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Cluster Synthesis. 34. Unsaturation in a High-Nuclearity Platinum–Osmium Carbonyl Cluster Complex. Studies of the Synthesis, Structure, and Reactivity of $Pt_2Os_4(CO)_{11}(COD)_2$

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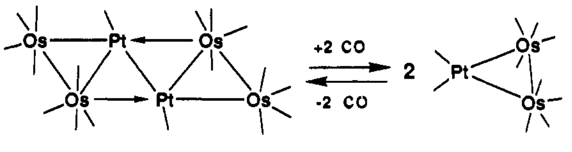
From the reaction of $Pt_2Os_4(CO)_{18}$ with cycloocta-1,5-diene at 97 °C, the new platinum osmium carbonyl cluster complexes $Pt_2Os_4(CO)_{12}(COD)_2$ (**2**) (55% yield) and $Pt_2Os_4(CO)_{11}(COD)_2$ (**3**) (9% yield), COD = cycloocta-1,5-diene were obtained. Compounds **2** and **3** were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. The structures of **2** and **3** both consist of an Os_4 tetrahedron that is capped on two faces by Pt(COD) groups. Compound **2** is electronically saturated with 84 valence electrons, and all metal–metal bond distances lie within the normal ranges. On the other hand, compound **3** is electronically unsaturated by the amount of two electrons, and three of the metal–metal bonds are unusually short: Os(2)–Os(3) = 2.530 (1) Å, Pt(1)–Os(3) = 2.606 (1) Å, and Pt(2)–Os(2) = 2.614 (1) Å. Compound **3** can be obtained in a good yield (83%) by photodecarbonylation of **2**. Compound **3** readily adds CO (25 °C/1 atm) to a re-form **2**. Compound **3** reacts with $Pt(COD)_2$ at 40 °C to yield the expanded cluster complex $Pt_3Os_4(CO)_{11}(COD)_3$ (**4**) (37%). Compound **4** was characterized by a single-crystal X-ray diffraction analysis. The structure of **4** is similar to that of **3** but contains a Pt(COD) grouping that was added across the short Os–Os bond. Compound **3** also reacts with H_2S to yield the new complex $PtOs_4(CO)_{11}(COD)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**5**) (33%). Compound **5** was also characterized by a single-crystal X-ray diffraction analysis. The structure of **5** consists of an Os_4 butterfly tetrahedron with a Pt(COD) capping group and a triply bridging sulfido ligand across one of the open Os_3 triangular groupings in the butterfly. Crystal data: for **2**, space group = $P\bar{1}$, a = 11.217 (2) Å, b = 17.295 (3) Å, c = 8.866 (2) Å, α = 92.88 (2)°, β = 105.82 (2)°, γ = 104.23 (2)°, Z = 2, 3084 reflections, R = 0.038; for **3**, space group = $P2_1/c$, a = 8.622 (2) Å, b = 21.917 (5) Å, c = 16.767 (3) Å, β = 95.61 (2)°, Z = 4, 2698 reflections, R = 0.033; for **4**, space group = $P2_1/c$, a = 17.198 (4) Å, b = 21.284 (4) Å, c = 24.802 (7) Å, β = 107.18 (2)°, Z = 8, 5158 reflections, R = 0.040, for **5**, space group = $P2_1/n$, a = 9.220 (4) Å, b = 21.846 (8) Å, c = 14.732 (4) Å, β = 91.84 (3)°, Z = 4, 2039 reflections, R = 0.041.

Introduction

Recently, there has been a great interest in the chemistry of heteronuclear cluster complexes containing platinum.[1] Much of this has been stimulated by the importance of heterobimetallic "clusters" containing platinum as catalysts in the petroleum reforming process.[2] We have been investigating the chemistry of mixed-metal cluster complexes containing platinum with iron,[3] ruthenium,[4] or osmium.[5] The compound $Pt_2Os_4(CO)_{18}$ (**1**) has been obtained both by the reaction of $Pt(COD)Me_2$ with $Os_3(CO)_{10}(\mu\text{-}H)_2$[6] and by the reaction of $Os(CO)_5$ with $Pt(COD)_2$.[7] The structure of **1** has been shown to have a puckered ladderlike structure consisting of two mutually bonded Pt(CO) groupings between pairs of mutually bonded $Os(CO)_4$ groups. The molecule can be split in two by reaction with CO at 50 atm/25 °C (eq 1).[6]



(1)

$Pt_2Os_4(CO)_{18}$, 1 $PtOs_2(CO)_{10}$

The reaction of **1** with hydrogen at 25 °C/100 atm has yielded a series of new hydrogen-rich platinum osmium carbonyl cluster complexes: $PtOs_5(CO)_{16}(\mu\text{-}H)_6$, $Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6$, $Pt_2Os_7(CO)_{23}(\mu\text{-}H)_8$, and $PtOs_6(CO)_{18}(\mu\text{-}H)_8$.[7] Their structures consist of vertex-fused tetrahedra with platinum atoms occupying the vertex-sharing positions.

We have now investigated the reaction of **1** with cycloocta-1,5-diene, COD. Two new complexes, $Pt_2Os_4(CO)_{12}(COD)_2$ (**2**) and $Pt_2Os_4(CO)_{11}(COD)_2$ (**3**), have been obtained and structurally characterized. Compound **3** was found to react with $Pt(COD)_2$ to yield a larger cluster complex, $Pt_3Os_4(CO)_{11}(COD)_3$ (**4**), and with H_2S to yield a smaller cluster, $PtOs_4(CO)_{11}(COD)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**5**), that contains a triply bridging sulfido ligand and two bridging hydride ligands. Details of this study are described in this report. 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. $Pt_2Os_4(CO)_{18}$[7] and $Pt(COD)_2$[9] were prepared by the previously reported procedures. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM-300 FT-NMR spectrometer. Elemental microanalyses were performed by Desert Analytics, Tucson, AZ. TLC separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Whatman 0.25 mm). UV irradiations were performed by using an 85-W external high-pressure mercury lamp on reactions solutions in Pyrex glassware.

Synthesis of $Pt_2Os_4(CO)_{12}(COD)_2$ (2). In a typical reaction, 36.0 mg of $Pt_2Os_4(CO)_{18}$ (**1**) (0.022 mmol) was allowed to react with 0.36 mL of COD (2.89 mmol) in 25 mL of heptane at 97 °C for 4.5 h. The color of the solution changed from dark red to red-brown during this time. The solvent was removed in vacuo. The residue was redissolved in a minimal amount of CH_2Cl_2 and was separated by TLC on silica gel with a hexane/CH_2Cl_2 (7/3) solvent mixture. This yielded 20.5 mg of red-brown $Pt_2Os_4(CO)_{12}(COD)_2$ (**2**) (55%) and 3.6 mg of yellow-brown $Pt_2Os_4(CO)_{11}(COD)_2$ (**3**) (9%). A small amount (0.6 mg) of a yellow compound that we have formulated as $PtOs_2(CO)_8(COD)$ was eluted before the principal products **2** and **3**. This compound slowly decomposes at 25 °C, and some **1** is formed in the process. Other decomposition products have not been identified. In the TLC, 4.5 mg of a green compound eluted

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Table I. Crystal Data for Compounds **2–5**

	2	**3**	**4**	**5**
formula	$Pt_2Os_4O_{12}C_{28}H_{24}$	$Pt_2Os_4O_{11}C_{27}H_{24}$	$Pt_3Os_4O_{11}C_{35}H_{36}\cdot C_6H_6$	$PtOs_4SO_{11}C_{19}H_{14}\cdot CH_2Cl_2$
fw	1703.47	1675.46	2056.85	1491.19
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
lattice params				
a, Å	11.217 (2)	8.622 (2)	17.198 (4)	9.220 (4)
b, Å	17.295 (3)	21.917 (5)	21.284 (3)	21.846 (8)
c, Å	8.866 (2)	16.767 (3)	24.802 (7)	14.732 (4)
α, deg	92.88 (2)	90.0	90.0	90.0
β, deg	105.82 (2)	95.61 (2)	107.18 (2)	91.84 (3)
γ, deg	104.23 (2)	90.0	90.0	90.0
V, $Å^3$	1591 (1)	3153 (2)	8674 (7)	2966
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
Z value	2	4	8	4
ρ_{calcd}, g/cm^3	3.55	3.53	3.15	3.34
μ(Mo Kα), cm^{-1}	248.4	250.6	214.8	221.5
temp, °C	20	20	20	20
no. of observns ($I > 3\sigma$)	3083	2698	5138	2039
residuals: R; R_w	0.038; 0.042	0.033; 0.034	0.040; 0.038	0.041; 0.042

before **2** and **3**. This compound has not yielded to exhaustive attempts to obtain crystals for a structural analysis, and thus its structure is currently unknown. This green compound is also obtained by the photolysis of **1** in the absence of COD. IR ν(CO) (cm^{-1}): for **2** (in hexane), 2059 (m), 2022 (w), 2005 (vs), 1955 (w), 1944 (vw); for **3** (in CH_2Cl_2), 2014 (vs), 1991 (vs), 1982 (sh), 1952 (w), 1926 (vw), 1844 (vw, br); for $PtOs_2(CO)_8(COD)$ (in hexane), 2090 (m), 2043 (vs), 2018 (s), 2004 (vs), 1982 (m), 1969 (s); for green compound (in hexane) 2086 (vs), 2042 (vs), 2033 (s), 2028 (sh). ^1H NMR (δ in $CDCl_3$): for **2**, 5.69 (s, 8 H $^2J_{Pt-H}$ = 61.5 Hz), 2.36 (m, 8 H), 1.92 (m, 8 H); for **3**, 5.03 (s, 4 H, br), 4.33 (s, 4 H, br), 1.36 (s, 8 H, br), 0.71 (s, 8 H, br); for $PtOs_2(CO)_8(COD)$, 5.47 (s, 4 H, $^2J_{Pt-H}$ = 63 Hz), 1.90 (m, 8 H). The green compound exhibited no proton resonance. The mass spectrum of $PtOs_2(CO)_8(COD)$ exhibited the parent ion m/e = 908 with the expected isotope distribution for one platinum and two osmium atoms and ions corresponding to the loss of each of eight CO ligands plus the COD ligand. Anal. Calcd (found) for **2**: C, 19.74 (19.66); H, 1.42 (1.29). Calcd (found) for **3**: C, 19.36 (19.55); H, 1.44 (1.33).

