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$Pd_{59}(CO)_{32}(PMe_3)_{21}$: A Nanosized Metal Cluster Containing a Trigonal D_3 Pd_{59} Core with 11 Interior Palladium Atoms

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The group 10 metals (Ni, Pd, Pt) are particularly attractive candidates for obtaining giant metal carbonyl clusters because clusters containing these electron-rich metals may be stabilized with relatively few ligands so that all of them can be sterically accommodated on the metal-core surface.[1] Extensive chemical/physical studies have been performed on nickel and platinum carbonyl clusters,[1,2] and clusters containing up to 50 metal atoms have been isolated and crystallographically characterized.[3] In sharp contrast, relatively few investigations involving palladium carbonyl clusters have been carried out, partly because palladium, per se, does not form discrete, pure carbonyl clusters.[2,4] Nevertheless, over the past 15 years a variety of high-nuclearity neutral homopalladium carbonyl phosphine clusters have been prepared by Mednikov and co-workers[5] and characterized by Slovokhotov and Struchkov[5] from X-ray crystallography. Analyses of the stereochemistry and prominent bonding features of several of these clusters have been presented.[6] Moreover, N,O-ligated palladium nanoclusters possessing idealized formulations based upon concentric closed-shell palladium cores have been reported, namely, 5-shell Pd_{561} clusters by Moiseev and co-workers[7] and by Schmid et al.[8] and mixtures of 7-shell Pd_{1415} and 8-shell Pd_{2057} clusters by Schmid *et al.*[9,10] Chaudret, Bradley, and co-workers[11] recently showed that zero-valent Pd (and likewise Pt) complexes in organic solutions (e.g., THF) decomposed under CO in the presence of PPh_3 to give novel PPh_3/CO-stabilized Pd (and Pt) particles which were studied by spectroscopic methods; although the Pd particles were much less stable than the Pt particles and were subject to size variations in solution, three distinct size-selected distributions were obtained with observed mean diameters determined from TEM to correspond to idealized 2-shell Pd_{55}, 3-shell Pd_{147}, and 5-shell Pd_{561} cores.[11]

Herein we present the preparation, isolation, and structural determination of the $Pd_{59}(CO)_{32}(PMe_3)_{21}$ cluster (**1**). This well-defined neutral cluster has particular significance in that it possesses the largest *crystallographically determined* metal-atom core with *direct* metal−metal bonding reported to date for a discrete metal-ligated species. Furthermore, **1** contains a nanosized metal core with 11 interior atoms. The ellipsoidal-shaped architecture of its Pd_{59} core may be formally considered as a trigonal deformation of a spheroidal-like geometry possessed by the similar-sized *full-shell* Au_{55} core (presumed to be cuboctahedral) of ca. 1.2 nm diameter in the prototype Schmid $Au_{55}(PPh_3)_{12}Cl_6$ nanocluster.[8,10,12]

1 was obtained in moderate yields (ca. 40%) from a highly reproducible synthesis involving the initial preparation of a heterometallic Pd−Ni carbonyl cluster (without phosphine ligands) followed by its reaction with PMe_3 under acidic conditions. Although it was presumed that the latter reaction would result in PMe_3 substitution for CO ligands and/or other large Pd−Ni carbonyl clusters via phosphine stabilization, the reaction instead gave rise to several new high-nuclearity homopalladium clusters with **1** as the major product.[13,14]

Its crystal structure[15] was unambiguously determined by X-ray diffraction involving the use of a SMART CCD area detector diffractometry system. The composition of **1** established by the X-ray structural determination is completely consistent with an elemental analysis.[16] This compound was also characterized by IR and $^{31}P\{H\}$, ^{1}H NMR measurements.[17]

