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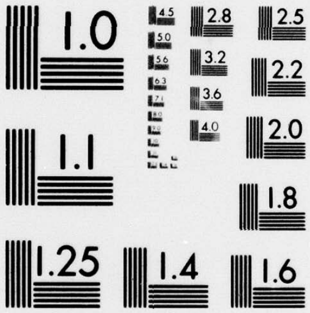

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FINAL REPORT

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Building 410

Bolling Air Force Base, D.C. 20332

on

NOVEL ORGANOPHOSPHORUS AND ORGANONITROGEN DERIVATIVES AND THEIR USE FOR THE SYNTHESIS OF UNUSUAL TRANSITION METAL COMPLEXES

Period Covered:

June 30, 1975, to September 30, 1979

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by

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Alkylaminobis(difluorophosphines)	Molybdenum	Nickel	Addition Reactions
Polyphosphines	Tungsten	Rhodium	
Metal Complexes	Manganese	Ruthenium	X-ray Crystallography
Vanadium	Iron	Metal Carbonyls	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

New research results in synthetic organophosphorus and coordination chemistry are summarized with particular emphasis on the following:

(1) Complexes of the alkylaminobis(difluorophosphines) RN(PF$_2$)$_2$ exhibiting novel structural features prepared by reactions of the ligands with carbonyls of chromium, molybdenum, tungsten, iron, cobalt and nickel and cyclopentadienylmetal carbonyls of vanadium, molybdenum, tungsten, manganese, and iron; and

(2) Polyphosphines containing terminal dialkylamino and methoxy groups with preliminary results on metal complexes of the latter.

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(a) Dr. Gimeno was partially supported by a fellowship from the Program of Cultural Cooperation between the U.S.A. and Spain, administered by the Fulbright Commission of Spain.

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(c) Dr. Kapoor was supported by an Indo-American Fellowship administered by the Council for International Exchange of Scholars.

(d) Mr. Davis was a participant in a Departmental Undergraduate Research Program funded by the National Science Foundation.

CUMULATIVE LIST OF PUBLICATIONS FROM AIR FORCE GRANT AFOSR-75-2869

(1) R. B. King, J. C. Cloyd, Jr., M. E. Norins, and R. H. Reimann, "Complexes of Trivalent Phosphorus Derivatives. XVIII. Some Complexes of Neopentylphosphines with Rhodium, Nickel, and Palladium Chlorides," J. Coord. Chem., 7, 23 (1977).

(2) R. B. King and J. Gimeno, "Tris[methylaminobis(difluorophosphine)] metal(0) Derivatives of Chromium, Molybdenum, and Tungsten: New Volatile Carbonyl-free Zerovalent Metal Derivatives of High Thermal and Oxidative Stabilities," Chem. Comm., 142 (1977).

(3) M. G. Newton, R. B. King, M. Chang, N. S. Pantaleo, and J. Gimeno, "Novel Bimetallic Products from Octacarbonyldicobalt and Methylaminobis(difluorophosphine)," Chem. Comm., 531 (1977).

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(23) R. B. King and T. W. Lee, "New Chelate Ring Opening Reactions Leading to the Synthesis of Novel Mixed Ligand Complexes of the Octahedral Metal Carbonyls," *manuscript in preparation*.

(24) R. B. King and T. W. Lee, "Metal Complexes of Fluorophosphines. 10. Mononuclear and Binuclear Chromium, Molybdenum, and Tungsten Carbonyl Derivatives of Alkylaminobis(difluorophosphines)," manuscript in preparation.

INTRODUCTION

The original objective of this basic research program as conceived in 1975 was the development of new organophosphorus and organonitrogen ligands and their transition metal complex chemistry in areas potentially useful for fuel cell, antioxidant, and lubricant technology as well as for themally stable fluids and flame resistant materials. The most significant scientific achievement during the course of this four-year research program was the development of the transition metal chemistry of the chelating strong π-acceptor fluorophosphine ligands of the type $RN(PF_2)_2$ (R= CH_3 and C_6H_5). This work resulted in the discovery of materials with unexpected thermal and oxidative stability (e.g. $[CH_3N(PF_2)_2]_3Cr$) and with unusual redox properties (e.g. $[CH_3N(PF_2)_2]_3Co_2(CO)_2$) and led to 19 scientific publications during the project period.

Another significant achievement arising from this research project was the development of the first general methods for the synthesis of polyphosphines containing terminal dialkylamino and/or alkoxy groups. Such polyphosphines are useful not only as ligands in transition metal chemistry but are also potentially reactive intermediates for the synthesis of a variety of organophosphorus compounds including materials potentially useful for antioxidants and flame-resistant polymers.

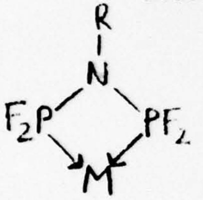
In terms of research publications this work was very successful since 24 papers discussing research supported by this grant were written during its four-year period. Because of this large volume of work, all of the new results will not be discussed in this report. Instead only the highlights of the work discussed in the 24 papers and related areas will be mentioned. Reference to the pertinent publications will be included according to their numbers on the list so that the interested reader will be able to seek additional details by consulting the original paper.

NEW RESULTS FROM THIS RESEARCH PROGRAM

A. Transition Metal Fluorophosphine Complexes

(1) General Comments

Ligands of the type $RN(PF_2)_2$ can bond to transition metals in diverse ways. Thus they can act as bidentate ligands forming four-membered chelate rings of the type I. Chelate rings of this type appear to be particularly effective in stabilizing low metal oxidation states as indicated by the zerovalent chromium complex $[CH_3N(PF_2)_2]_3Cr$, which can be handled in air at room temperature and distills unchanged at 256°C/1 atmosphere. Alternatively the $RN(PF_2)_2$ ligands can chelate with a bonded metal pair to form a five-membered ring of type II, which presumably is less strained than the four-membered ring of type I. Numerous bimetallic derivatives containing chelate rings of type II have been prepared during the course of this project. The chemical reactivity of bridged metal-metal bonds in complexes containing structural units of type II can uniquely be studied using the $RN(PF_2)_2$ ligands as the bridges.



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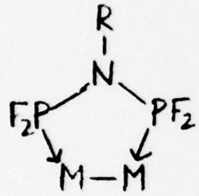

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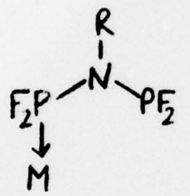

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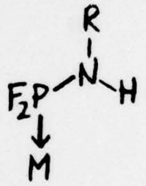

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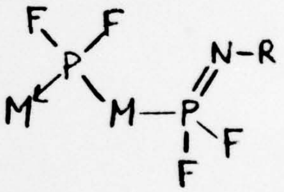


V

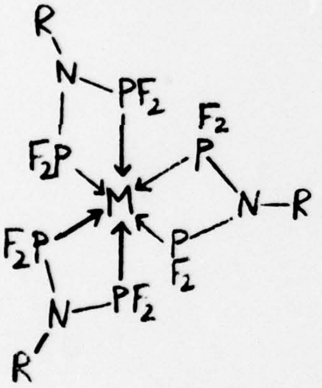
Some less obvious coordinating possibilities of the $RN(PF_2)_2$ ligands have also been observed. In many complexes the fluorophosphines $RN(PF_2)_2$ function only as monodentate ligands (III) thereby avoiding the strain of the four-membered chelate ring in I. However, at least for $CH_3N(PF_2)_2$, the nitrogen-phosphorus bond to the non-coordinating PF_2 group in complexes of the type III is readily hydrolyzed to form complexes of the CH_3NHPF_2 ligand (IV: $R=CH_3$), a ligand which is not stable in the free state. In other cases reaction of $CH_3N(PF_2)_2$ with a metal carbonyl containing a metal-metal bond can result in rupture of the phosphorus-nitrogen bond to form a bimetallic complex of the type V($R=CH_3$) containing a bridging PF_2 group and a CH_3NPF_2 unit which can be either terminal (e.g. $[CH_3N(PF_2)_2]_4Fe_2CO$) or bridging (e.g. $[C_5H_5Fe(PF_2)_2NCH_3]_2$).

Examples of all of these types of chemical bonding of $RN(PF_2)_2$ ligands have now been characterized by X-ray diffraction structure determinations in collaboration with Prof. M. G. Newton of the Chemistry Department of the University of Georgia. A summary is given below of the specific transition metal chemistry of the $RN(PF_2)_2$ ligands, including the preparations of metal complexes exhibiting all of the above structural features (I-V).

(2) Chromium, Molybdenum, and Tungsten Derivatives

Ultraviolet irradiation of the metal hexacarbonyls $M(CO)_6$ (M= Cr, Mo, and W) with excess $RN(PF_2)_2$ (R= CH_3 and C_6H_5) in diethyl ether solution results in complete displacement of all six carbonyl groups to give white volatile $[RN(PF_2)_2]_3M$ (VI: R= CH_3^{2,12} and C_6H_5^{21}; M= Cr. Mo, and W). These compounds exhibit high thermal and oxidative stabilities relative to other carbonyl-free zerovalent compounds of these metals.

