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SYNTHETIC APPLICATIONS OF d^{10} METAL COMPLEXES

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Introduction

It was with some reservation that I agreed to write an article for the 100th Volume of the Journal of Organometallic Chemistry. It can be argued that there is little value in adding a necessarily fragmentary and incomplete summary to the already large review literature. However, this article has provided me with an opportunity on two counts. Firstly, I hope to show that a synthetic programme of research encompassing several years can follow logical lines with reasonably definitive objectives. Preparative work, therefore, need not yield results without a common theme. Secondly, this article provides an opportunity to give credit to several talented co-workers. Synthetic work involving organometallics demands a very high degree of experimental skill and tenacity of purpose. Moreover, in recent times single crystal X-ray diffraction techniques have so improved that molecular structure determinations can often be accomplished within the time scale of preparative experiments. Rapid acquisition of structural information not only places the synthetic work on a firm foundation, but stimulates new ideas for further syntheses while the momentum is present for their accomplishment. Gifted crystallographers can, therefore, play a vital and synergic role, as is amply demonstrated in the later sections.

Space limitations necessarily restrict the material to be reviewed. I have selected that aspect of our work which is concerned with zerovalent d^{10} metal complexes. It is worth mentioning that the results to be described stemmed from work done fifteen years ago at Harvard University. There S.L. Stafford [1] found that pentacarbonyliron and perfluoroalkyl iodides underwent reactions to give complexes, e.g. $[Fe(C_3F_7)(I)(CO)_4]$, with carbon—iron σ bonds. This result, together with the observation by Chatt and Shaw [2] that Pt^{IV} complexes $[Pt(Me)_2(I)_2(PR_3)_2]$ formed upon treating $[Pt(Me)(I)(PR_3)_2]$ with methyl iodide, provided the first examples of the direct insertion into carbon—halogen bonds of transition metal atoms with d^8 electron shells (Fe^0, Pt^{II}). The generality of oxidative-addition reactions, of which these were early examples, is now well established [3], and they have proved useful both in elegant organic syntheses [4], as well as in an industrial process for converting methanol into acetic acid [5].

Following our researches with $Fe(CO)_5$ which gave the fluorocarbon iron carbonyl compounds, we predicted [6] the similarity to be expected in the reactivity patterns of $Fe(CO)_5$ $[Fe^0, d^8]$ and $[Co(\eta\text{-}C_5H_5)(CO)_2]$ $[Co^I, d^8]$, leading us to discover [6-8] several cobalt complexes analogous to known organoiron compounds. It was a logical extension of our ideas then developing at Harvard to consider whether zerovalent compounds of metals of the nickel triad might also oxidatively insert into carbon—halogen bonds and form complexes with unsaturated fluorocarbons, in a manner related to the results obtained with the d^8 species $Fe(CO)_5$ and $[Co(\eta\text{-}C_5H_5)(CO)_2]$. That carbon—metal bonds could form in this way* was quickly established in preliminary experiments [9]. However, an opportunity to develop a strategy for further syntheses based on d^{10} complexes of nickel, palladium and platinum as precursors for new organo derivatives of these metals was delayed by a change in the venue of the research from Massachusetts to England, which necessitated the establishment of an entirely new group and the re-acquisition of the necessary equipment.

Zerovalent compounds of nickel, palladium and platinum

Although tetracarbonyl nickel was reported [10] in 1890 some fifty years elapsed before chemists [11] came to realise that a metal could be in a zero oxidation state in some of its complex compounds. Even following acceptance of this idea, a decade passed before it was appreciated that such complexes could exist in large numbers, and that they were especially reactive. In the opinion of the writer the main stimulus for the ever widening research activity in this area in recent times came from discovery in the period 1950-1960 of the compounds $[Ni(PhNC)_4]$ (Hieber [12], 1950), $[Ni(PF_3)_4]$ (Wilkinson [13], 1951), $[Cr(C_6H_6)_2]$ (Fischer [14], 1955), $[Pd(PhNC)_2]$ (Malatesta [15], 1955), $[Pt(PPh_3)_3]$ (Malatesta [16], 1957), and $[Ni(COD)_2$**] (Wilke [17], 1960).

The chemical significance of Malatesta's*** platinum and palladium complexes $[M(PPh_3)_n]$ ($M = Pd, Pt$; $n = 3$ or 4), particularly in regard to their potential as precursors in inorganic synthesis, was not at first appreciated. This was due in part to an interesting coincidence. At the time of the early work on $[Pt(PPh_3)_n]$, Chatt and his coworkers [18] described the hydride $[Pt(H)(Cl)(PEt_3)_2]$. This result, together with the earlier discovery [19] of $[Re(H)(\eta\text{-}C_5H_5)_2]$, prompted an enormous interest in transition metal hydrides, so the question naturally arose as to whether Malatesta's compounds should also be formulated as hydrido species. However, a reinvestigation [20], coupled with the discovery of $[Pt(diphos)_2]$ [21] and of $[Pt\{P(p\text{-}FC_6H_4)_3\}]$ [22], placed this class of zerovalent platinum and palladium complex on a very firm basis at about the time when the author became established at Bristol, and following the preliminary study [9] of the oxidative-addition chemistry of $[Ni(diphos)(CO)_2]$.

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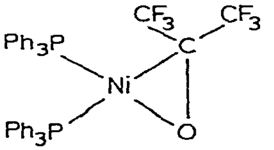
* In their classic paper on alkyls and aryls of transition metals, Chatt and Shaw [2] had reported that a d^{10} complex $[Pt(PPh_3)_3]$ would oxidatively add methyl iodide.

** Throughout this article the ligand cycloocta-1,5-diene (C_8H_{12}) will be represented by COD.

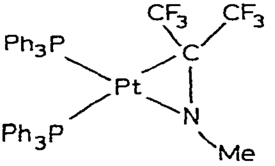
*** Readers are referred to the recent monograph by L. Malatesta and S. Cenini [87] for a review of these compounds.