1 has crystallographic D_3 (32) site symmetry such that the asymmetric part consists of $^{1}/_{6}$ of the neutral molecule. Its 59-atom metal framework (Figure 1) may be conceptually constructed in the following fashion. Two outer centered icosahedra are *indirectly* connected via trans double face-sharing with an inner face-shared bioctahedron. The 11 *interior* Pd(i) atoms comprise the bicapped face-sharing bioctahedron. The principal 3-fold axis passes through the two icosahedral-centered Pd(5), Pd(5A) atoms and the midpoints of the three perpendicular face-fused triangles interconnecting the two icosahedra and two octahedra with one another. Each of the two icosahedra is further condensed via face-sharing with 6 other octahedra and three square pyramids.[18] Three additional 3-fold-related octahedra, each lying on a horizontal 2-fold axis that passes through two vertexes, are each

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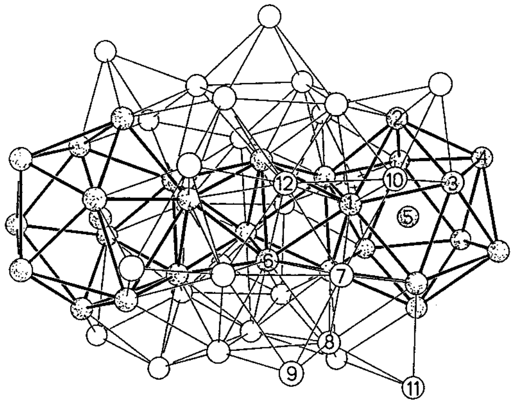

Figure 1. Geometry of the ellipsoidal-shaped Pd_{59} core in **1** which has crystallographic D_3 site symmetry. The maximum core diameter of ca. 1.3 nm along the principal 3-fold axis arises from trans double face-sharing of an inner face-fused $Pd(i)_9$ bioctahedron with two outer Pd(i)-centered icosahedra (outlined with wider line-connectivities). The core diameter along each of the three horizontal 2-fold axes, one of which passes through Pd(9) (and its attached PMe_3), Pd(6), and a 3-fold-related Pd atom of the Pd_{10}-capped Pd(12), is ca. 0.9 nm.

connected indirectly to both icosahedra via face-fusion of two of its 2-fold-related faces with two intermediate octahedra that in turn are each face-fused with an icosahedron. The metal core is completed by three capping atoms (viz., Pd(12), and its two 3-fold-related atoms), each located on a 2-fold axis and each connected to 10 Pd atoms that are disposed in a hemispherical-like array. Hence, the entire metal core of **1** can be formally derived from a specific face-sharing condensation of two icosahedra, 17 octahedra, and six square pyramids involving 56 Pd atoms that are additionally linked by three Pd_{10}-capped Pd atoms. It is apparent that the growth pattern of the metal framework in **1**, involving face-fused condensations of centered icosahedral units with other polyhedra, is entirely different from the growth sequence of a series of centered icosahedral units as vertex-sharing polyicosahedra formulated by Teo, Zhang, and co-workers[18] on the basis of comprehensive stereophysical studies of their remarkable Au−Ag and Au−Ag−M (M = Ni, Pd, Pt) clusters.

The palladium framework is stabilized by 32 bridging CO and 21 PMe_3 ligands. The trimethyl phosphine ligands are distributed about the metal core as 6 $Pd(\mu_3\text{-}CO)_2PMe_3$, 9 $Pd(\mu_2\text{-}CO)_2PMe_3$, and 6 $Pd(\mu_3\text{-}CO)PMe_3$ moieties.

Application of the analogous electron-counting procedures by Mingos[19] and by Teo/Zhang[20] for a condensed polyhedron (supracluster) gives the same calculated cluster valence electron (CVE) count[21] of 696 which is in exact accordance with the observed number of CVEs (*i.e.*, 59×10 (Pd) + 32×2 (CO) + 21×2 (PMe_3) = 696). This agreement is consistent with the ^1H NMR measurements which showed no detectable high-field signals characteristic of hydride-like atoms.

