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# Palladium(I) carbonyl carboxylate clusters *cyclo*-$[Pd_2(\mu\text{-}CO)_2(\mu\text{-}OCOR)_2]_n$ ($n = 2$ or 3): Structure and reactivity

Tatiana A. Stromnova [a,*], Oleg N. Shishilov [a], Mikhail V. Dayneko [c], Kirill Yu. Monakhov [a], Andrei V. Churakov [a], Ludmila G. Kuz'mina [a], Judith A.K. Howard [b]

[a] *Institute of General and Inorganic Chemistry, Russian Academy of Science (RAS), Leninsky prospekt, 31, Moscow 119991, Russia*
[b] *Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK*
[c] *Moscow State Academy of Fine Chemical Technology, Vernadskogo pr., 86, Moscow 119571, Russia*

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**Abstract**

The interaction of palladium(+1) cluster $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OAc)_4$ with saturated and unsaturated carboxylic acids was studied. It was found, that the substitution of acetates groups on others carboxylates leads to the clusters with different nuclearity. Palladium(+1) carbonyl carboxylate complexes of composition $[Pd(\mu\text{-}CO)(\mu\text{-}OCOR)]_n$, where R = $CF_3$, $CCl_3$, $CH_2Cl$, MeCH = CMe, Me, $Pr^i$, Bu, $Bu^i$, $Bu^{tert}$, $n\text{-}C_5H_{11}$ and $n = 4$ or 6 were synthesized. According to X-ray data all clusters possess cyclic planar metal cores with alternate pairs of μ-carbonyl and μ-carboxylate ligands. The presence of bulky alkyl fragments in the carboxylate ligand increases the nuclearity of the cluster compared to that of the starting palladium(+1) carbonyl acetate of composition $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OAc)_4$ due, apparently, to steric hindrance.

*Keywords:* Palladium; Carbonyl carboxylate; Cluster; Crystal structure

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## 1. Introduction

Palladium carbonyl complexes have attached the particular attention as potential intermediates of catalytical processes associated with CO transformation. The catalytic oxidation of CO to $CO_2$, syntheses of alkyl oxalates and alkyl carbonates, the carbonylation of alcohols, unsaturated hydrocarbons and nitroarenes, etc., are among these reactions. The processes, where formal oxidation state of Pd atoms plays key role, keep the special place. This is especially preferable for redox processes where easiness of Pd(+1) transformation into Pd(0) or Pd(+2) is very important feature [1,2].

On other side, Pd carboxylates are very attractive in systems where the absence of halogen should be realized. For example, according to preliminary data, the substitution of chlorine on different carboxylates in Pt and Pd leads to the less-toxic complexes with good anti-cancer activity [3].

Thus, this paper deals with Pd(+1) complexes that contain neutral ligands (CO) and carboxylate ligands and can serve as the convenient starting compounds for synthesis of various new classes of complexes as, for example, palladium nitrosyl complexes [4].

## 2. Results and discussion

The first Pd(+1) carbonyl acetate cluster $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OOCMe)_4$ (**1**) was obtained earlier by reduction of Pd(+2) acetate with carbon monoxide in glacial acetic acid media [5].

According to X-ray diffraction data, cluster **1** has an almost rectangular metal core. The opposite sides of the

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[*] Corresponding author. Tel.: +7 095 9554805; fax: +7 095 9541279.
*E-mail address:* strom@igic.ras.ru (T.A. Stromnova).

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core are linked by the same pairs of ligands – two pairs of acetate groups and two pairs of carbonyls (see Fig. 1).

