

H₁₂Pd₂₈(PtPMe₃)(PtPPh₃)₁₂(CO)₂₇, a High-Nuclearity Pd₂₈Pt₁₃ Cluster Containing 12 Hydrido Atoms: A Possible Molecular Hydrogen-Storage Model for Palladium Metal

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Received February 19, 1997

Exploratory investigations in our laboratories over the last several years have given rise to the synthesis, isolation, and physical/chemical characterization of a considerable number of new high-nuclearity monometallic, bimetallic, and trimetallic palladium carbonyl clusters, of which the vast majority possess unprecedented metal architectures. A recent report¹ describes the preparation, structure/bonding analysis, and physical properties of the remarkable [Pd₃₃Ni₉(CO)₄₁(PPh₃)₆]⁴⁻ tetraanion which contains a pseudo-D_{3h} hcp Pd₃₃Ni₉ core.

Herein we report the preparation, isolation, and stereo-physical analysis of another bimetallic palladium cluster, H₁₂Pd₂₈(PtPMe₃)(PtPPh₃)₁₂(CO)₂₇ (**1**). This 41-atom Pd₂₈Pt₁₃ cluster (**1**) is the first reported example of a high-nuclearity palladium–platinum cluster. Of special interest is that ¹H NMR solution data coupled with an initial D₂-exchange study provide compelling evidence for the presence in **1** of 12 hydrido atoms that are presumed to occupy the 12 available octahedral-like Pd₅Pt sites. The D₂-exchange results also indicate that this cluster may be viewed as a possible molecular model for the actual storage of tritium atoms in palladium metal.² Palladium compounds including several giant-sized ligand-stabilized non-crystalline Pd₅₆₁ clusters (in the nanoscale domain)^{3,4} are widely used both as heterogeneous and homogeneous catalysts in a diversity of organic reactions;⁵ hence, the possible utilization of **1** as a catalytic precursor⁶ is also of interest.

1 was prepared in 10–20% yields from the reaction of PtCl₂(PMe₃)₂ and PdCl₂(PPh₃)₂ with the [Ni₆(CO)₁₂]²⁻ reductant in DMSO at room temperature.⁷ The entire crystal structure for the non-hydrogen atoms in H₁₂Pd₂₈(PtPMe₃)(PtPPh₃)₁₂(CO)₂₇·5THF was unambiguously determined⁸ by use of the SMART CCD area detector system mounted on a Siemens P4 diffrac-

tometer together with a standard Mo sealed-tube generator. Although the five independent solvated THF molecules were crystallographically disordered, no evidence for any crystal-disorder of **1** was observed. The stoichiometry of **1** established by the X-ray crystallographic study was ascertained from an elemental analysis.⁹ This neutral compound was also characterized by IR, CV, and ¹H, ¹³C{¹H} NMR measurements.⁹

The molecular geometry of **1**, which closely conforms to pseudo-C_{3v} symmetry, is composed of a four-layer hcp Pd₂₈-Pt core (viz., Pd₃, Pd₇, Pd₁₂, and PtPd₆ layers) that contains four tetrahedrally-linked interior Pd(i) atoms each with a localized hcp environment (Figure 1). The pseudo 3-fold axis passes through one Pd(i), the bottom-layer centered Pt, and its attached PMe₃ ligand. The Pd₂₈Pt core has 12 highly distorted square-pyramidal Pd₅ cavities each capped by an external PtPPh₃ fragment.^{10,11} The 27 COs consist of 18 doubly bridging and nine triply bridging ligands.

The initial observed number of metal cluster valence electrons (CVEs) in the hcp Pd₂₈Pt core of **1** (excluding the crystallo-

(7) A yellow slurry of PtCl₂(PMe₃)₂ (0.25 g, 0.57 mmol) and PdCl₂(PPh₃)₂ (0.75 g, 1.07 mmol) in 25 mL of DMSO was added to [PPh₃Me]₂[Ni₆(CO)₁₂] (1.0 g, 0.81 mmol) under a N₂ atmosphere at room temperature and stirred for 24 h, at which time the solution turned to a deep brown color. A slow addition of water to the ice-cooled solution resulted in a brown precipitate which was filtered and washed several times with water and water/methanol solutions. The remaining solid was then extracted sequentially with hexane, toluene, THF, and acetone. After separation from other materials via THF extraction followed by column chromatography (silica gel), small dark brown crystals of **1** were obtained from vapor diffusion of diethyl ether into a concentrated THF solution.

