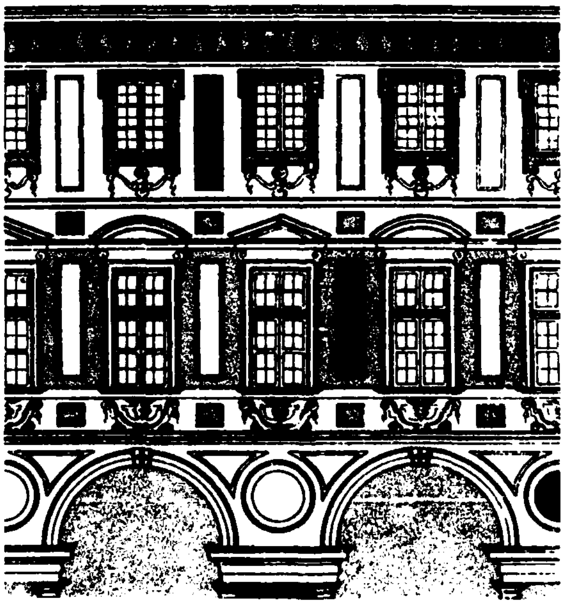
RD 6012-CH-02

XIII International Conference on Organometallic Chemistry

①

DAJA45-88-M-0295

abstracts



Torino, September 4-9, 1988

XIII International Conference on Organometallic Chemistry

XIII

Torino, September 4-9, 1988
Congress Centre Torino Esposizioni

abstracts

sponsored by

The International Union
of Pure and Applied Chemistry

The Federation of
European Chemical Societies
(FECS event No. 126)

XIII INTERNATIONAL CONFERENCE ON ORGANOMETALLIC CHEMISTRY

The Thirteenth 1988 edition of these Conferences is held in Torino, a modern European town of long-standing historical and cultural traditions, in which the brilliant scientist Amedeo Avogadro greatly contributed to establish the foundations of the present-day Chemistry.

Organometallic Chemistry has grown considerably and covers many fields of interest from metal containing supports to biologically relevant molecules. Metal-carbon- and metal-hydrogen bond making and breaking are fundamental steps in many processes of interest to all chemists.

Within the limits imposed by the tight schedule, the Scientific Organizing Committee has tried to aggregate the scientific contributions in meaningful and consistent clusters. The hope is there that the 1988 edition of these Conferences will be a profitable one from a scientific point of view and the wish is extended to all participants for a pleasant and active stay in Torino.

Fausto Calderazzo

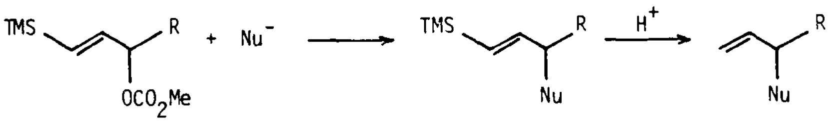
Keywords: Metal Complexes, Ligands,
Chemical Bonds, Aromatic Compounds,
Porphyrins, Molecular Structure,
Photochemical Reactions, Electrochemistry,
Surface Chemistry, Crystal
Structure, Cyclic Compounds,
Synthesis Chemistry, Molecule
Molecule Interactions, Ions,
Electronic States, Catalysis,
Reaction Kinetics, Abstracts.
(AW)

ORAL PRESENTATION

SELECTIVITIES IN ORGANIC REACTIONS VIA π-ALLYLPALLADIUM COMPLEXES

Jiro Tsuji, Department of Chemical Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

Palladium-catalyzed reactions of various allylic compounds via π-allylpalladium complexes are important synthetic methods. The usefulness of π-allylpalladium chemistry will be expanded if the reactions have high regio- and stereoselectivities. In this lecture, studies on regio- and stereoselectivities in several reactions of allylic carbonates and 2-vinyloxiranes with various nucleophiles are discussed. Particularly it was found that the introduction of trimethylsilyl group to allyl systems showed a profound effect on the regioselectivity of the reaction (ref. 1).



Ref. 1. J. Tsuji, M. Yuhara, M. Minato, H. Yamada, F. Sato, Y. Kobayashi, Tetrahedron Lett., 29, 343 (1988).

2

New Reagents for Carbon-hydrogen Activation: Organo-rhodium and -iridium Trispyrazolylborates

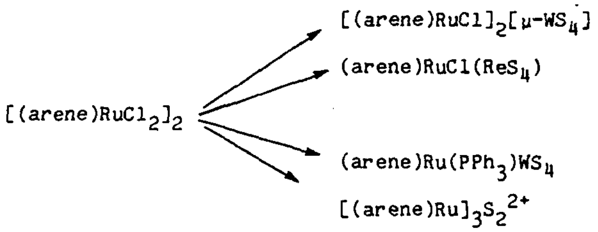
W.A.G. Graham, Department of Chemistry, University of Alberta, Edmonton AB T6G 2G2, Canada

ARENE RUTHENIUM SULFIDO CLUSTERS

Thomas B. Rauchfuss, Jayantha Amarasekera, Kevin E. Howard, John R. Lockemeyer, Emmanuel Ramli, Xiaoguang Yang, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801 USA

Although ruthenium carbonyl sulfides are numerous, the corresponding chemistry of arene ruthenium sulfides has not been developed. We have found that compounds of the type $[(arene)RuCl_2]_2$ (1) are excellent precursors to this new class of compounds. (Scheme)

Scheme



Direct reaction *of 1 with salts of* WS_4^{2-} *affords trinuclear* compounds of the type $[(arene)RuCl]_2(WS_4)$ which are soluble and thermally stable. Reaction of 1 with PPh_3 followed by WS_4^{2-} gives $(arene)Ru(PPh_3)WS_4$ which features terminal $W{=}S$ functionalities. Reaction of 1 with ReS_4^- gives purple $(arene)RuCl(ReS_4)$. Direct reaction of 1 with sulfide gives salts of the closo cluster $[(arene)Ru]_3S_2^{2+}$. The structural systematics and reaction chemistry of these compounds will be discussed as well as their potential as precursors to new inorganic polymers.

4

FIVE-COORDINATE OLEFIN CARBYL COMPLEXES OF PLATINUM(II)

Maria Elena Cucciolito, Vincenzo De Felice and Aldo Vitagliano,
Dipartimento di Chimica, Università di Napoli,
Via Mezzocannone 4, 80134 Napoli, Italy

Vincenzo G. Albano, Istituto Chimico G. Ciamician,
Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

Trigonal bipyramidal complexes of the type $PtClMe(N\text{-}N')(\eta^2\text{-}C_2H_4)$ (N-N'= α,α'bidentate nitrogen ligand) have been recently described. In contrast with the previously known analogs $PtCl_2(N\text{-}N')(Olefin)$, olefin dissociation from the above species was shown to be reversible.[1] With the help of this remarkable property, we have prepared a wide series of related complexes and investigated the influence of the coordination environment on their stability. The syntheses are outlined in eq. 1-3.

$$[PtClMe(C_2H_4)]_2 \xrightarrow{Olefin} \xrightarrow{N\text{-}N'} PtClMe(N\text{-}N')(Olefin) \qquad (1)$$

$$\begin{tikzcd} PtClR(Me_2S)_2 \arrow[rr, "Olefin,\ N\text{-}N'"] \arrow[dr, "N\text{-}N'"'] & & PtClR(N\text{-}N')(Olefin) \qquad (2) \\ & PtClR(N\text{-}N') \arrow[ur, "Olefin"'] & \end{tikzcd}$$

(L = neutral ligand) (R = Alkyl or Aryl ligand)

$$PtClR(N\text{-}N')(Olefin) \xrightarrow{AgBF_4,\ L} [PtLR(N\text{-}N')(Olefin)](BF_4) \qquad (3)$$

The equilibria $PtXR(N\text{-}N')(Olefin) \overset{K}{\rightleftharpoons} PtXR(N\text{-}N') + Olefin$ have been investigated through qualitative and quantitative observations (e.g. determination of K by ^1H NMR analysis of equilibrium mixtures). The main ligand effects may imply a variation of K of several orders of magnitude and are the following:

a) A dominating factor is the steric hindrance present on both sides of the N-N' ligand. If properly oriented in the coordination plane, this tends to stabilize the bipyramidal complexes through a corresponding destabilization of the square-planar species.

b) Electron-releasing substituents on the olefinic double bond destabilize the complexes while electron-withdrawing groups stabilize them. Since literature data suggest the opposite trend for square planar species,[2] this gives a direct evidence of the increased relative importance of π-back-donation in five-coordinate complexes.

Work supported by MPI

1) Albano, V.G.; Braga, D.; De Felice, V.; Panunzi, A.; Vitagliano, A. Organometallics **1987**, 6, 517.
2) Kurosawa, H; Asada, N. J. Organomet. Chem. **1981**, 217, 259.

CONJUGATE ADDITION OF ORGANOCOPPER COMPOUNDS AND IODOTRIMETHYLSILANE TO ENONES AND ENOATES

Mikael Bergdahl, Eva-Lotte Lindstedt, Martin Nilsson and Thomas Olsson

Department of Organic Chemistry, Chalmers University of Technology
S-412 96 Göteborg, Sweden

The presentation concentrates on the conjugate addition of organocopper compounds solubilised with tributylphoshine in the the presence of iodotrimethylsilane, a reaction which gives high yields under mild conditions, the silyl enol ethers being the primary products.

$$R\text{-}Cu/Bu_3P + C{=}C\text{-}CO + I\text{-}SiMe_3 \longrightarrow R\text{-}C\text{-}C{=}C\text{-}SiOMe_3 + CuI/Bu_3P$$

The work is an extension of our recent findings that lithium iodide is important for the conjugate addition of organocopper compounds in the presence of chlorotrimethylsilane [1]. This led us to use organocopper-iodotrimethylsilane combinations in ether, THF and even dichloromethane to give good yields of the conjugate adducts, primarily as silyl enol ethers [2]. The latter reactions led to homogeneous solutions in the presence of dimethyl sulphide, since the copper iodide formed immediately dissolved.

We now show that presence of tributylphoshine provides homogeneous reactions and even higher yields. The phosphine stabilises and solubilises the copper compound and also seems to favour the addition. The *E*/*Z*-selectivity in the reactions are affected by the presence of lithium iodide. NMR spectra of reagents, reaction mixtures and products indicate interactions for example between halosilane and organocopper reagents. The mechanism can be discussed in terms of activation of the organocopper compound by iodotrimethylsilane, 3,4-addition to the enone (or enoate) and elimination of copper iodide with formation of the (*E*) silyl enol ethers (in the absence of lithium iodide).

The results provide further improvements of recent metods for activation of lithium organocuprates and of organocopper compounds with chlorotrimethylsilane and complexing agents like HMPA and DMAP [3-5]. The reaction also bridges the gap between the classical conjugate additions and the cross-coupling of organocopper reagents with organic halides in the presence of soft phosphines [6]. In the present reactions the organic group from the soft copper connects to the beta carbon of the enone, the hard silicon connects to the oxygen and copper iodide is formed.

[1] Lindstedt, E-L, Nilsson, M. and Olsson. T., *J. Organometal. Chem.* *334* (1987) 255.
[2] Bergdahl, M., Lindstedt, E-L, Nilsson, M. and Olsson. T., *Tetrahedron* *44* (1988) In press.
[3] Corey, E.J. and Boaz, N.W. *Tetrahedron Lett.* *26* (1985) 6015 and 6019.
[4] Alexakis, A., Berlan, J. and Becase, Y. *Tetrahedron Lett.* *27* (1986) 1047.
[5] Nakamura, E., Matsuzawa, S., Horigushi, Y. and Kuwajima, I. *Tetrahedron Lett.* *27* (1986) 4029.
[6] Malmberg, H. and Nilsson, M. *Tetrahedron 38* (1982) 3981.

6

Studies on the Complexation of Polynuclear Heteroaromatic Nitrogen Ligands to Pentamethylcyclopentadienylrhodium Dication: Nitrogen versus π-Bonding

Richard H. Fish and Hoon-Sik Kim, Lawrence Berkeley Laboratory, University of California,
Berkeley, CA 94720 USA

Recent studies from our laboratory on the regioselective hydrogenation of polynuclear heteroaromatic nitrogen compounds, with mononuclear rhodium homogeneous catalysts, clearly showed that the nitrogen substrate binds to the rhodium metal center prior to hydrogen transfer to the nitrogen ring. Thus, we speculated that the bonding of the nitrogen heterocyclic ring to the rhodium metal center was an important criterion for selective hydrogenation.

Therefore, we wanted to determine the exact nature of nitrogen substrate bonding to the rhodium metal center, i. e., nitrogen (N) versus π-bonding and initiated studies on the reactions of of several representative polynuclear heteroaromatic nitrogen ligands with pentamethylcyclopentadienylrhodium dication [$Cp^{*}Rh^{2+}$]. Accordingly, the nitrogen ligands, quinoline, **1**; isoquinoline, **2**; 1,2,3,4-tetrahydroquinoline, **3**; 2-methylquinoline, **4**; N-methylindole, **5**; and N-methylpyrrole, **6**; were reacted with $Cp^{*}Rh^{2+}$ to provide N-bonding for **1** and **2**, while **3-6** preferred π-bonding.

The relative order of N ligand reactivity, in competitive experiments, was $2 > 3 > 4 \sim 5 > 1$ and shows that steric effects and availability of non-bonding electrons on the N-atom are important parameters that control N- versus π-bonding to $Cp^{*}Rh^{2+}$. In addition, the reactions of the $Cp^{*}Rh\ N_{1\text{-}3}{}^{2+}$ (N= ligands **1-6**) complexes with hydrogen gas and the use of $Cp^{*}Rh(\text{quinoline})_{1\text{-}2}{}^{2+}$ and its' synthetic precursors, $Cp^{*}Rh(\text{acetone})_3{}^{2+}$ and $Cp^{*}Rh(\text{p-xylene})^{2+}$, as catalysts for the selective nitrogen ring reduction will also be discussed.[1]

Reference

1 R. H. Fish and H-S. Kim Organometallics 1988 (Submitted)

*These studies at LBL were supported by the Director of Energy Research, Office of Basic Energy Science, Chemical Sciences Division of the U. S. Department of Energy.

Addition of Ethylene to Dichloro(Bu^t_2-ethylenediamine)platinum(II).

F. P. Fanizzi and G. Natile

Dipartimento Farmaco-Chimico, via G. Amendola 173, I-70126 Bari, Italy

The $[Pt(\eta^2-C_2H_4)Cl_2(N-N)]$ (N-N = bidentate N-donor ligand) represent a well established class of 5-coordinate platinum compounds known since 1973.[1] They are prepared by reacting the chelating ligand with a 4-coordinate platinum(II) species already containing the ethylene ligand; moreover, they can undergo irreversible dissociation of the olefin and formation of $[PtCl_2(N-N)]$ species.[2] More recently, it has been reported that substitution of a chloride by a methyl group renders the olefin dissociation reversible, thus providing a new route to this type of complexes.[3] The role of the methyl is not fully understood but it might be related to its strong trans-labilizing effect.

The complex $[PtCl_2(Bu^t_2en)]$ is anomalous in the series of dichlroroplatinum(II) complexes with substituted ethylenediamines. For instance, in DMSO, it adds one molecule of solvent without dissociating a chloride ion.

The cis isomer of $[PtCl_2(Bu^t_2en)]$, **1**, (cis is referred to the conformation of the bidentate ligand), reacts in chloroform (containind ca. 1% of ethanol) with ethylene under pressure (7 atm) forming the corresponding five-coordinate species $[Pt(\eta^2-C_2H_4)Cl_2(Bu^t_2en)]$, **2**, under our experimental conditions the reaction leads to a **1**:**2** ratio of ca. 6:4. The solution is capable to catalyze ethylene polymerization with formation of paraffins having an average molecular weight of 300.

Other strictly related complexes such as $[PtCl_2(Pr^i_2en)]$ and $[PtCl_2\{(MePhHC)_2en\}]$ under the same experimental conditions do not give formation of detectable amount of the five-coordinate species.

Different aspects of the olefin addition and polymerization will be discussed.

Work supported by the Consiglio Nazionale delle Ricerche, Roma.

[1] L. Cattalini, F. Gasparrini, L. Maresca, and G. Natile, J. Chem. Soc. Chem. Commun., 369 (1973).

[2] L. Maresca, G. Natile, M. Calligaris, P. Delise, and L. Randaccio, J. Chem. Soc. Dalton Trans., 2386 (1976); A. De Renzi, B. Di Blasio, A. Saporito, M. Scalone, A. Vitagliano, Inorg. Chem., 19, 960 (1980). H. van der Poel, G. van Koten, M. Kokkes, C. H. Stam, Inorg. Chem., 20, 2941 (1981).

[3] V. G. Albano, O. Braga, V. De Felice, A. Panunzi, and A. Vitagliano, Organometallics, 6, 517 (1987). A. De Renzi, G. Morelli, A. Panunzi, and A. Vitagliano, Gazz.Chim.Ital., 107, 549 (1987).

8

ALKOXIDE COMPLEXES OF GROUP 6 METALS AND THEIR FORMATION FROM THE CORRISPONDING HYDRIDES.

Bruno Longato, Dipartimento di Chimica Inorganica Metallorganica ed Analitica, Università degli Studi di Padova, Via Marzolo, 1, 35131 Padova, Italy

Jack Norton, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

The loss of an aldehyde RCHO from an alkoxide RCH_3OM is not always thermodynamically downhill; the $RCH_2OM \rightleftharpoons RCHO + H\text{-}M$ equilibrium may lie to the left, even with ordinary aldehydes. However, a RCHO/H-M mixture may be kinetically stable, with acid catalysis required in order for the thermodynamically favored RCH_2OM to be formed. $CpMo(CO)_3H$ does not react with aldehydes in the absence of acid, but in the presence of CF_3CO_2H it reacts with CH_3CHO and ArCHO (Ar = Ph, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$). With CH_3CHO, $CpMo(CO)_3)Et$ can be seen by NMR; the alkoxides formed from the other aldehydes are converted to the corresponding alcohol or ether by the acid present.

Alkoxide complexes of this type can be isolated after careful deprotonation of the corresponding alcohol complex. For example, $[CpW(CO)_3(EtOH)]BF_4$ can be made from solid $CpW(CO)_3BF_4$[1] and ethanol vapor; when a toluene solution of $[CpW(CO)_3(EtOH)]BF_4$ is treated with proton sponge at room temperature, $[CpW(CO)_2(\mu\text{-}OEt)]_2$ is formed.

---

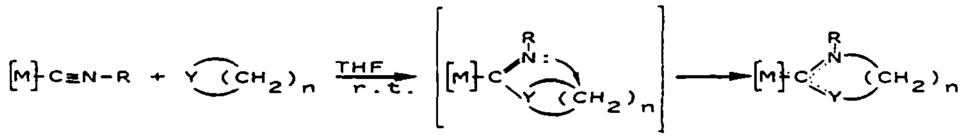
[1] Beck, W.; Schloter, K. *Z. Naturforsch.* 1978, *33b*, 1214.

9

SYNTHESIS OF 5- and 6- MEMBERED CYCLIC CARBENE COMPLEXES DERIVED FROM ISOCYANIDE LIGANDS IN COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

Roberta Bertani, Mirto Mozzon, and Rino A.Michelin
Centro di Chimica Metallorganica C.N.R. and Istituto di Chimica Industriale, Facolta' di Ingegneria, Universita' di Padova, 35100 Padova, Italy

Recently we reported[1] that metal-stabilized 5-membered cyclic aminooxy- and diaminocarbene complexes can be prepared by reaction of 2-bromoethanol and 2-bromoethylamine hydrobromide in the presence of n-BuLi with isocyanide ligands in complexes of Pd(II) and Pt(II). By taking advantage of the tendency of highly strained 3-membered heterocycles YCH_2CH_2, where Y=NH (aziridine), S (thiirane), O (oxirane) and 4-membered heterocycle $HNCH_2CH_2CH_2$ (azetidine), to undergo ring opening reactions, we have studied the following reactions of electrophilic isocyanide ligands in certain complexes of Pd(II) and Pt(II) :



[M]=Pd(II), Pt(II); R=alkyl, aryl; n=2, Y=NH,S,O ; n=3, Y=NH

In contrast to similar reactions of CO and CS ligands which require the presence of a halide salt as catalyst[2], the reactions of RNC ligands proceed spontaneously at room temperature to give 5- and 6-membered cyclic carbenes. The proposed reaction mechanisms as well as the spectroscopic data of the cyclic carbene products are discussed.

References

1 Michelin, R.A.; Zanotto,L; Braga,D.; Sabatino, P.; Angelici, R.J. Inorg.Chem. 1988,27, 85. Idem, Ibidem,1988, 27, 93

2 (a) Singh, M.M.; Angelici, R.J. Angew.Chem.Int.Ed.Engl.1983, 22, 163. (b) Singh, M.M.; Angelici, R.J. Inorg.Chem.1984, 23, 2691. (c) Idem, Ibidem, 1984, 23, 2699. (d) Singh, M.M.; Angelici, R.J. Inorg.Chim. Acta 1985, 100, 57.

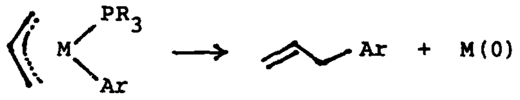
10

NEW ASPECTS IN REDUCTIVE ELIMINATION OF π-ALLYL COMPLEXES OF GROUP 10 METALS

Hideo Kurosawa, Yoshikane Kawasaki, Shinji Murai

Department of Applied Chemistry, Osaka University, Suita,
Osaka 565, Japan

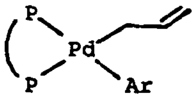
Herein reported are new reactivity trends in reductive elimination of π-allylmetal complexes **1** which are relevant to the full understanding and rational design of metal catalyzed allylic alkylation and olefin oligomerization reactions. The reactivity



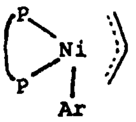
(1)

1 (M= Ni, Pd, Pt)

in eq. 1 follows the order, M= Ni > Pd ≫ Pt. Adding excess monophosphine ligand to the nickel and palladium complexes resulted in no significant acceleration nor retardation of the rate. On the other hand, addition of a chelating diphosphine caused retardation of eq. 1 in the case of the palladium complex, but ca. 10^8 times acceleration in the case of the nickel analog. These contrasting behaviors are unambiguously attributed to the formation of the less reactive σ-allylpalladium **2** and the extremely reactive 18-electron π-allylnickel **3**, respectively, each of **2** and **3** having been fully characterized separately.



2



3

THE PREPARATION OF NICKEL TRIAD METAL YLIDE COMPLEXES

Ivan J. B. Lin, Rey F. Wu and H. C. Hsy, Department of Chemistry, Fu Jen Catholic University, Hsin Chuang, Taipei, Taiwan, 24205

Sulfur ylide complexes were obtained in high yields by the reaction of trimethylsulfoxonium iodide with $M(PR_3)_2Cl_2$ (M = Pt, Pd, R = Me or Ph) under basic condition by the phase transfer catalysis (PTC) technique. Detailed reaction conditions were examined. The optimal range of base was found between 2.5N and 1N. Increasing the amount of phase transfer catalyst enhanced the rate of complex formation. Without a phase transfer catalyst, sulfur ylide complexes were obtained in low yield. The proposed role of the phase transfer catalyst is to carry the OH^- into the organic layer and to prevent the ylide abstracting a porton from water contained in the organic phase. The preparation of other metal ylide complexes, including mixed ylide metal complexes will be described.

12

BINUCLEAR COPPER(I) COMPLEXES CONTAINING ONE, TWO OR THREE 2-(DIPHENYLPHOSPHINE)PYRIDINE (Ph_2Ppy) BRIDGING LIGANDS. SYNTHESIS OF NEW PHOSPHORUS YLIDE COMPLEXES OF COPPER(I)

M.Pilar Gamasa, José Gimeno, Elena Lastra and Luzdivina Sanchez,
Departamento de Química Organometálica, Facultad de Química,
Universidad de Oviedo, 33071 Oviedo, Spain.

Maurizio Lanfranchi and Antonio Tiripicchio, Istituto di Chimica
Generale ed Inorganica, Università di Parma, Centro di Studio per
la Strutturistica Diffrattometrica del CNR, Viale delle Scienze,
43100 Parma, Italy.

Treatment of $|Cu(MeCN)_4|BF_4$ complex with 2-(diphenylphosphine)pyridine (Ph_2Ppy) in dichloromethane at room temperature or with an excess of Ph_2Ppy in refluxing acetonitrile affords $|Cu_2(\mu\text{-}Ph_2Ppy)_2(MeCN)_2||BF_4|_2$ (I) or $|Cu_2(\mu\text{-}Ph_2Ppy)_3(MeCN)||BF_4|_2$ (II), respectively.

The crystal structure of (II) has been determined by a X-ray single-crystal diffraction study and provides the first example of a new structural type of Ph_2Ppy bridged bimetallic complexes. To the best of our knowledge, this is the first example of a copper complex containing Ph_2Ppy ligands and the first example of a binuclear complex with three Ph_2Ppy ligands.

^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. studies at room temperature show that MeCN and Ph_2Ppy dissociation followed by rapid ligand exchange processes take place in solution.

The lability of the MeCN ligand in complex (II) as well as the presence of one co-ordinatively unsaturated copper atom allows the synthesis of the substituted complexes $|Cu_2(\mu\text{-}Ph_2Ppy)_3L_x||BF_4|_2$ (x = 1, L = 2-methylpyridine; x = 2, L = $P(OMe)_3$, PMe_3 and 4-methylpyridine). No reaction is observed with carbon monoxide and 1-phenyl-1-propyne.

Complexes (I) and (II) react with anionic bidentate phosphorus ylide ligands, $|(CH_2)_2PR_2|^-$ (R = Ph, Me), to give new copper(I) ylide complexes.

MULTINUCLEAR MAGNETIC RESONANCE STUDIES OF PHOSPHINE AND ISONITRILE SUBSTITUTED DERIVATIVES OF $Co_4(CO)_{12}$

S.A. Kernaghan, B.T. Heaton and J.A. Iggo, Department of Chemistry,
University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England.

Multinuclear (^{59}CO, ^{31}P, ^{13}C, ^{1}H) n.m.r. studies have been performed on $Co_4(CO)_9$(tripod) [tripod = $HC(PPh_2)_3$] and $Co_4(CO)_9$(triphos) [triphos = $MeC(CH_2PPh_2)_3$] and $Co_4(CO)_{12-n}L_n$[1] [L = MeNC or Bu^tNC; n = 1,2,3].

The solution structure of $Co_4(CO)_9$(triphos) has been determined by ^{13}C and ^{31}P n.m.r. and is analogous to that previously found for $Co_4(CO)_9$(tripod).[2] ^{13}C n.m.r. saturation transfer experiments[3] have been used to follow the processes by which CO scrambling occurs in these clusters.

^{13}C n.m.r. studies of $Co_4(CO)_{12-n}L_n$ have been used to establish the site of CO substitution.

The effect on the value of $\delta(^{59}Co)$ and $W_{1/2}$ of the ^{59}Co resonance resulting from ligand substitution of clusters is found to depend on the nature of the ligand. For triphosphine ligands there is only a small shift of $\delta(^{59}Co)$ for the basal and apical resonances, but there is a noticable narrowing of the basal ^{59}Co resonance. Substitution of CO by isonitrile ligands does not significantly affect $W_{1/2}$ of the basal and apical ^{59}Co resonances but there is a large shift of $\delta(^{59}Co)$ for the apical ^{59}Co resonance and little effect on the basal ^{59}Co chemical shift.

1. J. Newman, and A.R. Manning, J. Chem. Soc., Dalton Trans., 2549, (1974).
2. D.J. Darensbourg, D.J. Zalewski, and T. Delford, Organometallics, 3, 1210, (1984).
3. G.A. Morris, and R.J. Freeman, J. Mag. Res. 29, 433, (1978).

REACTIVITY OF $[Ir_6(CO)_{15}]^{2-}$ WITH COMPLEXES OF THE METALS OF THE IB AND IIB GROUPS.

R.Della Pergola,[a] L.Garlaschelli,[a] S.Martinengo,[b], F.Demartin,[c] M.Manassero,[c] N.Masciocchi,[c] M.Sansoni[c].
[a]Dipartimento di Chimica Inorganica, [b]Centro del C.N.R. sui Bassi Stati di Ossidazione and [c]Istituto di Chimica Strutturistica Inorganica, via Venezian 21, 20133 Milano,Italy.

The reactions of the dianion $[Ir_6(CO)_{15}]^{2-}$ with complexes of the metals of the IB and IIB groups have been investigated. The cluster anion reacts at room temperature with $HgCl_2$ to give $[Ir_6(CO)_{15}HgCl]^-$ (I) in quantitative yields. Its structure consists of an octahedron of iridium atoms capped by a HgCl moiety and bearing twelve terminal and three face bridging carbonyls. This arrangement is closely related to that found in the red isomer of $[Ir_6(CO)_{16}]$ [1].

The same reaction performed with EtHgCl affords, in a first step, anion (I), and on standing, evolves giving $[Ir_6(CO)_{14}(HgCl)_2]^{2-}$ which contains two face bridging HgCl groups.

$[Ir_6(CO)_{15}]^{2-}$ reacts very slowly with $Au(PPh_3)Cl$ or $Cu(PPh_3)Cl$, and after 48 h only a 30% conversion could be observed even in the presence of a large excess of complex. On the other hand, the cation $[Au(PPh)_3]^+$ reacts immediately and quantitatively to give $[Ir_6(CO)_{15}Au(PPh_3)]^-$.

1) L.Garlaschelli, S.Martinengo, P.L.Bellon, F.Demartin, M.Manassero, M.Y.Chiang, C.Y.Wei, R.Bau, J.Am.Chem.Soc., 1984, 106, 6664.

Intramolecular Dynamics Of Cluster Compounds Derived from $Ir_4(CO)_{12}$ and $Ir_2Rh_2(CO)_{12}$.

Andrés Strawczynski, Gianfranco Suardi, and Raymond Roulet.
Institut de Chimie Minérale et Analytique de l'Université
3, place du Château, CH-1005 Lausanne, Suisse

Renzo Ros, Istituto di Chimica Industriale dell'Università
Via Marzolo 9, I-35100, Padova, Italia

The following series of cluster compounds were examined by 2D and variable temperature ^{13}C-NMR and ^{31}P-NMR : $[Ir_4(CO)_{11}Br]^-$, I; $Ir_4(CO)_{11}(\mu_2\text{-}SO_2)$, II; $Ir_4(CO)_{10}(PMePh_2)_2$, III; $Ir_4(CO)_{10}(\mu_2\text{-dppm})$, IV; $Ir_2Rh_2(CO)_{10}(\mu_2\text{-dppm})$, V; $Ir_4(CO)_{10}(\mu_2\text{-}Ph_2P(CH_2)_3PPh_2)$, VI; $Ir_4(CO)_{10}(\mu_2\text{-}Ph_2P(CH_2)_5PPh_2)$, VII; $Ir_4(CO)_{10}(\text{diars})$, VIII; $Ir_4(CO)_{10}(1,5\text{-cyclooctadiene})$, IX; $Ir_4(CO)_9(\text{diars})(PPh_3)$, X; $Ir_4(CO)_9(L_3)$, XI and XII; $Ir_2Rh_2(CO)_9(L_3)$, XIII, XIV ($L_3 = (Ph_2P)_3CH, S_3(CH_2)_3$), and $Ir_4(CO)_8(\mu_2\text{-dppm})_2$, XV.

The observed *fluxional processes* are all due to CO site exchange and fall into 4 categories :

1. The "merry-go-round" of basal CO's. This process is of lowest activation energy for the Ir_4 clusters (I, IV, VI, XI, XII), but not for the Ir_2Rh_2 clusters (V, XIII, XIV). The unbridged "intermediate" of this process was in fact observed as a *stable isomer for* XII.

2. A switch of basal face by edge-bridging of 3 CO's to an alternative face of the tetrahedral metal core. This process occurs in all monosubstituted complexes. In the disubstituted complexes, it may occur when the non-CO ligands occupy two stereochemically different positions. The site exchange proceeds via an unbridged intermediate (IX, first process of XV) or is concerted (I, II, VIII, X).

3. A rotation of apical CO's : this process is of highest activation energy for the Ir_4 clusters (II, XI, XII), but of lowest energy for the Ir_2Rh_2 clusters (IV, XIII, XIV).

4. Edge-bridging of 3 radial CO's on the basal face . This unprecedented process is the simplest explanation of the P site exchange in VII : the axial and radial P atoms exchange without any switch of basal face (the apical CO's remain apical, the bridged ones remain *bridged*).

SYSTEMATIC SYNTHESIS OF $[MIr_4(CO)_9L(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ (M=Rh, Ir AND L=CO, PPh_3, PPh_2Me AND $PPhMe_2$); ^{13}C nmr (L=CO) AND X-RAY ANALYSIS OF $[Ir_5(CO)_{10}\text{-}(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$

Maria D. Vargas, Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, Campinas, 13100, SP, Brazil
Dario Braga, Instituto di Chimica Generale dell' Università, via Selmi 2, 40126 Bologna, Italy
Rajesh Khattar, Departament of Chemistry, University of Notre Dame, Notre Dame, IN46556, USA.

The deprotonation reactions of $[Ir_4(CO)_{11}(PPhH_2)]$ and $[Ir_4(CO)_{10}L(PPhH_2)]$ in the presence of $[M(\eta^5\text{-}C_5Me_5)(MeCN)_3][SbF_6]_2$, give high yields of $[MIr_4(CO)_{10}(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$, (M=Rh(1a), Ir(1b)), and $[MIr_4(CO)_9L(\eta^5\text{-}C_5Me_5)(\mu_4\text{-}PPh)]$ (M=Rh(2a), Ir(2b); L=PPh_3, PPh_2Me and $PPhMe_2$) respectively. Direct CO substitution on (1a) and (1b), either by oxidation of CO with Me_3NO in the presence of L, or by reaction with $[Bu_4N][Br]$ followed by Br^- abstraction with Ag^+ in the presence of L, also yields (2a) and (2b) respectively. The role of the PPh ligand in the condensation and CO substitution reactions will be discussed.

X-ray analysis of (1b) reveals a squase-based pyramidal arrangement of Ir atoms, with the μ_4-PPh ligand capping the square face. The slow exchange limiting ^{13}C nmr spectra of (1a) and (2b) are consistent with the solid state structure ; a structure is proposed for (2a) and (2b) and possible mechanisms for the CO fluxionality in all these species will be proposed.

On the Relative Strengths of Metal-Alkyl and Metal-Hydrogen Bonds .A Theoretical Study Based on Density Functional Theory.

Tom Ziegler and Vincenzo Tschinke
Department of Chemistry ,University of Calgary
Calgary,Alberta,CANADA

M-R bond formation (R=H,alkyl) and M-R cleavage pervades most of the elementary reaction steps in organometallic chemistry,and the difference in M-H and M-alkyl bond strengths has important implications for the relative ease with which ligands insert into the two types of bonds as well as the facility with which H_2 can add oxidatively to a metal center in comparison with H-alkyl and alkyl-alkyl bonds.

We present here calculations on M-H and M-CH_3 bond energies in a number of representative RML_n complexes,encompassing early [Cp_2MR (M=Sc,La,Y)] as well as middle [Cp_2VR,$Mn(CO)_5R$, and $CpCr(CO)_3R$] to late [CpNi(CO)R] transition metal and f-block elements[Cp_2MClR M=Th,U].

The main objective in this study has been to augment the scanty(and inaccurate) experimental data with near quantitative theoretical extimates of M-R bond energies for the whole spectrum of transition metals and f-block elements.We shall further explain why M-H and M-CH_3 bonds are quite similar in strengths for f-block elements and early transition metals ,whereas M-H bonds bonds are much stronger(by 50 kJ mol^{-1}) than M-CH_3 bonds for middle to late transition metals. Trends in the M-R bond strengths within a triad of transition metals will also be discussed .

18

LIGAND DEPENDENT NATURE OF THREE POSSIBLE SHAPES FOR A d^6 PENTACOORDINATED COMPLEX

Odile Eisenstein, Yves Jean and Idris El-Idrissi Rachidi,
Laboratoire de Chimie Théorique (UA 506), Bâtiment 490, Centre de
Paris-Sud, 91405 Orsay, France

The distortion of model XMH_4 d^6 complexes (X-equatorial ligand) away from their unstable trigonal bipyramidal (TBP) structure is studied by means of Extended Hückel calculations. The distortion is represented by the angle α between the two equatorial M-H bonds (α = 120° in the TBP geometry). Departure from α = 120° leads to two minima, one for α = 180° (square pyramid geometry) and one for α = 70°, the origin of both being traced to a first order Jahn-Teller effect and not to a favourable ligand-ligand interaction (α = 70°). The relative energies of these two minima are strongly dependent on the nature of the equatorial ligand X opposite to the α angle. In particular it is shown that a π donor X ligand favours α = 70° while a π acceptor favours α = 180°. Finally a third minima is found for α = 30°. In this case, there is a strong interaction between the equatorial hydrides and this structure is better viewed as a d^8 square planar complex with a molecular H_2 ligand side-bonded to the metal.

A NEW APPROACH TO MEASURING ABSOLUTE METAL-LIGAND BOND DISRUPTION ENTHALPIES IN ORGANOMETALLIC COMPOUNDS. THE $[(CH_3)_3SiC_5H_4]_3U$- SYSTEM

Afif Seyam, Department of Chemistry, University of Jordan, Amman, Jordan
Laurel E. Shock, Michal Sabat, and Tobin J. Marks, Department of Chemistry, Northwestern University, Evanston, Illinois 60208

Absolute uranium-ligand bond disruption enthalpies in the series Cp''_3UR ($Cp'' = \eta^5$-$Me_3SiC_5H_4$) have been measured by halogenolytic isoperibol titration calorimetry of $Cp''_3U/Cp''_3UI/Cp''_3UR$ ensembles. Derived $D(Cp''_3U\text{-}R)$ values in toluene solution are (kcal/mol, R): 62.4(0.4) (I); 28.9(1.7) (n-Bu); 25.6(3.1) (Bz); 39.3(2.3) (CH_2SiMe_3); 44.8(1.1) (Me); 48.5(2.2) (vinyl); 87.2 ($C\equiv CPh$). $D(Cp''_3U\text{-}L)$ values (kcal/mol, 95% confidence limits) in toluene solution were also determined for L = CO (10.3(0.2)) and THF (9.8(0.2)). The magnitudes of the D(U-R) values appear to reflect a combination of steric and electronic factors, and strongly suggest that D(U-I) is less sensitive to ancillary ligation (more transferable) than D(U-alkoxide). The complex Cp''_3U(vinyl) crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions $\underline{a} = 11.298(1)$, $\underline{b} = 13.997(2)$, $\underline{c} = 9.460(2)$ Å, and $\alpha = 97.00(1)^\circ$, $\beta = 105.98(1)^\circ$, and $\gamma = 86.94(1)^\circ$. Least-squares refinement led to a value for the conventional R index (on F) of 0.0196 for 4373 reflections having $2\theta_{MoK\alpha} < 50^\circ$ and $I>3\sigma(I)$. The molecule possesses a conventional pseudotetrahedral Cp_3MX geometry with U-C(ring) = 2.759(4)Å(average), U-C(α,vinyl) = 2.436(4)Å, ∢U-C(α,vinyl)-C(β,vinyl) = 137.7(3)°, ∢ Cg-U-Cg = 116.4°, 117.2°, 120.0°, and ∢ Cg-U-C(α,vinyl) = 95.1°, 100.0°, 100.1°. All hydrogen atoms were located, and U-H(Cα,vinyl) = 2.93(4)Å. The metrical parameters evidence severe nonbonded repulsions between the vinyl ligand and the Cp'' ligands, as well as between different Cp'' ligands. The quantity $D(M\text{-}I)\text{-}D(M\text{-}CH_3)$ is proposed as a new gauge of metal-ligand bonding.

20

HOMOLEPTIC ALKYLS AND ALKOXIDS OF THE TRANSITION ELEMENTS- MOLECULAR STRUCTURE AND BONDING

Arne Haaland and Kristin Rypdal
Department of Chemistry, University of Oslo,
P.O.Box 1033, Blindern, 0315 Oslo 3, NORWAY

The molecular structure of monomeric $Cr(CH_2CMe_3)_4$, $Cr(OBu^t)_4$, and $W(OMe)_6$ ($Me=CH_3$) has been determined by gas electron diffraction.

The best model for $W(OMe)_6$ has a WO_6 symmetry of O_h, the relativ orientation of the ligands is difficult to determine. The W-O bond distance is 190.7(1)pm, the W-O-C angle is $132.4(6)^0$.

The best model has S_4 symmetry for both chromium compounds, any distortion from T_d symmetry of the CrO_4 and CrC_4 in a D_{2d} manner cannot be seen from the data. The Cr-C distance is 203.8(6)pm, with a Cr-C-C angle of $128.0(8)^0$. The Cr-O distance is 176(2)pm, with a Cr-O-C angle of $140(1)^0$.

Ab-Initio HF-SCF and CASSCF calculations are carried out to study the nature of the transition metal-ligand bond.

We also hope to present recent results concerning the molecular structure of $Zr(CH_2CMe_3)_4$, $Ti(NMe_2)_4$, $TiMeCl_3$ and $V(OBu^t)_4$.

Geometry Deformations in A–PZ_3 Compounds: A Structural Test of Theories of Bonding in Phosphine Complexes.

B.J. Dunne and A.G. Orpen, Department of Inorganic Chemistry, The University, Bristol BS8 1TS, UK.

The widespread application of phosphines and their derivatives in industrial and academic organometallic chemistry makes an understanding of how they bind to metals, and other substrates, of great importance. This paper reports ways of using crystallographic data to assess current theories of bonding in phosphine complexes.

The large number of compounds in which triphenylphosphine (PPh_3) is present as a clearly defined fragment make it a suitable test case for the assessment of bonding theory of phosphines in general. We have used the Cambridge Structural Database as a source of information on how the PPh_3 fragment is distorted by complexation to an atom A, where A may be a *d*– or *p*–block metal or other *p*–block element such as C,N or O. Our strategy has been to examine the variation in the structure of the PPh_3 fragment in A–PPh_3 species as revealed by the A–P and P–C bond lengths, and the C–P–C and A–P–C angles.

While a number of statistical approaches are possible, we have concentrated on two.

i) The mean P–C length ($<r>$) was plotted against mean C–P–C ($<\alpha>$) for each element A. This shows strong correlation between $<r>$ and $<\alpha>$ (correlation coefficient *ca.* −0.95), and a marked dependency of $<r>$ and $<\alpha>$ on A. Small and electronegative A (*e.g.* O,N,H) leads to $<r>$ being short (and $<\alpha>$ large). Conversely large, electropositive A (*e.g.* Cr,Re,Ru) are associated with long $<r>$ (and small $<\alpha>$).

ii) Correlations, between the A–P and P–C bond lengths (d and r respectively) and between d and C–P–C angle (α) were analysed. These showed a range of behaviour, notably for the *d*–block metals. For elements in the centre and left of the transition series α and d are positively correlated, while at the right α and d are negatively correlated.

In a separate study we have examined the effect of oxidation of the transition metal in M–PZ_3 complexes on d, r and α. This shows the importance of M–P π–bonding on both M–P *and* PZ_3 geometries.

These observations are compared with predictions based on electronic and "steric" theories of molecular structure as applicable to tertiary phosphine complexes.

22

ORIENTATION EFFECTS ON ALKALI METAL REACTIONS WITH ALKYL IODIDES

Trina Valencich
Department of Chemistry and Biochemistry
California State University
5151 State University Drive
Los Angeles, California 90032 U.S.A.

Iodine is extracted from alkyl iodides by alkali and alkaline earth metals. This preference exhibits a dependence upon the cosine of the "angle of attack," $\cos\gamma$, for products which are backscattered in molecular beam experiments. The cutoff angle for this dependence expresses the classical chemical steric effect.

This reaction class is discussed in terms which evolved empirically from a combination of trajectory simulations, crossed molecular beam and laser induced fluoresence experiments. The interpretation suggests that the experimental behavior results from the transfer of an electron from the metal to the alkyl iodide at large distances, followed by a repulsive release of exothermicity. This mechanism is consistent with the observed small energies of activation, large reaction probabilities, and a correlation of product excitation with the mass of the alkyl group. The reaction is predicted to become orientation independent at large impact parameters. However, experimental verification of this prediction is incomplete.

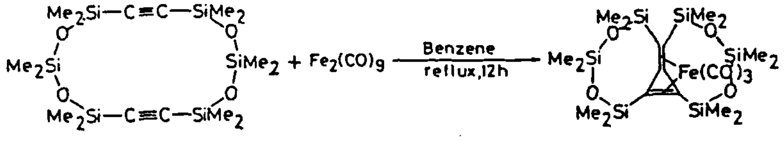
Quality ab initio information on this system is not available, however, it has been the subject of a semi-empirical diatomics in molecules (DIM) calculation. Although this system has been simulated several times, only a recent three atom trajectory treatment by Blais and Bernstein exhibits the $\cos\gamma$ sensitivity. A six atom treatment is necessary to examine how explicit inclusion of the hydrogens produces orientation effects; and to properly sample the initial rotational conditions for a symmetric top. Rotation of the target can influence the distribution of orientations which are sampled by the calculation.

We are representing this system by extending an approach developed by Valencich, Chapman, and Bunker to treat hydrogen atom reactions with methane. This six atom potential extrapolates to the three atom limit described by Blais and Bernstein. The barrier height increases as the approach of the metal deviates from colinearity, the methyl end is unreactive, and the hydrogens are explicitly included. We can also repeat selected trajectories with their three atom Blais and Bernstein approximation. This will help ascertain what aspects of three atom treatments can be extrapolated to larger systems. We will discuss the preliminary dynamics on this surface.

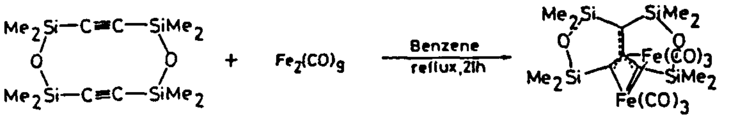
NOVEL IRON CARBONYL COMPLEXES OF METHYLENECYCLOPROPENE AND TRIMETHYLENEMETANE. INTERMEDIATES AND MECHANISM

Hideki Sakurai, Kazuhiro Hirama, Takeaki Fujii, and Kenkichi Sakamoto
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

A novel (methylenecyclopropene)iron tricarbonyl complex (1) was prepared by the reaction of 3,3,5,5,7,7,10,10,12,12,14,14-dodecamethyl-4,6,11,13-tetraoxa-3,5,7,10,12,14-hexasilacyclotetradeca-1,8-diyne (2) with diironnonacarbonyl, as orange crystals, mp 122-123 °C (dec).



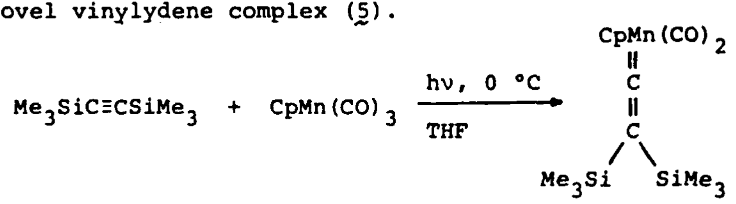
2 1



3 4

On the other hand, the reaction of 3 with $Fe_2(CO)_9$ resulted in the formation of a novel trimethylene methane complex (4). Structures of these complexes were determined by X-ray crystallographic analyses together with various spectroscopic properties.

The key step in these reactions is 1,2-silyl migration of complexed bis(silyl)acetylenes. Actually the reaction of bis(trimethylsilyl)acetylene with π-cyclopentadienylmanganese tricarbonyl gave a novel vinylydene complex (5).



$$Me_3SiC{\equiv}CSiMe_3 + CpMn(CO)_3 \xrightarrow[\text{THF}]{h\nu,\ 0\ ^\circ C} CpMn(CO)_2{=}C{=}C(SiMe_3)_2$$

5

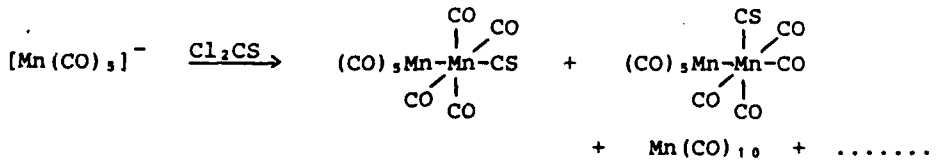
Structures of these interesting new complexes as well as the reaction mechanism will be discussed.

SPECTROSCOPIC EVIDENCE FOR THE FORMATION OF $Mn_2(CO)_9CS$

Wolfgang Petz, Gmelin-Institut fur Anorganische Chemie der Max-Planck-Gesellschaft, Varrentrappstraße 40-42, D-6000 Frankfurt/Main, Federal Republic of Germany

Although the field of thiocarbonyl complexes has been explored in the last decade, rather few information is available about thiocarbonyl derivatives of simple binary carbonyl compounds of the type $M_x(CO)_y$ (M = Cr, Mo, W [1]; M = Fe [2]).

We have now obtained a $Mn_2(CO)_{10}/Mn_2(CO)_9CS$ mixture in low yields from the reaction of $[Mn(CO)_5]^-$ with thiophosgene in pentane. The thiocarbonyl complex as the minor product (5 to 10%) could not be separated from $Mn_2(CO)_{10}$ but was identified by the (CS) frequencies in the IR spectrum at 1300 and 1280 cm^{-1} and by mass spectroscopic measurements. The results were indicative for the presence of two isomers possessing the CS ligand either in trans position to CO or to the $Mn(CO)_5$ group.



Reaction of the mixture with Br_2 gave mainly $Mn(CO)_5Br$ along with small amounts of $Mn(CO)_4(CS)Br$ which was identified by IR and mass spectroscopy. A product containing CS could also be identified from the reaction of the mixture with $PPh_3/ONMe_3$.

[1] B. D. Dombek, R. J. Angelici, J. Am. Chem. Soc. 95 [1973] 7516.

[2] W. Petz, J. Organometal. Chem. 146 [1978] C 23.

SULFUR MONOXIDE AS A LIGAND IN TRANSITION METAL COMPLEXES

Wolfdieter A. Schenk, Johanna Leissner, Stefan Müssig, Ute Karl,
Isabel Tomerius, Institut für Anorganische Chemie, Universität
Würzburg, D-8700 Würzburg, West Germany

Mononuclear sulfur monoxide complexes of iron, rhodium, and iridium are readily obtained by transition metal-induced cleavage of ethylene episulfoxide (1). The close similarity between these compounds and analogous complexes of sulfur dioxide can be explained on the basis of a simple MO picture. Reactions investigated so far include coordinative and oxidative addition as well as nucleophilic and electrophilic attack at sulfur. Treatment of the square-planar complexes $MCl(PR_3)_2(SO)$ (M = Rh, Ir) with CO leads to the liberation of SO which can be trapped by addition to orthoquinones at low temperature. A method will also be described for the catalytic cleavage of episulfoxides which allows the use of the highly unstable and reactive sulfur monoxide as a synthetic reagent.

(1) W. A. Schenk, Angew. Chem. 99 (1987) 101; Angew. Chem. Int. Ed. Engl. 26 (1987) 98.

26

SULFUR MONOXIDE, A NEW AND VERSATILE LIGAND IN ORGANOMETALLIC CHEMISTRY

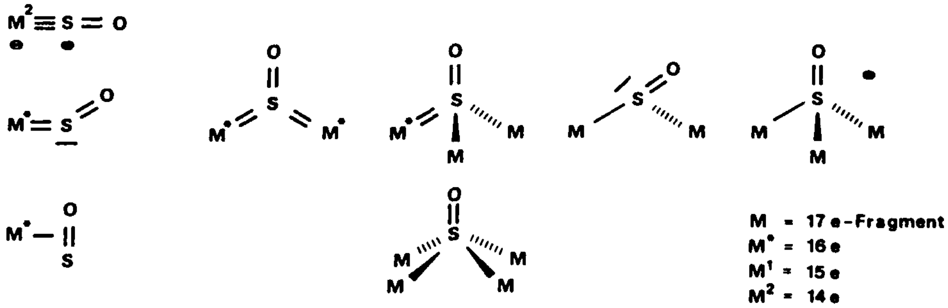
Ingo-Peter Lorenz

Institute for Inorganic Chemistry, University of Tübingen
Auf der Morgenstelle 18, D-7400 Tübingen (FRG)

Sulfur momoxide is extremely unstable, but it can be stabilized as ligand in organometallic complexes where it is inserted by different methods of synthesis:

1. directed S-oxidation of metal-coordinated sulfur.
2. SO-transfer reaction by metal-induced fragmentation of thiirane-S-oxide acting as SO-source.
3. nucleophilic substitution reaction at the sulfur atom of thionylchloride by hydrido complexes/amines.

Sulfur monoxide demonstrates a great structural variety as a ligand in organometallic complexes, depending on the number of electrons of the complex fragment, thus, SO can act as 2 or 4 electron donor in terminal or bridging ligand positions:



Starting from suitable organometallic compounds we succeeded in the synthesis of some examples of most of the bonding systems introduced above, which are isolobal analogues of sulfur dioxide, sulfur trioxide, sulfoxides and sulfones.

Hitherto, the SO ligand shows four different reaction modes:

1. Substitution of SO against CO ligands
2. Oxidation of SO into SO_2 ligands
3. Insertion of SO_2 into the S-O-bond to give thiosulfato ligands
4. Deoxygenation of SO to sulfur ligand (by HCl)

BINUCLEAR CARBONYLOSMIUM PORPHYRINS WITH BRIDGING NITROGEN DONOR LIGANDS

Johann W. Buchler, Stefan Pfeifer, Institut für Anorganische
Chemie, Technische Hochschule Darmstadt, D-6100 Darmstadt, FRG

Osmium porphyrins, e. g. $[\mathrm{Os(OEP)}]_2$[1], may serve as building blocks for the synthesis of conductive polymers in which bidentate nitrogen donors L^L, e. g. pyrazine (pyz) or 1,4-diazabicyclo[2,2,2]octane (dabco), are used as bridging donor ligands.[2] The polymers of the type $[\mathrm{Os(OEP)(L^\wedge L)}]_n$ are highly conductive when doped, i. e. partially oxidized. The defect electrons appear to be delocalized along the ..Os(L^L)Os(L^L).. chain. In order to check the presence of Os(L^L)Os interactions in isolated molecules, the synthesis of binuclear carbonylosmium(II) porphyrins 3 containing such an entity was undertaken according the sequence 1 -> 2 -> 3.

$$\underset{\mathbf{1}^{3}}{\mathrm{(MeOH)OsCO(TTP)}} \xrightarrow{\mathrm{L^\wedge L}} \underset{\mathbf{2}}{\mathrm{(L^\wedge L)OsCO(TTP)}} \longrightarrow \underset{\mathbf{3}}{\mathrm{(TTP)OCOsL^\wedge LOsCO(TTP)}}$$

	L^L
3a	pyz
3b	dabco

The species 2 were observed in solution, but lost L^L on attempted crystallization, thus forming 3a and 3b. The new compounds were characterized by elemental analyses, UV/VIS-, IR-, and 1H-NMR spectra. Electrochemical investigations gave no hint of OsL^LOs coupling in the oxidized forms of 3, $3a^+$ or $3b^+$.

---

(1) $(\mathrm{OEP})^{2-}$, $(\mathrm{TTP})^{2-}$: dianions of octaethylporphyrin or tetra(p-tolyl)porphyrin, respectively.

(2) J. P. Collman, J. T. McDewitt, C. R. Leidner, G. T. Yee, J. B. Torrance, and W. A. Little, J. Am. Chem. Soc. 109, 4606 (1987).

(3) J. W. Buchler, G. Herget, and K. Oesten, Liebigs Ann. Chem. 1983, 2164.

EQUILIBRIUM AND KINETIC STUDY OF IMIDAZOLE BINDING TO PHTHALOCYANINATOIRON(II) IN DIMETHYL SULPHOXIDE

Paolo Ascenzi e Maurizio Brunori, Dipartimento di Scienze Biochimiche, Università di Roma "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy

Giovanna Pennesi, Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione, Area della Ricerca del C.N.R., Via Salaria Km. 29,5, C.P. 10, 00016 Monterotondo Stazione (Roma), Italy

Claudio Ercolani e Fabrizio Monacelli, Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy

Ligand binding to phthalocyaninatoiron(II), [Fe(pc)], a porphirin-like molecule, has been widely investigated from both equilibrium and thermodynamic viewpoints (1).
As a development of our research on this field, we looked at imidazole, Im, as an interesting axial ligand, and since conflicting results were present in the literature (1), a reinvestigation of the reversible reactions (*1*) and (*2*) in dimethyl sulphoxide, dmso,

$$[\mathrm{Fe(pc)(dmso)_2}] + \mathrm{Im} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} [\mathrm{Fe(pc)(dmso)(Im)}] \qquad (1)$$

$$[\mathrm{Fe(pc)(dmso)(Im)}] + \mathrm{Im} \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} [\mathrm{Fe(pc)(Im)_2}] \qquad (2)$$

from both equilibrium and kinetic points of view, seemed necessary. At 20°C, the equilibrium constants are $K_1 = k_{+1}/k_{-1} = (6.4 \pm 2.6) \times 10^5$ $\mathrm{dm^3 mol^{-1}}$, and $K_2 = k_{+2}/k_{-2} = (7.4 \pm 0.5) \times 10^3$ $\mathrm{dm^3 mol^{-1}}$. Values of k_{+1} and k_{+2} are $(9.8 \pm 0.2) \times 10^3$ $\mathrm{dm^3 mol^{-1} s^{-1}}$ and 5.4 ± 0.2 $\mathrm{dm^3 mol^{-1} s^{-1}}$, respectively. From these parameters, values of $k_{-1} = 1.5 \times 10^{-2}$ $\mathrm{s^{-1}}$ and $k_{-2} = 7.3 \times 10^{-4}$ $\mathrm{s^{-1}}$ were calculated. These results show that the replacement of axial dmso in $[\mathrm{Fe(pc)(dmso)_2}]$ by Im is a two-step process with the uptake of the second Im molecule slower than the first.

(1) F.H. Moser and A.L. Thomas, 'The Phthalocyanines', CRC Press, Boca Raton, 1983.

REACTIONS OF DOUBLY REDUCED IRON(II) PORPHYRINS WITH (n, SEC, AND TERT) ALKYL HALIDES.

Doris LEXA, Jean-Michel SAVEANT and Dan Li WANG. Laboratoire d'Electrochimie de l'Université de Paris 7. UA CNRS N° 438 "Electrochimie Moléculaire" - 2, place Jussieu 75 251 Paris Cedex 05 -France.

Electrochemical investigation of the reduction of seven iron porphyrins (the octaethylporphyrin, the etioporphyrin I, the pentafluorotetraphenylporphin, the tetraphenylporphyrin and three basket-handle porphyrins) in the presence of (n, sec. and tert.) alkyl halides shows that not only the singly reduced iron(II) complex, formally and iron(I) complex, undergoes alkylation at the atom, but that this is also the case for the doubly reduced iron(II) complex. No ring alkylation, as possible with a radical anion or a di-anion structure, is observed. At low concentrations of alkyl halide, the one-electron reduction product of the iron(II) alkyl complex, formally and iron(I) alkyl complex, could be transiently observed. Upon raising the concentration, catalytic reduction of the alkyl halide by the Fe(II)R$^-$/Fe(I)R^{2-} couple occurs. It is found that the presence of the amide linked chains exerts a pronounced influence on the electrochemical and chemical reactivity of the alkyl complexes, stabilizing the negatively charged species. Implications concerning the alkylation mechanisms and the chemical catalysis of the electrochemical reduction of alkyl halides by metal complexes are discussed.

References :

Lexa D., Savéant J.M., Wang D.L. Organometallics 1986, 5, 1428.

Lexa D., Savéant J.M., Su K.B., Wang D.L., J.Am.Chem.Soc. (submitted)

Gueutin C., Lexa D., J.M. Savéant, Wang D.L., Inorg.Chem. (submitted)

SYNTHETIC STRATEGIES TO TRANSITION METALS CORROLATES. CRYSTAL AND MOLECULAR STRUCTURE OF (TRIPHENYLARSINE) OCTAMETHYL-CORROLATE RHODIUM (III).

S.Licoccia, T.Boschi, R.Paolesse, P.Tagliatesta
Dipartimento di Scienze e Tecnologie Chimiche - II Universita' di Roma Tor Vergata - 00173 Rome, Italy

G.Pelizzi, F.Vitali
Istituto di Chimica Generale - Universita' di Parma and Centro di Studio per la Strutturistica Diffrattometrica del CNR - 43100 Parma

The synthesis of transition metal corrolates has been widely investigated in order to ascertain the possible consequences of the macrocyclic ring deformation (a direct bond between pyrroles A and D) on its coordination properties.

Three main synthetic methods have been so far used to prepare metallocorrolates:

a) Reaction of the preformed macrocycle with metal carbonyls in a non coordinating solvent.
b) Reaction of metal salts with the linear tetrapyrrolic intermediate 1,19-dideoxybiladiene-a,c in a buffered alcoholic solution. The presence of a coordinating ligand has proved to be necessary when the metal is rhodium.
c) Reaction of metal salts with the macrocycle in N,N-dimethylformamide.

The reactivity towards axial ligand, such as phosphines, arsines or isocyanides has also been investigated and an Xray crystal structure determination has been performed on (triphenylarsine)octamethylcorrolate rhodium (III).

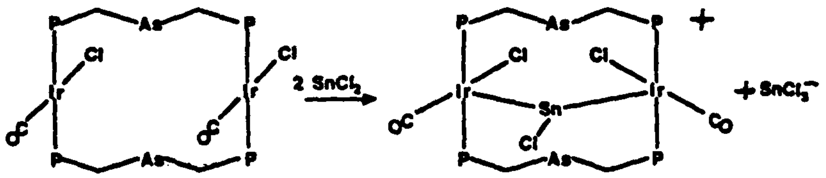
The compound crystallyzes in the orthorhombic space group $\underline{P}2_12_12_1$ with a = 20.172(7), b = 12.468(5), c = 14.893(5) Å and Z = 4. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares procedures to a conventional R value of 0.0353 for 1436 independent reflections collected by counter methods.

The crystal structure consists of discrete monomeric units, where the rhodium atom has a distorted square pyramidal environment, the equatorial sites being occupied by four nitrogen from the corrole ligand (Rh-N 1.93(1) - 1.96(1) Å) and the apex by the arsenic atom from the triphenylarsine molecule (Rh-As 2.311(2) Å). The 15 atom core of the corrole moiety is nearly planar, the largest deviation from the plane of best fit being 0.10 Å.

NOVEL CHEMICAL BEHAVIOR OF THE METALLOMACROCYCLES $Ir_2(CO)_2Cl_2\{(Ph_2PCH_2)_2AsPh\}_2$: BINDING OF MAIN GROUP IONS PARTICULARLY Sn(II).

Alan L. Balch, Vincent Catalano, Phillip E. Reedy, Jr., Steven Reimer, Department of Chemistry, University of California, Davis, California 95616, U.S.A.

The iridium metallomacrocycle $Ir_2(CO)_2Cl_2\{(Ph_2PCH_2)_2AsPh\}_2$ binds a variety of metal ions from both the transition series and the main group elements. This presentation will focus on the interactions with tin(II) which is summarized in eq. 1. The X-ray crystal structure of 2a will be compared to that of related transition metal counterparts. The metallomacrocycle 1 is capable of extracting tin selectively (in the presence of certain other metal ions) from aqueous solution and is capable of transporting tin through a non-aqueous medium. The adduct 2 shows a prominent absorption in the visible spectrum at 588 nm. In solution at 25°C, strong emission at 645 nm is observed. A molecular orbital model for the bonding within this unit will be presented. Removal of tin(II) from 2 is possible and a novel light-driven system for tin(II) extrusion will be described.



1 2

32

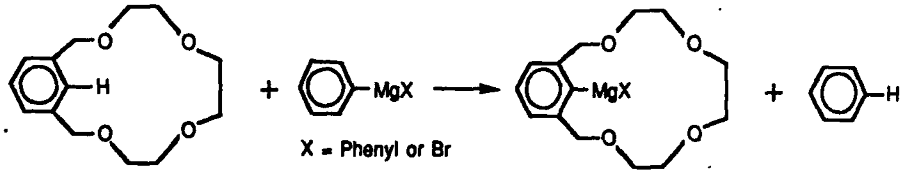
METALLATION OF AN AROMATIC C-H BOND BY CROWN ETHER ACTIVATED ORGANOMAGNESIUM COMPOUNDS

Peter R. Markies, Tateo Nomoto, Otto S. Akkerman and Friedrich Bickelhaupt,
Vakgroep Organische en Anorganische Chemie, Faculteit Scheikunde, Vrije Universiteit,
de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

During a study on intra- and intermolecular complexation in organomagnesium compounds we found that diphenylmagnesium and 1,3-xylyl-18-crown-5 form a 1:1 complex which can be crystallized from toluene. The X-ray structure analysis revealed a "threaded" or rotaxane structure.

For reasons of structural comparison, the analogous complex with 1,3-xylyl-15-crown-4 was also prepared. Surprisingly, the X-ray structure of the crystalline material showed that an asymmetric, crown ether ring containing, diphenylmagnesium had been formed. The ^1H NMR spectrum of the precursor in [D_8]toluene showed the relatively slow formation of benzene.

The crown ethers mentioned also form complexes with phenylmagnesium bromide. The 1,3-xylyl-18-crown-5 formed a 1:1 complex with the Grignard compound of which the crystal structure was determined. However, the complex with the 1,3-xylyl-15-crown-4 decomposed under the formation of benzene and a crown ether containing a Grignard function:



These remarkable metallation reactions of the aromatic C-H bond, normally known only for organolithium compounds, must result from the increased reactivity of the magnesium compounds through complexation with the crown ether system. We suggest that the marked difference in behaviour between the crown-5 and crown-4 complexes is due to the much more congested structure of the, intermediately formed, crown-4 complexes in which the aromatic C-H bonds in the 2-position are forced into the very close vicinity of the magnesium centre.

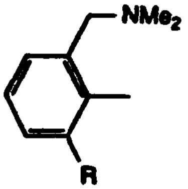
The metallation reactions proceed quantitatively and are believed to be favoured by the stronger co-ordination of magnesium in the products.

The mechanism of the complex formation and of the subsequent decomposition reactions will be discussed as well as the crystal structures of the complexes and of the magnesium compounds formed in the metallation reactions.

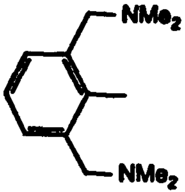
TUNING THE REACTIVITY OF METALS HELD IN A RIGID LIGAND ENVIRONMENT

Gerard van Koten, Laboratory of Organic Chemistry, Department of Metal Mediated Synthesis, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

In our studies we have found that specific chelating ligands afford metal complex substrates that are ideally suited for investigating intermediate species formed in reactions with electrophiles. An overview of some of our results in this area using square-planar d^8 Ni^{II}, Pd^{II}, Pt^{II}, Rh^{I}, and Ir^{I} substrates, and the unique organometallic species we encountered are presented. Research in our laboratory has been focussed on the chemistry of monoanionic aryl ligands having *ortho*- or bis-*ortho* dimethylaminomethyl substituents (*i.e.* $[C_6H_4(CH_2NMe_2)\text{-}2]$ (A) and $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$ (B)) that form organometallic compounds with a direct $M\text{-}C_{aryl}$ σ-bond.



(A)



(B)

Through coordination of the N donor site(s) of the *ortho* CH_2NMe_2 arm(s) five-membered M-C-C-C-N chelate ring formation occurs. In most cases, this *intramolecular coordination* hampers decomposition *via* pathways involving M-C bond breaking processes such as homolytic and heterolytic fission. In particular, the rigid chelating coordination of the aryl ligand B, provides the metal centre with a set of unusual properties. Firstly, the bis-*ortho* chelating ligand restricts the available sites for incoming reagents and other ligands. This is a situation that, as we will see, can frustrate the normal course of, for example, an oxidative reaction and lead to "trapped" intermediates having considerable stability. Secondly, the hard C and N donor atom(s) increase the nucleophilicity of the metal centre. This destabilizes the d_z2 orbital that lies perpendicular to the coordination plane in the square planar metal d^8 complexes derived from the ligands A and B. As a consequence, these complexes become susceptible to attack by a variety of electrophiles such as H_2, MeI, halogen and Me_2SnBr_2, - with startling results. An example of the unexpected and novel properties of these complexes is the use of organonickel II and III complexes derived from the bis-*ortho* chelating ligand B, for the addition of polyhalogenalkenes to alkene double bonds in homogeneous catalysis.

BASE-NUCLEOPHILE CATALYSIS OF POLYCONDENSATION OF FUNCTIONAL SILOXANES

M.Cypryk, S.Rubinsztajn, J.Chojnowski

Centre of Molecular and Macromolecular Studies, Polish Academy
of Sciences, Boczna 5, 90-362 Łódź, Poland

The heteropolycondensation of functional siloxane oligomers seems to be the most convenient route to many siloxane polymers and copolymers of regular structure. However, in many cases the reaction is slow and accompanied by siloxane bond cleavage as well as by other side processes. We found that using of basic or nucleophilic species, such as amines, phosphine oxides and others, is very effective in this reaction. Kinetics of the reaction of model compounds was studied and the mechanism of the catalysis was elucidated. In the case of strong nucleophiles, such as DMAP, Imidazole or N-methylimidazole, the process involves transient formation of a complex of the nucleophile with the polymer end group. At least some of these complexes have ionic structure, e.g. of an ammonium or phosphonium salt. In the case of relatively strong bases, such as Et_3N, the mechanism of base catalysis is more probable, involving activation of silanol group through hydrogen bonding with amine.

$$\sim\sim SiOSiX + Nu \rightleftharpoons \sim\sim SiOSiNu^{+}X^{-} \xrightarrow{\sim\sim SiOH} \sim\sim SiOSiSi\sim\sim + Nu + HX$$

$$\sim\sim SiOH + B \rightleftharpoons \sim\sim SiO\text{-}H\cdot\cdot B \xrightarrow{\sim\sim SiX} \sim\sim SiOSi\sim\sim + B + HX$$

Kinetic evidence for both mechanisms will be presented.

THE CHEMICAL DISPLACEMENT OF Os(II) CARBONYL SURFACE SPECIES ANCHORED TO HYDROXYLATED SILICA.

C. Dossi, A. Fusi, E. Grilli,[*]R. Psaro
Dipartimento di Chimica Inorganica e Metallorganica and [*]Centro C.N.R., Universita' degli Studi di Milano, Via G. Venezian, 21, 20133 Milano, Italy

The thermal decomposition of $HOs_3(CO)_{10}(OSi\leqslant)$ produces new Os(II) surface species characterized by three infrared carbonyl bands at 2126, 2038 and 1956 cm^{-1} (1). The real structure of these surface organometallic species still remains an open question. The formation of either mononuclear sites, or dimeric and polymeric $[Os(CO)_3]_n$ and $[Os(CO)_2]_n$ units without metal-metal bonds has been reported (2).

The chemical displacement of these surface species is performed through the complete disgregation of the silica with aqueous hydrofluoric acid (3). No osmium carbonyl species is recovered from the aqueous phase by extraction with either CH_2Cl_2 or $PPN^+ Cl^-$ in CH_2Cl_2 .

The solution was then evaporated at 70°C and a dark residue was obtained. Its infrared spectrum, in a KBr matrix, in the νCO region presents the same three carbonyl band pattern of the starting supported species. The presence of coordinated water and hydroxo groups is suggested by several $\delta(OH)$ $\delta(OH_2)$ and $\nu(OH)$ vibrations, in addition to the expected $\delta(Os-C-O)$, $\nu(OsC)$, $\delta(O-Os-O)$ bands.

A preliminary investigation with E.I. mass spectrometry shows an ion at 592 m/z, whose predominant fragmentation involves the successive loss of four carbon monoxide units has been observed.

A dimeric $Os_2(CO)_4(\mu-O)_2(OH_2)_4$ structure could be tentatively suggested.

1. R. Psaro, R. Ugo, G.M. Zanderighi, B. Besson, A.K. Smith and J.M. Basset, J. Organomet. Chem., 213 (1981) 215.
2. S.L. Cook, J. Evans, G.S. McNulty, G.N. Greaves, J. Chem. Soc. Dalton Trans., (1986) 7.
3. C. Dossi, R. Psaro, R. Zanoni and F.S. Stone, Spect. Acta, 43 A (1987) 1507.

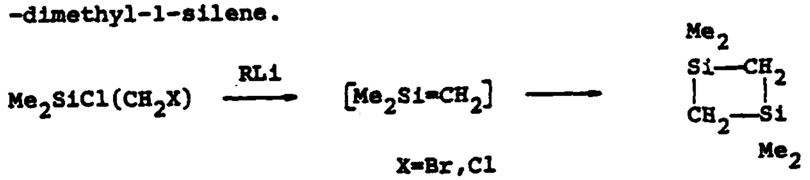
METHODS FOR PREPARATION OF 1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE

J.Chmielecka, J.Chojnowski, W.Stańczyk

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Boczna 5, 90-362 Łodź, Poland

There is a growing interest in preceramic polymers, which consist a useful source for silicon carbide ceramics. Ring opening polymerization of 1,3-disilacyclobutanes can give preceramic polycarbosilanes.

The studies of effective synthetic methods, in solution, leading to 1,1,3,3-tetramethyl-1,3-disilacyclobutane were performed, involving reactions of bromo- and chloromethyl(dimethyl)chlorosilane with organolithium reagents. The reactions show the features of an addition-elimination process, proceeding via unstable 1,1-dimethyl-1-silene.

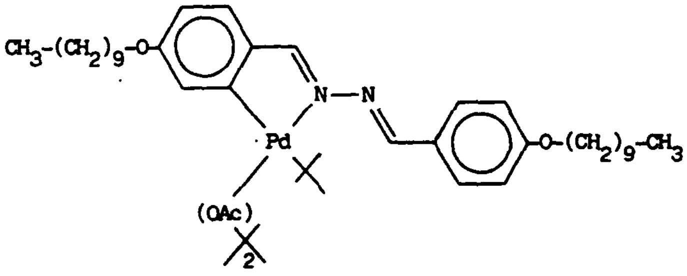


X=Br,Cl

LIQUID CRYSTALS DERIVED FROM ORTHOPALLADATED-AZINE DIMERS: THE INFLUENCE OF THE BRIDGING GROUP.

P. Espinet and J. Pérez, Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid (Spain).
M. Marcos, B. Ros and J.L. Serrano, Química Orgánica, Facultad de Ciencias, I.C.M.A. Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza (Spain).
E. Lalinde, Química Inorgánica, Colegio Universitario de la Rioja, Universidad de Zaragoza, Logroño (Spain).

Orthometallation of the azine p-$C_{10}H_{21}$-O-C_6H_4-CH=N-N=CH-C_6H_4-$OC_{10}H_{21}$-p with palladium acetate produces reasonable yields of the product orthopalladated in only one of the two rings of the azine,



In spite of the fact that carboxylate groups induce an open-book shape in the molecule that is expected to disturb the mesogenic properties, yet the molecule displays liquid-crystal behaviour.

Related complexes where the acetate group has been replaced by other increasingly larger carboxylate groups (up to 14 C atoms) reveal a surprising influence of the increasing length in the carboxylate chains, leading first to a decrease and then to a recovery of mesogenic properties, when the chain is sufficiently large.

The mesogenic properties of the compounds have been studied by optical microscopy and differential scanning calorimetry and the type of mesophase has been assigned.

CATALYTIC POLYMERIZATION OF ETHYLENE WITH (BISCYCLOPENTADIENYL COMPLEXES+ALUMOXANS) SYSTEMS

A. Romão Dias and Jorge Justino, Centro de Química Estrutural,
Instituto Superior Tecnico, Av. Rovisco Pais - 1096 Lisboa-CODEX
Portugal

Peter Tait, Department of Chemistry, University of Manchester
Institute of Science and Technology, Manchester M60 1QD, UK.

The subject of this work is ethylene polymerization using Kaminsky Type catalysts: Cp_2MR_2+alumoxan.

M=Zr,Mo,W; R=Cl,CH_3(1,2).

The catalytic activity of complexes Cp_2WCl_2, $Cp_2Mo(CH_3)_2PF_6$ is compared with that of Cp_2ZrCl_2. As expected the activity of the Mo and W complexes is smaller than the activity of the Zr complex.

In this communication we report active centers determination by quench method with tritium methanol (3), and kinetic studies of (Cp_2WCl_2+methylalumoxan) system.

(1) - Jens Herving and Walter Kaminsky, Polymer Bulletin, 9, 464 (1983)

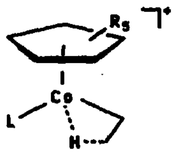
(2) - W. Kaminsky, Massoud Miri, H. Sinn and R. Woldt, Makromol. Chem., Rapid Commun., 4, 417 (1983)

(3) - D.R. Burfield and P.J.T. Tait, Polymer, Vol 13, July 315 (1972)

STRUCTURE AND DYNAMICS OF Co(III) AND Rh(III) ETHYLENE HYDRIDE COMPLEXES. MIGRATORY INSERTION REACTIONS AND POLYMERIZATION

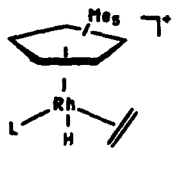
D. Lincoln, A. Volpe, and M. Brookhart, Department of Chemistry, Campus Box 3290, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, U.S.A.

The structure, spectroscopic properties and dynamics of complexes of 1 and 2 will be reported. The mechanism of ethylene polymerization of certain compounds in this series will be described together with preliminary results regarding methods for preparing terminally functionalized oligomers and polymers of ethylene.



1

$L = C_2H_4$, PMe_3
$P(OMe)_3$, PPh_3
$R = H$, CH_3



2

$L = PMe_3$, $P(OMe)_3$
$P(OPh)_3$, CH_2CH_2

ANALYTICAL ELECTRON MICROSCOPY OF LARGE TRANSITION METAL CARBONYL CLUSTERS AND CLUSTER DERIVED CATALYSTS

S. Mulley and B.T. Heaton, Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England

R. Devenish, Department of Metallurgy & Materials Science, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England

Analytical Electron Microscopy studies of large transition metal carbonyl clusters have been carried out on a Phillips 400em machine using electron energy loss spectroscopy (EELS) and X-ray energy dispersive analysis (EDA). Previous studies showed that the cluster $[Ni_{38}Pt_6(CO)_{42}]^{5-}$[1] was deposited intact on a carbon film support and EELS analysis showed Ni:C:O ratios which are consistent with those expected for this anion. Degradation of the cluster was observed with time and electron beam intensity to give a Ni/Pt alloy. Similar studies have now been carried out on other clusters and the order of stability to electron beam damage is $[Ni_{38}Pt_6(CO)_{42}]^{5-} < [Pt_{38}(CO)_{44}Hx]^{2-}$[2] $< [Ni_{34}C_4(CO)_{38}]^{6-}$.[3] Efforts are being made to characterise the new materials left after CO evolution and results on these materials will be reported.

Analytical techniques have also been used to study the bimetallic cluster $Fe_2Pd_2(CO)_5(NO)_2(dppm)_2$ used as a catalyst for the reductive carbonylation of nitro derivatives to iso-cyanates.[4] Results from studies before and after catalysis show that metal segregation occurs during catalysis to give particles (200 -500 Å) which are either pure Pd or pure Fe.

1. B.T. Heaton, P. Ingallina, R. Devenish, C.J. Humphreys, A. Cerriotti, G. Longoni, M. Marchionna, J. Chem. Soc., Chem. Commun., (1987) 766.
2. A. Cerriotti, P. Chini, G. Longoni, D.M. Waschecheck, E.J. Wurcherer, L.F. Dahl. M. Marchionna, R.A. Montag, unpublished results.
3. A. Cerriotti, A. Fait, G. Longoni, G. Piro, L. Resconi, F. Demartin, M. Manassero, N. Masiocchi, M. Sansoni, J. Am. Chem. Soc., (1986), 108, 5370.
4. B.T. Heaton, S. Mulley, R. Devenish, C.J. Humphreys, P. Braunstein, Angew Chem., accepted for publication.

STUDIES INTO THE STEREOSELECTIVITY OF REDUCTION OF CYCLIC KETONES WITH ALUMINIUM COMPOUNDS SUPERIMPOSED ON THE ADSORBENT SURFACE

Kutchin A.V., Nurushev R.A., Prokopenko Yu.A., and Tolstikov G.A.

Institute of Chemistry, Bashkirian Research Centre,
Ural Department, USSR Acad.Sci., Ufa 450054 U.S.S.R.

In search for new reducing agents we have come to investigations of stereoselectivity of reduction of cyclic ketones with aluminium compounds as $LiAlH_4$, $(i\text{-}C_4H_9)_2AlH$, $(i\text{-}C_4H_9)_3Al$, $(i\text{-}C_4H_9)_2AlH\text{-}ZnCl_2$ fixed on the surface silica gel, aluminium oxide, and Florisil. 3-Methylcyclohexanone (3MCH), menthone, and camphor have been taken as model compounds. Our investigation results are given in Table 1.

TABLE 1

Reagent	menthone		camphor		3-MCH alcohols	
	men-tol	neo-men-tol	bor-neol	iso-bor-neol	cis-	trans-
$LiAlH_4$	74	26	8	92	84	16
$LiAlH_4\cdot SiO_2$	38	62	13	87		
$(i\text{-}C_4H_9)_2AlH$	46	54				
$(i\text{-}C_4H_9)_2AlH\cdot SiO_2$	34	66	6	94	70	30
$(i\text{-}C_4H_9)_2AlH\text{-}ZnCl_2$	21	79				
$[(i\text{-}C_4H_9)_2AlH\text{-}ZnCl_2]\cdot SiO_2$	0	100				
$(i\text{-}C_4H_9)_3Al$	8	92	4	96	47	53
$(i\text{-}C_4H_9)_3Al\cdot SiO_2$	0	100	1	99	56	44
*$(i\text{-}C_4H_9)_3Al\cdot Al_2O_3$	8	92				
$(i\text{-}C_4H_9)_3Al\cdot$Florisil	0	100	0	100	53	47

Solvent - ether, *-hexane

The results presented demonstrate the applicability of aluminium reagents superimposed on the adsorbent to improve the stereoselectivity of reduction of hindered cyclic ketones to the related alcohols of lower thermodynamic stability.

A NEW CARBONYL CLUSTER SYSTEM. SYNTHESES AND MOLECULAR STRUCTURES OF $[Ni_{12}Ge(CO)_{22}]^{2-}$ AND $[Ni_{10}Ge(CO)_{20}]^{2-}$ DIANIONS.

A. Ceriotti, P. Ingallina, M. Marchionna, Dipartimento di Chimica Inorganica e Metallorganica, via Venezian 21, I-20133 Milano, Italy.

G. Longoni, Dipartimento di Chimica Fisica ed Inorganica, viale del Risorgimento 4, I-40136 Bologna, Italy.

B. T. Heaton, Department of Inorganic, Physical and Industrial Chemistry, Groove Street P. O. Box 147, Liverpool L69 3BX, England.

N. Masciocchi, F. Demartin, M. Manassero, M. Sansoni, Istituto di Chimica Strutturistica Inorganica, via Venezian 21, I-20133 Milano, Italy.

The new Ni-Ge carbonyl cluster system has been investigated. The reaction of $[Ni_6(CO)_{12}]^{2-}$ (I) with $GeCl_4$ in acetonitrile solution ($GeCl_4$/(I) ca. 0.6 as molar ratio) affords the $[Ni_{12}Ge(CO)_{22}]^{2-}$ (II) dianion (ν(CO) in THF: 2020(s), 1835(m), 1775(mw), brown soln.); when the reaction is performed with a higher molar ratio (ca. 2.5) another compound, viz. $[Ni_{10}Ge(CO)_{20}]^{2-}$ (III) (ν(CO) in THF: 2010(s), 1975(m), 1865(ms), 1845(m), green soln.) is obtained.

The direct degradation of (II) into (III) results with excess $GeCl_4$, however an analogous transformation can be achieved on using either CO or PPh_3 as degradation agents.

Crystals of (II) and (III) as PPh_4^+ salts have been prepared by slow diffusion of isopropylalcohol in THF solution. Their molecular structures, determined by X-ray diffraction analysis, are based on a Ge-centered icosahedral packing of metal atoms. The metal skeleton of (III) is directly obtained from that of (II) by removing two opposite Ni atoms. The only reported analogous structures in carbonyl cluster family are those of $[Ni_{12}Sn(CO)_{22}]^{2-}$ (1) and of $[Rh_{12}Sb(CO)_{27}]^{3-}$ (2).

1) A. Ceriotti, F. Demartin, P. Ingallina, M. Manassero, M. Marchionna, N. Masciocchi, M. Sansoni, XIX Cong. Naz. Chim. Inorg. A54, (1986).
2) J. L. Vidal, J. M. Troup, J. Organomet. Chem., 213, 351, (1981).

BRIDGED CYANO-SUBSTITUTED BUTA-1,3-DIENYLIDENE AND CYCLOPENTYLIDENE DIIRON COMPLEXES.

Michel Etienne, Département de Chimie, UA CNRS 322, Université de Bretagne Occidentale, 29287 BREST-CEDEX - FRANCE.

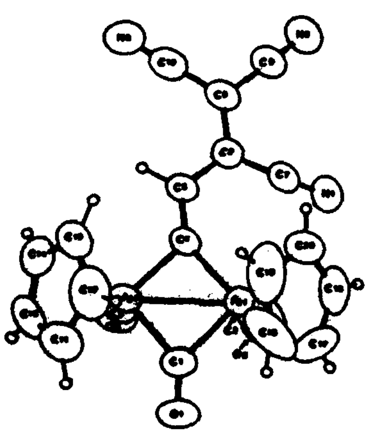
Loïc Toupet, Groupe de Physique Cristalline, UA CNRS 804, Université de Rennes I, Beaulieu, 35042 RENNES-CEDEX - FRANCE.

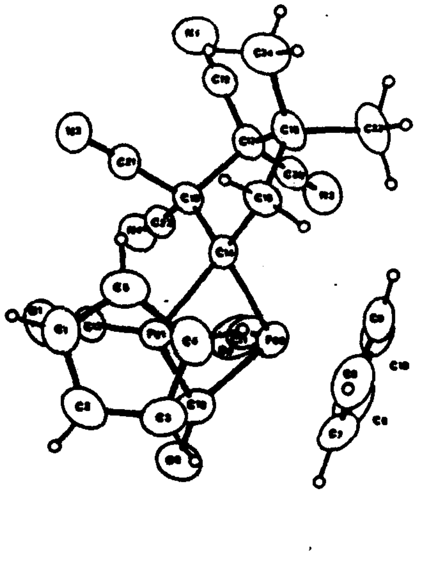
Tetracyanoethylene (TCNE) is a widely used reagent in several kinds of organic reactions. Some of these have proven to be subtly different in transition-metal chemistry. On the other hand, bridging alkenylidene diiron complexes can be viewed as 1,1-dimetallated olefins, an important feature of their potential use in organic synthesis and model reactions.

The reaction of the μ-alkenylidene diiron complexes $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}C{=}CHR)$ (R = H, CH_3) with TCNE gives the μ-3,4,4-tricyanobuta-1,3-dienylidene compounds $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}C{=}CR\text{-}(NC)C{=}C(CN)_2]$ (R = H, CH_3), resulting from the tricyanovinylation of the ligand. The μ-buta-1,3-dienylidene ligand is rare and relevant spectroscopic data together with the X-ray structure of one complex (R = H) are presented.

When TCNE reacts with the isopropyl substituted complex $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}C{=}CHCH(CH_3)_2]$, a [1,2] hydrogen shift occurs leading to an unexpected μ-cyclopentylidene complex $[(C_5H_5)Fe(CO)]_2(\mu\text{-}CO)$ $[\mu\text{-}\overline{C\text{-}CH_2\text{-}C(CH_3)_2\text{-}C(CN)_2\text{-}C}(CN)_2]$ whose X-ray structure has been determined.

Preliminary mechanistic results will be provided.

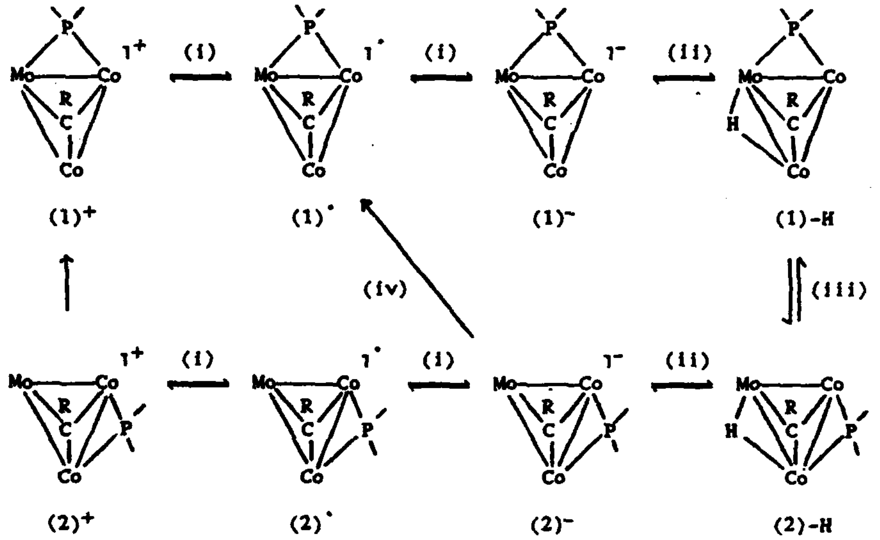




The Synthesis, Reactivity and Redox Properties of Phosphido-bridged Clusters

M.R. Bradford and J.C. Jeffery, Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

We are currently examining the synthesis and properties of series of related organometallic clusters in order to identify redox induced cluster activation reactions with organic or inorganic substrates. The phosphido-bridged complexes under investigation are typically prepared *via* controlled addition of either PPh_2H or $LiPPh_2$ to appropriate neutral precursors such as $[MoCo_2(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$.[1-4] Some reactions of phosphido-clusters derived from the latter complex are shown below:



Peripheral ligands omitted for clarity. (i) ±1e, (ii) $\pm H^+$, (iii) isomerises under ambient conditions, (iv) −1e, isomerisation may proceed *via* $(2)^{\bullet}$, $(2)^+$, and $(1)^+$.

Chemical and electrochemical studies suggest the existance of a complex series of isomeric cationic, radical, anionic and neutral hydride species. We have identified novel redox induced phosphide-bridge isomerisation of $(2)^-$ to $(1)^{\bullet}$ and can also isolate closely related kinetic and thermodynamic isomers [eg. $(1)^-$ and $(2)^-$]. Clusters of the types shown appear to be accessible for a wide variety of metal-ligand combinations and potentially have a rich and diverse chemistry. Thus treatment of $(1)^{\bullet}$ with $[W{\equiv}CR(CO)_2(\eta\text{-}C_5H_5)]$ gives initially a tetrametal radical which subsequently fragments to give good yields of the dimetal radical $[MoCo\{\mu\text{-}(RC{\equiv}CR)\}(\mu\text{-}PR_2)(CO)_3(\eta\text{-}C_5H_5)]^{\bullet}$. Controlled cluster expansion may also be achieved, thus (2)-H with $[Rh(CO)_2(\eta\text{-}C_9H_7)]$ sequentially affords the new tetra- and penta-nuclear clusters $[MoCo_2Rh(\mu_3\text{-}CR)(\mu\text{-}CO)_2(\mu\text{-}PR_2)(CO)_5(\eta\text{-}C_5H_5)]$ and $[MoCoRh_3(\mu_3\text{-}CR)(\mu_3\text{-}CO)(\mu\text{-}CO)_3\text{-}(\mu\text{-}PR_2)_2(CO)_4(\eta\text{-}C_5H_5)]$.

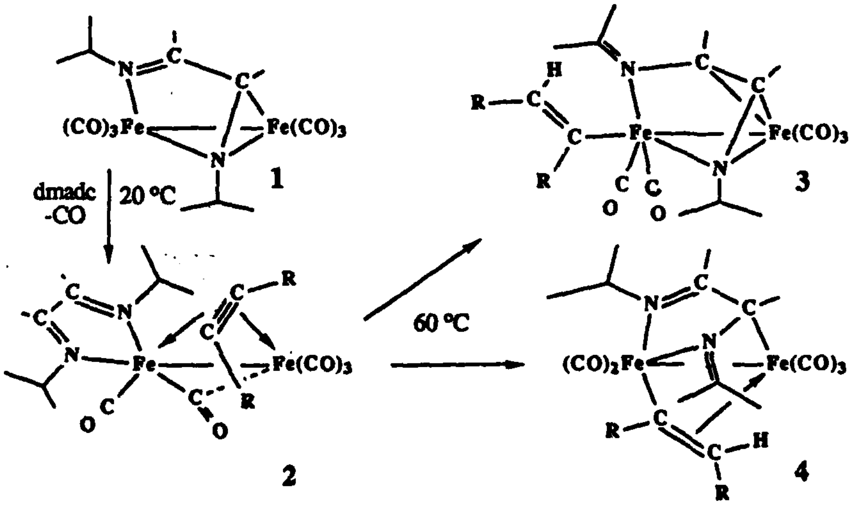
References

1. J.C. Jeffery and J.G. Lawrence-Smith, *J. Chem. Soc., Chem. Commun.*, 1985, 275-277.
2. J.C. Jeffery and J.G. Lawrence-Smith, *J. Organomet. Chem.*, 1985, 280, C34-C38.
3. J.C. Jeffery and J.G. Lawrence-Smith, *J. Chem. Soc., Chem. Commun.*, 1986, 17-19.
4. P. Dunn, J.C. Jeffery, and P. Sherwood, *J. Organomet. Chem.*, 1986, 311, C55-C59.

UNUSUAL HYDROGEN MIGRATIONS FROM AN α-DIIMINE LIGAND TO A COORDINATED ALKYNE ON A DIIRON CARBONYL COMPLEX

Fred Muller, Kees Vrieze, Gerard van Koten, Laboratory for Inorganic Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, Holland

$Fe_2(CO)_6$(iPr-DAB) (1) [iPr-DAB = iPr-N=CHCH=N-iPr], with a σ-N,μ_2-N',η^2-C=N' bridging 6e donating α-diimine ligand, reacts with MeOC(O)C≡CC(O)OMe (dmadc) to give $Fe_2(CO)_5$-(σ,σ-N,N'-iPr-DAB)(μ_2,η^2-dmadc) (2) (X-ray) with a chelating DAB ligand and a perpendicular bridging alkyne. Its formation proceeds via the substitution of the η^2-C=N bonded imine moiety in 1 by an η^2-C≡C bonded alkyne, followed by the loss of one CO ligand. Complex 2 shows a remarkable thermally induced rearrangement involving the migration of one of the DAB iPr methine protons to the coordinated alkyne, resulting in the formation of two isomeric products 3 and 4. In $Fe_2(CO)_5$[η^1-MeOC(O)C=CHC(O)OMe][Me_2C=N-CHCHN-iPr] (3) (X-ray) the alkyne is transformed into a monodentate bonded vinyl fragment and the DAB into a σ-N-imino-η^3-aza-allyl ligand. In the other isomer, $Fe_2(CO)_5$[μ_2,η^2-MeOC(O)C=CHC(O)OMe][iPr-N=CHCH-N=CMe_2] (4) the vinyl ligand is bridging both metal centers. The formation of the two different isomers probably originates from the reaction of the alkyne with the two different i-Pr methine protons in 2. The proton transfer most likely proceeds directly from the DAB to the alkyne and does not involve a metal-hydride intermediate. These results show that not only η^2-C=N coordinated imine fragments, but also chelate bonded DAB ligands are activated towards reactions with alkynes.



CRYSTAL STRUCTURES OF SEVERAL TRIOSMIUM CLUSTERS AND THE GEOMETRIES OF CALCULATED HYDRIDE POSITIONS IN THESE CLUSTERS.

Kenneth I. Hardcastle, Tim McPhillips, Michael Day and Houri
Minassian, Department of Chemistry, California State University
Northridge, Northridge, CA 91330, USA
and
Alejandro Arce, Centro de Quimica-IVIC, Caracas, Venezula.

The crystal and molecular structures of several triosmium clusters as well as clusters containing two trimetal-cluster rings connected by the $[CH\equiv CCO_2]^-$ ligand are presented. Examples are $HOs_6(CO)_{20}(O_2C_3H)$, $H_2Os_6(CO)_{19}(O_2C_3)$ and $HRu_3Os_3(CO)_{20}(O_2C_3H)$. The mode of attachment of the acetylenic end of the ligand to the triosmium unit is examined as well and the overall geometry of the molecule.

The program HYDEX by Guy Orphen at Bristol University has been used to calculate bridging hydride positions in the above mentioned binuclear clusters as well as in numerous other triosmium cluster molecules. The X-ray structures of several compounds are presented along with an examination of the hydride positions calculated using HYDEX versus the hydride positions predicted from a consideration of the geometry of the ligands around the metal atoms in the cluster.

ELECTROCHEMICAL BEHAVIOUR OF SOME ORGANOMETAL-CLUSTERS

Silvio Aime, Mauro Botta, Roberto Gobetto, Domenico Osella
Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei
Materiali, Università di Torino, Via P. Giuria 7, 10125 Torino (Italy)

Franco Laschi, Piero Zanello
Dipartimento di Chimica, Università di Siena (Italy)

The electrochemistry of transition metal clusters represents one of the most recent aspects of their characterization and a good test for their catalytic activity in reactions involving redox sequences. In binary metal carbonyls, the HOMO and LUMO are generally metal-metal bonding and anti-bonding in character, respectively, thus the anodic oxidation and the cathodic reduction cause quick and irreversible cluster degradation.

The coordination to the metallic frame of a large organic chain, able to clasp several metal atoms together and to improve the electronic delocalization over the entire molecule, increases the life-times of the electrogenerated ionic species when compared with parent clusters / 1-3 /. So,organometal-clusters often exhibit electrochemical and chemical reversibility and formal redox potentials can be evaluated ; consequently, electronic and thermodynamic information can be obtained making use of free-energy correlations.

The electrochemical behaviour of two series of organometal-clusters, namely $M_3(CO)_8(Alkyne)_2$ (M=Fe, Ru) and $Fe_2(CO)_6$(Butatriene) will be discussed along with the related electron-tranfer catalyzed (ETC) reactions.

Work supported by European Economic Community.

1) P.Zanello,S.Aime,D.Osella,Organometallics,1984,3,1374
2) D.Osella,R.Gobetto,P.Montangero,P.Zanello,A.Cinquantini, Organometallics,1986,5,1247
3) D.Osella,M.Botta,R.Gobetto,F.Laschi,P.Zanello,Organometallics 1988,7,283

REDUCTION OF THE PHOSPHORUS-BRIDGING CARBONYL GROUP IN CARBONYLBIS(DIISOPROPYLAMINOPHOSPHIDO)HEXACARBONYLDIIRON

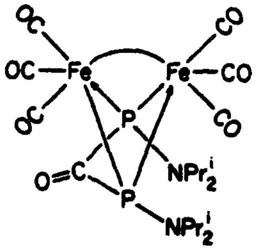
R. B. King, Department of Chemistry, University of Georgia, Athens, GA 30602, U.S.A.

F. -J. Wu, Department of Chemistry, University of Georgia, Athens, GA 30602, U.S.A.

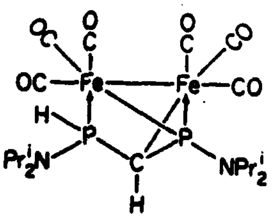
E.M. Holt, Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, U.S.A.

Reaction of iPr_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether solution results in migration of a carbonyl group from iron to phosphorus to give the phosphorus-bridging carbonyl complex $(iPr_2NP)_2COFe_2(CO)_6$(I) in ~35% yield thereby making this air-stable complex readily available in ~40 gram quantities. This complex can be regarded as a novel analogue of a ketone in which the carbonyl group is bonded to two phosphorus atoms rather than two carbon atoms. This paper summarizes studies on the reduction of the phosphorus-bridging carbonyl group in this complex with diverse reducing agents.

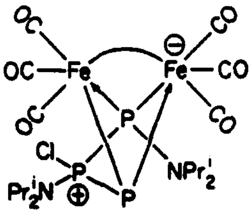
Treatment of $(iPr_2NP)_2COFe_2(CO)_6$ with $NaBH_4$ in methanol results in reduction of the phosphorus-bridging carbonyl group to give the corresponding secondary alcohol $(iPr_2NP)_2CHOHFe_2(CO)_6$. Similar treatment of $(iPr_2NP)_2COFe_2(CO)_6$ with $LiAlH_4$ in diethyl ether results in more extensive reduction to give a product of stoichiometry "$(iPr_2NP)_2CH_2Fe_2(CO)_6$" shown, however, by X-ray diffraction to be $[iPr_2NPCHPHNiPr_2)Fe_2(CO)_6$ (II) in which an iron-phosphorus bond has been broken and a new iron-carbon bond formed. Treatment of $(iPr_2NP)_2COFe_2(CO)_6$ with the alkyllithiums RLi (R=Me, nBu) results in addition to the phosphorus-bridging carbonyl group to give the corresponding tertiary alcohols $(iPr_2NP)_2C(R)(OH)Fe_2(CO)_6$. Reduction of $(iPr_2NP)_2COFe_2(CO)_6$ with sodium amalgam in tetrahydrofuran results in cleavage of a diisopropylamino group to give the anion $[iPr_2NPCOPFe_2(CO)_6]^-$ which can be isolated as its orange bis(triphenylphosphine) iminium salt or as the light orange trimethyltin derivative $(iPr_2N)(Me_3Sn)P_2COFe_2(CO)_6$. Reaction of $[iPr_2NPCOPFe_2(CO)_6]^-$ with iPr_2NPCl_2 results in rearrangement with expulsion of the phosphorus-bridging carbonyl group to give orange $[(iPr_2NP)(iPr_2N)(Cl)PP]Fe_2(CO)_6$ shown by X-ray diffraction to have a structure III with a triphosphorus chain bridging a $Fe_2(CO)_6$ unit through the end phosphorus atoms. One of the end phosphorus atoms of this triphosphorus chain is an ordinary diisopropylaminophosphido group whereas the other end phosphorus atom is trigonal pyramidal with a lone pair. The center atom of this triphosphorus chain is four-coordinate being bonded to the other two phosphorus atoms, a diisopropylamino group, and a chlorine atom.



I



II



III

ACTIVATION OF PHENYLACETYLENE IN COMPLEXES WITH Re_2 AND Re_2Mo_2 FRAMEWORK

A.D.Shaposhnikova, R.A.Stadnichenko, V.K.Belsky, I.L.Eremenko,
A.A.Pasynsky, A.V.Bogatsky Physico-Chemical Institute, Academy
of Sciences of the Ukrainian SSR, 86, Chernomorskaya doroga,
270080, Odessa, U S S R

Alkyncontaining complexes of transition metals are of interest as the model systems allowing to study the mechanism of the formation of catalyticallyactive intermediates in heterogeneous catalysis on the molecular level.

By the direct synthesis from $Re_2(CO)_{10}$ and HC CPh at UV radiation in ether hydride acetylenide complex $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)$ (I) was obtained which is an intermediate in rearrangement of phenylacetylene complexes. Regeneration of HC≡CPh as its complex with heterometallic cluster takes place in the reaction of complex 1 with $Cp_2Mo_2(CO)_6$ in boiling o-xylene during the first five-six hours. X-Ray structural analysis has shown that the resulting cluster $Cp_2Mo_2Re_2(CO)_8(\mu\text{-}CO)_2(\mu^4,\eta^2\text{-}PhC{\equiv}CH)$ (II) contains a heterometallic framework "butterfly" Re_2Mo_2 with a dihedral angle 110,7°. Bond C≡C of phenylacetylene ligand is coordinated by the type μ^4,η^2 and is extended (1,47(2)Å) unlike noncoordinated C≡C bond (1,22(1)Å) and it is situated parallel the bond $Mo^1\text{-}Re^2$. The presence of hydrogen in molecule PhC≡CH is proved by the singlet in ^1H-NMR spectrum in weak fields (δ 11,83 a.f. relative TMS).

At the further running of the reaction (10-11 hours) the transformation of complex II to heterometallic cluster $Cp_2Re_2Mo_2(\mu\text{-}H)\cdot(CO)_7(\mu\text{-}CO)(\mu^4,\eta^4,\eta^1\text{-}C{\equiv}C)(\mu,\eta^1,\eta^2\text{-}Ph)$(III) takes place. In cluster III the separation of hydrogen from phenylacetylene ligand and coordination of acetylenide according to σ-π type are observed.

III also contains heterometallic framework "butterfly" Re_2Mo_2 with dihedral angle 119,5°, the length of bond C≡C of phenylacetylenide ligand is 1,48(1)Å. Electron-unsaturated cluster III (60 electrons) is an intermediate; in its coordination sphere the introduction of small molecules is possible.

VIBRATIONAL SPECTRA AND STRUCTURES OF BIS(ETHENE)TETRACARBONYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN.

George Davidson and Claire Davies, Department of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom.

The stable bis(ethene) complexes, $(C_2H_4)_2M(CO)_4$, where M = Cr, Mo or W, have recently been synthesised.[1] As part of a study of the vibrational spectra of transition-metal ethene complexes, e.g. [2,3], we now report on the infrared and Raman spectra of the complexes with M = Mo or W, both as solids and as solutions in hexane and liquid xenon.

Almost complete vibrational assignments have been obtained for both complexes. The results show that 'local symmetry' approximation is not valid for the $M(CO)_4$ units, and that the molecules maintain D_{2h} symmetry in solution.

The vibrational assignments for the ethene fragment show that there is very little coupling between the two C_2H_4 units, and that a $(C_2H_4)M$ model of C_{2v} symmetry is adequate. The predominantly C=C stretching mode is at $1185cm^{-1}$ (M = W) or $1210cm^{-1}$ (M = Mo). The $M-(C_2H_4)$ stretching modes, however, reveal that some vibrational coupling does occur in the skeletal modes; the totally symmetric $W-C_2H_4$ stretch, for example, appears as a doublet (333, 369 cm^{-1}), due to in-phase and out-of-phase motions of the $(C_2H_4)-W-(C_2H_4)$ unit.

Force field calculations for the $M-C_2H_4$ fragment for M = Mo(0), W(0), Fe(0), Pt(0) and Pt(II) suggest that the M-C bond strength is in the sequence W(0) > Mo(0) > Pt(II) > Fe(0) > Pt(0). Similar calculations for the $M(CO)_4$ units (M = Mo or W), and comparison with the parent hexacarbonyls give useful information on the relative bonding abilities of C_2H_4 and CO.

1. F.W.Grevels, J.Jacke and S.Ozkar, J. Amer. Chem. Soc. 1987, 109,7536.
2. J.A.Crayston and G.Davidson, Spectrochim. Acta, 1986, 42A,1385.
3. J.A.Crayston and G.Davidson, Spectrochim. Acta, 1987, 43A, 559.

SYNTHESIS AND REACTIVITY OF THE COMPLEXES $|MCp_2(SR)(NCR')||PF_6|$ (M=Mo(IV); W(IV); R=aryl or alkyl, R'=aryl derivative

A. R. Dias, M. H. Garcia and M. Paula Robalo
Centro de Química Estrutural, I.S.T., 1096 Lisboa Codex

Previously we have described the chemical oxidation of the complexes $|MCp_2(SR)_2|$ (M=Mo(IV), W(IV); R=alkyl or aryl) with ferricinium cation in the presence of nucleophiles (1). In this communication, we report the synthesis of several nitriles derivatives, $|MCp_2(SR)(NCR')||PF_6|$ (R'=aryl substituted) by the same method.
In order to infer on the π delocalization of the nitrile attached to the organometallic moiety, we present the results of proton magnetic resonance spectra and compare with free ligands. Also we report the results of these compounds by cyclic voltammetry and study their chemical and electrochemical reactivity.

(1) M.J. Calhorda, M.A.A.F. de C.T. Carrondo, A.R. Dias, A.M.T.S. Domingos, M.T.L.S. Duarte, M. Helena Garcia and C.C. Romão
J. Organomet. Chem., 320, 63-81 (1987).

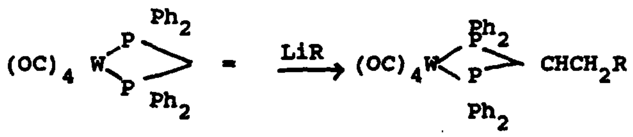
52

SYNTHESIS OF FUNCTIONALIZED DIPHOSPHINE-W(CO)$_4$ COMPLEXES VIA CARBANION ADDITIONS

Salme Koskimies, Neste Co, Research Centre, SF-06850 Kulloo, Finland

Bernard L Shaw, School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom

Treatment of complexes of the type [W(CO)$_4${(Ph$_2$P)$_2$C = CH$_2$}] with functionalized lithium reagents, LiR, followed by hydrolysis gives complexes of the type [W(CO)$_4$(Ph$_2$P)$_2$CHCH$_2$R}] in high yields; R = C$_6$H$_4$OMe-2, C$_6$H$_3$(OMe)$_2$-2.6, C$_6$H$_4$OH-2, C$_6$H$_4$(COOH)-2, CH$_2$COPh or CH$_2$COMe. This result is particularly interesting because addition reaction of functionalized carbanion to vinylene complexes gives a new novel possibility to synthesize functionalized phosphines which would be difficult to make in other ways. Vinylidene diphoshine (Ph$_2$P)$_2$C = CH$_2$ itself is relatively inert towards Michael conjugate addition, but becomes activated while complexed to metal (1,2). Details of the synthesis are discussed.



R = C$_6$H$_4$OMe -2, C$_6$H$_3$(OMe)$_2$, C$_6$H$_4$OH-2, C$_6$H$_4$(COOH)-2, CH$_2$COPh,
CH$_2$COMe

1) G.R. Cooper, D.M. Mc.Evan and B.L. Shaw, Inorg. Chim. Acta 76 (1983) L 165

2) Ibid 122 (1986) 207

P-C(sp^3) BOND CLEAVAGE LEADING TO A VERY REACTIVE UNSATURATED DIMOLYBDENUM CARBONYL COMPLEX.

Victor Riera, Miguel A.Ruiz, Departamento de Química Organometálica. Universidad de Oviedo.33071 Oviedo. Spain.

Fernando Villafañe, Departamento de Química Inorgánica. Universidad de Valladolid. 47005 Valladolid. Spain.

Yves Jeannin, Claudette Bois, Laboratoire de Chimie des Metaux de Transition, UACNRS 419, Université P. et Marie Curie, 4 Place Jussieu, 75252 Paris cedex 05. France.

During decarbonylation and hidrogenation experiments on dppm-brigded dimanganese and dimolybdenum carbonyl complexes (dppm:$Ph_2PCH_2PPh_2$), we have found that carbon-phosphorous ($P-CH_2$) bond cleavage is a relevant process operative under relatively mild conditions (70 - 110ºC). For example, heating $[MoCp(CO)_2]_2(\mu\text{-dppm})$ 1, (Cp:η-C_5H_5) (1) in thf at 70ºC for 30 min.yields $[Mo_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)Cp_2(CO)_2]$ 2 in c.a.65% yield. While the resulting diphosphine cleavage process leading to 2 strongly parallels that one found in $[Fe_2(CO)_7(\mu\text{-}R_2PCH_2PR_2)]$ species (2), an even more interesting feature in 2 arises from its insaturation (Mo═Mo ,on the basis of electron counting), which should markedly increase the synthetic potential of this type of species.

Compound 2 readily reacts with H_2 or CO at r.t.; in the CO reaction, the complex $[Mo_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_3Cp_2]$ 3 is isolated, in which the Mo-Mo bond order has been reduced to one. On the other hand, compound 2 can be protonated and it also reacts with oxidizing agents such as NO^+, $FeCp_2^+$ or I_2; in the latter reaction, a two electron oxidation leads to the dication $[Mo_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)Cp_2(CO)_2]^{+2}$ 4, which formally contains a triple molybdenum-molybdenum bond.

(1) The authors, J.Organomet.Chem., (1988) in press.

(2) N.M.Doherty,G.Hogart,S.A.R.Knox,K.A.Macpherson,F.Melchior and A.G.Orpen, J.Chem.Soc.,Chem.Commun., (1986) 540.

54

SYNTHESIS AND CHARACTERIZATION OF TETRANUCLEAR HYDROXO CARBONYL COMPLEXES, $[Et_4N]_4[M(CO)_3(\mu_3\text{-}OH)]_4$ (M = Mo, W)

Jiann T. Lin, Show K. Yeh, Institute of Chemistry, Academia Sinica,
Nankang, Taipei, Taiwan, Republic of China

Gene H. Lee, Yu Wang, Department of Chemistry, National Taiwan
University, Taipei, Taiwan, Republic of China

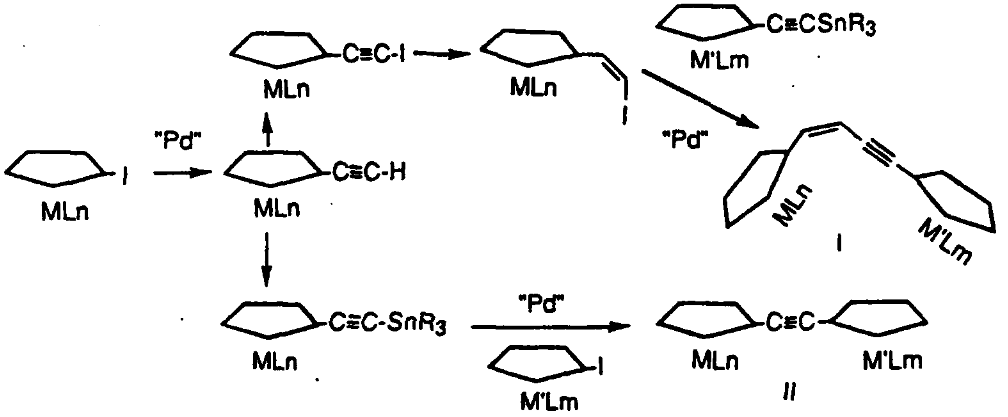
Reaction of $M(CO)_3(PMTA)$ (M = Mo, W; PMTA = 1,1,4,7,7-Pentamethyldiethylenetriamine) With tetraethylammonium hydroxide in aqueous THF solution provides $[Et_4N]_4[M(CO)_3\ (\mu_3\text{-}OH)]_4$ (1, M = Mo; 2, M = W). The crystal structures of both complexes have been determined. Compounds 1 and 2 are iso-sturctural; the crystals are monoclinic, space group C2/C, Z = 4, with unit cell dimensions a = 23.888(7), b = 12.3000(2), c = 23.254(3) Å, β = 123.85(2)° for 1 and a = 23.86(3), b = 12.317(7), c = 23.21(1) Å, β = 123.8(2)° for 2. The anions consist of a distorted A_4B_4(A = metal, B = oxygen)core with triply bridging hydroxide groups and $M(CO)_3$ units. The characterization and reactivity of these species will be described. Noble derivatives of 1 and 2, $(Ph_3PAu)_4M_4(CO)_{12}(OH)_4$ (M = Mo, W), were isolated in good yields.

SYNTHESIS OF HETEROBIMETALLIC CLUSTERS

Claudio Lo Sterzo , Centro di Studio sui Meccanismi di Reazione del C.N.R., c/o Dip. di Chimica, Univ. "La Sapienza", P.le A. Moro,2 00185 Roma, Italy

John K. Stille, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523 U.S.A.

By using the palladium-catalyzed cross-coupling reaction between trialkyltinacetylide and aromatic or vinylic iodide[1], we developed two general routes for the formation of heterobimetallic clusters of the formula I and II:



In our hands, we found that the nature of M and M' can range between groups 4 and 8, allowing a wide variety of combinations. The only requirement for a given metal to be introduced in the synthetic route is the availability of its η^5-iodocyclopentadienyl derivative. Since it can be obtained by metallation/iodination of the corresponding cyclopentadienyl derivative[2], by treatment of cyclopentadienyl diazide with iodometal derivative[3] or by treatment of the metal halide with η^5-iodocyclopentadienyl thallium[4], the possibilities in the combination of M and M' are enormous.

Structures I and II are promising for the investigation of CO reduction by homogeneous catalysis because of the possible cooperative effect of M and M' during the catalytic cycle.

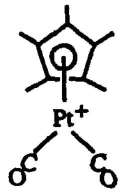
1) J.K.Stille, *Angew.Chem.Int.Ed.Engl.*, 25,(1986), 508
2) T.Yu.Orlova, V.N.Setkina, V.F.Sizoi and D.N.Kursanov, *J.Organomet. Chem.*, 252, (1983), 201
3) K.J.Reimer, and A.Shaver, *J.Organomet.Chem.*, 93 (1975) 239
4) B.G.Conway and M.D.Rausch, *Organometallics*, 4 (1985) 688

56

PENTAMETHYLCYCOPENTADIENYL COMPLEXES OF PLATINUM AND PALLADIUM

Neil M Boag, Majorie E Green, Nicholas Terrill, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

We have recently devised high yield syntheses of $[Pt_2(CO)_2(\eta^5\text{-}C_5Me_5)_2]$ 1 and $[Pd_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_2]$ 2 and converted them into to key precursors $[Pt(\eta^5\text{-}C_5Me_5)(CO)_2]^+$, 3, $[Pt(\eta5\text{-}C_5Me_5)(CO)]^-$, 4, and $[M(\eta^5\text{-}C_5Me_5)(CO)X]$ (5, M = Pd, X = I; 6, M = Pt, X = I, Br, Cl).



