Palladium–Carbonyl Clusters

Nanosized $[Pd_{69}(CO)_{36}(PEt_3)_{18}]$: Metal-Core Geometry Containing a Linear Assembly of Three Face-Sharing Centered Pd_{33} Icosahedra Inside of a Hexagonal-Shaped Pd_{30} Tube**

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Dedicated to Professor Boon Teo on the occasion of his 55th birthday

Palladium possesses exceptional versatility as a unique transition metal in forming an unparalleled assembly of highly condensed carbonyl–phosphane clusters containing either ccp-, mixed ccp/hcp-, or icosahedral-based metal-core architectures. Examples of high-nuclearity homopalladium clusters (that is, clusters arbitrarily designated by us to possess at least ten metal-core atoms with direct metal–metal bonding) with ccp or mixed ccp/hcp layer-stacking geometries include $[Pd_{10}(CO)_{12}(PR_3)_6]$ (R = *n*Bu,[1] Et[1a,2]) with a Pd_{10} tetracapped octahedron, $[Pd_{12}(CO)_{12}(PR_3)_6]$ (R = *n*Bu,[3] Ph[4]) with a Pd_{12} hexacapped octahedron, $[Pd_{23}(CO)_{22}(PEt_3)_{10}]$[5] and $[Pd_{23}(CO)_{20}(PEt_3)_{10}]$[6] with a centered hexacapped cuboctahedral Pd_{19} kernel,[5–8] and $[Pd_{30}(CO)_{26}(PEt_3)_{10}]$ and $[Pd_{54}(CO)_{40}(PEt_3)_{14}]$ with interpenetrating ("twinned-core") cuboctahedral Pd_{20} kernels.[9] High-nuclearity homopalladium clusters built on centered icosahedral frameworks are illustrated by $[Pd_{16}(CO)_{13}(PR_3)_9]$ (R = Me,[10] Et[11]) with a single Pd_{13}-centered icosahedron, and $[Pd_{34}(CO)_{24}(PEt_3)_{12}]$ with four interpenetrating Pd_{26}-centered icosahedra.[6,12] $[Pd_{35}(CO)_{23}(PMe_3)_{15}]$[10] and $[Pd_{39}(CO)_{23}(PMe_3)_{16}]$[10] each contain a face-fused Pd_{23}-centered biicosahedron with linear (D_{3h}) and bent (C_{2v}) geometries, respectively; the D_{3h} central Pd_{29} polyhedron of the Pd_{35} core ideally conforms to five interpenetrating centered icosahedra.[10] $[Pd_{59}(CO)_{32}(PMe_3)_{21}]$[10,13] has two Pd_{13}-centered icosahedra that are indirectly connected through *trans* double-face sharing with an inner face-fused Pd_9 bioctahedron. The unique nanosized $[Pd_{145}(CO)_x(PEt_3)_{30}]$ cluster (with $x \approx 60$) contains a capped three-shell 145-atom metal core that closely conforms to I_h icosahedral symmetry.[14]

Herein we report the preparation, isolation, and structural determination of another type of nanosized icosahedral-based cluster, $[Pd_{69}(CO)_{36}(PEt_3)_{18}]$ (**1**), which has two new important stereochemical features: 1) a linear face-condensation of three centered icosahedra that gives rise to a linear face-sharing Pd_{33}-centered triicosahedron, and 2) a hexagonal-shaped Pd_{30} tube formed by cyclic *trans* edge-sharing of six Pd_7-centered hexagons (host), inside of which resides the linear triicosahedron (guest).

It is particularly noteworthy that this face-condensed icosahedral growth pattern in **1** is completely different from the general vertex-sharing growth sequence of the extraordinary centered polyicosahedral Au/Ag and Au/Ag/M halide phosphane supraclusters (where M = Ni, Pd, Pt are centered M atoms) proposed by Teo, Zhang, and co-workers[15] (see below). In addition, the well-defined stoichiometries and widely diversified but precise geometries of **1** and other homopalladium carbonyl phosphane clusters have especially important stereochemical implications concerning multitwinned structures and growth patterns of much larger ligated and nonligated palladium nanoparticles, and hence are of relevance in nanotechnology.

