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Synthesis and Structural Analysis of the First Nanosized Platinum–Gold Carbonyl/Phosphine Cluster, $Pt_{13}[Au_2(PPh_3)_2]_2(CO)_{10}(PPh_3)_4$, Containing a Pt-Centered $[Ph_3PAu–AuPPh_3]$-Capped Icosahedral Pt_{12} Cage

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The preparation and molecular structure of the initial nanosized platinum–gold carbonyl cluster, $Pt_{13}[Au_2(PPh_3)_2]_2(CO)_{10}(PPh_3)_4$ (**1**), are described. A comparative analysis reveals its pseudo-D_{2h} geometry, consisting of a centered Pt_{13} icosahedron encapsulated by two centrosymmetrically related bidentate $[Ph_3PAu–AuPPh_3]$-capped ligands along with 4 PR_3 and 10 CO ligands, to be remarkably similar to that of the previously reported $Pt_{17}(\mu_2\text{-}CO)_4(CO)_8(PEt_3)_8$ (**2**). Reformulation of **2** as $Pt_{13}[(PtPEt_3)_2(\mu_2\text{-}CO)]_2(CO)_{10}(PEt_3)_4$ emphasizes the steric/electronic resemblance of the bulky-sized bidentate $[Ph_3PAu–AuPPh_3]$ and $[(PtPEt_3)_2(\mu_2\text{-}CO)]$ capping ligands in **1** and **2**, respectively, as well as their identical electron counts of 162 cluster valence electrons for a centered Pt_{13} icosahedron. We hypothesize that analogous steric effects of their ligand polyhedra in **1** and **2** play a crucial role along with electronic effects in the formation and stabilization of these two nanosized clusters that contain an otherwise unknown centered icosahedron of platinum atoms.

Because of the commercial prominence of Pt-based catalysts and the experimentally determined knowledge that the incorporation of gold into these catalysts has generally been found to enhance their activities, chemoselectivities, and stabilities, many studies during the last 2 decades have been directed toward the preparation and characterization of Pt−Au clusters as potential catalytic precursors.[1] Although this has given rise to a considerable number of new Pt−Au clusters,[2] there are no previous examples of nanosized Pt−Au carbonyl clusters.[3,4]

As part of an extensive preparative exploration to synthesize and physically/chemically characterize high-nuclearity (nanoscale) CO-ligated Pt−Au clusters, we present herein the preparation, isolation, and structural determination of the first nanosized Pt−Au carbonyl cluster, $Pt_{13}[Au_2(PPh_3)_2]_2(CO)_{10}(PPh_3)_4$ (**1**). This extraordinary cluster was initially obtained in low yield (∼10%) from the redox reaction of $PtCl_2(COD)$, $AuSMe_2Cl$, and PPh_3 with $[Ni_6(CO)_{12}]^{2-}$ in an acetonitrile solution under an initial CO atmosphere.[5] Its composition and atomic arrangement were unequivocally established from a low-temperature CCD X-ray diffractometry study.[6,7] The calculated Pt/Au atom ratio (13/4) of 76.5%/23.5% is in close agreement with that of 74(2)%/26(2)% and 77(2)%/23(2)% obtained from energy-resolved measurements on two crystals with a scanning electron microscope.[8]

The configuration of **1** of pseudo-D_{2h} and crystallographic C_i (-1) symmetry consists of a centered Pt_{13} icosahedron that is stabilized by two bidentate $[Ph_3PAu−AuPPh_3]$ units that cap two centrosymmetrically related (opposite) pairs of adjacent triangular icosahedral Pt_{13} faces along with 4 terminal PPh_3 and 10 CO ligands, of which 8 are terminal and 2 doubly bridging (Figure 1a). The elongated, cylindrically shaped 17-atom $Pt_{13}Au_4$ core has metal-core dimensions of 0.82 nm between opposite Au atoms along the vertical

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[3] High-nuclearity(nanosized) mono- and polyicosahedral Pt−Au−Ag phosphine/halide clusters containing Pt-centered icosahedral cages have been prepared and crystallographically/theoretically analyzed.[4]

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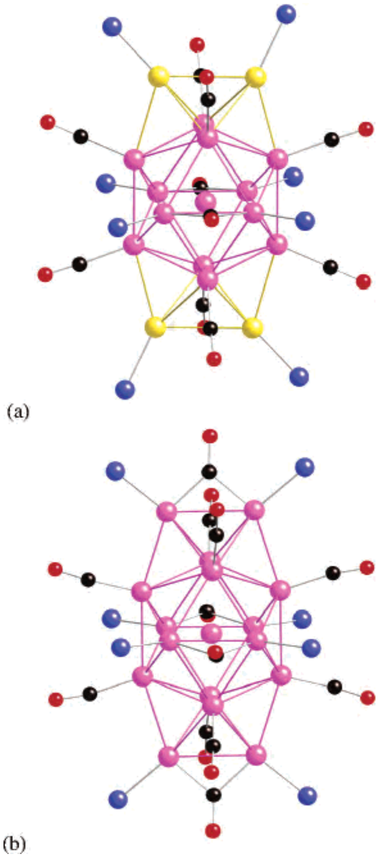

