Organometallics 1990, 9, 251-260

Cluster Complexes Containing Ynamine Ligands. 1. Synthesis and Structural Characterizations of the Complexes $Os_4(CO)_{11}(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, $Os_4(CO)_{11}[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)CMe](\mu_3\text{-}S)$, $Os_4(CO)_{11}[\mu\text{-}C(NMe_2)C(Me)C(Me)C(NMe_2)](\mu_3\text{-}S)$, $Os_4(CO)_9(\mu\text{-}MeC_2NMe_2)[\mu\text{-}C(Me)C(NMe_2)C(Me)C(NMe_2)]\text{-}(\mu_3\text{-}S)$, and $Os_3(CO)_7(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$

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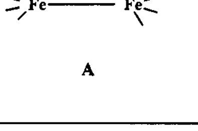
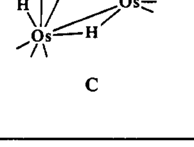
The reaction of $Os_4(CO)_{12}(\mu_3\text{-}S)$ (1) with MeC_2NMe_2 yielded the complexes $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (2), $Os_4(CO)_{11}(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (3), $Os_4(CO)_{11}[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)CMe](\mu_3\text{-}S)$ (4), $Os_4(CO)_{11}[\mu\text{-}C(NMe_2)C(Me)C(Me)C(NMe_2)](\mu_3\text{-}S)$ (5), $Os_4(CO)_9(\mu\text{-}MeC_2NMe_2)[\mu\text{-}C(Me)C(NMe_2)C(Me)C(NMe_2)](\mu_3\text{-}S)$ (6), and $Os_3(CO)_7(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (7), all in low yields. Compounds 3–7 are new and have been characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. Compound 3 contains a chain of four osmium atoms with two bridging ynamine ligands and a bridging sulfido ligand. Both ynamine ligands contain strong π-bonding interactions between the NMe_2 groups and the neighboring carbon atom in the alkynyl groups. These interactions alter the metal–carbon bonding, and the ynamine ligands adopt structures that resemble aminocarbene ligands. Similar structures were found for the ynamine ligands in 7. Compounds 4–6 contain spiked triangular clusters of four osmium atoms with a triply bridging sulfido ligand on the triangular grouping. Each of these compounds also contains a metallacyclopentadiene group formed by the coupling of two ynamine ligands. In each compound, the two ynamine ligands have been coupled in a different way. In 4, they were coupled tail to tail. In 5 they were coupled head to head, and in 6 they were coupled head to tail. There is structural evidence for significant, albeit weaker, π-bonding interactions between the amino groups and the adjacent carbon atoms in these complexes. This seems to produce a weakening of the corresponding metal–carbon bonding. Crystal Data: for 3, triclinic, $P\bar{1}$, $a = 9.324$ (2) Å, $b = 22.452$ (6) Å, $c = 8.259$ (3) Å, $\alpha = 98.87$ (2)°, $\beta = 105.60$ (2)°, $\gamma = 81.81$ (2)°, $Z = 2$, $R = 0.029$; for 4, orthorhombic, $Pna2_1$, $a = 15.413$ (2) Å, $b = 12.109$ (2) Å, $c = 15.104$ (2) Å, $Z = 4$, $R = 0.033$; for 5, monoclinic, $C2/c$, $a = 34.291$ (6) Å, $b = 10.101$ (2) Å, $c = 17.524$ (2) Å, $\beta = 96.14$ (1)°, $Z = 8$, $R = 0.034$; for 6, triclinic, $P\bar{1}$, $a = 10.474$ (4) Å, $b = 17.659$ (5) Å, $c = 8.841$ (3) Å, $\alpha = 94.73$ (2)°, $\beta = 107.33$ (3)°, $\gamma = 97.91$ (3)°, $Z = 2$, $R = 0.025$; for 7, monoclinic, $P2_1/n$, $a = 10.281$ (1) Å, $b = 14.956$ (2) Å, $c = 15.133$ (2) Å, $\beta = 94.38$ (1)°, $Z = 4$, $R = 0.032$.

Introduction

Ynamines, $R_2NC{\equiv}CNR_2$ and $RC{\equiv}CNR_2$, were first prepared and isolated as stable molecules in the late 1950s.[1] Although these molecules have a potential for novel bifunctional coordinative properties, investigations of their coordination chemistry have been very limited. King et al. reported one of the first investigations of the reactions of ynamines with metal carbonyl complexes. They prepared a variety of new complexes, but the absence of structural characterizations left open the question of the subtleties in the ynamine coordination.[2] The first structural characterization of an ynamine ligand was reported by Cabrera et al. for the complex $Fe_2(CO)_7(\mu\text{-}MeC_2NEt_2)$ (A).[3] The ynamine ligand in A was found to exhibit a novel bridging coordination with an uncoordinated and planar nitrogen atom. This structure prompted the formulation of the ynamine ligand as a combination of a terminal carbene grouping and a bridging carbene grouping. A bridging MeC_2NEt_2 coordinated similarly to that in A was recently observed in the complex $FeRu(CO)_5(i\text{-}Pr\text{-}DAB)$ (B; DAB = diazabutadiene).[4]



A



C

We have recently obtained the ynamine ligand complex $Os_3(CO)_9(\mu_3\text{-}HC_2NEt_2)(\mu\text{-}H)_2$ (C) and have chosen to describe it as a (dimetalliomethyl)(diethylamino)carbene ligand on the basis of its unusual coordination and the similarity of the nitrogen-substituted carbon atom to that of a carbene ligand.[5] Compound C has also been made by the addition of $N(H)Et_2$ to $Os_3(CO)_9(C_2H)(\mu\text{-}H)$.[6]

From the reaction of $Os_3(CO)_{10}(NCMe)_2$ and $Me_2C_2NMe_2$, we have obtained the product $Os_3(CO)_{10}(\mu\text{-}MeC_2NMe_2)$ (D), which contains an edge-bridging ynamine ligand similar to that in A.[7] When heated, D loses CO and is transformed to the new complex $Os_3(CO)_9(\mu_3\text{-}H_2CC_2NMe_2)(\mu\text{-}H)$ (E), in which the ynamine ligand has adopted a structure similar to that in C, but it has also

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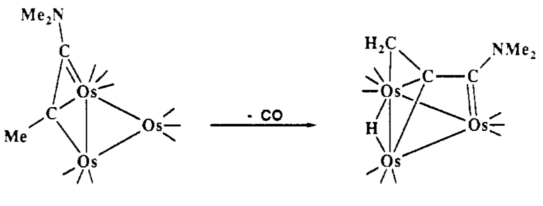
Table I. Crystallographic Data for the Structural Analyses of Compounds 3–7

	3	4	5	6	7
formula	$Os_4SO_{11}C_{21}N_2H_{18}$	$Os_4SO_{11}N_2C_{21}H_{18}$	$Os_4SN_2C_{21}O_{11}H_{18}$	$Os_4SN_3O_9C_{24}H_{27}$	$Os_3SN_2O_7C_{17}H_{18}$
fw	1267.24	1267.24	1267.24	1294.35	965.00
cryst syst	triclinic	orthorhombic	monoclinic	triclinic	monoclinic
lattice params					
a, Å	9.324 (2)	15.413 (2)	34.291 (6)	10.474 (4)	10.281 (1)
b, Å	22.452 (6)	12.109 (2)	10.101 (2)	17.659 (5)	14.956 (2)
c, Å	8.259 (3)	15.104 (2)	17.524 (2)	8.841 (3)	15.133 (2)
α, deg	98.87 (2)			94.73 (2)	
β, deg	105.60 (2)		96.14 (1)	107.33 (3)	94.38 (1)
γ, deg	81.91 (2)			97.91 (3)	
υ, Å^3	1363 (2)	2819 (1)	6035 (2)	1533 (2)	2320 (1)
space group	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Z	2	4	8	2	4
D_{calc}, g/cm^3	2.57	2.99	2.79	2.80	2.76
F_{000}	1132	2264	4528	1168	1736
μ(Mo Kα), cm^{-1}	156.07	181.18	169.26	166.63	165.32
temp, °C	23	23	23	23	23
$2\theta_{max}$, deg	46	48	48	46	46
no. of observns ($I > 3\sigma(I)$)	3822	1867	3508	3678	2424
no. of variables	352	246	352	370	271
residuals: R; R_w	0.029; 0.043	0.033; 0.033	0.034; 0.040	0.025; 0.028	0.032; 0.033
goodness of fit indicator	2.33	1.45	1.68	1.61	1.55
max shift in final cycle	0.00	0.11	0.04	0.03	0.02
largest peak in final diff map, e/Å^3	1.78	1.01	2.08	0.78	1.66
abs cor; max/min	analytical; 0.49/0.09	analytical; 0.09/0.03	analytical; 0.62/0.045	empirical; 1.00/0.34	empirical; 1.00/0.48

undergone an activation of one of the CH bonds of the *C*-methyl group (eq 1).



D E

(1)

In this report, we describe the nature of the reaction of MeC_2NMe_2 with the sulfidoosmium carbonyl cluster complex $Os_4(CO)_{12}(\mu_3\text{-}S)$ (1). All except one of the products were formed by multiple additions of ynamine. Coupling of the ynamine ligands by the formation of carbon–carbon bonds to produce metallacyclic groupings was a common occurrence.

Experimental Section

General Considerations. All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were stored over 4-Å molecular sieves. Trimethylamine *N*-oxide dihydrate was purchased from Aldrich Chemical Co. and was sublimed prior to use. MeC_2NMe_2 was prepared by a published method.[8] $Os_4(CO)_{12}(\mu_3\text{-}S)$ (1) was prepared as previously reported.[9]