Decarbonylation of 2. (1) By Photolysis. A solution of **2** (8.0 mg, 0.005 mmol) in 40 mL of CH_2Cl_2 was irradiated by a high-pressure UV lamp (85 W) at 25 °C for 16 h under a purge of nitrogen. The color of the solution changed from red-brown to yellow-brown during this period. The solvent was removed in vacuo, and the residue was separated by TLC on silica gel as described above. This yielded 6.5 mg of **3** (83%) and 1.2 mg of untransformed **2** (15%). Note: When a 1000-W *medium*-pressure mercury lamp was used, only a very small amount of **3** was obtained in a period of 16 h.

(2) By Thermolysis. A 14.0-mg sample of **2** (0.008 mmol) in 40 mL of heptane was heated to 97 °C for 12 h under a purge of nitrogen. TLC yielded only 0.9 mg of **3** (7%) and 12.5 mg of unreacted **2**. At 125 °C, **2** was largely decomposed in 2.5 h and no **3** was obtained.

Reaction of 3 with CO. A solution of 8.5 mg of **3** (0.005 mmol) in 15 mL of CH_2Cl_2 was purged with carbon monoxide at 25 °C for 15 min. The solvent was removed in vacuo, and the residue was separated by TLC plates on silica gel. Yield: 7.3 mg of **2** (84%) and 1.0 mg of **1** (12%).

Reaction of 3 with $Pt(COD)_2$. A 12.0-mg sample of **3** (0.007 mmol) was dissolved in 25 mL of CH_2Cl_2 and heated to 40 °C. Then, 3.0 mg of $Pt(COD)_2$ (0.007 mmol) was added to the solution, and the mixture was refluxed for 3 h. An additional 3.0 mg of $Pt(COD)_2$ was then added into the reaction solution every 3–4 h for a total of 36 h. The solvent was removed in vacuo and the residue was separated by TLC on silica gel by using a CH_2Cl_2/hexane (1/9) solvent mixture. A 5.2-mg yield of $Pt_3Os_4(CO)_{11}(COD)_3$ (**4**) (37%) was obtained, and 3.2 mg of **3** was recovered. Spectroscopic data for **4** are as follows. IR ν(CO) (cm^{-1}) in hexane: 2024 (m), 1991 (vs), 1963 (s), 1953 (w), 1941 (w), 1931 (vw), 1899 (vw, br). ^1H NMR (δ in $CDCl_3$): 5.49 (s, 12 H, $^2J_{Pt-H}$ = 59.5 Hz), 2.20 (m, 12 H), 1.90 (m, 12 H). Anal. Calcd (found): C, 21.25 (21.36); H, 1.83 (2.07).

Reaction of 3 with H_2S. A 10.0-mg sample of **3** (0.006 mmol) was dissolved in 20 mL of CH_2Cl_2. H_2S was then purged through the solution slowly at 25 °C for 20 min. The solvent was removed in vacuo, and the reaction mixture was separated by TLC on silica gel with a CH_2Cl_2/hexane (1/9) solvent mixture. This yielded 2.8 mg of $PtOs_4(CO)_{11}(COD)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**5**) (33%) and 1.4 mg of **2** (14%). Spectroscopic data for **5** are as follows. IR ν(CO) (cm^{-1}) in hexane: 2092 (m), 2072 (vs), 2044 (s), 2017 (vs), 2009 (m), 1990 (s), 1982 (m), 1933 (m). ^1H NMR δ in $CDCl_3$): 6.2 (s, 1 H, br), 5.76 (m, 2 H, br), 4.54 (s, 1 H, br), 2.44 (m, 8 H, br), −14.58 (s, 1 H, $^2J_{Pt-H}$ = 32.6 Hz), −20.96 (s, 1 H, $^2J_{Pt-H}$ = 19.9 Hz). Anal. Calcd (found): C, 16.23 (17.10); H, 1.00 (0.90).

Crystallographic Analysis. Crystals of compound **2** were grown by slow evaporation of solvent from CH_2Cl_2/hexane (3/7) solution at 10 °C. Crystals of compound **3** were grown by slow evaporation of solvent from CH_2Cl_2/hexane (4/1) solution at 25 °C. Crystals of compound **4** were grown by slow evaporation of solvent from benzene/heptane (9/1) solution at 25 °C. Crystals of compound **5** were grown by slow evaporation of solvent from CH_2Cl_2/hexane (1/1) solution at 10 °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.[10a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[10b] Lorentz/polarization (*Lp*) and absorption corrections were applied to the data for each structure. Full-matrix least-squares refinements minimized the function

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

where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compound **2** 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 positions of the metal atoms were obtained by direct methods (MITHRIL). All remaining non-hydrogen atoms were obtained by a series of subsequent difference Fourier syntheses. Only atoms heavier than carbon were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the COD ligands were calculated by using idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compounds **3** and **4** crystallized in the monoclinic crystal system. The systematic absences in the data of both compounds uniquely identified the space group as $P2_1/c$. Both structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. For **3** all non-hydrogen atoms except the COD carbon atoms were refined anisotropically. The positions of the hydrogen atoms on the COD ligands were calculated by using idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. Compound **4** crystallized with two complete molecules in the asymmetric crystal unit. Due to the large size of the structural analysis, only the metal atoms were refined with anisotropic thermal parameters. A molecule of benzene from the crystallization solvent was found cocrystallized with the complex in the final stages of the analysis. It was included in the analysis and was satisfactorily refined. The positions of all hydrogen atoms were calculated by using idealized geometries. Their

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[10] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

Table II. Positional Parameters and *B*(eq) for $Pt_2Os_4(CO)_{12}(COD)_2$ (**2**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.70288 (8)	0.35076 (5)	0.66137 (10)	2.39 (3)
Pt(2)	1.00679 (8)	0.20260 (4)	0.76939 (9)	2.11 (3)
Os(1)	0.90431 (8)	0.29681 (5)	0.55977 (9)	2.18 (3)
Os(2)	0.79872 (8)	0.12623 (5)	0.49593 (10)	2.33 (3)
Os(3)	0.64055 (8)	0.22880 (5)	0.42032 (10)	2.50 (3)
Os(4)	0.75763 (8)	0.21165 (4)	0.74302 (9)	1.96 (3)
O(17)	1.1090 (16)	0.4145 (9)	0.8327 (18)	4.6 (6)
O(18)	0.8624 (17)	0.4382 (10)	0.381 (2)	5.1 (8)
O(19)	1.0912 (17)	0.2765 (9)	0.3816 (19)	4.4 (7)
O(21)	0.9153 (17)	−0.0031 (9)	0.643 (2)	5.4 (7)
O(22)	0.5623 (17)	−0.0159 (10)	0.373 (2)	5.8 (8)
O(23)	0.8898 (20)	0.1109 (9)	0.208 (2)	5.5 (8)
O(31)	0.572 (2)	0.3562 (10)	0.218 (2)	7.6 (9)
O(32)	0.589 (3)	0.1316 (15)	0.103 (2)	10 (1)
O(33)	0.3636 (19)	0.1565 (15)	0.427 (3)	9 (1)
O(41)	0.7131 (16)	0.0434 (8)	0.8419 (19)	4.2 (6)
O(42)	0.8963 (16)	0.3011 (9)	1.0739 (18)	4.3 (6)
O(43)	0.4987 (16)	0.2166 (10)	0.794 (2)	4.5 (7)
C(1)	0.715 (2)	0.4154 (13)	0.891 (3)	3.4 (5)
C(2)	0.823 (2)	0.4496 (13)	0.855 (3)	3.4 (5)
C(3)	0.849 (3)	0.5257 (14)	0.779 (3)	4.3 (5)
C(4)	0.728 (3)	0.5340 (14)	0.645 (3)	4.3 (5)
C(5)	0.650 (2)	0.4544 (12)	0.554 (3)	3.1 (4)
C(6)	0.544 (2)	0.4055 (13)	0.590 (3)	3.4 (5)
C(7)	0.499 (3)	0.4216 (14)	0.731 (3)	4.3 (5)
C(8)	0.600 (3)	0.4502 (14)	0.885 (3)	4.3 (5)
C(9)	1.176 (2)	0.1760 (12)	0.710 (2)	2.9 (4)
C(10)	1.213 (2)	0.2501 (11)	0.779 (2)	2.6 (4)
C(11)	1.291 (3)	0.2759 (14)	0.955 (3)	4.5 (6)
C(12)	1.226 (3)	0.2591 (14)	1.081 (3)	4.5 (5)
C(13)	1.096 (2)	0.2033 (13)	1.026 (3)	3.5 (5)
C(14)	1.069 (2)	0.1272 (13)	0.958 (3)	3.2 (4)
C(15)	1.168 (3)	0.0885 (14)	0.928 (3)	4.3 (5)
C(16)	1.205 (3)	0.1043 (15)	0.780 (3)	4.9 (6)
C(17)	1.037 (2)	0.3660 (13)	0.738 (3)	3.5 (5)
C(18)	0.868 (3)	0.3833 (15)	0.448 (3)	4.1 (5)
C(19)	1.018 (2)	0.2835 (11)	0.445 (2)	2.5 (4)
C(21)	0.880 (2)	0.0509 (14)	0.590 (3)	3.6 (5)
C(22)	0.650 (2)	0.0390 (12)	0.422 (2)	2.5 (4)
C(23)	0.856 (2)	0.1162 (14)	0.316 (3)	3.8 (5)
C(31)	0.598 (2)	0.3083 (14)	0.299 (3)	4.0 (5)
C(32)	0.612 (3)	0.1632 (15)	0.233 (3)	4.9 (6)
C(33)	0.463 (3)	0.1816 (16)	0.426 (3)	4.8 (6)
C(41)	0.728 (2)	0.1038 (13)	0.799 (2)	2.7 (4)
C(42)	0.8493 (19)	0.2683 (11)	0.951 (2)	2.0 (4)
C(43)	0.594 (2)	0.2188 (12)	0.769 (3)	2.8 (4)

