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Cluster Synthesis. 7. Role of Bridging Sulfido Ligands in the Synthesis of Platinum Osmium Carbonyl Cluster Compounds

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The four platinum osmium sulfido carbonyl cluster compounds $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I), $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II), $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)$ (III), and $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (IV) have been obtained from the reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with $Pt(PMe_2Ph)_4$ at room temperature. All the products were characterized by IR and ^1H NMR spectroscopy. Compounds I, II, and IV were also characterized by X-ray crystallographic analyses. All three compounds crystallize in the triclinic space group $P\bar{1}$: (I) a = 8.558 (2) Å, b = 13.814 (3) Å, c = 15.214 (5) Å, α = 109.15 (2)°, β = 93.05 (2)°, γ = 95.75 (2)°, Z = 2, ρ_{calcd} = 2.67 g/cm^3; (II) a = 10.404 (4) Å, b = 13.746 (7) Å, c = 29.332 (16) Å, α = 85.23 (5)°, β = 88.43 (4)°, γ = 74.25 (4)°, Z = 4, ρ_{calcd} = 2.48 g/cm^3; (IV) a = 9.761 (4) Å, b = 11.926 (5) Å, c = 16.412 (6) Å, α = 78.57 (3)°, β = 89.16 (3)°, γ = 87.98 (6)°, Z = 2, ρ_{calcd} = 2.55 g/cm^3. All three structures were solved by the heavy-atom method and were refined to the final residuals R_F = 0.060 and R_{wF} = 0.071 for I, R_F = 0.037 and R_{wF} = 0.039 for II, and R_F = 0.032 and R_{wF} = 0.037 for IV. I and II are approximately planar clusters of one platinum and three osmium atoms. They have five metal–metal bonds and a triply bridging sulfido ligand on the $PtOs_2$ triangular face. IV consists of a tetrahedral cluster of one platinum and three osmium atoms with a triply bridging sulfido ligand on the Os_3 face. III is believed to be structurally analogous to IV. III and IV can be formed by the decarbonylation of I and II, respectively. This decarbonylation reaction is reversible. UV irradiation of solutions of II yields the compound $HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$ (V) in addition to IV. V was characterized by X-ray diffraction analysis: space group $P\bar{1}$, a = 10.432 (3) Å, b = 12.727 (6) Å, c = 14.448 (4) Å, α = 98.46 (3)°, β = 93.82°, γ = 91.82 (3)°, Z = 2, ρ_{calcd} = 2.47 g/cm^3. The structure of V was solved by the heavy-atom method and was refined to the final residuals R_F = 0.037 and R_{wF} = 0.042. V consists of a tetrahedral cluster of one platinum and three osmium atoms and has a triply bridging sulfido ligand on the triosmium face. The phenyl ring of one of the PMe_2Ph ligands is orthometalated on a metal atom adjacent to the primary coordination site.

Introduction

Research on the chemistry of transition-metal cluster compounds has grown by enormous amounts in the past 10 years.[1-3] Yet in spite of this, systematic routes for the synthesis of these compounds have been slow to emerge.[4,5] It is becoming increasingly apparent that bridging ligands can play an important role in both the stabilization and synthesis of new cluster compounds.[5] Bridging sulfido ligands have been found to be particularly effective in this regard.[6-9] This method has been found to be unusually valuable in the synthesis of a variety of mixed-metal cluster compounds[5,10,11] including the first examples of chiral clusters.[12] In this report the synthesis of a series of sulfido-bridged platinum osmium carbonyl cluster compounds will be described in which the importance of the sulfido ligand is clearly revealed. A preliminary report of some of this work has been published.[13]

Experimental Section

Reactions were performed under a prepurified nitrogen atmosphere unless otherwise indicated. Solvents were reagent grade and were dried over molecular sieves. Carbon monoxide gas was purchased from Linde Co. $Os_3(CO)_{10}(\mu_3\text{-}S)$[14] and $Pt(PMe_2Ph)_4$[15] were prepared by the published procedures. Dimethylphenylphosphine was used as purchased (Strem Chemical Co.).

^1H NMR spectra were recorded at 500 MHz on a Bruker WM500 FT-NMR spectrometer. ^{31}P NMR spectra were recorded on the same instrument operating at a frequency of 203 Hz, with H_3PO_4 as an external reference. IR spectra were recorded on a Nicolet 5-SX FTIR spectrophotometer. Melting points were determined by using a Thomas-Hoover capillary melting point apparatus and were uncorrected. Synthetic photolyses were performed by using an external high-pressure mercury lamp filtered only by the Pyrex glass of the reaction vessels. Elemental analyses were performed by Mic Anal, Tucson, AZ.

Reaction between $Os_3(CO)_{10}(\mu_3\text{-}S)$ and $Pt(PMe_2Ph)_4$. To $Os_3(CO)_{10}(\mu_3\text{-}S)$ (36 mg, 0.041 mmol) dissolved in 50 mL of THF was added $Pt(PMe_2Ph)_4$ (40 mg, 0.054 mmol) at 0 °C. The mixture was stirred for 10 min at 0 °C and was then warmed to room temperature. After 1 h, a bright red solution had formed. The solvent was removed in vacuo, and the residue was separated on silica TLC plates. Elution with CH_2Cl_2/hexane (10/40) separated in order of elution the brown compound III (mp 152–153 °C; ca. 1 mg (2%)), the orange compound I (8 mg (15%), the red-brown compound IV (16 mg (26%)), and the bright red compound II (mp 146–147 °C; 12 mg (20%)). IR and ^1H NMR spectra of all the products are listed in Table I.

The relative yields of the four products vary with the reaction temperature and the reaction time. For example, in another experiment the reagents were mixed at 0 °C and stirred for 0.5 h and then warmed to room temperature and stirred for 2.5 h. During this time the reaction atmosphere was periodically evacuated and replaced with pure N_2. The percentage yields of compounds III, I, IV, and II were respectively 10%, 1%, 42%, and 4%. Anal. Calcd for III: C, 22.65; H, 1.66; S, 2.42. Found: C, 22.62; H, 1.67; S, 2.06.

Preparation of $HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$ (V). A hexane solution (100 mL) of compound II (12 mg, 0.0082 mmol) was irradiated (UV) at room temperature for 6 h under a slow purge with N_2. The resultant brownish orange solution was evaporated to dryness to give an orange residue that was chromatographed by TLC with 35% dichloromethane in hexane as eluent. The major product

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Table I. IR and ^{1}H NMR Spectroscopic Data

compd	δ	ν, cm^{-1}
$PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I)	7.08–7.36 (m, 10 H), 1.91 (d, 6 H, J_{Pt-H} = 34 Hz), 1.81 (d, 6 H, J_{Pt-H} = 32 Hz)^a	2090 (s), 2020 (vs), 2015 (s, sh), 2010 (s), 1983 (vw), 1959 (m), 1921 (m), 1915 (m, sh)^c
$PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II)	7.09–7.62 (m, 15 H), 2.26 (d, 3 H, J_{P-H} = 9.8 Hz), 2.23 (d, 3 H, J_{P-H} = 9.7 Hz), 1.84 (q, 6 H, J_{P-H} = 10.0 Hz), 1.80 (q, 3 H, J_{P-H} = 10.1 Hz), 1.78 (q, 3 H, J_{P-H} = 10.2 Hz)^a	2053 (s), 2003 (s), 1992 (s), 1976 (vs), 1961 (m), 1928 (m), 1908 (m), 1895 (w, sh)^c
$PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)$ (III)	7.24–7.41 (m, 10 H), 1.80 (q, 12 H, J_{P-H} = 30 Hz)^{a,b}	2060 (s), 2035 (vw), 2016 (vw), 1980 (s), 1962 (m), 1949 (m)^c
$PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (IV)	298 K: 7.20–7.66 (m, 15 H), 2.32 (d, 6 H, J_{P-H} = 10.3 Hz), 1.73 (q, 12 H, J_{P-H} = 10.1 Hz, J_{Pt-H} = 25 Hz)^d 213 K: 6.85–7.59 (m, 15 H), 2.28 (d, 6 H, J_{P-H} = 10.4 Hz), 1.73 (d, 6 H, J_{P-H} = 9.5 Hz), 1.58 (d, 6 H, J_{P-H} = 10.3 Hz)^d 183 K: 6.80–7.58 (m, 15 H), 1.70 (br, 6 H), 1.56 (d, 6 H, J_{P-H} = 9.9 Hz)^d	2040 (s), 1998 (s), 1969 (s), 1945 (m, br), 1919 (m), 1891 (w)^c
$HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)^e$ (V)	6.93–8.07 (m, 14 H), 2.24 (d, 6 H, J_{P-H} = 9.9 Hz), 2.16 (q, 3 H, J_{P-H} = 10.5 Hz), 2.14 (q, 3 H, J_{P-H} = 10.8 Hz), 1.95 (d, 3 H, J_{P-H} = 9.3 Hz), 1.82 (d, 3 H, J_{P-H} = 10.2 Hz), −16.84 (m, 1 H)^a	2017 (m), 1992 (s), 1957 (m), 1934 (m), 1894 (w)^f

[a] $CDCl_3$. [b] $J_{P-H} + J_{P-H'}$; center peaks separation 10.3 Hz. [c] Hexane. [d] CD_2Cl_2. [e] ^{31}P NMR data ($CDCl_3$) (relative to D_3PO_4): −25.03 (s, 1 P), −48.30 (t, 1 P, J_{Pt-P} = 2694 Hz), −55.67 (s, 1 P). [f] $CHCl_3$.

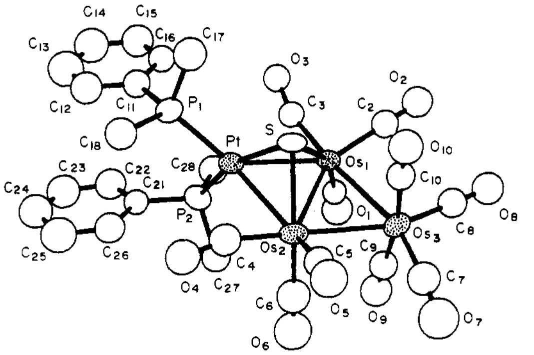

Figure 1. ORTEP diagram of $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I) showing 50% probability thermal ellipsoids.

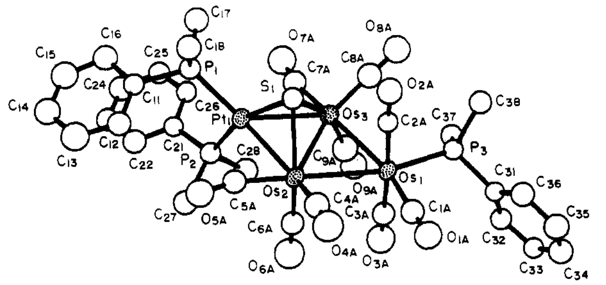

Figure 2. ORTEP diagram of one of the two crystallographically independent molecules of $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II) showing 50% probability thermal ellipsoids.

was identified as compound V, 6 mg (48%). A minor product was $PtOs_3(\mu_3\text{-}S)(CO)_8(PMe_2Ph)_3$ (IV), ca. 0.4 mg (3%).

Thermolytic Decarbonylation of $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I). A solution of I (7 mg, 0.0052 mmol) in 50 mL of hexane was refluxed for 5 h and yielded an orange-red solution. The solvent was removed in vacuo, and the residue was chromatographed on silica TLC plates to give three bands, eluted with hexane/CH_2Cl_2 (4/1) that were identified as IV (1 mg (14%)), the starting material I (1 mg (14%)), and III (4 mg (58%)).