All chromatographic separations were performed in air on TLC plates (0.25-mm Whatman silica gel 60A). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^{1}H NMR spectra were taken at 300 MHz on a Bruker AM-300 spectrometer, at 500 MHz on a Bruker AM-500 spectrometer, or at 80 MHz on a IBM NR-80 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of $Os_4(CO)_{12}(\mu_3\text{-}S)$ (1) with MeC_2NMe_2. A 33.2-mg (0.0294-mmol) amount of compound 1 and 26 μL of MeC_2NMe_2 was added to 50 mL of *n*-heptane, and the solution was refluxed for 2.5 h. The solvent was removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with a 6/4 hexane/CH_2Cl_2 solvent mixture yielded the following, in order of elution: 0.2 mg of $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (2), 1%; 1.1 mg of $Os_4(CO)_{11}(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (3), 3%; 0.8 mg of $Os_4(CO)_{11}[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)CMe](\mu_3\text{-}S)$ (4), 2%, as a yellow band; 3.8 mg of $Os_4(CO)_{11}[\mu\text{-}C(NMe_2)C(Me)C(Me)C(NMe_2)](\mu_3\text{-}S)$ (5), 10%, as a yellow band; 1.4 mg of $Os_4(CO)_9(\mu\text{-}MeC_2NMe_2)[\mu\text{-}C(Me)C(NMe_2)C(Me)C(NMe_2)](\mu_3\text{-}S)$ (6), 4%, as a yellow band; 1.4 mg of $Os_3(CO)_7(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (7), 5%, as a yellow band. Spectral and analytical data for 3: IR (ν(CO), cm^{-1}, in hexane) 2077 (m), 2060 (vs), 2036 (s), 2004 (vs), 1994 (m, sh), 1990 (s), 1983 (m, sh), 1969 (m), 1953 (w), 1919 (vw); ^{1}H NMR (δ, in $CDCl_3$) 3.55 (s, 3 H), 3.47 (s, 3 H), 3.38 (s, 3 H), 3.18 (s, 3 H), 2.74 (s, 3 H), 2.42 (s, 3 H). Anal. Calcd for $Os_4SO_{11}N_2C_{21}H_{18}$: C, 19.90; H, 1.43; N, 2.21. Found: C, 19.29; H, 1.19; N, 1.83. Spectral and analytical data for 4: IR (ν(CO), cm^{-1}, in hexane) 2088 (m), 2072 (vs), 2061 (w), 2041 (vs), 2029 (w), 2004 (vs), 1978 (m), 1967 (m), 1936 (vw), 1896 (vw); ^{1}H NMR (δ, in $CDCl_3$) 2.99 (s, 12 H), 2.50 (s, 6 H). Anal. Calcd for $Os_4SO_{11}N_2C_{21}H_{18}$: C, 19.90; H, 1.43; N, 2.21. Found: C, 20.49; H, 1.35; N, 1.96. Spectral and analytical data for 5: IR (ν(CO), cm^{-1}, in hexane) 2080 (m), 2061 (s), 2041 (m), 2003 (vs), 1970 (m), 1963 (m), 1919 (w), 1870 (w); ^{1}H NMR (δ, in $CDCl_3$) 3.63 (s, 6 H), 3.54 (s, 6 H), 1.98 (s, 3 H), 1.76 (s, 3 H). Anal. Calcd for $Os_4SO_{11}N_2C_{21}H_{18}$: C, 19.90; H, 1.43; N, 2.21. Found: C, 18.11; H, 1.43; N, 1.97. Spectral and analytical data for 6: IR (ν(CO), cm^{-1}, in hexane) 2075 (s), 2015 (vs), 2000 (vs), 1993 (m), 1982 (s), 1949 (w), 1937 (w), 1886 (vw); ^{1}H NMR (δ, in toluene-d_8) 3.22 (s, 3 H), 2.74 (s, 6 H), 2.70 (s, 3 H), 2.49 (s, 6 H), 2.42 (s, 6 H), 1.55 (s, 3 H). Anal. Calcd for $Os_4SO_9N_3C_{24}H_{27}$: C, 22.27; H, 2.10; N, 3.25. Found: C, 22.44; H, 2.01; N, 3.24. Spectral and analytical data for 7: IR (ν(CO), cm^{-1}, in hexane) 2065 (m), 1999 (s), 1989 (m), 1979 (vs), 1937 (m), 1922 (w); ^{1}H NMR (δ, in $CDCl_3$) 3.52 (s, 6 H), 3.46 (s, 3 H), 3.45 (s, 3 H), 2.86 (s, 3 H), 2.58 (s, 3 H). Anal. Calcd for $Os_3SO_7N_2C_{17}H_{18}$: C, 21.16; H, 1.88; N, 2.90. Found: C, 21.30; H, 1.67; N, 2.96.

Alternative Preparation of $Os_4(CO)_{11}(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (3). A 26.6-mg (0.024-mmol) amount of compound 1 was dissolved in 15 mL of CH_2Cl_2. A 15-mL CH_2Cl_2 solution of Me_3NO (3.6 mg, 0.080 mmol) was added from a dropping funnel over a period of approximately 10 min under a continuous purge with nitrogen. The reaction solution was then stirred at room temperature for an additional 15 min while the nitrogen purge was continued. The solvent was removed in vacuo. To the flask containing the residue was added 30 mL of hexane and 20 μL of MeC_2NMe_2. This mixture was refluxed for 1 h. The

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(9) Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* 1983, *2*, 1301.

hexane was removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with a 9/1 hexane/CH_2Cl_2 solvent mixture yielded 4.8 mg of **3** (16%) as a yellow band.

Crystallographic Analyses. Crystals of **3**–**7** suitable for diffraction analyses were grown from solutions in hexane/CH_2Cl_2 solvent mixtures at 5 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined from 25 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 an additional one-fourth 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.[10a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[10b] Full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compound **3** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atom positions 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.

Compound **4** crystallized in the orthorhombic crystal system with four molecular units in the unit cell. The systematic absences observed during data collection were consistent with either of the space groups *Pnma* and $Pna2_1$. The former space group would require a crystallographically imposed symmetry plane, and a trial solution in this space group did not permit a satisfactory refinement of the two NMe_2 groups. However, the space group $Pna2_1$ yielded a solution by direct methods and a satisfactory refinement of all non-hydrogen atoms. This space group was thus assumed to be the correct one and is the one reported here. Hydrogen atom positions were calculated by assuming idealized geometries and employing observed atoms whenever possible. The contributions of the hydrogen atoms were added to the structure factor calculations, but the positions were not refined.

Compound **5** crystallized in the monoclinic crystal system with eight molecular units in the unit cell. Systematic absences were consistent with either of the space groups *C*2/*c* and *Cc*. The centrosymmetric space group *C*2/*c* was selected and confirmed by the successful solution and refinement of the structure. Hydrogen atom positions were calculated by assuming idealized geometries and employing observed atoms whenever possible. The scattering contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound **6** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Hydrogen atom positions were calculated by assuming idealized geometries. The scattering contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound **7** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely from the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated by assuming idealized geometries. Their scattering contributions were added to the structure factor calculations, but their positions were not refined. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement. See the supplementary material for the tables of structure factor amplitudes, atomic positional parameters for hydrogen, and anisotropic thermal parameters for all of the structural analyses.

Table II. Positional Parameters and *B*(eq) Values for $Os_4(CO)_{11}(S)(MeC_2NMe_2)_2$ (3)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.33529 (07)	0.14538 (03)	0.86253 (08)	3.74 (3)
Os(2)	0.31341 (06)	0.25104 (03)	0.69822 (07)	3.06 (2)
Os(3)	0.41403 (06)	0.36557 (03)	0.77542 (07)	2.93 (2)
Os(4)	0.13960 (05)	0.41119 (03)	0.84705 (07)	2.77 (2)
S	0.2902 (04)	0.32127 (17)	0.9402 (04)	3.1 (1)
O(11)	0.1545 (19)	0.0505 (07)	0.619 (02)	9 (1)
O(12)	0.4720 (17)	0.0611 (07)	1.1263 (19)	8.3 (9)
O(13)	0.1050 (15)	0.2063 (07)	1.0581 (18)	7.3 (8)
O(21)	0.4091 (16)	0.1810 (07)	0.3946 (17)	7.6 (8)
O(22)	0.0053 (13)	0.2095 (06)	0.5972 (18)	6.9 (7)
O(31)	0.3822 (14)	0.4700 (06)	0.5685 (17)	6.5 (7)
O(32)	0.6739 (13)	0.2921 (06)	0.656 (02)	7.6 (7)
O(33)	0.6094 (12)	0.4287 (07)	1.0999 (16)	6.7 (7)
O(41)	0.2896 (12)	0.4812 (06)	1.1873 (15)	5.7 (6)
O(42)	−0.1303 (12)	0.3866 (06)	0.9543 (15)	6.2 (7)
O(43)	0.0281 (13)	0.5300 (05)	0.6934 (15)	5.3 (6)
N(1)	−0.0394 (13)	0.3567 (06)	0.4963 (14)	3.8 (6)
N(2)	0.6260 (15)	0.1199 (07)	0.7187 (19)	5.2 (7)
C(1)	0.2295 (15)	0.3286 (07)	0.5665 (17)	3.4 (6)
C(2)	0.0904 (14)	0.3589 (06)	0.6076 (17)	3.1 (6)
C(3)	0.4980 (15)	0.2036 (07)	0.8845 (19)	3.8 (7)
C(4)	0.5214 (15)	0.1498 (07)	0.789 (02)	4.2 (7)
C(5)	−0.0671 (18)	0.3121 (08)	0.343 (02)	5.2 (8)
C(6)	−0.1737 (16)	0.3958 (08)	0.518 (02)	4.7 (8)
C(7)	0.2519 (17)	0.3285 (08)	0.3872 (17)	4.2 (7)
C(8)	0.6080 (17)	0.2345 (08)	1.026 (02)	5.4 (8)
C(9)	0.753 (02)	0.1484 (10)	0.703 (03)	7 (1)
C(10)	0.607 (02)	0.0602 (09)	0.621 (03)	7 (1)
C(11)	0.219 (02)	0.0856 (09)	0.716 (02)	5.5 (9)
C(12)	0.4199 (20)	0.0944 (09)	1.024 (02)	6 (1)
C(13)	0.1919 (19)	0.1833 (08)	0.986 (02)	4.6 (8)
C(21)	0.3708 (18)	0.2065 (08)	0.513 (02)	4.7 (8)
C(22)	0.1281 (18)	0.2211 (08)	0.640 (02)	4.5 (8)
C(31)	0.3957 (17)	0.4316 (09)	0.645 (02)	4.4 (8)
C(32)	0.5769 (18)	0.3178 (08)	0.702 (02)	5.2 (8)
C(33)	0.5392 (15)	0.4060 (08)	0.979 (02)	4.7 (8)
C(41)	0.2314 (16)	0.4555 (07)	1.0646 (19)	3.6 (7)
C(42)	−0.0327 (15)	0.3978 (07)	0.9085 (20)	4.1 (7)
C(43)	0.0674 (15)	0.4855 (08)	0.7520 (18)	3.5 (7)

Results and Discussion

Six products, $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**2**), $Os_4(CO)_{11}(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**3**), $Os_4(CO)_{11}[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)CMe](\mu_3\text{-}S)$ (**4**), $Os_4(CO)_{11}[\mu\text{-}C(NMe_2)C(Me)C(Me)C(NMe_2)](\mu_3\text{-}S)$ (**5**), $Os_4(CO)_9(\mu\text{-}MeC_2NMe_2)]\mu\text{-}C(Me)C(NMe_2)C(Me)C(NMe_2)](\mu_3\text{-}S)$ (**6**), and $Os_3(CO)_7(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$ (**7**) were isolated from the reaction of $Os_4(CO)_{12}(\mu_3\text{-}S)$ with MeC_2NMe_2. All were isolated in relatively low yields of 1%, 3%, 2%, 10%, 4%, and 5%, respectively. Compound **2** was prepared in a very good yield from the reaction of $Os_3(CO)_{10}(\mu_3\text{-}S)$ and MeC_2NMe_2 and has been structurally characterized.[11] Compounds **3**–**7** are new, and each has been characterized by IR and ^1H NMR spectroscopy and a single-crystal X-ray diffraction analysis. These results are reported here. Compound **3** was obtained in a higher yield, 16%, by the reaction of MeC_2NMe_2 with $Os_4(CO)_{12}(\mu_3\text{-}S)$ that had been pretreated with Me_3NO.

An ORTEP drawing of the molecular structure of **3** is shown in Figure 1. Final atomic positional parameters

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

(11) Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, J. *Organometallics*, in press.

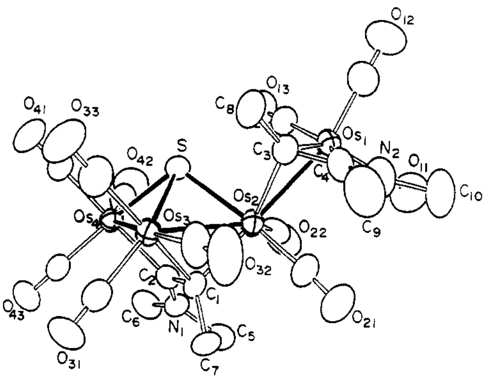


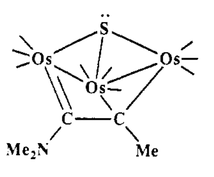
Figure 1. ORTEP drawing of 3 showing 50% probability thermal ellipsoids.

