

Nanosized $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ Containing Tetrahedrally Deformed Pd_4 Cage with Encapsulated Carbide Atom: Formal Substitution of Geometrically Analogous Interior Au_4 Entity in Isostructural $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ by Electronically Equivalent $\text{Pd}_4(\mu_4\text{-C})$ and Computational/Catalytic Implications

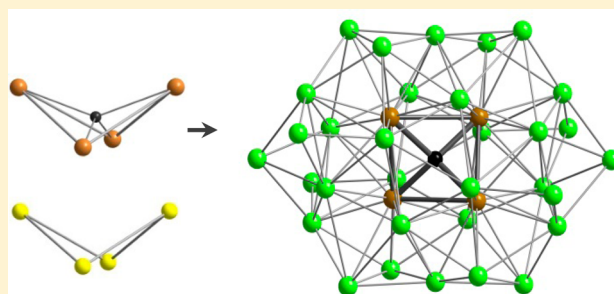
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S Supporting Information

ABSTRACT: This first homopalladium carbido cluster, $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**1**), was isolated (3–7% yields) from an ultimately simplified procedure—the reaction of CHCl_3 under N_2 with either $\text{Pd}_8(\text{CO})_8(\text{PMe}_3)_7$ or $\text{Pd}_{10}(\text{CO})_{12}(\text{PMe}_3)_6$ at room temperature. Charge-coupled device (CCD) X-ray diffraction data at 100 K for 1.2.5 C_6H_{14} (**1a**) and 1.3 CHCl_3 (**1b**) produced closely related molecular parameters for **1**. This $\{\text{Pd}_4\text{C}\}\text{Pd}_{32}$ cluster (**1**) possesses a highly unusual tetracoordinated carbide atom that causes a major distortion of a central regular Pd_4 tetrahedron into a new symmetry type of encapsulated Pd_4 cage of pseudo- D_2 (222) symmetry. Mean Pd–Pd distances for the three pairs of opposite twofold-equivalent Pd–Pd tetrahedral-like edges for **1a** are 2.71, 2.96, and 3.59 Å; the mean of the four Pd–C distances [range, 1.87(2)–1.94(2) Å] is 1.91 Å. An astonishing molecular feature is that this $\{\text{Pd}_4\text{C}\}\text{Pd}_{32}$ cluster (**1**) is an isostructural and electronically equivalent analogue of the nanosized $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**2**). Cluster **2**, likewise a pseudo- D_2 molecule, contains a geometrically analogous tetrahedrally deformed interior Au_4 entity encapsulated within an identical $\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ shell; mean distances for the three corresponding symmetry-equivalent pairs of slightly smaller opposite tetrahedral-distorted Au–Au edges are 2.64, 2.90, and 3.51 Å. A computational study by both a natural population analysis (NPA) and an atoms-in-molecules (AIM) method performed on model analogues $\{\text{Pd}_4\text{C}\}\text{Pd}_{32}(\text{CO})_{28}(\text{PH}_3)_{14}$ (**1-mod**) and $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PH}_3)_{14}$ (**2-mod**) suggested that the negatively charged Au_4 entity in **2-mod** may be described as two weakly interacting electron-pair Au_2 intradimers. In contrast, an NPA of the $\{\text{Pd}_4\text{C}\}$ entity in **1-mod** revealed that two similarly oriented identical Pd_2 intradimers of 2.71 Å are primarily stabilized by Pd–C bonding with a negatively charged carbide atom. The isostructural stabilizations of **1** and **2** are then attributed to the similar sizes, shapes, and overall negative charge distributions of the electronically equivalent interior $\{\text{Pd}_4\text{C}\}$ and Au_4 entities. This resulting remarkable structural/electronic equivalency between **1** and **2** is consistent with the greatly improved performances of commercial palladium catalysts for vinyl acetate synthesis by gold-atom incorporation to suppress carbonization of the Pd atoms, namely, that the extra Au 6s¹ valence electron of each added Au atom provides an effective “negative charge protection” against electron-donating carbon atoms forming Pd carbido species such as $\{\text{Pd}_4\text{C}\}$.



INTRODUCTION

Since the initial structural discovery in 1962 of the pentacoordinated square-pyramidal carbido atom in $\text{Fe}_5(\mu_5\text{-C})(\text{CO})_{15}$ ¹, which showed that discrete transition metal carbonyl clusters can incorporate an interstitial carbon atom, many examples of such clusters have been reported.² Hence, the resulting metal carbido cluster chemistry has five decades of history but continues to attract considerable attention.³ The interest is at least twofold. First, these compounds have given rise to greatly expanded synthetic routes that have produced highly diverse transition metal clusters. Carbide atoms not only electronically stabilize (each by donation of four valence

electrons) the metal cores but also allow heterometallic atom-for-atom substitution either with retention of the original metal framework or with controllable geometrical transformations.^{2c,e} Second, transition metal carbide clusters are valuable models for studies of reactivity patterns of carbon atoms toward C–H and C–C bond formation as well as related C–H bond activation. In fact, their positive relevance to both stoichiometric⁴ and catalytic reactions⁵ primarily involving C_1 chemistry has been widely recognized. However, catalyst

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carbide formation may play a highly negative role. One such example is the catalytic oxidation of ethylene into vinyl acetate (VA) in the presence of acetic acid on a supported Pd catalyst;^{6a} its carbidization resulted in a marked decrease of catalytic reactivity, whereas addition of Au suppressed carbide formation and kept the catalyst active.^{6b–f} Combined experimental/computational results described herein shed light on the probable origin of such a phenomenon.

Herein we present the preparation of the first homopalladium carbido cluster, $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**1**) by an ultimately simplified room-temperature reaction of CHCl_3 with either $\text{Pd}_8(\text{CO})_8(\text{PMe}_3)_7$ or $\text{Pd}_{10}(\text{CO})_{12}(\text{PMe}_3)_6$ precursors under N_2 together with its low-temperature X-ray crystallographic characterization of two different solvated crystalline forms. Of prime significance is that **1** provides an unprecedented example of a molecular cluster with a tetracoordinated carbon atom that is encapsulated within a new symmetry-type of tetrahedral-deformed M_4 cage to accommodate the C atom. Especially surprising is that **1** may be formally derived from the previously reported isostructural Au–Pd $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**2**)^{7a} by the electronically equivalent replacement of the internal Au_4 entity in **2** with the geometrically analogous interior $\{\text{Pd}_4\text{C}\}$ entity in **1**. A detailed stereochemical/bonding comparison of **1** and **2** including natural population analyses based upon density functional theory (DFT) calculations was performed; resulting computational/catalytic implications are discussed and related to the highly preferable utilization of commercial Au–Pd catalysts (vs corresponding Pd catalysts) used in the production of VA that greatly increased reactivities and suppressed palladium carbidization.

RESULTS AND DISCUSSION

Synthesis of $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (1**).** This research stems from our ongoing systematic attempts to find general synthetic pathways to obtain nanosized bimetallic Pd–Pt clusters via an exploration of the chemistry of the two separate families of CO/ PR_3 -ligated zerovalent Pd(0) and Pt(0) compounds. One exceptional outcome of this investigation led to isolation of the extraordinary Pt-centered icosahedral four-shell 165-atom Pd–Pt cluster of pseudo- I_h symmetry, $(\mu_{12}\text{-Pt})\text{Pd}_{164-x}\text{Pt}_x(\text{CO})_{72}(\text{PPh}_3)_{20}$ ($x \approx 7$), from the reaction of $\text{Pd}_{10}(\text{CO})_{12}(\text{PPh}_3)_6$ with zerovalent $\text{Pt}(\text{CO})_2(\text{PPh}_3)_2$.^{7b} Herein we report the preparation of the carbido cluster, $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**1**), via a synthesis based upon our initial (unreported) preparation of the analogous Pd–Pt carbido derivative, $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{31.2}\text{Pt}_{0.8}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**3**). This latter cluster (**3**) was obtained from a procedure designed for the synthesis of the heterometallic Pd–Pt cluster, $\text{Pd}_{16-x}\text{Pt}_x(\text{CO})_{13}(\text{PMe}_3)_9$ (**4**), namely, the substituted Pt-for-Pd analogue of the $\text{Pd}_{16}(\text{CO})_{13}(\text{PMe}_3)_9$,⁸ which consists of a centered icosahedral Pd_{13} architecture with three exopolyhedral wingtip Pd atoms. This procedure, which is conceptually similar to that used for the isolation of the concentric spheroidal-shaped multishell 165-atom Pd–Pt cluster $(\mu_{12}\text{-Pt})\text{Pd}_{164-x}\text{Pt}_x(\text{CO})_{72}(\text{PPh}_3)_{20}$ ($x \approx 7$),^{7b} involved several consecutive steps: (a) formation of the PMe_3 -containing butterfly Pd_4 cluster, $\text{Pd}_4(\text{CO})_5(\text{PMe}_3)_4$, in situ from the reaction of $\text{Pd}_{10}(\text{CO})_{12}(\text{PMe}_3)_6$ and PMe_3 ; (b) preparation of the corresponding mixed PMe_3 -containing $\text{Pd}_x\text{Pt}_{4-x}$ butterfly cluster, also in situ, from the reaction between the isostructural homonuclear $\text{Pd}_4(\text{CO})_5(\text{PMe}_3)_4$ and $\text{Pt}_4(\text{CO})_5(\text{PMe}_3)_4$ in an analogous fashion to that found for the preparation of the $\text{P}(\text{Et})_3$ -