Not surprisingly the zero-valent compounds [$M(PPh_3)_4$] and [$M(diphos)_2$] (M = Pd, Pt) readily afforded [23] M^{II} species, e.g. [$Pt(C_2F_5)(I)(PPh_3)_2$] and [$Pd(CF_3)(I)(diphos)$], on treatment with perfluoroalkyl iodides. More significantly, fluoroolefins [24] and hexafluoroacetone [25] formed very stable adducts [Pt(fluoroolefin)L_2] and [Pt{$(CF_3)_2CO$}L_2] (L = PPh_3, PPh_2Me) with the tetrakis(tertiary phosphine)platinum complexes. This was in marked contrast to the labile species [Pt(olefin)$(PPh_3)_2$] from which the olefins (ethylene, *trans*-stilbene, etc.) are easily displaced by other ligands [26, 27]. Moreover, ^{19}F NMR studies on the fluorocarbon adducts revealed a rigid attachment of these ligands to the metal with coupling constants as expected for extensive back-bonding [28].

The initial work [24, 25] pointed the way to the isolation of many "three-membered ring"* adducts involving several different kinds of fluorinated ligand (e.g. $(CF_3)_2C{=}NR$ (R = H, Me) [29-31], $(CF_3)_2C{=}S$ [32], $(CF_3)_2C{=}C{=}S$ [33], $(CF_3)_6C_6$ [34], $(CF_3)_2C{=}N{-}N{=}C(CF_3)_2$ [35], $(CF_3)_2C{=}C(CN)_2$ [30, 31, 36], and $CF_2{=}CFCF{=}CF_2$ [37]) coordinated not only to platinum but to nickel and palladium as well. X-ray crystallographic studies [38] were carried out on I-VIII** to underpin the synthetic work since in several instances the complexes had no structural precedent, e.g. the "side-ways on" bonding of hexafluoroacetone in I or the 1,2-η bonding mode of hexakis(trifluoromethyl)benzene*** in IV.



(I)



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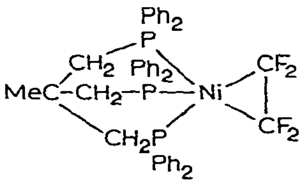

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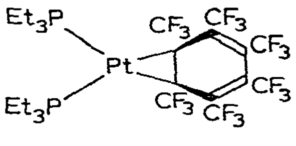

(IV)

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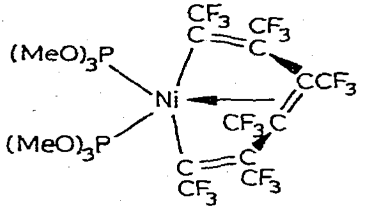
* The term "three-membered ring" is used to imply that in valence bond formalism the metal is in the 2+ oxidation state with a consequential rehybridization of the metal-bonded carbon (or nitrogen) atoms from sp^2 to sp^3. However, this is an extreme and no doubt incorrect view since in each fluorocarbon complex the balance between σ and π bonding will vary, depending on the metal and on the ligands involved. Nevertheless, we prefer to formulate some of the 1/1 adducts as metallocycles since this is in accord with certain spectroscopic properties, and emphasizes their relationship with the five-membered ring metallocycles into which they may often be converted.

** I am indebted to Professor Penfold and his co-workers for establishing the molecular structures of these key compounds, especially those (e.g. II and IV) exhibiting fluxional behaviour in solution. An isomer of VIII, containing a five-membered ring $\overline{Pt{-}CF_2CF{=}CFCF_2}$, was also identified by X-ray crystallography.

*** This ligand reacts with certain other Pt^0 complexes with cleavage of a C—C bond of the C_6 ring [89].



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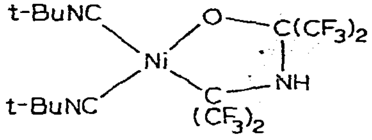

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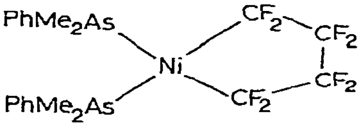

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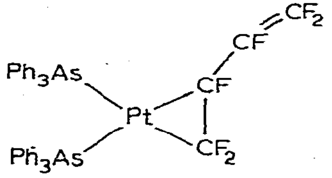

(VIII)

Some of the three-membered ring compounds were found to react with a second molecule of substrate to give five-membered metallocycles, for example VI forms on treating [$\overline{Ni—C(CF_3)_2O}(CNBu\text{-}t)_2$] with $(CF_3)_2C{=}NH$. In other cases, a five-membered metallocycle formed immediately on treating the zerovalent metal complex with the substrate without isolation of the one-to-one adduct. For example VII formed on reaction of [$Ni(AsPhMe_2)_4$] with $CF_2{=}CF_2$.

Observations such as these prompted a detailed study of the factors influencing activation of the organofluorine substrate by the metals; the principles developed [28] are of general application in the field of oxidative-coupling [39] involving non-fluorinated [40] species. Thus experiments were specifically designed to establish the importance of a vacant coordination site on the reactivity of the metal atom. For example, whereas [$Ni(C_2F_4)(PPh_3)_2$] reacts rapidly with C_2F_4 to give [$\overline{Ni—CF_2CF_2CF_2CF_2}(PPh_3)_2$] [41], the complex [$Ni(C_2F_4)$-$\{MeC(CH_2PPh_2)_3\}$] (III), having a tripodal ligand with bulky substituents, does not react with the fluoroolefin [42]. Other experiments were undertaken to establish the electronic and steric effects of the various donor ligands, and of the electrophilic substrates with which the metals react. Generally ligands with relatively good donor power increase the reactivity of the metal towards a second molecule of substrate. Thus bis(1-5-cyclooctadiene)nickel even with excess of hexafluoroacetone affords [$Ni\{C(CF_3)_2O\}(COD)$] [32]. The remaining cyclooctadiene ligand may be displaced with t-butyl isocyanide to give [$Ni\{C(CF_3)_2O\}(t\text{-}BuNC)_2$] [36]. The latter complex then proved very reactive towards hexafluoroacetone giving [$\overline{Ni—C(CF_3)_2—O—C(CF_3)_2—O}(t\text{-}BuNC)_2$]. Evidently substitution of t-BuNC for COD enhances the reactivity of the nickel. This is in contrast to [$Ni\{(CF_3)_2CO\}(PhNC)_2$] which is inert to more $(CF_3)_2CO$. Many other instances of similar behaviour were found. With palladium, for example, [$Pd\{(CF_3)_2CO\}$(diphos)] reacts with hexafluoroacetone with ring expansion, whereas the compound [$Pd\{(CF_3)_2CO\}\{P(OPh)_3\}_2$] does not [43]. However, the complex [$Pd\{P(OMe)_3\}_4$], with the relatively strong π-acceptor ligands $P(OMe)_3$, readily activates two molecules of $(CF_3)_2CO$ showing that steric effects and/or ligand dissociation are as important as is enhancement of the nucleophilicity of the metal by attachment of donor ligands*.

