trigonal-bipyramidal complexes [(pp$_3$)RhXH] is highly stereospecific. In fact, the hydride ligand is located trans to a terminal phosphorus atom, P_Q, rather than to the bridgehead phosphorus atom P_A. In the absence of X-ray structure determinations, this is nevertheless unequivocally demonstrated by ^{31}P proton-coupled NMR spectra.[43,46] Indeed, whereas the P_A resonance is only broadened by coupling to the proton nuclei, the P_Q signal is resolved into two distinct broad resonances. The large coupling constant between these two signals closely approaches the $J(H-P_{trans})$ value found for the hydride resonance in ^1H NMR spectra.

(b) Reactions of 1 and 2 with $CF_3SO_3CH_3$. As mentioned above, compounds **5**–**7** might form either by direct protonation of the rhodium atom [Scheme II(b)] or through a cationic intermediate [Scheme II(a)], which evolves to the final product, via "internal" oxidative addition. Unfortunately, deuterium-labeled experiments with CF_3COOD failed to elucidate the mechanism because the added deuterium atom equilibrates between the two sites, at the rhodium or at the chalcogen atom. Such behavior has already been observed for cis hydride sulfide complexes of ruthenium and platinum.[4b,30a] In order to understand the mechanism of protonation, the reactions of the hydrosulfide and hydroselenide derivatives **1** and **2** with the methyl ester of the triflic acid were studied. The reactions of [(pp$_3$)RhXH] (X = S, Se) with the stoichiometric amount of $CF_3SO_3CH_3$ in dichloromethane solution yielded, after addition of benzene, pale yellow microcrystalline products. Elemental analyses and chemical-physical measurements support their formulation as hydride methylchalcogenide compounds of formula [(pp$_3$)Rh(H)(XCH$_3$)]CF_3SO_3 [X = S (**8**), Se (**9**)]. The IR and ^1H NMR data clearly indicate that they contain the hydride and the methylchalcogenide groups. In particular, the IR spectra do not show any absorbance in the XH region, whereas they show an RhH stretching vibration at ca. 2000 cm^{-1} (Table VI). The proton NMR spectra of the two derivatives are similar and exhibit resonances that can be attributed, according to their intensities and chemical shifts, to hydride hydrogen atoms [$\delta = -9.12$ (**8**), $\delta = -9.57$ (**9**); $J(H-P_{trans}) = 152.0$ Hz], while no signal ascribable to hydrochalcogenide protons is observed. Resonances at 1.94 and 1.19 ppm in the spectra of **8** and **9**, respectively, may be assigned to the CH_3 bound to the S or Se atom. These results rule out a direct attack of CH_3^+ at the sterically hindered rhodium, which would preserve the hydrosulfide group. On the other hand, they provide evidence for the initial attack of CH_3^+ at the more nucleophilic chalcogen atom to form the trigonal-bipyramidal [(pp$_3$)Rh(HXCH$_3$)]$^+$ cation, which converts to the cis hydride methylsulfide or methylselenide complex by X–H internal oxidative addition of the CH_3XH ligand. Occurrence of the oxidative addition for the X–H rather than the X–CH_3 bond is in accordance with the smaller X–H bond energy, compared to the X–CH_3 one.[56]

In conclusion, on the basis of our present data and in consistency with other recent results,[14] we propose that the electrophilic attack on hydrochalcogenide complexes occurs on a lone pair of the chalcogen atom rather than on the less electronegative and sterically hindered metal center.

Acknowledgment. We thank the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support.

Supplementary Material Available: Full details of the crystal data and crystallographic data collections (Table SI), thermal parameters for **1**–**3** (Table SII), bond distances and angles for compound **1** (Table SIII) and for compounds **2** and **3** (Table SIV), and hydrogen atom coordinates (Table SV) for the three compounds (7 pages); listings of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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

Cluster Synthesis. 30. New Platinum–Osmium Carbonyl Cluster Complexes from the Reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Pt(COD)_2$

Richard D. Adams,* Gong Chen, Jau-Ching Lii, and Wengan Wu

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Two new platinum–osmium carbonyl cluster complexes, $Pt_2Os_3(CO)_{10}(COD)_2$ (**1**) and $PtOs_3(CO)_8(COD)(\mu\text{-}C_8H_{11})(\mu\text{-}H)$ (**2**), were obtained in yields of 18% and 4%, respectively, from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Pt(COD)_2$ at 25 °C. Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. Compound **1** contains a tetrahedral Pt_2Os_2 cluster with an $Os(CO)_4$ group bridging the Os–Os edge. Compound **2** contains a tetrahedral $PtOs_3$ cluster with a COD ligand activated at one of the olefin C–H bonds bridging an Os–Os edge of the cluster. Compound **1** is formally electron deficient and readily reacts with CO at 25 °C/1 atm to yield a series of two products, $Pt_2Os_3(CO)_{14}$ (**3**) and the known complex $PtOs_2(CO)_{10}$ (**4**). **3** and **4** were both characterized by single-crystal X-ray diffraction analyses. Compound **3** contains two structurally similar but symmetry-independent molecules in the crystal. Both molecules contain planar clusters of five metal atoms, with a "truncated raft" structure. Compound **4** contains a triangle of one platinum and two osmium atoms. Compound **3** reacts with $Os(CO)_5$ to form the known compound $Pt_2Os_4(CO)_{18}$ (**5**) in 92% yield. Crystal data: for **1**, space group *Pnma*, $a = 11.559$ (2) Å, $b = 14.984$ (2) Å, $c = 17.222$ (4) Å, $R = 0.037$ for 1891 reflections; for **2**, space group $P2_1/c$, $a = 10.433$ (2) Å, $b = 10.066$ (2) Å, $c = 24.976$ (3) Å, $\beta = 92.52$ (1)°, $R = 0.028$ for 2825 reflections; for **3**, space group $P2_1/c$, $a = 14.895$ (3) Å, $b = 12.060$ (2) Å, $c = 25.615$ (3) Å, $\beta = 92.87$ (1)°, $R = 0.040$ for 2740 reflections; for **4**, space group $P\bar{1}$, $a = 8.997$ (3) Å, $b = 12.888$ (3) Å, $c = 7.082$ (2) Å, $\alpha = 98.52$ (2)°, $\beta = 105.61$ (2)°, $\gamma = 81.51$ (2)°, $R = 0.034$ for 2051 reflections.

Introduction

The superior properties of platinum alloy re-forming catalysts have led to their widespread utilization by the petroleum industry.[1] Hopes of learning more about the bifunctional reactivity of these catalysts have generated a great interest in the chemistry of heteronuclear cluster complexes containing platinum.[2] We have recently found that interesting new heteronuclear cluster complexes containing platinum are readily obtained from the reactions of $Pt(COD)_2$ (COD = 1,5-cyclooctadiene) with the pentacarbonyl

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Table I. Crystallographic Data for Compounds **1**–**4**

	1	**2**	**3**	**4**
empirical formula	$Pt_2Os_3O_{10}C_{26}H_{24}$	$PtOs_3O_8C_{24}H_{24}$	$Pt_2Os_3O_{14}C_{14}$	$PtOs_2O_{10}C_{10}$
fw	1457.25	1206.14	1352.93	855.59
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic
a, Å	11.559 (2)	10.433 (2)	14.895 (3)	8.997 (3)
b, Å	14.984 (4)	10.066 (2)	12.060 (2)	12.888 (3)
c, Å	17.222 (4)	24.976 (3)	25.615 (3)	7.082 (2)
α, deg				98.52
β, deg		92.52 (1)	92.87 (1)	105.61 (2)
γ, deg				81.51 (2)
V, Å^3	2983 (2)	2620.4 (7)	4596 (2)	777.2 (4)
space group	*Pnma* (No. 62)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Z value	4	4	8	2
D_{calcd}, g, cm^3	3.24	3.06	3.91	3.66
F_{000}	2576	2152	4640	740
μ(Mo Kα), cm^{-1}	222.4	199.4	288.7	254.4
temp, °C	23	23	23	23
2θ(max), deg	50.0	45.0	42.0	47.0
no. of observns ($I > 3\sigma(I)$)	1891	2825	2740	2051
no. of variables	196	328	315	208
residuals: R, R_w	0.037, 0.035	0.028, 0.030	0.040, 0.041	0.034, 0.041
goodness-of-fit indicator	1.58	1.60	1.58	2.44
max shift in final cycle	0.06	0.39	0.11	0.07
largest peak in final diff map, e/Å^3	1.99	1.42	2.32	1.63
abs cor	empirical	empirical	Analytical	empirical
coeff: max/min	1.00/0.17	1.00/0.36	0.234/0.085	1.00/0.39

complexes of the iron subgroup.[3,4] We have now found that the reaction of $Pt(COD)_2$ with $Os_3(CO)_{10}(NCMe)_2$ also leads to the formation of the new platinum–osmium carbonyl cluster complexes $Pt_2Os_3(CO)_{10}(COD)_2$ (**1**) and $PtOs_3(CO)_8(COD)(\mu\text{-}C_8H_{11})(\mu\text{-}H)$ (**2**). These results as well as the results of the reaction of **1** with CO to yield sequentially $Pt_2Os_3(CO)_{14}$ (**3**) and $PtOs_2(CO)_{10}$ (**4**) are described in this report.

