Russian Chemical Reviews **64** (1) 47–60 (1995)
©1995 Russian Academy of Sciences and Turpion Ltd

UDC 546.92:546.98

Reduction methods in the synthesis of low-valence platinum and palladium complexes

N Yu Kozitsyna, I I Moiseev

Contents

I. Introduction	47
II. Synthesis of phosphine complexes of the type ML_n [M = Pt(0), Pd(0); L = PR_3; $n = 2-4$]	47
III. Synthesis of cluster compounds of platinum metals in the oxidation states $0 < n < 2$	51
IV. Conclusion	58

Abstract. The use of the reduction reactions of platinum(II) and palladium(II) complexes for the synthesis of compounds of these metals in the lowest oxidation states ($0 \leqslant n < 2$) with stabilising π-acceptor type ligands, such as phosphines, phosphides, phenanthroline, and bipyridyl, is discussed. The mechanisms of these reactions as well as the behaviour of tertiary phosphine ligands under the conditions of the reactions between the complexes and reductants are examined. The available structural data on the mononuclear and polynuclear compounds of platinum and palladium in the lowest oxidation states are surveyed. The bibliography includes 138 references.

I. Introduction

Among the known preparative methods of synthesis of complexes of metals in the nickel triad in the lowest oxidation states,[1,2] the following are most frequently employed: direct synthesis from the metals; substitution of the ligands in complexes with the metal in low oxidation states or addition of neutral ligands; reductive elimination; reduction reactions. The reduction reactions are simplest and possess extensive synthetic possibilities. Alkali metals, their alkoxides, hydrazine, sodium tetrahydroborate, carbon monoxide, and hydrogen are usually employed as reductants for the synthesis of complexes containing the metal atoms in the formal '0' oxidation state.

Among the compounds of platinoid metals, those with tertiary phosphines occupy a special place. Platinum(0) and palladium(0) compounds with aromatic tertiary phosphines and related ligands were obtained for the first time in 1957–1958 on reduction of phosphine complexes of platinum(II) and palladium(II) by hydrazine or an alcoholic solution of KOH.[3,4] In the 1970s–1980s, there was an appreciable growth of interest in the chemistry of transition metal complexes with ligands of the type PR_3 because many of them manifested a catalytic activity in processes such as hydrogenation, hydroformylation, and polymerisation. It was believed that these complexes are thermally fairly stable and do not undergo significant changes under the conditions of the catalysed reactions. An extensive set of ligands of the type PR_3 has been used to stabilise complexes in which the metal atom is bound to the H and C atoms as well as the atoms of other nontransition elements.

N Yu Kozitsyna, I I Moiseev Metal-Complex Catalysis Laboratory, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii prosp. 31, 117907 Moscow, Russian Federation.
Fax (7-095) 954 12 79. Tel. (7-095) 952 12 03 (I I Moiseev)

Received 4 October 1994
Uspekhi Khimii **64** (1) 51–65 (1995); translated by A K Grzybowski

II. Synthesis of phosphine complexes of the type ML_n [M = Pt(0), Pd(0); L = PR_3; $n = 2-4$]

1. Reduction by metals

The reduction of halophosphinepalladium and halophosphineplatinum complexes by metallic sodium in liquid ammonia leads to the formation of the complexes $M(PF_3)_4$ (M = Pd, Pt).[5] This reduction method is not extensively used because of a series of disadvantages. These are principally experimental difficulties associated with the employment of metallic sodium in liquid ammonia and a low yield of the target product because of the insolubility of the reactants in the reaction medium. The same compounds have been obtained by the reaction of MCl_2 (M = Pt, Pd) with PF_3 and metallic copper at 100 °C and 100–300 atm. However, in this case one cannot rule out the possibility that not only the copper but also PF_3 behaves as the reducing agent.[6]

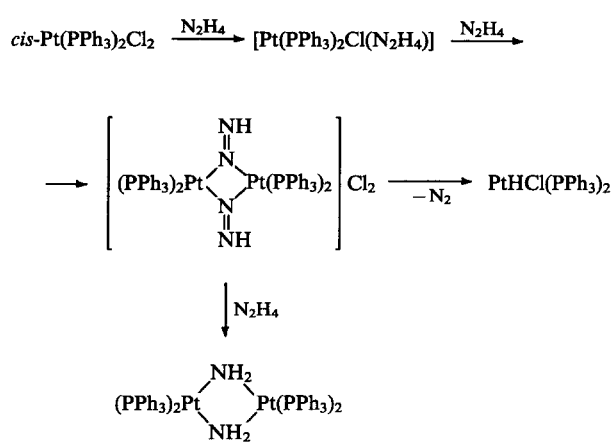
2. Reduction by hydrazine

This method is used successfully to reduce platinum(II) and palladium(II) compounds with tertiary phosphines, phosphites, and arsines.[3,4,7] The first studies on the reduction of platinum complexes by hydrazine led at first sight to contradictory results. Data were obtained indicating that, depending on: the reaction conditions, the nature of the ligands and the halogen atom bound to the metal, and the reaction time, it is possible to obtain both platinum(0) compounds and platinum(II) hydrides.[8] Furthermore, the unusual stability of the compounds described by Malatesta[4] as zero-valent complexes suggested that they are in fact platinum(II) hydrides.[9] However, later independent and careful studies definitely confirmed that platinum(0) compounds are formed in these syntheses.[7,10,11]

The interaction of metal complexes with hydrazine is as a rule a complex multistage process.[12] After the reduction of *cis*-$Pt(PPh_3)_2Cl_2$ at room temperature, certain stable intermediates were isolated. These are cationic dehydrodiimido- and amino-complexes soluble in the reaction medium (ethanol)[13] (Scheme 1).

The hydride complex *trans*-$Pt(PPh_3)_2HCl$ formed in the first stage of the reduction process is isolated from the reaction solution after several hours at room temperature or on heating the solution. This platinum(II) hydride is subsequently converted

Scheme 1



into a platinum(0) complex on treatment with an excess of hydrazine.[4,12]

$$cis\text{-}Pt(PPh_3)_2HCl \xrightarrow[PPh_3]{N_2H_4} Pt(PPh_3)_n$$

$n = 3, 4.$

Thus, by varying the amount of hydrazine, the time, and the reaction temperature, it is possible to obtain either a platinum(0) complex or a platinum(II) hydride. The reduction of *cis*-$Pt(PPh_3)_2Cl_2$ to $Pt(PPh_3)_2$ by an excess of hydrazine at 70–80 °C apparently proceeds via the same mechanism.[8]

The presence of an excess of the phosphine in the reaction solution makes it possible to obtain platinum(0) complexes with a maximum yield. The need for an excess of the phosphine arises from the ability of the zerovalent complexes to dissociate in solution, affording coordinatively-unsaturated compounds.[14]

$$M(PR_3)_4 \rightleftharpoons M(PR_3)_3 \rightleftharpoons M(PR_3)_2 \rightleftharpoons [M(PR_3)]_n$$

M = Ni, Pd, Pt.

The platinum complex of triphenylphosphine $Pt(PPh_3)_4$ is almost fully dissociated and the tricoordinate complex $Pt(PPh_3)_3$ exists in benzene. Further dissociation with formation of $Pt(PPh_3)_2$ takes place to a very slight extent—the equilibrium constant $[Pt(PPh_3)_2][PPh_3]/[Pt(PPh_3)_3]$ is $(1.6 \pm 1.1) \times 10^{-4}$ mol litre^{-1} in benzene at 25 °C.[14]

Such behaviour of the complexes $[M(PR_3)_4]$ in solution suggested that the PR_3 ligands in these compounds are non-equivalent. A later X-ray diffraction study of the tetrakis(triphenylphosphine)palladium complex $Pd[PPh_3]_4.0.5C_6H_6$ showed, however, that the coordination of the palladium atoms hardly differs from the ideal tetrahedral coordination;[15] admittedly, the average Pd–P bond length in this compound (2.443 Å) greatly exceeds the Pd–P distances in all other structurally characterised phosphine complexes.[16–18] This lengthening of the bond and also the extremely loose packing of the molecules in the crystal are apparently a consequence of the steric repulsion between the ligands in the complex. All these factors are responsible for the lability of the complex both in the solid state and in solutions.

The influence of steric factors on the stability of complexes of zerovalent metals has been confirmed by X-ray diffraction data for the entirely stable complex $Pd[P(C{\equiv}CPh)_3]_4$,[19] where the bulk of the phenyl substituent are separated from the phosphorus atom by the C≡C groups, which creates more favourable conditions for unstrained spatial packing. Similar data have been obtained also for the complex $Pd[P(CH_2OH)_3]_4$.[20] The environment of the palladium atom is tetrahedral in both cases and the Pd–P distances are 2.28 and 2.32 Å respectively.

A series of relatively stable tricoordinate platinum(0) and palladium(0) compounds have been isolated in the solid state and have been reliably characterised by X-ray diffraction.[3,4] According to the X-ray diffraction data for the complex $Pt(PPh_3)_3$, the PtP_3 fragment has the form of a greatly flattened trigonal pyramid.[21] The Pt atom is located 0.1 Å above the plane in which the three phosphorus atoms are present. The $Pt(PPh_3)_3$ molecule is much less strained than the $Pt(PPh_3)_4$ molecule and the Pt–P distances in it are in the usual range 2.25–2.28 Å. In the analogous palladium complex $Pd(PPh_3)_3$, the palladium atom is raised by 0.16 Å above the P_3 plane.[22] The PtP_3 fragment in the complex $Pt(PCy_3)_3$ (Cy = cyclohexyl) is almost planar,[23] the platinum atom being displaced from the plane by only 0.04 Å. All the cyclohexane rings have the chair conformation.

The dicoordinate platinum and palladium complexes are extremely unstable. Only a few complexes with bulky phosphine ligands such as PCy_3, PBu^t_3, and PBu^t_2Ph have been isolated and characterised (see below).[24–27]

Complexes of the type PdL_4 and PtL_4 (L = $Ph_2PC{\equiv}CMe$) can also be obtained from solutions of K_2PtCl_4 or K_2PdCl_4 by reduction with hydrazine in the presence of an excess of the phosphine ligand.[28] Compounds containing methoxy- and n-butoxy-diphenylphosphine ligands $Ph_2P(OR)$ (where R = Me, Bu) have been synthesised similarly.[29] The complex $Pd(PPh_3)_4$ has been obtained by reducing $PdCl_2$ and PPh_3 at 140 °C in dimethyl sulfoxide (DMSO).[30] DMSO is also used as a convenient solvent in the synthesis of ML_4 with ligands such as *m*- and *p*-tolylphosphines from the corresponding platinum and palladium chlorides.[31]

3. Reduction by sodium tetrahydroborate

Apart from hydrazine, the reduction by sodium tetrahydroborate is used to synthesise platinum(0) and palladium(0) containing phosphines and tertiary diphosphines and diarsines.[11,32,33] The nature of the compounds obtained on reduction with sodium tetrahydroborate remained controversial for some time, but it has been shown that these are indeed compounds with the metal in the zero oxidation state and not hydrido-complexes.[11] $M(PPh_3)_4$ and $M[C_2H_4(PPh_2)_2]_2$ (M = Pd, Pt),[34] $Pd[C_3H_6(PPh_2)_2]_2$,[35] PtL_4 [L = $PMePh_2$, $PPhMe_2$, $PPh(OMe)_2$, $P(OPh)_3$, $AsPh_3$],[36,37] and $Pt(PMe_2C_6F_5)_4$[37] have been obtained by reduction with sodium tetrahydroborate.

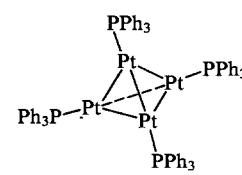
$$Pt[C_2H_4(PPh_2)_2]_2Cl_2 \xrightarrow{NaBH_4/C_2H_5OH} Pt[C_2H_4(PPh_2)_2]_2$$

The synthesis of the tetramer of the monocoordinate compound $Pt(PPh_3)$ by reducing $Pt(PPh_3)_2O_2$ with sodium tetrahydroborate has been reported.[38]

$$Pt(PPh_3)_2O_2 \xrightarrow{NaBH_4/C_2H_5OH} [Pt(PPh_3)]_4 \quad (1)$$

1

The data obtained in the determination of the molecular mass of this compound indicate the formation of the complex $[Pt(PPh_3)]_4$. The authors[38] proposed a tetrahedral structure of the complex.



The interaction of $[Pt(PPh_3)]_4$ with KCN leads to the displacement of free PPh_3 from the platinum complex, which agrees with the proposed interpretation of the experimental data.

