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The First Palladium Carbene Cluster: Synthesis and Structure

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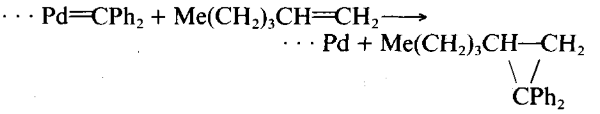
The first palladium carbene cluster, μ_2-tetrakis(diphenylmethylidene)-μ_2-tetraacetato-*quadro*-tetrapalladium(4*Pd–Pd*) $Pd_4(\mu\text{-}CPh_2)_4(\mu\text{-}OAc)_4$, has been obtained by substitution of diphenylcarbene ligands for CO groups in μ_2-tetrakis(carbonyl)-μ_2-tetraacetato-*quadro*-tetrapalladium(4*Pd–Pd*) $Pd_4(\mu\text{-}CO)_4(\mu\text{-}OAc)_4$; the cluster is also the first palladium complex containing carbene ligands of the Schrock type.

Palladium clusters with carbene ligands are assumed to be intermediates in carbene synthesis catalysed by palladium complexes.[1,2] Nevertheless, no palladium carbene clusters have been isolated so far.

Carbene species in a singlet state are similar to the CO molecule in their orbital and coordination properties. However, in contrast to CO the application of carbene ligands in the cluster chemistry of transition metals is restricted to rare examples. Thus, only two carbene clusters with a core containing more than three metal atoms have been synthesiszed to date.[3,4]

In search of synthetic paths to palladium clusters containing carbene ligands we attempted to substitute diphenylcarbene (formed from diphenyldiazomethane) for CO ligands in the tetranuclear cluster $Pd_4(\mu\text{-}CO)_4)(\mu\text{-}OAc)_4$ (**1**).[5] The reaction of complex **1** (0.5 mmol) with Ph_2CN_2 (5 mmol) in benzene (10 ml) at 20 °C was found to result in elimination of N_2 and evolution of all carbon monoxide molecules coordinated in **1** as shown by eqn. (1).† Light brown tetranuclear complex **2** was obtained in 7–8% yield by fractional crystallization of the reaction mixture. The presence of bridging OAc ligands and CPh_2 fragments in complex **2** was evidenced by ^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 **2** contains four OAc groups and four CPh_2 fragments. The CPh_2 fragments may be present in complex **2** either as diphenylcarbene ligands or in the form of π-coordinated tetraphenylethylene molecules which could be formed during reaction (1) by the dimerisation of CPh_2 species. The carbene and π-alkene structures are indistinguishable on the basis of the spectral data. Nevertheless, hydrogenation of complex **2** in benzene solution at 20 °C and 0.1 MPa was found to give diphenylmethane as the product of reduction of the diphenylcarbene ligands. Tetraphenylethane, the expected product of tetraphenylethylene hydrogenation, was not found in the reaction mixture. More evidence for the presence of carbene ligands in complex **2** was obtained from the alkene cyclopropanation reaction, typical for carbene species. Reaction of complex **2** under reflux in hex-1-ene solution gave 2-butyl-1,1-diphenylcyclopropane, the product of addition of Ph_2C: to the alkene, as shown by eqn. (2).

$$\underset{\mathbf{1}}{Pd_4(CO)_4(OAc)_4} + 4Ph_2CN_2 \longrightarrow \underset{\mathbf{2}}{Pd_4(CPh_2)_4(OAc)_4} + 4CO + 4N_2 \quad (1)$$



$$\cdots Pd{=}CPh_2 + Me(CH_2)_3CH{=}CH_2 \longrightarrow \cdots Pd + Me(CH_2)_3\underset{\diagdown\;\diagup \atop CPh_2}{CH{-}CH_2} \quad (2)$$

Table 1 Interatomic distances, *R*, obtained from EXAFS data for model substances and complex **2**

Substance	$R-\delta$/Å	I/rel. units	R/Å	Assignment
Pd metal	2.48	0.91	2.68	Pd—Pd
$Pd_3(OAc)_6$	1.60	0.41	1.99	Pd—O
	2.68	0.13	2.81	Pd—C
1	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
	3.43	0.035	3.65	Pd—Pd ↘Pd
2	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

These facts reveal that cluster complex **2** contains carbene ligands of the Schrock type.

Starting complex **1** has a rectangular metal core[5] with the short sides (2.67 Å) bridged by pairs of carbonyl ligands and the long sides (2.90 Å) bridged by acetate groups. If the transformation of **1** to **2** is the result solely of substitution of carbonyl ligands by carbene species, the geometry of the metal skeleton of complex **2** should be expected to be similar to that of complex **1**.

An EXAFS study‡ of complex **2** 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

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† Complex **2** was characterized by elemental analysis, molecular weight [M^+, 1200; M^+ (calc.), 1320], IR: (ν^{as}_{COO} 1560, ν^{s}_{COO} 1400, $\Delta\nu$ 160 cm^{-1}) and ^1H NMR spectra: δ(rel. to $SiMe_4$) 1.96 (s, 3H, OAc), 7.24 (m, 10H, Ph).

‡ The palladium K-edge X-ray absorption spectrum was measured with an EXAFS spectrometer at the Siberian Center of Synchrotron Radiation.[6] The spectra obtained were treated by the standard Fourier transformation procedure.[6] The values of $k.\chi(k)$ were analysed in the interval 3.8 to 15.0 $Å^{-1}$. The pre-edging region was extrapolated to the EXAFS region using the Victorin polynomial. The smooth part of the absorption spectrum was constructed by cubic spline. Ionization potential was taken as the twist point at the absorption edge. Actual interatomic distances were found by comparing the spectrum of the complex studied with those of model substances: Pd foil, $Pd_3(OAc)_6$, and complex **1**.

