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Phosphinepalladium and Phosphineplatinum Carbonyl Cluster Compounds

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The state of the chemistry of the cluster compounds of palladium and platinum is examined. The principal properties, structure, chemical reactions, and methods of synthesis of the phosphinepalladium and phosphineplatinum carbonyl clusters are described and the methods used to regulate the nuclearity of the clusters and their interconversions are discussed. The bibliography includes 69 references.

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I. INTRODUCTION

Several classifications of the cluster compounds of metals are available at the present time,[1] but the phosphinemetal carbonyl clusters have not been differentiated into an independent group in any of them. This is justified in relation to the phosphinemetal carbonyl clusters for metals belonging to the Fe and Cl triads, which are merely modifications of the corresponding carbonyl compounds obtained by substituting some of the CO groups by tertiary phosphines. However it does not apply to phosphinemetal carbonyl clusters of metals belonging to the Ni triad, which have no corresponding neutral carbonyl precursors and which have a unique intrinsic structure.

The stability of a cluster with a specific number of metal atoms n is determined by a fairly fine balance between the number of the valence electrons belonging to the metallic framework proper, the number of electrons supplied by the ligands, and the steric characteristics of the ligands. The clusters of metals having a large number of valence electrons (Ni, Pd, Pt, Au) are able to coordinate the smallest number of ligands in the clusters of preceding transition metals, which leads, for comparable dimensions of the metallic framework, to an incomplete filling of the surface of the framework by ligands and an inadequate steric stabilisation of the cluster. Tertiary phosphines as ligands are isoelectronic with carbon monoxide and, for the same number of valence electrons introduced into the cluster molecule, ensure a more effective shielding of the surface of the metallic framework. We believe that this is the explanation of the transition from the neutral purely carbonyl clusters of the Fe and Co triads to the phosphinepalladium and phosphineplatinum carbonyl clusters and the phosphinegold clusters. In other words, just as carbonyl clusters are typical for the Fe and Co triads, the phosphinemetal carbonyl clusters are typical for platinum and palladium and characterise the capacity of these metals for cluster formation. The phosphinemetal carbonyl clusters examined in this review are not the only palladium and platinum clusters. There exist a series of clusters of these metals with a wide variety of ligands: $[Pd_4(CO)_4(OAc)_4]$,[2] $[Pd_4(phen)_4(CO)_2](OAc)_4$,[3] $[Pd_3(SO_2)_2.(CNBu)_5]$,[4] $[Pd_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_2(PEt_3)_3]BF_4$,[5] $[Pt_3(CNBu_6]$,[6] $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$,[7,8] $[Pt_3(Ph)(\mu\text{-}PPh_2)_2(PPh_3)_3]$,[9] $[Pt_3(\mu\text{-}Ph)(\mu\text{-}PPh_2)(\mu\text{-}SO_2)(PPh_3)_3]$,[10] $[Pt_3(cod)_3(\mu_3\text{-}SnCl_3)_2]$,[11] $[Pt_4(OAc)_8]$,[12] $[Pt_5H_8P(t\text{-}Bu_2Ph)_5]$,[13] [$Pt_7$(2,6-xylyl isocyanide)$_{12}$],[14] and $[Pd_3(\mu\text{-}CO)(dppm)_3]^{2+}$,[18] where phen = phenanthroline, cod = cyclo-octa -1,5-diene, and dppm = bis(diphenylphosphino)methane.

It is noteworthy that, apart from the series of anionic platinum carbonyls i.e. $[Pt_3(\mu\text{-}CO)_3(CO)_3]_n^{2-}$ (n = 1, 2, 3, 4, 5, 6),[15,16] $[Pt_{19}(CO)_{22}]^{4-}$, $[Pt_{26}(CO)_{32}]^{2-}$, and $[Pt_{38}.(CO)_{44}H_2]^{2-}$,[17] investigated by Chini and co-workers, the majority of the remaining compounds are represented in the literature by single examples and are not discussed in this review. The structures, physicochemical properties, and reactivities of neutral phosphinepalladium and phosphineplatinum carbonyl clusters are examined below in succession.

II. TYPES OF PHOSPHINEPALLADIUM AND PHOSPHINEPLATINUM CARBONYL CLUSTERS.

1. The Trinuclear Clusters $M_3(CO)_3L_3$

Clusters having this composition are known mainly for bulky ligands [L = P(t-Bu)$_3$, PPh(t-Bu)$_2$, and P(cyclo-C_6H_{11})$_3$ (Table 1)]. The method of their synthesis is based on the interaction of coordination-unsaturated compounds of the type of PdL_2 or PtL_2 with carbon monoxide; intermediate phosphinemetal carbonyl complexes are formed and are then converted into the $M_3(CO)_3L_3$ clusters. The reaction is rapid and the yields of the desired products are high (>90%). In certain cases hydride complexes were used as the starting compounds:[23-25]

$$3PtH_2[P(t\text{-}Bu)_3]_2 \xrightarrow{CO} \{Pt(CO)[P(t\text{-}Bu)_3]\}_3 + 3P(t\text{-}Bu)_3 + 3H_2;$$

$$3\{PtH(\mu\text{-}H)[P(t\text{-}Bu)_3]\}_2 \xrightarrow{CO} 2\{Pt(CO)[P(t\text{-}Bu)_3]\}_3 + 3H_2;$$

$$3\ trans\text{-}[PtH(NH_3)(PR_3)_2]^+ \xrightarrow[acetone]{CO} [Pt_3(CO)_3(PR_3)_3] + 3NH_4^+;$$

$$PR_3 = P(t\text{-}Bu)_3, PPh(t\text{-}Bu)_2.$$

X-Ray diffraction analysis has been carried out for the compound $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_3$.[26] The metallic skeleton of the cluster has the form of an equilateral triangle all the sides of which are spanned by bridging CO groups (Fig.1); the phosphorus atoms are located in the plane of the triangle.

The D_{3h} symmetry of these compounds is also confirmed by ^{31}P and ^{195}Pt NMR data for the $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_3$ cluster in solution.[21] The presence of the ^{31}P and ^{195}Pt nuclei in the cluster ensures that the NMR spectra yield much information and a virtually unambiguous interpretation of the structure of the compound in solution. Since the content of the ^{195}Pt isotope is 33.7% in natural compounds,

the ^{31}P spectrum consists of a superposition of the spectra of the three isotopomers (A), (B), and (C), while the ^{195}Pt spectrum consists of a superposition of two such isotopomers, namely (B) and (C) (Fig. 2). The content of the isotopomer with three magnetic platinum nuclei is low (3.70%) and the isotopomer is not manifested in the spectra. The observed spin–spin coupling constants are listed in Table 2.

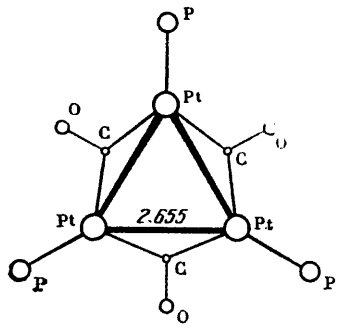


Figure 1. The structure of the $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_3$ cluster.[26]

A more complex pattern is observed in the infrared spectra of the compounds investigated. The stretching vibrations of the CO groups in the phosphinemetal carbonyl clusters are clearly shown in the infrared spectra, which can serve as a basis for structural analysis. According to the D_{3h} symmetry, a single ν(CO) band should be observed in the spectra of these compounds. However, the data obtained (Table 3) indicate a more complex character of the spectra. In most cases two bands are observed in the ν(CO) region and for palladium compounds even three bands are found. Such increase in the complexity of the spectra of the $M_3(CO)_3L_3$ clusters is associated with the influence of a number of factors (dissociation, change in nuclearity, etc.). It is noteworthy that in the description of the infrared spectroscopic data only the solvent is usually indicated and the influence of the gas phase (inert gas, CO, air), which is insignificant in the case of trinuclear clusters, is disregarded.[27] This is probably one of the causes of the conflicting infrared spectroscopic data.

Table 1. The synthesis of phosphinemetal carbonyl clusters $M_3(CO)_3L_3$ and $M_3(CO)_3L_4$.

Cluster	Initial compound	M:P*	Conditions of synthesis	Refs.
$Pd_3(CO)_3[P(t\text{-}Bu)_3]_3$	$Pd[P(t\text{-}Bu)_3]_2$	1:2	Hexane, CO	[19]
$Pd_3(CO)_3[P(t\text{-}Bu)_2Ph]_3$	$Pd[P(t\text{-}Bu)_2Ph]_2$	1:2	Hexane, CO	[19]
$Pt_3(CO)_3[P(t\text{-}Bu)_3]_3$	$Pt[P(t\text{-}Bu)_3]_2$	1:2	Hexane, CO	[20]
$Pt_3(CO)_3[PPh(t\text{-}Bu)_2]_3$	$Pt[PPh(t\text{-}Bu)_2]_3$	1:2	Hexane, CO	[19]
$Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_3$	$PtHCl[P(cyclo\text{-}C_6H_{11})_3]_2$	1:2	Ethanol, KOH, CO	[21]
$Pt_3(CO)_3[P(Ph_2Bz)]_3$	K_2PtCl_4	1:2	Ethanol, KOH, CO	[22]
$Pt_3(CO)_3[P(iso\text{-}Pr)_3]_3$	*trans*-$PtHCl[P(iso\text{-}Pr)_3]_2$	1:2	Ethanol, KOH, CO	[21]
$Pt_3(CO)_3[PPh(iso\text{-}Pr)_2]_3$	$Pt(cod)_2$	1:1	Petroleum ether, CO	[21]
$Pd_3(CO)_3(PPh_3)_4$	$PdCl_2(PPh_3)_3$	1:2	Aniline, methanol, CO	[28]
$Pd_3(CO)_3(PPh_3)_3$	$Pd(OAc)_2$	1:2	Acetone, CO, NaOAc	[29]
$Pd_3(CO)_3[P(C_6H_4\text{-}p\text{-}CH_3)_3]_4$	$Pd(OAc)_2$	1:2	Acetone, CO, NaOAc	[29]
$Pd_3(CO)_3[P(C_6H_4\text{-}p\text{-}OCH_3)_3]_4$	$Pd(OAc)_2$	1:2	Acetone, CO, NaOAc	[29]
$Pt_2(CO)_2(PPh_3)_4$	$Pt(CO)_2(PPh_3)_2$	1:2	Ethanol	[22]
$Pt_3(CO)_3(PEt_3)_4$	$Pt_4(CO)_5(PEt_3)_4$	1:1,3	Hexane, methanol	[30]
$Pt_3(CO)_3(PPhMe_2)_4$	*cis*-$[PtCl_2(PPhMe_2)_2]$	1:2	Methanol, KOH, CO	[31]
$Pt_3(CO)_3(PPh_2Et)_4$	K_2PtCl_4	1:2	Methanol, KOH, CO	[22]
$Pt_3(CO)_3(PPh_2Me)_4$	Na_2PtCl_4	1:2	Methanol, KOH, CO	[22]
$Pt_3(CO)_3[PEt_2(cyclo\text{-}Bu)]_4$	$Pt(cod)_2$	1:1,6	Petroleum ether, CO	[31]
$Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_4$	$PtH_2[P(cyclo\text{-}C_6H_{11})_3]_2$	1:2	Hexane, CO	[32]
$Pt_3(CO)_3(PPh_2Bz)_4$	$Pt_3(CO)_3(PPh_2Bz)_3$	1:1,5	Diethyl ether	[31]

*The M : P molar ratio used in the synthesis is quoted.

Table 2. ^{31}P and ^{195}Pt NMR data for the $Pt_3(CO)_3L_3$ clusters.

Ligand	δ(P), p.p.m.	δ(Pt), p.p.m.	^1J (Pt, Pt)	^1J (Pt, P)	^2J (Pt, P)	^3J (P, P)	Refs.
P(cyclo-C_6H_{11})3	69.8	—4392	1571	4412	430	58	[21]
P(iso-Pr)3	81.6	—4530	1607	4422	419	56	[21]
P(iso-Pr)2Ph	76.7	—4450	1610	4605	453	57	[21]
PPh_2Bz	55.6	—4448	1619	4751	488	63	[21]
P(t-Bu)$_2$Me	68.4	—	1770	4724	413	51	[44]
P(t-Bu)Et$_2$	73.8	—4445	1595	4430	435	59	[31]

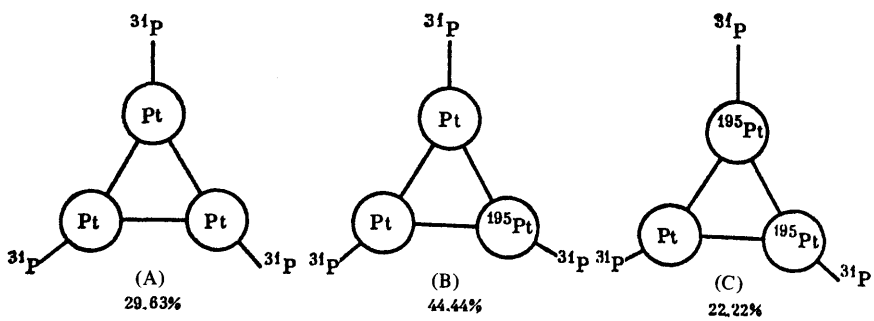


Figure 2. Principal types of the isotopomers of the $Pt_3(CO)_3L_3$ cluster.

