with $I_o > 3\sigma(I_o)$ were used in the full-matrix, least-squares refinements. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions (C–H = 0.96 Å; H–C–H = 109.5°), allowed to ride with the carbons to which they are attached, and their individual isotropic thermal motion was fixed at 0.08. The exception was the silyl hydrides in **8**, which were allowed to ride with the Si atoms but refined isotropically.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research Air Force Systems Command, USAF, under Contract No. F49620-86-0010 and by the National Science Foundation Grant No. CHE-8318820-02.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **8** and **9b** (10 pages); listings of structure factors for **8** and **9b** (45 pages). Ordering information is given on any current masthead page.

Clusters Containing Carbene Ligands. 8. Formation of Ligands Containing (Dialkylamino)carbene Centers by a Novel 1,1-Hydrogenation of Ynamine Ligands

Richard D. Adams,* Gong Chen, James T. Tanner, and Jianguo Yin

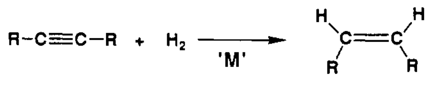
Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

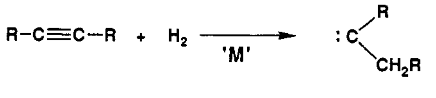
Received October 23, 1989

The reaction of the complex $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**1**) with hydrogen at 125 °C and 1 atm yielded the two new compounds $Os_3(CO)_7[\mu\text{-}C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)_3$ (**3**; 7%) and $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**4**; 9%). At 125 °C and 10 atm of H_2 pressure the yield of **4** was increased to 33%, the yield of **3** decreased to essentially zero, and the two new compounds $Os_3(CO)_8[C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)$ (**5**) and $Os_3(CO)_8[\eta\text{-}H_2CC(H)C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)$ (**6**) were formed in very low yield. Compounds **3** and **4** can be interconverted by the addition and elimination of CO. Compounds **3**–**6** were characterized by IR, NMR, and single-crystal X-ray diffraction analyses. Each compound consists of a sulfur-bridged triangular triosmium cluster. Compound **3** contains a bridging $EtCN(Me)CH_2$ ligand. The ethyl-substituted carbon is a carbene center. Compound **4** contains a terminally coordinated carbene, $EtC(NMe_2)$. Compound **5** contains a chelating $EtCN(Me)CH_2$. The ethyl-substituted carbon is a carbene center. Compound **6** contains a $\eta^2\text{-}H_2CC(H)C(H)NMe_2$ ligand. The carbene centers in compounds **3**–**5** were formed by 1,1-hydrogenations at the methyl-substituted carbon atom of the ynamine ligand in **1**. In compounds **3** and **5** one of the *N*-methyl groups was metalated. The (dimethylamino)allyl ligand in **6** was formed by a 1,2-dihydrogenation of the ynamine ligand in **1** plus a CH activation on the methyl group on the carbon atom. Crystal data: for **3**, space group *Pbca*, $a = 12.884$ (3) Å, $b = 23.897$ (5) Å, $c = 12.522$ (3) Å, 1858 reflections, $R = 0.034$, $R_w = 0.033$; for **4**, space group $P\bar{1}$, $a = 9.955$ (1) Å, $b = 13.971$ (2) Å, $c = 8.227$ (1) Å, $\alpha = 102.91$ (1)°, $\beta = 113.134$ (9)°, $\gamma = 92.06$ (1)°, 2606 reflections, $R = 0.027$, $R_w = 0.031$; for **5**, space group $P2_1/n$, $a = 9.260$ (2) Å, $b = 12.784$ (3) Å, $c = 16.734$ (3) Å, $\beta = 90.60$ (2)°, 2163 reflections, $R = 0.025$, $R_w = 0.026$; for **6**, space group $P2_1/n$, $a = 10.226$ (3) Å, $b = 12.589$ (5) Å, $c = 15.990$ (7) Å, $\beta = 106.88$ (3)°, 2129 reflections, $R = 0.036$, $R_w = 0.039$.

Introduction

The hydrogenation of alkynes by metal complexes invariably proceeds to yield alkenes, usually with a cis stereochemistry, by the 1,2-addition of hydrogen to the triple bond (eq 1).[1,2] To our knowledge, the alternative 1,1-hydrogenation to yield alkylidenes has not yet been reported (eq 2). For most substituents, eq 2 as written is probably thermodynamically unfavorable. However, in the presence of stabilizing substituents and a metal atom for complexation, eq 2 may become thermodynamically favorable.


$$\text{R–C}\equiv\text{C–R} + \text{H}_2 \xrightarrow[\text{'M'}]{} \text{(H)(R)C=C(H)(R)} \quad (1)$$


$$\text{R–C}\equiv\text{C–R} + \text{H}_2 \xrightarrow[\text{'M'}]{} \text{:C(R)(CH}_2\text{R)} \quad (2)$$

Recent studies of the coordination of ynamine ligands in metal cluster complexes have shown that the amine-substituted carbon atom possesses an appreciable carbene-like character.[3-6]

We have now investigated the reactions of the complex $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**1**) with H_2 and have observed a preference for the formation of the ethyl(dimethylamino)carbene ligand grouping by the addition of

---

(1) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 51, and references therein.

(2) (a) Muetterties, E. L.; Krause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (b) Muetterties, E. L. *Pure Appl. Chem.* **1978**, *50*, 941. (c) Burch, R. R.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 4257.

(3) Adams, R. D.; Tanner, J. T. *Organometallics* **1989**, *8*, 563.

(4) (a) Adams, R. D.; Tanner, J. T. *Organometallics* **1988**, *7*, 2241. (b) Deeming, A. J.; Kabir, S. E.; Nuel, D.; Powell, N. I. *Organometallics* **1989**, *8*, 717.

(5) (a) Cabrera, E.; Daran, J. C.; Jeannin, Y.; Kristiansen, O. *J. Organomet. Chem.* **1986**, *310*, 367. (b) Muller, F.; van Koten, G.; Kraakman, M. J. A.; Vrieze, K. *Organometallics* **1989**, *8*, 1331.

(6) Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, J. *Organometallics* **1990**, *9*, 595.

0276-7333/90/2309-1523$02.50/0

Table I. Crystal Data for the Structural Analyses of Compounds 3–6

	3	4	5	6
empirical formula	$Os_3SO_7C_{12}NH_{13}$	$Os_3SNO_8C_{13}H_9$	$Os_3SNO_8C_{13}H_{11}$	$Os_3SNO_8C_{13}H_{11}$
fw	885.90	909.88	911.89	911.89
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic
lattice params				
a, Å	12.884 (3)	9.955 (1)	9.260 (2)	10.226 (3)
b, Å	23.897 (5)	13.971 (2)	12.784 (3)	12.589 (5)
c, Å	12.522 (3)	8.227 (1)	16.734 (3)	15.990 (7)
α, deg		102.91 (1)		
β, deg		113.134 (9)	90.60 (2)	106.88 (3)
γ, deg		92.06		
V, Å^3	3855 (2)	1015.8 (6)	1980.9 (7)	1970 (2)
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z	8	2	4	4
D(calcd), g/cm^3	3.05	2.97	3.06	3.07
μ(Mo Kα)	198.8	188.7	193.5	195.1
abs cor	analytical	empirical	empirical	analytical
temp, °C	23	23	23	23
$2\theta_{max}$, deg	46.0	47.0	46.0	46.0
no. of observns ($I > 3\sigma(I)$)	1858	2606	2163	2129
no. of variables	217	241	238	235
residuals: R; R_w	0.034; 0.033	0.027; 0.031	0.025; 0.026	0.036; 0.039
goodness-of-fit indicator	1.35	1.79	1.20	1.81
max shift in final cycle	0.03	0.30	0.09	0.05
largest peak in final diff map, e/Å^3	1.52	0.86	0.67	1.38

two hydrogen atoms to the methyl-substituted carbon atom of the MeC_2NMe_2 ligand. This reaction could provide a new and general route for the formation of aminocarbene ligands in metal complexes[7] and especially cluster complexes.[8] A preliminary report of this work has been published.[9]

