Journal of Organometallic Chemistry, 262 (1984) 243–252
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CLUSTER CONDENSATION REACTIONS. THE SYNTHESIS AND CRYSTAL AND MOLECULAR STRUCTURE OF $Os_6(CO)_{14}(\mu_2\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$

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(Received June 6th, 1983)

Summary

Thermal degradation of the cluster compound $Os_3(CO)_8(PPh_2H)(\mu_3\text{-}S)_2$ (I) at 125°C leads to decarbonylation and formation of the new ligand bridged hexanuclear cluster $Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ (II) in 11% yield. Space Group: $P\bar{1}$, No. 2, a 10.427(5), b 13.552(3), c 17.919(3) Å, α 84.87(2), β 75.41(3), γ 78.43(3)°, V 2399(2) $Å^3$, $Z = 2$, ρ_{calc} 2.82 g cm^{-3}. The structure was solved by the heavy atom method and refined (3223 reflections) to the final residuals $R = 0.042$ and $R_w = 0.036$. The molecule consists of two sulfido bridged open triosmium clusters which are linked by a bridging sulfido ligand and a bridging diphenylphosphino ligand.

Introduction

Considerable attention has been focused on the synthesis of high nuclearity transition metal carbonyl cluster compounds [1–7]. A procedure that is showing considerable promise involves the use of bridging ligands to promote condensation reactions [8–15]. We have shown that bridging sulfido ligands can play an important role in the formation of higher nuclearity sulfido osmium carbonyl clusters [10–13]. Dialkyl- and diaryl-phosphino ligands (PR_2H) have been shown to serve as precursors to bridging dialkyl- and diaryl-phosphino ligands [16–20].

The cluster $Os_3(CO)_8(\mu_3\text{-}S)_2(PPh_2H)$ contains both bridging sulfido and diphenylphosphine ligands and condenses when decarbonylated to yield the hexanuclear cluster $Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ (II), in which two triosmium clusters are linked by both a bridging sulfido ligand and a bridging diphenylphosphino ligand.

Experimental

The reactions were performed under a nitrogen atmosphere although the products are relatively air stable. $Os_3(CO)_9(\mu_3\text{-}S)_2$ was prepared as previously reported [13].

PPh_2H was purchased from Strem Chemicals, Inc. and was used without further purification. IR spectra were recorded on a Nicolet 7199 FT-IR. ^1H NMR spectra were recorded on a Bruker HX-270 spectrometer operating at 270 MHz.

Preparation of $Os_3(CO)_8(PPh_2H)(\mu_3\text{-}S)_2$ *(I)*

12 mg (0.014 mmol) of $Os_3(CO)_9(\mu\text{-}S)_2$ were dissolved in 20 ml of hexane in a round-bottom flask at room temperature. 3μl of PPh_2H were added via syringe. The mixture was stirred 3 h, and the solvent was then removed in vacuo. The residue was chromatographed on silica TLC plates with hexane/CH_2Cl_2 (80/20) solvent. The yellow product was crystallized from hexane: yield 13 mg (0.013 mmol, 93%); IR (ν(CO) in hexane): 2084m, 2065w, 2052vs, 2024m, 2009s, 1991w, 1983w(sh), 1965w cm^{-1}. ^1H NMR (in $CDCl_3$): 7.73 ppm (d, 1H, J(P–H) 397.9 Hz), 7.73–7.30 ppm (m, 10H).

Preparation of $Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ *(II)*

A solution of $Os_3(CO)_8(PPh_2H)(\mu_3\text{-}S)_2$ (I) (30 mg, 0.03 mmol) in 20 ml of octane was heated to reflux for 20 h. The solution turned brownish-green and the solvent was removed in vacuo. The residue was dissolved and transferred to silica TLC plates. Chromatograms developed by using hexane/CH_2Cl_2 (70/30) yielded five separate bands. The first yellow band was unreacted I. The second green band was crystallized from hexane at 0°C to give 6 mg (0.0032 mmol, 11%) $Os_6(CO)_{14}(\mu_2\text{-}PPh_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$; IR ($\nu$(CO) in hexane): 2088m, 2081w, 2059s, 2045w, 2034vs, 2030m(sh), 2017w, 2009s, 1980w(sh), 1970w, 1962w(sh) cm^{-1}. ^1H NMR (in $CDCl_3$): 7.89–7.3 ppm (m, 20H). The three remaining bands have not yet been fully characterized. Their IR spectra are as follows: Band 3, orange, 2091s, 2048m, 2034vs, 2019s, 2016s, 1984m, 1964m, Band 4, green, 2090m, 2047s, 2026vs, 2018w, 2013m, 2010m(sh), 2001w, 1981w, 1972vw, 1967vw, 1949w; Band 5, brown, 2089s, 2045s, 2029vs, 2019vs, 2012s, 1977s, 1934m.