2. Trinuclear $M_3(CO)_3L_4$ Clusters

This group of clusters is known for a fairly large number of ligands (Table 1). The trinuclear palladium clusters† are obtained by reducing $PdCl_2L_2$ with carbon monoxide (L = PPh_3) or by reducing $Pd(OAc)_2$ in the presence of NaOAc and two equivalents of a phosphine ligand [L = PPh_3, $P(C_6H_4\text{-}p\text{-}CH_3)_3$, or $P(C_6H_4\text{-}p\text{-}OCH_3)_3$]. The trinuclear platinum clusters were obtained by the following procedures:

(a) by treating the compound $Pt(cod)_2$ with phosphine and carbon monoxide. A solution of $Pt(cod)_2$ in petroleum ether is treated with carbon monoxide for approximately 0.5 h after adding the phosphine [L = PEt_3, $PMePh_2$, $PEt_2(t\text{-}Bu)$, or PPh_2Bz] and the solvent is then distilled off and the required product is extracted from the residue; the yield is 50%.[31]

(b) By reducing sodium tetrachloroplatinite. A solution of Na_2PtCl_4 is treated with the phosphine and is boiled until the complete precipitation of $PtCl_2L_2$, after which is it treated with hydrazine hydrate and saturated with carbon monoxide. A solution of KOH is then introduced, the reaction mixture is again heated, boiled, and filtered. This procedure leads to the formation of the complex $Pt^0(CO)_2L_2$, which is subsequently converted on heating into the $Pt_3(CO)_3L_4$ cluster (L = PPh_3, $PMePH_2$, or $PEtPh_2$). The yield of the required product is usually 20–40%.[22]

(c) By the interaction of platinum dicarbonyl with phosphines. A solution of Na_2PtCl_4 in acetone, alcohol, or another organic solvent is treated at room temperature with carbon monoxide for 1–2 days. After the formation of platinum dicarbonyl, concentrated ammonia is added, whereupon the solution becomes bright green and capable of reacting with phosphine. When an aromatic phosphine is added to the alcoholic solution, the precipitation of the $Pt_3(CO)_3L_4$ cluster, where L = PPh_3, $P(C_6H_4\text{-}p\text{-}CH_3)_3$, $P(C_6H_3\text{-}p\text{-}OCH_3)_3$, or PPh_2Et, begins immediately. The yield of the product after recrystallisation is approximately 50%. The reaction with straight-chain aliphatic phosphines takes place nonselectively and admixtures are formed, causing rapid decomposition of the required product.[30]

Among more specific methods of synthesis, mention may be made of the interaction of carbon monoxide with $PtH_2[P(cyclo\text{-}C_6H_{11})_3]_2$ under normal conditions[32] and with $PtMe_2(PEt_3)_2$ at 90 °C and 50 atm.[37] However, in the latter case no detailed description of the method of synthesis is available in the literature.

The structure of clusters of the type $M_3(CO)_3L_4$ has been established by X-ray diffraction for $Pd_3(CO)_3(PPh_3)_4$[33] and $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_4$.[32] The cluster molecule is an equilateral triangle all the sides of which are spanned by μ-CO groups. Each of the two metal atoms in the base of the triangle is linked to one of the two phosphorus atoms of the phosphine ligand, while the third metal atom is linked to two other phosphorus atoms (Fig.3).

The non-equivalence of the CO groups in the cluster is reflected in the infrared spectra (Table 4). In the stretching region of the μ_2-CO groups two intense bands are usually observed at 1820–1880 cm^{-1} for the palladium compounds and at 1750–1800 cm^{-1} for the platinum compounds. We may note that the infrared spectra are to a large extent characteristic and can be used to identify the clusters.

† The methods of synthesis of the $Pd_3(CO)_3(PPh_3)_4$, Pd_4, Pd_{10} clusters, based on the interconversions of the phosphinepalladium carbonyl clusters, are examined below in Section III.

The platinum clusters have been investigated by the NMR method. The ^{31}P and ^{195}Pt NMR data agree with the results of the X-ray diffraction analysis.[32] Two types of P and Pt atoms are manifested in the spectra (Table 5) and the splitting of their signals by neighbouring atoms and the number of components of the spectrum indicate a triangular skeleton in which one platinum atom is linked to two phosphorus atoms and the two others are involved in only a single Pt–C bond.

Table 3. Infrared spectroscopic data for the $M_3(CO)_3L_3$ clusters.

Ligand	ν(CO), cm^{-1}	Solvent	Refs.
	M=Pd		
P(t-Bu)3	1843 s, 1802 s, 1795 s	LP	[19]
P(t-Bu)2Ph	1870 s, 1832 v.s, 1820 v.s	LP	[19]
	M=Pt		
P(t-Bu)3	1875 s, 1730 s	LP	[20]
P(t-Bu)3	1785 s, 1730 s	CH_2Cl_2	[20]
P(t-Bu)3	1792, 1740		[23]
P(t-Bu)2Ph	1872 s, 1760 v.s	LP	[19]
P(t-Bu)2Ph	1836 w, 1773 v.s	THF	[19]
$P(C_6H_{11})_3$	1840 w, 1770 v.s 1737 w	LP	[21]
PPh_2Bz	1784 s	LP	[22]
PPh_2Bz	1852 w, 1789 s	THF	[22]
PPh_2Bz	1855 w, 1795 s, 1788 s, 1760 sh 1750 sh	–	[21]
P(iso-Pr)3	1838 w, 1770 v.s, 1738 sh	LP	[21]
P(iso-Pr)2Ph	1865 w, 1800 s, 1785 s, 1760 sh	LP	[21]
P(iso-Pr)2Ph	1865 w, 1805 s, 1798 sh, 1788 s 1764 v.s	C_6H_{14}	[21]

Notation: (here and henceforth): v.s. = very strong (intense), s = strong (intense), m = medium, w = weak, sh = shoulder, b = broad, and LP = liquid paraffin.

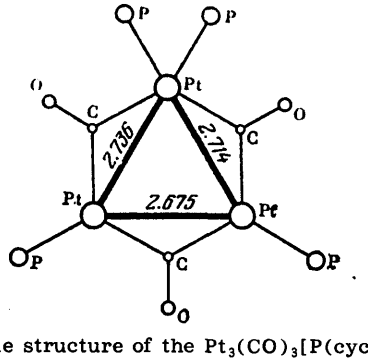


Figure 3. The structure of the $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]_4$ cluster.[32]

3. Tetranuclear $M_4(CO)_5L_4$ Clusters

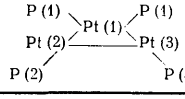
The conditions for the preparation of the tetranuclear palladium clusters (Table 6) are different for straight-chain aliphatic and triphenylphosphine ligands although $Pd(OAc)_2$ is used as the starting compound in both cases. The $Pd_4(CO)_5(PPh_2Me)_4$ palladium cluster[39] has been obtained by reducing $Pd(NO_2)_2(PPh_2Me)_2$ with carbon monoxide in

methylene chloride. The attempts to obtain the corresponding clusters with the PPh_3 and $PPhMe_2$ ligands by this reaction proved unsuccessful.

Table 4. Infrared spectroscopic data for the $M_3(CO)_3L_4$ clusters.

Ligand	ν(CO), cm^{-1}	Solvent	Refs.
	M=Pd		
PPh_3	1840, 1820	KBr	]33, 35]
PPh_3	1865 s, 1822 vs, 1790 vw	LP	[29]
$P(C_6H_4$-p-$CH_3)_3$	1879 w-m, 1846 s, 1925 vs	LP	[29]
$P(C_6H_4$-p-$OCH_3)_3$	2035 s.w, 1880 vw, 1843 s 1831 vs	LP	[29]
	M=Pt		
PPh_3	1854 w, 1803 s, 1788 s	LP	[22]
PPh_3	1845 w, 1799 s, 1782 s	LP	[34]
PPh_3	1839 m, 1784 s	Benzene	[22]
PPh_3	1854 w, 1805 sh, 1795 s	THF	[36]
PEt_3	1808 w, 1760 vs, 1745 sh	LP	[31]
PEt_3	1766 s, 1773 sh	C_6H_{14}	[37]
PEt_3	1766 s	C_6H_{14}	[38]
PEt_3	1766 s, 1774 sh, 1826 w,	C_6H_{14}	[30]
$PPhMe_2$	1825 w, 1772 vs, 1750 vs	LP	[31]
PPh_2Et	1788 s, 1765 s,	LP	[22]
PPh_2Et	1835 w, 1782 sh, 1770 s	Benzene	[22]
PPh_2Et	1849 w, 1768 s	THF	[36]
PPh_2Me	1840 w, 1792 vs, 1772 vs	LP	[31]
PPh_2Me	1847 w, 1796 s, 1769 s	LP	[22]
PPh_2Me	1839 m, 1775 s	Benzene	[22]
P(t-Bu)Et_2	1822 w, 1760 sb, 1752 sh	LP	[31]
$P(C_6H_{11})_3$	1825 w, 1780 s, 1760 s	LP	[32]
PPh_2Bz	1785 sh, 1765 sb, 1735 wb	LP	[31]

Table 5. ^{31}P and ^{195}Pt NMR data for the $Pt_3(CO)_6L_4$ clusters[31]



Parameters of spectrum	Ligand				
	PEt_3	PMe_2Ph	$PMePh_2$	PEt_2(t-Bu)	PPh_2Bz
δP(1), p.p.m.	33.7	8.8	24.5	47.0	43.8
δP(2), p.p.m.	60.8	35.6	49.8	82.5	60.0
δPt(1), p.p.m.	−3908	−3760	−3828	−3836	−3855
δPt(2), p.p.m.	−3883	−3949	−3970	−3758	−4066
^1J[Pt(1), Pt(2)], Hz	586	507	—	385	—
^1J[Pt(2), Pt(3)], Hz	1830	1840	—	1808	—
^1J[Pt(1), P(1)], Hz	3621	3611	3651	3741	3615
^1J[Pt(2), P(2)], Hz	4463	4643	4614	4317	4348
^2J[Pt(1), P(2)], Hz	445	487	519	440	455
^2J[Pt(2), P(1)], Hz	272	292	282	270	272
^2J[Pt(2), P(3)], Hz	411	427	453	459	453
^3J[P(2), P(3)], Hz	65	65	68	70	60
^3J[P(1), P(2)], Hz	21	21	21	25	20

The tetranuclear platinum clusters have been obtained mainly by two methods (Table 6).

(a) By the disproportionation of the trinuclear clusters in carbon monoxide involving the dissolution of the compound $Pt_3(CO)_3L_4$ in acetone and its maintenance in an atmosphere of carbon monoxide for several days. Crystals of the $Pt_3(CO)_5L_4$ clusters are gradually segregated (they are usually black). The synthesis can be carried out in a different way from Na_2PtCl_4. A solution of $Pt_3(CO)_3L_4$ is obtained initially, as described above, and is then kept in an atmosphere of carbon monoxide:[22]

$$2[Pt_3(CO)_3L_4] + 3CO \xrightarrow[1\ atm]{25^\circ C} Pt_4(CO)_5L_4 + 2PtL_2(CO)_2$$
$$L=PPh_3,\ PMe_2Ph,\ PPh_2Bz$$

The yield of the product ranges from 20 to 50%.