Table III. Positional Parameters and *B*(eq) for $Pt_2Os_4(CO)_{11}(COD)_2$ (**3**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.24796 (10)	−0.00075 (4)	0.70642 (5)	3.11 (4)
Pt(2)	0.26446 (10)	0.16462 (4)	0.91540 (5)	2.82 (4)
Os(1)	0.35916 (9)	0.11410 (4)	0.76900 (5)	2.31 (4)
Os(2)	0.07709 (10)	0.17758 (4)	0.78426 (5)	3.00 (4)
Os(3)	0.06729 (10)	0.09407 (4)	0.67973 (5)	3.05 (4)
Os(4)	0.13268 (9)	0.05734 (4)	0.84186 (5)	2.54 (4)
Os(17)	0.6432 (19)	0.0506 (9)	0.8532 (10)	6 (1)
O(18)	0.495 (2)	0.2426 (8)	0.7774 (11)	6 (1)
O(19)	0.485 (2)	0.1032 (9)	0.6087 (10)	7 (1)
O(21)	0.173 (2)	0.3106 (7)	0.7726 (9)	6 (1)
O(22)	−0.198 (2)	0.2104 (10)	0.8785 (13)	9 (1)
O(23)	−0.159 (3)	0.2006 (10)	0.6378 (12)	9 (1)
O(31)	−0.214 (2)	0.0158 (10)	0.6243 (12)	8 (1)
O(32)	0.150 (2)	0.1084 (9)	0.5091 (9)	7 (1)
O(41)	−0.0662 (20)	0.0904 (9)	0.9770 (10)	6 (1)
O(42)	−0.1015 (19)	−0.0440 (8)	0.7937 (10)	6 (1)
O(43)	0.352 (2)	−0.0219 (8)	0.9514 (10)	7 (1)
C(1)	0.408 (3)	−0.0711 (3)	0.7585 (15)	5.6 (6)
C(2)	0.286 (5)	−0.1161 (19)	0.765 (2)	11 (1)
C(3)	0.206 (4)	−0.1400 (17)	0.694 (2)	8.8 (8)
C(4)	0.134 (5)	−0.085 (2)	0.638 (3)	13 (1)
C(5)	0.203 (4)	−0.0514 (14)	0.5975 (17)	6.5 (7)
C(6)	0.356 (6)	−0.057 (2)	0.577 (3)	14 (1)
C(7)	0.486 (4)	−0.0819 (18)	0.628 (2)	9.5 (9)
C(8)	0.488 (5)	−0.0589 (20)	0.706 (2)	11 (1)
C(9)	0.197 (3)	0.2381 (11)	0.9918 (14)	4.6 (5)
C(10)	0.326 (3)	0.2559 (14)	0.9641 (16)	6.4 (7)
C(11)	0.488 (5)	0.257 (2)	0.995 (2)	11 (1)
C(12)	0.562 (4)	0.2040 (20)	1.025 (2)	10 (1)
C(13)	0.477 (3)	0.1476 (13)	1.0032 (15)	5.8 (6)
C(14)	0.354 (3)	0.1268 (12)	1.0337 (15)	5.4 (6)
C(15)	0.281 (3)	0.1590 (13)	1.0979 (14)	5.5 (6)
C(16)	0.199 (4)	0.2105 (19)	1.079 (2)	11 (1)
C(17)	0.535 (3)	0.0735 (12)	0.8265 (14)	4 (1)
C(18)	0.444 (3)	0.1923 (13)	0.7746 (14)	5 (1)
C(19)	0.432 (3)	0.1066 (11)	0.6689 (13)	4 (1)
C(21)	0.137 (3)	0.2613 (13)	0.7771 (12)	4 (1)
C(22)	−0.092 (3)	0.1970 (10)	0.8418 (16)	5 (1)
C(23)	−0.060 (3)	0.1725 (12)	0.6762 (15)	6 (1)
C(31)	−0.100 (3)	0.0458 (13)	0.6455 (14)	5 (1)
C(32)	0.117 (3)	0.1021 (10)	0.5736 (15)	5 (1)
C(41)	0.003 (3)	0.0802 (10)	0.9233 (13)	4 (1)
C(42)	−0.013 (3)	−0.0053 (10)	0.8088 (13)	4 (1)
C(43)	0.266 (3)	0.0069 (10)	0.9129 (13)	4 (1)

Table IV. Intramolecular Distances for **2**[a]

Pt(1)–Os(1)	2.975 (1)	Os(1)–C(19)	1.88 (2)
Pt(1)–Os(3)	2.741 (1)	Os(2)–Os(3)	2.786 (1)
Pt(1)–Os(4)	2.711 (1)	Os(2)–Os(4)	2.785 (1)
Pt(1)–C(1)	2.23 (2)	Os(2)–C(21)	1.87 (3)
Pt(1)–C(2)	2.24 (2)	Os(2)–C(22)	1.88 (2)
Pt(1)–C(5)	2.20 (2)	Os(2)–C(23)	1.89 (3)
Pt(1)–C(6)	2.18 (2)	Os(3)–Os(4)	2.868 (1)
Pt(2)–Os(1)	2.737 (1)	Os(3)–C(31)	1.86 (3)
Pt(2)–Os(2)	2.855 (1)	Os(3)–C(32)	1.86 (3)
Pt(2)–Os(4)	2.784 (1)	Os(3)–C(33)	1.97 (3)
Pt(2)–C(9)	2.25 (2)	Os(4)–C(41)	1.93 (2)
Pt(2)–C(10)	2.23 (2)	Os(4)–C(42)	1.92 (2)
Pt(2)–C(13)	2.22 (2)	Os(4)–C(43)	1.95 (2)
Pt(2)–C(14)	2.24 (2)	C(1)–C(2)	1.35 (3)
Os(1)–Os(2)	2.859 (1)	C(5)–C(6)	1.41 (3)
Os(1)–Os(3)	2.795 (1)	C(9)–C(10)	1.31 (3)
Os(1)–Os(4)	2.832 (1)	C(13)–C(14)	1.35 (3)
Os(1)–C(17)	1.95 (2)	O–C(av)	1.14 (3)
Os(1)–C(18)	1.90 (3)		

[a] Distances are in ångstroms. Estimated standard deviations in the least significant figure are given in parentheses.

contributions were added to the structure factor calculations, but their positions were not refined.

For **5**, the space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms larger than carbon were refined with anisotropic thermal parameters. A molecule of methylene chloride was found cocrystallized with the complex in the lattice in the final stages of the analysis. It was included and satisfactorily refined. The positions of all hydrogen atoms were calculated by using idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. Tables of hydrogen atom positional parameters and anisotropic thermal parameters for the analyses of **2**–**5** and structure factor amplitudes for **4** and **5** are available with the supplementary material. The structure factors for **2** and **3** were reported previously.[8]

Results

From the reaction of $Pt_2Os_4(CO)_{18}$ with cycloocta-1,5-diene (COD) at 97 °C, we have isolated the new platinum osmium carbonyl cluster complexes $Pt_2Os_4(CO)_{12}(COD)_2$ (**2**) in 55% yield and $Pt_2Os_4(CO)_{11}(COD)_2$ (**3**) in 9% yield. A small amount of the slightly unstable compound $PtOs_2(CO)_8(COD)$ was also obtained. Compounds **2** and **3** were characterized by a combination of IR, ^{1}H NMR, and a single-crystal X-ray diffraction analyses. ORTEP diagrams of both of the structures are shown in Figure 1. Final atomic positional parameters for **2** and **3** are listed in Tables II and III, respectively. Selected interatomic distances and angles for **2** and **3** are listed in Tables IV–VII. The clusters of both complexes consist of Os_4 tetrahedral groupings that are capped on two adjacent triangular faces by Pt(COD) groupings. Compound **2** has 12 carbonyl ligands, three on each osmium atom, while compound **3** has only 11, 10 terminal and one bridge. The structures of both clusters are very similar to the cluster of

Table V. Intramolecular Bond Angles for **2**[a]

Os(1)-Pt(1)-Os(3)	58.39 (3)	Os(1)-Os(2)-Os(4)	60.22 (3)
Os(1)-Pt(1)-Os(4)	59.54 (3)	Os(3)-Os(2)-Os(4)	61.98 (3)
Os(3)-Pt(1)-Os(4)	63.48 (3)	Pt(1)-Os(3)-Os(1)	64.99 (4)
Os(1)-Pt(2)-Os(2)	61.47 (3)	Pt(1)-Os(3)-Os(2)	110.91 (4)
Os(1)-Pt(2)-Os(4)	61.72 (3)	Pt(1)-Os(3)-Os(4)	57.75 (3)
Os(2)-Pt(2)-Os(4)	59.17 (3)	Os(1)-Os(3)-Os(2)	61.63 (3)
Pt(1)-Os(1)-Pt(2)	109.84 (4)	Os(1)-Os(3)-Os(4)	59.99 (3)
Pt(1)-Os(1)-Os(2)	102.57 (4)	Os(2)-Os(3)-Os(4)	58.99 (3)
Pt(1)-Os(1)-Os(3)	56.62 (3)	Pt(1)-Os(4)-Pt(2)	116.62 (4)
Pt(1)-Os(1)-Os(4)	55.59 (3)	Pt(1)-Os(4)-Os(1)	64.87 (3)
Pt(2)-Os(1)-Os(2)	61.29 (3)	Pt(1)-Os(4)-Os(2)	111.87 (4)
Pt(2)-Os(1)-Os(3)	110.99 (4)	Pt(1)-Os(4)-Os(3)	58.77 (3)
Pt(2)-Os(1)-Os(4)	59.97 (3)	Pt(2)-Os(4)-Os(1)	58.31 (3)
Os(2)-Os(1)-Os(3)	59.03 (3)	Pt(2)-Os(4)-Os(2)	61.67 (3)
Os(2)-Os(1)-Os(4)	58.58 (3)	Pt(2)-Os(4)-Os(3)	107.51 (4)
Os(3)-Os(1)-Os(4)	61.28 (3)	Os(1)-Os(4)-Os(2)	61.19 (3)
Pt(2)-Os(2)-Os(1)	57.24 (3)	Os(1)-Os(4)-Os(3)	58.73 (3)
Pt(2)-Os(2)-Os(3)	107.84 (4)	Os(2)-Os(4)-Os(3)	59.04 (3)
Pt(2)-Os(2)-Os(4)	59.16 (3)	Os-C(av)-O	177 (3)
Os(1)-Os(2)-Os(3)	59.34 (3)		

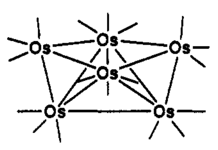
[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table VI. Intramolecular Distances for **3**[a]

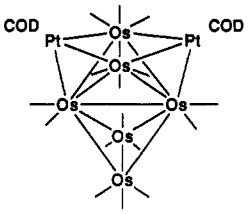
Pt(1)-Os(1)	2.857 (1)	Os(1)-C(19)	1.86 (2)
Pt(1)-Os(3)	2.609 (1)	Os(2)-Os(3)	2.530 (1)
Pt(1)-Os(4)	2.865 (1)	Os(2)-Os(4)	2.831 (1)
Pt(1)-C(1)	2.19 (3)	Os(2)-C(21)	1.91 (3)
Pt(1)-C(4)	2.34 (5)	Os(2)-C(22)	1.87 (3)
Pt(1)-C(5)	2.14 (3)	Os(2)-C(23)	2.07 (2)
Pt(1)-C(8)	2.43 (4)	Os(3)-Os(4)	2.838 (1)
Pt(2)-Os(1)	2.883 (1)	Os(3)-C(23)	2.04 (3)
Pt(2)-Os(2)	2.614 (1)	Os(3)-C(31)	1.84 (3)
Pt(2)-Os(4)	2.840 (1)	Os(3)-C(32)	1.88 (3)
Pt(2)-C(9)	2.17 (2)	Os(4)-C(41)	1.92 (2)
Pt(2)-C(10)	2.21 (3)	Os(4)-C(42)	1.91 (3)
Pt(2)-C(13)	2.27 (3)	Os(4)-C(43)	1.92 (3)
Pt(2)-C(14)	2.22 (2)	C(1)-C(8)	1.19 (4)
Os(1)-Os(2)	2.835 (1)	C(4)-C(5)	1.20 (5)
Os(1)-Os(3)	2.834 (1)	C(9)-C(10)	1.31 (3)
Os(1)-Os(4)	2.705 (1)	C(13)-C(14)	1.31 (3)
Os(1)-C(17)	1.93 (3)	O-C(av)	1.16 (3)
Os(1)-C(18)	1.86 (3)		

[a] Distances are in ångstroms. Estimated standard deviations in the least significant figure are given in parentheses.

