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Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Cluster Synthesis. 32. Hydrogen-Rich Metal Cluster Complexes from the Reaction of $Pt_2Os_4(CO)_{18}$ with Hydrogen. Synthesis and Molecular Structures of $PtOs_5(CO)_{16}(\mu\text{-}H)_6$, $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$, $PtOs_6(CO)_{18}(\mu\text{-}H)_8$, and $Pt_2Os_7(CO)_{23}(\mu\text{-}H)_8$

Richard D. Adams,* Michael P. Pompeo, and Wengan Wu

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From the reaction of $Pt_2Os_4(CO)_{18}$ with hydrogen at 25 °C/100 atm, four new hydrogen-rich platinum osmium carbonyl cluster complexes were obtained. They were identified as $PtOs_5(CO)_{16}(\mu\text{-}H)_6$ (**1**), $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ (**2**), $Pt_2Os_7(CO)_{23}(\mu\text{-}H)_8$ (**3**), and $PtOs_6(CO)_{18}(\mu\text{-}H)_8$ (**4**). All four compounds were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. The structures of all of the clusters are based on vertex-shared condensed polyhedra using platinum atoms at the vertex-sharing sites. Compound **1** consists of a $PtOs_3$ tetrahedron fused to a $PtOs_2$ triangle. Compound **2** consists of a $PtOs_3$ tetrahedron fused to a Pt_2Os_2 tetrahedron. Compound **3** consists of a $PtOs_3$ tetrahedron fused to a Pt_2Os_2 tetrahedron and a $PtOs_2$ triangle sharing the second platinum atom of the Pt_2Os_2 cluster. Compound **4** consists of two $PtOs_3$ tetrahedra sharing the one platinum atom. Compounds **1** and **2** contain six bridging hydride ligands. The positions of all of the hydride ligands were determined by a combination of ^1H NMR spectroscopy and crystallography. Compounds **3** and **4** both contain eight bridging hydride ligands. The positions of all eight hydride ligands in both compounds were determined by a combination of ^1H NMR spectroscopy and crystallography. Compounds **1**–**3** are electron deficient by the amount of two electrons. These three complexes are readily degraded by CO (25 °C/1 atm) to yield the products $PtOs_2(CO)_{10}$, $H_2Os_2(CO)_8$, $H_2Os(CO)_4$, and H_2. Compound **4** is electronically saturated and does not react with CO at 25 °C/1 atm. Crystal data: for **1**, space group $P2_1/n$, $a = 11.810$ (4) Å, $b = 15.656$ (4) Å, $c = 16.286$ (6) Å, $\beta = 109.15$ (3)°, $Z = 4$, 2422 reflections, $R = 0.032$; for **2**, space group $P2_1/n$, $a = 9.603$ (3) Å, $b = 16.246$ (7) Å, $c = 19.272$ (7) Å, $\beta = 91.49$ (3)°, $Z = 4$, 2751 reflections, $R = 0.042$; for **3**, space group $P2_1/n$, $a = 9.616$ (1) Å, $b = 24.411$ (9) Å, $c = 17.065$ (4) Å, $\beta = 92.82$ (2)°, $Z = 4$, 3097 reflections, $R = 0.029$; for **4**, space group $P\bar{1}$, $a = 10.232$ (1) Å, $b = 16.662$ (4) Å, $c = 10.252$ (2) Å, $\alpha = 91.04$ (2)°, $\beta = 113.38$ (1)°, $\gamma = 101.37$ (2)°, $Z = 2$, 2760 reflections, $R = 0.029$.

Introduction

The activation of hydrogen by transition metals is a central feature of their ability to serve as hydrogenation catalysts and hydrogen storage materials.[1,2] Recent studies have shown that certain metal cluster complexes are capable of storing relatively large amounts of hydrogen in the form of hydride ligands.[3] The stability of these complexes is derived in part by the ability of the hydrogen atom to serve as a bridging ligand.[4] Heteronuclear clusters containing platinum have been the source of great interest,[5] and we have recently begun studies of the preparation of new cluster complexes of this type.[6] Due to the well-known ability of platinum to activate hydrogen, we are also investigating the ability of these mixed-metal custer complexes to activate hydrogen. We have now completed our first studies of the reaction of hydrogen with the complex $Pt_2Os_4(CO)_{18}$.[7] A preliminary report of this work has been published.[8]

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were dried over sodium and deoxygenated by purging with nitrogen prior to use. IR spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer. A Bruker AM-300 FT-NMR spectrometer was used to obtain ^1H NMR spectra. Elemental microanalyses were performed by Desert Analytics, Tucson, AZ. TLC separations were performed by using silica gel (60 Å, F_{254}) on plates (Whatman 0.25 mm).

Synthesis of $Pt_2Os_4(CO)_{18}$. A flask containing a 50-mL solution of $Os(CO)_5$ in hexane (~2 mg/mL) was evacuated and filled with nitrogen three times to remove traces of CO. A 40-mg (0.097-mmol) sample of $Pt(COD)_2$ was added. The solution was stirred at 25 °C for 70 min and changed from colorless to dark red. The red product $Pt_2Os_4(CO)_{18}$ was isolated by column chromatography on Florisil using a hexane/CH_2Cl_2 9/1 solvent mixture. Yield: 64 mg, 51%. This material was spectroscopically identical with that reported by Sundberg, prepared by a different method.[7]

Reaction of $Pt_2Os_4(CO)_{18}$ with Hydrogen. A 20.0-mg (0.012-mmol) amount of $Pt_2Os_4(CO)_{18}$ was dissolved in 10 mL of CH_2Cl_2, and the solution was placed in a 25-mL Parr high-pressure apparatus. The reaction apparatus was flushed with hydrogen three times and was then filled with hydrogen to 100 atm, sealed, and maintained at 25 °C for 48 h. After the pressure was released, the solvent was removed in vacuo. The residue was dissolved in a minimum of CH_2Cl_2, and the mixture was separated by TLC on silica gel with a hexane/CH_2Cl_2, (95/5) solvent mixture. Four products separated in order of elution: red $PtOs_5(CO)_{16}(\mu\text{-}H)_6$ (**1**), 1.8 mg, 11%; green $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ (**2**), 5.6 mg, 32%; light green $Pt_2Os_7(CO)_{23}(\mu\text{-}H)_8$ (**3**), 1.2 mg, 7%. The fourth product, orange $PtOs_6(CO)_{18}(\mu\text{-}H)_8$ (**4**), was obtained only in a trace amount. All yields were calculated on the basis of osmium content. When 50 mg of $Pt_2Os_4(CO)_{18}$ was allowed to react with hydrogen under the same conditions, **3** was obtained in 11% yield (4.4 mg). Compounds **1** and **2** were obtained in 5% (1.9 mg) and 22% (9.5 mg) yields, re-

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spectively. IR (ν(CO) in hexane, cm^{-1}): for **1**, 2119 (vw), 2096 (m), 2086 (s), 2061 (m), 2041 (m), 2034 (m), 2027 (w), 2021 (m), 2012 (m), 2005 (w), 1994 (vw), 1985 (w); for **2**, 2090 (m), 2080 (vs), 2068 (w), 2061 (w), 2021 (m), 2011 (m), 1997 (w); for **3**, 2125 (w), 2101 (w), 2082 (vs), 2075 (sh), 2059 (m), 2051 (sh), 2048 (w), 2031 (vw), 2019 (m), 2014 (m), 2005 (m), 1988 (vw), 1980 (vw), 1868 (vw). IR (ν(CO) in CH_2Cl_2, cm^{-1}): for **4**, 2120 (vw), 2098 (m), 2081 (vs), 2054 (m), 2038 (vw), 2010 (m), 1998 (m). ^{1}H NMR (δ, ppm): for **1** (in $CDCl_3$ at 25 °C), −7.48 (s, 2 H, $^1J_{Pt-H}$ = 653.6 Hz), −12.17 (s, 1 H, $^1J_{Pt-H}$ = 573.2 Hz), −17.36 (s, 3 H, $^2J_{Pt-H}$ = 22.4 Hz); for **2** (in CD_2Cl_2 at −92 °C), −9.73 (d, 2 H, $^1J_{Pt-H}$ = 714.4 Hz, $^2J_{Pt-H}$ = 19.5 Hz, $^1J_{H-H}$ = 2.1 Hz), −17.86 (s, 3 H, $^2J_{Pt-H}$ = 16.4 Hz), −19.66 (d, 1 H, $^2J_{Pt-H}$ = 24.3 Hz, $^1J_{H-H}$ = 2.1 Hz); for **2** (in $CDCl_3$ at 25 °C), −8.46 (s, 2 H, $^1J_{Pt-H}$ = 716 Hz), −16.79 (s, 3 H, $^2J_{Pt-H}$ = 21 Hz), −18.01 (s, br, 1 H); for **3** (in CD_2Cl_2 at −75 °C), −7.95 (s, 1 H), −8.00 (s, 1 H), −10.06 (s, 1 H), −10.29 (s, 1 H), −15.35 (s, 1 H), −16.90 (s, 1 H), −16.91 (s, 1 H), −17.48 (s, 1 H); for **4** (in $CDCl_3$ at 25 °C), −18.59 (s, 3 H, $^1J_{Pt-H}$ = 624.9 Hz), −18.63 (s, 3 H, $^2J_{Pt-H}$ = 22.5 Hz), −20.25 (s, 2 H). Anal. Calc (found) for **1**: C, 12.01 (12.32); H, 0.38 (0.27). Calc (found) for **2**: C, 11.20 (11.03); H, 0.33 (0.30). Calc (found) for **3**: C, 11.64 (12.24); H, 0.34 (0.19). Calc (found) for **4**: C, 11.70 (11.78); H, 0.44 (0.35). The mass spectrum of **4** obtained at 180 °C by direct inlet showed the parent ion at *m/e* 1849 and ions corresponding to the loss of 2–18 CO ligands. The isotope distribution was consistent with the calculated distribution for six osmium atoms and one platinum atom.

An Improved Synthesis of 4. $Pt_2Os_4(CO)_{18}$ (13 mg, 0.008 mmol) and $Os_3(CO)_{10}(\mu\text{-}H)_2$ (13 mg, 0.015 mmol) were dissolved in 12 mL of CH_2Cl_2, and the solution was placed in a 25-mL Parr high-pressure apparatus. The apparatus was pressurized with hydrogen (100 atm) and the mixture allowed to stir at 25 °C for 48 h. After opening, the solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2 to yield 10.5 mg of **4** (44%). A 1.2-mg amount of **1** (5%), 1.0 mg of **2** (4%), and 1.3 mg of **3** (5%) were obtained from the mother liquor by TLC. All yields were calculated on the basis of osmium content.

