

Pd₄ Clusters: the sensitivity of the cluster metal core geometry to the surrounding ligands *

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Abstract

X-ray and EXAFS data reveal that the metal skeleton in the palladium carbonyl acetate cluster, Pd₄(CO)₄(OAc)₄, undergoes significant changes upon replacement of the CO and AcO groups. The rectangular skeleton rearranges into a square one when Pd₄(CO)₄(OAc)₄ is stored at room temperature, showing non-rigidity of the cluster core and the ability of the ligands to migrate.

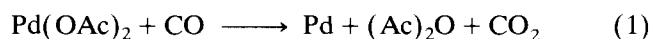
Keywords: Palladium; Clusters; Cluster core geometry; Cluster core rearrangement

1. Introduction

Control of the geometry of the metal complexes by varying the ligands surrounding the central atom has been one of the challenges in coordination chemistry since the days of Alfred Werner [1]. In contrast to the situation for classical coordination compounds, little is known of the effects of ligands on the geometry of the skeleton clusters (see Refs. [2–4] and references therein). We present below some relevant observations pertaining to Pd₄-cluster chemistry.

2. Palladium carbonyl acetate and related compounds

When solutions of palladium(II) carboxylate Pd(OCOR)₂ (R = Me, Et or Ph) are brought into contact with CO, reduction of Pd(II) to Pd metal usually occurs. In glacial acetic acid containing alkali metal acetates, reduction of Pd(OAc)₂ with CO results in formation of palladium metal, acetic anhydride, and CO₂ [5]:



In carboxylic acids or mixtures of carboxylic acid and benzene as solvents, in the absence of alkali metal acetates, relatively stable complexes of stoichiometry RCOO.Pd.CO.*n*R'COOH where *n* = 0:5 or 0 are obtained. Thus, carbonylation (1 atm of CO) of Pd(OAc)₂ in glacial acetic acid at 50°C gave AcO.Pd.CO.0.5AcOH (**1**). Crystals of **1** lose 0.5 mol of acetic acid per mol of palladium when kept for about 10 days in vacuo over KOH at 20°C, forming palladium carbonyl acetate (PCA), Pd₄(μ-CO)₄(μ-OAc)₄ (**2**). The IR spectra of the complexes show two strong absorption bands in the C–O stretching region, at 1934 and 1975 cm⁻¹ for **1**, and 1940 and 1975 cm⁻¹ for **2**, in addition to frequencies corresponding to the bidentate coordinated acetate ligands [5]. According to X-ray diffraction data, crystals of **1** consist of tetranuclear clusters Pd₄(CO)₄(OAc)₄ (Fig. 1) and hydrogen-bonded dimeric molecules of AcOH. Acetic acid dimers of crystallization are located in the cavities of the crystal lattice, one dimer for each four-nuclear cluster molecule.

The Pd₄ framework of the cluster is nearly rectangular, with almost 90° Pd–Pd–Pd angles (83.4° and 96.6°). The acetate-bridged Pd–Pd distances (2.909 Å) are longer, and the CO-bridged ones (2.663 Å) are shorter, than the shortest Pd–Pd distance (2.751 Å) in Pd metal [6]. Reaction of palladium(II) propionate with CO gave a PCA analogue, palladium carbonyl propionate Pd₄(CO)₄(OCOEt)₄. Similarly, palladium car-

* Dedicated to Prof. Dr. Fausto Calderazzo for his outstanding contribution to inorganic chemistry.

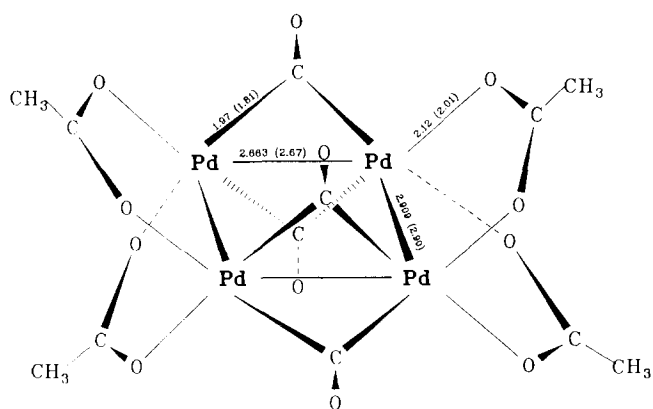
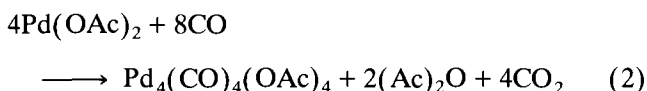
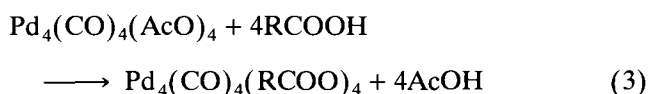


Fig. 1. Structure of $\text{Pd}_4(\text{CO})_4(\text{OAc})_4$ molecule revealed by X-ray diffraction [5].

bonyl benzoate $\text{Pd}_4(\text{CO})_4(\text{OCOPh})_4$ was prepared by reacting palladium(II) benzoate with CO in a solution of benzoic acid and benzene. Therefore, the reaction shown in Eq. 2 provides a general route to palladium(I) carbonyl carboxylates synthesis.