Compound **1** was obtained in moderate yields ($\approx 50\%$) from a reproducible (optimized) synthesis involving the use of the preformed tetracapped octahedral $[Pd_{10}(CO)_{12}(PEt_3)_6]$.[16] Its composition as well as its atomic arrangement were unequivocally established from low-temperature CCD X-ray diffractometry studies[17,18] of two different crystal forms obtained from related reactions: one being trigonal (**1**) and the other triclinic (**1a**) with each molecule having crystallographic $\bar{3}$ (C_{3i}) and $\bar{1}$ (C_i) site symmetry, respectively. The molecular geometries of **1** and **1a** obtained from their well-refined crystal structures are nearly identical.

The configuration of **1** given in Figure 1 consists of a Pd_{69} core composed of the central Pd_{33} triicosahedron with its central icosahedron completely enclosed by a hexagonal-shaped Pd_{30} cylindrical cavity along with six additional square-capping Pd atoms. The Pd_{69} core geometry has crystallographic $\bar{3}$ symmetry but ideally conforms to a D_{3d} geometry.

The linear Pd_{33} triicosahedron arises from face-sharing of the three centered icosahedra on centrosymmetrically opposite faces of the middle centered icosahedron. This imposes a linear D_{3d} geometry with the crystallographic $\bar{3}$ (S_6) axis passing through the three centered atoms and four midpoints of the two face-fused triangular faces and the two opposite triangular faces of the two outer icosahedra. Each of the two outer icosahedra is also linked to the middle one by three additional intericosahedral bonding connections that result from three threefold-related pairs of corresponding Pd(cage) atoms (namely, Pd(4) and Pd(5)) at a distance of 2.834(2) Å (shown as red links in Figure 1a). The D_{3h} linear face-sharing Pd_{23} biicosahedral fragment in the Pd_{35} core of $[Pd_{35}(CO)_{23}(PMe_3)_{15}]$ similarly possesses three threefold-related intericosahedal Pd–Pd interactions (mean: 2.98 Å; range: 2.941(4)–3.020(4) Å), whereas the C_{2v} bent face-sharing Pd_{23} biicosahedral fragment in the Pd_{39} core of $[Pd_{39}(CO)_{23}(PMe_3)_{16}]$ is additionally connected by only two intericosahedral bonding links (namely, two at 2.954(4) Å, with a third nonbonding connectivity at 4.029(5) Å).[19]

Large dispersions of 0.3–0.4 Å in individual Pd–Pd connectivities are observed for each mean separation, other than those for the centered icosahedral radial distances, which

