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Palladium carbene cluster: synthesis, structure and reactivity *

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Abstract

The first palladium carbene cluster, μ -tetrakis(diphenylmethyliden)- μ -tetraacetato-quadro-tetrapalladium (4Pd–Pd) Pd₄(μ -CPh₂)₄(μ -OAc)₄ (I), has been synthesized by substitution of diphenylcarbene ligands for CO-groups in μ -tetrakis(carbonyl)- μ -tetraacetato-quadro-tetrapalladium (4Pd–Pd) Pd₄(μ -CO)₄(μ -OAc)₄ (II) and characterized with EXAFS data. Reactivity of I, II and related clusters is discussed. Thermolysis of the clusters has been found to involve inner-sphere oxidation of carbene or carbonyl ligands during which an oxygen atom is transferred from the carboxylate group to the carbene or carbonyl ligand. Thermolysis of carbonyl clusters in benzene or toluene solutions gives rise to the products of CO₂ insertion into the C–H bond of the solvent forming benzoic acid from benzene and a mixture of phenylacetic and tolyl acids from toluene.

Introduction

In the 1980s the development of the coordination chemistry of cluster compounds was to a great extent associated with the use of carbonyl ligands [1,2]. Meanwhile, such ligands as carbenes, whose coordination ability is closely related with the nature of their carbonyl groups, were but rarely used in the study of clusters. Only two carbene clusters with cores containing more than three metal atoms are known to date [3,4].

Palladium clusters with carbene ligands are presumed to be intermediates in palladium complex-catalyzed carbene synthesis [5,6]. Nevertheless, palladium carbene clusters have not yet been isolated.

In the present paper the synthesis, structure and chemical properties of the first palladium carbene cluster are described.

* Dedicated to the memory of Professor Piero Pino.

Experimental

Chemically pure benzene, toluene and glacial acetic acid were purified by standard procedures [7]. Pure benzophenone hydrazone (Fluka) was used without additional purification. Diphenyldiazomethane was obtained by oxidation of benzophenone hydrazone with yellow mercury oxide according to ref. 8.

Elemental analysis was performed using a C,H,N-analyzer, model Laboratorni pristroje Praha. Molecular weights of the complexes were measured with vapour pressure osmometer. IR spectra were measured with a Specord IR-75 spectrometer. ^1H NMR spectra were measured with Bruker WP-200 (TMS as an internal standard). Mass spectra were measured with a Kratos MC-80 spectrometer in the chromatographic operation mode using a quartz capillary column TV-1 of 30 m length with ionization energy 50 eV and scanning speed 1 s/decade of mass. Organic compounds were identified by means of the mass-spectra map [9]. Chromatographic analysis was conducted using a LHM-80 chromatograph.

The K-edge of the palladium X-ray absorption spectrum was measured with the EXAFS spectrometer of the Siberian Synchrotron Centre. A double monoblock Si(111) crystal was used as a monochromator. Spectra 1000 eV beyond the absorption edge were measured using 2 eV steps and deduced by Fourier transformation. The $k \cdot \chi(k)$ values were analyzed within the 3.8–15.0 Å range. The pre-edging region was extrapolated to that of the EXAFS with Victorin polynomials. The smooth segment of the absorption spectrum was simulated with the cubic spline method. Ionization potential was taken as represented by the twist point at the absorption edge. Coordination numbers were determined by comparing amplitudes of peaks with those of model substances on the assumption that their Debye factors were approximately the same. False peaks are denoted by asterisks. They are derived from the smooth part of the absorption coefficient and from XANES oscillations. No correspondence procedures were used, interatomic distances and coordination numbers being determined by comparison with model substances.

Benzophenone azine was identified by elemental analysis (found: C, 87.1; H, 5.8; N, 7.9. $\text{C}_{26}\text{H}_{20}\text{N}_2$ calc.: C, 86.7; H, 5.6; N, 7.8%), m.p. 163–165°C, molecular weight (M^+ 360) and ^1H NMR spectra (2 signal groups corresponding to phenyl protons centred at $\delta = 7.41$ and 7.45 ppm).