The coordinated acetate groups in cluster **1** can be replaced by other carboxylates in the reactions with the corresponding carboxylic acids (both saturated and unsaturated ones):

$$Pd_4(\mu\text{-}CO)_4(\mu\text{-}OOCMe)_4 + RCOOH$$
$$\rightarrow [Pd(CO)(OCOR)]_n + MeCOOH$$
$$R = CF_3, CCl_3, CH_2Cl,$$
$$MeCH = CMe, Me, Pr^i, Bu, Bu^{tert}, Bu^i, C_5H_{11}$$

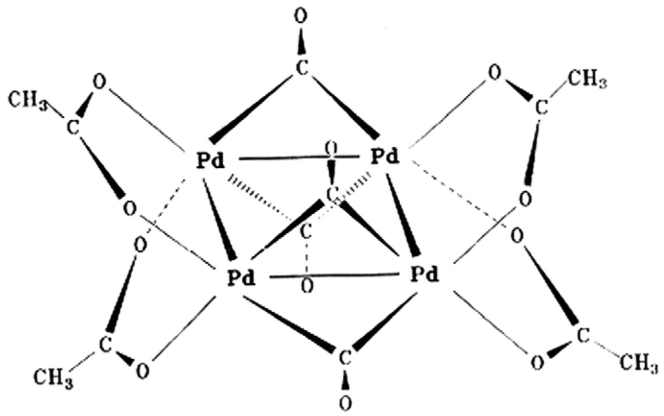

Fig. 1. Structure of cluster **1**.

All complexes obtained contain one carbonyl and one carboxylate groups per one Pd atom and have a composition $[Pd(CO)(OCOR)]_n$. The total composition of compounds allows assuming that the formal oxidation state of Pd atoms remains like in initial cluster (that is +1).

According to IR spectroscopic data, all the complexes contain bridging carbonyl groups (see Table 1).

One can see that the increasing of electron-acceptor capacity of R group in carboxylate ligands is accompanied with increasing of $\nu_{CO}$ value in IR spectra. Perhaps, the presence of electron-withdrawing groups such as $CF_3$ or $CCl_3$ favours to decrease the electron density on Pd atom and to reduce the back-donation from Pd atom to CO group, and, as result, increasing of $\nu_{CO}$.

Thus, all the complexes contain bridging carbonyl groups and this fact allows to consider that the $[Pd_2(\mu\text{-}CO)_2(OOCR)_2]$ structural moiety is common for each cluster obtained.

Nevertheless, the structures of clusters are quite different.

The structure of cluster $[Pd_2(\mu\text{-}CO)_2(\mu\text{-}OOCR)_2]_n$ (**2**: $R = CH_2Cl$, $n = 2$) is very similar to of **1** [5,6]. The molecule **2** is centrosymmetric with approximately rectangular $Pd_4$ core. The neighboring palladium atoms are linked by pairs of carbonyl and carboxyl ligands forming two $Pd_2(\mu\text{-}CO)_2$ and two $Pd_2(\mu\text{-}OOCCH_2Cl)_2$ fragments (see Fig. 2). The Pd–Pd distances are 2.6594(3) and 2.9653(3) Å, while Pd–Pd–Pd angles are equal 91.670(9)° and 88.330(9)°. The coordination environment of Pd atoms (two carbon and two oxygen atoms) is almost square-planar. The displacements

Table 1

| $[Pd(CO)(OCOR)]_n$, R= | $CF_3$ | $CCl_3$ | $CH_2Cl$ | MeCH=CMe | Me | $Pr^i$ | Bu | $Bu^{tert}$ | $C_5H_{11}$ |
|---|---|---|---|---|---|---|---|---|---|
| $\nu_{CO}$, $cm^{-1}$ | 2000<br>1968[a] | 1999<br>1967[a] | 1979<br>1934[a] | 1975<br>1954[a] | 1976<br>1934[a] | 1974<br>1944[a] | 1972<br>1936[a] | 1976<br>1932[a] | 1968<br>1936[a] |

[a] Wide band.