Mononuclear derivatives of these metals containing both $RN(PF_2)_2$ and CO ligands can be prepared by displacement of coordinated olefins by the $RN(PF_2)_2$ ligands.[24] Thus reactions of the norbornadiene-metal tetracarbonyls $C_7H_8M(CO)_4$ (M= Cr, Mo, and W) with the ligands $RN(PF_2)_2$ (R= CH_3 and C_6H_5) give either the chelates $RN(PF_2)_2M(CO)_4$ (VII) or the monoligate monometallic complexes $[RN(PF_2)_2]_2M(CO)_4$ (M = Cr, trans isomer VIIIa; M=Mo and W, cis isomer VIIIb) depending upon the reaction conditions including particularly the ligand: metal mole ratio. Reactions of the cycloheptatriene derivative $C_7H_8Cr(CO)_3$ with the ligands $RN(PF_2)_2$ (R = CH_3 and C_6H_5) give pale yellow mer-$[RN(PF_2)_2]_2Cr(CO)_3$ (IX) containing one monodentate and one bidentate ligand as well as the white binuclear complex mer-$[C_6H_5N(PF_2)_2]_3Cr_2(CO)_6$ of presumed structure X.



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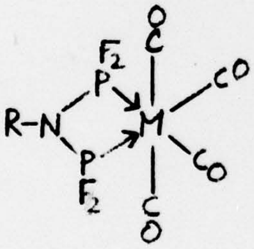

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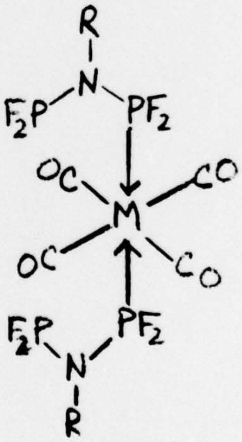

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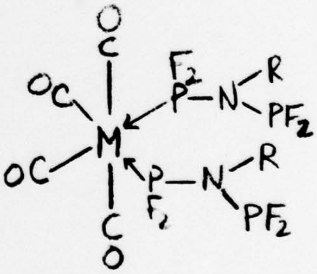

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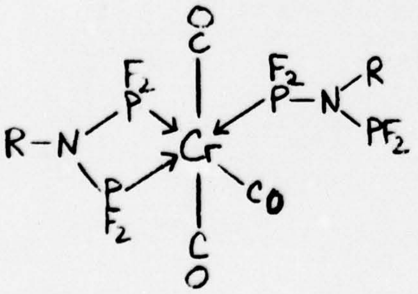

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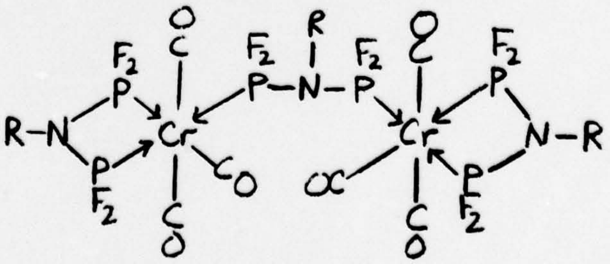

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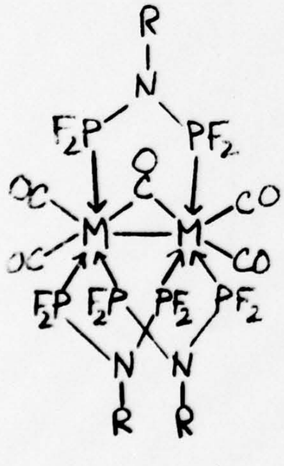
Binuclear derivatives of chromium, molybdenum, and tungsten containing both $RN(PF_2)_2$ and CO ligands have also been prepared.[24] Many of these binuclear derivatives contain bridging carbonyl groups, a rare structural feature for these group VI metals. The yellow binuclear molybdenum complexes $[RN(PF_2)_2]_3Mo_2(CO)_5$ (R= CH_3 and C_6H_5) are obtained by pyrolysis of the corresponding mononuclear complexes $RN(PF_2)_2Mo(CO)_4$ at 100-120°C. X-ray diffraction on the derivative $[C_6H_5N(PF_2)_2]_3Mo_2(CO)_5$ indicates structure XI (M= Mo; R= C_6H_5) containing one bridging CO group and three bridging $RN(PF_2)_2$ ligands. The yellow chromium and tungsten analogues $[CH_3N(PF_2)_2]_3M_2(CO)_5$ (XI: M= Cr and W; R = CH_3) can be obtained by photolysis of the corresponding metal hexacarbonyls with $CH_3N(PF_2)_2$ in a 1 to 1.5:1 ligand/metal mole ratio. Pyrolysis or photolysis of mixtures of the $RN(PF_2)_2$ ligands and the metal hexacarbonyls in a 2 to 2.5:1 ligand/metal mole ratio gives mixtures of the yellow binuclear complexes $[CH_3N(PF_2)_2]_4M_2(CO)_3$ and $[CH_3N(PF_2)_2]_5M_2CO$ in the case of $CH_3N(PF_2)_2$ (M= Mo and W) and the yellow binuclear complexes $[C_6H_5N(PF_2)_2]_4Mo_2(CO)_3$ and $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$ in the case of $C_6H_5N(PF_2)_2$ (M = Mo). A structure determination by X-ray diffraction on $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$ indicates structures of the type XII for the $[RN(PF_2)_2]_4M_2(CO)_3$ derivatives. Structure XII for the $[RN(PF_2)_2]_4M_2(CO)_3$ derivatives is closely related to structure XI for the $[RN(PF_2)_2]_3M_2(CO)_5$ derivatives by replacement of the two terminal CO groups on one metal in XI by a bidentate $CH_3N(PF_2)_2$ ligand in XII. The infrared spectra of $[CH_3N(PF_2)_2]_5M_2CO$ (M = Mo and W) and $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$ indicate only terminal CO groups thereby suggesting structures XIII (analogous to $[CH_3N(PF_2)_2]_4Fe_2CO$--see below) and XIV, respectively, for these binuclear complexes. The structures XIII and XIV have not yet been confirmed by X-ray crystallography, however.



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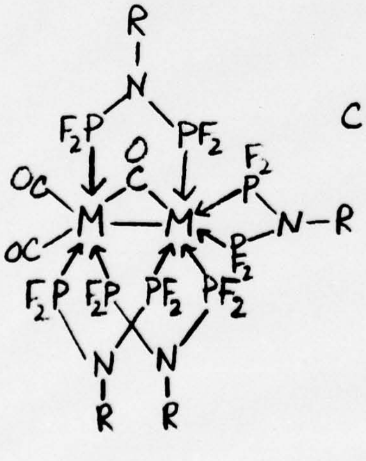

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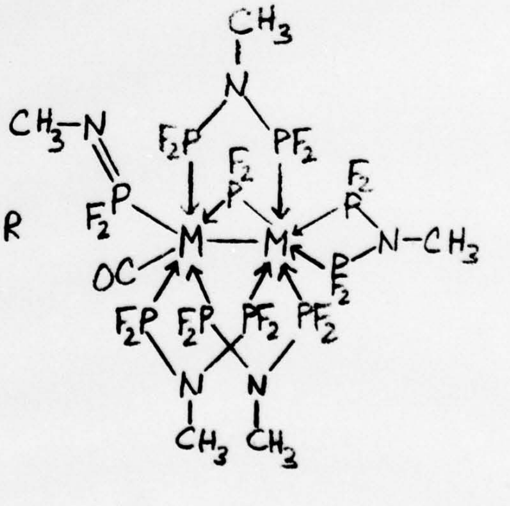
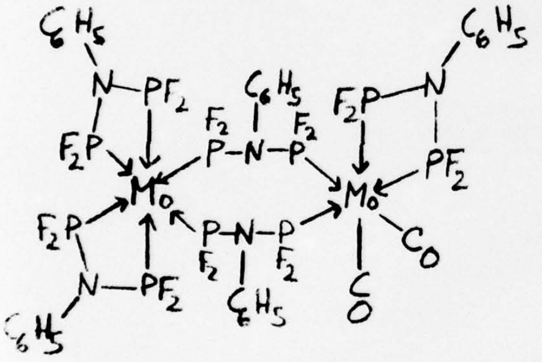


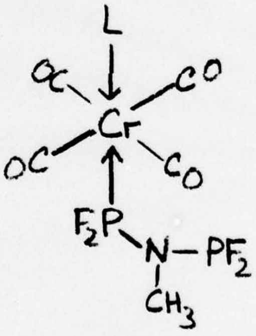
XIII

The potentially strained four-membered chelate rings in the $RN(PF_2)_2M(CO)_4$ complexes (VII) are subject to novel ring-opening reactions upon treatment with donor ligands.[23] Thus reaction of $CH_3N(PF_2)_2Cr(CO)_4$ (VII: R = CH_3, M = Cr) with excess $CH_3N(PF_2)_2$ at ~80°C results in formation of trans-$[CH_3N(PF_2)_2]_2Cr(CO)_4$ (VIIIa: R = CH_3, M = Cr) thereby indicating that the $RN(PF_2)_2M(CO)_4$ derivative can be an intermediate in the formation of the $[RN(PF_2)_2]_2M(CO)_4$ derivatives from the norbornadiene-metal tetracarbonyls and excess $RN(PF_2)_2$. Also this chelate ring-opening reaction has been used for the preparation of the "mixed ligand" complexes of the type trans-$CH_3N(PF_2)_2Cr(CO)_4L$ (XV: L = monodentate $C_6H_5N(PF_2)_2$ and $(C_6H_5)_3P$) by reactions of $CH_3N(PF_2)_2Cr(CO)_4$ (VII: R = CH_3, M = Cr) with the ligand L in an inert solvent at 80°C.