Photolytic Decarbonylation of I. A hexane solution (50 mL) of I (9 mg, 0.0066 mmol) was photolyzed with UV radiation for a period of 2 h. After removal of the hexane in vacuo, the residue was dissolved in a minimum of CH_2Cl_2 and applied to silica TLC plates. Elution with 25% CH_2Cl_2 in hexane led to the isolation of compound III as the major product (3 mg (34%)).

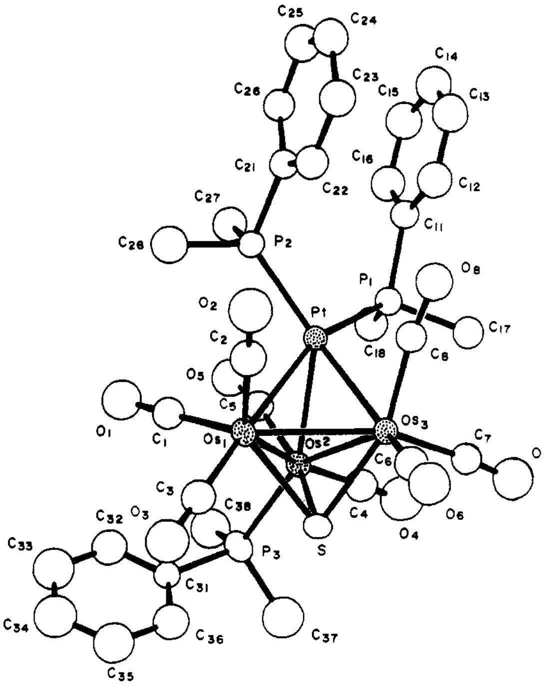

Figure 3. ORTEP diagram of $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (IV) showing 50% probability thermal ellipsoids.

Thermolytic Decarbonylation of $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II). Compound II (11 mg, 0.0075 mmol) was heated to reflux in hexane (100 mL) for 3 h. The resultant orange solution was evaporated to dryness, and the residue was chromatographed by TLC with CH_2Cl_2/hexane (3/7) as the eluent. This separated IV (8 mg (74%)) from a small amount of starting material (1 mg (9%)).

Carbonylation of III and IV. A slow stream of CO gas was bubbled through a hexane solution (50 mL) of IV (20 mg, 0.0139 mmol) for a period of 60 h at room temperature; during this time the solution gradually changed from bright red to orange-red and some red crystalline deposits were formed. Evaporation to dryness gave a red residue that was subsequently taken up in CH_2Cl_2 to give a blood red solution that was chromatographed on silica TLC plates with 35% CH_2Cl_2 in hexane as eluent. $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II) (13 mg (64%)) was isolated as the major product, and 2 mg (10%) of the starting material was recovered.

Table II. Crystallographic Data for X-ray Diffraction Studies

	I	II	IV	V
		(A) Cell Parameters		
formula	$PtOs_3SP_2O_{10}C_{26}H_{22}$	$PtOs_3SP_3O_9C_{33}H_{33}$	$PtOs_3SP_3O_8C_{32}H_{33}$	$PtOs_3SP_3O_7C_{31}H_{33}$
temp (±3 °C)	25	20	25	23
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.558 (2)	10.404 (4)	9.761 (4)	10.432 (3)
b, Å	13.814 (3)	13.746 (7)	11.926 (5)	12.727 (6)
c, Å	15.214 (5)	29.332 (16)	16.412 (6)	14.448 (4)
α, deg	109.15 (2)	85.23 (5)	78.57 (3)	98.46 (3)
β, deg	93.05 (2)	88.43 (4)	89.16 (3)	93.82 (2)
γ, deg	95.75 (2)	74.25 (4)	87.98 (6)	91.82 (3)
V, Å^3	1683.4 (15)	4023 (5)	1871 (2)	1891.5
M_r	1354.2	1464.3	1436.3	1408.3
Z	2	4	2	2
ρ_{calcd}, g/cm^3	2.67	2.42	2.55	2.47
		(B) Measurement of Intensity Data		
radiation (λ, Å)	Mo $K\bar{\alpha}$ (0.710 73)	Mo $K\bar{\alpha}$ (0.710 73)	Mo $K\bar{\alpha}$ (0.710 73)	Mo $K\bar{\alpha}$ (0.710 73)
monochromator	graphite	graphite	graphite	graphite
detector aperture, mm				
horiz ($A + B \tan \theta$): A, B	3.0, 1.0	3.0, 1.0	3.0, 1.0	2.6, 1.2
vert	4.0	4.0	4.0	4.0
cryst faces	100, $\bar{1}$00, 001, 00$\bar{1}$, 01$\bar{1}$, 0$\bar{1}$1	001, 00$\bar{1}$, $\bar{1}$01, 100, 1$\bar{2}\bar{2}$, $\bar{1}$22, $\bar{1}\bar{2}$2, 12$\bar{2}$	001, 00$\bar{1}$, 010, 0$\bar{1}$0, 100, $\bar{1}$00	100, $\bar{1}$00, 011, 102, 010, 0$\bar{1}$0
cryst size, mm	0.20 × 0.30 × 0.30	0.08 × 0.18 × 0.20	0.13 × 0.35 × 0.32	0.13 × 0.05 × 0.25
cryst orientation direction, deg from ϕ axis	normal to 02$\bar{1}$, 9.9	normal to 0$\bar{2}\bar{1}$, 14.2	normal to 201, 4.6	normal to 01$\bar{1}$, 7.1
reflcns measd	$h, \pm k, \pm l$	$h, \pm k, \pm l$	$h, \pm k, \pm l$	$h, \pm k, \pm l$
max 2θ, deg	50	44	47	46
scan type	moving-cryst stationary-counter	moving-cryst stationary counter	moving-cryst stationary counter	moving-cryst stationary counter
ω-scan width (A + 0.347 tan θ), deg	1.00	0.95	1.00	1.00
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	$^1/_4$ addnl scan at each end of scan
ω-scan rate (variable), deg/min: max, min	10.0, 1.5	10.0, 1.4	10.0, 1.7	10.0, 1.5
no. of reflcns measd	5871	9796	5483	5236
no. of data used ($F^2 \geqslant 3.0\sigma(F^2)$)	3512	5488	4223	3676
		(C) Treatment of Data		
abs cor coeff, cm^{-1}	156.9	131.8	141.6	140.1
grid	8 × 14 × 8	10 × 16 × 6	12 × 12 × 6	6 × 10 × 16
transmissn coeff: max, min	0.102, 0.018	0.53, 0.17	0.18, 0.01	0.24, 0.14
decay of cor: max, min	1.00, 0.95		1.04, 0.99	1.01, 0.97
P factor	0.03	0.02	0.03	0.02
final residuals: R_F, R_{wF}	0.060, 0.071	0.037, 0.039	0.032, 0.037	0.037, 0.042
esd of unit weight observn	2.84	1.66	1.67	2.13
largest shift/error value of final cycle	0.05	0.44	0.01	0.01
largest peak in final diff Fourier, e/Å^3	2.57	1.20	1.15	2.61

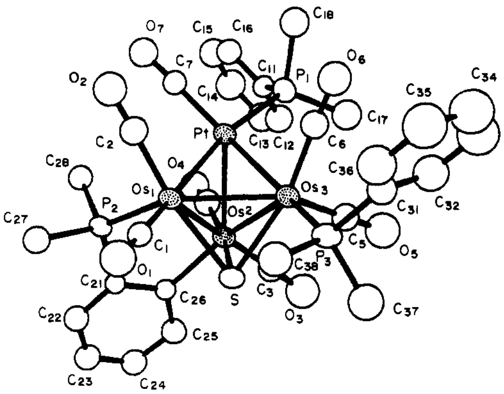

Figure 4. ORTEP diagram of $HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$ (V) showing 50% probability thermal ellipsoids.

Similarly, conversion of $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)$ (III) to $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I) via CO addition was also achieved with a yield of ca. 50%.

Reaction of $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I) with PMe_2Ph. A fourfold molar excess of PMe_2Ph (5 mg) was mixed with compound I (11 mg, 0.0081 mmol) in hexane and stirred for 5 h at room temperature. No reaction was noticeable (TLC/IR) at this stage. The solution was subsequently refluxed for 1.5 h, giving an orange solution. Removal of solvent was followed by chromatography on TLC plates with CH_2Cl_2/hexane (1/5). This separated $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (IV) (4 mg (34%)), $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II) (2 mg (17%)), and 4 mg (36%) of the starting material.

Crystallographic Analyses. Orange and red crystals of I and IV, respectively, were grown by slow evaporation of solvents from methylene chloride/hexane solutions at −10 °C. Red crystals of II were obtained from chloroform/ethanol solutions at the same temperature. Red crystals of V suitable for diffraction analyses were grown from acetone/ethanol solutions at −10 °C. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo $K\bar{\alpha}$ radiation. 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 PDP 11/45 computer by using the Enraf-Nonius SDP program library (version 18). Absorption corrections of a Gaussian integration type were done for each structure. Neutral-atom scattering

Table III. Positional and Thermal Parameters and Their Esds for $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I)

atom	x	y	z	$B(1,1)^a$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$	B_{eq}
Pt	0.8666 (1)	0.51459 (7)	0.76768 (6)	2.66 (4)	3.86 (3)	2.93 (3)	0.41 (3)	0.41 (3)	1.47 (2)	3.06 (2)
Os(1)	0.8831 (1)	0.33404 (7)	0.62121 (6)	2.47 (4)	3.66 (4)	3.19 (3)	0.25 (3)	0.53 (3)	1.45 (2)	3.03 (2)
Os(2)	0.6815 (1)	0.33149 (7)	0.76537 (6)	2.76 (4)	4.75 (4)	3.76 (3)	−0.02 (3)	0.71 (3)	2.07 (3)	3.62 (2)
Os(3)	0.7125 (1)	0.14319 (7)	0.61805 (7)	3.67 (5)	3.69 (4)	4.57 (4)	−0.27 (4)	−0.05 (4)	1.74 (3)	3.96 (2)
S	0.9653 (7)	0.3691 (5)	0.7842 (4)	2.0 (2)	4.9 (3)	4.2 (2)	0.2 (2)	0.1 (2)	2.1 (2)	3.6 (1)
P(1)	1.0328 (8)	0.6417 (5)	0.8761 (4)	3.7 (3)	4.8 (3)	3.2 (2)	−0.2 (3)	0.2 (2)	1.3 (2)	4.0 (2)
P(2)	0.7170 (8)	0.6106 (5)	0.7109 (4)	3.9 (3)	5.0 (3)	3.7 (2)	1.2 (2)	0.4 (2)	2.2 (2)	4.0 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.674 (3)	0.342 (2)	0.460 (1)	6.8 (5)	C(9)	0.549 (3)	0.175 (2)	0.546 (2)	5.2 (6)
O(2)	1.083 (2)	0.187 (1)	0.494 (1)	6.1 (5)	C(10)	0.890 (3)	0.136 (2)	0.696 (2)	4.5 (6)
O(3)	1.125 (2)	0.510 (1)	0.605 (1)	4.8 (4)	C(11)	1.097 (3)	0.755 (2)	0.850 (2)	4.7 (6)
O(4)	0.390 (2)	0.486 (1)	0.071 (1)	6.8 (5)	C(12)	1.073 (4)	0.856 (2)	0.905 (2)	6.2 (7)
O(5)	0.617 (3)	0.194 (2)	0.880 (1)	7.2 (5)	C(13)	1.121 (5)	0.939 (3)	0.881 (2)	8.2 (9)
O(6)	0.342 (3)	0.316 (2)	0.691 (1)	8.7 (6)	C(14)	1.196 (4)	0.930 (3)	0.803 (2)	7.9 (9)
O(7)	0.476 (3)	−0.002 (2)	0.675 (2)	9.1 (7)	C(15)	1.220 (4)	0.837 (2)	0.743 (2)	6.9 (8)
O(8)	0.822 (2)	−0.006 (1)	0.445 (1)	6.4 (5)	C(16)	1.173 (3)	0.746 (2)	0.767 (2)	4.7 (6)
O(9)	0.444 (3)	0.192 (1)	0.505 (1)	6.7 (5)	C(17)	1.218 (4)	0.602 (2)	0.899 (2)	6.3 (7)
O(10)	0.992 (2)	0.125 (1)	0.744 (1)	6.3 (5)	C(18)	0.970 (4)	0.688 (2)	0.992 (2)	5.6 (7)
C(1)	0.751 (3)	0.338 (2)	0.521 (2)	3.9 (5)	C(21)	0.692 (3)	0.736 (2)	0.785 (2)	4.0 (5)
C(2)	1.008 (3)	0.239 (2)	0.546 (2)	4.8 (6)	C(22)	0.626 (4)	0.746 (2)	0.871 (2)	5.8 (7)
C(3)	1.014 (3)	0.449 (2)	0.618 (2)	4.3 (5)	C(23)	0.595 (4)	0.844 (3)	0.932 (2)	7.9 (9)
C(4)	0.661 (4)	0.450 (2)	0.866 (2)	5.8 (7)	C(24)	0.646 (4)	0.936 (2)	0.910 (2)	7.2 (8)
C(5)	0.639 (3)	0.239 (2)	0.830 (2)	4.7 (6)	C(25)	0.697 (4)	0.920 (2)	0.828 (2)	7.3 (8)
C(6)	0.466 (4)	0.321 (2)	0.719 (2)	6.7 (8)	C(26)	0.728 (4)	0.827 (2)	0.767 (2)	6.4 (8)
C(7)	0.578 (4)	0.052 (2)	0.654 (2)	6.2 (7)	C(27)	0.517 (4)	0.550 (2)	0.675 (2)	5.6 (7)
C(8)	0.776 (3)	0.055 (2)	0.508 (2)	5.3 (6)	C(28)	0.784 (4)	0.633 (2)	0.607 (2)	5.8 (7)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}[h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)]]$.

