the other drum shaped molecules which have been structurally characterized:[3,18] the six-membered rings have a chair conformation while the four-membered rings are not planar due to the fact that the oxygen atoms are tilted toward the center of the cavity, relative to the tin atoms. The Sn–O bond lengths in the framework are 2.088 (4) and 2.097 (4) Å for the six-membered rings and 2.085 (3) Å for the four-membered rings. The bonds are shorter than the Sn–O bonds to the bridging carboxyl oxygen atoms which have values of 2.197 (4) and 2.193 (4) Å.

The Sn–O framework for the unfolded species **2** is shown in Figure 6. In Figure 6b deviations from planarity for this framework can be visualized. Atom Sn1, O1, Sn1′, and O1′ are required by symmetry to be coplanar. The symmetry related O2 atoms lie very nearly in this plane while the Sn2 atoms and the Sn3 atoms are progressively more displaced from this plane in opposite directions. The geometry about the trivalent oxygen atoms, however, tends toward planarity. For **2**, the sum of the angles about O1 is 356.7° and about O2 is 351.6°. For **3**, these values are 356.1° and 351.7°.

As in the case of the drum **1** the framework Sn–O bonds tend to be shorter than the Sn–O bonds to bridging carboxylate groups, with the exception of the Sn1–O2 framework bond. For **2**, the framework Sn–O bonds range from 1.985 (4) to 2.067 (4) Å

except for the Sn1–O2 bond length of 2.161 (4) Å, while the bridging Sn–O bond lengths range from 2.189 (5) to 2.242 (5) Å. For **3**, these values are 1.983 (7) to 2.072 (7), 2.140 (7), and 2.143 (8) to 2.244 (9) Å. For both **2** and **3**, the shortest Sn–O bond length is the axial bond of the heptacoordinated Sn3.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom parameters, and additional bond lengths and angles (Tables S1–S3, respectively, for **1**), anisotropic thermal parameters and additional bond lengths and angles (Tables S4 and S5, respectively, for **2**, and Tables S6 and S7, respectively, for **3**), deviations from selected least-squares mean planes (Tables S8 and S9 for **2** and **3**, respectively) (13 pages); a listing of observed and calculated structure factors for **1–3** (36 pages). Ordering information is given on any current masthead page.

Clusters Containing Carbene Ligands. 1. Novel Transformations of Carbene Ligands at Multinuclear Metal Sites. α-Activation of C–H and S–C Bonds in Carbene Containing Thiolatotriosmium Carbonyl Cluster Compounds

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Abstract: Treatment of the (arenethiolato)triosmium carbonyl cluster compounds $Os_3(CO)_{10}(\mu\text{-SAr})(\mu\text{-H})$ (**1a**, Ar = C_6H_5; **1b**, Ar = C_6F_5; **1c**, Ar = $p\text{-}C_6H_4Me$) with the diamines $H_2C(NR_2)_2$ (R = Me or Et) at 97 °C has yielded the new thiolatotriosmium cluster compounds $Os_3(CO)_9[C(H)NR_2](\mu\text{-SAr})(\mu\text{-H})$ (**2a**, R = Me, Ar = C_6H_5; **2b**, R = Me, Ar = C_6F_5; **2c**, R = Me, Ar = $p\text{-}C_6H_4Me$; **2d**, R = Et, Ar = $p\text{-}C_6H_4Me$) which contain a secondary (dialkylamino)carbene ligand substituted for a carbonyl ligand in the compounds **1a–c**. The structure of **2a** was established by a single-crystal X-ray diffraction analysis. When subjected to UV irradiation the compounds **2a–d** are decarbonylated and transformed into the products $Os_3(CO)_8[\mu\text{-CNR}_2](\mu\text{-SAr})(\mu\text{-H})_2$ (**3a–d**) and isomeric pairs of products $Os_3(CO)_8[\mu\text{-CNR}_2](\mu\text{-SAr})(\mu\text{-H})_2$ (**4a, 4c, and 4d and 5a, 5c, and 5d**). Compounds **3a** and **5d** were characterized by single-crystal X-ray diffraction analyses. Compound **3a** contains a triangular cluster of three osmium atoms with bridging benzenethiolato and (dimethylamino)carbyne ligands along adjacent edges of the cluster. Compounds **3** were formed by an α-CH activation of the aminocarbene ligand in the compound **2**. In compound **5d** the arenethiolato ligand was orthometalated at the third metal atom. The secondary aminocarbene ligand was not changed. The compounds **3a–d** were converted into the new carbene containing cluster compounds $Os_3(CO)_8[C(Ar)NR_2](\mu_3\text{-S})(\mu\text{-H})_2$ (**6a–d**) by heating to reflux in octane solvent for 1 h. Compound **6a** was characterized by a single-crystal X-ray diffraction analysis. It contains a triangular cluster of three metal atoms with a triply bridging sulfido ligand and a terminally coordinated phenyl(dimethylamino)carbene ligand. These compounds were formed by the transfer of the aryl group from the thiolato ligand to the carbon atom of the bridging carbyne ligand. A crossover experiment established that the transfer occurred by an intramolecular process. A mechanism which involves a sigmatropic shift of the phenyl group is proposed.

