and to the naturally abundant ^{195}Pt nuclei. The ^{1}H NMR spectrum of **2** at 155 K shows four broad singlets in the aliphatic region that can be attributed to the four inequivalent methyl groups on the two PMe_2Ph ligands. A pairwise averaging is demonstrated by the broadening, coalescence, and sharpening into two singlets (doublets at 199 K due to ^{31}P-H coupling) shown by the spectra recorded at higher temperatures; see Figure 4. This indicates the presence of a dynamical process that produces a time-averaged plane of symmetry. Two processes that could explain all the observations are shown in Scheme II. Via mechanism A, a bond is formed between the platinum atom and the third osmium atom. The intermediate has the structure that is predicted to be stable by the SEP theory. Alternatively, via mechanism B a platinum–osmium bond is broken. The intermediate contains a 16-electron platinum atom. The two processes can not be distinguished with the available information. In fact, they are permutationally indistinguishable, but the distinction between bond-making and bond-breaking is certainly chemically and physically real. Intuitively, the bond-making process, A, is preferred because the averaging is very rapid, $\Delta G^{\ddagger}_{167}$ = 7.5 kcal/mol, and this intermediate is expected to be a relatively stable one. Conversely, the bonding-breaking process, B, seems less likely since it seems that the metal–metal bond cleavage should have an activation barrier higher than 7.5 kcal/mol.[24]

Acknowledgment. This work was supported by the National Science Foundation, Grant No. CHE-8416460. NMR studies were supported by Grant No. CHE-8207445 from the National Science Foundation to the NMR Regional Facility at the University of South Carolina. We thank Drs. A. R. Garber and H. Cohen for their assistance in recording the variable-temperature NMR spectra.

Registry No. **1**, 101567-25-3; **2**, 101630-00-6; **3**, 82093-50-3; **4**, 72282-40-7; $Os_4(CO)_{13}(\mu_3\text{-}S)_2$, 83928-37-4; $Os_4(CO)_{11}(PMe_2Ph)(\mu_3\text{-}S)_2$, 91281-79-7; $Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)_2$, 101567-26-4; $Os_3(CO)_7(PMe_2Ph)_2(\mu_3\text{-}S)_2$, 101567-27-5; $Os(CO)_5$, 16406-49-8; $Pt(PMe_2Ph)_4$, 33361-89-6; Pt, 7440-06-4; Os, 7440-04-2.

Supplementary Material Available: Listings of anisotropic thermal parameters for both structures and additional interatomic angles for **2** (3 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (12 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Cluster Syntheses. 12. Metal–Metal Exchange Reactions. Systematics of the Synthesis of Platinum–Osmium Carbonyl Clusters Containing Quadruply Bridging Sulfido Ligands

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The reaction of $Os_5(CO)_{15}(\mu_4\text{-}S)$ (**1**) heptahydrate, $Pt(PPh_3)_2C_2H_4$ has yielded several new platinum–osmium clusters containing quadruply bridging sulfido ligands and $Os_5(CO)_{14}(PPh_3)(\mu_4\text{-}S)$ (**3**). The three platinum–osmium clusters $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**2**), $PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$ (**4**), and $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**6**) have been characterized by single-crystal X-ray diffraction analyses. For **2**: space group $P\bar{1}$, a = 13.116 (4) Å, b = 9.655 (3) Å, c = 14.669 (4) Å, α = 89.68 (3)°, β = 104.79 (2)°, γ = 89.11 (3)°, Z = 2, ρ_{calcd} = 2.99 g/cm^3. The structure was solved by the heavy-atom method and refined (4505 reflections) to the final residuals R_F = 0.044 and R_{wF} = 0.052. The molecule consists of a square-pyramidal cluster of four osmium atoms and one platinum atom with a quadruply bridging sulfido ligand on the square base. The platinum atom lies in the square base. For **4**: space group $P2_1/c$, a = 8.986 (7) Å, b = 16.605 (5) Å, c = 26.005 (8) Å, β = 97.62 (4)°, Z = 4, ρ_{calcd} = 3.21 g/cm^3. The structure of **4** was solved by direct methods and was refined (3947 reflections) to the final residuals R_F = 0.040 and ground = 0.048. The molecule consists of a square-pyramidal cluster of five osmium atoms with a quadruply bridging sulfido ligand on the square base and a $Pt(CO)PPh_3$ moiety bridging one of the triosmium triangles. For **6**: space group $P\bar{1}$, a = 12.538 (2) Å, b = 15.908 (2) Å, c = 18.061 (2) Å, α = 63.008 (9)°, β = 76.629 (9)°, γ = 65.68 (1)°, Z = 2, ρ_{calcd} = 2.45 g/cm^3. The structure was solved by the heavy-atom method and was refined (4976 reflections) to the final residuals R_F = 0.049 and R_{wF} = 0.065. The molecule consists of a square-pyramidal cluster of four osmium atoms and one platinum atom with the base bridged by a quadruply bridging sulfido ligand and one of the osmium–osmium bonds in the square base bridged by an $Os(CO)_3(PPh_3)$ moiety. Compound **6** is believed to be an intermediate in the formation of **2**. **6** reacts with carbon monoxide to yield both **2** and **3**. The yield of **6** is increased when the reaction is performed in the presence of PPh_3. The yield of **4** is increased when the reaction is performed under CO. A scheme based on hexanuclear intermediates is proposed to explain the formation of all the products.

Introduction

Recent studies have shown that certain platinum alloys and bimetallic mixtures exhibit catalytic properties that are far superior to those of the homonuclear components.[1-3] These observations have stimulated an intense interest in the chemistry of heteronuclear transition-metal cluster compounds. Unfortunately, the synthetic routes to heteronuclear cluster compounds have been almost as wide ranging and varied in type as the compounds themselves are.[4]

In this report the synthesis of several new platinum–osmium clusters by the reaction of $Os_5(CO)_{15}(\mu_4\text{-}S)$ (**1**) with $Pt(PPh_3)_2C_2H_4$ will be described. Although lightly stabilized[5] and electron-deficient[6] osmium clusters will react with platinum

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Table I. IR and ^{31}P NMR Spectra

compd	IR (ν_{CO}, CH_2Cl_2 solvent), cm^{-1}	$^{31}P\{^1H\}$ NMR,[a] δ
$PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**2**)	2087.4 (w), 2051.5 (s), 2019.7 (m), 1997.1 (w), 1972.9 (w)	43.86 (J_{Pt-P} = 2601 Hz)[b]
$PtOs_5(CO)_{14}(PPh_3)(\mu_4\text{-}S)$ (**3**)	2090.7 (s), 2055.8 (s), 2044.9 (s), 2028.9 (s), 2011.8 (s), 1996.4 (m), 1979.0 (m), 1977.0 (w), 1951.4 (s)	35.34 (s)[c]
$PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$ (**4**)	2093.0 (w), 2086.6 (w), 2061.5 (s), 2050.9 (s), 2028.8 (s), 2021.8 (s), 2001.7 (w), 1792.7 (w)	*d*
brown **5**	2076.3 (s), 2043.3 (s), 2029.4 (s), 2015.9 (s), 1986.1 (m), 1963.1 (m), 1903.9 (w), 1784.4 (w)	*e*
$PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**6**)	2064.5 (m), 2048.1 (s), 2035.9 (s), 2028.8 (s), 2017.1 (m), 1994.1 (m), 1971.9 (m), 1901.4 (w)	26.23 (J_{Pt-P} = 2442 Hz), 5.31 (s)[c]
$Os_4(CO)_{11}(PPh_3)(\mu_3\text{-}S)$ (**7**)	2087.5 (m), 2053.3 (s), 2043.5 (s), 2011.1 (s), 1997.9 (m), 1992.4 (m), 1968.1 (w), 1937.3 (w)	12.4 (s)

[a] Vs. phosphoric acid. [b] In CD_2Cl_2. [c] In C_6D_6. [d] Decomposed in NMR tube at 25°. [e] No resonances observed.

complexes to yield platinum–osmium clusters, the reaction of $Os_3(CO)_{12}$ with $Pt(PR_3)_4$ compounds yields only phosphine-substituted derivatives of $Os_3(CO)_{12}$.[7]

Bridging ligands have been shown to be of great value in cluster syntheses by facilitating the addition of metal-containing fragments to existing clusters and by stabilizing the products.[4,8] It has been shown recently that osmium carbonyl clusters containing triply bridging sulfido ligands will readily add platinum-containing moieties to yield platinum–osmium clusters,[9–11] and it is believed that the sulfido ligands play an important role in these additions. Similarly, it appears that the quadruply bridging sulfido ligand in the electron-precise cluster **1** may play an important role in the synthesis of the higher nuclearity platinum–osmium clusters that are reported here. A preliminary report of this work has been published.[12]

Experimental Section

Reactions were performed under a prepurified nitrogen atmosphere unless otherwise indicated. Reagent grade solvents were dried over molecular sieves and were deoxygenated by purging with nitrogen gas before use. CP grade CO gas was purchased from Linde and was used without further purification. $Pt(PPh_3)_2(C_2H_4)$ and $Os_5(CO)_{15}(\mu_4\text{-}S)$ was prepared by published procedures.[13,14] Triphenylphosphine was used as purchased from Aldrich Chemical Co. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrometer. A Bruker WP200 FT-NMR spectrometer was used to obtain ^{31}P NMR spectra at 81 MHz, using 85% D_3PO_4 as the external reference. Elemental analyses were performed by Mic Anal., Tuscon, AZ.

Reaction of $Os_5(CO)_{15}(\mu_4\text{-}S)$ (1) with $Pt(PPh_3)_2(C_2H_4)$. To $Os_5(CO)_{15}(\mu_4\text{-}S)$ (30 mg, 0.021 mmol) dissolved in 50 mL of THF was added $Pt(PPh_3)_2(C_2H_4)$ 15.5 mg, 0.021 mmol) at 0 °C. The mixture was stirred for 0.5 h at 0 °C and was then warmed to room temperature. After the mixture was stirred for an additional 2 h, the solvent was removed in vacuo from the dark brown solution. The dark brown residue was extracted with a minimum quantity of CH_2Cl_2, and the solution was applied to silica gel TLC plates. Elution in air with 35% CH_2Cl_2 in hexane solution led to the isolation in order of elution of (1) unreacted $Os_5(CO)_{15}(\mu_4\text{-}S)$ (10%), (2) brown $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**2**; 2 mg, 6%), (3) orange-red $Os_5(CO)_{14}(PPh_3)(\mu_4\text{-}S)$ (**3**; 3 mg, 9%), (4) green-brown $PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$ (**4**; 2 mg, 5%), (5) an unidentified brown compound (**5**, 3 mg), and (6) purple $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**6**; 3 mg, 7%). Anal. Calcd for **2**: C, 23.06; H, 0.93. Found: C, 22.95; H, 0.77. Calcd for **3**: C, 23.47; H, 0.92. Found: C, 23.6; H, 0.96. Calcd for **4**: C, 21.3; H, 0.80. Found: C, 21.56; H, 0.78. Calcd for **6**: C, 28.85; H, 1.14. Found: C, 29.12; H, 1.23. IR and $^{31}P\{^1H\}$ NMR spectral data for the products are listed in Table I.