Table IV. Interatomic Distances (Å) with Esds for $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I)

Os(1)–Os(2)	2.869 (1)	C(1)–O(1)	1.122 (17)
Os(1)–Os(3)	2.867 (1)	C(2)–O(2)	1.146 (17)
Os(2)–Os(3)	2.870 (1)	C(3)–O(3)	1.271 (18)
Os(1)–Pt	2.768 (1)	C(4)–O(4)	1.210 (25)
Os(2)–Pt	2.836 (1)	C(5)–O(5)	1.135 (18)
Os(1)–S	2.416 (4)	C(6)–O(6)	1.107 (23)
Os(2)–S	2.414 (4)	C(7)–O(7)	1.209 (22)
Pt–S	2.337 (4)	C(8)–O(8)	1.161 (18)
Os(1)–C(1)	1.871 (15)	C(9)--O(9)	1.151 (20)
Os(1)–C(2)	1.902 (17)	C(10)–O(10)	1.161 (18)
Os(1)–C(3)	1.871 (16)	P(1)–C(11)	1.783 (17)
Os(2)–C(4)	1.867 (19)	P(1)–C(17)	1.780 (20)
Os(2)–C(5)	1.875 (17)	P(1)–C(18)	1.802 (17)
Os(2)–C(6)	1.912 (23)	P(2)–C(21)	1.776 (15)
Os(3)–C(7)	1.857 (20)	P(2)–C(27)	1.801 (19)
Os(3)–C(8)	1.865 (17)	P(2)–C(28)	1.819 (18)
Os(3)–C(9)	1.906 (18)	C–C$_{av\ ring}$(11–16)	1.39 (4)
Os(3)–C(10)	1.912 (17)	C–C$_{av\ ring}$(21–26)	1.39 (5)
Pt–P(1)	2.275 (4)	Pt···C(3)	2.607 (15)
Pt–P(2)	2.262 (4)	Pt···C(4)	2.636 (19)

Table V. Selected Interatomic Angles (deg) with Esds for $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I)

Os(2)–Os(1)–Os(3)	60.05 (2)	Os(1)–Os(3)–C(10)	84.7 (5)
Os(1)–Os(2)–Os(3)	59.95 (2)	Os(2)–Os(3)–C(7)	99.6 (6)
Os(1)–Os(3)–Os(2)	60.01 (2)	Os(2)–Os(3)–C(8)	159.4 (6)
Os(2)–Os(1)–Pt	60.37 (2)	Os(2)–Os(3)–C(9)	87.7 (5)
Os(3)–Os(1)–Pt	120.34 (3)	Os(2)–Os(3)–C(10)	84.8 (5)
Os(1)–Os(2)–Pt	58.06 (2)	Pt–Os(2)–C(4)	64.4 (6)
Os(3)–Os(2)–Pt	117.93 (3)	Pt–Os(2)–C(5)	145.2 (5)
Os(1)–Pt–Os(2)	61.57 (2)	Pt–Os(2)–C(6)	113.6 (6)
Os(2)–Os(1)–S	53.52 (8)	Os(1)–Pt–P(1)	138.75 (11)
Os(3)–Os(1)–S	88.51 (9)	Os(2)–Pt–P(1)	135.26 (10)
Os(1)–Os(2)–S	53.61 (9)	Os(1)–Pt–P(2)	106.55 (11)
Os(3)–Os(2)–S	88.49 (10)	Os(2)–Pt–P(2)	109.90 (12)
Pt–Os(1)–S	53.06 (9)	S–Os(1)–C(1)	155.3 (5)
Pt–Os(2)–S	52.12 (9)	S–Os(1)–C(2)	109.4 (5)
Os(1)–Pt–S	55.73 (9)	S–Os(1)–C(3)	92.2 (5)
Os(2)–Pt–S	54.61 (9)	S–Os(2)–C(4)	91.6 (6)
Os(1)–S–O(2)	72.87 (10)	S–Os(2)–C(5)	104.2 (5)
Os(1)–S–Pt	71.21 (10)	S–Os(2)–C(6)	161.1 (6)
Os(2)–S–Pt	73.27 (10)	S–Pt–P(1)	100.02 (14)
Os(2)–Os(1)–C(1)	105.9 (5)	S–Pt–P(2)	159.59 (15)
Os(2)–Os(1)–C(2)	134.5 (5)	P(1)–Pt–P(2)	100.34 (16)
Os(2)–Os(1)–C(3)	125.4 (5)	Os(1)–C(1)–O(1)	178.2 (14)
Os(3)–Os(1)–C(1)	91.5 (5)	Os(1)–C(2)–O(2)	172.5 (15)
Os(3)–Os(1)–C(2)	79.8 (5)	Os(1)–C(3)–O(3)	165.2 (13)
Os(3)–Os(1)–C(3)	173.1 (5)	Os(2)–C(4)–O(4)	163.3 (16)
Pt–Os(1)–C(1)	106.9 (5)	Os(2)–C(5)–O(5)	171.5 (16)
Pt–Os(1)–C(2)	149.0 (5)	Os(2)–C(6)–O(6)	178.9 (17)
Pt–Os(1)–C(3)	65.1 (5)	Os(3)–C(7)–O(7)	172.4 (18)
Os(1)–Os(2)–C(4)	122.4 (6)	Os(3)–C(8)–O(8)	172.9 (16)
Os(1)–Os(2)–C(5)	133.3 (5)	Os(3)–C(9)–O(9)	176.4 (17)
Os(1)–Os(2)–C(6)	109.6 (6)	Os(3)–C(10)–O(10)	174.6 (15)
Os(3)–Os(2)–C(4)	176.9 (6)	Pt–P(1)–C(11)	118.1 (6)
Os(3)–Os(2)–C(5)	81.5 (5)	Pt–P(1)–C(17)	113.2 (6)
Os(3)–Os(2)–C(6)	89.1 (6)	Pt–P(1)–C(18)	116.4 (6)
Os(1)–Os(3)–C(7)	159.6 (6)	Pt–P(2)–C(21)	118.8 (5)
Os(1)–Os(3)–C(8)	99.4 (6)	Pt–P(2)–C(27)	112.5 (6)
Os(1)–Os(3)–C(9)	85.8 (5)	Pt–P(2)–C(28)	114.3 (6)

factors were calculated by the standard procedures.[16a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[16b] Full-matrix least-squares refinements minimized the function $\sum_w([F_o] - |F_c|)^2$, 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 except for II, all atoms heavier than oxygen were refined anisotropically and all other non-hydrogen atoms were refined isotropically. Positions of the hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculation, but their positions were not refined. Because of the large size of II, only the metal atoms were refined anisotropically and the hydrogen atoms were ignored.

All four compounds 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. All four structures were solved by the heavy-atom method. 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. Tables of structure factor

