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Nanosized Pd$_{145}$(CO)$_x$(PEt$_3$)$_{30}$ Containing a Capped Three-Shell 145-Atom Metal-Core Geometry of Pseudo Icosahedral Symmetry[**]

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Lawrence F. Dahl[*]

*Dedicated to Professor Dr. Heinrich Vahrenkamp
on the occasion of his 60th birthday*

Presented herein are the geometrical features of a stoichiometric capped three-shell palladium carbonyl phosphane cluster **1**. Its pseudo I_h metal core (see Figure 1) consists of a central Pd atom surrounded by 12 Pd atoms (shell 1), which in turn are encapsulated by 42 Pd atoms (shell 2), which in turn are encapsulated by 60 Pd atoms (shell 3). Thirty additional Pd atoms cap the 30 square polygons of the third-shell polyhedron with a triethylphosphane ligand attached to each capping Pd atom. It is currently presumed that 60 CO groups (crystal-disordered) edge-bridge the 30 capping Pd atoms with one-half of the square basal Pd atoms (in accordance with an IR carbonyl spectrum). The diameter of the entire Pd$_{145}$ core of **1** between two centrosymmetrically opposite capping Pd atoms is 1.65 nm; the spherical-like geometry of the centered three-shell Pd$_{115}$ kernel (that is, without the 30 capping Pd atoms) is evidenced by the similarity of the corresponding distances for the centrosymmetrically opposite pentagonal faces (1.22 nm), square faces (1.27 nm), and triangular faces (1.27 nm) of the third shell.

This remarkable Pd$_{145}$ nanocluster, whose metal-core geometry was unambiguously characterized from complete crystallographic analyses of X-ray data for two crystals (from different preparations, crystals A and B),[1, 2] was isolated from the reduction of a monomeric square-planar palladium precursor, [Pd(PEt$_3$)$_2$Cl$_2$].[3, 4] The geometrical conformity of the 55 interior metal atoms within the third shell of **1** to the well-known two-shell icosahedral Mackay hard-sphere model[5] had not been previously observed in single-crystal X-ray crystallographic determinations.[6, 7] The third-shell polyhedron in this unprecedented close-packed multi-shell metal carbonyl cluster possesses 60 equivalent vertices along with 12 pentagonal, 20 equilateral triangular, and 30 square faces;[8] this semi-regular (Archimedean) polyhedron, named rhombicosidodecahedron (with Schläfli symbol 3.4.5.4),[9] is a heretofore crystallographically unknown stereoisomer of the universally familiar C$_{60}$ buckyball, an icosahedrally truncated semi-regular polyhedron of I_h symmetry with 60 equivalent vertices and 12 pentagonal and 20 hexagonal faces.

Because the formation of **1** is extremely sensitive to reaction boundary conditions, extensive systematic preparative efforts have been made during the last 24 months to provide a reproducible but (as yet) low-yield synthesis. The Goddess Fortuna recently revisited our laboratory in that crystals of **1** were again isolated and its crystal structure redetermined. The fact that **1** has 55 interior Pd atoms makes it an ideal model for experimental operational tests of previous interpretations of size-dependent physical properties (attributed to quantum-size effects) reported[10] for several giant noncrystalline, (N,O)-ligated, full-shell palladium clusters (ideally formulated from other measurements as five-shell Pd$_{561}$ species by the Moiseev and Schmid groups[11, 12] and as seven-/eight-shell Pd$_{1415}$/Pd$_{2057}$ species by Schmid et al[13]) and for larger Pd (colloid) particles.

That the 115-atom 3-shell core of **1** (i.e., minus the 30 capping atoms) was actually proposed by Farges et al.[14] as a possible full-shell structural model for noble-gas clusters produced in free-jet expansion into a vacuum is somewhat astonishing (i.e., mass spectra of charged noble-gas clusters provide no subshell magic-number evidence for the 115-atom cluster being particularly abundant because of special stability[14, 15]). Their model represents a geometrical modification of the classic Mackay hard-sphere multilayer icosahedral (MIC) models based upon a 13-atom centered icosahedron being considered as 20 identical (slightly distorted) *fcc* tetrahedra that share a common vertex and are connected to one another through adjacent shared faces.