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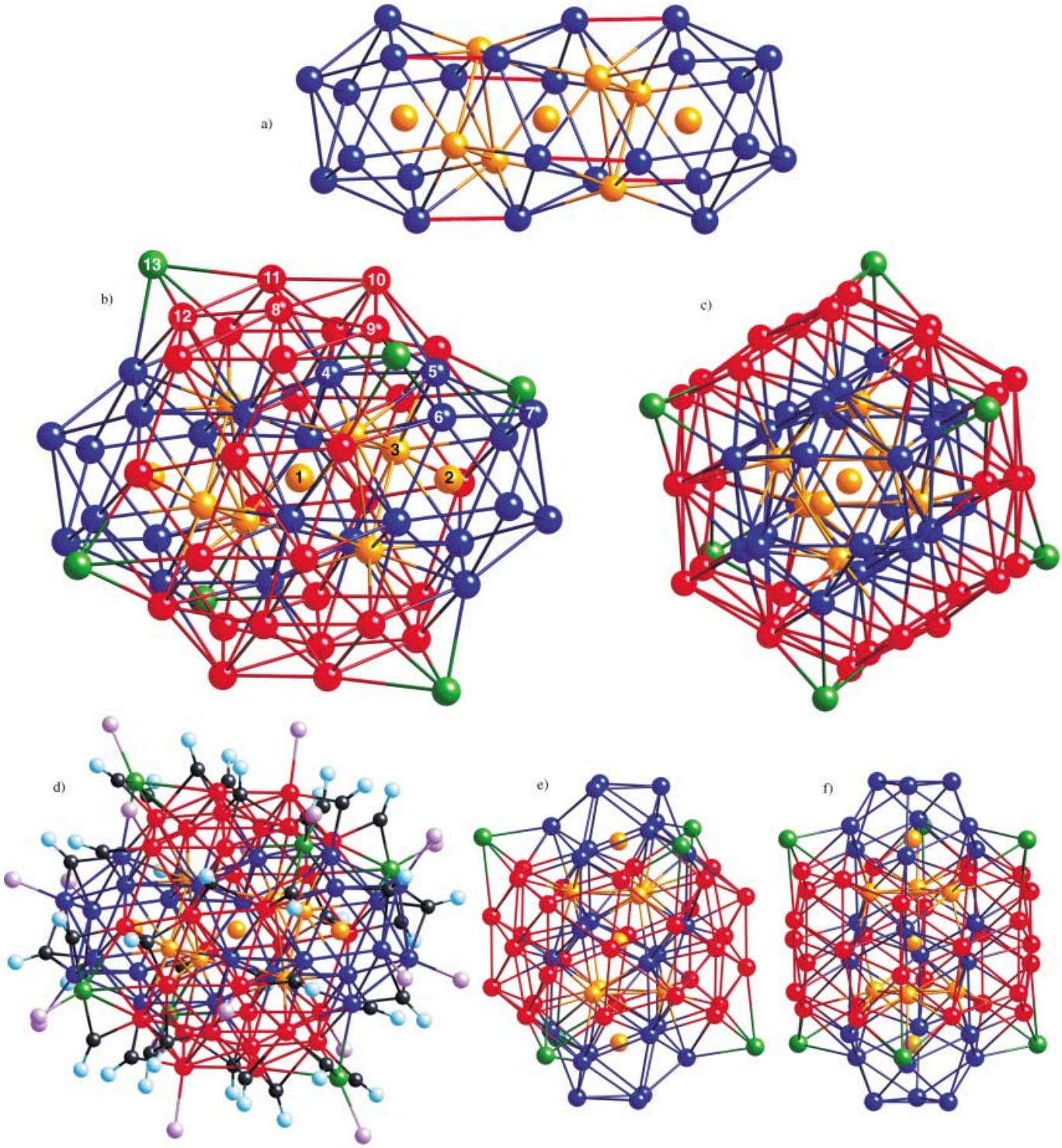

Figure 1. The anatomy of nanosized icosahedral-based $[Pd_{69}(CO)_{36}(PEt_3)_{18}]$ (**1**), with crystallographic $\bar{3}$ (C_{3i}) and pseudo $\bar{3}2/m$ (D_{3d}) symmetry: a) 33-atom core of the linear face-sharing Pd_{33} triicosahedron formed by face-condensation of two outer centered icosahedra on centrosymmetrically opposite triangular faces of the inner centered icosahedron. The three centered and six face-fused atoms are colored gold; b) and c) side and near-front views, respectively, of the entire Pd_{69} core (with numbering scheme for Pd atoms shown in b)). Its formal construction may be described as a Pd_{33} triicosahedron (guest) residing inside a hexagonal-shaped Pd_{30} tube (host; shown in red) with six symmetry-equivalent atoms (green) each asymmetrically capping a square-bonding polygon formed from one atom (blue) of the triicosahedron and three atoms (red) of the encapsulating host; d) entire structure of **1** displaying the geometrical disposition of 18 PEt_3 ligands (without ethyl substituents) and 18 doubly and 18 triply bridging CO ligands; e) front view of one of three pseudohorizontal twofold axes in the Pd_{69} core with centrosymmetric D_{3d} geometry. Each of the three pseudohorizontal twofold axes, which are normal to the principal $\bar{3}$ axis (that is, a combined threefold and inversion center), passes through the centered Pd(1) atom of the middle icosahedron and the centered atoms of two opposite Pd_7-centered hexagons; f) another front view (after counterclockwise rotation of **1** by 30° about the vertically oriented $\bar{3}$ axis) of one of three vertical σ_d mirror planes that bisect pairs of the three horizontal twofold axes in the Pd_{69} core.