Table III. Intramolecular Distances (Å) for 3[a]

Os(1)–C(12)	1.83 (2)	Os(3)–C(1)	2.23 (1)
Os(1)–C(11)	1.91 (2)	Os(3)–S	2.400 (3)
Os(1)–C(13)	1.92 (2)	Os(3)–Os(4)	2.799 (1)
Os(1)–C(4)	2.01 (2)	Os(4)–C(42)	1.88 (1)
Os(1)–C(3)	2.09 (1)	Os(4)–C(43)	1.91 (2)
Os(1)–Os(2)	2.867 (1)	Os(4)–C(41)	1.95 (2)
Os(2)–C(21)	1.86 (2)	Os(4)–C(2)	2.11 (1)
Os(2)–C(22)	1.86 (2)	Os(4)–S	2.396 (4)
Os(2)–C(1)	2.14 (1)	N(1)–C(2)	1.31 (2)
Os(2)–C(3)	2.24 (1)	N(2)–C(4)	1.32 (2)
Os(2)–S	2.386 (4)	C(1)–C(2)	1.47 (2)
Os(2)–Os(3)	2.784 (1)	C(3)–C(4)	1.36 (2)
Os(3)–C(32)	1.92 (2)	O–C (av)	1.14 (2)
Os(3)–C(31)	1.92 (2)	Os(2)···Os(4)	3.890 (1)
Os(3)–C(33)	1.94 (2)		

[a] Estimated standard deviations in the least significant figure are given in parentheses in this and the following tables.

are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. The cluster consists of a chain of four osmium atoms. Three adjacent osmium atoms are bridged by a triply bridging sulfido ligand and a triply bridging MeC_2NMe_2 ligand. This portion of the complex is structurally very similar to that of 2. The metal–metal bond distances, metal–sulfur bond distances, and metal–carbon distances to the triply bridging ynamine ligand in 3 are not significantly different from those in 2.[11] The C(1)–C(2) distance in 3 of 1.47 (2) Å is slightly longer than that in 2, 1.42 (1) Å, while the C(2)–N distance of 1.31 (2) Å is slightly shorter than that in 2, 1.34 (1) Å. Nitrogen atom N(2) has a planar geometry as a result of the strong donation of its lone pair of electrons to C(2). This results in a hindered rotation about the C–N bond and the observation of two methyl resonances for the *N*-methyl groups in the ^1H NMR spectrum (see below). Accordingly, we feel that the carbon atom C(1) contains some carbene-like character and could be formulated as a (1,1-dimetallioethyl)(dimethylamino)carbene ligand, as was also proposed for the ynamine ligand in 2. The structure of 3 is completed by the presence of an $Os(CO)_3$ group that is bonded to Os(2). The Os(1)–Os(2) bond length of 2.867 (1) Å is not unusual and is very similar to the Os–Os bond distances in $Os_3(CO)_{12}$, 2.877 (3) Å.[12] The Os(1)–Os(2) bond contains a second bridging ynamine ligand that is coordinated very similarly to those in compounds A,[3] B,[4] and D.[7] Carbon C(3) is bonded to both Os(1) and Os(2), but C(4) is bonded only to Os(1). The Os(1)–C(4) distance of 2.01 (2) Å is slightly shorter than the corresponding distance to the triply bridging ynamine ligand in 3, Os(4)–C(2) = 2.11 (1) Å, but it is very similar to that of the edge-bridging ynamine ligand in compound D, 2.00 (2) Å.[7] The nitrogen atom N(2) also exhibits a planar geometry due to strong C–N π-bonding interactions that involve the nitrogen lone pair of electrons, C(4)–N(2) = 1.32 (2) Å, and it is very likely that carbon C(4) also contains a significant amount of carbene-like character. There is a hindered rotation about the C(4)–N(2) bond since the ^1H NMR spectrum shows four *N*-methyl resonances, δ 3.55, 3.47, 3.38, and 3.18 ppm, for the two ynamine ligands.



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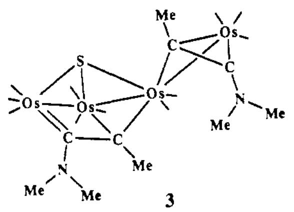

3

Table IV. Intramolecular Bond Angles (deg) for 3

C(12)–Os(1)–C(4)	97.0 (7)	C(1)–Os(3)–Os(4)	71.2 (4)
C(12)–Os(1)–C(3)	104.8 (7)	Os(2)–Os(3)–Os(4)	88.34 (3)
C(11)–Os(1)–C(4)	110.4 (7)	C(42)–Os(4)–C(2)	96.1 (6)
C(11)–Os(1)–C(3)	145.0 (7)	C(43)–Os(4)–C(2)	92.6 (6)
C(13)–Os(1)–C(4)	148.8 (7)	C(41)–Os(4)–C(2)	167.1 (5)
C(13)–Os(1)–C(3)	110.0 (7)	C(2)–Os(4)–S	84.7 (4)
C(13)–Os(1)–Os(2)	92.0 (5)	C(2)–Os(4)–Os(3)	73.1 (3)
C(4)–Os(1)–C(3)	38.8 (6)	C(2)–N(1)–C(6)	123 (1)
C(4)–Os(1)–Os(2)	68.3 (4)	C(2)–N(1)–C(5)	124 (1)
C(3)–Os(1)–Os(2)	50.9 (4)	C(4)–N(2)–C(10)	122 (1)
C(21)–Os(2)–C(1)	92.6 (7)	C(4)–N(2)–C(9)	123 (2)
C(21)–Os(2)–C(3)	93.0 (6)	C(2)–C(1)–C(7)	120 (1)
C(22)–Os(2)–C(1)	93.3 (6)	C(2)–C(1)–Os(2)	111.4 (9)
C(22)–Os(2)–C(3)	117.0 (6)	C(2)–C(1)–Os(3)	104.9 (9)
C(22)–Os(2)–S	100.3 (5)	C(7)–C(1)–Os(2)	120 (1)
C(1)–Os(2)–C(3)	148.8 (5)	C(7)–C(1)–Os(3)	113.8 (9)
C(1)–Os(2)–S	83.2 (4)	Os(2)–C(1)–Os(3)	79.1 (5)
C(1)–Os(2)–Os(3)	52.0 (3)	N(1)–C(2)–C(1)	121 (1)
C(1)–Os(2)–Os(1)	163.4 (3)	N(1)–C(2)–Os(4)	128 (1)
C(3)–Os(2)–S	84.0 (4)	C(1)–C(2)–Os(4)	110.4 (9)
C(3)–Os(2)–Os(3)	97.8 (4)	C(4)–C(3)–C(8)	128 (1)
C(3)–Os(2)–Os(1)	46.4 (4)	C(4)–C(3)–Os(1)	67.2 (9)
S–Os(2)–Os(3)	54.67 (9)	C(4)–C(3)–Os(2)	100 (1)
S–Os(2)–Os(1)	94.9 (1)	C(8)–C(3)–Os(1)	136 (1)
Os(3)–Os(2)–Os(1)	138.37 (3)	C(8)–C(3)–Os(2)	125 (1)
C(32)–Os(3)–C(1)	97.1 (6)	Os(1)–C(3)–Os(2)	82.7 (5)
C(31)–Os(3)–C(1)	86.5 (6)	N(2)–C(4)–C(3)	139 (2)
C(33)–Os(3)–C(1)	167.5 (5)	N(2)–C(4)–Os(1)	146 (1)
C(1)–Os(3)–S	81.0 (4)	C(3)–C(4)–Os(1)	74 (1)
C(1)–Os(3)–Os(2)	49.0 (4)	O–C–Os (av)	177 (2)

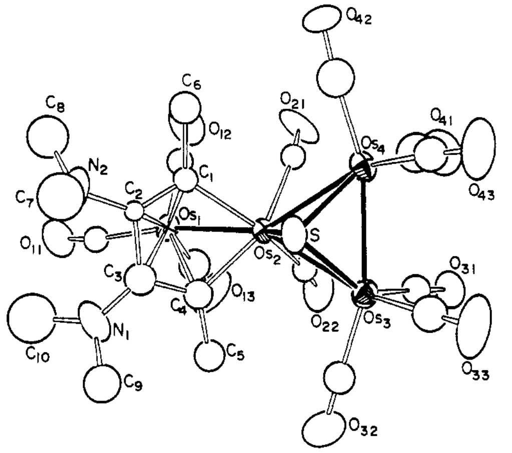

Figure 2. ORTEP drawing of 4 showing 50% probability thermal ellipsoids.

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

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

Table V. Positional Parameters and *B*(eq) Values for $Os_4(CO)_{11}[MeCC(NMe_2)C(NMe_2)CMe](S)$ (4)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.21432 (05)	−0.32346 (07)	0.1475	2.47 (4)
Os(2)	0.30165 (04)	−0.12795 (06)	0.14060 (16)	2.14 (3)
Os(3)	0.37602 (13)	0.05170 (12)	0.04775 (15)	2.85 (7)
Os(4)	0.37348 (12)	0.06021 (12)	0.22903 (15)	2.74 (7)
S	0.4489 (03)	−0.0720 (04)	0.1447 (11)	3.1 (2)
O(11)	0.1572 (12)	−0.5624 (15)	0.137 (03)	6 (1)
O(12)	0.1056 (18)	−0.283 (03)	0.311 (02)	7 (2)
O(13)	0.0726 (16)	−0.256 (03)	0.0214 (20)	6 (2)
O(21)	0.1872 (16)	−0.046 (02)	0.2945 (16)	5 (1)
O(22)	0.1588 (16)	−0.024 (02)	0.0280 (20)	5 (1)
O(31)	0.2377 (19)	0.232 (02)	0.027 (02)	4 (1)
O(32)	0.395 (03)	−0.036 (03)	−0.138 (02)	7 (2)
O(33)	0.521 (02)	0.211 (03)	0.019 (03)	7 (2)
O(41)	0.228 (03)	0.228 (03)	0.240 (03)	8 (2)
O(42)	0.387 (02)	0.000 (03)	0.4352 (18)	5 (1)
O(43)	0.514 (02)	0.232 (03)	0.245 (03)	7 (2)
N(1)	0.382 (02)	−0.441 (02)	0.031 (02)	5 (2)
N(2)	0.399 (02)	−0.455 (02)	0.221 (03)	4 (1)
C(1)	0.3314 (18)	−0.265 (02)	0.225 (02)	2.3 (5)
C(2)	0.3571 (16)	−0.360 (02)	0.1843 (18)	1.4 (5)
C(3)	0.350 (02)	−0.359 (03)	0.084 (02)	3.8 (8)
C(4)	0.311 (02)	−0.258 (03)	0.052 (02)	3.4 (7)
C(5)	0.2896 (20)	−0.246 (02)	−0.0458 (19)	3.8 (6)
C(6)	0.3466 (18)	−0.256 (02)	0.3274 (19)	3.6 (6)
C(7)	0.491 (02)	−0.455 (03)	0.216 (03)	7 (1)
C(8)	0.356 (03)	−0.510 (03)	0.298 (03)	6.3 (9)
C(9)	0.4359 (20)	−0.421 (03)	−0.047 (02)	4.7 (7)
C(10)	0.368 (03)	−0.560 (04)	0.039 (04)	9 (1)
C(11)	0.1803 (13)	−0.4771 (18)	0.133 (03)	2.9 (5)
C(12)	0.1418 (20)	−0.298 (02)	0.250 (02)	3.2 (6)
C(13)	0.121 (03)	−0.284 (03)	0.075 (02)	4.9 (8)
C(21)	0.2402 (18)	−0.063 (02)	0.2478 (18)	2.5 (5)
C(22)	0.2198 (19)	−0.052 (02)	0.0691 (18)	2.6 (6)
C(31)	0.286 (03)	0.158 (03)	0.036 (02)	3.3 (7)
C(32)	0.386 (03)	−0.003 (03)	−0.068 (03)	3.6 (8)
C(33)	0.465 (03)	0.151 (03)	0.030 (03)	3.9 (9)
C(41)	0.285 (04)	0.170 (04)	0.243 (03)	6 (1)
C(42)	0.384 (03)	0.019 (04)	0.354 (03)	5 (1)
C(43)	0.467 (02)	0.164 (03)	0.242 (03)	3.6 (8)

