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An Unprecedented High-Nuclearity Closest-Packed Bimetallic Palladium Carbonyl Cluster: $[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}$ Containing a Pseudo-D_{3h} hcp $Pd_{33}Ni_9$ Core

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During the last several years we have extended our exploratory research involving the preparation and physicochemical characterization of large metal clusters from nickel carbonyl clusters with bridging main-group IV (14), V (15), or VI (16) atoms[2] and high-nuclearity platinum carbonyl clusters (including new ones with closest-packed Pt_{35}, Pt_{44}, and Pt_{50} cores[3]) to bimetallic clusters including Au−Ni[4] and Pd−Ni carbonyl species. As previously found[3] for a number of other new isolated platinum carbonyl clusters, we also encountered great difficulties in obtaining appropriate crystals of Pd−Ni clusters for successful single-crystal X-ray diffraction analyses; the crystals were too small and/or weakly diffracting. However, the recent availability of a new-generation, commercial charge-coupled-device (CCD) area detector diffractometry system for use with Mo Kα radiation has been a crucial factor in our obtaining complete structural determinations of the first known close-packed bimetallic Pd−Ni clusters as well as new large palladium clusters with carbonyl/phosphine ligands. Herein we report the preparation, isolation, and structural determination of a remarkable high-nuclearity bimetallic Pd−Ni cluster, $[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}$ (**1**). This investigation has particular significance in that palladium is utilized as a heterogeneous catalyst in a wide variety of commercial reactions,[5] and its use as a hydrogen storage system has been extensively studied.[6] Furthermore, $PdNi_x$ alloys encaged in NaY zeolite were recently shown by Sachtler and co-workers[7] to possess marked selectivity differences in CO hydrogenation compared with monometallic Pd/NaY and Ni/NaY samples and their physical mixtures.

Unlike its nickel and platinum congeners, palladium *per se* does not form stable pure discrete carbonyl clusters.[8] Nevertheless, extensive studies[9,10] have produced a variety of large neutral homopalladium carbonyl phosphine clusters; crystallographically characterized compounds,[10] for which their structural-bonding features have been analyzed,[11] include Pd_n species with $n = 7$, 8, 10, 16, 23 (two different kinds), 34, and 38. In addition, several giant-sized ligand-stabilized noncrystalline palladium clusters in the nanoscale regime (i.e., with sizes greater than 10^{-9} m or 10 Å) have been isolated with *idealized* formulations based upon concentric closed-shell metal cores—*viz.*, five-shell Pd_{561} species[12,13] and inseparable mixtures of a seven-shell Pd_{1415} and eight-shell Pd_{2057} species.[14] Prior to our work, the only known high-nuclearity heterometallic carbonyl clusters containing palladium were the isostructural $[HFe_6Pd_6(CO)_{24}]^{3-}$ trianion[15a] and $[Ru_6Pd_6(CO)_{24}]^{2-}$ dianion[15b] and the $[Au_2Pd_{14}(CO)_9(PMe_3)_{11}]^{2-}$ dianion.[15c] To date, the high-nuclearity bimetallic carbonyl cluster possessing the largest number of close-packed metal-core atoms is $[H_{6-n}Pt_6Ni_{38}(CO)_{48}]^{n-}$ ($n = 4$, 5).[15d] Particularly noteworthy are the extensive investigations of metal carbonyl clusters as precursors for tailored metal catalysts;[16a] these include the use of SiO_2-supported $[HFe_6Pd_6(CO)_{24}]^{3-}$ to generate an Fe−Pd bimetallic catalyst that exhibited high selectivity toward methanol synthesis from CO/H_2 reactions.[16b]

The $Pd_{33}Ni_9$ cluster (**1**) was isolated as the $[PPh_4]^+$ salt in yields as high as 24% from the reduction of $Pd(PPh_3)_2Cl_2$ with the $[Ni_6(CO)_{12}]^{2-}$ dianion.[17] The entire crystal structure of $[PPh_4]^+{}_4[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}\cdot 3MeCN\cdot 5Me_2CO$ was unambiguously determined from an X-ray crystallographic analysis[18] via the SMART CCD area detector system in conjunction with a standard Mo sealed-tube generator. The stoichiometry of **1** established by the X-ray structural determination was