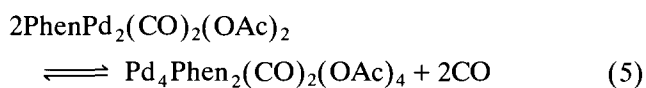
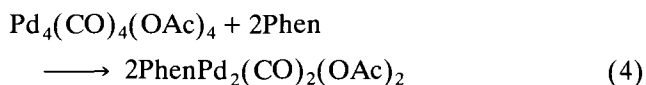
Another way of synthesizing palladium carbonyl carboxylates of the type $\text{Pd}_4(\text{RCOO})_4(\text{CO})_4$ involves replacement of acetate ligands in PCA by an carboxylate group RCOO by treating PCA with an appropriate carboxylic acid as depicted by Eq. 3 [6,7], where R = CF_3 , CH_2Cl , Ph, $\text{C}(\text{CH}_3)_3$. The reactions of PCA involving the substitution of ligands at Pd atoms are considered below.



3. Reaction of PCA with phenanthroline: cluster with a nearly tetrahedral skeleton

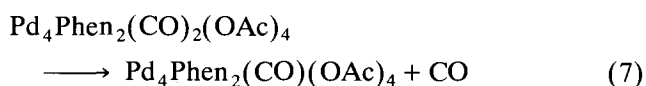
Reactions between PCA and bidentate N-ligands such as Phen, Bipy and their analogs gave a variety of complexes depending on the temperature and Pd: ligand ratio [5]. Addition of Phen to PCA in AcOH solution at 25–90°C causes reversible CO evolution. Volumetric data for this reaction at 25°C with Phen: Pd = ca. 2:1 are in good agreement with Eqs. 4–5, in which PCA is assumed to be split into binuclear species $\text{PhenPd}(\text{CO})_2(\text{OAc})_2$ in AcOH solution containing Phen (see Eq. 4). On this assumption, the experimental data were found to be described by Eq. 6

with equilibrium constant $K = (1.2 \pm 0.1) \cdot 10^{-4} \text{ mol l}^{-1}$ at 25°C [8]:

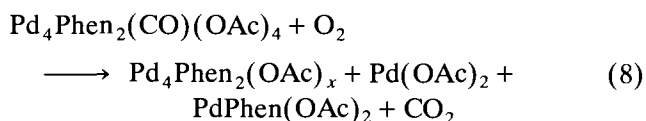


$$K = \frac{[\text{Pd}_4\text{Phen}_2(\text{CO})_2(\text{OAc})_4][\text{CO}]^2}{[\text{PhenPd}_2(\text{CO})_2(\text{OAc})_2]^2} \quad (6)$$

Further CO loss observed at higher temperature is assumed to arise from decarbonylation of complex $\text{Pd}_4\text{Phen}_2(\text{CO})_2(\text{OAc})_4$. Volumetric data at 90°C correspond to reversible loss of 1 mol of CO per four Pd atoms, in accord with Eq. 7:



The last CO molecule can only be removed irreversibly, by heating solutions of $\text{Pd}_4\text{Phen}_2(\text{CO})(\text{OAc})_4$ in AcOH under O_2 at 90°C, as shown in Eq. 8:



Treatment of PCA with Phen in a Phen: Pd ratio of 1:1 in AcOH under Ar gave complex $\text{Pd}_4(\text{CO})_2\text{Phen}_4(\text{OAc})_4$ (3), in accord with Eq. 9 [9]:

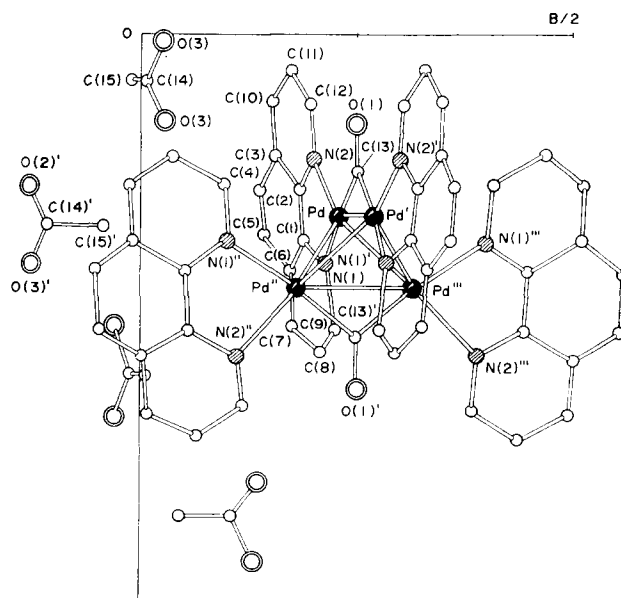
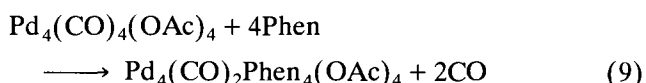
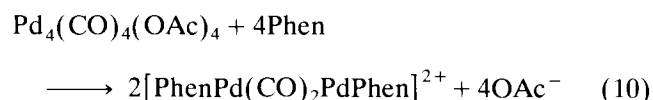


Fig. 2. Structure of $[\text{Pd}_4(\text{CO})_2\text{Phen}_4(\text{OAc})_4]$ revealed by X-ray diffraction [9].