$Os_6(CO)_{18}$ (**6**)[11] and the Pt_2Os_4 portion of the cluster complex $Pt_2Os_6(CO)_{16}(COD)_2$ (**7**).[12] Details of the structural differences of the clusters of **2**, **3**, **6**, and **7** will be described below.



6



7

When solutions of **2** were exposed to UV irradiation from a high-pressure mercury source, the compound slowly lost CO and was converted to **3** in a good yield (83%). Compound **3** was also obtained from **2** when solutions in heptane solvent were refluxed, but the yield was low (7%). When solutions of **3** were exposed to CO (1 atm/25 °C), compound **2** was formed in a good yield (84%).

The reaction of **3** with $Pt(COD)_2$ at 25 °C yielded the expanded cluster complex $Pt_3Os_4(CO)_{11}(COD)_3$ (**4**) in 37% yield. Compound **4** was characterized by a single-crystal X-ray diffraction analysis. The compound crystallizes with two independent molecular units in the asymmetric crystal unit. Final atomic positional parameters are listed in Table VIII. Selected interatomic distances and angles are listed in Tables IX and X. ORTEP diagrams of both molecules are shown in Figure 2. The structures of the clusters of both molecules are very similar. The basic cluster unit is the same bicapped Pt_2Os_4 grouping that was found in **2** and **3**, but there is an additional Pt(COD) grouping that bridges the Os(2)-Os(3) edge. The greatest difference between the two molecules of **4** lies at this position. In particular, in molecule **4A** the carbonyl ligand C(33)-O(33) is an edge bridging ligand bonded to atoms Os(3) and Pt(3). The Os(2)-C(33) distance of 2.50 (4) Å implies only a very weak bonding interaction at the most. On the other hand, in molecule **4B**, this CO ligand is more evenly bonded to all three metal atoms, Os(3B)-C(33B) = 2.05 (4) Å, Os(2B)-C(33B) = 2.31 (4) Å, and Pt(3B)-C(33B) = 2.29 (3) Å, and would be better described as a triple bridge. This slight

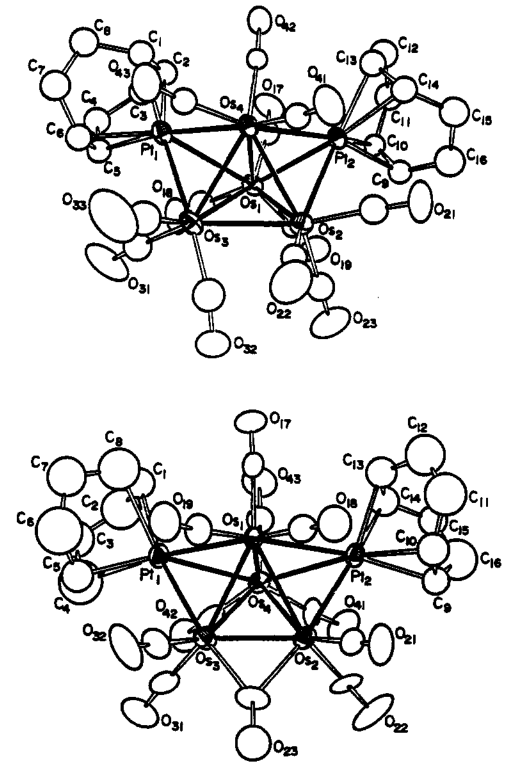


Figure 1. ORTEP diagrams of $Pt_2Os_4(CO)_{12}(COD)_2$ (**2**) (top) and $Pt_2Os_4(CO)_{11}(COD)_2$ (**3**) (bottom) showing 40% probability thermal ellipsoids.

Table VII. Intramolecular Bond Angles for **3**[a]

Os(1)-Pt(1)-Os(3)	62.26 (3)	Os(3)-Os(2)-Os(4)	63.64 (3)
Os(1)-Pt(1)-Os(4)	56.44 (3)	Pt(1)-Os(3)-Os(1)	63.15 (3)
Os(3)-Pt(1)-Os(4)	62.26 (3)	Pt(1)-Os(3)-Os(2)	118.58 (4)
Os(1)-Pt(2)-Os(2)	61.87 (3)	Pt(1)-Os(3)-Os(4)	63.29 (3)
Os(1)-Pt(2)-Os(4)	56.42 (3)	Os(1)-Os(3)-Os(2)	63.52 (3)
Os(2)-Pt(2)-Os(4)	62.39 (3)	Os(1)-Os(3)-Os(4)	56.98 (3)
Pt(1)-Os(1)-Pt(2)	122.58 (4)	Os(2)-Os(3)-Os(4)	63.36 (3)
Pt(1)-Os(1)-Os(2)	101.86 (4)	Pt(1)-Os(4)-Pt(2)	123.85 (4)
Pt(1)-Os(1)-Os(3)	54.59 (3)	Pt(1)-Os(4)-Os(1)	61.63 (3)
Pt(1)-Os(1)-Os(4)	61.93 (3)	Pt(1)-Os(4)-Os(2)	101.74 (4)
Pt(2)-Os(1)-Os(2)	54.39 (3)	Pt(1)-Os(4)-Os(3)	54.45 (3)
Pt(2)-Os(1)-Os(3)	101.45 (4)	Pt(2)-Os(4)-Os(1)	62.59 (3)
Pt(2)-Os(1)-Os(4)	61.00 (3)	Pt(2)-Os(4)-Os(2)	54.88 (3)
Os(2)-Os(1)-Os(3)	53.01 (3)	Pt(2)-Os(4)-Os(3)	102.39 (4)
Os(2)-Os(1)-Os(4)	61.41 (3)	Os(1)-Os(4)-Os(2)	61.55 (3)
Os(3)-Os(1)-Os(4)	61.60 (3)	Os(1)-Os(4)-Os(3)	61.42 (3)
Pt(2)-Os(2)-Os(1)	63.74 (3)	Os(2)-Os(4)-Os(3)	53.00 (3)
Pt(2)-Os(2)-Os(3)	118.71 (4)	Os(2)-C(23)-O(23)	140 (2)
Pt(2)-Os(2)-Os(4)	62.73 (3)	Os(3)-C(23)-O(23)	144 (2)
Os(1)-Os(2)-Os(3)	63.47 (3)	Os-C(av)-O	177 (2)
Os(1)-Os(2)-Os(4)	57.04 (3)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

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[11] Mason, R.; Thomas, K. M.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802.

[12] Couture, C.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1395.

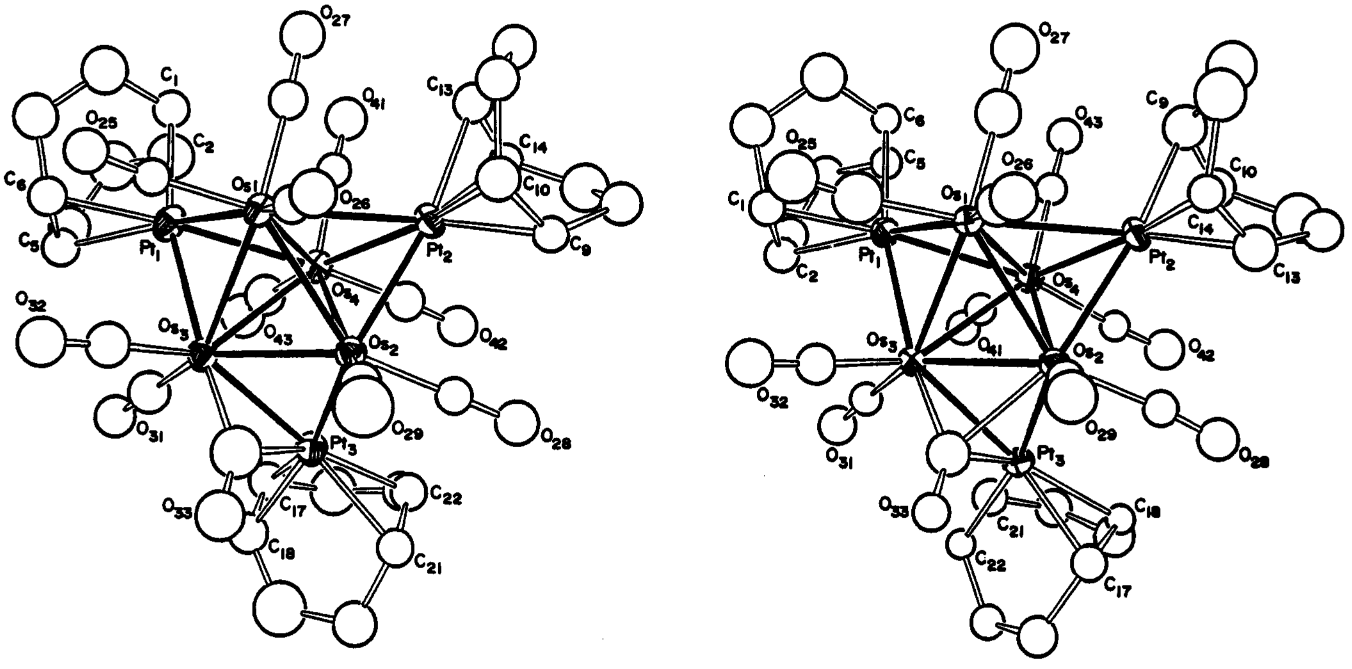

Figure 2. ORTEP diagrams of the two independent molecules of $Pt_3Os_4(CO)_{11}(COD)_3$, **4A** (left) and **4B** (right), showing 40% probability thermal ellipsoids.

