TRANSITION METAL COMPOUNDS WITH POTENTIAL
ELECTRONIC AND RADIATION RESISTANT PROPERTIES.

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Experimental work is reported involving the synthesis, properties, and structural characterisation of many new organometallic compounds. Cage structures containing boron, carbon and platinum are described, as are polynuclear metal clusters involving nickel, platinum and ruthenium. Especially novel discoveries include diplatinacarboranes, and tri- and tetra-nuclear nickel compounds with bridging acetylene and cyclooctatetraene groups. Studies on the activation of carbon-hydrogen, carbon-carbon, and carbon-halogen bonds using fluorocarbon reactants led to the isolation of numerous metallo-cyclic compounds.
Chemistry of sixteen electron molybdenum and tungsten complexes has been explored with particular reference to the activation of acetylenes. A bibliography of thirty three journal articles is appended.
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INTRODUCTION.

This report describes work carried out under Grant Number APOS-71-2090, and covers the period from August 1st 1971 through July 31st 1976. We have previously submitted through the European Office of Aerospace Research four Progress Reports as well as three Interim Scientific Reports dated September 17th, 1973, October 10th, 1974, and September 1st, 1975, respectively. The latter gave a summary of research carried out over the four year period, 71 Aug 01 - 75 Jul 31.

In addition to the Principal Investigator, the following persons have been associated with the research program for various periods of time during the five year period. Generally postdoctoral fellows worked with the group for one year or less whereas graduate students carried out research for longer periods. In the majority of cases stipends were provided by matching funds. Grant funds provided chemicals and other support.


Junior Research Personnel:

G.K. Barker* B.L. Goodall
R.L. Bennett* J.A.K. Howard*
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* Postdoctoral Research Assistants. † Dr. M.I. Bruce was associated with some aspects of the research until his departure in 1973 to become professor of chemistry at Adelaide, Australia.
RESEARCH ACCOMPLISHED.

As was stated in the Third Interim Scientific Report (September 1975), our researches can be classified under the main headings of (i) Polynuclear complexes, and (ii) Chemical activation of small molecules by metal complex formation.

In terms of research publications, the work has been very successful since thirty three (33) primary journal articles describing research supported in part by this Grant have either been published or have been submitted for publication during its five year period. Because of this very large volume of work, all of the results will not be discussed in detail in this Report. Instead, only highlights of the research will be mentioned. References to the relevant publications will be given in the cursive text according to their numbers on the list so that the interested reader will be able to seek additional details by consulting the original journal articles.

POLYNUCLEAR METAL COMPLEXES.

Research on metal complexes having cluster or cage-like structures is important in the context of the search for new materials expected to display useful conductivity, optical, or thermal stability. We have discovered several new syntheses of polynuclear compounds, a field of research which continues to be under very active study in many laboratories throughout the world.

(i) Metallacarborane Clusters.

During the course of our research program we developed a new approach to the synthesis of the metallacarboranes (compounds containing aggregates of metal, carbon and boron atoms) based on the direct reaction of low

* See page 20 for list of references.
valent transition metal complexes with a carborane. Molecular structures of many of the compounds were elucidated by single crystal X-ray diffraction studies. Some of the more novel structures are shown in Figures 1 - 8. The new synthetic approach was first employed using 11-atom carboranes where it was shown that reaction of these species with a d^{10} complex of nickel, palladium or platinum resulted in a direct insertion of the metal atom into the cage (see Scheme 1 illustrating reaction between [Ni(C_8H_{12})_2] and C_{2}B_{9}H_{11}). The resulting structures were of the closo-type, and the method of synthesis could be extended to mono-carbon carboranes and to metallacarboranes with 11-vertex structures, the latter affording clusters containing two different transition metals (2). These reactions formally involve a net transfer of electrons from the metal to the cage, representing an important new aspect of oxidative-addition chemistry.

Scheme 1.