Studies of transition-metal cluster compounds are revealing an increasing number of new and unusual ligand transformations that involve interactions at two or more metal sites.[1,2] An understanding of the scope and mechanisms of these rearrangements will play a central role in developing the potential of these compounds to serve as reaction catalysts.[3]

In our recent studies we have discovered that the osmium cluster complex $Os_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-S})$ will react with NMe_3 by a double C–H activation process to yield the product $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-S})(\mu\text{-H})_2$ which contains a terminally coordi-

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Thiolatotriosmium Carbonyl Cluster Compounds

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nated secondary aminocarbene ligand.[4] This compound has been found to be a precursor for an effective catalyst for the exchange of alkyl groups in tertiary amines.[4]

We have now discovered that bis(dialkylamino)methanes can also serve as reagents for the introduction of secondary amino-carbene ligands into certain osmium cluster complexes and these engage in some very unusual and potentially important multicenter ligand transformations. These results are described in detail in this report.[5]

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere, unless otherwise specified. Reagent grade solvents were dried over molecular sieves and deoxygenated by purging with nitrogen prior to use. Thiophenol, perfluorothiophenol, *p*-thiocresol, [*N*,*N*,*N'*,-*N'*-bis(dimethylamino)]methane and [*N*,*N*,*N'*,*N'*-bis(diethylamino)]-methane were purchased from Aldrich and were used without further purification. The compounds $Os_3(CO)_{10}(\mu$-SAr$)(\mu$-H$)$ (**1a**, Ar = Ph; **1b**, Ar = C_6F_5; **1c**, Ar = *p*-C_6H_4Me) were prepared by published procedures.[6] Photolyses were carried out by using an external high-pressure mercury lamp on reaction solutions contained in Pyrex glassware. IR spectra were recorded on a Nicolet 5DXB FTIR spectrometer. A Brüker AM300 FT NMR spectrometer was used to obtain ¹H NMR spectra. Elemental microanalyses were performed by MICANAL, Tuscon, AZ. Mass spectra were run on a Finnigan Model 4521 mass spectrometer by using electron impact ionization at 15 eV.

Preparation of $Os_3(CO)_9[C(H)NMe_2](\mu$-SPh$)(\mu$-H$)$, 2a. A heptane solution (200 mL) of **1a** (100 mg, 0.1041 mmol) and an excess of [*N*,-*N*,*N'*,*N'*-bis(dimethylamino)]methane (3.5 mL) was refluxed for 11 h. The solvent was removed in vacuo, and the residue was transferred to silica gel TLC plates in CH_2Cl_2 solvent. Elution with a 10% CH_2Cl_2/90% hexane solution separated in order of elution: unreacted **1a** (41 mg), a minor product, X (11 mg), $Os_3(CO)_9[C(H)NMe_2](\mu$-SPh$)(\mu$-H$)$, **2a** (39 mg (66%, based on the amount of **1a** consumed)), and a second minor product Y (7 mg); IR (ν(CO) in hexane solvent, cm⁻¹ for X 2062 (m), 2012 (s), 2002 (vs), 1990 (m), 1970 (w), 1945 (s), 1944 (w); for Y 2066 (m), 2032 (vs), 1992 (s), 1975 (m), 1959 (w), 1954 (m), 1932 (w); ¹H NMR (δ, in CD_2Cl_2 solvent) for X 7.42 (m, 5 H), 4.55 (d, J_{H-H} = 11.5 Hz, 1 H), 3.84 (s, 3 H), 3.79 (s, 3 H), 3.05 (s, 3 H), 2.83 (s, 3 H), 2.05 (d, J_{H-H} = 11.5 Hz, 1 H), −10.25 (s, 1 H); for Y 7.35 (m, 5 H), 3.82 (t, J_{H-H} = 1.8 Hz, 1 H), 3.75 (s, 3 H), 3.64 (s, 3 H), 3.51 (s, 3 H), 3.23 (s, 3 H), 2.35 (t, J_{H-H} = 1.8 Hz, 1 H), −15.99 (t, J_{H-H} = 1.6 Hz, 1 H). Compounds X and Y are still under investigation. IR and ¹H NMR spectra of **2a** are listed in Table I [Anal. Calcd for **2a**: C, 21.80; N, 1.41; H, 1.32. Found: C, 21.91; N, 1.42; H, 1.31. Mass spectrum for ¹⁹²Os *m/e* 995-28x, x = 0–6 ([M⁺] − *x*CO)]. By using similar procedures the following compounds were also prepared Os_3-$(CO)_9[C(H)NMe_2](\mu$-$SC_6F_5)(\mu$-H$)$, **2b** (47% yield), $Os_3(CO)_9[C(H)$-$NMe_2](\mu$-S-*p*-C_6H_4Me$)(\mu$-H$)$, **2c** (55%), and $Os_3(CO)_9[C(H)NEt_2](\mu$-S-*p*-$C_6H_4Me)(\mu$-H$)$, **2d** (31%). IR and ¹H NMR for compounds **2b–d** are listed in Table 1.