Formation of the Mackay 55-atom 2-shell MIC model arises from each of the 20 tetrahedra adding a 6-atom ν_2 triangle to its 3-atom ν_1 triangular surface (111) face. The resulting second complete MIC shell ($n = 2$) consists of 42 atoms, that may originate from the addition of 30 atoms to the midpoints of the 30 edges of a 12-atom icosahedron in the second shell. In general, the number of atoms in a complete n^{th} shell is given

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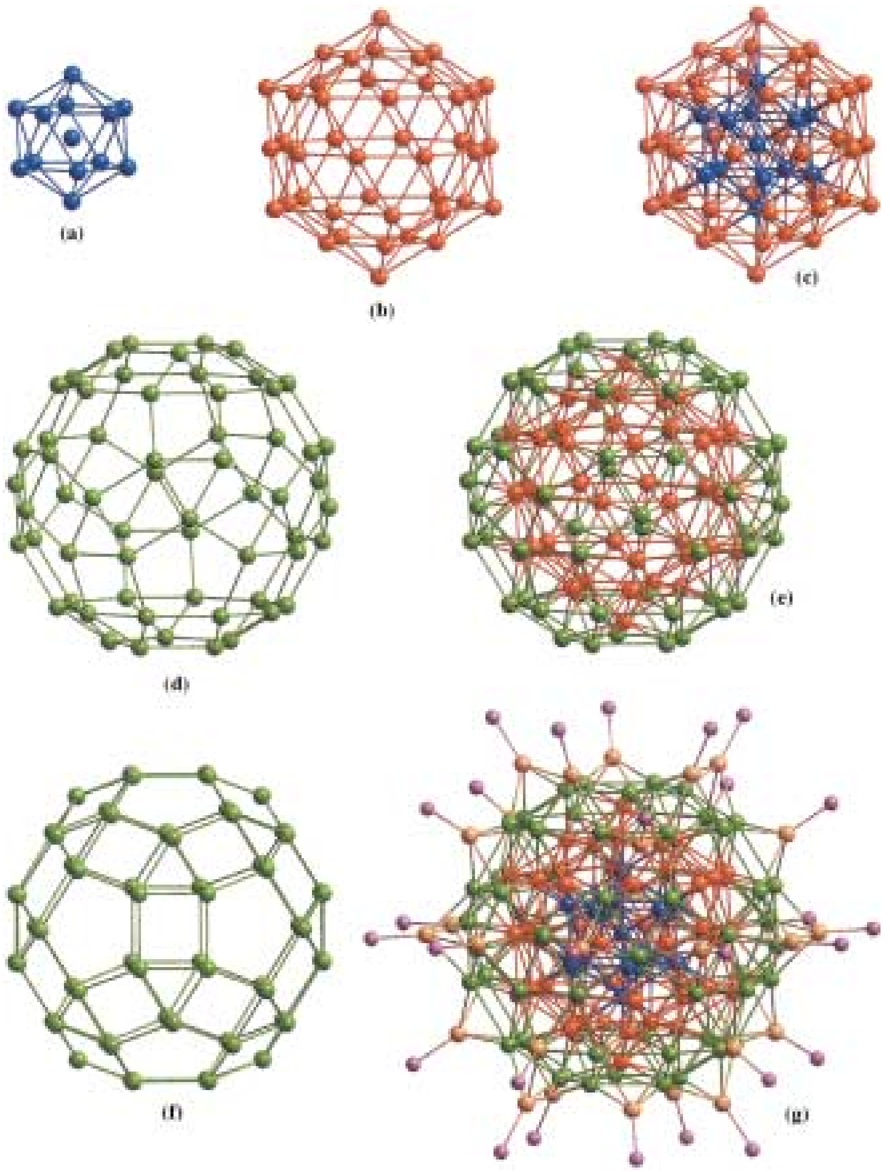

Figure 1. Formal concentric construction of the capped three-shell nanosized Pd_{145} core of pseudo I_h symmetry in $Pd_{145}(CO)_x(PEt_3)_{30}$: a) 12-atom ν_1 icosahedron surrounding the central atom (ν_n denotes $(n+1)$ equally spaced atoms along each edge). This centrosymmetrically centered icosahedron, one of the five regular Platonic solids (with equivalent vertices and identical faces composed of only one polygon), comprises: (1) six five-fold axes through opposite pairs of 12 vertices; (2) 10 three-fold axes through midpoints of opposite pairs of 20 triangular faces; and (3) 15 two-fold axes through midpoints of opposite pairs of 30 edges. b) 42-atom ν_2 icosahedron (shell 2) generated by the addition of an atom to the midpoint of each of the 30 edges of the 12-atom ν_1 icosahedron. c) Shell 2 encapsulating the Pd-centered shell 1 to give a 55-atom Mackay icosahedron. d) 60-atom polyhedron (shell 3), mathematically named a rhombicosidodecahedron (3.4.5.4). The numbers N (in parentheses) designate the Schläfli symbol which represents in cyclic order the polygons (N-gons) meeting at each equivalent vertex. e) Shell 3 encapsulating shell 2. f) Another orientation of the outermost third-shell polyhedron that more clearly shows the 60 equivalent vertices along with the 62 faces (namely, the 12 pentagons, 20 equilateral triangles, and 30 squares). This Archimedean polyhedron, a semi-regular one in that all 60 vertices are identical but there are three different polygons, has pseudo I_h symmetry. g) Entire 3-shell Pd_{145} core including 30 exopolyhedral Pd atoms (with attached triethylphosphane P atoms (purple)) that form square pyramids by capping of the 30 square polygons of the third shell.