Crystallographic analyses

Crystals of II suitable for X-ray diffraction measurements were grown from hexane solutions by cooling to −20°C. A crystal suitable for diffraction measurements was mounted in a thin-walled glass capillary. Diffraction measurements were made on an Enraf–Nonius CAD-4 fully automated diffractometer. The unit cell was determined by using the CAD-4 automatic search, center, index and least-squares routines. Crystal data and data collection parameters are listed in Table 1. All data processing was performed on a Digital Equipment Corp. PDP 11/45 computer using the Enraf–Nonius SDP program library (version 18). The absorption correction was of a Gaussian integration type. Neutral atom scattering factors were calculated by the standard procedures [21a]. Anomalous dispersion corrections were applied to all nonhydrogen atoms [21b]. Full-matrix least-squares refinements minimized the function $\Sigma_{hkl}w(|F_o|-|F_c|)^2$ where $w=1/\sigma(F)^2$, $\sigma(F)=\sigma(F_o^2)/2F_o$ and $\sigma(F_o^2)=[\sigma(I_{raw})^2+(PF_o^2)^2]^{1/2}/Lp$.

The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of Patterson and difference Fourier techniques. The coordinates of two of the six independent osmium atoms were obtained from a three dimensional Patterson function. The coordinates of all remaining atoms were obtained from a series of difference Fourier

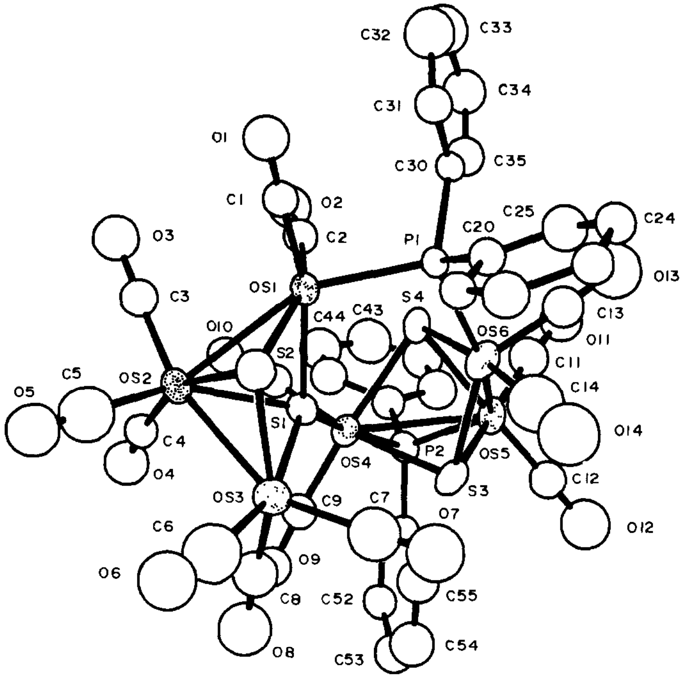
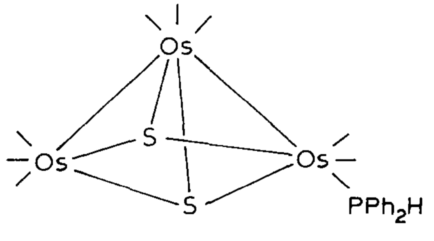


Fig. 1. An ORTEP diagram of $Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ (II) showing 50% probability thermal ellipsoids.

syntheses. The osmium, sulfur and phosphorus atoms were refined with anisotropic thermal parameters. The carbon and oxygen atoms were refined with isotropic thermal parameters. Estimated standard deviations for the bond distance and angle calculations were calculated by using the inverse matrix obtained on the final cycle of refinement.