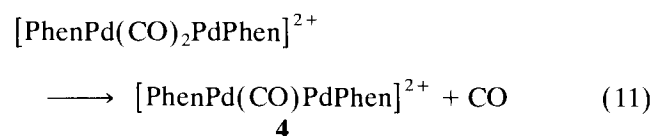
An IR spectrum of **3** shows the expected strong band at 1800 cm^{-1} . X-ray diffraction data showed that **3** contained a nearly tetrahedral cluster of palladium atoms (Fig. 2).

Two edges of the tetrahedron with CO bridges are slightly longer ($2.809(6)\text{ \AA}$) than the shortest Pd–Pd distance in Pd metal. As comparison with the geometry of PCA (Fig. 1) shows, formation of complex **3** from PCA is accompanied by shortening of formerly AcO-bridged Pd–Pd bonds, and lengthening of CO-bridged ones. All OAc ligands of PCA molecule are displaced to the outer sphere when tetra-cation $[\text{Pd}_4(\text{CO})_2\text{Phen}_4]^{4+}$ is formed.

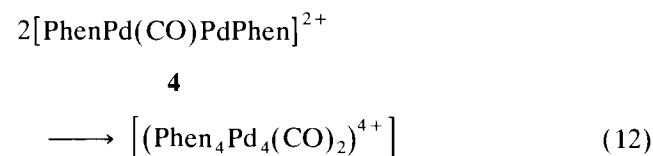
In the light of the observations outlined above, the first step of the reaction of PCA with Phen was suggested [9] to be replacement of OAc ligands by Phen molecules to split the PCA cluster into two complex di-cations, $\text{PhenPd}(\text{CO})_2\text{PdPhen}^{2+}$, as shown in Eq. 10:



In the next step, a CO ligand was assumed to be lost from the cationic intermediate to give the di-cation **4**:



The tetrahedral tetracationic cluster **3** is presumably formed by dimerization of the coordinatively unsaturated species **4**:



The shortest distance between the axes of $\text{PhenPd}(\text{CO})\text{PdPhen}$ groups in cluster **3** (see Fig. 2) was found to be ca. 1.8 \AA [9]. At this distance, overlapping between the two $\text{PhenPd}(\text{CO})\text{PdPhen}$ group orbitals might be sufficiently effective to contribute to the core stabilization of cluster **3**.

Thus, the transformation of the complex with a rectangular metal skeleton, PCA, into the cluster with a tetrahedral metal skeleton, $[\text{Pd}_4(\text{CO})_2\text{Phen}_4(\text{OAc})_2]$, seems to be a multistep process involving splitting of the starting PCA compound by the Phen ligands (Eq. 10), partial loss of CO ligands from the dicationic species $[\text{Phen}_2\text{Pd}_2(\text{CO})_2]^{2+}$ (Eq. 11) and recombination of the coordinatively unsaturated species $[(\text{Phen})_2\text{Pd}_2(\text{CO})]^{2+}$ (Eq. 12) formed in the first two steps.

4. Palladium–molybdenum carbonyl cluster, $\text{Na}_2\{[\text{Pd}_4[\text{CpMo}(\text{CO})_3]_4]\cdot 2\text{THF}$

Treatment of PCA with $\text{Na}[\text{CpMo}(\text{CO})_3]$ in THF (Cp = η^5 -cyclopentadienyl; THF = tetrahydrofuran) gave a cluster in which Pd atoms have a formal oxidation state of $(+1/2)$ [10].

The reaction of $[\text{Pd}_4(\text{CO})_4(\text{OAc})_4]$ with a large excess of $\text{Na}[\text{CpMo}(\text{CO})_3]$ in THF gives the dimer $[\text{CpMo}(\text{CO})_3]_2$ and a number of palladium–molybdenum complexes that are stable only in an inert atmosphere. From the THF–benzene–hexane mixture, a complex of the composition $\text{Na}_2\{[\text{Pd}_4[\text{CpMo}(\text{CO})_3]_4]\cdot 2\text{THF}$ (**5**) was isolated as dark-brown crystals. The IR spectrum of **5** displays bands corresponding to coordinated carbonyl groups at 2000 , 1945 , 1900 , 1870 , and 1830 cm^{-1} . Its ^1H NMR spectrum in dimethylformamide contained a singlet at $\delta 4.763$ (C_5H_5), but no metal hydride signals. The structure of the complex was determined by X-ray diffraction [10].

The structural unit of the crystal contains the centrosymmetric anion $\{[\text{Pd}_4[\text{CpMo}(\text{CO})_3]_4]\}^{2-}$ (Fig. 3), two sodium cations, and two THF molecules. Unlike PCA, in which the Pd–Pd distances are $2.663(1)\text{ \AA}$ and $2.909(1)\text{ \AA}$, cluster **5** has a square planar configuration [Pd–Pd 2.675 – $2.691(2)\text{ \AA}$]. Each of the Mo atoms forms an isosceles triangle with two Pd atoms [Pd–Mo 2.723 – $2.741(2)\text{ \AA}$], with all the metals atoms lying in one plane. The Pd–Mo distances are similar to those in related compounds [2,11] and correspond to single bonds.

