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Preliminary communication

A HIGH-NUCLEAR CARBONYLPHOSPHINE CLUSTER OF PALLADIUM, $Pd_{23}(CO)_{22}(PEt_3)_{10}$

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Summary

Reactions of palladium derivatives in combination with phosphine ligands make possible the production of new species of high nuclearity. Here both the production and further characterization of a new high-nuclear cluster, $Pd_{23}(CO)_{22}(PEt_3)_{10}$ is described.

Under mild conditions zerovalent palladium derivatives are able to form Pd_n clusters with a carbonyl—phosphine ligand shell and a nuclearity n varying between 3 and 10 [1—5]. The largest structurally characterized clusters of this type, viz. $Pd_7(CO)_7(PMe_3)_7$ [2], $Pd_{10}(CO)_{12}(PBu^n{}_3)_6$ [3] and $Pd_{10}(CO)_{14}(PBu^n{}_3)_4$ [4] are built up on the basis of Pd_6 octahedron with either one or four $Pd(\mu\text{-}CO)_2L$ asymmetrically capping units (L = phosphine). The mechanism of enlargement of carbonylphosphine clusters of Pd and the corresponding transformations "Pd_{1-4}"→"Pd_{10}" were reported earlier [3,5].

In order to obtain a species with a still higher nuclearity we chose $Pd(OAc)_2$ as the acceptor of phosphine ligand (AcO = MeCOO). Through its reaction with $Pd_{10}(CO)_{12}(PEt_3)_6$ under argon at room temperature the new high-nuclear $Pd_{23}(CO)_{22}(PEt_3)_{10}$ cluster (I) was obtained. The synthetic route was as follows: a solution of 21.3 mg $Pd(OAc)_2$ (0.095 mmol) in benzene (6 ml) and then 2 ml of heptane were added to $Pd_{10}(CO)_{12}(PEt_3)_6$ [1] (0.2 g, 0.095 mmol). The reaction mixture was first left to stand for a day under pentane vapour, then a small amount of the black precipitate was filtered off and the solution was then left under pentane vapour for a longer time. After 4 days black

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twinned crystals were separated and washed with pentane, yield 0.055 g (31%). Found: Pd, 58.29; P, 7.32. $C_{82}H_{150}O_{22}P_{10}Pd_{23}$ calcd.: Pd, 57.65; P, 7.30%. IR (cm^{-1}) (Nujol): 1863s, 1847sh, 1823sh.

Plate-like crystals of I suitable for an X-ray study were isolated from the crystalline product obtained in a modified experiment with a mixture of acetone (7 ml) and Et_2O (2 ml) as the solvent and without any hydrocarbon component, the reaction time was limited to 2 days. A single crystal of I was placed under argon in a sealed Lindemann glass capillary. Intensities of 4281 unique reflections were measured with a Hilger & Watts Y/290 diffractometer at room temperature (λMo-K_α, $\theta/2\theta$ scan up to $2\theta = 54°$), 3738 non-zero reflections (with $I > 2\sigma$) were used in calculations. Crystals of I are monoclinic, a 18.492(2), b 16.518(2), c 19.468(2) Å, β 93.59(1)°, V 5935(1) $Å^3$, space group $P2_1/n$, $Z = 2$. The structure was solved by direct method using a MULTAN program and refined by the block-diagonal least squares technique in isotropic(C,O)—anisotropic(Pd,P) approximation. Final R = 0.071.

