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Synthesis and characterization of platinum and palladium clusters with phosphide ligands *

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Abstract

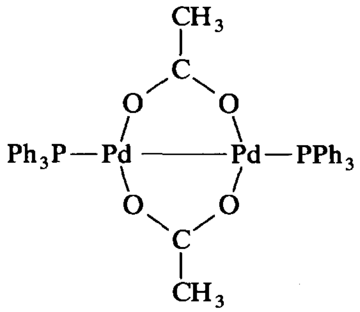
Clusters of composition $[Pt(PPh_2)]_n$, $n = 6$–10, have been synthesized by reduction of a series of Pt^{II} complexes $[(PPh_3)Pt(OAc)G]_m$ ($G = (OAc)_2 \cdot PdC_3H_5$, $m = 1$; $G = Cl$, OAc, $(OAc)_2Ag$, $m = 2$) with H_2, HCOOH and Na–amalgam. A hydridophosphide Pd^{II} complex $[Pd_2(PPh_2)H_x]_n$ was obtained in an analogous manner by reduction of $[(PPh_3)Pd(OAc)_2]_2$ with HCOOH. Additionally a complex with diphenylphosphonic acid as a ligand $[Pd(\mu\text{-}O_2PPh_2)(C_6H_5)(PPh_3)]_2$ was obtained and characterized with X-ray data. The formation of O_2PPh_2 anion under strictly anaerobic reductive conditions implies the transfer of an O atom from the carboxylic ligand to the P atom of the phosphorus-containing ligand. Cleavage of the C–Ph bond seems to be a common process for the reductive reactions of both Pd and Pt phosphine complexes. Phosphide clusters of compositions $[Pt(PPh_2)]_n$ and $[Pd_2(PPh_2)H_x]_n$ were characterized with IR, SAXS, EXAFS and NMR data and molecular mass measurements.

1. Introduction

A variety of diarylphosphide platinum and palladium complexes has been synthesized by thermal decomposition of the metal complexes with triarylphosphines, or isolated from catalytic hydrogenation and hydroformylation experiments [1]. This paper has been prompted by our interest in cluster synthesis via reductive reactions of compounds of platinum group metals [2,3].

Reactions of palladium(II) complexes in the presence of Phen or PR_3 ligands with a Pd:PR_3(Phen) ratio greater than 1 with different reductants such as H_2, Na/Hg were found to give rise to a series of clusters containing a Pd–Pd bond [2,3]. Reaction of the complex $[(PPh_3)Pd(OAc)_2]_2$ with H_2 resulted in a dinuclear cluster of composition $[(PPh_3)Pd(OAc)]_2$ [3].

$[(PPh_3)Pd(OAc)_2]_2 \xrightarrow{H_2}$



(1)

To compare the behaviour of similar Pt^{II} complexes with that of the palladium(II) complex we have studied reductive reactions of triphenylphosphine-containing Pt^{II} complexes with H_2, HCOOH and Na–amalgam.

The starting compound for synthesis of $[(PPh_3)Pd(OAc)]_2$ was the dinuclear palladium complex $[(PPh_3)Pd(OAc)_2]$ [3]. Unlike Pd^{II} dinuclear acetate com-

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plexes, analogous complexes of Pt^{II} with PPh_3 have not been synthesized to date. Complex $[(PPh_3)Pt(OAc)_2]_2$ cannot be obtained by the direct reaction of $Pt(OAc)_2$ with PPh_3 [4]. As the first step we therefore studied different ways to synthesize the complex $[(PPh_3)Pt(OAc)_2]_2$.

2. Experimental Section

Chemically pure solvents were purified by standard procedures [5]. $Re_2(OAc)_2X_4$ (X = Cl, Br) was obtained according to ref. 6. $[\pi\text{-}C_3H_5PdCl]_2$ was obtained according to ref. 7. *cis,trans*-$[(PPh_3)PtCl_2]_2$ (**1**) was obtained according to ref. 8.

Elemental analysis was performed using a C,H,N-analyzer (Carlo Erba). Molecular weights of the complexes were measured with a vapour pressure osmometer, IR spectra with a Specord IR-75 spectrometer and NMR spectra with a Bruker WP-200 instrument. Chromatographic analysis was conducted using a Tsvet chromatograph.

2.1. Small-angle X-ray scattering (SAXS)

SAXS data were obtained by a standard procedure [9] with the use of the small-angle X-ray chamber KRM-1.

2.2. Extended X-ray absorption fine structure (EXAFS)

EXAFS spectra of the K-edge of palladium (24.6 keV) and of the L_{III}-edge of Pt (11.56 keV) X-ray absorption of clusters **8** and **15** were obtained at the EXAFS Station of the Siberian Centre of Synchrotron Radiation, Novosibirsk [10a]. The VEPP-3 storage ring with electron beam energy of 2 GeV and average stored current of 50 mA was used as the radiation source. The energy of the synchrotron radiation quanta was monitored with the help of the two-crystal cut-off Si(111) monochromator. The higher harmonics ($3h\nu$ etc.) were not rejected. X-Ray absorption spectra were recorded in the transmission mode using two ionization chambers, *i.e.* those for monitoring and for full absorption. The monitoring chamber contained 0.5 atm Ar and was located in front of the sample, while the full absorption chamber contained 1 atm Xe and was behind the sample. Samples of clusters **8** and **15** were prepared in the form of pellets, which exhibited at the Pd or Pt K-edge a jump of absorption $\Delta\mu$, $x = 0.8$. The pellets consisted of *ca.* 90% of the cluster material plus *ca.* 10% of Apieson-L hydrocarbon binder. Pd and Pt foils with a known X-ray absorption edge energy, distances between atoms and coordination numbers were used as reference samples to calibrate the position E_0 of the absorption edge for the clusters, as well as the phase corrections δ for Pd–Pd distances for a given interval of k values. Solid $Pd(PPh_3)_4$ was used to calibrate the phase correction δ for Pt(Pd)–P distance and determination of coordination numbers.

For each sample X-ray absorption data were analyzed in the form of $k^2\chi(\mathbf{k})$, where $\chi(\mathbf{k})$ is the oscillating part of the absorption coefficient μ, for interval of wavenumbers $k = 2.5\text{–}12.0$ Å^{-1}. The background was removed by extrapolating absorption in the pre-edge region onto the EXAFS region in the form of Vectoreen's polynomial. Three cubic splines were used to construct the smooth part of μ. The inflection point of the edge of the X-ray absorption spectrum was used as the initial point ($k = 0$) of the EXAFS spectrum. The RDA function was calculated from the EXAFS spectra in $k^2\chi(\mathbf{k})$ form using Fourier analysis [10a]. An alternative fitting procedure [10b], was also used to determine interatomic distances and coordination numbers from the EXAFS spectra.

Theoretical parameters from McKale *et al.* [10c] were used for these procedures.

