currently attempting to obtain X-ray-quality crystals of [Na(18-crown-6)][$CH_3CO_2W(CO)_5$] in an effort to better define this interaction. Further, we hope to analyze crystals of [Na(18-crown-6)][*cis*-$CH_3W(CO)_4PMe_3$], where it is expected that the possibility of observing Na^+ interaction at the more basic oxygen sites of the carbonyl ligands is greatly enhanced.

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Supplementary Material Available: Stereoview of the unit cell packing for [Na(18-crown-6)$(THF)_2$][$W(CO)_5CH_3$] and tables of anisotropic thermal parameters and derived atomic coordinates for hydrogen atoms (3 pages); a table of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

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Cluster Condensation Reactions. Transformation of Two Triangular Trinuclear Clusters into a Hexanuclear Cluster Containing a Novel *Edge*-Fused Bitetrahedral Structure

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The carbene-containing cluster complex $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SMe})(\mu\text{-H})$ (**1**) was prepared in 56% yield from the reaction of $Os_3(CO)_{10}(\mu\text{-SMe})(\mu\text{-H})$ with $CH_2(NMe_2)_2$. UV irradiation of **1** yielded the complex $Os_3(CO)_8(\mu\text{-CNMe}_2)(\mu\text{-SMe})(\mu\text{-H})_2$ (**2**) in 68% yield. Compound **2** contains a bridging (dimethylamino)carbyne ligand that was formed by an α-CH activation of the carbene ligand in **1**. Thermal decarbonylation of **2** resulted in the formation of the hexaosmium cluster complex $Os_6(CO)_{12}(\mu\text{-CNMe}_2)_2(\mu_3\text{-SMe})_2(\mu\text{-H})_2$ (**3**) in 65% yield. Compound **3** was characterized by a single-crystal X-ray diffraction analysis. Crystal data: space group $P2_1/c$, a = 16.042 (4) Å, b = 12.670 (3) Å, c = 17.816 (3) Å, β = 101.59 (2)°, Z = 4, ρ_{calcd} = 3.23 g/cm^3. The structure was solved by a combination of direct methods and difference Fourier techniques and was refined (2701 reflections) to the final values of the residuals R = 0.048 and R_w = 0.050. The structure consists of six osmium atoms arranged in the form of two tetrahedral clusters that have one edge in common. There are two bridging (dimethylamino)carbyne ligands and two triply bridging methanethiolato ligands that appear to serve as three-electron donors instead of the usual five-electron-donor configuration.

Introduction

The development of systematic routes for their syntheses has been one of the greatest challenges to researchers investigating the chemistry of transition-metal cluster compounds.[1-3] In our recent studies we have focused on the ability of sulfido ligands in metal complexes to facilitate cluster synthesis.[1,4] In related work we have been investigating the synthesis and transformation behavior of heteronuclear carbene ligands in cluster compounds.[5] We have now found that decarbonylation of the compound $Os_3(CO)_8(\mu\text{-CNMe}_2)(\mu\text{-SMe})(\mu\text{-H})_2$ results in the formation of the hexanuclear product $Os_6(CO)_{12}(\mu\text{-CNMe}_2)_2(\mu_3\text{-SMe})_2(\mu\text{-H})_2$ with a cluster that consists of a pair of fused tetrahedra that has a pair of unusually coordinated triply bridging methanethiolato ligands. The thiolato ligands are believed to have played an important role in the formation of this hexanuclear product. The results of these studies are described in this report.

Experimental Section

General Procedures. Although all the products appear to be air stable, all the reactions were performed in the standard Schlenkware under a dry nitrogen atmosphere, unless otherwise specified. Reagent grade solvents were dried over molecular sieves and deoxygenated by purging with nitrogen prior to use. The compound $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SMe})(\mu\text{-H})$ (**1**) was obtained in 56% yield from the reaction of $Os_3(CO)_{10}(\mu\text{-SMe})(\mu\text{-H})$[6] and $CH_2(NMe_2)_2$ according to a procedure that was analogous to that which was used for the preparation of the arenethiolato analogue of **1**.[5] For **1**: IR (ν(CO) cm^{-1} in hexane) 2091 (m), 2051 (s), 2012 (vs), 2006 (m), 2001 (s), 1964 (m), 1938 (w); ^{1}H NMR (δ in $CDCl_3$) 11.69 (s, 1 H), 3.61 (s, 3 H), 3.57 (s, 3 H), 2.38 (s, 3 H), −17.51 (s, 1 H). Anal. Calcd for **1**: C, 16.80; N, 1.51; H, 1.20. Found: C, 17.01; N, 1.54; H, 1.11. Photolysis experiments were performed by using an externally positioned high-pressure mercury lamp on reaction solutions contained in Pyrex glassware. IR spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. A Bruker AM300 FT-NMR spectrometer was used to obtain ^{1}H NMR spectra. Elemental analyses were performed by MICANAL, Tucson, AZ.

Photolysis of $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SMe})(\mu\text{-H})$ (1). A cyclohexane solution (50 mL) of **1** (25 mg, 0.0027 mmol) was subjected to UV irradiation for 45 min in the presence of a continuous purge with nitrogen. The solvent was removed in vacuo. The residue was extracted with a minimum of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with a 30%/70% CH_2Cl_2/hexane solvent mixture yielded the yellow product $Os_3(CO)_8(\mu\text{-CNMe}_2)(\mu\text{-SMe})(\mu\text{-H})_2$ (**2**) (17 mg, (68% yield)). IR (ν(CO) cm^{-1} in hexane): 2085 (m), 2048 (vs), 2018 (s), 2012 (s), 1990 (m), 1974 (m), 1951 (m). ^{1}H NMR (δ, in $CDCl_3$ solvent): 3.99 (s, 3 H), 3.87 (s, 3 H), 2.58 (s, 3 H), −13.91 (s, 1 H), −15.95 (s, 1 H).

