Coordination Chemistry Reviews, 55 (1984) 151–204
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PLATINUM CARBONYLS AND THEIR USE IN HOMOGENEOUS CATALYSIS

HOWARD C. CLARK and VIMAL K. JAIN

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1 (Canada)

(Received 21 July 1983)

CONTENTS

ABBREVIATIONS

Bz	Benzyl
Bipy	2,2′-Bipyridyl
diars	1,2-Bis(diphenylarsino)ethane
dpam	Bis(diphenylarsino)methane
dppe	1,2-Bis(diphenylphosphino)ethane
dppm	Bis(diphenylphosphino)methane

0010-8545/84/$15.90

dppp	1,3-Bis(diphenylphosphino)propane
COD	1,5-Cyclooctadiene
c-Hx	Cyclohexyl
pdma	*o*-Phenylenebis(dimethylarsine)
TMBA	Trimethylbenzylammonium

A. INTRODUCTION

Metal carbonyl chemistry, which began in 1890 with the discovery of nickel tetracarbonyl by Mond, Langer and Quincke, quickly encompassed a large number of transition metal carbonyls. Further momentum came from the studies of Roelen et al. (ca. 1938) and Reppe et al. (ca. 1940) who applied cobalt and nickel carbonyls to organic syntheses, and at present metal carbonyls and their derivatives have numerous important applications as catalysts in synthetic processes [1–3].

In contrast to the stability and chemical importance of nickel tetracarbonyl, its platinum analogue, $Pt(CO)_4$, could only be prepared under matrix isolation conditions [4]. This is attributed to the preferential formation of Pt–Pt bonds, demonstrated by the isolation by Chatt and co-workers [5] of the polymeric carbonyl $[Pt(CO)_2]_4$. This, of course, confirmed very early work [6] which demonstrated that carbonyl derivatives of platinum could be formed; more recently, many other platinum carbonyl derivatives, mainly polynuclear, have been characterized to establish quite a broad field of chemistry.

In the first section of this article, the carbonyl compounds of platinum are described, and in the later section their applications as homogeneous catalysts in organic syntheses are summarized.

B. PREPARATIVE ROUTES TO SIMPLE PLATINUM CARBONYLS

Extensive studies have been made of platinum(II) carbonyl chemistry in recent years, and the following general preparative methods can be described.

(i) Direct method

Carbon monoxide reacts with $PtCl_2$ under pressure (40–120 atm) at 110°C yielding $[Pt(CO)_2Cl_2]$ and phosgene [7]. The analogous bromo and iodo complexes are prepared [8] by the reactions of H_2PtBr_6 or PtI_2 with CO at 180–210 atm. These are thermally unstable, monomeric compounds which readily lose carbon monoxide to generate halogen-bridged complexes [8].

$$2\,[Pt(CO)_2X_2] \rightarrow [Pt(CO)X_2]_2 + 2\,CO \qquad (1)$$

In turn, these latter species react further with neutral ligands to cleave the halogen bridge and give unstable products.

$$\begin{array}{l} [\mathrm{Pt(CO)X_2}]_2 \xrightarrow{2\,\mathrm{L}} 2[\mathrm{Pt(CO)LX_2}] \xrightarrow{2\,\mathrm{L}} 2[\mathrm{PtL_2(CO)X}]^+\mathrm{X}^- \\ \hspace{14em}\downarrow -2\,\mathrm{CO} \\ \hspace{13em} 2[\mathrm{PtL_2X_2}] \end{array} \qquad (2)$$

When L is *p*-toluidine or methyldiphenylarsine, the compounds $[PtL(CO)X_2]$ are stable at ambient conditions, but are temperature and moisture sensitive. When excess L is used, products of the type PtL_2X_2 are always obtained even at −30°C. Reaction of the starting dimers with limited amounts of PCl_3 or AsR_3 gives [9,10] the highly unstable $[PtL(CO)X_2]$.

(ii) Displacement of halide ion by CO

Carbon monoxide displaces a chloride ligand from *cis* or *trans*-$(PEt_3)_2PtCl_2$ in an acetone solution containing excess sodium perchlorate under ambient conditions, to give a cationic carbonyl complex [11,12]

$$\begin{matrix}\mathit{cis}\\ \mathit{trans}\end{matrix}\text{-}(\mathrm{PEt_3})_2\mathrm{PtCl_2} + \mathrm{CO} + \mathrm{NaClO_4}$$

$$\rightarrow \mathit{trans}\text{-}[(\mathrm{PEt_3})_2\mathrm{Pt(CO)Cl}]^+\mathrm{ClO_4^-} + \mathrm{NaCl} \qquad (3)$$

Similarly, $[(PPh_3)_2PtH(CO)]^+BPh_4^-$ is formed when a solution of *trans*-$[(PPh_3)_2PtHCl]$ containing sodium tetraphenylborate is treated [13] with carbon monoxide in the presence of silver nitrate which acts as a chloride abstracting reagent. Related types of cationic platinum(II) carbonyls have been similarly prepared by Clark and co-workers [14–17].

(iii) Cleavage of halogen bridged complexes

The chlorine bridge of $[Pt(CO)Cl_2]_2$ can be cleaved with hydrogen chloride to form [18] anionic compounds of the type $[Pt(CO)Cl_3]^-$. Carbon monoxide itself can cleave [18] the chloride bridge as in the following reaction [19–22]

$$[(\mathrm{PR_3})\mathrm{PtCl_2}]_2 + \mathrm{CO} \rightarrow \mathit{cis}\text{-}[(\mathrm{PR_3})\mathrm{Pt(CO)Cl_2}] \qquad (4)$$

The low temperature bridge cleavage of $[Pt(PR_3)Cl_2]_2$ with CO has been investigated using ^{31}P NMR spectroscopy and has been shown [21] to be reversible. Treatment of the halo-bridged complexes $[PtX_2L]_2$ (where $X = Cl$ or Br, $L = PR_3$ or AsR_3) with CO gives solutions of *trans*-$[PtX_2(CO)L]$ which readily lose carbon monoxide and isomerize to *cis* derivatives. Such *trans–cis* isomerizations are catalyzed by free CO, PR_3 or halide ions, which as nucleophiles catalyze the process even in the solid phase. Isomerization is also accelerated by visible or UV irradiation. Several mechanisms have been proposed [23,24], each involving loss of CO.

When carbon monoxide is passed through solutions of halogen-bridged platinum–olefin complexes in carbon tetrachloride, mixed complexes containing CO and olefins are formed [25].

(iv) Displacement of olefins by CO

Carbon monoxide can readily displace [26–28] olefins and acetylenes from platinum complexes

$$[\mathrm{Pt(C_2H_4)Cl_3}]^- + \mathrm{CO} \rightarrow [\mathrm{Pt(CO)Cl_3}]^- + \mathrm{C_2H_4} \qquad (5)$$

$$\begin{array}{ll} \textit{trans}\text{-}[\mathrm{Pt(C_2H_4)(RNH_2)Cl_2}] + \mathrm{CO} \rightarrow & \textit{trans}\text{-}[\mathrm{Pt(CO)(RNH_2)Cl_2}] + \mathrm{C_2H_4} \\ & \qquad \downarrow 120°\mathrm{C} \\ & \textit{cis}\text{-}[\mathrm{Pt(CO)(RNH_2)Cl_2}] \qquad (6) \end{array}$$

Carbon monoxide also replaces cyclo-octadiene (COD) from $R_2Pt(COD)$ ($R = CH_3$ or C_6H_5) to give [29] $(CO)_2PtR_2$, while RPt(COD)Cl complexes undergo carbonyl insertion to yield [PtCl(COR)COD]; $PtCl_2(COD)$ in the presence of one equivalent of phosphine (PEt_3, P^nBu_3, $PMePh_2$, PPh_3, $P(4\text{-}FC_6H_4)_3$, $P(c\text{-}Hx)_3$) reacts with CO to give [29] *cis*-[$PtCl_2(CO)L$]. When the insertion products [PtCl(COR)COD] are treated with monodentate bulky phosphines, the carbonyls [Pt(CO)Cl(R)L] are obtained; with chelating phosphines, insertion products result [30].

(v) Miscellaneous

Evaporation of a solution of H_2PtCl_6 in DMF after being heated for 20 min in the presence of tetraalkylammonium chlorides, gives salts of the monocarbonyl anion $[Pt(CO)Cl_3]^-$. If bipy is added to $H_2[PtCl_6]$ in DMF solution, the bridged binuclear complex $(bipy)[Pt(CO)Cl_2]_2$ is obtained; if hydrogen chloride is added to such solutions prior to the addition of bipy, the complex salt $[Pt(bipy)(CO)Cl]^+[Pt(CO)Cl_3]^-$ can be isolated [31].

Good yields of *cis*-[$PtCl_2(CO)_2$] can be obtained [32,33] by heating $PtCl_4 \cdot 4\ H_2O$ in thionyl chloride solution at 110°C with CO. $PtCl_2(CO)_2$ can also be obtained when platinum is co-condensed with oxalyl chloride [34]. Reaction of sulphur dichloride with $Pt(CO)_2(PPh_3)_2$ yields $Pt(CO)(PPh_3)Cl_2$ [35]. Compounds of the type $[Pt(CO)(SnCl_3)Cl_2]^-$ have also been prepared [36].

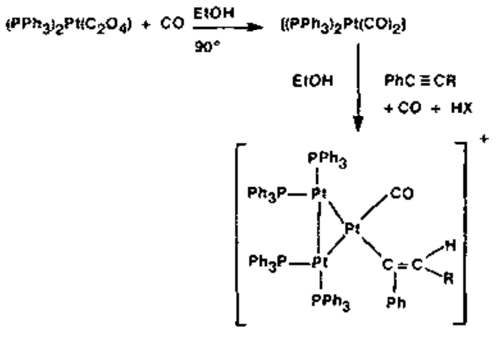
Nucleophilic attack by di-isopropylamine upon the coordinated carbonyl of *cis*-[$PtCl_2(CO)_2$] gives $[{}^iPr_2NH_2]^+[\textit{cis}\text{-}PtCl_2(CO)\{C(O)N{}^iPr_2\}]^-$ in which platinum has a square planar coordination with two *cis* chlorines [37]. The carbonyl ligand is planar and almost perpendicular (88.1°) to the coordination plane about Pt. Halogeno carbonyl complexes of platinum(II) of the type $Cs[Pt(CO)X_3]$ ($X = Cl, Br, I$) can be prepared by the reaction of $PtCl_6^{2-}$ with HX and formic acid [38]. Extraction of $K[Pt(CO)Br_3]$ by dibutylsulphide in benzene is rapid and complete [39] with the formation of $[Pt(Bu_2S)(CO)Br_2]$.

C. POLYNUCLEAR PLATINUM CARBONYLS

The relationships and interconversions between the simple carbonyls and polynuclear carbonyls of platinum are numerous and complex. This is perhaps compounded by the fact that the simple binary carbonyls, $Pt(CO)_n$ ($n = 1$–4), do not exist under normal conditions and have been prepared only under matrix isolation conditions [4]. On the basis of vibrational spectral data obtained from the matrix, a tetrahedral geometry has been suggested for $Pt(CO)_4$ [4]. Polymeric, air sensitive platinum(0) carbonyls of the type $[Pt(CO)_2]_n$ can be prepared [5,40] by the action of water on a benzene solution of $Pt(CO)_2Cl_2$ under carbon monoxide, or by the action of CO on an ethanolic solution of Na_2PtCl_6. Although carbon monoxide only forms this polymeric complex with Pt(0) in the absence of other ligands, it forms a variety of mononuclear and polynuclear species with tertiary phosphine Pt(0) complexes. This results from the strong σ-donor ability of the phosphine ligands which strengthen [41] the Pt–CO bond by increased metal-to-CO π-donation. Thus, simple Pt(0) carbonyls are prepared by the reactions of Pt(0) phosphine complexes with CO under pressure in hydrocarbon solvents [42,43] in THF or acetone [44]. For example, tetrakis(triphenylphosphine)platinum(0) reacts in solution with carbon monoxide to give the monocarbonyl $[(Ph_3P)_3Pt(CO)]$, characterized [43], by a single νCO frequency at 1908 cm^{-1}. Further carbonylation gives a mixture of $[(Ph_3P)_4Pt_2(CO)_2]$ and $[(Ph_3P)_2Pt(CO)_2]$ [43], with the former said to give $[(Ph_3P)_2Pt_3(CO)_4]$ on decomposition. Similarly, in cases where there are only two equivalents of phosphine available, the dicarbonyls such as $[(Ph_3P)_2Pt(CO)_2]$ usually result [45,46]. Reversible formation of $[Pt(CO)_3(PPh_3)]$ from $[Pt_3(CO)_3(PPh_3)_4]$ or $[Pt(CO)_2(PPh_3)_2]$ has been observed under CO pressure in *p*-xylene [47].

In much the same way, CO replaces the nitrosyl ligand in $Pt(NO)_2L_2$ (L = phosphine) to yield $L_2Pt(CO)_2$ [48]. Likewise, carbon monoxide reacts [49] reversibly with *trans*-$PtH_2[P(c\text{-}Hx)_3]_2$ at 298 K to give $[Pt(CO)_2\{P(c\text{-}Hx)_3\}_2]$ with reductive elimination of hydrogen. When this Pt(0) complex warms to room temperature, trimerization occurs to give $[Pt(CO)\{P(c\text{-}Hx)_3\}]_3$ [49]. It has been known for some time that trimeric $[Pt_3(PPh_3)_4(CO)_3]$ can be obtained by boiling an ethanolic solution of $[Pt(PPh_3)_2(CO)_2]$ [50], by treating a suspension of $[Pt(CO)_2]_n$ in acetone with triphenylphosphine [5], by replacing CF_3CN with CO in $[Pt(CF_3CN)_2(PPh_3)_2]$ [51] or by bubbling CO into a dichloromethane solution of $[Pt(PPh_3)_2N_2H]_2[BF_4]_2$ [52]. Further reaction of carbon monoxide with this trimeric complex gives, under ambient conditions, a tetrameric species $[Pt_4(PPh_3)_4(CO)_5]$ [44]. Complexes of this sort employing other donor ligands L (L = PMe_2Ph, PPh_2Bz, PPh_3, $AsPh_3$) have also been prepared and studied by IR spectroscopy [50,53]. The cluster compound $[Pt_4(CO)_5(PPh_3)_4]$ reacts with iodomethane to form the platinum(II) complex $[Pt(CO)IMe(PPh_3)]$ which in the presence of L (L = py, PPh_3, $AsPh_3$ or $SbPh_3$) yields acyl complexes [54].

The golden yellow product $[Pt_4(PPh_3)_5(CO)_3]$ is obtained in high yields when oxalato bis(triphenylphosphine)platinum(II) is photolyzed by UV light in a hydrogen atmosphere [55], but $[Pt(PPh_3)_2(CO)_2]$ is formed in a CO atmosphere in ethanol [56]. The latter complex, in the presence of acetylene and CO, gives a bright yellow trinuclear cluster compound [56] (eqn. (7))



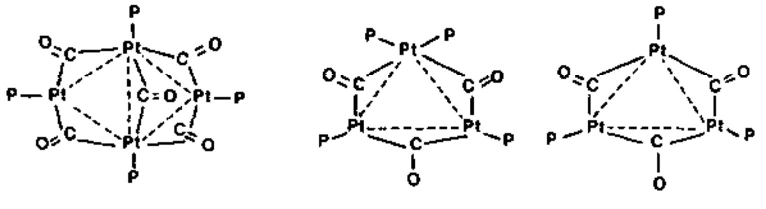
(HX = acetic, fluoroboric or fluorophosphoric acid)

(7)

It is of interest that certain of these phosphine–carbonyl complexes, on reaction with other phosphine ligands, undergo phosphine, and not carbonyl, displacement. For example, reaction [49] of $[Pt(CO)_2\{P(c\text{-}Hx)_3\}_2]$ with tributylphosphine gives $[Pt(CO)_2P(c\text{-}Hx)_3(P^nBu_3)]$. In contrast, $[PtL_3CO]$ and $[PtL_2(CO)_2]$ species react [57] with dppe to give $Pt(dppe)_2$.

Characterization of the polynuclear products obtained by carbonylation of Pt(0) tertiary phosphine complexes has only been possible through the application of X-ray diffraction techniques. The simple carbonyls, di-

Fig. 1. Structure of $[(Ph_3P)_3Pt(CO)]$; for $[(Ph_2EtP)_2Pt(CO)_2]$ Pt–P = 2.360 Å and Pt–C = 1.92 Å.



$[Pt_4(PPhMe_2)_4(CO)_5]$ $[Pt_3(PPh_3)_4(CO)_3]$ $[Pt_3(PPh_2Bz)_3(CO)_3]$

Fig. 2. Structures of tri- and tetranuclear platinum phosphine carbonyls (organic substituents on phosphines omitted).

carbonylbis(diphenylethylphosphine)platinum(0) [58] and monocarbonyltris(triphenylphosphine)platinum(0) [59,60] have the expected structures (Fig. 1) with a roughly tetrahedral arrangement about the metal atoms which lie on a two-fold axis of the unit cell. The Pt–P distance in the two complexes is essentially the same, indicating that the presence of the second π-accepting CO ligand does not decrease the overall Pt–P bond strength.

For the tri- and tetra-nuclear complexes described above, the crystal structure determinations (see Fig. 2) show [61] that the carbon monoxide ligand acts as a bridging rather than a terminal ligand. More recently, the structures of $[Pt_3\{P(c\text{-}Hx)_3\}_3(CO)_3]$ and $[Pt_3\{P(c\text{-}Hx)_3\}_4(CO)_3]$ have been determined [62,63]; despite the steric problems created by the bulkiness of the phosphines, they are entirely similar to those of their analogues drawn in Fig. 2. At least one other tetranuclear cluster, $[Pt_4(PPh_3)_3(CO)_5]$, has been reported [53] but without structural definition. A more general preparative route to the trinuclear cluster $[Pt(PR_3)(CO)]_3$ has been described [64], which is particularly suited to derivatives containing bulky phosphines; it entails carbon monoxide displacement of hydrogen under ambient conditions from $[Pt(PR_3)_2H_2]$ where $Pr_3 = P(c\text{-}Hx)_3$, P^iPr_3, $P^tBu_2{}^nBu$ or P^tBuPh_2. The tri-t-butylarsine analogue, $(As^tBu_3)_2PtH_2$ on the other hand gives the tetranuclear carbonyl cluster compound $[Pt_4(CO)_5(As^tBu_3)_4]$ [65]. Similarly, carbon monoxide displacement of phosphine from $Pt(P^tBu_3)_2$ yields $[Pt_3(P^tBu_3)_3(CO)_3]$ [66]. This can also be obtained by the reaction of CO with $[PtH(NH_3)(PR_3)_2]X$ in acetone [67]. Very recently, ^{31}P and ^{195}Pt NMR data have been used [68,69] to deduce structural information about these polynuclear carbonyls. The nuclearity of $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ ($PR_3 = P(c\text{-}Hx)_3$, P^iPr_3, P^iPr_2Ph and PPh_2Bz) in solution can be deduced via the ^{195}Pt coupling pattern with the values of $^1J(^{195}Pt\text{–}^{195}Pt)$ falling in the range 1517–1619 Hz. The values of $^2J(^{195}Pt\text{–}^{31}P)$ and $^3J(^{31}P\text{–}^{31}P)$ can also be useful indicators of the presence of Pt–Pt bonds. For clusters of the type $[Pt_3(\mu\text{-}CO)_3(PR_3)_4]$ ($PR_3 = PEt_3$, PMe_2Ph, $PMePh_2$, $PEt_2{}^tBu$ and PPh_2Bz), two different ranges of coupling constants, $^{1}J(^{195}\mathrm{Pt}-^{195}\mathrm{Pt})$ 1808–1840 and 385–586 Hz and $^{2}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ 411–459 and 272–292 Hz have been observed and direct metal–metal bonding has been indicated by the magnitude of ^{1}J(1808–1840 Hz). $^{1}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ has been found to be dependent upon the number of coordinated phosphines and two different ranges 3611–4430 Hz (platinum with two phosphines) and 4463–4849 Hz (platinum with one phosphine) have been obtained [69].

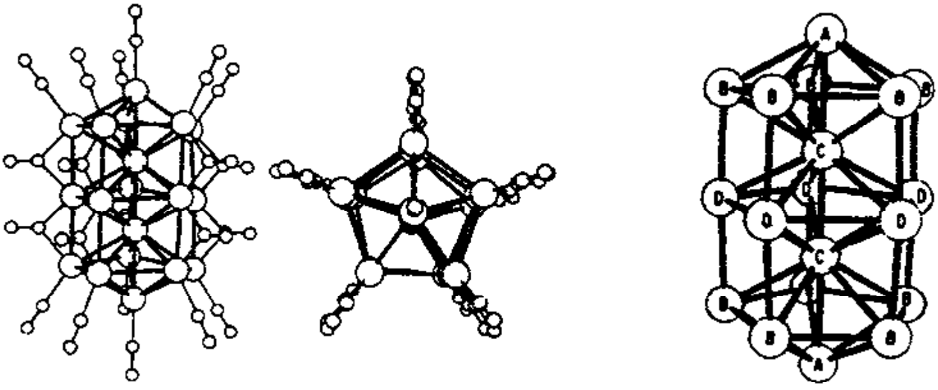
Sulphur dioxide replaces three carbonyl ligands from $[\mathrm{Pt_5(CO)_6(PPh_3)_4}]$ at one atmosphere pressure in toluene to give another cluster compound $[\mathrm{Pt_5}(\mu\text{-CO})_2(\mu\text{-SO}_2)_3\mathrm{(CO)(PPh_3)_4}]$ [70]. Metallic mercury reacts with $[\mathrm{Pt_3}(\mu\text{-CO})_3\mathrm{(PR_3)_3}]$ ($\mathrm{PR_3 = PPh^iPr_2}$, $\mathrm{P^iPr_3}$, $\mathrm{PEt_2{}^tBu}$) to give mixed metal clusters $[\mathrm{Pt_3Hg(CO)_3(PR_3)_3}]_2$ [71]. The molecule consists of two triangular $[\mathrm{Pt_3}(\mu\text{-CO})_3\mathrm{(PR_3)_3}]$ ($\mathrm{PR_3 = PPh^iPr_2}$) units each capped by a mercury atom. These two units are joined through two mercury atoms which are at a distance of 3.225(1) Å. In solution these are fluxional molecules and the fluxionality is associated with the mercury atoms [71].