agree within 0.04 Å. Similar large dispersions in Pd–Pd connectivities are found in the other previously mentioned icosahedral-based homopalladium carbonyl–phosphane clusters. Nevertheless, the different bonding Pd–Pd mean separations in **1** are within 0.1 Å of those found in ccp Pd metal (2.751 Å).[19]

For the middle icosahedron of **1**, the mean radial distance of 2.68 Å (range: 2.657(1)–2.702(1) Å) from the central Pd(1) atom to the 12 Pd(cage) atoms is significantly shorter than the mean tangential distance of 2.82 Å (range: 2.657(1)–3.127(2) Å) corresponding to the 30 icosahedral edges of the 12 Pd(cage) atoms. Similarly, for the two symmetry-equivalent outer icosahedra, the corresponding radial and tangential mean separations are 2.72 Å (range: 2.702(2)–2.730(2) Å) and 2.86 Å (range: 2.725(2)–3.127(2) Å), respectively. These observed radial compressions of 5.0% (i.e., [(2.82–2.68) Å/2.82 Å] × 100) and 4.9% (i.e., [(2.86–2.72) Å/2.86 Å] × 100) are identical with the predicted value of approximately 5% for a geometrically regular centered icosahedron[20] and furthermore are completely consistent with experimental values determined for Pd_{13}-centered icosahedra in the previously mentioned Pd_{16}, Pd_{35}, Pd_{39}, Pd_{59}, and Pd_{145} clusters.

The hexagonal-shaped Pd_{30} tube that surrounds the middle icosahedron of the linear face-sharing triicosahedron can be viewed as a cyclic *trans* edge-sharing of six Pd_7-centered hexagons. The Pd–Pd bonding connectivities within the independent Pd(8)-centered hexagon vary considerably, but their mean separations of 2.84 Å (range: 2.697(2)–3.150(2) Å) for the radial Pd(8)–Pd(edge) separations and 2.83 Å (range: 2.743(2)–3.018(2) Å) for the tangential Pd(edge)–Pd(edge) separations are virtually identical. The independent Pd(8)-centered atom is displaced by 0.29 Å from the mean plane of six hexagon atoms in the outward direction away from the Pd_{33} triicosahedral guest. The average diameter of this cylinder-like Pd_{30} tube is approximately 0.86 nm, based upon the distance of 0.92 nm between centrosymmetrically opposite Pd(8)-centered atoms minus 0.06 nm for the net perpendicular displacements of two Pd(8) atoms out of their mean Pd_6 hexagons.

The middle icosahedron of the linear face-condensed Pd_{33} triicosahedron fills the cylindrical cavity of the hexagonal-shaped Pd_{30} tube. Its encapsulation by this tube can be considered as a guest–host model that is fully bonded in this case (that is, a *permanent* guest). Each centered hexagon forms 14 Pd–Pd bonding connectivities with the icosahedral fragment, with a mean length of 2.79 Å (range: 2.627(2)–2.911(2) Å). The number of bonding interactions of each atom of the independent Pd_7-centered hexagon to the triicosahedron varies from one to three.

The resulting Pd_{63} guest–host composite of the Pd_{69} core of **1** is completed by six additional Pd atoms that cap the six bonding square polygons formed between the Pd_{33} triicosahedron and the hexagonal-shaped Pd_{30} tube. The capping Pd atoms are each asymmetrically coordinated to its bonding square Pd_4 base with three short Pd–Pd connectivities that range from 2.723(2) to 2.764(2) Å and one long connectivity of 3.151(2) Å; an analogous asymmetry of one long and three much shorter Pd–Pd connectivities for tetracapping Pd atoms is observed in $[Pd_{23}(CO)_{20}(PEt_3)_8]$.[6b,21]

Compound **1** has 15 interior Pd(i) atoms, consisting of the entire 13-atom middle centered icosahedron and the two centered Pd atoms of the two outer centered icosahedra, and 54 surface Pd(s) atoms. Nanosized diameters of the ellipsoidal-shaped Pd_{69} core are 1.35 nm between the two centrosymmetrically opposite square-capping Pd atoms, 1.24 nm between two opposite outermost icosahedral triangular faces of the triicosahedron, and 0.92 nm between two centered Pd atoms of two opposite centered hexagons.