by $(10n^2+2)$; the total number of atoms (N) in a full n-shell MIC model corresponds to the well-known magic-number sequence $N=13$ ($n=1$), 55 ($n=2$), 147 ($n=3$), 309 ($n=4$), 561 ($n=5$), etc.[5a, 15a] Noteworthy is that this same sequence of magic numbers is obtained for full-shell *ccp* (i.e., *fcc*) clusters. In fact, this full-shell sequence is responsible for the idealized formulations of the renowned $Au_{55}(PPh_3)_{12}Cl_6$ ($n=2$) from Schmid et. al[16] and the above-mentioned ligand-stabilized Pd_{561} ($n=5$),[11, 12] Pd_{1415} ($n=7$),[13] and Pd_{2057} ($n=8$)[13] clusters.

In the formal cluster-growth sequences of the third MIC layer (i.e., shell 3), Farges et al.[14] recognized that the addition of atoms to the 55-atom Mackay icosahedron can occur in two ways and thereby can give rise to two types of surface arrangements: one cluster-growth pattern involves the addition of atoms to the edge-sites and vertices of the 6-atom ν_2 triangular surface (111) face of a tetrahedron such that *fcc* (*abca*) layer-packing is maintained; complete surface coverage of each of the 20 tetrahedra by a 10-atom ν_3 triangular layer involves the addition of 92 atoms ($n=3$) to give the 147-atom 3-shell Mackay icosahedron. The other cluster-growth pattern arises from the addition of atoms to the three internal *hcp* sites of the 6-atom ν_2 triangular surface (111) face of a tetrahedron in the second shell (Figure 2). The complete third-shell layer then forms the above-described 60-vertex rhombicosidodecahedron (i.e., 3 atoms per face × 20 faces) and thereby produces the 115-atom 3-shell cluster (without the capping atoms) observed in **1**. Farges et al.,[14] denoted the first pattern as a *regular* MIC arrangement and the latter pattern as a *twin* arrangement. Subsequently, the *regular* atom-site surface arrangement for shell 3 was also designated as edge-capping/vertex (ECV3)[15b,c] or simply the Mackay overlayer,[17] while the *twin* arrangement was designated as face-capping/vertex (FCV3)[15b,c, 18] or the anti-Mackay layer.[17]

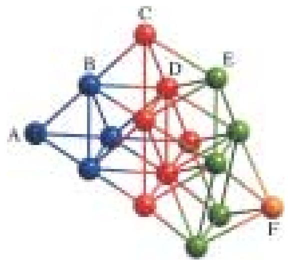

Figure 2. Pd_{16} fragment of the Pd_{145} core displaying the capped three-shell atomic arrangement with atom-labeling; see text and refs [4],[24] for further details.

Of prime interest is that in the formal construction of the third icosahedral layer, Farges et al.[14a] stated that experimental electron diffraction patterns of the noncrystalline structures of argon clusters indicate a transformation from a *twin* to a *regular* surface MIC arrangement. They concluded from a comparison of the experimental and calculated diffraction functions for $N = 116$ (incomplete third layer), $N = 147$ (three complete layers), and $N = 178$ (incomplete fourth layer) that each of these clusters has a *regular* MIC structure. The matching of experimentally observed shell and subshell magic numbers[14, 15] with structural models obtained by pairwise additive potential calculations[14, 15, 17] for noble-gas clusters favors the existence of icosahedral geometries for particular N-atom sizes with cluster-growth occurring by anti-Mackay overlayers for a relatively empty third shell but by *regular* Mackay overlayers for a nearly full third shell.[19–21]