Diphenylphosphine was not detected in the products of this reaction, but the conditions of reaction (1), in the course of which compound **1** was obtained (heating for 6 h at 90 °C),[38] and the fact that the formation of benzene or biphenyl were not monitored during the synthesis casts doubt on the view that complex **1** contains no phosphide or phosphene groups as ligands.[38]

The palladium(0) complexes formed on reduction are known to be incapable of catalysing the reduction of unsaturated hydrocarbons under mild conditions.[39] However, it has been shown in a series of studies that, after contact with air, solutions of $(PPh_3)_2PdCl_2$ treated with sodium tetrahydroborate acquire the capacity to absorb molecular hydrogen and to catalyse hydrogenation reactions in DMF, like solutions of authentic $Pd(PPh_3)_4$.[40,41] This effect can be accounted for by the formation of complexes with oxygen. Indeed a solution of $Pd(PPh_3)_2O_2$, obtained after the reduction of $(PPh_3)_2PdCl_2$ with sodium tetrahydroborate in air, proved to be catalytically active.[41] The increase in the reactivity of palladium compounds in relation to molecular hydrogen when oxygen-containing ligands are introduced into the coordination sphere agrees well with the reaction mechanism according to which the hydrogen molecule is cleaved heterolytically with simultaneous heterolysis of the Pd–X bond. Quantum-chemical analysis[42] of the interaction of the complexes *trans*-$XYPd(PH_3)_2$, where X = OH or OAc and Y = Cl, with molecular hydrogen showed that the presence of the oxygen-containing ligands facilitates the heterolysis of the hydrogen molecule.

The influence of oxygen and oxygen-containing ligands on the reactivity of palladium compounds in the reaction with hydrogen and on the formation of the centres responsible for the catalysis of the hydrogenation reaction has been observed not only for palladium complexes with organophosphorus ligands but also for systems containing N- or S-ligands. Thus it has been shown that the reduction of palladium complexes of pyridine, aliphatic amines, and sulfides or sulfoxides of petroleum origin by sodium tetrahydroborate or diisobutylaluminium hydride when the system is promoted by water or molecular hydrogen leads to highly active selective catalysts for the hydrogenation of conjugated dienes to alkenes.[43,44]

Systems obtained in the reduction of palladium salts by sodium tetrahydroborate in the presence of *o*-phenanthroline, α,α-bipyridyl, and polyethyleneimines in aqueous media may also be active in hydrogenation reactions,[45,46] but the composition of the complexes formed has not been investigated.

4. Reduction with an alcoholic solution of KOH

The reduction of platinum and palladium complexes with an alcoholic solution of KOH leads to the formation of compounds similar to those obtained with the aid of hydrazine and sodium tetrahydroborate. It was first used to synthesise the complex $Pt(PPh_3)_4$ by reducing $(Ph_3P)_2PtCl_2$.[4,47] Potassium tetrachloroplatinate in the presence of a phosphine ligand can also be used as the initial platinum compound. The complexes $Pt[P(OEt)_3]_4$,[48,49] $Pt(PMe_2Ph)_4$,[37] and $Pt(PMePh_2)_4$[50] have been obtained in this way. The combined reduction of K_2PtCl_4 by hydrazine and KOH in the presence of a tertiary phosphine has been used to synthesise $Pt[P(CH_2Ph)Ph_2]_4$.[50]

Depending on the reaction conditions, the reaction can proceed in accordance with the equations

$$K_2PtCl_4 + 5\,PPh_3 + 2\,KOH \longrightarrow$$
$$\longrightarrow Pt(PPh_3)_4 + OPPh_3 + 4\,KCl + H_2O;$$

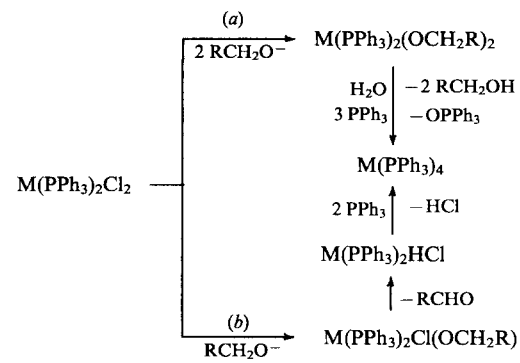
or

$$K_2PtCl_4 + 4\,PPh_3 + 2\,KOH + EtOH \longrightarrow$$
$$\longrightarrow Pt(PPh_3)_4 + 4\,KCl + MeCHO + 2\,H_2O.$$

In the former case, the reducing agent is the phosphine, while in the latter ethanol participates directly in the reaction, being oxidised to acetaldehyde.

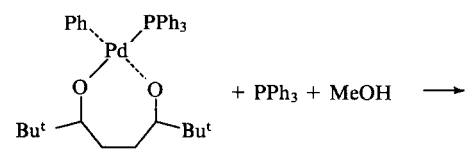
Sodium propoxide may also be used as the reductant for the preparation of $Pt(PPh_3)_4$ from $Pt(PPh_3)_2Cl_2$. Secondary and tertiary alcohols and also phenols may be used instead of propanol.

The reduction of $Pd(PPh_3)_2Cl_2$ by sodium propoxide in propanol is carried out at room temperature in the presence of an excess of the phosphine.[51] The intermediates in this reaction were later investigated,[52] which made it possible to obtain a clearer picture of the process. The reaction apparently proceeds via two parallel routes:



In the case of route (*a*), the reducing agent is the phosphine, which gives up one or two electrons to the metal atom and is apparently subjected to inner-sphere nucleophilic attack by the hydroxide ion. For tertiary alcohols, this is the only possible pathway. Route (*b*) explains the formation of the products of the oxidation of primary and secondary alcohols. It has been shown that the contributions of both routes are approximately the same.[52] When the reaction was carried out in benzene, the intermediate $M(PPh_3)_2(OPh)_2$ was isolated and was then reduced in the presence of water to $M(PPh_3)_4$ with triphenylphosphine. In the first stage of this reaction, the hydroxo-complex $M(PPh_3)_2(OH)_2$ is probably formed [this complex has not been detected in the reaction of $M(PPh_3)_2(OC_6H_5)_2$ with water]. It has been shown that $Pt(PPh_3)_2(OH)_2$ is formed from $Pt(PPh_3)_2Cl_2$ and sodium propoxide in benzene in the presence of water and that its subsequent reaction with PPh_3 leads to the formation of $Pt(PPh_3)_4$ and triphenylphosphine oxide.

Treatment of phenylpalladium complexes with methanol in the presence of PPh_3 leads to the reductive dissociation of the Pd–C bond accompanied by the formation of $Pd(PPh_3)_4$ and benzene. In this case, methanol readily reduces the palladium, being oxidised to formaldehyde.[53]



$$\longrightarrow Pd[PPh_3]_4 + CH_2O + C_6H_6 + Bu^t{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_2{-}\overset{O}{\overset{\|}{C}}{-}Bu^t$$

Hydrides such as $[PtH(PPh_3)_3]HSO_4$ may be reduced to $Pt(PPh)_3$ by a solution of KOH in ethanol.[54] In essence, the platinum(II) compound is reduced in this reaction as a result of the deprotonation of a complex hydride on reaction with a base,

$$L_3PtH^+ + OH^- \longrightarrow L_3Pt + H_2O,$$

where the coordinated hydride ligand behaves as the 'reductant'.

The absence of an excess of the ligand from the solution makes it possible to obtain formally more coordinatively unsaturated compounds containing only two phosphine ligands at the central atom instead of four.

Attempts have also been made to synthesise coordinatively unsaturated complexes of the type ML_2 by creating conditions for the simultaneous reduction of the metal and the oxidation of the excess ligand. O_2 and H_2O_2 may be used as oxidants for the oxidation of PPh_3 to Ph_3PO. Thus Ugo et al.[24] reported the preparation of the yellow compound $Pt(PPh_3)_2$ in different ways. The first involved the addition of an alcoholic solution of KOH to an alcoholic solution of $[PtH(PPh_3)_3]HSO_4$ and subsequent treatment of the solution with oxygen.

$$2\,[PtH(PPh_3)_3]HSO_4 + 2\,KOH + O_2 \longrightarrow$$

$$\longrightarrow 2\,[Pt(PPh_3)_2] + 2\,Ph_3PO + 2\,KHSO_4$$

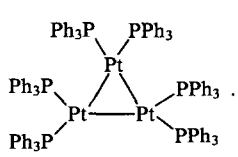
In the second procedure, stoichiometric amounts of H_2O_2 and KOH in alcohol were added slowly to an alcoholic solution of $[PtH(PPh_3)_3]HSO_4$.

$$[PtH(PPh_3)_3]HSO_4 + KOH + H_2O_2 \longrightarrow$$

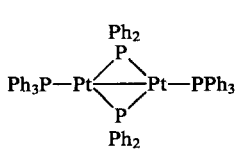
$$\longrightarrow [Pt(PPh_3)_2] + 2\,Ph_3PO + 2\,KHSO_4 + H_2O$$

The coordinatively unsaturated compound obtained as a result of these reactions was identified by elemental analysis. The molecular mass proved to be lower than the value calculated for the monomer $[Pt(PPh_3)_2]$.[24]

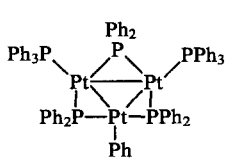
It has been reported that the isolation of pure $[Pt(PPh_3)_2]$ is extremely difficult as a consequence of its instability. A more stable red compound is formed on refluxing $[Pt(PPh_3)_2]$ in benzene under an argon atmosphere.[55] The results of the determination of the molecular mass indicate the existence of the complex $[Pt(PPh_3)_2]$ in the form of a trimer, for which the following structure has been proposed:



In 1966, when the study of Ugo and coworkers[55] was carried out, the ability of triphenylphosphine to undergo degradative reactions in the coordination spheres of platinum metals was not yet known. At the beginning of the 1970s, studies were published[56–66] in which doubt was cast on the postulate that the phosphine ligand is stable both under the conditions of the synthesis and under the conditions of the subsequent reactions of the phosphine complexes of platinum and palladium. In view of this, the above structure was re-examined.[63] It was observed[63] that, on heating $Pt(PPh_3)_4$ in benzene under an argon atmosphere, a dark-red solution is formed from which the two cluster complexes $[Pt_2(PPh_3)_2(PPh_2)_2].C_6H_6$ **2** and $[Pt_3(PPh_3)_2(PPh_2)_3(Ph)].C_6H_6$ **3** were isolated and characterised by X-ray diffraction.



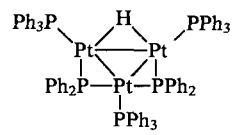
2



3

According to X-ray diffraction data, compound **2** is a dinuclear complex with a very short metal–metal distance (Pt–Pt = 2.604 Å), two bridging ligands PPh_2, and two terminal ligands PPh_3. The Pt_2P_2 skeleton is planar. Compound **3** is constructed as a trinuclear cluster with three Pt–Pt bonds and three bridging PPh_2 groups. The Pt–Pt distances (2.785 Å) are greater than in compound **2**, but are comparable to the bond lengths in the carbonylphosphineplatinum clusters. One of the platinum atoms is coordinated to two PPh_2 groups and to a σ-linked Ph group. This is one of the first compounds where a phenyl residue, formed as a result of the dissociation of the P–C bond, remains bound to the metal.[63]

The platinum complex $[Pt_3(PPh_3)_3(\mu\text{-}PPh_2)_2[\mu\text{-}H)]^+BF_4^-$ **4**, having a similar structure



4

has been obtained on UV irradiation of $Pt(PPh_3)_2C_2O_4$ under a hydrogen atmosphere and subsequent precipitation with $NaBF_4$.[64] The Pt_3P_2 skeleton is significantly nonplanar. The Pt–Pt distance between the atoms linked by the bridging hydrogen atom (2.638 Å) is appreciably shorter than the other two (2.795 Å). The presence of the bridging hydrogen atom was established from ^{31}P NMR spectroscopic data.

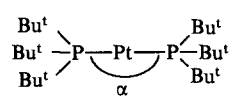
Nevertheless, the mononuclear complexes $[ML_2]$ can be obtained in solution in the case of phosphine ligands containing 'bulky', frequently branched, aliphatic or aryl-substituted aliphatic substituents at the phosphorus atom (L = PCy_3,[25,67] PBu^t_3,[26] PPr^i_3, PBu^t_2Ph,[27] and PBu^t_2Me[68]) by substituting the ligands in platinum(0) and palladium(0) complexes.

$$Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5) + 2\,L \longrightarrow PdL_2 + \text{hydrocarbons}$$

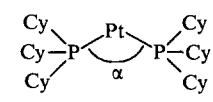
$$Pt(\eta^4\text{-}COD)_2 + 2\,L \longrightarrow PtL_2 + 2\,COD$$

L = PR_3, COD = cycloocta-1,5-diene.

