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Cluster Synthesis. 6. The Unusual Structures, Bonding, and Reactivity of Some Sulfido-Bridged Tungsten–Osmium Carbonyl Cluster Compounds

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Abstract: In the presence of UV irradiation $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**1**) reacts with $W(CO)_5(PMe_2Ph)$ to give a mixture of four principal products: $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (**2**), 28%; $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**3**), 7%; $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**4**), 10%; $Os_3W_2(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**5**), 13%. Each of the products have been characterized by IR and ^1H NMR spectroscopies and an X-ray crystallographic analysis. Compounds **3**–**5** are products of secondary reactions and have been prepared independently from reactions with **2**. **2** plus PMe_2Ph yields **3** in 69% yield. Photolysis of **3** leads to **2**, 18% yield, and **4**, 37% yield. Photolysis of **2** and $W(CO)_5(PMe_2Ph)$ leads to **5**, 51% yield. The structure of **2** consists of a cluster of four metal atoms arranged in the form of a butterfly tetrahedron with the tungsten atom in a wing-tip position. Triply bridging sulfido ligands bridge the open triangular faces. The cluster contains 64 electrons and conforms to the bonding requirements of the polyhedral skeletal electron pair theory but violates the conditions of the 18-electron rule. **4** is isoelectronic with **2**. The cluster of **4** could be described as a butterfly tetrahedron with one bond missing. It has only four metal–metal bonds and conforms to the bonding requirements of the 18-electron rule but violates that of the polyhedral skeletal electron pair theory. **3** contains a planar cluster of one tungsten and three osmium atoms. It has only three metal–metal bonds and two triply bridging sulfido ligands symmetrically disposed about the M_4 plane. The tungsten atom contains both phosphine ligands. **5** has a structure analogous to **4** but has in addition a tungsten tricarbonyl phosphine unit bridging one of the tungsten–sulfur bonds. **5** is electronically unsaturated and contains two unusually short metal–metal bonds which are adjacent to each other. This suggests that the unsaturation is distributed over a trimetallic center.

The structures and bonding of the vast majority of organometallic compounds can be explained through the use of 18-electron rule and the notion of localized two-center–two-electron bonds.[1-3] However, recent studies of higher nuclearity transition-metal cluster compounds have revealed a series of compounds that cannot be understood in these simple terms. This has led to the development of delocalized bonding explanations, the most successful of which is the polyhedral skeletal electron pair (PSEP) theory.[3-5]

In our recent studies we have utilized the coordination properties of the bridging sulfido ligand to synthesize a variety of new higher nuclearity sulfido osmium carbonyl cluster compounds.[6-11] Some of these exhibit unusual bonding properties and reactivity.[11] We have recently found that the bridging sulfido ligand can be of great value also in the synthesis of mixed-metal carbonyl cluster compounds.[12]

In this report we shall describe the results of our investigations of the synthesis, structures, bonding, and reactivity of a series of tungsten–osmium carbonyl cluster compounds that further demonstrate the value of the bridging sulfido ligand in cluster synthesis and epitomize the differences that exist between the localized and delocalized bonding schemes. A preliminary report of some of this work has been published.[13]

Experimental Section

Although the products are air stable, all the reactions were performed under a prepurified nitrogen atmosphere. Photolyses were carried out by using an external high-pressure mercury lamp on reaction solutions contained in Pyrex glassware. Solvents were stored over 4-Å molecular sieves and were deoxygenated with a dispersed stream of nitrogen gas before use. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrophotometer. A Bruker WM 500 FT-NMR spectrometer was used to obtain ^1H NMR spectra at 500 MHz. UV–visible spectra were recorded on a Cary Model 219 spectrophotometer in CH_2Cl_2 solvent. $Os_3(CO)_9(\mu_3\text{-}S)_2$ was prepared from $HOs_3(CO)_{10}(\mu\text{-}SPh)$ by a previously reported procedure.[14] $W(CO)_5PMe_2Ph$ was prepared from $W(CO)_6$ and PMe_2Ph by UV irradiation.[15]

Photolytic Reaction of $Os_3(CO)_9(\mu_3\text{-}S)_2$ (1) with $W(CO)_5(PMe_2Ph)$. In a typical reaction, a mixture of $Os_3(CO)_9(\mu\text{-}S)_2$ (67 mg, 0.07 mmol) and $W(CO)_5(PMe_2Ph)$ (76 mg, 0.16 mmol) in 50 mL of hexane solvent was photolyzed under a continuous purge with N_2 for 2 h. The solvent was removed in vacuo, and the brown residue was put on silica TLC plates. Elution with hexane/CH_2Cl_2 (85/15) separated (in order of elution) trace amounts of $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**1**) and $W(CO)_5(PMe_2Ph)$ from the major dark green band of $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (**2**) (23 mg, 28%), the orange $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**3**) (6 mg, 7%), the brown $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**4**) (9 mg, 10%), and the dark brown $Os_3W_2(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**5**) (12 mg, 13%). IR and ^1H NMR of **2**–**5** are given in Table I. UV–visible spectra for **2** and **4** are as follows: **2**, $\lambda_1 = 583$ (ϵ 1600 M^{-1} cm^{-1}), $\lambda_2 = 404$ nm (ϵ 4000 M^{-1} cm^{-1}); **4**, $\lambda_1 = 435$ (ϵ 1630 M^{-1} cm^{-1}), $\lambda_2 = 351$ nm (ϵ 5230 M^{-1} cm^{-1}).

Addition of Dimethylphenylphosphine to 2. **2** (12 mg, 0.01 mmol) was dissolved in 5 mL of CH_2Cl_2. To this dimethylphenylphosphine (1.5 mg, 0.01 mmol) dissolved in 2 mL of CH_2Cl_2 was added dropwise, and the mixture was stirred at room temperature for 7 h. The color of the solution changed from dark green to orange. Chromatography on silica TLC plates separated a trace amount of **2** from orange **3** (9 mg, 69%).

Reaction of $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)$ (2) with CO. A 10-mL solution of **2** (11 mg, 0.01 mmol) in CH_2Cl_2 was stirred at room temperature under an atmosphere of CO for 18 h. Chromatography of the reaction solution on silica TLC plates gave the following compounds: $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**1**) (4.2mg 47%), $W(CO)_5(PMe_2Ph)$ (2.0 mg, 43%), yellow $Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)_2$ (1.0 mg, 10%), unreacted **2** (1.6 mg, 15%), and orange **3** (1.0 mg, 8%).

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Table I. IR and ^{1}H NMR Spectra for the Compounds **2–5**

compd	IR (CO), hexane solvent	^{1}H NMR
$Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (**2**)	2093 m, 2062 s, 2055 s, 2042 sh, 2012 s, 2000 m, 1994 m, 1982 m, 1927 br, 1908 br	7.61 (m, C_6H_5), 2.69 (d, CH_3, $^2J_{P\text{-}H}$ = 9.5 Hz)[a]
$Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**3**)	2092 s, 2050 s, 2037 m, 2014 s, 2077 sh, 1982 m, 1978 m, 1970 m, 1942 m, 1912 w, 1895 w, 1873 s, 1833 sh	7.41 (m, C_6H_5), 2.16 (d, CH_3, $^2J_{P\text{-}H}$ = 9.2 Hz)[a]
$Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**4**)	2083 s, 2057 s, 2029 s, 2006 s, 1997 m, 1983 s, 1970 w, 1967 w, 1957 w, 1913 w, 1871 br	7.13 (m, C_6H_5), 2.34 (d, CH_3, $^2J_{P\text{-}H}$ = 8.8 Hz), 1.79 (d, CH_3, $^2J_{P\text{-}H}$ = 9.2 Hz), 1.07 (d, CH_3, $^2J_{P\text{-}H}$ = 8.4 Hz), 0.87 (d, CH_3, $^2J_{P\text{-}H}$ = 8.3 Hz)[b] [27.5 d, −9.88 d, $^2J_{P\text{-}P}$ = 28.5 Hz][c]
$Os_3W(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**5**)	2082 s, 2057 s, 2049 sh, 2029 s, 2023 sh, 2006 m, 1996 w, 1983 m, 1970 w, 1956 w, 1939 w, 1923 m, 1893 w, 1715 w	7.49 (m, C_6H_5), 2.29 (d, CH_3, $^2J_{P\text{-}H}$ = 9.8 Hz), 2.10 (d, CH_3, $^2J_{P\text{-}H}$ = 8.4 Hz), 2.05 (d, CH_3, $^2J_{P\text{-}H}$ = 8.3 Hz), 1.72 (d, CH_3, $^2J_{P\text{-}H}$ = 9.5 Hz)[a]

[a] In $CDCl_3$. [b] In toluene-d_8 at −20 °C. [c] ^{31}P spectrum at −40 °C in toluene-d_8, δ vs. trimethyl phosphite.

Ligand Elimination from 3. A solution of **3** (12 mg, 0.01 mmol) in 40 mL of hexane on photolysis under a continuous purge of N_2 for 1 h changed color from orange to dark brown. Chromatography of the mixture on silica TLC plates using hexane/CH_2Cl_2 (80/20) separated trace amounts of **1**, $Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)_2$, $W(CO)_5(PMe_2Ph)$, dark green **2** (2 mg, 18%), a trace of unreacted **3**, and the major brown band of **4** (4 mg, 37%).

CO Addition to 4. A brown solution of **4** (12 mg, 0.01 mmol) in 5 mL of CH_2Cl_2 was stirred under an atmosphere of CO at room temperature for 48 h. Chromatography of the solution on silica TLC yielded the orange **3** (7 mg, 58%).

Photolytic Reaction of 2 with $W(CO)_5(PMe_2Ph)$. A mixture of **2** (20 mg, 0.02 mmol) and $W(CO)_5(PMe_2Ph)$ (12 mg, 0.03 mmol) in hexane solvent was photolyzed under a continuous stream of N_2 for 2 h. The solvent was removed in vacuo, and the brown residue was put on silica TLC plates. Elution with hexane/CH_2Cl_2 (70/30) separated trace amounts of **1**, $Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)_2$, $W(CO)_5(PMe_2Ph)$, and the unreacted **2** from the major dark brown band, **5** (12 mg, 51%).

Crystallographic Analyses. Crystals of each of the compounds suitable for diffraction analysis were obtained from solutions in CH_2Cl_2/hexane solvent by cooling to −20 °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 factors were calculated by the standard procedures.[16a] Anomalous dispersion corrections were applied to all nonhydrogen atoms.[16b] Full-matrix least-squares refinements minimized the function

$$\sum_{hkl} w(|F_{\text{obsd}}| - |F_{\text{calcd}}|)^2 \text{ where } w = 1/(\sigma(F)^2)$$

$$\sigma(F^2_{\text{obsd}}) = [\sigma(I_{\text{raw}})^2 + (PF^2_{\text{obsd}})^2]^{1/2}/(Lp)$$

$$\sigma(F) = \sigma(F^2_{\text{obsd}})/(2F_{\text{obsd}})$$

Atoms heavier than oxygen were refined anisotropically. All other nonhydrogen atoms were refined isotropically. Positions of the hydrogen atoms were calculated by assuming idealized geometry. Their contributions were added to the structure factor calculations, but their positions were not refined.

For **2** the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The coordinates of the metal atoms were obtained from the phasing (MULTAN) of 444 reflections (E_{min} = 1.80). The coordinates of all remaining nonhydrogen atoms were obtained from difference Fourier calculations.

For compound **3** the unique space group $P2_1/n$ was identified from the systematic absences observed in the data. The coordinates of the metal atoms were obtained from the phasing (MULTAN) of 264 reflections (E_{min} = 1.78). The coordinates of all remaining nonhydrogen atoms were obtained from difference Fourier calculations.