Thermolysis of 2. An octane solution (40 mL) of **2** (20 mg, 0.223 mmol) was refluxed for 90 min. The solvent was removed in vacuo, and the product was isolated by TLC on silica gel. Elution with a 40%/60% CH_2Cl_2/hexane solvent mixture yielded red $Os_6(CO)_{12}(\mu\text{-CNMe}_2)_2(\mu_3\text{-SMe})_2(\mu\text{-H})_2$ (**3**) (13 mg (65%)). IR (ν(CO) cm^{-1} in hexane) for **3**: 2042 (w), 2018 (s), 1998 (vs), 1989 (s), 1961 (m), 1950 (m), 1939 (w). ^{1}H NMR at 25 °C (δ, in $CDCl_3$ solvent): 3.81 (s, 12 H), 3.12 (s, 6 H), −15.80 (s, 2 H). ^{1}H NMR at −80 °C (δ, in CD_2Cl_2 solvent): 3.84 (s, 6 H), 3.79 (s, 6 H), 3.15 (s, 6 H), −15.77 (s, 2 H).

Crystallographic Analysis. Red crystals of **3** were grown by slow evaporation of solvent from CH_2Cl_2/hexane solutions at −20 °C. The data crystal was mounted in a thin-walled glass capillary. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo Kα radiation. The unit cell for **3** was determined by using the AFC6 automatic search, index, center, and least-squares routines. Crystal data, data collection parameters, and results of the analysis are listed in Table I. Data processing was performed on a Digital Equipment Corp. MICROVAX I computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., College Station, TX. An absorption correction of a Gaussian integration type was performed. Neutral-atom scattering factors were calculated by the standard procedures.[7a] Anomalous dispersion corrections were applied

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0020-1669/87/1326-0980$01.50/0

Table I. Crystallographic Data for X-ray Diffraction Studies for **3**

(A) Crystal Data	
formula	$Os_6S_2O_{12}N_2C_{20}H_{20}\cdot CH_2Cl_2$
temp, °C	23 (±3)
space group	$P2_1/c$, No. 14
a, Å	16.042 (4)
b, Å	12.670 (3)
c, Å	17.816 (3)
β, deg	101.59 (2)
V, Å^3	3547 (1)
M_r	1685.4
Z	4
ρ_{calcd}, g/cm^3	3.23
(B) Measurement of Intensity Data	
radiation	Mo Kα
monochromator	graphite
detector aperture, mm	
horiz	2.0
vert	2.0
cryst faces	$1\bar{1}0$, $10\bar{2}$, $01\bar{2}$, $\bar{1}10$ $\bar{1}02$, $1\bar{1}\bar{1}$, $0\bar{1}\bar{1}$, $\bar{1}00$ 100, 011, 110, $0\bar{2}1$
cryst size, mm	0.11 × 0.13 × 0.14
cryst orientation: direction; deg from θ axis	$[\bar{1}2\bar{2}]$; 1.4
reflections measured	$+h,+k,\pm l$
max 2θ, deg	45
scan type	moving cryst–stationary counter
ω-scan width: $(A + 0.347 \tan \theta)^\circ$	
ω-scan rate,[a] deg/min	4.0
no. of reflcns measd	4962
no. of data used ($F^2 \geq 3.0\sigma(F^2)$)	2701
(C) Treatment of Data	
abs cor	applied
coeff, cm^{-1}	230.9
grid	6 × 12 × 12
transmissn coeff	
max	0.18
min	0.08
P factor	0.02
final residuals[b]	
R_F	0.048
R_{wF}	0.050
esd. of unit wt observn	1.66
largest shift/error value of final cycle	0.02
largest peak in final diff Fourier, e/Å^3	1.03

[a] Rigaku software uses a multiple scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to first scan, etc. A maximum of three scans was permitted per reflection. [b] The final residuals were calculated according to the formulas $R_F = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_{wF} = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

to all non-hydrogen atoms.[7b] Full-matrix least-squares refinements minimized the function

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

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

Compound **3** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was determined from systematic absences observed in the data. The positions of the metal atoms were determined by direct methods (MULTAN). The remaining non-hydrogen atoms were located by subsequent difference Fourier syntheses. All atoms heavier than oxygen were refined with anisotropic thermal parameters. The hydrogen atoms were not located crystallographically and therefore were ignored in the analysis. In the later stages the structure was found to contain 1 mol of CH_2Cl_2 solvent that cocrystallized with each mole of **3**. This was added to the analysis and was refined without difficulty. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement. See supplementary material for tables of the structure factor amplitudes, anisotropic thermal parameters, and least-squares planes.

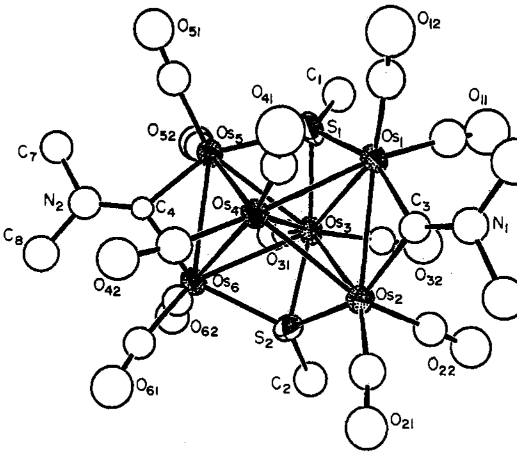


Figure 1. Perspective ORTEP diagram of $Os_6(CO)_{12}(\mu\text{-}CNMe_2)_2(\mu_3\text{-}SMe)_2(\mu\text{-}H)_2$ (**3**) showing 50% probability thermal ellipsoids.