Reaction of 2 with $Os_3(CO)_{11}(NCMe)$ or $W(CO)_5(NCMe)$. A solution of **2** (13 mg, 0.007 mmol) and $Os_3(CO)_{11}(NCMe)$ (8.5 mg, 0.0092 mmol) in 25 mL of hexane was refluxed under a purge of nitrogen for 45 min. The products were separated by TLC on silica gel with a hexane/CH_2Cl_2 (9/1) mixture solvent. In order of elution, 2.5 mg of $Os_3(CO)_{12}$ and 2.4 mg of **1** (21%) were obtained; 2.3 mg of **2** (18%) was recovered. When $W(CO)_5(NCMe)$ was used instead of $Os_3(CO)_{11}(NCMe)$, **1** was obtained in 15% yield.

Reaction of 3 with CO. An 8.0-mg sample of **3** (3.4×10^{-3} mmol) in 10 mL of CH_2Cl_2 was allowed to react with CO (slow purge through the solution) at 25 °C for 15 min. The solvent was removed in vacuo, and the residue was separated by TLC on silica gel. A 3.3-mg yield of **2** (54%) was obtained. When the reaction of **3** (2.8 mg) with CO was carried out in an NMR tube over a period of 1 h and was followed by ^{1}H NMR spectroscopy, resonances due to the formation of H_2, $H_2Os(CO)_4$,[10] and $H_2Os_2(CO)_8$[11] were clearly observed. The ratio of the last two was approximately 1/3. The amount of H_2 was slightly less than that of the $H_2Os(CO)_4$. After this period of time, only a very small amount of **2** was present. A small amount of **1** had been found, and a new resonance $\delta = -19.09$ with long-range coupling $^2J_{Pt-H}$ = 23 Hz was observed. The unknown product apparently reacts with CO also. After 4 h at 25 °C, the resonance of the unknown compound was absent. At this time, the ratio of $H_2Os(CO)_4$ to $H_2Os_2(CO)_8$ was approximately 1/2. Chromatography of this sample showed the CO absorptions for $H_2Os_2(CO)_8$ and $PtOs_2(CO)_{10}$[6e] in the IR region. The amount of $PtOs_2(CO)_{10}$ could not be accurately determined due to its instability.[6e]

Reaction of 2 with CO. The reaction of approximately 3 mg of **2** with CO in $CDCl_3$ solvent in an NMR tube was followed by ^{1}H NMR spectroscopy for $^1/_2$ h at 25 °C. Three products, H_2, $H_2Os(CO)_4$, and $H_2Os_2(CO)_8$, were formed in approximately equal amounts. The amount of **2** remaining was approximately equal to that of the $H_2Os_2(CO)_8$. A small amount of **1** had formed, and an amount of the unknown compound (−19.09 ppm) had formed that was approximately equal to the amount of $H_2Os_2(CO)_8$. Chromatography of the reaction solution revealed the presence of $PtOs_2(CO)_{10}$ by IR spectroscopy.

Reaction of 1 with CO. The reaction of **1** (approximately 4 mg) with CO in $CDCl_3$ solvent in an NMR tube at 25 °C was followed by ^{1}H NMR spectroscopy for 11 h at 25 °C. These measurements showed the formation of H_2, $H_2Os(CO)_4$, and $H_2Os_2(CO)_8$ in an approximate ratio of 1/2/2. The amount of **2** remaining after 11 h was equal to or greater than the amount of $H_2Os_2(CO)_8$. A trace of the unknown compound (−19.09 ppm) was also observed. $PtOs_2(CO)_{10}$ was detected by IR spectroscopy after chromatography.

Table I. Crystal Data for Compounds 1–4

	1	**2**	**3**	**4**
formula	$PtOs_5O_{16}C_{16}H_6$	$Pt_2Os_5O_{17}C_{17}H_6$	$Pt_2Os_7O_{23}C_{23}H_8$	$PtOs_6O_{18}C_{18}H_8$
fw	1600.30	1823.40	2378.88	1848.54
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
a, Å	11.810 (4)	9.603 (3)	9.616 (1)	10.232 (1)
b, Å	15.656 (4)	16.246 (7)	24.411 (9)	16.662 (4)
c, Å	16.286 (6)	19.272 (7)	17.065 (4)	10.252 (2)
α, deg				91.04 (2)
β, deg	109.15 (3)	91.49 (3)	92.82 (2)	113.38 (1)
λ, deg				101.37 (2)
V, Å^3	2845 (3)	3006 (2)	4001 (2)	1564 (1)
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z	4	4	4	2
ρ_{calc}, g/cm^3	3.74	4.03	3.94	3.93
μ(Mo K$\bar{\alpha}$), cm^{-1}	272.89	305.13	292.73	288.78
temp, °C	20	20	20	20
residuals: *R*, R_w	0.032, 0.033	0.042, 0.043	0.029, 0.029	0.029, 0.033

Crystallographic Analyses. Crystals of compound **1** suitable for diffraction analysis were grown by slow evaporation of benzene/heptane solutions at 25 °C. Crystals of compounds **2** and **3** were grown in solutions of hexane/CH_2Cl_2 solvent by cooling to 10 °C. Crystals of compound **4** were grown by slow evaporation of solvent from CH_2Cl_2/benzene solutions at 25 °C. All data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[12a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[12b] Lorentz–polarization (*Lp*) and absorption corrections were applied for each structure. Full-matrix least-squares refinements minimized the function

$$\textstyle\sum_{hkl} w(|F_o| - |F_c|)^2$$

$$w = 1/\sigma(F_o)^2 \qquad \sigma(F_o) = \sigma(F_o^2)/2F_o$$

$$\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02F_o^2)^2]^{1/2}/Lp$$

Compounds **1**, **2**, and **3** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely for each compound on the basis of the systematic absences observed during the collection of data. Each structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. For compound **1** all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydride ligands were obtained from difference Fourier maps. Their contributions were added to the structure factor calculations, but their positions were not refined. For compounds **2** and **3** all atoms heavier than carbon were refined with anisotropic thermal parameters. The positions of the hydride ligands were obtained from difference Fourier maps for both **2** and **3**. For compound **2** their contributions were added to the structure factor calculations without refinement. For compound **3** the coordinates of all of the hydride ligands were refined. Seven of the hydride ligands refined to convergence (shift/error < 0.01). On the final cycle, the remaining hydride ligand H(45) had a shift/error value of 0.87.

Compound **4** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All eight hydride ligands were located in difference Fourier maps, but only six H(1)–H(6) could be refined to convergence. Thus, the two remaining hydride ligands were added as fixed contributions. Tables of anisotropic thermal parameters and structure factor amplitudes are available with

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Table II. Positional Parameters and *B*(eq) for $PtOs_5(CO)_{16}H_6$ (**1**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt	0.57021 (07)	0.10989 (05)	0.24132 (05)	2.50 (3)
Os(1)	0.44750 (08)	0.16376 (05)	0.34445 (06)	3.04 (4)
Os(2)	0.34874 (08)	0.16323 (05)	0.15544 (06)	2.95 (4)
Os(3)	0.39747 (08)	0.00452 (05)	0.25395 (06)	3.01 (4)
Os(4)	0.73778 (08)	0.14816 (05)	0.16714 (06)	3.18 (4)
Os(5)	0.81918 (08)	0.05109 (06)	0.32524 (06)	3.58 (4)
O(11)	0.6373 (18)	0.0938 (12)	0.5064 (2)	7 (1)
O(12)	0.2908 (20)	0.2371 (13)	0.4423 (15)	9 (1)
O(13)	0.5807 (16)	0.3335 (11)	0.3608 (13)	6 (1)
O(21)	0.0863 (18)	0.2127 (13)	0.0737 (14)	8 (1)
O(22)	0.4494 (17)	0.3372 (09)	0.1270 (11)	5.8 (9)
O(23)	0.3751 (16)	0.0856 (11)	−0.0123 (12)	6 (1)
O(31)	0.5758 (17)	−0.0960 (10)	0.4012 (13)	6 (1)
O(32)	0.4444 (18)	−0.0984 (12)	0.1112 (12)	6 (1)
O(33)	0.1851 (17)	−0.1054 (12)	0.2511 (14)	8 (1)
O(41)	0.8514 (20)	0.0367 (13)	0.0629 (14)	9 (1)
O(42)	0.5960 (8)	0.2550 (12)	0.0125 (12)	6 (1)
O(43)	0.9568 (19)	0.2629 (11)	0.2307 (13)	8 (1)
O(51)	0.8701 (19)	−0.0468 (13)	0.4928 (14)	8 (1)
O(52)	0.7327 (17)	−0.1068 (11)	0.2094 (12)	6 (1)
O(53)	1.0679 (17)	0.0554 (14)	0.3054 (14)	8 (1)
O(54)	0.8377 (17)	0.2276 (12)	0.4136 (13)	7 (1)
C(11)	0.565 (02)	0.1183 (15)	0.4459 (16)	4 (1)
C(12)	0.348 (02)	0.2068 (16)	0.4039 (16)	5 (1)
C(13)	0.532 (02)	0.2692 (16)	0.3573 (16)	5 (1)
C(21)	0.181 (02)	0.1934 (14)	0.1028 (15)	4 (1)
C(22)	0.411 (02)	0.2712 (14)	0.1374 (15)	4 (1)
C(23)	0.3639 (19)	0.1135 (14)	0.0506 (15)	3 (1)
C(31)	0.510 (2)	−0.0591 (13)	0.3460 (15)	4 (1)
C(32)	0.428 (02)	−0.0589 (15)	0.1636 (18)	5 (1)
C(33)	0.264 (02)	−0.0644 (15)	0.2504 (18)	5 (1)
C(41)	0.809 (02)	0.0790 (15)	0.1055 (18)	5 (1)
C(42)	0.650 (2)	0.2157 (15)	0.0695 (17)	4 (1)
C(43)	0.873 (02)	0.2204 (15)	0.2058 (15)	4 (1)
C(51)	0.849 (02)	−0.0114 (17)	0.4291 (18)	6 (1)
C(52)	0.767 (02)	−0.0510 (14)	0.2503 (17)	5 (1)
C(53)	0.977 (02)	0.0525 (17)	0.3130 (16)	5 (1)
C(54)	0.838 (02)	0.1628 (16)	0.3821 (15)	5 (1)
H(1)	0.3218	0.2012	0.2531	3.0
H(2)	0.2510	0.0546	0.1505	3.0
H(3)	0.3539	0.0496	0.3364	3.0
H(4)	0.6536	0.2131	0.2230	3.0
H(5)	0.6146	0.0713	0.1420	3.0
H(6)	0.6767	0.0442	0.3460	3.0