For research designed to ascertain the role of the ligands on the reactivity of the metal it became necessary to prepare many hitherto unknown d^{10} complexes of nickel, palladium and platinum, and to synthesize others (e.g. $[Ni(C_2H_4)(PPh_3)_2]$) [46] which had been mentioned [47] in the literature but for which no details had been given at the time of our work. In 1966 Wilke et al. [17] had reported that the cyclooctadiene ligands in $[Ni(COD)_2]$ could be displaced by triphenylphosphine to give $[Ni(PPh_3)_4]$. This led Cundy [32, 48, 49] to develop high yield syntheses of the species $[NiL_4]$ [L = PEt_3, PPh_2Me, $P(OMe)_3$], $[Ni(COD)(P\text{-}n\text{-}Bu_3)_2]$, [Ni(COD)(diphos)] and $[Ni(diphos)(P\text{-}n\text{-}Bu_3)_2]$ by displacement of cyclooctadiene from $[Ni(COD)_2]$. This route was subsequently employed to obtain $[Ni(PPh_2CH_2)_3CMe]$ [42], and used by others [50, 51] to obtain $[NiL_4]$ (L = PMe_3, PEt_3). The arsine complexes $[Ni(AsMe_2Ph)_4]$ and $[Ni(diars)_2]$ were similarly prepared from $[Ni(COD)_2]$ [52]. Several new zerovalent palladium and platinum complexes were also prepared at Bristol in the initial stages of the research including $[Pd(PMePh_2)_4]$ [53]**, $[Pt(PMePh_2)_4]$ [25], $[Pt(diars)_2]$ and $[Pt(PPhMe_2)_4]$ [54]. The latter complex was independently described by Clark and Itoh [55]. Subsequently, more reactive zerovalent palladium and platinum complexes were synthesized, and these are mentioned in a later section of this article.

Complexes with metal—metal bonds

Ten years ago there was considerable interest in transition metal complexes which contained covalent metal—metal bonds and a very important paper [56] focussed attention and stimulated research in this area. Today this field continues to maintain considerable momentum, particularly with respect to metal cluster compounds [57]. One of the early examples of a complex with a bond between two dissimilar metal atoms was $[FeMn(CO)_7(\eta\text{-}C_5H_5)]$ prepared at Harvard in 1960 [58]. The proposed structure was subsequently confirmed [59] by X-ray crystallography.

In 1968 the heteronuclear carbonyls $[Fe_2Ru(CO)_{12}]$ and $[FeRu_2(CO)_{12}]$ were discovered [60], raising the question as to whether related triangular clusters might exist. The suggestion by Russian chemists [61] that there was a parallel between the chemical behaviour of carbenes*** and the d^{10} species $[PtL_2]$, formed by dissociation of the tetrakis derivatives, led us to expect that zerovalent platinum compounds would insert into the metal—metal bonds of carbonyls of the iron triad. In this way the metal clusters shown in Fig. 1 came to be isolated [63].

Use of zerovalent platinum complexes in syntheses designed to obtain new

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* In parallel studies with d^8 complexes others noted the effect on reactivity of changing ligands. Thus Chatt and Butter [44] showed that substitution of $Me_2PCH_2CH_2PMe_2$ for $Ph_2PCH_2CH_2PPh_2$ increased the reactivity of Rh^I, while Collman and Sears [45] established that $[IrCl(CO)(PMe_2Ph)_2]$ would react with methyl chloride whereas $[IrCl(CO)(PPh_3)_2]$ would not.

** A recent paper [88] describes the synthesis of several complexes $[PdL_n]$ ($n = 2, 3, 4$).

*** Halpern [62] drew attention to the reactivity pattern of d^8 complexes such as $[IrCl(CO)(PPh_3)_2]$ in relation to their being inorganic analogues of the carbenes.

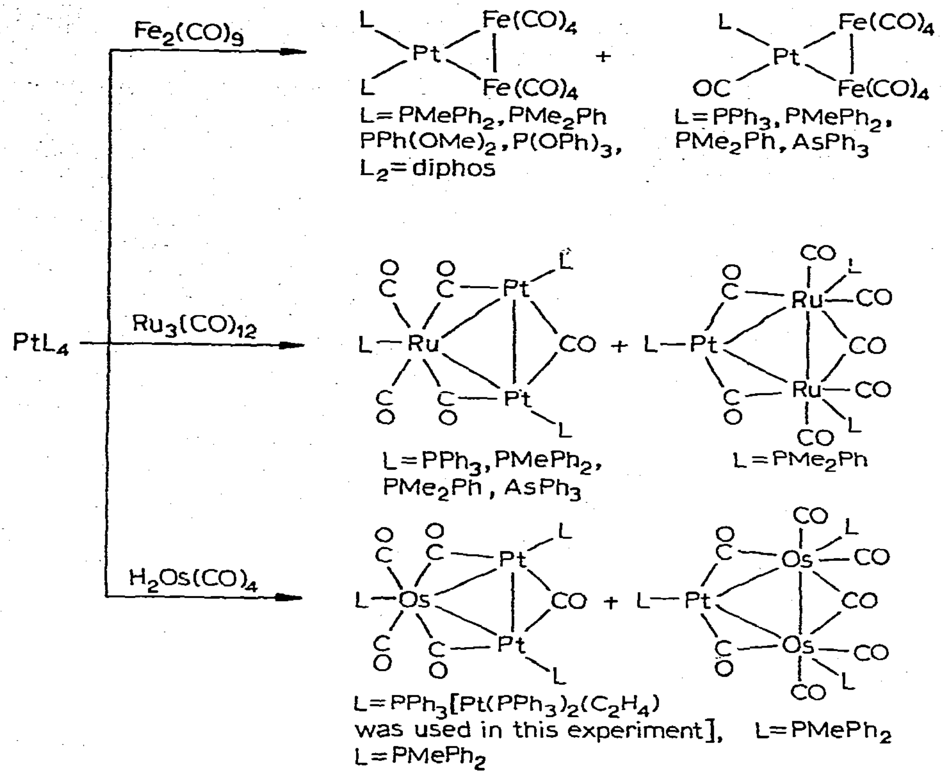
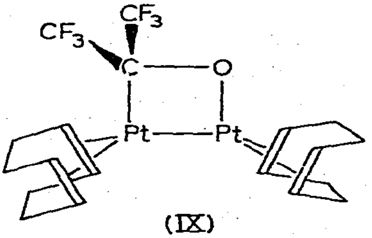


Fig. 1. Synthesis of heteronuclear metal carbonyls.

cluster compounds proved especially profitable when applied to polyhedral boron chemistry, as described in the next section. However, such is the propensity for the Sub-group VIII metals to form metal—metal bonds that even our work



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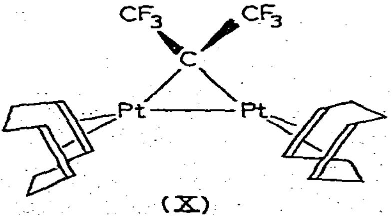

(X)

with fluorocarbons has produced species like IX and X [64], the molecular structure of the former being established by X-ray crystallography. Compound X forms by attack of bis(cyclooctadiene)platinum on perfluoropropene.