Figure 1. Configurations of (a) **1** and (b) known **2**[10] without the phosphorus-attached substituents. Each molecular configuration of crystallographic site symmetry C_i (-1) ideally conforms to D_{2h} ($2/m$, $2/m$, $2/m$) symmetry. These electronically equivalent and geometrically analogous molecular clusters are the only examples of a centered Pt_{13} icosahedron, whose stabilization is sterically/electronically attributed to closely similar ligand polyhedra.

pseudo-C_2 axis and 0.54 nm between Pt atoms perpendicular to the C_2 axis.

In contrast to many examples of icosahedral-based palladium carbonyl/phosphine clusters,[9] the only other examples of icosahedral-based platinum carbonyl clusters are $Pt_{17}(\mu_2\text{-}CO)_4(CO)_8(PEt_3)_8$ (**2**)[10] and the classic 19-metal-atom pseudo-D_{5h} $[Pt_{19}(CO)_{22}]$,[4−11] which may be viewed as a geometrical isomer of two interpenetrating icosahedra (corresponding to one double icosahedron), for which the three pentagonal Pt_5 rings are constrained to be eclipsed instead of staggered because of 10 doubly bridging COs linking eclipsed pairs of Pt atoms between pentagonal rings. The centrosymmetric **2**, reported in 1989, was prepared in low yield (∼14%) by Kurasov and Eremenko[10] from the thermolysis of $Pt_5(CO)_6(PEt_3)_4$[12a] in decane and structurally determined from an X-ray diffraction study by Slovokhotov and Struchkov.[10] We subsequently found that **1** can also be prepared from the triphenylphosphine analogue, $Pt_5(CO)_6(PPh_3)_4$,[12] by reaction with $AuPPh_3Cl$ and $TlPF_6$ (as a chloride scavenger).[13]

Figure 1b shows that **2** also is composed of a centered Pt_{13} icosahedron that is capped on each of two centrosymmetrically opposite pairs of adjacent triangular Pt_3 faces by two bidentate $[(PtPEt_3)_2(\mu_2\text{-}CO)]$ fragments. A comparison of the molecular structures of **1** and **2** (Figure 1a,b) reveals

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(4) (a) Teo, B. K.; Zhang, H. *Coord. Chem. Rev.* **1995**, *143*, 611. (b) Teo, B. K.; Zhang, H. *J. Organomet. Chem.* **2000**, *614*, 66. (c) Teo, B. K.; Zhang, H.; Shi, X. *Inorg. Chem.* **1994**, *33*, 4086. (d) Kappen, T. G. M. M.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J. *Inorg. Chem.* **1994**, *33*, 754. (e) Teo, B. K.; Zhang, H. *J. Cluster Sci.* **2001**, 12, 349. (f) Teo, B. K.; Zhang, H.; Shi, X. *J. Am. Chem. Soc.* **1993**, *115*, 8489.

(5) Reactions were carried out by standard Schlenk techniques on a preparative vacuum line under a nitrogen atmosphere. A typical procedure for the preparation of **1** is as follows: To a stirred solution of $PtCl_2(COD)$ (0.145 g, 0.38 mmol), $AuSMe_2Cl$ (0.056 g, 0.19 mmol), and PPh_3 (0.100 g, 0.38 mmol) in 10 mL of MeCN was added $[Ni_6(CO)_{12}]^{2-}$ ($[NMe_4]^+$ salt) (0.200 g, 0.24 mmol) in 15 mL of MeCN. The solution was stirred under a CO atmosphere for 45 min followed by 10 min under a nitrogen atmosphere. The resulting red-brown solution was then filtered to a separate flask, and the acetonitrile solvent was removed by evaporation. The residue was washed with a minimum amount of MeOH and extracted into MeCN. Single crystals of **1** were obtained by layer diffusion of isopropyl ether into a concentrated MeCN solution of **1** (yield ∼ 10%). IR spectra in Nujol: 1956 (br, vs), 1947 (sh), 1738 (m) cm^{-1}.