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Reagent grade solvents were stored over 4-Å molecular sieves. All chromatographic separations were performed in air on TLC plates (0.25 mm siliga gel 60 F_{254}, Whatman). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were taken at 300 MHz on a Bruker AM-300 spectrometer. ^{13}C NMR spectra were taken at 125.76 MHz on a Bruker AM-500 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**1**) was prepared by the previously reported procedure.[6]

Reaction of 1 with H_2. A. Under Hydrogen at 1 atm. A 30.0-mg (0.033-mmol) amount of **1** was dissolved in 20 mL of octane. The solution was heated to reflux with stirring, and the flask was purged with hydrogen slowly at this temperature for a period of 5 h. After the mixture was cooled, the solvent was removed in vacuo, and the residue was dissolved in a minimal amount of CH_2Cl_2 and chromatographed by TLC on silica gel. Elution with a mixture of hexane/CH_2Cl_2 (4/1) yielded the following bands in order of elution: 2.5 mg of $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2**; 9%); 1.9 mg of pale yellow $Os_3(CO)_7[\mu\text{-}C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)_3$ (**3**, 7%); 2.8 mg of pale yellow $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**4**; 9%). IR (cm^{-1}, in hexane): for **3**, 2107 (m), 2035 (vs), 2020 (m), 2023 (s), 2016 (m), 1968 (m), 1957 (m); for **4**, 2083 (s), 2046 (vs), 2030 (s), 2002 (vs), 1985 (m), 1969 (m), 1960 (w). ^1H NMR (ppm in $CDCl_3$ at 25 °C): for **3**, 4.44 (d, 1 H, J_{H-H} = 14.1 Hz), 4.10 (d, 1 H, J_{H-H} = 14.1 Hz), 3.29 (s, 3 H), 3.18 (dq, 1 H, J_{H-H} = 12.0, 7.8 Hz), 3.08 (dq, 1 H, J_{H-H} = 12.0, 7.8 Hz), 1.08 (t, 3 H, J_{H-H} = 7.8 Hz), −17.27 (t, 1 H, J_{H-H} = 1.3 Hz), −19.85 (t, 1 H, J_{H-H} = 1.1 Hz), −21.40 (t, 1 H, J_{H-H} = 1.8 Hz); for **4**, 3.75 (s, 3 H), 3.37 (s, 3 H), 3.44 (q, 1 H, J_{H-H} = 7.7 Hz), 3.43 (q, 1 H, J_{H-H} = 7.6 Hz), 1.12 (t, 3 H, J_{H-H} = 7.7 Hz), −20.66 (s, 1 H), −21.85 (s, 1 H). ^{13}C NMR (ppm) for **4** ($CDCl_3$): δ 217.19 (s, $CNMe_2$), 178.44 (s, CO), 178.40 (s, CO), 176.72 (s, CO), 171.02 (s, CO), 170.80 (s, CO), 169.27 (s, CO), 167.28 (s, CO), 167.04 (s, CO), 56.86 (s, NMe), 51.74 (s, NMe), 41.73 (s, CH_2), 9.56 (Me). Anal. Calcd (found) for **3**: C, 16.27 (16.33); H, 1.71 (1.45); N, 1.58 (1.46). Calcd (found) for **4**: C, 17.08 (17.09); H, 1.43 (1.44); N, 1.58 (1.46).

B. Under Hydrogen at 10 atm. A 20-mg (0.022-mmol) amount of **1** was dissolved in 15 mL of octane and placed in a 45-mL stainless steel Parr high-pressure reaction vessel. The vessel was pressurized with hydrogen to 10 atm and then heated to 125 °C with stirring for 5 h. After the mixture was cooled, the reaction solution was separated as described above to yield 2.3 mg of **2** (14%), 2.7 mg of unreacted **1**, 0.4 mg of pale yellow $Os_3(CO)_8[C(Et)N(CH_3)CH_2](\mu_3\text{-}S)(\mu\text{-}H)$ (**5**; 2%), 5.5 mg of **4** (33%), and 1.1 mg of orange $Os_3(CO)_8[\eta^2\text{-}CH_2{=}CHCH{=}NMe_2](\mu_3\text{-}S)(\mu\text{-}H)$ (**6**; 6%). IR (in hexane, cm^{-1}): for **5**, 2082 (m), 2047 (vs), 2019 (m), 2002 (vs), 1985 (m), 1971 (m); for **6**, 2076 (m), 2041 (vs), 2016 (s), 1995 (s), 1980 (m), 1959 (w). ^1H NMR (ppm in $CDCl_3$ at 25 °C): for **5**, 3.23 (s, 3 H), 3.05 (d, 1 H, J_{H-H} = 9.1 Hz), 2.97 (q, 2 H, J_{H-H} = 7.8 Hz), 2.48 (d, 1 H, J_{H-H} = 9.1 Hz), 1.16 (t, 3 H, J_{H-H} = 7.7 Hz), −20.73 (s, 1 H); for **6**, 6.59 (d, 1 H, J_{H-H} = 6.0 Hz), 3.47 (br, 1 H), 3.32 (br, 1 H), 3.17 (s, 3 H), 3.30 (s, 3 H), 2.92 (br, 1 H), −22.43 (s, 1 H). Anal. Calcd (found) for **5**: C, 17.12 (17.32); H, 1.21 (1.09); N, 1.54 (1.54). Calcd (found) for **6**: C, 17.08 (17.59); H, 1.43 (1.23); N, 1.53 (1.54).

If 50 mg of **1** was used in this reaction, the formation of a trace amount of complex **3** could be detected by IR spectroscopy after TLC isolation.

Decarbonylation of 4 to 3. A 19.0-mg (0.021-mmol) amount of complex **4** was dissolved in 15 mL of nonane. The solution was heated to reflux with stirring for 5 h. The solvent was removed in vacuo, and the residue was chromatographed by TLC with a hexane/CH_2Cl_2 (4/1) solvent mixture to give 4.1 mg of **2** (27%), 5.5 mg of **3** (34%), and 2.4 mg of unreacted **4**. Almost no reaction took place if the same procedures were followed in refluxing octane solvent.

Carbonylation of 3. A 7.0-mg (0.0080-mmol) amount of **3** was dissolved in 10 mL of octane. The solution was placed in a Parr reaction vessel, pressurized to 25 atm with CO, and heated to 125 °C for 8 h. The solvent was removed under vacuum, and the residue was separated as described above to yield 1.5 mg of **2** (22%) and 4.3 mg of **4** (59%).

Crystallographic Analyses. Crystals of **3** suitable for X-ray diffraction analyses were grown from solutions in hexane solvent by slow evaporation of the solvent at 25 °C. Crystals of **4** were grown from a hexane/CH_2Cl_2 (1/1) solvent mixture by cooling to −15 °C. Crystals of **5** were grown from solutions in a benzene/octane solvent mixture by slow evaporation of solvent at 25 °C. Crystals of **6** were grown from solutions in benzene solvent

---

(7) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983; and references therein.