Photolysis of 2a. A cyclohexane solution (100 mL) of **2a** (40 mg, 0.0404 mmol) was subjected to UV irradiation for 30 min in the presence of a continuous purge with nitrogen. The solvent was removed in vacuo. The residue was extracted with a minimum of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with a 40% CH_2Cl_2/60% hexane solution separated $Os_3(CO)_8(\mu$-CNMe$_2)(\mu$-SPh$)(\mu$-H$)_2$, **3a** (15 mg (37%), and an inseparable mixture of two isomers. This mixture can be partially separated by TLC on alumina. Elution with a 30% CH_2Cl_2/70% hexane yielded $Os_3(CO)_8[C(H)NMe_2](\mu$-$SC_6H_4)(\mu$-H$)_2$, **4a** (13 mg, 32%) and **5a** (9 mg, 22%). Isomers **4a** and **5a** slowly interconvert in solution and arrive at 1.65/1.00 equilibrium in approximately 30 min at 25 °C. Anal. Calcd for **3a**: C, 21.21; N, 1.46; H, 1.29. Found: C, 21.15; N, 1.36; H, 1.29. Anal. Calcd for **4a**: C, 21.21; N, 1.46; H, 1.29. Found: C, 21.57; N, 1.44; H, 1.29. Also prepared by this method were $Os_3(CO)_8(\mu$-CNMe$_2)(\mu$-$SC_6F_5)(\mu$-H$)_2$, **3b** (53% yield), $Os_3(CO)_8(\mu$-CNMe$_2)(\mu$-S-*p*-C_6H_4Me$)(\mu$-H$)_2$, **3c** (35%), $Os_3(CO)_8(\mu$-CNEt$_2)(\mu$-S-*p*-C_6H_4Me$)(\mu$-H$)_2$, **3d** (21%), $Os_3(CO)_8[C(H)NMe_2](\mu$-$SC_6H_3Me)(\mu$-H$)_2$, **4c** (30%) and **5c** (20%), and $Os_3(CO)_8[C(H)$-$NEt_2](\mu$-SC_6H_3Me$)(\mu$-H$)_2$, **4d** (29%) and **5d** (21%). Isomers **4c** and **5c** equilibrate to a 1.60/1.00 mixture in solution at 25 °C in approximately 30 min. The rate of isomerization of **4d** and **5d** is considerably slower, and they can be separated and crystallized in a pure form. IR and ¹H

NMR spectra for these compounds are listed in Table I.

Thermolysis of 3a. An octane solution (10 mL) of **3a** (20 mg, 0.0208 mmol) was refluxed for 1 h. The solvent was removed in vacuo. The residue was dissolved in a minimum of CH_2Cl_2 and was chromatographed by TLC on silica gel. Elution with a 40% CH_2Cl_2/60% hexane solution separated $Os_3(CO)_8[C(Ph)NMe_2](\mu_3$-S$)(\mu$-H$)_2$, **6a** (12 mg, 60%) [Anal. Calcd for **6a**: C, 21.21; N, 2.46; H, 1.29. Found: C, 20.52; N, 1.17; H, 1.32. Mass spectrum for ¹⁹²Os *m/e* 967 − 28*x*, x = 0–5 ([M⁺] − *x*CO)]. By similar procedures the following compounds were also prepared: $Os_3(CO)_8[C(C_6F_5)NMe_2](\mu_3$-S$)(\mu$-H$)_2$, **6b** (55% yield), Os_3-$(CO)_8[C(C_6H_4$Me$)NMe_2](\mu_3$-S$)(\mu$-H$)$, **6c** (45%), and $Os_3(CO)_8[C$-$(C_6H_4$Me$)NEt_2](\mu_3$-S$)(\mu$-H$)_2$, **6d** (50%). IR and ¹H NMR spectra of **6a–d** are listed in Table I.