(b) By the interaction of platinum dicarbonyl with phosphines. A solution of platinum dicarbonyl obtained by the method of Eremenko et al.[30] readily reacts with straight-chain aliphatic phosphines in equimolar proportions; the $Pt_4(CO)_5L_4$ cluster is formed in a high yield (>80%):[30]

$$[Pt_3(CO)_6]_n^{2-} + PEt_3 \rightarrow Pt_4(CO)_5(PEt_3)_4$$

Table 6. The synthesis of phosphinemetal carbonyl clusters $M_4(CO)_5L_4$

Cluster	Initial compound	M:P in synthesis	Conditions of synthesis	Refs.
$Pd_4(CO)_5(PPh_2Me)_4$	$Pd(NO_2)_2(PPh_2Me)_2$	1:2	CH_2Cl_2	[39]
$Pd_4(CO)_5(PPh_3)_4$	$Pd(OAc)_2$	1:1.3	Et_2NH	[29]
$Pd_4(CO)_5(PPh_3)_4$	$Pd(OAc)_2$	1:2	Acetone, NaOAc, CO; CO + O_2 mixture	[29]
$Pd_4(CO)_5(PEt_3)_4$	$Pd(OAc)_2$	1:1÷1:2	Acetone, NaOAc, HOAc	[40]
$Pd_4(CO)_5(PBu_3)_4$	$Pd(OAc)_2$	1:1÷1:2	Acetone, NaOAc, HOAc	[40]
$Pd_4(CO)_5[P(n\text{-}C_8H_{17})_3]_4$	$Pd(OAc)_2$	1:1	Acetone, NaOAc, HOAc	[41]
$Pd_4(CO)_5[P(n\text{-}C_{12}H_{25})_3]_4$	$Pd(OAc)_2$	1:1	Acetone, NaOAc, HOAc	[41]
$Pt_4(CO)_5(PEt_3)_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[30]
$Pt_4(CO)_5(PPhMe_2)_4$	Na_2PtCl_4	1:2	Methanol, CO, KOH, Hydrazine	[42]
$Pt_4(CO_5)(PPh_3)_4$	$Pt_3(CO)_3(PPh_3)_4$	1:1.33	Acetone, CO	[22]
$Pt_4(CO)_2(\mu\text{-dppm})$ (dppm-O)	$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$	—	—	[43]

The interaction of $[Pt_3(CO)_6]_n^{2-}$ for aromatic phosphine ligands has been mentioned, but a detailed description of the experiment is not available.[22]

The formation of the tetranuclear platinum cluster in the catalytic conversion of carbon monoxide should be noted:[43]

$$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]PF_6 \xrightarrow[O_2]{P_{CO}} Pt_4(\mu\text{-CO})_2(\mu\text{-dppm})_3[dppm(:O)]$$

X-Ray diffraction studies have been carried out for four compounds: $Pd_4(CO)_5(PPh_2Me)_4$,[39] $Pd_4(CO)_5(PPh_3)_4$,[33] $Pt_4(CO)_5(PMe_2Ph)_3$,[42] and $Pt_4(CO)_2(\mu\text{-dppm})_3[dppm(:O)]$.[43] Fig. 4 illustrates the structure of the $Pt_4(CO)_5(PEt_3)_4$ cluster. Its metallic skeleton has the form of a "butterfly" or an open tetrahedron. All five M–M bonds in the cluster are spanned by μ-CO groups and each metal atom is coordinated to one phosphorus atom. The remaining compounds have analogous structures. A cluster with dppm as the bridging ligand has shorter Pt–Pt bonds owing to the chelating influence of dppm.

The structure of the tetranuclear phosphineplatinum carbonyl clusters in solution was investigated by ^{31}P and ^{195}Pt NMR. If the "butterfly" structure of the $Pt_4(CO)_5(PEt_3)_4$ is retained in solution, two types of Pt nuclei with different chemical shifts should be manifested in the NMR spectrum, making it asymmetric. Experiments showed[45] that the $^{31}P\{^1H\}$ NMR spectrum of the $Pt_4(CO)_5(PEt_3)_4$ cluster is symmetrical relative to the central intense line with δ = 36.4

p.p.m., which made it possible to postulate a tetrahedral structure of the cluster in solution. Within the framework of this model, it was possible to interpret the observed spectrum as the sum of the contributions due to clusters containing between zero and four nuclei of the ^{195}Pt magnetic isotope.[45]#

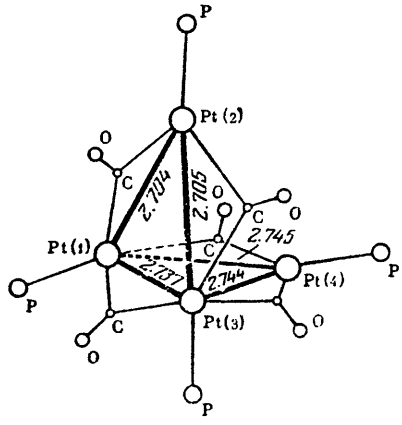


Figure 4. Structure of the $Pt_4(CO)_5(PEt_3)_4$ cluster (the X-ray diffraction analysis has been carried out by R.F.Klevtsova of the Institute of Inorganic Chemistry of the Siberian Division of the USSR Academy of Sciences).

The ^{195}Pt NMR spectrum also indicates a tetrahedral structure of the cluster (a doublet of quartets, which is a superposition of the spectra of clusters with two and three magnetic nuclei, is observed). The observed increase of the symmetry of the clusters in solution at room temperature can be explained by the stereochemical non-rigidity of the compound associated with the rapid exchange of carbonyl groups. The exchange processes remain fairly rapidly at temperatures down to -70 °C.[45]

Exchange processes have been observed for the first time also for palladium clusters whose ^{31}P NMR spectra consist of singlets—δ, p.p.m. (in benzene): -14.0 (Et) and -6.5 (Bu);[40] δ, p.p.m. (in hexane): -6.6 ($n-C_8H_{17}$) and -6.8 ($n-C_{12}H_{25}$)[45] (downfield chemical shifts relative to the H_3PO_4 signal correspond to the negative values).

Another cause of the transition to the tetrahedral structure of the Pt_4 cluster in solution may be associated with the addition of a sixth CO molecule from the solution. This possibility has been confirmed indirectly by the synthesis of the $Pd_4(CO)_6(PBu_3)_4$ cluster on slow crystallisation of $Pd_4(CO)_5(PBu_3)_4$ *in a CO atmosphere.*[46]

The infrared spectra of palladium compounds in the region of the stretching vibrations of the CO group are characterised by a single intense band; an intense band with a shoulder has also been observed for platinum clusters (Table 7).

A study has been published (A.Moor, P.S.Pregosin, L.M.Venanzi, and A.J.Welch, Inorg.Chim.Acta, 1985, 85, 103), whose NMR data agree with those of Yudanov et al.[45]

4. Pentanuclear $Pt_5(CO)_6L_4$ Clusters

The pentanuclear platinum clusters have been discovered recently. They have been synthesised by a fairly specific method (Table 8) involving the reduction of platinum(II) by metal carbonyl anions. For this purpose, a solution of $PtCl_2L_2$ in tetrahydrofuran was treated with $NaMn(CO)_5$ or $KFe(CO)_3NO$ and the reaction mixture was kept at room temperature (for 1 h for PEt_3 or 18 h for PPh_3). The reaction products were isolated chromatographically. The yield depends greatly on the nature of the carbonylate ion and the phosphine ligand; it amounts to 35% for PPh_3 and 50% for PEt_3 in the case of $NaMn(CO)_5$ and to 10% for PPh_2Me and 75% for PPh_3 in the case of $KFe(CO)_3NO$.[49]

Table 7. *Infrared spectroscopic data for the* $M_4(CO)_5L_4$ clusters.

Ligand	ν(CO), cm^{-1}	Solvent	Refs.
	M=Pd		
PPh_2Me	1840 s, 1820 sh	KBr	[39]
PPh_3	1858 s	LP	[29]
PEt_3	2018 vw, 1889 *m*, 1874 w 1844 s, 1797 sh	LP	[40]
PBu_3	2012 vw, 1886 w, 1851 sh, 1837 s, 1800 sh	LP	[40]
$P(n-C_8H_{17})_3$	2014 w-m, 1894 w, 1880 vw 1852 sh, 1842 sb, 1804 sh	Hexane film	[41]
$P(n-C_{12}H_{25})_3$	2012 s, 1887 w, 1852 sh, 1841 sb 1799 sh	Hexane film	[41]
	M=Pt		
PEt_3	1804 sh, 1790 s	Hexane, LP	[30]
PPh_2Me_2	1800 s, 1779 s	LP	[22]
PPh_3	1810 sh, 1797 s	LP	[22]
$Pt_3(CO)_2(dppm)_3$	1835, 1735	LP	[43]

Table 8. The synthesis of the phosphineplatinum carbonyl clusters $Pt_5(CO)_6L_4$.

Cluster	Initial compound	Pt:P*	Conditions of synthesis	Refs.
$Pt_5(CO)_6(PEt_3)_4$	$[PtCl_2(PEt_3)_2]$	1:2	$NaMn(CO)_5$	[47]
$Pt_5(CO)_6(PPh_3)_4$	$[PtCl_2(PPh_3)_2]$	1:2	$NaMn(CO)_5$	[47]
$Pt_5(CO)_6[P(C_6H_4\text{-}p\text{-}CH_3)_3]_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[48]
$Pt_5(CO)_6[P(C_6H\text{-}p\text{-}OCH_3)_3]_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[48]
$Pt_5(CO)_6(PPh_2Et)_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[48]
$Pt_5(CO)_6(PBu_3)_4$	$[Pt_3(CO)_6]_n^{2-}$	1:1	Acetone, CO	[48]

*The Pt : P molar ratio in the synthesis is quoted.

A *more effective and simple method of synthesis is based* on the interaction of platinum dicarbonyl with phosphine.[36] A solution of platinum dicarbonyl, obtained as described above, is treated with phosphine in the proportions Pt : L = 5 : 4 and is allowed to stand for 10–15 h. The solvent is then distilled off and the product recrystallised from benzene–heptane, acetone–ethanol, etc. mixtures.

The reaction is fairly selective and takes place equally readily with aliphatic and aromatic phosphine. The yield of the product is usually high (80%). A method based on the increase of the nuclearity of the $Pt_3(CO)_3L_4$ clusters when they are deposited on different carriers is also of interest.

It has been suggested that the process procees on acid centres, since an analogous enlargement of the framework has been observed on treating the initial cluster with a 48% solution of HBF_4 in THF.[50]

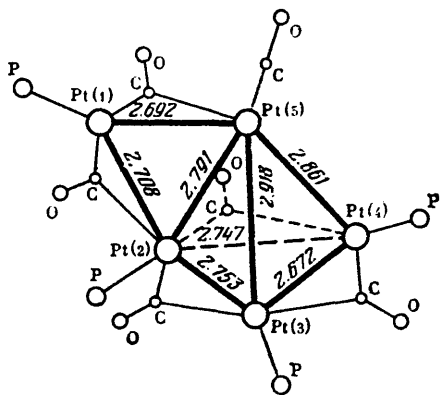


Figure 5. The structure of the $Pt_5(CO)_6(PPh_3)_4.3C_6H_6$ cluster.[48]

Table 9. Infrared spectroscopic data for the $Pt_5(CO)_6L_4$

Ligand	ν(CO), cm^{-1}	Solvent	Refs.
PPh_3*	1998 vs, 1893 w, 1854 s, 1814 s, 1790 vs	KBr	[47]
PPh_3	2005 vs, 1898 w, 1864 m, 1818 s, 1795 s	THF	[47]
PPh_3	1998 vs, 1899 m, 1858 s, 1812 s, 1788 vs	LP	[47]
PPh_3	1999 s, 1895 w, 1864 m, 1816 s, 1792 s	THF	[48]
PEt_3	1985 vs, 1880 m, 1850 s, 1786 vs 1769 sh, 1754 vs	KBr	[47]
PEt_3	1996 vs, 1879 w, 1848 m, 1808 vs 1780 s, 1769 s	Cyclohexane	[47]
PEt_3	1989 vs, 1879 w, 1844 s, 1798 vs 1776 vs, 1765 vs	THF	[47]
PEt_3	1984 vs, 1881 w, 1859 m-s, 1786 m, 1769 sh, 1751 vs	LP	[47]
PEt_3	1988 vs, 1878 w, 1842 m, 1797 vs 1778, 1778 vs, 1762 vs	Hexane	[48]
$P(C_6H_4\text{-}p\text{-}CH_3)_3$	1999 s, 1892 w, 1860 m, 1818 s, 1793 s,	$(C_2H_5)_2O$	[48]
$P(C_6H_4\text{-}p\text{-}OCH_3)_3$	1955 s, 1892 s, 1855 m, 1812 s, 1787 s	THF	[48]
PPh_2Et	1998 s, 1890 w, 1853 m, 1812 s, 1794 sh, 1784 s	$(C_2H_5)_2O$	[48]
PBu_3	1988 s, 1878 w, 1842 m, 1797 s, 1778 s, 1762 s	THF	[48]

*Solvate with three benzene molecules.

The structure of two solvates $Pt_5(CO)_6(PPh_3)_4.3Solv$ with toluene[47] and benzene[48] has been investigated. The structure of the pentanuclear cluster (Fig.5) can be regarded either as a tetrahedron with a Pt(1) metal bridge or as two orthogonal triangles with a common Pt(2) vertex;[47] the latter view is based on the presence in the molecule of the longer Pt(3)–Pt(5) and Pt(4)–Pt(5) bonds.