Results and discussion

Treatment of $Os_3(CO)_9(\mu_3\text{-}S)_2$ with one equivalent of PPh_2H leads to formation of the monosubstituted derivative $Os_3(CO)_8(PPh_2H)(\mu_3\text{-}S)_2$ (I) in high yield. Because of the very close similarity of the IR spectra, it can be safely concluded that the compound has a structure analogous to the related compound $Os_3(CO)_8(PPhMe_2)(\mu_3\text{-}S)_2$ [22].



(I)

TABLE 1

CRYSTALLOGRAPHIC DATA FOR X-RAY DIFFRACTION STUDY OF $Os_6(CO)_{14}(\mu\text{-}PPh_2)(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ (II)

(A)	Formula	$Os_6S_4P_2O_{14}C_{38}H_{20}$
	Temperature (± 5°C)	25°C
	Space Group	$P\bar{1}$
	a	10.427(5) Å
	b	13.552(3) Å
	c	17.919(3) Å
	α	84.87(2)°
	β	75 41(3)°
	γ	78.43(3)°
	V	2399(2) Å^3
	M. Wt.	2032
	Z	2
	ρ_{calc}	2.82 g cm^{-3}
(B)	Measurement of intensity data	
	Radiation	Mo-K_α (0.71073 A)
	Monochromator	Graphite
	Detector aperture (mm)	
	Horizontal ($A + B \tan\theta$):	
	A	3.0
	B	1.0
	Vertical:	4.0
	Crystal faces.	$00\bar{1}$, 001, $0\bar{1}0$, 010, 111,$\bar{1}\bar{1}\bar{1}$
	Crystal size:	$0.30 \times 0.09 \times 0.04$
	Crystal orientation	
	Direction; deg from ϕ-axis	normal to 211, 5.4°
	reflections measured	$h, \pm k, \pm l$
	Max 2θ	46°
	Scan type	moving crystal-stationary counter
	ω-Scan width:	
	$A + 0.347\tan\theta$	$A = 0.90$
	Background	1/4 additional scan at each end of scan
	ω-Scan Rate (variable).	
	Max	10.0° min^{-1}
	Min°/min	1.2° min^{-1}
	No. Reflections measured	6593
	Data Used ($F^2 \geqslant 3.0\sigma(F)^2$)	3223
(C)	Treatment of data	
	Absorption correction:	
	Coefficient	161.5 cm^{-1}
	Grid	$14 \times 10 \times 6$
	Transmission coefficients	
	Max.	0.526
	Min.	0.248
	P-factor	0.01
	Final residuals R	0.042
	R_w	0.036
	Estimation of unit weight	1.602
	Largest shift/error:	
	Value on final cycle	0.10
	Largest peaks in final diff. Fourier	1.24 eÅ^{-3}

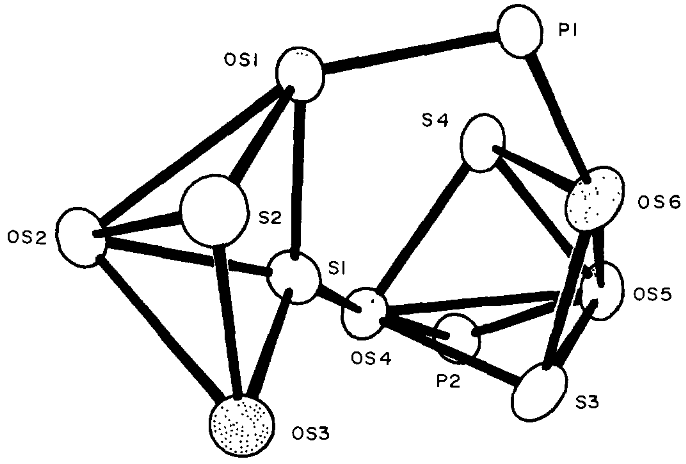


Fig. 2. An ORTEP diagram of $Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ (II) minus the carbonyl ligands and phenyl groups.

When refluxed in octane solvent for 20 h, compound I is converted into the hexaosmium compound $Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ (II) as one of several products. The characterizations of the other products of this reaction are still in progress.

The molecular structure of II was established by a single crystal X-ray diffraction analysis. An ORTEP diagram of II is shown in Fig. 1. An ORTEP diagram of II minus the carbonyl ligands and phenyl rings is shown in Fig. 2. Final positional and thermal parameters are given in Table 2. Interatomic distances and angles are listed in Tables 3 and 4, respectively.