Another important group of platinum cluster compounds contains the $[\mathrm{Pt_3(CO)_6}]_n^{2-}$ anions, where $n = 1$–6, 10; they may be prepared [63,72,73] by the reductive carbonylation of $[\mathrm{PtCl_6}]^{2-}$, and isolated as coloured crystalline salts of $\mathrm{Ph_4P^+}$ or $\mathrm{Ph_4As^+}$. Crystal structure determinations [72] show that they are composed of vertical stacks of $[\mathrm{Pt_3(CO)_3}(\mu\text{-CO})_3]$ units, with Pt–Pt distances within each unit of 2.66 Å (shorter than the Pt–Pt distance of 2.774 Å in metallic platinum), and between units of 3.10 Å. The former short Pt–Pt distance is ascribed to the removal of some of the platinum *sp* electron density from the plane of the $\mathrm{Pt_3}$ triangle into the inter-triangular region [74,75]. In addition to attempts [74,76] to provide a unifying description of bonding in both clusters of this type and the bulk metals, calculations of the bonding and electronic structures of $[\mathrm{Pt_3(CO)_6}]_n^{2-}$ ($n = 1$ or 2) have also been made, the main electronic interactions involving platinum *s* and *d* orbitals with the 5σ MOs of the carbonyl ligands [77]. These dianion clusters have also been studied by X-ray photo emission spectroscopy [78]. The general structure of all the valence spectra is remarkably similar, particularly for the Pt 5*d* derived bands, indicating that there is negligible interaction between the $[\mathrm{Pt_3(CO)_6}]$ layers. However, changes are observed in the binding energies of Pt 4*f*, Pt 4*d* and the molecular orbitals ($5\sigma + 1\pi$) of the carbonyl ligands, all levels (except the carbonyl 4σ shifts) being shifted to higher binding energy asymptotically as the cluster size increases. This has been interpreted as due to the decreasing effect of the anionic charge as cluster size increases and to the bonding character of the ($5\sigma + 1\pi$) orbitals.

While these dianion clusters, in the solid state, generally have an eclipsed arrangement of the $[\mathrm{Pt_3(CO)_6}]$ layers, their solution behaviour is interestingly different. ^{195}Pt NMR data, for $\mathrm{CDCl_3}$ solutions, suggest [79] that the

$[Pt_3(CO)_6]$ triangles rotate independently about the three-fold axis; in particular, for $[Pt_9(CO)_{18}]^{2-}$, ^{195}Pt NMR show [80] that there is rapid rotation of the outer Pt_3 triangles with respect to the middle Pt_3 triangle at both 25° and −85°. The retention of Pt–Pt coupling indicates that the process is intramolecular; if $[Pt_{12}(CO)_{24}]^{2-}$ is also present, there is exchange of $[Pt_3(CO)_6]$ units between the $n = 3$ and $n = 4$ species at 25°.

At least one other carbonyl cluster can be derived from these dianion species. When $[Pt_9(CO)_{18}]^{2-}$ is heated under reflux in acetonitrile, carbon monoxide is evolved and $[Pt_{19}(CO)_{22}]^{4-}$ may be obtained [81] as its $[^nBu_4N]^+$ salt in 50% yield. This complex is of particular interest with regard to catalysis since its stoichiometry (CO : Pt ratio = 1 : 1.16) is much closer to that of a carbonylated metal surface (CO : M ratio = ca. 1 : 0.75) than for any previously reported metal carbonyl (CO : M ⩾ 1 : 1.7), but its catalytic behaviour, if any, has not yet been reported. Its structure (Fig. 3) consists of a stack of three eclipsed planar Pt_5 rings with isolated Pt atoms sandwiched between them, and one above and one below this stack. There are twelve terminal carbonyls, one bound to each of the six Pt atoms on the top and the six on the bottom of the stack, together with ten bridging carbonyls that half link the three planar Pt_5 rings together. Two platinum atoms are completely encapsulated within the structure and have no carbonyl ligands. Finally, another species, $[Pt_5(CO)_6(PPh_3)_4]$, which is structurally related to the



Pt–Pt′	[No]	I^a	Mean (Å) II^b	III^c
A–B	[10]	[illegible]	2.76	2.75
A–C	[2]	2.70	2.74	2.68
B–C	[10]	2.81	2.81	2.81
B–D	[10]	2.73	2.72	2.72
C–D	[10]	2.81	2.78	2.80
C–C′	[1]	2.52	2.61	2.64
B–B′	[10]	2.82	2.85	2.87
D–D′	[5]	[illegible]	2.89	2.90

Fig. 3. Structure of the $[Pt_{19}(CO)_{22}]^{4-}$ anion.

TABLE 1

Polynuclear platinum carbonyls

Carbonyl compound	Properties	Physical measurements	Ref.
$[Pt(CO)_2]_n$	Brown crystalline solid, glows in air	IR	5, 40
$[Pt_3(CO)_3(PR_3)_3]$ $(PR_3 = PPh_2Bz, P(c\text{-}Hx)_3, P^iPr_3, PPh_2{}^tBu, P^tBu_2{}^nBu, P^tBu_3, P^iPr_2Ph, P^tBu_2Me)$	Red colour compounds	IR, ^1H, ^{31}P, ^{195}Pt NMR, X-ray	5, 49, 50, 63, 64, 66–68, 114, 128
$[Pt_3(CO)_3(PR_3)_4]$ $(PR_3 = PMe_2Ph, PPh_2Et, PPh_3, PEt_3, P(c\text{-}Hx)_3)$	Dark red colour compounds	IR, ^1H, ^{31}P, ^{195}Pt NMR, X-ray	5, 40, 47, 49, 50, 53, 62, 64, 69
$[Pt_3(CO)_4(PR_3)_3]$ $(PR_3 = PMe_2Ph, PPh_3)$	Black or brown, melts with decomposition	IR	5
$[Pt_3(CO)_4(PPh_3)_2]$			43
$[Pt_3(CO)_2(PPh_3)_4]$	Yellow crystals $\nu CO = 1830\ cm^{-1}$	IR, X-ray	102
$[Pt_3(\mu\text{-}CO)_2\{\mu\text{-}C(OMe)Ph\}(PR_3)_3]$ $(PR_3 = P^tBu_2Me, P(c\text{-}Hx)_3)$	Yellow crystals	IR, ^1H, ^{13}C, ^{31}P NMR	112
$[Pt_3(\mu\text{-}CO)\{\mu\text{-}C(OMe)Ph\}(PR_3)_3]$ $(PR_3 = P^tBu_2Me, PMe_3)$	Orange-red crystals	IR, ^{13}C, ^{31}P NMR	112
$[Pt_2(CO)_2\{\mu\text{-}C(OMe)Ph\}(P^tBu_2Me)]$	Pale yellow crystals m.p. 193-195	IR, ^{13}C, ^{31}P NMR	112

$[Pt_3(CO)_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3]$	Red crystals	IR, ^1H, ^{13}C NMR, X-ray	122
$[Pt_4(CO)_5L_3]$ $(L = PPh_3, AsPh_3)$	Pink or brown crystals	IR	50, 53
$[Pt_4(CO)_5L_4]$ $(L = PMe_2Ph, PPh_2Bz, PPh_3, As^tBu_3, AsPh_3)$	Orange red to black crystals, decompose on heating	IR, ^1H NMR, X-ray	44, 50, 61, 65
$[Pt_4(CO)_3(PPh_3)_5]$	Golden yellow needles, m.p. 217–220°C (dec.)	IR (νCO in $CHCl_3$ 1780m cm^{-1}) mass	55
$[Pt_5(CO)_6(PR_3)_4]$ $(PR_3 = PEt_3, PPh_3)$	Red crystals, decompose on heating	IR, X-ray	82, 105
$[Pt_6(CO)_5(PPh_3)_4]$ or $[Pt_6(CO)_5(PPh_3)_5]$	Violet crystals, decompose at 210°C	IR (νCO, 2012(s) 1990s, 1819 sh m, 1785s cm^{-1})	53
$[Pt_5(CO)_3(\mu\text{-}SO_2)_3(PPh_3)_4]$	Orange red crystals	IR, ^{31}P NMR, X-ray	70
$[Pt_3(CO)_2(PhC{\equiv}CR)(PPh_3)_4]$ $(R = Et$ or $Ph)$	Yellow crystals, m.p. 170–178°C (dec.)	IR, mass	55
$[Pt_3(CO)(PhC = CHR)(PPh_3)_4]^+$ $(R = Me$ or $Ph)$	Yellow crystals	IR, ^1H NMR	56
$[Pt_3(CO)(PhC = CHPh)(PMePh_2)_5]^+$	Yellow crystals, m.p. 94–101°C	IR, ^1H NMR	56
$[Pt_3(\mu\text{-}CO)_3(CO)_3]_n^{2-}$ $(n = 1\text{–}6, 9, 10, 12, 15)$	$n = 2$ Orange red $n = 3$ Red violet $n = 4$ Blue green $n = 5$ Yellow green	IR, ^{13}C, ^{195}Pt NMR, X-ray Photo emission	72, 78, 79
$[Pt_{19}(CO)_{22}]^{4-}[^nBu_4N]_4$	Brown product	IR, ^{13}C NMR	81

TABLE 2

Crystallographic data for polynuclear platinum carbonyls

Carbonyl compound	Unit cell	Space group	*a* (Å)
$[Pt_3(CO)_3\{P(c\text{-}Hx)_3\}_3]$	Orthorhombic	*Cmca*	23.756 (7)
$[Pt_3(CO)_3\{P(c\text{-}Hx)_3\}_4]$	Triclinic	$P\bar{1}$	20.342 (10)
$[Pt_3(CO)_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3]$	Orthorhombic	$P2_12_12_1$	11.085 (2)
$[Pt_4(CO)_5(PMe_2Ph)_4]$	Orthorhombic	$Pc2_1n$ or $Pcmn$	19.96
$[Pt_5(CO)_6(PPh_3)_4]$	Monoclinic	$P2_{1/c}$	16.478 (3)
$[Pt_5(CO)_3(SO_2)_3(PPh_3)_4]$	Triclinic	$P\bar{1}$	13.991(6)
$[Pt_3(\mu\text{-}CO)_3(CO)_3]_2[PPh_4]_2$	Monoclinic	$C2/c$	18.882 (4)
$[Pt_3(\mu\text{-}CO)_3(CO)_3]_3[PPh_4]_2$	Monoclinic	$C2/c$	20.123 (2)
$[Pt_3(\mu\text{-}CO)_3(CO)_3]_4[AsPh_4]_2$	Triclinic	$P\bar{1}$	15.239 (5)
$[Pt_3(\mu\text{-}CO)_3(CO)_3]_5[AsPh_4]_2$	Triclinic	$P\bar{1}$	14.783 (8)
$[Pt_{19}(CO)_{22}][N^nBu_4]_4$	Orthorhombic	*Pmmn*	17.380 (9)
$[Pt_{19}(CO)_{22}][PPh_4]_4$	Triclinic		17.234 (3)

$[Pt_3(CO)_6]_n^{2-}$ dianion clusters, can be obtained [82] by the reduction of *cis*-$[Pt(PPh_3)_2Cl_2]$ by $NaMn(CO)_5$ in THF at room temperature. Structurally (Fig. 4) it contains two Pt_3 triangles ($Pt^1Pt^2Pt^5$) and ($Pt^2Pt^3Pt^4$) which

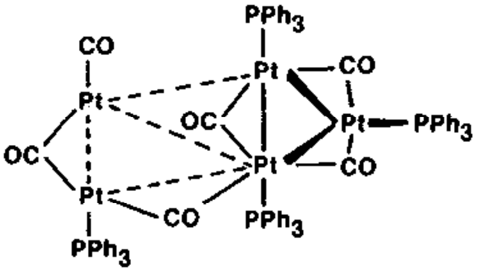


Fig. 4. Structure of $[Pt_5(CO)_6(PPh_3)_4]$.

b (Å)	*c* (Å)	α (°)	β (°)	γ (°)	*Z*	Ref.
16.569 (9)	38.661 (6)				16	63
15.372 (10)	13.876 (10)	97.92 (4)	86.89 (5)	79.36 (5)	2	62
15.554 (3)	18.733 (5)				4	122
20.29	10.66					61
17.640 (3)	30.986 (6)		98.28 (2)		4	82
14.625 (5)	21.285 (4)	84.07 (2)	83.34 (3)	70.76 (4)	2	70
14.677 (3)	22.860 (7)		110.67 (2)		4	72
14.311 (3)	26.433 (5)		115.22 (6)		4	72
19.377 (14)	14.628 (5)	106.66 (4)	101.10 (3)	85.65 (5)		72
26.426 (13)	13.835 (4)	102.73 (3)	118.16 (3)	95.28 (4)	2	72
21.201 (4)	16.728 (8)				2	81
25.480 (5)	17.171 (3)	91.69 (2)	118.10 (1)	74.60 (1)	2	81

are almost orthogonal and which share Pt^2 as their apex; Pt^2 shows the highest coordination number (eight) so far observed for a platinum atom.

Physical properties of polynuclear platinum carbonyls that have been surveyed here are given in Table 1 and crystallographic data in Table 2.

D. HETERONUCLEAR PLATINUM CARBONYLS

A large number of heteronuclear platinum carbonyls have been prepared (Table 3) which contain Pt–M (M = metal) bonds, many of them by Stone and co-workers [83–87]. Thus, reactions of carbonyl derivatives of iron, ruthenium and osmium with low valent platinum phosphine or arsine complexes give a variety of heteronuclear platinum cluster complexes, in-

TABLE 3

Heteronuclear platinum carbonyls

Clusters	Properties	Physical measurements	Ref.
$[PtCr\{\mu\text{-}C(OMe)R\}(CO)_5L_2]$ ($R = Ph$, $C_6H_4Me\text{-}4$, $C_6H_4CF_3\text{-}4$; $L = PMe_3$, PMe_2Ph; $L_2 = COD$)	Yellow-orange to brown crystals	IR, ^1H, ^{13}C, ^{31}P NMR	111, 118
$[PtCr\{\mu\text{-}C(OEt)Ph\}(CO)_5(PMe_3)_2]$	Orange crystals m.p. 126–129°C	IR, ^1H, ^{31}P NMR	119
$[PtCr\{\mu\text{-}C(OMe)R\}(CO)_4(PMe_3)_3]$ ($R = Ph$, $C_6H_4Me\text{-}4$)	Orange crystals m.p. 118–121°C	IR, ^1H, ^{13}C, ^{31}P NMR	111, 118
$[PtCr\{\mu\text{-}C(OMe)Ph\}(CO)_3({}^tBuNC)_3(PMe_3)]$	Orange crystals m.p. 101–103°C	IR, ^1H, ^{13}C, ^{31}P NMR	111
$[PtCr\{\mu\text{-}C_4H_6O\}(CO)_5(PMe_2Ph)_2]$	Orange crystals	IR, ^1H, ^{31}P NMR	118
$[Pt_2Cr\{\mu\text{-}C(OMe)Ph\}(CO)_6(PR_3)_2]$ ($PR_3 = P^tBu_2Me$, $P(c\text{-}Hx)_3$)	Red product	IR, ^{13}C, ^{31}P NMR	112
$[PtCr\{\mu\text{-}C(COOR')R''\}(CO)_4(PMe_3)_3]$ ($R' = Me$ or Et; $R'' = Ph$, $C_6H_4Me\text{-}4$)	Yellow crystals	IR, ^1H, ^{31}P NMR, X-ray	119
$[PtCr\{\mu\text{-}CPh(C_6H_4Me\text{-}4)\}(CO)_5(PMe_3)_2]$	Orange crystals m.p. 119–121°C	IR, ^1H, ^{31}P NMR	119
$[PtCr(\mu\text{-}CPh)(CO)_4(PMe_3)_3][BF_4]$	Brown solid m.p. 184–185°C	IR, ^1H, ^{31}P NMR	119
$[PtMo\{\mu\text{-}C(OMe)Ph\}(CO)_5(PR_3)_2]$ ($PR_3 = PMe_3$, PMe_2Ph)	Orange-brown solid	IR, ^1H, ^{13}C, ^{31}P NMR	111
$[PtMo_2(CO)_4(PPh_3)_2(\eta\text{-}Cp)_2]$	Red solid	IR, ^1H NMR	111(a)
$[Pt_2Mo_2(CO)_6(PR_3)_2(\eta\text{-}Cp)_2]$ ($PR_3 = PEt_3$, PPh_3)	Black crystals	IR, X-ray	102, 108
$[PtW\{\mu\text{-}C(OMe)R\}(CO)_5(L_2)]$ ($R = Me$, Ph, $C_6H_4Me\text{-}4$, $C_6H_4CF_3\text{-}4$; $L = PMe_3$, PMe_2Ph; $L_2 = COD$, dppp, pdma)	Yellow orange solid	IR, ^1H, ^{13}C, ^{31}P NMR X-ray	111, 118, 122
$[PtW\{\mu\text{-}C(OEt)Ph\}(CO)_5(PMe_3)_2]$	Orange crystals m.p. 129–131°C (dec.)	IR, ^1H, ^{31}P NMR	119
$[PtW\{\mu\text{-}C(OMe)R\}(CO)_4(PR_3)_3]$ ($R = Ph$, $C_6H_4Me\text{-}4$; $PR_3 = PMe_3$, PMe_2Ph)	Brown product	IR, ^1H, ^{13}C, ^{31}P NMR, X-ray	111, 118

$[PtW\{\mu\text{-}C(COOR)Ph\}(CO)_4(PMe_3)_3]$ $(R = Me \text{ or } Et)$	Yellow solid	IR, ^1H, ^{31}P NMR	119
$[PtW\{\mu\text{-}C(COOMe)Ph\}(CO)_3(PMe_3)_4]$	Yellow product m.p. 159–161°C	IR, ^1H, ^{31}P NMR	119
$[PtW(\mu\text{-}CPh_2)(CO)_4(PMe_3)_3]$	Dark red solid m.p. 140–146°C (*dec.*)	IR, ^1H, ^{31}P NMR	118
$[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(\eta\text{-}Cp)(PMe_3)_2]$		IR, ^1H, ^{13}C, ^{31}P NMR X-ray	121
$[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}Cp)][BF_4]$		IR, ^1H, ^{13}C, ^{31}P NMR, X-ray	121
$[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}Cp)L][BF_4]$ $(L = PMe_3, CO)$		IR, ^1H, ^{13}C, ^{31}P NMR	121
$[PtW\{\mu\text{-}CC_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3][BF_4]$	Green solid m.p. 135–137°C	IR, ^1H, ^{31}P NMR	119
$[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PR_3)(\eta\text{-}Cp)]$ $(PR_3 = PMe_3, PMe_2Ph, PPh_3)$	Red crystalline solid	IR, ^1H, ^{13}C, ^{31}P, ^{195}Pt NMR	125
$[PtW\{\mu\text{-}CC_6H_4Me\text{-}4\}(CO)_2(PR_3)_2(\eta\text{-}Cp)]$ $(PR_3 = PMe_3, PMe_2Ph, PEt_3)$	Red microcrystals	IR, ^1H, ^{13}C, ^{31}P NMR X-ray	109, 110
$[PtWBr\{\mu\text{-}CC_6H_4Me\text{-}4\}(CO)_4(PMe_3)_2]$	Red crystals m.p. 132–134°C	IR, ^1H, ^{13}C, ^{31}P NMR	109
$[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)CO\}(CO)(PR_3)(\eta\text{-}Cp)(COD)]$ $(PR_3 = PMe_3, PMe_2Ph, PMe_2Bz)$	Orange solid	IR, ^1H, ^{13}C, ^{31}P, ^{195}Pt NMR X-ray	126
$[PtW_2\{\mu\text{-}CC_6H_4Me\text{-}4\}_2(CO)_4(\eta\text{-}Cp)_2]$	Dark purple-red solid m.p. 178-180°C	IR, ^{13}C, ^{195}Pt NMR, X-ray	120
$[Pt_2W\{\mu\text{-}C(OMe)Ph\}(CO)_6(PR_3)_2]$ $(PR_3 = P^tBu_2Me, P(c\text{-}Hx)_3)$	Red crystals	IR, ^1H, ^{13}C, ^{31}P NMR	112
$[Pt_2W\{\mu\text{-}C(OMe)Ph\}(CO)_6(P^tBu_2Me)_3]$	Red crystals m.p. 166°C (dec.)	IR, ^{13}C, ^{31}P NMR	112
$[Pt_2W(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PR_3)_2(\eta\text{-}Cp)]$ $(PR_3 = PMe_3, PMe_2Ph, PMePh_2, PPh_3, PEt_3)$	Orange-red crystalline solid	IR, ^1H, ^{13}C, ^{31}P, ^{195}Pt NMR X-ray	124, 125
$[Pt_2W_2(CO)_6(\eta\text{-}Cp)_2(PR_3)_2]$ $(PR_3 = PEt_3, PPh_3)$			108