It is noteworthy that both X-ray diffraction data and the parameters of the infrared spectra of the pentanuclear cluster $Pt_5(CO)_6(PPh_3)_4$, obtained in two independent studies,[47,48] agree well. The infrared spectrum contains a set of bands in the ν(CO) region, characteristic of all the compounds obtained hitherto (Table 9). This agreement is not only between the number of bands but also between the ratios of their intensities. A pronounced dependence of the position and form of the low-frequency band (~1790 cm^{-1}) on the nature of the solvent (as far as the splitting of the band into two components) has also been noted.[36]

The highly characteristic nature of the infrared spectra of the pentanuclear clusters makes it possible to assume, in our view, that the compounds obtained previously,[22] to which the composition $Pt_4(CO)_5L_4$ (L = $AsPh_3$, PPh_2Bz, or PEt_3) was attributed, are apparently in reality clusters having the composition $Pt_5(CO)_6L_4$ or contain the latter in large amounts. This conclusion can be based on the analysis of the infrared spectra in the ν(CO) region. Bender and Braunstein[49] arrived at an analogous conclusion on the basis of the identity of the infrared spectra of $Pt_5(CO)_6(PEt_3)_4$ and the product to which the composition $Pt_4(CO)_5(PEt_3)_4$ had been attributed previously.[22] The compound $Pt_4(CO)_5(PPh_3)_3.1.5C_6H_6$ obtained by Ugo et al.[34] has a set of ν(CO) bands characteristic of pentanuclear clusters, but their positions differ appreciably from those of the ν(CO) bands for the compounds investigated. Thus in individual instances the form of the spectrum in the ν(CO) region is sufficiently characteristic to assign the clusters to a particular type.

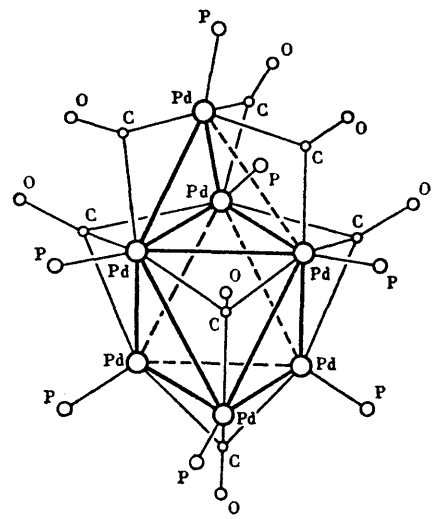


Figure 6. The structure of the $Pd_7(CO)_7(PMe_3)_3$ cluster.[51]

5. The Heptanuclear $Pd_7(\mu_3\text{-}CO)_4(\mu\text{-}CO)_3(PMe_3)_7$ Cluster

The heptanuclear cluster $Pd_7(CO)_7(PMe_3)_7$ has been obtained by reducing $Pd(\eta^1,\eta^3\text{-}C_8H_{12})(PMe_3)$ with carbon monoxide and is the only example of a cluster having the degree of nuclearity indicated.[51] Its structure has been established by X-ray diffraction (Fig.6). The cluster is a one-cap octahedron; the additional palladium atom is located asymmetrically over a face of the octahedron; one of the Pd_{cap}–Pd_{oct} distances is 3.18 Å, which greatly exceeds the lengths of the other two bonds (2.73 Å). The bond lengths within the octahedron are in the range 2.75–2.81 Å. The infrared spectrum of a specimen of the test substance

pelleted with KBr has absorption bands due to the CO groups in the low-frequency region (1825 s, 1800 v.s, 1785 sh, 1770 s, 1850 s, 1685 s).

6. The Decanuclear $Pd_{10}(CO)_{12}L_6$ and $Pd_{10}(CO)_{14}L_4$ Clusters

(a) Clusters with straight-chain aliphatic phosphines. The conditions of the synthesis of clusters of this type have been investigated in greatest detail. The compounds are formed when palladium acetate is reduced in the presence of trifluoroacetic acid. The special advantage of this method of synthesis is the possibility of obtaining individual compounds $Pd_{10}(CO)_{12}L_6$ (I) and (II) and $Pd_{10}(CO)_{14}(PBu_3)_4$ (V) within wide limits of the Pd : P ratios (Table 10).[41,52,53]

Table 10. The synthesis of the decanuclear palladium clusters by the reduction of $Pd(OAc)_2$.

Cluster		Pd:P *	Conditions of synthesis	Refs.
$Pd_{10}(CO)_{12}(PEt_3)_6$	(I)	1:3.3—1:15	Acetone, CF_3COOH	[52, 53, 46]
$Pd_{10}(CO)_{12}(PBu_3)_6$	(II)	1:4—1:10	Acetone, CF_3COOH	[52, 46]
$Pd_{10}(CO)_{14}(PEt_3)_4$ **	(III)	1:1.5—1:1.5	Acetone, CF_3COOH	[41, 27]
$Pd_{10}(CO)_{14}(PPr_3)_4$	(IV)	1:2	Acetone, CF_3COOH	[27]
$Pd_{10}(CO)_{14}(PBu_3)_4$	(V)	1:1.5—1:2.5	Acetone, CF_3COOH	[54]
$Pd_{10}(CO)_{12}[P(n\text{-}C_8H_{17})_3]_6$	(VI)	1:0.6	Acetone	[41]
$Pd_{10}(CO)_{12}[P(n\text{-}C_{12}H_{25})_3]_6$	(VII)	1:0.6	Acetone	[41]
$Pd_{10}(CO)_{12}(PPh_3)_6$	(VIII)	1:1—1:0.6	Acetone, NaOAc, HOAc	[29]
$Pd_{10}(CO)_{12}[P(C_6H_4\text{-}p\text{-}Me)_3]_6$	(IX)	1:0.7	Acetone, NaOAc, HOAc	[29]
$Pd_{10}(CO)_{12}[P(C_6H_4\text{-}p\text{-}OMe)_3]_6$	(X)	1:0.7	Acetone, NaOAc, HOAc	[29]

*The Pd : P molar ratio in the synthesis is quoted.
**In a mixture with compound (I).

Table 11. Infrared spectroscopic data for the decanuclear palladium clusters $Pd_{10}(CO)_{12}L_6$.

Ligand	ν(CO), cm^{-1}	Conditions	Refs.
PEt_3	2052 vw, 1921 sh, 1889 s, 1875 sh, 1850 s, 1841 sh, 1822 sh, 1806 sh, 1791 m or * 1892 s, 1853 s, 1790 m	LP	[27]
PEt_3	1892 s, 1875 m, 1856 s	Benzene	[27]
PBu_3	2038 vw, 1921 sh, 1889 s, 1878 sh, 1864 sh, 1852 s, 1827 sh, 1800 m or * 1884 s, 1850 s, 1799 m	LP	[27]
PBu_3 **	2034 s, 1914 s, 1898 s, 1871 s, 1818 s	LP	[27, 54]
$P(n\text{-}C_8H_{17})_3$	2032 w-m, 1920 sh, 1891 s, 1876 sh, 1856 s, 1800 m	Hexane film	[41]
$P(n\text{-}C_{12}H_{25})_3$	2034 w, 2017 vw, 1895 s, 1882 sh, 1859 s, 1835 sh, 1805 w	Hexane film	[41]
PPh_3	2036 w, 1906 s, 1893 m, 1870 s, 1839 shb, 1803 m	LP	[29]
PPh_3	1911 s, 1894 m, 1877 s, 1845 w-m, 1816 m	THF	[29]
$P(C_6H_4\text{-}p\text{-}Me)_3$	2023 w, 1906 s, 1893 m, 1872 s, 1847 s, 1809 m	LP	[29]
$P(C_6H_4\text{-}p\text{-}Me)_3$	1910 s, 1891 m, 1875 s, 1845 sh, 1815 m	THF	[29]
$P(C_6H_4\text{-}p\text{-}OMe)_3$	2036 w, 1901 s, 1889 m, 1867 s, 1832 sh 1803 m	LP	[29]
$P(C_6H_4\text{-}p\text{-}OMe)_3$	1906 s, 1890 m, 1872 s, 1845 sh, 1812 m	THF	[29]

*Depends on the degree of dispersion of the specimen in liquid paraffin.
**The $Pd_{10}(CO)_{14}(PBu_3)_4$ cluster.

The infrared and ^{31}P NMR spectra of the clusters (I), (II), and (V) have been obtained.[41,46,52–54] The absorption bands in the range 1810–1920 cm^{-1} which have been assigned to the vibrations of the bridging CO groups, and the bands at 2030–2040 cm^{-1}, assigned to the terminal CO groups, are characteristic of the infrared spectrum of cluster (V) (Table 11). The spectra of clusters (I) and (II) have a similar form and similar relative intensities of the ν(CO) bands. The spectra of clusters (II) and (V) are characterised by very similar sets of absorption bands of the bridging CO groups, but in the infrared spectrum of compound (V) these bands have undergone a hypsochromic shift of approximately 20 cm^{-1}.

The ^{31}P NMR spectrum of compound (V) (in benzene as the solvent) consists of a singlet with $\delta = -5.0$ p.p.m. The ^{31}P NMR spectra of clusters (III) and (I) are characterised by two signals with a 2 : 1 intensity ratio and $\delta = -4.0$ and +3.3 p.p.m. for compound (II) and $\delta = -11.0$ and −3.1 p.p.m. for compound (I).[52,53]

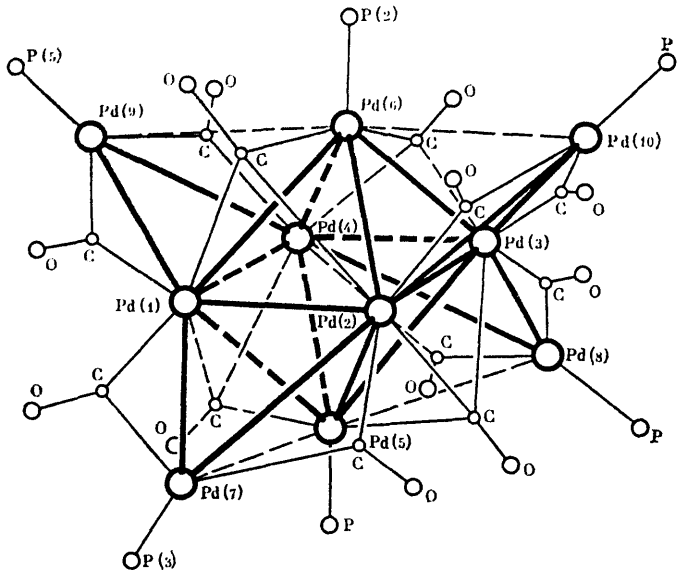


Figure 7. The structure of the $Pd_{10}(CO)_{12}(PBu_3)_6$ cluster.[53]

The spectroscopic data agree well with the structures of clusters (V) [54] and (II).[53] The structure of cluster (II) is illustrated in Fig. 7 (the n-butyl substituents are not shown).[53] Cluster (II) is an octahedron with capping palladium atoms located over its non-adjacent faces: the equatorial Pd(1)–Pd(4) atoms and the apical Pd(5) and Pd(6) atoms of the "internal" Pd_6 octahedron, as well as the Pd(7)–Pd(10) capping atoms. The Pd_{cap}–Pd_{eq} distances [2.694–2.722 (a) Å] are much smaller than the Pd_{cap}–Pd_{apic} distances [3.301–3.42 (2) Å]. The Pd–Pd distances in the internal "Pd_6" octahedral are in the range [2.791–2.851 (2) Å].[53] The eight μ_2-CO groups span the short Pd_{cap}–Pd_{eq} bonds and the four μ-CO groups are coordinated to the four free faces of the octahedron. The coordination of the CO groups to the faces is also asymmetric but, in contrast to the capping metal atoms, the carbon atoms of the μ_3-CO groups are displaced towards the apical palladium atoms, so that the Pd_{apic}–C distances [2.04–2.08 (2) Å] are shorter than the Pd_{eq}–C distances [2.23–2.35 (2) Å]. The six phosphorus

atoms of the tributyl phosphine ligands are linked to the four capping palladium atoms and the two apical palladium atoms. The ^{31}P NMR spectrum of these atoms is characterised by signals with $\delta = -4.0$ and $+3.3$ p.p.m.

Cluster (V) retains the same framework of metal atoms as cluster (II), but CO groups and not the PBu_3 ligand have been added to the apical palladium atoms. The $Pd_{cap}-Pd_{apic}$ distances in cluster (V) are shorter by approximately 0.015 Å than the analogous distances in cluster (II).[54] This shortening is apparently caused by the partial elimination of steric strain when the PBu_3 groups are replaced by CO groups. Another feature of the structure of cluster (V) is the presence in one molecule of three types of CO groups: four bridging μ_3-CO groups, eight bridging μ-CO groups, and two terminal groups.