Riley, Parks, and co-workers[22] have pioneered the development of a chemical probe method to determine by mass spectrometry how the number and nature of particular surface sites of photoionized nickel clusters vary with cluster size and temperature. Based upon saturation-coverage binding patterns of different adsorbates (e.g., N_2, H_2, CO, NH_3, H_2O) under equilibrium conditions, they suggested from pronounced chemical-reactivity magic numbers that "naked" as well as ligated gas-phase nickel clusters in the size-range from 10 to 28 atoms and from 49 to approximately 200 atoms form predominantly icosahedral-type geometries.[22]

Recent, more sophisticated theoretical calculations[23] of equilibrium geometries of Ni_N clusters ($N \leq 55$)[23a–c] and Pd_N clusters ($N \leq 23$)[23a] instead produced highly diversified lowest-energy geometries which are notably dissimilar to the previously proposed icosahedral structures except for those containing a stable icosahedral core (i.e., corresponding to $N = 13$, 19, 23, 51–55). These calculations (which are based upon density functional theory (DFT) concepts) also predicted the existence of geometrically different isomers with analogous binding energies for a considerable number of size-selected clusters along with the occurrence of multiple isomeric transformations. Geometric changes were linked to the underlying electronic structures of transition metal clusters.[23c] DePristo and co-workers[23a,b]proposed that the major driving force for the creation of the most stable structures for Ni_N and Pd_N clusters involves a maximization of the minimum coordination for any surface atom (giving rise to more uniform surface coordination numbers). Proposed consequences[23a,b] are nearly spherical cluster shapes, a large range of nearest-neighbor interatomic distances, high coordination numbers, and large electron densities about the core atom(s) of the clusters. In contrast, equilibrium geometries of noble-gas clusters, which are stabilized by weak dispersion forces, were proposed to involve maximization of the number of nearest-neighbor interatomic contacts (that correspond to similar distances for close-packed geometries).[14, 15, 17]

Ligation effects arising from the capping of the 30 square polygons in the third-shell polyhedron of **1** by 30 $Pd(PEt_3)$ fragments along with doubly bridging CO units linking the capping Pd atoms to two of the four square-basal Pd atoms no doubt play a dominant role in the energetically preferred formation of the 60-atom semi-regular icosahedral polyhedron of shell 3.[14] The layer-by-layer growth pattern of the ligated capped 3-shell Pd_{145} core of pseudo-I_h symmetry presumably involves an energetic compromise between maximization of atom-connectivities (resulting in the lowest surface Pd coordination number being seven[24]) and the minimization of icosahedral strain energy.

Table 1 presents distances averaged under I_h symmetry based upon the atom-labeling palladium fragment given in Figure 2. This table not only reveals that the corresponding average (means) for the 11 different types of Pd–Pd distances for crystals A and B agree within 0.01 Å but also that the dispersion of individual Pd–Pd separations for each of the means for crystal A is unusually small. Only those for crystal A are utilized in this discussion.

Table 1. The mean metal–metal and metal–phosphorus connectivities under pseudo-I_h icosahedral symmetry in $Pd_{145}(CO)_x(PEt_3)_{30}$ for crystals A and B[a] and corresponding individual ranges for crystal A.

Connectivity[b]	N[c]	Mean [Å][a]	Range [Å]
Pd(A)-Pd(B)	12	2.63 (2.63)	2.629(3)–2.633(3)
Pd(B)-Pd(B)	30	2.77 (2.77)	2.757(4)–2.778(5)
Pd(B)-Pd(C)	12	2.74 (2.73)	2.734(4)–2.737(4)
Pd(B)-Pd(D)	60	2.70 (2.70)	2.696(4)–2.709(4)
Pd(C)-Pd(D)	60	2.82 (2.82)	2.811(6)–2.836(6)
Pd(D)-Pd(D)	60	2.82 (2.82)	2.810(5)–2.825(6)
Pd(C)-Pd(E)	60	2.73 (2.73)	2.714(7)–2.749(7)
Pd(D)-Pd(E)	120	2.74 (2.73)	2.724(6)–2.756(6)
Pd(E)-Pd(E) (triangle/square shared edge)	60	2.82 (2.82)	2.795(8)-2.844(9)
Pd(E)-Pd(E) (pentagon/square shared edge)	60	3.09 (3.09)	3.070(8)–3.112(9)
Pd(E)-Pd(F)	120	2.84 (2.84)	2.809(9)–2.874(9)
Pd(F)-P	30	2.32 (2.30)	2.181(13)–2.363(15)

[a] The means for crystal B are given in parentheses. [b] Atom-labeling is given in Figure 2. [c] N denotes the number of symmetry-equivalent connectivities under I_h symmetry.

