New Palladium Cluster Compounds. *X*-Ray Crystal Structure of $Pd_{10}(CO)_{12}(PBu^n_3)_6$

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Summary The ten-vertex palladium cluster $Pd_{10}(CO)_{12}[PBu^n{}_3]_6$ obtained by treatment of $Pd(OAc)_2$ with $PBu^n{}_3$ and CO [molar ratio Pd : P 1 : 4·5], is shown by *X*-ray crystallography to contain a tetracapped octahedron of metal atoms, *i.e.* a distorted fragment of close packing Pd_{10} with 16 skeletal electrons.

Despite the increasing interest in the chemistry of transition metal clusters data on polyhedral palladium derivatives are comparatively scarce. At present, only 3 Pd_4 clusters are known, their structures having been determined by *X*-ray crystal analysis.[1–3] A few years ago we reported a scheme permitting the synthesis of clusters containing up to 12 atoms of Pd,[4] and we subsequently used this method [treatment of $Pd(OAc)_2$ with CO in H_2O-Ac_2O solution in the presence of CF_3CO_2H and trialkylphosphine ligands] to synthesise $Pd_{12}(CO)_{15}(PR_3)_7$ (R = Bu^n, Et) and $Pd_{12}(CO)_{17}[PBu^n_3]_5$. We also showed that treatment of the latter compound with 2 equiv. of PBu^n led to substitution of two CO ligands.[5] In continuation of our study of these cluster compounds, we have repeated the synthesis using dioxan as a solvent. Addition of small portions of acetone under these conditions provided single crystals of the Pd_{10} clusters (**1**) and (**2**)† (the Pd : P ratio in the synthesis was 1 : 4·5).

$$Pd^{2+} + CO + PBu^n_3 \rightarrow Pd_{10}(CO)_m(PBu^n_3)_n$$

$$(\mathbf{1})\ m = 12,\ n = 6$$
$$(\mathbf{2})\ m = 14,\ n = 4$$

The structure of (**1**) was determined by *X*-ray diffraction and is shown in the Figure. Compound (**1**) is the first 10-vertex palladium cluster to be reported. The metal atoms are arranged as an octahedron wherein four faces situated tetrahedrally are centred by Pd atoms. The bonding of the capping atoms to the triangular faces is not symmetrical, and thus three types of Pd atoms can be distinguished in (**1**): the 'apical' and 'equatorial' atoms in the inner octahedron and the capping atoms. The Pd–Pd distances can also be subdivided into 3 groups: the edges of the Pd_6 octahedron (2·791—2·851 Å), short bonds between the capping atoms and equatorial octahedron vertices (two bonds per capping atom of length 2·694—2·722 Å), and elongated distances between the capping atoms and the 'apical' atoms Pd(5) and Pd(6) of 3·301—3·421 Å. The PBu^n_3 ligands are co-ordinated to the apical and capping Pd atoms and the 4 free faces of the inner Pd_6 octahedron are centred by the μ_3-CO ligands forming two long (2·21—2·32 Å) and one short Pd—C bonds [the latter with apical Pd(5) and Pd(6) of 2·02—2·05 Å]. The eight remaining μ_2-carbonyls 'tighten' the short Pd–Pd bonds between the atoms of the inner octahedron and the caps (ave. Pd–C 2·05 Å).