Compound **1** is stabilized by 18 PEt_3 ligands, together with 18 doubly and 18 asymmetrically coordinated (two shorter/one longer) triply bridging CO ligands.[22] The 18 PEt_3 ligands are each attached to the six Pd atoms of the two outer triangular faces of the triicosahedron, to the six square-capping Pd atoms, and to the six Pd(edge) atoms of the six centered hexagons that are not basal atoms connected to the six square-capping Pd atoms. It is noteworthy that each square-capping Pd atom has two doubly bridging CO ligands that are linked on the two opposite short Pd(axial)–Pd(basal) edges.

A comparison of the face-condensation mode of formation of the centered Pd_{33} triicosahedral guest in **1** with the entirely different vertex-sharing growth-pattern of centered polyicosahedral Au/Ag and Au/Ag/M halide phosphane supraclusters (M = Ni, Pd, Pt) is informative. These remarkable coinage-metal polyicosahedral clusters were prepared, isolated, and structurally/theoretically analyzed by Teo, Zhang, and co-workers[15] who formulated a vertex-sharing sequence of modular centered icosahedral building blocks to account for the generation of known and proposed polyicosahedral geometries containing up to 13 icosahedra (that is, an icosahedron of 12 icosahedra). Known examples include a crystallographically analyzed 36-atom centered triicosahedral Au/Ag phosphane/chloride cluster consisting of three Au-centered icosahedra sharing three vertices in a cyclic array.[23] This particular $Au_{18}Ag_{18}$ triicosahedron was found to contain two additional exopolyhedral Ag atoms. In striking contrast, the *trans* face-fused centered triicosahedron in **1** has 33 rather than 36 metal atoms. The face-condensation of centered icosahedra to give the centered Pd_{23} biicosahedral fragment in both the Pd_{35} and Pd_{39} clusters and the centered Pd_{33} triicosahedron in **1** would suggest that face-sharing of centered icosahedra may be considered as another possible growth process in the formation of the unligated and ligated nanoparticles. It is apparent that the existence of different kinds of ligated icosahedral-based metal clusters greatly depends upon the cohesive energies and relative electronegativities of the metal atoms and the electronic/steric effects of their ligands, as well as the reaction boundary conditions.