(8) Adams, R. D. *Chem. Rev.* **1989**, *89*, 1703.

(9) Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, J. *Organometallics* **1989**, *8*, 2493.

(10) Deleted in proof.

by slow evaporation of the solvent at 25 °C. All data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromatized Mo Kα radiation. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All intensity measurements were made by using the standard ω-scan (moving crystal–stationary counter) technique. Background measurements were made by a one-fourth additional scan at each end of the scan. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure solving program library (version 2.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[11a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[11b] Full-matrix least-squares refinements minimized the function

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

where

$$w = 1/\sigma(F)^2$$

$$\sigma(F) = \sigma(F_o^2)/2F_o$$

$$\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$$

Compound **3** crystallized in the orthorhombic crystal system. The space group *Pbca* was identified uniquely from the systematic absences observed in the data. Compound **4** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Compounds **5** and **6** both crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely for both of these compounds on the basis of the systematic absences observed in the data. All of the structures were solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. For all of the structures all non-hydrogen atoms were refined by using anisotropic thermal parameters. The hydride ligands were located in difference Fourier syntheses for each structure but were successfully refined only for the structures of **4**–**6**. The positions of the remaining hydrogen atoms were calculated by assuming idealized geometries and employing observed positions whenever possible. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined. See the supplementary material for the tables of structure factor amplitudes, tables of hydrogen atom positional parameters, and the values of the anisotropic thermal parameters for all of the structural analyses.

Results

From the reaction of **1** with hydrogen at 125 °C and 1 atm, the two complexes $Os_3(CO)_7[\mu\text{-}C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)_3$ (**3**; 7%) and $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**4**; 9%) were obtained in low yields. There was considerable formation of uncharacterizable decomposition materials under these conditions, but one decomposition product, the previously known compound $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2**; 9% yield) was characterized. The yield of **4** was significantly increased (33%) when the reaction was performed in a sealed container at 125 °C and 10 atm of H_2 pressure, but the amount of **3** decreased essentially to zero, and the two new compounds $Os_3(CO)_8[C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)$ (**5**; 2%) and $Os_3(CO)_8[\eta^2\text{-}H_2CC(H)C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)$ (**6**; 6%) were formed in very low yields.

In separate experiments, it was shown that **3** undergoes CO addition to give **4** in a good yield. Compound **4** can be decarbonylated to yield **3** at 150 °C, but this reaction does not occur to a significant extent under the conditions of the original hydrogenation.

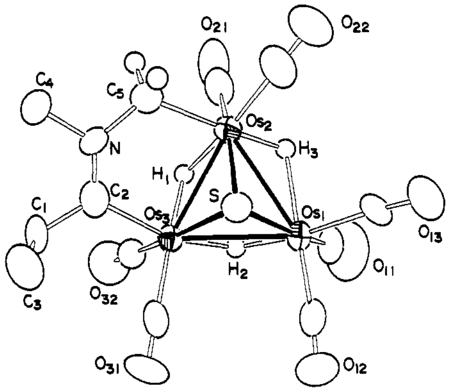


Figure 1. ORTEP drawing of $Os_3(CO)_7(\mu\text{-}C(Et)N(Me)CH_2)(\mu_3\text{-}S)(\mu\text{-}H)_3$ (**3**) showing 50% probability thermal ellipsoids.

Table II. Positional Parameters and *B*(eq) Values for 3

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.29320 (5)	0.05454 (3)	0.52907 (6)	3.08 (3)
Os(2)	0.09283 (5)	0.11130 (3)	0.51683 (6)	3.52 (3)
Os(3)	0.24282 (5)	0.15117 (3)	0.66205 (5)	2.66 (3)
S	0.2584 (3)	0.14870 17)	0.4715 (3)	3.1 (2)
O(11)	0.2931 (18)	−0.0630 (6)	0.6335 (17)	11 (1)
O(12)	0.5267 (13)	0.0703 (7)	0.5474 (18)	9 (1)
O(13)	0.3108 (13)	0.0043 (7)	0.3082 (13)	7 (1)
O(21)	−0.0947 (12)	0.0576 7)	0.6168 (17)	10 (1)
O(22)	0.0135 (13)	0.0929 (8)	0.2900 (13)	8 (1)
O(31)	0.4605 (11)	0.1978 (6)	0.7017 (12)	6.0 (8)
O(32)	0.2065 (13)	0.1405 (7)	0.9008 (12)	8 (1)
N	0.0845 (10)	0.2358 (5)	0.5953 (11)	3.2 (7)
C(1)	0.2047 (16)	0.2750 (6)	0.7216 (14)	4 (1)
C(2)	0.1672 (14)	0.2276 (7)	0.6566 (15)	3.7 (9)
C(3)	0.2801 (16)	0.3107 (7)	0.6644 (17)	5 (1)
C(4)	0.0281 (16)	0.2893 (8)	0.5908 (19)	6 (1)
C(5)	0.0353 (14)	0.1943 (7)	0.5243 (18)	5 (1)
C(11)	0.2928 (16)	−0.0194 (8)	0.5937 (19)	6 (1)
C(12)	0.4403 (18)	0.0640 (7)	0.5355 (18)	5 (1)
C(13)	0.2998 (15)	0.0236 (8)	0.3886 (16)	4 (1)
C(21)	−0.0242 (17)	0.0783 (10)	0.5764 (20)	6 (1)
C(22)	0.0436 (18)	0.0998 (10)	0.376 (2)	6 (1)
C(31)	0.3800 (17)	0.1805 (8)	0.6860 (16)	5 (1)
C(32)	0.2194 (15)	0.1437 (8)	0.8103 (17)	5 (1)

Table III. Intramolecular Distances for 3[a]

Os(1)–C(12)	1.91 (2)	Os(3)–S	2.395 (4)
Os(1)–C(13)	1.91 (2)	N–C(2)	1.33 (2)
Os(1)–C(11)	1.94 (2)	N–C(4)	1.47 (2)
Os(1)–S	2.405 (4)	N–C(5)	1.47 (2)
Os(1)–Os(3)	2.920 (1)	C(1)–C(2)	1.48 (2)
Os(1)–Os(2)	2.920 (1)	C(1)–C(3)	1.48 (3)
Os(2)–C(21)	1.86 (2)	O–C (av)	1.14 (2)
Os(2)–C(22)	1.90 (3)	Os(2)–H(1)	1.73
Os(2)–C(5)	2.12 (2)	Os(3)–H(1)	1.74
Os(2)–S	2.382 (4)	Os(1)–H(2)	1.55
Os(2)–Os(3)	2.819 (1)	Os(3)–H(2)	1.64
Os(3)–C(32)	1.89 (2)	Os(2)–H(3)	1.54
Os(3)–C(31)	1.92 (2)	Os(3)–H(3)	2.10
Os(3)–C(2)	2.07 (2)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Compounds **3**–**6** were characterized by IR and ^1H NMR spectroscopy, elemental analyses, and single-crystal X-ray diffraction analyses.