containing $\text{Pd}_x\text{Pt}_y(\text{CO})_5(\text{P}(\text{Et})_3)_4$, $x + y = 4$;⁹ and (c) generation of $\text{Pd}_{16-x}\text{Pt}_x(\text{CO})_{13}(\text{PMe}_3)_9$ (**4**) in accordance with the synthetic methodology developed for the preparation of the homonuclear $\text{P}(\text{Et})_3$ -containing $\text{Pd}_{16}(\text{CO})_{13}(\text{P}(\text{Et})_3)_9$ from the reaction of $\text{Pd}_4(\text{CO})_5(\text{P}(\text{Et})_3)_4$ and $\text{HOAc}/\text{Me}_3\text{NO}$.¹⁰ In contrast to the latter reaction, which gave crystalline $\text{Pd}_{16}(\text{CO})_{13}(\text{P}(\text{Et})_3)_9$ with a high yield (>60%),¹⁰ step (c) instead afforded a red precipitate as the main product, even though the target **4** was also observed as a minor byproduct. This red precipitate was found to be insoluble in common nonchlorinated organic solvents. Its crystallization under N_2 from CHCl_3 /hexane vapor diffusion unexpectedly gave the crystallographically characterized bimetallic Pd–Pt carbido cluster $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{31.2}\text{Pt}_{0.8}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**3**) as a mixed solvate $3 \cdot 0.5\text{C}_6\text{H}_{14} \cdot 0.5\text{CHCl}_3$ (**3a**). Further investigation showed that formation of this black carbido cluster does not necessitate the presence of the $\text{Pt}_4(\text{CO})_5(\text{PMe}_3)_4$ precursor and that the red precipitate is primarily composed of the $\text{Pd}_8(\text{CO})_8(\text{PMe}_3)_7$ cluster.¹¹ These observations resulted in an ultimately simplified procedure for the preparation of crystalline $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**1**), namely, its direct isolation from reactions of CHCl_3 with either the PMe_3 -ligated Pd_8 or Pd_{10} cluster under N_2 and concomitant/subsequent crystallizations under N_2 from CHCl_3 solutions in the presence of hexane. Yields (3–7%) of **1**, somewhat better with the Pd_8 precursor, are kinetically controlled and mainly affected by the time (an optimum of 1–3 d) of keeping CHCl_3 solutions prior to contact with hexane vapor. If crystallization was set up immediately after dissolution of the Pd_8 cluster in CHCl_3 , it gave a mixture of crystalline **1** together with square-planar $\text{PdCl}_2(\text{PMe}_3)_2$ (**5**) and the red precursor $\text{Pd}_8(\text{CO})_8(\text{PMe}_3)_7$. On the contrary, too long storage (up to 10 d) of an initially dark red (and then dark brown) solution of the Pd_8 precursor in CHCl_3 led to its complete color fading due to in situ decomposition of **1**, accompanied by precipitation of Pd black and formation of colorless **5**. The halocarbon CHCl_3 was previously shown by Chini and co-workers¹² to be the source of the carbide atom in their preparation of the trigonal prismatic $[\text{Rh}_6(\mu_6\text{-C})(\text{CO})_{15}]^{2-}$ dianion. Our change from CHCl_3 to the perchlorinated reagent hexachloropropene C_3Cl_6 , which was utilized¹³ for generation of the size-comparable Ni_{38} polycarbido cluster anion $[\text{Ni}_{38}\text{C}_6(\text{CO})_{42}]^{6-}$, did not afford **1** or any other crystalline products.

There is no doubt that the initial driving force toward the formation of **1** is an oxidative addition of CHCl_3 to the CO/ PMe_3 -ligated Pd(0) species. The resulting most stable product of such a reaction is the Pd(II) complex (**5**), $\text{PdCl}_2(\text{PMe}_3)_2$, which is always observed upon completion of the reaction of either the Pd_8 or Pd_{10} precursor with chloroform. Furthermore, the $\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{P}^t\text{Bu}_3)_4$ cluster with a μ_3 -methylidyne ligand was previously isolated by Mingos and co-workers¹⁴ from the reaction of CHCl_3 with a Pd(0) species. This tetrapalladium cluster, even with the absence of the “pure” carbide atom and with its resulting small metal-core size compared to that of **1**, is nevertheless especially relevant to **1**. First, its simple synthesis involving reaction of $\text{Pd}_2\text{dba}_3 \cdot \text{C}_6\text{H}_6$ (dba = dibenzylideneacetone) with P^tBu_3 followed by addition of CHCl_3 ¹⁴ is conceptually identical to the preparation of **1**. In fact, the bulky P^tBu_3 ligands and the absence of carbon monoxide are presumably responsible for its formation; otherwise, in the presence of CO and with PMe_3 (instead of P^tBu_3) either the same precursor $\text{Pd}_8(\text{CO})_8(\text{PMe}_3)_7$ ¹¹ used to synthesize **1** or an analogous one would be generated. Second,

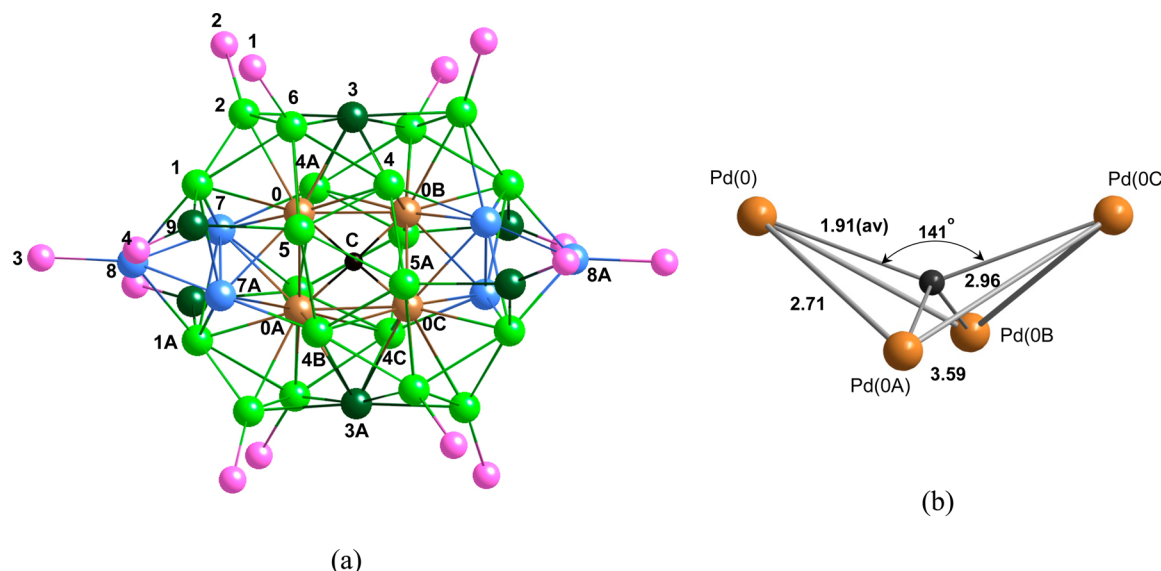


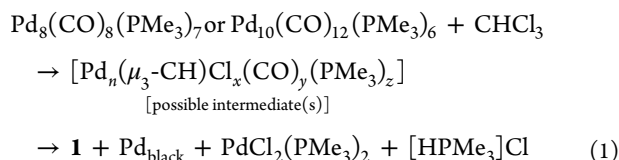
Figure 1. (a) Side view of the molecular structure (with atom-labeling) of homopalladium carbido $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}\text{P}_{14}$ cluster (**1**) of pseudo- D_2 symmetry (without P-attached Me substituents and 28 bridging COs) oriented with in-plane horizontal and vertical C_2 axes and the third out-of-plane C_2 axis each intersecting the central carbido atom and passing through the midpoints of the pair of opposite twofold-equivalent Pd–Pd edges. (b) Interior $\{\text{Pd}_4(\mu_4\text{-C})\}$ entity of **1** containing a new symmetry type of encapsulated tetrahedral-deformed Pd_4 cage (accommodating the tetracoordinated carbide atom) of pseudo- D_2 geometry with three pairs of opposite twofold-equivalent tetrahedral-like Pd–Pd edges being 2.71 (average (av)), 2.96 (av), and 3.59 (av) Å for solvated $1\cdot 2.5 \text{ C}_6\text{H}_{14}$ (**1a**); the mean of the four Pd–C distances (range, 1.87(2)–1.94(2) Å) is 1.91 Å.

Table 1. Mean Distances (Å) and Corresponding Individual Ranges (Å) under Pseudo- D_2 Symmetry for Central $\text{Pd}_4(\mu_4\text{-C})$ Entity of $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**1**) in Solvated $1\cdot 2.5 \text{ C}_6\text{H}_{14}$ (**1a**) and $1\cdot 3 \text{ CHCl}_3$ (**1b**)

entry	connectivity ^a	N ^b		1a		1b
1	Pd-($\mu_4\text{-C}$)	4	1.91	1.87(2)–1.94(2)	1.91	1.88(2)–1.94(2)
2	Pd(0)–Pd(0A) ^c	2	2.71	2.706(2), 2.706(2)	2.71	2.707(2), 2.707(2)
3	Pd(0)–Pd(0B) ^d	2	2.96	2.954(2), 2.970(2)	2.99	2.976(2), 2.999(2)
4	Pd(0)–Pd(0C) ^e	2	3.59	3.572(2), 3.614(2)	3.60	3.597(2), 3.599(2)

^aAtom-labeling for the four equivalent carbide-connected Pd(0), Pd(0A), Pd(0B), Pd(0C) atoms is shown in Figure 1. ^bN denotes number of symmetry-equivalent atom-pair connectivities under pseudo- D_2 symmetry. ^cEquivalent atom-pair is Pd(0B)–Pd(0C). ^dEquivalent atom-pair is Pd(0A)–Pd(0C). ^eEquivalent atom-pair is Pd(0A)–Pd(0B).

this tetrapalladium $\text{Pd}_4(\mu_3\text{-CH})(\mu\text{-Cl})_3(\text{P}^t\text{Bu}_3)_4$ compound formally contains all of the elemental components of the CHCl_3 molecule including the $\mu_3\text{-CH}$ group and thereby provides a prototype for unobserved intermediates in our reactions of either the Pd_8 or Pd_{10} precursor with CHCl_3 that gave rise to **1**. This suggestion is also based on known examples of the facile conversion of $\mu_3\text{-CH}$ groups into carbido species.¹⁵ In the synthesis of **1**, reductive elimination of HCl via dissociation of a possible μ_3 -methylidyne intermediate would be facilitated by its coordination with stoichiometrically available basic PMe_3 to form a phosphonium salt, $[\text{HPMe}_3]\text{Cl}$. Thus, the reaction leading to **1** most likely occurs via consecutive oxidative addition and reductive elimination processes with presumed products that may be formulated as follows:



During our investigation of possible pathways toward bimetallic Pd–Pt clusters we also obtained and crystallographically characterized $\text{Pd}_{12.7}\text{Pt}_{3.3}(\text{CO})_{13}(\text{PMe}_3)_9$ (**4**) as the

solvated $4\cdot 0.5(\text{CH}_3)_2\text{CO}\cdot 0.3\text{C}_4\text{H}_8\text{O}$ (**4a**), together with the butterfly tetraplatinum $\text{Pt}_4(\text{CO})_5(\text{PMe}_3)_4$. Crystal structures of heterometallic **4** and earlier mentioned **3** will be published elsewhere along with crystal structures of other Pd/Pt clusters that we have isolated.