For compound **4** the unique space group $P2_12_12_1$ was identified from the systematic absences observed in the data. The coordinates of the metal atoms were determined from phasing (MULTAN) of 256 reflections (E_{min} = 1.67). The coordinates of all remaining nonhydrogen atoms were obtained from difference Fourier calculations. The correct enantiomorph was established by refining each enantiomer of the molecule (i.e., positive fractional atomic coordinates vs. negative fractional atomic coordinates). The R factors for the refinements based on positive coordinates were R = 0.047 and R_w = 0.047. The R factors for the refinement based on negative coordinates were R = 0.055 and R_w = 0.057. The former were deemed to be correct and are reported here.

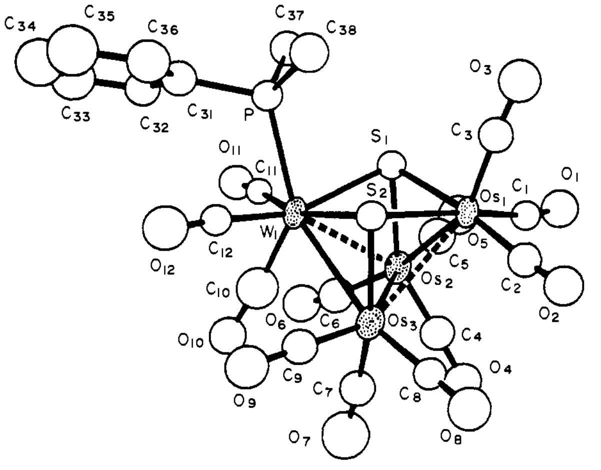

Figure 1. ORTEP diagram of $Os_3W(CO)_{12}(PMe_2Ph)$ $(\mu_3\text{-}S)_2$ (**2**) showing 50% probability thermal ellipsoids.

For compound **5** the unique space group $P2_1/c$ was determined from the systematic absences observed in the data. The coordinates of the metal atoms were determined by the phasing (MULTAN) of 256 reflections (E_{min} = 1.74). The coordinates of all remaining nonhydrogen atoms were obtained from difference Fourier calculations.

Structure factor tables for compounds **2** and **3** were published previously.[13] Structure factor tables for **4** and **5** are available with this report (see Supplementary material).

Results

Under the influence of UV irradiation $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**1**) reacts with $W(CO)_5(PMe_2Ph)$ and yields four principal products that have been identified as $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (**2**), 28% yield, $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**3**), 7% yield, $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**4**), 10%, and $Os_3W_2(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**5**), 13%. Each product has been characterized by IR and ^{1}H NMR spectral analysis (see Table I) and a single-crystal X-ray diffraction analysis.

Structure of $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (2). Compound **2** crystallizes with two independent molecules in the asymmetric crystallographic unit. Final fractional atomic coordinates are listed in Table III. Interatomic distances and selected interatomic angles are given in Tables IV and V. Both independent molecules have very similar geometry. An ORTEP diagram of one of these in shown in Figure 1. The molecule contains a cluster of one tungsten and three osmium atoms in the form of a "butterfly" tetrahedron with the tungsten atom in a "wing-tip" position. The metal–metal bonding is significantly distorted. In each independent molecule one tungsten–osmium bond is significantly longer than the other (e.g., Os(2)–W(1) = 3.031 (1) Å [Os(6)–W(2) = 3.068 (1) Å]

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Table II. Crystallographic Data for X-ray Diffraction Studies

	compd			
	2	3	4	5
formula	$Os_3WS_2PO_{12}C_{20}H_{11}$	$Os_3WS_2P_2O_{12}C_{28}H_{22}$	$Os_3WS_2P_2O_{11}C_{27}H_{22}$	$Os_3W_2S_2P_2O_{15}C_{31}H_{22}$
temp, ±3 °C	25	27	28	25
space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
a, Å	9.229 (5)	19.917 (9)	13.943 (3)	11.666 (4)
b, Å	11.785 (3)	9.560 (3)	15.674 (7)	21.539 (9)
c, Å	28.559 (9)	21.392 (8)	16.174 (3)	15.934 (10)
α, deg	87.02 (2)	90.00	90.00	90.00
β, deg	83.82 (2)	113.74 (3)	90.00	92.65 (4)
γ, deg	66.82 (4)	90.00	90.00	90.00
V, Å^3	2838 (2)	3728 (5)	3535 (3)	4000 (6)
M_r	1292.9	1431.0	1403.0	1698.9
Z	4	4	4	4
ρ_{calcd}, g/cm^3	3.03	2.55	2.64	2.82
Measurement of Intensity Data				
radtn	Mo K$\bar{\alpha}$ (0.71073 Å)	Mo K$\bar{\alpha}$ (0.71073 Å)	Mo K$\bar{\alpha}$ (0.71073 Å)	Mo K$\bar{\alpha}$ (0.71073 Å)
monochromator	graphite	graphite	graphite	graphite
detector aperture, mm				
horizontal ($A + B$ tan θ)				
A	3.0	3.0	3.0	3.0
B	1.0	1.0	1.0	1.0
vertical	4.0	4.0	4.0	4.0
cryst faces	$010, 0\bar{1}0, 001$ $00\bar{1}, \bar{1}01, 10\bar{1}$	$\bar{1}01, 10\bar{1}, \bar{1}00, 100$ $\bar{1}\bar{1}0, 121, \bar{1}\bar{1}2, 11\bar{2}$	$00\bar{1}, \bar{1}02, \bar{1}0\bar{1}, 101\ 10\bar{1}$ $\bar{1}01, 0\bar{1}0, 02\bar{1}, 012$	$021, 0\bar{2}\bar{1}, 0\bar{2}1$ $02\bar{1}, \bar{1}00, 100$
cryst size, mm	0.073 × 0.217 × 0.332	0.07 × 0.22 × 0.25	0.16 × 0.29 × 0.33	0.12 × 0.16 × 0.46
cryst orientatn directn; deg from ϕ axis	[210]; 0.0	[120]; 10.7	*b*; 9.2	*a**; 3.7
reflcns measured	$h, \pm k, \pm l$	$h, k, \pm l$	h, k, l	$h, k, \pm l$
max 2θ	48°	48°	50°	47°
scan type	moving crystal–stationary counter	moving crystal–stationary counter	moving crystal–stationary counter	moving crystal–stationary counter
ω scan width (A + 0.347 tan θ), deg	1.00	1.00	0.95	1.00
bkgd	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan	$^1/_4$ addition scan at each end of scan
ω scan rate (variable)				
max, deg/min	10.0	10.0	10.0	10.0
min, deg/min	1.5	1.5	1.5	1.5
no. reflcns measured	8875	6340	3470	6339
data used ($F^2 \geq 3.0\ \sigma(F^2)$)	6034	3135	2332	3659
Treatment of Data				
absorptn corctn				
coeff, cm^{-1}	177.9	136.0	143.4	156.1
grid	14 × 6 × 10	8 × 12 × 10	10 × 10 × 10	14 × 6 × 10
transmission coeff				
max	0.29	0.39	0.18	0.33
min	0.04	0.07	0.05	0.08
P factor	0.02	0.03	0.02	0.03
final residuals				
R_F	0.033	0.046	0.048	0.057
R_{wF}	0.034	0.051	0.048	0.069
esd of unit wt observatn	1.60	1.83	2.01	2.06
largest shift/error value of final cycle	0.11	0.09	0.16	0.19
largest peak in final diff Fourier, e$^-$/Å^3	1.39	1.63	2.32	2.76

vs. Os(3)–W(1) = 2.969 (1) Å [Os(5)–W(2) = 2.976 (1) Å]). Here and in all cases that follow the molecular dimension given within brackets is the corresponding value in the second crystallographically independent molecule. There are only a few reports of tungsten–osmium bonding distances in the literature. The cluster compounds $HOs_3W(CO)_{12}(Cp)$[17] and $H_3Os_3W(CO)_{11}(Cp)$[18] are probably the most closely related to **2**. In these "electron precise" clusters the non-hydride bridged W–Os distances are 2.919 Å$_{av}$ and 2.880 (3) Å, respectively. The osmium–osmium bonding in **2** is also quite irregular. The Os–Os bond diametrically opposite the long W–Os bond is also unusually long, Os(1)–Os(3) = 3.060 (1) Å [Os(4)–Os(5) = 3.047 (1) Å]. The hinge-to-wingtip bond Os(1)–Os(2) = 2.908 (1) Å [Os(4)–Os(6) = 2.899 (1) Å] is much shorter but still slightly longer than the Os–Os bond distance of 2.877 (3) Å observed in $Os_3(CO)_{12}$.[19] The hinge bond Os(2)–Os(3) = 2.980 (1) Å [Os(5)–Os(6) = 2.946 (1) Å] is roughly midway between the two extremes. $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (**6**) the homonuclear homologue of **2** has also been prepared and structurally studied and shows bonding distortions similar to **2**. Triply bridging sulfido ligands span the two open triangular faces. The osmium–sulfur distances span the range 2.360 (3)–2.431 (3) Å and are similar to those observed in other sulfido-bridged osmium carbonyl clusters. The tungsten–sulfur distances are slightly longer 2.484 (3)–2.549 (3) Å, as would be expected due to its larger covalent radius.[17] The sulfur–sulfur distances 3.176 (8) Å [3.166(8)Å] are indicative of nonbonding or, at most, very weak bonding interactions. The tungsten atom contains a (dimethyl-