Table III. Intramolecular Distances (Å) for **1**

Pt–Os(1)	2.689 (1)	Os(2)–H(1)	1.82
Pt–Os(2)	2.664 (2)	Os(2)–H(2)	1.82
Pt–Os(3)	2.684 (1)	Os(3)–C(31)	1.93 (3)
Pt–Os(4)	2.703 (2)	Os(3)–C(32)	1.91 (3)
Pt–Os(5)	2.954 (2)	Os(3)–C(33)	1.90 (2)
Pt–H(5)	1.95	Os(3)–H(3)	1.74
Pt–H(4)	1.97	Os(3)–H(2)	2.13
Pt–H(6)	2.03	Os(4)–Os(5)	2.870 (2)
Os(1)–Os(2)	2.912 (2)	Os(4)–C(41)	1.86 (2)
Os(1)–Os(3)	2.858 (1)	Os(4)–C(42)	1.91 (3)
Os(1)–C(11)	1.91 (3)	Os(4)–C(43)	1.89 (2)
Os(1)–C(12)	1.88 (2)	Os(4)–H(4)	1.86
Os(1)–C(13)	1.90 (3)	Os(4)–H(5)	1.83
Os(1)–H(1)	1.82	Os(5)–C(51)	1.89 (3)
Os(1)–H(3)	2.08	Os(5)–C(52)	1.98 (2)
Os(2)–Os(3)	1.911 (1)	Os(5)–C(53)	1.94 (3)
Os(2)–C(21)	1.94 (2)	Os(5)–C(54)	1.96 (3)
Os(2)–C(22)	1.90 (3)	Os(5)–H(6)	1.82
Os(2)–C(23)	1.94 (3)	O–C(av)	1.15 (3)

the supplementary material for all four structures.

Results and Discussion

From the reaction of $Pt_2Os_4(CO)_{18}$ with H_2 (100 atm) at 25 °C, we have isolated four new platinum–osmium carbonyl cluster complexes that contain large amounts of hydrogen in the form of hydride ligands: $PtOs_5(CO)_{16}(\mu\text{-}H)_6$ (**1**), 11%; $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ (**2**), 32%; $Pt_2Os_7(CO)_{23}(\mu\text{-}H)_8$ (**3**), 7%; $PtOs_6(CO)_{18}(\mu\text{-}H)_8$ (**4**), trace. Compound **4** was obtained in a much better yield (44%) by adding 2 equiv of $Os_3(CO)_{10}(\mu\text{-}H)_2$ to the original reaction. All four products were characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses.

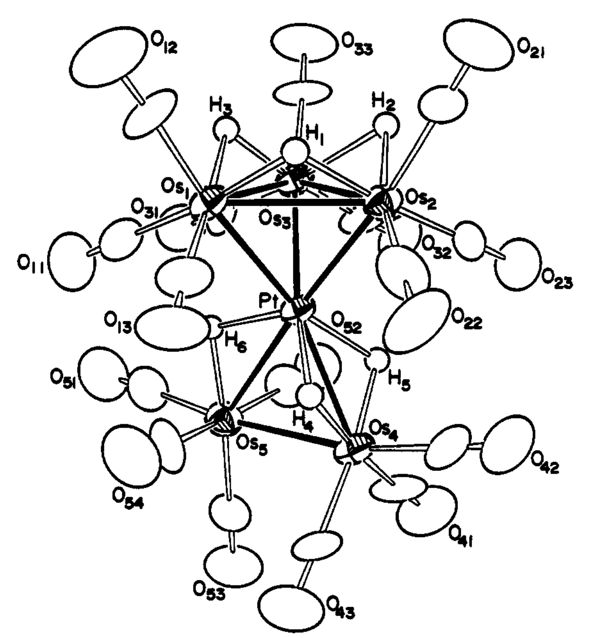

Figure 1. ORTEP diagram of $PtOs_5(CO)_{16}(\mu\text{-}H)_6$ (**1**) showing 50% probability thermal ellipsoids.

Table IV. Intramolecular Bond Angles (deg) for **1**

Os(1)–Pt–Os(2)	65.92 (4)	Pt–Os(3)–Os(2)	56.69 (4)
Os(1)–Pt–Os(3)	64.27 (4)	Pt–Os(3)–C(31)	91.6 (7)
Os(1)–Pt–Os(4)	146.46 (4)	Pt–Os(3)–C(32)	85.3 (7)
Os(1)–Pt–Os(5)	117.87 (5)	Pt–Os(3)–C(33)	173.3 (9)
Os(2)–Pt–Os(3)	65.97 (4)	Os(1)–Os(3)–Os(2)	60.63 (4)
Os(2)–Pt–Os(4)	115.64 (5)	Os(1)–Os(3)–C(31)	94.4 (6)
Os(2)–Pt–Os(5)	176.10 (4)	Os(1)–Os(3)–C(32)	142.4 (7)
Os(3)–Pt–Os(4)	149.00 (4)	Os(1)–Os(3)–C(33)	122.8 (7)
Os(3)–Pt–Os(5)	116.06 (4)	Os(2)–Os(3)–C(31)	146.3 (7)
Os(4)–Pt–Os(5)	60.80 (4)	Os(2)–Os(3)–C(32)	94.1 (7)
Pt–Os(1)–Os(2)	56.62 (4)	Os(2)–Os(3)–C(33)	117.2 (8)
Pt–Os(1)–Os(3)	57.78 (4)	C(31)–Os(3)–C(32)	94 (1)
Pt–Os(1)–C(11)	92.0 (7)	C(31)–Os(3)–C(33)	95 (1)
Pt–Os(1)–C(12)	172.9 (7)	C(32)–Os(3)–C(33)	93 (1)
Pt–Os(1)–C(13)	88.3 (7)	Pt–Os(4)–Os(5)	63.93 (4)
Os(2)–Os(1)–Os(3)	60.59 (4)	Pt–Os(4)–C(41)	130.0 (7)
Os(2)–Os(1)–C(11)	146.9 (7)	Pt–Os(4)–C(42)	102.5 (7)
Os(2)–Os(1)–C(12)	116.4 (8)	Pt–Os(4)–C(43)	130.3 (7)
Os(2)–Os(1)–C(13)	97.6 (8)	Os(5)–Os(4)–C(41)	95.6 (9)
Os(3)–Os(1)–C(11)	95.1 (7)	Os(5)–Os(4)–C(42)	166.2 (7)
Os(3)–Os(1)–C(12)	121.3 (9)	Os(5)–Os(4)–C(43)	91.2 (7)
Os(3)–Os(1)–C(13)	145.6 (7)	C(41)–Os(4)–C(42)	95 (1)
C(11)–Os(1)–C(12)	95 (1)	C(41)–Os(4)–C(43)	93 (1)
C(11)–Os(1)–C(13)	91 (1)	C(42)–Os(4)–C(43)	97 (1)
C(12)–Os(1)–C(13)	92 (1)	Pt–Os(5)–Os(4)	55.28 (4)
Pt–Os(2)–Os(1)	57.46 (4)	Pt–Os(5)–C(51)	116.1 (9)
Pt–Os(2)–Os(3)	57.35 (4)	Pt–Os(5)–C(52)	84.6 (7)
Pt–Os(2)–C(21)	172.9 (6)	Pt–Os(5)–C(53)	142.5 (8)
Pt–Os(2)–C(22)	89.8 (6)	Pt–Os(5)–C(54)	83.3 (6)
Pt–Os(2)–C(23)	88.7 (6)	Os(4)–Os(5)–C(51)	171.4 (9)
Os(1)–Os(2)–Os(3)	58.78 (4)	Os(4)–Os(5)–C(52)	86.0 (7)
Os(1)–Os(2)–C(21)	117.6 (7)	Os(4)–Os(5)–C(53)	87.2 (8)
Os(1)–Os(2)–C(22)	96.9 (7)	Os(4)–Os(5)–C(54)	84.5 (7)
Os(1)–Os(2)–C(23)	144.3 (6)	C(51)–Os(5)–C(52)	94 (1)
Os(3)–Os(2)–C(21)	116.1 (6)	C(51)–Os(5)–C(53)	101 (1)
Os(3)–Os(2)–C(22)	145.7 (6)	C(51)–Os(5)–C(54)	95 (1)
Os(3)–Os(2)–C(23)	94.8 (6)	C(52)–Os(5)–C(53)	93 (1)
C(21)–Os(2)–C(22)	96.1 (9)	C(52)–Os(5)–C(54)	168 (1)
C(21)–Os(2)–C(23)	95 (1)	C(53)–Os(5)–C(54)	94 (1)
C(22)–Os(2)–C(23)	94 (1)	Os–C(av)–O	177 (3)
Pt–Os(3)–Os(1)	57.95 (4)		

An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. The cluster can be viewed as a combination of one