2.3. Synthesis of $[(PPh_3)Pt(OAc)_3Ag]_2$ (3)

The suspension of *trans*-$[(PPh_3)PtCl_2]_2$ (**1**) (0.1 g, 0.1 mmol) with AgOAc (0.16 g, 0.8 mmol) in HOAc solution (10 ml) was stirred under Ar at 20–40° for 1 h. The colourless complex **3** was isolated from the reaction mixture after removal of HOAc and recrystallization of the residue from a large amount of hot benzene. The benzene solution was evaporated *in vacuo*. The yield was 70% based on Pt. A single crystal was grown by slow crystallization in benzene/hexane or chloroform/hexane solutions. Complex **3** is soluble in $CHCl_3$, CH_2Cl_2, HOAc, DMFA, and hot C_6H_6. It decomposes on exposure to light in the solid state, but faster in solution, and is stable for a few months in darkness under Ar. IR: ν(COO) 1585, 1540, 1440 cm^{-1}. ^1H NMR spectra (CH_2Cl_2): δ 1.57 (s, 6H, μ^2-OAc), 2.06 (s, 3H, μ^3-OAc), 7.27 (m, 15H, Ph). ^{31}P NMR spectra (rel. to H_3PO_4): 6.06(J(Pt–P), Hz 4652).

2.4. Synthesis of triphenylphosphine acetate complexes

$[(PPh_3)PtClOAc]_2$ was obtained via the reaction of *cis*-$[(PPh_3)PtCl_2]_2$ with AgOAc in $CHCl_3$ solution according to ref. 11.

$[(PPh_3)Pt(OAc)_2]_2$ was obtained via the reaction of $[(PPh_3)Pt(OAc)_3Ag]_2$ with $Re_2(OAc)_2X_4$ (X = Cl, Br) in benzene solution according to ref. 11.

$\pi\text{-}C_3H_5Pd(OAc)_3Pt(PPh_3)$ was obtained via the reaction of $[(PPh_3)Pt(OAc)_3Ag]_2$ with $[\pi\text{-}C_3H_5PdCl]_2$ in $CHCl_3$ solution according to ref. 12.

2.5. Synthesis of $[Pt(PPh_2)]_n$ (8)

Reduction reactions were carried out in a thermostatic reaction vessel with a gas burette. The yellowgreen complex $[(PPh_3)Pt(OAc)_2]_2$ (0.1 g, 8.7×10^{-5} mol) was placed in the reaction vessel which was pumped out and refilled with argon. 5 ml of deoxygenated formic acid was then added. The reaction mixture was stirred until completion of benzene formation (GLC, 20 h, 20–25°C). The colour changed to dark-brown. The volume of the gas evolved was measured with a gas burette and its composition determined by gas chromatography. Formic acid was evaporated *in vacuo*. The solid residue was dissolved in dry benzene and the solution filtered. On adding hexane to the benzene solution, the dark brown complex **8** was precipitated. The complex was washed with dry diethyl ether then with hexane, and dried *in vacuo*. Yield: 85% based on Pt. Anal. Found: C 37.1; H 3.0; Cl 1.0; P 9.2; Pt 51.5. $C_{12}H_{10}PtP$ calc.: C 37.9; H 2.6; P 8.16; Pt 51.31%. IR spectrum (ν, cm^{-1}): 1470, 1410, 1090, 730, 700, 550, 520. ^1H NMR: δ 7.5 (multiplet, Ph); ^{31}P NMR (-90°C): (δ, H_3PO_4) broad line in interval $+48$ to $+17$ ppm. Molecular weight (C_6H_6): 3783 (calc.: for $n = 10$; 3800).

2.6. Synthesis of $[Pd_2(PPh_2)H_x]_n$ (15) and $[Pd(\mu\text{-}O_2PPh_2)(C_6H_5)(PPh_3)]_2$ (16)

The complex $[(PPh_3)Pd(OAc)_2]_2$ (0.1 g, 0.13 mmol) was placed in a glass container which was pumped out and filled with argon. 5 ml of deoxygenated HCOOH was then added. The solution was stirred until evolution of gases (CO_2, H_2) was complete (12 h at 20–25°C). Complex $[Pd_2(PPh_2)H_x]_n$ (**15**) was isolated from the reaction mixture after removal of HCOOH, dissolution of residue in benzene followed by precipitation with hexane and washing with ether. In addition, the light-brown complex $[Pd(\mu\text{-}O_2PPh_2)(C_6H_5)(PPh_3)]_2$ (**16**) was obtained after slow crystallization from the united mother solutions in 8–10% yield based on Pd. The structure of the complex **16** was resolved by X-ray data [13]. Yield of $[Pd_2(PPh_2)H_x]_n$: 60–70% based on Pd. Anal. Found: C 35.8; H 9.5; P 8.1; Pd 54.1. $C_{12}H_{10}Pd_2P$ (neglecting H_x) calc.: C 36.3; H 2.5; P 7.8; Pd 53.4%. IR spectrum (ν, cm^{-1}): 1485, 1420, 1100, 750, 720, 550, 520. ^1H NMR: δ 7.5 (multiplet, Ph), $-9{,}5$ (wide line, H); ^{31}P NMR (-90°C): (δ, H_3PO_4) broad line in interval $+48$ to $+17$ ppm. The complex **15** decomposes on exposure to air and is stable under argon.

2.7. Reduction of platinum complexes with sodium amalgam

The complex (1 mmol) was placed with sodium amalgam (22 g) in a 50 ml glass container which was pumped out and filled with argon. 30 ml of deoxygenated solvent (THF or benzene) was then added. The suspension was stirred (48 h at 20–25°C) until a dark-brown solution formed. The reaction mixture was filtered. The solvent was evaporated in vacuum to half of its volume. After addition of hexane (30 ml) to the mixture the precipitation of dark-brown phosphide complexes was observed. The complexes were purified by dissolution in benzene followed by precipitation with addition of hexane.

2.8. Reduction of platinum complexes with dihydrogen

Reduction was carried out in a glass double-jacketed reaction vessel equipped with a gas burette. The solution of the complex (0.1–0.2 mmol) in acetic acid (5–10 ml) was placed in the reaction vessel which was pumped out and filled with dihydrogen. The solution was stirred under hydrogen ($P = 1$ atm, 20–25°C) until completion of hydrogen absorption.

2.9. Synthesis of $[Pt_2(PPh_3)(PPh_2)(OAc)]_3$ (6)

The complex **6** was obtained by reacting the complex $[(PPh_3)Pt(OAc)_3Ag]_2$ with dihydrogen. The complex **6** was isolated from the reaction mixture after removal of AcOH, dissolution of residue in benzene, and filtration followed by precipitation with hexane and washing the precipitate with ether. The yield was 80% based on Pt. Anal. Found: C 42.1; H 3.2; P 6.6; Pt 42.8. $C_{32}H_{28}Pt_3P_2$ calc.: C 42.9; H 3.1; P 6.9; Pt 43.5%. Molecular weight (C_6H_6): 2596, (calc.) 2688. IR: ν(COO) 1580, 1440 cm^{-1}. ^1H NMR spectra: $\delta(CDCl_3)$ 2.09. ^{31}P NMR spectra: (rel. to H_3PO_4) broad line in interval $+58$ to $+17$ ppm. TEM: narrow size distribution with single maximum at 5 Å.