M = Pd, X = I, 5
Pt, X = I, 6a
Br, 6b
Cl, 6c

We will discuss the physical and chemical properties of complexes 3-6 and discuss typical and atypical chemistry we find to be associated with complexes of these types.

SYNTHESIS OF ASYMMETRIC BINUCLEAR PENTAFLUOROPHENYL DERIVATIVES OF THE NICKEL GROUP ELEMENTS

Gregorio López, Gabriel García, Concepción de Haro, María D. Santana and Natalia Cutillas

Departamento de Química Inorgánica, Universidad de Murcia, Santo Cristo 1,
30001-Murcia, Spain

The synthesis of neutral binuclear organo-complexes $R_2M(\mu\text{-}X)_2M'L_2$ in which the metal atoms have different coordination environments requires the availability of a labile organometallic complex, $R_2ML'_2$, that can react with a halo-complex, $M'X_xL_2$, to give the desired product. Complexes of the type $(C_6F_5)_2ML'_2$, where L' = dioxane,[1] tetrahydrofurane[2] or benzonitrile[3] should be good precursors for this purpose.

When the benzonitrile complex *cis*-$M(C_6F_5)_2(PhCN)_2$ (M = Ni, Pd, Pt) and the appropriate halo-complex $M'X_2L_2$ (M' = Ni, Pd, Pt; X = Cl, Br, I; L = mono- or bidentate phosphine) are allowed to react in dichloromethane the corresponding homo- or hetero-bimetallic complexes are formed according to the following equation:

$$\underline{cis}\text{-}(C_6F_5)_2M(PhCN)_2 + \underline{cis}\text{-}X_2M'L_2 \longrightarrow (C_6F_5)_2M(\mu\text{-}X)_2M'L_2 + 2PhCN$$

The new compounds have been characterized by microanalyses and IR, ^{19}F- and ^{31}P-NMR spectroscopies. The ^{31}P resonances are clearly influenced by the coordination of $X_2M'L_2$ to the R_2M moiety.

References

(1) García, G.; López, G. *Inorg. Chim. Acta* 1981, *52*, 87.
(2) Usón, R; Forniés, J.; Tomás, M.; Menjón, B. *Organometallics* 1986, *5*, 1581.
(3) De Haro, C.; García, G.; Sánchez, G.; López, G. *J. Chem. Research* (S) 1986, 119; *J. Chem. Research* (M) 1986, 1128.

58

A NEW VIEW OF THE FISCHER-TROPSCH POLYMERISATION REACTION

Peter M. Maitlis, Isabel M. Saez, Neil J. Meanwell, Jesus Martinez,
Kiyoshi Isobe, Amelio Vázquez de Miguel, and Andrew Nutton
Department of Chemistry, The University, Sheffield S3 7HF, England

Recent results on model complexes will be presented which are leading to a new view of the mechanism of the Fischer-Tropsch polymerisation reaction.

Vinyl Complexes of Ruthenium(II): Intermediates in Reductive Elimination, Ring Closure and Catalytic Reactions

Roger Mawby, Department of Chemistry, University of York,
York YO1 5DD, England

Joanne Bray, C.N.R.S., 91190 Gif-sur-Yvette, France

Joseph Crook, Department of Chemistry, Western Washington
University, Bellingham, WA 98225, U.S.A.

Complexes $[Ru(CO)_2XYL_2]$ ($L = PMe_2Ph$ or $AsMe_2Ph$, $X = Y = H$, Me or Cl; $X = H$, $Y = Cl$; $X =$ aryl, $Y = Cl$) react with activated alkynes such as $MeO_2CC{\equiv}CCO_2Me$ to yield vinyl complexes $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)X\}YL_2]$. Where $X \neq Y$, insertion occurs preferentially in an Ru-H bond, and least readily in Ru-Cl. Hydride complexes $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)X\}HL_2]$ exist in solution as pairs of conformers, and slowly rearrange to alkene complexes $[Ru(CO)_2\{CH(CO_2Me)=C(CO_2Me)X\}L_2]$. The compounds $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_4Z\text{-}4)\}ClL_2]$ are formed in a single isomeric form, yet they undergo ring closure at 323 K to give both $[\overline{Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C}_6H_3Z\text{-}4)\}L_2]$ and $[\overline{Ru(CO)_2\{C(CO_2Me)=C(CO}_2)(C_6H_4Z\text{-}4)\}L_2]$, by HCl and MeCl elimination respectively, implying ready interconversion of isomers of the vinyl complexes.

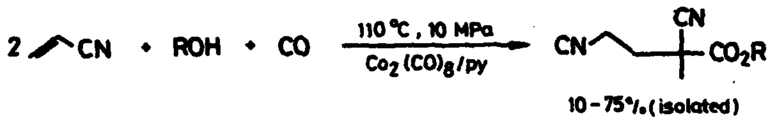
The ease and reversibility of the transfer of organic ligands between mercury and ruthenium are nicely illustrated by our discovery of a catalytic cycle, using $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, for converting diaryl mercury compounds $[Hg(C_6H_4Z\text{-}4)_2]$ to new vinyl compounds $[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4Z\text{-}4)\}(C_6H_4Z\text{-}4)]$ and $[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4Z\text{-}4)\}_2]$. Transfer of an aryl ligand from mercury to ruthenium is followed by alkyne insertion on ruthenium and then by return of the vinyl ligand to mercury.

COBALT CARBONYL MEDIATED MICHAEL ADDITION. DIRECT SYNTHESIS OF DICYANO ESTERS FROM ACRYLONITRILE

Attila Sisak, Ferenc Ungváry

Institute of Organic Chemistry, University of Veszprém,
Schönherz Z.u. 10., H-8200 Veszprém

The hydrocarbalkoxylation of acrylonitrile with stoichiometric amounts of alcohols in the presence of $Co_2(CO)_8$/pyridine catalyst leads directly to 2,4-dicyano-2-methyl-butanoic acid esters[1]:



1

The yield of 1 increases at the expense of two cyanopropionic acid ester byproducts, $NCCH(CH_3)CO_2R$ and $NCCH_2CH_2CO_2R$ (*c.f.* ref 2), with the increasing relative concentration of pyridine, and it has a maximum at $[py]/[Co] \approx 2$. Secondary alcohols give the best yields. Model reactions proved, that the catalytic cycle starts with the addition of $pyH[Co(CO)_4]$ on acrylonitrile giving the alkyl complex $NCCH(Me)Co(CO)_4$ (2). 2 leads to the byproducts through isomerization and/or carbonylation (*c.f.* ref 3), however, it could be also deprotonated by pyridine to a „Michael-donor" anion $NC\bar{C}(Me)Co(CO)_4$, which reacts with acrylonitrile giving 1 after all.

Analogous reactions using equimolar amounts of alcohol, acrylonitrile and an other activated olefin lead to products with at least 3 different functional groups.

1. Sisak,A.; Ungváry,F.; Markó,L. Ger.Offen. DE 3718223 A1, 1987.
2. Matsuda,A. Bull.Chem.Soc.Jap. 1967, 40, 135.
3. Ungváry,F.; Markó,L. Organometallics 1986, 5, 2341.

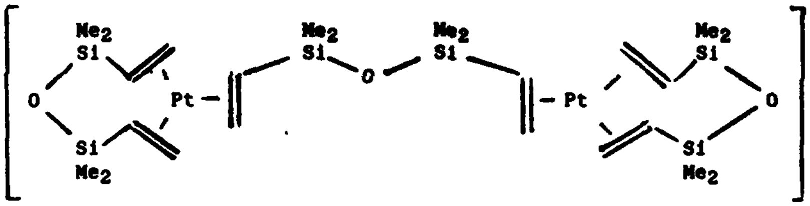
Pt(0) AND Rh(I) HYDROSILYLATION CATALYSTS CONTAINING CHELATING AND/OR BRIDGING DIVINYLDISILOXANES

Peter B. Hitchcock, Michael F. Lappert, Nigel Sarjudeen, and
Nicholas J.W. Warhurst

School of Chemistry and Molecular Sciences, University of Sussex, Falmer,
Brighton, U.K.

It has recently been shown by Chandra, Lo, Hitchcock, and Lappert that the hydrosilylaton catalyst (solution A), obtained by refluxing $H_2[PtCl_6].xH_2O$ in $(ViSiMe_2)_2O$, is a Pt(0) species, from which further Pt(0) complexes may be isolated.[1]

We shall show that solution A comprises a mixture of two diastereoisomers (variable temperature ^{195}Pt, ^{29}Si, ^{13}C, ^{1}H, and 2D-^{1}H COSY n.m.r. spectroscopy). The crystalline complex isolated from A was a single (*rac*) diastereoisomer (1) (*X*-ray data), also obtained from $[Pt(cod)_2]$ and $(ViSiMe_2)_2O$.



(1)

A crystalline Rh(I) complex, $[\ Rh(\eta\text{-}ViSiMe_2)_2O)(\mu\text{-}Cl)\ _2]$ (2) (*X*-ray data) was obtained from $[\{Rh(\eta\text{-}C_8H_{14})_2(\mu\text{-}Cl)\}_2]$ and $(ViSiMe_2)_2O$; (2) was not accessible directly from $RhCl_3.3H_2O$ and the divinyldisiloxane.

We shall report extensions of this chemistry, including results of investigations of (a) the hydrosilylation catalytic activity of (1) and (2); (b) the function of solution (A) or complexes (1) or (2) as a convenient source of further Pt(0) or Rh(I) complexes, such as $[Pt(Sn(NR_2)_2)_3]$ $(R = SiMe_3)$;[2] (c) the role of $(ViSiMe_2)_2O$ as a reducing agent in noble metal chemistry; and (d) the mechanistic implications of the formation of (1) from $H_2[PtCl_6].xH_2O$ and $(ViSiMe_2)_2O$.

We thank Dow Corning PLC (Barry) and S.E.R.C. for the award of a CASE studentship to N.J.W.W. and Drs. A.G. Avent, P.Y. Lo, and R.G. Taylor for useful discussions.

References

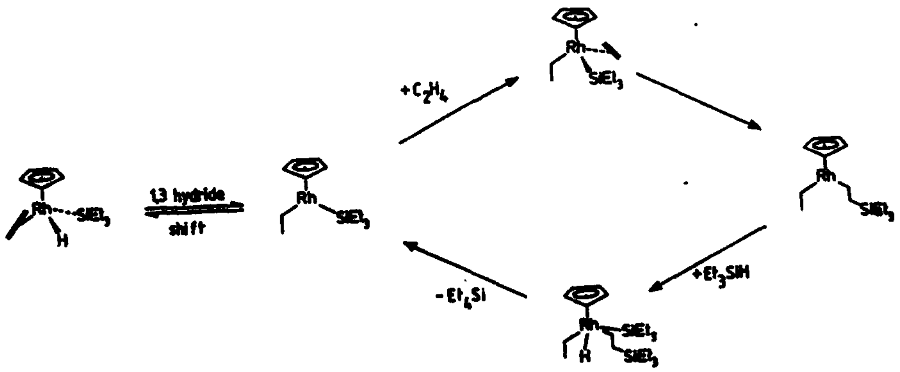
1. G. Chandra, P.Y. Lo, P.B. Hitchcock, and M.F. Lappert, *Organometallics*, 1987, 6, 191.
2. P.B. Hitchcock, M.F. Lappert, and M.C. Misra, *J. Chem. Soc., Chem. Commun.*, 1985, 863.

The Mechanism of Hydrosilation by $CpRh(C_2H_4)(SiEt_3)(H)$

Simon B. Duckett and Robin N. Perutz

Department of Chemistry, University of York, York YO1 5DD, U.K.

Photolysis of $CpRh(C_2H_4)_2$, (1), ($Cp = \eta^5-C_5H_5$) in the presence of excess Et_3SiH at 213K yields $CpRh(C_2H_4)(SiEt_3)H$, 2, and no hydrosilation products. Similar photolysis of 1 at 300K yields 2, $CpRh(SiEt_3)_2(H)_2$ (3) and hydrosilation products. Isolation of 2 has enabled us to test whether it is directly involved in the catalytic cycle of hydrosilation as would be expected from the Chalk-Harrod mechanism. If 2 is placed under C_2H_4 + Et_3SiH, catalytic hydrosilation occurs producing Et_4Si. When C_2D_4 is used in place of C_2H_4 the main hydrosilation product is $Et_3SiCD_2CD_2H$, but no incorporation of C_2D_4 into 2 was observed after four catalytic cycles. Furthermore, reaction of 2 with propene + Et_3SiH gives the corresponding hydrosilation products, but no new Rh products. These results are consistent with the mechanism below in which a 1,3-H shift generates the 16e intermediate $CpRh(Et)(SiEt_3)$ (4). In subsequent steps (i) C_2H_4 coordinates, (ii) the silyl group migrates onto coordinated ethene and (iii) Et_3SiH adds to form a Rh(V) species (compare 3), (iv) Et_4Si is eliminated reforming 4. This mechanism retains the integrity of the C_2H_4 group of 2 but does not regenerate 2 in the catalytic cycle.

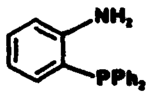


IRIDIUM COMPLEXES WITH P-N LIGANDS AS CATALYSTS FOR SELECTIVE HYDROGENATION.

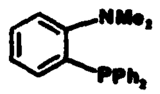
Erica Farnetti and Mauro Graziani
Dipartimento di Scienze Chimiche, Universita' di Trieste,
Piazzale Europa 1, 34127 Trieste, Italy.

The potentially chelating phosphines P-NH_2 and P-NMe_2 [1] are employed as ligands in the preparation of iridium-based hydrogenation catalysts, starting from $[Ir(cod)(OMe)]_2$.

P-NH_2 =



P-NMe_2 =



In the presence of such systems, benzylideneacetone is reduced to the corresponding unsaturated alcohol with yields up to 90% when using P-NH_2. On the basis of ^1H and ^{31}P NMR data we suggest the catalytically active species to be $H_2\overline{Ir(P-N}H)(P-NH_2)_2$, which is formed via N-H oxidative addition to the metal.

The selectivity in carbonyl group reduction could be ascribed to a steric control on the coordination mode of the substrate, which is induced by the presence of three phosphines in the coordination sphere of the iridium atom. Such a steric control of the selectivity has also been suggested in the recently reported hydrogenation of α,β unsaturated carbonyl compounds by $H_3Ir(PR_3)_3$.[2]

References

1. a) T.Rauchfuss and D.M.Roundhill, J.Mol.Catal., 1973, **59**, C30. b) M.K.Cooper and J.M.Downes, Inorg.Chem., 1978, **17**, 880.
2. a) E.Farnetti, M.Pesce, J.Kaspar, R.Spogliarich, and M.Graziani, J.Chem.Soc.Chem.Commun., 1986, 746.
   b) E.Farnetti, M.Pesce, J.Kaspar, R.Spogliarich, and M.Graziani, J.Mol.Catal., 1987, **43**, 35.
   c) E.Farnetti, J.Kaspar, R.Spogliarich, and M.Graziani, J.Chem.Soc.Dalton Trans., in the press.

KEY INTERMEDIATES OF THE RUTHENIUM COMPLEX CATALYZED HYDROSILYLATION AND METATHESIS

Bogdan Marciniec and Jacek Guliński

Faculty of Chemistry, A.Mickiewicz University, 60-780 Poznań,Poland

Ruthenium chlorophosphine as well as ruthenium chloride based complexes appeared to be novel effective catalysts for hydrosilylation of C=C bonds in alkenes |1,2| and vinylsilanes |2| as well as for metathesis of vinylsubstituted silanes |3|. Some requirements for these reactions e.g. the presence of alkoxy substituents at silicon in hydrosilanes and in vinylsilanes, traces of dioxygen and inhibition by any solvent used, determined the program of ruthenium-silyl intermediate examinations.

A series of reactions of the substrates (triethoxysilane, vinylsilanes) and other ethoxysubstituted silanes (tetraethoxysilane, alkylethoxysilane) with $RuCl_2(PPh_3)_3$ and $RuCl_3 \cdot nH_2O$ under conditions close to those in the processes studied, allow to isolate ruthenium-silyl complexas characterized by various spectroscopic and other physico-chemical methods. The isolated complexes were subsequently tested in the hydrosilylation of C=C bond and metathesis of vinylsilanes. Complexes prepared under oxygen-free conditions do not show any activity in the hydrosilylation of 1-alkenes, whereas the influence of various factors on ruthenium-carbenes initiation as catalysts for the metathesis is more complex.

The most active isolated complexes provide the basis for mechanistic considerations of the reactions studied.

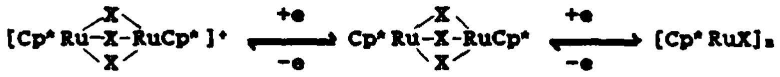
1. B.Marciniec and J.Guliński, J.Mol.Catal., 10,123(1981).
2. B.Marciniec and J.Guliński, J.Organometal.Chem., 253,349(1983).
3. B.Marciniec and J.Guliński, J.Organometal.Chem., 266,C19(1984).

Stoichiometric and catalytic reactions of Cp*Ru complexes

U. Koelle, J. Kossakowski and R. Boese[§]

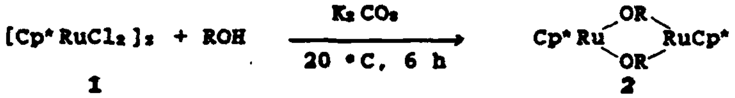
Institute of Inorganic Chemistry, Technical University of Aachen,
D-5100 Aachen, G.F.R.

The potential role of complexes $Cp^*RuL_nX_m$ as redox catalystst was investigated. A survey of the electrochemical behavior of three groups, i.e. Cp^*RuL_2X (I), Cp^*RuLX_2 (II) and $[Cp^*RuX_2]_2$, (III) ($Cp^* = h^5\text{-}C_5Me_5$, X = Cl, Br, I) showed group I to give reversible Ru(II/III) electron transfer ($E_{1/2} \simeq 0$ V vs.SCE), whereas the redox behavior of II is complex being associated with loss of X ($E_p \simeq -0.4$ V vs.SCE). A two step reversible electron transfer is observed for group III in MeOH ($E_{1/2} \simeq 0$ V vs.SCE) according to eq (1):

(1) 

$$[Cp^*Ru\overset{X}{\underset{X}{-X-}}RuCp^*]^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} Cp^*Ru\overset{X}{\underset{X}{-X-}}RuCp^* \underset{-e}{\overset{+e}{\rightleftharpoons}} [Cp^*RuX]_2$$

$[Cp^*RuCl_2]_2$, 1 acts as an electrocatalyst for alcohol oxidation (e.g. E_{o1}. 0.7 V vs. SCE for MeOH). In the presence of a base it is reduced by alcohols in a thermal reaction according to eq (1) giving dinuclear alcoxo complexes 2[1].

(2) 

$$\underset{1}{[Cp^*RuCl_2]_2} + ROH \xrightarrow[20\ °C,\ 6\ h]{K_2CO_3} \underset{2}{Cp^*Ru\overset{OR}{\underset{OR}{\diamond}}RuCp^*}$$

2a (R = Me) was characterized by single crystal x-ray diffraction as a folded dimer (Ru-Ru 295 pm) with 16-electron-ruthenium. Alcoxo complexes 2 are reative not only in complexation reactions (3) but also towards acids and oxygen.

(3) $[Cp^*RuOR]_2 + 4\ L \longrightarrow 2\ Cp^*RuL2OR$

(4) $[Cp^*RuOR]_2 + 2\ HX \longrightarrow 2\ [Cp^*Ru]X + 2\ MeOH$

Various aspects of the reactions of 2 are discussed.

---

§) Institute of Inorganic chemistry, University of Essen, D-4300 Essen, G.F.R.; X-ray structure.

1) U. Koelle and J. Kossakowski, J. Chem. Soc. Chem. Commun. in print.

66

OXIDATION OF ORGANIC SUBSTRATES BY PHOSPHINO-COMPLEXES OF RHODIUM, IRIDIUM, RUTHENIUM AND OSMIUM.

Mario Bressan and Antonino Morvillo.

Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Universita' di Padova, via F.Marzolo 1, 35131 Padova, Italy.

We report here the preliminary results of an investigation carried out with a number of complexes $[M(diphos)_2]BF_4$ (M=Rh, Ir) and $[MCl(DPPP)_2]X$ (M=Ru, Os; DPPP=1,3-bis(diphenylphosphino)propane; X=PF_6, ClO_4) using LiClO as oxidant of alkenes, alkanes, alcohols and ethers.

In a typical catalytic experiment, a dichloromethane solution containing the complexes (1-2 mM) and the substrate (0.1-1 M) was stirred with an excess of aqueous LiClO (0.1-1 M), and aliquots monitored by gas-chromatography. Ruthenium and osmium complexes were stable and active for week-long periods. On the contrary, $[Ir(diphos)_2]BF_4$ rapidly collapsed becoming inactive under these conditions. The related rhodium(I) derivative was instantaneously and quantitatively transformed to a new complex, presumably of rhodium(III), which appears to be the active catalyst.

Secondary alcohols, cyclic and linear ethers were oxidized in high yields to ketones, lactones and esters respectively. Olefins gave epoxides as main products, although in the case of phenyl-substituted alkenes another route was operating which led to products of the oxidative cleavage (benzaldehyde, acetophenone). Under the same conditions, cyclohexane produced small amounts of cyclohexanone.

Work supported by C.N.R. (Centro Stabilita' Reattivita' Composti di Coordinazione) and Ministero Pubblica Istruzione.

NEW INTERCONVERSIONS IN THE LIGAND SPHERE OF CLUSTERS

Heinrich Vahrenkamp, Institut für Anorganische und Analytische Chemie
Universität Freiburg, Albertstr. 21,
D-7800 Freiburg, Deutschland.

The ability of organometallic clusters to stabilize reactive organic species by multicenter attachment provides the possibility to elucidate bonding modes, stabilities, and reactivities of such species. In this context the following subjects will be addressed:

1. Synthetic aspects: reactive tri- and tetranuclear clusters, capping with unsaturated substrates, metal fragment plus substrate assembly reactions.

2. Reactivity: rearrangement of multiply bonded substrates, C-C and N-N cleavage, metal attachment and removal, insertion into cluster-C and cluster-H bonds.

3. Mechanistic aspects: maintenance of the cluster identity during reactions, fate of substrate fragments, metal-metal versus metal-substrate bond labilities, stereochemistry of reactions involving chiral clusters.

CHELATING AND BRIDGING BEHAVIOUR OF THE LIGANDS $Ph_2PCH_2CH_2EPh_2$ (E = P or As) in $HRu_3(C\equiv CBu^t)(CO)_7(Ph_2PCH_2CH_2EPh_2)$

ENRICO SAPPA
Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Corso M. d'Azeglio 48, I-10125 Torino, Italy

GIOVANNI PREDIERI and ANTONIO TIRIPICCHIO
Istituto di Chimica Generale ed Inorganica, Università di Parma, Viale delle Scienze, I-43100 Parma, Italy

Symmetrical or asymmetrical bidentate ligands are useful for stabilizing bimetallic and cluster frames[1] (in view of homogeneous catalytic applications involving reversible metal-metal bond cleavage) or for inducing chirality even in suitable homometallic clusters.[2,3]

We have recently synthesized the chiral cluster $HRu_3(C\equiv CBu^t)(CO)_7(dppm)$ (dppm = $Ph_2PCH_2PPh_2$), which crystallizes as an ordered racemic array of the two enantiomers.[3] The diphosphine dppm, which substitutes two carbonyls in equatorial positions, bridging two ruthenium atoms, blocks the localized CO scrambling processes but promotes a novel fluxional mechanism, inducing the acetylide rotation and the contemporary hydride transfer.

On the other hand, by reacting the parent cluster $HRu_3(C\equiv CBu^t)(CO)_9$ with the bidentate ligands $Ph_2PCH_2CH_2EPh_2$ (E = P, dppe; E = As, dppae) in the presence of Me_3NO, we obtained in both cases two isomers of the complexes $HRu_3(C\equiv CBu^t)(CO)_7(Ph_2PCH_2CH_2EPh_2)$, which have been separated by TLC. In the first the ligands chelate the ruthenium atom opposite to the bridging hydride, whereas in the second they bridge a hydride-free edge, as can be deduced from ^1H and ^{31}P NMR spectra. When dppae behaves as bridging ligand the phosphorus atom is bonded to the ruthenium opposite to the hydride. When chelating, the ligands do not show any fluxional behaviour, when bridging, interconversion between axial and equatorial positions has been observed.

In conclusion, the rather rigid ligand dppm produces only one isomer and promotes acetylide fluxionality, whereas the less sterically demanding ligands dppe and dppae give two isomers and show some mobility.

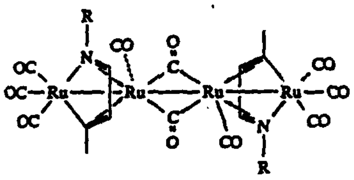
References

1. R.J.Puddephatt, Chem.Soc.Rev., 12 (1983) 99
2. J.Collin, C.Jossart, and G.Balavoine, Organometallics, 5 (1986) 203
3. G.Predieri, A.Tiripicchio, C.Vignali and E.Sappa, J. Organomet. Chem., 342 (1988) C33

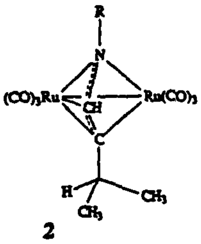
Dehydrogenation and coupling of monoazadienes on ruthenium carbonyl fragments.

C.J. Elsevier and W.P. Mul.
Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

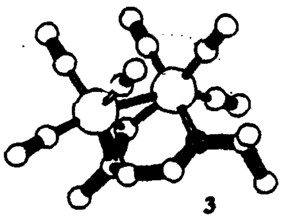
The organometallic and coordination chemistry of monoazadienes (which contain the N=C-C=C moiety) currently receives renewed interest [1,2]. For instance, a new 7 electron coordination mode of the monoazadienyl ligand in the linear tetranuclear complex 1 has recently been described [2]. Compound 1, which can be imagined as an analogue of $Cp_2Ru_2(CO)_4$, arises as a major product of the thermal reaction of CH_3-CH=CH-CH=NR with $Ru_3(CO)_{12}$ in heptane. Here we report new organoruthenium compounds (2-4) which are formed in reactions of homologs $(CH_3)_2$C=CH-CH=NR with $Ru_3(CO)_{12}$. Due to the absence of a H-atom at the appropriate position, a metallated product like 1 cannot be formed. Instead, at 85 °C in heptane, azaallylic complex 2 emerges as the result of a 1,2-H shift. At 100 °C also compounds 3 and 4 (X-ray) arise, probably via insertions of Ru into C-H bonds of one methyl group. Furthermore, as a minor product, an intriguing pyridinium complex 5 (X-ray) is found, the organic part of which can overall be viewed as the condensation product of two monoazadienes with net loss of RNH_2.



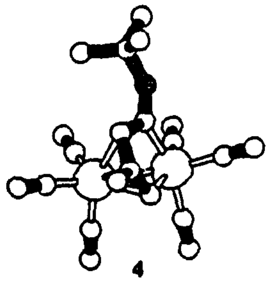
1



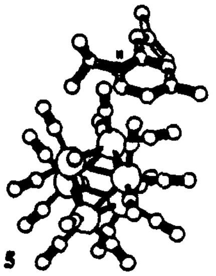
2



3



4



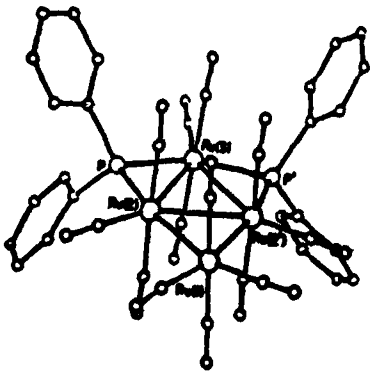
5

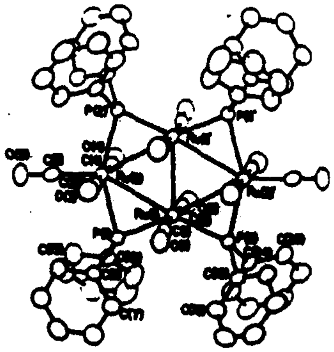
[1] H. tom Dieck, L. Stamp, R. Diercks, C. Müller, Nouv. J. Chim., 1985, 9, 289.
[2] L.H. Polm, W.P. Mul, C.J. Elsevier, K. Vrieze, Organometallics, 1987, 7, 423.

The Synthesis and Structural Characterisation of a Series of 64- electron Phosphido Stabilised Tetraruthenium Butterfly Clusters.

Graeme Hogarth, Jacquie A. Phillips, Nicholas J. Taylor, Todd B. Marder and Arthur J. Carty.
Department of Chemistry, University of Waterloo, Waterloo, Ontario,
Canada, N2L 3G1.

Tetranuclear complexes containing a butterfly arrangement of metal atoms are generally characterised by a 62-electron count and contain a folded core, while a 64-electron count is attributed to a square or metalloligated triangular geometry. During the course of our studies on phosphide stabilised clusters we have synthesised a series of 64-electron tetranuclear complexes which contain a planar butterfly framework with elongated ruthenium-ruthenium bonds, namely $[HRu_4(CO)_n(\mu\text{-}PPh_2)_m]$ (n= 11,14; m= 3,1) and $[Ru_4(CO)_x(\mu\text{-}PPh_2)_y]$ (x= 10,13; y= 4,2). The synthesis, spectroscopic features, structural chemistry and reactivity of these electron-rich clusters typified by (1) and (2) will be described.


(1)


(2)

TRIPLY-BRIDGING FORMS OF PYRROLE AND RELATED LIGANDS IN TRIOSMIUM CLUSTERS

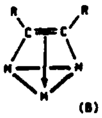
Antony J Deeming, Department of Chemistry, University College London,
20 Gordon Street, London WC1H 0AJ, Great Britain.

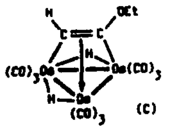
Alejandro J Arce and Ysaura De Sanctis, Chemistry Center, Instituto
Venezolano Cientificas, Apartado 1827, Caracas 101, Venezuela.

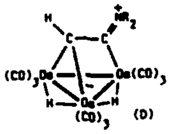
Kenneth I Hardcastle and Michael Day, Department of Chemistry, California
State University Northridge, Northridge, California 91330, U.S.A.

Triply-bridging alkynes adopt either vertical perpendicular orientations (A) or tilted parallel orientations (B) in trinuclear clusters which may be described as closo or nido respectively in PSEP theory. Thus $M_3(RC_2R)(CO)_9$ (M = Fe, Ru, or Os) have structure (A) while $M_3(RC_2R)(CO)_{10}$ or $M_3H_2(RC_2R)(CO)_9$ (M = Ru or Os) have structure (B). π-Donor substituents X in $Os_3H_2(HC_2X)(CO)_9$ can lower the energy of a perpendicular form to make alkyne rotation more rapid as when X = OEt (C)[1] or even make the perpendicular form the more stable as when X = NR_2 (R = H or Et) (D).[2]

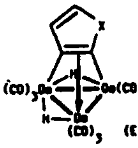

(A)

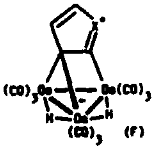

(B)

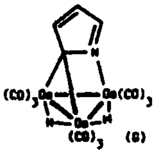

(C)

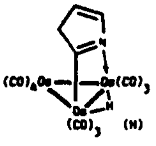

(D)

The clusters $Os_3H_2(C_4H_2X)(CO)_9$ (X = S, O, NH, or NMe)[3] containing dehydrogenated forms of thiophene, furan, or pyrrole as ligands adopt the parallel mode (E) (X-ray structures for X = S or NMe) but with some contribution from (F) (greatest when X = NMe). When X = NH the aromatic form (E) readily isomerises to the non-aromatic N-bonded perpendicular form (G). The structure of the non-aromatic derivative of pyrrole $Os_3H(C_4H_4N)(CO)_{10}$ (H) is also described.


(E)


(F)


(G)


(H)

Indole forms analogues of (E) and (H) but the analogue of (G) is inaccessible because the benzo-group would need to span a single bond.

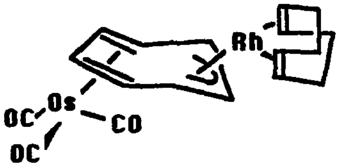
REFERENCES:
1. E Boyar, A J Deeming, M S B Felix, S E Kabir, T Adatia, R Bhusate, H Powell, and M McPartlin, J.C.S.,Dalton Trans., in press.
2. E Boyar, A J Deeming, and S E Kabir, J.C.S.,Chem.Commun., 1986, 577; A J Deeming, S E Kabir, and D Nuel, unpublished results.
3. A J Arce, Y De Sanctis, and A J Deeming, J.Organometal.Chem., 1986, 311, 371.

USE OF $K^+(C_7H_7)Os(CO)_3^-$ IN THE SYNTHESIS OF CYCLOHEPTATRIENYL BRIDGED HETEROBIMETALLIC COMPLEXES

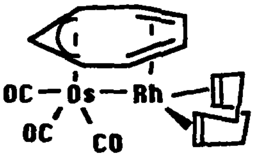
Stephen T. Astley and Josef Takats, Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Anionic cycloheptatrienyl complexes of the form $(C_7H_7)M(CO)_3^-$ (M = Fe,Ru,Os) are ideal precursors for the formation of cycloheptatrienyl bridged heterobimetallic complexes upon reaction with unsaturated transition metal halides. We have previously reported on the utility of the Fe and Ru derivatives in this regard.[1,2]

The corresponding anionic osmium complex, $K^+(C_7H_7)Os(CO)_3^-$ (1), has been obtained by deprotonation of (η^4-cycloheptatriene)Os(CO)$_3$ with KO^{t}Bu. 1 reacts with $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) to give 2 as the major product where the two metals straddle the seven membered ring.



2



3

The more robust cis isomer, 3, containing a metal-metal bond is a minor product in this reaction. The different bonding of the cycloheptatrienyl ring in the two isomers is clearly seen in the ^1H N.M.R. spectra of the complexes. Whilst at room temperature, ring whizzing is observed for both 2 and 3, the low temperature limiting spectra for 2 is obtained readily upon cooling.

In an effort to change the reactivity pattern of the anionic osmium complex, the use of alternative deprotonating agents such as butyl lithium is being investigated. Further reactions with other suitable transition metal substrates is also being pursued.

1. R.G.Ball, F.Edelmann, G.Y.Kiel, J.Takats and R.Drews. Organometallics 5 (1986) 829.
2. F.Edelmann, G.Y.Kiel, J.Takats, A.Vasudevamurthy and M.Y.Yeung. J. Chem. Soc. Chem. Commun., in press.

MULTIPLE CARBON-CARBON BOND CLEAVAGE ON A HEPTAOSMIUM CLUSTER: THE SYNTHESIS AND MOLECULAR STRUCTURE OF $Os_7(CO)_{18}(\mu_3\text{-CPh})_2$ AND $Os_7(CO)_{15}(\mu_3\text{-CPh})_4$

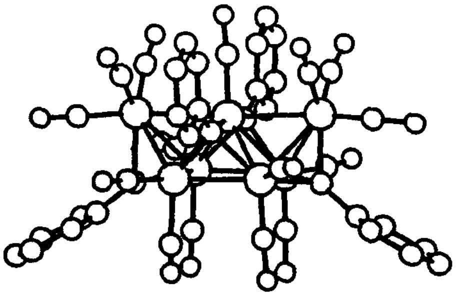
Dario Braga and Fabrizia Grepioni, Dipartimento di Chimica "G. Ciamician", Universita' di Bologna, via Selmi 2, I-40126 Bologna, Italy

Brian F. G. Johnson, Jack Lewis, and Julie Lunniss, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

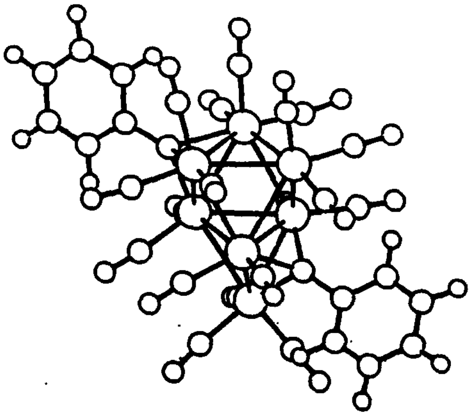
The dihydrido cluster $H_2Os_7(CO)_{20}$[1] (1) reacts with Ph_2C_2 in toluene under reflux to initially produce a brown compound (2), then a green compound (3) and finally, after an extended period (~3 days), a purple compound (4). Neither the ^{1}H n.m.r. nor mass spectral data were particularly informative, save for verifying the presence of phenyl ligands in all three complexes. However, X-ray quality crystals of (2) and (4) could be obtained by slow evaporation of a tetrahydrofuran solution at room temperature.

The X-ray diffraction study identified (2) and (4) as $Os_7(CO)_{18}(\mu_3\text{-CPh})_2$ and $Os_7(CO)_{15}(\mu_3\text{-CPh})_4$, respectively. Both species contain three-electron donor μ_3-CPh groups originated by carbon-carbon cleavage of the Ph_2C_2 reagent.

It should be emphasized that the μ_3-CPh ligands in (4) supply 12 electrons to the cluster: never before such an extensive electron contribution by ligands other than CO has been observed for Os-clusters. What is more, the starting $H_2Os_7(CO)_{20}$ species undergoes remarkable metal core rearrangements in the course of the reaction yielding two different Os_7 polyhedra, wich share the same electron counting of 98 electrons. It is also noteworthy that the square base of the square pyramid in (4) is unsupported.



$Os_7(CO)_{15}(\mu_3\text{-CPh})_4$ (4)



$Os_7(CO)_{18}(\mu_3\text{-CPh})_2$ (2)

---

1) E. J. Ditzel, H. D. Holden, B. F. G. Johnson, J. Lewis, A. Saunders, and M. J. Taylor, J. Chem. Soc., Chem. Commun., 1982, 1373.

The Varied Substitution Chemistry of $H_3BiRu_3(CO)_9$

Brian F. G. Johnson, Jack Lewis, Paul R. Raithby and Alan J. Whitton.
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW,
Great Britain.

The substitution chemistry of the recently reported mixed metal bismuth ruthenium cluster $H_3BiRu_3(CO)_9$ (1,2) is prolific and varied. The three bridging hydride ligands in the parent molecule makes the identification of the products by ^1H n.m.r. a simple process. This, together with the recent development of a high yield synthetic route to the parent carbonyl, (2) makes this cluster ideally suited to a detailed study of it's substitution chemistry, and allows the resolution of isomeric mixtures found in solution.

While it has not been possible as yet to coordinate organic ligands directly to the cluster, the substitution of carbonyl ligands by phosphines, phosphites, arsines, stibines and isocyanides has suggested the existence of 13 of the possible 27 *unique structures* that can be envisaged for mono-, bis- and tris- substitution of this cluster. In no instance has evidence been obtained which would suggest that greater than one CO per Ru atom has been replaced. We have found that isocyanide ligands have a coordination preference at equatorial sites whilst the more bulky, *s* -donor ligands (ER_3; E= P, As, Sb) exhibit an axial preference. Polydentate isocyanide and phoshine ligands have been used to force the cluster into adopting further configurations.

From the results of these experiments we are able to propose a simple model to explain all the observations which is based on the steric interactions of the ligands. Although the steric model encompasses the observation that more than one ligand will not occupy the same metal atom, we believe that the more important reason is that the additional electron density on the substituted Ru atom deactivates the atom towards further CO loss.

References.

1) H. G. Ang, C. M. Hay, B. F. G. Johnson, J. Lewis, P. R. Raithby, and A. J. Whitton, *J. Organometal. Chem.*, 1987, **330**, C5.

2) B. F. G. Johnson, J. Lewis, P. R. Raithby, and A. J. Whitton, *J. Chem. Soc., Dalton Trans.*, In the Press.

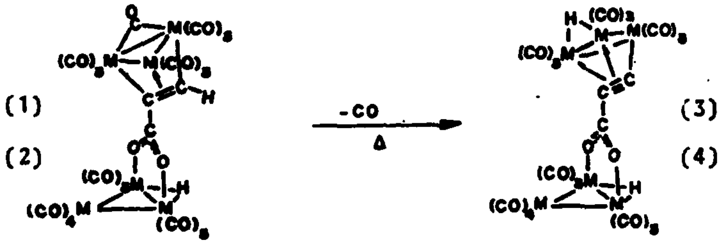
REACTIONS OF ACETYLENIC ALDEHYDES, ETHERS AND CARBOXYLIC ACIDS WITH TRIOSMIUM AND TRIRUTHENIUM CLUSTERS

ALEJANDRO J. ARCE and YSAURA DE SANCTIS, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020-A, Venezuela.

ANTONY J. DEEMING, University College London, Department of Chemistry, 20 Gordon St., London WC1H OAJ, U.K.

The hydrido cluster $[Os_3H_2(CO)_{10}]$ reacts with CH≡CCHO to give $[Os_3H(CO)_{10}(CH_2{=}CCHO)]$ in which the ligand is bridging as a three-electron donor through the oxygen and the unsaturated α-carbon atoms[1]. On thermolysis, two compounds are formed. One is the isomer $[Os_3H(CO)_{10}(cis\text{-}CH{=}CHCHO)]$ which has an open structure with two Os-Os bonds, since the organic ligand is now a five-electron donating bridge. The other product is the dinuclear derivative $[Os_2H(CO)_6(cis\text{-}CH{=}CHCHO)]$. The clusters $[Os_3H_2(CO)_{10}]$ and $[M_3(CO)_{10}(MeCN)_2]$ (M=Ru or Os) react with CH≡CH$_2$OMe to give $[M_3(CO)_{10}(CH{=}CCH_2OMe)]$ (M=Ru or Os), $[Os_3(CO)_9(RCCHCOCH{=}CR)]$ and $[Os_3(CO)_9\{(RC_2H)_2CO\}]$ (R=CH$_2$OMe), where the last two correspond to alkyne-coupled products.

$[Os_3H_2(CO)_{10}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ react smoothly with CH≡CCO$_2$H to give, as expected, the carboxylate derivative $[Os_3H(CO)_{10}(CH{\equiv}CCO_2)]$ which contains an uncoordinated alkyne group[2]. We reacted this compound with $[M_3(CO)_{10}(MeCN)_2]$ (M=Ru or Os) to give two new linked clusters in high yields: $[Os_6H(CO)_{20}(\mu^5\text{-}CH{\equiv}CCO_2)]$ (1) and $[Os_3Ru_3H(CO)_{20}(\mu^5\text{-}CH{\equiv}CCO_2)]$ (2). Decarbonylation of (1) and (2) affords in quantitative yields the compounds (3) and (4), in which the organic ligand acts as an eight-electron donor system, a remarkable number of electrons for such a small ligand.



1. A.J. Arce, A.J. Deeming, Y. De Sanctis, J. Organomet. Chem., 1985, 295, 365.
2. A.J. Arce, A.J. Deeming, Y. De Sanctis, POLYHEDRON, Symposium in Print, 1988.

76

APPLICATIONS OF TWO-DIMENSIONAL NMR SPECTROSCOPY TO ORGANOMETALLIC CHEMISTRY

Paul S. Pregosin and Christian Ammann, Laborat. für anorganische Chemie, ETH-Z, Universitätstr. 6, CH-8092 Zürich, Switzerland

C. Anklin and H. Rüegger, Spectrospin AG, CH-8117 Fällanden, Switzerland

Organometallic chemistry is frequently associated with complex dynamic molecules. Historically, various NMR methods have been employed to recognize, trace and quantify these rate processes, e.g., line shape analysis and magnetization transfer techniques are two commonly used methodologies.

Two-dimensional ^{31}P and ^{1}H-NMR exchange methods complement these techniques and provide some subtle advantages. Using examples drawn from simple coordination chemistry of Pt(II), followed by some rather complicated simultaneous exchange phenomena involving $Pt\{CH_2C(CH_3)CH_2\}(SnCl_3)(styrene)$ we will demonstrate the strength and weakness of this methodology.

In a second chapter we will illustrate some few applications of inverse 2-D X nucleus-NMR spectroscopy where subtle structural questions were solved using metal atom NMR data.

III. RHODIUM(II) CARBOXYLATE-CATALYSED REACTIONS OF DIAZOESTERS : AN EQUILIBRIUM BETWEEN FREE CARBENE AND A METAL-CARBENE COMPLEX

A. Demonceau, A.F. Noels, J.-L. Costa, and A.J. Hubert,
University of Liège, Sart-Tilman (B.6), B-4000 Liège, Belgium

A comparative study of alkane homologation by **ethyl diazoacetate** and **diethyl diazomalonate**, catalysed by various rhodium(II) carboxylates, indicates that two different active carbene species, a metal-carbene intermediate and presumably the "free" carbene, are involved in these reactions.

Indeed, we have observed that the homologation of alkanes by **ethyl diazoacetate** dramatically depends on the method of decomposition (photolysis, thermolysis, or catalysis) of the diazo compound and on the nature of the rhodium(II) counter-ions. This is consistent with the involvement of the previously proposed metal-carbene intermediate [*].

On the contrary, several characteritics of the functionalisation of alkanes by **diethyl diazomalonate** are almost independent on the mode of decomposition of the diazo precursor, as well as on the ligands of the rhodium catalyst. This suggests a different active species that does not include the metal. Therefore, the free carbene formed by dissociation of the metal-carbene complex is a good candidate within the possible following mechanism :

$$\begin{tikzcd} L_nM{=}CXY \arrow[r, shift left] \arrow[d, "RH"] & L_nM \arrow[l, shift left] & + & :CXY \arrow[d, "RH"] \\ RCXYH & & & RCXYH \end{tikzcd}$$

$L_nM = Rh(O_2C\text{-}R)_4Rh$
$CXY = CHCO_2Et$ or $C(CO_2Et)_2$

(a) R.G. Salomon and J.K. Kochi, *J. Am. Chem. Soc.*, 95, 3300 (1973); (b) A. Nakamura, A. Konishi, R. Tsujitani, M. Kudo, and S. Otsuka, *Ibid*, 100, 3449 (1978); (c) A.J. Anciaux, A.J. Hubert, A.F. Noels, N. Petiniot, and Ph. Teyssié, *J. Org. Chem.*, 45, 695 (1980); (d) H.J. Callot, F. Metz, and C. Piechocki, *Tetrahedron*, 38, 2365 (1982); (e) M.P. Doyle, R.L. Dorow, W.E. Buhro, J.H. Griffin, W.H. Tamblyn, and M.L. Trudell, *Organometallics*, 3, 44 (1984); (f) M.P. Doyle, J.H. Griffin, V. Bagheri, and R.L. Dorow, *Ibid*, 3, 53 (1984).

A. Demonceau, A.F. Noels, J.-L. Costa, and A.J. Hubert, submitted for publication.

THE REACTION OF A RUTHENIUM(II) DICHLOROCARBENE COMPLEX WITH PYRROLE: THE DIPYRROMETHYLIDENE LIGAND.

G.R. Clark, D.J. Hodgson, M.M.P. Ng, C.E.F. Rickard, W.R. Roper and L.J. Wright, Department of Chemistry, The University of Auckland, Auckland, New Zealand.

Metal bound electrophilic dihalocarbene centres can, in an intramolecular reaction, add to the phenyl rings of *cis*-coordinated PPh_3 ligands[1]. In a related intermolecular version of this reaction, the electrophilic carbene centre in $RuCl_2(=CCl_2)(CO)(PPh_3)_2$[2] has been found to add to the aromatic heterocycle, pyrrole, to form $RuCl_2[=C(Cl)(2\text{-}C_4H_4N)](CO)(PPh_3)_2$(1). The structure of this complex has been determined by X-ray crystallography and noteworthy features are the long $C_{carbene}\text{-}Cl$ bond, the large $Ru\text{-}C_{carbene}\text{-}C_{pyrrole}$ angle and the hydrogen bonding of the N-H proton to the *cis* metal bound chloro-ligand.

Compound (1) undergoes further reaction with pyrrole, in the presence of base, forming $\overline{RuCl[=C(2\text{-}C_4H_3N})(2\text{-}C_4H_4N)](CO)(PPh_3)_2$, (2). Compound (2) adds HCl giving $RuCl_2[=C(2\text{-}C_4H_4N)_2](CO)(PPh_3)_2$ (3), while base reconverts (3) to (2). Compound (3) contains the novel dipyrromethylidene ligand and compound (2) has an unusual chelate ligand with both carbene and amido donor functions. The X-ray crystal structure of compound (2) and further reactions of compounds (1) - (3) will be reported.

References

1. W.R. Roper, J. Organometal. Chem., 1986, 300, 167.

2. W.R. Roper and A.H. Wright, J. Organometal. Chem., 1982, 232, C39.

PHOTOCHEMICAL REACTIONS OF DECACARBONYLDIRHENIUM WITH ALLENE AND DERIVATIVES OF ALLENE

Cornelius G. Kreiter, Wolfgang Michels und Udo Heeb
Fachbereich Chemie der Universität Kaiserslautern
D-6750 Kaiserslautern, Bundesrepublik Deutschland

Decacarbonyldirhenium (I) reacts at low temperatures photochemically with monoolefins, dienes or trienes predominantly under loss of CO and oxidative addition of a C-H-bond to octacarbonyl-μ-hydrido-μ-$\eta^{1:2}$-olefinyl-dirhenium complexes [1]. With cumulated dienes like allene (IIa), and its methylated derivatives (IIb - IIf), $[Re_2(CO)_{10}]$ shows a totally different photoreactivity. A wide variety of mono- and dinuclear rhenium complexes are obtained, with allene, and hydrocarbon ligands, formed from the allenes by H-shift, dimerization and co-oligomerization with CO.

$$\underset{\text{I}}{[Re_2(CO)_{10}]} + \underset{\text{IIa - IIf}}{C_3H_{4-n}(CH_3)_n} \longrightarrow \text{IIIa - XIIIf}$$

1,2-propadiene	(IIa)	IIIa, IVa, Va, VIa
1,2-butadiene	(IIb)	IIIb, IVb
2,3-pentadiene	(IIc)	IIIc, IVc, VIIc, VIIIc
3-methyl-1,2-butadiene	(IId)	IIId, VIId, IXd, Xd, XId
2-methyl-2,3-pentadiene	(IIe)	IIIe, VIIe, VIIIe, IXe, Xe, XIIe
2,4-dimethyl-2,3-pentadiene	(IIf)	IXf, Xf, XIIIf

The types of products depend on the number and position of the methyl substituents in the allenes. Eleven different types of complexes were isolated by HPL chromatography. With the exception of IIf all allenes form $[Re_2(CO)_8(\mu\text{-}\eta^{2:2}\text{-}C_3H_{4-n}(CH_3)_n)]$ (IIIa - IIIe; n = 0 - 3) with bridging allene ligands. With IIa - IIc $[Re_2(CO)_9(\mu\text{-}\eta^{3:1}\text{-}C_3H_{4-n}(CH_3)_n)]$ (IVa - IVc; n = 0, 1, 2) are the common products. Allenes with two and three methyl groups add hydrogen and form the simple enyl complexes $[Re(CO)_4(\eta^3\text{-}C_3H_{5-n}(CH_3)_n)]$ (VIIc - VIIe; n = 2, 3). In addition, IId - IIf show a metal induced isomerization to the corresponding conjugated dienes in $[Re_2(CO)_8(\mu\text{-}\eta^{2:2}\text{-}C_4H_{6-n}(CH_3)_n)]$ (IXd - IXf; n = 1, 2, 3), and $[Re_2(CO)_9(\mu\text{-}H)(\mu\text{-}\eta^{1:2}\text{-}C_4H_{5-n}(CH_3)_n)]$ (Xd - Xf; n = 1, 2, 3).

Unique products are obtained in several cases. 2-Methyl-2,3-pentadiene (IIe) forms by 1,2-H-shift a trimethylated bridging propenyliden ligand, found in the carbene complex $[Re_2(CO)_8(\mu\text{-}\eta^{1:2}\text{-}CH_3CCHC(CH_3)_2)]$ (XIIe). Only 3-methyl-1,2-butadiene (IId) shows a co-oligomerization with CO to 2,5-di-i-propenylcyclopentanone. The cyclopentanone is coordinated in its enol form as a 4-electron donor by a CC-double bond and the oxygen to the $[(CO)_5Re_2(CO)_3]$ fragment in XId. The permethylated allene IIf forms tricarbonyl-η^5-2,4-dimethyl-2,4-pentadien-1-ylrhenium (XIIIf).

Three types of complexes with allene dimeres as ligands were isolated. Allene (IIa) yields a $[Re_2(CO)_8]$ complex with tetramethyleneethane (Va) and a $[Re_2(CO)_7]$ complex with vinyltrimethylenemethane (VIa) as bridging ligands. IIc and IIe form $[Re_2(CO)_7]$ complexes with $\eta^{1:2:1.2}$-1,5-hexadien-2,5-diyl and CO bridges.

---

[1] a) K. H. Franzreb und C. G. Kreiter, Z. Naturforsch., 37B (1982) 1038; b) K. H. Franzreb und C. G. Kreiter, J. Organometal. Chem., 246 (1983) 189; c) K. H. Franzreb und C. G. Kreiter, Z. Naturforsch., 39B (1984) 81; d) C. G. Kreiter, K. H. Franzreb, W. Michels und U. Schubert, Z. Naturforsch., 40B (1985) 1188, e) C. G. Kreiter, K. H. Franzreb und W. S. Sheldrick, Z. Naturforsch., 41B (1986) 904.

80

Water Oxidative Addition to Pd(0) Phosphine Complexes in the Presence of Lewis Bases.

Piero Leoni, *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56100 Pisa, Italy.*

Cristina Di Bugno, and Marco Pasquali, *Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, 56100 Pisa, Italy.*

Hydrido-hydroxy complexes derived from water oxidative addition to transition metals are supposed to be intermediates in water activation. Late-transition metal complexes tend to form unstable metal hydrido-hydroxy derivatives (e.g. $Pt(H)(OH)(PR_3)_2$)[1], and only recently a full characterization of a stable hydrido-hydroxy iridium complex has been reported[2].
We report here the preparation and characterization of a Pd(II) phosphine complex derived from oxidative addition of water in the presence of Lewis acids.
$Pd(PCy_3)_2$ (Cy = cyclohexyl) reacts in toluene solution with water in the presence of a stoichiometric amount of $BF_3 \cdot Et_2O$ yielding the colourless insoluble complex $[Pd(H)(OH)(PCy_3)_2] \cdot BF_3$. This compound, which can be handled at room temperature for some hours both in the solid state and in solution without noticeable decomposition, has been fully characterized by analytical and spectroscopic data.

Acknowledgements: This work was supported by the 'Ministero Italiano della Pubblica Istruzione', thanks are due to ENI (Milano) for a Research Fellowship to C.D.B.

1. S. Otsuka, et al., J. Am. Chem. Soc., 101, 2027, (1979).
2. D. Milstein, et al., J. Am. Chem. Soc., 108, 6387, (1986).

^{57}Fe MÖSSBAUER AND ^{31}P NMR SPECTROSCOPIC CHARACTERIZATION OF $Fe(CO)_3L^1L^2$ COMPLEXES (L^1, L^2 = PHOSPHITE OR PHOSPHINE)

Hidenari Inoue, Takeshi Kuroiwa and Tsuneo Shirai, Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan

Ekkehard Fluck, Gmelin-Institut der Max-Planck-Gesellschaft, Varrentrappstr. 40/42, D-6000 Frankfurt am Main 90, FRG

A variety of mixed ligand complexes of the type $Fe(CO)_3L^1L^2$ (L^1 = triphenylphosphine or triphenylphosphite and L^2 = phosphine or phosphite) have been synthesized by the stepwise reactions of phosphine and phosphite with iron dodecacarbonyl. These mixed ligand complexes provide a good opportunity to study the Fe-P bond by ^{57}Fe Mössbauer and ^{31}P NMR spectroscopy. All the ^{57}Fe Mössbauer spectra of trans-$Fe(CO)_3L^1L^2$ gave a quadrupole-splitting doublet typical of the disubstituted iron carbonyls in trigonal bipyramidal symmetry. The isomer shift and the quadrupole splitting fall into the range characteristic of disubstituted iron carbonyls with D_{3h} symmetry. A linear correlation with a positive slope was found between the quadrupole splittings and the isomer shifts. This linear correlation indicates that the iron-to-phosphorus σ -donation is offset by the phosphorus-to-iron π -back donation. The $^{31}P\{^1H\}$ NMR spectra of trans-$Fe(CO)_3L^1L^2$ complexes gave a couple of doublets assignable to the coordinated phosphite and/or the coordinated phosphine. As expected, the doublet of the phosphite-coordinated site was observed at the downfield compared with that of the phosphine-coordinated site. The change in the chemical shift upon coordination of the phosphine and phosphite ligand, i.e. the coordination shift is associated with the Mössbauer isomer shifts. This suggests that the iron-to-phosphorus π -back donation plays an important role in the formation of the Fe-P bond. A larger coupling constant of $^2J(P,P)$ was observed for trans-$Fe(CO)_3L^1L^2$ (L^1 = triphenylphosphite and L^2 = phosphines), while a smaller coupling constant was found for trans-$Fe(CO)_3L^1L^2$ (both L^1 and L^2 = phosphines or phosphites). The relatively large coupling constant due to $^2J(P,P)$ means that there exists a strong interaction between trans phosphorus ligands through the P-Fe-P bond. The $^2J(P,P)$ coupling constant reflects the bond strength between Fe-P and the Mössbauer isomer shift is also a measure of the strength of the Fe-P bond. In view of this feature a correlation between these spectroscopic parameters will be discussed for trans-$Fe(CO)_3L^1L^2$ complexes.

Organometallic Chemistry of Chelating Oxygen Ligands: Coordination and Catalysis.

W. Kläui
Institut für Anorganische Chemie, TH Aachen
Templergraben 55, D-5100 Aachen, FRG.

We have recently reported that anionic complexes of the type L^- = $[CpM\{P(O)R_2\}_3]^-$ (Cp = C_5H_5, C_5Me_5, M = Co, Rh) react as tris-chelating oxygen ligands with a large variety of metal ions to form stable 2:1 and 1:1 complexes, e.g. $[ML_2]^{(n-2)+}$, M^{n+} = Ti - Zn, $LZrCl_3$, $LMo(O)Cl_2$, $L_2W_2O_5$, and $[LRhCl_3]^-$.[1,2] The ligand field spectra of the transition metal complexes $[ML_2]$ (where the metal ion M is octahedrally coordinated by six P=O oxygen donor centers) allow an unequivocal determination of the electronic properties of the ligands L^-: they are very weak and hard oxygen ligands, comparable to fluoride and oxide in their ligand field strength and about as hard as water.[1] We where therefore surprised to see that most of the organometallic complexes[3] containing oxygen tripod ligands of the type L^-, e.g. the molybdenum and tungsten compounds $LM(CO)_3H$, $LM(CO)_2(\eta^2\text{-}C(O)R)$, $LM(\equiv CPh)(CO)_2$, $L_2M_2(CO)_4$ (*M≡M*), and others like $L(Mn(CO)_3$, $LRu(CO)_2Cl$, $L_2Ru_2(CO)_4$ (*Ru-Ru*), $LRh(\mu\text{-}CO)_3RhL$ (*Rh-Rh*), $LRh(C_2H_4)_2$, $LCu(CO)$, $LCu(PhC\equiv CPh)$ are very stable.

In order to prepare more reactive organometallic derivatives two routes have been envisaged: functionalization of the ligands L^- with the aim of introducing additional labile coordination sites or the substitution of a labile chloride donor site for one of the strongly coordinating P=O oxygen donor centers. An example for the latter possibility is the anionic complex $[(C_6Me_6)RuCl\{P(O)R_2\}_2]^-$, R = OCH_3, which has been shown to act as a ligand with an *O,O,Cl* donor set.[4]

Several of the chelating oxygen ligands have successfully been used as components in catalysts for the cyclotrimerisation of acetylenes and hydroformylation or hydrogenation of olefins.

1 W. Kläui, W. Eberspach, P. Gütlich, Inorg. Chem. 1987, *26*, 3977; W. Kläui, H. Otto, W. Eberspach, E. Buchholz, Chem. Ber. 1982, *115*, 1922.
2 W. Kläui, A. Müller, W. Eberspach, R. Boese, I. Goldberg, J. Am. Chem. Soc. 1987, *109*, 164.
3 W. Kläui, H. Hamers, J. Organomet. Chem., in print; W.Kläui, B.Lenders, B.Hessner, K.Evertz, Organometallics, accepted for publication; W. Kläui, A. Müller, Organometallics 1987, *6*, 1824; M. Scotti, M. Valderrama, S. Rojas, W. Kläui, J. Organomet. Chem. 1986, *301*, 369, and references cited therein.
4 W. Kläui, E. Buchholz, Angew. Chem 1988, *100*(4), in print.

REDOX CHEMISTRY OF DIPHOSPHAZANE LIGAND BRIDGED DERIVATIVES OF DIRUTHENIUM NONACARBONYL

Dennis W. Engel and Edgar C. Horsfield, Department of Physics,
University of Durban-Westville, Private Bag X54001. Durban 4000,
Republic of South Africa.

John S. Field, Ashleigh M.A. Francis, Raymond J. Haines and Jörg
Sundermeyer, U.N./C.S.I.R. Research Unit of Metal Cluster Chemistry,
Department of Chemistry, University of Natal, P.O. Box 375,
Pietermaritzburg 3200, Republic of South Africa.

Reaction of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i), electron-rich derivatives of $[Ru_2(CO)_9]$ with compounds or salts of Cu(I), Au(I) or Hg(II) gives cationic products in which the Group IB or Group IIB metal substrate is co-ordinated either terminally as in $[Ru_2(HgCl)(CO)_5\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$, or in the bridging mode as in $[Ru_2\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$, the structure of the latter being established X-ray crystallographically. Treatment of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (*1*) with Ag(I) salts leads to products whose nature depends on the ligand co-ordinated to the silver. For instance, reaction of (*1*) with an equimolar amount of $AgSbF_6$ in weakly co-ordinating oxygen-donor solvents such as acetone or THF leads to the formation of a half-molar amount of $[Ru_2(CO)_5(solvent)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$ (*2*) and the precipitation of elemental silver. On the other hand reaction of (*1*) with $AgSbF_6$ in MeCN or with $[Ag(pyridine)_4]SbF_6$ in THF, gives $[Ru_2\{\mu\text{-}Ag(L)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ (L = MeCN or C_5H_5N). Solid $[Ru_2\{\mu\text{-}Ag(MeCN)\}(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]$ degrades under vacuum to the one-electron oxidised product $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2][SbF_6]$ (*3*, SbF_6), elemental silver and acetonitrile; (*3*) rapidly disproportionates in solution to give (*1*) and (*2*) an observation which is confirmed by cyclic voltammetric studies of the electrochemical oxidation of (*1*) in acetone and benzonitrile. Thus the one-electron oxidation of (*1*) by certain silver salts to give (*3*) is shown to proceed via an inner-sphere mechanism. The usefulness of the dicationic solvento species (*2*) as a precursor for the synthesis of diruthenium compounds is demonstrated by its facile reaction with neutral *e.g.* L = CO and RNC, and anionic e.g. X^- = H^-, CN^-, OMe^- and $MeCO_2^-$, nucleophiles to give $[Ru_2(CO)_5L\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$ and $[Ru_2(CO)_5L\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$ and/or $[Ru_2(\mu\text{-}X)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^+$.

84

A DOMINANT ROLE FOR STERIC EFFECTS IN THE CHEMISTRY OF RUTHENIUM(II) COMPLEXES WITH 1,2-BIS(DICYCLOHEXYLPHOSPHINO)ETHANE

Antonio Mezzetti, Alessandro Del Zotto and Pierluigi Rigo, Istituto di Chimica, Università di Udine, viale Ungheria 43, I-33100 Udine, Italy

Ruthenium(II) forms six-coordinate complexes of the type $RuX_2(P-P)_2$ (X=halogenide) with some diphosphine ligands [P-P = $R_2P-(CH_2)_n-PR_2$; n= 1, 2, 3; R=Me, Et, Ph].[1] However, with the ligands which form six-membered chelate rings (n=3, R=Ph), also the five-coordinate cations $[RuX(P-P)_2]^+$ have been obtained. We now find that analogous five-coordinate complexes can be prepared also with ligands forming five-membered chelate rings, if the R substituents at the phosphorus atoms are the bulky cyclohexyl groups. The five-coordinate complexes $[RuX(dcype)_2]BPh_4$ [dcype=1,2-bis(dicyclohexylphosphino)ethane; X=Cl, Br, I], formed by reacting dcype with $RuX_2(DMSO)_4$ and an excess of $NaBPh_4$ in ethanol, are fluxional at room temperature on the NMR time scale, and show at low temperature a spectral pattern which suggests a trigonal-bipyramidal structure.

Since there is evidence from both theoretical studies and solid state analyses that five-coordinate d^6 complexes prefer the square-pyramidal geometry over the isomeric trigonal-bipyramidal form, the molecular structure of $[RuCl(dcype)_2]PF_6$ has been determined by X-ray diffractometry. The complex is based on the TBP geometry with two P atoms at the axial positions and two P atoms and the chloride in the equatorial plane. Distortions from the idealized geometry can be attributed both to the bite of the diphosphine ligands and to the steric requirements of the cyclohexyl groups.

According to their coordinatively unsaturated nature, the complexes $[RuX(dcype)_2]^+$ readily add carbon monoxide to yield trans-$[RuX(CO)(dcype)_2]^+$, and their dissolution in a coordinating solvent such as acetonitrile occurs with the formation of the six-coordinate adducts trans-$[RuX(CH_3CN)(dcype)_2]^+$. Consistently with the trans-structure, the ^{31}P NMR spectra of both carbonyl and acetonitrile six-coordinate derivatives show a single sharp signal at room temperature. However, when the temperature is lowered, the singlet broadens, and at 143 K gives rise to a complex pattern which is consistent with an AA'BC spin system. These NMR results have been explained in terms of the steric crowding of the cyclohexyl groups which interact in such a way to destroy the symmetry of the six-coordinate molecule, with the ligand motions sufficiently restricted that the reduction of symmetry is mantained in the NMR time scale.

These results show that the chemistry of both six- and five-coordinate derivatives of ruthenium(II) with dcype is largely determined by the bulkiness of the diphosphine ligand.

References

1) E.A.Seddon and K.R.Seddon, "The Chemistry of Ruthenium"; Elsevier: Amsterdam, 1984.
2) M.Bressan and P.Rigo, Inorg.Chem., 1975, 14, 2286.
3) G.Dyer, J.C.Briggs, and C.A.McAuliffe, J.Chem.Soc., Dalton Trans.,1984, 423.

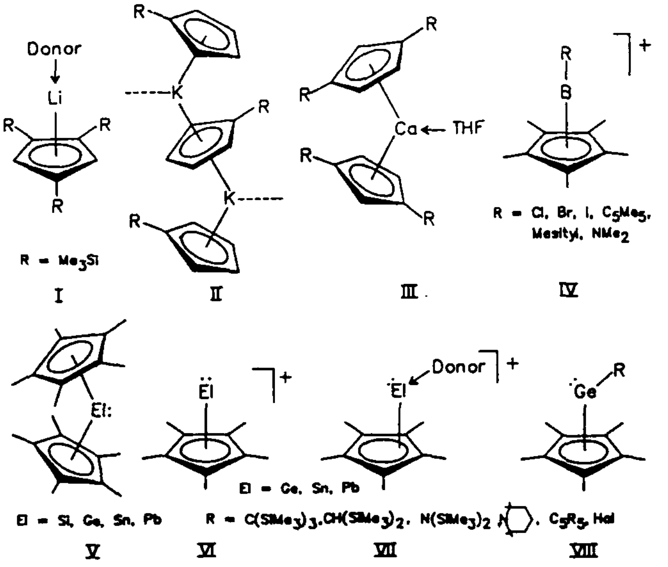
MAIN GROUP METALLOCENES - RECENT DEVELOPMENTS

P. Jutzi, R. Dickbreder, B. Hampel, U. Holtmann, D. Kanne, W. Leffers, A. Möhrke
Faculty of Chemistry, University of Bielefeld, 4800 Bielefeld, FRG

π-Complexation has become an interesting tool in main-group chemistry, as documented by many mainly recent examples [1,2]. The central atoms in the resulting compounds are characterized by low oxidation states and high coordination numbers. Here, some new results concerning synthesis, structure, bonding, and reactivity of π-cyclopentadienyl species are reported.

With trimethylsilylated cyclopentadienyl ligands, hitherto unknown structures are verified in group 1 and group 2 chemistry (see I, II and III).

The pentamethylcyclopentadienyl ligand stabilizes cationic species of type IV in boron chemistry; in group 14, π-complexes of type V - VIII have been realized.



Special emphasis will be given to the synthesis and structure of decamethylsilicocene, $(Me_5C_5)_2Si$:, the first silicon(II) compound stable under ordinary conditions. The chemistry of this π-complex differs importantly from that of the heavier homologues.

[1] P. Jutzi, Adv.Organometal.Chem. 26 (1986), 217
[2] H. Schmidbaur, Angew.Chem. 97 (1985) 893

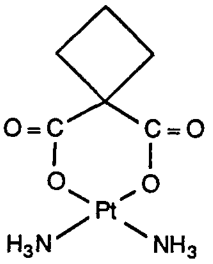
SYNTHESIS, CHARACTERIZATION AND ANTITUMOUR ACTIVITY OF "PARATIN", AN ORGANOTIN(IV) ANALOG OF "PARAPLATIN" ("CARBOPLATIN"), AND OF SOME RELATED COMPOUNDS

Marcel Gielen[@*], Muriel Mélotte[@], and Rudolph Willem[*]

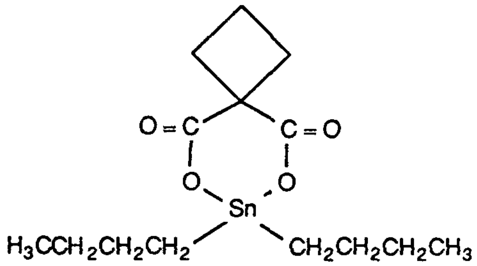
[@]Université Libre de Bruxelles, Faculté des Sciences, Av. F.D. Roosevelt, 50
B - 1050 Bruxelles - Belgium

[*]Vrije Universiteit Brussel, Polytechnische School, Pleinlaan, 2
B - 1050 Brussel - Belgium

The antitumor activity of "paraplatin", (I) was found superior to that of "cis-platin", cis-$Cl_2Pt(NH_3)_2$, in two xenograft systems, colon CX-1 xenograft and epidermoid carcinoma P-246 xenograft, and also against PC 6A plasmacytoma(1).

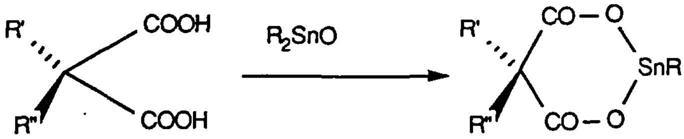


(I)



(II)

Because many diorganotin compounds exhibit some antitumor activity(2), we have prepared in high yield "paratin", (II), an analog of paraplatin, and also some other related di-n-butyltin(IV) derivatives, (III).



(III)

Their spectroscopic properties (^1H, ^{13}C NMR, Mössbauer, IR, and mass spectrometry), used to characterize them, will be discussed, together with the results of the *in vitro* and *in vivo* screening.

(1) Paraplatin (Carboplatin), Compendium of Recent Data, Bristol-Myers, NY, NY 10154 (1987)

(2) A.J. Crowe, The Antitumour Activity of Tin Compounds, Chapter 3 of "Metal-Based Antitumour Drugs", pp. 103-150, Ed. M. Gielen, Freund Publishing House, 1988

PENTACOORDINATE SILICON SPECIES : SYNTHESIS AND REACTIVITY OF NOVEL HYDRIDOALKOXOSILICATES

B. Becker, R. Corriu, C. Guérin, B. Henner and Q. Wang

UA C.N.R.S. N° 1097
Institut de Chimie Fine - Université des Sciences et Techniques
du Languedoc - Place Eugène Bataillon - 34060 Montpellier-cédex (France)

Pentacoordinate hydridosilicates have been assumed as active hydride species of reduction of carbonyl compounds with hydridosilanes promoted by fluoride or alkoxide ions.

We have now prepared several pentacovalent hydridoalkoxosilicate anions for the first time. For instance, reaction of potassium alkoxide with triethoxysilane yielded quantitatively the potassium salt of the hydridotriethoxosilicate, 1, as a white powder :

$$\mathrm{HSi(OEt)_3 + EtOK \xrightarrow[r.t]{THF} \underset{1}{[HSi(OEt)_4]^- K^+}}$$

We examined their chemical behaviors :

- Reactions of 1 with aldehydes and ketones proceed smoothly in THF at 0°C or r.t. to afford the alcohol in high yields after hydrolysis.

- Nucleophilic displacement reactions (Nu = RMgX, ROH, H_2O) can be performed.

- Interestingly, reduction is observed in the reactions of 1 with alkyl halides.

The above data will be discussed and compared to those obtained with the corresponding neutral tetravalent species.

88

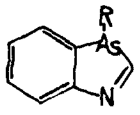
THE CONJUGATIVE ABILITY OF PHOSPHOROUS AND ARSENIC, A UPS STUDY

László Nyulászi, Tamás Veszprémi, Tibor Pasinszky, Gábor Csonka,
József Réffy, Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest, HUNGARY

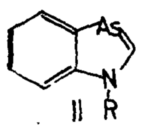
J. Heinicke, Chemistry Section, Martin-Luther University,
402 Halle, Weinbergweg 16, GDR

The conjugative ability of phosphorous and arsenic is generally thought to be similar to that of nitrogen. In the latter case conjugation with a π system can be attained by two different ways. One of them is that nitrogen takes part in *double* π bonds as the case is in imines, piridine etc., while the other possibility is the conjugation of the nitrogen lone pair with the π system as in aniline, pyrrole etc.

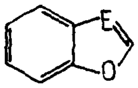
Our photoelectron spectroscopic investigations on aniline analogues showed small interaction between the π system and the phosphorous or arsenic lone pair. Similar conclusion could be drawn by investigating the 3-substituted 1,3-benzazaarsole (I) system.



I



II



III

The 1-substituted 1,3-benzazaarsole system (II), however, shows a large conjugation of the arsenic-carbon double bond and the π system, similarly to the compounds of type III.

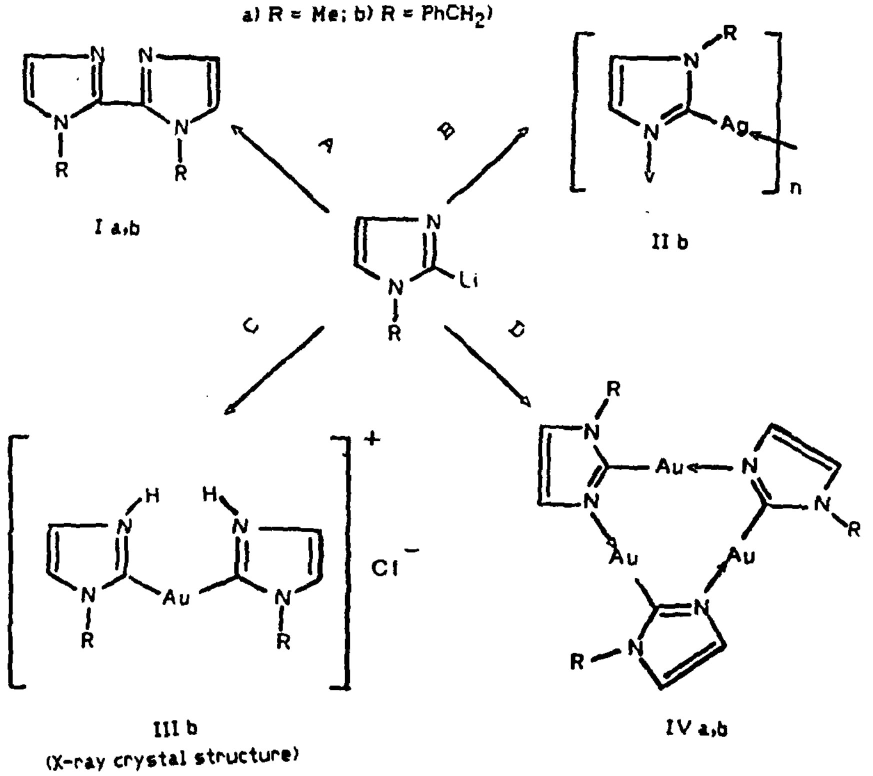
The authors thank for the financial support of National Scientific Research Foundation of Hungary (Nr. 487/86).

GOLD AND SILVER IMIDAZOLE DERIVATIVES HAVING METAL-CARBON BOND(S).

F. Bonati, A. Burini, B.R. Pietroni
Dipartimento di Scienze Chimiche, Università, 62032 Camerino (Italy)

B.Bovio
Dipartimento di Chimica Generale, Università, 27100 Pavia (Italy)

a) R = Me; b) R = PhCH$_2$)



A) Me_2SCuBr (R = Me or $PhCH_2$)

B) Me_2SAgNO_3 (R = $PhCH_2$)

C) t- Bu_3PAuCl (R = $PhCH_2$)

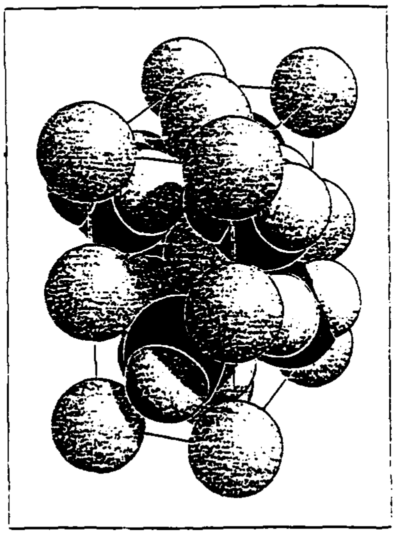
D) Ph_3PAuCl or Me_2SAuCl (R = Me or $PhCH_2$)

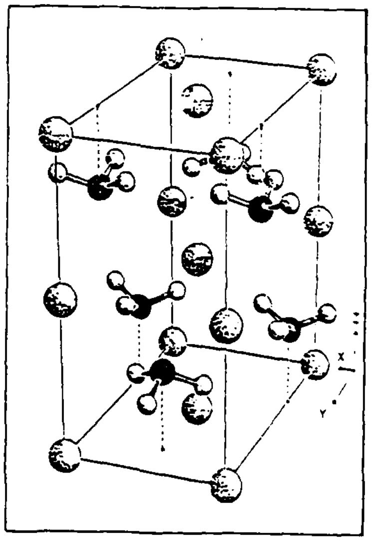
STRUCTURE REFINEMENT OF METHYL POTASSIUM PREPARATION OF KCH_3-d_3 AND NEUTRON DIFFRACTION STUDY AT 1.35 AND 290 K

Erwin Weiss, Thomas Lambertsen, Bernd Schubert
Institut für Anorganische und Angewandte Chemie der Universität
Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13.

Jeremy Cockroft, Institut Max von Laue-Paul Langevin, B.P. 156X,
F-38042 Grenoble Cedex.

The crystal structure of methyl potassium has been refined by neutron diffraction at 1.35 and 290 K using powder samples of KCD_3. Slightly distorted pyramidal methyl ions of C_{3v} symmetry were found with bond angles analogous to NH_3. In the crystal each carbanion is coordinated by six K ions with a trigonal-prismatic array and the methyl ions have alternating orientations. An orthorhombic unit cell (Pmcn, a=419.80(5), b=729.98(8), c=815.92(8)pm. Z=4) has now been found as compared to the smaller hexagonal cell (Z=2) detected previously [1] by X-ray methods and without precise location of the H atoms. The preparation of KCD_3 and $LiCD_3$ is described together with IR data of KCD_3.





[1] E. Weiss and G. Sauermann, Chem.Ber. 103 (1970) 265

On the Structure and Bonding in Cyclopentadienyl Compounds of In(I) and Tl(I).

Richard Blom and Knut Faegri, Jr.

Department of Chemistry, University of Oslo, P.b. 1033 Blindern, N-0315 Oslo 3, Norway.

In the solid state both In(C_5H_5) and Tl(C_5H_5) exhibit polymeric zig-zag chain structures, where the metal atoms are pentahapto bonded to two bridging cyclopentadienyl rings with linear metal-ring centroid-metal fragments and ring centroid-metal-ring centroid angles of approxemately 137°.[1] The introduction of bulky groups on the cyclopentadienyl rings increase the steric repulsions between the chains, which in the case of In(C_5Me_5) leads to a solid state structure where six Indium atoms form an octahedral cluster with each pentamethylcyclopentadienyl ring pentahapto bonded to only one Indium atom, $[In(C_5Me_5)]_6$.[2] In the three cyclopentadienyl indium structures that have been reported,the direct In-In distances are all in the range 394-399 pm, indicating that these interactions are the determining factors for how the total structures turn out.The structural consequenses when sterically bulky groups are introduced on the ring are less for the Thallium analouge; Tl(C_5Me_5) can still maintain the zig-zag chain structure.[3] The structural differences between the indium and thallium analogues in the solid state seem to be a consequence of decreased metal-metal bonding capability when going down group 13.In the cyclopentadienyl-thallium compounds the Tl···Tl interactions are weaker, so when the substituents on the cyclopentadienyl ring are bulkier the zig-zag structures can still be maintaind by loosen up the interchain Tl···Tl interactions.

In the gas phase both In(C_5H_5) and Tl(C_5H_5) form monomeric units with open-faced half sandwich structures of C_{5v} symmetry.[4] The gas phase structure of In(C_5Me_5) is similar to the non methylated compound; the only difference being a shortening of the In-C bond distance by approxemately 3pm; r(In-C)= 259.2(4) and 261.9(5)pm in In(C_5Me_5) and In(C_5H_5) respectively. The same decrease of the metal-carbon bond distance has been observed for the thallium analogues. *Ab initio* calculations on In(C_5H_5) and In(C_5Me_5) indicate that the shortening of the metal-carbon bond is a consequence of the polarisation of negative charge on the ring towards the methyl groups.

---

[1] E. Frasson, F. Menegus and C. Panattoni, *Nature*, 199(1963) 1087. O. T. Beachley, Jr., J. C. Pazik, T. E. Glassman, M. R. Churtchill, J. C. Flettinger and R. Blom, *Organometallics*, in press.

[2] O. T. Beachley, Jr., M. R. Churchill, J. C. Flettinger, J. C. Pazik and L. Victoriano, *J. Am. Chem. Soc.*, 108(1986) 4666; O. T. Beachley, Jr., R. Blom, M. R. Churchill, K. Faegri, Jr., J. C. Flettinger, J. C. Pazik and L. Victoriano, *Organometallics*, in press.

[3] H. Werner, H. Otto and J. Kraus, *J. Organomet. Chem.*, 315(1986) C57.

[4] S. Shibata, L. S. Bartell and R. M. Gavin, Jr., *J. Chem. Phys.*, 41(1964) 717; J. K. Tyler, A. P. Cox and J. Sheridan, *Nature*, 183(1959) 1182.

NEW METHODS FOR GENERATING VOLATILE ORGANOMETALLIC SPECIES FOR ANALYSIS FROM THE ENVIRONMENT

J.R. Ashby, S. Clark and P.J. Craig

School of Chemistry, Leicester Polytechnic,
P.O. Box 143, Leicester. LE1 9BH. U.K.

Numerous organometallic species are found in the natural environment[1]. Some of these arise from the use of various commercial products (e.g. agricultural chemicals, biocides, etc.) and some are formed in the environment (e.g. various methyl metal species). In the aqueous natural environment, these compounds are usually bound by naturally occurring proteinaceous ligands (via S, N or O atoms) in suspended or bottom sedimentary material. Analysis of these bound organometallics (e.g. CH_3Hg^+, $(nC_4H_9)_3Sn^+$, $(CH_3)_2AsOOH$, etc.) is made more difficult by their low concentrations and also by the need for extraction and removal of the organometallic from the environmental matrix prior to determination. In most cases, complete removal from the matrix for analysis does not occur; sometimes extraction is not only incomplete but it is also not very reproducible. A common procedure is to remove the non-volatile and relatively intractible organometallic from the environmental matrix by a derivatization technique that produces a volatile product retaining the organometallic features of the analyte (e.g. conversion of complexed $(nC_4H_9)_3Sn$ to $(nC_4H_9)_3SnH$; conversion of $(CH_3)_3Pb$ derivatives to $(CH_3)_3PbC_2H_5$).

Several techniques are described in this paper for the extraction of various volatile hydride or ethyl derivatives of the following: R_3Sn^+, R_2Sn^{2+}, RSn^{3+}, $(CH_3)_2As^+$, CH_3As^{2+}, $(CH_3)_3Pb^+$, inorganic tin, lead, antimony and arsenic compounds. Some techniques were applied to environmental aqueous solutions and some to complexes in sediment matrices. The techniques described involve a generation of the hydride or ethyl species on or off the column of a chromatograph and also include a convenient, one-step, non-Grignard process for generating ethyl derivatives for the analysis of organometallic derivatives from solution or sediments[2-4]. In the process for the extraction of organotin compounds from sediments, the analyte is extracted from acid solution by a tropolone/CH_2Cl_2 solution. After concentration and re-solution in ethanol, ethyl derivatives were generated by addition of a $NaBEt_4$ solution and the $R_3SnC_2H_5$/ethanol solution was analysed by GC AA or GC MS.

References

1. See for example "Organometallic Compounds in the Environment", (P.J. Craig, Ed.), Longman 1986.

2. S. Clark and P.J. Craig, Appl.Organometallic Chem., 2, 33, 1988.

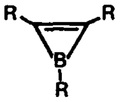
3. J. Ashby, S. Clark and P.J. Craig, Science of the Total Environment, submitted 1988.

4. S. Clark, J.R. Ashby and P.J. Craig, Analyst, 112, 1781, 1987.

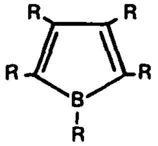
BORON-CARBON *PI*-BONDING IN THE FORMATION AND REACTIONS OF BORACYCLOPROPENES AND BORACYCLOPENTADIENES

John J. Eisch and Babak Shafii, Department of Chemistry, State
University of New York, Binghamton, New York 13901 U.S.A.

The question of the extent and chemical consequences of boron-carbon *pi*-bonding in boracyclopolyenes has received considerable attention over the last 25 years [1]. However, only relatively recently have the unambiguous syntheses of the boracyclopropene (borirene) ring [2] and the boracyclopentadiene (borole) ring [3] been achieved.



I



II

In this report we describe our investigation of the di-*pi*-methane-like photorearrangement of diaryl(arylethynyl)boranes (III), which can lead to I or which in the presence of a diarylacetylene (IV) can effect the capture of a zwitterionic intermediate and thereby the generation of II. As an alternative approach to I, the photogeneration of carbene-like boron(I) intermediates and their capture by IV will be discussed.

The *pi*-electron delocalization and the question of Hückel aromaticity in the borirene and borole systems will be assessed on the basis of the following criteria: 1) spectral properties of I and II, as well as their complexes with Lewis bases; 2) X-ray crystallographic data on B-C and C-C bond distances; 3) chemical reactivity of the boron-carbon rings; and 4) suggestive results of Extended Hückel Molecular Orbital calculations [4].

1. J.J. Eisch, in "Advances in Organometallic Chemistry," R. West and F.G.A. Stone, Ed., Vol. XVI, Academic Press, New York, 1977, pp. 67-109.
2. J.J. Eisch, B. Shafii and A.L. Rheingold, *J. Am. Chem. Soc.*, 109, 2526 (1987), and references cited therein.
3. J.J. Eisch, J.E. Galle and S. Kozima, *J. Am. Chem. Soc.*, 108, 379 (1986).
4. J.J. Eisch and R. Hoffmann, unpublished studies, 1986.

94

MIGRATORY INSERTION OF CARBON MONOXIDE INTO METAL ACYL BONDS TO FORM α-KETOACYL LIGANDS

Gregory L. Geoffroy, Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

Oxidation of the anionic acyl complex $[Cp'(CO)_2Mn-C\{O\}R]^-$ ($Cp' = C_5H_4CH_3$, R = Ph, Tol) followed by addition of NO gas yields the α-ketoacyl complex $Cp'(CO)(NO)Mn-C\{O\}C\{O\}R$, for which the R = Ph derivative has been crystallographically characterized. This reaction sequence represents the first observed CO insertion into a metal-acyl bond and indicates that such reaction may be important in some of the metal catalyzed "double carbonylation" reactions. Similar treatment of $Cp(CO)(PPh_3)Fe-C\{O\}CH_3$ with an oxidizing agent followed by NO addition gives the cationic α-ketoacyl complex $[Cp(CO)(PPh_3)Fe-C\{O\}C\{O\}CH_3]^+$. The intermediate $17e^-$ complex resulting from the oxidation process has been spectroscopically detected in both the Fe and Mn reactions. A mechanism for this carbonylation is proposed which involves initial addition of NO to the oxidized complex *as a $1e^-$ donating bent nitrosyl ligand.* This is believed to be followed by acyl migration to CO as the nitrosyl changes from a bent to a $3e^-$ linear ligand, with the latter providing the driving force for the reaction.

A similar oxidation/NO addition reaction sequence has been found to convert the methyl complex $Cp(CO)(PPh_3)_2Fe-CH_3$ into the cationic acyl species $[Cp(NO)(PPh_3)Fe-C\{O\}CH_3]^+$. This latter complex readily deprotonates to yield the unstable ketene complex $Cp(NO)(PPh_3)Fe(CH_2CO)$ which rapidly disproportionates to form Cp_2Fe and $Fe(NO)_2(PPh_3)_2$.

Oxidation has also been found to promote the carbonylation of carbene ligands to form ketenes, and these reactions will also be discussed.

The graduate students and postdoctoral fellows who have contributed to this research are Sherri Bassner, Sung-Hwan Han, and John Sheridan. This work has been supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

CHEMICAL FILIATIONS BETWEEN NEW HOMOBIMETALLIC COMPLEXES OF THE HETERODIFUNCTIONAL LIGAND (DIPHENYL PHOSPHINO) CYCLOPENTADIENYL

A. MAISONNAT, X.D. HE and R. POILBLANC
Laboratoire de Chimie de Coordination du CNRS, unité 8241, liée par convention à l'Université Paul Sabatier, 31077 TOULOUSE CEDEX (FRANCE).

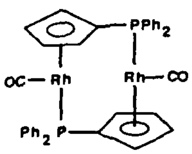
The homodimetallic complex 1 previously described (1) is easily chemically or electrochemically oxidizable according to a reversible two-electron process yielding the related symmetrical dication 2 which contains a metal-metal bond.

Complex 2 may be readily decarbonylated, using trimethylamine oxide, yielding complexes 3.

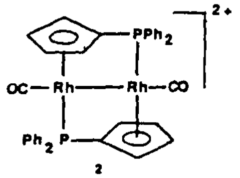
Treatment of 2 or 3 complexes with halides yields quantitatively mono or dihalide species such as 4 and 5.

Complex 5 is a convenient precursor to the preparation of dihydride 6, tetrahydride 7 and dimethyl 8 species.

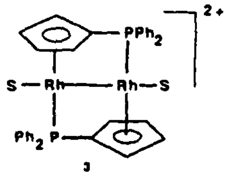
Structural determinations (using NMR, IR, mass spectra and X-ray data) of these novel bimetallic species will be presented ans discussed.



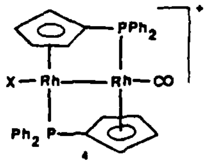
1



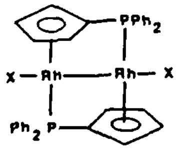
2



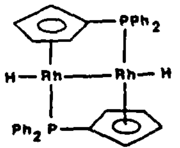
3



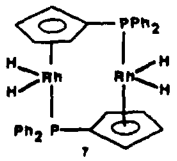
4



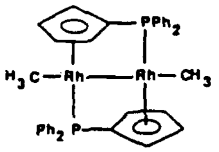
5



6



7



8

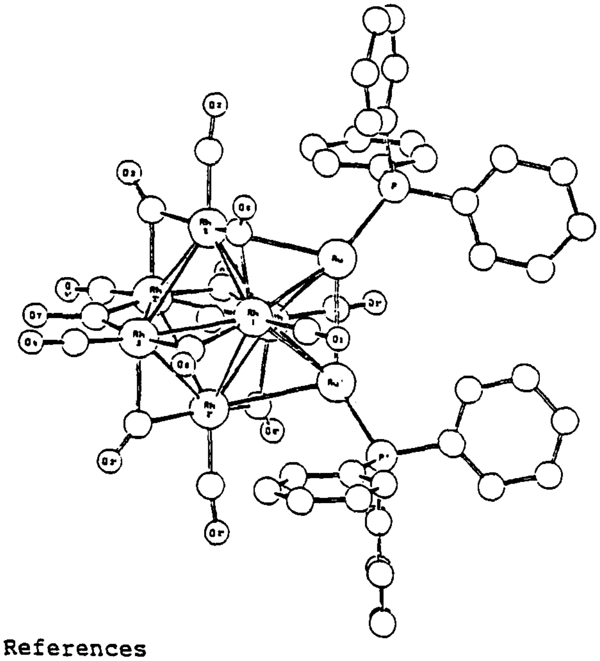
(1) X.D.HE, A.MAISONNAT, F.DAHAN and R.POILBLANC, Organometallics (1987) 6, 678

BIMETALLIC CARBIDO CARBONYL CLUSTERS. SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF $[Rh_6Au_2C(CO)_{13}(PPh_3)_2]$.

A. Fumagalli and S. Martinengo, Centro C.N.R. Sintesi e Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Via G. Venezian 21, I-20133 Milano, Italy.

V.G.Albano, D.Braga and F.Grepioni, Dipartimento di Chimica "G.Ciamician", Via F.Selmi 2, 40126 Bologna, Italy.

The prismatic carbido-carbonyl cluster $[Rh_6C(CO)_{15}]^{2-}$ [1] undergoes electrophilic attack from metal fragments such as $[ML]^+$ (M = Cu, Ag, Au), selectively on one or both triangular faces.[2,3] A parallel investigation on the octahedral anion $[Rh_6C(CO)_{13}]^{2-}$ [4] gave, as result of the reaction with $[AuCl(PPh_3)]$, the new species $[Rh_6Au_2C(CO)_{13}(PPh_3)_2]$.



Single crystal X-ray diffraction yielded the reported structure.[5] The molecule, with C_2 symmetry, has a skeleton consisting of a distorted Rh_6 octahedron capped on two adjacent faces by gold atoms which are bonded together with a distance of 2.929 Å. Other bond distances, in Å, are: Rh1-Au, 2.801; Rh2-Au, 3.147; Rh1-Au', 2.859; Rh1-Rh2, 2.727; Rh1-Rh3, 2.795; Rh1-Rh1', 3.245; Rh3-Rh3', 2.808; Rh1-Rh2', 3.230; Rh2-Rh3, 3.156; Rh2'-Rh3, 2.793. The interstitial carbide is located at an average distance of 2.063 Å from the rhodium atoms. The compound reacts with CO (1 atm, RT) to give the bicapped prismatic $[Rh_6C(CO)_{15}\{Au(PPh_3)\}_2]$.[3]

References

1) V.G.Albano, M.Sansoni, P.Chini and S.Martinengo, J.Chem.Soc. Dalton Trans., 1973, 651.

2) B.T.Heaton, L.Strona, S.Martinengo, D.Strumolo, V.G.Albano and D.Braga, J.Chem.Soc. Dalton Trans., 1983, 2175, and refs therein.

3) A.Fumagalli, S.Martinengo, V.G.Albano and D.Braga, J.Chem.Soc. Dalton Trans., 1988, in press.

4) V.G.Albano, D.Braga and S.Martinengo, J.Chem.Soc. Dalton Trans., 1981, 717.

5) Crystal data: orthorhombic, space group Fdd2, a = 22.335(4), b = 31.710(6), c = 14.947(7) Å, Z = 8, R = 0.04, R_w = 0.05.

SYNTHESIS, CRYSTAL STRUCTURE AND SOLUTION CHEMISTRY OF THE TETRANUCLEAR ALKYNE COMPLEX $[(\eta\text{-}C_5H_5)Rh(\mu\text{-}PPh_2Py)(\mu\text{-}MeO_2CC_2CO_2Me)Rh(CO)(\mu\text{-}Cl)]_2$.

Enrico Rotondo, Sandra Lo Schiavo, Giuseppe Bruno, Felice Faraone,
Dipartimento di Chimica Inorganica e Struttura Molecolare
Universita' di Messina - 98100 Messina - Italy

Roberto Gobetto, Istituto di Chimica Generale ed Inorganica
Universita' di Torino - Via P. Giuria 7 - Torino - Italy

The tetranuclear alkyne complex $[(\eta\text{-}C_5H_5)Rh(\mu\text{-}PPh_2Py)\text{-}(\mu\text{-}DMA)Rh(CO)(\mu\text{-}Cl)]_2$ (1) (PPh_2Py = 2-(diphenylphosphino)pyridine) has been synthesized by reacting at room temperature the binuclear compound $[(\eta\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}PPh_2Py)Rh(CO)Cl]$ with the dimethyl acetylenedicarboxilate (DMA). The X-ray crystal structure of 1 was determined. The molecule shows a crystallographic inversion center originated from the presence of two asymmetrical bridging chloro-ligands which link two rhodium dimer units. Each dimer unit is completely asymmetrical and consists of two rhodium atoms bridged by the Ph_2PPy and the DMA which become bound as a dimetalated olefin.

Molecular weight determination showed that 1 is extensively dissociated at 298 K in CH_2Cl_2. ^{31}P and ^{1}H NMR data are consistent with the following temperature dipendent equilibrium which takes place in solution:

$$2\ [(\eta\text{-}C_5H_5)Rh(\mu\text{-}PPh_2Py)(\mu\text{-}DMA)Rh(CO)Cl]\ (2) \rightleftharpoons (1)$$

The insaturation of the rhodium 16-electrons center seems to be a crucial point in the reactivity of 2. In fact it accounts for both the formation of the tetranuclear chloro-bridges dimers and for the reaction with small molecules such as SO_2 and CO.

In the latter case the CO addition product, formed in the first step, partially evolves at room temperature to new species.

The ^{13}C (212 ppm and 208 ppm) and the $^{1}J(^{103}Rh-^{13}C)$ of 24 Hz are consistent with the formation of acylderivatives, presumably by insertion of ^{13}CO into a C−Rh bond. The CO reaction products have not been fully characterized owing to the reversibility of the process.

STRUCTURAL STUDIES OF PHOSPHINE SUBSTITUTED $HRuCo_xRh_{3-x}(CO)_{12}$ (x = 0-3) MIXED METAL CLUSTERS

Jouni Pursiainen, Markku Ahlgren and Tapani A. Pakkanen
University of Joensuu, Department of Chemistry,
P.O. Box 111, SF-80101 JOENSUU, FINLAND

The trimetallic parent clusters $HRuCo_2Rh(CO)_{12}$ and $HRuCoRh_2(CO)_{12}$ were prepared as a mixture together with other tetranuclear clusters.[1] $HRuCo_3(CO)_{12}$ and $HRuRh_3(CO)_{12}$ were prepared separately according to known procedures. The tri-metallic clusters are difficult to isolate and they tend to decompose during the separation, but some of their phosphine derivatives can be isolated in small amounts by TLC on silica.

The crystal structures show $Rh_4(CO)_{12}$-like carbonyl geometries (an example in Figure) with the hydride ligands bridging the basal metal face and phosphines being coordinated preferably on rhodium atoms in axial positions.

^1H n.m.r. results, however, show that in solution the rhodium containing components have two isomers with the hydride bridging either a Ru(apical)-Rh(basal) edge or the basal face of the metal tetrahedron. Of these the face-bridged form, which in most cases dominates for the substituted compounds in solution, was found in the crystals. In solution the edge-bridging hydride tends to be connected with an equatorial phosphine.

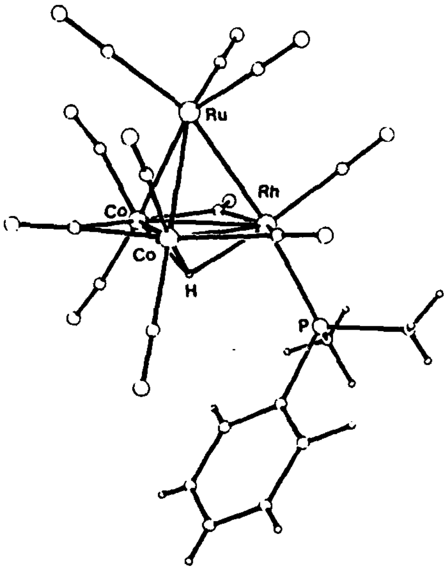


Figure. $HRuCo_2Rh(CO)_{11}(PMe_2Ph)$

References

1. Pursiainen, J. and Pakkanen, T.A. unpublished results.

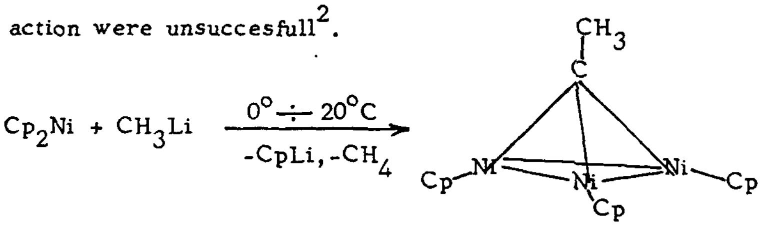
New tris/η^5-cyclopentadienylnickel/-μ_3-ethylidyne cluster

Herbert Lehmkuhl, Carl Krüger, Max-Planck Institut für Kohlenforschung
D-4330 Mülheim/Ruhr, West Germany

Stanisław Pasynkiewicz, Joanna Popławska, Warsaw Technical University
00-662 Warszawa /Poland/

Tris/η^5-cyclopentadienylnickel/-μ_3-alkylidyne clusters were obtained from the reaction of Cp_2Ni with benzylmagnesium chloride[1] or with alkyllithium RCH_2Li /R=CMe$_3$, SiMe$_3$/[2]. Both substrates don't contain β-H-atoms. The reaction of Cp_2Ni with RCH_2M /M=MgX, Li/, where organic substituent contains β-H atoms /R=Me, Et, Pr/ leads to the decomposition of unstable $\{CpNiCH_2R\}$ species /via β-H elimination/ and no μ_3-alkylidynetrinickel /CpNi/$_3$CR can be isolated[3].

We observed that Cp_2Ni reacts with CH_3Li to give μ_3-ethylidynetrinickel cluster[4], although previous attempts to isolate it from this reaction were unsuccesfull[2].



1

Besides 1, other clusters with more than three CpNi fragments are formed. 1 was isolated also from the reaction of Cp_2Ni with vinyllithium[4]. Full spectroscopic characterization of the cluster 1 ^1H, ^{13}C NMR, MS, E.A as well as X-ray structure are given.

$CpNiCp^*$ /Cp^*=C_5Me_5/ reacts with CH_3Li unselectively to give the mixture of /$Cp_nCp^*_{3-n}Ni$/$_3$ CCH_3 clusters.

/Cp^*Ni/$_3CCH_3$ was isolated in the pure state after the sublimation off the mixed clusters followed by crystalization.

References: 1. Voyevodskaya, T.J.; Pribytkova I.M.; Ustyniuk Yu.A., J.Organomet.Chem.. 1972, 37, 187. 2. Booth B.L.; Casey G.C., J.Organomet.Chem., 1979, 178, 371. 3. Pasynkiewicz S.; Lehmkuhl H., J.Organomet.Chem., 1985, 289, 189. 4. Lehmkuhl H; Krüger C.; Pasynkiewicz S.; Popławska J.; Organometallics in press.

100

FERROCENYLSILYLMETHYLIDINETRICOBALTNONACARBONYL COMPLEXES.

Jim Simpson, Jan Borgdorff and Brian H. Robinson, Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand.

Reaction between ferrocenyl silanes $FcSi(R)_2H$ and $1,1'$-$Fc'[Si(R)_2H]_2$ [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, $1,1'$-Fc' = $(\eta^5\text{-}C_5H_4)Fe\text{-}(\eta^5\text{-}C_5H_4)$, R = Me, Et, Ph] and $HCCo_3(CO)_9$ leads to the preparation of the corresponding ferrocenylsilylmethinyltricobaltnonacarbonyl complexes, $FcSi(R)_2CCo_3(CO)_9$ and $1,1'$-Fc'-$[Si(R)_2CCo_3(CO)_9]_2$ in good yield. The ^{29}Si nmr spectra of the complexes will be reported together with the crystal and molecular structure of the dicluster complex $1,1'$-Fc'-$[Si(Me)_2CCo_3(CO)_9]_2$.

Electrochemical studies of the mono- and dicluster complexes are consistent with electrochemically non-interacting ferrocene and cluster redox centres. A reversible one electron oxidation is centred on the ferrocenyl moiety with the CCo_3 centres undergoing reversible one electron reduction.

Thermal and electron transfer catalysed substitution reactions with phosphine and phosphite ligands yield a variety of Lewis base derivatives of the cluster complexes. Chemical oxidation of the Lewis base derivatives yields both mono and dication products.

REACTIVITY OF $[HFe_4(CO)_{12}BH_2]$; A NOVEL CLUSTER WITH A BUTTERFLY METAL ARRANGEMENT.

Thomas P. Fehlner, Rajesh Khattar and Nigam P. Rath.

Department of Chemistry, University of Notre Dame, Notre Dame, IN 46556, USA.

The novel cluster $[HFe_4(CO)_{12}BH_2]$ has been synthesised[1,2] and shown by X-ray analysis to adopt a butterfly metal framework.[3] Multideprotonation of the butterfly cluster $[HFe_4(CO)_{12}BH_2]$ has recently been achieved by the use of BuLi affording the anions, $[HFe_4(CO)_{12}BH]^-$, $[Fe_4(CO)_{12}BH]^{2-}$ and $[Fe_4(CO)_{12}B]^{3-}$ in high yields.[4] These anionic clusters have been characterised by i.r. and NMR spectroscopy (both ^1H and ^{11}B). Reaction of these anionic clusters with the mononuclear cationic species containing labile acetonitrile ligands have been examined and the corresponding neutral clusters have been isolated and characterised by spectroscopic techniques. Complete detail regarding the synthesis, structure and NMR studies on these new clusters will be presented.

1. K. S. Wong, W. R. Scheidt and T. P. Fehlner, J. Am. Chem. Soc., 1982, 104, 1111.
2. C. E. Housecroft and T. P. Fehlner, Organomet., 1986, 5, 379.
3. T. P. Fehlner, C. E. Housecroft, W. R. Scheidt and K. S. Wong, Organomet., 1983, 2, 825.
4. N. P. Rath and T. P. Fehlner, J. Am. Chem. Soc., 1987, 109, 5273.

Carbonyl Scrambling in $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and their Derivatives.

by Brian E. Mann and Gary W. Bentley, Department of Chemistry,
The University, Sheffield, S3 7HF, England.

An examination of the crystal structure of $Fe_3(CO)_{12}$ has revealed a new dynamic carbonyl scrambling mechanism involving concerted bridge opening and closing processes on different edges of the iron triangle. This is a very low energy pathway with $\Delta G^\ddagger <$ 25 kJ mol^{-1}. The ^{13}C n.m.r. spectra of $Fe_3(CO)_{12-n}\{P(OMe)_3\}_n$, n = 1 to 3, in CD_2Cl_2 at -100 °C are consistent with only this dynamic process occurring, but the merry-go-round process is just starting with $\Delta G^\ddagger$ = 37 to 42 kJ mol^{-1}. At -50 °C, an edge carbonyl scrambling process commences, and then at -30 °C, the trigonal twist comes into operation. The data unambiguously show that $Fe_3(CO)_{12-n}\{P(OMe)_3\}_n$, n = 1 or 2, and the major isomer of $Fe_3(CO)_9\{P(OMe)_3\}_3$ exist in CD_2Cl_2 solution in the carbonyl bridged form and have an activation energy of ca. 40 kJ mol^{-1} for merry-go-round carbonyl scrambling via the terminal carbonyl form. It is therefore probable that $Fe_3(CO)_{12}$ exists in CD_2Cl_2 solution in exclusively the carbonyl bridged form found in the solid state.

A minor isomer of $Fe_3(CO)_9\{P(OMe)_3\}_3$ exists without fully bridging carbonyls. This isomer is enhanced by increasing the bulk of the phosphite, and is dominant in $Fe_3(CO)_9\{P(OPr^i)_3\}_3$. The ^{13}C n.m.r. spectrum shows three carbonyl signals in the ratio 3:3:3. A structure analogous to that published for $Ru_3(CO)_9(PMe_3)_3$ is proposed with the axial carbonyls leaning into semi-bridging positions.

For $Ru_3(CO)_{12-n}\{P(OMe)_3\}_n$, n = 1 to 3, the lowest energy pathway is the merry-go-round process, with $\Delta G^\ddagger < 30$ kJ mol^{-1}. The edge-bridging process is clearly observed in one isomer of $Ru_3(CO)_{10}\{P(OMe)_3\}_2$, with $\Delta G^\ddagger$ = 37 kJ mol^{-1}, and then at higher temperatures all the isomers show the trigonal twist mechanism.

CARBON-HYDROGEN BOND ACTIVATION AT DITUNGSTEN CENTERS SUPPORTED BY ALKOXIDE LIGANDS

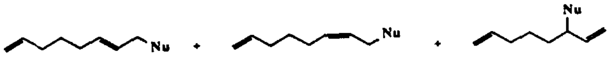
Malcolm H. Chisholm, Department of Chemistry, Indiana University, Bloomington, Indiana 47405 U.S.A.

Small alkoxide clusters of molybdenum and tungsten that are coordinatively unsaturated provide centers for the generation of organometallic chemistry by substrate binding and activation. Alternatively an organometallic chemistry can be brought about in a stepwise manner in which hydrocarbyl ligands are first introduced and then substrate binding and activation occurs. Examples of both approaches are described. (1) The reactions between $W_2(OR)_6$ compounds ($R = CH_2Bu^t$, Pr^i, cy-hexyl and cy-pentyl) and ethylene lead in a stepwise manner to (a) olefin adducts, (b) metallacyclopentanes and (c) alkylidyne ligands with the elimination of ethane. (2) The reactions between $1,2\text{-}(RCH_2)_2W_2(OPr^i)_4$ compounds and alkynes ($MeC\equiv CMe$, $MeC\equiv CEt$ and $EtC\equiv CEt$) yield alkyne adducts, $W_2(CH_2R)_2(\eta^2\text{-}C_2R'_2)_2(OPr^i)_4$; alkylidyne-hydrides or -alkyls, $W_2(\mu\text{-}C_4R'_4)(\mu\text{-}CR)(X)(OPr^i)_4$, where $X = H$ or CH_2R; or alkyne adducts $W_2(\mu\text{-}C_2R'_2)_2(OPr^i)_4$ or $[(\eta^2\text{-}C_2R'_2)W_2(\mu\text{-}C_2R'_2)(\mu\text{-}CR)(OPr^i)_3]_2$ by competitive reaction pathways involving α and β C-H activation. Mechanistic aspects of this reaction are discussed based on labelling studies.

SELECTIVE PALLADIUM-CATALYZED TRANSFORMATIONS OF DIENES - FORMAL SYNTHESIS OF SATIVENE

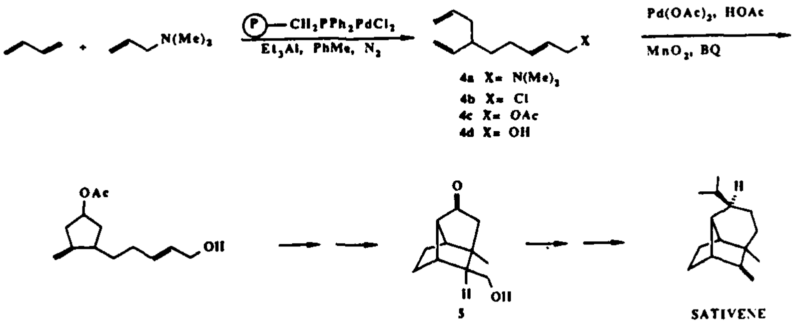
Christina Moberg and Thomas Antonsson
Department of Organic Chemistry, Royal Institute of Technology,
S-100 44 Stockholm, Sweden

Products obtained by palladium-catalyzed telomerizations of conjugated dienes and nucleophiles have proved to be useful starting materials for a variety of natural products. However, in the telomerizations mixtures of octadienyl adducts 1-3 are usually obtained. We have found that using a catalyst prepared from Pd(OAc)$_2$, a phosphine (or, preferably, a polymeric palladium-phosphine complex) and triethylaluminum in the reaction with diethylamine, the ratio 1:2:3 (X=NEt$_2$) varies with the Pd:P:Al ratio and under proper reaction conditions, the adduct 1 can be obtained without concomitant formation of 2 and 3.



1 2 3

These findings have been used in the synthesis of the Sativene precursor 5. The key steps are the regio- and stereoselective palladium-catalyzed telomerization of butadiene and N,N-dimethylallylamine to obtain 4a[1] and the regioselective palladium-catalyzed oxidative cyclization of 4d.[2]

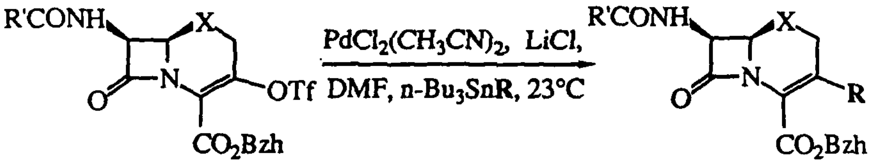


1. T. Antonsson and C. Moberg, Organometallics, 4 (1985) 1083.
2. T. Antonsson, A. Heumann and C. Moberg, J. Chem. Soc., Chem. Commun., (1986) 518.

Application of Palladium Catalyzed Organostannane Coupling with Vinyl Triflates to Complex ß-Lactams

John H. McDonald, III and Gwendolyn K. Cook,
Lilly Research Laboratories, Lilly Corporate Center,
Indianapolis, Indiana 46285 U.S.A.

We have developed methodology which allows palladium catalyzed couplings[1] to to be applied to functionally complex ß-lactam antibiotics. The coupling of 3-triflates of cephems and carbacephems with saturated and unsaturated organostannanes mediated by a palladium catalyst has been thoroughly explored. The (carba)cephem-3-triflates were highly catalyst selective unlike published examples and demanded the use of "ligandless" Pd(II) catalysts. This allowed the high yield application of this extremely chemoselective methodology to a large variety of organostannanes and ß-lactam nuclei. Taking advantage of a side-reaction allowed the chemistry to be extended to novel palladium catalyzed reductions of enol triflates. Isolation and characterization of a presumed palladium containing intermediate is also described.



---

[1] See for example; W. J. Scott, G. T. Crisp, J. K. Stille, *J. Am. Chem. Soc.* **106** (1984) 4630.

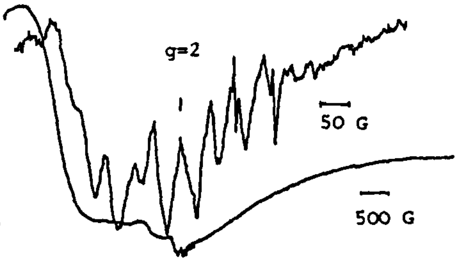
ARENE SOLVATED COBALT ATOMS AS SOURCE OF NAKED CLUSTERS OF DIFFERENT SIZE AND SPECIFIC CATALYTIC ACTIVITY; PRELIMINARY EPR STUDIES.

Giovanni Vitulli, Sergio Bertozzi
Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy.

Arturo Colligiani
Istituto di Chimica Industriale, Università di Messina, S.Agata (ME), Italy.

The clustering of solvated metal atoms is a promising tool for the preparation of naked clusters of different size and peculiar catalytic activity(1). Arene solvated cobalt atoms, (arene=toluene, mesitylene), obtained by cocondensation of Co and arene vapours at about -196°C followed by warming up to the melting temperature of the solvent, have recently been found to be very active catalysts in the synthesis of pyridines from acetylenes and nitriles(2).

We report here epr evidence of the presence of cobalt clusters of different size in such cocondensates. The epr spectrum recorded at about -35°C, Figure, shows a group of structured signals centred at $g \approx 2$, which can be related to the presence of low-nuclearity Co clusters, and strong broad absorptions, accounting for high nuclearity Co aggregates(3).



The clustering process is temperature dependent, allowing the separation of Co compounds of low and high nuclearity, showing different catalytic behaviours in the cocyclization of α,ω-dialkynes and nitriles to pyridines. Details on the magnetic properties of arene/cobalt cocondensates, at variable temperatures, will be given.