The synthesis of palladium carbonylcarboxylate complexes

$\text{Pd}_4(\mu\text{-CO})_4(\mu\text{-OAc})_4$ (II) was obtained by reduction of palladium acetate with carbon monoxide in acetic acid solution according to ref. 10.

Palladium carbonylcarboxylate complexes $\text{Pd}_4(\mu\text{-CO})_4(\mu\text{-OOCR})_4$ ($\text{R} = \text{CH}_2\text{Cl}$, Ph, CMe_3) were obtained via the reaction of II with a saturated benzene solution of the corresponding carboxylic acid.

$\text{Pd}_4(\text{CO})_4(\text{OOCCH}_3)_4$ was obtained via the reaction of I with CF_3COOH .

The synthesis of carbenecarboxylate complexes was carried out under argon atmosphere in thoroughly dehydrated benzene. The apparatus was equipped with a glass double-jacket reaction vessel and gas burette.

The synthesis of $\text{Pd}_4(\mu\text{-CPh}_2)_4(\mu\text{-OAc})_4$ (I)

The bright-red solution of Ph_2CN_2 (1 g, 5 mmol) in benzene (10 ml) was added to powered I (0.1 g, 0.5 mmol). The reagent mixture was stirred with the magnetic

stirrer until completion of nitrogen evolution (25–30 min at 25°C or 5–10 min at 35°C). Afterwards the reagent mixture was evaporated in vacuum to half its volume and filtered to isolate the precipitated benzophenone azine. On adding hexane to the mixture the light-brown complex I was precipitated. The complex was purified by resolving in benzene followed by precipitation with addition of hexane. The yield was 0.015 g (9.4%). Found: C, 57.2; H, 3.6. $C_{60}H_{52}O_8Pd_4$ calc.: C, 54.3; H, 3.6%. IR spectrum (ν , cm^{-1}): 1560, 1400, 760, 720, 690. 1H NMR: δ 7.4 (multiplet, 10, Ph); 1.96 (singlet, 3, OAc). Molecular weight (C_6H_6): 1200; calc.: 1325.

$Pd_4(\mu-CPh_2)_4(\mu-OOCPh)_4$ was obtained in a similar way from Ph_2CN_2 and $Pd_4(CO)_4(OOCPh)_4$.

The hydration of $Pd_4(\mu-CPh_2)_4(\mu-OAc)_4$ (I)

Hydration was carried out in a glass double-jacket reaction vessel with gas burette. The solution of complex I (0.15 g, 0.5 mmol) in benzene (10–15 ml) was placed in the reaction vessel which was pumped out and filled with hydrogen. The solution was stirred with a magnetic stirrer under a hydrogen atmosphere ($P = 0.1$ mPa) at 25°C until completion of hydrogen absorption (1 h).

Reaction of $Pd_4(\mu-CPh_2)_4(\mu-OAc)_4$ (I) with hexene-1

A solution of complex I (0.33 g, 1 mmol) in hexene-1 (20 ml) was boiled in an argon atmosphere until decomposition was complete (metallic palladium was formed and the solution colour changed to light-yellow; 5 h), then metallic palladium was filtered out and the liquid phase analyzed using a chromatomass-spectrometry technique.

Hydrolysis and alcoholysis of palladium carbonyl and carbene complexes

Hydrolysis and alcoholysis were carried out in a thermostatic reaction vessel with a gas burette. The complex was placed in the reaction vessel which was pumped out and refilled with argon. Then the solvent was added through a rubber membrane from a syringe. The gas evolved was measured with a gas burette and its composition determined by gas chromatography.

Thermolysis of palladium carbene complexes

The complex (1 mmol) was placed with 2 ml of benzene in a 10 ml-volume glass container which was pumped out, filled with argon, isolated and mounted inside the 80°C bath for 1–2 h. After the reaction was complete gas and liquid phase compositions were determined by gas chromatography.