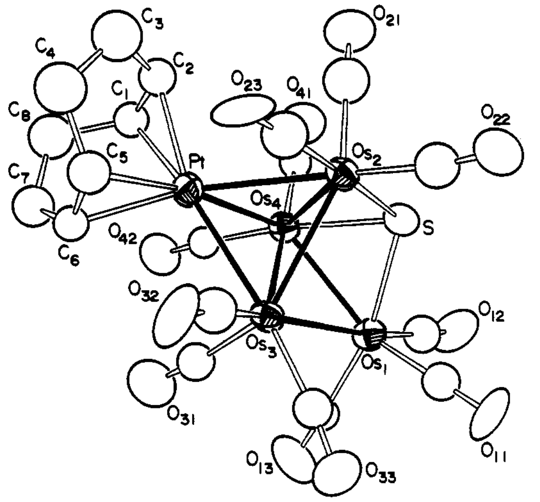

Figure 3. ORTEP diagram of $PtOs_4(CO)_{11}(COD)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**5**), showing 50% probability thermal ellipsoids.

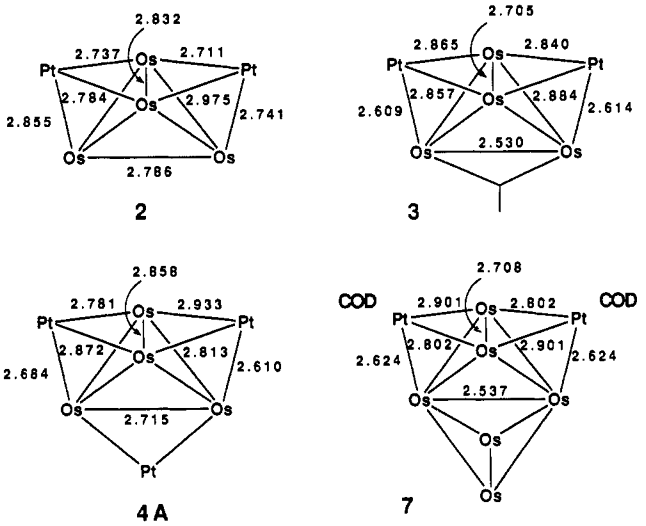

Figure 4. Comparison of selected metal–metal bond distances in related platinum–osmium cluster complexes.

shift (approximately 0.2 Å) in the position of this ligand has no significant effect on the metal–metal bond distances of Pt(3) to the osmium atoms Os(2) and Os(3). Other details of the metal–metal bonding in **4** will be described below. Interestingly, compound **4** could not be obtained by reaction of **2** with $Pt(COD)_2$ under similar reaction conditions.

When compound **3** was allowed to react with H_2S at 25 °C for 20 min, the new compound $PtOs_4(CO)_{11}(COD)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**5**) was formed in 33% yield. Compound **5** was also characterized by a single-crystal X-ray diffraction analysis, and an ORTEP drawing of its molecular structure is shown in Figure 3. Final atomic positional parameters are listed in Table XI. Selected interatomic distances and angles are listed in Tables XII and XIII. The structure of **5** consists of an Os_4 butterfly tetrahedron with one Pt(COD) capping group across one of the closed triangular faces and a triply bridging sulfido ligand across one of the open Os_3 triangular groupings. The Pt–Os bond distances span a considerable range (2.624 (2) Å –2.925 (2) Å, but are similar to the Pt–Os distances found in **2** and **4**. The SOs_4 portion of this complex is similar to that of the molecule $Os_4(CO)_{12}(\mu_3\text{-}S)(\mu\text{-}H)_2$.[13] Compound **5** contains two inequivalent hydride ligands as indicated by the presence of two high-field resonances in the ^1H NMR spectrum at $\delta = -14.58$ (s, $^2J_{Pt-H} = 32.6$ Hz) and -20.96 (s, $^2J_{Pt-H} = 19.9$ Hz). These were not located directly in the structural analysis, but the small values of the coupling constants indicate that they are not bonded directly to the platinum atom.[7] The two locations that we consider to be the most probable for their positions are bridging sites across the Os(2)–Os(3) and Os(1)–Os(4) bonds. This is most strongly suggested by the large Os–Os–C angles involving the carbonyl ligands C(33)–O(33) and C(22)–O(22) at the Os(2)–Os(3) bond, and C(11)–O(11), C(13)–O(13), C(41)–O(41), and C(42)–O(42) at the Os(1)–Os(4) bond. This is caused by the steric interactions of the hydride ligand with the CO ligands.[14]

Discussion

Compounds **2** and **6** each contain a total of 84 valence electrons and are thus electron precise according to the effective atomic number rule and the polyhedral skeletal electron pair (PSEP) theory.[15] The electron count in the Pt_2Os_4 cluster in **4** is 84

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(14) Churchill, M. R. In *Transition Metal Hydrides*; Bau, R., Ed.; Advances in Chemistry 167; American Chemical Society: Washington, DC, 1978.

(15) 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.

Table VIII. Positional Parameters and B(eq) for $Pt_3Os_4(CO)_{11}(COD)_3$ (**4**)