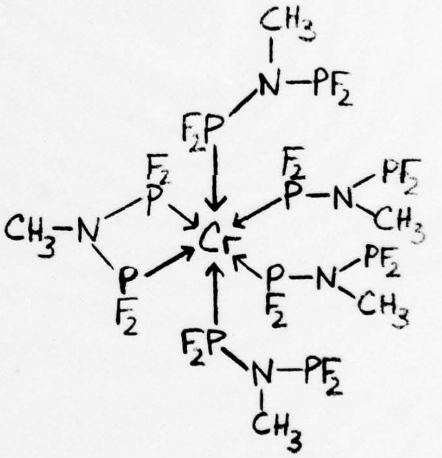
Cocondensations of chromium vapor with fluorophosphines are also useful for the preparation of zerovalent chromium complexes.[17,20] Thus cocondensation of chromium vapor with $CH_3N(PF_2)_2$ provides an alternate route to the complex $[CH_3N(PF_2)_2]_3Cr$ (VI: R = CH_3, M = Cr). Similarly, cocondensation of chromium vapor with the monodentate ligand $(CH_3)_2NPF_2$ gives the new complex $[(CH_3)_2NPF_2]_6Cr$, which is reasonably air-stable but relatively thermally unstable. Cocondensation of chromium vapor with a 4:1 mixture of $(CH_3)_2NPF_2$ and $CH_3N(PF_2)_2$ gives the complex $CH_3N(PF_2)_2Cr[PF_2N(CH_3)_2]_4$ (XVI).



XIV



XV



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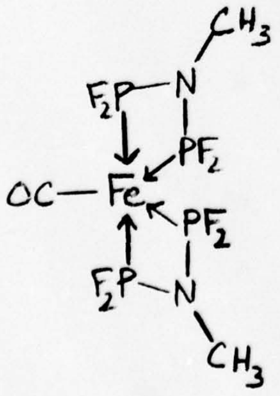
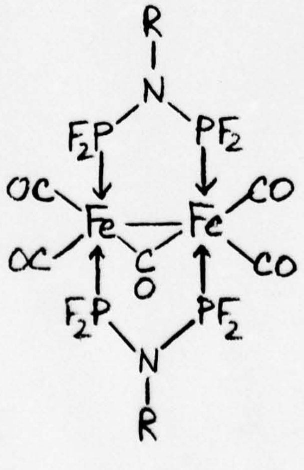
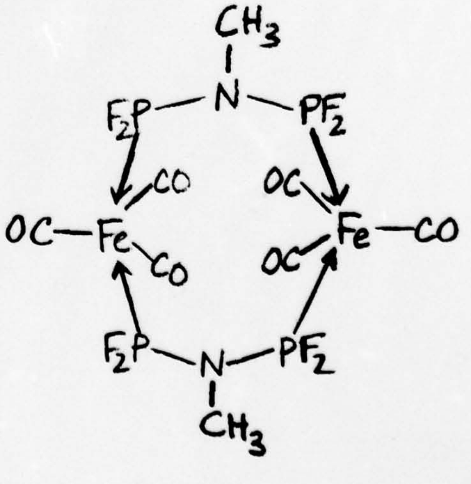


XVII



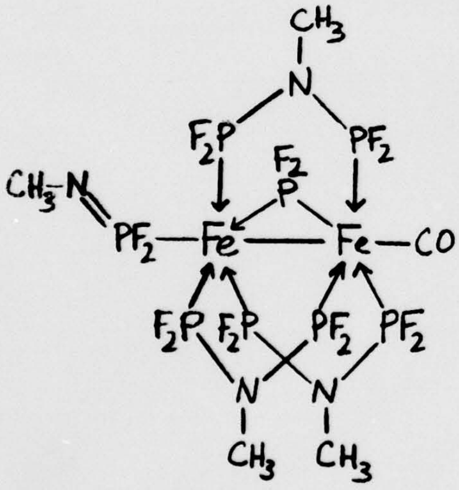
XVIII



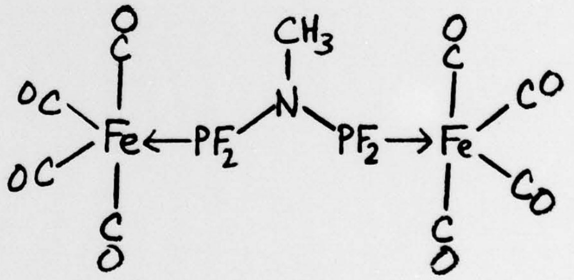
XIX

(3) Iron Derivatives

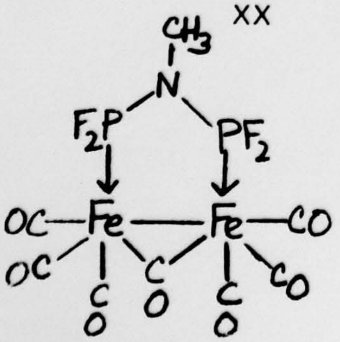
The reactions of iron carbonyls with the $RN(PF_2)_2$ ligands can lead to a great variety of products which depend upon the iron carbonyl used and the reaction conditions. Ultraviolet irradiation of $Fe(CO)_5$ with $CH_3N(PF_2)_2$ gives either yellow liquid $[CH_3N(PF_2)_2]_2FeCO$ (XVII) or orange crystalline $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$ (XVIII) depending upon the reaction conditions.[4,12] Reaction of $Fe_3(CO)_{12}$ with $CH_3N(PF_2)_2$ in boiling tetrahydrofuran gives yellow crystalline $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (XIX) which readily loses carbon monoxide upon standing or heating in solution to form $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$. The indicated structures of both XVIII and XIX have been confirmed by X-ray diffraction.[4] An unusual feature of $[CH_3N(PF_2)_2Fe(CO)_3]_2$ (XIX) is square pyramidal rather than the usual trigonal bipyramidal coordination for the five-coordinate iron(0) atoms. Ultraviolet irradiation of $Fe_3(CO)_{12}$ with excess $CH_3N(PF_2)_2$ in diethyl ether gives yellow $[CH_3N(PF_2)_2]_4Fe_2CO$ shown by X-ray diffraction to have a novel structure XX in which the phosphorus-nitrogen bond of one of the $CH_3N(PF_2)_2$ ligands has broken to give separate CH_3NPF_2 and PF_2 units.[9] The photolysis of $Fe_3(CO)_{12}$ with $CH_3N(PF_2)_2$ in diethyl ether also gives a low yield of red $[CH_3N(PF_2)_2]_3Fe_2(CO)_3$ of unknown structure.



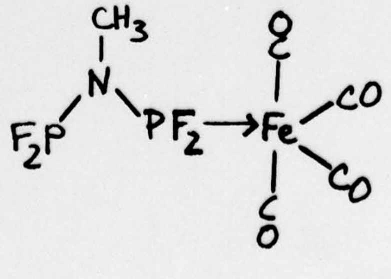
XX



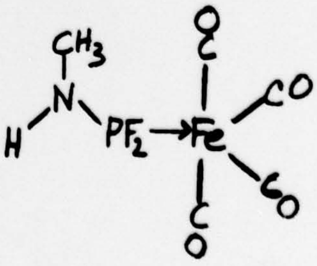
XXI



XXII



XXIII

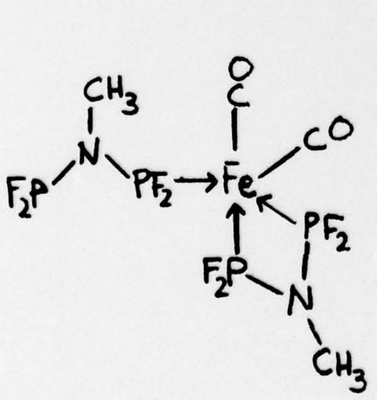


XXIV

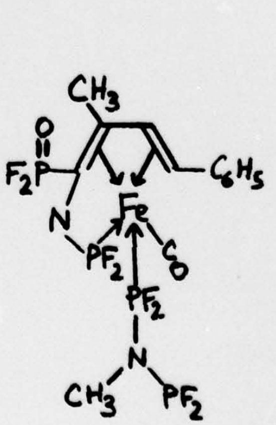
Additional iron carbonyl derivatives are available from $Fe_2(CO)_9$ and $CH_3N(PF_2)_2$ with the actual products obtained depending greatly upon the reaction conditions. Thus treatment of $Fe_2(CO)_9$ with an equimolar quantity of $CH_3N(PF_2)_2$ in diethyl ether at room temperature gives a mixture of yellow liquid $CH_3N(PF_2)_2[Fe(CO)_4]_2$ (XXI) and red-orange crystalline $CH_3N(PF_2)_2Fe_2(CO)_7$ (XXII).[12] However, reaction of $Fe_2(CO)_9$ with excess $CH_3N(PF_2)_2$ in diethyl ether at room temperature gives yellow liquid $CH_3N(PF_2)_2Fe(CO)_4$ apparently with structure XXIII containing a monodentate $CH_3N(PF_2)_2$ ligand. This liquid is readily hydrolyzed upon chromatography on Florisil to give pale yellow volatile crystals of $CH_3NHPF_2Fe(CO)_4$ (XXIV) in accord with the general behavior of monodentate $CH_3N(PF_2)_2$ ligands noted above. Ultraviolet irradiation of $Fe_2(CO)_9$ with excess $CH_3N(PF_2)_2$ in diethyl ether gives a dicarbonyl $[CH_3N(PF_2)_2]_2Fe(CO)_2$ apparently with structure XXV containing one monodentate and one bidentate $CH_3N(PF_2)_2$ ligand.