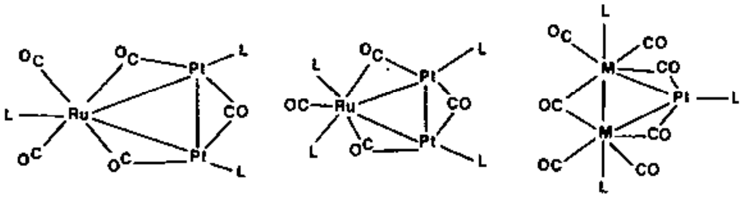
TABLE 3 (continued)

Clusters	Properties	Physical measurements	Ref.
$[\mathrm{PtMn}\{\mu\text{-C(OMe)R}\}(\mathrm{CO})_2(\mathrm{PMe}_3)_2(\eta\text{-Cp})]$ $(\mathrm{R = Ph\ or\ C_6H_4Me\text{-}4})$	Orange solid	IR, ^{1}H, ^{13}C, ^{31}P NMR	113, 119
$[\mathrm{PtMn}\{\mu\text{-C(OMe)Ph}\}(\mathrm{CO})_2(\mathrm{COD})(\eta\text{-Cp})]$	Black solid m.p. 128°	IR	113
$[\mathrm{PtMn}\{\mu\text{-C}_4\mathrm{H}_5\mathrm{O}\}(\mathrm{CO})_4(\mathrm{PMe}_3)_2]$	Yellow and red forms m.p. 122°C (dec.)	IR, ^{1}H, ^{31}P NMR, X-ray	113
$[\mathrm{PtMn}\{\mu\text{-CC}_6\mathrm{H}_4\mathrm{Me\text{-}4}\}(\mathrm{CO})_2(\mathrm{PMe}_3)_2(\eta\text{-Cp})][\mathrm{BF}_4]$	Purple crystals	IR, ^{1}H, ^{13}C, ^{31}P NMR, X-ray	119
$[\mathrm{PtMnI}\{\mu\text{-C}_4\mathrm{H}_6\mathrm{O}\}(\mathrm{CO})_4(\mathrm{P^tBu_2Me})]$	Orange crystals m.p. 128°C	IR, ^{1}H, ^{13}C, ^{31}P NMR	114
$[\mathrm{PtMn}(\mathrm{CO})_2(\mu\text{-CS})(\mathrm{PR}_3)_2(\eta\text{-Cp})]$ $(\mathrm{PR_3 = PMe_2Ph,\ PMePh_2})$	Yellow crystals	IR, ^{1}H, ^{13}C, ^{31}P NMR	116, 123
$[\mathrm{PtMn}(\mathrm{CO})_2(\mu\text{-CSMe})(\mathrm{PPhMe}_2)_2][\mathrm{BF}_4]$	Red salt	IR, ^{1}H, ^{13}C, ^{31}P NMR	116
$[\mathrm{PtRe}(\mathrm{CO})_2(\mathrm{PMe}_2\mathrm{Ph})_2(\mu\text{-CS})(\eta\text{-Cp})]$	Yellow solid	IR, ^{1}H, ^{13}C, ^{31}P NMR	116, 123
$[\mathrm{PtRe}\{\mu\text{-C(OMe)C}_6\mathrm{H}_4\mathrm{Me\text{-}4}\}(\mathrm{CO})_2(\mathrm{PR}_3)_2(\eta\text{-Cp})]$ $(\mathrm{PR_3 = PMe_3,\ PMe_2Ph})$	Yellow crystals	IR, ^{1}H, ^{13}C, ^{31}P NMR	119
$[\mathrm{PtRe}\{\mu\text{-CC}_6\mathrm{H}_4\mathrm{Me\text{-}4}\}(\mathrm{PR}_3)_2(\mathrm{CO})_2(\eta\text{-Cp})][\mathrm{BF}_4]$ $(\mathrm{PR_3 = PMe_3,\ PMe_2Ph})$	Dark red solid	IR, ^{1}H, ^{13}C, ^{31}P NMR	119
$[\mathrm{PtFe}_2(\mathrm{CO})_8\mathrm{L}_2]$ $(\mathrm{L = PMe_2Ph,\ PMePh_2,\ PPh_3,\ PPh_2}$Ⓟ$,$ $\mathrm{P(OMe)_2Ph,\ P(OPh)_3;\ L_2 = dppe,\ diars})$			83, 86, 203
$[\mathrm{PtFe}_2(\mathrm{CO})_9\mathrm{L}]$ $(\mathrm{L = PMe_3,\ PMe_2Ph,\ PMePh_2,\ PPh_3,\ AsPh_3})$	Deep red solid	IR, ^{1}H, ^{31}P NMR, X-ray	83, 86, 88, 89
$[\mathrm{PtFe}_3(\mu\text{-H})(\mu\text{-COMe})(\mathrm{CO})_{10}(\mathrm{PPh}_3)]$	Black crystals	IR, ^{1}H, ^{13}C, ^{31}P NMR, X-ray	91
$[\mathrm{PtFe}_3(\mu\text{-H})(\mathrm{CO})_{11}(\mathrm{PPh}_3)][\mathrm{NEt}_3\mathrm{H}]$	Black crystals	IR, ^{1}H, ^{13}C, ^{31}P NMR	90
$[\mathrm{Pt}_2\mathrm{Fe}(\mathrm{CO})_5\{\mathrm{P(OPh)}_3\}_3]$	Orange prisms m.p. 145–146°C (dec.)	IR, ^{1}H NMR, X-ray	85, 86
$[\mathrm{Pt}_2\mathrm{Fe}_2(\mu\text{-H})_2(\mathrm{CO})_8(\mathrm{PPh}_3)_2]$	Black crystals	IR, ^{1}H, ^{31}P NMR, X-ray	90
$[\mathrm{Pt}_2\mathrm{Fe}_2(\mu\text{-H})(\mathrm{CO})_8(\mathrm{PPh}_3)_2][\mathrm{X}]$ $(\mathrm{X = NEt_4,\ N(PPh_4)_2})$	Red-brown crystals 130–136°C (dec.)	IR, ^{31}P NMR, X-ray	90
$[\mathrm{PtFe}_4(\mathrm{CO})_{16}][\mathrm{TMBA}]_2$	Brown solid	IR, X-ray	92

$[Pt_3Fe_3(CO)_{15}]^{2-}$	Green salt	IR, X-ray	93
$[Pt_3Fe_3(CO)_{15}]^-$	Brown salt		93
$[Pt_6Fe_4(CO)_{22}]^-$	Brown salt	IR, X-ray	93
$[PtRu_2(CO)_8(dppe)]$	Red crystals m.p. 184–186°C (dec.)	IR, ^1H NMR	84
$[PtRu_2(CO)_7(PMe_2Ph)_3]$	Yellow solid	IR, ^1H NMR	83, 84
$[Pt_2Ru(CO)_5(L_3)]$	Yellow crystalline solid	IR, ^1H NMR	83, 84, 203
(L = PMe_2Ph, $PMePh_2$, PPh_3, $P(OMe_2)Ph$, PPh_2Ⓟ, $AsPh_3$)			
$[Pt_2Ru(CO)_4\{P(OMe)_2Ph\}_4]$	Yellow solid m.p. 116–117°C	IR, ^1H NMR	84
$[Pt_2Os(CO)_5L_3]$	Yellow crystalline solid	IR, ^1H NMR	83, 84
(L = $PMePh_2$, PPh_3)			
$[PtOs_2(CO)_7(PMePh_2)_3]$	Orange solid	IR, ^1H NMR	83, 84
$[Pt_2Os_2H_2(CO)_8(PR_3)_2]$	Yellow-orange crystals m.p. 192–195°C	IR, ^1H, ^{31}P NMR, X-ray	84, 95, 100
(PR_3 = PMe_3, PPh_3, $P(c\text{-}Hx)_3$)			
$[PtOs_3H_2(CO)_{10}(PR_3)]$	Dark green to black crystals	IR, ^1H, ^{13}C, ^{31}P NMR, X-ray	95, 96
(PR_3 = PPh_3, $P(c\text{-}Hx)_3$, P^tBu_2Me)			
$[PtOs_3H_2(CO)_{10}(PPh_3)L]$	Yellow solid	IR, ^{31}P NMR, X-ray	95, 96
(L = PPh_3, $AsPh_3$)			
$[PtOs_3(\mu\text{-}H)_2(CO)_{11}\{P(c\text{-}Hx)_3\}]$	Bright yellow crystals	IR, ^1H, ^{31}P NMR, X-ray	98, 99
$[PtOs_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(c\text{-}Hx)_3\}]$	Red and orange forms	IR, ^1H, ^{31}P NMR	97
$[PtOs_3(\mu\text{-}H)_4(CO)_{10}\{P(c\text{-}Hx)_3\}]$	Yellow crystals	IR, X-ray	99
$[Pt_2Os(CO)_6(\mu\text{-}MeC{\equiv}CMe)(PPh_3)]$	Bright yellow solid	IR, ^1H, ^{31}P NMR	98
$[Pt_2Os(CO)_5(\mu\text{-}MeC{\equiv}CMe)(PPh_3)_2]$	Bright yellow crystals	IR, ^1H, ^{31}P NMR	98
$[Pt_2Co_2(CO)_8(PR_3)_2]$	Red crystals	IR, X-ray	101, 102, 104
(PR_3 = PPh_3, PEt_3)			
$[Pt_3Co_2(CO)_9(PEt_3)_3]$	Dark violet needles m.p. 158–159°C	IR, X-ray	104
$[PtCo_2(CO)_7L_2]$	Brown solid	IR	101a
(L_2 = dppe, diars)			

TABLE 3 (continued)

Clusters	Properties	Physical measurements	Ref.
$[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$	Dark red crystals	IR, ^1H, ^{13}C, ^{195}Pt NMR	117, 127
$[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$	Orange-brown crystals	IR, ^1H, ^{13}C, ^{31}P, ^{195}Pt NMR X-ray	117, 128
$[PtRh_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)_2]$	Orange-brown crystals	IR, ^1H, ^{13}C, ^{195}Pt NMR	128
$[PtRh_2(\mu\text{-}CO)_2(COD)(\eta\text{-}C_5Me_5)_2]$	Yellow-brown solid	IR, ^1H, ^{13}C, ^{195}Pt NMR	128
$[PtRh_2(\mu\text{-}CO)_2(\mu\text{-}H)(\eta\text{-}C_5Me_5)_2LL'][BF_4]$	Red-brown crystals	IR, ^1H, ^{13}C, ^{31}P NMR, mass, X-ray	117, 129
(L = L′ = CO; L = CO, L′ = PPh_3; LL′ = COD)			
$[PtRh_4(CO)_{14}]^{2-}$	Yellow-brown crystals	IR, ^{195}Pt NMR, X-ray	130
$[PtRh_5(CO)_{15}]^-$	Brown solid	IR, ^{195}Pt NMR, X-ray	130
$[PtRh_{10}(CO)_{21}N]^{3-}$		IR, X-ray	131
$[Pt_3Hg(CO)_3L_3]$	Dark violet crystals	IR, ^{31}P, ^{195}Pt, ^{199}Hg NMR X-ray	71
(L = P^iPr_3, $PEt_2{}^tBu$, P^iPr_2Ph)			
$[PtWFe\{\mu\text{-}CC_6H_4Me\text{-}4\}(CO)_6(PR_3)(\eta\text{-}Cp)]$ (PR_3 = PMe_3, $PMePh_2$, PEt_3)	Brown-black crystals	IR, ^1H, ^{13}C, ^{31}P NMR, X-ray	110, 124
$[PtWFe\{\mu\text{-}CC_6H_4Me\text{-}4\}(CO)_6(PMe_2Ph)_2(\eta\text{-}Cp)]$	Purple plates	IR, ^1H, ^{13}C, ^{31}P, ^{195}Pt NMR	124
$[PtWFe\{\mu\text{-}CC_6H_4Me\text{-}4\}(CO)_5(PMePh_2)_2(\eta\text{-}Cp)]$	Brown solid	IR, ^1H, ^{13}C, ^{31}P NMR X-ray	124


I L = PMePh$_2$

II L = PPh(OMe)$_2$, P(OPh)$_3$

III M = Ru,Os

Fig. 5. Structures of (I) [$Pt_2Ru(CO)_5L_3$], (II) [$Pt_2Ru(CO)_4L_4$] and (III) [$PtM_2(CO)_7L_3$] (M = Ru, L = PMe_2Ph; M = Os, L = $PMePh_2$).

cluding **I–III** (Fig. 5). The ruthenium and osmium complexes contain triangular clusters of metal atoms in which each metal atom is generally bonded to one phosphine and linked to the other metal atoms by both metal–metal bonds and bridging carbonyl groups [83]. However, the reaction of $Fe_2(CO)_9$ and $Pt[P(OPh)_3]_3$ gives $FePt_2(CO)_5[P(OPh)_3]_3$ for which the X-ray structure determination shows [85,87] that there are four terminal CO groups bonded to iron with the fifth CO bound to a Pt atom *trans* to iron (Fig. 6). In contrast, the ruthenium and osmium analogues have structures of type **I**. The structure of [$PtFe_2(CO)_9(PPh_3)$], prepared from the reaction of PtL_4 or PtL_2(olefin) (L = PPh_3) with $Fe_3(CO)_{12}$, shows two independent and significantly different Pt–Fe bond distances, reflecting the much higher *trans* influence of the phosphine relative to the CO ligand [88,89] (Fig. 7).

The metal framework of the anion, [$Fe_2Pt_2(\mu\text{-H})(CO)_8(PPh_3)_2$]$^-$, prepared by the reaction of [$Fe_2(\mu\text{-H})(\mu\text{-CO})_2(CO)_6$]$^-$ with $Pt(C_2H_4)_2(PPh_3)$ in THF [90], consists of a cluster of Fe_2Pt_2 atoms which are arranged in such a way that an Fe_2Pt triangle, edge-bridged by three CO ligands, is capped by a platinum atom carrying terminal CO and PPh_3 ligands. The platinum atom

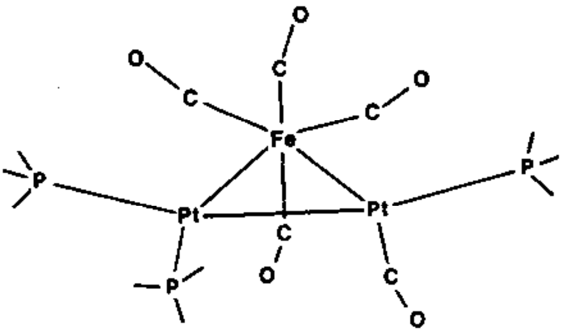


Fig. 6. Molecular structure of [$FePt_2(CO)_5\{P(OPh)_3\}_3$].

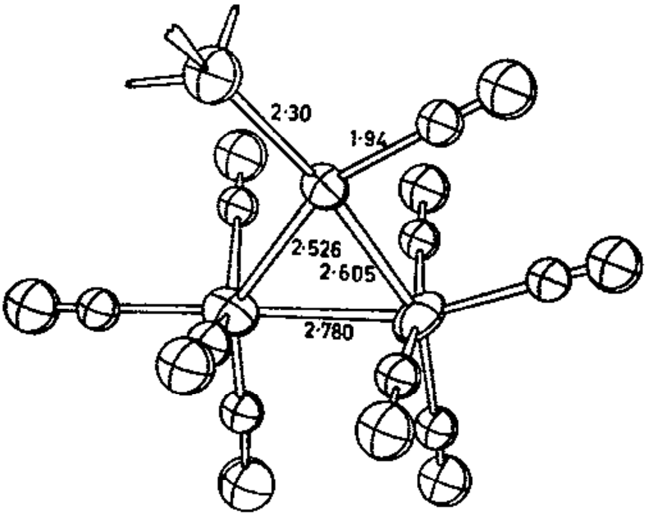


Fig. 7. Stereochemistry of $[PPh_3(CO)PtFe_2(CO)_8]$.

of the triangle carries a PPh_3 group. A pair of CO ligands is terminally bonded to each iron atom of the triangle [90]. Protonation of this anion with $HBF_4 \cdot 2\ Et_2O$ yields a neutral dark red crystalline compound $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ [90]. In the molecule each iron atom is bonded to three CO ligands and each platinum is bonded to CO and a PPh_3 ligand [90]. The hydride ligands bridge the two longer Pt–Fe edges (Fig. 8).

Reaction of $[Pt(C_2H_4)_2(PPh_3)]$ with $[Fe_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ or $[Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ yields $[Fe_3Pt(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}(PPh_3)]^-$ [90] and $[Fe_3Pt(\mu_3\text{-}H)(\mu_3\text{-}COMe)(CO)_{10}(PPh_3)]$ [91] respectively.

In other studies, $[Fe_4Pt(CO)_{16}]^{2-}$ has been prepared in high yield as its trimethylbenzylammonium (TMBA) salt from the reaction of $(TMBA)_2[Fe_3(CO)_{11}]$ with K_2PtCl_4 or $(PhCN)_2PtCl_2$ in a 1 : 0.7 molar ratio under nitrogen [92]. The dianion $[Fe_3Pt_3(CO)_{15}]^{2-}$, green in colour, has been

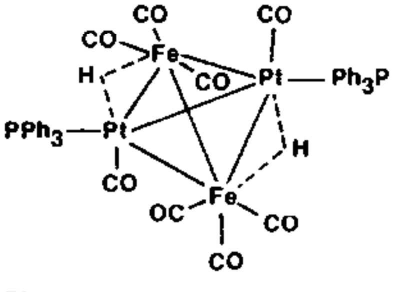


Fig. 8. Structure of $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$.

obtained both by redox condensation of $[Pt_3(CO)_6]_n^{2-}$ and $Fe(CO)_5$ and by the reaction under nitrogen of $Fe_3(CO)_{11}^{2-}$ with K_2PtCl_4 in a 1:1.5 molar ratio; other clusters of the types $[Fe_3Pt_3(CO)_{15}]^-$ and $[Fe_4Pt_6(CO)_{22}]^{2-}$ are also obtained [93] as their trimethylbenzyl ammonium salts. The unpaired electron in $[Fe_3Pt_3(CO)_{15}]^-$ is mainly located in a non-degenerate molecular orbital of the triplatinum system [94].

The reaction of $H_2Os_3(CO)_{10}$ with $(C_2H_4)_2PtPR_3$ yields [95,96] cluster $[H_2Os_3Pt(CO)_{10}(PR_3)]$ ($PR_3 = PPh_3$, P^tBu_2Me, $P(c\text{-}Hx)_3$) as the compound shown in Fig. 9. In solution these clusters show dynamic behaviour with site exchange of the two hydrido-ligands. The X-ray structure of the tricyclohexylphosphine derivative has revealed that the platinum atom is bonded to a CO group and to a $P(c\text{-}Hx)_3$ ligand and each osmium is attached to three CO groups [96]. The hydrido ligands bridge the longest Os–Os and Os–Pt bonds (Fig. 9). The former compound, $[(\mu\text{-}H)_2Os_3Pt(CO)_{10}(PR_3)]$ (R = Ph, c-Hx) reacts further with CH_2N_2 in THF-Et_2O at 0°C with the formation of the kinetic product **IV** (Fig. 10) which equilibrates in solution, over a period of 4–5 days, with the thermodynamically stable product **V** (Fig. 10) [97]. **IV** can also be obtained by the reaction of $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ with $[Pt(C_2H_4)_2\{P(c\text{-}Hx)_3\}]$ [97].

The cluster compounds, $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$ react with CO, PPh_3 or $AsPh_3$ to give $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)L]$ whereas with but-2-yne a mixture of five polynuclear metal complexes including $[OsPt_2(CO)_5(PPh_3)_2(\mu\text{-}MeC{\equiv}CMe)]$ is obtained [98]. The four metal atoms in the former cluster, $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ adopt a butterfly arrangement in which one PPh_3 ligand is attached to platinum and the other to osmium and all the carbonyl ligands are terminally bonded (Fig. 11) [98]. The metal atoms in the latter molecule, $[OsPt_2(CO)_5(PPh_3)_2(\mu\text{-}MeC{\equiv}CMe)]$, form an isosceles triangle bridged by a face-bonding but-2-yne molecule [98].

Another interesting reaction of the cluster compound $Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(c\text{-}Hx)_3\}$ is with H_2 or CO. It reacts reversibly to give $[Os_3Pt(\mu\text{-}H)_3(CO)_{10}\{P(c\text{-}Hx)_3\}]$ and $[OsPt(\mu\text{-}H)_2(CO)_{11}\{P(c\text{-}Hx)_3\}]$ with H_2 and CO respectively [99]. The structures of both these compounds have been

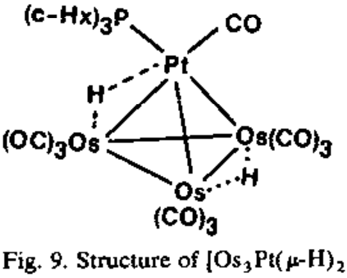
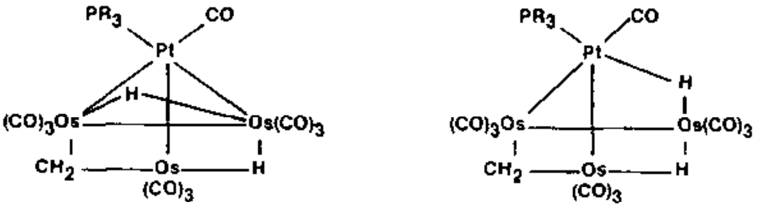


Fig. 9. Structure of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(c\text{-}Hx)_3\}]$.



