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Palladium carbonyl complexes †

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Contents

I.	Introduction	485
II.	Activation of carbon monoxide in the coordination sphere of the transition metal and the strength of the M – CO bond	486
III.	Palladium(0) carbonyl complexes	486
IV.	Palladium(+1) carbonyl complexes	493
V.	Palladium(+2) carbonyl complexes	502
VI.	Palladium carbonyl complexes containing the metal in fractional oxidation state	504
VII.	Palladium carbonyl hydride complexes	508
VIII.	Palladium carbonyl complexes in zeolites	509
IX.	Conclusion	509

Abstract. Data on palladium carbonyl complexes are described systematically and subjected to a critical analysis. The methods of synthesis and data on the structures and chemical properties of mono- and poly-nuclear carbonyl-containing palladium complexes in which the formal oxidation state of the metal varies from 0 to +2 are discussed. Virtually all the publications on this question up to 1997 are examined. The bibliography includes 241 references.

I. Introduction

The interest in the chemistry of palladium carbonyl complexes is to a large extent determined by the activity of palladium and its compounds in the catalysis of reactions involving CO. Such reactions include in the first place the catalytic oxidation of CO to CO_2, the synthesis of alkyl oxalates and alkyl carbonates, reactions involving the carbonylation of alcohols, saturated hydrocarbons, and aromatic nitro-compounds, *etc*.[1] The study of the properties and reactivities of carbon-containing palladium complexes is an essential stage in the investigation of the mechanisms of the reactions occurring with participation of palladium catalysts.[2] The carbonyl complexes of palladium and other platinum metals are of undoubted interest from the standpoint of the theory of coordination compounds, especially the nature of the bond in complex many centre systems of clusters containing the metal in the lowest oxidation states.

The susceptibility of $PdCl_2$ to reduce by carbon monoxide to the metal, *i.e*.

$$PdCl_2 + CO + H_2O = Pd + CO_2 + 2HCl$$

was observed more than 100 years ago.[3–5] Palladium carbonyl chlorides were among the first platinum metal carbonyl complexes synthesised.[6] However, owing to their higher reactivity compared with other platinum metal carbonyls, they remained for a long time represented by a few poorly characterised compounds. The available information about their structures and reactivities was based solely on indirect data (mainly by analogy with compounds of other platinum metals).

Data on the chemistry of palladium carbonyl complexes have been partly surveyed in a monograph[7] in which none of the compounds of this class have been reliably characterised. A review[8] presents the structural characteristics of two palladium carbonyl complexes — $[Pd(dam)Cl]_2CO$,[9,10] where dam = bis(diphenylarsino)methane, and $Pd_4(CO)_4(OAc)_4$.[11,12] Since the end of the 1970s, the number of studies on palladium carbonyls has increased sharply.

The classification of the compounds constituting the subject of the present review is based on the formal oxidation state (FOS) of palladium. The formal oxidation state of the metal atom in a complex is defined as the average charge of the metal atoms which they possess after the removal of the ligands.[13,14] It is assumed that in the leaving ligands (for example, such as H^-, Cl^-, O^{2-}, OH^-, NH^{2-}, NR_2^-, NR^{2-}, PR^{2-}, $SnCl_3^-$, and CH_3^-) the electron shell of the atom linked to the metal corresponds to the shell of the nearest inert gas atom; the ligands are removed in the form of neutral molecules (CO, NO, N_2, CO_2, C_2H_2, C_2H_4, *etc*). As regards certain π-linked organic groups (allyl C_3H_5, cyclopentadienyl C_5H_5), they are regarded as anions, like the σ-linked $C_3H_5^-$ and $C_5H_5^-$ groups.

Mainly mononuclear compounds are considered in classical coordination chemistry. The stable oxidation states 0 and +2 are attributed to palladium. However, the study of polynuclear, mainly cluster, compounds has shown that many of them have an oxidation state of +1; there are also compounds in which the formal charge per metal atom is nonintegral. Palladium carbonyl hydride complexes, for which the exact stoichiometry of the polyhydrides can be established in by no means all cases which precludes in its turn the determination of the FOS of the metal, constitute a separate group. A separate Section has been devoted to the palladium carbonyls isolated in zeolite cells, which may function as polyanions.

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A systematic treatment of heteronuclear, palladium-containing complexes in accordance with the above principles is in many cases difficult. The FOS of palladium can be comparatively readily inferred, provided that the structure of the heterometal-containing species forming part of the complex remains unchanged on formation of the compound.

For example, the reaction[15,16] of the benzonitrilepalladium(+2) complex $PdCl_2(NCPh)_2$ with $Na[Co(CO)_4]$ affords, after the substitution of Cl^- by $[Co(CO)_4]^-$, the trinuclear cluster $Pd[Co(CO)_4]_2(NCPh)_2$, in which the palladium atom is believed to retain a FOS of +2. However, on interaction of this cluster with dppm [dppm = bis(diphenylphosphino)methane], which leads to $PdCo_2(CO)_5(\mu\text{-dppm})_2$, not only are the benzonitrile ligands displaced but also three carbonyl groups are lost by the two anionic carbonylmetallates $[Co(CO_4]^-$. The CO-containing complexes formed ultimately have to analogues in classical coordination chemistry and this hinders the overall classification.

The present review deals with individual heteronuclear palladium-containing complexes, the assignment of which to a particular Section of the review is not open to doubt.

Since the aim of the present review is the analysis of the methods of synthesis and the characteristics of the structures and reactivities of molecular palladium complexes with carbonyl ligands, we shall deal only briefly with data on the palladium carbonyls formed on the surface of oxide carriers.

II. Activation of carbon monoxide in the coordination sphere of the transition metal and the strength of the M – CO bond

In the complexes of transition metals carbon monoxide effectively stabilises their lowest oxidation states. The carbonyl complexes of each metal from the first series of transition elements have been well characterised.[17] The composition of the compounds obeys the '18 electron' rule, which predicts monomeric compounds for Group IV metals, for example, $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$. The metals in odd Groups form paramagnetic $[V(CO)_6]$ or dimeric $[Mn_2(CO)_{10}$ or $Co_2(CO)_8]$ carbonyls. Mononuclear complexes are not very characteristic of transition metals in the second and third series. These metals afford preferentially compounds in which the number of metal atoms is from 2 or 3 to several hundreds.[18–21] From a formal point of view, features, structure and chemical properties) common to mononuclear carbonyls and a metallic surface coated by adsorbed CO molecules are characteristic of these clusters.[22]

A considerable number of communications (see, for example, Refs 23–27) have been devoted to the question of the stability of monomeric transition metal, especially palladium, carbonyls. It has been established on the basis of quantum-chemical calculations that, among the transition metal carbonyls $M(CO)_6$ (M = Cr, Mo, W), $M(CO)_5$ (M = Fe, Ru, Os), and $M(CO)_4$ (M = Ni, Pd, Pt), the metal–carbonyl bond energy and the dissociation energy of the first carbonyl ligand are a minimum for $Pd(CO)_4$. Calculations led to the conclusion that the π-back-donation from the ligand to the metal makes a much greater contribution in the stable $M(CO)_m$ systems than the σ-donor bond.

Thus the results of quantum-chemical calculations have shown the palladium carbonyls should have a minimum thermal stability and a maximum kinetic lability among transition metal carbonyls. These properties of the Pd–CO bond have probably in fact been responsible for the activity of palladium and its compounds in the catalysis of processes occurring with participation of carbon monoxide. However, the same properties have apparently 'inhibited' the development of the chemistry of palladium carbonyl complexes compared with other transition metal complexes.

The catalytic activation of carbon monoxide entails a change in the molecular orbitals of this ligand due to coordination to the metal atom. Carbon monoxide is a weak σ-donor ligand, but it can bind fairly strongly to the metal atom. The overall mechanism of the binding of carbon monoxide to a metal atom is presented in Fig. 1.

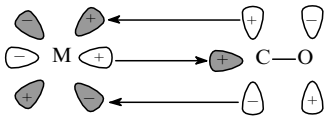


Figure 1. Schematic illustration of the bonds between carbon monoxide and a metal atom.

According to this scheme, apart from the ligand–metal interaction determined by the σ-donor properties of the ligand, the back-donation from the occupied *d* orbitals of the metal to the occupied antibonding π orbitals of the ligand takes place. Evidently, these two bonding modes should lead to opposite effects in the resulting transfer of electron density between the metal and the ligand.[28] Until recently the view that the π-acceptor properties of the ligand predominate in the formation of the metal–carbonyl bond was dominant. This was used to account for the weakening of the C–O bond in the carbonyl ligand itself, observed on coordination of CO to metals in the lowest oxidation states, and hence for the appreciable decrease in the ν_{CO} stretching vibrational frequencies in the IR spectra of the compounds.

However, on coordination of CO to metals in high oxidation states, for example on formation of Pd(+2) carbonyls, the predominance of the σ-donor properties of the ligand over their π-acceptor properties was noted, which leads in its turn to an increase in ν_{CO} to values equal to and even exceeding the stretching vibrational frequencies of CO in free carbon monoxide.[29]

III. Palladium(0) carbonyl complexes

All the Pd(0) complexes described hitherto have been described by convention in two groups — binary carbonyls (compounds containing only CO molecules as the ligands) and complexes with additional stabilising ligands (as a rule N- or P-donor ligands).

1. The binary carbonyls

The binary carbonyls are characteristic of many Group VIII metals and are readily formed even at room temperature when the metal interacts with carbon monoxide. In contrast to these metals, palladium does not form binary carbonyls on direct interaction with CO at room or elevated temperature.

The binary palladium carbonyls began to be synthesised simultaneously by two groups of investigators.[30–34] The method involving the joint condensation of metal vapour and CO at 4.2–27 K with isolation of the carbonyl in a crystalline argon or CO matrix was employed. At 4.2–10 K and for a CO content in the gas phase ranging from 100% to 10%, $Pd(CO)_4$ was obtained. On raising the temperature and on reducing the partial pressure of CO, the formation of $Pd(CO)_3$, $Pd(CO)_2$, and Pd(CO) was observed.

All the conclusions concerning the structure of the binary palladium carbonyls are based on the results of the study of their vibrational spectra. Analysis of the Raman and IR spectra of carbonyl molecules containing isotope-substituted CO fragments ($^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$) showed that the $Pd(CO)_4$ molecule is tetrahedral like $Ni(CO)_4$ (T_d symmetry).[33] The frequency of the stretching vibration active in these spectra (the T_2 band) is 2066 cm^{-1}; the frequency of the A_1 vibration, active in the Raman spectrum, is 2122 cm^{-1} and the force constant k_{CO} = 17.48 mdyn $Å^{-1}$ in the Cotton–Kraihanzel approximation. It is of interest that the force constant k_{CO} for the more stable $Ni(CO)_4$ molecule is virtually the same (17.23 mdyn $Å^{-1}$). The M–C stretching vibrational frequency and force constant are more sensitive to the nature of the central atom. The ν_{M-C} = 258 cm^{-1} for palladium tetracarbonyl, whereas the

corresponding band has been observed at 435 cm^{-1} for nickel tetracarbonyl.[34]

Spectroscopic data have led to the conclusion that the $Pd(CO)_3$ molecule is planar (D_{3h} symmetry), while the $Pd(CO)_2$ (D_h symmetry) and Pd(CO) (C_v symmetry) molecules are linear. The frequencies of the IR-active vibration are respectively 2060, 2044, and 2050 cm^{-1} for these molecules, but the force constant k_{CO} varies from 17.35 to 16.96 mdyn $Å^{-1}$.[32] The decrease in the force constant is correlated with the decrease in the stability of the carbonyls in the sequence $Pd(CO)_4 > Pd(CO)_3 > Pd(CO)_2 > Pd(CO)$.[33] Apparently the palladium mono-, di-, and tri-carbonyls are mononuclear, the CO groups are terminal, and there is no metal–metal interaction.[31,33] The stretching vibrational frequency of the terminal CO group in the mononuclear complexes is in the range 2050–2066 cm^{-1}.

The formation of binary carbonyls stable at temperatures up to 190 K has been noted in the deposition of palladium from a gas phase containing carbon monoxide onto an Al_2O_3 surface.[35] These carbonyl compounds have been characterised under high vacuum conditions by thermal desorption spectroscopy (TDS), diffraction of slow electrons (LEED), UV photoelectron spectroscopy (UPS), and X-ray electron spectroscopy (ESCA).

Another type of binary palladium carbonyls — the cationic complexes $[Pd(CO)_4]^{2+}$ — is considered below.

2. Palladium(0) carbonyl complexes containing stabilising ligands

The binary Pd(0) carbonyls are extremely unstable and decompose at a temperature above 20 K. The insertion into the coordination sphere of palladium of additional ligands having low-lying unoccupied orbitals capable of accepting the *d* electrons of the central atom (for example, N- and P-donor bases) made it possible to obtain relatively thermally stable Pd(0) complexes.

Carbonyl-containing Pd(0) complexes are synthesised mainly by three methods: by the reduction of Pd(+2) complexes under a CO atmosphere; by the substitution of ligands by carbon monoxide in preformed Pd(0) complexes; by the mild oxidation of coordinated ligands (for example, by the oxidation of phosphines to phosphine oxides, which leads to the 'liberation' of coordination sites and hence the formation of clusters with a greater nuclearity).

Only the first method or the first method combined with the third have been used to obtain Pd(0) carbonyl complexes. When the first method was used, carbon monoxide served only in rare instances both as a reductant and as a stabilising ligand. As a rule, more vigorous reductants have been used in the reduction of Pd(+2) to Pd(0); the products of such reduction were small clusters. In order to obtain clusters with a greater nuclearity (Pd_{10} and above), 'mild' oxidation (*i.e.* oxidation of only some of the isotypical ligands) has been used, leading to the liberation of coordination sites and the formation of new metal–metal bonds. Mainly Pd(+2) and $Me_3N^+O^-$ have been used as the oxidants in this instance.

a. Mononuclear palladium(0) complexes

The reduction of Pd(+2) in the presence of carbon monoxide and additional stabilising ligands leads as a rule to di- and poly-nuclear complexes; the number of isolated and reliably characterised mononuclear Pd(0) complexes is extremely small (Table 1).

The first mononuclear Pd(0) complex was obtained by the reduction of palladium acetylacetonate with triethylaluminium in toluene at 223 K.[36]

$$Pd(acac)_2 + AlEt_3 + PPh_3 + CO \longrightarrow \underset{\mathbf{1}}{Pd(CO)(PPh_3)_3} + ...$$

Together with mononuclear complexes, the formation of the polynuclear complexes $Pd_3(CO)_3(PPh_3)_3$ **2** and $Pd_3(CO)_3(PPh_3)_4$ **3** has been observed.

Table 1. Mononuclear palladium(0) complexes.

Complex	Physical methods used to characterise the substance	ν_{CO} /cm^{-1}	Ref.
$Pd(CO)(PPh_3)_3$	elemental analysis, IR spectroscopy	1955	36–38, 40, 41
$Pd(CO)(NP_3)$ [a]	elemental analysis, IR spectroscopy, $^{31}P\{^1H\}$ NMR	1930	42
$Pd(CO)[MeC(CH_2PPh_2)_3]$	elemental analysis, IR spectroscopy XRD	1919	44
$Ba[Pd(CN)(CO)]_2$	elemental analysis, IR spectroscopy	1780, 1720	45
$[RPh_3P]^+[Pd(CN)(CO)]_2$	the same	1790	45

[a] NP_3 = tris(2-diphenylphosphinoethyl)amine $N(CH_2CH_2PPh_2)_3$.

Complex **1** has also been obtained by the reduction of the phosphinepalladium(+2) chloride complex in methanol at 228 K by the reaction.[37]

$$PdCl_2(PPh_3)_2 + NaBH_4 + CO \longrightarrow \mathbf{1} + ...$$

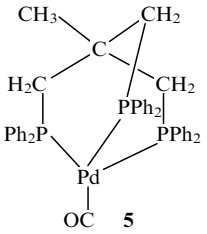
The interaction of $PdCl_2(PPh_3)_2$ and CO in a mixture of methanol with primary or secondary alkylamine also results in the formation of complexes **1** and **3**.[38] However, one cannot rule out the possibility that in this instance the amine itself exhibits reducing properties. When a primary or secondary amine is replaced by a tertiary amine, a methoxycarbonyl derivative of divalent palladium, $(PPh_3)PdCl(COOMe)$, is formed.[38] This complex has also been synthesised by Zhir-Lebed' *et al.*[39]

The formation of complex **1** has been noted in the carbonylation of $[(\eta^3\text{-allyl})PdCl]_2$ in the presence of PPh_3 in solution in methanol or ethanol (P_{CO} = 4 atm; 293 K).[40]

The divalent palladium acetate complex $(PPh_3)_2Pd(OAc)_2$ is not reduced by carbon monoxide in methanol under mild conditions.[41] Only at 323 K and a CO pressure of 20–50 atm is Pd(+2) reduced to Pd(0) with formation of a mixture of complexes **1** and **3**.

In all the studies described, complex **1** was characterised solely by elemental analysis and IR spectroscopic data. The stretching vibration frequency of the carbonyl group is fairly low (1955 cm^{-1}), which precludes an unambiguous determination of the mode of coordination of this ligand (bridging or terminal carbonyl) and it is therefore impossible to estimate the reliability of the conclusion that this compound is mononuclear. However, later investigations of the complexes $Pd(CO)L_3$ made it possible to regard complex **1** as mononuclear with a terminal carbonyl ligand.

Thus, when carbon monoxide is passed through a benzene solution of $Pd(NP_3)$ [NP_3 = tris(2-diphenylphosphinoethyl)-amine $N(CH_2CH_2PPh_2)_3$], $Pd(NP_3)CO$ **4** was obtained.[42] Complex **4** is stable only under a CO atmosphere. Its IR spectrum contains an intense band at 1930 cm^{-1}. The presence of a band at 2820 cm^{-1}, assigned to the stretching vibrations of the CH–N bond, showed that the nitrogen atom is not linked to the metal atom. The $^{31}P\{^1H\}$ NMR spectrum indicated the equivalence of all the phosphorus atoms. On the basis of the entire set of data obtained and comparison with the data for the analogous nickel complex characterised by X-ray diffraction,[43] the structure assigned to compound **4** consists of a tetrahedron in the centre of which is the palladium atom and whose vertices are occupied by the carbon atom of the carbonyl ligand and the three phosphorus atoms of tris(phosphino) amine. The complex $Pd[MeC(CH_2PPh_2)_3](CO)$ **5**, obtained later and characterised by X-ray diffraction, has precisely this structure.[44]



5

Complex **5** is formed on interaction of Pd(DBA) (DBA = dibenzylideneacetone) and the triphosphine ligand $MeC(CH_2PPh_2)_3$ in toluene under a CO atmosphere. It has been isolated in the form of yellow needles and characterised by IR spectroscopy (ν_{CO} = 1919 cm^{-1}) and X-ray diffraction. In the molecule of compound **5**, the palladium atom is linked to the carbon atom of the terminal CO group and the phosphorus atom of the triphosphine, forming a trigonal pyramid.

Carbon monoxide is capable of substituting CN^- in $Pd(CN)_2^{2-}$, obtained by the reduction of $Pd(CN)_4^{2-}$.[45] On treatment with oxygen-free dry CO in liquid ammonia (196 K), the following reaction takes place:

$$Pd(CN)_2^{2-} + CO = Pd(CN)(CO)^- + CN^-.$$

6

Complex **6** has been isolated[45] in the form of a salt with $PRPh_3^+$ (R = Me or Ph) and also in the form of a barium salt and has been characterised by elemental analysis and IR spectroscopy. The stretching vibrational frequencies, which are extremely low for a terminal carbonyl ligand (ν_{CO} = 1790 cm^{-1} for the phosphonium salts and ν_{CO} = 1780 and 1720 cm^{-1} for the barium salt), provide grounds for the assumption that in these compounds the CO group is a bridging structure between two or three metal atoms and the compounds themselves are at least dinuclear.

The ability of carbon monoxide to reduce Pd(+2) in aqueous solutions has been used to obtain carbonyl complexes stabilised by 1,10-phenanthroline (Phen) or α,α′-bipyridyl (Bipy).[46] When a solution of $PdCl_2$ containing Phen or Bipy is treated with CO containing 5% of O_2, a bright-red solution is obtained, from which the substance $(L)Pd(CO)\cdot 4H_2O$ (L = Phen or Bipy) was isolated on treatment with acetone. Certain properties of this complex (good solubility in water, inability to dissolve in organic solvents resistance to the action of oxygen, *etc.*) provide grounds for the assumption that it contains ionogenic groups and that the oxidation state of palladium is greater than zero.

b. Polynuclear palladium(0) complexes

Polynuclear (cluster) Pd(0) complexes consist mainly of compounds containing carbonyl and phosphine ligands. Clusters comprising metals having a large number of valence electrons (nickel, palladium, and platinum) are capable of coordinating a smaller number of ligands than clusters of the preceding transition metals, which leads to the instability of their carbonyl derivatives.[50] The coordination of tertiary amines, which produce the same number of valence electrons as carbon monoxide but ensure, by virtue of steric factors, more effective shielding of the surface of the metal core, leads to the formation of fairly stable compounds. The methods of synthesis structures and reactivities of phosphine palladium carbonyl clusters are considered below.

The formation of the dinuclear $Pd_2(dppm)_2(CO)$ is described in a communication[47] devoted to the synthesis of catalysts for the hydrogenation of carbon dioxide. The complex, believed to contain a bridging carbonyl group, was obtained by the reduction of $PdCl_2(dppm)_2$, with sodium tetrahydroborate in ethanol under a CO atmosphere. There are only elemental analytical and IR spectroscopic data (ν_{CO} = 1820 cm^{-1}) and the conclusions concerning its structure are therefore insufficiently reliable.

Complexes which are at least dinuclear and contain sulfide ligands in addition to the carbonyl group have been obtained.[48, 49]

The reduction of palladium acetate with carbon monoxide in an aqueous solution of trifluoroacetic acid in the presence of an excess of dialkyl sulfides R_2S (R = Me, Et, Pr^n, Bu^n) afforded complexes with the overall composition $Pd(R_2S)_3(CO)$.[48] The band at 1828–1838 cm^{-1} (ν_{CO}) in the IR spectra of the complexes indicates the bridging coordination of the carbonyl ligand and hence the di- or poly-nuclearity of the complexes.

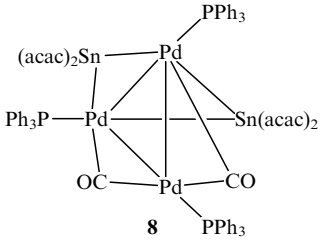
Compounds with the overall composition $\{Pd_2[RS(CH_2)_mSR]_2(CO)(HOAc)_n\}$ have been obtained similarly from palladium acetate in the presence of sulfides having the general formula $RS(CH_2)_mSR$, where m = 1, 2, or 3 and R = C_3H_7, C_7H_{15}, Ph, or Ph–CH_2.[49] The IR spectra of all the complexes isolated contain an intense band in the region of 1800 cm^{-1}, which has been assigned to the stretching vibrations of the bridging carbonyl ligand. Measurements of the molecular masses of the complexes, whose solubility is low, did not allow a choice to be made between dinuclear and tetranuclear complexes.