An interesting feature of this iron carbonyl chemistry of $CH_3N(PF_2)_2$ is the fact that all possible formal substitution products of $Fe_2(CO)_9$ of the type $[CH_3N(PF_2)_2]_nFe_2(CO)_{9-2n}$ ($n = 1, 2, 3,$ and 4) can be obtained depending upon the reaction conditions. This is the first time that a ligand has been found where this is possible. The structures of these binuclear derivatives appear to depend upon the degree of substitution of CO groups with $CH_3N(PF_2)_2$ with the observed ligand phosphorus-nitrogen bond cleavage in $[CH_3N(PF_2)_2]_4Fe_2CO$ (XX) being a total surprise to arise from this research.

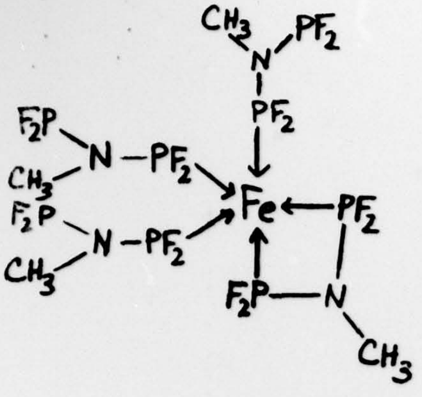
None of these reactions of iron carbonyls with $CH_3N(PF_2)_2$ gave any indications for a simple mononuclear $CH_3N(PF_2)_2Fe(CO)_3$ derivative. Therefore the reaction of $CH_3N(PF_2)_2$ was investigated with the benzalacetone derivative $[C_6H_5CH{=}CHC(O)CH_3]Fe(CO)_3$, a known source of $Fe(CO)_3$ groups under mild conditions. However, instead of giving the desired $CH_3N(PF_2)_2Fe(CO)_3$ this reaction was found to give the yellow diene complex $[C_6H_5CH{=}CHC(CH_3){=}C(POF_2)N(CH_3)\text{-}PF_2]Fe(CO)(PF_2)_2NCH_3$ shown by single crystal X-ray diffraction to have the unusual structure XXVI.[22]



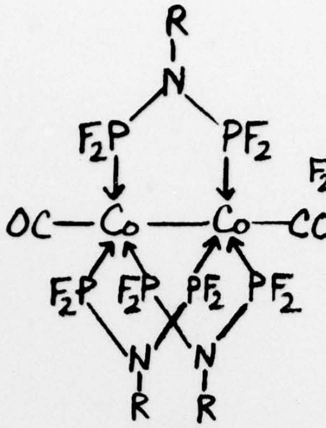
XXV



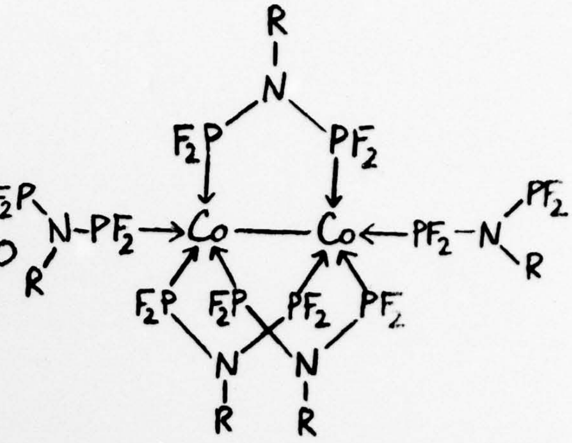
XXVI



XXVII



XXVIII



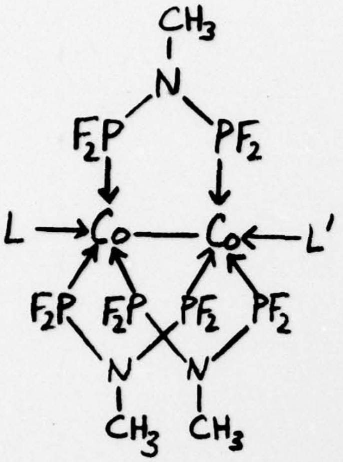
XXIX

Cocondensations of iron vapor with aminodifluorophosphines provide still additional zerovalent iron complexes of interest.[10] Thus cocondensation of iron vapor with $CH_3N(PF_2)_2$ gives a low yield of yellow crystals of stoichiometry $[CH_3N(PF_2)_2]_4Fe$, shown by X-ray crystallography to have structure XXVII containing one bidentate and three monodentate $CH_3N(PF_2)_2$ ligands. Cocondensation of iron vapor with $(CH_3)_2NPF_2$ gives yellow crystalline $[(CH_3)_2NPF_2]_5Fe$, an analogue of such well-known zerovalent iron complexes as $Fe(CO)_5$ and $Fe(PF_3)_5$.

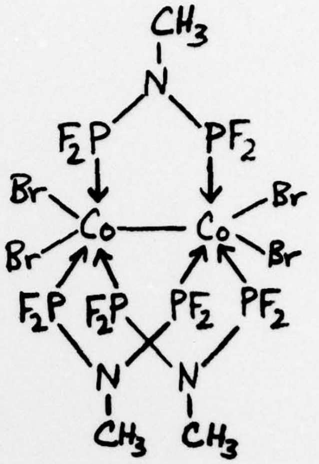
(4) Cobalt Derivatives

The cobalt chemistry of $RN(PF_2)_2$ ligands is dominated by a variety of stable derivatives containing $[RN(PF_2)_2]_3Co_2$ units in which a cobalt-cobalt bond is bridged by three $RN(PF_2)_2$ ligands. Thus reaction of $Co_2(CO)_8$ with $RN(PF_2)_2$ ($R = CH_3$ and C_6H_5) at room temperature in the absence of ultraviolet irradiation results in rapid evolution of carbon monoxide to give the purple crystalline $[RN(PF_2)_2]_3Co_2(CO)_2$ derivatives ($R = CH_3$[3,14] and C_6H_5[21]). The structure XXVIII ($R = CH_3$) has been confirmed by X-ray crystallography for $[CH_3N(PF_2)_2]_3Co_2(CO)_2$. Ultraviolet irradiation of $Co_2(CO)_8$ with excess $RN(PF_2)_2$ at room temperature results in complete displacement of all carbonyl groups to give the purple-black derivatives $[RN(PF_2)_2]_5Co_2$ ($R = CH_3$[14] and C_6H_5[21]) formulated as XXIX containing three biligate bimetallic and two monoligate monometallic $RN(PF_2)_2$ ligands. The compound $[CH_3N(PF_2)_2]_5Co_2$ is also obtained by cocondensation of cobalt vapor with $CH_3N(PF_2)_2$.[16,20] Chromatography of $[CH_3N(PF_2)_2]_5Co_2$ on Florisil results in hydrolysis of the two monoligate monometallic $CH_3N(PF_2)_2$ ligands to give purple $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ (XXX: $L = L' = CH_3NHPF_2$).[14]

The $[CH_3N(PF_2)_2]_3Co_2$ unit in $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ (XXVIII: $R = CH_3$) is stable towards a variety of chemical transformations. Thus ultraviolet irradiation of $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ with the ligands $(CH_3)_2NPF_2$, $(C_2H_5O)_3P$, $(C_6H_5)_3P$, and $(CH_3)_3CNC$ (designated as L) results in the stepwise displacement of the two terminal carbonyl groups to give complexes of the types $[CH_3N(PF_2)_2]_3Co_2(CO)L$ (XXX: $L' = CO$) and $[CH_3N(PF_2)_2]_3Co_2L_2$ (XXX: $L' = L$). A related purple complex $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$ (XXX: $L = L' = (CH_3)_2NPF_2$)



XXX



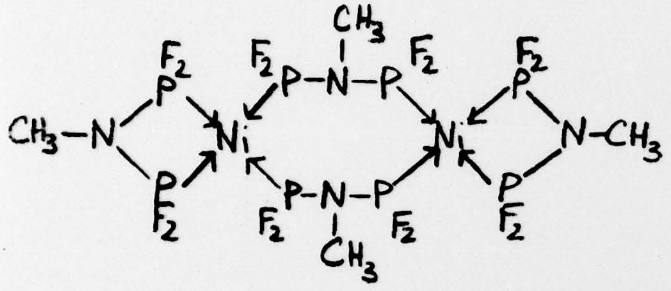
XXXI

has been obtained by cocondensation of cobalt vapor with a 4:1 mixture of $(CH_3)_2NPF_2$ and $CH_3N(PF_2)_2$.[16,20] Unsymmetrical complexes of the types $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)L$ (XXX: L = CO, $(CH_3)_2NPF_2$, and $(C_2H_5O)_3P$; L' = CH_3NHPF_2) have been prepared by analogous methods.[14] The cobalt-cobalt bond in $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ is even resistant towards attack by elemental bromine. Thus reaction of $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ with excess bromine at room temperature gives brown $[CH_3N(PF_2)_2]_3Co_2Br_4$, shown by single crystal X-ray diffraction to have structure XXXI.[15] Electrochemical studies on $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ in collaboration with Dr. N. El Murr of the Université de Dijon (France) indicate both a reversible one-electron reduction to a green radical anion $[CH_3N(PF_2)_2]_3Co_2(CO)_2^-$ and a reversible two-electron reduction to a pale yellow dianion $[CH_3N(PF_2)_2]_3Co_2(CO)_2^{2-}$.