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

Table VI. Positional Parameters with Esds for $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pt(1)	0.48169 (7)	0.07060 (6)	0.12483 (3)	C(8B)	−0.062 (2)	0.909 (2)	0.3391 (8)
Pt(2)	0.07413 (8)	0.57532 (6)	0.34473 (3)	C(9B)	−0.120 (2)	0.800 (2)	0.4127 (8)
Os(1)	0.63891 (7)	0.37793 (6)	0.09208 (3)	C(11)	0.271 (2)	−0.092 (1)	0.1370 (7)
Os(2)	0.45187 (8)	0.27577 (6)	0.13435 (3)	C(12)	0.188 (2)	−0.033 (2)	0.1687 (8)
Os(3)	0.67976 (7)	0.16233 (6)	0.08855 (3)	C(13)	0.107 (2)	−0.075 (2)	0.1988 (9)
Os(4)	0.16627 (7)	0.85836 (6)	0.41434 (3)	C(14)	0.115 (2)	−0.179 (2)	0.1993 (8)
Os(5)	0.25394 (8)	0.65066 (6)	0.39120 (3)	C(15)	0.197 (2)	−0.230 (2)	0.1684 (9)
Os(6)	−0.00853 (7)	0.77781 (6)	0.36388 (3)	C(16)	0.277 (2)	−0.198 (2)	0.1351 (8)
S(1)	0.4517 (5)	0.1965 (4)	0.0643 (2)	C(17)	0.462 (2)	−0.125 (2)	0.0623 (8)
S(2)	0.1721 (5)	0.7027 (4)	0.3147 (2)	C(18)	0.231 (2)	0.044 (2)	0.0561 (8)
P(1)	0.3654 (5)	−0.0289 (4)	0.0969 (2)	C(21)	0.558 (2)	−0.151 (1)	0.2002 (7)
P(2)	0.5441 (5)	−0.0152 (4)	0.1934 (2)	C(22)	0.481 (2)	−0.188 (2)	0.2326 (8)
P(3)	0.8273 (5)	0.4072 (4)	0.0548 (2)	C(23)	0.496 (2)	−0.297 (2)	0.2365 (8)
P(4)	−0.0258 (5)	0.4830 (4)	0.3933 (2)	C(24)	0.589 (2)	−0.359 (2)	0.2117 (8)
P(5)	0.0978 (6)	0.4863 (5)	0.2814 (2)	C(25)	0.663 (2)	−0.319 (2)	0.1772 (8)
P(6)	0.3332 (5)	0.8931 (4)	0.4567 (2)	C(26)	0.649 (2)	−0.213 (1)	0.1716 (7)
O(1A)	0.503 (1)	0.599 (1)	0.1002 (5)	C(27)	0.436 (2)	0.040 (2)	0.2413 (8)
O(2A)	0.505 (1)	0.381 (1)	0.0002 (5)	C(28)	0.711 (2)	−0.012 (2)	0.2129 (8)
O(3A)	0.778 (1)	0.357 (1)	0.1847 (6)	C(31)	0.865 (2)	0.524 (1)	0.0702 (7)
O(4A)	0.285 (1)	0.493 (1)	0.1241 (6)	C(32)	0.956 (2)	0.523 (1)	0.1043 (7)
O(5A)	0.199 (1)	0.225 (1)	0.1721 (5)	C(33)	0.984 (2)	0.613 (1)	0.1126 (7)
O(6A)	0.549 (2)	0.281 (1)	0.2281 (6)	C(34)	0.920 (2)	0.702 (2)	0.0871 (8)
O(7A)	0.763 (2)	−0.063 (1)	0.0838 (6)	C(35)	0.829 (2)	0.707 (2)	0.0547 (8)
O(8A)	0.831 (1)	0.173 (1)	0.0009 (6)	C(36)	0.799 (2)	0.617 (2)	0.0444 (7)
O(9A)	0.907 (1)	0.144 (1)	0.1554 (6)	C(37)	0.990 (2)	0.307 (1)	0.0651 (7)
O(1B)	−0.007 (1)	1.073 (1)	0.4164 (6)	C(38)	0.819 (2)	0.425 (1)	−0.0078 (7)
O(2B)	0.050 (1)	0.786 (1)	0.5020 (6)	C(41)	−0.145 (2)	0.425 (1)	0.3684 (7)
O(3B)	0.288 (1)	0.901 (1)	0.3222 (5)	C(42)	−0.243 (2)	0.487 (1)	0.3396 (7)
O(4B)	0.529 (1)	0.682 (1)	0.3772 (5)	C(43)	−0.331 (2)	0.441 (2)	0.3202 (9)
O(5B)	0.367 (1)	0.425 (1)	0.3788 (6)	C(44)	−0.324 (2)	0.341 (2)	0.3307 (8)
O(6B)	0.277 (2)	0.594 (1)	0.4921 (6)	C(45)	−0.223 (2)	0.277 (2)	0.3566 (8)
O(7B)	−0.226 (1)	0.732 (1)	0.3098 (6)	C(46)	−0.133 (2)	0.320 (2)	0.3784 (8)
O(8B)	−0.100 (1)	0.991 (1)	0.3205 (6)	C(47)	−0.131 (2)	0.555 (2)	0.4357 (9)
O(9B)	−0.194 (1)	0.812 (1)	0.4450 (5)	C(48)	0.088 (2)	0.384 (2)	0.4286 (8)
C(1A)	0.558 (2)	0.515 (1)	0.0990 (7)	C(51)	0.096 (2)	0.355 (1)	0.2856 (7)
C(2A)	0.556 (2)	0.378 (1)	0.0357 (7)	C(52)	−0.002 (2)	0.321 (2)	0.2634 (8)
C(3A)	0.723 (2)	0.366 (2)	0.1493 (7)	C(53)	0.001 (2)	0.223 (2)	0.2691 (8)
C(4A)	0.355 (2)	0.410 (2)	0.1265 (8)	C(54)	0.100 (2)	0.153 (2)	0.2930 (8)
C(5A)	0.304 (2)	0.228 (1)	0.1562 (7)	C(55)	0.199 (2)	0.179 (2)	0.3165 (8)
C(6A)	0.508 (2)	0.281 (2)	0.1892 (7)	C(56)	0.200 (2)	0.282 (2)	0.3130 (8)
C(7A)	0.713 (2)	0.024 (2)	0.0885 (8)	C(57)	−0.024 (2)	0.550 (2)	0.2359 (9)
C(8A)	0.771 (2)	0.168 (2)	0.0364 (8)	C(58)	0.255 (2)	0.480 (2)	0.2516 (9)
C(9A)	0.820 (2)	0.154 (2)	0.1312 (9)	C(61)	0.421 (2)	0.979 (2)	0.4245 (8)
C(1B)	0.062 (2)	0.988 (2)	0.4168 (8)	C(62)	0.517 (2)	0.940 (2)	0.3938 (8)
C(2B)	0.093 (2)	0.816 (2)	0.4665 (8)	C(63)	0.583 (2)	0.999 (2)	0.3658 (10)
C(3B)	0.246 (2)	0.881 (2)	0.3586 (8)	C(64)	0.539 (2)	1.098 (2)	0.3752 (9)
C(4B)	0.422 (2)	0.673 (2)	0.3839 (8)	C(65)	0.446 (2)	1.147 (2)	0.4017 (9)
C(5B)	0.312 (2)	0.515 (2)	0.3796 (8)	C(66)	0.374 (2)	1.084 (2)	0.4321 (8)
C(6B)	0.268 (2)	0.617 (2)	0.4525 (8)	C(67)	0.266 (2)	0.954 (2)	0.5084 (8)
C(7B)	−0.134 (2)	0.733 (2)	0.3300 (8)	C(68)	0.473 (2)	0.789 (2)	0.4794 (8)

Table VII. Interatomic Distances (Å) with Esds for $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II)

Molecule A				Molecule B			
Os(1)–Os(2)	2.891 (1)	C(3A)–O(3A)	1.180 (19)	Os(4)–Os(5)	2.884 (1)	C(3B)–O(3B)	1.184 (19)
Os(1)–Os(3)	2.888 (1)	C(4A)–O(4A)	1.182 (19)	Os(4)–Os(6)	2.870 (1)	C(4B)–O(4B)	1.154 (17)
Os(2)–Os(3)	2.833 (1)	C(5A)–O(5A)	1.189 (17)	Os(5)–Os(6)	2.907 (1)	C(5B)–O(5B)	1.214 (20)
Os(2)–Pt(1)	2.789 (1)	C(6A)–O(6A)	1.227 (19)	Os(5)–Pt(2)	2.803 (1)	C(6B)–O(6B)	1.177 (22)
Os(3)–Pt(1)	2.835 (1)	C(7A)–O(7A)	1.182 (19)	Os(6)–Pt(2)	2.782 (1)	C(7B)–O(7B)	1.149 (18)
Os(2)–S(1)	2.405 (4)	C(8A)–O(8A)	1.206 (19)	Os(5)–S(2)	2.403 (5)	C(8B)–O(8B)	1.170 (19)
Os(3)–S(1)	2.406 (4)	C(9A)–O(9A)	1.142 (20)	Os(6)–S(2)	2.392 (4)	C(9B)–O(9B)	1.202 (19)
Pt(1)–S(1)	2.339 (4)	P(1)–C(11)	1.822 (16)	Pt(2)–S(2)	2.354 (4)	P(4)–C(41)	1.847 (16)
Os(1)–C(1A)	1.870 (18)	P(2)–C(21)	1.820 (16)	Os(4)–C(1B)	1.821 (18)	P(5)–C(51)	1.812 (17)
Os(1)–C(2A)	1.889 (16)	P(3)–C(31)	1.846 (15)	Os(4)–C(2B)	1.812 (21)	P(6)–C(61)	1.867 (18)
Os(1)–C(3A)	1.888 (18)	P(1)–C(17)	1.798 (18)	Os(4)–C(3B)	1.854 (19)	P(4)–C(47)	1.808 (21)
Os(2)–C(4A)	1.841 (18)	P(1)–C(18)	1.878 (17)	Os(5)–C(4B)	1.863 (17)	P(4)–C(48)	1.809 (19)
Os(2)–C(5A)	1.908 (17)	P(2)–C(27)	1.854 (18)	Os(5)–C(5B)	1.860 (20)	P(5)–C(57)	1.857 (21)
Os(2)–C(6A)	1.742 (18)	P(2)–C(28)	1.858 (17)	Os(5)–C(6B)	1.819 (22)	P(5)–C(58)	1.818 (20)
Os(3)–C(7A)	1.844 (19)	P(3)–C(37)	1.883 (16)	Os(6)–C(7B)	1.915 (18)	P(6)–C(67)	1.821 (19)
Os(3)–C(8A)	1.786 (19)	P(3)–C(38)	1.832 (17)	Os(6)–C(8B)	1.835 (20)	P(6)–C(68)	1.839 (18)
Os(3)–C(9A)	1.919 (21)	C–C_{av}(11–26)	1.40 (2)	Os(6)–C(9B)	1.808 (20)	C–C_{av}(41–46)	1.40 (2)
Os(1)–P(3)	2.332 (4)	C–C_{av}(21–26)	1.40 (2)	Os(4)–P(6)	2.335 (5)	C–C_{av}(51–56)	1.40 (2)
Pt(1)–P(1)	2.268 (5)	C–C_{av}(31–36)	1.39 (2)	Pt(2)–P(4)	2.249 (5)	C–C_{av}(61–66)	1.39 (2)
Pt(1)–P(2)	2.264 (5)	Pt···C(5A)	2.651 (17)	Pt(2)–P(5)	2.279 (5)	Pt···C(5B)	2.597 (18)
C(1A)–O(1A)	1.147 (18)	Pt···C(7A)	2.547 (17)	C(1B)–O(1B)	1.199 (19)	Pt···C(7B)	2.633 (17)
C(2A)–O(2A)	1.173 (16)			C(2B)–O(2B)	1.208 (21)		

Table VIII. Interatomic Angles (deg) with Esds for $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II)