The molecule consists of two triosmium clusters linked by a bridging diphenylphosphino ligand and a quadruply bridging sulfido ligand. Each triosmium group contains two metal–metal bonds and two sulfido ligands which are bonded to all three metal atoms. These groupings are structurally similar to the parent molecule $Os_3(CO)_9(\mu_3\text{-}S)_2$ [22]. The metal–metal bonds in the group Os(1), Os(2), Os(3) are decidedly inequivalent, Os(1)–Os(2) = 2.907(1) Å, and Os(2)–Os(3) = 2.773(1) Å. Similar distortions were observed in the monosubstituted derivatives $Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)_2$ and $Os_3(CO)_8(CS)(\mu_3\text{-}S)_2$ [23] in which the substitutent is positioned *trans* to the elongated metal–metal bond. Similarly, the Os(1), Os(2), Os(3) group in II contains the diphenylphosphino bridging ligand *trans* to the long metal–metal bond. Both metal–metal bonds in the Os(4), Os(5), Os(6) group in II are significantly longer than those in the Os(1), Os(2), Os(3) group, Os(4)–Os(5) 2.960(1) Å, Os(5)–Os(6) 3.020(1) Å. However, for this group there is a substituent *trans* to each metal–metal bond (i.e., S(1) *trans* to Os(4)–Os(5) and P(1) *trans* to Os(5)–Os(6)). The shortness of the Os(4)–Os(5) separation compared to the Os(5)–Os(6) separation could be attributed to the presence of the bridging diphenylphosphino ligand, P(2).

The two triosmium groups are linked by a bridging diphenylphosphino ligand P(1) which bridges Os(1)...Os(6) and the quadruply bridging sulfido ligand S(1). The long Os(1)...Os(6) separation at 3.674(1) Å suggests the absence of a significant

(Continued on p. 250)

TABLE 2

POSITIONAL AND THERMAL PARAMETERS AND THEIR esd FOR $Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ (II)

Atom	x	y	z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$	B_{eq}
Os(1)	0.3247(1)	0.11363(8)	0.16681(6)	2.41(5)	2.43(4)	2.26(5)	−0.10(4)	−0.45(4)	0.13(4)	2.45(3)
Os(2)	0.2919(1)	−0.06876(8)	0.26242(6)	3.25(5)	2.31(4)	2.52(5)	−0.20(4)	−0.59(4)	0.07(4)	2.77(3)
Os(3)	0.0870(1)	−0.07122(8)	0.18987(7)	3.61(5)	3.21(5)	3.02(5)	−0.77(4)	−0.83(4)	−0.53(4)	3.22(3)
Os(4)	−0.0477(1)	0.18683(8)	0.34488(6)	2.37(5)	3.04(5)	2.05(5)	−0.02(4)	−0.45(4)	−0.31(4)	2.56(3)
Os(5)	−0.1910(1)	0.38114(8)	0.29173(6)	2.73(5)	3.67(5)	2.15(5)	0.47(4)	−0.38(4)	−0.08(4)	3.04(3)
Os(6)	0.0179(1)	0.29502(9)	0.15214(7)	2.69(5)	5.51(6)	1.90(5)	0.03(5)	−0.49(4)	−0.55(5)	3.46(3)
S(1)	0.1143(6)	0.0749(4)	0.2488(4)	2.8(3)	2.5(3)	1.8(3)	−0.5(2)	−0.1(3)	−0.3(2)	2.5(2)
S(2)	0.3107(7)	−0.0445(5)	0.1228(4)	3.4(3)	3.3(3)	2.8(3)	0.1(3)	−0.1(3)	−1.1(3)	3.3(2)
S(3)	−0.1627(6)	0.2206(5)	0.2341(4)	2.3(3)	4.8(4)	3.0(3)	−0.1(3)	−0.9(3)	−0.3(3)	3.4(2)
S(4)	0.0536(7)	0.3297(5)	0.2745(4)	3.1(3)	3.2(3)	2.6(3)	0.2(3)	−1.0(3)	−0.1(3)	3.0(2)
P(1)	0.2509(6)	0.2554(5)	0.0941(4)	2.6(3)	2.2(3)	2.3(3)	−0.5(2)	−0.9(2)	0.3(3)	2.3(2)
P(2)	−0.2124(7)	0.3142(5)	0.4149(4)	2.9(3)	3.1(3)	2.6(3)	−0.3(3)	−0.2(3)	0.1(3)	3.0(2)