IV

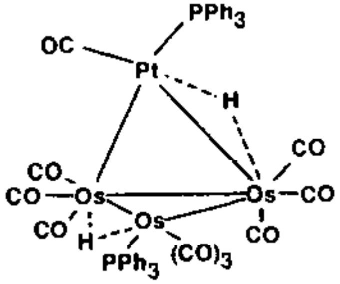
V

Fig. 10. Structure of $[Os_3Pt(\mu\text{-}H)_2(CH_2)(CO)_{10}\{P(c\text{-}Hx)_3\}]$.

determined by X-ray crystallography [99].

When $(C_2H_4)_2PtPR_3$ reacts with $H_2Os(CO)_4$ at room temperature, the product $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PR_3)_2]$ (R = Me, Ph or c-Hx) is obtained [100]; the four metal atoms form a butterfly cluster, with the two osmium atoms at the hinge (Os–Os = 2.781 Å) and the two platinum atoms at the wing-tip (Pt–Pt = 3.206 Å). Each platinum atom carries one CO and one PR_3, with three CO groups on each osmium (Fig. 12). The hydrido ligands bridge the Pt–Os and Pt′–Os′ edges of the cluster. In fact the molecular structure is closely similar to that of its iron analogue $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ [90].

Platinum–cobalt heteronuclear carbonyl clusters have also been prepared [101–107]. Treatment of PtL_2Cl_2 (L = phosphine) complexes with cobalt carbonyl anions has yielded a number of clusters, $[Pt_2Co_2(CO)_5(\mu\text{-}CO)_3(PR_3)_2]$, $[Pt_3Co_2(CO)_4(\mu\text{-}CO)_5PEt_3]$ and $[PtCo_2(CO)_8(PPh_3)]$. *cis*-$Pt(PR_3)_2Cl_2$ (R = Et or Ph) reacts with $Na[M(CO)_3(\eta^5\text{-}C_5H_5)]$ (M = Mo or W) to yield [102–108] the product with the structure of Fig. 13; semi-triple bridging carbonyls lie on either side of the Mo-Pt plane, largely over one Mo–Pt bond.



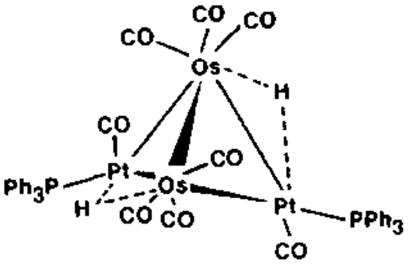


Fig. 11. Structure of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$.

Fig. 12. Structure of $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$.

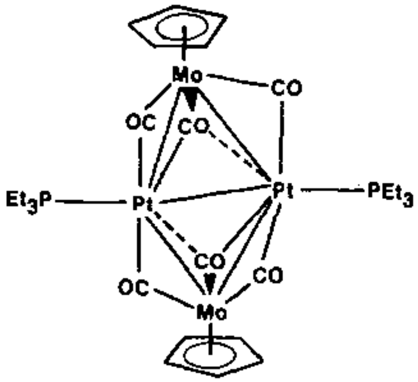


Fig. 13. Structure of $[Mo_2Pt_2(CO)_6(PEt_3)_2(\eta\text{-}Cp)_2]$.

A large number of heteronuclear carbonyl cluster compounds of platinum, containing Cr, Mo, W, Fe, Mn, Rh, etc. have been prepared by Stone and co-workers [109–122], who have also, in many cases, determined the molecular structures. $[M(CO)_2(CS)(\eta\text{-}Cp)]$ (M = Mn or Re) reacts with $[Pt(C_2H_4)(PR_3)_2]$, in equimolar quantities in light petroleum, to give yellow bimetallic clusters $[(\eta\text{-}Cp)M(CO)_2(\eta\text{-}CS)Pt(PR_3)_2]$ [116]. The crystal and molecular structures of $[MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2(\eta\text{-}Cp)]$ have been determined, and show the CS ligand to occupy a bridging position rather than CO, with one CO ligand in a semi-bridging arrangement [116,123] (Fig. 14).

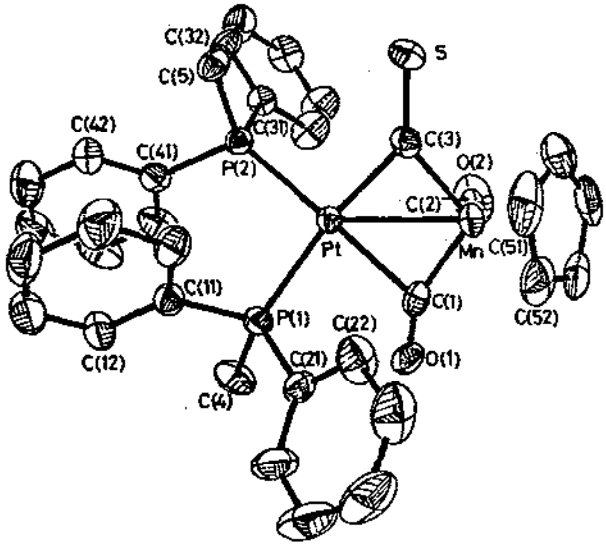
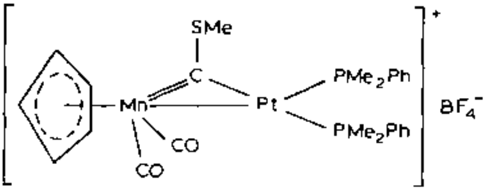


Fig. 14. Structure of $[MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2(\eta\text{-}Cp)]$.

^1H, ^{13}C and ^{31}P NMR studies show that at room temperature, CO and CS ligands undergo bridge–terminal site exchange, but that the process ceases at about −60°C. The product of Fig. 14 also reacts with Me_3OBF_4 in dichloromethane to afford the thiocarbyne complex, **VI**.

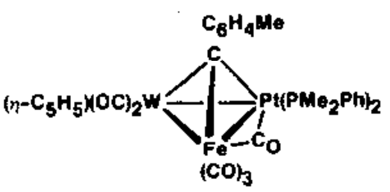


VI

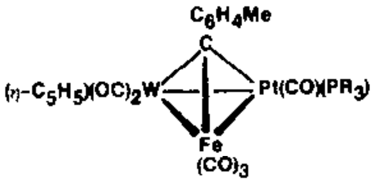
The reaction of $Pt(COD)_2$ with $[Mn\{C(OMe)Ph\}(\mu\text{-}Cp)(CO)_2]$ in light petroleum at 0°C yields $[PtMn\{\mu\text{-}C(OMe)Ph\}(CO)_2(COD)(\eta\text{-}Cp)]$ [113]. Reaction of the same manganese carbene complex with $[Pt(C_2H_4)_3]$ in the presence of trimethylphosphine produces $[MnPt\{\mu\text{-}C(OMe)Ph\}(CO)_2(PMe_3)_2(\eta\text{-}Cp)]$ which reacts further with ^tBuNC to afford $[Mn\{\mu\text{-}C(OMe)Ph\}(CO)_2(\eta\text{-}Cp)Pt(PMe_3)(^tBuNC)]$ [113]. Similar reactions with chromium, molybdenum and tungsten carbonyls have also been performed [111]. Reaction of $[Pt(C_2H_4)_3]$ with $[(CO)_5Mn\text{–}Mn(\overline{CCH_2CH_2CH_2O})(CO)_4]$ in the presence of two equivalents of PMe_3 gives two crystalline forms of $[(CO)_4MnMn(\mu\text{-}C_4H_5O)Pt(PMe_3)_2]$ which differ in the relative orientation of some least-squares planes involving various groups of atoms comprising the molecules, and in the Mn–Pt distances (red form 2.6909(7) Å and yellow form 2.659(2) Å) [113].

When a pentane solution of $[Pt(C_2H_4)_3]$ is treated first with two equivalents of tertiaryphosphine and then with $[W(CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}Cp)]$, the product $[PtW(\mu_2\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}Cp)]$ ($PR_3 = Me_3P$, $PMePh_2$ or PEt_3) is obtained; this on treatment in THF with $Fe_2(CO)_9$ gives $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PR_3)_2(\eta\text{-}Cp)]$ (**VII**), $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(PPh_2Me)_2(\eta\text{-}Cp)]$ and $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PR_3)(\eta\text{-}Cp)]$ ($PR_3 = PMe_3$, PEt_3 or $PMePh_2$) (**VIII**). When the same reaction with the triethylphosphine analogue was carried out a small amount of non-iron containing compound, $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PEt_3)_2(\eta\text{-}Cp)]$, **IX**, was also obtained.

Compound **VII** contains the μ_3-CFePtW core with the alkylidyne ligand asymmetrically bridging the metal triangle [110,124]. The methyldiphenylphosphine analogue of **VII** has been prepared [110,124] similarly, and ^{13}C, ^{31}P, and ^{195}Pt NMR studies all reveal both the dynamic behaviour and chiral nature of the cluster. On treating the toluene solutions of the compounds $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}Cp)]$ ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3, PEt_3) with CO at room temperature, di- and tri-metal complexes,

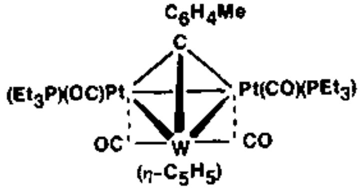


VII



VIII

$PR_3 = PMePh_2, PMe_3, PEt_3$



IX

[PtW(μ-CC_6H_4Me-4)$(CO)_3(PR_3)$(η-Cp)] and [Pt_2W(μ-CC_6H_4Me-4)$(CO)_4(PR_3)_2$(η-Cp)], **IX**, were obtained [125].

In molecule (**IX**) the metal atoms form a triangle with long Pt–Pt distance and the carbyne carbon atom is equidistant from the three metal atoms [125]. Reaction of $Pt(COD)_2$ with [W{μ-C(C_6H_4Me-4)CO}(CO)(PR_3)(η-Cp)] ($PR_3 = PMe_3$, PPh_3, PMe_2Ph, PMe_2Bz and $PMePh_2$) yields various products depending upon the tertiary phosphine, but with PMe_3, PMe_2Bz and PMe_2Ph a bimetallic complex [PtW{μ-C(C_6H_4Me-4)CO}(CO)(PR_3)(η-COD)(η-Cp)] of the following structure is obtained (Fig. 15) [126].

Reaction of [$Pt(C_2H_4)_2(P^tBu_2Me)$] with [MnI{$COCH_2CH_2CH_2$}$(CO)_4$] yields [Pt(μ-CO)$(P^tBu_2Me)]_3$ and [MnPtI{$COCH_2CH_2CH_2$}$(CO)_4$-(P^tBu_2Me)] in which the iodide ligand bridges the Mn–Pt bond, and the CO ligands occupy four of the octahedral positions about manganese [114]. Similarly, [$Pt(C_2H_4)_2(PR_3)$] ($PR_3 = P^tBu_2Me$ or $P(c\text{-}Hx)_3$) reacts with [M{C(OMe)Ph}$(CO)_5$] (M = Cr or W) to give [MPt_2{μ-C(OMe)Ph}$(CO)_6$-$(PR_3)_2$]. However, the same reaction employing [Cr{C(OMe)Ph}$(CO)_5$]

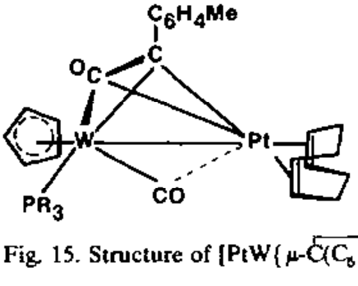


Fig. 15. Structure of [PtW{μ-C(C_6H_4Me-4)(CO)}(CO)(PR_3)(η-COD)(η-Cp)].

also gives the di- and triplatinum derivatives, $[Pt_2\{\mu\text{-}C(OMe)Ph\}(CO)(P^tBu_2Me)_2]$ and $[Pt_3\{\mu\text{-}C(OMe)Ph\}(\mu\text{-}CO)_2(PR_3)]$ [112]. X-ray diffraction studies of $[Pt_2W\{\mu\text{-}C(OMe)Ph\}(CO)_6(P^tBu_2Me)_2]$ show that the carbene group bridges the Pt–Pt bond and that each Pt atom is coordinated by a CO and a phosphine [112].

$Pt(C_2H_4)_3$ reacts with $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ to give the pentanuclear cluster compound $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ in which the four rhodium atoms are disposed around the platinum in an essentially tetrahedral arrangement and the four CO ligands, in addition to bridging the Rh–Rh vector, weakly interact with the platinum atom [127]. A similar reaction of $Pt(COD)_2$ with $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ or $Rh(CO)_2(\eta\text{-}C_5Me_5)$ yields $[PtRh_2(\mu\text{-}CO)_2(COD)(\eta\text{-}C_5Me_5)_2]$ and $[PtRh_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)_2]$ respectively [128]. However, reaction of $Pt(C_2H_4)(PPh_3)_2$ with $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ affords a mixture of complexes from which $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ is isolated as a major product by chromatography [128]. The cluster compounds $[PtRh_2(\mu\text{-}CO)_2LL'(\eta\text{-}C_5Me_5)_2]$ ($L = L' = CO$; $L = CO$, $L' = PPh_3$; $L\text{–}L' = COD$) react with HBF_4 in diethylether to afford $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2LL'(\eta\text{-}C_5Me_5)_2][BF_4]$ and exhibit dynamic behaviour in solution [129]. The variable temperature ^1H NMR spectral data were consistent with rapid two-site exchange involving movement of the hydride from one Pt–Rh vector to the other in such a way that the hydride remains bonded to Pt. The molecule (where $L = CO$, $L' = PPh_3$) consists of the $PtH(CO)PPh_3$ unit bonded to the dirhodium fragment $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ in such a way that coordination about the platinum is planar (Fig. 16). The two carbonyl groups which bridge the rhodium–rhodium bonds show weak interaction with the Pt atom [129].

A somewhat simpler cluster is that obtained [130] by reaction of $[Pt_{12}(CO)_{24}]^{2-}$ with $[Rh_{12}(CO)_{30}]^{2-}$; the product, $[PtRh_5(CO)_{15}]^-$ can be regarded structurally as a simple derivative of $Rh_6(CO)_{16}$. By a similar type of reaction [131] between cluster species, $[Rh_6N(CO)_{15}]^-$ reacts with $[PtRh_4(CO)_{14}]^{2-}$ in refluxing acetone, in a nitrogen atmosphere, to give

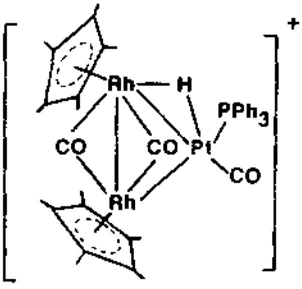


Fig. 16. Structure of $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5Me_5)_2(PPh_3)][BF_4]$.

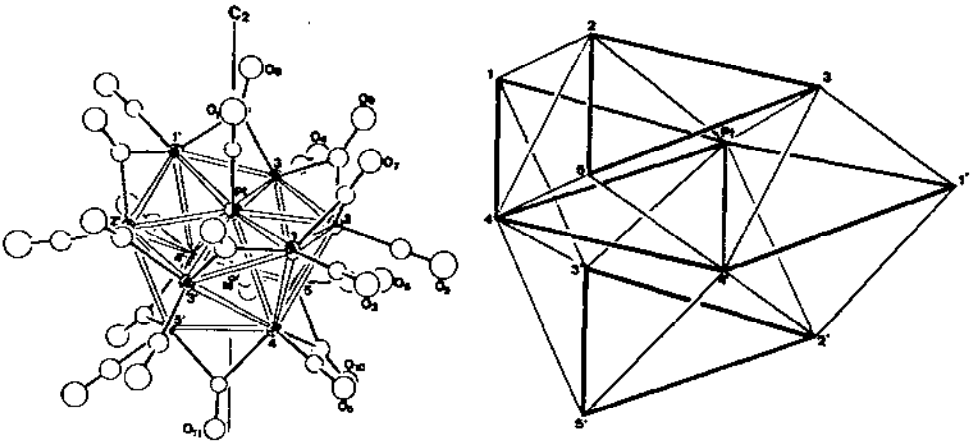


Fig. 17. (a) View of the anion $[PtRh_{10}N(CO)_{21}]^{3-}$. The rhodium atoms are indicated by their sequence numbers and the carbonyl ligands by the oxygen atoms. (b) Cluster geometry of the $[PtRh_{10}N(CO)_{21}]^{3-}$ anion, consisting of a closely-packed hexagonal array of metal atoms.

$[PtRh_{10}N(CO)_{21}]^{3-}$. This species has a novel geometry which can be described as consisting of a folded hexagon of Rh atoms centred by a Pt atom, superimposed along the C_{2v} axis on to a folded square of Rh atoms. Of the 21 CO ligands, eleven are bound terminally (one per metal atom) and ten are double bridged on the Rh–Rh edges of the folded hexagon and square. Alternatively the cluster geometry can be derived from a fragment of a hexagonal close-packed array of metals consisting of three layers. The interstitial N atom causes a distortion of this compact fragment and occupies an unusual type of cavity in which it is connected to five metal atoms (Fig. 17).

E. PLATINUM(I) CARBONYLS

Complex carbonyl ions, containing platinum in the less common oxidation state of I, have been prepared by a number of methods. The action of CO on aqueous solutions of $[PtX_4]^{2-}$ gives [132,133] the anions $[Pt_2X_4(CO)_2]^{2-}$ for which a Pt–P bond was suggested [133]. This was confirmed by an X-ray structure determination [134] of $[Pt_2Cl_4(CO)_2]^{2-}$ which also showed the occurrence of an unusual form of isomerism. Coordination about each platinum is distorted square planar, with the two planes twisted about the Pt–Pt bond to give a *transoid* configuration with a dihedral angle of 120° between the two Pt–Cl groups; the other isolated isomer is thought to have the *cisoid* configuration. The dianion, $[Pt_2(CO)_2Cl_4]^{2-}$, undergoes a number of oxidative reactions. The hydridocarbonyl compound,

$[Pt(CO)HCl_2]^-$, is formed by oxidation with iron(III) in aqueous HCl solution [135].

Platinum(I) chloro complexes containing (dppm) or (dpam) ligands have been prepared and studied by Puddephatt and co-workers [136–139]. Treatment of $PtCl_2(dppm)_2$ with CO in dichloromethane gives the chloro-bridged carbonyl, **X** (E = P), which can also be obtained by the reaction of dppm with $[Pt_2Cl_4(CO)_2]^{2-}$; on heating this reverts to the starting compound, but when the same reaction is performed in methanol, the ionic compound **XI** results [136,137]. However, the arsine analogue, obtained from $[Pt_2Cl_4(CO)_2]^{2-}$ and dpam, does not readily lose CO on heating nor does it isomerize readily to an ionic terminal carbonyl complex **XI** (E = As). Initially, Puddephatt and co-workers considered these as platinum(I) complexes on the basis of IR stretching frequencies [136,137] but the X-ray analysis of dpam complexes has shown that platinum is in the formal oxidation state of two [138]. The platinum atoms are bridged by the carbonyl group and two dpam ligands with no Pt–Pt bond. The $Pt_2(CO)$ fragment is planar and the carbon atom is approximately sp^2 hybridized and forms two σ-covalent bonds to the platinum atoms (Fig. 18), giving a structure similar to the palladium analogue [140]. The crystals of the cation $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$ are monoclinic and of space group $P2\ 1/n$. The molecule consists of Pt–Cl and Pt–CO fragments linked by a Pt–Pt σ bond of 2.620 Å [141].

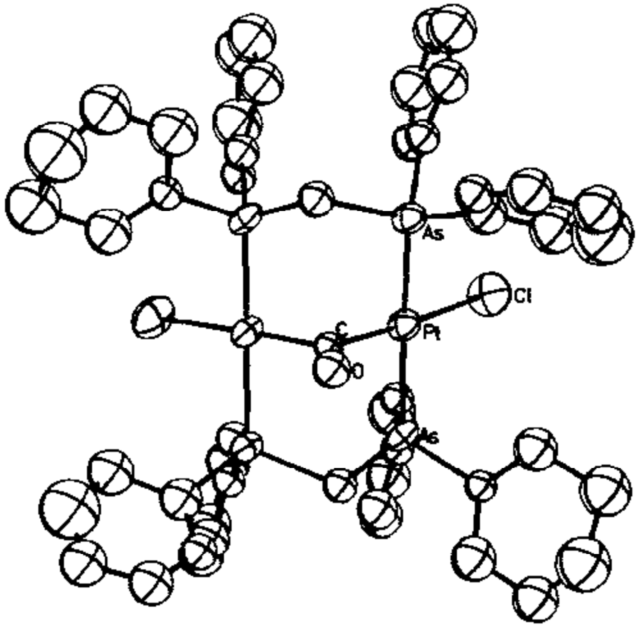
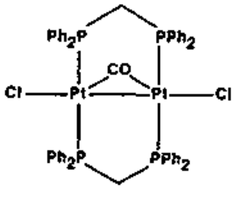
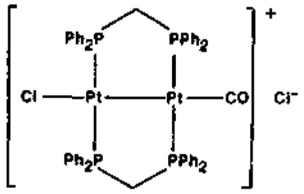


Fig. 18. Molecular structure of $[Pt_2(\mu\text{-dpam})_2(CO)Cl_2]$.

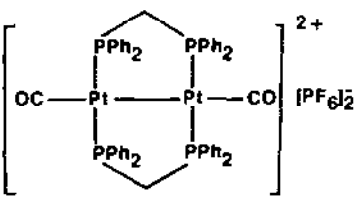


X



XI

When CO is bubbled into a dichloromethane solution of $[Pt_2(\mu\text{-}dppm)_2(NH_3)_2]Cl_2$ a dinuclear platinum carbonyl, **XII**, could be isolated as



XII

its hexafluorophosphate salt [139]. The crystals of the complex are monoclinic of space group P2 $1/c$. The cation contains two Pt–CO fragments bridged by two dppm ligands and linked directly by a Pt–Pt σ bond of 2.642(1) Å. Variations in the Pt–P distances (2.302(4)–2.340(4) Å) have been observed which have been attributed to steric effects [142].