Experimental Section

General Procedures. Although the reaction products are air stable, all the reactions were performed under an atmosphere of nitrogen, unless otherwise indicated. Reagent grade solvents were dried over molecular sieves and were deoxygenated by purging with nitrogen prior to use. $Os_3(CO)_{10}(NCMe)_2$[5] and $Pt(COD)_2$[6] were prepared by the reported procedures. TLC separations were performed in air on plates (0.25 mm, silica gel 60 F_{254}). IR spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer. Elemental analyses were performed at Desert Analytics, Tucson, AZ.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Pt(COD)_2$. A 110-mg sample (0.120 mmol) of $Os_2(CO)_{10}(NCMe)_2$ and 75 mg (0.180 mmol) of $Pt(COD)_2$ were dissolved in 30 mL of CH_2Cl_2 in a 100-mL three-necked flask. The solution was stirred at 25 °C under nitrogen for 20 min and was then concentrated and separated by TLC with a solvent mixture of Hex/CH_2Cl_2 (4/1). Principal products (in order of elution): orange $PtOs_3(CO)_8(COD)(C_8H_{11})(H)$ (**2**), 6.1 mg (4.2%); brown $Pt_2Os_3(CO)_{10}(COD)_2$ (**1**), 23.2 mg (18%). Small amounts of several compounds were eluted from the baseline with pure CH_2Cl_2 solvent. These are believed to be high-nuclearity species and are currently being characterized. For **1**: IR (ν(CO), cm^{-1}; in hexane) 2077 (m), 2023 (m), 2012 (vs), 1999 (s), 1948 (w), 1900 (w); ^1H NMR (δ; in $CDCl_3$) 5.57 (t, CH, $J_{Pt-H} = 54$ Hz), 4.88 (t, CH, $J_{Pt-H} = 54$ Hz), 1.90–2.40 (br, CH_2). Anal. Calc (found): C, 20.99 (21.43); H, 1.54 (1.66). For **2**: IR (ν(CO), cm^{-1}; in hexane) 2061 (m), 2044 (vs), 1988 (s, sh), 1982 (s), 1963 (w, sh), 1952 (vw), 1927 (w); ^1H NMR (δ; in $CDCl_3$) 5.5–5.9 (m, 3 H), 4.42 (d, 1 H, $J_{H-H} = 6.1$ Hz), 3.92 (m, 1 H), 3.41 (m, 2 H), 3.05 (m, 2 H), 2.75 (m, 4 H), 2.45 (m, 6 H), 1.8–2.3 (m, 6 H), −18.956 (d, 1 H, $J_{Pt-H} = 22.0$ Hz). Anal. Calc (found): C, 24.01 (23.90); H, 1.99 (2.01).

Reaction of 1 with CO. (a) Short Exposure. A 12.0-mg amount of **1** was dissolved in 15 mL of hexane in a 50-mL three-necked flask under a nitrogen atmosphere at 25 °C. Over a period of 2 min, 3.7 cm^3 of CO was admitted to the flask by bubbling through the solution while it was stirred. During this time, the solution became green. After additon of CO, the CO and solvent were removed promptly under vacuum. The residue was transferred to TLC plates and chromatographed with a CH_2Cl_2/hexane (1/5) solvent mixture. The green band was collected and yielded 6.0 mg (54%) of $Pt_2Os_3(CO)_{14}$ (**3**): IR (ν(CO), cm^{-1}; in hexane) 2084 (m), 2070 (m), 2040 (vs), 2030 (s), 1992 (vw). Anal. Calc (found): C, 12.43 (13.08).

(b) Long Exposure. A 10.8-mg sample of **1** was dissolved in 12 mL of hexane. CO was slowly purged through the solution for a period of 30 min while it was stirred at 25 °C. The solution was then passed over a Florisil column to yield 6.0 mg (63% based on Os) of $PtOs_2(CO)_{10}$ (**4**): IR (ν(CO), cm^{-1}; in hexane) 2074 (m), 2069 (s), 2034 (m), 2028 (vs), 2015 (w), 2003 (w), 1988 (w). Compound **4** has been prepared previously by another method.[7]

Reaction of 3 with CO. A 10.0-mg quantity of **3** was dissolved in 12 mL of hexane in a 50-mL three-necked flask. While the solution was stirred at 25 °C, CO was slowly bubbled through it. The color of the solution changed to a light yellow. After 30 min, solvent was removed under vacuum. The product $PtOs_2(CO)_{10}$ (**4**) was isolated by column chromatography on Florisil with hexane solvent. This yielded 6.3 mg (67%) of light yellow **4** and a small amount (0.50 mg) of $Pt_2Os_4(CO)_{18}$ (**5**). On silica gel TLC plates, **4** is rapidly transformed to the red dimer $[PtOs_2(CO)_9]_2$ (**5**) when the plates are dried. Compound **5** has been prepared previously by another method.[7]

Reaction of 3 with $Os(CO)_5$. A 9.8-mg sample (7.2×10^{-3} mmol) of $Pt_2Os_3(CO)_{14}$ was dissolved in 12 mL of hexane in a 25-mL three-necked flask. To this solution was added 2.8 mL of $Os(CO)_5$ (8.5×10^{-3} mmol) in hexane solution (1.0 mg/mL). After the solution was stirred at 25 °C for 2.5 h, the solvent was removed under vacuum. The residue was dissolved in a minimal amount of CH_2Cl_2 and separated by TLC with a solvent mixture of hexane/CH_2Cl_2 (85/15) to yield $Pt_2Os_4(CO)_{18}$ (**5**) (11.0 mg, 92%).

Crystallographic Analyses. Dark brown crystals of **1** were obtained by slow evaporation of solvent from a solution in hexane/CH_2Cl_2 (10/1) at 25 °C. Orange crystals of **2** were grown from solutions in hexane/CH_2Cl_2 (10/1) by cooling to −20 °C. Emerald green crystals of **3** suitable for diffraction analysis were very difficult to obtain. Most crystals had very broad diffraction peaks. The needlelike data crystal with peak half-widths of approximately 0.40° was eventually obtained by slow evaporation of solvent from benzene solutions at 10 °C. Light yellow plates of **4** were obtained from hexane solutions at −20 °C. All data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. The data were processed on Digital Equipment Corp. MICROVAX II

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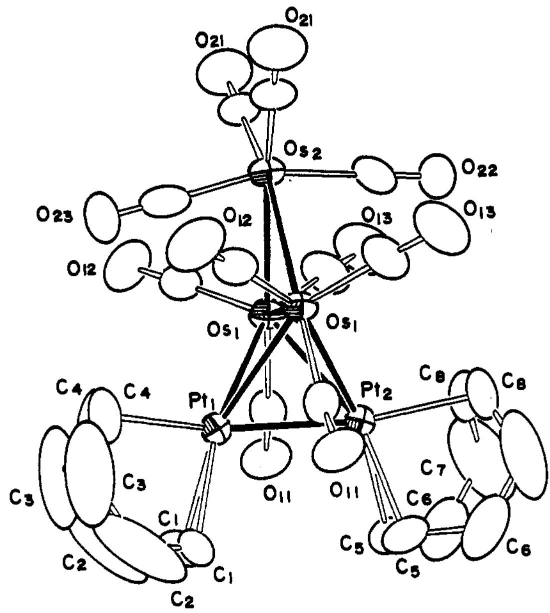

Figure 1. ORTEP diagram of $Pt_2Os_3(CO)_{10}(COD)_2$ (**1**) showing 50% probability thermal ellipsoids.

and VAXstation 3520 computers by using the TEXSAN structure-solving library, Version 5.0, obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by standard procedures.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] All structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Full-matrix least-squares refinements minimized the function

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

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

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

Compound **1** crystallized in the orthorhombic crystal system. The systematic absences observed during the collection of data were consistent with both of the space groups *Pnma* and the related noncentric space group $Pna2_1$. The centrosymmetric space group was assumed and confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the COD ligands were calculated in idealized positions and were included in the structure factor calculations, but they were not refined.