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Table III. Final Fractional Atomic Coordinates for $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (**2**)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Os(1)	0.81055 (6)	0.24736 (5)	0.04013 (2)	C(2)	0.899 (1)	0.234 (1)	−0.0229 (4)
Os(2)	0.98416 (6)	0.12535 (5)	0.11991 (2)	C(3)	0.605 (1)	0.325 (1)	0.0207 (4)
Os(3)	1.10111 (6)	0.29349 (5)	0.06089 (2)	C(4)	1.163 (2)	0.006 (1)	0.0891 (5)
Os(4)	0.27664 (6)	0.29491 (5)	0.31919 (2)	C(5)	0.896 (2)	0.010 (2)	0.1376 (5)
Os(5)	0.58944 (6)	0.24926 (5)	0.35840 (2)	C(6)	1.074 (2)	0.100 (1)	0.1762 (5)
Os(6)	0.32991 (6)	0.20478 (5)	0.41483 (2)	C(7)	1.293 (2)	0.180 (1)	0.0803 (5)
W(1)	0.86042 (6)	0.39806 (5)	0.14169 (2)	C(8)	1.188 (1)	0.270 (1)	−0.0016 (4)
W(2)	0.34731 (6)	0.45964 (5)	0.41295 (2)	C(9)	1.171 (1)	0.418 (1)	0.0661 (4)
S(1)	0.7163 (4)	0.2684 (3)	0.1233 (1)	C(10)	1.075 (2)	0.342 (1)	0.1626 (5)
S(2)	0.8393 (4)	0.4379 (3)	0.0539 (1)	C(11)	0.825 (1)	0.358 (1)	0.2083 (4)
S(3)	0.4100 (4)	0.4329 (3)	0.3251 (1)	C(12)	0.896 (1)	0.553 (1)	0.1470 (4)
S(4)	0.1364 (4)	0.3951 (3)	0.3924 (1)	C(13)	0.185 (2)	0.180 (1)	0.3226 (5)
P(1)	0.5787 (4)	0.5533 (3)	0.1613 (1)	C(14)	0.117 (2)	0.404 (1)	0.2845 (5)
P(2)	0.1355 (4)	0.6754 (4)	0.4028 (1)	C(15)	0.406 (1)	0.218 (1)	0.2648 (4)
O(1)	0.782 (1)	−0.0008 (10)	0.0348 (3)	C(16)	0.707 (2)	0.147 (2)	0.3078 (5)
O(2)	0.945 (1)	0.2255 (9)	−0.0623 (3)	C(17)	0.695 (2)	0.127 (2)	0.3997 (5)
O(3)	0.483 (1)	0.3707 (10)	0.0075 (3)	C(18)	0.738 (2)	0.319 (1)	0.3566 (5)
O(4)	1.271 (1)	−0.0717 (10)	0.0704 (4)	C(19)	0.453 (2)	0.043 (2)	0.3949 (5)
O(5)	0.837 (1)	−0.0593 (11)	0.1490 (4)	C(20)	0.396 (2)	0.173 (1)	0.4747 (5)
O(6)	1.132 (1)	0.0850 (11)	0.2118 (4)	C(21)	0.158 (2)	0.164 (2)	0.4353 (5)
O(7)	1.413 (1)	0.1183 (11)	0.0951 (4)	C(22)	0.513 (2)	0.373 (1)	0.4529 (5)
O(8)	1.248 (1)	0.2508 (10)	−0.0402 (3)	C(23)	0.476 (2)	0.562 (1)	0.4078 (5)
O(9)	1.206 (1)	0.5014 (10)	0.0712 (3)	C(24)	0.243 (1)	0.496 (1)	0.4773 (4)
O(10)	1.196 (1)	0.3206 (10)	0.1773 (3)	C(31)	0.566 (1)	0.683 (1)	0.1980 (4)
O(11)	0.804 (1)	0.3336 (10)	0.2477 (3)	C(32)	0.588 (2)	0.660 (1)	0.2444 (5)
O(12)	0.923 (1)	0.6389 (10)	0.1504 (3)	C(33)	0.589 (2)	0.751 (2)	0.2731 (5)
O(13)	0.127 (1)	0.1066 (11)	0.3260 (4)	C(34)	0.562 (2)	0.866 (2)	0.2517 (6)
O(14)	0.015 (1)	0.4737 (10)	0.2646 (4)	C(35)	0.538 (2)	0.893 (2)	0.2069 (6)
O(15)	0.481 (1)	0.1833 (10)	0.2297 (3)	C(36)	0.539 (2)	0.797 (1)	0.1778 (5)
O(16)	0.778 (1)	0.0857 (11)	0.2767 (4)	C(37)	0.445 (2)	0.496 (1)	0.1942 (4)
O(17)	0.775 (1)	0.0512 (12)	0.4264 (4)	C(38)	0.478 (2)	0.623 (1)	0.1102 (5)
O(18)	0.821 (1)	0.3733 (11)	0.3547 (4)	C(41)	0.111 (2)	0.727 (1)	0.3425 (4)
O(19)	0.523 (1)	−0.0574 (11)	0.3812 (4)	C(42)	0.197 (2)	0.787 (2)	0.3200 (5)
O(20)	0.439 (1)	0.1581 (11)	0.5126 (4)	C(43)	0.186 (2)	0.823 (2)	0.2727 (6)
O(21)	0.046 (1)	0.1471 (13)	0.4491 (4)	C(44)	0.078 (2)	0.800 (2)	0.2494 (6)
O(22)	0.616 (1)	0.3273 (10)	0.4791 (4)	C(45)	−0.012 (2)	0.747 (2)	0.2699 (6)
O(23)	0.551 (1)	0.6209 (10)	0.4033 (4)	C(46)	0.000 (2)	0.706 (2)	0.3170 (6)
O(24)	0.176 (1)	0.5181 (10)	0.5147 (3)	C(47)	0.165 (2)	0.799 (1)	0.4312 (5)
C(1)	0.801 (1)	0.091 (1)	0.0373 (4)	C(48)	−0.060 (2)	0.698 (2)	0.4270 (6)

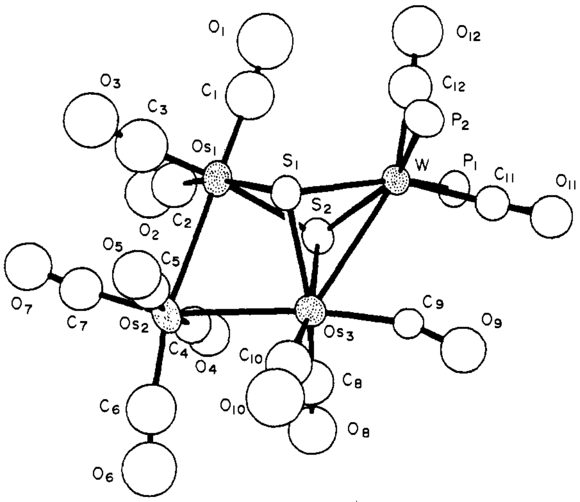

Figure 2. ORTEP diagram of $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu\text{-}_3\text{-}S)_2$ (**3**) showing 50% probability thermal ellipsoids.

phenyl)phosphine ligand, W(1)–P(1) = 2.543 (3) Å [W(2)–P(2) = 2.549 (3) Å]. Each metal atom contains three linear terminal carbonyl ligands, and, as expected on the basis of the larger covalent radius, the tungsten–carbon bond distances are approximately 0.1 Å larger than the osmium–carbon distances.

Structure of $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (3). Final fractional atomic coordinates are listed in Table VI. Interatomic distances and selected angles are listed in Tables VII and VIII, respectively. An ORTEP drawing of **3** is shown in Figure 2. This molecule consists of a planar cluster of one tungsten and three osmium atoms. There are only three metal–metal bonds, Os(3)–W = 3.044 (1), Os(1)–Os(2) = 2.895 (1), and Os(2)–Os(3) = 2.887 (1) Å. The tungsten–osmium bond is similar in length to the longer tungsten–osmium bonds in **2** while the osmium–osmium bonds are similar in length to the shorter osmium–osmium bonds in **2**. The Os(1)···W distance at 3.612 (1) Å seems to be too long to involve a significant bonding interaction.

Two triply bridging sulfido ligands lie symmetrically disposed about the M_4 plane and are each bonded to the tungsten atom and the two osmium atoms Os(1) and Os(3). The tungsten–sulfur distances 2.470 (4) and 2.497 (4) Å are similar to those in **2** while the osmium–sulfur distances 2.440 (4)–2.482 (5) Å are longer than those in **2** and are similar in length to the tungsten–sulfur distances in **3**. The tungsten atom contains two (dimethylphenyl)phosphine ligands (W–P = 2.497 (5) Å) and two terminal carbonyl ligands. There are 10 carbonyl ligands distributed among the three osmium atoms as shown in Figure 2. C(9)–O(9) is a semibridge across the Os(3)–W bond, W···C(9) = 2.86 (1) Å.

Structure of $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (4). Final fractional atomic coordinates are listed in Table IX. Interatomic distances and selected interatomic angles are listed in Tables X and XI. An ORTEP diagram of **4** is shown in Figure 3. For the purposes of comparison with **2**, the structure of **4** is probably best described as a butterfly tetrahedral cluster of four metal atoms with one bond missing, Os(1)···Os(2) = 3.813 (1) Å. As in **2**, there is no bond between Os(1) and W, Os(1)···W = 3.666 (1) Å. There are two osmium–osmium bonds Os(1)–Os(3) = 2.829 (1) and Os(2)–Os(3) = 2.923 (1) Å. Their average, 2.876 Å, is nearly identical with the average Os–Os distance found in $Os_3(CO)_{12}$, 2.877 (3) Å. The two bonding tungsten–osmium distances are decidedly inequivalent, Os(2)–W = 2.814 (1) and Os(3)–W = 3.016 (1) Å. The latter is only slightly shorter than the long Os–W bonds in **2**. The metal–sulfur internuclear separations are similar to those in **2** and **3**. The sulfur–sulfur distance at 3.209

Table IV. Interatomic Distances with esds for $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (**2**)

molecule 1		molecule 2	
atoms	distance, Å	atoms	distance, Å
Os(1)–Os(2)	2.908 (1)	Os(4)–Os(5)	3.047 (1)
Os(1)–Os(3)	3.060 (1)	Os(4)–Os(6)	2.899 (1)
Os(2)–Os(3)	2.980 (1)	Os(5)–Os(6)	2.946 (1)
Os(2)–W(1)	3.031 (1)	Os(5)–W(2)	2.976 (1)
Os(3)–W(1)	2.969 (1)	Os(6)–W(2)	3.068 (1)
Os(1)–S(1)	2.429 (2)	Os(4)–S(3)	2.415 (3)
Os(1)–S(2)	2.419 (3)	Os(4)–S(4)	2.431 (3)
Os(2)–S(1)	2.376 (3)	Os(5)–S(3)	2.373 (3)
Os(3)–S(2)	2.367 (3)	Os(6)–S(4)	2.360 (3)
W(1)–S(1)	2.493 (3)	W(2)–S(3)	2.521 (2)
W(1)–S(2)	2.539 (2)	W(2)–S(4)	2.484 (3)
W(1)–P(1)	2.543 (3)	W(2)–P(2)	2.549 (3)
Os(1)–C(1)	1.888 (13)	Os(4)–C(13)	1.851 (15)
Os(1)–C(2)	1.880 (10)	Os(4)–C(14)	1.868 (13)
Os(1)–C(3)	1.883 (11)	Os(4)–C(15)	1.884 (11)
Os(2)–C(4)	1.858 (13)	Os(5)–C(16)	1.878 (14)
Os(2)–C(5)	1.865 (15)	Os(5)–C(17)	1.841 (14)
Os(2)–C(6)	1.847 (12)	Os(5)–C(18)	1.852 (13)
Os(3)–C(7)	1.872 (14)	Os(6)–C(19)	1.870 (15)
Os(3)–C(8)	1.862 (10)	Os(6)–C(20)	1.848 (13)
Os(3)–C(9)	1.841 (12)	Os(6)–C(21)	1.859 (15)
W(1)–C(10)	1.972 (12)	W(2)–C(22)	1.927 (13)
W(1)–C(11)	1.961 (11)	W(2)–C(23)	1.992 (13)
W(1)–C(12)	1.992 (13)	W(2)–C(24)	1.966 (11)
P(1)–C(31)	1.885 (12)	P(2)–C(41)	1.804 (11)
P(1)–C(37)	1.788 (11)	P(2)–C(47)	1.824 (14)
P(1)–C(38)	1.801 (12)	P(2)–C(48)	1.781 (14)
C(31)–C(32)	1.358 (14)	C(41)–C(42)	1.349 (17)
C(32)–C(33)	1.394 (18)	C(42)–C(43)	1.396 (17)
C(33)–C(34)	1.396 (19)	C(43)–C(44)	1.366 (18)
C(34)–C(35)	1.322 (17)	C(44)–C(45)	1.304 (18)
C(35)–C(36)	1.430 (18)	C(45)–C(46)	1.402 (17)
C(31)–C(36)	1.380 (16)	C(41)–C(46)	1.417 (17)
C(1)–O(1)	1.169 (13)	C(13)–O(13)	1.179 (15)
C(2)–O(2)	1.156 (11)	C(14)–O(14)	1.158 (13)
C(3)–O(3)	1.139 (12)	C(15)–O(15)	1.151 (12)
C(4)–O(4)	1.160 (14)	C(16)–O(16)	1.144 (15)
C(5)–O(5)	1.163 (15)	C(17)–O(17)	1.205 (15)
C(6)–O(6)	1.171 (13)	C(18)–O(18)	1.174 (14)
C(7)–O(7)	1.167 (14)	C(19)–O(19)	1.171 (16)
C(8)–O(8)	1.172 (11)	C(20)–O(20)	1.171 (13)
C(9)–O(9)	1.166 (13)	C(21)–O(21)	1.151 (15)
C(10)–O(10)	1.163 (13)	C(22)–O(22)	1.208 (13)
C(11)–O(11)	1.161 (11)	C(23)–O(23)	1.147 (13)
C(12)–O(12)	1.148 (13)	C(24)–O(24)	1.161 (11)
S(1)···S(2)	3.176 (7)	S(3)···S(4)	3.166 (7)

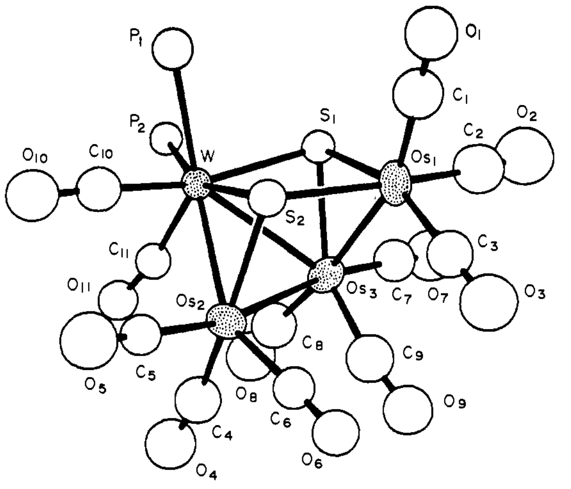

Figure 3. ORTEP diagram of $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**4**) showing 50% probability thermal ellipsoids.