When the direct oxidative-insertion reaction was extended to carboranes containing less than eleven vertices the new compounds were found to display unusual structural features. For example, instead of closo-structures being uniformly produced the new species often possessed nido-structures (a polyhedron with one vertex removed) rather than closo, and the inserted metal atom, usually platinum, showed a marked
General view of the molecule 1,1-(PhMe$_2$)$_2$-2,6-Me$_2$-1,2,4-PtC$_4$H$_8$H$_6$.

Structure of [Me$_2$C$_2$H$_2$Pt($\text{P}$(PEt$_3$)$_5$]. Phosphino ethyl groups are omitted for clarity.

General view of the molecule 1-(t$_7$C$_4$H$_4$)$_2$-8,8-(Et$_3$P)$_2$-1,2,7,8-CoC$_4$PtB$_4$H$_{10}$.

nido-6,6-(Et$_3$P)$_2$-5,8-Me$_2$-6,8-PtC$_4$B$_4$H$_8$. 
Molecular structure of \( \text{clos}_{-}2.3^\text{+} (\text{Et},P)_{1.2.3.6} \) \( \text{CP}_{4} \text{CB}_{12} \text{H}_{12} \). Phosphinoethyl groups are omitted for clarity.

Molecular structure of \( \text{clos}_{-}1.1^\text{+} (\text{Me},P)_{1.6.8.8} \) \( \text{Me}_{1.6.8.8} \) \( \text{PtC}_{12} \text{B}_{12} \text{H}_{12} \).

Molecular structure of \( \text{nido}_{-} \mu(4.8)^\text{-} (\text{Me},P)_{8.8.8} \) \( \text{Me}_{8.8.8} \) \( \text{PtC}_{12} \text{B}_{12} \text{H}_{12} \).

Molecular structure of \( \text{nido}_{-}8.8^\text{-} (\text{Me},P)_{8.8.8} \) \( \text{Me}_{8.8.8} \) \( \text{PtC}_{12} \text{B}_{12} \text{H}_{12} \).
preference to bond to the boron atoms of the cage in preference to the carbon. Thus 3 illustrates the nido-cluster complex obtained from [Pt(Et₃P)₃] and Me₂C₂B₇H₇, and 4 a nido-metallacarborane prepared by reacting [Pt(trans-stilbene)(Et₃P)₂] with Me₂C₂B₆H₆. The important and interesting observation was made that in solution the compound [Pt(Me₂C₂B₇H₇)(Et₃P)₂] underwent a rapid degenerate rearrangement (Scheme 2) as detected by ¹¹B and ³¹P n.m.r. studies.

Scheme 2.

The complex 5, prepared by reacting closo-1,6-Me₂-1,6-C₂B₆H₆ with [Pt(trans-stilbene)(Me₃P)₂], represents the first structurally authenticated example of a boracyclobutadiene derivative, the isolation and characterisation of which has served to emphasize further the wide scope of metallacarborane chemistry.

Whereas direct insertion of d¹⁰ Ni, Pd or Pt species into 8-, 9- and 11-atom closo-carboranes led to the discovery of a new approach to the synthesis of both closo- and nido-metallacarboranes, analogous reactions with 7- and 10-atom carboranes gave hitherto unknown types of bimetallic species. Thus reaction of closo-2,4-C₂B₆H₇ with [Pt(styrene)(Et₃P)₂] gave 6, whereas [Pt(1,5-C₈H₁₂)(Me₃P)₂] and 1,6-C₈B₆H₁₀ gave the very novel structure 7. Treatment of the latter with charcoal afforded 8. Structure 7 with one metal atom within the cage and the other
without, is without precedent in inorganic cluster chemistry.

Some reactions between zero-valent complexes of nickel, palladium and platinum with arachno-carboranes were also investigated. Arachno structures are based on polyhedra with two vertices missing, and in carborane chemistry one example of such a structure is that of Me$_2$C$_2$B$_7$H$_{11}$. Reaction of the latter with, for example, [Ni(C$_8$H$_{12}$)(Et$_3$P)$_2$] gives the nido-compound [6,6-(Et$_3$P)$_2$-5,9-Me$_2$-6,5,9-NiC$_2$B$_7$H$_9$], a cluster in which a nickel atom is attached to a B$_2$C-system in a 1,2,3-\eta bonding mode.$^{26}$

(ii) Polynuclear Metal Carbonyl Complexes.