The dication reacts with hydrogen to give the hydrido complex $[Pt_2H(CO)(\mu\text{-}dppm)_2]^+$ [142,143] which reacts reversibly with excess of hydrogen to give $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ and CO. The cation $[Pt_2H(CO)(\mu\text{-}dppm)_2]^+$ also reacts with $PhMe_2P$ or MeSH to give $[Pt_2H(PPhMe_2)(\mu\text{-}dppm)]^+$ or $[Pt_2H_2(\mu\text{-}SMe)(\mu\text{-}dppm)]^+$ respectively [142] and CO. X-ray photoelectron spectroscopy shows the presence of a Pt–Pt bond with platinum in oxidation state I in $[Pt_2H(CO)_2(\mu\text{-}dppm)_2][PF_6]$, since the Pt $4f_{7/2}$ binding energy (72.4 eV) lies in between the Pt(0) and Pt(II) binding energies [144].

A reaction similar to $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ with CO in CH_2Cl_2 was carried out employing the hetero-bimetallic complex $[PtPdCl_2(\mu\text{-}dppm)_2]$ and the product $[PtPd(\mu\text{-}CO)Cl_2(\mu\text{-}dppm)_2]$ was readily isolated which reverted into the starting complex on prolonged heating [145].

A related but structurally similar univalent platinum carbonyl is that shown in Fig. 19, which has a thio-bridge as well as a Pt–Pt bond [146–148], and which was prepared by refluxing (carbonyl sulfide)bis(triphenylphosphine) platinum(II), $[(PPh_3)_2Pt(COS)]$, in chloroform. The resulting bright yellow complex was initially formulated as $Pt_2S(CO)_2(PPh_3)_3$ [149], but the

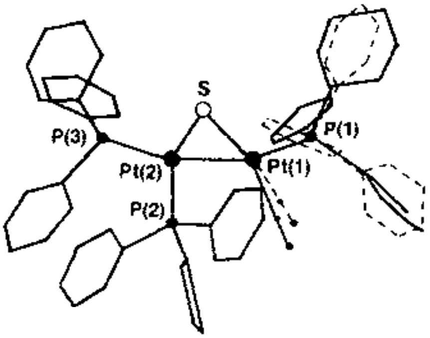


Fig. 19. Structure of $[Pt_2(\mu\text{-}S)(CO)PPh_3]$.

X-ray structural study revealed the presence of only one carbonyl group, $[Pt_2S(CO)(PPh_3)_3]$ [146,147].

F. PLATINUM(IV) CARBONYLS

There are only a few papers in the literature which describe platinum(IV) carbonyls [132,150–153]. The pentanuclear cluster $[Pt(CO)_2]_5$, in the presence of ferric and halide ions in water gives $[PtH_2X_2(CO)]$ which in solution exists as $[PtH_2(CO)X_3]^-$ and can be isolated as its tetraalkyl ammonium salt [150,151]. X-ray analysis of $[Pt(CO)H_2Br_3][NEt_4]$ shows an octahedral configuration with *trans* hydride ligands around the platinum atom [152]. Recently, another carbonyl compound, $[Pt(CO)X_5][N^nBu_4]$ has been produced in solution by the halogenation of $[PtX_3(CO)]^-$ ($X = Cl$ or Br) and detected by IR and ^{13}C NMR spectroscopy [153].

G. CHEMICAL BONDING AND PHYSICAL STUDIES

The nature of Pt–CO binding is, of course, essentially the same as that in all transition metal carbonyls. For terminal carbonyls, it is generally agreed that such bonding involves a filled *sp* hybrid orbital on carbon with a vacant hybrid metal orbital, complemented by π-back donation of electron density from filled (*d* and *dp*) orbitals of the metal to empty antibonding orbitals on CO. Such electron transfer raises CO to an electronically excited state [154]. The presence of electrons in the π^* (antibonding) orbitals of CO weakens the C–O bond and hence lowers the C–O stretching frequency which in free carbon monoxide occurs at 2155 cm^{-1}. Because of their generally reasonable stability and well-defined geometry, platinum carbonyls are particularly useful in studies of ligand effects on electron distribution in metal carbonyls. For example, a steady decrease in the C–O stretching frequency is observed in platinum(II) halogen carbonyls as the atomic number of the halogen increases; this reflects the changing magnitude of π back-donation from Pt(II) to CO as the electronegativity of the halogen decreases (see Table 4). Similarly, the carbonyl stretching frequency in the series of complexes *trans*-[Pt(CO)LCl$_2$] (where L = 4-substituted pyridine or 4-substituted pyridine-*N*-oxide) increases as the electron-withdrawing power of the 4-substituent increases [155–158]. The electronic absorption spectra of *trans*-[Pt(CO)Cl$_2$(4-R-py)] also show bands whose frequencies are dependent on the nature of R [159]. Again, in the IR spectra of these complexes, ν(Pt–N) is strongly dependent [158] on the nature of R and has a minimum value when R = H; this is explained in terms of the σ and π bonding properties of the 4-substituted pyridine, as well as the ionization potential of Pt [158]. Other IR spectroscopic studies of *cis*-[PtCl$_2$(CO)(PR$_3$)] and *cis*-[PtX$_2$(CO)$_2$] complexes [29,30,160] have confirmed these general effects and have also indicated that the Pt–C stretching force constants are, not too surprisingly, more sensitive to the nature of the other ligands about Pt than the C–O stretching force constant [161].

Infrared methods have also been used [162] to determine equilibrium constants, K_{eq}, for the reaction

$$[{}^n\mathrm{Bu_4N}]^+[(\mathrm{CO})\mathrm{PtCl_2X}]^- + \text{4-Z-py} \rightleftharpoons [{}^n\mathrm{Bu_4NX}] + cis\text{-}[\mathrm{Pt(CO)Cl_2(4\text{-}Z\text{-}py)}]$$

(where X = Cl, Br or I, and 4-Z-py = 4-substituted pyridines with Z = H, Me, Et, ^{t}Bu, Ac). By observing ν(CO) for such systems in chloroform, it has been found that the more electron-releasing Z results in a larger K_{eq} which is independent of X, and that the effect of changing Z is much greater than that of changing X. It has also been observed that displacement reactions lead to [PtCl$_2$X(CO)]$^-$ (X = Cl or Br) during IR measurement [163], in metal-halide IR cells, of [(Zpy)PtCl$_2$(CO)] in acetonitrile.

In view of their general chemical characteristics, but especially because of the presence of ^{195}Pt (nuclear spin 1/2) in 33% natural abundance, platinum carbonyls are well-suited to NMR studies. In recent years, ^{13}C NMR

TABLE 4

C–O stretching frequencies (cm^{-1}) in some Pt(II) carbonyls

Complex	X			Ref.
	Cl	Br	I	
cis-[Pt(CO)X$_3$]$^-$	2132	2112	2088	38
[PtX$_2$(CO)$_2$]	2152	2130	2112	9
[Pt(bipy)(CO)X]	2145	2132	2120	155
cis-[(PEt$_3$)PtX$_2$(CO)]	2100	2094	2085	19

investigations have been numerous [23,24,29,30,164–172] and productive. By this technique, the electronic effects of X and L in the complexes $Pt(CO)LX_2$ (X = Cl, L = CO, MeCN, Py, or PyO) on $^1J(PtC)$ and $\delta(^{13}CO)$ have been examined and correlated with the electron-donating ability and π-electron accepting ability of the *trans* ligands [166]. In the ^{13}C NMR spectra of *trans*-$[Pt(CO)Cl_2(4\text{-}X\text{-}py)]$ complexes (4-Xpy = 4-substituted pyridines), small changes in the carbonyl chemical shifts and $^1J(PtC)$ values are observed [165–167] and have been interpreted in terms of small fluctuations in the σ-donor component of the Pt–C bonds. For the complexes $[Pt(PR_3)(CO)X(R)]$ (R = alkyl or aryl), the carbonyl ^{13}C NMR chemical shifts, as well as the corresponding $^1J(PtC)$ values, are affected markedly by changes in both the *cis* and *trans* ligands relative to CO, while the electronic charge on the complex does not have a dominating influence on these parameters [23,29,170]. It has also been observed that for the carbonyl group *trans* to phosphine in $[PtX_2(CO)(PR_3)]$, $^1J(PtC)$ is large and positive; the *cis* two-bond $^{31}P–Pt–^{13}C$ coupling is small and negative, whereas the *trans* two-bond coupling is large and positive [172].

The ^{13}C NMR spectra of $[MePt(AsMe_3)_2CO]PF_6$ and $[ClPt(AsMe_3)_2CO]PF_6$ have been recorded and $^1J(PtC)$ coupling constants for sp^3, sp^2 and sp hybridized carbon atoms have been compared [173,174]. The carbonyl carbon in the methyl cation resonates at higher field than for other carbonyl derivatives and is slightly shielded relative to free CO. This indicates that in the cation there is little Pt *d* to carbonyl π^* bonding. This lack of π-back-bonding is responsible for the susceptibility of the CO in cationic complexes towards nucleophilic attack (see later) [173].

The ^{13}C NMR chemical shifts and $^1J(PtC)$ values for carbonyl carbon in a series of anionic, neutral and cationic platinum(II) carbonyl complexes of the types $[HPy][PtCl_3(CO)]$, *cis*-$[PtCl_2(CO)(AsEt_3)]$, and *trans*-$[PtX(CO)L_2]BF_4$ (X = H, C_6H_4Cl, CH_2Ph, NCS, NO_3, Cl, Br or I, and L = PEt_3, PPh_3 or $AsEt_3$) have been measured. The chemical shift decreases with increasingly negative charge on the complex, but shows little sensitivity to the *cis* ligands. For ligands X of high *trans* influence, the value of $^1J(PtC)$ falls in the range 960–990 Hz but for ligands of low *trans* influence the values range between 1658 and 1817 Hz [175].

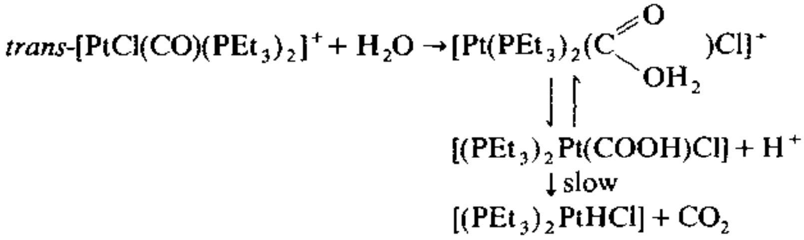
In the reaction of CO with $[PtLX_2]_2$, (L = PR_3 or AsR_3) it is usually assumed that the product has *cis* geometry, but in fact the initial product is the *trans* isomer [23,24,29,170]. *Trans–cis* isomerization is rapid and can be completed in less than one hour in the presence of CO, although if the excess CO is removed, isomerization is slower and takes one to three days [23,24,170]. The *cis* geometry in $[PtX_2(PR_3)(CO)]$ complexes has been confirmed by X-ray analysis. Thus, crystals of $[PtCl_2(CO)(PEt_3)]$ are orthorhombic, space group $P_{Ca}{}^2$, in which platinum has a *cis* square-planar geometry [176]. However, crystals of [$PtCl_2(CO)(PPh_3)$] belong to the triclinic system, space group *P1* with $a = 10.482(1)$, $b = 9.593(1)$, $c = 11.007(1)$ Å and $\alpha = 97.57(1)$, $\beta = 117.96(1)$ and $\gamma = 93.80(1)$ [177,178]. The molecules have a slightly distorted square planar arrangement about platinum, and the Pt–C and Pt–Cl (*trans* to CO) bond lengths indicate that CO possesses π-acceptor properties and exerts an extremely small *trans*-influence on the Pt–Cl bond. These conclusions are consistent with those reached from the crystal structure determination of tetrabutylammonium trichlorocarbonyl platinate(II) [179]; the crystals are monoclinic, of the *P2* space group.

H. SOME CHEMICAL REACTIONS OF PLATINUM CARBONYLS

No attempt will be made in this section to describe all the various reactions which platinum carbonyls can undergo. Many of these are identical to those of other platinum compounds and are not unique to the carbonyls. Instead, only those recent chemical studies with some relation to catalytic behaviour will be described and these consist essentially of reactions of coordinated carbon monoxide.

The platinum carbonyls have been particularly valuable in studies of hydrolytic reactions of carbonyls. Much of this work was generated from the preparation of cationic platinum carbonyl complexes, in which because of the cationic charge, the coordinated CO is particularly susceptible to nucleophilic attack by water and other hydroxylic reagents. Although such cations can be easily prepared from dihalides [11], they have also been produced by much more exotic routes. A particularly remarkable reaction is that of *trans*-[$PtHCl(PEt_3)_2$] with tetrafluoroethylene in benzene at 90°C. One of the products, originally thought [180] to be the π-tetrafluoroethylene complex of the hydride, was later shown [181] to be *trans*-[$PtCl(CO)(PEt_3)_2]^+BF_4^-$; thus, under remarkably mild conditions, the Pt(II) hydride and C_2F_4 with small amounts of water present in the solvent, generate HF, and thus the BF_4^- anion, and also produce CO allowing the carbonyl cation to be generated. An additional bonus from this reaction is that it also produced for the first time the SiF_5^- anion! It was also shown that a more mundane synthesis of the carbonyl cation involves the reaction of *trans*-[$PtHCl(PEt_3)_2$] with HBF_4 and CO under pressure [181].

As already stated, the resistance to hydrolysis of platinum(II) carbonyls decreases in going from anionic to cationic complexes, i.e. in the order $[PtX_3(CO)]^- > [PtX_2(CO)]_2 > [PtX_2(CO)_2] > [PtX(CO)L_2]^+$ [182]. The ready hydrolysis of the latter type of cation proceeds as follows



$$trans\text{-}[PtCl(CO)(PEt_3)_2]^+ + H_2O \rightarrow [Pt(PEt_3)_2(C(=O)OH_2)Cl]^+ \rightleftharpoons [(PEt_3)_2Pt(COOH)Cl] + H^+ \xrightarrow{slow} [(PEt_3)_2PtHCl] + CO_2$$

This reaction route was initially proposed by Clark and Jacobs [183] and recently confirmed by Catellani and Halpern [184] who were able to isolate the intermediate species, $[(PEt_3)_2Pt(COOH)Cl]$. This carboxylate species is stable in air for several hours at room temperature, but decomposes on prolonged standing, or in vacuo, or on heating at 170°C for 15 min giving the Pt(II) hydride and carbon dioxide. The interest in these and related systems arises from the ease with which one can employ them to study the individual chemical steps related to the metal catalyzed conversion of carbon monoxide to carbon dioxide.

Analogous reactions occur when cationic Pt(II) carbonyls are treated with methanol or ethanol; carboxylic acid esters can be readily isolated [185].

$$trans\text{-}\left[(PEt_3)_2Pt(CO)Cl\right]^+ + ROH \rightleftharpoons trans\text{-}\left[(PEt_3)_2Pt(COOR)Cl\right] + H^+$$

Such ester complexes exchange the ester group readily with other alcohols and can be converted to hydrides by treatment with water in the presence of an ammonium or potassium halide as catalyst [186].

$$\begin{array}{l}[(Ph_3P)_2Pt(COOR)Cl] + R'OH \rightleftharpoons [(Ph_3P)_2Pt(COOR')Cl] + ROH \\ \qquad\qquad H_2O \\ \qquad\qquad \downarrow NH_4Cl/KCl \\ \quad trans\text{-}[(PtHCl(PEt_3)_2]\end{array}$$

From a kinetic study of such reactions with alcohols using the system

$$\left[(Ph_3P)_2PtCl(CO)\right]^+ + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[(Ph_3P)_2Pt(COOR)Cl\right] + H^+$$

a mechanism has been deduced [187] which involves nucleophilic attack by alcohol on the carbon atom of coordinated CO. Not surprisingly, then, the ease of formation of the carboxylate complexes decreases in the order, $MeOH > MeOCH_2CH_2OH > \sim EtOH > PhCH_2OH > {}^iPrOH > {}^tBuOH$, which is the order of increasing steric bulk of the alcohol. Moreover, such nucleophilic reactions with water or alcohols are markedly ligand dependent [188]. Thus, of the complexes *trans*-$[(ER_3)_2PtCl(CO)]BF_4$, ($E = As$ or Sb, $R = Et$ or Ph), only *trans*-$[(AsEt_3)_2PtHCl]$ and CO_2; *trans*-

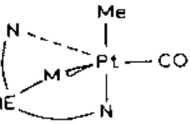
$[(AsPh_3)_2Pt(CO)Cl]^+$ reacted readily with methanol or ethanol to give the alkoxycarbonyl species $[Pt(AsPh_3)_2(COOR)Cl]$ (R = Me or Et) but these did not produce the corresponding hydride on treatment with water in the presence of a salt catalyst. The cationic stibine carbonyls did not react with either water or alcohols, so that the overall susceptibility towards such hydrolytic reactions decreases with the nature of the ligand in the order, $PR_3 > AsR_3 > SbR_3$.

Instead of alcohols, primary or secondary amines can also be used in these reactions. Thus, the cation *trans*-$[(ER_3)_2PtCl(CO)]^+$ (E = P or As) reacts with primary or secondary amines to give carboxamide complexes, *trans*-$[(ER_3)_2PtCl(CONR'R'')]$ (R', R″ = H or alkyl) which can also be prepared by the reactions of $[(PR_3)_2PtCl_2]$ with amines in presence of CO [189,190]. The latter reaction, however, with primary amines yields $[(PR_3)_2Pt(CO)_2]$ in acetone [190]. There is a high barrier to rotation around the C–N bond of the carboxamido group in these complexes and this barrier is dependent on the bulk of the ligand [189].

Irradiation of alkoxycarbonylplatinum(II) complexes, *trans*-$[Pt(CO_2CH_2R)(PPh_3)_2Cl]$ (R = H, Me or Ph), in solution or in the solid state with 254 nm light causes dissociation of the alkoxycarbonyl ligand which then decomposes to CO and alkoxide ion [191]. The carbon monoxide so formed is recoordinated to form the stable product *trans*-$[PtCl(CO)(PPh_3)_2]^+$.

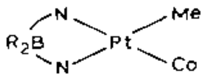
Cationic carbonyl complexes have also been prepared by a variety of alternative routes [14,186,192–195], including CO cleavage of chloro-bridged dimeric complexes [193]. Analogous cyclopentadienyl species $[(\eta\text{-}Cp)Pt(PR_3)(CO)]ClO_4$ ($PR_3 = PPh_3$, Ph_2MePh, $PhMe_2P$) have been prepared by the reactions of $[(\eta\text{-}Cp)Pt(PR_3)X]$ (X = Cl or Br) with $AgClO_4$ in acetone under a carbon monoxide atmosphere [196]. Exchange of the cyclopentadienyl group has been observed in the reactions of *cis*-$[Pt(CO)(Cp)_2(PPh_3)]$ with *cis*-$[PtCl_2(CO)PPh_3]$ and *cis*-$[PtCl_2(CO)(PPh_3)]$ with $[PtCl(Cp)(CO)PMe_2Ph]$; the products *trans*-$[PtCl(CO)(Cp)(PPh_3)]$ in the former case and *cis*-$[PtCl_2(CO)(PMe_2Ph)]$ plus *trans*-$[PtCl(Cp)(PPh_3)(CO)]$ in the latter were obtained [197]. Reaction of $(PPh_3)_2Pt(NCO)_2$ or $(PPh_3)_2PtN_3X$ ($X = N_3$, NCO, $NHSO_2C_6H_4Me$) with CO in ROH affords $[(PPh_3)_2Pt(NCO)(COOR)]$ [198,199]. Carbon monoxide reacts reversibly with *trans*-$[PtHCl(As^tBu_3)_2]$ to give *trans*-$[Pt(CO)H(As^tBu_3)_2]Cl$, but in the presence of $LiBF_4$ or $LiPF_6$ the cationic complexes *trans*-$[PtH(CO)(As^tBu_3)_2][X]$ ($X = BF_4$ or PF_6) are isolated [65]. Carbon monoxide reacts with $[(Ph_2MeP)_2Pt(C_2F_5)Cl]$ in the presence of $NaClO_4$ to give $[(Ph_2MeP)_2Pt(CF{=}CF_2)CO]ClO_4$ [200]. Reaction of $[Pt(PPh_3)_2Cl(RCO)]$ with $AgPF_6$ in ethanol gives $[Pt(PPh_3)_2(CO)R]^+$ but in acetonitrile products of the type $[Pt(PPh_3)_2(RCO)(MeCN)]^+$ are obtained [201]. *trans*-$[Pt(SnCl_3)PhL_2]$ ($L = PPh_3$ or $PMePh_2$) reacts with CO with the displacement of the trichlorostannate ligand to yield *trans*-$[PtPh(CO)L_2]^+SnCl_3^-$. In the absence of excess CO, the $SnCl_3^-$ anion subsequently attacks slowly as a nucleophile to generate *trans*-$[Pt(SnCl_3)(COPh)L_2]$ but in the presence of excess CO, dissociation of phosphine occurs [202]. A related sequence of reactions in that both involve the $SnCl_3$ ligand, has the $[Pt(SnCl_3)_2Cl(CO)]^-$ anion being treated with Ph_3P, 1,10-phenanthroline, or pyridine to yield $[(PPh_3)Pt(SnCl_3)_2CO]$, $[Pt(SnCl_3)_2(phen)(CO)]$, and $[Pt(SnCl_3)_2(Py)(CO)]$ respectively [203].