Descriptions of the Structures. An ORTEP drawing of the molecular structure of **3** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic bond distances and angles are listed in Tables III and IV, respectively. The molecule consists of a triangular cluster of three osmium atoms with three

---

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

Table IV. Intramolecular Bond Angles for 3[a]

C(12)–Os(1)–S	95.0 (6)	C(32)–Os(3)–C(2)	92.3 (7)
C(12)–Os(1)–Os(3)	95.9 (5)	C(32)–Os(3)–S	171.9 (6)
C(12)–Os(1)–Os(2)	145.5 (5)	C(32)–Os(3)–Os(2)	119.5 (6)
C(13)–Os(1)–S	95.5 (6)	C(32)–Os(3)–Os(1)	121.4 (6)
C(13)–Os(1)–Os(3)	147.3 (5)	C(31)–Os(3)–C(2)	96.7 (7)
C(13)–Os(1)–Os(2)	99.8 (6)	C(31)–Os(3)–S	95.0 (6)
C(11)–Os(1)–S	167.2 (6)	C(31)–Os(3)–Os(2)	148.5 (6)
C(11)–Os(1)–Os(3)	118.7 (6)	C(31)–Os(3)–Os(1)	100.0 (5)
C(11)–Os(1)–Os(2)	116.2 (6)	C(2)–Os(3)–S	91.6 (5)
S–Os(1)–Os(3)	52.4 (1)	C(2)–Os(3)–Os(2)	87.4 (5)
S–Os(1)–Os(2)	52.0 (1)	C(2)–Os(3)–Os(1)	141.6 (5)
Os(3)–Os(1)–Os(2)	57.73 (2)	S–Os(3)–Os(2)	53.6 (1)
C(21)–Os(2)–C(5)	95.5 (9)	S–Os(3)–Os(1)	52.7 (1)
C(21)–Os(2)–S	169.1 (8)	Os(2)–Os(3)–Os(1)	61.14 (3)
C(21)–Os(2)–Os(3)	116.1 (7)	Os(2)–S–Os(3)	72.3 (1)
C(21)–Os(2)–Os(1)	120.0 (8)	Os(2)–S–Os(1)	75.2 (1)
C(22)–Os(2)–C(5)	93 (1)	Os(3)–S–Os(1)	74.9 (1)
C(22)–Os(2)–S	97.6 (7)	C(2)–N–C(4)	123 (1)
C(22)–Os(2)–Os(3)	151.5 (7)	C(2)–N–C(5)	126 (1)
C(22)–Os(2)–Os(1)	106.1 (7)	C(4)–N–C(5)	110 (1)
C(5)–Os(2)–S	88.4 (5)	C(2)–C(1)–C(3)	113 (2)
C(5)–Os(2)–Os(3)	84.0 (5)	N–C(2)–C(1)	118 (2)
C(5)–Os(2)–Os(1)	137.9 (5)	N–C(2)–Os(3)	122 (1)
S–Os(2)–Os(3)	54.0 (1)	C(1)–C(2)–Os(3)	120 (1)
S–Os(2)–Os(1)	52.8 (1)	N–C(5)–Os(2)	120 (1)
Os(3)–Os(2)–Os(1)	61.13 (3)	O–C–Os (av)	178 (2)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

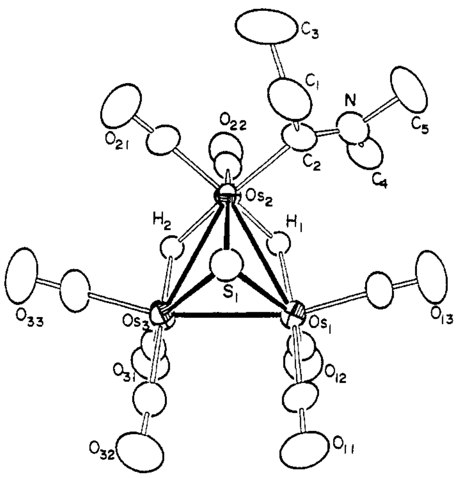


Figure 2. ORTEP diagram of $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (4) showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and *B*(eq) Values for 4

atom	*x*	*y*	*z*	*B*(eq), Å²
Os(1)	0.73612 (4)	0.24892 (3)	0.34939 (6)	2.77 (1)
Os(2)	1.03746 (4)	0.21287 (3)	0.40697 (6)	2.37 (1)
Os(3)	0.78370 (4)	0.13989 (3)	0.05488 (6)	2.65 (1)
S(1)	0.8857 (3)	0.30858 (19)	0.2153 (4)	3.01 (9)
O(11)	0.4598 (10)	0.3142 (7)	0.1047 (14)	6.2 (4)
O(12)	0.5738 (11)	0.0777 (8)	0.4039 (14)	5.9 (4)
O(13)	0.7771 (13)	0.4087 (9)	0.6881 (15)	7.9 (5)
O(21)	1.2779 (11)	0.2087 (8)	0.2714 (15)	6.5 (5)
O(22)	1.1630 (9)	0.0569 (6)	0.6078 (12)	4.8 (3)
O(31)	0.6377 (9)	−0.0639 (7)	0.0180 (12)	5.1 (3)
O(32)	0.5126 (11)	0.1856 (8)	−0.2389 (13)	6.5 (4)
O(33)	0.9286 (12)	0.0688 (8)	−0.2057 (14)	6.8 (5)
N	1.1483 (10)	0.3590 (7)	0.7848 (14)	4.0 (4)
C(3)	1.3869 (16)	0.4183 (12)	0.647 (3)	7.5 (7)
C(1)	1.2192 (15)	0.4227 (9)	0.5789 (18)	5.0 (5)
C(2)	1.1446 (11)	0.3401 (8)	0.6211 (16)	3.3 (4)
C(4)	1.0942 (14)	0.2865 (10)	0.8578 (17)	5.0 (5)
C(5)	1.2115 (17)	0.4544 (10)	0.9270 (19)	6.0 (5)
C(11)	0.5628 (12)	0.2888 (9)	0.1976 (17)	4.0 (4)
C(12)	0.6340 (13)	0.1440 (10)	0.3868 (16)	4.0 (4)
C(13)	0.7642 (14)	0.3491 (10)	0.5647 (18)	4.8 (5)
C(21)	1.1887 (12)	0.2115 (9)	0.3252 (17)	3.6 (4)
C(22)	1.1175 (11)	0.1180 (8)	0.5350 (15)	3.1 (4)
C(31)	0.6931 (12)	0.0116 (9)	0.0291 (14)	3.4 (4)
C(32)	0.6124 (13)	0.1693 (9)	−0.1280 (16)	3.8 (4)
C(33)	0.8744 (14)	0.0964 (9)	−0.1083 (17)	4.2 (4)

Table VI. Intramolecular Distances for 4[a]