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
O(1)	0.614(2)	0.104(1)	0.074(1)	4.9(5)	C(13)	0.018(3)	0.419(2)	0.106(2)	4.8(7)
O(2)	0.381(2)	0.244(1)	0.280(1)	5.2(5)	C(14)	−0.029(3)	0.261(3)	0.065(2)	8.3(10)
O(3)	0.535(2)	−0.010(1)	0.304(1)	5.6(5)	C(20)	0.273(2)	0.241(2)	−0.009(1)	3.2(6)
O(4)	0.144(2)	−0.100(1)	0.425(1)	5.8(5)	C(21)	0.294(2)	0.146(2)	−0.043(1)	3.0(6)
O(5)	0.417(2)	−0.291(1)	0.239(1)	6.7(6)	C(22)	0.294(3)	0.138(2)	−0.118(2)	4.5(7)

O(6)	0.156(2)	−0.289(2)	0.136(1)	7.5(6)	C(23)	0.270(2)	0.227(2)	−0.166(1)	3.5(6)
O(7)	−0.088(2)	0.021(2)	0.078(1)	7.9(6)	C(24)	0.260(2)	0.322(2)	−0.133(2)	3.6(6)
O(8)	−0.142(2)	−0.134(2)	0.311(1)	7.7(6)	C(25)	0.251(3)	0.325(2)	−0.056(2)	4.9(7)
O(9)	−0.197(2)	0.021(1)	0 426(1)	4.7(5)	C(30)	0.355(2)	0.352(2)	0.093(1)	2.2(5)
O(10)	0.148(2)	0.143(1)	0.448(1)	4.4(4)	C(31)	0.484(2)	0.337(2)	0.047(1)	3.5(6)
O(11)	−0.178(2)	0.599(1)	0.312(1)	6.2(5)	C(32)	0.574(3)	0.398(2)	0.057(2)	6.4(9)
O(12)	−0.491(2)	0.442(2)	0.302(1)	8.0(6)	C(33)	0.534(3)	0.470(2)	0.106(2)	6.6(9)
O(13)	0.017(2)	0.506(2)	0.084(1)	8.7(7)	C(34)	0.402(3)	0.490(2)	0.146(2)	5.3(8)
O(14)	−0.060(2)	0.237(2)	0.013(1)	9.2(7)	C(35)	0.315(3)	0.432(2)	0.145(2)	4.1(7)
C(1)	0.499(2)	0.109(2)	0.115(1)	3.1(6)	C(40)	−0.182(3)	0.382(2)	0.485(2)	4.0(7)
C(2)	0.355(2)	0.200(2)	0.235(1)	3.3(6)	C(41)	−0.250(3)	0.486(2)	0.500(2)	5.9(8)
C(3)	0.438(2)	−0.036(2)	0.285(1)	3.9(6)	C(42)	−0.226(3)	0.539(2)	0.557(2)	6.2(8)
C(4)	0.210(2)	−0.089(2)	0.363(1)	3.2(6)	C(43)	−0.146(3)	0.495(2)	0.598(2)	8.1(10)
C(5)	0.369(3)	−0.209(2)	0.251(2)	7.7(10)	C(44)	−0 078(3)	0.400(2)	0.591(2)	6.8(9)
C(6)	0.124(3)	−0.210(2)	0.150(2)	8.2(10)	C(45)	−0.091(3)	0.346(2)	0.535(2)	5.0(7)
C(7)	−0.027(3)	−0.013(2)	0.120(2)	6.9(9)	C(50)	−0.372(2)	0.274(2)	0.461(1)	3.0(6)
C(8)	−0.048(3)	−0.105(2)	0.264(2)	5.4(8)	C(51)	−0.429(3)	0.289(2)	0.543(2)	4.9(7)
C(9)	−0.133(2)	0.085(2)	0.394(2)	3.8(6)	C(52)	−0.544(3)	0.250(2)	0.576(2)	4.3(7)
C(10)	0.071(2)	0.168(2)	0.409(1)	3.7(6)	C(53)	−0.603(3)	0.197(2)	0.534(2)	5.7(8)
C(11)	−0.181(3)	0.509(2)	0.311(2)	5.3(8)	C(54)	−0.544(3)	0.183(2)	0.459(2)	6.7(9)
C(12)	−0.364(3)	0.415(2)	0.294(2)	4.5(7)	C(55)	−0.433(3)	0.224(2)	0.425(2)	5.9(8)