Reaction of $Os_5(CO)_{15}(\mu_4\text{-}S)$ with PPh_3. $Os_5(CO)_{15}(\mu_4\text{-}S)$ (23 mg, 0.016 mmol) was mixed with PPh_3 (6 mg; 0.023 mmol) in octane and stirred for 3 h at room temperature. No reaction was observed (TLC/IR) at this stage. The solution was subsequently refluxed for 2.5 h. After cooling, the solvent was removed in vacuo and the residue was chromatographed on silica TLC plates with 15%/85% CH_2Cl_2/hexane solvent. This separated $Os_5(CO)_{14}(PPh_3)(\mu_4\text{-}S)$ (**3**; 13 mg, 50%) and unreacted **1** (7 mg, 31%).

$Os_5(CO)_{15}(\mu_4\text{-}S)$ with $Pt(PPh_3)_2(C_2H_4)$ and PPh_3. To $Os_5(CO)_{15}(\mu_4\text{-}S)$ (35 mg, 0.025 mmol) dissolved in 50 mL of THF were added $Pt(PPh_3)_2(C_2H_4)$ (18.5 mg, 0.025 mmol) and PPh_3 (6.5 mg, 0.025 mmol) at 0 °C. The mixture was stirred for 0.5 h at 0 °C and was then warmed to room temperature. While the mixture was being stirred for an additional 2 h, it turned dark brown in color. The solvent was removed in vacuo, and the residue was separated on silica TLC plates. Elution with 35% CH_2Cl_2 in hexane solution separated in order of elution (1) brown **2** (trace), (2) orange-red **3** (13 mg, 32%), and (3) purple **6** (9 mg, 17%).

$Os_5(CO)_{15}(\mu_4\text{-}S)$ with $Pt(PPh_3)_2(C_2H_4)$ under a CO Atmosphere. To a CO-saturated THF solution (30 mL) of $Os_5(CO)_{15}(\mu_4\text{-}S)$ at 0 °C (16 mg, 0.011 mmol) was added solid $Pt(PPh_3)_2(C_2H_4)$ (8.5 mg, 0.011 mmol). After the mixture was stirred at 0 °C for 0.5 h, the reaction vessel was slowly warmed to room temperature and stirring was continued for 2 h under a CO atmosphere. After removal of the solvent in vacuo from the orange-brown solution, the residue was extracted with a minimum quantity of CH_2Cl_2 and was chromatographed on silica gel TLC plates. Elution with 35% CH_2Cl_2 in hexane solution led to the isolation of the compounds $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**2**; 1.5 mg, 8%), $Os_5(CO)_{14}(PPh_3)(\mu_4\text{-}S)$ (**3**; <1 mg), $PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$ (**4**; 1.8 mg, 9%), brown **5** (<1 mg), and $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**6**; <1 mg).

Reaction of $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (6) with CO. $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (8 mg, 0.004 mmol) was refluxed in CH_2Cl_2 solution under a CO atmosphere for 4 h. The solvent was removed in vacuo, and the residue was separated on silica TLC plates. Elution with a 35% CH_2Cl_2 in hexane solution separated in order of elution $Os(CO)_4PPh_3$ (0.9 mg, 48%), **2** (2.4 mg, 40%), and **3** (2 mg, 33%).

Pyrolysis of $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (2). $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (7 mg, 0.004 mmol) in octane solution was refluxed for 3 h. The greenish brown solution changed color to orange-brown. The solvent was removed in vacuo, and the residue was chromatographed on silica TLC plates. Elution with 35% CH_2Cl_2 in hexane solution separated $Os_4(CO)_{11}(PPh_3)(\mu_3\text{-}S)$ (**7**; 5 mg, 84%). The identity of compound **7** was confirmed by an independent syntheses from the reaction of $Os_4(CO)_{11}(NMe_3)(\mu_3\text{-}S)$ with PPh_3.

Preparation of $Os_4(CO)_{11}(PPh_3)(\mu_3\text{-}S)$ (7). PPh_3 (2 mg, 0.008 mmol) was added to $Os_4(CO)_{11}(NMe_3)(\mu_3\text{-}S)$[15] (8 mg, 0.007 mmol) in CH_2Cl_2 solution at 0 °C. The mixture was stirred at 0 °C for 15 min and then warmed to room temperature and stirred for an additional 1 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel TLC plates. Elution with a 20%/80% CH_2Cl_2/hexane solvent solution separated $Os_4(CO)_{11}(PPh_3)(\mu_3\text{-}S)$ (**7**; 4 mg, 42%). Anal. Calcd: C, 25.56; H, 1.10. Found: C, 25.72; H, 1.21.

Reaction of Brown 5 with PPh_3. PPh_3 (4 mg) was added to a THF solution of brown **5** (24 mg) with stirring at 25 °C. After 2 h the solution changed color from brown to orange. The solvent was removed in vacuo, and the residue was chromatographed on silica gel TLC plates with 35% CH_2Cl_2 in hexane solvent to yield 20 mg of **3**.

Crystallographic Analyses. Brown crystals of **2** suitable for diffraction measurements were grown by slow evaporation of solvent from solutions in a methanol/dichloromethane solvent mixture at 25 °C. Dark brown crystals of **4** were grown from solutions in a dichloromethane/hexane solvent mixture by cooling to 0 °C. Purple crystals of **6** were grown from solutions in a dichloromethane/hexane solvent mixture maintained under a carbon monoxide atmosphere at −30 °C. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on

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Table II. Crystallographic Data for X-ray Diffraction Studies

	2	**4**	**6**
(A) Crystal Data			
formula	$PtOs_4SPO_{13}C_{31}H_{15}$	$PtOs_5SPO_{15}C_{33}H_{15}$	$PtOs_5SP_2O_{15}C_{51}H_{30}\cdot 0.25CH_2Cl_2$
temp (±3), °C	23	23	23
space group	$P\bar{1}$, No. 2	$P2_1/c$, No. 14	$P\bar{1}$, No. 2
a, Å	13.116 (4)	8.986 (7)	12.538 (2)
b, Å	9.655 (3)	16.605 (5)	15.908 (2)
c, Å	14.669 (4)	26.005 (8)	18.061 (2)
α, deg	89.63 (3)	90.0	63.008 (9)
β, deg	104.79 (2)	97.62 (4)	76.629 (9)
γ, deg	89.11 (3)	90.0	65.68 (1)
V, Å^3	1795.8	3846	2920.8
M_r	1616.4	1860.0	2122.9
Z	2	4	2
ρ_{calcd}, g/cm^3	2.99	3.21	2.45
(B) Measurement of Intensity Data			
radiation	Mo K$\bar{\alpha}$ (0.710 73 Å)	Mo K$\bar{\alpha}$ (0.710 73 Å)	Mo K$\bar{\alpha}$ (0.710 73 Å)
monochromator	graphite	graphite	graphite
detector aperture, mm			
horiz ($A + B \tan\theta$))			
A	2.0	3.0	3.0
B	1.0	1.2	1.0
vert	2.0	4.0	4.0
cryst faces		001, 00$\bar{1}$, 010 0$\bar{1}$0, 100, $\bar{1}$00	110, $\bar{1}\bar{1}$0, 011, 0$\bar{1}\bar{1}$ 001, $\bar{2}$1$\bar{4}$, 101
cryst size, mm	0.2 × 0.2 × 0.34	0.05 × 0.20 × 0.35	0.23 × 0.15 × 0.28
cryst orientation direction; deg from ϕ axis		a^*; 6.6	[102]; 11.3
reflcns measd	$\pm h,\pm k,+l$	$h,k,\pm l$	$+h,\pm k,\pm l$
max 2θ, deg	50.0	47.5	46.0
scan type	moving cryst–moving counter	moving cryst–stationary counter	moving cryst–stationary counter
ω-scan width ($A + 0.347 \tan\theta$), deg	0.70	1.00	0.60
bkgd	$^1/_4$ addnl scan at each end of scan	$^1/_4$ addnl scan at each end of scan	$^1/_4$ addnl scan at each end of scan
ω-scan rate (variable)			
max, deg/min	10.0	10.0	10.0
min, deg/min	2.0	2.0	1.5
no. of reflcns measd	6515	6099	6520
no. of data used ($F^2 \geq 3.0\sigma(F^2)$)	4505	3947	4976
(C) Treatment of Data			
abs cor			
coeff, cm^{-1}	182	203	134
grid	empirical cor applied	14 × 8 × 8	14 × 8 × 8
transmission coeff			
max	0.99	0.37	0.218
min	0.54	0.03	0.045
P factor	0.04	0.04	0.04
final residuals			
R_F	0.044	0.040	0.049
R_{wF}	0.052	0.048	0.065
esd of unit wt observn	1.47	1.52	2.08
largest shift/error value of final cycle	0.00	0.01	0.18
largest peak in final diff Fourier, e/Å^3	1.45	2.35	3.74
no. of params varied	240	265	354

an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite monochromatized Mo Kα radiation by the Molecular Structure Corp., College Station, TX. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table II. All data processing was performed on a Digital Equipment Corp. VAX 11/782 computer by using the Enraf-Nonius SDP program library at the University of South Carolina. Absorption corrections of a Gaussian integration type were done for all structures. Neutral-atom scattering factors were calculated by standard procedures.[16a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[16b] Full-matrix least-squares refinements minimized the function

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

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

For each analysis all atoms heavier than oxygen were refined anisotropically, and all other non-hydrogen atoms were refined isotropically. For **2** and **4**, the positions of the hydrogen atoms were calculated by assuming idealized phenyl geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. For **6**, the hydrogen atoms were ignored.

Compounds **2** and **6** crystallized in the triclinic crystal system. For each the space group $P\bar{1}$ was assumed and subsequently confirmed by the successful solution and refinement of the structure. The structures of **2** and **6** were solved by the heavy-atom method. In the final stages of the analysis of **6** a $^1/_4$ mol of methylene chloride solvent was located and found to be 2-fold disordered about a center of symmetry site.