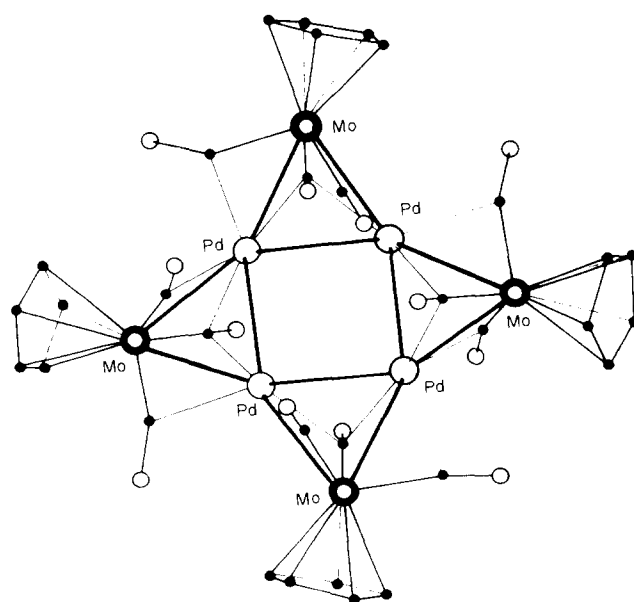
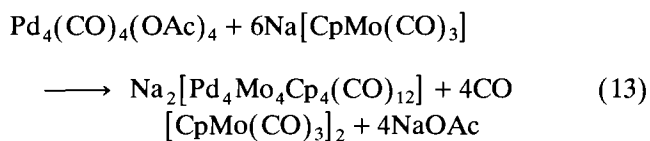


Fig. 3. Structure of $\{[\text{Pd}_4[\text{MoCp}(\text{CO})_3]_4]\}^{2-}$ revealed by X-ray diffraction [10].

The environment of each Mo and Pd atom is similar to that in the known cluster of type $\text{Pd}_2\text{Mo}_2(\text{Cp})_2(\mu\text{-CO})_4(\mu^3\text{-CO})_2(\text{PET}_3)_2$ [11]. The three carbonyl groups attached to each Mo atom form a trigonal pyramid with C–Mo–C angles of 92–109(1)°, and Mo–C distances 1.97–2.01(2) Å. The positions above the vertices are occupied by the cyclopentadienyl ligands, which are oriented in such a way that the Cp ring planes form angles of 78.3° and 83.6° with the planar metal core [Mo–C 2.29–2.36(3) Å, C–C 1.34–1.44(5) Å]. The carbonyl carbon atoms attached to Mo approach Pd, one of them in a triply bridging mode, $\mu^3\text{-CO}$ [Pd–C 2.22–2.45(2) Å], and the other two as double bridging ligands, $\mu\text{-CO}$ [Pd–C 2.34–2.6(2) Å].

Thus, during the formation of the octanuclear cluster not only are the acetate ligands displaced by the $\text{CpMo}(\text{C})_3^-$ anions, but the neutral CO molecules are also eliminated. The vacancies in the coordination sphere of the Pd are occupied by the Mo-coordinated CO molecules that form the bridging ligands.

However, the reaction is not restricted to the ligand substitution process. During the reaction, the reduction of Pd(+1) atoms takes place, apparently owing to the one-electron oxidation of the $[\text{CpMo}(\text{CO})_3]^-$ anions, revealed by formation of the dimer, $[\text{CpMo}(\text{CO})_3]_2$. If the Mo atoms entering the complex are assumed to retain their oxidation state of 0, as in the initial $\text{Na}[\text{CpMo}(\text{CO})_3]$, the observed transformation can be formally described as a reduction of Pd(+1) to Pd (+1/2) according to Eq. (13):



Thus, the observed change in the metal skeleton geometry during the transition from PCA (Fig. 1) to the complex 5 (Fig. 3) is the result of changes in both the surrounding ligands and the oxidation state of Pd.

Another Pd_4 -cluster with an average oxidation state at 0.5 for each Pd atom has been recently reported [12]. The cluster core of the tetranuclear cluster $\text{Pd}_4(\mu^4\text{-S})(\text{dppm})_4$ (where dppm denotes bis(diphenylphosphino)methane) consists of four metal atoms with a short bonding Pd–Pd distance of 2.675 Å, and a non-bonding Pd–Pd distance of 3.030 Å. Each dppm ligand bridges a pair of Pd atoms (see Fig. 4).

5. Palladium carbene cluster

The reaction of complex $\text{Pd}_4(\mu\text{-CO})_4(\mu\text{-OAc})_4$ (0.5 mmol) with Ph_2CN_2 (5 mmol) in benzene (10 ml) at 20°C was found to involve elimination of N_2 and re-