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[a] The form of the anisotropic thermal parameter is:

$$\exp\left[-1/4\left(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23}\right)\right]$$

metal–metal bonding interaction. S(1) serves as a four electron donating, triply bridging ligand to the group Os(1), Os(2), Os(3) and uses its two remaining valence electrons to form a donor: acceptor bond with Os(4) and thus becomes a quadruply bridging six-electron donor. The compounds $Re_2MoCo(CO)_8(\mu_3\text{-}S)(\mu_4\text{-}S)[MoCp(CO)_3]$ [25] and $Mn_2Fe_2(CO)_{14}(\mu_3\text{-}S)$ [26] contain similarly coordinated quadruply bridging sulfido ligands. A valuable feature of both the diphenylphosphino and sulfido ligands is their ability to adopt stable bonding structures under a wide range

TABLE 3

INTERATOMIC DISTANCES WITH Esds FOR $Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ (II)

Atoms	Distance (Å)	Atoms	Distance (Å)
Os(1)–Os(2)	2.907(1)	P(1)–C(30)	1.86(2)
Os(2)–Os(3)	2.773(1)	P(2)–C(40)	1.74(2)
Os(4)–Os(5)	2.960(1)	P(2)–C(50)	1.83(2)
Os(5)–Os(6)	3.020(1)	C(20)–C(21)	1.42(3)
Os(1)...Os(3)	3.792(1)	C(20)–C(25)	1.38(3)
Os(1).. Os(6)	3.674(1)	C(21)–C(22)	1.36(3)
Os(4).. Os(6)	3.585(1)	C(22)–C(23)	1.44(3)
Os(1)–S(1)	2.439(5)	C(23)–C(24)	1.45(3)
Os(1)–S(2)	2.392(5)	C(24)–C(25)	1.35(3)
Os(1)–P(1)	2.334(5)	C(30)–C(31)	1.38(3)
Os(1)–C(1)	1.81(2)	C(30)–C(35)	1.42(3)
Os(1)–C(2)	1.88(2)	C(31)–C(32)	1.43(3)
Os(2)–S(1)	2.445(5)	C(32)–C(33)	1.31(3)
Os(2)–S(2)	2.457(6)	C(33)–C(34)	1.36(3)
Os(2)–C(3)	1.82(2)	C(34)–C(35)	1.32(3)
Os(2)–C(4)	1.81(2)	C(40)–C(41)	1.46(3)
Os(2)–C(5)	1.92(3)	C(40)–C(45)	1.45(3)
Os(3)–S(1)	2.422(5)	C(41)–C(42)	1.40(3)
Os(3)–S(2)	2.421(6)	C(42)–C(43)	1.27(3)
Os(3)–C(6)	2.00(3)	C(43)–C(44)	1.35(3)
Os(3)–C(7)	1.95(3)	C(44)–C(45)	1.34(3)
Os(3)–C(8)	1.78(3)	C(50)–C(51)	1.46(3)
Os(4)–S(1)	2.469(5)	C(50)–C(55)	1.33(3)
Os(4)–S(3)	2.530(6)	C(51)–C(52)	1.39(3)
Os(4)–S(4)	2.484(6)	C(52)–C(53)	1.39(3)
Os(4)–P(2)	2.370(6)	C(53)–C(54)	1.34(3)
Os(4)–C(9)	1.83(2)	C(54)–C(55)	1.36(3)
Os(4)–C(10)	1.86(2)	C(1)–O(1)	1.23(2)
Os(5)–S(3)	2.424(6)	C(2)–O(2)	1.16(2)
Os(5)–S(4)	2.452(6)	C(3)–O(3)	1.27(2)
Os(5)–P(2)	2.285(6)	C(4)–O(4)	1.16(2)
Os(5)–C(11)	1.82(3)	C(5)–O(5)	1.14(3)
Os(5)–C(12)	1.76(3)	C(6)–O(6)	1.08(3)
Os(6)–S(3)	2.414(6)	C(7)–O(7)	1.13(3)
Os(6)–S(4)	2.415(6)	C(8)–O(8)	1.23(3)
Os(6)–P(1)	2.361(6)	C(9)–O(9)	1.22(2)
Os(6)–C(13)	1.80(2)	C(10)–O(10)	1.18(2)
Os(6)–C(14)	1.86(4)	C(11)–O(11)	1.24(2)
P(1)–C(20)	1.83(2)	C(12)–O(12)	1.28(3)
		C(13)–O(13)	1.21(3)
		C(14)–O(14)	1.15(3)