It has long been known that transition metals have a strong tendency to form metal-metal bonds in their carbonyl derivatives. Even though this is now a relatively old field of study important discoveries continue to be made. Early in the Grant period we characterised$^{1-3,10}$ several unusual cluster compounds of platinum and ruthenium shown on page 8 of this Report. Recently, in the Journal of the American Chemical Society,$^{28}$ we have described two nickel atom clusters of special novelty (9, 10) (page 9). These compounds were prepared by the reactions illustrated in Scheme 3.

![Scheme 3](image-url)
Molecular structure of [Ni(CO)₆(C₂F₆)]₂. Fluorine atoms omitted for clarity. The Ni-CO bond distances average 1.81 (6) Å and the three Ni(apex)-Ni(basal)-CO fractions are each nearly linear. The three OC-Ni(apex)-Ni(basal) are each nonlinear with the OC-Ni(apex) vector nearly collinear with the idealized C₄ axis of the molecule.

Molecular structure of [Ni(CO)₆(C₆H₆)(C₂F₆)]₃. The Ni-CO distances average 1.78 (1) Å, with the carbonyl groups bent ca. 30° out of the Ni₃ plane away from the C₆ ring.
The tetranuclear nickel species is the first example of a large class of \([M_4L_4(u_x(\eta^2)^-L)^3]\) clusters, while the trinuclear nickel cluster provides the first example of a polynuclear metal complex in which a planar cyclooctatetraene ring bridges three metal atoms as it might on the surface of a metal. These two compounds are of considerable interest within the context of those cluster complexes which are fluxional and chemically active in relation to their ability to provide multinuclear sites for the bonding of alkenes or alkynes.

CHEMICAL ACTIVATION OF SMALL MOLECULES BY COMPLEX FORMATION.

In the search for new catalyst systems relevant to polymer and petrochemicals fundamental information is required concerning the ability of transition metals to activate chemically C-H, C-X (X = halogen) or C-C bonds. Our researches have been conducted in three main areas: (i) Cyclo-metallation and related reactions, (ii) Fluoro- and chlorofluorocarbon-metal complexes, and (iii) Sixteen-electron complexes of molybdenum and tungsten.

(i) Cyclo-metallation and Related Reactions.

In the early stages of our research\(^4,13,21\) we were involved in the study of ortho-metallation reactions relating to the activation of C-H bonds by metals. For example, Scheme 4 illustrates the reactivity towards acetylenes of an ortho-metallated compound (I) to give a novel heterocyclic complex (II).

\[
\begin{align*}
\text{(I)} & \quad \xrightarrow{\text{(i)} \text{ Refluxing decalin, } \text{CH}_2} \quad \xrightarrow{\text{(ii)} \text{ C}_8\text{F}_{14}} \\
\text{(II)}
\end{align*}
\]

More recently\textsuperscript{29} ortho-metallation reactions of several $\eta^5$-cyclopenta
dienylruthenium complexes have been investigated in detail leading,
inter-alia, to the characterisation of the metallo-cycles shown in
Scheme 5.

(ii) Fluoro- and Chlorofluorocarbon-metal Complexes.

The study of fluorocarbon-metal complexes has been useful in
providing models for the ways in which analogous hydrocarbons may react
with transition metal compounds. It is often possible to isolate and
study reaction intermediates when fluoro- or chlorofluoro-carbon
compounds are employed as substrate molecules in reactions with reactive
organometallic compounds, whereas the same is frequently not possible
when the analogous hydrocarbons are used.

In references 5-7, 12, 14, 15 and 24 we describe numerous new
fluorocarbon-metal complexes formed by C-C, C-O or C-N bond formation
within the coordination sphere of a metal, with concomitant synthesis
of carbon-metal bonds. These studies involved metal complexes of
ruthenium, cobalt, iridium, nickel, palladium and platinum. The scope
of our activity in this area is demonstrated by the compounds listed
on page 13.

