Synthesis of High-nuclearity Carbonyl–Phosphine Clusters of Palladium under Mild Conditions and *X*-Ray Crystal Structure of $Pd_{38}(\mu_3\text{-}CO)_4(\mu_2\text{-}CO)_{24}(PEt_3)_{12}$

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The large $Pd_{38}(CO)_{28}(PEt_3)_{12}$ carbonyl–phosphine cluster, obtained by a general phosphine abstracting route by the action of $Pd(OAc)_2$ on the ten-vertex $Pd_{10}(CO)_{12}(PEt_3)_6$ cluster, is shown by an *X*-ray study to contain a four-layer fragment of a distorted cubic close packing with an interstitial Pd_4 tetrahedron.

Except for a few examples,[1—5] high-nuclearity clusters with more than 20 metal atoms remain scarcely investigated, principally because their synthesis requires highly specific conditions, making the isolation of products in the form of single crystals very difficult. However, large clusters are of greater interest in view of both the structure and bonding in their metal polyhedra and the fact that they may model ligand co-ordination on metal surfaces.

In our study of palladium carbonyl–phosphine clusters, which earlier allowed us to isolate ten-vertex representatives,[6,7] we found a simple route to enlargement of the metal core by the mild abstraction of the phosphine ligands. This method recently led to the syntheses of two 23-nuclear clusters, *viz.* $Pd_{23}(CO)_{22}(PEt_3)_{10}$[8] and $Pd_{23}(CO)_{20}(PEt_3)_8$.[9] Here we report the isolation and *X*-ray structure of the new large cluster $Pd_{38}(CO)_{28}(PEt_3)_{12}$ (**1**).

Single crystals of the solvate $Pd_{38}(CO)_{28}(PEt_3)_{12}{\cdot}Me_2CO$ (**1a**), suitable for *X*-ray investigation, were obtained as reported previously[8] by the reaction of $Pd_{10}(CO)_{12}(PEt_3)_6$ and $Pd(OAc)_2$ (molar ratio 1 : 2) in acetone solution under argon.† Compound (**1a**) has been isolated in 24% yield and rapidly decomposes in air.

The metal framework in (**1a**) is shown in Figure 1. In contrast to the structure of $[Pt_{38}(CO)_{44}]^{2-}$ (ref. 1) and $[Ni_{38}Pt_6(CO)_{48}H_{6-n}]^{n-}$ (ref. 5), built up on the basis of a highly symmetrical cubic close packing (c.c.p.) fragment ('v_3-octahedron'), and also the c.c.p. basic metal polyhedron in $Pd_{23}(CO)_{22}(PEt_3)_{10}$[8] ('$v_2$-octahedron') and body-centred cubic packing (b.c.c.) fragment in $Pd_{23}(CO)_{20}(PEt_3)_8$,[9] the metal core in (**1**) has a less regular structure with non-crystallographic symmetry close to D_2. The flattened interstitial tetrahedron Pd_4 with two long (2.958, 2.970 Å) and four short (2.539, 2.610, 2.603, 2.514 Å) Pd–Pd edges is enveloped by 20 Pd atoms arranged in four approximately planar layers, and two interlayer Pd atoms, thus forming the 4 : 8 : 2 : 8 : 4 configuration. The resulting 26-atomic cluster nucleus (shown in bold lines in Figure 1) is further completed by 12 capping Pd atoms, each cap being co-ordinated by one PEt_3 ligand. Each of four interstitial atoms has 11 nearest neighbours in accordance with an incomplete and very distorted c.c.p. (8 short Pd–Pd distances of 2.514—2.772 Å and 3 longer distances of 2.841—3.178 Å). The average Pd–Pd distance of

