Volume 29
Number 18
September 5, 1990

Inorganic Chemistry

# Communications

## Hydrogen-Rich Metal Cluster Complexes. Hexahydrido Platinum–Osmium Carbonyl Cluster Complexes from the Reaction of $Pt_2Os_4(CO)_{18}$ with Hydrogen

The ability of the transition metals to activate hydrogen is a central feature in their use as hydrogenation catalysts[1] and as hydrogen storage materials.[2] To date, there are only a few examples of polynuclear metal complexes $M_xH_y$ ($x \geq 4$; $y \geq 6$) that contain relatively large amounts of hydrogen.[3] As a part of our recent studies of heteronuclear cluster complexes containing platinum,[4] we have investigated the reaction of $Pt_2Os_4(CO)_{18}$ with hydrogen.

From the reaction of $Pt_2Os_4(CO)_{18}$[5] (20.0 mg) with hydrogen (100 atm/25 °C) in 10 mL of $CH_2Cl_2$ solvent, we have isolated the two new compounds $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ (**1**; 32% yield) and $PtOs_5(CO)_{16}(\mu\text{-}H)_6$ (**2**; 11% yield).[6] Both products have been characterized by IR, $^1H$ NMR, and single-crystal X-ray diffraction analysis.[7,8] An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. The cluster can be described as a vertex-shared, Pt(1), bitetrahedron. The two triangular groupings Os(1), Os(2), Os(3) and Os(4), Os(5), Pt(2) have a staggered conformation with respect to each other. The Pt–Os bond lengths to the $Os_3$ triangle are not unusual,[5] 2.699 (2)–2.700 (2) Å. The Pt–Os bond lengths to Os(4) and Os(5) are longer, 2.881 (2) and 2.878 (2) Å, due to the presence of the bridging hydride ligands; see below. The Pt(1)–Pt(2) distance is long, 2.998 (2) Å, but probably contains a significant bonding interaction. Each osmium atom contains three linear terminal carbonyl ligands, while the platinum atom Pt(2) has only two. The existence of six bridging hydride ligands shown in the figure (located but not refined) was confirmed by $^1H$ NMR analysis. At −92 °C in $CD_2Cl_2$ solvent

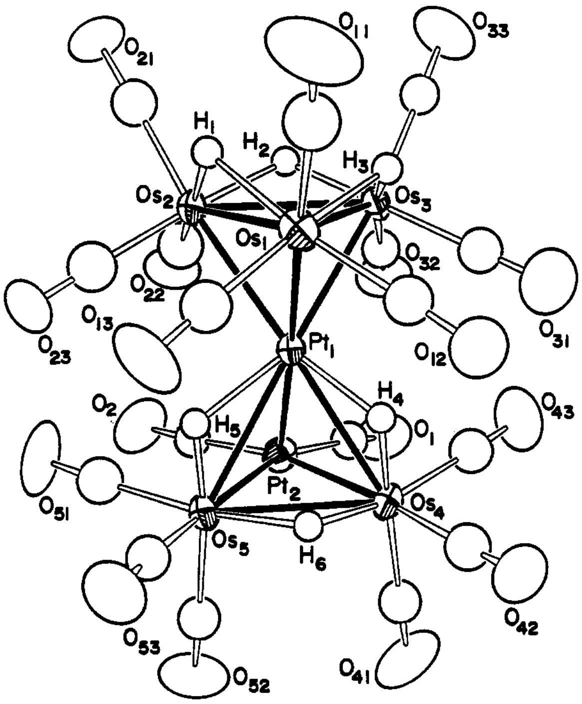


**Figure 1.** ORTEP diagram of $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ (**1**) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å): Pt(1)–Pt(2) = 2.998 (2), Pt(1)–Os(1) = 2.700 (2), Pt(1)–Os(2) = 2.700 (2), Pt(1)–Os(3) = 2.699 (2), Pt(1)–Os(4) = 2.881 (2), Pt(1)–Os(5) = 2.878 (2), Os(1)–Os(2) = 2.861 (2), Os(1)–Os(3) = 2.861 (2), Os(2)–Os(3) = 2.923 (2), Os(4)–Os(5) = 2.939 (2), Pt(2)–Os(4) = 2.698 (2), Pt(2)–Os(5) = 2.693 (2).