3. Results and discussion

3.1. Synthesis of trans-$[(PPh_3)Pt(OAc)_2]_2$

The replacement of the chloride atom in *cis*-$[(PPh_3)PtCl_2]_2$ (**1**) [4] by an acetate group by reacting the complex with AgOAc in HOAc solution or in a chlorinated solvent (CH_2Cl_2, $CHCl_3$, $C_2H_2Cl_4$) at ambient temperature was found to give complex $[(PPh_3)PtClOAc]_2$ (**2**) as the main product (eqn. (2)).

$$\underset{\mathbf{1}}{cis\text{-}[(PPh_3)PtCl_2]_2} + 2AgOAc \xrightarrow{H_2C_2Cl_4} \underset{\mathbf{2}}{[(PPh_3)PtCl(OAc)]_2} + 2AgCl \qquad (2)$$

According to IR and ^1H NMR data complex **3** was found, similarly to $[(Me_2PhP)PtCl(OAc)]_2$ [14], to contain two bridging acetate groups and terminal chloride ions.

In contrast to the *cis*-isomer **1**, *trans*-**1** reacts with AgOAc in HOAc solution (1 h at 20–40°C under Ar atmosphere) giving rise to $[(PPh_3)Pt(OAc)_3Ag]_2$ **3** as depicted by eqn. (3).

$$\underset{\mathbf{1}}{trans\text{-}[(PPh_3)PtCl_2]_2} + 6AgOAc \xrightarrow{HOAc} \underset{\mathbf{3}}{[(PPh_3)Pt(OAc)_3Ag]_2} + 4AgCl \quad (3)$$

In a mixture of a chlorinated solvent and acetic acid, under conditions when the *cis–trans* isomerization of initial compounds **1** was possible, a mixture of complexes **2** and **3** was obtained.

According to X-ray data [15], the molecular complex **3** consists of two symmetrically bonded binuclear fragments (Fig. 1) with the Pt–Ag distance of 2.898(2) Å. This short distance (compare with Pt–Ag 2.915 Å in $[Pt_3Ag(\mu\text{-}CO)_2(PPh_3)_5]ClO_4 \cdot 2H_2O$ [16] and 2.919, 2.927 Å in $[Pt_3Ag(O_3SCF_3)(\mu\text{-}CO)_3(PCy_3)_2$ (dppm)] [17]) cannot exclude the possibility of metal–metal interaction. Dimerization of $[(Ph_3P)Pt(\mu^2\text{-}OAc)_2(\mu^3\text{-}OAc)Ag]$ fragments is due to bonding between Pt and Ag atoms via the tri-coordinated acetate bridge. The mean Ag–Ag (a) distance of 3.797 Å excludes direct interaction between those metal atoms. The arrangement of O and P atoms in the coordination environment of Pt^{II} atoms is close to what is expected for ideal square-planar.

The Ag atom has an essentially distorted tetrahedral coordination and is displaced by 0.533 Å above the plane O(2), O(4a), O(6) of the nearest oxygen atoms of the bridging acetate ligands. The observed non-bonding distance O(4) ··· Ag to the fourth tetrahedral top is longer (2.530(9) Å) and may correspond to a weak interaction.

In attempts to remove the Ag^+ ion from the complex **3** we studied its reactions with different Cl^- donors. Complex **3** reacts with $(Et_3BuN)Cl$ forming complex $(Et_3BuN)[(PPh_3)Pt(OAc)_3]$ (see eqn. (4)).

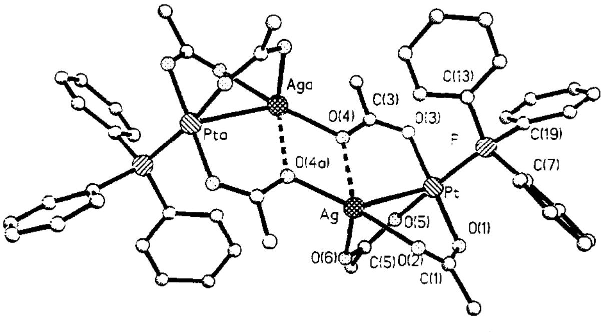


Fig. 1. Structure of $[(PPh_3)Pt(OAc)_3Ag]_2$ according to X-ray data.

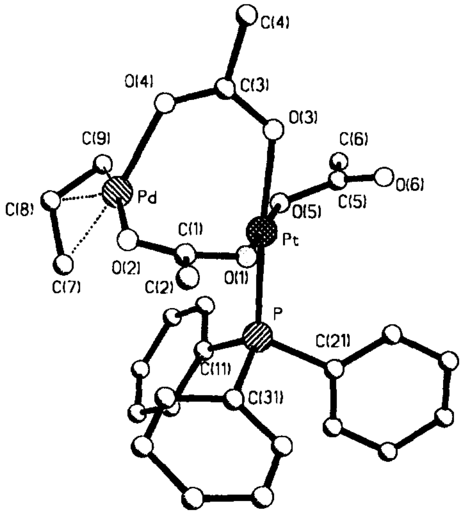


Fig. 2. Structure of $\pi\text{-}C_3H_5Pd(OAc)_3Pt(PPh_3)$ according to X-ray data.

$$[(PPh_3)Pt(OAc)_3Ag]_2 + 2(Et_3BuN)Cl \longrightarrow 2(Et_3BuN)[(PPh_3)Pt(OAc)_3] \quad (4)$$

Complex **3** on reacting with transition metal chloro compounds readily yields heteronuclear complexes retaining the initial coordination of the Pt atom. Thus, the reaction of the complex **3** with $[\pi\text{-}C_3H_5PdCl]_2$ was found to give rise to the Pd,Pt- complex $\pi\text{-}C_3H_5Pd(OAc)_3Pt(PPh_3)$ (**4**) [12], as shown by eqn. (5).

$$[\pi\text{-}C_3H_5PdCl]_2 + \underset{\mathbf{3}}{2[(PPh_3)Pt(OAc)_3Ag]_2} \longrightarrow \underset{\mathbf{4}}{2\pi\text{-}C_3H_5Pd(OAc)_3Pt(PPh_3)} + 2AgCl \quad (5)$$

According to X-ray data for complex **4**, Pt and Pd atoms are bridged by two OAc^- groups and the third OAc^- group is terminally coordinated to the Pt atom (Fig. 2). The Pt ··· Pd distance is greater than the sum of covalent radii of Pt and Pd atoms (2.89 Å). As a result of additional coordination by the non-bonded O atom of the terminal AcO^- group and Pd atom, the planar-square coordination of the Pt atom (two bridging OAc^- group in the *cis*-position, P atom of PPh_3 and terminal OAc^- group) lead to tetragonal-bipyramidal (distorted octahedral).