Solid-State Structure of $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (1**) and Its Stereochemical/Electronic Equivalence to $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**2**).** (a) *General Comments.* The molecular structure of **1** was obtained from complete charge-coupled device (CCD) X-ray diffractometry determinations at 100 K of two isolated solvated crystalline forms, namely, $1\cdot 2.5\text{C}_6\text{H}_{14}$ (**1a**) and $1\cdot 3\text{CHCl}_3$ (**1b**), each of which crystallizes in a triclinic unit cell (with $Z = 2$) under centrosymmetric $\bar{P}1$ symmetry such that one molecule of **1** is crystallographically independent. Figure 1 shows the geometry of the $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}\text{P}_{14}$ fragment of **1** (without the 28 CO ligands and P-attached Me substituents) together with its unprecedented interstitial interior $\text{Pd}(\text{i})_4$ cage that contains the carbide atom. Table 1 presents the mean distances and ranges under pseudo- D_2 symmetry for the central $\text{Pd}_4(\mu_4\text{-C})$ entity in **1a** and **1b**. Figure 2 presents comparative views of the entire molecular geometries of the isostructural $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}$ **1** and $\text{Au}_4\text{Pd}_{32}$ **2** (without the P-attached methyl substituents). Figure 3 displays the proposed formal generation of the $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}\text{P}_{14}$ framework of **1**, which parallels that given in Figure

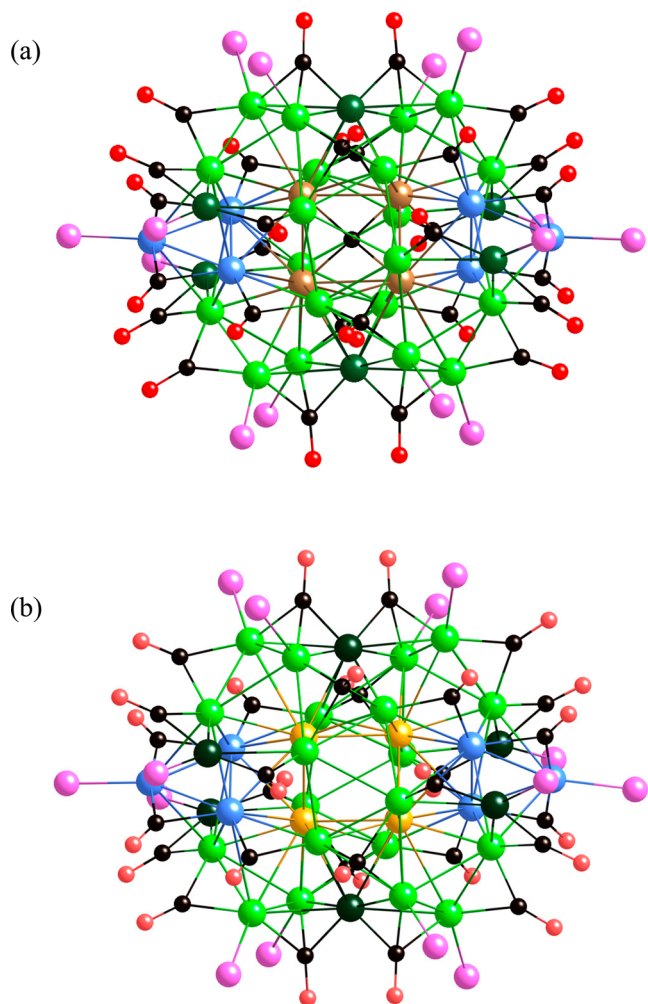


Figure 2. Comparison of closely related molecular structures (without phosphine-attached Me substituents) of (a) $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**1**) from crystal-solvated 1.2.5 C_6H_{14} (**1a**); and of (b) $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**2**) from crystal-solvated 2.3THF·Et₂O (**2a**). Both isostructural molecules **1** and **2** are displayed in virtually identical orientations (as in Figure 1) to highlight their remarkably analogous ligations. The coloring scheme is the same as in Figure 1; the Au atoms are shown in light yellow. The isostructural stabilizations of **1** and **2** are presumed to be a consequence of the similar sizes, shapes, and overall negative charge distributions of the electronically equivalent interior C-filled Pd_4 and empty Au_4 cages, respectively, supported by encapsulations within identical $\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ shells.

4 for the previously proposed analogous formation of the corresponding $\text{Au}_4\text{Pd}_{32}\text{P}_{14}$ framework of **2**.^{7a} Table S1 (Supporting Information) presents a comparison of corresponding mean distances and ranges of individual distances under pseudo- D_2 molecular symmetry for $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**1**) in 1.2.5 C_6H_{14} (**1a**) and 1.3 CHCl_3 (**1b**) together with the isostructural $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**2**) in 2.3THF·Et₂O (**2a**; THF = tetrahydrofuran). Particularly noteworthy is that this Table S1 shows that geometric differences of corresponding mean molecular metal–metal distances of **1** in **1a** and **1b** due to different solid-state solvation effects are small (≤ 0.05 Å) for the 27 different types of mean metal–metal distances. Table S1 also shows that the corresponding different atom-pair connectivities involving both the mean $\{\text{Pd}_4\text{-C}\}-\text{Pd}_{\text{shell}}$ and $\text{Pd}_{\text{shell}}-\text{Pd}_{\text{shell}}$ distances in

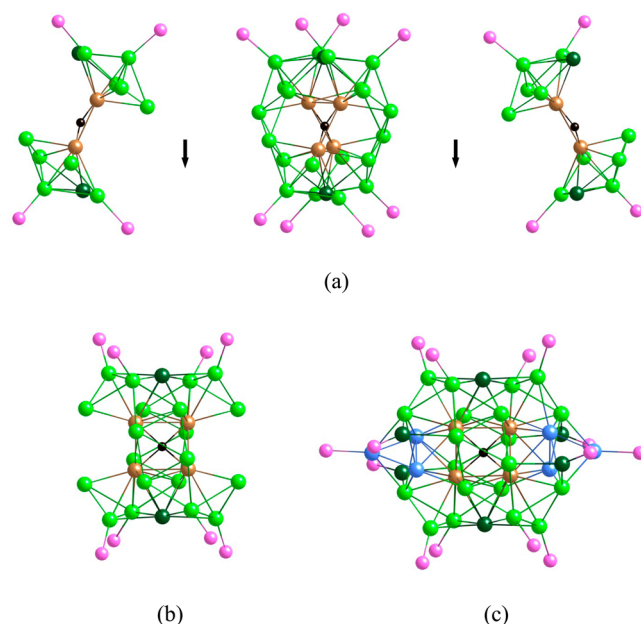


Figure 3. Anatomy showing proposed buildup of icosahedral $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}\text{P}_{14}$ framework of **1** from the following: (a) Formation of twinned composite $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{22}\text{P}_8$ kernel (center) from interpenetration of two identical "open" bis(pentagonal-bipyramidal) $\{\text{Pd}_2(\mu_4\text{-C})\}\text{Pd}_{12}\text{P}_4$ intradimers (left and right) via vertex-fusion of carbide atom (black) and two Pd atoms (dark green). (b) Another view of $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{22}\text{P}_8$ kernel after 90° rotation about in-plane vertical pseudo- C_2 axis passing through carbide and two dark green Pd atoms. (c) Entire $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}\text{P}_{14}$ fragment of **1** formed by addition of six blue-colored Pd atoms (with two horizontally attached P atoms) and four exopolyhedral edge-bridged dark green Pd atoms, each with an attached P atom.

1a versus the mean $\text{Au}_4\text{-Pd}_{\text{shell}}$ and $\text{Pd}_{\text{shell}}\text{-Pd}_{\text{shell}}$ distances in **2a** are likewise small (≤ 0.07 Å).

(b) **Structural Features of 1 and Comparative Analysis with 2.** This nanosized cluster (**1**) possesses a tetracoordinated carbide atom that causes the interior tetrapalladium cage to be highly deformed from a regular tetrahedron into a new type of completely encapsulated $\{\text{Pd}_4\text{C}\}$ entity of pseudo- D_2 (222) symmetry. Mean distances for the three pairs of opposite twofold-equivalent Pd–Pd edges are 2.71, 2.96, and 3.59 Å for solvated crystal 1.2.5 C_6H_{14} (**1a**) and 2.71, 2.99, and 3.60 Å for solvated crystal 1.3 CHCl_3 (**1b**); the mean of the four Pd–C distances [range: 1.87(2)–1.94(2) Å in **1a**; 1.88(2)–1.94(2) Å in **1b**] in both **1a** and **1b** is 1.91 Å (Table 1), and the three mean Pd–C–Pd pair angles are 90.2°, 102.9°, and 140.6° (whereas the ideal tetrahedral angle is 109.5°). The view of **1** in Figure 1a shows that the three mutually perpendicular pseudo- C_2 axes, each passing through the central carbide atom and midpoints of two opposite Pd–Pd edges, are approximately oriented as horizontal and vertical in-plane C_2 axes and a perpendicular out-of-plane C_2 axis. This idealized D_2 $\{\text{Pd}_4\text{C}\}$ - $\text{Pd}_{32}\text{P}_{14}$ geometry of **1** is preserved upon addition of the 28 bridging COs. Figure 2 provides comparative views (same as in Figure 1) of the entire molecular configurations of **1** and **2** (without methyl substituents), which clearly display their isostructural relationship that arises from analogous geometrical encapsulations by identical $\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ shells of the electronically equivalent and structurally similar interior carbon-filled $\text{Pd}(\text{i})_4$ cage and empty Au_4 cage, respectively. Both molecules in Figure 2 are shown in virtually identical