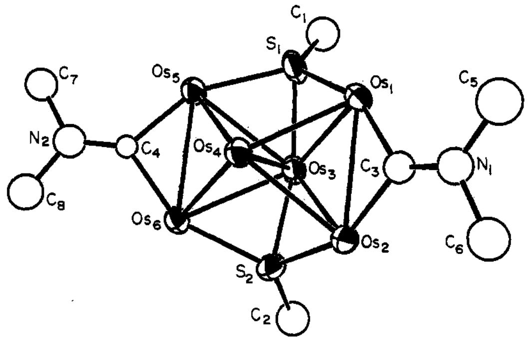
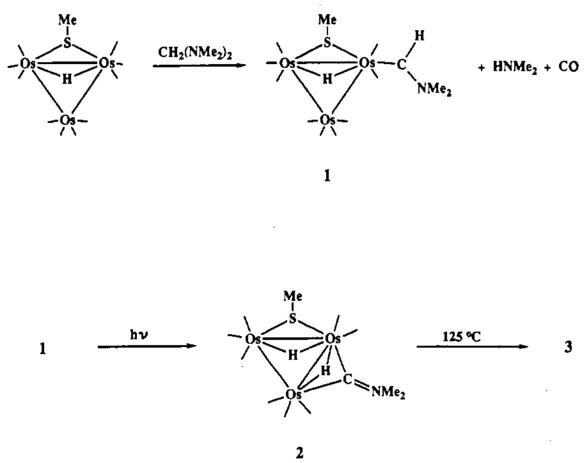


Figure 2. ORTEP diagram of **3** with the carbonyl ligands omitted for clarity.

Results and Discussion

The reaction of $Os_3(CO)_{10}(\mu\text{-}SMe)(\mu\text{-}H)$ with $CH_2(NMe_2)_2$ yielded the (dimethylamino)carbene cluster complex $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}SMe)(\mu\text{-}H)$ (**1**), which is believed to be structurally analogous to the corresponding (arenethiolato)triosmium cluster complexes that have been characterized previously by X-ray crystallographic methods.[5] When solutions of **1** were subjected to UV irradiation, it was decarbonylated and transformed into the new compound $Os_3(CO)_8(\mu\text{-}CNMe_2)(\mu\text{-}SMe)(\mu\text{-}H)_2$ (**2**), which contains a (dimethylamino)carbyne ligand that bridges one edge of the cluster. The transformation, which is believed to involve an intramolecular binuclear α-CH activation in the carbene ligand (eq 1), was also observed for the corresponding carbene-containing (arenethiolato)triosmium cluster complexes.[5] From this point, however, the transformations of the arenethiolato cluster complexes and the methanethiolato cluster complexes diverge. Heating of the arenethiolato analogues of **2** induces a shift of the aryl ring from the sulfur atom to the carbon atom of the carbyne



(1)

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Table II. Positional Parameters and *B*(eq) for $Os_6(CO)_{12}(\mu\text{-}CNMe_2)_2(\mu_3\text{-}SMe)_2(\mu\text{-}H)_2$ (**3**)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.613238 (88)	0.13864 (11)	0.375545 (87)	3.6
Os(2)	0.767862 (87)	0.01419 (10)	0.442368 (79)	2.9
Os(3)	0.755582 (86)	0.24117 (10)	0.483334 (76)	3.2
Os(4)	0.768965 (82)	0.178857 (98)	0.331076 (74)	2.7
Os(5)	0.759764 (87)	0.40128 (10)	0.361867 (79)	3.2
Os(6)	0.913598 (82)	0.272624 (97)	0.420785 (73)	2.6
S(1)	0.63860 (56)	0.32641 (66)	0.40430 (57)	4.1
S(2)	0.87791 (55)	0.13466 (66)	0.50141 (46)	3.4
O(11)	0.4821 (22)	0.1200 (25)	0.4778 (18)	7.7
O(12)	0.4830 (21)	0.1290 (23)	0.2290 (17)	6.9
O(21)	0.8661 (16)	−0.1812 (19)	0.4196 (14)	4.8
O(22)	0.7296 (18)	−0.0840 (22)	0.5862 (16)	5.9
O(31)	0.8177 (16)	0.4222 (20)	0.5899 (14)	4.8
O(32)	0.6671 (20)	0.1589 (23)	0.6053 (17)	6.8
O(41)	0.6573 (19)	0.0843 (22)	0.1874 (16)	6.2
O(42)	0.9092 (17)	0.1883 (19)	0.2363 (14)	5.0
O(51)	0.6731 (18)	0.5319 (21)	0.2277 (16)	5.8
O(52)	0.7801 (18)	0.5952 (22)	0.4623 (15)	5.7
O(61)	1.0749 (19)	0.1835 (22)	0.3855 (16)	5.9
O(62)	1.0139 (17)	0.3989 (21)	0.5493 (15)	5.3
N(1)	0.6011 (18)	−0.1038 (21)	0.3604 (15)	3.5
N(2)	0.9273 (18)	0.4604 (22)	0.3150 (16)	3.9
C(1)	0.5730 (25)	0.4045 (29)	0.4543 (21)	4.8
C(2)	0.9301 (26)	0.1156 (29)	0.6037 (22)	4.7
C(3)	0.6472 (20)	−0.0126 (24)	0.3845 (17)	2.9
C(4)	0.8803 (17)	0.3968 (21)	0.3487 (15)	1.8
C(5)	0.5107 (28)	−0.1085 (32)	0.3232 (23)	5.6
C(6)	0.6416 (25)	−0.2100 (29)	0.3876 (21)	4.6
C(7)	0.8941 (23)	0.5579 (27)	0.2720 (20)	3.9
C(8)	1.0185 (24)	0.4369 (29)	0.3125 (21)	4.6
C(11)	0.5261 (27)	0.1232 (30)	0.4340 (22)	4.9
C(12)	0.5267 (25)	0.1394 (29)	0.2879 (22)	4.4
C(21)	0.8223 (23)	−0.1034 (27)	0.4301 (19)	3.8
C(22)	0.7435 (23)	−0.0469 (27)	0.5306 (21)	3.9
C(31)	0.7945 (21)	0.3534 (25)	0.5472 (18)	3.1
C(32)	0.7021 (21)	0.1878 (25)	0.5605 (18)	3.1
C(41)	0.6938 (23)	0.1177 (27)	0.2504 (20)	3.9
C(42)	0.8601 (23)	0.1858 (27)	0.2812 (20)	3.9
C(51)	0.7091 (24)	0.4864 (28)	0.2801 (21)	4.0
C(52)	0.7734 (23)	0.5194 (28)	0.4197 (19)	3.8
C(61)	1.0164 (23)	0.2273 (26)	0.3980 (18)	3.5
C(62)	0.9735 (23)	0.3546 (27)	0.4949 (20)	3.9
C(99)	0.7377 (39)	−0.3374 (46)	0.6373 (33)	9.6
Cl(1)	0.7868 (12)	−0.3297 (15)	0.7335 (10)	11.8
Cl(2)	0.6314 (21)	−0.3175 (24)	0.6294 (16)	20.3