Compounds **2** and **3** crystallized in a monoclinic crystal system. The space group $P2_1/c$ was identified for both compounds on the basis of the systematic absences observed during the collection of the data. For **2**, all non-hydrogen atoms were refined anisotropically. The hydride ligand was located and refined, but the hydrogen atoms on the COD ligands were calculated in idealized positions. Compound **3** crystallized with two independent molecules in the asymmetric unit. Because of the large number of atoms and limited amount of data, only the atoms heavier than oxygen were refined with anisotropic thermal parameters. A low-quality preliminary report of the structure of **4** has been published,[7] but because of the general interest in a fundamental molecule such as this, a complete high-quality analysis was performed and is reported here. All atoms were refined anisotropically.

Results

From the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Pt(COD)_2$ in CH_2Cl_2 solvent at 25 °C, we have obtained two new mixed-metal cluster complexes: $Pt_2Os_3(CO)_{10}(COD)_2$ (**1**), 18% yield; $PtOs_3(CO)_8(COD)(\mu\text{-}C_8H_{11})(\mu\text{-}H)$ (**2**), 4% yield. Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses.

Table II. Positional Parameters and B(eq) for $Pt_2O_3(CO)_{10}(COD)_2$ (**1**)

atom	x	y	z	B(eq), Å^2
Pt(1)	0.49923 (06)	$^1/_4$	0.51733 (05)	2.63 (4)
Pt(2)	0.62696 (06)	$^1/_4$	0.39280 (05)	2.44 (3)
Os(1)	0.70800 (04)	0.15913 (04)	0.52065 (03)	2.49 (2)
Os(2)	0.87641 (07)	$^1/_4$	0.60929 (05)	2.94 (4)
O(11)	0.5359 (09)	0.0464 (08)	0.4277 (07)	4.4 (6)
O(12)	0.6794 (12)	0.0353 (11)	0.6590 (07)	6.2 (8)
O(13)	0.9010 (10)	0.0481 (11)	0.4525 (09)	7.1 (9)
O(21)	1.0078 (11)	0.0955 (11)	0.6834 (08)	6.1 (8)
O(22)	1.0124 (14)	$^1/_4$	0.4544 (09)	5 (1)
O(23)	0.6808 (14)	$^1/_4$	0.7304 (10)	5 (1)
C(1)	0.3231 (11)	0.2070 (15)	0.4780 (09)	5 (1)
C(2)	0.2698 (17)	0.1487 (18)	0.536 (02)	12 (2)
C(3)	0.325 (03)	0.1481 (18)	0.6173 (19)	11 (2)
C(4)	0.4192 (16)	0.2034 (19)	0.6282 (09)	7 (1)
C(5)	0.5084 (13)	0.2050 (15)	0.2988 (09)	5 (1)
C(6)	0.573 (02)	0.1458 (17)	0.2415 (11)	7 (1)
C(7)	0.698 (02)	0.149 (03)	0.2447 (19)	14 (3)
C(8)	0.7551 (14)	0.2090 (15)	0.3039 (09)	5 (1)
C(11)	0.5920 (13)	0.0978 (12)	0.4594 (09)	3.4 (7)
C(12)	0.6927 (13)	0.0832 (15)	0.6075 (10)	4.3 (9)
C(13)	0.8271 (13)	0.0890 (13)	0.4808 (11)	4.5 (9)
C(21)	0.9596 (13)	0.1514 (15)	0.6561 (09)	4.0 (8)
C(22)	0.9622 (18)	$^1/_4$	0.5112 (16)	4 (1)
C(23)	0.7536 (19)	$^1/_4$	0.6838 (14)	3 (1)

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

Pt(1)–C(4)	2.23 (2)	Os(2)–C(22)	1.96 (3)
Pt(1)–C(1)	2.24 (1)	C(1)–C(1′)	1.29 (4)
Pt(1)–Pt(2)	2.604 (1)	C(1)–C(2)	1.47 (3)
Pt(1)–Os(1)	2.7713 (9)	C(2)–C(3)	1.53 (4)
Pt(2)–C(8)	2.22 (1)	C(3)–C(4)	1.38 (4)
Pt(2)–C(5)	2.22 (1)	C(4)–C(4′)	1.40 (6)
Pt(2)–Os(1)	2.753 (1)	C(5)–C(5′)	1.35 (4)
Os(1)–C(13)	1.86 (2)	C(5)–C(6)	1.53 (3)
Os(1)–C(12)	1.89 (2)	C(6)–C(7)	1.44 (3)
Os(1)–C(11)	1.94 (2)	C(7)–C(8)	1.51 (4)
Os(1)–Os(1′)	2.723 (1)	C(8)–C(8′)	1.23 (5)
Os(1)–Os(2)	2.824 (1)	O–C(av)	1.14 (3)
Os(2)–C(23)	1.91 (3)	Pt(1)–C(11)	2.710 (3)
Os(2)–C(21)	1.94 (2)	Pt(2)–C(11)	2.584 (3)

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

C(4)–Pt(1)–C(4′)	36 (1)	Os(1)–Pt(2)–Os(1′)	59.28 (3)
C(4)–Pt(1)–C(1)	78.0 (7)	C(13)–Os(1)–Os(1′)	124.4 (6)
C(4)–Pt(1)–C(1′)	88.4 (6)	C(13)–Os(1)–Pt(2)	103.7 (6)
C(4)–Pt(1)–Pt(2)	159.9 (6)	C(13)–Os(1)–Pt(1)	155.9 (6)
C(4)–Pt(1)–Os(1)	100.9 (5)	C(13)–Os(1)–Os(2)	87.8 (5)
C(4)–Pt(1)–Os(1′)	119.8 (6)	C(12)–Os(1)–Os(1′)	127.1 (6)
C(4)–Pt(1)–Pt(2)	159.9 (6)	C(12)–Os(1)–Pt(2)	154.2 (5)
C(1)–Pt(1)–C(1)	33 (1)	C(12)–Os(1)–Pt(1)	103.4 (5)
C(1)–Pt(1)–Pt(2)	105.4 (4)	C(12)–Os(1)–Os(2)	85.8 (5)
C(1)–Pt(1)–Os(1)	131.0 (5)	C(11)–Os(1)–Os(1′)	118.3 (5)
C(1)–Pt(1)–Os(1′)	159.9 (5)	C(11)–Os(1)–Pt(2)	64.1 (5)
C(1)–Pt(1)–Pt(2)	105.4 (4)	C(11)–Os(1)–Pt(1)	67.6 (5)
Pt(2)–Pt(1)–Os(1)	61.53 (3)	C(11)–Os(1)–Os(2)	179.5 (5)
Os(1)–Pt(1)–Os(1′)	58.85 (3)	Os(1′)–Os(1)–Pt(2)	60.36 (2)
C(8)–Pt(2)–C(8)	32 (1)	Os(1′)–Os(1)–Pt(1)	60.57 (2)
C(8)–Pt(2)–C(5)	79.9 (6)	Os(1′)–Os(1)–Os(2)	61.17 (2)
C(8)–Pt(2)–C(5′)	89.6 (6)	Pt(2)–Os(1)–Pt(1)	56.24 (3)
C(8)–Pt(2)–Pt(1)	161.4 (5)	Pt(2)–Os(1)–Os(2)	115.37 (3)
C(8)–Pt(2)–Os(1)	100.8 (5)	Pt(1)–Os(1)–Os(2)	112.00 (3)
C(8)–Pt(2)–Os(1′)	117.5 (5)	C(23)–Os(2)–Os(1)	81.4 (5)
C(8)–Pt(2)–Pt(1)	161.4 (5)	C(21)–Os(2)–Os(1)	101.5 (5)
C(5)–Pt(2)–C(5)	35 (1)	C(21)–Os(2)–Os(1′)	159.1 (5)
C(5)–Pt(2)–Pt(1)	104.5 (4)	C(21)–Os(2)–Os(1)	101.5 (5)
C(5)–Pt(2)–Os(1)	129.9 (5)	C(22)–Os(2)–Os(1)	83.3 (6)
C(5)–Pt(2)–Os(1′)	160.2 (5)	Os(1)–Os(2)–Os(1′)	57.65 (3)
Pt(1)–Pt(2)–Os(1)	62.24 (3)	O(11)–C(11)–Os(1)	166 (2)
		O–C(av)–Os	178 (2)

An ORTEP diagram of **1** is shown in Figure 1. Final atom positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. The molecule consists of a tetrahedral Os_2Pt_2 cluster that has an $Os(CO)_4$ grouping bridging the Os–Os edge of the cluster. Each platinum atom contains one COD ligand. The osmium atoms bonded to the platinum atoms have three carbonyl ligands. One of these