Table V. Positional Parameters and *B*(eq) for $Pt_2Os_5(CO)_{17}H_6$ (**2**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.89441 (11)	0.09161 (06)	0.25664 (05)	1.95 (4)
Pt(2)	0.89574 (12)	0.02681 (07)	0.11099 (05)	2.65 (5)
Os(1)	0.90091 (13)	0.14861 (07)	0.38829 (05)	2.53 (5)
Os(2)	1.09958 (12)	0.03163 (07)	0.34072 (05)	2.56 (5)
Os(3)	0.80716 (12)	−0.01399 (06)	0.35446 (05)	2.25 (5)
Os(4)	0.69156 (12)	0.13029 (07)	0.14880 (05)	2.38 (5)
Os(5)	0.98354 (12)	0.18143 (07)	0.13696 (05)	2.36 (5)
O(1)	0.717 (03)	−0.1173 (14)	0.0646 (12)	7 (1)
O(2)	1.182 (03)	−0.0372 (17)	0.0740 (11)	7 (2)
O(11)	0.905 (03)	0.2074 (17)	0.5385 (10)	8 (2)
O(12)	0.618 (02)	0.2264 (12)	0.3564 (10)	5 (1)
O(13)	1.056 (03)	0.2964 (12)	0.3384 (11)	6 (1)
O(21)	1.309 (02)	−0.0441 (16)	0.4450 (10)	6 (1)
O(22)	1.165 (02)	−0.0888 (12)	0.2251 (09)	5 (1)
O(23)	1.298 (03)	0.1627 (17)	0.2913 (13)	7 (2)
O(31)	0.510 (03)	0.0397 (16)	0.3333 (14)	8 (2)
O(32)	0.775 (03)	−0.1349 (12)	0.2343 (10)	5 (1)
O(33)	0.750 (03)	−0.1404 (13)	0.4676 (11)	6 (1)
O(41)	0.601 (03)	0.1483 (17)	−0.0044 (10)	8 (2)
O(42)	0.487 (02)	0.2638 (12)	0.1945 (10)	5 (1)
O(43)	0.489 (03)	−0.0114 (15)	0.1725 (13)	7 (2)
O(51)	1.290 (02)	0.1290 (16)	0.1256 (13)	7 (2)
O(52)	0.961 (03)	0.2114 (15)	−0.0193 (09)	7 (1)
O(53)	1.052 (03)	0.3596 (12)	0.1772 (10)	5 (1)
C(1)	0.780 (03)	−0.0639 (18)	0.0856 (14)	3.4 (6)
C(2)	1.071 (03)	−0.0106 (17)	0.0867 (13)	3.1 (6)
C(11)	0.898 (04)	0.1868 (19)	0.4844 (16)	4.3 (7)
C(12)	0.725 (03)	0.1964 (18)	0.3692 (14)	3.4 (6)
C(13)	0.998 (03)	0.2440 (19)	0.3596 (14)	3.7 (6)
C(21)	1.227 (03)	−0.0160 (18)	0.4058 (14)	3.9 (6)
C(22)	1.139 (04)	−0.047 (02)	0.2693 (16)	4.5 (7)
C(23)	1.225 (04)	0.1112 (20)	0.3101 (15)	4.2 (7)
C(31)	0.625 (04)	0.0182 (18)	0.3412 (14)	3.5 (6)
C(32)	0.788 (03)	−0.0900 (17)	0.2805 (13)	3.1 (6)
C(33)	0.770 (03)	−0.0906 (17)	0.4273 (13)	2.9 (5)
C(41)	0.636 (0)	0.1422 (17)	0.0542 (15)	3.6 (6)
C(42)	0.562 (03)	0.2178 (19)	0.1780 (14)	3.5 (6)
C(43)	0.565 (04)	0.0414 (19)	0.1612 (15)	4.0 (6)
C(51)	1.173 (04)	0.1518 (19)	0.1295 (15)	4.2 (7)
C(52)	0.966 (03)	0.2017 (17)	0.0389 (14)	3.5 (6)
C(53)	1.032 (03)	0.2918 (17)	0.1624 (13)	3.0 (6)
H(1)	1.0641	0.0934	0.4147	3.0
H(2)	0.9712	−0.0429	0.3661	3.0
H(3)	0.7943	0.0583	0.4120	3.0
H(4)	0.7304	0.1350	0.2322	3.0
H(5)	1.0200	0.1594	0.2089	3.0
H(6)	0.8094	0.2133	0.1658	3.0

Table VI. Intramolecular Distances (Å) for **2**

Pt(1)–H(4)	1.78	Os(2)–C(23)	1.87 (4)
Pt(1)–H(5)	1.89	Os(2)–C(21)	1.90 (3)
Pt(1)–Os(3)	2.699 (2)	Os(2)–C(22)	1.92 (3)
Pt(1)–Os(1)	2.700 (2)	Os(2)–Os(3)	2.923 (2)
Pt(1)–Os(2)	2.700 (2)	Os(3)–H(3)	1.62
Pt(1)–Os(5)	2.878 (2)	Os(3)–H(2)	1.65
Pt(1)–Os(4)	2.881 (2)	Os(3)–C(31)	1.84 (3)
Pt(1)–Pt(2)	2.998 (2)	Os(3)–C(32)	1.89 (3)
Pt(2)–C(2)	1.86 (3)	Os(3)–C(33)	1.92 (3)
Pt(2)–C(1)	1.90 (3)	Os(4)–H(4)	1.64
Pt(2)–Os(5)	2.693 (2)	Os(4)–H(6)	1.78
Pt(2)–Os(4)	2.698 (2)	Os(4)–C(41)	1.90 (3)
Os(1)–H(3)	1.85	Os(4)–C(43)	1.91 (3)
Os(1)–H(1)	1.86	Os(4)–C(42)	1.98 (3)
Os(1)–C(12)	1.89 (3)	Os(4)–Os(5)	2.939 (2)
Os(1)–C(13)	1.90 (3)	Os(5)–H(5)	1.47
Os(1)–C(11)	1.95 (3)	Os(5)–H(6)	1.85
Os(1)–Os(2)	2.861 (2)	Os(5)–C(51)	1.89 (4)
Os(1)–Os(3)	2.861 (2)	Os(5)–C(53)	1.91 (3)
Os(2)–H(1)	1.78	Os(5)–C(52)	1.92 (3)
Os(2)–H(2)	1.80	O–C(av)	1.14 (3)

Table VII. Intramolecular Bond Angles (deg) for **2**

Os(3)–Pt(1)–Os(1)	63.99 (5)	C(22)–Os(2)–Os(1)	145 (1)
Os(3)–Pt(1)–Os(2)	65.56 (4)	C(22)–Os(2)–Os(3)	96 (1)
Os(3)–Pt(1)–Os(5)	170.53 (5)	Pt(1)–Os(2)–Os(1)	58.01 (4)
Os(3)–Pt(1)–Os(4)	115.23 (5)	Pt(1)–Os(2)–Os(3)	57.19 (4)
Os(3)–Pt(1)–Pt(2)	116.09 (5)	Os(1)–Os(2)–Os(3)	59.27 (4)
Os(1)–Pt(1)–Os(2)	63.97 (5)	C(31)–Os(3)–Pt(1)	92 (1)
Os(1)–Pt(1)–Os(5)	125.38 (5)	C(31)–Os(3)–Os(1)	94 (1)
Os(1)–Pt(1)–Os(4)	127.00 (6)	C(31)–Os(3)–Os(2)	146 (1)
Os(1)–Pt(1)–Pt(2)	178.36 (7)	C(32)–Os(3)–Pt(1)	85.1 (8)
Os(2)–Pt(1)–Os(5)	115.87 (5)	C(32)–Os(3)–Os(1)	143.0 (8)
Os(2)–Pt(1)–Os(4)	168.77 (5)	C(32)–Os(3)–Os(2)	100 (1)
Os(2)–Pt(1)–Pt(2)	114.47 (5)	C(33)–Os(3)–Pt(1)	172.6 (8)
Os(5)–Pt(1)–Os(4)	61.37 (4)	C(33)–Os(3)–Os(1)	119.8 (7)
Os(5)–Pt(1)–Pt(2)	54.49 (4)	C(33)–Os(3)–Os(2)	115.4 (8)
Os(4)–Pt(1)–Pt(2)	54.58 (4)	Pt(1)–Os(3)–Os(1)	58.03 (4)
C(2)–Pt(2)–Os(5)	94.1 (8)	Pt(1)–Os(3)–Os(2)	57.24 (4)
C(2)–Pt(2)–Os(4)	160.1 (8)	Os(1)–Os(3)–Os(2)	59.28 (4)
C(2)–Pt(2)–Pt(1)	112.2 (8)	C(41)–Os(4)–Pt(2)	89 (1)
C(1)–Pt(2)–Os(5)	161.5 (9)	C(41)–Os(4)–Pt(1)	152 (1)
C(1)–Pt(2)–Os(4)	97 (1)	C(41)–Os(4)–Os(5)	98 (1)
C(1)–Pt(2)–Pt(1)	119.7 (8)	C(43)–Os(4)–Pt(2)	92 (1)
Os(5)–Pt(2)–Os(4)	66.09 (5)	C(43)–Os(4)–Pt(1)	99.6 (8)
Os(5)–Pt(2)–Pt(1)	60.48 (4)	C(43)–Os(4)–Os(5)	147 (1)
Os(4)–Pt(2)–Pt(1)	60.49 (4)	C(42)–Os(4)–Pt(2)	172.1 (9)
C(12)–Os(1)–Pt(1)	87.7 (8)	C(42)–Os(4)–Pt(1)	111.7 (8)
C(12)–Os(1)–Os(2)	144.3 (8)	C(42)–Os(4)–Os(5)	115.2 (9)
C(12)–Os(1)–Os(3)	93.5 (9)	Pt(2)–Os(4)–Pt(1)	64.93 (4)
C(13)–Os(1)–Pt(1)	90.3 (8)	Pt(2)–Os(4)–Os(5)	56.88 (5)
C(13)–Os(1)–Os(2)	96 (1)	Pt(1)–Os(4)–Os(5)	59.28 (4)
C(13)–Os(1)–Os(3)	147.3 (8)	C(51)–Os(5)–Pt(2)	93 (1)
C(11)–Os(1)–Pt(1)	177 (1)	C(51)–Os(5)–Pt(1)	104 (1)
C(11)–Os(1)–Os(2)	123 (1)	C(51)–Os(5)–Os(4)	149 (1)
C(11)–Os(1)–Os(3)	120 (1)	C(53)–Os(5)–Pt(2)	174.2 (9)
Pt(1)–Os(1)–Os(2)	58.01 (4)	C(53)–Os(5)–Pt(1)	110.2 (8)
Pt(1)–Os(1)–Os(3)	57.98 (4)	C(53)–Os(5)–Os(4)	118 (1)
Os(2)–Os(1)–Os(3)	61.45 (5)	C(52)–Os(5)–Pt(2)	87.6 (8)
C(23)–Os(2)–Pt(1)	92 (1)	C(52)–Os(5)–Pt(1)	148.7 (9)
C(23)–Os(2)–Os(1)	95 (1)	C(52)–Os(5)–Os(4)	94 (1)
C(23)–Os(2)–Os(3)	146 (1)	Pt(2)–Os(5)–Pt(1)	65.02 (4)
C(21)–Os(2)–Pt(1)	173 (1)	Pt(2)–Os(5)–Os(4)	57.04 (4)
C(21)–Os(2)–Os(1)	119 (1)	Pt(1)–Os(5)–Os(4)	59.35 (4)
C(21)–Os(2)–Os(3)	116 (1)	O–C(av)–M	177 (3)
C(22)–Os(2)–Pt(1)	88 (1)		