The unit cell and systematic absences observed in the data for compound **4** indicated that the crystal belonged to the monoclinic crystal system and the space group $P2_1/c$. The coordinates of the heavy atoms in the structure of **4** were obtained from an E map obtained from the phasing by direct methods (MULTAN) of 495 reflections with $E \gtrsim 1.77$. All remaining non-hydrogen atoms were subsequently obtained from

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

Table III. Positional and Thermal Parameters with Esd's for $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**2**)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Pt	0.22651 (4)	0.37883 (6)	0.22760 (4)	2.06 (1)
Os(1)	0.07257 (5)	0.16053 (7)	0.20018 (5)	2.36 (1)
Os(2)	0.11599 (5)	0.32881 (7)	0.36004 (5)	2.52 (1)
Os(3)	0.33560 (5)	0.25554 (7)	0.40525 (5)	2.39 (1)
Os(4)	0.19185 (5)	0.04285 (7)	0.36943 (5)	2.41 (1)
S	0.2677 (3)	0.1437 (4)	0.2487 (3)	2.40 (8)
P	0.3387 (3)	0.4150 (4)	0.1262 (3)	2.25 (9)
C(1)	0.169 (1)	0.555 (2)	0.218 (1)	3.7 (4)*
O(1)	0.131 (1)	0.661 (2)	0.208 (1)	5.8 (3)*
C(2)	0.074 (1)	0.014 (2)	0.118 (1)	3.7 (4)*
C(2)	0.078 (1)	−0.084 (1)	0.073 (1)	5.1 (3)*
C(3)	0.013 (1)	0.286 (2)	0.102 (1)	2.8 (3)*
O(3)	−0.031 (1)	0.364 (1)	0.048 (1)	5.2 (3)*
C(4)	−0.060 (1)	0.126 (2)	0.221 (1)	3.7 (4)*
O(4)	−0.142 (1)	0.102 (1)	0.233 (1)	5.2 (3)*
C(5)	0.174 (1)	0.470 (2)	0.439 (2)	4.8 (5)*
O(5)	0.204 (1)	0.570 (2)	0.486 (1)	8.8 (5)*
C(6)	−0.004 (1)	0.427 (2)	0.296 (1)	4.1 (4)*
O(6)	−0.081 (1)	0.490 (2)	0.255 (1)	6.0 (4)*
C(7)	0.044 (2)	0.251 (3)	0.440 (2)	7.1 (6)*
O(7)	−0.016 (1)	0.204 (2)	0.482 (2)	9.5 (5)*
C(8)	0.400 (1)	0.428 (2)	0.394 (1)	3.6 (4)*
O(8)	0.4465 (9)	0.527 (1)	0.397 (1)	4.7 (3)*
C(9)	0.354 (1)	0.266 (2)	0.534 (2)	4.8 (5)*
O(9)	0.364 (1)	0.271 (2)	0.616 (1)	5.7 (3)*
C(10)	0.460 (1)	0.154 (2)	0.421 (1)	3.0 (3)*
O(10)	0.535 (1)	0.083 (1)	0.425 (1)	5.6 (3)*
C(11)	0.287 (1)	−0.106 (2)	0.378 (1)	3.8 (4)*
O(11)	0.348 (1)	−0.195 (2)	0.381 (1)	6.8 (4)*
C(12)	0.203 (1)	0.033 (2)	0.498 (1)	3.1 (3)*
O(12)	0.209 (1)	0.026 (2)	0.578 (1)	5.9 (3)*
C(13)	0.079 (1)	−0.082 (2)	0.334 (1)	4.5 (4)*
O(13)	0.004 (1)	−0.153 (1)	0.320 (1)	5.4 (3)*
C(14)	0.475 (1)	0.368 (2)	0.183 (1)	2.5 (3)*
C(15)	0.505 (1)	0.230 (2)	0.205 (1)	3.7 (4)*
C(16)	0.604 (1)	0.192 (2)	0.251 (1)	4.4 (4)*
C(17)	0.678 (2)	0.292 (2)	0.284 (2)	5.6 (5)*
C(18)	0.656 (2)	0.424 (2)	0.265 (2)	5.0 (5)*
C(19)	0.552 (1)	0.466 (2)	0.210 (1)	4.3 (4)*
C(20)	0.309 (1)	0.320 (2)	0.016 (1)	2.3 (3)*
C(21)	0.385 (1)	0.275 (2)	−0.026 (1)	3.7 (4)*
C(22)	0.358 (1)	0.209 (2)	−0.113 (2)	4.7 (4)*
C(23)	0.252 (2)	0.193 (2)	−0.158 (2)	4.9 (5)*
C(24)	0.177 (1)	0.239 (2)	−0.116 (1)	4.3 (4)*
C(25)	0.201 (1)	0.304 (2)	−0.030 (1)	4.0 (4)*
C(26)	0.339 (1)	0.597 (2)	0.093 (1)	2.7 (3)*
C(27)	0.316 (1)	0.639 (2)	−0.004 (1)	2.9 (3)*
C(28)	0.316 (1)	0.781 (2)	−0.022 (1)	3.8 (4)*
C(29)	0.336 (1)	0.876 (2)	0.045 (1)	4.1 (4)*
C(30)	0.360 (2)	0.832 (2)	0.142 (2)	5.0 (5)*
C(31)	0.359 (1)	0.694 (2)	0.163 (1)	3.4 (4)*

[a] Values marked with an asterisk denote isotropically refined atoms. Hydrogen atoms were not refined. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

difference Fourier syntheses. The results of the final refinements for each structure are listed in Table II. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure. See the supplementary material paragraph at the end of this paper regarding the tables of structure factor amplitudes, anisotropic thermal parameters, and hydrogen atom coordinates for **2** and **4**.

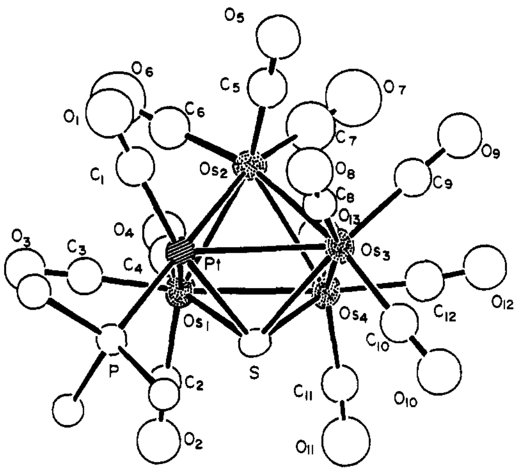

Figure 1. ORTEP diagram of $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**2**) showing 50% probability thermal motion ellipsoids. For clarity only carbon atoms directly attached to the phenyl rings have been included.

Table IV. Interatomic Distances (Å) with Esd's for $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**2**)

Pt–Os(1)	2.900 (1)	Os(4)–C(11)	1.87 (2)
Pt–Os(2)	2.749 (1)	Os(4)–C(12)	1.86 (2)
Pt–Os(3)	2.875 (1)	Os(4)–C(13)	1.90 (2)
Pt–S	2.326 (3)	Os(2)–Os(3)	2.862 (1)
Pt–P	2.373 (4)	P–C(14)	1.820 (13)
Pt–C(1)	1.84 (2)	C(1)–O(1)	1.13 (2)
Pt···C(8)	2.923 (15)	C(2)–O(2)	1.16 (2)
Os(1)–Os(2)	2.802 (1)	C(3)–O(3)	1.12 (2)
Os(1)–Os(4)	2.799 (1)	C(4)–O(4)	1.17 (2)
Os(1)–S	2.477 (3)	C(5)–O(5)	1.20 (2)
Os(1)–C(2)	1.87 (2)	C(6)–O(6)	1.19 (2)
Os(1)–C(3)	1.884 (14)	C(7)–O(7)	1.20 (3)
Os(1)–C(4)	1.87 (2)	C(8)–O(8)	1.14 (2)
Os(3)–Os(4)	2.770 (1)	C(9)–O(9)	1.18 (2)
Os(2)–Os(4)	2.911 (1)	C(10)–O(10)	1.18 (2)
Os(2)–C(5)	1.84 (2)	C(11)–O(11)	1.16 (2)
Os(2)–C(6)	1.86 (2)	C(12)–O(12)	1.16 (2)
Os(2)–C(7)	1.85 (3)	C(13)–O(13)	1.18 (2)
Os(3)–S	2.499 (4)	P–C(20)	1.814 (14)
Os(3)–C(8)	1.90 (2)	P–C(26)	1.818 (14)
Os(3)–C(9)	1.84 (2)	C–C$_{av}$ (ring 1)	1.38 (3)
Os(3)–C(10)	1.850 (14)	C–C$_{av}$ (ring 2)	1.38 (3)
Os(4)–S	2.445 (4)	C–C$_{av}$ (ring 3)	1.39 (3)

Results

When $Os_5(CO)_{15}(\mu_4\text{-}S)$ (**1**) was allowed to react with $Pt(PPh_3)_2C_2H_4$ at 25 °C for 2 h, five new cluster compounds were formed. Four of these were fully characterized, while one that would not yield crystals suitable for diffraction analysis has been only partially characterized. In order of elution on silica gel TLC plates the products were identified as $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**2**; 6% yield), $Os_5(CO)_{14}(PPh_3)(\mu_4\text{-}S)$ (**3**; 9% yield), $PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$ (**4**; 5% yield), a brown compound (**5**), and $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**6**; 7% yield). Compounds **2**, **4**, and **6** were characterized by single-crystal X-ray diffraction analyses. IR and $^{31}P\{^1H\}$ NMR spectra of the compounds are listed in Table I.

Compound **5** gave no ^{31}P signal but when treated with PPh_3 gave a good yield of **3**. All attempts to grow crystals of **5** suitable for single-crystal diffraction analysis were unsuccessful; therefore, a structural characterization of **5** was not possible. Compound **3** is simply a PPh_3 derivative of **1**. Its characterization was supported by an independent synthesis of it through the reaction of **1** with PPh_3.

Description of the Structure of 2. An ORTEP diagram of the molecular structure of **2** is shown in Figure 1. Final fractional atomic coordinates are given in Table III, and selected interatomic distances and angles are given in Tables IV and V, respectively. The cluster in **2** consists of a square-pyramidal arrangement of five metal atoms with the square base bridged by a sulfido ligand. The platinum atom lies in the square base. The platinum–osmium bond distance to the osmium atom in the apex of the square pyramid is significantly shorter than those to the osmium atoms in the base, Pt–Os(2) = 2.749 (1) Å vs. Pt–Os(1) = 2.900 (1) Å and Pt–Os(3) = 2.875 (1) Å, and the latter two bonds are nearly equal in length. Curiously, the osmium–osmium bonds in the base of the square pyramid are shorter than the osmium–platinum bonds in the square base. Os(1)–Os(4) = 2.799 (1) Å and Os(3)–Os(4) = 2.770 (1) Å. The osmium–osmium bonds between the square base and the apex, Os(1)–Os(2) = 2.802 (1) Å, Os-

Table V. Selected Interatomic Angles (deg) with Esd's for $PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$ (**2**)