3. The trinuclear complexes $Pd_3(CO)_3L_3$ and $Pd_3(CO)_3L_4$

Clusters with the composition $Pd_3(CO)_3L_3$ are known only for very bulky ligands (L = PBu^t_3, PBu^t_2Ph). Such clusters were obtained by the interaction of coordinatively unsaturated complexes PdL_2 and carbon monoxide.[51] An X-ray diffraction analysis has been carried out only for the platinum analogue $Pt_3(CO)_3[P(cyclo\text{-}C_6H_{11})_3]$.[52] It has been established that the cluster has a metal core shaped as an equilateral triangle (in which the Pt–Pt band length is 2.665 Å), to the sides of which the bridging CO groups are coordinated. All the phosphorus atoms of the terminal phosphine ligands, one of which is coordinated to each metal atom, lie in the Pt_3 plane.

The interaction of $M[M'(NR_2)_2]_3$ and CO afforded[53] the heteronuclear clusters $M_3[\mu\text{-}M'(NR_2)_2]_3(CO)_3$ **7** (M = Pd or Pt, M′ = Ge or Sn, R = $SiMe_3$), which were characterised by IR spetroscopy and NMR involving various nuclei. X-Ray diffraction study of the structure of complex **7** with M = Pd and M′ = Sn showed that it has a planar metal core, whose base consists of the Pd_3 triangle. The bridging $Sn(NR_2)_2$ ligands are coordinated symmetrically to the sides of the triangle. The carbonyl groups are terminal (ν_{CO} = 2038 cm^{-1}), one being coordinated to each palladium atom.

Heteronuclear clusters of another type, $Pd_3Sn_2(\eta^2\text{-acac})_4(CO)_2(PR_3)_3$ **8** (R = Ph, Et), was obtained by the interaction of the clusters $Pd_4(\mu\text{-}CO)_5(PR_3)_4$ and $Sn(acac)_2$ in a hydrocarbon solution.[54, 55]



8

Compounds **8** are sensitive to moisture and are unstable in solution. In the region of the vibrational frequencies of the carbonyl groups, their IR spectra contain only bands due to the bridging CO groups in the range 1770–1890 cm^{-1}. According to X-ray diffraction data, the palladium atoms in clusters **8** (R = Ph) form an isosceles triangle, the sides of which are spanned by bridging CO groups, while the base is coordinated to two $Sn(\eta^2\text{-acac})_2$ bridging ligands. One phosphine ligand is linked to each palladium atom. In principle, the Pd_3Sn_2 metal core may be regarded as a 'propeller' with a Pd–Pd axis and triangular wings made up from a Pd atom and two Sn atoms.

The trinuclear clusters $Pd_3(CO)_3L_4$ are obtained by reducing $PdCl_2L_2$ (L = PPh_3)[36] or palladium acetate with carbon monoxide in the presence of NaOAc and two equivalents of the phosphine ligand (L = PPh_3, $P(C_6H_4OMe\text{-}p)_3$].[56] The structure of clusters of this type has been established in relation to $Pd_3(CO)_3(PPh_3)_4$.[57] The molecule of the cluster consists of an isosceles triangle, to the sides of which μ-CO groups are coordi-

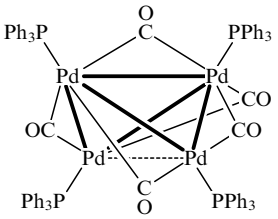
nated. Each metal atom in the base of the triangle is linked to one phosphorus atom, while the atom at the apex of the triangle is linked to two phosphorus atoms of the phosphine ligands. Such coordination of the phosphines leads to the nonequivalence of the carbonyl groups, which is reflected in the IR spectra: two intense bands are observed in the region of the stretching vibrations of the CO groups (1820 – 1880 cm^{-1}).

4. The tetranuclear clusters $Pd_4(CO)_5L_4$ and $Pd_4(CO)_6L_4$

It was noted above that the coprecipitation of Pd and CO *in vacuo* at low temperatures leads to mononuclear complexes which decompose even on a slight increase in temperature. On the other hand, if hexafluorobut-2-yne $F_3CC{\equiv}CCF_3$ (HFB) is added to Pd and CO, then precipitation *in vacuo* at −196 °C results in the formation [58] of a volatile substance having the tentative composition $Pd(CO)_2(HFB)$, which is converted into the cluster $Pd_4(CO)_4(HFB)_3$ on slow heating. The substance has been characterised by osmometric data obtained in acetone (molecular mass), IR spectroscopy (ν_{CO} = 2138 and 2122 cm^{-1}), and ^{19}F NMR spectroscopy.

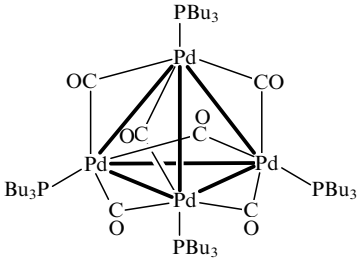
$Pd(OAc)_2$ is usually employed for the synthesis of tetranuclear carbonyl clusters with phosphine ligands, but the conditions used in the preparation of compounds with aliphatic and aromatic phosphines are different.

The tetranucler cluster $Pd_4(CO)_5(PPh_2Me)_4$ was obtained [58] by reducing $Pd(NO_2)_2(PPh_2Me)_2$ with carbon monoxite in methylene chloride. The cluster $Pd_4(CO)_5(PPh_3)_4$ **9** was obtained later in a similar reaction.[59] X-Ray diffraction analysis of $Pd_4(CO)_5(PPh_2Me)_4$ [58] and compound **9** [59] showed that the metal cores in both clusters have the form of a tetrahedron with one elongated edge ('open' tetrahedron or 'butterfly'). All the carbonyl groups are involved in μ-type coordination on the edges, each metal atom being linked to one phosphorus atom of the phosphorus ligand. The IR spectra of the complexes in the region of the stretching vibration of the CO groups are characterised by one intense band.



9

The $Pd_4(CO)_5L_4$ clusters are not very stable in solution and are capable of adding additional ligands. Thus, slow crystallisation of $Pd_4(CO)_5(PBu_3)_4$ under a CO atmosphere results in the addition of another CO molecule with formation of $Pd_4(CO)_6(PBu_3)_4$ **10**.[60] According to X-ray diffraction data, the cluster has a tetrahedral metal core, to which bridging CO groups are coordinated along all the edges and each palladium atom is linked to one terminal phosphine ligand.

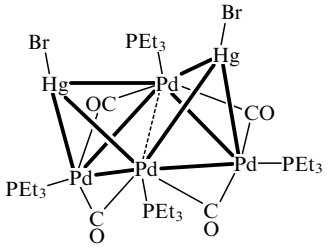


10

The interaction of the $Pd_4(CO)_5L_4$ clusters with organomercury compounds takes place virtually without change in the metal core. Thus 8-(α-bromomercurioethyl) quinoline, both parts of the molecule of which may assume the role of an additional ligand (substituted quinoline as a N,C-chelating ligand and mercury as a metalloligand) reacts with the $Pd_4(CO)_5(PEt_3)_4$ cluster to form a heteronuclear compound.[61]

$$Pd_4(CO)_5(PEt_3)_4 + C_9H_8NCH(Me)HgBr \longrightarrow$$
$$\longrightarrow CO + Pd_4Hg_2Br_2(CO)_4(PEt_3)_4.$$

11



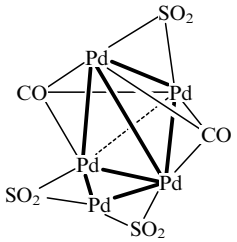
11

There is no information about the 'fate' of the quinoline component of the molecule. Formally, the two HgBr species generated as a result of the homolytic dissociation of the C – Hg bond, substitute one carbonyl group. However the coordination modes of CO and HgBr are different. According to X-ray diffraction data, the metal core is retained in cluster **11** in the form of an 'open' tetrahedron or a 'butterfly', to which external triangular faces the HgBr ligands are coordinated.

5. Pentanuclear palladium clusters

The pentanuclear carbonyl-containing platinum clusters are fairly numerous (see, for example, the review of Eremenko *et al.*[50]). The methods of their synthesis include either the reductive carbonylation of platinum(+2) compounds or the interaction of platinum dicarbonyl with phosphines. Similar approaches have proved ineffective for the carbonyl-containing palladium clusters. Compounds of this group were obtained [62] as a result of ligand substitutions in the presynthesised pentanuclear cluster $Pd_5(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(PR_3)_5$ **12**.[63]

Thus, when CO was passed through a solution of compound **12** (R = Ph or C_6H_4OMe-*p*) in dichloromethane, the corresponding complexes having the general formula $Pd_5(SO_2)_2(CO)_2(PR_3)_5$ were obtained. They were characterised by ^{31}P NMR and mass spectrometry (fast atom bombardment method, FAB). If the initial complex contained another phosphine ligand, for example $PR_3 = PMe_2Ph$, the analogous reaction led to the complex $Pd_5(SO_2)_3(CO)_2(PMe_2Ph)_5$ **13**, characterised by X-ray diffraction data. The metal core of compound **13** consists of a tetrahedron,to one edge of which a fifth palladium atom (Pd_{bridge}) is μ-coordinated. The Pd – Pd distances are in the range from 2.73 to 2.97 Å.

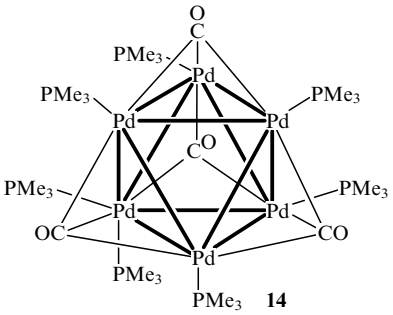


13

The bridging SO_2 groups are coordinated to two Pd_{bridge} – Pd bonds and to the edge of the tetrahedron most remote from Pd_{bridge}. The carbonyl ligands are coordinated on the opposite faces of the tetrahedron and their coordination may be regarded as highly distorted μ_3-coordination.

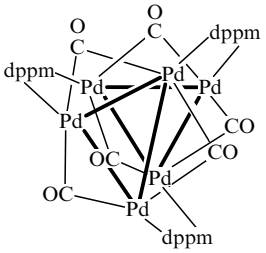
6. Hexanuclear palladium clusters

The first cluster containing six palladium atoms with the composition $Pd_6(\mu_3\text{-}CO)_4(PMe_3)_7$ **14**, was obtained by the interaction of $Pd(PMe_3)_4$ and carbon monoxide (P_{CO} = 1 atm) at 323 K.[64] The cluster has a distorted octahedral metal core, on whose faces four carbonyl ligands are μ_3-coordinated. The even phosphine ligands are linked to each of the palladium atoms.



14

The reduction of potassium hexachloropalladate K_2PdCl_6 with sodium tetrahydroborate in the presence of dppm under a CO atmosphere in a toluene–ethanol mixture afforded the complexes $Pd_2(\mu\text{-}CO)(\mu\text{-}dppm)_2Cl_2$, $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3Cl]$. .Cl, $Pd_2(\mu\text{-}dppm)_3$, and $Pd_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3$ **15**. The IR spectrum of the last compound contains bands characteristic of the stretching vibrations of the bridging CO groups (ν_{CO} = 1818–1884 cm^{-1}).

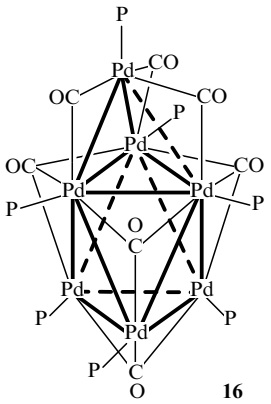


15

Accordlng to X-ray diffraction data,[65] the palladium atoms in cluster **15** form two almost equilateral triangles in which the length of one side is 2.658–2.714 Å. The triangles are linked by three bridging diphosphine ligands. One carbonyl group is coordinated to each side of each triangle. The coordination of the diphosphine ligands is such that they form almost planar trimeric $Pd_3(\mu\text{-}CO)_3P_3$ species, which are linked by the $-CH_2-$ bridges belonging to the dppm ligand. The Pd_3 triangles are almost parallel and have rotated relative to one another by 10°. Thus the metal core of the cluster can be regarded as a slightly distorted trigonal prism, the distances between the bases of which (along the Pd–Pd edges) are 3.030, 3.010, and 2.948 Å.

7. The heptanuclear $Pd_7(\mu_3\text{-}CO)_4(\mu\text{-}CO)_3(PMe_3)_7$ cluster

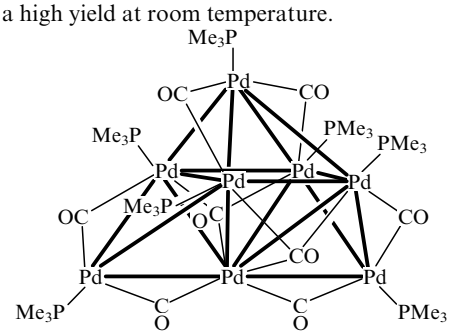
The heptanuclear $Pd_7(\mu_3\text{-}CO)_4(\mu\text{-}CO)_3(PMe_3)_7$ **16** cluster has been obtained by the reduction of the complex $Pd(\eta^1,\eta^3\text{-}C_8H_{12})(PMe_3)$ with carbon monoxide and is the only example of palladium clusters with the above degree of nuclearity.[66] The IR spectrum of the complex contains absorption bands in the region characteristic of the stretching vibrations of the bridging CO group (l685–1825 cm^{-1}). The structure of the cluster has been established by X-ray diffraction. The metal core consists of an octahedron with one 'capping' palladium atom. The additional palladium atom is located asymmetrically above the face of the octahedron: one of the interatomic 'nonbonding' $Pd_{cap}-Pd_{octahedron}$ (3.17 Å) is appreciably longer than the other two bonds (2.73 Å). The metal–metal bond lengths in the octahedron are 2.75–2.81 Å; these are typical values for distances over which direct metal–metal interaction usually takes place.



16

8. The octanuclear $Pd_8(\mu_3\text{-}CO)_2(\mu\text{-}CO)_6(PMe_3)_7$ cluster

The syntheses of phosphinepalladium(0) carbonyl are carried out under similar conditions. The formation of clusters with different nuclearities can be accounted for by the extreme sensitivity of the process leading to the formation of the cluster metal core to the nature of the reaction medium and the source of the palladium atoms. Thus, when a solution of $Pd(DBA)_2$ (DBA = dibenzylideneacetone) was treated with carbon monoxide (P_{CO} = 1 atm) in dry CH_2Cl_2 containing PMe_3, $Pd_8(CO)_8(PMe_3)_7$ **17** was obtained in a high yield at room temperature.



17

The cluster was isolated in the form of dark reddish-black plates and was characterised by IR spectroscopy (ν_{CO} = 1763–1878 cm^{-1}) and X-ray diffraction data.[67] According to the X-ray diffraction data, six of the eight palladium atoms in the cluster form a regular octahedron. The remaining two palladium atoms behave as 'caps' on two opposite faces of the octahedron and are linked to the same apical palladium atom not joined to the terminal phosphine ligand.

9. The decanuclear clusters $Pd_{10}(CO)_{12}L_6$ and $Pd_{10}(CO)_{14}L_4$

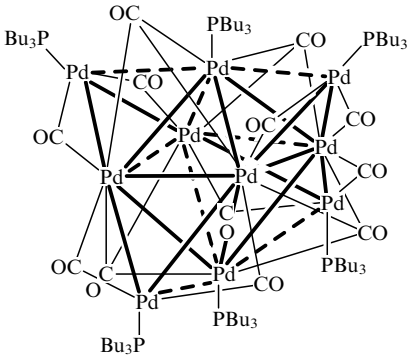
a. Clusters with aliphatic phosphines

The synthesis of palladium clusters with aliphatic phosphines has been studied in greatest detail. The compounds are formed on reduction of palladium acetate by carbon monoxide in the presence of CF_3COOH. In these syntheses, the acid generates the optimum equilibrium concentration of the free phosphine, the excess of which is bound in the phosphine salt $[HPAlk_3]^+[CF_3COO]^-$.[60,68,69] Superstoichiometric amounts of $PAlk_3$ and the presence of a strong acid are necessary in the syntheses of the complexes $Pd_{10}(CO)_{12}(PEt_3)_6$ **18**, $Pd_{10}(CO)_{12}(PBu_3)_6$ **19**, and $Pd_{10}(CO)_{14}(PBu_3)_4$ **20**. On the other hand, in weakly acid and neutral media, it is necessary to reduce the concentration of $PAlk_3$ to give stoichiometric ratios.[68] The compounds which could be isolated at a low $PAlk_3$ concentration in a neutral medium proved to be noncrystalline.

Clusters **18**–**20** were characterised by IR spectroscopic data (the bands in the range 1810–1920 cm^{-1} were assigned to the stretching vibrations of the bridging CO groups) and ^{31}P NMR

spectroscopic data.[60, 68–71] The ^{31}P NMR spectra of clusters **18** and **19** are characterised by two signals with an intensity ratio of 2 : 1 and $\delta = -11.0$ and -3.1 ppm for cluster **18** and $\delta = -4.0$ and $+3.3$ ppm for cluster **19**. The ^{31}P NMR spectrum of cluster **20** contains one singlet at $\delta = -5.0$ ppm.[69, 70]

The spectroscopic data are consistent with the structure of the clusters determined by X-ray diffraction analysis. Thus cluster **19** is an octahedron, over all the nonadjacent faces of which 'capping' palladium atoms are located.[69]



19

The palladium atoms of the metallopolyhedron can be subdivided into equatorial, apical (in the octahedron), and 'capping'. Since the $Pd_{cap}-P_{eq}$ distance (2.694–2.722 Å) is much shorter than the $Pd_{cap}-Pd_{apic}$ distance (3.301–3.421 Å), it would be more logical to regard the 'capping' atoms not as atoms μ_3-linked to the Pd_3 face of the octahedron but as bridging atoms on the $Pd_{eq}-Pd_{eq}$ edges. The Pd–Pd distances in the inner octahedron are in the range from 2.791 to 2.851 Å. Eight μ-CO groups behave as bridges on the $Pd_{cap}-Pd_{eq}$ edges and four CO groups are μ-coordinated to the four free faces of the octahedron. The coordination of these CO groups is also asymmetric, but, in contrast to the 'capping' metal atoms, the carbon atoms of the μ_3-CO groups are displaced towards the apical palladium atoms. The six phosphorus atoms of the tributylphosphine ligands are bound to four capping and two apical palladium atoms.

Treatment of complex **18** with the isocyanide XylNC (Xyl = $C_6H_3Me_2$-2,6) leads to the displacement of some of the coordinated CO groups and the formation of the cluster $Pd_{10}(\mu\text{-}CO)_6(\mu_3CO)_2(\mu\text{-}CNXyl)_2(PEt_3)_6$ **21**. According to X-ray diffraction data[72] cluster **21** retains the same metal core as cluster **18**.

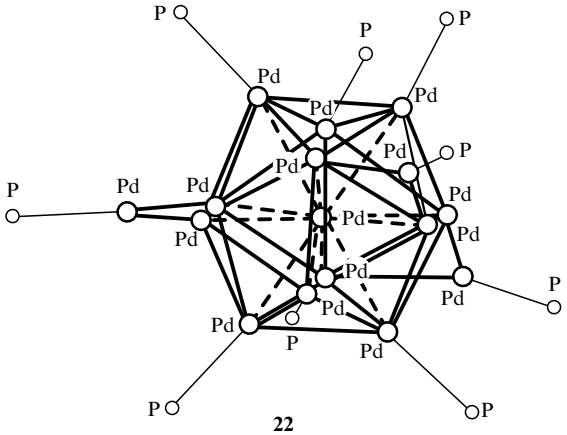
b. Clusters with aromatic phosphines

Aromatic phosphines [for example, PPh_3, $PMePh_2$, and $P(OMe)Ph_2$] are very weak bases and a very high content of hydrogen ions is required to regulate their concentration. Attempts have been made[69–71] to synthesise these compounds under neutral conditions with vigorous control of the concentration of the initial phosphine. The clusters $Pd_{10}(CO)_{12}L_6$ [L = PPh_3, $PMePh_2$, and $P(OMe)Ph_2$] were isolated in the solid state and identified by elemental analysis and IR spectroscopy.

10. The hexadecanuclear cluster $Pd_{16}(CO)_{13}L_9$

The use of the traditional procedure — oxidation of CO by trimethylamine *N*-oxide[73] — made it possible to obtain[74] the 16-nuclear cluster $Pd_{16}(CO)_{13}(PEt_3)$ **22** by the reaction of $Pd_4(CO)_5(PEt_3)_4$ and $Pd_{10}(CO)_{12}(PEt_3)_6$. X-Ray diffraction study demonstrated the presence in this cluster of the centred icosahedron $Pd_{13}(\mu_3\text{-}CO)_7(PEt_3)_6$, overlaid by three bridging $Pd(\mu\text{-}CO)_2L$ fragments. These fragments impart chirality to the centred icohedral metal core of the cluster, reducing its idealised symmetry I_h to D_3. The centrosymmetric racemic crystals of the clusters contain equal numbers of the optically active isomeric molecules.

Compound **22** is the first example of a polynuclear palladium complex with icosahedral packlng of the metal atoms.



22

11. Tricosahedral clusters

The use of $Pd(OAc)_2$ as a mild acceptor of phosphine ligands made it possible to convert decanuclear carbonyl–phosphine clusters into the compounds with a high nuclearity. Thus the interaction of $Pd_{10}(CO)_{12}(PEt_3)_6$ and $Pd(OAc)_2$ (molar ratio 1 : 1) in benzene at 293 K for 24 h and subsequent addition of heptane afforded the cluster $Pd_{23}(CO)_{22}(PEt_3)_{10}$ **23**.[75] A slight change in the conditions of the synthesis (molar ratio Pd : Pd = 1 : 1.5; methanol–ether mixture, 303 K, 2.5 h) leads[76] to another 23-nuclear cluster having the composition $Pd_{23}(CO)_{20}(PEt_3)_8$ **24**. Both clusters have been characterised by X-ray diffraction data (Fig. 2*a*).

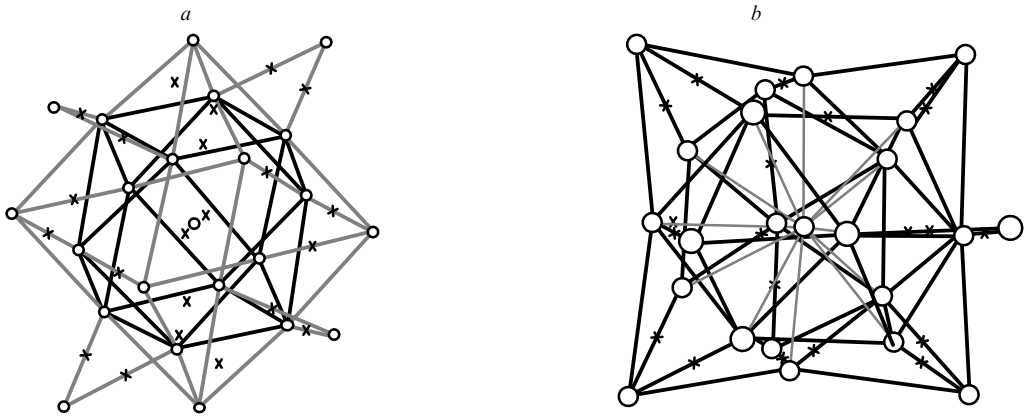


Figure 2. The structure of the metal cores of the $Pd_{23}(CO)_{22}(PEt_3)_{10}$ (*a*) and $Pd_{23}(CO)_{20}(PEt_3)_8$ (*b*) clusters according to X-ray diffraction data.[75, 76] The crosses designate the positions of the carbon atoms of carbonyl ligands.