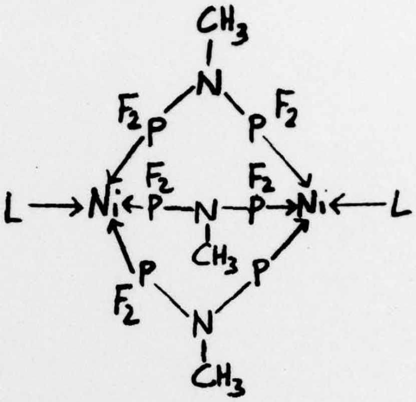
In some cases the ligand $CH_3N(PF_2)_2$ can replace pairwise the carbonyl groups in metal clusters while retaining the fundamental cluster structure. Thus reaction of $Co_4(CO)_{12}$ with $CH_3N(PF_2)_2$ appears to give products of the type $[CH_3N(PF_2)_2]_nCo_4(CO)_{12-n}$ in which the cobalt tetrahedron is apparently maintained intact.[14] The products where n = 2, 3, 4 and 5 have been isolated in the pure state.

(5) Nickel Derivatives

A variety of products have been obtained from $Ni(CO)_4$ and $CH_3N(PF_2)_2$ depending upon the reaction conditions. Ultraviolet irradiation of $Ni(CO)_4$ with excess $CH_3N(PF_2)_2$ in diethyl ether solution gives colorless $[CH_3N(PF_2)_2]_6Ni_2$, apparently XXXII, which upon pyrolysis at 150°C gives a light yellow sublimate of stoichiometry $[CH_3N(PF_2)_2]_2Ni$. The insolubility of this sublimate suggests a coordination polymer in the solid state, although the mass spectrum of the vapor indicates a dimer. A photochemical reaction of $Ni(CO)_4$ with $CH_3N(PF_2)_2$ in a 1:1 mole ratio gives the yellow crystalline binuclear complex $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$, apparently with a structure XXXIII (L = CO) resembling that of the cobalt complex XXVIII except for the absence of a metal-metal bond. The carbonyl groups in $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ (XXXIII: L = CO) are readily replaced with a variety of ligands at room temperature even in the absence of utlraviolet irradiation to give complexes of the type $[CH_3N(PF_2)_2]_3Ni_2L_2$ (XXXIII: L = $(CH_3O)_3P$, $(C_2H_5O)_3P$, $(C_6H_5)_3P$, monodentate $CH_3N(PF_2)_2$, and $(CH_3)_3CNC$). A thermal reaction of $Ni(CO)_4$ with $CH_3N(PF_2)_2$ in a 1:1 mole ratio gives yellow $[CH_3N(PF_2)_2]_2Ni_2(CO)_3$, apparently with structure XXXIV.

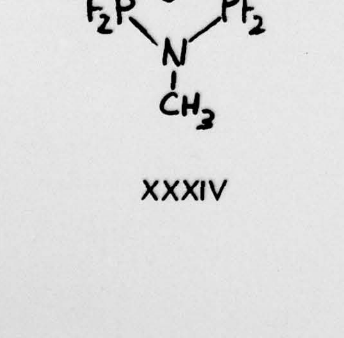


XXXII



XXXIII

Nickel complexes of fluorophosphines have also been prepared by cocondensation reactions involving nickel vapor. Thus cocondensation of nickel vapor with $CH_3N(PF_2)_2$ gives the coordination polymer $\{[CH_3N(PF_2)_2]_2Ni\}_n$, apparently identical to the product obtained from $Ni(CO)_4$ mentioned above. Cocondensation of nickel vapor with $(CH_3)_2NPF_2$ gives the known complex $[(CH_3)_2NPF_2]_4Ni$. Cocondensation of nickel vapor with a 4:1 mixture of $(CH_3)_2NPF_2$ and $CH_3N(PF_2)_2$, respectively, gives a mixture of white $Ni[PF_2N(CH_3)_2]_3[(PF_2)_2NCH_3]$ and light yellow $Ni_2[PF_2N(CH_3)_2]_2[(PF_2)_2NCH_3]_3$ formulated as XXXV and XXXIII (L = $(CH_3)_2NPF_2$), respectively.



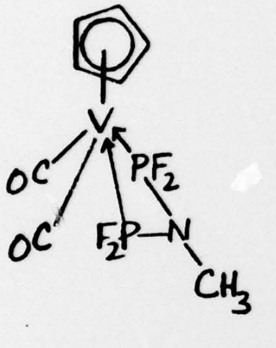
XXXIV

XXXV

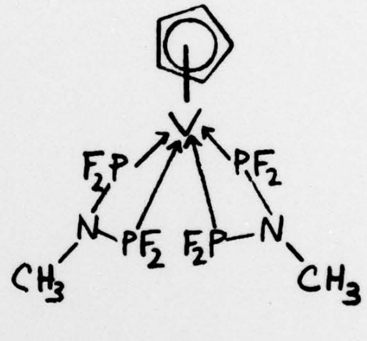
(6) Cyclopentadienylmetal Derivatives

Reactions of cyclopentadienylmetal carbonyl derivatives with the $RN(PF_2)_2$ ligands give a variety of novel complexes containing both cyclopentadienyl rings and the $RN(PF_2)_2$ ligands. Complexes of this type have been prepared containing vanadium, molybdenum, tungsten, manganese, and iron.

Ultraviolet irradiation of $C_5H_5V(CO)_4$ with $CH_3N(PF_2)_2$ in diethyl ether results in the pairwise replacement of the four carbonyl groups to give successively orange $C_5H_5V(CO)_2(PF_2)_2NCH_3$ (XXXVI) and $C_5H_5V[(PF_2)_2NCH_3]_2$ (XXXVII).[7] The compound XXXVII is the first known example of a fully substituted derivative of $C_5H_5V(CO)_4$.

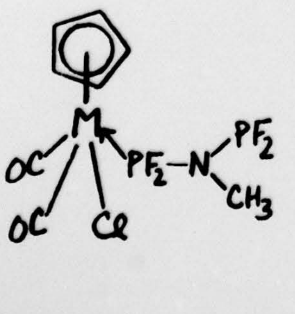


XXXVI

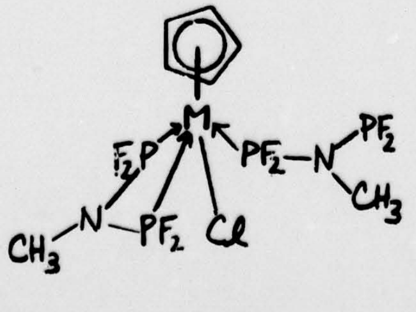


XXXVII

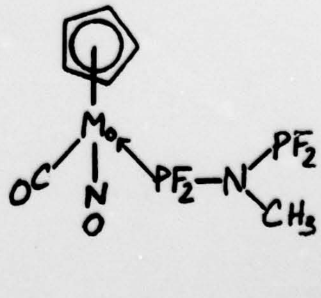
Reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with $CH_3N(PF_2)_2$ successively form orange $C_5H_5M(CO)_2[(PF_2)_2NCH_3]Cl$ (XXXVIII: M = Mo and W) and yellow $C_5H_5M[(PF_2)_2NCH_3]_2Cl$ (XXXIX: M = Mo and W).[13] The structure XXXIX (M = Mo) for $C_5H_5Mo[(PF_2)_2NCH_3]_2Cl$ has been confirmed by X-ray crystallography.[8] However, in the presence of methanol or ethanol the reaction of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with $CH_3N(PF_2)_2$ result in alcoholysis of the fluorophosphine ligand to give orange $C_5H_5Mo(CO)_2(PF_2NHCH_3)Cl$ and $C_5H_5W(CO)_2[PF(OR)_2]Cl$ (R = CH_3 and C_2H_5, respectively). Apparently a different phosphorus-nitrogen bond of the monodentate ligand in XXXVIII is susceptible towards solvolysis depending on whether molybdenum or tungsten is the central metal atom. Reaction of $C_5H_5Mo(CO)_2NO$ with $CH_3N(PF_2)_2$ in boiling benzene slowly forms yellow-orange solid $C_5H_5Mo(CO)(NO)(PF_2)_2NCH_3$ (XL).