Thermolysis of palladium carbonyl complexes

The complex (2 mmol) was placed with 10 ml of benzene in a glass container (80 ml) which was pumped out, filled with argon and kept thermostatically at 110°C for 5–6 h. On cooling the container was attached to the volumetric apparatus and opened. Composition of the gaseous phase was analyzed by chromatography. Metallic palladium was filtered out of the reacted solution and the filtrate was subjected to low-temperature evaporation. The residual non-volatile precipitate was analyzed by mass-spectrometry. Thermolysis of the complexes in toluene solution was carried out in the same manner.

Results and discussion

The synthesis of $Pd_4(CPh_2)_4(OAc)_4$ (I)

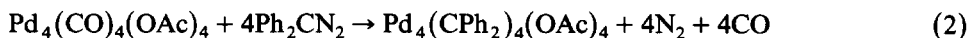
In searching for synthetic paths for clusters of palladium with carbene ligands we attempted to replace carbonyl groups in palladium carbonylacetate $Pd_4(\mu-CO)_4(\mu-OAc)_4$ (II) [10,11] by diphenylcarbene (from diphenyldiazomethane).

Our experiments showed diphenyldiazomethane in a benzene solution of complex II to be decomposed giving benzophenone azine and molecular nitrogen:

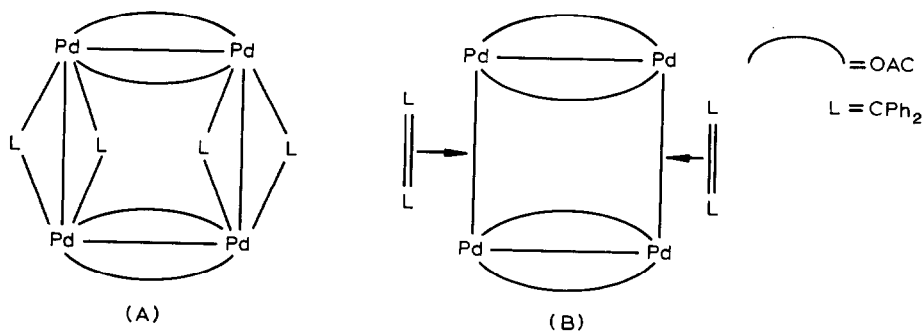


All of the carbon monoxide coordinated in II was evolved during the first 1–2 min of this reaction. Benzophenone azine and the complex $Pd_{15}H_{13}O_2$ were isolated by fractional crystallization from the reaction solution after all the nitrogen had been evolved. The light-brown complex was soluble in weakly polar organic solvents but not in saturated hydrocarbons. In strong polar solvents the complex is decomposed slowly producing palladium metal. Both molecular weight and elemental analysis data are in agreement with the formulation $C_{60}H_{52}O_8Pd_4$ for complex I. The complex has no nitrogen-containing ligands, although the latter have been reported in all published reactions of diazo-compounds with palladium complexes [12–14].

The complex I contains bridging acetate groups (IR data: $\nu(COO_{asym}) = 1560$; $\nu(COO_{sym}) = 1400$; $\Delta\nu = 160\text{ cm}^{-1}$). The 1H NMR spectrum showed peaks at chemical shift ranges characteristic for phenyl and acetate protons. The ratio $H_{Ph}/H_{Ac} = 10/3$, i.e. one acetate group corresponds to one Ph_2C ligand. All the facts mentioned point out that during the transformation from II to I the substitution of carbonyls by carbene ligands takes place alone:



According to X-ray diffraction data, the parent complex II has a rectangular metal core with the sides bridged by carbonyl and acetate groups. In forming I, carbene ligands could replace bridging carbonyl groups (A). Another case is possible as well when the isolated compound I is not a carbene complex but rather a palladium π -complex with tetraphenylethylene, formed via dimerization of carbene groups (B):



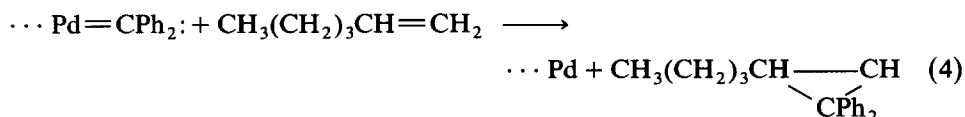
Palladium(II) π -complexes with monoolefins are known to be unstable with their stability decreasing further as bulk substituents are introduced into the olefin [15].