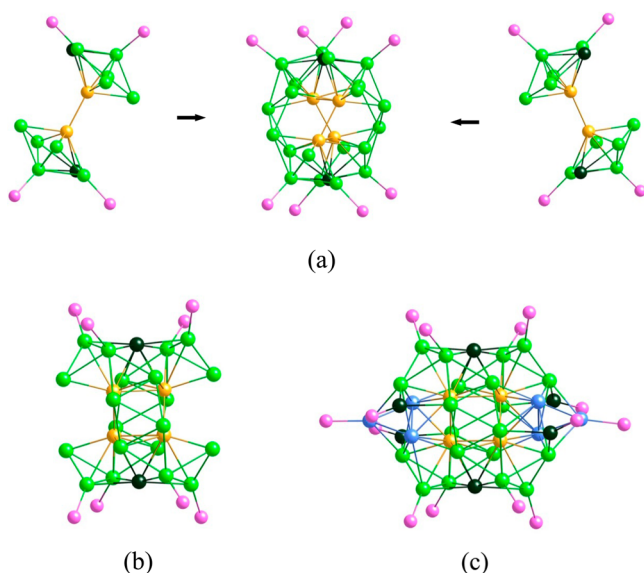


Figure 4. Previously proposed anatomy^{7a} of nanosized $\text{Au}_4\text{Pd}_{32}\text{P}_{14}$ fragment (without COs) of $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ (**2**) envisioned to arise from the following: (a) Formation of twinned composite $\text{Au}_4\text{Pd}_{22}\text{P}_8$ kernel of **2** from interpenetration of two identical Au–Au bonded $\text{Au}_2\text{Pd}_{12}\text{P}_4$ dimers with vertex-fusion of two Pd (dark green). Resulting geometry consists of tetrahedrally deformed empty Au_4 cavity of pseudo- D_2 (222) symmetry with three pairs of opposite twofold-equivalent Au–Au edges: (1) intradimer electron-pair Au–Au bonding, 2.64 Å; (2) weak interdimer Au–Au bonding, 2.90 Å; (3) interdimer Au–Au nonbonding, 3.51 Å. This central $\text{Au}_4\text{Pd}_{22}\text{P}_8$ kernel is oriented with in-plane horizontal C_2 axis and in-plane vertical C_2 axis; the third perpendicular out-of-plane C_2 axis bisects midpoints of two intradimer electron-pair Au–Au bonds. (b) Another view of $\text{Au}_4\text{Pd}_{22}\text{P}_8$ kernel after 90° rotation about the in-plane vertically oriented C_2 axis. (c) Entire $\text{Au}_4\text{Pd}_{32}\text{P}_{14}$ architecture formed by addition of six blue-colored Pd and four exopolyhedral dark green Pd atoms with attached P atoms.

orientations to highlight (in particular) the extraordinary structural similarities in CO ligation. Their remarkable isostructural architectures point to similar formal geometrical sequences in growth patterns for **1** and **2** that are outlined in Figures 3 and 4, respectively.

The mean distances of the twofold-equivalent opposite pairs of its Pd–Pd edges of the $\{\text{Pd}_4\text{C}\}$ core in **1** are only 0.06–0.09 Å larger than those of the corresponding Au–Au edges of the Au_4 core in **2**. In addition to this nearly perfect size/shape geometrical match, the filled $\{\text{Pd}_4(\mu_4\text{-C})\}$ cage in **1** is electronically equivalent to the empty Au_4 cage in **2**. Consequently, geometrical encapsulations of the $\{\text{Pd}_4\text{C}\}$ entity in **1a,b** and of the Au_4 entity in **2** by identical $\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ shells are analogous, in accordance with the Pd–Pd separations between Pd atoms of the $\text{Pd}(\text{i})_4$ cage and atoms of the Pd_{32} shell differing by less than 0.1 Å from the corresponding Au–Pd separations in the $\text{Au}_4\text{Pd}_{32}$ **2**. Therefore, aside from electronic factors (vide infra), it is then not completely surprising that the remarkably similar geometrical deformations found in both the electronically equivalent interior C-filled $\text{Pd}(\text{i})_4$ and empty Au_4 cages are stabilized by the same $\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14}$ shells.

(c) Ligand Arrangements. The stereochemical dispositions (shown in Figure 2) of the PR_3/CO ligands in **1** virtually duplicate those found in **2**. All 14 Pd–P connectivities in **1** possess the same mean distance of 2.31 Å, as was found in **2**

(Table S1). Of the 28 carbonyls in **1**, 20 are doubly bridging, and 8 are triply bridging; the mean Pd–(μ_2 -CO) and Pd–(μ_3 -CO) distances of 2.04 and 2.11 Å, respectively, in **1** are identical with those observed in **2** (Table S1).

Computational Analysis of $\{\text{Pd}_4(\mu_4\text{-C})\}\text{Pd}_{32}(\text{CO})_{28}(\text{PH}_3)_{14}$ (1-mod**) and $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PH}_3)_{14}$ (**2-mod**).** **(a) Methodology.** To gain an insight into the possible physical reasons behind the isostructural Pd and Pd–Au interiors in **1** and **2**, respectively, we performed a natural population analysis (NPA) of atomic charges in models of these molecules. The experimental geometries of the two fully ligated clusters **1** and **2** were used for the analysis with each trimethylphosphine ligand of the experimental structure being replaced by a PH_3 ligand for computational efficiency, namely, $\{\text{Pd}_4\text{C}\}\text{Pd}_{32}(\text{CO})_{28}(\text{PH}_3)_{14}$ (**1-mod**) and $\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PH}_3)_{14}$ (**2-mod**). The wavefunctions for further analysis were obtained by use of meta-GGA DFT functional M06L,¹⁶ as implemented in Gaussian 09 A.01.¹⁷ Gold and palladium atoms were described with the effective core potential (ECP) LANL2 combined with a modified double- ζ 18-valence-electron basis set DZ¹⁸ on Au and Pd, while lighter atoms were treated with the Pople 6-31G* all-electron basis set.¹⁹ Modifications in the Au and Pd valence basis sets involved reoptimized exponents for 6p and 5p orbitals, respectively, to account for more involved participation of these orbitals in bonding than previously assumed. All necessary geometry optimizations (see text) were performed by use of the SVWN5 local spin-density DFT functional²⁰ with the same basis set as described above. The modified NPA (including Wiberg bond-order evaluation) was conducted by the NBO5.9 procedure in Gaussian 09.

(b) Resulting Computational Implications. The NPA of the Pd_4C entity in **1-mod** expectedly reveals significant negative charge on the carbon atom and four electron-deficient bonds (1.67 electrons per bond) between the central carbon atom and each of the four palladium atoms formed by the $\text{sp}^{0.5}$ hybrid of the carbon atom and 5s orbital of each metal. The electron configuration of each palladium atom points to the noticeable 4d-to-5s promotion of ~ 0.5 electrons per atom that is responsible for the described Pd–C bonding. The Wiberg bond-order index²¹ also points to somewhat increased bond order between the closest palladium atoms: ~ 0.35 “intradimer” bond order (BO) versus ~ 0.12 “interdimer” BO (Table 2). Despite these differences in BO, the NPA suggests no major bonding interactions between the closely positioned palladium atoms.

An individual neutral Au_4 cluster has been previously predicted²² to possess the geometry of an elongated rhombus with its short diagonal being smaller than its sides; the arrangement of four gold atoms observed in **2-mod** is estimated to be 20–25 kcal/mol higher in energy. Furthermore, such an arrangement is only slightly more stable (by 2 kcal/mol) than two noninteracting Au_2 dimers. From these energy arguments, it is likely that the electronic structure of the Au_4 core in **2** might resemble the superposition of two weakly interacting Au_2 dimers.

NPA reveals that the electronic structure of the individual Au_4 fragment can be envisioned as comprised of two weakly interacting Au_2 dimers in close proximity to each other. Two natural bonds were identified in the individual Au_4 core, with bonds between gold atoms in each dimer being the same as in the individual Au_2 dimer and formed primarily via interaction of unhybridized 6s NAOs of each gold atom, as the 5d NAOs of

Table 2. Electronic Configurations of Interior Metal (M) Core Atoms and Wiberg Bond Orders in (1-mod)-Bound Pd₄C Core and in (2-mod)-Bound Au₄ Core and in Corresponding Au₄ Core from 2-mod

core ^a	electronic configuration	intra-BO ^b	inter-BO ^b
Pd ₄ C in 1-mod	5s ^{0.54} 4d ^{9.33} tail(0.02) ^c	0.35	0.12
Au ₄ from 2-mod ^d	6s ^{1.06} 5d ^{9.96} 6p ^{0.02} tail(0.00)	0.93	0.08
Au ₄ core in 2-mod	6s ^{1.18} 5d ^{9.84} 6p ^{0.01} tail(0.09) ^c	0.17	0.03

^a**1-mod** and **2-mod** designate isostructural model {Pd₄C}Pd₃₂-(CO)₂₈(PH₃)₁₄ and Au₄Pd₃₂(CO)₂₈(PH₃)₁₄ clusters, respectively, of pseudo-D₂ symmetry (with P-attached Me substituents replaced by H atoms). Each interior M₄ entity may be envisioned as two identical M₂ intradimers (M = Pd, 2.71 Å in **1-mod**; M = Au, 2.64 Å in **2-mod**) that form under pseudo-D₂ symmetry two identical shorter diagonal interdimer bonding distances (M = Pd, 2.96 Å in **1-mod**; M = Au, 2.90 Å in **2-mod**) and two identical longer interdimer nonbonding distances (M = Pd, 3.59 Å in **1-mod**; M = Au, 3.51 Å in **2-mod**).

^bIntra-BO denotes Wiberg bond order of two identical intradimer M-M bonding distances; inter-BO denotes Wiberg bond order of two identical shorter M-M diagonal interdimer bonding distances. ^cTail (0.02 or 0.09) in the electronic configuration implies the total occupation number in higher-energy AOs than 5s in Pd or 6p in Au.