Molecule A			
Os(2)–Os(1)–Os(3)	58.71 (2)	Os(2)–Os(3)–C(8A)	140.2 (6)
Os(1)–Os(2)–Os(3)	60.59 (2)	Os(2)–Os(3)–C(9A)	102.0 (6)
Os(1)–Os(3)–Os(2)	60.70 (2)	Pt(1)–Os(3)–C(7A)	61.74 (53)
Os(1)–Os(2)–Pt(1)	120.97 (3)	Pt(1)–Os(3)–C(8A)	138.2 (6)
Os(3)–Os(2)–Pt(1)	60.56 (2)	Pt(1)–Os(3)–C(9A)	113.0 (6)
Os(1)–Os(3)–Pt(1)	119.48 (3)	Os(2)–Pt(1)–P(1)	138.66 (12)
Os(2)–Os(3)–Pt(1)	58.96 (2)	Os(2)–Pt(1)–P(2)	107.86 (12)
Os(2)–Pt(1)–Os(3)	60.49 (2)	Os(3)–Pt(1)–P(1)	134.45 (12)
S(1)–Os(2)–Os(1)	88.36 (10)	Os(3)–Pt(1)–P(2)	111.17 (11)
S(1)–Os(2)–Os(3)	53.94 (10)	Os(2)–Os(1)–P(3)	161.71 (11)
S(1)–Os(3)–Os(1)	88.41 (10)	Os(3)–Os(1)–P(3)	103.11 (11)
S(1)–Os(3)–Os(2)	53.91 (10)	S(1)–Os(2)–C(4A)	109.5 (6)
S(1)–Os(2)–Pt(1)	52.89 (11)	S(1)–Os(2)–C(5A)	90.01 (52)
S(1)–Os(3)–Pt(1)	52.22 (11)	S(1)–Os(2)–C(6A)	153.8 (6)
S(1)–Pt(1)–Os(2)	55.10 (11)	S(1)–Os(3)–C(7A)	94.40 (53)
S(1)–Pt(1)–Os(3)	54.40 (10)	S(1)–Os(3)–C(8A)	104.0 (6)
Os(2)–S(1)–Os(3)	72.15 (12)	S(1)–Os(3)–C(9A)	155.2 (6)
Os(2)–S(1)–Pt(1)	72.01 (13)	S(1)–Pt(1)–P(1)	99.11 (16)
Os(3)–S(1)–Pt(1)	73.37 (13)	S(1)–Pt(1)–P(2)	160.70 (16)
Os(2)–Os(1)–C(1A)	104.04 (50)	Os(1)–C(1A)–O(1A)	174.6 (16)
Os(2)–Os(1)–C(2A)	87.76 (44)	Os(1)–C(2A)–O(2A)	178.1 (13)
Os(2)–Os(1)–C(3A)	89.12 (50)	Os(1)–C(3A)–O(3A)	178.3 (16)
Os(3)–Os(1)–C(1A)	162.03 (49)	Os(2)–C(4A)–O(4A)	173.9 (16)
Os(3)–Os(1)–C(2A)	80.70 (46)	Os(2)–C(5A)–O(5A)	162.6 (15)
Os(3)–Os(1)–C(3A)	94.73 (52)	Os(2)–C(6A)–O(6A)	177.3 (16)
Os(1)–Os(2)–C(4A)	75.76 (52)	Os(3)–C(7A)–O(7A)	164.0 (16)
Os(1)–Os(2)–C(5A)	169.20 (50)	Os(3)–C(8A)–O(8A)	179.1 (14)
Os(1)–Os(2)–C(6A)	92.66 (54)	Os(3)–C(9A)–O(9A)	175.9 (19)
Os(3)–Os(2)–C(4A)	131.98 (54)	Pt(1)–P(1)–C(11)	118.4 (6)
Os(3)–Os(2)–C(5A)	125.99 (50)	Pt(1)–P(1)–C(17)	114.6 (6)
Os(3)–Os(2)–C(6A)	104.40 (53)	Pt(1)–P(1)–C(18)	112.7 (6)
Pt(1)–Os(2)–C(4A)	151.19 (52)	Pt(1)–P(2)–C(21)	118.9 (6)
Pt(1)–Os(2)–C(5A)	65.63 (50)	Pt(1)–P(2)–C(27)	113.1 (6)
Pt(1)–Os(2)–C(6A)	105.5 (6)	Pt(1)–P(2)–C(28)	114.4 (6)
Os(1)–Os(3)–C(7A)	176.9 (6)	Os(1)–P(3)–C(31)	113.25 (50)
Os(1)–Os(3)–C(8A)	89.2 (6)	Os(1)–P(3)–C(37)	116.7 (6)
Os(1)–Os(3)–C(9A)	83.2 (6)	Os(1)–P(3)–C(38)	116.3 (5)
Os(2)–Os(3)–C(7A)	120.21 (54)		
Molecule B			
Os(5)–Os(4)–Os(6)	60.68 (2)	Os(5)–Os(6)–C(8B)	130.90 (53)
Os(4)–Os(5)–Os(6)	59.42 (2)	Os(5)–Os(6)–C(9B)	110.9 (6)
Os(4)–Os(6)–Os(5)	59.90 (2)	Pt(2)–Os(6)–C(7B)	65.19 (52)
Os(4)–Os(5)–Pt(2)	117.65 (3)	Pt(2)–Os(6)–C(8B)	145.2 (6)
Os(6)–Os(5)–Pt(2)	58.27 (2)	Pt(2)–Os(6)–C(9B)	113.4 (6)
Os(4)–Os(6)–Pt(2)	118.86 (3)	Os(5)–Pt(2)–P(4)	110.80 (13)
Os(5)–Os(6)–Pt(2)	59.00 (2)	Os(5)–Pt(2)–P(5)	131.98 (12)
Os(5)–Pt(2)–Os(6)	62.73 (2)	Os(6)–Pt(2)–P(4)	109.66 (12)
S(2)–Os(5)–Os(4)	89.96 (11)	Os(6)–Pt(2)–P(5)	136.89 (14)
S(2)–Os(5)–Os(6)	52.52 (10)	Os(5)–Os(4)–P(6)	108.82 (12)
S(2)–Os(6)–Os(4)	90.51 (10)	Os(6)–Os(4)–P(6)	169.42 (12)
S(2)–Os(6)–Os(5)	52.86 (11)	S(2)–Os(5)–C(4B)	98.9 (6)
S(2)–Os(5)–Pt(2)	53.08 (10)	S(2)–Os(5)–C(5B)	93.1 (6)
S(2)–Os(6)–Pt(2)	53.48 (11)	S(2)–Os(5)–C(6B)	164.3 (6)
S(2)–Pt(2)–Os(5)	54.72 (11)	S(2)–Os(6)–C(7B)	92.19 (53)
S(2)–Pt(2)–Os(6)	54.77 (11)	S(2)–Os(6)–C(8B)	102.6 (6)
Os(5)–S(2)–Os(6)	74.63 (13)	S(2)–Os(6)–C(9B)	161.9 (6)
Os(5)–S(2)–Pt(2)	72.20 (13)	S(2)–Pt(2)–P(4)	161.33 (17)
Os(6)–S(2)–Pt(2)	71.75 (12)	S(2)–Pt(2)–P(5)	97.67 (11)
Os(5)–Os(4)–C(1B)	159.75 (53)	Os(4)–C(1B)–O(1B)	177.2 (17)
Os(5)–Os(4)–C(2B)	89.0 (6)	Os(4)–C(2B)–O(2B)	177.3 (18)
Os(5)–Os(4)–C(3B)	82.24 (53)	Os(4)–C(3B)–O(3B)	175.0 (15)
Os(6)–Os(4)–C(1B)	99.12 (53)	Os(5)–C(4B)–O(4B)	175.1 (16)
Os(6)–Os(4)–C(2B)	88.3 (6)	Os(5)–C(5B)–O(5B)	167.6 (17)
Os(6)–Os(4)–C(3B)	86.52 (52)	Os(5)–C(6B)–O(6B)	179.2 (19)
Os(4)–Os(5)–C(4B)	85.43 (53)	Os(6)–C(7B)–O(7B)	162.8 (16)
Os(4)–Os(5)–C(5B)	176.9 (6)	Os(6)–C(8B)–O(8B)	174.7 (17)
Os(4)–Os(5)–C(6B)	86.1 (6)	Os(6)–C(9B)–O(9B)	177.9 (17)
Os(6)–Os(5)–C(4B)	130.83 (54)	Pt(2)–P(4)–C(41)	116.9 (6)
Os(6)–Os(5)–C(5B)	122.3 (6)	Pt(2)–P(4)–C(47)	114.3 (7)
Os(6)–Os(5)–C(6B)	113.1 (6)	Pt(2)–P(4)–C(48)	114.7 (6)
Pt(2)–Os(5)–C(4B)	140.43 (54)	Pt(2)–P(5)–C(51)	121.2 (6)
Pt(2)–Os(5)–C(5B)	64.0 (6)	Pt(2)–P(5)–C(57)	112.6 (7)
Pt(2)–Os(5)–C(6B)	116.1 (6)	Pt(2)–P(5)–C(58)	112.8 (7)
Os(4)–Os(6)–C(7B)	175.95 (52)	Os(4)–P(6)–C(61)	113.4 (6)
Os(4)–Os(6)–C(8B)	81.9 (6)	Os(4)–P(6)–C(17)	111.5 (6)
Os(4)–Os(6)–C(9B)	86.1 (6)	Os(4)–P(6)–C(68)	119.9 (6)
Os(5)–Os(6)–C(7B)	124.14 (52)		

Table IX. Positional and Thermal Parameters and Their Estimated Standard Deviations for $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (IV)

atom	*x*	*y*	*z*	*B*(1,1)[a]	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)	B_{eq}
Pt	0.28069 (4)	−0.11643 (3)	0.26577 (3)	2.20 (2)	2.22 (1)	1.94 (2)	−0.11 (1)	0.24 (2)	0.02 (1)	2.184 (9)
Os(1)	0.40646 (4)	0.08534 (3)	0.17857 (3)	2.03 (2)	2.29 (1)	2.02 (2)	0.18 (1)	0.01 (1)	−0.05 (1)	2.174 (9)
Os(2)	0.12852 (4)	0.08422 (3)	0.22719 (3)	2.61 (2)	2.07 (1)	1.80 (2)	−0.20 (1)	−0.12 (2)	−0.33 (1)	2.160 (8)
Os(3)	0.36802 (4)	0.04766 (3)	0.34928 (3)	2.18 (2)	1.85 (1)	1.84 (2)	−0.09 (1)	−0.01 (1)	−0.23 (1)	1.973 (8)
S	0.2870 (3)	0.2110 (2)	0.2556 (2)	3.0 (1)	2.06 (9)	2.6 (1)	0.00 (9)	−0.1 (1)	−0.29 (9)	2.58 (6)
P(1)	0.1411 (3)	−0.2297 (2)	0.3577 (2)	2.9 (1)	2.5 (1)	2.7 (1)	−0.65 (9)	0.4 (1)	−0.31 (9)	2.70 (6)
P(2)	0.3495 (3)	−0.2563 (2)	0.1949 (2)	3.6 (1)	2.5 (1)	2.4 (1)	0.4 (1)	−0.2 (1)	−0.67 (9)	2.80 (6)
P(3)	0.0152 (3)	0.2306 (3)	0.1366 (2)	2.9 (1)	3.5 (1)	2.9 (1)	0.7 (1)	−0.1 (1)	0.3 (1)	3.24 (7)

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
O(1)	0.2943 (10)	0.0343 (7)	0.0168 (6)	5.2 (2)	C(15)	0.125 (2)	−0.5818 (11)	0.3947 (10)	5.1 (3)
O(2)	0.6658 (10)	−0.0667 (7)	0.2115 (6)	5.3 (2)	C(16)	0.094 (1)	−0.4654 (10)	0.3664 (9)	4.4 (3)
O(3)	0.5555 (10)	0.2994 (7)	0.0950 (6)	5.2 (2)	C(17)	0.125 (1)	−0.1915 (9)	0.4593 (8)	3.6 (2)
O(4)	−0.0971 (12)	0.0896 (9)	0.3527 (8)	7.3 (3)	C(18)	−0.036 (1)	−0.2240 (10)	0.3283 (9)	4.3 (3)
O(5)	0.0026 (10)	−0.0833 (7)	0.1348 (6)	5.4 (2)	C(21)	0.462 (1)	−0.3744 (8)	0.2475 (7)	2.6 (2)
O(6)	0.6116 (10)	0.1648 (7)	0.4008 (6)	4.8 (2)	C(22)	0.573 (1)	−0.3489 (9)	0.2873 (8)	3.2 (2)
O(7)	0.2033 (10)	0.0767 (7)	0.5004 (6)	5.3 (2)	C(23)	0.663 (1)	−0.4354 (10)	0.3258 (8)	3.8 (3)
O(8)	0.5096 (9)	−0.1834 (7)	0.4219 (6)	4.1 (2)	C(24)	0.643 (1)	−0.5473 (10)	0.3216 (8)	3.9 (3)
C(1)	0.333 (1)	0.0549 (9)	0.0797 (8)	3.3 (2)	C(25)	0.532 (1)	−0.5726 (10)	0.2825 (9)	4.1 (3)
C(2)	0.562 (1)	−0.0106 (10)	0.1991 (8)	3.8 (3)	C(26)	0.438 (1)	−0.4883 (9)	0.2448 (8)	3.2 (2)
C(3)	0.500 (1)	0.2155 (9)	0.1281 (8)	3.4 (2)	C(27)	0.205 (1)	−0.3266 (10)	0.1584 (9)	4.3 (3)
C(4)	−0.015 (1)	0.0865 (10)	0.3018 (8)	3.9 (3)	C(28)	0.445 (1)	−0.2162 (10)	0.0995 (9)	4.3 (3)
C(5)	0.059 (1)	−0.0262 (9)	0.1751 (8)	3.2 (2)	C(31)	0.114 (1)	0.3085 (8)	0.0497 (7)	2.4 (2)
C(6)	0.518 (1)	0.1220 (9)	0.3804 (8)	3.3 (2)	C(32)	0.196 (1)	0.3974 (10)	0.0604 (9)	4.3 (3)
C(7)	0.266 (1)	0.0608 (9)	0.4445 (7)	3.1 (2)	C(33)	0.276 (2)	0.4524 (11)	−0.0039 (10)	5.3 (3)
C(8)	0.447 (1)	−0.1009 (8)	0.3891 (7)	2.8 (2)	C(34)	0.275 (2)	0.4209 (12)	−0.0772 (11)	6.0 (4)
C(11)	0.179 (1)	−0.3851 (9)	0.3874 (7)	2.8 (2)	C(35)	0.201 (2)	0.3337 (12)	−0.0885 (10)	5.8 (4)
C(12)	0.295 (1)	−0.4218 (10)	0.4301 (9)	4.2 (3)	C(36)	0.121 (1)	0.2742 (10)	−0.0246 (9)	4.4 (3)
C(13)	0.328 (1)	−0.5380 (11)	0.4575 (9)	4.8 (3)	C(37)	−0.058 (2)	0.3413 (13)	0.1864 (11)	6.3 (4)
C(14)	0.240 (1)	−0.6180 (11)	0.4387 (9)	4.8 (3)	C(38)	−0.133 (2)	0.1861 (13)	0.0873 (11)	6.1 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}[h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)]]$.