Thermolysis of 4a and 5a. A mixture of **4a** and **5a** (25 mg, 0.0026 mmol) was refluxed in hexane for 4 h. The solvent was removed in vacuo, and the residue was chromatographed by TLC on silica gel. Elution with a 30% CH_2Cl_2/70% hexane solvent mixture separated **3a** (22 mg, 88%).

Crossover Experiment between 3a and 3d. An octane solution (30 mL) of **3a** (7 mg, 0.0071 mmol) plus **3d** (7 mg, 0.0070 mmol) was refluxed for 1 h. The solvent was removed in vacuo, and the residue was chromatographed by TLC on silica gel. Elution with a 25% CH_2Cl_2/75% hexane solvent mixture separated the following compounds: **6d** (3 mg, 43%) and **6a** (mg, 57%). There was no evidence for the formation of compound **6c**.

Crystallographic Analyses. Crystals of **2a**, **5d**, and **6a** were grown by slow evaporation of solvent from CH_2Cl_2/hexane solutions at −20 °C. Crystals of **3a** were grown by slow evaporation of solutions in benzene solvent at 25 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo Kα radiation. Unit cells were determined and refined 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 II. All data processing was performed on a Digital Equipment Corp. MICROVAX I computer by using the Molecular Structure Corp. TEXSAN structure solving program library. Absorption corrections of a Gaussian integration type were done for each structure. Neutral atom scattering factors were obtained from the standard sources.[7a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[7b] Full-matrix least-squares refinements minimized the function

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

$$\sigma(F_{obsd}^2)/2F_{obsd}, \text{ and } \sigma(F_{obsd}^2) = [\sigma(I_{raw})^2 + (PF_{obsd}^2)^2]^{1/2}/Lp$$

Compounds **2a**, **5d** and **6a** crystallized in the monoclinic crystal system. The space groups $P2_1/n$ for **2a** and **5d** and $P2_1/c$ for **6a** were determined from systematic absences derived in the data. Compound **3a** 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. The structure of **3a** was solved by a combination of Patterson and difference Fourier techniques. The structures of **2a**, **5d**, and **6a** were solved by a combination of direct methods (MULTAN) and difference Fourier techniques. For compounds **2a**, **5d**, and **6a** all non-hydrogen atoms were refined with anisotropic thermal parameters. For **3a**, only atoms heavier than oxygen were refined anisotropically. For **2a** the coordinates of the carbene hydrogen atom were obtained from a difference Fourier synthesis. All other hydrogen atom positions were calculated by assuming idealized geometry. The contributions of all hydrogen atoms 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 for each structure. See Supplementary Material for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters for compounds **5d** and **6a**. For compounds **2a** and **3a** this information was published previously.[5]

Results

The reaction of the osmium clusters $Os_3(CO)_{10}(\mu$-SR$)(\mu$-H$)$, **1a**, R = Ph; **1b**, R = C_6F_5; and **1c**, R = *p*-C_6H_4Me with the diamines $CH_2(NR'_2)_2$ (R' = Me or Et) in refluxing heptane yielded the new carbene containing cluster complexes Os_3-$(CO)_9[C(H)NR'_2](\mu$-SR$)(\mu$-H$)$ (**2a**, R = Ph, R' = Me; **2b**, R = C_6F_5, R' = Me; **2c**, R = *p*-C_6H_4Me, R' = Me; **2d**, R = *p*-C_6H_4Me, R' = Et) as the major products (31–66% yield based on the amount of cluster reagent consumed). These compounds

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(7) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV (a) Table 2, 2B, pp 99–101 and (b) Table 2.3.1, pp 149–150.