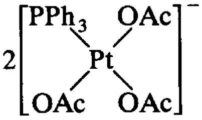
As candidates for halogen atom donors we also chose rhenium halogenides. We expected that in the reactions with rhenium compounds the acetate ligand can be abstracted because of the affinity of rhenium towards the oxygen atom. In fact the reaction of **3** with rhenium(I) complex $Re(CO)_5Br$ gave rise to diphosphinediacetate platinum(II) complex and metallic silver (eqn. (6)):

$$[(PPh_3)Pt(OAc)_3Ag]_2 + PPh_3 \xrightarrow{Re(CO)_5Br} (PPh_3)_2Pt(OAc)_2 + Ag^0 \qquad (6)$$

However, by reacting complex **3** with the rhenium(III) complex the desired complex $[(PPh_3)Pt(OAc)_2]_2$ (**5**) was synthesized finally (see eqn. (7)) [11].

$$\underset{\mathbf{3}}{[(PPh_3)Pt(OAc)_3Ag]_2} \xrightarrow{Re_2(OAc)_2Cl_4\cdot 2H_2O} \underset{\mathbf{5}}{[(PPh_3)Pt(OAc)_2]_2} + AgCl(Ag^0) \qquad (7)$$

In this reaction the rhenium complex *cis*-$Re_2(OAc)_2X_4 \cdot 2H_2O$ acts as a donor of halogen to the bound silver atom (see for example eqns. (7b) and (7c) and as an acetate acceptor to liberate the fragment $(PPh_3)Pt(OAc)_2$ which dimerizes to give the complex $[(PPh_3)Pt(OAc)_2]_2$ (see, for example, eqn. (7a)).



$$2\left[\begin{array}{c} PPh_3 \quad OAc \\ Pt \\ OAc \quad OAc \end{array}\right]^- \xrightarrow[-2\,OAc^-]{} [(PPh_3)Pt(OAc)_2]_2 \qquad (7a)$$

$$n Re_2(OAc)_2Cl_4 \xrightarrow{+OAc^-} [Re(OAc)_lCl_m]_{2n} + Cl^- \quad (l > 1,\ m < 2) \qquad (7b)$$

$$Ag^+ \xrightarrow{+Cl^-} AgCl \qquad (7c)$$

According to X-ray data for complex **5** [11], the Pt atoms are bridged by two acetate groups in the *cis*-position (Fig. 3). The environment of each Pt atom consists of three O atoms of OAc-groups and one P atom of triphenylphosphine. The coordination of Pt atoms is close to ideal square-planar. Both Pt atoms are distorted towards each other by 0.11 Å. The Pt ··· Pt distance (3.10 Å) is more than the sum of covalent radii of two Pt atoms. The nonbonded O atom of the terminal OAc^- group was shown to interact with Pt atom (Pt–O4 3.03 Å) in a pseudochelated manner.

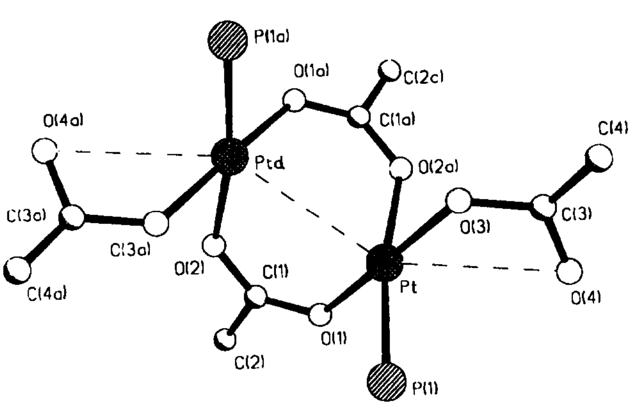


Fig. 3. Structure of $[(PPh_3)Pt(OAc)_2]_2$ according to X-ray data.

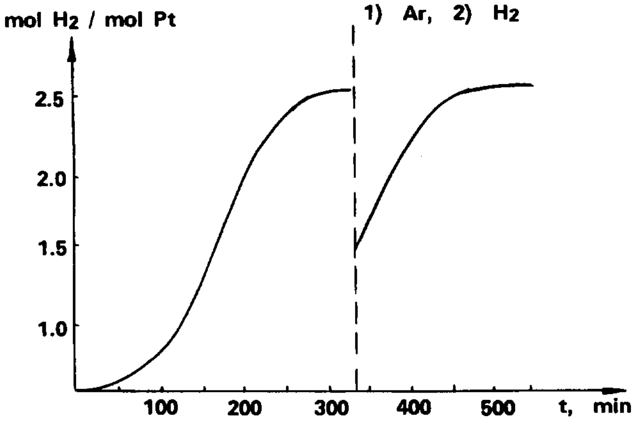


Fig. 4. Absorption of dihydrogen for $[(PPh_3)Pt(OAc)_3Ag]_2 + H_2$.

3.2. Reduction of platinum phosphine complexes

3.2.1. Reduction of Pt^{II} phosphine complexes with dihydrogen

Complex $[(PPh_3)Pt(OAc)_3Ag]_2$ has rather short Pt ··· Ag contacts. One might have expected the reduction of the complex to give compounds containing Pt–Ag bonds. However, the treatment of $[(PPh_3)Pt(OAc)_3Ag]_2$ in acetic acid solution gave rise to silver powder with formation of a silver mirror. A complex with both triphenylphosphine and diphenylphosphide ligands $[Pt_2(PPh_3)(PPh_2)(OAc)]_3$ (**6**) was isolated as the only platinum-containing product (eqn. (8)). The complex $[Pt_2(PPh_3)(PPh_2)(OAc)]_3$ was found to absorb dihydrogen reversibly (Fig. 4).

$$\underset{\mathbf{3}}{[(PPh_3)Pt(OAc)_3Ag]_2} \xrightarrow{H_2} 2\,Ag^0 + \underset{\mathbf{6}}{[Pt_2(PPh_3)(PPh_2)(OAc)]_3} \qquad (8)$$

$$[Pt_2(PPh_3)(PPh_2)(OAc)]_3 \underset{-H_2}{\overset{+H_2}{\rightleftharpoons}} \underset{\mathbf{7}}{[Pt_2(PPh_3)(PPh_2)(OAc)(H_2)_2]_3}$$

The complex **5** reacts with dihydrogen giving rise to the soluble product of composition $[(PPh_2)Pt]_n$ in good

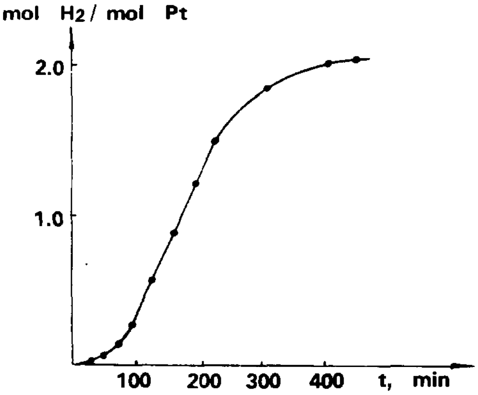


Fig. 5. Absorption of dihydrogen in $[(PPh_3)Pt(OAc)_2]_2/H_2$ system.

yield (*ca.* 85%) and the insoluble product $[(PPh)Pt]_m$ (*ca.* 5%) as depicted by eqn. (9).

$$\underset{\mathbf{5}}{[(PPh_3)Pt(OAc)_2]_2} \xrightarrow[-C_6H_6]{H_2} \underset{\mathbf{8}}{[(PPh_2)Pt]_n} + \underset{\mathbf{9}}{[(PPh)Pt]_m} \qquad (9)$$

More than 1 mole of H_2 of Pt was absorbed per mole (Fig. 5) and about 1 mole of benzene per mole of triphenylphosphine ligand was found by GLC. ^{31}P NMR spectrum of the solution of complex **8** in toluene showed a broad phosphorus band even at −90°C (Fig. 6).