However, the formation of olefin π -complex is not to be neglected because the compound under discussion contains palladium atoms in an unusual oxidation state (1+). Steric factors which might be more important in polynuclear compounds should also be taken into consideration. The carbene and π -olefin structures are indistinguishable on the basis of IR and ^1H NMR data.

In order to choose between **A** and **B** structures we examined the behaviour of complex I in various reactions. Thus, hydrogenation of the complex I in benzene at 20 °C and 0.1 mPa was found to give diphenylmethane as a product of diphenylcarbene ligand hydrogenation:



Tetraphenylethane, a product of tetraphenylethylene hydrogenation, was not found in the reaction mixture. Further evidence for carbene ligands in complex I was obtained from the cyclopropanation reaction of olefins, which is known to be characteristic of carbene species. On reacting complex I under reflux in hex-1-ene, 1,1-diphenyl-2-butylcyclopropane was formed. The latter is a product of $\text{Ph}_2\text{C}:$ addition to olefin:



Both the formation of diphenylmethane during the hydrogenation of complex I and the reaction 4 are evidence that cluster complex I contains carbene ligands.

The structure of complex (I)

The structure of complex I was studied by EXAFS. Interatomic distances were determined by comparing the spectrum under study with those of model substances such as Pd-foil, $\text{Pd}_3(\text{OAc})_6$ and complex II. Coordination numbers were found by comparing appropriate peak amplitudes assuming that Debye factors are about the same. EXAFS data showed that each Pd atom is surrounded by two Pd atoms located at 2.7 Å distance and one Pd atom at 3.8 Å. Besides, each Pd atom is coordinated to two relatively light atoms located at 1.9 Å, two light atoms at 2.14 Å and, presumably, two light atoms at 3.46 Å (see Fig. 1 and Table 1). The Pd–Pd distances for the complex I (see Table 1) agree well with there being a square-planar metal core having sides of 2.7 Å and diagonal of 3.8 Å. The set of interatomic distances and coordination numbers found is consistent with the cluster structure where the sides of the square metal skeleton are coordinated to bridging carbene ($\text{Pd}-\text{C}_{\text{carbene}}$ 1.9 Å) and acetate ($\text{Pd}-\text{O}$ 2.14 Å, $\text{Pd} \cdots \text{O}$ 3.46 Å) ligands, and differs

from Pd–Pd distances determined for the complex II by X-ray data and EXAFS (see Fig. 1). The parent complex II has a rectangular metal skeleton [10,11] with short (2.67 Å) sides bridging by carbonyl pairs and long (2.90 Å) ones bridging by acetate pairs. If it is assumed that the complex II transformation to the complex I giving rise solely to carbonyls substitution for carbenes, the metal core geometry of complex I would be expected to be close to that of complex II. The uniform distribution of carbene and carbonyl ligands around a square palladium metal core (see Fig. 2) is more favourable due to steric restrictions imposed by bulk diphenyl-