Os(1)–Pt–Os(3)	89.84 (2)	Os(2)–Pt–P	173.75 (8)
Os(1)–Pt–Os(2)	59.41 (2)	Os(1)–S–Pt	74.19 (9)
Os(3)–Pt–Os(2)	61.14 (2)	Os(1)–S–Os(4)	69.30 (9)
Pt–Os(1)–Os(2)	57.62 (2)	Os(1)–S–Os(3)	110.04 (13)
Pt–Os(1)–Os(4)	87.43 (2)	Os(4)–S–Os(3)	68.14 (10)
Os(2)–Os(1)–Os(4)	62.62 (2)	Os(4)–S–Pt	111.23 (14)
Os(1)–Os(2)–Pt	62.96 (2)	Os(3)–S–Pt	73.03 (10)
Os(1)–Os(2)–Os(4)	58.63 (2)	Pt–C(1)–O(1)	176.6 (16)
Os(1)–Os(2)–Os(3)	92.06 (2)	Os(1)–C(2)–O(2)	174.6 (14)
Os(4)–Os(2)–Os(3)	57.35 (2)	Os(1)–C(3)–O(3)	172.5 (14)
Os(4)–Os(2)–Pt	88.14 (2)	Os(1)–C(4)–O(4)	178.6 (15)
Os(3)–Os(2)–Pt	61.59 (2)	Os(2)–C(5)–O(5)	173.9 (16)
Os(4)–Os(3)–Pt	88.46 (2)	Os(2)–C(6)–O(6)	180.0 (26)
Os(2)–Os(3)–Os(4)	62.20 (2)	Os(2)–C(7)–O(7)	170.6 (20)
Os(2)–Os(3)–Pt	57.27 (2)	Os(3)–C(8)–O(8)	171.9 (13)
Os(1)–Os(4)–Os(3)	94.12 (2)	Os(3)–C(9)–O(9)	178.6 (17)
Os(1)–Os(4)–Os(2)	58.75 (2)	Os(3)–C(10)–O(10)	174.9 (14)
Os(3)–Os(4)–Os(2)	60.45 (2)	Os(4)–C(11)–O(11)	176.8 (16)
Os(1)–Pt–P	123.21 (9)	Os(4)–C(12)–O(12)	179.4 (15)
Os(3)–Pt–P	112.66 (8)	Os(4)–C(13)–O(13)	172.8 (16)

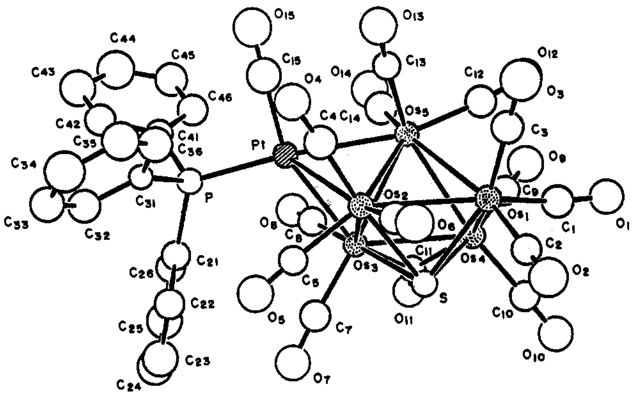

Figure 2. ORTEP diagram of $PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$ (4) showing 50% probability thermal motion ellipsoids.

(2)–Os(4) = 2.911 (1) $[NiL_2]_2(S_2O_6)_3$ and Os(2)–Os(3) = 2.862 (1) Å, are longer than those in the square base, but for the Os(1)–Os(2) distance this difference is not significant. The structure of **1** is similar to that of **2** and the osmium–osmium distances in **1** and **2** are of similar lengths, but in **1** no consistent pattern of variation was observed, even though the variation was significant.[14] The platinum–sulfur distance in **2**, Pt–S = 2.326 (3) Å, is significantly shorter than the osmium–sulfur distances, Os(1)–S = 2.477 (3) Å, Os(3)–S = 2.499 (4) Å, and Os(4)–S = 2.445 (4) Å. The latter are similar to those observed in **1**. Each osmium atom contains three terminal carbonyl ligands. The platinum atom contains one terminal carbonyl ligand and the triphenylphosphine ligand, which is positioned trans to the apex metal atom Os(2).

Description of the Structure of 4. An ORTEP diagram of the molecular structure of **4** is shown in Figure 2. Final fractional atomic coordinates are listed in Table VI. Selected interatomic distances and angles are listed in Tables VII and VIII, respectively. The cluster in **4** consists of a square-pyramidal arrangement of five osmium atoms that is capped on one triangular face by a platinum atom. Seven of the eight osmium–osmium bond distances lie in the range 2.804 (1)–2.919 (1) Å. This range is very similar to that observed for **1**.[14] However, the Os(3)–Os(4) bond in **4** is anomalously short, 2.703 (1) Å. This result could be due to a contraction effect caused by the carbonyl ligand that bridges this bond but may be due to a ligand "deficiency" which occurs at the metal atoms Os(3) and Os(4). For example, atoms Os(3) and Os(4) have only two terminal carbonyl ligands while all the other osmium atoms have three. By including the bridging carbonyl group the net of number of carbonyl groups at Os(3) and Os(4) is still only two and one-half. In compound **1** each osmium atom contained three carbonyl groups. Although the capped square-pyramidal on for the cluster is the one predicted for this molecule by the skeletal electron pair theory,[17] this theory does not consider how distortions in the cluster bonding might occur due to the existence of unsymmetrical ligand distributions such as those that exist in **4**. The bonding of the platinum atom to the osmium atoms is also very unsymmetric and could be explained by this same reasoning. For example, the Pt–Os(3) bond is only 2.646 (1) Å in length while the Pt–Os(2) bond is very long (2.986 (1) Å). The Pt–Os(5) distance of 2.791 (1) Å is approximately midway between them. Interestingly, the compound $Os_6(CO)_{17}(\mu_4\text{-}S)$, which is the homonuclear, isoelectronic homologue of **4**, shows similar distortions in the metal–metal

Table VI. Positional Parameters with Esd's for $PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$ (**4**)[a]

atom	*x*	*y*	*z*	*B*, Å²
Os(1)	0.30565 (8)	0.03547 (4)	0.59267 (3)	2.50 (2)
Os(2)	0.30278 (8)	0.08489 (4)	0.69736 (3)	2.30 (2)
Os(3)	0.50820 (8)	−0.04863 (4)	0.72528 (3)	2.17 (1)
Os(4)	0.50180 (8)	−0.09159 (4)	0.62475 (3)	2.48 (2)
Os(5)	0.21976 (8)	−0.07469 (4)	0.66795 (3)	2.11 (1)
Pt	0.26879 (8)	−0.04481 (4)	0.77449 (3)	2.33 (1)
S	0.5291 (5)	0.0506 (3)	0.6573 (2)	2.5 (1)
P	0.3420 (6)	−0.0320 (3)	0.8627 (2)	2.5 (1)
C(1)	0.356 (2)	−0.034 (1)	0.5397 (9)	3.8 (4)*
O(1)	0.360 (2)	−0.0656 (8)	0.4994 (6)	4.4 (3)*
C(2)	0.367 (2)	0.126 (1)	0.5568 (8)	3.2 (4)*
O(2)	0.393 (2)	0.1829 (9)	0.5361 (7)	5.3 (4)*
C(3)	0.104 (2)	0.051 (1)	0.5622 (9)	3.7 (4)*
O(3)	−0.024 (2)	0.0588 (9)	0.5487 (7)	6.0 (4)*
C(4)	0.125 (2)	0.105 (1)	0.7208 (9)	3.9 (4)*
O(4)	0.008 (2)	0.1267 (8)	0.7366 (6)	4.6 (3)*
C(5)	0.411 (2)	0.142 (1)	0.7554 (8)	3.0 (4)*
O(5)	0.478 (2)	0.1755 (8)	0.7879 (6)	4.7 (3)*
C(6)	0.261 (2)	0.177 (1)	0.6579 (9)	3.5 (4)*
O(6)	0.228 (2)	0.2351 (9)	0.6352 (7)	5.1 (4)*
C(7)	0.670 (2)	0.003 (1)	0.7641 (9)	3.6 (4)*
C(7)	0.774 (2)	0.038 (8)	0.7859 (6)	4.7 (3)*
C(8)	0.516 (2)	−0.136 (1)	0.7730 (8)	3.2 (4)*
O(8)	0.530 (2)	−0.1938 (8)	0.7981 (6)	4.3 (3)*
C(9)	0.448 (2)	−0.192 (1)	0.6003 (9)	3.4 (1)*
O(9)	0.419 (2)	−0.2589 (9)	0.5851 (7)	5.2 (4)*
C(10)	0.660 (2)	−0.087 (1)	0.5850 (9)	3.4 (4)*
O(10)	0.761 (2)	−0.0868 (8)	0.5620 (20)	4.6 (3)*
C(11)	0.636 (2)	−0.134 (11)	0.6881 (8)	2.7 (4)*
O(11)	0.735 (2)	−0.1808 (8)	0.7001 (6)	4.1 (3)*
C(12)	0.158 (2)	−0.124 (1)	0.6039 (9)	3.7 (4)*
O(12)	0.109 (2)	−0.1575 (8)	0.5656 (6)	4.7 (3)*
C(13)	0.019 (2)	−0.044 (1)	0.6727 (8)	2.8 (4)*
O(13)	−0.099 (2)	−0.0196 (9)	0.6719 (7)	4.9 (3)*
C(14)	0.222 (2)	−0.176 (1)	0.6997 (9)	4.0 (5)*
O(14)	0.217 (2)	−0.2425 (9)	0.7157 (7)	5.5 (4)*
C(15)	0.080 (3)	−0.078 (1)	0.787 (1)	4.6 (:5*
O(15)	−0.028 (2)	−0.1062 (9)	0.7945 (7)	5.7 (4)*
C(21)	0.544 (2)	0.026 (1)	0.8856 (8)	3.2 (4)*
C(22)	0.618 (2)	0.051 (1)	0.8857 (9)	3.4 (4)*
C(23)	0.767 (3)	0.054 (1)	0.902 (1)	4.9 (5)*
C(24)	0.848 (3)	−0.013 (1)	0.920 (1)	5.1 (5)*
C(25)	0.777 (3)	−0.086 (1)	0.917 (1)	5.1 (5)*
C(26)	0.631 (2)	−0.093 (1)	0.9037 (9)	3.4 (4)*
C(31)	0.269 (2)	0.0593 (9)	0.8897 (7)	2.1 (3)*
C(32)	0.332 (2)	0.089 (1)	0.9391 (9)	3.9 (4)*
C(33)	0.280 (2)	0.158 (1)	0.958 (1)	4.2 (5)*
C(34)	0.163 (3)	0.197 (1)	0.930((1)	5.8 (6)*
C(35)	0.096 (3)	0.171 (1)	0.882 (1)	5.0 (5)*
C(36)	0.151 (2)	0.101 (1)	0.8649 (9)	4.3 (5)*
C(41)	0.276 (2)	−0.118 (1)	0.8969 (8)	2.9 (4)*
C(42)	0.242 (2)	−0.113 (1)	0.9478 (9)	3.7 (4)*
C(43)	0.202 (3)	−0.178 (1)	0.975 (1)	5.1 (5)*
C(44)	0.197 (3)	0.253 (1)	0.950 (1)	5.8 (6)*
C(45)	0.223 (2)	−0.260 (1)	0.901 (1)	4.3 (5)*
C(46)	0.259 (2	−0.192 (1)	0.8749 (9)	3.7 (4)*

[a] See footnote *a*, Table III.

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(17) (a) Wade, K. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980. (b) John, B. F. G.; Benfield, R. E. In *Topics in Stereochemistry*; Geoffroy, G. L., Ed.; Wiley: New York, 1981; Vol. 12.