We have also discovered\textsuperscript{11,17} a series of tin halide promoted
rearrangement reactions of coordinated fluorocarbons, in which C-F
bonds are "activated" and converted into C-Cl or C-Br linkages (Scheme 6).
In the absence of a metal centre this type of reaction does not occur.

Recently\textsuperscript{31} we have extended our work with fluorocarbon-metal
complexes to a study of insertion reactions of hexafluorobut-2-yne,
tetrafluoroethylene, and hexafluoroacetone with cyclopentadienyl-iron,
ruthenium, -palladium and -molybdenum complexes. In this manner we
have discovered many new compounds, the structures of which are shown
Scheme 5.
(II) \( \text{L} = \text{PPh}_3 \)
(VI) \( \text{L} = \text{PMe}_2\text{Ph} \)
(X) \( \text{L} = \text{PSO}_{2}\text{Ph} \)
(XI) \( \text{L} = \text{PM}_{123}\text{Ph} \)

(III) \( \text{L} = \text{PPh}_3 \)
(VII) \( \text{L} = \text{PMe}_2\text{Ph} \)
(XI) \( \text{L} = \text{PSO}_{2}\text{Ph} \)

(IV) \( \text{L} = \text{CO} \)
(IX) \( \text{L} = \text{PPh}_3 \)
(X) \( \text{L} = \text{PSO}_{2}\text{Ph} \)

(I) \( \text{L} = \text{CO} \)

(IVa) \( \text{L} = \text{CO} \)
(IX) \( \text{L} = \text{PPh}_3 \)
(X) \( \text{L} = \text{PSO}_{2}\text{Ph} \)

(III) \( \text{L} = \text{CO} \)
(VII) \( \text{L} = \text{PPh}_3 \)
(XI) \( \text{L} = \text{PSO}_{2}\text{Ph} \)

(XI) \( \text{L} = \text{AsPh}_3 \)

(VI) \( \text{L} = \text{PPh}_3 \)
(V) \( \text{L} = \text{Ph}_3\text{PCHCH}_2\text{PPPh}_3 \)

(IX) \( \text{L} = \text{PPh}_3 \)
(XI) \( \text{L} = \text{PPh}_3 \)

(IV) \( \text{L} = \text{Ph}_3\text{PCHCH}_2\text{PPPh}_3 \)
(VII) \( \text{L} = \text{Ph}_3\text{PCHCH}_2\text{PPPh}_3 \)

(VIII) \( \text{L} = \text{PPh}_3 \)
(X) \( \text{L} = \text{PSO}_{2}\text{Ph} \)

(XII) \( \text{L} = \text{PPh}_3 \)

(XIII) \( \text{L} = \text{PPh}_3 \)

(XIV) \( \text{L} = \text{PPh}_3 \)

(XV) \( \text{L} = \text{PPh}_3 \)

(XVI) \( \text{L} = \text{PPh}_3 \)

(XVII) \( \text{L} = \text{PPh}_3 \)

(XVIII) \( \text{L} = \text{PPh}_3 \)

(XIX) \( \text{L} = \text{PPh}_3 \)

(XIV) \( \text{L} = \text{Ph}_3\text{PCHCH}_2\text{PPPh}_3 \)

(XV) \( \text{L} = \text{PPh}_3 \)

(XVI) \( \text{L} = \text{PPh}_3 \)

(XVII) \( \text{L} = \text{PPh}_3 \)

(XVIII) \( \text{L} = \text{PPh}_3 \)

(XIX) \( \text{L} = \text{PPh}_3 \)

(XIV) \( \text{L} = \text{Ph}_3\text{PCHCH}_2\text{PPPh}_3 \)

(XV) \( \text{L} = \text{PPh}_3 \)

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(XIV) \( \text{L} = \text{Ph}_3\text{PCHCH}_2\text{PPPh}_3 \)

(XV) \( \text{L} = \text{PPh}_3 \)