1. M.P.Andrews and G.A.Ozin, J.Phys.Chem., 90 (1936) 2929 and references therein.
2. G.Vitulli, S.Bertozzi, M.Vignali, R.Lazzaroni and P.Salvadori, J.Organomet. Chem., 326 (1987) C33.
3. A.Abragam and P.Bleaney, "Electron Paramagnetic Resonance of Transition Ions", Oxford University Press, Oxford (1970).

ON THE SUBJECT OF IRON-GRAPHITE INTERCALATION COMPOUND AS A CATALYST FOR CONVERTION OF CO+H_2 INTO ACETYLENE

Alexandre Bely, Vladimir Kuznetzov, Oleg Andryushin, Mark Vol'pin
Institute of Organo-Element Compounds of the USSR Academy of Sciences, Vavilov St. 28, Moscow 117813, USSR

It was published recently that $FeCl_3$ - graphite intercalation compound reduced by K-naphtalenide and further exposed to air was able to catalyse the unusual reaction of CO+H_2 convertion into acetylene [I] . In this connection, we have examined a number of graphite intercalation compounds as Fisher-Tropsch catalysts. $FeCl_3$ and $FeCl_2$-graphite intercalates of different stages (from 1 to 4) were reduced by alkali metals or by Li, Na and K-naphtalenides. These materials - per se or exposed to air prior to testing - were used as catalysts of CO+H_2 reaction carried out under 100-300°C.

In all the cases products appeared to be the mixture of light hydrocarbons. Occasionally C_2H_2 was indeed observed but in rather small quantity.

In the course of the investigation we found out that lithium reacted with naphtalene to give carbide-like compound which yielded C_2H_2 after hydrolysis. The mild heating (70°-100°C) of this compound, exposed to air prior to the experiment, was followed by long-term process of C_2H_2 evolution.

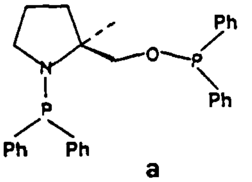
Therefore, the C_2H_2 formation in [I] seems at least partly to be the result of the naphtalene with alkali metal reaction.

I. Jones W., Schlögl R., Thomas J.M., J.Chem.Soc. Chem.Commun. 1984, 464.

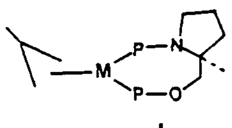
Stereochemical studies of η^3-allylPd(II) complexes containing chiral chelating ligand.

Edoardo Cesarotti , Mariella Grassi , Laura Prati
Università di Milano , Dipartimento di Chimica Inorganica e Metallorganica,
Via Venezian 21 , I-20133 Milano , Italy

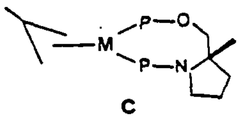
Pd-mediated asymmetric allylation , leading to selective C-C bond formation is a reaction of primary importance in organic chemistry. Despite the relevant number of studies and applications reported , the systematic outcome of the reaction is not defined and the control of asymmetric induction together with the rise in optical yields are far from optimal. In order to offer an insight into the correlation between precursor, intermediate and product in " real-like" conditions, we illustrate the solution characterization of [η^3-C_4H_7PdLL']X (where LL'= chiral chelating ligand with symmetry lower than C2V). The structures of the ligand (S)-N-(diphenylphosphino)-2-diphenylphosphinoxymethylpyrrolidin {herein abbreviated as ((S)-Prolophos)} and of the two diastereoisomeric forms of the complex {η^3-C_4H_7Pd((S)-Prolophos-PP')}$^+$ X^-,1, are shown in formulae a, b , c , respectively.



a



b



c

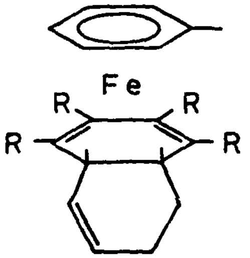
The full characterization of both the ligand and the complex 1 have been performed by ^1H , ^{13}C , ^{31}P one- and two-dimensional n.m.r. techniques . On the basis of the n.m.r findings, the absolute configuration of the two diastereoisomers has been assigned (i.e. the major and minor isomers have structure b and c, respectively). The comparative values of ^3J (XP) (where X= allylic carbon , proton) allow an evaluation of the relative trans influence of the two phosphorus atoms indicating that -PN- is a better σ donor than -PO- . The analysis of the relative ^{13}C shifts of the allylic carbons suggests that -PO- is a stronger π acceptor than -PN- . On the basis of these results , hypotheses on the regioselectivity of the nucleophilic attack on the coordinated allyl are formulated .

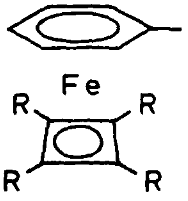
This work was supported by the C.N.R. (Centro di studi sulla sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione , Milano , Italy).

NEW ROUTES TO π-COMPLEXES OF IRON VIA CYCLOTRIMERIZATION OF ALKYNES

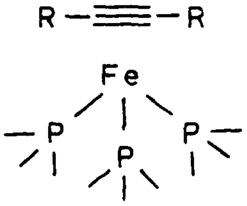
Ulrich Zenneck, Hartmut Schäufele, Catherine Tolxdorff and Hans Pritzkow, *Anorganisch-Chemisches* Institut der Universität, Im Neuenheimer Feld 270, D-69 Heidelberg, FRG

(Toluene)bis(ethene)iron 1 1) is rapidely accessible in good yield via a metal vapor reaction. It cyclotrimerizes alkynes RCCR' (R,R'= H, alkyl, phenyl, alkylester) below room temperature. We use the catalytic cycle as a generator of highly reactive complexes, which may be trapped by suitable reagents such as phosphites, olefines or dienes. The reactions of 1 with diphenylacetylene or bis(trimethylsilyl)acetylene directly yield new π-complexes of iron. Examples for the many products are the compounds 2-5.



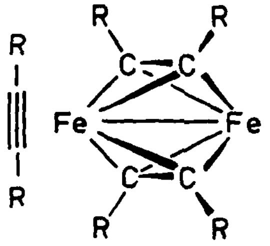


3



4

2



5

1) U. Zenneck and W. Frank, Angew.Chem.Int.Ed.Engl. 25 (1986) 831

110

AMINO-COPPER COMPLEXES AS CATALYSTS FOR ADDITION REACTION

Jaroslav Včelák, Václav Chvalovský, Institute of Chemical Process Fundamentals, Czech. Acad. Sci., 165 02 Prague 6, Czechoslovakia

Jiří Hradil, František Švec, Institute of Macromolecular Chemistry, Czech. Acad. Sci., 162 06 Prague 6, Czechoslovakia

Copper complexes prepared under homogeneous conditions "in situ" from copper I chloride and aliphatic primary amine in excess of CCl_4 were compared with those immobilized on the surface of organic polymer support. As polymerous carriers macroporous 2,3-epoxypropylmethacrylate copolymer crosslinked by ethylenedimethacrylate or copolymers of styrene and divinylbenzene both modified by built-in primary amino groups were used.
The rate constant of addition reaction (at 70°C) between CCl_4 and styrene giving 1,3,3,3-tetrachloropropylbenzene was used as a measure of catalytic activity of prepared complexes.

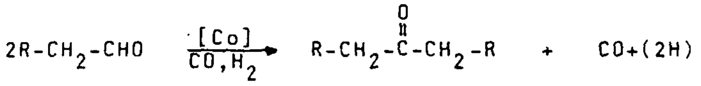
$$d|\mathrm{Prod.}|/dt = k \times |\mathrm{Styr.}| \times |\mathrm{Cat.}|o$$

The concentration of styrene and that of copper complex was 0.77 Mol/L and 0.06 Mol/L, respectively.
The activity of catalytic complex depends on the molar ratio of copper and amine group in complex. Under homogeneous conditions the most active complex was obtained from CuCl and n-butylamine in ratio 1:2. Supported copper complex pretreated by primary amine decreases its activity as a reason of wash-off of a small part of Cu from supported complex and a rearrangement of amino groups in retained complex. For immobilized copper complexes the dependency of activity on the structure and surface of carrier and on the content of amino groups in polymerous matrix was characterized.

NOVEL ACCESS TO KETONES BY CATALYTIC COUPLING OF ALDEHYDES

M. Fontaine, A.F. Noels and A.J. Hubert
University of Liège, Institut de Chimie B.6,
B-4000 SART TILMAN, Belgium.

Although a number of transition-metal complexes activate aldehydes to lead either to decarbonylation or to hydroacylation reactions in the presence of olefins, no direct formation of ketones seems to have been reported.
We now describe a straightforward catalytic synthesis of ketones from aldehydes, a reaction that globally involves the formation of a C-C bond as well as the loss of one molecule of carbon monoxide :



$$2R\text{-}CH_2\text{-}CHO \xrightarrow[CO,H_2]{[Co]} R\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}R \quad + \quad CO+(2H)$$

Pressure as well as the presence of basic ligands was crucial for the obtention of ketones. For example, a solution of phenylacetaldehyde at 150° in the presence of a catalytic amount of cobalt carbonyl under 10 MPa of $CO\text{-}H_2$ yielded 1,3-diphenyl-2-propanone (dibenzylketone, $>70\%$). Benzaldehyde did not react under the same reaction conditions. Hydroacylation of an olefin intermediate was ruled out as a major reaction pathway.

112

Some Reminiscences

Geoffrey Wilkinson, Department of Chemistry, Imperial College of Science and Technology, South Kensington, London SW7 2AY, UK

"In his last public lecture Professor Wilkinson is expected to talk about his early days in organometallic chemistry and to report on some recent work on rhenium and platinum homoleptic alkyls and aryls".

COMPETITIVE UNCATALYZED GEOMETRICAL ISOMERIZATION AND ß-HYDRIDE ELIMINATION OF ALKYL COMPLEXES OF PLATINUM(II).

ALIBRANDI, G. ; CUSUMANO, M.; MINNITI, D.; MONSU' SCOLARO, L.; ROMEO, R.

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Vill.S.Agata, Salita Sperone 31, 98166 Messina, Italy.

Rates and activation parameters for the spontaneous cis to trans isomerization of monoalkyl $[Pt(PEt_3)_2(R)Cl]$ ($R = CH_3$, C_2H_5, C_2D_5, n-C_3H_7, n-C_4H_9, $CH_2Si(CH_3)_3$) complexes have been measured in isopropanol. The reactions are inhibited by chloride ion and for all systems the isomeric equilibrium lies well to the side of the trans form. As in the case of the related aryl complexes, the isomerization mechanism involves dissociative loss of chloride and interconversion of two T-shaped $[Pt\ L_2(alkyl)]^+$ 3-coordinate intermediates. An incipient interaction of the ß-hydrogens of the alkyl group with the metal in the transition state leading to the first platinum cation intermediate accounts for the much higher reactivity of complexes in which R = Et, n-Pr and n-Bu with respect to that of complexes containing alkyl groups with no ß-hydrogens.

The n-propyl and n-butyl derivatives, in addition to spontaneous isomerization undergo thermal decomposition through a concurrent pathway yielding trans-$[Pt(PEt_3)_2HCl]$ and olefins (propene and 1-butene, cis-2-butene and trans-2-butene in the ratio 1: 1: 0.04, respectively). No alkanes are produced in these reactions that go to completion and are unaffected by the presence of excess of chloride ion in solution. The relative rates of the two competing processes either in the neat solvent or in solutions containing chloride have been calculated through kinetic, spectrophotometric and GLC measurements. The most probable mechanism for the thermolysis involves a nondissociative pathway in which the loss of olefin after facile reversible ß-hydride elimination is probably rate determining.

REACTIVITY OF A CATIONIC OSMIUM POLYHYDRIDE TOWARDS ETHYLENE

L. S. Van Der Sluys, T. Johnson, Kenneth G. Caulton, T. Koetzle, and P. Vergamini, Departments of Chemistry, Indiana University, Bloomington, IN 47405 (U.S.A.), Brookhaven National Laboratory, Upton, NY (U.S.A.), and Los Alamos National Laboratory, Los Alamos, NM (U.S.A.)

We have established, by neutron diffraction, that $FeH_4(PEtPh_2)_3$ contains two hydride ligands and one dihydrogen molecule. $OsH_4(PMe_2Ph)_3$, in contrast, contains four hydride ligands. In order to explore further this difference, we have protonated $OsH_4(PMe_2Ph)_3$ to give $OsH_5(PMe_2Ph)_3^+$, which reacts with ethylene (1 atm, 25°) to give *cis,mer*-$OsH(C_2H_4)_2(PMe_2Ph)_3^+$. Multinuclear NMR studies, including work with $^{13}C_2H_4$, reveals this ion to have chemically-inequivalent ethylene ligands. The C_2H_4 *trans* to a phosphine shows rigidity of the OsC_2 plane, while that *trans* to hydride shows rapid olefin rotation. Detailed studies of these and related dynamic processes, including attempted olefin hydrogenation, will be reported, as well as attempts to establish the possible presence of intact H_2 in $OsH_5(PMe_2Ph)_3^+$.

NEW REACTIONS OF IODO-RUTHENIUM(0) NUCLEOPHILES

Heindirk tom Dieck and *Wolfgang Rohde*, Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13 (F.R.G.)

Ruthenium(II) forms very stable complexes with several N,N'-chelating ligands. The reduction of $[(N{-}{-}N')Ru(CO)_2I_2]$ 1 leads to the pentacoordinate anion $[(N{-}{-}N')Ru(CO)I]^-$ 2 [1], which undergoes a number of low temperature nucleophilic reactions, e.g. with alkyl halides and triflates, allyl halides and triflates, silyl halides, ammonium salts (as proton source), acyl halides etc. The oxidative addition products always contain the iodo ligand. The conformationally stable and kinetically inert complexes $[(N{-}{-}N')Ru(CO)_2(Y)(I)]$ 3 allow the comparison of many electrophiles Y at the same center. Starting from diolefin complexes $[N{-}{-}N')Ru(diene)Cl_2]$ [2] analogues $[(N{-}{-}N')Ru(diene)I]^-$ 4 have also been prepared and reacted with electrophiles.
Reduction of complexes 3 (Y = $-CH_3$; N--N' = ipr-DAD = ipr-N=CH-CH=N-ipr) gives a Ru-Ru bonded dimer [(N--N')(CO)2Ru-Ru(CO)2(N--N')] 5 . For another complex 3 (Y = I^-) the same type of Ru-Ru bonding occurs for bulky (N--N'), while for the relatively small ipr-DAD the known Ru(0) dimers $[(DAD)Ru(CO)_2]_2$ [3] are formed. Complex 5 shows an exceptionally strong CT absorption band near the infrared. Kinetic results from electrochemical studies are presented to illustrate the reactivity of the Ru(II), Ru(I), and Ru(0) species

[1] W. Rohde and H. tom Dieck, *J. Organometal. Chem. 328* (1987) 209.
[2] H. tom Dieck, I. Kleinwächter, *Z. Naturforsch. 42b* (1987) 71.
[3] G. van Koten, K. Vrieze, *Adv. Organomet. Chem. 21* (1982) 151.

FACTORS AFFECTING THE EQUILIBRIUM CONSTANT OF HOMOLYSIS OF COMPLEXES WITH METAL-CARBON σ BONDS IN AQUEOUS SOLUTIONS: PULSE RADIOLYSIS STUDIES.

Dan Meyerstein

R. Bloch Coal Research Center and Chemistry Department
Ben Gurion University of the Negev, Beer-Sheva, Israel.

Aliphtic free radicals, ·R, react with a large variety of transition metal complexes to form transient complexes with metal-carbon σ bonds. Recently it was observed that the mechanism of decomposition of these complexes involves in many systems the homolysis of the metal-carbon σ bond:

(1) $L_{m-1}M^{(n+1)}\text{-}R + L \rightleftarrows ML_m^{(n)} + \cdot R$

The homolysis reaction is followed by one of the following reactions:

(2) $\cdot R + S \longrightarrow$ *products (where S is a substrate for the free radical)*

(3) $\cdot R + L_{m-1}M^{(n+1)}\text{-}R + L \longrightarrow ML_m^{(n)} + R\text{-}R$ or $RH + ROH$

(4) $2\cdot R \longrightarrow R\text{-}R$ or $RH + ROH$

The equilibrium constant K_1 can be determined by studying the dependence of the rate of formation of $L_{m-1}M^{(n+1)}\text{-}R$ on $[ML_m^{(n)}]$, by studying the dependence of the absorption due to $L_{m-1}M^{(n+1)}\text{-}R$ on $[ML_m^{(n)}]$ or by studying the dependence of the rate of decomposition of $L_{m-1}M^{(n+1)}\text{-}R$ on [S] when k_2 is known.

The technique enables the study of the effect of the nature of the central cation M, the ligands L and substituents on R on K_1. Specific examples for each effect and mechanism will be discussed, these examples include:

The determination of the equilibrim constant K_5 for M = Mn, Fe and Co.

(5) $[(nta)(H_2O)M(III)\text{-}CH_3]^- \rightleftarrows [(nta)(H_2O)_2M(II)]^- + \cdot CH_3$

in this system the homolysis is followed by

(6) $[(nta)(H_2O)M(III)\text{-}CH_3]^- + \cdot CH_3 \longrightarrow [(nta)(H_2O)M(II)]^- + C_2H_6$.

whereas reaction (7)

(7) $[(nta)(H_2O)Fe(III)\text{-}CO_2]^{2-} \rightleftarrows [(nta)(H_2O)_2Fe(II)]^- + \cdot CO_2^-$

is followed by

(9) $[(nta)(H_2O)Fe(III)\text{-}CO_2]^{2-} + \cdot CO_2^- \longrightarrow [(nta)(H_2O)_2Fe(II)]^- + CO + CO_2$

For M = Co the effect of substituents on the methyl on K_5 is reported.

Other systems discussed will include those in which $ML_m^{(n)} = Cr_{aq}^{2+}$, Cu_{aq}^{+}, Cu(II)tetrasulfophthalocyanine and Ni(II)tetrasulfophthalocyanine.

SUBSTITUENT EFFECTS ON THE RATES OF CO SUBSTITUTION OF $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$

Minsek Cheong and Fred Basolo, The Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

The syntheses and characterization of the new compounds $(\eta^5\text{-}C_5H_4CF_3)Rh(CO)_2$ and $(\eta^5\text{-}C_5H_4N(CH_3)_2)Rh(CO)_2$ are reported. The compounds $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ and $(\eta^5\text{-}C_5H_4X)Rh(CO)PPh_3$ (where X = H, NO_2, CF_3, Cl, CH_3, or $N(CH_3)_2$) show a good linear correlation between the values of CO stretching frequencies, ν_{CO}, and the Hammett σ values of the X ring substituents. This may be the first time such a correlation has been reported, and it is believed to mirror the electron density on the metal which in turn results in greater or lesser back π-bonding, $M \rightarrow CO$. In spite of this the rates of CO substitution of these compounds show strong deviations from linear correlation with Hammett σ values. This is rationalized in terms of resonance stabilization of the transition state for reaction by certain ring substituents.

We are now collaborating with Professor Dennis L. Lichtenberger on a core and valence ionization study[1] of these compounds in an attempt to determine the separate contributions of the σ and the π effects of the ring substituents on the rates of CO substitution.

(1) Lichtenberger, D. L.; Calabro, D. C.; Kellogg, G. E. Organometallics, 1984, 3, 1623.

LARGE AND SMALL DEUTERIUM KINETIC ISOTOPE EFFECTS IN INTRAMOLECULAR PROCESSES IN TRANSITION METAL HYDRIDES

Edward Rosenberg, Sharad Hajela, Michael Green, Roberto Gobetto and Giuseppe Nicola, Department of Chemistry, California State University, Northridge, California 91330

We have previously reported a small primary deuterium kinetic isotope effect (kH/kD ~ 1.5) in various intramolecular rearrangements[1] and chemical reactions.[2] We have now found that this small isotope effect is not confined to polynuclear metal hydrides but is also observed in intramolecular rearrangements involving hydride motion in mononuclear species (e.g. $[(\eta\text{-}C_6H_6)Cr(CO)_2(P(CH_3)_2C_6H_5)H]^+$). In addition, we have applied the small isotope effect to understanding the connectivity between hydride motion and migrations of other ligands in the cluster systems $(\mu\text{-}H)_2M_3(CO)_9(\mu_3\text{-}S)$ (M = Ru, Os) and $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-alkyne})$.

We have also previously documented a large isotope effect (kH/kD > 50) in the intramolecular ligand to metal hydrogen transfer involved in the conversion of $(\mu\text{-}H)(\mu\text{-}COH)M_3(CO)_{10}$ to $H(\mu\text{-}H)M_3(CO)_{11}$ (M = Ru, Os)[3] We have now documented a large isotope (kH/kD = 6) for the intramolecular metal to ligand hydrogen transfer involved in the conversion of $H(\mu\text{-}H)Os_3(CO)_{10}(CNR)$ (I; R = CH_3) $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta'\text{-}C{=}N(H)R)$. This isotope effect is not observed in the conversion of I(R = C_6H_5) to the isomeric $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}NR)$ where a small inverse isotope effect is observed. The temperature dependence of these isotope effects will be discussed as a means of evaluating the barrier tunnelling component in these types of chemical reactions.

References

(1) E. Anslyn, E. Rosenberg, S. Aime, D. Osella, L. Milone. Organometallics, 1984, **3**, 1790.

(2) C. Barner-Thorsen, E. Rosenberg, G. Saatjian, S. Aime, L. Milone and D. Osella, Inorg. Chem., 1981, **20**, 1592.

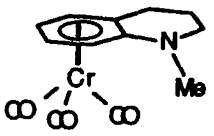
(3) D. Pribich and E. Rosenberg, Organometallics, 1988, **7**, in press.

Reversible Addition of Carbon Nucleophiles to some Nitrogen-Substituted η⁶-Arenetricarbonylchromium(0) Compounds

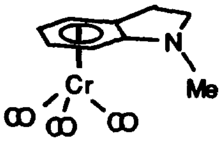
Bengt Ohlsson, and Christina Ullenius

Department of Organic Chemistry, Chalmers University of Technology,
S-412 96 Göteborg, Sweden,

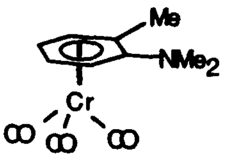
The nucleophilic addition/oxidation reactions of η^6-1-methyl-1,2,3,4-tetrahydroquinolinetricarbonylchromium(0) **1**, η^6-1-methylindolinetricarbonylchromium(0) **2**, and η^6-2-N,N-dimethylaminotoluenetricarbonylchromium(0) **3** with the nucleophiles 2-lithio-2-methylpropionitrile **A**, 2-lithioacetonitrile **B** and 2-lithio-2-methyl-1,3-dithiane **C** have been studied.



1



2



3

The regioselectivity in the addition of stabilized nucleophiles is time- and temperature-dependent indicating the onset of thermodynamic control in prolonged/high temperature reactions. The addition is reversible according to crossover experiments with benzene$Cr(CO)_3$, the rate for dissociation of the C-C bond being strongly dependent on both the structure of the intermediate η^5-cyclohexadienyltricarbonylchromium anions as well as the structure of the nucleophile. The regioselectivity of the thermodynamically controlled reaction of **2** has been correlated with the relative energies obtained from EHT calculations on a model system for the intermediate cyclohexadienyltricarbonylchromium anions.

The regioselectivity of the addition/oxidation reaction can be optimized by the proper choice of reaction conditions for each of the compounds **1**, **2** and **3**.

References:

1. B. Ohlsson and C. Ullenius, *J. Organometal. Chem.* 267 (1984) C34.
2. B. Ohlsson and C. Ullenius, *J. Organometal. Chem.* in print.

Photochemically induced C-H Activation Using (η^5-C_5H_5)Rh(PMe_3)C_2H_4 - A Mechanistic Study

Simon T. Belt, Andrew McCamley and Robin N. Perutz

Department of Chemistry, University of York,
York YO1 5DD, U.K.

The work of Bergman, Jones and Graham has shown that efficient C-H activation of arenes/alkanes may be achieved with the reactive 16e intermediates (η^5-C_5R_5)ML (R = H, CH_3; M = Rh, Ir; L = PMe_3, CO) via photo-ejection of H_2, CO from their 18e precursors[1]. We have now utilised the photo-lability of C_2H_4 in CpRhL(C_2H_4) complexes[2] to examine the mechanisms of these reactions more closely. Here we report investigations of the photochemistry of CpRhPMe$_3$(C_2H_4) in solution, in low temperature matrices and by laser flash photolysis.

Photolysis of CpRhPMe$_3$(C_2H_4) in aromatic solvents yields stable aryl hydride complexes via elimination of C_2H_4 and oxidative addition of solvent C-H bonds. In alkanes, C-H activation occurs unselectively to give thermally unstable alkyl hydride complexes characterised by ^{1}H and ^{31}P n.m.r.. The reaction intermediate, CpRhPMe$_3$, remains elusive even at 20K in an argon matrix, where intramolecular C-H activation of co-ordinated PMe$_3$ (cyclometallation) is dominant. The cyclometallated product exhibits a conspicuous ν(Rh-H) band at ca. 2040 cm^{-1} in the i.r.. Laser flash photolysis of CpRhPMe$_3$(C_2H_4) in alkane solvents fails to show any transients, only products. However, a transient is observed in arene solvents which is assigned to CpRhPMe$_3$(η^2-arene). Evidence for such intermediates has been published by Jones[3]. The rate of isomerisation of CpRhPMe$_3$(η^2-C_6H_6) to CpRhPMe$_3$(C_6H_5)(H) is 1×10^3 s^{-1}.

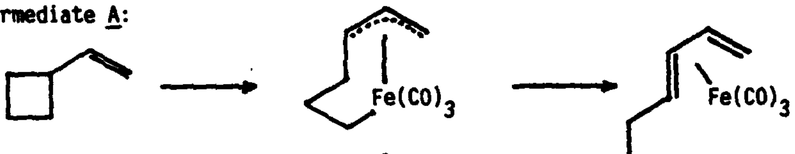
1. R.H. Crabtree, Chem. Rev., 1985, 85, 245.
2.(a) D.M. Haddleton and R.N. Perutz, J.C.S. Chem. Comm., 1985, 1372.
(b) D.M. Haddleton et al. J. Organomet. Chem., 1986, 311, C15.
3. W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 1984, 106, 1650.

IRON CARBONYL INDUCED REARRANGEMENT OF VINYLCYCLOBUTANE SYSTEMS

Titus A. Jenny, Institut de chimie organique, Université de Fribourg,
CH-1700 Fribourg, Switzerland

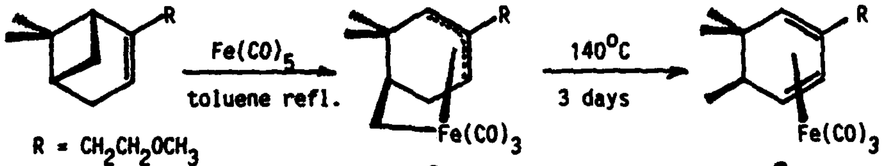
Although facile ring opening of vinylcyclopropanes by the action of iron carbonyls has long been known, only one report appeard so far on the corresponding behaviour of vinylcyclobutanes[1].

We found now, that vinylcyclobutanes can be reacted with $Fe(CO)_5$, either thermally at temperatures above 100°C, or photochemically at temperatures above 60°C, to yield products which are derived from the expected π-allyl complexed intermediate A:



A

Surprisingly, intermediates of the type A can be isolated as major products, if the substituents and further ring connections of the reacting vinylcyclobutane systems lead to products which meet the steric requirements of complexation on iron:



R = $CH_2CH_2OCH_3$
1
2
3

Thus, starting from enantiomerically pure nopol methylether 1, one obtaines with complete steric control the highly versatile complex 2 as a slightly air sensitive, stable compound in moderate yield. Hydrogen transfer on subsequent heating leads to the substituted 1,3-cyclohexadiene complex 3, without loss of enantiomeric purity.

References

1) A.Stockis and E. Weissberger, J. Am. Chem. Soc., (1975), 97, 4288.

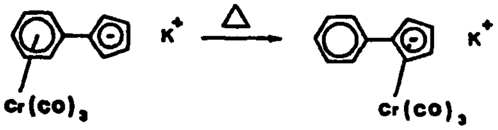
THE MIGRATION OF $Cr(CO)_3$ FROM THE PHENYL TO THE σ-BONDED CYCLOPENTADIENYL RING IN 9-PHENYL-FLUORENYL, 3-PHENYL-INDENYL, AND PHENYL-CYCLOPENTADIENYL ANIONS.

Alberto Ceccon, Alessandro Gambaro, Francesca Gottardi
Dipartimento di Chimica Fisica dell'Università, Via Loredan, 2 - 35131 PADOVA (Italy)

Alfonso Venzo
Centro Studi Stati Molecolari, Radicalici ed Eccitati del CNR, Via Loredan, 2 - 35131 PADOVA (Italy)

Intramolecular haptotropic rearrangements in biphenyl or in iso-electronic systems have not been previously observed. Recently, the migration of $Cr(CO)_3$ occurring between co-ordinative sites separated by a carbon-carbon σ bond has been shown by us to occur in the 3-phenyl-pentadienyl anion.[1]

In this communication we will show that the migration of $Cr(CO)_3$ in the phenyl-cyclopentadienyl anion



takes place irreversibly in the temperature range 325÷342 K. Analogous shift of the inorganic unit occurs also in the 9-phenyl-fluorenyl and the 3-phenyl-indenyl anions. The rates and the activation parameters of these processes are compared with those of other haptotropic rearrangements.

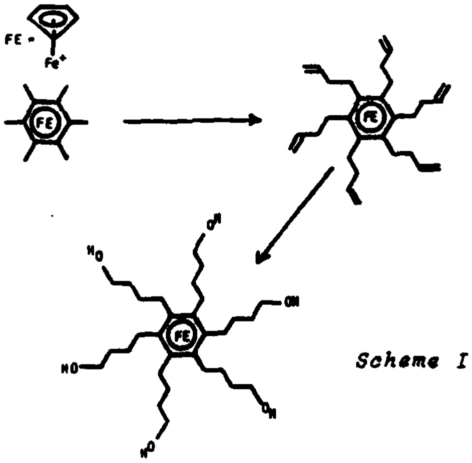
[1] A.Ceccon, A.Gambaro, A.Venzo, J.Chem.Soc.Chem.Commun., (1985) 540

Tentacled Iron Sandwiches

Françoise Moulines and Didier Astruc

Laboratoire de Chimie Organique et Organométallique, U.A. CNRS N° 35
Université de Bordeaux I, 351, cours de la Libération, 33400 Talence,
France.

The perfunctionalization of $[Fe(C_5H_5)(C_6H_6)]^+PF_6^-$ *has been achieved*[1] *by reaction with allylbromide and t-BuOK in THF. (scheme I) This reaction follows the known permethylation reaction with* CH_3I[2]. *The reactivity of the double bonds has been investigated with the aim to design new discoid molecules.*



Scheme I

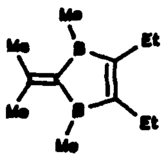
[1] *F. Moulines, D. Astruc, submitted to Angew. Chem. Int. Ed. Engl.*

[2] *J.-R. Hamon, J.-Y. Saillard, A. Le Beuze, M. McGlinchey, D. Astruc, J. Am. Chem. Soc. 1982, 104, 7549-7555.*

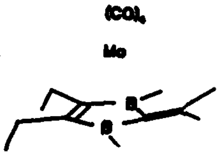
METAL COMPLEXES OF 1,3-DIHYDRO- 1,3-DIBORAFULVENE DERIVATIVES

Walter Siebert, Volker Schäfer, Gregor Brodt and Hans Pritzkow,
Anorganisch-Chemisches Institut der Universität, Im Neuenheimer
Feld 270, D-6900 Heidelberg, FRG

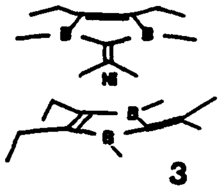
Reaction of (Z)bis(dichloroboryl)hexene-3 with 1,1-bis(trimethylstannyl)-2-methyl-1-propene leads to of the diborafulvene derivative 1. This Lewis acidic heterocycle is a four-electron donor and it has good acceptor properties for the formation of mononuclear and dinuclear complexes. A typical example is the tetracarbonylmetal complex 2, which is obtained on reaction of 1 with Mo(CO)$_6$. With bis(allyl)nickel the sandwich 3 and the triple-decker 4 are formed. An unusual transfer of C_5H_5 occurs when 1 is reacted with $[(C_5H_5)Ni(CO)]_2$ to give 5 and the paramagnetic triple-decker sandwich 6. $[(C_5H_5)Fe(COD)]_2Zn$ and 1 yield paramagnetic FeFe triple-decker complexes. The structure of several complexes will be discussed.



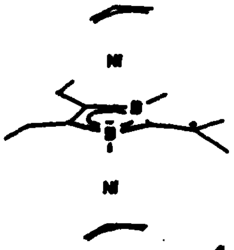
1



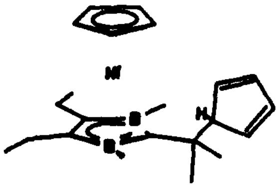
2



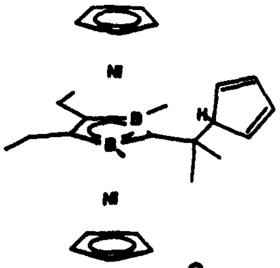
3



4



5



6

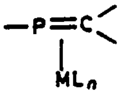
1) V. Schäfer, H. Pritzkow, W. Siebert, Angew.Chem. 100 (1988) 272

NOVEL SANDWICH COMPOUNDS CONTAINING PHOSPHORUS

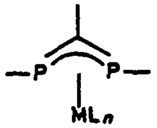
John F. Nixon, Rainer Bartsch, Mohd. Jamil Maah and Peter B. Hitchcock.
School of Chemistry and Molecular Sciences, University of Sussex,
Brighton, BN1 9QJ, Sussex, England.

There is considerable current interest in the ligating behaviour of unsaturated organophosphorus ligands.[1] It has become increasingly apparent that formal replacement of a CH fragment by P or a CH_2 fragment by PR in organic compounds can lead to a variety of novel unsaturated organophosphorus compounds, many of which form complexes with transition metals. During the past few years the structural types (a)—(h) have been established (ML_n = transition metal and attendant ligands).

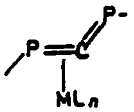
(a)



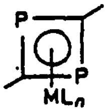
(b)



(c)

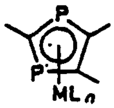


(d)

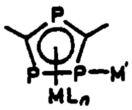


(e)

(f)

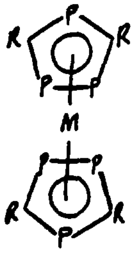


(g)

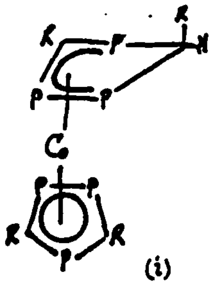


(h)

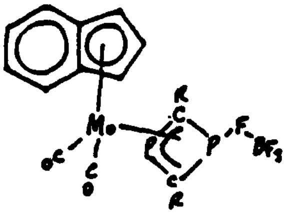
Recent results in syntheses, photo-electron spectra and electrochemistry of sandwich compounds of the type $[M(\eta^5\text{-}P_3C_2R_2)_2]$,(M = Cr,Fe),will be reported. New ring systems typified by (i) and (j)† below (the former containing a 1,2,4 triphospha-butadiene) will be described as will "half-sandwich" compounds (k) , (R = Bu^t).



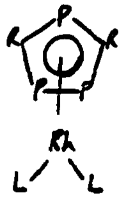
(M = Cr, Fe)



(i)



(j)



(k)

(L = PR'$_3$; L$_2$ = COD)

---

1. J. F. Nixon Chem. Revs. In Press.

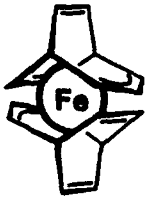
† In collaboration with Prof. M. Green, King's College, London.

ANALOGUES OF METALLOCENES WITH SEPARATED ALLYL AND OLEFIN SYSTEMS

J. Blümel, N. Hertkorn, F. H. Köhler, G. Müller, D. Wilkinson,
Anorganisch-chemisches Institut der TU München, Lichtenbergstr. 4,
8046 Garching, W-Germany.

Carbanions of type 1 play an important role in the discussion of homoaromaticity[1]. As a working base we regard 1 as a cyclopentadienyl (Cp) the π-system of which has been broken down into an olefinic and an allylic system so that corresponding transition metal complexes of 1 show increased reactivity as compared to Cp complexes. We describe the synthesis of complexes containing the following ligands: bicyclo[3.2.1]octa-2,6-dien-4-yl, bicyclo[3.2.2]nona-2,6,8-trien-4-yl, and tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-5-yl. Two examples, 2 and 3, are shown below. Compared with ferrocene these complexes display some remarkable differences and similarities which will be discussed.

1



2

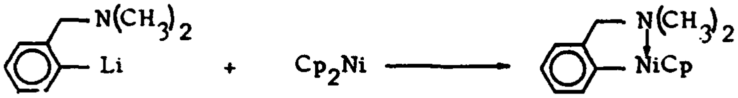
3

[1] a) L. A. Paquette, Angew. Chem. 90(1978)114. b) R. Lindh, B. O. Roos, G. Jonsäll, P. Ahlberg, J. Am. Chem. Soc. 108(1986)6554 and references cited therein.

SYNTHESIS AND REACTIONS OF CYCLOMETALLATED COMPOUNDS OF NICKEL

Antoni Pietrzykowski, Piotr Maksymiuk and Małgorzata Miłosz.
Institute of Organic Technology, Warsaw Technical University,
Koszykowa 75, 00-662 Warsaw, Poland

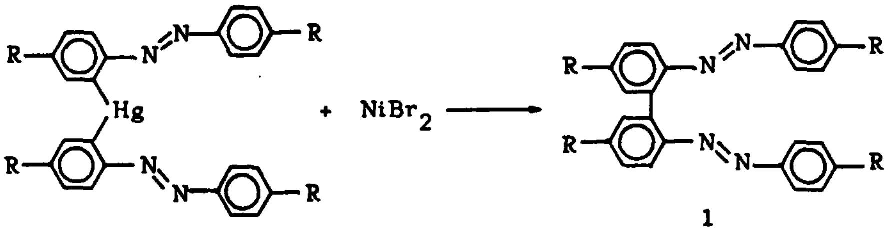
Treatment of bis-cyclopentadienylnickel with 2-((dimethylamino) methyl)phenyllithium in THF at room temperature for 2 h leads to the formation of η^5-cyclopentadienyl(2-((dimethylamino)methyl)phenyl)nickel with 60% yield.



The product was recrystalized from hexane and characterized by elemental analysis and ^{1}H NMR: /$CDCl_3$/ 6.86 /m, 4H, ring H/, 5.20 /s, 5H, Cp ring H/, 3.61 /s, 2H, CH_2/, 2.50 /s, 6H, NCH_3/.

Neither this compound nor its azobenzene analogue insert olefins and dienes. The reaction of (azb)NiCp with $Cl_2C=CCl-CCl=CCl_2/H_2O$ mixture leads to the formation of 2-hydroxyazobenzene.

The reaction of bis-((2-arylazo)aryl)mercury with nickel bromide in THF leads to the coupling of (arylazo)arene groups in ortho positions.



1

1 a: R=H; b: R=CH_3

After recrystallization from pentane compounds 1a and 1b were isolated with 52% and 62% yield respectively and were characterized by means of elemental analysis, IR and mass spectra.

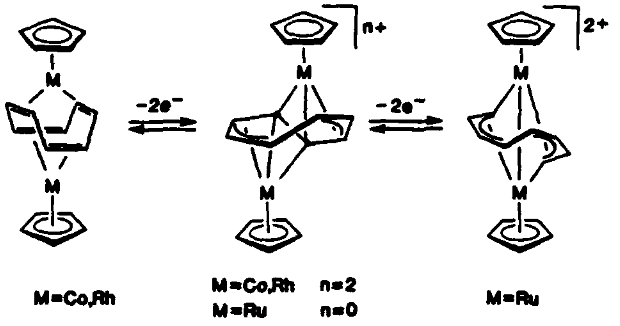
CYCLOOCTATETRAENE AS BRIDGING LIGAND: STRUCTURES, DYNAMIC BEHAVIOUR AND REDOX CHEMISTRY OF DIMETALLIC COMPLEXES

Albrecht Salzer and Urs Ruppli, Anorganisch-chemisches Institut der Universität Zürich, Winterthurerstr. 190, 8057 Zürich, Switzerland

Joseph Edwin and William E.Geiger, Department of Chemistry, University of Vermont, Burlington, Vermont, 05405

Arnold L. Rheingold, Department of Chemistry, University of Delaware, Newark, Delaware 19716

A series of dimetallic complexes of general composition $[Cp_2M_1M_2(\mu\text{-}C_8H_8]^{n+}$ will be presented with $M_{1,2}$ = Co,Rh,Ru and n = 0,1,2.
$Cp_2Rh_2C_8H_8$ occurs as two isomers with either cis or trans coordination to the bridging C_8H_8 moiety. Both complexes undergo reversible two-electron oxidations with concomitant structural rearrangements. The trans-dication shows an unsual slipped tripledecker structure.



In search for more electron-deficient numbers of this series, the oxidation of $Cp_2Ru_2C_8H_8$, also a slipped tripledecker, was investigated. This also undergoes reversible two-electron oxidation. In the dication the eight-carbon ring of the neutral precursor has opened, giving a chain whose termini now bridge a newly formed Ru-Ru bond. The central structure is basically a ten-membered dimetallacyclic ring. This reaction appears to be the first example of a reversible ring opening of a bridging olefinic ligand.

A.Salzer, U.Ruppli, J.Edwin, W.E.Geiger and A.L.Rheingold, J.Am.Chem.Soc. (1987) 109, 7893

The Chemistry and Structures of Trimesitylaluminum Derivatives; Novel Sterically Hindered Organometallic Compounds

John P. Oliver, Sreeni De Mel, and Mark LaLama

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

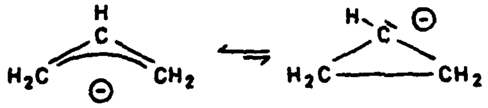
The structure of the sterically crowded molecule, trimesitylaluminum, determined previously,[1] will be compared with the crystal structure of trimesitylaluminum•THF(1) adduct which has been determined by single crystal X-ray diffraction techniques. The latter compound crystallizes in the monoclinic lattice system, space group $P2_1/c$, with unit cell dimensions of a = 8.457(7), b = 14.318(2), c = 22.234(3) Å, β = 98.271(9)°, v = 2264.48(49) $Å^3$ and Z = 4. The final full matrix least-squares refinement on 2062 data gave R = 7.5% and R_w = 4.5%. 1 is similar to other organoaluminum adducts yielding a four-coordinate aluminum atom but the steric crowding leads to a slightly longer Al-C distances, d_{av} = 2.017 Å and an Al-O distance of 1.969(5) Å, significantly longer than the Al-O distance observed in other THF and diethyl ether adducts. Further evidence of the steric crowding is seen in the distortion of the C-Al-O angles with one of these angles 91.4°, far less than observed in other ether adducts of triorganoaluminum derivatives. Simple calculations on the "acceptor" site size will be discussed and their implications with regard to the formation of other adducts will discussed and compared with experimental results. The formation and structure of derivatives in which one or more alkoxide or halide groups have been substituted for a mesityl group will be described.

1) Synthesis, Molecular Structure, and NMR Spectra of Trimesitylaluminum, A Novel Three-Coordinate Molecule: John J. Jerius, Juliet M. Hahn, A. F. M. Maqsudur Rahman, Ole Mols, William H. Ilsley, and John P. Oliver, *Organometallics*, 1986, 5, 1812-14.

VALENCE TAUTOMERISM OF RX-BRIDGED
(X = P.. Sb, S.. Te) DIMETAL COMPOUNDS

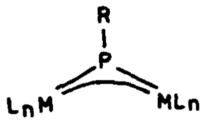
Gottfried Huttner, Anorganisch-Chemisches Institut der Universität Heidelberg
Im Neuenheimer Feld 270, D - 6900 Heidelberg, F.R.G.

The allylic anion **A** and its ring closed valence tautomere **B**, the cyclopropyl anion, are close and interconvertable neighbours on the corresponding hypersurface.

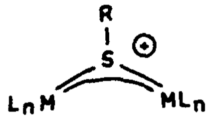


A **B**

The behaviour of these master compounds is mimicried by their organometallic analogues such as phosphinidene (**C**) or "sulfinidene" (**D**) complexes.



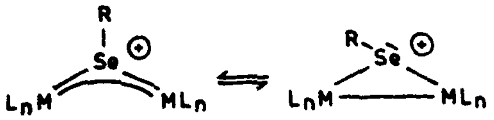
C



D

$L_nM = Cp(CO)_2Mn$

The Selenium homologue of **D**, **E**, displays a temperature dependent equilibrium between the open (**E**) and the closed form **F**.



E **F**

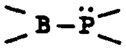
$L_nM = Cp(CO)_2Mn$

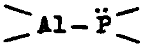
The observation itself and its implications are discussed.

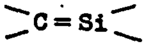
NOVEL "III/V"-COMPOUNDS

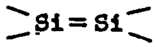
Hans H. Karsch, G. Hanika, A. Schneider, G. Müller
Anorganisch-chemisches Institut, Technische Universität München,
Lichtenbergstr. 4, D-8046 Garching, F.R.G.

Taking advantage of the concept of isoelectronic relationship, "III/V"-analogues (I, II) of silenes (III) and disilenes (IV) may be anticipated.

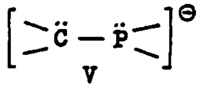

I

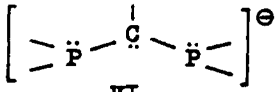

II

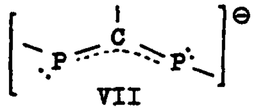

III


IV

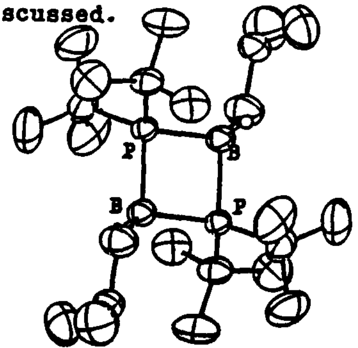
Monomeric, dimeric and trimeric derivatives of (I, II) with more or less bulky substituents have been prepared and characterized structurally and/or spectroscopically. Other anionic phosphorus based ligands than diorganophosphides $(R_2P)^-$, e.g. (V), (VI) and (VII) likewise give neutral III/V compounds.


V

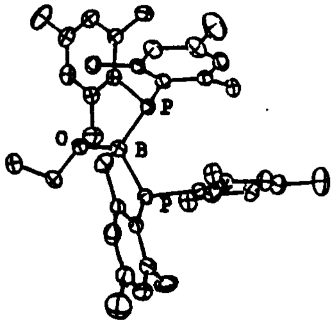

VI


VII

Examples for dimeric and monomeric boron diorganophosphides are **1** and **2**, respectively. Preparation, properties and structures are discussed.



[^{t}Bu$_2$P-B(H)^{i}Bu]$_2$
1



[(Mes)$_2$P]$_2$B-OEt
2

FUNCTIONAL AND CHIRAL PHOSPHORUS METAL DOUBLE BOND COMPLEXES .
$Cp(L)_2M{=}PR_2$ (M = Mo, W)

Wolfgang Malisch, S. Amann, E. Nodes, U. Hirth and M. Schmeußer, Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-8700 Würzburg, FRG

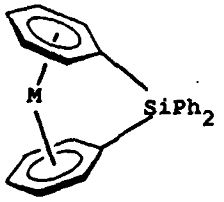
Functional metal phosphorus double bond complexes $Cp(CO)_2M{=}P(R)X$ (1) (X = H, Cl; R = alkyl, aryl, alkoxy, dialkylamino; M = Mo, W) can be synthesized either via decarbonylation of the corresponding metallo-phosphanes $Cp(CO)_3M\text{-}P(R)X$ (2) or via the dehydrochlorination of the bifunctional phosphane complexes $Cp(CO)_2M(Cl)\text{-}P(H)(R)X$ (3). In special cases side reactions give rise to the formation the metallacycles $Cp(CO)_2\overline{M\text{-}P(tBu)(Cl)\text{-}P}tBu$ (4) or the dinuclear M=P complex $Cp(CO)_2M{=}P(Mes)\text{-}M(CO)_2[P(Mes)H_2]Cp$ (5). Compounds of the type 2 are extremely reactive concerning the exchange of P-bonded hydrogen chlorine atom. In this context H/Cl-exchange with CCl_4 can be realized as well as the substitution of chlorine against RO^-, RS^-, R_2N^- and the metal anions $C_5R_5(CO)_3M^-$ (R = H, Me). Experiments to convert 2 to $[Cp(CO)_2M{=}PR]^+$ have so far been unsuccessful.

The chiral metal phosphorus double bond complexes $Cp(CO)(R_2PH)M{=}PR_2$ (7) ($R_2P = Ph_2P$, t-Bu(Ph)P) are obtained via dehydrohalogenation of $Cp(CO)(R_2PH)_2MCl$ (6) with $Me_3P{=}CH_2$. 7 can be further deprotonated to the anionic diphosphametalla-allyl species $[Cp(CO)(R_2P)_2M]^-$ (8), which represents an attractive building block in cluster synthesis. The structure, the spectroscopic data and the reactivity of 7, 8 are discussed.

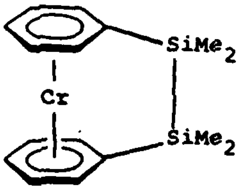
SILA-METALLOCYCLOPHANES

Christoph Elschenbroich, James Hurley, Werner Massa and
Gerhardt Baum
Fachbereich Chemie, Philipps-Universität,
Hans-Meerwein-Strasse, D-3550 Marburg (FRG)

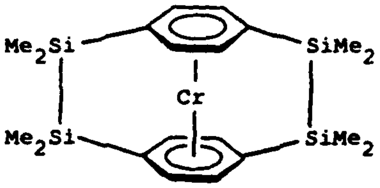
By means of wet-chemical methods and by metal-atom ligand-vapor cocondensation techniques we have prepared bis(η^6-arene) metal complexes containing -R_2Si- as well as -R_4Si_2- groups as interannular bridges (sila-metallocyclophanes):



1 M = V
2 M = Cr



3



4 [1]

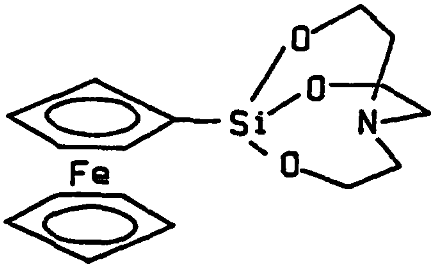
1 and 4 are characterized by X-ray crystallography, the paramagnetic species $1^{\cdot}$, $2^{\cdot+}$, $3^{\cdot+}$, and $4^{\cdot+}$ are studied by EPR-spectroscopy. Topics of interest include the effect of ring tilt on metal-ligand spin delocalization, the influence η^{12}-coordination of a transition metal atom excerts on the structure of the parent cyclophane and the prospect of constructing hetera-cyclophanes taking advantage of the template effect. Work towards accomplishing higher degrees of interannular bridging and towards substitution of germanium and tin for silicon in order to fine tune the dimension of the sandwich cavity is in progress and will be reported in due course.

[1] Ch.Elschenbroich, J.Hurley, W.Massa, G.Baum
Angew.Chem.100(1988) in print

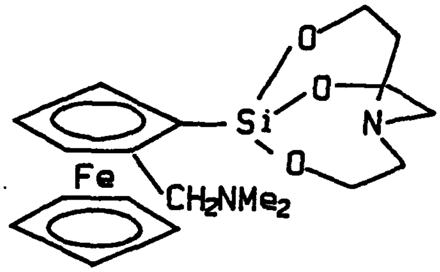
FERROCENYLSILATRANES

Rudolf Herrmann, Organisch-Chemisches Institut der Technischen
Universität München, Lichtenbergstr.4, D-8046 Garching (F.R.G.)

Silatranes are pentacoordinated silicon compounds of pharmaceutical interest1). Although many derivatives with different substituents at silicon have been reported, no silatranes with metallocene substituents have ever been prepared. The first members of this class of compounds will be presented here.



(I)



(II)

The silatranes (I) and (II) are prepared in the usual way2), i.e. by transesterification of triethoxysilanes with triethanolamine, or by direct reaction of ethoxysilatrane with lithiated ferrocenes. (I) and (II) show the normal spectroscopic behaviour of ferrocene and silatrane derivatives, and the NMR chemical shifts of ^{1}H, ^{13}C, ^{15}N, and ^{29}Si lie in the range expected for such compounds. Comparing the silatranes with the corresponding triethoxysilanes, the upfield shift in the ^{29}Si NMR spectra confirms the widening of the coordination sphere by the formation of the nitrogen-silicon bond. Interestingly, a considerable lowering of the redox potential corresponding to the reversible Fe$^{II/III}$ transition is observed comparing the triethoxysilanes with the silatranes ($\Delta E^{ox}_{1/2}$ = 0.26 V for (I) and 0.14 V for (II)). The redox potentials of the triethoxysilanes are almost the same as the unsubstituted ferrocene, while the much lower potentials of the silatranes suggest a considerable transmission of electron density from nitrogen to iron via silicon. Mechanisms for this transmission will be discussed.

1) M.G.Voronkov, Top.Curr.Chem. **84**, 77 (1979).
2) M.G.Voronkov, Pure Appl.Chem. **13**, 35 (1966).

SYNTHESIS, STRUCTURE AND REACTIVITY OF THE GERMENE Mes$_2$Ge=CR$_2$

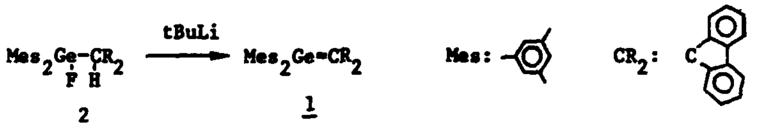
J. Escudie, C. Couret, M. Lazraq, J. Satgé

Laboratoire de Chimie des Organominéraux, UA 477, Université P. Sabatier
118 route de Narbonne, 31062 Toulouse cédex, France

and M. Dräger

Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg
Universität, Johann-Joachim-Becher-Weg 24, D-6500 Mainz, Germany

The germene 1, first stable compound with a germanium-carbon double bond[1], has recently been synthesized by dehydrofluorination of the fluorogermane 2 :



2 1

X-ray structure of 1 has been determined [2]: the germanium atom is planar and the germanium-carbon double bond (1.80 Å) is shortened by about 10.5% in relation to the corresponding single bond in the germane Mes$_2$Ge(H)C(H)R$_2$. Strong mesomeric effects, corroborated by calculations, are observed between the Ge=C double bond and the fluorenylidene group, and also for the first time across the germanium atom.

Reactivity of 1 is very important towards electrophiles (protic reagents, halogens...), nucleophiles (lithio compounds, hydrides...) which add onto the double bond.

Many cycloaddition reactions have been observed : [2+1] (sulfur), [2+2] (azo compounds, imines, aldehydes and ketones), [2+3] (nitrones, diazo compounds) and [2+4] (1,3-dienes, α-ethylenic aldehydes and ketones) with formation of novel three, four, five and six-membered rings.

The germene 1 appears as a very interesting new synthon in organometallic chemistry.

References

1) C. Couret, J. Escudié, J. Satgé and M. Lazraq, J. Am. Chem. Soc. (1987), 109, 4411

2) M. Lazraq, J. Escudié, C. Couret, J. Satgé, M. Dräger and R. Dammel, Angew. Chem. (in press).

LOW-COORDINATED SPECIES WITH MAIN GROUP IV/VI BONDS INCLUDING POST-TRANSITION-ELEMENTS

W.-W. du Mont, L. Lange, D. Sewing, T. Severengiz, I. Wagner, Fachbereich Chemie
Universität Oldenburg, Postfach 25 03, D-2900 Oldenburg, RFA

I. GENERATION AND DECOMPOSITION OF C=Te DOUBLE BOND SPECIES

Bis(trimethylsilyl)telluride 1 and di(pivaloyl)telluride 2a react to give pivaloyl(trimethylsilyl)telluride [trimethylsilyl telluropivaloate] 3a, which exsits in an dynamic equilibrium with the C=Te-bonded isomer 4a. 3a and 4a are related by an intramolecular 1,3-trimethylsilyl shift; (2+4)cycloaddition reactions with the C=Te bond lead to complete consumption of 3 and 4 [1]. Sterically less congested 4, obtained from 1 with diacetyltelluride 2b (confirmed by mass spectra and trapping experiments) decomposes spontaneously to give E- and Z-bis(trimethylsiloxy)buten (2).

II. APPROACH TO STERICALLY CONGESTED MOLECULES WITH Ge=S OR Ge=Se BONDS

Bis(2,4,6-tri-tert-butylphenyl)germanium(II), 5, the first isolated diarylgermylene, rearranges within several hours at room temperature to an the isomeric germaindane 6 [2]. With sulfur, 5 reacts at low temperature to germaindanthiol 7. The spontaneous C,H activation at one ortho-tert-butyl group of germathione 6 by an adjacent Ge=S bond deserves interest. Corresponding experiments, that might lead to Ge=Se or Ge=Te bonds, will be reported.

III. FORMATION AND STABILISATION OF THE FIRST SELENO GERMYLENE

Di-coordinate divalent germanium species are known with bulky substituents that contain, C, N, O, or S-atoms bonded to germanium. Stable monomeric germylenes with less electronegative, and highly polarizable atoms [from the 4th and 5th period] attached to germanium have not yet been isolated. Bis(2,4,6-tri-tert-butylphenylseleno)germanium(II) 8 was generated from the corresponding lithium reagent with $GeCl_2$-dioxane at -78°C ... -40°C. Isolation of pure 8 at room temperature failed, but pure Dichloro(2,4,6-tri-tert-butylphenylseleno)germanium(IV) 9 was obtained in low yield. Trapping of 8 with $W(CO)_5THF$ led to yellow crystalline $[W(CO)_5 \cdot 8]$, the monomeric germylene complex 10.

[1] T. Severengiz, W.-W. du Mont, J.Chem.Soc., Chem.Commun. 1987, 820
[2] L. Lange, W.-W. du Mont, J.Organomet.Chem. 329 (1987) C17

SYNTHESIS AND CATALYTIC ACTIVITY OF CARBONYL PALLADIUM CLUSTERS

I.I.Moiseev, Institute of General & Inorganic Chemistry,
Academy of Sciences, Leninskii pr., 31, Moscow, USSR

Palladium compounds are known to catalyze carbonylation reactions of unsaturated hydrocarbons, haloalkyls, carboxylic acids, alcohols, nitroaromatic derivatives [1, 2]. This attracts attention to carbonyl palladium complexes [3, 4].

Synthesis and properties of carbonyl clusters with Pd_4-core [5, 6] will be considered. The dehydratation of alcohols catalyzed by heteronuclear Pd,Mo-cluster $Na_2Pd_4Mo_4(CO)_{12}Cp_4$ [7, 8] under mild conditions will be discussed.

References

1. P.M.Maitlis "The Organic Chemistry of Palladium" v.II. Catalytic Reactions. Academic Press, New York and London, 1971.
2. Catalysis in C_1 Chemistry. Ed. by W.Keim, A.P.G.Dordrecht, Boston, Lancaster, 1983.
3. M.N.Vargaftig, T.A.Stromnova, I.I.Moiseev Russk.Z.Neorg.Khim. 1980, v.25(1), p.236-244.
4. F.Calderazzo, D.B.Dell'Amico Pure and Appl. Chem., 1986, v.58, N 4, p.561-566.
5. I.I.Moiseev, T.A.Stromnova, M.N.Vargaftig, G.Ja.Mazo, L.G.Kuzmina, Ju.T.Struchkov J.C.S.Chem.Commun. 1978, p.27-28.
6. M.N.Vargaftig, T.A.Stromnova, T.S.Khodashova, M.A.Poraj-Koshitz, I.I.Moiseev Koord. Khim. 1981, v.7(1), p.132-140.
7. T.A.Stromnova, I.N.Busygina, S.B.Katser, A.S.Antsyshkina, M.A. Poraj-Koshits, I.I.Moiseev Dokl. AN SSSR, 1987, v.295(4), p.890-893.
8. T.A.Stromnova, I.N.Busygina, S.B.Katser, A.S.Antsyshkina, M.A. Poraj-Koshits, I.I.Moiseev Izv. AN SSSR, Ser. Khim., 1987, N 6, p.1435.

ORGANO RARE EARTH HYDRIDES WITH CHELATING BISCYCLOPENTADIENE LIGAND

Changqing Ye, Yuqin Li and Changtao Qian, Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai, China

The $[C_5H_4(CH_2)_3C_5H_4]MC_4H_9\text{-t}(THF)$ complexes react with dihydrogen in toluene under mild conditions to yield a new class of organo rare earth hydrides with a chelating biscyclopentadiene ligand $[C_5H_4(CH_2)_3C_5H_4]MH(THF)$ (M=Y, Er, Lu). These hydrides have been

$$[C_5H_4(CH_2)_3C_5H_4]MC_4H_9\text{-t}(THF) + H_2 \longrightarrow [C_5H_4(CH_2)_3C_5H_4]MH(THF) + (CH_3)_3CH$$

characterized by IR, MS, ^1H NMR spectroscopy and elemental analysis. They are stable enough to be isolated and identified at ambient temperature. The factors which have been presumed to influence the cleavage of M-C bond in precursors and the formation of M-H bond are discussed.

Treatment of the hydrides obtained with 1-hexene in tetrahydrofuran produces hexane in good yield, moreover the hydrides are able to hydrogenate catalytically 1-hexene under mild conditions.

1. Changtao Qian, Changqing Ye, Hanzhang Lu, Yuqin Li and Yaozeng Huang, J. Organomet. Chem., 263, 333 (1984).
2. Changtao Qian, Changqing Ye and Yuqin Li, J. Organomet. Chem., 302, 171 (1986).

C-X ACTIVATION WITH Cp^*_2MH AND $Cp^*_2MCH(SiMe_3)_2$ DERIVATIVES OF Y, La, AND Ce.

Martin Booij, Djurre Postma, Rob Duchateau, Auke Meetsma and Jan H. Teuben.
Department of Chemistry, University of Groningen, The Netherlands.

In our study on the reactivity of metallocene hydride and alkyl compounds of Y, La, and Ce we found remarkable selectivity differences for the activation C-X bonds.

Thermolysis of $Cp^*_2MCH(SiMe_3)_2$ in toluene gave a mixture of products for M = Y, but for M = La and Ce exclusive activation of sp^3-C-H bonds with formation of the benzyl derivative (Fig. 1) was observed (eq 1).

$$Cp^*_2MCH(SiMe_3)_2 + C_6H_5CH_3 \text{ ----> } Cp^*_2MCH_2C_6H_5 + CH_2(SiMe_3)_2 \quad (M = La, Ce) \qquad (1).$$

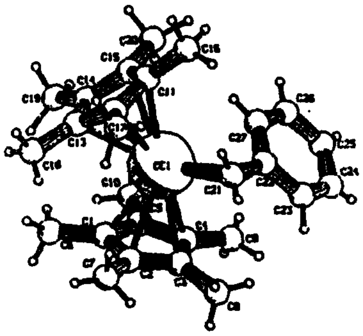


Fig. 1.

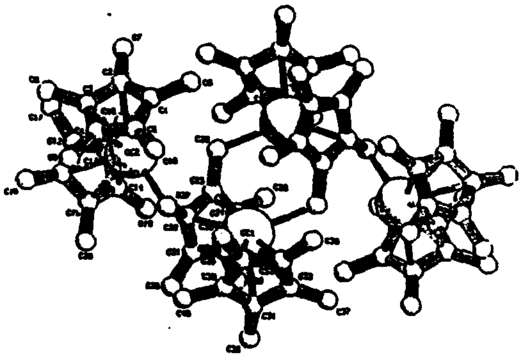


Fig. 2.

Thermolyses in an inert solvent like cyclohexane again showed the formation of $CH_2(SiMe_3)_2$. For M = Ce selective double hydrogen abstraction from the Cp^*-methyl groups took place (Fig. 2). The intriguing product is a tetramer with bridging $C_5Me_3(CH_2)_2$-groups.

For Cp^*_2YH both C-H and C-X activation was observed. Ortho directing groups like $-OCH_3$ and $-SCH_3$ provide selective C-H activation of ortho C-H bonds (eq 2). In contrast to this, aliphatic ethers show activation of the C-O bond (eq 3).

$$Cp^*_2YH + PhXCH_3 \text{ ----> } Cp^*_2Y(o\text{-}C_6H_4XCH_3) + H_2 \quad (X = O, S) \qquad (2).$$

$$Cp^*_2YH + R\text{-}O\text{-}R \text{ ----> } Cp^*_2Y\text{-}OR + RH \quad (R = Et, {}^iPr) \qquad (3).$$

REACTIVITY AND CATALYTIC PROPERTIES OF NAPHTHALENE AND ANTHRACENE COMPLEXES OF YTTERBIUM

M.N.Bochkarev,E.A.Fedorova, T.A.Basalgina, G.S.Kalinina,
I.M.Penyagina, Yu.F.Radkov, L.N.Zakharov, G.A.Razuvaev,
Institute of Chemistry, U.S.S.R Academy of Sciences,
Tropinina st, 49, GSP-445, Gorky, U.S.S.R.

Recently we have found that interaction of the anhydrous lanthanoid halides with naphthalene sodium or naphthalene lithium leads to the formation of high reactive naphthalene complexes of lanthanoids $C_{10}H_8Ln_x(MHal)_y$ (Ln = Sm, Eu, Yb; M = Li, Na; Hal = Cl, Br, I; x = 1-5; y = 0-3)[1].
The complex $C_{10}H_8Yb_2$(I) shows high catalytic activity in the reactions with oxygencontaining reagents and unsaturated hydrocarbons. The compound I catalyzes polymerzation reactions of epoxides, styrene, methyl methacrylate, isoprene and piperilene. It also catalyzes copolymerisation reaction of ethyleneoxide with styrene and isoprene, and reaction of epoxides with CO_2 which leads to alkylenecarbonates $R\overline{CH-CH_2-CO_2O}$.
Reaction of I with Ph_3GeH (THF, 20°C) gives a metalhydride complex of the new type $(Ph_3GeH)_2Yb\cdot(THF)_4$. It was isolated as the yellow diamagnetic crystals, soluble in THF, toluene, m.p. 129-133°C(dec.). X-Ray analysis shows that the molecule of the product is distorted octahedron. The grouping GeHYbHGe is almost colinear: the Ge-H-Yb angle is 169.4, and 168.8°, the H-Yb-H angle is 179.0°, the Ge-H distances are 1.61 and 1.65 Å , the Yb-H distances are 1.56 and 1.51 Å . Molecules of THF lei in equatorial plane. Anthracene complex $C_{14}H_{10}Yb_2(NaCl)_3$ was obtained as the black pyrophoric insoluble powder by reaction of $YbCl_3$ with anthracene sodium. It reacts with O_2, H_2O, CO_2, CpH, $(Me_3Si)_2NH$ and $\overline{CH_2CH_2O}$ like naphthalene complex but reactions are slower and give lower yields of the corresponding products.

I. M.N.Bochkarev, A.A.Trifonov, V.K.Cherkasov, G.A.Razuvaev, Abstr. VIII FECHEM Conf. Organometal Chem., Toledo, (1987), p. 152; Zh. Obshch. Khim. 58(1988)719.

THE PREPARATION OF DIVALENT AMIDO-LANTHANOIDS BY PROTOLYTIC CLEAVAGE OF $(C_6F_5)_2M$ (M = Sm, Eu, Yb) – EVIDENCE FOR THE FORMATION OF $(C_6F_5)_2Sm$ FROM $(C_6F_5)_2Hg$ AND METALLIC SAMARIUM.

G.B. Deacon and C.M. Forsyth. Department of Chemistry, Monash University, Clayton,
Victoria 3168, Australia.

The bis(pentafluorophenyl)lanthanoid complexes, $(C_6F_5)_2M$ (M = Eu, Yb), which are readily prepared by transmetallation of $(C_6F_5)_2Hg$ with europium or ytterbium, (eq.(1)), react with weak N–acids, displacing pentafluorobenzene and forming divalent amido-lanthanoids (eq.(2)).

$$Hg(C_6F_5)_2 + M \xrightarrow{thf} (C_6F_5)_2M + Hg\downarrow \qquad \ldots(1)$$

M = Eu, Yb.

$$(C_6F_5)_2M + 2R_2NH \xrightarrow{thf} (R_2N)_2M + 2C_6F_5H \qquad \ldots(2)$$

R_2NH = carbazole, 2–phenylindole

Prior formation of the $(C_6F_5)_2M$ reagent can be omitted by using a "one-pot" synthesis, *viz* – direct reaction of the metal, $(C_6F_5)_2Hg$ and the amine (eq.(3)).

$$M + (C_6F_5)_2Hg + 2R_2NH \xrightarrow{thf} (R_2N)_2M + Hg\downarrow + 2C_6F_5H \qquad \ldots(3)$$

M = Eu, Yb; R_2NH = 2–phenylindole

The reaction of $(C_6F_5)_2Hg$ with samarium metal, in contrast with that for europium and ytterbium, yields as variety of products which are considered to be derived from decomposition of initially formed $(C_6F_5)_2Sm$ and/or $(C_6F_5)_3Sm$ species (eq.(4)).

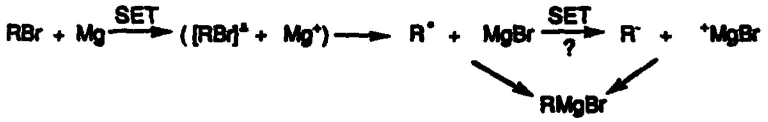
$$(C_6F_5)_2Hg + Sm \begin{array}{l} \nearrow (C_6F_5)_2Sm \\ \\ \searrow (C_6F_5)_3Sm \end{array} \left.\vphantom{\begin{array}{l} a \\ \\ b \end{array}}\right\} \rightarrow \text{decomposition products} \qquad \ldots(4)$$

However, by utilizing the "one-pot" reaction (eq.(3) M = Sm) the thf soluble, divalent amido-samarium complex, (2–phenylindol-1-yl)$_2$Sm(thf)$_4$ was prepared. This provides substantial evidence for the formation of $(C_6F_5)_2Sm$ from the transmetallation reaction.

CARBANIONOID INTERMEDIATES IN THE GRIGNARD FORMATION REACTION

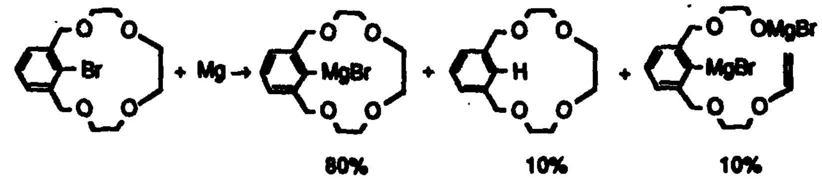
H.J.R. de Boer, P.R. Markies, T. Nomoto, O.S. Akkerman and F. Bickelhaupt
Scheikundig Laboratorium , Vrije Universiteit,
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

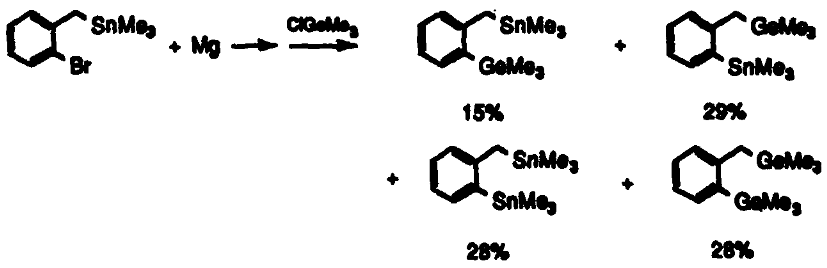
The famous and preparatively important formation of Grignard reagents from organic halides has been the subject of intensive mechanistic investigation. Although the heterogeneous character of the reaction and the (extremely) short half life of the many intermediates posed major obstacles, the following scheme has gradually emerged, and there is widespread agreement on most of its features.



$$RBr + Mg \xrightarrow{SET} ([RBr]^{\pm} + Mg^{+}) \longrightarrow R^{\bullet} + MgBr \xrightarrow[?]{SET} R^{-} + {}^{+}MgBr \quad \longrightarrow RMgBr$$

Uncertainty exists amongst others on the latter stages of the reaction. Thus, there is no doubt that the radical R and MgBr combine to give RMgBr, but it is mostly assumed that this combination is a direct one without the intermediate formation by a single electron transfer (SET) of the (more or less free) carbanion R⁻. We present evidence from two completely unrelated systems exhibiting two completely different, but highly diagnostic modes of reactivity, which point to R⁻ as a true intermediate:

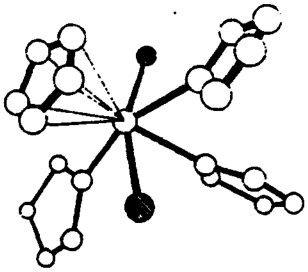




MONOCYCLOPENTADIENYL LANTHANIDE(III) COMPLEXES.I. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE mer,trans EUROPIUM(III) COMPLEX $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$

Giovanni De Paoli and Pierluigi Zanonato, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, Via L. Loredan, 4, 35100 - Padova - Italy.
Giovanni Valle, Centro di Studi sui Biopolimeri del C.N.R., Via Marzolo, 1, 35141- Padova - Italy

As a part of a spectroscopic study on europium(II and III) organometallic derivatives, the solid state structure of the compound obtained by reacting (1) NaC_5H_5 and $EuCl_3$ in tetrahydrofuran (molar ratio=1) is reported. Structural data on monocyclopentadienyl complexes of the type $(C_5H_5)LnCl_2(THF)_3$ (Ln=Lanthanide; THF = tetrahydrofuran) are known only for Ln=Er(2). Since the size of the lanthanide metal seems to have "a pronunced influence on the structural makeup of Cp-compounds", (1) we have investigated possible conformational changes in the solid state, in the "gadolinium break" region of the lanthanide series. The title compound shows in the solid state the same arrangement of the ligands found in the erbium(III) analogue.



Crystal data.The purple single crystals of $(\eta^5\text{-}C_5H_5)EuCl_2(THF)_3$ are monoclinic, space group $P2_1/n$ with four molecules in a unit cell of dimensions:a=15.258(3), b=17.216(3), c=7.860(1)Å,β=95.5(3)°. The europium(III) ion is coordinated by two chloride two chloride ions, three tetrahydrofuran oxygen atoms and the cyclopentadienyl group bonded in a penta- hapto fashion.(see Figure). The europium(III) coordination sphere can be described as distorted octahedral with the $\eta^5\text{-}C_5H_5$ ligand formally occupying one of the polyhedral vertices. The THF molecules have a meridional disposition and the chlorine atoms occupy approximately trans sites.

REFERENCES.

1)S. Monastyrskyj, R.E. Maggin and M. Dubeck, Inorg. Chem.,2,904,(1963).
2)C.S. Day, V.W. Day, R.D. Ernst and S.H. Vollmer, Organometallics,1,998,(1982) and references therein.

ELECTRON RICH METAL COMPLEXES FOR CO_2 AND CS_2 INCORPORATION

Ernesto Carmona, Departamento de Química Inorgánica and Instituto de Ciencias de Materiales de Sevilla, Universidad de Sevilla-CSIC, Aptdo. 553, 41071 Sevilla, Spain.

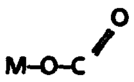
The synthesis of some new dinitrogen and ethylene complexes of Mo and W has been carried out and their reactivity towards CO_2 and CS_2 has been studied. While CO_2 reacts with the compounds trans-$M(C_2H_4)_2(PMe_3)_4$, (M= Mo, W), with formation of the white acrylate complexes $|M(CH_2{=}\,CHCO_2)H(C_2H_4)(PMe_3)_2|_2$, the reaction with CS_2 affords an almost black material of composition $M(CS_2)_2(C_2H_4)(PMe_3)_3$, which has been shown to contain an η^3-C_2S_4 fragment, resulting from the reductive head-to-tail coupling of two molecules of CS_2. CO symmetrically cleaves the C_2S_4 group of this complex and yields the M(0) species $Mo(S_2CPMe_3)(CO)_2(PMe_3)_2$.

The reactivity of some nickelacyclopentene complexes, $L_2Ni(CH_2CMe_2$-$\underline{o}$-$C_6H_4)$, towards CO_2 and CS_2, has also been investigated. While anhydrous CO_2 produces only the nickelalactone complex $(PMe_3)_2Ni(CH_2CMe_2$-$\underline{o}$-$C_6H_4CO_2)$, excess of CS_2 reacts with formation of $Ni(C_2S_4PMe_3)(PMe_3)$, (J.A. Ibers, 1982), and the thiolactone $S{=}C(S)CH_2CMe_2$-$\underline{o}$-C_6H_4. A possible pathway for this reaction has been stablished by the isolation of the intermediate η^2-C,S dithiolactone complex $(PMe_3)_2Ni(S{=}C(S)CH_2C(Me)_2$-$\underline{o}$-$C_6H_4)$. The dmpe derivative, $(dmpe)Ni(CH_2C(Me)_2$-$\underline{o}$-$C_6H_4)$ reacts with excess CS_2 with formation of the trithiocarbonate $(dmpe)Ni(CS_3)$ and of the tioketone $S{=}CCH_2C(Me)_2$-$\underline{o}$-C_6H_4. This process can formally be regarded as a reductive disproportionation of CS_2 although it takes place without change in the oxydation state of the metal. The reaction seems to imply an insertion of CS_2 as the first step, and this has been confirmed by isolation of the dithiolate complex $(dmpe)Ni(S_2CCH_2CMe_2$-o-$C_6H_4)$.

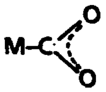
VIBRATIONAL SPECTROSCOPIC STUDIES OF SOME CARBON DIOXIDE COMPLEXES

Corine Jegat and Joëlle Mascetti, Laboratoire de Spectroscopie Moléculaire et Cristalline, (UA 124 CNRS), 351, Cours de la Libération, 33405 Talence Cedex, France

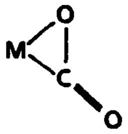
Some transition metal atoms in low valency state form complexes with CO_2, leading to the following structures :



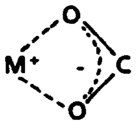
(1)



(2)



(3)



(4)

A systematic study of the reactivity of CO_2 toward transition metal atoms at zero oxidation state has been realized in low temperature matrices by means of F.T.I.R. spectroscopy in an attempt to learn more about the binding of CO_2 with transition metal atoms. Structures (1) (2) (3) have been observed, depending on the nature of the metal and the matrix, leading to different reactivities upon annealing or irradiation.

IR bands alone do not allow to discriminate between the different structures but the situation is more favorable if we look at the isotopic shifts of the stretching and bending modes of coordinated CO_2, using $^{13}CO_2$ and $C^{18}O_2$.

So structural conclusions and schematic pathways of reactions can be based on the isotopic shifts observed in IR spectra and normal coordinate calculations have been carried out for structures (1) (2) and (3). Compared with the free molecule, the force constants of coordinated CO_2 are significantly decreased (-50 %) and OCO angle is typically between 120 and 150°.

To improve our analysis, we also calculate force constants for some structurally already known complexes and transfer them to our models :
e.g., the valence force field of $(PCy_3)_2Ni(CO_2)$ (a) and $(PMe_3)_4Mo(CO_2)_2$ (b) are determined from the IR and Raman frequencies of complexes and some labeled derivatives.

(a) collaboration with M.ARESTA, Univ.Bari, Italy
(b) collaboration with E.CARMONA, Univ. Sevilla, Spain.

A HETEROBIMETALLIC APPROACH TO C/O BOND SCISSION OF CO_2.

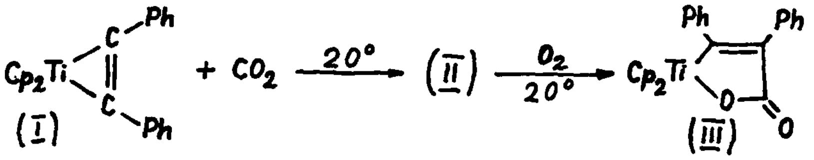
E. G. Lundquist, J. C. Huffman, and Kenneth G. Caulton,
Department of Chemistry and Molecular Structure Center,
Bloomington, IN 47405 (U.S.A.).

The heterobimetallic polyhydride $(COD)RhH_3OsP_3$ (COD ≡ 1,5-cyclooctadiene; P ≡ PMe_2Ph) reacts with CO_2 at 1 atm and 25° to produce $H_2Os(CO)P_3$, $(COD)_2Rh_2P_3OsH_2CO_2$ and H_2O. Hydride transfer thus effects reduction of CO_2 to CO. The Rh_2Os cluster has been shown by spectroscopic studies and X-ray diffraction to contain CO_2 in a highly bent geometry, this ligand being coplanar with and bonded to all three metals. Attempts to probe the reactivity of this tightly-bound CO_2 moiety reveal it to be subject to electrophilic attack, detected initially by changes in ^1H, ^{31}P, and ^{13}C NMR parameters. The bonding in the resulting adducts has been established in one example, by X-ray diffraction of the product from Zn^{2+}.

INTERACTION OF A TOLANE COMPLEX OF TITANOCENE WITH CARBON DIOXIDE

Vladimir Burlakov, Alexander Yanovsky, Yurii Struchkov, Vladimir Shur and Mark Vol'pin, Institute of Organo-Element Compounds of the USSR Academy of Sciences, Vavilov St. 28, Moscow 117813, USSR

We have found that a complex of titanocene with tolane $Cp_2Ti(C_2Ph_2)$ (I) [1] readily reacts with carbon dioxide at room temperature and atmospheric pressure. On carrying out the reaction in hexane the product (II) is formed, a subsequent interaction of which with the air oxygen results in rapid formation of titanadihydrofuranone metallacycle (III). The structure of the complex III has been proved by an X-ray analysis (λMo, 2713 reflections, R=0.031); the structure of II is under investigation and the results of this study will be presented.



Complex III is an air-stable, red, crystalline substance (m.p. 261-262°C(dec.) under Ar) soluble in CH_2Cl_2 and poorly soluble in ethers and hydrocarbons. The titanadihydrofuranone cycle $TiOC_3$ in III has an envelope conformation. The Ti atom is displaced from the OC_3 plane by 0.222(1) Å, the $TiOC/OC_3$ dihedral angle is equal to 7.9(2)°. Geometry of coordination environment of the Ti atom is unexceptional. The Cp ring planes in the wedge-like sandwich form the dihedral angle of 133.4(1)°, the Ti-C and Ti-O bond lengths in the metallacycle are equal to 2.199(1) and 1.964(1) Å respectively.

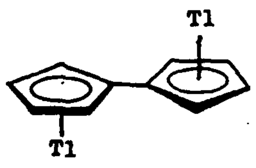
1. V.B.Shur, V.V.Burlakov, M.E.Vol'pin, J.Organomet. Chem., 1988, in press.

STUDIES ON FULVALENE DERIVATIVES OF GROUP 7 AND 9 METALS

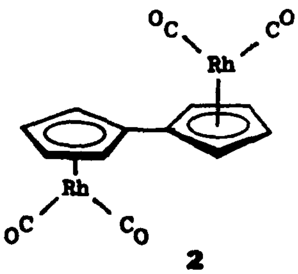
M. D. Rausch and W. C. Spink, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003 (U.S.A.)

T. E. Bitterwolf, Department of Chemistry, United States Naval Academy, Annapolis, Maryland 21402 (U.S.A.)

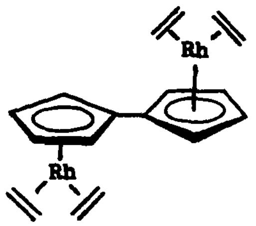
The reaction of thallous ethoxide with halide-free solutions of dihydrofulvalene has produced (fulvalene)dithallium (1) in 85-100% yield. Compound 1 is a brown air-sensitive solid that can be stored at -20°C for several months. Reactions of 1 with carbonyl halides of manganese, rhenium, cobalt, rhodium and iridium produced the corresponding homobimetallic fulvalene-metal carbonyls in yields of 52-94%. The dirhodium analog (2) reacted with trimethylamine-N-oxide to form a tricarbonyl complex that contained a bridging carbonyl group and a rhodium-rhodium bond. Tetraethylene(fulvalene)-dirhodium (3) and bis(cyclooctatetraene)dirhodium (4) as well as the corresponding bis(1,5-cyclooctadiene) analog have been prepared in excellent yields by reactions of 1 with the corresponding diolefin(chloro)rhodium dimer. Variable temperature proton NMR studies on 3 indicate that the ethylene ligands are fluxional. Photolysis of 4 with $CpRh(C_2H_4)_2$ in THF solution has produced a novel tetranuclear rhodium complex in 27% yield. Reaction of 2 with $(Ph_2P)_2CH_2$ has led to a bridged derivative (5) that has been the subject of chemical oxidation and protonation studies. The structures of 2 and 3 have been confirmed by X-ray diffraction analyses.



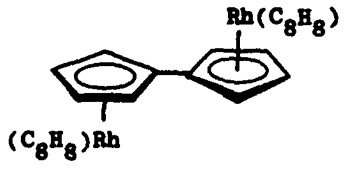
1



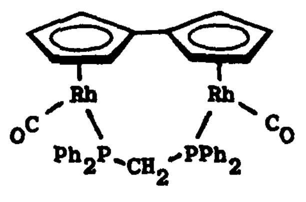
2



3



4



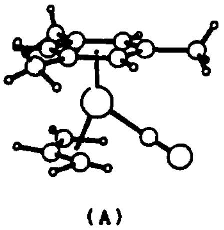
5

A STUDY OF HALF-SANDWICH ARENE-IRON (II) COMPLEXES

Anthony H. Wright and Shakher Puntambekar, Chemistry Department, University of Nottingham, Nottingham, NG7 2RD, U.K.

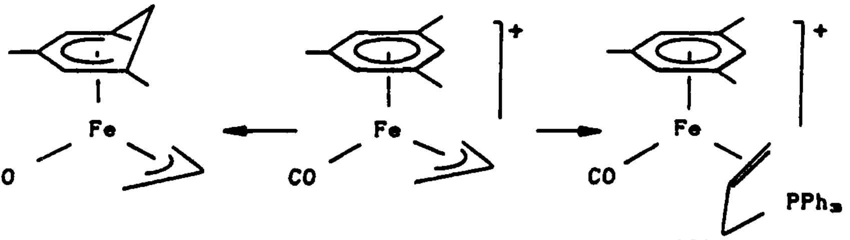
One of the major branches of organoiron chemistry is based on half sandwich chemistry, based on complexes such as CpFeXL$_2$. The comparable chemistry for arene-iron complexes is minimal. This is because ther appropriate synthetic routes to half-sandwich iron (II) complexes have not been available.

A new method for making both sandwich and half-sandwich arene-iron complexes will be outlined. The products, such as [(C$_6$H$_3$Me)Fe(C$_3$H$_5$)(CO)]PF$_6$ (A) are air stable but highly reactive fulfilling the anticipation of a rich chemistry. As might be expected for these electron-rich species, the neutral derivatives are however air sensitive.



(A)

Preliminary investigations of reactivity indicate that both metal-based and arene-based reactions are common. Results including arene substitution, and nucleophilic addition will be described.



(B) (A) (C)

The site of nucleophilic substitution is critically dependant on the nature of the nucleophile. Thus simple hydride addition gives the predicted Green-Mingos product (B), but phosphines add to the allyl ligand (C).

THE INCLUSION AND COVALENT ORGANOMETALLIC DERIVATIVES OF CYCLODEXTRINS

Viatcheslav I. Sokolov and Veronica L. Bondareva, Institute of Organo-Element Compounds, Vavilov St., 28, 117813 Moscow, U.S.S.R.

The cyclodextrin complexes with organometallic derivatives of iron, ruthenium, osmium, rhodium and some other transition metals have been prepared in solid state from aqueous solution. They are used to carry hydrophobic π-cyclopentadienyl or π-arene ligands.

Induced Cotton effects in the circular dichroism spectra which correspond to the chromophores of the molecules included have been investigated, as well as equilibrium constants for some ferrocenes have been determined in the ethylene glycol solution.

Several modified α- and β-cyclodextrins having σ-bonded ferrocenyl or arylchromiumtricarbonyl groups have been synthesized such as π-complexed per-benzoyl derivatives

$$(C_6H_7O_5)_n(OCOC_6H_5)_{3n-m}[OCOC_6H_5Cr(CO)_3]_m$$

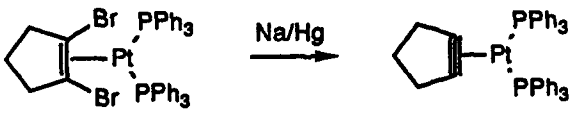
$n = 7,\ m = 2;\qquad n = 6,\ m = 1$

THE STABILIZATION AND REACTIVITY OF HIGHLY STRAINED CYCLIC ALKYNES ON TRANSITION METAL CENTRES

Martin Bennett, Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

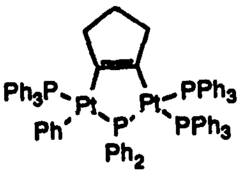
The smallest carbocyclic acetylene that can be isolated in the free state is the eight-membered ring cyclooctyne. Smaller cycloalkynes and benzyne (didehydrobenzene) are transient molecules that can be stabilized by formation of mononuclear metal complexes, especially with the d^{10} elements nickel(0) and platinum(0).

This lecture will describe the synthesis and reactivity of a series of η^2-benzyne complexes $M(\eta^2\text{-}C_6H_4)L_2$ (M = Ni, Pt; L_2 = various monodentate and bidentate tertiary phosphines)[1], together with the formation of a dinuclear nickel(0) complex of 1,4-benzdiyne (1,2,4,5-tetradehydrobenzene), $\mu\text{-}1,4\text{-}C_6H_2Ni_2(Cy_2PCH_2CH_2PCy_2)_2$. The generation of the first metal complex of cyclopentyne, (1), will be reported (eq 1). This molecule is clearly more strained than its long-known cyclohexyne analogue[2]; in the presence of polar solvents, one of its PPh_3 ligands undergoes spontaneous P-Ph bond cleavage to give the dimer 2.



eq. 1

1



2

1. M.A. Bennett, T.W. Hambley, N.K. Roberts and G.B. Robertson, Organometallics, 4(1985)1992.
2. M.A. Bennett and T. Yoshida, J.Amer.Chem.Soc. 100(1978)1750.

SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF MANGANESE AND CHROMIUM ACETYLENE COMPLEXES

Helmut G. Alt and Heidi E. Engelhardt
Laboratorium für Anorganische Chemie der Universität Bayreuth,
Universitätsstrasse 30, D-8580 Bayreuth (West Germany)

The acetylene complexes $Cp'(CO)_2MnC_2H_2$ (**1**) ($Cp' = \eta^5$-C_5H_5, η^5-C_5H_4Me, η^5-C_5Me_5) and $Ar(CO)_2CrC_2H_2$ (**2**) ($Ar = \eta^6$-C_6H_6, η^6-$C_6H_3Me_3$, η^6-C_6Me_6) can be prepared by the photo-induced reaction of the corresponding tricarbonyl compounds and acetylene. Complexes **1** and **2** react with various phosphines, amines, alcohols and hydrazines yielding ylidic carbene-, ylidic vinylidene-, aminocarbene-, carbene- and acetonitrile complexes. The various products were characterized by IR and NMR spectroscopy as well as X-ray structures in some cases.

Isocyanides,good ligands for the stabilisation of tungsten carbyne complexes in low and high oxidation states

ALEXANDER CONSTANTIN FILIPPOU, ERNST OTTO FISCHER
INSTITUT FÜR ANORGANISCHE CHEMIE,TECHNISCHE UNIVERSITÄT MÜNCHEN,
LICHTENBERGSTR.4,D-8046 GARCHING,WEST GERMANY

Carbyne complexes of the general type $I(CO)_2L_2W{\equiv}CNEt_2$ (I: L=py, II: L_2=2.2'-bipy, III: L_2=ophen) /1/ are easily accessible,useful starting materials for the preparation of neutral and cationic isocyanide substituted carbyne complexes of tungsten in low and high oxidation states.Thus the pyridine ligands in I can be readily replaced by RNC to yield $I(CO)_2(RNC)_2W{\equiv}CNEt_2$ (IV: R=Me, V:R=t-C_4H_9).Upon oxidative decarbonylation with iodine,IV and V are transformed to the seven coordinated complexes $(I)_3(CO)(RNC)_2W{\equiv}CNEt_2$,which react with excess RNC upon elimination of CO to give the cationic compounds $[(I)_2(RNC)_4W{\equiv}CNEt_2]^+ I^-$ /2/.Following a similar synthetic route,II and III are first oxidized to $(I)_3(CO)L_2W{\equiv}CNEt_2$ (L_2=2.2'-bipy,ophen) and then converted to the cationic species $[(I)_2(+NC)_2L_2W{\equiv}CNEt_2]^+I^-$ (L_2=2.2'-bipy,ophen) /3/.

A rich coordination chemistry is observed when $I(CO)_2(+NC)_2W{\equiv}CNEt_2$ (V) is heated with $+NC$.It loses CO ligands successively to yield $I(CO)(+NC)_3W{\equiv}CNEt_2$ (VI) and $I(+NC)_4W{\equiv}CNEt_2$ (VII).In the presence of $+NC$,thermodynamic equilibria between VI or VII and their cationic counterparts $[(+NC)_4(CO)W{\equiv}CNEt_2]^+ I^-$ (VIII) or $[(+NC)_5W{\equiv}CNEt_2]^+ I^-$ (IX) exist.These equilibria are dependant on the temperature and the nature of the solvent,and permit the quantitative interconversion of VI and VIII,or VII and IX /4/.

/1/ A.C.Filippou,E.O.Fischer und J.Okuda,J.Organomet.Chem.,339(1988) 309.
/2/ A.C.Filippou,E.O.Fischer und R.Paciello,J.Organomet.Chem.,to be published.
/3/ A.C.Filippou,E.O.Fischer und H.G.Alt,Z.Naturforsch.B,to be published.
/4/ A.C.Filippou und E.O.Fischer,J.Organomet.Chem.,to be published.

REACTIONS OF THE HYDRIDO COMPLEXES $|Ru(CO)ClH(py)(PPh_3)_2|$ AND $|Ru(CO)HL_2(PPh_3)_2|ClO_4$ (L = MeCN, py) WITH ACETYLENES.

Antonio Romero, Amelia Santos and Angel Vegas, Instituto de Ciencia de Materiales de Madrid, Sede D, C.S.I.C.,Serrano 113, 28006 Madrid.
Pedro Noheda, Instituto de Química Orgánica General, C.S.I.C.,Juan de la Cierva 3, 28006 Madrid.

Recently we have reported on the reactions of $|Ru(CO)ClH(Me_2Hpz)(PPh_3)_2|$ (Me_2Hpz = 3,5-dimethyl-pyrazole) with acetylenes, which were strongly dependent on the solvent nature |1,2|.

The reactions of the analogous neutral complex $|Ru(CO)ClH(py)(PPh_3)_2|$ with terminal acetylenes RC≡CH (R = CMe_3,Ph,COOMe,COOEt) give rise to the expected - alkenyl complexes derived from a cis-insertion of the alkyne into the Ru-H bond. However the reactions in MeOH yield alkynyl complexes $|Ru(CO)(C{\equiv}CR)(py)(PPh_3)_2|$. These last reactions in the presence of NH_4PF_6 give rise to the same alkynyl complexes in the case of R = CMe_3 and Ph, but in the reactions with the activated acetylenes (R = COOMe, COOEt) not yet well characterized carbene or vinylidene complexes seem to be formed, as in the corresponding reactions of the pyrazole complex.

$|Ru(CO)H(py)_2(PPh_3)_2|ClO_4$ shows a strong tendence to give catalytic cyclotrimerization reactions of the alkynes. Only in some cases the expected monoinsertion derivatives could be isolated from the reactions in a molar ratio 1:1 - in CH_2Cl_2. However $|Ru(CO)H(MeCN)_2(PPh_3)_2|ClO_4$ yields well characterized monoinsertion derivatives in the same conditions, in which both nitrile ligands are - mutually trans, although these ligands were mutually cis in the starting complex.

In the case of the cationic complexes the reactions with dimethyl acetylene dicarboxylate were also studied.

1. A. Romero, A. Santos and A. Vegas, Organometallics, 1987, 6, 1584-1586.
2. A. Romero, A. Santos and A. Vegas, Organometallics (in press).

SYNTHESIS AND REACTIVITY OF BIS(PYRAZOL-1-YL)BORATE ALKYLIDYNE COMPLEXES OF TUNGSTEN AND MOLYBDENUM

Anthony F. Hill and F. Gordon A. Stone

Department of Inorganic Chemistry, University of Bristol,
Bristol BS8 1TS, Great Britain.

The complexes $[W(\equiv CR)(CO)_2(NC_5H_4Me\text{-}4)_2Br]$ (R = CH_3, C_6H_4Me-4, $C_6H_3Me_2$-2,6) and $[Mo(\equiv CC_6H_4Me\text{-}4)(CO)_2(NC_5H_4Me\text{-}4)_2(CF_3CO_2)]$ react with $K[H_2B(pz)_2]$ (pz = pyrazol-1-yl) in dichloromethane to afford the compounds $[M(\equiv CR)(CO)_2(NC_5H_4Me\text{-}4)\{\eta^2\text{-}H_2B(pz)_2\}]$ (M = W, R = CH_3 1a, C_6H_4Me-4 1b, $C_6H_3Me_2$-2,6 1c; M = Mo, R = C_6H_4Me-4 1d) in high yield.

Alternatively, phosphite substituted molybdenum-alkylidyne complexes are accessible from the reaction of $[Mo(\equiv CC_6H_4OMe\text{-}2)(CO)\{P(OMe)_3\}_3Cl]$ with the salts $K[H_2B(pz)_2]$ or $K[Ph_2B(pz)_2]$ giving the compounds $[Mo(\equiv CC_6H_4OMe\text{-}2)(CO)\{P(OMe)_3\}_2(\eta^2\text{-}R_2B(pz)_2\}]$ (R = H 2a, *Ph 2b*)

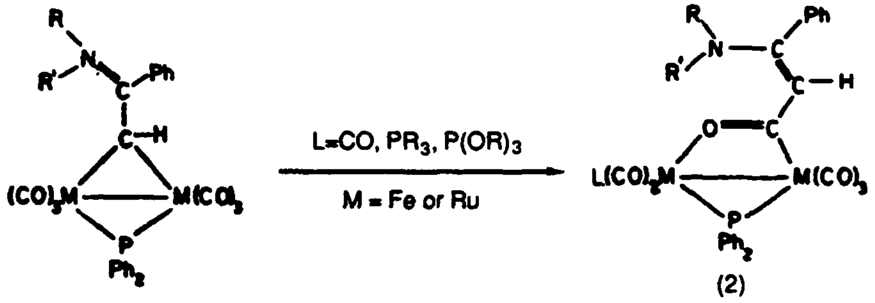
The compounds 1 and 2 feature coordination of a labile ligand (γ-picoline or phosphite) *cis* to the alkylidyne group and this property is seen to dominate the subsequent chemistry.

The reactions of 1 and 2 with phosphines, isonitriles, alkynes, nitrosarenes and chalcogens will be discussed, with particular reference to the rôle of the poly(pyrazol-1-yl) ligand.

Binuclear μ-Acyl Complexes via Carbonyl Insertion into a μ-Alkylidene Ligand.

Graeme Hogarth, Nicholas J. Taylor and Arthur J.Carty, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

The unusual three electron donor μ-alkylidene complexes $[M_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}CHC(Ph)NRR'\}]$ (1) smoothly insert carbon monoxide in the presence of donor ligands to give the corresponding μ-acyl complexes $[M_2(CO)_5L(\mu\text{-}PPh_2)\{\mu\text{-}O{=}CCHC(Ph)NRR'\}]$ (2) in high yield.



(1)

(2)

U.v. kinetic studies have been performed and show a first order dependence in both starting complex and incoming ligand as well as an interesting solvent dependence. Site selectivity of the incoming ligand is also noted allowing a mechanism for this process to be proposed. Reactivity studies on the μ-acyl complexes (2) will be presented.

AQUEOUS AND NON-AQUEOUS CHEMISTRY OF LATE TRANSITION METAL σ-ALKYNYL COMPLEXES

Pauline Chow, David Zargarian, Ian R. Jobe, Ian D. Williams, Nicholas J. Taylor and Todd B. Marder, The Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Wateroo, Waterloo, Ontario, N2L 3G1 Canada.

During the course of our studies of the Rh catalyzed cyclization of alkynoic acids to enol lactones, we found* that the complex $[Rh(PMe_3)_4]Cl$ reacts with terminal alkynes via C-H oxidative addition yielding cis-hydrido-σ-alkynyl complexes $[Rh(PMe_3)_4(H)(C{\equiv}CR)]Cl$ (1) in quantitative yield. The reaction can be performed in THF suspension, in which the products are insoluble, or in H_2O wherein the products are very soluble. Similar chemistry has been developed for $[Rh(dmpe)_2]Cl$, however these cis-hydrido-σ-alkynyl complexes slowly isomerize to their trans isomers. Compounds of type (1) can be deprotonated with KOH/H_2O yielding neutral Rh(I) species $[Rh(PMe_3)_4C{\equiv}CR]$ (2). Analogous $[Rh(dmpe)_2C{\equiv}CR]$ complexes have also been prepared. Reactivity patterns of the above complexes along with crystallographic characterization of several classes of Rh σ-alkynyl species will be addressed.

* T.B. Marder, D. Zargarian, J.C. Calabrese, T. Herskovitz and D. Milstein, *J. Chem. Soc.*, *Chem. Commun.*, 1484 (1987).

NEW RESULTS IN ORGANO-f-ELEMENT REACTIVITY, THERMOCHEMISTRY, AND CATALYSIS

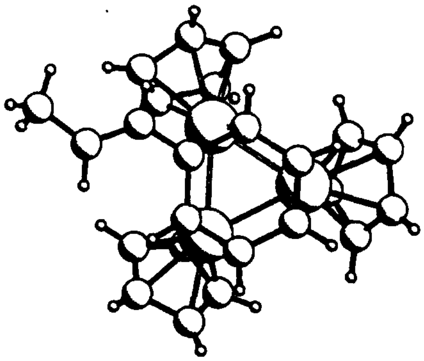
Tobin J. Marks, Department of Chemistry, Northwestern University, Evanston, IL 60208, U.S.A.

It is becoming increasingly apparent that metal-ligand bond enthalpy data can afford invaluable insights into important reaction patterns in organometallic chemistry and homogeneous catalysis. Moreover, trends in metal-ligand bonding can be discerned, and unexplored modes of reactivity are sometimes suggested. In this lecture, new results on both relative and absolute metal-ligand bond enthalpies are presented for organoactinides, organolanthanides, and related group 4 organometallic complexes. Striking and chemically significant variations in parameters are noted across the transition series. These can be understood in terms of relatively straightforward bonding concepts, and provide instructive insight into a wide range of H_2, C-H, C-C, C=C, C≡C, N-H, O-H, and related activation processes. The influence of ancillary ligation on metal-ligand bond enthalpies is also discussed--sometimes it is surprisingly small.

NOVEL TRICOBALT CLUSTERS WITH FACE-CAPPING VINYLBENZENE LIGANDS

Hubert Wadepohl, Klaus Büchner and Hans Pritzkow, Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg, FRG

Convenient one-pot high-yield syntheses of a variety of novel $(CpCo)_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-subst.-vinylbenzene})$clusters are presented. The crystal structure of $(CpCo)_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-trans-}\omega\text{-methylstyrene})$ reveals a planar arene ligand with nearly equal carbon-carbon bond lengths. In solution mutual rotation of the Co_3 and arene rings is observed. The bonding in these clusters in relation to chemisorbed arenes on metal surfaces will be discussed.



Preliminary reactivity studies reveal the extraordinary stability of the μ_3-arene clusters. Arene exchange is not accomplished without disrupting the metal backbone.

NEW GERMANIUM - COBALT AND IRON CARBONYL CLUSTERS

Skelte Anema, Siew Kim Lee, Kenneth M. Mackay, Brian K. Nicholson, and Miranda Service. School of Science, University of Waikato, P.B. Hamilton, New Zealand

In earlier work we have used germanium hydrides to synthesise open clusters containing linked GeM_2(M=Co,Fe)triangles, such as $GeCo_4(CO)_{14}$(A) (1). Closed clusters, like the pseudo-octahedral $(RGe)_2Co_4(CO)_{11}$(B) form by condensation from the open precursors(2), and have been prepared by other routes(3).

We now report:-

(a) a new Ge/Fe homologue of A, namely $Ge_2Fe_6(CO)_{23}$ (A_1), and a related $Ge_2Fe_7(CO)_{26}$(A_2)

(b) that the open networks may be extended by reaction of alkylgermanes as in

$A + 2Me_2GeH_2 = 2H_2 + 2CO + (Me_2Ge)_2GeCo_4(CO)_{12}(A_3)$

$Ge_2Fe_2Co_4(CO)_{21} + 2Me_2GeH_2 = 2H_2 + 2CO + (Me_2Ge)_2Ge_2Fe_2Co_4(CO)_{19}(A_4)$

(c) the R groups may be varied in molecules of type B, giving mixed substituents such as $R^1 = Me, R^2 = Co(CO)_4$ (B_1)

(d) the synthesis of a new structural type which may be viewed as a fusion of the A and B structures by sharing a common Co-Co edge, $[(EtGe)_2Co_4(CO)_{10}][(GeCo_2(CO)_7](C)$.

(e) the first cluster with a trigonal bipyramidal core incorporating Ge, $(EtGe)_2Fe_3(CO)_9$ (D)

The syntheses, characterisation, and structures of A_1, A_2, A_3, A_4, B_1, C and D will be presented.

(1) S.G. Anema, K.M. Mackay, L.C. McLeod, B.K. Nicholson & J.M. Whittaker, Angew. Chemie. Int. Ed. Eng., 25 (1986) 759 and refs therein.

(2) S.P. Foster, K.M. Mackay & B.K. Nicholson, Inorg. Chem., 24 (1985) 909

(3) P. Gusbeth and H. Vahrenkamp Chem. Ber. 118, (1985) 1746

PHOTOCHEMISTRY OF METAL-METAL BONDED CARBONYLS WITH A LOWEST METAL TO LIGAND CHARGE-TRANSFER (MLCT) EXCITED STATE

Derk J. Stufkens, Tim van der Graaf and Ad Oskam, Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Although the photochemistry of unsubstituted metal-metal bonded carbonyls has been studied in detail,[1] much less attention has been paid to substituted binuclear carbonyls such as $XM(CO)_3$(α-diimine) (X=$M(CO)_5$, $Co(CO)_4$, $CpFe(CO)_2$, Ph_3Sn; M=Mn,Re; α-diimine=bpy, phen etc.), which possess an extra metal to α-diimine charge-tranfer (MLCT) band in the visible region. Contrary to most mononuclear complexes with a lowest MLCT state, these $XM(CO)_3$(α-diimine) compounds are photoreactive showing both homolysis of the metal-metal bond and release of CO.[2] The radicals $M(CO)_3$(α-diimine), formed by the homolysis reaction, have been identified as stable 16e-radical complexes with ESR and IR for M=Re. The corresponding $Mn(CO)_3$(α- diimine) radicals can act as catalysts in electron transfer catalyzed reactions. Examples of such reactions will be given. The α-diimines R-PyCa (=pyridine-2-carbaldehyde imine) and R-DAB(=1,4-diaza-1,3-butadiene) afford novel complexes $Mn(CO)_4(\sigma,\sigma,\eta^2$-R-PyCa)$Mn(CO)_3$ and $Mn(CO)_3(\sigma,\sigma,\eta^4$-R-DAB)$Mn(CO)_3$, respectively, by reaction of the $Mn(CO)_3$(α-diimine) and $Mn(CO)_5$ radicals.

Exceptional reactions are also observed for the complexes $(CO)_4CoRe(CO)_3$(α-diimine) and $Ph_3SnMn(CO)_3$(α-diimine). The Co-Re complexes produce $Re(CO)_3$(α-diimine)$^+Co(CO)_4^-$ and the Sn-Mn complexes lose CO with high quantum yield even upon irradiation with λ=600nm.

The mechanisms of these reactions will be discussed.

References

1) T.J. Meyer and J.V. Caspar, Chem. Rev. 85 (1985) 187

2) D.J. Stufkens, 'Steric and Electronic Effects on the Photochemical Reactions of Metal-Metal bonded Carbonyls', in 'Stereochemistry of Organometallic and Inorganic Compounds', Vol.3, Ed. I. Bernal, Elsevier 1988.

INFRARED FREQUENCIES AND INTENSITIES OF ALKYNES COORDINATED ON METAL CLUSTERS.

Pier Luigi Stanghellini,
Dipartimento di Chimica,Università di Sassari, Via Vienna 2,
I-07100 Sassari, Italy

Francesca Filippi, Rosanna Rossetti,
Dipertimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali,Università di Torino, Via Giuria 7, I-10125 Torino, Italy

Alkynes provide a great structural and chemical variety in the interactions with transition metals in complexes[1]. It is noteworthy their ability to bind simultaneously two, three or four metal atoms with largely different σ-π interaction and significant rehybridization of the acetylenic carbon atom. Vibrational spectroscopic properties of the coordinated alkyne may be related to the nature of the metal-ligand bond; moreover, if the surface-coordination chemistry analogy is valid, the comparison with the spectral data of the alkyne adsorbed on a surface can offer useful insights about the structure of the chemisorbate.

Systems belonging to the series $Co_2(CO)_6(RC_2R')$, $Os_3(CO)_{10}(RC_2R')$ and $Co_4(CO)_{10}(RC_2R')$with $R=R'=H,CH_3$ and $R=H$, $R'=CH_3$, with alkyne coordination of the type μ-η_2,μ_3-η_2, μ_4-η_2 and metal-alkyne bond formally π_2, $\sigma_2\pi$, $\sigma_2\pi_2$, were studied. The frequencies associated with the main vibrational modes of the alkynes (in particular, C≡C and C-H stretchings and C-H deformations) were evaluated with respect to those of the free alkyne and to the coordination type. At the same time, the contribution per the C-H bond to the total intensity in the C-H stretching and deformation region was measured: this is known to be easily related with the electrical properties of the C-H bonds in different surroundings[2]. Both the frequency and intensity data provide informations on the effect induced by the kind of coordination to the metal atoms (structure of the cluster, different σ and π contribution to the bond) on the geometry and on the charge distribution in the alkyne.

AKNOLEDGMENT P.L.S. thanks NATO for a grant.

REFERENCES

1) E.Sappa, A.Tiripicchio and P.Braunstein Chem.Rev. 1983,83,203
2) C.Castiglioni, M.Gussoni and G.Zerbi J.Mol.Struct.1986,141,341

EFFECT OF STRUCTURE ON THE RELATIVE REACTIVITY OF STYRENES BY DIIODOBORANE-METHYL SULFIDE

M.G. Longobardi, G. Ortaggi and R. Scialis

Centro CNR di Studio sui Meccanismi di Reazione e Dipartimento di Chimica,
Università "La Sapienza", P.le Aldo Moro 2, 00185 ROMA, ITALY

We have examined the properties and the reactivity of a new hydroborating agent, $HBI_2 \cdot SMe_2$, which is prepared by reacting BI_3 and $BH_3 \cdot SMe_2$ in the appropriate molar ratio. Diiodoborane is more sensitive than dibromoborane to moisture and this makes its preparation more difficult. It appears to be indefinitely stable at room temperature when stored under nitrogen. Ethereal solvents cannot be used for $HBI_2 \cdot SMe_2$ since cleavage of the ether linkage occurs at a significant rate.

The reactivity of HBI_2 is lower than that of $HBBr_2$. For example, 1-octene is hydroborated in CH_2Cl_2 at 25° by HBI_2 to the extent of 60% in 4 hrs, while hydroboration with $HBBr_2$ in the same experimental conditions reaches 69% in 1 h. For cis-3-octene the results are as follows: HBI_2, 36% in 1 hr; $HBBr_2$, 87% in 1 hr.

In order to establish the role of electronic effects in influencing the directions of addition of the boron-hydrogen moiety to the carbon-carbon double bond, a number of para-substituted styrenes, $X\text{-}C_6H_4CH{=}CH_2$ (X = H, CH_3O, CH_3, Cl, CF_3, NO_2), were hydroborated with $HBI_2 \cdot SMe_2$ under standard conditions (CH_2Cl_2, 25°C). The alcohols produced in the oxidation of the organoboranes were analyzed by gas-chromatography to establish the isomeric distribution. It is of interest that in the cases of 4-nitro- and 4-trifluoromethylstyrene major amounts of the corresponding ethylbenzenes were formed.

The results show that electron-withdrawing groups favour the addition of boron to the α-position (for X = Cl, CF_3, NO_2 the % of α-ol is 39, 56, 67, respectively), while the electron-releasing groups favour the addition of boron to the β-position (for X = CH_3O only 2-(para-methoxyphenyl)ethanol is formed). This behaviour is in agreement with the four-centred transition state proposed by Brown. It is also of interest to point out that the effect of these substituents in influencing the direction of the hydroboration parallels qualitatively ther σ^+ values. Indeed, a plot of $\log (k_\beta/k_\alpha)$ against σ^+ reveals a reasonably good linear relationship and shows that HBI_2 is extremely sensitive to electronic effects.

Finally, the unexpected large formation of substituted ethylbenzenes for 4-nitro- and 4-trifluoromethylstyrenes is probably due to a base-catalyzed deboronation which involves the formation of carbanionic intermediates, stabilized by the electron-withdrawing substituents.

A mechanistic study of HX (X=Cl,Br) addition to the $[Mo_2Br_8]^{4-}$, $[Mo_2(\mu\text{-}H)(\mu\text{-}X)_2X_6]^{3-}$, *X=Cl,Br ions and the homogeneous reduction of* $[Mo_2(\mu\text{-}X)_3X_6]^{3-}$ X=Cl,Br by aqueous Cr(II).

Constantinos Mertis, Maria Chorianopoulou, Spyros Koinis, Myrsini Cravaritou and Nikos Psaroudakis.

Low-valent metal ions like Cr^{2+}, V^{2+} and Eu^{2+} give dihydrogen at relatively slow rates even at HCl concentrations as high as 12M. However, the reaction is considerably accelerated in the presence of multiply bonded dimolybdenum complexes forming hydrides (eq.(1) and (2))[1] which then react with the reducing metal ion eq.(3) and (4) [2] :

$$\underset{\underline{1}}{[Mo_2X_8]^{4-}} \xrightarrow[(1)]{HX} \underset{\underline{2}}{[Mo_2HX_8]^{3-}} \xrightarrow[-H_2]{HX} \underset{\underline{3}}{[Mo_2X_9]^{3-}}$$

(2)

x: a) Cl; b) Br

$$[Mo_2HCl_8]^{3-} + 2Cr^{2+} + H^+ \longrightarrow [Mo_2Cl_8]^{4-} + 2Cr^{3+} + H_2 \qquad (3)$$

$$[Mo_2Cl_9]^{3-} + 2Cr^{2+} \longrightarrow [Mo_2Cl_8]^{4-} + 2Cr^{3+} + Cl^- \qquad (4)$$

We now report an extension of these studies including also the analogous bromo-derivatives which are extremely more reactive than their chloro counterparts. The rates of the reactions (1) and (2) are first order in H^+ and the Mo_2^{4+} reactants.

The energies of activation are shown in Table I.

The higher reactivity and the smaller energy required for the bromo- than the chloro-system must be attributed to the relative ease of breaking the δ-component which is weakened by the repulsion between the bulkier bromine atoms.

Both $\underline{3a}$ and $\underline{3b}$ undergo homogeneously a two electron reduction by $Cr^{2+}_{(aq)}$ to give $\underline{1a}$ and $\underline{1b}$ respectively in aqueous acidic solutions and are effective catalysts for the anaerobic oxidation of Cr(II) to Cr(III) with concomitant hydrogen evolution (Figure 1).

The reaction is slow for $\underline{3a}$ and very fast for $\underline{3b}$. The cycle can be followed by visible spectroscopy, each step is descernible and by controlling the reaction conditions all the intermediates (for the chloro compound) can be isolated.

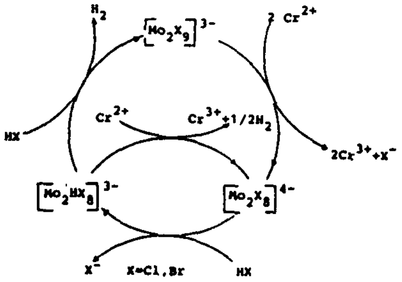


Figure 1

Table I

Reaction	E_a(KJ mol^{-1})
(1)	80.5(X=Cl), 33.0(X=Br)
(2)	71.9 "

REFERENCES

1. F.A.Cotton and A.R.Walton," Multiple bonds between Metal Atoms", New York, 1982 and references therein.
2. C.Mertis, M. Cravaritou, A.Shehadeh and D.Katakis, Polyhedron, 1987, 6, 1975.