tetrahedral $PtOs_3$ cluster and one triangular $PtOs_2$ cluster joined by the common Pt vertex. The ^1H NMR spectrum indicated the presence of six hydride ligands. These were located in chemically reasonable positions in accordance with the ^1H NMR data, but they were not structurally refined. One hydride ligand bridges each of the Os–Os bonds in the Os(1)–Os(2)–Os(3) triangle. Although formally they are not all equivalent, they are attributed to the high-field resonance of intensity 3 at −17.36 ppm. This resonance shows long-range coupling to the platinum atom, $^2J_{Pt-H}$ = 22.4 Hz. One hydride ligand bridges the long Pt–Os(5) bond, 2.954 (2) Å. The resonance of intensity 1 at −12.17 ppm that shows a large coupling to platinum, $^1J_{Pt-H}$ = 573.2 Hz, is attributed to this ligand. Two hydride ligands bridge the comparatively short Pt–Os(4) bond of 2.703 (2) Å. The resonance of −7.48 ppm of intensity 2 with large coupling to platinum, $^1J_{Pt-H}$ = 653.6 Hz, is attributed to these ligands. The Pt–Os distances involving Os(1), Os(2), and Os(3) do not contain hydride ligands. They are the shortest metal–metal bonds in the molecule, 2.689 (1), 2.664 (2), and 2.684 (1) Å, but are not of unusual lengths.[5] The Os(4)–Os(5) bond length is similar to that in $Os_3(CO)_{12}$, 2.877 (3) Å.[13] Each osmium atom contains three linear terminal carbonyl ligands except Os(5), which contains four. The platinum atom has no ligands except for the sharing interaction with three of the bridging hydrides. Electron counting shows that compound **1** is electron deficient by the amount of two electrons. It contains a total of 88 valence electrons, which is two less than the expected value of 90 based on Mingo's theory of condensed polyhedra (i.e. tetrahedron, 60 electrons, plus triangle, 48 electrons, minus shared vertex, 18 electrons).[14] We believe that this electron deficiency

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(13) De Boer, B. G.; Churchill, M. R. *Inorg. Chem.* **1977**, *16*, 878.

(14) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 2.

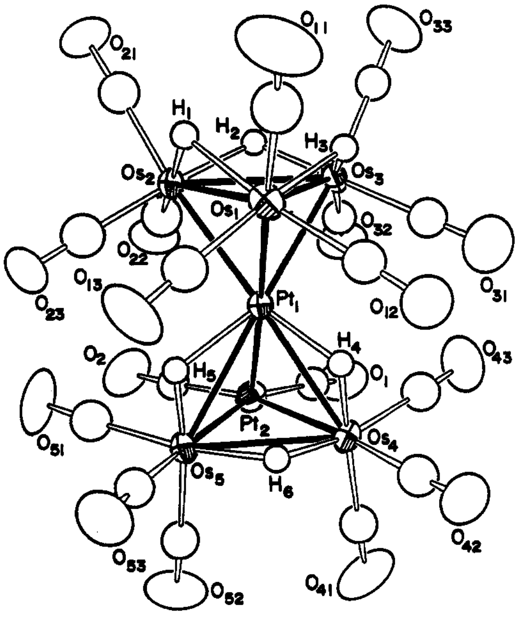

Figure 2. ORTEP diagram of $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$ (**2**) showing 50% probability thermal ellipsoids.

may be 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).[15]

An ORTEP drawing of the molecular structure of **2** is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. 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 ^1H NMR spectrum of **2** at −92 °C indicates that it also contains six hydride ligands. These ligands were located structurally in chemically reasonable positions, but they were not refined. As in **1**, one hydride ligand bridges each of the Os–Os bonds in the Os_3 triangle. The high-field resonance at −17.86 ppm of intensity 3 with long-range coupling to platinum, $^1J_{Pt-H}$ = 16.4 Hz, is attributed to these ligands. Technically, these three hydride ligands are not all equivalent. It is believed that they are dynamically averaged even at −92 °C. Investigation of this process in related molecules is in progress and will be the subject of a future report.[16] The Pt(1)–Os(4) and Pt(1)–Os(5) bonds, 2.881 (2) and 2.878 (2) Å, each contain one bridging hydride ligand. They are equivalent and are attributed to the doublet, J_{H-H} = 2.1 Hz, at −9.73 ppm and show short-range coupling to Pt(1), $^1J_{Pt-H}$ = 714.4 Hz and long-range coupling to Pt(2), $^2J_{Pt-H}$ = 19.5 Hz. The remaining hydride ligand bridges the Os(4)–Os(5) bond, 2.939 (2) Å, and is attributed to the triplet, J_{H-H} = 2.1 Hz, at −19.66 ppm with long-range coupling to one platinum atom, $^2J_{Pt-H}$ = 24.3 Hz. The Pt–Os bond lengths to the Os_3 triangle are similar to those in **1**, 2.699 (2)–2.700 (2) Å, and contain no hydride bridges. The Pt(1)–Pt(2) bond is long at 2.998 (2) Å and may be a relatively weak bond. Each osmium atom in **2** contains three linear terminal carbonyl ligands. The platinum atom Pt(2) has only two carbonyl ligands. Compound **2** also appears to be electron deficient. It contains a total of 100 valence electrons, but should contain 102.[14] Unlike the delocalized unsaturation proposed about the $PtOsH_2$ center in **1**, the unsaturation in **2** may be localized on Pt(2) in the form of a 16-electron configuration instead of the anticipated 18-electron configuration.[17]

Table VIII. Positional Parameters and B(eq) for $Pt_2Os_7(CO)_{23}H_8$ (**3**)

atom	x	y	z	B(eq), Å^2
Pt(1)	0.54132 (07)	0.15231 (04)	0.14803 (04)	2.18 (4)
Pt(2)	0.56811 (08)	0.26555 (04)	0.09178 (05)	2.45 (4)
Os(1)	0.51016 (08)	0.04597 (04)	0.19328 (05)	2.67 (4)
Os(2)	0.74410 (08)	0.10924 (04)	0.24664 (05)	2.40 (4)
Os(3)	0.46276 (08)	0.12700 (04)	0.30283 (05)	2.65 (4)
Os(4)	0.63236 (08)	0.17952 (04)	0.00059 (05)	2.36 (4)
Os(5)	0.34973 (08)	0.20462 (04)	0.03729 (05)	2.59 (4)
Os(6)	0.48423 (09)	0.35872 (04)	0.19373 (05)	3.28 (4)
Os(7)	0.75678 (08)	0.35177 (04)	0.12704 (05)	3.02 (4)
O(11)	0.2189 (16)	0.0467 (08)	0.1131 (11)	7 (1)
O(12)	0.6296 (18)	−0.0223 (09)	0.0616 (10)	7 (1)
O(13)	0.4303 (18)	−0.0485 (07)	0.2940 (11)	7 (1)
O(21)	0.9538 (15)	0.0603 (08)	0.3693 (09)	6 (1)
O(22)	0.9174 (15)	0.0735 (07)	0.1097 (09)	5 (1)
O(23)	0.8782 (14)	0.2220 (07)	0.2566 (09)	4.8 (9)
O(31)	0.4414 (16)	0.2243 (08)	0.4152 (10)	6 (1)
O(32)	0.1514 (13)	0.1221 (08)	0.2619 (09)	6 (1)
O(33)	0.447 (02)	0.0439 (09)	0.4367 (10)	8 (1)
O(41)	0.9314 (13)	0.2012 (07)	0.0596 (09)	4.4 (8)
O(42)	0.6407 (16)	0.2550 (07)	−0.1428 (08)	5.2 (9)
O(43)	0.6990 (20)	0.0772 (08)	−0.0963 (10)	7 (1)
O(51)	0.2949 (15)	0.3063 (08)	−0.0662 (09)	5 (1)
O(52)	0.1638 (14)	0..2402 (07)	0.1682 (09)	4.9 (9)
O(53)	0.1292 (16)	0.1316 (08)	−0.0432 (09)	6 (1)
O(61)	0.6228 (17)	0.2803 (07)	0.3163 (10)	6 (1)
O(62)	0.578 (02)	0.4625 (09)	0.2871 (12)	9 (1)
O(63)	0.382 (02)	0.4281 (10)	0.0518 (10)	8 (1)
O(64)	0.1923 (16)	0.3458 (08)	0.2575 (10)	6 (1)
O(71)	0.7655 (19)	0.4760 (08)	0.0984 (11)	6 (1)
O(72)	0.8849 (16)	0.3593 (09)	0.2962 (09)	6 (1)
O(73)	0.6012 (15)	0.3461 (07)	−0.0366 (08)	4.5 (8)
O(74)	1.0446 (16)	0.3354 (08)	0.0632 (10)	7 (1)
C(11)	0.328 (02)	0.0481 (11)	0.1454 (14)	4.3 (5)
C(12)	0.584 (02)	0.0019 (11)	0.1097 (14)	4.0 (5)
C(13)	0.464 (02)	−0.0148 (11)	0.2558 (13)	3.8 (5)
C(21)	0.871 (02)	0.0798 (10)	0.3250 (12)	3.2 (4)
C(22)	0.8563 (20)	0.0873 (09)	0.1603 (12)	2.8 (4)
C(23)	0.8287 (20)	0.1790 (10)	0.2540 (12)	2.8 (4)
C(31)	0.450 (2)	0.1884 (11)	0.3716 (13)	3.7 (5)
C(32)	0.268 (02)	0.1231 (09)	0.2768 (11)	2.9 (4)
C(33)	0.453 (02)	0.0731 (12)	0.3879 (15)	4.6 (5)
C(41)	0.8184 (20)	0.1925 (09)	0.0350 (11)	2.6 (4)
C(42)	0.643 (02)	0.2280 (10)	−0.0926 (13)	3.3 (4)
C(43)	0.671 (02)	0.1152 (11)	−0.0616 (13)	3.8 (5)
C(51)	0.316 (02)	0.2679 (11)	−0.0273 (13)	3.6 (5)
C(52)	0.2317 (19)	0.2276 (09)	0.1165 (12)	2.9 (4)
C(53)	0.206 (2)	0.1602 (11)	−0.0144 (13)	4.0 (5)
C(61)	0.571 (02)	0.3103 (11)	0.2711 (14)	3.9 (5)
C(62)	0.545 (02)	0.4230 (12)	0.2543 (14)	4.4 (5)
C(63)	0.421 (02)	0.4016 (12)	0.1037 (16)	5.2 (6)
C(64)	0.300 (02)	0.3501 (10)	0.2335 (13)	3.9 (5)
C(71)	0.765 (02)	0.4297 (12)	0.1106 (14)	4.3 (5)
C(72)	0.839 (02)	0.3556 (11)	0.2347 (14)	3.9 (5)
C(73)	0.647 (02)	0.3367 (10)	0.0279 (13)	3.6 (5)
C(74)	0.940 (03)	0.3391 (12)	0.0850 (14)	5.2 (6)
H(12)	0.677 (13)	0.039 (07)	0.245 (08)	2.0
H(13)	0.473 (14)	0.196 (07)	0.231 (08)	2.0
H(15)	0.370 (14)	0.161 (07)	0.120 (08)	2.0
H(23)	0.656 (14)	0.131 (07)	0.336 (08)	2.0
H(26)	0.433 (14)	0.310 (07)	0.132 (08)	2.0
H(27)	0.748 (13)	0.285 (07)	0.156 (08)	2.0
H(45)	0.450 (14)	0.167 (07)	−0.021 (08)	2.0
H(67)	0.664 (14)	0.379 (07)	0.214 (08)	2.0