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(XVIII) \( \text{L} = \text{PPh}_3 \)

(XIX) \( \text{L} = \text{PPh}_3 \)

(XIV) \( \text{L} = \text{Ph}_3\text{PCHCH}_2\text{PPPh}_3 \)

(XV) \( \text{L} = \text{PPh}_3 \)

(XVI) \( \text{L} = \text{PPh}_3 \)

(XVII) \( \text{L} = \text{PPh}_3 \)

(XVIII) \( \text{L} = \text{PPh}_3 \)

(XIX) \( \text{L} = \text{PPh}_3 \)

(XIV) \( \text{L} = \text{Ph}_3\text{PCHCH}_2\text{PPPh}_3 \)

(XV) \( \text{L} = \text{PPh}_3 \)

(XVI) \( \text{L} = \text{PPh}_3 \)

(XVII) \( \text{L} = \text{PPh}_3 \)

(XVIII) \( \text{L} = \text{PPh}_3 \)

(XIX) \( \text{L} = \text{PPh}_3 \)

(XIV) \( \text{L} = \text{Ph}_3\text{PCHCH}_2\text{PPPh}_3 \)

(XV) \( \text{L} = \text{PPh}_3 \)

(XVI) \( \text{L} = \text{PPh}_3 \)

(XVII) \( \text{L} = \text{PPh}_3 \)

(XVIII) \( \text{L} = \text{PPh}_3 \)

(XIX) \( \text{L} = \text{PPh}_3 \)
The complex (Fe(COCF,C,H,)(t-C,H,)). Fe–C(1), 1.99(1); Fe–C(4), 2.18(2); Fe–C(5), 2.06(2); and C(3)–C(4), 1.34–
(3) Å. The t-C,H, ring has an envelope conformation with an acute folding angle of 26.4°.
on page 16. A number of new insertion reactions have been identified. A particularly novel result was the characterisation of complex 11 (XII on page 16), formed by the apparent cleavage of the C=C double bond in C₂F₄.

(iii) Sixteen Electron Complexes of Molybdenum and Tungsten.

Organometallic chemistry is dominated by compounds which obey the 18-electron rule. In these complexes all the metal bonding orbitals are occupied and the species are kinetically stable, reacting only by ligand dissociation, processes which generate a vacant site. Of potential interest, from the chemical reactivity point of view, are 16-electron complexes which have vacant coordination sites to which substrate molecules can become bonded as a prelude to chemical reaction via modification of their bonding properties by interaction with metal orbitals. In the case of an organic reactant this can take the form of C-H or C-C bond activation. During our researches we have investigated the chemistry of new 16-electron complexes of molybdenum and tungsten. 30-32

Reaction of [MC1(0)₃(η⁵-C₅H₅)] (M = Mo or W) with acetylenes affords the 16-electron species [MC1(RC₂R)₂(η⁵-C₅H₅)], which were structurally characterised by X-ray crystallography, and shown to react with donor ligands and with TlC₅H₅ (Scheme 7). These compounds are thus highly reactive.

```
[MC1CO(C₆H₄-C₆H₄)₃]

(X)

[MC1CO(C₆H₄-C₆H₄)₃] + [PhC≡CH] → [MC1CO(C₆H₄-C₆H₄)₃](PhC≡CH)

(Y)

[MC1CO(C₆H₄-C₆H₄)₃] + [PhC≡CH] → [MC1CO(C₆H₄-C₆H₄)₃](PhC≡CH)

(Z)

[MC1CO(C₆H₄-C₆H₄)₃] + [PhC≡CH] → [MC1CO(C₆H₄-C₆H₄)₃](PhC≡CH)

(W)

[MC1CO(C₆H₄-C₆H₄)₃] + [PhC≡CH] → [MC1CO(C₆H₄-C₆H₄)₃](PhC≡CH)

(V)

Scheme 7.
```
Molecular structure of \([\text{W(Cl)}(\text{CF}_3\text{C}_6\text{F}_{15})_2(\eta^4-\text{C}_8\text{H}_8)]\).