Os(1)–H(1)	1.8 (1)	Os(2)–Os(3)	2.9253 (8)
Os(1)–C(11)	1.88 (1)	Os(3)–H(2)	1.7 (1)
Os(1)–C(12)	1.90 (1)	Os(3)–C(33)	1.90 (1)
Os(1)–C(13)	1.91 (1)	Os(3)–C(31)	1.91 (1)
Os(1)–S(1)	2.396 (3)	Os(3)–C(32)	1.91 (1)
Os(1)–Os(3)	2.7785 (8)	Os(3)–S(1)	2.390 (3)
Os(1)–Os(2)	2.9284 (6)	N–C(2)	1.30 (1)
Os(1)–H(1)	1.7 (1)	N–C(4)	1.47 (2)
Os(1)–H(2)	1.8 (1)	N–C(5)	1.48 (1)
Os(2)–C(21)	1.87 (1)	C(3)–C(1)	1.55 (2)
Os(2)–C(22)	1.88 (1)	C(1)–C(2)	1.52 (2)
Os(2)–C(2)	2.10 (1)	O–C (av)	1.14 (1)
Os(2)–S(1)	2.402 (3)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

osmium–osmium bonds. Each metal–metal bond contains one bridging hydride ligand. These were located crystallographically in chemically reasonable positions, but their positions could not be refined. There is a triply bridging sulfido ligand. All metal–metal and metal–sulfur bond distances are normal and similar to those found in $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**2**).[12] The most interesting ligand is the $EtCN(Me)CH_2$ ligand. Carbon C(2) is a carbene site. The Os(3)–C(2) distance of 2.07 (2) Å is similar to that observed in other osmium cluster complexes that contain aminocarbene ligands[13] and the Os–C distances to the carbene carbon atoms observed in **4** and **5** (see below). Atom C(5) is the carbon atom of the methylene group. As expected, the Os(2)–C(5) bond length of 2.12 (2) Å is slightly longer than that to the carbene carbon. Also, the C(5)–N distance of 1.47 (2) Å is significantly longer than the C(2)–N distance of 1.33 (2) Å. The latter should contain considerable multiple-bond character due to donation of the lone pair of electrons on the nitrogen atom to the carbon atom.[7] The three inequivalent hydride ligands show separate resonances in the ^1H NMR spectrum, −17.27, −19.85, and −21.40 ppm. Each resonance appears as a triplet, probably an unresolved doublet of doublets, due to similar couplings to the other two hydride ligands. As expected, the inequivalent hydrogen atoms on the methylene group C(5) exhibit separate resonances with mutual coupling.

An ORTEP drawing of the molecular structure of **4** is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. This molecule also consists of a sulfur-bridged triangular cluster of three metal atoms. Compound **4** contains two bridging hydride ligands that were crystallographically located and refined. As expected, the hydride-bridged osmium–osmium bonds are slightly longer (2.9284 (6) and 2.9253 (8) Å) than the bond not bridged by hydride (2.7785 (9) Å).[12,14] An ethyl(dimethylamino)carbene ligand is terminally coordinated to atom Os(2). The Os(2)–C(2) distance of 2.10 (1) Å is similar to that found in **3** and **5** and other carbene-containing osmium cluster complexes.[13] The C(2)–N distance is short

---

(12) Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R.; Sheldrick, G. M.; Rouse, K. D. *J. Chem. Soc., Dalton Trans.* **1979**, 616.

(13) (a) Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* **1985**, *107*, 6107. (b) Adams, R. D.; Babin, J. E.; Kim, H. S. *Inorg. Chem.* **1986**, *25*, 4319. (c) Adams, R. D.; Babin, J. E.; Kim, H. S. *J. Am. Chem. Soc.* **1987**, *109*, 1414.

(14) Churchill, M. R. *Adv. Chem. Ser.* **1978**, *No. 140*, 36.

Table VII. Intramolecular Bond Angles for 4[a]

C(11)–Os(1)–S(1)	94.5 (4)	C(33)–Os(3)–S(1)	107.8 (4)
C(11)–Os(1)–Os(3)	93.0 (4)	C(33)–Os(3)–Os(1)	160.8 (4)
C(11)–Os(1)–Os(2)	145.7 (4)	C(33)–Os(3)–Os(2)	102.5 (4)
C(12)–Os(1)–S(1)	151.5 (4)	C(31)–Os(3)–S(1)	153.7 (3)
C(12)–Os(1)–Os(3)	98.0 (4)	C(31)–Os(3)–Os(1)	100.2 (3)
C(12)–Os(1)–Os(2)	111.1 (4)	C(31)–Os(3)–Os(2)	111.9 (3)
C(13)–Os(1)–S(1)	107.2 (4)	C(32)–Os(3)–S(1)	95.8 (4)
C(13)–Os(1)–Os(3)	160.5 (4)	C(32)–Os(3)–Os(1)	95.2 (4)
C(13)–Os(1)–Os(2)	103.0 (4)	C(32)–Os(3)–Os(2)	147.4 (4)
S(1)–Os(1)–Os(3)	54.41 (7)	S(1)–Os(3)–Os(1)	54.61 (7)
S(1)–Os(1)–Os(2)	52.49 (6)	S(1)–Os(3)–Os(2)	52.57 (6)
Os(3)–Os(1)–Os(2)	61.61 (2)	Os(1)–Os(3)–Os(2)	61.72 (2)
C(21)–Os(2)–C(2)	92.8 (5)	Os(3)–S(1)–Os(1)	70.97 (7)
C(21)–Os(2)–S(1)	97.5 (4)	Os(3)–S(1)–Os(2)•	75.23 (8)
C(21)–Os(2)–Os(3)	99.5 (3)	Os(1)–S(1)–Os(2)	75.22 (8)
C(21)–Os(2)–Os(1)	148.4 (3)	C(2)–N–C(4)	124 (1)
C(22)–Os(2)–C(2)	97.9 (4)	C(2)–N–C(5)	126 (1)
C(22)–Os(2)–S(1)	167.3 (3)	C(4)–N–C(5)	110 (1)
C(22)–Os(2)–Os(3)	116.7 (3)	C(2)–C(1)–C(3)	110 (1)
C(22)–Os(2)–Os(1)	118.0 (3)	N–C(2)–C(1)	116 (1)
C(2)–Os(2)–S(1)	91.8 (3)	N–C(2)–Os(2)	127.1 (9)
C(2)–Os(2)–Os(3)	143.0 (3)	C(1)–C(2)Os(2)	117.1 (9)
C(2)–Os(2)–Os(1)	96.6 (3)	O–C–Os (av)	178 (1)
S(1)–Os(2)–Os(3)	52.19 (7)	Os(2)–H(1)–Os(1)	115 (6)
S(1)–Os(2)–Os(1)	52.29 (7)	Os(3)–H(2)–Os(2)	112 (6)
Os(3)–Os(2)–Os(1)	56.67 (2)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in paraentheses.

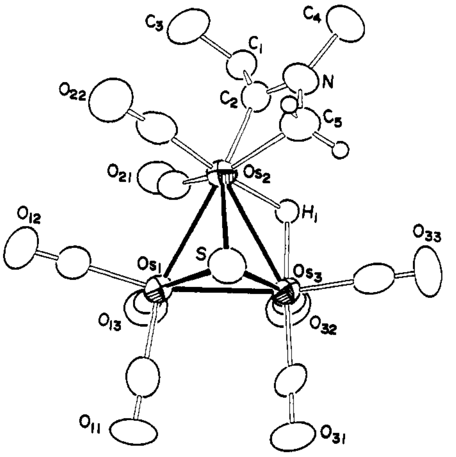


Figure 3. ORTEP diagram of $Os_3(CO)_8[C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)$ (5) showing 50% probability thermal ellipsoids.