XXXVIII

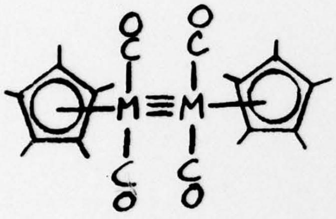


XXXIX

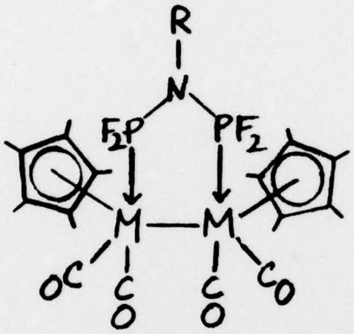


XL

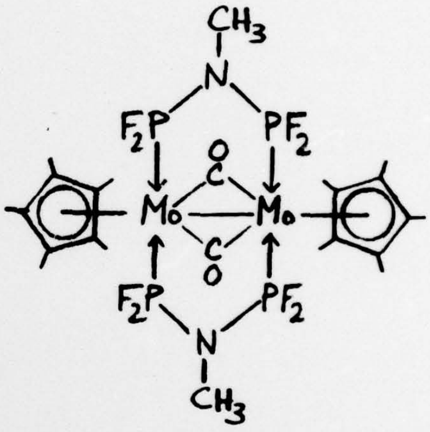
Some addition reactions of the fluorophosphines $RN(PF_2)_2$ to the metal-metal triple bonds in the pentamethylcyclopentadienyl complexes $[(CH_3)_5C_5M(CO)_2]_2$ (XLI: M = Mo and W) have been investigated. The initial products formed from the reactions between $[(CH_3)_5C_5M(CO)_2]_2$ and $RN(PF_2)_2$ are the red adducts $RN(PF_2)_2[M(CO)_2C_5(CH_3)_5]_2$ (XLII: R = CH_3, M = Mo and W; R = C_6H_5, M = Mo) in which the bidentate fluorophosphine has added to the metal-metal triple bond without CO loss to give a metal-metal single bond. Reaction of $[(CH_3)_5C_5Mo(CO)_2]_2$ (XLI: M = Mo) with $CH_3N(PF_2)_2$ under more vigorous conditions (boiling methylcyclohexane) also results in CO loss to give $[(CH_3)_5C_5Mo(CO)(PF_2)_2NCH_3]_2$ formulated tentatively as XLIII because its infrared spectrum indicates the presence of bridging carbonyls but the absence of terminal carbonyls.



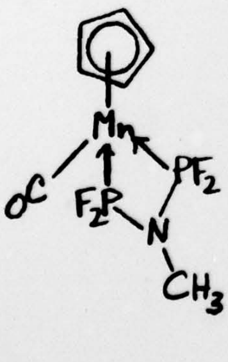
XLI



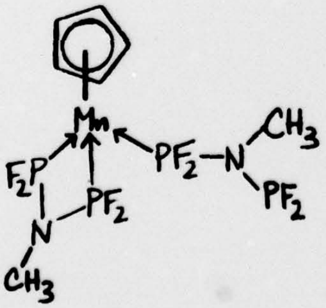
XLII



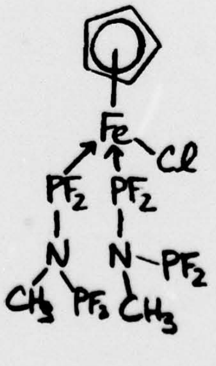
XLIII



XLIV



XLV



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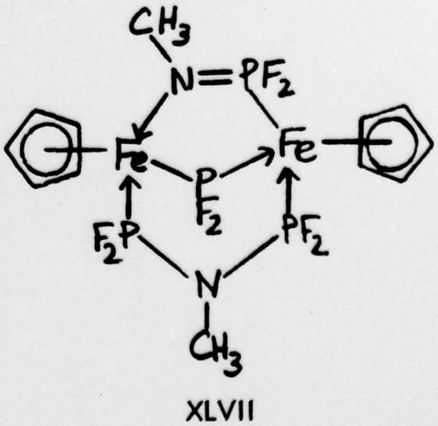


XLVII

Some reactions of the cyclopentadienylmetal carbonyls of manganese and iron with $CH_3N(PF_2)_2$ have also been investigated. Ultraviolet irradiation of $C_5H_5Mn(CO)_3$ with $CH_3N(PF_2)_2$ in diethyl ether gives successively $C_5H_5Mn(CO)(PF_2)_2NCH_3$ (XLIV) and $C_5H_5Mn[(PF_2)_2NCH_3]_2$ (XLV) as yellow liquids.[13] Reaction of $C_5H_5Fe(CO)_2Cl$ with $CH_3N(PF_2)_2$ gives successively red-purple $C_5H_5Fe(CO)[(PF_2)_2NCH_3]Cl$ and red $C_5H_5Fe[(PF_2)_2NCH_3]_2Cl$ (XLVI) *containing* only monodentate $CH_3N(PF_2)_2$ ligands. Again these monodentate ligands are susceptible towards solvolytic removal of the uncomplexed PF_2 group as indicated by the reaction of $C_5H_5Fe(CO)_2Cl$ with $CH_3N(PF_2)_2$ in the presence of methanol to give brown-black $C_5H_5Fe(CO)[PF_2NHCH_3]Cl$. Ultraviolet irradiation of $[C_5H_5Fe(CO)_2]_2$ with $CH_3N(PF_2)_2$ in tetrahydrofuran or pentane results in pairwise substitution of the four carbonyl groups to give successively low yields of purple $[C_5H_5FeCO]_2(PF_2)_2NCH_3$ and red $[C_5H_5Fe(PF_2)_2NCH_3]_2$.[11] The latter complex has been shown by single crystal X-ray diffraction to have the unexpected structure XLVII in which one of the two $CH_3N(PF_2)_2$ ligands has undergone phosphorus-nitrogen bond rupture to form separate PF_2 and CH_3NPF_2 units. The bonding of the CH_3NPF_2 unit to the bimetallic system is unusual since it is attached to one iron through its phosphorus atom and to the other iron through its nitrogen atom. This is the only well-defined example where an aminodifluorophosphine derived ligand is bonded to a transition metal through its nitrogen atom.

B. Polyphosphines Containing Terminal Dialkylamino and Alkoxy Groups and their Metal Complexes

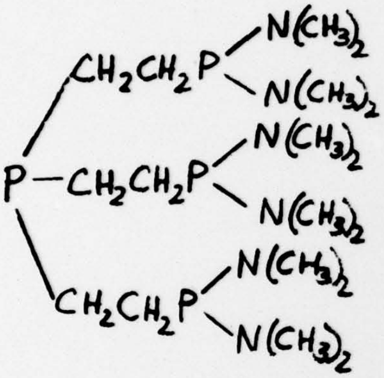
Research at the University of Georgia by the principal investigator during the period 1968-1975 resulted in the development of methods for the synthesis of diverse polytertiary phosphines by the base-catalyzed addition of phosphorus-hydrogen bonds to the carbon-carbon bonds of vinylphosphorus derivatives as represented schematically by the following equation:

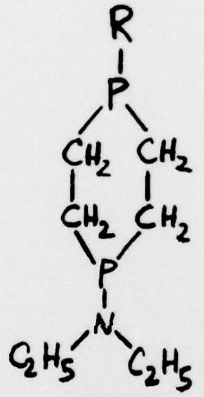
$$\rangle P{-}H + CH_2{=}CH{-}P\langle \quad \longrightarrow \quad \rangle PCH_2CH_2P\langle \qquad (1)$$

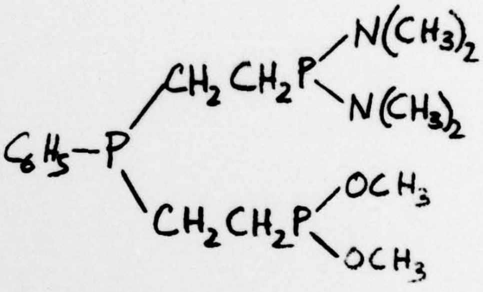
A major achievement during this project has been the adaptation of this synthetic principle for the preparation of polyphosphines containing terminal dialkylamino and alkoxy groups.

In order to adapt this type of base-catalyzed addition for the preparation of such polytertiary phosphines, vinylphosphorus and/or phosphorus-hydrogen derivatives containing terminal dialkylamino and alkoxy groups are required. Vinylphosphorus derivatives of this type are much easier to obtain than such phosphorus-hydrogen derivatives and therefore were used for this synthetic work. Key compounds for this work are $[(CH_3)_2N]_2PCH{=}CH_2$ and $(C_2H_5)_2NP(CH{=}CH_2)_2$ which were obtained by reactions of $[(CH_3)_2N]_2PCl$ and $(C_2H_5)_2NPCl_2$, respectively, with vinylmagnesium bromide followed by hydrolysis with aqueous alkaline tetrasodium ethylenediamine tetraacetate.[5] Another key vinylphosphorus intermediate is $(CH_3O)_2PCH{=}CH_2$, obtained by methanolysis of $[(CH_3)_2N]_2PCH{=}CH_2$ in boiling methanol.

The polyphosphines containing phosphorus-nitrogen and/or phosphorus-oxygen bonds are constructed by base-catalyzed additions of various phosphorus-hydrogen compounds to the above vinylphosphorus derivatives. For example, the additions of the secondary phosphines R_2PH (R = CH_3 and C_6H_5) to $[(CH_3)_2N]_2PCH{=}CH_2$ catalyzed by KH give the corresponding diphosphines $R_2PCH_2CH_2P[N(CH_3)_2]_2$. The base-catalyzed additions of the primary phosphines RPH_2 (R = CH_3 and C_6H_5) to $[(CH_3)_2N]_2PCH{=}CH_2$ can be controlled to give either the 1:1 adduct diphosphines $RP(H)CH_2CH_2P[N(CH_3)_2]_2$ or the 1:2 adduct triphosphines $RP[CH_2CH_2P[N(CH_3)_2]_2]_2$ depending mainly upon the mole ratio of the reactants. Reaction of KPH_2 with $[(CH_3)_2N]_2PCH{=}CH_2$ followed by hydrolysis gives the tripod tetraphosphine $P[CH_2CH_2P[N(CH_3)_2]_2]_3$ (XLVIII). The base-catalyzed additions of the secondary phosphines R_2PH (R = CH_3 and C_6H_5) to $(C_2H_5)_2NP(CH{=}CH_2)_2$ can be controlled to give either the 1:1 adducts $(C_2H_5)_2NP(CH{=}CH_2)CH_2CH_2PR_2$ or the 2:1 adducts $(C_2H_5)_2NP(CH_2CH_2PR_2)_2$ again depending largely on the mole ratios of the reactants. Base-catalyzed additions of the primary phosphines RPH_2 (R = C_6H_5, $CH_2C_6H_5$, and $CH_2C(CH_3)_3$) to $(C_2H_5)_2NP(CH{=}CH_2)_2$ result in cyclization to give the corresponding 1,4-diphosphacyclohexane derivatives $(C_2H_5)_2NP(CH_2CH_2)_2PR$ (XLIX).