(10) Å is indicative of little or no sulfur–sulfur bonding. The eight coordinate tungsten atom contains two (dimethylphenyl)phosphine ligands and two carbonyl ligands. The osmium atoms each contain three linear terminal carbonyl ligands.

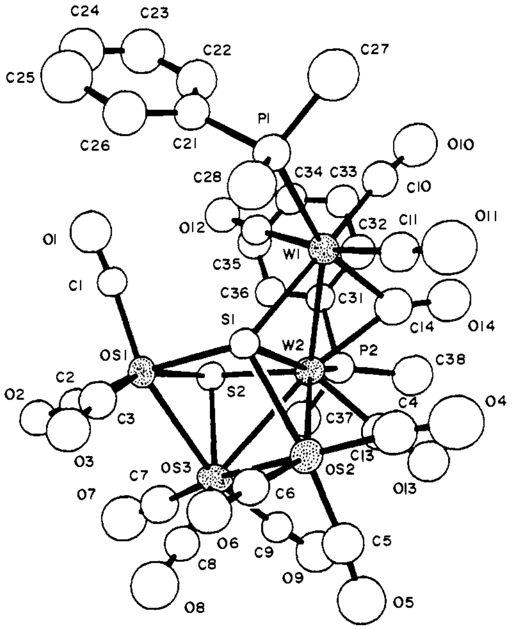

Figure 4. ORTEP diagram of $Os_3W_2(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)$ $(\mu_4\text{-}S)$ (**5**) showing 50% probability thermal ellipsoids.

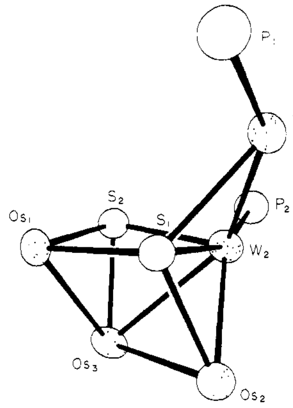

Figure 5. ORTEP diagram of $Os_3W_2(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**5**) showing 50% probability thermal ellipsoids. Carbonyl ligands and R groups of the phosphine ligands have been omitted for clarity.

Structure of $Os_3W_2(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$ (5). Final fractional atomic coordinates are listed in Table XII. Interatomic distances and selected interatomic angles are listed in Tables XIII and XIV. An ORTEP drawing of the complete molecule of **5** is shown in Figure 4. An ORTEP drawing of 5 minus the carbonyl ligands is shown in Figure 5. Compound **5** consists of an open cluster of two tungsten and three osmium atoms. The group Os(1), Os(2), Os(3), and W(2) is structurally analogous to the cluster in **4**. The Os(1)···Os(2) and Os(1)···W(2) distances of 3.867 (1) and 3.527 (1) Å, respectively, are clearly nonbonding. The Os(1)–Os(3) and Os(2)–Os(3) bonding distances in **5** are nearly identical with those in **4**. The Os(3)–W(2) distance of 2.991 (1) Å is only slightly shorter than the corresponding distance in **4** (3.016 (1) Å). However, the Os(2)–W(2) distance, 2.703 (1) Å, is over 0.11 Å shorter than corresponding distance in **4** (2.814 (1) Å). The second tungsten atom W(1) is bonded to W(2) via a surprisingly short tungsten–tungsten bond, W(1)–W(2) = 2.711 (1) Å. By comparison, the tungsten–tungsten bond distance in the electron precise cluster $Ir_2W_2(CO)_{10}(\eta\text{-}Cp)_2$ is 2.991 (1) Å.[20] In $[(\eta\text{-}Cp)W(CO)_3]_2$ the tungsten–tungsten single bond distance is 3.222 (1) Å although there is evidence for steric crowding in this case.[21] There are few examples of tungsten–tungsten double

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(20) Churchill, M. R.; Bueno, C.; Hutchinson, J. R. *Inorg. Chem.* **1982**, *21*, 1359.

Table V. Interatomic Angles with esds for $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (**2**)

molecule 1		molecule 2		molecule 1		molecule 2	
atoms	angle, deg	atoms	angle, deg	atoms	angle, deg	atoms	angle, deg
Os(2)–Os(1)–Os(3)	59.84 (1)	Os(5)–Os(4)–Os(6)	59.33 (1)	S(1)–Os(2)–C(4)	151.9 (4)	S(3)–Os(5)–C(16)	106.5 (4)
Os(1)–Os(2)–Os(3)	62.61 (1)	Os(4)–Os(5)–Os(6)	57.83 (1)	S(1)–Os(2)–C(5)	84.3 (4)	S(3)–Os(5)–C(17)	163.7 (4)
Os(1)–Os(2)–W(1)	75.56 (2)	Os(4)–Os(5)–W(2)	74.44 (2)	S(1)–Os(2)–C(6)	114.9 (4)	S(3)–Os(5)–C(18)	89.8 (4)
Os(1)–Os(3)–Os(2)	57.55 (1)	Os(4)–Os(6)–Os(5)	62.84 (1)	Os(1)–Os(3)–S(2)	51.01 (7)	Os(4)–Os(6)–S(4)	53.89 (6)
Os(1)–Os(3)–W(1)	74.25 (1)	Os(4)–Os(6)–W(2)	75.21 (2)	Os(1)–Os(3)–C(7)	128.6 (4)	Os(4)–Os(6)–C(19)	92.6 (4)
Os(3)–Os(2)–W(1)	59.19 (1)	Os(6)–Os(5)–W(2)	62.40 (2)	Os(1)–Os(3)–C(8)	92.9 (3)	Os(4)–Os(6)–C(20)	164.4 (4)
Os(2)–Os(3)–W(1)	61.26 (1)	Os(5)–Os(6)–W(2)	59.28 (2)	Os(1)–Os(3)–C(9)	142.1 (4)	Os(4)–Os(6)–C(21)	104.6 (4)
Os(2)–W(1)–Os(3)	59.55 (1)	Os(5)–W(2)–Os(6)	58.32 (2)	Os(2)–Os(3)–S(2)	91.48 (7)	Os(5)–Os(6)–S(4)	93.17 (7)
Os(1)–S(1)–Os(2)	74.47 (8)	Os(4)–S(3)–Os(5)	79.04 (9)	Os(2)–Os(3)–C(7)	80.4 (4)	Os(5)–Os(6)–C(19)	80.9 (4)
Os(1)–S(1)–W(1)	95.35 (9)	Os(4)–S(3)–W(2)	95.12 (9)	Os(2)–Os(3)–C(8)	126.6 (4)	Os(5)–Os(6)–C(20)	103.8 (4)
Os(2)–S(1)–W(1)	76.94 (8)	Os(5)–S(3)–W(2)	74.82 (7)	Os(2)–Os(3)–C(9)	141.2 (3)	Os(5)–Os(6)–C(21)	165.0 (4)
Os(1)–S(2)–Os(3)	79.46 (9)	Os(4)–S(4)–Os(6)	74.46 (9)	W(1)–Os(3)–S(2)	55.46 (6)	W(2)–Os(6)–S(4)	52.53 (7)
Os(1)–S(2)–W(1)	94.41 (9)	Os(4)–S(4)–W(2)	95.67 (10)	W(1)–Os(3)–C(7)	112.1 (4)	W(2)–Os(6)–C(19)	139.8 (4)
Os(3)–S(2)–W(1)	74.37 (7)	Os(6)–S(4)–W(2)	78.53 (9)	W(1)–Os(3)–C(8)	158.0 (3)	W(2)–Os(6)–C(20)	91.1 (4)
Os(2)–Os(1)–S(1)	51.93 (7)	Os(5)–Os(4)–S(3)	49.87 (7)	W(1)–Os(3)–C(9)	89.4 (3)	W(2)–Os(6)–C(21)	128.0 (5)
Os(2)–Os(1)–S(2)	92.19 (6)	Os(5)–Os(4)–S(4)	89.31 (7)	S(2)–Os(3)–C(7)	167.6 (4)	S(4)–Os(6)–C(19)	143.7 (4)
Os(2)–Os(1)–C(1)	79.9 (3)	Os(5)–Os(4)–C(13)	123.6 (4)	S(2)–Os(3)–C(8)	102.6 (3)	S(4)–Os(6)–C(20)	123.0 (4)
Os(2)–Os(1)–C(2)	124.9 (3)	Os(5)–Os(4)–C(14)	145.0 (4)	S(2)–Os(3)–C(9)	91.5 (4)	S(4)–Os(6)–C(21)	84.7 (5)
Os(2)–Os(1)–C(3)	143.1 (3)	Os(5)–Os(4)–C(15)	84.4 (3)	Os(2)–W(1)–S(1)	40.80 (7)	Os(5)–W(2)–S(3)	50.33 (7)
Os(3)–Os(1)–S(1)	90.08 (6)	Os(6)–Os(4)–S(3)	92.20 (6)	Os(2)–W(1)–S(2)	87.07 (7)	Os(5)–W(2)–S(4)	89.96 (7)
Os(3)–Os(1)–S(2)	49.53 (7)	Os(6)–Os(4)–S(4)	51.66 (7)	Os(2)–W(1)–P(1)	130.39 (7)	Os(5)–W(2)–P(2)	142.07 (7)
Os(3)–Os(1)–C(1)	125.3 (3)	Os(6)–Os(4)–C(13)	79.9 (4)	Os(2)–W(1)–C(10)	79.6 (4)	Os(5)–W(2)–C(22)	72.3 (4)
Os(3)–Os(1)–C(2)	85.0 (3)	Os(6)–Os(4)–C(14)	140.5 (4)	Os(2)–W(1)–C(11)	88.8 (3)	Os(5)–W(2)–C(23)	95.0 (4)
Os(3)–Os(1)–C(3)	143.2 (3)	Os(6)–Os(4)–C(15)	125.2 (3)	Os(2)–W(1)–C(12)	150.6 (3)	Os(5)–W(2)–C(24)	139.4 (3)
S(1)–Os(1)–S(2)	81.85 (9)	S(3)–Os(4)–S(4)	81.56 (9)	Os(3)–W(1)–S(1)	90.98 (6)	Os(6)–W(2)–S(3)	86.34 (7)
S(1)–Os(1)–C(1)	92.5 (3)	S(3)–Os(4)–C(13)	172.0 (4)	Os(3)–W(1)–S(2)	50.17 (6)	Os(6)–W(2)–S(4)	48.94 (7)
S(1)–Os(1)–C(2)	175.0 (3)	S(3)–Os(4)–C(14)	95.7 (4)	Os(3)–W(1)–P(1)	141.87 (6)	Os(6)–W(2)–P(2)	131.10 (8)
S(1)–Os(1)–C(3)	93.4 (3)	S(3)–Os(4)–C(15)	93.2 (4)	Os(3)–W(1)–C(10)	70.2 (3)	Os(6)–W(2)–C(22)	80.7 (4)
S(2)–Os(1)–C(1)	172.0 (3)	S(4)–Os(4)–C(13)	94.3 (4)	Os(3)–W(1)–C(11)	137.8 (3)	Os(6)–W(2)–C(23)	150.6 (4)
S(2)–Os(1)–C(2)	94.8 (4)	S(4)–Os(4)–C(14)	91.4 (4)	Os(3)–W(1)–C(12)	96.8 (3)	Os(6)–W(2)–C(24)	92.4 (3)
S(2)–Os(1)–C(3)	94.8 (4)	S(4)–Os(4)–C(15)	173.5 (3)	Os(1)–C(1)–O(1)	174.1 (10)	Os(4)–C(13)–O(13)	178.4 (11)
Os(1)–Os(2)–S(1)	53.59 (6)	Os(4)–Os(5)–S(3)	51.09 (7)	Os(1)–C(2)–O(2)	176.5 (10)	Os(4)–C(14)–O(14)	177.2 (11)
Os(1)–Os(2)–C(4)	100.5 (4)	Os(4)–Os(5)C(16)	92.1 (4)	Os(1)–C(3)–O(3)	177.7 (10)	Os(4)–C(15)–O(15)	173.2 (11)
Os(1)–Os(2)–C(5)	101.6 (4)	Os(4)–Os(5)–C(17)	127.7 (4)	Os(2)–C(4)–O(4)	177.1 (12)	Os(5)–C(16)–O(16)	179.4 (13)
Os(1)–Os(2)–C(6)	161.6 (4)	Os(4)–Os(5)–C(18)	139.7 (4)	Os(2)–C(5)–O(5)	177.9 (13)	Os(5)–C(17)–O(17)	173.8 (12)
Os(3)–Os(2)–S(1)	93.07 (7)	Os(6)–Os(5)–S(3)	91.92 (6)	Os(2)–C(6)–O(6)	179.0 (12)	Os(5)–C(18)–O(18)	174.0 (12)
Os(3)–Os(2)–C(4)	81.7 (4)	Os(6)–Os(5)–C(16)	121.5 (4)	Os(3)–C(7)–O(7)	173.6 (12)	Os(6)–C(19)–O(19)	176.4 (13)
Os(3)–Os(2)–C(5)	161.1 (4)	Os(6)–Os(5)–C(17)	77.2 (4)	Os(3)–C(8)–O(8)	177.1 (11)	Os(6)–C(20)–O(20)	177.3 (12)
Os(3)–Os(2)–C(6)	107.6 (4)	Os(6)–Os(5)–C(18)	146.2 (3)	Os(3)–C(9)–O(9)	175.4 (10)	Os(6)–C(21)–O(21)	175.6 (15)
W(1)–Os(2)–S(1)	53.26 (7)	W(2)–Os(5)–S(3)	54.85 (6)	W(1)–C(10)–O(10)	172.6 (11)	W(2)–C(22)–O(22)	174.7 (12)
W(1)–Os(2)–C(4)	138.2 (4)	W(2)–Os(5)–C(16)	161.3 (4)	W(1)–C(11)–O(11)	179.8 (10)	W(2)–C(23)–O(23)	177.9 (10)
W(1)–Os(2)–C(5)	129.9 (4)	W(2)–Os(5)–C(17)	108.9 (4)	W(1)–C(12)–O(12)	177.3 (11)	W(2)–C(24)–O(24)	177.9 (10)
W(1)–Os(2)–C(6)	86.1 (4)	W(2)–Os(5)–C(18)	91.9 (4)				