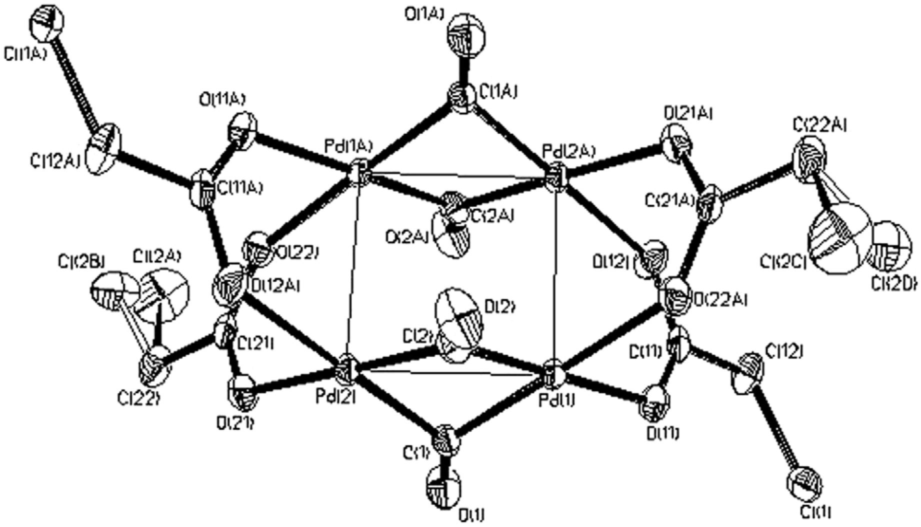

Fig. 2. Molecular structure of **2**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

of Pd(1) and Pd(2) atoms from least-squares planes of these coordinated atoms are 0.009(1) and 0.017(1) Å, respectively. Since the O–O distances in carboxyl ligands (2.247(3) and 2.242(3) Å) are significantly shorter than the distance between carboxyl bridged Pd atoms (2.9653(3) Å), all carbonyl ligands are noticeably shifted outwards the molecular center to maintain the square-planar coordination of Pd atoms. The bridging carbonyl ligands are symmetrical with Pd–C distances ranging from 1.972(3) to 1.981(3) Å and Pd–C–O angles varying from 136.4(3)° to 138.9(3)°. One of the independent $CH_2Cl$ groups was found rotationally disordered with chlorine atoms occupying two positions in the ratio 0.54/0.46. In the crystal, molecules of **2** form columns spread along *c*-axis (see Fig. 3). These columns are bridged by short intermolecular Pd···Cl contacts (3.1245(8) Å). The space between columns is filled with disordered solvent toluene molecules lying on crystallographic inversion centers.

Thus, the clusters **1** and **2**, as well as the clusters $[Pd_2(\mu\text{-}CO)_2(\mu\text{-}OOCR)_2]_n$, where $R = CF_3$ (**3**) or $CCl_3$(**4**) (the structures of last two complexes were determine by EXAFS [7]) possess cyclic tetranuclear metal core with pairs of carbonyl and carboxylate bridging ligands.

Three next representatives of carbonyl carboxylate clusters – namely clusters $[Pd_2(\mu\text{-}CO)_2(\mu\text{-}OOCR)_2]_n$ – (**5**, $R = CMe_3$; **6**, $R = Pr^i$; **7**, $R = C_5H_{11}$) possess the hexanuclear metal core. The structure of **5** was published early [8]. The structure of **6** contains two independent hexanuclear molecules with similar geometrical parameters (bond lengths and angles). In both molecules, cyclic $Pd_6$ cores are planar within 0.1387(5) and 0.1442(5) Å (see Fig. 4). In the $Pd_6$ cycles, the neighboring palladium atoms are linked by alternating pairs of carbonyl and carboxyl ligands forming three $Pd_2(\mu\text{-}CO)_2$ and three $Pd_2(\mu\text{-}OOCPr^i)_2$ fragments. The Pd–Pd distances lie within the ranges 2.6484(10)–2.6658(9) and 2.8767(10)–2.9493(10) Å, for carbonyl and carboxyl bridged fragments, respectively. The displacements of 12 Pd atoms from least-squares planes of coordinated atoms (two carbons and two oxygen atoms) range within 0.022(4)–0.084(4) Å. In contrast to **1** and **2**, all carbonyl ligands in **6** are slightly shifted towards the center of molecule to maintain the planarity of Pd coordination environment. The latter difference with the structure of **2** is a consequence of steric requirements of larger $Pd_6$ cycle. As for **2**, bridging carbonyl ligands in **5** are rather symmetrical with Pd–C distances ranging from 1.948(9) to 2.004(8) Å and Pd–C–O angles varying from 136.2(8) to 139.8(8)°. In the structure of **6**, five of 12 isopropyl groups were found to be rotationally disordered over two positions. The crystal of **6** contains solvent benzene molecules. The center of benzene molecule (CR1) is positioned approximately on the line connecting the centers of adjacent $Pd_2(\mu\text{-}CO)_2$ moieties (CR2 and CR3) (see Fig. 5). The distances CR1–CR2 and CR1–CR3 (3.250 and 3.254 Å) are significantly shorter than the doubled van der Waals radius of carbon atom (3.4 Å) [9]. and indicate the presence of π–π interaction. The angle CR2–CR1–CR3 is equal 165.4°. The same arrangement of solvent benzene molecule was observed previously in the closely related structure of **5**. Moreover, the neighboring molecules of **6** are linked by short intermolecular Pd(6)–Pd(4′) and Pd(1′)–O(12) contacts – 3.1772(8) and 2.899(7) Å, respectively. These three intermolecular interactions form distorted hexagonal layers in the plane [1 0 1] (see Fig. 6).