Table I. IR and ^{1}H NMR Spectra

compound	IR (ν_{CO}) hexane solvent (cm^{-1})	^{1}H NMR, δ, CD$_2$Cl$_2$ Solvent
Os$_3$(CO)$_9$[C(H)NMe$_2$](μ-SPh)(μ-H), **2a**	2092 (m), 2052 (m), 2013 (vs), 2002 (w), 1996 (m), 1966 (w), 1940 (w)	11.71 (s, 1 H), 7.22 (m, 5 H), 3.61 (s, 3 H), 3.56 (s, 3 H), −17.24 (s, 1 H)
Os$_3$(CO)$_9$[C(H)NMe$_2$](μ-SC$_6$F$_5$)(μ-H), **2b**	2096 (m), 2059 (m), 2018 (vs), 2009 (w), 1999 (m), 1971 (w), 1947 (w)	11.93 (s, 1 H), 4.02 (s, 3 H), 3.39 (s, 3 H), −20.07 (s, 1 H)
Os$_3$(CO)$_9$[C(H)NMe$_2$](μ-S-p-C$_6$H$_4$CH$_3$)(μ-H), **2c**	2091 (m), 2052 (m), 2013 (vs), 2002 (w), 1996 (m), 1965 (w), 1939 (w)	11.72 (s, 1 H), 7.15 (m, 4 H), 3.61 (s, 1 H), 3.56 (s, 3 H), 2.28 (s, 3 H), −17.23 (s, 1 H)
Os$_3$(CO)$_9$[C(H)NEt$_2$](μ-S-p-C$_6$H$_4$CH$_3$)(μ-H), **2d**	2091 (m), 2051 (m), 2012 (vs), 2001 (w), 1995 (m), 1966 (w), 1937 (w)	11.81 (s, 1 H), 7.15 (m, 4 H), 3.96 (9, J_{H-H} = 7.3 Hz, 2 H), 3.70 (9, J_{H-H} = 7.3 Hz, 2 H), 2.28 (s, 3 H), 1.45 (t, J_{H-H} = 7.3 Hz, 3 H), 1.30 (t, J_{H-H} = 7.3 Hz, 3 H), −17.19 (s, 1 H)
Os$_3$(CO)$_8$(μ-CNMe$_2$)(μ-SPh)(μ-H), **3a**	2086 (m), 2050 (vs), 2020 (s), 2012 (s), 1999 (w), 1990 (m), 1975 (w), 1953 (m)	7.30 (m, 5 H), 4.01 (s, 3 H), 3.85 (s, 3 H), −13.71 (s, 1 H), −15.84 (s, 1 H)
Os$_3$(CO)$_8$(μ-CNMe$_2$)(μ-SC$_6$F$_5$)(μ-H)$_2$, **3b**	2090 (m), 2054 (vs), 2029 (s), 2018 (s), 2001 (w), 1996 (m), 1975 (w), 1953 (m)	3.97 (s, 3 H), 3.84 (s, 3 H), −13.34 (s, 1 H), −15.61 (s, 1 H)
Os$_3$(CO)$_8$(μ-CNMe$_2$)(μ-S-p-C$_6$H$_4$CH$_3$)(μ-H)$_2$, **3c**	2086 (m), 2050 (vs), 2020 (s), 2011 (s), 1999 (w), 1990 (m), 1974 (w), 1952 (m)	7.05 (m, 4 H), 4.04 (s, 3 H), 3.84 (s, 3 H), 2.11 (s, 3 H), −13.85 (s, 1 H), −15.83 (s, 1 H)
Os$_3$(CO)$_8$(μ-CNEt$_2$)(μ-S-p-C$_6$H$_4$CH$_3$)(μ-H)$_2$, **3d**	2085 (m), 2049 (vs), 2019 (s), 2011 (s), 1997 (w), 1989 (m), 1973 (w), 1950 (m)	7.11 (m, 3 H), 4.03 (9, J_{H-H} = 7.3 Hz, 2 H), 3.75 (9, J_{H-H} = 7.3 Hz, 2 H), 2.06 (s, 3 H), 1.35 (t, J_{H-H} = 7.3 Hz, 3 H), 1.04 (t, J_{H-H} = 7.3 Hz, 2 H), −13.92 (s, 1 H), −15.95 (s, 1 H)
Os$_3$(CO)$_8$[C(H)NMe$_2$](μ-SC$_6$H$_4$)(μ-H)$_2$, **4a**	2083 (s), 2045 (vs), 2037 (s), 2004 (s), 1991 (m), 1984 (w), 1970 (m)	11.32 (s, 1 H), 7.15 (m, 4 H), 3.78 (s, 3 H), 3.58 (s, 3 H), −14.28 (s, 1 H), −15.94 (s, 1 H)