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(8) *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 V. Positional Parameters and *B*(eq) for $Os_3Pt(CO)_8(COD)(C_8H_{11})H$ (**2**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt	0.66893 (04)	0.20648 (05)	0.131046 (16)	2.30 (2)
Os(1)	0.88606 (04)	0.20175 (05)	0.073181 (17)	2.34 (2)
Os(2)	0.86143 (04)	0.41983 (05)	0.145828 (17)	2.45 (2)
Os(3)	0.68269 (04)	0.40254 (05)	0.059147 (17)	2.30 (2)
O(11)	1.0559 (10)	0.1533 (11)	−0.0217 (04)	5.5 (6)
O(12)	1.0060 (10)	−0.0144 (12)	0.1422 (04)	6.0 (6)
O(13)	0.6880 (09)	0.0019 (11)	0.0256 (04)	4.8 (5)
O(21)	0.6969 (10)	0.4050 (11)	0.2426 (04)	6.1 (6)
O(23)	0.7756 (11)	0.7026 (11)	0.1250 (05)	6.5 (7)
O(31)	0.5166 (10)	0.2474 (11)	−0.0223 (04)	5.0 (5)
O(32)	0.7370 (09)	0.6349 (10)	−0.0157 (04)	4.6 (5)
O(33)	0.4635 (10)	0.5411 (11)	0.1122 (04)	5.1 (5)
C(11)	0.9932 (14)	0.1706 (14)	0.0131 (05)	3.7 (7)
C(12)	0.9612 (12)	0.0697 (15)	0.1173 (05)	3.5 (6)
C(13)	0.7505 (12)	0.0768 (14)	0.0470 (05)	3.3 (6)
C(21)	0.7503 (13)	0.4011 (14)	0.2021 (05)	4.0 (7)
C(23)	0.7982 (14)	0.5927 (16)	0.1288 (06)	4.2 (8)
C(31)	0.5796 (12)	0.3076 (14)	0.0089 (04)	3.1 (6)
C(32)	0.7211 (11)	0.5485 (13)	0.0128 (05)	2.8 (6)
C(33)	0.5472 (12)	0.4907 (13)	0.0919 (04)	3.0 (6)

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

Pt–Os(1)	2.7405 (7)	Os(1)–H(1)	1.7 (1)
Pt–Os(2)	2.9524 (8)	Os(2)–Os(3)	2.8000 (7)
Pt–Os(3)	2.6764 (7)	Os(2)–C(21)	1.87 (1)
Pt–C(1)	2.32 (1)	Os(2)–C(23)	1.90 (2)
Pt–C(2)	2.28 (1)	Os(2)–C(41)	2.21 (1)
Pt–C(5)	2.19 (1)	Os(2)–C(44)	2.21 (1)
Pt–C(6)	2.20 (1)	Os(2)–C(45)	2.20 (1)
Os(1)–Os(2)	2.8667 (8)	Os(2)–C(48)	2.30 (1)
Os(1)–Os(3)	2.9402 (8)	Os(3)–C(31)	1.88 (1)
Os(1)–C(11)	1.94 (1)	Os(3)–C(32)	1.92 (1)
Os(1)–C(12)	1.88 (1)	Os(3)–C(33)	1.89 (1)
Os(1)–C(13)	1.98 (1)	Os(3)–H(1)	1.7 (1)
Os(1)–C(41)	2.14 (1)	C–O(av)	1.15 (1)

on each osmium atom is a semitriple bridge across the adjacent $OsPt_2$ face, Os(1)–C(11)–O(11) = 166 (2)°. The molecule contains a crystallographically imposed plane of symmetry that passes through the atoms Pt(1), Pt(2), and Os(2). The Pt–Pt distance of 2.604 (1) Å is not unusually short for a Pt–Pt single-bond length for Pt(0).[2a,3] The Os–Pt and Os–Os bond lengths are also not unusual. The cluster has a total of 72 valence electrons, which is 2 less than the value expected for an electron-precise edge-bridged tetrahedron.[9] It is believed that the electron deficiency is associated with the tetrahedral Os_2Pt_2 group and contains 58 electrons instead of the usual 60. Similar electron deficiencies in related cluster complexes containing platinum have been rationalized by Mingos.[10]

An ORTEP diagram of compound **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 molecule consists of a tetrahedral cluster of three osmium and one platinum atom. A COD ligand is coordinated to the platinum atom. A second COD ligand activated at one of the olefinic C–H bonds is coordinated to Os(2) and bridges to Os(1) at the site of the C–H cleavage. The hydrogen atom has become a hydride ligand that bridges the Os(1)–Os(3) bond ($\delta = -18.96$, $J_{Pt-H} = 22.0$ Hz). The cluster is electron precise with 60 electrons, as expected for a closed tetrahedral cluster. However, the Pt–Os(2) bond length of 2.9524 (8) Å is significantly longer and presumably weaker than the other two, Pt–Os(1) = 2.7405 (7) Å and Pt–Os(3) = 2.6764 (7) Å. Similar distances were found in the related complex $PtOs_3(CO)_9(COD)(\mu\text{-}CH_2)(\mu\text{-}H)_2$.[11] This could be due to the tendency of platinum to acquire stable 16-electron configurations, which would be achieved with one less metal–metal bond.[2a] As expected, the hydride-bridged Os–Os bond, 2.9402 (8) Å, is significantly longer than the other two,

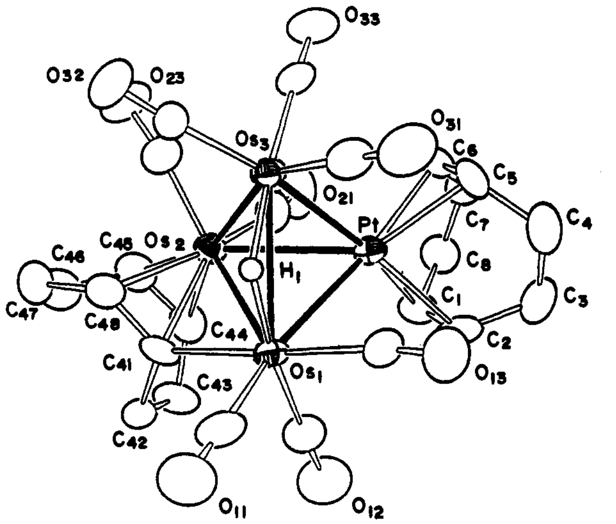

Figure 2. ORTEP diagram of $PtOs_3(CO)_8(COD)(\mu\text{-}C_8H_{11})(\mu\text{-}H)$ (**2**) showing 50% probability thermal ellipsoids.

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

Os(1)–Pt–Os(2)	60.33 (2)	Pt–Os(2)–Os(3)	55.38 (2)
Os(1)–Pt–Os(3)	65.73 (2)	Pt–Os(2)–C(21)	65.2 (4)
Os(1)–Pt–C(1)	111.1 (3)	Pt–Os(2)–C(23)	114.2 (4)
Os(1)–Pt–C(2)	101.3 (3)	Pt–Os(2)–C(41)	103.1 (3)
Os(1)–Pt–C(5)	137.7 (4)	Pt–Os(2)–C(44)	113.9 (4)
Os(1)–Pt–C(6)	169.4 (3)	Pt–Os(2)–C(45)	147.8 (4)
Os(2)–Pt–Os(3)	59.42 (2)	Pt–Os(2)–C(48)	125.9 (3)
Os(2)–Pt–C(1)	105.7 (3)	Os(1)–Os(2)–Os(3)	62.50 (2)
Os(2)–Pt–C(2)	131.7 (4)	Os(1)–Os(2)–C(21)	118.3 (4)
Os(2)–Pt–C(5)	145.2 (4)	Os(1)–Os(2)–C(23)	126.8 (4)
Os(2)–Pt–C(6)	118.6 (4)	Os(1)–Os(2)–C(41)	47.7 (3)
Os(3)–Pt–C(1)	164.8 (3)	Os(1)–Os(2)–C(44)	102.5 (4)
Os(3)–Pt–C(2)	157.7 (3)	Os(1)–Os(2)–C(45)	129.2 (4)
Os(3)–Pt–C(5)	97.6 (3)	Os(1)–Os(2)–C(48)	72.7 (3)
Os(3)–Pt–C(6)	104.2 (3)	Os(3)–Os(2)–C(21)	99.3 (4)
C(1)–Pt–C(2)	35.2 (4)	Os(3)–Os(2)–C(23)	70.8 (4)
C(1)–Pt–C(5)	94.0 (5)	Os(3)–Os(2)–C(41)	94.7 (3)
C(1)–Pt–C(6)	79.5 (4)	Os(3)–Os(2)–C(44)	164.5 (4)
C(2)–Pt–C(5)	79.7 (5)	Os(3)–Os(2)–C(45)	156.1 (4)
C(2)–Pt–C(6)	87.0 (5)	Os(3)–Os(2)–C(48)	87.5 (3)
C(5)–Pt–C(6)	36.9 (5)	Pt–Os(3)–Os(1)	58.18 (2)
Pt–Os(1)–Os(2)	63.50 (2)	Pt–Os(3)–Os(2)	65.20 (2)
Pt–Os(1)–Os(3)	56.08 (2)	Pt–Os(3)–C(31)	91.5 (4)
Pt–Os(1)–C(11)	158.5 (4)	Pt–Os(3)–C(32)	170.3 (3)
Pt–Os(1)–C(12)	92.1 (4)	Pt–Os(3)–C(33)	89.6 (4)
Pt–Os(1)–C(13)	65.8 (4)	Os(1)–Os(3)–Os(2)	59.86 (2)
Pt–Os(1)–C(41)	112.5 (3)	Os(1)–Os(3)–C(31)	96.8 (4)
Pt–Os(1)–H(1)	84 (3)	Os(1)–Os(3)–C(32)	115.4 (3)
Os(2)–Os(1)–Os(3)	57.64 (2)	Os(1)–Os(3)–C(33)	145.3 (3)
Os(2)–Os(1)–C(11)	133.3 (4)	Os(2)–Os(3)–C(31)	153.0 (4)
Os(2)–Os(1)–C(12)	102.5 (4)	Os(2)–Os(3)–C(32)	105.6 (4)
Os(2)–Os(1)–C(13)	127.7 (4)	Os(2)–Os(3)–C(33)	97.0 (4)
Os(2)–Os(1)–C(41)	49.9 (3)	C(31)–Os(3)–C(32)	96.6 (5)
Os(3)–Os(1)–C(11)	117.2 (4)	C(31)–Os(3)–C(33)	96.4 (5)
Os(3)–Os(1)–C(12)	146.9 (4)	C(32)–H(1)–Os(3)	118 (5)
Os(3)–Os(1)–C(13)	84.0 (4)	Os–C(av)–O	175 (1)
Os(3)–Os(1)–C(41)	92.5 (3)		
Pt–Os(2)–Os(1)	56.17 (2)		