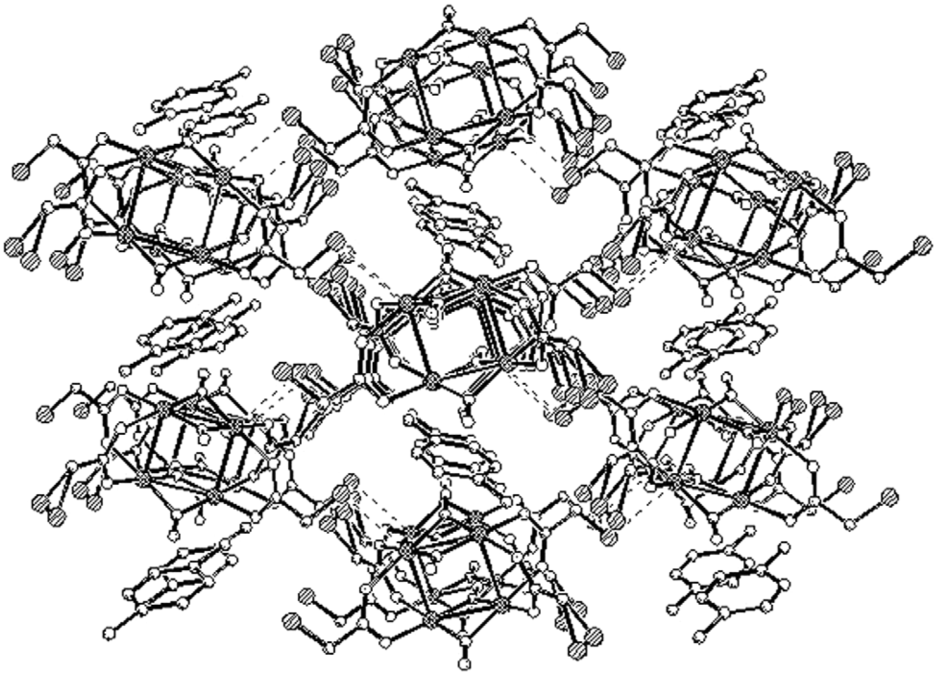

Fig. 3. Packing motif in the crystal structure of **2**. Intermolecular Pd···Cl contacts are shown by dashed lines.