Somewhat related to the large class of cationic platinum carbonyls described above, most of which contain simple monodentate ligands, is the group of platinum carbonyls containing polypyrazolylborate ligands. Tris(pyrazolyl)borate and tris(pyrazolyl)methane complexes of the type **XIII** have been prepared by Clark et al. [17,204,205], as well as the bis(pyrazolyl)borate derivatives **XIV** [16]; only the tris(pyrazolyl)borate carbonyl is cationic, all other derivatives being neutral. Both the neutral borate and cationic methane carbonyls **XIII**, on the basis of NMR studies, are non-rigid in solution at room temperature, the non-rigidity apparently occurring through rotation of the tridentate ligand about the Pt–B or Pt–C axis making all pyrazolyl rings equivalent. However, an X-ray structure determination [206,207] of $[(HBpz_3)Pt(Me)CO]PF_6$ shows that the coordination about Pt is slightly distorted square-planar with only two of the three pyrazolyl groups coordinated to Pt. The uncoordinated pyrazole ring is disordered in the structure with the shortest intramolecular distance involving Pt and any non-hydrogen atom of that ring being 3.30(1) Å. This unusual structure contrasts with that of the analogous acetylenic compound containing hexafluorobut-2-yne π-bonded to Pt instead of CO; in this molecule, Pt has a trigonal bipyramidal five coordinate geometry in which all three pyrazole rings are coordinated to Pt [208]. Subsequently, variable temperature ^{13}C and ^1H NMR studies [209] of $[PtMe(HBpz_3)(CO)]^+PF_6^-$ gave spectra which indicate that, in the low exchange limit, there is pentacoordination of Pt, but with an intramolecular exchange which probably involves rotation of the $HBpz_3^-$ ligand about the Pt–B axis.



(E = B or C)

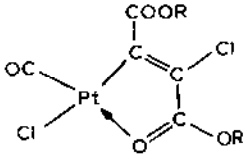
XIII



(R = C_2H_5)

XIV

The reactions of some platinum carbonyls with acetylenes, which also appear to involve, at least in some cases, reactions of the coordinated CO, have been investigated by Canziani et al. [210–214]. The carbonyl $Pt(CO)_2Cl_2$ reacts with dialkylacetylene dicarboxylate in benzene or toluene to give **XV**, which is stable in dry non-polar solvents under a CO atmosphere. Alcoholysis of the γ-alkoxy group is effected in **XV** by primary or secondary alcohols



(R = Me or Et)

XV

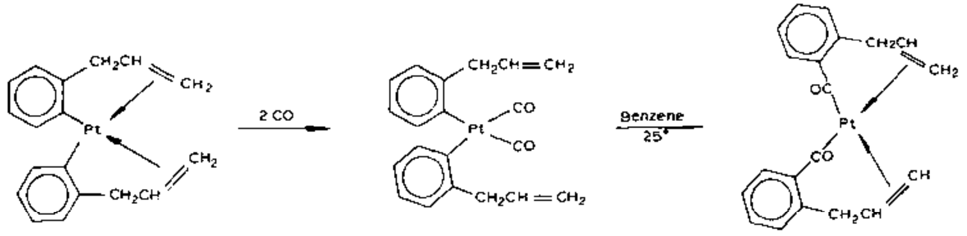
[214]. **XV** reacts with neutral donor ligands to afford $[Pt(CO)Cl\{C(COOR){=}C(COOR)Cl\}L]$ (L = Py or 4-Mepy) or $[PtCl\{C(COOR){=}C(COOR)Cl\}L_2]$ (L = $PMePh_2$, PPh_3, L_2 = dppe, 2,2′-dipyridyl or 4,4′-dimethyl-2,2′-bipyridine) [212,213]. Reaction with LiCl in chloroform gives an ionic product $[PtCl_2(CO)\{C(COOR){=}C(COOR)Cl\}]^-$ which can be isolated by the addition of bulky cations. X-ray analysis of $[PtCl(CO)\{C(COOMe){=}C(COO)(Cl)\}][N(PPh_3)_2]$ has shown that the anion has square-planar coordination around Pt and the carbonyl group is linearly coordinated to the platinum atom [213].

Similarly, $Pt(CO)_2Cl_2$ reacts with 3-hexyne to give four products, [carbonylplatinum bis(di-μ-chloro(chloro)tetraethyl cyclobutadiene)platinum], [bis{dichloro(tetraethylcyclopentadienone)}platinum], [dichloro(tetraethylcyclobutadiene)platinum] and [dichloro(tetraethyl-*p*-benzoquinone)platinum] [211]. A similar reaction occurs with 2-butyne to give analogous methyl derivatives [211]. Reaction with diphenylacetylene affords three products: hexaphenylbenzene, tetracyclone and tetraphenylcyclobutadiene platinum complex, $[Pt(C_{28}H_{20})Cl_2]_n$ [210]. Cationic alkoxy carbonyl complexes, $[Pt(COOR)(CO)(PPh_3)_2][BF_4]$ (R = Me or Et) also react with acetylenes [215]. Monosubstituted acetylenes in methanol produce *trans*$[Pt(C{\equiv}CR')(CO)(PPh_3)_2][BF_4]$ (R′ = Me, Ph or COOMe) whereas disubstituted acetylenes yield β-alkoxyvinyl complexes of the type *trans*-$[Pt(CO)\{CR'{=}CR'(OR'')\}(PPh_3)_2][BF_4]$.

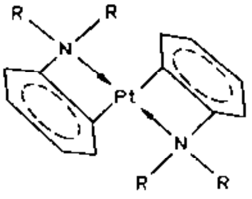
I. CARBON MONOXIDE INSERTION AND DECARBONYLATION REACTIONS

The carbonylation and decarbonylation reactions of four coordinate Pt(II) complexes are less facile than those of Pd(II). This is attributed to the lesser tendency of platinum to expand its coordination shell to five. Thus, the carbonylation reaction of *trans*-$[PtMeX(PEt_3)_2]$ (X = Cl, Br) requires [216,217] pressure of 80 atm and a temperature of 90°C. Similarly vigorous conditions are needed for the carbonylation of *cis*-[$PtMeCl(PEt_3)_2$], *trans*-[$PtEtI(PEt_3)_2$], *cis* and *trans*-[$PtPhCl(PEt_3)_2$], *trans*-[$PtPhI(PEt_3)_2$] and *trans*-[$PtMeCl(PMe_2Ph)_2$] [217,218]. Only one Pt–CH_3 bond participates in the carbonylation of [$PtMe_2(Et_2PCH_2CH_2PEt_2)$] but loss of methyl groups from *cis*-[$PtMe_2(PR_3)_2$] (R = Et, Ph) has been observed during carbonylation. Insertion of CO into the Pt–CH_3 bond of *trans*-[$PtMeI(PPh_3)_2$] does not occur even under pressure and at 120°C; however, insertion of CO under ambient conditions has been observed in [$(MeOC_{10}H_{12})Pt(PPh_3)Cl$] ($MeOC_{10}H_{12}$ = 7-methoxytricyclo[5,2,1,$0^{2,5}$]dec-4-en-8-yl [219]. An irreversible insertion of CO into the platinum–cyclohexenyl bond at ambient conditions has been observed in [$Pt(COOMe)(C_6H_9)$(dppp)]. However, similar complexes containing dppe or *cis*-1,2-bis(diphenylphosphino)ethylene have been found to be inactive towards CO [220].

Furthermore, carbonylation can often be induced by the addition of neutral ligands to an existing carbonyl complex. Thus, [$Pt(Et)(CO)(AsPh_3)Cl$] reacts with a second equivalent of triphenylarsine to generate [$Pt(EtCO)(AsPh_3)_2Cl$] [221]. A similar carbonylation process occurs when PPh_3 or P^nBu_3 reacts with [$(C_8H_{17})Pt(CO)Cl$] [222,223]. Platinum chelate complexes such as **XVI** react with carbon monoxide to give carbonyls, **XVII**, which contain uncoordinated olefins. Further reaction occurs in benzene at 25°C with CO insertion into the Pt–C–σ-bond to give aryl derivatives, **XVIII**, containing coordinated olefins [224]. In the same way, carbon monoxide insertion occurs in cationic platinum π-allyl complexes, [$(\pi\text{-}C_3H_3R_2)Pt(PPh_3)_2]^+Cl^-$ to give [$(PPh_3)_2PtCl(COR{=}CRMe)$] [225]. Nitrogen ligands can also induce carbonylation. For example, complexes of the type **XIX** react with carbon monoxide to produce various Pt(II) acyl derivatives [226], and reactions of $Pt(PPh_3)_n(CO)_{4-n}$ ($n = 2,3$) with RN_3 (toluene-*p*-sulphonyl azide) in protic solvents such as methanol or ethanol (R′OH) yield *trans*-[$Pt(PPh_3)_2(COOR')_2$] for $n = 2$ and [$Pt(PPh_3)_2N_3(NRCOOR)$] for $n = 3$ [227]. Acyl complexes, *trans*-[$PtCl(COR)(PPh_3)_2$] (R = ^{n}Pr, $^nC_6H_{13}$), are also formed during hydroformylation reactions of olefins employing *cis*-$PtCl_2(PPh_3)_2$ [228–230]. The aryl compound, [$PtCl(CO^nC_6H_{13})(PPh_3)_2$] crystallizes in the triclinic space group $P\bar{1}$ and



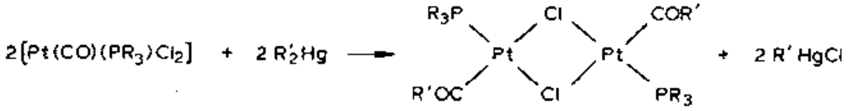
XVI XVII XVIII



XIX

has a square planar platinum atom with chlorine *trans* to the acyl group [228].

Indeed, other reasonably strong Lewis acids can also induce carbonylation of a Pt(II) carbonyl. Complexes of the type [Pt(CO)(PR_3)Cl_2] react with HgR_2 under mild conditions to give binuclear products [Pt(R′CO)PR_3Cl]$_2$ [231–234], although treatment of the P(*o*-tolyl)$_3$, $AsMePh_2$ or $AsPh_3$ complexes with Ph_2Hg gives only [PtCl(CO)LPh] [234]. Mercury alkynyls, Hg(C≡CR)$_2$ (R = Me or Ph) on the other hand do not produce platinum acyl when treated with [Pt(CO)Cl_2L] but yield platinum alkynyl compounds, [Pt(CO)(C≡CR)ClL] and [Pt(CO)(C≡CR)$_2$L] [235].

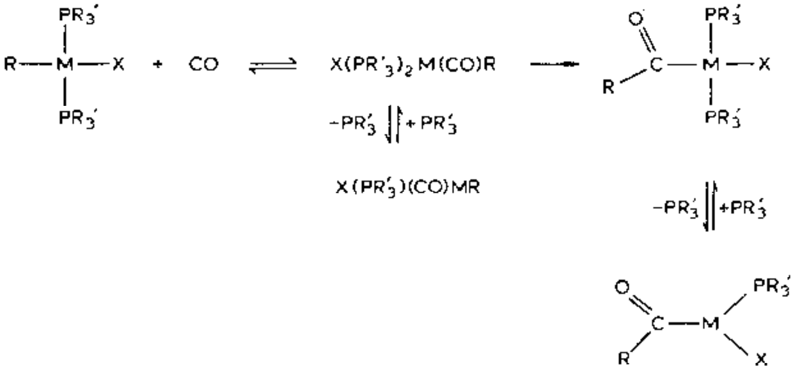


Low temperature NMR studies show that the reaction between diphenylmercury and $PtCl_2$(CO)L gives first [PtClPh(CO)L] which then undergoes carbonyl insertion. The solution equilibrium between [Pt(CO)PhXL] and the binuclear benzoyl complexes has been shown to be influenced by the bridging ability of X; stronger bridges favour formation of the carbonylation product. Steric and electronic properties of the ligands are also important, with increasing bulk of the ligand L favoring the mononuclear species [234].

Replacing the phenyl group by other R groups also affects the equilibrium position between the acyl and carbonyl complexes and the tendency to form acyl decreases in the order R = Et > Ph > Me > CH_2Ph(= 0) [233,236]. The substituents at *meta* and *para* positions in the aryl group also play an important role on the R migration process [237]. Electron donating groups on *meta* or *para* positions promote the carbonyl-insertion reaction and the order follows the sequence of the Hammett σ constant whereas the electron withdrawing substituents inhibit this process. Due to steric crowding the *ortho* substituted aryls do not fit the sequence. Further, the enthalpies of the reactions (aryl → aroyl) have been found to be less negative with increasing electron withdrawing power of the aryl groups [237].

The detailed mechanistic steps involved in carbonylation reactions of

Pt(II) complexes have been studied by several groups over the past 8–10 years. Mawby and co-workers [238] examined the kinetics of the reactions of $[Pt(CO)(PPh_3)MeI]$ with L = tertiary phosphine and concluded that the intramolecular rearrangement to give the three-coordinate intermediate $[Pt(PPh_3)ICOMe)]$ is rate-determining, and is followed by rapid combination with L to give $[Pt(PPh_3)I(COMe)L]$. A more extensive study [239] of the carbonylation of a wide variety of complexes $MXR(ER'_3)_2$, where M = Ni, Pd or Pt; X = Cl, Br or I; E = P, As or Sb; R′ = Ph, c-Hx, Et, OPh, etc., showed that pseudo first-order kinetics generally applied, and from the reactions with trialkylphosphine ligands with electron-donating substituents, that stepwise reactions were involved. The data were explained by the mechanism



in which both associative and dissociative steps are involved. A later study established that the associative pathway is sensitive to the electronic character of the migrating organic group. The mechanism is also sensitive to the nature of the solvent medium, as another study [241] employing ^{31}P NMR spectroscopy, has demonstrated. Thus, with *trans*-$[PtX(Ph)(PR_3)_2]$, carbonyl addition gives a metastable five-coordinate intermediate in non-polar solvents, which in polar solvents eliminates a halide to give the ionic species *trans*-$[Pt(Ph)(CO)(PPh_3)_2]X$. Loss of phosphine from the five-coordinate intermediates gives two isomers of $[PtX(Ph)(CO)(PPh_3)]$ which convert to the remaining isomer with Ph *trans* to PR_3 before migration of Ph occurs to give the benzoyl complex. A direct carbonyl insertion route from a five coordinate intermediate is also operative; it is independent of phosphine elimination pathways and becomes the predominant pathway with more nucleophilic phosphine ligands [240,241].

There is also evidence that, in at least some cases, the nature of the anionic ligand in the above phenyl–platinum complexes influences the carbonylation pathway. Thus, in the carbonylation of *trans*-$[Pt(SnCl_3)(Ph)$

$(PPh_3)_2]$, the mechanism involves formation of *trans*-$[Pt(CO)(Ph)(PPh_3)_2]^+$-$SnCl_3^-$ which rearranges to *trans*-$[Pt(COPh)(SnCl_3)(PPh_3)_2]$. Phosphine dissociation does not contribute significantly to the overall rate of carbonylation, and the non-dissociative route is favoured, regardless of the electronic nature of the tertiary phosphine [202].

On the other hand, in the presence of excess CO, an alternative route involving phosphine dissociation operates [202]. In these reactions, carbonylation is obviously induced by the nucleophilic character of the $-SnCl_3$ ligand; in contrast the reactions of *trans*-$[PtCl(CO)(PPh_3)_2][ClO_4]$ with a range of tin, lead, mercury and boron organometallic compounds result in the replacement of the chloride ligand by an organic group, although a small amount of acyl compound is formed with $Hg(4\text{-}MeC_6H_4)_2$ [242]. Related reactions are those of the carbonyl complexes *cis*-$[Pt(CO)Cl_2L]$ with $SnMe_3R$ to give the binuclear acyl complexes $[Pt_2(COR)_2Cl_2L_2]$ which exist as a mixture of *cis* and *trans* isomers [243,244].

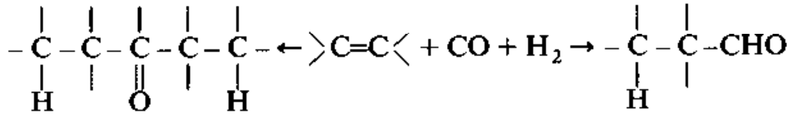
The reverse process, carbon monoxide elimination from acyl complexes of the type $(RCO)PtX(PR_3)_2$, requires high temperatures [217,245–247]. However, such reductive elimination from acyl platinum(IV) compounds can give platinum(II) alkyl derivatives cleanly [248–250]. In the case of Pt(II) acyl compounds, decarbonylation is promoted [251] by tin(II) chloride; a recent, detailed study shows this to be due to the combination of properties of the $-SnCl_3$ ligand, namely its property as a good leaving group combined with its nucleophilicity [202].

J. PLATINUM CARBONYLS IN HOMOGENEOUS CATALYSIS

In this section an attempt is made to summarize the literature dealing with organic syntheses utilizing carbon monoxide which involve the use of platinum carbonyls, or other platinum compounds from which carbonyls may be generated, as catalysts. Such organic reactions, in which carbon monoxide and/or syn-gas are used as reactants and platinum compounds as catalysts, include hydroformylation, carbonylation, hydrogenation, and the water gas-shift reaction.

(i) Hydroformylation reactions

The hydroformylation reaction, which has been extensively investigated, is one of the oldest carbonylation reactions. As discovered by Roelen in 1938 [251a] it can be represented as



$$-\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\leftarrow\;>\mathrm{C{=}C}<\;+\mathrm{CO}+\mathrm{H_2}\rightarrow-\overset{|}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{CHO}$$

Originally, cobalt compounds were employed as catalysts, but the catalytic activities of other metals were quickly explored [1–3]. Square planar Pt(II) complexes were found to show only slight catalytic activity, requiring a high temperature to produce reasonable conversions; however, under such conditions the selectivity favouring aldehyde formation is reduced [252–254]. A major advance was achieved with the discovery that the addition of tin(II) chloride to the system greatly enhanced the catalytic activity of the Pt(II) species [228–230,255]. A variety of platinum complexes has been described in the patent literature [252–257] as hydroformylation catalysts, but these are essentially catalyst precursors and the active catalyst must contain both hydrido and carbonyl ligands. Certainly, Pt(II) hydride and carbonyl species must be immediate precursors to the active catalysts. Hsu and Orchin [258] were among the first to use a Pt(II) hydride as catalyst precursor; $[HPt(SnCl_3)(CO)(PPh_3)_2]$ was employed to catalyze hydroformylation of 1-pentene at 100°C and 3000 p.s.i. of synthesis gas (hydrogen and carbon monoxide) with conversion (95%) to straight chain aldehyde. Similarly, *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ and *trans*-$[PtHCl(PPh_3)_2]$ have been used as hydroformylation catalysts. More recently, platinum carbonyl complexes, $[Pt(ER_3)(CO)(Cl)_2]$, combined with $SnCl_2$, have been used as hydroformylation catalyst precursors [259–264]. These readily convert terminal aliphatic monoenes to linear aldehydes, but hydroformylation is more difficult with hindered internal olefins, cyclic, and conjugated or aromatic olefins [229,261,262]. The efficiency of such catalyst systems also varies with the solvent and with temperature [261]. The effect of the various ligands about platinum on such catalytic activity has also been investigated [261]. It was found that, for ligands of similar basicity, a smaller size of the ligand gave a more effective catalyst precursor (thus, $PEt_3 \sim P^nBu_3 > P(c\text{-}Hx)_3$), while for ligands of about the same size, those of lower basicity gave more effective catalysts [(i.e. $P(p\text{-tol})_3 \sim PPh_3 < P(p\text{-}FC_6H_4)_3$]. Overall, neither steric nor electronic factors govern the reactions, but those Pt(II) complexes with smaller ligands certainly displayed greater catalytic activity [261].

From the earlier work by Hsu and Orchin [258], by Consiglio and Pino [265,266], Schwager and Knifton [267–269] and others [229,270,271], it was suggested that the equilibrium

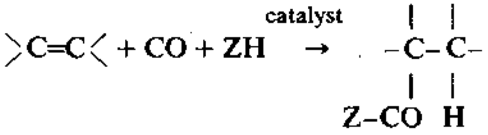
$$[Pt(PR_3)_3(CO)H]^+SnCl_3^- \rightleftharpoons Pt(PR_3)_2(CO)(H)(SnCl_3)$$

was important in these processes, but there is still some degree of uncertainty about the significance of the making and breaking of the Pt–Sn bond.

Similar hydroformylation reactions have been investigated using $PtCl_2$–diphosphine–$SnCl_2$ systems [272–275]. In general, catalytic activity is reduced [267] by the use of such chelating diphosphines, but nevertheless, the rate and selectivity of *n*-aldehyde formation are found to be strongly dependent on the methylene chain length of the diphosphine, both being at a maximum for $n = 4$ [273].

(ii) Carbonylations (Reppe-type reactions)

Catalyzed carbonylations of olefins in the presence of CO and an appropriate protic compound (e.g. water, alcohols, amines, carboxylic acids, mercaptans, etc.) have been used for some time for the synthesis of carboxylic acids.



$$>C{=}C< + CO + ZH \xrightarrow{\text{catalyst}} -\underset{\underset{\text{Z-CO}}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}-$$

where $Z = -OH, -OR, -NHR, -NR_2, -OOCR', -SR'$

The first such synthesis by Reppe in 1940 used nickel tetracarbonyl as catalyst, and subsequently such catalyzed carbonylations have become very important industrially. In addition to the use of other metal carbonyls as catalysts, platinum compounds also display reasonable catalytic activity under relatively mild conditions. Using H_2PtCl_6–$SnCl_2$, γ-olefins can be carbonylated with CO and methanol to give an 85% yield of the corresponding linear methyl esters and a 15% yield of the branched ester [276,277]. The presence of water is also apparently necessary since H_2PtCl_6 with anhydrous $SnCl_2$ shows no catalytic activity while with $SnCl_2 \cdot 2\ H_2O$ such catalysis is observed [276]. The carbonylation of alkyl chloride can similarly be catalyzed effectively [278] by H_2PtCl_6–$SnCl_2 \cdot 2\ H_2O$.