Table VII. Selected Interatomic Distances (Å) with Esd's for $PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$ (**4**)

Os(1)–Os(2)	2.847 (1)	Os(5)–C(12)	1.87 (2)
Os(1)–Os(4)	2.804 (1)	Os(5)–C(13)	1.897 (15)
Os(1)–Os(5)	2.859 (1)	Os(5)–C(14)	1.87 (2)
Os(1)–S	2.454 (4)	Pt–P	2.311 (4)
Os(1)–C(1)	1.90 (2)	Pt···C(8)	2.69 (2)
Os(1)–C(2)	1.89 (2)	Pt–C(15)	1.86 (2)
Os(1)–C(3)	1.987 (2)	P–C(21)	1.84 (2)
Os(2)–Os(3)	2.914 (1)	P–C(31)	1.828 (14)
Os(2)–Os(5)	2.830 (1)	P–C(41)	1.82 (2)
Os(2)–Pt	2.986 (1)	C(1)–O(1)	1.17 (2)
Os(2)–S	2.471 (4)	C(2)–O(2)	1.13 (2)
Os(2)–C(4)	1.82 (2)	C(3)–O(3)	1.19 (2)
Os(2)–C(5)	1.93 (2)	C(4)–O(4)	1.23 (2)
Os(2)–C(6)	1.86 (2)	C(5)–O(5)	1.12 (2)
Os(3)–Os(4)	2.703 (1)	C(6)–O(6)	1.15 (2)
Os(3)–Os(5)	2.847 (1)	C(7)–O(7)	1.18 (2)
Os(3)–Pt	2.646 (1)	C(8)–O(8)	1.16 (2)
Os(3)–S	2.442 (4)	C(9)–O(9)	1.20 (2)
Os(3)–C(7)	1.86 (2)	C(10)–O(10)	1.15 (2)
Os(3)–C(8)	1.90 (2)	C(11)–O(11)	1.19 (2)
Os(3)–C(11)	2.133 (15)	C(12)–O(12)	1.17 (2)
Os(4)–Os(5)	2.919 (1)	C(13)–O(13)	1.13 (2)
Os(4)–S	2.509 (4)	C(14)–O(14)	1.18 (2)
Os(4)···C(1)	2.60 (2)	C(14)–O(15)	1.11 (2)
Os(4)–C(9)	1.83 (2)	C–C_{av} (ring 1)	1.37 (3)
Os(4)–C(10)	1.87 (2)	C–C_{av} (ring 2)	1.38 (3)
Os(4)–C(11)	2.03 (2)	C–C_{av} (ring 3)	1.37 (3)
Os(5)–Pt	2.791 (1)		

bonding.[18] As in **1** and **2**, compound **4** contains a quadruply bridging sulfido ligand on the base of the square pyramid. The osmium–sulfur distances range from 2.442 (2) Co^{2+} 2.509 (4) Å and are similar to those observed in **1**.[14] There are 14 linear terminal carbonyl ligands, distributed as shown in Figure 2, and one bridging carbonyl ligand C(11)–O(11) across the Os(3)–Os(4) bond. The platinum atom contains a PPh_3 ligand and one of the terminal carbonyl ligands.

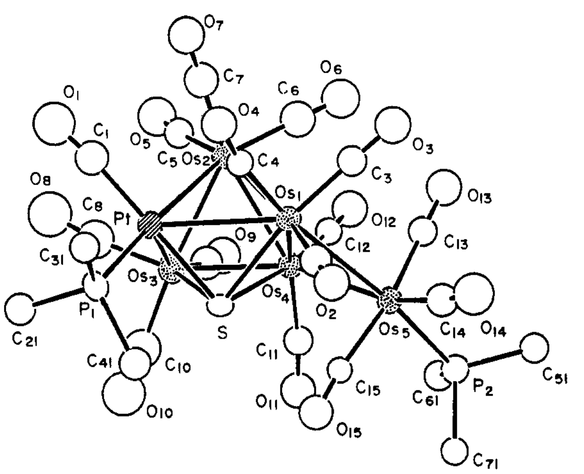

Figure 3. ORTEP diagram of $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (6) showing 50% probability thermal motion ellipsoids. For clarity only carbon atoms directly attached to the phenyl rings have been included.

Description of the Structure of 6. An ORTEP diagram of the molecular structure of **6** is shown in Figure 3. Final fractional atomic coordinates are given in Table IX, and selected interatomic distances and angles are given in Tables X and XI, respectively. The cluster in **6** consists of a square-pyramidal arrangement of one platinum and four osmium atoms. This portion of the molecule is very similar to that of **2**; however, compound **6** has, in addition, a fifth osmium atom that bridges the Os(1)–Os(4) pair of osmium

Table VIII. Selected Interatomic Angles (deg) with Esd's for $PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$ (**4**)

Os(2)–Os(1)–Os(4)	91.00 (3)	Pt–Os(2)–C(4)	74.6 (6)	Os(5)–Os(3)–Pt	60.96 (2)	Os(1)–Os(5)–C(12)	75.3 (5)
Os(2)–Os(1)–Os(5)	59.48 (2)	Pt–Os(2)–C(5)	85.0 (5)	Os(5)–Os(3)–S	82.85 (9)	Os(1)–Os(5)–C(13)	102.5 (5)
Os(2)–Os(1)–S	55.0 (1)	Pt–Os(2)–C(6)	159.4 (5)	Os(5)–Os(3)–C(7)	160.8 (5)	Os(1)–Os(5)–C(14)	152.7 (6)
Os(2)–Os(1)–C(1)	154.5 (6)	S–Os(2)–C(4)	173.9 (6)	Os(5)–Os(3)–C(8)	100.2 (5)	Os(2)–Os(5)–Os(3)	61.78 (2)
Os(2)–Os(1)–C(2)	106.5 (5)	S–Os(2)–C(5)	94.97 (5)	Os(5)–Os(3)–C(11)	99.7 (4)	Os(2)–Os(5)–Os(4)	89.01 (2)
Os(2)–Os(1)–C(3)	100.4 (6)	S–Os(2)–C(6)	94.3 (5)	Pt–Os(3)–S	118.66 (9)	Os(2)–Os(5)–Pt	64.17 (2)
Os(4)–Os(1)–Os(5)	62.04 (2)	C(4)–Os(2)–C(5)	91.4 (7)	Pt–Os(3)–C(7)	110.7 (5)	Os(2)–Os(5)–C(12)	133.4 (5)
Os(4)–Os(1)–S	56.53 (9)	C(4)–C(5)–C(6)	84.8 (8)	Pt–Os(3)–C(8)	70.3 (5)	Os(2)–Os(5)–C(13)	87.0 (4)
Os(4)–Os(1)–C(1)	63.7 (6)	C(5)–Os(2)–C(6)	94.2 (7)	Pt–Os(3)–C(11)	139.1 (4)	Os(2)–Os(5)–C(14)	137.3 (6)
Os(4)–Os(1)–C(2)	122.2 (5)	Os(2)–Os(3)–Os(4)	91.62 (3)	S–Os(3)–C(7)	87.4 (5)	Os(3)–Os(5)–Os(4)	55.90 (2)
Os(4)–Os(1)–C(3)	139.1 (5)	Os(2)–Os(3)–Os(5)	58.84 (2)	S–Os(3)–C(8)	170.6 (5)	Os(3)–Os(5)–Pt	55.96 (2)
Os(5)–Os(1)–S	82.38 (9)	Os(2)–Os(3)–Pt	64.76 (2)	S–Os(3)–C(11)	91.2 (4)	Os(3)–Os(5)–C(12)	132.3 (5)
Os(5)–Os(1)–C(1)	102.6 (5)	Os(2)–Os(3)–S	54.08 (9)	C(7)–Os(3)–C(8)	92.1 (7)	Os(3)–Os(5)–C(13)	137.2 (5)
Os(5)–Os(1)–C(2)	166.0 (5)	Os(2)–Os(3)–C(7)	102.1 (5)	C(7)–Os(3)–C(11)	96.9 (7)	Os(3)–Os(5)–C(14)	87.2 (5)
Os(5)–Os(1)–C(3)	90.3 (5)	Os(2)–Os(3)–C(8)	135.0 (5)	C(8)–Os(3)–C(11)	79.5 (7)	Os(4)–Os(5)–Pt	111.61 (3)
S–Os(1)–C(1)	107.9 (5)	Os(2)–Os(3)–C(11)	138.8 (4)	Os(1)–Os(4)–Os(4)	91.20 (3)	Os(4)–Os(5)–C(12)	77.6 (5)
S–Os(1)–C(2)	89.5 (5)	Os(4)–Os(3)–Os(5)	63.40 (2)	Os(1)–Os(4)–Os(5)	59.90 (2)	Os(4)–Os(5)–C(13)	159.0 (5)
S–Os(1)–C(3)	154.5 (6)	Os(4)–Os(3)–Pt	124.04 (3)	Os(1)–Os(4)–S	54.68 (9)	Os(4)–Os(5)–C(14)	97.2 (5)
C(1)–Os(1)–C(2)	90.7 (7)	Os(4)–Os(3)–S	58.11 (9)	Os(1)–Os(4)–C(9)	117.3 (5)	Pt–Os(5)–C(12)	161.7 (5)
C(1)–Os(1)–C(3)	97.5 (8)	Os(4)–Os(3)–C(7)	124.0 (6)	Os(1)–Os(4)–C(10)	107.5 (5)	Pt–Os(5)–C(13)	85.1 (5)
C(2)–Os(1)–C(3)	92.1 (7)	Os(2)–Pt–Os(3)	61.98 (2)	Os(1)–Os(4)–Os(11)	141.5 (4)	Pt–Os(5)–C(14)	74.4 (6)
Os(1)–Os(2)–Os(3)	86.17 (2)	Os(2)–Pt–Os(5)	58.55 (2)	Os(3)–Os(4)–Os(5)	60.70 (2)	C(12)–Os(5)–C(13)	90.3 (7)
Os(1)–Os(2)–Os(5)	60.48 (2)	Os(2)–Pt–P	124.03 (9)	Os(3)–Os(4)–S	55.7 (1)	C(12)–Os(5)–C(14)	89.0 (8)
Os(1)–Os(2)–Pt	116.69 (2)	Os(2)–Pt–C(15)	121.1 (6)	Os(3)–Os(4)–C(9)	123.3 (6)	C(13)–Os(5)–C(14)	99.7 (7)
Os(1)–Os(2)–S	54.4 (1)	Os(3)–Pt–Os(5)	63.07 (2)	Os(3)–Os(4)–C(10)	127.2 (5)	Os(1)–C(1)–O(1)	163 (2)
Os(1)–Os(2)–C(4)	119.6 (6)	Os(3)–Pt–P	109.9 (1)	Os(3)–Os(4)–C(11)	51.2 (4)	Os(1)–C(2)–O(2)	175 (2)
Os(1)–Os(2)–C(5)	145.1 (5)	Os(3)–Pt–C(15)	154.3 (6)	Os(5)–Os(4)–S	80.26 (9)	Os(1)–C(3)–O(3)	178 (2)
Os(1)–Os(2)–C(6)	74.8 (6)	Os(5)–Pt–P	171.2 (1)	Os(5)–Os(4)–C(9)	91.2 (5)	Os(2)–C(4)–O(4)	174 (1)
Os(3)–Os(2)–Os(5)	59.38 (2)	Os(5)–Pt–C(15)	95.7 (7)	Os(5)–Os(4)–C(10)	166.7 (5)	Os(2)–C(5)–O(5)	178 (2)
Os(3)–Os(2)–Pt	53.26 (2)	P–Pt–C(15)	89.6 (7)	Os(5)–Os(4)–C(11)	100.0 (4)	Os(2)–C(6)–O(6)	176 (2)
Os(3)–Os(2)–S	53.16 (9)	Os(1)–S–Os(2)	70.6 (1)	S–Os(4)–C(9)	170.5 (5)	Os(3)–C(7)–O(7)	176 (2)
Os(3)–Os(2)–C(4)	127.9 (6)	Os(1)–S–Os(3)	107.0 (1)	S–Os(4)–C(10)	95.8 (5)	Os(3)–C(8)–O(8)	171 (2)
Os(3)–Os(2)–C(5)	86.4 (5)	Os(1)–S–Os(4)	68.8 (1)	S–Os(4)–C(11)	91.7 (4)	Os(3)–C(11)–O(11)	138 (1)
Os(3)–Os(2)–C(6)	147.3 (5)	Os(2)–S–Os(3)	72.8 (1)	C(9)–Os(4)–C(10)	91.6 (7)	Os(4)–C(9)–O(9)	178 (1)
Os(5)–Os(2)–Pt	57.28 (2)	Os(2)–S–Os(4)	108.0 (1)	C(9)–Os(4)–C(11)	93.8 (7)	Os(4)–C(11)–O(11)	141 (1)
Os(5)–Os(2)–S	82.68 (8)	Os(3)–S–Os(4)	66.16 (9)	Os(1)–Os(5)–Os(2)	60.04 (2)	Os(5)–C(12)–O(12)	174 (2)
Os(5)–Os(2)–C(4)	93.0 (5)	Os(3)–C(11)–Os(4)	80.9 (5)	Os(1)–Os(5)–Os(3)	87.22 (2)	Os(5)–C(13)–O(13)	173 (2)
Os(5)–Os(2)–C(5)	139.1 (5)	Os(4)–Os(3)–C(8)	115.2 (5)	Os(1)–Os(5)–Os(4)	58.06 (2)	Os(5)–C(15)–O(14)	174 (2)
Os(5)–Os(2)–C(6)	126.8 (5)	Os(4)–Os(3)–C(11)	47.9 (4)	Os(1)–Os(5)–Pt	122.99 (3)	Pt–C(15)–O(15)	173 (2)
Pt–Os(2)–S	106.28 (9)						