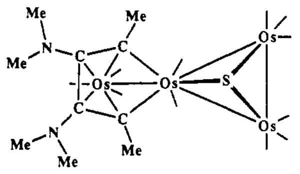
Table VI. Intramolecular Distances (Å) for 4

Os(1)–C(13)	1.87 (4)	Os(3)–S	2.38 (1)
Os(1)–C(12)	1.93 (3)	Os(3)–Os(4)	2.740 (1)
Os(1)–C(11)	1.95 (2)	Os(4)–C(41)	1.91 (6)
Os(1)–C(4)	2.22 (3)	Os(4)–C(43)	1.92 (4)
Os(1)–C(1)	2.26 (3)	Os(4)–C(42)	1.95 (5)
Os(1)–C(2)	2.31 (3)	Os(4)–S	2.35 (1)
Os(1)–C(3)	2.34 (4)	N(1)–C(3)	1.37 (5)
Os(1)–Os(2)	2.726 (1)	N(1)–C(9)	1.46 (5)
Os(2)–C(22)	1.90 (3)	N(1)–C(10)	1.47 (5)
Os(2)–C(21)	2.04 (3)	N(2)–C(7)	1.42 (5)
Os(2)–C(4)	2.07 (3)	N(2)–C(2)	1.43 (4)
Os(2)–C(1)	2.14 (3)	N(2)–C(8)	1.49 (5)
Os(2)–S	2.370 (5)	C(1)–C(2)	1.36 (4)
Os(2)–Os(3)	2.831 (2)	C(1)–C(6)	1.57 (4)
Os(2)–Os(4)	2.864 (2)	C(2)–C(3)	1.51 (4)
Os(3)–C(33)	1.84 (4)	C(3)–C(4)	1.44 (5)
Os(3)–C(32)	1.88 (4)	C(4)–C(5)	1.52 (4)
Os(3)–C(31)	1.90 (4)	O–C (av)	1.14 (5)

Table VII. Intramolecular Bond Angles (deg) for 4

C(13)–Os(1)–C(4)	92 (1)	C(33)–Os(3)–Os(2)	151 (1)
C(13)–Os(1)–C(1)	147 (1)	C(32)–Os(3)–Os(4)	161 (1)
C(13)–Os(1)–C(2)	157 (1)	C(32)–Os(3)–Os(2)	103 (1)
C(13)–Os(1)–C(3)	120 (1)	C(31)–Os(3)–Os(4)	93 (1)
C(13)–Os(1)–Os(2)	98 (1)	C(31)–Os(3)–Os(2)	106 (1)
C(12)–Os(1)–C(4)	148 (1)	Os(4)–Os(3)–Os(2)	61.84 (6)
C(12)–Os(1)–C(1)	90 (1)	C(41)–Os(4)–Os(3)	98 (2)
C(12)–Os(1)–C(2)	113 (1)	C(41)–Os(4)–Os(2)	109 (2)
C(12)–Os(1)–C(3)	151 (1)	C(43)–Os(4)–Os(3)	96 (1)
C(12)–Os(1)–Os(2)	100.3 (9)	C(43)–Os(4)–Os(2)	149 (1)
C(11)–Os(1)–C(4)	117 (1)	C(42)–Os(4)–Os(3)	162 (1)
C(11)–Os(1)–C(1)	125 (1)	C(42)–Os(4)–Os(2)	106 (1)
C(11)–Os(1)–C(2)	95.8 (9)	Os(3)–Os(4)–Os(2)	60.63 (6)
C(11)–Os(1)–C(3)	91 (1)	Os(4)–S–Os(2)	74.7 (2)
C(11)–Os(1)–Os(2)	163.6 (8)	Os(4)–S–Os(3)	70.8 (1)
C(4)–Os(1)–Os(2)	48.2 (9)	Os(2)–S–Os(3)	73.2 (2)
C(1)–Os(1)–Os(2)	49.8 (7)	C(3)–N(1)–C(9)	124 (3)
C(2)–Os(1)–Os(2)	72.9 (6)	C(3)–C(1)–C(10)	128 (4)
C(3)–Os(1)–Os(2)	73 (1)	C(9)–C(1)–C(10)	108 (3)
C(22)–Os(2)–C(4)	93 (1)	C(7)–N(2)–C(2)	115 (3)
C(22)–Os(2)–C(1)	149 (1)	C(7)–N(2)–C(8)	118 (3)
C(22)–Os(2)–Os(1)	96.6 (8)	C(2)–N(2)–C(8)	118 (3)
C(22)–Os(2)–Os(3)	67.3 (9)	Os(2)–C(1)–Os(1)	76 (1)
C(22)–Os(2)–Os(4)	97.8 (8)	C(1)–C(2)–N(2)	130 (3)
C(21)–Os(2)–C(4)	147 (1)	C(1)–C(2)–C(3)	115 (3)
C(21)–Os(2)–C(1)	86 (1)	N(2)–C(2)–C(3)	115 (3)
C(21)–Os(2)–Os(1)	94.4 (8)	N(1)–C(3)–C(4)	124 (3)
C(21)–Os(2)–Os(3)	106.5 (8)	N(1)–C(3)–C(2)	123 (4)
C(21)–Os(2)–Os(4)	60.0 (8)	C(4)–C(3)–C(2)	112 (3)
C(4)–Os(2)–C(1)	77 (1)	C(3)–C(4)–C(5)	120 (3)
Os(1)–Os(2)–Os(3)	152.45 (9)	Os(2)–C(4)–Os(1)	79 (1)
Os(1)–Os(2)–Os(4)	149.78 (9)	O(21)–C(21)–Os(2)	158 (3)
Os(3)–Os(2)–Os(4)	57.53 (3)	O(22)–C(22)–Os(2)	166 (3)
C(33)–Os(3)–Os(4)	98 (1)	O–C–Os (av)	174 (4)

angles are listed in Tables VI and VII. The molecule consists of a spiked triangular cluster of four osmium atoms. The Os_3 triangle contains a triply bridging sulfido ligand. Atom Os(1) is bonded to Os(2) of the triangular group, and the Os(1)–Os(2) bond is bridged by a C(Me)-C(NMe_2)C(NMe_2)C(Me) ligand that was formed by a tail-to-tail coupling of two ynamine molecules. A similarly coordinated C(Me)C(NEt_2)C(NEt_2)C(Me) ligand was found in the complex $Fe_2(CO)_6[\mu\text{-}C(Me)C(NEt_2)C(NEt_2)C(Me)]$ (8) obtained by the tail-to-tail coupling of two ynamine molecules in the reaction of MeC_2NEt_2 with $Fe_3(CO)_{12}$.[13] The structure of 4 is analogous to that of the compound $Os_4(CO)_{11}[\mu\text{-}C(CO_2Me)C(CO_2Me)C(H)CPh](\mu_3\text{-}S)$ (9), which was formed by the addition of PhC_2H to $Os_4(CO)_{11}[\mu_4\text{-}(MeO_2C)C_2(CO_2Me)](\mu_4\text{-}S)$.[14] The metal–metal and metal–sulfur bond distances in 4 are not significantly different from those in 9. The four carbon atoms of the OsC_4 metallacycle are π-bonded to Os(1) as in 9. However, unlike the case for 9, the Os–C bond distances to the amine-substituted carbon atoms are longer than those to the bridging methyl-substituted carbon atoms, 2.31 (3) and 2.34 (4) Å vs 2.22 (3) and 2.26 (3) Å. However, these differences are not large. A similar but larger effect was observed in compound 8. To explain this effect, it was proposed that the bridging carbon atoms contained carbene-like character and C–N π-bonding weakened the Fe–C bonding to the amine-substituted carbon atoms.[13] This explanation may apply to 4 also, but the longer C–N bond distances, C(3)–N(1) = 1.37 (5) Å and



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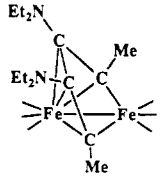

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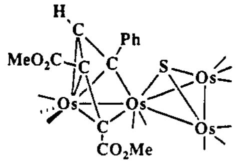

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(13) Daran, J.-C.; Jeannin, Y. *Organometallics* **1984**, *3*, 1158.

(14) Adams, R. D.; Wang, S. W. *Organometallics* **1987**, *6*, 739.

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

atom	x	y	z	B(eq), Å^2
Os(1)	0.08176 (02)	0.13563 (06)	0.52400 (04)	2.96 (3)
Os(2)	0.152783 (19)	0.00360 (05)	0.56275 (04)	2.46 (2)
Os(3)	0.18920 (02)	−0.20725 (06)	0.65224 (04)	3.03 (3)
Os(4)	0.12947 (02)	−0.26285 (06)	0.53948 (04)	3.25 (3)
S	0.12364 (13)	−0.1334 (04)	0.6506 (02)	3.2 (2)
O(11)	0.0264 (05)	0.3684 (14)	0.5084 (09)	7.2 (9)
O(12)	0.0253 (04)	−0.0708 (13)	0.5775 (08)	5.8 (7)
O(13)	0.0612 (05)	0.0312 (13)	0.3609 (08)	6.4 (8)
O(21)	0.1518 (04)	−0.0495 (11)	0.3908 (07)	4.7 (6)
O(22)	0.2417 (04)	0.0187 (10)	0.5732 (08)	4.8 (6)
O(31)	0.2366 (04)	−0.0692 (13)	0.7852 (08)	5.7 (7)
O(32)	0.1792 (04)	−0.4591 (11)	0.7411 (07)	5.7 (7)
O(33)	0.2567 (05)	−0.3287 (14)	0.5778 (09)	7.2 (9)
O(41)	0.0516 (04)	−0.2478 (14)	0.4343 (09)	6.7 (8)
O(42)	0.1758 (05)	−0.3870 (13)	0.4186 (08)	6.3 (8)
O(43)	0.1088 (05)	−0.5249 (12)	0.6083 (09)	8 (1)
N(1)	0.0899 (04)	0.2102 (12)	0.6958 (08)	3.7 (7)
N(2)	0.1420 (04)	0.2733 (12)	0.4330 (08)	3.7 (7)
C(1)	0.1075 (05)	0.1841 (12)	0.6334 (09)	2.9 (7)
C(2)	0.1494 (04)	0.1783 (13)	0.6371 (09)	2.6 (6)
C(3)	0.1635 (05)	0.2218 (13)	0.5636 (09)	2.9 (7)
C(4)	0.1340 (05)	0.2283 (12)	0.5009 (08)	2.3 (6)
C(5)	0.0476 (07)	0.198 (02)	0.6946 (13)	7 (1)
C(6)	0.1069 (06)	0.2678 (18)	0.7676 (10)	5 (1)
C(7)	0.1782 (05)	0.1831 (15)	0.7087 (09)	3.6 (8)
C(8)	0.1995 (05)	0.3066 (14)	0.5699 (10)	3.8 (8)
C(9)	0.1804 (6)	0.2611 (18)	0.4046 (10)	5 (1)
C(10)	0.1135 (07)	0.3126 (20)	0.3758 (12)	6 (1)
C(11)	0.0469 (06)	0.2788 (18)	0.5142 (10)	5 (1)
C(12)	0.0455 (06)	0.0070 (16)	0.5586 (11)	4.1 (9)
C(13)	0.0690 (06)	0.0735 (18)	0.4205 (12)	5 (1)
C(21)	0.1514 (05)	−0.0450 (14)	0.4556 (11)	3.8 (8)
C(22)	0.2082 (05)	−0.0102 (14)	0.5755 (09)	3.2 (7)
C(31)	0.2182 (05)	−0.1176 (16)	0.7353 (10)	3.7 (8)
C(32)	0.1831 (06)	−0.3638 (16)	0.7074 (10)	4.1 (9)
C(33)	0.2321 (06)	−0.2815 (16)	0.6039 (11)	4 (1)
C(41)	0.0798 (6)	−0.2508 (15)	0.4734 (10)	4.0 (9)
C(42)	0.1601 (06)	−0.3413 (16)	0.4639 (12)	5 (1)
C(43)	0.1157 (06)	−0.4260 (17)	0.5777 (13)	5 (1)

C(2)–N(2) = 1.43 (4) Å, indicate that the C–N π-bonding is not nearly as strong as that in **3**. In addition, nitrogen N(2) in **4** is not as rigorously planar as found in other examples and the planes of the NMe_2 groups are twisted out of the plane of the metallacycle. The latter result should cause a weakening of C–N π-bonding. In addition, the ^1H NMR spectrum of **4** shows only one resonance for the NMe_2 groups, δ 2.99 ppm at 25 °C, which indicates that the NMe_2 groups are rapidly rotating about the C–N bonds. This rotation will produce a time-averaged plane of symmetry in the molecule.