The metal core of the centrosymmetric molecule of cluster **23** can be regarded as a cubooctahedron (designated by thickened lines in Fig. 2*a*) with one metal atom at the centre. This cubooctahedron has an idealised O_h symmetry. Six 'capping' palladium, atoms are μ^4-coordinated to each square face of the cubooctahedron while the remaining four metal atoms are symmetrically μ-coordinated to the four edges of the cubooctahedron. The metal–metal distances beetween the central and peripheral metal atoms (on average 2.847 Å) and between pairs of peripheral metal atoms (2.849 Å) in the cubooctahedron are virtually equal. All the other metal–metal distance in the metallopolyhedron are in the range from 2.720 to 2.920 Å.

Clusters **23** and **24** have a 22-atomic metallopolyhedron and one endopolyhedral metal atom. However, in contrast to complex **23**, containing a fragment with cubic close packing of metal atoms, the metallopolyhedron in complex **24** has a different structure. In the immediate environment of the endopolyhedral palladium atom, there are not 12, as in complex **23**, but 14 metal atoms; the average Pd–Pd distance (2.918 Å) exceeds by almost 0.17 Å the metal–metal distance in metallic palladium. The central palladium atom with metal atoms in its immediate vicinity is approximately regarded as a fragment with body-centred cubic packing (BCC), although the appreciable distortions of the idealised BCC packing observed in complex **24** are more likely to indicate that the polyhedron is not so regular in its shape. This polyhedron, made up of 15 metal atoms, is overlaid by eight 'caps' comprising palladium atoms, which are also coordinated to eight terminal phosphine ligands. The composition of the coordination sphere also includes three μ_3-CO and seventeen μ-CO ligands.

12. The cluster $Pd_{34}(CO)_{24}(PEt_3)_{12}$

The 34-nuclear cluster $Pd_{34}(\mu\text{-}CO)_{20}(\mu_3\text{-}CO)_4(PEt_3)_{12}$ **25** has been obtained as a by-product of the elimination of phosphine ligands from the decanuclear clusters $Pd_{10}(CO)_{12}(PEt_3)_6$ and $Pd_{10}(CO)_{14}(PEt_3)_4$, leading to the formation of a 38-nuclear cluster with 'irregular' packing of atoms in the quasi-spherical metal polyhedron (see below). According to X-ray diffraction data,[77] the metal polyhedron of the cluster contains four inner palladium atoms located at the apices of a distorted octahedron. Each of these atoms has a distorted icosahedral environment comprising 12 palladium atoms. This environment does not occur in the crystal lattice of the bulk metal but is encountered in the metal cores of cluster with finite dimensions. The observed metal–metal distances in the metal core of cluster **25** indicate unambiguously an icosahedral type of packing of the metal atoms (Fig. 3). Histograms of the metal–metal distances in large palladium clusters based on X-ray diffraction data have been compared with atomic radial distribution curves calculated from EXAFS data (Fig. 4).[78]

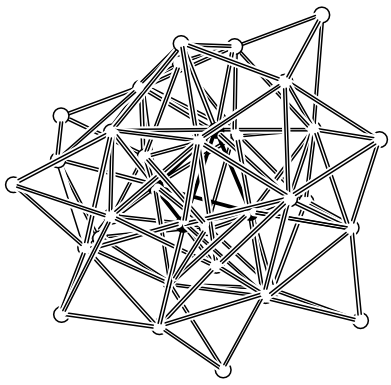


Figure 3. The structure of the metal core of the cluster $Pd_{34}(\mu\text{-}CO)_{20}(\mu_3\text{-}CO)_4(PEt_3)_{12}$ according to X-ray diffraction data (the dark lines designate the inner metallotetrahedron).[77]

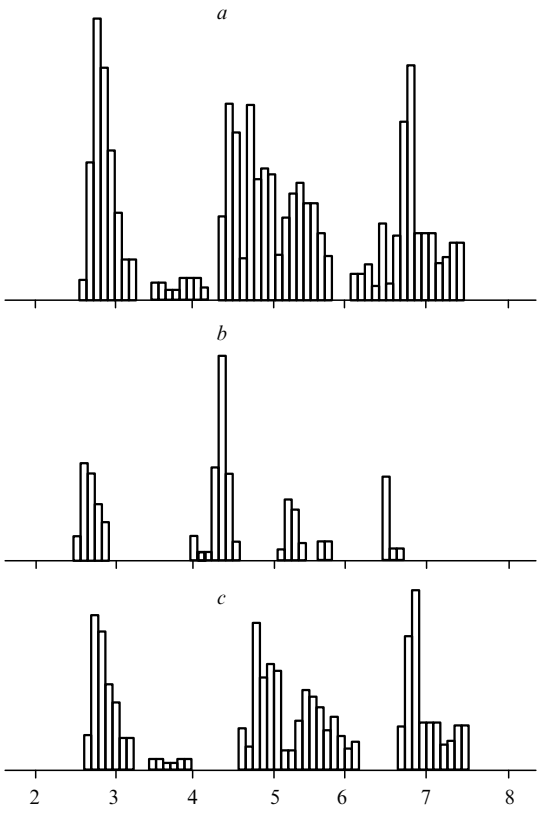


Figure 4. Histograms of the distribution of interatomic distances in the Pd_{34} metal core of the cluster $Pd_{34}(\mu\text{-}CO)_{20}(\mu\text{-}CO)_4(PEt_3)_{12}$ with participation of only four intracluster atoms (*a*) with participation of all the remaining distances in the Pd_{30} metal 'shell' (*b*), and the theoretical distribution for the standard (idealised) icosahedral packing of the metal (*c*).

13. The cluster $Pd_{38}(CO)_{28}(PEt)_{12} \cdot Me_2CO$

The cluster $Pd_{38}(CO)_{28}(PEt)_{12} \cdot Me_2CO$ **26** was obtained, like the 23-nuclear cluters, by the reaction of the $Pd_{10}(CO)_{12}(PEt_3)_6$ with $Pd(OAc)_2$ (molar ratio 1 : 2) in acetone in an argon atmosphere. The complex was isolated in the form of crystals sensitive to atmospheric oxygen and characterised by X-ray diffraction data (Fig. 5).[79]

The cluster metal core has an incompletely regular structure with noncrystallographic symmetry close to D_2. The flattened inner Pd_4 tetrahedron with two long (2.958 and 2.970 Å) and four short (2.539, 2.610, 2.603, and 2.514 Å) Pd–Pd bonds is surrounded by twenty metal atoms, located in four approximately parallel layers, and two metal atoms located outside these layers. All this corresponds to the 4 : 8 : 2 : 8 : 4 configuration. The 26-

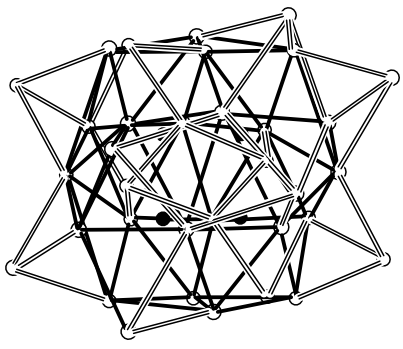


Figure 5. The structure of the metal core of the cluster $Pd_{38}(CO)_{28}(PEt)_{12}$ (the filled circles identify the inner metal atoms).[79]

nuclear metal core thus obtained is linked to twelve 'capping' palladium atoms, while each 'capping' metal atom is linked to the phosphorus atom of the terminal phosphine ligand. The average Pd – Pd distance for 118 metal – metal bonds is 2.775 Å. Among the 28 carbonyl groups, four are μ_3-coordinated, whilst the others are μ-coordinated.

Analysis of the structures of the polynuclear phosphinepalladium(0) carbonyl complexes showed that the 'tendency' to form a spherical metallopolyhedron, leading to the minimisation of the surface of the molecule, is characteristic for these compounds, as in the case of the platinum and nickel clusters (Table 2) The structures of clusters **24** – **26** provide a good illustration of the characteristic feature of the structure of the entire class of large clusters: the possibility of the rearrangement of the metallopolyhedron following a change in the ligand environment and the 'tendency' to achieve close packing of the metal atoms.

In order to investigate the structure and nature of the chemical bonding in the palladium(0) carbonyl clusters, an attempt has been made [80] to apply an incorporation method as the basic procedure for the 'construction' of large clusters by the addition of 'caps' to the triangular and/or rectangular faces of the metallopolyhedron. The method is based on the graph theory. Thus the structures of clusters **16**, **17**, **19**, and **20** are produced by the addition of one, two, three, and four palladium 'caps' respectively to the central Pd_6 octahedron. However, for the description of the Pd_{23} and Pd_{38} clusters, this approach requires the introduction of additional concepts and appears somewhat artificial.

The results of the determination of the metal – metal bond length in a series of phosphinepalladium(0) carbonyl complexes from X-ray diffraction and EXAFS data agree well.[78] This gives rise to the hope for a wider application of the EXAFS method in the study of the structures of cluster compounds.

14. Infrared spectra of palladium(0) carbonyl complexes

Analysis of the IR spectra (Table 2) of structurally characterised carbonylphosphine clusters [81, 82] permitted the conclusion that the characteristic differences in the region of the sretching vibrations of the carbonyl group are observed only as the coordination mode of the carbonyl ligands is varied. Thus the vibrations of the terminal CO groups are manifested in the short-wavelength region (2000 – 2050 cm^{-1}), those of the μ-CO groups are in the middle region ($\sim$1850 – 1950 cm^{-1}), and those of the μ_3-groups are shown in the longest-wavelength part of the spectrum. The regions corresponding to absorption by the last two types of CO ligands overlap appreciably. Complexes of different nuclearity, containing the same type of CO ligand, have no stable distinctive features in the IR spectra.

On the other hand, the presence at one metal atom of only one terminal group and three *n*-donor atoms {for example, in the complexes $Pd(CO)(PPh_3)_3$, $Pd(CO)(NP_3)$ and $Pd(CO)[MeC(CH_2PPh_2)_3]$, see Table 1} leads to a decrease in ν_{CO} to values characteristic of the stretching vibrations of the bridging CO groups, *i.e.* the region of the stretching vibrations of the bridging and terminal carbonyl groups overlap. It is noteworthy that in all other complexes where the number of *n*-donor atoms at each metal atom is smaller (for example, two or one phosphorus atoms), the stretching vibrational frequencies of the terminal CO group lie above 2000 cm^{-1}.

IV. Palladium(+1) carbonyl complexes

The coordination compounds in which palladium is present in the formal oxidation state +1 have been frequently postulated as active intermediates in palladium-catalysed reactions.[84 – 86] This applies to a considerable extent to reactions occurring with participation of carbon monoxide. Palladium(+1) intermediate

Table 2. Characteristics of the polynuclear palladium(0) complexes containing carbonyl ligands.

Compound	Coordination of CO	ν_{CO} /cm^{-1}	Metal core	Pd – Pd /Å	Ref.
$Pd_3Sn_2(\eta^2\text{-acac})_4(CO)_2(PPh_3)_3$	μ	1890 – 1770	equilateral Pd_3 triangle	2.71 – 2.80	54, 55
$Pd_3(CO)_3(PPh_3)_4$	μ	1820 – 1880	the same	2.670, 2.741 2.777	57
$Pd_4(\mu\text{-}CO)_5(PPh_2Me)_4$	μ	1840, 1820	'open' Pd_4 tetrahedron ('butterfly')	2.74 – 2.77 3.20	58
$Pd_4(\mu\text{-}CO)_5(PPh_3)_4$	μ	1858	the same	2.74 – 2.78 3.19	59
$Pd_4(\mu\text{-}CO)_6(PBu_3)_4$	μ		tetrahedron	2.77 – 2.79	60
$Pd_4Hg_2Br_2(CO)_4(PEt_3)_4$	μ	1897, 1855	'open' tetrahedron ('butterfly')	2.69 – 3.01 3.43	61
$Pd_5(SO_2)_3(CO)_2(PMe_2Ph)_5$	μ	1908	tetrahedron with one Pd bridge	2.73 – 2.97	62
$Pd_6(\mu_3\text{-}CO)_4(PMe_3)_7$	μ_3	1730, 1708	distorted octahedron	2.705 – 2.806	64
$Pd_6(\mu\text{-}CO)_6(\mu\text{-dppm})_3$	μ	1884, 1876, 1841, 1826, 1818	distorted trigonal prism	2.658 – 2.724	65
$Pd_7(\mu_3\text{-}CO)_4(\mu\text{-}CO)_3(PMe_3)_7$	μ, μ_3	1825, 1800, 1785, 1770, 1750, 1685	octahedron with one Pd cap	2.75 – 2.81	66
$Pd_8(CO)_8(PMe_3)_7$	μ, μ_3	1878, 1843, 1810, 1803, 1775, 1763	octahedron with two Pd caps	2.73 – 2.87	67
$Pd_{10}(CO)_{12}(PBu_3)_6$	μ, μ_3	1920 – 1810	octahedron with four Pd caps	–	69
$Pd_{16}(CO)_{13}(PEt_3)_9$	μ, μ_3		centred icosahedron with three Pd caps	–	74
$Pd_{23}(CO)_{22}(PEt_3)_{10}$	μ, μ_3	1863, 1847, 1823	centred cubooctahedron with six μ_4-coordinated and four μ-coordinated Pd caps	2.720 – 2.920	75
$Pd_{23}(CO)_{20}(PEt_3)_8$	μ, μ_3	1865, 1839, 1815	fragment of the BCC structure with eight Pd caps	2.819 [a]	76
$Pd_{34}(\mu\text{-}CO)_{20}(\mu_3\text{-}CO)_4(PEt_3)_{12}$	μ, μ_3	1892, 1865, 1837, 1809	fragment of the icosahedral type of packing		77, 78
$Pd_{38}(CO)_{28}(PEt_3)_{12}$	μ, μ_3	1899, 1885, 1849, 1842, 1817, 1778	a not very regular structure with noncrystallographic symmetry	2.775 [a]	79, 83

[a] Average distance.

complexes could arise either in the reduction of Pd(+2) by carbon monoxide or in the oxidation of Pd(0), for example, during oxidative addition in a medium containing CO as the stabilising ligand. These postulates constitute the basis of the syntheses of palladium(+1) carbonyl complexes, although other products of the oxidation–reduction reactions [except Pd(+1)] have by no means been characterised in any way and discussed in all cases.

The first among palladium(+1) carbonyl complexes was the carbonyl chloride Pd(CO)Cl obtained in 1926.[87] The structure of this complex and in the first place the coordination mode of the carbonyl group remained obscure for many years. It was not until more than half a century later that X-ray diffraction studies on the structures of palladium carbonyl complexes were published. $[Pd(\mu\text{-dam})Cl]_2(\mu\text{-CO})$ [9,10] and $Pd_4(\mu\text{-CO})_4(\mu\text{-OAc})_4$ [11,12] were investigated. X-Ray diffraction data with IR spectroscopic data provided answers to a number of questions concerning the structure of palladium carbonyl chloride, its analogues, and derivatives.

1. The syntheses and structures of palladium(+1) carbonyl complexes

a. Palladium(+1) carbonyl halides and their anionic derivatives

The carbonyl chloride Pd(CO)Cl was first obtained by the reaction of solid $PdCl_2$ with carbon monoxide saturated with methanol vapour at 0 °C and atmospheric pressure.[87] A more convenient method of synthesis of the carbonyl halides involved the reaction of PdX_2 (X = Cl, Br) with CO at atmospheric pressure in a concentrated aqueous solution of the corresponding hydrogen halides. The formation of diamagnetic powdered Pd(CO)Cl and Pd(CO)Br deposits was observed when an aqueous solution of the corresponding palladium salt was treated with carbon monoxide or after treatment with formic acid.[88] Palladium carbonyl chloride has also been obtained by carbonylation of a suspension of $PdCl_2$ in the presence of acetyl chloride [89] or small amounts of H_2O [90,91] and also by the reaction of $PdCl_2$ and allyl chloride with CO at both atmospheric and elevated pressures. [91,92] The benzonitrile complex $(PhCN)_2 \cdot PdCl_2$ — a convenient reagent which has proved very useful in the preparation of alkene palladium π-complexes [94] — has been employed as the starting material for the synthesis of Pd(CO)Cl.[91,93]

The carbonyl chloride Pd(CO)Cl (ν_{CO} = 1975 cm^{-1}) has also been obtained [95] by treating the palladium(+2) carbonyl complex $Pd_2(CO)_2Cl_4$ with carbon monoxide (Ac_2O, 25 °C, 24 h, P_{CO} = 1 atm).

In contrast to the binary palladium(0) carbonyl compounds, which are not formed from metallic palladium at temperatures above 323 °C, the palladium(+1) carbonyl chloride can be produced from powdered palladium at a CO pressure of 170 atm and 190 °C in a phosgene-containing solution in *o*-dichlorobenzene.[91] The palladium(+1) carbonyl fluoride or carbonyl iodide could not be obtained by any of the methods indicated above.

The elemental composition of palladium(+1) carbonyl chloride specimens obtained by different methods [88–93] as a rule corresponds to the formula Pd(CO)Cl: the IR spectra of three specimens agree satisfactorily. A powdered amorphous or very fine-crystalline substance, which does not dissolve in organic solvents and is thermally stable up to 60 °C but readily decomposes on treatment with water or even atmospheric moisture, was obtained in all cases.

$$2Pd(CO)Cl + H_2O = 2Pd + CO_2 + 2HCl + CO.$$

The reaction is strongly inhibited by H^+ or Cl^- ions, as a result of which the carbonyl chloride dissolves almost without decomposition and is stable in concentrated hydrochloric acid. The properties of the thermally more stable (T_{decomp} = 120 °C) carbonyl bromide Pd(CO)Br are similar. This too is stable in concentrated aqueous HBr solution.[88] Both palladium(+1) carbonyl halides are relatively stable in air in the absence of H_2O.

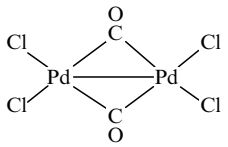
Thermolysis of the carbonyl halides leads to the elimination of CO and the formation of palladium metal. Probably as a result of slight decomposition the colour of the Pd(CO)X specimens obtained by different workers varies from yellow-green to dark-violet. The stretching vibrational frequency of the CO groups in these compounds varies in the range from 1850 to 2000 cm^{-1}.[96,97]

It was postulated in early investigations that the compounds Pd(CO)X are polymers with halide [88] or carbonyl [98] bridges. On dissolution in the corresponding hydrogen halide solution, depolymerisation takes place with formation of mono- or di-nuclear anions, for example:

$$2Pd(CO)X + 2X^- = [Pd_2(CO)_2X_4]^{2-}.$$

The crystalline substance with the composition $(NH_4)_2[Cl_2Pd(CO)]_2$ has been isolated from a solution of $(NH_4)_2PdCl_4$ in concentrated HCl, treated with carbon monoxide for several days, while in the presence of enH_2^{2+} and $[Pt(NH_3)_4]^{2+}$ cations the crystalline salts of the latter with the $[Pd_2(CO)_2Cl_4]^{2-}$ anion were obtained. It was assumed that the anion contains Pd(+3) atoms linked by bridging CO groups to form a dimer.[99] Without going into the question of the electronic structure of the anion, we may note that, since the CO group is electrically neutral, the formal oxidation state of palladium is in this instance +1. One cannot rule out the possibility that a metal–metal bond is present in the dimeric anion. The diamagnetism of the cesium rubidium, and tetraalkylammonium salts of the anions $[Pd_2(CO)_2Cl_4]^{2-}$ and $[Pd_2(CO)_2Br_4]^{2-}$ obtained by a similar method [88,98] agrees with this hypothesis. Treatment of the complex Pd(CO)Cl with an equimolar amount of NH_2Et_2Cl afforded the anionic complex $[NH_2Et_2]_2[Pd_2(CO)_2Cl_4]$, characterised by elemental analysis and IR spectroscopy (ν_{CO} = 1916 cm^{-1}).[95]

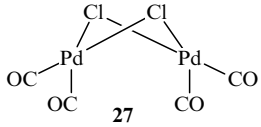
The structure of the anionic carbonyl halide complex $[Bu^n_4N]_2[Pd_2(CO)_2Cl_4]$, synthesised by Goggin and Mink,[98] has been investigated by X-ray diffraction.[100] The 1966 and 1906 cm^{-1} frequencies correspond to the stretching vibrations of the CO groups in the complex in solution in CH_2Cl_2. The palladium atoms in the anion of the complex are linked by two carbonyl bridges, each metal atom being bound to two terminal chloride ligands.



The metal–metal distance (2.697 Å) indicates the presence of the Pd–Pd single bond. Each palladium atom has a highly distorted tetrahedral environment, the $PdCl_2$ plane making a dihedral angle of 8–10° with the $Pd_2(\mu\text{-C})_2$ plane.

The planar configuration of the $Pd_2(\mu\text{-C})_2$ species agrees well with the IR spectrum of the solid complexes (the spectrum contains only the ν_{CO} = 1903 cm^{-1} band due to the asymmetric vibrations). The presence in the spectrum of the solution in CH_2Cl_2 of a band at 1966 cm^{-1} assigned to the symmetrical vibrations of the CO group, indicates the distortion of the planar configuration of the $Pd_2(\mu\text{-C})_2$ species in solution.

Thus the carbonyl ligand in virtually all the reliably characterised neutral and anionic palladium(+1) carbonyl halide complexes is a bridge between two metal atoms. The only exception is the complex $[Pd(CO)_2(\mu\text{-Cl})]_2$ **27** obtained when CO is passed (6 h, 60 °C) through a reaction mixture containing $PdCl_2$ and $NaHCO_3$ in anhydrous methanol in the presence of 2-(1,5-dimethylhex-4-enyl)-3-hydroxy-5-methyl-1,4-benzoquinone.[101]



27

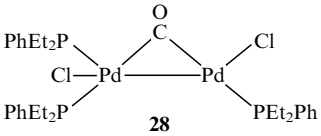
Complex **27** has been isolated from n-hexane in the form of crystals stable in air. Unfortunately, the very brief relevant publication [101] contains no comments whatsoever concerning the fairly unexpected choice of reagents and the role of sodium bicarbonate or the substituted benzoquinone. The IR spectrum of the complex contains bands characteristic of terminal CO groups (2103, 2082, 2024, and 1997 cm^{-1}). According to X-ray diffraction data, the two palladium atoms of the complex, at a distance of 3.114 Å, are joined by two chloride bridges *cis*-posed relative to the Pd...Pd axis (the dihedral angle of the Pd_2Cl triangle is 124 °). Each metal atom is also joined to two terminal CO groups, which builds up their environment to a distorted planar square.

b. Palladium(+1) carbonyl halides containing *n*-donor stabilising ligands

Neutral molecules containing an element E (E = N, P, As, Sb), which is capable of donating an unshared electron pair, are usually employed as additional stabilising ligands. In the chemistry of carbonyl-containing palladium(+1) compounds, nitrogen-containing ligands are relatively rare,whilst phosphorus-containing ones (mono- and di-phosphines) are very common.