(1.30 (1) Å) and indicative of partial multiple bonding. The observation of two N-methyl resonances in the ^1H NMR spectrum indicates the existence of a significantly hindered rotation about the C(2)–N bond. The resonance of the carbene carbon atom C(2) lies at the characteristically low-field value of +217.2 ppm.[7] This is 26.3 ppm upfield from the resonance of the amine-substituted carbon atom in 1[6] and 18.0 ppm downfield from the resonance of the carbene carbon atom of the secondary (dimethylamino)-carbene ligand in the osmium cluster complex $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$.[15]

Table VIII. Positional Parameters and B(eq) Values for 5

atom	x	y	z	B(eq), Å^2
Os(1)	0.06138 (5)	0.22627 (4)	0.57202 (3)	3.09 (2)
Os(2)	0.26490 (5)	0.37241 (4)	0.63170 (3)	3.02 (2)
Os(3)	0.34643 (5)	0.16239 (4)	0.57762 (3)	3.35 (2)
S	0.2027 (3)	0.2089 (2)	0.69027 (17)	3.8 (1)
O(11)	−0.0772 (10)	0.0117 (7)	0.5844 (6)	5.6 (5)
O(12)	−0.2132 (10)	0.3405 (7)	0.6221 (6)	5.7 (5)
O(13)	0.0380 (11)	0.2361 (8)	0.3889 (5)	6.1 (5)
O(21)	0.1461 (10)	0.4508 (7)	0.4720 (5)	5.1 (5)
O(22)	0.0543 (11)	0.5011 (9)	0.7270 (6)	7.3 (6)
O(31)	0.2625 (11)	−0.0679 (7)	0.5797 (6)	6.6 (6)
O(32)	0.3993 (12)	0.1609 (8)	0.3986 (6)	7.1 (6)
O(33)	0.6494 (10)	0.1218 (9)	0.6461 (7)	7.4 (6)
N	0.4932 (10)	0.4826 (8)	0.6767 (5)	4.1 (5)
C(1)	0.4144 (12)	0.5862 (9)	0.5596 (7)	3.7 (6)
C(2)	0.4031 (11)	0.4962 (9)	0.6170 (7)	3.5 (6)
C(3)	0.3050 (16)	0.6690 (10)	0.5836 (8)	5.6 (8)
C(4)	0.6197 (13)	0.5454 (12)	0.7045 (8)	5.9 (8)
C(5)	0.4376 (14)	0.3914 (10)	0.7187 (7)	4.4 (6)
C(11)	−0.0261 (13)	0.0920 (11)	0.5787 (7)	4.5 (7)
C(12)	−0.1105 (14)	0.2994 (9)	0.432 (7)	3.9 (6)
C(13)	0.0416 (12)	0.2332 (9)	0.4571 (8)	4.0 (6)
C(21)	0.1703 (13)	0.4075 (10)	0.5330 (8)	4.4 (7)
C(22)	0.1376 (14)	0.4536 (10)	0.6928 (7)	4.3 (6)
C(32)	0.3837 (13)	0.1603 (9)	0.4662 (9)	4.5 (7)
C(33)	0.5368 (16)	0.1379 (10)	0.6209 (8)	4.9 (7)
H(1)	0.407 (9)	0.297 (7)	0.577 (5)	3.0

Table IX. Intramolecular Distances for 5[a]

Os(1)–C(11)	1.90 (1)	Os(2)–Os(3)	2.9345 (9)
Os(1)–C(12)	1.93 (1)	Os(3)–H(1)	1.81 (9)
Os(1)–C(13)	1.93 (1)	Os(3)–C(31)	1.89 (1)
Os(1)–S	2.372 (3)	Os(3)–C(32)	1.90 (1)
Os(1)–Os(3)	2.7637 (7)	Os(3)–C(33)	1.92 (2)
Os(1)–Os(2)	2.8285 (7)	Os(3)–S	2.394 (3)
Os(2)–H(1)	1.87 (9)	N–C(2)	1.31 (1)
Os(2)–C(22)	1.88 (1)	N–C(5)	1.46 (1)
Os(2)–C(21)	1.92 (1)	N–C(4)	1.49 (1)
Os(2)–C(2)	2.05 (1)	C(1)–C(2)	1.50 (2)
Os(2)–C(5)	2.16 (1)	C(1)–C(3)	1.52 (2)
Os(2)–S	2.381 (3)	O–C (av)	1.15 (1)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table X. Intramolecular Bond Angles for 5[a]

C(11)–Os(1)–Os(3)	98.0 (4)	S–Os(2)–Os(3)	52.27 (8)
C(11)–Os(1)–Os(2)	149.1 (4)	Os(1)–Os(2)–Os(3)	57.28 (2)
C(12)–Os(1)–Os(3)	157.6 (4)	C(31)–Os(3)–Os(1)	92.6 (4)
C(12)–Os(1)–Os(2)	97.4 (4)	C(31)–Os(3)–Os(2)	145.1 (4)
C(13)–Os(1)–Os(3)	97.3 (3)	C(32)–Os(3)–Os(1)	98.9 (4)
C(13)–Os(1)–Os(2)	112.1 (3)	C(32)–Os(3)–Os(2)	111.4 (4)
S–Os(1)–Os(3)	54.93 (8)	C(33)–Os(3)–Os(1)	158.7 (4)
S–Os(1)–Os(2)	53.64 (8)	C(33)–Os(3)–Os(2)	105.7 (4)
Os(3)–Os(1)–Os(2)	63.29 (2)	S–Os(3)–Os(1)	54.18 (7)
C(22)–Os(2)–C(2)	92.0 (5)	S–Os(3)–Os(2)	51.89 (8)
C(22)–Os(2)–C(5)	92.0 (5)	Os(1)–Os(3)–Os(2)	59.43 (2)
C(22)–Os(2)–Os(1)	97.9 (4)	Os(1)–S–Os(2)	73.04 (8)
C(22)–Os(2)–Os(3)	146.9 (4)	Os(1)–S–Os(3)	70.89 (8)
C(21)–Os(2)–C(2)	89.8 (5)	Os(2)–S–Os(3)	75.84 (9)
C(21)–Os(2)–C(5)	151.8 (5)	C(2)–N–C(5)	104 (1)
C(21)–Os(2)–Os(1)	63.5 (4)	C(2)–N–C(4)	131 (1)
C(21)–Os(2)–Os(3)	93.8 (4)	C(5)–N–C(4)	124 (1)
C(2)–Os(2)–C(5)	62.4 (4)	C(2)–C(1)–C(3)	108 (1)
C(2)–Os(2)–S	151.6 (3)	N–C(2)–C(1)	123 (1)
C(2)–Os(2)–Os(1)	151.8 (3)	N–C(2)–Os(2)	101.5 (8)
C(2)–Os(2)–Os(3)	120.4 (3)	C(1)–C(2)–Os(2)	135.6 (8)
C(5)–Os(2)–S	90.1 (3)	N–C(5)–Os(2)	91.6 (7)
C(5)–Os(2)–Os(1)	142.8 (3)	O(21)–C(21)–Os(2)	160 (1)
C(5)–Os(2)–Os(3)	96.9 (3)	O–C–Os (av)	178 (1)
S–Os(2)–Os(1)	53.32 (7)	Os(3)–H(1)–Os(2)	106 (4)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

An ORTEP drawing of 5 is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected interatomic distances and angles are listed in Tables IX and X. Compound 5 consists of a sulfur-bridged triangular cluster of three metal atoms. In 5, there is only one bridging hydride ligand (δ = −20.73 ppm), which was located and refined crystallographically. It bridges the Os(2)–Os(3) bond, which is significantly longer than the other two Os–Os bonds (2.9345 (9) Å vs 2.8285 (7) and 2.7637 (7) Å). Compound 5 contains a $EtCN(Me)CH_2$ ligand that is chelated to Os(1). The corresponding ligand

---

[15] Adams, R. D.; Babin, J. E.; Kim, H. S.; Tanner, J. T.; Wolfe, T. A. *J. Am. Chem. Soc.*, in press.