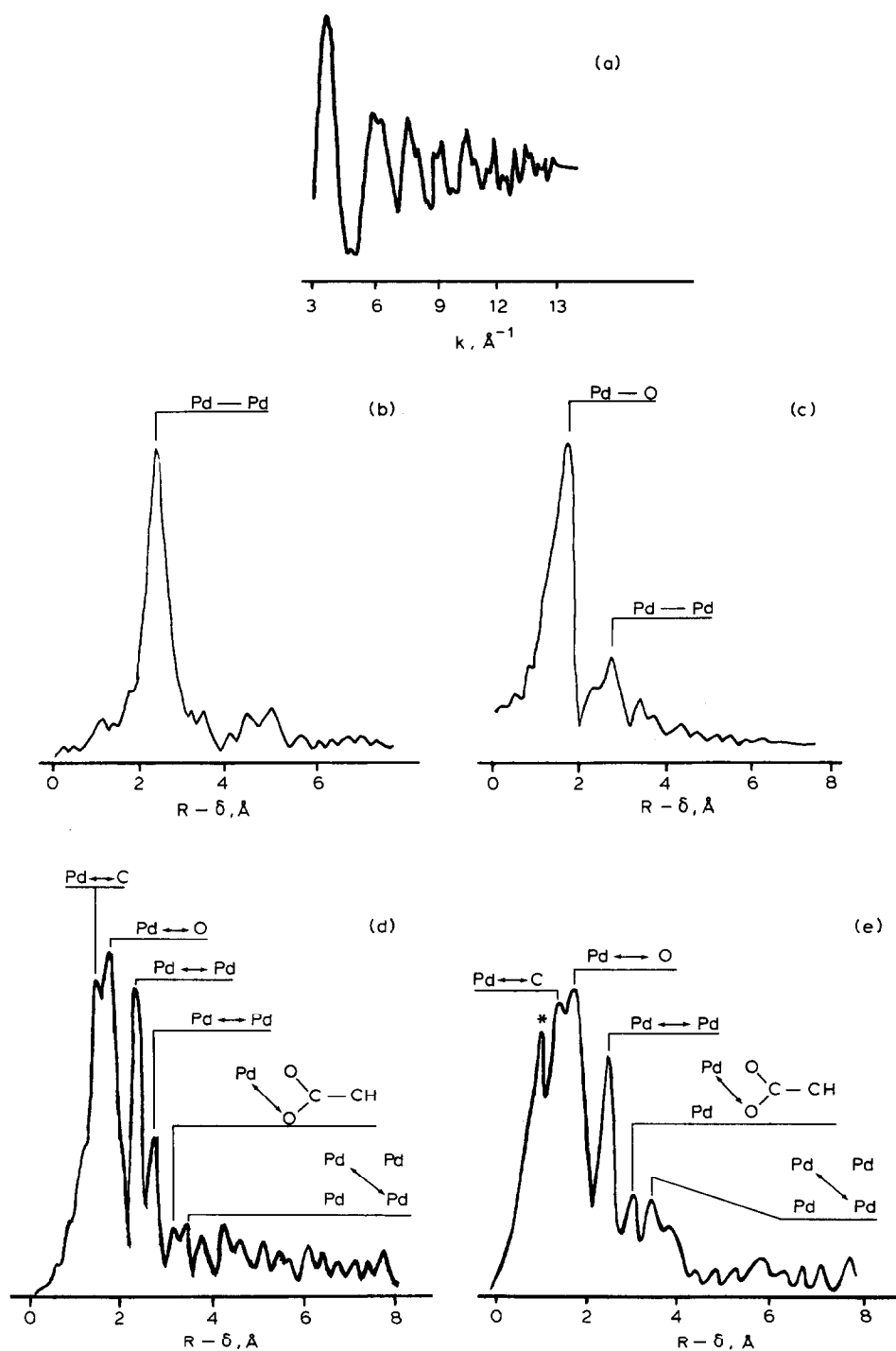


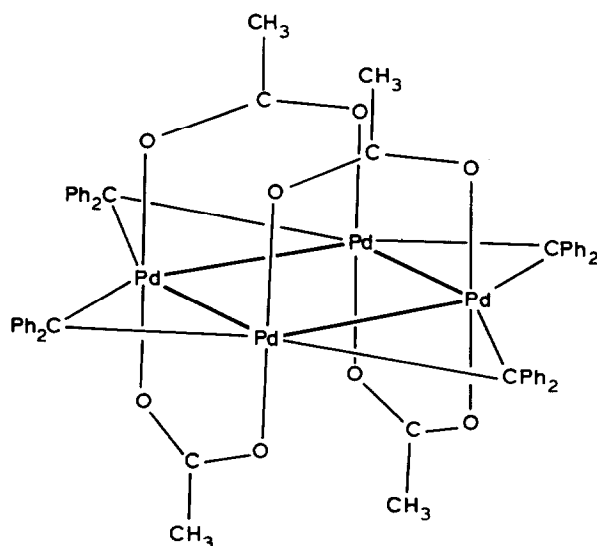
Fig. 1. EXAFS data: (a) Oscillation part of the absorption coefficient, $k \cdot \chi(k)$, for cluster I; (b) RDA curve from Fourier transformation of EXAFS spectrum for Pd-foil; (c) RDA curve from Fourier transformation of EXAFS spectrum for $\text{Pd}_3(\text{OAc})_6$; (d) RDA curve from Fourier transformation of EXAFS spectrum for cluster II; (e) RDA curve from Fourier transformation of EXAFS spectrum for cluster I.