Metalloborane chemistry

The ability of boron to bond with itself was first recognised by Alfred Stock at the beginning of this century, but the structures of the hydrides he discovered, e.g. $B_{10}H_{14}$, were not known for many years [65]. A very significant development in this field occurred in 1963 with the isolation [66, 67] of species with icosahedral structures in which the twelve vertices of the icosahedra comprised two carbon and ten boron atoms. These "carboranes" were subsequently shown by Hawthorne and his coworkers [68] to form a variety of metallo derivatives. The synthetic method involved removal of a boron atom from the structure and its replacement by a transition metal ion. In this manner a new dimension was added to organometallic chemistry with the discovery of polyhedral structures of great novelty.

An alternative method of synthesizing metallocarboranes, also developed by Hawthorne and his co-workers [69], depends on reduction with sodium and naphthalene of the *closo*-carborane cages with their consequent opening to create a vacant site into which a metal ion can then be inserted. This procedure may be represented by:

$$C_2B_nH_{n+2} \xrightarrow{+2e^-} [C_2B_nH_{n+2}]^{2-} \xrightarrow[\text{(ii) Oxidation}]{\text{(i) Co}^{\text{II}}\text{, NaC}_5\text{H}_5} [\eta\text{-}C_5H_5CoC_2B_nH_{n+2}]$$

Our experience with the more nucleophilic of the zerovalent derivatives of nickel, palladium and platinum prompted the idea [70] that such species might insert directly into a *closo*-carborane polyhedron in a concerted process. Such reactions, if they occurred, would formally involve a net transfer of electrons from the metal to the cage, representing an interesting new aspect of oxidative-addition chemistry:

$M^0 + C_2B_nH_{n+2}$	$\rightarrow$	$[M^{II}C_2B_nH_{n+2}]$
Polyhedron with $(2 + n)$ vertices		Polyhedron with $(3 + n)$ vertices

M = Ni, Pd or Pt; with suitable ligands (R_3P, C_8H_{12}, RNC, etc.).

This concept was put to the experimental test by Dr. John Spencer who thereby discovered many new complexes*. In this research it was imperative for the synthetic work to be supported by single crystal X-ray crystallographic studies. These have been carried out by Dr. Alan Welch who thereby established several molecular structures which were not only different from those expected from the known chemical behaviour of the carboranes towards nucleophiles, but were without precedent in metallocarborane chemistry.

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* Direct insertion of metal atoms from element vapours into the polyhedra should also be possible.

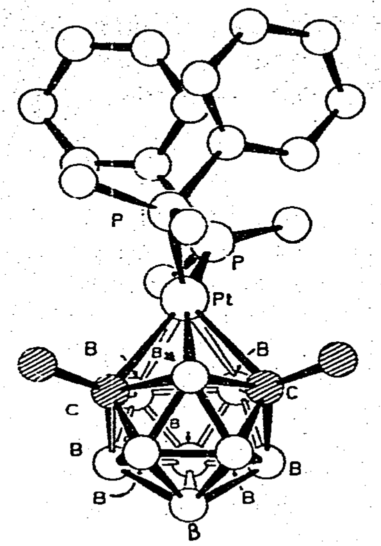

Fig. 2. The molecule 1,1-(PhMe$_2$P)$_2$-2,4-Me$_2$-1,2,4-PtC$_2$B$_9$H$_9$.

Reaction of [Pt(PEt$_3$)$_3$], [Pt(PMe$_3$)$_2$(*trans*-stilbene)], [Pt(PMe$_2$Ph)$_4$], [Ni(1,5-COD)$_2$], [Ni(PEt$_3$)$_2$(1,5-COD)], or [Pd(CN-t-Bu)$_2$] with *closo*-2,3-Me$_2$-2,3-C$_2$B$_9$H$_9$ affords the *closo*-metallocarboranes [1,1-L$_2$-2,4-Me$_2$-1,2,4-MC$_2$B$_9$H$_9$] (M = Pt, L = PEt$_3$, PMe$_3$ or PMe$_2$Ph; M = Ni, L$_2$ = COD, L = PEt$_3$; M = Pd, L = t-BuNC) [71]. An X-ray crystallographic study of the product from [Pt(PMe$_2$Ph)$_4$] confirmed (Fig. 2) that the metal coordinates three boron and two carbon atoms to complete a *closo*-2,4-dicarba-icosahedron.

Following this successful polyhedral expansion of a *closo*-carborane with vertices comprising two carbon and nine boron atoms the question arose as to whether other eleven vertex polyhedra would behave similarly.

The complex [72] [*closo*-1-(η-C$_5$H$_5$)-1,2,4-CoC$_2$B$_8$H$_{10}$] is a metallocarborane analogue of 2,3-C$_2$B$_9$H$_{11}$. Reaction of this cobalt compound with [Pt(PEt$_3$)$_2$-(*trans*-stilbene)] leads to an insertion reaction to form the bi-metallic species

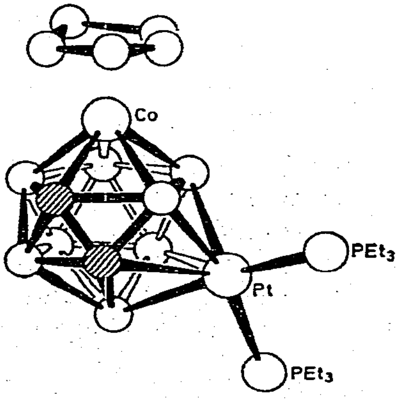

Fig. 3. The molecule 1-(η-C$_5$H$_5$)-8,8-(Et$_3$P)$_2$-1,2,7,8-CoC$_2$PtB$_8$H$_{10}$.