An ORTEP drawing of the molecular structure of **3** is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected interatomic distances and angles are listed in Tables IX and X. The cluster consists of seven osmium and two platinum atoms. Metal atoms Os(1)–Os(5) plus Pt(1) and Pt(2) are arranged in the form of a vertex-shared bitetrahedron similar to that of **2**. However, Pt(2) is bonded to two additional osmium atoms, Os(6) and Os(7), which form another triangular group. The ^1H NMR spectrum of **3** shows only a few broad peaks at 25 °C. However, at −75 °C eight sharp singlets are observed at −7.95, −8.00, −10.06, −10.29, −15.35, −16.90, −16.91, and −17.48 ppm and are indicative of eight inequivalent hydride ligands. Platinum satellites were not observed at this temperature, but the intensity of the four lower field resonances was only about two-thirds the

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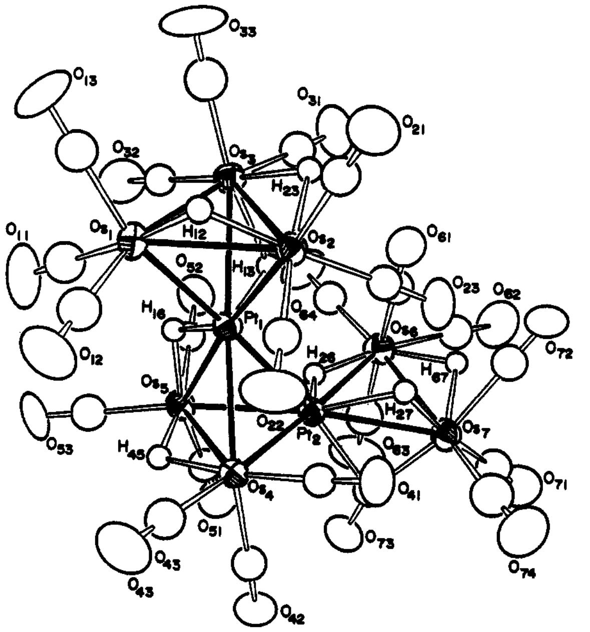

Figure 3. ORTEP diagram of $Pt_2Os_7(CO)_{23}(\mu\text{-}H)_8$ (3) showing 50% probability thermal ellipsoids.

Table IX. Intramolecular Distances (Å) for 3

Pt(1)–Pt(2)	2.942 (2)	Os(3)–C(32)	1.90 (2)
Pt(1)–Os(1)	2.729 (2)	Os(3)–C(33)	1.97 (3)
Pt(1)–Os(2)	2.724 (1)	Os(3)–H(13)	2.1 (2)
Pt(1)–Os(3)	2.851 (1)	Os(3)–H(23)	1.9 (1)
Pt(1)–Os(4)	2.785 (1)	Os(4)–Os(5)	2.885 (1)
Pt(1)–Os(5)	2.873 (1)	Os(4)–C(41)	1.88 (2)
Pt(1)–H(13)	1.9 (1)	Os(4)–C(42)	1.99 (2)
Pt(1)–H(15)	1.7 (1)	Os(4)–C(43)	1.94 (3)
Pt(2)–Os(4)	2.703 (1)	Os(4)–H(45)	1.9 (1)
Pt(2)–Os(5)	2.701 (1)	Os(5)–C(51)	1.92 (3)
Pt(2)–Os(6)	2.998 (1)	Os(5)–C(52)	1.89 (2)
Pt(2)–Os(7)	2.824 (1)	Os(5)–C(53)	1.93 (3)
Pt(2)–C(73)	2.21 (2)	Os(5)–H(15)	1.8 (1)
Pt(2)–H(26)	1.9 (1)	Os(5)–H(45)	1.8 (1)
Pt(2)–H(27)	2.1 (1)	Os(6)–Os(7)	2.913 (1)
Os(1)–Os(2)	2.841 (1)	Os(6)–C(61)	1.93 (3)
Os(1)–Os(3)	2.775 (1)	Os(6)–C(62)	1.95 (3)
Os(1)–C(11)	1.90 (2)	Os(6)–C(63)	1.93 (3)
Os(1)–C(12)	1.95 (2)	Os(6)–C(64)	1.94 (2)
Os(1)–C(13)	1.89 (3)	Os(6)–H(26)	1.6 (2)
Os(1)–H(12)	1.8 (1)	Os(6)–H(67)	1.8 (1)
Os(2)–Os(3)	2.947 (1)	Os(7)–C(71)	1.93 (3)
Os(2)–C(21)	1.90 (2)	Os(7)–C(72)	1.97 (2)
Os(2)–C(22)	1.94 (2)	Os(7)–C(73)	1.98 (2)
Os(2)–C(23)	1.89 (2)	Os(7)–C(74)	1.96 (3)
Os(2)–H(12)	1.8 (2)	Os(7)–H(27)	1.7 (2)
Os(2)–H(23)	1.9 (1)	Os(7)–H(67)	1.9 (1)
Os(3)–C(31)	1.91 (3)	O–C(av)	1.14 (3)

intensity of the four higher field resonances. The missing intensity is assumed to exist in broad unobserved platinum satellites due to coupling to ^{195}Pt (33% abundant) that have not sharpened at −75 °C. The structural analysis of 3 was of high quality, and a search of difference Fourier maps revealed the locations of the eight inequivalent bridging hydride ligands. All were subsequently refined with credible bond parameters. Four of these ligands are bonded directly to one platinum atom, while the other four are not. In seven of the eight cases, the associated metal–metal bond shows the well-known lengthening effect caused by the hydride ligand.[4] In the one case, H(27), where the metal–metal bond is not lengthened, the bond also contains a strong semibridging carbonyl ligand, C(73)–O(73), that could counterbalance the expected lengthening effect. When the sample is warmed to −46 °C, two of the platinum-bonded hydride resonances, −7.95 and −10.06 ppm, broaden and collapse into the baseline, and the closely spaced pair at −16.90 and −16.91 ppm have averaged to a singlet. The other resonances are unchanged. We attribute these effects to a dynamical averaging process. A two-step mechanism that we consider to be very attractive is the following: (1) The semibridging carbonyl ligand C(73)–O(73) is shifted to a terminal position on Os(7), and carbonyl C(63)–O(63) on Os(6) is shifted to a semibridging position across the Os(6)–Pt(2) bond. (2) To complete the process, the hydride H(16) must be shifted to a bridging position across the Pt(1)–Os(4) bond. If averaging within the Os_3 triangle is rapid as in 2 (vide supra), then hydrides H(12) and H(23) will be averaged. By this mechanism, the hyrides H(16), H(13), H(45), and H(67) are not averaged, as observed. At temperatures above −26 °C, all remaining resonances begin to broaden. We have not been able to obtain spectra in the fast-exchange region of the spectrum, and we do not wish to speculate about possible mechanisms for this higher temperature exchange process at this time. Overall, compound 3 contains 130 valence electrons, which is two less than that required by Mingos' theory of condensed polyhedra.[14] As in 2, we believe this may be attributed to a 16-electron center at Pt(2).[17]

Table X. Intramolecular Bond Angles (deg) for 3

Pt(2)–Pt(1)–Os(1)	177.19 (4)	Os(5)–Pt(2)–Os(7)	164.62 (4)
Pt(2)–Pt(1)–Os(2)	119.53 (4)	Os(6)–Pt(2)–Os(7)	59.96 (3)
Pt(2)–Pt(1)–Os(3)	122.51 (4)	Pt(1)–Os(1)–Os(2)	58.50 (3)
Pt(2)–Pt(1)–Os(4)	56.26 (3)	Pt(1)–Os(1)–Os(3)	62.39 (4)
Pt(2)–Pt(1)–Os(5)	55.34 (3)	Os(2)–Os(1)–Os(3)	63.28 (3)
Os(1)–Pt(1)–Os(2)	62.82 (3)	Pt(1)–Os(2)–Os(1)	58.68 (4)
Os(1)–Pt(1)–Os(3)	59.59 (3)	Pt(1)–Os(2)–Os(3)	60.22 (3)
Os(1)–Pt(1)–Os(4)	121.76 (4)	Os(1)–Os(2)–Os(3)	57.26 (3)
Os(1)–Pt(1)–Os(5)	122.22 (4)	Pt(1)–Os(3)–Os(1)	58.02 (3)
Os(2)–Pt(1)–Os(3)	63.77 (3)	Pt(1)–Os(3)–Os(2)	56.01 (3)
Os(2)–Pt(1)–Os(4)	113.77 (4)	Os(1)–Os(3)–Os(2)	59.47 (3)
Os(2)–Pt(1)–Os(5)	174.02 (4)	Pt(1)–Os(4)–Pt(2)	64.81 (4)
Os(3)–Pt(1)–Os(4)	176.69 (4)	Pt(1)–Os(4)–Os(5)	60.87 (3)
Os(3)–Pt(1)–Os(5)	121.02 (4)	Pt(2)–Os(4)–Os(5)	57.70 (3)
Os(4)–Pt(1)–Os(5)	61.29 (3)	Pt(1)–Os(5)–Pt(2)	63.62 (4)
Pt(1)–Pt(1)–Os(4)	58.94 (4)	Pt(1)–Os(5)–Os(4)	57.85 (3)
Pt(1)–Pt(2)–Os(5)	61.04 (3)	Pt(2)–Os(5)–Os(4)	57.78 (3)
Pt(1)–Pt(2)–Os(6)	119.55 (4)	Pt(2)–Os(6)–Os(7)	57.06 (3)
Pt(1)–Pt(2)–Os(7)	134.14 (4)	Pt(2)–Os(7)–Os(6)	62.98 (3)
Os(4)–Pt(2)–Os(5)	64.52 (3)	Pt(2)–C(73)–O(73)	119 (2)
Os(4)–Pt(2)–Os(6)	177.43 (4)	Os(7)–C(73)–O(73)	156 (2)
Os(4)–Pt(2)–Os(7)	122.61 (4)	Os–C(av)–O	177 (2)
Os(5)–Pt(2)–Os(6)	113.00 (4)		