Table 1

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

Substance	$R-\delta$ (Å)	I (rel. un.)	R (Å)	Attributed to:
Pd-metal	2.48	0.91	2.68	Pd-Pd
$\text{Pd}_3(\text{OAc})_6$	1.60	0.41	1.99	Pd-O
	2.68	0.13	2.81	Pd-C
$\text{Pd}_4(\text{CO})_4(\text{OAc})_4$	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 Pd-Pd
	3.43	0.035	3.65	↓ Pd
$\text{Pd}_4(\text{CPh}_2)_4(\text{OAc})_4$	1.42	0.11	1.86	Pd-C
	1.73	0.11	2.03	Pd-O
	2.47	0.09	2.67	Pd-Pd
	3.01	0.04	3.25	Pd-O ↓ O Pd-Pd
	3.45	0.03	3.65	↓ Pd

carbene ligands. The Pd-Mo cluster $\text{Na}_2\{\text{Pd}_4[\text{CpMo}(\text{CO})_3]_4\}$ with square palladium skeleton and uniform Mo atoms and distribution of carbonyl ligands around its square sides and corners is already known [16].

Fig. 2. The structure of $\text{Pd}_4(\text{CPh}_2)_4(\text{OAc})_4$ cluster according to EXAFS data.

In palladium chemistry the reaction 2 is the first example of carbonyl ligands substituting for carbenes and, as far as we know, the complex I is the first example of a palladium carbene cluster.

In contrast to many other known organic derivatives of palladium, the complex I is quite stable in solid state, in spite of the absence of stabilizing ligands such as phosphines, arsines or π -coordinated olefins. The complex seems to owe its stability to several factors. Presumably, both the low formal oxidation state (1+) of Pd atoms and the delocalization of electron density within the multicentre bonds formed not only in $\text{Ph}_2\text{C}_{\text{carbene}}$ fragments but throughout the Pd cluster skeleton, should be taken into consideration in discussing the enhanced stability of complex I.

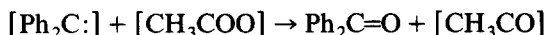
Reactivity of complex I and related compounds

Noticeable amounts of benzophenone, a product of oxidation or hydrolytic transformation of diphenylcarbene, were formed in addition to the expected compounds in the hydrogenation and cyclopropanation reactions of complex I.

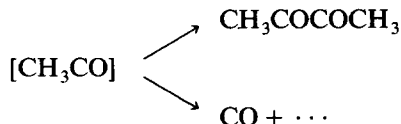
In order to elucidate the source of the oxygen incorporated during $\text{Ph}_2\text{C}=\text{O}$ formation, we carried out thermolysis of complex I in benzene solution under argon atmosphere at 80°C. The main products of this reaction were found to be benzophenone, diacetyl and CO:



As the acetate group is the only oxygen-containing ligand, benzophenone would be expected to be formed due to an oxygen atom being transferred from the acetate group to the diphenylcarbene *:



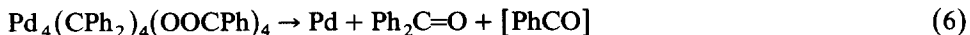
The acetyl groups formed are either dimerized to give diacetyl or undergo decarbonylation:



The transfer of an oxygen atom from the acetate group to the diphenylcarbene ligand seems to be a rather unusual process.

It should be noted that both acetate group and acetic acid itself are considered to be very stable thermodynamically, therefore it was absolutely unexpected to encounter acetate groups behaving as oxidants or as an oxygen source with respect to carbene ligands.