ELIMINATION OF ACID HALIDES FROM ACETYL, PHENYLACETYL, AND BENZOYL CHLOROBIS(TRIPHENYLPHOSPHINE) PLATINUM(II) AND PALLADIUM(II) COMPLEXES.

Mits Kubota and Thorsten J. Anderson, Department of
Chemistry, Harvey Mudd College, Claremont, California,
91711 (U.S.A.)

Oxidative addition and migratory insertion reactions which are important basic steps in homogeneously catalyzed reactions of carbon monoxide such as in the Monsanto acetic acid and Eastman acetic anhydride synthesis have been extensively studied, but reductive elimination of acid halides has not been investigated in depth. Attempts to reductively eliminate acid halides usually lead to decarbonylation and elimination of the alkyl halide. The reactions of the acyl metal complexes $[M(PPh_3)_2Cl(RCO)]$, 1, where M is Pt or Pd and R is CH_3 , $PhCH_2$ or Ph with the halogens (X_2) chlorine, bromine, or iodine yield the acid halides RCOX. Reactions of the acyl complexes, 1, with ICl give the acid chlorides RCOCl. The rates of the reactions are too rapid to be measured by standard techniques, and no intermediates were detected at temperatures above 168 K. Mechanisms for the elimination reactions will be discussed.

166

FLASH PHOTOLYSIS INVESTIGATIONS OF RHODIUM AND IRIDIUM PHOSPHINE COMPLEXES

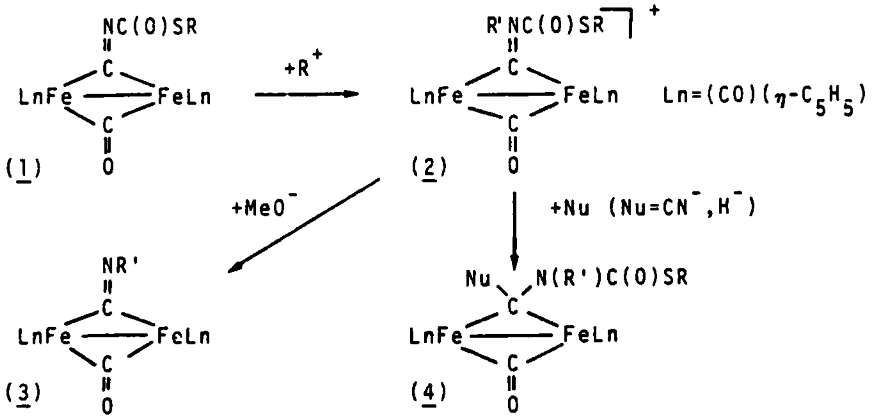
Cris Tina Spillett, Ralph G. Pearson and Peter C. Ford, Department of Chemistry, University of California, Santa Barbara, California, USA 93106

Flash photolysis techniques have been used to investigate photodissociation pathways and reactions of transient intermediates. The kinetics displayed by such transients formed from tetracoordinate complexes such as RhCl(CO)dppe (dppe=1,2-bis(diphenylphosphino)ethane) IrClC(CO)dppe, trans-Rhcl(CO)(tri-p-tolylphosphine)$_2$, and other such analogs offer information regarding the nature of these intermediates. The kinetics observed with flash photolysis techniques of these and other Ir(I) and Rh(I) phosphine complexes will be discussed and related to possible mechanisms of reaction for the transient intermediates formed.

CHEMISTRY OF BRIDGING ACYL ISOCYANIDE COMPLEXES

Luigi Busetto, Valerio Zanotti, Silvia Bordoni and Antonio Palazzi
Dipartimento di Chimica Fisica ed Inorganica, Universita' di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy.

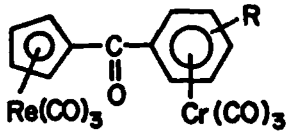
The novel bridging acyl isocyanide complexes (1), recently synthesized by NCO^- insertion into the C-S bond of $[(Cp)_2(CO)_3Fe_2(\mu\text{-CSR})]^+$ (R = Me, Et; Cp = η-C_5H_5), readily undergo N-alkylation or N-protonation to form stable cationic imminium-bridged derivatives (2: R=R'=Me, Et; R=Et, R'=Me).
NaOMe in methanol converts (2) into the known bridging isocyanide derivatives (3 : R'=Me,Et) via N-C(O)SR bond cleavage. The electrophilic nature of the bridging carbyne-like carbon atom in (2) is demonstrated from the reactions with nucleophiles (CN^-, H^-) which afford bridging carbene derivatives (4). The results of studies concerned with the stereochemistry of the above reactions together with other aspects of the reactivity of type (1) complexes, will be reported.



SYNTHESIS AND SPECTROSCOPIC STUDIES OF MIXED Re AND Cr CARBONYL COMPLEXES

Niall J. Gogan and I. Sheila Jayasinghe, Department of Chemistry, Memorial University of Newfoundland, St. John's, NF, Canada A1B 3X7

A series of benzoylcyclopentadienyl complexes have been prepared in which the cyclopentadienyl ring is complexed by a $Re(CO)_3$ group and the benzene ring by a $Cr(CO)_3$ group.



R = H, o-CH_3, p-CH_3, p-OCH_3, o-F, p-Cl

The complexes have been studied by IR, ^1H NMR and mass spectrometry. Similar studies on the parent $Re(CO)_3$ complexes have been carried out for comparison. Substituents on the benzene ring affect the ketonic ν_{CO} and ν_{CO} $[Cr(CO)_3]$ but not $\nu_{CO}[Re(CO)_3]$.

Comparison with results for similar Mn complexes[1] reveals significant differences between the two series. The ν_{COs} of $Re(CO)_3$ are lower by 5-12 cm^{-1} then the ν_{COs} of $Mn(CO)_3$. On average the ν_{COs} of $Cr(CO)_3$ are higher for the Re complexes then for the Mn complexes. The reasons for the observations and for observed changes in ^1H NMR shifts are explained by differences in the electron-withdrawing ability of the $M(CO)_3$ groups.

1. N.J. Gogan and C.K. Chu. J. Organometal. Chem. 132, 103(1977) and 93, 363 (1975).

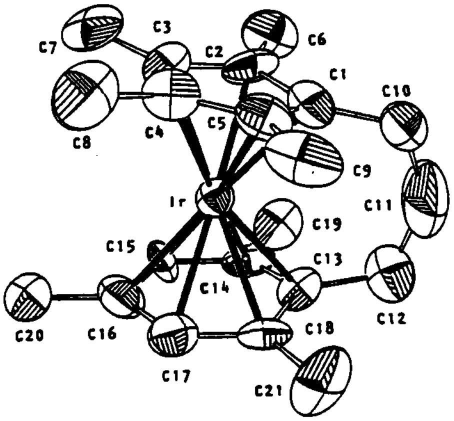
CRYSTAL AND MOLECULAR STRUCTURE OF TWO IRIDIUM(II) CYCLOPHANES: $[Ir(\eta^{11}-C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$ AND $[Ir(\eta^{11}-C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeOH)$

Paavo O. Lumme and Urho Turpeinen, Division of Inorganic Chemistry, Department of Chemistry, University of Helsinki, Vuorik. 20, SF-00100 Helsinki, Finland

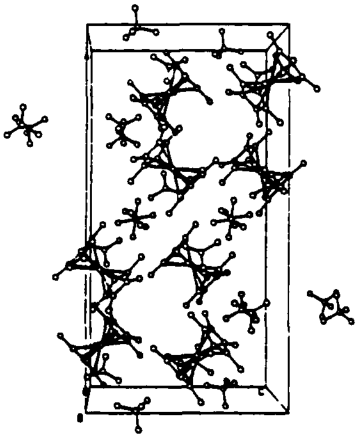
V.S. Kaganovich, R.R. Kudinov and M.I. Rybinskaya, A.N. Nesmeyanov Institute of Organo-Element Compounds of the Academy of Sciences of the USSR, Vavilov St. 28, Moscow 117334, U.S.S.R.

The structures of the compounds $[Ir(\eta^{11}-C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$ (1) and $[Ir(\eta^{11}-C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeOH)$ (2) have been determined by X-ray diffraction. The compound 1 crystallizes in space group *Pbcn* (Z = 8) with *a* 26.812(18), *b* 14.275(11), *c* 13.942(5) Å, and the compound 2 in the space group *Pnma* (Z = 4) with *a* 28.313(6), *b* 9.137(3), *c* 9.789(4) Å. The two structures are similar, bridged sandwich complexes, with an Ir atom bonded to the cyclopentadienyl and benzene rings of the organic ligand. The solvent molecules $MeNO_2$ and MeOH and the BF_4^- anions are more or less disordered in the structures, but they could be located from the difference Fourier maps. The Ir complex cations form discrete units in both structures. The crystal structures are thermally rather labil and are held together mainly through van der Waals forces.

1. V.S. Kaganovich, A.R. Kudinov and M.I. Rybinskaya, J. Organomet. Chem., 323 (1987) 111.



An ORTEP drawing of the $[Ir(\eta^{11}-C_5Me_4C_3H_6C_6H_2Me_3)]^{2+}$ cation (with 295 K parameters) of 1 showing the ion geometry and the atom numbering scheme. Thermal ellipsoids are drawn at 50% probability level for the non-H atoms.



Molecular packing in the unit cell of $[Ir(\eta^{11}-C_5Me_4C_3H_6C_6H_2Me_3)](BF_4)_2(MeNO_2)$ viewed down *b*.

THE TRANSIENT RADICAL ANIONS $Fe(CO)_4^-$ AND $M(CO)_5^-$ (M = Cr, Mo, W): ELECTRON SPIN RESONANCE, ELECTROCHEMISTRY AND MO CALCULATIONS

P. J. Krusic, Central Research and Development Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, DE 19898, U.S.A.

C. Amatore, and J.-N. Verpeaux, Laboratoire de Chimie, Ecole Normale Supérieure, 75231 Paris Cedex 05, France.

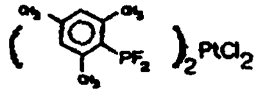
R. Subra, L.E.D.S.S., Université de Grenoble I, 38054 Saint Martin d'Hères Cedex, France.

The solution ESR spectra of the transient radical anions $Fe(CO)_4^-$ (**1**) and $Cr(CO)_5^-$ (**2**), $Mo(CO)_5^-$, and $W(CO)_5^-$ are reported and discussed together with their anisotropic spectra in frozen 2MeTHF glasses. The radicals are produced by photochemical cleavage of the metal-metal bond in $Na_2Fe_2(CO)_8$ and $K_2M_2(CO)_{10}$ (M = Cr, Mo, W) in THF. The ESR parameters are consistent with C_{3v} and C_{4v} geometries for $Fe(CO)_4^-$ and the $M(CO)_5^-$ radicals, respectively, which are also the geometries of the prototypical radicals $Co(CO)_4$ and $Mn(CO)_5$, isoelectronic with **1** and **2**. The remarkable similarity of the electronic and geometric structures of these radicals is also brought out by Extended Hückel MO calculations which reveal substantial delocalization of the unpaired electron onto the basal CO ligands (ca. 50%). The $Cr(CO)_5^-$ radical exchanges very rapidly its CO ligands with ^{13}CO, and the ESR spectra of the ^{13}C isotopomers indicate that the five CO ligands are rendered equivalent in solution on the ESR time scale by a fast intramolecular exchange process. Cyclic voltammetry with microelectrodes in the absence of supporting electrolyte shows that at sufficiently rapid potential scans **1** can be generated reversibly by oxidation of $Fe(CO)_4^{2-}$. **1** is not an important intermediate in the electrochemical reduction of $Fe(CO)_5$ as currently believed. The reduction of the latter is a two-electron process leading directly to $Fe(CO)_4^{2-}$ which reacts rapidly with $Fe(CO)_5$ to yield $Fe_2(CO)_8^{2-}$, the major product of electrolysis. An analysis of the cyclic voltammograms yields the rate of this reaction (6×10^6 $M^{-1}s^{-1}$). In the anodic potential scan, $Fe_2(CO)_8^{2-}$ is reversibly oxidized to the radical anion $Fe_2(CO)_8^-$ whose ESR behavior will also be briefly discussed.

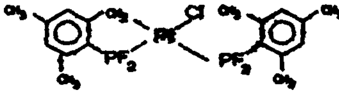
CHEMISTRY AND STRUCTURE OF ARYLDIFLUOROPHOSPHINE PLATINUM(II)-COMPLEXES CONTAINING Pt-C BONDS

Lutz Heuer , Ludger Ernst , Reinhard Schmutzler
Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30,
3300 Braunschweig, *Germany*
and
Dietmar Schomburg
Gesellschaft für Biotechnologische Forschung, Mascheroder Weg 1, 3300 Braunschweig, Germany

During our investigations on platinum(II) complexes of type *cis* - dichloro-bis(aryldifluorophosphine)platinum(II)[1,2] we have observed the elimination reaction of HCl in the compound



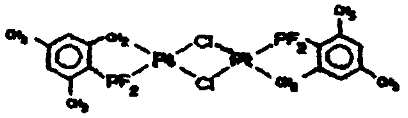
, 1 with formation of



2.

The identity of 2 was established by ^1H-, ^{13}C-, ^{19}F-, ^{31}P- and ^{195}Pt-n.m.r. spectroscopy. In contrast to the n.m.r. spectra for all the other nuclei and even without proton decoupling the ^{195}Pt- n.m.r. spectrum could be interpreted on a first order basis . The structure of 2 has also been established by a single crystal X-ray diffraction study.

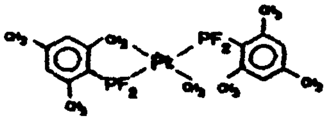
As a byproduct in the preparation of 2 compound 3 was observed.



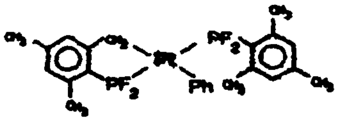
3

The unusually short Pt-P bond (212 pm), found in the single crystal X-ray diffraction study of 3 is reflected in the very large $^1J(PtP)$ coupling constant (7646 Hz).

The reaction of 2 with $SnMe_4$ and $HgPh_2$ lead to the formation of 4 and 5, respectively.



4



5

These complexes are the first involving *trans* PF_2 groups. Therefore, in the ^{31}P-n.m.r. spectra small $^1J(PtP)$ coupling constants were detected. A correlation between the Pt-P bond length and $^1J(PtP)$ has been found to be obeyed by 2 and 3.

---

[1] L.Heuer, M.Sell, R.Schmutzler, and D.Schomburg, *Polyhedron*, **1987**, 6, 1295.

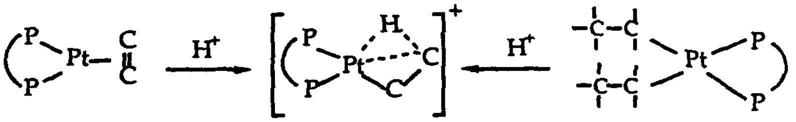
[2] L.Heuer and R.Schmutzler, *J.Fluorine Chem.*, **1988**, 39, 197.

β-AGOSTIC COMPOUNDS OF PLATINUM AND PALLADIUM

Nicholas Carr,[a,b] Barry J Dunne,[b] Laura Mole,[a] A Guy Orpen[b] and John L Spencer[a]

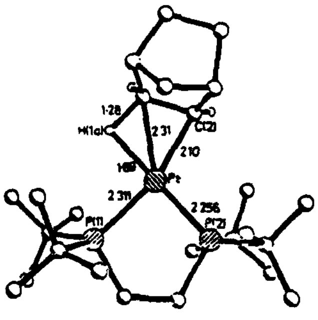
[a] Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT, UK
[b] Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, UK

The protonation of 16-electron platinum and palladium alkene complexes [ML_2(alkene)] (M = Pt, Pd; L_2 = chelating diphosphine; alkene = C_2H_4, norbornene etc) affords a series of cationic alkyl complexes in which the electronic requirements of the nominally 14-electron metal centre are satisfied by interaction with a β–C-H bond of the alkyl group (an *agostic* interaction). The same compounds may be made by the protonation of platinum dialkyls through the elimination of alkane.



This system has proved to be particularly suitable for study by multinuclear nmr methods, and the spectroscopic results correlate well with the results of single crystal X-ray diffraction studies. The norbornyl complex [$PtC_7H_{11}\{Bu^t_2P(CH_2)_3PBu^t_2\}$]$BPh_4$ (Figure) is typical of several which have been characterised. Interestingly the extent of the 3-centre, 2-electron agostic interaction is controlled by the bite angle of the phosphine.

Platinum complexes with agostic alkyl groups undergo extremely facile intramolecular rearrangements and are also reactive in an intermolecular sense.

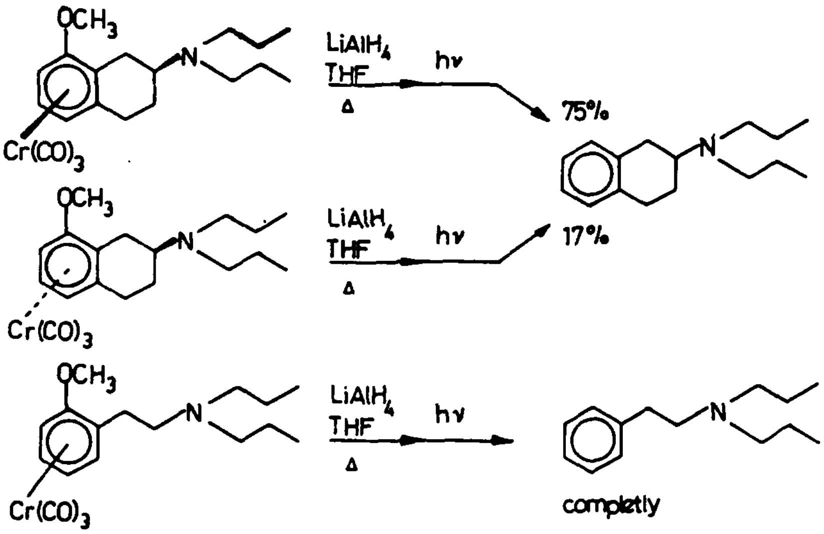


η^6 - CROMIUMTRICARBONYL COMPLEX INTERMEDIATES IN SYNTHESIS OF TETRAHYDRONAPHTALENE DERIVATIVES

Marie Persson and Uli Hacksell, Department of Organic Pharmaceutical Chemistry, University of Uppsala, S-751 23 Uppsala, Sweden

Ingeborg Csöregh, Department of Structural Chemistry, Arrhenius lab., University of Stockholm, S-106 91 Stockholm, Sweden

We have observed that hydride can act as a nucleophile, displacing aromatic methoxy groups on some Cr(CO)$_3$-complexed amino-substituted tetralins and related compounds.



Mechanism, scope and limitations of the reaction will be discussed.

New Studies of C-H Bond Activation Reactions Using Complexes of Rhodium.

William D. Jones, Valerie L. Chandler, and Lingzhen Dong, Department of Chemistry, University of Rochester, Rochester, New York, 14627, USA.

A variety of complexes of the general formula $(C_5Me_5)Rh(PR_3)(Ar)H$ have been prepared by C-H bond activation of the appropriate arene. For complexes with R = Me, aromatic species including substituted benzenes, naphthalenes, furans, and pyroles have been examined. Several unusual rearrangements have been observed in the course of this chemistry, indicating a new type of C-H bond activation that does not involve the 16-electron $[(C_5Me_5)Rh(PMe_3]$ intermediate.

The complexes with PR_3 = PMe_2Ph, $PMePh_2$, PPh_3, $P(t\text{-}Bu)_3$, PCy_3, $P(n\text{-}Bu)_3$, $PMe_2(n\text{-}Pr)$, PCH_2Ph, and PMe_2Bu have been prepared and reactions with H_2 studied. The stability of the phenyl hydride complexes were found to vary with both steric and electronic differences in the phosphine ligand. Evidence for the intermediacy of Rh(V) intermediates in the hydrogenolysis was also found. Intramolecular reactions of the phosphine ligand were also observed and the stability of these species will be compared with the intermolecular activation adducts.

Reactions of the complex $(C_5Me_5)Rh(PMe_3)(Ph)H$ with a variety of electrophiles (CS_2, PhNCS, MeOOCC≡CCOOMe) have also been examined. In all cases insertion into the metal-hydrogen bond is observed. With the sulfur containing substrates, a series of complex thioacetal reactions are seen in the organic ligands while bound to the metal.

REACTIVITY OF "MIXED" METAL-NAKED PHOSPHORUS CLUSTER COMPOUNDS

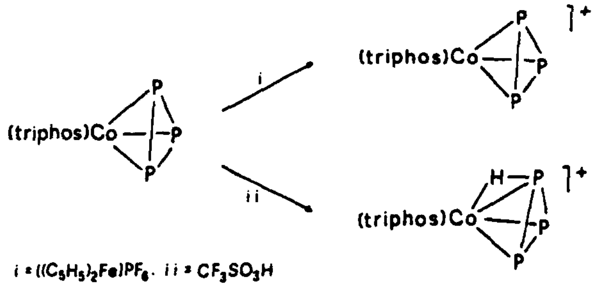
Massimo Di Vaira, Piero Stoppioni, Dipartimento di Chimica,
Università di Firenze, Via Maragliano, 77, I-50144 Firenze, Italy

Stefano Midollini, Maurizio Peruzzini, Istituto I.S.S.E.C.C., CNR,
Via J. Nardi, 39, I-50132 Firenze, Italy

Piero Zanello, Dipartimento di Chimica, Università di Siena,
Pian de' Mantellini, 44, I-53100 Siena, Italy

The cluster compounds $[M^*P_3]$ $[M^* = C_5Me_5Mo(CO)_2$, $(CO)_3Co$ and (triphos)M; triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; M = Co, Rh, Ir] and $[M^*P_2X]BF_4$ $[M^*$ = (triphos)Co; X = S, Se], which contain unsubstituted main group atoms and metal fragments in a pseudotetrahedral geometry, present non-bonding electrons available for redox processes and for interactions with electrophilic reagents or transition-metal ligand units. While the reactivity of such species toward metal fragments has been considered,[1] scarce attention has been addressed to their chemistry with oxidizing or electrophilic reagents.

The compound $[(triphos)CoP_3]$ reacts with $[(C_5H_5)_2Fe]PF_6$ yielding the paramagnetic monocation $[(triphos)CoP_3]PF_6$ (μ_{eff} = 2.11 BM).



i = $[(C_5H_5)_2Fe]PF_6$. ii = CF_3SO_3H

Trifluoromethansulphonic acid reacts with the cobalt derivative affording a compound of formula $[(triphos)CoP_3H](H_3O)(CF_3SO_3)_2\cdot H_2O$. The deformations undergone by the CoP_3 core in the $[(triphos)CoP_3H]^+$ cation, as shown by an X-ray analysis, suggest that the hydrogen atom bridges the cobalt and one phosphorus atom. ^1H and ^{31}P n.m.r. data obtained at different temperatures point to rapid exchange of the hydrogen with the solvent.

Work supported by Ministero Pubblica Istruzione (MPI, Roma).

1 M. Di Vaira, M. Peruzzini, and P. Stoppioni, Polyhedron, 6, 351, 1987.

176

REVERSAL OF SELECTIVITY IN SE2 CLEAVAGE OF MIXED ORGANOTIN COMPOUNDS BY HALOGENS

Bernard Jousseaume and Patrice Villeneuve, Laboratoire de Chimie Organique et Organométallique, UA 35 CNRS, Université de Bordeaux I, 351, Cours de la Libération, 33405 - Talence Cedex (France)

Numerous data on electrophilic cleavage of metal-carbon bonds is now available. These studies have been developped primarily because the very high selectivity of electrophilic demetallation allows usefull synthetic applications. The ease of cleavage by halogens of mixed organotin derivatives follows the sequence : benzyl > aryl ≃ vinyl > methyl > higher alkyl. For mixed tetraalkyltin compounds, a cyclic or an open S_E2 transition state, or a charge-transfer mechanism has been proposed to account for selectivity, solvent effects and configurationnal changes at the cleaved organic group, whereas an open S_E2 transition state with assistance of the solvent or another molecule of electrophile is generally accepted for aryl or vinyltin derivatives.

We present the first exemples of halogenodemetallation[1] where the usual sequence of reactivity is reversed, i.e. where alkyl groups are cleaved preferentially to aryl, vinyl or benzyl groups in mixed tetraorganotin derivatives and propose an interpretation of these very unexpected results.

1-B.Jousseaume,P.Villeneuve,J.Chem.Soc.Chem.Commun.1987,517.

TIN-CARBON BONDED CARBOHYDRATE DERIVATIVES

James L. Wardell and Oonah J. Taylor, Department of Chemistry
University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE

Carbohydrate derivatives containing tin-carbon bonds have been synthesized by standard routes, including reactions of R_3SnLi with carbohydrates having tosylate, carbonyl or epoxy groups.

Transmetallation reactions of the tin derivatives have been attempted with chloro-platinum and -palladium complexes as well as with organolithium reagents. Reactions with electrophilic reagents (e.g. halogens and proton acids) have also been studied.

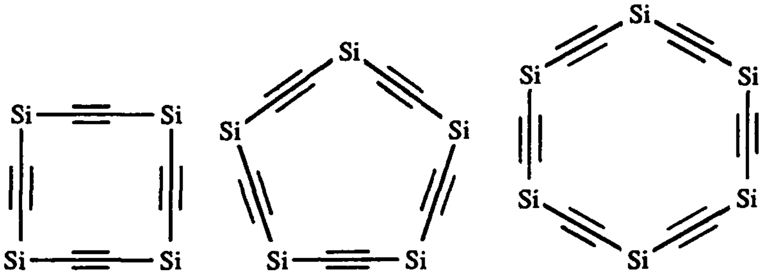
The metallated carbohydrates have some potential in carbohydrate synthesis.

Pericyclynosilanes : Synthesis of a New Class of Cyclic Organosilicon Compounds.

Roberto Bortolin, Bhukan Parbhoo and Scott S.D. Brown

Dow Corning Research Group, School of Molecular Sciences, The University of Sussex, Brighton BN1 9Qj, UK

Pericyclynosilanes are cyclic compounds composed of alternating R_2Si and $C\equiv C$ units.



They can be prepared in high yields by reaction of $R_2Si(C\equiv CH)_2$, BuLi and R_2SiCl_2 according to the following scheme:

$$R_2Si(C\equiv CH)_2 + 2\,BuLi \longrightarrow R_2Si(C\equiv CLi)_2 + 2\,BuH$$

$$R_2Si(C\equiv CLi)_2 + R_2SiCl_2 \longrightarrow (R_2SiC\equiv C)_n + 2n\,LiCl$$

The combination of substituents R on the silicon of the reagents allows the synthesis of a large number of pericyclynosilanes, each one in different ring sizes. The compounds $(Me_2SiC\equiv C)_6$ and $(Ph_2SiC\equiv C)_6$ have been isolated and structurrally characterized by X-ray crystallography.

The synthesis of pericyclynosilanes allows the demonstration of a novel rearrangement mechanism occuring on the silicon. The species responsible for such rearrangements were identified. Pericyclynosilanes can be coordinated to metal centers such as copper.

WEAK INTERACTIONS IN ORGANOMETALLIC COMPOUNDS: STRUCTURAL CRITERIA

Gerhard Müller, Anorganisch-chemisches Institut der Technischen
Universität München, Lichtenbergstr. 4, D-8046 Garching, FRG.

Extensive structural, spectroscopic, and theoretical studies make hydrogen bonds probably the best understood weak intra- and intermolecular interactions, both in solution and in the solid state. From structural studies in particular, detailed geometrical criteria can be given for hydrogen bonds. Other weak interactions are less amenable to such a systematic treatment. Ion-induced dipole interactions, closed-shell (d^{10}-d^{10}) attractive interatomic interactions, and particularly London dispersion (van der Waals) forces are typical examples for this situation.

On the basis of a large number of crystal structures on various classes of organometallic compounds evidence for common features of weak interactions has been established. In particular, weak electrostatic interactions are shown to have a decisive influence on the structures of organolithium compounds, while closed-shell interactions between Au(d^{10}) centers may be substantiated by a comparison of the ground state conformations of their P ylide complexes and those of the respective free ligands. Ample structural evidence for van der Waals forces and weak ion-induced dipole attraction is found in the complexes of Ga(I), In(I), and Tl(I), as well as AsX_3, SbX_3, and BiX_3 (X = halogen), with uncharged arenes, most notably with substituted benzenes.

STRUCTURE AND DYNAMIC BEHAVIOR OF SOLVATED ORGANOLITHIUM COMPOUNDS

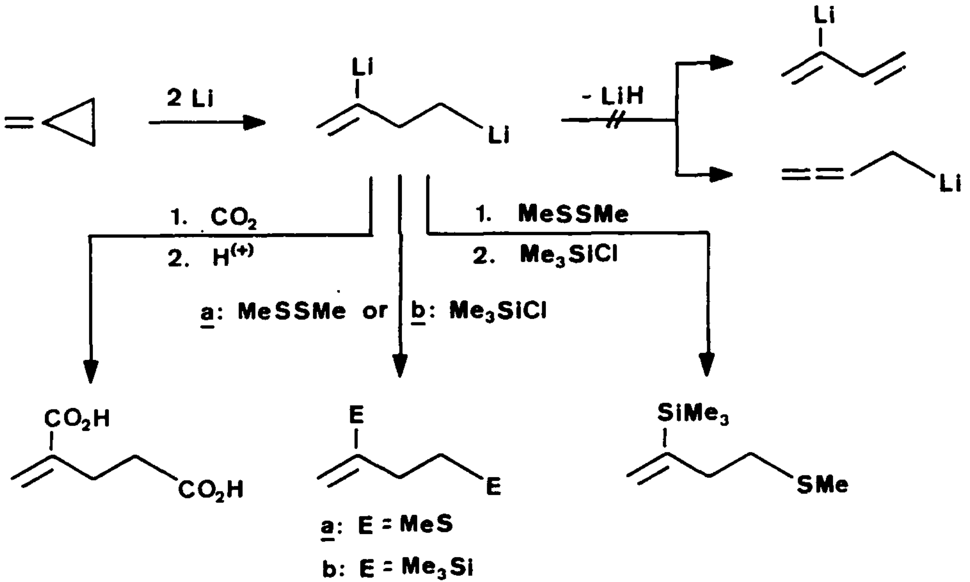
Gideon Fraenkel, Department of Chemistry, Ohio State University,
120 W. 18th Avenue, Columbus, Ohio 43210, USA.

If there is observable spin coupling between ^{13}C and directly bonded ^{6}Li in organolithium compounds one can infer information about aggregate structure from the multiplicity of the α-carbon resonance while from its averaging kinetic investigations can be made of interaggregate carbon lithium bond exchange. In this general way we have found out that $(RLi)_n$ species solvated by ethers or t-amines exist as equilibrium mixtures of bridged dimers, cubic tetramers and less frequently, monomers, the coordination number of lithium being four in all these species. In general, cooling these equilibrium mixtures favors the smaller aggregates because lithium therein is coordinated to more ligand molecules. Data for typical solvated organolithium compounds will be discussed. In particular we have investigated lithium t-butyl acetylide, a stable model system, in the presence of a wide variety of potential ligands. Simple ethers and monoamines give rise of tetramers whereas vicinal diamines favor dimers due to bidentate solvation of lithiums. The averaging of the ^{13}C, ^{6}Li coupling, due to interaggregate carbon lithium bond exchange has been analyzed using our methods of NMR line-shape analysis which incorporate the mechanism of exchange into the density matrix equations which are solved to obtain the NMR absorption. Using these procedures we find the mechanism of exchange is the fast reversible dissociation of tetramer to dimers.

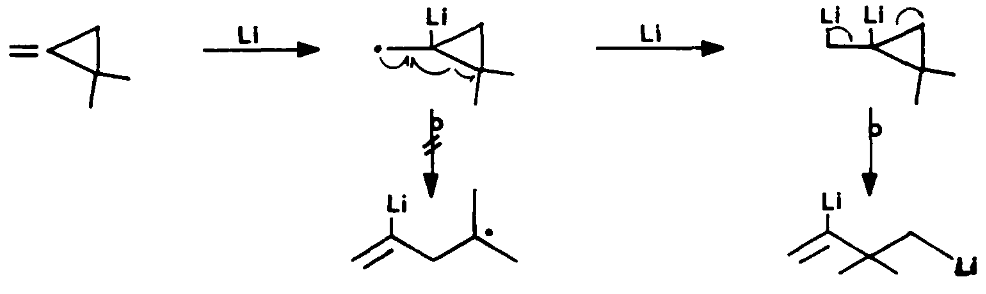
STABLE RING-OPENED 1,3-DILITHIUM ORGANIC COMPOUNDS UPON THE REACTION OF METHYLENECYCLOPROPANES WITH LITHIUM METAL: 2,4-DILITHIO-1-BUTENES

A. Maercker and K.-D. Klein, Department of Organic Chemistry,
University of Siegen, D-5900 Siegen (FRG)

Methylenecyclopropane readily reacts with lithium powder in diethyl ether at room temperature or without solvent at its boiling point (10°C) to yield the stable 2,4-dilithio-1-butene which - in contrast to 1,3-dilithiopropane - does not split off lithium hydride. The two lithium atoms can be replaced stepwise by different electrophiles, the allylcarbinyl center being more reactive than the vinyl center:



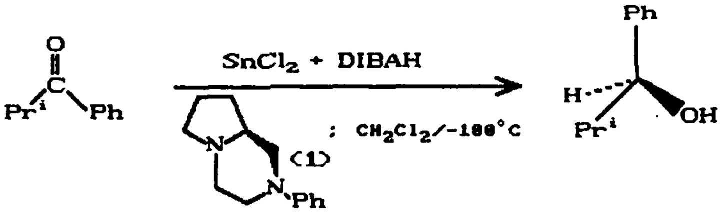
Mechanism :



CHIRAL TIN(II) ORGANOMETALLIC SYSTEMS AS ENANTIODIFFERENTIATING REAGENTS

Massimo Falorni, Luciano Lardicci
Dipartimento di Chimica e Chimica Industriale della Facolta' di Scienze dell'Universita', via Risorgimento 35, I-56100 Pisa, Italy.
Giampaolo Giacomelli
Dipartimento di Chimica della Facolta' di Scienze dell'Universita', via Vienna 2, I-07100 Sassari, Italy.
Mauro Marchetti, Annamaria Piroddi
Istituto del CNR per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, via Vienna 2, I-07100 Sassari, Italy.

During our studies, we have reported that chiral reducing reagents can be obtained from optically active diamines and $LiAlH_4$.[1] In our present investigations on the asymmetric reductions of a wide variety of prochiral carbonyl substrates,[2] we discovered that a chiral organometallic system, generated from tin(II) chloride and diisobutyl aluminium hydride,[3] in the presence of a chiral diamine such as compound **1**, reacts smoothly with prochiral ketones to yield the optically active secondary carbinol in good enantioselectivity.



In these reactions, the coordination of the bidentate chiral diamine to the bivalent tin atom plays an important role as shown from the use of $AlEt_3$ instead of DIBAH. In this case, the reaction of the chiral tin system with benzaldehyde occurs to yield the alkylated carbinol in poor yield (<5%) in a very high enantiodifferentiating manner (e.e.>95%).

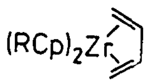
References

1) M. Falorni, L. Lardicci, G. Giacomelli, *Gazz. Chim. Ital.*, **1986**, *116*, 73.
2) M. Falorni, L. Lardicci, G. Giacomelli, *J. Org. Chem.*, **1986**, *51*, 2030.
3) T. Mukaiyama, K. Tomimori, T. Oriyama, *Chem. Lett.*, **1985**, 813.

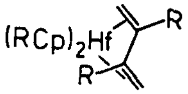
Some Novel Structural and Chemical Aspects of Cp-substituted Bent Metallocene Complexes.

Gerhard Erker
Institut für Organische Chemie der Universität Würzburg
Am Hubland, 8700 Würzburg (BRD)

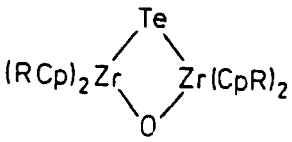
Preparations and properties of various examples of Cp-substituted group 4 bent metallocene complexes of general types $(RCp)_2ML_n$ and $(RCp)CpML_n$ are described. In the presence of sufficiently bulky Cp-substituents, chiral conformations of the bent metallocene unit are preferred in the solid state. In solution, often hindered RCp-M rotation is observed (typical examples are 1, 2, or 3).



1



2



3

The potential of the Cp-substituted group 4 metallocene complexes to serve as components in catalytically active systems is discussed.

REACTIVITY OF PARAMAGNETIC MONO- AND DICYCLOPENTADIENYL NIOBIUM DERIVATIVES

Abdenasser Zaki, Liliane G. Hubert-Pfalzgraf and Olivio Pagliarini,
Laboratoire de Chimie Moléculaire, Associé au CNRS, Université
de Nice, Parc Valrose, 06034 Nice, France

The molecular chemistry of low-valent niobium and tantalum derivatives remains limited, especially in oxidation state II.

Photochemical or chemical reduction of $(\eta^5\text{-Cp})_2NbMe_2$ and $(\eta^5\text{-Cp})_2NbCl_2$, respectively, in the presence of trimethylphosphane, has been considered. The unusual lability of the niobium cyclopentadienyl linkage in some experimental conditions offers a route to $(\eta^5\text{-Cp})NbCl_2(PMe_3)_2$, 1, a highly reactive paramagnetic species.

Its reactivity has been widely investigated (alkyl reagents, carbon monoxide, isocyanides, heterocumulenes, alkynes, diazabutadienes,...). 1 acts as a precursor for mono- as well as non-cyclopentadienyl niobium derivatives of various oxidation states, including oxidation state II. The synthesis and characterization of representative examples will be discussed.

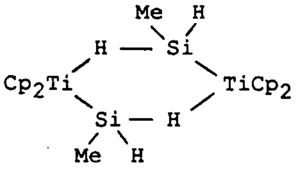
RACTIONS OF DIMETHYLTITANOCENE WITH ALKYL- AND ALKOXYSILANES.

E.Samuel, Ecole Nationale Superieure de Chimie de Paris (UA 403 CNRS), 11 rue P. et M. Curie, 75005 Paris, France.

J.Harrod, Department of Chemistry, McGill University, Montreal, Canada.

Y.Drumzee,F.Robert and Y.Jeannin, Laboratoire de chimie des métaux de transition (ERA 608 CNRS), Université P. et M. Curie, 75005 Paris, France.

Dimethyltitanocene (I) reacts with $Me(OEt)_2SiH$ in toluene or hexane to yield the dimeric compound (a) containing Si-H bridges. The structure has been determined from H NMR by comparison with the previously reported compound[1] $[Cp_2TiSiH_2Ph]_2$.



(a)

In the presence of PR_3 ($R=CH_3,C_2H_5$), I gives with $PhSiH_3$ the paramagnetic compound $Cp_2Ti(SiH_2Ph)PR_3$ (EPR: g=1.9944; A(P)=29.3G; A(H)=3.2G). Preliminary crystal structure studies will be reported.

I also gives with $(OMe)_3SiH$ the dimeric paramagnetic compound $[Cp_2Ti\mu\text{-}(OMe)]_2$. The EPR spectrum is characteristic of an excited triplet state. Crystal structure data will be reported.

1. C.Aitken,J.F.Harrod,E.Samuel, J.Amer. Chem.Soc.,1986,108,4059.

BI- AND TRI-NUCLEAR η^2-HYDRAZONATO μ-OXO COMPLEXES OF TITANIUM

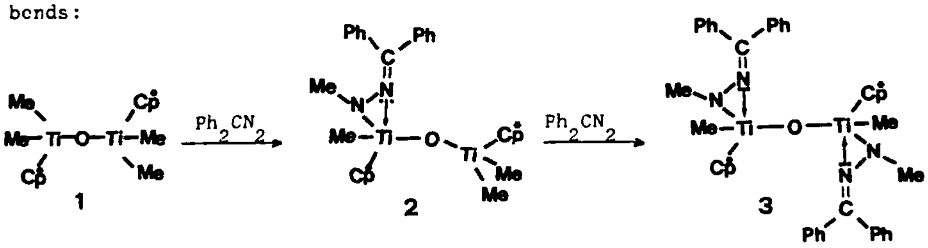
Juan Carlos Flores, Pascual Royo, Ricardo Serrano , Miguel Mena

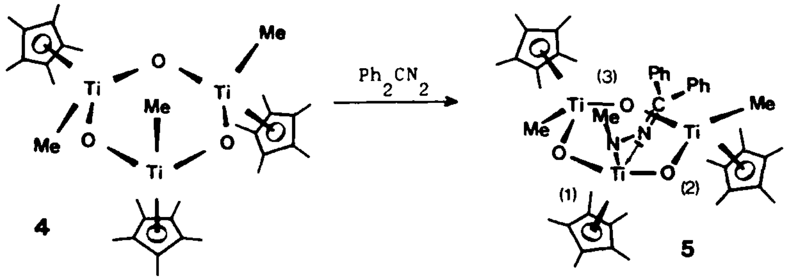
Departamento de Química Inorgánica, Universidad de Alcalá; Campus Universitario, 28871 Alcalá de Henares Madrid, Spain)

M.A. Pellinghelli, Antonio Tiripicchio

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M'Azeglio 85, I-43100 Parma, Italy.

We have recently described several di- and tri-nuclear μ-oxo pentamethylcyclopentadienyl titanium dimers and trimers[1]; their reaction with diphenyldiazomethane has been investigated and lead to the formation of η^2-hydrazonato complexes by insertion into the titanium-methyl bonds:





IR, NMR(^1H and ^{13}C) data as well as the X-ray structure of (2) are presented.

---

[1] S. García Blanco, M.P. Gómez Sal, S. Martinez Carreras, M. Mena, P. Royo and R. Serrano, J. Chem. Soc. Chem. Commun. 1986, 1572

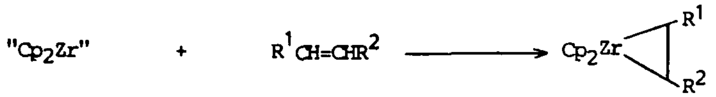
PREPARATION AND REACTIONS OF ZIRCONACYCLOPROPANE COMPLEXES

Tamotsu Takahashi and Yasuzo Uchida, Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, JAPAN

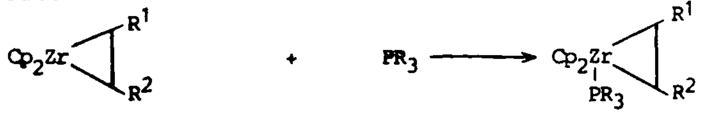
Tokiko Uchida, Department of Industrial Chemistry, Faculty of Science and Technology, The Science University of Tokyo, Noda, Chiba 278, JAPAN

Ei-ichi Negishi, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.

Zirconacyclopropane complexes were prepared by the reactions of olefins with zirconocene which was produced in situ from Cp_2ZrCl_2 and 2 equiv of n-BuLi.



Addition of one equiv of PR_3 to the complex ($R^1 = R^2 = Ph$) gave yellow crystals. Its structure was determined by the X-ray analysis.



These zirconacyclopropane complexes reacted with aldehydes or ketones to give corresponding alcohols.

SYNTHESIS AND REACTIVITY OF BIS-(SILYLATED CYCLOPENTADIENYL) NIOBIUM COMPLEXES WITH CUMULENE LIGANDS.

A.Otero[a],A.Antiñolo[a],M.Fajardo[a],F.Jalón[a],C.López Mardomingo[b],C.Sanz[a],F.Florencio[c] and J.Sanz-Aparicio[c].

[a]Departamento Química Inorgánica.[b]Departamento Química Orgánica.Universidad de Alcalá de Henares(Spain).[c]Departamento de RayosX.Instituto Rocasolano.C.S.I.C. Madrid(Spain).

Metal-promoted activations on some cumulenes can simulate the metal-induced transformations on carbon dioxide[1].

The synthesis and characterization of new "carbenoid like" niobium(III)sixteen electron species $Nb(\eta^5-C_5H_3RR')_2X$,R=H,R´=$SiMe_3$,X=Br;R=R´=$SiMe_3$,X=Cl permits to determine the influence of electronic and steric effects in the relative stability of the compounds $Nb(\eta^5-C_5H_3RR')_2X(ZCY)$,Z=Y=S;Z=PhN,Y=O(or S) in comparison with the previously described[2] complexes with the cumulene coordinated on the $Nb(\eta^5-C_5H_4SiMe_3)_2Cl$ unit.

The formation,prrperties and coordination modes of an extensive serie of ketene and keteneimine complexes with the fragments $Nb(\eta^5-C_5H_3RR')_2X$,R=H,R´=$SiMe_3$,X=Cl, Br;R=R´=$SiMe_3$,X=Cl,will also be deeply discussed because this type of complexes have been proposed as possible intermediacy in homogeneous carbon monoxide reduction related to the Fischer-Tropsch process[3].

These and other related reactions with other cumulene systems will be studied.

All the described complexes have been characterized by IR and NMR spectroscopy. Also for a keteneimine niobocene complex the X-ray crystal structure is being determined.

References

1.D.J.Darensbourg and R.A.Kudaroski.,Adv.Organomet.Chem.,(1983),22,129

2.A.Antiñolo,S.García-Lledó,J.Martínez de Ilarduya and A.Otero.,J.Organomet.Chem., (1987),335,85

3.D.A.Straus and R.H.Grubbs.,J.Am.Chem.Soc.,(1982),104,5499

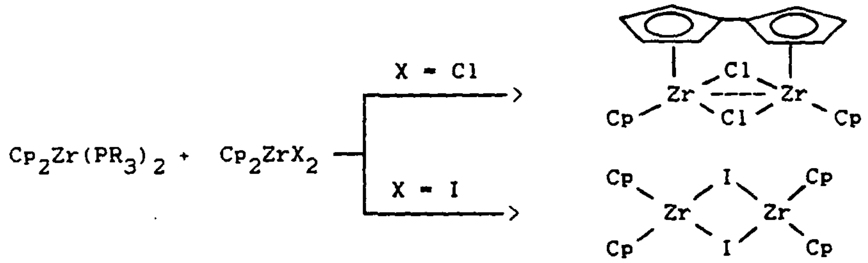
Synthesis of Diamagnetic and Dimeric Zirconium(III) and Hafnium(III) Compounds without Metal-Metal Bond

Sandro Gambarotta, Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16 9747AG Groningen, The Netherlands

Michael Y. Chiang, Chemistry Department, Columbia University, New York, N.Y.10027, USA

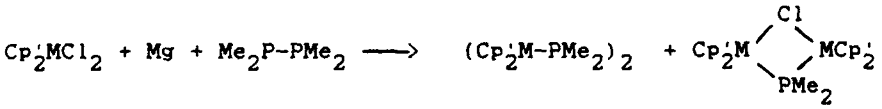
The formation of a Zr-Zr bond has been postulated to explain the generally observed diamagnetism of the dimeric Zr(III) species(1). However, there is in the literature a remarkable lack of structural reports(2).

Easy comproportionation reaction between Cp_2ZrX_2 (X = Cl,I) and $Cp_2Zr(PR_3)_2$ leads to the formation of two different Zr(III) complexes depending on the nature of the halide.



The X-ray structure of both complexes showed a rather long intermetallic distance which, in the case of the diamagnetic $(Cp_2ZrI)_2$, excluded the presence of any M-M bond.

The "in situ" generated "Cp_2Zr", reacts with Me_2PPMe_2 originating two diamagnetic Zr(III) and Hf(III) complexes which can be easily isolated in pure form and characterized by X-ray analysis.



$$Cp'_2MCl_2 + Mg + Me_2P\text{-}PMe_2 \longrightarrow (Cp'_2M\text{-}PMe_2)_2 + Cp'_2M(\mu\text{-}Cl)(\mu\text{-}PMe_2)MCp'_2$$

(M = Zr, Hf: Cp'= C_5H_5, MeC_5H_4)

The value of the intermetallic distance shows that even in this case no M-M bond occurs as a common feature of these derivatives. The magnetic properties of these complexes will be discussed.

References:
1) Issleib,K. et al. Z.Naturforschg (1966),21b,519
2) Lappert,M.F. Chemistry of organo zirconium and hafnium compounds Ellis Horwood 1984

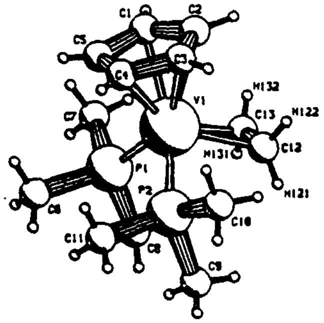
AN ETHYLENE COMPLEX OF VANADIUM (I)

Bart Hessen, Auke Meetsma and Jan H. Teuben, Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands.

The first ethylene complex of vanadium, $CpV(\eta^2\text{-ethylene})(PMe_3)_2$, was prepared by reaction of $CpVCl(PMe_3)_2$ with 0.5 mol of 1,4-di(bromomagnesio)butane. The compound is paramagnetic. Its formation probably involves rearrangement of an intermediate 1,4-divanadabutane complex:

$$\begin{tikzcd}
2\ CpVCl(PMe_3)_3 + (BrMg)(CH_2)_4(MgBr) \arrow[dr, "\text{THF}", "0^\circ C"'] & \\
CpV(\eta^2\text{-ethylene})(PMe_3)_2 & {[Cp(PMe_3)_2VCH_2(CH_2)_2CH_2V(PMe_3)_2Cp]} \arrow[l]
\end{tikzcd}$$

An X-ray structure determination showed that only a small amount of π-backdonation into the ethylene $\bar{u}^*$-orbital takes place (C–C (ethylene) = 1.365(5) Å).



The varied reactivity of $CpV(ethylene)(PMe_3)_2$ includes: (a) ligand exchange with (hard or soft) Lewis bases to yield new, CO-free CpV(I)-complexes, e.g. $CpV(PhC{\equiv}CPh)(PMe_3)_2$ and $CpV(bpy)PMe_3$; (b) insertion of CO_2 into the metal-olefin bond; (c) oxidative addition to the low valent metal center; (d) catalytic dimerization of olefins.

Transition Metal Siloxide Compounds

Alice C. Sullivan, Michael B. Hursthouse, M. Altaf Hossain, M. Mazid, Helen Blanchard, and Simon Bott. Department of Chemistry, Queen Mary College, University of London, Mile End Road, London E1 4NS.

A range of novel transition metal siloxide compounds having either unidentate or bidentate siloxide ligands are described. Some of the compounds along with features to be discussed are outlined below.

(1) $\{(Me_3Si)_3CSiMe_2O\}_3Cr$: Trigonal planar by Crystallography. First Cr(III) alkoxide with C.N. = 3 [1,2]

(2) $\{(Me_3Si)_3CSiMe_2O\}TaCl_4$: Two isomers observed by ^1H N.M.R. [1]

(3) $\{(2\text{-}Me\text{-}C_6H_4)_3SiO\}TaCl_4.Et_2O$: Octahedral by Crystallography with the chlorides equatorial. Approx. linear Si-O-Ta (172.1(2)°) and short Ta-O (1.812(3)Å) [3]

(4) $\{(2\text{-}Me\text{-}C_6H_4)_3SiO\}TaMe_3Cl$: Trigonal bipyramidal by Crystallography. [4]

(5) Formation and thermal decomposition of $\{(2\text{-}Me\text{-}C_6H_4)_3SiO\}TaMe_4$.

(6) $(\overline{OPh_2SiOSiPh_2OSiPh_2O})_2Ti$.2pyridine : cis-Octahedral by Crystallography. Formation from $Ph_2SiO(OLi)SiPh_2(OLi)$ and $TiCl_4$ involves interesting chain expansion. [5]

A full account of chemical features of these and other related compounds will be given.

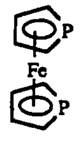
References

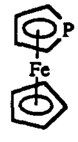
1. Blanchard H., Hursthouse M.B., and Sullivan A.C., J. Organomet. Chem., 1988, 341, 367.
2. Hitch P.B., Buttrus N.H., and Sullivan A.C., J. Organomet. Chem., 1986, 303, 321.
3. Bott S., and Sullivan A.C., unpublished work.
4. Hursthouse M.B., Mazid M., and Sullivan A.C., unpublished work.
5. Hursthouse M.B., Hossain M.A., Mazid M., and Sullivan A.C., unpublished work.

η^5-PHOSPHOLYL COMPLEXES OF EARLY TRANSITION METALS.

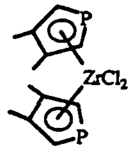
François Nief and François Mathey,Laboratoire de Chimie du Phosphore et des Métaux de Transition,Ecole Polytechnique,91128 Palaiseau Cedex,France.

Until now,most of the η^5-phospholyl (phosphacyclopentadienyl) complexes of transition metals belonged to the phospha- and diphosphaferrocene (1 and 2 respectively) or phosphacymantrene (3) families[1],with a few exceptions.

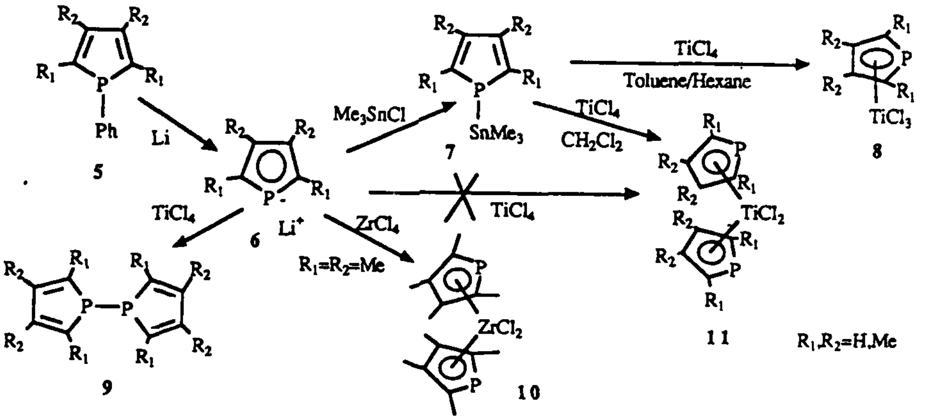

1


2


3


4

One of these exceptions is a diphosphazirconocene dichloride 4 which has been obtained[2] in modest yield and not completely characterized.



We have now been able to prepare the diphosphazirconocene dichloride 10 in good yield by reacting the new tetramethylphospholyl anion 6 (R_1=R_2=Me) with $ZrCl_4$.Reaction of 6 with $TiCl_4$ does not give the expected diphospha-titanocene dichloride but a biphospholyl 9 instead. However,this drawback was overcome by allowing a stannylphosphole 7 (easily obtained from 6) to react with $TiCl_4$.Depending on the solvent,a phospholyltitanium trichloride 8 or a bisphospholyltitanium dichloride 11 is obtained.

---

[1] F.Mathey,J.Fischer and J.H.Nelson,Structure and Bonding(Springer-Verlag,Berlin),1983,55,153

[2] P.Meunier and B.Gautheron,J.Organomet.Chem.,1980,193,C13

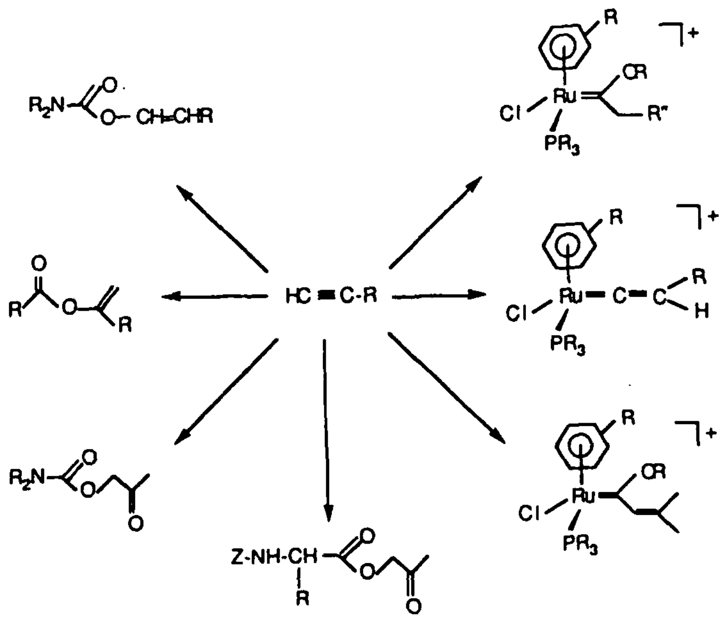
Activation of Alkynes with Ruthenium Complexes

P.H. Dixneuf
Université de Rennes, Campus de Beaulieu
35042 RENNES CEDEX (France)

Mononuclear ruthenium(II) complexes provide activation of alkynes towards both catalytic and stoicheiometric additions.

They are catalyst precursors for the one-step synthesis of vinylcarbamates or enol esters directly from carbon dioxide or carboxylic acids. When propargyl alcohols are used this activation offers a route to β-oxopropyl carbamates and esters.

Activation of alkynes can be used for the access to new arene ruthenium-carbene complexes, via vinylidene intermediates, or to vinylcarbene derivatives via allenylidene intermediates.



194

WATER SOLUBLE RHODIUM HYDROFORMYLATION SYSTEM

István T. Horváth, Rodney V. Kastrup, and Alexis A. Oswald
Exxon Research and Engineering Company, Annandale, NJ 08801, USA

Edmund J. Mozeleski
Exxon Chemical Company, Annandale, NJ 08801, USA

Although a water soluble trisodium-phosphinetriyltri-m-benzenesulfonate [$P(m\text{-}C_6H_4SO_3Na)_3$] modified rhodium hydroformylation catalyst system has been successfully used in large scale production of n-butanal, no information was available on the structure of catalytic species under catalytic conditions.

We have found that $Rh(CO)_2(acac)$ reacts with excess $P(m\text{-}C_6H_4SO_3Na)_3$ ($P/Rh=3.5$ or higher) in water under atmospheric pressure of carbon monoxide to give $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ (1). The hydride ligand in 1 is formed via the water-gas shift reaction. NMR and IR spectroscopic data indicate a structure analogous to $HRh(CO)(PPh_3)_3$ (2). The reaction of $[Rh(CO)_2Cl]_2$ or $Rh_4(CO)_{12}$ with $P(m\text{-}C_6H_4SO_3Na)_3$ also yields 1. The formation of 1 was observed in the reaction of $HRh(CO)(PPh_3)_3$ (2) with excess $P(m\text{-}C_6H_4SO_3Na)_3$ as well.

Surprisingly, the $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ (1)/3 $P(m\text{-}C_6H_4SO_3Na)_3$ system shows an extremely high stability under CO/H_2, the formation of new species could not be detected up to 200 bar of $CO/H_2(1:1)$ by high pressure NMR. This sharply contrasts to the behavior of the $HRh(CO)(PPh_3)_3$ (2)/3 PPh_3 system in organic media. Under the same conditions, 200 bar $CO/H_2(1:1)$, the only species in solution detectable by high pressure NMR is $HRh(CO)_2(PPh_3)_2$.

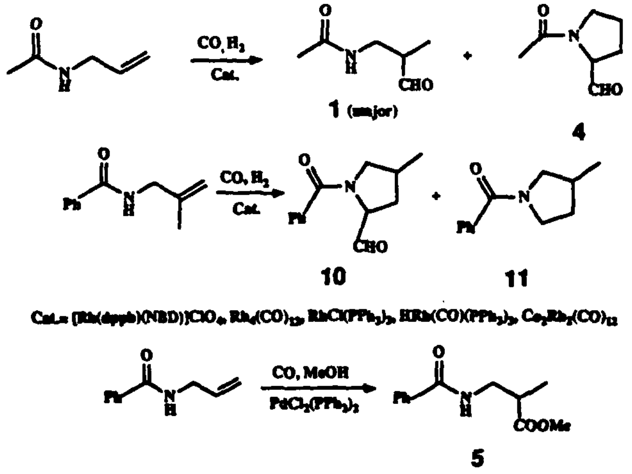
These results provide further evidence that the n/i ratio of aldehyde products is controlled either by the stereoselective coordination of the olefin to a coordinatively unsaturated $\{HRh(CO)(phosphine)_2\}$ species and/or by the subsequent formation of the $\{alkyl\text{-}Rh(CO)(phosphine)_2\}$ intermediate.

Hydrocarbonylations of N-Allylamides. Novel Amide-directed Hydrocarbonylations and Double Carbonylation

Iwao Ojima and Zhaoda Zhang
Department of Chemistry, State University of New York
at Stony Brook, New York 11794, U.S.A.

The hydroformylation of N-allylacetamide is effected by the chelation of the amide moiety to rhodium catalysts giving iso-aldehyde (1) as a major product. Novel double carbonylation (a new type of amidocarbonylation) of N-allyl- and N-methallylamides giving 1-acyl-2-formylpyrrolidines (4, 10) is promoted by rhodium complexes. A Co-Rh mixed metal catalyst, $Co_2Rh_2(CO)_{12}$, gives 1 with a good regioselectivity and also promotes a new homologation-cyclization process to give 1-benzoyl-3-methylpyrrolidine (11) in one step with excellent selectivity. The $PdCl_2(PPh_3)_2$-catalyzed hydroesterification of N-allylbenzamide gives iso-ester (5) predominantly through a chelation-control.

Possible mechanisms for those new reactions are proposed.



Cat. = $[Rh(dppb)(NBD)]ClO_4$, $Rh_4(CO)_{12}$, $RhCl(PPh_3)_3$, $HRh(CO)(PPh_3)_3$, $Co_2Rh_2(CO)_{12}$

HYDROCARBONYLATION REACTIONS FOR KETONE SYNTHESIS

Giambattista Consiglio and Roger Schwab

Swiss Federal Institute of Technology (ETH), Department of
Industrial and Engineering Chemistry, ETH Zentrum, CH-8092 Zürich

Despite its potential significance, the catalytic "oxo synthesis" of ketones has been very limited in scope until now [1]. In the last years large interest has been devoted to the copolymers of olefins (particularly of ethylene) and carbon monoxide [2]. Among the most active catalyst precursors for this copolymerization $[Pd(CH_3CN)_4][BF_4]_2/PPh_3$ and $Pd(OAc)_2$/Dpp/Acid (Dpp=1,3-propanediylbis(diphenylphosphine); Acid=non-hydrohalogenic acid with a pK_a of less than 2) have been largely investigated [2,3]. The latter catalytic system (or the similar one containing the dpb ligand, where dpb is 1,4-butanediylbis(diphenylphosphine)) was reported to be active for the hydroformylation of 1-octene under about 100 bars of hydrogen and carbon monoxide and about 120 °C [4], the catalytic activity being much larger than that previously reported for the related systems based on Pd $(PPh_3)_4/CF_3COOH$ or $(PPh_3)_2Pd(C_6H_5)Br/AgPF_6$ [5]. *In fact, by modifying the* $Pd(OAc)_2/CF_3COOH$ system with diphosphines such as dpp, dpb or even dpe we could carry out the hydroformylation of 1-pentene at 100 °C under 200 bars of hydrogen and carbon monoxide in equimolar ratio. However, when $[Pd(CH_3CN)_4][BF_4]_2$ was used with the dpp ligand under the same reaction conditions, the most abundant hydrocarbonylation product (36 %) was a 4:1 mixture of undecan-6-one and 4-methyldecan-5-one. Partial hydroformylation (13 %) and hydrogenation (10 %) of the substrate takes also place. In the case of styrene as the substrate the reaction is much more selective, 1,5-diphenylpentan-3-one being recovered in 80 % yield. Yields for his system are thus much better than that recently reported for the formation of 4-oxo-heptandioate from methyl acrylate using $Pd(OAc)_2$/dpp/p.toluenesulphonic acid as the catalyst precursor [6].

References: 1) O. Roelen, Chem. Exp. Didakt. 3, 119 (1977). 2) A. Sen, Adv. Polym. Sci. 73/74, 125 (1986). 3) J.A.M. Van Broekhoven, E. Drent, Eur. Pat. Appl. 235,866 (1986) (C.A. 108, 38604 (1988)) and previous applications. 4) E. Drent, Eur. Pat. Appl. 220,767 (1985); C.A. 107, 39199 (1987). 5) J.J. Mrowca, U.S. Patent 3,876,672 (1972); C.A. 84, 30432 (1976). 6) E. Drent U.K. Pat. Appl. 2183631 (1985); C.A. 107, 153941 (1987).

DINUCLEAR RHODIUM COMPLEXES AS CATALYST PRECURSORS FOR THE HYDROFORYLATION OF ALKENES.

Carmen Claver, Aurora Ruiz and Alfonso Polo, Departament de Química, Facultat de Química de Tarragona, Universitat de Barcelona,Plaza Imperial Tàrraco 1, 43005 Tarragona, Spain.

Juan Carlos Bayón and Julio Real, Deprtament de Química, Universitat Autónoma de Barcelona, Bellaterra, 08193 Barcelona, Spain.

In recent years dinuclear rhodium complexes have received considerable attention due to their catalytic activity in hydroformylation reactions. It has been shown that complexes of the types $|Rh_2(\mu\text{-SR})_2(CO)_2(PR_3)_2|^1$, $|Rh_2(\mu\text{-azolate})_2(COD)_2|$ plus PR_3 ligands and related complexes$^{2-4}$, behave as active catalyst in alkene hydroformylation, even in mild conditions.

A potential advantage of these species with respect to other catalysts is the possibility of introducing changes in the bridgind ligands.

The present investigation was undertaken in order to explore the use of anionic and zwitteronic amino-thiols as bridging ligands to produce new complexes of rhodium(I). Neutral and cationic dinuclear complexes of formulation $|Rh_2(COD)_2(S(CH_2)_3NMe_2)_2|$ and $|Rh_2(COD)_2(S(CH_2)_3NMe_2Bz)_2|(PF_6)_2$ and related carbonil complexes have been prepared and characterized by elemental analyses, infrared spectra, ^1H NMR and ^{13}C NMR.

The systems formed by adding phosphine or phosphite ligands (PR_3/Rh= 1/1) to the dinuclear complexes are catalysts precursors in hydroformylation of 1-heptene under mild conditions(5 bar,80ºC).

The best conversion from 1-heptene to aldehydes was achieved when PR_3= PPh_3 (90%) and the best selectivity (n-octanal/2-methylheptanal= 3/1) when PR_3= $P(OMe)_3$.

References:1)Ph.Kalck,J.M.Frances,P.Pfister,T.Southern and A.Thorez J. Chem. Soc. Chem. Commun., 1983,510. 2)Ph. Kalck, A. Thorez, M.T. Pinillos, L. A. Oro, J. Mol. Cat., **31**, 1985, 311. 3)C. Claver, Ph. Kalck, L. A. Oro, M. A. Pinillos and C. Tejel, J. M. Cat. (in press) 4)C. Claver, Ph. Kalck, M. Ridmy, A. Thorez, L. A. Oro, M. T. Pinillos, M. C. Apreda, F. H. Cano and C. Foces-Foces, J. Chem. Dalton Trans (in press).

OXIDATIVELY INDUCED MIGRATION OF HYDROGEN FROM METAL TO ALKENE. HIGHLY REACTIVE RHODIUM SYSTEMS FOR HYDROGENATION AND HYDROFORMYLATION OF ALKENES AND ALKYNES.

Claudio Bianchini, Andrea Meli, Maurizio Peruzzini and Francesco Vizza, Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R., Via J. Nardi 39, I-50132 Firenze, Italy

Piero Frediani, Dipartimento di Chimica Organica, Università di Firenze, Via G. Capponi 7, I-50121 Firenze, Italy

The formation of alkyl complexes via migratory insertion of alkene into a transition metal-hydrogen bond has long been a goal in organometallic chemistry, in large part because of the importance of the reaction in catalytic hydrogenation of alkenes. Generally, such a migratory step is accomplished by ligand addition to hydride(alkene) complexes.
We now wish to report an alternative pathway by which the hydride (alkene) ⟶ alkyl migration takes place. The [(triphos)RhH(π-dialkyl fumarate)] complex, (1), [triphos = $MeC(CH_2PPh_2)_3$] converts to the stable $[(triphos)Rh(\sigma\text{-alkyl})]^{2+}$ derivative upon two-electron chemical or electrochemical oxidation. The process is reversible, i.e. the two-electron reduction restores the starting hydride(π-fumarate) complex via Rh(II)-alkyl and Rh(I)-alkyl intermediates.
Results on the hydrogenation and hydroformylation of alkenes and alkynes using 1 as catalyst precursor are discussed.

BIMETALLIC ACTIVATION IN HOMOGENEOUS CATALYSIS : PALLADIUM CATALYZED MONO AND DOUBLE CARBONYLATION OF CHLOROARENE CHROMIUM TRICARBONYL COMPLEXES

Robert MUTIN, Christine LUCAS, Jean THIVOLLE-CAZAT, Fabienne DANY, Véronique DUFAUD and Jean Marie BASSET

Institut de Recherches sur la Catalyse, conventionné à l'Université Claude Bernard, CNRS, 2 avenue Albert Einstein, 69626 Villeurbanne, cédex France.

The palladium catalyzed carbonylation of aryl bromide or iodide to aromatic carboxylic acids, esters, amides, aldehydes or to aromatic α-keto amides, α-keto esters and α-keto acids is now well documented. However and so far, there is no reliable example of carbonylation of chlorobenzene leading to the same products. The difficulty to carry out carbonylation of chloroaromatic compounds is probably due to the high temperature required for the oxidative addition of the C-Cl bond onto zerovalent palladium complexes.

We report here that the palladium catalyzed carbonylation of chloroarene chromium tricarbonyl complexes, can lead to the corresponding esters, aldehydes, amides or α-keto amides. In the case of methoxy carbonylation, methyl-benzoate chromium tricarbonyl can be obtained at 100ºC, with a selectivity of 95%. This result strongly suggests that the whole catalytic cycle of carbonylation proceeds via bimetallic intermediates where chromium and palladium are simultaneously bonded to the same organic substrate. Consequently, it is suggested that the $Cr(CO)_3$ moiety favors the oxidative addition of the arene-Cl bond to zerovalent palladium and makes it possible a subsequent catalytic cycle of carbonylation.

Acknowledgements : The authors wish to thank R.P. Industries for financial support.

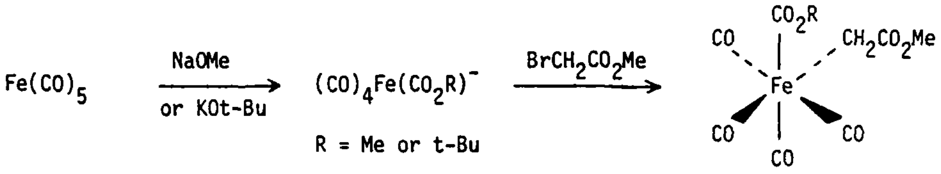
200

ALKYLALKOXYCARBONYLTETRACARBONYLIRON COMPLEXES ISOLATED INTERMEDIATES IN THE CATALYTIC CARBONYLATION OF ORGANIC HALIDES

Pascale Laurent, Sylviane Sabo-Etienne and Hervé des Abbayes

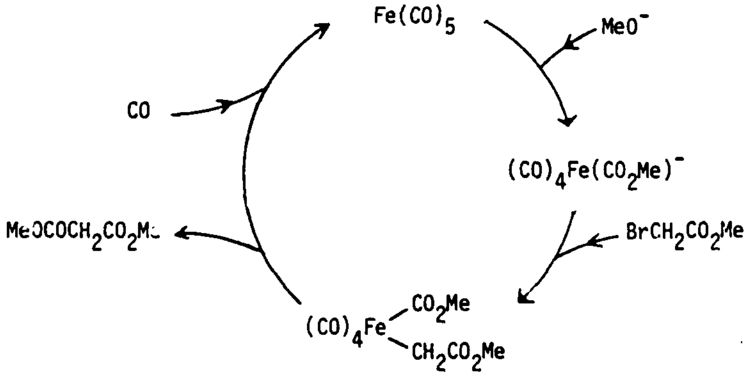
Laboratoire de Chimie Organique des Eléments de Transition, UA CNRS 322
Université de Bretagne Occidentale, 29287 Brest-Cédex FRANCE

Alkylalkoxycarbonyl complexes are believed to be intermediates in important catalytic reactions. We report here the synthesis and characterization of $(CO)_4Fe(CH_2CO_2Me)(CO_2R)$ complexes and provide direct evidence for their involvement in the catalytic cycle of carbonylation of organic halide into ester.



(A)

For R = Me, the complex (A) decomposes above 20°C under a CO atmosphere to yield $Fe(CO)_5$ and dimethylmalonate. (A) can be considered as an intermediate in the catalytic carbonylation of $BrCH_2CO_2Me$ into ester, according to the following cycle :

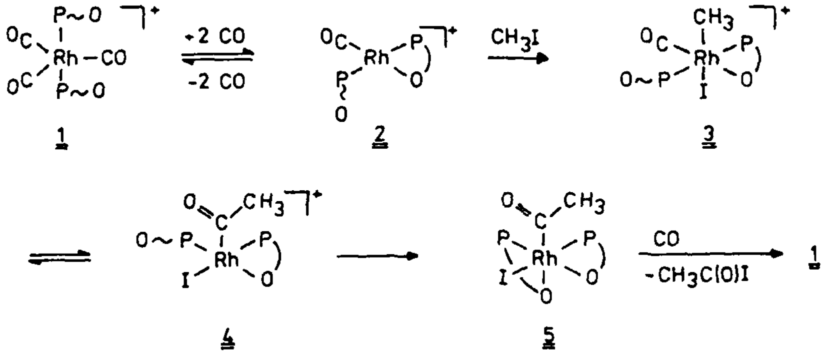


ETHER-PHOSPHINES AS CONTROLLING LIGANDS IN THE HYDROCARBONYLATION OF METHANOL

Ekkehard Lindner, Erhard Glaser, Uwe Schober, and Anselm Sickinger,
Universität Tübingen, Institut für Anorganische Chemie II, Auf der Morgenstelle 18, D-7400 Tübingen 1, BRD

Tetrahedrally coordinated cobalt(I) complexes of the type ICo(P⌒O)(P~O) (P~O: P-coordinated; P⌒O: O,P-coordinated), containing specifically conceived ether-phosphines as controlling ligands, are precursors in the catalytic cycle of the hydrocarbonylation of methanol. They are obtained by reaction of $I_2Co(P\sim O)_2$ with $K[HB(\text{sec-}C_4H_9)_3]$[1]. Methanol conversions and selectivities to acetaldehyde have attained more than 80%.

(Ether-phosphine)-rhodium complexes are useful as model compounds in the carbonylation of methanol[2]. CO elimination from **1** yields **2**. With rapid methyl migration via **3** and **4** oxidative addition of CH_3I to **2** affords the acyl complex **5**. Heating of **5** in the presence of CO results in the reductive elimination of $CH_3C(O)I$. The formation of the individual complexes is promoted by the "opening and closing mechanism" of (ether-phosphine) ligands.



---

[1] E. Lindner, U. Schober, E. Glaser, H. Norz, and P. Wegner, Z. Naturforsch. 42b, 1527 (1987).

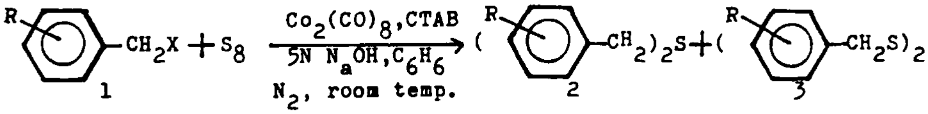
[2] E. Lindner and B. Andres, Chem. Ber., in press.

SYNTHESIS OF SULFIDES BY THE $Co_2(CO)_8$ AND PHASE TRANSFER CATALYZED REACTIONS OF BENZYL CHLORIDES

Jinxian Wang
Chemistry Institute, Department of Chemistry, Northwest Teachers' University, 51, An Nin Road (E.) , Lanzhou, China

Since the first publication on organometallic phase transfer catalysis[1], the field has developed sufficiently rapidly to justify an account at this time. Recent investigations have demonstrated that phase transfer catalysis is an exceedingly useful technique in organometallic chemistry. Several good reviews was published by Cassar[2] and Alper[3].

Sulfides are an important organic compounds. The preparation of sulfides by reaction of halides with Na_2S are will know in synthetic organic chemistry. We now report the synthesis of dibenzylsulfides and dibenzyldisulfides by the $Co_2(CO)_8$ and phase transfer catalyzed reactions of benzyl chlorides with S_8.



$X= -\overset{+}{N}(C_2H_5)_3Cl^-$, Br, Cl.

$R=$ H, o-CH_3, m-CH_3, p-CH_3, o-Cl, m-Cl, p-Cl, o-OCH_3, p-OCH_3.

Sixteen sulfides were prepared by the $Co_2(CO)_8$ and phase transfer catalyzed reactions of benzyl chlorides.The total yield is above 90%. Their structures have been proved by IR.MS.NMR and elemental analysis. The reaction mechanism is briefly discussed.

1) H.ALper and D.Des Roches, J.Organomet.Chem., 117,C44(1976).
2) L.Casser, in "Fundamental Research in Homogeneous Catalysis", P.115. Plenum, New York, 1977.
3) H.Alper,Fundam.Res. Homogeneous Catal., 1984, 4,79; Adv. Organomet. Chem.,1981, 19, 183.
4) Jinxian Wang,H.Alper, J.Org.Chem., 51, 273(1986).

Organosilicon Reagents in Organic Synthesis

E. Keinan, Technion Israel Institute of Technology, Technion City, IL 32000
Haifa, Israel

204

CYCLOMETALLATION CHEMISTRY OF METHYL-SUBSTITUTED TRIPHENYLPHOSPHINES

Elmer C. Alyea and John Malito, Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

It has now been well established that large tertiary phosphine ligands can promote cyclopalladation and/or cycloplatination reactions. Our presentation will quickly review the known trends in this chemistry and then focus on the closely related series of methyl-substituted triphenylphosphines, $P(C_6H_{5-n}(CH_3)_n)_3$ $(n=0-4)$. Cyclometallation is not observed in all cases but depends on the metal and its environment as well as the reaction conditions employed. As expected, the relative bulk of the phosphine is very important but the overall ligand electronic properties also prove to be important. Comparisons are made to parallel reactions of bulky trialkylphosphine ligands and all the factors which facilitate internal metallation are summarized so as to suggest a more definite description for the intimate mechanism(s) for metal-carbon bond formation via cyclometallation.

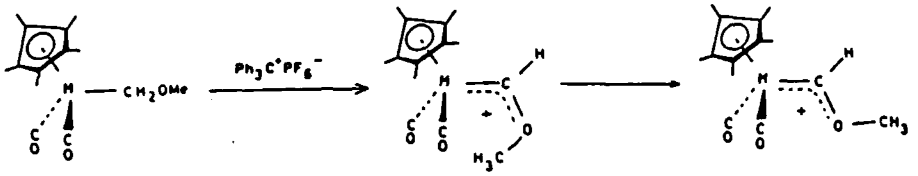
STEREO- AND CHEMO-SELECTIVE α-HYDRIDE ABSTRACTION FROM TRANSITION METAL ALKYL COMPLEXES

Véronique Guerchais, Claude Lapinte, Jean-Yves Thépot, Laboratoire de Chimie des Organométalliques, UA CNRS 415, Université de Rennes I, 35042 Rennes Cedex, France.

Loïc Toupet, Laboratoire de Physique Cristalline, UA CNRS 804, Université de Rennes I, 35042 Rennes Cedex, France.

The alkyl complexes $M(C_5Me_5)(L^1)(L^2)(CH_2XR)$ -M = Fe, Ru, X = O,S- provide an attractive chemistry in connection with the access to electrophilic carbene species. Their reactivity - the nature of the leaving group (H^- vs. CH_3O^- or S-adducts), the stereoselectivity of the α-hydride abstraction (geometric isomers)- are both controlled by the ancillary ligands at the metal center and by the nature of the abstracting reagent (the trityl cation and the in situ generated methylene complex $[Fe{=}CH_2]^+$ have been employed).

Complex 1 (L^1 = L^2 = CO, XR = OCH_3) undergoes an α-hydride abstraction with $Ph_3C^+PF_6^-$ affording specifically the kinetic cis isomer of 2 which then isomerizes into the thermodynamic trans form.



cis-2 TRANS-2

Such a behavior suggests an initial interaction of the trityl cation with the oxygen atom of the methoxy group of 1. This assumption is supported by the change of the chemoselectivity either observed upon substitution of a carbonyl ligand by a phosphine or in the case of the parent sulfur-containing complex which leads to the formation of stable adducts. The electrophilic properties of the carbene complexes have been investigated.

C-H BOND ACTIVATION: THE EIGHTEEN ELECTRON RULE AND THE GENERATION OF CATALYSTS

Giovanni Fochi, Scuola Normale Superiore, Pisa.
Working address: Dipartimento di Chimica & Chimica Industriale dell'Università, Sezione di Chimica Inorganica, Via del Risorgimento 35, 56100 PISA (Italy)

Bis(arene)metal sandwiches are usually stable if they do not exceed an $18\text{-}e^-$ count, the bis(hexamethylbenzene) d^7-d^8 group VIII metal complexes being only apparent exceptions because distorsions either alterate the energy levels, and thus the basis of the $18\text{-}e^-$ rule itself, or reduce the hapticity of one of the ligands.

In group VI bis(arene) sandwiches, a ligand is labilized by contact with potassium metal.[1] We report here that such a labilization can generate catalytic systems.

A mixture of 1,4-cyclohexadiene (5.3 mmol), di(benzene)molybdenum(0) (0.24 mmol) and potassium sand (0.59 mmol) in 1,2-dimethoxyethane (25 cm^3) was stirred overnight at room temperature (15^0 C). This resulted in the total conversion of the diolefin to benzene and dihydrogen (G.C.). Preliminary results show that also chromium and iron arene complexes are active in the same reaction.

Discussions with Prof. F. Calderazzo and Prof. G. Fachinetti were very helpful. M.P.I. (ministero della pubblica istruzione), Rome, is gratefully acknowledged for financial support.

---

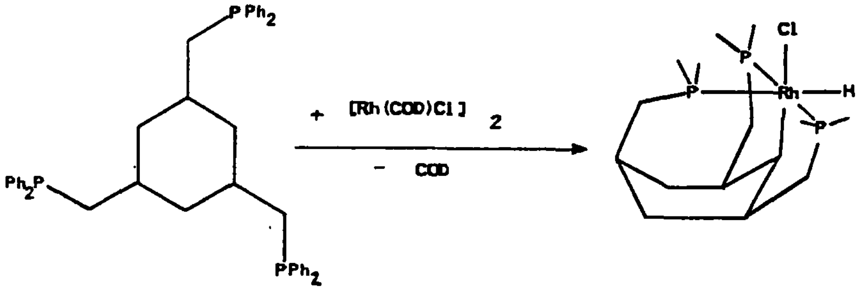
1) M. L. H. Green, G. Parkin, J. Chem. Soc., Chem. Comm., 1985, 771.

THE METALATION OF C-H-BONDS BY RHODIUM.
CIS,CIS-1,3,5-TRIS(DIPHENYLPHOSPHINOMETHYL)-CYCLOHEXANE

Hermann A. Mayer, Department of Chemistry, University of California
Santa Barbara, Santa Barbara, California 93106, [University of Tubingen
(on leave)]

William C. Kaska, Department of Chemistry, University of California
Santa Barbara, California, 93106, USA

The novel tridentate phosphine cis,cis-1,3,5-Tris(diphenylphosphinomethyl)-cyclohexane (I) has been synthesized.



I

II

Treatment with $[Rh(COD)Cl]_2$ in toluene at elevated temperatures gives a yellow solid (II). Compound II was characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR-Spectroscopy of the intramolecular C-H metalated product. Broad NMR lineshapes suggest that intramolecular exchange processes occur between the metal and the cyclohexane frame. Treatment with carbon monoxide gives different complexes with the cleavage of the Rh-C bond. Carbon-hydrogen metalation, exchange processes and reaction with carbon monoxide will be discussed.

ALLYLSTANNATION IN AQUEOUS MEDIUM

Giuseppe Tagliavini and Daniele Marton

Dipartimento di Chimica Inorganica, Metallorganica e Analitica
Universita' di Padova, Via Marzolo, 1, I 35131 Padova (Italia)

Allyl-, allenyl-, and propargyl-stannation of carbonyl compounds have recently been developed using allyl-, allenyl- and propargyl-tin chlorides (1-3). The procedure is based on: $Bu_2RSnCl + R'COR" + 1/2H_2O \quad R(HO)CR'R" + 1/2(Bu_2SnCl)_2O$, where R= allyl, allyllike, allenyl, or propargyl; R' = H or alkyl; R" = alkyl group.

Organotin substrates having allyl, crotyl, 1-methylallyl, cyclohex-2-enyl, and cinnamyl groups easily react in the presence of water with carbonyl compounds such as aldehydes, dialdehydes, ketones and acetals to give homoallyl alcohols(3).

The stereochemical course of some of these reactions has been evaluated by changing the esperimental conditions.

Work supported by C.N.R. (Roma).

(1) A. Boaretto, D. Marton, G. Tagliavini and A. Gambaro, J. Organometal. Chem., 286 (1985) 9.

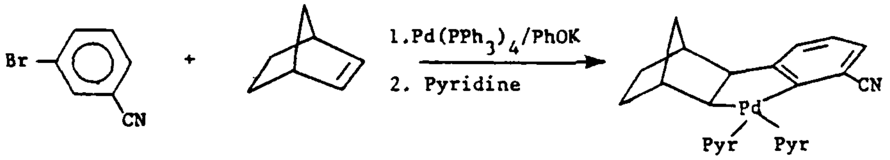
(2) A. Boaretto, D. Marton and G. Tagliavini, J. Organometal. Chem., 297 (1985) 149.

(3) D. Furlani, D. Marton, G. Tagliavini and M. Zordan, J. Organometal. Chem., 341 (1988) 345.

DIRECT SYNTHESIS OF A NEW ALKYLAROMATIC PALLADACYCLE.

Marta Catellani and Gian Paolo Chiusoli, Istituto di Chimica Organica, Universita', Viale delle Scienze, 43100 Parma, Italy

In the course of studies aimed at isolating intermediates of palladium-catalyzed C-C bond formation reactions [1], a new palladacycle has been obtained as a whitish solid powder from the reaction of m-bromobenzonitrile with bicyclo [2.2.1] hept-2-ene in anisole at 105° C in the presence of $Pd(PPh_3)_4$ and potassium phenoxide. The complex is insoluble in non coordinating solvents. On addition of pyridine it goes into solution while preserving its metallacyclic structure, as shown by n.m.r. evidence:



The composition and structure of the complex clearly result from decomposition with $NaBD_4$, which gives the expected dideuterated cyanophenylbicycloheptane.

To our knowledge this is the first direct preparation of a palladacycle by one-pot oxidative addition, insertion and aromatic substitution in sequence.

Work supported by Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione.

---

[1] M. Catellani and G.P. Chiusoli, J. Organomet. Chem., in press.

A STEREOSELECTIVE SYNTHESIS OF ALLYLIC ALCOHOLS

Mitsuhisa Tamura and Gohu Suzukamo*
Chiba Research Laboratory, Sumitomo Chemical Co.Ltd.,
Sodegaura, Kimitsugun, Chiba 299-02, Japan
*Takatsuki Research Laboratory, Takatsuki, Osaka, Japan

The reaction of vinyl epoxide with Grignard reagents and methyllithium was reported to give the mixture of 1,2- and 1,4-adducts and with organocopper reagents to give 1,4-adducts of E-configuration. Although it was claimed that the reaction of phenyllithium with isoprene epoxide gave a 1,4-adduct of Z-configuration as a major product, 1,2-adduct was always accompanied to some extent when the reaction was reinvestigated.

It was found that alkyllithiums react with vinyl epoxide regioselectively and stereoselectively to give 1,4-adducts. The major isomer was shown to have Z-configuration on the basis of ^{1}H-NOE, ^{13}C- and ^{1}H-NMR. The predominance of Z-isomer was improved when the reaction was conducted in the presence of a base such as tertiary amine or lithium alkoxide. The results are summarized in Table. This unexpected reactivity is limited to alkyllithiums and the organolithium compounds other than alkyllithium such as allyllithium, benzyllithium, 3-pyrridyllithium and 2-phenylvinyllithium gave only 1,2-adducts.

The present method was successfully applied to a stereoselective synthesis of α -santalol, which is one of the main constituents in East Indian sandalwood oil.

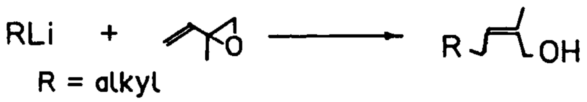


Table.

R	Base	Temp(^{o}C)	Solvent	Yd(%)	Z/E
n-C_4H_9	none	0	Hexane	76	88/12
"	TMEDA	0	"	68	96/4
"	n-C_4H_9OLi	0	"	73	97/3
sec-C_4H_9	none	0	"	63	86/14
n-C_8H_{17}	TMEDA	-20	"	55	96/4
cyclo-C_3H_5	none	-30	Et_2O	77	82/18
cyclo-C_6H_{11}	none	"	"	55	89/11
$PhCH_2CH_2$	none	"	"	70	79/21
"	TMEDA	-20	"	59	98/2

INTRAMOLECULAR ADDITION REACTIONS OF IRON CARBENE COMPLEXES

Paul Helquist, Christopher Knors, Shi-Kai Zhao, Pascale Seutet, and Matthew Mattson., University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

We have obtained several examples of carbene complexes of the general structure $[(\eta^5\text{-}C_5H_5)(CO)(L)Fe{=}CR^1R^2]^+$ (L = CO, phosphite, or phosphine). These species may be generated from the corresponding α-(alkylthio)alkyl-, alkenyl-, or acyliron complexes. Some of the carbene complexes are quite stable and have been characterized spectroscopically and by x-ray diffraction. Furthermore, many of these compounds show quite useful reactivity such as addition to alkenes to give cyclopropanes.

Most recently, we have been placing emphasis upon the uses of these complexes in the synthesis of polycyclic organic compounds proceeding through intramolecular additions of the carbene ligands to alkenes. Complex fused-ring cyclopropane derivatives are normally obtained, but we have also been studying the formation of five-membered rings. Current studies are being directed toward applications of these reactions in very direct syntheses of a variety of naturally occurring compounds. These syntheses have in turn required us to develop methods for the incorporation of the carbene complexes into organic substrates that serve as precursors of the natural products.

Literature References:

K. A. M. Kremer and P. Helquist, *J. Organomet. Chem.* **1985**, *285*, 231 (1985).

R. S. Iyer, G.-H. Kuo, and P. Helquist, *J. Org. Chem.* **1985**, *50*, 5898.

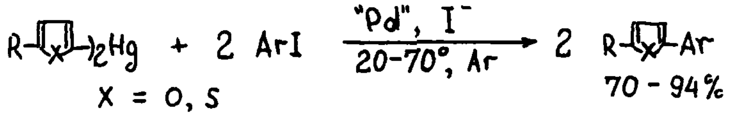
E. J. O'Connor, S. Brandt, and P. Helquist, *J. Am. Chem. Soc.* **1987**, *109*, 3739.

C. Knors, G.-H. Kuo, J. W. Lauher, C. Eigenbrot, and P. Helquist, *Organometallics* **1987**, *6*, 988.

PALLADIUM-CATALYZED CROSS-COUPLING, ACYL-DEMETALLATION AND CARBONYLATION REACTIONS OF ORGANOMERCURIALS

Prakash More, Nikolai Bumagin, Irina Beletskaya
Moscow State University, Moscow, USSR.

The palladium-catalyzed cross-coupling reactions of organomercurials with organic halides provide a novel and convenient method for the synthesis of arylated heterocyclic compounds. The reaction proceeds in the presence of iodide ion and oxygen-free atmosphere in dimethyl formamide to give a high yield of cross-coupling product (eq. 1).



(1)

The palladium-catalyzed acyl-demetallation of organomercurials is a mild, selective and general method for the synthesis of unsymmetrical ketones (eq. 2). The reaction proceeds at room temperature in acetone and in the presence of iodide ion to give high yields of unsymmetrical ketones (79-85%) along with the formation of homo-coupling product (~15%). The yield of unsymmetrical ketone can be increased by carring out the reaction in vacuum.

$$R_2Hg \quad + \quad 2\ R'COCl \xrightarrow[20^\circ]{\text{"Pd"},\ I^-} 2\ RCOR' \quad + \quad R_2 \qquad (2)$$

$$R, R' = Alk,\ Ar,\ 2\text{-}C_4H_3O,\ 2\text{-}C_4H_3S,\ 3\text{-}C_5H_4N$$

Carbonylation of ArI-RHgX system in the presence of palladium catalyst and iodide ion is another route to get high yields of unsymmetrical ketones (eq. 3). The highest reaction rate and selectivity was found in HMPA and in the presence of ligandless palladium catalyst.

$$ArI \quad + \quad CO \quad + \quad RHgX \xrightarrow[\substack{HMPA,\ 20^\circ \\ 1\,atm\ CO}]{\text{"Pd"},\ I^-} \underset{70-92\%}{ArCOR} \qquad (3)$$

POSTER SESSION

LITHIUM, POTASSIUM, AND STANNYL DERIVATIVES OF BI- AND TRICYCLIC CARBANIONS

J. Blümel, N. Hertkorn, F. H. Köhler, Anorganisch-chemisches Institut der TU München, Lichtenbergstr. 4, 8046 Garching, W-Germany.

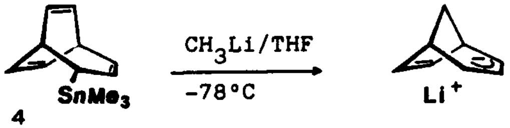
Metal derivatives of perturbed cyclopentadienyl anions represent a fascinating topic in Organometallic Chemistry. A special kind of perturbation is the twofold interruption of the originally cyclic π-system by sp^3-C-atoms as in 1, 2, and 3.

1 

2 

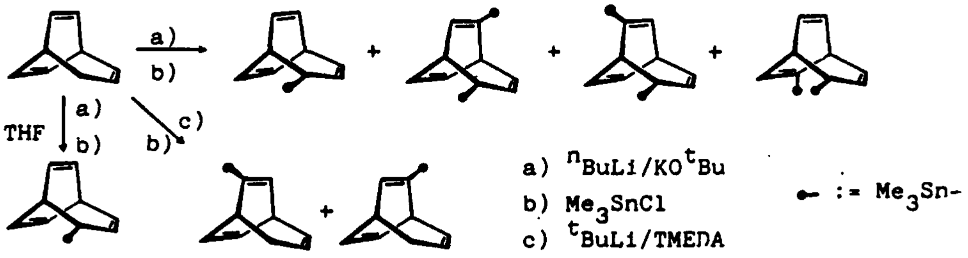
3 

We have obtained the lithium derivatives of 1, 2 and 3 according to the example given in the following equation.



4

A simple and fast access to the stannyl derivatives like 4 is provided by direct metalation of the olefins and reaction with trimethyltinchloride or by stannyl halogen exchange. In addition, a variety of stannyl compounds can be obtained selectively depending on the metalation conditions, e. g.:



a) $^nBuLi/KO^tBu$
b) Me_3SnCl
c) $^tBuLi/TMEDA$

• := Me_3Sn-

All stannylated derivatives are characterized by their NMR spectra. The data obtained therefrom lead to useful trends for the ^1H, ^{13}C and ^{119}Sn signal shifts and for the nuclear coupling constants $^nJ(^{117/119}Sn-^{13}C)$ and $^nJ(^{117/9}Sn-^{119}Sn)$.

REMARKABLE STRUCTURAL ANALOGIES BETWEEN Li^+ AND Cp_2ZrCl^+ COMPLEXES.

Gerhard Müller, Jürgen Riede, Brigitte Huber, Gabi Reber, Hans Heinz Karsch, Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstr. 4, D-8046 Garching, FRG.

Unexpected structural analogies between organometallic complexes of Li^+ and $Cp_2MCl(d^0)$ fragments were first predicted by Schleyer [1]. These should be due to electronic similarities of the metal fragments.

In a variety of molecular structures of *phosphinomethanide* complexes of $(TMEDA)Li^+$ and Cp_2ZrCl^+ [2] some remarkable structural analogies may actually be substantiated. These are not limited to virtually identical Li-P/C and Zr-P/C bond lengths, but are also evident in similar coordination modes of the ambident phosphinomethanide ligands I (monodentate via P or C; bidentate under formation of a three-membered ring).

$[R_2P - CR'_2]^-$ R = Me, Ph; R' = H, PMe_2, $SiMe_3$

I

Surprisingly, at both metal centers the coordination mode of the ligands is less influenced by the P substituents R, but rather by those at the carbanionoid C atoms (R'). Bidentate, chelating coordination is favored by +I substituents, e.g., $-PMe_2$ or $-SiMe_3$ which induce higher coordination numbers at the central metal atoms despite their greater steric bulk.

Similarities with, and differences to, theoretical studies on Li-phosphinomethanides (by P.v.R. Schleyer et al.) and Cp_2ZrCl^+-phosphinomethanides (by P. Hofmann) are discussed.

[1] A.J. Kos, E.D. Jemmis, P.v.R. Schleyer, R. Gleiter, U. Fischbach, J. Pople, J. Am. Chem. Soc. 103 (1981) 4996.

[2] H.H. Karsch, B. Deubelly, G. Müller, J. Organometal. Chem., in the press; H.H. Karsch, B. Deubelly, J. Hoffmann, U. Pieper, G. Müller, J. Am. Chem. Soc., in the press.

THE DYNAMIC PROPERTIES OF THE ARYLORGANOLITHIUM "ATE" COMPLEXES $/ArMR_3/Li{\cdot}D$ /M=B,Al/ INVESTIGATED BY MEANS OF MULTINUCLEAR H-1, C-13, Li-7, B-11, Al-27 DYNAMIC NMR SPECTROSCOPY

E.Kalbarczyk-Bidelska, S.Pasynkiewicz, Warsaw Technical University, 00-662 Warszawa /Poland/

G.van Koten, University of Utrecht, 3508 TB Utrecht /The Netherlands/

J.M.Ernsting, University of Amsterdam, 1018 Amsterdam /The Netherlands/

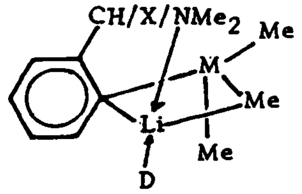
The model $/ArMMe_3/Li{\cdot}D$ $\left[/I\ Ar{=}Ar^1{=}2\text{-}C_6H_4CH_2NMe_2,\ M{=}B,\ D{=}OEt_2;\ II\ Ar{=}Ar^2{=}2\text{-}C_6H_4\text{-}/S/\text{-}CHMeNMe_2,\ M{=}B,\ D{=}OEt_2;\ III\ Ar{=}Ar^2,\ M{=}Al,\ D{=}OEt_2\right]$ were synthesized in the complexation reaction 1.

$$1/4\ Ar_4Li_4 + MMe_3 \xrightarrow{OEt_2/hexane} /ArMMe_3/Li{\cdot}OEt_2 \qquad /1/$$

The complexes IV $Ar{=}Ar^1$, M=B, D=THF, V $Ar{=}Ar^2$, M=B, D=nTHF were synthesized via the donor exchange reaction 2.

$$/ArBMe_3/Li{\cdot}OEt_2 \xrightarrow{THF} /ArBMe_3/Li{\cdot}THF \qquad /2/$$

The following structure has been established on the basis of molecular weight determinations and NMR spectroscopy:



	Li-7	B-11		Li-7	Al-27
I	-0.49	-17.2	III	-0.17	150.8
II	-0.72	-17.17			
IV	-0.56	-17.72			
V	-0.98	-17.41			

The flexibility of the molecules has been detected in polar and nonpolar solvents. The intramolecular two steps "rotation" of the aryl ring was found in D8-toluene solution for the I-IV complexes. The intramolecular processes, involving carbon-lithium bond, in OEt_2 solution at low temperature and in THF solution at rised temperatures were established.

216

METAL ALKOXIDE MODIFIED ORGANOMETALLIC REACTIONS. DIRECT SYNTHESIS OF LITHIOOXYALKYL- AND ARYLLITHIUM COMPOUNDS

C.G.Screttas ,I.D.Kostas and C.S.Salteris,Institute of Organic
Chemistry The National Hellenic Research Foundation Athens 116 35
Greece

Attempts to synthesize $LiO(CH_2)_6Li$ according to the conventional method from $HO(CH_2)_6Br$ led to extensive Wurtz coupling. Similar results were obtained by employing lithium naphthalene radical anion in place of lithium metal.

6-Lithiooxyhexyllithium was prepared in fair yields according to eq. (1).

$$PhS(CH_2)_6OH \xrightarrow[\substack{2.\ Li\ disp., \\ Mg(OCH_2CH_2OEt)_2, \\ THF\text{-}MCH}]{1.\ BuLi} Li(CH_2)_6OLi \qquad (1)$$

(MCH=methylcyclohexane)

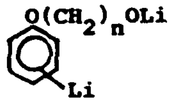
The organometallic product was characterized by carbonation and by conversion to $Hg(CH_2CH_2CH_2CH_2CH_2CH_2OH)_2$. The function of the alkoxide is to stabilize the organometallic reagent with respect to THF-cleaving reaction, so that solutions of the reagent can be stored at room temperature for 48 hours or longer.

The method has been extended to the preparation of the lithiooxy- organolithiums of the general types 1 and 2 .

$Li(CH_2)_n$-Y-$(CH_2)_mOLi$

Y=O,NR

1



2

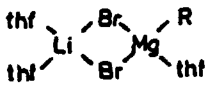
STERICALLY HINDERED ORGANOMETALLIC COMPOUNDS OF GROUPS 2 AND 12

Salih S. Al-Juaid, Colin Eaborn, Peter B. Hitchcock, Catherine A. McGeary, J.David Smith and Kayumars Tavakkoli. School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK.

The compound RLi (R = $C(SiMe_3)_3$) (1) reacts with anhydrous magnesium(II) bromide to give the bridged lithium-magnesium complex (2) (thf = tetrahydrofuran) which on heating gives the dialkyl MgR_2 (3), with the same structure as the compounds R_2M (M = Zn, Cd, Hg, or Mn) described earlier.

With cadmium(II) chloride, (1) gives $Li(thf)_nCdRCl_2$ (4) which has an ionic structure with the unusual dicadmate anion (5). On heating (4) gives RCdCl which has the tetrameric cubane structure (6). In contrast, the compound R'CdBr (R' = $C(SiMe_2Ph)_3$) (7), is dimeric in the solid: on recrystallisation from moist thf, the hydrate (8) is formed.

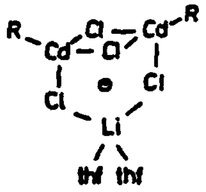
The mercury compound R'HgCl reacts with organolithium or Grignard reagents to give the unsymmetrical compounds R'HgR" (R" = Me, Bu, Ph, CH_2Ph or $C(SiMe_3)_3$) which are remarkably stable thermally. No decomposition of $(Me_2PhSi)_3CHgCH_2Ph$ was detected at 230 °C whereas $Hg(CH_2Ph)_2$ was completely decomposed at 150-170 °C. If, as is generally supposed, the rate determining step in the decomposition of dibenzyl mercury is homolytic cleavage of the Hg-C bond, it is not clear why the large alkyl group in the unsymmetrical $R'HgCH_2Ph$ should make this cleavage so difficult.



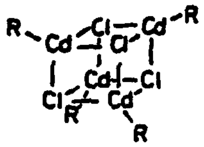
(2)

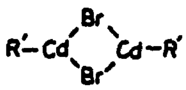
$R{-}Mg{-}R$

(3)

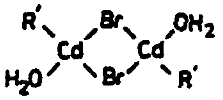


(5)





(7)



(8)

(6) R = $C(SiMe_3)_3$ R' = $C(SiMe_2Ph)_3$

N.H. Buttrus, C. Eaborn, M.N.A. El-Kheli, P.B. Hitchcock, J.D. Smith, A.C. Sullivan, and T. Tavakkoli, J. Chem. Soc. Dalton Trans. 1988, 381, and unpublished results.

STOICHEIOMETRY OF REACTION BETWEEN RADICAL ANIONS AND METAL COMPOUNDS

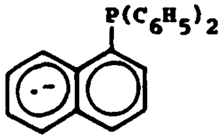
Constantinos G. Screttas and **Maria Micha-Screttas** , Institute of
Organic Chemistry The National Hellenic Research Foundation
Athens 116 35 Greece

The stoicheiometry of the reaction between **RMgX** and e.g. lithium naphthalene radical anion has been determined by the method of magnetic titration . When **X** = **Br** the stoicheiometry is 1:1 , and this result combined with product analysis and product characterization indicates that the reaction is as follows

$$2RMgBr + 2Li^{+}C_{10}H_{8} \longrightarrow R_{2}Mg + Mg^{0}$$

Magnesium alkoxides as well as **RMgOR** resist reduction by radical anion rather strongly .

The stoicheiometry of interaction between radical anions bearing a functional group capable of acting as a strong ligand, such as 1 , with e.g. **TiX$_4$** (X = Cl, OR) will be reported.



1

STUDIES ON ORGANOMERCURY(II) COMPLEXES OF MALTOL

N.K. Kaushik and S. Bhatia
Department of Chemistry, University of Delhi, Delhi 110 007, India
G.S. Sodhi
Department of Chemistry, S.G.T.B. Khalsa College, University of Delhi, Delhi 110 007, India

A number of organomercury(II) complexes involving maltol of the type, RHgL [R = phenyl (C_6H_5), o-,p-hydroxyphenyl (o-,p-HOC_6H_4), p-acetoxyphenyl (p-$AcOC_6H_4$), 2-furyl (2-C_4H_3O); HL = maltol] have been synthesised and characterised. Conductance measurements indicate that the complexes are non-electrolytes. From IR and UV studies, it is concluded that maltol acts as a bidentate ligand, coordinating to the mercury(II) ion through phenolic and carbonyl oxygen atoms. ^{1}H and ^{13}C NMR support the stoichiometry of the complexes. Fluorescence spectra has been recorded for o-,p-HOC_6H_4HgL complexes. For C_6H_5HgL, p-HOC_6H_4HgL and p-$AcOC_6H_4HgL$ complexes, thermal studies (TG and DSC) have been carried out and relevent kinetic and thermodynamic parameters have been enumerated. In addition, the fragmentation pattern of the complexes has been analysed on the basis of mass spectra.

REGIOSELECTIVITY OF THE $L_2Pt(0)$ INSERTION INTO THE NONSYMMETRICAL ORGANOMERCURIALS

E.V.Maskaeva, V.V.Bashilov, V.I.Sokolov, Institute of Organo-Element Compounds, Academy of Sciences, Moscow, U.S.S.R.

Previously we have described the preparation of compounds such as cis-isomers $(PPh_3)_2R^fM\text{-}HgR^f$, wherein M=Pd, Pt. Now regioselectivity has been studied for the nonsymmetrical organomercurials R^fHgX and R^fHgR which fiffer by the electronic effects of both groups. With perfluoroalkylmercuric halides the insertion of L_2Pt occurred onto the Hg-Hal bond:

$$CF_3HgX \ + \ PtL_2L' \longrightarrow CF_3HgPtL_2X$$

$L=PPh_3$, $L' = PhCH{=}CHPh$, X=Cl,Br,J

The presence of a Hg-Pt bond and the trans-arrangement of two phosphine ligands have been deduced from the ^{31}P and ^{19}F NMR spectra.

With the mercurials of type R^fHgR the insertion unexpectedly took place onto the Hg-R bond of the non-fluorinated group.

$$R^fHgR + PtL_2L \longrightarrow R^fHgPtL_2R$$

$R^f = CF_3$, $(CF_3)_2CF$, R = Ph; $R^f = (CF_3)_2CF$, R = $Ph_2C{=}CH$

According to the ^{31}P and ^{19}F NMR spectra the insertion products for all non-symmetrical dialkylmercuries have cis-arrangement of both PPh_3 ligands.

REACTIONS OF ANIONIC RHODACARBABORANES WITH ORGANOMETALLIC ELECTROPHILES

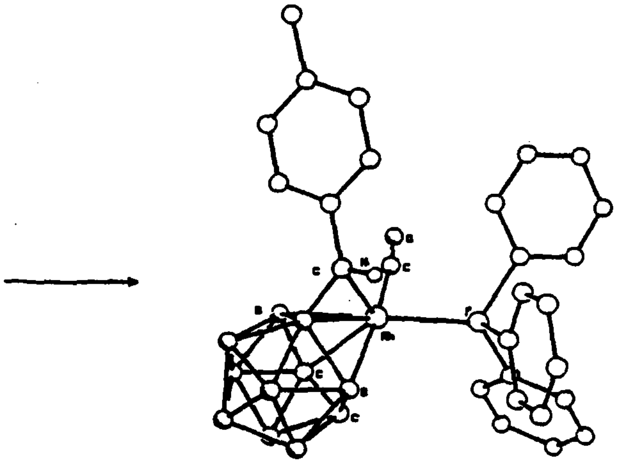
Ian J. Hart, Judith A.K. Howard, Max U. Pilotti
and F. Gordon A. Stone

Department of Inorganic Chemistry, University of Bristol,
Bristol BS8 1TS, Great Britain

The reactions of the anionic rhodacarbaborane complexes $[(\eta^5\text{-}C_2B_9H_{11})RhL_2]^-$ (L_2 = $(PPh_3)(CO)$, $(CO)_2$, (η^4-cycloocta-1,5-diene)] with a variety of organotransition metal electrophiles have been investigated. In particular, organometallic complexes have been chosen which feature exotic π-acid ligands, e.g., alkylidenes and alkylidynes.

The reactions which result will be discussed in terms of the non-innocence of the carbaborane and π-acid moieties. An illustration of this is provided by the following reaction:

$[(\eta^5\text{-}C_2B_9H_{11})Rh(CO)(PPh_3)]^-$ + $[Mn(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]^+$



+ $[Mn(CO)_3(\eta\text{-}C_5H_5)]$

which involves the transfer and intramolecular hydroboration of a coordinated alkylidyne group.

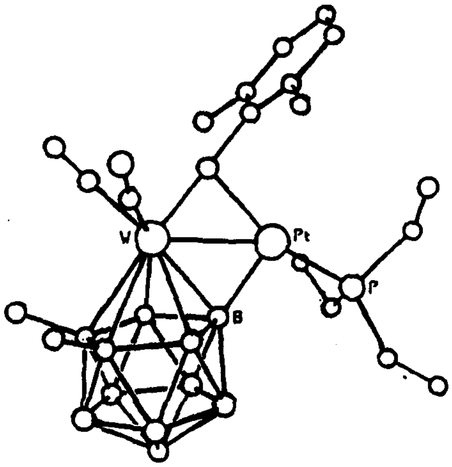
HYDROGEN TRANSFER PROCESSES IN HETEROBIMETALLIC CARBABORANE COMPLEXES

David D. Devore, Judith A.K. Howard, John C. Jeffery,
Max U. Pilotti and F. Gordon A. Stone

Department of Inorganic Chemistry, University of Bristol,
Bristol BS8 1TS, Great Britain

The salts $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ and $[PtH(Me_2CO)(PEt_3)_2][BF_4]$ afford the dimetal compound $[PtW(CO)_2(PEt_3)_2(\eta^6\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}$ which features a novel hyper-closo metallacarbaborane configuration [1]. Fundamental to this unusual rearrangement is the intramolecular hydroboration of a μ-alkylidyne ligand which ultimately becomes bound in a terminal manner to a boron vertex.

To better understand the processes involved, we have employed the sterically congested alkylidyne complex anion $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ 1. It was anticipated that the bulky 2,6-dimethyl substituents might impede hydrogen transfer to the alkylidyne carbon and facilitate the interception of intermediates. Indeed, reaction of 1 with $[PtH(Me_2CO)(PEt_3)_2)]^+$ provides the bimetallic alkylidyne complex $[PtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PEt_3)_2H(C_2B_9H_9Me_2)]$ 2 which readily loses dihydrogen to provide the novel σ-carbaboranyl compound $[PtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PEt_3)(\mu\text{-}\sigma{:}\eta^5\text{-}C_2B_9H_8Me_2)]$ 3. The coordinatively unsaturated compound 3 forms adducts with CO, CN^{t}Bu and hydrogen, the latter reaction being reversible, to, giving, respectively, $[PtW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(PEt_3)(L)(\mu\text{-}\sigma{:}\eta^5\text{-}C_2B_9H_8Me_2)]$ (L = CO 4, CN^{t}Bu 5), and 2.



3

---

[1] M.J. Attfield, J.A.K. Howard, A.N.de M. Jelfs, C.M. Nunn and F.G.A. Stone, J. Chem. Soc., Dalton Trans., 1987, 2219.

SODIUM ALUMINUM HYDRIDE - PREPARATION AND APPLICATION

GUNNER E. NELSON
ETHYL CORP., BATON ROUGE, LOUISIANA

WE REPORT THE DEVELOPMENT OF A FACILE SYNTHESIS OF SAH FROM THE ELEMENTS. PRELIMINARY RESULTS NEGATE THE INTERMEDIACY OF NAH IN THE PROCESS AS REPORTED EARLIER.

SAH IS USEFUL AS A REDUCING AGENT IN ITS OWN RIGHT AND CAN ALSO BE USED AS AN INTERMEDIATE IN THE PREPARATION OF REDUCING AGENTS IN COMMON USE SUCH AS $LIALH_4$, $NABH_4$, $NAAL(OCH_2CH_2OCH_3)_2H_2$ AND $NAALET_2H_2$.

SAH REACTS READILY AND SELECTIVELY WITH α-OLEFINS YIELDING THE DI-, TRI- AND TETRAALKYL ALUMINATES AS DESIRED. WE HAVE USED THE TETRAALKYL ALUMINATES AS ALKYLATING AGENTS IN THE PREPARATION OF ALKYLSILICON, -PHOSPHORUS AND -TIN COMPOUNDS.

REACTION OF ALKYLALUMINIUM COMPOUNDS WITH CARBON SUBOXIDE

Luciano Pandolfo, Gastone Paiaro, Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Universita' di Padova, Via F. Marzolo 1, I-35131 Padova Italy

Umberto Vettori, Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., Via F. Marzolo 1, I-35131 Padova, Italy

Trialkylaluminium compounds react with ketones giving products of addition, reduction and enolization reactions (1).
Reaction of trimethylaluminium with benzophenone was found to proceed trough two distint paths, depending upon the ratio of aluminiumalkyl to ketone (2).
In continuation of our studies (3) on the reactivity of carbon suboxide, we have examined its reaction with trialkylaluminium compounds.
C_3O_2, which presents two carbonylic groups, gives alkylated compounds.
In the reactions with trimethyl-and triethylaluminium in n-hexane, with ratios $Al/C_3O_2 < 2$, we have found the formation of a $=C=O......AlR_3$ adduct.
With higher ratios ($Al/C_3O_2 \geqslant 2$), $(R_2Al)_2O$ was produced and, after hydrolysis, two principal products, $RCOCH_2COR$ and $R_2C=CHCOR$, were obtained (R=Me, Et).

Work supported by Ministero della Pubblica Istruzione (Roma).

(1) S. Pasynkiewicz, E. Sliwa - J. Organometal. Chem. 3, 121, (1965)
(2) E.C. Ashby, J. Laemmle, H.M. Neumann - J. Am. Chem. Soc. 90, 5179, (1968)
(3) L. Pandolfo, G. Paiaro, U. Vettori - Gazz. Chim. Ital. 11, 781, (1987);
P. Ganis, G. Paiaro, L. Pandolfo, G. Valle, Organometallics 7, 210, (1988)

SPECTROSCOPIC INVESTIGATION OF DICHLOROALUMINIUM ACETYLACETONATE

J.Lewiński. S.Pasynkiewicz
Warsaw Technical University, Faculty of Chemistry, Koszykowa 75,
00-661 Warszawa, Poland

We have found that dichloroaluminium acetylacetonate obtained by known methods [1,2] /illustrated by equations /1/ and /2/ / exist not only in the monomeric form $Cl_2Alacac$, like it was assumed previously [1,2/], but has a more complex structure

$$RAlCl_2 + Hacac \longrightarrow [Cl_2Alacac] + RH \qquad /1/$$

$$2\ AlCl_3 + Al/acac/_3 \longrightarrow 3\,[Cl_2Alacac] \qquad /2/$$

The structure of the dichloroaluminium acetylacetonate was studied by the means of variable temperature ^1H, ^{13}C and ^{27}Al NMR and IR spectroscopy. In the methylene chloride solution monomeric molecular complex $Cl_2Alacac$ is in equilibrium with the trimer $acacAl/acac\cdot AlCl_3/_2$.

$$\underset{I}{Cl_2Alacac} \rightleftharpoons \underset{II}{acacAl/acac\cdot AlCl_3/_2} \qquad /3/$$

Equilibrium /3/ depends on the temperature and the concentration of dichloroaluminium acetylacetonate. In dilluted solution equilibrium is shifted to the left. Decrease of temperature and increase of concentration favours form II.