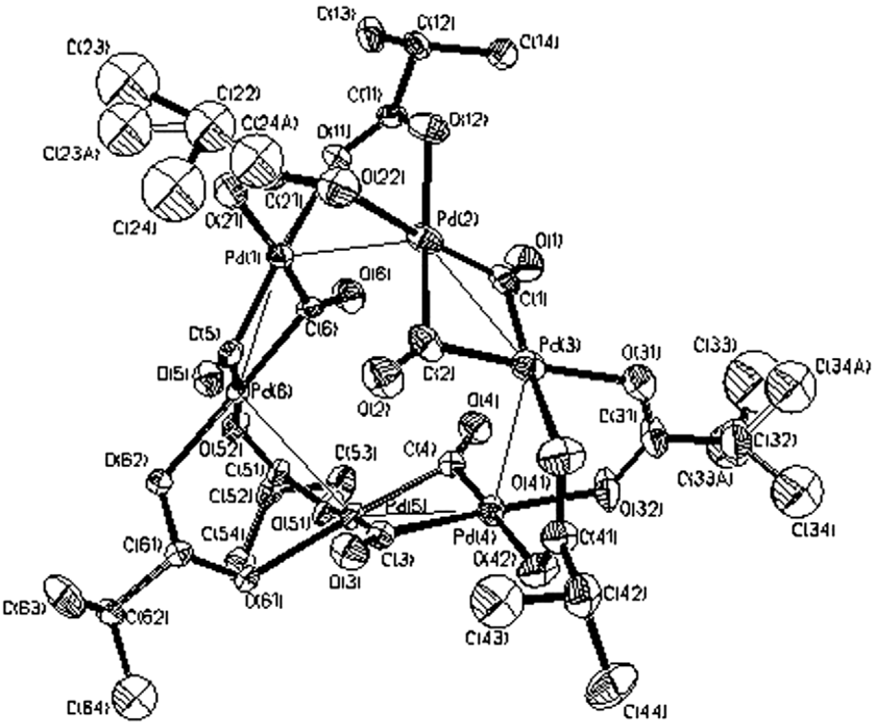

Fig. 4. Molecular structure of **6**. Only one independent molecule is shown. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

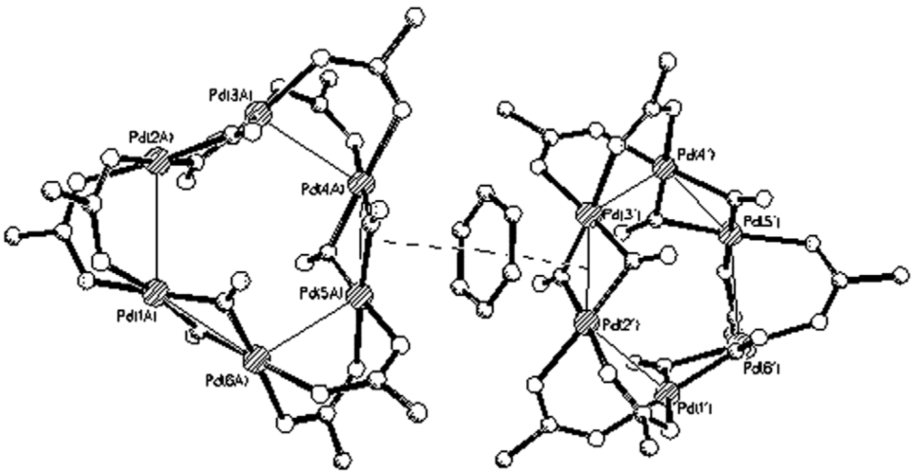

Fig. 5. Arrangement of solvent benzene molecule in structure of **6**. *i*-Pr groups are omitted for clarity.

Preliminary X-ray analyses of complex $[Pd(CO)(OOCC_5H_{11})]_6$ (**7**) showed that the structure of **7** is similar to that of **6**. The metal core in 7 represents approximately planar $Pd_6$ fragment with alternating pairs of carbonyl and carboxyl ligands. The details concerning the crystal structure **7** will be published elsewhere later.

The presence of two bands $\nu_{CO}$ in IR spectra (see Table 1) can be explained by the fact that strong polar groups (such as CO, NO, etc.) coordinated on the similar metal center have more then one bands.