It should be mentioned that the first step of the reduction of the analogous palladium complex $[(PPh_3)Pd(OAc)_2]_2$ has been found to give rise to the dinuclear complex formulated as μ^2-diacetato-bis(triphenylphosphine)dipalladium(I) [3]. A complex analogous to **8** together with palladium black were obtained by reacting of π-$C_3H_5Pd(OAc)_3Pt(PPh_3)$ with dihydrogen as depicted by eqn. (10).

$$\underset{\mathbf{4}}{(\eta^3\text{-}C_3H_5)Pd(OAc)_3Pt(PPh_3)} \xrightarrow[-C_6H_6]{H_2,\ HOAc} Pd^0 + \underset{\mathbf{8}}{[(PPh_2)Pt]_n} \qquad (10)$$

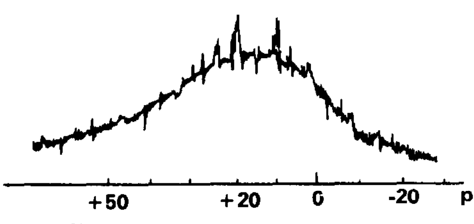


Fig. 6. ^{31}P NMR spectrum of **8**. Toluene solution at −90°C (rel. to H_3PO_4).

3.2.2. *Reduction of platinum phosphine complexes with sodium amalgam*

The dinuclear chlorine complex $[(PPh_3)PtCl_2]_2$ (**11**) does not react with dihydrogen under the same conditions. However, complex **11** was reduced readily with sodium amalgam in benzene solution at room temperature to give rise to a phosphide complex $[(PPh_2)PtCl]_n$ (eqn. (11)):

$$\underset{\mathbf{11}}{[(Ph_3P)PtCl_2]_2} \xrightarrow[-C_6H_6]{Na/Hg,\ C_6H_6} \underset{\mathbf{12}}{[(PPh_2)PtCl]_n} \qquad (11)$$

The molecular weight of complex **12** is in agreement with the conclusion about the polymeric nature of this compound with $n = 16$. The direction of reaction and the nature of the compounds formed were found to depend on the nature of the solvent. Thus, in contrast to the reaction in benzene solution (eqn. (11)), the reduction of the complex **11** proceeds in tetrahydrofuran (THF) solution more thoroughly forming a phosphide product $[(PPh_2)Pt]_n$ (**13**) (eqn. (12)):

$$\underset{\mathbf{11}}{[(Ph_3P)PtCl_2]_2} \xrightarrow[-C_6H_6]{Na/Hg\ (THF)} \underset{\mathbf{13}}{[(PPh_2)Pt]_n} \qquad (12)$$

The reactions (11) and (12) were found to result in elimination of 1 mole of benzene per mole of triphenylphosphine. Elemental analysis data for complex **13** coincide with those for complex **8**. However, molecular weight measurements showed the value of n for complex **13** to be 6 in contrast to complex **8** where $n = 8$. According to ESCA data, complex **13** contains Pt^I atoms ($Pt_{4f7/2}$ 72.1 eV).

Complex **8** was found to be formed in the reaction of $[(PPh_3)Pt(OAc)_2]_2$ with sodium amalgam (see eqn. (13)).

$$[(PPh_3)Pt(OAc)_2]_2 \xrightarrow[-C_6H_6]{Na/Hg\ (C_6H_6)} [(PPh_2)Pt]_n \qquad (13)$$

3.2.3. *Reduction of Pt^{II} and Pd^{II} complexes with formic acid*

The platinum(II) complex $[(PPh_3)Pt(OAc)_2]_2$ (**5**) reacts with formic acid (20°C, under an Ar atmosphere) without any additional solvent giving rise to a phosphide cluster with $n = 8$–10 (see eqn. (14)).

$$\underset{\mathbf{5}}{[(PPh_3)Pt(OAc)_2]_2} \xrightarrow{HCOOH} \underset{\mathbf{8}}{[(PPh_2)Pt]_n} \qquad (14)$$

GLC: CO_2, H_2, HOAc (2 mol/mol Pt),
C_6H_6 (1 mol/1 mol PPh_3)

After the complex dissolved in formic acid the full substitution of acetato ligands for formate anions was monitored by GLC for 45 min. Evolution of CO_2 and accumulation of C_6H_6 were observed with the formation of a dark brown solution $[(PPh_2)Pt]_n$ in formic acid.

Interaction of palladium complex $[(PPh_3)Pd(OAc)_2]_2$ (**14**) with HCOOH (20°C, under an Ar) was found to give the hydride complex $[Pd_2(PPh_2)H_x]_n$ (**15**) as the main product (60–70%, based on Pd) and to yield complex $[Pd(\mu\text{-}O_2PPh_2)(C_6H_5)(PPh_3)]_2$ (**16**) in 8–10% yield based on Pd (eqn. (15)) [10]:

$$\underset{\mathbf{14}}{[(PPh_3)Pd(OAc)_2]_2} \xrightarrow{HCOOH} \underset{\mathbf{15}}{[Pd_2(PPh_2)H_x]_n} + \underset{\mathbf{16}}{[Pd(\mu\text{-}O_2PPh_2)(C_6H_5)(PPh_3)]_2} \qquad (15)$$

GLC: CO_2, H_2, HOAc (2 mol/mol Pd),
C_6H_6 (0.9 mol/mol PPh_3)

The suggestion that the complex **15** contains hydride compounds is supported by ^1H NMR spectra (Fig. 7). A wide line with a maximum at $\delta = -9.5$ ppm, in the region typical for hydride complexes, was detected. Considerable broadening of the hydride signal may be explained, for instance by proposing that compound **15** is really a complex with molecular dihydrogen.

The reaction was found by GLC data to give rise to AcOH (2 mol per mole Pd) and C_6H_6 (0.9 mol per mol PPh_3). Evolution of CO_2 and H_2 was observed throughout the duration of the reaction, apparently as a result of decomposition of HCOOH catalyzed with Pd complexes (Fig. 8).

It is noteworthy that complex **16** was formed by an unusual redox reaction in which phosphorus(III) was oxidized to phosphorus(V) in spite of the presence of a strong reductant, formic acid. The only source of O atoms added to P atom on forming complex **16** under the reaction conditions (Ar atmosphere, reagents carefully purified from O_2) appeared to be a carboxylate ligand.

Let us consider some possible reactions which could lead to complexes **15** and **16**. P–C bond cleavage is a well known effect in the chemistry of tertiary phosphine complexes [1,3]. This reaction is usually assumed to involve a decrease of the oxidation state of the metal atom as an intermediate step. When complex **14** is converted to **16**, a Pd–Ph fragment was formed too, indicating formation of intermediate low-valent palladium complexes capable of insertion to the P–C bond of triphenylphosphine.