Os$_3$(CO)$_8$[C(H)NMe$_2$](μ-SC$_6$H$_3$CH$_3$)(μ-H)$_2$, **4c**	2083 (s), 2045 (vs), 2037 (s), 2004 (s), 1991 (m), 1983 (w), 1969 (m)	11.33 (s, 1 H), 7.19 (m, 3 H), 3.71 (s, 3 H), 3.59 (s, 3 H), 2.16 (s, 3 H), −14.33 (s, 1 H), −15.94 (s, 1 H)
Os$_3$(CO)$_8$[C(H)NEt$_2$](μ-SC$_6$H$_3$CH$_3$)(μ-H)$_2$, **4d**	2082 (s), 2044 (vs), 2039 (s), 2003 (s), 1990 (m), 1983 (w), 1968 (m)	11.39 (s, 1 H), 7.27 (m, 3 H), 4.12 (9, J_{H-H} = 7.3 Hz, 2 H), 3.68 (9, J_{H-H} = 7.3 Hz, 2 H), 2.06 (s, 3 H), 1.49 (t, J_{H-H} = 7.3 Hz, 3 H), 1.08 (t, J_{H-H} = −14.48 Hz, 3 H), −14.48 (s, 1 H), −15.94 (s, 1 H)
Os$_3$(CO)$_8$[C(H)NMe$_2$](μ-SC$_6$H$_4$)(μ-H)$_2$, **5a**	2082 (s), 2046 (vs), 2037 (w), 2004 (vs), 1986 (m), 1973 (w), 1967 (s)	10.35 (s, 1 H), 7.17 (m, 4 H), 3.76 (s, 3 H), 3.68 (s, 3 H), −14.96 (s, 1 H), −15.31 (s, 1 H)
Os$_3$(CO)$_8$[C(H)NMe$_2$](μ-SC$_6$H$_3$CH$_3$)(μ-H)$_2$, **5c**	2082 (s), 2046 (vs), 2037 (w), 2004 (vs), 1986 (m), 1973 (w), 1966 (s)	10.37 (s, 1 H), 7.14 (m, 4 H), 3.80 (s, 3 H), 3.64 (s, 3 H), −14.91 (s, 1 H), −15.38 (s, 1 H)
Os$_3$(CO)$_8$[C(H)NEt$_2$](μ-SC$_6$H$_3$CH$_3$)(μ-H)$_2$, **5d**	2081 (s), 2045 (vs), 2035 (w), 2003 (vs), 1984 (m), 1972 (w), 1965 (s)	10.42 (s, 1 H), 7.10 (m, 3 H), 4.15 (9, J_{H-H} = 7.3 Hz, 2 H), 3.71 (9, J_{H-H} = 7.3 Hz, 2 H), 2.11 (s, 3 H), 1.33 (t, J_{H-H} = 7.3 Hz, 3 H), 1.02 (t, J_{H-H} = −14.96 Hz, 3 H), −14.96 (s, 1 H), −15.37 (s, 1 H)
Os$_3$(CO)$_8$[C(Ph)NMe$_2$](μ_3-S)(μ-H)$_2$, **6a**	2082 (s), 2046 (vs), 2036 (m), 2002 (vs), 1986 (s), 1973 (w), 1957 (w)	7.13 (m, 5 H), 3.86 (s, 3 H), 3.07 (s, 3 H), 20.68 (s, 1 H), −21.72 (s, 1 H)
Os$_3$(CO)$_8$[C(C$_6$F$_5$)NMe$_2$](μ_3-S)(μ-H)$_2$, **6b**	2085 (s), 2050 (vs), 2041 (m), 2005 (vs), 1990 (w), 1980 (w), 1985 (w)	3.91 (s, 3 H), 3.07 (s, 3 H), −20.83 (s, 1 H), −21.80 (s, 1 H)
Os$_3$(CO)$_8$[C(p-C$_1$H$_4$CH$_3$)NMe$_2$](μ_3-S)(μ-H)$_2$, **6c**	2082 (s), 2046 (vs), 2036 (m), 2002 (vs), 1985 (s), 1973 (w), 1958 (w)	7.08 (m, 4 H), 3.85 (s, 3 H), 3.09 (s, 3 H), 2.09 (s, 3 H), −20.42 (s, 1 H), −21.88 (s, 1 H)
Os$_3$(CO)$_8$[C(p-C$_6$H$_4$CH$_3$)NEt$_2$](μ_3-S)(μ-H)$_2$, **6d**	2082 (s), 2046 (vs), 2035 (m), 2001 (vs), 1985 (s), 1971 (w), 1960 (w)	6.99 (m, 4 H), 4.63 (9, J_{H-H} = 7.3 Hz, 2 H), 3.99 (9, J_{H-H} = 7.3 Hz, 2 H), 2.42 (s, 1 H), 1.53 (t, J_{H-H} = 7.3 Hz, 3 H), 1.42 (t, J_{H-H} = 7.3 Hz, 3 H), −21.81 (s, 1 H), −21.81 (s, 1 H)