Table VI. Final Fractional Atomic Coordinates for $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**3**)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Os(1)	0.70977 (5)	−0.10523 (10)	0.41823 (4)	C(5)	0.7872 (11)	0.127 (2)	0.3488 (10)
Os(2)	0.68736 (5)	0.13897 (10)	0.33212 (4)	C(6)	0.6774 (14)	0.320 (3)	0.2928 (13)
Os(3)	0.74086 (5)	0.22679 (9)	0.47299 (4)	C(7)	0.6604 (13)	0.032 (3)	0.2537 (11)
W	0.77846 (5)	0.02299 (9)	0.59163 (4)	C(8)	0.6654 (13)	0.345 (3)	0.4398 (12)
S(1)	0.8184 (3)	0.0182 (6)	0.4963 (2)	C(9)	0.7770 (9)	0.315 (2)	0.5615 (8)
S(2)	0.6622 (3)	0.0418 (6)	0.4870 (2)	C(10)	0.8039 (12)	0.343 (3)	0.4517 (11)
P(1)	0.6786 (4)	0.0207 (6)	0.6339 (3)	C(11)	0.8137 (10)	0.135 (2)	0.6745 (9)
P(2)	0.9143 (4)	−0.0110 (7)	0.6470 (3)	C(12)	0.7857 (13)	−0.160 (3)	0.6329 (11)
O(1)	0.7362 (11)	−0.364 (2)	0.5061 (10)	C(21)	0.6195 (11)	0.172 (2)	0.6124 (10)
O(2)	0.5604 (10)	−0.195 (2)	0.3163 (9)	C(22)	0.5430 (15)	0.174 (3)	0.5808 (13)
O(3)	0.7847 (10)	−0.243 (2)	0.3372 (9)	C(23)	0.5058 (15)	0.302 (3)	0.5665 (14)
O(4)	0.5345 (8)	0.142 (2)	0.3292 (8)	C(24)	0.5381 (14)	0.423 (3)	0.5821 (12)
O(5)	0.8504 (8)	0.123 (2)	0.3571 (7)	C(25)	0.6086 (14)	0.428 (3)	0.6143 (13)
O(6)	0.6695 (10)	0.436 (2)	0.2749 (9)	C(26)	0.6476 (13)	0.303 (3)	0.6278 (11)
O(7)	0.6467 (9)	−0.050 (2)	0.2067 (8)	C(27)	0.6181 (14)	−0.129 (3)	0.6059 (13)
O(8)	0.6133 (9)	0.429 (2)	0.4184 (8)	C(28)	0.7033 (13)	0.006 (3)	0.7261 (11)
O(9)	0.7967 (8)	0.399 (2)	0.6038 (7)	C(31)	0.9635 (11)	0.126 (2)	0.6246 (10)
O(10)	0.8460 (10)	0.413 (2)	0.4409 (9)	C(32)	1.0052 (14)	0.098 (3)	0.5854 (13)
O(11)	0.8365 (7)	0.201 (2)	0.7238 (7)	C(33)	1.0357 (16)	0.214 (3)	0.5668 (14)
O(12)	0.7953 (10)	−0.270 (2)	0.6583 (9)	C(34)	1.0289 (16)	0.342 (3)	0.5830 (14)
C(1)	0.7250 (14)	−0.260 (3)	0.4741 (13)	C(35)	0.9933 (16)	0.371 (3)	0.6249 (15)
C(2)	0.6193 (14)	−0.167 (3)	0.3566 (13)	C(36)	0.9622 (12)	0.261 (3)	0.6458 (11)
C(3)	0.7488 (15)	−0.189 (3)	0.3666 (14)	C(37)	0.9463 (14)	−0.173 (3)	0.6226 (13)
C(4)	0.5931 (11)	0.137 (2)	0.3303 (10)	C(38)	0.9592 (13)	−0.015 (3)	0.7393 (11)

bonds. One example is the dinuclear compound $W_2(\mu\text{-}CO)_2\{\mu\text{-}HC(N\text{-}3,5\text{-}xylyl)_2\}\{HC(N\text{-}3,5\text{-}xylyl)_2\}\{N\text{-}3,5\text{-}xylyl)CH(N\text{-}3,5\text{-}xylyl)CH_2\}$ for which the W–W separation is 2.464 (3) Å.[22] The metal–sulfur bonding in **5** is very similar to that in **4** except that

Scheme I

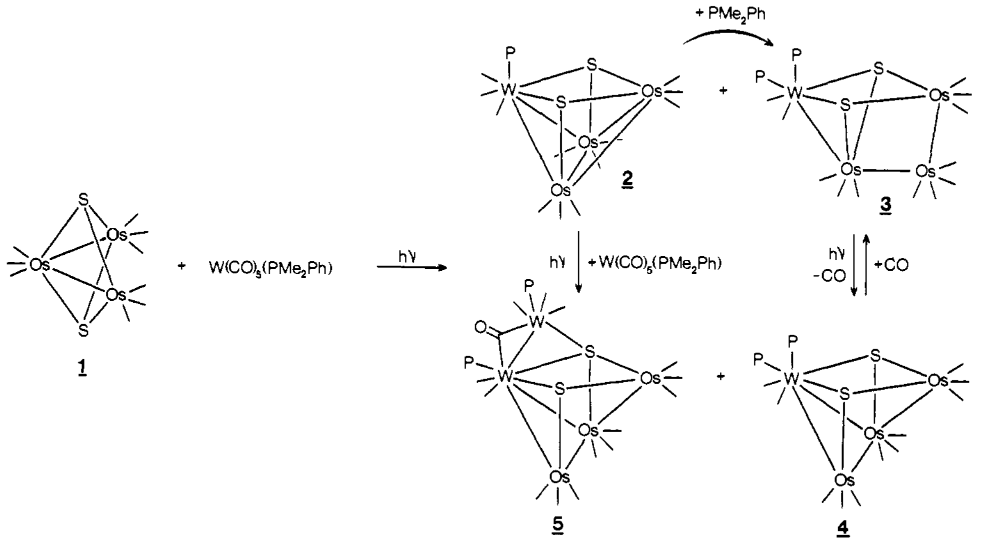

Table VII. Interatomic Distances with esds for $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (3)

atoms	distance, Å	atoms	distance, Å
Os(1)–Os(2)	2.895 (1)	C(4)–O(4)	1.16 (2)
Os(2)–Os(3)	2.887 (1)	C(5)–O(5)	1.20 (2)
Os(3)–W	3.044 (1)	C(6)–O(6)	1.16 (2)
Os(1)–S(1)	2.440 (4)	C(7)–O(7)	1.22 (2)
Os(1)–S(2)	2.482 (5)	C(8)–O(8)	1.24 (2)
Os(1)–C(1)	1.85 (2)	C(9)–O(9)	1.16 (1)
Os(1)–C(2)	1.85 (2)	C(10)–O(10)	1.16 (2)
Os(1)–C(3)	1.78 (3)	C(11)–O(11)	1.15 (1)
Os(2)–C(4)	1.86 (2)	C(12)–O(12)	1.16 (2)
Os(2)–C(5)	1.88 (2)	P(1)–C(21)	1.80 (2)
Os(2)–C(6)	1.90 (2)	P(1)–C(27)	1.81 (2)
Os(2)–C(7)	1.85 (2)	P(1)–C(28)	1.84 (2)
Os(3)–S(1)	2.447 (4)	P(2)–C(31)	1.81 (2)
Os(3)–S(2)	2.461 (4)	P(2)–C(37)	1.83 (2)
Os(3)–C(8)	1.78 (2)	P(2)–C(38)	1.81 (2)
Os(3)–C(9)	1.93 (1)	C(21)–C(22)	1.40 (2)
Os(3)–C(10)	1.87 (2)	C(22)–C(23)	1.40 (3)
W–S(1)	2.470 (4)	C(23)–C(24)	1.31 (3)
W–S(2)	2.497 (4)	C(24)–C(25)	1.30 (3)
W–P(1)	2.494 (5)	C(25)–C(26)	1.39 (3)
W–P(2)	2.500 (5)	C(26)–C(21)	1.36 (2)
W···C(9)	2.86 (1)	C(31)–C(32)	1.42 (3)
W–C(11)	1.95 (1)	C(32)–C(33)	1.39 (3)
W–C(12)	1.94 (2)	C(33)–C(34)	1.29 (3)
C(1)–O(1)	1.18 (2)	C(34)–C(35)	1.38 (3)
C(2)–O(2)	1.17 (2)	C(35)–C(36)	1.38 (3)
C(3)–O(3)	1.24 (3)	C(36)–C(31)	1.37 (2)
Os(1)···W	3.612 (1)	S(1)···S(2)	3.046 (6)

the sulfido ligand S(1) in **5** is a quadruple bridge since it is also bonded to the second tungsten atom. Each tungsten atom contains one PMe_2Ph ligand. Overall, there are 14 carbonyl ligands. Each metal atom contains three terminal carbonyls, except W(2), which has only one. C(14)–O(14) is a bridge across the W(1)–W(2) bond.