Several such complexes have been characterised by X-ray diffraction (Table 1). It was found that the P–M–P angle in these compounds varies in the range from values close to 180° in the case of $Pt[PBu^t_3]_2$ **5**[26] to 160.5° for $Pt[PCy_3]_2$ **6**.[25]



5



6

The bent structure of the P–M–P fragment in the complex $Pt[PCy_3]_2$ cannot be a result of the packing effect in the crystal structure, since not one H...H packing distance shorter than 2.32 Å has been observed.[25] Nor can one account for the decrease in the angle α by electronic factors because the quasilinear geometry of the complex $Pt[PBu^t_3]_2$ does not fit within the framework of this scheme. Although the conical angle for the PBu^t_3 ligand is greater than for PCy_3 (Table 1),[69] the steric repulsion of the *tert*-butyl groups cannot exert a significant influence on the geometry of the complex because all the distances between the hydrogen atoms of the neighbouring groups are greater than 5.0 Å.[25]

For the less stable dicoordinate complexes with the triphenylphosphine ligand, the stable adducts $[Pt(PPh_3)_2].BCl_3$ with trichloroborane[70] or $[Pt(PPh_3)_2].SiF_4$ with tetrafluorosilane[71] are known.

Table 1. X-Ray diffraction data for the complexes $M[PR_3]_2$ and the conical angles of the PR_3 ligands.

Compound	M–P/Å	P–M–P angle/deg	Conical PR_3 angle[a]/deg	Ref.
$Pt[P(Bu^t)_3]_2$	2.249	180	182(2)	26
$Pt[P(Bu^t)_2Ph]_2$	2.25	177.0	170(2)	18
$Pt[PCy_3]_2$	2.23	160.5	179(10)	67
$Pd[PCy_3]_2$	2.26	158.4	179(10)	25
$Pd[P(Bu^t)_2Ph]_2$	2.28	175.7	170(2)	25

[a]The conical angles were taken from Tolman.[69]

5. Reduction by metal alkyls

The reduction of palladium(II) acetylacetonate by $AlEt_3$ in the presence of PCy_3 leads to the formation of a product described as $Pd(PCy_3)_2$.[72] The complexes $PdL_2(C_2H_4)$ [L = PPh_3, PCy_3, $P(OC_6H_4Me\text{-}o)_3$] have been obtained similarly in the presence of ethene and various phosphines.[73] HX can be removed from hydrido-complexes such as *trans*-$Pt(PPh_3)_2HX$ (X = halogen) by treating them with n-butyllithium. The complex $Pt(PPh_3)_2$, first synthesised by treating $[PtH(PPh_3)_3]HSO_4$ with alcoholic alkali,[24] has been obtained by this method.[54]

6. Reduction by phosphine ligands

Phosphine ligands may reduce the central metal atom in the absence of halide ions or other strongly coordinated ligands lowering the oxidation-reduction potential of the platinoid atom. The reaction is usually carried out in ethanol. This method has been applied successfully in the synthesis of PdL_4 [L = PPh_3, $P(OPh)_3$] by treating $Pd(NO_3)_2$ or freshly precipitated palladium oxide with an excess of the ligand.[3] When metal halides are used as the initial compounds, amines are added to the reaction mixture in order to displace the halide ions. $Pd[P(OEt)_3]_4$ has been obtained in this way.[74]

Phosphite ligands are capable of reducing palladium halides in the absence of an amine. The complexes $Pd[PhP(OR)_2]_4$ (R = Me, Et) have been synthesised in this way from $PdCl_2$ and the corresponding phosphite.[75]

$$PdCl_2 + 4\,PhP(OMe)_2 \longrightarrow Pd[PhP(OMe)_2]_4$$

The complex $Pd(PF_3)_4$ has been obtained by reducing $Pd(CO)_2Cl_2$[76] or $Pd(C_6H_5CN)_2Cl_2$[77] using PF_3 as the reductant at room temperature. The ability of PF_3 to reduce platinum group metals appears unexpected at first sight. However, one should bear in mind that the tendency of trivalent phosphorus to form bonds with oxygen, which are some of the strongest in inorganic chemistry, is very great. It would seem that powerful electronegative substituents (fluorine atoms) should diminish the electron-donating capacity of the phosphorus atom and its ability to give up a lone electron pair in order to form a bond with a 'singlet' oxygen atom. However, the effect of these substituents leads apparently to a very considerable lowering of the unoccupied *d* levels of the phosphorus atom, which is reflected by an increased electron-accepting capacity of the phosphorus atom in PF_3. As a consequence of this, the P–O π-bond in the corresponding (possibly hypothetical) oxide F_3PO should be very strong. In other words, the contribution of the covalent canonical structures

$$\overset{-}{O}\!-\!\overset{+}{P}F_3 \longleftrightarrow O{=}PF_3\,,$$

in the description of F_3PO should be extremely large.

As a consequence of the increased tendency towards the acceptance of electrons manifested by PF_3, the latter is believed to be the most powerful π-acceptor in coordination compounds and is superior to the cyanide ion, alkyl isocyanides, carbon monoxide, etc. Numerous complexes of PF_3 with metals in low oxidation states are known.[78] Thus both factors — the tendency towards the formation of stable complexes with the metal in a low oxidation state and the energy of the bond formed in F_3PO — play the role of the driving force by virtue of which PF_3 is able to function as a reductant in relation to platinum group metal complexes.

The platinum complexes PtL_4 [L = PF_3, CF_3PF_2, $(CF_3)_2PF$] have been synthesised by the reaction of platinum(II) chloride[79] or K_2PtCl_4[80] with phosphorus trifluoride.

In virtually all the reactions described above, mononuclear compounds were employed as the starting materials. The reaction was carried out in the presence of an excess of the phosphine ligand, coordinatively saturated mononuclear compounds of the type ML_4 with the metal in the zero oxidation state being obtained. Similar complexes have been frequently used as the initial form of the catalyst in a wide variety of catalytic reactions (oxidation, hydrogenation, isomerisation, etc.) of organic substrates.[81] The chemistry of these compounds suggests that they are unstable under the conditions of the catalytic reactions and undergo partial oxidation, elimination, and/or dehalogenation of the phosphine ligands usually with formation of aggregated species of cluster type. The latter are in fact apparently responsible for catalysis in most cases. We shall therefore consider in the next section the conditions for the reduction of platinum(II) and palladium(II) leading to the formation of platinum and palladium clusters in nonzero oxidation states.

III. Synthesis of cluster compounds of platinum metals in the oxidation states $0 < n < 2$

Polynuclear and cluster compounds of platinum metals in low oxidation states are formed when reductants such as carbon monoxide, formic acid, or hydrogen are used, while the initial compounds are platinum(II) or palladium(II) dinuclear or polynuclear carboxylate complexes. As a rule, the reaction is carried out for low concentration ratios L:M, where L is the stabilising ligand. When halide compounds, which are reduced by the above reductants under severe conditions, are the starting materials, sodium amalgam is employed.

1. Reduction by carbon monoxide

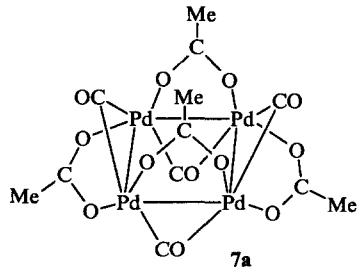
Treatment of solutions of palladium(II) salts with CO usually leads to the reduction of palladium to the metal. Thus the reduction of $Pd(OAc)_2$ by carbon monoxide in glacial acetic acid containing alkali metal acetates leads to the formation of metallic palladium, acetic anhydride, and CO_2.[82,83]

$$Pd(OAc)_2 + CO \xrightarrow{NaOAc} Pd^0 + Ac_2O + CO_2$$

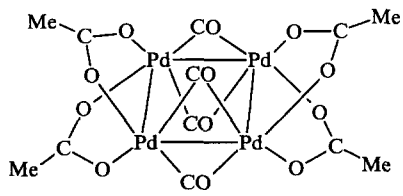
However, in the absence of alkali metal acetates, palladium carbonyl acetate (PCA) having the composition $Pd_4(CO)_4.(OAc)_4.2AcOH$ was obtained from $Pd(OAc)_2$ and CO.[84,88]

$$4\,Pd(OAc)_2 + 8\,CO \longrightarrow Pd_4(CO)_4(OAc)_4 + 2\,Ac_2O + 4\,CO_2$$

According to X-ray diffraction data,[85] crystals of this substance consist of tetranuclear clusters $Pd_4(CO)_4(OAc)_4$ **7** with a rectangular metal core (the Pd–Pd distances are 2.66 and 2.91 Å). However, according to EXAFS data complex **7** exists in the form of two isomers with a square metal core **7a** (the Pd–Pd distance is 2.72 Å) and a rectangular core **7b**.[86] The authors attribute their existence to the presence or absence of molecules of acetic acid of crystallisation in complex **7**.



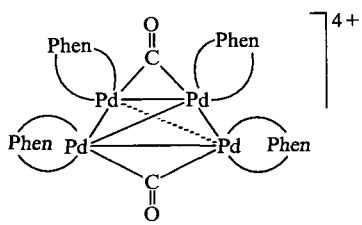
7a



7b

Similar clusters having the composition $Pd_4(CO)_4(RCOO)_4$ have been obtained by reducing palladium(II) propionate and benzoate (R = Ph, Et) with carbon monoxide and also by the exchange of the carboxylate ligands by treating the PCA with the corresponding carboxylic acids (R = CF_3, CH_2Cl, Bu^t).[87-90] IR spectroscopic data for these compounds permit the conclusion that they all have similar structures. Nevertheless, their investigation by the EXAFS method revealed appreciable differences between the geometries of the metal cores for not very significant differences in the acido-ligand.[86] Thus the palladium carbonyl monochloroacetate complex (R = CH_2Cl) has a square metal core (the Pd–Pd distance is 2.70 Å), similar to one of the isomers of PCA. The metal core in the palladium carbonyl trifluoroacetate complex (R = CF_3) has the form of a rhombus with a side of 2.70 Å and diagonals of 3.75 and 4.08 Å. The observed Pd–Pd distances for palladium carbonyl benzoate (R = Ph) and carbonyl pivalate (R = Bu^t) correspond to a mixture of isomers with metal cores in the form of a square and a rectangle.[86] The causes of such sensitivity of the geometry of the metal core to the ligand environment require the analysis of not only steric but also electronic factors.

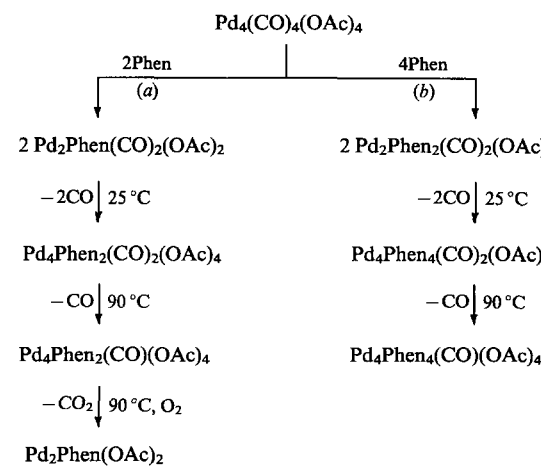
In contrast to the substitution of acido-ligands, the exchange of carbonyl groups for other neutral ligands and, what is more important the displacment of the acido-ligands from the inner coordination sphere of palladium lead to appreciable changes in the cluster metal core. Thus the interaction of the PCA with phenanthroline in the proportions [Pd]:[Phen] = 1:1 in acetic acids results in the formation of the complex $Pd_4Phen_4(CO)_2$.$(OAc)_4$ with a nearly tetrahedral metal core.[88]



This complex is also formed on the reduction of $Pd(OAc)_2$ by carbon monoxide in the presence of phenanthroline. According to X-ray diffraction data, the crystals of the complex contain the almost tetrahedral cluster cation $[Pd_4Phen_4(CO)_2]^{4+}$ as the main structural unit. On formation of this complex from the PCA, all the metal–metal distances change significantly: the Pd–Pd bonds in the Pd(μ-CO)Pd fragments are lengthened to 2.890 Å (in the PCA this distance is 2.663 Å) and become longer than the Pd–Pd bonds in the absence of ligands (2.718 Å). This ratio of bond lengths could be accounted for by the fact that, in terms of its disposition in space, each Pd(μ-CO)Pd bond is in fact bridging in relation to the opposite ligand-free Pd–Pd bond. The acetate groups are not coordinated to the Pd atoms, as in the PCA, but are located in the outer sphere in the form of AcO^- anions.[88]

The replacement of the CO groups by neutral ligands such as phenanthroline (Phen) or bipyridyl (Bipy) also takes place readily on interaction of the PCA with the free ligands at extremely low concentrations — $[L]_\Sigma:[Pd]_\Sigma \leqslant 1:1$. The extremely labile complexes formed under these conditions (Scheme 2) have been characterised on the basis of indirect data for the stoichiometry of the reaction, but have not been isolated in a pure form.[91,92]

Scheme 2



It has been shown[91-93] that the complete removal of the coordinated CO molecules requires heating under an oxygen atmosphere above 90 °C, the polynuclear palladium complexes formed exhibiting a catalytic activity in the oxidation of CO and in the oxidative acetoxylation of alkenes and alkylarenes (Scheme 2).

