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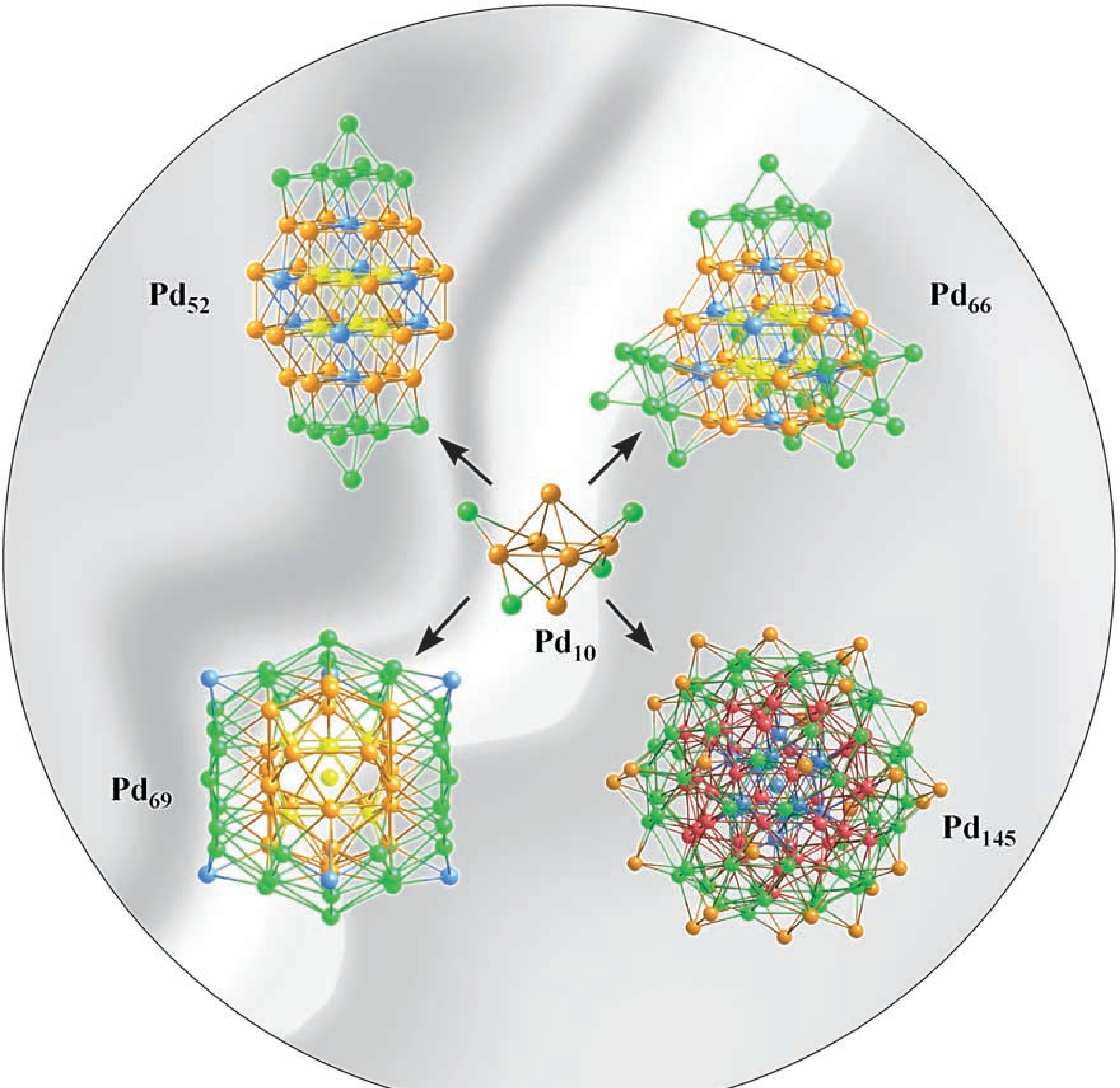

Zwei weitere Mitglieder einer Familie großer Palladiumcluster mit Carbonyl- und Triethylphosphan-Liganden wurden ausgehend von der gemeinsamen Vorstufe $[Pd_{10}(CO)_{12}(PEt_3)_6]$ aufgebaut. Die Produkte enthalten einen Pd$_{52}$- oder einen Pd$_{66}$-Kern. Eine detaillierte Analyse der geometrischen Vielfalt dieser Homometallnanocluster liefert die Zuschrift von L. F. Dahl, E. G. Mednikov et al. auf den folgenden Seiten.