(6) X-ray data for crystal of **1** were collected at 173(2) K on a Bruker SMART CCD-1000 area-detector diffractometer with graphite-monochromated Mo Kα radiation from a sealed-tube generator. The crystal structure was determined from direct methods. Least-squares refinements (based on F^2) were carried out with *SHELXTL*.[7] Supplementary crystallographic data in CIF format for **1** have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, United Kingdom, and copies can be obtained upon request free of charge, by quoting the publication citation and deposition number: CCDC-271649. $Pt_{13}[Au_2(PPh_3)_2]_2(CO)_{10}(PPh_3)_4$: $M_r = 5714.31$, triclinic, $P\bar{1}$, $a = 15.902(2)$ Å, $b = 16.041(2)$ Å, $c = 17.593(2)$ Å, $\alpha = 78.963(2)°$, $\beta = 63.696(1)°$, $\gamma = 63.132(2)°$, $V = 3588.4(6)$ Å^3, $Z = 1$, $F(000) = 2580$, $\rho_{calcd} = 2.644$ Mg m^{-3}. 32 128 reflections were obtained over $1.29 \leq \theta \leq 28.33°$. An empirical absorption correction (SADABS) was applied [μ(Mo Kα) = 16.82 mm^{-1}, max/min transmission, 0.4317/0.1071]. Full-matrix least-squares refinement (on F^2) of 17 003 independent merged reflections [R(int) = 0.0835] with 493 parameters [0 restraints] converged at w$R2(F^2) = 0.1497$ for all data; $R1(F) = 0.0731$ for $I > 2\sigma(I)$; max/min residual electron density, 5.30/−7.02 e Å^{-3}; GOF (on F^2) = 0.975. Hydrogen atoms were included in structure factor calculations at idealized positions and were allowed to ride on attached carbon atoms with relative isotropic displacement coefficients. All non-hydrogen atoms, except carbon atoms of phenyl groups, were refined anisotropically.

(7) All crystallographic software and sources of the scattering factors are contained in the *SHELXTL* program library: Sheldrick, G. *SHELXTL*, version 6.10; Bruker AXS: Madison, WI, 2000.

(8) Measurements were performed by Dr. Richard Noll (Manager, SEM Facility at Materials Center-Instrumentations, University of Wisconsin—Madison) on a LEO DMS 1530 field emission scanning electron microscope (JEOL JSM-6100).

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(13) $Pt_5(CO)_6(PPh_3)_4$[12] (0.05 mmol) and $AuPPh_3Cl$ (0.03 mmol) were reacted with $TlPF_6$ (0.03 mmol) in the THF solution. After the reactants were stirred at room temperature under N_2 for four days, the solution was evaporated and the residue was washed with *i*-Pr_2O. Crystals, grown by layer diffusion of *i*-Pr_2O with a MeCN solution of **1**, were identified as **1** via IR amd X-ray crystallographic analysis (approximate yield, 10−15%). This much simpler, direct preparative route is preferable to the original one (ref 5), and optimization of the reaction boundary conditions should give rise to a higher yield of **1**.

analogous orientations of the corresponding four terminal PR_3 ligands and eight terminal and two doubly bridging carbonyl ligands attached to the common Pt(i)-centered Pt_{12} cage. These approximately identical ligand arrangements of pseudo-D_{2h} symmetry in **1** and **2** are in accordance with the close similarity of their IR spectra.[10,14] The reformulation of **2** as $Pt_{13}[(PtPEt_3)_2(\mu_2\text{-}CO)]_2(CO)_{10}(PEt_3)_4$ stresses the close geometrical similarity (Figure 1) of both molecular structures of **1** and **2** and thereby suggests an overall resemblance of the combined electronic/steric influence of the two bidentate $[Au_2(PPh_3)_2]$ fragments in **1** with that of the corresponding two bidentate $[(PtPEt_3)_2(\mu_2\text{-}CO)]$ fragments in **2**.

The means of the 12 radial Pt(i)−Pt(cage) and 30 tangential Pt(cage)−Pt(cage) distances of 2.71 and 2.85 Å, respectively, in **1** compare favorably with those of 2.70 and 2.84 Å, respectively, reported[10] for **2**. These observed radial compressions of 4.9% in both **1** and **2** [e.g., (2.85−2.71 Å/2.85 Å) × 100 in **1**] are virtually identical with the predicted value of approximately 5% for a geometrically regular centered icosahedron and furthermore are completely consistent with experimental values determined for centered Pd_{13} icosahedra in Pd_{16} , Pd_{35}, Pd_{39}, Pd_{59}, Pd_{69}, and Pd_{145} carbonyl/phosphine clusters.[9] In fact, the above means in **1** and **2** are significantly smaller than the identical means of 2.74 and 2.88 Å found for the corresponding radial Pd(i)−Pd(cage) and tangential Pd(cage)−Pd(cage) distances in the centered Pt_{13} icosahedron of the isostructural $Pd_{16}(CO)_{13}(PMe_3)_9$[9a] and $Pd_{16}(CO)_{13}(PEt_3)_9$.[9b] These bond-length differences of 0.03−0.04 Å between corresponding Pt−Pt and Pd−Pd bonding interactions are not surprising in light of the cohesive energy being considerably greater in platinum metal (565 kJ mol^{-1}) than that in palladium metal (377 kJ mol^{-1}).[15]