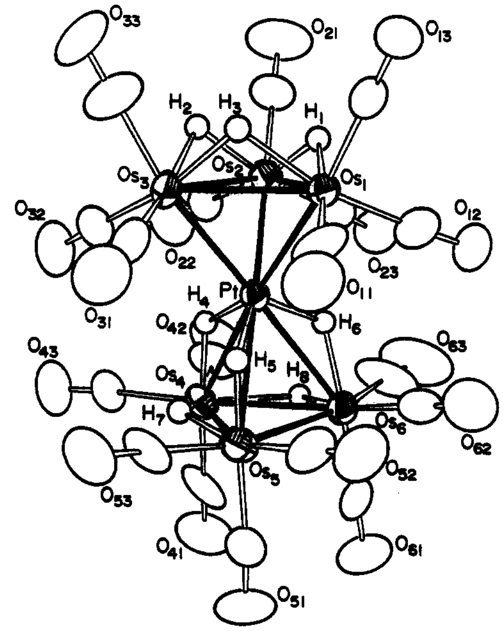

Figure 4. ORTEP diagram of $PtOs_6(CO)_{18}(\mu\text{-}H)_8$ (4) showing 50% probability thermal ellipsoids.

An ORTEP drawing of the molecular structure of 4 is shown in Figure 4. Final atomic positional parameters are listed in Table XI. Selected bond distances and angles are listed in Tables XII and XIII. This cluster consists of two tetrahedral $PtOs_3$ clusters

Table XI. Positional Parameters and *B*(eq) for $PtOs_6(CO)_{18}H_8$ (**4**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt	0.32773 (07)	0.76189 (05)	0.15679 (08)	2.53 (3)
Os(1)	0.23099 (08)	0.89946 (05)	0.17133 (08)	2.85 (3)
Os(2)	0.25027 (08)	0.83653 (05)	−0.08530 (08)	3.20 (3)
Os(3)	0.03594 (08)	0.74792 (05)	0.00832 (08)	3.26 (3)
Os(4)	0.46395 (09)	0.61885 (05)	0.15552 (09)	3.44 (3)
Os(5)	0.42117 (09)	0.67353 (06)	0.41518 (09)	3.46 (3)
Os(6)	0.64182 (08)	0.77393 (05)	0.34071 (08)	3.08 (3)
O(11)	0.1928 (18)	0.8562 (12)	0.4427 (17)	6.6 (8)
O(12)	0.5384 (17)	1.0063 (11)	0.3195 (19)	7.0 (8)
O(13)	0.0957 (19)	1.0495 (11)	0.1481 (17)	7.5 (8)
O(21)	0.125 (02)	0.9347 (14)	−0.3360 (19)	8 (1)
O(22)	0.241 (02)	0.6859 (13)	−0.260 (02)	8 (1)
O(23)	0.5726 (17)	0.9124 (12)	−0.0137 (19)	6.6 (8)
O(31)	−0.0447 (17)	0.6778 (13)	0.2460 (19)	6.8 (9)
O(32)	0.0064 (17)	0.5786 (12)	−0.133 (02)	6.9 (8)
O(33)	−0.2742 (18)	0.7642 (14)	−0.179 (02)	10 (1)
O(41)	0.694 (02)	0.5189 (14)	0.305 (02)	10 (1)
O(42)	0.539 (02)	0.6400 (14)	−0.099 (03)	9 (1)
O(43)	0.222 (02)	0.4672 (12)	−0.007 (02)	7.8 (9)
O(51)	0.6282 (17)	0.5833 (12)	0.6254 (17)	6.7 (8)
O(52)	0.4515 (18)	0.8065 (12)	0.6452 (17)	6.5 (8)
O(53)	0.1492 (20)	0.5643 (13)	0.4192 (20)	7.4 (9)
O(61)	0.8852 (19)	0.7015 (14)	0.553 (02)	9 (1)
O(62)	0.691 (04)	0.9166 (15)	0.544 (02)	17 (1)
O(63)	0.836 (02)	0.8685 (17)	0.213 (03)	13 (2)
C(11)	0.213 (02)	0.8738 (17)	0.341 (02)	5 (1)
C(12)	0.427 (02)	0.9649 (16)	0.263 (02)	4 (1)
C(13)	0.148 (02)	0.9921 (15)	0.1539 (18)	3.9 (8)
C(21)	0.174 (02)	0.8945 (16)	−0.243 (02)	5 (1)
C(22)	0.242 (02)	0.7440 (15)	−0.198 (02)	4 (1)
C(23)	0.452 (02)	0.8859 (14)	−0.040 (02)	4 (1)
C(31)	−0.009 (02)	0.7052 (15)	0.158 (02)	4 (1)
C(32)	0.016 (02)	0.6436 (16)	−0.080 (02)	5 (1)
C(33)	−0.160 (03)	0.7578 (19)	−0.108 (03)	7 (1)
C(41)	0.611 (03)	0.5554 (15)	0.252 (03)	6 (1)
C(42)	0.511 (03)	0.6351 (18)	−0.003 (03)	6 (1)
C(43)	0.307 (03)	0.5254 (14)	0.053 (02)	5 (1)
C(51)	0.555 (02)	0.6196 (14)	0.551 (02)	4.2 (9)
C(52)	0.437 (02)	0.7561 (17)	0.560 (03)	5 (1)
C(53)	0.246 (03)	0.6050 (15)	0.418 (02)	4 (1)
C(61)	0.795 (02)	0.7288 (15)	0.470 (02)	5 (1)
C(62)	0.677 (03)	0.8633 (18)	0.471 (03)	8 (1)
C(63)	0.760 (03)	0.8286 (20)	0.253 (04)	9 (2)
H(1)	0.226 (15)	0.919 (10)	0.000 (15)	3.0
H(2)	0.044 (15)	0.805 (10)	−0.132 (15)	3.0
H(3)	0.040 (15)	0.855 (10)	0.037 (16)	3.0
H(4)	0.355 (15)	0.678 (10)	0.058 (15)	3.0
H(5)	0.306 (15)	0.723 (10)	0.323 (15)	3.0
H(6)	0.516 (15)	0.807 (10)	0.188 (15)	3.0
H(7)	0.3506	0.6200	0.2623	10.0
H(8)	0.6586	0.7180	0.1843	10.0

Table XII. Intramolecular Distances (Å) for **4**

Pt–Os(1)	2.694 (1)	Os(3)–C(33)	1.93 (2)
Pt–Os(2)	2.697 (1)	Os(3)–H(2)	1.8 (2)
Pt–Os(3)	2.719 (1)	Os(3)–H(3)	1.8 (2)
Pt–Os(4)	2.991 (1)	Os(4)–Os(5)	3.017 (1)
Pt–Os(5)	2.964 (1)	Os(4)–Os(6)	2.970 (1)
Pt–Os(6)	2.974 (1)	Os(4)–C(41)	1.96 (3)
Pt–H(4)	1.8 (2)	Os(4)–C(42)	1.88 (3)
Pt–H(5)	1.9 (1)	Os(4)–C(43)	1.93 (2)
Pt–H(6)	1.8 (1)	Os(4)–H(4)	1.7 (1)
Os(1)–Os(2)	2.908 (1)	Os(4)–H(7)	1.89
Os(1)–Os(3)	2.892 (1)	Os(4)–H(8)	2.24
Os(1)–C(11)	1.87 (2)	Os(5)–Os(6)	2.899 (1)
Os(1)–C(12)	1.93 (2)	Os(5)–C(51)	1.91 (2)
Os(1)–C(13)	1.88 (2)	Os(5)–C(52)	1.94 (3)
Os(1)–H(1)	1.8 (1)	Os(5)–C(53)	1.93 (2)
Os(1)–H(3)	1.9 (1)	Os(5)–H(5)	1.6 (1)
Os(2)–Os(3)	2.891 (1)	Os(5)–H(7)	1.60
Os(2)–C(21)	1.87 (2)	Os(6)–C(61)	1.91 (2)
Os(2)–C(22)	1.88 (2)	Os(6)–C(62)	1.86 (3)
Os(2)–C(23)	1.93 (2)	Os(6)–C(63)	1.88 (3)
Os(2)–H(1)	1.7 (2)	Os(6)–H(6)	1.8 (1)
Os(2)–H(2)	1.8 (1)	Os(6)–H(8)	1.92
Os(3)–C(31)	1.88 (3)	O–C(av)	1.15 (3)
Os(3)–C(32)	1.88 (3)		

sharing a common Pt vertex. The two Os_3 triangles lie in a staggered rotational conformation. The ^1H NMR spectrum at 25 °C shows three hydride resonances: −18.59 (3 H), −18.63 (3 H), and −20.25 ppm (2 H). The first shows strong coupling to platinum, 624.9 Hz, the second shows weak coupling to platinum, 22.5 Hz, and the third shows no platinum coupling. The presence of eight hydride ligands was confirmed by the mass spectrum which shows a parent ion at *m*/*e* 1849 with an isotope distribution consistent with the presence of six osmium atoms and one platinum atom. A close inspection of difference Fourier maps revealed the probable locations of eight bridging hydride ligands. Six of these, H(1)–H(6), were subsequently refined. Two, H(7) and H(8), would not converge upon refinement and were finally added as fixed contributions. Three of the hydride ligands, H(1)–H(3), bridge the Os–Os bonds on the Os_3 triangle Os(1)–Os(3) in a manner similar to that found in **1** and **2**. H(4)–H(6) bridge the Pt–Os bonds to the second Os_3 triangle. H(7) and H(8) bridge two Os–Os bonds in the Os(4)–Os(6) triangle and lie approximately in the plane of the triangle. The observation that ligands H(1)–H(3) and H(4)–H(6) form two equivalent sets of three as indicated by the ^1H NMR spectra suggests that H(7) and H(8) are circulating among all three Os–Os bonds on the Os(4)–Os(6) triangle. Low-temperature ^1H NMR studies of **4** that might confirm this have not been performed. As in **1**–**3**, the hydride-bridged metal–metal bonds in **4** are all significantly longer than the coresponding nonbridged bonds. Compound **4** contains 102 valence electrons and obeys Mingos' theory of condensed polyhedra.[14]