^dAu₄ core per se.

each gold atom are almost fully occupied. The Wiberg bond order of 0.93 (for Au₄ from **2-mod**) clearly points to the existence of a single bond between two gold atoms in each dimer (Table 2), whereas its value of 0.08 for the bonding interdimer Au–Au interactions is relatively small. Table 3 shows that insertion of the Au₄ core into the Pd₃₂(CO)₂₈(PH₃)₁₄ shell (i.e., Au₄ in **2-mod**) gives rise to the transfer of almost 0.39e from the ligands (60% from PH₃ and 36% from CO) onto the gold core, thereby causing the core to acquire negative charge, similar to the Au₂ entity in the earlier reported Au₂Pd₂₈ cluster Au₂Pd₂₈(CO)₂₆(PR₃)₁₀.²³ An analysis in Table 2 of the gold electron configuration in **2-mod** shows that more than half of the newly acquired electron density is located on Au(6s) NAO, whereas the remaining density occupies higher 6p, 7s AOs—the “tail” of the electronic configuration—further away from the atomic center. At the same time, the Au₄ incorporation in the **2-mod** interior further facilitates depletion of the 5d orbital whose occupation diminishes by 0.12e. A large decrease in the intradimer BO was also observed, from 0.93 to 0.17, caused by considerable

electron-density Au–Pd_{shell} delocalization within the cluster core due to extensive Pd_{shell} coordination. Nevertheless, the significant difference between intradimeric and interdimeric Wiberg bond orders points to the bonding anisotropy being retained within the Au₄ entity.

An analysis of electron-density deformation $\Delta\rho$ leads to the same conclusion about two weakly interacting gold dimers in **2-mod** (Figure S1). The deformation of electron density was calculated by subtraction of the individual Au₄ core electron density and the electron density of the model “shell” cluster Pd₃₂(CO)₂₈(PH₃)₁₄ from the electron density of the complete cluster **2-mod**: $\Delta\rho = \rho(\mathbf{2-mod}) - \rho(\text{Au}_4) - \rho(\text{Pd}_{32}(\text{CO})_{28}(\text{PH}_3)_{14})$. As the interaction between Au₄ and the cluster shell “turns on”, the buildup of the electron density in the intradimer space outside the core in line with the Au–Au intradimer bond is apparent [Figure S1a,b], which is consistent with the accumulation of the negative charge on the Au₄ core established from the NPA (Table 3). The extension of significant deformation density outside of the core along the Au–Au connectivity vector is consistent with an increased population of higher NAOs on gold, which is also apparent from significant combined population of 6p and higher orbitals, totaling 0.09 electrons per atom (Table 2). The maximum $\Delta\rho$ in the intradimer region is $664 \times 10^{-5} \text{ e}/\text{\AA}^3$. No bond-density buildup is apparent in the interdimer space, with maximum $\Delta\rho$ found to be only $12 \times 10^{-5} \text{ e}/\text{\AA}^3$. Similar anisotropy in deformation of electron density is observed if the Au₄ core is simply placed between four intradimer oriented PH₃ ligands, essentially creating two weakly interacting Au₂(PH₃)₂ dimers (Figure S1b): the presence of donor ligands increases the electron density in the intradimer space up to $760 \times 10^{-5} \text{ e}/\text{\AA}^3$, whereas the maximum increase of electron density between dimers is $216 \times 10^{-5} \text{ e}/\text{\AA}^3$, which occurs at the centroid of the Au₄ fragment. Such anisotropic deformation of electron density clearly points to the existence of two weakly bound Au₂ dimers in **2-mod** rather than a single Au₄ core with delocalized bonding.

Table 3 discloses that ~50% of the negative-charge buildup on Pd₄C in **1-mod** originates from the cluster Pd₃₂ surface metal shell, in contrast to only 3% of the charge increase on Au₄ in **2-mod** from an identical Pd₃₂ shell. This shift in the source of the cluster core negative-charge buildup from primarily the Pd₃₂ metal shell (in **1-mod**) toward the ligands (in **2-mod**) may

Table 3. Natural Atomic Charges on Metallic Fragments and Ligands (Atomic, *q*, and Entire Molecular Group, *Q*) in Complete Clusters 1-mod and 2-mod and in These Clusters with the Interior Pd₄C and Au₄ Entity, Respectively, Removed (Same Cluster Shell)^a

charge	1-mod shell	1-mod complete	$\Delta\%$ ^b	2-mod shell	2-mod complete	$\Delta\%$ ^b	Au ₄ (PH ₃) ₄
<i>Q</i> (cluster interior)		−0.609			−0.386		−0.194
<i>q</i> (M _{int}) ^c		−0.033			−0.097		−0.049
<i>q</i> (C _{int})		−0.479					
<i>Q</i> (Pd ₃₂ surface)	+3.262	+3.571	50.7	+3.191	+3.204	3.3	
<i>q</i> (Pd _{surface}) ^c	+0.102	+0.111		+0.100	+0.100		
<i>Q</i> (CO)	−5.347	−5.167	29.6	−5.249	−5.109	36.3	
<i>q</i> (CO) ^c	−0.191	−0.185		−0.187	−0.182		
<i>Q</i> (PH ₃)	+2.085	+2.205	19.7	+2.058	+2.291	60.3	+0.194
<i>q</i> (PH ₃) ^c	+0.149	+0.158		+0.147	+0.164		

^a**1-mod** and **2-mod** designate model {Pd₄C}Pd₃₂(CO)₂₈(PH₃)₁₄ and Au₄Pd₃₂(CO)₂₈(PH₃)₁₄ clusters, respectively, with electronically equivalent {Pd₄C} or Au₄ embedded within an identical surface Pd₃₂(CO)₂₈(PH₃)₁₄ shell model. ^b $\Delta\%$ is the percentage of charge adjustment on each molecular group upon removal of these interior fragments from the corresponding complete cluster. For comparison, charges on analogously deformed Au₄(PH₃)₄ are shown in the last column. ^c*q*(M_{int}), *q*(Pd_{surface}), *q*(CO), *q*(PH₃) denote metal (M) or ligand per unit.

explain how the introduction of gold atoms into a palladium catalyst modifies the selectivity of the homopalladium catalyst. Most likely, such shifts arise from the lower energies of gold valence orbitals compared to those of palladium orbitals and their more efficient coupling with those of phosphine ligands, thereby yielding *more efficient* charge transfer from the ligands onto the metal cluster Au–Pd core.

Topological analyses of electron density within the Pd₄C and Au₄ cores in **1-mod** and **2-mod** present another approach to identify bonding interactions in the two cores. This analysis of Pd₄(μ₄-C) core (shown in Figure 5a) revealed only four

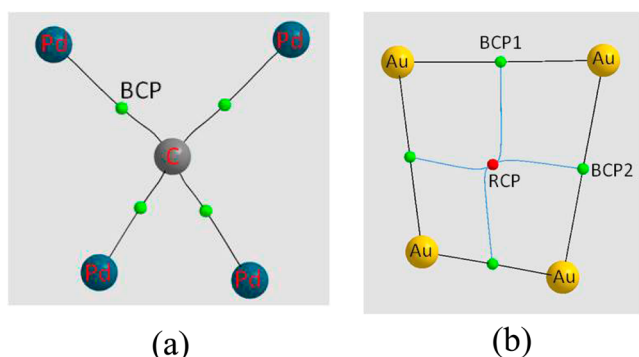


Figure 5. (a) Calculated model of Pd₄C cluster core in **1-mod** with ρ BCP critical points (green) together with bonding paths. (b) Calculated model of Au₄ cluster core in **2-mod** with ρ critical points—BCP1 and BCP2 (green) and the RCP (red)—together with bonding paths and RCP-to-BCP paths.

calculated (3, −1) bond critical points (BCPs) corresponding to Pd–C bonding but no BCPs between Pd atoms. [Noteworthy is that a (3, −1) BCP is a point located between two atoms in which the electron density is a minimum in the direction of the bonded atoms and a maximum in the two orthogonal directions; it is taken as indicative of covalent bonding.] The analysis of electron density in Pd₄C core identifies very small but negative values of energy density at the midpoints between adjacent Pd atoms that suggest uniformly weak interpalladium interactions. In contrast, QTAIM analysis of the individual Au₄ core in **2-mod** identified four (3, −1) BCPs (Figure 5b) that are located midway between two gold atoms of the two Au₂ intradimers and midway between the two Au₂ bonding interdimer, namely, two BCPs 1 and two BCPs 2, respectively. In addition, one (3, +1) ring critical point (RCP) was identified close to the fragment's centroid (Figure 5b). The two sets of BCPs in the Au₄ core in **2-mod** indicate that interdimeric Au₂ bonding is also significant. The different locations of the BCPs in the Pd₄(μ₄-C) core versus those in the Au₄ core provide additional definite evidence concerning their dissimilar bonding scenarios in spite of their remarkable geometrical/electronic equivalences.