Table II. Crystallographic Data for X-ray Diffraction Studies

	compound			
	2a	**3a**	**5d**	**6a**
formula	$Os_3SO_9NC_{18}H_{13}$	$Os_3SO_8NC_{17}H_{13}$	$Os_3SO_8NC_{20}H_{19}$	$Os_3SO_8NC_{17}H_{13}$
temp (±3 °C)	23 °C	23 °C	23 °C	23 °C
space group	$P2_1/n$, no. 14	$P\bar{1}$, no. 2	$P2_1/n$, no. 14	$P2_1/c$, no. 14
a (Å)	15.841 (3)	9.278 (1)	12.711 (2)	7.987 (2)
b (Å)	10.246 (2)	32.668 (5)	14.410 (2)	8.930 (2)
c (Å)	15.594 (3)	7.644 (1)	14.447 (2)	31.794 (4)
α (deg)	90.0	90.26 (1)	90.0	90.0
β (deg)	111.23 (1)	99.99 (1)	109.08 (1)	96.37 (1)
γ (deg)	90.0	96.07 (1)	90.0	90.0
V (Å³)	2359.3 (7)	2268.4 (5)	2500.7 (6)	2253.7 (6)
M_r	989.7	961.7	1003.8	961.7
Z	4	4	4	4
ρ_{calcd} (g/cc)	2.58	2.82	2.63	2.83

(A) Measurement of Intensity Data

radiatn	Mo Kα	Mo Kα	Mo Kα	Mo Kα
monochromatr	graphite	graphite	graphite	graphite
detctr aptre (mm)				
horizntl	2.0	2.0	2.0	2.0
vertcl	2.0	2.0	2.0	2.0
cryst faces	101, $\bar{1}0\bar{1}$, $\bar{1}\bar{1}1$, $1\bar{1}\bar{1}$, $11\bar{1}$, $\bar{1}11$	010, $0\bar{1}0$, 100, $\bar{1}00$, 001, $00\bar{1}$	$10\bar{1}$, $\bar{1}01$, $\bar{1}2\bar{1}$, $1\bar{2}1$, 110, $\bar{1}\bar{1}0$	001, $00\bar{1}$, 010, $0\bar{1}0$, $10\bar{1}$, $\bar{1}01$
cryst size (mm)	0.05, 0.21, 0.26	0.05, 0.10, 0.26	0.02, 0.12, 0.20	0.11, 0.22, 0.35
cryst orientn lattice dirctn; deg from R θ-axis	[101]; 1.2	[010]; 0.6	[1$\bar{2}$1]; 0.9	[001]; 2.8
rflctns measd	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
max 2θ	48°	47°	46°	50°
scan type	moving cryst-statnary cnter	moving cryst-statnary cnter	moving cryst-statnary cnter	moving cryst-statnary cnter
ω-scan width: $A =$ ($A + 0.347\tan \theta$)°	1.10	1.10	1.10	1.10
background (count time at each end of scan)	9.0 s	9.0 s	9.0 s	9.0 s
ω-scan rate[a] (deg/min)	4.0	4.0	4.0	4.0
no. reflctns measd	4096	7189	3838	4578
data used ($F^2 \geq$ 3.0 $\sigma(F^2)$)	2800	4616	2325	3204

(B) Treatment of Data

absrptn corrctn	applied	applied	applied	applied
coeff (cm⁻¹)	172.0	178.9	162.3	180.1
grid	8 × 8 × 8	10 × 6 × 16	8 × 10 × 10	16 × 10 × 6
transmssn coeff				
max	0.399	0.44	0.74	0.17
min	0.089	0.17	0.18	0.03
P factor	0.03	0.02	0.03	0.02
final residuals R_F	0.036	0.053	0.034	0.030
R_{wF}	0.044	0.059	0.036	0.033
esd of unit wt obsrvtn	1.65	2.28	1.16	1.72
largest shift/error value of final cycle	0.06	0.08	0.05	0.03
largest peak in final diff Fourier (e⁻/Å³)	1.50	1.98	1.0	0.6

[a] Rigaku software uses a multiple scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made, and the results are added to the first scan, etc. A maximum of three scans was permitted per reflection.

were characterized by IR and ¹H NMR spectroscopies and by a single-crystal X-ray diffraction analysis of compound **2a**. The crystallographic positional parameters are listed in Table III. Interatomic distances and angles are listed in Tables IV and V, respectively. An ORTEP drawing of the molecular structure of **2a** is shown in Figure 1. The molecule consists of a triangular cluster of three metal atoms with one edge bridged by a benzenethiolato ligand. To this extent the structure is very similar to that of the compound $Os_3(CO)_{10}(\mu\text{-SEt})(\mu\text{-H})$ both qualitatively and quantitatively.[8] A secondary (dimethylamino)carbene ligand, C-(H)NMe₂, is coordinated in a terminal fashion to atom Os(3). The Os(3)–C distance of 2.02 (2) Å is very similar to that observed in the related complex $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-S})(\mu\text{-H})_2$, **7**,