Our studies revealed that form II possesses three acetylacetonate ligands bonded to the central aluminium atom. One of them have a symmetrical chelate structure and two others - enol ether structure with complexed $AlCl_3$ molecules.

References

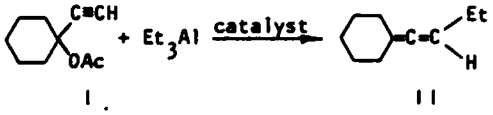
1.W.R.Kroll, J.Kuntz, E.Brinbaum, J.Organomet.Chem., 26/1971/313.
2. K.Dowbor, Thesis, Warsaw Technical University, 1973.

226

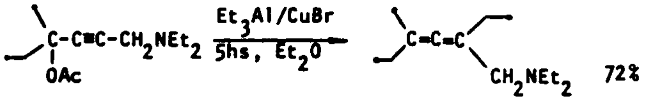
HIGHLY REACTIVE AND SELECTIVE ALUMOCOPPER REAGENTS APPLIED TO SYNTHESIS

Kutchin A.V., Romanova T.Yu., Andreeva N.I., and Tolstikov G.A.
Institute of Chemistry, Bashkirian Research Centre,
Ural Department, USSR Acad.Sci., Ufa 450054 U.S.S.R.

To improve the reactivity and selectivity of organoaluminium reagents in substitution of propargyl substrates the alumocopper reagents prepared from trialkylalane and CuBr have been taken. Thus, the reaction of 1-diethylamino-4-acetoxy-4-methyl-2-hexyn with $Et_3Al \cdot CuBr$ has been successful. This reaction fails under any different conditions.

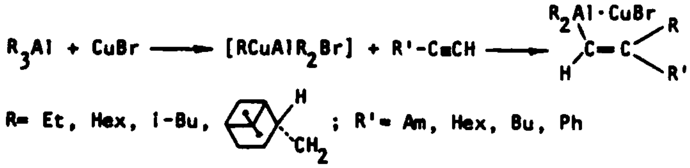


Yield,%(II)	T,°C	Catalyst
0	20	CuBr - 10%
89	20	CuBr -100%
70	60	CuBr - 10%
70	60	$FeCl_3$- 10%



The carbalumination of monosubstituted acetylenes with $R_3Al \cdot CuBr$ proceeds at a good rate to reveal its satisfactory regioselectivity with the ration of α- and β-aluminated products as 9:1.

The alkenyl organometallic compounds thus obtained can be further usefully applied to synthesis of allyl alcohols, ethers, sulfides, etc. [1].



Reference

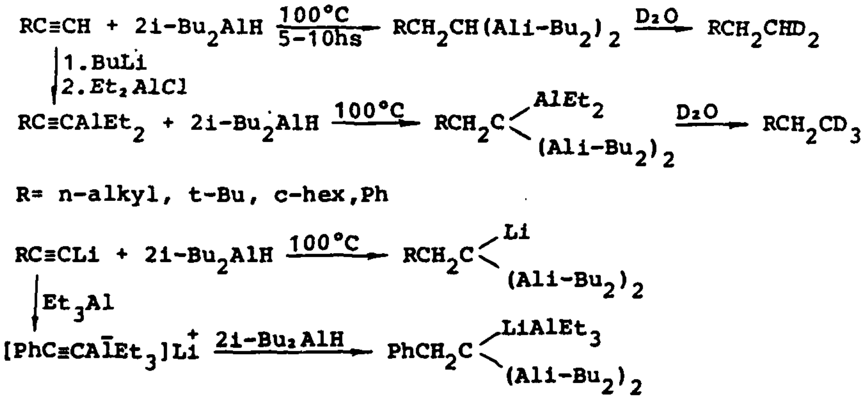
1. Kutchin A.V., Tolstikov G.A., and Andreeva N.I. Izv.AN SSSR Ser.Khim., 1987, 397.

THE DEVELOPMENT OF SYNTHETIC ROUTES TO AND SOME REACTIONS OF DI- AND TRIALUMINIUM OR ALUMOLITHIUM COMPOUNDS

Kutchin A.V., Markova S.A., Gorobets E.V., and Tolstikov G.A.

Institute of Chemistry, Bashkirian Research Centre,
Ural Department, USSR Acad.Sci., Ufa 450054 U.S.S.R.

Polyorganometallics have bee synthesized via double hydroalumination of terminal Al- and Li-acteylenes and acetylenides with diisobutylaluminium hydride. The reaction is over in 5-10hs at 100°C to reveal its high regioselectivity and complete conversion of substrates. The structures of the compounds obtained have been assigned by the deuterolysis and bromination products, the structures of which imply the geminal position of aluminium.



$$RC\equiv CH + 2i\text{-}Bu_2AlH \xrightarrow[5\text{-}10hs]{100°C} RCH_2CH(Ali\text{-}Bu_2)_2 \xrightarrow{D_2O} RCH_2CHD_2$$

$$\Big\downarrow \begin{matrix}1.BuLi\\2.Et_2AlCl\end{matrix}$$

$$RC\equiv CAlEt_2 + 2i\text{-}Bu_2AlH \xrightarrow{100°C} RCH_2C{<}\begin{matrix}AlEt_2\\(Ali\text{-}Bu_2)_2\end{matrix} \xrightarrow{D_2O} RCH_2CD_3$$

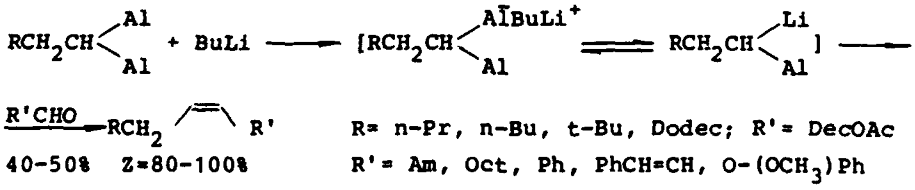
R= n-alkyl, t-Bu, c-hex,Ph

$$RC\equiv CLi + 2i\text{-}Bu_2AlH \xrightarrow{100°C} RCH_2C{<}\begin{matrix}Li\\(Ali\text{-}Bu_2)_2\end{matrix}$$

$$\Big\downarrow Et_3Al$$

$$[PhC\equiv C\bar{A}lEt_3]\overset{+}{Li} \xrightarrow{2i\text{-}Bu_2AlH} PhCH_2C{<}\begin{matrix}LiAlEt_3\\(Ali\text{-}Bu_2)_2\end{matrix}$$

Gem-dialumoalkanes treated with n-BuLi are capable of attaching to the aldehyde carbonyl group to form olefins. Some pheromones can be thus synthesized due to high stereoselectivity of the above reaction (the content of Z reaches 100%).



$$RCH_2CH{<}\begin{matrix}Al\\Al\end{matrix} + BuLi \longrightarrow [RCH_2CH{<}\begin{matrix}\bar{A}lBuLi^+\\Al\end{matrix} \rightleftharpoons RCH_2CH{<}\begin{matrix}Li\\Al\end{matrix}] \longrightarrow$$

$$\xrightarrow{R'CHO} RCH_2\diagup\!\!=\!\!\diagdown R'$$

40-50% Z=80-100%

R= n-Pr, n-Bu, t-Bu, Dodec; R'= DecOAc
R'= Am, Oct, Ph, PhCH=CH, O-(OCH$_3$)Ph

E28

ALUMINIUM-ORGANIC DERIVATIVES OF SOME FREE AND COORDINATED DIOXIMES

Nicolae Voiculescu, Diana Giurgiu, Anton Airinei, Mihaela
Spiratos, "P. Poni" Institute of Macromolecular Chemistry,
Aleea Grigore Ghica Vodă 41 A, R-6600, Iaşi, ROMANIA

Aluminium- organic compounds of dimethyl- and diphenylglyoxime were obtained from the reaction of $Ni(DMGH)_2$, $Pd(DMGH)_2$, $Ni(DPGH)_2$ and $Pd(DPGH)_2$ (DMGH and DPGH being divalent radicals of dimethylglyoxime and diphenylglyoxime, respectively) with $R_{3-n}AlCl_n$ derivatives ($R = -C_2H_5$, $i-C_4H_9$, $-C_5H_6$, $n = 1, 2$). The substitution of O-H...O bonds from the chelates by O-Al-O bridges determines the closing of some M-N-O-Al-O-N hexaatomic rings without carbon. The infrared absorption spectra evidenced the disappearing of the -OH absorption bands and the shift towards higher frequencies of the C=N and N-O absorption bands in dioximates, depending on the nature of the central metal ion, of the ligand and of the radical belonging to the aluminium atom.
Also, the complexes have been studied using thermogravimetrical method in order to obtain information concerning the thermal decomposition mechanism and the influence of the ligands on the thermal stability.

CARBORANYL DERIVATIVES OF III GROUP NONTRANSITION METALS

V.I.Bregadze, A.Ya.Usiatinsky, L.M.Golubinskaya,
V.A.Antonovich, N.N.Godovikov

A.N.Nesmeyanov Institute of Organo-Element Compounds, USSR
Academy of Sciences, Vavilov St. 28, Moscow B-334, USSR

Carboranyl derivatives of III Group nontransition metals were obtained by interaction of carboranyllithium compounds with III Group metal halides or organometallic compounds with metal-halogen bond:

$$RCB_{10}H_{10}CLi \quad + \quad MCl_3 \xrightarrow{L} (RCB_{10}H_{10}C)_2MCl\cdot L$$

M = Al, R = Ph, L = o-phen; M = Ga, R = Ph, L = Et_2O;
M = In, R = Ph, L = o-phen, THF; M = Tl, R = H, Ph, $ClCH_2$

$$PhCB_{10}H_{10}CLi \quad + \quad MeGaCl_2 \xrightarrow{Et_2O} (PhCB_{10}H_{10}C)_2GaMe\cdot OEt_2$$

The interaction of Al, Ga, In and Tl trialkyls with carboranes in the presence of TMEDA, HMPA or DME leads either to metalation of carborane cage at a carbon atom or to degradation of a carborane cage.

Thus, the interaction of trimethylgallium with o- and 1-phenyl-o-carborane in benzene in the presence of TMEDA results in formation of undecaborate containing gallium. According to ^{11}B NMR data, in this anion Me_2Ga fragment occupies the place of extra hydrogen over open face of carborane cluster.

The metallation of decachloro-o-carborane containing more acidic hydrogen of C-H bond than in unsubstituted carborane proceeds in the absence of TMEDA without degradation of carborane cage:

$$HCB_{10}Cl_{10}CH \quad + \quad Me_3M \xrightarrow{L} HCB_{10}Cl_{10}CMMe_2\cdot L_n \quad + \quad CH_4$$

M = Al, L = HMPA, n = 3; M = In, L = DME, n = 1

The interaction of o-carborane with $(i\text{-}Bu)_2AlH$ gives the mixture of carborane derivative with C-Al bond and products of carborane cage degradation.

230

Disilanyl Metal Complexes: Preparation and Reactions

W.Seelbach, G. Thum and W. Malisch
Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg, W.-Germany

The reaction of Si_2Cl_6 with various sodium metallates 1a-c in cyclohexane leads to the formation of the pentachlorodisilanyl metal complexes 2a-c.

$$\underset{\textbf{1a-c}}{Na[ML_n]} + Si_2Cl_6 \longrightarrow L_nM\text{-}Si_2Cl_5 + NaCl$$

2	ML_n
a	$Fe(CO)_2Cp$
b	$Mo(CO)_3Cp$
c	$W(CO)_3Cp$

2b,c show an unusual high tendency to decompose to the *trichlorosilyl complexes* $L_nM\text{-}SiCl_3$ *(3a-c)* via silylene elimination both in the solid state and in solution. 2a shows this behaviour under photochemical conditions or in the presence of a Lewis base (Me_3P, Me_3N, Et_3N).
Reaction of 2a with $LiAlH_4$ in Et_2O yields the pentahydridodisilanyl species 4, which in the presence of CCl_4 undergoes regiospecific chlorination of the α-silicon to generate the disilanyl species 5.

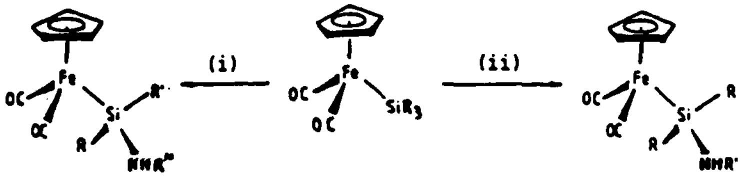
$$\underset{\textbf{2a}}{Cp(CO)_2Fe\text{-}Si_2Cl_5} \xrightarrow{(i)} \underset{\textbf{4}}{Cp(CO)_2Fe\text{-}Si_2H_5} \xrightarrow{(ii)} \underset{\textbf{5}}{Cp(CO)_2Fe\text{-}SiCl_2SiH_3}$$

(i) $LiAlH_4$ (ii) CCl_4

Bifunctional Ferrio-aminosilanes

U.Wachtler and W.Malisch
Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg, W.-Germany

The reaction of the ferrio-chlorosilanes $Cp(CO)_2Fe-SiR_xCl_{3-x}$ (R=H, Me, iPr, o-Tol) with primary amines $R'NH_2$ and the corresponding amides LiNHR'(R'=Me,tBu,Mes) results in formation of the ferrio-aminosilanes 2a-e, 3a, b having an iron bound bifunctional Si-N group. The thermal stability of 2a-e, 3a, b strongly depends on the nature of substituents both at the silicon and at the nitrogen.



2a - e 1a - f 3a - b

i: excess $R'NH_2$, ii: R'NHLi

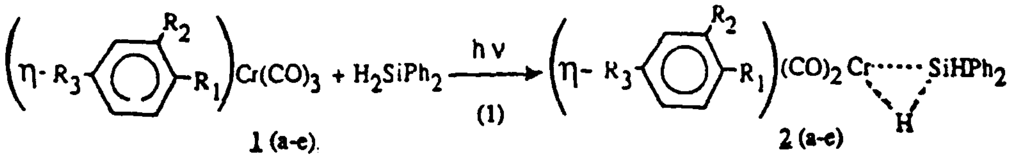
1: SiR_3 = $SiHCl_2$ (a), $SiMeCl_2$ (b), SiMe(H)Cl (c), Si(iPr)HCl (d), $Si(iPr)Cl_2$ (e), Si(o-Tol)HCl (f).
2: SiRR'(NHR'') = $SiH(NHtBu)_2$ (a), SiMeCl(NHtBu) (b), SiMe(H)NHtBu (c), Si(iPr)H(NHMe) (d), $Si(iPr)(NHMe)_2$ (e).
3: $SiR_2(NHR')$ = SiMe(H)NHMes (a), Si(o-Tol)H(NHMes) (b).

CO/R_3P-exchange reactions at the iron centre are presented, as well as ligand exchange experiments at the silicon, leading to useful precursors for the generation of silaimine complexes $Cp(L)_2Fe-Si(R)=NR'$.

Transition metal Hydrosilyl complexes, (η-arene)$(CO)_2Cr(H)SiHPh_2$ 2e/3c bond, Cr-H-Si. From Si-H to Si-O-Si.

Elisabeth MATARASSO-TCHIROUKHINE and Gérard JAOUEN
Ecole Nationale Supérieure de Chimie de Paris - U.A. 403
11, rue Pierre et Marie Curie - 75231 PARIS CEDEX 05

Diphenylsilane reacts photochemically on (η-arene)tricarbonylchrome complexes, 1 (a-e), to hydrosilyl derivatives, 2 (a-e), characterized by ^1H, ^{13}C and ^{29}Si nmr.



1 (a-e). 2 (a-e)

	$\|^2J(Si\text{-}Cr\text{-}H)\|$Hz
1a,2a $R_1 = R_2 = CH_3$; $H = R_3$	80 ± 0,5
1b,2b $R_1 = CH_2N(CH_3)_2$; $R_2 = R_3 = H$	79 ±2
1c,2c $R_1 = R_1 = R_2 = R_3 = H$	80 ±1
1d,2d $R_1 = COOCH_3$; $R_2 = R_3 = H$	81 ±1
1e,2e $R_1 = R_3 = COOCH_3$; $R_2 = H$	82,5 ±2

The high value of $|^2J(Si\text{-}Cr\text{-}H)|$, ≅80Hz, confirms the presence of 2 electron/3 center bond -(Cr-Si-H). $|^2J(Si\text{-}Cr\text{-}H)|$, $|^1J(Si\text{-}H)|$ and ^{29}Si are examined depending on Hammett's σ_{para}.

The hydrosilation (1) is accompanied by 1,1,3,3 tetraphenyldisiloxane formation. In the presence of 2 (a-e), it oligomerizes to polysiloxanes : $HSiPh_2(OSiPh_2)_nH$, n = 2-6 and $(Ph_2SiO)_n$, n = 3,4.

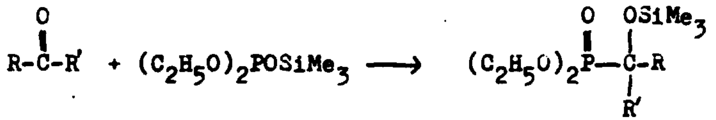
Studies On Synthesis Of Dialkyl α-Trimethylsilyloxyalkylphosphonates

Zhao Yong-Zhen and Li Zhong-Hua
Department of Chemistry, Hua Zhong Normal University, Wuhan,
Hubei, People's Republic of China

Using Dialkyl α-Trimethylsilyloxyalkylphosphonates as synthetic intermediates can prepare many acetones and α-hydroxyacetones both are with complex structures.

The report of research works concerning synthesis of contained phosphorus-silicon compounds is real small. The new method which we present adopt phosphorus-silicon reagents proceeding addition reaction with carbonyl compounds to prepare Dialkyl α-Trimethylsilyloxyalkylphosphonates, gaining 12 compounds successfully which have not reported yet from references. This method is better than the original, as it possesses simple operation of reaction, higher yield and other merit. All products have been conformed by IR and NMR spectrums. It contain two reactions:

$$(C_2H_5O)_2POH + Na \xrightarrow[\text{ether}]{Me_3SiCl} (C_2H_5O)_2POSiMe_3$$



$$R-\overset{O}{\overset{\|}{C}}-R' + (C_2H_5O)_2POSiMe_3 \longrightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}-\overset{OSiMe_3}{\overset{|}{\underset{R'}{\underset{|}{C}}}}-R$$

(R, R' = H, alkyl, aryl, substituted aryl)

This paper reports reaction conditions, and make a preliminary discussion about the factors of affecting reaction.

References:

(1) Koenigkramer R. E.,Zimmer H.,Tetrahadron Lett., 1017 (1980)
(2) Koenigkramer R. E.,Zimmer H., J.Org.Chem., 45, 3994 (1980)
(3) Birum G.H.,Richardson G.A., U.S.Patent, 3,113,139 (1963)
(4) Weker W.P., Silicon Reagents for Organic Synthesis, Berlin Heidelberg, New York, (1983)
(5) Mecombie S., J. Chem. Soc., 380 (1945)
(6) Bugerenko E.F., Chernyshev E.A., Izv Akad Nauk SSSR., Ser. Khim, 1391 (1966)
(7) Bugerenko E.F., Chernyshev E.A., Bull. Acad. Sci. USSR., 1334 (1966)

PREPARATION AND IR, ^{1}H, ^{13}C and ^{119}Sn NMR SPECTRAL STUDIES OF TRIORGANOTIN(IV) DERIVATIVES OF N-FORMYL-L-PHENYLALANINE AND N-FORMYL-L-PHENYLALANYLGLYCINE.

G.K.Sandhu, G.Kaur
Department of Chemistry, Guru Nanak Dev University,
Amritsar-143005, India

J.Holecek,
Department of General and Inorganic Chemistry,
University of Chemical Technology, 53210, Pardubice,
Czechoslovakia.

A.Lycka,
Research Institute of Organic Synthesis, 53218, Rybitui,
Pardubice, Czechoslovakia.

ABSTRACT

Preparation and structure elucidation studies of some diorganotin and triorganotin complexes of amino acids and dipeptides have already been reported (1-2). Complexes R_3SnX (R=Me, n-Pr, n-Bu, cyclohexyl, phenyl, X = anion of N-formyl-L-phenylalanine and N-formyl-L-phenylalanylglycine) have been prepared by reacting triorganotin(IV) chlorides with sodium salts of the N-formyl-L-phenylalanine and N-formyl-L-phenylalanylglycine or with the acids in the presence of triethylamine. All the complexes are weak polymers in the solid state with a unidentate carboxylate and a weak intermolecular donor-acceptor NHCC...$Sn(R_3)O$ bond. In non-coordinating solvents ($CHCl_3$, C_6H_6) all the complexes are monomeric and tetrahedral, in coordinating solvents (DMSO) coordination by one molecule of solvent occurs to form trans trigonal bipyramidal complexes as revealed by ^{1}H, ^{13}C and ^{119}Sn NMR studies.

References

1. G.K.Sandhu, G.Kaur, J.Holecek, A.Lycka, J.Organomet.Chem. 332, 75 (1987).
2. G.K.Sandhu, G.Kaur, J.Holecek, A.Lycka, J.Organomet.Chem., (In Press).

ORGANOTIN(IV) DERIVATIVES OF BIS(PYRAZOL-1-YL)ALKANES

F. BONATI, G. GIOIA LOBBIA, A. CINGOLANI, D. LEONESI, A. LORENZOTTI.
Dipartimento di Scienze Chimiche, Università degli Studi, 1 - 62032 CAMERINO (Italy)

The series of organotin(IV) derivatives R_aSnX_b (X = halogen: R = Me, Ph : a+b = 4) was used in order to investigate the donor properties of several bis(pyrazolyl) alkanes, $(pz)_2CR_2$: L_1 (R = H, pzH = pyrazole), L_2 (R = H, pzH = 3,5- dimethylpyrazole), L_3 (R = H, pzH = 4-nitropyrazole), L_4 (R = Me, pzH = pyrazole), and L_5 (R = H, pzH = 3,5-di-tert-butylpyrazole).

If a $\leq$ 2 in most cases, but L_3 and L_5, an 1:1 adduct was isolated and characterized. The behaviour in solution was studied by ^1H, ^{13}C, or ^{119}Sn nmr, by conductivity and by molecular weight determinations by osmometry.

While in solution (acetone or dimethylsulphoxide), the adducts of L_1 are non-electrolyte and dissociate into the starting components (1), complex equilibria are found in the isolated derivatives of the more basic (L_2) or more sterically demanding ligands (e.g. L_4).

The combined evidence suggest that in several cases e.g. when a = 3 and X = Cl , several species co-exist in the solution owing to solvation, ionization, and/or positional isomerism.

Work supported by CNR and Ministero P.I..

(1) - *G. Gioia Lobbia, A. Cingolani, D. Leonesi, A. Lorenzotti, F. Bonati, Inorg. Chim. Acta, 130 (1987) 203.*

SYNTHESIS OF ARYL COMPLEXES OF Rh(III), Tl(III) AND Sn(IV).

-Jose Vicente, Jose-Antonio Abad, Maria-Teresa Chicote, Juan-Francisco Gutierrez-Jugo, Carmen Ramirez de Arellano. Departamento de Quimica Inorganica, Universidad de Murcia, 30.071 Murcia, Spain.
-Peter G. Jones, Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, W. Germany.
-Giancarlo Pelizzi, Istituto di Chimica Generale ed Inorganica, Universita di Parma. 43100 Parma. Italy.

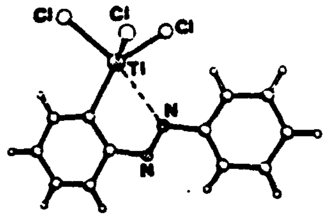
The following transmetallation reactions allow to prepare aryl complexes of:

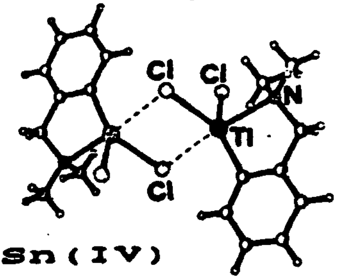
●●●●● Rh(III)

$$1/2\ [Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2 + [Hg(2\text{-}C_6H_4NO_2)_2] \longrightarrow [(\eta^5\text{-}C_5Me_5)Rh(2\text{-}C_6H_4N(O)O)Cl]\ (1)$$

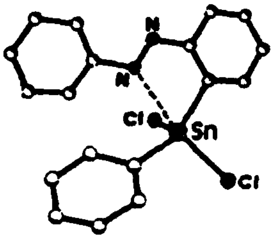
●●●●● Tl(III)

$$\begin{tikzcd}
{[Tl(2\text{-}C_6H_4N{=}NC_6H_5)Cl_3]^-\ (2)} \\
{[TlCl_5]^-} \arrow[u, "+\ 1/2\ {[Hg(2\text{-}C_6H_4N{=}NC_6H_5)_2]}"'] \arrow[d, "+\ 1/2\ {[Hg(2\text{-}C_6H_4CH_2NMe_2)_2]}"] \\
{[Tl(2\text{-}C_6H_4CH_2NMe_2)Cl_3]^-\ (3)} \arrow[d, "-\ NaCl", "+Na^+"'] \\
{[Tl(2\text{-}C_6H_4CH_2NMe_2)Cl_2]_2\ (4)}
\end{tikzcd}$$





●●●●● Sn(IV)



$$[Hg(2\text{-}C_6H_4N{=}NC_6H_5)_2] + [SnPhCl_3] \longrightarrow [Sn(2\text{-}C_6H_4N{=}NC_6H_5)(Ph)Cl_2]\ (5)$$

$$[HgPh_2] + [Sn(2\text{-}C_6H_4N{=}NC_6H_5)Cl_3] \longrightarrow (5)$$

Reactions with neutral and anionic ligands of complexes (1)-(5) are described.

ELUCIDATION OF THE GEOMETRY AND CONFIGURATION OF ORGANOTIN (IV) COMPLEXES OF SCHIFF BASES OF AMINO ACIDS

A.K. Varshney
Department of Chemistry,
University of Rajasthan,
JAIPUR-302004 (India)

The present paper is a report on the synthesis, characterization and geometrical features of penta-coordinated dibutyl tin (IV) complexes of Schiff bases derived by the condensation of Amino acids viz. Glycine β-alanine and Anthranilic acid with 2-Hydroxy-1-naphthaldehyde and Benzoin. The conductance measurements in DMF show ,these complexes to be non-electrolytes and the molecular weight determinations indicate their monomeric nature.

On the basis of UV, IR, NMR (^{1}H, ^{13}C & ^{119}Sn), Mössbauer spectra along with the mass spectral fragmentation pattern trigonal bipyramidal geometry is proposed. The nitrogen atom probably occupies the axial site, while the remaining two oxygen atoms and the dibutyl groups rest in an equatorial plane.

Synthesis and characterization of organotin(IV) complexes of thiohydrazides and thiohydrazone

N.K.Singh and Usha Sharma, Department of Chemistry, Banaras Hindu University, Varanasi - 221 005, India

Complexes of 2-furanthiocarboxyhydrazide (Hfth), 4-hydroxyphenylthiocarboxyhydrazide (Hoth) and salicylaldehyde-2-furanthiocarboxyhydrazone (H_2L) have been prepared by the reactions of Bu_2SnO and Ph_2SnCl_2 taken in appropriate molar ratio and refluxing the reaction mixture for several hours in non-aqueous media; sodium was used in the preparation of deprotonated complexes. The resulting complexes have been characterized on the basis of elemental analysis, molar conductance, melting point and various physicochemical techniques. The complexes have been found to melt between 64 to 210 C, the corresponding dibutyl tin(IV) complexes have lower melting points than the diphenyl tin(IV) complexes. IR coupled with ^{1}H and ^{13}C NMR spectra suggest bonding through thione/thiol sulphur and amino nitrogen. ^{119}Sn spectra of some compounds have also been studied in order to get the structural information.

SYNTHESIS OF ORGANOTIN DERIVATIVES OF BIOLOGICAL INTEREST

Valerian Drăguţan and Ileana Drăguţan

Center of Organic Chemistry, 202B Spl. Independenţei,
R-78100 Bucharest, Romania

Several organotin derivatives of biological interest have been synthesized starting from diorganotin dihalides (e.g. dimethyl-, dibutyl- and diphenyltindichloride) or diorganotin-oxides (e.g. dibutyltinoxide) and carboxylic acids and hydroxy-carboxylic acids or their salts. The structure of these compounds has been examined by IR, NMR and mass spectrometry. The possibilities of using the prepared compounds as antitumor agents are discussed in comparison with known organotin antitumor agents /1-4/.

1. M. Gielen, in "Tin as a Vital Nutrient: Implications in Cancer Prophylaxis and Other Physiological Processes", N. F. Cardarelli (Ed), CRC Press, Inc., Boca Raton, Florida, p. 169.

2. F. Huber and R. Barbieri, ibid., p. 175.

3. M. Gielen, R. Willem, T. Mancillia, J. Ramharter and E. Joosen, Silicon, Germanium, Tin and Lead Compounds, IX, 349 (1986).

4. A. Saxena, Appl. Organomet. Chem., 1, 39 (1987).

DEPENDENCE BETWEEN STRUCTURE AND ELECTRONIC TRANSITIONS IN $GePh_3$- AND $SnPh_3$-TERMINATED POLYSILANES

Martin Dräger and Manfred Mathes
Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg-Universität, Becher-Weg 24, D-6500 Mainz, Germany

In the last decade the photochemical behaviour of organosilicon polymers gained industrial interest [1]. The σ-bonded Si_n chains are thermally very stable and show strong UV absorption in the range 300-350 nm. Related Sn_n chains show even stronger electronic absorption extending to the visible range [2], their thermal stability is much lower however. To combine both properties, electronic absorption at longer wavelength and thermal stability, we synthesized some model oligomers. These compounds form two series of linear Polysilanes

$$Ph_3Sn-(SiPh_2)_n-SnPh_3 \quad \text{and} \quad Ph_3Ge-(SiPh_2)_n-GePh_3$$
$$n = 1 \text{ to } 5$$

produced in good yields by coupling of the corresponding dichloro polysilanes with stannyl- and germyllithium reagents in thf at -75 °C.

As found by X-ray structure determinations, all chain conformations are antiperiplanar. The values of the electronic absorption maxima and the NMR chemical shifts and couplings for ^{29}Si and ^{119}Sn are strong dependent on chain length and slightly dependent upon bond lengths and angles (distance ranges Si-Si 235-241, Ge-Si 242-243 and Sn-Si 259-260 pm).

1 R. West, J. Organomet. Chem., 300 (1986) 327.
2 S. Adams and M. Dräger, Angew. Chem. Int. Ed. Engl., 26 (1987) 1255.

PREPARATION AND SPECTROSCOPIC STUDIES OF DI-ISO-PROPYLTIN DICHLORIDE AND ITS ADDUCTS WITH SOME N-DONORS.

G.C.Saxena,
Department of Chemistry, R.3.S.College,
AGRA-282 002 (INDIA)

and

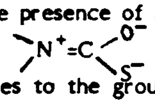
K.L.Gupta and P.Srivastava,
Department of Chemistry, S.D.College,
Ambala Cantt.-133 001 (INDIA)

Di-iso-propyltin dichloride has been prepared by the redistribution reaction method in good yield and characterised by elemental analysis, molecular weight determination, ^{1}H NMR, IR and mass spectroscopically. X-ray data of the above compound is well in agreement with the tetragonal symmetry to give the lattice constants $a = 12.9751$ Å, $C = 15.7359$ Å and cell volume $V = 2649.1894$ Å^3. It has been found to form 1:2 (acid/base) adducts with unidentate ligands viz triethylamine, quinoline, β-naphthylamine and O-tolidine and 1:1 adduct with 2,2'-bipyridyl. Their molar conductance values show that they are week electrolytes in nitrobenzene while their molecular weight determinations indicate that they exist as monomers with small dissociation. Their IR in the range 4000-200cm^{-1} and ^{1}H NMR have also been studied.

242

STRUCTURAL FEATURES OF TIN(IV) PYRROLYLTHIOCARBAMATES

Vishnu D. Gupta, The Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005, India.

With a view to understand the factors influencing the coordination number, the geometry of the coordination, the coordination polyhedron and the isomer formed, crystal and molecular structures of the complete series of tin(IV) pyrrolylthiocarbamates, Ph_3SnL, Me_2SnL_2, $PhSnL_3$ and SnL_4 (with tin:ligand ratio 1 to 4) have been examined. While the coordination environment around tin varies from Ph_3SnL to SnL_4 complex, the nature of the coordination of monothiocarbamate ligand smoothly changes from simple sulfur-bonded to typical bidentate mode. The Sn-S bond distances are comparably similar. However, it is Sn-O interaction which becomes prominent with the gradual incorporation of the ligand around the tin centre. The presence of aromatic pyrrole system destabilizes the double bonded canonical form ( $>N^+=C(O^-)(S^-)$) of the ligand. It is the mercaptide form which predominantly contributes to the ground state electronic structure of pyrrolylthiocarbamate in these complexes. Spectroscopic evidence particularly multinuclear NMR data suggests little structural changes in the solution.

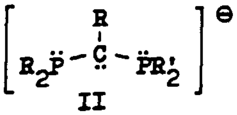
PHOSPHINOMETHANIDE LIGANDS IN MAIN GROUP ELEMENT COMPLEXES: UNUSUAL BONDING, COORDINATION NUMBERS AND OXIDATION STATES

Hans H. Karsch, B. Deubelly, K. Zellner, G. Müller
Anorganisch-chemisches Institut, Technische Universität München,
Lichtenbergstr. 4, D-8046 Garching, F.R.G.

Monophosphinomethanides I and Diphosphinomethanides II

$[R_2\ddot{C}-\ddot{P}R'_2]^{\ominus}$

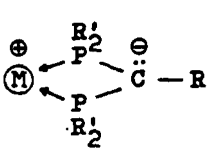
I



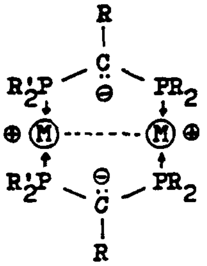
$\left[R_2\ddot{P}-\underset{\cdot\cdot}{\overset{R}{C}}-\ddot{P}R'_2\right]^{\ominus}$

II

are ambidentate ligands exhibiting unusual properties and unusual bonding modes. Particularly interesting are diphosphinomethanides II,



III

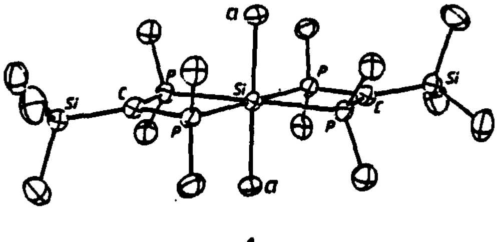


IV

which on coordination to main group element acceptors stabilize high phosphine coordination numbers and/or low oxidation states due to the betaine-type character of these complexes. Examples are given, inter alia, for hexacoordinated silicon (e.g. 1) and for low valent germanium complexes (e.g. 2).

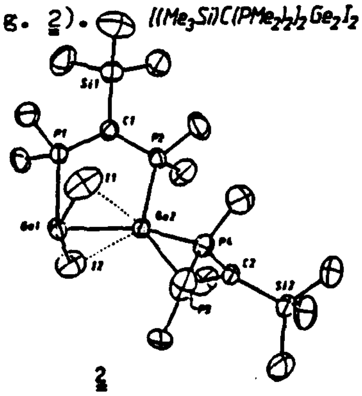
$[(Me_3Si)(Me_2P)_2C]_2MCl_2$

(M = Si, Ge, Sn)



1

$[(Me_3Si)C(PMe_2)_2]_2Ge_2I_2$



2

244

REACTION OF TRIBUTYLTIN HYDRIDE WITH CHLORINATED ESTERS

Jouko Vihanto, Department of Chemistry, University of Turku, SF-20500 Turku, Finland

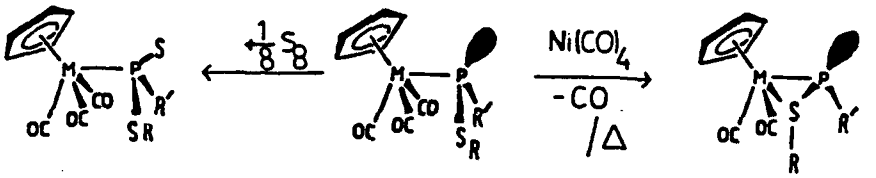
The reaction of tributyltin hydride with esters have been shown to yield mainly corresponding hydrocarbons and stannyl esters.[1] This reaction requires quite drastic conditions, so it is possible to reduce some functional groups in an ester before the ester function. Thus, it is possible to reduce cleanly halogens (except F) in the ester provided that there are not α halogens in both acyl and alkyl group of the ester. α Halogens give rise to the break of the carbon-oxygen bond and subsequent reactions.

1. Khoe, L. E. and Lee, H. H. Tetrahedron Lett. No.41 (1968) 4351

Complexes with a Thioalkyl-Bridged M-P-Bond from Metallo-(alkylthio)phosphanes

Sandro Amann and Wolfgang Malisch
Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg, W.-Germany

Metallation of alkylthio(chloro)phosphanes ClP(R')S-R (R = iPr, tBu; R' = tBu, StBu) with Na[M(CO)$_3$Cp] (M=Cr, Mo, W) yields the metallo-(alkylthio)chloro-, metallo-bis(alkylthio)-, metallo-(alkylthio)-alkyl-posphanes (1a-f) or the bismetallo-(alkylthio)phosphane (3g) respectively. Metallo-(alkylthio)thiophosphoranes (2a-c) are obtained from 1a-c via oxidation with elementary sulfur.



2a-c 1a-f 3a-d

2	a	b	c
R	iPr	tBu	tBu
R'	Cl	Cl	StBu
M	W	W	W

1	a	b	c	d	e	f	g
R	iPr	tBu	tBu	tBu	tBu	tBu	tBu
R'	Cl	Cl	StBu	StBu	StBu	tBu	Cp(CO)$_3$W
M	W	W	Cr	Mo	W	W	W

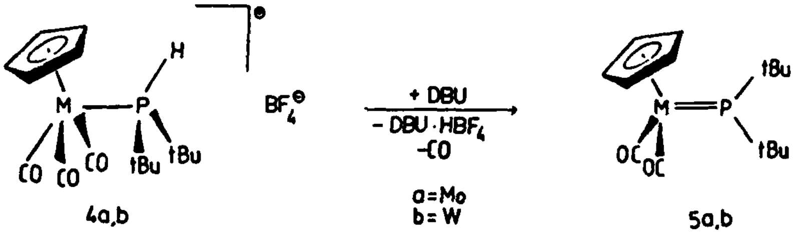
3	a	b	c	d
R	tBu	tBu	tBu	tBu
R'	tBu	StBu	StBu	Cp(CO)$_3$W
M	W	Mo	W	W

Due to the bulkiness of the P-bonded non metal ligands the metallo-(alkylthio)phosphanes 1d-g can be easily decarbonylated to the corresponding metallacyclopropanes (3a-d) either thermally or via reaction with Ni(CO)$_4$. 3a-d can be described as S-donor stabilized metal to phosphorus double bonded species. The combination of a thioalkyl ligand with a bulky amino group causes preference of the M=P-Isomer. This fact is demonstrated by the existence of Cp(CO)$_2$W=P(TMPip)S-iPr obtained from Cp(CO)$_2$W=P(TMPip)Cl and NaS-iPr.

THE METAL PHOSPHORUS DOUBLE BONDED COMPLEX $Cp(CO)_2M{=}P^tBu_2$: NOVEL SYNTHESIS AND REACTIONS WITH TRANSITION METAL HALIDES.

Wolfgang Reich, Angelika Meyer, Klaus Jörg and Wolfgang Malisch
Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, Federal Republic of Germany.

The successive reaction of the metalhydrides $Cp(CO)_3M{-}H$ (1a,b) with $[Ph_3C]BF_4$ (2) and $^tBu_2PH$ (3) leads to the cationic complexes 4a,b, which can be deprotonated by DBU to give the metal phosphorus double bonded species 5a,b .1)



(1)

(1) represents a novel, in comparison to the dehydrohalogenation and decarbonylation route 2) more versatile procedure for the generation of phosphorus metal double bonded complexes.

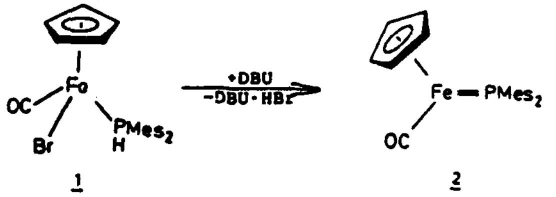
The reactivity of the M=P-complexes will be demonstrated by the addition of Te, CuCl, AgCl, AuCl(PPh_3) and $HgCl_2$ to the W=P bond of 5b. The structures of the Te- or the AuCl(PPh_3)-adduct respectively will be presented.

1) K. Jörg, W. Malisch, W. Reich, A. Meyer u. U. Schubert, Angew. Chem. 98, 103, (1986), Angew. Chem. Int. Ed. Engl. 25, 92 (1986).
2) W. Malisch, K. Jörg, E. Groß, M. Schmeußer u. A. Meyer, Phosphorus and Sulfur, 1986, 26,25.

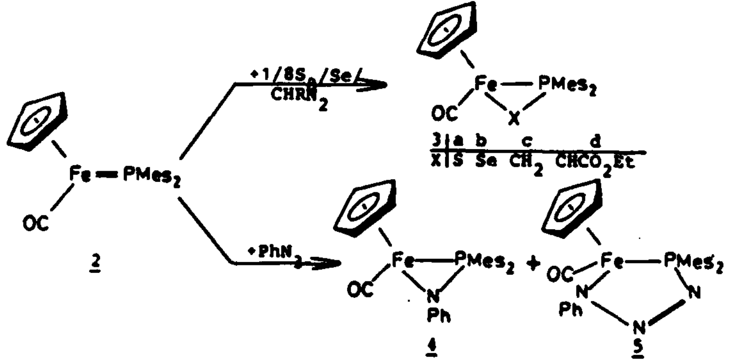
SYNTHESIS AND REACTIVITY OF THE IRON-PHOSPHORUS DOUPLE BONDED SPECIES $Cp(CO)Fe{=}PMes_2$

M.Märkl and W.Malisch
Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg, W.-Germany

Treatment of 1, obtained via irridiation of $Cp(CO)_2FeBr$ with Mes_2PH, with DBU yields the phosphorous iron double bonded species 2.



2 shows high activity towards nucleophiles and electrophiles. Reaction with sulfur, selenium or diazoalkanes leads to the formation of the metallocyclopropanes 3a-d. With phenylazide a mixture of the three and five membered ring species 4 and 5 is obtained.



The reaction of 2 with isonitriles, CS_2, dienes and acetylenes will be reported.

ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY OF ACYCLIC DITERTIARY PHOSHPINES AND ARSINES

László Zanathy, László Szepes, Eötvös Loránd University, General and Inorganic Chemistry Department, Múzeum krt. 6-8, 1088 Budapest Hungary

Yuri V. Chizhov, Physics Institute, Leningrad University 198904 Leningrad, Petrodvoretz, USSR

The He(I) photoelectron spectra of $Ph_2X\text{-}(CH_2)_n\text{-}YPh_2$ compounds (X, Y = P or As, n = 1 or 2) - frequently used as complexing ligands in transition metal chemistry - have been recorded and interpreted. The gaseous phase molecular geometries are not available the only experimental data are provided by the NMR studies of $Ph_2PCH_2PPh_2$ (1).

The low energy part of the spectra are very similar to each others. The maximum of the first weak band in the region of 7.75 and 8.15 eV refers to the ionization of heteroatom lone pair. The second, more intense, band system showing maximum at about 9 eV can be assigned to the ionization of the benzene π-system. The third less intense band at about 10.35-10.85 eV originates from the ionization of X(and/or Y)-C σ-skeleton. The interpretation of the spectra is in good agreement with the ultraviolet photoelectron spectroscopy studies of their tungsten complexes (2) and that of related molecules (3).

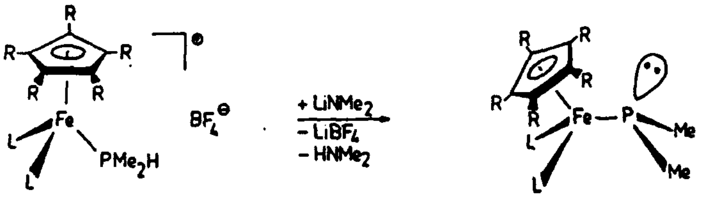
According to our results there is no sizeable interaction between heteroatom lone pairs, furthermore π/π and n/π interactions are similar to those measured in Ph_3X(or Y).

1) I.J. Colquhoun and W. McFarlane
J. Chem. Soc. Dalton Trans. 1982 1915
2) G.M. Bancroft, L. Dignard-Bailey and R. Puddephatt
Inorg. Chem. 25 (1986) 3675
3) G. Distefano, S. Pignataro, L. Szepes and J. Borossay
J. Organomet. Chem. 102 (1975) 313

Ferrio-dimethylphosphanes

Elisabeth Kaifer and Wolfgang Malisch
Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg, W.-Germany

Stable metallo-dimethylphosphanes are available via the deprotonation of the PH-functional cationic iron salts $[(C_5R_5)(L)_2(HMe_2P)Fe]BF_4$ (R = H, Me; L = CO, HMe_2P, Me_3P) (1a-d).
While $[Cp(CO)_2(HMe_2P)Fe]BF_4$ (1a) yields the dinuclear ferrio-phosphan 2a, the analogoues reaction of 1b-d leads to the monomeric phosphido complexes 2b-d, as a consequence of the stabilizing effect of the electron releasing C_5Me_5 unit or the phosphane ligands respectively. The mechanism for the formation of 2a involves the intermediate formation of the metallo-phosphane "$Cp(CO)_2Fe-PMe_2$".



1	a	b	c	d
R	H	Me	H	H
L	CO	CO	HMe_2P	Me_3P

2	a	b	c	d
R	H	Me	H	H
L	CO/$Cp(CO)_2FePMe_2$	CO	HMe_2P	Me_3P

2a-d show pronounced reactivity at the phosphido phosphorus towards diverse electrophilic reagents (HCl, MeI, AgCl etc.), a behaviour, which is characteristic for metallo-phosphanes 1a-c).
The reactions of 2a,b with some transition metal complexes [$Cp(CO)_3MX$ (M = Mo, W; X = H, Cl, Me); $[Cp(CO)_3Fe]BF_4$; $Pt(PPh_3)_2(C_2H_4)$ etc.] will be reported.

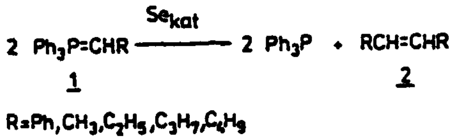
1a) R. Maisch, E. Ott, W. Buchner and W. Malisch, J. Organomet. Chem. 286 (1985) C 31. - b) W. Angerer, W.S. Sheldrick and W. Malisch, Chem. Ber. 118 (1985) 1261. - c) W. Malisch, W. Angerer, A.H. Cowley and N.C. Norman, J. Chem. Soc., Chem. Commun., 1985, 1811.

250

Selenoketones and -aldehydes by Reaction of Phosphorus Ylides with Elemental Selenium

Regina Hock, Gerhard Erker
Institut für Organische Chemie der Universität Würzburg
Am Hubland, 8700 Würzburg (BRD)

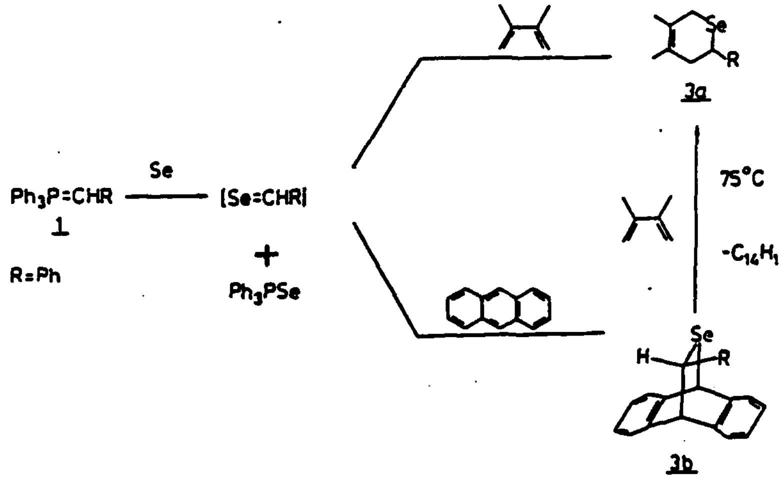
The reaction of alkylidenetriphenylphosphoranes 1 with catalytic amounts of elemental selenium yields the olefins 2 and triphenylphosphin. A mechanism similar to the Wittig olefination reaction is proposed, involving selenoaldehyde intermediate.



$$\underset{\textstyle 1}{2\ Ph_3P{=}CHR} \xrightarrow{Se_{kat}} 2\ Ph_3P + \underset{\textstyle 2}{RCH{=}CHR}$$

$R{=}Ph, CH_3, C_2H_5, C_3H_7, C_4H_9$

From the reaction of $Ph_3P{=}CHPh$ 1a with two equivalents of selenium in the presence of conjugated dienes, the Diels-Alder products 3 of the seleno-aldehyde intermediate were obtained [1].



From the stoichiometric reaction of $Ph_3P{=}Ph_2$ 1f with Se selenobenzophenon was isolated as a brightly green coloured solid. At ambient temperature it forms the Diels-Alder adducts with various conjugated olefins.

1) G.Erker, R.Hock, R.Nolte. J.Am.Chem.Soc.110 (1988), 624

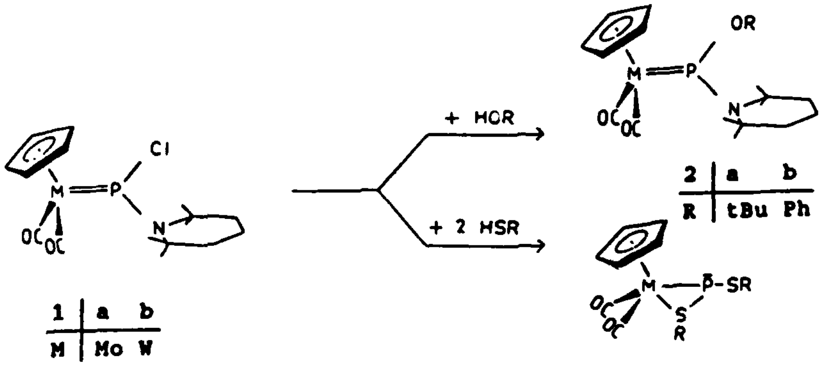
FUNCTIONAL METAL PHOSPHORUS DOUBLE BOND COMPLEXES $Cp(CO)_2M{=}P(NR_2)$ (M = Mo, W): EXCHANGE REACTIONS AT THE PHOSPHORUS

U.-A. Hirth und W. Malisch, Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, FRG

Metallation of the aminodichlorophosphane R_2NPCl_2 (R_2N = 2.2.6.6.-tetramethylpiperidine) with $Na[M(CO)_3Cp]$ (M = Mo, W) yields the metallo-aminochlorophosphanes $Cp(CO)_3M$-$P(NR_2)Cl$, which can be easily converted to the corresponding metal phosphorus double bond complexes 1a,b via decarbonylation.

The reactions of 1b with tert.-butanole and diverse phenols in presence of Et_3N leads to the formation of the alkoxy-derivates 2a,b.

With mercaptanes substitution of both the chlorine and the aminoligand is observed to give the threemembered heterocycles 3a-c, in which an organylthio ligand is bridging the metal phosphorus bond.



1	a	b
M	Mo	W

2	a	b
R	tBu	Ph

3	a	b	c
R	iPr	tBu	Ph

Futher experiments to exchange the P-bonded chlorine atom against diverse nucleophiles will be presented.

ORGANOANTIMONY COMPOUNDS AS FLAME RETARDANTS FOR POLYPROPYLENE.

A.C. Mishra[a], P. Bajaj[b] and N.K. Jha[a]

a Department of Chemistry, I.I.T., New Delhi-110016, INDIA

b Department of Textile Technology.

Antimony oxide in conjunction with organohalogen compounds is known to have good flame retardant property for many organic polymers including polypropylene. Triphenyl stibine can also serve in place of antimony trioxide. As an alternative of a mixture of antimony compound and an organic halogen compound we have synthesized and characterised a new series of antimony halogen based flame retardants in the form of halogen derivatives of organoantimony (V) compounds e.g. triphenylstibine dibromide and triphenyl antimony (V) derivatives of tribromo-, trichloro-and pentachlorophenols. The performance of these compounds as flame retardants for polypropylene has been evaluated by measuring limiting oxygen index, vertical flame test and smoke density of the flame retardant-polypropylene systems. The LOI of polypropylene was raised from 18 to approximately 30 in the flame retardant loaded polypropylene systems. Triphenyl stibine dibromide proved to be the most effective flame retardant among all the organoantimony (V) compounds tested. The effect of loading on the processability and mechanical properties of the flame retardant loaded propylene systems has also been evaluated and is reported.

Formation of Decamethyl-bis-Cyclopentadiene by Reductive Elimination: A General Feature in Main Group Element Chemistry?

J.Lorberth, Th.F.Berlitz, S.H. Shin, U.Müller and H.Sinning,

Fachbereich Chemie, Philipps-University, Hans-Meerwein-Strasse,
D-3550 Marburg/Lahn, West Germany.

Tris-cyclopentadienyls of the heavier elements in group 13, viz. $InCp_3$ have an unusual structure [1] or are not known at all for Tl, where only Tl(I) compounds exist [2]. Tetracoordinate cyclopentadienyls of group 14 have regular tetrahedral structures and tris-cyclopentadienyls of group 15 are trigonal pyramidal shaped molecules in the case of Antimony [3] and believed to be isomorphous for Arsenic and Bismuth.

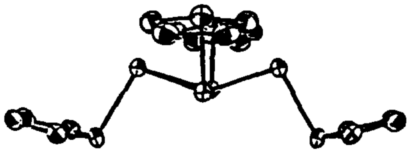
Reaction of Antimony and Bismuth trihalides with the potassium salt of pentamethylcyclopentadiene (abbrev.: Pcp) yielded metal-metal-bonded main group element clusters with the elimination of decamethyl-bis-cyclopentadiene, a molecule first observed in organotin chemistry [4]:

$$MCl_3 + 3\ KPcp \xrightarrow[-78^oC]{Et_2O} 3\ KCl + 1/n\ (M\text{-}Pcp)_n + Pcp_2$$

M = Sb,Bi: n = 4

M = In : n = 6

M = Tl : n = ?



The hexameric Indium compound $[InPcp]_6$ was already described in the literature [5] by the reaction

$$InCl + LiPcp \text{ -----> } LiCl + 1/6\ (InPcp)_6$$

We report on the structures of $(SbPcp)_4$, $(BiPcp)_4$, $Tl(Pcp)_?$ and the elusive decamethyl-bis-cyclopentadiene, $C_{20}H_{30}$, obtained by reductive elimination from $MPcp_3$ and consecutive C-C-bond formation; a radical reaction pathway is substantiated by EPR spectroscopy.

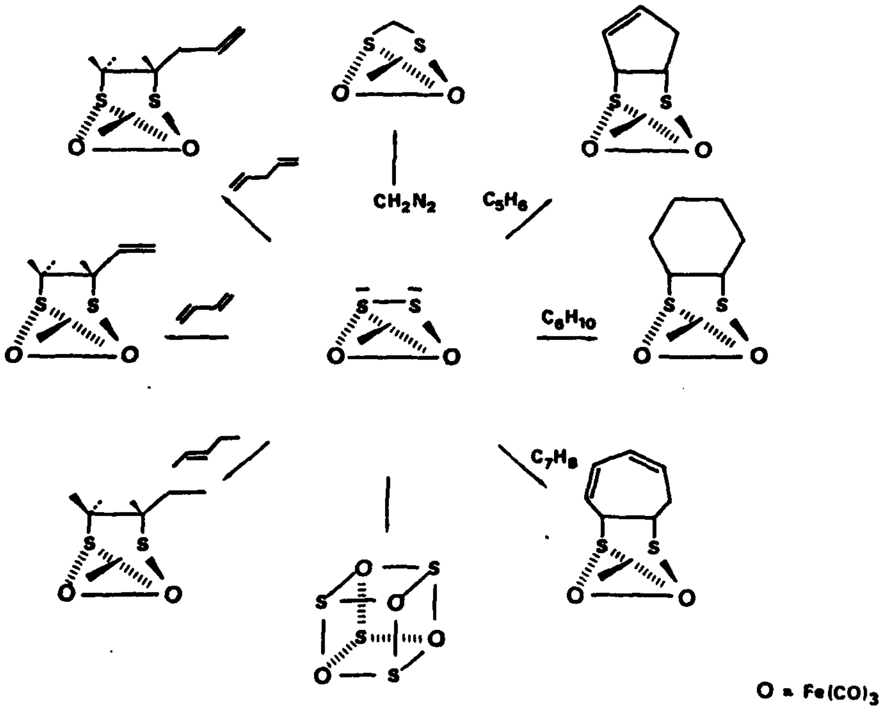
Reactions of $(SbPcp)_4$ and $(BiPcp)_4$ with BF_3 and other reagents are reported.

[1] F.W.B.Einstein, M.M.Gilbert and D.G.Tuck, Inorg.Chem., 11 (1972) 2832.
[2] H.Schumann, C.Janiak, J.Pickardt and U.Börner, Angew.Chem., 99 (1987) 788.
[3] M.Birkhahn, P.Krommes, W.Massa and J.Lorberth, J.Organomet. Chem., 208 (1981) 161.
[4] P.Jutzi and F.Kohl, J.Organomet.Chem., 164 (1979) 141.
[5] O.T.Beachley,Jr., M.R.Churchill, J.C.Fettinger, J.C.Pazik and L.Victoriano, J.Amer.Chem.Soc., 108 (1986) 4666.

PHOTOINDUCED CYCLOADDITION OF ALKENES, ALKINES AND DIENES WITH THE S–S-BOND OF $[Fe(CO)_3S]_2$

Ingo-Peter Lorenz and Anja Kramer
Institute for Inorganic Chemistry, University of Tübingen,
Auf der Morgenstelle 18, D-7400 Tübingen (FRG)

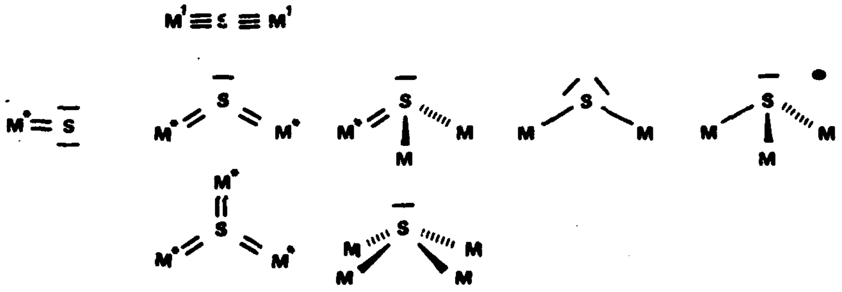
Organic and organomatallic disulfides show a very similar reactivity; Seyferth et al. have proved this for reduction reactions of the disulfido cluster $[(CO)_3FeS]_2$ (1) into the corresponding dithiolate dianion $[(CO)_3FeS]_2^{2-}$, which is a very useful synthon. Now, we succeeded in the photoinduced insertion reactions of alkenes, alkines and dienes into the S–S-bond of 1, to obtain the corresponding 1,2-dithiolato complexes by 2+2-cycloadditions. Carbon monoxide and diazomethane are inserted by the carbon atom to give the bridging dithiocarbonato or methanedithiolato ligand, respectively. In one case the dithiolato ligand can be oxidized to the corresponding mixed sulfenatothiolato ligand:



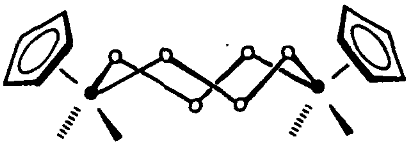
NEUTRAL AND CATIONIC ORGANOMETALLIC SULFUR COMPLEXES

Ingo-Peter Lorenz, Guido Effinger and Andrea Spiesberger
Institute for Inorganic Chemistry, University of Tübingen
Auf der Morgenstelle 18, D-7400 Tübingen (FRG)

Organometallic sulfur complexes and clusters play an important role as models for the active sites of redox enzymes and for the dehydrosulfurization catalysis. Sulfur demonstrates a great structural variety in metal-sulfur bonding (single, double and triple bonds) depending on the number of electrons of the organometallic complex fragment. Thus, sulfur can act as 2, 4 or 6 electron donor prefering bridging positions (μ_2-μ_4-S):



Starting from the new sulfur sources thiirane, C_2H_4S, or bis(trimethylsilyl)sulfane, $S(SiMe_3)_2$, and suitable organometallic compounds, we succeeded in the syntheses of examples of some of the bonding systems introduced above, which are the isolobal analogues of sulfur dioxide, sulfanes, sulfoxides and sulfonium cations; a very interesting compound is obtained by the reaction of $[Cp(CO)_2Mn]_2S$ with S_8:



INVESTIGATIONS OF HYPERVALENT TELLURIUM COMPOUNDS IN THE SOLID STATE AND IN SOLUTION

Dainis Dakternieks[A], Robert Di Giacomo[B], Robert W. Gable[B] and Bernard F. Hoskins[B]

[A] Division of Chemical and Physical Sciences, Deakin University, Geelong, Victoria 3217, Australia.

[B] Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.

Multinuclear magnetic resonance techniques and X-ray crystallography were used to investigate a series of organoyltellurium(IV) complexes in solution and in the solid state respectively. The X-ray crystal structures of the compounds $C_8H_8Te(Etxan)_2$, $C_8H_8Te(Etdtp)_2$, $C_8H_8Te(Etdtc)_2$ and $C_8H_8Te(I)(Etdtc)$ (where Etxan = S_2COEt; Etdtp = $S_2P(OEt)_2$; Etdtc = S_2CNEt_2 and C_8H_8 = o-xylene -α,α'-diyl) show that the tellurium atom is either seven or eight coordinate, with an active lone electron pair occupying an effective coordinate site in each case.

Carbon-13, ^{31}P and ^{125}Te NMR date indicate that intramolecular *mono*dentate-bidentate dithiolate exchange becomes slow on the NMR time scale at low temperature and the structures inferred in solution approximate those observed directly in the solid state. Conformational isomers are observed in solutions of mixed-ligand complexes of the type $C_8H_8Te(^iPrdtc)(Etdtp)$ and the distribution of these isomers is solvent dependent.

The complexes $Ph_2Te(S\text{-}S)_2$ (where S-S = xanthate, dithiohosphate, dithiocarbamate) are not as stable as their $C_8H_8Te(S\text{-}S)_2$ analogues. NMR data indicate that in solution, these complexes rapidly disproportionate to Ph_2Te and the corresponding disulphide. Low temperature NMR studies of the dithiocarbamate complexes are in accord with a seven coordinate geometry about the tellurium atom, consistent with the structure determined in the solid state by X-ray crystallography.

NEW CATIONIC ALKYLBIS(CYCLOPENTADIENYL)TITANIUM COMPLEXES BY ONE-ELECTRON OXIDATION OF Ti(III) ALKYLS

Manfred Bochmann and Andrew J. Jaggar, School of Chemical Sciences,
University of East Anglia, Norwich NR4 7TJ, U.K.

Cationic alkylbis(cyclopentadienyl)titanium complexes, $[Cp_2TiR(L)]^+$, are currently being discussed as intermediates in olefin polymerisation reactions based on Cp_2TiCl_2 / AlR_2Cl systems. While the synthesis of these complexes via substitution of Cl^- by L in $Cp_2Ti(R)Cl$ is restricted to L being a good electron donor[1], the one-electron oxidation of $Cp_2'TiR$ ($Cp' = C_5H_5$, C_5Me_5) with Ag^+ provides a generally applicable route. Complexes with labile L (e.g. L = THF) have now been obtained.

$$Cp_2'Ti\text{-}R \quad + \quad AgBPh_4 \quad \xrightarrow{L} \quad [Cp_2'TiR(L)]^+BPh_4^- \quad + \quad Ag^0$$

The cationic complexes react readily with CO, isocyanides and nitriles. The structure of $[(C_5Me_5)_2TiMe(THF)]BPh_4$ has been determined by X-ray diffraction[2].

(1) M. Bochmann and L.M. Wilson, J. Chem. Soc., Chem. Commun. 1986, 1610; M. Bochmann, L.M. Wilson, M.B. Hursthouse and R.L. Short, Organometallics 1987, <u>6</u>, 2556.

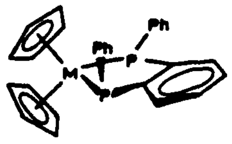
(2) M.B. Hursthouse and M. Motevalli, to be published.

258

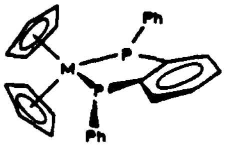
METALLOCENE o-PHENYLENEBIS(PHENYLPHOSPHANATO) CHELATES OF EARLY TRANSITION METALS

Hartmut Köpf and Verena Richtering, Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, Germany

o-Phenylenebis(phenylphosphane), o-$(PhHP)_2C_6H_4$, was deprotonated and was introduced as a dianionic, bidentate chelate ligand $[o\text{-}(PhP)_2C_6H_4]^{2-}$ into the bent metallocene systems of early transition metals of subgroups IV or VI. Thus, the dilithium salt o-$(LiPhP)_2C_6H_4$ reacted with equivalent amounts of metallocene dichlorides, Cp_2MCl_2 ($Cp = \eta^5\text{-}C_5H_5$), to give the new five-membered chelate complexes $Cp_2M(PPh)_2C_6H_4$-o (M = Ti, 1, green; Zr, 2, orange; Hf, 3, red; Mo, 4, brown; W, 5, ochre-yellow). Compounds 1-3 could be prepared more conveniently by reacting o-$(PhHP)_2C_6H_4$ with equimoler amounts of the dimethylmetallocenes Cp_2MMe_2 (M = Ti, Zr, Hf). The $^{31}P\{^1H\}$-NMR-spectra of 1-5 each showed two singlets of different intensity due to the existence of trans (predominant) and cis isomers of the metallacycles in solution at room temperature.



cis-Isomer



trans-Isomer

IONIC TITANOCENE COMPLEXES:
A NEW TYPE OF ANTITUMOR CYCLOPENTADIENYL METAL COMPOUNDS

Petra Köpf-Maier, Institut für Anatomie, Freie Universität Berlin,
Königin-Luise-Straße 15, D-1000 Berlin 33, Germany

Thomas Klapötke and Hartmut Köpf, Institut für Anorganische und
Analytische Chemie, Technische Universität Berlin, Straße des
17. Juni 135, D-1000 Berlin 12, Germany

Bis(η^5-cyclopentadienyl)titanium(IV) ("titanocene") diacido complexes $(C_5H_5)_2TiX_2$ have proven to exhibit antitumor activity against diverse animal and human tumors. These compounds are neutral complexes containing two acido ligands X which are covalently bound to the central metal titanium. They are soluble in water to an only limited extent, thus requiring the addition of a solubilizer to the aqueous injection fluid when administered in higher dose levels.

In the present study, we investigated a new type of bis- and mono-(η^5-cyclopentadienyl)titanium(IV) complexes and report now upon antitumor properties of some ionic titanocene complexes, mainly represented by the acetonitrile complex $[(C_5H_5)_2TiCl(NCCH_3)]^+[FeCl_4]^-$ (I), the 2,2'-bipyridyl derivative $[(C_5H_5)_2Ti(bipy)]^{2+}[CF_3SO_3]_2$ (II), the N-methyl-o-aminothiophenolate complex $\{(C_5H_5)_2Ti[o\text{-}S(NHCH_3)C_6H_4]\}^+I^-$ (III) and the five-coordinate bis(dithiolene) chelate $[(C_5H_5)Ti(1,2,4\text{-}S_2C_6H_3CH_3)_2]^-[N(C_2H_5)_4]^+$ (IV).

I-III were tested against fluid Ehrlich ascites tumor growing in the peritoneal cavity of mice and effected optimum cure rates ranging between 70 and 100 % and therapeutic indices between 1.5 and 1.9. These values are similar to those caused by neutral titanocene dihalides and related compounds. As ionic titanocene complexes are distinguished by improved water solubility due to their salt-like character, they are obviously superior to neutral titanocene complexes with respect to biological application.

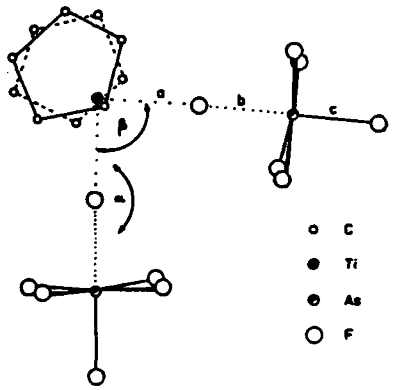
METALLOCENE CHEMISTRY OF HIGHLY FLUORINATED LIGAND SYSTEMS: TITANIUM(IV) CYCLOPENTADIENYL HEXAFLUOROPNICTOGENATES *

Thomas Klapötke, Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, FRG.

Ulf Thewalt, Sektion für Röntgen- und Elektronenbeugung der Universität Ulm, Oberer Eselsberg, D-7900 Ulm, FRG.

Transition metal halides have been reported to possess Lewis base qualities and it has been assumed that the metal-halide bond is not broken in the complexes formed. Adduct formation between Cp_2TiF_2 and Lewis acids has been investigated. However, for a long time Lewis acid adducts of the type $Cp_2Ti(LF)_2$ (L = BF_3, PF_5) were known to be unstable and not existent in the solid state.

In the present study, we investigated the reaction behaviour of Cp_2TiF_2 toward the very powerful F^- acceptors AsF_5 and SbF_5. The novel titanocene derivatives $Cp_2Ti(AsF_6)_2$, $Cp_2Ti(SbF_6)_2$, and $Cp_2Ti(Sb_2F_{11})_2$ have been prepared and were characterized by chemical analysis, IR, mass, and ^1H NMR spectroscopy. More convenient these complexes are easily available by salt elimination reaction in SO_2 from the corresponding silver hexafluoropnictogenates. Whereas these thermodynamically unstable titanocene compounds are kinetically stabilized the mono(cyclopentadienyl) species are kinetically unstable and decompose even at -50°C. Reaction behaviour and mechanism of the decomposition reactions are discussed. Like the IR the single crystal X-ray structure of $Cp_2Ti(AsF_6)_2$ shows a distorted AsF_6 unit with fluorine co-ordinated (linear) to both, Ti and As:



---

* Organo transition metal chemistry of highly fluorinated ligand systems (Organo-Übergangsmetall-Chemie hochfluorierter Ligand-Systeme): 5th communication.

Cyclopentadienyl(2,2-bipyridyl) complexes of titanium, zirconium, niobium

O.N.Suvorova, V.V.Kutyryova, N.B.Patrikeeva, G.A.Domrachev
Institute of Chemistry, Academy of Sciences of USSR, Gorky

The aim of this work is the investigation of thermal decomposition of the cyclopentadienyl(2,2-bipyridyl) titanium, zirconium, niobium complexes and formation of the films of inorganic materials in conditions of gas-phase precipitation.

The starting compounds CpTi(bipy), Cp_2Zr(bipy), Cp_2Nb(bipy) have been prepared by the reaction of Li_2(bipy) with Cp_2MCl_2.

All complexes are crystal substances of deep-blue or black colour, extreme easily reacting with oxygen of air, therefore all operations with them have been carried out in atmosphere of argon and in vacuum. Spectral characteristics of this compounds have been obtained.

The thermographic investigations of thermal decomposition of all studied compounds are carried out. The volume of evolved gaseous products of decomposition was fixed simaltaneously with the registration of DTA curves. The thermal decomposition of homoleptic bipyridyl complexes $Ti(bipy)_3$ and $Nb(bipy)_3$, dicyclopentadienyl compounds Cp_2MCl_2 and mixed cyclopentadienylchelate compounds such as $CpMCh_2Cl$, ChM(bipy) have been investigated for comparison of reaction directions and conditions.

The influence of the structure of initial compounds on composition and structure of inorganic materials films, on conditions of their formation and properties has been shown.

Some ferrocenyl chelate complexes of transition metals of the type of Fc_2MCh, Fc_2M(bipy) have been prepared in this work.

η^1- VERSUS η^2-COORDINATION IN PHOSPHINOMETHYL ZIRCONIUM COMPLEXES

Hans H. Karsch, B. Deubelly, G. Müller
Anorganisch-chemisches Institut, Technische Universität München,
Lichtenbergstr. 4, D-8046 Garching, F.R.G.

Due to the ambidentate nature of phosphinomethanides I,

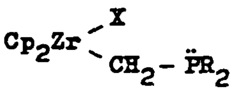
$[R_2\ddot{C}-\ddot{P}R'_2]^-$

I

(Ⓜ : d^1-d^8)

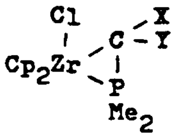
II

unsaturated metal complexes form three membered rings II in most cases.



X = Cl, CH_3, CH_2PR_2; R = Me, Ph

III



X = H; Y = $SiMe_3$, PMe_2;
X = Y = $SiMe_3$

IV

Computational studies predict η^2-coordination also for the d^0-complex $Cp_2Zr(Cl)CH_2PH_2$[1], but all (real) complexes III of this type, studied so far, exhibit η^1-coordination[2].
According to our structural findings on lithium derivatives of I, P-coordination of I is supported by silyl or phosphino substituents at the carbanion (R = $SiMe_3$, PMe_2). In fact, complexes IV exhibit η^2-coordination in the solid state. Hence, comparing III and IV, the coordination number of zirconium increases on enhancing the size of the ligand. Preparation, structures and properties of these and related compounds are discussed.

---

1) Hofmann, P.; Stauffert, P.; Shore, N.E. Chem. Ber. 1982, **115**, 2153.

2) Karsch, H.H.; Müller, G.; Krüger, C. J. Organomet. Chem. 1984, 273, 195. - Young, S.J.; Olmstead, M.M.; Knudsen, M.J.; Shore, N.E. Organometallics 1985, **4**, 1432.

Arene derivatives of zirconium(II)

Fausto Calderazzo, Guido Pampaloni and Piersandro Pallavicini, Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Via Risorgimento 35, I-56100 Pisa, Italy.

The chemistry of low-valent Group 4 transition elements (oxidation state less than III) is still largely unexplored, especially when the non-cyclopentadienyl organometallic derivatives of these elements are concerned [1]. In the framework of our studies on the synthesis and properties of low-valent early transition metal derivatives [2], we have found that the reaction of the tetrahalides of zirconium(IV), ZrX_4, with Al/AlX_3 in arene as solvent proceeds according to equation (1) and the products were isolated and/or characterized spectroscopically.

$$3\,ZrX_4 + 4\,AlX_3 + 6\,Al \xrightarrow[X = Cl,\,Br]{\text{arene}} 3\,(\eta^6\text{-arene})Zr(AlX_4)_2 \cdot n\,\text{arene} \qquad (1)$$

A new preparation of the zirconium and hafnium tetrabromide and tetraiodide was found by reacting $M(BH_4)_4$ and anhydrous HX in n-heptane as solvent, according to equation (2):

$$MCl_4 + LiBH_4 \longrightarrow M(BH_4)_4 \longrightarrow MX_4 \qquad (2)$$

Work is in progress in order to extend these reactions to hafnium and to study the reactivity of such systems towards CO, CO_2, olefins, alkynes.

Financial support from ENICHEM ANIC, Milano, is gratefully acknowledged.

---

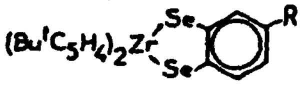
[1] M. Bottrill, P.D. Gravens and J. McMeeking in "Comprehensive Organometallic Chemistry", G. Wilkinson, F.G.A. Stone and E.W. Abel, Eds., Pergamon Press, Oxford, 3, 281 (1982); D.J. Cardin, M.F. Lappert and C.L. Raston, Chemistry of Organo-Zirconium and Organo-Hafnium Compounds, Ellis Horwood, 1986.

[2] P. Biagini, F. Calderazzo, G. Pampaloni and P.F. Zanazzi, Gazz. Chim. Ital., 117, 27 (1987); P. Biagini, F. Calderazzo and G. Pampaloni, J. Chem. Soc., Chem. Commun, 1015 (1987).

NEW SYNTHETICAL APPLICATIONS OF DISELENOPHENYLENE ZIRCONOCENES

Philippe Meunier, Bernard Gautheron, Jacques Bodiguel and Pascale Tavarès
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS
(UA 33), Faculté des Sciences, 6 bd *Gabriel 21000 Dijon (France)*

Recently we have shown that electrophiles ECl and ECl_2 react easily with diselenophenylene zirconocene (I) leading to various diseleno aromatic compounds (II,III) (1,2).



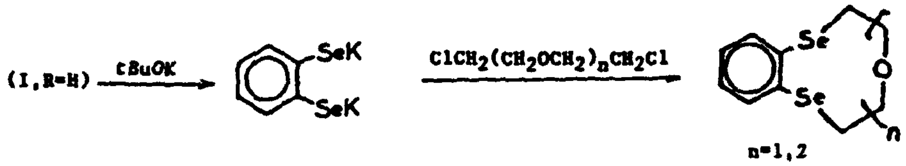
(*I*)

(II)

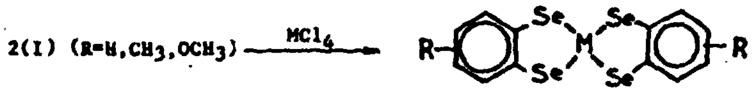
(III)

We are presently reporting new applications of complex I.

1) *Synthesis of first* Se-containing crown ethers



2) Formation of new silicon, germanium and tin spiro derivatives



M = Si, Ge, Sn

All compounds were characterized by ^1H NMR and mass spectrometry.

References

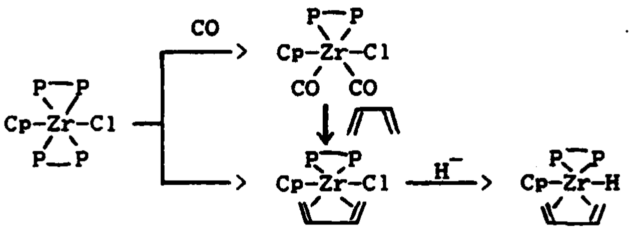
1. P. Meunier, B. Gautheron and A. Mazouz, J. Chem. Soc., Chem. Comm., 1986, 424.
2. P. Meunier, B. Gautheron and A. Mazouz, Phosphorous and Sulfur, 1987, 33, 33.

Low-valent monocyclopentadienyl zirconium chemistry: synthesis, structure and reactivity.

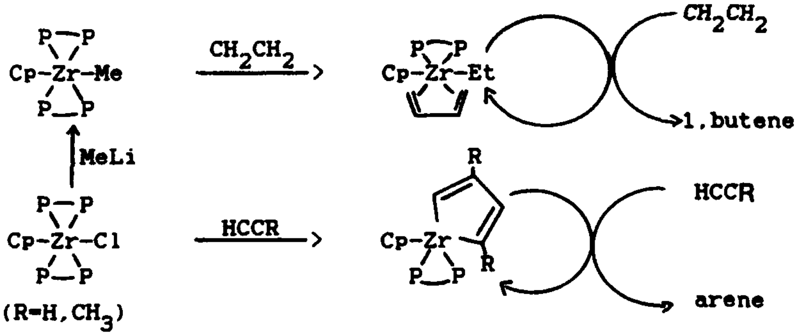
Sandro Gambarotta, Ytsen Wielstra. Laboratorium voor Anorganische Chemie, . Rijksuniversiteit Groningen, Nijenborgh 16 9747AG Groningen, The Netherlands

Michael Y. Chiang, Chemistry Department, Columbia University, New York, N.Y.10027, USA

Apart from the bis(cyclopentadienyl) systems, very little is known in the chemistry of low-valent zirconium (1). We found that CpZr(dmpe)$_2$Cl (2) is a versatile synthetic tool to enter this chemistry. Mild condition reaction with unsaturated substrates in fact, allowed the easy substitution of one phosphine ligand and the preparation of new compounds including halocarbonyls and diene derivatives. The structures of all the complexes have been demonstrated by X-ray analysis



Chlorine replacement has been achieved by reaction with MeLi forming the first low-valent zirconium-alkyl. Preliminary results on the reactivity of these species with light olefins and acetylenes displayed some interesting catalytic features.



For example, reaction of CpZr(dmpe)$_2$Me with 3 equivalents of ethylene led to the formation of CpZr(dmpe)(diene)Et which selectively catalyzed the dimerization of ethylene to 1-butene. Catalytic cyclotrimerization has been obtained instead with propyne and acetylene. The catalytic species have been fully characterized including by X-ray analysis.

References:
1) Lappert,M.F. Chemistry of organo zirconium and hafnium compounds Ellis Horwood 1984
2) Gambarotta,S.; Chiang,M.Y. J.Chem.Soc.Chem.Comm.1987,698

Synthesis and structural studies of mono- and bis-(n^5-cyclopentadienyl)hafnium(IV) derivatives of heterocyclic thioketones

O.P.Pandey, Organometallic Research Laboratory, Department of Chemistry, University of Gorakhpur, Gorakhpur273009, India

The reactions of dichlorobis(n^5-cyclopentadienyl)hafnium(IV) with four different classes of heterocyclic thioketones viz., 3-substituted-4-amino-s-triazole-5-thiol, 1-substituted-2-thiohydantoin, 5-substituted 1,3,4-oxadiazole-2-thione and 1-substituted tetrazoline-5-thione were studied in anhydrous tetrahydrofuran in the presence of base. The reaction products were characterized on the basis of elemental analyses, electrical conductance, magnetic susceptibility and spectral(electronic, infrared and ^{1}Hn.m.r.) data.

^1H AND ^{13}C NMR SPECTRAL STUDIES ON ORGANO-RHODIUM(I) COMPLEXES CONTAINING NITROGEN HETEROCYCLES.

Y.S. RAMASWAMY, N.M.N. GOWDA* & G.K.N. REDDY
Department of Chemistry, Central College,
Bangalore University, Bangalore-560 001, India.

ABSTRACT

The chlorobridged binuclear complex, $[Rh\,Cl\,(DCPD)]_2^1$ containing the tricyclic diolefin, *endo*-dicyclopentadiene (DCPD) reacts with exobidentate nitrogen heterocycles (N-N) in acetone to yield (N-N)- bridged complexes of the type [(DCPD)(Cl)Rh(N-N) Rh(Cl)(DCPD)], where N-N is 4,4' bipyridyl, pyrazine or *trans*- 1, 2 - Bis (4-Pyridyl) ethylene. The chlorobridged binuclear complex also reacts with 2-substituted benzimidazole derivatives (R-BztH; R = H, Me, Et, n-Pr) to produce polynuclear complexes $[Rh\,(DCPD)(R\text{-}Bzt)]_n$. Several of these complexes have been investigated by ^1H and ^{13}C nmr spectra, in addition to physico-chemical measurements. In the case of DCPD and $Rh_2Cl_2\,(DCPD)_2$, the pmr spectral assignments have been further corroborated by 2-D and 1-D difference NOE (Nuclear Overhauser Effect) nmr spectral studies

REFERENCE

[1] J. Chatt and L.M. Venanzi J. Chem. Soc. (1957) 4735-40.

- o -

4-FLUOROTHIOPHENOLATE DERIVATIVES OF RHODIUM

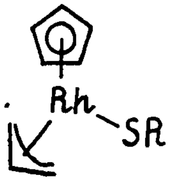
Z.L.Lutsenko, E.M.Rokhlina, A.S.Peregudov, A.Z.Rubezhov,
D.N.Kravtsov

A.N.Nesmeyanov Institute of Organoelement Compounds, U.S.S.R.
Academy of Sciences, 28 Vavilov Str., Moscow 117813, U.S.S.R.

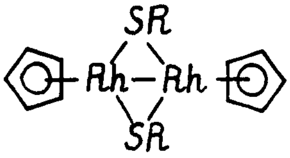
With the exception of rhodanides, no metal-sulphur bonded π-All-π-Cp and π-All-π-Arene complexes of Rh and Ru appear to be known. In view of the studies on relative polarity and reactivity of transition metal-sulphur bonds, the corresponding thiophenolates are of interest. In this connection, interaction of π-C_3H_5-π-C_5H_5RhCl (I) and π-C_3H_5-π-C_6H_6RuCl (II) with 4-fluorothiophenol and its derivatives has been examined.

Reaction of I with 4-FC_6H_4SH in the presence of excess triethylamine leads to a mixture of complexes III, IV and V:

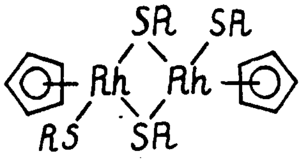
$R = C_6H_4F$



III



IV



V

The structures of products obtained were based on ^1H, ^{19}F NMR and mass-spectroscopic data.

Under the same conditions, II does not react with 4-FC_6H_4SH. All attempts to obtain π-C_3H_5-π-$C_6H_6RuSC_6H_4F$ by reactions of II with 4-FC_6H_4SM (M=Na,Ag) or 4-FC_6H_4SH in the presence of $AgBF_4$ met with little success.

STABLE PARAMAGNETIC PLATINUM GROUP METAL HYDRIDES: SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND BEHAVIOR IN SOLUTION OF THE COMPLEX $Rh(IV)(H)_2(Cl)_2(P\text{-}\underline{i}\text{-}Pr_3)_2$, 1.

P. MURA and A. Segre, Istituto di Strutturistica Chimica "G. Giacomello", Area della Ricerca di Roma, C.N.R., 00016 Monterotondo Stazione - Roma - Italy.

D. Attanasio, Istituo di Teoria e Struttura e Comportamento Spettrochimico dei Composti di Coordinazione, Area della Ricerca di Roma - C.N.R. - 00016 Monterotondo Stazione - Roma - Italy.

Recently we reported the synthesis, x-ray crystal structure and behavior in solution of the first two examples of stable paramagnetic platinum group metal hydrides: the complexes $Ir(IV)(H)_2(Cl)_2(P\text{-}\underline{i}\text{-}Pr_3)_2$ and $Ir(IV)(H)_2(Cl)_2(PCy_3)_2$[1-3]. Considering the stability of these compounds we thought that rhodium, like iridium, should give stable paramagnetic hydrides. Indeed we have synthesized the stable paramagnetic complex $Rh(IV)(H)_2(Cl)_2(P\text{-}\underline{i}\text{-}Pr_3)_2$, 1, which shows to be isomorphous with the iridium compound[1].

Paramagnetic rhodium (IV) complexes are very rare, the only well-defined species are the two cesium salts Cs_2RhCl_6 and Cs_2RhF_6. To our knowledge, compound 1 is the first example of a stable paramagnetic hydride of rhodium (IV).

In this work we present synthesis, x-ray crystal structure, magnetic proporties both in the solid state and in solution, and NMR in solution of compound 1.

1) P. Mura J. Am. Chem. Soc. 1986, 108, 351-352.

2) P. Mura and A. Segre Angew. Chemie, 1986, 25, 460-462.

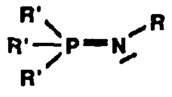
3) P. Mura, A. Segre and S. Sostero, submitted to J. Am. Chem. Soc.

270

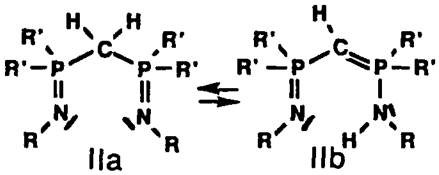
The coordination and organometallic chemistry of bis(iminophosphoranyl)methane with rhodium complexes.

Pieter Imhoff, Cornelis J.Elsevier, Kees Vrieze;
Laboratory of Inorganic Chemistry, University of Amsterdam,
Nieuwe Achtergracht 166, 1018WV Amsterdam.

The organometallic and coordination chemistry of dienes containing several hetero atoms continues to be of interest. One of our current research items comprises a study of the coordination and reactivity of phosphinimides (I) and bis(iminophosphoranyl)methane (IIa) with d^8 transition metal complexes.



I



IIa IIb

Bis(iminophosphoranyl)methane may, in analogy to bis(methylenephosphoranyl)methane (1), exist as 2 isomers (IIa and IIb). However isomer IIa appears to be the groundstate in solution as well as in the solid state.
When bis(N-p-tolyl-imino-P,P-diphenylphosphoranyl)methane (*IIa, R=p-tolyl, R'=Ph*) is reacted with Rh(I) compounds two different coordination complexes are formed: i.e. N-N and N-C coordination to Rh (X-Ray) occurs. These coordination modes can be regarded as the Rh stabilized forms of IIa and IIb respectively (R=p-tolyl, R'=Ph).
The coordination and organometallic chemistry of bis(iminophosphoranyl)-methane with Rh(I) and the reactivity of the Rh complexes towards small molecules will be discussed.

1. R.Appel, G.Haubrich, F.Knoch; Chem.Ber. 117(1984)2063

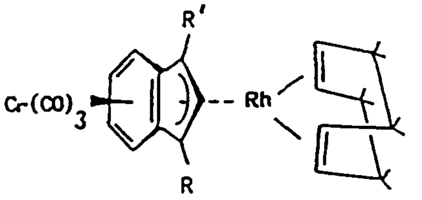
SYNTHESIS, STRUCTURE AND CHEMICAL PROPERTIES OF SOME η^6-TRICARBONYLCHROMIUM-η^3-(CYCLOOCTADIENE)RHODIUM INDENYLS.

Alberto Ceccon, Alessandro Gambaro, Saverio Santi
Dipartimento di Chimica Fisica dell'Università, Via Loredan,
2 - 35131 PADOVA (Italy)

Alfonso Venzo
Centro Studi Stati Molecolari, Radicalici, Eccitati del CNR,
Via Loredan, 2 - 35131 PADOVA (Italy)

Transition metal indenyl complexes often exhibit higher reactivity than the iso-structural cyclopentadienyl derivatives. Usually, indenyl ligand is bonded to the metal via the C_5-ring and, unlike the cyclopentadienyl analog, it may undergo a facile bonding tranformation from a penta-hapto to a tri-hapto coordinative mode.[1]

We have prepared some indene bimetallic complexes by quenching the appropriate η^6-$Cr(CO)_3$-indenyl anion with $(RhClCOD)_2$ (COD ≡ 1,5-cyclooctadiene):



I R = H R' = H
II R = H R' = CH_3
III R = CH_3 R' = CH_3
IV R = H R' = C_6H_5
V R = C_6H_5 R' = C_6H_5

Structural assignements based on X-ray and NMR spectra of the compounds will be presented.

The activity of these bimetallic species as catalysts will be compared with that of the parent (η^5-indenyl)-Rh-COD complex.

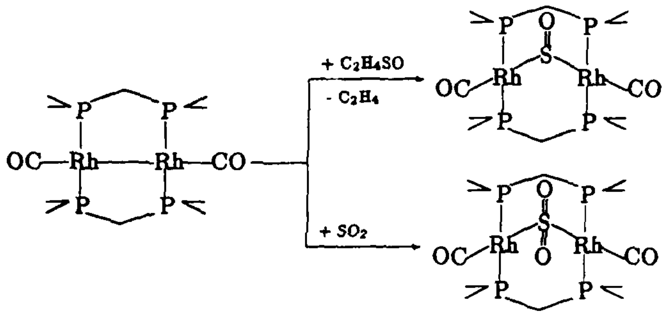
[1] J.M.O'Connor, C.P.Casey, Chem. Rev., 87 (1987) 307.

NEW SULFUR MONOXIDE AND SULFUR DIOXIDE COMPLEXES OF RHODIUM AND PLATINUM

Ingo-Peter Lorenz and Armin Neher

Universität Tübingen, Institut für Anorganische Chemie,
Auf der Morgenstelle 18, D-7400 Tübingen, Germany

The reaction of thiirane S-oxide with the dimeric [Rh(CO)(μ-dppm)]$_2$ [dppm=bis(diphenylphosphino)methane] results in the new SO-complex [Rh$_2$(μ-SO)(CO)$_2$(μ-dppm)$_2$] **1** with A-frame type structure and a *bridging* SO-group as 3c2e-system. The analogous reaction with SO$_2$ yields the new sulfur dioxide complex [Rh$_2$(μ-SO$_2$)(CO)$_2$(μ-dppm)$_2$] **2** of the same type, eq 1 and 2:



1 (1)

2 (2)

These A-frame complexes have been characterized by $^{31}P\{^1H\}$ NMR, IR and mass-spectroscopy (FAB). The AA'BB'XX'- and AA'A''A'''XX'-$^{31}P\{^1H\}$ NMR spectra of **1** and **2**, respectively, were resolved by 2D-COSY-NMR experiments and simulation.

Reaction of the dimeric platinum complex [PtCl(μ-dppm)]$_2$ with thiirane S-oxide results in the SO$_2$-A-frame complex. This reaction shows, that if 'SO', generated from thiirane S-oxide, can't be stabilized in the coordination sphere of a metal complex, it will decompose into sulfur and sulfur dioxide.

A monomer sulfur monoxide complex with terminal SO-group has been prepared by the reaction of thiirane S-oxide with [Rhdppm$_2$]PF$_6$, eq 3.

$$[\mathrm{Rhdppm_2}]\mathrm{PF_6} + \mathrm{C_2H_4SO} \longrightarrow [\mathrm{Rhdppm_2(SO)}]\mathrm{PF_6}\ \mathbf{3} + \mathrm{C_2H_4} \quad (3)$$

3 has been characterized by $^{31}P\{^1H\}$ NMR, IR and mass-spectroscopy (FAB), too.

INTRAMOLECULAR 1,2-HAPTOTROPIC SHIFT IN SQUARE-PLANAR COMPLEXES OF NICKEL (II) WITH PYRIDAZINE.

María-José Bermejo, and Jordi Vinaixa, Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, 08028-Barcelona, Spain.

The square-planar complexes $[Ni(pdz)R(PR'_3)_2]^+$ (pdz= pyridazine; $(PR'_3)_2$= 1,2-bis(diphenylphosphino)ethane, R= C_6Cl_5, C_6F_5, 2,3-$C_6H_3Cl_2$; PR'_3= PEt_3, R= C_6Cl_5) have been prepared by the reaction of $[Ni(acetone)R(PR'_3)_2]^+$,prepared "in situ" from $[NiXR(PR'_3)_2]$ (X= Cl, or Br) and $AgClO_4$, with the amine.
The variable temperature ^1H NMR studies of these complexes have shown that at low temperature they are monomers with the pdz ligand bound through only one nitrogen atom, and that at high temperature they are fluxional species in which there is a rapid exchange of the site of nickel coordination between the two nitrogen atoms of the monodentate pyridazine. The mechanism for this 1,2-haptotropic shift is, apparently, intramolecular. The energy barrier for this exchange has been found to depend on the trans effect of the ligand trans to the amine. In the presence of free pdz another exchange process between free and coordinated ligand has been observed for the less sterically crowded complexes (R= C_6F_5, and 2,3-$C_6H_3Cl_2$), the process ocurring at temperatures higher than those of the 1,2-haptotropic shift.

NEW HYDROXO-BRIDGED COMPLEXES OF THE NICKEL GROUP ELEMENTS

Gregorio López, Gabriel García, José Ruiz, Gregorio Sánchez, Joaquín García and Juan J. Ponti

Departamento de Química Inorgánica, Universidadde Murcia, Santo Cristo 1, 30001-Murcia, Spain

Hydroxo-complexes of the later transition metals are of interest because their potential reactivity promises extensive utility in organic and organometallic synthesis. Although some hydroxo-complexes of the nickel group elements have been described in the literature,[1-4] we have found that binuclear anionic complexes of the type $[(C_6F_5)_2M(\mu\text{-}OH)_2M(C_6F_5)_2]^{2-}$ (M = Ni, Pd) can be prepared by reaction of cis-$M(C_6F_5)_2(PhCN)_2$ with $(NBu_4)OH$. Addition of HX to the di-μ-hydroxo-metallate(II) leads to the formation of the complexes $[(C_6F_5)_2M(\mu\text{-}OH)(\mu\text{-}X)M(C_6F_5)_2]^{2-}$ and $[(C_6F_5)_2M(\mu\text{-}X)_2M(C_6F_5)_2]^{2-}$, X being anionic groups such as pyrazolate exobidentate ligands. Preliminary results indicate that platinum may exhibit a similar behaviour.

The new compounds have been characterized by microanalyses, conductivities and IR, ^1H- and ^{19}F-NMR spectroscopies.

A study of the reactivity of the di-μ-hydroxo-complexes towards organic compounds containing active methyl or methylene groups (acetone, nitromethane, malononitrile, ...) is now in progress.

References

(1) Carmona, E.; Marín, J.M.; Paneque, M.; Poveda, M.L. Organometallics 1987, 6, 1757.
(2) Yoshida, T.; Okano, T.; Otsuka, S. J. Chem. Soc., Dalton Trans. 1976, 993.
(3) Appleton, T.G.; Bennett, M.A. Inorg. Chem. 1978, 17, 738.
(4) Ros, R.; Michelin, R.A.; Bataillar, R.; Roulet, R. J. Organomet. Chem. 1978, 161, 75.

Comparative reactivity of dimethylpalladium complexes with diphosphine, phosphino-amine, and diamine bidentate ligands[1]

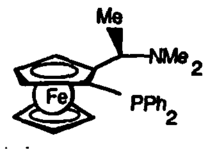
W. de Graaf, J. Boersma, and G. van Koten

University of Utrecht, Laboratory for Organic Chemistry, Dept. of Metal-Mediated Synthesis,
Padualaan 8, 3584 CH Utrecht, The Netherlands

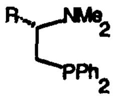
Many chiral ligands used in palladium- and nickel-catalyzed asymmetric coupling reactions contain both a phosphorus and a nitrogen donor atom:[2]

$$\text{R-M} + \text{R'-X} \xrightarrow{L_2PdCl_2,\ L_2NiCl_2} \text{R-R'} + \text{M-X}$$

L_2 =

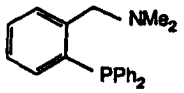


,

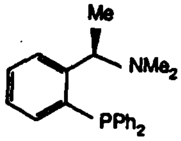


, etc.

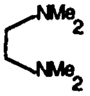
In these reactions, the last step is generally accepted to be reductive elimination of R-R' from a diorganopalladium species. We have investigated the effects of variation of the donor ligands on the mechanism of this reductive elimination in complexes of the type R_2PdL_2. To that end we have prepared and studied the reactivity of dimethylpalladium complexes with the P,N and N,N bidentate ligands *o*-diphenylphosphino-N,N-dimethylbenzylamine (1),[3] *o*-diphenylphosphino-α-methyl-N,N-dimethylbenzylamine (2),[3] and with N,N,N',N'-tetramethylethylenediamine (TMEDA):



(1)



(2)



(3)

References

[1] Part of this work has been published in preliminary form:
W. de Graaf, J. Boersma, D.M. Grove, A.L. Spek and G. van Koten, Recl. Trav. Chim. Pays-Bas **107**, 299 (1988)

[2] M. Kumada, Pure and Appl. Chem. **52**, 669 (1980); T. Hayashi and M. Kumada, Acc. Chem. Res. **15**, 395 (1982)

[3] T. H. Rauchfuss, F. T. Patino and D. M. Roundhill, Inorg. Chem. **14**, 652 (1975)

"Pd(C_6F_5)Br", A CONVENIENT PRECURSOR FOR STUDYING THE NUCLEOPHILIC ENDO ATTACK TO COORDINATED DIENES. X-RAY STRUCTURE OF |Pd_2(μ-Br)$_2$(1-3-η-4(C_6F_5)cyclohexenyl)$_2$|.

A.C. Albéniz and **P. Espinet**, Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain.
C. Foces-Foces and **F.H. Cano**, Departamento de Rayos X, Instituto Rocasolano, C.S.I.C., Serrano 119, 28006 Madrid, Spain.

Exo nucleophilic attack to dienes coordinated to Pd has been widely studied, but **endo** attack from nucleophiles attached to Pd has been less accessible to study and mostly limited to: *a) addition* of diolefins to |$PdHL_2$|$^+$, where the nucleophile H^- is undoubtedly attached to Pd but cannot be recognized after the formation of the η^3-allyl complex; and b) one-pot reactions of Li_2PdCl_4 + diene + RHgX where an intermediate "PdRX" is likely to be formed but no direct evidence of its participation is available.

Our work is concerned with the reactions of |Pd(C_6F_5)Br(S)$_2$| (S=solvent) with acyclic, cyclic, conjugated or non-conjugated diolefins to give, generally, allylic complexes of palladium. The advantages of using this "Pd(C_6F_5)Br" synthon are that: a) there is no doubt that the nucleophile, C_6F_5, is initially attached to the Pd atom; b) the C_6F_5 group gives excellent information from IR and ^{19}F NMR spectroscopies; and c) the position of the attack can be determined from examination of the products.

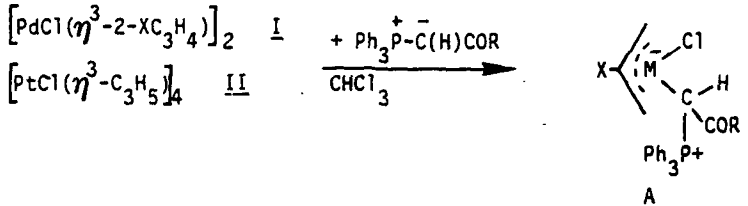
The results of the reactions with several diolefins as interpreted from ^1H and ^{19}F NMR spectroscopies and from the X-ray structure of |Pd_2(μ-Br)$_2$(1-3-η-4-(C_6F_5)cyclohexenyl)$_2$| will be presented.

COORDINATION OF KETO-STABILIZED YLIDES ON Pd(II) AND Pt(II) SUBSTRATES

Giacomo Facchin, Roberta Bertani, Livio Zanotto

Centro di Chimica Metallorganica, C.N.R. , Istituto di Chimica Industriale
Facolta' di Ingegneria, Universita' di Padova, 35100 Padova, Italy

Ylides are electron donor ligands and react with metallic substrates [1] giving metal-carbon σ-bonds having surprising thermal and chemical stability. However electronic and steric factors of the organometallic framework and of the organic ylide can affect stability of the M-C(ylide) bond and the coordination mode of the ylide to the metal centre. We recently prepared Pd(II) and Pt(II) complexes with keto-stabilized ylides starting from dimers I and tetramer II, respectively [2]

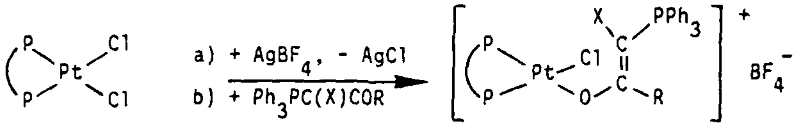


(1

A

M=Pd; X=H,Me; R=Me,Ph;
M=Pt; X=H; R=Me,Ph,OMe

Compounds A show a labile M-C(ylide) σ-bond. The Pd(II) derivatives spontaneously dissociate in CH_2Cl_2 or $CHCl_3$ giving rise to an equilibrium with starting reagents. Substitution in complexes A of the Cl^- with a neutral π-accepting ligands (CNR) lightly stabilizes the σ-bond.
Keto-stabilized ylides can delocalize the negative charge of the carbonyl oxygen; so, in some cases, their coordination to the metal centre through the oxygen atom is possible. Complexes with Pt-O(ylide) bond have been obtained by the following reaction :



(2

B

$\widehat{P\ P}$ $=Ph_2PCH_2CH_2PPh_2$; X=H, Br; $R=CH_3,C_6H_5$
$\widehat{P\ P}$ $=Ph_2PCH_2CH_2PPh_2$; $X=CH_3$; $R=C_6H_5$

The nature of R moiety on the carbonyl group of ylides plays an important role in the coordination mode in the reaction (2).

References

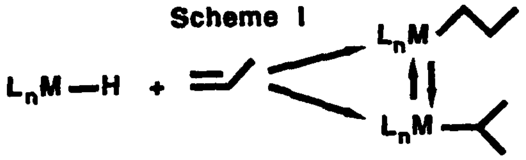
1 W.C.Kaska, Coord.Chem.Rev.1983, 1, 48.
2 G.Facchin, R.Bertani, M.Calligaris, G.Nardin and M.Mari, J.Chem.Soc.,Dalton. Trans.1987, 1381.

ALKYL ISOMERIZATION STUDIES WITH NEW ALKYLPLATINUM (II) COMPLEXES

Daniel L. Reger and Janet C. Baxter, Department of Chemistry, University of South Carolina, Columbia, S. C. 29208, USA

Many important processes that are catalyzed by metal complexes involve the formation of hydridometal intermediates that react with alkenes to form alkylmetal complexes. As shown in Scheme I for propene, with most alkenes a number of alkylmetal isomers that are frequently in equilibrium form in this step. There has only been limited study of the factors that determine the position of this equilibrium.

Scheme I



A series of new alkyl complexes of platinum (II) has been prepared to study these factors in detail. Stable alkylmetal complexes of the type (ligand)Pt(PR_3)(alkyl) (ligand = bischelate, monoanionic ligand) undergo alkylisomerization reactions (*e.g.* secbutyl ⇌ n-butyl) at elevated temperatures. Results on the relative stability of various alkylmetal isomers will be reported as well as mechanistic information on these isomerization reactions.

SYNTHESES AND STRUCTURES OF 2-DIPHENYLPHOSPHINOMETHYLENIDE-6-DIPHENYLPHOSPHINOMETHYLENEPYRIDINE COMPLEXES OF PALLADIUM(II)<AND PLATINUM(II): CRYSTAL STRUCTURES OF $|\mathrm{PtCl\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)}$ PYRIDINE }| AND $|\mathrm{Pd(COOCH_3)\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)}$PYRIDINE}|.

Adriano Sacco,Giuseppe.Vasapollo,Cosimo F. Nobile,Angela Piergiovanni
Dipartimento di Chimica,Centro M.I.S.O. del C.N.R.,Università di Bari,via Amendola 173,Bari (Italy)

Maria A. Pellinghelli, Maurizio Lanfranchi
Istituto di Chimica Generale ed Inorganica,Università di Parma
Centro di studio per la Strutturistica Diffrattometrica del C.N.R.,
Viale delle Scienze,Parma(Italy)

Summary

The reactivity of the palladium(II) and platinum(II) complexes of formula $\mathrm{M(pnp)Cl_2}$ |M= Pd,Pt; pnp=2,6-bis(diphenylphosphinomethyl)pyridine| and $\mathrm{Pt(dppf)Cl_2}$ |dppf=1,1'-bis(diphenyl phosphinomethyl)ferrocene| in methanol solution with sodium methoxide under carbon monoxide atmosphere at room temperature and atmospheric pressure has been investigated.

In contrast with the behavior of the $\mathrm{Pt(dppf)Cl_2}$ complex,which gives the corresponding bis-methoxycarbonyl compound, the terdentate ligand pnp of the $\mathrm{M(pnp)Cl_2}$ complexes undergoes a nucleophilic attack by the methoxide ion, loosing a proton and yielding complexes of formula $\mathrm{MX|C_5H_3N(CHPPh_2)(CH_2PPh_2)|}$ |M= Pt, X=Cl, $\mathrm{COOCH_3}$;M= Pd, X=$\mathrm{COOCH_3}$|,which have been characterized by chemical and spectroscopic means.The crystal structures of $\mathrm{PtCl\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)}$pyridine} (**1**) and $\mathrm{Pd(COOCH_3)\{2\text{-}(CHPPh_2)\text{-}6\text{-}(CH_2PPh_2)}$pyridine} (**2**) have been determined by X-ray methods. Both structures were solved from diffrattometric data by Patterson and Fourier techniques and refined by full-matrix least-squares to R=0.0418 (3338 observed reflections) for **1** and to R= 0.0663 (3088 observed reflections) for **2**. In both complexes the terdentate anionic ligand chelates the metal forming two five-membered rings, and the range for P-C and C-C bond lengths in one of the chelate rings is in agreement with a sp^2 hybridization of the formally anionic methylenidic carbon and with a large delocalization in the ring.

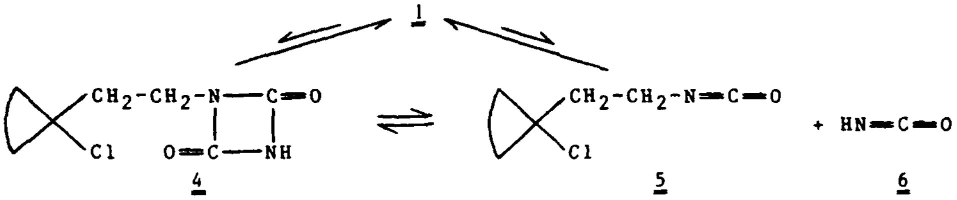
A Possible Example of an Intramolecular Oxidative Addition - Reductive Elimination Process.

L. Maresca,[a] G. Natile,[a] B. Pelli,[b] and P. Traldi.[b]

[a]Dipartimento Farmaco-Chimico, via G.Amendola 173, 70126 Bari
[b]Istituto di Polarografia ed Elettrochimica Preparativa, CNR, Corso Stati Uniti 4, 35100 Padova

The Pt^{IV} complex $[\overline{Pt(CH_2CH_2\text{-}NHC}{=}O)Cl(NCO)(tmen)]$, 1 (tmen = N,N,N',N'-tetramethylethylenediamine), is generated by reaction of the cationic complex $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ with cyanate ion which gives nucleophilic attack to the coordinated olefin and oxidative addition to the central metal (the complete reaction requires also the uptake of a proton and of an extra cyanate ion).[1]

Compound 1 exhibits a thermal lability and its rearrangement can be accounted for by the following scheme:



Different combinations of 4, 5, and 6 lead to the formation of 7, 8, and 9 in which one, two or three hydrogens of the 1,3,5-triazine-2,4,6-one eterocycle, $\overline{CO\text{-}NH\text{-}CO\text{-}NH\text{-}CO\text{-}NH}$, have been substituted by R = $-CH_2\text{-}CH_2\text{-}Pt(tmen)Cl$.

The relative yields of the complexed species (including [Pt(tmen)(NCO)Cl] not reported in the scheme) depends strongly upon the experimental conditions.

M.S. experiments have evidentiated the occurrence of a preferred pathway in the decomposition of $[\overline{Pt(CH_2CH_2\text{-}NHC}{=}O)Cl(NCO)(tmen)]$ under E.I., that is elimination of a N-ethylisocyanate fragment either as such or incorporating a second fragment which can be either the coordinated cyanate ion or the tmen ligand.

Both thermal and M.S. experiments indicate that compound 4 is the most likely primary rearrangement product and therefore the process could be described as an intramolecular oxidative addition - reductive elimination reaction.

Work supported by the Ministero Pubblica Istruzione, Roma

---

[1] L. Maresca and G. Natile, J. Chem. Soc. Chem. Commun., 40 (1983). L. Maresca, G. Natile, A. M. Manotti-Lanfredi, and A. Tiripicchio, J. Am. Chem. Soc., 104, 7661 (1982). G. Gervasio, S. A. Mason, L. Maresca, and G. Natile, Inorg. Chem., 25, 2207 (1986).

CH_2 INSERTION INTO PLATINUM-HALOGEN BONDS

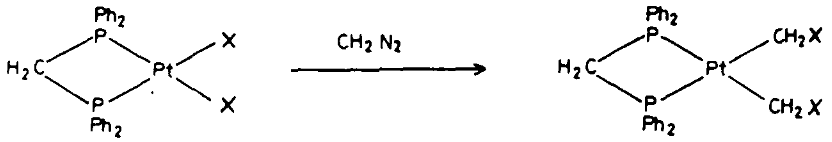
Paola Bergamini, Silvana Sostero, Orazio Traverso, Dipartimento di Chimica, Università di Ferrara, Italia.

Paul G. Pringle, School of Chemistry, University of Bristol, Bristol, U.K.

Nathaniel W. Alcock, Department of Chemistry, University of Warwick, Coventry, U.K.

The insertion of CH_2 into metal-halogen bonds is potentially a convenient route to $M-CH_2X$ species which are precursors to terminal- or bridging- CH_2 complexes.[1,2]

There has been only one previous report of CH_2 insertion into a transition metal-halogen bond[3] but this reaction is well known in main group chemistry.[4] We report here the conversion, in high yield, of the dihaloplatinum(II) complexes (1) to the halomethylcomplexes (2):



(1) X = Cl, Br, I

(2) X = Cl, Br, I

Complexes (2) have been fully characterized spectroscopically and the X- ray crystal structure of (2, X=Cl) has been determined.

The scope of this reaction and some of the chemistry of the reactive complexes (2) will be discussed.

This project has been supported by a NATO travel grant.

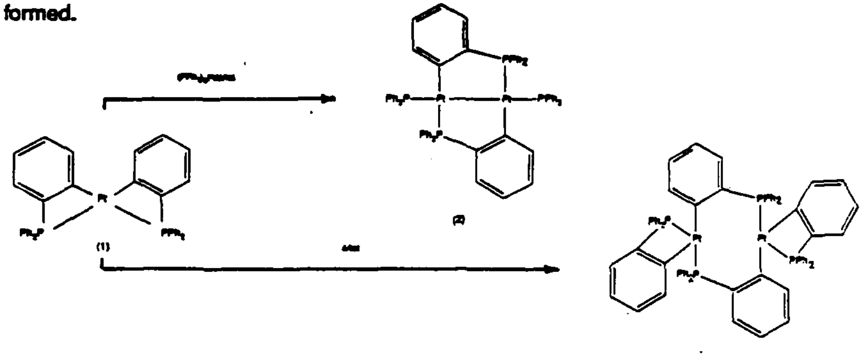
1. Z.Y. Yang and G.B. Young, J. Chem. Soc. Dalton Trans., 1984, 2019.
2. G.J. Arsenault, M. Crespo and R.J. Puddephatt, Organometallics, 1987, 6, 2255.
3. F.D. Mango and I. Dvoretzky, J. Amer. Chem. Soc., 1966, 88, 1965.
4. D. Seyferth, Chem. Rev., 1955, 55, 1155.

Synthesis and Properties of Dinuclear Complexes of Platinum(I) and Platinum(II) Containing Bridging Ortho-metallated Triphenylphosphine Ligands

Johannes Messelhäuser, Martin A. Bennett, Suresh K. Bhargava, Evert J. Ditzel, Glen B. Robertson, Anthony C. Willis, David E. Berry

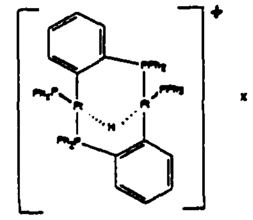
Australian National University, Research School of Chemistry, G.P.O. Box 4, CANBERRA, ACT 2601

The comproportionation of the bis(chelate)complex $[(o\text{-}C_6H_4)PPh_2)]_2Pt$ (1) and $(PPh_3)_3Pt$ in hot toluene gives the dinuclear Pt(I)-complex (2) containing a Pt-Pt bond, two terminal and two bridging ortho-metallated PPh_3 ligands.[1] On heating (1) in the absence of $(PPh_3)_3Pt$ the Pt(II) dimer (3) with two chelating and two ortho-metallated triphenylphosphine ligands is formed.

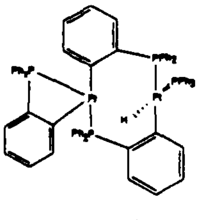


In (1) the terminal PPh_3 ligand can easily substituted by ${}^tBuNC$ affording $({}^tBuNC)_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2Pt$.

The Pt-Pt bond of (2) is cleaved by various acids HX (X = BF_4, CF_3COO, CF_3SO_3, $tolSO_3$) forming a Pt-H-Pt bridge (4). Bases as K_2CO_3 or NH_3 replace the proton of the Pt-hydride complex (4) leading to the original complex (2). With BuLi, however, an isomer of (2) is formed, which is tentatively assigned structure (5).



(4)



(5)

---

[1] M.A. Bennett, D.E. Berry, S.K. Bhargava, E.J. Ditzel, G.B. Robertson, A.C. Willis; J. Chem. Soc. Chem. Commun. 1987, 1613

NEUTRAL PERHALOPHENYL BINUCLEAR PLATINUM-SILVER COMPLEXES

Rafael Usón, Juan Forniés, Milagros Tomás and Irene Ara
Departamento de Química Inorgánica. Instituto de Ciencia de Materiales de Aragón. Universidad de Zaragoza-C.S.I.C.
50009 Zaragoza. SPAIN

We have recently prepared polynuclear perhalophenyl complexes containing Pt → Ag bonds, by reacting anionic perhalophenyl platinate(II) derivatives with ClO_4Ag or $O_3ClOAgL$ (1). The structure of the obtained complexes is strongly dependent on the nature of the platinum precursors and in most of these complexes the perhalophenyl groups are oriented in such a way that one of the o-F or o-Cl atoms of the perhalophenyl groups makes a short contact with the silver atom.