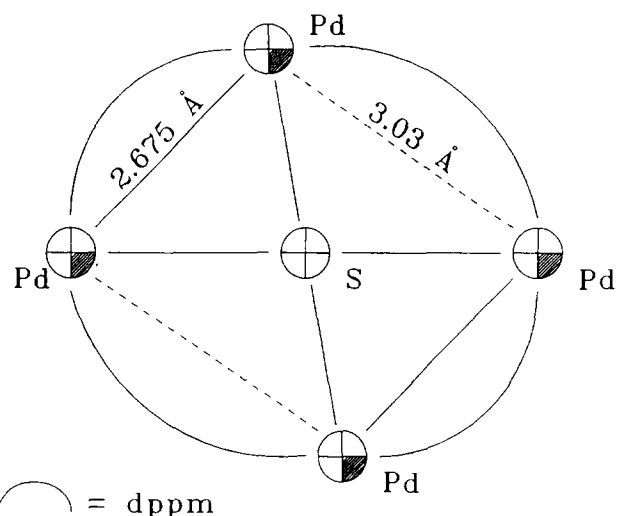
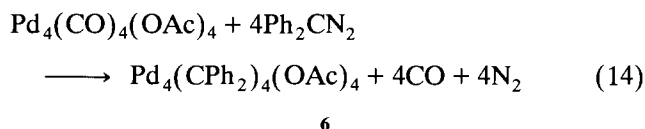


Fig. 4. Schematic representation of the structure of the cluster $\text{Pd}_4(\mu^4\text{-S})\text{dppm}_4$ [12].

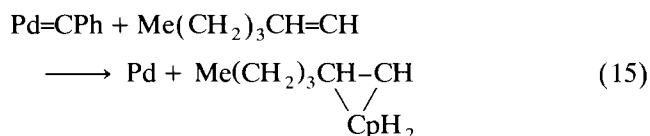
placement of all the CO ligands from the PCA, as shown by Eq. (14) [13,14]:



The light brown tetranuclear complex 6, which was characterized by elemental analysis, molecular weight [M^+ , 1200; M^+ (calc.), 1320], IR: ($\nu_{\text{CO}}^{\text{as}}$ 1560, $\nu_{\text{CO}}^{\text{s}}$ 1400, $\Delta\nu$ 160 cm^{-1}) and ^1H NMR spectroscopy: [δ 1.96 (s, 3H, OAc), 7.24 (m, 10H, Ph)] was obtained in 7–8% yield by fractional crystallization from the product mixture. The presence of bridging OAc ligands and CPh_2 fragments in complex 6 was revealed by the ^1H NMR and IR spectra. According to the ^1H NMR data the ratio OAc: CPh_2 is 1:1. Both the molecular weight and elemental analysis data are in agreement with the conclusion that complex 6 contains four OAc groups and four CPh_2 fragments. The CPh_2 fragments may be present in complex 6 either as diphenylcarbene ligands or in the form of π -coordinated tetraphenylethylene molecules, which could be formed during reaction (14) by the dimerisation of CPh_2 species. The carbene and π -alkene structures are indistinguishable on the basis of the spectral data. However, hydrogenation of complex 6 in benzene at 20°C at 0.1 MPa was found to give diphenylmethane, the product of reduction of the diphenylcarbene ligands. Tetraphenylethane, the expected product of tetraphenylethylene hydrogenation, was not found.

More evidence for the presence of carbene ligands in complex 6 was obtained from the alkene cyclopropanation reaction typical of carbene species. Reaction of complex 6 in refluxing hex-1-ene gave 2-butyl-1,1-di-

phenylcyclopropane, the product of addition of Ph_2C to the alkene, as shown by Eq. (15):



These observations show that cluster complex **6** contains carbene, not alkene, ligands.

If the conversion of the starting PCA with a rectangular metal core [5(b)] to **6** involved solely of substitution of carbonyl ligands by carbene species, the geometry of the metal skeleton of cluster **6** should be expected to be similar to that in PCA.

An EXAFS study of cluster **6** showed the coordination sphere of each palladium atom to include two Pd atoms 2.67 Å apart and one Pd atom 3.65 Å away. In addition, each palladium atom is surrounded by two light atoms at a distance of 1.86 Å, two light atoms at a distance of 2.03 Å, and presumably by two light atoms at a distance of 3.25 Å. [Fig. 5(c), Table 1]. The Pd–Pd distances found for **6** (see Table 1) differ from those observed for complex PCA by both X-ray [5(b)] (Table 1) and EXAFS techniques [13] (Fig. 5(b)), and agree well with a square-planar metal skeleton of side 2.67 Å and diagonal 3.65 Å. The set of interatomic distances and coordination numbers is compatible with a structure of the cluster in which each side of the square metal skeleton is bridged both by carbene (Pd–C 1.86 Å) and acetate (Pd–O 2.03, Pd...O 3.25 Å) ligands.

The uniform arrangement of carbene and acetate ligands around the square palladium skeleton (Fig. 6) is thought to be more favourable because of the steric requirements of the bulky diphenylcarbene ligands. The square Pd-skeleton and an uniform arrangement of Mo atoms and CO ligands around the sides and corners of the square [10] was mentioned above for a Pd–Mo cluster, $\text{Na}_2\{\text{Pd}_4[\text{CpMo}(\text{CO})_3]_4\}$, (see Fig. 3).

6. Metallic-core isomerism in palladium carbonyl carboxylate clusters

An EXAFS study of palladium (+1) carbonyl carboxylate complexes $\text{Pd}_4(\text{CO})_4(\text{RCOO})_4$ (**I**), where $\text{R} = \text{Me}, \text{CF}_3, \text{CH}_2\text{Cl}, \text{Ph}, \text{CMe}_3$ has revealed isomerism involving both the cluster metallic core and the mutual arrangement of bridging ligands [6].