Independent Synthesis of 3, 4, and 5. Although the four products **2**–**5** are all obtained in the photolytic reaction of **1** with $W(CO)_5(PMe_2Ph)$, clearly **3** and **4** which contain two phosphine ligands, cannot be primary products. We have found that **3**–**5** can be prepared by using **2** as a reagent. **3** can be made in 69% yield by the addition of 1 equiv of PMe_2Ph to **2**. When photolyzed, **3** loses either CO or PMe_2Ph to yield **4** (37% yield) or regenerate **2** (18% yield). When photolyzed in the presence of $W(CO)_5(PMe_2Ph)$, **2** adds a second tungsten moiety and yields **5** (51% yield). These reactions are summarized in Scheme I.

Table VIII. Interatomic Angles with esds for $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (3)

atoms	angle, deg	atoms	angle, deg
Os(1)–Os(2)–Os(3)	70.90 (2)	Os(2)–Os(3)–C(10)	85.4 (6)
Os(2)–Os(3)–W	123.20 (3)	W–Os(3)–S(1)	52.08 (10)
Os(2)–Os(1)–S(1)	84.99 (10)	W–Os(3)–S(2)	52.65 (9)
Os(2)–Os(1)–S(2)	85.57 (10)	W–Os(3)–C(8)	128.5 (7)
Os(2)–Os(1)–C(1)	179.3 (8)	W–Os(3)–C(9)	65.8 (4)
Os(2)–Os(1)–C(2)	87.0 (7)	W–Os(3)–C(10)	128.4 (5)
Os(2)–Os(1)–C(3)	87.9 (8)	S(1)–Os(3)–S(2)	76.71 (15)
S(1)–Os(1)–S(2)	76.45 (14)	S(1)–Os(3)–C(8)	163.5 (6)
S(1)–Os(1)–C(1)	94.3 (6)	S(1)–Os(3)–C(9)	101.5 (4)
S(1)–Os(1)–C(2)	169.5 (7)	S(1)–Os(3)–C(10)	95.9 (6)
S(1)–Os(1)–C(3)	98.9 (7)	S(2)–Os(3)–C(8)	91.6 (7)
S(2)–Os(1)–C(1)	94.2 (7)	S(2)–Os(3)–C(9)	101.4 (4)
S(2)–Os(1)–C(2)	96.2 (7)	S(2)–Os(3)–C(10)	169.2 (6)
S(2)–Os(1)–C(3)	172.3 (8)	Os(3)–W–S(1)	51.42 (9)
Os(1)–Os(2)–C(4)	84.2 (5)	Os(3)–W–S(2)	51.58 (10)
Os(1)–Os(2)–C(5)	87.2 (5)	Os(3)–W–P(1)	110.10 (11)
Os(1)–Os(2)–C(6)	168.1 (7)	Os(3)–W–P(2)	109.50 (12)
Os(1)–Os(2)–C(7)	92.7 (6)	Os(3)–W–C(11)	106.5 (4)
Os(3)–Os(2)–C(4)	88.3 (5)	Os(3)–W–C(12)	154.8 (5)
Os(3)–Os(2)–C(5)	84.3 (5)	S(1)–W–S(2)	75.65 (14)
Os(3)–Os(2)–C(6)	97.2 (6)	S(1)–W–P(1)	150.25 (14)
Os(3)–Os(2)–C(7)	163.3 (6)	S(1)–W–P(2)	75.02 (15)
Os(2)–Os(3)–S(1)	85.02 (9)	S(2)–W–P(1)	74.84 (14)
Os(2)–Os(3)–S(2)	86.13 (9)	S(2)–W–P(2)	150.52 (16)
Os(2)–Os(3)–C(8)	82.6 (6)	Os(1)–S(1)–Os(3)	86.66 (13)
Os(2)–Os(3)–C(9)	170.9 (4)	Os(1)–C(1)–O(1)	175 (2)
Os(1)–S(2)–Os(3)	85.45 (15)	Os(1)–C(2)–O(2)	175 (2)
Os(1)–S(1)–W	94.73 (16)	Os(1)–C(3)–O(3)	172 (2)
Os(1)–S(2)–W	93.02 (15)	Os(2)–C(4)–O(4)	177 (2)
Os(3)–S(1)–W	76.50 (12)	Os(2)–C(5)–O(5)	177 (1)
Os(3)–S(2)–W	75.77 (12)	Os(2)–C(6)–O(6)	172 (2)
W–P(1)–C(21)	115.7 (6)	Os(2)–C(7)–O(7)	173 (2)
W–P(1)–C(27)	114.1 (8)	Os(3)–C(8)–O(8)	178 (1)
W–P(1)–C(28)	118.9 (6)	Os(3)–C(9)–O(9)	161 (1)
W–P(2)–C(31)	112.2 (5)	Os(3)–C(10)–O(10)	177 (2)
W–P(2)–C(37)	114.2 (7)	W–C(11)–O(11)	178 (1)
W–P(2)–C(38)	119.0 (7)	W–C(12)–O(12)	175 (2)

The UV–vis spectrum of **2** showed a low-energy absorption $\lambda_1 = 583$ nm (ϵ 1600 $M^{-1}\ cm^{-1}$) and one at higher energy $\lambda_2 = 404$ nm (ϵ 4000 $M^{-1}\ cm^{-1}$). Two absorptions were also observed in the spectrum of **4** but these are shifted to significantly higher energy, $\lambda_1 = 435$ (ϵ 1630 $M^{-1}\ cm^{-1}$), $\lambda_2 = 351$ nm (ϵ 5230 $M^{-1}\ cm^{-1}$), compared to those in **2**.

Discussion

Compound **2** provides yet another example of the increasing number of polynuclear metal complexes that violate the requirements of the 18-electron rule. Compound **2** contains 64 electrons and to be electron precise should contain only four

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(21) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086.

(22) De Roode, W. H.; Vrieze, K. *J. Organomet. Chem.* **1978**, *145*, 207.

Table IX. Final Fractional Atomic Coordinates for $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**4**)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Os(1)	0.82144 (7)	0.22139 (6)	0.09582 (5)	C(5)	0.616 (2)	0.354 (2)	−0.098 (2)
Os(2)	0.65277 (8)	0.26181 (8)	−0.01572 (6)	C(6)	0.922 (2)	0.473 (2)	0.076 (2)
Os(3)	0.80842 (8)	0.40877 (6)	0.01690 (6)	C(7)	0.728 (2)	0.499 (2)	0.049 (2)
W	0.82724 (7)	0.21916 (6)	−0.05517 (5)	C(8)	0.793 (2)	0.497 (2)	−0.062 (2)
S	0.7477 (4)	0.1044 (4)	0.0057 (3)	C(9)	0.827 (2)	0.305 (2)	−0.139 (1)
P(1)	0.7823 (5)	0.1038 (5)	0.1769 (3)	C(10)	0.946 (2)	0.296 (2)	−0.013 (1)
P(2)	0.7458 (5)	0.1026 (5)	−0.1627 (4)	C(11)	0.935 (2)	0.125 (2)	−0.057 (1)
O(1)	1.027 (1)	0.162 (1)	0.157 (1)	C(21)	0.826 (2)	−0.028 (2)	0.175 (1)
O(2)	0.827 (2)	0.394 (2)	0.205 (1)	C(22)	0.911 (2)	−0.059 (2)	0.226 (2)
O(3)	0.482 (2)	0.125 (2)	−0.069 (2)	C(23)	0.943 (3)	−0.166 (3)	0.220 (2)
O(4)	0.565 (2)	0.359 (2)	0.091 (1)	C(24)	0.892 (3)	−0.226 (2)	0.169 (2)
O(5)	0.594 (2)	0.415 (2)	−0.140 (1)	C(25)	0.808 (3)	−0.200 (3)	0.122 (2)
O(6)	0.988 (1)	0.509 (1)	0.114 (1)	C(26)	0.776 (2)	−0.099 (2)	0.123 (2)
O(7)	0.675 (1)	0.558 (1)	0.063 (1)	C(27)	0.660 (2)	0.088 (2)	0.164 (2)
O(8)	0.805 (1)	0.551 (1)	−0.112 (1)	C(28)	0.826 (2)	0.144 (2)	0.266 (2)
O(9)	0.829 (1)	0.352 (1)	−0.192 (1)	C(31)	0.708 (2)	−0.025 (2)	−0.142 (1)
O(10)	1.028 (1)	0.329 (1)	0.009 (1)	C(32)	0.778 (2)	−0.097 (2)	−0.109 (2)
O(11)	0.998 (1)	0.072 (1)	−0.059 (1)	C(33)	0.753 (2)	−0.198 (2)	−0.089 (2)
C(1)	0.948 (2)	0.186 (2)	0.134 (1)	C(34)	0.669 (2)	−0.224 (2)	−0.096 (2)
C(2)	0.827 (2)	0.329 (2)	0.162 (1)	C(35)	0.596 (3)	−0.154 (3)	−0.126 (2)
C(3)	0.555 (3)	0.180 (3)	−0.045 (2)	C(36)	0.618 (2)	−0.056 (2)	−0.151 (2)
C(4)	0.604 (2)	0.323 (2)	0.048 (2)	C(37)	0.642 (2)	0.157 (2)	−0.223 (2)
				C(38)	0.821 (2)	0.076 (2)	−0.222 (2)

Table X. Interatomic Distances with esds for $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**4**)

Os(1)···Os(2)	3.813 (1)	P(1)–C(28)	1.79 (3)
Os(1)···W	3.666 (1)	P(2)–C(31)	1.83 (2)
Os(1)–Os(3)	2.829 (1)	P(2)–C(37)	1.79 (2)
Os(2)–Os(3)	2.923 (1)	P(2)–C(38)	1.80 (3)
Os(2)–W	2.814 (1)	C(21)–C(22)	1.34 (3)
Os(3)–W	3.016 (1)	C(22)–C(23)	1.37 (3)
Os(1)–S(1)	2.401 (5)	C(23)–C(24)	1.35 (3)
Os(3)–S(1)	2.396 (5)	C(24)–C(25)	1.35 (4)
W–S(1)	2.457 (6)	C(25)–C(26)	1.36 (3)
Os(1)–S(2)	2.456 (7)	C(21)–C(26)	1.37 (3)
Os(2)–S(2)	2.381 (6)	C(31)–C(32)	1.38 (3)
W–S(2)	2.475 (6)	C(32)–C(33)	1.35 (4)
W–P(1)	2.575 (6)	C(33)–C(34)	1.41 (5)
W–P(2)	2.563 (6)	C(34)–C(35)	1.31 (4)
S(1)···S(2)	3.209 (10)	C(35)–C(36)	1.39 (4)
Os(1)–C(1)	1.82 (3)	C(31)–C(36)	1.41 (3)
Os(1)–C(2)	1.86 (4)	C(1)–O(1)	1.21 (3)
Os(1)–C(3)	1.86 (2)	C(2)–O(2)	1.16 (4)
Os(2)–C(4)	1.85 (3)	C(3)–O(3)	1.15 (3)
Os(2)–C(5)	1.87 (2)	C(4)–O(4)	1.22 (3)
Os(2)–C(6)	1.87 (2)	C(5)–O(5)	1.10 (3)
Os(3)–C(7)	1.82 (3)	C(6)–O(6)	1.16 (2)
Os(3)–C(8)	1.96 (3)	C(7)–O(7)	1.21 (3)
Os(3)–C(9)	1.85 (3)	C(8)–O(8)	1.11 (3)
W–C(10)	1.96 (3)	C(9)–O(9)	1.17 (3)
W–C(11)	1.93 (2)	C(10)–O(10)	1.23 (3)
P(1)–C(21)	1.80 (2)	C(11)–O(11)	1.21 (2)
P(1)–C(27)	1.82 (4)		