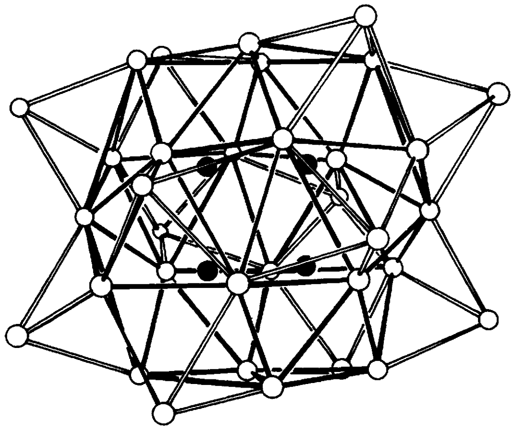

Figure 1. Metal polyhedron in (**1**) (interstitial metal atoms as filled circles, the four-layer core in bold lines).

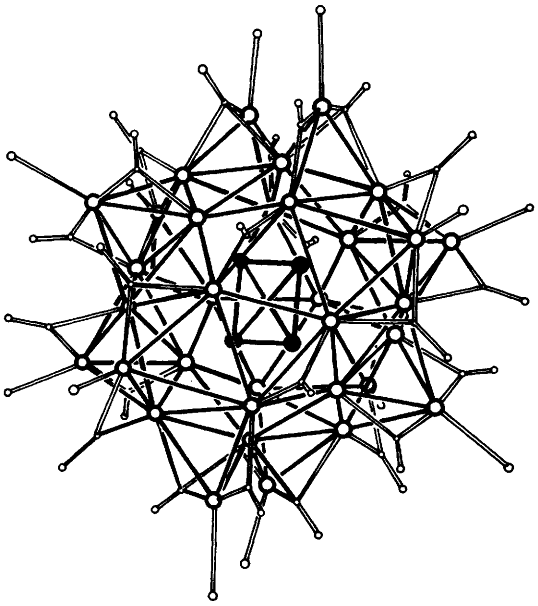

Figure 2. Cluster (**1**) with its ligand environment (Et substituents omitted). Bond distances: Pd–P 2.296—2.322, Pd–C(μ_2) 1.93—2.10, Pd–C(μ_3) 2.00—2.40, C–O 1.10—1.20 Å, Pd–Pd distances in text. E.s.d.s: Pd–Pd 0.001—0.002, Pd–P 0.004, Pd–C 0.01, C–O 0.02 Å.

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† *Crystal data:* (**1a**), monoclinic, space group $P2_1/c$, a = 18.448(3), b = 25.024(3), c = 34.150(4) Å, β = 90.08(1)°, Z = 4, 12 439 observed [$I > 2\sigma(I)$] independent reflections (−120 °C, Mo-K_α, $\theta/2\theta$ scan, $2\theta_{max.}$ 40°), direct methods, absorption corrected by DIFABS procedure,[10] block-diagonal least-squares anisotropic refinement to R = 0.032. The accuracy of the experiment showed the location of the acetone solvating molecule and the second orientation of one rotationally disordered PEt_3 ligand (refined isotropically) as most of hydrogen atoms in the ordered Et substituents. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

2.699 Å in the inner tetrahedron is shorter than in palladium metal (2.751 Å[11]); the average of 118 metal–metal bonds in (**1**) (2.775 Å) is closer to the latter distance and shorter than in $Pd_{23}(CO)_{22}(PEt_3)_{10}$[8] (2.836 Å) and $Pd_{23}(CO)_{20}(PEt_3)_8$[9] (2.918 Å).

The overall view of the cluster (**1**) with its ligand environment is shown in Figure 2. Four of 28 carbonyl ligands are triply bridging, and the rest are doubly bridging. To our knowledge, (**1**) is the largest neutral transition metal cluster which has been structurally investigated. In the crystal of (**1a**) the small Me_2CO molecules are situated in channels within the packing of the large cluster spheroids.

An interesting structural feature of the largest clusters studied by *X*-ray crystallography is that they tend to minimize their molecular surface and, therefore, to form spheroidal metal polyhedra. This tendency indicates the analogy of these (and perhaps larger) polynuclear metal aggregates with small liquid droplets rather than with metal microcrystallites (see also ref. 12).

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