TABLE 4

INTERATOMIC ANGLES WITH Esds FOR $Os_6(CO)_{14}(\mu\text{-}PPh_2)_2(\mu_3\text{-}S)_3(\mu_4\text{-}S)$ (II)

Atoms	Angle (deg)	Atoms	Angle (deg)
Os(1)–Os(2)–Os(3)	83.74(4)	Os(5)–S(4)–Os(6)	76.7(2)
Os(4)–Os(5)–Os(6)	73.65(3)	Os(1)–P(1)–Os(6)	103.0(2)
Os(2)–Os(1)–S(1)	53.6(1)	Os(4)–P(2)–Os(5)	79.0(2)
Os(2)–Os(1)–S(2)	54.2(1)	Os(1)–P(1)–C(20)	117.3(7)
Os(2)–Os(1)–P(1)	154.2(1)	Os(1)–P(1)–C(30)	109.3(6)
Os(2)–Os(1)–C(1)	111.1(6)	Os(6)–P(1)–C(20)	108.7(7)
Os(2)–Os(1)–C(2)	102.7(6)	Os(6)–P(1)–C(30)	117.9(6)
Os(1)–Os(2)–S(1)	53.4(1)	Os(4)–P(2)–C(40)	123.1(8)
Os(1)–Os(2)–S(2)	52.2(1)	Os(4)–P(2)–C(50)	113.9(7)
Os(1)–Os(2)–C(3)	78.0(7)	Os(5)–P(2)–C(40)	119.3(8)
Os(1)–Os(2)–C(4)	132.6(5)	Os(5)–P(2)–C(50)	116.6(7)
Os(1)–Os(2)–C(5)	134.9(9)	P(1)–C(20)–C(21)	124(2)
Os(3)–Os(2)–S(1)	54.9(1)	P(1)–C(20)–C(25)	119(2)
Os(3)–Os(2)–S(2)	54.8(1)	C(21)–C(20)–C(25)	116(2)
Os(3)–Os(2)–C(3)	161.4(7)	C(20)–C(21)–C(22)	123(2)
Os(3)–Os(2)–C(4)	102.0(7)	C(21)–C(22)–C(23)	120(2)
Os(3)–Os(2)–C(5)	95.5(9)	C(22)–C(23)–C(24)	116(2)
Os(2)–Os(3)–S(1)	55.7(1)	C(23)–C(24)–C(25)	120(2)
Os(2)–Os(3)–S(2)	56.0(1)	C(24)–C(25)–C(20)	124(2)
Os(2)–Os(3)–C(6)	105.2(9)	P(1)–C(30)–C(31)	117(2)
Os(2)–Os(3)–C(7)	152.4(8)	P(1)–C(30)–C(35)	123(2)
Os(2)–Os(3)–C(8)	105.0(8)	C(31)–C(30)–C(35)	119(2)
Os(5)–Os(4)–S(1)	119.2(1)	C(30)–C(31)–C(32)	118(2)
Os(5)–Os(4)–S(3)	51.7(1)	C(31)–C(32)–C(33)	121(3)
Os(5)–Os(4)–S(4)	52.7(1)	C(32)–C(33)–C(34)	120(3)
Os(5)–Os(4)–P(2)	49.2(1)	C(33)–C(34)–C(35)	123(3)
Os(5)–Os(4)–C(9)	123.4(7)	C(34)–C(35)–C(30)	119(2)
Os(5)–Os(4)–C(10)	127.1(6)	P(2)–C(40)–C(41)	122(2)
Os(4)–Os(5)–S(3)	55.0(1)	P(2)–C(40)–C(45)	127(2)
Os(4)–Os(5)–S(4)	53.6(1)	C(41)–C(40)–C(45)	111(2)
Os(4)–Os(5)–P(2)	51.8(1)	C(40)–C(41)–C(42)	121(2)
Os(4)–Os(5)–C(11)	129.0(8)	C(41)–C(42)–C(43)	120(3)
Os(4)–Os(5)–C(12)	127.2(7)	C(42)–C(43)–C(44)	126(3)
Os(6)–Os(5)–S(3)	51.2(1)	C(43)–C(44)–C(45)	118(3)
Os(6)–Os(5)–S(4)	51.1(1)	C(44)–C(45)–C(40)	124(2)
Os(6)–Os(5)–P(2)	125.1(1)	P(2)–C(50)–C(51)	119(2)
Os(6)–Os(5)–C(11)	113.7(8)	P(2)–C(50)–C(55)	123(2)
Os(6)–Os(5)–C(12)	123.0(8)	C(51)–C(50)–C(55)	118(2)
Os(5)–Os(6)–S(3)	51.5(1)	C(50)–C(51)–C(52)	116(2)
Os(5)–Os(6)–S(4)	52.2(1)	C(51)–C(52)–C(53)	123(2)
Os(5)–Os(6)–P(1)	145.1(1)	C(52)–C(53)–C(54)	118(3)
Os(5)–Os(6)–C(13)	90.9(8)	C(53)–C(54)–C(55)	120(3)
Os(5)–Os(6)–C(14)	122.3(9)	C(54)–C(55)–C(50)	124(3)
Os(1)–S(1)–Os(2)	73.1(2)	Os(1)–C(1)–O(1)	174(2)
Os(1)–S(1)–Os(3)	102.5(2)	Os(1)–C(2)–O(2)	173(2)
Os(1)–S(1)–Os(4)	125.4(2)	Os(2)–C(3)–O(3)	177(2)
Os(2)–S(1)–Os(3)	69.5(1)	Os(2)–C(4)–O(4)	172(2)
Os(2)–S(1)–Os(4)	131.6(2)	Os(2)–C(5)–O(5)	175(3)
Os(3)–S(1)–Os(4)	130.5(2)	Os(3)–C(6)–O(6)	169(3)
Os(1)–S(2)–Os(2)	73.7(2)	Os(3)–C(7)–O(7)	177(3)
Os(1)–S(2)–Os(3)	104.0(2)	Os(3)–C(8)–O(8)	174(2)
Os(2)–S(2)–Os(3)	69.3(2)	Os(4)–C(9)–O(9)	176(2)
Os(4)–S(3)–Os(5)	73.4(2)	Os(4)–C(10)–O(10)	171(2)
Os(4)–S(3)–Os(6)	92.9(2)	Os(5)–C(11)–O(11)	170(2)
Os(5)–S(3)–Os(6)	77.3(2)	Os(5)–C(12)–O(12)	175(2)
Os(4)–S(4)–Os(5)	73.7(2)	Os(6)–C(13)–O(13)	172(2)
Os(4)–S(4)–Os(6)	94.1(2)	Os(6)–C(14)–O(14)	177(3)