2.8000 (7) and 2.8667 (8) Å. Three of the eight carbonyl ligands have adopted weak semibridging coordinations: Os(1)–C(13)–O(13) = 168 (1)°, Os(3)–C(21)–O(21) = 167 (1)°, and Os(3)–C(23)–O(23) = 168 (1)°.

The reaction of **1** with CO proceeds in two steps. First the COD ligands are replaced by CO ligands and the cluster opens to form the isolable product $Pt_2Os_3(CO)_{14}$ (**3**). This product can be isolated in reasonably good yields, 50–60%, if the amount of CO is kept small and the exposure time is short, 2–3 min. With prolonged exposure (15–30 min) to CO, cluster degradation occurs and the compound $PtOs_2(CO)_{10}$ (**4**) is obtained is good yields, 60–70%. This compound has been prepared previously by the CO-induced splitting of the dimer $Pt_2Os_4(CO)_{18}$ (**5**) with CO at

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[9] Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

[10] Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *240*, 321.

[11] Norén, B.; Sundberg, P. *J. Chem. Soc., Dalton Trans.* **1987**, 3103.

Table VIII. Positional Parameters and *B*(eq) for $Pt_2Os_3(CO)_{14}$ (3)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Pt(1)	0.52564 (10)	0.21097 (14)	0.38252 (05)	2.58 (8)
Pt(2)	0.44706 (12)	0.40902 (17)	0.37077 (06)	3.16 (8)
Pt(1A)	−0.02464 (10)	0.13682 (14)	0.61768 (05)	2.53 (8)
Pt(2A)	0.05429 (12)	0.33609 (15)	0.62851 (05)	3.14 (8)
Os(1)	0.61424 (11)	0.40099 (16)	0.40836 (05)	2.98 (8)
Os(1A)	−0.11054 (11)	0.32659 (15)	0.58745 (05)	3.10 (8)
Os(2)	0.44193 (11)	0.01498 (14)	0.35915 (06)	2.94 (8)
Os(2A)	0.05751 (11)	−0.05770 (14)	0.64426 (05)	2.65 (8)
Os(3)	0.35451 (11)	0.22672 (16)	0.34161 (05)	2.86 (8)
Os(3A)	0.14588 (11)	0.15430 (15)	0.66005 (05)	2.78 (8)
O(1)	0.691 (02)	0.088 (03)	0.4170 (11)	6.7 (8)
O(1A)	−0.189 (02)	0.004 (03)	0.5834 (10)	5.2 (6)
O(2)	0.427 (03)	0.658 (04)	0.3696 (13)	9 (1)
O(2A)	0.068 (02)	0.579 (03)	0.6265 (12)	8.1 (9)
O(11)	0.670 (02)	0.648 (03)	0.4357 (11)	7.2 (8)
O(11A)	−0.158 (02)	0.558 (03)	0.5570 (12)	7.7 (8)
O(12)	0.801 (02)	0.314 (03)	0.4411 (10)	5.8 (7)
O(12A)	−0.291 (02)	0.234 (03)	0.5467 (11)	6.2 (7)
O(13)	0.518 (02)	0.345 (03)	0.5094 (11)	6.7 (7)
O(13A)	−0.005 (02)	0.282 (03)	0.4900 (11)	6.5 (7)
O(14)	0.6493 (18)	0.403 (02)	0.2923 (10)	4.8 (6)
O(14A)	−0.1541 (20)	0.330 (03)	0.7033 (11)	5.6 (7)
O(21)	0.5200 (18)	0.044 (02)	0.2508 (10)	4.7 (6)
O(21A)	−0.0198 (19)	−0.024 (02)	0.7531 (10)	5.0 (6)
O(22)	0.300 (02)	−0.153 (03)	0.3246 (11)	6.4 (8)
O(22A)	0.202 (02)	−0.223 (03)	0.6780 (11)	6.9 (8)
O(23)	0.398 (02)	0.017 (03)	0.4746 (12)	6.8 (8)
O(23A)	0.1037 (19)	−0.055 (03)	0.5290 (11)	5.7 (7)
O(24)	0.589 (03)	−0.151 (03)	0.3830 (13)	8 (1)
O(24A)	−0.090 (02)	−0.226 (03)	0.6206 (10)	6.0 (7)
O(31)	0.236 (02)	0.437 (03)	0.3216 (11)	7.2 (8)
O(31A)	0.260 (02)	0.354 (03)	0.6786 (11)	6.9 (8)
O(32)	0.4430 (19)	0.270 (03)	0.2356 (10)	5.3 (7)
O(32A)	0.054 (02)	0.196 (03)	0.7616 (11)	5.9 (7)
O(33)	0.1963 (20)	0.082 (03)	0.2943 (10)	5.1 (6)
O(33A)	0.298 (03)	0.020 (03)	0.7066 (12)	7.7 (9)
O(34)	0.2975 (20)	0.225 (03)	0.4550 (10)	5.7 (7)
O(34A)	0.200 (023)	0.150 (03)	0.5469 (12)	6.9 (8)
C(1)	0.626 (03)	0.140 (03)	0.4001 (13)	3.6 (8)
C(1A)	−0.125 (03)	0.055 (03)	0.5961 (13)	3.3 (8)
C(2)	0.430 (03)	0.558 (05)	0.3705 (17)	6 (1)
C(2A)	0.057 (02)	0.484 (03)	0.6276 (10)	0.7 (6)
C(11)	0.654 (03)	0.556 (04)	0.4265 (14)	4.1 (9)
C(11A)	−0.132 (02)	0.473 (04)	0.5746 (12)	2.7 (7)
C(12)	0.726 (03)	0.344 (03)	0.4316 (12)	3.4 (8)
C(12A)	−0.230 (04)	0.268 (05)	0.5597 (17)	6 (1)
C(13)	0.556 (03)	0.370 (04)	0.4718 (14)	4.2 (8)
C(13A)	−0.042 (03)	0.296 (04)	0.5284 (15)	4.7 (9)
C(14)	0.634 (03)	0.399 (03)	0.3370 (14)	3.8 (8)
C(14A)	−0.137 (02)	0.329 (03)	0.6632 I(13)	3.1 (7)
C(21)	0.483 (03)	0.032 (04)	0.2891 (15)	4.5 (9)
C(21A)	0.012 (03)	−0.034 (04)	0.7132 (14)	4.2 (8)
C(22)	0.358 (03)	−0.101 (04)	0.3399 (16)	5 (1)
C(22A)	0.145 (03)	−0.160 (04)	0.6663 (13)	3.8 (8)
C(23)	0.413 (03)	0.018 (04)	0.4310 (16)	5 (1)
C(23A)	0.088 (02)	−0.055 (03)	0.5712 (13)	3.4 (8)
C(24)	0.529 (04)	−0.096 (05)	0.3714 (20)	8 (1)
C(24A)	−0.031 (02)	−0.162 (03)	0.6272 (11)	1.9 (6)
C(31)	0.283 (03)	0.365 (04)	0.3335 (14)	4.2 (9)
C(31A)	0.191 (03)	0.295 (04)	0.6662 (14)	4 (1)
C(32)	0.410 (02)	0.248 (03)	0.2769 (12)	3.2 (7)
C(32A)	0.087 (03)	0.177 (04)	0.7249 (15)	4.7 (9)
C(33)	0.258 (03)	0.132 (04)	0.3146 (16)	5 (1)
C(33A)	0.239 (03)	0.063 (04)	0.6908 (14)	3.8 (8)
C(34)	0.322 (02)	0.224 (03)	0.4137 (13)	2.9 (7)
C(34A)	0.179 (03)	0.149 (03)	0.5899 (14)	4.1 (8)