For each of the identically deformed 20 tetrahedra within the inner 13-atom centered icosahedral shell of **1**, the experimentally determined uniform contraction of the three radial edges relative to the three tangential edges by 5.0% (i.e., $[(2.77-2.63\,\text{Å})/2.77\,\text{Å}] \times 100$) is in complete agreement with the theoretically predicted value of approximately 5%.[5a, 12] This radial compression is also evidenced on going from shell 1 to shell 2; the relative growth increment along the radial (intershell) direction increases by 4.2% (i.e., $[(2.74-2.63\,\text{Å})/2.63\,\text{Å}] \times 100$), while that along the tangential (intrashell) direction increases by only 1.8% (i.e.,$[(2.82-2.77\,\text{Å})/2.77\,\text{Å}] \times 100$). For shell 3 both the intershell Pd(C)–Pd(E) and Pd(D)–Pd(E) means are virtually identical with that of the radial Pd(B)–Pd(C) mean between the first and second shell (2.74 Å). That the tangential (intrashell) Pd(E)–Pd(E) mean of 2.82 Å for the shared edge between each triangle and square polygon is 0.27 Å shorter than that of 3.09 Å for the shared edge between each pentagon and square polygon reflects considerably larger bonding interactions presumably arising from sterically imposed strain effects. Noteworthy is that the Pd–Pd distance found in *ccp* Pd metal is 2.75 Å.[25]

Current/planned collaborations include detailed physical characterization of **1** involving mass spectrometric, electrochemical, TEM, EXAFS, PES, and variable-temperature magnetic susceptibility measurements. A preliminary investigation has already indicated the existence of PMe_3 and PPh_3 analogues.

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[1] Crystal structure analysis: Intensity data were collected at 133(2) K for two black prism-shaped crystals on a Bruker SMART CCD area detector mounted on a Bruker P4 goniometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by direct methods and refined by full-matrix anisotropic least-squares methods (based on F^2). $Pd_{145}(CO)_x(PEt_3)_{30}$ (with $x = 60$): $M = 20653.1$, cubic, $Pa\bar{3}$, $Z = 4$; $F(000) = 37960$. Crystal A: $a = b = c = 35.1022(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 43251.7(9)$ Å^3, $\rho_{calcd} = 3.172$ Mg m^{-3}. 34693 reflections were obtained by 0.4° φ oscillation frames (90 s/frame) over $10.46° \leq 2\theta \leq 44.98°$. An empirical absorption correction (SADABS) was applied ($\mu(Mo_{K\alpha}) = 6.050$ mm^{-1}; max./min. transmission, 0.352/0.191). Refinement (479 parameters; 1072 restraints) on 9300 independent merged reflections ($R_{int} = 0.080$) converged at $wR_2(F^2) = 0.336$ for all data; $R_1(F) = 0.093$ for 4308 observed data ($I > 2\sigma(I)$); GOF (on F^2) = 1.049; max./min. residual electron density, 1.84/ − 1.36 e Å^{-3}. Crystal B: $a = b = c = 35.019(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 42945(6)$ Å^3, $\rho_{calcd} = 3.194$ Mg m^{-3}. 96721 reflections were obtained by 0.2° φ oscillation frames (120 s/frame) over $2.60° \leq 2\theta \leq 45.00°$. An empirical absorption correction (SADABS) was applied ($\mu(Mo_{K\alpha}) = 6.03$ mm^{-1}; max./min. transmission, 0.289/0.263). Refinement (479 parameters; 1072 restraints) on 8733 independent merged reflections ($R_{int} = 0.143$) converged at $wR_2(F^2) = 0.409$ for all data; $R_1(F) = 0.098$ for 2875 observed data ($I > 2\sigma(I)$); GOF (on F^2) = 1.134; max./min. residual electron density, 1.49/ − 1.22 e Å^{-3}. Geometric restraints were placed upon the positional parameters of all light atoms. The ethyl carbon atoms on the phosphorus atoms were modeled as "crystal-ordered" in spite of the methyl carbon peaks being particularly weak on Fourier difference maps. The crystal-disordered CO groups were modeled as two composite doubly bridging CO goups in two orientations based upon structural determinations of other palladium carbonyl phosphane clusters[2] exhibiting two doubly bridging CO groups per square-pyramidal capping Pd atom. Equal occupancies were assumed for *trans* CO groups on opposite sides and $x/(1-x)$ refined occupancies for each set of *cis* pairs that are 90° apart by rotations about the Pd-P axes; the refined occupancies of the sets of *cis*-related CO groups ranged from 0.50(4)/0.50(4) to 0.70(4)/0.30(4). Displacement parameters of the carbon and oxygen atoms were assigned as 1.2 and 1.5 times, respectively, the isotropic equivalent values of the associated non-hydrogen atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149270 and -149271. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[3] $[Pd(PEt_3)_2Cl_2]$ (0.25 g; 0.60 mmol) and $[Au(PPh_3)Cl]$ (0.050 g; 0.10 mmol) were dissolved in DMF (10 mL) under N_2. This solution was transferred under CO into DMF (20 mL) containing NaOH pellets and kept under CO atmosphere. After two days the reaction, that had turned slowly to dark brown with a black precipitate, was terminated by filtration into $[PPh_4]Br$ (1.0 g). Addition of H_2O to the ice-cooled solution produced a dark brown solid that was extracted successively with MeOH, MeCN, and THF. Cluster **1** was isolated from the MeOH extract in low yields. An IR spectrum (THF) exhibited one strong band at 1870.4 cm^{-1} characteristic of a bridging carbonyl. Compound **1** forms thermally stable crystals that are soluble in polar solvents. Two geometrically intriguing Au_2Pd_{21} and Au_2Pd_{41} carbonyl phosphane clusters were isolated as by-products; details of their structural determinations and spectroscopic characterizations will be presented elsewhere.