Molecular structure of \([\text{Mo(CF}_3\text{C}_6\text{F}_{15})_2(\eta^4-\text{C}_8\text{H}_8)]\).
The molecular structure of the 16-electron tungsten complex [MC1(CF3C2CF3)2(n5-C5H5)] is shown in 12, (page 17).

The extensive chemistry of the species [MC1(CF3C2CF3)2(n5-C5H5)] was further demonstrated by reactions with TlSC6F5 to give compounds [M(SC6F5)(CF3C2CF3)2(n5-C5H5)]; the related species [M(SC6F5)(CO)(PhC2Ph)(n5-C5H5)] being similarly obtained from [MC1(CO)(PhC2Ph)(n5-C5H5)]. Cyclopentadienyllithium reacts with the compounds [MC1(CF3C2CF3)2(n5-C5H5)] to afford insertion products [MC1(COF3:C(CF3):C(CF3):C5H5(CF3C2CF3)(n5-C5H5)]; the molybdenum compound being characterised by a single crystal X-ray diffraction study (13).

The molybdenum compound [MoCl(CF3C2CF3)2(n5-C5H5)] underwent an unusual reaction with the tris(pyrazolyl)borate anion giving a complex containing no boron but an n3-allyl group, linking two pyrazole ligands and formed by condensation of the two hexafluorobut-2-yne ligands originally coordinated to the metal. Buta-1,3-diene reacted with [MoCl(CF3C2CF3)2(n5-C5H5)] to give [MoCl2(n4-C4H6)(n5-C5H5)] and with [MoCl(CO)(PhC2Ph)(n5-C5H5)] to yield the same compound or [MoCl(CO)(n4-C4H6)(n5-C5H5)], depending on the solvent. The tungsten compound [WC1(CO)(n4-C4H6)(n5-C5H5)] was also prepared. Reactions of bicyclo[2.2.1]heptadiene with the compounds [MC1(CF3C2CF3)2(n5-C5H5)] were also studied.

SUMMARY OF RESULTS ACHIEVED.

Advances have been made in two main areas of organometallic chemistry:

(a) Polynuclear metal complexes, and (b) Chemical activation of small molecules by metal complex formation.

(a) New metal-cage structures containing nickel, palladium or platinum atoms have been prepared by polyhedral expansion of carboranes with zero-valent complexes of these metals. Entirely new structural types have
been identified for the first time including a diplatinum complex in which one metal atom is located within the cage of boron and carbon atoms while the second is external to the cage but joined to it by a Pt-Pt and a Pt-B bond. In another area of metal cluster chemistry several polynuclear carbonyl compounds of ruthenium and platinum have been characterised, as have two novel nickel complexes \([\text{Ni}_4(\text{CO})_4(\mu_3-\text{CF}_3\text{C}_2\text{CF}_3)_3]\) and \([\text{Ni}_3(\text{CO})_3(\mu_3-\text{C}_8\text{H}_8)(\mu_3-\text{CF}_3\text{C}_2\text{CF}_3)]\). In the latter a planar C₈ ring bridges a nickel triangle, whereas in the former structure three acetylene ligands bridge faces of a Ni₄ tetrahedron.

(b) Several new cyclometallation reactions have been identified, particularly involving the group \([\text{Ru(Ph}_3\text{P)}(\eta^5-\text{C}_5\text{H}_5)]\) and azobenzene derivatives. Numerous fluorocarbon metal complexes have been prepared by oxidative-addition reactions of d⁸ and d¹⁰ metal compounds. The activation of carbon-fluorine bonds towards substitution by chlorine or bromine has been demonstrated for fluoro-olefin metal complexes. Novel insertion products have been obtained by reacting hexafluoro-but-2-yne, tetrafluoroethylene and hexafluoroacetone with cyclopentadienyliron, -ruthenium, -palladium and -molybdenum complexes. A detailed study has been made of the chemical reactivity of the 16-electron complexes \([\text{MC}_1(\text{CF}_3\text{C}_2\text{CF}_3)_2(\eta^5-\text{C}_5\text{H}_5)]\) (M = Mo, W).
### CUMULATIVE LIST OF PUBLICATIONS UNDER GRANT AFSR 71-2090.