The combination of the effect of CO as a stabilising ligand and reductants such as alkali metals or their hydroxides, $Fe(CO)_5$, or cobaltocene on platinum compounds such as Na_2PtCl_6, $H_2PtCl_6.xH_2O$, Na_2PtCl_4, and $Pt(CO)_2Cl_2$ made it possible to obtain a series of dianions having the general formula $[Pt_3(CO)_6]_n^{2-}$ (n = 1–6, 10).[94]

$$3n[PtCl_6]^{2-} + (12n+1)\,CO + (12n+2)\,OH^- \longrightarrow$$

$$\longrightarrow [Pt_3(CO)_6]_n^{2-} + 18n\,Cl^- + (6n+1)\,CO_2 + (6n+1)\,H_2O$$

The structure of a series of platinum carbonyls $[Pt_3(CO)_6]_n^{2-}$ (n = 2, 3, 5) in the form of tetraphenylphosphonium salts has been determined by X-ray diffraction.[95] The Pt_3 triangles are linked by three bridging carbonyl ligands and are arranged one on top of the other, forming a layered structure. The Pt–Pt distances in the triangular Pt_3 fragment are 2.66 Å and those between the layers reach 3.01–3.04 Å. The layers have rotated relative to one another by angles ranging from 8.1° to 28.6°, which disturbs the regular prismatic packing of the platinum atoms.[95] This geometrical disorder is apparently a result of an increase in the distances between the CO ligands.

In the search for catalytically active complexes and, what is more important, complexes selective in hydrogenation reactions, studies have been made of phosphine and phenanthroline complexes of palladium, which are formed when $Pd(OAc)_2$ interacts with various reductants in the presence of the above ligands.[96-98]

2. Reduction of the complexes $[Ph_3PMX_2]_2$ (M = Pd, Pt) by sodium amalgam

Sodium amalgam is used as a reductant for palladium and platinum halide complexes because the latter are reduced by hydrogen only under very severe conditions.[99]

The interaction of the dinuclear complex $[Ph_3PPdCl_2]_2$ with sodium amalgam in CH_2Cl_2 at 20 °C leads to the formation of solutions from which a compound described as a dinuclear palladium(0) complex $(Ph_3P)_2Pd_2$ was isolated.[100]

$$[Ph_3PPdCl_2]_2 \xrightarrow{Na/Hg,\ CH_2Cl_2} (Ph_3P)_2Pd_2$$

A similar compound is obtained also when the carboxylate complex $[Ph_3PPd(OAc)_2]_2$ is used as the starting material.[100]

$$[Ph_3PPd(OAc)_2]_2 \xrightarrow{Na/Hg,\ CH_2Cl_2} (Ph_3P)_2Pd_2$$

The experiments on the synthesis of this compound are poorly reproducible, which may be associated with the characteristic features of the purification of the solvent.

The reduction of $[Ph_3PPtCl_2]_2$ by sodium amalgam in benzene at 20 °C leads to the dissociation of the P–Ph bond of the coordinated PPh_3 ligand and the formation of a phosphide complex, which is $[Ph_2PPtCl]_n$ according to elemental analysis and IR spectroscopy.[101]

$$[Ph_3PPtCl_2]_2 \xrightarrow{Na/Hg,\ C_6H_6} [Ph_2PPtCl]_n$$

The molecular mass of this compound corresponds to a polymer with $n = 16$ and it may be that the Pt atoms are linked to phosphide and chloride bridges.

In tetrahydrofuran (THF), the reaction of the platinum(II) chloride complex with sodium amalgam proceeds further and terminates with the formation of the complex $[Ph_2PPt]_n$, where $n = 6$. According to elemental analysis, the compound contains no chlorine and its IR and ^1H NMR spectra contain only the signals due to phosphide groups.[101]

$$[Ph_3PPtCl_2]_2 \xrightarrow[-C_6H_6]{Na/Hg,\ THF} [Ph_2PPt]_n$$

Gas–liquid chromatography of the reaction mixture revealed the presence of 1 mol of C_6H_6 per gram-atom of the platinum of the complex introduced into the reaction. Measurements of the electrical conductivities of the solutions in dimethylformamide showed that the compounds $[Ph_2PPtCl]_n$ and $[Ph_2PPt]_n$ are electrically neutral.

The complex $[Ph_2PPtCl]_n$ does not react with hydrogen under mild conditions, but, after the replacement of Cl^- by AcO^- (on treatment with AgOAc), it is reduced by hydrogen. Benzene was detected in the reaction product.

The platinum acetate complex $[Ph_3PPt(OAc)_2]_2$ is also reduced by sodium amalgam with formation of a platinum phosphide complex and benzene.[101]

$$[Ph_3PPt(OAc)_2]_2 \xrightarrow[-C_6H_6]{Na/Hg,\ THF} [Ph_2PPt]_n$$

3. Reduction of platinum(II) and palladium(II) carboxylate complexes with phosphine ligands by hydrogen

In connection with the study of the homogeneous hydrogenation of alkenes in systems containing a palladium carboxylate and PR_3, the reduction of palladium by molecular hydrogen has been studied in greatest detail. Analysis of literature data shows that both the mode of the reaction and the nature of the compounds formed depend greatly both on the nature of the acido-ligand coordinated to the metal atom and on the reaction conditions.[100,102]

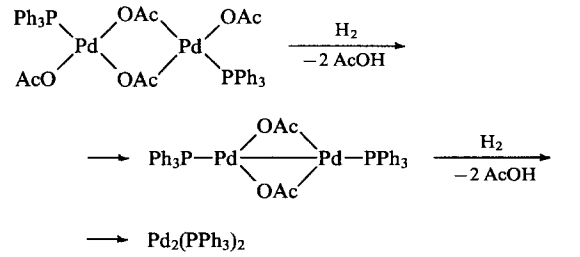
Treatment of the palladium acetate trimer $[Pd(OAc)_2]_3$ with a phosphine ligand leads primarily to the rupture of the acetate bridges. Depending on the metal : ligand ratio, the following reactions can take place:[103]

$$2\,[Pd(OAc)_2]_3 + 6\,PPh_3 = 3\,[Ph_3PPd(OAc)_2]_2,$$

$$[Ph_3PPd(OAc)_2]_2 + 2\,PPh_3 = 2\,(Ph_3P)_2Pd(OAc)_2.$$

For the ratio $[PPh_3] : [Pd(II)] = 1$, predominantly dinuclear palladium(II) complexes exist in solutions in DMF and CH_2Cl_2.[104] These actually react with hydrogen in this system.

The interaction of molecular hydrogen with $[Ph_3PPd(OAc)_2]_2$ leads to the formation of palladium(I) and palladium(0) complexes.[41,100]



The presence of the bridging ligands coordinated as bidentate species in the initial compounds apparently creates favourable conditions for the formation of the metal–metal bond on reduction.

The final product of this reaction — tentatively bis(triphenylphosphine)dipalladium — combines reversibly with molecular hydrogen, but is incapable of catalysing the hydrogenation reaction. Solutions of this complex acquire catalytic activity only after contact with a gas containing at least traces of oxygen in addition to H_2. In the joint presence of oxygen and hydrogen, hydrogen peroxide is formed and oxidises part of this complex, affording phosphine oxide and palladium(II) acetate. The latter reacts with H_2 and with the $Pd_2(PPh_3)_2$ which failed to enter into the oxidation reaction, being converted into the cluster **8**.

$$n\,(Ph_3P)_2Pd_2 + n\,[Pd(OAc)_2]_3 + 5n\,H_2O \longrightarrow$$

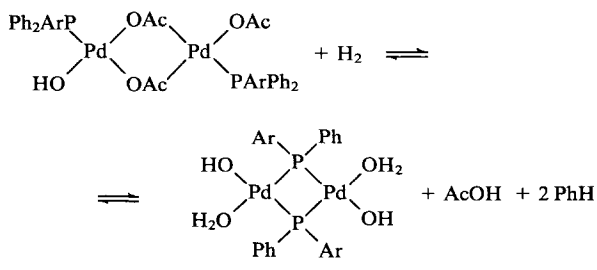
$$\longrightarrow [(PhP)_2Pd_5]_n + 6n\,AcOH + 4n\,C_6H_6$$

8

The kinetics and mechanisms of the hydrogenation of various organic substrates in the presence of the complexes described above have been investigated in detail.[96,105–112]

The use of the triarylphosphine ligand (L), containing the lyophilic SO_3Na group in the benzene ring, made it possible to synthesise by the above procedure phosphine complexes of the type (LPd_2X_2) (X = oxygen-containing acido-ligand). These compounds are soluble in water and may be used to hydrogenate unsaturated compounds in aqueous solution at 1 atm and 20 °C.[97,113–115]

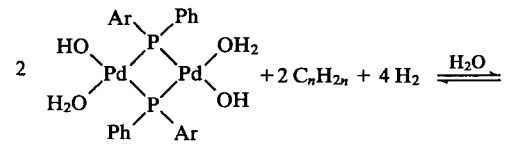
In aqueous solutions, the palladium(II) complex of phosphine, containing the lyophilic SO_3Na group, reacts with hydrogen, affording complex **9** with a phosphide ligand.



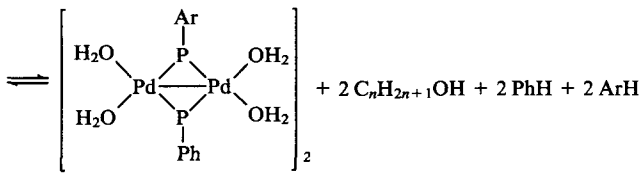
9

where Ar = *m*-$NaO_3SC_6H_4$.

Complex **9** in water is inert to molecular hydrogen, probably as a consequence of the influence of the strong electron-donating ligands — phosphide groups, which reduce the effective positive charge on the palladium atom. However, after the addition of an unsaturated hydrocarbon (propargyl or allyl alcohol, etc.) the absorption of hydrogen due to the reduction of the complex begins. Stoichiometric (in relation to the absorbed hydrogen) formation of an alcohol is observed simultaneously.[113,116]



9



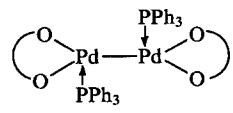
10

Under an argon atmosphere at 293 K, the cluster **10** catalyses the hydration of allyl alcohol to 1,2-propylene glycol and of propene to propan-2-ol.[115]

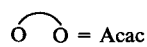
The clusters **8–10** have also been obtained as X-ray-amorphous powders and conclusions about their structures are based on the results of elemental analysis, IR and ^1H NMR spectroscopic data, and also the stoichiometry of the reactions involving them.

The formation of the complex $Pd(Acac)_2PPh_3$ is observed in the $Pd(Acac)_2 + PPh_3$ system. Therefore, in the study of the interaction of $Pd(Acac)_2$ with H_2 in the presence of PPh_3, the reduction of the complex already formed by hydrogen was in fact investigated.[98,117,118] In contrast to the palladium(II) acetate complex, the reduction of $Ph_3PPd(Acac)_2$ by hydrogen leads to the formation of the cluster $[(Pd_3P)_8.PPh_3]_n$.[122] In both cases, the palladium phosphide complexes are regarded as intermediates and the principal reaction products are obtained as a result of the far-reaching dephenylation of the triphenylphosphine ligands.