atom	*x*	*y*	*z*	B(eq), Å^2	atom	*x*	*y*	*z*	B(eq), Å^2
Pt(1A)	0.20310 (8)	0.12197 (6)	0.40381 (6)	3.69 (7)	C(12B)	0.745 (2)	0.0630 (15)	−0.1836 (17)	4.9 (8)
Pt(1B)	0.77929 (8)	−0.00489 (5)	0.13679 (6)	3.13 (6)	C(13A)	0.5190 (19)	0.2095 (15)	0.5449 (16)	4.8 (7)
Pt(2A)	0.42439 (7)	0.16245 (5)	0.57520 (6)	3.12 (6)	C(13B)	0.702 (2)	0.0894 (16)	−0.1469 (18)	5.6 (8)
Pt(2B)	0.73905 (8)	0.04733 (6)	−0.06035 (6)	3.25 (6)	C(14A)	0.5468 (18)	0.1527 (14)	0.5664 (16)	3.7 (7)
Pt(3A)	0.25064 (8)	−0.00691 (5)	0.56790 (7)	3.48 (6)	C(14B)	0.6349 (17)	0.0668 (13)	−0.1345 (15)	3.6 (7)
Pt(3B)	0.89511 (7)	0.18202 (5)	0.08041 (6)	2.86 (6)	C(15A)	0.606 (2)	0.1403 (18)	0.621 (2)	7.4 (9)
Os(1A)	0.26188 (7)	0.19762 (5)	0.50346 (6)	2.77 (6)	C(15B)	0.594 (2)	0.0045 (18)	−0.1588 (20)	7.1 (9)
Os(1B)	0.67122 (7)	0.04551 (5)	0.03411 (6)	2.86 (6)	C(16A)	0.5919 (20)	0.1769 (15)	0.6710 (17)	5.0 (8)
Os(2A)	0.29575 (7)	0.11173 (5)	0.59266 (6)	2.92 (6)	C(16B)	0.652 (2)	−0.0507 (18)	−0.156 (2)	7.5 (9)
Os(2B)	0.75608 (7)	0.14571 (5)	0.00688 (6)	2.71 (6)	C(17A)	0.217 (2)	−0.0972 (15)	0.5160 (17)	5.2 (8)
Os(3A)	0.17169 (8)	0.08495 (6)	0.49872 (6)	3.18 (6)	C(17B)	0.9246 (18)	0.2668 (14)	0.0415 (16)	4.2 (7)
Os(3B)	0.78516 (7)	0.11794 (5)	0.11733 (6)	2.67 (6)	C(18A)	0.166 (2)	−0.0891 (16)	0.5464 (19)	5.6 (8)
Os(4A)	0.33456 (8)	0.07974 (6)	0.49135 (6)	3.19 (6)	C(18B)	0.9741 (16)	0.2196 (12)	0.0311 (14)	2.9 (6)
Os(4B)	0.84144 (7)	0.03180 (5)	0.04913 (6)	2.78 (6)	C(19A)	0.163 (3)	−0.117 (2)	0.600 (3)	10.2 (9)
O(25A)	0.1185 (13)	0.2685 (10)	0.4293 (11)	5.4 (5)	C(19B)	1.063 (2)	0.2112 (17)	0.0620 (19)	6.4 (8)
O(25B)	0.5686 (16)	0.0343 (12)	0.1149 (14)	7.6 (7)	C(20A)	0.223 (2)	−0.1009 (17)	0.6575 (19)	6.4 (8)
O(26A)	0.2664 (13)	0.2956 (10)	0.5940 (11)	5.1 (5)	C(20B)	1.080 (2)	0.1749 (16)	0.1146 (18)	5.4 (8)
O(26B)	0.5204 (14)	0.1020 (10)	−0.0477 (11)	5.5 (6)	C(21A)	0.2904 (19)	−0.0573 (14)	0.6520 (16)	4.5 (7)
O(27A)	0.3718 (14)	0.2750 (11)	0.4531 (12)	6.0 (6)	C(21B)	1.0169 (20)	0.1760 (15)	0.1445 (17)	4.8 (8)
O(27B)	0.6270 (15)	−0.0856 (12)	−0.0168 (13)	7.2 (6)	C(22A)	0.3425 (19)	−0.0689 (15)	0.6190 (16)	4.7 (7)
O(28A)	0.4267 (14)	0.0549 (10)	0.6910 (12)	5.8 (6)	C(22B)	0.9775 (16)	0.2269 (13)	0.1543 (14)	2.9 (6)
O(28B)	0.8288 (13)	0.2009 (10)	−0.0803 (11)	5.1 (5)	C(23A)	0.359 (2)	−0.1253 (16)	0.5873 (18)	5.5 (8)
O(29A)	0.2406 (16)	0.1905 (13)	0.6762 (14)	8.4 (7)	C(23B)	1.0032 (18)	0.2914 (14)	0.1441 (16)	4.1 (7)
O(29B)	0.6088 (15)	0.2252 (11)	−0.0487 (12)	6.4 (6)	C(24A)	0.294 (3)	−0.139 (2)	0.540 (2)	8.9 (9)
O(31A)	0.0803 (14)	−0.0230 (11)	0.4231 (12)	6.2 (6)	C(24B)	0.953 (2)	0.3176 (15)	0.0903 (18)	5.2 (8)
O(31B)	0.9215 (14)	0.1215 (10)	0.2308 (12)	5.5 (5)	C(25A)	0.1722 (18)	0.2370 (14)	0.4554 (15)	3.6 (7)
O(32A)	0.0514 (15)	0.1638 (11)	0.4637 (12)	6.7 (6)	C(25B)	0.611 (3)	0.0400 (19)	0.088 (2)	7.7 (9)
O(32B)	0.6727 (15)	0.1449 (11)	0.1863 (12)	6.5 (6)	C(26A)	0.2633 (18)	0.2568 (13)	0.5612 (16)	3.6 (7)
O(33A)	0.1116 (15)	0.0637 (11)	0.6024 (13)	6.7 (6)	C(26B)	0.5784 (20)	0.0790 (15)	−0.0172 (17)	4.5 (7)
O(33B)	0.7459 (11)	0.2595 (9)	0.0894 (10)	3.8 (5)	C(27A)	0.3314 (19)	0.2476 (14)	0.4740 (16)	4.3 (7)
O(41A)	0.4445 (15)	0.1316 (11)	0.4251 (12)	6.4 (6)	C(27B)	0.643 (2)	−0.0357 (18)	0.0021 (19)	6.4 (8)
O(41B)	0.9859 (13)	0.0148 (9)	0.1528 (11)	4.6 (5)	C(28A)	0.3762 (19)	0.0781 (14)	0.6538 (16)	3.9 (7)
O(42A)	0.4726 (14)	0.0001 (11)	0.5678 (11)	5.6 (6)	C(28B)	0.8016 (18)	0.1786 (14)	−0.0506 (16)	3.8 (7)
O(42B)	0.9591 (14)	0.0717 (10)	−0.0160 (12)	5.8 (6)	C(29A)	0.2636 (19)	0.1616 (15)	0.6452 (17)	4.4 (7)
O(43A)	0.2744 (16)	−0.0319 (13)	0.4105 (14)	7.9 (7)	C(29B)	0.6642 (18)	0.1921 (14)	−0.0289 (15)	3.7 (7)
O(43B)	0.8393 (12)	−0.1068 (10)	0.0164 (10)	4.6 (5)	C(31A)	0.118 (2)	0.0186 (17)	0.4524 (19)	6.1 (8)
C(1A)	0.2571 (19)	0.1722 (15)	0.3474 (16)	4.5 (7)	C(31B)	0.8699 (18)	0.1172 (13)	0.1867 (16)	3.7 (7)
C(1B)	0.7220 (19)	−0.0177 (14)	0.2039 (16)	4.3 (7)	C(32A)	0.078 (2)	0.1353 (16)	0.4779 (18)	5.8 (8)
C(2A)	0.252 (3)	0.108 (2)	0.333 (2)	8.3 (9)	C(32B)	0.7149 (20)	0.1367 (15)	0.1587 (17)	4.8 (8)
C(2B)	0.8026 (19)	−0.0068 (14)	0.2280 (16)	4.4 (7)	C(33A)	0.156 (3)	0.0672 (19)	0.573 (2)	7.8 (9)
C(3A)	0.196 (3)	0.081 (2)	0.281 (2)	9.7 (9)	C(33B)	0.768 (2)	0.2074 (17)	0.0855 (17)	5.7 (8)
C(3B)	0.8669 (20)	−0.0564 (15)	0.2515 (17)	5.0 (8)	C(41A)	0.4038 (19)	0.1128 (15)	0.4473 (16)	4.2 (7)
C(4A)	0.118 (2)	0.0586 (17)	0.2933 (20)	6.8 (9)	C(41B)	0.9281 (19)	0.0211 (13)	0.1175 (16)	3.7 (7)
C(4B)	0.8616 (20)	−0.1151 (16)	0.2208 (17)	5.1 (8)	C(42A)	0.421 (2)	0.0334 (16)	0.5391 (18)	5.5 (8)
C(5A)	0.0907 (20)	0.0923 (16)	0.3368 (17)	5.0 (8)	C(42B)	0.9156 (17)	0.0592 (13)	0.0089 (15)	3.2 (6)
C(5B)	0.8302 (18)	−0.1012 (13)	0.1570 (16)	3.9 (7)	C(43A)	0.293 (2)	0.0146 (18)	0.4392 (19)	6.2 (8)
C(6A)	0.0905 (20)	0.1560 (16)	0.3404 (17)	5.1 (8)	C(43B)	0.8391 (17)	−0.0533 (14)	0.0289 (15)	3.6 (7)
C(6B)	0.7511 (17)	−0.1057 (12)	0.1255 (14)	3.0 (6)	C(101)	−0.854 (3)	0.1536 (20)	0.720 (2)	7.5 (9)
C(7A)	0.110(2)	0.2022 (17)	0.3039 (20)	6.8 (8)	C(102)	0.917 (2)	0.1243 (16)	0.7677 (18)	5.2 (8)
C(7B)	0.682 (2)	−0.1204 (18)	0.146 (2)	7.3 (9)	C(103)	0.942 (2)	0.1567 (20)	0.820 (2)	7.1 (9)
C(8A)	0.198 (3)	0.2175 (18)	0.316 (2)	7.5 (9)	C(104)	0.916 (3)	0.212 (2)	0.825 (3)	9.8 (9)
C(8B)	0.681 (2)	−0.0810 (17)	0.1997 (19)	6.4 (8)	C(105)	0.854 (3)	0.237 (2)	0.778 (3)	8.8 (9)
C(9A)	0.4994 (17)	0.1887 (13)	0.6618 (14)	3.3 (6)	C(106)	0.822 (3)	0.210 (2)	0.727 (2)	8.4 (9)
C(9B)	0.733 (2)	−0.0429 (16)	−0.1019 (18)	6.1 (8)	C(107)	0.509 (4)	0.160 (2)	0.262 (3)	11.5 (8)
C(10A)	0.4553 (20)	0.2432 (15)	0.6342 (17)	5.2 (8)	C(108)	0.437 (3)	0.176 (3)	0.271 (3)	11.5 (8)
C(10B)	0.803 (2)	−0.0140 (15)	−0.1034 (17)	5.2 (8)	C(109)	0.422 (4)	0.236 (3)	0.289 (3)	12.4 (8)
C(11A)	0.4869 (19)	0.2944 (15)	0.6031 (16)	4.8 (7)	C(110)	0.487 (4)	0.271 (3)	0.304 (3)	11.6 (8)
C(11B)	0.811 (2)	0.0205 (19)	−0.156 (2)	7.8 (9)	C(111)	0.560 (3)	0.255 (2)	0.301 (2)	8.6 (9)
C(12A)	0.5462 (20)	0.2721 (15)	0.5722 (17)	5.3 (8)	C(112)	0.574 (3)	0.206 (3)	0.273 (3)	10.5 (9)

electrons if the Pt(COD) bridging group is counted as 16. Compound **3** on the other hand has only 82 valence electrons and is thus electron deficient by the amount of two electrons. Compound **7** contains a total of 108 valence electrons and according to the PSEP theory is also electron deficient by the amount of two electrons.[16] A comparison of the metal-metal bond distances in **2**, **3**, **4A**, and **7** are shown in Figure 4. The metal–metal bond distances in **4A** and **4B** are similar, and only the distances of **4A** are shown in the figure.

The Pt–Os distances in **2** span a considerable range, 2.711 (1)–2.975 (1) Å, but none of the values are highly unusual.[1a] The COD ligands adopt different conformations on the two platinum atoms. On Pt(1) the coordinated C–C double bonds are nearly parallel to the Os(1)–Os(4) bond in the cluster, while on Pt(2) they are nearly perpendicular to it. These different conformational arrangements are probably responsible for some of the differences in the Pt–Os distances between the two capping groups in **2**. Both COD ligands in **3** and **7** have the parallel orientation relative to the Os(1)–Os(4) bond, and the Pt–Os bonding of both compounds is similar. In **4** both of the COD ligands have adopted orientations that lie in between the perpendicular and parallel directions and the Pt–Os bonding spans a wide range, 2.610 (2) –2.933 (2) Å.

A comparison of the metal bonds in **2** with those in the unsaturated clusters **3** and **7** shows several significant differences. In particular, the CO bridged Os–Os bond, Os(2)–Os(3), and the corresponding bond in **7** at 2.530 (1) and 2.537 (1) Å, respectively, are much shorter than the corresponding bond in **2**, 2.786 (1) Å.

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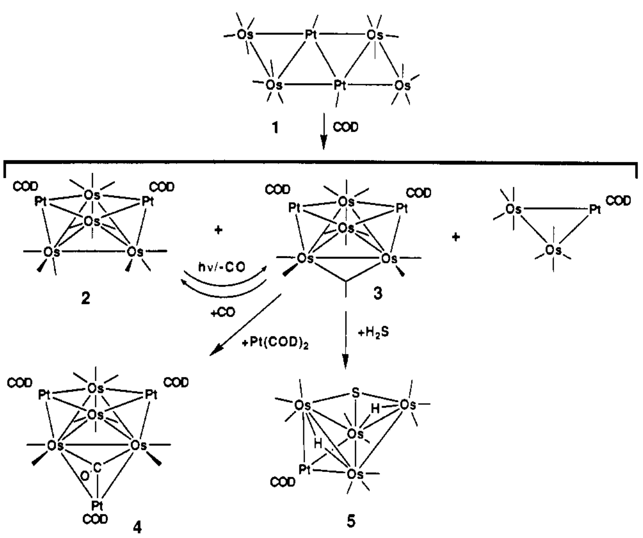
[16] The cluster of compound **7** could be described as a bicapped bitetrahedron and according to the PSEP theory should contain 110 electrons.[15]

Table IX. Intramolecular Distances for **4**[a]