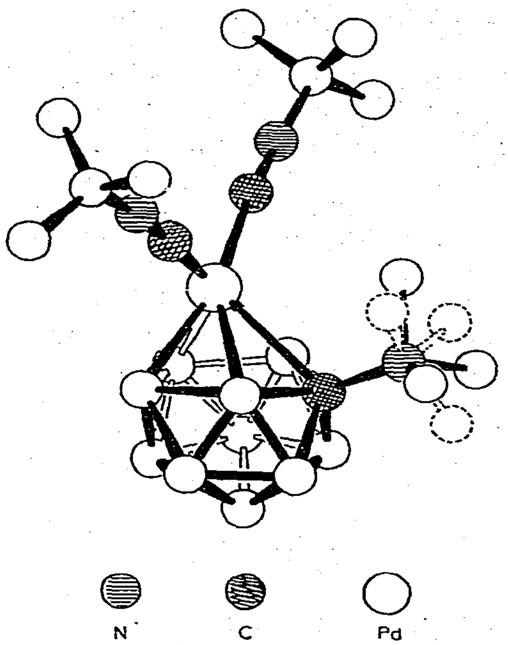

Fig. 4. The molecule 1,1-$(t\text{-BuNC})_2$-2-NMe_3-1,2-$PdCB_{10}H_{10}$.

shown in Fig. 3, with a distorted icosahedral structure. A further example of polyhedral expansion from an eleven to a twelve vertex structure is provided by reactions of the monocarbon carboranes $[CB_{10}H_{11}]^-$ and $[CB_{10}H_{10}NMe_3]$. Thus Dr. Carroll showed [73] that the latter species on treatment with $[Pd(CN\text{-}t\text{-}Bu)_2]$ afforded a complex the structure of which is shown in Fig. 4. It will be noted that Dr. Welch's structural study revealed disorder in the trimethylamine group, and more significantly that the palladium—boron bonds are shorter than the bond from the metal to the carbon atom, which at 2.600 Å is virtually non-bonding. It is therefore a formalism as to whether the structure is regarded as icosahedral or not.

Encouraged by the above results, a study has been initiated of reactions of

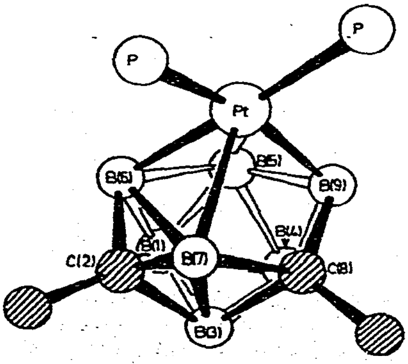

Fig. 5. The molecule $[Me_2C_2B_7H_7]Pt[PEt_3]_2$. Phosphino ethyl groups are omitted for clarity.

zerovalent platinum complexes with *closo*-carboranes having less than eleven vertices.

Treatment (room temperature) of [Pt(PEt$_3$)$_3$] with 1,6-Me$_2$-1,6-C$_2$B$_7$H$_7$ in light petroleum gives the complex shown in Fig. 5 in better than 90% yield [74]. The platinum coordinates boron atoms 5,6,7 and 9 to produce a *nido*- rather than a *closo*-10 atom polyhedron. The length of the diagonals of the open face [defined by Pt, B(7), C(8) and B(9)] do not constitute bonding interactions. It is interesting to note that in the geometry adopted, both cage carbon atoms occupy relatively low coordination positions.

Treatment of the eight vertex carborane *closo*-1,6-Me$_2$-1,6-C$_2$B$_6$H$_6$ with [Pt(*trans*-C$_6$H$_5$CH=CHC$_6$H$_5$)(PMe$_3$)$_2$] affords two isomeric complexes, *closo*-1,1-(Me$_3$P)$_2$-6,8-Me$_2$-1,6,8-PtC$_2$B$_6$H$_6$ and *nido*-6,6-(Me$_3$P)$_2$-5,8-Me$_2$-6,5,8-PtC$_2$B$_6$H$_6$ [74]. The *closo* structure is shown in Fig. 6, and within the concept of a metallocarborane as a transition metal complex containing a π-complexed carborane ligand, it is the first structurally authenticated example of a 1-4-η bonded boracyclobutadiene moiety*.

The ten atom *closo*-carborane 1,6-C$_2$B$_8$H$_{10}$ which has a bicapped square antiprism structure like B$_{10}$H$_{10}^{2-}$, reacts with [Pt(PMe$_3$)$_2$(C$_6$H$_5$CH=CHC$_6$H$_5$)] to give a binuclear platinum complex [C$_2$B$_8$H$_{10}${Pt(PMe$_3$)$_2$}$_2$] which at first, on the basis of its molecular composition, was thought to have an icosahedral structure. However, a single crystal X-ray crystallographic study revealed the novel molecular structure shown in Fig. 7 with an *exo*-polyhedral platinum atom linked to the cage by Pt—Pt and Pt—B bonds [78]. This structure is unique in metallo-

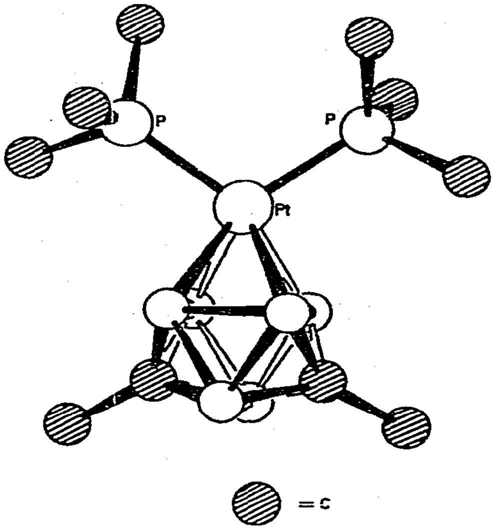

Fig. 6. The molecule *closo*-1,1-(Me$_3$P)$_2$-6,8-Me$_2$-1,6,8-PtC$_2$B$_6$H$_6$.

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* The recently reported [75] tricarbonyliron complex [Fe(B$_4$H$_8$)(CO)$_3$] must also have a structure in which the metal atom is bonded to four boron atoms, thereby being an analogue of tricarbonyl-(cyclobutadiene)iron. Other complexes in which it has been proposed that there is a 1,4-η bonded bora-ligand group include [(η-C$_5$H$_5$)CoB$_4$H$_8$] [76], one of the two isomers [(η-C$_5$H$_5$)Co(B$_7$CH$_8$)-Ni(η-C$_5$H$_5$)] [77a], and [(η-C$_5$H$_5$)Ni(B$_8$CH$_9$)] [77b].