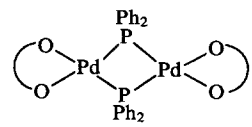
In the first stage of the reaction of $Pd(Acac)_2$ with H_2, the formation of an unstable intermediate was detected by IR and NMR spectroscopic methods. The formula **11** was proposed for it.[117]



11

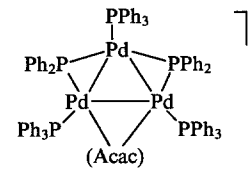


The subsequent treatment with hydrogen leads to the appearance of benzene and the formation of the stable intermediate complex $[Ph_2PPdAcac]_2$, isolated in the solid state, in which the palladium atoms are assumed to be linked by two bridging diphenyl phosphide groups.

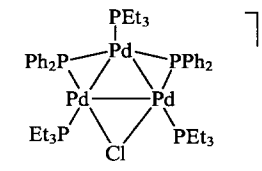


12

After the complete cessation of the absorption of hydrogen, complex **12** as well as the dinuclear cluster $[Pd_3(PPh_3)_3(PPh_2)_2.Acac]^+Acac^-$ [13] were detected in solution. The structures of complexes **12** and **13** were proposed on the basis of ^{31}P NMR spectroscopic data. In reaching conclusions about the structure of complex **13**, the authors were guided by the available data on the structure of the trinuclear palladium complex with diphenylphosphide ligands $[Pd_3(PPh_3)_3(PPh_2)_2Cl]^+Cl^-$ **14**,[119] containing chloride ions instead of acetylacetonato-groups. Complex **14** was first isolated together with *trans*-$Pd(Ph)Cl(PPh_3)_2$ when attempts were made to obtain $Pd(PPh_3)_2$ from $Pd(PPh_3)_4$ with $PdCl_2$ as the PPh_3 acceptor.[58] A series of analogues of this compound $[Pd_3(PPh_2)_2.(PR_3)_3X]^+BF_4^-$ (R = Ph, Et; X = Cl, Br, SCF_3) were later synthesised and the structure of the cluster $[Pd_3(PPh_2)_2.(PEt_3)_3Cl]^+BF_4^-$ **15** was determined by X-ray diffraction.[119]



13



15

The structure of this complex is based on a triangle made up of palladium atoms. The Pd_3P_2 skeleton is almost planar. The Pd–Pd bond lengths (2.89, 2.93, and 2.93 Å) are very similar and indicate a significant metal — metal interaction. The triangular Pd_3 fragment is almost equilateral in contrast to that observed in the cluster $[Pt_3(PPh_2)_3(PPh_3)_3Ph].C_6H_6$, where the metal atoms have the same formal oxidation state (4/3) as in the cluster **15**, but one Pt–Pt distance is longer than the other two.[63]

In the reaction of $Pd(Acac)_2$ with H_2 in the presence of PPh_3, a small amount of a product containing as the ligands P atoms or PPh groups, arising as a result of the removal of the phenyl group from the phosphorus atom of triphenylphosphine, is formed in addition to benzene and complexes **12** and **13**. This compound proved to be an active catalyst of hydrogenation, carbonylation, and arylation reactions.[98]

In order to increase the yield of the catalytically active substance, a study was made of the reduction of $Pd(Acac)_2$ in the presence of PPh_3 with the ratio Pd : P = 0.7–5.0. The substance obtained with the ratio Pd : P = 4 and having the composition $Pd_8P_3C_6H_{15}$ **16** proved to be most active in catalysing the hydrogenation of phenylethyne.[118]

According to ^{31}P NMR data, complex **16** contains phosphorus atoms, as an interstitial element, and triphenylphosphine ligands. According to small angle scattering data, the size of the particles is ~30 Å. EXAFS data for complex **16** were interpreted within the framework of a cluster model constructed from a set of trihedral Pd_6 prisms with a 2.54 Å edge and a height of 3.14 Å. The phosphorus atoms are located in their centres. In addition, about 11% of the initial PPh_3 is not dephenylated and is coordinated to the palladium phosphide Pd_3P formed. On the basis of the data obtained, the formula $[(Pd_3P)_8.PPh_3]_n$ was attributed to complex **16**.[102,118]

In contrast to platinum(II) chloride complexes, which are reduced by hydrogen only under very severe conditions,[99] platinum(II) acetate complexes are readily reduced by hydrogen, like the palladium(II) complexes. Treatment of the complex $[Ph_3PPt.(OAc)_2]_2$ with hydrogen (20 °C, 1 atm H_2) in acetic acid leads to the formation of the compounds $[Ph_2PPt]_n$ **17** (yield 85% with respect to platinum), $[Ph_2PPt(OAc)]_n$ **18** (yield 5% with respect to platinum), and a mixture of products of the far reaching dephenylation of triphenylphosphine having the general formula $[PhPPt]_m$ (yield 5% with respect to platinum).[101]

$$[Ph_3PPt(OAc)_2]_2 \xrightarrow[-C_6H_6]{H_2,\ AcOH} [Ph_2PPt]_n + [Ph_2PPt(OAc)]_n + [PhPPt]_m$$

17 **18**

The reaction is accompanied by the formation of benzene, which indicates the cleavage of the P–C bond of the coordinated triphenylphosphine under the conditions of the reaction with H_2. Furthermore, the main bulk of the compounds isolated contain PPh_2 groups and even the product of the incomplete reduction of the acetate groups $[Ph_2PPt(OAc)]_n$ contains diphenylphosphide groups and not triphenylphosphine. Thus, in contrast to palladium, where the complex $[Ph_3PPd]_2$ is formed under analogous conditions,[104] in the reduction of the complex $[Ph_3PPt(OAc)_2]_2$ by hydrogen the dephenylation of triphenylphosphine apparently proceeds in parallel with the hydrogenolysis of the Pt–OAc bonds linking the acetate groups and the complex $[Ph_3PPt]_n$ cannot be synthesised under these conditions.

It was expected[101] that the formation of heteronuclear platinum and palladium phosphide complexes is possible in the reduction of $(\eta^3\text{-}C_3H_5)Pd(OAc)_3Pt(PPh_3)$ **19** by hydrogen in acetic acid. However, metallic palladium is formed almost simultaneously with the heteronuclear complex on contact of complex **19** with H_2 and then platinum(II) is reduced slowly with formation of benzene and a platinum complex. According to IR spectroscopic data and elemental analysis, the latter complex is analogous to the $[Ph_2PPt]_n$ obtained on reduction of $[Ph_3PPt(OAc)_2]_2$ by hydrogen.[101]

$$(\eta^3\text{-}C_3H_5)Pd(OAc)_3Pt(PPh_3) \xrightarrow[-C_6H_6]{H_2,\ AcOH} \underset{\mathbf{19}}{} \longrightarrow Pd^0 + \underset{\mathbf{17}}{[Ph_2PPt]_n}$$

The reduction of $[Ph_3PPt(OAc)_3Ag]_2$ **20** by hydrogen in acetic acid also leads to the partial dephenylation of the triphenylphosphine ligands. On reduction, 1–2 molecules of benzene are formed from two molecules of compound **20**. The silver is reduced quantitatively to the metal. According to elemental analysis and the determination of the molecular mass, the main reaction product is the complex $[Pt_2(PPh_3)(PPh_2)(OAc)]_3$ **21**. According to data obtained by transmission electron microscopy (TEM), the particle size is ~5 Å, which can be correlated with the size of the particle containing the Pt_6 group.[101]

$$\underset{\mathbf{20}}{[Ph_3PPt(OAc)_3Ag]_2} \xrightarrow[-C_6H_6]{H_2,\ AcOH} \underset{\mathbf{21}}{[Pt_2(PPh_3)(PPh_2)(OAc)]_3}$$

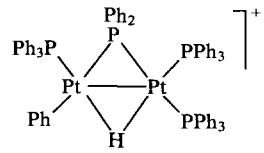
The acetate groups of complex **21** are manifested in the IR spectrum at 1580 and 1440 cm^{-1} and in the ^1H NMR spectrum at 2.09 p.p.m. (the hydride signals are not observed). A superposition of complex multiplet signals in the range 17–58 p.p.m. is observed in the ^{31}P NMR spectrum, which can be attributed to both Ph_2P and Ph_3P groups.

Complex **21** absorbs hydrogen reversibly in solutions in acetic acid (1 mol of H_2 per gram-atom of Pt). The cycles involving evaporation, admission of argon, and subsequent absorption of hydrogen may be repeated several times.

$$\underset{\mathbf{21}}{[Pt_2(PPh_3)(PPh_2)(OAc)]_3} \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} \underset{\mathbf{22}}{[Pt_2(PPh_3)(PPh_2)(OAc)(H_2)_2]_3}$$

The reversible absorption of hydrogen is not characteristic of this complex alone. Thus, when $[Ph_3PPt(OAc)_2]_2$ and $(\eta^3\text{-}C_3H_5)$. $Pd(OAc)_3Pt(PPh_3)$ are reduced, more hydrogen is absorbed (2 mol and 1.5 mol per gram-atom of the metal respectively) than is required for the stoichiometric reduction reaction. The superstoichiometric amount of hydrogen is also absorbed reversibly in such cases. Similar results were obtained previously in the case of the palladium complex $Pd_2(PPh_3)_2$.[100] The signal due to the coordinated hydrogen in the ^1H NMR spectra was not recorded in all cases, which can probably be explained by the low stability of the complexes and the very large signal width, characteristic of complexes with molecular hydrogen.[120]

When a mixture of $Pt(1,5\text{-}C_8H_{12})_2$, [*trans*-PtPh(MeCOMe). $(PPh_3)_2]^+$, and PPh_3 was treated with hydrogen, the formation of the platinum phosphide complex **23** was also observed.[66]



23

The question of the origin of the phenyl group linked to the platinum atom was solved by replacing the initial cation by $[trans\text{-}Pt(p\text{-}MeC_6H_4)(MeCOMe)(PPh_3)_2]^+$. Since the cation **23** is in this case detected among the reaction products, it is evident that the phenyl group was formed as a result of the dissociation of the P–C bond involving the PPh_3 ligand.

4. Reduction of $Pd(OAc)_2$ by hydrogen in the presence of phenanthroline and bipyridyl

The products of the reduction of $Pd(OAc)_2$ by hydrogen in acetic acid containing phenanthroline or bipyridyl have been investigated.[121–123] The noncrystalline substances obtained are capable of catalysing the oxidation of alkenes, alcohols, and other organic substrates.

The product of the reduction of palladium(II) acetate by hydrogen in solution in acetic acid containing 0.5 mol of phenanthroline per gram-atom of palladium has the composition $Pd_4Phen(OAc)_2H_4$ **24.**

$$4\,Pd_3(OAc)_6 + 3\,Phen + 15\,H_2 = 3\,\underset{\mathbf{24}}{[Pd_4Phen(OAc)_2H_4]_n} + 6\,AcOH$$

The hydride nature of complex **24** was confirmed by ^1H NMR spectroscopic data. A broad band with a maximum in the range $\delta = -30$ to -50 ppm (width 5 kHz) was found in the broad-band spectrum (frequency range 250 kHz).[130] The appreciable broadening of the hydride signals was explained by the fact that the palladium atoms in these complexes form a polynuclear structure with a system of metal–metal bonds similar to the lattice of metallic palladium or its hydride phases.

The study of this substance by high-resolution transmission electron microscopy showed that its particles contain a nearly spherical metal core 20 ± 5 Å in diameter.[124] A radial distribution curve for the atoms (RDA), on which there is a single maximum corresponding to the Pd–N interatomic distance (2.1 ± 0.1 Å) and a single peak corresponding to the short Pd–Pd distance (2.62 ± 0.05 Å) was obtained from EXAFS data.

The sizes of the metal core of the hydrido-complex molecules found from TEM data enabled the authors to estimate the number n in the formula $[Pd_4Phen(OAc)_2H_4]_n$, which proved to be approximately 100 on the assumption that the packing density of the palladium atoms in the core of this cluster is the same as in the metallic palladium lattice.