Table IX. Positional Parameters with Esd's for $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**6**)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Pt	0.10621 (8)	0.49827 (6)	0.21677 (6)	2.36 (2)
Os (1)	0.19651 (8)	0.33686 (6)	0.14909 (6)	2.13 (2)
Os(2)	−0.02003 (8)	0.37779 (7)	0.24685 (6)	2.46 (3)
Os(3)	0.09642 (9)	0.35312 (7)	0.38022 (6)	2.70 (3)
Os(4)	0.18179 (8)	0.21037 (6)	0.31702 (6)	2.12 (2)
Os(5)	0.35197 (8)	0.12074 (6)	0.22092 (6)	2.22 (2)
S	0.2609 (5)	0.3450 (4)	0.2673 (4)	2.3 (2)
P(1)	0.2287 (5)	0.5938 (4)	0.1748 (4)	2.7 (2)
P(2)	0.4695 (6)	−0.0480 (4)	0.2983 (4)	2.7 (2)
C(1)	−0.035 (2)	0.609 (2)	0.200 (2)	4.1 (6)*
O(1)	−0.119 (2)	0.673 (1)	0.199 (1)	6.4 (6)*
C(2)	0.333 (2)	0.340 (2)	0.077 (2)	3.2 (6)*
O(2)	0.409 (1)	0.348 (1)	0.030 (1)	4.1 (4)*
C(3)	0.143 (2)	0.289 (2)	0.095 (1)	3.1 (6)*
O(3)	0.114 (2)	0.259 (1)	0.058 (1)	4.6 (5)*
C(4)	0.117 (2)	0.472 (1)	0.074 (1)	2.3 (5)*
O(4)	0.074 (1)	0.545 (1)	0.018 (1)	4.1 (4)*
C(5)	−0.141 (2)	0.401 (2)	0.326 (2)	3.2 (6)*
O(5)	−0.218 (2)	0.408 (1)	0.372 (1)	5.8 (5)*
C(6)	−0.058 (2)	0.279 (2)	0.237 (2)	4.3 (7)*
O(6)	−0.082 (2)	0.220 (1)	0.231 (1)	5.5 (5)*
C(7)	−0.118 (2)	0.484 (2)	0.161 (2)	3.9 (6)*
O(7)	−0.181 (2)	0.549 (1)	0.109 (1)	4.7 (5)*
C(8)	−0.012 (3)	0.0462 (2)	0.404 (2)	5.1 (7)*
O(8)	−0.088 (2)	0.530 (2)	0.415 (1)	7.2 (6)*
C(9)	0.049 (2)	0.247 (2)	0.460 (2)	4.0 (6)*
O(9)	0.010 (2)	0.187 (1)	0.511 (1)	5.1 (5)*
C(10)	0.198 (3)	0.336 (2)	0.452 (2)	5.3 (8)*
O(10)	0.257 (2)	0.329 (2)	0.495 (1)	7.1 (6)*
C(11)	0.287 (2)	0.128 (2)	0.399 (1)	3.2 (6)*
O(11)	0.357 (2)	0.082 (1)	0.451 (1)	4.6 (5)*
C(12)	0.101 (2)	0.123 (2)	0.362 (1)	2.8 (5)*
O(12)	0.045 (2)	0.072 (1)	0.392 (1)	4.9 (5)*
C(13)	0.232 (2)	0.080 (2)	0.220 (1)	2.9 (5)*
O(13)	0.155 (2)	0.054 (1)	0.217 (1)	4.4 (4)*
C(14)	0.428 (2)	0.108 (2)	0.130 (2)	3.7 (6)*
O(14)	0.472 (2)	0.113 (1)	0.061 (1)	5.6 (5)*
C(15)	0.458 (2)	0.175 (1)	0.235 (1)	2.0 (5)*
O(15)	0.525 (1)	0.201 (1)	0.240 (1)	3.8 (4)*
C(21)	0.200 (2)	0.661 (2)	0.241 (2)	3.6 (6)*
C(54)	0.549 (3)	−0.295 (2)	0.202 (2)	6.6 (9)*
C(55)	0.585 (3)	−0.324 (2)	0.284 (2)	7 (1)*
C(56)	0.558 (3)	−0.246 (2)	0.312 (2)	6.0 (8)*
C(61)	0.416 (2)	−0.106 (2)	0.407 (2)	3.1 (6)*
C(62)	0.484 (2)	−0.142 (7)	0.472 (2)	4.3 (7)*
C(63)	0.433 (3)	−0.186 (2)	0.555 (2)	5.9 (8)*
C(64)	0.312 (3)	−0.181 (2)	0.565 (2)	5.3 (8)*
C(65)	0.249 (3)	−0.137 (2)	0.497 (2)	5.0 (7)*
C(66)	0.299 (2)	−0.102 (2)	0.416 (2)	3.8 (6)*
C(71)	0.621 (2)	−0.063 (2)	0.307 (1)	2.7 (5)*
C(72)	0.636 (2)	−0.019 (2)	0.353 (2)	3.5 (6)*
C(73)	0.753 (2)	−0.025 (2)	0.356 (2)	4.6 (7)*
C(74)	0.843 (3)	−0.071 (2)	0.314 (2)	5.8 (8)*
C(75)	0.832 (3)	−0.113 (2)	0.267 (2)	6.2 (9)*
C(76)	0.712 (3)	−0.111 (2)	0.264 (2)	5.4 (8)*
Cl	0.454 (2)	0.454 (1)	0.477 (1)	7.7 (5)*
C(90)	0.434 (9)	0.542 (7)	0.481 (6)	4 (2)*

[a] See footnote *a*, Table III.

atoms in the basal plane. There are some significant changes in the metal–metal bonding in **6** as compared to **2**. For example the Pt–Os(1) distance is increased to a very long 3.030 (1) Å, while two of the bond distances to Os(4) are decreased, Os(2)–Os(4) = 2.823 (1) Å, and Os(3)–Os(4) = 2.719 (1) Å. The bridging osmium atom, Os(5), is very unsymmetrically bonded to the cluster (i.e. Os(1)–Os(5) = 2.984 (1) Å and Os(4)–Os(5) = 2.761 (1) Å).

Table X. Selected Interatomic Distances (Å) with Esd's for $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**6**)

Pt–Os(1)	3.030 (1)	Os(4)–C(12)	1.84 (2)
Pt–Os(2)	2.762 (1)	Os(5)–P(2)	2.371 (5)
Pt–Os(3)	2.818 (1)	Os(5)–C(13)	1.88 (2)
Pt–S	2.333 (4)	Os(5)–C(14)	1.76 (2)
Pt–P(1)	2.362 (5)	Os(5)–C(15)	1.97 (2)
Pt–C(1)	1.88 (2)	P(1)–C(21)	1.82 (2)
Pt···C(4)	2.77 (2)	P(1)–C(31)	1.87 (2)
Os(1)–Os(2)	2.878 (1)	P(1)–C(41)	1.85 (2)
Os(1)–Os(4)	2.791 (1)	P(2)–C(51)	1.80 (2)
Os(1)–Os(5)	2.984 (1)	P(2)–C(61)	1.84 (2)
Os(1)–S	2.521 (5)	P(2)–C(71)	1.85 (2)
Os(1)–C(2)	1.89 (2)	C(1)–O(1)	1.11 (2)
Os(1)–C(3)	1.83 (2)	C(2)–O(2)	1.13 (2)
Os(1)–C(4)	1.90 (2)	C(3)–O(3)	1.16 (2)
Os(2)–Os(3)	2.896 (1)	C(4)–O(4)	1.15 (2)
Os(2)–Os(4)	2.823 (1)	C(5)–O(5)	1.12 (2)
Os(2)–C(5)	1.88 (2)	C(6)–O(6)	1.15 (2)
Os(2)–C(6)	1.91 (2)	C(7)–O(7)	1.17 (2)
Os(2)–C(7)	1.89 (2)	C(8)–O(8)	1.17 (3)
Os(3)–Os(4)	2.719 (1)	C(9)–O(9)	1.18 (2)
Os(3)–S	2.550 (5)	C(10)–O(10)	1.13 (3)
Os(3)–C(8)	1.87 (3)	C(11)–O(11)	1.19 (2)
Os(3)–C(9)	1.87 (2)	C(12)–O(12)	1.16 (2)
Os(3)–C(10)	1.89 (3)	C(13)–O(13)	1.21 (2)
Os(4)–Os(5)	2.761 (1)	C(14)–C(14)	1.21 (2)
Os(4)–S	2.443 (4)	C(15)–O(15)	1.12 (2)
Os(4)–C(11)	1.83 (2)		

A quadruply bridging sulfido ligand spans the square base of the cluster, and all osmium atoms contain three terminal carbonyl ligands except Os(4), which has only two. Carbonyl C(4)–O(4) is leaning toward the platinum atom, Pt···C(4) = 2.77 (2) Å and Os(1)–C(4)–O(4) = 1.67 (2)°, and could be described as a semibridge. The platinum atom and Os(5) contain PPh_3 ligands.