Coordination numbers were found by comparison of the peak amplitudes with those of the model substances assuming the Debye factors to be almost the same. False peaks are marked by asterisks. These peaks obtained from incomplete extraction of the absorption coefficient's smooth part and XANES oscillation. The fitting procedures were not used, and interatomic distances and coordination number were found only from comparison with model objects. It is difficult to assess the accuracy of these values but the discrepancy is not greater than 0.1 Å for interatomic distances and 50% for coordination numbers.

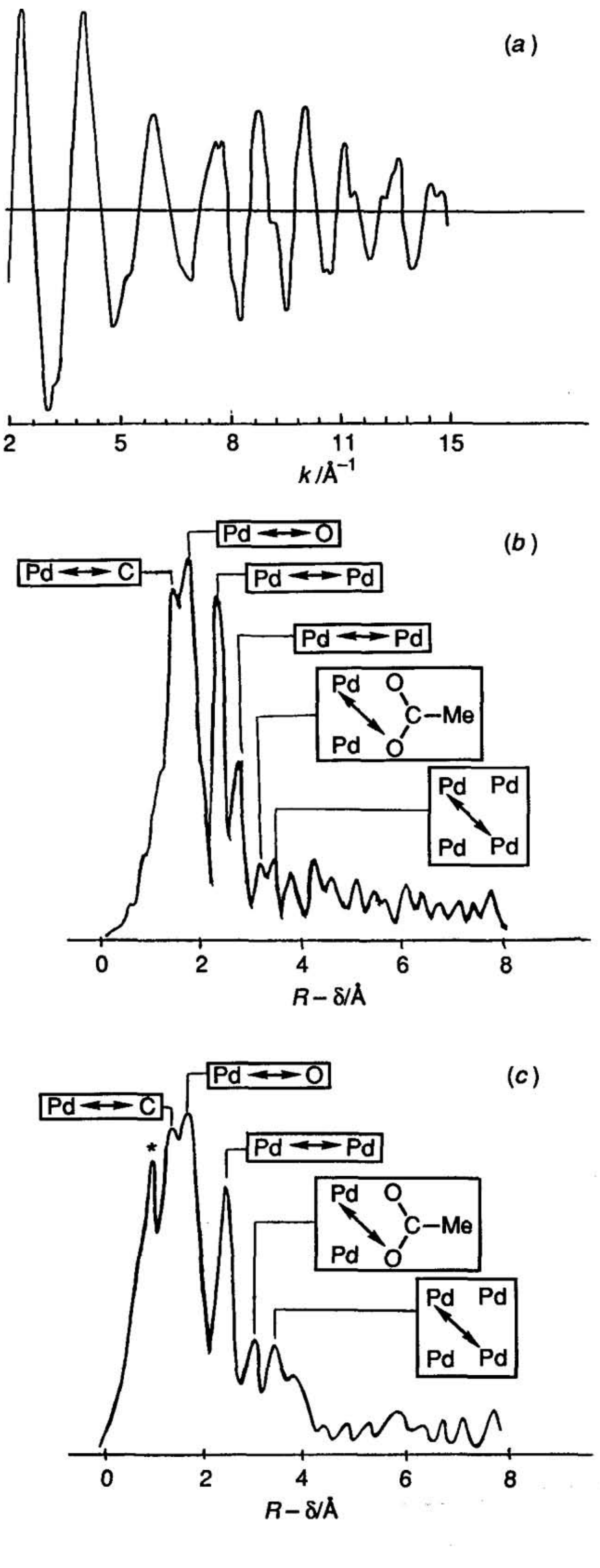

Fig. 1 EXAFS data: (*a*) oscillation part of the absorption coefficient, $k.\chi(k)$, for cluster **2**; (*b*) RDA curve from Fourier transformation of EXAFS spectrum for cluster **1**; (*c*) RDA curve from Fourier transformation of EXAFS spectrum for cluster **2**.

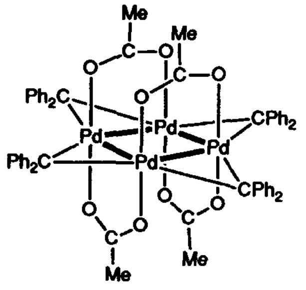

Fig. 2 The structure of $Pd_4(CPh_2)_4(OAc)_4$ cluster **2** according to EXAFS data

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. 1(*c*), Table 1]. The Pd—Pd distances found for **2** (see Table 1) differ from those observed for complex **1** by X-ray[5] and EXAFS techniques [Fig. 1(*b*)] and fit well to 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 the sides of the square metal skeleton are bridged both by carbene (Pd—C 1.86 Å) and acetate (Pd—O 2.03, $\underset{\searrow\mathrm{O}}{\mathrm{Pd}}\cdots\mathrm{O}$ 3.25 Å) ligands.

The uniform arrangement of carbene and acetate ligands around the square palladium skeleton (Fig. 2) is presumed to be more favourable because of the steric requirements of the bulky diphenylcarbene ligands. A Pd—Mo cluster, $Na_2[Pd_4\{Cp\text{-}Mo(CO)_3\}_4]$, is known, with the square Pd-skeleton and a uniform arrangement of Mo atoms and CO ligands around the sides and corners of the square.[7]

In palladium chemistry reaction (1) is the first example of the substitution of carbonyl ligands by carbene species. To the best of our knowledge complex **2** is the first example both of a palladium cluster with carbene ligands and of a Pd complex containing carbene ligands of the Schrock type.

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