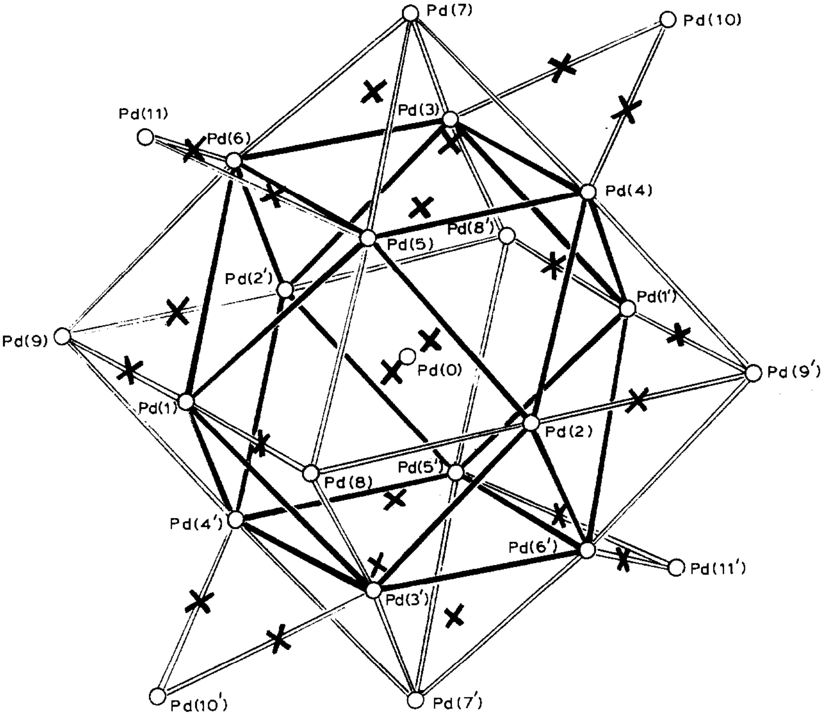

Fig. 1. The Pd_{23} metallapolyhedron (cuboctahedral moiety in bold lines). PEt_3 ligands are coordinated to Pd(7), Pd(8), Pd(9), Pd(10), Pd(11) atoms and those related by inversion. Interatomic distances in the polyhedron: Pd(0)—Pd(1) 2.796, Pd(0)—Pd(2) 2.700, Pd(0)—Pd(3) 2.864, Pd(0)—Pd(4) 2.897, Pd(0)—Pd(5) 2.919, Pd(0)—Pd(6) 2.907, Pd(1)—Pd(3') 2.916, Pd(1)—Pd(4') 2.862, Pd(1)—Pd(5) 2.936, Pd(1)—Pd(6) 2.866, Pd(1)—Pd(8) 2.798, Pd(1)—Pd(9) 2.797, Pd(2)—Pd(3') 2.765, Pd(2)—Pd(4) 2.770, Pd(2)—Pd(5) 2.779, Pd(2)—Pd(6') 2.839, Pd(2)—Pd(8) 2.855, Pd(2)—Pd(9') 2.784, Pd(3)—Pd(4) 2.937, Pd(3)—Pd(6) 2.785, Pd(3)—Pd(7) 2.803, Pd(3)—Pd(8') 2.828, Pd(3)—Pd(10) 2.738, Pd(4)—Pd(5) 2.815, Pd(4)—Pd(7) 2.811, Pd(4)—Pd(9') 2.779, Pd(4)—Pd(10) 2.734, Pd(5)—Pd(6) 2.920, Pd(5)—Pd(7) 2.807, Pd(5)—Pd(8) 2.856, Pd(5)—Pd(11) 2.720, Pd(6)—Pd(7) 2.795, Pd(6)—Pd(9) 2.907, Pd(6)—Pd(11) 2.726 Å. E.s.d. 0.003—0.005 Å. Pd—P 2.28—2.35 Å, e.s.d. 0.01 Å. Positions of CO ligands are marked by crosses.

The metal polyhedron of the centrosymmetric molecule I (Fig. 1) includes the closed packed metal atoms fragment, i.e. the body- and edge-centered octahedron Pd_{19}, whose vertices are occupied by the atoms Pd(7), Pd(8), Pd(9) and those related by the symmetry center, and the midpoints of all edges occupied by the atoms Pd(1)—Pd(6) and also those related by inversion. In molecule I this polyhedron ("large octahedron", by analogy with the M_{10} "large tetrahedron" in such clusters as $[Os_{10}C(CO)_{24}]^{2-}$ [6] or $Pd_{10}(CO)_{12}(PBu^n{}_3)_6$ [3]) is complemented by four non-closed $Pd(\mu\text{-}CO)_2PEt_3$ capping moieties (Pd atoms with numbers 10, 10′, 11 and 11′ in Fig. 1) with the resulting reduction of the symmetry of the Pd_{23} framework from O_h to D_{2h}. Thus, the latter atoms form the open caps on the faces of the large octahedron of I, resembling asymmetric caps of a Pd_6 octahedron in the earlier studied structures of $Pd_{10}(CO)_{12}L_6$ and $Pd_{10}(CO)_{14}L_4$ ($L = PBu^n{}_3$, vide supra). However, in I the planes of Pd_3 triangles in the caps (e.g. Pd(10)Pd(3)Pd(4)) are perpendicular to the faces of the large octahedron, thus resulting in almost equal non-bonded distances Pd(7)···Pd(10, 11) (3.381, 3.455 Å) and Pd(1)···Pd(10,11) (3.357, 3.344 Å), respectively. All vertices of the large octahedron and all capping atoms are coordinated by PEt_3 ligands. There are also 14 μ-CO and 8 μ_3-CO ligands in I (indicated in Fig. 1 by crosses).

The Pd_{23} cluster in I may also be regarded as a centered cuboctahedron with six caps on all square faces, complemented by four open caps. This cuboctahedron of idealized O_h symmetry is shown in Fig. 1 by bold lines. The Pd—Pd bond distances in this polyhedron show no differences between "center(i.e. Pd(0))—peripheral" (av. 2.847) and "peripheral—peripheral" (av. 2.849 Å) interactions. All the other bonding distances in the large octahedron also have these close values (2.779—2.920 Å). The non-bonding distances from the large vertices to the Pd(0) atom are equal to 3.969—4.017 Å, and the distances from the capping atoms to atoms of the large octahedron (those bridged by μ-CO ligands) vary from 2.720 to 2.738 Å (av. 2.730 Å).

In contrast to high-nuclear rhodium clusters, built up mainly on the basis of a less symmetric twinned cuboctahedron (D_{3h}), and thus corresponding to hexagonal close packing (h.c.p.), the metal polyhedron in I corresponds to a cubic close packing (c.c.p.), typical of Pd and Pt metals [7]. Therefore, the high-nuclear cluster I can be considered as a fragment of the crystal lattice of the corresponding metal (contrasting, for example with the $[Pt_{26}(CO)_{32}]^{2-}$ h.c.p. cluster, but similar to the larger c.c.p. truncated octahedral cluster $[Pt_{38}(CO)_{44}H_x]^{2-}$ [7]). It is noteworthy that the average Pd—Pd distance in the large Pd_{19} octahedron of I (2.836 Å) is still considerably longer, than the shortest interatomic distance in the metal bulk (2.751 Å), probably due to the antibonding influence of the ligand shell on the metal cluster core.

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