$(NBu_4)|Pt(C_6F_5)_3L|$ (L= N,P,S donor) react with $O_3ClOAgL'$ (L'= PPh_3, PEt_3) yielding the binuclear $|L(C_6F_5)_3Pt \rightarrow AgL'|$ derivatives (2) and in order to evaluate the influence of the ligands bonded to the platinum centre we have prepared the following complexes: $(NBu_4)|cis\text{-}Pt(C_6F_5)_2(C_6Cl_5)L|$, $(NBu_4)|cis\text{-}Pt(C_6F_5)(C_6Cl_5)_2L|$, $(NBu_4)|trans\text{-}PtX_2(C_6F_5)L|$, $(NBu_4)|trans\text{-}PtX_2(C_6Cl_5)L|$ (X= Cl, Br) and have studied their reactions with $O_3ClOAgPPh_3$. In all cases binuclear platinum silver derivatives of general formula $|L(C_6F_5)_x(C_6Cl_5)_yPtAgPPh_3|$ (x= 1, y= 2; x= 2, y= 1) or $|L(C_6X'_5)X_2PtAgPPh_3|$ (X= Cl, Br, X'= Cl, F) have been obtained. Crystallographic studies reveal that o-Cl...Ag contacts are stronger than the o-F...Ag ones since the higher electronegativity of the fluorine makes it more reluctant to donate electron density to the silver centres.

1.- R. Usón, J. Forniés, M. Tomás, J.M. Casas, F.A. Cotton and L.R. Falvello, Inorg. Chem., 1987,26,3482, and references therein
2.- F.A. Cotton, L.R. Falvello, R. Usón, J. Forniés, M. Tomás, J.M. Casas and I. Ara, Inorg. Chem., 1987,26,1366.

PREPARATION AND STRUCTURAL CHARACTERIZATION OF BIS(1,5-CYCLOOCTADIENE)-COPPER(I) PERCHLORATE AND THE NATURE OF Cu-OLEFIN BONDING.

Megumu Munakata and Susumu Kitagawa

Department of Chemistry, Faculty of Science and Technology, Kinki University
Kowakae, Higashi-Osaka 577, Japan

The binary copper(I) complex with a olefin, $[Cu(cod)_2]ClO_4$ (cod = 1,5-cyclooctadiene), was synthesized by the reduction of copper(II) perchlorate with copper wire in the presence of cod. The structure has been determined by a single-crystal X-ray structure analysis and the nature of Cu-olefin bonding has been discussed on the basis the C=C distance, ^{1}H NMR chemical shifts and ν(C=C). Three important results emerge from this study. Firstly, the obtained molecular structure is the first binary Cu(I) complex with olefin of which geometry is characteristic of a four-coordinate tetrahedron regarding four olefin bond moieties of two cod molecules (Figure 1). Secondly, the Cu-olefinic carbon distances {Cu-C = 2.273 Å(av.)} are significantly longer than those(1.93 - 2.07 Å) for the mixed-ligand Cu(I) olefin complexes reported,[1] suggesting that the metal-olefin bonding mode in four-coordinate copper(I) complexes is almost purely dominated by σ donation. On the other hand, some mixed-ligand Cu(I) complexes with both olefins and nitrogenous ligands show a slight increase in the contribution of π back donation in the bonding mode, because the shortening of the Cu-olefin bond due to replacement of one olefin with a nitrogenous ligand implies the strengthening of π back bonding. This is also supported from the fact that the ^{1}H NMR spectrum of olefinic protons of the cod molecule appeared lower field compared with that for free cod.[2] Thirdly, the coordination of the cod molecules to the Cu(I) ion exerts virtually no effect on the C=C bond distances of the coordinated cod molecules: 1.332 Å(av.) vs 1.341 Å (av.) for free cod molecule. This phenomenon is also reflected on the little decreasing of the C=C stretching frequencies, 69 cm^{-1}.

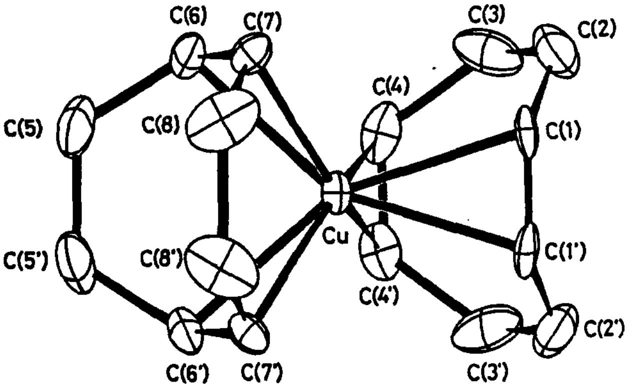


Figure 1. Structure of $[Cu(cod)_2]^+$

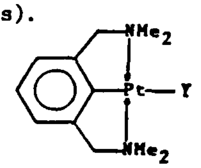
---

1) M. Munakata et al., J. Organomet. Chem., 1987, 322, 121.
2) M. Munakata et al., Inorg. Chem., 1985, 25, 2622.

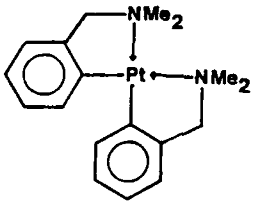
Stereoselective Oxidative Addition Reactions of Halogens and Copper(II) Halides to Square Planar Organoplatinum(II) Complexes.

Johannus A. M. van Beek and Kees Vrieze, Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands
Gerard van Koten, Vakgroep Organische Chemie, Universiteit van Utrecht, Padualaan 8, 3508 TB Utrecht, The Netherlands

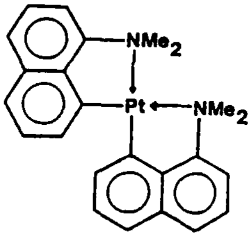
Oxidative addition reactions of electrophiles to organometallic complexes play an important role in both organometallic synthesis and in many homogeneous catalyzed processes. We studied the reactions of halogens and copper(II) halides with the organoplatinum(II) complexes 1, 2 and 3 (see figures).



1a: Y = Cl, Br, I
1b: *Y = Ph, p-Tol*



2



3

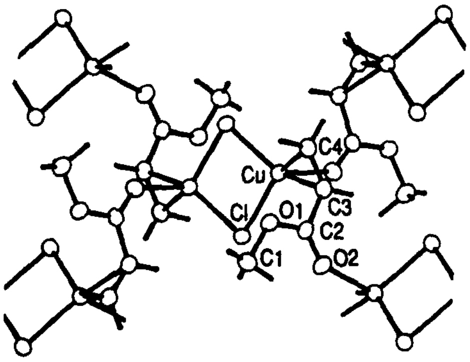
Reactions with CuX_2 (X = Cl, Br) yielded for 2 and 3 cis-X_2Pt(IV) products (for 1a mer-X_3 arrangement), whereas the reactions of 2 and 3 with the halogens Br_2 and I_2 yielded trans-X_2Pt(IV) oxidative addition products. For steric reasons implied by the rigid terdentate ligand system, 1b reacted with X_2 to afford cis-X_2Pt(IV) complexes. Most strikingly, 1a (with Y = I) reacted with I_2 to yield the first example of a complex with an I_2 molecule η^1 bonded to the Pt(II) centre,[1] a situation that can be seen as an early stage in the oxidative addition reactions of halogens to Pt(II). The above described results (isolation of the I_2-intermediate and the stereochemistry of the Pt(IV) products), obtained by suitable choise of the chelate ligands, indicate that the oxidative addition reactions of halogens to square planar organoplatinum(II) complexes most probably proceed via the S_n2 type mechanism.

1. van Beek, J. A. M. ; van Koten, G.; Smeets, W. J. J. ; Spek, A. L. ; J. Am. Chem. Soc. 1986, 108, 5010.

PREPARATION AND STRUCTURES OF COMPLEXES BETWEEN α,β-UNSATURATED CARBONYL COMPOUNDS AND COPPER(I) CHLORIDE

Mikael Håkansson and Susan Jagner, Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden
Martin Nilsson, Department of Organic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

π-Complexes between α,β-unsaturated carbonyl compounds and copper(I) are of interest in relation to the tendency of copper(I) to promote conjugate addition reactions. We have previously reported the preparation and structural characterisation of complexes between copper(I) chloride and acrylaldehyde [1], methyl vinyl ketone [2] and ethyl vinyl ketone [3]. In the first compound, the acrylaldehyde ligand has the *s-trans* conformation, and acts as a bridge, via C=C and the carbonyl oxygen atom, between adjacent Cu(I). In the second, there are two types of butenone ligand: one bridging, with the *s-trans* conformation and one terminal, *s-cis*, bonded to Cu(I) solely via C=C. The pentenone ligand in the third compound is an *s-cis* bridge with a long O-Cu bond. In the complex between methyl acrylate and copper(I) chloride, the ligand assumes the *s-trans* conformation, rather than the preferred [4] *s-cis* conformation of the uncomplexed molecule, bridging $(CuCl)_2$ dimers to form layers:



[1] S. Andersson, M. Håkansson, S. Jagner, M. Nilsson, C. Ullenius, F. Urso, Acta Chem. Scand. A 40 (1986) 58.

[2] S. Andersson, M. Håkansson, S. Jagner, M. Nilsson, F. Urso, Acta Chem. Scand. A 40 (1986) 194.

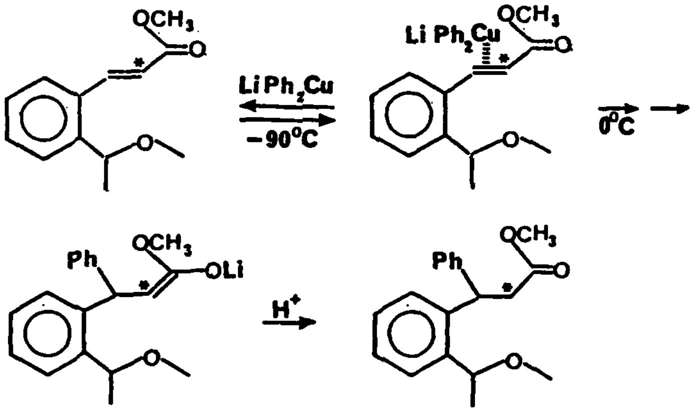
[3] M. Håkansson, S. Jagner, M. Nilsson, J. Organomet. Chem. 336 (1987) 279.

[4] R.J. Abraham, S.L.R. Ellison, P. Schonholzer, W.A. Thomas, Tetrahedron 42 (1986) 2101.

ORGANOCUPRATE ADDITION TO α,β-UNSATURATED COMPOUNDS: NMR INVESTIGATIONS

Beritte Christenson, Thomas Olsson and Christina Ullenius,
Department of Organic Chemistry, Chalmers University of Technology,
S-412 96 Göteborg, Sweden.

The addition of lithium dimethylcuprate and lithium diphenylcuprate to methyl 2-(1-methoxyethyl)cinnamate has been investigated by NMR spectroscopy. The experiments were run at various temperatures, -90 - +20°C, in order to study the formation and dynamics of an copper-alkene π-complex. The substrate was labeled with ^{13}C in the α-carbon position to facilitate the assignments.



* = ^{13}C

The signals at 50 - 54 ppm (-90°C) have been assigned to the α-carbon of isomeric copper-alkene π-complexes. As the temperature was increased these signals disappear with the simultaneous increase of signals assigned to the product enolate.

G. Hallnemo, T. Olsson and C. Ullenius, J. Organometal. Chem. 282, 133 (1985).
C. Ullenius and B. Christenson, Pure & Appl. Chem. 60, 57 (1988).

SYNTHESIS AND STRUCTURAL STUDIES ON COPPER (1) COMPOUNDS

A.E. Mauro, C.C. Porta and M.R. Roveri - Instituto de Química de Araraquara - UNESP - C.P. 174 - 14.800 - Araraquara, S.P., Brazil

R.H.A. Santos and M.T.P. Gambardela - Instituto de Física e Química de São Carlos - USP.

We have been developing a programme on metal carbonyl chemistry (1, 2) for some years and now we wish to report our findings concerning to the study of bimetallics that have Cu-Fe bonds. These complexes of general formula $[LCu_2Fe(CO)_4]$ (L = ethylenediamine, N,N'-dimethylethylenediamine;N,N-diethylethylenediamine; N,N,N',N'-tetramethylethylenediamine; diethylenetriamine) were synthesized in water by reacting $[Fe(CO)_5]$ and CuCl in the presence of the nitrogen ligands. They are yellow solids and their infrared spectra in the νCO region suggest that the symmetry around the iron is octahedral with the Cu atoms at cis-positions. As some CO modes are observed in the range 1800-1700 cm^{-1} it is possible that these compounds have CO bridging groups.

We are also interested in copper(I)-triphenylphosphine complexes (3) and recently we run the reaction of the dimer $[CuSCN(PPh_3)_2]$ with θ-phenanthroline. The structure of the product $[CuSCN(phen)(PPh_3)]$, was determined by X-ray diffraction and consits of a monomer with the copper atom tetrahedrally coordinated. Some important distances and bond angles are:

$Cu\text{-}P = 2,2091(4)$Å

$Cu\text{-}N_2 = 2,02(2)$Å

$Cu\text{-}N_3 = 2,31(1)$Å

$N_2\text{-}Cu\text{-}N_3 = 103,5(6)^{\circ}$

$N_2\text{-}Cu\text{-}N_4 = 111,3(5)^{\circ}$

$N_3\text{-}Cu\text{-}P = 120,6(4)^{\circ}$

N_2 (nitrogen of SCN)

N_3 and N_4 (nitrogen of phen)

1. A.E. Mauro, O. Sala, Y. Hase; J. Molec. Struct. 48, 199 (1978).
2. A.E. Mauro, R.H.A. Santos, M.T.P. Gambardella, R.H.P. Francisco; Polyhedron 6, 1273 (1987).
3. J. Zukerman - Schpector, E.E. Castelano, A.E. Mauro, M.R. Roveri, Acta Cryst. 42, 302 (1986).

PREPARATION AND CHARACTERISATION OF SOME Cu(II), Ni(II) AND Co(II) SCHIFF BASE CHELATES OF QUINOLINE TYPE

N. Koprivanac, J. Jovanović-Kolar, S. Papić and V. Kramer
Faculty of Technology, University of Zagreb, 41000 Zagreb, Savska c. 16, Yugoslavia
Institute "Jozef Stefan", 61000 Ljubljana, Yugoslavia

In continuation of the other studies on the preparation and investigation of some Schiff's bases as the ligands in the metal chelates, the following azomethine compounds of quinolyne type were synthetized:

1,6-di-(2-quinolyl)-2,5-diazo-1,5-hexadiene and

4-(2-quinolylmethylene-amino-1-phenyl-2,3-dimethyl-5-pyrozolone.

The structure of these azomethine compounds were confirmed by means of elemental analyses, UV/VIS, IR and MS nalytical methods. Their Cu(II) and Ni(II) metal complexes were prepared in general with Cu(II)-chloride, Ni(II)-acetate, precipited and isolated as perchlorates. The nature of bonding by forming complex molecules was determined via UV/VIS, IR as well as by mass spectra.

NEW YLIDE-COMPLEXES OF Ag, Au, Pd, AND Pt.

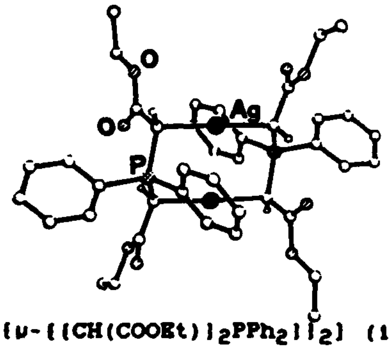
Jose Vicente, Maria-Teresa Chicote, Isabel Saura-Llamas and
Juan Fernandez-Baeza. Departamento de Quimica Inorganica,
Universidad de Murcia, 30.071 Murcia, Spain.

Peter G. Jones, Institut für Anorganische Chemie der
Universität, Tammannstrasse 4, 3400 Göttingen, W. Germany.

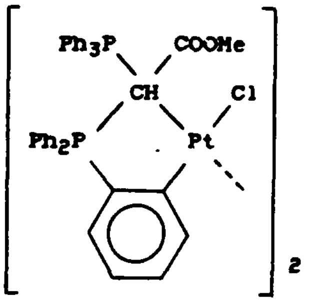
The phosphonium salt $[Ph_2P(CH_2COOEt)_2]Cl$ reacts with Ag_2CO_3 (1:1) to give the dinuclear complex $[Ag_2\{\mu\text{-}\{[CH(COOEt)]_2PPh_2\}\}_2]$ (1) which crystal structure has been determined. (1) reacts with [AuCl(tht)] (tht = tetrahydrothiophene) (1:2) to give the analogous Au(I) complex that can be oxidized with Cl_2IPh or I_2 to the corresponding Au(II) derivatives even if an excess of the oxidizing agent is used.

When $[Ph_2P(CH_2COOEt)_2]ClO_4$ is reacted with [Au(acac)L] [L = PPh_3, $P(3\text{-}CH_3O\text{-}C_6H_4)_3$] trinuclear cationic complexes are obtained as a result of the substitution of three hydrogen atoms of the phosphonium salt by three "AuL" moieties.

On the other hand, $PtCl_2$ reacts with $Ph_3PCHCOOCH_3$ to give a dinuclear complex (2) where the ylide is orthometallated.



$[Ag_2\{\mu\text{-}\{[CH(COOEt)]_2PPh_2\}\}_2]$ (1)



(2)

When (2) is reacted with 1,10-phenanthroline in the presence of $NaClO_4$, a cationic complex is obtained. Both species can be oxidized with Cl_2/CCl_4 to the corresponding neutral or cationic Pt(IV) complexes.

If $[PtCl_2(NCC_6F_5)_2]$ is reacted with different ylides of general formula $Ph_3PCHCOR$, complexes of the types $[PtCl_2\{N=C[CH(PPh_3)COR](C_6F_5)\}_2]$ (R = OMe, OEt) or $[PtCl_2\{NH[C=C(PPh_3)COR](C_6F_5)\}_2]$ (R = Me, Ph) are obtained.

SILVER FERROCENE-LIGAND COMPLEXES: DONOR PREFERENCE AND REDOX PROPERTIES

Brian H. Robinson, Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand.

William R. Cullen, Department of Chemistry, University of British Columbia, Vancouver, Canada.

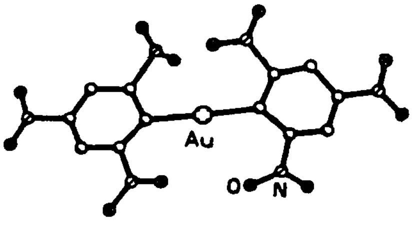
Silver(I) complexes of the chelating ferrocene ligands $Fe[C_5H_4(PR_2)]_2$, $CpFe[C_5H_3(CH(R)NMe_2)(PR_2)]$ and $[C_5H_4(PR_2)]Fe[C_5H_3-CH(R)NMe_2)(PR_2)]$ have been synthesised and the donor preference and structure investigated by ^1H, ^{31}P and ^{109}Ag NMR and X-ray crystal data. In all cases the overall stoichiometry is $[AgL_2]^+X^-$ in the solid but in solution all complexes are stereochemically non-rigid with tri-substituted complexes as well as species involving -N, -N/P or P/P donor sets, being observed. Cyclic voltammetry and chemical studies show that both the ferrocene and silver redox centres can be oxidised giving the first Ag(II)-phosphine complexes; the interaction between these two redox centres will be discussed. Where there is a -N/P donor set the silver(I) complexes undergo a novel cleavage of the NMe_2 group.

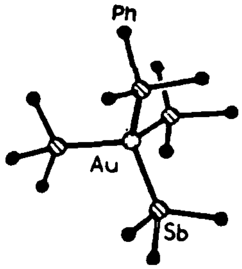
2,4,6-TRINITROPHENYLCOMPLEXES OF Au(I) AND Pd(II)

-Jose Vicente, Aurelia Arcas and M. Victoria Borrachero.
Departamento de Quimica Inorganica, Universidad de Murcia,
30.071 Murcia, Spain.

-Peter G. Jones, Institut für Anorganische Chemie der
Universität, Tammannstrasse 4, 3400 Göttingen, W. Germany.

There exists just one 2,4,6-trinitrophenyl complex of a transition element [1]. We have succeded in preparing Au and Pd derivatives using the corresponding diarylmercury(II) compound. Thus, by reacting $[AuCl_2]^-$ with HgR_2 (R = 2,4,6-trinitrophenyl) (1/1) we prepared $[Au(R)Cl]^-$ (1) which reacts with $NaClO_4$ + tetrahydrotiophene(tht) to give [Au(R)(tht)] (2) which its high stability must be asigned to the special nature of the R group. Complex 2 reacts with ligands L_2 to give complexes "$Au(R)L_2$" [L = $SbPh_3$ (3) or L_2 = 1,10-phenanthroline (4)]. The crystal structure of complex 3 corresponds to a formulation $[Au(R)_2][AuL_4]$.





Treatment of $[(PhCH_2)PPh_3]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ with HgR_2 (1/2) in refluxing acetone gives $[(PhCH_2)PPh_3]_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2].2Me_2CO$ (5). The reaction of 5 with excess of NaX gives $[(PhCH_2)PPh_3]_2[Pd_2R_2X_2(\mu\text{-}X)_2]$[X = Br(6), I(7)]. Reactions of 5 or 6 with dimethylsulfoxide lead to complexes cis-$[(PhCH_2)PPh_3][Pd(R)X_2\{S(O)Me_2\}]$ [X = Cl(8), Br(9)]. Complex 5 reacts with several mono- and bi-dentate ligands to give neutral complexes $[Pd(R)ClL_2]$. Some of these react with $AgClO_4$ to give stable perchlorato-complexes $[Pd(R)(OClO_3)L_2]$ which in turn react with bidentate neutral ligands L'_2 to give complexes $[Pd(R)L'_2L]^+$ or with PPh_3 to give complexes $[Pd(R)L_2(PPh_3)]^+$

---

[1] W. Beck, K. Schorpp, and K. H. Setter, Z. Naturforsch B., 26(1971)684

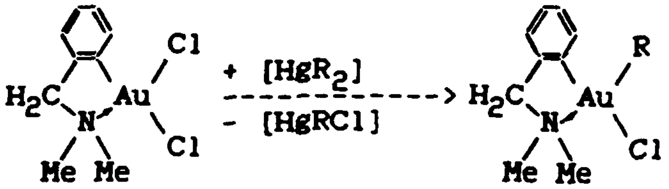
THE ORGANOMERCURY ROUTE TO MIXED DIARYLGOLD(III) COMPLEXES

-Jose Vicente, Maria-Teresa Chicote, Maria-Dolores Bermudez, Maria-Jose Sanchez-Santano. Departamento de Quimica Inorganica, Universidad de Murcia, 30.071 Murcia, Spain.

-Peter G. Jones, Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, W. Germany.

We have used organomercury compounds as transmetallating reagents in the synthesis of arylgold(I) and (III) complexes [1]. The complexes obtained in these transmetallation reactions are mono- or di-aryl complexes depending on the nature of the aryl group to be transferred, on the oxydation state of gold and on the reaction conditions.

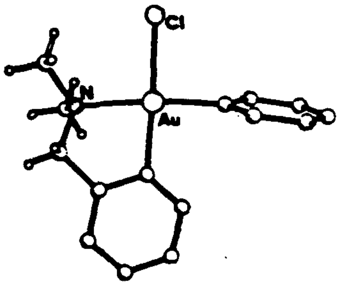
By reacting monoarylgold(III) complexes with organomercurials, mixed diaryl derivatives can be isolated. We illustrate this synthetic method through the following general reaction:



R = 2-$C_6H_4CH_2NMe_2$, 2-$C_6H_4N{=}NPh$, Ph, C_6F_5, 2-$C_6H_4NO_2$, 2- or 3-$C_6H_4CF_3$.

We also report the synthesis of derivatives of these mixed diaryl complexes obtained by reacting them with neutral and anionic ligands.

We also present the first crystal structure of a neutral mixed diarylgold(III) complex which confirms many structural and IR spectral assignments that we have previously done.



---- Crystal Structure of $[Au(2\text{-}C_6H_4CH_2NMe_2)(Ph)Cl]$

---

[1] J. Vicente, M.T. Chicote, M.D. Bermudez, M.J. Sanchez-Santano, P.G. Jones, C. Fittschen and G.M. Sheldrick, J. Organomet. Chem. 310 (1986) 401 and refs. there in.

GERMYLMERCURY COMPLEXES OF TRIVALENT SAMARIUM, EUROPIUM AND YTTERBIUM

N.A.Orlov, S.F.Zhiltsov, L.N.Bochkarev, Gorky state pedagogical institute, Ulyanova, 1, 603600, Gorky, USSR.

Earlier we have found [1], that interaction of metallic samarium, europium and ytterbium with germylmercury $[(C_6F_5)_3Ge]_2Hg$ in 1,2-dimethoxyethane (DME) leads to the formation of ionic germylmercury complexes of divalent lanthanoids $[(R^F_3Ge)_6Hg_2]^{2-}\ Ln^{2+}$ $(R^F = C_6F_5)$.

In this paper we report that similar germylmercury complexes of trivalent samarium, europium and ytterbium have been obtained by hydride method - reaction of hydride R^F_3GeH with tert-buthoxy-derivatives of lanthanoids in the presence of $(R^F_3Ge)_2Hg$

$$3R^F_3GeH + (Bu^tO)_3Ln + 2(R^F_3Ge)_2Hg \xrightarrow[70^oC]{DME} [(R^F_3Ge)_7Hg_2]Ln\cdot 3DME + 3Bu^tOH$$

The isolated compounds of samarium, europium and ytterbium react easily with hydrogen chloride and at molar reagent ratio 1:3 give germylmercury hydride R^F_3GeH and $LnCl_3$ in high yields:

$$[(R^F_3Ge)_7Hg_2]Ln\cdot 3DME + 3HCl \xrightarrow[20^oC]{DME} 2(R^F_3Ge)_2Hg + 3R^F_3GeH + LnCl_3$$

Furthermore, it was found that the reaction of $(R^F_3Ge)_2Hg$ with YbI_3 in DME or methyl cyanide leads to the formation of germylmercury complex of trivalent ytterbium $[(R^F_3Ge)_2HgI]_3^{1-}Yb^{3+}$.

1. L.N.Bochkarev, N.A.Orlov, S.F.Zhiltsov, M.N.Bochkarev. Zh. Obshch.Khimii, 52, (1987), 2804.

ORGANOSILICON, -GERMANIUM AND -TIN COMPLEXES OF LANTHANOIDS OF GRIGNARD REAGENTS TYPE

L.N.Bochkarev, I.L.Fedyushkin, S.F.Zhiltsov, Gorky state pedagogical institute, Ulyanova, 1, 603600, Gorky, USSR.

Earlier we have found that reaction of organogermanium and -tin halogenides R_3EX (E = Ge, Sn; X = Br, I) with metallic samarium, europium and ytterbium in THF solution leads to the formation of complexes $R_3ELnX\cdot(THF)_{1-2}$ in low yields. Chlorides R_3ECl (E = Si, Ge, Sn) in similar conditions do not react with metallic lanthanoids.

Now we report that Grignard type complexes R_3ELnX can be obtained in more high yields by reaction of organosilicon, -germanium and -tin iodides, bromides and also chlorides with naphtalene derivatives of lanthanoids

$$R_3EX + (C_{10}H_8)_nYb \xrightarrow[20^0]{THF} R_3ELnX\cdot(THF)_{1-2}$$

Ln = Sm, Eu, Yb; E = Si, Ge, Sn; X = Cl, Br, I; R = Me, Et, Ph;
n = 0,5-1

Complexes $Et_3GeYbBr\cdot(THF)_2$, $Ph_3SnYbCl\cdot(THF)_2$, $Me_3SiYbCl\cdot(THF)_2$ have been isolated in 74%, 30%, 25% accordingly. The compounds are deep-brown solid substances, unstable in air, well soluble in THF, 1,2-dimethoxyethane, insoluble in hexane.

Organogermanium and -tin complexes of lanthanoids react with Et_3GeBr and Ph_3SnCl with the formation of halogenides of divalent lanthanoids LnX_2 and Et_6Ge_2 or Ph_6Sn_2 accordingly.

Reaction of $Me_3SiYbCl$ with trimethylchlorosilane leads to oxidation of ytterbium to trivalent state:

$$Me_3SiYbCl + Me_3SiCl \xrightarrow{THF} Me_3SiYbCl_2 + 1/2\ Me_6Si_2$$

Reaction of $Me_3SiYbCl_2$ derivative with Me_3SiCl leads to $YbCl_3$ and Me_6Si_2.

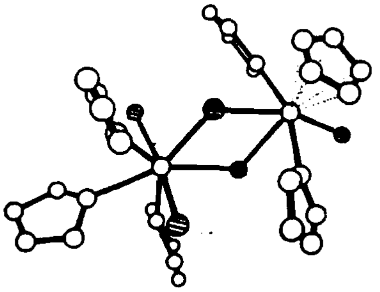
MONOCYCLOPENTADIENYL LANTHANIDE(III) COMPLEXES.II. CONFORMATIONAL CHANGES IN THE SOLID STATE STRUCTURE OF SAMARIUM(III) AND EUROPIUM(III) ORGANOMETALLIC DERIVATIVES.

Giovanni De Paoli, Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, Via L.Loredan, 4, 35100, Padova, Italy.
Giovanni Valle, Centro di Studi sui *Biopolimeri del C.N.R.*, Via Marzolo, 1, 35141, Padova, Italy

In the preceding Abstract (Part I) the structure of the europium (III) complex ($\eta^5 C_5H_5$)$EuCl_2(THF)_3$ is described. The X-ray structural results show that the compound assumes a distorted mer,trans octahedral configuration as in the erbium(III) analogous.(1)

We have extended our investigation to samarium(III) and gadolinium(III) monocyclopentadienyl complexes in order to check if the observed tendency to give the above geometry is general. We report here the crystallographic results on the samarium(III) compound obtained by reacting $SmCl_3$ with NaC_5H_5 in tetrahydrofuran (molar ratio=1).

Crystal data. Yellow pale crystals of (η^5-C_5H_5)$Sm_2Cl_5(THF)_5$ are monoclinic, space group $P2_1/c$, with a=16.615(3) , b=17.766(3) , c=13.440(2) Å, β=104.0(2)° Z=4, V=3849,4 Å^3.



The samarium(III) compound has different stoicheiometry and overall geometry as compared with that of the $EuCl_3$-NaC_5H_5 reaction under apparently similar conditions. The molecular structure of the samarium compound consists of dinuclear units in which the samarium atoms are bridged by two chlorine atoms and have different environment. The distances are: Sm-Sm, 4.443 Å; Sm-Cl(bridge)av., 2.80 Å. This distance is 0.2 Å longer than that to the other chlorine atoms. The Cl-Sm-Cl angles of the bridging unit are 75°. One samarium atom is heptacoordinated being surrounded by four chlorine atoms and three THF molecules, the other is hexacoordinated by three chlorine atoms, two THF ligands and a cyclopentadienyl ring bonded in a penta-hapto fashion.

REFERENCE.

1)C.S. Day, V.W. Day, R.D. Ernst and S.H. Vollmer, Organometallics,1,998,(1982).

IODIZED MISCH METAL AS A SYNTHETIC AGENT

Nobuo Mori, Department of Chemistry, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

Misch metal, an alloy of lanthanoid metals, easily reacts with 1,2-diiodoethane in THF. The resulting iodized misch metal solution was tested about its reactivity toward a variety of functional groups.

Epoxides were deoxygenated. Aldehydes and ketones were reduced in the presence of alcohol to primary and secondary alcohols. Acyl and benzyl halides gave only coupling products. Bis(halomethyl)benzenes gave [2.2]cyclophanes as coupling products.
In the absence of alcohol, aldehydes and ketones gave pinacols. Treatment of a mixture of aldehyde or ketone and alkyl or benzyl halide with the iodized misch metal gave a mixture of products: pinacol, Grignard adduct, reduction product and/or diphenylethane. A similar treatment of aldehydes or ketones and α-halogenoalkanoates gave Reformatsky adducts in high yields.

In a similar way, cerium reacted easily with 1,2-diiodoethane in THF and the product showed a similar reactivity to the iodized misch metal.

It can thus be concluded that both iodides are synthetic agents comparable to SmI_2.

SYNTHESIS AND CHARACTERIZATION OF SOME DIVALENT LANTHANIDE ORGANOMETALLIC COMPLEXES

Gerard F. Payne, Oak Ridge National Laboratory, Oak Ridge,
Tennessee 37831 USA

In an attempt to synthesize divalent complexes of californium and possibly americium, some preliminary studies involving europium, ytterbium, and samarium have been carried out using cyclopentadienyl, indenyl, pentamethylcyclopentadienyl, and pentaphenylcyclopentadienyl ligands. Because of the innate problems associated with both californium and americium (high specific activity and quantities available), the more completely we can characterize the lanthanide complexes, and also perfect techniques for small scale syntheses, the easier the actinide studies should be. Because the (II/III) potentials of samarium and californium are similar (approximately 1.7V vs the normal hydrogen electrode) if we can prepare the bis samarium complex we should be able to prepare the corresponding californium complex. Americium on the other hand has a (II/III) potential of approximately 2.6V vs the NHE, so this will present more problems. The lanthanide work and also possible synthetic routes for the actinide work will be discussed here.

298

Ortho-substitution of Aromatic Substrates Using Electrophiles and Palladium Acetate

Samuel J. Tremont*, Lanny Liebeskind, John Gasdaska,
Barry L. Haymore and Dominic McGrath

Abstract:

Ortho-alkyl acetanilides have been prepared in high yields under mild conditions by the reaction of acetanilides, $Pd(OAc)_2$ and alkyl halides. This new synthetic method can be used to synthesize a variety of highly functionalized mono- or di-ortho-alkyl acetanilides. The ortho alkylation reaction can be made catalytic in palladium by using excess AgOAc. The reaction involves the initial formation of an ortho-palladated acetanilide complex; this complex is then alkylated with alkyl halide by a non radical pathway. This new ortho-substitution reaction has also been demonstrated with many non-carbon electrophiles to produce a family of ortho-substituted products. Application of this chemistry to other aromatic substrates has also been studied.

REACTIONS OF IN SITU GENERATED IMINIUM IONS WITH PROPARGYLSILANES

Jacques PORNET , Dominique DAMOUR and Léone MIGINIAC ,

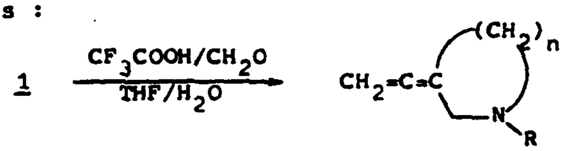
Laboratoire de Synthèse Organique, UA CNRS 574, Université de
Poitiers, 40, avenue du Recteur Pineau, 86022 Poitiers, France

We have shown that ω-silyloxypropargyltrimethylsilanes are convenient precursors for the preparation of 3-vinylidene oxygen-containing heterocycles (1,2).

We report a new method to prepare 3-vinylidene nitrogen-containing heterocycles (3), from ω-monoalkylaminopropargyltrimethylsilanes 1 :

$$Me_3Si{-}CH_2{-}C{\equiv}C{-}(CH_2)_n{-}NH{-}R \qquad \underline{1}$$

Upon exposure to silanes 1 , simple iminium ions generated in situ under Mannich-like conditions from formaldehyde, afford in a one-pot reaction 3-vinylidene pyrrolidines, piperidines and perhydroazepines :



Scope and limitations of this reaction will be discussed.

(1) J. PORNET, D. DAMOUR and L. MIGINIAC, Tetrahedron, 1986, 42, 2017.
(2) J. PORNET, D. DAMOUR, B. RANDRIANOELINA and L. MIGINIAC, Tetrahedron, 1986, 42, 2501.
(3) D. DAMOUR, J. PORNET and L. MIGINIAC, Tetrahedron Lett., 1987, 28, 4689.

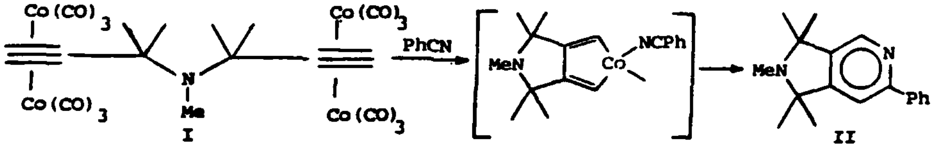
PYRIDINES FROM NITRILE-DIALKYNE COCYCLIZATION ON Co(0) AND Co(I) COMPLEX

Luigi Pietro Battaglia, Daniele Delledonne, Mario Nardelli, Giovanni Predieri, Istituto di Chimica Generale ed Inorganica dell'Universita', Viale delle Scienze, I-43100 Parma, Italy

Gian Paolo Chiusoli, Mirco Costa, Istituto di Chimica Organica, Universita', Viale delle Scienze, I-43100 Parma, Italy

Corrado Pelizzi, Istituto di Chimica Biologica, Via Murani 23/a, I-07100 Sassari

Dicobalt octacarbonyl and N-methyldi(α,α-dimethylpropargyl)amine give complex I, the structure of which has been determined by X-ray methods. We examined its reactivity with benzonitrile and the reactivity of the amine with benzonitrile and dicobalt octacarbonyl in comparison with other Co(0) and Co(l) complexes. We observe that dicobalt octacarbonyl reacts with a selectivity comparable to that of bis(acetonitrile)bis(diethyl fumarate)cobalt(0) to give II. This means that complex I must undergo rearrangement and fragmentation to give the expected cobaltacycle precursor of II.



The ability of Co(0) to incorporate nitriles is essentially due to the presence of the geminal groups on the substrate. In the absence of such groups the reaction of nitriles become difficult and the acetylenic triple bond is incorporated preferentially. Thus 1,7-octadiyne and 1, 6 heptadiyne have been caused to react with monomeric, dimeric and heterogeneous cobalt(0) catalysts, i.e. (bis(acetonitrile)bis(diethyl fumarate)cobalt) (dicobalt octacarbonyl) and $CoCl_2/Mn$) in comparison with cyclopentadienylbis(triphenylphosphine)cobalt(I). The latter turns out to be the best catalyst for nitrile incorporation. The other catalysts prefer the acetylenic triple bond. The heterogenous cobalt catalyst is the most selective for the acetylenic triple bond but also is the most sensitive to the action of geminal groups, which cause a reactivity change leading to preferential nitrile incorporation.

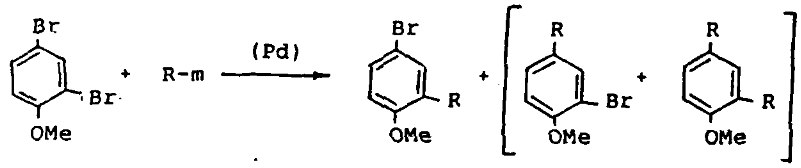
The reactivity change seems to be determined by the combination of steric and conformational effects: the latter favor the cobaltacycle ring formation the former makes more difficult the incorporation of an acetylenic molecule into the cobaltacyle, thus favoring the nitrile incorporation.

Work supported by Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione.

REGIO-SELECTIVE MONO-ALKYLATION OF 2,4-DIBROMOANISOLE CATALYSED BY PALLADIUM-PHOSPHINE COMPLEXES

Akio Minato, Yasuhiro Fujiwara, Sigeru Ozasa, Kyoto
Pharmaceutical University, Misasagi, Yamashina, Kyoto 607,
JAPAN

The regio-selective introduction of organic groups into an aromatic ring has been a fundamental subject of synthetic organic chemistry. We report here the palladium-phosphine complex-catalysed regio-selective mono-alkylation of 2,4-dibromoanisole (1) by Grignard and organozinc reagents.



(1) m = MgX, ZnX (2)

Ethyl- and 2-thienylmagnesium bromide and phenyl- and benzylzinc chloride coupled with (1) regioselectively to give the corresponding 2-substituted-4-bromoanisoles (2) in moderate to good yields.

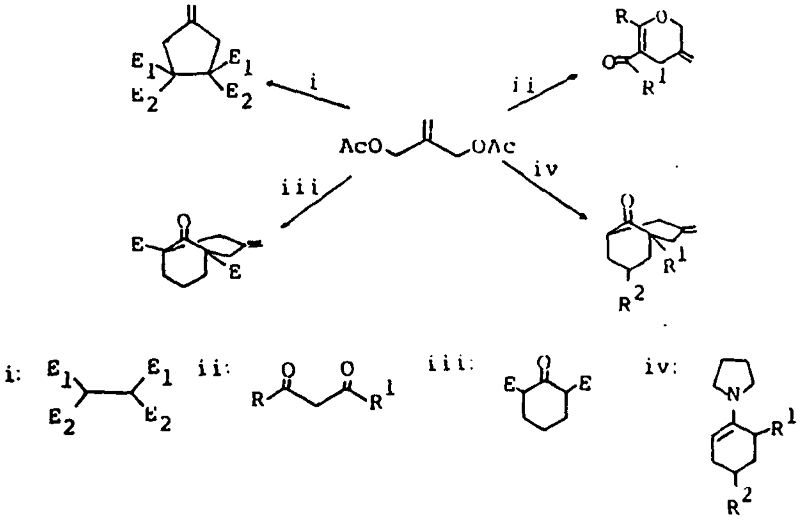
302

PALLADIUM CATALYZED ANNULATION REACTION USING BIFUNCTIONAL ALLYLIC ALKYLATING AGENT

Xiyan Lu and Yujin Huang

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Lingling Lu, Shanghai 200032, China

The reaction of 2-methylene-propane-1,3-diol diacetate (1) with β-diketone or β-ketoester bearing two active hydrogen atoms, which could react with 1 first as a carbon nucleophile then subsequently as an O-nucleophile, to give pyrane derivatives in one pot reaction is described. The usefulneess of 1 as a bifunctional alkylating agent in organic synthesis also lies in preparing various types of ring compounds by the selection of different dicarbanions. In these reactions, 1 can be regarded as an a^1, a^3 synthon.



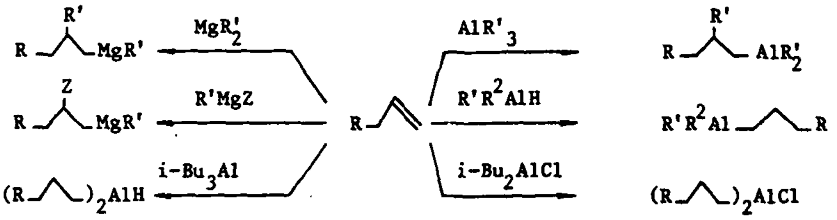
METAL COMPLEX CATALYSIS FOR THE CHEMISTRY OF Mg- AND Al-ORGANICS

U.M.Dzhemilev, O.S.Vostrikova, A.G.Ibragimov,
and G.A.Tolstikov

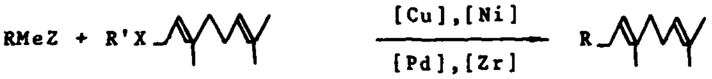
Institute of Chemistry, Bashkirian Research Centre,
USSR Acad.Sci. Ural Department, Ufa 450054, U.S.S.R.

The paper presented covers the results obtained by the authors during recent five years in the field of employment of metal complex catalysis to develop new regio- and stereoselective synthesis techniques for Mg and Al organics.

With Ti and Zr complexes taken as catalysts, the selective hydro- and carbometallations of olefins, dienes, and acetylenes have been carried out with the assistance of alkyl and hydride derivatives.

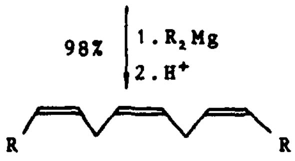


On the basis of ONCs synthesized, the effective methods of catalysis have been proposed to design new bonds as C-C, C-N, and C-S.



Me=Mg, Al; R= RC ≡ C – ; R_2N – ; RS –

$R-C\equiv C-CH_2-C\equiv C-CH_2-C\equiv C-R'$

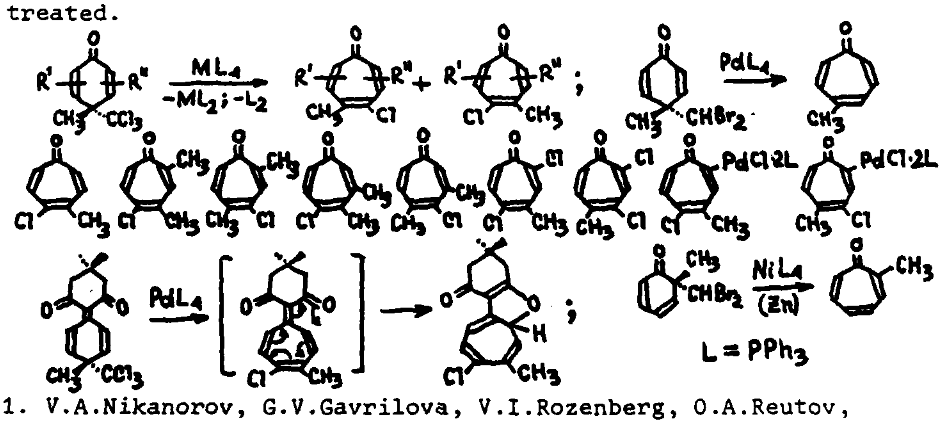


NEW ORGANOMETALLIC INTERRELATIONS BETWEEN SEMIQUINOIDS AND NON-BENZENOID AROMATIC COMPOUNDS

V.A.Nikanorov, G.V.Gavrilova, S.V.Sergeev, V.I.Rozenberg,
O.A.Reutov

A.N.Nesmeyanov Institute of Organo-Element Compounds of the
Academy of Sciences of USSR, Moscow 117813, Vavilova 28, USSR

In 1984 we discovered the reaction of redox-troponization - a new effective method for inert gem-$CHHal_2$- and -$CHal_3$-group activation in ortho- and para-semiquinoids under the action of low-valent transition metal complexes. This opens new organometallic route for the synthesis of hardly available tropones, heptafulvenes, their analogues and derivatives [1,2]. Some mechanistic aspects of the process as a possible combination of Ad_{ox} M(0) into C-Hal bond, F_{red} of α-halo-substituted organometallic intermediate, and subsequent ring expansion in homoallyl-like carbene or carbenoid will be discussed. Stereochemical differences between Pd- and Pt-induced reactions, as well as the effect of metal (Ni≫Pd>Pt), halogen (Br>Cl) and semiquinoid ring substituents (H,CH_3,Cl) on the rates, product ratio and toposelectivity of the ring skeletal isomerisation are also treated.

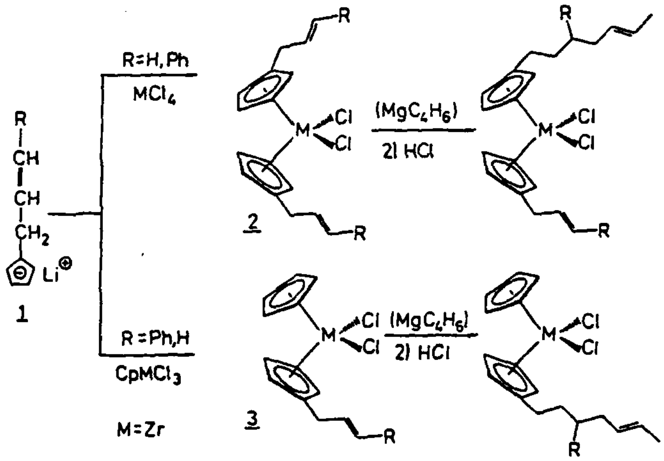


1. V.A.Nikanorov, G.V.Gavrilova, V.I.Rozenberg, O.A.Reutov, Izv. AN SSSR, ser.khim., 1984, s.2647; 1987, s.2345
2. V.I.Bakhmutov, M.V.Galakhov, V.A.Nikanorov, G.V.Gavrilova, V.I.Rozenberg, O.A.Reutov, DAN SSSR, 1987, T.295, s.1376

Reaction of Cp-substituted Metallocenedichlorides with Magnesium-Butadiene: A Method of Increasing the Chain Length of unsaturated Cp-substituents

Rainer Aul, Gerhard Erker
Institut für Organische Chemie der Universität Würzburg
Am Hubland, 8700 Würzburg (BRD)

The metallocene derivatives 2, featuring unsaturated substituents at the Cp-rings were obtained by reaction of lithium salts 1 with Zirconiumtetrachloride. The mixed metallocenedichlorides 3 were obtained from the reaction of 1 with $CpZrCl_3$.



The Cp-substituted metallocenedichlorides 2 and 3 , when treated with magnesium-butadiene, undergo carbon-carbon coupling at the Cp-allyl group. Subsequent work-up with HCl affords a new metallocene dichloride bearing one unsaturated Cp-substituent whose chain length has been increased by four carbon atoms.

NEW C-C BOND FORMING REACTIONS OF ALKYNES WITH ALKENES AND ALLENES WITH PALLADIUM AND PLATINUM DIAZADIENE COMPLEXES

Christina Munz and *Heindirk tom Dieck*, Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13 (F.R.G.)

The sparingly soluble Pd(dba)$_2$ affords complexes (DAD)Pd(alkyne) **1** or the palladacyclopentadienes (DAD)Pd-C=C-C=C **2**, when reacted with DAD (diazadiene RN=CR'-CR'=NR) and dmad (dimethyl acetylene dicarboxylate). These complexes react catalytically with various alkynes R^1-CC-R^2 to give penta-(R^1 = H) or hexasubstituted benzenes [1]. In special cases (e.g. Ph-CC-H) not only the catalytic products of the triple bond insertion into the Pd-C bond of **2** are isolated, but also the linear products of the C-H addition to the Pd-C bond.
When **2** is reacted with terminal alkenes (e.g. 1-hexene, 1,4-hexadiene, Methoxypropadiene), palladacyclopentenes **3**, postulated in the catalysis literature, are formed and are fully characterized by NMR techniques. With other alkenes such as allylic alcohols the complexes **3** are much more reactive and yield linear dienones, dienals or dienols, depending on the substitution pattern of the allylic system and the preferred β-elimination either from a ring or a side chain position [2]. A number of similar intermediates have also been obtained starting from Pt(dba)$_2$. Based on the structures of the Pd and Pt complexes and the stereochemistry of the [$2\pi + 2\pi + 2\pi$] reaction products a general mechanism for catalytic reactions of alkynes with other π-systems at the Pd(0) center will be discussed.

[1] H. tom Dieck, Chr. Munz, Chr. Müller, *J. Organometal. Chem. 326* (1987) C1.
[2] Chr. Munz, H. tom Dieck, *J. Organometal. Chem.* in preparation

AN EASY ACCESS TO β-ACYL AND β-ARYL-PROPIONALDEHYDES THROUGH A NEW SILYLATED ORGANOTIN HOMOENOLATE EQUIVALENT

Jean-Baptiste Verlhac and Michel Pereyre, Laboratoire de Chimie Organique et Organométallique UA 35 CNRS, Université de Bordeaux I, 351, Cours de la libération, 33405 - Talence Cedex (France)

Homologation by a three-carbon reagent is a process of considerable synthetic interest and several lithiated species have been proposed as homoenolate equivalents (d^3 propionaldehyde synthons). However, such highly reactive species do not tolerate various fonctionnal groups.

We had previously employed for this purpose α-alkoxyallyltins[1] but difficulties appeared with the simplest reagent α-ethoxyallyltributyltin with tends to isomerize readily into γ-ethoxyallyltributyltin.

We describe a fast and efficient method[2] to introduce the simplest homoenolate anion $-CH_2CH_2CHO$ on acyl chlorides and aryl bromides via a new easily accessible reagent : (α-methoxy-γ-tributylstannyl)allyltrimethylsilane.

---

1 - J.P. QUINTARD, A. Duchêne, G.Dumartin, B. Elissondo and J.B. Verlhac, Rev. Silicon Germanium, Tin Lead, Compd., 1986, 9, 241.

2 - J.B. Verlhac, J.P. Quintard and M. pereyre, J. Chem. Soc. Chem. Commun., in press.

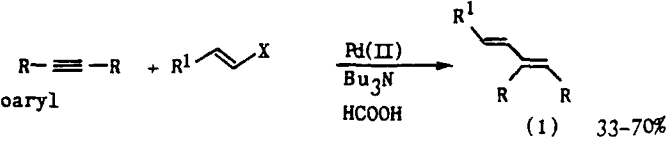
PALLADIUM-CATALYSED STEREOSELECTIVE HYDROVINYLATION OF DISUBSTITUTED ACETYLENES: PREPARATION OF FUNCTIONALYZED 1,2,4-TRISUBSTITUTED-1,3-BUTADIENES

A. Arcadi[a], E. Bernocchi[b], A. Burini[c], S. Cacchi[b], F. Marinelli[a], B. Pietroni[c]

a) Dip. di Chimica Ingegneria Chimica e Materiali, Università degli Studi, Via Assergi 4, 67100 L'Aquila (Italy)
b) Dip. di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università "La Sapienza", P.le A. Moro 5, 00185 Roma (Italy)
c) Dip. di Scienze Chimiche, Università degli Studi, Via S. Agostino 1, 62032 Camerino (Italy)

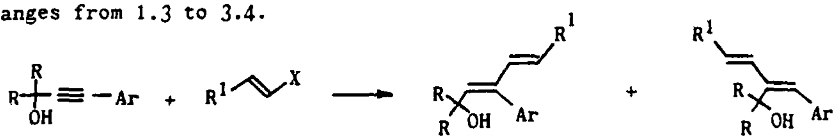
Vinyl halides have been reacted with disubstituted acetylenes in the presence of palladium-tributylammonium formate[1] to give stereoselectively[2] functionalyzed 1,2,4-trisubstituted-1,3-butadienes (1).

X = I, Br
R = alkyl, aryl, heteroaryl
R^1 = alkyl, aryl



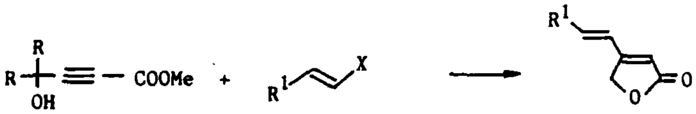
(1) 33-70%

A variety of functional groups can be tolerated in the starting disubstituted acetilenes. Acetylenes disubstituted with different steric demanding groups, such as arylethynyl,dialkylcarbinols (2)[3] react with moderate regioselectivity to produce the isomer (3) in higher yield. The ratio (3)/(4) ranges from 1.3 to 3.4.



(2) (3) (4)

Better regioselectivity was observed in the hydrovinylation of carbomethoxyethynyl,dialkylcarbinols (6). In these cases the hydrovinylation step is followed by an in situ cyclization to 3-alkenyl butenolides (7)[4]



(6) (7)

1) Cacchi, S.; Felici, M.; Pietroni, B. Tetrahedron Lett. (1984) 25, 3137. 2) Arcadi, A.; Cacchi, S.; Ianelli, S.; Marinelli, F.; Nardelli, F. Gazz. Chim. It. (1986) 116, 725. 3) Arcadi, A.; Cacchi, S.; Marinelli, F.; Tetrahedron (1985) 41, 5121; Arcadi, A.; Cacchi, S.; Marinelli, F. Tetrahedron Lett. (1986) 42, 6397. 4) Arcadi, A.; Bernocchi, E.; Burini, A.; Cacchi, S.; Marinelli, F.; Pietroni, B. Tetrahedron (1988) 44, 481

CARBON-CARBON BOND FORMATION IN CATIONIC OLEFIN CARBYL COMPLEXES OF PLATINUM AND PALLADIUM

Vincenzo De Felice, Augusto De Renzi, Achille Panunzi and
Aldo Vitagliano, Dipartimento di Chimica, Università di Napoli,
Via Mezzocannone 4, 80134 Napoli, Italy

Five-coordinate olefin complexes of platinum(II)[1] and palladium(II)[2] containing σ-bonded carbon ligands have been recently described. These complexes have two important properties:

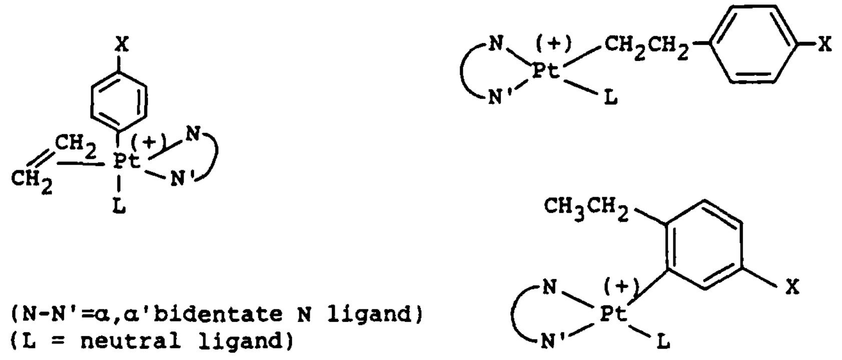
a) They are well characterized species, with an olefin and a σ-bonded carbyl group occupying two adjacent coordination positions.

b) Olefin coordination is reversible, and the free energy change of the process can be modulated by a proper choice of the ligands.

The complexes are thus ideal substrates for the investigation of possible insertion and/or related reactions involving C-C bond formation between an olefin and some other carbon ligand.

We found that neutral complexes are generally not reactive, while an interesting reactivity is displayed by cationic species. Our preliminary results are summarized in schemes 1 and 2.

$$[\mathrm{PdLMe(N\text{-}N')(C_2H_4)}]^{(+)} \xrightarrow{C_2H_4} \mathrm{MeCH{=}CH_2} + (Z{+}E)\text{-}\mathrm{MeCH{=}CHMe} + \mathrm{Pd}^{\circ} \qquad (1)$$



(2)

(N-N'=α,α'bidentate N ligand)
(L = neutral ligand)

Work supported by CNR and MPI

1) Albano, V.G.; Braga, D.; De Felice, V.; Panunzi, A.; Vitagliano, A. Organometallics 1987, 6, 517.
2) De Renzi, A.; Morelli, G.; Panunzi, A.; Vitagliano, A. Gazz. Chim. Ital. 1987, 117, 445.

310

NUCLEOPHILIC AROMATIC SUBSTITUTIONS IN THE $(\eta^6$-CHLOROBENZENE$)$ $(\eta^5$-CYCLOPENTADIENYL$)$ IRON (II) CATION

Eduardo J.S. Vichi, Joseph Miller, Paulo J.S. Moran and Paulo C.B. Gomes; Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, 13081-Campinas, SP, Brasil

Nucleophilic substitutions in halogenoarene transition metal complexes have gained synthetic importance in organic chemistry since the parent organic molecules are virtually inert to nucleophiles under normal conditions. The π-complexation to $Cr(CO)_3$ activates the arene ligand toward metoxide to an extent similar to the effect of a 4-nitro substituent[1], although different mechanisms of electron withdrawall have been suggested for the two systems[2]. The effect of complexation with $(\eta^5\text{-}C_5H_5)Fe^+$ is even more marked, being equivalente to that of ortho-and para nitro groups combined[3]. We report here the results of a kinetic study of the reactions of $|(\eta^6\text{-}C_6H_5Cl)Fe(\eta^5\text{-}C_5H_5|BF_4$ with a varied range of nucleophiles including anionic such as MeO^-, PhO^-, MeS^-, N_3^- and neutral such as morpholine, piperidinie, guanidine and thiourea. For the anionic nucleophiles the reactivities increase in the order $N_3^- \ll PhO^- < PhS^- < MeS^- < MeO^-$, which neither correlate with the relative reactivities with 2,4-dinitrochloro benzene nor with the polarizabilities of the nucleophiles. For the neutral nucleophiles the order is thiourea - aniline << morpholine piperidina<<guanidine. The differences in the reactivities of the arene complex and 2,4-dinitrochlorobenzene towards these nucleophiles are discussed in terms of the localization of the "arenide electrons", i.e. the electrons displaced from the reaction center by the nucleophile in forming the addition intermediate. In the dinitrochlorobenzene intermediate these electrons are located mainly on the (β-exocyclic) oxygen atoms and in the arene complex (Meisenheimer complex) they ramain effectively in the ring where the attack occur. The reactions where folowed by titrating the displaced Cl^- ions with $AgNO_3$ solutions.

1. D.A. Brown and J.R. Raju; J. Chem. Soc. A. 1960 40.

2. A.Z. Kreindlin, et al., J. Organomet. Chem. 1975, 92, 197.

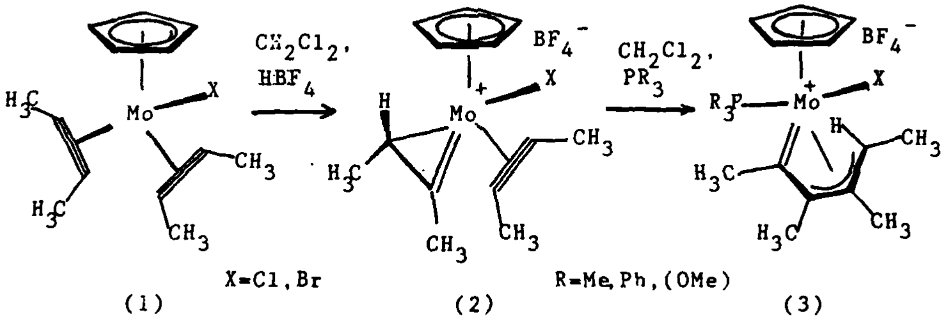
3. A.N. Nesmeyanov et al., Doklady Acad. Nauk. SSSR 1968, 183, 834

THE FORMATION OF CATIONIC η^2-VINYL COMPLEXES AND THE EVIDENCE FOR THE COUPLING OF AN η^2-VINYL AND ALKYNE LIGAND

Michael Green, Carolyn Reeve, Christopher Woolhouse, Department of Chemistry, King's College London, Strand, London. WC2R 2LS. UK.

Grainne Conole, Mary McPartlin, School of Chemistry, Polytechnic of North London, Holloway Road, London. N7. UK.

The molybdenum bis acetylene complexes, $[Mo(\eta^2-CH_3C\equiv CCH_3)_2(\eta-C_5H_5)(X)]$, (X= Br, 1a; X= Cl, 1b), have been shown to be useful starting materials for the investigation of carbon-carbon coupling reactions at a metal centre. Complexes containing an η^2-vinyl moiety may be synthesised by the reaction of (1a) or (1b), with HBF_4.The resulting cationic species (2), was found to be reactive towards phosphines, PR_3 (R= CH_3 or C_6H_5) and phosphites, $P(OR)_3$, (R= CH_3), which leads to coupling of the η^2-vinyl and alkyne ligands to form an allyl carbene fragment.

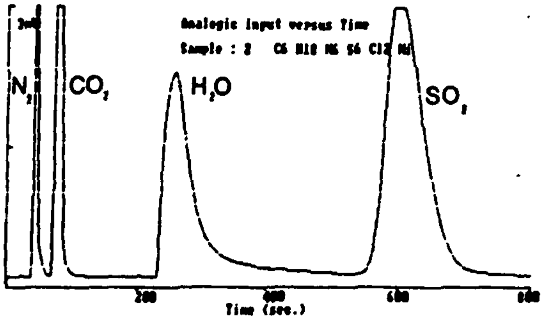


The structure of (3) has been confirmed by x-ray crystallography and the mechanism of formation is discussed in relation to other allyl carbene forming processes. The further chemistry of (1), (2) and (3) is outlined, with particular reference to the deprotonation of the methyl carbene and alkyne functions.

CHARACTERIZING ORGANOMETALLIC COMPOUNDS BY SIMULTANEOUS ELEMENTAL ANALYSIS OF C,H,N,S, WITH THE INNOVATE CARLO ERBA ST. EA 1108 INSTRUMENT.

Marco Baccanti and Bruno Colombo, Carlo Erba Strumentazione, Strada Rivoltana, 20090 Rodano (Milan), Italy.

A method based on high temperature flash combustion followed by catalytic oxidation, reduction, gas cromatographic separation and detection by thermal conductivity is presented.
Nitrogen, carbon dioxide, water and sulphur dioxide are simultaneously and dynamically determined in less than 14 min.
N, C, H, S found weight percentages are printed out by a personal computer with a dedicated software.
The analytical procedures are performed automatically and up to 196 samples can be analysed continuously and automatically.
A typical output is shown below. A series of experimental result obtained for a number of organometallic compounds will be described.



```
Date      : 05-29-1988    Time : 11:06:31     Company name :
Sample    : 2     C6 H18 N6 S6 C12 Ni         Type : Unlnown
Sample     Weight    :  2.028                 Base Line drift (micV): 24
Operator :
-----------------------------------------------------------------------------
_#___Ret.T. _____Area (micV*s)________Area %________Comp. %________Feal name ___
 1     23             197              .034
 2     43           70876            12.588        16.88023         Nitrogen
 3     75          168408            29.911        14.72409           Carbon
 4    256          121287            21.542        3.642198         Hydrogen
 5    595          202251            35.922        38.69496          Sulphur
-----------------------------------------------------------------------------
Carb./Hyd. Area =      1.388508    Carb./Nitr.Area =      2.376093
Carb./Sulp.Area =      .8326683
```

SYNTHESIS AND REACTIVITY OF HYDROQUINONE CHROMIUM TRICARBONYL COMPLEXES

Hans Schumann, Atta M. Arif and Thomas G. Richmond, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (USA)

Chromium tricarbonyl complexes of the general type (η^6 - aren $(OSi(CH_3)_3)_2)Cr(CO)_3$ (aren = $C_6H_2R'_2$: 1a $R'_2 = H_2$, 1,4 - $(OSiR_3)_2$; 1b R'_2 = 2,5 - $(t\text{-}C_4H_9)_2$, 1,4 - $(OSiR_3)_2$; 1c R'_2 = 3,5 - $(t\text{-}C_4H_9)_2$, 1,2 - $(OSiR_3)_2$; and aren = $C_{10}H_6$: 1d 1,2 - $(OSiR_3)_2$) have been obtained from the thermal CO substitution in $Cr(CO)_6$ by bis(trimethylsilyl) - protected hydroquinones. The molecular structure of complex 1d was determined by X-ray structure analysis and will be discussed in comparison with related structures of substituted naphthaline chromium tricarbonyl complexes.

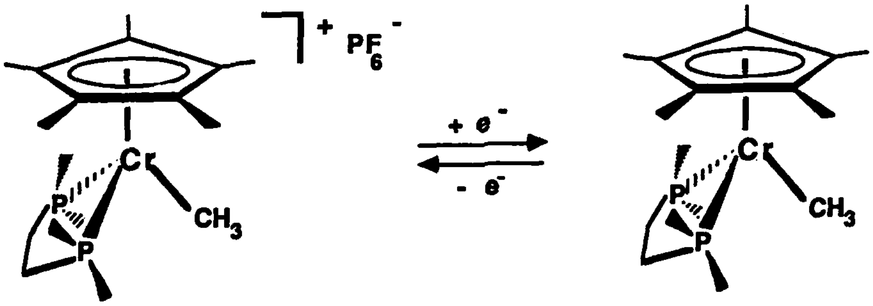
Deprotection of the $Si(CH_3)_3$ protection groups in complexes 1 by F^- under controlled conditions give the related hydroquinone complexes 2 in high yield. Further deprotonation by selected bases afford the dianionic complexes 3, (η^6 - aren$(O^-)_2)Cr(CO)_3$.

Selected reactions and properties for the complexes 1 to 3 will be presented in comparison with related hydroquinone complexes. Based on spectroscopic data, the change of electron density on the $Cr(CO)_3$ unit will be analysed with repect to the observed lability of some of the coordinated arene ligands. Possible applications for these complexes will also be outlined.

REDOX CHEMISTRY AND SMALL MOLECULE ACTIVATION WITH PARAMAGNETIC CHROMIUM ALKYLS

Barbara J. Thomas, Darrin S. Richeson, Klaus H. Theopold, Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853, USA.

A great variety of paramagnetic alkyl complexes of chromium(III) have been prepared in our laboratory and their reactivity has been investigated. More recently, we have used these compounds as starting materials for chromium alkyls in other oxidation states (see below for an example).



The products of reductions as well as oxidations of several Cr(III) precursors will be descibed. The reactions of these new compounds with small molecules (e.g. alkenes) will also be discussed.

OXIDATIVE ELECTROCHEMISTRY OF THE COMPOUNDS $[MCp_2HX]$ (M=Mo(IV); W(IV), X=H,Cl,Br,SMe).

A.R. Dias, M. Helena Garcia, M. Paula Robalo and C.C. Romão
Centro de Química Estrutural, I.S.T. 1096 Lisboa Codex.

The oxidative electrochemistry of the compounds $[MCp_2X_2]$ (M=Mo(IV), W(V); X=halide or thiolate, had been examined previously (1), by cyclic voltammetry and coulometry.
In order to explore the electrochemical behaviour of this general family of compounds and to understand their reactivity we have extended these studies to the compounds $[MCp_2HX]$ (X=H,Cl,Br,SMe), which results we report on this communication.

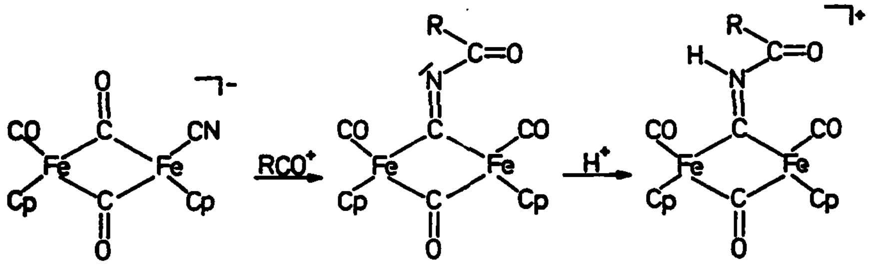
(1) J.C. Kotz, W. Vining, W. Coco, R. Rosen, A.R. Dias and M.H. Garcia
Organometallics, 68-79 (1983).

ACYLISOCYANIDE METAL COMPLEXES

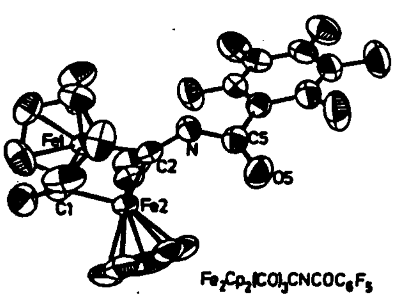
A. Schröder and W.P. Fehlhammer

Institut für Anorganische und Analytische Chemie der Freien
Universität Berlin, D-1000 Berlin 33 (West-Germany)

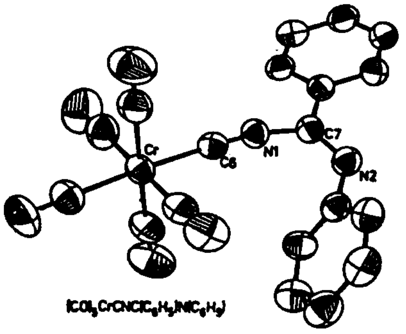
Treatment of cyanometallate anions with acyl- and iminoacyl halides represents a simple approach to functional isocyanide complexes. Terminal acylisocyanide complexes are mild acylating agents, which also add to multiple bonds (e.g. in $R_2N-C{\equiv}C-Ph$). By acylation of the dinuclear cyanoiron species $[Fe_2Cp_2(CO)_3CN]^-$, a variety of new isocyanide bridged compounds has been obtained, which can further be protonated and alkylated.



The spectroscopic properties (ir, nmr, ms, uv) of the compounds will be discussed. Some of their structures have been ascertained by x-ray analysis, e.g.



$Fe_2Cp_2(CO)_3CNCOC_6F_5$

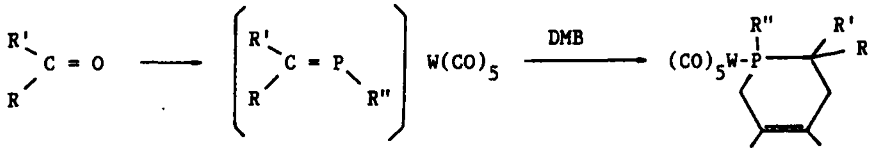


$(CO)_5CrCNC(C_6H_5)NC_6H_5)$

A NEW SYNTHESIS OF PHOSPHAALKENES-$W(CO)_5$ COMPLEXES

Angela Marinetti-Mignani and François Mathey, Laboratoire de Chimie du Phosphore et des Métaux de Transition.
Ecole Polytechnique, 91128 Palaiseau Cedex, France.

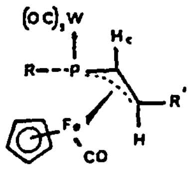
Unhindered phosphaalkene- $W(CO)_5$ complexes are generated at low temperature from carbonyl compounds.
Cycloaddition with DMB is used as trapping reaction to allow an easy characterization of the most unstable complexes.



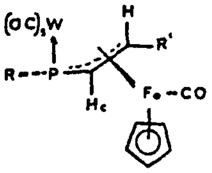
SYNTHESIS OF η^3-PHOSPHAALLYL-MOLYBDENUM AND TUNGSTEN COMPLEXES.

François Mercier, Catherine Hugel-Le Goff and François Mathey, Laboratoire DCPH
Ecole Polytechnique, 91128 Palaiseau Cedex, France

During the last few years numerous phosphorous analogues of classical transition metal π -complexes have been described in the litterature. In this order we have recently described the synthesis and chemical properties of one new type of the class, i.e. the η^3-1-phosphaallyl iron complexes (1).

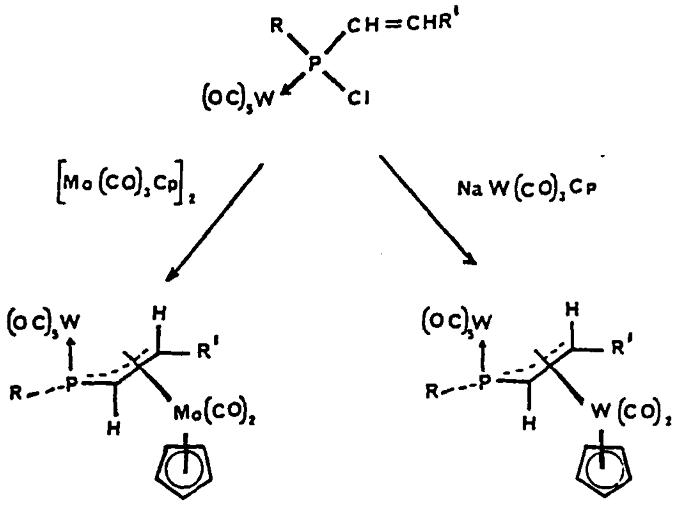


SYN



ANTI

We wish to report here after the synthesis of η^3-1-phosphaallyl-molybdenum and tungsten analogues :



Some aspects of their reactivity will be presented.

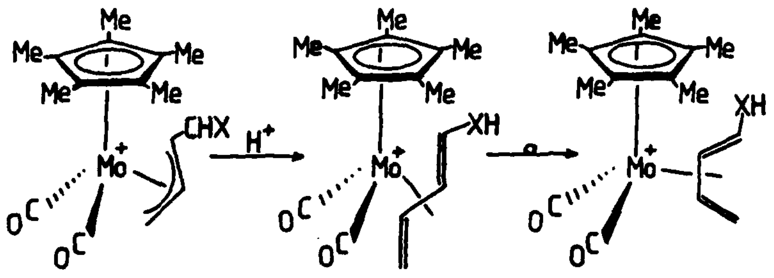
(1) F. Mercier, C. Hugel-Le Goff, F. Mathey. Organometallics to be published.

SYNTHESIS AND PROTONATION OF SUBSTITUTED η^3-ALLYL COMPLEXES OF MOLYBDENUM; EVIDENCE FOR THE INTERMEDIACY OF CATIONIC TRANSOID η^4-1,3-DIENE SPECIES

Stephen A. Benyunes, Michael Green, Michael J. Grimshire, Stanley C. Nyburg, and Adrian W. Parkins, Department of Chemistry, King's College London, Strand, London. WC2R 2LS. UK.

The cationic molybdenum acetonitrile complex $[Mo(NCMe)_2(CO)_2(Cp)]^+[BF_4]^-$ (Cp = η^5-C_9H_7, η^5-C_5Me_5), reacts with 1-methoxy-1,3-cyclohexadiene, yielding the corresponding diene complex. Treatment of the latter with NaOMe results in a facile demethylation, with the isolation in high yield of a neutral oxo-substituted allyl complex. A direct synthesis can likewise be accomplished by the use of 1-trimethylsiloxy-1,3-cyclohexadiene *via* a fluoride-induced desilylation. Similarly, the use of the appropriate acyclic diene allows the preparation of the allyl-aldehyde complex $[Mo(\eta^3\text{-}CH_2\text{-}CH\text{-}CH\text{-}CHO)(CO)_2(\eta^5\text{-}C_5Me_5)]$ [1], which has been characterised by x-ray diffraction. Upon treatment with the Wittig reagent Ph_3PCH_2, complex [1] undergoes selective attack at the aldehyde centre affording the methylene-allyl complex [2].

Complexes [1] and [2] are protonated readily by the strong acids HBF_4 and CF_3SO_3H affording the cationic diene complexes [3] and [4]. Low temperature n.m.r. studies demonstrate the initial adoption by the diene of a transoid conformation, followed by an irreversible isomerisation to the more stable cisoid species (scheme).



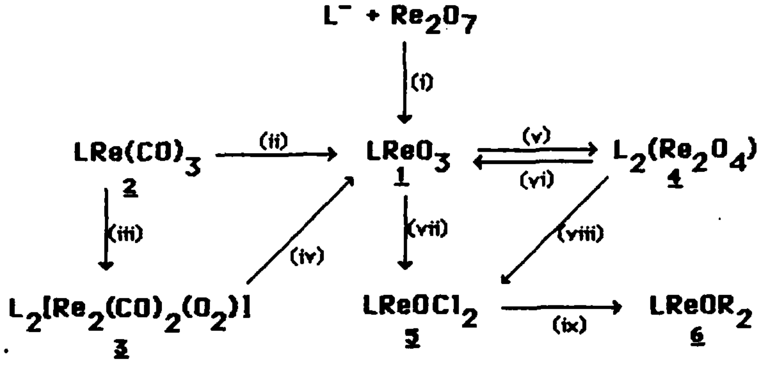
[1],[3], X = O
[2],[4], X = CH_2

NEW ORGANOMETALLIC RHENIUM COMPLEXES CONTAINING THE ANIONIC FAC-TRIPOD ORGANOMETALLIC LIGAND $[\eta\text{-}C_5H_5\{P(O)(OEt)_2\}_3]^-$ (R = C, CH_3]

Enrique Román[1], Sergio Hernández[1], Fernando Tapia[1] and Alan H. Cowley[2].

[1]Facultad de Química. Pontificia Universidad Católica de Chile. P.O.Box 6177.
Santiago-Chile. [2]Department of Chemistry. University of Texas at Austin.
Texas, Austin-78712. United States.

A series of new mono and polynuclear rhenium complexes in low and high oxidation states have been synthetized. In all of them the anionic *fac*-tripod ligand $L^- = [\eta\text{-}C_5R_5\{P(O)(OEt)_2\}_3]^-$ (R = H, CH_3) is facially coordinated to the rhenium metal center. The synthetic route can been described by the scheme.



(i) THF, r.t.; (ii), (iii), (iv) hν, O_2; (v) oxo-abstraction by PR_3;
(vi) O_2; (vii) PR_3, HCl; (viii) HCl; (ix) $(CH_3)_3CCH_2Li$, THF.

X-ray difraction studies for the 1, 2 and 5 rhenium complexes were carried out. Distortional and electronic effects produced by the anionic L^- ligand were correlated with spectroscopical properties. Complexes 6 showed to be potential model for olefine metathesis catalysts *via* the obtained alkylydene complexes 6.

NEW IRON(II) THIOLATES CONTAINING NITROGEN-DONOR LIGANDS.

J.Takacs,E. Soos,Z. Nagy-Magos, L.Marko,Research Group for Petrochemistry of the Hungarian Academy of Sciences, Veszprem, Hungary

G.Gervasio,Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Universita di Torino, Italy

T.Hoffmann,Inorganic Chemistry Division, Humboldt University, Berlin, GDR

Absorption of CO under mild conditions is a useful and convenient method for the preparation of thiolato iron(II) carbonyls from solutions of Fe(II) salts containing the necessary ligands and a base. The compounds synthesized by this method all contain a two-electron donor S-, N-, or P- ligand in addition to the thiolato and CO groups.

Using the same method, several new iron(II) carbonyl complexes containing thiolato and N-donor ligands were prepared.

Two types of complexes were synthesized and characterized: complexes of type A with the general formula $Fe(S^\frown N)_2(CO)_2$ where $(S^\frown N)$ represents a ligand containing a thiolato and an amino group; and complexes of type B having the general formula $Fe(SPh)_2(N^\frown N)(CO)_2$ which contain a bidentate N-ligand $(N^\frown N)$.

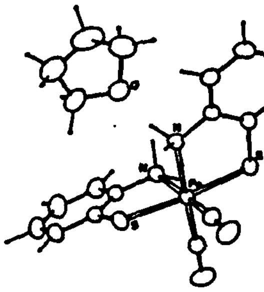
The structures of two representatives were determined by X-ray analysis: $Fe(SC_6H_4NH_2\text{-}o)_2(CO)_2$ for type A and $Fe(SPh)_2(H_2NC_2H_4NH_2)(CO)_2$ for type B (Fig.).

According to the IR spectra the octahedral complexes contain two CO ligands in cis position, while the coordinated N atoms are trans to the CO groups.

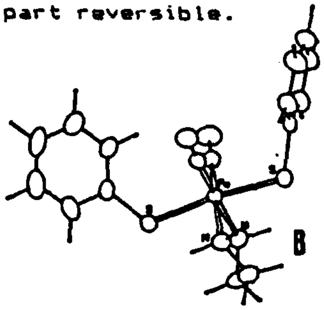
Both molecules possess a C_2 symmetry in the solid state, the twofold axis lying between the two CO and the two NH_2 groups. However, only the molecule of type A remains chiral in solution (owing to the configuration of the chelate rings about the iron atom); the chirality of molecule B in the crystal is only due to the conformation of the chelate ring and will be lost if the compound is dissolved in a solvent.

Complex A crystallizes with one molecule of tetrahydrofuran linked via hydrogen bonds N-H..O to the complex, while the complex molecules are enchained via weak N-H..S bonds.

A necessary condition for the stability of such complexes is the presence of at least one chelating ligand: all the complexes loose CO on heating and this reaction is in part reversible.



A



B

PREPARATION AND CHEMISTRY OF CYCLOPENTADIENYLIRON BIS(PHOSPHANE) LIGAND CATIONS CONTAINING GROUP IVb TO VIb LIGANDS

Hans Schumann, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (USA)
L. Eguren and Manfred L. Ziegler, Anorganisch-Chemisches Institut der Universität Heidelberg, D-6900 Heidelberg 1 (FRG)
Arnold L. Rheingold, Department of Chemistry, University of Delaware, Newark, Delaware 19716 (USA)

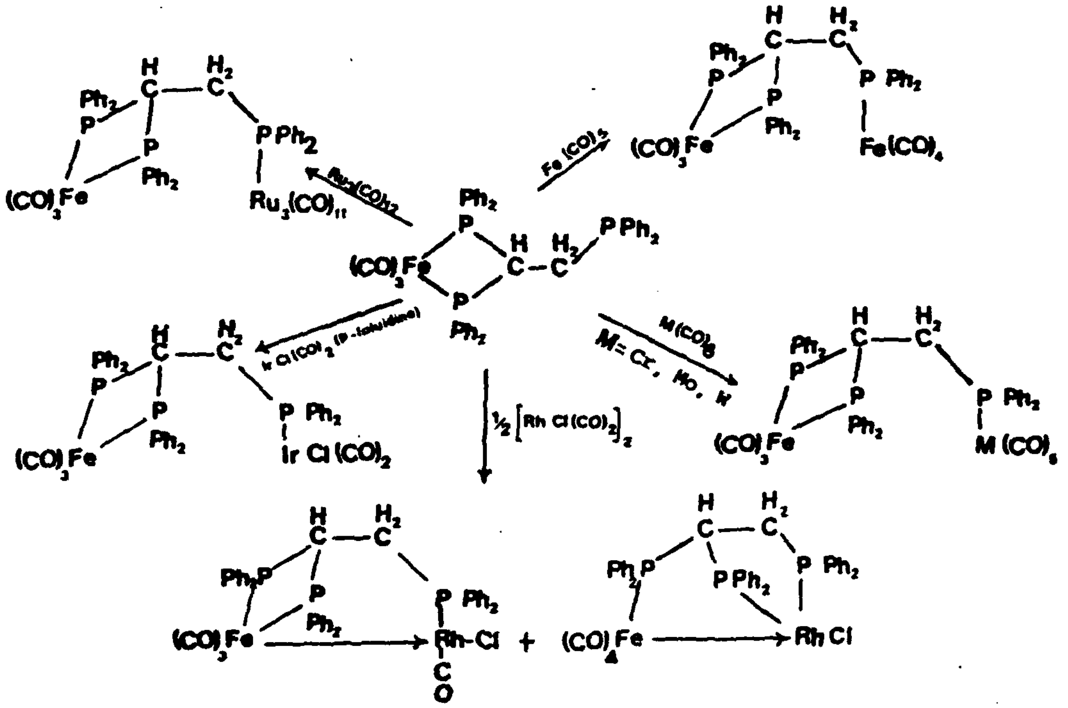
The photochemical substitution of the coordinated arene ligand in $[C_5H_5Fe(\eta^6 - p\text{-}(CH_3)_2C_6H_4)]PF_6$ in acetonitrile solution in the presence of two equivalents of phosphanes PR_3 afford complexes of the general type $[C_5H_5Fe(PR_3)_2(NCCH_3)]PF_6$ in high yield and purity. Due to the lability of the coordinated nitrile ligand,substitution reactions with donor/ akzeptor ligands containing group IVb to VIb centers afford electronrich complexes of the type $[C_5H_5Fe(PR_3)_2(L)]PF_6$ in high yield.

The reactivity of selected complexes towards ligand displacement and modification of the coordinated ligand will be reported together with the results of spectroscopic investigations including X-ray structure analysis. Obtained results and spectroscopic trends will be discussed in comparison with related investigations in the $[C_5H_5Fe(CO)_2(L)]BF_4$ series.

THE SYNTHESIS OF HETEROMETALLIC COMPLEXES BY USE OF MULTIDENTATE PHOSPHINE LIGANDS

Nagwa Nawar and Anthony K. Smith, Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England.

It has been shown[1] that the coordinated ligand $Ph_2PC(=CH_2)PPh_2$ readily *undergoes* Michael addition type reactions. We have made use of this reaction to synthesise "dangling" phosphine complexes of the type $[M(CO)_n\{\eta^2-(Ph_2P)_2CHCH_2PPh_2\}]$ which provide convenient starting materials for the synthesis of heteronuclear metal complexes. Examples of such complexes are illustrated below:



The syntheses and spectroscopic characterisation of these complexes will be described, together with some of their subsequent thermal rearrangements.

Reference

1. See for example, A.M. Herring, S.J. Higgins, G.B. Jacobsen and B.L. Shaw, J. Chem. Soc. Chem. Commun., 1986, 882.

PHOTOCHEMISTRY OF $M(CO)_3(R\text{-}DAB)(M{=}Fe,Ru)$, A GROUP OF COMPLEXES WITH TWO CLOSE-LYING REACTIVE EXCITED STATES.

Derk J. Stufkens, Hans K. van Dijk and Ad Oskam, Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

The complexes $M(CO)_3(R\text{-}DAB)$ (M=Fe,Ru; R-DAB=1,4-diaza-1,3-butadiene) possess an intense metal to ligand charge-transfer (MLCT) band in the visible region. Irradiation into this band at room temperature in the presence of a nucleophile causes photosubstitution of CO. Flash photolysis shows that this reaction can proceed via loss of CO or by breaking of a Fe-N bond, depending on the substituent R.

When the complexes $Fe(CO)_3(R\text{-}DAB)$ with not too bulky substituents R are, however, irradiated into the MLCT band in n-pentane at 150K, a wavelength dependent photochemistry is observed. Irradiation at the high-energy side of the band causes loss of CO and formation of a dimer $Fe_2(CO)_5(R\text{-}DAB)_2$. A completely different photoproduct, $Fe(CO)_3(\eta^4\text{-}R\text{-}DAB)$ is formed upon irradiation at lower energy. In this latter complex the R-DAB ligand has obtained a novel η^4-coordination. Raising the temperature to 200K causes a backreaction of this photoproduct to the starting complex.

Under similar conditions the complexes $Ru(CO)_3(R\text{-}DAB)$ only show the formation of the dimer $Ru_2(CO)_5(R\text{-}DAB)_2$ at all wavelengths of irradiation, whereas the substituted complexes $Ru(CO)_2(R\text{-}DAB)(PR_3)$ only produce the η^4-coordinated R-DAB photoproduct $Ru(CO)_2(\eta^4\text{-}R\text{-}DAB)(PR_3)$. The occurrence of these two, completely different, photochemical reactions is explained in terms of an energy diagram with close-lying reactive ^{3}LF and ^{3}MLCT excited states.[1]

References

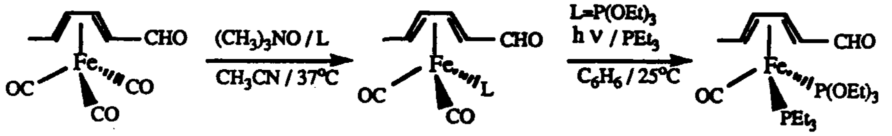
[1] H.K. van Dijk, D.J. Stufkens and A. Oskam, submitted for publication.

SYNTHESIS, STRUCTURE AND CONFORMATIONAL ANALYSIS OF CHIRAL ($Fe(CO)L_1L_2(\eta^4$-DIENE)) COMPLEXES.

L.Solana, C.M. Adams, S.Chimichi, A. Hafner and W. von Philipsborn

Organisch-Chemisches Institut der Universität Zürich, CH-8057 Zürich
(Switzerland)

A versatile method for selective and stepwise carbonyl displacement in acyclic ($Fe(CO)_3$(diene)) and ($Fe(CO)_3$(enone)) complexes by phosphane or phosphite ligands is described. The reactions are applicable to alkyl-substituted and functionalized 1,3-dienes, for example, the sorbic aldehyde complexes 1 and 2 :

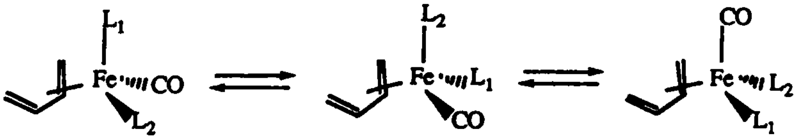


1 2 3

L = $P(OMe)_3$, $P(OEt)_3$, PEt_3, PPh_3

Complexes of type 2 exhibit planar chirality (racemate), those of type 3 a chiral iron centre and a chirality plane (two racemic diastereoisomers). The molecular structure of the predominant racemic diastereoisomer of 3 was determined by X-ray diffraction.

In solution, complexes of type 1, 2 and 3 are fluxional :



and show temperature-dependent ^{13}C-, ^{17}O- and ^{31}P-NMR spectra. The conformational isomers and their relative population were assigned at 180-200K based on ^{13}C and ^{31}P chemical shifts and $^2J(P,P)$ and $^2J(P,C)$ spin coupling data. The structural and spectroscopic results indicate a pronounced stereochemical preference of the iron ligands depending upon ligand size and diene substitution.

SONOCHEMICALLY PROMOTED ACCESS TO NEW ORGANO IRON COMPLEXES.

Patrick Brégaint, Christophe Roger, Jean-René Hamon
and Claude Lapinte, Laboratoire de Chimie des Organométalliques,
UA CNRS 415, Université de Rennes I, 35042 Rennes Cedex, France.

The high intensity ultrasound is a powerful tool in organometallic synthesis. It allows the use of stoechiometric amount of activated reducing reagent (i.e. colloïdal potassium) which improved the chemistry of the formed highly reactivity species. It enhances the reactivity of insoluble transition metal complexes such as $[Fe(C_5Ph_5)(CO)_2]^-K^+$ and it also can be used for generation of transiant zerovalent transition metal intermediates like metal vapor chemistry. These properties are illustrated by the equations 1 and 2 which shown the synthetic interest of ultrasound to developp new reactions.

$$\underset{\underline{1}}{Fe(C_5Ph_5)(CO)_2Br} + 2\ K \xrightarrow{20\ kHz} \underset{\underline{2}}{[Fe(C_5Ph_5)(CO)_2]^-K^+}$$

eq. 1

$$\underline{2} + CH_3CH_2I \xrightarrow{20\ kHz} \underset{\underline{3}}{Fe(C_5Ph_5)(CO)_2CH_2CH_3}$$

$$\underset{\underline{4}}{FeCl_2(\overset{\frown}{P\quad P})} + 2\ K \xrightarrow[C_5Me_5H]{20\ kHz,\ 50°C} \underset{\underline{5}}{Fe(C_5Me_5)(\overset{\frown}{P\quad P})H}$$

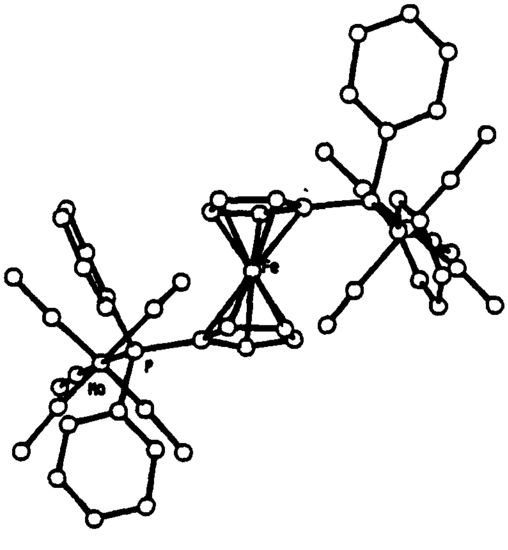
eq. 2

$\overset{\frown}{P\quad P}$: $Ph_2P-CH_2CH_2-PPh_2$

1,1'-BIS(DIPHENYLPHOSPHINO)FERROCENE AS A BRIDGING LIGAND IN HETEROBINUCLEAR ORGANOMETALLIC COMPLEXES

Olli Orama and Jukka Hietala, Department of Inorganic Chemistry,
University of Helsinki, Vuorikatu 20, SF-00100 Helsinki, Finland

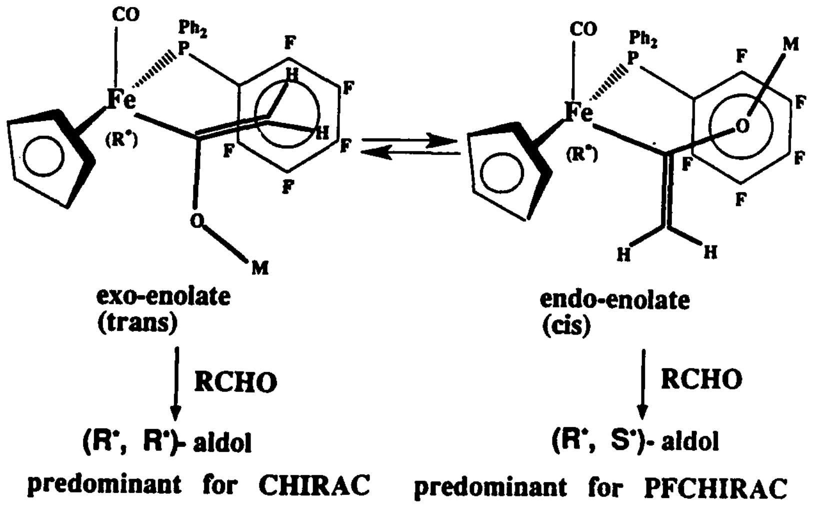
In recent papers we have studied binuclear diphosphine-bridged complexes formed by bis(diphenylphosphino)acetylene and L_nM (L_nM=Cp(CO)$_2$Mn; (CO)$_5$Cr; (CO)$_5$Mo; (CO)$_5$W). In this work we use ferrocene instead of acetylene to yield heterobimetallic trinuclear complexes with the hope to get complexes with unusual catalytic properties. The preparation of transition metal complexes of type $[Fe(C_5H_4PPh_2)_2][L_nM]_2$ using organothallium compounds as intermediates is described. The compounds are fully analyzed and the crystal structure of bis[η^5-(pentacarbonyl-molybdenum)diphenylphosphinocyclopentadienyl]iron has been determined from X-ray diffraction data.



Remarkable Effects of a Pentafluorophenyl Group on the Stereoselective Reactions of a Chiral Iron Acyl Complex

Iwao Ojima and Hyok Boong Kwon
Department of Chemistry, State University of New York
at Stony Brook, Stony Brook, New York 11794, U.S.A.

A novel chiral iron acyl complex, [(C_6F_5)Ph_2P](CO)CpFe-COMe (PFCHIRAC), is synthesized. The stereoselective aldol and imine condensation reactions with benzaldehyde and benzylideneaniline using the lithium, tin, aluminum, and copper enolates of PFCHIRAC are studied. The reactions give (R*,S*)-products regardless of the metal enolate species with high stereoselectivities (89 - 99% d.e.). The observed unique stereo-differentiation is rationalized based on an electron donor - acceptor type attractive interaction between the pentafluorophenyl moiety and the enolate oxygen. The variable temperature NMR (^1H, ^{19}F, ^{31}P) study of the dynamic behavior of PFCHIRAC strongly supports the rationale.

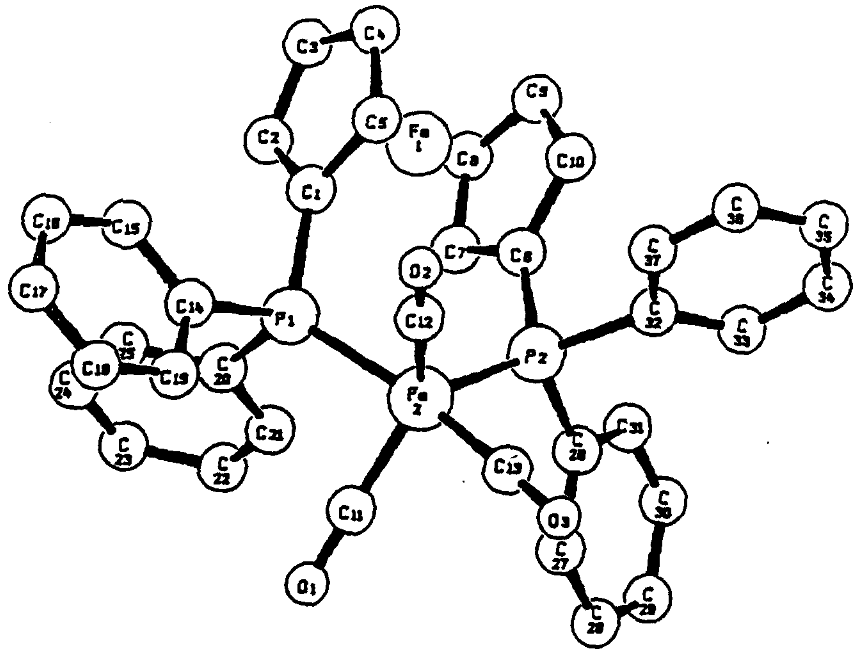


SYNTHESIS AND STRUCTURE OF (1,1'-BIS(DIPHENYLPHOSPHINO)FERROCENE)TRICARBONYLIRON(0), (FDPP)Fe(CO)$_3$

Ling-Kang Liu*, Show-Kei Yeh, and Chu-Chieh Lin
Institute of Chemistry, Academia Sinica
Nankang, Taipei, Taiwan 11529 ROC

(Fdpp)Fe(CO)$_3$ has been prepared by the reaction of 1,1'-bis-(diphenylphosphino)ferrocene and (maleic acid)tetracarbonyliron(0) as firstly attacked by trimethylamine-oxide. The structure of (fdpp)Fe(CO)$_3$ has been studied with ir, nmr, and x-ray diffraction.

Crystals of (fdpp)Fe(CO)$_3$ crystallize in the monoclinic space group $P2_1/c$ with cell constants a 9.710(3), b 16.162(9), c 19.910(5) A, and β 95.78(2) deg. The x-ray diffraction studies have resulted in a final R 0.036 for 2416 reflections. The two cyclopentadienyl moieties are staggered. The coordination geometry around the tricarbonyl Fe is a distorted trigonal bipyramid with one P occupying the equatorial site and the other P axial. The P-Fe-P angle is 99.88(7) deg. The ferrocenyl Fe still holds its sandwiched position. There is no direct Fe-Fe interaction.



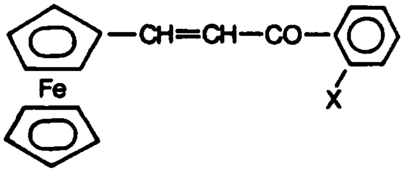
330

FERROCENES STUDIED BY ^{13}C NMR AND CYCLIC VOLTAMMETRY

Ágnes G.Nagy, Chemistry Department, Central Research Institute for Physics, 1121 Budapest,Hungary

Pál Sohár, EGIS Pharmaceuticals, Spectroscopic Department, POB 100, 1475 Budapest,Hungary

Ferrocene analogues of chalcone substituted in the ortho position /1/ were prepared and investigated by ^{13}C NMR and cyclic voltammetry. The change in the oxidation potential of the ferrocenyl group and the changes of the electron densities at the carbon atoms in the molecules caused by the substituens are presented and the inramolecular interactions are discussed. A comparison of these effects in the ortho- and para-substituted series is also given.

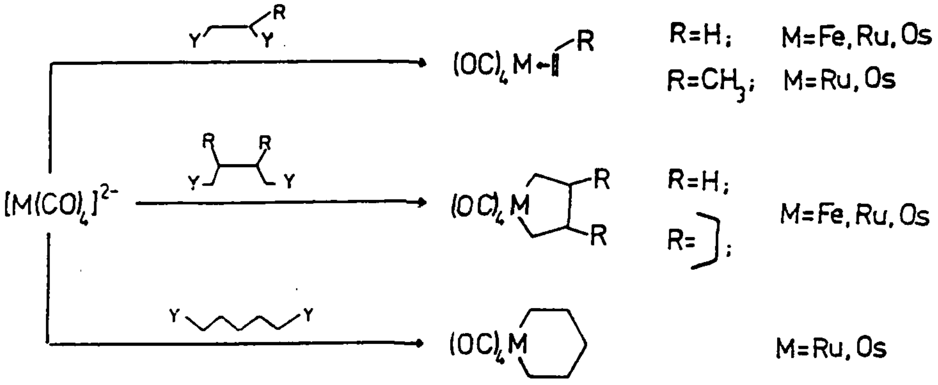


1

A Simple Route to Ruthena- and Osmacycloalkanes

Rolf-Michael Jansen and Ekkehard Lindner*, Institut für Anorganische Chemie der Universität, Auf der Morgenstelle 18, D-7400 Tübingen, West- Germany

For lack of suitable synthetic methods, only few mononuclear carbonyl complexes of the iron triad, containing metall-carbon-σ-bonds, are known. By using the nucleophilic elimination cycloaddition method we found a simple route to these systems[1,2].
Reaktion of $[M(CO)_4]^{2-}$ (M = Fe, Ru, Os) with α, ω-alkanediyl-bis(trifluoromethanesulfonates) yields three- to six-membered metallacycles.



The ring systems show the expected reactivity. Thermal decomposition results in the formation of the corresponding alkenes and alkadienes. Formal insertion of CO in one of the M-C bonds, followed by reductive elimination of the metal fragment, yields cyclic ketones.

References:

1) E. Lindner, E. Schauß ,W. Hiller and R. Fawzi, Angew. Chem. Int. Ed. Engl. **23**, 711 (1984).
2) E. Lindner, R.-M. Jansen and H. A. Mayer, Angew. Chem. Int. Ed. Engl. **25**, 1003 (1986).

Alkene Complexes of Ruthenium(0): Photochemical Alkene Hydrogenation

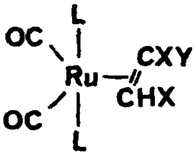
Jonathan Vessey, Michael Whittlesey and Roger Mawby

Department of Chemistry, University of York, York YO1 5DD, England

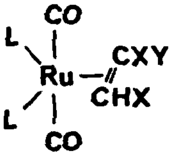
We have prepared alkene complexes of ruthenium(0), $[Ru(CO)_2(CHX{=}CXY)(PMe_2Ph)_2]$, where X = CO_2Me or CN, Y = H or Cl:

(i) by rearrangement of vinyl hydride complexes $[Ru(CO)_2(CX{=}CXY)H(PMe_2Ph)_2]$,
(ii) by displacement of H_2 from $[Ru(CO)_2H_2(PMe_2Ph)_2]$,
(iii) by displacement of ethene from $[Ru(CO)_2(C_2H_4)(PMe_2Ph)_2]$.

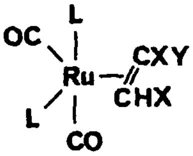
Detailed n.m.r. studies have indicated three stereochemistries for these complexes (shown below, where L = PMe_2Ph):



(1)



(2)



(3)

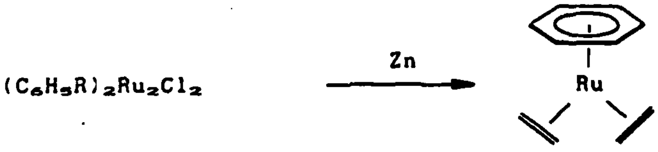
The relative energies of (1), (2) and (3), and the energy barriers for their interconversion, appear to be very sensitive to the nature of X and Y.

We are currently studying the photochemical reactions of the alkene complexes and their vinyl hydride precursors. In C_6D_6 solution and in the absence of free H_2, $[Ru(CO)_2\{CH(CO_2Me){=}CH(CO_2Me)\}(PMe_2Ph)_2]$ yields the hydrogenated product $MeO_2CCH_2CH_2CO_2Me$ under irradiation, with concurrent formation of a new organo-ruthenium complex.

REACTIONS OF ARENE-RUTHENIUM BISOELFIN COMPLEXES

Richard S. Bates and Anthony H. Wright, Department of Chemistry,
University of Nottingham, Nottingham, NG7 2RD, U.K.

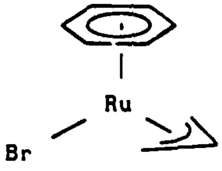
Arene ruthenium bisolefin complexes (I) can be made in high yield utilising low-temperature ultrasound. The reaction appears to be general for different types of aromatic and for a range of different olefins. The scope of the reaction will be described.



(I)

These complexes are highly reactive, undergoing both substitution and oxidative addition reactions. When simple CO substitution reactions are carried out, products involving arene loss are isolated. However with other substitution reactions, complexes of the form (arene)RuL$_2$ may be isolated.

The bisolefin complexes are particularly suitable for oxidative addition reactions that generate four-electron donor ligands. Thus the addition of allylbromide generates the new series of air sensitive complexes (arene)RuBr(allyl) (II). These and other products of oxidative addition reactions will be described.



(II)

COMPARATIVE STUDY OF THE BIDENTATE PHOSPHINE LIGANDS BIS(DIPHENYLPHOSPHINO)METHANE (DPPM) AND 1,1-BIS(DIPHENYLPHOSPHINO)ETHENE (DPPEE) WITH COMPLEXES OF METAL CARBONYLS

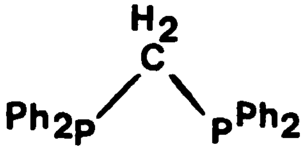
RICHARD H. DAWSON AND ANTHONY K. SMITH

DEPARTMENT OF INORGANIC. PHYSICAL AND INDUSTRIAL CHEMISTRY.
UNIVERSITY OF LIVERPOOL.
P.O. BOX 147,
LIVERPOOL. L69 3BX.
UNITED KINGDOM.

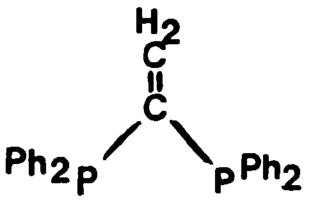
The use of multidentate phosphine ligands to stabilise and to provide sites of reactivity in homo- and hetero- metallic species is well known.

Studies comparing and contrasting such ligands are rare. We report a comparative study of bis(diphenylphosphino)methane and 1,1-bis(diphenylphosphino)ethene in reactions with mono-, bi- and tri-metallic complexes of iron, ruthenium, osmium and rhodium.

Examples of some of the complexes to be discussed include:
$Fe(CO)_3(L\text{-}L)$, $M_3(CO)_9(L\text{-}L)_2$ (M = Ru and Os) and
$Rh_2(\mu\text{-}CO)Cl_2(L\text{-}L)_2$.



DPPM



DPPEE

REACTIVITY PATTERNS OF DINUCLEAR DIPHOSPHAZANE LIGAND BRIDGED DERIVATIVES OF COBALT

John S. Field, Raymond J. Haines and Lesley A. Rix, U.N./C.S.I.R. Research Unit of Metal Cluster Chemistry, Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg 3200, Republic of South Africa.

Dinuclear diphosphazane ligand bridged derivatives of cobalt of the type $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ (R = Me or Pr^i) are electron-rich and, as such, are susceptible to electrophilic attack. Reactions with I_2, CBr_4 and CCl_4 in toluene lead to loss of CO and formation of the halogeno-bridged species $[Co_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2\{\mu\text{-}(RO)_2\text{-}PN(Et)P(OR)_2\}_2]^+$ (R = Me or Pr^i; X = I, Br or Cl). These cations are readily reduced by BH_4^- to afford essentially two neutral products which spectroscopic measurements indicate to be $[Co_2(CO)_4\text{-}\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ and the dihydrido species $[Co_2H_2(\mu\text{-}CO)(CO)_2\text{-}\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$. Reaction of $[Co_2(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P\text{-}(OMe)_2\}_2]$ with CCl_4 in methanol (rather than toluene) in the presence of BPh_4^- gives the salt $[Co(CO)_2\{P(OMe)_3\}_2\{(MeO)_2PN(Et)P(OMe)_2\}][BPh_4]$ as confirmed X-ray crystallographically. Significantly, the cation is mononuclear with two $P(OMe)_3$ ligands, as well as a pendant diphosphazane ligand, bonded to the cobalt atom. Presumably, the $P(OMe)_3$ ligands derive from chlorine radical attack at the phosphorus atom of a diphosphazane ligand resulting in fission of the P-N bond and formation of $P(OMe)_2Cl$; the latter is then attacked by methoxide ions to give the $P(OMe)_3$ ligand. Protonation of $[Co_2(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]$ using HPF_6 in methanol, or even methanol alone, proceeds rapidly and quantitatively to give the bridged hydrido species $[Co_2(\mu\text{-}H)(CO)_4\{\mu\text{-}(RO)_2PN(Et)P(OR)_2\}_2]^+$ R = Me or Pr^i) the structure of the BPh_4^- salt having been determined X-ray crystallographically.

SYNTHESIS AND REACTIVITY OF VINYLIDENE-, KETENIMIN- AND AZACARBENE(RHODIUM)-COMPLEXES

U. Brekau and H. Werner

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg

The paper describes the synthesis of monomeric, halfsandwich-type vinylidene(rhodium) compounds $(C_5H_5)(PPr^i_3)Rh(=C=CHR)$ with bulky and strongly electron withdrawing substituents at the vinylidene ligand ($R={}^tBu$, CO_2CH_3).

Via cycloaddition reactions of these compounds with organic azides ($R'N_3$), the corresponding η^2-N,C ketenimin complexes $[Z]-(C_5H_5)(PPr^i_3)\overline{RhC(CHR)N}(R')$ are obtained which are useful precursors for cyclic azacarbene(rhodium) derivatives $[(C_5H_5)(PPr^i_3)\overline{RhC(CH_2R)N}(R')]BF_4$. In addition, a stereoselective η^2-N,C to η^2-C,C rearrangement of the ketenimin(rhodium) compounds will be reported.

BIMETALLIC RODIUM (1) COMPLEXES OF FLUORINATED THIOLATE LIGANDS.

D.Cruz-Garritz, J. García Alejandre and H. Torrens Miguel
Departamento de Química Inorgánica, División de Estudios de Posgrado,
Facultad de Química, Universidad Nacional Autónoma de México,
Cd. Universitaria, México, D.F. C.P. 04510

The syntheses and characterization of new rhodium (I) bimetallic compounds of the type $[Rh(\mu\text{-}SRf)(COD)]_2$ are presented. The - complexes were prepared by metathetic reaction of $[Rh(\mu\text{-}Cl)(COD)]_2$, where COD = cyclooctadiene, with M(SRf)n where M = Pb, n =2 and SRf = $p\text{-}HC_6F_4S^-$, $p\text{-}FC_6H_4S^-$, $C_6F_5S^-$ or M = Ag, n = 1 and SRf = CF_3S^-. Because of the relevance of these species to a number of catalytic processes, their reactivity pathways towards triphenlphosphine and carbon monoxide has been examined in detail, stablishing significant diferences that can be related to the basicity of the fluorinated pseudohalides and of the (phosphine/dimer) ratio employed. The complexes $[Rh(\mu\text{-}SRf)(CO)_2]_2$; $[Rh(\mu\text{-}SRf)(P\phi_3)(CO)_2]$; $[Rh(SRf)(P\phi_3)(CO)_2]$ and $[Rh(SRf)(P\phi_3)(COD)]$ were isolated.

These compounds were characterized by the usual spectroscopic techniques, the molecular "bend" structures of $[Rh(\mu\text{-}SC_6F_5)(COD)]_2$, $[Rh(\mu\text{-}SC_6F_4H)(COD)]_2$ and $[Rh(\mu\text{-}SC_6H_4F)(CO)_2]_2$ as shown by X ray diffraction will be discussed.

A prelimary study of the behavior of the complexes $[Rh(\mu\text{-}SRf)(COD)]_2$ on olefine hidrogenation reactions is also presented.

VOLTAMMETRIC BEHAVIOUR OF $[Cr(HCOOH)]^{+2}$

J. Szynkarczuk, I. Drela, J. Kubicki
Institute of Inorganic Technology and Mineral Fertilizers,
Technical University of Wrocław, Wybrzeże Wyspiańskiego 27,
50-370 Wrocław, POLAND

Electrochemical reduction of the complex cations $[Cr(H_2O)_6]^{+3}$ and $[Cr(HCOO)]^{+2}$ in 0.5 M solution of sodium perchlorate (supporting electrolyte) was investigated.

Voltammetric behaviour of prepared complex indicates that at pH = 4.0 there are two cathodic peaks corresponding to the following processes:

$$[Cr(H_2O)_6]^{+3} + e = Cr^{+2} + 6H_2O \qquad (1)$$

$$[Cr(HCOO)]^{+2} + e = [Cr(HCOO)]^{+} \qquad (2)$$

It was noticed that with the increase of the scan rate, peaks potentials move towards more negative values. Cyclic voltammetry of $[Cr(HCOO)]^{+2}$ on hanging mercury drop electrode shows that there are no anodic peak corresponding to the cathodic ones. Anodic process: $Cr^{+2} + 6H_2O = [Cr(H_2O)_6]^{+3} + e$ is observable in the values *ca* -0.40 V (referred to Ag/AgCl electrode). These experimental facts prove that reduction of cations is totally irreversible in both cases.

Some electrokinetic parameters were calculated:

	reaction (1)	reaction (2)	dimension
transfer coefficient	0.42	0.59	
Tafel coefficient	0.14	0.10	V
peak potential (v=0.1 V/s)	-1.15	-1.47	V
half-peak potential	-1.18	-1.41	V
diffusion coefficient	$6.5 \cdot 10^{-6}$	$3.3 \cdot 10^{-6}$	cm^2/s
standard rate constant (calc. at half-peak potential)	$4.5 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	cm/s

THE MECHANISM OF OXIDATION OF 2-HYDROXYCYCLOHEXYL RADICAL TO CYCLOPENTANECARBALDEHYDE BY COPPER IONS IN AQUEOUS SOLUTIONS.

Mohamed Masarwa, Haim Cohen and Dan Meyerstein
Nuclear Research Centre Negev, R. Bloch Coal Research Center and
Chemistry department Ben-Gurion University of the Negev, Beer-Sheva.

Copper ions are known to change the reaction course of the oxidation of cyclohexene by peroxydisulphate. It has been suggested that this change is due to the selective oxidation of 2-hydroxycyclohexyl radicals by copper(II) to yield cyclopentanecarbaldehyde. We decided to study the detailed mechanism of this reaction by the pulse-radiolysis technique.

2-Hydroxycyclohexyl radicals, produced by the addition of hydroxyl free radicals to cyclohexene, were reacted with Cu^{2+}_{aq} and Cu^{+}_{aq} ions in aqueous solutions. Surprisingly enough it was found that Cu^{2+}_{aq} ions react only slowly with the free radicals. On the other hand Cu^{+}_{aq} react with 2-hydroxycyclohexyl radicals with a rate approaching the diffusion controlled limit. The product of the latter reaction, (I) , rearranges in a process obeying a first order rate law into a second short lived intermediate, (II). The absorption spectrum of (II) indicates that the copper-carbon bond was maintained in the rearrangement process. The intermediate (II) decomposes in a process obeying a first order rate law to form the final products. The rate of both first order processes is independent of $[Cu^{2+}_{aq}]$ and $[Cu^{+}_{aq}]$. Cyclopentanecarbaldehyde is quantitatively formed in this reaction sequence. A detailed mechanism for these reactions is proposed and discussed.