The complexes $[(PdXL)_2CO]_n$, where X = Cl, Br, or I and L = PPh_3, $PPh(p\text{-}MeOC_6H_4)_2$, $PPh_2(C_6H_4COOH)$, $PPh_2(C_6H_4F)$, $PPh_2(C_6H_4Cl)$ or $PPh_2(C_6H_4Me)$, have been obtained by the reactions of the corresponding phosphine with a solution of $H_2Pd_2(CO)_2Cl_4$ in concentrated HCl.[102] The IR spectra of the solid complexes contain two bands in the range 1860–1962 cm^{-1}, which have been assigned to the stretching vibrations of the bridging CO groups. On the other hand, if a solution of $H_2Pd_2(CO)_2Cl_4$ in concentrated HCl is acted upon initially by a solution of $SnCl_2$ and then triphenylphosphine in concentrated HCl, all the acido-ligands are displaced from the initial carbonyl chloride and $[Pd_2(PPh_3)_2(SnCl_3)_2]CO$ (ν_{CO} = 1800–2000 cm^{-1}) is formed.[103] The complexes $[(PdXL)_2CO]_n$, containing stabilising ligands of the type of arsine (L = $AsPh_3$) or stibine (L = $SbPh_3$) have been obtained on partial substitution of carbonyl and acido-ligands in palladium(+1) carbonyl halides and carbonyl acetate complexes by organoelement ligands.[104] The complexes have been characterised by elemental analysis, ESCA, and IR spectroscopy. Judging from the ν = 1710–1890 cm^{-1} region, the carbonyl group in these compounds is involved in bridging coordination.

The dinuclear complex $Pd_2(CO)Cl_2L_3$ (L = PEt_2Ph) **28** has been obtained [59] in a fairly high yield (49%) yield by the reaction of CO with $Pd(NO_2)_2L_2$ in dichloromethane (293 K, P_{CO} = 1 atm, 48 h) and subsequent precipitation of the compound formed on treatment with CO-saturated hexane at 273 K. In the formation of compound **28**, the source of chloride ligands could be dichloromethane itself, although the authors did not rule out also the possibility of the interaction of the initial $Pd(NO_2)_2L_2$ and HCl or Cl_2, present in. the solvent, with formation of $PdCl(NO_2)L_2$. In order to confirm this hypothesis, *trans*-$PdCl(NO_2)L_2$ was obtained. Its treatment with CO also affords the dimer **28**.



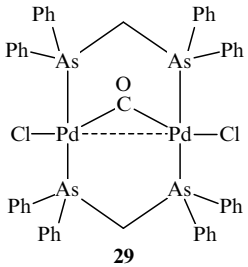
28

According to X-ray diffraction data, the two palladium atoms in the molecule of compound **28** (the Pd–Pd distance is 2.652 Å) are linked asymmetrically by the coordinated semibridging carbonyl ligand (the Pd–C distances are 1.874 and 2.110 Å, while the Pd–C–Pd angle is 83.3°.[105] They have nonequivalent environments. The palladium atom involved in the shorter bond with the carbonyl group is also linked to the second metal atom, one chloride ligand, and one phosphine ligand. It has a highly distorted 4-coordinated environment. There are five atoms in the environment of the second palladium atom: one Cl atom, two phosphorus atoms of the phosphine ligands, palladium, and a somewhat remote carbon atom of the carbonyl ligand.

Unfortunately the authors do not quote spectroscopic data for complex **28**.

Complexes containing the $Pd_2(\mu\text{-}Q)_2$ moiety, where Q = diphosphine or diarsine ligands having the composition $R_2E(CH_2)_nER_2$ (E = P or As, n = 1–3), constitute a special group. As a rule, such complexes are formed by the insertion of CO in the metal–metal bond in the dinuclear palladium(+1) complexes $Pd_2(\mu\text{-}Q)_2X_2$ (X = Cl, Br, I), which are formed in their turn in the reaction of the polymeric $[Pd(CO)X]_n$ (or its anionic derivatives) with the bidentate ligand Q. In the interaction of $[Pd(CO)X]_n$ and dppm, the coordinated CO group is fully displaced with formation of the complexes $[Pd(dppm)X]_2$.[88] In the case of dam, the reaction product depends on the nature of the halogen: if X is chlorine or bromine, $[Pd(\mu\text{-}dam)X]_2(\mu\text{-}CO)$ **29** is formed, whereas in the case where it is iodine the product is $[Pd(\mu\text{-}dam)I]_2$.[9, 10, 105]

In complex **29** (X = Cl) palladium atoms are bound to two dam molecules and the carbonyl bridge.



29

The Pd–Pd distance (3.274 Å exceeds twice the covalent radius. Nevertheless, the compound is diamagnetic, so that the spins are apparently paired via the carbonyl bridge, which in this case is fairly unusual: the Pd–C–Pd angle is 119° and not 85–89° as in the majority of transition metal carbonyl complexes.

When $[Pd(\mu\text{-}dppm)X]_2$ (X = Cl, Br) is treated with CO in dihloromethane, $[Pd(\mu\text{-}dppm)X]_2(\mu\text{-}CO)$ (ν_{C0} = 1704 cm^{-1}) is formed;[106]; it liberates CO reversibly on heating in solution in dichloromethane. The complex $Pd_2(\mu\text{-}CO)(\mu\text{-}dppm)_2Cl_2$ has been obtained as a result of the addition of oxalyl chloride ClC(=O)-C(=O)Cl to $Pd_2(dppm)_3$ in dichloromethane.[107]

The kinetics of the reversible insertion on of carbon monoxide in the Pd–Pd bond of the complex $Pd_2(dppm)_2X_2$ with formation of $Pd_2(\mu\text{-}CO)(\mu\text{-}dppm)_2X_2$ have been investigated spectrophotometrically.[108] It was established that the reaction obeys a first-order equation with respect to both the metal and carbon monoxide.

The reaction of the polymer $[Pd(CO)Cl]_n$ with dmpm (dmpm = bis(dimethylphosphino)methane] in dichloromethane at 198 K leads to the formation of $Pd_2Cl_2(dmpm)_2$ **30**. Treatment of compound **30** with carbon monoxide results in the formation of $[PdCl(\mu\text{-}dmpm)]_2(\mu\text{-}CO)$ **31** with a bridging carbonyl ligand (ν_{CO} = 1710 cm^{-1}). According to X-ray diffraction data, the distance between the metal atoms in the molecule of compound **31** (the Pd–Pd distance is 3.169 Å) exceeds the sum of the covalent radii of palladium and the environment of each metal atom consists of an almost planar square.[109, 110]

In contrast to analogues containing dppm, an unusually high solubility and stability in aqueous solution were characteristic of complex **31**. On the basis of IR, Raman, and NMR spectroscopy involving different nuclei and electrical conductivity data, it has been shown that the following reactions take place readily in water:

$$Cl—Pd(\mu\text{-}dmpm)_2Pd—Cl + H_2O \longrightarrow$$
$$\longrightarrow HO—Pd(\mu\text{-}dmpm)_2Pd—OH,$$

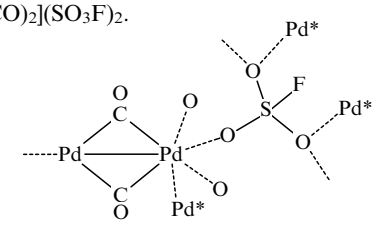
$$HO—Pd(\mu\text{-dmpm})_2Pd—OH + {}^{13}CO \longrightarrow$$
$$\longrightarrow HO—Pd(\mu\text{-dmpm})_2(\mu\text{-}{}^{13}CO)Pd—OH.$$

The interaction of $[Pd(\mu\text{-dppm})X]_2$ and $SnCl_2$ followed by treatment of the resulting solution with carbon monoxide afforded[111] *in situ* the complex $Pd_2(\mu\text{-dppm})_2Cl(SnCl_3)(\mu\text{-CO})$ (ν_{CO} = 1688 cm^{-1}).

The principal characteristic feature of the reaction involving the insertion of small molecules in the Pd – Pd bond is the increase in the metal – metal distance on the formation of bridges. Despite the fact that the palladium – palladium distance increases to a value greatly exceeding the sum of the covalent radii, the compounds containing palladium in the formal +1 oxidation state remain diamagnetic. The probable causes of the diamagnetism of these compounds will be discussed below.

c. The binary palladium(+1) carbonyl

The only compound in which the Pd(+1) atom is linked to carbonyl groups only is the cationic complex $[Pd_2(\mu\text{-CO})_2](SO_3F)_2$.



The reductive decomposition of the divalent palladium carbonyl $Pd(CO)_2(SO_3F)_2$ in solution in fluorosulfonic acid HSO_3F at 298 K leads to the formation (according to IR spectroscopic data) of a mixture of complexes containing both bridging and terminal CO groups.[112] Slow crystallisation (for about three weeks) of the mixture from fluorosulfonic acid leads to the precipitation of needle-like crystals.

It has been suggested that the reduction of Pd(+2) to Pd(+1) includes the elimination of the $SO_3F^{\bullet}$ radicals and their dimerisation to $S_2O_6F_2$ with simultaneous liberation of one mole of CO in accordance with the equation

$$2Pd(CO)_2(SO_3F)_2 \xrightarrow{HSO_3F} 2Pd(CO)SO_3F + 2CO + S_2O_6F_2,$$

which is probably followed by the oxidation of CO to CO_2:

$$CO + S_2O_6F_2 \xrightarrow{HSO_3F} CO_2 + S_2O_5F_2.$$

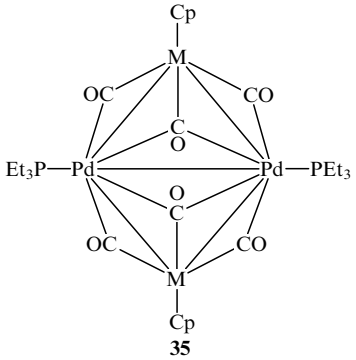
The formation of $S_2O_5F_2$, in the reaction mixture has been confirmed by ^{19}F NMR (signal at δ = 47.5 ppm).

The complex $[Pd_2(\mu\text{-CO})_2](SO_3F)_2$ has been characterised by elemental analysis IR spectroscopy (ν_{CO} = 1977 cm^{-1}), and X-ray diffraction data. Its molecular structure consists of cyclic, almost planar four-membered $Pd_2(\mu\text{-CO})_2$ species, in which the palladium atoms are linked together as a result of direct metal – metal interaction (the Pd – Pd distance is 2.698 Å) and by two symmetrical carbonyl bridges. The individual metallocycles are joined by symmetrical bridging bidentate fluorosulfate groups, forming a planar polymer chain. Thus the coordination sphere of each palladium atom incorporates the two carbon atoms of two *cis*-disposed carbonyl groups, two oxygen atoms of two fluorosulfate groups, and a neighbouring palladium atom. If the metal – metal bonding is ignored, the geometrical environment of each palladium atom can be regarded as a slightly distorted square.

d. Other palladium(+1) complexes containing carbonyl and organic ligands

The interaction of the complex $Pd_2(\mu\text{-Cp})(\mu\text{-Br})(PR_3)_2$ and CO in toluene leads to the displacement of the bromide and cyclopentadienyl bridges to axial positions and to the formation of $Pd_2(\mu\text{-CO})(\eta^5\text{-Cp})(Br)(PR_3)_2$ **32** [R = Et (**32a**), R = Pr^i (**32b**)].[113] The analogous initial compound containing an acetate instead of a bromide bridge reacts with CO also with formation of complex **32**.[114] Complexes **32a,b** have been characterised by IR spectroscopy (ν_{CO} = 1804 and 1828 cm^{-1} respectively) and NMR spectroscopy on different nuclei. The. structure of complex **32b** has been investigated by X-ray diffraction. The metal atoms in the molecule of the complex are linked both to one another (direct metal – metal interaction, the Pd – Pd distance is 2.67 Å) and with the bridging carbonyl. The phosphine ligands are *trans*-located relative to the metal – metal axis. It has been shown that the carbonyl bridge in complex **32** is readily substituted by other small molecules, for example SO_2 or CH_3NC. The dinuclear complexes $(PR_3)_2Pd_2(\mu\text{-CP})(\mu\text{-X})$ (X = Cl or CH_3COO) readily react with $NaCpM(CO)_3$ (M = Cr, Mo, W) or $NaCo(CO)_4$. Such interaction affords the heteronuclear clusters $(PR_3)_2Pd_2(\mu\text{-Cp})[\mu\text{-M(CO)}_3\text{Cp})]$ **33** and $(PR_3)_2Pd_2(\mu\text{-Cp})[\mu\text{-Co(CO)}_4]$ **34** respectively.[115] These complexes have been characterised by spectroscopic methods. It has been established that the cyclopentadieny and carbonylmetallate ligands function as bridges between the two palladium atoms ,while the phosphines occupy the axial position. The attempt to substitute the cyclopentadienyl ligand in complexes **33** and **34** by a second carbonylmetallate in order to obtain tetranuclear clusters was unsuccessful, but such clusters have been obtained by another method.

The interaction of *trans*-$Pd(PEt_3)_2Cl_2$ and $[\eta^5\text{-CpM(CO)}_3]^-$ results in the formation[116,117] of the tetranuclear clusters $Pd_2M_2(\eta^5\text{-Cp})_2(\mu_3\text{-CO})_2(\mu\text{-CO})_4(PEt_3)_2$ (M = Cr, Mo, W) **35**. All three complexes have been characterised by X-ray diffraction data. The metal atoms in complex **35** (M = Mo) are in the same plane and form a rhombus with a short Pd – Pd diagonal. One μ_3-CO group is linked to each Pd_2Mo triangle (ν_{CO} = 1772 cm^{-1}), while a μ-CO group is linked to each Pd – Mo edge (ν_{CO} = 1842 and 1801 cm^{-1}).



35

A similar cluster with another phospine ligand, $Pd_2Mo_2(\eta^5\text{-Cp})_2(\mu_3\text{-CO})_2(\mu\text{-CO})_4(PBzPh_2)_2$ (the Pd – Pd and Pd – Mo distances are 2.58 and 2.86, 2.82 Å respectively), has been synthesised.[118]

Palladium(+1) complexes with terminal carbonyl groups have been obtained[119] in a study of the reactions of a dimeric univalent palladium complex with phosphide bridges as a result of the following transformations in solution in dimethoxyethane:

$$R_2HP—Pd(\mu\text{-}PR_2)_2Pd—PHR_2 + HCl \longrightarrow$$
$$\longrightarrow [R_2HP—(H)Pd(\mu\text{-}PR_2)Pd(PR_2)—PHR_2]^+X^-,$$
36

$$\mathbf{36} + CO \longrightarrow [R_2HP—(CO)Pd(\mu\text{-}PR_2)Pd(CO)—PHR_2]^+X^-,$$
37

where $X^- = CF_3SO_3^-$ or BF_4^-. Complexes **36** and **37** have been characterised by NMR and IR spectroscopy (ν_{CO} = 2080, 2055, and 2045 cm^{-1} for complex **37**) and also by X-ray diffraction data (the Pd – Pd distances are 2.611 and 2.682 Å for complexes **36** and **37** respectively). The NMR spectra have shown that complex **37** exists in the form of a mixture of isomers differing in the relative

disposition of the carbonyl and phosphine ligands. Complex **37** is stable only under a carbon monoxide atmosphere; it is readily decarbonylated *in vacuo*, on passing nitrogen, on heating, or on UV-irradiation.

e. Palladium(+1) carbonyl carboxylates

All the carbonyl-containing univalent palladium complexes presented above are as a rule dimers or linear polymers. The tetranuclear carbonyl carboxylates having a planar cyclic metal core are an exception. The structure and chemical properties of compounds of this group have been thoroughly investigated.

The complexes containing simultaneously both carbonyl and carboxylate ligands are usually obtained by reduction of palladium(+2) carboxylates with carbon monoxide in a carboxylic acids or in an inert solvent containing the corresponding carboxylic acid. The second method of synthesis involved the substitution of ligands in the presynthesised palladium(+1) carbonyl carboxylates. The cluster $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OAc)_4$ **38** was obtained[11,12] by the first methods, *i.e.* by carbonylating (P_{CO} = 1 atm) palladium acetate in glacial acetic acid at 323 K.

$$4Pd(OAc)_2 + 8CO \longrightarrow Pd_4(CO)_4(OAc)_4 + 2AcO + 4CO.$$

The cluster crystallises with two molecules of acetic acid to give $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OAc)_4 \cdot 2AcOH$ **38a**, while on drying *in vacuo* over KOH it loses an acetic acid molecule and is converted into $Pd_4(CO)_4(OAc)_4$ **38b**. The IR spectra of the complexes each contain intense bands corresponding to the stretching vibrations of the CO groups (1934 and 1975 cm^{-1} for **38a** and 1940 and 1975 cm^{-1} for **38b**) and bands due to the stretching vibrations of acetate groups coordinated as bidentate species. According to X-ray diffraction data, the cluster as an almost rectangular metal core with angles of 83.4° and 96.6°. The sides of the rectangle, linked by acetate bridges are longer (2.909 Å), while the sides linked by carbonyl bridges are shorter (2.663 Å) than the metal–metal distance in metallic palladium (2.751 Å) (Fig. 6).[120]

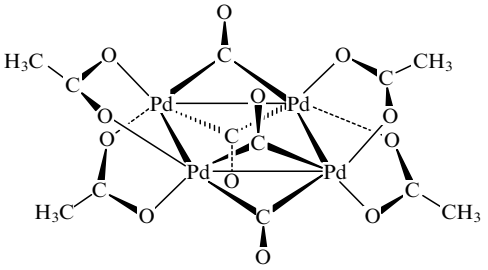


Figure 6. The structure of the cluster $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OAc)_4$ according to X-ray diffraction data.[122]

The mechanism of the formation of cluster **38** has been investigated by spectroscopic and kinetic methods. The data obtained led to the conclusion that the formation of complex **38** involves the transfer of an oxygen atom from the carboxylate group to the coordinated carbonyl group. This results in the formation of the coordinated acyl [CH_3CO] and in the elimination of carbon dioxide.[121–123]

It has been established that the coordinated acetate groups in complex **38** are substituted by other carboxylates in the reactions with the corresponding acids, for example:

$$Pd_4(CO)_4(OAc)_4 + 4RCOOH = Pd_4(CO)_4(RCOO)_4 + 4AcOH,$$

39

R = CD_3, C_2H_5, C_6H_5, CF_3, CCl_3, CH_2Cl.

According to IR spectroscopic data, all the complexes contain bridging carbonyl and carboxylate groups. Comparative analysis of X-ray diffraction data for palladium carbonyl acetate and of EXAFS data for all carbonyl carboxylate complexes permitted the conclusion that they all have a similar structure — a planar metal core (rectangle, square, or rhombus) to the sides of which bridging carboxylate and carbonyl ligands are coordinated.[124]

Together with the existence of isomers having different metal cores, there is also a possibility of the existence of isomers with different relative dispositions of ligands: disposition of ligands in pairs (for example as in complex **38** characterised by X-ray diffraction analysis) and uniform distribution of similar ligands. The influence of substituents in carboxylated groups on the isomerism of the metal core of the carbonyl carboxylates has been examined in detail.[125,126]

f. Derivatives of palladium(+1) carbonyl carboxylates with N- and P-donor ligands

The interaction of complex **38** with ligands such as Py, dppe, PPh_3, Bipy, and Phen leads to a series of complexes, the composition of which depends on the initial Pd/ligand(L) ratio. The palladium complexes formed with the Pd/L = 2 ratio are unstable. With decrease in the ratio, more stable compounds appear.

The interaction of complex **38** with Py and its alkyl derivatives (with the ratio Pd/Py = 1) entails the disproportionation of Pd(+1) to Pd(0) and Pd(+2):

$$Pd_2(CO)_4(OAc)_4 + 4Py \longrightarrow Pd(0) + 2Pd(Py)_2(OAc)_2 + 4CO.$$

The interaction of complex **38** and dppe (Pd/dppe = 1) in benzene affords the complex $Pd_2(dppe)_2(CO)(OAc)_2$:[127,128]

$$Pd_4(CO)_4(OAc)_4 + 4dppe \longrightarrow 2Pd_2(dppe)_2(CO)(OAc)_2 + 2CO.$$

40

According to IR spectroscopic data, the group CO in complex **40** is of the bridging type (ν_{CO} = 1790 cm^{-1}). The fairly low stretching vibrational frequency in the compound where the metal atoms are linked also by a further two diphosphine bridges indicates an increase in the Pd–Pd distances compared with the analogous distances in complex **38**. Analysis of the stretching vibrational frequencies of the acetate group in the IR spectrum of complex **40** [$\nu_{as}(COO)$ = 1580 cm^{-1}, $\nu_s(COO)$ = 1380 cm^{-1}, $\Delta\nu$ = 200 cm^{-1}) permits the conclusion that monodentate coordination of the acetate groups takes place. Apparently the structure of complex **40** is analogous to that of palladium(+1) carbonyl halide complexes with diphosphine and diarsine groups.[9,10] The coordination sphere of each metal atom consists of two phosphorus atoms of the two diphosphine ligands, the carbon atom of the carbonyl group, and the oxygen atom of the terminal acetate group.

The analogous complex $[Pd(dppm)(O_2CCF_3)]_2(\mu\text{-}CO)$ has been isolated in the course of the study of the kinetics of the interaction of the dimer $[Pd(dppm)(O_2CCF_3)]_2$ and carbon monoxide in dichloromethane.[129] The complex has been characterised by IR spectroscopy (ν_{CO} = 1720 cm^{-1}) and NMR spectroscopy involving different nuclei and also by X-ray diffraction analysis.

The two palladium atoms in the molecule of the complex, linked by a bridging CO group, are at a distance of 2.896 Å. This is less than the sum of the covalent radii of palladium (2.98 Å) and is appreciably shorter than the Pd–Pd distance (~ 2.7 Å) characteristic of the Pd(+1) dimers. Each palladium atom in the molecule is surrounded by the same set of atoms: the carbon atom of the carbonyl group, two phosphorus atoms of the two diphosphine ligands, and one oxygen atom of the terminal carboxylate ligand. If the Pd–Pd bond is excluded from consideration, then environment of each palladium atom consists of an almost planar square (the deviation from the plane of the square is not more then 0.02 Å), whereas the environment of the second metal atom is close to being tetrahedral. The authors believed that in this case the distortion of the symmetrical structure may be caused by a redistribution of electron density in the complex and that the latter can be regarded as an intermediate in the dissociation of the trifluoroacetate complex leading to $[Pd_2(\mu\text{-}dppm)_2(\mu\text{-}CO)(O_2CCF_3)]^+(CF_3CO_2)^-$.

The interaction of complex **38** and dppe, taken in nine–tenfold excess in tetrahydrofuran, leads to the formation of a cationic complex in accordance with the equation

$$Pd_4(CO)_4(OAc)_4 + 8dppe \longrightarrow 2[Pd_2(CO)(dppe)_4](OAc)_2 + 2CO.$$

According to ^{31}P NMR data the diphosphine ligands in the complex are involved in both bridging and terminal coordination, whereas the carbonyl group serves as a bridge between the two metal atoms.