Table X. Interatomic Distances (Å) with Esds for $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (IV)

Os(1)-Os(2)	2.816 (1)	C(1)-O(1)	1.179 (11)
Os(1)-Os(3)	2.770 (1)	C(2)-O(2)	1.195 (11)
Os(2)-Os(3)	3.064 (1)	C(3)-O(3)	1.187 (11)
Os(1)-Pt	2.853 (1)	C(4)-O(4)	1.157 (11)
Os(2)-Pt	2.740 (1)	C(5)-O(5)	1.191 (11)
Os(3)-Pt	2.766 (1)	C(6)-O(6)	1.147 (10)
Os(1)-S	2.406 (2)	C(7)-O(7)	1.140 (11)
Os(2)-S	2.315 (2)	C(8)-O(8)	1.176 (10)
Os(3)-S	2.350 (2)	P(1)-C(17)	1.817 (10)
Os(1)-C(1)	1.887 (10)	P(1)-C(18)	1.798 (11)
Os(1)-C(2)	1.859 (10)	P(2)-C(27)	1.832 (10)
Os(1)-C(3)	1.868 (10)	P(2)-C(28)	1.804 (12)
Os(2)-C(4)	1.847 (11)	P(3)-C(37)	1.807 (13)
Os(2)-C(5)	1.858 (9)	P(3)-C(38)	1.816 (13)
Os(3)-C(6)	1.867 (8)	P(1)-C(11)	1.847 (9)
Os(3)-C(7)	1.870 (10)	P(2)-C(21)	1.835 (8)
Os(3)-C(8)	1.904 (9)	P(3)-C(31)	1.820 (9)
Pt···C(8)	2.654 (9)	$C\text{-}C_{av}$(11-16)	1.38 (2)
Pt-P(1)	2.285 (2)	$C\text{-}C_{av}$(21-26)	1.37 (2)
Pt-P(2)	2.292 (2)	$C\text{-}C_{av}$(31-36)	1.36 (3)
Os(2)-P(3)	2.317 (2)		

amplitudes for all four structural analyses are given in the supplementary material.

Results

When allowed to react at room temperature for 1 h, solutions of $Os_3(CO)_{10}(\mu_3\text{-}S)$ plus $Pt(PMe_2Ph)_4$ yielded four major products. These were identified as $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I), $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II), $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)$ (III), and $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (IV). All the compounds have been characterized by IR and ^1H NMR analyses. These results are listed in Table I. In addition, compounds I, II, and IV have been characterized by single-crystal X-ray diffraction analyses. Compounds III and IV can be prepared by the decarbonylation at 68 °C of I and II, respectively, in yields of 58% and 74%.

When solutions of IV are exposed to UV radiation the new compound $HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$ (V) was formed in 48% yield. Compound V was characterized by IR and ^1H NMR spectroscopies and by a single-crystal X-ray diffraction analysis; see below.

Structures. $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$ (I) and $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$ (II). Because of the close similarities of the structures of I and II, these two analyses will be described jointly. Compound II is simply a PMe_2Ph derivative of I. An ORTEP diagram of I is shown in Figure 1. Final fractional atomic coordinates are listed in Table III. Interatomic distances and angles are listed in Tables IV and V, respectively.

Compound II crystallizes with 2 independent molecules in the asymmetric crystallographic unit. Final fractional atomic coordinates are listed in Table VI. Interatomic distances and selected interatomic angles are given in Tables VII and VIII. Both independent molecules have very similar geometry. An ORTEP diagram of one of these is shown in Figure 2.

Compound I and II consist of nearly planar clusters of one platinum and three osmium atoms. The dihedral angle between the Os(1)–Os(2)–Os(3) and Pt–Os(1)–Os(2) planes in I is 176.8°. The corresponding value in II is 175.2° [177.7°]. In all cases the value in brackets for compound II is the corresponding value for the second crystallographically independent molecule. I and II both contain five metal–metal bonds. As a result, each metal atom can achieve an 18-electron configuration. The three osmium–osmium bonds in I are of nearly equal length, 2.869 (1), 2.867 (1), and 2.870 (1) Å and are very similar to those in $Os_3(CO)_{12}$, 2.877 (3) Å.[17] Similar values are observed in II except for the diagonal bond Os(2)–Os(3) in molecule A which seems to be significantly shorter at 2.833 (1) Å. However, this shortening does not show up in molecule B and is therefore believed not to be significant.

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(17) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

Table XI. Selected Interatomic Angles (deg) with Esds for $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (IV)

Os(2)-Os(1)-Os(3)	66.52 (1)	S-Os(3)-C(7)	100.78 (28)
Os(1)-Os(2)-Os(3)	56.02 (1)	S-Os(3)-C(8)	159.79 (29)
Os(1)-Os(3)-Os(2)	57.46 (1)	S-Os(2)-P(3)	90.59 (8)
Pt-Os(1)-Os(2)	58.81 (1)	C(1)-Os(1)-C(2)	104.8 (4)
Pt-Os(1)-Os(3)	58.91 (1)	C(1)-Os(1)-C(3)	96.1 (4)
Pt-Os(2)-Os(1)	61.76 (1)	C(2)-Os(1)-C(3)	95.9 (4)
Pt-Os(2)-Os(3)	56.58 (1)	C(4)-Os(2)-C(5)	96.5 (4)
Pt-Os(3)-Os(1)	62.03 (1)	C(6)-Os(3)-C(7)	93.7 (4)
Pt-Os(3)-Os(2)	55.79 (1)	C(6)-Os(3)-C(8)	93.4 (4)
Os(1)-Pt-Os(2)	60.43 (1)	C(7)-Os(3)-C(8)	97.8 (4)
Os(1)-Pt-Os(3)	59.06 (1)	C(4)-Os(2)-P(3)	88.5 (3)
Os(2)-Pt-Os(3)	67.63 (1)	C(5)-Os(2)-P(3)	91.9 (3)
S-Os(1)-Os(2)	51.91 (5)	P(1)-Pt-P(2)	95.65 (9)
S-Os(1)-Os(3)	53.43 (5)	Os(1)-C(1)-O(1)	176.6 (9)
S-Os(2)-Os(3)	49.42 (5)	Os(1)-C(2)-O(2)	176.2 (9)
S-Os(2)-Os(1)	54.87 (6)	Os(1)-C(3)-O(3)	178.2 (9)
S-Os(3)-Os(1)	55.32 (6)	Os(2)-C(4)-O(4)	174.8 (10)
S-Os(3)-Os(2)	48.46 (5)	Os(2)-C(5)-O(5)	169.9 (9)
Os(1)-S-Os(2)	73.22 (6)	Os(3)-C(6)-O(6)	178.1 (8)
Os(1)-S-Os(3)	71.25 (6)	Os(3)-C(7)-O(7)	175.4 (9)
Os(2)-S-Os(3)	82.12 (7)	Os(3)-C(8)-O(8)	168.7 (8)
Pt-Os(1)-S	94.63 (5)	Os(2)-P(3)-C(37)	113.6 (5)
Pt-Os(2)-S	99.81 (5)	Os(2)-P(3)-C(38)	114.3 (4)
Pt-Os(3)-S	98.25 (5)	Os(2)-P(3)-C(31)	117.3 (3)
Os(2)-Os(1)-C(1)	82.59 (29)	Pt-P(1)-C(17)	115.0 (3)
Os(2)-Os(1)-C(2)	138.04 (32)	Pt-P(1)-C(18)	115.0 (4)
Os(2)-Os(1)-C(3)	124.83 (29)	Pt-P(1)-C(11)	120.2 (3)
Os(3)-Os(1)-C(1)	143.04 (32)	Pt-P(2)-C(27)	112.7 (3)
Os(3)-Os(1)-C(2)	86.93 (34)	Pt-P(2)-C(28)	118.7 (3)
Os(3)-Os(1)-C(3)	117.83 (30)	Pt-P(2)-C(21)	118.6 (3)
Pt-Os(1)-C(1)	87.99 (29)	C(17)-P(1)-C(18)	100.4 (5)
Pt-Os(1)-C(2)	80.91 (31)	C(11)-P(1)-C(17)	100.9 (4)
Pt-Os(1)-C(3)	175.38 (30)	C(11)-P(1)-C(18)	102.6 (4)
Os(1)-Os(2)-C(4)	154.64 (32)	Os(1)-Pt-P(1)	159.35 (6)
Os(1)-Os(2)-C(5)	102.44 (30)	Os(1)-Pt-P(2)	104.69 (7)
Os(3)-Os(2)-C(4)	99.10 (32)	Os(2)-Pt-P(1)	102.39 (6)
Os(3)-Os(2)-C(5)	125.73 (28)	Os(2)-Pt-P(2)	134.89 (6)
Pt-Os(2)-C(4)	110.95 (31)	Os(3)-Pt-P(1)	105.25 (6)
Pt-Os(2)-C(5)	69.27 (28)	Os(3)-Pt-P(2)	145.04 (6)
Os(1)-Os(3)-C(6)	100.59 (32)	S-Os(1)-C(1)	121.10 (28)
Os(1)-Os(3)-C(7)	152.46 (28)	S-Os(1)-C(2)	133.72 (32)
Os(1)-Os(3)-C(8)	104.66 (28)	S-Os(1)-C(3)	85.19 (30)
Os(2)-Os(3)-C(6)	141.55 (29)	S-Os(2)-C(4)	106.76 (31)
Os(2)-Os(3)-C(7)	97.19 (29)	S-Os(2)-C(5)	156.69 (31)
Os(2)-Os(3)-C(8)	121.18 (26)	S-Os(3)-C(6)	93.31 (29)
Pt-Os(3)-C(6)	146.08 (29)	C(27)-P(2)-C(28)	100.6 (5)
Pt-Os(3)-C(7)	115.00 (27)	C(21)-P(2)-C(27)	104.7 (4)
Pt-Os(3)-C(8)	66.33 (26)	C(21)-P(2)-C(28)	99.1 (5)
Os(1)-Os(2)-P(3)	107.39 (7)	C(37)-P(3)-C(38)	102.2 (6)
Os(3)-Os(2)-P(3)	139.88 (7)	C(31)-P(3)-C(37)	104.1 (5)
Pt-Os(2)-P(3)	153.80 (7)	C(31)-P(3)-C(38)	103.6 (5)

The platinum–osmium bonds are slightly shorter than osmium–osmium bonds and seem to be significantly different in I, 2.768 (1) and 2.836 (1) Å. The inequivalence seems to be present in II also but to a lesser degree, 2.789 (1) Å [2.782 (1) Å] and 2.833 (1) Å [2.803 (1) Å]. The Pt–Os distances are similar to those found in the compound $H_2Os_3Pt(CO)_{10}[P(C_6H_{11})_3]$.[18] Compounds I and II each contain one triply bridging sulfido ligand that spans the $PtOs_2$ triangle. The Os–S distances range from 2.392 (4) to 2.416 (4) Å and are very similar to those found in $Os_3(CO)_9(\mu_3\text{-}S)_2$.[19] As expected, the Pt–S distances, 2.337 (4)–2.354 (4) Å, are slightly shorter than the Os–S distances but are similar to those observed in other sulfido platinum cluster compounds.[20]

The platinum atoms in I and II contain two PMe_2Ph ligands. All carbonyl ligands are located on the osmium atoms. In I, Os(3) contains four CO ligands and Os(1) and Os(2) contain three each. One CO ligand on each of Os(1) and Os(2) forms a semibridging interaction to the platinum atom, Pt···C(3) = 2.607 (15) Å and Pt···C(4) = 2.636 (19) Å. In II a third phosphine ligand is located on the unique osmium atom. Each osmium atom in II contains three carbonyl ligands, and as in I each of the osmium atoms bonded to the platinum atom has one carbonyl ligand that acts as a semibridge to the platinum atom.

$PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$ (IV). An ORTEP drawing of IV is shown in Figure 3. Final fractional atomic coordinates are listed in Table IX. Interatomic distances and angles are listed in Tables X and XI, respectively. Compound IV consists of a tetrahedral cluster of one platinum and three osmium atoms. A triply bridging sulfido ligand spans the triosmium face. The cluster is significantly distorted as is apparent from the metal–metal bonding. The three osmium–osmium bond distances span a range of nearly 0.3 Å. The shortest Os–Os bond, Os(1)–Os(3) = 2.770 (1) Å, is significantly shorter than that found in $Os_3(CO)_{12}$, 2.877 (3) Å,[17] while the longest bond, Os(2)–Os(3) = 3.064 (1) Å, is much longer. The platinum–osmium bonds are also inequivalent, Os(1)–Pt = 2.853 (1) Å, Os(2)–Pt = 2.740 (1) Å, and Os(3)–Pt = 2.766 (1) Å, but are similar in length to those found in I and II. The osmium–sulfur distances span a wide range from 2.315 (2) Å for Os(2)–S to 2.406 (2) Å for Os(1)–S. The platinum atom contains two PMe_2Ph ligands while osmium Os(2) has one. All eight carbonyl ligands are coordinated to the osmium atoms. Os(1) and Os(3) contain three carbonyls each, while Os(2) has only two. C(8)–O(8) is a semibridging ligand to the platinum atom, Pt···C(8) = 2.654 (9) Å.

Compound IV is stereochemically nonrigid at ambient temperature. At room temperature the methyl groups on the PMe_2Ph ligands appear as a doublet (δ 2.32, 6 H) and quartet (δ 1.73, 12 H). The quartet nature of the latter is due to a superposition of ^{31}P and ^{195}Pt couplings and can be attributed to the phosphine ligands coordinated to the platinum atom. As the temperature is lowered, the resonance at δ 1.73 broadens and re-forms into resonances that sharpen into two doublets (δ 1.73 (J_{P-H} = 9.5 Hz) and δ 1.58 (J_{P-H} = 10.1 Hz) at −60 °C. At this temperature the ^{195}Pt couplings are not clearly resolved. At still lower temperatures the doublet at δ 1.73 broadens further and exists as a very broad singlet at −90 °C, the lowest temperature recorded. The other methyl resonances are only slightly broadened at −90 °C.

We attribute these changes to intramolecular ligand-exchange processes of two different types. The lowest energy rearrangement leads to an averaging of the diastereotopic methyl groups on the phosphine ligand coordinated to the osmium atom. This averaging is only beginning to slow on the NMR time scale at −90 °C. The rearrangement could be as simple as a polytopal process that interchanges the sites of phosphine P(3) with C(4)–O(4); see Figure 3. The higher energy process leads to an averaging of the diastereotopic methyl groups on the phosphines P(1) and P(2) coordinated to the platinum atom. This process could be as simple as a polytopal process that causes phosphines P(1) and P(2) to interchange their sites.

$HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$ (V). An ORTEP drawing of the molecular structure of V is shown in Figure 4. Final fractional atomic coordinates are listed in Table XII. Interatomic distances and angles are listed in Tables XIII and XIV. The cluster core of V is similar to that of IV in that it consists of a tetrahedral group of one platinum and three osmium atoms and has a triply bridging sulfido ligand on the triosmium face. As in IV the metal–metal bond distances span a wide range, but the longest osmium–osmium bond, Os(2)–Os(3) = 2.972 (1) Å, is nearly 0.1 Å shorter than that in IV, while the shortest, Os(1)–Os(3) = 2.837 Å, is nearly

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Table XII. Positional and Thermal Parameters with Esds for $HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$ (V)

atom	x	y	z	$B(1,1)^a$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$	B_{eq}
Pt	−0.16353 (6)	−0.21780 (5)	−0.16166 (4)	2.32 (3)	2.03 (3)	2.14 (2)	0.29 (2)	0.70 (2)	0.19 (2)	2.15 (1)
Os(1)	0.03135 (6)	−0.31296 (5)	−0.26672 (4)	2.46 (3)	2.06 (3)	2.41 (3)	0.17 (2)	0.66 (2)	0.37 (2)	2.28 (1)
Os(2)	−0.20698 (6)	−0.42356 (5)	−0.23355 (4)	2.89 (3)	2.24 (3)	1.89 (2)	0.45 (2)	0.48 (2)	0.35 (2)	2.31 (1)
Os(3)	−0.20048 (6)	−0.25747 (5)	−0.35805 (4)	2.58 (3)	2.24 (3)	2.04 (2)	0.59 (2)	0.63 (2)	0.05 (2)	2.28 (1)
S	−0.1157 (4)	−0.4314 (3)	−0.3762 (3)	3.3 (2)	2.3 (2)	2.3 (2)	0.4 (2)	0.7 (2)	0.2 (1)	2.62 (9)
P(1)	−0.3436 (4)	−0.1330 (4)	−0.1148 (3)	2.7 (2)	3.4 (2)	3.2 (2)	0.8 (2)	0.7 (2)	0.3 (2)	3.1 (1)
P(2)	0.1019 (4)	−0.4314 (3)	−0.1682 (3)	2.7 (2)	2.4 (2)	2.4 (2)	0.6 (2)	0.4 (2)	0.1 (2)	2.51 (9)
P(3)	−0.1643 (5)	−0.2541 (4)	−0.5152 (3)	4.9 (7)	2.7 (2)	1.9 (2)	0.7 (2)	0.7 (2)	0.3 (2)	3.1 (1)

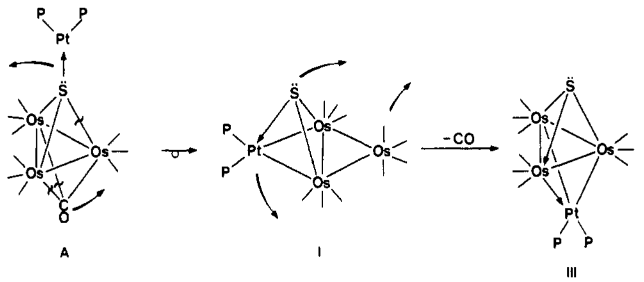
atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.243 (1)	−0.3634 (11)	−0.3986 (9)	5.3 (3)	C(16)	−0.330 (2)	−0.126 (1)	0.079 (1)	3.7 (4)
O(2)	0.193 (1)	−0.1341 (10)	−0.1496 (9)	5.1 (3)	C(17)	−0.485 (2)	−0.152 (2)	−0.191 (1)	4.9 (5)
O(3)	−0.462 (1)	−0.5293 (12)	−0.2932 (10)	6.5 (4)	C(18)	−0.321 (2)	0.010 (1)	−0.088 (1)	4.5 (4)
O(4)	−0.273 (1)	−0.4107 (10)	−0.0308 (9)	5.1 (3)	C(21)	0.017 (1)	−0.559 (1)	−0.188 (1)	2.2 (3)
O(5)	−0.478 (1)	−0.3108 (11)	−0.4077 (10)	6.2 (4)	C(22)	0.081 (2)	−0.652 (1)	−0.175 (1)	3.3 (4)
O(6)	−0.239 (1)	−0.0194 (10)	−0.3194 (9)	5.2 (3)	C(23)	0.014 (2)	−0.750 (1)	−0.188 (1)	3.8 (4)
O(7)	−0.005 (1)	−0.1154 (9)	0.0104 (8)	4.4 (3)	C(24)	−0.111 (2)	−0.754 (1)	−0.212 (1)	3.8 (4)
C(1)	0.160 (1)	−0.343 (1)	−0.349 (1)	2.6 (3)	C(25)	−0.179 (2)	−0.664 (1)	−0.226 (1)	3.5 (4)
C(2)	0.128 (2)	−0.202 (1)	−0.192 (1)	3.7 (4)	C(26)	−0.116 (1)	−0.564 (1)	−0.213 (1)	2.3 (3)
C(3)	−0.355 (2)	−0.483 (1)	−0.269 (1)	3.9 (4)	C(27)	0.270 (2)	−0.456 (1)	−0.173 (1)	3.5 (4)
C(4)	−0.248 (2)	−0.409 (1)	−0.111 (1)	3.7 (4)	C(28)	0.097 (2)	−0.385 (1)	−0.044 (1)	3.2 (3)
C(5)	−0.367 (2)	−0.290 (1)	−0.388 (1)	3.6 (4)	C(31)	−0.203 (2)	−0.133 (1)	−0.559 (1)	3.6 (4)
C(6)	−0.225 (2)	−0.113 (1)	−0.330 (1)	3.6 (4)	C(32)	−0.328 (2)	−0.101 (2)	−0.557 (1)	5.3 (5)
C(7)	−0.065 (2)	−0.153 (1)	−0.057 (1)	2.9 (3)	C(33)	−0.364 (2)	−0.005 (2)	−0.589 (2)	6.8 (6)
C(11)	−0.394 (1)	−0.171 (1)	−0.007 (1)	2.7 (3)	C(34)	−0.271 (2)	0.051 (2)	−0.617 (2)	7.1 (6)
C(12)	−0.490 (2)	−0.249 (2)	−0.005 (1)	4.7 (4)	C(35)	−0.151 (2)	0.024 (2)	−0.624 (2)	7.1 (6)
C(13)	−0.522 (2)	−0.282 (2)	0.075 (1)	5.5 (5)	C(36)	−0.114 (2)	−0.068 (2)	−0.591 (1)	5.8 (5)
C(14)	−0.459 (2)	−0.238 (2)	0.156 (2)	5.9 (5)	C(37)	−0.260 (2)	−0.354 (2)	−0.593 (1)	5.4 (5)
C(15)	−0.365 (2)	−0.162 (2)	0.161 (1)	5.1 (5)	C(38)	−0.006 (2)	−0.281 (1)	−0.548 (1)	4.6 (4)

[a] The form of the anisotropic thermal parameter is $\exp[[h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2hlb^*c^*B(2.3)]]$.