(8) H₁₂Pd₂₈(PtPMe₃)(PtPPh₃)₁₂(CO)₂₇·5THF: triclinic, P1, *a* = 21.685(4) Å, *b* = 21.710(4) Å, *c* = 36.814(7) Å, α = 99.06(3)°, β = 96.38(3)°, γ = 119.77(3)°, *V* = 14,490(5) Å³, *Z* = 2, *d*(calcd) = 2.32 Mg/m³. Data (70 709, from 2400 frames) were acquired during ca. 30 h from a small block-shaped crystal (0.04 × 0.05 × 0.10 mm) at 133(2) K via 0.3 φ scans over 2θ = 2.1–47.0°; empirical absorption correction (SADABS) applied (μ = 8.06 mm⁻¹ for Mo Kα radiation). Structural solution by direct methods and least-squares refinement (anisotropic atoms for Pd₂₈Pt₁₃(CO)₂₇; isotropic atoms for 36 Ph, 3 Me, and five disordered THF species) performed with SHELXTL (version 5, 1994). This refinement (1545 parameters/845 restraints) on 37 300 independent merged reflections (*R*_{int} = 0.074) converged at *R*₁(*F*) = 0.17, *wR*(*F*²) = 0.29 for all data; *R*₁(*F*) = 0.10, *wR*(*F*²) = 0.20, *GOF*(*F*²) = 1.084 for 31 954 observed data (*I* > 2σ(*I*)).

(9) Anal. by Desert Analytics (Tucson, AZ). H₁₂Pd₂₈(PtPMe₃)(PtPPh₃)₁₂(CO)₂₇ (FW = 9507.1). Calcd (Found): Pt, 26.78 (26.05); Pd, 31.45 (30.94); P, 4.25 (4.32); Ni, 0.00 (<0.1). IR (THF; KBr) exhibited three bridging carbonyl bands at 1859 (vs), 1785 (sh), 1741 (m) cm⁻¹. CV (BAS100; 500 mV/s) in acetonitrile (0.1 M TBAPF₆ as supporting electrolyte) at Pt disc electrode displayed four irreversible oxidation waves between +0.5 and +1.5 V and a broad irreversible reduction wave at ca. -1.0 V (vs SCE). Both ¹H (RD, 2s; NS, 2760; SW, 20 000 Hz) and ¹³C{¹H} (RD, 1s; NS, 3000; SW, 18 000 Hz) NMR (360 MHz, CD₃CN at 23°C): (a) 12 PtC₆H₅₃ (¹H: d 6.87, 7.12, 7.34 ppm; ¹³C: d 136.3, 135.7, 134.3, 131.3 ppm). (b) 1 PMe₃ (¹H: d 1.62 ppm; ¹³C: d 41.4 ppm), [J(P–H) 11.23 Hz; J(P–C) 12.35 Hz] (c) 12 equivalent hydrido-like protons (pseudotriplet at δ = -16.4 ppm with integrated intensities of 1.94:8.10:2.00 versus that of 9.06 for the single ¹H resonance of 1 PMe₃); this signal is ascribed to a doublet (Δ*v*_{1/2} = 4.6 Hz) with [J(Pt–H) 400 Hz] from proton coupling to one ¹⁹⁵Pt (*I* = 1/2, 33.8%) and a central peak (Δ*v*_{1/2} = 23.0 Hz) from no proton coupling to one nonmagnetic Pt isotope (66.8%). Acetonitrile-*d*₃ solution of **1** was transferred to a new NMR tube which was frozen before N₂ was removed by vacuum. After addition of 300 Torr of D₂ gas, the tube was flame-sealed, then warmed to room temperature, and vigorously shaken for 15 min; a subsequent ¹H NMR spectrum acquired three hours later revealed only the hydrido pseudotriplet signal to be markedly reduced by ca. 80% in intensity with all other resonances essentially unchanged.

(10) Under pseudo-C_{3v} symmetry for the Pd₂₈Pt core in **1**, each of the three symmetry-related individual metal–metal connectivities among the Pt, the four internal Pd(i), and 24 surface Pd(s) atoms is within 0.02 Å of their mean. However, considerable variations are observed between the 2 Pd(i)–Pd(i) means (2.65 and 2.80 Å; 2.72 Å (av)), among the 11 Pd(i)–Pd(s) means (2.76–3.07 Å; 2.86 Å(av)), and among the 18 Pd(s)–Pd(s) means (2.71–3.19 Å; 2.83 Å(av)); these large differences are attributed to the extensive deformation of the Pd₂₈Pt core from pseudo-C_{3v} symmetry due to the unusual formation of 12 irregularly-shaped square-pyramidal Pd₅ cavities, such that the four independent ones (under C₃ symmetry) are markedly different in geometrical dimensions from one another. The average Pd–Pd means as well as the one Pt–Pd(i) mean (2.82 Å) and the two Pt–Pd(s) means (2.68 and 2.83 Å; 2.75 Å(av)) are similar to the distances found in ccp Pd metal (2.75 Å)¹¹ and ccp Pt metal (2.77 Å).¹¹