Planned investigations include variable-temperature measurements of the magnetic moment and specific heat properties of the Pd_{59} cluster for comparison with the corresponding size-dependent properties reported (and attributed to quantum-size effects) for the Pd_{561}, Pd_{1415}, Pd_{2057} *full-shell* clusters and Pd-(colloid) particles.[22]

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Supporting Information Available: Figures of the metal-core and molecular geometry of **1** with anisotropic displacement ellipsoids along with crystallographic data (24 pgs). See any current masthead page for ordering information and Web access instructions.

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(13) (a) Preparation of heterometallic Pd−Ni carbonyl precursor (**5**): In a typical reaction, $Pd(OAc)_2$ (0.40 g, 1.80 mmol) dissolved in 15 mL of DMSO was added dropwise under a N_2 atmosphere at rt to a stirred solution of $[Me_4N]_2[Ni_6(CO)_{12}]$ (0.75 g, 0.90 mmol) in 30 mL of DMSO containing pellets of NaOH (∼0.2 g). The solution quickly changed from a cherry-red to a dark-brown color. After 5 h, NaOH pellets were removed by a solution transfer to another flask, and a solution of Ph_4PBr (7.5 g) in 20 mL of MeOH was added. Slow addition of distilled, degassed water to the ice-cooled solution resulted in a dark-brown precipitate which was filtered and washed several times with degassed water, methanol, and then exclusively with THF. A subsequent acetone extract from the solid gave 0.60 g of **5**. An IR spectrum (MeCN) exhibited CO bands at 1874 (s), 2010 (s) cm^{-1}. The Pd−Ni anion of **5** possesses a 30-atom *ccp* metal-core geometry that conforms to an edge-truncated ν_4 tetrahedron; its tentative formulation as $[PPh_4]_4[Pd_{30-x}Ni_x(CO)_y]\cdot$solvent ($x \approx 14$; $y \approx 36$) is based upon a partial crystal structure (i.e., poor X-ray data), elemental analysis, and IR.[14] Extensive efforts to crystallize this compound again are as yet unsuccessful. (b) Preparation of **1** and other products (**2**, **3**, **4**): In a typical reaction, 10 mL of deoxygenated acetic acid was added to 0.60 g of **5** in 30 mL of CH_3CN, after which 250 μL of PMe_3 dissolved in 10 mL of acetonitrile was added dropwise to the mixture. The reaction was stirred at rt for 3 days. The resulting precipitate was separated and washed with CH_3CN. An extraction with THF gave 0.05 g of a dark-brown compound characterized as $Pd_{35}(CO)_{23}(PMe_3)_{15}$ (**3**). No residue remained after this extraction. The filtrate from the reaction was dried in vacuo to give a dark-brown solid which was extracted with MeOH and then with THF. This THF extract gave 0.05 g of a dark-brown compound characterized as $Pd_{16}(CO)_{13}(PMe_3)_9$ (**4**). The MeOH extract was dried under a N_2 flow, washed with degassed water, and extracted first by diisopropyl ether and then by THF. $Pd_{59}(CO)_{32}(PMe_3)_{21}$ (**1**) (0.11 g), and $Pd_{39}(CO)_{23}(PMe_3)_{16}$ (**2**) (0.08 g) were obtained from the diisopropyl ether and THF extracts, respectively. Estimated yields based on $Pd(OAc)_2$ are 40% for **1**, 27% for **2**, 15% for **3**, and 16% for **4**.

(14) Bacon, J. W.; Dahl, L. F. unpublished research.