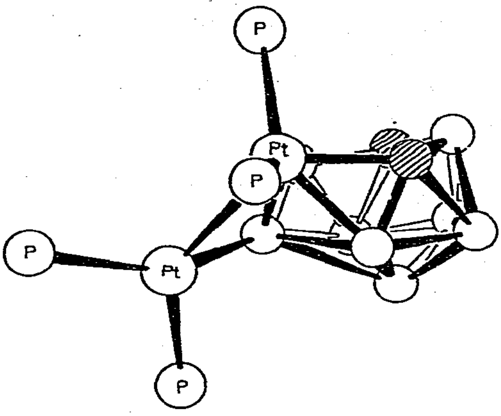

Fig. 7. The molecule $(Me_3P)_4Pt_2C_2B_8H_{10}$. Phosphino methyl groups omitted for clarity.

carborane chemistry. The $[Pt(PMe_3)_2]$ group outside the cage system may be removed under mild conditions to produce $[C_2B_8H_{10}\{Pt(PMe_3)_2\}]$ (Fig. 8).

The results described in this section indicate that d^{10} complexes, particularly those of platinum, are capable of reacting with polyhedral boron compounds to give new cluster complexes with unusual structures. Moreover, these preliminary studies have revealed that there is a tendency for the products to have *nido*-structures when simple considerations would lead at least in some instances to the expectation that *closo*-structures would be formed. Furthermore, the research has shown that the metal has a marked preference to bond to boron atoms rather than to carbon. Clearly much further work remains to be done and it is possible that direct oxidative-insertion syntheses can be extended to other electron deficient polyhedral systems.

Reference was made earlier to our synthesis of several zerovalent nickel, palladium and platinum complexes more reactive than the classic species $[M(PPh_3)_4]$. The metallocarborane complexes described in this section necessitated the development of syntheses of $[Pt(PEt_3)_3]$ [70, 74], $[Pt(PMe_3)_2($*trans*-$C_6H_5CH{=}CHC_6H_5)]$ [71], and $[Pt(PEt_3)_2($*trans*-$C_6H_5CH{=}CHC_6H_5)]$ [34], and more recently of $[Pt(COD)_2]$, and $[Pt(PEt_3)_2(PhCH{=}CH_2)]$ [79]. The complex $[Pt(PEt_3)_3]$ was first reported by Muetterties et al. [80] who obtained it from $[Pt(PEt_3)_4]$, the latter being prepared from $[Pt(B_3H_7)(PEt_3)_2]$. Our method of

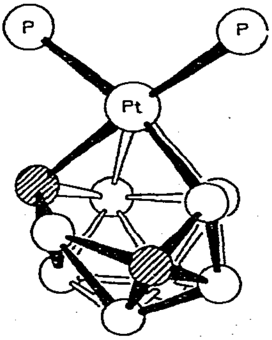

Fig. 8. The molecule $(Me_3P)_2Pt(C_2B_8H_{10})$.

synthesis was essentially the same as that later described by Pearson et al. [81] in which K_2PtCl_4 is treated with triethylphosphine and potassium hydroxide in ethanol. The complex bis(1,5-cyclooctadiene)platinum has also been reported [82], previously being prepared by UV irradiation of [Pt-i-Pr_2(COD)] in the presence of cyclooctadiene. However, in our hands variable yields were obtained in this two step (from [$PtCl_2$(COD)]) synthesis; and this led Dr. Spencer to devise a new method of preparation which is likely to have important consequences in the development of zerovalent platinum chemistry.

Organometallic compounds where only C=C double bonds coordinate to a transition metal

The work of Wilke and his co-workers [83] has produced a remarkable number of novel organometallic compounds, especially complexes of nickel, in which only olefin-like molecules are coordinated to the metal atom. These include, for example, 1,5,9-cyclododecatriene-, bis(1,5-cyclooctadiene)-, tris(norbornene)-, and tris(ethylene)nickel. These compounds are useful precursors in organonickel chemistry, the lability of the ligands often giving rise to catalytic behaviour. The development of related platinum chemistry has hitherto been inhibited by the absence of convenient synthetic routes to labile olefin-substituted Pt^0 complexes. This difficulty has now been overcome by Spencer's synthesis of [$Pt(COD)_2$], [$Pt(C_2H_4)_3$] and [$Pt(C_7H_{10})_3$]*, with indications of the existence of many similar complexes.

As mentioned earlier, [$Pt(COD)_2$] has been previously prepared [82]. The new [84] synthesis involves treating [$PtCl_2$(COD)] with $Li_2C_8H_8$ or certain other reducing agents in diethyl ether in the presence of 1,5-cyclooctadiene. Bis(1,5-cyclooctadiene)platinum undergoes a number of interesting reactions. Bulky tertiary phosphines afford the 14-electron complexes [$Pt(PR_3)_2$], unsaturated fluorocarbons give species like IX and X, while isocyanides yield [$Pt(RNC)_2$]. Here again X-ray crystallographic studies are of paramount importance. For example, Dr. Judith Howard found that bis(t-butylisocyanide)platinum was tri-

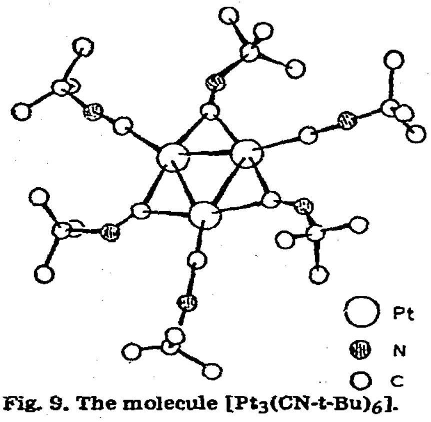

Fig. 9. The molecule [$Pt_3(CN\text{-}t\text{-}Bu)_6$].

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* C_7H_{10} = norbornene. The palladium analogue has also been prepared by Dr. Spencer [90].

meric with an equilateral triangle of platinum atoms and bridging and terminal isocyanide ligands (Fig. 9). This complex forms a number of novel products with acetylenes.