Table XIII. Interatomic Distances (Å) with Esds for $HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$ (V)

Os(1)–Os(2)	2.920 (1)	C(1)–O(1)	1.174 (13)
Os(1)–Os(3)	2.837 (1)	C(2)–O(2)	1.152 (13)
Os(2)–Os(3)	2.972 (1)	C(3)–O(3)	1.248 (14)
Os(1)–Pt	2.816 (1)	C(4)–O(4)	1.201 (14)
Os(2)–Pt	2.684 (1)	C(5)–O(5)	1.192 (14)
Os(3)–Pt	2.806 (1)	C(6)–O(6)	1.198 (13)
Os(1)–S	2.440 (3)	C(7)–O(7)	1.147 (12)
Os(2)–S	2.317 (3)	P(1)–C(11)	1.808 (11)
Os(3)–S	2.395 (3)	P(1)–C(17)	1.771 (14)
Os(1)–C(1)	1.861 (11)	P(1)–C(18)	1.807 (13)
Os(1)–C(2)	1.870 (13)	P(2)–C(21)	1.803 (11)
Os(2)–C(3)	1.708 (13)	P(2)–C(27)	1.789 (12)
Os(2)–C(4)	1.840 (13)	P(2)–C(28)	1.810 (11)
Os(2)–C(26)	2.099 (10)	P(3)–C(31)	1.797 (13)
Os(3)–C(5)	1.777 (13)	P(3)–C(37)	1.798 (14)
Os(3)–C(6)	1.849 (13)	P(3)–C(38)	1.776 (14)
Pt–C(7)	1.849 (11)	C–C$_{av}$(11–16)	1.37 (2)
Os(1)–P(2)	2.324 (3)	C–C$_{av}$(21–26)	1.39 (3)
Os(3)–P(3)	2.332 (3)	C–C$_{av}$(31–36)	1.37 (4)
Pt–P(1)	2.289 (3)	Pt···C(4)	2.775 (13)

Scheme I



0.07 Å longer. One platinum–osmium bond, Os(2)–Pt = 2.684 (1) Å, is significantly shorter than the other two, Os(1)–Pt = 2.816 (1) Å and Os(3)–Pt = 2.806 (1) Å. The latter two are similar to the distances observed in I and II. Compound V contains three phosphine ligands, one on the platinum atom, one on Os(1), and one on Os(3). They are normal in all respects, except for the one on Os(1) in which the phenyl ring is orthometalated to Os(2), Os(2)–C(26) = 2.099 (10) Å. Each osmium atom contains two carbonyl ligands. The platinum atom has only one carbonyl ligand. C(4)–O(4) is weakly semibridging ligand to the platinum atom, Pt···C(4) = 2.775 (13) Å. Compound V also contains one bridging hydride ligand verified only by its characteristic high-field NMR absorption, δ −16.84. Its position was not determined independently in the crystallographic analysis, but a probable location for it across the Os(1)–Os(3) bond is suggested by the presence of a large cavity in the ligand structure circumscribed by the ligands C(1)–O(1), C(2)–O(2), C(6)–O(6), and P(3).

Discussion

In reactions of $Os_3(CO)_{12}$ with $Pt(PR_3)_4$ no mixed-metal compounds, only phosphine-substituted derivatives of $Os_3(CO)_{12}$, were formed.[21] It is believed that the facile formation of the mixed-metal compounds in the reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with $Pt(PMe_2Ph)_4$ is a result of preliminary bonding interactions of the platinum atom with the lone pair of electrons on the sulfido ligand in $Os_3(CO)_{10}(\mu_3\text{-}S)$. An intermediate like A (Scheme I) might be formed initially. From intermediate A compound I could be formed by cleavage of one of the osmium–sulfur bonds, a shift of the triply bridging carbonyl ligand to the osmium atom where the osmium–sulfur bond was cleaved, and the formation of platinum–osmium bonds to the remaining osmium atoms. II is simply a PMe_2Ph derivative of I. Its formation is probably a result of subsequent reactions with adventitious PMe_2Ph released from $Pt(PMe_2Ph)_4$. This was supported by an independent synthesis of II from I.

When heated, I and II both lose 1 mol of CO and are converted into the closed-tetrahedral cluster compounds III

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Table XIV. Interatomic Angles (deg) with Esds for $HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$ (V)

Os(2)-Os(1)-Os(3)	62.15 (2)	Os(1)-Pt-P(1)	164.73 (8)	Os(2)-C(4)-O(4)	172.6 (11)	Os(1)-Os(3)-P(3)	107.77 (9)
Os(1)-Os(2)-Os(3)	57.54 (2)	Os(2)-Pt-P(1)	114.05 (8)	Os(3)-C(5)-O(5)	179.8 (12)	Os(2)-Os(3)-P(3)	135.53 (8)
Os(1)-Os(3)-Os(2)	60.31 (2)	Os(3)-Pt-P(1)	104.40 (8)	Os(3)-Os(1)-C(1)	112.82 (33)	Pt-Os(3)-P(3)	159.82 (9)
Os(2)-Os(1)-Pt	55.76 (1)	S-Os(1)-C(1)	88.64 (33)	Os(3)-Os(1)-C(2)	116.34 (38)	Os(3)-C(6)-O(6)	174.2 (11)
Os(3)-Os(1)-Pt	59.53 (2)	S-Os(1)-C(2)	169.29 (39)	Pt-Os(1)-C(1)	165.40 (34)	Pt-C(7)-O(7)	177.3 (11)
Os(1)-Os(2)-Pt	60.16 (2)	S-Os(2)-C(3)	100.58 (63)	Pt-Os(1)-C(2)	80.21 (38)	Os(2)-C(26)-C(21)	119.1 (8)
Os(3)-Os(2)-Pt	59.23 (2)	S-Os(2)-C(4)	168.99 (39)	Os(1)-Os(2)-C(3)	152.58 (43)	Os(2)-C(26)-C(25)	123.8 (8)
Os(1)-Os(3)-Pt	59.87 (2)	S-Os(2)-C(26)	88.65 (29)	Os(1)-Os(2)-C(4)	115.51 (38)	Pt-P(1)-C(11)	111.61 (38)
Os(2)-Os(3)-Pt	55.26 (1)	S-Os(3)-C(5)	100.67 (40)	Os(1)-Os(2)-C(26)	93.72 (29)	Pt-P(1)-C(17)	118.44 (47)
Os(1)-Pt-Os(2)	64.09 (2)	S-Os(3)-C(6)	165.39 (39)	Os(3)-Os(2)-C(3)	99.97 (43)	Pt-P(1)-C(18)	113.90 (45)
Os(1)-Pt-Os(3)	60.60 (2)	S-Os(1)-P(2)	99.73 (10)	Os(3)-Os(2)-C(4)	127.84 (39)	Os(1)-P(2)-C(21)	114.82 (36)
Os(2)-Pt-Os(3)	65.51 (2)	S-Os(3)-P(3)	87.31 (10)	Os(3)-Os(2)-C(26)	139.55 (29)	Os(1)-P(2)-C(27)	113.20 (42)
Os(2)-Os(1)-S	50.25 (7)	C(1)-Os(1)-C(2)	93.83 (5)	Pt-Os(2)-C(3)	124.97 (43)	Os(1)-P(2)-C(28)	115.14 (39)
Os(3)-Os(1)-S	53.34 (7)	C(3)-Os(2)-C(4)	90.3 (6)	Pt-Os(2)-C(4)	72.99 (38)	Os(3)-P(3)-C(31)	115.54 (41)
Os(1)-Os(2)-S	54.06 (7)	C(3)-Os(2)-C(26)	96.09 (52)	Pt-Os(2)-C(26)	134.00 (28)	Os(3)-P(3)-C(37)	112.6 (5)
Os(3)-Os(2)-S	52.06 (7)	C(4)-Os(2)-C(26)	88.65 (48)	Os(1)-Os(3)-C(5)	146.88 (40)	Os(3)-P(3)-C(38)	116.2 (5)
Os(1)-Os(3)-S	54.82 (7)	C(5)-Os(3)-C(6)	93.64 (54)	Os(1)-Os(3)-C(6)	110.87 (38)	C(11)-P(1)-C(17)	104.1 (6)
Os(2)-Os(3)-S	49.74 (7)	C(1)-Os(1)-P(2)	93.78 (35)	Os(2)-Os(3)-C(5)	87.09 (40)	C(11)-P(1)-C(18)	103.7 (6)
Pt-Os(1)-S	94.89 (7)	C(2)-Os(1)-P(2)	90.52 (39)	Os(2)-Os(3)-C(6)	129.04 (38)	C(17)-P(1)-C(18)	103.6 (6)
Pt-Os(2)-S	101.52 (7)	C(5)-Os(3)-P(3)	90.99 (41)	Os(1)-Pt-C(7)	99.71 (35)	C(21)-P(2)-C(27)	106.8 (5)
Pt-Os(3)-S	96.18 (7)	C(6)-Os(3)-P(3)	95.43 (38)	Os(2)-Pt-C(7)	131.55 (35)	C(21)-P(2)-C(28)	105.4 (5)
Os(1)-S-Os(2)	75.69 (8)	C(7)-Pt-P(1)	92.36 (36)	Os(3)-Pt-C(7)	148.06 (35)	C(27)-P(2)-C(28)	100.1 (6)
Os(1)-S-Os(3)	71.84 (8)	Os(1)-C(1)-O(1)	178.6 (11)	Os(2)-Os(1)-P(2)	77.23 (8)	C(31)-P(3)-C(37)	103.2 (6)
Os(2)-S-Os(3)	78.20 (8)	Os(1)-C(2)-O(2)	176.0 (11)	Os(3)-Os(1)-P(2)	139.35 (8)	C(31)-P(3)-C(38)	105.5 (6)
Os(2)-Os(1)-C(1)	154.18 (32)	Os(2)-C(3)-O(3)	177.2 (12)	Pt-Os(1)-P(2)	99.56 (7)	C(37)-P(3)-C(38)	102.2 (7)
Os(2)-Os(1)-C(2)	130.51 (38)						

and IV. III is believed to be a structural analogue of IV containing nine CO ligands and two PMe_2Ph ligands. The $Pt-CH_3$ couplings in the NMR spectrum of III indicate that both PMe_2Ph ligands are coordinated to the platinum atom. Only IV was characterized by crystallographic methods. Mechanistically, the loss of CO probably occurs at the CO-rich $Os(CO)_4$ group in I. Compound III could then be formed by formation of an osmium-sulfur bond, cleavage of the platinum-sulfur bond and attachment of the platinum moiety onto the face of the Os_3 triangle on the side opposite the sulfido ligand. A similar process can be envisaged for the formation of IV from II. The decarbonylation reaction is reversible, and under 1 atm CO at room temperature compounds I and II are re-formed by the addition of 1 mol of CO to III and IV, respectively.

When irradiated, solutions of IV produce significant amounts of the new compound $HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$ (V). V contains three phosphine ligands that are more widely distributed about the cluster than in II or IV. This wider distribution of the phosphine ligands may be produced by irradiation-promoted ligand-dissociation reactions. In this regard V has fewer CO ligands than all of the other clusters prepared in these reactions, and this greater degree of CO loss probably paves the way for the orthometalation of the phenyl ring of one of the phosphine ligands that has occurred.

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Registry No. I, 93426-74-5; II, 93426-75-6; III, 93426-76-7; IV, 93426-77-8; V, 93426-78-9; $Os_3(CO)_{10}(\mu_3\text{-}S)$, 93426-79-0; $Pt(PMe_2Ph)_4$, 33361-89-6; Os, 7440-04-2; Pt, 7440-06-4.

Supplementary Material Available: Tables of structure factor amplitudes for all four structures, hydrogen atom parameters for I, IV, and V and thermal parameters for II (72 pages). Ordering information is given on any current masthead page.