XLVIII


XLIX


L

The polyphosphines containing terminal methoxy groups can be prepared either by base-catalyzed additions of phosphorus-hydrogen compounds to $(CH_3O)_2PCH{=}CH_2$ or by methanolysis of the corresponding polyphosphines containing terminal dialkylamino groups. Thus the potassium hydride catalyzed additions of $(C_6H_5)_2PH$ and $C_6H_5PH_2$ to $(CH_3O)_2PCH{=}CH_2$ give the diphosphine $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ and the triphosphine $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$, respectively. The phosphines containing terminal methoxy groups $R_2PCH_2CH_2P(OCH_3)_2$, $RP[CH_2CH_2P(OCH_3)_2]_2$ (R = CH_3 and C_6H_5), and $P[CH_2CH_2P(OCH_3)_2]_3$ have been obtained by methanolysis in boiling toluene of the corresponding phosphines containing terminal dimethylamino groups.

A triphosphine containing both dimethylamino and methoxy terminal groups $C_6H_5P[CH_2CH_2P(OCH_3)_2][CH_2CH_2P[N(CH_3)_2]_2]$ (L) has been obtained by the base-catalyzed addition of $C_6H_5P(H)CH_2CH_2P[N(CH_3)_2]_2$ to $(CH_3O)_2PCH{=}CH_2$.

Some preliminary studies on the transition metal coordination chemistry of the ligands $(C_6H_5)_2PCH_2CH_2P(OCH_3)_2$ (abbreviated as Pf-Pom) and $C_6H_5P[CH_2CH_2P(OCH_3)_2]_2$ (abbreviated as Pom-Pf-Pom) have been made. Reactions of these ligands with nickel(II) nitrate in boiling methanol give the yellow diamagnetic complexes (Pf-Pom)$Ni(NO_3)_2$ and (Pom-Pf-Pom)$Ni(NO_3)_2$. These are tentatively formulated as square planar nickel(II) derivatives with one uncoordinated phosphorus atom in the case of the triphosphine derivative. Similarly, reactions of these ligands with cobalt(II) chloride in boiling methanol give the blue-green paramagnetic (4.8 B.M. by Evans' method) complexes (Pf-Pom)$CoCl_2$ and (Pom-Pf-Pom)$CoCl_2$. Analogous reactions of these ligands with iron(II) chloride in boiling methanol give the orange paramagnetic (5.2 B.M.) complexes (Pf-Pom)$FeCl_2$ and (Pom-Pf-Pom)$FeCl_2$. A yellow diamagnetic apparently hexacoordinate ruthenium(II) complex (Pf-Pom)$_2RuCl_2$ has been prepared by reaction of two equivalents of Pf-Pom with $[(C_6H_5)_3P]_3RuCl_2$.

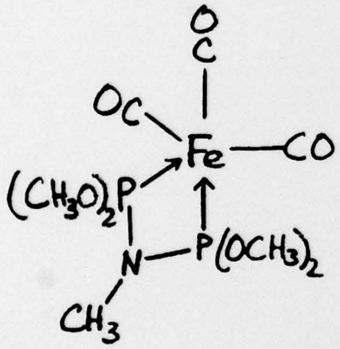
The coordination chemistry of the related ligand $(CH_3O)_2PCH_2CH_2P(OCH_3)_2$ (abbreviated as Pom-Pom) has also been investigated.[19] This ligand can be prepared by alcoholysis of $Cl_2PCH_2CH_2PCl_2$ in the presence of triethylamine according to the following equation:

$$Cl_2PCH_2CH_2PCl_2 + 4\ CH_3OH + 4\ (C_2H_5)_3N \longrightarrow (CH_3O)_2PCH_2CH_2P(OCH_3)_2 + 4\ [(C_2H_5)_3NH]Cl \qquad (2)$$

Metal halides (e.g. $FeCl_2$, $CoCl_2$, $NiCl_2$) do not react with Pom-Pom under conditions that they react with Pf-Pom and Pom-Pf-Pom (see above) apparently owing to the lack of a sufficiently basic phosphorus atom in Pom-Pom arising from the absence of alkyl or aryl terminal groups. However, several metal carbonyl derivatives of Pom-Pom have been prepared. Ultraviolet irradiations of Pom-Pom with the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) result in replacement of four of the six carbonyl groups to give (Pom-Pom)$_2M(CO)_2$ (M = Cr, Mo, and W). No evidence could be obtained for complete substitution of all six carbonyl groups in $M(CO)_6$ by Pom-Pom to give the carbonyl-free complexes (Pom-Pom)$_3$M corresponding to the zerovalent derivatives $[RN(PF_2)_2]_3M$ (M = Cr, Mo, and W) discussed above. Reaction of Pom-Pom with the norbornadiene complex $C_7H_8Cr(CO)_4$ results in displacement of the coordinated diolefin in the usual manner to give the tetracarbonyl (Pom-Pom)$Cr(CO)_4$. Reaction of Pom-Pom with $Fe_2(CO)_9$ in tetrahydrofuran solution gives the binuclear complex (Pom-Pom)$[Fe(CO)_4]_2$ in which the Pom-Pom ligand bridges two iron atoms. Reaction of Pom-Pom with $Co_2(CO)_8$ in diethyl ether at or below room temperature generates the pale yellow monocarbonyl cation $[(\text{Pom-Pom})_2CoCO]^+$ which can be isolated as its hexafluorophosphate salt.

The extensive coordination chemistry of $CH_3N(PF_2)_2$ outlined above makes of interest an investigation of the coordination chemistry of $CH_3N[P(OCH_3)_2]_2$. Our preliminary results indicate that complete substitution of the fluorines in $CH_3N(PF_2)_2$ with methoxy groups has a major effect on the resulting coordination chemistry. Thus reaction of $CH_3N[P(OCH_3)_2]_2$ with $Fe_2(CO)_9$

at 60°C in hexane solution gives a complex of stoichiometry $CH_3N[P(OCH_3)_2]_2Fe(CO)_3$, which is formulated as a monomer LI because of its high volatility (molecular weight determinations are not yet available on this complex). The corresponding fluorophosphine derivative $CH_3N(PF_2)_2Fe(CO)_3$ has never been found despite numerous investigations on the reactions of $CH_3N(PF_2)_2$ with various iron carbonyls as outlined above. Reaction of $CH_3N[P(OCH_3)_2]_2$ with $Co_2(CO)_8$ at ambient temperature in tetrahydrofuran solution gives violet-brown crystalline $[CH_3N[P(OCH_3)_2]_2Co(CO)_2]_2$, tentatively formulated as LII with two diphosphine bridges. Thus the substitution of fluorines with methoxy groups in going from $CH_3N(PF_2)_2$ to $CH_3N[P(OCH_3)_2]_2$ lowers the degree of substitution of $Co_2(CO)_8$ that can be attained under a given set of conditions. The rather routine white crystalline complexes $CH_3N[P(OCH_3)_2]_2M(CO)_4$ (M = Cr and Mo) have been obtained by displacement of coordinated norbornadiene in $C_7H_8M(CO)_4$ (M = Cr and Mo) with $CH_3N[P(OCH_3)_2]_2$ in boiling hexane.



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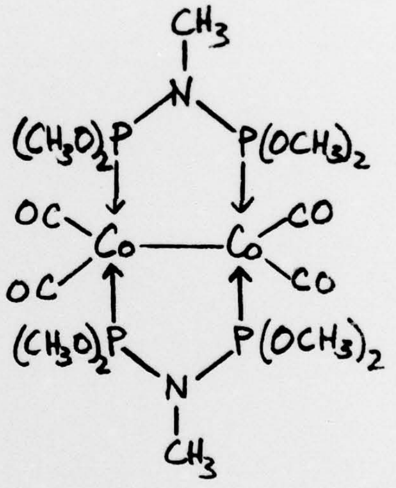

LII

C. Miscellaneous Coordination Chemistry of Organophosphorus and Organonitrogen Ligands

In addition to the above major efforts on the coordination chemistry of $RN(PF_2)_2$ derivatives and on the synthesis and coordination chemistry of polyphosphines with terminal dialkylamino and methoxy groups, several other aspects of the coordination chemistry of unusual organophosphorus and organonitrogen ligands have been investigated as outlined below. Some aspects of this work represented completion of incomplete work remaining from the Air Force Grant AFOSR-71-2000 funded during the period 1971-1975. Other aspects of this work represented exploratory experiments which did not appear promising enough to warrant extensive attention. In the interest of brevity only exploratory experiments leading to publications or representing a major portion of the time of one or more of the project personnel are mentioned in this final report.