The IR spectra indicated that all the complexes contain bridging carbonyl ligands and carboxylate groups, and their structures are similar and close to the structure of palladium carbonyl acetate $\text{Pd}_4(\mu\text{-CO})_4(\mu\text{-OAc})_4$. To provide more detail, the cluster structures were studied by the EXAFS method [6].

The EXAFS data for PCA were compared with the

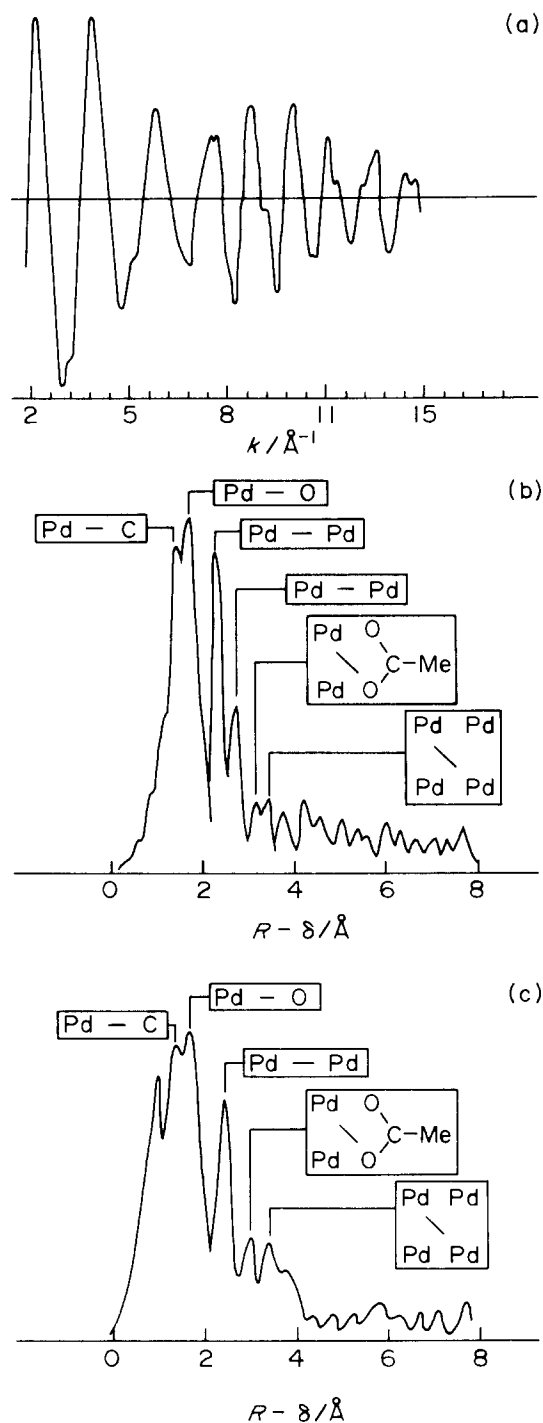


Fig. 5. EXAFS data: (a) Oscillation part of the absorption coefficient, $k\chi(k)$, for cluster **6**; (b) RDA curve from Fourier transformation of EXAFS spectrum for cluster **1**; (c) RDA curve from Fourier transformation of EXAFS spectrum for cluster **6** [14].

X-ray diffraction data [5(b)]. According to the EXAFS data (see Tables 1 and 2), two C atoms and two O atoms, separated by 1.96 Å and 2.20 Å, respectively, surround each palladium atom. These results agree well with the X-ray data for the coordinated bridging carbonyl (the Pd–C_{carbonyl} distances are 1.97 Å and

Table 1

Interatomic distances, R , obtained from EXAFS data for model substances and complex **6**

Substance	$R\text{-}\delta/\text{\AA}$	$I/\text{rel. units}$	$R/\text{\AA}$	Assignment
Pd metal	2.48	0.91	2.68	Pd–Pd
$\text{Pd}_3(\text{OAc})_6$	1.60	0.41	1.99	Pd–O
PCA	2.68	0.13	2.81	Pd–C
	1.50	0.148	1.81	Pd–C
	1.78	0.164	2.01	Pd–O
	2.34	0.145	2.67	Pd–Pd
	2.68	0.078	2.901	Pd–Pd
	3.18	0.030	3.42	Pd–O O
6	3.43	0.035	3.65	Pd–Pd Pd Pd
	1.42	0.11	1.86	Pd–C
	1.73	0.11	2.03	Pd–O
	2.47	0.9	2.67	Pd–Pd
	3.01	0.4	3.25	Pd–O O
	3.45	0.3	3.65	Pd–Pd

2.01 Å) and acetate groups (the Pd–O_{carboxyl} distance is 2.12 Å). However, the EXAFS data suggest that PCA occurs as two isomers: one isomer with a square metallic core (the side of the square is 2.72 Å and the diagonal is 3.85 Å, with a uniform ligand arrangement analogous to that in carbene complex $\text{Pd}_4(\text{CPh}_2)_4(\text{OAc})_4$, see Fig. 6) and another isomer with a rectangular metallic core (the sides are 2.67 Å and 2.90 Å and the diagonal is 3.65 Å, Fig. 1). The isomerism is possibly associated with the presence or absence of acetic acid molecules of crystallization in the PCA. In the presence of acetic acid of crystallization, the complex has a rectangular metallic core, whereas in its absence, it may have a square metallic core. The acetic acid molecules crystallizing with PCA can be removed by storage under reduced pressure