Table III. Intramolecular Distances (Å) for $Os_6(CO)_{12}(\mu\text{-}CNMe_2)_2(\mu_3\text{-}SMe)_2(\mu\text{-}H)_2$ (**3**)

Os(1)–C(12)	1.87 (4)	Os(5)–Os(6)	2.975 (3)
Os(1)–C(11)	1.91 (4)	Os(6)–C(62)	1.80 (4)
Os(1)–C(3)	1.99 (3)	Os(6)–C(61)	1.87 (4)
Os(1)–S(1)	2.444 (9)	Os(6)–C(4)	2.03 (3)
Os(1)–Os(4)	2.815 (3)	Os(6)–S(2)	2.393 (8)
Os(1)–Os(3)	2.976 (2)	S(1)–C(1)	1.80 (4)
Os(1)–Os(2)	2.985 (3)	S(2)–C(2)	1.86 (4)
Os(2)–C(21)	1.76 (4)	O(11)–C(11)	1.15 (4)
Os(2)–C(22)	1.85 (4)	O(12)–C(12)	1.15 (4)
Os(2)–C(3)	2.04 (3)	O(21)–C(21)	1.24 (4)
Os(2)–S(2)	2.413 (9)	O(22)–C(22)	1.15 (4)
Os(2)–Os(4)	2.869 (2)	O(31)–C(31)	1.17 (3)
Os(2)–Os(3)	2.975 (2)	O(32)–C(32)	1.12 (4)
Os(3)–C(31)	1.85 (3)	O(41)–C(41)	1.23 (4)
Os(3)–C(32)	1.88 (3)	O(42)–C(42)	1.23 (4)
Os(3)–S(2)	2.354 (9)	O(51)–C(51)	1.15 (4)
Os(3)–S(1)	2.37 (1)	O(52)–C(52)	1.21 (4)
Os(3)–Os(4)	2.857 (2)	O(61)–C(61)	1.15 (4)
Os(3)–Os(5)	2.964 (2)	O(62)–C(62)	1.19 (4)
Os(3)–Os(6)	2.991 (3)	N(1)–C(3)	1.39 (4)
Os(4)–C(41)	1.85 (4)	N(1)–C(5)	1.48 (5)
Os(4)–C(42)	1.86 (4)	N(1)–C(6)	1.53 (4)
Os(4)–Os(6)	2.810 (2)	N(2)–C(4)	1.32 (4)
Os(4)–Os(5)	2.873 (2)	N(2)–C(7)	1.49 (4)
Os(5)–C(12)	1.80 (3)	N(2)–C(7)	1.49 (4)
Os(5)–C(51)	1.86 (4)	N(2)–C(8)	1.51 (4)
Os(5)–C(4)	2.00 (3)	C(99)–Cl(2)	1.71 (6)
Os(5)–S(1)	2.415 (9)	C(99)–Cl(1)	1.73 (6)