An ORTEP drawing of the molecular structure 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. The cluster consists of a spiked triangle of four osmium atoms with a triply bridging sulfido ligand. This arrangement is very similar to that in **4**. The Os–Os bond distances in the triangular portion are similar to those in **4** and **9**, but the distance to the external metal atom Os(1), 2.796 (1) Å, is significantly longer than the corresponding distances in **4**, 2.726 (1) Å, and **9**, 2.7572 (8) Å. This can be attributed to differences in the coordination of the dimetallabutadiene ligands that bridge the Os(1)–Os(2) bonds in these three molecules. The dimetallabutadiene ligand $C(NMe_2)C(Me)C(Me)C(NMe_2)$ in **5** was formed by a head-to-head coupling of two MeC_2NMe_2 ligands, but unlike the case for **4** and **9**, for which the four-carbon chain is π-bonded to Os(1), in **5** it is π-bonded to Os(2). Interestingly, only atoms C(2) and C(3) are strongly π-bonded to Os(2), Os(2)–C(2) = 2.20 (1) Å and Os(2)–C(3) = 2.23 (1) Å. The Os(2)–C(1) and Os(2)–C(4) distances of 2.77 (2) and 2.57 (2) Å, respectively, indicate that there is very little if any bonding between these atoms. The slight lengthening of the Os(1)–Os(2) bond distance may be a consequence of the weakness of these interactions. In contrast, the C–N

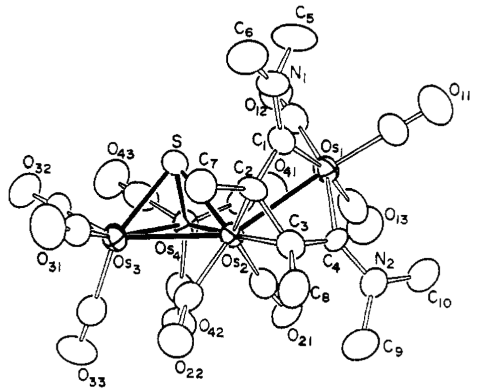


Figure 3. ORTEP drawing of **5** showing 50% probability thermal ellipsoids.

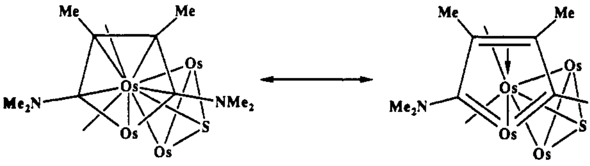
Table IX. Intramolecular Distances (Å) for 5

Os(1)–C(11)	1.87 (2)	Os(3)–C(22)	2.53 (2)
Os(1)–C(13)	1.92 (2)	Os(3)–Os(4)	2.748 (1)
Os(1)–C(12)	1.94 (2)	Os(4)–C(43)	1.86 (2)
Os(1)–C(1)	2.08 (2)	Os(4)–C(42)	1.94 (2)
Os(1)–C(4)	2.10 (1)	Os(4)–C(41)	1.96 (2)
Os(1)–Os(2)	2.796 (1)	Os(4)–S	2.371 (4)
Os(2)–C(22)	1.90 (2)	Os(4)–C(21)	2.79 (2)
Os(2)–C(21)	1.94 (2)	N(1)–C(1)	1.33 (2)
Os(2)–C(2)	2.20 (1)	N(1)–C(6)	1.45 (2)
Os(2)–C(3)	2.23 (1)	N(1)–C(5)	1.45 (3)
Os(2)–S	2.369 (4)	N(2)–C(4)	1.33 (2)
Os(2)–C(1)	2.77 (2)	N(2)–C(10)	1.38 (2)
Os(2)–C(4)	2.57 (2)	N(2)–C(9)	1.46 (2)
Os(2)–Os(4)	2.8249 (9)	C(1)–C(2)	1.43 (2)
Os(2)–Os(3)	2.8525 (9)	C(2)–C(3)	1.49 (2)
Os(3)–C(32)	1.88 (2)	C(2)–C(7)	1.51 (2)
Os(3)–C(31)	1.90 (2)	C(3)–C(4)	1.41 (2)
Os(3)–C(33)	1.93 (2)	C(3)–C(8)	1.50 (2)
Os(3)–S	2.366 (4)	O–C (av)	1.14 (2)

Table X. Intramolecular Bond Angles (deg) for 5

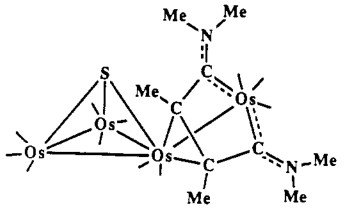
C(11)–Os(1)–C(1)	96.1 (7)	Os(1)–Os(2)–Os(3)	143.94 (3)
C(11)–Os(1)–C(4)	100.8 (7)	Os(4)–Os(2)–Os(3)	57.88 (2)
C(13)–Os(1)–C(1)	167.4 (7)	Os(4)–Os(3)–Os(2)	60.55 (2)
C(13)–Os(1)–C(4)	94.4 (7)	S–Os(4)–Os(3)	54.5 (1)
C(13)–Os(1)–Os(2)	100.2 (6)	S–Os(4)–Os(2)	53.4 (1)
C(12)–Os(1)–C(1)	95.4 (7)	Os(3)–Os4)–Os(2)	61.56 (2)
C(12)–Os(1)–C(4)	161.5 (6)	Os(3)–S–Os(2)	74.1 (1)
C(1)–Os(1)–C(4)	77.6 (6)	Os(3)–S–Os(4)	70.9 (1)
C(1)–Os(1)–Os(2)	67.4 (4)	Os(2)–S–Os(4)	73.2 (1)
C(4)–Os(1)–Os(2)	61.3 (4)	N(1)–C(1)–C(2)	121 (2)
C(22)–Os(2)–C(2)	96.0 (6)	N(1)–C(1)–Os(1)	128 (1)
C(22)–Os(2)–C(3)	84.8 (6)	C(2)–C(1)–Os(1)	111 (1)
C(22)–Os(2)–Os(1)	154.2 (4)	C(1)–C(2)–C(3)	111 (1)
C(22)–Os(2)–Os(4)	102.2 (4)	C(1)–C(2)–C(7)	127 (1)
C(22)–Os(2)–Os(3)	60.4 (4)	C(1)–C(2)–Os(2)	97 (1)
C(21)–Os(2)–C(2)	141.2 (6)	C(3)–C(2)–C(7)	118 (1)
C(21)–Os(2)–C(3)	104.1 (6)	C(3)–C(2)–Os(2)	71.5 (7)
C(21)–Os(2)–Os(1)	87.5 (5)	C(7)–C(2)–Os(2)	116 (1)
C(21)–Os(2)–Os(4)	69.0 (4)	C(4)–C(3)–C(2)	114 (1)
C(21)–Os(2)–Os(3)	107.9 (5)	C(4)–C(3)–C(8)	123 (1)
C(2)–Os(2)–Os(1)	70.2 (4)	C(4)–C(3)–Os(2)	86.4 (8)
C(2)–Os(2)–Os(4)	144.7 (4)	C(2)–C(3)–C(8)	117 (1)
C(2)–Os(2)–Os(3)	108.7 (4)	C(2)–C(3)–Os(2)	69.3 (7)
C(3)–Os(2)–Os(1)	70.7 (4)	C(8)–C(3)–Os(2)	134 (1)
C(3)–Os(2)–Os(4)	170.0 (4)	N(2)–C(4)–C(3)	121 (1)
C(3)–Os(2)–Os(3)	132.1 (4)	N(2)–C(4)–Os(1)	126 (1)
S–Os(2)–Os(1)	91.1 (1)	C(3)–C(4)–Os(1)	113 (1)
S–Os(2)–Os(4)	53.5 (1)	O(21)–C(21)–Os(2)	167 (1)
S–Os(2)–Os(3)	52.9 (1)	O(22)–C(22)–Os(2)	160 (1)
Os(1)–Os(2)–Os(4)	101.17 (3)	O–C–Os (av)	177 (2)

interactions C(1)–N(1) = 1.33 (2) Å and C(4)–N(2) = 1.33 (2) Å appear to be significantly stronger than those in **4**. The nitrogen atoms exhibit a planar geometry, and there is spectroscopic evidence for a hindered rotation about the C–N bonds and other dynamical processes (vide infra). The bonding in **5** could be described as a mixture of the resonance structures F and G. The latter structure emphasizes the strong C–N interactions for the amine-substituted carbon atoms. This bonding should weaken the Os(2)–C bonding, as observed, and may lead to the development of carbene-like character on C(1) and C(4).



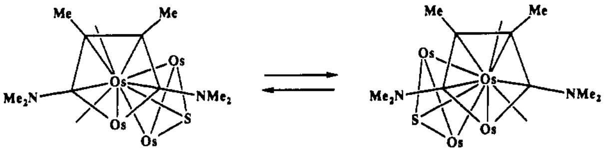
F

G



5

The ^1H NMR spectrum of **5** at 0 °C in toluene-d_8 solvent shows resonances at 2.92 (6 H), 2.67 (6 H), 1.56 (3 H), and 1.36 ppm (3 H). The first two can be assigned to time-averaged signals for the two inequivalent NMe_2 groups. The last two resonances can be attributed to the inequivalent *C*-methyl groups. As the temperature is raised, all of the resonances broaden at approximately the same rate. They coalesce in pairs, methyl 1 with methyl 2 and methyl 3 with methyl 4, at ~40 °C and then sharpen as singlets at 2.97 (12 H) and 1.56 ppm (6 H) at 73 °C. Clearly, the inequivalent *C*-methyl and NMe_2 groups are being averaged, respectively. The dynamical process is shown in eq 2. The process could be viewed as a reversible rotation of the OsC_4 metallacyclic ring about a vector from Os(2) to the center of the ring, as depicted, with ΔG^*_{313} = 15.3 (5) kcal/mol.



(2)

At reduced temperatures, one of the NMe_2 resonances exhibits a broadening and re-formation into two separate resonances, with coalescence at −38 °C, ΔG^*_{235} = 11.6 (5) kcal/mol. The other NMe_2 resonance undergoes substantial broadening, but at the lowest temperature attainable (−92 °C in CD_2Cl_2) this resonance had still not separated into two resonances. These changes can be attributed to hindered rotations of the NMe_2 groups. Since they are inequivalent, it is to be expected that they will have different barriers to rotation as was indicated by the observation of broadening in two significantly different temperature regions.