Comparative Analysis of Mean Pd–C Distance in 1 with Those in Known Palladium-Containing Mixed-Metal Carbide Clusters. Because **1** is the first example of a cluster with a tetracoordinated carbide atom exclusively encapsulated within a homopalladium cage, of interest is a comparison of its mean Pd–C bonding connectivities with those in heteropalladium carbide clusters having at least one Pd–C bond. To our knowledge, all such previously characterized bimetallic/trimetallic heteropalladium carbide clusters are known only for Fe, Co (or Fe/Co), Ru, and Os

Table 4. Pd–C_{carbide} Mean Distances (Å) in Palladium-Containing Mixed-Metal Carbide Clusters with the Mono-Interstitial C Atom(s) Either in the Distorted Trigonal Bipyramidal PdM₄(μ₅-C) or in the Distorted Octahedral Pd_xM_{6-x}(μ₆-C) Cages, where M and x are Specified in the Table

entry	cluster	environment of carbido atom	mean Pd–C distance	reference
1	{Os ₄ C(CO) ₁₀ (μ-Cl)(μ-PPh ₂ py)}(μ ₄ -Pd) {Os ₄ C(CO) ₁₂ (μ-Cl)} ^a	[PdOs ₄ (μ ₅ -C)]	2.04	24a
2	{Os ₄ C(CO) ₁₂ (μ-Cl)} ₂ (μ-Pd ₂ Cl ₂)	[PdOs ₄ (μ ₅ -C)]	1.99	24a
3	{Os ₄ C(CO) ₁₂ (μ-I)} ₂ (μ-Pd ₂ I ₂)	[PdOs ₄ (μ ₅ -C)]	1.99	24a
4	PdOs ₅ C(CO) ₁₅ (μ-Cl) ₂ (PPh ₃)	[PdOs ₄ (μ ₅ -C)]	2.04	24b
5	PdFe ₃ CoC(CO) ₁₂ (η ³ -C ₃ H ₅)	[PdFe ₃ Co(μ ₅ -C)]	2.01	24c
6	HPdFe ₂ Ru ₂ C(CO) ₁₂ (η ³ -C ₁₀ H ₁₅) ₂ ^b	[PdFe ₂ Ru ₂ (μ ₅ -C)]	2.00 ^c	24d
7	Pd ₈ Ru ₁₀ C ₂ (CO) ₂₇ (C ₃ H ₅) ₄	[PdRu ₅ (μ ₆ -C)]	2.03	24e; CCDC Refcode LISVEO ²⁵
8	PdRu ₅ C(CO) ₁₅ (P ^t Bu ₃)	[PdRu ₅ (μ ₆ -C)]	2.10	24f
9	Pd ₂ Ru ₅ C(CO) ₁₅ (P ^t Bu ₃) ₂	[PdRu ₅ (μ ₆ -C)]	2.13	24f
10	PdOs ₅ C(CO) ₁₄ (μ-dppf) ^d	[PdOs ₅ (μ ₆ -C)]	2.04	24g
11	Pd ₄ Os ₅ C(CO) ₁₅ (μ-dppm) ₂ ^e	[PdOs ₅ (μ ₆ -C)]	2.00	24h; CCDC Refcode PUNVEZ ²⁵
12	Pd ₂ Fe ₃ RuC(CO) ₁₂ (η ³ -C ₁₀ H ₁₅) ₂ ^b	[Pd ₂ Fe ₃ Ru(μ ₆ -C)]	2.12	24i
13	[H _{3-n} Co ₁₃ Pd ₉ C ₃ (CO) ₃₈] ⁿ⁻	[PdCo ₅ (μ ₆ -C)]		24j
	n = 0		1.99	
	n = 1		1.99	
	n = 2		2.03	
	n = 3		2.00	
	[H _{6-n} Co ₂₀ Pd ₁₆ C ₄ (CO) ₄₈] ⁿ⁻	[PdCo ₅ (μ ₆ -C)]		24k
	n = 4		2.03	
	n = 5		1.96	
14	Co ₄ Pd ₂ C(CO) ₁₁ (PPh ₃) ₂	[Pd ₂ Co ₄ (μ ₆ -C)]	2.14	24k
15	Co ₂ Pd ₃ C(CO) ₈ (PPh ₃) ₅	[Pd ₄ Co ₂ (μ ₆ -C)]	2.10	24k

^aPPh₂py = diphenyl-2-pyridylphosphine. ^bη³-C₁₀H₁₅ = η³-β-pinenyl. ^cFor two crystallographically independent molecules. ^ddppf = 1,1'-bis(diphenylphosphino)ferrocene. ^edppm = bis(diphenylphosphino)methane.

and involve carbide-encapsulated metal cages with either five or six metal atoms. These clusters along with the compositions of their metal cages and mean Pd–C distances are presented in Table 4. As expected, their syntheses are more complex than that for **1**.

The mean value of 1.91 Å for the Pd(μ_4 -C) distance in the two structures of **1** determined in **1a** and **1b** (Table 1) is 0.10 Å smaller than the mean Pd(μ_5 -C) distance of 2.01 Å (mean range, 1.99–2.04 Å) for the six listed pentacoordinated heteropalladium carbide clusters (in Table 4) and likewise is 0.14 Å smaller than the mean Pd(μ_6 -C) distance of 2.05 Å (mean range, 1.96–2.14 Å) for the 14 listed hexacoordinated heteropalladium carbide clusters (in Table 4). This bond-length trend is completely consistent with an enlargement of the metal cage size upon incorporation of a greater number of metal cage atoms coupled with the size restrictions (i.e., a constraint matrix effect) imposed upon the Pd(μ_4 -C) cage by the encapsulating Pd₃₂ shell (vide supra).

Comparison of **1 with Known M₄(μ_4 -C) Clusters Containing a Carbido Atom Tetracoordinated to Four Metals.** Highly distorted tetrahedral arrangements of four metal atoms around a carbide atom by itself is not at all surprising. But a carbide atom cannot be geometrically accommodated inside of a regular (nondistorted) tetrahedral metal cage with retention of all six metal–metal bonds.² Known examples of a C atom coordinated to four metal centers include more-or-less deformed metal tetrahedra either with all six M–M bonds broken, [e.g., M₄(μ_4 -C) with M = Hg,^{26a,b} Pb,^{26c} Sn,^{26d} Ge,^{26e} Au;^{26f} M₄ = Al₃Ti,^{26g,h} Al₂Ti₂²⁶ⁱ] or with deformed metal tetrahedra possessing one to three significantly weakened or broken M–M bonds. Among this second group are the long-known “butterfly”-based clusters containing a linear M–C–M arrangement (i.e., with one broken M–M bond)² with an exposed C atom, and a few M₄(μ_4 -C) clusters with two or three highly elongated or broken M–M bonds. Examples are a pentametal-bonded butterfly WOs₃(μ_4 -C) cluster of formula WOs₃(μ_4 -C)(μ_2 -H)₂(η^5 -C₅H₅)(CO)₉(μ_2 -SMe)²⁷ with a linear W–C–Os architecture, another tetrametal-bonded WOs₃(μ_4 -C) cluster of formula WOs₃(μ_4 -C)(η^5 -C₅H₅)(CO)₁₁(μ_2 -SMe)²⁷ with nonbonding W...Os and Os...Os distances, and a trimetal-bonded RuCo₃(μ_4 -C) cluster²⁸ with a tetrahedral sp³ carbide atom. This latter RuCo₃(μ_4 -C)(η^5 -C₅H₅)(CO)₈L₃ cluster²⁸ is the first crystallographic example of a tetrahedral sp³ carbide cluster with the (μ_4 -C) atom coordinated to a trimetal-bonded Co₃(CO)₆L₃ fragment [where L₃ denotes tdpm CH(PPh₂)₃] and to an otherwise nonbonded Ru(η^5 -C₅H₅)(CO)₂ moiety. An unusual example of a tetrametal-bonded butterfly-based M₄(μ_4 -C) cluster with two broken M–M bonds is the Ru₂Pt₂(μ_4 -C) cluster of formula Ru₂Pt₂(μ_4 -C)(μ_2 -H)₂(η^5 -C₅H₅)₂(CO)₂(PⁱPr₃)₂²⁹ that is folded about the linear Ru–C–Ru axis; however, the resulting highly elongated Pt–Pt separation of 3.132(1) Å implies little or no direct metal–metal bonding. Particularly noteworthy is that closed-shell electronic metal configurations are achieved in these M₄(μ_4 -C) metal carbide clusters.

An exceptional geometrical arrangement was observed for the W₄(μ_4 -C) framework in the [W₅(C)I₁₃][−] anion ([NBu₄]⁺ counterion);³⁰ unlike all other known metal-bonded square-pyramidal M₅(μ_5 -C) clusters for which the pentacoordinated (μ_5 -C) atoms approximately reside within the basal tetrametal frameworks, the tetracoordinated (μ_4 -C) carbide atom is 1.06 Å below the square-basal W₄ plane at 2.98 Å from the axial

octahedrally coordinated W atom compared to its normal basal W–C bonding distances of 2.09(4)–2.24(3) Å.

From symmetry considerations, the only tetrametal-coordinated carbide cluster that is structurally related to **1** is the [Re₄(μ_4 -C)(CO)₁₅I][−] anion (as the [PPN]⁺ salt),³¹ which was reported in 1985 in very low yield from a partial oxidative fragmentation of the monocapped octahedral carbido [Re₇(μ_6 -C)(CO)₂₁]^{3−} anion by reaction with I₂ in MeCN under CO atmosphere. An X-ray crystallographic determination of this [Re₄(μ_4 -C)(CO)₁₅I][−] anion showed four octahedrally coordinated Re atoms [namely, one Re(CO)₃I and three Re(CO)₄ fragments] that are each linked to one another in a cyclic cis-fashion via two Re–Re single bonds. The additional attachment of these four Re atoms to the carbido atom gives rise to a central Re₄(μ_4 -C) entity of pseudo-*D*_{2d} (42*m*) symmetry with two mean Re–C–Re trans bond angles of 157.4° and four mean Re–C–Re cis bond angles of 92.1°, indicating that the carbido atom is much closer to square-planar instead of tetrahedral Re–C coordination; although exposed, the carbide atom is sterically protected by the axial octahedral Re ligands. The central Re₄(μ_4 -C) entity of pseudo-*D*_{2d} symmetry thereby geometrically differs from the pseudo-*D*₂ isostructural Pd₄(μ_4 -C) and Au₄ entities in **1** and **2**, respectively, in possessing two instead of three kinds of symmetry-equivalent M–M connectivities, namely, four equivalent opposite single-bond Re–Re (rhombus) edges (mean, 3.00 Å) and two equivalent nonbonding diagonal Re...Re distances (mean, 4.09 Å). Both its structure and composition conform to a closed-shell electronic metal configuration.

Geometric Comparison with Only Other Known Nanosized Au–Pd Cluster Au₄Pd₂₈(CO)₂₂(PMe₃)₁₆ Possessing a Tetragold Kernel. A previous study³² showed that analogous precursors under different reaction conditions produced another new type of tetragold–palladium cluster, Au₄Pd₂₈(CO)₂₂(PMe₃)₁₆ (**6**), that not only has a completely dissimilar Au₄Pd₂₈ core geometry with a nearly regular encapsulated Au₄ tetrahedron but also a totally different postulated multitwinned composite growth pattern. This cluster, which was obtained from the reaction of Pd₁₀(CO)₁₂(PMe₃)₆ with Au(SMe₂)Cl or Au(PPh₃)Cl (yield, ~20–40%), has a 32 metal-atom Au₄Pd₂₈ framework that conforms to pseudo-cubic *T* (23) symmetry, which is reduced to general C₁(1) symmetry upon inclusion of its 22 bridging CO ligands.