Linear carboxylic acid esters can also be prepared [279] from linear γ-olefins in high yields (> 98%) by catalysis with ligand stabilized platinum(II)–group IVB metal halide complexes. The activity of each catalyst is highly sensitive to the nature of the ligands coordinated to platinum, but no correlation could be found between the catalytic performance of these platinum(II)–tin(II) chloride systems and either the steric or electron donor properties of the coordinated group VB and group VIB ligands; generally speaking, however, high yields of the linear esters are obtained with strong π-acceptor ligands of low basicity. In the absence of tin(II) chloride, there is no carbonylation.

(iii) Hydrogenation reactions

There have been only a few reported instances of the use of platinum carbonyls as catalysts in hydrogenation reactions. Recently, platinum carbonyl clusters supported on MgO, La_2O_3 or ZrO_2 have been used as catalysts in methanol synthesis [280], and phosphine-functionalized poly(styrene-divinylbenzene) and silica-supported bimetallic carbonyl clusters, $[Fe_2Pt(CO)_8(Ph_2P\text{–}Ⓟ)_2]$ (Ⓟ = poly(styrene-divinylbenzene), $[Fe_2Pt(CO)_8(PPh_3)_2]$, $[RuPt_2(CO)_5(Ph_2P\text{–}Ⓟ)_3]$ and $[RuPt_2(CO)_5(PPh_3)_3]$ have been employed [281] as catalysts in the hydrogenation of ethylene. The heteronuclear platinum carbonyl clusters, $[Pt_2Co_2(CO)_8(PPh_3)_2]$ and $[Pt(C_6H_{11}NC)_2\{Mo(CO)_3(\eta\text{-}Cp)_3\}_2]$ have been found to be good catalysts for hydrogenation of terminal olefins [282].

Another platinum carbonyl cluster, $[N^nBu_4][\{Pt_3(CO)_6\}_5]$ has been employed for homogeneous hydrogenation of benzaldehyde, heptanal, cyclohexanone, cyclohexene, acetonitrile and benzonitrile [283]. Benzaldehyde hydrogenated most readily and the nature of the products depends on the pressure of hydrogen used. At low hydrogen pressure benzyl alcohol is formed while at comparatively high hydrogen pressure a mixture of benzene and methanol is obtained [283].

$$PhCHO + H_2 \xrightarrow{\text{catalyst}} PhCH_2OH \xrightarrow[\text{catalyst}]{H_2} C_6H_6 + CH_3OH$$

(iv) Water-gas shift reaction

The water-gas shift reaction, described as

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

$\Delta G^0_{298} = 4.76$ kcal mol^{-1}, finds industrial application in CO removal, hydrogen production, and adjustment of $H_2:CO$ ratios in synthesis gas. A variety of metal complexes has been used to catalyze the reaction including, more recently, complexes of platinum [284–288]. Cheng and Eisenberg [286], using K_2PtCl_4 and $SnCl_4 \cdot 5\,H_2O$ in $AcOH/HCl/H_2O$ mixtures, found that the catalyzed reaction did not occur in the absence of tin(IV) chloride, in the presence of a large excess of tin(IV) chloride, in the absence of acetic acid or of the strong protic acid or of the chloride source. They were able to isolate two platinum carbonyl complexes $[PtCl(CO)(SnCl_3)_2]^-$ and $[PtCl_2(CO)SnCl_3]^-$ from the reaction mixtures as their tetrabutylammonium salts; the bis complex, $[PtCl(CO)(SnCl_3)_2]^-$ gives hydrogen and a little CO_2 when heated in the $AcOH/HCl/H_2O$ reaction medium under nitrogen, whereas the monocomplex $[PtCl_2(CO)SnCl_3]^-$ gives CO_2 and traces of hydrogen in the same solvent mixture under CO. The authors thus conclude that the Sn(II)/Sn(IV) redox couple ($SnCl_6^{2-} + 2\,e^- \rightleftharpoons SnCl_3^- + 3\,Cl^-$) is involved in the reaction and that there are two components to the water-gas shift reaction

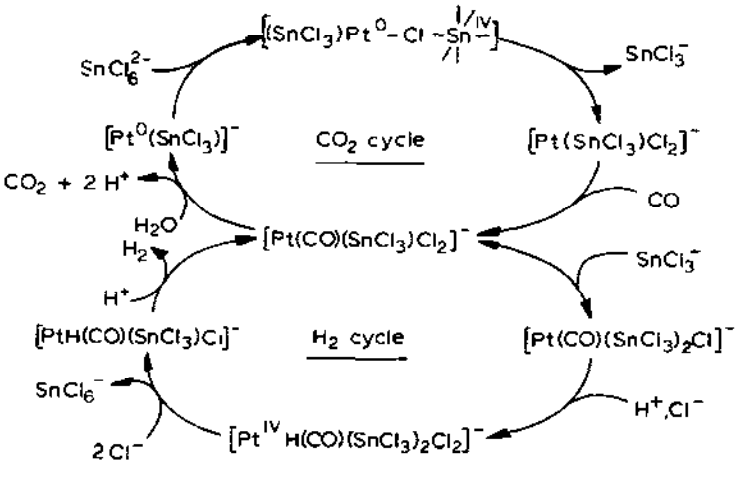
$$CO + H_2 + SnCl_6^{2-} \overset{\text{Pt species}}{\rightleftharpoons} CO_2 + 2\,H^+ + 3\,Cl^-$$

and

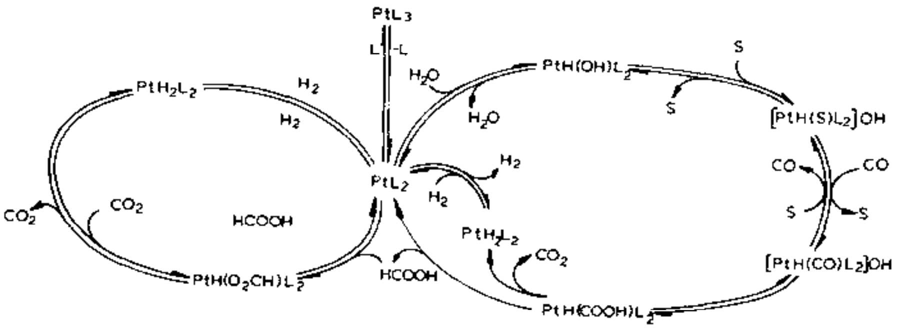
$$2\,H^+ + SnCl_3^- + 3\,Cl^- \overset{\text{Pt species}}{\rightleftharpoons} H_2 + SnCl_6^{2-}$$

The overall reaction mechanism which Cheng and Eisenberg [286] then proposed is shown in Scheme 1.

Otsuka and co-workers [287] have used platinum(0) tertiary phosphine complexes, PtL_3, as catalysts in the water-gas shift reaction and have proposed the overall reaction sequence shown in Scheme 2. The first cycle involves formation of *trans*-$[Pt(PR_3)_2H(CO)]OH$, (I), which has been isolated as the BPh_4^- salt, and which is probably formed by the oxidative addition of water to PtL_2, which in turn is formed by dissociation of PtL_3. In the case of the triethylphosphine species, the complex $[PtH(PEt_3)_3]OH$ is isolated. Nucleophilic attack of OH^- on the coordinated CO of (I) then gives $[PtH(COOH)L_2]$ which on thermal decomposition yields PtH_2L_2 and CO_2. Hydrogen from the dihydride is then eliminated to regenerate PtL_2. The involvement of the dihydride in the catalyzed reaction mixture has been confirmed by using dihydride as catalyst and then isolating *trans*-$[PtH(CO)L_2]OH$ (as the BPh_4^- salt) from the mixture. In the second cycle, the formation of formic acid from $PtH(COOH)L_2$ is proposed. The formic acid in the presence of PtL_3 is known and is believed to proceed through



Scheme 1. Probable mechanism for water-gas shift reaction using $K_2PtCl_4/SnCl_4$ as a catalyst.



Scheme 2. Probable mechanisms for water-gas shift reaction using PtL_3 ($L = P^iPr_3$).

oxidative addition of HCOOH to PtL_3 to give $[PtH(OOCH)L_2]$, followed by a β-hydrogen elimination step yielding PtH_2L_2 and CO_2. Decomposition of HCOOH has also been catalyzed and *trans*-$PtH(OOCH)L_2$ ($L = P^iPr_3$) has been prepared separately by CO_2 insertion into the Pt–H bond of PtH_2L_2.

Puddephatt and co-workers [142,288] have found that the binuclear complex $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]PF_6$ ($dppm = Ph_2PCH_2PPh_2$) acts as an active catalyst precursor for the water-gas shift reaction at low pressures of CO. When the catalytic solutions are evaporated in air, a tetranuclear cluster complex $[Pt_4(\mu\text{-}CO)_2(\mu\text{-dppm})_3\{Ph_2PCH_2P(O)Ph_2\}$ is isolated.

ACKNOWLEDGEMENT

The support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

REFERENCES

1 I. Wender and P. Pino, Organic Synthesis via Metal Carbonyls, Wiley, Toronto, Vol. I, 1968; Vol. II, 1977.
2 J. Falbe, Carbon Monoxide in Organic Synthesis, Engl. edn., Springer-Verlag, New York, 1970.
3 J. Falbe, New Syntheses with Carbon Monoxide, Springer-Verlag, New York, 1980.
4 E.P. Kündig, D. McIntosh, M. Moskovits and G.A. Ozin, J. Am. Chem. Soc., 95 (1973) 7234.
5 G. Booth, J. Chatt and P. Chini, Chem. Commun., (1965) 639.
6 P. Schützenberger, Bull. Soc. Chim. Fr., 14 (1870) 97; C.R. Acad. Sci., 70 (1870) 1134; J. Prakt. Chem., 4 (1871) 139.
7 J.M. Lutton and R.W. Parry, J. Am. Chem. Soc., 76 (1954) 4271.
8 L. Malatesta and L. Naldini, Gazz. Chim. Ital., 90 (1960) 1505.
9 R.J. Irving and E.A. Magnusson, J. Chem. Soc., (1956) 1860.
10 R.J. Irving and E.A. Magnusson, J. Chem. Soc., (1957) 2018.
11 M.J. Church and M.J. Mays, Chem. Commun., (1968) 435.

12 M.J. Church and M.J. Mays, J. Chem. Soc. A, (1968) 3074.
13 H.C. Clark and K.R. Dixon, J. Am. Chem. Soc., 91 (1969) 596.
14 W.J. Cherwinski and H.C. Clark, Inorg. Chem., 10 (1971) 2263.
15 H.C. Clark and L.E. Manzer, Inorg. Chem., 13 (1974) 1996.
16 H.C. Clark and K. von Werner, J. Organomet. Chem., 101 (1975) 347.
17 H.C. Clark and M.A. Mesubi, J. Organomet. Chem., 215 (1981) 131.
18 F. Mylius and F. Foerster, Chem. Ber., 24 (1891) 2424.
19 J. Chalt, N.P. Johnson and B.L. Shaw, J. Chem. Soc., (1964) 1662.
20 A.C. Smithies, M. Ryckeck and M. Orchin, J. Organomet. Chem., 12 (1968) 199.
21 J.R. Briggs, C. Crocker and B.L. Shaw, Inorg. Chim. Acta, 40 (1980) 245.
22 H.C. Clark, A.B. Goel, R.G. Goel and S. Goel, Inorg. Chem., 19 (1980) 3220.
23 G.K. Anderson and R.J. Cross, J. Chem. Soc., Dalton Trans., (1980) 1988.
24 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20 (1981) 944.
25 A.J. Chalk, Tetrahedron Lett., (1964) 2627.
26 W.H. Clement and M. Orchin, J. Organomet. Chem., 3 (1965) 98.
27 R. Ellis, T.A. Weil and M. Orchin, J. Am. Chem. Soc., 92 (1970) 1078.
28 T. Theophanides and P.C. Kong, Inorg. Chim. Acta, 5 (1971) 485.
29 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20 (1981) 1636.
30 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 20 (1981) 3607.
31 Ju.S. Varshavsky, N.N. Kiseleva, T.G. Cherkasova and N.A. Buzina, J. Organomet. Chem., 31 (1971) 119.
32 D.B. Dell-Amico and F. Calderazzo, Gazz. Chim. Ital., 109 (1979) 99.
33 D.B. Dell-Amico, F. Calderazzo and G. Dell-Amico, Gazz. Chim. Ital., 107 (1977) 101.
34 P.R. Brown, F.G.N. Cloke, M.L.H. Green and R.C. Tovey, J. Chem. Soc., Chem. Commun., (1982) 519.
35 W.H. Baddley and D.S. Hamilton, Inorg. Nucl. Chem. Lett., 10 (1974) 143.
36 J.V. Kingston and G.R. Scollary, J. Chem. Soc. A, (1971) 3765.
37 D.B. Dell-Amico, F. Calderazzo and G. Pelizzi, Inorg. Chem., 18 (1979) 1165.
38 M.J. Cleare and W. Griffith, J. Chem. Soc. A, (1970) 2788.
39 O.S. Shelkovnikova, N.K. Eremenko and V.A. Mikhailov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (1979) 97; Chem. Abstr., 92 (1980) 117256.
40 G. Booth and J. Chatt, J. Chem. Soc. A, (1969) 2131.
41 R.S. Nyholm, Proc. Chem. Soc., London, (1961) 273.
42 L. Malatesta and C. Cariello, J. Chem. Soc., (1958) 2323; J. Inorg. Nucl. Chem., 8 (1958) 561.
43 F. Cariati and R. Ugo, Chem. Ind. (Milan), 48 (1966) 1288; Chem. Abstr., 66 (1967) 65618.
44 P. Chini and G. Longoni, J. Chem. Soc. A, (1970) 1542.
45 F. Cariati, R. Ugo and F. Bonati, Chem. Ind., (1964) 1714.
46 P. Giannoccaro, A. Sacco and E. Vasapollo, Inorg. Chim. Acta, 37 (1979) L 455.
47 R. Whyman, J. Organomet. Chem., 63 (1973) 467.
48 S.A. Bhaduri, I. Bratt, B.F.G. Johnson, A. Khair, J.A. Segal, R. Walters and C. Zuccaro, J. Chem. Soc., Dalton Trans., (1981) 234.
49 G.K. Anderson, H.C. Clark and J.A. Davies, Organometallics, 1 (1982) 550.
50 J. Chatt and P. Chini, J. Chem. Soc. A, (1970) 1538.
51 W.J. Bland, R.D.W. Kemmitt and R.D. Moore, J. Chem. Soc., Dalton Trans., (1973) 1292.
52 M. Keubler, R. Ugo, S. Cenini and F. Conti, J. Chem. Soc., Dalton Trans., (1975) 1081.
53 R. Ugo, S. Cenini, M.F. Pilbrow, B. Diebl and G. Schneider, Inorg. Chim. Acta, 18 (1976) 113.

54 C.J. Wilson, M. Green and R.J. Mawby, J. Chem. Soc., Dalton Trans., (1974) 421.
55 D.M. Blake and C.J. Nyman, J. Am. Chem. Soc., 92 (1970) 5359.
56 D.M. Blake and L.M. Leung, Inorg. Chem., 11 (1972) 2879.
57 L. Malatesta, R. Ugo and S. Cenini, Adv. Chem. Ser., 62 (1966) 318.
58 V.G. Albano, P.L. Bellon and M. Manasserro, J. Organomet. Chem., 35 (1972) 423.
59 V.G. Albano, P.L. Bellon and M. Sansoni, Chem. Commun., (1969) 899.
60 V.G. Albano, G.M. Besso-Ricci and B.L. Bellon, Inorg. Chem., 8 (1969) 2109.
61 R.G. Vranka, L.F. Dahl, P. Chini and J. Chatt, J. Am. Chem. Soc., 91 (1969) 1574.
62 A. Albinati, G. Carturan and A. Musco, Inorg. Chim. Acta, 16 (1976) L3.
63 A. Albinati, Inorg. Chim. Acta, 22 (1977) L31.
64 H.C. Clark, A.B. Goel and C.S. Wong, Inorg. Chim. Acta, 34 (1979) 159.
65 R.G. Goel, W.O. Ogini and R.C. Srivastava, Inorg. Chem., 21 (1982) 1627.
66 R.G. Goel, W.O. Ogini and R.C. Srivastava, J. Organomet. Chem., 214 (1981) 405.
67 R.G. Goel and R.C. Srivastava, J. Organomet. Chem., 244 (1983) 303.
68 A. Moor, P.S. Pregosin and L.M. Venanzi, Inorg. Chim. Acta, 48 (1981) 153.
69 A. Moor, P.S. Pregosin and L.M. Venanzi, Inorg. Chim. Acta, 61 (1982) 135.
70 C.E. Briant, D.G. Evans and D.M.P. Mingos, J. Chem. Soc., Chem. Commun., (1982) 1144.
71 A. Albinati, A. Moor, P.S. Pregosin and L.M. Venanzi, J. Am. Chem. Soc., 104 (1982) 7672.
72 J.C. Calabrese, L.F. Dahl, P. Chini, G. Longoni and S. Martinengo, J. Am. Chem. Soc., 96 (1974) 2614.
73 G. Longoni and P. Chini, J. Am. Chem. Soc., 98 (1976) 7225.
74 R.G. Woolley, Inorg. Chem., 18 (1979) 2945.
75 R.G. Woolley, Platinum Met. Rev., 24 (1980) 26.
76 J.W. Lauher, J. Am. Chem. Soc., 101 (1979) 2604.
77 D.G. Evans and D.M.P. Mingos, Organometallics, 2 (1983) 435.
78 G. Apai, S.T. Lee, M.G. Mason, L.J. Gerenser and J.A. Gardner, J. Am. Chem. Soc., 101 (1979) 6880.
79 C.W. Brown, B.T. Heaton, A.D.C. Towly, P. Chini, A. Fumagalli and G. Longoni, J. Organomet. Chem., 181 (1979) 233.
80 C.W. Brown, B.T. Heaton, P. Chini, A. Fumagalli and G. Longoni, J. Chem. Soc., Chem. Commun., (1977) 309.
81 D.M. Washecheck, E.J. Wucherer, L.F. Dahl, A. Ceriotti, G. Longoni, M. Manassero, M. Sansoni and P. Chini, J. Am. Chem. Soc., 101 (1979) 6110.
82 J.P. Barbier, R. Bender, P. Braunstein, J. Fischer and L. Ricard, J. Chem. Res. (S), (1978) 230.
83 M.I. Bruce, G. Shaw and F.G.A. Stone, Chem. Commun., (1971) 1288.
84 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 1781.
85 V.G. Albano, G. Ciani, M.I. Bruce, G. Shaw and F.G.A. Stone, J. Organomet. Chem., 42 (1972) C99.
86 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 1082.
87 V.G. Albano and G. Ciani, J. Organomet. Chem., 66 (1974) 311.
88 R. Mason, J.A. Zubieta, A.T.T. Hsieh, J. Knight and M.J. Mays, Chem. Commun., (1972) 200.
89 R. Mason and J.A. Zubieta, J. Organomet. Chem., 66 (1974) 289.
90 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 1134.
91 M. Green, K.A. Mead, R.M. Mills, I.D. Salter, F.G.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1982) 51.

92 G. Longoni, M. Manassero and M. Sansoni, J. Am. Chem. Soc., 102 (1980) 3242.
93 G. Longoni, M. Manassero and M. Sansoni, J. Am. Chem. Soc., 102 (1980) 7973.
94 G. Longoni and F. Marazzoni, J. Chem. Soc., Dalton Trans., (1981) 1735.
95 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, J.L. Spencer, F.G.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1978) 260.
96 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 155.
97 M. Green, D.R. Hankey, M. Murray, A.G. Orpen and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1981) 689.
98 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 162.
99 L.J. Farrugia, M. Green, D.R. Hankey, A.G. Orpen and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1983) 310.
100 L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 1274.
101 J. Fisher, A. Mitschler, R. Weiss, J. Dehand and J.F. Nenning, J. Organomet. Chem., 91 (1975) C 37.
101a J. Dehand and J.F. Nenning, Inorg. Nucl. Chem. Lett., 10 (1974) 875.
102 P. Braunstein, J. Dehand and J.F. Nenning, J. Organomet. Chem., 92 (1975) 117.
103 J.P. Barbier and P. Braunstein, J. Chem. Res. (S), (1978) 412.
104 J.P. Barbier, P. Braunstein, J. Fischer and L. Ricard, Inorg. Chim. Acta, 31 (1978) L 361.
105 J.P. Barbier, R. Bender, P. Braunstein, J. Fischer and L. Ricard, J. Chem. Res. (M), (1978) 2913.
106 R. Bender, P. Braunstein, J. Fischer, L. Ricard and A. Mitschler, Nouv. J. Chim., 5 (1981) 81; Chem. Abstr., 94 (1981) 184775.
107 P. Lemoine, A. Giraudeau, M. Gross, R. Bender and P. Braunstein, J. Chem. Soc., Dalton Trans., (1981) 2059.
108 R. Bender, P. Braunstein, V. Dusausoy and J. Protas, J. Organomet. Chem., 172 (1979) C 51.
109 T.V. Ashworth, J.A.K. Howard and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1980) 1609; J. Chem. Soc., Chem. Commun., (1979) 42.
110 M. Chetcuti, M. Green, J.A.K. Howard, J.C. Jeffery, R.A. Mills, G.N. Pain, S.J. Porter, F.G.A. Stone, A.A. Wilson and P. Woodward, J. Chem. Soc., Chem. Commun., (1980) 1057.
111 T.V. Ashworth, J.A.K. Howard, M. Laguna and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1980) 1593.
111a M.D. Curtis and R.J. Klinger, J. Organomet. Chem., 161 (1978) 23.
112 T.V. Ashworth, M. Berry, J.A.K. Howard, M. Laguna and G.F.A. Stone, J. Chem. Soc., Dalton Trans., (1980) 1615; J. Chem. Soc., Chem. Commun., (1979) 45.
113 M. Berry, J.A.K. Howard and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1980) 1601.
114 M. Berry, J. Martin-Gil, J.A.K. Howard and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1980) 1625.
115 N.M. Boag, M. Green, R.M. Mills, G.N. Pain, G.F.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1980) 1171.
116 J.C. Jeffery, H. Razay and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1981) 243.
117 M. Green, J.A.K. Howard, R.M. Mills, G.N. Pain, F.G.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1981) 869.
118 J.A.K. Howard, K.A. Mead, J.R. Moss, R. Navarro, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 743.