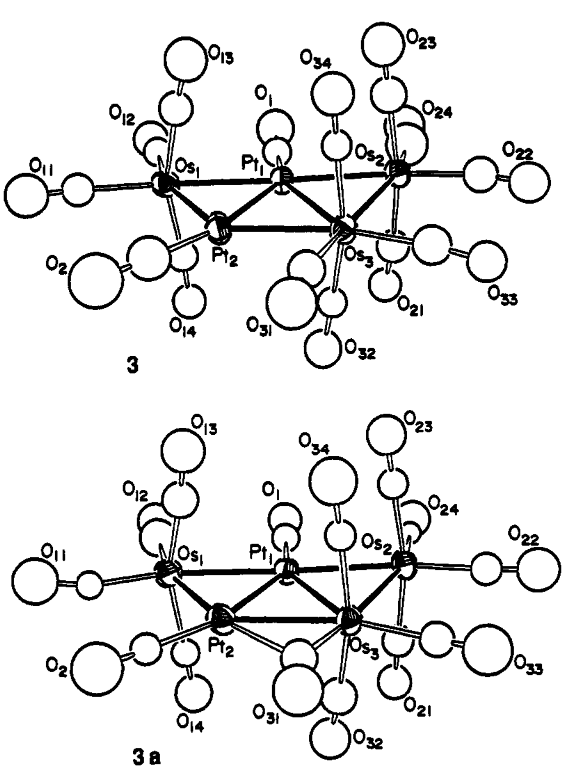

Figure 3. ORTEP diagrams of the two crystallographically independent molecules of $Pt_2Os_3(CO)_{14}$ (3 and 3a).

Table IX. Intramolecular Disdtances (Å) for $Pt_2Os_3(CO)_{14}$ (3)

Pt(1)–Pt(2)	2.670 (3)	Os(1A)–C(12A)	2.01 (6)
Pt(1)–Os(1)	2.710 (3)	Os(1A)–C(13A)	1.90 (4)
Pt(1)–Os(2)	2.725 (3)	Os(1A)–C(14A)	2.00 (3)
Pt(1)–Os(3)	2.714 (2)	Os(2)–Os(3)	2.891 (3)
Pt(1)–C(1)	1.76 (4)	Os(2)–C(21)	1.94 (4)
Pt(2)–Os(1)	2.626 (3)	Os(2)–C(22)	1.92 (5)
Pt(2)–Os(3)	2.681 (3)	Os(2)–C(23)	1.91 (4)
Pt(2)–C(2)	1.81 (6)	Os(2)–C(24)	1.88 (7)
Pt(2)–C(31)	2.63 (4)	Os(2A)–Os(3A)	2.895 (3)
Pt(1A)–Pt(2A)	2.684 (3)	Os(2A)–C(21A)	1.95 (4)
Pt(1A)–Os(1A)	2.716 (3)	Os(2A)–C(22A)	1.87 (4)
Pt(1A)–Os(2A)	2.717 (3)	Os(2A)–C(23A)	1.95 (3)
Pt(1A)–Os(3A)	2.720 (2)	Os(2A)–C(24A)	1.86 (4)
Pt(1A)–C(1A)	1.85 (4)	Os(3)–C(31)	1.99 (5)
Pt(2A)–Os(1A)	2.625 (3)	Os(3)–C(32)	1.91 (3)
Pt(2A)–Os(3A)	2.685 (3)	Os(3)–C(33)	1.93 (5)
Pt(2A)–C(2A)	1.79 (4)	Os(3)–C(34)	1.93 (3)
Pt(2A)–C(31A)	2.27 (4)	Os(3A)–C(31A)	1.83 (5)
Os(1)–C(11)	2.00 (5)	Os(3A)–C(32A)	1.94 (4)
Os(1)–C(12)	1.87 (4)	Os(3A)–C(33A)	1.91 (4)
Os(1)–C(13)	1.92 (4)	Os(3A)–C(34A)	1.89 (4)
Os(1)–C(14)	1.87 (4)	O–C(av)	1.15 (6)
Os(1A)–C(11A)	1.82 (4)		

50 atm.[7] Our reaction proceeds under much milder conditions (1 atm of CO) but suffers from the loss of one Pt and one Os atom from the pentanuclear cluster 3. The fate of these two atoms has not been established.

The structure of 3 was determined crystallographically. The compound crystallizes with two symmetry-independent molecules in the asymmetric crystal unit. Both molecules are structurally similar with the exception of one carbonyl ligand that is terminally coordinated in one molecule 3 and is a strong semibridge in the other, 3A. ORTEP diagrams of both molecules are shown in Figure 3. Final positional parameters are listed in Table VIII. Selected interatomic distances and angles for both molecules are listed in Tables IX and X. Both molecules consist of planar clusters of five metal atoms. No metal atom deviates from the best least-squares plane through the molecule by more than 0.035 Å. The metal atoms that contain only one carbonyl ligand were assigned as the platinum atoms. The platinum atoms have only 16-electron configurations, and this assumes that the Os(3)–Pt(2) bond in 3 is a donor–acceptor bond from Os(3) to Pt(2). In 3A the Os(3)–Pt(2) bond could be viewed as homopolar, since it contains a bridging carbonyl ligand; see below. The metal–metal bond lengths in both molecules are remarkably similar and are similar to those found in other platinum–osmium cluster complexes.[2a] The greatest difference between the two molecules lies in the coordination of the CO ligand C(31)–O(31). In 3, C(31)–O(31) is a weak semibridge [Os(3)–C(31)–O(31) = 169 (4)°, Pt(2)⋯C(31) = 2.63 (4) Å], while in 3A, it is a strong semibridge [Os(3A)–