(b) The influence of the acidity of the medium on the composition of the clusters. The replacement of trifluoroacetic acid by the weak acetic acid in the synthesis of the clusters $Pd_{10}(CO)_{12+x}L_{6-x}$ ($x = 0.2$) leads to a continuous variation of the composition of the product as a function of the Pd : P ratio. Under these conditions, the individual compounds (V) and (II) were obtained for stoichiometric Pd : P ratios; as the ratio decreases to 1 : 2.2, the $Pd_4(CO)_5 \cdot (PBu_3)_4$ cluster is formed. An analogous relation has been observed using PEt_3 as the ligand. It has been shown by spectroscopic methods that in the region of intermediate Pd : P ratios (from 1 : 06 to 1 : 2) a mixture of the $Pd_4(CO)_5 \cdot (PBu_3)_4$ and (II) clusters is formed.[41] In the case of triethylphosphine the mixture of compounds was resolved into the individual Pd_3 and Pd_7 clusters.[41]

Clusters having the compositions (VI) and (VII) have been obtained in a neutral medium for the stoichiometric Pd : P ratios and have been identified from infrared and ^{31}P NMR spectra. Their infrared spectra (Table 11) are analogous to those of the structurally characterised cluster (II). The ^{31}P NMR spectra of clusters (VI) and (VII) each containg two singlets with intensities in a ratio of 2 : 1, which corresponds to signals from phosphorus atoms coordinated to the four "capping" and two apical palladium atoms.[4]

It is noteworthy that in a neutral medium and in the HOAc + NaOc system with the Pd : PBu_3 = 1 : 0.4 ratio, cluster (II) with an admixture of metallic palladium is formed instead of the expected compound (V).[41] An important factor is the intermediate formation of the $Pd_4(CO)_5(PBu_3)_4$ cluster detected from the infrared spectra of the products in the initial stages of the reaction (in the HOAc + NaOAc system).[27,41]

On passing to a weakly alkaline medium (NaOAc) with the ratios Pd : PBu_3 = 1 : 1–1 : 1.4, $Pd_4(CO)_5(PBu_3)_4$ is formed in a mixture with metallic palladium, while under conditions with the ratio Pd : PBu_3 = 1 : 0.6, a mixture incorporating compound (II), $Pd_4(CO)_5(PBu_3)_4$ and metallic palladium is formed.[41]

The role of the acid consists of creating a specific equilibrium concentration of the free phosphine which is optimal for the formation of the cluster having the appropriate structure. Superstoichiometric amounts of $P(n\text{-}Alk)_3$ in the synthesis of compounds (I), (II), and (V) require the presence of a strong acid.[41,46,53] The excess ligand is bound in this case into the phosphonium salt $[HPAlk_3]^+ \cdot [CF_3COO]^-$. Otherwise in weakly acid and neutral media it is essential to reduce the concentration of $P(n\text{-}Alk)_3$ to give the stoichiometric ratios.[41]

A significant factor is that under the conditions of synthesis investigated and when the above trialkylphosphines are used, the "intermediate" $Pd_5-Pd_6-\ldots\ldots Pd_9$ structures cannot be detected either in solution or in the solid phase. Thus crystallisation during the synthesis in the $Pd(OAc)_2$–dioxan–Me_2CO–HX–PBu_3–H_2O–CO system leads only to clusters (II), (V), $Pd_4(CO)_5(PBu_3)_4$, and $Pd_4(CO)_6(PBu_3)_4$, depending on the Pd : PBu_3 ratio and the type of group X (X = CF_3COO^- or CH_3COO^-).[27,41]

(c) Clusters with aromatic phosphines. The lower basicity of aromatic phosphines precludes the regulation of their concentration by varying the acidity of the medium. The composition of the product is extremely sensitive to the Pd : P ratio during the synthesis and to the reaction time. The synthesis is therefore carried out under rigorously controlled conditions and yet despite this a reprecipitation is usually required to obtain a purer substance. Clusters (VIII)–(X) have been identified by elemental analysis and infrared spectroscopy (Table 11).[29]

7. Comparison of the Methods of Synthesis

Examination of the principal methods of synthesis of palladium and platinum clusters makes it possible to differentiate a number of common features. A low-valence complex of the metal, namely PdL_2, PtL_2, $Pt(cod)_2$, and $[Pt_3(CO)_6]_n^{2-}$, synthesised beforehand or obtained by reducing platinum(II) and palladium(II) in solution, is usually employed as the starting compound. Derivatives of the zerovalent metal are then converted into carbonyl-containing mononuclear complexes by treatment with carbon monoxide:

$$PtL_2 + 2CO \rightleftarrows Pt(CO)_2L_2;$$
$$Pd(OAc)_2 + 2CO + 3L + H_2O \rightarrow Pd(CO)L_3 + CO_2 + 2HOAc;$$
$$K_2PtCl_4 + 2L + CO \xrightarrow[N_2H_4]{KOH} Pt(CO)_2L_2.$$

As a consequence of the pronounced ability of zerovalent palladium and platinum compounds to form metal–metal bonds, in the presence of a deficiency of phosphine ligands the mononuclear phosphine metal carbonyl species are combined into clusters of different nuclearity depending on the conditions; this is shown particularly for the trinuclear compounds:

$$5Pt(CO)_2L_2 \rightleftarrows Pt_3(CO)_3L_4 + 2PtL_3 + 7CO;$$
$$3Pd(CO)L_3 \rightleftarrows Pd_3(CO)_3L_4 + 5L.$$

Another picture is observed when palladium dicarbonyl is used. X-Ray diffraction showed[15] that the $[Pt_3(CO)_6]_n^{2-}$ species have polymeric structures made up of three-membered rings linked by elongated Pt–Pt bonds. In this case mononuclear species are not produced[36] and attack by the phosphine results in the immediate splitting off of a fragment made up of three platinum atoms:

$$[Pt_3(CO)_6]_n^{-2} + 4PPh_3 \rightarrow Pt_3(CO)_3(PPh_3)_4 + [Pt_3(CO)_6]_{n-1}^{-2} + 3CO.$$

Furthermore, interconversions of clusters of different nuclearity are a common feature. Thus in an atmosphere of carbon monoxide the clusters $Pt_3(CO)_3(PPh_3)_4$ gradually disproportionates into $Pt_4(CO)_5(PPh_3)_4$ and a mononuclear complex:[22]

$$2Pt_3(CO)_3(PPh_3)_4 \xrightarrow{3CO} Pt_4(CO)_5(PPh_3)_4 + 2Pt(CO)_2(PPh_3)_2.$$

This process is particularly rapid for aliphatic phosphines, which precludes the synthesis of the trinuclear cluster with PEt_3 by reaction with platinum dicarbonyl. On the other hand, the high reactivity of the platinum clusters with aliphatic phosphines helps in effecting a wide variety of rearrangements of the clusters and leads to the selective formation of $Pt_4(CO)_5(PEt_3)_4$ and $Pt_5(CO)_6(PEt_3)_4$. The yield

and nuclearity of the clusters are in this case determined solely by the Pt : L ratio:[30]

$$[Pt_3(CO)_6]_n^{2-} + PEt_3 \rightarrow Pt_4(CO)_5(PEt_3)_4 + CO;$$
$$[Pt_3(CO)_6]_{n2}^{-} + PEt_3 \rightarrow Pt_5(CO)_6(PEt_3)_4 + CO.$$

The process involving an increase of nuclearity can be made more selective and rapid by binding the phosphines. The removal of the phosphines from the reaction media (by treatment with H^+, O_2, etc.) makes it possible to obtain clusters of high nuclearity immediately from the mononuclear species. This process has been investigated for palladium compounds.[55,56] In the case of platinum, $Pt_5(CO)_6(PEt_3)_4$ has been obtained in a high yield from the complex $Pt_4(CO)_5.(PEt_3)_4$ on treatment with CF_3COOH:

$$5Pt_4(CO)_5(PEt_3)_4 + 4CF_3COOH \rightarrow 4Pt_5(CO)_6(PEt_3)_4 + 4[HPEt_3]^+CF_3COO^- + CO.$$

In the synthesis of the pentanuclear platinum clusters by the method of Bender and co-workers[47,49] involving the reduction of $PtCl_2L_2$ by carboxylate ions, the interconversion of the clusters probably also takes place. The method yields as a rule a mixture of compounds, the most stable form $Pt_5(CO)_6L_4$ being separated in the chromatographic stage. This has been confirmed by a later study[50] where impregnation of different carriers by the $Pt_3(CO)_3L_4$ clusters leads to their conversion into pentanuclear compounds $Pt_5(CO)_6L_4$.

Much less complex transformations take place in the synthesis of the pentanuclear platinum clusters in the reaction of phosphine ligands with $[Pt_3(CO)_6]_n^{2-}$. As already mentioned, in this case the first reaction stage involves the formation of $Pt_3(CO)_3L_4$ and this stage is rapid. The compound then reacts slowly with platinum dicarbonyl to form $Pt_5(CO)_6L_4$:[36]

$$Pt_3(CO)_3L_4 + [Pt_3(CO)_6]_n^{2-} \rightarrow Pt_5(CO)_6L_4 + CO.$$

In the case of aliphatic phosphines the rates of both stages are similar and the trinuclear cluster is therefore obtained always in a mixture with compounds with a higher nuclearity. It is noteworthy that the Pt_4 cluster in solution does not undergo disproportionation and its conversion into the Pt_5 cluster requires the elimination of the phosphine ligand and its chemical binding. The disproportionation reactions take place for all the palladium cluster compounds, including the decanuclear clusters.[55,56]

III. THE INTERCONVERSION OF PHOSPHINEPALLADIUM CARBONYL CLUSTERS

It was found that in the synthesis of phosphine metal carbonyl clusters the acidity of the medium has a strong influence on the formation of compounds with a particular nuclearity; this observation has been used to synthesise one compound from another. The above possibility has been realised experimentally in two studies,[55,56] which led to the development of the method for increasing the nuclearity of phosphinepalladium carbonyl compounds. The method is based on the binding of the phosphine-containing ligand. The choice of reactant depends on the basicity of the phosphine ligand and includes acids, oxidants, organohalogen compounds, and complexes of metals in different oxidation states:[27,55,56]

$$PR_3 + H^+ \text{ (or } {}^1/_2O_2) \rightarrow HPR_3^+ \text{ (or } OPR_3); \quad (1)$$
$$PR_3 + R'X \rightarrow [R'PR_3]^+X^-; \quad (2)$$
$$nPR_3 + M(CO)_x \rightarrow M(CO)_{x-n}(PR_3)_n + nCO; \quad (3)$$
$$2PR_3 + MX_2 \rightarrow (PR_3)_2MX_2. \quad (4)$$

1. The Interconversions of Clusters in the Pd(0)–CO–P(n-Alk)$_3$ System

In a system with tri-n-alkylphosphine ligands the clusters undergo interconversions with a change in the degree of their nuclearity and the composition of the coordination shell. The $Pd_4 \rightleftharpoons Pd_{10}$ interconversion is the key factor:[55]

$$5Pd_4(CO)_5[P(n\text{-Alk})_3]_4 + 8H^+ \rightarrow 2Pd_{10}(CO)_{12}[P(n\text{-Alk})_3]_6 + 8[HP(n\text{-Alk})_3]^+ + CO;$$
$$2Pd_{10}(CO)_{12}[P(n\text{-Alk})_3]_6 + 8P(n\text{-Alk})_3 + CO \rightarrow 5Pd_4(CO)_5[P(n\text{-Alk})_3]_4.$$

The interconversion takes place with a high selectivity (>90%). The transformation $Pd_4 \rightarrow Pd_{10}$ has been carried out by treating $Pd_4(CO)_5(PEt_3)_4$ with iron pentacarbonyl (88% of compound (I) was obtained] and by treating $Pd_4(CO)_5(PBu_3)_4$ with palladium acetate or 8-bromomethylquinoline, i.e. on the basis of reactions (2)–(4). A compound from the family of phosphine palladium carbonyl clusters can also be used as an acceptor of the phosphorus-containing ligand:[55]

$$10Pd_{10}(CO)_{14}(PBu_3)_4 + 11Pd_4(CO)_5(PBu_3)_4 \rightarrow 14Pd_{10}(CO)_{12}(PBu_3)_6 + 27CO + 4Pd.$$