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# Nanosized $[Pd_{52}(CO)_{36}(PEt_3)_{14}]$ and $[Pd_{66}(CO)_{45}(PEt_3)_{16}]$ Clusters Based on a Hypothetical $Pd_{38}$ Vertex-Truncated $\nu_3$ Octahedron**

*Evgueni G. Mednikov,* Sergei A. Ivanov, Irina V. Slovokhotova, and Lawrence F. Dahl**

*Dedicated to Professor Giuliano Longoni*

Palladium is a unique transition metal in that it forms an exceptionally versatile family of high-nuclearity palladium carbonyl phosphine clusters (i.e., with cores of at least 10 metal atoms with direct metal–metal bonding) that display a truly remarkable diversity of geometries about the metal cores.[1a–h] Fifteen distinctly different geometries have been identified crystallographically for $Pd_n$ cores with $n = 10$,[2a–c] 12,[2d,e] 16,[2f,g] 23 (two different metal cores have been observed),[2h–j] 29,[2e] 30,[2k] 34,[1a,2l] 35,[2g] 38,[2m] 39,[2g] 54,[2k] 59,[2g,n] 69,[2o] and 145.[2p] All but two of these highly condensed palladium clusters have close-packed frameworks that contain metal fragments whose structural units may be described as ccp (cubic close-packed), mixed ccp/hcp (hexagonal close-packed) stacking layers (which include layer sequences corresponding to capped octahedra, centered cuboctahedra, or centered anti-cuboctahedra), and as icosahedra. One exception is the $Pd_{38}$ cluster, which has a highly irregular geometry about the metal core;[1a,2m] the other exception is one of the $Pd_{23}$ clusters, which has a highly distorted body-centered-cubic metal framework.[2j] Close-packed structural units of the $Pd_n$ cores also include "twinned interpenetrating" centered cuboctahedral and icosahedral geometries as well as one mixed, face-fused icosahedral/octahedral $Pd_{59}$ architecture, which consists of two centered icosahedra that *trans*-cap a bioctahedron.[2g,n] The largest known crystallographically determined discrete metal cluster, $Pd_{145}$, contains a capped three-shell 145-atom metal core, whose geometry closely conforms to $I_h$ icosahedral symmetry.[2p]

A most impressive stereochemical aspect of this extraordinary family of $[Pd_n(CO)_xL_y]$ clusters, where L denotes phosphine ligands, is that practically all of the above-mentioned members of the $Pd_n$ series have been prepared with the same phosphine ligand, $L = PEt_3$, which is sterically non-bulky and also a good σ donor. The exceptions reported to date are the $Pd_{12}$ cluster, which was isolated only with $PnBu_3$[2d] and $PPh_3$,[2e] and the $Pd_{35}$,[2g] $Pd_{39}$,[2g] and $Pd_{59}$[2g,n] clusters, which were obtained only with sterically smaller $PMe_3$ ligands. Furthermore, all of the triethylphosphine-containing $[Pd_n(CO)_xL_y]$ ($L = PEt_3$) clusters may be obtained from reactions with the same tetracapped octahedral $Pd_{10}$ precursor, $[Pd_{10}(CO)_{12}(PEt_3)_6]$,[2b,c] through different kinetically controlled synthetic pathways to give relatively thermodynamically stable products in most cases. For the majority of the $Pd_n$ clusters, reasonably good yields (at least 30%) were ultimately obtained by optimization of the reaction conditions and in particular cases by the structure-to-synthesis approach from different synthetic routes.

Herein, we report the synthesis of two new extraordinary members to the series of palladium carbonyl phosphine clusters, namely, $[Pd_{52}(CO)_{36}(PEt_3)_{14}]$ (**1**) and $[Pd_{66}(CO)_{45}(PEt_3)_{16}]$ (**2**), from the precursor $[Pd_{10}(CO)_{12}(PEt_3)_6]$ (**3**). Cluster **1** was prepared as an extremely minor product (< 5% yield) from the reaction of **3** with $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) at 50 °C.[3] Subsequent attempts to increase the yield of **1** were unsuccessful; in the best cases, reactions usually (but not always) afforded **1** as a minor product in powder samples. Initial attempts to prepare the $Pd_{66}$ cluster **2** were carried out by Mednikov and Kanteeva from the reproducible deligation of **3** with $CF_3CO_2H/Me_3NO$ under optimized ratios of **3**/$CF_3CO_2H$ and **3**/$Me_3NO$ at 1:120 and 1:16, respectively (42% yield; note that the product obtained by this procedure is labeled as **2′** (see below)).[2l] However, at that time attempts to characterize the product by X-ray diffraction were unsuccessful. Crystals of this unknown cluster **2′** were again isolated from the above-stated reaction,[4] and new efforts were undertaken to determine both its atomic arrangement and stoichiometry. However, we experienced great difficulty in obtaining the entire crystal structure. Complete X-ray data sets (two with synchrotron radiation) were collected from at least 10 monoclinic crystals (different preparations): despite poor refinements, solutions of the structure from several data sets confirmed the $\{Pd_{66}P_{16}\}$ architecture of **2′** but did not provide any information concerning the number and coordination modes of the carbonyl ligands. Major problems included unusually high diffuse-scattering background and merohedral twinning (i.e., due to a monoclinic unit cell with $\beta \approx 90°$), which was taken into account in least-squares refinements. Nevertheless, the entire crystal structure was eventually established from monoclinic crystals (with a larger angle $\beta = 90.9°$) that were obtained from a different preparative route, through the reaction of **3** with $[Pd(MeCN)_4](BF_4)_2$,[5] to give **2**. Although the IR spectra of **2** and **2′** are virtually identical and their crystallographic unit-cell parameters are analogous, it should be noted that the $Pd_{66}$ cluster **2′** obtained from the reaction of