1. **Chemistry of the Metal Carbonyls. Part LXIII. New Cluster Carbonyl Compounds Containing Platinum and Iron.**
   

2. **Chemistry of the Metal Carbonyls. Part LXIV. New Cluster Carbonyl Compounds Containing Platinum and either Ruthenium or Osmium.**
   

3. **Chemistry of the Metal Carbonyls. Part LXV. Reactions Between Dodecacarbonyl Triruthenium and Tertiary Phosphines or Arsines.**
   

4. **Metallation and Related Reactions with π-Cyclopentadienyl-ruthenium Complexes.**
   

5. **Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXIV. Chloronitrosylbis(triphenyl-, methylidiphenyl- and dimethylphenylphosphine)ruthenium and Nitrosyl(triphenylphosphine)iridium.**
   

6. **Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXV. Phosphine-, Phosphite- and Cyclo-octa-1,5-diene Platinum Complexes.**
   

7. **Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXVI. 1,1,1-Tris(diphenylphosphinomethyl)- and 1,1,1-Tris(diphenylarsinomethyl)-ethane.**
   
8. Metalallocarboranes: New Syntheses


10. Triaryl Phosphite Derivatives of Dodecacarbonyltrimethanenium.

11. Lewis Acid Promoted Vinyl-rearrangement and Halogen-exchange of Platinum-fluoroolefin Complexes.

12. Reactions of Low-Valent Metal Complexes with Fluorocarbons. Part XXVIII.
Nickelocene and Tricarbonyl(π-allylic)cobalt Complexes with Bis(tri-fluoromethyl)diazomethane.


14. Reactions of Low-Valent Metal Complexes with Fluorocarbons.
Part XXIX. Zerovalent Nickel and Platinum Complexes with Hexa-fluorobut-2-yne and Hexakis(trifluoromethyl)benzene.
15. Reaction of Amines with Nickel, Palladium and Platinum Complexes Containing Isocyanide and Fluorocarbon Ligands.


17. Tin(IV) Halide Promoted Vinyl Rearrangement of Hexafluorobuta-1,3-diene-platinum Complexes.


19. Formation of closo- and nido-Metallocarboranes from closo-C$_2$B$_9$ and -C$_2$B$_7$ Carboranes; Molecular Structures of closo-1,1-(Me$_2$PhP)$_2$-2,4-Me$_2$-1,2,4-PtC$_2$B$_9$H$_9$ and nido-10,10-(Et$_3$P)$_2$-2,8-Me$_2$-10,2,8-PtC$_2$B$_7$H$_7$.

20. Synthesis of a Boron Analogue of Co-ordinated Cyclobutadiene; Molecular Structures of closo- and nido-L$_2$PtC$_2$B$_6$H$_6$R$_2$ [L = PMe$_3$ or PEt$_3$; R = H or Me].
21. 2-(Phenylazo)phenyl Complexes of Iridium(III).
   by M.I. Bruce, B.L. Goodall, F.G.A. Stone and B.J. Thomson,

22. Reactions of Fluorinated Ketones with Ferrocenes
   by M.I. Bruce, F.G.A. Stone and B.J. Thomson,

23. Metallaborane Chemistry. Oxidative-insertion Reactions of 11-atom
    Carborane and Metallacarborane Species with Zerovalent Nickel,
    Palladium and Platinum Complexes.
    by M. Green, J.L. Spencer, F.G.A. Stone and A.J. Welch,

24. Reactions of Hexafluoroacetone, Hexafluoropropene, and Tetrafluoro-
    ethylene with Bis(cyclo-octa-1,5-diene)platinum; Molecular Structure
    of \([\text{Pt}_2\{\text{CF}_3\}_2\text{CO}\{1,5-\text{C}_6\text{H}_{12}\}_2]\).
    by M. Green, J.A.K. Howard, A. Laguna, M. Murray, J.L. Spencer,