ligand to yield triosmium clusters that contain aryl(dialkylamino)carbene ligands. In contrast, heating of compound **2** does not cause a shift of the methyl group from the sulfur atom. Instead, heating led to decarbonylation of **2**, and two triosmium units were combined to form the hexanuclear product $Os_6(CO)_{12}(\mu\text{-}CNMe_2)_2(\mu_3\text{-}SMe)_2(\mu\text{-}H)_2$ (**3**) in 65% yield. Compound **3** was characterized by IR and ^1H NMR spectroscopies and by elemental and single-crystal X-ray diffraction analyses. An ORTEP drawing of **3** is shown in Figure 1. An ORTEP drawing of **3** in which the carbonyl ligands have been removed for clarity is shown in Figure 2. Final atomic positional parameters are listed in Table II. Intramolecular distances and angles are listed in Tables III and IV. The cluster of **3** consists of six osmium atoms that are arranged in the form of two tetrahedral tetraosmium groupings that are fused along one edge, the Os(3)–Os(4) bond. We are not aware of any previously reported examples of hexanuclear metal cluster complexes that exhibit a bitetrahedral structure that has been fused along an edge, although a similarly related fragment was observed as a part of the larger cluster $Os_8(CO)_{22}(H)^-$.[8] The 11 osmium–osmium bond lengths span a wide range, 2.810 (2)–2.991 (3) Å. The osmium–osmium bond distance in $Os_3(CO)_{12}$ at 2.877 (3) Å lies close to the middle of this range.[8] Most of the variations in the metal–metal bond lengths in **3** seem to be related to influences of the ligand structure of the molecule, vide infra. Each metal atom in **3** contains two carbonyl ligands. All the carbonyl ligands are of a terminal form, except those on Os(4), which have adopted weak semibridging interactions along the two shortest metal–metal bonds, Os(1)–Os(4) and Os(4)–Os(6). The molecule contains two triply bridging methanethiolato ligands that span the open trinuclear groups Os(1), Os(3), and Os(5) and Os(2), Os(3), and Os(6). We are not aware of any structural characterizations of triply bridging thiolato ligands in osmium clusters; however, the metal–sulfur distances in **3** are very similar in length, 2.354 (9)–2.444 (9) Å, and show a variation from those observed for triply bridging sulfido ligands in open triosmium clusters.[10] Interestingly, the groupings Os(1), Os(5), S(1), and C(1) and Os(2), Os(6), S(2), and C(2) are planar within experimental error. The molecule contains two (dimethylamino)carbyne ligands that symmetrically bridge the Os(1)–Os(2) and Os(5)–Os(6) bonds. The metal–carbon bond distances are similar to those that were observed for the bridging (dimethylamino)carbyne ligand in the triosmium cluster $Os_3(CO)_8(\mu\text{-}CNMe_2)(\mu\text{-}SPh)(\mu\text{-}H)_2$ (**4**) even though a significant amount of asymmetry in the bonding of the bridging carbyne ligand was observed in the latter complex. The shortness of the C–N bond distances, C(3)–N(1) = 1.39 (4) Å and C(4)–N(2) = 1.32 (4) Å, indicates the presence of partial multiple bonding between these atoms. This is consistent with the observed planarity at the nitrogen atoms, which indicates the absence of a lone pair of electrons on them. A similar shortening was observed in the C–N distance in **4**, 1.27 (3) Å [1.32 (3) Å].[5] Curiously, the metal–metal bonds that are bridged by the carbyne ligands in **3**, Os(1)–Os(2) = 2.985 (3) Å and Os(5)–Os(6) 2.975 (3) Å, are significantly longer than the carbyne-bridged bond in **4**, 2.79 (1) Å [2.794 (1) Å]. The ^1H NMR spectrum of **3** shows a resonance at −15.60 ppm of relative intensity 2 that is indicative of the presence of two equivalent bridging hydride ligands. These ligands were not observed crystallographically. Frequently, however, the locations of bridging hydride ligands can be inferred on the basis of distortions in the structural geometry of a molecule.[11,12] One of the primary effects is an observed elongation of a metal–metal bond

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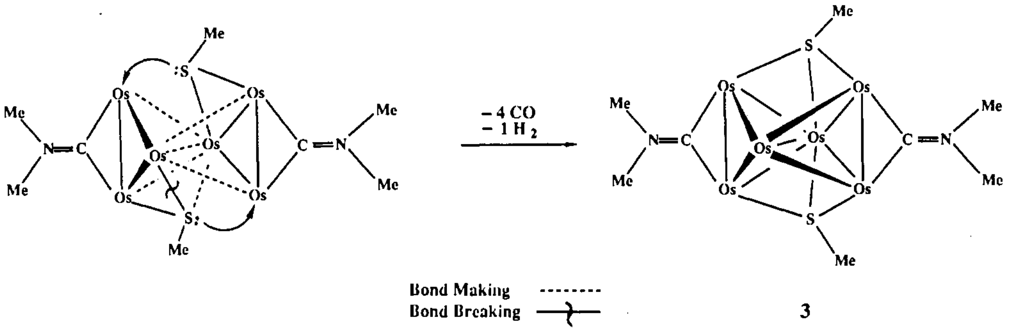
Table IV. Intramolecular Bond Angles (deg) for $Os_6(CO)_{12}(\mu\text{-}CNMe_2)_2(\mu_3\text{-}SMe)_2(\mu\text{-}H)_2$ (3)