Table X. Intramolecular Bond Angles (deg) for **3**

Pt(2)–Pt(1)–Os(1)	58.43 (7)	Pt(1)–Os(1)–Pt(2)	60.03 (7)	Os(3A)–Os(2A)–C(23A)	90 (1)
Pt(2)–Pt(1)–Os(2)	123.91 (8)	Pt(1)–Os(1)–C(11)	168 (1)	Os(3A)–Os(2A)–C(24A)	161 (1)
Pt(2)–Pt(1)–Os(3)	59.73 (7)	Pt(1)–Os(1)–C(12)	100 (1)	Pt(1)–Os(3)–Pt(2)	59.33 (7)
Pt(2)–Pt(1)–C(1)	146 (1)	Pt(1)–Os(1)–C(13)	79 (1)	Pt(1)–Os(3)–Os(2)	58.07 (6)
Os(1)–Pt(1)–Os(2)	177.52 (9)	Pt(1)–Os(1)–C(14)	81 (1)	Pt(1)–Os(3)–C(31)	126 (1)
Os(1)–Pt(1)–Os(3)	118.14 (8)	Pt(2)–Os(1)–C(11)	108 (1)	Pt(1)–Os(3)–C(32)	84 (1)
Os(1)–Pt(1)–C(1)	87 (1)	Pt(2)–Os(1)–C(12)	160 (1)	Pt(1)–Os(3)–C(33)	140 (1)
Os(2)–Pt(1)–Os(3)	64.23 (7)	Pt(2)–Os(1)–C(13)	82 (1)	Pt(1)–Os(3)–C(34)	85 (1)
Os(2)–Pt(1)–C(1)	90 (1)	Pt(2)–Os(1)–C(14)	80 (1)	Pt(2)–Os(3)–Os(2)	117.36 (8)
Os(3)–Pt(1)–C(1)	154 (1)	Pt(1A)–Os(1A)–Pt(2A)	60.31 (7)	Pt(2)–Os(3)–C(31)	67 (1)
Pt(1)–Pt(2)–Os(1)	61.54 (7)	Pt(1A)–Os(1A)–C(11A)	161 (1)	Pt(2)–Os(3)–C(32)	84 (1)
Pt(1)–Pt(2)–Os(3)	60.94 (7)	Pt(1A)–Os(1A)–C(12A)	102 (2)	Pt(2)–Os(3)–C(33)	161 (1)
Pt(1)–Pt(2)–C(2)	161 (2)	Pt(1A)–Os(1A)–C(13A)	78 (1)	Pt(2)–Os(3)–C(34)	84 (1)
Os(1)–Pt(2)–Os(3)	122.5 (1)	Pt(1A)–Os(1A)–C(14A)	81 (1)	Os(2)–Os(3)–C(31)	174 (1)
Os(1)–Pt(2)–C(2)	100 (2)	Pt(2A)–Os(1A)–C(11A)	100 (1)	Os(2)–Os(3)–C(32)	92 (1)
Os(3)–Pt(2)–C(2)	138 (2)	Pt(2A)–Os(1A)–C(12A)	162 (2)	Os(2)–Os(3)–C(33)	82 (1)
Pt(2A)–Pt(1A)–Os(1A)	58.17 (6)	Pt(2A)–Os(1A)–C(13A)	78 (1)	Os(2)–Os(3)–C(34)	88 (1)
Pt(2A)–Pt(1A)–Os(2A)	123.90 (8)	Pt(2A)–Os(1A)–C(14A)	81 (1)	Pt(1A)–Os(3A)–Pt(2A)	59.54 (7)
Pt(2A)–Pt(1A)–Os(3A)	59.59 (7)	Pt(1)–Os(2)–Os(3)	57.70 (6)	Pt(1A)–Os(3A)–Os(2A)	57.78 (6)
Pt(2A)–Pt(1A)–C(1A)	148 (1)	Pt(1)–Os(2)–C(21)	87 (1)	Pt(1A)–Os(3A)–C(31A	116 (1)
Os(1A)–Pt(1A)–Os(2A)	177.45 (8)	Pt(1)–Os(2)–C(22)	166 (1)	Pt(1A)–Os(3A)–C(32A)	84 (1)
Os(1A)–Pt(1A)–Os(3A)	117.75 (8)	Pt(1)–Os(2)–C(23)	84 (1)	Pt(1A)–Os(3A)–C(33A)	140 (1)
Os(1A)–Pt(1A)–C(1A)	90 (1)	Pt(1)–Os(2)–C(24)	106 (2)	Pt(1A)–Os(3A)–C(34A)	84 (1)
Os(2A)–Pt(1A)–Os(3A)	64.34 (6)	Os(3)–Os(2)–C(21)	86 (1)	Pt(2A)–Os(3A)–Os(2A)	117.29 (8)
Os(2A)–Pt(1A)–C(1A)	88 (1)	Os(3)–Os(2)–C(22)	109 (1)	Pt(2A)–Os(3A)–C(31A)	57 (1)
Os(3A)–Pt(1A)–C(1A)	152 (1)	Os(3)–Os(2)–C(23)	91 (1)	Pt(2A)–Os(3A)–C(32A)	84 (1)
Pt(1A)–Pt(2A)–Os(1A)	61.53 (7)	Os(3)–Os(2)–C(24)	163 (2)	Pt(2A)–Os(3A)–C(33A)	160 (1)
Pt(1A)–Pt(2A)–Os(3A)	60.88 (7)	Pt(1A)–Os(2A)–Os(3A)	57.88 (6)	Pt(2A)–Os(3A)–C(34A)	84 (1)
Pt(1A)–Pt(2A)–C(2A)	155 (1)	Pt(1A)–Os(2A)–C(21A)	86 (1)	Os(2A)–Os(3A)–C(31A)	174 (1)
Pt(1A)–Pt(2A)–C(31A)	103 (1)	Pt(1A)–Os(2A)–C(22A)	161 (1)	Os(2A)–Os(3A)–C(32A)	91 (1)
Os(1A)–Pt(2A)–Os(3A)	122.4 (1)	Pt(1A)–Os(2A)–C(23A)	82 (1)	Os(2A)–Os(3A)–C(33A)	82 (1)
Os(1A)–Pt(2A)–C(2A)	94 (1)	Pt(1A)–Os(2A)–C(24A)	103 (1)	Os(2A)–Os(3A)–C(34A)	89 (1)
Os(1A)–Pt(2A)–C(31A)	165 (1)	Os(3A)–Os(2A)–C(21A)	85 (1)	Os(3)–C(31)–O(31)	169 (4)
Os(3A)–Pt(2A)–C(2A)	144 (1)	Os(3A)–Os(2A)–C(22A)	104 (1)	Os(3A)–C(31A)–O(31A)	146 (4)
Os(3A)–Pt(2A)–C(31A)	42 (1)			M–C(av)–O	174 (6)

Table XI. Positional Parameters and *B*(eq) for $PtOs_2(CO)_{10}$ (**4**)

atom	*x*	*y*	*z*	*B*(eq), Å²
Pt(1)	0.11487 (07)	0.35776 (04)	0.35954 (089)	2.70 (3)
Os(1)	0.16660 (07)	0.15261 (04)	0.41726 (09)	2.75 (3)
Os(2)	0.37831 (07)	0.30142 (04)	0.62459 (08)	2.65 (2)
O(1)	–0.1966 (17)	0.3439 (14)	0.064 (02)	8.7 (9)
O(2)	0.1939 (17)	0.5811 (10)	0.391 (02)	7.1 (7)
O(11)	–0.1100 (16)	0.0489 (13)	0.143 (02)	7.7 (8)
O(12)	0.3119 (16)	0.1275 (10)	0.0648 (19)	6.3 (7)
O(13)	0.3652 (17)	–0.0404 (11)	0.599 (02)	7.8 (8)
O(14)	–0.0202 (17)	0.2014 (10)	0.732 (02)	6.8 (7)
O(21)	0.5350 (16)	0.5038 (10)	0.785 (02)	6.8 (7)
O(22)	0.6058 (18)	0.1385 (12)	0.863 (02)	8.1 (8)
O(23)	0.5415 (17)	0.2678 (10)	0.2870 (20)	6.6 (7)
O(24)	0.1745 (16)	0.3783 (11)	0.9157 (19)	6.8 (7)
C(1)	–0.079 (02)	0.3481 (13)	0.176 (03)	5.0 (8)
C(2)	0.1556 (20)	0.4973 (13)	0.375 (02)	4.4 (8)
C(11)	–0.004 (02)	0.0888 (13)	0.248 (03)	5.2 (8)
C(12)	0.2652 (19)	0.1389 (12)	0.200 (02)	4.2 (7)
C(13)	0.287 (02)	0.0313 (15)	0.529 (02)	5.2 (9)
C(14)	0.056 (02)	0.1876 (12)	0.623 (02)	5.0 (8)
C(21)	0.474 (02)	0.4238 (13)	0.720 (02)	4.9 (8)
C(22)	0.523 (02)	0.2012 (14)	0.776 (02)	5.1 (8)
C(23)	0.479 (02)	0.2771 (12)	0.405 (02)	4.5 (7)
C(24)	0.247 (02)	0.3449 (13)	0.810 (02)	4.4 (8)

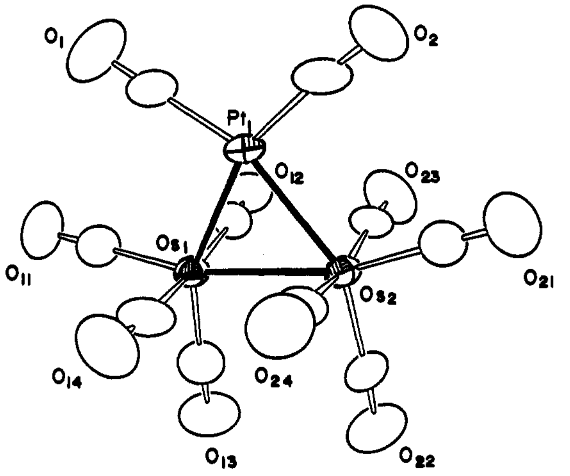

Figure 4. ORTEP diagram of the molecular structure of $PtOs_2(CO)_{10}$ (**4**).

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

Pt(1)–C(2)	1.87 (2)	Os(2)–C(24)	1.97 (2)
Pt(1)–C(1)	1.88 (2)	O(1)–C(1)	1.14 (2)
Pt(1)–Os(2)	2.678 (1)	O(2)–C(2)	1.16 (2)
Pt(1)–Os(1)	2.689 (1)	O(11)–C(11)	1.18 (2)
Os(1)–C(11)	1.88 (2)	O(12)–C(12)	1.13 (2)
Os(1)–C(13)	1.91 (2)	O(13)–C(13)	1.16 (2)
Os(1)–C(14)	1.94 (2)	O(14)–C(14)	1.15 (2)
Os(1)–C(12)	1.95 (2)	O(21)–C(21)	1.21 (2)
Os(1)–Os(2)	2.864 (1)	O(22)–C(22)	1.14 (2)
Os(2)–C(21)	1.86 (2)	O(23)–C(23)	1.11 (2)
Os(2)–C(22)	1.92 (2)	O(24)–C(24)	1.12 (2)
Os(2)–C(23)	1.96 (2)		

C(31A)–O(31A) = 146 (4)°, Pt(3A)–C(31A) = 2.27 (4) Å]. These molecules are related to the triangulated planar hexaosmium "raft" clusters prepared by Lewis and Johnson[12] and the platinum–iron anions reported by Longoni[13] several years ago except that these clusters have one less metal atom. Accordingly, we feel that the structure of **3** could be described as a "truncated" or incomplete raft.