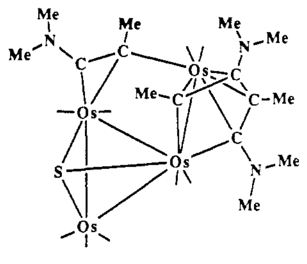
An ORTEP drawing of the molecular structure of **6** is shown in Figure 4. Final atomic positional parameters are listed in Table XI. Selected interatomic distances and angles are listed in Tables XII and XIII. Compound **6** also contains a spiked triangular cluster of four osmium atoms with a triply bridging sulfido ligand on the triangular grouping. Compound **6** was formed by the addition of three ynamine ligands to **1**. Two of these have been coupled in a head-to-tail fashion by the formation of a carbon–carbon bond. In analogy to compound **4**, the dimetallabutadiene ligand is π-bonded to the external metal atom Os(1) and σ-bonded to Os(3). The longest Os–C bonds to Os(1) involve the NMe_2-substituted carbon atoms

Table XI. Positional Parameters and *B*(eq) Values for $Os_4S(CO)_9[(MeCCNMe_2)_2](MeCCNMe_2)$ (6)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.16517 (04)	0.27518 (02)	0.14937 (04)	2.43 (1)
Os(2)	0.24154 (04)	0.13181 (02)	0.32585 (04)	2.34 (1)
Os(3)	0.30311 (04)	0.29093 (02)	0.48921 (04)	2.16 (1)
Os(4)	0.45778 (04)	0.17354 (02)	0.60641 (04)	2.61 (1)
S(1)	0.2283 (02)	0.17294 (14)	0.5825 (03)	2.59 (8)
O(11)	0.3481 (09)	0.2712 (05)	−0.0569 (09)	5.4 (4)
O(12)	−0.0602 (10)	0.2996 (06)	−0.1380 (11)	7.4 (4)
O(21)	0.2208 (08)	−0.0392 (04)	0.3419 (09)	4.7 (3)
O(22)	0.4398 (09)	0.1263 (05)	0.1341 (10)	5.6 (4)
O(31)	0.2523 (09)	0.3982 (05)	0.7411 (09)	4.8 (3)
O(32)	0.5972 (08)	0.3566 (04)	0.6641 (09)	4.7 (3)
O(41)	0.4667 (09)	0.0097 (05)	0.6779 (10)	5.5 (4)
O(42)	0.6227 (08)	0.2379 (05)	0.9499 (10)	5.6 (4)
O(43)	0.7003 (09)	0.1848 (06)	0.4806 (12)	6.3 (4)
N(1)	0.0110 (09)	0.4282 (05)	0.2569 (11)	4.2 (4)
N(2)	0.4680 (08)	0.3871 (05)	0.3052 (10)	3.2 (3)
N(3)	−0.0803 (09)	0.0980 (05)	0.2124 (10)	3.6 (3)
C(1)	−0.0161 (10)	0.2806 (06)	0.4180 (12)	3.6 (4)
C(2)	0.1011 (09)	0.3116 (05)	0.3621 (10)	2.4 (3)
C(3)	0.1102 (10)	0.3819 (06)	0.2958 (11)	2.9 (4)
C(4)	−0.1322 (13)	0.3988 (09)	0.2047 (19)	7.2 (7)
C(5)	0.0481 (14)	0.5087 (07)	0.2928 (17)	5.8 (6)
C(6)	0.2353 (11)	0.4577 (06)	0.1263 (12)	3.7 (4)
C(7)	0.2326 (09)	0.4024 (05)	0.2496 (10)	2.4 (3)
C(8)	0.3430 (10)	0.3662 (05)	0.3290 (10)	2.7 (3)
C(9)	0.5304 (11)	0.4666 (07)	0.3132 (14)	4.5 (5)
C(10)	0.5579 (11)	0.3338 (07)	0.3017 (15)	4.5 (5)
C(11)	0.2759 (12)	0.2673 (06)	0.0173 (12)	3.7 (4)
C(12)	0.0276 (13)	0.2893 (07)	−0.0275 (13)	4.3 (5)
C(21)	0.2282 (10)	0.0261 (07)	0.3353 (12)	3.4 (4)
C(22)	0.3718 (11)	0.1288 (06)	0.2103 (13)	3.6 (4)
C(31)	0.2760 (11)	0.3569 (06)	0.6498 (11)	3.1 (4)
C(32)	0.4930 (11)	0.3178 (06)	0.6008 (12)	3.1 (4)
C(41)	0.4651 (11)	0.0728 (07)	0.6502 (13)	3.9 (5)
C(42)	0.5576 (12)	0.2143 (08)	0.8208 (13)	4.5 (5)
C(43)	0.6104 (12)	0.1807 (07)	0.5296 (14)	4.0 (5)
C(51)	0.0984 (10)	0.1547 (05)	0.1012 (10)	2.7 (3)
C(52)	0.0765 (12)	0.1100 (06)	−0.0621 (11)	4.3 (4)
C(53)	0.0409 (10)	0.1250 (05)	0.2096 (11)	2.9 (4)
C(54)	−0.1067 (11)	0.0610 (07)	0.3455 (14)	4.3 (5)
C(55)	−0.2020 (11)	0.1034 (08)	0.0850 (16)	5.6 (5)

Table XII. Intramolecular Distances (Å) for 6

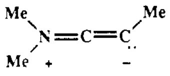
Os(1)–C(12)	1.85 (1)	Os(4)–C(42)	1.89 (1)
Os(1)–C(11)	1.89 (1)	Os(4)–C(43)	1.91 (1)
Os(1)–C(51)	2.11 (1)	Os(4)–S(1)	2.347 (3)
Os(1)–C(2)	2.252 (9)	N(1)–C(3)	1.39 (1)
Os(1)–C(7)	2.278 (9)	N(1)–C(5)	1.41 (2)
Os(1)–C(8)	2.36 (1)	N(1)–C(4)	1.44 (2)
Os(1)–C(3)	2.43 (1)	N(2)–C(8)	1.39 (1)
Os(1)–Os(3)	2.891 (1)	N(2)–C(10)	1.42 (1)
Os(2)–C(21)	1.86 (1)	N(2)–C(9)	1.45 (1)
Os(2)–C(22)	1.94 (1)	N(3)–C(53)	1.30 (1)
Os(2)–C(53)	2.03 (1)	N(3)–C(55)	1.45 (1)
Os(2)–C(51)	2.209 (9)	N(3)–C(54)	1.47 (1)
Os(2)–C(1)	2.374 (2)	C(1)–C(2)	1.51 (1)
Os(2)–Os(4)	2.778 (1)	C(2)–C(3)	1.42 (1)
Os(2)–Os(3)	2.945 (1)	C(3)–C(7)	1.47 (1)
Os(3)–C(31)	1.87 (1)	C(6)–C(7)	1.53 (1)
Os(3)–C(32)	1.91 (1)	C(7)–C(8)	1.43 (1)
Os(3)–C(8)	2.11 (1)	C(51)–C(53)	1.38 (1)
Os(3)–C(2)	2.176 (8)	C(51)–C(52)	1.52 (1)
Os(3)–S(1)	2.420 (3)	O–C (av)	1.15 (1)
Os(3)–Os(4)	2.876 (1)	Os(4)–C(32)	2.53 (1)
Os(4)–C(41)	1.86 (1)	Os(1)–Os(2)	3.154 (1)



6

C(3) and C(8), Os(1)–C(3) = 2.43 (1) Å and Os(1)–C(8) = 2.36 (1) Å. These values are similar to those found in **4**. Likewise, the C–N distances C(3)–N(1) = 1.39 (1) Å and C(8)–N(2) = 1.39 (1) Å are also similar to those in **4**. The third ynamine molecule is not coupled to the first two. It serves as a bridge between Os(1) and Os(2) and is coordinated in a σ–π type fashion similar to the ynamine ligands found in D and **3**. The C(53)–N(3) distance of 1.30 (1) Å is significantly shorter than those found in coupled ligands in **6** but is similar to those found in D and **3**. The Os(1)–Os(2) distance is relatively long, 3.154 (1) Å. This combined with an application of electron-counting rules (vide infra) leads us to believe that there is a minimum of direct bonding between Os(1) and Os(2). The bond to the external metal atom Os(1), Os(1)–Os(3) = 2.891 (1) Å, is the longest in the three spiked triangular cluster complexes **4**–**6**. This may be related to a strain effect produced by the bending of Os(1) toward Os(2) to form the bond to the bridging ynamine ligand. The Os(1)–Os(3)–Os(2) angle is 65.43 (3)°.

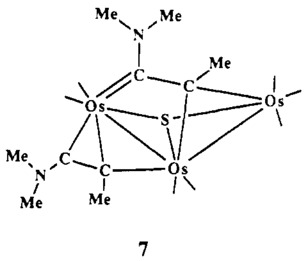
If the dimetallabutadiene ligand serves as a six-electron donor and the ynamine ligand as a four-electron σ–π donor (see resonance structure H), then compound **6** contains a total of 64 valence electrons. Electron-precise clusters with 64 electrons should contain only four metal–metal bonds. Three of these can be accounted for in the triangle Os(2)–Os(3)–Os(4) with the fourth being Os(1)–Os(3).



H

The ^{1}H NMR spectrum of **6** at 25 °C shows six resonances in toluene-d_8 solvent, 3.22 (3 H), 2.74 (6 H), 2.70 (3 H), 2.49 (6 H), 2.42 (6 H), and 1.55 ppm (3 H). Those of intensity 3 can be attributed to the three *C*-methyl groups. Those of intensity 6 can be attributed to the three NMe$_2$ ligands in the presence of rapid rotation about the C–N bonds.

An ORTEP drawing of the molecular structure of **7** is shown in Figure 5. Final atomic positional parameters are listed in Table XIV. Selected interatomic distances and angles are listed in Tables XV and XVI. This compound contains only three osmium atoms arranged in the form of a open triangular cluster. Structurally, it is very similar to **2**,[11] but it contains two ynamine ligands. One of these is a triply bridging ligand similar to those in **2** and **3**. This ligand also has structural features that strongly suggest a carbene-like character (e.g. the planar nitrogen atom N(2) and short C(8)–N(2) distance of 1.33 (2) Å), and the Os(3)–C(8) distance of 2.95 (1) Å is a nonbonding value. The second ynamine ligand in **7** bridges the Os(1)–Os(3) edge of the cluster in a manner similar to that found in A, B, D, **3**, and **6**. N(1) is also planar, and C(3)–N(1) is short, 1.31 (3) Å. The ^{1}H NMR spectrum of **7** shows five resonances: 3.52 (6 H), 3.46 (3 H), 3.45 (3 H), 2.86 (3 H), and 2.58 ppm (3 H). The resonance of intensity 6 can be