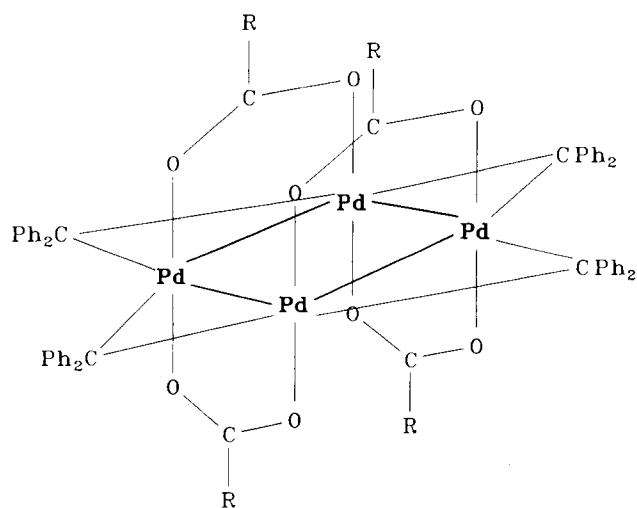


Fig. 6. Structure of $\text{Pd}_4(\text{CPh}_2)_4(\text{OAc})_4$ revealed by EXAFS data [14].

Table 2

Interatomic distances in the carboxylate complexes determined from the EXAFS spectra [6]

Complex	$R\text{-}\delta, \text{\AA}$	$A, \text{relative unit}$	$R, \text{\AA}$	Assignment	Parameter N^a	
PCA (square) R = Me	1.48	0.0803	1.97	Pd–C _{carbonyl}	4	
	1.80	0.0966	2.20	Pd–O _{carboxyl}	4	
	2.40	0.1080	2.72	Pd–Pd	2	
	2.72	0.0317	3.10	Pd–O _{carbonyl}	2	
	2.72	0.0317	3.10	Pd–C _{carboxyl}	2	
	3.22	0.0248	3.10	Pd–O _{carboxyl}	2	
	3.53	0.0308	3.85	Pd–Pd	1	
	3.85	0.0186	4.10	Pd–O _{carbonyl}	1	
	4.43	0.0176	4.85	Pd–O _{carboxyl}	1	
	PCA (rectangular) R = Me	1.50	0.1480	1.81	Pd–C _{carbonyl}	4
		1.78	0.1640	2.01	Pd–O _{carboxyl}	4
		2.34	0.1450	2.67	Pd–Pd	2
2.68		0.0780	2.90	Pd–Pd	2	
3.18		0.0300	3.42	Pd–O _{carboxyl}	2	
3.43		0.0350	3.65	Pd–Pd	2	
R = CH ₂ Cl	1.44	0.0737	1.93	Pd–C _{carbonyl}	4	
	1.76	0.0990	2.14	Pd–O _{carboxyl}	4	
	2.38	0.1231	2.70	Pd–Pd	2	
	2.93	0.0185	3.30	Pd–O _{carbonyl}	2	
	2.93	0.0185	3.30	Pd–C _{carboxyl}	2	
	3.20	0.0220	3.60	Pd–O _{carboxyl}	2	
	3.51	0.0296	3.83	Pd–Pd	1	
	3.78	0.0188	4.10	Pd–O _{carboxyl}	1	
	R = CMe ₃	1.46	0.0803	1.95	Pd–C _{carbonyl}	4
		1.76	0.1023	2.14	Pd–O _{carboxyl}	4
		2.38	0.0760	2.70	Pd–Pd	1.5
		2.72	0.0340	3.04	Pd–Pd	1
3.20		0.0259	3.60	Pd–O _{carboxyl}	2	
3.51		0.0383		Pd–Pd	1	
R = Ph	3.51	0.0383		Pd–Pd	1	
	3.85	0.0286	4.10	Pd–O _{carbonyl}	1	
	3.85	0.0286	4.10	Pd–Pd	1	
	1.40	0.0589	1.83	Pd–C _{carbonyl}	4	
	1.71	0.0773	2.11	Pd–O _{carboxyl}	4	
	2.26	0.0881	2.58	Pd–Pd	1.5	
	2.67	0.0509	3.07	Pd–O _{carbonyl}	2	
	2.67	0.0509	2.98	Pd–Pd	1	
	2.99	0.0202	3.38	Pd–O _{carboxyl}	2	
	2.99	0.0202	3.38	Pd–O _{carboxyl}	2	
	3.32	0.0202	3.70	Pd–C _{carboxyl}	2	
	3.32	0.0202	3.64	Pd–Pd	1	
3.68	0.0173	4.00	Pd–Pd	1		
4.01	0.0223	4.33	Pd–Pd	1		
R = CF ₃	1.42	0.0584	1.92	Pd–C _{carbonyl}	4	
	1.76	0.0645	2.14	Pd–O _{carboxyl}	4	
	2.36	0.1214	2.70	Pd–Pd	2	
	3.01	0.0089	3.40	Pd–O _{carbonyl}	2	
	3.01	0.0089	3.40	Pd–C _{carboxyl}	2	
	3.43	0.0119	3.75	Pd–Pd	0.5	
3.76	0.0126	4.08	Pd–Pd	0.5		

^a N is the empiric parameter proportional to the number of the given atoms surrounding the palladium atom.