Cluster (II) has also been obtained from the complex PdL_4, where L = PBu_3 but with a lower yield (10%):[55]

$$10\,PdL_4 + 34\,H^+ + 12\,CO \rightarrow Pd_{10}(CO)_{12}L_6 + 34\,HL^+.$$

The reactions, which take place with a change in the composition of the coordination shell, include the following processes:[46,55]

$$Pd_{10}(CO)_{12}(PBu_3)_6 + 2H^+ + 2CO \rightarrow Pd_{10}(CO)_{14}(PBu_3)_4 + 2HPBu_3;$$
$$Pd_{10}(CO)_{14}(PBu_3)_4 + 2PBu_3 \rightarrow Pd_{10}(CO)_{12}(PBu_3)_6 + 2CO;$$
$$Pd_4(CO)_5(PBu_3)_4 + CO \rightarrow Pd_4(CO)_6(PBu_3)_4. \quad (5)$$
(XI)

In order to obtain the pure compound (V) by reaction (5), it is necessary to monitor the latter with respect to time: on treatment with an excess of H^+, metallic palladium is gradually formed.[54,55]

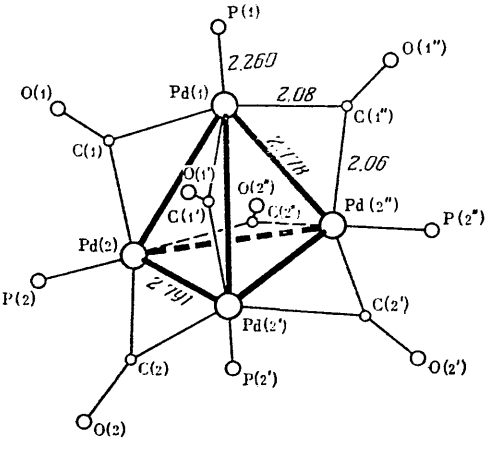


Figure 8. The structure of the $Pd_4(CO)_6(PBu_3)_4$ cluster.[46]

The structurally characterised cluster (XL) (Fig.8) has been obtained by crystallising $Pd_4(CO)_5(PBu_3)_4$ in a CO atmosphere.[46] The cluster consists of a virtually undistorted tetrahedron, all the edges of which are spanned by

the μ-CO ligands and each palladium atom is coordinated to one phosphorus atom of the phosphine ligand.

Thus the overall mechanism of the interconversion of the phosphinepalladium carbonyl clusters in the Pd(0)–CO–P(n-Alk)$_3$ system can be represented as follows:

$$PdL_4 \underset{L,N_2,\Delta}{\overset{CO}{\rightleftarrows}} Pd(CO)L_3 \underset{L}{\overset{CO,\,H^+}{\rightleftarrows}} Pd_4(CO)_5L_4 + Pd_4(CO)_6L_4 \underset{L}{\overset{CO,\,H^+}{\rightleftarrows}}$$
$$\rightleftarrows Pd_{10}(CO)_{12}L_6 \underset{L}{\overset{CO,\,H^+}{\rightleftarrows}} Pd_{10}(CO)_{14}L_4 \begin{cases} \xrightarrow{CO,\,H^+} Pd \\ \xrightarrow[L]{} PdL_4 \end{cases}.$$

This mechanism constitutes a clear illustration of one of the definitions of clusters as compounds intermediate between the classical mononuclear complexes and compact metal.

2. The Interactions of the Clusters in the Pd(0)–CO–PPh$_3$ System

The use of an acid to increase the nuclearity of clusters in this system is ineffective owing to the low basicity of the aromatic phosphine ligand. Up to $n = 4$, the binding of the triphenylphosphine ligand is not essential in view of the existence of the following equilibria in the solutions:[33,35,56–58]

$$PdL_4 + CO \rightleftarrows Pd(CO)L_3 + L;$$
$$3\,Pd(CO)L_3 \rightleftarrows Pd_3(CO)_3L_3 + 5\,L;$$
$$4\,Pd_3(CO)_3L_4 + 3\,CO \rightleftarrows 3\,Pd_4(CO)_5L_4 + 4\,L.$$

The $Pd_3(CO)_3(PPh_3)_4$ cluster is much more stable than its analogue with the PBu_3 ligand, which could not be isolated. In solution in a CO atmosphere the $Pd_3(CO)_3(PPh_3)_4$ cluster is converted into the tetranuclear $Pd_4(CO)_5(PPh_3)_4$ cluster previously characterised as $Pd_3(CO)_3L_3$.[35,58] We may note that the platinum cluster $Pt_3(CO)_3L_4$ disproportionates under similar conditions into $Pt_4(CO)_5L_4$ and $Pt(CO)_2L_2$.[22]

The composition and yield of the products of crystallisation of the compounds PdL_4, $Pd(CO)L_3$, and $Pd_3(CO)_3L_4$ in a CO atmosphere depend on the concentrations of the starting materials, the nature of the solvent, the reaction time, the temperature, and the composition of the gas phase. In some cases it is possible to obtain crystals containing two different clusters. Thus the joint crystallisation of two clusters, i.e. $Pd_3(CO)_3(PPh_3)_4Pd_4(CO)_5(PPh_3)_4.C_6H_6$, has been observed by X-ray diffraction.[33]

In solution in an atmosphere of CO the $Pd_4(CO)_6(PPh_3)_4$ cluster is also in equilibrium with the form having a higher nuclearity, namely the cluxter (VIII).[56]

The decanuclear cluster (VIII) has been obtained by oxidising PdL_4, $Pd(CO)L_3$, $Pd_3(CO)_3(PPh_3)_4$, or $Pd_4(CO)_5(PPh_3)_4$ with an oxygen–carbon monoxide mixture (in proportions of 2 : 1):[27,56]

$$10PdL_4 + 17O_2 + 12CO \rightarrow Pd_{10}(CO)_{12}L_6 + 34OL;$$
$$10Pd_4(CO)_5L_4 + 9O_2 \xrightarrow{CO} 4Pd_{10}(CO)_{12}L_6 + 16OL + 2CO_2. \qquad (6)$$

The formation of cluster (VIII) in these reactions has been demonstrated by elemental analysis, infrared spectroscopy (Table 11), and ^{31}P NMR of the solution at the end of the oxidation reaction.[27,56] The ^{31}P NMR spectrum of the solution in toluene[56] indicates the formation of $OPPh_3$ (–23.7 p.p.m.) and cluster (VIII), which gives rise to two signals, at –23.0 and –15.9 p.p.m., with an intensity ratio of approximately 2 : 1. The difference between their chemical shifts (7.1 p.p.m.) is the same as in the ^{31}P NMR spectra of clusters (I) and (II) (7–8 p.p.m.).[41,52,53] The relative signal intensities $OPPh_3 : PPh_3 = 1 : 1.6$ confirm the stoichiometry of reaction (6).

A decrease of nuclearity with formation of the individual compounds is achieved in the interaction with phosphine in the ratios (VIII) : L = 1 : 7), (VIII) : L = 1 : 11, and $Pd_4(CO)_5(PPh_3)_4$: L = 1 : 2.5 respectively:[56]

$$2Pd_{10}(CO)_{12}L_6 + 8L + CO \xrightarrow{\text{toluene}} 5Pd_4(CO)_5L_4;$$
$$3Pd_{10}(CO)_{12}L_6 + 22L \xrightarrow{\text{acetone}} 10Pd_3(CO)_3L_4 + 6CO;$$
$$3Pd_4(CO)_5L_4 + 4L \xrightarrow{\text{acetone}} 4Pd_3(CO)_3L_4 + 3CO.$$

Treatment of any of the clusters $Pd_3(CO)_3L_4$, $Pd_4(CO)_5L_4$, or (VIII) with an excess of the ligand L leads to the complex PdL_4.

The triphenylphosphinepalladium carbonyl clusters are also formed in the disproportionation reactions of clusters of different nuclearity.[56] The interaction of the stoichiometric amounts of Pd_3 and (VIII) in the presence of L in toluene leads to the Pd_4 cluster:

$$6\,Pd_3(CO)_3L_4 + Pd_{10}(CO)_{12}L_6 + 5\,CO \rightarrow 7\,Pd_4(CO)_5L_4 + 2\,L.$$

The $Pd_4(CO)_5L_4$ cluster has been obtained by the interaction of compound (VIII) and PdL_4 in toluene in the ratio (VIII) : PdL_4 = 1 : 2:

$$Pd_{10}(CO)_{12}L_6 + 2\,PdL_4 + 3\,CO \rightarrow 3\,Pd_4(CO)_5L_4 + 2\,L.$$

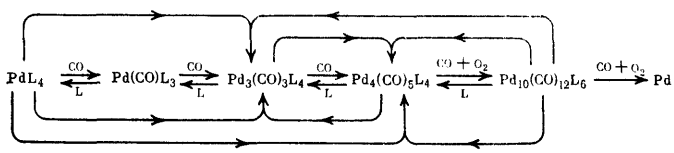
The highly labile $Pd_3(CO)_3L_4$ cluster is not formed in appreciable amounts in solution even under favourable stoichiometric conditions; the products of the reaction of compound (VIII) and PdL_4 in toluene for the ratio (VIII) : PdL_4 = 1 : 4 are $Pd_4(CO)_5(PPh_3)_4$ and $Pd(CO)L_3$:[56]

$$Pd_{10}(CO)_{12}L_6 + 4\,PdL_4 + 5\,CO \rightarrow 3\,Pd_4(CO)_5L_4 + 2\,Pd(CO)L_3 + 4\,L.$$

However, the interaction in acetone, in which all the compounds involved in the reaction are sparingly soluble, leads to the formation of $Pd_3(CO)_3L_4$ for the molar ratios (VIII) : : PdL_4 = 1 : 5 and $Pd_4(CO)_5L_4$: PdL_4 = 1 : 2:[56]

$$Pd_{10}(CO)_{12}L_6 + 5\,PdL_4 + 3\,CO \rightarrow 5\,Pd_3(CO)_3L_4 + 6\,L;$$
$$Pd_4(CO)_5L_4 + 2\,PdL_4 + CO \rightarrow 2\,Pd_3(CO)_3L_4 + 4\,L.$$

The overall mechanism of the interconversions of triphenylphosphinemetal carbonyl compounds can be formulated as follows:

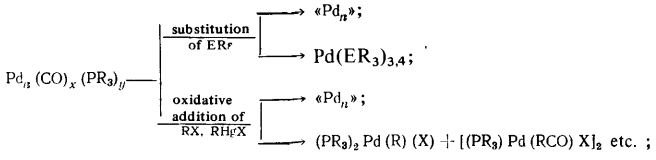


An important property of the Pd(0)–CO–PR$_3$ system, where R = n-Alk and R = Ph, is the formation of isotypical Pd_4 and Pd_{10} clusters, although the PPh_3 group differs from P(n-Alk)$_3$ (for example, from PBu_3) in its steric and electronic characteristics.[59]

In contrast to the Pd(0)–CO–P(n-Bu)$_3$ system, in the system with the triphenylphosphine ligand it is not possible to isolate in a pure state the second decanuclear cluster $Pd_{10}(CO)_{14}L_4$. An increase of the duration of the treatment of solutions of the clusters $Pd_4(CO)_5(PPh_3)_4$ or (VIII) with the CO + O_2 mixture leads to the formation of a mixture of $Pd_{10}(CO)_{12}L_6$, $Pd_{10}(CO)_{14}L_4$, and metallic palladium.[56] Another difference consists of the existence of the trinuclear $Pd_3(CO)_3(PPh_3)_4$ cluster, which is stable in the solid state. As in the system with PBu_3, in that with PPh_3 it has not so far been possible to isolate compounds with an intermediate nuclearity in the range $4 < n \leq 9$.[56]

IV. CHEMICAL PROPERTIES

It is possible to differentiate two types of reactions characteristic of phosphinepalladium carbonyl clusters, namely the substitution and oxidative addition reactions. By virtue of the polynuclearity of the initial compounds, each of these reactions can lead in the general case to products of two types—with retention of the initial structure or with a change in nuclearity up to the formation of mononuclear compounds:[27]



Cluster (V), being most depleted in the phosphine ligand, is suitable for substitution reactions. Depending on the ratio (V) : substituting ligand, compounds with different nuclearities n = 10, 4, or 1) and heterogeneous (for n = 10 or 4) or homogeneous (for n = 4 or 1) phosphorus-containing ligands are formed. Thus treatment of compound (V) with a solution PPh_3 as L in the proportions (V) : L = 1 : 2 yielded the $Pd_{10}(CO)_{12}(PBu_3)_4(PPh_3)_2$ cluster:

$$Pd_{10}(CO)_{14}(PBu_3)_4+2\ PPh_3 \rightarrow Pd_{10}(CO)_{12}(PBu_3)_4(PPh_3)_2+2\ CO,$$

while reaction involving the proportions 1 : 3.7 yielded the $Pd_{10}(CO)_{12}(PBu_3)(PPh_3)_5$ cluster.[27]