Ethylene reacts with [Pt(COD)$_2$] under mild conditions (room temperature, 1 atm) to give volatile white crystalline [Pt(C$_2$H$_4$)$_3$]. Although markedly more stable than its nickel analogue (dec. >0°) [85], tris(ethylene)platinum decomposes at ambient temperatures unless maintained in an ethylene atmosphere. Its solution will deposit platinum metal under certain conditions, but it is also an important intermediate for further research now underway. With tetrafluoroethylene, for example, the "mixed" olefin complex [Pt(C$_2$H$_4$)$_2$(C$_2$F$_4$)] is formed which is more robust than the parent compound. An X-ray crystallographic study by Dr. Howard has shown a planar geometry [90]. This result is of special significance in view of Rösch and Hoffmann's [86] recent prediction that molecules [M(CH$_2$=CH$_2$)$_3$] will have a trigonal-planar structure and that this geometry is even more likely if an ethylene ligand is substituted by a better π-acceptor. The tetrafluoroethylene complex provides experimental confirmation of this idea.

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References

1 T.A. Manuel, S.L. Stafford and F.G.A. Stone, J. Amer. Chem. Soc., 83 (1961) 249.
2 J. Chatt and B.L. Shaw, J. Chem. Soc., (1959) 705, 4020.
3 J.P. Collman and W.R. Roper, J. Amer. Chem. Soc., 87 (1965) 4008; Advan. Organometal. Chem., 7 (1968) 53.
4 E.J. Corey and M.F. Semmelhack, J. Amer. Chem. Soc., 89 (1967) 2755, 3911.
5 J.F. Roth, J.H. Craddock, A. Hershman and F.E. Paulik, Chem. Tech., (1971) 600.
6 R.B. King, P.M. Treichel and F.G.A. Stone, J. Amer. Chem. Soc., 83 (1961) 3593.
7 R.B. King, P.M. Treichel and F.G.A. Stone, J. Amer. Chem. Soc., 83 (1961) 3600.
8 T.D. Coyle, R.B. King, E. Pitcher, S.L. Stafford, P.M. Treichel and F.G.A. Stone, J. Inorg. Nucl. Chem., 20 (1961) 172.
9 (a) D.W. McBride, S.L. Stafford and F.G.A. Stone, J. Chem. Soc., (1963) 723; (b) J.R. Phillips, Ph.D. Thesis, Harvard University 1962.
10 L. Mond, C. Langer and F. Quincke, J. Chem. Soc., (1890) 749.
11 L. Malatesta, Endeavour, 28 (1969) 30.
12 W. Hieber and E. Böckly, Z. Anorg. Chem., 262 (1950) 344.
13 G. Wilkinson, J. Amer. Chem. Soc., 73 (1951) 5501.
14 E.O. Fischer and W. Hafner, Z. Naturforsch, B, 10 (1955) 655; Z. Anorg. Chem., 286 (1956) 146.
15 L. Malatesta, J. Chem. Soc., (1955) 3924.
16 L. Malatesta and C. Cariello, J. Chem. Soc., (1958) 2323; J. Inorg. Nucl. Chem., 8 (1958) 561.
17 G. Wilke, Angew. Chem., 72 (1960) 581; B. Bogdanović, M. Kröner and G. Wilke, Liebigs Ann. Chem., 699 (1966) 1.
18 J. Chatt, L.A. Duncanson and B.L. Shaw, Proc. Chem. Soc., (1957) 343.
19 G. Wilkinson and J.M. Birmingham, J. Amer. Chem. Soc., 77 (1955) 3421.
20 L. Malatesta and R. Ugo, J. Chem. Soc., (1963) 2080.
21 J. Chatt and G.A. Rowe, Nature, 191 (1961) 1191.
22 A.D. Allen and C.D. Cook, Proc. Chem. Soc., (1962) 218.
23 D.A. Harbourne, D.T. Rosevear and F.G.A. Stone, Inorg. Nucl. Chem. Letters, 2 (1966) 247; D.T. Rosevear and F.G.A. Stone, J. Chem. Soc. (A), (1968) 164.
24 M. Green, R.B.L. Osborn, A.J. Rest and F.G.A. Stone, Chem. Commun., (1966) 502; J. Chem. Soc. (A), (1968) 2525.