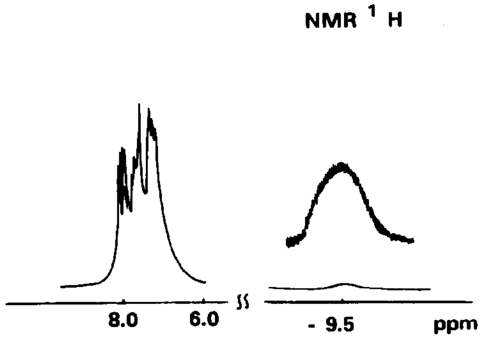


Fig. 7. ^1H NMR spectrum of **15** in benzene solution.

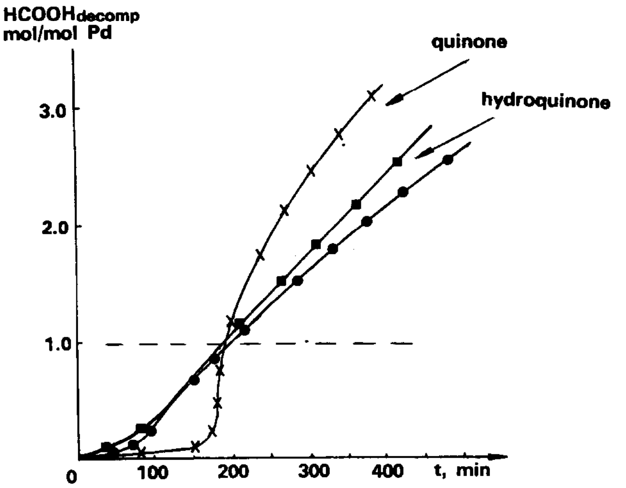
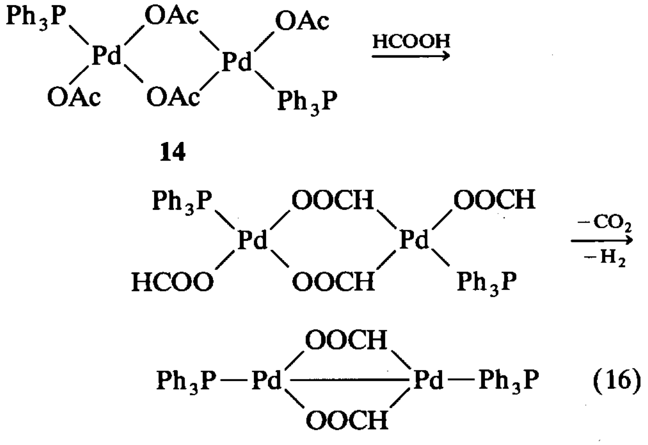


Fig. 8. Change in gas volume accompaning the reaction between complex $[(PPh_3)Pd(OAc)_2]_2$ and HCOOH.

Dissolution of complex **14** in HCOOH was found by GLC to be followed by immediate replacement of acetate ligands by formate ligands. Further decarboxylation of formate ligands and reduction of palladium(II) could give rise to the Pd^1 complex $(PPh_3)Pd(OOCH)_2$-$Pd(PPh_3)$ (**17**) as shown by eqn. (16):



14

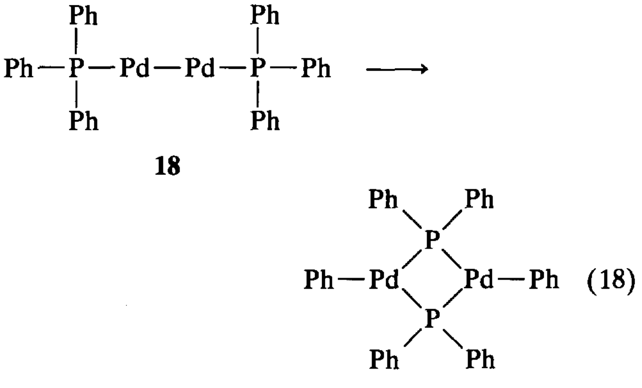
17

In contrast to the relatively stable $(Ph_3P)_2Pd_2(OAc)_2$ which was obtained by reaction of complex **1** with H_2 [3], complex **4** could undergo decarboxylation again to be transformed to the complex Pd^0 (**18**) as shown by eqn. (17):

$$\mathbf{17} \xrightarrow[-H_2]{-2CO_2} (Ph_3P)_2Pd_2 \qquad (17)$$

We have not found direct evidence that **18** was formed in our study. However, transformation of complex **14** to **15** and **16** could be easily understood in the framework of a mechanism including steps (1) and (2) with intermediate formation of complex **18**.

Thus, insertion of atom Pd into the P–C bond of complex **18** may given rise to both the diphenylphosphide group in complex **15** and the Pd–Ph bond in compound **16** as shown by eqn. (18):

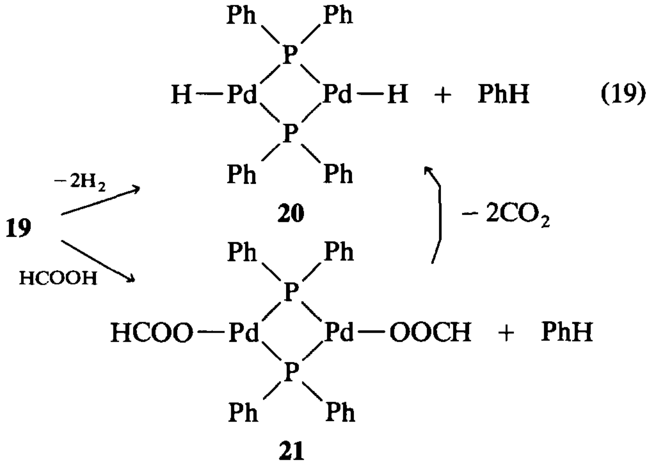


18

19

(18)

Reaction of the intermediate complex **19** with HCOOH or H_2, the last being formed by reactions (1) and (2), could be responsible for formation of benzene (yield *ca.* 1 mol/mol PPh_3) and the hydride complex (eqns. (19) and (20)):



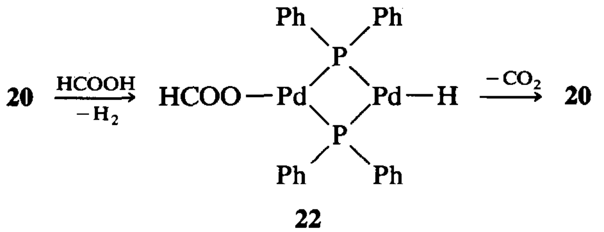
20

21

(19)

(20)

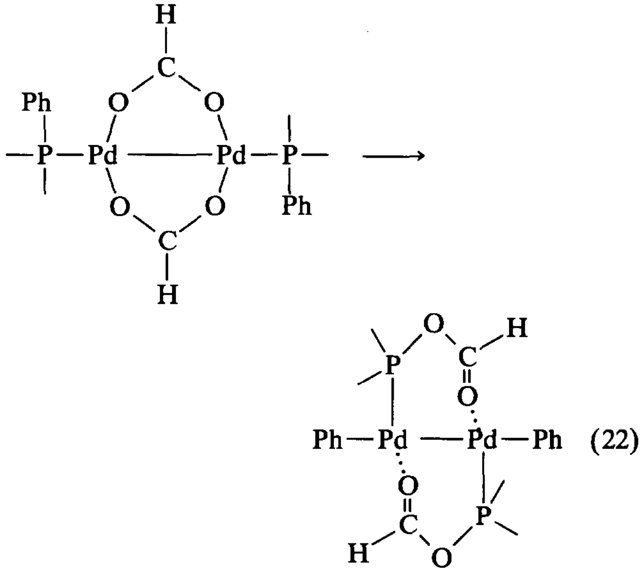
The compound **20**, being the source of complex **2**, is assumed to be the catalyst for decarboxylation of HCOOH, in accord with eqn. (21):



22

(21)

Thus, oxidative addition of phosphine ligand to Pd–Pd (eqn. (3)) followed by nucleophilic attack by the formate group on the phosphorus atom of the obtained diphenylphosphido group, could give rise to complex **23**, as generalized by eqn. (22).