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[*] Dr. E. G. Mednikov, Dr. S. A. Ivanov, Prof. L. F. Dahl
Department of Chemistry
University of Wisconsin–Madison
Madison, WI 53706 (USA)
Fax: (+1) 608-262-6143
E-mail: mednikov@chem.wisc.edu
dahl@chem.wisc.edu

I. V. Slovokhotova
Zelinsky Institute of Organic Chemistry
Russian Academy of Sciences
Moscow (Russia)

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**3** with $CF_3CO_2H$ and $Me_3NO$ may possibly contain a different number of carbonyl ligands to that found in **2**.[6]

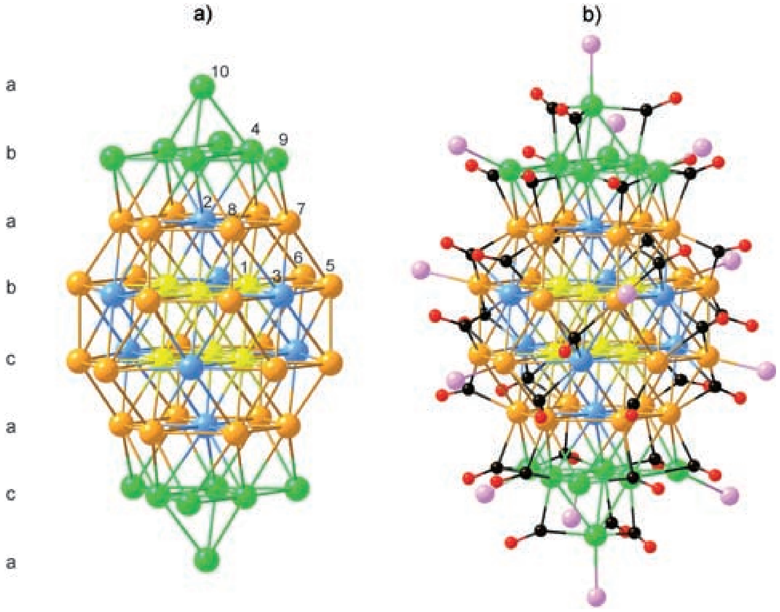

*Figure 1.* a) Crystallographic $C_{3i}$ and pseudo-$D_{3d}$ geometry of the nanosized $Pd_{52}$ core in $[Pd_{52}(CO)_{36}(PEt_3)_{14}]$ (**1**). Symmetry-independent Pd atoms are numbered. The maximum diameter of the metal core is 1.58 nm parallel and 0.84 nm perpendicular to the principal threefold axis that passes through Pd(10), Pd(2) and the crystallographic inversion centre; the latter is situated between the two middle 12-atom Pd layers. b) Molecular structure of **1** displaying the arrangement of 14 $PEt_3$ ligands (P pink; ethyl substituents not shown) and 36 bridging carbonyl ligands (O red, C black) about the $Pd_{52}$ core. Two crystallographically independent carbonyl ligands are each disordered between two sites with occupancy factors of 0.54/0.46 and 0.76/0.24; only their main orientations are shown.

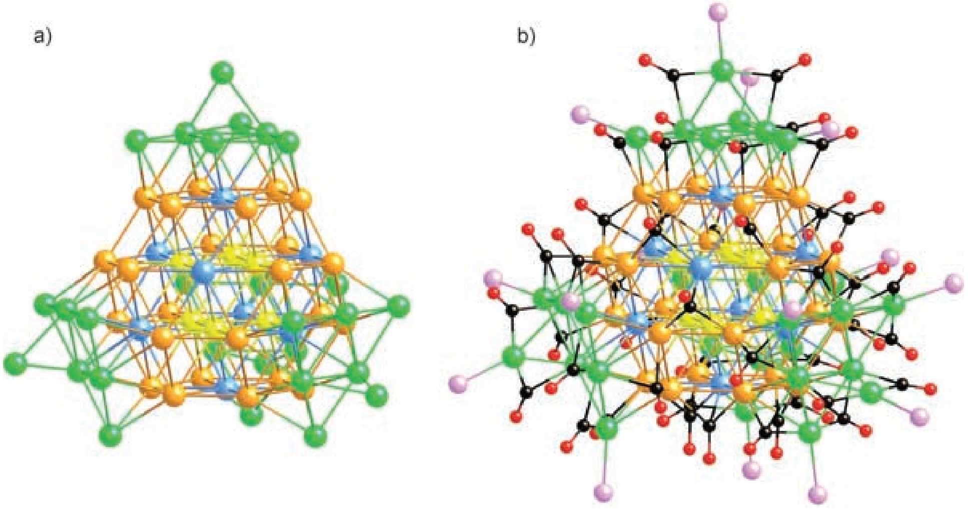

*Figure 2.* a) Geometry of the nanosized $Pd_{66}$ core in $[Pd_{66}(CO)_{45}(PEt_3)_{16}]$ (**2**). The maximum diameter of the metal core of this spherically shaped $Pd_{66}$ cluster is approximately 1.14 nm along each of the four tetrahedral body-diagonal ⟨111⟩ directions. b) Molecular structure of **2** exhibiting the arrangement of 16 $PEt_3$ ligands (P pink; ethyl substituents not shown) and 45 bridging carbonyl ligands (O red, C black) about the $Pd_{66}$ core. Four carbonyl ligands are each disordered between two sites with occupancy factors of approximately 0.5/0.5 in each case; only one of the two orientations is shown.