The second possible reason of the presence of two bands $\nu_{CO}$ in IR spectra can be sequent of their structures. Thus, an arrangement of CO-groups towards metal core in clusters is slightly non-symmetrical. For example, in $Pd_4(CO)_4(OOCCH_2Cl)_4$ the length of both Pd–C(carbonyl) bonds is the same, but dihedral angles between two planes – $Pd_4$ (metal core plane) and $Pd_2C$(carbonyl) – are different and equal 76.8° and 77.5°. More difference were found in structure of $Pd_6(CO)_6(OOCPr^i)_6$. In this molecule the dihedral angles between two planes – $Pd_6$ (metal core plane) and $Pd_2C$(carbonyl) – change from 81.4° to 77.2° and diversity between two dihedral angles for CO-groups coordinated on one side of metal core varies from 0.9° up to 3.9°. Such difference can lead to different overlapping of

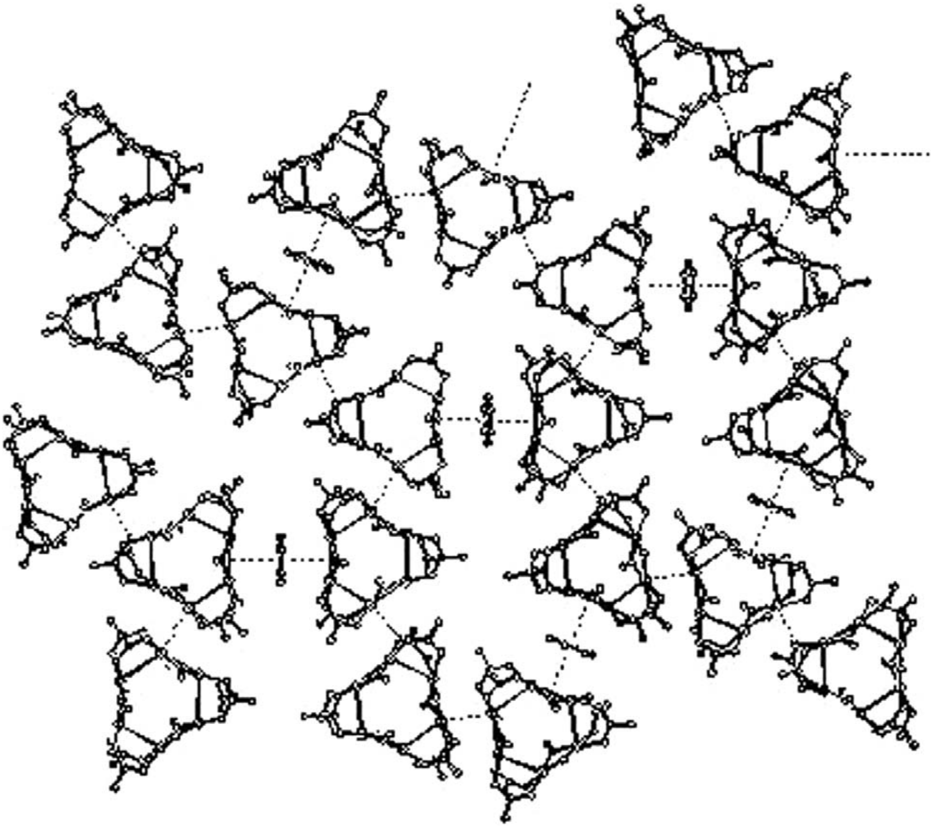

Fig. 6. Distorted hexagonal layers [1 0 1] in the crystal structure of **6**. Short intermolecular contacts are shown by dashed lines.

corresponding orbitals responsible for binding Pd–CO and to change of back-donation from Pd to CO, which displays in changing of $\nu_{CO}$.

One can assume that the wide band in every IR spectrum is a result of overlapping of some near-placed bonds in solid sample of corresponding complex. The absence of effect of crystal-packing in solution of complex should lead to appearance only one $\nu_{CO}$ band – as a result of overage of position of CO-groups. IR spectra of complexes in $CH_2Cl_2$ solution verify this suggestion. Thus, in IR spectrum of complex $Pd_6(CO)_6(OOCBu^{tert})_6$ two bands at 1976 and 1932 cm$^{-1}$ in solid state transform to one band at 1952 cm$^{-1}$ in $CH_2Cl_2$ solution. The same picture – transformation of two bands at 1975 and 1954 cm$^{-1}$ in solid state into one band at 1932 cm$^{-1}$ in $CH_2Cl_2$ solution – you can see in IR spectrum of complex $[Pd_2(CO)_2(OOCCMe{=}CHMe)_2]$ (**8**).