Treatment of complex **38** with PPh_3 leads to the complex $Pd_2(CO)(PPh_3)(OAc)_2$:

$$Pd_4(CO)_4(OAc)_4 + 4PPh_3 \longrightarrow Pd_2(CO)(PPh_3)_2(OAc)_2 + 2CO.$$

41

Complex **41** contains a bridging CO group (ν_{CO} = 1800 cm^{-1}). Depending on the conditions in the synthesis, compounds differing in the coordination of the acetate groups are formed. Thus, when the process is carried out in tetrahydrofurane a complex with acetate bridges is produced [ν_{as}(COO) = 1530 cm^{-1}, ν_s(COO) = 1400 cm^{-1}, $\Delta\nu$ = 130 cm^{-1}], whereas the reaction of complex **38** with PPh_3 in benzene leads to a compound with terminal OAc groups [ν_{as}(COO) = 1610 cm^{-1}, ν_s(COO) = 1350 cm^{-1} $\Delta\nu$ = 260 cm^{-1}].

In the interaction of complex **38** and Bipy at an initial Bipy concentration > 0.5 M and a concentration of complex **38** of 5×10^{-3} M all the CO molecules are displaced:[49, 50]

$$Pd_4(CO)_4(OAc)_4 + 2Dipy \longrightarrow 2Pd_2Dipy(OAc)_2 + 2CO.$$

At low Bipy concentrations (< 5×10^{-3} M), only half of the CO's are displaced from complex **38**:

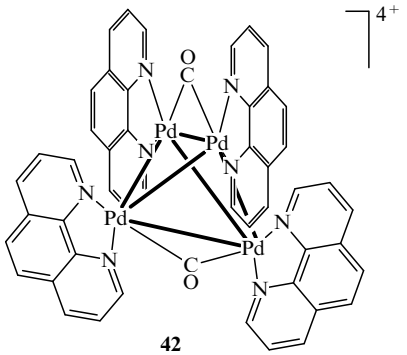
$$Pd_4(CO)_4(OAc)_4 + 2Dipy \longrightarrow 2Pd_2Dipy(CO)(OAc)_2 + 2CO.$$

In contrast to Bipy, *o*-phenanthroline (Phen) displaces from complex **38** only half of the CO groups present even at the highest ligand concentrations. In the reaction of complex **38** with Phen, in the proportions Phen : Pd = 1 : 1, in acetic acid, a tetranuclear cationic complex is formed:[130]

$$Pd_4(CO)_4(OAc)_4 + 4Phen \longrightarrow [Pd_4(CO)_2Phen_4](OAc)_4 + 2CO.$$

42

The complexes have been characterised by IR spectroscopy (ν_{CO} = 1800 cm^{-1}) and X-ray diffraction data.[130] In the cation **42**, the four metal atoms form a tetrahedron, to the two mutually perpendicular edges of which bridging CO groups are coordinated. The remaining metal–metal bonds are unbridged. One Phen molecule is coordinated as a chelate species to each palladium atom, while all the acetate groups are displaced to the outer sphere



42

On passing from complex **38** to **42**, all the metal–metal distances change significantly. The Pd–Pd distance in the Pd(μ-CO)Pd fragments increases from 2.667 Å in complex **38** to 2.890 Å in complex **42**, while the unbridged Pd–Pd bond is shortened from 2.909 to 2.718 Å to compare with the Pd(μ-OAc)Pd fragment in the initial carbonyl acetate.

It has been suggested that the conversion of the neutral molecule of complex **38** into the cationic cluster **42** involves the interaction of complex **38** and Phen, which results in the displacement of the acetate groups and the formation of the dication $[PhenPd(CO)_2PdPhen]^{2+}$. This is followed by the elimination of half of the coordinated CO groups and the dimerisation of coordinatively unsaturated species produced, which leads to the appearance of cluster **42**.

g. The structure of palladium(+1) complexes containing a bridging CO group

The palladium(+1) complexes containing a bridging CO group have been reliably characterised by the results of spectroscopic and structural studies (Table 3).

In the complexes where the palladium atoms are not linked to *n*-donor atoms (Nos 1–3), the metal–metal distances are close to that in metallic palladium, which is 2.7 Å. The stretching vibrational frequencies of the CO group in these complexes vary from 1900 to 2000 cm^{-1}. The presence of powerful electron-withdrawing groups, for example CF_3COO (complex No. 4), increases the stretching vibrational frequency of the CO group to 2000 cm^{-1}.

Table 3. Certain spectroscopic and structural data for palladium(+1) complexes containing a bridging carbonyl group.

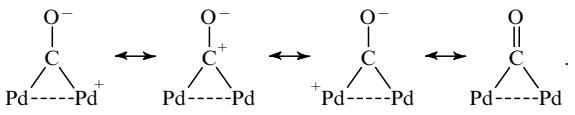
No.	Complex	*n*-Donor atom	Pd–Pd /Å (XRD)	ν_{CO} /cm^{-1}	Ref.
1	[cyclo-Pd_2(μ-CO)$_2$]$(SO_3F)_2$		2.698	1977	35
2	$[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$		2.697	1903	22
3	$Pd_4(\mu\text{-}CO)_4(\mu\text{-}OAc)_4$		2.663	1934, 1975	7, 8
4	$Pd_4(\mu\text{-}CO)_4(\mu\text{-}O_2CCF_3)_4$		2.700 [a]	2002, 1940	45
5	$Pd_2(\mu\text{-}CO)(Cl)(PEt_2Ph)_3$	P	2.652	–	27
6	$Pd_2(\mu\text{-}CO)(\eta^5\text{-}Cp)(Br)(PPr^i_3)_2$	P	2.670	1828	38
7	$[Pd_4Phen_4(\mu\text{-}CO)_2](OAc)_4$	N	2.890	1800	52
8	$Pd_2(\mu\text{-}CO)(\mu\text{-dppm})_2(OAc)_4$	P	2.980	1720	51
9	$Pd_2(\mu\text{-}CO)(\mu\text{-dmpm})_2Cl_2$	P	3.169 [b]	1720	32, 33
10	$Pd_2(\mu\text{-}CO)(\mu\text{-dam})_2Cl_2$,	As	3.274 [b]	1710	5, 6, 29

[a] According to EXAFS data. [b] For comparison, the Pd–Pd distance in $Pd_2(\mu\text{-dppm})_2Br_2$ is 2.699 Å.

After the insertion of *n*-donor phosphorus atoms (axial phosphine ligands in complex Nos 5 and 6) into the coordination sphere of palladium, the Pd–Pd distance does not change, but ν_{CO} falls sharply. Only the presence of chelating phenanthroline molecules, linked to one palladium atom (No. 7), or of bridging diphosphino and diarsine ligands (complexes Nos 8–10) leads to a simultaneous increase in the Pd–Pd distance and decrease in the stretching vibration frequency of the bridging carbonyl ligand.

It is of interest that powerful electron-accepting ligands, for example trifluoroacetate groups, in the axial positions in complex No. 4 (Table 3) somewhat 'extinguish' the effect involving the donation of *n* electrons by phosphorus atoms, which is probably the reason for the shortening (compared with other complexes containing diphosphines and diarsines) of the Pd–Pd distance.

As mentioned above, all the complexes discussed are diamagnetic. On the other hand, the metal–metal distance in complexes with diphosphines and diarsines (complexes Nos 9 and 10 in Table 3) greatly exceeds the sum of the covalent radii palladium and for this reason the pairing of electrons as a result of the formation of the Pd–Pd bond is impossible. The diamagnetism of such complexes has been explained by the exchange of charges in the Pd_2(μ-CO) fragment with participation of the structure



Evidently the hypothesis of the resonance of structures with different numbers of unpaired electrons ($Pd^{+}...Pd^{+}$ and $Pd^{2+}...Pd^{0}$) conflicts with the main principles of the resonance theory.[131] At the same time, the bond in the group made up of two palladium atoms and one carbon atom of the carbonyl group can be described approximately in terms of a localised three-centre system of molecular orbitals, similar to that which occurs in the allyl radical. The diamagnetism of the dinuclear palladium(+1) compounds under consideration implies, in terms of this approximation, that four electrons (one from each palladium atom and two from the carbonyl ligands fill the bonding and nonbonding molecular orbitals of the system (Fig. 7).

Within the framework of this approximation, all the changes in the Pd–Pd distance and ν_{CO} frequencies should be considered from the standpoint of the variation of the electron density on the metal atoms and the variation of the levels of the atomic orbitals in view of the change in the nature of the ligand atoms coordinated to palladium. It is easily seen that in the isomeric ylide the frequencies of the carbonyl group should be significantly reduced compared with the frequencies of the dimetallocyclopropanone. The complexes presented in Table 3 may be regarded as models of the intermediate states on the path to the isomerisation of the dimetallocyclopropanone to the corresponding dimetalloylide:

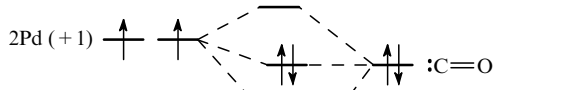
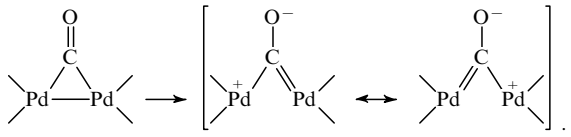
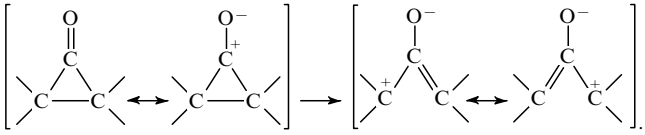


Figure 7. The three-centre system of molecular orbitals in the group comprising two palladium atoms and one carbon atom.



The strong electron-donating influence of the ligands linked to the palladium atom may weaken the Pd–Pd bond and increase the distance between the atoms involved. This is equivalent to the isomerisation of the cyclopropanone to an ylide with an opened ring:



2. The reactivity of palladium(+1) carbonyl complexes

The available information about the chemical properties of palladium(+1) carbonyl halides is limited to data concerning their behaviour in relation to water and under thermal decomposition conditions. The reactivity of the carbonyl carboxylate complexes and their derivatives has been investigated much more fully.

a. Ligand substitution reactions in palladium(+1) carbonyl carboxylates

Synthesis of a carbene cluster by the substitution of CO groups

When certain acido-ligands (for example, the acetate groups in complex **38**) are substituted by other carboxylates, new carbonyl carboxylate complexes are formed.

The substitution of neutral carbonyls has been observed in the interaction of complex **38** with diphenyldiazomethane.[132] The interaction of complex **38** and Ph_2CN_2, which is capable to generate diphenylcarbene groups *in situ*, results in the displacement of the CO groups and the formation of a new complex (Fig. 8);

$$Pd_4(CO)_4(OAc)_4 + 4Ph_2CN_2 = Pd_4(CPh_2)_4(OAc)_4 + 4CO + 4N_2.$$

43

Complex **43** contains bridging acetate groups. It has been established by IR spectroscopic studies that $\nu_{as}(COO) = 1560\ cm^{-1}$, $\nu_s(COO) = 1400\ cm^{-1}$, and $\Delta\nu = 160\ cm^{-1}$. The signals due to the protons of the phenyl and acetate groups in the ratio $H_{Ph}/H_{OAc} = 10/3$, *i.e.* there is one CPh_2 ligand per acetate group, have been observed in the ^1H NMR spectrum. According to EXAFS data, the coordination sphere of each palladium atom in cluster **43** includes two metal atoms at a distance of 2.67 Å, one metal atom at a distance of 3.65 Å, and also two light atoms in each case (in all six) at distances of 1.86, 2.03, and 3.25 Å. These values agree with the structure proposed by Stromnova *et al.*[132,133] (Fig. 8).

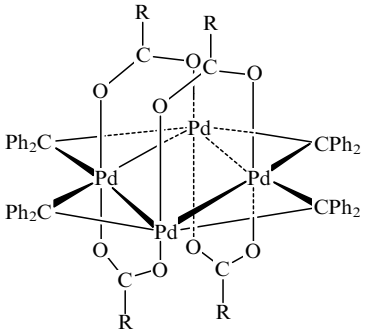


Figure 8. The structure of the cluster $Pd_4(\mu\text{-}CPh_2)_4(\mu\text{-}OAc)_4$ according to EXAFS data.[132,133]

Oxidative substitution of carbonyl ligands

The coordinated carbon monoxide in transition metal carbonyl complexes may be oxidised by an outer-sphere oxidant, for example trimethylamine *N*-oxide:

$$R_3N{=}O + L_nM(CO)_m \longrightarrow R_3N + N + CO_2 + L_nM(CO)_{m-1},$$

or by other compounds containing the N–O group.[73,134]

In a study of the interaction of complex **38** with organic compounds containing the N–O group, such as nitrobenzene, nitrosobenzene, azoxybenzene, phenylhydroxylamine, and trimethylamine *N*-oxide, it has been established[135] that only nitrosobenzene and phenylhydroxylamine are capable of oxidising the coordinated carbon monoxide under mild conditions, like trimethylamine *N*-oxide:

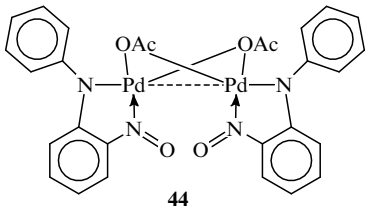
$$Pd_4(CO)_4(OAc)_4 + Me_3NO \longrightarrow Pd + CO_2 + Me_3N + Ac_2 + ...,$$

$$Pd_4(CO)_4(OAc)_4 + PhNHOH \longrightarrow$$

$$\longrightarrow Pd + CO_2 + PhNH_2 + Ac_2 + Ac_2O,$$

$$Pd_4(CO)_4(OAc)_4 + PhNO \longrightarrow$$
$$\longrightarrow Pd_2(\mu\text{-}OAc)_2(Ph{-}N{-}C_6H_4{-}NO)_2 + CO_2 + PhN(O){=}NPh.$$

The complex $Pd_2(\mu\text{-}Ac)_2(Ph-N-C_6H_4-NO)_2$ **44**, containing a new ligand — phenyl-*o*-nitrosophenylamide, is formed in the reaction between complex **38** and nitrosobenzene together with organic products (azoxybenzene, azobenzene, and aniline) of the transformation of the NO-containing compound .[136]



44

This ligand is obtained by the reaction of a nitrene species (the product of the deoxygenation of nitrosobenzene when the latter is acted upon by the CO group) and a second nitrosobenzene molecule.

Reactions of complex 38 with anionic carbonylmetallates

Presumably, like the substitution of the OAc groups in complex **38** by carboxylate groups, the same groups might; be substituted by more complex ones, for example the carbonylmetallates $Co(CO)_4^-$, $V(CO)_6^-$, and $CpMo(CO)_3^-$. Such reactions would make it possible to obtain heteronuclear palladium-containing clusters. Indeed, the reaction of complex **38** with $NaCpMo(CO)_3$ in tetrahydrofuran entails the formation of the octanuclear cluster $Na_2\{Pd_4[CpMo(CO)_3]_4\} \cdot 2THF$.[137, 138]

X-Ray diffraction analysis has shown that the structural unit in the crystals investigated consists of the centrosymmetric anion $\{Pd_4[CpMo(CO)_3]_4\}^{2-}$, two sodium cations, and two tetrahydrofuran molecules. The palladium atoms are located at the vertices of a square (the Pd–Pd distances are 2.675–2.691 Å). Each molybdenum atom forms an almost regular triangle with the two palladium atoms (the Pd–Mo distances are 2.723–2.741 Å), and all the metal atoms lie in the same plane. The observed metal–metal distances correspond to single bonds. Three carbonyl ligands are linked to each molybdenum atom and one of the carbonyls is a μ_3-bridge on the Pd_2Mo face, while the other two are bridges on the Pd–Mo bonds (Fig. 9).

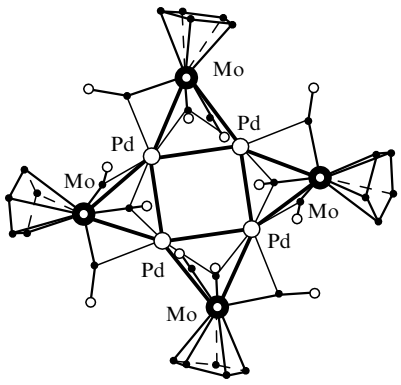


Figure 9. The structure of the anion $\{Pd_4[CpMo(CO)_3]_4\}^{2-}$ according to X-ray diffraction data.[137, 138]

The IR spectrum of the complex contains bands at 2000, 1945, 1900. 1870, and 1830 cm^{-1} referring to the coordinated CO groups.

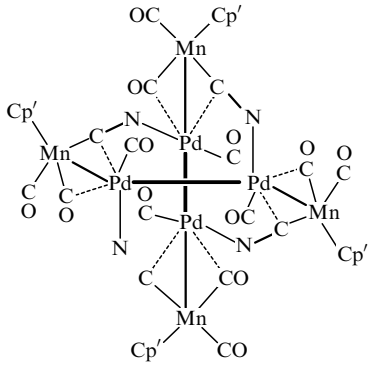
In the course of the formation of the octanuclear cluster, not only are the acetate ligands substituted by the $CpMo(CO)_3^-$ anions, but the neutral CO molecules are also displaced. The vacancies liberated in the coordination sphere of palladium in this process are occupied by the CO molecules coordinated to the molybdenum atom, which are converted into bridging ligands. However, it is significant that the process is not restricted to the substitution of ligands: during the reaction, the Pd(+1) atoms are reduced, apparently as a result of the one-electron oxidation of the $CpMo(CO)_3^-$ anions. The overall process is described by the equation

$$Pd_4(CO)_4(OAc)_4 + 6Na[CpMo(CO)_3] =$$
$$= Na_2\{Pd_4Mo_4Cp_4(CO)_{12}\} + 4CO + [CpMo(CO)_3]_2 + 4NaOAc.$$

The dimer $[CpMo(CO)_3]_2$ has been found in the reaction products

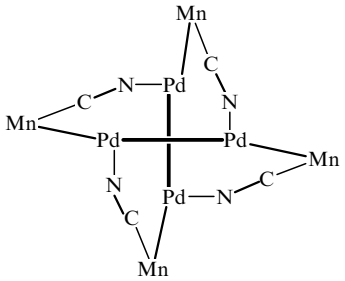
If it is assumed that the molybdenum atoms incorporated in the complex retain a zero oxidation state, then the observed reaction can be regarded as the reduction of the Pd(+1) atoms to Pd(+0.5). The resulting cluster is the first example of a compound in which eight metal atoms linked by the metal–metal interaction lie in the same plane.

The interaction of the another carbonylmetallate — $[(\eta^5\text{-}C_5H_4Me)Mn(CN)(CO)_2]^-$ (in the form of the sodium salt) — and complex **38** leads,[139] as in the preceding case, to the displacement of all the ligands and the formation of the octanuclear cluster $[(OC)Pd(\mu\text{-}NC)Mn(\eta^5\text{-}C_5H_4Me)(CO)_2]_4$ **45**. In contrast to the preceding reaction, in this case the formation of the cluster is not accompanied by any kind of oxidation-reduction reactions and, if it 1s assumed that the carbonylmanganate ligand retains a formal −1 change, then the formal oxidation state of palladium in cluster **45** remains +1.



45

The structure of cluster **45** is unusual. It can be regarded as two mutually orthogonal bent metal chains $Mn-Pd_2-Mn$ with short metal–metal distances. The metal chains are linked to one another by four cyanide bridges.



Furthermore, one terminal carbonyl group is linked to each palladium atom, while the coordination environment of each manganese atom is supplemented by the methylcyclopentadienyl ligand and two carbonyl groups (one terminal and the second behaving as a semibridge in relation to the nearest palladium atom).

b. Reactions of palladium carbonyl acetate with oxygen-containing nucleophiles

In the presence of alkali metal acetates in solution in glacial acetic acid, complex **38** decomposes to metallic palladium in accordance with the equation

$$Pd_4(CO)_4(OAc)_4 \xrightarrow{NaOAc} 4Pd(0) + 2CO + 2CO_2 + 2Ac_2O.$$

Analysis of the kinetic data permits the conclusion that the reaction mechanism involves a repeated alternation of the following cycles: insertion of CO in the Pd–OAc bond, elimination of CO_2 with formation of an acyl fragment, liberation of Ac_2O, and the formation of the Pd–Pd bond. Overall, the process proceeds *via* the reductive condensation of the palladium clusters.[124, 140]

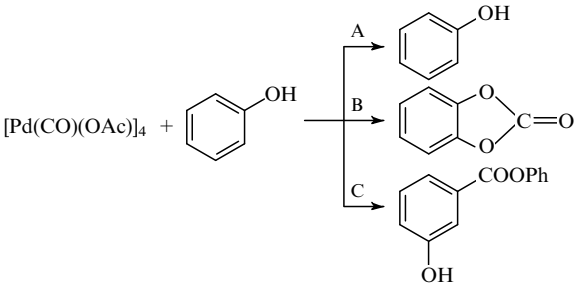
Presumably the interaction of complex **38** and water described by the equation

$$Pd_4(CO)_4(OAc)_4 + 2H_2O = 4Pd + 4AcOH + 2CO + 2CO_2,$$

also takes place *via* a reductive condensation mechanism.

The reaction of complex **38** with aliphatic C_1-C_3 alcohols proceeds simultaneously *via* several paths with formation of CO_2 and dialkyl carbonate — the products of the oxidation of the coordinated CO molecules, as well as carbonyl compounds arising owing to the oxidation of the corresponding alcohols. It has been observed that the reaction with ethanol results in the appearance of both dialkyl carbonates and carbonyl compounds — acetaldehyde and its acetals. In the case of isopropyl alcohol, dialkyl carbonate and carbonyl compounds are produced. The reaction of cluster **38** with methanol leads to the formation of only methyl acetate. It has been shown [141, 142] that the reactions of complex **38** with alcohols proceed *via* several paths with formation of carbonyl [$L_nM(CO)$], alkoxy- (L_nMOR), alkoxycarbonyl (L_nMCOOR), and acyl [$L_nMC(O)R$] derivatives of palladium.

In the interaction of complex **38** with phenol,[143], reactions *via* three paths, leading to the formation of phenyl acetate, diphenyl carbonate, and phenyl salicylate (paths A, B, and C), are also observed.