of coordination geometries. For example, the Os–P–Os angles are 79.0(2)° between the mutually-bonded metal atoms Os(4) and Os(5) and 103.0(2)° between the nonbonded metal atoms Os(1) and Os(6). The flexibility of the bridging sulfido ligand is even greater. Os–S–Os angles range from 69.5° between the mutually-bonded metal atoms Os(2) and Os(3) to 131.6(2)° between the nonbonded metal atoms Os(2) and Os(4). There are fourteen linear terminal carbonyl ligands distributed among the six osmium atoms as shown in Fig. 1. The shortest intermolecular contacts were between oxygen atoms of the carbonyl ligands, O(7)...O(7) 2.96(4) Å, and O(6)...O(14) 3.07(3) Å.

To form II two moles of I lose formally two moles CO and one mole of H_2 with both moles of CO are apparently lost from one and the same cluster of I. A mechanism involving a sequence of decarbonylations, sulfur to osmium coordination, P–H oxidative additions and an H_2 reductive elimination can be anticipated, but can not be proven at this time.

Acknowledgment

This work was supported by the National Science Foundation and the Alfred P. Sloan Foundation through a fellowship to R.D.A. NMR studies were supported by Grant No. CHE-7916210 to the Northeast Regional NSF-NMR Facility from the National Science Foundation. We wish to thank Engelhard Industries for a loan of osmium tetroxide.

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