340

ORGANOMETALLIC PHOTOCHEMISTRY IN SUPERCRITICAL FLUIDS

Steven M Howdle, Martyn Poliakoff, Michael A. Healy
and John M. Whalley
Department of Chemistry, University of Nottingham,
Nottingham, England NG7 2RD

Supercritical fluids have exciting advantages over conventional solvents as media for photochemical processes, particularly those involving reactions between gases and relatively involatile materials. Supercritical Xe (T_c 16.9°C, P_c 59 atm.) has the added benefit of total spectroscopic transparency from far ultra-violet to far infra-red. Unfortunately, the high pressures associated with supercritical fluids have prevented their use outside highly specialised laboratories. However, many of the the hazards of working with high pressure gases are reduced greatly by use of a cell with a very small internal volume.

In this poster, we describe the construction of such a miniature high pressure cell for spectroscopy and photochemistry in supercritical fluids close to room temperature. The stainless steel cell (internal volume <1ml, CaF_2 windows) has maximum operating pressure of 250 atm. and a maximum temperature of 100°C. The cell is magnetically stirred and can be used with fluids such as Xe, CO_2 , C_2H_4 , C_2H_6 and SF_6.

We illustrate the use of the cell by describing the photochemical reactions of transition metal carbonyl complexes with H_2 which generate complexes containing "non-classical" n^2-H_2 ligands. Such complexes are often thermally unstable but we have already shown that their lifetimes can be extended by increased pressures of H_2 [1]. The effect is particularly dramatic in supercritical Xe because the concentration of dissolved H_2 is much higher than in a conventional solvent under similar conditions. We present results of kinetic and spectroscopic measurements on compounds such as (n-toluene)$Cr(CO)_2(H_2)$ or (n-C_5H_5)$Mn(CO)_2(H_2)$. These compounds are stabilised sufficiently in supercritical fluids to be studied at temperatures in excess of 80°C with a conventional IR spectrometer.

[1] RK Upmacis, GE Gadd, M Poliakoff, MB Simpson, JJ Turner, R Whyman and AF Simpson, J. Chem. Soc. Chem. Commun. (1985) 27.

REACTIVITY OF THE TRANSITION METAL CARBONYLS IN THE SUBSTITUTION REACTIONS WITH CARBON-HALOGEN AND ELEMENT-HYDROGEN BOND FISSION.

Rashid Gasanov and Anna Tumanskaya, A.N.Nesmeyanov Institute of Organo-element Compounds, USSR Academy of Sciences, 28 Vavilov Str., II78I3 Moscow, U.S.S.R.

EPR-spectroscopy has been applied to determine rate constants of halogen abstraction from R-Hal(R=alkyl,allyl,aryl) by metal carbonyl radicals $\dot{Re}(CO)_5$, $\dot{Mn}(CO)_5$, $C_5H_5\dot{W}(CO)_3$, $C_5H_5\dot{Mo}(CO)_3$ and coordinatively unsaturated $Cr(CO)_5$-particles. In accordance with the rate constant values of halogen abstraction from mono-, di-, tri- and polyhalogen containg compounds found the reactivity of metal carbonyls in the substitution reaction proceeding with carbon-halogen bond rupture increases in the series:

$$Re_2(CO)_{IO} > Mn_2(CO)_{IO} \approx Cr(CO)_5 > /C_5H_5W(CO)_3/_2 \approx /C_5H_5Mo(CO)_3/_2$$

Halogen containing compounds replacing each other, a symbatic change of rate constants of halogen abstraction for different acceptors studied was observed.

The rate constants of hydrogen abstraction from trietylsilane were determined by the analogous procedure and the following order of metal carbonyls activity in $(C_2H_5)_3Si$-radicals generation is displayed:

$$Re_2(CO)_{IO} > Mn_2(CO)_{IO} \approx /C_5H_5W(CO)_3/_2 > /C_5H_5Fe(CO)_2/_2$$

342

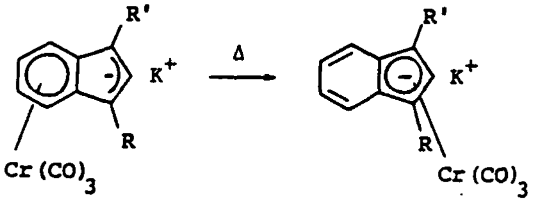
THE MIGRATION OF THE $Cr(CO)_3$ GROUP FROM THE SIX- TO THE FIVE-MEMBERED RING IN SOME POTASSIUM INDENYLS IN THF.

Alberto Ceccon, Alessandro Gambaro, Saverio Santi
Dipartimento di Chimica Fisica, Via Loredan 2, PADOVA

Alfonso Venzo
Centro Studi Stati Molecolari Radicalici Eccitati del CNR,
Via Loredan, 2 - 35131 PADOVA (Italy)

The $\eta^6 \rightarrow \eta^5$ haptotropic migration occurring in the $Cr(CO)_3$ complexed fluorenyl anion has received much attention in the near past [1]. In contrast, despite a theoretical study on the iso-lobal cyclopentadienyl-iron complex [2], no experimental details have been published up today for the $Cr(CO)_3$ migration in the indenyl system.

In this communication we report the generation, the IR and the ^1H NMR spectra of some η^6-(R,R'-indenyl)-$Cr(CO)_3$ anions in THF. At T > 253 K the $Cr(CO)_3$ group migrates from the six- to the five-membered ring:



R = R' = H, Ph
R = H, R' = Ph

The kinetics have been followed by both ^1H NMR and IR spectroscopies, and the data obtained suggest that the haptotropic rearrangement occurs through a peripheral pathway.

---

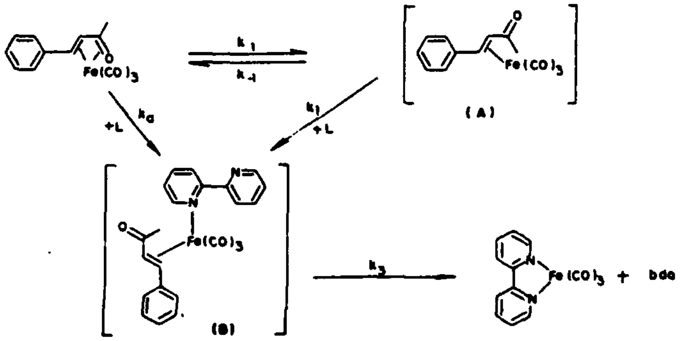
[1] A.Ceccon, A.Gambaro, A.Venzo, V.Lucchini, T.E.Bitterwolf, J.Shade, J.Orgamometal.Chem., 327(1987)55 and ref. therein

[2] T.A.Albright, et al., J.Amer.Chem.Soc., 105(1983)3396

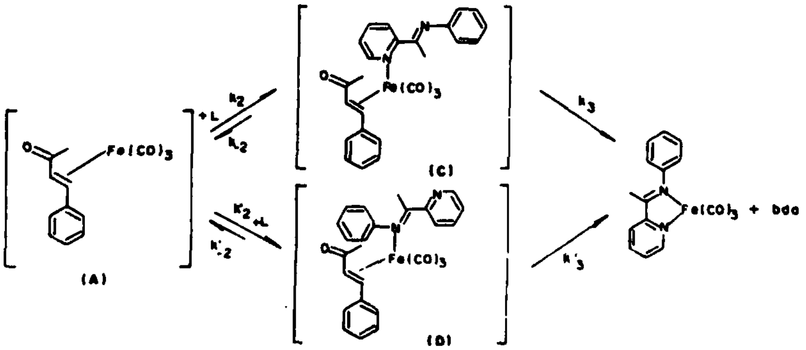
KINETICS OF THE BENZYLIDENEACETONE (bda) LIGAND SUBSTITUTION IN THE |Fe(bda)(CO)$_3$| COMPLEX BY DIIMINES

Edison Stein, Fatima Squizani Livotto and Eduardo J.S. Vichi, Instituto de Química, Universidade Estadual de Campinas, C.P. 6154 - Campinas, SP, Brazil

The kinetics and mechanism of the benzylideneacetone substituition in the title complex by 2,2'-bipyridyl and 2-acetylpyridineanil have been studied. The reactions were followed by I.R. spectroscopy by monitoring the sharpest νC≡O band of the Fe(CO)$_3$ group in both the reagents and products. The mechanism depends on the incoming ligand. For bipy, the reaction occurs via two concurrent paths, an associative (Id) and a dissociative (D):



For the assimetric 2-acetylbipyridineanil, only the dissociative path is observed. Both nitrogen atoms of the incoming ligand can bind to the 16-electrons intermediate (A) leading to intermediates C and D:



The kinetics results and the mechanism will be discussed in terms of the eletronic an steric properties of the attaching ligands.

ADDITION OF ACRYLONITRILE TO ANIONIC TRANSITION METAL HYDRIDES

Marcetta Y.Darensbourg[a], Barbara Floris[b], and Kay A.Youngdhal[a]

(a) Department of Chemistry, Texas A & M University, College Station,77843 USA
(b) Dipartimento di Chimica, Università "La Sapienza", I-00185 Roma, Italy.

The insertion of olefins into transition metal-hydrogen bond - a reaction postulated as an intermediate step in catalytic processes involving chemical modification of olefins (1) - may be investigated with suitable model reactions. The reactivity of $HCr(CO)_5^-$ PPN^+ indicated a predominant hydride transfer character with polar organic substrates (2) and therefore it was a promising system for investigating the behaviour of selected alkenes.

PPN^+ $HCr(CO)_5^-$ added to acrylonitrile used in excess, in THF as the solvent, at room temperature, and under a nitrogen atmosphere, to yield PPN^+ $CH_3CH(CN)Cr(CO)_5^-$ (3) quantitatively.

Some acrylonitrile oligomers were isolated, but blank experiments ruled out the possibility that the addition product is an intermediate in the polymerization process.

A radical process can be excluded, on the basis of the lack of any CIDNP effect. A dissociative process is ruled out by the results of studies on ^{13}CO exchange. At 22°C, ^{13}CO does not exchange with $PPN^+HCr(CO)_5^-$ in THF, either in the absence or in the presence of acrylonitrile, in the time period necessary for the MH^-/alkene reaction to occur.

Second-order kinetics and activation parameters are more consistent with an associative process. The reactivity order of a series of substituted alkenes, $CH_2{=}CH{-}CO_2CH_3 > CH_2{=}CH{-}CN > CH_2{=}CH{-}CONH_2 \gg Ph,CH{=}CH_2$, $CH_2{=}CHOCOCH_3$ (no reaction) is in agreement with a reaction affected by electronic substituent effects on the alkene β-position, thus indicating hydride transfer in the rate-determining step. This hypothesis is supported by the high reactivity of $HCr(CO)_5^-$ with acrylonitrile, when the latter compound is π-coordinated to the $Fe(CO)_4$ moiety.

Work supported by the National Science Foundation (Grant No. CHE 8603664 to MYD).

1. J.Halpern, Science,217, 401 (1982) and references therein.
2. M.Y.Darensbourg et al., J.Amer.Chem.Soc., 107, 2428 (1985).
3. M.Y.Darensbourg, B.Floris, and K.A.Youngdahl, submitted for publication.

STUDY OF ORGANOMETALLIC COMPOUNDS USING AN IMPROVED VERSION OF MOLDRAW GRAPHIC PROGRAM

By **P. Ugliengo**, **G. Borzani** & **G. Gervasio**, Dip. di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Univ. di Torino, **D. Viterbo**, Dip. di Chimica, Univ. della Calabria, Rende (Cosenza), Italy.

MOLDRAW[1] is a program for the graphical manipulation of molecules on personal computers, with no requirement of any non standard hardware. The new features, which have recently been introduced in the program, also thanks to the suggestions of several users, are:

- Use of the coordinate files previously retrieved from the Cambridge Crystallographic Data Base through a simple interface program.
- Faster algorithm to generate the unit-cell content.
- Generation of the neighboring molecules around a given fragment or molecule.
- Adjustable vertical clipping.
- View along the normal to the least-squares plane.
- Stereo red and green view.
- Interactive keyboard controlled labelling of selected atoms for both geometrical calculations and deletion of atoms to generate a fragment.
- Display of the crystallographic atomic labels.
- Interactive keyboard control for continuous rotation along the three principal axes.
- Update of the Buckingham potential parameters for energy calculations.
- Four different ways of displaying van der Waals surface.
- Enantiomorph generation.
- Access to DOS commands without leaving MOLDRAW.

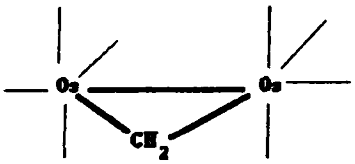
MOLDRAW proved to be extremely useful to study the structural features of mono and polynuclear organometallic compounds. Some selected examples will be shown during the present meeting.

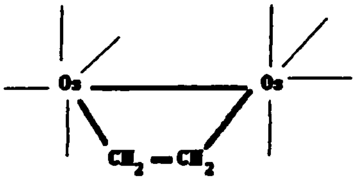
[1] Ugliengo et al., J.Appl.Cryst.(1988), 21, 75.

UV PE Spectra and Electronic Structure of 1,2-Diosmacyclopropane and 1,2-Diosmacyclobutane Complexes.

by Gaetano Granozzi, Renzo Bertoncello
Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova (Italy),
Maurizio Casarin,
Istituto di Chimica dell'Universita' della Basilicata, Potenza (Italy),
Bruce R. Bender, Jack R. Norton
Department of Chemistry, Colorado State University, Fort Collins (USA)
Michael R. Burke and Josef Takats.
Department of Chemistry, University of Alberta, Edmonton (Canada).

The electronic structures of two isolobal analogues of cyclopropane and cyclobutane, $Os_2(CO)_8(\mu\text{-}CH_2)$ and $Os_2(CO)_8(\mu\text{-}C_2H_4)$, (see below) have been investigated by means of gas-phase UV photoelectron (PE) spectroscopy and Discrete Variational Xα MO calculations.





From a comparison between the bonding schemes of the organic and organometallic partners it appears that the "isolobal analogy" reproduces the gross features of the bonding of these molecules but is an oversimplification when a detailed description is attempted. Actually, when both complexes are compared with their organic analogues, the complexes have an additional framework MO with significant Os-C antibonding character. Such a distinct feature is due to the involvement of the t_{2g}-like MOs of the metallic fragment into the interactions within the dimetallacycle. The UV-PE data agree well with the picture arising from the theoretical calculations.

Energetics of Intermediates and Reactions Steps Involved in the Hydroformylation Reaction Catalyzed by $HCo(CO)_4$ .A Theoretical Study Based on the HFS-Method

Louis Versluis and Tom Ziegler
Department of Chemistry ,University of Calgary
Calgary,Alberta,CANADA

The coordinatively unsaturated hydrido-carbonyl $HCo(CO)_3$,as well as the acyl system $CH_3(O)CCo(CO)_3$ and the olefin π-complex $HCo(CO)_3$(olefin) are all postulated intermediates in the hydroformylation reaction,yet little is known experimentally about their structures.We have carried out unconstrained geometry optimizations[1] on all three systems and for each of the three intermediate determined the structures and relative stabilities of all possible conformers .We have found that $HCo(CO)_3$ as its most stable conformation has a butterfly structure with the hydride in the axial position whereas the preferred geometry for $CH_3(O)CCo(CO)_3$ is a butterfly dihapto structure with the acyl-group in an equatorial position .Geometry optimizations will also be presented for $HCo(CO)_4$,$CH_3Co(CO)_4$ and the formyl complexes $H(O)CCo(CO)_3$ and $H(O)CCo(CO)_4$.

The reaction profiles for the migratory insertion reactions

$$RCo(CO)_4 \rightarrow R(O)CCo(CO)_3 \quad , \quad R=H,CH_3 \qquad (1)$$

as well as the olefin insertion reaction

$$HCo(CO)_3\text{-}C_2H_4 \rightarrow CH_3CH_2Co(CO)_3 \qquad (2)$$

has been traced by a linear transit procedure and reaction enthalpies as well as activation barriers evaluated for the processes in Eq.(1) and Eq.(2).It will in particular be shown that the migratory insertion reaction (1) with R=H is unfavorable on thermodynamic as well as kinetic grounds.

[1] L.Versluis and T.Ziegler ,J.Chem.Phys 1988

Thermal Stability and Kinetic Lability of the M-CO Bond.A Theoretical Study Based on Density Functional Theory.

Tom Ziegler and Vincenzo Tschinke
Department of Chemistry ,University of Calgary
Calgary,Alberta,CANADA

Thermochemical data on the M-CO bond,even in basic metal carbonyls such as $M(CO)_6$ (M=Cr,Mo,W); $M(CO)_5$ (M=Fe,Ru,Os) and $M(CO)_4$ (M=Ni,Pd,Pt) are still lacking,and it is not known with certainty how the M-CO bond strength changes through a series of homologous $M(CO)_n$ complexes made up of metals from the same triad.

We have carried out near quantitative calculations on the intrinsic mean bond energy[1] D(M-CO) of $M(CO)_n$ as well as the first CO dissociation energy H(M-CO) for $M(CO)_6$ (M=Cr,Mo,W) ;$M(CO)_5$ (M=Fe,Ru,Os) and $M(CO)_4$ (M=Ni,Pd,Pt) .We find for both D(M-CO) and H(M-CO) the order first row> third row >second row through a triad.This trend will be rationalized in terms of steric and electronic factors as well as relativistic effects.An assessment will also be given of the conflicting experimental M-CO bond strength.

[1] Bond energy between M in its d^n valence state and m CO ligands.

THE SEVEN TOPOLOGICALLY DISTINCT SIX-VERTEX POLYHEDRA IN METAL CARBONYL CLUSTER CHEMISTRY

R. B. King, Department of Chemistry, University of Georgia, Athens, GA 30602, U.S.A.

There are seven topologically distinct six-vertex polyhedra, namely the octahedron, the bicapped tetrahedron, distinct C_s and C_{2v} six-vertex polyhedra having one quadrilateral face and six triangular faces, the pentagonal pyramid, a C_2 six-vertex polyhedron having two quadrilateral and four triangular faces, and the trigonal prism. All of these polyhedra can be shown to play a role in metal carbonyl cluster chemistry. Metal carbonyl clusters based on the octahedron generally exhibit globally delocalized bonding consisting of a six-center core bond as well as surface bonding derived from pairwise overlap of the surface orbitals delocalized throughout the surface leading to a skeletal bonding manifold that may be regarded as topologically homeomorphic to the sphere. Metal carbonyl clusters based on the other six-vertex polyhedra as well as a few metal octahedral clusters exhibit edge-localized bonding consisting of two-center bonds along each of the polyhedral edges. Many examples of octahedral metal carbonyl clusters are known such as $M_6(CO)_{16}$ (M=Co, Rh, Ir) and $Co_6C(CO)_{13}^{2-}$. An important example of a bicapped tetrahedral metal carbonyl cluster is $Os_6(CO)_{18}$. The reactions of alkynes with $RPFe_3(CO)_{10}$ derivatives lead to various PC_2Fe_3 clusters based on the pentagonal pyramid, the C_s six-vertex polyhedron, and the C_2 six-vertex polyhedron. An important example of a trigonal prismatic metal carbonyl cluster is $Co_6C(CO)_{15}^{2-}$. The remaining six-vertex polyhedron, namely the C_{2v} polyhedron having one quadrilateral face and six triangular faces, is a topologically required intermediate in the reduction of bicapped tetrahedral $Os_6(CO)_{18}$ to octahedral $Os_6(CO)_{18}^{2-}$.

Gale transformations can be used to map the vertices of six-vertex polyhedra onto the circumference and the center of a unit circle without losing essential topological information. Six-vertex polyhedral rearrangements can thus be depicted as motions of points on the circumference or between the center and circumference of the unit circle. This approach will be used to depict the following rearrangements in six-vertex metal carbonyl cluster polyhedra: (1) Decarbonylation of the trigonal prismatic $Co_6C(CO)_{15}^{2-}$ to the octahedral $Co_6C(CO)_{13}^{2-}$; (2) Decarbonylation of either the pentagonal pyramidal or the C_2 polyhedral $(\mu_3\text{-}RP)(\mu_3\text{-}R'C)_2Fe_3(CO)_9$ to the C_s polyhedral $(\mu_3\text{-}RP)(\mu_3\text{-}R'C)_2Fe_3(CO)_8$; (3) Reduction of bicapped tetrahedral $Os_6(CO)_{18}$ to octahedral $Os_6(CO)_{18}^{2-}$ through a topologically required C_{2v} six-vertex polyhedral intermediate.

ANALOGY BETWEEN MIXED-METAL CLUSTERS AND MONONUCLEAR TRANSITION METAL PI-COMPLEXES

Aleksander A.Pasynskii, N.S.Kurnakov Institute of General & Inorganic Chemistry, Academy of Sciences of the USSR, Leninsky Pr.31, Moscow V-71, USSR.

To develope the Hoffmann's ideas about the isolobality of organic and organometallic fragments we discussed the next analogies:

1. 3ē donor C_3H_5 allyl ligand and $RCCo_2(CO)_6$triangular fragment.
2. 4ē donor C_4H_4 cyclobutadiene ligand and $Fe_2X_2(CO)_6$ fragment, where X = S,Se,Te and NPh.
3. 5ē donor C_5H_5 cyclopentadienyl ligand and binuclear fragments $Cp_2Cr_2(SCMe_3)(S)_2$ or 1/2 $Cp_2Cr_2S_3$.
4. 7ē donor C_7H_7 cycloheptatrienyl ligand and $Cp_3M_3X_4$ cluster, where M = Cr or Mo, X = O,S,NPh.

The choice of analogous fragment depends on similarity of geometry and spectral properties of mononuclear metal-containing fragment, for example $Mn(CO)_3$, when it bonds with organic ligand or cluster fragment respectively ("key-lock" principle). The original and literature data were used for the predict of the stability, structure, magnetic and redox properties of mixed-metal clusters, and the methods of their planned synthesis. In particular, $Fe_2S_2(CO)_6$ was shown to be 2ē, 4ē or 6ē donor ligand in its complexes with $(PPh_3)_2Pt$, QRh or QFe fragments, respectively, where Q = $Cp_2Cr_2(SCMe_3)(S)_2$.
The chemistry of binuclear antiferromagnetic complex $Cp_2Cr_2(OCMe_3)$ as a model of the active site of the ethylene polimerisation catalyst was shown to be analogous to vanadocene chemistry.

THERMAL DECOMPOSITION OF METAL ALKYLS OF V GROUP ELEMENTS IN THE GAS PHASE

V.A.Yablokov, I.A.Zelyaev, E.I.Makarov, A.V.Dozorov

Building Engineering Institute, Gorky, USSR

The kinetics of thermal decomposition of gaseous metal alkyls have been studied in a static system. The progress of the reaction was followed by measuring the amount of gaseous product formed.

It was established that the pyrolysis rate of these organometallics is a first order reaction. The rate constant was found to be markedly independent on the initial pressure and surface effects.

Temperature dependence on the rate constant (k) for the process was calculated. The Arrhenius equations obtained by squares analysis are $\ln k\ (s^{-1}) = 31{,}1 - 50400/RT$, $\ln k\ (s^{-1}) = 27{,}7 - 41400/RT$ and $\ln k\ (s^{-1}) = 25{,}5 - 29200/RT$ for Et_3As, Et_3Sb and Et_3Bi respectively. These organometallics thermal stability decreases in the order As → Sb → Bi.

The obtained values of activation energies for pyrolysis triethylarsine, triethylstibine and triethylbismuth in fair agreement with $\overline{D}\left[M - Et\right]$ derived from thermochemical data.

The thermal decomposition of arsine alkyls indicated that the pyrolysis rate is dependent upon the ligand nature and changes in the order $Me < Et < n\text{-}Pr$.

BOND DISSOCIATION ENERGIES AND THERMAL DECOMPOSITION SCHEMES OF d-METALS ALKYLAMIDES

Alexei Baev, Victor Mikhailov, Analytical Chemistry Department,
Byelorussian Technological Institute, Sverdlova 13a,Minsk-50,USSR.

Seat of ways permitting to predict the direction of organometallic compounds thermal decomposition process still remains unsatisfaction. The present paper deals with the investigation of energies intramoleculur distribution along $M-NR_2$,N-R and M M bonds as well as the study of d-metals alkylamides fragmentation and thermal decomposition processes. Reliabl values of heat combustion have been determined and standard formation heats of titanium tetradimethyl- and tetradiethylamides have been calculated as a result ofthermochemical investigations. Thermodynamic characteristics of the compounds vaporization process have been found and information about their vapor state have been obtained by static method. Using regular properties changes in related compounds series selected more correct thermodynamic characteristics for d-metalls alkylamides have been chosen and on this basis thermodynamic values for alkylamides not studied yet have been reliabl estimatid by correlation method. Proceeding from intramolecular distribution of energies along bonds in diethylamides of metals considerable influence of coordination endoeffect in the $N-C_2H_5$ has been substatiatid permitted to determine a more correct value of dissociation energy in dinuclear methylamides of molybdenum and tungsten as well as to substantiated $N-C_2H_5$ dissociation energy necessary bonds dissociation energies calculation in d-metals ethyamides. The regularity established and metal-metal bond dissociation energy greater increase with respect to energy metal-alkylamides radical energy represent specific examples of bond changes analisis and may be regarded as a definite conception for a deeper development of which quontitative experimental data should be obtained. The thermal decomposition process schemes for methyl- and ethylamides of titanium, vanadium and chromium subgroups elements proposed on the basis of power values have definite conformation, based on literaly and our experimental data, mass-spectrometry investigations and study of some mentioned metals alkylamides thermal decomposition.

THE METAL PENTACARBONYL HALIDES ARE NOT ISOMORPHOUS

Mona Arif, Universidade da Beira Interior, 6200 Covilhã, Portugal

The solution of metal pentacarbonyl halides $M(CO)_5X$ [M = Mn, Re; X = Cl, Br, I] have very similar vibrational spectra in the carbon monoxide stretching region, but unexpectedly the crystalline state of the iodides behaved differently. The spectra of the iodides are remarkabley simpler than those of the chlorides and bromides. They shaw no factor group splitting niether on B_1 nor on A_1 (axial) modes of the molecular ν(CO). also no transfer of Raman intensity between ν(CO) B_1 and E modes was observed [1], a spectral behaviour that was observed on the cholorides and bromides. This spectral difference of the iodides surely lies in a difference of crystal structure from that of the other halides, which have a D_{2h}^{16} (Pnma) structure with Z = 4. Space group method was used to explain the iodides structure, a crystal structure of higher symmetry is suggested which perfectly in accord with their solid state spectra. The spectra also reveals that intermolecular vibrational interactions contribute more to dispersion than to factor group effects [2].

The suggested space group is also in accord with the fact that mixed crystal could be formed from $Mn(CO)_5I$ and $Mn(CO)_5Cl$.

References

1 - M. Arif and S.F.A. Kettle, J. Chem. Phys., 72 (1980) 2131

2 - R. Durman, U.A. Tayasooriya, S.F.A. Kettle, S. Mahasuverachai, R. Mortimer and L. Norrby, J. Chem. Phys., 81 (1984) 5248

DETAILED MECHANISM OF ETHYLENE HYDROGENATION BY $H_4Ir(PMe_2Ph)_3^+$: DIHYDROGEN LIGAND AS A "GOOD LEAVING GROUP"

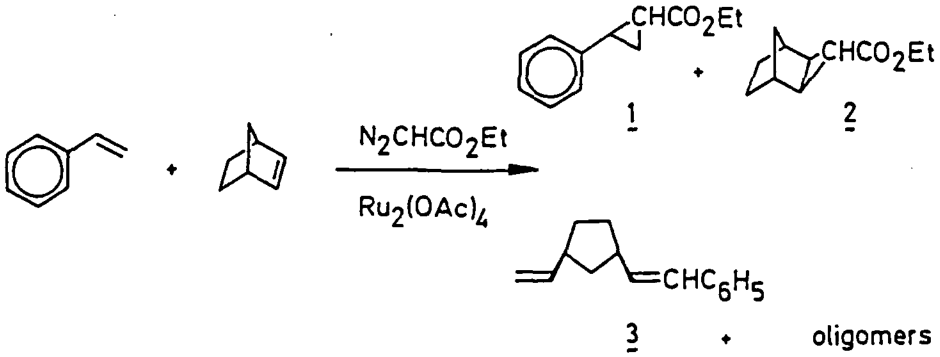
E. G. Lundquist, K. Folting, W. Streib, J. C. Huffman, Odile Eisenstein, and Kenneth G. Caulton, Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405 (U.S.A.) and Laboratoirè de Chimie Theorique, Batiment 490, Centre de Paris-Sud, 91405 Orsay, FRANCE

Protonation of a transition metal polyhydride furnishes a method for generating a catalytically-active reaction system. Thus, protonation of H_3IrP_3 ($P \equiv PMe_2Ph$) yields $H_4IrP_3^+$ (an H_2 complex), which reacts with ethylene to give $H_2Ir(C_2H_4)P_3^+$, which is then induced by additional ethylene to release ethane, with formation of $Ir(C_2H_4)_2P_3^+$. The *bis*-ethylene complex is unusual in being a stereochemically-rigid, trigonal bipyramid and having a high barrier to olefin rotation. This complex under H_2, liberates ethylene to give $H_2Ir(C_2H_4)P_3^+$, thereby closing a catalytic cycle. Further dynamic features of this complex, together with a description of its substrate selectivity, will be presented.

COMPETITIVE CYCLOPROPANATION AND CROSS-METATHESIS OF OLEFINS CATALYSED BY RUTHENIUM CARBOXYLATES

A.F. Noels, A. Demonceau, E. Carlier and A.J. Hubert
University of Liège, Sart-Tilman (B.6), B-4000 Liège, Belgium
R.-L. Marquez-Silva and R.A. Sanchez-Delgado
Instituto Venezolano de Investigationes Cientificas, Caracas 1010-A
Venezuela

It is well-established that rhodium(II) carboxylates are outstanding carbene-transfer catalysts (*e.g.*, in cyclopropanation reaction)[1] whereas other binuclear tetracarboxylates are less efficient (Cu, Pd) or practically inactive (Cr, Mo, Fe, ...) for promoting typical carbene reactions. The recent report of the synthesis of diruthenium(II,II) acetate ($Ru_2(OAc)_4$)[2] prompted us to test this complex in carbene chemistry. It appeared readily that rhodium and ruthenium-based systems promoted different reaction pathways. We report herein for the first time a clear-cut competition between catalytic reactions of cyclopropanation (carbene transfer) and metathesis of olefins. For instance, addition of ethyl diazoacetate to a mixture of styrene and norbornene containing a catalytic amount of $Ru_2(OAc)_4$ led both to cyclopropanes 1 and 2 and to products (3, selectively) resulting from a cross-metathesis of the olefins (Equation)[3].



---

1. A. Demonceau, A.F. Noels and A.J. Hubert, Aspects of Homogeneous Catalysis, Vol. 6, R. Ugo (Ed.), 199-232, D. Reidel Publishing Company, 1988.
2. A.J. Lindsay, G. Wilkinson, M. Motevalli and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 2321 (1985).
3. A.F. Noels, A. Demonceau, E. Carlier, A.J. Hubert, R.-L. Marquez-Silva and R.A. Sanchez-Delgado, *J. Chem. Soc., Chem. Commun.*, submitted for publication.

CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE WITH RESIN-TRANSITION METAL ION COMPLEXES CONTAINING AMINE AND AMMINE LIGANDS

M.Y.El-Sheikh, A.M.Habib, F.M.Ashmawy, A.H.Gemeay and A.B.Zaki

Chemistry Department, Faculty of Science, Tanta University, Tanta,
A.R.Egypt

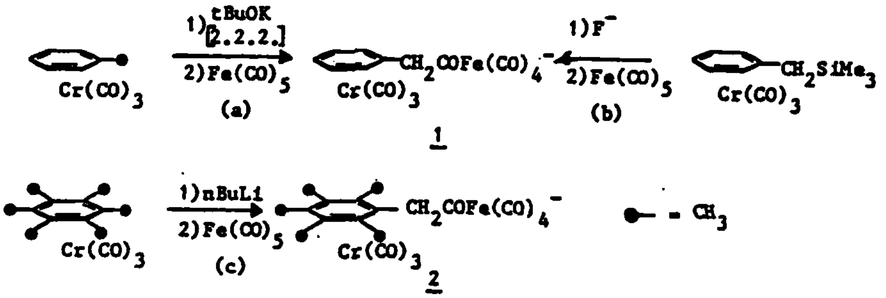
Dowex-50W resin (8% divinylbenzene crosslinking, 50-100 mesh) in the form of transition metal ion (Co^{2+},Ni^{2+},Cu^{2+}) complexes containing the ligands NH_3 and $C_2H_5NH_2$ was used as potentially active catalyst in the H_2O_2 decomposition. The structure of each complex in the resin was determined. The reaction was first order in all cases. The rate constant (per g of dry resin), the half time of the reaction and the molar distribution coefficient of the reactant were evaluated. The active species which was formed as an intermediate at the beginning of the reaction, had an inhibiting effect on the reaction rate. As a result of the H_2O_2 decomposition, a coloured compound (peroxo-metal complex) was formed and was found to contain catalytic active species. Probable mechanisms for the reactions are proposed. The activation energy,E and the change in the entropy of activation, ΔS^* with $C_2H_5NH_2$-complexes were greater than those with NH_3-complexes. The values of E and ΔS^* with both ligands increased in the following sequence: Ni-complex ion $<$ Co-complex ion $<$ Cu-complex ion. This is the same sequence of the transition metal ionic size,taking into consideration that the H_2O_2 decomposition by the copper-complex ion involves a redox reaction,$Cu(II) \underset{-e}{\overset{+e}{\rightleftharpoons}} Cu(I)$. The latter favours the catalytic decomposition of H_2O_2. The smaller the transition metal ion, the greater its electrical field, the more stable its complexes and the lower is the activation energy.

SYNTHESE OF PHENYLACETYL (η^6 CHROMIUM TRICARBONYL) TETRACARBONYL IRON ANIONS. APPLICATION TO THE α,α'-DIFUNCTIONNALIZATION OF HEXAMETHYLBENZENE

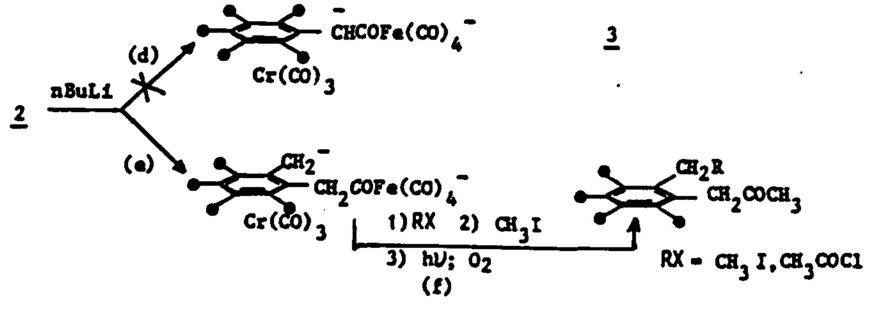
H. des ABBAYES & J.J. YAOUANC

UA CNRS 322, Laboratoire de Chimie Organique des Eléments de Transition
Faculté des Sciences et Techniques, Université de Bretagne Occidentale,
6, avenue Le Gorgeu, 29287 BREST CEDEX FRANCE

Anions 1 and 2 were synthetized according to the following reaction schemes (a) or (b) and (c), and fully characterized by IR, ^1H and ^{13}C NMR spectroscopy.



It was anticipated from the electrowithdrawing effect of the $Cr(CO)_3$ moiety that, on reaction with n Bu Li, anion 2 could give dianion 3 (reaction d). In fact, deprotonation occurs on a methyl group in the ortho position, as shown by sequences (e) and (f).



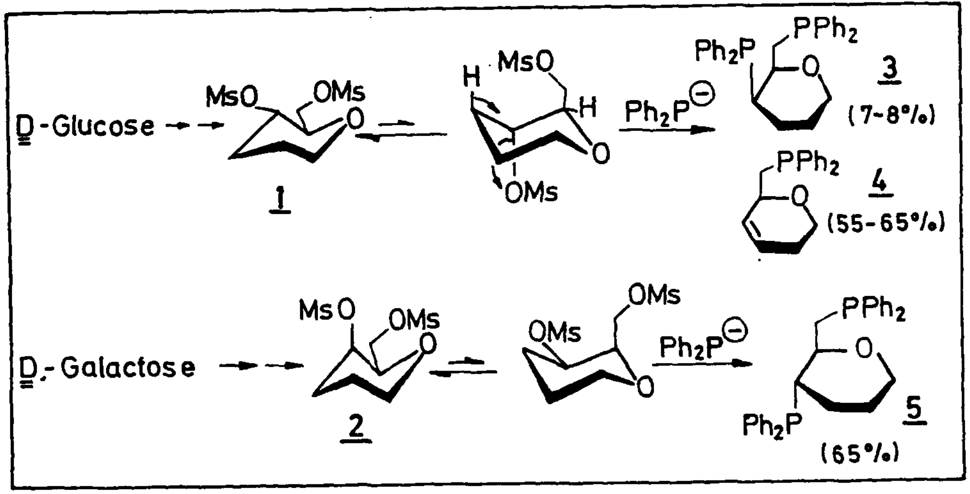
These sequences open up a new entry into the α,α'difunctionnalization of hexamethylbenzene.

SYNTHESIS, CONFORMATIONAL PROPERTIES AND ENANTIOSELECTIVITY OF Rh(I) COMPLEXES OF DIPHOSPHINES DERIVED FROM D-GLUCOSE AND D-GALACTOSE

Ivan Habuš, Zlata Raza and Vitomir Šunjić
"Rudjer Bošković" Institute, P.O.B. 1016, 41001 Zagreb - YU

Starting from D-glucose and D-galactose two dimesylates (1, 2) are prepared and converted into diphosphines 3 and 5 (Scheme 1.). Surprisingly, the reactivity of 1 and 2 towards diphenylphosphine anion, a sterically crowded nucleophile, was quite different; the main product from 1 was "anti - Saytzeff" elimination product 4. Conformational analysis, based on CD spectra of dibenzoate congeners of 1 and 2, explains these results.

Scheme 1.



Rh(I) complexes of 3 and 5, [Rh(NBD)(3)]ClO_4 (6) and [Rh(NBD)(5)] ClO_4 (7), exhibited interesting differences in CD and ^{13}C-NMR spectra. Direction of enantioselectivity of hydrogenation was the same with both catalytic complexes. Complex 7, being significantly more effective however, yielded over 90% e.e.s of chiral products on reduction of some unsaturated substrates.

HOMOGENEOUS CATALYTIC CARBONYLATION OF STEROIDS WITH TRANSITION-METAL COMPLEXES

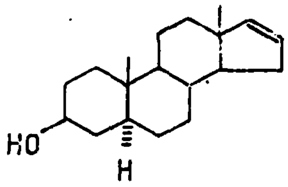
Szilárd Tőrös, László Kollár, Bálint Heil,
Institute of Organic Chemistry, University of Chemical Engineering,
H-8201 Veszprém, P.O.Box 158, Hungary

Zoltán Tuba, Chemical Works of Gedeon Richter Ltd., H-1103 Budapest, Gyömrői út 19/21, Hungary

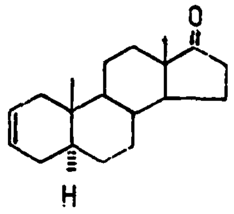
There is only few information$^{1-2)}$ in the literature about the catalytic carbonylation of steroids.

We investigated the carbonylation of several steroids with C=C double bonds in different positions (1,2,4,5,6.7,9/11/ and 16) with catalysts like $Rh_4(CO)_{12}$, $Rh_4(CO)_{12}$ + Et_3N, $[Rh(diene)Cl]_2$ + + PR_3 (prepared in situ), $Pt(SnCl_3)Cl(PR_3)_2$ and $PdCl_2(PPh_3)_2$.

Δ^{16}- (A) and Δ^2-steroid (B) proved to be the most reactive.



(A)



(B)

In the hydroformylation with rhodium catalysts mainly the appropriate aldehydes have been formed (up to 70%), while addition of Et_3N favoured the formation of hydroxymethyl-derivatives (65%).

In the hydroalkoxycarbonylation of (A) regioselectivity (with the -COOR group in position 16) was 80%. The new compound was separated by column chromatography, purified by recrystallization and determined by GLC, MS and ^{13}C NMR.

1) P.F.Beal, M.A.Rebensdorf, J.E.Pike, J.Am.Chem.Soc., 81, 1231 (1959)
2) A.L.Nussbaum, T.L.Popper, E.P.Oliveto, S.Friedman, I.Wender, J.Am.Chem. Soc., 81, 1228 (1959)

Homogeneous Catalytic Hydrogen Formation Using a Ditungsten Cluster and Low Valency Metal Ions in Aqueous Acidic Solutions

by

Constantinos Mertis and Nikos Psaroudakis
University of Athens,Inoganic Chemistry Laboratory,
Navarinou 13A 10680 Athens,Greece

Multiply bonded dinuclear comlexes of group VIB (M=Mo,W) react with hydrogen halides e.g. proton oxidative addition to the $[Mo_2Cl_8]^{4-}$,1,ion produces[1] the hydride $[Mo_2(\mu\text{-}H)(\mu\text{-}Cl)_2Cl_6]^{3-}$,2;Diprotonation followed by loss of hydrogen gives[2] the nonachloro derivative $[Mo_2(\mu\text{-}Cl)_3Cl_6]^{3-}$,3;

$$\underset{\underline{1}}{[Mo_2Cl_8]^{4-}} \xrightarrow[\substack{\vartheta=60^{o}C \\ (2)}]{HCl} \underset{\underline{2}}{[Mo_2HCl_8]^{3-}} \xrightarrow[\substack{-H_2 \\ (2)}]{HCl} \underset{\underline{3}}{[Mo_2Cl_9]^{3-}}$$

For the isoelectronic and isotuctural tungsten compound $W_2Cl_8{}^{4-}$,4,reactions (1) and (2) occur[3] at -78°C in HCl (12M) giving the corresponding $[W_2(\mu\text{-}Cl)_3Cl_6]^{3-}$,6,ion,presumably via the reactive unstable hydride[4] $[W_2HCl_8]^{3-}$,5. Reactions(1) and (2) are easily reversible for molybdenum[2,5] but not for tungsten[2,6]. This enhanced sucseptibility of W-W quatruple bonds towards protons and the irreversibility of these reactions has been the reason for a)the slow development of the chemistry ofthe W_2^{4+} unit and the long efforts for the isolation of 4 achieved eventually under non acidic conditions and b)the belief that these allegedly important catalytically species are in fact thermodynamic and kinetic sinks which makes them relatively uninteresting in terms of catalytic properties.

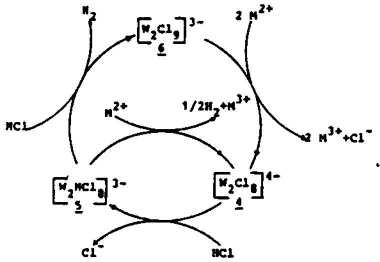


Fig.1.The binuclear tungsten complex 6 catalyses the evolution of H_2 in HCl solutions with excess $M^{2+}_{(aq)}$,M=Cr,V.

We now report the facile two electron redutions of 6 by the chromous and vanadous chlorides to give 4 followed by decomposition and/or hydrolysis in aqueous solutions;In acid,decomposition is prevented by interception of reactions (1) and (2),thus 6 becomes an effective catalyst for the anaerobic oxidation of Cr(II) and V(II) to Cr(III) and V(III) with simultaneous hydrogen evolution as shown in Figure 1.Analogous results are obtained with 3 but because the rates of reactions (1) and (2) are relatively slow the cycle can be monitored by electronic srectroscopy and the intermediate products can be isolated.The system although not directly related to hydrogen producing systems (water splitting or homogeneous catalysts for the water gas-shift reaction)[7,8] it is nevertheless relevant and of great interest.

REFERENCES

1.F.A.Cotton,Acc.Chem.Res.,1978,11,225;M.J.Bennet,J.V.Brencic and F.A.Cotton, Inorg.Chem.,1969,8,1060.
2.F.A.Cotton and A.R.Walton,"Multiple Bonds between Metal Atoms",Wiley,New York 1982;p.238 and references therein.
3.R.R.Shrock,L.G.Sturgeoff and P.R.Sharp,Inorg.Chem.,1983,22,2801
4.A.P.Sattelberger,K.W.McLaughlin and J.C.Huffman,J.Am.Chem.Soc.,1981,103,2280
5.C.Mertis,M.Kravaritou,A.Shehadeh and D.Katakis,Polyhedron,1987,6,1975
6.F.A.Cotton and G.N.Mott,J.Am.Chem.Soc.1982,104,5978.
7.Inorganic reactions and methods,Vol.1,p.61and references therein.
8.P.Escaffre,A.Thorez and P.Kalck,J.Chem.Soc.,Chem.Commun.,1987,146 and references therein

DISPLACEMENT OF AN AQUO GROUP BY OLEFINS IN SOME WATER SOLUBLE RUTHENIUM(III) COMPLEXES

M. M. Taqui Khan*, M. Rafiq H. Siddiqui, Z. Shirin and S. A. Samad
Coordination Chemistry and Catalysis Division, Central Salt & Marine
Chemicals Research Institute, Bhavnagar - 364 002. INDIA.

Ruthenium complexes have been found to be efficient catalysts for various reactions such as oxidation, hydrogenation and carbonylation of olefins [1-3]. The synthesis of mixed ligand organometallic complexes of olefins can give a lead in understanding the mechanism of such reactions.

The present investigation deals with the synthesis and characterization of some water soluble mixed ligand organometallic complexes of Ru(III) involving mono and di-olefins such as cyclohexene, cyclooctene and 1,5 cyclooctadiene. Mixed ligand complexes of the composition $K_2[RuCl_5L]$ (where L = cyclohexene, cyclooctene) and $[RuCl_3(\text{cyclooctadiene})]_2$ were synthesized by the interaction of $K_2[RuCl_5(H_2O)]$ and the corresponding olefin in a 1:1 mole ratio in H_2O-EtOH mixture. The complex [Ru(EDTA-H)(cyclohexene)] was synthesized by the displacement of H_2O from the coordination sphere of $[Ru(EDTA\text{-}H)(H_2O)]2H_2O$ by cyclohexene.

The above mentioned complexes were characterized by elemental analysis, conductivity measurements, IR, UV-vis and NMR spectroscopy. All the olefin complexes are water soluble except for the cyclooctadiene dimer.

References

1. M. M. Taqui Khan, M. R. H. Siddiqui, Amjad Hussain and M. A. Moiz, Inorg. Chem., 25, 2765 (1986).
2. M. M. Taqui Khan and M. R. H. Siddiqui, J. Mol. Cat., 42, 161 (1987).
3. M. M. Taqui Khan, S. B. Halligudi, S. H. R. Abdi and Sumita Shukla, J. Chem. Soc. (Chem. Commun.).

Silica Supported Ruthenium and Osmium Carbonyls as Catalysts for Cycloocta-1,5-diene Isomerization.

by Jan Kaspar, Alessandro Trovarelli, Giuliano Dolcetti* and Mauro Graziani
Dipartimento di Scienze Chimiche, Universita' di Trieste, Piazzale Europa 1, 34127 Trieste (Italy)
* Istituto di Chimica, Facolta' di Ingegneria, Universita' di Udine, Viale Ungheria 43, 33100 Udine (Italy).

Homogeneous and heterogenized ruthenium and osmium catalysts derived from $M_3(CO)_{12}$ (M= Ru, Os) are used in the isomerization of cycloocta-1,5-diene (1.5 cod) to the 1.4 and 1.3 isomers. Their activities and selectivities in 1.4 isomer -which has recently been reported as an interesting starting material for a polimerization reaction- [1] are compared both in flow and in batch conditions, operating in the range of temperature 40-125°C. Selectivities up to 90% and yields as high as 50% in 1.4 cod have been obtained. Interestingly, surface organometallic ruthenium species show a higher catalytic activity than the homogeneous one, which deactivates during the reaction due to formation of a mixture of tri- and tetranuclear Ru clusters with coordinated 1.5 cod [2]. By air oxidation of the $Ru_3(CO)_{12}/SiO_2$ species a mononuclear surface carbonyl is obtained [3] which mantains a good catalytic activity and can be recycled without significant loss of catalytic activity. The nature and the stability of the heterogenized catalyst have been investigated by i.r. spectroscopy.

1. W.Holtrup, R.Streck, W.Zaar, and D.Zerpner, J.Mol.Catal., 1986, 36, 127.
2. A.J.Canty, A.J.P.Domingo, B.F.G.Johnson, and J.Lewis, J.Chem.Soc. Dalton, 1973, 2056.
3. G.M.Zanderighi, C.Dossi, R.Ugo, R.Psaro, A.Theolier, A.Choplin, L.D'Ornelas, and J.M.Basset, J.Organometal. Chem., 1985, 296, 127.

NIOBIUM(V) CHLORIDE AS HOMOGENEOUS CATALYST FOR THE TRIMERIZATION OF ALKYNES

J.A.K. du Plessis, C.J. du Toit and G. Lachmann, Department of Chemistry, Potchefstroom University for C.H.E., Potchefstroom 2520, Republic of South Africa

Niobium(V) chloride trimerizes phenylacetylene to 1,2,4- and 1,3,5-triphenylbenzene, 1,7-octadiyne to 1,4-bis-(6-tetralin)-butane and 1-hexyne to 1,2,4- and 1,3,5-tributylbenzene.

The course of the reactions is characterized by three phases. In the first phase 2 moles of the mono-alkynes or one mole of the dialkyne per mole niobium is rapidly absorbed to give a niobium(V) complex. This is followed by an induction period during which the active trimerization catalyst is formed by a spontaneous reduction of the niobium(V) to a niobium(III) complex.[1] In the third phase the alkynes are converted to the trimers. If a mixture of phenylacetylene and 1,7-octadiyne is used the expected trimers as well as a co-trimer, 6-phenyl-tetralin are formed. With phenylacetylene and 1-hexyne the co-trimers phenyldibutylbenzene and diphenylbutylbenzene are formed. In all these cases phenylacetylene played the most important role during the activation of the catalytic system.

---

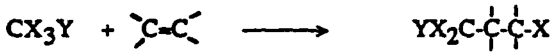
1 G. Lachmann, J.A.K. du Plessis and C.J. du Toit, J. Mol. Catal., 1987, 42, 151.

NEW HOMOGENEOUS CATALYSTS IN THE ADDITION OF POLYHALOGENOALKANES TO OLEFINS; ORGANONICKEL(II) COMPLEXES $[Ni\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}X]$ (X = Cl, Br, I).

David M. Grove, Gerard van Koten, and Augustinus H. M. Verschuuren,

Department of Metal-Mediated Synthesis, Laboratory of Organic Chemistry, Transitorium III,
University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands.

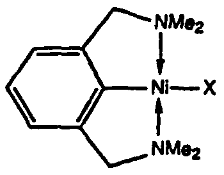
The Karasch addition of polyhalogenoalkanes to an alkene double bond, eq 1, is amenable to catalysis by various metal complexes.



$$CX_3Y + {>}C{=}C{<} \longrightarrow YX_2C\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}X \qquad (1)$$

X = Halogen; Y = H, halogen, CF_3 or other electronegative group.

We now report that the square planar Ni(II) organometallics 1a-c [1], Fig. 1, are very active homogeneous catalysts for the Karasch addition under very mild conditions. Some quantitative results for the 1a catalysed addition of the perhaloalkanes CCl_4, CBr_4, and CF_3CCl_3 to the terminal alkenes hept-1-ene, and methyl methacrylate are presented. For example, the addition of CCl_4 to methyl methacrylate in CH_3CN catalysed by < 0.1 mole % of 1a (relative to alkene) affords the 1:1 adduct $CCl_3CH_2CCl(Me)CO_2Me$ in high yield with 100 % regiospecificity. Kinetic experiments at 30 °C show turnover numbers of more than 500 h^{-1} for the first hour of the reaction. This catalytic behaviour is clearly related to the fact that 1a-c are easily oxidized to novel air-stable nickel(III) species $[Ni\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}X_2]$ [2].



$[Ni\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}X]$
X = Cl, **1a**
X = Br, **1b**
X = I, **1c**

Figure 1

The fairly rigid *N,C,N* chelation of the ligand in and the consequent restrictions imposed on the catalytic site(s) makes these species well suited for mechanistic investigations.

References:

1) D. M. Grove, G. van Koten, H. J. C. Ubbels, R. Zoet, and A. L. Spek, *Organometallics* 1984, *3*, 1003-1009.
2) D. M. Grove, G. van Koten, P. Mul, R. Zoet, J. G. M. van der Linden, J. Legters, J. E. J. Schmitz, N. W. Murrall, and A. J. Welch, *Inorganic Chemistry* (1988) in press.

INFLUENCE OF THE NATURE OF THE ORGANOMETALLIC COMPONENT ON THE CATALYTIC ACTIVITY AND PRODUCT SELECTIVITY IN METATHESIS REACTION

Ileana Drăguţan and Valerian Drăguţan

Center of Organic Chemistry, 202B Spl. Independenţei,
R-78100 Bucharest, Romania

A comparative study of the effect of the nature of the organometallic compound on the catalytic activity and product selectivity in metathesis reaction of unsaturated alicyclic esters (e.g. methyl and ethyl cyclohexylidene and cyclopentylidene acetates) in the presence of WCl_6-based catalysts was performed. When using organotin (e.g. Me_4Sn, Bu_4Sn, Ph_4Sn) and organoaluminium compounds (e.g. Et_2AlCl, $EtAlCl_2$) in the catalytic system the following results were obtained:

(i) organotin compounds were more selective for metathesis products than organoaluminium compounds;

(ii) the selectivity in metathesis products varies in the order: $Me_4Sn > Ph_4Sn > Bu_4Sn$;

(iii) the catalytic activity induced by the organoaluminium compounds is high but the selectivity in metathesis products remains low;

(iv) the catalytic systems with organoaluminium compounds lead preferentially to isomerization and oligomerization reactions.

These results are attributed to a distinct alkylating and reducing power of the organometallic compound used in the catalytic system, the generation of metallacarbenes of different types and reactivities through the interaction of the organometallic compound with WCl_6 and differences in the Lewis type acidity of the organometallic compound employed. The mode of interaction of the above organometallic compounds with WCl_6 and the ways of generation of the intermediate metallacarbene species are discussed in detail.

366

ORGANO-PALLADIUM COMPOUNDS IN CATALYSIS OF DIAZO ALKANES DECOMPOSITION

I.N.Busygina, T.A.Stromnova, S.B.Katser, A.S.Antsyshkina, M.A. Poraj-Koshits, I.I.Moiseev, Institute of General & Inorganic Chemistry, Academy of Sciencas, Leninskii pr. 31, Moscow, USSR

Catalyzed by $Pd(OAc)_2$ in benzene solutions at 35°C decomposition of diphenil diazo methane has been shown to proceed with N_2 elimination and benzophenone azine (I) formation. In addition to (I) palladium complex $Pd_4(\mu\text{-}OAc)_4[C_6H_4C(Ph)=N-N=C(Ph)C_6H_4]_2$ (II) containing orhto-palladated azine ligands has been isolated and characterised by analytical, spectral (IR, NMR) and molecular mass data. The thermolysis of (II) in $AcOH/C_6H_6$ solutions at 50-60°C yields trinuclear palladium complex $Pd_3(\mu\text{-}OAc)_4[C_6H_4C(Ph)=N-N=C(Ph)C_6H_4]$ (III) also containing orhto-palladated azine ligand. According to single crystal X-ray structure determinations of (III) Pd atoms are shaped like a bent metal chain with Pd-Pd-Pd angle of 73,1° and Pd-Pd distances of 3,102 - 3,157 Å. The neigboring Pd-atoms are bridges by the pairs of AcO-groups, and the terminal Pd-atoms of the chain are coordinated by N-atom and orhto-C-atom of the azine ligand.

Under reaction conditions (C_6H_6, 35°C) $Pd(OAc)_2$ and (I) does not form complex (II), suggesting the complex (II) to be formed through carbene intermediates.

FACILE HYDRIDE MIGRATIONS IN MODEL BINUCLEAR CATALYSTS

Martin Cowie and Brian A. Vaartstra, Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

The complexes, $[MM'(CO)_2(\mu\text{-}X)(DPM)_2]^{n+}$ (M, M' = Rh, Ir; X = Cl, I (n = 1); X = S (n = 0); DPM = $Ph_2PCH_2PPh_2$), have been studied as models of the binuclear hydrogenation catalyst, $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$. All model complexes react readily with H_2 to give a range of dihydride species which in some cases react further to yield tetrahydrides. NMR studies (^1H, $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$) on these species have yielded valuable information on the facile hydride migrations occurring. In all cases oxidative addition of H_2 appears to take place at one metal centre in the A-frame "pocket" between the metals. However in the chloride- and sulfide-bridged diiridium complexes the hydride ligands rearrange to positions, one on each metal, on the "outside" of the complexes. The mechanism for these rearrangements will be discussed. Subsequent reactions of the dihydride complexes with alkynes have helped elucidate the ways in which binuclear hydrides may interact with unsaturated substrate molecules and the relationship of this chemistry to binuclear hydrogenation catalysis will be discussed. The involvement of the adjacent metal centres in this chemistry will be emphasized.

ANHYDRIDE SYNTHESIS BY HOMOGENEOUS PALLADIUM(II) CATALYZED CARBONYLATION REACTIONS OF ARYL HALIDES

Ilan Pri-Bar and Howard Alper, Department of Chemistry, University of Ottawa
Ottawa, ONtario, Canada K1N 6N5

There has been considerable interest in metal complex catalyzed routes to acid anhydrides. However, in general, product yields are low and stringent conditions are required. It has now been found that aryl halides react with

$$\mathrm{ArX} + \mathrm{CO} + \mathrm{Ar'COONa} \xrightarrow[\substack{\mathrm{PPh_3,DMF} \\ \text{40 psi, 95°C}}]{\mathrm{Pd(OAc)_2}} \mathrm{ArCOOCOAr'} + \mathrm{NaX}$$

$$X = \mathrm{I,Br}$$

carbon monoxide and sodium or calcium carboxylate in N,N-dimethylformamide, in the presence of catalytic quantities of palladium acetate, to give anhydrides in reasonable yields. The influence of different factors (solvent, substituent effects), as well as a proposed reaction mechanism, will be discussed.

The $[\mathrm{Copy}_6][\mathrm{BPh}_4]$ - Promoted Cyclotrimerization and Hydrodimerization of Alkynes

Paolo Biagini, Giuseppe Fachinetti, Dipartimento di Chimica e
Chimica Industriale, Università di Pisa, Via Risorgimento, 35
I-56100, Italy.
Pier Francesco Zanazzi, Dipartimento di Scienze della Terra,
Università di Perugia, I-06100, Italy.

Pyridine solutions of the cationic Co(I) complex $[\mathrm{Copy}_6][\mathrm{BPh}_4]^1$ promote the cyclotrimerization of both terminal and internal alkynes at room temperature. However diphenylacetylene behaves differently, and induces the disproportionation of Co(I) to Co(0) and Co(II) (eq 1).

$$2\,[\mathrm{Copy}_6]^+ \;+\; 4\,\mathrm{C_2Ph_2} \longrightarrow (\eta^6\text{-}\mathrm{C_6Ph_6})\mathrm{Co}(\mathrm{C_2Ph_2}) \;+\; [\mathrm{Copy}_6]^{2+} \qquad (1)$$

The molecular structure of $(\eta^6\text{-}\mathrm{C_6Ph_6})\mathrm{Co}(\mathrm{C_2Ph_2})$ has been solved by X-ray diffraction methods and the compound constitues the first example of a long-lived radical, half-sandwich mononuclear cobalt complex.

The slow addition of alkynes to $[\mathrm{Copy}_6][\mathrm{BPh}_4]$ in pyridine solution under a hydrogen atmosphere, brings about gas absorption and butadienes are formed according to equation 2.

$$2\,\mathrm{C_2Ph_2} \;+\; \mathrm{H_2} \longrightarrow \mathrm{CHPh{=}CPh{-}CPh{=}CHPh} \qquad (2)$$

The reaction constitutes the first example of alkyne hydrodimerization which occurs catalitically and employing dihydrogen instead of metal hydrides[2] or aluminium alkyls[3]. Polypyridines inhibit the above mentioned reactions.

---

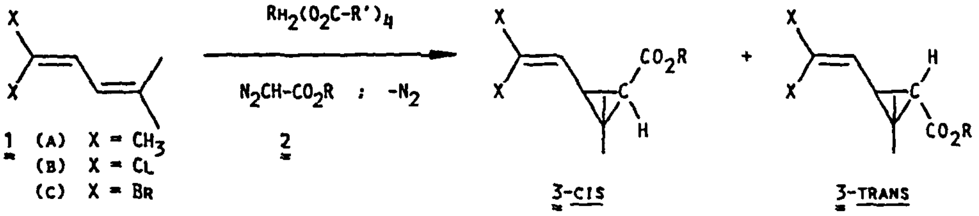
1) G. Fachinetti, T. Funaioli and P.F. Zanazzi, J. Chem. Soc., Chem. Commun., in the press.
2) N. Satyanarayana and M. Periasamy, Tetrahedron Lett., 27, 6253 (1986).
3) A.M. Caporusso, G. Giacomelli and L. Lardicci, J. Org. Chem., 42, 914 (1977).

CATALYTIC CYCLOPROPANATION OF DIENES : STEREOSELECTIVE SYNTHESIS OF PYRETHROIDS FROM DIAZOACETATES AND 1,1-DISUBSTITUTED-4-METHYLPENTA-1,3-DIENES

A. Demonceau, A.F. Noels, A.J. Anciaux and A.J. Hubert ,
University of Liège, Sart-Tilman (B.6), B-4000 Liège, Belgium

Pyrethroids derived from chrysanthemic acid 3.A (R=H), permethric acid 3.B (R=H) and deltamethric acid 3.C (R=H), exhibit exceptionally potent insecticidal activity together with very low mammalian toxicity and rapid biodegradability. These remarkable properties are at the basis of intense effort to devise syntheses suitable for the industrial production of pyrethroids.

We have already described the cyclopropanation of olefins and dienes catalysed by rhodium acetate [1].



We now report that the use of rhodium(II) carboxylate catalysts for the addition of diazoacetates 2 to dienes 1 affords cyclopropanecarboxylates 3 containing substantially more of the insecticidally preferable cis-isomer which has the substituted vinyl and alkoxycarbonyl groups on the same side of the cyclopropane ring, than is obtained using other catalysts, namely the better known copper catalysts [2,3]. The cyclopropanecarboxylates 3 are then readily converted into pyrethroids insecticides.

---

1. (a) A.J. Hubert, A.F. Noels, A.J. Anciaux and Ph. Teyssié, *Synthesis*, 600 (1976); (b) A.J. Anciaux, A.J. Hubert, A.F. Noels, N. Petiniot and Ph. Teyssié, *J. Org. Chem.*, 45, 695 (1980).
2. (a) A.J. Anciaux, A. Demonceau, A.F. Noels, R. Warin, A.J. Hubert and Ph. Teyssié, *Tetrahedron*, 39, 2169 (1982); (b) A. Demonceau, A.F. Noels, A.J. Anciaux, A.J. Hubert and Ph. Teyssié, *Bull. Soc. Chim. Belg.*, 93, 949 (1984).
3. D. Holland and D.J. Milner, *J. Chem. Res.* (S), 317 (1979); (M), 3734 (1979).

IRON-PROMOTED REGIO-, STEREO- AND ENANTIOSELECTIVE ADDITION OF ALKENES TO 1,3-DIENES AND NORBORNADIENE

Jens Ehlers, *Kai Baldenius* and *Heindirk tom Dieck*, Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13 (F.R.G.)

The complexes of the type (DAD)FeX_2 (DAD = diazadiene RN=CR'-CR'=NR or similar pyridylimines) are easily converted to catalytically active species "(DAD)Fe" by reaction with butadiene-magnesium. In the presence of 1,3-dienes a smooth catalytic reaction to cyclodimers occurs at ambient temperature [1]. In the presence of terminal olefins the simple isodimerization is suppressed and an addition of the olefin to the diene is favoured instead. The terminal olefin may carry n-alkyl, iso-alkyl or aromatic substituents. The scope of the reaction has been expanded to many mono- and disubstituted dienes as well. As a function of steric requirements of the DAD the stereochemistry of the products can be controlled (linear or branched addition products); chiral DADs, like in the isodimerization reaction [1], give considerable enantiomeric excess, e.g. in the formation of 3-methyl-1,Z-4-hexadiene from ethene and piperylene. A similar chiral iron-organic catalyst induces the asymmetric coupling of ethene and norbornadiene to 3-vinyl-tricyclo[$2.2.1.0^{2,6}$]-heptane [2].

Isolated (DAD)Fe(norbornadiene)(L) complexes afford details to understand the stereochemical course of these catalytic reactions as well as the catalytic coupling of norbornadiene with alkynes or 1,3-dienes [3].

[1] H. tom Dieck, J. Dietrich, *Angew. Chem. Int. Ed. Engl.24* (1985) 791.
[2] J. Ehlers, H. tom Dieck, *Angew. Chem.* submitted.
[3] H. tom Dieck, M. Mallien, R. Diercks, *J. Mol. Cat.* submitted

MODELS FOR CO REDUCTION. PREPARATION OF DINUCLEAR COBALT CARBONYLS WITH THE CARBENE MOIETY $C(OSiR_3)CH_2OSiR_3$

Attila Sisak, Márta Máté, László Németh

Institute of Organic Chemistry, University of Veszprém,
Schönherz Z.u.10., H-8200, Veszprém

The complexes $R_3SiCo(CO)_4$ (R = Me, Et, Ph) react with aliphatic aldehydes to give α-silyloxymethyl- and α-silyloxyacetylcobalt tetracarbonyls[1,2]:

$$R_3SiCo(CO)_4 + R'CHO \longrightarrow \underset{\underline{\underline{1}}}{R_3SiOCHR'Co(CO)_4} \underset{-CO}{\overset{CO}{\rightleftharpoons}} \underset{\underline{\underline{2}}}{R_3SiOCHR'C(O)Co(CO)_4}$$

$\underline{\underline{1}}$ and $\underline{\underline{2}}$ are stable only in the case of R'=H. The reaction with gaseous formaldehyde could be promoted by catalytic amounts of bases (e.g. PBu_3) and/or UV irradiation. Depending on the relative concentration of the base and other reaction conditions $\underline{\underline{1}}$, $\underline{\underline{2}}$, or $Co_2(CO)_7$ (μ-$C(OSiR_3)CH_2OSiR_3$) ($\underline{\underline{3}}$) were found, respectively as main products. The complexes are characterised by their IR, NMR and mass spectra and elementary analysis. We observed the complexes $\underline{\underline{3}}$ also in the reaction mixtures of the catalytic hydrosilylation of CO in the presence of $Co_2(CO)_8$ and bases[3]:

$$R_3SiH + CO \xrightarrow[120^{o}C,\ 100\ bar]{Co_2(CO)_8/PBu_3} CH_3(CH_2)_nOSiR_3 + (R_3Si)_2O + \ \ldots$$

R_3 = Et_3, $MeEt_2$; n = 0-5

1. Kovács,I.; Sisak,A.; Ungváry,F.; Markó L. Organometallics, accepted.
2. Sisak,A.; Sámpár-Szerencsés,E.; Németh,L.; Ungváry,F.; Pályi.G. to be published.
3. Sisak,A.; Angyalosy,Z.: unpublished results.

REACTIVITY OF METALLIC COPPER WITH ORGANIC COMPOUNDS IN THE PRESENCE OF MOLECULAR OXYGEN.

M.Gargano, N.Ravasio and M.Rossi
Dipartimento di Chimica - Università di Bari
4, Trav. 200 Re David - 70126 Bari - Italy

The role of Cu(I) and Cu(II) in promoting oxygen activation both in chemical and biological systems has been widely discussed [1,2]. However, little is known about the interaction of metallic copper with molecular oxygen[3].

We have already studied the reaction of metallic Cu with CH_3OH and PhOH in the presence of oxygen and pyridine to give $Cu(OCH_3)_2$ and 4,5-dimethoxy-1,2-benzoquinone[4].

The observation that the more acidic phenol (pKa=9.89) reacts much more smoothly than the less acidic methanol (pKa=16) and the necessity to operate in the presence of a coordinating base suggest that the activation and complexation of the organic reagent requires an hydrogen abstraction as a preliminary step.

To prove this hypotesis we have reacted very weak acids, such as ethanol and phenylacetylene,with O_2 which caused very slow oxygen consumption, whereas organic molecules lacking mobile hydrogen atoms failed to react.

This point of view is confirmed also by the very easy interaction of Cu and O_2 with benzoic acid (pKa=4.19) and CH_3NO_2 (pKa=10.2). The latter reaction is particularly interesting as it gives cyanide, isocyanate and nitrito compounds depending on the reaction conditions.

The recent application of analytical surface techniques which allow the detection of peroxo species and adsorbed atomic oxygen on Cu, and the results reported by Rao et al.[5] on the interaction of polycrystalline Cu surface with molecular oxygen and proton donor molecules agree with our hypothesis on the role played by the base in promoting hydrogen abstraction.[1]

---

[1] Houben-Weyl, "Methoden der Organische Chemie", IV/1b, Georg Thieme Verlag, p. 55-67 (1976)

[2] K.D.Karlin and J.Zubieta (eds.), "Copper Coordination Chemistry: Biochemical and Inorganic Persoective", Adenine Press, Guilderland, N.Y., (1983)

[3] K.Prabhakaran, P.Sen and C.N.R. Rao, Surface Sci., 177, L971 (1986)

[4] M.Gargano, N.Ravasio and M.Rossi, proc. XIIth Inter. Conf. Organometallic Chem.,p.53, Vienna (1985)

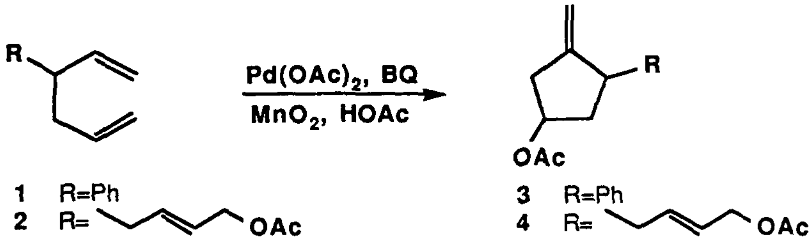
[5] K.Prabhakaran, P.Sen and C.N.R. Rao, Surface Sci., 169, L301 (1986)

PALLADIUM-CATALYZED OXIDATIVE CYCLIZATION OF 1,5-DIENES

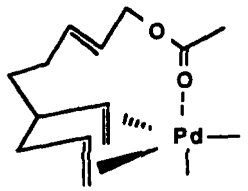
Thomas Antonsson[a], Christina Moberg[a], Louise Tottie[a], and Andreas Heumann[b]

[a]Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, SWEDEN, [b]I.P.S.O.I. -UA 126 Université d'Aix-Marseille III, Centre de Saint-Jérome, F-13013 Marseille, FRANCE

Previously, we have reported that substituted 1,5-dienes, e.g. **1** and **2**, undergo oxidative ring-closure catalyzed by palladium acetate using p-benzoquinone and MnO_2 as oxidants to give functionalized cyclopentanes. The reaction shows a high degree of regioselectivity affording mainly **3** and **4**.



The stereoselectivity of the cyclizations differs, however. The product obtained from cyclization of the allylic acetate **2** gives a trans/cis ratio of about 2/1 whereas the product obtained from the diene **1** gives a trans/cis ratio of 1/1. A possible explanation for this difference may be a weak coordination of the acetate group to palladium which would favour a pseudo-equatorial palladium-diene complex thereby increasing the trans-adduct formation.



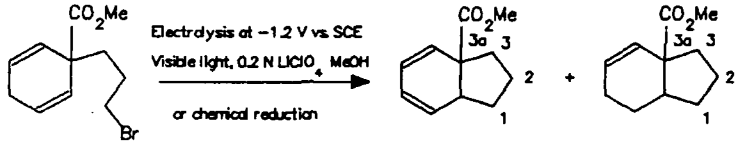
In order to investigate whether increased stereoselectivity results from coordination of a functional group to palladium, a series of 3-O-substituted 1,5-dienes carrying alcohol, nitrile, acetate and carboxylic acid groups at various distances from the diene center were prepared and allowed to undergo the cyclization reaction.

CARBON-CARBON BOND FORMATION CATALYZED BY VITAMIN B_{12} STEREROCHEMISTRY AND MECANISM

Heng Su, Eugen Eichenberger, Rolf Scheffold.

Department of Organic Chemistry, University of Bern,
Freiestr. 3, CH-3012 Bern, Switzerland

Vitamin B_{12} acts as a catalyst in reductive, intra- and intermolecular, radical-type C,C-bond formation [1]. Reductive cyclisation of achiral bromodiene I affords chiral *cis*-diene II and chiral *cis*-monoene III. The ratio by which the two products II and III are formed as well as the enantiomeric excesses in II and III strongly depend on the reaction conditions.



I   II-*cis*   III-*cis*

Catalyst or reagent Reaction condition	Total Yield, %	Products Ratio [% e. e. of major enantiomer]	
B_{12}(5 mol%) Pt–Cathode	92	98 [<1%, 3a(S)]	<2
B_{12}(5 mol%) C–Cathode	73	50 [14%, 3a(S)]	50 [12%, 3a(R)]
B_{12}(5 mol%) Zn/NH_4Cl/DMF	74	7	93
Bu_3SnH C_6H_6/reflux	98	<2	98 [2]

The mechanism and the stereochemistry of the B_{12}-catalyzed C,C-bond formation will be discussed.

[1] R. Scheffold, M. Dike, Th. Herold and L. Walder. *J. Am. Chem. Soc.* 1980, *102*, 3642.
[2] A. L. J. Beckwith and D. H. Roberts. *J. Am. Chem. Soc.* 1986, *108*, 5893.

VITAMIN B_{12}-CATALYZED TANDEM RADICAL CYCLIZATION

E. Eichenberger, R. Härter, H. Su, R. Scheffold

Department of Organic Chemistry, University of Bern,
Freiestr. 3, CH-3012 Bern, Switzerland

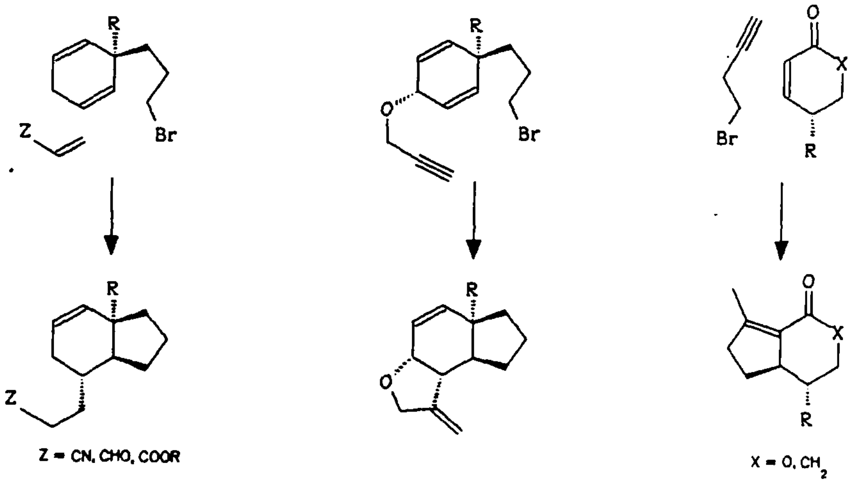
The vitamin B_{12}- catalyzed chemical or electrochemical reduction of alkylhalides in presence of a suitable choosen set of two or more intra- or intermolecularly located C,C- multiple bonds offers a flexible strategy for the stereoselective formation of two or more C,C - bonds in one operation (Tandem Reaction)[1,2].

Three of four combinations of intra - and intermolecular formation of two C,C - bonds are of relevance in synthesis. Examples for each type, intra - inter, intra - intra and inter - intra are presented.

Intra - Inter
Cyclization with chain extension

Intra - Intra
Double cyclization

Inter - intra
Annelation



Synthesis of natural products based on B_{12} - Tandem cylization will be presented.

---

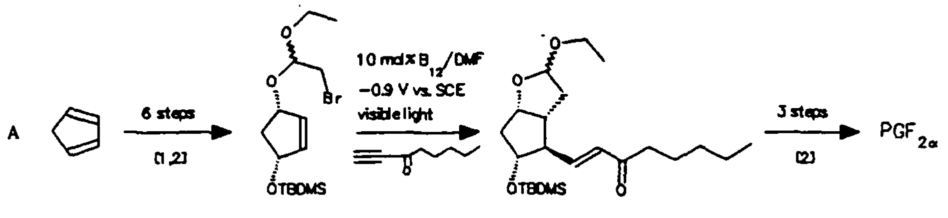
[1] R. Scheffold, *Nachr.Chem.Tech.Lab.* 1988, *36*, 261.
[2] Ch. Weymuth, Euchem Conf. "Semiochemicals in the Plant and Animal Kingdom", Angers 12.-16. Oct. 1987.

PROSTAGLANDIN SYNTHESIS *via* VITAMIN B_{12}-CATALYZED C-C-BOND FORMATION

S. Busato, O. Tinembart, R. Scheffold

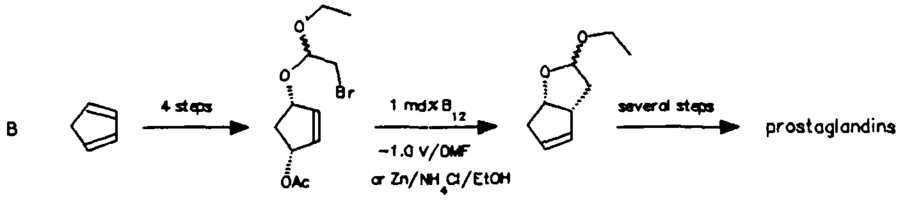
Department of Organic Chemistry, University of Bern,
Freiestr.3, CH-3012 Bern, Switzerland

The key reaction in a short synthesis of (+)-prostaglandin $F_{2\alpha}$ is the vitamin B_{12}-catalyzed electrolysis of the bromoacetal I in the presence of 1-octyn-3-one, affording directly II in good yield.



I II

The bromoacetal III on B_{12}-catalyzed reduction affords the olefin IV in high yield.



III IV

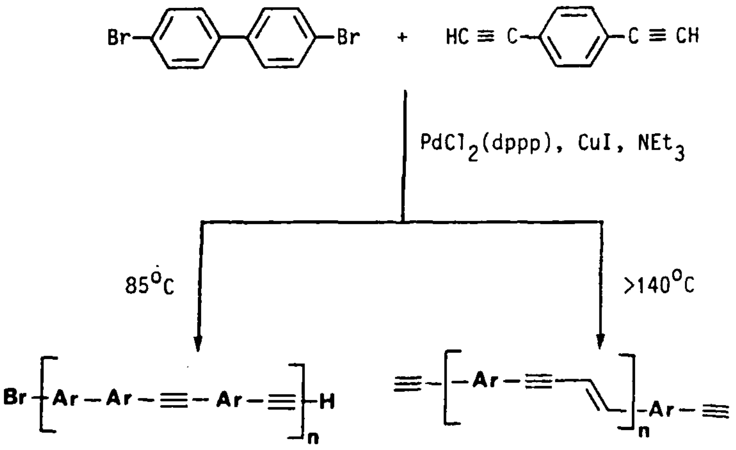
B_{12} acts as a mediator in the electron-transfer[3] from the electron source to the bromides I or III, creating a radical which undergoes cyclization. The cyclized radical intermediate adds to the Michael-system (reaction A) or undergoes elimination (reaction B).

[1] K. Laumen, M.P. Schneider, *J.Chem.Soc.,Chem.Commun.* 1986, 1298.
[2] G. Stork, P.M. Sher, H.L. Chen, *J.Am.Chem.Soc.* 1986, *108*, 6384.
[3] R. Scheffold, S. Abrecht, R. Orlinski, H.-R. Ruf, P. Stamouli, O. Tinembart, L. Walder, C. Weymuth, *Pure & Appl.Chem.* 1987, *59*, 363.

TEMPERATURE DEPENDENT REACTION PATHWAYS IN PALLADIUM-CATALYSED C-C BOND FORMATIONS

Manfred Bochmann and Keith Kelly, School of Chemical Sciences,
University of East Anglia, Norwich NR4 7TJ, U.K.

Aromatic polymers are chemically inert, extremely tough and very resistant to heat. They have therefore found widespread use in engineering applications. The C-C cross-coupling reaction of dihaloarenes with dialkynylarenes in the presence of palladium catalysts gives access to a new range of these materials. The structure of polymers obtained under two different temperature regimes suggests tnat two reaction pathways are followed, and that at higher temperature alkyne polymerisation dominates over cross-coupling:



The polymers are characterised by FTIR, FT-Raman, DSC and solid-state ^{13}C-MAS NMR.

VALENCE CHANGES OF ORGANIC COMPLEXES OF CHROMIUM AND VANADIUM IN CATALYTIC HYDROPEROXIDE ALKANE OXIDATION

V.N. Glushakova, N.A. Skorodumova, G.A. Domrachev,
G.A. Razuvaev, Chemistry Institute of the USSR Academy of
Sciences, Gorky, USSR

Hydroperoxide alkane oxidation catalyzed by organic chromium and vanadium complexes has been investigated in the detail in the present work. Under this conditions C_5–C_{15} alkanes are oxidized to alkanones with good selectivity at temperatures 60 to 110°C, i.e. under more mild conditions than on autoxidation. Chromium(III)- and vanadium(IV)-acetylacetonates and alcoholates and in addition carboxylates, derivatives of polyatomic alcohols, carbonyls for chromium (III, 0) are studied as catalysts. Hydroperoxide oxidation does not demonstrate features characteristic of chain radical processes. The first stage of the process is a rapid formation of different stoichiometry equilibrium complexes of the initial organometallic compound with tert-butyl hydroperoxide. Intracomplex oxidation of initial metal atom to higher oxidation state proceeds in the complex which limits the rate of hydroperoxide alkane oxidation. Alkylperoxochromate(VI) or alkylperoxovanadate(V) formed oxidized alkane. The simultaneons attack of methylene group of alkane by peroxide and chromate (vanadate) groups occurs in alkylperoxochromate (VI)- or alkylperoxovanadate (V)-alkane complex and this determines the selective formation alkanones. Such alkylperoxovanadate has been synthesized in case of vanadium; its ability to alkane oxidation has been indicated.

Reactivity of the unsaturated carbonyl $|Mn_2H_2(CO)_6(dppm)|$ towards small molecules

F.J. García Alonso, M. García Sanz, J.A. Oliveira, V. Riera. Departamento de Química Organometálica. Universidad de Oviedo. 33071 Oviedo. Spain

A. Tiripicchio, M. Tiripicchio-Camellini. Istituto di Chimica Generale ed Inorganica. Universita di Parma. 43100 Parma. Italy.

Recently the carbonyl complex $|Mn_2H_2(CO)_6(dppm)|$, 1, containing the unsaturated fragment $(\mu\text{-}H)_2Mn_2(Mn{=}Mn)$, has been synthetized in our laboratory. We report now some results on the reactivity of 1 towards small molecules under mild conditions.

Compound 1 shows patterns of reactivity not observed previously in related unsaturated hydrido-carbonyl complexes. Thus 1 reacts with RCN, (R=Me,Et) to give $|Mn_2(\mu\text{-}\sigma,\pi\text{-}NCR)(CO)_6(dppm)|$, rare examples of complexes with π-bonded nitriles, but the expected(1) $|Mn_2(\mu\text{-}H)(\mu\text{-}N{=}CHR)(CO)_6(dppm)|$ are obtained for R=Ph, $HC{=}CH_2$. The reaction of 1 with t-BuNC yields $|Mn_2(\mu\text{-}\sigma,\pi\text{-}CN\text{-}t\text{-}Bu)(CO)_6(dppm)|$ in contrast with the behaviour of $|Re_2H_2(CO)_6(dppm)|$(1) or $|Mn_2H_2(CO)_4(dppm)_2|$(2). On the other hand, 1 reacts with RCOOH to afford $|Mn_2(\mu\text{-}H)(\mu\text{-}OOCR)(CO)_6(dppm)|$ while CF_3COOH adds oxidatively to $Os_3H_2(CO)_{10}$(3). Complex 1 also reacts with aldehydes to give $|Mn_2(\mu\text{-}H)(\mu\text{-}OR)\text{-}(CO)_6(dppm)|$.

(1).- D.W. Prest, M.J. Mays, P.R. Raithby. J.Chem. Soc., Dalton Trans., 1982, 2021.

(2).- H.C. Aspinall, A.J. Deeming. J. Chem. Soc., Chem. Commun., 1983, 839.

(3).- E.D. Korniets, L.K. Kedrova, N.I. Pavlenko. Izv. Akad. Nauk. SSSR, Ser. Khim. 1986, 2310.

Reactions of $|Mn_2H_2(CO)_6(dppm)|$ and $|Mn_2(CO)_8(dppm)|$ with terminal alkynes.

F.J.García Alonso, V. Riera, M.A. Ruiz. Departamento de Química Organometálica. Universidad de Oviedo. 33071 Oviedo. Spain.

A. Tiripicchio, M. Tiripicchio-Camellini. Istituto di Chimica Generale ed Inorganica. Universita di Parma. 23100 Parma. Italy.

It is well known that acetylenes are among the simplest and most reactive organic molecules, therefore they have been used as ideal starting materials for many different purposes. We report here the early results on the reactivity of terminal alkynes with carbonyl complexes $|MnH_2(CO)_6(dppm)|$, 1, and $|Mn_2(CO)_8(dppm)|$, 2, at r.t. or under U.V. irradiation (-10°C) respectively.

Since H_2 loss from 1 or CO evolution from 2 would yield seemingly the same intermediates, it could be anticipated that some common products might be obtained in the reactions of acetylenes with either 1 or 2. Actually three type of compounds can be isolated from both reactions, namely $|Mn_2(\mu\text{-}H)(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)(CO)_6(dppm)|$, 3, $|Mn_2(\mu\text{-}HC{\equiv}C\text{-}t\text{-}Bu)(CO)_6(dppm)|$, 4, and $|Mn(CO)_3(\mu\text{-}dppm)(\mu\text{-}OC(MeO)C{\equiv}CH)Mn(CO)_3|$, 5. On the other hand the vinyl compound $|Mn_2(\mu\text{-}H)(\mu\text{-}HC{=}CH_2)(CO)_6(dppm)|$, 6, is only accesible from 1 and finally $|Mn(CO)_4(\mu\text{-}dppm)Mn(\eta^3\text{-}C(O)CH{=}CR)\text{-}(CO)_2|$, 7, is exclusively obtained in the reactions of 2 with $HC{\equiv}CR$, (R= H, CH_2OCH_3).

NEW ORGANOMETALLIC RHENIUM CLUSTER COMPOUNDS

T. Beringhelli*, G. Ciani#, G. D'Alfonso*, M. Freni*, M. Moret# and A. Sironi#

* Dipartimento di Chimica Inorganica e Metallorganica, V.Venezian 21, 20133 Milano.
\# Istituto di Chimica Strutturistica Inorganica, V.Venezian 21, 20133 Milano

The unsaturated triangular cluster anion[1] $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ provides a good entry into the organometallic chemistry of hydrido-carbonyl clusters of rhenium, by reactions such as:

(a) hydride transfer to an electrophilic site of an unsaturated organic molecule:

$$\xrightarrow{RNC} [Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2C(H)NR)(CO)_{10}]^- \qquad \text{(Fig. 1, R = p-tolyl)}$$

Similar reactions have been previously observed with tropylium ion[2] and acetone[3].

(b) H_2 elimination and oxidative addition of a CH bond of a coordinated pyridine molecule:

$$\xrightarrow{NC_5H_5} [Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2NC_5H_4)(CO)_{10}]^- + H_2$$

(c) nucleophilic attack on a carbonyl ligand, followed by hydride transfer on the carbon atom (a reaction analogous to that[4] previously observed with $LiHBR_3$):

$$\xrightarrow{MeLi} [Re_3(\mu\text{-}H)_4(C(Me)O)(CO)_9]^{2-} \longrightarrow [Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2C(H)(Me)O)(CO)_9]^{2-} \quad \text{(Fig.2)}$$

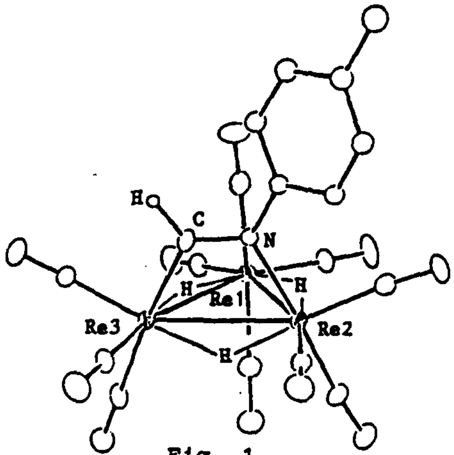


Fig. 1

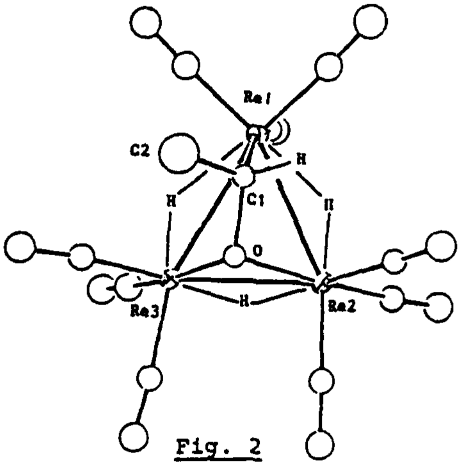


Fig. 2

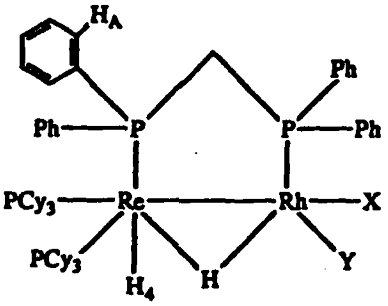
Work supported by Centro CNR Sintesi Struttura Composti Metalli di Transizione of Milan.

1) T. Beringhelli, G. Ciani, G. D'Alfonso, H. Molinari and A. Sironi, Inorg. Chem., 1985, 24, 2666.
2) T. Beringhelli, G. Ciani, G. D'Alfonso, P. Romiti, A. Sironi and M. Freni, Inorg. Chem., 1984, 23, 2849.
3) T. Beringhelli, G. D'Alfonso, M. Freni, G. Ciani, and A. Sironi, J. Organometal. Chem., 1988, 339, 323.
4) T. Beringhelli, G. D'Alfonso, G. Ciani and H. Molinari, Organometallics, 1987, 6, 194.

Systematic Syntheses of Polyhydrido Heterobimetallics Containing Bridging Diphosphines

Stuart Carr, Xavier Fontaine, Edmund Fowles, Bernard Shaw and Mark Thornton-Pett; Department of Inorganic and Structural Chemistry, University of Leeds, Leeds, LS2 9JT, UK

We have found that treatment of $[ReH_7(PCy_3)_2]$, $[OsH_6(PCy_3)]$ or $[IrH_5(PCy_3)_2]$ (PCy_3 = tricyclohexylphosphine) with diphosphines gave complexes of the type $[MH_x(PCy_3)_2(L\text{-}L)]$ (MH_x = ReH_5, OsH_4 or IrH_3; L-L = a monodentate diphosphine such as $PPh_2CH_2PPh_2$, $PPh_2C(=CH_2)PPh_2$, $PPh_2CH_2CH_2PPh_2$ or *cis*-$PPh_2CH=CHPPh_2$). Complexation of the free end of the diphosphine with other metals e.g. Cu, Ag, Mn, Rh or Ir gave heterobimetallic complexes which contained both terminal and bridging hydrides. These were fluxional at room temperature. Thus treatment of $[ReH_5(PCy_3)_2(PPh_2C(=CH_2)PPh_2)]$ with $[RhCl(CO)_2]_2$ or $[RhCl(norbornadiene)]_2$ gave respectively (1) or (2):



(1) X, Y = CO, Cl
(2) X, Y = norbornadiene$^+$

The hydride ligands in (1) and (2) were static at -80 °C and these complexes were each a mixture of two isomers which rapidly interconverted at room temperature. Evidence is given for an interesting interaction between H_A and Rh. Other reactions will be described.

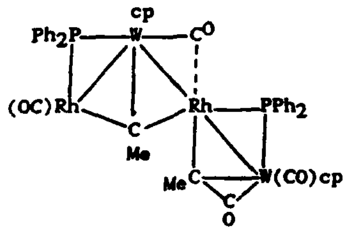
SYNTHESIS OF 'CHAIN'-TYPE POLYNUCLEAR METAL COMPLEXES CONTAINING TUNGSTEN AND RHODIUM OR IRIDIUM

Simon J. Davies, Judith A.K. Howard, Max U. Pilotti, and F. Gordon A. Stone,

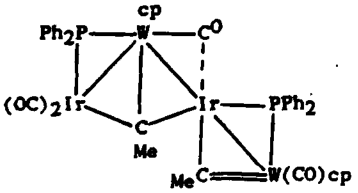
Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, Great Britain.

We have recently illustrated the rational directed syntheses of novel transition metal cluster compounds containing open chains of molybdenum or tungsten and nickel or platinum atoms, bridged by alkylidyne ligands. In an attempt to prepare similar compounds containing rhodium the reaction between $[Rh(cod)(\mu\text{-}PPh_2)]_2$ (1) and $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (2) was investigated.

The initial product of the reaction is $[Rh_2W_2\{\mu\text{-}C(Me)C(O)\}(\mu_3\text{-}CMe)(CO)_3\text{-}(\mu\text{-}PPh_2)_2(\eta\text{-}C_5H_5)_2]$ (3).



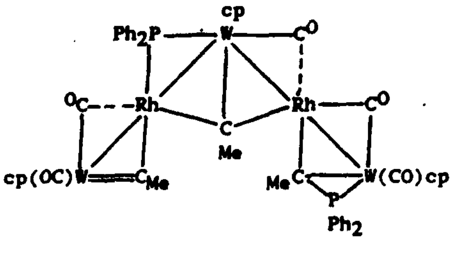
(3)



(5)

In contrast (2) reacts with $[Ir(cod)(\mu\text{-}PPh_2)]_2$ (4) to give the related compound $[Ir_2W_2\text{-}(\mu\text{-}CMe)(\mu_3\text{-}CMe)(CO)_4(\mu\text{-}PPh_2)_2(\eta\text{-}C_5H_5)_2]$ (5).

Compound (3) reacts with excess (2) to give the pentanuclear complex $[Rh_2W_3\{\mu\text{-}C(Me)C(O)\}(\mu\text{-}CMe)(\mu_3\text{-}CMe)(CO)_4(\mu\text{-}PPh_2)_2(\eta\text{-}C_5H_5)_3]$ (6) which isomerises slowly in solution to yield $[Rh_2W_3(\mu\text{-}CO)\{\mu\text{-}C(Me)PPh_2\}(\mu\text{-}CMe)(\mu_3\text{-}CMe)(CO)_4(\mu\text{-}PPh_2)\text{-}(\eta\text{-}C_5H_5)_3]$ (7) whose structure has been determined by X-ray analysis.



(7)

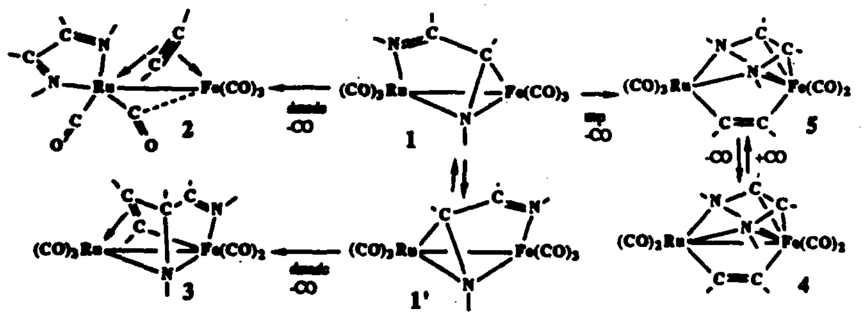
Reference

1. S.J. Davies, G.P. Elliott, J.A.K. Howard, C.M. Nunn, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1987, 2177.

THE REACTIVITY OF THE HETERODINUCLEAR α-DIIMINE COMPLEX FeRu(CO)$_6$(iPr-N=CHCH=N-iPr) TOWARDS ALKYNES

Fred Muller, Marco J. A. Kraakman, Kees Vrieze, Gerard van Koten, Laboratory for Inorganic Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, Holland

In order to compare the reactivity of homo- and heterodinuclear *α-diimine complexes* towards alkynes the novel heterodinuclear complex FeRu(CO)$_6$(iPr-DAB) (1) [iPr-DAB = iPr-N=CHCH=N-iPr], with the α-diimine bonded as a σ-N,μ_2-N',η^2-C=N' bridging 6e donor, was synthesized. Reaction of 1 with MeOC(O)C$\equiv$CC(O)OMe (dmadc) yields two products: FeRu(CO)$_5$(σ,σ-N,N'-iPr-DAB)(μ_2,η^2-dmadc) (2), which has a chelating iPr-DAB on Ru as well as a perpendicular bridging alkyne, and FeRu(CO)$_5$[iPr-N=CHCH(N-iPr)-C(C(O)OMe)=CC(O)OMe] (3) (X-ray). Complex 2 is formed via the substitution of the η^2-C=N bonded imine moiety (to Fe) in 1 by an η^2-C$\equiv$C bonded alkyne, followed by the loss of one CO. This type of mechanism is also involved in the reaction of Fe$_2$(CO)$_6$(iPr-DAB) with dmadc. The organic ligand in 3 results from the C-C coupling of one of the DAB imine C atoms and the alkyne. This C-C coupling is probably preceded by an isomerization of 1 (η^2-C=N coordination to Fe) to give the intermediate 1' with η^2-C=N coordination to Ru. The C-C coupling of the alkyne with the π-bonded imine C atom in 1' followed by the loss of one CO yields 3. An analogous C-C coupling occurs in the reaction of Ru$_2$(CO)$_6$(iPr-DAB) with dmadc. These results lead to the conclusion that the nature of the η^2-C=N-metal interaction has a major influence on the path along which the reactions of M$_2$(CO)$_6$(iPr-DAB) [M$_2$=Fe$_2$, FeRu, Ru$_2$] proceed. A third process is illustrated by the formation of FeRu(CO)$_5$(iPr-DAB)(μ_2-mp) (5) (X-ray) from 1 and MeOC(O)C$\equiv$CH (mp) which involves the insertion of the alkyne in the Fe-Ru bond followed by the loss of one CO. Complex 5 looses easily and reversibly one CO to give FeRu(CO)$_4$(iPr-DAB)(μ_2-mp) (4). In both 4 and 5 the DAB ligand is bonded as a σ,σ-N,N'-η^2,η^2-C=N,C=N' bridging 8e donor. Products of type 4 have also been found in reactions of the Fe$_2$ and Ru$_2$ analogues with alkynes.



CARBON-HYDROGEN AND CARBON-NITROGEN ACTIVATION PROCESSES IN THE REACTIONS OF $Ru_3(10)_{12}$ WITH TERTIARY AMINES

Edward Rosenberg, Kenneth Hardcastle, Michael Day, Tim McPhillips and Mauro Botta, Department of Chemistry, California State University, Northridge, California 91330.

Robert W. Gellert, Department of Chemistry, California State University, Los Angeles, California 90024

The reactions of tertiary amines, NR_2R' ($R = CH_2CH_3$, $CH(CH_3)_2$; $R' = CH_2CH_3$) with $Ru_3(CO)_{12}$ promoted by the radical catalyst $[Fe(\mu SCH_2CCH_3)(CO)_2P(C_6H_5)_3]_2$ have been examined. The structures of the major triruthenium products have been determined by x-ray diffraction and multinuclear nmr studies. In the case of $N(CH_2CH_3)_3$[1] three major Ru_3 products are obtained which result from a combination C-H and C-N cleavage reactions and one product which is the result of insertion of a C_2 fragment into the tertiary amines. With the bulkier $N(CH(CH_3)_2)_2(CH_2CH_3)$ only two major Ru_3 containing complexes are isolated which are the result of only C-H cleavage reactions on the ethyl group of the amine. In both series of complexes structures containing zwitterionic carbon nitrogen double bonds both coordinated to the cluster or as a pendent ligand are observed.[2] The importance of this type of bonding in C-N cleavage processes and a general scheme for the sequence of and factors controlling C-H and C-N bond cleavage processes will be presented based on the structural work and on the observed interconversion of the various products obtained.

References

(1) S. Aime, R. Gobetto, F. Padovan, M. Botta, E. Rosenberg and R. W. Gellert, Organometallics, 1987, **6**, 2074.

(2) M. A. Churchill and R. A. Lashewycz, Inorg. Chem., 1979, **18**, 848.

PYROLYSIS OF $Os_3(CO)_{10}(R_2C_2)$ (R=Ph,Me)

Hong Chen,Brian F.G.Johnson,Rajesh Khattar,Jack Lewis and Paul R.Raithby
University Chemical Laboratory, Lensfield Road,Cambridge CB2 1EW,U.K.

Pyrolysis of $Os_3(CO)_{10}(R_2C_2)$ (R=Ph,Me) gives a range of products. At high temperature (265°C), the dianion $[Os_{10}C(CO)_{24}]^{2-}$ is obtained as a major product, while at lower temperature (210°C), several neutral complexes are obtained including some high nuclearity clusters. These include $Os_4(CO)_{12}(Ph_2C_2)$ (1), $HOs_7(CO)_{18}[PhCC(C_6H_4)]$ (2), $HOs_3(CO)_9(C_4H_5)$ (3), $HOs_4(CO)_{11}(C_4H_5)$ (4), $Os_4(CO)_{12}(C_4H_6)$ (5). All these compounds have been identified and characterised by i.r.,mass spectroscopy and ^1H n.m.r. spectroscopy. Among these, compounds (2) and (4) have not been reported so far. ^1H n.m.r. studies of these two compounds give evidence for orthometallation of a phenyl ligand in (2), and an allylic bonding mode in (4) due to ligand rearrangement. Compounds (3) and (5) may be new isomers of the known compounds, as suggested by ^1H n.m.r. evidence[1,2]. The X-ray crystallographic study of (3) is in progress.

References

1. Antony J.Deeming, Sunduss Hasso and Mark Underhill, *J.C.S. Dalton Trans.*, 1975,1614
2. Ronald Jackson, Brian F.G.Johnson, Jack Lewis, Paul R.Raithby and Stephen W.Sankey, *J. Organomet. Chem.*., 1980, **193**, C1

OXIDATIVE ADDITION OF VINYL-DIPHENYL-PHOSPHINE ON $Ru_3(CO)_{12}$. CHARACTERIZATION AND CRYSTAL STRUCTURE OF $(\mu\text{-H})Ru_3(CO)_9(PPh_2CH{=}CH_2)(\mu,\eta^2\text{-}PPh_2CH{=}CH)$.

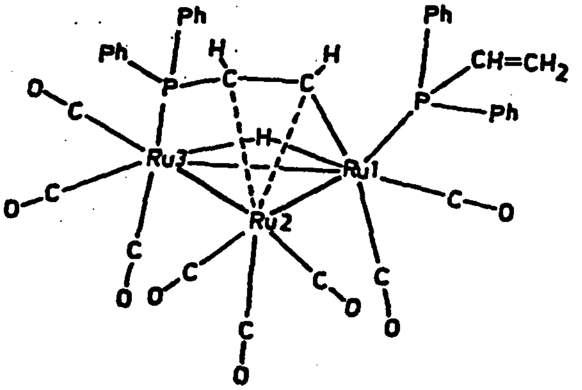
Enrico SAPPA, Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Universita' di Torino, Corso M. D' Azeglio 48, I-10125 Torino, Italy.

Antonio TIRIPICCHIO, Marisa TIRIPICCHIO CAMELLINI, Istituto di Chimica Generale ed Inorganica, Universita' di Parma, Viale delle Scienze, I-43100 Parma, Italy.

Martin J. MAYS, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

The title complex (1), obtained by reacting $Ru_3(CO)_{12}$ with vinyl-diphenyl-phosphine in aliphatic hydrocarbons under moderate heat, has been characterized by multinuclear n.m.r. spectroscopy. The structure of 1, fully elucidated by X-ray diffraction methods, is represented in the Figure.

The complex 1 represents an example of oxidative addition, without P-C bond cleavage, involving a phosphine characterized by an unsaturated hydrocarbyl substituent; generally, indeed, phosphino-alkynes undergo P-C bond cleavage even in mild conditions.[1,2] Upon thermal treatment, 1 gives several phosphido-bridged derivatives, which are now under investigation.



---

[1] A.J. Carty, Pure & Appl. Chem., 54, 113 (1982); A.J. Carty, Adv. Chem. Ser., 196, 163 (1982).

[2] F. Van Gastel, S.A. MacLaughlin, M. Lynch, A.J. Carty, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, J. Organometal. Chem., 326, C65 (1987).

Reactions of Trinuclear (Ru and Os) Carbonyl Clusters with Amino-Alcohols and -Thiols.

Silvio Aime, Mauro Botta, Roberto Gobetto, Luciano Milone, Domenico Osella and Luciana Violano

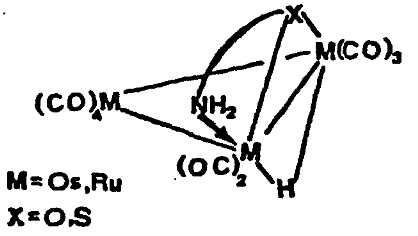
Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei
Materiali, Universita' di Torino, Via P. Giuria 7/9, 10125 Torino,
Italy

In the study of these reactions under different experimental conditions we were able to isolate and characterize several organometal carbonyl clusters corresponding both to the oxidative addition of -OH, -SH and -NH bonds to the metallic moiety and to the nucleophilic attack of the NH_2 group on coordinated CO ligands as already found in the interaction of primary and secondary amines with $M_3(CO)_{12}$ clusters (M=Ru and Os)^{1,2,3}.

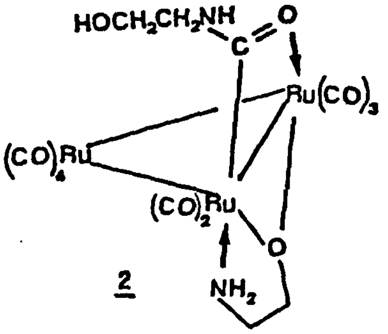
When the oxidative addition reaction involves the oxygen or sulphur centres the resulting derivatives contain the NH_2 group coordinating one of the metal atoms bridged by the heteroatom as shown in 1. The easy cleavage of the coordinative bonds to form unsaturated species in solution under mild experimental conditions shows interesting properties for these organometallic coordination compound.

In the reaction between $Ru_3(CO)_{12}$ and Ethanolamine (ETA) in THF as solvent at ambient temperature a single product is obtained (isolated in 65% yield) which contains two ETA moyeties bonded as shown in 2.

This work was supported by Italian Ministry of Education.



1



2

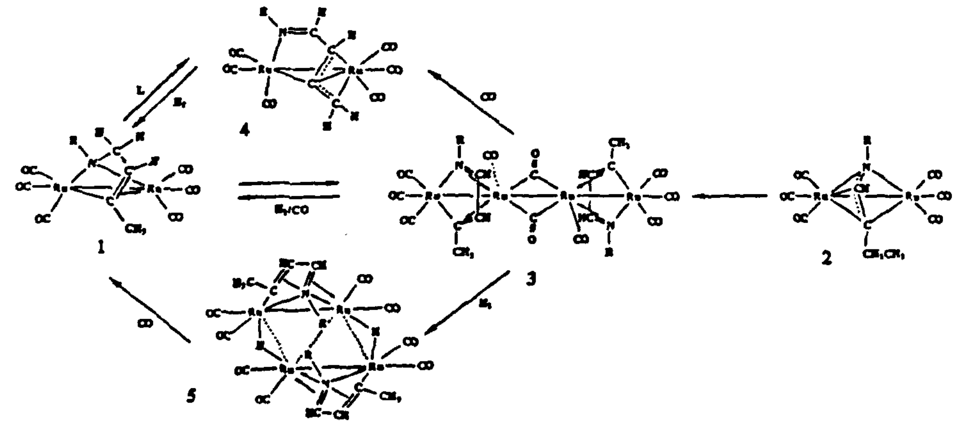
1) R. Szostak, C.E. Strouse and H.D. Kaesz J. Organomet. Chem. 1980, 191, 243.
2) A.D. Kaesz, C.B. Knobler, M.A. Andrews, G. Van Hoskirk, R. Szostak, C.E. Strouse, Y.C. Lin and A. Mayr Pure Appl. Chem. 1982, 54, 131.
3) A. Mayr, Y.C. Lin, N.M. Boag and H.D. Kaesz Inorg. Chem. 1982, 21, 1704.

Hydrogenation and dehydrogenation processes on di- and tetranuclear ruthenium compounds

W.P. Mul, M. van Leijen, C.J. Elsevier and K. Vrieze
University of Amsterdam, Dept. of Inorg. Chem., Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands

Whereas the coordination and reactivity of 1,3-dienes and 1,4-diaza-1,3-dienes on metal carbonyl frameworks of the iron triad has been extensively investigated, the chemistry of 1-aza-1,3-dienes remained virtually unexplored. Only in the last few years this gap has partly been filled up. New di-, tri- and tetranuclear organometallic compounds containing one or two ligands arising from hydrogen migration or abstraction were isolated from thermal reactions of $Ru_3(CO)_{12}$ with CH_3-CH=CH-CH=N-R (R=i-Pr, c-Hex, t-Bu). On the poster we present additional information about their formation and interconversion and the influence of the R-group.

The dinuclear compounds **1** (R=i-Pr, c-Hex) and **2** (R=i-Pr, c-Hex, t-Bu) are initially formed. A sequence of thermal reaction steps including dehydrogenation of the ligands, loss of CO from the metal framework and subsequent dimerization results in the almost quantative formation of the tetranuclear **3** after 4-24 h (**1**) or 3-4 days (**2**). In a reverse reaction hydrogenation of **3** in the presence of CO yields **1**. In the latter two different reaction pathways may be involved with the intermediacy of **4** or **5**. Dehydrogenation of **1** is also observed during thermal reactions in the presence of an excess of 1-aza-1,3-diene, though another reaction is kinetically favoured, which results in the formation of **4**. Possible mechanisms and catalytic applications will be discussed.



S70

^{1}H Spin-Lattice Relaxation Times in Hydrido Carbonyl Clusters as an Aid to the determination of Molecular Structures

Silvio Aime, Mauro Botta, Marco Cisero, Roberto Gobetto, Luciano Milone and Domenico Osella

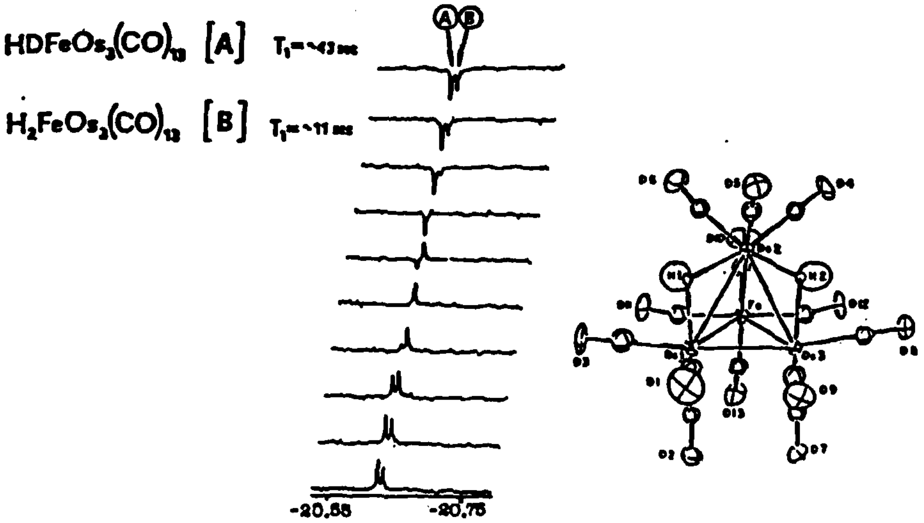
Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Universita' di Torino, Via P. Giuria 7/9, 10125 Torino (Italy)

This work deals with the evaluation of H-H distances obtained *via* the measurement of proton spin-lattice relaxation times:

$$\frac{1}{T_1^{DD}} = \frac{3}{2} \cdot \frac{\gamma^4 \hbar^2}{r^6} \cdot \tau_c$$

The molecular correlation time τ_c has been evaluated from T_1 and n.O.e. determinations of rigid C-H fragment in the organic ligand or by applying the Stokes-Debye formula.

In systems containing two chemically and magnetically equivalent hydrides (and no other hydrogen) it is possible to extract structural distances by evaluating the difference in the relaxation rates between the two H,H and H,D isotopomers if τ_c is known by an independent experiment. The measurement of the relaxation times T_1 of the two isotopomers is possible in the same experiment by making use of the small isotopic shift between the hydrido resonances of the two isotopomers. This is shown in the figure for $H_2FeOs_3(CO)_{13}$ and $HDFeOs_3(CO)_{13}$.



This work was supported by Italian C.N.R. under the grant no. 87.007.03.

BUILD UP OF OSMIUM CARBONYL CLUSTERS USING ARSENIC LIGANDS

Karlheinz Guldner, Brian F.G. Johnson, Jack Lewis, Anju D. Massey,
University Chemical Laboratory, Lensfield Road. CambridgeCB2IEW. U.K.

Reaction of the activated cluster $Os_3(CO)_{12-n}(NCMe)_n$ (n=1 (1a), n=2 (1b)) with primary arsines[1]($RAsH_2$,R=Ph, Me,H) yields the arsinidine compounds $H_2Os_3(CO)_{11}(\mu_3\text{-AsR})$ (2a) (R=Ph,Me,H). At elevated temperatures, (2a) is transformed to the AsPh capped cluster $[(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-AsPh})]$(2b). Treatment of (2a) with osmium sources like $Os_3(CO)_{12}$, $H_2Os(CO)_4$ and $H_2Os_3(CO)_{10}$ under thermolytic conditions gives the tetranuclear cluster $[(\mu\text{-H})_2Os_4(CO)_{12}(\mu_3\text{-AsPh}]$ (2c) and the pentanuclear cluster $[(\mu\text{-H})_2Os_5(CO)_{15}(\mu_4\text{-AsPh})]$ (2d) as the major products. Similarly the reaction of (1a) and (1b) with the secondary arsine[2] Me_2AsH gives the $AsMe_2$ bridged triosmium clusters $[(Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-AsMe}_2)]$ (2e) and $[(Os_3(\mu\text{-H})_2(CO)_8(\mu\text{-AsMe}_2)_2]$ (2f) which are formed via the intermediate compound $Os_3H(CO)_{11}(\mu\text{-AsMe}_2)$ (2g).

Extension of this work using AsH_3,$PhAsH_2$ and $As(p\text{-Tol})_3$ ligands leads to the synthesis of osmium clusters, ranging in nuclearity from three to six metal atoms , containing μ-AsR ,μ-AsR_2 and AsR_3 groups.The reaction of (1a) with $PhAsH_2$ in refluxing CH_2Cl_2 gives $Os_3(CO)_9(AsPh)_2$ (3a). In comparison, the reaction with $As(p\text{-Tol})_3$ gives $Os_3(CO)_9(\mu\text{-AsC}_6H_4CH_3)(\mu\text{-C}_6H_3CH_3)$ (4a), which results from the migration of one tolyl group from the arsenic to the cluster framework, and $Os_3(CO)_{10}(\mu\text{-AsC}_6H_4CH_3)(\mu\text{-C}_6H_3CH_3)$ (4b). Reaction of $As(p\text{-Tol})_3$ with (1b) gives a trinuclear osmium cluster with two bridging arsine ligands and involves metal-metal bond breakage (4c). Cluster build-up reactions using the arsine substituted cluster $Os_3(CO)_{11}AsTol_3$ with $H_2Os(CO)_4$ gives $Os_4(CO)_{11}As_2Tol_2$ (5a) and $Os_6(CO)_{13}As_2Tol_2$ (5b). A hexanuclear cluster $H_2Os_6(CO)_{21}AsH$ (6a) is also obtained by reacting $Os_3(CO)_{11}AsH_3$ with (1a). All these compounds have been characterised by i.r, n.m.r and mass spectroscopy. The *X* -ray crystallographic study of (4a) and (4c) is in progress.

Reference:1,2: Karlheinz Guldner, Brian F.G. Johnson, Jack Lewis and Paul R. Raithby.(Unpublished results).

Arene Activation by Triosmium Cluster:Nucleophilic Addition to cationic $[HOs_3(CO)_9(PPh_3)(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2C_6H_6)]BF_4$.

Márcia Martinelli; Mark A Gallop; Brian F.G.Johnson; Jack Lewis.
Inorganic Chemistry Department, Cambridge University, Lensfield Road, Cambridge, CB 2 1 EW, England.

The ability of certain transition metal centers to activate *normally unreactive* π-hydrocarbons towards nucleophilic attack has been known for several decades (1). This area has attracted considerable interest in recent years due to its potential application in organic synthesis.