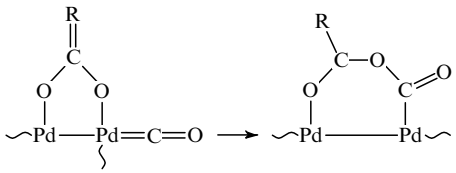


c. Oxidation of the coordinated CO groups in the carbonyl carboxylate complexes

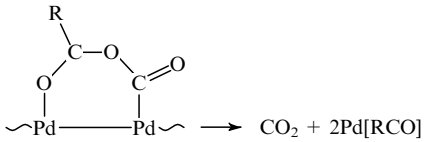
The thermal decomposition of carbonyl complexes leads as a rule to the elimination of carbon monoxide. The thermolysis of the carbonyl carboxylate clusters proceeds *via* a fundamentally different path. It has been observed that the thermolysis of the clusters in the absence of oxygen entails the inner-sphere oxidation of the neutral ligand with formation of CO_2. In the reaction, an oxygen atom is transferred from the carboxylate group to the carbonyl group, *i.e.* the acetate group functions as an oxygen donor (oxidant):[124, 144, 145]

$$Pd_4(CO)_4(OAc)_4 \longrightarrow Pd + CO_2 + Ac_2.$$

The oxidation-reduction process which has been put forward, in which carbon monoxide is oxidised by the oxygen of the coordinated carboxylate groups, apparently involves the insertion of CO in the metal–oxygen bond with formation of an unstable intermediate:



The decomposition of the intermediate leads to the elimination of CO_2 and the formation of reduced forms of palladium and coordinated acyl groups:



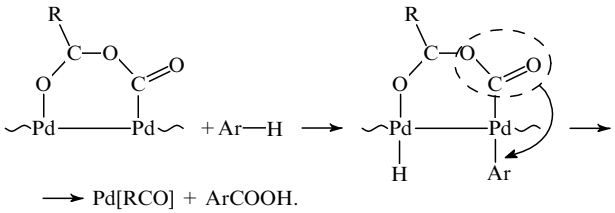
The recombination of the two acyl ligands bound to the core of the cluster affords the biacyl:

$$2Pd[RCO] \longrightarrow 2Pd + RCOCOR.$$

If the thermolysis of the carbonyl carboxylate clusters is carried out in benzene or toluene solution, the main product of the oxidation of the coordinated CO groups is not CO_2 but an arenecarboxylic acid:

$$Pd_4(CO)_4(OAc)_4 + Ar{-}H \longrightarrow \underset{(\sim 10\%)}{Pd} + CO_2 + \underset{(\sim 80\%)}{ArCOOH}.$$

Presumably oxidative addition of an arene molecule to the palladium core with dissociation of the H–Ar bond, followed by the insertion of CO_2 in the Pd–C_{aryl} bond, takes place simultaneously with the transfer of an oxygen atom from the carboxylate to CO:



The inner-sphere transfer of an oxygen atom from the carboxylate group to the neutral carbonyl group is a fairly general reaction. Complexes containing as ligands carboxylate groups having both powerful electron-donating substituents at the carboxylate group [the acetate CH_3COO and the pivalate $(CH_3)_3COO$] and powerful electron-accepting substituents (the trifluoroacetate CF_3COO and the monochloroacetate CH_2ClCOO) are capable of entering into this reaction. The CO_2 produced by the reaction is coordinated to the palladium atoms of the decomposing cluster, exhibits unusual properties, and is capable of being inserted into the C–H bonds of aromatic compounds.

Summarising the data on the synthesis, structures, and reactivities of the carbonylpalladium(+1) complexes, one should note that their number is appreciably smaller than that of the carbonylpalladium(0) complexes.

All the palladium(+1) complexes contain an even number of metal atoms (2 or 4). Since the main structural element of polymeric carbonyl halides is the species [X–Pd(μ-CO)$_2$Pd–X] and there is no metal–metal bond between such species, it appears legitimate to regard them as dinuclear. Complexes with a higher nuclearity have not been described for Pd(+1). All the palladium(+1) carbonyl complexes are diamagnetic and the pairing of electrons at the two metal atoms, having the d^9 electronic configuration, takes place either as a result of the formation of a metal–metal bond (with a Pd–Pd distance of ~ 2.7 Å) or *via* the formation of a three-centre four-electron bond incorporating two palladium atoms and one carbon atom of the bridging carbonyl ligand.

In complexes containing only carbonyl and halide, carboxylate, or fluorosulfate ligands, the Pd–Pd distance is close to 2.7 Å and the stretching vibrational frequency of the μ-CO group is in the range from 1900 to 2000 cm^{-1}. Being relatively resistant to thermal decomposition, these complexes are fairly sensitive to the action of oxygen-containing nucleophiles and, when treated with, for example, water or lower aliphatic alcohols, decompose with formation of palladlum metal.

The introduction of *n*-donor ligands into the complexes leads as a rule to an increase in the metal–metal distance in the Pd(μ-CO)Pd fragment and to a decrease in the stretching vibrational frequency of the μ-CO group. The resistance of these complexes to reductive decomposition on treatment with nucleophiles increases simultaneously and some of them, for example, $[Pd_4(CO)_2Phen_4](OAc)_4$ or $[Pd(\mu\text{-dmpm})Cl]_2(\mu\text{-CO})$, are readily soluble and are stable even in aqueous solutions.

In contrast to palladium(0) carbonyls, the reactivity of palladium(+1) carbonyls is not limited to ligand substitution reactions and has been investigated much more fully. In our view, the oxidation–reduction reactions of carbonyl carboxylate clusters is of greatest interest. In the first place, this is the reaction involving the intramolecular transfer of an oxygen atom from the carboxylate ligands to the coordinated carbonyl group. This reaction can serve as a model for the whole series of oxidation–reduction processes occurring with participation of CO and catalysed by palladium compounds.

V. Palladium(+2) carbonyl complexes

A considerably smaller number of palladium(+2) complexes with carbonyl ligands than palladium carbonyls containing the metal in other oxidation states have been synthesised and reliably characterised at the present time. This can probably be accounted for primarily by the striking tendency of Pd(+2) to be reduce by carbon monoxide and hence by the high lability of Pd(+2) carbonyls in proton-donating basic solvents.

1. Binary carbonyls

The first studies on the chemistry of palladium(+2) carbonyls date back as early as the past century,[6] but sufficiently definite conclusions concerning the structure of the palladium(+2) carbonyl complexes have been reached on the basis of studies carried out in the last three–five years. In these investigations, the key compounds were characterised by X-ray diffraction. This applies primarily to the binary cationic carbonyls.

A series of cationic carbonyls have been obtained quite recently in strong protic acids (HSO_3F) or superacids ($HSO_3F \cdot SbF_5$).[146, 147] In the solid state, the carbonyl cations were stabilised by very weakly basic anions SO_3F^- or $Sb_2F_{11}^-$. These are singly-charged linear cations $[M(CO)_n]^+$ [M = Au or Ag, n = 1 or 2;[148–150] M = Hg, n = 1 (Ref. 151)] or square-planar cations $[M(CO)_4]^{2+}$ [M = Pd(**46**) or Pt(**47**)[152, 153]].

Complexes **46** and **47** have been obtained as a result of the reductive carbonylation of $[Pd(SO_3F)_3]_2$ or $Pt(SO_3F)_4$ respectively and the subsequent solvolysis of the resulting neutral complex in liquid antimony(+5) fluoride.

Treatment of the solid salt containing Pd(+2) and Pd(+4) with CO (P_{CO} = 0.5 atm, 25 °C) affords $Pd(CO)_2(SO_3F)_2$ in accordance with equation

$$Pd(+2)Pd(+4)(SO_3F)_6 + 5CO \longrightarrow 2Pd(CO)_2(SO_3F)_2 + S_2O_5 + CO_2.$$

48

According to IR spectroscopic data, when the reaction is carried out in the absence of solvent, complex **48** is formed exclusively as the *cis*-isomer. On the other hand, when fluorosulfonic acid HSO_3F is used as the solvent, a mixture of isomers is produced. In liquid antimony fluoride in the presence of free carbon monoxide (P_{CO} = 0.5 atm, 60–80 °C), complex **48** is converted into $[Pd(CO)_4][Sb_2F_{11}]_2$ in accordance with the equation

$$Pd(CO)_2(SO_3F)_2 + 8SbF_5 + 2CO \longrightarrow [Pd(CO)_4][Sb_2F_{11}]_2.$$

Complex **47**, the platinum analogue of complex **46**, was obtained in the same manner. Complexes **46** and **47**, isolated in the form of white powders, are thermally fairly stable (they begin to decompose at 155 and 200 °C respectively), but are extremely sensitive to moisture. The stretching vibration frequencies of the CO groups in both complexes are very high (2259 cm^{-1} for complex **46** and 2261 cm^{-1} for complex **47**) and are higher by approximately 120 cm^{-1} than for free carbon monoxide. These data suggest that, as in the neutral and anionic divalent palladium carbonyl halides, in these compounds the σ-donor properties of the CO group greatly predominate over its π-acceptor properties

Dicarbonylpalladium fluorosulfate **48** (a precursor of complex **46**) has been obtained[154] in the form of a thermally fairly stable yellow substance (decomposition temperature 117 °C). Complex **48** is the first example of a thermally stable compound in which two monodentate carbonyls are coordinated to one Pd(+2) atom. Two other complexes of the type $Pd(CO)_2R_2$ ($R = C_6F_5$ or C_6Cl_5),[155] where two terminal carbonyls are coordinated to one palladium atom, are much less stable and already begin to decompose at a temperature below −30 °C. The fluorosulfate group in complex **48**, which has a pronounced electron-withdrawing capacity, probably enhances the electron-accepting properties of the metal atom. The stretching vibrational frequency of the CO group is 2218 cm^{-1}, which is the highest observed for all the known neutral carbonyl complexes of platinum metals.

Complex **48** is the first example of a structurally characterised neutral palladium carbonyl.[156] Crystals of the *cis*-isomer of compound **48**, suitable for X-ray diffraction, have been obtained on slow recrystallisation of the complex from its saturated solution in fluorosulfonic acid. The palladium atom in the molecule of compounds **48** is surrounded by two *cis*-disposed terminal carbonyl groups and monodentate fluorosulfate groups located at the corners of a planar square. The C–O bond is fairly short (1.106 Å), which agrees well with its high frequency ν_{CO} in the IR spectra and with the conclusion that the π-back-donation from the metal to the carbonyl group is absent or at least greatly reduced. A weak interaction of the noncoordinated oxygen atom with the carbon atom of the carbonyl groups has been noted (the C–O distance is 2.819–3.172 Å). In the absence of π-back-donation, secondary contacts, with participation of the electrophilic carbon atom of the CO group as an electron acceptor probably promote somewhat charge compensation and exert a stabilising influence on the entire molecule.

2. Neutral and anionic palladium(+2) carbonyl halides

The synthesis of the three carbonyl derivatives of palladium $PdCl_2 \cdot (CO)$, $PdCl_2 \cdot (CO)_2$, and $PdCl_2 \cdot (CO)_3$ on interaction of solid $PdCl_2$ with carbon monoxide at 260 °C, described by Fink,[6] could not be reproduced subsequently. Manchot[157] showed that complexes having this composition are actually formed by the platinum present as an impurity in the initial palladium salt. However, one of these complexes has been obtained from pure palladium chloride. The divalent palladium carbonyl $Pd(CO)Cl_2$, which is extremely unstable when acted upon by atmospheric moisture, has been obtained[158] at 20 °C from solid $PdCl_2$ and carbon monoxide, from which water vapour had been carefully removed and which had been saturated with anhydrous methanol vapour, and also from a suspension of $PdCl_2$ in anhydrous methanol on treatment with dry carbon monoxide:

$$Pd(CO)Cl_2 + H_2O = Pd + 2HCl + CO_2.$$

A similar complex $Pd(CO)Br_2$ has been obtained by the interaction of $PdBr_2$ and carbon monoxide saturated with methanol vapour and also on treatment of a suspension of K_2PdBr_4 in dioxane containing 0.5%–2.0% of H_2O with carbon monoxide. Palladium(+2) bromide complexes are not carbonylated in anhydrous dioxane.[96, 158] It has been suggested[158] that the above palladium(+2) carbonyl halides are dimeric and that the anions

$[Pd(CO)X_3]^-$ are also present in a solution containing an excess of halide ions. In these anionic complexes, isolated in the form of a salt with the tetetrabutylammonium cation,[159] the CO molecule may be bound as a monodentate ligand, like the alkene in a π-complex of the Zeise's salt type.

The complexes: listed above (both neutral and anionlc) were initially insufficiently fully characterised and the information available about their structure was tentative. However, later the structure of analogues of these compounds was established quite definitely.

Thus the carbonylation of $PdC1_2$ in thionyl chloride under fairly strong conditions (P_{CO} = 50 atm, 120 °C) yielded[160] $Pd_2(CO)_2Cl_4$ **49**:

$$2PdCl_2 + 2CO \longrightarrow Pd_2(CO)_2Cl_4.$$

The interaction of NH_2Et_2Cl and compound **49** in solution in CH_2Cl_2 leads to the formation of the anionic complex $NH_2Et_2[Pd(CO)Cl_3]$ **50** .Complexes **49** and **50** have been characterised by elemental analyse and IR spectroscopy (ν = 2167 cm^{-1} for complex **49** and 2141 cm^{-1} for complex **50).**

Complex **49** is stable only in a CO atmosphere, decomposing in the absence of CO. The terminal CO groups are readily substituted by tertiary phosphines, forming initially $Pd_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2$ and then *trans*-$PdCl_2(PPh_3)_2$.

It has been suggested that complex **49** is a dimer with two chloride bridges; the two terminal carbonyl ligands are *trans*-disposed relative to the metal–metal axis. This is in fact the structure of the platinum analogue $Pt_2(CO)_2I_4$ isolated in a crystalline form and characterised by IR spectroscopy (ν_{CO} = 2122 cm^{-1}) and X-ray diffraction data.[161] This is a dimer with a nonbonding metal–metal spacing, two bridging iodide ligands, and two *trans*-disposed terminal carbonyl groups.

The complex to which the authors attribute the composition $PdCO)Cl_2(PPh_2$-polymer) may have a similar structure (but with carbonyl and not halide bridges). The complex has been obtained[162] by carbonylating the corresponding benzonitrile derivative 'attached' to the polymeric support *via* a phosphide bridge. The stretching vibrational bands of the CO group in the range 1944–1964 cm^{-1} have been found in the IR spectrum of the complex, indicating that these groups are of the bridging type.

On the basis of spectroscopic data for the anion of complex **50**, a structure has been proposed in which the metal atom has a planar environment (three chlorine atoms and one carbon atom of the terminal carbonyl ligand). It has been found that the anion of the salt $(NBu^n_4)^+[Pd(CO)Br_3]^-$ **51** has precisely this structure. Complex **51** has been obtained by treating a solution of $(NBu^n_4(PdBr_3)$ in ttetrachloroethane with CO (P_{CO} = 1 atm).[163]

The carbonylation of $PdBr_2$ (P_{CO} > 70 atm) leads to the formation of $Pd_2(CO)_2Br_4$, which, judging from the IR spectra (ν_{CO} = 2145 cm^{-1}), is constructed similarly to complex **49**. The iodide analogue of complex **49** could not be obtained. However, treatment of a solution of PdI_2 in toluene with CO in the presence of stoichiometric amounts of I^- leads to $[Pd(CO)I_3]^-$. The latter has been isolated as a salt with $(NBu^n_4)^+$ and has been characterised by IR spectroscopy (ν_{CO} = 2015 cm^{-1}).

According to X-ray diffraction data for complexes **50** and **51**, the palladium atoms in the anions $[Pd(CO)Cl_3]^-$ and $[Pd(CO)Br_3]^-$ have a square-planar environment with the usual $Pd-C_{CO}$ (1.87 Å for both anions) and C–O (1.10 and 1.11 Å respectively) distance. The stability of the palladium carbonyl halide complexes (both neutral and anionic) decrease in the sequence Cl > Br > I.[163]

The study of the kinetics of the exchange of the carbonyls in the carbonyl halides between $[M(^{13}CO)X_3]^-$ and ^{12}CO (IR and ^{13}C NMR spectroscopy) showed that the carbonyl ligands in these complexes are bound fairly strongly and that the rate of exchange of the carbonyls is lower almost by six orders of magnitude than the rate of exchange of ethene in the analogous ethene π-complexes.[164]

The formation of complex **49** in thionyl chloride has been investigated and the thermodynamic constants of the process have been determined, which made it possible to estimate the energy of the Pd–CO bond (~ 24 kcal mol^{-1}).[163] Analysis of the thermodynamic and spectroscopic data led to the conclusion [155, 165] that the contribution of metal-to-ligand the π-back-donation in the palladium carbonyls is slight and that the strength of the Pd–CO bond is determined almost exclusively by the σ-donor capacity of the carbonyl ligand.

This conclusion appears fairly justified for the neutral and anionic palladium(+2) carbonyl halides, but the question of the contribution of the σ-donor and π-acceptor interactions in organopalladium compounds with carbonyl ligands (see below) requires additional discussion.

The contribution of a particular type of bonding of the carbonyl ligands may be inferred from spectroscopic data.[29] As a result of the predominance of the σ-donor properties over the π-acceptor properties in the coordinated carbon monoxide molecule, the stretching vibration frequency of the CO group becomes higher than in free CO, while the chemical shift of the carbon atom in the ^{13}C NMR spectra is observed at δ = 120–130 ppm, in contrast to 190–220 ppm for the classical carbonyls.

3. Palladium(+2) carbonyl halides containing additional stabilising ligands

Palladium(+2) carbonyl halide complexes with additional stabilising ligands have been obtained in both neutral and anion forms. For example, the reaction of CO with a suspension of the $[Pd_2Cl_2(PEt_3)_4]^{2+}$ fluoroborate in chloroform afforded the cationic complex $[PdCl(CO)PEt_3)_2][BF_4]$, which has been characterised by elemental analysis and IR spectroscopy (ν_{CO} = 2140 cm^{-1}) and which is comparatively stable under a CO atmosphere. In the absence of CO from the gas phase over the complex a carbon monoxide molecule is evolved and the initial complex is reformed.[166, 167] In this case it is reasonable to postulate that the CO groups are terminal if the palladium atom contains four ligands in the coordination sphere, as in the majority of other palladium(+2) complexes. For the complex anion $[Pd(CO)(SnCl_3)Cl]^-$ isolated [168] as a salt with NEt_4^+ the frequency ν_{CO} is equal 2054 cm^{-1}.

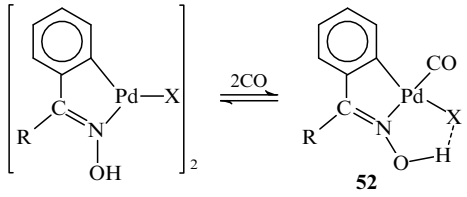
The neutral complexes $Pd(CO)(L)Cl_2$, where L = dimethyl sulfoxide, diethyl sulfoxide, or diethyl sulfide, have been obtained[169, 170] by carbonylating $[PdLCl_2]_2$. The authors attribute a mononuclear structure to these compounds, but on the basis of IR spectroscopic data (ν_{CO} = 1927–1977 cm^{-1}) one may postulate that the complexes are at least dinuclear and contain bridging CO groups.

The complex Pd(PhN=NPh)Cl_2(CO), obtained by the reaction of CO and Pd(PhN=NPh)Cl_2(PhCN),[171] should also probably be at least dimeric. The stretching vibrational frequency of the CO group in the complex is 1900 cm^{-1}, which definitely indicates a bridging coordination of the ligand.

Unfortunately, none of the complexes of this type have been characterised by X-ray diffraction analysis.

4. Organopalladium compounds containing carbonyl ligands

The complexes obtained by the reaction of carbon monoxide and dimeric palladium complexes containing oxime ligands may be regarded as an example of palladium(+2) compounds containing both the carbonyl ligand and an organopalladium group with a Pd–C σ-bond:[172]



52

R = Ph, Me, H.

Table 4. Palladium(+2) carbonyl complexes characterised by X-ray diffraction.

No.	Complex	No. of CO groups bound to Pd	Mode of coordination of CO groups	ν_{CO} /cm^{-1}	Pd–C carbonyl bond length	C–O bond length	Geometrical environment of Pd atom	Ref.
1	$Pd(CO)_2(SO_3F)_2$	2	η	2218 [a]	1.94	1.106	*cis*-configuration, planar square	152, 153
2	$(NH_2Et)_2[PdCl_3(CO)]$	1	η	2141	1.87	1.100	planar square	160
3	$(Bu^n_4N)[PdCl_3(CO)]$	1	η	2132	1.87	1.100	the same	163
4	$(Bu^n_4N)[PdBr_3(CO)]$	1	η		1.87	1.110	"	163
5	$[PPh_3(CH_2Ph)]\{Pd(R)Cl_2(CO)]$	1	η	2100	1.853	1.145	"	175
6	dmbaPd(μ-Cl)(μ-M′)Pddmba ([M′] = $[Co(CO)_4]^-$)	2	η (on Co atom, w.r.t. Pd–Co bonds)	2018 1963 1880 1860	2.17 2.13	1.150 1.140	distorted square (disregarding the Pd–CO bond)	173
7	dmbaPd(μ-Cl)(μ-M′)Pddmba ([M′] = $[CpMo(CO)_3]^-$)	2	μ (w.r.t. Pd–Mo bonds) μ$_3$ (on the Pd_2Mo triangle)	1844 1770	2.28 2.20 2.39	1.150 1.140 1.130	distorted octahedron (disregarding the Pd–Pd bond)	173

[a] For free carbon monoxide, ν = 2140 cm^{-1}.

Complexes of type **52** have been isolated in the solid state and characterised by elemental analysis and IR spectroscopy (ν_{CO} = 2108–2136 cm^{-1}).

The dimeric complexes containing an organopalladium group with a Pd–C σ-bond proved to be convenient precursors for the synthesis of heteronuclear compounds.[173] Thus the cyclopalladated dimers with the general formula [Pd(*C*–*N*)Cl]$_2$ [*C*–*N* = dimethylbenzylamine (dmba), 2-(dimethylamino)-toluene (dmat), or 8-methylquinoline (8-mq)] react with anionic carbonylmetallates M^- {$M^- = [Co(CO)_4]^-$, $[Fe(CO)_3(NO)]^-$, or $[M(CO)_3Cp]^-$, where M = Cr, Mo, or W}, the carbonylmetallates substituting one of the bridging chloride ligands and forming thereby the heterometallic complexes (*C*–*N*)Pd(μ-Cl)(μ-M)Pd(*C*–*N*) **53**. The structures of complexes **53a** {*C*–*N* = dmba, $M^- = [Co(CO)_4]^-$} and **53b** [*C*–*N* = dmba, M^- = $Mo(CO)Cp^-$] have been investigated by X-ray diffraction analysis. In both molecules the palladium atoms are at a distance exceeding the sum of the covalent radii (3.442 Å for **53a** and 3.241 Å for **53b**). In complex **53a**, the Co atom is linked to two Pd atoms, two carbonyl groups are bridging in relation to the Pd–Co bonds, and two others are coordinated terminally to the cobalt atom. In complex **53b**, having a similar metal core, among the three carbonyl ligands two are bridges on the Pd–Mo bonds, whilst the third is μ$_3$-coordinated to the Pd_2Mo metallotriangle.

Organopalladium carbonyl complexes of another type have been synthesised[174] by ligand substitution on treatment the complexes of the type $Pd(C_6F_5)(ClO_4)L_2$, where L = Bipy, Phen, tetraethylenediamine, or 2PR$_3$ with CO (*P* = 1 atm, 0 °C, toluene, chloroform, or acetone).

$$Pd(C_6F_5)(ClO_4)L_2 + CO = [Pd(C_6F_5)(CO)L_2](ClO_4).$$

The available information about structures of this type is also limited to the results of elemental analysis, the conductivity of solutions, and IR spectroscopy (ν_{CO} = 2132–2160 cm^{-1}). There are no structural data for the complexes, but the frequencies, ν_{CO}, in the IR spectra indicate unambiguously the terminal coordination of the carbonyl.