The molecular structures[7] of **1** and **2** are based upon a common hypothetical $Pd_{38}$ kernel that can be formally derived by vertex-truncating of a likewise unknown $\nu_3$ $Pd_{44}$ octahedron, where $\nu_n$ refers to $n+1$ equally spaced atoms (namely, four) along each of the 12 octahedral edges. This cubic $O_h$-symmetric $Pd_{38}$ kernel contains six {100} square $Pd_4$ faces and eight {111} centered hexagonal $Pd_7$ faces, and has six interior (encapsulated) metal atoms that are located at the vertices of a regular octahedron.

The $Pd_{52}$ core in **1** (Figure 1) formally arises from the remaining 14 Pd atoms, which form two monocapped $\nu_2$ $Pd_7$ triangles that sequentially condense on centrosymmetrically opposite, *trans*-oriented {111} centered hexagonal $Pd_7$ faces[8] of the $Pd_{38}$ kernel. This *trans* attachment of the two $Pd_7$ triangles to the $Pd_{38}$ kernel lowers the symmetry of the resulting $Pd_{52}$ core, which has crystallographically imposed $C_{3i}$ ($\bar{3}$) symmetry, from pseudo-$O_h$ to pseudo-$D_{3d}$ ($\bar{3}2/m$). The $Pd_{52}$ core contains eight interior Pd atoms that conform to a *trans*-bicapped octahedron.

The $Pd_{66}$ core in **2** is formally constructed by the sequential condensation of the same monocapped $\nu_2$ $Pd_7$ triangles on four non-adjacent (tetrahedral) {111} centered hexagonal $Pd_7$ faces of the $Pd_{38}$ kernel (Figure 2). The crucial stage is the condensation of the second triangular $Pd_7$ fragment which must occur on any of three tetrahedrally oriented {111} faces of the $Pd_{38}$ core. As a result, further condensation of the remaining two $\nu_2$ $Pd_7$ triangles can sterically occur only on the remaining two tetrahedral centered hexagonal $Pd_7$ faces to thereby complete the $Pd_{66}$ core of **2**. Because the probability of the condensation of the second $\nu_2$ $Pd_7$ triangle on one of the tetrahedrally oriented centered hexagonal faces of the $Pd_{38}$ kernel is three-times greater than that on the opposite face, this formal construction of the $Pd_{66}$ core is significantly favored over that of the $Pd_{52}$ core. Hence, it is not surprising that this building-block scheme is consistent with the good synthetic reproducibility of the $Pd_{66}$ cluster as well as with its preparation from different procedures. In contrast, the $Pd_{52}$ cluster **1** is difficult to isolate. A close examination of the particular orientations of the four monocapped $Pd_7$ triangles relative to the $Pd_{38}$ kernel in **2** reveals that the $Pd_{66}$ core has approximately $C_{3v}$ symmetry instead of the expected $T_d$ symmetry. However, the 10 interior (encapsulated) atoms ideally conform to a tetracapped $T_d$ $Pd_{10}$ octahedron, which alternatively may be viewed as a $\nu_2$ $Pd_{10}$ tetrahedron with three equally spaced Pd atoms along each of the six tetrahedral edges.

The resulting metal arrangements of the entire $Pd_{52}$ core along the threefold axis in **1** and of each of the four $\{Pd_{38}Pd_7\}$ fragments with the common $Pd_{38}$ kernel along the $\langle 111\rangle$ directions in **2** may be considered as mixed ccp/hcp layer-stacking structures. Figure 1 shows that the eight layers in **1** adopt an ababcaca stacking sequence. In **2**, which has pseudo-$C_{3v}$ symmetry, the alternation of the stacked layers (Figure 2) depends on the $\langle 111\rangle$ direction: namely, the layer-stacking sequence along the proper $C_3$ axis is abacba, whereas along each of the other three symmetry-equivalent $\langle 111\rangle$ directions the sequence is ababca. Similar four-, five-, and six-layer stacking sequences involving mixed ccp/hcp metal arrangements have been observed in other large carbonyl clusters, including $[Rh_{22}(CO)_{37}]^{4-}$ (abcb),[9a] $[Pd_{13}Ni_{13}(CO)_{34}]^{4-}$ (abcac),[9b] $[Pd_{16}Ni_{16}(CO)_{40}]^{4-}$ (abcbca),[9c] $[Ni_{32}Pt_{24}(CO)_{56}]^{6-}$ (abacbc sequence along its threefold axis),[9d] and neutral $[Pd_{54}(CO)_{40}(PEt_3)_{14}]$ (abaca).[2k]

Overall mean Pd–Pd distances of 2.80 Å (range: 2.70–2.95 Å) and 2.81 Å (range: 2.66–3.00 Å) in **1** and **2**, respectively, are typical for palladium carbonyl phosphine clusters, as exemplified by the overall mean Pd–Pd distance of 2.81 Å previously reported for the ccp $Pd_{30}$ and ccp/hcp $Pd_{54}$ clusters.[2k] The significantly shorter mean Pd–Pd distances of 2.74 Å in the interior (encapsulated) bicapped $Pd_8$ octahedron in **1** and 2.77 Å in the interior (encapsulated) tetracapped $Pd_{10}$ octahedron ($\nu_2$ tetrahedron) in **2**, which are essentially identical to the Pd–Pd distance of 2.75 Å in ccp Pd metal,[10] are consistent with the interior $Pd_n$ atoms presumably having metallic character.