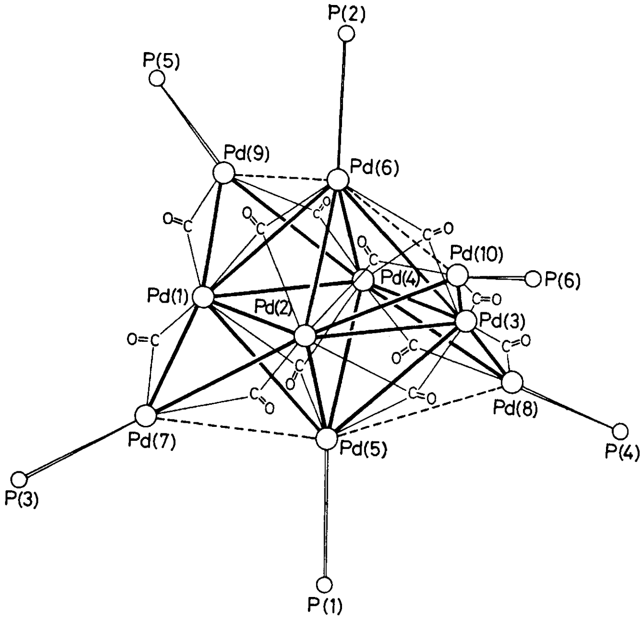

Figure. The structure of (**1**) (n-butyl substituents are not shown). Distances: Pd(1)–Pd(2) 2·846, Pd(1)–Pd(4) 2·832, Pd(1)–Pd(5) 2·812, Pd(1)–Pd(6) 2·823, Pd(1)–Pd(7) 2·720, Pd(1)–Pd(9) 2·722, Pd(2)–Pd(3) 2·850, Pd(2)–Pd(5) 2·821, Pd(2)–Pd(6) 2·806, Pd(2)–Pd(7) 2·700, Pd(2)–Pd(10) 2·714, Pd(3)–Pd(4) 2·816, Pd(3)–Pd(5) 2·842, Pd(3)–Pd(6) 2·837, Pd(3)–Pd(8) 2·702, Pd(3)–Pd(10) 2·694, Pd(4)–Pd(5) 2·820, Pd(4)–Pd(6) 2·791. Pd(4)–Pd(8) 2·712, Pd(4)–Pd(9) 2·710, Pd(5)–Pd(7) 3·324, Pd(5)–Pd(8) 3·307, Pd(6)–Pd(9) 3·301, Pd(6)–Pd(10) 3·421, Pd–P 2·293—2·330, Pd–C 1·96—2·35 Å, e.s.d.s Pd–Pd 0·001—0·002, Pd–P 0·004, Pd–C 0·01—0·02 Å.

A four-capped octahedron of 10 transition metal atoms has been found earlier in the carbide carbonyl cluster $[Os_{10}(CO)_{24}C]^{2-}$, where all CO ligands are terminal.[6] This system, like (**1**), may be considered as a somewhat distorted fragment of close three-layer packing, but, in contrast, the

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† Spectral data: (**1**), ν_{CO} 1800(m), 1853(s), and 1890(s) cm^{-1}, ^{31}P n.m.r. [rel. to H_3PO_4] δ −4·0 and +3·3 (2 : 1) p.p.m., (**2**) ν_{CO} 1818(s), 1870(s), 1899(sh), 1918(s), and 2036(s) cm^{-1}, ^{31}P n.m.r. [rel. to $P(OEt)_3$] δ −5·0 p.p.m.

‡ *Crystal data* at −120 °C, monoclinic a = 18·218(10), b = 29·299(16), c = 19·845(9) Å, β = 92·43(4)°, space group $P2_1/n$, Z = 4. Intensities of 12,127 reflections with $I > 2\delta(I)$ were measured with a Syntex $P2_1$ diffractometer at −120 °C (λMo-K_α, $\theta/2\theta$ scan, $4 < 2\theta < 44^0$). The Pd atom positions were found by direct methods, light atoms were located in a series of Fourier syntheses, and the structure was refined by block-diagnonal least-squares (all atoms anisotropic) to a current R = 0·068. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

capping atoms in (**1**) are bound to the faces non-symmetrically. The skeletal electron number in (**1**) is 16 and thus exceeds the value necessary for an octahedron, according to Wade's rule, by two electrons (the appearance of a cap in a *closo*-polyhedron does not led to an increase in the number of skeletal electrons[7]), while the $[Os_{10}(CO)_{24}C]^{2-}$ cluster does obey Wade's rule. It is tempting to correlate the excess of skeletal electrons with a 'slightly opened' configuration of caps. It is of interest that in the mixed iron–palladium cluster $[Fe_6Pd_6(CO)_{24}H]^{3-}$ whose structure consists of a six-capped octahedron similar to that of (**1**) and which also has 16 skeletal electrons, the inner Pd_6 octahedron exhibits distortions of a trigonal anti-prismatic type, although the Fe atoms centre its faces almost symmetrically.[8]

The reaction[5] $Pd_{10}(CO)_{14}(PBu^n_3)_4 + 2PBu^n_3 \rightarrow Pd_{10}(CO)_{12}(PBu^n_3)_6 + 2CO$ can be represented as a substitution of both 'apical' CO ligands [at Pd(5) and Pd(6), see the Figure] by PBu^n_3, this substitution being accompanied by the disappearance of the i.r. absorption band at 2036 cm^{-1} due to terminal CO groups and splitting of the ^{31}P n.m.r. signal from (**1**) [but not from (**2**)], the intensity ratio being 2:1. This splitting is in accordance with the existence of non-equivalent P atoms, *i.e.* the PBu^n_3 ligands attached to the capping and apical Pd atoms in (**1**).

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