The interaction of $[PPh_3(CH_2Ph)]_2Pd(R)Cl(\mu\text{-}Cl)]_2$ and carbon monoxide (P_{CO} = 1 atm, 20 °C, CH_2Cl_2) yielded[175] the complexes $[PPh_3(CH_2Ph)][Pd(R)Cl_2(CO)]$ [R = C_6H_3(2-Me)(6-NO_2) (**54**) or $C_6H_2(NO_2)_3$-2,4,6 (**55**)]. These complexes are stable in the solid state, but in solution they eliminate CO, reconverting into the initial state. The IR spectra of both complexes contain characteristic bands of terminal CO groups 2100 cm^{-1} for **54** and 2115 cm^{-1} for **55**). The frequencies ν_{CO} are lower than for the cationic complex $[Pd(C_6H_5)(CO)L_2]^+$ (2132–2163 cm^{-1})[174] or the neutral complex $[Pd(C_6F_5)_2(CO)_2]$ (2152–2186 cm^{-1}),[155] but higher than the frequencies ν_{CO} for the palladium carbonyl complexes containing the metal in lower oxidation states (for example, for $Pd(CO)_n$, where *n* = 4, 3 or 2, ν_{CO} = 2060, 2044, and 2050 cm^{-1} respectively[33]). IR spectroscopic data indicate the occurrence of the 'classical' π-donation in the complexes **54** and **55**.

The structure of complex **54** has been investigated by X-ray diffraction. In the anion, the palladium atom has a planar environment consisting of two *cis*-disposed chlorine atoms, the carbon of the terminal carbonyl group (the Pd–C bond length is 1.853 Å and the Pd–C–O angle is 175.4°) and the 2-methyl-6-nitrophenyl ligand. The C–O distance, amounting to 1.145 Å, has the usual value for terminal carbonyl groups.

Summarising the data presented on the structure of palladium(+2) carbonyl complexes, one should note that all the reliably characterised homonuclear complexes (Table 4) are monomers with terminal CO groups. In complexes containing halide and alkyl ligands (No. 2–No. 5, Table 4) apart from the terminal carbonyl, the strength of the Pd–C_{CO} bond is low, which is the reason for the low thermal stability of the carbonyls. The presence of the fluorosulfate group, which possesses strong electron-withdrawing properties, in the complex $Pd(CO)_2(SO_3F)_2$ (No. 1, Table 4) leads to an increase in the electron-accepting capacity of the palladium atom. The consequence of such increase is, on the one hand, the strengthening of the Pd–C_{CO} bond, expressed by an unusually high thermal stability of palladium complexes with a terminal carbonyl group, and, on the other hand, extremely high stretching vibrational frequencies of the CO group.

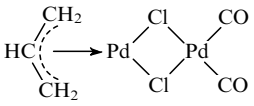
In the Pd(+2) complexes where the metal atom has the d^8 electronic configuration and a much smaller ability to donate the metal π electrons to the corresponding orbitals of the CO molecule than in the palladium(0) and palladium(+1) complexes, an enhancement of the σ-donor properties of the carbonyl has been observed. The enhancement of the σ-donor and the weakening of the π-acceptor properties of the carbonyl ligand are accompanied by an increase in the stretching vibration frequencies of the CO group (Table 4).

VI. Palladium carbonyl complexes containing the metal in fractional oxidation state

The appearance of unusual or 'intermediate', including fractional, oxidation states of transition metals is associated with the development of the chemistry of polynuclear compounds, especially the chemistry of clusters.

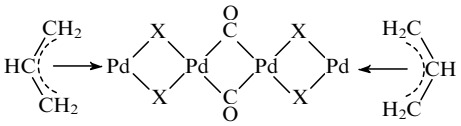
1. The synthesis and structure of clusters containing a metal in a fractional formal oxidation state

π-Allylbis(carbonylchloropalladium) having the composition π-$C_3H_5[PdCl(CO)]_2$ **56**, described as early as 1964, should probably be regarded as the first palladium carbonyl in which the the formal oxidation state of the metal atom proved to be nonintegral.[176] The authors proposed a composition for the complex where there are three singly-charged acido-ligands for two palladium atoms; the FOS of the metal in the complex is +1.5. The complex was obtained by passing carbon monoxide through a solution of a mixture of $PdCl_2$ and HCl in methanol in which π-allylpalladium chloride had been suspended. The IR spectrum of the resulting bright-yellow precipitate, which did not dissolve in the usual organic solvents, contained an intense band at 1940 cm^{-1}, which the authors attributed to the stretching vibrations of the terminal CO group. The absence of bands in the range 286–360 cm^{-1}, characteristic of the vibrations of the Pd–Cl bond, led to the conclusion that the chloride ligands were involved in bridging coordination. The following structure of **56** was proposed:



However, the structure of complex **56** is somewhat more complicated. On the basis of current data concerning the structure of palladium carbonyls, one may postulate that the carbonyl groups in this compound are bridges, like the chloride ligands. The bridging coordination of the allyl ligands cannot be ruled out either.

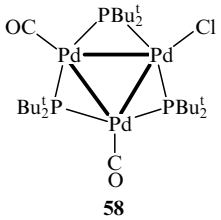
Similar complexes with the composition π-$C_3H_5[PdX]_2(CO)$ **57**, where X = Cl or Br, have been obtained by passing carbon monoxide through a methanol solution of π-allylpalladium chloride.[89] The authors suggest that the compounds formed are tetramers, in which bridging halide and semibridging carbonyl groups alternate:



ν_{CO} = 1937 cm^{-1} (for X = Cl), ν_{CO} = 1929 cm^{-1} (for X = Br).

The presence of three singly-charged acido-ligands in the molecule containing two metal atoms makes it possible to assign a formal oxidation state of +1.5 to palladium. Unfortunately, in both cases the substances were characterised only by elemental analysis and IR spectroscopy, so that the interpretation of their structure does not appear sufficiently reliable. However, the presence in these compounds of bridging carbonyl groups is undoubtedly reliable. Furthermore, the data on the magnetic properties of complexes **56** and **57** might prove useful in the interpretation of their structure. Thus if the proposed formulae are correct, it follows that complex **56** should be paramagnetic and complex **57** diamagnetic.

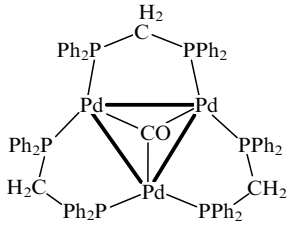
The trinuclear carbonyl clusters synthesised later were more fully and reliably characterised. Thus the interaction of $LiPBu^t_2$ and the polymeric carbonyl chloride $[Pd(CO)Cl]_n$ in THF at −78 °C afforded (together with other products) the cluster $Pd_3(\mu\text{-}PBu^t_2)_3(CO)_2Cl$ **58**, in which the metal has a formal oxidation state of +1.33.[177]



58

According to X-ray diffraction data, the palladium atoms in complex **58** form a triangle with Pd–Pd distances ranging from 2.949 to 3.000 Å which indicates a weak metal–metal interaction. All the phosphide groups are bridges along the Pd–Pd bonds, while one chloride and two carbonyl ligands are terminal. The relatively low stretching vibrational frequencies of the terminal CO groups (two bands in the IR spectrum at 2035 and 2030 cm^{-1}) compared with the ν_{CO} in the mononuclear complexes (usually above 2100 cm^{-1}) are due to the presence of phosphide species with their high electron content.

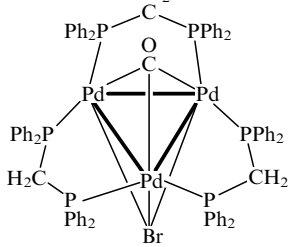
Another type of carbonyl trinuclear clusters represented by the dication $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ **59**, was described for the first at time by Manojlovic-Muir *et al.*[178] and Puddephatt[179] and was characterised in detail by Lloyd and Puddephatt[180]. Cluster **59** has been obtained by the reaction of $Pd(OAc)_2$ and dppm with carbon monoxide (P_{CO} = 1 atm) in solution in aqueous acetone containing an excess of trifluoroacetic acid and was isolated as a salt with CF_3COO^- **59a**. The interaction of complex **59a** with an excess of $NH_4(PF_6)$ leads to the formation of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3](PF_6)_2$ **59b**. Complex **59** has been characterised by IR spectroscopy (ν_{CO} = 1820 cm^{-1} and X-ray diffraction. The palladium atoms in the cation form a triangle (the Pd–Pd sides are 2.576, 2.607, and 2.610 Å, to the sides of which diphosphine bridges are coordinated symmetrically, while the carbonyl group is linked to all three metal atoms (the Pd–C distance ranges from 2.09 to 2.18 Å.



59

In the clusters of type **59** containing only neutral ligands, there are two positive charges on three metal atoms and hence the FOS of each palladium atom is +0.67.

The interaction of halides or of the trifluoroacetate anion with the dication **59** is reversible, without change in the FOS of the metal atoms, and leads to the formation of $[Pd_3(X)(\mu_3\text{-}CO).(\mu\text{-}dppm)_3]^+$ (X = CF_3COO, Cl, Br, I) **60**. It has been established that the capacity for coordination diminishes in the sequence I > Br > Cl > CF_3COO and that each successive ligand can be quantitatively substituted by the preceding one.[181, 182]



60

Clusters **60** have been isolated in the form of a salt with CF_3COO^- and have been characterised by X-ray diffraction analysis for X = I[180] and Cl.[181] In both cases, the anionic ligand X is μ_3-coordinated to the side of the Pd_3 triangle opposite the side to which the μ_3-CO group is coordinated.

It is noteworthy that the Pd–X distances in the $Pd_3(\mu_3\text{-}X)$ groups are fairly large (the Pd–X distance is 2.741–3.161 Å for X = Cl and 2.951–3.083 Å for X = I) and an unambiguous conclusion concerning the incorporation of X in the coordination sphere of the cluster cannot be reached on the basis of X-ray diffraction data. However, the results of studies of the molar conductance of solutions of the clusters and of their spectra in the

Table 5. Palladium complexes containing the metal in fractional oxidation states.

Compound	FOS	Physicochemical methods	ν_{CO} /cm^{-1}	Metal core, Pd – Pd distances /Å	Ref.
π-$C_3H_5[PdCl(CO)]_2$	+0.67	elemental analysis, IR spectroscopy	1940		176
$\{\pi$-$C_3H_5[PdX]_2(CO)\}_2$ (X^- = Cl^- or Br^-)	+1.5	the same	1937 (X = Cl) 1929 (X = Br)		89
$Pd_3(\mu$-$Bu^t_2P)_3(CO)_2Cl$	+1.33	elemental analysis, IR spectroscopy, XRD	2035, 2030	triangle, 2.949 – 3.000	177
$[Pd_3(\mu_3$-$CO)(\mu$-dppm$)_3]X_2$ (X^- = CF_3COO^- or PF_6^-)	+0.67	elemental analysis, IR spectroscopy, XRD, ^{31}P NMR	1820	triangle, 2.576, 2.607, 2.610	178, 179, 180
$[Pd_3(\mu_3$-X$)(\mu_3$-$CO)(\mu$-dppm$)_3]X$ (X^- = CF_3COO^-, Cl^-, Br^-, I^-)	+0.67	the same	1712 (X = CF_3COO)	triangle, 2.584 – 2.603	181, 182
$[Pd_3(\eta^5$-$C_5Me_5)_3(\mu_3$-$CO)_2]CF_3COO$	+0.33	elemental analysis, IR spectroscopy, XRD	1769	triangle, 2.63	183

visible region on titration of the cluster solution with a solution of KX (X = Cl, Br, I) showed that the anionic ligand is incorporated into the coordination sphere of the palladium cluster and that the contribution of the covalent component to the formation of the Pd – X bond greatly exceeds that of the ionic component.

The mechanism of the formation of clusters **59** and **60** has been investigated [182] by ^{31}P NMR. The NMR monitoring of the reaction solution containing initially $Pd(OAc)_2$, dppm, and CO in an acetone – CF_3COOH – H_2O mixture made it possible to identify the formation of the complexes $Pd(CF_3COO)_2$(dppm) **61**, $Pd_2(CF_3COO)_2(\mu$-dppm$)_2$ **62**, $Pd_2(CF_3COO)_2(\mu$-$CO)(\mu$-dppm$)_2$ **63**, and $[Pd_3(\mu$-$CF_3COO)(\mu_3$-$CO)(\mu$-dppm$)_3](CF_3COO)$ **64**. There are grounds for the postulate that a short-lived palladium(0) complex with diphosphine is formed initially and then reacts with complex **61** to form compound **62** or **63**. The subsequent reaction of the palladium(0) complex containing bis(diphenylphosphino)methane with compound **62** or **63** leads to the appearance of $[Pd_3(\mu_3$-X$)(\mu_3$-$CO)(\mu$-dppm$)_3]^+$ (X = CF_3COO) **60**. It can be assumed arbitrarily that the two palladium atoms in the base of the triangle, linked by a shortened Pd – Pd bond (2.567 Å), have a FOS of +1. The third metal atom at the apex of the triangle than has a zero FOS. Incidentally. such treatment should be regarded as a marked simplification, which is used only for a clear representation of a more complex situation. The bridging halide ligand in the inner coordination sphere of complex **60** is readily substituted by another halide when the complex interacts with KX in acetone.

Palladium carbonyl complexes with a nonintegral FOS of the metal are few in number, are not distinguished by a structural diversity, and are represented (among reliably characterised complexes) only by clusters with a triangular metal core (Table 5). Whereas, the Pd – Pd distances are fairly short (2.58 – 2.61 Å) in clusters **59** and **60**, where each metal atom has a FOS of +0.67, and indicate the occurrence of a direct metal – metal interaction, in cluster **58** (the FOS of the metal is +1.33) such interaction is weaker, which is reflected in the length of the metal – metal bonds (2.95 – 3.00 Å).

Certain heteronuclear complexes should apparently be assigned to compounds in which the metal atom has a nonintegral FOS. Thus in the octanuclear complex $Na_2\{Pd_4[Cp$-$Mo(CO)_3]_4\}$,[138] there are two positive charges on the four palladium atoms (the palladium atoms form a square with 2.675 – 2.691 Å sides), *i.e*. the FOS is +0.5.

Another example is provided by the anionic cluster $[Pd_6Ru_6(CO)_{24}]^{2-}$ **64** obtained [183] by the interaction of $[Ru_3H(CO)_{11}]^-$ and $Pd(PhCN)_2Cl_2$. The palladium atoms in the cluster form an octahedron, the ruthenium atoms serve as 'caps' on the faces of the octahedron, while the carbonyl ligands are involved in terminal (12 molecules) and bridging (six molecules are μ-coordinated and six are μ_3-coordinated) coordination. If it is assumed by analogy with the preceding cluster that the 'capping' ruthenium atoms represent together with the carbonyl ligands anionic carbonylmetallates, then a formal charge somewhat exceeding +1 should be attributed to the palladium atoms forming the inner octahedron, but in principle such a procedure does not appear sufficiently legitimate.

The picture becomes even more complex with increase in the number of atoms in the cluster. Thus the interaction of $Pd(PPh_3)_2Cl_2$ and $[Ni_6(CO)_{12}]^-$ afforded [184] the anionic cluster $(Pd_{33}Ni_9(CO)_4(PPh_3)_6]^{4-}$ isolated in the form of a salt with $[PPh_4]^+$ and characterised by X-ray diffraction (Fig. 10).

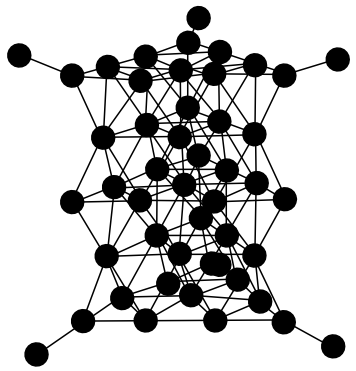


Figure 10. The structure of the metallopolyhedron of the heterometallic cluster anion $(Pd_{33}Ni_9(CO)_4(PPh_3)_6]^{4-}$ according to X-ray diffraction data.[184]

The metal atoms in the cluster form five triangular layers and the vertices of the upper, lowest, and middle triangles are occupied by nickel atoms. The carbonyl ligands (not shown in Fig. 10) consist of five terminal and 36 bridging groups the terminal carbonyl being linked to the three nickel atoms of the middle layer and the central palladium atoms of the upper and lowest layers.

2. The reactivity of clusters containing the metal in a fractional formal oxidation state

The reactivity of the clusters under discussion is characterised by two distinctive features: the coordinative unsaturation of the clusters (and hence their ability to coordinate additional ligands) and the ability of clusters containing metal atoms in the lowest oxidation states to enter into oxidative addition reactions.

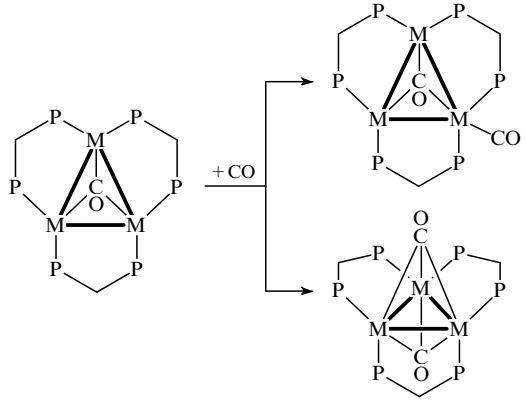
Such features are most characteristic of the type **59** clusters $[M_3(\mu_3$-$CO)(\mu$-dppm$)_3]^{2+}$, the reactivity of which has been characterised in fair detail.

a. Coordination of additional ligands

It has been shown that cluster **59** (M = Pd or Pt) is capable of coordinating two- and four-electron donor ligands and the newly introduced ligands can be both terminal and bridging on the M_3 triangle, or on the sides of this triangle, and their coordination has an appreciable influence on the coordination of the carbonyl ligand.

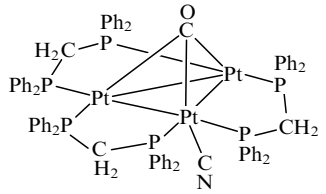
Since cluster **59** and the products of its interaction with various reagents are much more stable in the case where M = Pt than for M = Pd, the authors were as a rule able to characterise fairly reliably the platinum-containing products, the analogous properties and structures being merely attributed to the palladium complexes.

Thus it has been shown in relation to the platinum complex by NMR involving different nuclei [185] that complex **59** can combine with a second CO molecule with formation of two isomers; the first with terminal and μ_3-coordinated carbonyls and the second with two μ_3-coordinated carbonyl ligands:



Phosphines and phosphites (L) are coordinated as monodentate species in reactions with complex **59**, forming $[Pt_3(\mu_3\text{-}CO)(L)(\mu\text{-}dppm)_3]^{2+}$. The coordination of the carbonyl group and of the diphosphines does not then change.[186, 187]

Treatment of cluster **59** (M = Pd or Pt) with the cyanide ion in acetone solution at −78 °C and subsequent heating of the solution to room temperature lead to the formation [188] of the adduct $[M_3(CN)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^+$. According to X-ray diffraction data for M = Pt, the cyanide ligand in such an adduct is linked to one of the platinum atoms in such a way that the Pt–C–N line is virtually perpendicular to the plane of the Pt_3 triangle.



The study of the behaviour of this adduct by ^{31}P NMR in solution at −90 °C showed that the central ligand migrates rapidly around the Pt_3 triangle. This migration is not accompanied by the dissociation of the carbonyl or cyanide ligand and involves in all probability an intermediate with a μ_3-coordinated cyanide ion.

On interaction of cluster **59** (M = Pt) with isocyanides RNC,[189] initially one isocyanide molecule is coordinated and then a second one is attached to the same metal atom. On coordination of a second isocyanide molecule, a CO molecule is displaced and the cluster $[Pt_3(RNC)_2(\mu\text{-}dppm)_3]^{2+}$ is formed.

If the isocyanide molecule contains a bulky group, its reaction with complex **59** proceeds in a somewhat different manner.[190] Thus, the interaction of complex **59** (M = Pd) with XyN=C (Xy = 2,6-$C_6H_3Me_2$) results in the formation of $[Pd_3(XyNC)(\mu\text{-}dppm)_3]^{2+}$ **64**, in which the μ_3-η-isocyanide ligand is coordinated (according to X-ray diffraction data) over the Pd_3 plane. Cluster **64**, containing 42 valence electrons, combines reversibly with a second isocyanide molecule, forming the 44-electron cluster $[Pd_3(\mu_3\text{-}CNXy)_2(\mu\text{-}dppm)_3]^{2+}$. The reaction of complex **59** (M = Pd) with 0.5 mole of 1,4-C=NC_6Me_4N=C also leads to the substitution of CO. The cationic cluster $\{Pd_3(\mu\text{-}dppm)_3]_2(CNC_6Me_4NC)\}^{4+}$ **65** is then formed. It was isolated in the; form of a salt with PF_6^- or CF_3COO^-. X-Ray diffraction analysis showed that the diisocyanide ligands in complex **65** serve as bridges between the $Pd_3(\mu\text{-}dppm)_3$ species.

By analogy with the isocyanides, the anion SnX_3^- (X = F or Cl) initially forms the 1:1 adduct $[Pt_3(\mu_3\text{-}CO)(\mu_3\text{-}SnX_3)(\mu\text{-}dppm)_3]^+$ in the reaction with complex **59** (M = Pt) and then combines with a second equivalent of SnX_3^-. This leads to the displacement of CO and the formation of $[Pt_3(\mu_3\text{-}SnX_3)(\mu\text{-}dppm)_3]$.[53, 191]

It has been shown by the NMR method [192] that the interaction of complex **59** and $NaBH_4$ entails the initial formation of the fragment $[Pt_3(\mu_3\text{-}CO)(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^+$, which affords $[Pt_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^+$ after eliminating CO.

The reaction of complex **59** with halide ligands proceeds similarly to the reaction with hydrides but terminates at the first stage. Complex **59** combines with a halide ligand to form $[M_3(\mu_3\text{-}CO)X(\mu\text{-}dppm)_3]^+$. In the case where M = Pd, it has been established by X-ray diffraction study that the halide μ_3-coordinated to the second side of the Pd_3 triangle is built into the $Pd_3(\mu_3\text{-}CO)(\mu_3\text{-}X)$ bipyramid.[180, 181]

The pseudohalide SCN^- also forms 1:1 adducts, but it has been established by X-ray diffraction that in $[Pt_3(\mu_3\text{-}CO)(SCN)(\mu\text{-}dppm)_3]^+$ the thiocyanate ion assumes the role of a terminal ligand coordinated to one metal atom.[193] Complex **59** does not react directly with diphosphine ligands (even in the presence of their large excess). Other bidentate ligands, such as $R_2NCS_2^-$ and R_3PCS_2, form [194] the complexes $[Pt_3(\mu\text{-}CO)(\mu\text{-}dppm)_3(\mu\text{-}S_2CNR_2)]$ or $[Pt_3(\mu\text{-}CO)(\mu\text{-}dppm)_3(\mu\text{-}S_2CBr_3]^{2+}$.

Thus complex **59** can combine with one- or two-electron ligands or a bidentate four-electron ligand with formation of 44- and 46-electron clusters. On addition of weakly coordinated halide or trifluoroacetate, the number of valence electrons of the cluster may reach 48. In the cluster, the M_3P species is planar and the M–M bond lengths vary within a very narrow range. Additional ligands may bind to complex **59** *via* the unoccupied P_z orbitals of the metal and not the unoccupied σ* orbitals of the metal–metal bond of the cluster. This conclusion has been confirmed by a theoretical analysis.[195, 196] The additional ligands can interact with one, two, or three metal centres, the first case being most frequently encountered. The degree of displacement of the carbonyl group from the symmetrical μ-coordination (expressed by a change in the M–C bond lengths) reflects the donor properties of the additional ligand. It increase in the sequence μ_3-I < μ_3-η^2-CF_3COO < SCN < $P(OPh)_3$.

b. Oxidative addition reaction

In the cluster $[M_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ or $[M_3(\mu_3\text{-}H)(\mu\text{-}dppm)_3]^+$, the formal +2 charge is distributed among three metal atoms, which corresponds to a FOS of +2/3. After the removal of a further two electrons from these complexes the formal 4+ charge is distributed among three palladium atoms, which corresponds to a FOS of +4/3. In the oxidised complexes, one of the sides of the metal triangle increases to a size exceeding the sum of the covalent radii of palladium and precluding direct metal–metal interaction. In this case, one may assume that the complexes contain the $(M_2)^{2+}M^{2+}$ species, where M^{2+} is linked to the $(M_2)^{2+}$ cations only *via* two μ-dppm groups and the outer μ_3-ligand introduced during the oxidation process.