In **1**, four $PEt_3$ ligands are attached to each of the two monocapped $\nu_2$ $Pd_7$ triangles, with one to the capped Pd atom and the other three to the corner atoms of the $Pd_6$ triangles. The six other $PEt_3$ ligands are coordinated to the six $\bar{3}$ ($S_6$)-equivalent Pd(6) atoms (see Figure 1) in the middle two $Pd_{12}$ layers. In **2**, the 16 $PEt_3$ ligands are equally distributed among the four monocapped $\nu_2$ $Pd_7$ triangles in coordination modes that are analogous to those found in **1**.

The 36 CO groups in **1** were all located without any difficulties. They comprise 12 doubly bridging $\mu_2$-CO groups and 24 triply bridging $\mu_3$-CO groups (Figure 1), and under crystallographically $\bar{3}$ ($S_6$) site symmetry, they may be divided into the following three distinct groups: 1) Six $\mu_2$-CO groups (one independent), with three of these connecting each of the two monocapped $\mu_3$-Pd atoms to the three inner Pd atoms of the triangular $Pd_6$ layer.[11] 2) Twelve $\mu_3$-CO groups (two independent), with six of these connecting each of the two monocapped $\nu_2$ $Pd_7$ triangles to a centered hexagonal $Pd_7$ face of the $Pd_{38}$ kernel. This carbonyl arrangement may be readily visualized as six edge-bridging CO groups that span the six Pd–Pd pairs in each $Pd_6$ triangle being formally converted into face-capped $\mu_3$-CO groups by each becoming attached to one of the six hexagonal Pd atoms of the centered hexagonal face. 3) Twelve $\mu_3$-CO groups (two independent) and six $\mu_2$-CO groups (one independent) joined to the six "open" symmetry-related centered hexagonal faces of the $Pd_{38}$ kernel. These consist of two $\mu_3$-CO groups, which connect the centered Pd atom of a given $Pd_7$ face with four of the Pd atoms in the hexagon, and one $\mu_2$-CO group that links the remaining two Pd atoms. These bridging carbonyl ligands in **1** are consistent with the observation of only one strong broad CO band in the solid-state IR spectrum at 1856 $cm^{-1}$ with a shoulder at 1875 $cm^{-1}$.

In sharp contrast, the ultimate location of all 45 independent carbonyl ligands in the $Pd_{66}$ cluster **2** (Figure 2) proved to be difficult and time-consuming. Nevertheless, a careful examination of their composite steric dispositions provides complete reassurance for the presence of 45 CO groups in **2**. Particularly intriguing is that normally 44 CO groups would be predicted from general symmetry considerations, thus the 45th CO group in **2** constitutes an unexpected extra one.[12] It is most convenient to initially describe the carbonyl arrangement of the 44 normal CO groups in **2** and then consider the observed major steric deformations of two CO groups that allow for the addition of the extra 45th CO ligand. In this analysis the carbonyl ligands in **2** are likewise separated into the same three groups: 1) Eight $\mu_2$-CO groups, of which two edge-bridge each of the four monocapped $\mu_2$-Pd atoms that are coordinated to only two of the three inner triangular Pd atoms within the four $\nu_2$ $Pd_7$ triangles. 2) Twenty-four $\mu_3$-CO groups with six face-capped ones connecting each of the four monocapped $\nu_2$ $Pd_7$ triangles to a centered hexagonal $Pd_7$ face of the $Pd_{38}$ kernel, as described above in **2**. 3) Six $\mu_3$-CO groups and three $\mu_2$-CO groups attached (as found in **1**) to three of the four "open" centered hexagonal $Pd_7$ faces of the $Pd_{38}$ kernel; the fourth "open" face has three $\mu_3$-CO ligands instead of one $\mu_2$-CO and two $\mu_3$-CO groups. This above description accounts for 44 of the 45 CO units found in **2**. To provide sufficient space for the addition of the extra (45th) $\mu_3$-CO ligand, the one-bond-connectivity of each of two adjacent normally disposed $\mu_3$-CO groups that connect one monocapped $\nu_2$ $Pd_7$ triangle to its centered hexagonal $Pd_7$ face is broken, such that these two adjacent $\mu_3$-CO groups are then transformed into $\mu_2$-CO units that are highly bent above the $\nu_2$ $Pd_6$ triangle (away from the centered hexagonal $Pd_7$ face) to increase intraligand contact distances and thereby minimize steric repulsions. This extensive localized deformation thus allows the extra $\mu_3$-CO unit to face-cap the resulting $Pd_3$ triangle, which is composed of the two adjacent Pd atoms of the centered hexagonal $Pd_7$ face and the central atom of the $\nu_2$ $Pd_6$ triangle that is also linked to the two highly bent $\mu_2$-CO groups. These bridging CO coordinations give rise to only one broad strong CO band at 1884 $cm^{-1}$ in the solid-state IR spectrum of **2**.[11–13]