Table XI. Interatomic Angles with esds for $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (**4**)

atoms	angle, deg	atoms	angle, deg
Os(1)–Os(3)–Os(2)	83.02 (4)	S(1)–Os(3)–C(7)	86.0 (8)
Os(1)–Os(3)–W	77.64 (4)	S(1)–Os(3)–C(8)	121.4 (8)
Os(2)–Os(3)–W	56.54 (3)	S(1)–Os(3)–C(9)	143.8 (9)
Os(3)–Os(2)–W	63.38 (3)	Os(2)–W–S(1)	102.88 (13)
Os(2)–W–Os(3)	60.08 (3)	Os(2)–W–S(2)	53.04 (13)
Os(1)–S(1)–Os(3)	72.27 (16)	Os(2)–W–P(1)	129.30 (17)
Os(1)–S(1)–W	97.99 (22)	Os(2)–W–P(2)	141.77 (14)
Os(3)–S(1)–W	76.83 (17)	Os(2)–W–C(10)	83.0 (7)
Os(1)–S(2)–Os(2)	104.02 (23)	Os(2)–W–C(11)	71.4 (6)
Os(1)–S(2)–W	96.05 (23)	Os(3)–W–S(1)	50.68 (13)
Os(2)–S(2)–W	70.79 (16)	Os(3)–W–S(2)	77.20 (15)
Os(3)–Os(1)–S(1)	53.78 (13)	Os(3)–W–P(1)	137.16 (17)
Os(3)–Os(1)–S(2)	81.22 (14)	Os(3)–W–P(2)	99.18 (15)
Os(3)–Os(1)–C(1)	159.4 (8)	Os(3)–W–C(10)	141.3 (7)
Os(3)–Os(1)–C(2)	94.1 (10)	Os(3)–W–C(11)	77.6 (7)
Os(3)–Os(1)–C(3)	102.3 (8)	S(1)–W–S(2)	81.17 (20)
S(1)–Os(1)–S(2)	82.69 (21)	S(1)–W–P(1)	89.65 (22)
S(1)–Os(1)–C(1)	106.3 (9)	S(1)–W–P(2)	81.43 (20)
S(1)–Os(1)–C(2)	90.0 (10)	S(1)–W–C(10)	163.0 (8)
S(1)–Os(1)–C(3)	156.1 (8)	S(1)–W–C(11)	116.9 (8)
S(2)–Os(1)–C(1)	91.6 (10)	S(2)–W–P(1)	81.73 (21)
S(2)–Os(1)–C(2)	172.7 (10)	S(2)–W–P(2)	159.94 (21)
S(2)–Os(1)–C(3)	94.7 (9)	S(2)–W–C(1)	90.2 (8)
Os(3)–Os(2)–S(2)	80.48 (17)	S(2)–W–C(11)	124.4 (6)
Os(3)–Os(2)–C(4)	88.9 (11)	P(1)–W–P(2)	88.25 (21)
Os(3)–Os(2)–C(5)	167.9 (7)	P(1)–W–C(10)	74.6 (8)
Os(3)–Os(2)–C(6)	100.6 (9)	P(1)–W–C(11)	143.6 (6)
W–Os(2)–S(2)	56.17 (14)	P(2)–W–C(10)	103.9 (8)
W–Os(2)–C(4)	112.3 (8)	P(2)–W–C(11)	72.9 (7)
W–Os(2)–C(5)	104.6 (7)	W–P(1)–C(21)	123.5 (8)
W–Os(2)–C(6)	149.6 (8)	W–P(1)–C(27)	112.8 (12)
S(2)–Os(2)–C(4)	167.0 (10)	W–P(1)–C(28)	114.4 (8)
S(2)–Os(2)–C(5)	93.2 (7)	W–P(2)–C(31)	115.5 (7)
S(2)–Os(2)–C(6)	97.4 (7)	W–P(2)–C(37)	118.3 (8)
Os(1)–Os(3)–S(1)	53.95 (13)	W–P(2)–C(38)	114.6 (9)
Os(1)–Os(3)–C(7)	94.4 (8)	Os(1)–C(1)–O(1)	173 (3)
Os(1)–Os(3)–C(8)	173.9 (8)	Os(1)–C(2)–O(2)	174 (3)
Os(1)–Os(3)–C(9)	90.0 (9)	Os(1)–C(3)–O(3)	177 (3)
Os(2)–Os(3)–S(1)	101.33 (16)	Os(2)–C(4)–O(4)	171 (3)
Os(2)–Os(3)–C(7)	168.4 (8)	Os(2)–C(5)–O(5)	178 (3)
Os(2)–Os(3)–C(8)	94.6 (11)	Os(2)–C(6)–O(6)	177 (3)
Os(2)–Os(3)–C(9)	73.8 (11)	Os(3)–C(7)–O(7)	172 (3)
W–Os(3)–S(1)	52.49 (15)	Os(3)–C(8)–O(8)	174 (3)
W–Os(3)–C(7)	134.0 (7)	Os(3)–C(9)–O(9)	170 (3)
W–Os(3)–C(8)	96.3 (9)	W–C(10)–O(10)	177 (3)
W–Os(3)–C(9)	129.8 (11)	W–C(11)–O(11)	169 (2)

metal–metal bonds.[23] However, **2** has five metal–metal internuclear separations that are short enough to imply significant bonding interactions. The PSEP theory has successfully explained the bonding in the vast majority of anomalous clusters like **2** and seems to apply well in the case of **2** also.[3-5] According to this theory the cluster core of **2**, including the sulfido ligands, has the form of a nido-pentagonal bipyramid. A pentagonal-bipyramidal cluster should contain eight bonding cluster valence orbitals and thus should accomodate 16 cluster valence electrons. Indeed, according to this theory, **2** contains 16 cluster valence electrons. However, it should not go unnoticed that, of the five metal–metal bonds, two (indicated by the dashed lines in Figure 1) are significantly longer than the others. This could be indicative of a selective weakening of these bonds. A similar selective lengthening of two of the five metal–metal bonds was observed in the homonuclear homologue of **2**, $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (**6**).[11] The low-energy absorption λ = 583 nm observed in **2**, which shifts to 435 nm in **4**, seems to support the notion of low-lying delocalized

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[23] Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

Table XII. Final Fractional Atomic Coordinates for $Os_3W_2(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**5**)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Os(1)	0.9640 (1)	0.07531 (6)	0.87701 (7)	C(5)	1.163 (3)	0.147 (2)	0.603 (2)
Os(2)	1.0496 (1)	0.09980 (6)	0.64781 (7)	C(6)	1.145 (2)	0.032 (1)	0.669 (2)
Os(3)	1.0856 (1)	0.17142 (6)	0.80269 (7)	C(7)	1.139 (3)	0.213 (2)	0.902 (2)
W(1)	0.7018 (1)	0.07385 (6)	0.67060 (7)	C(8)	1.227 (2)	0.126 (1)	0.796 (2)
W(2)	0.8648 (1)	0.16187 (5)	0.70035 (7)	C(9)	1.126 (2)	0.242 (1)	0.740 (2)
S(1)	0.9037 (6)	0.0507 (3)	0.7302 (4)	C(10)	0.545 (2)	0.092 (1)	0.627 (2)
S(2)	0.8924 (6)	0.1782 (4)	0.8490 (4)	C(11)	0.729 (2)	0.037 (2)	0.558 (2)
P(1)	0.6408 (7)	−0.0378 (4)	0.6969 (5)	C(12)	0.651 (2)	0.101 (1)	0.784 (2)
P(2)	0.7822 (7)	0.2705 (4)	0.7160 (5)	C(13)	0.930 (3)	0.210 (2)	0.611 (2)
O(1)	0.762 (2)	0.009 (1)	0.953 (1)	C(14)	0.730 (3)	0.156 (2)	0.604 (2)
O(2)	1.060 (2)	0.114 (1)	1.048 (1)	C(21)	0.592 (2)	−0.059 (1)	0.798 (2)
O(3)	1.137 (2)	−0.031 (1)	0.868 (1)	C(22)	0.497 (3)	−0.030 (2)	0.827 (2)
O(4)	0.975 (2)	0.068 (1)	0.469 (1)	C(23)	0.455 (3)	−0.044 (2)	0.904 (2)
O(5)	1.239 (2)	0.179 (1)	0.579 (1)	C(24)	0.512 (3)	−0.088 (2)	0.950 (2)
O(6)	1.209 (2)	−0.010 (1)	0.685 (1)	C(25)	0.601 (3)	−0.118 (2)	0.929 (2)
O(7)	1.175 (2)	0.229 (1)	0.963 (2)	C(26)	0.647 (3)	−0.102 (2)	0.850 (2)
O(8)	1.312 (2)	0.099 (1)	0.800 (1)	C(27)	0.524 (3)	−0.061 (2)	0.630 (2)
O(9)	1.141 (2)	0.286 (1)	0.699 (1)	C(28)	0.754 (3)	−0.092 (2)	0.675 (2)
O(10)	0.459 (2)	0.107 (1)	0.597 (1)	C(31)	0.642 (2)	0.266 (1)	0.764 (2)
O(11)	0.737 (2)	0.013 (1)	0.493 (1)	C(32)	0.546 (3)	0.253 (2)	0.716 (2)
O(12)	0.613 (2)	0.114 (1)	0.848 (1)	C(33)	0.442 (3)	0.245 (2)	0.753 (2)
O(13)	0.957 (2)	0.236 (1)	0.552 (1)	C(34)	0.439 (3)	0.250 (2)	0.838 (2)
O(14)	0.684 (2)	0.187 (1)	0.547 (1)	C(35)	0.534 (3)	0.262 (2)	0.888 (2)
C(1)	0.833 (2)	0.033 (1)	0.921 (2)	C(36)	0.636 (2)	0.272 (2)	0.849 (2)
C(2)	1.030 (2)	0.099 (1)	0.982 (2)	C(37)	0.866 (3)	0.323 (2)	0.781 (2)
C(3)	1.061 (2)	0.009 (1)	0.874 (2)	C(38)	0.749 (3)	0.316 (2)	0.626 (2)
C(4)	1.000 (3)	0.076 (2)	0.538 (2)				

Table XIII. Interatomic Distances with esds for $Os_3W_2(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$, **5**

atoms	distance, Å	atoms	distance, Å
Os(1)···Os(2)	3.867 (1)	W(1)–C(12)	2.017 (16)
Os(1)···W(2)	3.527 (1)	W(2)–C(13)	1.939 (21)
Os(1)–Os(3)	2.802 (1)	W(1)–C(14)	2.093 (21)
Os(2)–Os(3)	2.924 (1)	W(2)–C(14)	2.145 (20)
Os(2)–W(2)	2.703 (1)	P(1)–C(21)	1.789 (17)
Os(3)–W(2)	2.991 (1)	P(1)–C(27)	1.758 (24)
W(1)–W(2)	2.711 (1)	P(1)–C(28)	1.812 (23)
Os(1)–S(1)	2.469 (4)	P(2)–C(31)	1.841 (17)
Os(1)–S(2)	2.402 (5)	P(2)–C(37)	1.797 (23)
Os(2)–S(1)	2.437 (4)	P(2)–C(38)	1.764 (24)
Os(3)–S(2)	2.408 (4)	C(1)–O(1)	1.12 (2)
W(1)–S(1)	2.548 (4)	C(2)–O(2)	1.15 (2)
W(2)–S(1)	2.478 (5)	C(3)–O(3)	1.24 (2)
W(2)–S(2)	2.401 (4)	C(4)–O(4)	1.14 (2)
W(1)–P(1)	2.548 (6)	C(5)–O(5)	1.20 (2)
W(2)–P(2)	2.548 (6)	C(6)–O(6)	1.19 (2)
Os(1)–C(1)	1.938 (17)	C(7)–O(7)	1.10 (2)
Os(1)–C(2)	1.878 (18)	C(8)–O(8)	1.16 (2)
Os(1)–C(3)	1.831 (20)	C(9)–O(9)	1.16 (2)
Os(2)–C(4)	1.881 (22)	C(10)–O(10)	1.14 (2)
Os(2)–C(5)	1.833 (22)	C(11)–O(11)	1.17 (2)
Os(2)–C(6)	1.864 (19)	C(12)–O(12)	1.16 (2)
Os(3)–C(7)	1.902 (24)	C(13)–O(13)	1.16 (2)
Os(3)–C(8)	1.926 (20)	C(14)–O(14)	1.24 (2)
Os(3)–C(9)	1.895 (19)	C–C (ring 21–26)$_{av}$	1.37 (3)
W(1)–C(10)	1.971 (19)	C–C (ring 31–36)$_{av}$	1.37 (3)
W(1)–C(11)	2.005 (19)		