The bidentate $[Ph_3PAu{-}AuPPh_3]$ capping unit in **1** has a Au−Au separation of 3.131(1) Å indicative of a weak but definite Au−Au bonding interaction corresponding to a six-center interaction of its bonding electron pair with the four Pt atoms of the two adjacent edge-fused triangles.[16−18] Nevertheless, its designation (based upon the condensation capping rule[19]) as a two-electron donor results in the observed number of cluster valence electrons (CVEs) for the central Pt_{13} icosahedron in **1** being 162 CVEs (viz., 13 × 10[Pt] + 2 × 2[$Au_2(PPh_3)_2$] + 10 × 2[CO] + 4 × 2[PPh_3]). An analogous consideration of each bidentate $[(PtPEt_3)_2(\mu_2\text{-}CO)_2]$ fragment in **2** as a two-electron donor also gives rise to an electron count of 162 CVEs. This same lower electron count of 162 CVEs (compared to a normal icosahedral electron count of 170 CVEs) is observed in other complete centered icosahedra including the Pd(i)-centered Pd_{12} cage in neutral $[Pd_{16}(CO)_{13}(PR_3)_9]$ (R = Me,[9a] Et[9b]), the classic Au-centered Au_{12} cage in $[(\mu_{12}\text{-}Au)(AuPMe_2Ph)_{10}(AuCl)_2]^{3+}$ $([PF_6]^-$ salt),[20a] and other centered coinage-metal cages.[20,21]

Mingos[19] pointed out that this lower electron count should occur for a 13-atom centered icosahedron where radial bonding dominates. The same lower electron count is obtained via the Teo/Zhang approach[22] when a smaller skeletal electron-pair B value of 9 (instead of 13) is used for the centered icosahedron. Teo et al.[22c] emphasize that the weakening of the tangential bonding in these electron-deficient clusters (with $B = 9$) is primarily due to relativistic effects of Au and Pt.

Attempts to prepare the PEt_3 analogue of **1** were unsuccessful. The two bulky-sized bidentate $[Ph_3PAu{-}AuPPh_3]$ capping ligands in **1**, which are spatially analogous to the corresponding two bidentate $[(PtPEt_3)_2(\mu_2\text{-}CO)]$ capping ligands in **2**, are presumed to be necessary components of their ligand polyhedra in being sufficiently large to offer steric protection of the encapsulated Pt(i)-centered icosahedral Pt_{12} cage in **1** and **2** against chemical predators.

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Supporting Information Available: Table 1 that presents distances under pseudo-D_{2h} symmetry, Figure 2 that gives the atom labeling of the metal-core fragments of **1** and **2**, an atomic ellipsoidal figure of **1**, and CIF for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) IR spectra (Nujol) of **1** display one very strong, broad terminal carbonyl band at 1956 cm^{-1} with a shoulder at 1947 cm^{-1} and a considerably weaker but sharp bridging carbonyl band at 1738 cm^{-1}. The reported IR spectrum (Nujol) for **2** has two strong terminal carbonyl bands at 1963 and 1944 cm^{-1} and one strong bridging carbonyl band at 1728 cm^{-1} with a shoulder at 1720 cm^{-1}.[10]

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(16) This bidentate fragment in **1**, which is isolobal with dihydrogen,[17] was initially observed crystallographically in a $Pt(AuPPh_3)_2$ cluster,[18] in which the Au−Au connectivity of 2.737(3) is even shorter than that in gold metal. The much longer Au−Au connectivity in **1** is mainly a geometrical consequence of each 13-electron $AuPPh_3$ entity in the bidentate $[(AuPPh_3)_2]$ unit capping a Pt_3 triangle.

(17) For a recent excellent review of metal−H_2 bonding, see: Kubas, G. J. *Adv. Inorg. Chem.* **2004**, *56*, 127.

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(21) The icoshedra are the Pd-centered Au_{12} cages in neutral $[(\mu_{12}\text{-}Pd)(AuPPh_3)_8(AuCl)_4]$[20b] and $[(\mu_{12}\text{-}Pd)(AuPPh_3)_6(Au_2dppe)(AuCl)_4]$,[20c] the Au-centered Au_8Ag_4 cages in $[(\mu_{12}\text{-}Au)(AuPMePh_2)_8(AgX)_4]^+$ (X = Cl,[20d] Br[20e]), and the Pt-centered Au_6Ag_6 cage in neutral $[(\mu_{12}\text{-}Pt)(AuPPh_3)_6(Ag(\mu_2\text{-}I)_6(\mu_3\text{-}Ag)_2]$.[20f]

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