A comparative analysis of resulting low-temperature CCD X-ray diffractometry determinations³² of two different solvated crystals of **6** revealed an amazing molecular similarity that clearly indicates that the observed analogous geometrical distortions are primarily induced by intracuster strain-releasing effects and not by crystal-packing interactions. A multitwinned growth-pattern of its Au₄Pd₂₈ core was proposed involving the formation of a Au₄Pd₂₄ composite-twinned architecture formed from four markedly deformed interpenetrating three-layer Au(*n*)-centered [Pd₃]_A[Au(*n*)Pd₆]_B[Au₃]_C cuboctahedra (*n* = 1–4) that are oriented along the four localized threefold axes of the encapsulated Au₄ tetrahedron; the remaining four outermost (external) Pd atoms are tetrahedrally disposed about the Au₄Pd₂₄ composite and presumably provide stabilization via face condensations (specifically, three tetracapped; one tricapped). The mean Au–Au distances of the Au₄ tetrahedron in 6·Pr₂O and 6·STHF·hexane are 2.75 and 2.77 Å (ranges, 2.648(1)–2.810(1) Å; 2.687–2.823(1) Å).³²

Relevance to Heterogeneous Pd and Pd/Au Catalysts for Conversion of Ethylene to Vinyl Acetate. Palladium

has long been widely used as a heterogeneous catalyst for the multiton production of such an important monomer as VA, which is formed by oxidation of ethylene in the presence of acetic acid.^{6a} The fact that Pd–Au catalysts were shown to exhibit much higher reactivities than Pd-based catalysts in VA synthesis led to a comprehensive investigation^{6b–f} as to whether Pd–Au catalysts resist carbide formation; it was concluded that there is no evidence for PdC_x entities in a Pd–Au alloy following VA synthesis such that the alloying of Au with Pd is apparently very effective in preventing PdC_x formation in Pd-based catalysts for VA synthesis.

CONCLUSIONS

The first homopalladium carbido cluster, {Pd₄(μ₄-C)}Pd₃₂(CO)₂₈(PMe₃)₁₄ (**1**), was obtained via an ultimately simplified straightforward reaction of either Pd₈(CO)₈(PMe₃)₇ or Pd₁₀(CO)₁₂(PMe₃)₆ with CHCl₃ at room temperature under N₂. X-ray crystallographic determinations of solvated crystals (**1a** and **1b**) of **1** at 100 K revealed closely related structures consisting of a highly unusual tetracoordinated C atom encapsulated within a highly distorted tetrahedral Pd₄ cage of pseudo-D₂ symmetry. The unprecedented {Pd₄C} kernel in **1a** may be described as two symmetry-equivalent Pd₂ intradimers (mean, 2.71 Å) that are linked to each other by a weakly bonding interdimer Pd₂ pair (mean, 2.96 Å); the other interdimer Pd₂ pair is nonbonding (mean, 3.59 Å). The mean of the four Pd–C distances is 1.91 Å [range, 1.87(2)–1.94(2) Å], and mean values for the three pairs of opposite tetrahedrally deformed Pd–C–Pd bond angles are 90.2°, 102.9°, and 140.6°.

A completely unanticipated and prime feature is that the molecular geometry of **1** is essentially isomorphous with that in the known Au₄Pd₃₂(CO)₂₈(PMe₃)₁₄ (**2**), in which an identical Pd₃₂ shell analogously accommodates a Au₄ kernel that is geometrically similar in size and shape and is electronically equivalent to the {Pd₄C} kernel in **1**. Mean distances for the three corresponding symmetry-equivalent pairs of opposite tetrahedrally deformed Au–Au edges within the Au₄ kernel in **2** are 2.64, 2.91, and 3.51 Å. However, the NPA and AIM method indicated that the bonding interactions of **1-mod** and **2-mod**, respectively (in which P-attached Me substituents were replaced by H atoms), are different. Whereas the two Pd₂ dimers in the negatively charged {Pd₄C} entity in **1** are primarily stabilized by Pd–C interactions, the corresponding Au₂ dimers in **2** are stabilized by direct Au–Au bonds. The NPA also showed that both the Pd₃₂ shell and its ligands play a crucial role in the tuning of overall similar negative electron densities upon {Pd₄C}-for-Au₄ substitution. This interchangeable accommodation of the negatively charged {Pd₄C} and Au₄ entities offers a reasonable explanation of why the Au-doped Pd catalyst used for the oxidation of ethylene into vinyl acetate (in the presence of acetic acid) prevents carbidization, namely, the valence 6s Au electron of each added gold atom provides an efficient “negative charge protection” against the formation of negatively charged palladium carbide species such as {Pd₄C} obtained from electron-donating carbon atoms.

EXPERIMENTAL SECTION

Synthesis and IR Spectroscopic Characterization of {Pd₄C}-Pd₃₂(CO)₂₈(PMe₃)₁₄ (1**). General Remarks.** The standard Schlenk technique was used for performing all reactions. Solvents were deoxygenated by the passage of N₂ through them for at least 20 min prior to their use. The syntheses of Pd₁₀(CO)₁₂(PMe₃)₆ and

Pd₈(CO)₈(PMe₃)₇ are analogous to that of Pd₁₀(CO)₁₂(PⁿBu₃)₆ with an adjusted stoichiometry of Pd/P = 8/7 for the second one.³³ Pd₁₀(CO)₁₂(PMe₃)₆ was purified by recrystallization from C₆H₆/heptane. Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer; nujol mulls were prepared under nitrogen.

Pseudo-polymorphic crystals of **1** (i.e., different crystal types as the result of diverse solvation) were obtained from both Pd₈(CO)₈(PMe₃)₇ and Pd₁₀(CO)₁₂(PMe₃)₆ clusters via crystallizations of their CHCl₃ solutions in the presence of hexane vapor. The crystal shapes varied from blocks to thin plates and rods, whereas crystal solvations varied from hexane to CHCl₃ molecules; mixed hexane/CHCl₃ compositions of solvated molecules were found in **3a**. IR spectra of crystalline pseudo-polymorphs of **1** exhibited bridging carbonyl bands at 1880–1878 (s), 1868–1864 (sh), 1849–1806 (several sh bands), 1765–1743 (usually two distinguished m bands) cm^{−1}. For bulky samples bridging carbonyl bands at 1905–1900 (sh) and terminal 2031–2015 (mw–vw) cm^{−1} were also observed and attributed to contaminations. Dichloro-bis(trimethylphosphine)palladium(II) was identified by single-crystal X-ray diffraction as the *cis*-isomer in the form of two crystal types, namely, *cis*-PdCl₂(PMe₃)₂ · CHCl₃ (**5a**) and nonsolvated *cis*-PdCl₂(PMe₃)₂ (**5b**).

Synthesis of 1-2.5C₆H₁₄ (1a**) from Pd₈(CO)₈(PMe₃)₇.** A solution of Pd₈(CO)₈(PMe₃)₇ (200 mg; 0.124 mmol) in 4 mL of CHCl₃ was kept under N₂ for 1 d, filtered, and left in the presence of hexane vapor. After two weeks 12 mg (7%) of black crystals of {Pd₄C}-Pd₃₂(CO)₂₈(PMe₃)₁₄ · 2.5C₆H₁₄ were decanted from amorphous Pd black. Its IR spectrum in nujol displayed the following carbonyl bands: 2015 (vw), 1878 (vs), 1864 (sh), 1845 (sh), 1828 (sh), 1816–1809 (sh, br), 1760 (m), 1743 (m) cm^{−1}. This IR spectrum is very close to the nujol spectrum of the isostructural and electronically equivalent Au–Pd cluster Au₄Pd₃₂(CO)₂₈(PMe₃)₁₄.^{7a} A crystal of size 0.33 × 0.10 × 0.07 mm³ was chosen for X-ray data collection.

Crystals of **1** with significantly less solvated hexane molecules [i.e., 1-0.8C₆H₁₄ (**1c**)] were obtained (estimated yield 1–2 mg) in an analogous synthesis but with crystallization set up immediately after the dissolving of the Pd₈ cluster. The unit cell triclinic crystal parameters for **1c** are *a* = 16.189(2) Å, *b* = 17.829(2) Å, *c* = 27.777(4) Å, α = 82.693(2)°, β = 75.197(2)°, γ = 83.783(2)°; *V* = 7664.3(18) Å³. In addition to 1-0.8C₆H₁₄ (**1c**), colorless crystals of PdCl₂(PMe₃)₂ and dark red crystals of the precursor Pd₈(CO)₈(PMe₃)₇ [identified by an IR spectrum, nujol, carbonyl bands: 1875 (s), 1839 (m), 1819 (sh), 1808 (s), 1798 (sh), 1774 (m), 1761 (mw) cm^{−1}]¹¹ were also obtained.

In striking contrast to the stability of crystals of 1-2.5C₆H₁₄ (**1a**), crystals of 1-0.8C₆H₁₄ (**1c**) at room temperature in absence of mother liquid were extremely fragile and readily self-destructed via explosion. X-ray data collection was accomplished only because the crystal was immediately transferred from the crystallization flask into the diffractometer nitrogen flow at 100 K; nevertheless, the *R*_i(*F*) value of 0.12 was still high.

Synthesis of 1-3CHCl₃ (1b**) from Pd₈(CO)₈(PMe₃)₇ and Pd₁₀(CO)₁₂(PMe₃)₆.** This synthesis was analogous to the preparation of **1a**, but the solution was held under N₂ for 4 d, filtered from Pd black, and crystallization was then set up. It was completed in 9 d with the formation of 5 mg (3%) of black rodlike crystals of **1b** and 80 mg (18%) of light yellow large block crystals of *cis*-PdCl₂(PMe₃)₂ · CHCl₃ (**5a**). IR of **1b** in nujol, carbonyl bands: 1878 (s), 1868 (sh), 1847–1840 (sh), 1827–1806 (sh br), 1762 (w), 1743 (mw) cm^{−1}. The sizes of crystals selected for X-ray data collection were 0.26 × 0.08 × 0.05 mm³ and 0.36 × 0.30 × 0.20 mm³ (cut) for **1b** and **5a**, respectively. Crystals of **5a** exposed to air at room temperature quickly became cloudy due to loss of solvate molecules.