---

(1) (a) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (c) Rylander, P. N. *Catalytic Hydrogenation Over Platinum Metals*; Academic Press: New York, 1967.

(2) (a) Sandrock, G. D.; Huston, E. L. *CHEMTECH* **1981**, *11*, 754. (b) Bau, R., Ed. *Transition Metal Hydrides*; Advances in Chemistry Series 167; American Chemical Society: Washington, DC, 1978.

(3) (a) Adams, R. D.; Foust, D. F.; Segmüller, B. E. *Organometallics* **1983**, *2*, 308. (b) Frost, P. W.; Howard, J. A. K.; Spencer, J. L.; Turner, D. G.; Gregson, D. *J. Chem. Soc., Chem. Commun.* **1981**, 1104. (c) Gregson, D.; Howard, J. A. K.; Murray, M.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 716. (d) Frediani, P.; Bianchi, M.; Salvini, A.; Piacenti, F.; Ianelli, S.; Nardelli, M. *J. Chem. Soc., Dalton Trans.* **1990**, 165. (e) Bachechi, F.; Ott, J.; Venanzi, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1760. (f) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 1759. (g) *J. Am. Chem. Soc.* **1983**, *105*, 5137. (h) Lemmem, T. H.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 7774. (i) Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 262.

(4) (a) Adams, R. D.; Chen, G.; Wang, J. G. *Polyhedron* **1989**, *8*, 2521. (b) Adams, R. D.; Chen, G.; Wang, J. G.; Wu, W. *Organometallics* **1990**, *9*, 1339.

(5) Sundberg, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1307.

(6) The products were isolated by TLC on silica gel. IR ($\nu_{CO}$ $cm^{-1}$ in hexane): for **1**, 2090 (m), 2080 (vs), 2068 (w), 2066 (w), 2021 (m), 2011 (m), 1997 (w); for **2**, 2119 (vw), 2096 (m), 2086 (s), 2061 (m), 2041 (m), 2034 (m), 2027 (w), 2021 (m), 2012 (m), 2005 (w), 1994 (vw), 1985 (w).

(7) Dark green crystals of **1** were grown by slow evaporation of solvent from $CH_2Cl_2$/hexane solutions at 10 °C. Crystal data: space group $P2_1/n$, $a = 9.603$ (3) Å, $b = 16.246$ (7) Å, $c = 19.272$ (7) Å, $\beta = 91.49$ (3)°, $Z = 4$. An empirical absorption correction was applied to the data. The structure was solved by direct methods (MITHRIL) and was refined (2751 reflections) to the final residuals $R = 0.042$ and $R_w = 0.043$.

(8) Diffraction measurements were made on a Rigaku AFC6S diffractometer using Mo K$\alpha$ radiation. Calculations were performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Satisfactory elemental analyses have been obtained.

(9) According to the solid-state structure, hydride ligands H(1) and H(3) are not equivalent to H(2). We attribute their spectroscopic equivalence to a dynamical averaging process, such as a rotation of one triangular group Os(1), Os(2), Os(3) relative to other Os(4), Os(5), Pt(2). Efforts to confirm this are in progress. At 25 °C, resonances 1 and 3 show substantial broadening that appears to be related to the onset of yet another dynamical process.