Our experiments showed that thermolysis of the related carbene complex $\text{Pd}_4(\text{CPh}_2)_4(\text{OOCPh})_4$ (III) in benzene solution in the absence of oxygen yields benzophenone via oxidation of diphenylcarbene with the oxygen atoms of acetate groups:



The same reaction was found to be common for $\text{Pd}(1+)$ carbonyl clusters as well. For instance, thermolysis at 110°C of comparatively stable palladium

* Moieties represented in square brackets.

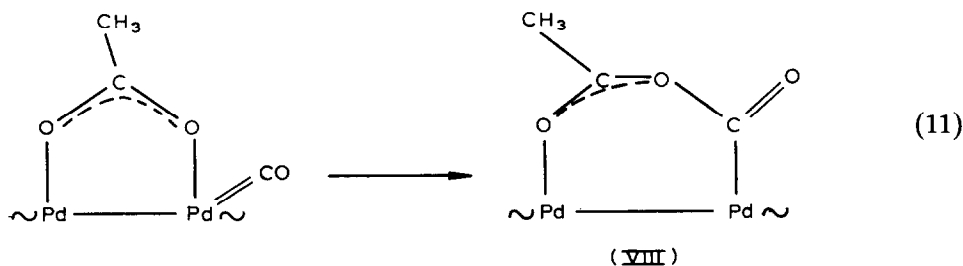
carbonylcarboxylates such as complex II or its analogues such as $\text{Pd}_4(\text{CO})_4(\text{OOCR})_4$ ($\text{R} = \text{CF}_3$, CH_2Cl , Ph , CMe_3) (denoted below as complexes IV–VII, respectively) yields CO_2 which is a product oxidation of the neutral ligand with carboxylate group oxygen*:



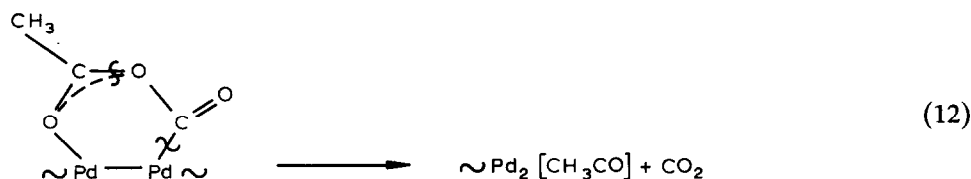
Some diacetyl, the product of acetate group reduction, was found after thermolysis of complex II. So the reaction under consideration could be formally depicted as consisting of the following oxidative (eq. 8) and reductive (eq. 9 and 10) processes:



All the reactions involving transfer of an oxygen atom from carboxylate groups to diphenylcarbenes in complexes I and III and those to CO in complexes II and IV–VII are assumed to be of the same reaction type. Maybe both sets of reactions proceed via similar mechanisms. For instance, CO oxidation with the oxygen of carboxylate group might involve CO insertion into the metal–oxygen bond:



The decomposition of the unstable intermediate VIII could be accomplished with formation of reduced palladium and a coordinated acetyl group:



Some carbon dioxide is eliminated in this step but the fate of CO_2 will be discussed below.

* A similar reaction, namely transfer of an oxygen atom from a carboxylate group to a coordinated phosphine ligand, has recently been reported [17].

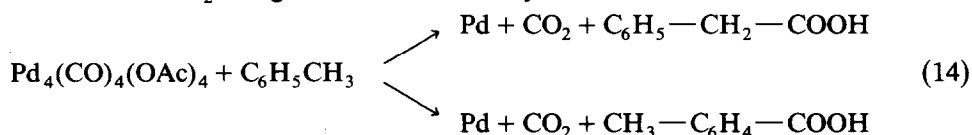
Reactions similar to 11 and 12 involving the insertion of diphenylcarbene into the palladium–oxygen bond and subsequent oxidation of carbenes are likely to give the products noted during thermolysis of the carbene complex.