C(12)–Os(1)–C(11)	87 (2)	C(31)–Os(3)–Os(4)	135 (1)	Os(6)–Os(4)–Os(1)	127.00 (7)	C(4)–Os(6)–Os(3)	101.4 (8)
C(12)–Os(1)–C(3)	103 (1)	C(31)–Os(3)–Os(5)	82 (1)	Os(6)–Os(4)–Os(3)	63.70 (5)	S(2)–Os(6)–Os(4)	76.2 (2)
C(12)–Os(1)–S(1)	104 (1)	C(31)–Os(3)–Os(2)	149 (1)	Os(6)–Os(4)–Os(2)	91.89 (5)	S(2)–Os(6)–Os(5)	109.1 (2)
C(12)–Os(1)–Os(4)	109 (1)	C(31)–Os(3)–Os(1)	149 (1)	Os(6)–Os(4)–Os(5)	63.12 (5)	S(2)–Os(6)–Os(3)	60.4 (2)
C(12)–Os(1)–Os(3)	152 (1)	C(31)–Os(3)–Os(6)	85 (1)	Os(1)–Os(4)–Os(3)	63.29 (5)	Os(4)–Os(6)–Os(5)	59.46 (6)
C(12)–Os(1)–Os(2)	139 (1)	C(32)–Os(3)–S(2)	101 (1)	Os(1)–Os(4)–Os(2)	63.36 (5)	Os(4)–Os(6)–Os(3)	58.91 (6)
C(11)–Os(1)–C(3)	94 (1)	C(32)–Os(3)–S(1)	100 (1)	Os(1)–Os(4)–Os(5)	92.40 (5)	Os(5)–Os(6)–Os(3)	59.57 (6)
C(11)–Os(1)–S(1)	96 (1)	C(32)–Os(3)–Os(4)	136 (1)	Os(3)–Os(4)–Os(2)	62.60 (5)	C(1)–S(1)–Os(3)	116 (1)
C(11)–Os(1)–Os(4)	163 (1)	C(32)–Os(3)–Os(5)	149 (1)	Os(3)–Os(4)–Os(5)	62.29 (4)	C(1)–S(1)–Os(5)	122 (1)
C(11)–Os(1)–Os(3)	105 (1)	C(32)–Os(3)–Os(2)	84 (1)	Os(2)–Os(4)–Os(5)	124.89 (6)	C(1)–S(1)–Os(1)	123 (1)
C(11)–Os(1)–Os(2)	112 (1)	C(32)–Os(3)–Os(1)	85 (1)	C(52)–Os(5)–C(51)	87 (2)	Os(3)–S(1)–Os(5)	76.5 (3)
C(3)–Os(1)–S(1)	152 (1)	C(32)–Os(3)–Os(6)	149 (1)	C(52)–Os(5)–C(4)	94 (1)	Os(3)–S(1)–Os(1)	76.3 (3)
C(3)–Os(1)–Os(4)	87 (1)	S(2)–Os(3)–S(1)	152.3 (3)	C(52)–Os(5)–S(1)	99 (1)	Os(5)–S(1)–Os(1)	115.3 (4)
C(3)–Os(1)–Os(3)	102 (1)	S(2)–Os(3)–Os(4)	75.9 (2)	C(52)–Os(5)–Os(4)	156 (1)	C(2)–S(2)–Os(3)	114 (1)
C(3)–Os(1)–Os(2)	43 (1)	S(2)–Os(3)–Os(5)	110.6 (2)	C(52)–Os(5)–Os(3)	100 (1)	C(2)–S(2)–Os(6)	124 (1)
B(1)–Os(1)–Os(4)	76.2 (2)	S(2)–Os(3)–Os(2)	52.3 (2)	C(52)–Os(5)–Os(6)	105 (1)	C(2)–S(2)–Os(2)	120 (1)
S(1)–Os(1)–Os(3)	50.8 (2)	S(2)–Os(3)–Os(1)	110.9 (2)	C(51)–Os(5)–C(4)	102 (1)	Os(3)–S(2)–Os(6)	78.1 (2)
S(1)–Os(1)–Os(2)	109.7 (2)	S(2)–Os(3)–Os(6)	51.5 (2)	C(51)–Os(5)–S(1)	102 (1)	Os(3)–S(2)–Os(2)	77.2 (3)
Os(4)–Os(1)–Os(3)	59.04 (6)	S(1)–Os(3)–Os(4)	76.5 (2)	C(51)–Os(5)–Os(4)	117 (1)	Os(6)–S(2)–Os(2)	116.2 (3)
Os(4)–Os(1)–Os(2)	59.19 (6)	S(1)–Os(3)–Os(5)	52.4 (2)	C(51)–Os(5)–Os(3)	153 (1)	C(3)–N(1)–C(6)	126 (3)
Os(3)–Os(1)–Os(2)	59.86 (6)	S(1)–Os(3)–Os(2)	112.1 (2)	C(51)–Os(5)–Os(6)	143 (1)	C(3)–N(1)–C(6)	118 (3)
C(21)–Os(2)–C(22)	87 (2)	S(1)–Os(3)–Os(1)	52.9 (2)	C(4)–Os(5)–S(1)	152.3 (8)	C(5)–N(1)–C(6)	115 (3)
C(21)–Os(2)–C(3)	104 (1)	S(1)–Os(3)–Os(6)	110.8 (2)	C(4)–Os(5)–Os(4)	82.1 (8)	C(4)–N(2)–C(7)	124 (3)
C(21)–Os(2)–S(2)	104 (1)	Os(4)–Os(3)–Os(5)	59.11 (4)	C(4)–Os(5)–Os(3)	103.0 (8)	C(4)–N(2)–C(8)	123 (3)
C(21)–Os(2)–Os(4)	117 (1)	Os(4)–Os(3)–Os(2)	58.89 (4)	C(4)–Os(5)–Os(6)	42.8 (8)	C(7)–N(2)–C(8)	114 (3)
C(21)–Os(2)–Os(3)	155 (1)	Os(4)–Os(3)–Os(1)	57.67 (5)	S(1)–Os(5)–Os(4)	75.5 (2)	N(1)–C(3)–Os(1)	131 (2)
C(21)–Os(2)–Os(1)	142 (1)	Os(4)–Os(3)–Os(6)	57.39 (4)	S(1)–Os(5)–Os(3)	51.1 (2)	N(1)–C(3)–Os(2)	134 (2)
C(22)–Os(2)–C(3)	91 (1)	Os(5)–Os(3)–Os(2)	117.99 (6)	S(1)–Os(5)–Os(6)	110.1 (2)	Os(1)–C(3)–Os(2)	96 (1)
C(22)–Os(2)–S(2)	99 (1)	Os(5)–Os(3)–Os(1)	87.44 (5)	Os(4)–Os(5)–Os(3)	58.60 (4)	N(2)–C(4)–Os(5)	133 (2)
C(22)–Os(2)–Os(4)	156 (1)	Os(5)–Os(3)–Os(6)	59.94 (5)	Os(4)–Os(5)–Os(6)	57.42 (5)	N(2)–C(4)–Os(6)	131 (2)
C(22)–Os(2)–Os(3)	99 (1)	Os(2)–Os(3)–Os(1)	60.22 (5)	Os(3)–Os(5)–Os(6)	60.49 (5)	Os(5)–C(4)–Os(6)	95 (1)
C(22)–Os(2)–Os(1)	105 (1)	Os(2)–Os(3)–Os(6)	86.34 (5)	C(62)–Os(6)–C(61)	88 (2)	O(11)–C(11)–Os(1)	170 (4)
C(3)–Os(2)–S(2)	150.3 (9)	Os(1)–Os(3)–Os(6)	115.05 (7)	C(62)–Os(6)–C(4)	93 (1)	O(12)–C(12)–Os(1)	168 (4)
C(3)–Os(2)–Os(4)	84.7 (9)	C(41)–Os(4)–C(42)	96 (2)	C(62)–Os(6)–S(2)	98 (1)	O(21)–C(21)–Os(2)	175 (3)
C(3)–Os(2)–Os(3)	100.4 (9)	C(41)–Os(4)–Os(6)	163 (1)	C(62)–Os(6)–Os(4)	157 (1)	O(22)–C(22)–Os(2)	179 (3)
C(3)–Os(2)–Os(1)	41.4 (9)	C(41)–Os(4)–Os(1)	70 (1)	C(62)–Os(6)–Os(5)	103 (1)	O(31)–C(31)–Os(3)	177 (3)
S(2)–Os(2)–Os(4)	74.8 (2)	C(41)–Os(4)–Os(3)	133 (1)	C(62)–Os(6)–Os(3)	100 (1)	O(32)–C(32)–Os(3)	177 (3)
S(2)–Os(2)–Os(3)	50.5 (2)	C(41)–Os(4)–Os(2)	98 (1)	C(61)–Os(6)–C(4)	104 (1)	O(41)–C(41)–Os(4)	165 (3)
S(2)–Os(2)–Os(1)	108.9 (2)	C(41)–Os(4)–Os(5)	120 (1)	C(61)–Os(6)–S(2)	103 (1)	O(42)–C(42)–Os(4)	168 (3)
Os(4)–Os(2)–Os(3)	58.51 (4)	C(42)–Os(4)–Os(6)	67 (1)	C(61)–Os(6)–Os(4)	115 (1)	O(51)–C(51)–Os(5)	174 (3)
Os(4)–Os(2)–Os(1)	57.45 (5)	C(42)–Os(4)–Os(1)	166 (1)	C(61)–Os(6)–Os(5)	143 (1)	O(52)–C(52)–Os(5)	176 (3)
Os(3)–Os(2)–Os(1)	59.92 (5)	C(42)–Os(4)–Os(3)	130 (1)	C(61)–Os(6)–Os(3)	153 (1)	O(61)–C(61)–Os(6)	169 (3)
C(31)–Os(3)–C(32)	89 (1)	C(42)–Os(4)–Os(2)	118 (1)	C(4)–Os(6)–S(2)	151.0 (8)	O(62)–C(62)–Os(6)	173 (3)
C(31)–Os(3)–S(2)	100 (1)	C(42)–Os(4)–Os(5)	97 (1)	C(4)–Os(6)–Os(4)	83.3 (8)	Cl(2)–C(99)–Cl(1)	109 (3)
C(31)–Os(3)–S(1)	98 (1)			C(4)–Os(6)–Os(5)	42.0 (8)		