119 J.A.K. Howard, J.C. Jeffery, M. Laguna, R. Navarro and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1981) 751.

120 T.V. Ashworth, M.J. Chetcuti, J.A.K. Howard, F.G.A. Stone, S.J. Wisbey and P. Woodward, J. Chem. Soc., Dalton Trans., (1981) 763.

121 J.C. Jeffery, I. Moore, H. Razay and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1981) 1255.

122 J.C. Jeffery, I. Moore, M. Murrey and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1982) 1741.

123 J.C. Jeffery, H. Razay and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1982) 1733.

124 M.J. Chetcuti, J.A.K. Howard, R.M. Mills, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 1757.

125 M.J. Chetcuti, K. Marsden, I. Moore, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 1749.

126 J.C. Jeffery, C. Sambale, M.F. Schmidt and F.G.A. Stone, Organometallics, 1 (1982) 1597.

127 M. Green, J.A.K. Howard, G.N. Pain and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1982) 1327.

128 M. Green, R.M. Mills, G.N. Pain, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 1309.

129 M. Green, R.M. Mills, G.N. Pain, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 1321.

130 A. Fumagalle, S. Martinengo, P. Chini, A. Albinati, S. Bruckner and B.T. Heaton, J. Chem. Soc., Chem. Commun., (1978) 195.

131 S. Martinengo, G. Ciani and A. Sironi, J. Am. Chem. Soc., 104 (1982) 328.

132 L.N. Rachkovskaya, N.K. Eremenko and K.I. Matveev, Russ. J. Inorg. Chem., 17 (1972) 1173.

133 P.L. Goggin and R.J. Goodfellow, J. Chem. Soc., Dalton Trans., (1973) 2355.

134 A. Modinos and P. Woodward, J. Chem. Soc., Dalton Trans., (1975) 1516.

135 L.N. Rachkovskaya, N.E. Eremenko and K.I. Malveer, Dokl. Phys. Chem., 190 (1970) 174.

136 M.P. Brown, R.J. Puddephatt, M. Rashidi, L. Manojlovic-Muir, K.W. Muir, T. Solomun and K.R. Seddon, Inorg. Chim. Acta, 23 (1977) L33.

137 M.P. Brown, R.J. Puddephatt, M. Rashidi and K.R. Seddon, J. Chem. Soc., Dalton Trans., (1978) 1540.

138 M.P. Brown, A.N. Keith, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt and K.R. Seddon, Inorg. Chim. Acta, 34 (1979) L223.

139 M.P. Brown, J.R. Fisher, S.J. Franklin, R.J. Puddephatt and K.R. Seddon, J. Chem. Soc., Chem. Commun., (1978) 749; J. Organomet. Chem., 161 (1978) C46.

140 R. Colton, M.J. McCormick and C.D. Pannan, J. Chem. Soc., Chem. Commun., (1977) 823; Aust. J. Chem., 31 (1978) 1425.

141 L. Manojlovic-Muir, K.W. Muir and T. Solomun, J. Organomet. Chem., 179 (1979) 479.

142 J.R. Fisher, A.J. Mills, S. Sumner, M.P. Brown, M.A. Thomson, R.J. Puddephatt, A.A. Frew, L. Manojlovic-Muir and K.W. Muir, Organometallics, 1 (1982) 1421; Inorg. Chim. Acta, 44 (1980) L271.

143 M.P. Brown, S.J. Franklin, R.J. Puddephatt, M.A. Thompson and K.R. Seddon, J. Organomet. Chem., 178 (1979) 281.

144 G.M. Bancroft, T. Chan, R.J. Puddephatt and M.P. Brown, Inorg. Chim. Acta, 53 (1981) L119.

145 P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 81.

146 A.C. Skapski and P.G.H. Troughton, Chem. Commun., (1969) 170.

147 A.C. Skapski and P.G.H. Troughton, J. Chem. Soc. A, (1969) 2772.

148 C.T. Hunt, G.B. Matson and A.L. Balch, Inorg. Chem., 20 (1981) 2270.

149 M.C. Baird and G. Wilkinson, J. Chem. Soc. A, (1967) 865.

150 L.N. Rachkovskaya, N.K. Eremenko and K.I. Matveev, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 5 (1970) 78; Chem. Abstr. 74 (1971) 60302.

151 L.N. Rachkovskaya, N.K. Eremenko and K.I. Matveev, Dokl. Akad. Nauk SSSR, 190 (1970) 1396; Chem. Abstr., 72 (1970) 139098.

152 Yu.I. Mironov, L.M. Plyasova and V.V. Bakakin, Kristallografiya, 19 (1974) 511; Chem. Abstr. 81 (1974) 42541.

153 C. Crocker, P.L. Goggin and R.J. Goodfellow, J. Chem. Soc., Chem. Commun., (1978) 1056.

154 E.W. Abel and F.G.A. Stone, Q. Rev., Chem. Soc., 23 (1969) 325.

155 R.J. Irving and E.A. Magnusson, J. Chem. Soc., (1958) 2283.

156 A.R. Brause, M. Rycheck and M. Orchin, J. Am. Chem. Soc., 89 (1967) 6500.

157 T.A. Weil, P. Schmidt, M. Rycheck and M. Orchin, Inorg. Chem., 8 (1969) 1002.

158 M.A.M. Meester, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 14 (1975) 25.

159 M.A.M. Meester, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 14 (1975) 33.

160 K.L. Klassen and N.V. Duffy, J. Inorg. Nucl. Chem., 35 (1973) 2602.

161 P.L. Goggin and J. Mink, Inorg. Chim. Acta, 34 (1979) 225.

162 F. Pesa, L. Spaulding and M. Orchin, Inorg. Chem., 13 (1974) 1289.

163 L. Spaulding, B.A. Reinhardt and M. Orchin, Inorg. Chem., 11 (1972) 2092.

164 H.C. Clark and J.E.H. Ward, J. Am. Chem. Soc., 96 (1974) 1741.

165 M.A.M. Meester, D.J. Stufkens and K. Vrieze, Inorg. Chim. Acta, 15 (1975) 137.

166 Y. Saito and T. Iwayanagi, Seisan Kenkyu, 28 (1976) 440; Chem. Abstr., 86 (1977) 170267.

167 D.G. Cooper and J. Powell, Inorg. Chem., 16 (1977) 142.

168 J. Browning, P.L. Goggira, R.J. Goodfellow, M.J. Norton, A.J.M. Pattray, B.F. Taylor and J. Mink, J. Chem. Soc., Dalton Trans., (1977) 2061.

169 J. Browning, P.L. Goggin, R.J. Goodfellow, N.W. Hurst, L.G. Mallinson and M. Murray, J. Chem. Soc., Dalton Trans., (1978) 872.

170 G.K. Anderson, R.J. Cross and D.S. Rycroft, J. Chem. Res. Synop., (1979) 120.

171 G.K. Anderson, R.J. Cross and D.S. Rycroft, J. Chem. Res. M, (1979) 1601.

172 G.K. Anderson, R.J. Cross and D.S. Rycroft, J. Chem. Res. Synop., (1980) 240.

173 M.H. Chisholm, H.C. Clark, L.E. Manzer and J.B. Stothers, J. Chem. Soc., Chem. Commun., (1971) 1627.

174 M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers and J.E.H. Ward, J. Am. Chem. Soc., 95 (1973) 8574.

175 W.J. Cherwinski, B.F.G. Johnson, J. Lewis and J.R. Norton, J. Chem. Soc., Dalton Trans., (1975) 1156.

176 M.L. Manojlovic-Muir, K.W. Muir and T. Solomun, J. Organomet. Chem., 142 (1977) 265.

177 L. Manojlovic-Muir, K.W. Muir and R. Walker, J. Organomet. Chem., 66 (1974) C21.

178 M.L. Manojlovic-Muir, K.W. Muir and R. Walker, J. Chem. Soc., Dalton Trans., (1976) 1279.

179 D.R. Russell, P.A. Tucker and S. Wilson, J. Organomet. Chem., 104 (1976) 387.

180 H.C. Clark and W.S. Tsang, J. Am. Chem. Soc., 89 (1967) 529.

181 H.C. Clark, P.W.R. Corfield, K.R. Dixon and J.A. Ibers, J. Am. Chem. Soc., 89 (1967) 3360.

182 F. Calderazzo, in V. Gutmann (Ed.), Halogen Chemistry, Vol. 3, Academic Press, London, 1967, p. 383.
183 H.C. Clark and W.J. Jacobs, Inorg. Chem., 9 (1970) 1229.
184 M. Catellani and J. Halpern, Inorg. Chem., 19 (1980) 566.
185 H.C. Clark, K.R. Dixon and W.J. Jacobs, Chem. Commun., (1968) 548.
186 H.C. Clark, K.R. Dixon and W.J. Jacobs, J. Am. Chem. Soc., 91 (1969) 1346.
187 J.E. Byrd and J. Halpern, J. Am. Chem. Soc., 93 (1971) 1634.
188 W.J. Cherwinski and H.C. Clark, Can. J. Chem., 47 (1969) 2665.
189 C.R. Green and R.J. Angelici, Inorg. Chem., 11 (1972) 2095.
190 W. Beck and B. Purucker, J. Organomet. Chem., 112 (1976) 361.
191 C.F. Shiba and W.H. Waddell, J. Organomet. Chem., 241 (1983) 119.
192 H.C. Clark, K.R. Dixon and W.J. Jacobs, J. Am. Chem. Soc., 90 (1968) 2259.
193 H.C. Clark, K.R. Dixon and W.J. Jacobs, Chem. Commun., (1968) 93.
194 H.C. Clark and K.R. Dixon, J. Am. Chem. Soc., 91 (1969) 596.
195 K.R. Dixon and D.J. Hawke, Can. J. Chem., 49 (1971) 3252.
196 T. Majima and H. Kurosawa, J. Organomet. Chem., 134 (1977) C45.
197 R.J. Cross and A.J. McLennan, J. Chem. Soc., Dalton Trans., (1983) 359.
198 W. Beck and K.V. Werner, Chem. Ber., 104 (1971) 2901.
199 W. Beck, M. Bauder, G. La Monnica, S. Cenini and R. Ugo, J. Chem. Soc. A, (1971) 113.
200 V.A. Mukhedkar, B.J. Kavathekar and A.J. Mukhedkar, J. Inorg. Nucl. Chem., 39 (1977) 1003.
201 M. Kubota, R.K. Rothrock and J. Geibel, J. Chem. Soc., Dalton Trans., (1973) 1267.
202 G.K. Anderson, H.C. Clark and J.A. Davies, Organometallics, 1 (1982) 64.
203 J.V. Kingston and G.R. Scollary, J. Chem. Soc., Chem. Commun., (1970) 362.
204 H.C. Clark and L.E. Manzer, Inorg. Chem., 13 (1974) 1291.
205 H.C. Clark and L.E. Manzer, J. Am. Chem. Soc., 95 (1973) 3812.
206 P.E. Rush and J.D. Oliver, J. Chem. Soc., Chem. Commun., (1974) 996.
207 J.D. Oliver and P.E. Rush, J. Organomet. Chem., 104 (1976) 117.
208 B.W. Davies and N.C. Payne, Inorg. Chem., 13 (1974) 1843.
209 L.E. Manzer and P.Z. Meakin, Inorg. Chem., 15 (1976) 3117.
210 F. Canziani, P. Chini, A. Quarta and A.D. Martino, J. Organomet. Chem., 26 (1971) 285.
211 F. Canziani and M.C. Malatesta, J. Organomet. Chem., 90 (1975) 235.
212 F. Canziani, L. Garlaschelli and M.C. Malatesta, J. Organomet. Chem., 146 (1978) 179.
213 F. Canziani, L. Garlaschelli, M.C. Malatesta and A. Albinati, J. Chem. Soc., Dalton Trans., (1981) 2395.
214 F. Canziani, A. Albinati, L. Garlaschelli and M.C. Malatesta, J. Organomet. Chem., 146 (1978) 197.
215 H.C. Clark and K.V. Werner, Chem. Ber., 110 (1977) 667.
216 G. Booth and J. Chatt, Proc. Chem. Soc., London, (1961) 67.
217 G. Booth and J. Chatt, J. Chem. Soc. A, (1966) 634.
218 H.C. Clark and R.J. Puddephatt, Inorg. Chem., 9 (1970) 2670.
219 G. Carturan, M. Graziani and U. Belluco, J. Chem. Soc. A, (1971) 2509.
220 M.A. Bennett and A. Rokicki, J. Organomet. Chem., 244 (1983) C31.
221 R.W. Glyde and R.J. Mawby, Inorg. Chem., 10 (1971) 854.
222 D. Wright, Chem. Commun., (1966) 197.
223 E. Lodwijk and D. Wright, J. Chem. Soc. A, (1968) 119.
224 M. Aresta and R.S. Nyholm, Chem. Commun., (1971) 1459.

225 H.C. Volger and K. Vrieze, J. Organomet. Chem., 13 (1968) 495.
226 G. Longoni, P. Fantucci, P. Chini and F. Canziani, J. Organomet. Chem., 39 (1972) 413.
227 W. Beck, W. Rieber, S. Cenini, F. Porta and G. LaMonica, J. Chem. Soc., Dalton Trans., (1974) 298.
228 R. Bardi, A.M. Piazzesi, A.D. Pra, G. Cavinato and L. Toniolo, J. Organomet. Chem., 234 (1982) 107.
229 A. Cavinato and L. Toniolo, J. Organomet. Chem., 241 (1983) 275.
230 R. Bardi, A.M. Piazzesi, G. Cavinato, P. Cavoli and L. Toniolo, J. Organomet. Chem., 224 (1982) 407.
231 T.H. Coffield, J. Kozikowski and R.D. Closson, J. Org. Chem., 22 (1957) 598.
232 R.J. Cross and R. Wardle, J. Chem. Soc. A, (1970) 840.
233 G.K. Anderson and R.J. Cross, J. Chem. Soc., Dalton Trans., (1979) 1246.
234 G.K. Anderson and R.J. Cross, J. Chem. Soc., Dalton Trans., (1980) 712.
235 R.J. Cross and J. Gemmill, J. Chem. Soc., Chem. Commun., (1982) 1343.
236 G.K. Anderson and R.J. Cross, J. Chem. Soc., Chem. Commun., (1978) 819.
237 R.J. Cross and J. Gemmill, J. Chem. Soc., Dalton Trans., (1981) 2317.
238 C.J. Wilson, M. Green and R.J. Mawby, J. Chem. Soc., Dalton Trans., (1974) 1293.
239 P.E. Garrou and R.F. Heck, J. Am. Chem. Soc., 98 (1976) 4115.
240 N. Sugita, J.V. Minkiewicz and R.F. Heck, Inorg. Chem., 17 (1978) 2809.
241 G.K. Anderson and R.J. Cross, J. Chem. Soc., Dalton Trans., (1980) 1434.
242 C. Eaborn, K.J. Odell and A. Pidcock, J. Chem. Soc., Dalton Trans., (1979) 134.
243 C. Eaborn, K.J. Odell and A. Pidcock, J. Chem. Soc., Dalton Trans., (1978) 1288.
244 C. Eaborn, K.J. Odell and A. Pidcock, J. Organomet. Chem., 96 (1975) C38.
245 C.D. Cook and G.S. Jauhal, Can. J. Chem., 45 (1967) 301.
246 A.J. Mukhedkar, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1970) 947.
247 S.J. Ashcroft, A. Maddock and G. Beech, J. Chem. Soc., Dalton Trans., (1974) 462.
248 J.D. Ruddick and B.L. Shaw, J. Chem. Soc. A, (1969) 2801.
249 J.D. Ruddick and B.L. Shaw, J. Chem. Soc. A, (1969) 2964.
250 J.D. Ruddick and B.L. Shaw, J. Chem. Soc. A, (1969) 2969.
251 M. Kubota, D.A. Phillips and J.E. Jacobsen, J. Coord. Chem., 10 (1980) 125.
251a O. Roelen, German Pat., (1938) 849548.
252 L.H. Slaugh and R.D. Mullineaux, U.S. Pat., (1966) 3239571; Chem. Abstr., 65 (1966) 618.
253 G.A. Rowe, G.B. Pat., (1974) 136834; Chem. Abstr., 83 (1975) 142590.
254 J.J. Mrowca, U.S. Pat., (1975) 3876672; Chem. Abstr., 84 (1976) 30432.
255 I. Schwager and J.F. Knifton, Ger. Offen. (1973) 2322751; Chem. Abstr., 80 (1974) 70327.
256 G. Wilkinson, Fr. Pat., (1966) 145964.
257 M. Ichikawa, Jpn. Pat., (1977) 7765201; Chem. Abstr., 88 (1978) 123625.
258 C.Y. Hsu and M. Orchin, J. Am. Chem. Soc., 97 (1975) 3553.
259 Agency Ind. Sci. Technol., Jpn. Pat., (1980) 80100331; Chem. Abstr., 94 (1981) 30191.
260 Toa Nenryo Kogyo K.K., Jpn. Pat., (1981) 81166139; Chem. Abstr., 96 (1982) 142265.
261 H.C. Clark and J.A. Davies, J. Organomet. Chem., 213 (1981) 503.
262 S.C. Tang and L. Kim, J. Mol. Catal., 14 (1982) 231.
263 G.K. Anderson, H.C. Clark and J.A. Davies, Inorg. Chem., 22 (1983) 427, 434.
264 G.K. Anderson, C. Bilard, H.C. Clark, J.A. Davies and C.S. Wong, Inorg. Chem., 22 (1983) 439.
265 G. Consiglio and P. Pino, Isr. J. Chem., 15 (1976/1977) 221.
266 G. Consiglio and P. Pino, Chim. Ind. (Milan), (1978) 396.

267 I. Schwager and J.F. Knifton, J. Catal., 45 (1976) 256.

268 I. Schwager and J.F. Knifton, (Texaco Inc.) U.S. Pat. (1976) 3996293.

269 I. Schwager and J.F. Knifton, (Texaco Inc.) DE-OS (1978) 2811403.

270 I.C.I. Ltd., G.B. Pat. (1966-70) 1185156; G.B. Pat., (1974) 1368434.

271 H. Behrens, A. Jungbauer and M. Moll, Z. Naturforsch. Teil B. 32 (1977) 57.

272 G. Consiglio and P. Pino, Helv. Chim. Acta, 59 (1976) 642.

273 Y. Kawabata, T. Hayashi and I. Ogata, J. Chem. Soc., Chem. Commun., (1979) 462.

274 P. Haelg, G. Consiglio and P. Pino, Helv. Chim. Acta, 64 (1981) 1865.

275 T. Hayashi, Y. Kawabata, T. Isoyama and I. Ogata, Bull. Chem. Soc. Jpn., 54 (1981) 3438.

276 L.J. Kehoe and R.A. Schnell, J. Org. Chem., 35 (1970) 2846.

277 E.L. Jenner and R.V. Lindsey Jr., U.S. Pat., (1959) 2876254; Chem. Abstr., 53 (1959) 17906.

278 J. Tsuji, J. Kiji, S. Imamura and M. Morikawa, J. Am. Chem. Soc., 86 (1964) 4350.

279 J.F. Knifton, J. Org. Chem., 41 (1976) 793.

280 M. Ichikawa and K. Shikakura, Stud. Surf. Sci. Catal., 7 (1981) 925; Chem. Abstr., 95 (1981) 203250.

281 R. Pierantazzi, K.J. McQuade, B.C. Gates, M. Wolf, H. Knözinger and W. Ruhmann, J. Am. Chem. Soc., 101 (1979) 5436.

282 A. Fusi, R. Ugo, R. Psaro, P. Braunstein and J. Dehand, J. Mol. Catal., 16 (1982) 217; Chem. Abstr., 97 (1982) 144102.

283 S. Bhaduri and K.R. Sharma, J. Chem. Soc., Dalton Trans., (1982) 727.

284 N.K. Eremenko, L.N. Rachkovskaya, K.I. Matveev, I.A. Ovsyannikova, Katal. Reakts. Zhidki Faze, Tr. Vses. Knof. 3rd (1971) 450: Chem. Abstr. 79 (1973) 83880.

285 V.I. Avdeev, L.I. Kozhevina, K.I. Matveev, I.A. Ovsyannikova, N.K. Eremenko and L.N. Rachkovskaya, Kinet. Catal. (USSR), 15 (1974) 935; Chem. Abstr., 81 (1974) 177218.

286 C.H. Cheng and R. Eisenberg, J. Am. Chem. Soc., 100 (1978) 5968.

287 T. Yoshida, Y. Ueda and S. Otsuka, J. Am. Chem. Soc., 100 (1978) 3941.

288 A.A. Frew, R.H. Hill, L. Manojlovic-Muir, K.W. Muir and R.J. Puddephatt, J. Chem. Soc., Chem. Commun., (1982) 198.