Factors controlling reactivity, mechanism and site of nucleophilic addition in mononuclear metal-arene systems have been reviewed(1) and analogous studies concerning the electrophilicity of *benzene and toluene, coordinated in the face-capping* bonding mode, in $[Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2C_6H_6)]$ and $[Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2(C_6H_5Me))]$ have recently been performed(2).

The present work is concerned with nucleophilic addition to the benzene in $[HOs_3(CO)_8(PPh_3)(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2C_6H_6)]BF_4$. Reaction with diethylamine, MeLi, PhLi, H^-, MeO^- and DBU afforded neutral compounds. NMR evidence indicates attack occurs at the arene ring and this has been confirmed by a X-ray strusctural analysis of $[HOs_3(CO)_8(PPh_3)(\mu_3{:}\eta^2{:}\eta^1{:}\eta^2C_6H_7)]$.

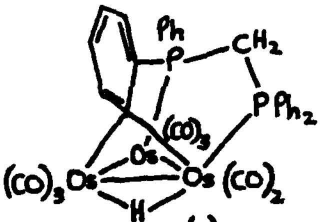
1. L.A.P.Kane-Maguire; E.D.Honig; D.A.Sweigart. Chem. Rev., 1984, 84, 525.
2. M.A.Gallop. Ph.D. Theses. Cambridge Universiy. 1988.

ELECTRONIC CONTROL OF THE COORDINATION MODE OF AN ALKYNE TO A TRI-OSMIUM CLUSTER AND THE REACTIVITY OF THE UNSATURATED CLUSTER $[Os_3(\mu\text{-}H)(CO)_8\{\mu\text{-}Ph_2PCH_2P(Ph)C_6H_4\}]$

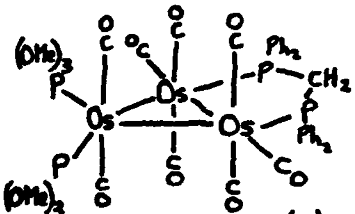
P. Ann Dolby, Marjorie M. Harding, and Anthony K. Smith, Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, Grove Street, PO Box 147, Liverpool L69 3BX, England

The unsaturated cluster $[Os_3(\mu\text{-}H)(CO)_8\{\mu\text{-}Ph_2PCH_2P(Ph)C_6H_4\}]$ (1) readily undergoes a de-metallation reaction, allowing the addition of two or four electrons to the cluster framework to occur under mild conditions. For example, complex (1) reacts with $P(OMe)_3$ at room temperature to produce $[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$ (2) ($dppm{=}Ph_2PCH_2PPh_2$). With the alkyne, $PhC{\equiv}CPh$, complex (1) reacts to give the 46-electron cluster $[Os_3(CO)_7(dppm)(PhC{\equiv}CPh)$ (3), in which the alkyne ligand is coordinated in the $\mu_3,\eta^2\text{-}\perp$ mode (shown by X-ray crystallography).[2] This coordination mode, previously unknown for triosmium clusters, is favoured over the usual $\mu_3\eta^2\text{-}\|$ mode (4) by the presence of the σ-donating diphosphine ligand, and demonstrates how a change in electronic properties of a triangular array of metal atoms can influence the mode of coordination of unsaturated organic molecules to that array.

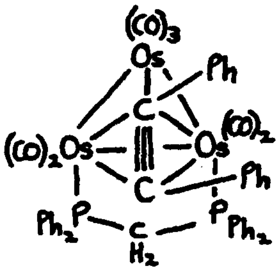
The cluster (3) also undergoes a ready reversible addition of CO leading to the formation of $[Os_3(CO)_8(dppm)(PhC{\equiv}CPh)]$ (5), in which the coordination of the alkyne is changed to the more usual $\mu_3,\eta^2\text{-}\|$ mode.



(1)

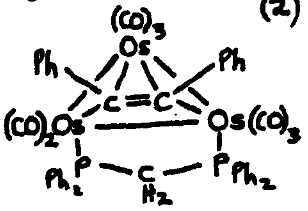


(2)



(3)

(4)



(5)

References

1. J.A. Clucas, D.F. Foster, M.M. Harding, and A.K. Smith, J. Chem. Soc., Chem. Commun., 1984, 949.
2. J.A. Clucas, P.A. Dolby, M.M. Harding, and A.K. Smith, J. Chem. Soc., Chem. Commun., 1987, 1829.

PROTONATION OF ALKENYLIDENE COMPLEXES
$Os_3H_2(CO)_9(C{=}CHR)$ ($R{=}H, C_6H_5$, $C_5H_5FeC_5H_4$)

Avtandil Koridze, Ol'ga Kizas, Pavel Petrovskii

Institute of Organoelement Compounds, Academy of Sciences,
28 Vavilov Str., Moscow, U.S.S.R.

Reaction of $Os_3H_2(CO)_9(C{=}CHR)$ (Ib,c $R{=}C_6H_5$, $C_5H_5FeC_5H_4$) in CD_2Cl_2 with CF_3COOH at low temperatures affords bridged alkenyl complexes $Os_3H_2(CO)_9(CH{=}CHR)\{OC(O)CF_3\}$(IIb,c) which were characterized by ^1H, ^{19}F NMR and IR spectroscopy. At room temperature complexes IIb,c rearrange to the corresponding cationic trihydrides $[Os_3H_3(CO)_9(C{=}CHR)]^+$ (IIIb,c) by alkenyl hydrogen atom migration to the trimetallic core.

Whereas protonation of Ib,c with CF_3COOH at -30°C occurs via attack on the carbene atom of alkenylidene ligand, the reaction of $Os_3H_2(CO)_9(C{=}CH_2)$ (Ia) under the same conditions gives only $[Os_3H_3(CO)_9(C{=}CH_2)]^+$(IIIa), and there is no evidence for the formation of a bridged alkenyl complex.

Treatment of Ia-c with $HBF_4{\cdot}OEt_2$ in CD_2Cl_2 even at -60°C afforded only cationic trihydrides IIIa-c.

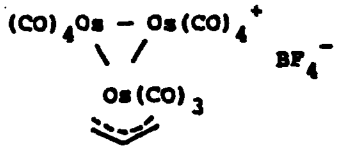
SYNTHESIS AND PROPERTIES OF IRON GROUP METAL CLUSTERS

Asunta Tuula, Department of Chemistry, University of Jyväskylä, Tellervonkatu 8, SF-40100 Jyväskylä, Finland

Krivykh Vasily and Rybinskaya Margarita, A.N. Nesmeyanov Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, 117813, Moscow, Vavilova 28 (U.S.S.R.)

Thermal and photochemical reactions of trinuclear carbonyls of Fe, Ru and Os with allyl alcohol in acidic medium as well as their reactions with $(CH_3)_3NO \cdot 2\,H_2O$ with subsequent protonation have been reported.1)
Cationic mononuclear allyltetracarbonyl complexes of Fe, Ru, Os and cationic Os cluster with π-allyl ligand have been obtained. In case of $Os_3(CO)_{12}$ the formation of the two compounds, namely, mono- and trinuclear (III and IV) cationic allyl complexes were *observed:*

III



IV

Formation and structural characterization by means of IR and NMR methods as well as by X-ray methods will be presented and discussed. The properties of the complexes will be reported.

1. V.V. Krivykh, T. Asunta, O.V. Gusev and M.I. Rybinskaya, J. Organomet. Chem., 338 (1988) 55.

THE CHEMISTRY OF THE HYDRIDOCARBONYLTRIOSMIUM ANION $[HOs_3(CO)_{11}]^-$

S.N.A.B. Syed-Mustaffa, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia.

J. Lewis, University Chemical Laboratories, Lensfield Road, Cambridge, United Kingdom.

For the past few years the study of mixed-metal clusters have been intensive and since then numerous mixed-metal clusters have been synthesised. The study of such cluster is interesting as it throw light into the understanding of catalytic activities of bimetallic heterogenous catalysts.

There are several methods of preparing meixed-metal clusters such as pyrolysis of transition metal carbonyls, addition of coordinatively unsaturated species, redox condensation and reaction of carbonylmetalates with metal halides. Herein we report the synthesis of goldtriosmium cluters using the anion $[HO_3(CO)_{11}]^-$ as precursor.

The reaction of the anion $[HOs_3(CO)_{11}]^-$ with an equivalent amount of R_3PAuCl in dichloromethane at room temperature lead to the monogold clusters $HOs_3(CO)_{11}AuPR_3$ and $HOs_3(CO)_{10}$ $AuPPh_3$[1]. When the anion $[HOs_3(CO)_{11}]^-$ is refluxed with a two-fold equivalent amounts of R_3PAuCl in chloroform the digold cluster $Os_3(CO)_{10}(AuPR_3)_2$ is obtained in high yield[2]. Stirring the anionic cluster $[HOs_3(CO)_{11}]^-$ with half equivalents of R_3PAuCl in chloroform at room temperature afforded the bridged-gold cluster $[\{HOs_3(CO)_{10}\}_2Au]^-$[3]. The yield of the goldtriosmium clusters is further enhanced in presence of $TlPF_6$.

[1] B.F.G. Johnson, D.A. Kaner, J. Lewis and P.R. Raithby, J. Organometal.Chem., 1981, 215, C33.

[2] K. Burgess, B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby, and S.N.A.B. Syed-Mustaffa, J. Chem.Soc.,Chem.Commun., 455, 1981.

[3] B.F.G. Johnson, D.A. Kaner, J. Lewis and P.R. Raithby, J.Chem.Soc., Chem.Commun., 753, 1981.

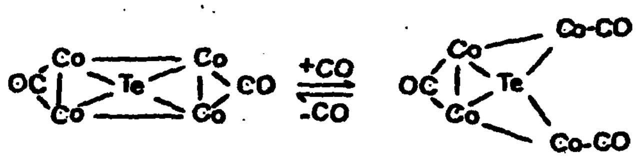
TETRACOBALT PLANAR CLUSTERS WITH μ_4-BRIDGING LIGANDS

Giuliana Gervasio, Olimpia Gambino, Rosanna Rossetti,
Dipartimento di Chimica Inorganica,Chimica Fisica e Chimica dei Materiali, Università di Torino, Via Giuria 7, I-10125 Torino, Italy

Pier Luigi Stanghellini,
Dipartimento di Chimica ,Università di Sassari, Via Vienna 2, I-07100 Sassari, Italy

The core structures of tetranuclear clusters have mainly tetrahedral or butterfly shapes, whereas the square or rectangular planar arrays are quite rare. Among them, few examples of cobalt carbonyls are known, of general formula $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}X)(\mu_4\text{-}Y)$ and of similar structure, where X=Y=S(Ia),Te(Ib),PC_6H_5(Ic) are coordinated on the two sides of the rectangular Co_4 core and two CO groups bridge the short Co-Co bonds. We report the synthesis of complex Id with X=Y=Se via a room temperature reaction of $Co_2(CO)_8$ with CSe_2 or red Se and its structure determination. Comparing the dichalcogen compounds, the dimensions of the Co_4 rectangle regularly increase in the order S<Se<Te, for allocating the greater bridging chalcogen atoms; the Co-X and the non-bonding X....Y distances increase in the same way.

Complex Ib adds reversibly a CO molecule to give $Co_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (II). An easy high yield synthesis of II by reacting $Co_2(CO)_8$ with $[TeO_3]^{=}$ at room temperature and atmospheric pressure was carried out and the complex completely characterized.



Ib

II

The Co_4 core of II remains planar with trapezoidal shape, the three Co-Co bond distances being similar and close to the CO-bridged distances in Ib.

New complexes Ie (X=S, Y=$HC_2C_6H_5$) and If(X=S, Y=HC_2H) were prepared in good yields by reacting $Co_3(CO)_9S$ with the alkyne in the presence of $(CH_3)_3NO$. The reaction is a noteworthy example of cluster expansion, which usually begins by a decarbonylation process largely favoured by $(CH_3)_3NO$. The structure of Ie shows a quite uncommon coordination of an alkyne to a planar M_4 core with the C≡C bond parallel to the long side of the rectangle. The i.r. frequency of the acetylene modes in If were assigned and related to the type of the alkyne-cluster bonding.

MONONUCLEAR THIOLATECOBALT CARBONYLS: CLUSTER BUILDING BLOCKS

Miklòs TASI, Tibor RANGA and Gyula Pàlyi
Research Group for Petrochemistry of the Hungarian Academy of Sciences, Veszprém and Institute of General and Inorganic Chemistry, Eotvos University, Budapest, Hungary

Paolo ZANI
Department of Organic Chemistry, University of Bologna, Italy.

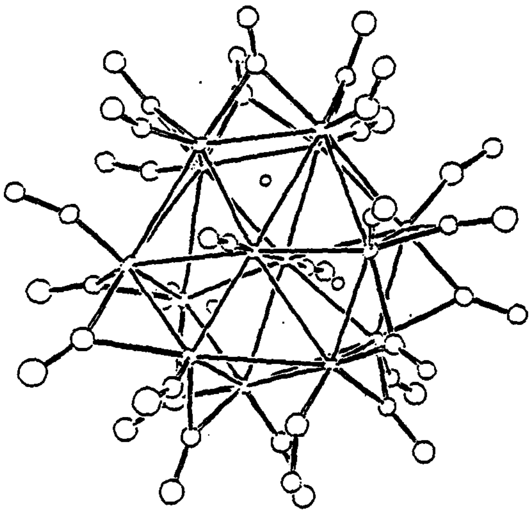
$RSCo(CO)_4$ (R=Et, $PhCH_2$, Ph) (1) compounds were prepared from RSNa and $ICo(CO)_4$ or $Co_2(CO)_8$ and from RSSR and Na/ $Co(CO)_4$ /.
These very instable compounds react with PPh_3 to give $RSCo(CO)_3(PPh_3)$ (2) which can be isolated. 1 readily oligomerizes to Co_3 to Co_6 cluster derivatives already over -20°C. In contrast to the (hypothetic) ROCo-$(CO)_4$ alkoxides 1 does not react with CO up to 15 bar at -30°C.
The phosphine complexes 2 react to PPh_3 *containing cluster derivatives* which are in course of characterization.

NEW HIGH NUCLEARITY COBALT NITRIDO-CARBONYL CLUSTERS. SYNTHESIS AND X-RAY STRUCTURE OF THE ANION $[Co_{14}N_3(CO)_{26}]^{3-}$.

S. Martinengo, Centro C.N.R. Sintesi e Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Via G. Venezian 21, I-20133 Milano, Italy.

G. Ciani, M. Moret and A. Sironi, Istituto di Chimica Strutturistica Inorganica, Via G. Venezian 21, I-20133 Milano, Italy.

In 1979 we reported the first examples of carbonyl cluster compounds containing a fully encapsulated nitrogen atom, namely the trigonal prismatic anions $[M_6N(CO)_{15}]^-$ (M = Co,Rh).[1] Mild pyrolysis of these species gave rise, in the case of rhodium, to larger cluster compounds such as the dinitride $[Rh_{12}HN_2(CO)_{23}]^{3-}$,[2] while in the case of cobalt only rearrangement of the metal framework to the octahedral $[Co_6N(CO)_{13}]^-$ was observed.[3] We have now investigated the pyrolysis of the cobalt species in more drastic conditions (diglyme, 140°C) obtaining the new high nuclearity $[Co_{14}N_3(CO)_{26}]^{3-}$ anion, the first example of a trinitride cluster compound. The anion is shown in the Figure.



The unprecedented metal atom cluster consists of two superimposed rather folded centered-hexagons of cobalt atoms giving rise to a distorted fragment of simple hexagonal packing. Three alternate, out of the six, trigonal prismatic cavities are occupied by encapsulated nitrogen atoms. This situation resembles that present in binary phases of some metal carbides and nitrides. However the empty prisms are quite distorted. The CO ligands are disposed 12 edge bridging, and 14 terminally, one for each cobalt atom. The Co-Co bond lengths are rather scattered (range 2.42-2.94 Å).

References

1) S. Martinengo, G. Ciani, A. Sironi, B.T. Heaton and J. Mason, J. Am. Chem. Soc., 1979, 101, 7095.

2) S. Martinengo, G. Ciani and A. Sironi, J. Chem. Soc., Chem. Commun., 1986, 1742.

3) G. Ciani and S. Martinengo, J. Organomet. Chem., 1986, 306, C49.

REACTIONS OF $[Ir_4(CO)_{12}]$ and $[Ir_4(CO)_{11}(SCN)][PPN]$ WITH MULTIDENTATE LIGANDS

Diane Burns, Michael P. Brown, Marjorie M. Harding and Anthony K. Smith, Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England

Following our discovery that the tripod ligand substituted iridium cluster $[Ir_4(CO)_9\{(PPh_2)_3CH\}]$ has an all-terminal CO ligand structure.[1] we have carried out further investigations into the reactions of $[Ir_4(CO)_{12}]$ and $[Ir_4(CO)_{11}(SCN)]^-$ with multidentate phosphine ligands.

The reactions to be described will include treatment of $[Ir_4(\mu\text{-}CO)_3(CO)_8(PPh_3)]$ with $HC(PPh_2)_3$ to give the all-terminal CO ligand cluster $[Ir_4(CO)_8(PPh_3)\{HC(PPh_2)_3\}]$, and the reaction between $[Ir_4(CO)_{11}X]^-$ (X = Br, SCN) and $CH_3C(CH_2PPh_2)_3$. In addition we report the crystal structure determination of an isomer of $[Ir_4(CO)_{11}(SCN)]^-$, which, as the PPN^+ salt, contains three bridging CO ligands, in contrast to the recently reported[2] structure of the $[NBz_2Me_2]^+$ salt which has an all-terminal CO ligand configuration.

1. J.A. Clucas, M.M. Harding, B.S. Nicholls, and A.K. Smith, J. Chem. Soc., Chem. Commun., 1984 319.

2. R. Della Pergola, L. Garlaschelli, S. Martinengo, F. Demartin, M. Manassero, and M. Sansoni, Gazz. Chim. Ital., 117, 245 (1987).

SOME CHEMISTRY OF SULPHUR DIOXIDE SUBSTITUTED TRINUCLEAR PLATINUM CLUSTERS

J.G.JEFFREY, A.BURROWS, O.EZOMO, D.M.P.MINGOS & S.BOTT.

Inorganic Chemistry Laboratory, University of Oxford, U.K.

The ligand SO_2 is comparable to CO both in its ability to stabilise clusters and their mutual labilisation by the addition of amine oxides. Recently routes into SO_2 clusters in particular, $[Pt_3(\mu\text{-}SO_2)_3(PR_3)_3]$, have been realised and the bonding and chemistry of these clusters explored.

We now report the systematic sequential substitution of CO into $[Pt_3(\mu\text{-}SO_2)_3(PCy_3)_3]$ which yields the mixed mono and bis substituted carbonyl clusters $[Pt_3(\mu\text{-}SO_2)_{3-n}(\mu\text{-}CO)_n(PCy_3)_3]$, where $n=1$ and 2 respectively. These compounds have been fully characterised by X-ray crystallography, $^{31}P\{H\}$ and $^{195}Pt\{H\}$ N.m.r., infra-red spectroscopy and microanalysis. Some correlation has been observed between the strength of the Pt—Pt bonds and the corresponding J_{Pt-P} coupling constant for the respective cluster. Also some mechanistic studies, primarily using I.R. stop flow techniques, have been undertaken to investigate the carbonylation of these clusters.

The labilisation of phosphines using isocyanide ligands on tri-platinum clusters has been further investigated using stoichiometric amounts of xylyl isocyanide on the aforementioned mixed bridged clusters.

In addition the reaction of acetylides and terminal acetylenes have been investigated on both the mixed and homo bridged platinum clusters, where Me_3NO activation has been employed. For example, reaction of the 42-electron cluster $[Pt_3(SO_2)_3(PCy_3)_3]$ with sodium acetylide has afforded the novel 44-electron cluster species $[Pt_3(SO_2)_2(\mu\text{-}C\equiv CH)(PCy_3)_3]^-[(n\text{-}Butyl)_4N]^+$ where the organic moiety bridges one edge of the platinum triangle through its α-carbon. The reactivity of such organoclusters will be further discussed.

402

ANIONIC TRIMETALLIC COMPOUNDS WITH Fe-M-M' (M= Zn, Cd, Hg; M'= Fe, Mo, W) SKELETONS.

Montserrat Ferrer, Roser Reina, Oriol Rossell and Miquel Seco.
Departament de Química Inorgànica. Universitat de Barcelona. Diagonal 647,
08028 Barcelona. Spain.
Xavier Solans
Departament de Cristal.lografía, Mineralogia i Dipòsits Minerals.
Martí i Franquès s/n. 08028 Barcelona. Spain.

As an extension of previous studies which have lead to the synthesis of neutral heterotrimetallic mercury compounds[1], we have investigated the formation of anionic trimetallic compounds of zinc, cadmium and mercury.

The reaction of $(NEt_4)[HFe(CO)_4]$ with MX_2 (M= Zn, Cd, Hg; X= halides), produces the di-hydrides $[(OC)_4HFe\text{-}Hg\text{-}FeH(CO)_4]$ which are sensitive towards H^+ abstraction with BuLi to afford, with very good yields, the di-anions $[(OC)_4Fe\text{-}M\text{-}Fe(CO)_4]^{2-}$, stabilised as the PPN^+ salts. Similar species have been prepared by different and longer routes[2].

The complex $(PPN)_2[(OC)_4Fe\text{-}Hg\text{-}Fe(CO)_4]$ reacts with trimetallic $[Hg\{M'(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (M'= Mo, W) derivatives to give, after ligands redistribution, the new unsymmetrical $(PPN)[(OC)_4Fe\text{-}Hg\text{-}M'(CO)_3(\eta\text{-}C_5H_5)]$ (M'= Mo, W) compounds.

The structural characterization of all these derivatives has been carried out by i.r. and n.m.r. spectroscopy. X-Ray crystal structure of the compound $(PPN)_2[(OC)_4Fe\text{-}Hg\text{-}Fe(CO)_4]$ is also reported.

REFERENCES

1.- O.Rossell, M.Seco, and I.Torra, J.Chem.Soc.Dalton Trans., 1986, 1011; P.Braunstein, O.Rossell, M.Seco, I.Torra, X.Solans, and C.Miravitlles, Organometallics, 1986, 5, 1113.

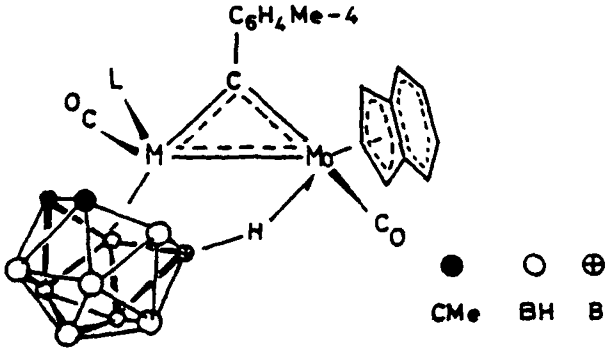
2.- H.Behrens, H.D.Feilner, E.Lindner, and D.Uhlig, Z.Naturforsch., 1977, 26b, 990; B.A.Sosinsky, R.G.Shong, B.J.Fitzgerald, N.Norem, and C.O'Rourke, Inorg.Chem., 1983, 22, 3124.

SYNTHESIS AND REACTIVITY OF THE BIMETALLIC COMPOUNDS
$[MMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(L)(\eta^{n-4}\text{-}C_2B_nH_nMe_2)(\eta^5\text{-}C_9H_7)]$
{ M = Mo, W; L = CO, $P(OMe)_3$; n = 9, 10 }

Stephen J. Dossett and F. Gordon A. Stone

Department of Inorganic Chemistry, University of Bristol,
Bristol BS8 1TS, Great Britain.

The anionic complexes $[M(\equiv CC_6H_4Me\text{-}4)(CO)(L)(\eta^{n-4}\text{-}C_2B_nH_nMe_2)]^-$ { M = Mo, W; n = 9, 10; L = CO, $P(OMe)_3$ } react with the salt $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ to provide bimetallic compounds of the form $[MMo(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(L)(\mu\text{-}H)(\eta^{n-4}\text{-}C_2B_nH_{n-1}Me_2)]$:



The metal-metal bonds in these species are supported by bridging alkylidyne and borohydride groups. The non-innocence of these moieties will be discussed with reference to the reactions of these complexes with unsaturated organic substrates.

LUMINESCENCE OF TUNGSTEN (O)-CARBYNE COMPLEXES

Raûl G.E.Morales, Departamento de Química.
Universidad de Chile, Casilla 653, Santiago-Chile.

Andreas Mayr and Donald S. Mc Clure, Department of Chemistry, Princeton
University, Princeton, New Jersey 08544, U.S.A.

The emission spectra of some octahedral tungsten carbyne complexes of the type $((W\equiv CAr)\ X\ (CO)_{4-n}L_n)$ with monodentate and two bidentate ligands in solution of 2-methyltetrahydrofuran have been analyzed at 77 K and room temperature.

The observed luminescence in glass solution was completely depolarized when incident polarized light was used. The phenyl ring linked to the carbyne center was found as a fundamental structure for the new luminescent species, however substituents in this ring do not alter in a significant way the luminescent properties of it. The emission lifetime for these species at 77 K are in the range of biradical species (4 to 17 μs) in agreement with our model for a system of carbene nature as the luminescent chromophore excited state.

The emission of some octahedral single bidentate ligand tungsten carbyne complexes presents a nonsimple exponential decay according to time resolved spectroscopy data in the range of 1 to 60 μs. These experimental data reveals a conformeric equilibrium in the ground and excited states derived from the bidentate ligand conformations.

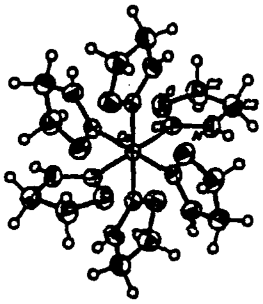
This work was supported by the Department of Energy and N.S.F. (Grants CHE 8506943 and CHE 8617472).

New Homoleptic Carbene Complexes

Thomas Bliß, Ulrike Plaia and Wolf Peter Fehlhammer

Institut für Anorganische und Analytische Chemie der Freien
Universität Berlin, Fabeckstraße 34-36, D-1000 Berlin 33

A series of oligo- and percarbene complexes has been synthesized from metal salts and 2-hydroxy isocyanides of which the hexacarbene complexes of cobalt(III) and rhodium(III) are most remarkable, e.g.[1]



$[Co(\overline{CNHCH_2CH_2O})_6]Cl_3 \cdot 3H_2O$

Both, their tendency of formation and stabilities are surprisingly high. By coupling of the carbene ligands in the coordination sphere of the metals, a further increase in stability of these complexes is to be expected. Several approaches to this aim will be reported including reactions of isocyanide complexes of palladium(II) and platinum(II) with diamines.

---

1) U. Plaia, H. Stolzenberg and W.P. Fehlhammer, J. Am. Ch. Soc. 107 (7), 2171 (1985)

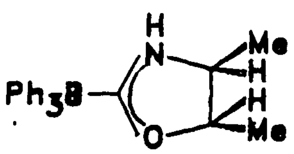
Transition Metal and Boron Stabilized N,O-Carbenes: Similarities in Structure and Reactivity

H. Hoffmeister, B. Boyadjiev and W.P. Fehlhammer

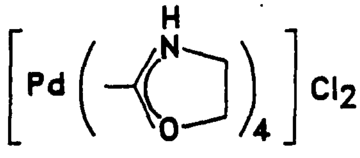
Institut für Anorganische und Analytische Chemie der
Freien Universität Berlin, D-1000 Berlin 33 (West-Germany)

Transition metal coordinated 2- and 3-hydroxyalkyl isocyanides spontaneously undergo intramolecular cyclization reactions to give homoleptic carbene complexes [1, 2]. With triphenylboron, the same isocyanides give rise to (oxazolidin-2-ylidene)- and (perhydrooxazin-2-ylidene)triphenylboron [3].

The very similar effects of boron and transition metals on the stabilization of coordinated N,O-carbenes are established through X-ray analyses of (*trans*-4,5-dimethyloxazolidin-2-ylidene)triphenylboron **1** and, e.g., tetrakis(oxazolidin-2-ylidene)palladium(II)-dichloride **2** [1].



1



2

N-alkylation of the carbene ligands in both, transition metal and boron complexes is achieved on treatment with NaH and RI or $[R_3O][BF_4]$ in dimethyl formamide.

The spectroscopic properties (ir, nmr, ms) of the compounds will be discussed.

---

[1] Fehlhammer, W.P.; Bartel, K.; Plaia, U.; Völkl, A.; Liu, A.T. *Chem. Ber.* 1985, *118*, 2235.

[2] Plaia, U.; Stolzenberg, H.; Fehlhammer, W.P. *J. Am. Chem. Soc.* 1985, *107*, 2171.

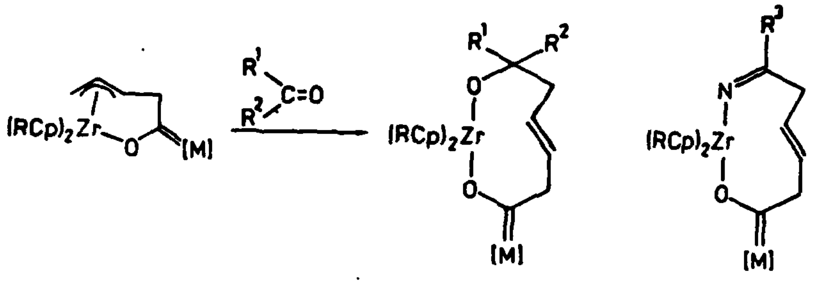
[3] Fehlhammer, W.P.; Hoffmeister, H.; Stolzenberg, H.; Boyadjiev, B. *Z. Naturforsch.*, in press.

Medium-sized Metallacyclic Carbene Complexes from (Butadiene)zirconocene, Metal Carbonyls and Organic Carbonyl Compounds

Friedrich Sosna, Gerhard Erker

Institut für Organische Chemie der Universität Würzburg
Am Hubland, D-8700 Würzburg

Carbene complexes 1 are obtained by reacting metal carbonyls with the (butadiene)zirconocene reagent[1]. Complexes 1 react with aldehydes, ketones or nitriles to give nine membered metallacycles 2 or 3.



1 2 3

Complexes 2, having a *trans*-configurated C=C bond, exhibit a rather rigid chiral ring conformation. From the dynamic NMR spectra, Gibbs activation energies between 16 and 18 kcal/mol have been obtained for the topomerization process. The potential use of the metallacyclic carbene complexes in organic synthesis is discussed.

1) G. Erker, U. Dorf, R. Benn, R. D. Reinhardt, J. L. Petersen, J. Am. Chem. Soc. 1984, *106*, 7649

A NEW SYNTHETIC ROUTE TO THE SECONDARY HETEROCARBENE COMPLEXES : $[Mo(\eta-C_5Me_5)(CO)_2(PR'_3)(CHOR)]^+X^-$ (R = H, Me, SiMe$_3$)

Ali Asdar, Véronique Guerchais, Claude Lapinte, Laboratoire de Chimie des Organométalliques, UA CNRS 415, Université de Rennes I, 35042 Rennes Cedex, France

Loïc Toupet, Laboratoire de Physique Cristalline, UA CNRS 804, Université de Rennes I, 35042 Rennes Cedex, France.

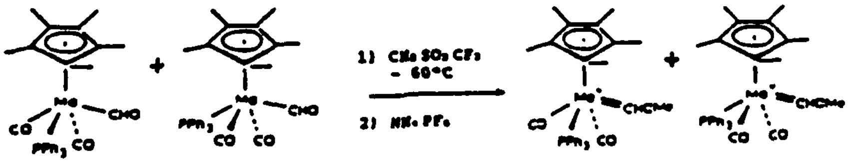
Few secondary cationic heterocarbene complexes ($LnM^+=CHOR$) are known because their access are scarce.

Indeed, only the hydride abstraction reaction from metal alkyl compounds $LnM-CH_2OR$ is operative (eq. 1). However, the hydride abstracting agents (the trityl cation and the methylene complex $LnM^+=CH_2$) are either versatile or elusive.

Meanwhile the addition of electrophiles to the oxygen atom of the metal-acyl compounds is one of the main route to Fischer-type carbenes, up to now similar reactions from neutral metal formyl complexes have failed in synthesizing monocationic secondary heterocarbene compounds (eq. 2).

$$LnM-CHO \xrightarrow[\text{eq. 2}]{R^+} [LnM=CHOR]^+ \xleftarrow[\text{eq. 1}]{-H^-} LnM-CH_2OR$$

We have found that a cis-trans mixture of the new molybdenum formyl complex 1 reacts with electrophilic reagents like H^+, CH_3^+, R_3Si^+ to yield the cis-trans mixture of the secondary metal-carbene in 60-80 % yield (eq. 3).



(eq. 3)

1 2

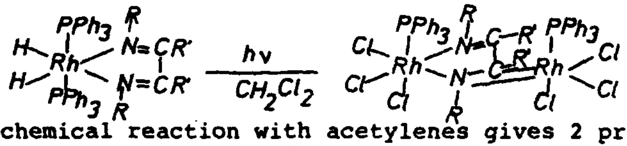
The X-ray crystal structure of 1 and the stereoselectivity of the reaction will be reported.

Photochemistry of $[RhH_2(R\text{-}DAB)(PR_3)_2]PF_6$ and their photoreactivity with acetylenes.

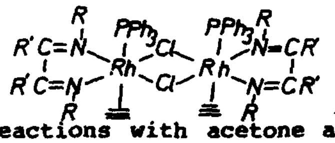
M. Iglesias, C. del Pino Instituto de Ciencia de Materiales, C.S.I.C. calle Serrano 113, 28006 MADRID, SPAIN.

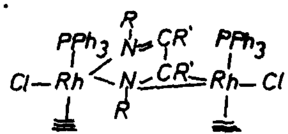
A photochemical study of Rh(III) dihydrides, $[RhH_2(R\text{-}DAB)(PR_3)_2]PF_6$ 1 (R-DAB = 1.4 diaza-1.3 butadiene) and their photochemical reactions with acetylenes in solution of CH_2Cl_2, acetone of THF has been made. The structures of the photoproducts appear to depend on the electronic properties of the ligands and the solvent used.

Reactions in CH_2Cl_2.- The starting product 1 after reductive elimination of H_2, loses a phosphine ligand, takes chlorine from the solvent by oxidative addition and the R-DAB ligand changes its coordination mode from σ,σ'-N,N' (4e) to σ-N, μ^2-N', η^2-CN' (6e), 2.

1  2

The photochemical reaction with acetylenes gives 2 products: a pale yellow one with R-DAB ligand σ,σ-N,N', 4e coordinated, and Cl-bridged, in a very low yield 3 and product 4 with the ligand R-DAB σ-N, μ^2-N', η^2-CN', 6e coordinated. In both cases there is one molecule of acetylene per rhodium.

 3

 4

Reactions with acetone and tetrahydroduran.- The Rh(III) dihydrides with these solvents lose H_2, a phosphine ligand and R-DAB coordinates by 8e (acetone) or 6e (THF).

In their photochemical reactions with acetylenes the ratio Rh/≡ = 1 too.

As regards the photochemical mechanism, we are trying to find out from which excited state it occurs. Normally MLCT states are not reactives. Reactions can however take place from a close-lying reactive state. The change of coordination mode of R-DAB ligands, has a great influence on the absorption spectra.

A complete study of U.V-Vis of these compounds has been done.

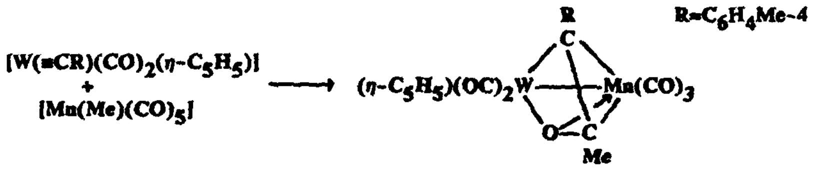
NOVEL ALKYLIDYNE ACYL COUPLING REACTIONS ON DINUCLEAR COMPLEXES

L.J.Hart, J.C.Jeffery, R.M.Lowry and F.G.A.Stone

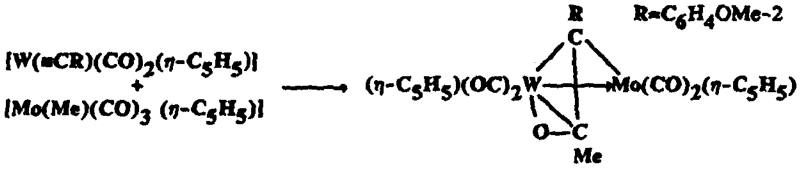
Department of Inorganic Chemistry, The University of Bristol, BS8 1TS, ENGLAND

The versatility of the compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R=C_6H_4Me\text{-}4$) in rational stepwise cluster synthesis has long been established. However,reacting this complex with simple metal alkyl species has provided some surprising results.

The thermal reaction between $[Mn(Me)(CO)_5]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ yields the species $[WMn\{\mu\text{-}C(R)C(O)Me\}(CO)_5(\eta\text{-}C_5H_5)]$, whose structure has been established by X-ray crystallography. The study reveals the combination of the alkylidyne ligand and an acyl unit. The resulting $C(R)\{C(O)Me\}$ bridging ligand has an acyl group that itself bridges the W-Mn bond, formally donating 4e- to the complex. The mechanism whereby the product is formed almost certainly involves the coordination of the W≡C triple bond to a transient $[Mn(C(O)Me)(CO)_4]$ species. Carbon-carbon bond formation then takes place and CO is lost with coordination of the oxygen to the Mn atom.



In contrast, the photochemical reaction between the alkyl species $[Mo(Me)(CO)_3(\eta\text{-}C_5H_5)]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R=C_6H_4Me\text{-}4,C_6H_4OMe\text{-}2$) yields the $[MoW\{\mu\text{-}C(R)C(O)Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$. The structure for $R=C_6H_4OMe\text{-}2$ has been determined and reveals a completely different arrangement of the bridging C(R)C(O)Me ligand. *In this complex* the acyl C=O double bond acts as a 2e- donor to the W atom.



The structural and *chemical properties* of the new compounds will be discussed.

HIGH-VALENT COMPLEXES OF ORGANOSULPHUR LIGANDS *VIA* OXIDATIVE THIONYLATION OF [W($\equiv$CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(L)]

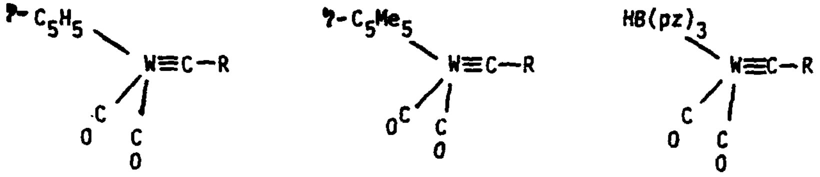
{L = η-C$_5$H$_5$, η-C$_5$Me$_5$, HB(pyrazol-1-yl)$_3$}

Anthony F. Hill, Judith A.K. Howard, Nicholas H. Sanders and F. Gordon A. Stone

Department of Inorganic Chemistry, University of Bristol,
Bristol BS8 1TS, Great Britain

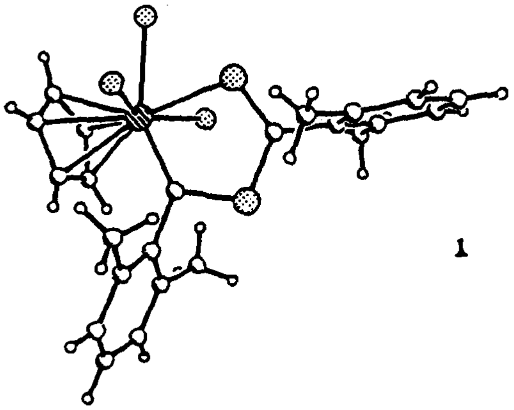
An extensive coordination chemistry of carbon-bound organosulphur ligands (CS$_2$, -C(S)R, =C(SR)$_2$, $\equiv$C-SR *etc.*) has developed, concerned primarily with low-valent, soft transition metal centres. In contrast, these types of ligands are rare in systems in which the metal is in a high oxidation state.

The alkylidynetungsten complexes

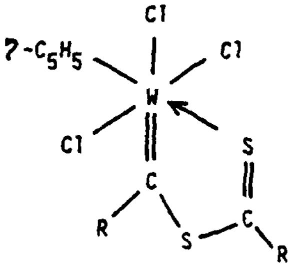


(R = C$_6$H$_3$Me$_2$-2,6, pz = pyrazol-1-yl)

react with thionyl chloride, O=SCl$_2$, providing access to a range of novel high-valent organosulphur complexes, of which **1** is an example. Mechanisms for the processes involved will be discussed in terms of the steric influence of the large -C$_6$H$_3$Me$_2$-2,6 group, the degree of crowding at the tungsten centre, and the extent to which these effect the structures of the final products.



1



412

ORGANIC COMPOUNDS OF MERCURY, TIN AND LEAD AS INITIATORS OF VINYL MONOMER POLYMERIZATION

S.F.Zhil'tsov, S.B.Shustov, M.Gorky State Pedagogical Institute,
Ul'yanov Str., 1, 603000 Gorky, USSR

Yu.D.Semchikov, L.M.Mazanova, Chemistry Research Institute at
N.I.Lobachevsky State University, Gagarin Avenue, 23, 603600
Gorky, USSR

The goal-oriented search of new effective binary initiating systems based on homolytical reactions of organometallic compounds for polymerization and copolymerization of vinyl monomers (methyl methacrylate, acrylonitrile and others) has been performed:

1. R_nM and halides of transition (Ti, Mn, Ni, Fe, Co) and non-transition (Sn, Si) elements;
2. R_nMX and sodium borohydride or tetraphenylborate, where R is alkyl; M = Hg, Sn, Pb; X = Cl, CH_3COO.

The given systems have been found to initiate polymerization of the monomers mentioned at rather low temperature (20-50°C).

The following facts are indicative of free-radical mechanism of initiation:polymerization process is inhibited by hydroquinone additives, polymerization rate is directly proportional to square root of initiator concentration; $K_g/K_t^{1/2}$ values, copolymer compositions are close to corresponding quantities for polymerization reaction on benzoyl peroxide.

The peculiarity of the initiating systems suggested is in the following:the polymerization process can be conducted in the presence of air oxygen, i.e. the latter does not inhibit and acts as a cocatalyst in some cases.

Polymers prepared on the initiating systems to use organic compounds of mercury, tin and lead, contain metal atoms in the composition of terminal groups;that is practically important for obtaining biologically resistant materials, block-copolymers and protective film-forming polymer coatings.

Dimethyldiethylaminoindium: a potential precursor for MOVPE technique.

G. Rossetto, N. Brianese, F. Ossola, M. Porchia, P. Zanella

Istituto di Chimica e Tecnologia dei Radioelementi, C.N.R., Corso Stati Uniti 4, 35020 Padova, Italy

Metal Organic Chemical Vapor Epitaxy (MOVPE) is finding larger utilization as a method of preparing thin films of good quality for optoelectronic devices. However, several problems concerning C incorporation or parasitic pre-reactions are still limiting factors depending on the type of used precursors. Here we report on the synthesis of $(Me_2InNEt_2)_2$ which shows promising chemical-physical properties for its use as a precursor in MOVPE. It can be obtained in good yield by two steps reaction of $InCl_3$ and LiMe (1:2 molar ratio) and of the formed Me_2InCl with $LiNEt_2$ (1:1 molar ratio) in diethyl ether solution as a colourless volatile solid (it melts at 55 C and readily sublimes at 40 C and 10^{-2} Pa). It has been characterized by elemental analysis and IR and NMR spectroscopies; the mass spectrum suggests a dimeric structure. Almost complete prompt pyrolysis to metallic indium has been showed. Studies on gas-phase reactions with P or As donor molecules are in progress.

AMORPHOUS GERMANIUM FROM VOLATILE HYDRIDES:INVESTIGATION ON REACTION MECHANISM

Mario Castiglioni, Giuseppe Cetini, Paola Michelin Lausarot, Lorenza Operti, Gian Angelo Vaglio, Mario Valle and Paolo Volpe, Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso M. d'Azeglio 48, I-10125 Torino, Italy.

Amorphous materials, which show semiconducting properties suitable for practical applications, can be obtained by thermal and γ-radiolytic decomposition of volatile organometallic and hydridic compounds. As the features of the solid material are strongly dependent on the experimental conditions, it is intersting to investigate the reactions of germanium hydrides in the gas phase, a relatively unexplored field (1). The gas phase behaviour of the ionic species originated from GeH_4 has been studied by high pressure mass spectrometry. In self-condensation reactions, GeH_2^+ appears to be the most reactive species, as it has already been suggested in processes involving radicals (2). *Reactions of* GeH_4 *with* O_2 *give weak* GeH_nO^+ *(n=0-3) and* $GeH_nO_2^+$ (n=0-1); with NH_3 they give $GeNH_n^+$ (n=2-6); and with CO they give GeH_nO^+ and GeH_nC^+ (n=0-3). The formation of these latter ions is likely to be due to the bridge coordination of a CO on the two germanium atoms of $Ge_2H_n^+$ species. The relative abundances of the ionic products are affected by the total pressure and by the partial pressure ratio of the reagents.

Interesting results were obtained by investigating the amorphous material at different pressures. The composition of the solid product obtained at 1 atm pressure is $GeH_{1.15}$ (2). Thermogravimetry and mass spectrometry analyses show that it loses a mixture of volatile germanes at 200 °C and monogermane at 875 °C, with a total weight loss of 23.4%. A sharp phase change is observed at 675 °C by DSC analysis and the X-ray spectra of the material, which is amorphous up to 675 °C, show the presence of two crystalline phases at *higher temperature (3). Moreover, the solid shows* EPR signals in the 600-700 °C range. Chemical properties, IR, MS and EPR spectra of the solid germanium hydride and of a carbon-germanium hydride will be discussed.

1 - J.K. Northrup and F.W. Lampe, J. Phys. Chem., 77, 30 (1973).

2 - R. Belluati, M. Castiglioni, P. Volpe and M.C. Gennaro, Polyhedron, 6, 441 (1987).

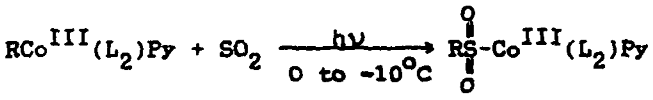
3 - P. Benzi, M. Castiglioni, P. Volpe, L. Battezzati and M. Venturi, Polyhedron, in press.

Sulphur Dioxide Insertion into Co-C bond in Organocobaloximes

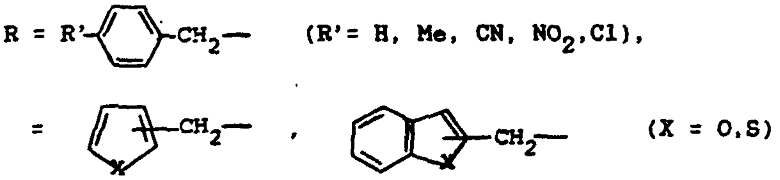
B.D. Gupta, S. Roy and M. Roy

Department of Chemistry, Indian Institute of Technology
Kanpur - 208 016, U.P., India

Sulphur dioxide insertion into a metal-carbon bond takes place with a wide variety of sigma bonded organometallic complexes of both main groups and transition elements. Despite a great deal of work on the kinetics and stereochemistry of these reactions, no unified mechanism has emerged so far. We present an unambiguous experimental evidence that sulphur dioxide insertion reactions into benzyl, thienylmethyl and furylmethyl cobaloximes are not true insertions into Co-C bond. The products result as a consequence of intermolecular process in which organic and the metal fragments of the inserted products do not arise from the same organometallic substratep The insertion occurs only under photochemical conditions and no inserted product is formed under thermal conditions.



$$RCo^{III}(L_2)Py + SO_2 \xrightarrow[0\ \text{to}\ -10^{\circ}C]{h\nu} R\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Co^{III}(L_2)Py$$



(R'= H, Me, CN, NO$_2$,Cl),

(X = O,S)

L = dmgH (dimethylglyoxime mono anion)

= chgH (cyclohexaneglyoxime mono anion)

1. J.J. Alexander in S. Patai(Ed.) The chemistry of metal carbon bond, Vol.**2**, John Wiley and Sons, 1985, p.339.

2. J.L. Wardel and E.S. Patterson, ref. 1, p.219.

3. A. Wojcicki, Adv. Organometal. Chem., **12**, 31 (1974) and Ann. Acad. Sci. **239**, 100 (1974).

CO INSERTION IN METAL-CARBON BONDS IN THE IRON PORPHYRIN SERIES.

Claire GUEUTIN[a], Doris LEXA[a], M. MOMENTEAU[b] and J.M.SAVEANT[a] . (a) Laboratoire d'Electrochimie Moléculaire, UA CNRS N° 438, Université de Paris 7- 2, place Jussieu,75 251 Paris Cedex 05 - France . (b) Institut Curie, Section de Biologie, Unité INSERM 210, Centre Universitaire, 91405 Orsay-France-

Electrogenerated Fe(I)$^{-}$ or Fe("o")$^{2-}$ porphyrins are known to react with alkyl halides (RX) leading to iron σ alkyl complexes (I) (1-3). The first study upon the reactivity of carbon monoxide towards such complexes under mild conditions is described (4).

The obtained results show that two different behaviors appear depending on the alkyl chain (R) nature. If R = $-CH_3$ or $-C_6H_5$ only complexation of I by CO takes place whereas CO insertion in the metal-carbon bond is effective, either for longer n-alkyl chains (($-C_2H_5$ to C_8H_{17}) or for ramified ones (secondary or tertiary),leading to the corresponding iron-acyl complexes. The spectral and electrochemical characteristics of the acyl compounds are determined for different iron porphyrins (octaéthyl, tetraphenyl,picket-fence or basket-handle). The mechanism of the insertion reaction is discussed. We can assume,according to the numerous literature concerning carbonyl complexes of transition metals, that the initial step consists in a σ-alkyl complex CO ligation followed by CO insertion. The kinetic of the latter step depends upon the oxidation state of the iron : the alkyl to acyl migration rate is enhanced by the electrochemical oxidation of the iron II species into the iron III one. The kinetic constants can be estimated using cyclic voltammetry.

References :

1. D. Lexa, J. Mispelter and J.M. Savéant. J.Am.Chem.Soc., 1981, 103, 6806.
2. D. Lexa, J.M.Savéant and D.L. Wang. Organometallics, 1986, 5, 1428.
3. C. Gueutin, D. Lexa, J.M.Savéant and D.L. Wang .Submitted
4. C. Gueutin, D.Lexa and J.M. Savéant. Submitted.

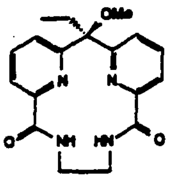
METAL COMPLEXES OF MACROCYCLES FROM DIPYRIDYLMETHAN-DIAMINE DERIVATIVES FOR POTENTIAL CATALYTIC APPLICATIONS

Christina Moberg and Kenneth Wärnmark

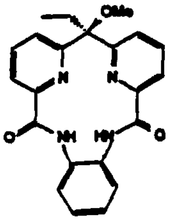
Department of Organic Chemistry, Royal Institute of
Technology, S-100 44 STOCHOLM, Sweden.

Chiral synthetic macrocyclic compounds capable of coordination to transition metal ions are attractive for use in selective synthetic transformations. By proper design, the macrocyclic ligand should be able to choose the desired substrate and direct the substrate in a regio- and stereospecific fashion towards the metal center.

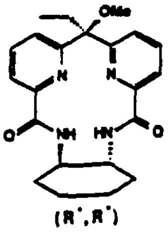
We have been able to synthesize macrocyclic ligands from dipyridylmethane derivatives and diamines, e.g 1 and 2. Use of the chiral diamine R,R-trans-1,2-diaminocyclohexane gives the chiral macrocyclic ligand 3 in high yield. According to NMR-data 3 has a rigid conformation with two different amide-protons.



1



2



(R*,R*)

3

The ligands form complexes with transistion metal ions like Co^{2+}, Cu^{2+}, Ni^{2+} and Pd^{2+}. According to spectroscopic data, Ni^{2+} and Pd^{2+} have square planar coordination to 3.

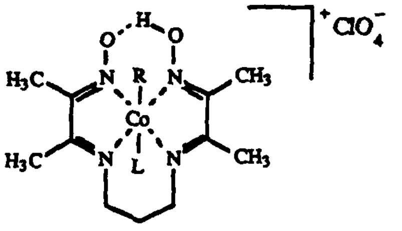
Metal-pyridyl ligands are good catalysts in oxidative transformations. The usefulness of our macrocyclic ligands in such processes will be investigated.

^{59}Co NMR OF VITAMIN B$_{12}$ MODEL COMPOUNDS

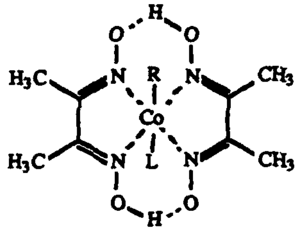
C.Tischler[a], G.Costa[b] and W. von Philipsborn[a]

a) Organisch-Chemisches Institut der Universität Zürich, CH-8057 Zürich (Switzerland)
b) Dipartimento di Scienze Chimiche, Università di Trieste, I-34127 Trieste (Italy)

Because of the biochemical importance of the Cobalt-Carbon bond in cobalamines and other experimental studies on the nature of this bond[1]) a large number of Vitamin B$_{12}$ model compounds of type A and type B (cobaloximes) have been investigated by ^{59}Co NMR. Whereas the Co chemical shift is strongly dependent on the nature of the axial and equatorial donor ligands, a less pronounced but significant dependence on the structure of the axial carbon ligand is observed.



A



B

Our results show that

a) changing of the equatorial ligand causes a chemical shift of about 500 ppm, cobaloximes appearing at lower frequencies than type A compounds.

b) variation of the coordinating axial donor ligand L results in a chemical shift dispersion, depending upon the structure of R, e.g. $\Delta\delta$ (aquo/pyridine) in benzyl-compounds is 645 ppm, compared with 380 ppm in acetyl-compounds.

c) in the series of alkyl-cobaloximes (methyl, ethyl, n-propyl, n-butyl, isopropyl, benzyl), the trend in the ^{59}Co chemical shifts is rather complex. Increased shielding is found in going from methyl to ethyl (30-100 ppm), thus reflecting an inductive effect. In all other alkyl compounds, a deshielding is observed (up to 460 ppm) with increasing chain length or branching, most pronounced in benzyl and isopropyl complexes (steric effect).

d) variation of the Co-C bond length in cobaloximes is reflected in the ^{59}Co chemical shift. This is in agreement with an EHMO study [2]) which predicts a smaller HOMO-LUMO gap with increasing Co-C bond distance. The expected deshielding effect is indeed observed.

---

[1]) J.Halpern, *Science* 227, 869 (1985); G.Costa et al., *Gazz. Chim. Ital.* 116, 735 (1986)

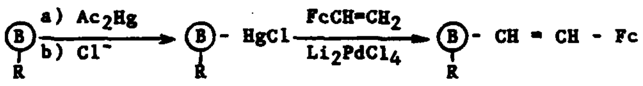
[2]) C.Mealli, M.Sabat, L.G.Marzilli, *J.Am.Chem.Soc.* 109, 1593 (1987)

FIRST EXAMPLES OF "METALLOCENONUCLEOSIDES"

Philippe Meunier, Issa Ouattara, Bernard Gautheron, Jean Tirouflet and
Jack Besançon
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS
(UA 33), Faculté des Sciences, 6 bd Gabriel 21000 Dijon (France)

First examples of ferrocenyl substituted pyrimidine and purine nucleosides have been synthesised according to the following sequences :

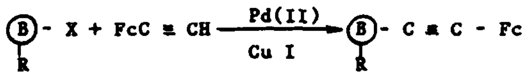
1) **Reaction of vinylferrocene on a 5-chloromercuri nucleoside**



$$\underset{R}{Ⓑ} \xrightarrow[b)\ Cl^-]{a)\ Ac_2Hg} \underset{R}{Ⓑ}-HgCl \xrightarrow[Li_2PdCl_4]{FcCH=CH_2} \underset{R}{Ⓑ}-CH=CH-Fc$$

R = CH_3, sugar Fc = ferrocenyl B = bases : pyrimidines

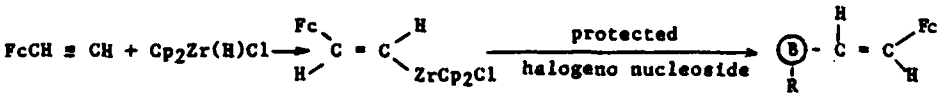
2) **Halogenonucleoside and ethynylferrocene coupling**



$$\underset{R}{Ⓑ}-X + FcC \equiv CH \xrightarrow[Cu\ I]{Pd(II)} \underset{R}{Ⓑ}-C \equiv C-Fc$$

R = H, sugar B = bases : purines, pyrimidines

3) **Hydrozirconation reaction**



$$FcCH \equiv CH + Cp_2Zr(H)Cl \longrightarrow \overset{Fc}{\underset{H}{}}C=C\overset{H}{\underset{ZrCp_2Cl}{}} \xrightarrow[\text{halogeno nucleoside}]{\text{protected}} \underset{R}{Ⓑ}-\overset{H}{C}=C\overset{Fc}{\underset{H}{}}$$

R = sugar B = bases : purines, pyrimidines

The whole of the compounds were characterized by ^1H NMR and mass spectrometry.

Cytotoxic properties of metallocenonucleosides have been tested "in vitro" on L 1210.

REACTIVITY OF METALLOCENES IN REACTIONS WITH ORGANOCADMIUM COMPOUNDS

G.A.Razuvaev, V.P.Mar'in, L.I.Vyshinskaya (Institute of Chemistry, Academy of Science, Gorky, U.S.S.R.)

Reactions of the Cp_2M metallocenes (M = V, Cr, Mn, Co, Fe, Ni) with R_2Cd have been discussed. It has been found that the reactivity of metallocenes depends on the nature of the central atom and in a number of cases by the R groups.

When Cp_2V (Cp = C_5H_5, C_5H_4Alk, C_5Me_5) interacts with R_2Cd (R = Me, Et, Pr) the bielectronic oxidative addition to vanadocene take place to form Cp_2VR_2. At the same time the reaction of Cp_2V with R_2Cd (R = Ph, $GeEt_3$) results in Cp_2VR.

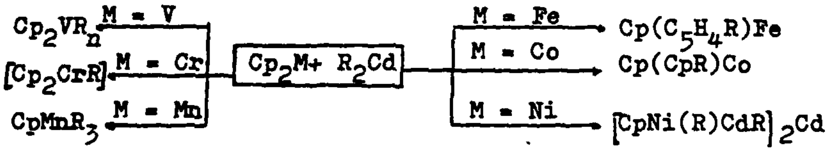
The oxidative addition of R_2Cd (R = Me, Et, Pr, Ph) to Cp_2Cr occurs through sandwich-covalent chromium derivatives the existence of which have been confirmed by their conversion products and also by the low-temperature IR spectroscopy.

By the reaction of Cp_2Mn (Cp = C_5H_5, C_5H_4Alk) with R_2Cd (R =Me,Et, Pr, Bu) the $CpMnR_3$ compounds have been obtained. In the reaction unstable intermediate has been registrated by low-temperature IR spectroscopy method.

Ferrocene reacts with R_2Cd (R = Alk) to form the homolytic substitution products under thermal decomposition conditions of organocadmium compounds.

Cobaltocene reaction with R_2Cd (R = Me, Et, Pr, CH_2SiMe_3, $GeEt_3$, Ph) results to homolytic addition product such as $(\eta^5\text{-}Cp)(\eta^4\text{-}CpR)Co$.

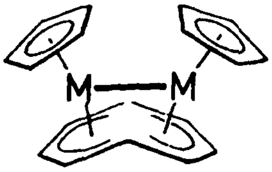
Nickelocene reacts with organocadmiun compounds to form the polynuclear complex with Ni-Cd bond.



SYNFACIAL HOMO- AND HETEROBINUCLEAR CYCLOOCTATETRAENE COMPLEXES $(\text{CpM})_2$-μ-Cot: TOWARDS A NEW CLASS OF COMPOUNDS

Bernd Bachmann, Jürgen Heck, and Rainer Stürmer
Fachbereich Chemie der Philipps-Universität, Hans Meerwein-Straße,
D-3550 Marburg, FRG

The preparation of the synfacial homobinuclear Cot-complexes $(\text{CpM})_2$-μ-Cot (M = V, Cr) was first achieved by a one-pot-reaction of MCl_2, K_2Cot, and NaCp.[1,2] For the synthesis of the corresponding heterobinuclear complexes $(\text{Cp}_2\text{MM'})$-μ-Cot the sandwich compound $(\eta^5\text{-Cp})\text{Cr}(\eta^6\text{-Cot})$[3] (6) can be employed as a valuable precursor (1).



M=V (1)
M=Cr (2)

$$\underline{6} \xrightarrow[\text{a) Zn or b) }\Delta]{\text{CpM'L}_n} (\text{Cp}_2\text{CrM'})\text{-}\mu\text{-Cot} \quad \underline{2}-\underline{5} \qquad (1)$$

a) $\text{M'=V, L}_n\text{=Cl}_2 \rightarrow \underline{3}$
a) $\text{M'=Cr, L}_n\text{=Cl}_2 \rightarrow \underline{2}$
b) $\text{M'=Fe, L}_n\text{=C}_6\text{H}_6 \rightarrow \underline{4}$
b) $\text{M'=Co, L}_n\text{=(C}_2\text{H}_4)_2 \rightarrow \underline{5}$

Because of chemical and structural results the addition of a second CpM-unit exclusively occurs synfacially to the CpCr-moiety. As the only diamagnetic compound the dichromium complex 2 can be identified. The divanadium species on the other hand has an excited triplet state, which can be populated thermally as proved by ^{1}H-NMR spectroscopy. NMR-measurements indicate two unpaired electrons for 4. ESR spectroscopically a localization of the unpaired electron in 3 and 5 can be observed on the less noble metal centre.

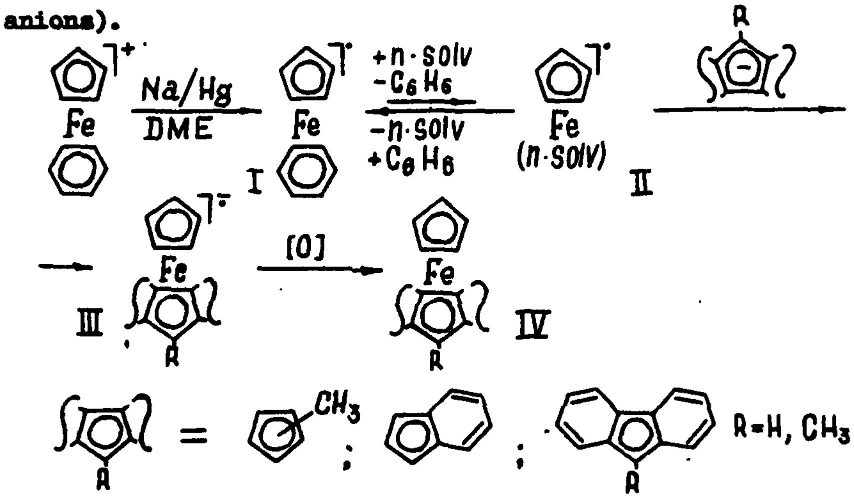
1) Ch. Elschenbroich, J. Heck, W. Massa, E. Nun und R. Schmidt, J. Am. Chem. Soc. 105 (1983) 2905
2) Ch. Elschenbroich, J. Heck, W. Massa und R. Schmidt, Angew. Chem. 95 (1983) 319
3) J. Müller und H. Menig, J. Organomet. Chem. 96 (1975) 83; J. Heck und G. Rist, J. Organomet. Chem. 342 (1988) 45

THE ANION-RADICAL SYNTHESIS OF UNSYMMETRICAL IRON SANDWICH COMPLEXES

L.N.Novikova, N.A.Pomazanova, N.A.Ustynyuk, D.N.Kravtsov

Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilov str., Moscow, 117813, USSR.

The metodology of radical nucleophilic substitution[1] has been employed for synthesis of iron unsymmetrical sandwich complexes. The neutral 19-electron complex I easily exchanges the benzene ligand for methylcyclopentadienyl-anion and its condenced analogues (indenyl-, fluorenyl-, 9-methylfluorenyl-anions).



The key step of the whole process is the interaction of the anion with radical II, leading to anion-radicals III. The mild oxidation of III at the final step gives the corresponding neutral complexes IV. [2].

1. L.I.Denisovich, N.A.Ustynyuk, M.G.Peterleitner, V.N.Vinogradova, D.N.Kravtsov, Izvestiya Akademii Nauk, seriya Khimicheskaya, 1987, p.2635.

2. N.A.Ustynyuk, N.A.Pomazanova, L.N.Novikova, D.N.Kravtsov, Yu.A.Ustynyuk, Izvestiya Akademii Nauk, seriya Khimicheskaya, 1986, p.1688.

Reactivity of the Protonated "Open Ruthenocene" Salt [Ru(η^5-C_7H_{11})$_2$H] BF_4

David N. Cox, Tito Lumini and Raymond Roulet.
Institut de Chimie Minérale et Analytique de l'Université
3, Place du Château, CH-1005 Lausanne, Switzerland.

As part of a general study of the chemistry of octadienediyl ruthenium complexes, the title compound, 1 , has been prepared in good yield by treatment of the octadienediyl ruthenium (IV) dichloride dimer, $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2]_2$, with $AgBF_4$ and 2,4-dimethylpentadiene.[1]

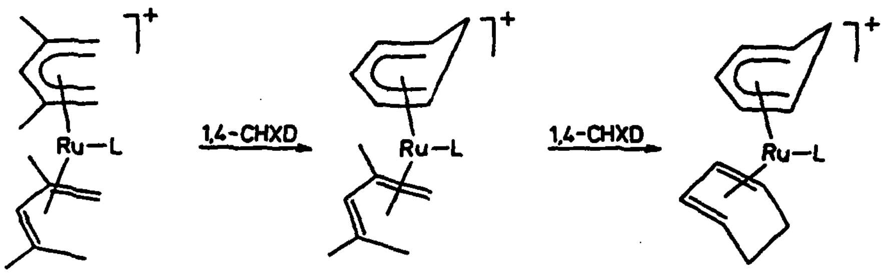
A wide range of monopentadienyl ruthenium derivatives are accessible from 1:

$1 \xrightarrow{\text{MeCN}} [(\eta^5\text{-}C_7H_{11})Ru(NCMe)_3]^+ \xrightarrow{\text{I}^-/\text{CO}} (\eta^5\text{-}C_7H_{11})Ru(CO)_2I$

$1 \xrightarrow{\text{L}} [(\eta^5\text{-}C_7H_{11})Ru(\eta^4\text{-}C_7H_{12})L]^+$ (L = CO, 2a; t-BuNC, 2b; $P(OMe)_3$, 2c.)

$1 \xrightarrow{\text{L'}} [(\eta^5\text{-}C_7H_{11})RuL']^+$ (L' = η^5-thiophene, η^6-arene, η^6-C_7H_8, η^6-C_8H_8.)

Whereas the reactions of complexes 2a to 2c with 1,3-cyclohexadiene yield the cations $[(\eta^5\text{-}C_7H_{11})Ru(\eta^4\text{-}C_6H_8)L]^+$ by simple displacement of the 2,4-dimethylpentadiene ligand, the reactions of complexes 2a and 2b with 1,4-cyclohexadiene proceed as shown below:



Further reactivity of 1 will also be discussed.

---

1. D.N.Cox and R.Roulet, JCS Chem. Commun. in press.

VIBRATIONAL SPECTRA OF TRIPLE-DECKER SANDWICHES OF RUTHENIUM AND OSMIUM WITH CENTRAL PENTAMETHYLCYCLOPENTADIENYL LIGAND

I.A.GARBUZOVA, A.R.KUDINOV, S.S.BUKALOV, M.I.RYBINSKAYA,
B.V.LOKSHIN

A.N.Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Vavilov st. 28, 117813 Moscow (USSR).

The triple-decker complexes of ruthenium and osmium $(\eta\text{-}C_5R_5)M(\eta\text{-}C_5Me_5)M'(\eta\text{-}C_5Me_5)PF_6$ (M=M'=Ru, R=H,Me; M=Ru, M'=Os, R=H), containing 30 valence electrons, are studied by the methods of Raman and Infrared spectroscopies. The assignment is proposed by comparison with the spectra of corresponding metallocenes and its cations. The normal coordinate analysis of the C_5Me_5-ligand is also carried out using the force field of C_5H_5-anion /1/.

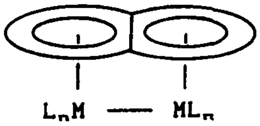
Resonance Raman enhancement have been observed for symmetric ring-metal stretching vibrations at 140-160cm^{-1} and 370-380cm^{-1}, for the out-of-plane C-Me deformation mode at 440cm^{-1} and for the ring-breathing mode of C_5H_5-ring at 1102cm^{-1}. The bands of methyl groups vibrations and the bands of very coupled ring-breathing and C-Me stretching modes of C_5Me_5-ring at 1428 and 590cm^{-1}, very intensive in the Raman spectra of decamethylmetallocens, became relativly weak in the Raman spectra of triple-decker sandwiches. The methyl groups vibration bands of central and terminal rings coincide, while the methyl group signals of the central and terminal rings in ^{13}C - ^{1}H NMR spectra are distingushed. The frequencies of symmetric ring-metal stretching modes at 140-170cm^{-1} in the spectra of triple-decker sandwiches and decamethylmetallocenes increase upon transition from Ru to Os in accordance with the strengthing of metal-ring bond.

1 -I.A.Garbusova, O.G.Garkusha, B.V.Lokshin, J.Mink, Izv. Acad. Nauk SSSR, Ser. Khim., 8 (1988)

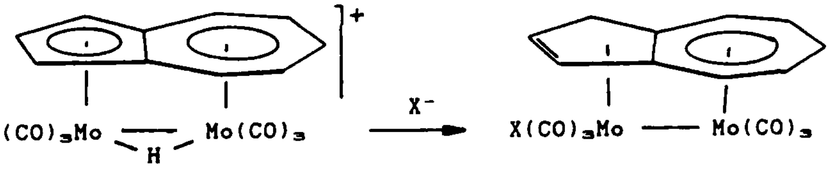
THE CHEMISTRY OF POLYAROMATIC-POLYMETALLIC COMPLEXES OF THE GROUP VI METALS

Kirsten E. Clode and Anthony H. Wright, Chemistry Department, University of Nottingham, Nottingham, NG7 2RD, U.K.

Polyaromatic-polymetallic complexes containing both fused and tied aromatic ligands are being investigated. The results of photochemical and electrochemical studies will be described. With systems containing fused polyaromatic rings (I), unexpected metal-ligand hydrogen migration reactions have been observed:

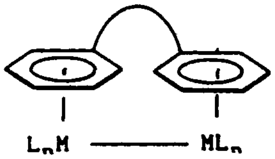


(I)



Two dimensional NMR and deuteration studies have revealled that these migration reactions are both stereospecific and regiospecific. Photochemical substitution reactions are likewise regiospecific.

In polyaromatic systems containing rings tied by a saturated hydrocarbon link (II), photochemical activation has been used to generate new complexes containing metal-metal bonds. The electrochemical properties and chemical reactivity of these complexes will be described.



(II)

METAL-ASSISTED INCORPORATION AND DEOXYGENATION OF CARBON DIOXIDE

Antonio Belforte and Fausto Calderazzo. Dipartimento di Chimica e Chimica Industriale, Sezione Chimica Inorganica, via Risorgimento 35, I - 56100 Pisa, Italy.

Incorporation of carbon dioxide into organic substrates, with formation of $C-CO_2$, $O-CO_2$, or $N-CO_2$ bonds, is an interesting subject.[1] Prior coordination of carbon dioxide to a metal cation as the *N,N*-dialkylcarbamato group, $[M(O_2CNR_2)_n]_m$,[2] may accomplish the twofold objective of stabilizing carbon dioxide as an *O*-donor and promote its reactivity towards electrophiles.[3] We have now found that metal *N*-alkylcarbamato complexes react easily with acyl halides, and alkyl isocyanates are chiefly formed. The overall process (equation 1-3), operating at room temperature and atmospheric pressure, corresponds to the metal-assisted deoxygenation of carbon dioxide , and to the direct synthesis of alkylisocyanates from primary amines.

$$2\ CO_2 + 4\ RNH_2 + MCl_2 \longrightarrow M(O_2CNRH)_2 + 2\ RNH_3Cl \qquad (1)$$

$$M(O_2CNRH)_2 + 2\ MeCOCl \longrightarrow 2\ RNCO + Me\overset{O}{C}O\overset{O}{C}Me + H_2O + MCl_2 \qquad (2)$$

$$2\ CO_2 + 4\ RNH_2 + 2\ MeCOCl \longrightarrow 2\ RNCO + Me\overset{O}{C}O\overset{O}{C}Me + H_2O + 2\ RNH_3Cl \qquad (3)$$

M = Mn, Co; R = *n*-Pr, Cy

Both kinetic and thermodynamic factors concur favourably to the formation of isocyanate, and the proposed mechanism shows that the metal plays an important role in both these aspects.

---

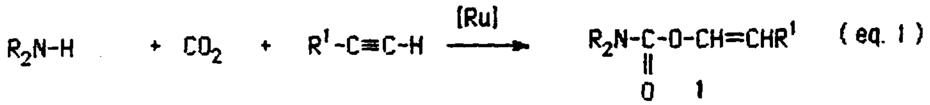
1) S.Inoue, N.Yamazaki, *Organic and Bioorganic Chemistry of Carbon Dioxide*, Kodansha, Tokyo, 1982.
2) D.Belli Dell'Amico, F.Calderazzo, U.Giurlani, G.Pelizzi, *Chem. Ber.*, 1987, *120*, 955.
3) D.Belli Dell'Amico, F.Calderazzo, U.Giurlani, *J.Chem.Soc.Chem. Commun.*, 1986, 1000.

ONE-STEP CATALYTIC SYNTHESIS OF CARBAMATES FROM ALKYNES AND CO_2

Christian Bruneau and Jean Fournier

Laboratoire de Chimie de Coordination Organique, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex (France).

Alkynes can be activated towards nucleophiles in the presence of ruthenium complexes. Enol carbamates have been synthetised by catalytic addition of secondary amines and CO_2 to terminal alkynes such as phenylacetylene or 1-hexyne. (eq. 1). Ruthenium complexes such as $(C_6Me_6)RuCl_2PR_3$ and $RuCl_2$(pyridine)(norbornadiene) are especially efficient catalysts . The reaction is highly regioselective and leads to the addition of the carbamate at the unsubstituted carbon of the alkyne (1).

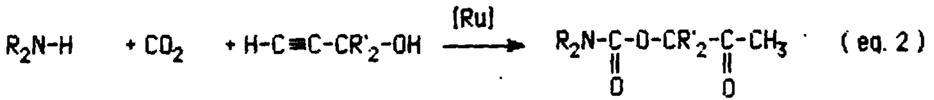


$$R_2N\text{-}H \quad + \; CO_2 \quad + \; R^1\text{-}C{\equiv}C\text{-}H \xrightarrow{[Ru]} R_2N\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}CH{=}CHR^1 \qquad (\text{eq. } 1)$$

1

This synthesis can be extended to the formation of vinylcarbamates, transparent polymer precursors, directly from acetylene itself with selective catalysts.

Propargylic alcohols react differently with secondary amines and actually afford β-oxoalkylcarbamates (2). The reaction is not possible with primary amines. However, the corresponding β-oxoalkylcarbamates can be obtained by addition of primary amines to the propargylic alcohol cyclic carbonate which is a possible intermediate in the catalytic reaction (eq.2).



$$R_2N\text{-}H \quad + CO_2 \quad + H\text{-}C{\equiv}C\text{-}CR'_2\text{-}OH \xrightarrow{[Ru]} R_2N\text{-}\underset{O}{\underset{\|}{C}}\text{-}O\text{-}CR'_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3 \qquad (\text{eq. } 2)$$

2

NOVEL REACTIONS OF ALKYNES WITH $\eta^2 CS_2$ METAL COMPLEXES.

Françoise Conan, Jean Sala-Pala, Jacques-E. Guerchais.

Université de Bretagne Occidentale, UA CNRS 322 "Chimie, Electrochimie et *Photochimie moléculaires*", Faculté des Sciences et Techniques, Laboratoire de Chimie Inorganique Moléculaire, 6 avenue Le Gorgeu, 29287 BREST-FRANCE -

The utilization of carbon disulphide in transition metal-mediated reactions of organic molecules is an important problem. One of the most fruitful current areas of research is that in which alkynes react with coordinated CS_2. We describe reactions of alkynes with the CS_2 complex $|Mo(CS_2)(\eta\text{-}C_5H_5)_2|$, and the structural characterization of three unprecedented types of CS_2-alkyne combination, involving one, two or three molecules of alkyne.

A. The addition of *one* molecule of alkyne to coordinated CS_2 has been previously observed to occur either across the two sulphur atoms, giving a carbene ligand, or across the metal and a sulphur atom, giving a metallacyle $\overline{MC(S)SC(R)C}(R)$. We describe alkyne addition across the metal and the carbon atom of CS_2 to give a metallacyle $\overline{MSC(S)C(R)C}(R)$.

B. Recently it has been reported that reactions of alkynes with coordinated CS_2 can give complexes in which *two* molecules of alkyne are combined with CS_2. We display a new type of combination of CS_2 with two alkynes, in which the cyclopentadienyl ligand intervenes.

C. Finally, we report the first example of a complex in which coordinated CS_2 is combined with *three* molecules of alkyne.

I. TRANSITION-METAL-CATALYSED REACTIONS OF DIAZOESTERS : INSERTION INTO C-H BONDS OF PARAFFINS BY CARBENOIDS

A. Demonceau [a], A.F. Noels [a], and A.J. Hubert [b]
[a] *Laboratory of Macromolecular Chemistry and Organic Catalysis,*
[b] *Laboratory of Organic Synthesis and Catalysis ,*
University of Liège, Sart-Tilman (B.6), B-4000 Liège, Belgium

When compared to transition-metal-mediated carbene transfer to unsaturated substrates, the direct "insertion" into C-H bonds of alkanes generally suffers from low yields and lack of selectivity. In principle such drawbacks should be overcome by stabilizing carbene species by coordination to suitable metal complexes. Moreover, in order to achieve efficient reactivity towards paraffins, the catalyst should be stable towards intramolecular carbene reactions (so as to suffer minimum deactivation) while the reactivity of the complexed carbene should permit insertion into non-activated C-H bonds.

Accordingly, it appeared that some electron-poor rhodium derivatives catalysed the decomposition of diazoesters at room temperature and promoted the reactions of the so-generated carbonylcarbenes (or carbenoids) with alkanes *. High yields in ester functionalized molecules were obtained with cycloalkanes. Linear branched paraffins gave somewhat poorer results. However, temperature dependence of the yields were considerable, as well as dilution effects (ratio substrate to diazoester) and size of the diazoester alkoxy-group.

These results led us to study in detail the catalytic addition of carbenes, generated from diazoacetates, to saturated hydrocarbons, and to try to understand the following facts :

- unexpected regioselectivities,
- competitive experiments between pairs of alkanes,
- addition of radical traps and of carbon tetrachloride,
- deuterium isotope effects, ...

This communication will be a summary of our studies of the mechanistic aspects of this reaction and provide a working hypothesis for the future.

---

* (a) N. Petiniot, A.F. Noels, A.J. Anciaux, A.J. Hubert, and Ph. Teyssié, "Fundamental Research in Homogeneous Catalysis", Plenum Press, New York and London, 1979, Vol. 3, p. 421; (b) A. Demonceau, A.F. Noels, A.J. Hubert, and Ph. Teyssié, *J. Chem. Soc., Chem. Commun.*, 688 (1981); (c) *Bull. Soc. Chim. Belg.*, 93, 945 (1984).

II. ON THE EFFECTS OF WEAK INTERACTIONS ON THE SELECTIVITIES IN REACTIONS OF RHODIUM CARBENOIDS WITH ALKANES

A. Demonceau, A.F. Noels, and A.J. Hubert,
University of Liège, Sart-Tilman (B.6), B-4000 Liège, Belgium

Rhodium(II) carboxylates are very efficient catalysts for promoting, under mild conditions, the insertion of carbenes (generated from diazoacetates) into the C-H bonds of alkanes.

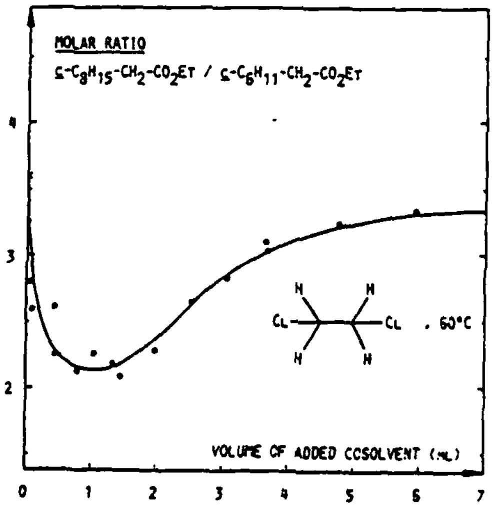
The selectivity of insertion strongly depends on both the diazoacetate alkoxy-group and the metal counter-ion.

Moreover, we have observed recently that the relative reactivities between cycloalkanes depend also on the presence of "inert" cosolvent as well as, surprisingly enough, on the amount of added cosolvent (Figure).

These unexpected influences of the catalyst and diazoester substitution on the selectivities, together with preferential reactions in competitive experiments between pairs of alkanes pointed out the importance of "solvation effects", even with paraffins. The formation of preferred *"carbenoid-substrate" solvates* was therefore postulated to rationalize the observed chemoselectivities in competitive experiments.

INTERMOLECULAR COMPETITIONS BETWEEN CYCLOOCTANE AND CYCLOHEXANE

INFLUENCE OF ADDED 1.2-DICHLOROETHANE



$Rh_2(O_2C\text{-}C(CH_3)_3)_4$: $N_2CH\text{-}CO_2Et$.

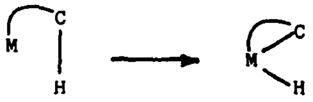
A. Demonceau, A.F. Noels, and A.J. Hubert, submitted for publication.

INTRAMOLECULAR C-H OXIDATIVE ADDITION AT IRIDIUM . SYNTHESIS AND CHARACTERIZATION OF $[Ir(H)(CO)(bq)L_2]PF_6$ (bq = 7,8-benzoquinolinato).

Mauro Ghedini , Francesco Neve , Dipartimento di Chimica , Università della Calabria, I-87030 Arcavacata di Rende (CS), Italy

Antonio Tiripicchio and Franco Ugozzoli, Istituti di Chimica Generale ed Inorganica e di Strutturistica Chimica , Università di Parma , Viale delle Scienze, I-43100 Parma, Italy.

Thermal activation of a C-H bond is the most common way to obtain cyclometallated complexes.[1] Or the other hand oxidative addition to give the hydride derivative (II) (eq. 1) is relatively uncommon.



(I) (II)

(1)

We now report the formation of $[Ir(H)(CO)(bq)L_2]PF_6$ (2) (L = PPh_3) , achieved in good yield by reaction of $[Ir(CO)(MeCN)L_2]PF_6$ with benzo[h]quinoline (bqH) (eq. 2) .

$$\underset{(1)}{[Ir(CO)(MeCN)L_2]PF_6} \xrightarrow[\Delta,16h]{bqH} \underset{(2)}{[Ir(H)(CO)(bq)L_2]PF_6} \qquad (2)$$

The spectroscopic data for 2 [IR, ^1H NMR and ^{31}P-{selective ^1H} NMR] account for an hydride group trans to the nitrogen of the cyclometallated bq and two mutually trans PPh_3 groups. The metallated carbon atom appears as a triplet in the ^{13}C-{^1H} NMR spectrum.On this basis we assume the structure of 2 similar to that of the known aquo complex $[Ir(H)(H_2O)(bq)L_2]SbF_6$.[2] The determination of the crystal structure of 2 by X-ray diffraction methods is in progress .

Reactivity of 1 with different BH ligands [e.g. 8-methylquinoline (mqH) and 2-phenylpyridine (ppyH)] is currently under investigation.

1 - E.C.Constable, Polyhedron, 3, 1037 (1984); G.R.Newkome et al.,Chem.Rev., 86, 451 (1986).

2 - R.H.Crabtree and M.Lavin, J.Chem.Soc.,Chem.Commun.,794 (1985); R.H.Crabtree, personal communication ,1988.

OXIDATIVE ADDITION/REDUCTIVE ELIMINATION OF ALDEHYDES AND KETONES AT RHODIUM.

Claudio Bianchini, Andrea Meli, Maurizio Peruzzini, Josè Antonio Ramirez, Alberto Vacca, Francesco Vizza and Fabrizio Zanobini,
Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R., Via J. Nardi; 39, I-50132 Firenze, Italy.

A great deal of research is presently focused to the synthesis and characterization of hydrido acyl complexes, because of their primary role in various rhodium catalyzed processes involving aldehydes.

In the course of our studies on the activation of C-H and H-H bonds at rhodium and iridium fragments with the tripodal ligands $N(CH_2CH_2PPh_2)_3$, NP_3, and $P(CH_2CH_2PPh_2)_3$, PP_3, we have found that the electronically and coordinatively unsaturated systems $(NP_3)Rh^+$ and $(PP_3)Rh^+$ are highly effective in the cleavage of C-H bonds from saturated and unsaturated hydrocarbons.[1] Herein we report on the reactions of aldehydes with the NP_3 and PP_3Rh systems.

The $(PP_3)Rh^+$ fragment is unable to keep in mutual cis disposition hydride (or alkyl) and acyl ligands, invariably promoting the reductive elimination of aldehydes (or ketones). By contrast the isoelectronic $(NP_3)Rh^+$ fragment easily inserts across the formylic C-H bond from different aldehydes to yield quite robust octahedral cis-hydrido(acyl) complexes of rhodium (III). These have been fully characterized by chemical physical measurements and NMR spectroscopic techniques.

References: (1) C. Bianchini, A. Meli, M. Peruzzini, and F. Zanobini, J. Chem. Soc., Chem. Commun. 1987, 971.

HIGHLY CATALYTIC C-H ACTIVATION IN THE PRESENCE OF $RhCl(CO)(PR_3)_2$

Masato TANAKA and Toshiyasu SAKAKURA, National Chemical Laboratory for Industry, Higashi, Tsukuba, Ibaraki 305, Japan

Direct functionalization of arenes and alkanes has been realized *via* C-H bond activation in the presence of transition metal complexes under irradiation. Rhodium complexes, in particular, $RhCl(CO)(PMe_3)_2$, are powerful catalysts for the following reactions

(1) Carbonylation of arenes

$ArH + CO \longrightarrow ArCHO$ (m-selective)

(2) Carbonylation of alkanes

$RH + CO \longrightarrow RCHO$ (terminal selective)

Depending on the wavelength, the reaction gives terminal alkenes and acetaldehyde;

$RCH_2CH_2CH_3 + CO \rightarrow [R(CH_2)_3CHO] \rightarrow RCH{=}CH_2 + CH_3CHO$

(3) Silylation of arenes

$ArH + HSiR_3 \longrightarrow ArSiR_3 + H_2$

$ArH + R_3SiSiR_3 \longrightarrow ArSiR_3 + HSiR_3$

(4) Dehydrogenative homo-coupling of arenes

$2ArH \longrightarrow ArAr + H_2$

(5) Dehydrogenative cross-coupling of arenes and alkenes

$ArH + CH_2{=}CHCOOR' \longrightarrow ArCH{=}CHCOOR' + H_2$

(6) Dehydrogenation of alkanes giving alkenes

$RCH_2CH_2R' \longrightarrow RCH{=}CHR' + H_2$

(7) Schiff base synthesis

$RH + CNR' \longrightarrow RCH{=}NR'$

Some of these reactions are highly catalytic (turnover frequencies more than $200 h^{-1}$). Some aspects of the reaction mechanism including the effects of ligands and the role of irradiation will be discussed.

References

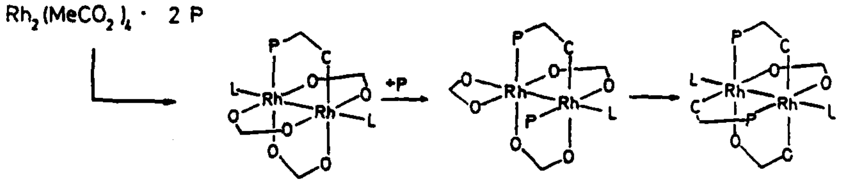
M. Tanaka et al., Chem. Lett., 1987, 249, 859, 1113, 2211, 2373, 2375; 1988, 155, 263. J.C.S. Chem. Commun., 1987, 758.

NEW ORTHOMETALATION REACTIONS IN DIRHODIUM (II) COMPOUNDS

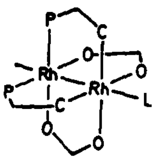
PASCUAL LAHUERTA, JORGE PAYA, M. ANGELES UBEDA
Depto. Química Inorgánica, Universidad de Valencia, Dr.Moliner, 50 , 46100
BURJASSOT-VALENCIA.

Orthometalated arylphosphines have been shown to be good bridging ligands in dinuclear Rh_2^{4+} (1). Following our studies of orthometalation reactions in binuclear rhodium compounds (2), we report here the chemical behaviour of dirhodium tetraacetate adducts, $Rh_2(O_2CCH_3)_4.2P$(**I**), P=PMe_2Ph(**Ia**), $PMePh_2$(**Ib**) and $P(p\text{-}XC_6H_4)_3$ [X= H(**Ic**), CH_3(**Id**), Cl(**Ie**)]. All these adducts generate doubly metalated compounds $Rh_2(O_2CCH_3)_2(P\text{-}C)_2$ of type **IV**. By careful modification of the reaction conditions, intermediates of type **II** and **III** have been isolated in variable yields. The intermediate **III**, that contains a phosphine occupying an equatorial coordination site, is stabilized for less bulky P-donor ligands.

The reactivity of these intermediate compounds has been studied. In the presence of 2:1 molar excess of the corresponding phosphine, compound of type **II** (PPh_3, $PMePh_2$) readily reacts at room temperature yielding the corresponding doubly metalated **IV**. Similar reactivity is found for compound **III** (PPh_3, PMe_2Ph). Doubly metalated compounds with head to head configuration, structure **V**, have also been prepared. Additional aspects related to these particular reactions will be discussed.



II III IV



V

REFERENCES.
1-Chakravarty, A.R.; Cotton, F.A.; Tocher J.M., Organometallics 1985, *4* 8.
2-Barceló, F.A.; Cotton, F.A.; Lahuerta, P.; Sanaú, M.; Schwotzer, W.; Ubeda, M.A., Organometallics, 1987, *6* 1105 and references therein.

ACTIVE β-HYDROGEN IN Cp^*_2TiR COMPOUNDS

G.A. Luinstra and J.H. Teuben, Department of Inorganic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands.

Thermally labile Cp^*_2TiEt 1 (Cp^*: η^5-C_5Me_5) reacts with unsaturated substrate molecules under the liberation of ethene (1).

$$Cp^*_2TiEt + X{=}Y \longrightarrow Cp^*_2Ti\text{-}X\text{-}Y\text{-}H + C_2H_4 \qquad (1)$$

Heteronuclear unsaturated molecules (t-BuCN, CO_2) and 2-butyne follow reaction 1 with formation of imide, formate and alkenyl $Cp^*_2Ti(III)$ derivatives.
Only in a few cases insertion into the metal-carbon bond is observed. In reaction with CO, t-BuNC and paraformaldehyde 1 was tranformed into acyl, iminoacyl and alkoxide derivatives (2).

$$Cp^*_2TiEt + X{=}Y \longrightarrow Cp^*_2Ti\text{-}(XY)\text{-}Et \qquad (2)$$

Reaction 1 is also observed for interaction of α-olefines with 1 (3).

$$Cp^*_2TiEt + CH_2{=}CHR \overset{K}{\rightleftharpoons} Cp^*_2TiCH_2CHR + C_2H_4 \qquad (3)$$

For propene the equilibrium constant (278 K) was determined (K = 0.033, ΔG = 1.9 Kcal/mol). As a consequence these Ti(III) compounds are not active in the polymerization of α-olefines. A similar reaction was observed with other α-olefines, but internal olefines (2-hexene) sterically demanding olefines (cyclohexene, styrene) and acetylenes (diphenylacetylene) do not react, probably for steric reasons.
The mechanism of reaction 1 (and 3) is likely to involve a six-membered transition state in which a hydrogen atom is directly transferred from an ethyl-ligand to the substrate molecule.

436

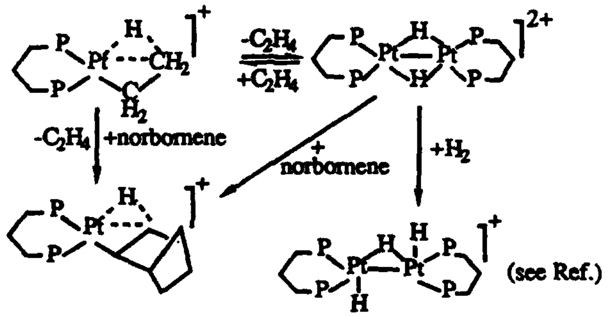
TWO-ELECTRON, THREE-CENTRE BONDING IN PLATINUM ETHYL DIPHOSPHINE COMPLEXES

Nicholas Carr,[a,b] Laura Mole,[a] A Guy Orpen,[b] Alan D Redhouse,[a] and John L Spencer[a]

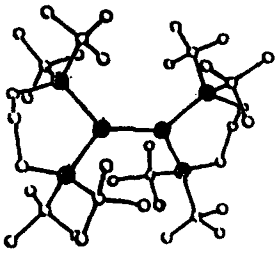
[a] Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT, UK
[b] Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, UK

Protonation of $[Pt(C_2H_5)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}]$ affords the off-white crystalline complex $[Pt(C_2H_5)\{Bu^t_2P(CH_2)_3PBu^t_2\}]^+ X^-$ where $X = BF_4, CF_3SO_3, (CF_3SO_2)_2CPh$. This formally 14-electron complex has been shown by ^{13}C, ^1H and ^{31}P nmr to be stabilised by a two-electron, three-centre agostic Pt—H—C bond.
Remarkably the system is extremely fluxional even at low temperatures resulting in equivalence not only of all five ethyl protons but also of the C_α and C_β via β-elimination and alkene rotation.

Scheme 1



β-agostic complexes can be viewed as models for the intermediate stage of β-elimination and alkene insertion; most importantly, the complex $[Pt(C_2H_5)\{Bu^t_2P(CH_2)_3PBu^t_2\}]^+$ has been shown to undergo alkene exchange (see Scheme 1) and dimerisation with loss of ethylene to form a hydride bridged platinum dinuclear complex $[Pt_2(\mu\text{-}H)_2\{Bu^t_2P(CH_2)_3PBu^t_2\}_2][BF_4]_2$ (Scheme 1 and Figure 1).

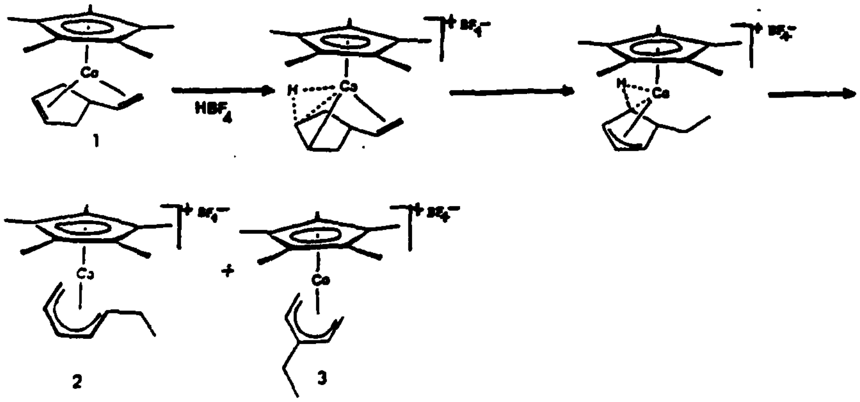


T H Tulip *et al*, *Inorg Chem*, 1979, 18, 2239.

CARBON-CARBON BOND CLEAVAGE IN AGOSTIC COBALT COMPLEXES

Iulian C Nicholis, Alan D Redhouse and John L Spencer, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

Carbon-carbon bond activation by soluble transition metal complexes remains one of the most prominent challenges in organometallic chemistry (Ref.). We have observed examples of facile carbon-carbon cleavage by the protonation of [Co(η-C_5R_5)(diene)] complexes. For example protonation of [Co(η-C_5Me_5)(η^4-bicyclo[2.2.2]octa-2,5-diene] with HBF_4 leads to [Co(η-C_5Me_5)(1-3,7,8,-η-5-vinylcyclohexenyl)]BF_4 via an agostic intermediate, and [Co(η-C_5Me_5)(η^4-4-vinylcyclopentene)] (1) affords *syn*-[Co(η-C_5Me_5)(η^5-1-Et-C_5H_6)]BF_4 (2) and [Co(η-C_5Me_5)(η^5-3-EtC_5H_6)]BF_4 (3) on protonation (Scheme).
The structure of (2) was confirmed by a single crystal X-ray diffraction study.



Scheme

Reference: John E Bercaw, et al., *J Am Chem Soc*, 1988, 110, 976-987.

438

EVIDENCE FOR METAL-PHOSPHORUS $d\pi$-$d\pi$ BACKBONDING IN THE BRIDGE-CLEAVAGE PRODUCTS OF CYCLOMETALLATED TRIMESITYLPHOSPHINE COMPLEXES

E.C. Alyea and John Malito, (GWC)[2], Department of Chemistry and Biochemistry,
University of Guelph, Guelph, Ontario, Canada, N1G 2W1.

The very bulky trimesitylphosphine ligand ($P(mes)_3$) promotes formation of the cyclometallated dimeric complexes, $[M(P^{\frown}C)X]_2$ ($M=Pd,Pt$; $P^{\frown}C=Pmes_2C_6H_2(CH_3)_2CH_2$; $X=Cl,Br,I$), which undergo facile bridge-cleavage reactions with smaller tertiary phosphine ligands to give *trans*-$[M(P^{\frown}C)(PR_3)X]$. Trends observed for the ^1H and ^{31}P NMR of these monomers strongly suggest a π-backbonding component in the $M-PR_3$ bond whereas there is no evidence for a similar effect in the M-P bond of the parent dimers. Discussion is also extended to the related apparent order of *trans*-effect for the series of PR_3 ligands studied.

SYNTHESIS AND REACTIVITY OF MESITYLENE-OSMIUM(0) AND MESITYLENE-HYDRIDO-OSMIUM(II) COMPLEXES: POTENTIAL PRECURSORS FOR C-H-BOND ACTIVATION ?

S.Stahl and H.Werner

Institut für Anorganische Chemie der Universität
Würzburg, Am Hubland, D-8700 Würzburg

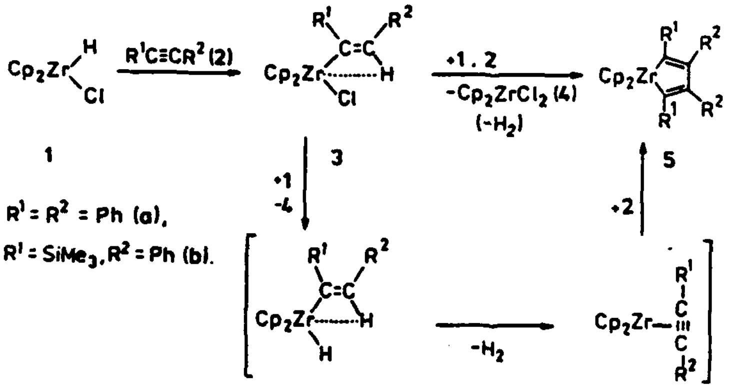
Starting with the easily accessible polymeric compound $[(mes)OsCl_2]_n$ a series of half-sandwich type mesitylene-osmium complexes have been synthesized. The first examples of mesitylene-osmium(0) derivatives (mes)OsLL', which contain two monodentate π-acceptor ligands, are prepared by several independent routes.

Reaction of $(mes)OsCl_2(L)$ with suitable reducing agents gives the dihydrido complexes $(mes)OsH_2(L)$. The new compounds are considered to be potential precursors for generating a 16-electron intermediate [(mes)Os(L)], able to activate C-H-bonds of aromatic or aliphatic hydrocarbons.

Formation of a β-CH-Agostic Alkenylzirconocene Complex and Metallacyclopentadienes by Hydrozirconation of Alkynes

Roland Zwettler, Gerhard Erker
Institut für Organische Chemie der Universität Würzburg
Am Hubland, D-8700 Würzburg

The reaction of $PhC\equiv CPh$ (2a) with Cp_2ZrHCl (1) does not afford the anticipated alkenylzirconocene complex (3a), but a 1:1 mixture of metallacycle (5a) and Cp_2ZrCl_2 (4). The formation of the "agostic" complex (3b) as well as the metallacycle (5b) and (4) from the reaction of $PhC\equiv CSiMe_3$ (2b) with (1) leads us to propose that "agostic" alkenylzirconocene complexes may be important intermediates in this unexpected hydrozirconation.



With less sterically demanding alkynes, e.g. $HC\equiv CH$, $PhC\equiv CH$, $MeC\equiv CMe$, and $HC\equiv CSiMe_3$, (1) reacts to afford the normal alkenylzirconocenes.

THREE STEPS PATHWAY FOR AN α-HYDRIDE ABSTRACTION FROM IRON ALKYL.

Christophe Roger, Claude Lapinte, Laboratoire de Chimie des Organométalliques, UA CNRS 415, Université de Rennes I, 35042 Rennes Cedex, France.

Loïc Toupet, Laboratoire de Physique Cristalline, UA CNRS 804, Université de Rennes I, 35042 Rennes Cedex, France.

Electron transfer pathway are of general interest in C-H bond activation of metal alkyl intermediates in a variety of catalytic reactions. It has been scarcely shown that C-H bond activation from transition metal alkyl gives rise to hydride transfer to the trityl cation as hydride acceptor by a two-step, electron transfer, hydrogen atom transfer, mechanism.

The first example of hydride abstraction from the iron methoxymethyl compound 1 through a three step pathway : electron transfer, proton abstraction, electron transfer (Scheme I) will be presented. The X-ray structure of the paramagnetic complex 2 will be also reported.

$$\underset{\underline{1}}{[Fe]-CH_2OCH_3} \underset{+e}{\overset{-e}{\rightleftharpoons}} \underset{\underline{2}}{[Fe]^{+}-CH_2OCH_3}$$

$$\underset{\underline{2}}{[Fe]^{+}-CH_2OCH_3} \xrightarrow{-H^{+}} \underset{\underline{3}}{[Fe]=CHOCH_3} \xrightarrow{-e} \underset{\underline{4}}{[Fe]^{+}=CHOCH_3}$$

$[Fe] = Fe(C_5Me_5)(\eta^2\text{-dppe})$

Scheme I

These reactions provide a new synthetic way to secondary heterocarbene compounds.

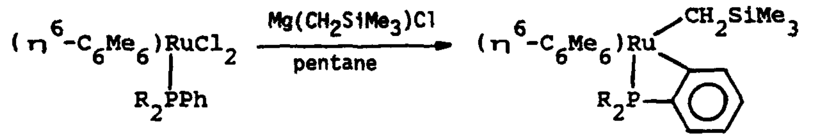
TRIMETHYLSILYLMETHYL DERIVATIVES OF RUTHENIUM(II) WITH ORTHO-METALLATED PHOSPHINES

P. Di Giorgio, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti
Dipartimento di Chimica e Chimica Industriale, Università di Pisa,
Via Risorgimento 35 - 56100 Pisa, Italy

V. Adovasio, M. Nardelli
Istituto di Chimica Generale ed Inorganica dell'Università di Parma,
Centro di Studio per la Strutturistica Diffrattometrica del C.N.R.,
Viale delle Scienze - 43100 Parma, Italy

Cyclometallation reactions have attracted renewed interest since the discovery that some transition metal centers can insert into C-H bonds of hydrocarbons [1].

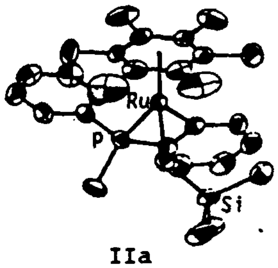
We have recently observed a new cyclometallation reaction in some ruthenium(II) systems leading to neopentyl derivatives containing *ortho*-metallated phosphines. With the aim to verify the generality of these reactions, we shifted to the trimethylsilylmethyl systems. In spite of the reduced steric hindrance of the alkyl group, the complexes $[RuCl_2(\eta^6\text{-}C_6Me_6)(PPhR_2)]$ do react with an excess of trimethylsilylmethyl Grignard reagent to give the *ortho*-metallated complexes I (R = Ph, 25% yield), II (R_2 = MePh, 28% yield), and III (R = Me, 5% yield):



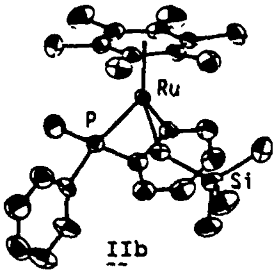
I-III

II has been separated by column chromatography into the two diastereomers IIa (24% yield) and IIb (4% yield).

The structures of I-III have been unambigously determined by X-ray crystal structure analysis. All complexes have a " three-legged piano stool" structure, with the *ortho*-metallated ring planar and practically co-planar with the benzene ring. In the Figure the Ortep projections of the diastereomers IIa and IIb are reported.



IIa



IIb

[1] G.W. Parshall, Chem. Tech., 14, 628 (1984).

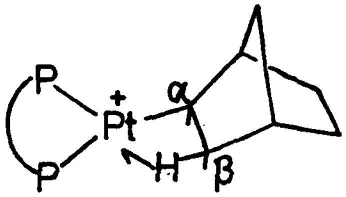
Models for the β-elimination Reaction: Cationic Norbornyl Diphosphine Platinum and Palladium Complexes.

Nicholas Carr,[a,b] A. Guy Orpen,[a] and John L. Spencer[b]

[a] Department of Inorganic Chemistry, The University, Bristol BS8 1TS, UK

[b] Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

We have prepared a series of cations (1) in compounds of general formula [M(norbornyl)(diphosphine)]Y, where M is Pt or Pd, Y is BF_4, BPh_4 and the diphosphine is {$^tBu_2P(CH_2)_nP^tBu_2$}, {$cyh_2P(CH_2)_nPcyh_2$} (n = 2 or 3; cyh = *cyclo*-C_6H_{11}) or {o-$(^tBu_2PCH_2)_2C_6H_4$}. In these species the norbornyl ligand is bound to the metal by both 2c-2e σ-alkyl and 3c-2e β-C-H (agostic) interactions.



(1)

We have studied the geometry and solution dynamics of cations (1) by multinuclear n.m.r. spectroscopy and *X*-ray diffraction. The extent of the β-agostic interaction may be monitored by examination of the P-H, Pt-H, Pt-P and C-H coupling constants. These show that the strength of the agostic (M-H-C) bond varies substantially as a function of both diphosphine chelate ring size and phosphorus substituent bulk. In addition, variable temperature n.m.r. spectra are consistent with an intramolecular rearrangement process, involving β-hydrogen elimination and olefin rotation, which is rapid at room temperature. *X*-ray crystal structure analyses of these compounds provide a second means of assessing the degree of β-C-H interaction, and complement the n.m.r. studies.

We view the agostic alkyls in cations (1) as models for the intermediate stages of the β-elimination/olefin-insertion reactions, an analogy which is strengthened by the observation of these reactions in the chemistry of these species. The studies we report allow detailed inspection of the course of these reactions.

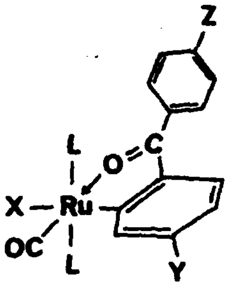
Unusual C-H Activation Reactions of Ruthenium(0)

Michelle Stell, Madeleine Helliwell and Roger Mawby

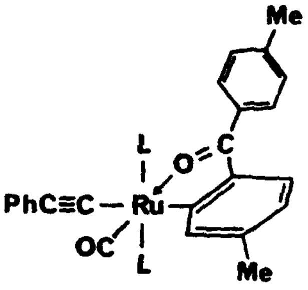
Department of Chemistry, University of York, York YO1 5DD, England

Complexes $[\mathrm{Ru(CO)_2RR'L_2}]$ ($\mathrm{L = PMe_2Ph}$; R,R' = methyl or aryl) decompose intramolecularly in propanone or benzene to give ketones RCOR' in good yield. Kinetic and mechanistic studies indicate a mechanism involving reductive elimination from intermediates $[\mathrm{Ru(CO)(COR)R'L_2}]$. In the presence of halogen-containing compounds ($\mathrm{CHCl_3}$, EtBr, EtI), however, the diaryl complexes $[\mathrm{Ru(CO)_2(C_6H_4Y\text{-}4)(C_6H_4Z\text{-}4)L_2}]$ (Y = Z = H, Me or Cl; Y = Cl, Z = H or Me) yield the ortho-metallated complexes (1), where X = halogen. We believe that these are formed by reversible activation of a C-H bond in intermediate ruthenium(0) ketone complexes $[\mathrm{Ru(CO)\{OC(C_6H_4Y\text{-}4)(C_6H_4Z\text{-}4)\}L_2}]$ followed by reaction of the resulting hydride complexes $[\overline{\mathrm{Ru(CO)\{OC(C}}\mathrm{_6H_3Y\text{-}4)(C_6H_4Z\text{-}4)\}HL_2}]$ with the halogen-containing compounds.

Decomposition of $[\mathrm{Ru(CO)_2(C_6H_4Me\text{-}4)_2L_2}]$ in the presence of $\mathrm{PhC{\equiv}CH}$ results in the formation of complex (2). Here both the ketone and the alkyne have undergone activation of a C-H bond.



(1)

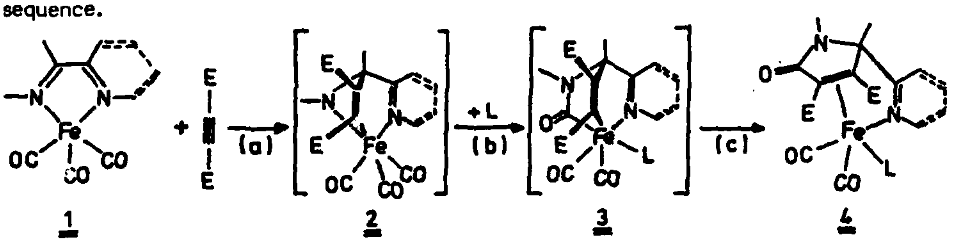


(2)

PREPARATION AND PROPERTIES OF (1,4-DIAZA-1,3-DIENE) $Fe(CO)_2(CNR)$ AS CANDIDATES TO PROBE THE COMPETITIVENESS OF CO vs. CNR INSERTION.

Hans-Werner Frühauf, Dave Dijkhuis, Wouter de Lange,
Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, the Netherlands.

The reaction of (DAD)$Fe(CO)_3$, 1(DAD=1,4-diaza-1,3-diene), with dipolarophiles has been shown to give 1,5-dihydropyrrol-2-one complexes 4 [1] via the indicated reaction sequence.



(a) oxidative 1,3-dipolar cycloaddition of alkyne to the C=N-Fe unit. (b) CO-insertion. (c) reductive elimination (1,2 shift) and recoordination.

Structural types 2 [2] and 3 [3] could be stabilized in particular cases and have been identified by single crystal X-ray analysis. In order to probe the competitiveness of CO and CNR in the migration-insertion step (b) we have prepared some mono-isonitrile derivates of 1 through Pd-catalyzed CO-substitution. The preparation of (DAD)-$Fe(CO)_2$(CN-tBu), 5, will be reported and their spectroscopic properties (IR, ^1H, ^{13}C-NMR) discussed. Contrasting 1, where CO scrambling is fast on the NMR time scale down to the lowest temperatures, intramolecular ligand exchange in 5a (DAB: iPr-N=CH-CH=N-iPr) is slow at or below room temperature. Two different isomers in unequal amounts can be distinguished in the ^{13}C-NMR spectra. This has to be taken into account when looking at CO vs. CNR insertion since only ligands in cis position to the migrating group can be inserted. Investigations on the reactivity of 5 in the above reaction sequence are now underway, and the latest results will also be presented.

[1] H.-W. Frühauf, F. Seils, M.J. Romão, R.J. Goddard; Angew. Chem. Int. Ed. Engl. 22 (1983) 992.

[2] H.-W. Frühauf, F. Seils, C.H. Stam; to be published.

[3] H.-W. Frühauf, F. Seils, R.J. Goddard, H.J. Romão; Organometallics 4 (1985) 948.

446

THE REACTIVITY OF THE TERTIARY PHOSPHINE COMPLEXES OF NICKEL(II) TOWARDS ALKOXIDES AND CARBON MONOXIDE.

by

P. GIANNOCCARO*, M. LATRONICO**, C.F. NOBILE* and A. SACCO*

*Centro MISO - CNR- Università di Bari, IV trav.200 Re David Campus

** Università degli Studi della Basilicata, Via N. Sauro 85, Potenza

The reactions between tertiary phosphine complexes of formula Ni $(PEt_nPh_{3-n})_2X_2$ (X = Cl, Br, I) and the alkoxides RO^- (R = Me, Et, Ph, n-But) under a carbon monoxide atmosphere at room temperature and atmospheric pressure have been investigated. The products of the reaction depend from the nature of both the tertiary phosphine and the alkoxide. Carbonyl-alkoxo complexes of formula NiL_2 X(COOMe) (L= tertiary phosphine) have been obtained with methoxide (MeO^-/Ni =1), in yields strongly increasing with the basicity of the phosphine. These complexes react further with nucleophiles such as methoxide or aliphatic primary amines yielding phosphine-substituted nicke(0) carbonyl complexes and dimethyl oxalate and dimethylcarbonate or carbamates. Several organic compounds, including aldehydes and hydrocarbons, besides carbon dioxide and Ni(II) and Ni(0) derivatives, have been obtained with other alkoxides. The mechanism of the reactions investigated will be discussed.

This work was supported by C.N.R. Rome.

STEREOCHEMISTRY OF CARBON MONOXIDE INSERTION IN ALKYL COMPLEXES OF IRON (II) AND RUTHENIUM (II).

Giuseppe Cardaci, Gustavo Reichenbach and Gianfranco Bellachioma,
Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto,
8, I-06100 Perugia, Italy.

Berend Wassink and Michael C. Baird
Department of Chemistry, Queen's University, Kingston,
Canada K7L 3N6

The stereochemistry of the insertion of carbon monoxide^1 in the complexes $M(CO)_2L_2RX$ (M=Fe,Ru; X=I,CN,NCS) was studied by ^{13}C NMR spectra of variously labeled complexes. The effect of the trans substituent on the chemical shifts and the values of the trans C-C coupling constants with respect to the cis ones are important for structural assignment.
For the iron complexes we observed a strong trans effect on the chemical shifts of the carbonyl groups and a moderate effect on the coupling constants (J_{C-C}(cis)=4-8 Hz, J_{C-C}(trans)=12-16 Hz). On the contrary, for the ruthenium complexes, we observed a weak effect on the chemical shifts and a strong effect on the coupling constants (J_{C-C}(cis)<1 Hz; J_{C-C}(trans)=22-26 Hz). These results allow us to assign the ^{13}C NMR bands to the various carbonyl substituents and so to study the stereochemistry of the carbonylation reaction. The carbonylation of $Fe(CO)_2(PMe_3)_2MeX$ (X=I,CN,NCS) with ^{13}CO gives both the isotopomers with the labeled CO in trans or in cis with respect to the acetyl group. The carbonylation of $Ru(CO)_2(PMe_3)_2MeX$ (X=I,CN) with ^{13}CO is more stereospecific and gives only the isotopomer with the labeled CO trans to the acetyl group.
These results are interpreted, contrary to the conclusions of the literature,^{2} on the basis of methyl group migration with probable formation of square pyramidal intermediates. The relative thermodynamic stability of the intermediates is responsible of the distribution of the isotopomers.
Although both ruthenium^3 and iron^4 dihaptoacyl structures were characterized being more stable than the unsaturated intermediates, they are not important to explain the stereochemistry of the carbonylation.

Work Supported by MPI, Rome, Italy

REFERENCES

1) G. Cardaci,G.Reichenbach,G.Bellachioma,Inorg.Chem.,23,2936(1984).
2)M.Pankowski,M.Bigorgne,J.Organometal.CHem.,251,333 (1983).
3) W.R.Roper,G.E.Taylor,J.M.Waters,L.J.Wright,J.Organometal.Chem., 182,C46 (1979).
4) G.Cardaci,G.Bellachioma,P.Z.Zanazzi,Organometallics,7,172(1988).

INDEX OF AUTHORS

PAPER NUMBER BOLD FACED: Presenter
PAPER NUMBER NORMAL FACED: Coauthor