3

Figure 3. Schematic representation of the condensation of 2 mol of 2 into 3.

distance. Although the four metal–metal bonds to atom Os(3) are the longest in 3, 2.964 (2)–2.991 (3) Å, it is believed that these bonds do not contain the two bridging hydride ligands unless perhaps they are triply bridging hydride ligands. However, there is another good explanation for the lengthening observed in these bonds, vide infra. The elongated metal–metal bonds that are bridged by the carbyne ligands could be the locations for the bridging hydride ligands. Bridging aminocarbyne/hydride ligand combinations have been observed previously in the compounds $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$[12] and $Os_3(CO)_{10}[\mu\text{-}CN(H)(t\text{-}Bu)](\mu\text{-}H)$,[13] but in these examples an elongation of the bridged metal–metal bond was not observed. To be considered finally are the metal–metal bonds to atom Os(4). The Os(2)–Os(4) and Os(4)–Os(6) bonds are relatively unobstructed by ligands on the surface of the cluster, and these bonds are longer than the others to this metal atom. These bonds would seem to be ideal locations for two bridging hydride ligands. Conversely, the geometric crowding about the Os(3)–Os(4) bond would seem to make this an unlikely site. Unfortunately, an unambiguous determination of the hydride ligand positions will probably require a single-crystal neutron diffraction analysis. All the bonds to atom Os(3) are very long (greater than 2.964 Å) except the Os(3)–Os(4) bond, which is 2.857 (2) Å in length. The elongation of the bonds to atom Os(3) could be due to steric crowding due to its high coordination number. Atom Os(3) has nine atoms bonded directly to it. These include the five other metal atoms, the two sulfur atoms, and two carbonyl ligands. Overall, the molecule contains an approximate

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C_2 symmetry axis that is coincident with the Os(3)–Os(4) vector.