This comparative analysis of the carbonyl ligands in **1** and **2** discloses two important stereochemical features that originated from the observed {111} face-condensations of the hypothetical $Pd_{38}$ vertex-truncated $\nu_3$-octahedral kernel: 1) in **1**, each triply bridging monocapped Pd atom connected to the three inner Pd atoms of the $Pd_6$ triangle contains *three* edge-bridged $\mu_2$-CO groups, whereas in **2** each of the four doubly bridging monocapped Pd atoms connected to two of the three inner Pd atoms of the $Pd_6$ triangle contains *two* edge-bridged $\mu_2$-CO ligands; 2) the observed localized carbonyl rearrangement in **2** which sterically allows the presence of the extra (45th) CO ligand suggests that the geometry of the nanosized $Pd_{66}$ core with 44 normal CO groups may potentially accommodate up to four additional carbonyl ligands without any substantial changes in the architecture of the metal core.[6] In fact, a current investigation has indicated the formation of another $Pd_{66}$ cluster with 47 CO groups (three extra) from the reaction of **3** with dicobalt octocarbonyl.[13]

The possibility of variable numbers of carbonyl ligands for close-packed nanosized $[Pd_n(CO)_x(PR_3)_y]$ clusters without the need for significant geometrical changes in the common $\{Pd_n(PR_3)_y\}$ fragments was recently observed for the cuboctahedral $[Pd_{23}(CO)_x(PEt_3)_{10}]$ clusters with $x = 20, 21, 22$.[6] The arrangements of their composite carbonyl groups revealed that the formal addition of an extra CO ligand produces considerable localized displacements of certain neighboring CO ligands (with concomitant changes in their coordination modes) in order to increase intraligand contacts and thereby minimize steric effects. The geometric effects of the expanded carbonyl ligation in the $Pd_{66}$ cluster also have special relevance to the well-known Muetterties cluster–science analogy[14] that chemisorbed CO molecules are not static but undergo both dissociative processes and nondissociative migratory processes about the metal surface as a function of the CO pressure.

Of particular relevance to our hypothesized modular construction of **1** and **2** from the hypothetical $Pd_{38}$ vertex-truncated $\nu_3$ octahedron is that the congeneric $Pt_{38}$ core of the classic Chini $[Pt_{38}(CO)_{44}]^{2-}$ dianion displays this same $O_h$ geometry.[15] More-recent comprehensive synthetic, stereochemical, spectroscopic, and electrochemical studies by Longoni, Zanello, and co-workers[16,17] have revealed the only other known cluster with a 38-atom metal core that displays the truncated $\nu_3$ octahedral geometry; namely, the ordered $[H_2Ni_{24}Pt_{14}(CO)_{44}]^{4-}$ cluster for which the 24 Ni atoms occupy the 24 equivalent square corner sites and the 14 Pt atoms occupy the six vertices of the encapsulated octahedron and the centers of the eight hexagonal faces.[9d,16,18] They also prepared and characterized heterometallic 44-atom $\nu_3$ octahedral clusters that contain a ccp 38-atom truncated $\nu_3$ octahedral $M_{38-x}M'_x$ kernel with six additional Ni atoms capping the six {100} square faces. These include $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n = 4$–6)[17a,b] and $[Ni_{35}Pt_9(CO)_{48}]^{6-}$,[17c] both with an encapsulated $Pt_6$ octahedron, and $[Ni_{36}Pd_8(CO)_{48}]^{6-}$ [17c] with an encapsulated $Pd_6$ octahedron and with the other two Pd atoms occupying two of the eight centered sites of the crystal-disordered 10-atom $\nu_3$ octahedral faces.

The salient structural feature of **1** and **2** is that their hypothesized formation from the $Pd_{38}$ truncated $\nu_3$ octahedron occurs through six-atom condensations of monocapped $Pd_7$ triangles on {111} octahedral faces instead of one-atom metal condensations on six {100} square faces, as found in the $\{Ni_{38}Pt_6\}$,[17a,b] $\{Ni_{35}Pt_9\}$,[17c] and $\{Ni_{36}Pd_8\}$[17c] clusters. The resulting condensation pattern of 44 metal atoms comprises eight "open" triangular $\nu_3$ $\{Ni_{10-x}M'_x\}$ faces, which are only occupied by ligands. Stereochemical analysis of the known $[Pd_n(CO)_xL_y]$ clusters reveals that, in general, $Pd_n$ cores do not form such relatively large triangular 10-atom "open" faces, but they prefer instead to undergo face condensations.

In general, the formation of different kinds of large ligated close-packed metal clusters critically depends upon the subtle interplay of cohesive energies, electronegativities, and relative sizes of the metal atoms, the electronic and steric properties of the ligands, and, of course, the reaction conditions. The dissimilar growth processes presented above in the formal construction of the $Pd_{52}$ and $Pd_{66}$ clusters **1** and **2**, respectively, versus that of the 44-atom Ni–Pt and Ni–Pd carbonyl clusters from their nonisolated precursors with the same 38-atom vertex-truncated $\nu_3$ octahedral geometry may be largely attributed to the markedly weaker metal–metal and metal–carbonyl interactions in palladium carbonyl/triethylphosphine clusters compared to those in nickel and platinum carbonyl clusters.