(1) Metal Chloride Complexes of Neopentylphosphines[1]

Some complexes of various neopentylphosphines with rhodium, nickel, and palladium chlorides have been investigated in order to complete work started under the earlier Air Force Grant AFOSR-71-2000.[1] In this connection trineopentylphosphine was found to react with hydrated rhodium(III) chloride to give yellow $\{[(Me_3CCH_2)_3P]_2RhCl_2\}_2$ in ethanol at room temperature but yellow $[(Me_3CCH_2)_3P]_2Rh(CO)Cl$ in boiling $ROCH_2CH_2OH$ ($R = CH_3$ or C_2H_5). Dineopentylphenylphosphine reacts with hydrated rhodium(III) chloride in ethanol to give red $[(Me_3CCH_2)_2PC_6H_5]_3Rh_2Cl_4$ at room temperature and orange $\{[(Me_3CCH_2)_2PC_6H_5]_2RhCl_2\}_2$ at the boiling point. Neither trineopentylphosphine nor dineopentylphenylphosphine reacts with nickel(II) chloride in ethanol solution. However, neopentyldiphenylphosphine reacts with nickel(II) chloride in ethanol solution to give purple $[Me_3CCH_2P(C_6H_5)_2]_2NiCl_2$, which gives yellow solutions in polar solvents. Trineopentylphosphine reacts with palladium(II) chloride derivatives in boiling n-butanol to give either yellow $[(Me_3CCH_2)_3P]_2PdCl_2$ or orange $[(Me_3CCH_2)_3PPdCl_2]_2$ depending upon the reaction conditions.

(2) Transition Metal Derivatives of Pentavalent Phosphorus

An attempt was made to prepare transition metal derivatives of pentavalent phosphorus by the addition of hexafluoroacetone or hexafluorobutanedione to the phosphido derivatives $(CF_3)_2PMn(CO)_5$ and $(C_6F_5)_2PFe(CO)_2C_5H_5$ containing both a phosphorus-metal bond and a potentially available lone electron pair on the phosphorus. Unfortunately neither of these perfluorinated ketones appeared to add to the trivalent phosphorus atoms of these phosphido complexes under conditions other than those leading to complete decomposition of the system. This line of research was therefore abandoned.

(3) Cyclopentadienylmetal Carbonyl Complexes of Molybdenum and Tungsten Containing Other Ligands[6]

During the course of this research project various research workers in this laboratory were investigating reactions of $C_5H_5M(CO)_3Cl$ ($M = Mo$ and W) with various ligands. In view of a general interest in polypyrazolylborate chemistry, pyrazole and imidazole were included in this study hoping to get compounds with some structural features related to those of the polypyrazolylborates.

Reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with pyrazole (abbreviated as PzH) in boiling hexane, benzene, methylcyclohexane, or pyridine give ionic products $[C_5H_5M(CO)_2(PzH)_2]^+Cl^-$ and/or non-ionic products $C_5H_5M(CO)_2(PzH)Cl$ which are readily interconverted by the following equilibrium:[6]

$$[C_5H_5M(CO)_2(PzH)_2]Cl \rightleftharpoons C_5H_5M(CO)_2(PzH)Cl + PzH \qquad (3)$$

Similar chemistry is observed upon reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with imidazole (abbreviated as ImH) except that the ionic complexes $[C_5H_5M(CO)_2(ImH)_2]^+Cl^-$ are much more stable towards dissociation of the heterocycle than their pyrazole analogues. Since no evidence for deprotonation of the pyrazole or imidazole was observed in any of these studies, this line of research was abandoned after fully characterizing the new metal complexes outlined above.

(4) New Polypyrazolylborates

One of the original objectives of this research project as outlined in the original research proposal was the development of the coordination chemistry of polypyrazolylborates containing unusual, particularly bulky, substituents on the pyrazole rings or the boron atom. However, attempts to prepare new polypyrazolylborates from 3,5-di-tert-butylpyrazole and from 3,5-bis(trifluoromethyl)pyrazole and potassium borohydride, even for prolonged periods at elevated temperatures, were unsuccessful. Apparently the bulky substituents on the pyrazole ring hinder greatly the reaction with potassium borohydride to form polypyrazolylborates. In another series of experiments, reactions of sodium cyanotriphenylborate and sodium cyanotrihydroborate with pyrazole were investigated. The reaction with sodium cyanotriphenylborate was found to give a product exhibiting spectroscopic properties suggesting formulation as $Na[C_6H_5B(CN)(C_3H_3N_2)_2]$ but this product was never obtained in the pure state. The reaction with $NaBH_3CN$ resulted in elimination of HCN to give the well known sodium bispyrazolylborate, identified by its infrared and proton n.m.r. spectra.

(5) Optically Active Isocyanide Metal Complexes[18]

A supply of both enantiomers of the optically active isocyanide $C_6H_5CH(CH_3)NC$ remained from the previous Air Force project AFOSR-71-2000. We therefore investigated the reactions of this optically active ligand with simple octahedral metal carbonyl derivatives in order to see how ligand substitution reactions might be used systematically to introduce multiple chiral sites into transition metal complexes. In this connection octahedral metal complexes of the types $LMo(CO)_5$, cis-$L_2M(CO)_4$, and fac-$L_3M(CO)_3$ (M = Cr, Mo, and W) containing the optically pure enantiomers of $C_6H_5CH(CH_3)NC$ were prepared by conventional methods. The molar rotations $[\phi]^{25}_{D}$ of the $LMo(CO)_5$ (+58°) and cis-$L_2M(CO)_4$ (118-126°) complexes were found to increase incrementally with the number of optically active ligands (L) in the complex. However, the fac-$L_3M(CO)_3$ complexes were found not to exhibit a regular incremental increase in their molar rotation (148-163°) when compared with the other complexes in the series.

PAPERS PRESENTED AT SCIENTIFIC MEETINGS COVERING WORK SUPPORTED BY THE AIR FORCE GRANT AFOSR-75-2869

1. R. B. King and W. F. Masler, "Polytertiary Phosphines with Terminal Dialkylamino and Alkoxy Groups," paper presented by R. B. King at the 172nd National Meeting of the American Chemical Society, San Francisco, California, September, 1976: paper INOR 145 in abstracts.
2. M. Chang, J. Gimeno, N. S. Pantaleo, R. B. King and M. G. Newton, "The Structures of Two Novel Bimetallic Products Obtained from Octacarbonyldicobalt and Methylaminobis(difluorophosphine)," paper presented by M. Chang at the 173rd National Meeting of the American Chemical Society, New Orleans, Louisiana, March, 1977: paper INOR 120 in abstracts.
3. R. B. King, M. G. Newton, J. Gimeno, M. Chang and K. -N. Chen, "Reactions of Cyclopentadienyl Metal Carbonyls with Methylaminobis(difluorophosphine)," paper presented by J. Gimeno at the 174th National Meeting of the American Chemical Society, Chicago, Illinois, August, 1977: paper INOR 18 in abstracts.
4. K. -N. Chen and R. B. King, "Some New Cyclopentadienylmolybdenum and Cyclopentadienyltungsten Derivatives Containing Organonitrogen Ligands," paper presented by K. -N. Chen at the 174th National Meeting of the American Chemical Society, Chicago, Illinois, August, 1977: paper INOR 21 in abstracts.
5. R. B. King, M. G. Newton, J. Gimeno, M. Chang, and K. -N. Chen, "Reactions of Cyclopentadienyl Metal Carbonyls with Methylaminobis(difluorophosphine)," reserve paper for the Eighth International Conference on Organometallic Chemistry, Kyoto, Japan, September, 1977.
6. M. Chang, M. G. Newton, R. B. King, and J. Gimeno, "The Structure of a Novel Product from the Reaction of Benzalacetone-tricarbonyliron and Methylaminobis(difluorophosphine)" paper presented by M. Chang at the Ninth Central Regional Meeting of the American Chemical Society, Charleston, West Virginia, October, 1977: paper INOR 60 in abstracts.
7. R. B. King, "Transition Metal Coordination Chemistry of Alkylaminobis(difluorophosphines)," lecture presented by R. B. King at the Second Annual Gulf Coast Chemistry Conference, Gulf Coast, Alabama, October, 1977.
8. R. B. King, M. Chang, M. G. Newton, and J. Gimeno, "Methylaminobis(difluorophosphine) as a Ligand in Metal Cluster Chemistry: Novel Phosphorus-Nitrogen Bond Cleavage Reactions," paper presented by R. B. King at the 175th National Meeting of the American Chemical Society, Anaheim, California, March, 1978: paper INOR 103 in abstracts.

9. R. B. King, "Metal Complexes of Methylaminobis(difluorophosphine)," lecture presented by R. B. King at a symposium on Recent Advances in Transition Metal Chemistry at the South Western Regional Meeting of the Chemical Society--Dalton Division, Bristol, England, March, 1978.

10. R. B. King, M. G. Newton, J. Gimeno, M. Chang, T. J. Lotz and N. Pantaleo, "Metal-Metal Bonds Bridged by Methylaminobis(difluorophosphine)," paper presented by R. B. King at the Third European Inorganic Chemistry Symposium, Cortona, Italy, April, 1978.

11. J. Gimeno, R. B. King, M. G. Newton, and M. Chang, "Carbonil Complejos con Enlaces Metal-Metal y Metilaminobis(difluorofosfina) Puente," paper presented by J. Gimeno at the 75th Anniversary Congress of the Real Sociedad Española de Fisica y Quimica, Madrid, Spain, October, 1978.

12. R. B. King, T. W. Lee, M. G. Newton, and L. Norskov-Lauritzen, "Novel Binuclear Molybdenum Carbonyl Derivatives Containing Bridging Carbonyl Groups," paper presented by R. B. King at the Ninth International Conference on Organometallic Chemistry, Dijon, France, September, 1979.