All clusters $[Pd_2(CO)_2(OOCR)_2]_n$ are readily soluble in benzene and toluene, and poorly soluble in diethyl ether and hexane. Noteworthy that the solubility of $[Pd_2(CO)_2(OCOR)_2]_n$ increases in parallel to decreasing of electron acceptor properties of radical R in their carboxylate groups according to row $CF_3 < CCl_3 < CH_2Cl \sim MeCH{=}CMe < Me \sim Pr^i \sim Bu \sim Bu^{tert} < C_5H_{11}$. In the presence of highly polar organic solvents (aliphatic alcohols, acetone) and water, the complexes decompose to form metallic palladium. This capability increases according to the same row. The partial decomposition in the presence of traces of water is a plausible reason of change of the solution's color from yellow to greenish in the course of syntheses.

The transformation of tetranuclear $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OOCMe)_4$ into tetra- or hexanuclear clusters II can include the substitution of acetate groups by different carboxylates:

$$Pd_4(\mu\text{-}CO)_4(\mu\text{-}OOCMe)_4 + RCOOH \rightarrow [Pd(CO)(O_2CR)]_n + MeCOOH$$

Perhaps, the substitution is accompanied by dissociation of tetranuclear clusters into binuclear fragments $(RCOO)Pd(\mu\text{-}CO)_2Pd(OOCR)$. It can be the other reason of color's change during the syntheses. The subsequent enlargement of these fragments gives rise to clusters in which the number of metal atoms is a multiple of two – $Pd_4$ or $Pd_6$. The origin of different nuclearity of clusters formatted can be both electron and steric factors. Based on analyses of the structures of all cluster structures, namely the positions of atoms in quite different radical R in carboxylate groups, gives no evidence of the influence of steric factors. Hence, we can suggest the electron factors as the main origin of observed difference in the cluster structured. For example, the presence of electron acceptors in carboxylate group leads to decreasing of electron density on Pd atom. And as consequence such atom will climb to have planar square environment. On the contrary, if there are electron donors in carboxylate group, the degree of approaching to such square becomes smaller.

## 3. Conclusion

The presence of carboxylate groups promotes the formation palladium clusters with planar cyclic metal core. The nuclearity of such clusters depends on the steric factor of substitute in carboxylate groups.

## 4. Experimental

### *4.1. General techniques*

All organic solvents and liquid organic reagents were purified and dried according to standard procedures. Microanalyses were conducted on a Carlo Erba Analyzer CHND-OEA 1108. The spectroscopic instrument used was a Carl Zeiss SPECORD-M82 for IR spectra. The compound *cyclo*-$[Pd_4(\mu\text{-}CO)_4(\mu\text{-}OOCMe)_4]$ (**1**) was prepared according to a published procedure [5] by reductive carbonylation of palladium diacetate in glacial acetic acid. The compound $[Pd(CO)(OCOCMe_3)]_6$ (**5**) was prepared according to a published procedure [8]. Solid carboxylic acids were commercially supplied.

### *4.2. Preparation of* $[Pd(CO)(OCOR)]_n$, *R* = $CH_2Cl$ (**2**), $CF_3$ (**3**), $CCl_3$ (**4**)

Complexes **2–4** were obtained according to [7] by interaction of cluster **1** with corresponding acids in toluene solutions. The yield is usually about 75–80%. Crystals of clusters **2** suitable for X-ray diffraction analyses were grown from a $CH_2Cl_2$–benzene–hexane mixture at reduced temperatures during 2–3 weeks.