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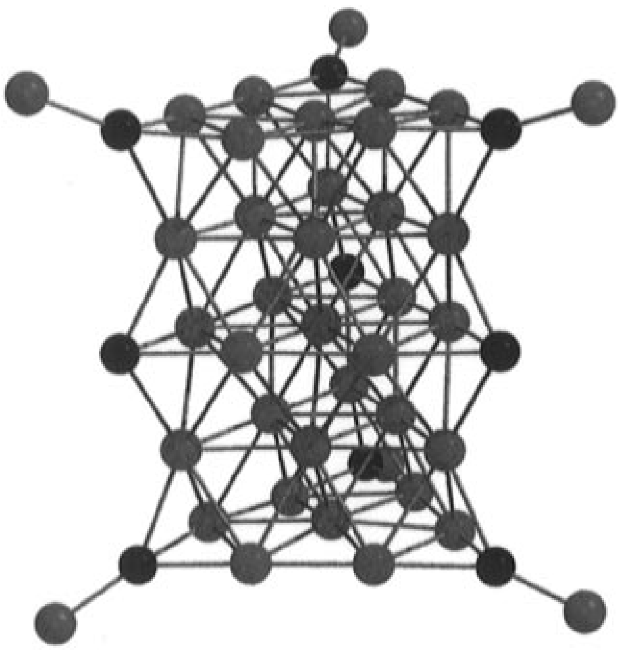

Figure 1. Pseudo-D_{3h} $Pd_{33}Ni_9$ core (with Ni-attached P atoms) of $[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}$: Pd (red), Ni (blue), and P (green).

ascertained from an elemental analysis.[19] This compound was also characterized by IR and $^{31}P\{H\}$, ^{1}H NMR measurements.[19]

The tetraanion (**1**) of crystallographic C_2-2 site symmetry consists of a $Pd_{33}Ni_9$ core of pseudo D_{3h}-$\bar{6}2m$ symmetry (Figure 1). Its unique metal-core geometry may be readily described as a hcp 42-atom aggregate composed of 5 stacked triangular layers with 1 interior (encapsulated) Pd atom in the middle layer and 41 surface metal atoms. The 3 bottom, middle, and top 10-atom triangular Pd_7Ni_3 layers are identical with 3 nickel atoms at the corners and 7 palladium atoms at the other positions of each equilateral triangle. A horizontal crystallographic 2-fold axis passes through the one interior Pd atom, one Ni atom, and its attached terminal carbonyl ligand of the middle layer such that one-half the cluster is crystallographically independent. The symmetry-related second and fourth six-atom triangular layers are composed entirely of Pd atoms. The entire $Pd_{33}Ni_9$ core has 12 octahedral and 28 tetrahedral holes.

The six triphenylphosphine ligands are attached to the six corner nickel atoms in the top and bottom layers. The 41 carbonyl groups consist of 5 terminal and 36 bridging ligands. The terminal COs are coordinated to the three corner Ni atoms in the middle layer and to the two central Pd atoms in the top and bottom layers. Of the 36 bridging COs, 24 are edge-bridging and the other 12 are face-bridging.

Considerable variations are observed in both the 114 Pd−Pd distances (range, 2.695(1)−3.024(1) Å; mean, 2.82 Å) and 30 Pd−Ni distances (range, 2.555(2)−2.710(2) Å; mean, 2.64 Å) within the $Pd_{33}Ni_9$ core; the mean Pd−Pd distance is 0.07 Å longer than that found in ccp Pd metal (2.751 Å).[20] As expected, the Pd−Pd and Pd−Ni distances adhere reasonably closely (i.e., generally within 0.1 Å) to pseudo-D_{3h} symmetry. The different bonding modes of the 36 bridging carbonyl ligands play an important role in influencing the metal−metal distances.

The observed number of metal cluster valence electrons (CVEs) in this hcp cluster, which may be considered to possess globally delocalized metal−metal bonding, is 518 (i.e., 33 × 10 (Pd) + 9 × 10 (Ni) + 41 × 2 (CO) + 6 × 2 (PPh_3) + 4 (charge) = 518). This number is in exact agreement with the predicted number of CVEs obtained by the combined application of the electron-counting Shell model and inclusion principle,[21] as illustrated by Teo and Zhang[21d] for other closed-packed metal clusters with an interior atom (i.e., as observed for the $Pd_{33}Ni_9$ skeleton).[22] The observed electron count for **1** is also consistent with that based upon the PSEP theory developed by Mingos[23] for high-nuclearity close-packed metal clusters.[24]

The $[PPh_4]^+$ salt of **1** is air-sensitive, especially in solution; powder samples are soluble in acetonitrile and DMSO and slightly soluble in acetone. The observed IR bands at 1998 and 1883 cm^{-1} in acetonitrile solution are readily assigned to the terminal and bridging carbonyl ligands, respectively. No signals corresponding to hydride-like atoms were detected in ^{1}H NMR spectra (CD_3CN) at room temperature over a ±50 ppm range; in addition, these spectra showed no paramagnetic shifts of the phenyl proton resonances. Room-temperature ^{31}P NMR spectra (with and without proton decoupling) of **1** in CD_3CN exhibited one signal for the six Ni-attached PPh_3 substituents and one signal for the four $[PPh_4]^+$ counterions.