The attack of the carboxylate ligand on the carbonyl group could be promoted by partial electron density transfer from carbonyl to the palladium core, as has been observed in the parent palladium carbonylcarboxylate clusters, according to IR studies. IR spectra of carbonylcarboxylate complexes contain bands of $\nu(\text{CO})$ ranging from 1930 up to 2000 cm^{-1} . The highest shift value is measured in the case of palladium carbonyltrifluoroacetate. Such frequencies are characteristic of terminal carbonyls and are not usually associated with bridging CO groups. The CO frequencies that are taken as implying transfer of electron density from carbonyl to metal core suggest an increasing of electrophilicity of carbon atoms of the carbonyl group in palladium carbonylcarboxylates.

Thermolysis of palladium carbonylcarboxylate does not yield CO_2 alone. Moreover, the carbon dioxide evolved did not exceed 10–15% of that calculated by the stoichiometry of reactions 8–10. Most of the coordinated carbonyl ligands from the palladium cluster in benzene solution are consumed in the formation of benzoic acid (eq. 13):



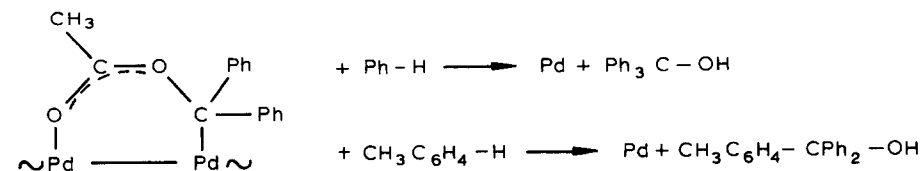
Even more unexpected results were obtained from a study of the thermolysis of complex II in toluene solution. In this case apart from isomeric tolyl acids which arise from CO_2 being inserted into the aryl-hydrogen bond, phenylacetic acid was formed from CO_2 being inserted into the alkyl toluene C–H bond:



Benzoic acid formation from benzene and CO_2 is not thermodynamically favourable ($\Delta G_{298}^0 + 5.96$ kcal/mol). Under our experimental conditions the energy losses associated with benzoic acid formation represent the energy gained in palladium reduction.

The reactions 13 and 14 might be considered as steps of the oxidative carbonylation of benzene described by Fujiwara et al. [18,19].

If, in thermolysis of the carbene complex oxidation of diphenylcarbene were followed by its insertion into the solvent C–H bond, as is the case for carbonyl complexes, the reaction products would be triphenylcarbinole in the case of benzene and tolyldiphenylcarbinole in the case of toluene:

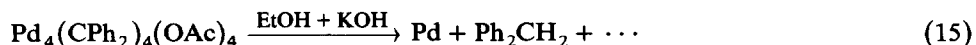


Neither of these alcohols were found after thermolysis of the carbene complexes.

Thus the neutral carbene ligand is oxidised by the oxygen atom of the carboxylate group. In the case of carbonyl complexes this reaction is accompanied by insertion of the CO oxidation product into the solvent C–H bond.

The other reactions where carbene and carbonyl complexes behave in a similar way are their hydrolysis and alcoholysis. The reactions of carbonyl complexes with water and alcohols give, together with other products, carbon dioxide which is the product of oxidation of the carbonyl ligand [20]. Benzophenone, the product of carbene ligand oxidation, is also formed in the hydrolysis and alcoholysis of carbene complexes. The oxygen source is however still unclear in this reaction, since the reaction mixture includes oxygen-containing solvent/substrate together with carboxylate ligands.

The main decomposition product of the carbene complex II in ethanol in the presence of KOH is diphenylmethane (eq. 15):



Thus alcohol or hydroxyl ions are hydrogen atom donors even under basic conditions. The alcohol molecule seems to be the most likely origin of the hydrogen atoms that are attached to the carbene ligand.

These results show there are some similarities in the bridge-type coordination of both carbene and carbonyl ligands as well as in the reactivity of their palladium clusters. Carbene complexes have been assumed to be intermediates in various catalytic reactions including Fischer-Tropsch synthesis, alcohol homologation, etc. In our opinion the carbene clusters under discussion could be considered as modelling the process of metal catalysis as they consist of positively charged metal particles covered with carbene species.

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