The chemical properties of the hydrido-complex indicate its high reactivity.[125,126] Treatment of the polynuclear hydrido-complex with various electrophiles leads as a rule to unstable products, which decompose into monomeric or oligomeric palladium complexes. In contrast to this, the reaction with O_2 leads to the formation of clusters in which a massive metal skeleton is retained. These clusters proved to be effective catalysts for many oxidation reactions.[127,128]

5. Giant palladium clusters

On reaction with oxygen, the polynuclear hydrido-complex **24** loses its hydride atoms, which are bound to form H_2O. A small proportion of the palladium atoms are then oxidised to Pd(2+) complexes and the main bulk are converted into a cluster compound the simplest formula of which is $Pd_9Phen(OAc)_3$ **25**. Complex **25** is stable in air and is soluble, like the hydrido-complex **24**, in water and polar organic solvents.[127]

The molecular mass of complex **25**, which is $(1.0 \pm 0.05) \times 10^5$, was estimated from the measured rates of sedimentation in an aqueous solution under ultracentrifugation conditions. Such a large molecular size required the use of a set of analytical methods for the identification of these compounds. More definite information about the molecular size of compound **25** was obtained with the aid of small angle X-ray scattering methods, high-resolution transmission electron microscopy, and electron diffraction.[128-130]

The metal cores of the molecules of compound **25** are observed on the electron photomicrographs in the form of almost regular spherical particles 26.0 ± 3.5 Å in diameter with a unimodal size distribution. The packing of the palladium atoms in the cluster **25** was determined with the aid of EXAFS spectra.[128,129] The set of atomic Pd–Pd distances found (2.60 ± 0.04, 3.1 ± 0.1, 3.7 ± 0.1, 4.1 ± 0.1) agrees best with the icosahedral model of the packing of palladium atoms in the metal core of the cluster **25**. Taking into account the chemical composition, the idealised formula $Pd_{561}Phen_{60}(OAc)_{180}$ was proposed for the cluster **25**. This formula apparently corresponds to an average size and composition of the cluster and not to definite fixed dimensions and chemical composition, i.e. there is a distribution of the particles of the cluster **25** about an average value $d \approx 25$ Å and the idealised composition $Pd_{561}Phen_{60}(OAc)_{180}$.

In this structure, 60 Phen ligands are coordinated as bidentate species by the palladium atoms at the vertices and on the edges of the icosahedron. The overall formal charge on the metal core together with the electrically neutral Phen ligand is 180+ and is balanced by 180 anionic ligands OAc^-, which are distributed in the outer sphere of the cluster cation **25** (Fig. 1). A similar outer-sphere arrangement of acetate anions has been observed with the aid of X-ray diffraction in the tetranuclear cluster $[Pd_4Phen_4(CO)_2](OAc)_4$.[131]

The cluster **25** can be precipitated from aqueous solution by adding salts such as NaX or KX (X = Cl, Br, ClO_4, HSO_4, PF_6, AsF_6), which is accompanied by the substitution of the OAc^- anions by X^-. When compound **25** was treated with the salt KPF_6, a giant cluster having a similar composition and structure and represented by the idealised formula $Pd_{561}Phen_{60}O_{60}(PF_6)_{60}$ **26** was obtained.[130]

$$Pd_{561}Phen_{60}(OAc)_{180} + 60\,PF_6^- + 60\,H_2O$$

$$= Pd_{561}Phen_{60}(PF_6)_{60}O_{60} + 120\,AcOH + 60\,AcO^-$$

EXAFS data led to the conclusion that the packing of the metal atoms in the metal core of the cluster **26** is cubooctahedral and not icosahedral.

The giant clusters obtained serve as a bridge between the usual molecular clusters and colloidal metals and their homogeneous solutions are a model of the colloidal solutions of metals. The size of the metal core in giant clusters greatly exceeds the size of the larger molecular clusters, such as $Pd_{38}(CO)_{28}(PEt_3)_{12}$[132] and $Au_{55}(PPh_3)_{12}Cl_6$,[133] approaching the lower limit of the size of the colloidal particles of metals. In contrast to the latter, giant clusters have a distinct ligand environment with a definite stoichiometry characteristic of molecular clusters. However, in those cases where the number of metal atoms approaches several hundreds, a set of more or less imperfect metallopolyhedra is formed with a certain distribution with respect to size and chemical composition.

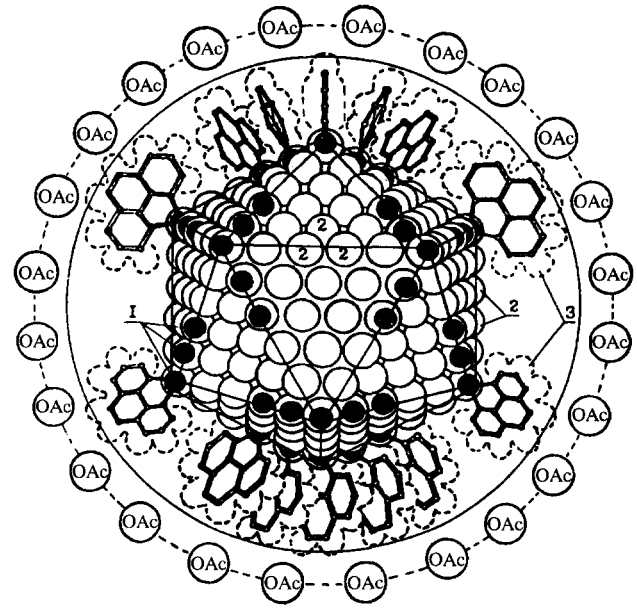


Figure 1. An idealised model of the cluster **25**: (*1*) palladium atoms coordinated to the Phen ligands; (*2*) palladium atoms accessible for the coordination of the AcO^- anion and substrate or solvent molecules; (*3*) the van der Waals volume of the coordinated phenanthroline molecules.

The clusters **25** and **26** behaved as catalysts in a series of reactions. Oxidative acetoxylation of ethene to vinyl acetate, of propene to allyl acetate, and of toluene to benzyl acetate takes place in the presence of acetic acid in solutions of these clusters.[130] They effectively catalyse the oxidation by molecular oxygen of primary alcohols to esters and of secondary alcohols to ketones.[134]

6. Reduction of platinum(II) and palladium(II) carboxylate complexes by formic acid

As shown above, the reduction of $[Ph_3PPd(OAc)_2]_2$ or $Ph_3PPd(Acac)_2$ by molecular hydrogen leads to the final products $[Pd_5(PPh)_2]_m$ and $[(Pd_3P)_8.PPh_3]_n$ respectively.[100] These are formed as a result of the far reaching dephenylation of the triphenylphosphine ligands. In both cases, palladium phosphide complexes are regarded as intermediates. Presumably it will be possible to obtain palladium phosphide complexes by the reduction of palladium carboxylates with formic acid.

Indeed, the study of the interaction of $Pd(Acac)_2PPh_3$ with formic acid under an atmosphere of an inert gas or hydrogen showed that the initial complex is reduced much faster by formic acid than by hydrogen. The latter does not affect the course of the reaction and the composition of the products under these conditions.[98,117,135] In the first stage, all the acetylacetonate ligands are substituted by formate ligands.

$$Pd(Acac)_2PPh_3 + 2\,HCOOH \longrightarrow Pd(HCOO)_2PPh_3 + 2\,HAcac$$

Analysis of the gas phase revealed the presence of CO_2 and H_2, which is characteristic of the catalytic decomposition of HCOOH.[136] According to a number of investigators,[98,117,137,138] the dimeric complex $[PdPPh_3]_2$ should also be formed in the reduction of $Pd(HCOO)_2PPh_3$, similarly to what happens in the reduction of $[(Ph_3P)_2Pd(OAc)_2]_2$ by hydrogen.[41,100]

$$[Pd(HCOO)_2PPh_3]_2 \longrightarrow [PdPPh_3]_2 + 4\,CO_2 + 2\,H_2$$

However, the complex $[PdPPh_3]_2$ could not be detected. It is apparently unstable under the reaction conditions and interacts in accordance with the following scheme with the hydrogen formed:

$$[PdPPh_3]_2 + H_2 \longrightarrow [PdPPh_2]_2 + 2\,C_6H_6.$$

The final product of the reduction reaction is a complex to which the formula $[Pd_4(PPh_3)_2(PPh_2)_2]_n$ was attributed on the basis of the results of elemental analysis and UV and IR spectroscopic data.[117] In this product, half of the PPh_3 ligands have been dephenylated. the complex obtained exhibits a high activity in the arylation of styrene by iodobenzene, but is inactive in the hydrogenation and oligomerisation of phenylethyne.[117]

The interaction of $[Ph_3PPt(OAc)_2]_2$ with HCOOH also begins with the replacement of all the acetate ligands by formate ligands (according to GLC data). After an induction period, the platinum(II) complex is subsequently reduced with formation of benzene and CO_2. According to the results of elemental analysis and IR spectra, the main reaction product corresponds to the composition $[Ph_2PPt]_n$ **27**. In addition, a small amount (~5%) of the product of more far reaching dephenylation $[PhPPt]_m$ **28** is formed (Scheme 3).[101,102]

Scheme 3

$$[Ph_3PPt(OAc)_2]_2 \xrightarrow[-AcOH]{HCOOH} [Ph_3PPt(OCOH)_2]_2 \xrightarrow{-CO_2}$$

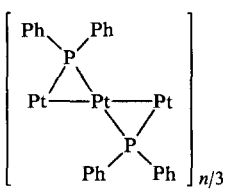
$$\longrightarrow [Ph_3PPtH_2]_n \xrightarrow{-C_6H_6} [Ph_2PPt]_n \xrightarrow{-C_6H_6} [PhPPt]_m$$

27 **28**

The molecular mass of complex **27** in benzene corresponds to 10 $[Ph_2PPt]$ fragments, i.e. $n = 10$. According to the results of the study of complexes **27** and **28** by high-resolution transmission electron microscopy, their particle size does not exceed 6 Å, which corresponds to small clusters and does not conflict with the determination of the molecular mass.[101]

A very broad signal (50 mHz), apparently associated with the occurrence of rapid exchange in the system, is observed in the ^{31}P NMR spectra. A decrease in temperature to −90 °C in toluene or to the glass point (−60 °C) in DMF does not induce slow exchange conditions in this case. ^{31}P NMR spectra of a similar type have been observed for all platinum phosphide complexes.

According to EXAFS spectroscopic data, there is only one shortest Pt–Pt distance in complex **27**, amounting to 2.53 Å, while the next nonbonding distance is 3.01 Å; only one maximum also corresponds to the Pt–P distance (2.22 Å). Bearing in mind that the Pt:P ratio is 1:1 on the basis of the composition of complex **27** and that according to EXAFS spectroscopic data the intensity of the Pt–P peak exceeds significantly that of the Pt–Pt peak, the authors suggested that complex **27** is a linear chain polymer in which the platinum atoms are linked by the metal–metal interaction and by bridging phosphido-groups. In addition, the authors do not rule out the possibility of the existence of pentacoordinate phosphorus atoms in this structure.



The fixed long Pt–Pt distance can apparently be explained by the fact that the chain structure is bent and not linear. The bent form of the chain can be accounted for by the molecular packing effects in the solid phase (EXAFS spectra were recorded for the specimens). However, the EXAFS spectroscopic data for a solution of complex **27** are virtually identical with the spectra of solid specimens.

The size distribution and form of the particles of complex **27** have been investigated by the small angle X-ray scattering method (SAXS). According to SAXS data, the particles of complex **27** are nearly spherical with a diameter of 15.2 ± 0.5 Å.

In contrast to platinum, treatment of the palladium acetate complex $[Ph_3PPd(OAc)_2]_2$ with formic acid leads to the formation of the polyhydride complex $[Pd_2(PPh_2)H_x]_n$ **29** as the main reaction product (60% and 70% relative to palladium). Furthermore, the complex $[Pd(\mu\text{-}O_2PPh_2)(Ph)(PPh_3)]_2$ **30** was obtained in 8%–10% yield relative to palladium. According to GLC data, the reaction also results in the formation of acetic acid (2 mol per mol of palladium) and benzene (0.9 mol per mol of PPh_3).[137]

$$[Ph_3PPd(OAc)_2]_2 \xrightarrow[-C_6H_6]{HCOOH}$$

$$\longrightarrow [Pd_2(PPh_2)H_x]_n + [Pd(\mu\text{-}O_2PPh_2)(Ph)(PPh_3)]_2$$

29 **30**

The dynamics of the variation of the volume of the gas phase of the system corresponds to the autocatalytic nature of the reaction, the volume of the gas exceeding the calculated value by a factor greater than 2.5. According to GLC data, the evolved gas is a ~1:1 mixture of CO_2 and H_2. Carbon monoxide was not detected even in trace amounts. The presence of hydrogen in the gas mixture and the volume of the evolved gas indicate that the reduction of the palladium(II) complex is accompanied by the decomposition of formic acid by the complex.