Table XIV. Selected Interatomic Angles with esds for $Os_3W_2(CO)_{14}(PMe_2Ph)_2(\mu_3\text{-}S)(\mu_4\text{-}S)$ (**5**)

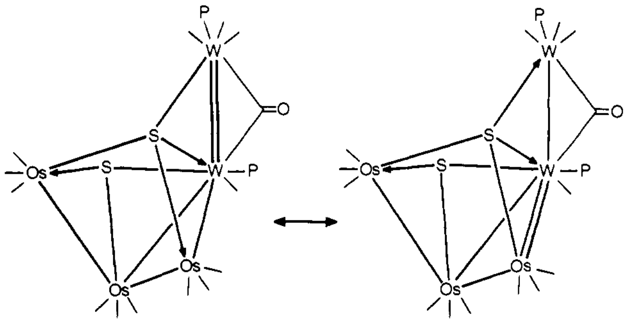
atoms	angle, deg	atoms	angle, deg
Os(1)–Os(3)–Os(2)	84.92 (3)	Os(3)–W(2)–C(13)	90.4 (6)
Os(1)–Os(3)–W(2)	74.93 (3)	Os(3)–W(2)–C(14)	167.6 (5)
Os(3)–Os(2)–W(2)	64.08 (3)	W(1)–W(2)–C(14)	58.61 (10)
Os(2)–Os(3)–W(2)	54.36 (2)	W(1)–W(2)–S(2)	109.60 (11)
Os(2)–W(2)–Os(3)	61.56 (3)	W(1)–W(2)–P(2)	113.21 (12)
Os(2)–W(2)–W(1)	99.39 (3)	W(1)–W(2)–C(13)	122.7 (6)
Os(3)–W(2)–W(1)	136.28 (3)	W(1)–W(2)–C(14)	49.4 (6)
Os(1)–S(1)–Os(2)	104.00 (16)	W(2)–W(1)–S(1)	56.11 (10)
Os(1)–S(1)–W(1)	121.94 (17)	Os(1)–Os(3)–S(2)	54.27 (12)
Os(1)–S(1)–W(2)	90.94 (15)	Os(1)–Os(3)–C(7)	98.7 (7)
Os(2)–S(1)–W(1)	111.80 (60)	Os(1)–Os(3)–C(8)	95.6 (6)
Os(2)–S(1)–W(2)	66.71 (12)	Os(1)–Os(3)–C(9)	163.7 (5)
W(1)–S(1)–W(2)	65.28 (11)	Os(2)–Os(3)–S(2)	100.98 (11)
Os(1)–S(2)–Os(3)	71.27 (13)	Os(2)–Os(3)–C(7)	169.1 (7)
Os(1)–S(2)–W(2)	94.50 (16)	Os(2)–Os(3)–C(8)	77.1 (5)
Os(3)–S(2)–W(2)	76.93 (13)	Os(2)–Os(3)–C(9)	90.6 (5)
Os(3)–Os(1)–S(1)	83.41 (10)	W(2)–Os(3)–S(2)	51.43 (10)
Os(3)–Os(1)–S(2)	54.46 (11)	W(2)–W(1)–P(1)	146.10 (12)
Os(3)–Os(1)–C(1)	157.3 (5)	W(2)–W(1)–C(10)	123.7 (6)
Os(3)–Os(1)–C(2)	88.8 (6)	W(2)–W(1)–C(11)	107.2 (6)
Os(3)–Os(1)–C(3)	104.0 (6)	W(2)–W(1)–C(12)	82.8 (5)
Os(3)–Os(2)–S(1)	81.41 (10)	W(2)–W(1)–C(14)	51.1 (6)
Os(3)–Os(2)–C(4)	161.9 (7)	W(1)–C(14)–W(2)	79.5 (7)
Os(3)–Os(2)–C(5)	88.0 (6)	Os(1)–C(1)–O(1)	174.8 (16)
Os(3)–Os(2)–C(6)	101.6 (5)	Os(1)–C(2)–O(2)	173.4 (16)
W(2)–Os(2)–S(1)	57.37 (11)	Os(1)–C(3)–O(3)	171.9 (16)
W(2)–Os(2)–C(4)	101.9 (6)	Os(2)–C(4)–O(4)	172.7 (20)
W(2)–Os(2)–C(5)	116.6 (7)	Os(2)–C(5)–O(5)	174.6 (18)
W(2)–Os(2)–C(6)	144.2 (5)	Os(2)–C(6)–O(6)	176.8 (15)
W(2)–Os(3)–C(7)	136.5 (7)	Os(3)–C(7)–O(7)	169.6 (24)
W(2)–Os(3)–C(8)	130.9 (5)	Os(3)–C(8)–O(8)	173.8 (17)
W(2)–Os(3)–C(9)	89.7 (5)	Os(3)–C(9)–O(9)	174.6 (17)
Os(2)–W(2)–S(1)	55.92 (10)	W(1)–C(10)–O(10)	173.1 (17)
Os(2)–W(2)–S(2)	107.78 (11)	W(1)–C(11)–O(11)	175.0 (18)
Os(2)–W(2)–P(2)	142.71 (12)	W(1)–C(12)–O(12)	174.8 (16)
Os(2)–W(2)–C(13)	72.2 (6)	W(2)–C(13)–O(13)	175.5 (16)
Os(2)–W(2)–C(14)	108.6 (5)	W(1)–C(14)–O(14)	139.4 (16)
Os(3)–W(2)–S(1)	79.41 (10)	W(2)–C(14)–O(14)	140.6 (17)
Os(3)–W(2)–S(2)	51.64 (11)		
Os(3)–W(2)–P(2)	101.73 (12)		

metal–metal bonding orbitals present in **2** as implied by the PSEP theory and absent in **4**.

It is believed that these elongated metal–metal bonds do exhibit an enhanced reactivity. This is demonstrated by the facile reaction of **2** with PMe_2Ph to form **3**. The addition of phosphine to **2** occurs via nucleophilic attack at the tungsten atom. A shift of a carbonyl ligand from the tungsten atom to Os(2) (Figure 1), accompanied by a shift of the sulfido ligand S(1) to Os(3), and cleavage of both elongated metal–metal bonds yield **3**. A similar reaction occurs in the addition of CO to **6**, but the site of addition of the nucleophile could not be discerned in that study.[11] The product **3** is electron precise and is structurally analogous to its homonuclear homologue, $Os_4(CO)_{13}(\mu_3\text{-}S)_2$ (**7**).[11]

Under the influence of UV irradiation **3** loses either PMe_2Ph to regenerate **2** or CO to yield **4**. The most surprising feature about **4** is its structure. **4** is isoelectronic to **2**, but unlike **2** it adopts an opened structure having only four metal–metal bonds and is thus electron precise. The most important difference between **2** and 4 is that they employ different bonding mechanisms. 2 utilizes a delocalized bonding mechanism (PSEP theory) and 4 utilizes a localized bonding mechanism (i.e., all bonds are of a two-center–two-electron type). Except for this difference in the structures of the clusters the only difference between 2 and 4 is in the identity of one of the ligands. 4 contains PMe_2Ph in place of one of the carbonyl ligands (e.g., C(11)–O(11) in Figure 1). It is not possible at this time to prove which factors are most responsible for the change in structure, but both steric and electronic effects could be important. Most simply, the substitution of a bulky phosphine for a carbonyl ligand should lead to enhanced ligand–ligand nonbonded repulsions. These might be sufficiently large in 4 that they cannot be offset by the formation of the additional metal–metal bond. Electronically, the replacement of a poorly electron-donating CO ligand by a good donor like phosphine would lead to an increase in the electron density on the tungsten atom. This could lead to a strengthening of the tungsten–osmium bonds, perhaps at the expense of the osmium–osmium bonds, and one of the latter is then broken. All of the metal–metal bonds in 4 are shorter than the corresponding bonds in 2, but the greatest contractions are for those which involve metal atoms which have lower coordination numbers as a result of the bond cleavage. Although it is electron precise, 4 does add CO to yield 3. Unfortunately, it is not possible to compare accurately the relative rates of CO addition to 2 and 4 because the addition of CO to 2 leads to degradation of the cluster, but the rates must be somewhat similar because the CO addition to 4 and the CO degradation of 2 seem to occur at similar rates.

When irradiated in the presence of $W(CO)_5PMe_2Ph$, 2, adds a second tungsten-containing moiety across one of its tungsten–sulfur bonds. 5 appears to possess an unusual electronic structure since there are not enough ligands in the complex to allow all the metal atoms to achieve 18-electron configurations. Eighteen-electron configurations could be achieved by employing a metal–metal double bond and assuming that the quadruply bridging sulfido ligand serves as a 6-electron donor. The resonance structures 5A and 5B could be viable representations of its bonding and would explain the observed shortening of the indicated tungsten–osmium and tungsten–tungsten bonds. The pentaosmium cluster $HOs_5(CO)_{13}(\mu\text{-}PhNC_6H_4N)$ is also unsaturated by the amount of 2 electrons and shows a selective shortening of two of the osmium–osmium bonds to 2.60 Å.[24] In spite of its apparent unsaturation, we have not been successful in performing ligand additions to 5.



5A 5B

In all of the new compounds 2–5 the tungsten atoms are bonded to one or more of the bridging sulfido ligands. It is, thus, believed that the sulfido ligands play a key role in their stabilization and probably an important role in directing their synthesis as well.

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Registry No. 1, 72282-40-7; **2**, 87802-46-8; **3**, 87802-47-9; **4**, 91781-16-7; **5**, 91781-17-8; $W(CO)_5(PMe_2Ph)$, 42565-94-6; W, 7440-33-7; Os, 7440-04-2.

Supplementary Material Available: Tables of structure factor amplitudes for the structural analyses of compounds 4 and 5 and tables of thermal parameters and hydrogen atom coordinates for each structure (34 pages). Ordering information is given on any current masthead page.

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[24] Dawoodi, A.; Mays, M. J.;; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* 1980, 712.

A Molecule Containing the OWOWO Unit. Synthesis, Structure, and Spectroscopy of $W_2O_3(CH_2CMe_3)_6$

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Abstract: Addition of excess water to $W(CCMe_3)(CH_2CMe_3)_3$ yields pentane-soluble, water- and air-stable $W_2O_3(CH_2CMe_3)_6$ (1). Anhydrous HCl reacts with 1 in the presence of Me_3SiCl to produce $WONp_3Cl$ (2). $W_2O_3(CH_2CMe_3)_6$ crystallizes in the trigonal system, space group $R\bar{3}$, with a = 10.232 (2) Å, c = 61.446 (9) Å, V = 5571.1 Å^3, and Z = 6. The molecule, which has crystallographically imposed C_3 symmetry, contains a linear O=W—O—W=O unit in which three neopentyl groups are trigonally disposed about each tungsten atom. The W=O bond lengths are 1.726 (10) and 1.689 (13) Å, the W(μ-O) distances are 1.923 (10) and 1.977 (10) Å, and the independent W—C bond lengths are 2.141 (9) and 2.127 (14) Å. The two ends of the molecule are twisted by 31.9 (5)° with respect to one another. Spectroscopic examination of 1 (and [^{18}O]1) showed two IR active bands at 962 (905) (w) and 693 (668) (s) cm^{-1} and two Raman active bands at 942 (894) (s) and 205 (205) (m) cm^{-1} that we assign to the asymmetric W=O stretch, the asymmetric W—O—W stretch, the symmetric W=O stretch, and the symmetric W—O—W stretch, respectively. The calculated force constants are comparable to those reported for several rhenium(V) complexes containing a linear O=Re—O—Re=O backbone.

There is considerable evidence that, in many catalysts consisting of an early transition-metal deposited on silica or alumina, the catalytically active site contains the metal in its highest possible oxidation state (d^0).[1] In order to understand this chemistry better

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