(15) $[Pd_{59}(CO)_{32}(PMe_3)_{21}]\cdot 3(Me_2CO)\cdot 1.5(i\text{-}Pr_2O)$: trigonal, $P\bar{3}12/c$, $a = b = 22.7815(3)$ Å, $c = 28.0363(4)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 12601.3(3)$ Å^3, $Z = 2$, $d_{calcd} = 2.398$ Mg/m^3. Sphere of 26 966 data collected at 133(2) K via 0.3 ω scans over a 2θ range 4.12−50.00°; empirical absorption correction applied to data. Anisotropic least-squares refinement (409 parameters/142 restraints) on 7135 independent merged reflections ($R_{int} = 0.0986$) converged at $\omega R_2(F^2) = 0.1455$ for all data; $R_1(F) = 0.0546$ for 4120 observed data ($I > 2\sigma(I)$). The highest positive residual peak on the final (original) difference map was interpreted on the basis of reasonable distances to involve the partial occupancy of an additional Pd atom in the asymmetric unit in place of one bridging CO ligand. The resulting least-squares refined occupancy factors of $\alpha = 0.04$ for the presumed extra independent Pd(13) atom and $1 - \alpha = 0.96$ for the independent bridging CO ligand indicate the presence of a superimposed cocrystallized $Pd_{65}(CO)_{26+x}(PMe_3)_{21}$ cluster of D_3 (32) site symmetry occupying 4% of the unit cells. The *x* COs attached to Pd(13) and the other five symmetry-related Pd atoms were expectedly not detected on subsequent difference maps due to their much smaller X-ray scattering powers. Because the occupancy factor was only 4% for Pd(13), we regard the presumed superimposed cocrystallized Pd_{65} cluster as a small impurity that can be neglected in this reported crystal structure. Restraints were applied to only the solvent molecules and the independent PMe_3 group lying on a 2-fold axis.

(16) Anal. by Desert Analytics (Tucson, AZ): Calcd for $[Pd_{59}(CO)_{32}(PMe_3)_{21}]\cdot 3(Me_2CO)\cdot 1.5(i\text{-}Pr_2O)\cdot 2(C_6H_{14})$ (fw = 9 271.32). Calcd (found) Pd, 67.72 (67.59); Ni, 0.00 (0.16); C, 16.19 (16.29); H, 2.79 (2.80).

(17) IR (THF, CaF_2) ν(CO): 1848 (br), 1820 (sh), 1739 (w), and 1653 (w) cm^{-1}. $^{31}P\{H\}$ NMR (202.3 MHz, THF-d_8 at 23 °C and −60 °C, 85% H_3PO_4 external: 31.30 ppm. ^1H NMR (500 MHz, THF-d_8 at 23 °C): two doublets at 1.34 ($^2J_{P-H} = 12.91$ Hz) assigned to PMe_3 and 0.10 ppm ($^2J_{P-H} = 9.30$ Hz) due to unknown species. No signals due to hydrido-like protons from 9.0 to −30.0 ppm. All other proton signals assigned to solvent.

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(21) Each of the two identical halves of the 59-atom metal core (Figure 1) in **1** consists of an interior tetrahedron of 4 Pd(i)s (viz., the icosahedra-centered Pd(5), Pd(1), and the two 3-fold-related Pd(1A), Pd(1B)) surrounded by 27 surface atoms (i.e., Pd(9), Pd(9A), and Pd(9B) are excluded). The resulting electron count for each half given by $\Delta_i + 12n_s$ is 384, where $\Delta_i = 60$ (for the $Pd(i)_4$ tetrahedron) and $n_s = 27$. The two halves condense by the face-sharing of a common ν_2 Pd_6 triangle (90 CVEs). Because Pd(9), Pd(9A), and Pd(9B) are each the apical atom of a square pyramid (74 CVEs), the entire condensed metal core of **1** can then be formally completed via double edge-sharing of the above formed 56-atom polyhedron with the basal atoms of three square pyramids (i.e., exclusion of the sixth atom in each octahedron to give a square pyramid simplifies this bonding scheme but does not alter the resulting electron count). The total predicted electron count for these condensations is $2 \times 384 - 90 + 3 \times 74 - 3\,(2 \times 34) = 696$.

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