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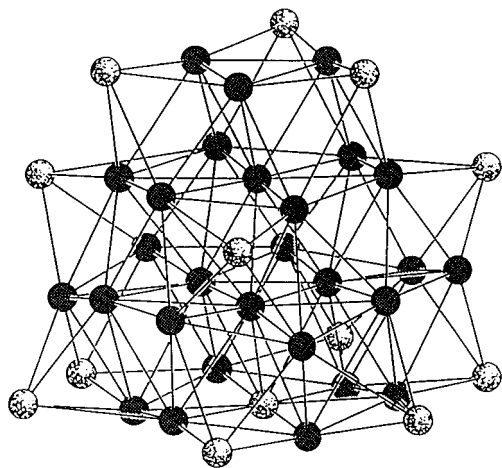


Figure 1. Pseudo- C_3 hcp $Pd_{28}Pt$ core (consisting of four Pd_3 , Pd_7 , Pd_{12} , and $PtPd_6$ layers) of $H_{12}Pd_{28}(PtPMe_3)(PtPPh_3)_{12}(CO)_{27}$ with 12 external Pt atoms capping the 12 markedly deformed square-pyramidal Pd_5 cavities: Pd (black) and Pt (speckled).

graphically undetected 12 hydrido-like H atoms) is 346 (i.e., 28×10 (Pd) + 1×10 (Pt) + 1×2 (PMe_3) + 27×2 (CO) + 12×0 ($PtPPh_3$) = 346). Particularly noteworthy is that this number is 14 electrons less than the calculated number of 360 electrons for the CVEs obtained from the use of either the Teo/Zhang model^{12,13} or the Mingos PSEP model^{14,15} for high-nuclearity close-packed metal clusters. This predicted tremendous electron deficiency in **1** was the catalyst which instead suggested that this cluster additionally has crystallographically undetected hydrido atoms. A subsequent 1H NMR spectrum⁹ of **1** revealed a high-field pseudotriplet resonance ($\delta = -16.4$ ppm) of an expected 1:4:1 ratio due to the interaction of each equivalent hydrido atom with one Pt isotope—viz., a doublet arising from the coupling with one ^{195}Pt isotope ($I = 1/2$; natural abundance, 33.8%) superimposed upon a central peak arising from no coupling with one nonmagnetic Pt isotope (viz., ^{192}Pt , 0.8%; ^{194}Pt , 32.9%; ^{196}Pt , 25.3%; ^{198}Pt , 7.2%; with $I = 0$; total natural abundance, 66.2%). The resulting 11.96/9.00 intensity ratio for the entire integrated pseudotriplet signal versus the integrated singlet resonance due to the nine protons of the one PMe_3 ligand provides convincing evidence for the presence in **1** of 12 hydrido-like hydrogen atoms. The revised electron count of $346 + 12 = 358$ electrons is now in essential agreement with the calculated value of 360 electrons based upon the two electron-counting models.

To our knowledge, no other structurally determined, discrete transition-metal cluster has as many hydrido atoms. Of prime significance is that the solution reaction of **1** with D_2 reduced the intensity of the pseudotriplet hydrido signal by ca. 80%

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(13) The calculated electron count given by application of the Teo/Zhang model^{12a} for a close-packed metal cluster is $N = 2T_n = 2(6S_n + B_n)$, where T_n designates the total number of topological electron pairs, S_n the total number of surface atoms, and B_n the number of shell electron pairs. For the hcp $Pd_{28}Pt$ core in **1**, $S_n = 25$ and $B_n = T_i = 30$ for an interior bonding $Pd(i)_4$ tetrahedron (inclusion principle); hence, $N = 12(25) + 2(30) = 360$ electrons. Alternatively, the same calculated number of CVEs can be obtained from utilization of the Teo/Sloane shell model,^{12b-d} for which $N = 2T_n = 2(6G_n + K)$, where G_n denotes the total number of atoms, and K is related to the B value at the cluster center. For a bonding $Pd(i)_4$ tetrahedron centered at a tetrahedral hole, $K = 6$; hence, $N = 12(29) + 2(6) = 360$ electrons.

(14) Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1985**, 1352.

(15) For high-nuclearity close-packed metal clusters with primarily radial interactions between the interior and surface metal atoms, the Mingos model¹⁴ presumes that the total valence electron count, N , is equal to $\Delta_i + 12n_s$, where Δ_i and n_s are the central fragment count and number of surface atoms, respectively. For the hcp $Pd_{28}Pt$ core in **1**, $\Delta_i = 60$ for the bonding interior $Pd(i)_4$ tetrahedron and $n_s = 25$; hence, $N = 60 + 12(25) = 360$ electrons.