Although the structure of **6** can be rationalized by the skeletal electron pair bonding theory, the gross distortions in the metal–metal bonding are not explained.[14] However, considerations of the ligand structure as applied to **4** (vide supra) might provide an explanation for the short bonds to Os(4). Atom Os(4) contains only two carbonyl ligands. It is comparatively ligand deficient, and application of two-center two-electron bond theory reveals that it must also be electron deficient, unless one of the metal–metal bonds is regarded as a donor–acceptor type. These deficiencies might produce a contraction of the metal–metal bonds about atom Os(4).

Compound **2** is the heteronuclear homologue of **1**. It seems plausible that **6** could be an intermediate in the formation of **2**. This notion is supported by the observation that compound **6** reacts with carbon monoxide at 1 atm in refluxing dichloromethane in 4 h to yield compound **2** and $Os(CO)_4PPh_3$ in 48% yield. Significant amounts of **3** were also formed in this reaction. This result indicates the extrusion of the platinum moiety from the main body of the cluster is also facile. It was thought that the addition of the PPh_3 ligand to the osmium atom could be a key factor in the stabilization of **6**. This is supported by the observation that the yield of **6** was increased to 18% when the reaction of **1** and $Pt(PPh_3)_2C_2H_4$ was performed in the presence of 1 equiv of PPh_3. Conversely, the yields of **3** and **6** decreased and the yield of **4** was increased when the reaction of **1** and $Pt(PPh_3)_2C_2H_4$ was performed under an atmosphere of carbon monoxide.

An interesting example of cluster contraction was observed in the pyrolysis of **2** at 125 °C. The product $Os_4(CO)_{11}(PPh_3)(\mu_3\text{-}S)$ was formed in 84% by the expulsion of the platinum atom. Interestingly, the PPh_3 ligand was somehow captured by the tetraosmium product. The characterization of $Os_4(CO)_{11}(PPh_3)(\mu_3\text{-}S)$ was supported by its independent synthesis from $Os_4(CO)_{11}(NMe_3)(\mu_3\text{-}S)$ and PPh_3.

Discussion

A summary of the reactions reported here is given in Scheme I. Compound **2** is simply a heteronuclear homologue of **1** formed by a sequence of transformations that overall would be termed a metal–metal exchange reaction.[8] It is believed that the formation of the expanded cluster **6** may be very important to understanding the mechanism of these reactions. Compound **6** appears to be an isolable intermediate since it can be converted readily into the

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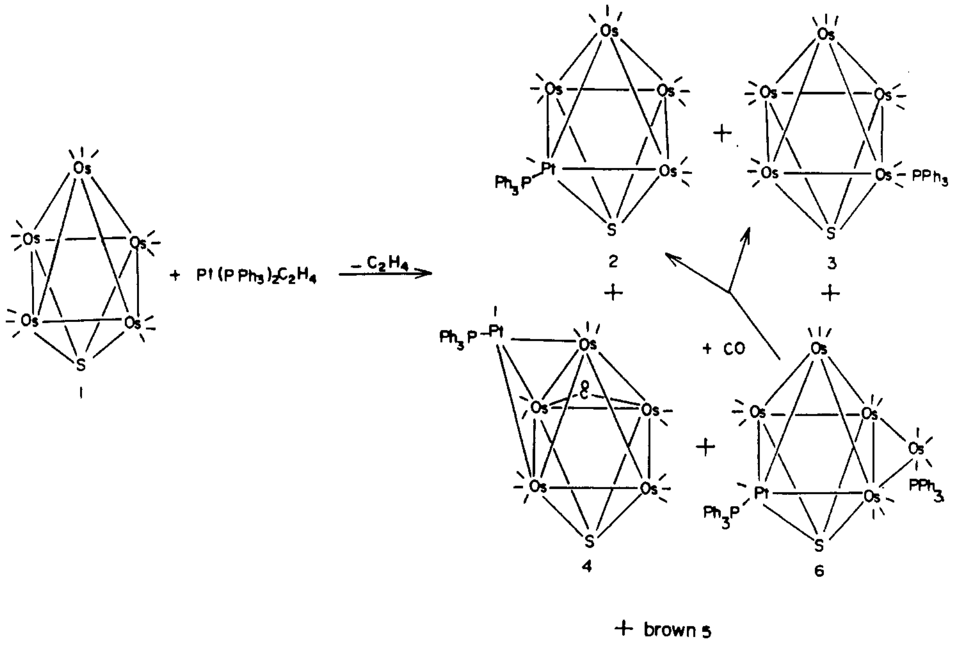
(18) Adams, R. D.; Horvăth, I. T.; Mathur, P. *Organometallics* **1984**, *3*, 623.

Table XI. Selected Interatomic Angles (deg) with Esd's for $PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$ (**6**)

Os(1)–Pt–Os(2)	59.36 (3)	Os(2)–Os(4)–Os(3)	62.96 (3)	Pt–Os(2)–C(7)	89.2 (7)	Os(3)–Os(4)–C(12)	111.6 (6)
Os(1)–Pt–Os(3)	90.78 (3)	Os(2)–Os(4)–Os(5)	121.37 (4)	Os(1)–Os(2)–C(5)	167.8 (6)	Os(5)–Os(4)–C(11)	84.9 (6)
Os(1)–Pt–S	54.2 (1)	Os(2)–Os(4)–S	80.8 (1)	Os(1)–Os(2)–C(6)	92.0 (7)	Os(5)–Os(4)–C(12)	99.4 (6)
Os(1)–Pt–P(1)	112.5 (1)	Os(3)–Os(4)–Os(5)	148.68 (4)	Os(1)–Os(2)–C(7)	98.9 (7)	S–Os(4)–C(11)	91.9 (6)
Os(2)–Pt–Os(3)	62.51 (3)	Os(3)–Os(4)–S	58.9 (1)	Os(3)–Os(2)–C(5)	75.5 (6)	S–Os(4)–C(12)	170.2 (6)
Os(2)–Pt–S	84.0 (1)	Os(5)–Os(4)–S	90.2 (1)	Os(3)–Os(2)–C(6)	127.8 (7)	C(11)–Os(4)–C(12)	90.7 (9)
Os(2)–Pt–P(1)	171.5 (1)	Os(1)–Os(5)–Os(4)	57.97 (3)	Os(3)–Os(2)–C(7)	138.2 (6)	C(12)–Os(4)–C(13)	67.3 (7)
Os(3)–Pt–S	58.5 (1)	Os(1)–Os(5)–P(2)	170.9 (1)	Os(4)–Os(2)–C(5)	113.2 (6)	Os(1)–Os(5)–C(13)	90.8 (6)
Os(3)–Pt–P(1)	122.5 (1)	Os(4)–Os(5)–P(2)	113.7 (1)	Os(4)–Os(2)–C(6)	82.4 (7)	Os(1)–Os(5)–C(14)	99.9 (7)
S–Pt–P(1)	93.1 (2)	Os(2)–Pt–P(1)	171.6 (1)	Os(4)–Os(2)–C(7)	156.4 (7)	Os(1)–Os(5)–C(15)	83.8 (5)
Pt–Os(1)–Os(2)	55.68 (3)	Os(2)–Pt–C(1)	89.1 (6)	C(5)–Os(2)–C(6)	95.9 (9)	Os(4)–Os(5)–P(2)	113.7 (1)
Pt–Os(1)–Os(4)	52.78 (3)	Os(1)–Pt–C(1)	130.2 (7)	C(5)–Os(2)–C(7)	90.1 (9)	Os(4)–Os(5)–C(13)	81.0 (6)
Pt–Os(1)–Os(5)	131.31 (4)	Os(3)–Pt–C(1)	108.6 (6)	C(6)–Os(2)–C(7)	92.1 (9)	Os(4)–Os(5)–C(14)	157.4 (7)
Pt–Os(1)–S	48.6 (1)	S–Pt–C(1)	167.7 (7)	Pt–Os(3)–C(8)	95.4 (7)	Os(4)–Os(5)–C(15)	88.8 (5)
Os(2)–Os(1)–Os(4)	59.72 (3)	P(1)–Pt–C(1)	95.2 (6)	Pt–Os(3)–C(9)	152.1 (7)	P(2)–Os(5)–C(13)	91.4 (6)
Os(2)–Os(1)–Os(5)	112.33 (3)	Pt–Os(1)–C(2)	113.3 (6)	Pt–Os(3)–C(10)	114.8 (8)	P(2)–Os(5)–C(14)	88.7 (7)
Os(2)–Os(1)–S	78.4 (1)	Pt–Os(1)–C(3)	139.6 (6)	Os(2)–Os(3)–Os(4)	98.7 (7)	P(2)–Os(5)–C(15)	92.3 (5)
Os(4)–Os(1)–Os(5)	57.02 (3)	Os(2)–Os(1)–C(2)	167.5 (5)	Os(2)–Os(3)–C(9)	94.3 (7)	C(13)–Os(5)–C(14)	96.1 (9)
Os(4)–Os(1)–S	54.5 (1)	Os(2)–Os(1)–C(3)	93.1 (6)	Os(2)–Os(3)–C(10)	168.8 (7)	C(13)–Os(5)–C(15)	169.8 (7)
Os(5)–Os(1)–S	83.8 (1)	Pt–Os(1)–C(4)	63.5 (6)	Os(4)–Os(3)–C(8)	157.9 (7)	C(14)–Os(5)–C(15)	93.3 (8)
Pt–Os(2)–Os(1)	64.96 (3)	Os(2)–Os(1)–C(4)	81.8 (5)	Os(4)–Os(3)–C(9)	75.6 (7)	Pt–C(1)–O(1)	172 (2)
Pt–Os(2)–Os(3)	59.68 (3)	Os(4)–Os(1)–C(2)	128.2 (6)	Os(4)–Os(3)–C(10)	113.2 (7)	Os(1)–C(2)–O(2)	175 (2)
Pt–Os(2)–Os(4)	87.22 (3)	Os(4)–Os(1)–C(3)	104.3 (6)	S–Os(3)–C(8)	131.4 (7)	Os(1)–C(3)–O(3)	177 (2)
Os(1)–Os(2)–Os(3)	92.37 (3)	Os(4)–Os(1)–C(4)	139.3 (6)	S–Os(3)–C(9)	127.4 (7)	Os(1)–C(4)–O(4)	167 (2)
Os(1)–Os(2)–Os(4)	58.61 (3)	Os(5)–Os(1)–C(2)	79.1 (6)	S–Os(3)–C(10)	91.1 (7)	Os(2)–C(5)–O(5)	172 (2)
Os(3)–Os(2)–Os(4)	56.75 (3)	Os(5)–Os(1)–C(3)	80.6 (6)	C(8)–Os(3)–C(9)	101 (1)	Os(2)–C(6)–O(6)	179 (2)
Pt–Os(3)–Os(2)	57.81 (3)	Os(5)–Os(1)–C(4)	163.4 (6)	C(8)–Os(3)–C(10)	89 (1)	Os(2)–C(7)–O(7)	178 (2)
Pt–Os(3)–Os(14)	88.18 (3)	S–Os(1)–C(2)	98.6 (6)	C(9)–Os(3)–C(10)	93 (1)	Os(3)–C(8)–O(8)	174 (2)
Pt–Os(3)–S	51.2 (1)	S–Os(1)–C(3)	158.6 (6)	Os(1)–Os(4)–C(9)	132.7 (5)	Os(3)–C(9)–O(9)	174 (2)
Os(2)–Os(3)–Os(4)	60.28 (3)	S–Os(1)–C(4)	108.4 (6)	Os(1)–Os(4)–C(11)	134.6 (6)	Os(3)–C(10)–O(10)	177 (2)
Os(2)–Os(3)–S	77.6 (1)	C(2)–Os(1)–C(3)	93.6 (9)	Os(1)–Os(4)–C(12)	125.7 (6)	Os(4)–C(11)–O(11)	175 (2)
Os(4)–Os(3)–S	55.1 (1)	C(2)–Os(1)–C(4)	87.8 (8)	Os(2)–Os(4)–C(9)	77.1 (4)	Os(4)–C(12)–O(12)	175 (2)
Os(1)–Os(4)–Os(2)	61.67 (3)	C(3)–Os(1)–C(4)	89.5 (8)	Os(2)–Os(4)–C(11)	152.5 (6)	Os(5)–C(13)–O(13)	178 (2)
Os(1)–Os(4)–Os(3)	98.24 (3)	Pt–Os(2)–C(5)	107.3 (6)	Os(2)–Os(4)–C(12)	92.6 (6)	Os(5)–C(14)–O(14)	171 (2)
Os(1)–Os(4)–Os(5)	65.02 (3)	Pt–Os(2)–C(6)	156.8 (8)	Os(3)–Os(4)–C(11)	90.5 (6)	Os(5)–C(15)–O(15)	174 (2)
Os(1)–Os(4)–S	57.1 (1)						