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**Keywords:** carbonyl ligands · cluster compounds · palladium · phosphane ligands · X-ray diffraction

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[3] a) A mixture of $[Pd_{10}(CO)_{12}(PEt_3)_6]$ (**3**)[3b] (0.200 g, 0.095 mmol) and $[Pd_2(dba)_3]$ (0.304 g, 0.332 mmol) in $Me_2CO$ (7 mL) and $i Pr_2O$ (2 mL) was stirred for 4.5 h under $N_2$ at 50 °C. The resulting brown solution was filtered from the black precipitate of $[Pd_{34}(CO)_{24}(PEt_3)_{12}]$ (**4**) and left under $H_2O$ vapor. Black block crystals of **1** were isolated and washed with MeOH (estimated yield < 5 %); IR (nujol): $\tilde{\nu} = 1875$ (sh), $1856\ cm^{-1}$ (s). The black precipitate of **4** (0.182 g, 67 % yield based on combined content of palladium in **3** and $[Pd_2(dba)_3]$, or 114 % based on **3**) was identified by its IR spectrum (nujol): $\tilde{\nu} = 1892$ (s), 1867 (s), 1837 (s), $1810\ cm^{-1}$ (s–m).[2l] The yield of **4** calculated on the basis of **3** unambiguously indicates its formation from both **3** and $[Pd_2(dba)_3]$. A crystal of **1** of dimensions $0.30 \times 0.20 \times 0.20\ mm^3$ was used for the determination of the crystal structure; b) E. G. Mednikov, N. K. Eremenko, *Izv. Akad. Nauk SSSR Ser. Khim.* **1982**, 2540. [*Bull. Acad. Sc. USSR Div. Chem. Sc. (Engl. Transl.)* **1982**, *31*, 2240].

[4] In a typical experiment $[Pd_{10}(CO)_{12}(PEt_3)_6]$ (**3**; 0.150 g, 0.071 mmol) and $Me_3NO{\cdot}2H_2O$ (0.127 g, 1.143 mmol) were dissolved in a mixture of $Me_2CO$ (7.5 mL), THF, $i Pr_2O$ or $Et_2O$ (2.5 mL), and $CF_3CO_2H$ (0.66 mL, 8.57 mmol) in a 100-mL flask with 4–6 min of ultrasonication or heating ($\approx$35 °C) under Ar. After ten days, black plate arrow-end crystals of **2′** were isolated by decanting the mother liquors and washed with acetone (50–55 mg, 45–50 %). Elemental analysis (Zelinsky Institute of Organic Chemistry): calcd (%) for $Pd_{66}(CO)_{46}(PEt_3)_{16}$: C 16.72, H 2.37, P 4.86, Pd 68.84; found: C 16.38, H 2.30, P 4.89, Pd 69.28; IR (nujol): $\tilde{\nu} = 1883–1881\ cm^{-1}$ (s br). Crystals obtained from this procedure were monoclinic with a β angle close to 90°; for example, $a = 20.417(5)$, $b = 35.711(9)$, $c = 30.877(11)$ Å, $\beta = 90.04(2)°$, $V = 22512(12)$ Å$^3$; or $a = 20.48(1)$, $b = 35.48(4)$, $c = 30.55(2)$ Å, $\beta = 90.10(5)°$, $V = 22194(49)$ Å$^3$, etc. Solution of the structural data from their X-ray data sets could not be refined but did disclose the $\{Pd_{66}P_{16}\}$ fragment of **2′**.

[5] $[Pd_{10}(CO)_{12}(PEt_3)_6]$ (**3**; 0.150 g, 0.071 mmol) and $[Pd(MeCN)_4](BF_4)_2$ (0.063 g, 0.142 mmol) were dissolved in a mixture of THF (10 mL) and $Me_2CO$ (5 mL) under $N_2$. On the next day, the solvent was evaporated and the black residue was extracted with MeCN. Crystallization in the presence of vapor from a 1:1 mixture of $i Pr_2O$/hexane gave black needlelike crystals of **2** (15 mg; 13 %). IR (nujol): $\tilde{\nu} = 1884\ cm^{-1}$ (s br) with shoulders at 1916 and $1867\ cm^{-1}$. A crystal of dimensions $0.61 \times 0.28 \times 0.18\ mm^3$ was used for the determination of the X-ray crystal structure.

[6] On a related note, a recent systematic preparative/structural investigation[2i] has provided compelling geometrical evidence for a previously unknown stereochemical example involving close-packed, nanosized cuboctahedral-based $[Pd_{23}(CO)_x(PEt_3)_{10}]$ clusters that comprise structurally analogous $\{Pd_{23}(PEt_3)_{10}\}$ fragments with variable numbers of carbonyl ligands ($x = 20$, 21, 22). This observed expanded capacity of CO coordination on the same centered $Pd_{23}$ polyhedron from the thermodynamically stable structure with 20 CO ligands to the kinetic products with additional CO ligands ($x = 21$, 22) without notable changes in the geometry of the common $\{Pd_{23}(PEt_3)_{10}\}$ fragment was attributed to the nanosized ($\approx$0.8–0.9 nm) architecture of the metal core.