Treatment of **2** with $Os_3(CO)_{13}(NCMe)$ produces $Os_3(CO)_{12}$ and some **1**, ~20% yield. Evidently, $Os_3(CO)_{11}(NCMe)$ serves to decarbonylate **2**, which then expels one platinum atom to yield **1**. The fate of this platinum atom was not determined. $W(CO)_5(NCMe)$ reacts with **2** in a similar manner to produce **1**, ~15% yield.

Complexes **1**–**3** were readily degraded by reaction with CO at 25 °C/1 atm. In a reaction period of 15 min, we were able to isolate **2** in about 50% yield from the reaction of **3** with CO; however, **2** is also degraded by CO. Additional information about the course of the degradation was obtained by carrying out the reactions in NMR tubes and following by ^1H NMR spectroscopy. A summary of these results is given in Scheme I.

Three hydride-containing products were observed in the reactions of each of **1**–**3** with CO. Two of these were the known compounds $H_2Os(CO)_4$ and $H_2Os_2(CO)_8$. Hydrogen was also evolved, and workup of the reaction showed the presence of the known cluster complex $PtOs_2(CO)_{10}$.[7] $PtOs_2(CO)_{10}$ slowly loses CO to yield the original starting material $Pt_2Os_4(CO)_{18}$.[7] An unidentified and unstable hydride-containing product that exhibited a resonance at −19.09 ppm with long-range coupling to Pt, J_{Pt-H} = 23 Hz, was observed as a transient intermediate in these decompositions, but it could not be isolated and was not further characterized. With this information, we can describe the decomposition of the **3** as follows: (1) a molecule of $H_2Os_2(CO)_8$ is cleaved, and with addition of 2 equiv of CO, compound **2** is formed; (2) **2** is subsequently fragmented to $PtOs_2(CO)_{10}$, $H_2Os(CO)_4$, a second equivalent of $H_2Os_2(CO)_8$, and H_2. An intermediate containing platinum, hydride ligands, and presumably osmium (since the small Pt–H coupling indicates that the hydrides are not bonded directly to the platinum) is traversed. We believe that this intermediate is the compound $PtOs_3(CO)_{12}(\mu\text{-}H)_2$, which was partially characterized by Farrugia.[18] Phosphine derivatives of $PtOs_3(CO)_{12}(\mu\text{-}H)_2$ have been isolated and fully characterized.[19] All the osmiums and hydrogens are accounted for in this degradation process. One of the platinum

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Scheme I

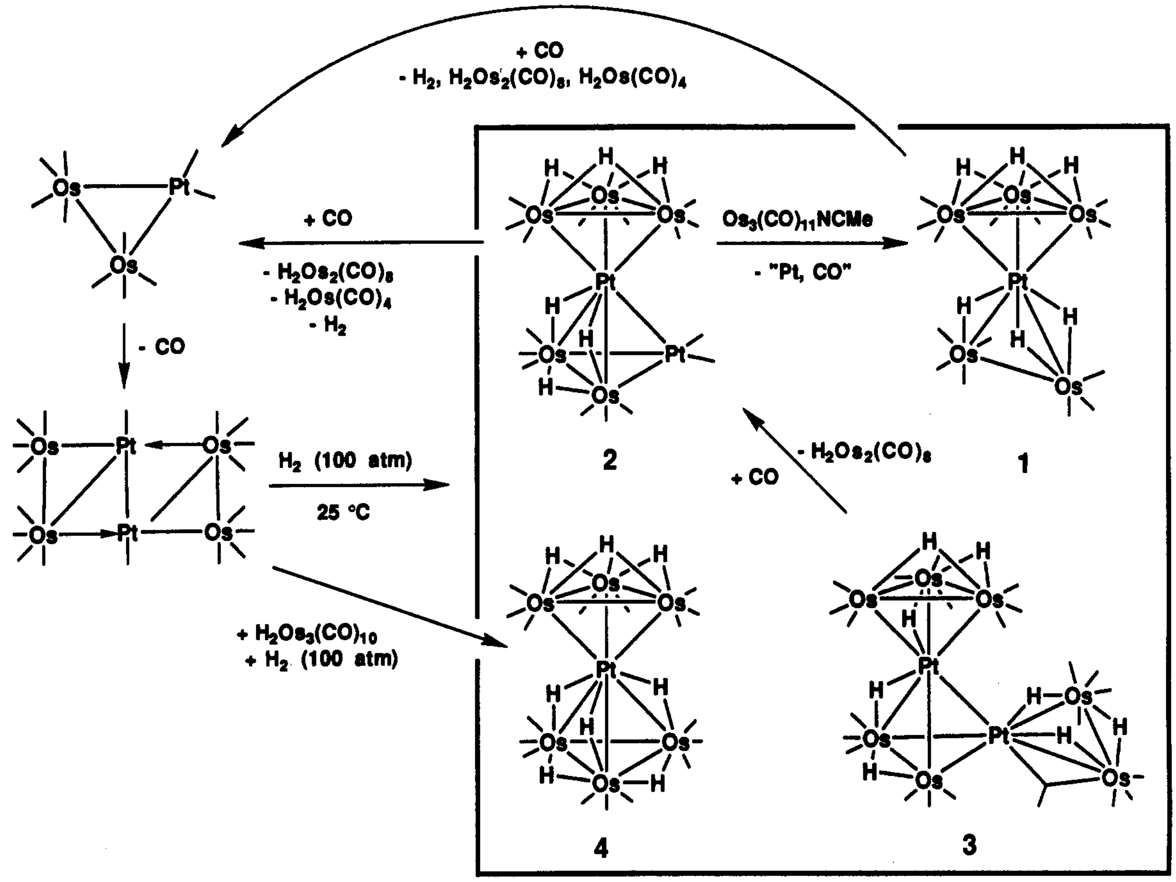

Table XIII. Intramolecular Bond Angles (deg) for 4

Os(1)-Pt-Os(2)	65.29 (3)	Os(2)-Os(1)-Os(3)	59.79 (3)
Os(1)-Pt-Os(3)	64.60 (3)	Pt-Os(2)-Os(1)	57.30 (3)
Os(1)-Pt-Os(4)	174.55 (4)	Pt-Os(2)-Os(3)	58.10 (3)
Os(1)-Pt-Os(5)	118.15 (4)	Os(1)-Os(2)-Os(3)	59.84 (3)
Os(1)-Pt-Os(6)	114.97 (4)	Pt-Os(3)-Os(1)	57.28 (3)
Os(2)-Pt-Os(3)	64.52 (3)	Pt-Os(3)-Os(2)	57.38 (3)
Os(2)-Pt-Os(4)	115.62 (4)	Os(1)-Os(3)-Os(2)	60.37 (3)
Os(2)-Pt-Os(5)	176.48 (4)	Pt-Os(4)-Os(5)	59.12 (3)
Os(2)-Pt-Os(6)	119.98 (4)	Pt-Os(4)-Os(6)	59.86 (3)
Os(3)-Pt-Os(4)	120.80 (4)	Os(5)-Os(4)-OS(6)	57.92 (3)
Os(3)-Pt-Os(5)	117.17 (4)	Pt-Os(5)-Os(4)	60.00 (3)
Os(3)-Pt-Os(6)	175.17 (4)	Pt-Os(5)-Os(6)	60.95 (3)
Os(4)-Pt-Os(5)	60.88 (3)	Os(4)-Os(5)-Os(6)	60.22 (3)
Os(4)-Pt-Os(6)	59.72 (3)	Pt-Os(6)-Os(4)	60.42 (3)
Os(5)-Pt-Os(6)	58.44 (3)	Pt-Os(6)-Os(5)	60.60 (3)
Pt-Os(1)-Os(2)	57.41 (3)	Os(4)-Os(6)-Os(5)	61.86 (3)
Pt-Os(1)-Os(3)	58.12 (3)	Os-C(av)-O	177 (3)

atoms is found in $PtOs_2(CO)_{10}$, but we have not been able to establish the fate of the second platinum atom.

Compound **1** is slowly degraded (about 50% in 12 h) by CO (25 °C/1 atm). The products are $PtOs_2(CO)_{10}$, H_2, $H_2Os(CO)_4$, and $H_2Os_2(CO)_8$. The unknown intermediate was also observed in this reaction. Thus, the degradation of **1** is believed to be similar to that of **2** and **3**.

Compound **4** showed no evidence of a reaction with CO at 25 °C/1 atm over a period of 10 h. The lack of reactivity may be related to its electronic structure. Of the four new cluster complexes **1**–**4**, only compound **4** is electronically saturated (vide supra).

Our studies show that heteronuclear platinum–osmium carbonyl cluster complexes can absorb relatively large amounts of hydrogen under mild conditions. The complexes consist of small heteronuclear clusters of platinum and osmium that are fused through vertex-sharing platinum atoms. Studies of the reactivity of these clusters toward other small molecules are in progress.

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Supplementary Material Available: For all of the structural analyses, tables of anisotropic thermal parameters (12 pages); listings of structure factor amplitudes (76 pages). Ordering information is given on any current masthead page.