25. Metallaborane Chemistry. Oxidative-insertion Reactions of
    11-atom Monocarbon Carborane Species with Zerovalent Nickel,
    Palladium and Platinum Complexes; the Molecular and Crystal
    Structure of \(1,1-(\text{Bu}^+\text{NC})_2-2-\text{NMe}_3-1,2-\text{PdCB}_{10}\text{H}_{10}\).
    by W.E. Carroll, M. Green, F.G.A. Stone and A.J. Welch,

26. Metallaborane Chemistry. Reactions of Zerovalent Nickel and
    Platinum Complexes with arachno-5,9-C$_2$B$_7$ Carboranes; Crystal and
    Molecular Structure of a carbadibora-allyl Nickel Complex.
    by M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone,
27. Synthesis of nido- and closo-Diplatina carborane Complexes by Direct Insertion; Crystal and Molecular Structures of

\[ \text{closo-}2,3-[(\text{Et}_3\text{P})_2]_2-1,2,3,6-\text{Cp}_2\text{CB}_5\text{H}_7, \]
\[ \text{nido-}\mu(4,8)-[(\text{Me}_3\text{P})_2\text{Pt}]_{-8,8-}[(\text{Me}_3\text{P})_2]_{-7,8,10-}\text{Cp}_2\text{CB}_8\text{H}_{10} \]
and
\[ \text{nido-}8,8-[(\text{Me}_3\text{P})_2]_{-7,8,10-}\text{Cp}_2\text{CB}_8\text{H}_{10}. \]


28. Formation of Tetra- and Trinuclear Cluster Complexes from Tetra-carbonylnickel and Hexafluorobut-2-yne; The Molecular Structures of \[ [\text{Ni}_4(\text{CO})_{4}(\text{CF}_3\text{C}_2\text{CF}_3)_3] \] and \[ [\text{Ni}_3(\text{CO})_{3}(\text{CF}_3\text{C}_2\text{CF}_3)(\text{C}_8\text{H}_8)]. \]


30. Formation of 16-Electron Alkyne Complexes by Reaction of Halo(tri-carbonyl)(\(n^5\)-cyclopentadienyl)-molybdenum and -tungsten Complexes with Alkynes; Crystal and Molecular Structure of \[ [\text{WC}_1(\text{CF}_3\text{C}_2\text{CF}_3)_2(n^5-\text{C}_5\text{H}_5)]. \]


31. Insertion Reactions of Hexafluorobut-2-yne, Tetrafluoroethylene and Hexafluoroacetone with \(n^5\)-Cyclopentadienyl-Iron, -Ruthenium, -Palladium and -Molybdenum Complexes: Molecular and Crystal Structures of \[ [\text{Fe}_2(\text{CO})_4(\text{CF}_3)_4\text{CO})(n^5-\text{C}_5\text{H}_5)_2] \] and \[ [\text{Fe}(\text{CO})_2(\text{CF}_3)_2(n^5-\text{C}_5\text{H}_5)]. \]

32. Syntheses Involving Coordinatively Unsaturated Cyclopentadienyl-
molybdenum and -tungsten Complexes: Molecular and Crystal Structure
of \([\text{Mo}^\text{C(CF}_3\text{):C(CF}_3\text{)}^\text{C}_5\text{H}_5(C\text{F}_3\text{C}_2\text{CF}_3)(\text{n}^5\text{C}_5\text{H}_5)]\).
by J.L. Davidson, M. Green, F.G.A. Stone and A.J. Welch,

33. Cyclopentadienylruthenium Phosphine Complexes. Some Complexes
Derived from 1-Alkynes: Molecular and Crystal Structure of the
Cumulene Derivative \([\text{Ru}(\text{C(CF}_3\text{):C(H)C(CF}_3\text{):C:C\cdot\text{CH(CF}_3\text{)})(\text{PPh}_3)(\text{n}^5\text{C}_5\text{H}_5)]\).
by M.I. Bruce, R.C.F. Gardner, J.A.K. Howard, F.G.A. Stone,