Pt(1A)–Os(1a)	2.872 (2)	Os(2A)–C(29A)	1.89 (4)
Pt(1A)–Os(3A)	2.684 (2)	Os(2A)–C(33A)	2.50 (4)
Pt(1A)–Os(4A)	2.781 (2)	Os(2B)–Os(3B)	2.701 (2)
Pt(1B)–Os(1B)	2.880 (2)	Os(2B)–Os(4B)	2.868 (2)
Pt(1B)–Os(3B)	2.666 (2)	Os(2B)–C(28B)	1.95 (4)
Pt(1B)–Os(4B)	2.802 (2)	Os(2B)–C(29B)	1.85 (3)
Pt(2A)–Os(1A)	2.933 (2)	Os(2B)–C(33B)	2.31 (4)
Pt(2A)–Os(2A)	2.610 (2)	Os(3A)–Os(4A)	2.862 (2)
Pt(2A)–Os(4A)	2.813 (2)	Os(3A)–C(31A)	1.88 (4)
Pt(2B)–Os(1B)	2.910 (2)	Os(3A)–C(32A)	1.88 (4)
Pt(2B)–Os(2B)	2.639 (2)	Os(3A)–C(33A)	1.97 (5)
Pt(2B)–Os(4B)	2.786 (2)	Os(3B)–Os(4B)	2.851 (2)
Pt(3A)–Os(2A)	2.660 (2)	Os(3B)–C(31B)	1.90 (4)
Pt(3A)–Os(3A)	2.690 (2)	Os(3B)–C(32B)	1.85 (4)
Pt(3A)–Os(4A)	3.272 (2)	Os(3B)–C(33B)	2.05 (4)
Pt(3A)–C(33A)	2.30 (4)	Os(4A)–C(41A)	1.97 (4)
Pt(3B)–Os(2B)	2.658 (2)	Os(4A)–C(42A)	1.88 (4)
Pt(3B)–Os(3B)	2.701 (2)	Os(4A)–C(43A)	1.89 (4)
Pt(3B)–Os(4B)	3.355 (2)	Os(4B)–C(41B)	1.91 (4)
Pt(3B)–C(33B)	2.29 (3)	Os(4B)–C(42B)	1.93 (3)
Os(1A)–Os(2A)	2.796 (2)	Os(4B)–C(43B)	1.88 (3)
Os(1A)–Os(3A)	2.840 (2)	C(1A)–C(2A)	1.41 (5)
Os(1A)–Os(4A)	2.858 (2)	C(1B)–C(2B)	1.36 (4)
Os(1A)–C(25A)	1.85 (3)	C(5A)–C(6A)	1.36 (4)
Os(1A)–C(26A)	1.90 (3)	C(5B)–C(6B)	1.36 (4)
Os(1A)–C(27A)	1.90 (3)	C(9A)–C(10A)	1.44 (4)
Os(1B)–Os(2B)	2.778 (2)	C(9B)–C(10B)	1.37 (4)
Os(1B)–Os(3B)	2.844 (2)	C(13A)–C(14A)	1.35 (4)
Os(1B)–Os(4B)	2.855 (2)	C(13B)–C(14B)	1.36 (4)
Os(1B)–C(25B)	1.91 (5)	C(17A)–C(18A)	1.33 (4)
Os(1B)–C(26B)	1.86 (4)	C(17B)–C(18B)	1.39 (4)
Os(1B)–C(27B)	1.90 (4)	C(21A)–C(22A)	1.40 (4)
Os(2A)–Os(3A)	2.175 (2)	C(21B)–C(22B)	1.34 (4)
Os(2A)–Os(4A)	2.866 (2)	O–C(av)	1.16 (4)
Os(2A)–C(28A)	1.87 (4)		

[a] Distances are in ångstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Scheme I



The Os(1)–Os(4) bond in **3** (2.705 (1) Å) and the corresponding bond in **7** (2.708 (1) Å) are also significantly shorter than that in **2** (2.832 (1) Å). The Pt–Os bonds involving osmium atoms Os(2) and Os(3) in **3** and **7** at 2.604 (1)–2.624 (1) Å are also much shorter than those in **2**, 2.855 (1) Å and 2.741 (1) Å. A comparison of these bonds with those in **4** is very revealing. For example, the Pt–Os bonds to Os(2) and Os(3) are short, 2.610 (2) –2.684 (2) Å, like those in **3** and **7**, but the Os(2)–Os(3) and Os(1)–Os(4) bonds are long like those in **2**. Although the bonding picture is not yet clear for these molecules, we feel that the shortness observed for the Os–Os bond in **3** and **7** is probably related to a semilocalization of the electronic unsaturation in these compounds. The shortness of the Pt–Os bonds in **3** and **7** may also be related to this unsaturation, but the fact that these bonds are also short in **4** makes this conclusion less certain.

A summary of the reactions performed in this study is shown in Scheme I. The reaction of **1** with COD results in the loss of 6 mol of CO and the addition of 2 mol of COD to yield the

Table X. Intramolecular Bond Angles for **3**[a]

Os(1A)–Pt(1A)–Os(3A)	61.36 (5)	Pt(2A)–Os(2A)–Pt(3A)	123.92 (6)	Pt(1B)–Os(3B)–Os(4B)	60.95 (5)
Os(1A)–Pt(1A)–Os(4A)	60.72 (5)	Pt(2A)–Os(2A)–Os(1A)	65.60 (5)	Pt(3B)–Os(3B)–Os(1B)	115.41 (7)
Os(3A)–Pt(1A)–Os(4A)	63.14 (5)	Pt(2A)–Os(2A)–Os(3A)	115.74 (7)	Pt(3B)–Os(3B)–Os(2B)	58.95 (5)
Os(1B)–Pt(1B)–Os(3B)	61.56 (5)	Pt(2A)–Os(2A)–Os(4A)	61.61 (5)	Pt(3B)–Os(3B)–Os(4B)	74.30 (5)
Os(1B)–Pt(1B)–Os(4B)	60.30 (5)	Pt(3A)–Os(2A)–Os(1A)	117.37 (7)	Os(1B)–Os(3B)–Os(2B)	60.07 (5)
Os(3B)–Pt(1B)–Os(4B)	62.78 (5)	Pt(3A)–Os(2A)–Os(3A)	60.05 (5)	Os(1B)–Os(3B)–Os(4B)	60.17 (5)
Os(1A)–Pt(2A)–Os(2A)	60.24 (5)	Pt(3A)–Os(2A)–Os(4A)	72.52 (5)	Os(2B)–Os(3B)–Os(4B)	62.13 (5)
Os(1A)–Pt(2A)–Os(4A)	59.62 (5)	Os(1A)–Os(2A)–Os(3A)	62.02 (5)	Pt(1A)–Os(4A)–Pt(2A)	121.15 (6)
Os(2A)–Pt(2A)–Os(4A)	63.67 (5)	Os(1A)–Os(2A)–Os(4A)	60.63 (5)	Pt(1A)–Os(4A)–Os(1A)	61.21 (5)
Os(1B)–Pt(2B)–Os(2B)	59.86 (5)	Os(3A)–Os(2A)–Os(4A)	61.65 (5)	Pt(1A)–Os(4A)–Os(2A)	105.17 (6)
Os(1B)–Pt(2B)–Os(4B)	60.12 (5)	Pt(2B)–Os(2B)–Pt(3B)	125.02 (6)	Pt(1A)–Os(4A)–Os(3A)	56.78 (5)
Os(2B)–Pt(2B)–Os(4B)	63.76 (5)	Pt(2B)–Os(2B)–Os(1B)	64.92 (5)	Pt(2A)–Os(4A)–Os(1A)	62.27 (5)
Os(2A)–Pt(3A)–Os(3A)	60.99 (5)	Pt(2B)–Os(2B)–Os(3B)	114.84 (6)	Pt(2A)–Os(4A)–Os(2A)	54.72 (5)
Os(2B)–Pt(3B)–Os(3B)	60.52 (5)	Pt(2B)–Os(2B)–Os(4B)	60.61 (5)	Pt(2A)–Os(4A)–Os(3A)	105.23 (6)
Pt(1A)–Os(1A)–Pt(2A)	114.16 (6)	Pt(3B)–Os(2B)–Os(1B)	119.15 (7)	Os(1A)–Os(4A)–Os(2A)	58.46 (5)
Pt(1A)–Os(1A)–Os(2A)	104.63 (5)	Pt(3B)–Os(2B)–Os(3B)	60.53 (5)	Os(1A)–Os(4A)–Os(3A)	59.52 (4)
Pt(1A)–Os(1A)–Os(3A)	56.06 (5)	Pt(3B)–Os(2B)–Os(4B)	74.66 (5)	Os(2A)–Os(4A)–Os(3A)	56.58 (5)
Pt(1A)–Os(1A)–Os(4A)	58.07 (5)	Os(1B)–Os(2B)–Os(3B)	62.52 (5)	Pt(1B)–Os(4B)–Pt(2B)	120.88 (6)
Pt(2A)–Os(1A)–Os(2A)	54.16 (4)	Os(1B)–Os(2B)–Os(4B)	60.73 (4)	Pt(1B)–Os(4B)–Os(1B)	61.20 (5)
Pt(2A)–Os(1A)–Os(3A)	102.75 (5)	Os(3B)–Os(2B)–Os(4B)	61.50 (5)	Pt(1B)–Os(4B)–Os(2B)	104.35 (5)
Pt(2A)–Os(1A)–Os(4A)	58.11 (4)	Pt(1A)–Os(3A)–Pt(3A)	125.34 (6)	Pt(1B)–Os(4B)–Os(3B)	56.27 (5)
Os(2A)–Os(1A)–Os(3A)	57.59 (5)	Pt(1A)–Os(3A)–Os(1A)	62.58 (5)	Pt(2B)–Os(4B)–Os(1B)	62.09 (5)
Os(2A)–Os(1A)–Os(4A)	60.91 (5)	Pt(1A)–Os(3A)–Os(2A)	112.36 (6)	Pt(2B)–Os(4B)–Os(2B)	55.62 (5)
Os(3A)–Os(1A)–Os(4A)	60.31 (4)	Pt(1A)–Os(3A)–Os(4A)	60.08 (5)	Pt(2B)–Os(4B)–Os(3B)	105.93 (6)
Pt(1B)–Os(1B)–Pt(2B)	114.18 (6)	Pt(3A)–Os(3A)–Os(1A)	114.89 (6)	Os(1B)–Os(4B)–Os(2B)	58.09 (4)
Pt(1B)–Os(1B)–Os(2B)	104.64 (6)	Pt(3A)–Os(3A)–Os(2A)	58.96 (5)	Os(1B)–Os(4B)–Os(3B)	59.80 (5)
Pt(1B)–Os(1B)–Os(3B)	55.51 (5)	Pt(3A)–Os(3A)–Os(4A)	72.15 (5)	Os(2B)–Os(4B)–Os(3B)	56.37 (5)
Pt(1B)–Os(1B)–Os(4B)	58.50 (5)	Os(1A)–Os(3A)–Os(2A)	60.39 (5)	Pt(3A)–C(33A)–O(33A)	125 (3)
Pt(2B)–Os(1B)–Os(2B)	55.22 (5)	Os(1A)–Os(3A)–Os(4A)	60.17 (4)	Os(3A)–C(33A)–O(33A)	150 (4)
Pt(2B)–Os(1B)–Os(3B)	102.88 (5)	Os(2A)–Os(3A)–Os(4A)	61.78 (5)	Pt(3B)–C(33B)–O(33B)	124 (2)
Pt(2B)–Os(1B)–Os(4B)	57.79 (5)	Pt(1B)–Os(3B)–Pt(3B)	128.63 (6)	Os(2B)–C(33B)–O(33B)	131 (3)
Os(2B)–Os(1B)–Os(3B)	57.41 (5)	Pt(1B)–Os(3B)–Os(1B)	62.93 (5)	Os(3B)–C(33B)–O(33B)	148 (3)
Os(2B)–Os(1B)–Os(4B)	61.19 (4)	Pt(1B)–Os(3B)–Os(2B)	113.12 (6)	Os–C(av)–O	176 (4)
Os(3B)–Os(1B)–Os(4B)	60.03 (5)				