[4] Because the central atom in both the Au_2Pd_{41} and Au_2Pd_{21} clusters is Au, the possibility that the central atom encapsulated by the 12 Pd atoms in shell 1 of **1** is also Au instead of Pd was carefully examined. However, this possibility can be ruled out conclusively from the X-ray crystallographic refinements of both crystals. The crystallographic analysis involves a comparison of the equivalent isotropic atomic displacement values obtained from anisotropic least-squares refinements of the independent atoms of the molecular cluster under crystallographic $\bar{3}$ site symmetry; the crystallographically asymmetric part of the Pd_{145} core (Figure 2) is comprised of the central Pd(A) atom located at the $\bar{3}$ (S_6) site, two independent Pd(B) atoms in shell 1, two independent Pd(C) and five independent Pd(D) atoms in shell 2, 10 independent Pd(E) atoms in shell 3, and five independent capping Pd(F) atoms. When the central atom is designated as Pd, the equivalent isotropic value of 0.057(2) Å determined for this atom from least-squares refinement of the CCD X-ray data for crystal A is in excellent agreement with those of 0.059(1) and 0.060(1) Å for the two independent Pd(B) atoms in shell 1; similarly, for crystal B the corresponding central Pd(A) value of 0.066(3) Å agrees closely with those of 0.063(2) and 0.064(2) Å for the two independent Pd(B) atoms in shell 1. However, when only the central atom was arbitrarily assigned as Au, its resulting equivalent isotropic value increased in a separate least-squares refinement to an unrealistic higher value of 0.128(2) Å versus those of 0.060(1) and 0.059(1) Å for the two independent Pd(B) atoms in shell 1; similarly, for crystal B the equivalent isotropic value of the central atom increased to a totally unreasonable value of 0.163(4) Å versus 0.063(2) and 0.063(2) Å for the two independent Pd(B) atoms.

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[19] These two different size-dependent cluster-growth patterns are in accordance with the number of nearest-neighbor *intershell* and *intrashell* contacts for the outermost atoms in the incomplete third shell being maximized by anti-Mackay and *regular* Mackay overlayers, respectively. A comprehensive review summarizes the merits and problems inherent in the use of magic numbers to predict equilibrium structures of microclusters.[20] Dynamic structural behavior of very small particles, which additionally may be multi-twinned, also complicates proposals of static geometric models for given atom-sized clusters.[21]

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[24] For the "naked" Pd_{145} core, the Pd(A), Pd(B), and Pd(D) atoms are each 12-coordinate, while the Pd(C), Pd(E), and Pd(F) atoms are 11-, 9-, and 4-coordinate, respectively, to other Pd atoms. Upon ligation, each Pd(E) is linked to one composite whole-weighted CO and each Pd(F) to one P and two composite whole-weighted CO groups thereby increasing the number of atom-connectivities of Pd(E) to 10-coordinate and that of Pd(F) to 7-coordinate.

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