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[16] Reactions were carried out under an inert atmosphere by standard Schlenk techniques. All solvents were thoroughly purged with N_2 before use. $[Pd_{10}(CO)_{12}(PEt_3)_6]$ was prepared by using the Mednikov procedure[1a], and then used as a precursor. In a typical reaction, $Me_3NO{\cdot}2H_2O$ (0.089 g, 0.80 mmol) and NaOH (≈1.0 g, pellet form) were stirred in DMF (20 mL)at 50 °C for about 1 h (in order to form a saturated NaOH solution). Then a suspension of $[Pd_{10}(CO)_{12}(PEt_3)_6]$ (0.211 g, 0.10 mmol) in DMF (10 mL) was quickly transferred to the Me_3NO/NaOH solution. The reaction was performed at 50 °C for one day. The resulting black reaction solution was filtered into PPh_4Cl (≈1.0 g), and then degassed distilled water (150 mL) was added to the ice-cooled solution in order to precipitate out a black solid (that is, the use of ionic PPh_4Cl enabled the formation of a precipitate instead of a colloidal suspension). The precipitate was filtered and washed several times with methanol, after which it was extracted first with CH_3CN and then with THF. Solvent removal from the CH_3CN extract afforded approximately 0.08 g of **1** as the major product (yield ≈50% based upon $[Pd_{10}(CO)_{12}(PEt_3)_6]$). IR spectra of **1** exhibit carbonyl bands at 1855(s) and 1830(sh) in Nujol and 1869(s) and 1826(sh) cm^{-1} in THF. The triclinic crystal form, **1a**, was subsequently obtained as a very minor product (a few crystals) from the similar reaction of $[Pd_{10}(CO)_{12}(PEt_3)_6]$ with NaOH in DMF (but without $Me_3NO{\cdot}2H_2O$) at room temperature for one day.
[17] Crystallographic data are given for the trigonal (**1**) and triclinic (**1a**) crystal forms of $[Pd_{69}(CO)_{36}(PEt_3)_{18}]$. Compound **1** was crystallized by slow diffusion of a diisopropyl ether layer and then a hexane layer over a concentrated THF solution at room temperature, while **1a** was crystallized as a minor product (that was isolated from the CH_3CN extract) by slow diffusion of a diisopropyl ether layer over a concentrated THF solution at room temperature. Black block-shaped crystals of dimensions $0.13\times0.18\times0.24\ mm^3$ for **1** and $0.05\times0.11\times0.28\ mm^3$ for **1a** were used for X-ray data collections. Intensity data were collected for **1** and **1a** at −173(2) °C via a Bruker SMART CCD 1000 area detector system mounted on a Bruker Platform diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) from a standard sealed-tube generator. An empirical absorption correction (SADABS) was applied to each data set. Structural determinations were obtained by use of direct methods followed by successive Fourier difference maps. Least-square refinements (based on F^2) were carried out with SHELXTL.[18] $[Pd_{69}(CO)_{36}(PEt_3)_{18}]$ (**1**): trigonal; $R\bar{3}c$; $a=b=18.961(1)$, $c=115.164(15)$ Å, $\alpha=\beta=90$, $\gamma=120°$, $V=35{,}856(6)$ Å^3; $Z=6$; $\rho_{calcd}=2.911\ Mg\,m^{-3}$. 68873 data collected via 0.3 ω scans (60 s/frame) over a 2θ range 4.24–46.60°. Least-squares refinement (411 parameters/276 restraints) on 5452 independent merged reflections ($R_{int}=0.037$) converged at $\omega R_2(F^2)=0.150$ for all data; $R_1(F)=0.053$ for 4981 observed data ($I>2\sigma(I)$). Compound **1** has crystallographic $\bar{3}$ site symmetry, such that the asymmetric part is comprised of 13 Pd atoms, six CO ligands, and three $P(C_2H_5)_3$ ligands. Of the 13 independent Pd atoms, Pd(1) is located at the $\bar{3}$ site, Pd(2) is located on the threefold axis, while the other 11 Pd atoms are in general positions. One oxygen atom of a bridging carbonyl group was disordered at two sites (namely, O(6)/O(6′) with refined occupancies of 0.66/0.34). One independent P atom was disordered at two sites (namely, P(1)/P(1′) with refined occupancies of 0.56/0.44); disordered ethyl carbon atoms attached to P(1)/P(1′) were refined isotropically. Ethyl carbon atoms coordinated to P(2) were refined isotropically in two different orientations. Non-hydrogen atoms were refined anisotropically except for all carbon atoms of the two disordered phosphane groups, as stated above. Restraints were applied to the positional and displacement parameters of the ethyl carbon atoms in order to achieve convergence. $[Pd_{69}(CO)_{36}(PEt_3)_{18}]$ (**1a**): triclinic; $P\bar{1}$; $a=19.103(2)$, $b=19.246(2)$, $c=21.854(2)$ Å, $\alpha=64.877(1)$, $\beta=75.099(2)$, $\gamma=61.913(1)°$, $V=6401.4(11)$ Å^3; $Z=1$; $\rho_{calcd}=2.718\ Mg\,m^{-3}$. 45722 data collected via 0.3 ω scans (120 s/frame) over a 2θ range 4.34–50.00°. Least-squares refinement (1218 parameters/1463 restraints) on 21861 independent merged reflections ($R_{int}=0.039$) converged at $\omega R_2(F^2)=0.130$ for all data; $R_1(F)=0.055$ for 16565 observed data ($I>2\sigma(I)$). Compound **1a** has crystallographic $\bar{1}$ site symmetry, such that the asymmetric part is comprised of 35 Pd atoms, 18 CO ligands, and nine $P(C_2H_5)_3$ ligands. One independent carbonyl ligand is disordered at two orientations (namely, CO(12)/CO(12′) with refined occupancies of 0.59/0.41). All carbon atoms of one independent phosphane ligand are disordered (occupancies of 0.49/0.51). Non-hydrogen atoms were refined anisotropically except for all carbon atoms of the disordered phosphane ligand. Restraints were applied to the positional and displacement parameters of the ethyl carbon atoms in order to achieve convergence. CCDC-208518 (**1**) and -208519 (**1a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data

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