0020-1669/90/1329-3269\$02.50/0

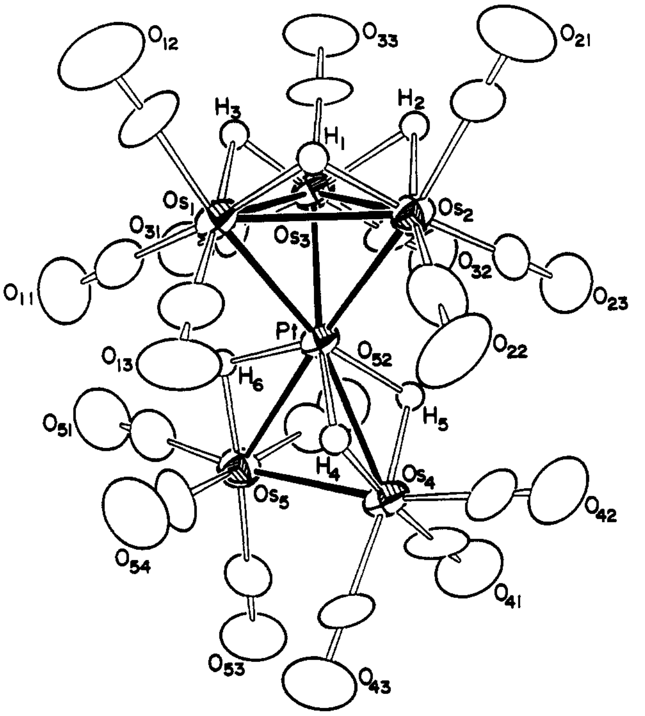


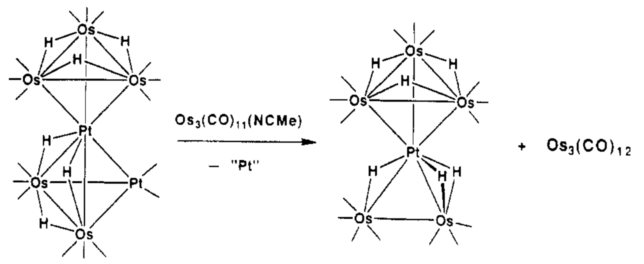
**Figure 2.** ORTEP drawing of $PtOs_5(CO)_{16}(\mu\text{-}H)_6$ (**2**) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å): Pt–Os(1) = 2.689 (1), Pt–Os(2) = 2.664 (2), Pt–Os(3) = 2.684 (1), Pt–Os(4) = 2.703 (2), Pt–Os(5) = 2.954 (2), Os(1)–Os(2) = 2.912 (2), Os(1)–Os(3) = 2.858 (1), Os(2)–Os(3) = 2.911 (1), Os(4)–Os(5) = 2.870 (2).

the spectrum shows three resonances: (1) −9.73 ppm (d, 2 H), $J_{H-H}$ = 2.1 Hz; (2) −17.86 ppm (s, 3 H); (3) −19.66 ppm (t, 1 H), $J_{H-H}$ = 2.1 Hz. Resonance 1 contains satellites due to large coupling to one platinum atom, $^1J_{Pt-H}$ = 714.4 Hz, and small coupling to a second platinum atom, $^2J_{Pt-H}$ = 19.5 Hz. Resonance 1 is thus assigned to the two equivalent hydride ligands H(4) and H(5) shown in Figure 1. Resonance 2 shows small coupling to one platinum nucleus, $^2J_{Pt-H}$ = 16.4 Hz, and is assigned to the three hydride ligands H(1)–H(3) shown in Figure 1. Resonance 3 shows weak coupling to platinum, $^2J_{Pt-H}$ = 24.3 Hz, and is attributed to H(6). These assignments are also consistent with the small H–H couplings.