An ORTEP drawing of the molecular structure of **4** is shown in Figure 4. The final crystallographic positional parameters are listed in Table XI. Interatomic bond distances and angles are listed in Tables XII and XIII. A preliminary report of the structure of **4** has appeared.[7] The molecule consists of a triangular cluster of one platinum plus two osmium atoms. The Pt–Os distances are essentially equal in length, 2.678 (1) and 2.689 (1)

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(12) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1982**, 640.

(13) Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 7973.

Scheme I

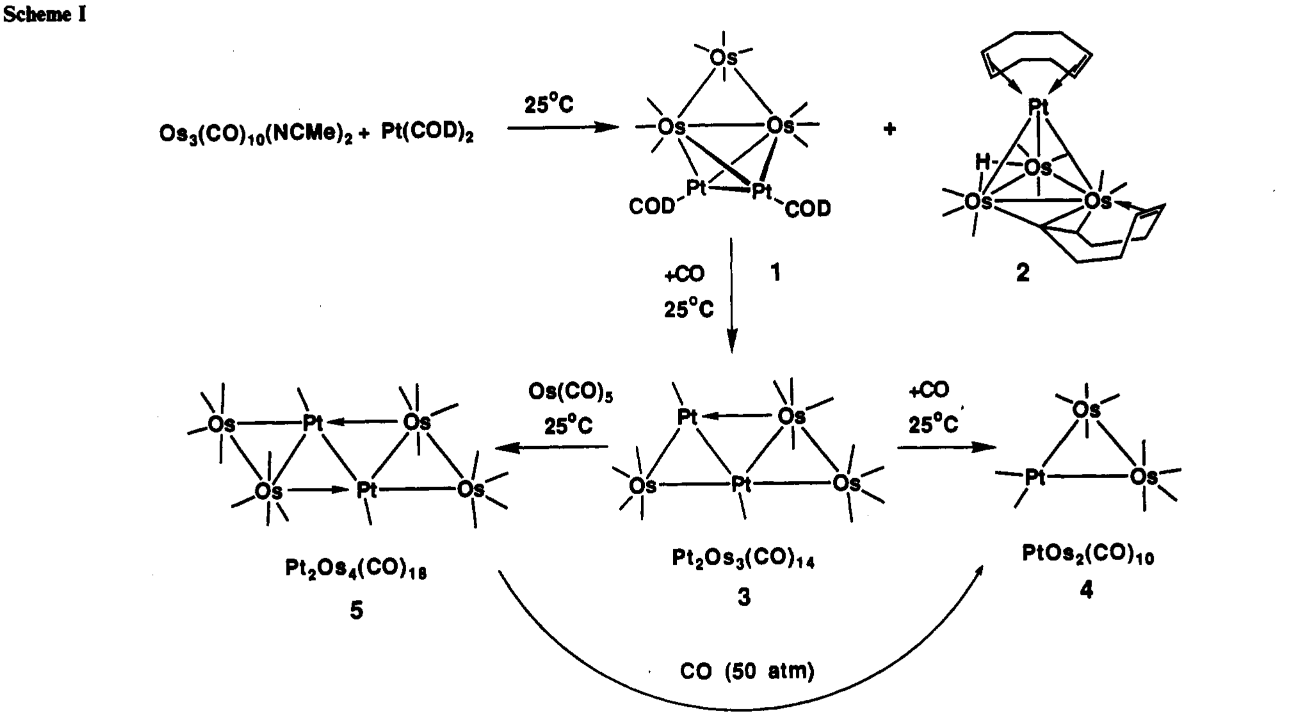

Table XIII. Intramolecular Bond Angles (deg) for 4

C(2)–Pt(1)–C(1)	105.6 (7)	C(12)–Os(1)–Os(2)	87.9 (4)
C(2)–Pt(1)–Os(2)	94.4 (5)	Pt(1)–Os(1)–Os(2)	57.56 (3)
C(2)–Pt(1)–Os(1)	158.6 (5)	C(21)–Os(2)–C(22)	100.5 (7)
C(1)–Pt(1)–Os(2)	160.0 (5)	C(21)–Os(2)–Pt(1)	106.3 (6)
C(1)–Pt(1)–Os(1)	95.5 (5)	C(21)–Os(2)–Os(1)	164.2 (6)
Os(2)–Pt(1)–Os(1)	64.51 (3)	C(22)–Os(2)–Pt(1)	153.2 (5)
C(11)–Os(1)–C(13)	99.7 (8)	C(22)–Os(2)–Os(1)	95.2 (5)
C(11)–Os(1)–Pt(1)	106.2 (5)	C(23)–Os(2)–Pt(1)	86.7 (5)
C(11)–Os(1)–Os(2)	163.8 (5)	C(23)–Os(2)–Os(1)	89.5 (5)
C(13)–Os(1)–Pt(1)	154.0 (6)	C(24)–Os(2)–Pt(1)	82.5 (5)
C(13)–Os(1)–Os(2)	96.5 (5)	C(24)–Os(2)–Os(1)	88.6 (5)
C(14)–Os(1)–Pt(1)	88.1 (5)	Pt(1)–Os(2)–Os(1)	57.93 (3)
C(14)–Os(1)–Os(2)	89.1 (5)	O–C(av)–M	175.00
C(12)–Os(1)–Pt(1)	83.4 (5)		

Å, and both are significantly shorter than the Os–Os bond distance of 2.864 (1) Å. The latter is very similar to the Os–Os distances in $Os_3(CO)_{12}$, 2.877 (3) Å.[14] All of the carbonyl ligands are of a linear terminal type, and the two carbonyl ligands on the platinum atom lie in the plane of the $PtOs_2$ triangle.

Compound 3 reacts readily (25 °C) with $Os(CO)_5$ to yield the known hexanuclear cluster complex 5, 92%. The structure of 5[7] and its ruthenium homologue[4] have been reported previously.

Discussion

Couture and Farrar have shown that the acetonitrile derivatives of $Os_6(CO)_{18}$ react with $Pt(COD)_2$ to yield higher nuclearity platinum–osmium carbonyl cluster complexes containing Pt(COD) groupings.[15] Our studies show that the nitrile-containing triosmium cluster $Os_3(CO)_{10}(NCMe)_2$ readily reacts with $Pt(COD)_2$ to yield the new pentanuclear complex 1, in which two Pt(COD) groupings are joined by a Pt–Pt bond. Compound 1 reacts with CO to yield a series of transformed binary platinum–osmium carbonyl cluster complexes. These results are summarized in Scheme I. The initial displacement of the COD ligands is accompanied by an opening of the cluster to yield the planar cluster complex 3, which is readily degraded by CO to yield the diosmium platinum complex 4. Compound 4 contains a total of 46 valence electrons, which is 2 less than the 48-electron configuration that occurs when all of the metal atoms in the triangular cluster achieve 18-electron configurations. The 2-electron deficiency in 4 can be attributed to a 16-electron configuration at the platinum atom. This results in a vacant p orbital that lies perpendicular to the plane of the cluster. Compound 3 also readily reacts with $Os(CO)_5$ to yield the known cluster complex 5. The formation of 5 has occurred by the addition of an $Os(CO)_4$ grouping to the Os(1)–Pt(2) edge of the cluster of 3. The Pt(2)–Os(3) edge is an alternative site for addition that would have yielded a cluster with the well-known triangulated triangle or "raft" structure, but we have obtained no evidence for a product having this structure. Unlike 4, the cluster of 5 possesses a structure that is considerably folded. Whether this is due to steric or electronic effects has yet to be ascertained. Electron-counting procedures indicate that the structure of 5 is anomalous. Efforts are in progress to try to understand the bonding in these molecules.[16] Compound 5 is also degraded by reaction with CO to yield 4, but considerably more forcing conditions (50 atm) are required than those for the reaction of 3.[6] A better understanding of the bonding in these molecules may also help to explain these differences in reactivity.

We have recently shown that 5 reacts with hydrogen to yield a variety of *hydrogen-rich* platinum–osmium carbonyl cluster complexes.[17] We expect that all of the complexes 1–5 will be prove to be useful in preparing a variety of derivatives that contain both osmium and platinum. It will be of interest to compare the reactivity of the mixed-metal cluster complexes with that of the pure osmium clusters[18] to try to identify effects in the reactivity of the mixed-metal clusters that might be attributed to the presence of the platinum.

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Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom positional parameters (15 pages); listings of structure factor amplitudes (66 pages). Ordering information is given on any current masthead page.

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