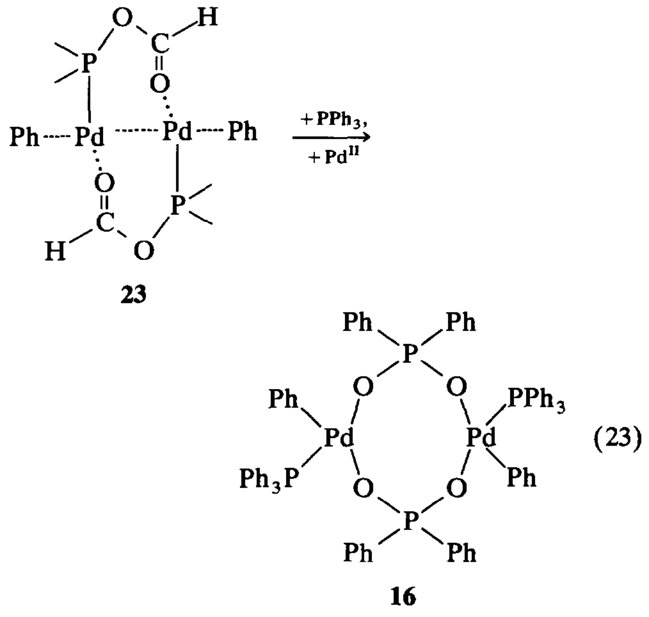


23

(22)

The new ligand, formoxydiphenylphosphine, is assumed to be formed at this step. This ligand seems to be more liable than PPh_3 to both nucleophilic attack by carboxylate ligand and to oxidation by initial Pd^{II} complexes to produce Ph_2POOH or the corresponding anion. Moreover, the additional molecule of triphenylphosphine released as a result of the transformation of complex **14** to **15**, was coordinated to Pd as shown by eqn. (23).

The structure of the centrosymmetrical dimeric complex **16** has been proved by X-ray diffraction [13] (Fig. 9). Atoms of Pd^{2+} are bridged by two diphenyl-



23

16

(23)

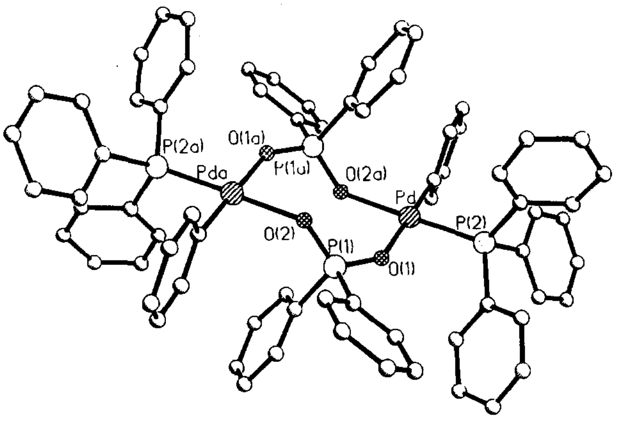


Fig. 9. Structure of $[Pd(\mu\text{-}O_2PPh_2)(C_6H_5)(PPh_3)]_2$ according to X-ray data.

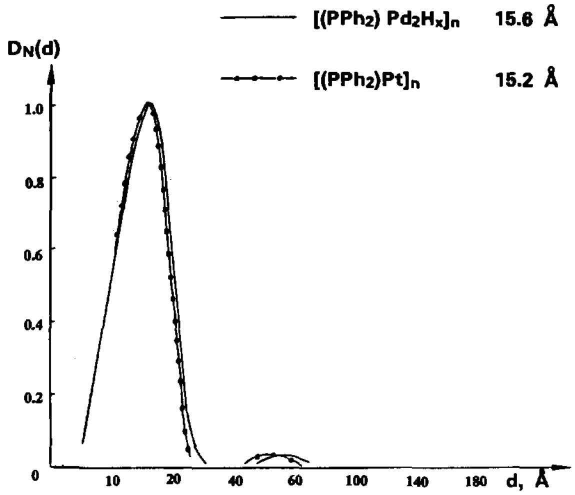


Fig. 10. Diameter distribution curves for the metal cores of clusters **8** and **15** according to SAXS data.

phosphinate groups. The mean Pd ··· Pd distance of 5.35 Å excludes the direct interaction between palladium atoms. Coordination of Pd-atoms is close to ideal plane-square. The central 8-membered cycle has a chair-like conformation.

The geometrical parameters of complex **16** are close to those of the structurally-related complex $[Pd_2(\mu\text{-}O_2CMe)_2(C_6H_5)_2(PPh_3)_2]$ with bridging acetate ligand [18]. However, the central cycle of the last-named complexes has a boat-like conformation, and the Pd ··· Pd distance is decreased to 3.079 Å. Bonds Pd–O(1) and Pd–O(2a) are translocated with respect to Ph- and Ph_3P-substituents and their lengths are almost equal (2.115(6) and 2.100(9) Å).

SAXS data showed that particles of the platinum phosphide complex $[(PPh_2)Pt]_{8-10}$ (**8**) contain an almost spherical metallic core 15.2 Å in diameter (Fig. 10). The particles of the palladium complex $[Pd_2(PPh_2)H_x]_n$ (**15**) are 15.6 Å in diameter.