[7] a) **1**: trigonal; $R\bar{3}$; $a = b = 17.303(2)$, $c = 51.067(13)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 13240(4)$ Å$^3$; $Z = 3$, $\rho_{calcd} = 3.083\ Mg\,m^{-3}$. $Mo_{K\alpha}$ data collected at 173(2) K with Bruker SMART CCD-1000 area-detector diffractometer by $0.3\omega$ scans over a $2\theta$ range from 2.40 to 46.62°; empirical absorption correction (SADABS) applied; $\mu(Mo_{K\alpha}) = 5.328\ mm^{-1}$; max/min transmission, 0.416/0.298. Full-matrix least-squares refinement (SHELXTL)[7c] (300 parameters; 27 restraints) on 4253 independent reflections converged at $\omega R_2(F^2) = 0.176$ with $R_1(F) = 0.071$ for $I > 2\sigma(I)$; GOF (on $F^2$) = 1.03; max/min residual electron density 8.87/−5.10 e Å$^{-3}$. All non-hydrogen atoms were refined anisotropically, except for those of disordered carbonyl groups and disordered ethyl substituents; b) **2**: monoclinic; $P2_1/n$; $a = 20.717(2)$, $b = 35.756(4)$, $c = 30.623(4)$ Å, $\beta = 90.904(1)°$, $V = 22682(5)$ Å$^3$; $Z = 4$, $\rho_{calcd} = 2.979\ Mg\,m^{-3}$. $Mo_{K\alpha}$ data collected at 100(2) K with Bruker SMART CCD-1000 area-detector diffractometer by $0.3\omega$ scans over a $2\theta$ range from 1.76 to 46.36°; empirical absorption correction (SADABS) applied; $\mu(Mo_{K\alpha}) = 5.247\ mm^{-1}$; max/min transmission, 0.452/0.142. Full-matrix least-squares refinement (SHELXTL)[7c] (1540 parameters; 236 restraints) on 31 516 independent reflections converged at $\omega R_2(F^2) = 0.278$ with $R_1(F) = 0.108$ for $I > 2\sigma(I)$; GOF (on $F^2$) = 0.894; max/min residual electron density 3.48/−2.41 e Å$^{-3}$. Palladium and phosphorus atoms were refined anisotropically. CCDC 276453 (**1**) and 276454 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; c) G. M. Sheldrick: SHELXTL version 6.10 Program Library, Bruker Analytical X-Ray Systems, Madison, WI, **2000**

[8] a) Similar formal condensations of monocapped $\nu_2$ $Pd_7$ triangles to centered metal hexagons are encountered in $Pd_{30}$[2k] and $Pd_{23}$[2h,i] clusters. The condensation of four noncapped $\nu_2$ $Ni_6$ triangles on four centered hexagonal faces of a ccp $Ag_{16}$ metal core was observed in the pseudo-$T_d$ $[Ag_{16}Ni_{24}(CO)_{40}]^{4-}$ cluster[8b]; b) J. Zhang, L. F. Dahl, *J. Chem. Soc. Dalton Trans.* **2002**, 1269.

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[11] An anisotropic pancake-shaped displacement ellipsoid observed for the crystallographically independent monocapped Pd(10) atom, which lies on the crystallographic $C_3$ axis of **1** (Figure 1), is attributed to it being randomly disordered among three sites toward each of the three equivalent inner Pd(4) atoms in the $Pd_6$ triangle. Nevertheless, we consider its site displacements from the threefold axis to be relatively small such that Pd(10) still undergoes $\mu_3$ coordination with three threefold-related edge-bridging carbonyl ligands that span the three Pd(10)–Pd(4) edges. This premise is based upon the least-squares refinement, which indicates that the carbon and oxygen atoms of the crystallographically independent doubly bridging carbonyl group that connects Pd(10) to the inner $Pd_3$ triangle have whole-weighted occupancy factors.

[12] a) The $[Cu_xNi_{35-x}(CO)_{40}]^{5-}$ cluster ($x = 3$ or 5)[12b] provides another striking example of a nanosized close-packed metal-core carbonyl cluster that contains an extra carbonyl ligand. The presence of the extra CO moiety on one of three otherwise symmetry-equivalent sides of the metal core results in a markedly different arrangement on the side of the extra CO to the similar arrangements of CO groups on the other two sides. Its inclusion lowers the symmetry of the 35-atom triangular stacking-layer sequence from pseudo-$D_{3h}$ to $C_s$ symmetry (i.e., a pseudo-vertical mirror plane); b) P. D. Mlynek, M. Kawano, M. A. Kozee, L. F. Dahl, *J. Cluster Sci.* **2001**, *12*, 313.

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[18] This current formulation for the Ni–Pt cluster is based on ref. [9d] (see footnote 2 therein), which states that “circumstantial evidence suggests the presence of two hydride atoms in the cluster originally formulated as $[Ni_{24}Pt_{14}(CO)_{44}]^{4-}$”.[16]