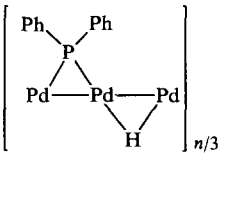
$$Pd(II) \xrightarrow{HCOOH} Pd(0) + CO_2 + 2\,H^+$$

$$HCOOH \xrightarrow{Pd^{0-1}} CO_2 + H_2$$

Nor can one rule out [the possibility] that the hydrogen formed on decomposition of formic acid is consumed on the reduction of the initial palladium(II).

The IR spectrum of complex **29** (the main reaction product) contains only the absorption bands of the phosphorus-containing ligands. Those of the OAc^- groups are absent (the Pd–H vibrations are inactive in the IR spectrum). In the ^1H NMR spectrum, the signal due to the aromatic protons is broadened and in addition a broad signal is observed (signal widths ~0.9 ppm) with the centre at −9.5 ppm and may correspond only to complexes with hydrogen. According to SAXS data (small angle scattering), the particles of complex **29** are spherical and their size is 15.6 ± 0.5 Å. The $[Pd_2(PPh_2)H_x]_n$ particle size is virtually the same as for the analogous platinum complex $[Ph_2PPt]_{10}$ (15.2 ± 0.5 Å). Thus the number of metal atoms in the palladium phosphide complex is apparently also close to ten.

The RDA curve for complex **29** was obtained from EXAFS data. It has a peak corresponding to a single shortest distance between the palladium atoms (2.55 Å), the next nonbonding distance being 3.66 Å. Only a single maximum corresponding to a Pd–P distance of 2.15 Å is also observed in the EXAFS spectrum. In conformity with these data, the authors[137] suggest that, like the platinum phosphide complex, complex **29** is a linear chain polymer in which the palladium atoms are linked by the metal–metal interaction, bridging phosphido-ligands, and, apparently, bridging hydrido-ligands.



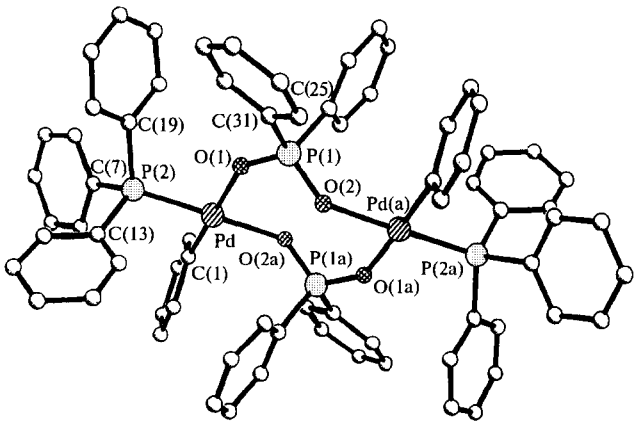


Figure 2. Molecular structure of $[Pd(\mu\text{-}O_2PPh_2)(Ph)(PPh_3)]_2$ **30**.

The structure of the second product of the interaction of $[Ph_3PPd(OAc)_2]_2$ with HCOOH — the dimeric complex $[Pd(\mu\text{-}O_2PPh_2)(Ph)(PPh_3)]_2$ **30** was established by X-ray diffraction.[138] The Pd^{2+} species of the centrosymmetrical dimeric complex **30** are linked by two bridging diphenylphosphinate groups. The Pd...Pd distance is 5.35 Å, which rules out the possibility of a metal–metal interaction (Fig. 2). The coordination of the palladium atoms is close to the ideal square-planar. The central eight-membered ring has the chair conformation and, as a consequence of its centrosymmetrical structure, the atoms of the central part of the ring P(1), O(2), P(1a), and O(2a) are strictly coplanar, while the plane comprising the atoms of the 'angular' fragment P(1), O(1), Pd, and O(2a) forms a dihedral angle of 47.3° with the plane of the central part.

The Pd–O(1) and Pd–O(2a) bonds in the *trans*-positions relative to the Ph and Ph_3P substituents at the metal atom are virtually the same [2.115(6) and 2.100(9) Å]. On the other hand, the P(1)–O(1) [1.482(6) Å] and P(1)–O(2) [1.516(9) Å] bond lengths differ by 0.034(9) Å, which justifies the assumption that the P(1)–O(1) bond is multiple, while Pd–O(1) is a coordinate bond. Nevertheless, the Pd–O bond lengths are equalised, which is apparently induced by the electronic influence of the Ph_3P and Ph groups in the *trans*-positions relative to these bonds.

It is noteworthy that the formation of complex **30** in the reaction of $[Ph_3PPd(OAc)_2]_2$ with HCOOH is the outcome of an unusual oxidation-reduction process because it indicates the oxidation of P^{III} to P^{V} in the presence of a powerful reductant (HCOOH) and in the absence of any kind of traditional oxidant. The only source of oxygen atoms, which become attached to the phosphorus atom of the phosphine ligand during the formation of complex **30** under the reaction conditions (Ar atmosphere, reagents carefully freed from O_2), is the carboxylate ligands.

The fact that the P–C bond dissociation reaction in the formation of complex **30** includes an intermediate decrease in the oxidation state of the metal is confirmed both by the very fact of the formation of complex **30** with a Pd–C(Ph) bond and by data on the reduction of palladium(II) by formic acid in the presence of hydroquinone and *p*-benzoquinone. The presence of hydroquinone, which is incapable of oxidising palladium(0), under these conditions merely shortens somewhat the induction period and hardly affects the form of the curve. On the other hand, the addition of *p*-benzoquinone increases sharply the induction period, at the end of which gas is evolved at a significantly higher rate. On the basis of these data, one may conclude that the low-valence palladium complex formed in the system is immediately oxidised by *p*-benzoquinone to palladium(II) and, as long as any amount of the quinone remains in the system, there is virtually no gas evolution.

IV. Conclusion

The extensive and independent field of the chemistry of cluster compounds such as the carbonylphosphineplatinum(0) and carbonylphosphinepalladium(0) compounds remains outside the scope of the present review.

Complexes with phosphine ligands have played an enormous role in the establishment and development of the modern chemistry of transition metals. The electronic properties of these ligands (their *n*-donor capacity and their fairly low-lying unoccupied *d* orbitals) as well as the steric factors which vary within wide limits have been used widely to stabilise labile complexes containing M–H, M–C, M–Si and other bonds and also to obtain numerous catalysts from them.

In the first stage of the study of complexes of this type, it appeared that the phosphine ligand can migrate, as a stable fragment, from one compound to another or can leave the coordination sphere without changing and without entering into any kind of reactions involving the P–C bonds.

The data examined above show that in reality tertiary phosphines lose their organic groups fairly readily under the conditions of reactions leading to a decrease in the oxidation state of the central atom. The dissociation of the P–C bond is observed when virtually any reductants are employed. It now appears surprising that these reactions remained unnoticed in the first stages of the development of the chemistry of complexes with tertiary phosphines when numerous mononuclear complexes of metals in the zero oxidation state were synthesised. Studies in later years showed that, when the M : L ratio is varied, it is possible to obtain in the same systems clusters in which the role of the bridging groups is assumed by phosphide or phosphene ligands, arising when the organic groups are removed from the molecule of the initial tertiary phosphine. The nature of these reactions is still insufficiently clear. There is no doubt about the role which the coordinative unsaturation of the metal atom in the corresponding intermediate plays in the dearylation and dealkylation of the tertiary phosphine. However, the comparative stability of the complexes containing only two phosphine ligands at the metal atom in the zero oxidation state suggests that, apart from the formal coordinative unsaturation, some other factors are also responsible for the course of these unusual processes.

The cluster formation reactions are a phenomenon characteristic not only of complexes with phosphine ligands. As can be seen from the concluding sections of the present review, palladium clusters are formed readily when palladium acetate is treated with reductants in the presence of stabilising ligands such as carbon monoxide and aromatic nitrogen-containing bases coordinated as bidentate species. The formation reactions of these clusters constitute the basis of the synthesis of catalytically active compounds exhibiting an unusual selectivity and activity under mild conditions. The interest of the authors in the topic to which this review is devoted is partly due to these factors.

References

1. F R Hartley *Organomet. Chem. Rev., A* (6) 119 (1970)
2. L Malatesta, S Cenini *Zerovalent Compounds of Metals* (London: Academic Press, 1974)
3. L Malatesta, M Angoletta *J. Chem. Soc.* 1168 (1957)
4. L Malatesta, C Cariello *J. Chem. Soc.* 2323 (1958)
5. T Kruck, K Baur *Angew. Chem., Int. Ed. Engl.* **4** 521 (1965)
6. T Kruck *Angew. Chem., Int. Ed. Engl.* **6** 53 (1967)
7. A D Allen, C D Cook *Proc. Chem. Soc.* 218 (1962)
8. J Chatt, B L Shaw *J. Chem. Soc.* 5057 (1962)
9. J A Chopoorian, J Lewis, R S Nyholm *Nature (London)* **190** 528 (1961)
10. L Malatesta, R Ugo *J. Chem. Soc.* 2080 (1963)
11. J Chatt, G A Rowe *Nature (London)* **191** 1191 (1961)