Analysis of the experimental EXAFS data by the above mentioned procedure showed both the platinum (**8**) and palladium (**15**) complexes to contain in the first

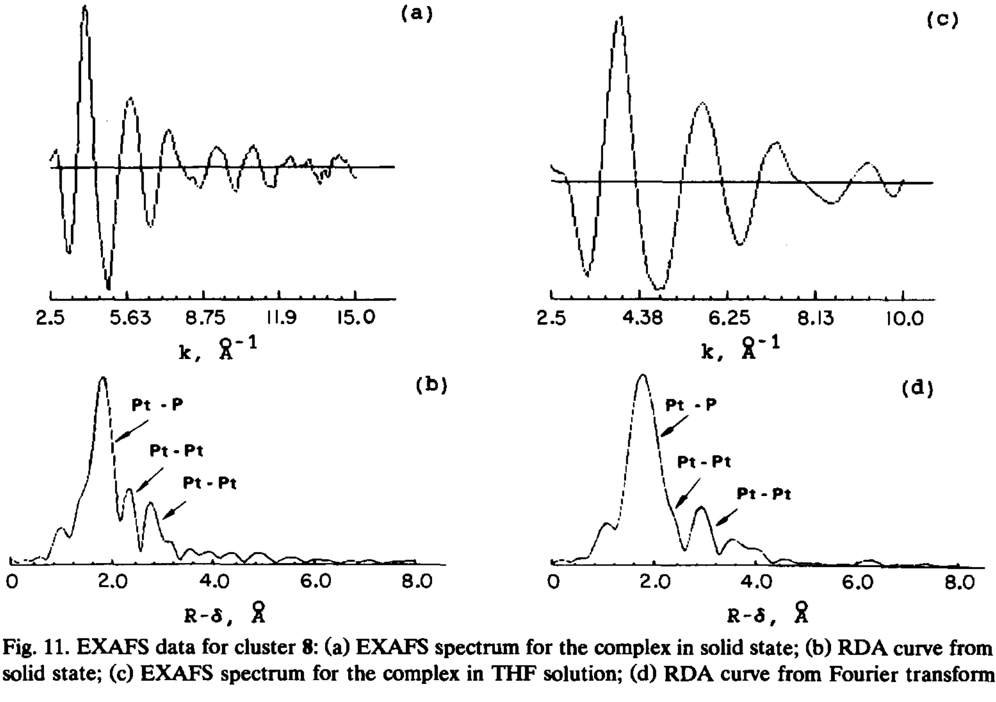


Fig. 11. EXAFS data for cluster **8**: (a) EXAFS spectrum for the complex in solid state; (b) RDA curve from Fourier transformation of EXAFS in solid state; (c) EXAFS spectrum for the complex in THF solution; (d) RDA curve from Fourier transformation of EXAFS in THF solution.

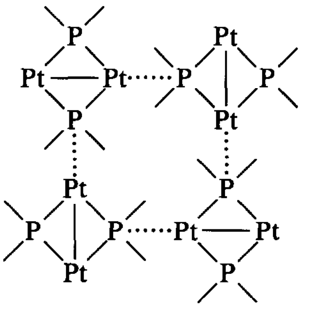
coordination sphere only phosphorus atom. (Fig. 11). The interatomic distances between Pt(Pd) and the phosphorus atoms are 2.26 Å, which is typical for Pt(Pd)–P distances in platinum and palladium complexes. Comparison with the spectral data for the reference compound $Pd(PPh_3)_4$ showed each platinum atom to be surrounded by 4 phosphorus atom (the coordination number $n(Pt/P)$ is 4). The corresponding figure for palladium atoms, $n(Pd/P)$ is 3. The next two maxima of the RDA curve for complex **8** correspond to distances of 2.46 and 2.90 Å. The atoms at these distances have coordination numbers $n(Pt/P)$ of 1.

EXAFS data of complex **8** in THF solution showed the distance 2.46 Å to disappear. The patterns corresponding to the distance of 2.90 Å and distance Pt–P observed for solid complex remained in the spectra for the dissolved complex. The difference observed between the EXAFS spectra for solid and dissolved complex **8** suggest the distance of 2.46 Å to correspond to a nonbridged Pt–Pt contact existing in the solid state and disappearing in THF solution. Hence the Pt–Pt distance of 2.90 Å should be attributed to the Ph_2P bridged Pt–Pt bond.

The only short Pd–Pd distance in the solid complex **15** is 2.78 Å and the coordination number $n(Pd/P)$ is 1 (Fig. 12).

A chain structure for complex **8** consisting of platinum atoms bonded with PPh_2 bridging groups does not fit the coordination number for Pt and P atoms that is observed experimentally. The molecular mass measurement suggest the complex **8** to consist of oligomers of type $[(PPh_2)Pt]_n$ where n is 6–10.

The intensities of peaks corresponding to the metal–light atom distances exceed those for the shortest metal–metal distances, suggesting the idea of triple-bridging phosphide ligands in these complexes as depicted by Scheme 1:



Scheme 1.

However a planar structure as figured out in Scheme 1 cannot be made consistent with the coordination num-

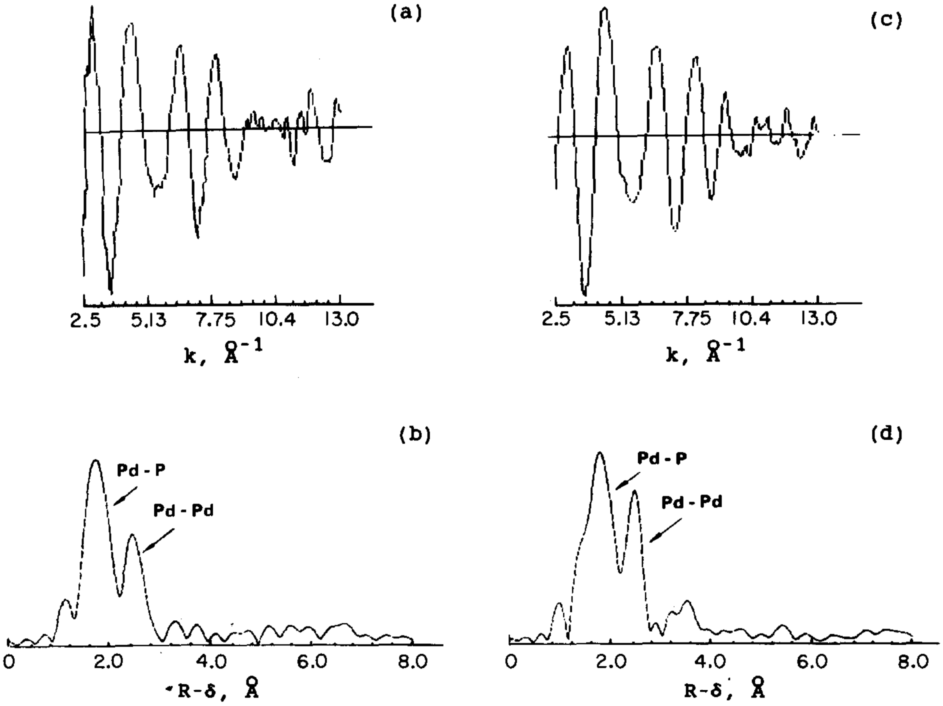


Fig. 12. EXAFS data for cluster **15**: (a) EXAFS spectrum for the complex in solid state; (b) RDA curve from Fourier transformation of EXAFS in solid state; (c) EXAFS spectrum for the complex in THF solution; (d) RDA curve from Fourier transformation of EXAFS in THF solution.

bers. The general pattern of the data available suggests complex **8** to involve a more non-planar structure.

Our study has therefore shown that the reactions of $[(PPh_3)Pt(OAc)_2]_2$ with different reductants result in formation of complexes of platinum (+1) with phosphide ligands of general formula $[Pt(PPh_2)]_n$ where the value of n can be slightly influenced by the nature of the reducing agent and solvent.

The Palladium complex $[(PPh_3)Pd(OAc)_2]_2$ revealed a similar behaviour the only exception being in the case of reaction with dihydrogen, where the first observed product was the triphenylphosphine acetate complex of palladium(+1) [2].

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