At this time we are pursuing the characterization of the other major product of this reaction (isolated from an acetone extraction) as well as investigations of the physicochemical properties of **1** including its variable-temperature magnetic and electrochemical behavior and protonation/dihydrogen reactions. This research has also inspired extensive current studies of related reactions including the formation of heteropalladium clusters with other metals. Details will be forthcoming.

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Supporting Information Available: Anisotropic atomic thermal ellipsoid figure of **1** and tables listing crystallographic data (29 pages). Ordering information is given on any current masthead page.

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(17) A slurry of $Pd(PPh_3)_2Cl_2$ (0.83 g; 1.18 mmol) in 20 mL of DMSO and 5 mL of CH_2Cl_2 was slowly added to $[NMe_4]^+{}_2[Ni_6(CO)_{12}]^{2-}$ (0.50 g; 0.60 mmol) in 15 mL of DMSO under a N_2 atmosphere at room temperature over 15−20 min and stirred for 5 h. PPh_4Br (3.50 g; 8.35 mmol) was then added to the resultant solution, which had turned from dark red to dark yellow-brown. A slow addition of water to the ice-cooled solution gave rise to a black precipitate which was filtered and washed with water, methanol, and THF. Black microcrystalline $[PPh_4]^+{}_4$ $[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}$ (0.07 g; 24% yield based on $Pd(PPh_3)_2Cl_2$) was isolated from an acetonitrile extraction. This compound was recrystallized from an acetone/acetonitrile mixture via layer diffusion with *i*-Pr_2O.

(18) $[PPh_4]^+{}_4[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}\cdot 3MeCN\cdot 5Me_2CO$: monoclinic, $C2/c$, $a = 22.761(2)$ Å, $b = 29.584(2)$ Å, $c = 40.844(3)$ Å, $\beta = 102.213(3)°$, $V = 26\,881(3)$ Å^3, $Z = 4$. A hemisphere of 55 534 data was collected during *ca*. 14 h via 0.3 ω scans over a 2θ range of 2.3−47.0°; an empirical absorption correction from ψ scans was applied to the data ($\mu = 2.885$ mm^{-1} for Mo Kα radiation). Structural solution by direct methods and anisotropic least-squares refinement (based on F^2) were performed with SHELXTL (version 5, 1994). This refinement (1605 parameters/24 restraints) on 19 366 independent merged reflections converged at $R_1(F) = 0.12$, $\omega R_2(F^2) = 0.17$ for all data; $R_1(F) = 0.088$, $\omega R_2(F^2) = 0.15$ for 14 844 observed data ($I > 2\sigma(I)$).

(19) Anal. by DESERT ANALYTICS (Tucson, AZ) of black crystals obtained from MeCN/*i*-Pr_2O layering, $[Ph_4P]^+{}_4[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}\cdot CH_3CN$ (FW = 8160.97), Calcd (found): C, 36.35 (36.16); H, 2.14 (2.40); N, 0.17 (0.26); Ni, 6.47 (6.75); Pd, 43.03 (46.57). IR (acetonitrile; CaF_2); ν(CO), cm^{-1}: 1998 (s), 1883 (vs, asymmetric). $^{31}P\{^{1}H\}$ NMR (202.3 MHz, CD_3CN at 23 °C, 85% H_3PO_4 external; *d*, ppm): 21.78 ([*P*Ph_4]$^+$), 38.36 (*P*Ph_3]). ^{1}H NMR (500 MHz, CD_3CN at 23 °C: multipet, 7.2−8.0 ppm (C_6H_5 of $[PPh_4]^+$ and PPh_3).

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(22) For a close-packed high-nuclearity metal cluster, the calculated electron count is $N = 2T_n = 2(6S_n + B_n)$, where T_n denotes the total number of topological electron pairs, S_n the total number of surface atoms, and B_n the number of shell electron pairs.[21d] In the case of the $Pd_{33}Ni_9$ cluster (**1**), $S_n = 41$ and $B_n = T_i = 13$ (inclusion principle), where $T_i = 6S_i + B_i = (6 \times 1) + 7 = 13$ for a cluster centered at 1 interior Pd atom ($S_i = 1$) that is completely encapsulated by 12 neighboring Pd atoms in a localized hcp arrangement (for which $B_i = 7$).[21d] Thus, $N = 2((6 \times 41) + 13) = 518$ electrons for **1**.

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(24) This model states that the total valence electron count, N, is given by $\Delta_i + 12n_s$, where Δ_i is the central fragment count (*viz.*, 170 for a centered 13-atom *anti*-cuboctahedron (hcp)) and n_s is the number of surface atoms (*viz.*, 29). Thus, $N = 170 + 12(29) = 518$ electrons for **1**.