Curiously, the observation of only one *N*-methyl resonance of intensity 12 in the ^{1}H NMR spectrum is inconsistent with the solid-state structure. This anomally was resolved by a variable-temperature ^{1}H NMR study, which revealed the presence of a dynamical exchange process. At −80 °C the ^{1}H NMR spectrum showed two closely space *N*-methyl resonances at 3.78 and 3.84 ppm of intensity 6. As the temperature was raised, the resonances broadened, merged (−36 °C), and re-formed as the sharp singlet that is observed at 25 °C. Two dynamical processes that could explain this observation are as follows: The first is rotations about the C–N bonds that are slowed at low temperature. This could be expected on the basis of the structural evidence for partial C–N multiple bonding. The second is a polytopal rearrangement at Os(4) in which the semibridging carbonyl ligands shift rapidly between the Os(1)–Os(4) and Os(4)–Os(6) bonds, and the Os(2)–Os(4) and Os(4)–Os(5) bonds. As a consequence the *N*-methyl groups on the carbyne ligands would interchange their environments. With the available data these mechanisms cannot be distinguished.

In addition to its novel structure, compound **3** also possesses an unusual electronic configuration. In all previously reported examples the triply bridging alkanethiolato ligand was regarded as a five-electron donor.[14,15] If these ligands are five-electron donors in **3**, then assuming that the carbyne ligands serve as three-electron donors, the cluster would contain a total of 90 valence electrons. However, the edge-fused bitetrahedron should contain only 86 electrons.[16] An alternative possibility is that the thiolato ligands serve only as three-electron donors and the total valence electron count is the expected number 86. If the thiolato ligands are three-electron donors, then the sulfur atoms should contain an uncoordinated pair of electrons. Consideration of the geometry of the sulfur atoms (vide supra) suggests that this is not unreasonable. For both sulfur atoms, a plane is defined by two of the metal atoms, the sulfur atom, and the carbon atom (e.g., Os(1), Os(5), S(1), C(1)). The only other atom bonded to the sulfur atom is the third metal atom. As a result, a full hemisphere of space around the sulfur atom is vacant. Indeed, a lone pair of electrons could easily occupy part of this space.

When viewed in terms of two-center–two-electron, (2c–2e) bonding, it is found that atom Os(4) is electron deficient and atom Os(3) is electron rich unless the Os(3)–Os(4) bond is regarded as a donor–acceptor bond donating from Os(3) to Os(4). The requirement for use of such formalisms is becoming increasingly necessary when 2c–2e theory is applied to large clusters.[17] Cotton has pointed out that these situations often lead to the formation of semibridging carbonyl ligands.[18] In accord with this it was found that the two carbonyl ligand bonded to Os(4) have adopted semibridging bonding modes.

The fact that **3** contains only two hydride ligands indicates that 1 equiv of H_2 was eliminated at some stage in the condensation. Such eliminations have been observed previously in the high-temperature condensation of hydride-containing clusters.[4] No attempt was made to measure the small amounts of H_2 that could have been formed in the reaction. Overall the formation of **3** requires the loss of 4 mol of CO and 1 equiv of H_2 from 2 mol of **2**. Mechanistically, the condensation must be complex. A schematic representation of the condensation is shown in Figure 3. It is believed that the lone pairs of electrons on the thiolato ligands in **2** assist in the reaction through the formation of transient donor–acceptor bonds that join the clusters. Details of the condensation cannot be accurately predicted at this time. Figure 3 shows only the locations where key bonds must be formed and broken in order to produce **3**.

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Supplementary Material Available: Tables of anisotropic thermal parameters and least-squares planes for compound **3** (3 pages); a table of structure factor amplitudes for compound **3** (19 pages). Ordering information is given on any current masthead page.

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New Mode of Bonding of Bis((diphenylphosphino)methyl)phenylphosphine, dpmp: Synthesis and Structure of a Sterically Crowded, Triply Bonded Dirhenium Complex, $[Re_2Cl_3(dpmp)_2]X$ (X = Cl, PF_6)

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The reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with dpmp leads to reduction of the quadruple bond and results in the formation of a triply bridged complex, $[Re_2Cl_3(dpmp)_2]X$. The title compound has been isolated as the chloride and hexafluorophosphate salts. $[Re_2Cl_3(dpmp)_2]Cl$ crystallizes in the monoclinic space group *Cc* with the following unit cell dimensions: a = 13.130 (3) Å, b = 22.162 (4) Å, c = 23.634 (3) Å, β = 104.94 (1)°, V = 6645 (2) Å^3, and Z = 4. The hexafluorophosphate salt, $[Re_2Cl_3(dpmp)_2]PF_6$, was obtained by metathesis and crystallized in the monoclinic space group $P2_1/c$ with a = 24.835 (4) Å, b = 12.048 (3) Å, c = 24.047 (5) Å, β = 114.25 (2)°, V = 6560 (5) Å^3, and Z = 4. A new mode of bonding has been observed in which the triphosphine has doubly bridged the dimetal unit, with the middle phosphorus atom coordinated to one rhenium atom and both terminal phosphorus atoms coordinated to the other rhenium atom.

Introduction

Bifunctional phosphines have been used extensively to stabilize multiple bonds between metal atoms.[1,2] They have been shown to coordinate in two different ways, namely as bridges spanning a dimetallic core and as chelating ligands. A natural extension of the bifunctional phosphines are polyfunctional phosphines. As always with polyfunctional ligands, the problem of forming

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