### *4.3. Preparation of* $[Pd(CO)(OCOCHMe_2)]_6$ (**6**)

Cluster **1** (0.15 g, 0.64 mg-atom of Pd), benzene (10 ml) and freshly distilled *i*-butyric acid (0.2 ml, a twofold excess with respect to palladium) were placed in a round-bottom flask. The resulting suspension was twice evacuated, purged with argon to remove the residual oxygen, and stirred under an inert atmosphere. The suspension rapidly (with 5–10 min) dissolved to give a bright yellow solution. The color of the solution changed to greenish in the course of synthesis (1 h). The optimum reaction time was determined in a series of experiments using the IR spectra of the final product (based on the absence of stretching bands of the carbonyl groups of starting complex). After completion of the synthesis, the reaction mixture was concentrated to dryness under vacuum using an oil pump and washed two or three times with hexane (to remove the residual *i*-butyric acid). The pale yellow precipitate was dried under vacuum. The yield was 75% (0.129 g).

For $[Pd(CO)(OCOCHMe_2)]_6$ Anal. Calc.: C, 27.10; H, 3.16. Found: C, 27.29; H 3.68%.

Crystals of clusters **6**, suitable for X-ray diffraction analyses, were grown from a benzene–hexane mixture by low reducing of temperatures from 20°C to −18°C during 3–6 days.

### *4.4. Preparation of* $[Pd(CO)(OCOC_5H_{11})]_6$ (*7*)

Cluster **1** (0.23 g, 1 mg-atom of Pd), benzene (30 ml) and freshly distilled hexanoic acid (0.3 ml, an approximately twofold excess with respect to palladium) were placed in a round-bottom flask. The synthesis and isolation of the product were carried out as described for cluster **6**. The pale yellow precipitate was dried under vacuum. The yield was 76% (0.24 g).

For $[Pd(CO)(OOCC_5H_{11})]_6$ Anal. Calc.: C, 33.68; H, 4.41. Found: C, 33.61; H 3.67%.

### *4.5. Preparation of* $[Pd(CO)(OOCCMe{=}CHMe_2)]_n$ (**8**)

Cluster **1** (0.2 g, 1 mg-atom of Pd), THF (10 ml) and 1-methylcroton acid (0.2 g, 2 mmol, a twofold excess with respect to the palladium) were placed in a round-bottom flask. The reaction mixture was being stirred during 30 min. The resulting suspension was filtered and concentrated up to 1/3 part by volume under vacuum using an oil pump. After that 5 ml of hexane were added and dark-yellow precipitate formed. The precipitate was filtered and washed by 3 ml of THF. The yellow powder was dried under vacuum. The yield was 50% (0.117 g).

For $[Pd(CO)(OCO(CH_3)C{=}CHCH_3)]_n$ Anal. Calc.: C, 30.85; H, 3.00. Found: C, 30.81; H, 3.03%.

IR spectrum: $\nu(CO) = 1972,\ 1946\ cm^{-1}$, $\nu(C{=}C) = 1653\ cm^{-1}$, $\nu_{as}(COO) = 1557\ cm^{-1}$, $\nu_s(COO) = 1430\ cm^{-1}$.

### *4.6. X-ray crystallography*

X-ray data for compounds **2** and **6** were collected on a Bruker SMART CCD diffractometer (graphite-monochromatized Mo Kα radiation, 0.71073 Å) at 120 K using $\omega$ scan mode. Experimental intensities were corrected for Lorentz and polarization effects. Semi-empirical absorption correction based on measurements of equivalent reflections was applied. The structures were solved by direct methods [10] and refined by full-matrix least-squares on $F^2$ [11]. All non-hydrogen atoms were refined with anisotropic thermal parameters (except disordered methyl carbon atoms in **6**). In the structure of **2**, one of $-CH_2Cl$ groups was found to be rotationally disordered over two positions with occupancy ratio 0.54/0.46. In the structure of **6**, five of 12 isopropyl groups were also found to be rotationally disordered over two positions. Refinement of occupancy factors led to the ratios 0.53/0.47, 0.52/0.48, 0.64/0.36, 0.58/0.42 and 0.64/0.36. In both structures, all hydrogen atoms were placed in calculated positions and refined using a riding model. The crystal structure of **2** contains disordered toluene solvent molecule; the structure of **6** contains solvent benzene molecule. Details of X-ray structural investigations are listed in Table 1.

**Acknowledgements**

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## Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-278722 and 278723. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.033.

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