[5(b),7]; it is possible that removal of the crystallization acetic acid dimers is accompanied by isomerization of the metallic core.

Examination of the IR [7] and EXAFS [6] data for the interatomic separations and coordination numbers

for the other carbonyl carboxylate complexes under consideration allows us to conclude that all the complexes have a similar structure. Thus, the carbonyl monochloroacetate complex $\text{Pd}_4(\text{CO})_4(\text{CH}_2\text{ClCOO})_4$ is analogous to one of the PCA isomers, and has a square metallic core with a side of 2, 70 Å and a diagonal of 3.83 Å. The distances in the metallic core of the carbonyl trifluoroacetate complex, $\text{Pd}_4(\text{CO})_4(\text{CF}_3\text{COO})_4$, correspond to the rhombus with a side of 2.70 Å and diagonals of 3.75 Å and 4.08 Å. For the carbonyl benzoate complex $\text{Pd}_4(\text{CO})_4(\text{PhCOO})_4$ and the carbonyl pivalate complex $\text{Pd}_4(\text{CO})_4(\text{CMe}_3\text{COO})_4$, the observed Pd–Pd separations match the mixture of the isomers with the square and rectangular metallic cores. We also think that along with the core isomers there can also be isomers arising from different mutual dispositions of the ligands. Ligands of the same kind can be arranged in pairs (Fig. 1), as was found for the PCA sample studies by X-ray diffraction, or uniformly, as in the case of the carbene complex $\text{Pd}_4(\text{CPh}_2)_4(\text{OAc})_4$ (Fig. 6). The EXAFS data indicate the presence of the isomers with the uniform ligand arrangement. The latter seems to be more favourable thermodynamically. Upon prolonged storage the content of such an isomer seems to increase. The examination of peaks with $R > 3$ Å suggests that the carboxylate ligands are located close to the plane of the metallic core with the carbonyl ligands arranged perpendicular to it.

7. Concluding remarks

In this accord we have attempted to define the influence of the ligands on the geometry of Pd_4 clusters.

It is apparent that both the steric requirements of the ligands and electronic interactions between the ligands and metal skeleton must be taken into account in rationalizing the observed changes in PCA cluster core geometry upon the replacement of CO and/or AcO ligands by other groups.

Both changes in the nature of the ligand surrounding the Pd atom and change in the formal oxidation state of Pd are responsible for the observed metal skeleton changes upon reaction of PCA with $\text{CpMo}(\text{CO})_3\text{Na}$ (see Eq. 13 and Figs. 1 and 3).

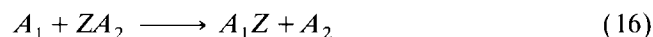
Changes in the metal skeleton upon variation of the carboxylate ligands in PCA and related complexes of the composition $\text{Pd}_4(\text{CO})_4\text{X}_4$, where $\text{X} = \text{AcO}^-$, $\text{CH}_2\text{ClCOO}^-$, CF_3COO^- , have been detected by EXAFS studies.

The rather unexpected redistribution of ligands over Pd_4 cluster core and changes in the geometry of the core of PCA detected by the EXAFS technique reveal the ability of the ligands to migrate, and the non-rigidity of the cluster cores under mild conditions. Both

these features are well established phenomena [2–4] and seem to be of great importance for cluster reactivity and cluster activity in catalysis [3,4,15,16].

Mobility of the cluster core is presumably favoured by both a low metal–metal bond energy (60–80 kJ mol⁻¹ for the average Pd–Pd bond) and the expected low energy required for angle deformations in metal cycles consisting of Pd atoms. As models of bulk Pd catalysts, giant clusters approximating to $\text{Pd}_{561}\text{L}_{60^-}$ (OCOCH_3)₁₈₀ (L = Phen, Bipy) and $\text{Pd}_{561}\text{Phen}_{60^-}\text{O}_{60}\text{X}_{60}$ (X = PF₆, ClO₄, BF₄, CF₃CO₂) have been shown to undergo metal skeleton rearrangement when heated or stored [17], the concept of cohesive energy, which works well for metals and their alloys [4], should be used to discuss the inner-cluster reactions of such species.

A general step in heterogeneous catalytic reactions is adsorption of a substrate A_1 at an active centre Z . Usually adsorptive substitution of adsorbate A_2 by adsorbate A_1 is of practical interest, Eq. 16:



The structure of active centre Z is usually assumed not to be changed in the reaction (16), and the enthalpy of the reaction is attributed to the difference in bond energies (heats of adsorptions) $Z - A_1$ and $Z - A_2$. It is easy to verify that adsorption reaction (16) is formally similar to the reaction of PCA with phenanthroline molecule (Eq. 9). However, the last mentioned reaction involves not only formal replacement of CO by Phen but displacement of carboxylate ligands and cluster core rearrangement. It is evident that even seemingly very simple steps in catalytic reactions can involve rather complicated transformations of active centres.

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