25 B. Clarke, M. Green, R.B.L. Osborn and F.G.A. Stone, J. Chem. Soc. (A), (1968) 167.
26 C.D. Cook and G.S. Jauhal, J. Amer. Chem. Soc., 90 (1968) 1464; Inorg. Nucl. Chem. Letters, 3 (1967) 31.
27 J. Chatt, B.L. Shaw and A.A. Williams, J. Chem. Soc., (1962) 3269.
28 F.G.A. Stone, Pure and Applied Chem., 30 (1972) 551; and ref. cited therein.
29 J. Ashley-Smith, M. Green and F.G.A. Stone, J. Chem. Soc. (A), (1970) 3161.
30 H.D. Empsall, M. Green, S.K. Shakshooki and F.G.A. Stone, J. Chem. Soc. (A), (1971) 3472.
31 J. Browning, H.D. Empsall, M. Green and F.G.A. Stone, J. Chem. Soc. Dalton, (1973) 381.
32 J. Browning, C.S. Cundy, M. Green and F.G.A. Stone, J. Chem. Soc. (A), (1969) 20.
33 M. Green, R.B.L. Osborn and F.G.A. Stone, J. Chem. Soc. (A), (1970) 944.
34 J. Browning, M. Green, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. (Dalton), (1974) 97.
35 J. Clemens, M. Green and F.G.A. Stone, J.C.S. (Dalton), (1973) 1620; J. Clemens, R.E. Davis, M. Green, J.D. Oliver and F.G.A. Stone, Chem. Commun., (1971) 1095.
36 M. Green, S.K. Shakshooki and F.G.A. Stone, J. Chem. Soc. (A), (1971) 2828.
37 P.K. Maples, M. Green and F.G.A. Stone, J. Chem. Soc. Dalton, (1974) 1194.
38 R. Countryman and B.R. Penfold, J. Cryst. Mol. Struct., 2 (1972) 281; Chem. Commun., (1971) 1598; J. Browning and B.R. Penfold, J. Cryst. Mol. Struct., 4 (1974) 335, 347; Chem. Commun., (1973) 31, 198; B.R. Penfold, K.K. Chan, R.G. Holloway and T.J. McLennan, private communication.
39 C.A. Tolman, Chem. Soc. Revs., 1 (1972) 337.
40 R.F. Heck, Organotransition Metal Chemistry—A Mechanistic Approach, Academic Press N.Y., 1974, Chapter 8.
41 A. Greco, M. Green, S.K. Shakshooki and F.G.A. Stone, Chem. Commun., (1970) 1375.
42 P.K. Maples, M. Green and F.G.A. Stone, J. Chem. Soc. Dalton, (1973) 388.
43 H.D. Empsall, M. Green and F.G.A. Stone, J. Chem. Soc. (A), (1972) 96.
44 J. Chatt and S.A. Butter, Chem. Commun., (1967) 501.
45 J.P. Collman and C.T. Sears, Inorg. Chem., 7 (1968) 27.
46 J. Ashley-Smith, M. Green and F.G.A. Stone, J. Chem. Soc. (A), (1969) 3019.
47 G. Wilke and G. Hermann, Angew. Chem. Intern. Edn., 1 (1962) 549.
48 C.S. Cundy, M. Green and F.G.A. Stone, J. Chem. Soc. (A), (1970) 1647.
49 C.S. Cundy, J. Organometal. Chem., 69 (1974) 305.
50 C.A. Tolman, D.H. Gerlach, J.P. Jesson and R.A. Schunn, J. Organometal. Chem., 65 (1974) C23.
51 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2956.
52 J. Browning, M. Green and F.G.A. Stone, J. Chem. Soc. (A), (1971) 453.
53 M. Green, A.J. Mukhedkar and F.G.A. Stone, J. Chem. Soc. (A), (1969) 3023.
54 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc. Dalton, (1972) 1082; Chem. Commun., (1971) 1288.
55 H.C. Clark and K. Itoh, Inorg. Chem., 10 (1971) 1707.
56 C.E. Coffey, J. Lewis and R.S. Nyholm, J. Chem. Soc., (1964) 1741.
57 J.D. Cotton, Chemical Society Specialist Periodical Reports, Organometallic Chemistry, Vol. 1, pp. 194-227; N.G. Connelly, ibid., Vol. II, pp. 234-272; N.G. Connelly, ibid., Vol. III, pp. 180-209.
58 R.B. King, P.M. Treichel and F.G.A. Stone, Chem. Ind., (1961) 747.
59 P.J. Hansen and R.J. Jacobson, J. Organometal. Chem., 6 (1966) 389.
60 D.B.W. Yawney and F.G.A. Stone, Chem. Commun., (1968) 619; J. Chem. Soc. (A), (1969) 502.
61 O.M. Nefedov and M.N. Manakov, Angew. Chem. Intern. Edn., 5 (1966) 1037.
62 J. Halpern, Chem. Eng. News, 44, No. 45 (1966) 68; Advan. Chem. Series, 70 (1968) 1.
63 M.I. Bruce, G. Shaw and F.G.A. Stone, Chem. Commun., (1971) 1288; J. Chem. Soc. Dalton, (1972) 1082, 1782; V.G. Albano, G. Ciani, M.I. Bruce, G. Shaw and F.G.A. Stone, J. Organometal. Chem., 42 (1972) C99.
64 M. Green, J.A.K. Howard, A. Laguna, M. Murray, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1975) 451.
65 W.N. Lipscomb, Boron Hydrides, Benjamin, New York, 1963.
66 T.J. Heying, J.W. Ager, S.L. Clark, D.J. Mangold, H.C. Goldstein, M. Hillman, R.J. Polak and J.W. Szymanski, Inorg. Chem., 2 (1963) 1089.
67 M.M. Fein, J. Bobinski, N. Mayes, N. Schwartz and M.S. Cohen, Inorg. Chem., 2 (1963) 1111.
68 M.F. Hawthorne, Accounts Chem. Res., 1 (1968) 281; Pure Applied Chem., 33 (1973) 475; M.F. Hawthrone and G.B. Dunks, Science, 178 (1972) 462.
69 M.J. Evans, G.B. Dunks and M.F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4565.
70 J.L. Spencer, M. Green and F.G.A. Stone, J. Chem. Soc. Chem. Commun., (1972) 1178.
71 M. Green, J.L. Spencer, F.G.A. Stone and A.J. Welch, J. Chem. Soc. Dalton, (1975) 179.
72 C.J. Jones, J.N. Francis and M.F. Hawthrone, J. Amer. Chem. Soc., 94 (1972) 8391.
73 W.E. Carroll, M. Green, F.G.A. Stone and A.J. Welch, J. Chem. Soc. Dalton, (1975) in press.
74 M. Green, J.L. Spencer, F.G.A. Sone and A.J. Welch, J. Chem. Soc. Chem. Commun., (1974) 571, 794.

75 N.N. Greenwood, C.G. Savory, R.N. Grimes, L.G. Sneddon, A. Davison and S.S. Wreford, J. Chem. Soc. Chem. Commun., (1974) 718.

76 V.R. Miller and R.N. Grimes, J. Amer. Chem. Soc., 95 (1973) 5078.

77 (a) C.G. Salentine and M.F. Hawthorne, J. Chem. Soc. Chem. Commun., (1973) 560; (b) C.G. Salentine, R.R. Rietz and M.F. Hawthorne, Inorg. Chem., 13 (1974) 3025.

78 M. Green, J.L. Spencer, F.G.A. Stone and A.J. Welch, to be published.

79 J.L. Spencer, to be published.

80 D.H. Gerlach, A.R. Kane, G.W. Parshall, J.P. Jesson and E.L. Muetterties, J. Amer. Chem. Soc., 93 (1971) 3543.

81 R.G. Pearson, W. Louw and J. Rajaram, Inorg. Chim. Acta, 9 (1974) 251.

82 J. Müller and P. Göser, Angew. Chem. Intern. Edn., 6 (1967) 364.

83 P.W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol. 1, Academic Press, New York, 1974.

84 M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Chem. Commun., (1975) 3.

85 K. Fischer, K. Jonas and G. Wilke, Angew. Chem. Internat. Edn., 12 (1973) 565.

86 N. Rösch and R. Hoffmann, Inorg. Chem., 13 (1974) 2656.

87 L. Malatesta and S. Cenini, Zerovalent compounds of metals, Academic Press, New York, 1974.

88 W. Kuran and A. Musco, Inorg. Chim. Acta, 12 (1975) 187.

89 M. Green, A. Laguna, L. Smart, T.L. Spencer and F.G.A. Stone, to be published.

90 M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1975). 449.