An ORTEP diagram of **2** is shown in Figure 2.[8,10] The cluster can be viewed as a vertex-shared, Pt, fusion of one tetrahedral $PtOs_3$ group to a triangular $PtOs_2$ group. The Pt–Os lengths to the $Os_3$ triangle are similar to those in **1**, but the Pt–Os(4) distance is unexpectedly short, 2.703 (2) Å, even though it contains *two* bridging hydride ligands. The Pt–Os(5) distance is long, 2.954 (2) Å, as expected since it contains one bridging hydride ligand. The existence of six bridging hydride ligands (located crystallographically, but not refined) was established by $^1H$ NMR spectroscopy. As in **1**, the spectrum of **2** at 25 °C in $CDCl_3$ shows three resonances: (1) −7.48 ppm (s, 2 H); (2) −12.17 ppm (s, 1 H); (3) −17.36 ppm (s, 3 H). Resonance 1 is assigned to H(4) and H(5), on the basis of large coupling to platinum, $^1J_{Pt-H}$ = 653.6 Hz. Resonance 2 is assigned to H(6), $^1J_{Pt-H}$ = 573.2 Hz, and resonance 3 to H(1)–H(3) on the basis of the small coupling to platinum, $^2J_{Pt-H}$ = 22.4 Hz.[11]

Electron counting shows that compound **2** is electron deficient by the amount of two electrons. It contains a total of 88 valence electrons, which is 2 less than the expected value of 90 based on Mingos' theory of condensed polyhedra (i.e. tetrahedron, 60 electrons, plus triangle, 48 electrons, minus shared vertex, 18 electrons).[12] We propose that this electron deficiency is associated with the *short* doubly hydride-bridged bond Pt–Os(4). A similar effect was observed in the well-known and studied 46-electron triangular cluster complex $Os_3(CO)_{10}(\mu\text{-}H)_2$ (**3**).[13] The unsaturation in **3** has been the site of remarkable reactivity that has permitted the synthesis of a wide variety of new compounds and even some examples of cluster catalysis.[13]

Scheme I



Although we have not yet identified the process by which **1** and **2** were formed, we have found that **1** can be converted to **2** in 20% yield by reaction with $Os_3(CO)_{11}(NCMe)$ (**4**); see Scheme I. The concomitant formation of $Os_3(CO)_{12}$ suggests that **4** is acting simply as a decarbonylation reagent. The fate of the platinum atom that was expelled from **1** in the course of this transformation has not yet been established.

We anticipate that **1** and **2** are only the first members of what will prove to be a much larger series of hydrogen-rich platinum-containing heteronuclear cluster complexes that may also exhibit some unusual reactivities.

**Acknowledgment.** These studies were supported by the National Science Foundation under Grant CHE8919786.

**Supplementary Material Available:** For compounds **1** and **2**, tables of crystal data, positional, isotropic thermal, and anisotropic thermal parameters, and bond distances and angles (16 pages); listings of structure factors (36 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

**Richard D. Adams***
**Gong Chen**
**Dean A. Katahira**
**James T. Tanner**
**Wengan Wu**

*Received March 28, 1990*

---

(10) Dark red crystals of **2** were grown from benzene/heptane solutions by slow evaporation of solvent at 25 °C. Crystal data: space group $P2_1/n$, $a$ = 11.810 (4) Å, $b$ = 15.656 (4) Å, $c$ = 16.286 (6) Å, $\beta$ = 109.15 (3)°, $Z$ = 4. An empirical absorption correction was applied. The structure was solved by direct methods (MITHRIL) and was refined (2422 reflections) to the final values of the residuals $R$ = 0.032 and $R_w$ = 0.033.

(11) As with **1**, the equivalence of the three hydride ligands H(1), H(2), and H(3) may be the result of a dynamical averaging process. Further studies are in progress.

(12) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

(13) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1 and references therein.

(14) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 123.

---

## Inverse Experiments with Fluorine Detection

Since the publication by Freeman and Morris[1] on *J* polarization transfer between two coupled spin systems (the INEPT experiment), a great number of papers have appeared in the literature, dealing with proton-to-X polarization transfer (X = $^{13}C$, $^{15}N$). It was clear very rapidly that this kind of NMR experiment was very useful for inorganic chemists because of both the enormous sensitivity and experimental time gain when detecting low-$\gamma$ nuclei. The second step was then to extend the INEPT scheme to transfer a phosphorus,[2] fluorine,[3] or carbon[4] polarization to another X magnetization. Accordingly, the so-called "inverse experiment"

---

(1) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.