Table XI. Positional Parameters for 6

atom	*x*	*y*	*z*
Os(1)	0.55658 (7)	0.19650 (6)	0.68838 (5)
Os(2)	0.70993 (8)	0.17143 (6)	0.87346 (5)
Os(3)	0.47223 (8)	0.05983 (6)	0.79978 (5)
S(1)	0.6757 (5)	0.0427 (4)	0.7591 (3)
O(11)	0.4042 (16)	0.0732 (11)	0.5284 (9)
O(12)	0.2983 (17)	0.3114 (13)	0.6912 (10)
O(21)	0.8075 (17)	0.0154 (12)	1.0208 (9)
O(22)	0.5979 (19)	0.3137 (12)	0.9895 (12)
O(23)	0.9862 (16)	0.2774 (14)	0.8950 (9)
O(31)	0.2902 (16)	0.1944 (13)	0.8773 (11)
O(32)	0.2490 (17)	−0.0506 (14)	0.6582 (11)
O(33)	0.5060 (15)	−0.1138 (11)	0.9357 (10)
N	0.886 (2)	0.1467 (14)	0.6280 (13)
C(1)	0.6024 (18)	0.3374 (15)	0.6213 (14)
C(2)	0.731 (2)	0.2744 (18)	0.6483 (14)
C(3)	0.744 (3)	0.200 (2)	0.6093 (16)
C(4)	0.885 (2)	0.056 (2)	0.5750 (16)
C(5)	1.002 (2)	0.160 (2)	0.7061 (15)
C(11)	0.4647 (20)	0.1237 (15)	0.5900 (13)
C(12)	0.395 (2)	0.2658 (15)	0.6931 (12)
C(21)	0.7685 (20)	0.0705 (17)	0.9649 (12)
C(22)	0.639 (3)	0.2611 (17)	0.9449 (15)
C(23)	0.880 (2)	0.2364 (16)	0.8836 (11)
C(31)	0.354 (2)	0.1397 (17)	0.8480 (15)
C(32)	0.335 (2)	−0.0111 (16)	0.7104 (13)
C(33)	0.4932 (20)	−0.0490 (15)	0.8832 (16)
H	0.612 (15)	0.257 (12)	0.806 (10)

Table XII. Intramolecular Distances for 6[a]

Os(1)–C(11)	1.82 (2)	Os(2)–Os(3)	2.752 (2)
Os(1)–C(12)	1.89 (2)	Os(2)–H	1.6 (2)
Os(1)–C(1)	2.19 (2)	Os(3)–C(33)	1.88 (2)
Os(1)–C(2)	2.28 (2)	Os(3)–C(31)	1.90 (2)
Os(1)–S(1)	2.387 (5)	Os(3)–C(32)	1.91 (2)
Os(1)–Os(3)	2.788 (2)	Os(3)–S(1)	2.361 (5)
Os(1)–Os(2)	2.933 (3)	N–C(3)	1.29 (3)
Os(1)–H	2.0 (2)	N–C(4)	1.42 (3)
Os(2)–C(23)	1.89 (2)	N–C(5)	1.46 (3)
Os(2)–C(22)	1.90 (2)	C(1)–C(2)	1.48 (3)
Os(2)–C(21)	1.90 (2)	C(2)–C(3)	1.27 (3)
Os(2)–S(1)	2.392 (5)	O–C (av)	1.14 (2)
		Os(1)–C(3)	2.82 (2)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

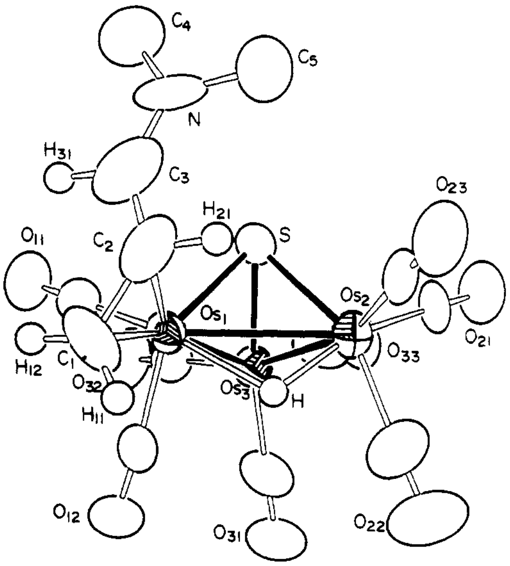


Figure 4. ORTEP diagram of $Os_3(CO)_8[\eta^2\text{-}H_2CC(H)C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)$ (**6**) showing 50% probability thermal ellipsoids. Hydrogen atoms on the ligand are shown in idealized positions.

Table XIII. Intramolecular Bond Angles for 6[a]

C(11)–Os(1)–C(1)	96.5 (7)	S(1)–Os(2)–Os(3)	54.1 (1)
C(11)–Os(1)–C(2)	102.7 (8)	S(1)–Os(2)–Os(1)	52.1 (1)
C(11)–Os(1)–S(1)	93.6 (6)	Os(3)–Os(2)–Os(1)	58.64 (5)
C(11)–Os(1)–Os(3)	93.7 (5)	C(33)–Os(3)–S(1)	101.7 (6)
C(11)–Os(1)–Os(2)	143.5 (5)	C(33)–Os(3)–Os(2)	99.5 (6)
C(12)–Os(1)–C(1)	87.7 (8)	C(33)–Os(3)–Os(1)	155.6 (6)
C(12)–Os(1)–C(2)	125.1 (9)	C(31)–Os(3)–S(1)	151.0 (6)
C(12)–Os(1)–S(1)	133.3 (6)	C(31)–Os(3)–Os(2)	98.1 (7)
C(12)–Os(1)–Os(3)	79.8 (6)	C(31)–Os(3)–Os(1)	106.5 (6)
C(12)–Os(1)–Os(2)	102.9 (6)	C(32)–Os(3)–S(1)	105.3 (6)
C(1)–Os(1)–C(2)	38.7 (7)	C(32)–Os(3)–Os(2)	157.4 (5)
C(1)–Os(1)–S(1)	137.4 (5)	C(32)–Os(3)–Os(1)	96.1 (5)
C(1)–Os(1)–Os(3)	164.1 (6)	S(1)–Os(3)–Os(2)	55.2 (1)
C(1)–Os(1)–Os(2)	117.0 (5)	S(1)–Os(3)–Os(1)	54.5 (1)
C(2)–Os(1)–S(1)	98.7 (6)	Os(2)–Os(3)–Os(1)	63.92 (5)
C(2)–Os(1)–Os(3)	149.0 (6)	Os(3)–S(1)–Os(1)	71.9 (1)
C(2)–Os(1)–Os(2)	95.8 (6)	Os(3)–S(1)–Os(2)	70.8 (1)
S(1)–Os(1)–Os(3)	53.6 (1)	Os(1)–S(1)–Os(2)	75.7 (1)
S(1)–Os(1)–Os(2)	52.2 (1)	C(3)–N–C(4)	115 (2)
Os(3)–Os(1)–Os(2)	57.43 (5)	C(3)–N–C(5)	126 (2)
C(23)–Os(2)–S(1)	106.5 (6)	C(4)–N–S(5)	118 (2)
C(23)–Os(2)–Os(3)	159.0 (5)	C(2)–C(1)–Os(1)	74 (1)
C(23)–Os(2)–Os(1)	104.3 (5)	C(3)–C(2)–C(1)	131 (2)
C(22)–Os(2)–S(1)	150.3 (7)	C(3)–C(2)–Os(1)	104 (2)
C(22)–Os(2)–Os(3)	96.7 (7)	C(1)–C(2)–Os(1)	67 (1)
C(22)–Os(2)–Os(1)	111.1 (7)	C(2)–C(3)–N	133 (3)
C(21)–Os(2)–S(1)	94.5 (6)	Os(1)–H–Os(2)	109 (5)
C(21)–Os(2)–Os(3)	91.6 (6)	O–C–Os (av)	176 (2)
C(21)–Os(2)–Os(1)	143.6 (6)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