It has been shown that the triphenylphosphine ligand in the compound $Pd_{10}(CO)_{12}(PBu_3)_4(PPh_3)_2$ is coordinated not only to the apical palladium atoms but also to the capping palladium atom in the proportions $L_{cap} : L_{apic} = 1.8 : 1.0$.[27] A ^{31}P NMR study showed that the observed coordination of triphenylphosphine is caused by the simultaneous substitution of the terminal CO groups at the apical palladium atom and of the PBu_3 groups at the capping atom (with some predominance of the substitution of the CO groups). The PBu_3 liberated in this process can also substitute terminal CO groups.[27]

The decomposition of the structures of the $Pd_{10}(CO)_{14}.(PBu_3)_4$ and $Pd_{10}(CO)_{12}(PBu_3)_6$ clusters with formation of $Pd_4(CO)_5(PBu_3)_{4-n}(PPh_3)_n$ clusters has been observed in the presence of a more than 4-molar excess of PPh_3. A further increase of the amount of PPh_3 (up to $Pd_{10} : PPh_3$ = 1 : 12) leads to the formation of a mixture of $Pd(CO)(PPh_3)_3$ and $Pd(PPh_3)_4$.[27] Treatment of the compound $Pd_4(CO)_5.(PBu_3)_4$ with triphenylphosphine in the proportions $Pd_4 : PPh_3$ = 1 : 2 gives rise to a mixture of $Pd_4(CO)_5.(PBu_3)_{4-n}(PPh_3)_n$ (where $n \cong 2$–4), $Pd(CO)(PPh_3)_3$, and $Pd(PPh_3)_4$.[27]

The interaction of the Pd_{10} clusters with an excess of L = ER_3, where E = P, As, or Sb, in the proportions $Pd_{10} : ER_3$ = 1 : 40 and less leads to the mononuclear PdL_4 complexes and can be regarded as yet another method of synthesis of these compounds:[27]

$$Pd_{10}(CO)_{12}(PAlk_3)_6+40\ ER_3 \rightarrow 10\ Pd(ER_3)_4+12\ CO+6\ PAlk_3.$$

The complexes $Pd(PR_3)_x$ have been obtained for R—OPh (x = 4) and R = p-$CH_3C_6H_4$ or p-$CH_3OC_6H_4$ (x = 3).[27]

The advantage of the proposed method[27] of synthesis of PdL_4 and similar complexes over the familiar method[60] lies in the presence in the coordination shell of the initial cluster of carbon monoxide as the dominant ligand, which can be readily removed into the gas phase and does not therefore prevent the isolation of the pure substance.

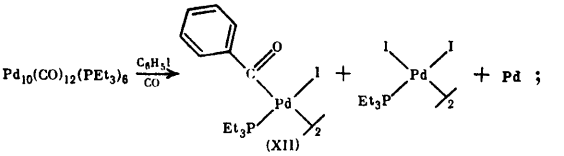
The majority of the oxidative addition reactions have been carried out with trialkylphosphinemetal carbonyl clusters Pd_4 and Pd_{10}.[61] Almost all the reactions are accompanied by the elimination of CO and the decomposition of the initial structure.

The reactions with RX and RHgX yielded products both containing the carbonyl group in the R—CO—Pd fragment and without it, as in R—Pd; carbonyl-containing compounds are then formed regardless of whether the reaction is carried out in an atmosphere of CO or in an inert gas. Furthermore, metallic palladium is produced and the compounds $[PdI_2.(PEt_3)]_2$, $PdBr_2(PBu_3)_2$, etc. are formed. A wide variety of products can be accounted for, apart from the possibility of different reaction pathways, by the chemical non-equivalence of the Pd atoms in the Pd_{10} cluster. As mentioned above, three types of palladium atoms can be differentiated in the Pd_{10} structure (Fig. 7)—equatorial, capping, and apical. Among these the capping and apical atoms are most accessible to the attacking molecule, while the equatorial atoms, which lack phosphine ligands, are primarily responsible for the formation of metallic palladium. The interaction of RX, RHgX, or R_2Hg with one of the outer Pd atoms apparently causes a rapid decomposition of the $Pd_{10}(Pd_4)$ structure. The ratio of the oxidative addition products and the metal is then determined solely by the relative rates of reaction of the decomposing Pd_{10} (or Pd_4) fragments with RX, RHgX, or R_2Hg and their agglomeration to the metal.[61]

In the reaction with an excess of C_3H_5Cl the metal is not produced as a consequence of the formation of the compound $[(\eta^3\text{-}C_3H_5)Pd]_2$, which does not require additional phosphine ligands:[27]

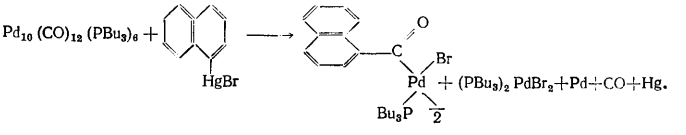
$$Pd_{10}(CO)_{12}(PBu_3)_6+10\ C_3H_5Cl \rightarrow 2[(\eta^3\text{-}C_3H_5)PdCl]_2+$$
$$+6(\eta^3\text{-}C_3H_5)PdCl(PBu_3)+12\ CO.$$

The reaction of iodobenzene with compound (I) in an atmosphere of CO and the reaction of bromobenzene with $Pd_4(CO)_5.(PEt_3)_4$ in an atmosphere of N_2 lead to di-μ-iodobis[benzoyl(triethylphosphine)palladium] (XII), phenylbis(triethylphosphine)palladium bromide (XIII), and benzoylbis(triethylphosphine)palladium bromide (XIV):[27]



$$Pd_4(CO)_5(PEt_3)_4 + C_6H_5Br \xrightarrow{N_2} \underset{(XIII)}{(Ph)(Br)Pd(PEt_3)_2} +$$
$$+ \underset{(XIV)}{(PhCO)(Br)Pd(PEt_3)_2} + Br_2Pd(PEt_3)_2 + Pd + CO\ .$$

The interaction of α-naphthylmercury bromide with cluster (II) takes place with liberation of mercury in accordance with the general mechanism of redox demercuration[62] and is accompanied by the insertion of the CO group and the formation of di-μ-bromobis[α-naphthoyltributylphosphinepalladium]:[61]

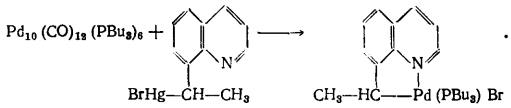


A mononuclear diarylpalladium derivative has been obtained by reaction (7) in the light in the course of seven days:[61]

$$Pd_{10}(CO)_{12}(PBu_3)_6 + (C_6F_5)_2Hg + Ph_2PC_2H_4PPh_2 \rightarrow (C_6F_5)_2Pd(Ph_2PC_2H_4PPh_2). \quad (7)$$

A chelate σ-complex of palladium(II) has been obtained as

one of the products of the reaction with 8-(α-bromomercuriethyl)quinoline:[61]



A second product of the same reaction proved to be a cluster whose infrared spectrum contains two bands due to the bridging CO groups at 1900 and 1860 cm^{-1} and which could not be isolated. However, its triethylphosphine analogue has been obtained by the reaction of the cluster $Pd_4(CO)_5(PEt_3)_4$ with 8-(α-bromomercuriethyl)quinoline.

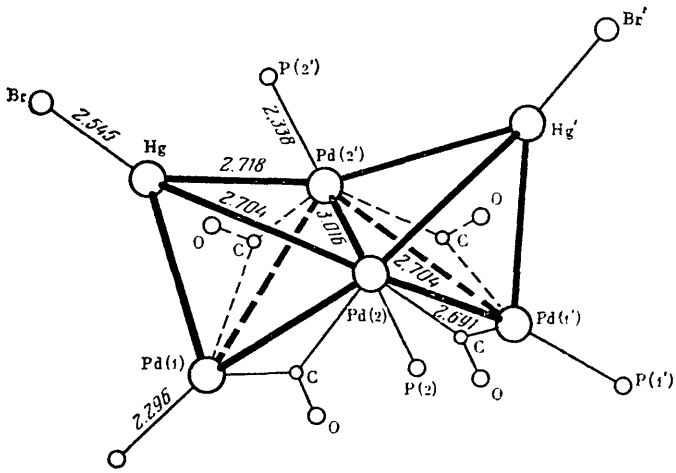


Figure 9. The structure of the $Pd_4Hg_2(CO)_4(PEt_3)_4Br_2$ cluster.[63]

The elemental composition and structure of the first heteronuclear palladium-mercury cluster $Pd_4Hg_2(CO)_4(PEt_3)_4 \cdot Br_2$ has been established by X-ray diffraction (Fig.9).[63] The cluster consists of a "butterfly", both "wings" of which are centred on the Hg—Br fragments. All the Pd—Pd bonds, with the exception of the elongated "hinged" bonds, are spanned by the μ_2-CO groups, each palladium atom being coordinated to a phosphorus atom. One may assume[27] that the charges in the cluster are separated up to the attainment of the limiting state $[(Pd_4(CO)_4(PEt_3)_4]^{2-}[HgBr]_2^{2+}$. In this compound both the anion and cation should be fairly stable: the anion is isoelectronic with the stable $Pd_4(CO)_5(PEt_3)_4$ cluster, while the mercury in the cation is in its usual +2 oxidation state.

The second heteronuclear palladium-mercury cluster has been obtained by the reaction of $Pd_4(CO)_5(PEt_3)_4$ with mercury:[64]

$$2\ Pd_4(CO)_5(PEt_3)_4 + Hg \rightarrow Pd_6Hg(CO)_6(PEt_3)_6 + 4\ CO + 2\ PEt_3 + 2\ Pd.$$

The formula of the compound has been proposed on the basis of analytical data and a cryoscopic determination of the molecular weight. In the suggested structure (Fig.10) all the CO groups are bridging (the bands at 1862 and 1822 cm^{-1} in the infrared spectrum) and span all six Pd—Pd bonds. Each palladium atom is coordinated to one phosphorus atom of the phosphine ligand.

The information available about reactions involving oxidative addition to triphenylphosphinepalladium(0) carbonyl clusters is limited: only the complex [Pd(I).(PhCO)(PPh_3). .toluene] (apparently with a dinuclear structure) has been obtained by treating a solution of PhI and $Pd_3(CO)_3(PPh_3)_4$ in toluene with carbon monoxide; $Pd(PhCO)(I)(PPh_3)_2$ was obtained as an admixture.[65]

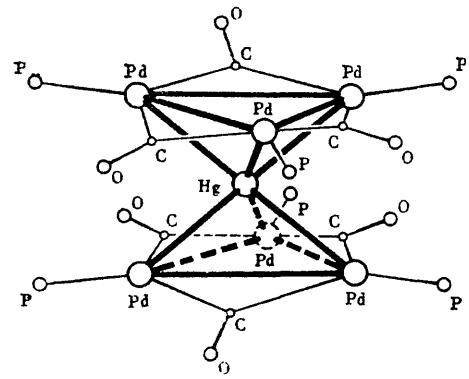


Figure 10. The suggested structure of the $Pd_6Hg(CO)_6 \cdot (PEt_3)_6$ cluster.[64]

The $Pd_3(CO)_3(PPh_3)_4$ [35] and $Pd_4(CO)_5(PPh_3)_4$ [33,35] clusters catalyse the methoxycarbonylation of aryl halides under mild conditions,[65] but the compounds themselves apparently decompose during the reaction. The following mechanism of the process has been proposed:[65-67]

$$PdL_n + PhI \rightarrow (Ph)Pd(I)L_{n-2} + 2\ L;$$
$$(Ph)Pd(I)L_{n-2} + CO \rightarrow (PhCO)Pd(I)L_{n-2};$$
$$(PhCO)Pd(I)L_{n-2} + CH_3OH \rightarrow PhCOOCH_3 + (H)Pd(I)L_{n-2};$$
$$(H)Pd(I)L_{n-2} + 2\ L + R_2NH \rightarrow PdL_n + R_2NH_2^+ + I^-.$$

where L is carbon monoxide, phosphine, or a solvent molecule. The activities of the substrates vary inversely to the C—halogen bond energy: PhI > PhBr ≫ PhCl.

The chemical properties of phosphineplatinum(0) carbonyl clusters have so far been inadequately investigated; we shall examine the main ones.