7

Table XIII. Intramolecular Bond Angles (deg) for 6

C(12)–Os(1)–C(51)	90.4 (4)	C(2)–Os(3)–Os(2)	91.5 (3)
C(12)–Os(1)–C(2)	105.7 (4)	S(1)–Os(3)–Os(4)	51.75 (6)
C(12)–Os(1)–C(7)	96.0 (4)	S(1)–Os(3)–Os(1)	107.08 (7)
C(12)–Os(1)–C(8)	129.8 (4)	S(1)–Os(3)–Os(2)	51.40 (6)
C(12)–Os(1)–C(3)	87.8 (4)	Os(4)–Os(3)–Os(1)	117.36 (3)
C(12)–Os(11)–Os(3)	153.4 (4)	Os(4)–Os(3)–Os(2)	56.99 (3)
C(11)–Os(1)–C(51)	89.9 (4)	Os(1)–Os(3)–Os(2)	65.43 (3)
C(11)–Os(1)–C(2)	159.6 (4)	C(41)–Os(4)–S(1)	97.7 (3)
C(11)–Os(1)–C(7)	99.5 (4)	C(41)–Os(4)–Os(2)	94.3 (3)
C(11)–Os(1)–C(8)	88.3 (4)	C(41)–Os(4)–Os(3)	150.2 (3)
C(11)–Os(1)–C(3)	134.4 (4)	C(42)–Os(4)–S(1)	106.3 (3)
C(11)–Os(1)–Os(3)	115.7 (3)	C(42)–Os(4)–Os(2)	160.3 (3)
C(51)–Os(1)–C(2)	104.3 (4)	C(42)–Os(4)–Os(3)	104.1 (4)
C(51)–Os(1)–C(7)	168.7 (3)	C(43)–Os(4)–S(1)	154.4 (3)
C(51)–Os(1)–C(8)	139.6 (3)	C(43)–Os(4)–Os(2)	102.2 (3)
C(51)–Os(1)–C(3)	135.5 (4)	C(43)–Os(4)–Os(3)	108.7 (3)
C(51)–Os(1)–Os(3)	100.2 (2)	S(1)–Os(4)–Os(2)	54.41 (6)
C(2)–Os(1)–C(7)	65.0 (3)	S(1)–Os(4)–Os(3)	54.04 (6)
C(2)–Os(1)–C(8)	71.4 (3)	Os(2)–Os(4)–Os(3)	62.75 (3)
C(2)–Os(1)–C(3)	35.1 (3)	Os(4)–S(1)–Os(2)	72.08 (8)
C(2)–Os(1)–Os(3)	48.1 (2)	Os(4)–S(1)–Os(3)	74.21 (8)
C(7)–Os(1)–C(8)	35.7 (3)	Os(2)–S(1)–Os(3)	75.81 (7)
C(7)–Os(1)–C(3)	36.1 (3)	C(3)–N(1)–C(5)	120 (1)
C(7)–Os(1)–Os(3)	70.1 (2)	C(3)–N(1)–C(4)	124 (1)
C(8)–Os(1)–C(3)	60.8 (3)	C(5)–N(1)–C(4)	116 (1)
C(8)–Os(1)–Os(3)	46.1 (2)	C(8)–N(2)–C(10)	122.7 (8)
C(3)–Os(1)–Os(3)	67.5 (2)	C(8)–N(2)–C(9)	123.2 (8)
C(21)–Os(2)–C(53)	93.9 (4)	C(10)–N(2)–C(9)	113.0 (9)
C(21)–Os(2)–C(51)	110.5 (4)	C(53)–N(3)–C(55)	122.7 (9)
C(21)–Os(2)–S(1)	99.4 (3)	C(53)–N(3)–C(54)	123.4 (9)
C(21)–Os(2)–Os(4)	95.1 (3)	C(55)–N(3)–C(54)	114 (1)
C(21)–Os(2)–Os(3)	149.9 (3)	C(3)–C(2)–C(1)	123.3 (8)
C(22)–Os(2)–C(53)	121.3 (4)	C(3)–C(2)–Os(3)	110.1 (7)
C(22)–Os(2)–C(51)	86.6 (4)	C(3)–C(2)–Os(1)	79.3 (5)
C(22)–Os(2)–S(1)	141.1 (3)	C(1)–C(2)–Os(3)	118.8 (6)
C(22)–Os(2)–Os(4)	88.4 (3)	C(1)–C(2)–Os(1)	132.8 (7)
C(22)–Os(2)–Os(3)	104.4 (3)	Os(3)–C(2)–Os(1)	81.5 (3)
C(53)–Os(2)–C(51)	37.6 (4)	N(1)–C(3)–C(2)	127 (1)
C(53)–Os(2)–S(1)	95.5 (3)	N(1)–C(3)–C(7)	117.7 (9)
C(53)–Os(2)–Os(4)	148.7 (3)	N(1)–C(3)–Os(1)	133.7 (7)
C(53)–Os(2)–Os(3)	99.6 (3)	C(2)–C(3)–C(7)	115.0 (8)
C(51)–Os(2)–S(1)	123.2 (3)	C(2)–C(3)–Os(1)	65.6 (5)
C(51)–Os(2)–Os(4)	153.9 (2)	C(7)–C(3)–Os(1)	66.3 (5)
C(51)–Os(2)–Os(3)	96.3 (2)	C(8)–C(7)–C(3)	114.0 (8)
S(1)–Os(2)–Os(4)	53.52 (6)	C(8)–C(7)–C(6)	125.2 (9)
S(1)–Os(2)–Os(3)	52.79 (6)	C(8)–C(7)–Os(1)	75.2 (5)
Os(4)–Os(2)–Os(3)	60.26 (3)	C(3)–C(7)–C(6)	120.8 (8)
C(31)–Os(3)–C(8)	103.3 (4)	C(3)–C(7)–Os(1)	77.5 (5)
C(31)–Os(3)–C(2)	80.8 (4)	C(6)–C(7)–Os(1)	115.5 (6)
C(31)–Os(3)–S(1)	95.4 (3)	N(2)–C(8)–C(7)	118.7 (8)
C(31)–Os(3)–Os(4)	114.1 (3)	N(2)–C(8)–Os(3)	125.8 (7)
C(31)–Os(3)–Os(1)	127.3 (3)	N(2)–C(8)–Os(1)	123.0 (6)
C(31)–Os(3)–Os(2)	145.2 (3)	C(7)–C(8)–Os(3)	115.3 (7)
C(32)–Os(3)–C(8)	85.2 (4)	C(7)–C(8)–Os(1)	69.0 (5)
C(32)–Os(3)–C(2)	156.2 (4)	Os(3)–C(8)–Os(1)	80.4 (3)
C(32)–Os(3)–S(1)	105.5 (3)	O(32)–C(32)–Os(3)	158.5 (9)
C(32)–Os(3)–Os(4)	59.8 (3)	C(53)–C(51)–C(52)	121.8 (9)
C(32)–Os(3)–Os(1)	128.7 (3)	C(53)–C(51)–Os(1)	113.8 (7)
C(32)–Os(3)–Os(2)	109.7 (3)	C(53)–C(51)–Os(2)	64.0 (5)
C(8)–Os(3)–C(2)	77.8 (3)	C(52)–C(51)–Os(1)	121.9 (7)
C(8)–Os(3)–S(1)	159.0 (3)	C(52)–C(51)–Os(2)	124.0 (7)
C(8)–Os(3)–Os(4)	125.5 (3)	Os(1)–C(51)–Os(2)	93.7 (3)
C(8)–Os(3)–Os(1)	53.6 (2)	N(3)–C(53)–C(51)	137 (1)
C(8)–Os(3)–Os(2)	108.2 (2)	C(3)–C(53)–Os(2)	143.8 (7)
C(2)–Os(3)–S(1)	96.1 (3)	C(51)–C(53)–Os(2)	78.4 (6)
C(2)–Os(3)–Os(4)	143.9 (3)	O–C–Os (av)	177 (1)
C(2)–Os(3)–Os(1)	50.4 (2)		

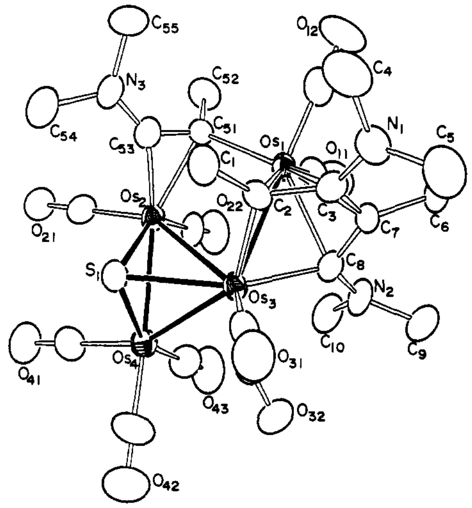


Figure 4. ORTEP drawing of 6 showing 50% probability thermal ellipsoids.

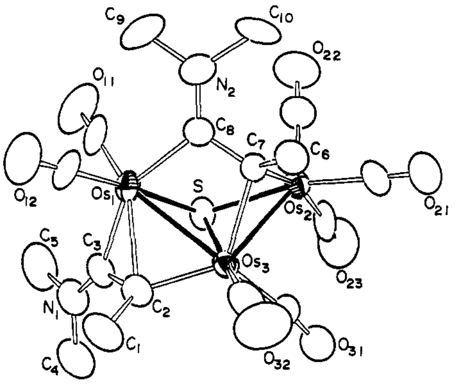


Figure 5. ORTEP drawing of 7 showing 50% probability thermal ellipsoids.

Table XIV. Positional Parameters and *B*(eq) Values for $Os_3S(CO)_7(MeCCNMe_2)_2$ (7)

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.50583 (05)	0.22315 (04)	0.35138 (04)	2.87 (3)
Os(2)	0.14481 (05)	0.21696 (04)	0.42227 (04)	2.97 (3)
Os(3)	0.38942 (05)	0.23778 (03)	0.50972 (04)	2.68 (2)
S	0.3137 (03)	0.3153 (02)	0.3747 (03)	3.2 (2)
O(11)	0.4849 (13)	0.2671 (10)	0.1568 (08)	7.6 (8)
O(12)	0.7467 (11)	0.1067 (08)	0.3443 (08)	5.8 (7)
O(21)	−0.0182 (12)	0.0931 (08)	0.5277 (10)	6.3 (7)
O(22)	0.0126 (13)	0.1677 (10)	0.2451 (09)	8.0 (9)
O(23)	−0.0198 (13)	0.3828 (09)	0.4560 (12)	9 (1)
O(31)	0.2195 (11)	0.3400 (08)	0.6308 (09)	6.2 (7)
O(32)	0.4782 (14)	0.1223 (09)	0.6656 (08)	7.5 (8)
N(1)	0.6384 (12)	0.4109 (08)	0.4074 (11)	4.6 (7)
N(2)	0.3463 (12)	0.0557 (08)	0.2930 (09)	3.9 (6)
C(1)	0.6945 (14)	0.2515 (11)	0.5521 (12)	5.0 (9)
C(2)	0.5726 (12)	0.2770 (09)	0.4926 (10)	3.4 (7)
C(3)	0.5931 (12)	0.3296 (09)	0.4174 (11)	3.5 (7)
C(4)	0.6716 (16)	0.4697 (11)	0.4833 (15)	6 (1)
C(5)	0.6592 (18)	0.4461 (12)	0.3203 (16)	7 (1)
C(6)	0.2960 (14)	0.0370 (09)	0.4841 (10)	3.7 (7)
C(7)	0.3023 (12)	0.1225 (08)	0.4319 (10)	2.7 (6)
C(8)	0.3717 (12)	0.1182 (09)	0.3543 (10)	2.9 (6)
C(9)	0.4191 (17)	0.0434 (11)	0.2164 (12)	5 (1)
C(10)	0.2266 (16)	−0.0032 (10)	0.2922 (13)	5 (1)
C(11)	0.4974 (14)	0.2436 (12)	0.2309 (14)	5 (1)
C(12)	0.6523 (15)	0.1517 (10)	0.3458 (11)	3.8 (8)
C(21)	0.0418 (14)	0.1402 (10)	0.4889 (12)	4.1 (8)
C(22)	0.0579 (16)	0.1898 (11)	0.3109 (13)	4.9 (9)
C(23)	0.0370 (15)	0.3209 (11)	0.4426 (13)	4.7 (9)
C(31)	0.2769 (15)	0.2970 (11)	0.5822 (11)	4.2 (8)
C(32)	0.4462 (15)	0.1653 (11)	0.6050 (12)	4.7 (9)