(without significantly affecting the intensities of the other 1H resonances);⁹ this initial work indicating that most of the H atoms are exchanged by D atoms is consistent with the premise that this molecular cluster may be an appropriate hydrogen-storage model for palladium metal. The proposed location of the 12 H atoms in the 12 square-pyramidal Pd_5 cavities capped by the 12 $PtPPh_3$ fragments (rather than at external Pt-Pd edge- and/or $PtPd_2$ face-capping positions) is consistent with a recent neutron diffraction analysis of the $[H_2Rh_{13}(CO)_{24}]^{3-}$ trianion^{16,17} which conclusively showed that the two hydrogen atoms are approximately located at the centered positions in two of the six square-pyramidal cavities of the hcp Rh_{13} core.^{18,19}

Further characterization of this intriguing cluster is planned including detailed investigations of its variable-temperature NMR spectroscopic, magnetic susceptibility, and D_2/H_2 -exchange behavior and its source of H atoms.

Acknowledgment. This research was financially supported by the NSF (Grant CHE-9310428). Departmental purchases of the CCD area detector system and the AM360 NMR spectrometer were made possible by funds from NSF (Grants CHE-9310428 and CHE-8306121, respectively) and the Graduate School of UW-Madison. We are grateful to Dr. Randy Hayashi and Dr. Douglas Powell for helpful crystallographic advice and to Professor Tom Farrar, Professor Clark Landis, and Dr. Charles Fry for informative NMR spectroscopic discussions. We are also pleased to acknowledge Alfa AESAR/A Johnson Matthey Company (Ward Hill, MA) for their University Metal Loans Program in providing a sample of chloroplatinic acid.

Supporting Information Available: Anisotropic atomic thermal ellipsoid figure of **1** and tables listing crystallographic data (47 pages). See any current masthead page for ordering and Internet access instructions.

JA970528C

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(17) The observed number of CVEs (viz., 170) in $[H_2Rh_{13}(CO)_{24}]^{3-}$ is in exact agreement with the predicted value of 170 from both the Teo/Zhang and Mingos electron-counting models.^{12a,14}

(18) Although several other hydrido metal clusters^{19a-c} were likewise shown from neutron diffraction studies to contain their H atoms within octahedral-like metal holes, the H atoms for additional ones^{19d-g} containing at least one octahedral-like cavity are instead distributed only on metal surface sites.

(19) (a) $[HCO_6(CO)_{15}]^-$: Hart, D. W.; Teller, R. G.; Wei, C.-Y.; Bau, R.; Longoni, G.; Campanella, S.; Chini, P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1981**, *103*, 1458. (b) $[HRu_6(CO)_{18}]^-$: Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; McPartlin, M.; Nelson, W. J. H.; Rouse, K. D.; Allibon, J.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1980**, 295. (c) $[H_nNi_{12}(CO)_{21}]^{n-4}$ ($n = 1, 2$): Broach, R. W.; Dahl, L. F.; Longoni, G.; Chini, P.; Schultz, A. J.; Williams, J. M. *Adv. Chem. Ser.* **1979**, *167*, 93. (d) $[HRh_6(CO)_{15}]^-$ (terminal position via multinuclear NMR): Heaton, B. T.; Strona, L.; Martinengo, S.; Strumolo, D.; Goodfellow, R. J.; Sadler, I. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1499. (e) $H_2Cu_6(P(p\text{-tolyl})_3)_6$ (face-capping positions): Stevens, R. C.; McLean, M. R.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1989**, *111*, 3472. (f) $[H_4Os_{10}(CO)_{24}]^{2-}$ (two edge-bridging and two face-capping positions): Bashall, A.; Gade, L. H.; Lewis, J.; Johnson, B. F. G.; McIntyre, G. J.; McPartlin, M. *Angew. Chem., Int. Ed., Engl.* **1991**, *30*, 1164. (g) $[H_5Zr_6Cl_{18}]^{3-}$ (face-capping positions): Cotton, F. A.; Chen, L.; Schultz, A. J. *C. R. Acad. Sci. Paris, t. 323, Série IIb*, **1996**, 539.

(20) If the 12 1H in **1** are encapsulated within the 12 octahedral-like $PtPd_5$ cavities, quadrupolar broadening effects due to coupling with the ^{105}Pd isotope ($I = -5/2$; 22.3%) would be expected for both the central and doublet peaks of the pseudotriplet signal. At this time we cannot rationalize the unusually large observed line width variation between the central and doublet peaks, corresponding to an apparent difference in $J(Pd-H)$ coupling between the central peak (ca. 6 Hz) and the outer two lines (<1 Hz); one possible explanation is that the 12 H atoms do not occupy the 12 octahedral-like $PtPd_5$ holes but are instead distributed on metal surface sites.