The oxidative addition reactions have been examined in relation to platinum compounds.[197–199] The complex $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ reacts with H_2E or REH (E = S or Se R = Et or Ph) with the elimination of the CO molecule and the formation of $[Pt_3H(\mu_3\text{-}ER)(\mu\text{-}dppm)_3]^{2+}$ or $[Pt_3H(\mu_3\text{-}E)(\mu\text{-}dppm)_3]^+$. The

palladium cluster reacts similarly, but the Pd–H bond is more labile and the complexes formed could not be isolated in a crystalline form. The reactions described above are of interest as model processes involving the poisoning of platinum or palladium catalysts by hydrogen sulfide.

The complex $[M_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$ reacts with SCN^- to form $[M_3(\mu_3\text{-}CO)(SCN)(\mu\text{-}dppm)_3]^+$ which undergoes a thermal or photochemical rearrangement [193] with dissociation of the S–C. bond and the formation of $[M_3(CN)(\mu_3\text{-}S)(\mu\text{-}dppm)_3]^+$. The mechanism of this reaction has been investigated [200] and it has been established that the principal characteristic features of the process extend also to the interaction of complex **59** and the heterocumulenes S=C=E (E = N^-, O, S, or NR). In all cases, the reaction proceeds with formation of the adduct $[M_3(S=C=E)(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$, which is followed by the oxidative addition of the heterocumulene to the C=S bond, the elimination of CO, and the appearance of $[M_3(\mu_3\text{-}S)(C=E)(dppm)_3]^{2+}$.

VII. Palladium carbonyl hydride complexes

The palladium complexes containing simultaneously both carbonyl and hydride ligands are of great interest primarily as possible intermediates (or models of intermediates) in catalytic reactions occurring with participation of carbon monoxide and hydrogen. This is a wide range of processes including the industrially important alkene hydroformylation, alkoxycarbonylation, *etc*. reactions. The carbonyl hydride complexes are believed to be intermediates in the key stages of the processes, but the evidence for the formation of such complexes is extremely scanty or completely absent.[201–203] There are few reliably characterised palladium carbonyl hydride complexes.[204]

The first communication about the synthesis of a carbonyl hydride complex appeared as early as 1969.[205] A solution of palladium chloride in 2-methoxyethanol was treated with carbon monoxide until the formation of a yellow solution. A brown diamagnetic complex was precipitated on treatment with $AsPh_4Cl$. The sparing solubility of this complex precluded the study of its ^1H NMR spectra. On the basis of the results of elemental analysis, conductimetric measurements (the compound behaved as a 1 : 1 electrolyte in solution in dimethylformamide), and IR spectroscopic data (the weak band at 1960 cm^{-1} was assigned to the stretching vibrations of the M–H bond, while the intense band at 1900 cm^{-1} was assigned to the stretching vibrations of the terminal CO group), the authors postulated that the compound is the carbonyl hydride $[AsPh_4][Pd(CO)HCl_2]$. In the light of later data on palladium carbonyl and hydride complexes, taking into account the new interpretation of the IR spectra of these compounds (both bands in the IR spectra should be more correctly assigned to the stretching vibrations of bridging groups), this hypothesis appears insufficiently well founded. The complex probably has a more complicated dinuclear structure, particularly since mononuclear compounds are absent among the palladium carbonyl halides described later.

On protonation of $Pd(PPh_3)_4$ with aqueous trifluoroacetic acid at 25 °C or on reduction of $(PPh_3)_2Pd(CF_3COO)_2$ with hydrogen in solution in aqueous CF_3COOH at 70 °C, the complex $[(PPh_3)_3PdH]^+$ is formed *in situ*, carbonylation of the complex afforded [206–208] the carbonyl hydride $[(PPh_3)_4Pd_2(\mu\text{-}H)(\mu\text{-}CO)](CF_3COO)$ in accordance with the equation

$$2[(PPh_3)_3PdH]^+X^- + CO = [(Ph_3P)_4Pd_2(\mu\text{-}H)(\mu\text{-}CO)]X,$$

66

X = CF_3COO.

Complex **66** has not been isolated in the solid state but it has been fairly completely characterised by NMR data, which agree well with those for platinum analogues.[209, 210]

The protonation of $Pd(PPh_3)_4$ in toluene under a CO atmosphere or of $(PPh_3)_3Pd(CO)$ in toluene on treatment with the sulfonic acid $H_2C(SO_2CF_3)_2$ also leads to the formation of complex **66** [X = $HC(SO_2CF_3)_2$], which has been isolated in the solid state and characterised by elemental analysis and IR spectroscopy (ν_{CO} = 1851 cm^{-1}), while the complex in solution in CD_2Cl_2 has been characterised by NMR spectroscopy involving different nuclei.[211]

Complex **66** (X = BPh_4) has been obtained [212, 213] in a study of the nature of the compounds responsible for the catalysis of the reduction of nitro-compounds by carbon monoxide in the $Pd(OAc)_2/PPh_3/CO/PhNO_2/Bu^nOH/H_2SO_4$ system.

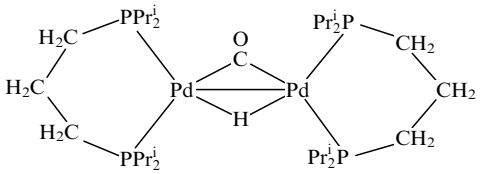
The only palladium carbonyl hydrate the structure of which has been investigated by X-ray diffraction has been synthesised [214, 215] by a fairly unusual method — the interaction of the organopalladium compound Pd(dippp)(Ph)(Cl), where dippp = 1,3-bis(diisopropylphosphino)propane, and methanol in the presence of an excess of triethylamine at 60 °C in accordance with the equation

$$2Pd(dippp)(Ph)(Cl) + 2CH_3OH + NEt_3 =$$
$$= 2C_6H_6 + CH_2O + H_2 + HNEt_3Cl + [Pd_2(dippp)_2(\mu\text{-}CO)(\mu\text{-}H)]^+Cl^-$$

67

Experiments using CH_3OD showed that methanol is in fact the source of hydride ions in the synthesis of complex **67**. The carbonyl groups also arise as a result of the decarbonylation of methanol. The ^1H NMR spectrum of complex **67** contains a signal at δ = −5.17 ppm (quintet. $^2J_{P-H}$ = 41.1 Hz); the IR spectrum contains an intense band at 1789 cm^{-1}, which does not change when the hydride is replaced by deuterium and which has been assigned to the stretching vibrations of the CO group. The relatively low stretching vibrational frequency of the carbonyl group reflects the presence of an increased electron density on the metal atom, arising as a consequence of the high donor capacity of the chelating phosphines.

According to X-ray diffraction data, the two palladium atoms in complex **67** are at a distance of 2.767 Å, indicating a metal–metal single bond.



The hydride ligand is localised and the Pd–H distance is 1.53 Å, which is within the range of distances determined for the structurally characterised palladium hydrides.[216–218]

A complex analogous to complex **67** has also been obtained by decarbonylating methanol.[219] On heating to 80 °C a solution of the acetyl complex Pd(COMe)(Cl){(*S*,*S*)-bdpp}, where (*S*,*S*)-bdpp = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane, in a methanol–toluene-d_8 mixture in an inert gas atmosphere, an equimolar mixture of $(bdpp)PdCl_2$ and $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)(bdpp)_2]^+Cl^-$ is formed.

The interconversions of the polynuclear palladium hydride and carbonyl hydride complexes have been described.[2, 220–226] The reduction of $Pd(OAc)_2$ by molecular hydrogen in glacial acetic acid in the presence of L (L = Phen or Bipy) leads to the formation of X-ray-amorphous substances with the approximate composition $[Pd_4L(OAc)_2H_4]_n$, where $n \sim 100$. The reaction of polynuclear hydrides with carbon monoxide leads to the carbonyl hydride clusters $[Pd_4L_3(CO)_3(H)_2(OAc)_3]_n$ (n = 2, 3). The interaction of CO with a 1 : 1 solution of $Pd(OAc)_2$ and Phen in acetic acid at 20 °C leads to the formation of the complex $[PhenPd(CO)(OAc)]_n$, which does not contain hydrides.

If the temperature of the reaction mixture is raised to 50 °C, a polymeric carbonyl hydride having the general formula $[(Phen)_2Pd_2(CO)(H)(OAc)\cdot AcOH]_m$ is formed; the signal of its hydride hydrogen atoms in the ^1H NMR spectrum is δ = −15.5 ppm. Finally, the interaction of $Pd(OAc)_2$ and Phen

in acetic acid under a mixed H_2/CO atmosphere affords the carbonyl hydride $[(Phen)_3Pd_4(CO)_3H_3(OAc)_2 \cdot AcOH]$.

All the carbonyl hydrides have been characterised by elemental analysis and IR, ^1H NMR, and EXAFS spectroscopy. On the basis of the data obtained from these compounds, a structure has been proposed. It is based on tetrahedral palladium fragments with chelating phenanthroline ligands and bridging CO groups, which are linked to one another by bridging hydrides.

Thus the palladium carbonyl hydride complexes described are represented either by dinuclear singly charged cations with bridging carbonyl and hydride ligands or by polynuclear compounds also containing bridging carbonyls and hydrides. In all cases, the FOS of the palladium atoms has an intermediate value between 0 and +2.

VIII. Palladium carbonyl complexes in zeolites

In the early studies devoted to the adsorption of carbon monoxide on palladium(0) deposited on oxide carriers,[227,228] it was established that two types of adsorption exist: weak reversible and strong irreversible adsorption. In the former case, the carbon monoxide molecules are involved in terminal coordination according to IR spectroscopic data (ν_{CO} = 2085 cm^{-1}), while in the latter bridging CO groups predominate (ν_{CO} = 1960 cm^{-1}).

The authors of later studies [229–236] obtained additional data on the structures of palladium carbonyls in the cavities of the NaY and 5A zeolites by employing modern physical research methods (Fourier transform IR spectroscopy, atomic radial distribution methods, and EXAFS), as well as data obtained for the structurally characterised palladium(0) carbonyls. Thus comparative analysis of the IR spectra of compounds of palladium and carbon monoxide, located in the cavities of the NaY zeolites, and data on the molecular clusters of ruthenium and iridium carbonyls in zeolites led to the conclusion that the principal form of the palladium carbonyl consists of the clusters $Pd_{13}(CO)_x$ containing both bridging and terminal CO groups. [237] The size of the cluster is determined by the size of the zeolite cavity and is almost independent of either the initial form of palladium or of the cluster formation conditions.[230]

Subsequent studies by the EXAFS method confirmed the hypothesis that the Pd_{13} clusters predominate. These can have a metal core in the form of both a cubooctahedron and an icosahedron.[231] In the initial stage of the formation of the compound on treatment of palladium immobilised on the surface of the zeolite with carbon monoxide at room temperature, the formation of the Pd_6 cluster was observed. The subsequent migration of such clusters and species with a smaller nuclearity into the zeolite cavity leads to Pd_{13}. On raising the temperature to $\sim$ 200 °C, there is a possibility of the growth of the metal core right up to Pd_{40}. However, all the conclusions concerning the nuclearity of clusters in the zeolite and their composition and nature are tentative.

It is believed that, under the conditions where the $Pd_{13}(CO)_x$ clusters are formed on the NaY zeolites, clusters having the composition $Pd_6(CO)_x$ predominate on the surface of the 5A zeolite. The presence of mainly terminal and μ_3-bound CO groups is characteristic of $Pd_6(CO)_x$.[232]

The ability of various zeolites to form palladium carbonyls with different nuclearities has been used in the preparation of catalysts altering the selectivity in various processes. Thus the hydrogenation of CO on Pd/5A leads to methanol and dimethyl ether, whereas the employment of Pt/NaY leads mainly to the formation of C_2 hydrocarbons.[234]

IX. Conclusion

The organic chemistry of palladium was initiated by the study of the π-complexes and alkyl derivatives of this metal.[201] The carbonyl complexes played only a modest role at this stage.

The last quarter of the century has been marked by the development of a series of processes which have found industrial applications or for which prospects for an industrial application exist. Carbon monoxide plays the role of one of the substrates in this series, whilst the active component of the catalytic system consists of palladium compounds.[237]

Simultaneously with this field of chemistry, the chemistry of palladium carbonyl complexes developed, its importance growing far beyond the framework determined by utilitarian needs.

The synthesis and study of palladium carbonyl complexes, regarded as a chemical rarity as late as 25 years ago, posed a series of problems before the theory of the chemical bond and of the reactivity of compounds. Modern ideas about the nature of the metal–metal and metal–organic ligand chemical bonds [238] are based in many respects on the existing factual data and the chemistry and structure of platinum group metal carbonyl complexes.

The analysis of these data carried out in the present review has confirmed the existing hypothesis that the stability of polynuclear compounds diminishes with increase in the formal oxidation state of the central atom in palladium carbonyls and hence the number of reliably characterised compounds diminishes sharply on passing from Pd(0) to Pd(+2). Thus, whereas binary carbonyls and mononuclear and polynuclear compounds with various forms of the metal core and all the forms of the coordination of carbonyl ligands have been described for palladium(0), all the known palladium(+2) carbonyls are limited by mononuclear compounds with terminal carbonyl groups.

Among the fairly wide range of methods of synthesis of transition metal carbonyl complexes [239–241] (direct carbonylation of the metal, reductive carbonylation, oxidative carbonylation, reduction of carbonyl complexes, substitution of ligands *etc.*), only some have been applied in the chemistry of palladium carbonyls, different numbers of compounds being obtained by the application of a particular method. Thus only four complexes have been synthesised by the coprecipitation of palladium metal and CO at low temperatures; the reaction involving the substitution of ligands by carbon monoxide has also been successful in only isolated instances. The method involving the insertion of CO in the metal–metal bond in dinuclear and polynuclear palladium complexes and reductive carbonylation of palladium compounds have proved much more productive. It is noteworthy that the vast majority of compounds have been obtained by the latter method and not only palladium(0) or palladium(+1) complexes but also palladium(+2) complexes.

Palladium(0) carbonyls constitute the most numerous class among palladium carbonyl complexes, polynuclear carbonyls, including also large clusters with several tens of palladium atoms in the metal core, predominating. Probably one of the most important causes of such diversity of the complexes is the stability of the Pd–CO bond determined by the combination of the σ-donor and π-acceptor properties of the CO molecule and the ability of the palladium atom (d^{10} electronic configuration) to donate the electron density from the 3*d* metal orbital to the π*-orbital of the CO molecule.

The stability of the Pd–CO bond in palladium(+1) complexes, where the metal atom has the d^9 electronic configuration, is lower and hence the number of such complexes is much smaller than that of palladium(0) carbonyls. All the palladium(+1) complexes contain an even number of metal atoms — 2 or 4. They are diamagnetic and the pairing of electrons at the two metal atoms, having the d^9 configuration, occurs either as a result of the formation of a metal–metal bond (with a Pd–Pd distance of $\sim$ 2.7 Å) or by the formation of a three-centre four-electron bond incorporating two palladium atoms and one carbon atom of the bridging carbonyl ligand.

The palladium(+1) complexes are fairly sensitive to the action of oxygen-containing nucleophiles and, when treated with, for example, water or lower aliphatic alcohols, they decompose with the formation of palladium metal. The insertion of π-donor

ligands into these complexes promotes an increase in their resistance to reductive decompositions.

In the palladium(+2) complexes where the metal atom has the d^8 electronic configuration and the possibility of the donation of electrons from the metal to the corresponding orbitals of the CO molecule is much smaller than for Pd(0) and Pd(+1), an enhancement of the σ-donor properties of the carbonyl is observed. All the palladium(+2) carbonyl complexes are monomeric with terminal CO groups. The strength of the Pd–CO bond is as a rule small, which leads to a low thermal stability of the complexes. The presence in the palladium(+2) carbonyl complex of groups with strong electron-withdrawing properties, for example SO_3F^-, enhances the electron-accepting properties of the palladium atom and hence leads to an increase in the thermal stability of the complexes.

There are few palladium carbonyl complexes containing the metal in fractional oxidation states. In fact, only compounds having the $Pd_3(\mu_3\text{-CO})$ core can be regarded as reliably characterised. The reactions involving the coordination of additional ligands are characteristic of these compounds and the newly introduced ligands can be both terminal or can function as μ_3-bridges on the Pd_3 triangle. Reactions of the second type are oxidative addition reactions. As a consequence of the change in the charge on the Pd_3 triangle, the metal core is altered and the charges are redistributed, which actually leads to a species with nonequivalent metal atoms.

Palladium carbonyl hydrides are of enormous interest primarily as possible intermediates (or models of intermediates) in catalytic processes occurring with participation of carbon monoxide and hydrogen and catalysed by palladium and its compounds. The number of such complexes, which have been postulated in a large number of studies, is small. All the palladium carbonyl hydrides are represented either by dinuclear singly-charged cations with bridging carbonyl and hydride ligands or by polynuclear compounds also containing bridging carbonyl and hydride ligands. In all cases, the FOS of the palladium atoms is intermediate between 0 and +2.

Summarising the data described above concerning the characteristic features of the Pd–CO bond in the carbonyl-containing complexes, one should note that such a bond may be described by several models distinguished by different contributions of the σ- and π-interactions. The symbolism introduced by Willner and Aubke (Fig. 11) appears very clear in the simplest case where the overlap of orbitals in an individual M–CO fragment with CO groups bound as terminal species is considered.[238]

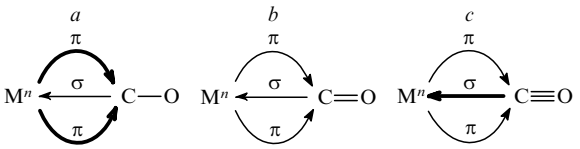


Figure 11. A schematic model of the formation of the bond in the M–CO fragment.

In this scheme, the σ-donor bond arising from the 5σ molecular orbital of CO is shown as an arrow directed from the carbon atom to the metal atom, while the π-acceptor bond, responsible for the donation from the nd_{xz} or nd_{xy} orbital of the metal to the π* molecular orbitals of CO is shown by arrows directed towards CO. The thin lines indicate a weak bond, whereas thick lines demonstrate the dominant type of bond and the boundary situations. Figure 11*a* illustrates the dominant π-back-donation (this involves predominantly highly reduced carbonylmetallates), whilst Fig 11*c* illustrates the predominance of σ-bonding (cationic carbonyls). Figure 11*b* characterises the bonding in typical metal carbonyls, where the bonds of the types indicated in Fig. 11*a* and Fig. 11*c* may overlap depending on the oxidation state of the metal. Apparently there are at present no physicochemical data which would make it possible to assign the type of bonding in the carbonyl fragments solely to the 'π-interaction' or the 'pure σ-interaction' and both types of bonding occur in any of the existing compounds.

The palladium carbonyls where the bond might be assigned to the type presented in Fig. 11*b* and which should have a large positive charge, for example $[M(CO)_4]^{4-}$ (M = Cr, Mo, W) and $[M(CO)_4]^{3-}$ M = Co, Rh, Ir)[242] have not so far been described and the possibility of the synthesis of such reduced carbonyl carbonylpalladates appears doubtful. In the vast majority of the palladium carbonyl complexes, the bond is of the type presented in Fig. 11*b* (the σ- and π-interactions are combined). Only one complex — the palladium(+2) carbonyl complex $[Pd(CO)_4]^{2+}$ — may be assigned to complexes in which a bond of the Pd–CO type presented in Fig. 11*c* is achieved. Only in this complex is an anomalously high stretching vibrational frequency of the CO (2248 cm^{-1}) observed, exceeding the value of ν_{CO} for free carbon monoxide.

In the case of all other palladium carbonyl complexes, the energy of the Pd–CO bond and the vibrational frequencies ν_{CO}, indirectly characterising this bond, depend on a whole series of ancillary factors. Thus the vibrations of the terminal CO groups are manifested in the shortest-wavelength region (2000–2050 cm^{-1}), those of the μ-CO groups are in the middle region (1850–~1950 cm^{-1}), while the vibrations of the μ_3-groups are in the longest-wavelength region. The regions corresponding to absorption by the last two types of CO ligands overlap appreciably. Complexes of different nuclearity, containing CO ligands of the same type, do not exhibit stable distinctive features in their IR spectra.

On the other hand, the presence at one atom of only one terminal carbonyl and of three *n*-donor atoms [for example in $Pd(CO)(PPh_3)_3$, $Pd(CO)(NP_3)$, and $Pd(CO)[MeC(CH_2PPh_2)_3]$ leads to a decrease in ν_{CO} to values characteristic of the stretching vibrations of the bridging CO group, *i.e.* the regions of the stretching vibrations of the bridging and terminal carbonyls overlap.

The appearance of strong electron-withdrawing groups increases ν_{CO} to values characteristic of the stretching vibrations of the terminal CO groups. For example, ν_{CO} for the complex $Pd_4(\mu\text{-CO})_4(\mu\text{-OCOCF}_3)_4$ is 2003 cm^{-1}, which is characteristic of the terminal CO groups. At any rate, bearing in mind the foregoing one should treat with caution the description of the structure of carbonyls and the estimation of the strength of the metal–ligand bond on the basis of spectroscopic data.

The reactivity of palladium carbonyl complexes is restricted to a narrow range of reactions. Thus ligand substitution, which does not lead to a serious structural rearrangement, has been described for all types of palladium carbonyl complexes. Reactions leading to a change in the metal core have been described for polynuclear complexes containing Pd(0), Pd(+1), and palladium in fractional oxidation states, and such changes can occur with decrease or increase in the nuclearity of the complex [for example, the formation of various carbonyl phosphine complexes of palladium(0)] and with retention of the nuclearity {for example, the formation of the tetrahedral complex $[Pd_4(CO)_2Phen_4](OAc)_4$ from the carbonyl acetate $Pd_4(CO)_4(OAc)_4$, which has a rectangular metal core}.

The reactivity of the palladium(+1) carbonyl carboxylate complexes has been studied much more widely than for the other complexes. Among the reactions investigated the greatest interest attaches to the oxidative-reduction reactions of the tetranuclear clusters. In the first place, this is the reaction involving the intramolecular transfer of an oxygen atom from the carboxylate ligands to the coordinated carbonyl, which may serve as a model of a whole series of oxidation–reduction processes proceeding with participation of CO and catalysed by palladium compounds.

The extensive field of the chemistry of palladium comprising the synthesis, the structure, and the reactivity of heteronuclear

palladium-containing complexes with carbonyl ligands has remained outside the scope of the present review.

The authors hope that the compilation of data on the synthesis, structures, and properties of palladium carbonyl complexes presented in the review will prove useful not only to chemists occupied with different aspects of the synthesis of carbonyl complexes but also to specialists in the application of these complexes in catalysis and in the study of the details of their electronic structure.

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