The interaction of the trinuclear clusters with carbon monoxide leads to tetranuclear platinum clusters. In contrast to the corresponding reaction of the $Pd_3(CO)_3L_4$ palladium cluster, a second platinum-containing product is formed in this reaction, namely a mononuclear complex:[22]

$$Pt_3(CO)_3L_4 + CO \rightarrow Pt_4(CO)_5L_4 + Pt(CO)_2L_2.$$

The removal of the phosphine ligands in the form of quaternary phosphonium salts or complexes with other metals is accompanied by a rearrangement of the skeleton:[48,50]

$$Pt_3(CO)_3(PPh_3)_4 \xrightarrow[\text{sorbent}]{H^+} Pt_5(CO)_6(PPh_3)_4;$$
$$Pt_4(CO)_5(PEt_3)_4 \xrightarrow[Fe(CO)_5]{H^+} Pt_5(CO)_6(PEt_3)_4.$$

Treatment with a measured amount of the phosphine ligand leads either to a cluster with a smaller number of platinum atoms in the metallic skeleton [32] or to the complete decomposition of the skeleton to mononuclear zerovalent platinum compounds: [22]

$$Pt_4(CO)_5(PEt_3)_4 + PEt_3 \xrightarrow{N_2} Pt_2(CO)_3(PEt_3)_4 + Pt(PEt_3)_x;$$
$$Pt_3(CO)_3(PPh_3)_4 + dppe \rightarrow Pt(dppe)_2 + CO + PPh_3;$$
$$dppe = Ph_2PC_2H_4PPh_2.$$

The latter reaction is used for the volumetric determination of the CO content in the cluster. [22]

The reaction of phosphineplatinum carbonyl clusters with SO_2 yielded the corresponding SO_2 containing clusters (with retention of the skeleton): [8]

$$Pt_3(CO)_3(PPh_3)_4 + 3\ SO_2 \rightarrow Pt_3(SO_2)_3(PPh_3)_3 + CO + PPh_3;$$
$$Pt_4(CO)_5(PMe_2Ph)_4 + 5\ SO_2 \rightarrow Pt_4(SO_2)_5(PMe_2Ph)_4 + 5\ CO;$$
$$Pt_3(CO)_6(PPh_3)_4 + 3\ SO_2 \rightarrow Pt_3(CO)_2(SO_2)_3(PPh_3)_4 + 4\ CO.$$

In the last case the SO_2 groups substitute all the CO groups with the exception of the terminal and one of the basal groups in the tetrahedral fragment. The reverse process, i.e. the displacement of the SO_2 groups by carbon monoxide, takes place with rearrangement of the skeleton: [8]

$$Pt_3(SO_2)_3(PPh_3)_3 \xrightarrow[CO]{60^\circ C} Pt_3(CO)_6(PPh_3)_4 + SO_2.$$

Oxidation of the trinuclear $Pt_3(CO)_3[P(t\text{-}Bu)_3]_3$ cluster with a stoichiometric amount of iodine leads to a dinuclear platinum(I) complex: [68]

$$Pt_3(CO)_3[P(t\text{-}Bu)_3]_3 + I_2 \rightarrow [PtI(CO)P(t\text{-}Bu)_3]_2.$$

The reaction with mercury takes place in a somewhat unusual manner. The trinuclear $Pt_3(CO)_3L_3$ clusters, where L = PPh(iso-Pr)$_2$, P(iso-Pr)$_3$, or PEt(t-Bu), react with mercury to form compounds in which two triangles made up of platinum atoms are linked by an Hg–Hg chain. [69] The reaction with $Pt_4(CO)_5(PEt_3)_4$ leads to the $Hg[Pt_3(CO)_3 \cdot (PEt_3)_3]_2$, which has a sandwich structure where the mercury atom links symmetrically two planar triangles made up of platinum atoms. [69]

Analysis of the literature data has shown that phosphine-metal carbonyl clusters are most typical for palladium and platinum. Whereas compounds with n = 3, 4, or 5 are known for platinum, compounds with n = 3, 4, 7, or 10 are known for palladium. Reactions involving a change in nuclearity are characteristic of palladium and platinum clusters.

The great possibilities of clusters in the formation of effective catalysts must be emphasised. The creation of effective catalytic systems based on cluster compounds will probably constitute in the immediate future the theoretically and practically most important trend in the development of catalysis.

REFERENCES

1. E.L.Muetterties, J.Organometal.Chem., 1980, 200, 177.
2. I.I.Moiseev, T.A.Stromnova, M.N.Vargaftig, G.Ya.Mazo, L.G.Kuz'mina, and Yu.T.Struchkov, Chem.Comm., 1978, 27.
3. T.A.Stromnova, M.N.Vargaftik, T.S.Khodashova, M.A.Porai-Koshits, and I.I.Moiseev, Koord.Khim., 1981, 7, 132.
4. S.Otsuka, Y.Tatsumo, M.Miki, T.Aoki, M.Matsumoto, H.Yoshioka, and K.Nakatsu, Chem.Comm., 1973, 445.
5. G.W.Bushnell, K.R.Dixon, P.M.Moroney, A.D.Rattray, and C.Wan, Chem.Comm., 1977, 709.
6. M.Green, J.A.K.Howard, M.Murray, J.L.Spenser, and F.G.A.Stone, J.Chem.Soc., Dalton Trans., 1977, 1509.
7. D.C.Moody and R.R.Ryan, Inorg.Chem., 1977, 16, 1502.
8. C.E.Briant, D.G.Evans, and D.P.M.Mingos, Chem. Comm., 1982, 1144.
9. N.G.Taylor, P.S.Chieh, and A.J.Carty, Chem.Comm., 1975, 448.
10. D.G.Evans, G.R.Hughes, D.M.P.Mingos, J.-M.Bassett, and A.Welch, Chem.Comm., 1980, 1225.
11. L.J.Guggenburger, Chem.Comm., 1968, 512.
12. M.A.A.F.de C.T.Carrondo and A.C.Skapski, Chem. Comm., 1976, 410.
13. D.Gregson, J.A.K.Howard, M.Murray, and J.L.Spencer, Chem.Comm., 1981, 716.
14. Y.Yamamoto, K.Aoki, and H.Yamazaki, Chem.Letters, 1979, 391.
15. J.C.Calabrese, L.F.Dahl, P.Chini, G.Longoni, and S.Martinengo, J.Amer.Chem.Soc., 1974, 96, 2614.
16. G.Longoni and P.Chini, J.Amer.Chem.Soc., 1976, 98, 7225.
17. P.Chini, J.Organometal.Chem., 1980, 200, 37.
18. L.Manojlovic-Muir, K.W.Muir, B.R.Lloyd, and R.J.Puddephatt, Chem.Comm., 1983, 1336.
19. T.Yoshida and S.Otsuka, J.Amer.Chem.Soc., 1977, 99, 2134.
20. R.G.Goel, W.O.Ogini, and R.C.Shrivastava, J.Organometal.Chem., 1981, 214, 405.
21. A.Moor, P.S.Pregosin, and L.M.Venanzi, Inorg.Chim. Acta, 1981, 48, 153.
22. J.Chatt and P.Chini, J.Chem.Soc.A, 1970, 1538.
23. A.B.Goel and S.Goel, Inorg.Nuclear Chem.Letters, 1980, 16, 397.
24. H.C.Clark, A.B.Goel, and C.S.Wong, Inorg.Chim. Acta, 1979, 34, 159.
25. R.G.Goel and R.C.Shrivastava, J.Organometal.Chem., 1983, 244, 303.
26. A.Albinati, Inorg.Chim.Acta, 1977, 22, L31.
27. E.G.Mednikov, Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1983.
28. M.Hidai, M.Kokura, and Y.Uchida, J.Organometal. Chem., 1973, 52, 431.
29. E.G.Mednikov, N.K.Eremenko, and S.P.Gubin, Koord. Khim., 1984, 10, 711.
30. N.K.Eremenko et al., Izv.Akad.Nauk SSSR, Ser.Khim., 1983, 682.
31. A.Moor, P.S.Pregosin, and L.M.Venanzi, Inorg.Chim. Acta, 1982, 61, 135.
32. A.Albinati, G.Carturan, and A.Musco, Inorg.Chim. Acta, 1976, 16, L3.
33. E.G.Mednikov, N.K.Eremenko, S.P.Gubin, Yu.L.Slovokhotov, and Yu.T.Struchkov, J.Organometal.Chem. (in the Press).
34. R.Ugo, S.Cenini, N.F.Pilbrow, B.Deible, and G.Schneider, Inorg.Chim.Acta, 1976, 18, 113.
35. A.Misono, Y.Uchida, M.Hidai, and K.Kudo, J.Organometal.Chem., 1969, 20, P7.
36. N.K.Eremenko, E.G.Mednikov, and S.P.Gubin, Koord. Khim., 1984, 10, 617.
37. G.Booth and J.Chatt, J.Chem.Soc.A, 1966, 634.
38. G.Booth and J.Chatt, J.Chem.Soc.A, 1969, 2131.

39. J.Dubrawski, J.C.Kriege-Simondsen, and R.D.Feltham, J.Amer.Chem.Soc., 1980, 102, 2089.
40. E.G.Mednikov and N.K.Eremenko, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2400.
41. E.D.Mednikov and N.K.Eremenko, Koord.Khim., 1983, 9, 243.
42. R.G.Vranka, L.F.Dahl, P.Chini, and J.Chatt, J.Amer. Chem.Soc., 1969, 91, 1574.
43. A.A.Frew, R.H.Hill, L.Manojlovic-Muir, K.W.Muir, and R.J.Puddephatt, Chem.Comm., 1982, 198.
44. N.M.Boag, J.Browning, C.Crocker, P.J.Goggin, R.J.Goodfewllow, M.Murray, and J.L.Spencer, J.Chem. Res.(S), 1978, 238.
45. V.F.Yudanov et al., Zhur.Strukt.Khim., 1984, 25, 49.
46. E.G.Mednikov, N.K.Eremenko, S.P.Gubin, Yu.L.Slovokhotov, and Yu.T.Struchkov, J.Organometal.Chem., 1982, 239, 401.
47. J.P.Barbier, R.Bender, P.Braunstein, J.Fischer, and L.Ricard, J.Chem.Res.(S), 1978, 230; 1979, 2901.
48. N.K.Eremenko, E.G.Mednikov, and S.S.Kurasov, Izv. Akad.Nauk SSSR, Ser.Khim. (in the Press).
49. R.Bender and P.Braunstein, Nouv.J.Chim., 1981, 5, 81.
50. R.Bender and P.Braunstein, Chem.Comm., 1983, 334.
51. R.Goddard, P.W.Jolly, C.Kruger, K.-P.Schick, and G.Wilke, Organometallics, 1982, 1, 1709.
52. E.G.Mednikov and N.K.Eremenko, Koord.Khim., 1981, 7, 1399.
53. E.G.Mednikov, N.K.Eremenko, V.A.Mikhailov, S.P.Gubin, Yu.L.Slovokhotov, and Yu.T.Struchkov, Chem.Comm., 1981, 989.
54. E.G.Mednikov, N.K.Eremenko, Yu.L.Slovokhotov, Yu.T.Struchkov, and S.P.Gubin, J.Organometal. Chem., 1983, 258, 247.
55. E.G.Mednikov and N.K.Eremenko, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2540.
56. E.G.Mednikov and N.K.Eremenko, Izv.Akad.Nauk SSSR, Ser.Khim., 1984, 2781.
57. F.Morandini, G.Consiglio, and F.Wenzinger, Helv. Chim.Acta, 1979, 62, 59.
58. K.Kudo, M.Hidai, and Y.Uchida, J.Organometal. Chem., 1971, 33, 393.
59. C.A.Tolman, Chem.Rev., 1977, 77, 313.
60. L.Takahashi, Ts.Ito, S.Sakai, and Y.Ishii, Chem. Comm., 1970, 1065.
61. V.V.Bashilov, E.G.Mednikov, V.I.Sokolov, N.K.Eremenko, and O.A.Reutov, Izv.Akad.Nauk SSSR, Ser. Khim., 1983, 923.
62. V.V.Bashilov, V.I.Sokolov, and O.A.Reutov, Izv. Akad.Nauk SSSR, Ser.Khim., 1982, 2069.
63. E.G.Mednikov, V.V.Bashilov, V.I.Sokolov, Yu.L.Slovokhotov, and Yu.T.Struchkov, Polyhedron, 1983, 2, 141.
64. E.G.Mednikov, V.V.Bashilov, N.K.Eremenko, and V.I.Sokolov, Inorg.Chim.Acta Letters, 1983, 76, L131.
65. M.Hidai, T.Hikita, Y.Wada, Y.Fujikura, and Y.Uchika, Bull.Chem.Soc.Japan, 1975, 48, 2075.
66. T.Ito, K.Mori, T.Mizoroki, and A.Ozaki, Bull.Chem. Soc.Japan, 1975, 48, 2091.
67. R.F.Heck, Adv.Catalysis, 1977, 26, 323.
68. A.B.Goel and S.Goel, Inorg.Nuclear Chem.Letters, 1980, 16, 397.
69. A.Albinati, A.Moor, P.S.Pregosin, and L.M.Venanzi, J.Amer.Chem.Soc., 1982, 104, 7672.

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