Table XV. Intramolecular Distances (Å) for 7

Os(1)-C(11)	1.84 (2)	Os(3)-C(7)	2.24 (1)
Os(1)-C(12)	1.85 (1)	Os(3)-S	2.426 (4)
Os(1)-C(3)	2.05 (1)	N(1)-C(3)	1.31 (2)
Os(1)-C(8)	2.09 (1)	N(1)-C(5)	1.45 (2)
Os(1)-C(2)	2.34 (1)	N(1)-C(4)	1.47 (2)
Os(1)-S	2.456 (4)	N(2)-C(8)	1.33 (2)
Os(1)-Os(3)	2.7678 (9)	N(2)-C(9)	1.44 (2)
Os(2)-C(22)	1.89 (2)	N(2)-C(10)	1.51 (2)
Os(2)-C(21)	1.90 (2)	C(1)-C(2)	1.53 (2)
Os(2)-C(23)	1.95 (2)	C(2)-C(3)	1.41 (2)
Os(2)-C(7)	2.15 (1)	C(6)-C(7)	1.51 (2)
Os(2)-S	2.427 (4)	C(7)-C(8)	1.42 (2)
Os(2)-Os(3)	2.7683 (8)	O-C (av)	1.15 (2)
Os(3)-C(32)	1.86 (2)	Os(1)-Os(2)	3.943 (1)
Os(3)-C(31)	1.88 (2)	Os(3)-C(8)	2.95 (1)
Os(3)-C(2)	2.01 (1)	Os(3)-C(3)	2.95 (1)

Table XVI. Intramolecular Bond Angles (deg) for 7

C(11)-Os(1)-C(3)	109.8 (7)	C(31)-Os(3)-Os(1)	150.5 (5)
C(11)-Os(1)-C(8)	99.4 (7)	C(31)-Os(3)-Os(2)	75.8 (5)
C(11)-Os(1)-C(2)	146.6 (7)	C(2)-Os(3)-C(7)	119.9 (5)
C(11)-Os(1)-S	94.1 (5)	C(2)-Qs(3)-S	89.7 (4)
C(11)-Os(1)-Os(3)	148.4 (5)	C(2)-Os(3)-Os(1)	55.9 (4)
C(12)-Os(1)-C(3)	98.2 (6)	C(2)-Os(3)-Os(2)	142.9 (4)
C(12)-Os(1)-C(8)	96.2 (6)	C(7)-Os(3)-S	80.5 (4)
C(12)-Os(1)-C(2)	93.3 (6)	C(7)-Os(3)-Os(1)	70.5 (4)
C(12)-Os(1)-S	174.3 (5)	C(7)-Os(3)-Os(2)	49.4 (3)
C(12)-Os(1)-Os(3)	119.4 (5)	S-Os(3)-Os(1)	56.0 (1)
C(3)-Os(1)-C(8)	146.9 (6)	S-Os(3)-Os(2)	55.23 (8)
C(3)-Os(1)-C(2)	36.9 (5)	Os(1)-Os(3)-Os(2)	90.82 (3)
C(3)-Os(1)-S	79.7 (4)	Os(3)-S-Os(2)	69.6 (1)
C(3)-Os(1)-Os(3)	73.7 (4)	Os(3)-S-Os(1)	69.08 (9)
C(8)-Os(1)-C(2)	112.8 (5)	Os(2)-S-Os(1)	107.7 (1)
C(8)-Os(1)-S	83.1 (4)	C(3)-N(1)-C(5)	121 (2)
C(8)-Os(1)-Os(3)	73.3 (4)	C(3)-N(1)-C(4)	122 (2)
C(2)-Os(1)-S	81.9 (3)	C(5)-N(1)-C(4)	117 (1)
C(2)-Os(1)-Os(3)	45.3 (3)	C(8)-N(2)-C(9)	124 (1)
S-Os(1)-Os(3)	55.0 (1)	C(8)-N(2)-C(10)	122 (1)
C(22)-Os(2)-C(7)	102.8 (6)	C(9)-N(2)-C(10)	113 (1)
C(22)-Os(2)-S	99.5 (5)	C(3)-C(2)-C(1)	116 (1)
C(22)-Os(2)-Os(3)	143.2 (5)	C(3)-C(2)-Os(3)	118 (1)
C(21)-Os(2)-C(7)	90.8 (6)	C(3)-C(2)-Os(1)	60.4 (8)
C(21)-Os(2)-S	164.4 (5)	C(1)-C(2)-Os(3)	126 (1)
C(21)-Os(2)-Os(3)	109.6 (5)	C(1)-C(2)-Os(1)	128 (1)
C(23)-Os(2)-C(7)	161.9 (6)	Os(3)-C(2)-Os(1)	78.7 (4)
C(23)-Os(2)-S	89.5 (4)	N(1)-C(3)-C(2)	133 (2)
C(23)-Os(2)-Os(3)	110.0 (5)	N(1)-C(3)-Os(1)	144 (1)
C(7)-Os(2)-S	82.3 (4)	C(2)-C(3)-Os(1)	82.7 (8)
C(7)-Os(2)-Os(3)	52.3 (3)	C(8)-C(7)-C(6)	116 (1)
S-Os(2)-Os(3)	55.20 (9)	C(8)-C(7)-Os(2)	113 (1)
C(32)-Os(3)-C(2)	91.6 (6)	C(8)-C(7)-Os(3)	105.3 (9)
C(32)-Os(3)-C(7)	92.8 (6)	C(6)-C(7)-Os(2)	122 (1)
C(32)-Os(3)-S	172.9 (5)	C(6)-C(7)-Os(3)	114 (1)
C(32)-Os(3)-Os(1)	119.6 (6)	Os(2)-C(7)-Os(3)	78.3 (4)
C(32)-Os(3)-Os(2)	121.6 (4)	N(2)-C(8)-C(7)	122 (1)
C(31)-Os(3)-C(2)	124.3 (6)	N(2)-C(18)-Os(1)	127 (1)
C(31)-Os(3)-C(7)	115.6 (6)	C(7)-C(8)-Os(1)	111 (1)
C(31)-Os(3)-S	95.4 (5)		

attributed to one of the NMe_2 groupings that is undergoing a rapid rotation about the C–N bond and averaging the methyl groups. The resonances at 3.46 and 3.45 ppm can be attributed to the *N*-methyl resonances on the second ynamine ligand. By comparison to D, which exhibits rapid C–N rotation at 25 °C,[7] and 2, which displays a hindered C–N rotation at 25 °C,[11] we believe that it is the *edge*-bridging ynamine ligand that is exhibiting the rapid C–N rotation in 7.

Conclusions

The reaction of $Os_4(CO)_{12}(\mu_3\text{-}S)$ (1) with MeC_2NMe yielded the five new osmium cluster complexes 3–7 and the previously reported complex 2. All of the products were obtained in low yields. Efforts to improve the yields by pretreating 1 with Me_3NO resulted only in a slight increase in the yield of 3. Except for 2 and 6, all of the products were formed by the addition of 2 equiv of

MeC_2NMe_2. Compounds 4–6 formed by the coupling of two ynamine ligands and contain metallacyclopentadienyl groupings. These compounds appear to be unrelated since the coupling of the ynamine ligands in each occurs in a different way (i.e. tail-to-tail coupling in 4, head-to-head coupling in 5, and head-to-tail coupling in 6). Although 3 could conceivable be a precursor to one or more of these products, our efforts to convert 3 to them independently have been unsuccessful. The triosmium clusters were evidently formed by fragmentation of some tetraosmium species, but this precursor has not been identified.

In all cases, where the ynamine ligands were not coupled, there is structural and spectroscopic evidence for a strong C–N π-bonding interaction between the nitrogen atom and the amine-substituted carbon atom of the alkynyl group. This bonding appears to disrupt the anticipated metal–carbon bonding and causes this carbon atom to adopt a structural form that resembles an aminocarbene ligand. In those cases where the ynamine ligands have been coupled, there still appears to be evidence for significant, albeit weaker, π-bonding interactions between the amino groups and the adjacent carbon atoms that appear to lead to a weakening of the metal-carbon bonding.

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Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters of the hydrogen atoms for all five crystal structure analyses (21 pages); tables of structure factor amplitudes (106 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Halide, Hydride, and Alkyl Derivatives of (Pentamethylcyclopentadienyl)(bisphosphine)iron(II)

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Reaction of $[Fe(acac)_2]_x$ (acac = η^2-acetylacetonate) with LiCp* (Cp* = η^5-pentamethylcyclopentadienyl) in the presence of PMe_3 or DMPE (DMPE = $Me_2PCH_2CH_2PMe_2$) yields Cp*LFe(acac) (L = PMe_3 (1), η^1-DMPE (2)). Compounds 1 and 2 can be isolated or treated in situ with $ClSiMe_3$ (in the presence of PMe_3 for 1) to afford Cp^*L_2FeCl (L = PMe_3 (3), L_2 = DMPE (4)). Reaction of 1 with Grignard reagents, RMgX (X = Cl, Br), in the presence of PMe_3 yields either $Cp^*(PMe_3)_2FeR$ (R = CH_3, CH_2CH_3) or $Cp^*(PMe_3)_2FeX$ (R = CMe_3, $CH_2C_6H_5$, C_3H_5). Compounds of the general formula Cp^*L_2FeX react with RMgX to yield Cp^*L_2FeR (R = H, CH_3, $CH_2C_6H_5$) or $Cp^*(PMe_3)Fe(\eta^3\text{-}C_3H_5)$. Routes to the cationic species $[Cp^*(PMe_3)_2FeL]^+PF_6^-$ (L = PMe_3, CO) are described. Reaction of 1 with CH_3CH_2MgX in the absence of PMe_3 yields $Cp^*(PMe_3)(C_2H_4)FeH$. Treatment of this complex with dihydrogen yields a highly unstable Fe^{IV} complex, $Cp^*(PMe_3)FeH_3$. The reactivity of these complexes is discussed and proposed to involve highly reactive, 16-electron unsaturated intermediates, $[Cp^*(PMe_3)FeR]$ (R = H, alkyl, aryl, etc.).

Introduction

Electron-rich, half-sandwich complexes of the type $Cp^*(PMe_3)_2RuX$ (Cp* = (η^5-C_5Me_5); X = halide, alkoxide, alkyl, hydride, etc.)[2] exhibit a rich and varied chemistry. For example, several of these derivatives are precursors to highly reactive, 16-electron species, $[Cp^*(PR_3)RuX]$, capable of activating C–H bonds both intramolecularly and intermolecularly.[3] Utilizing equilibrium methods, we have determined relative Ru–X bond strengths for $Cp^*(PMe_3)_2RuX$[4] and have investigated factors influencing the loss of trimethylphosphine from these compounds.[5] The analogous iron system with the same electron-donating ligand set, $Cp^*(PMe_3)_2FeX$, also offers the potential for high reactivity. Although the synthesis and reactivity of $Cp(CO)_2FeX$ derivatives (Cp = η^5-C_5H_5)) have been extensively investigated,[6] synthetic routes to the pentamethylcyclopentadienyl-bis(phosphine) complexes have been reported only recently. For example, the reaction of C_5Me_5H with (η^6-C_6H_6)$(PMe_3)_2Fe$ yields $Cp^*(PMe_3)_2FeH$, which is readily converted to $Cp^*(PMe_3)_2FeCl$ upon treatment with CH_2Cl_2.[7] The requirement for an apparatus for the metal vapor synthesis of the precursor, (η^6-C_6H_6)$(PMe_3)_2Fe$,[8] prompted a search for "wet" chemical

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