Crystals of **1b** were also obtained by a procedure analogous to that used for the preparation of **1a** but with Pd₁₀(CO)₁₂(PMe₃)₆ (190 mg; 0.102 mmol) as a precursor. Yields: **1b**, black crystals, ~5 mg (3%); *cis*-PdCl₂(PMe₃)₂ (**5b**), colorless crystals, ~15 mg (4%). IR of **1b**, (prepared from Pd₁₀(CO)₁₂(PMe₃)₆) in nujol, ν(CO): 1880 (s), 1866 (sh), 1849 (sh), 1833–1806 (sh br), 1765–1745 (mw br) cm^{−1}; unit cell triclinic crystal parameters: *a* = 16.0645(11) Å, *b* = 17.7303(13) Å,

$c = 25.7442(18) \text{ \AA}$, $\alpha = 87.681(1)^\circ$, $\beta = 80.989(1)^\circ$, $\gamma = 80.008(1)^\circ$; $V = 7131.7(9) \text{ \AA}^3$.

cis-PdCl₂(PMe₃)₂ (**5b**) was identified by comparison of its unit cell parameters, obtained by X-ray diffraction from a single crystal at 100 K (monoclinic, $a = 6.264(2) \text{ \AA}$, $b = 11.793(4) \text{ \AA}$, $c = 8.747(4) \text{ \AA}$; $\beta = 110.69(2)^\circ$, $V = 604.5(3) \text{ \AA}^3$), with those from previous crystals measured at 273 K (specifically, monoclinic, $a = 6.350(4) \text{ \AA}$, $b = 11.837(9) \text{ \AA}$, $c = 8.813(7) \text{ \AA}$; $\beta = 109.85(6)^\circ$, $V = 623.0(8) \text{ \AA}^3$).³⁴

Crystals of **1** were sufficiently insoluble in common solvents such that no NMR spectra of **1** were obtained.

X-ray Crystallographic Determinations of (Pd₄C)₂Pd₃₂(CO)₂₈-(PMe₃)₁₄·2.5C₆H₁₄ (1a**), Pd₃₆(μ₄-C)(CO)₂₈(PMe₃)₁₄·3CHCl₃ (**1b**) and *cis*-PdCl₂(PMe₃)₂·CHCl₃ (**5a**). General Remarks.** X-ray data were collected at 100(2) K with a Bruker SMART CCD-1000 area detector diffractometer and a Mo sealed-tube generator. Reflections in all data sets were empirically corrected for absorption (SADABS). The crystal structures were obtained by use of direct methods followed by successive Fourier difference maps. Least-squares refinements (based on F^2) were performed with SHELXL.³⁵

In structures **1a**, **1b**, and **5a** all non-hydrogen atoms [other than those of solvated hexane molecules (**1a**), disordered solvated CHCl₃ molecule (**1b**), and disordered methyl carbon atoms of trimethylphosphine ligand (**1a** and **5a**)] were refined with anisotropic displacement parameters. In **1a**, methyl groups attached to P8, P12, and P14 atoms are disordered over two sites around each of the P atoms, with occupancy factors of 0.54/0.46, 0.72/0.28, and 0.71/0.29, respectively. One of the solvated hexane molecules in **1a** has $C_i(-1)$ site symmetry and thereby contributes half of molecule per cluster. The other two hexane molecules occupy general positions with one molecule disordered over two nearby sites with an occupancy factor of 0.61/0.39. In the crystal structure of **1b** all three solvated CHCl₃ molecules reside on general positions; one of these molecules is disordered over two sites with an occupancy factor of 0.74/0.26.

Distance restraints were applied for disordered Me groups and solvated molecules. Restraints on anisotropic displacement parameters of carbido atoms were imposed in both structures **1a** and **1b** to avoid nonpositive definite thermal parameters. EADP constraints and/or SIMU and DELU restraints were also used for solvated hexane molecules in **1a** and for a few light atoms in **1b**. Hydrogen atomic positions were generated geometrically and refined with a riding model. The largest residual peaks for all structures were located in close proximities to peaks for Pd atoms and thereby were unambiguously assigned to systematic error (noise). For **5b** only unit cell parameters were determined (vide supra).

Structural tests performed by the checkCIF/PLATON service [via <http://journals.iucr.org/services/cif/checking/checkform.html>] are in agreement with the space groups chosen for these crystal structures and did not show any serious or unexpected problems. Additional crystallographic information, including details of structure refinements in cif files, is available in Supporting Information.

Pd₃₆(μ₄-C)(CO)₂₈(PMe₃)₁₄·2.5C₆H₁₄ (**1a**). C₈₆H₁₆₁O₂₈Pd₃₆: $M = 5907.13 \text{ g·mol}^{-1}$; triclinic; $P\bar{1}$; $Z = 2$; $a = 16.0206(11) \text{ \AA}$, $b = 17.7225(12) \text{ \AA}$, $c = 27.6060(19) \text{ \AA}$, $\alpha = 82.698(1)^\circ$, $\beta = 75.289(1)^\circ$, $\gamma = 83.801(1)^\circ$; $V = 7496.2(9) \text{ \AA}^3$; $d(\text{calc}) = 2.617 \text{ Mg/m}^3$; $F(000) = 5534$. Reflections (59591) obtained over $3.52 \leq 2\theta \leq 52.00$ (98.5% completeness at maximum 2θ); max/min transmission coefficients, 0.7484/0.3249; $\mu(\text{Mo K}\alpha) = 4.394 \text{ mm}^{-1}$. Full-matrix least-squares refinement on 29 018 independent merged ($R(\text{int}) = 0.0572$) reflections (1402 parameters, 126 restraints) converged at $wR_2(F^2) = 0.1506$ for all data; $R_1(F) = 0.0589$ for $I > 2\sigma(I)$; GOF (on F^2) = 0.912; max/min residual electron density, 1.840 and $-1.351 \text{ e·\AA}^{-3}$.

Pd₃₆(μ₄-C)(CO)₂₈(PMe₃)₁₄·3CHCl₃ (**1b**). C₇₄H₁₂₉Cl₉O₂₈Pd₃₆: $M = 6049.80 \text{ g·mol}^{-1}$; triclinic; $P\bar{1}$; $Z = 2$; $a = 16.0975(16) \text{ \AA}$, $b = 17.7114(17) \text{ \AA}$, $c = 25.768(3) \text{ \AA}$, $\alpha = 87.771(2)^\circ$, $\beta = 81.185(1)^\circ$, $\gamma = 80.053(1)^\circ$; $V = 7150.2(12) \text{ \AA}^3$; $d(\text{calc}) = 2.810 \text{ Mg/m}^3$; $F(000) = 5632$. Reflections (90 528) obtained over $3.38 \leq 2\theta \leq 56.74$ (95.4% completeness at maximum 2θ); max/min transmission coefficients, 0.7963/0.3700; $\mu(\text{Mo K}\alpha) = 4.773 \text{ mm}^{-1}$. Full-matrix least-squares refinement on 34 207 independent merged ($R(\text{int}) = 0.0528$) reflections (1438 parameters, 72 restraints) converged at $wR_2(F^2) =$

0.2073 for all data; $R_1(F) = 0.0738$ for $I > 2\sigma(I)$; GOF (on F^2) = 1.329; max/min residual electron density, 2.878 and $-2.705 \text{ e·\AA}^{-3}$.

cis-PdCl₂(PMe₃)₂·CHCl₃ (**5a**). C₇H₉Cl₃Pd: $M = 448.81 \text{ g·mol}^{-1}$; monoclinic; $P2_1/c$; $Z = 8$; $a = 10.1667(7) \text{ \AA}$, $b = 28.1052(19) \text{ \AA}$, $c = 11.6394(8) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90.322(1)^\circ$, $\gamma = 90^\circ$; $V = 3325.8(4) \text{ \AA}^3$; $d(\text{calc}) = 1.793 \text{ Mg/m}^3$; $F(000) = 1776$. Reflections (30 644) obtained over $1.44 \leq 2\theta \leq 56.62$ (98.4% completeness at maximum 2θ); max/min transmission coefficients, 0.6807/0.5209; $\mu(\text{Mo K}\alpha) = 2.084 \text{ mm}^{-1}$. Full-matrix least-squares refinement on 8169 independent merged ($R(\text{int}) = 0.0342$) reflections (269 parameters, 6 restraints) converged at $wR_2(F^2) = 0.0885$ for all data; $R_1(F) = 0.0332$ for $I > 2\sigma(I)$; GOF (on F^2) = 1.077; max/min residual electron density, 1.328 and $-0.711 \text{ e·\AA}^{-3}$. The structure of **5a** consists of two independent *cis*-PdCl₂(PMe₃)₂ molecules together with two solvated CHCl₃ molecules. Methyl groups attached to the P1 atom are disordered over two sites with an occupancy factor of 0.65/0.35.

The crystal of **5a** was a pseudo-merohedral twin crystal with a ratio of domains of 0.88/0.12. Although the contribution from a second component was low (~10%), the twin law, $[-100, 0, -10, 001]$, used in least-squares refinement improved the R_1 value significantly from 0.083 (before twin modeling) to 0.033.

■ ASSOCIATED CONTENT

■ Supporting Information

Crystallographic information files (CIF) for the reported structures; Table S1 with the comparative mean distances and individual ranges for **1a**, **1b**, and **2a**; Figure S1 (contour maps of anisotropic deformation of electron density about the Au₄ core); energy considerations for Pd₄ and Au₄ kernels in **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data (in CIF files) have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, United Kingdom, and copies can be obtained upon request, free of charge, by quoting the publication citation and the CCDC deposition numbers 1040120 (**1a**), 1040122 (**1b**), and 1040121 (**5a**) via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

We dedicate this paper to Professor Giuliano Longoni in honor of his recent retirement from the University of Bologna and in

recognition of his highly creative, inspirational leadership and the resulting major scientific impacts of the many important contributions that he and his co-workers have made to metal carbonyl cluster chemistry during the past 40 years.

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