12. R Ugo *Coord. Chem. Rev.* **3** 319 (1968)
13. G C Dobinson, R Mason, G B Robertson, R Ugo, F Conti, D Morelli, S Cenini, F Bonati *J. Chem. Soc., Chem. Commun.* 739 (1967)
14. C A McAuliffe, in *Transition Metal Compounds Containing Phosphine Ligands* 1973, p. 147
15. V G Andrianov, I S Akhrem, N M Chistovalova, Yu T Struchkov *Zh. Strukt. Khim.* **17** 135 (1976)
16. J S Field, P J Wheatley *J. Chem. Soc., Dalton Trans.* 702 (1974)
17. V G Albano, G M B Ricci, P L Bellon *Inorg. Chem.* **10** 2109 (1969)
18. S Otsuka, T Yoshida, M Matsumoto, K Nakatsu *J. Am. Chem. Soc.* **98** 5850 (1976)
19. L G Kuz'mina, Yu T Struchkov, L Yu Ukhin, N A Dolgopolova *Koord. Khim.* **11** 1694 (1985)
20. K N Harrison, P A Hoye, G A Orpen, P G Pringle, M B Smith *J. Chem. Soc., Chem. Commun.* 1096 (1989)
21. V G Albano, P L Bellon, V Scatturin *J. Chem. Soc., Chem. Commun.* 507 (1966)
22. T A Stromnova, V S Sergienko, A V Kisin, M A Porai-Koshits, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 894 (1987)
23. A Ammirzi, A Musco, B E Mann *Inorg. Chim. Acta* **21** L37 (1977)
24. R Ugo, F Cariati, La Monica *J. Chem. Soc., Chem. Commun.* 869 (1966)
25. A Ammirzi, A Musco *J. Chem. Soc., Chem. Commun.* 400 (1974)
26. K J Moynihan, Chung Chen, R G Goel *Acta Crystallogr., Sect. B* **35** 3060 (1979)
27. S Otsuka, T Yoshida, M Matsumoto, K Nakatsu *J. Am. Chem. Soc.* **98** 5850 (1976)
28. K S Wheelock, J H Nelson, H B Jonassen *Inorg. Chim. Acta.* **4** 399 (1970)
29. Pi-Chang Kong, D M Roundhill *Inorg. Chem.* **11** 749 (1972)
30. D R Coulson *Inorg. Synth.* **13** 121 (1972)
31. C A Tolman, W C Seidel, D H Gerlach *J. Am. Chem. Soc.* **94** 2669 (1972)
32. J Chatt, F A Hart, H R Watson *J. Chem. Soc.* 2537 (1962)
33. J Chatt, H R Watson *Nature (London)* **189** 1003 (1961)
34. D T Rosevear, F G A Stone *J. Chem. Soc. A* 164 (1968)
35. M Bressan, G Favero, B Corain, A Turco *Inorg. Nucl. Chem. Lett.* **203** 203 (1971)
36. M I Bruce, G Shaw, F G A Stone *J. Chem. Soc., Dalton. Trans.* 1082 (1972)
37. H C Clark, K Itoh *Inorg. Chem.* **10** 1707 (1971)
38. R Ugo, S Cenini, M F Pilbrow, B Deible, P Schneider *Inorg. Chim. Acta* **18** (7) 113 (1976)
39. P Abley, F J McQuillin *J. Chem. Soc., Chem. Commun.* 1503 (1969)
40. A S Berenblyum, L I Lakhman, I I Moiseev, E D Radchenko *Izv. Akad. Nauk SSSR, Ser. Khim.* 2417 (1975)
41. A S Berenblyum, L I Lakhman, I I Moiseev, E D Radchenko *Koord. Khim.* **2** 841 (1976)
42. O V Gritsenko, A A Bagatur'yants, I I Moiseev, V B Kazanskii, I V Kalechits *Kinet. Katal.* **21** 632 (1980)
43. V M Frolov, O P Parenago, L P Shuikina *Kinet. Katal.* **21** 1085 (1980)
44. L P Shuikina, G M Cherkashin, O P Parenago, V M Frolov *Dokl. Akad. Nauk SSSR* **257** 655 (1981)
45. L P Shuikina, A I El'natanova, L S Kovaleva, O P Parenago, V M Frolov *Kinet. Katal.* **22** 177 (1981)
46. V M Frolov, O P Parenago, L P Shuikina *Kinet. Katal.* **19** 1608 (1978)
47. R Ugo, F Cariati, G La Monica *Inorg. Synth.* **11** 105 (1968)
48. M Maier, F Basolo, R G Pearson *Inorg. Chem.* **8** 795 (1969)
49. M Maier, F Basolo *Inorg. Synth.* **13** 112 (1972)
50. P Chini, G Longoni *J. Chem. Soc. A* 1542 (1970)
51. P Roffia, F Conti, G Gregorio *Chim. Ind.* **54** 317 (1972)
52. P Roffia, F Conti, G Gregorio *Chim. Ind.* **53** 361 (1971)
53. D A White, G W Parshall *Inorg. Chem.* **9** 2358 (1970)
54. R Ugo, G La Monica, F Cariati, S Cenini, F Conti *Inorg. Chim. Acta* **4** 390 (1970)
55. R D Gillard, R Ugo, S Cenini, F Bonati *J. Chem. Soc., Chem. Commun.* 869 (1966)
56. P E Garrow *Chem. Rev.* **85** 171 (1985)
57. G W Parshall *Acc. Chem. Res.* **3** 139 (1970)
58. D R Coulson *J. Chem. Soc., Chem. Commun.* 1530 (1968)
59. P S Brakerman, R J Cross, G B Young *J. Chem. Soc., Dalton Trans.* 1306 (1976)
60. G Oehme, H Bandisch *Tetrahedron Lett.* **15** 4129 (1974)
61. A Gillie, J K Stille *J. Am. Chem. Soc.* **102** 4933 (1980)
62. F Glockling, T McBride, R J Pollock *J. Chem. Soc., Chem. Commun.* 650 (1973)
63. N J Taylor, P C Chieh, A J Carty *J. Chem. Soc., Chem. Commun.* 448 (1975)
64. P L Bellon, A Ceriotti, F Demartin, G Longoni, B T Heaton *J. Chem. Soc., Dalton Trans.* 1671 (1982)
65. R Meij, D J Stuffkens, K Vriese, A M F Browers, A R Overbeek *J. Organomet. Chem.* **155** 123 (1978)
66. J Jans, R Naegeli, L M Venanzi, A Albinati *J. Organomet. Chem.* **247** 123 (1983)
67. A Ammirzi, A Musco, P Zambelli, G Carturan *Inorg. Chim. Acta* **13** L12 (1975)
68. J Fornies, M Green, J L Spencer, F G A Stone *J. Chem. Soc., Dalton Trans.* 1006 (1977)
69. C A Tolman *Chem. Soc. Rev.* 337 (1972)
70. T R Durkin, E P Schram *Inorg. Chem.* **11** 1054 (1972)
71. T R Durkin, E P Schram *Inorg. Chem.* **11** 1048 (1972)
72. K Kudo, M Hidai, T Murayama, Y Uchida *J. Chem. Soc., Chem. Commun.* 1701 (1970)
73. R Van der Linde, R O de Jongh *J. Chem. Soc., Chem. Commun.* 563 (1971)
74. M Meier, F Basolo, R G Pearson *Inorg. Chem.* **8** 795 (1969)
75. R R Orio, B B Chastain, H B Gray *Inorg. Chim. Acta.* **3** 3 (1969)
76. G F Svatos, E E Flag *Inorg. Chem.* **4** 422 (1965)
77. T Kruck, K Baur *Chem. Ber.* **98** 3080 (1965)
78. A F Hollman, E Wiberg, N Wiberg, in *Lehrbuch der Anorganishen Chemie* (Berlin: Walter de Gruyter, 1985) p. 1178
79. J F Nixon, M D Sexton *J. Chem. Soc. A* 1068 (1969)
80. J F Nixon, M D Sexton *J. Chem. Soc. A* 321 (1970)
81. P M Maitlis, in *The Organic Chemistry of Palladium* (New York: Academic Press, 1971) Vol. 2, p. 216
82. I I Moiseev, M N Vargaftik, I V Kalechits, T A Stromnova, Yu A Pazderskii, O I Gentosh *Izv. Akad. Nauk SSSR, Ser. Khim.* 2635 (1977)
83. I I Moiseev, M N Vargaftik, O I Gentosh, N M Zhavoronkov, I V Kalechits, Yu A Pazderskii, T A Stromnova, S A Shcherbakova *Dokl. Akad. Nauk SSSR* **237** 645 (1977)
84. I I Moiseev, T A Stromnova, M N Vargaftik, G Ja Mazo *J. Chem. Soc., Chem. Commun.* 27 (1978)
85. T A Stromnova, L G Kuz'mina, M N Vargaftik, G Ya Mazo, Yu T Struchkov, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 720 (1978)
86. T A Stromnova, N Yu Tikhonova, D I Kochubei, I I Moiseev *Dokl. Akad. Nauk SSSR* **335** 602 (1994)
87. I I Moiseev *Pure Appl. Chem.* **61** 1755 (1989)
88. T A Stromnova, Candidate Thesis, Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 1982
89. T A Stromnova, M N Vargaftik, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 31 (1983)
90. I I Moiseev, M N Vargaftik, T A Stromnova *J. Organomet. Chem.* **252** 113 (1983)
91. Ya V Salyn', M K Starchevskii, I P Stolyarov, M N Vargaftik, V I Nefedov, I I Moiseev *Kinet. Katal.* **24** 743 (1983)
92. M K Starchevskii, M N Vargaftik, I I Moiseev *Kinet. Katal.* **20** 1163 (1979)
93. I P Stolyarov, Candidate Thesis in Chemical Sciences, Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, Moscow, 1986
94. G Longoni, P Chini *J. Am. Chem. Soc.* **98** 7225 (1976)
95. J C Calabrese, L F Dahl, P Chini, G Longoni, S Martinengo *J. Am. Chem. Soc.* **96** 2614 (1974)
96. A S Berenblyum, A G Knizhnik, S L Mund, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2711 (1978)
97. A S Berenblyum, T V Turkova, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 235 (1981)
98. T I Bakunina, Candidate Thesis in Chemical Sciences, Irkutsk Institute of Organic Chemistry, Irkutsk, 1990
99. B R James, in *Homogeneous Hydrogenation* (Translated into Russian; Moscow: Mir, 1976) p. 370

100. A S Berenblyum, A G Knizhnik, S L Mund, I I Moiseev *J. Organomet. Chem.* **234** 219 (1982)
101. I I Moiseev, N Yu Kozitsyna, D I Kochubey, V N Kolomijchuk, K I Zamaraev *J. Organomet. Chem.* **451** 231 (1993)
102. N Yu Kozitsina, Candidate Thesis in Chemical Sciences, Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 1994
103. T A Stephenson, G J Wilkinson *J. Inorg. Nucl. Chem.* **29** 2122 (1967)
104. A S Berenblyum, A G Knizhnik, S L Mund, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1687 (1979)
105. A S Berenblyum, A P Aseeva, L I Lakhman, V P Petrovskii, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1227 (1980)
106. A S Berenblyum, S L Mund, L G Danilova, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1761 (1980)
107. A S Berenblyum, T V Turkova, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 514 (1981)
108. A S Berenblyum, A G Knizhnik, S L Mund, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1249 (1982)
109. A S Berenblyum, A G Knizhnik, S L Mund, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2700 (1980)
110. A S Berenblyum, S L Mund, L G Danilova, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 677 (1981)
111. A S Berenblyum, S L Mund, L G Danilova, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 906 (1981)
112. A S Berenblyum, S L Mund, T P Goranskaya, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2472 (1981)
113. A S Berenblyum, T V Turkova, I I Moiseev *Koord. Khim.* **5** 773 (1979)
114. A S Berenblyum, L I Lakhman, I I Moiseev, E D Radchenko *Izv. Akad. Nauk SSSR, Ser. Khim.* 2417 (1975)
115. A S Berenblyum, A P Aseeva, L I Lakhman, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2163 (1977)
116. A S Berenblyum, T P Goranskaya, S L Mund, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1367 (1979)
117. V A Khutoryanskii, T I Bakunina, S V Zinchenko, L V Mironova, E A Grechkina, F K Shmidt *Koord. Khim.* **13** 809 (1987)
118. T I Bakunina, S V Zinchenko, V A Khutoryanskii, V N Kolomeichuk, F K Shmidt, in *Metallokompleksnyi Kataliz: Sb. Nauch. Tr.* (Metal Complex Catalysis: Collection of Scientific Reports) (Irkutsk: Izd. Irkutsk. Gos. Univ., 1989) p. 132
119. K R Dixon, A D Rattray *Inorg. Chem.* **17** 1099 (1978)
120. A G Ginzburg, A A Bagatur'yants *Metalloorg. Khim.* **2** 249 (1989)
121. M N Vargaftik, V P Zagorodnikov, I I Moiseev *Kinet. Katal.* **22** 951 (1981)
122. I P Stolyarov, M N Vargaftik, O M Nefedov, I I Moiseev *Kinet. Katal.* **23** 376 (1982)
123. I P Stolyarov, M N Vargaftik, O M Nefedov, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1455 (1983)
124. M N Vargaftik, V P Zagorodnikov, I P Stolyarov, D I Kochubei, V M Nekipelov, V M Mastikhin, V D Chinakov, K I Zamaraev, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2381 (1985)
125. V P Zagorodnikov, T S Khodashova, M N Vargaftik, M A Porai-Koshits, I I Moiseev *Koord. Khim.* **11** 95 (1985)
126. V P Zagorodnikov, S B Katser, M N Vargaftik, M A Porai-Koshits, I I Moiseev *Koord. Khim.* **15** 1540 (1989)
127. M N Vargaftik, V P Zagorodnikov, I I Moiseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1209 (1983)
128. M N Vargaftik, V P Zagorodnikov, I P Stolyarov, V A Likholobov, A L Chuvilin, V I Zaikovskii, D I Kochubei, G I Timofeeva, K I Zamaraev, I I Moiseev *Dokl. Akad. Nauk SSSR* **284** 895 (1985)
129. M N Vargaftik, V P Zagorodnikov, I P Stolyarov, I I Moiseev, V A Likholobov, D I Kochubey, A L Chuvilin, V I Zaikovsky, K I Zamaraev, G I Timofeeva *J. Chem. Soc., Chem. Commun.* 937 (1985)
130. M N Vargaftik, V P Zagorodnikov, I P Stolyarov, I I Moiseev, D I Kochubey, V A Likholobov, A L Chuvilin, K I Zamaraev *J. Mol. Catal.* 315 (1989)
131. M N Vargaftik, T A Stromnova, T S Khodashova, M A Porai-Koshits, I I Moiseev *Koord. Khim.* 7 132 (1981)
132. E G Mednikov, N K Eremenko, Yu L Slovokhotov, Yu T Struchkov *J. Chem. Soc., Chem. Commun.* 218 (1987)
133. G Schmid, R Pfeil, R Boese, F Bandermann, S Meyer, G H M Calis, J W A van der Velden *Chem. Ber.* **114** 3634 (1981)
134. V P Zagorodnikov, M N Vargaftik *Izv. Akad. Nauk SSSR, Ser. Khim.* 2652 (1985)
135. T I Bakunina, S V Zinchenko, V A Khutoryanskii, O V Burlakova, G V Ratovskii, F K Schmidt *Metalloorg. Khim.* **3** 426 (1990)
136. Yu N Novikov, N D Lapkina, M E Vol'pin *Kinet. Katal.* **17** 1537 (1976)
137. I I Moiseev, T A Stromnova, I N Busygina, N Yu Tihonova, N Yu Kozitsyna, A M Ellern, M Yu Antipin, Yu T Struchkov *J. Cluster Sci.* **3** 411 (1992)
138. N Yu Kozitsyna, A M Ellern, M Yu Antipin, Yu T Struchkov, I I Moiseev *Mendeleev Commun.* 92 (1991)