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table XI. Positional Parameters and *B*(eq) for $PtOs_4(CO)_{11}(COD)(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**5**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt	0.97834 (14)	0.22649 (6)	0.01759 (8)	2.94 (6)
Os(1)	0.65251 (14)	0.39375 (6)	0.03867 (9)	3.02 (7)
Os(2)	0.99687 (14)	0.32176 (6)	0.15702 (8)	2.65 (6)
Os(3)	0.92689 (14)	0.34831 (6)	−0.03246 (8)	2.63 (6)
Os(4)	0.73444 (14)	0.27516 (6)	0.06962 (8)	2.73 (6)
S	0.7519 (9)	0.3541 (4)	0.1787 (5)	3.1 (4)
O(11)	0.754 (3)	0.5255 (9)	0.0624 (17)	6 (1)
O(12)	0.369 (3)	0.4253 (11)	0.1313 (18)	7 (2)
O(13)	0.540 (3)	0.4099 (12)	−0.1582 (16)	7 (2)
O(21)	0.955 (2)	0.2304 (10)	0.3076 (15)	5 (1)
O(22)	1.123 (3)	0.4200 (10)	0.2755 (14)	5 (1)
O(23)	1.300 (3)	0.2790 (10)	0.1180 (15)	5 (1)
O(31)	0.785 (3)	0.2928 (11)	−0.2016 (16)	6 (1)
O(32)	1.241 (3)	0.3409 (9)	−0.0936 (17)	6 (1)
O(33)	0.915 (3)	0.4771 (10)	−0.1124 (16)	5 (1)
O(41)	0.592 (3)	0.1917 (11)	0.2055 (17)	7 (2)
O(42)	0.642 (3)	0.1862 (10)	−0.0754 (15)	5 (1)
C(1)	0.929 (3)	0.1291 (13)	0.037 (2)	3.4 (7)
C(2)	1.035 (4)	0.1439 (13)	0.098 (2)	3.6 (7)
C(3)	1.192 (4)	0.1295 (17)	0.096 (3)	5.9 (9)
C(4)	1.251 (4)	0.1415 (17)	0.005 (3)	5.9 (9)
C(5)	1.184 (4)	0.1954 (14)	−0.046 (2)	4.1 (7)
C(6)	1.072 (3)	0.1898 (13)	−0.1088 (20)	3.0 (6)
C(7)	0.984 (4)	0.1313 (15)	−0.131 (2)	4.6 (8)
C(8)	0.958 (4)	0.0893 (16)	−0.051 (2)	5.7 (9)
C(11)	0.717 (4)	0.4747 (15)	0.053 (2)	3.8 (7)
C(12)	0.475 (4)	0.4129 (15)	0.092 (2)	4.5 (8)
C(13)	0.572 (3)	0.4043 (14)	−0.085 (2)	3.2 (7)
C(21)	0.979 (4)	0.2641 (17)	0.252 (3)	5.5 (9)
C(22)	1.068 (4)	0.3851 (16)	0.229 (2)	4.5 (8)
C(23)	1.181 (4)	0.2944 (16)	0.135 (2)	4.7 (8)
C(31)	0.838 (4)	0.3167 (15)	−0.138 (2)	3.8 (7)
C(32)	1.120 (4)	0.3406 (15)	−0.065 (2)	4.4 (8)
C(33)	0.919 (4)	0.4283 (15)	−0.077 (2)	3.6 (7)
C(41)	0.647 (3)	0.2244 (14)	0.153 (2)	3.3 (7)
C(42)	0.691 (3)	0.2197 (14)	−0.020 (2)	3.1 (6)
Cl(1)	0.813 (3)	0.0107 (8)	0.1999 (11)	15 (1)
C(101)	0.649 (7)	0.036 (3)	0.202 (4)	12 (1)
Cl(2)	0.569 (2)	0.0409 (10)	0.0942 (16)	19 (2)

Table XII. Intramolecular Distances for **5**[a]

Pt–Os(2)	2.925 (2)	Os(2)–C(21)	1.89 (4)
Pt–Os(3)	2.798 (2)	Os(2)–C(22)	1.85 (4)
Pt–Os(4)	2.642 (2)	Os(2)–C(23)	1.84 (4)
Os(1)–Os(2)	3.904 (2)	Os(3)–Os(4)	2.852 (2)
Os(1)–Os(3)	2.942 (2)	Os(3)–C(31)	1.87 (4)
Os(1)–Os(4)	2.733 (2)	Os(3)–C(32)	1.87 (4)
Os(1)–S	2.393 (8)	Os(3)–C(33)	1.87 (3)
Os(1)–C(11)	1.88 (3)	Os(4)–S	2.358 (8)
Os(1)–C(12)	1.89 (4)	Os(4)–C(41)	1.85 (3)
Os(1)–C(13)	1.95 (3)	Os(4)–C(42)	1.83 (3)
Os(2)–Os(3)	2.903 (2)	C(1)–C(2)	1.34 (4)
Os(2)–Os(4)	2.889 (2)	C(5)–C(6)	1.37 (4)
Os(2)–S	2.397 (8)	O–C(av)	1.17 (4)

[a] Distances are in ångstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table XIII. Intramolecular Bond Angles for **5**[a]

Os(2)–Pt–Os(3)	60.92 (5)	Pt–Os(3)–C(33)	171 (1)
Os(2)–Pt–Os(4)	62.48 (5)	Os(1)–Os(2)–Os(2)	83.81 (5)
Os(3)–Pt–Os(4)	63.38 (5)	Os(1)–Os(3)–Os(4)	56.26 (5)
Os(3)–Os(1)–Os(4)	60.21 (4)	Os(1)–Os(3)–C(31)	93 (1)
Os(3)–Os(1)–S	82.8 (2)	Os(1)–Os(3)–C(32)	164 (1)
Os(3)–Os(1)–C(11)	95 (1)	Os(1)–Os(3)–C(33)	77 (1)
Os(3)–Os(1)–C(12)	172 (1)	Os(2)–Os(3)–Os(4)	60.26 (5)
Os(3)–Os(1)–C(13)	90.7 (9)	Os(2)–Os(3)–C(31)	144 (1)
Os(4)–Os(1)–S	54.3 (2)	Os(2)–Os(3)–C(32)	93 (1)
Os(4)–Os(1)–C(11)	142 (1)	Os(2)–Os(3)–C(33)	122 (1)
Os(4)–Os(1)–C(12)	112 (1)	Os(4)–Os(3)–C(31)	88 (1)
Os(4)–Os(1)–C(13)	111.2 (9)	Os(4)–Os(3)–C(32)	134 (1)
Pt–Pt(2)–Os(3)	57.38 (5)	Os(4)–Os(3)–C(33)	134 (1)
Pt–Os(2)–Os(4)	53.65 (5)	Pt–Os(4)–Os(1)	124.77 (6)
Pt–Os(2)–S	105.6 (2)	Pt–Os(4)–Os(2)	63.88 (5)
Pt–Os(2)–C(21)	92 (1)	Pt–Os(4)–Os(3)	61.29 (5)
Pt–Os(2)–C(22)	161 (1)	Pt–Os(4)–S	117.0 (2)
Pt–Os(2)–C(23)	71 (1)	Pt–Os(4)–C(41)	110 (1)
Os(3)–Os(2)–Os(4)	58.99 (5)	Pt–Os(4)–C(42)	72 (1)
Os(3)–Os(2)–S	83.6 (2)	Os(1)–Os(4)–Os(2)	87.90 (6)
Os(3)–Os(2)–C(21)	145 (1)	Os(1)–Os(4)–Os(3)	63.52 (5)
Os(3)–Os(2)–C(22)	118 (1)	Os(1)–Os(4)–S	55.5 (2)
Os(3)–Os(2)–C(23)	94 (1)	Os(1)–Os(4)–C(41)	124 (1)
Os(4)–Os(2)–S	52.0 (2)	Os(1)–Os(4)–C(42)	117 (1)
Os(4)–Os(2)–C(21)	90 (1)	Os(2)–Os(4)–Os(3)	60.75 (5)
Os(4)–Os(2)–C(22)	143 (1)	Os(2)–Os(4)–S	53.2 (2)
Os(4)–Os(2)–C(23)	125 (1)	Os(2)–Os(4)–C(41)	107 (1)
Pt–Os(3)–Os(1)	111.57 (5)	Os(2)–Os(4)–C(42)	136 (1)
Pt–Os(3)–Os(2)	61.71 (4)	Os(3)–Os(4)–S	85.4 (2)
Pt–Os(3)–Os(4)	55.33 (4)	Os(3)–Os(4)–C(41)	167 (1)
Pt–Os(3)–C(31)	86 (1)	Os(3)–Os(4)–C(42)	97 (1)
Pt–Os(3)–C(32)	80 (1)	Os–C(av)–O	175 (4)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

condensed cluster complex **2**. Small amounts of the unsaturated compound **3** are also formed, and it is believed that this is formed by the decarbonylation of **2**. Compound **2** can be decarbonylated to **3** at 97 °C, but the yield is poor. Alternatively, compound **3** can be obtained in a good yield by UV photolysis. A small amount of $Os_2Pt(CO)_8COD$ is also formed in the original reaction by a splitting process that may resemble the reaction of **1** with CO (eq 1). The iron analogue of this compound, $Fe_2Pt(CO)_8(COD)$, is known.[17] Compounds **3** and **7** both react readily with CO by ligand addition in support of the notion that they are unsaturated. Compound **3** yields **2** by addition at the short Os–Os bond. The addition of CO to **7** produces a major rearrangement of the cluster.[12] Compound **3** also reacts with $Pt(COD)_2$ by the addition of a Pt(COD) grouping to the short Os–Os bond to yield compound **4**. The reaction of **3** with H_2S yields the new compound **5**. In this reaction one PtCOD grouping is eliminated, and H_2S is added and converted into a triply bridging sulfido ligand and two hydride ligands. Similar transformations of H_2S were observed in its reactions with $Os_3(CO)_{12}$[18] and $Ru_3(CO)_{12}$.[19] Further studies of the reactivity of **3** are in progress.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for the structures of **2**–**5** (13 pages); tables of structure factor amplitudes for **4** and **5** (49 pages). Ordering information is given on any current masthead page.

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