Scheme I



products **2** and **3**. The existence of platinum–sulfur bonds in **6** suggests that platinum–sulfur interactions are important early in the course of the reaction. This could involve an initial bonding involving the lone pair of electrons on the sulfido ligand and an empty orbital on the 16-electron platinum complex.[19] Formation of two platinum–osmium bonds and cleavage of an osmium–sulfur bond are important steps in the entry of the platinum atom into the cluster and the extrusion of an osmium atom from the cluster; see Scheme II. The addition of PPh_3 to the extruded osmium atom is clearly important in stabilizing the $Os(CO)_3PPh_3$ grouping in the bridging position.

The reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with $Pt(PMe_2Ph)_4$ has important similarities to the ones reported here.[11] In this reaction the expanded clusters, $PtOs_3(CO)_{11-n}(PMe_2Ph)_n(\mu_3\text{-}S)$ (n = 1, 2) are formed by the displacement of an osmium-containing group from the cluster to an edge-bridging position. A ligand addition

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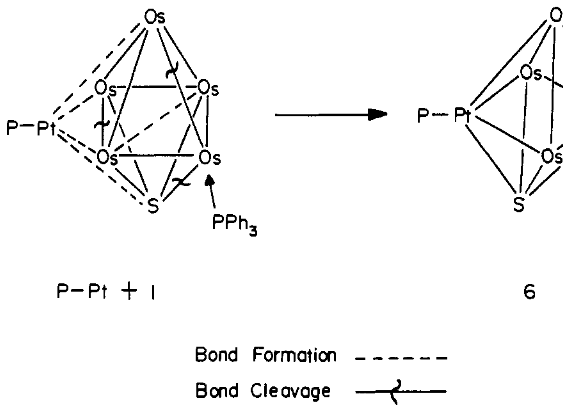
Scheme II



P–Pt + 1

6

to this osmium group also occurs. These clusters decarbonylate by reincorporating the osmium group into the cluster and shifting the platinum atom onto the triosmium face. A similar process could lead to the formation of **4**. Unfortunately, we have not observed the expected precursor (i.e. the carbonyl analogue of **6**, $PtOs_5(CO)_{16}(PPh_3)(\mu_4\text{-}S)$). However, it was observed that the yield of **4** was increased to 13% when the reaction of **1** and $Pt(PPh_3)_2C_2H_4$ was performed under a atmosphere of carbon monoxide. Compound **6** decomposes not by condensation, but by loss of metal-containing units. By loss of the edge-bridging $Os(CO)_3PPh_3$ group, compound **2** is formed. However, reincorporation of this osmium bridge is a competing process and this leads to formation of **3** via loss of a platinum containing moiety.

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Registry No. **1**, 86437-19-6; **2**, 101566-39-6; **3**, 99595-19-4; **4**, 101629-48-5; **6**, 101566-41-0; **7**, 101566-42-1; $Os_4(CO)_{11}(NMe_3)(\mu_3\text{-}S)$, 101566-43-2; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; Os, 7440-04-2; Pt, 7440-06-4.

Supplementary Material Available: Tables of anisotropic thermal parameters for all three structures and hydrogen atom coordinates for compounds **2** and **4** (5 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (116 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Synthesis, Structures, and Nonrigidity of Heterotrimetallic Alkyne Clusters of the Type $CpNiCoM(CO)_6(C_2RR')$ (M = Fe, Ru, Os)

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A series of heterotrimetallic alkyne clusters of the type $CpNiCoM(CO)_6(C_2RR')$ (where M = Fe, Ru, Os) has been synthesized and structurally investigated. In all cases examined, the alkyne is oriented parallel to one edge of the trimetallic framework but the particular location varies. In the iron complex $CpNiCoFe(CO)_6(C_2Et_2)$ (**1b**), it is parallel to the Ni–Co edge and all carbonyls are terminal. In the ruthenium and osmium complexes $CpNiCoRu(CO)_6(C_2Ph_2)$ (**2a**) and $CpNiCoOs(CO)_6C_2Ph_2$ (**3a**), the orientation is parallel to the Ni–Ru or Ni–Os edge and one of the CO groups adopts a semibridging position across the Co–Ru or Co–Os bond. A similar arrangement is observed in an iron complex when one of the carbonyl groups bound to cobalt is replaced by triphenylphosphine to give $CpNiCoFe(CO)_5(PPh_3)(C_2Ph_2)$ (**1d**). Crystal data: **1b**, monoclinic, $P2_1/n$, $a = 9.559$ (3) Å, $b = 12.573$ (5) Å, $c = 16.175$ (4) Å, $\beta = 104.42$ (3)°, $Z = 4$, $V = 1883$ Å^3, $\lambda(\text{Mo K}\alpha_1) = 0.709\,30$ Å, $\mu(\text{Mo K}\alpha) = 26.4$ cm^{-1}, $d_{\text{calcd}} = 1.72$ g cm^{-3}, $d_{\text{measd}} = 1.74$ g cm^{-3}, $R = 0.029$ and $R_w = 0.033$ for 1387 observed reflections, with $I \geq 2.3\sigma(I)$ (1748 measured with $40° \geq 2\theta \geq 3°$); **1d**, monoclinic, $P2_1/c$, $a = 11.698$ (2) Å, $b = 14.768$ (3) Å, $c = 22.616$ (4) Å, $\beta = 111.82$ (1)°, $Z = 4$, $V = 3627$ Å^3, $\lambda(\text{Mo K}\alpha_1) = 0.709\,30$ Å, $\mu(\text{Mo K}\alpha) = 14.7$ cm^{-1}, $d_{\text{calcd}} = 1.48$ g cm^{-3}, $d_{\text{measd}} = 1.51$ g cm^{-3}, $R = 0.057$ and $R_w = 0.070$ for 1109 observed reflections, with $I \geq 2.3\sigma(I)$ (2316 measured with $35° \geq 2\theta \geq 3°$); **2a**, monoclinic, $P2_1/c$, $a = 9.964$ (2) Å, $b = 9.5112$ (6) Å, $c = 24.835$ (2) Å, $\beta = 90.11$ (1)°, $Z = 4$, $V = 2353$ Å^3, $\lambda(\text{Mo K}\alpha_1) = 0.709\,30$ Å, $\mu(\text{Mo K}\alpha) = 21.7$ cm^{-1}, $d_{\text{calcd}} = 1.78$ g cm^{-3}, $d_{\text{measd}} = 1.80$ g cm^{-3}, $R = 0.036$ and $R_w = 0.042$ for 1816 observed reflections with $I \geq 2.3\sigma(I)$ (3100 measured with $45° \geq 2\theta \geq 3.5°$); **3a**, monoclinic, $P2_1/c$, $a = 9.950$ (2) Å, $b = 9.505$ (2) Å, $c = 24.813$ (4) Å, $\beta = 90.10$ (3)°, $Z = 4$, $V = 2347$ Å^3, $\lambda(\text{Mo K}\alpha_1) = 0.70930$ Å, $\mu(\text{Mo K}\alpha) = 69.4$ cm^{-1}, $d_{\text{calcd}} = 2.03$ g cm^{-3}, $d_{\text{measd}} = 2.11$ g cm^{-3}, $R = 0.033$ and $R_w = 0.039$ for 2503 reflections with $I \geq 2.3\sigma(I)$ (3063 measured with $45° \geq 2\theta \geq 3°$). The variable-temperature ^{1}H NMR spectra of **1c** (Fe), **2c** (Ru), and **3c** (Os), containing the unsymmetrical alkyne MeC_2Ph, indicate that the clusters are nonrigid and the alkyne substituents interchange position by rotation of the alkyne moiety on the face of the metal triangle. Examination of the C_2Et_2 complexes shows this to be nondissociative and to involve no transfer from one face of the metal triangle to the other.

Introduction

Alkynes provide great structural and chemical diversity in their interactions with transition metals in complexes. One aspect of current interest is their ability to bind simultaneously to three or four transition metals in clusters, and these compounds have recently been reviewed.[1,2] Somewhat different viewpoints have been adopted in describing what constitutes the "cluster" in these compounds. To cite the trimetallic case, the alkyne may simply be viewed as one ligand among others binding to a triangular M_3 cluster.[3] Alternatively, the alkyne carbon atoms may be considered to be an integral part of a M_3C_2 five-vertex cluster polyhedron.[4]

The M_3C_2 clusters adopt two distinct geometries that differ in the orientation of the alkyne C_2 vector with respect to the M_3 triangle. In the first, this vector is parallel to a metal–metal edge, and in this structure, the alkyne may be designated[5] as η^2-‖; the polyhedron is a *nido*-M_3C_2 cluster with a square-based-pyramidal

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