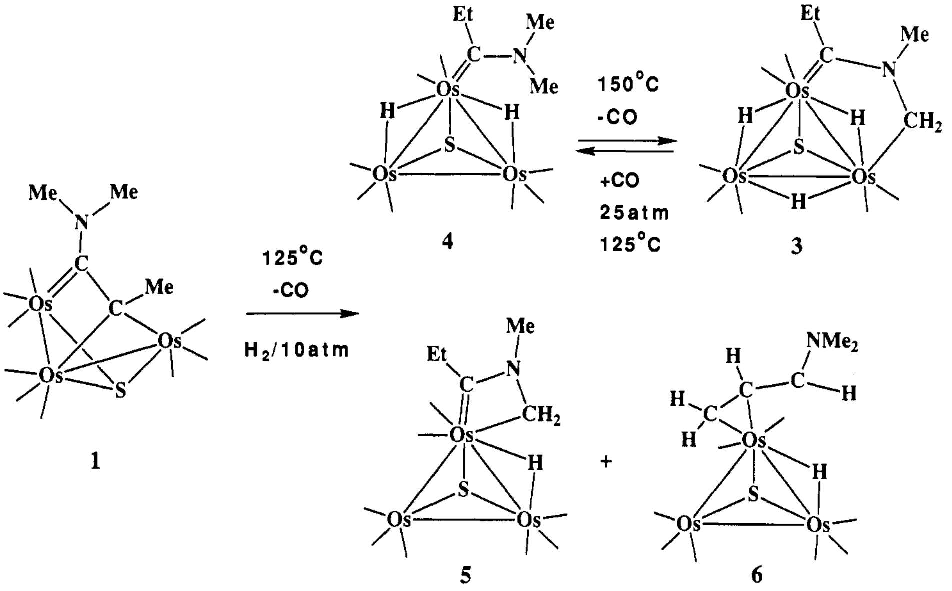
in 3 was a bridge. The osmium–carbon bond distance to the carbene center, C(2), is 2.05 (1) Å and is similar to that found in 3 and 4 and significantly shorter than the Os–C distance to the methylene group C(5) (2.16 (1) Å). The C(2)–N distance of 1.31 (1) Å is also shorter than the C(5)–N distance of 1.46 (1) Å.

An ORTEP drawing of the molecular structure of 6 is given by Figure 4. Final atomic positional parameters are listed in Table XI. Selected interatomic distances and angles are listed in Tables XII and XIII. The molecule consists of a sulfur-bridged triangular cluster of three osmium atoms. There is one bridging hydride ligand (δ = −22.43 ppm), which was located and refined crystallographically. It bridges the elongated Os(1)–Os(2) bond (2.933 (3) Å). The most interesting ligand is the group $H_2CC(H)C(H)NMe_2$, which can be described as a (dimethylamino)allyl ligand. It is π-bonded to Os(1), but unlike normal η^3-allyl ligands[16] this ligand is coordinated to the metal atom by only two of the allyl carbon atoms (Os(1)–C(1) = 2.19 (2) Å and Os(1)–C(2) = 2.28). The Os(1)···C(3) distance of 2.82 (2) Å is clearly nonbonding. As is commonly found for allyl ligands, the hydrogen resonances appear as broad singlets in the ^1H NMR spectrum due to long-range H–H couplings, except for the low-field resonance at +6.59 ppm, which is a doublet. This resonance is probably from the hydrogen atom H(31) on the NMe_2-substituted carbon atom. The C(3)–N distance (1.29 (3) Å) is indicative of C–N multiple bonding that evidently is obtained by donation of the lone pair of electrons on the nitrogen atom to C(3). In accord with this, the nitrogen atom exhibits a planar geometry. The observation of separate resonances for the two *N*-methyl groups indicates the existence of a substantial barrier to rotation about the C(3)–N bond. It is believed that the strong lone-pair interaction from the nitrogen atom to C(3) is responsible for the substantial weakening and cleavage of the anticipated Os–C(3) bond. Another example of an

---

[16] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

Scheme I



η^2-aminoallyl ligand was observed in the complex Fe$(CO)_3$(Ph)[η^2-Ph(H)CC(H)C(H)N(Et)(2,4-$C_6H_3Me_2$)].[17]

Discussion

In previous studies we demonstrated that the ynamine ligand in compound 1 contained a substantial amount of carbene character at the amine-substituted carbon atom. We chose to describe the ligand as an (α,α-dimetallioethyl)(dimethylamino)carbene ligand in order to emphasize this feature.[6] In this study we have investigated the reaction of 1 with hydrogen. The results are summarized in Scheme I. The principal product is the carbene complex 4, formed by the addition of 2 equiv of H_2 to 1. Two of the hydrogen atoms were added to the methyl-substituted carbon atom. The other two hydrogen atoms became bridging hydride ligands. Presumably, all hydrogen addition proceeded by way of metal activation steps and was accompanied by a sequential transfer of two hydrogen atoms to the methyl-substituted carbon atom. From this study we have not been able to obtain much information concerning the mechanism of this unusual hydrogenation reaction. Efforts to obtain minor products have led to the characterization of compounds 3, 5, and 6. Unfortunately, these interesting products have not revealed much information concerning the mechanism of the hydrogenation. Compound 4 is readily converted to 3 by decarbonylation, and 3 is converted back to 4 by CO addition, but the forcing conditions of the latter transformation suggest that 3 is not an intermediate en route to 4 in the original reaction. Compounds 5 and 6 were isolated in such low yields that it was not possible to establish their importance or relationship to the others.

Unlike this study, our investigation of the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $MeCNMe_2$[18] produced a clean sequence of products that showed in great detail the nature of the hydrogenation and conversion of the ynamine into aminocarbene and related ligands. It is believed that processes similar to those are also operative in the reaction of 1 with H_2.

The principal result of this study is the establishment of a reaction that leads to the formation of aminocarbene ligands by a novel 1,1-addition of hydrogen to an ynamine ligand. If the carbene ligand could be removed from the cluster in a constructive fashion, one could envisage from the formation of another aminocarbene ligand by the addition and hydrogenation of a second ynamine molecule, etc. This could serve as a basis for a part of a catalytic process. The facile metalation of the *N*-methyl groups as observed in 3 and 5 could provide new routes to the elaboration of the aminocarbene ligands. This process appears to be intrinsically binuclear in nature and may be a characteristic feature of the chemistry of heteroatom-substituted carbene ligands in cluster complexes.[8]

Acknowledgment. These studies were supported by the Office of Basic Energy Science of the U.S. Department of Energy (Grant No. DEFG84ER13296).

Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters of the hydrogen atoms for all four crystal structure analyses (12 pages); tables of structure factor amplitudes (60 pages). Ordering information is given on any current masthead page.

---

[17] Yin, J.; Chen, J.; Xu, W.; Xu, X.; Tang, Y. *Acta Chim. Sin. (Engl. Ed.)* 1988, *4*, 279.

[18] Adams, R. D.; Chen, G.; Tanner, J. T. *Organometallics*, following paper in this issue.