Os–C = 2.026 (15) and 2.04 (2) Å.[4] The nitrogen atom is planar, and the C–N distance of 1.28 (2) Å is typical of that observed in aminocarbene ligands.[9] The coordinates of the carbene containing hydrogen atom were obtained in a chemically reasonable position from a difference Fourier synthesis, C–H = 1.06 Å. Its ¹H NMR signal was observed at a characteristically low-field shift value $\delta = 11.71$ ppm.[10] The compound contains eight linear terminal carbonyl ligands distributed as shown in Figure 1. The hydride ligand was not observed crystallographically, but it is believed to bridge the Os(2)–Os(3) bond. Its ¹H NMR signal

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Table III. Positional Parameters and B(eq) for
$Os_3(CO)_9[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$ (**2a**)

atom	x	y	z	B(eq)
Os1	0.186881 (42)	0.222008 (57)	0.014122 (44)	3.5
Os2	0.195749 (42)	0.462806 (53)	−0.076408 (44)	3.0
Os3	0.117969 (41)	0.236327 (51)	−0.183529 (42)	3.2
S	0.03496 (25)	0.41908 (33)	−0.15360 (26)	3.3
O11	0.2873 (10)	0.2685 (15)	0.2207 (10)	6.6
O12	0.37067 (88)	0.1587 (13)	−0.0041 (11)	9.7
O13	0.1236 (11)	−0.0607 (12)	−0.0026 (11)	6.9
O14	0.00859 (96)	0.3134 (13)	0.03325 (99)	9.1
O21	0.20209 (91)	0.7143 (11)	−0.17563 (97)	6.2
O22	0.18238 (88)	0.6012 (13)	0.09188 (86)	5.2
O23	0.40022 (92)	0.4608 (14)	0.0075 (12)	7.6
O31	0.07310 (98)	0.2587 (13)	−0.38876 (83)	6.3
O32	0.24923 (92)	0.0219 (11)	−0.18275 (95)	7.9
N	−0.0161 (10)	0.0058 (12)	−0.22976 (97)	4.7
C	0.0106 (11)	0.1196 (14)	−0.1975 (10)	3.4
C1	−0.0974 (15)	−0.0583 (17)	−0.2264 (15)	5.9
C2	0.0305 (16)	−0.0722 (21)	−0.2783 (18)	6.3
C11	0.2469 (12)	0.2521 (16)	0.1406 (13)	4.2
C12	0.3057 (13)	0.1822 (16)	0.0035 (13)	6.0
C13	0.1498 (11)	0.0455 (16)	0.0026 (12)	4.5
C14	0.0711 (13)	0.2831 (15)	0.0197 (12)	4.9
C21	0.19732 (90)	0.6167 (15)	−0.14180 (99)	2.3
C22	0.1856 (11)	0.5500 (15)	0.0287 (14)	5.3
C23	0.3227 (12)	0.4618 (16)	−0.0237 (14)	5.0
C31	0.0863 (11)	0.2555 (13)	−0.3126 (12)	3.7
C32	0.2006 (12)	0.1040 (15)	−0.1805 (11)	4.6
C41	−0.0200 (10)	0.5149 (12)	−0.25596 (96)	3.4
C42	0.0196 (11)	0.5476 (14)	−0.3190 (12)	4.3
C43	−0.0311 (13)	0.6160 (15)	−0.3982 (11)	4.0
C44	−0.1183 (11)	0.6529 (16)	−0.4120 (11)	4.0
C45	−0.1556 (10)	0.6239 (15)	−0.3474 (12)	3.0
C46	−0.10624 (96)	0.5554 (13)	−0.2697 (10)	3.5

Table IV. Intramolecular Distances for
$Os_3(CO)_9[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$ (**2a**)^a

atom	atom	distance	atom	atom	distance
Os1	C11	1.88 (2)	O12	C12	1.11 (2)
Os1	C13	1.89 (2)	O13	C13	1.16 (2)
Os1	C14	1.97 (2)	O14	C14	1.13 (2)
Os1	C12	1.99 (2)	O21	C21	1.15 (2)
Os1	Os2	2.8711 (9)	O22	C22	1.13 (2)
Os1	Os3	2.877 (1)	O23	C23	1.15 (2)
Os2	C23	1.88 (2)	O31	C31	1.13 (2)
Os2	C21	1.88 (1)	O32	C32	1.15 (2)
Os2	C22	1.92 (2)	N	C	1.28 (2)
Os2	S	2.433 (4)	N	C1	1.46 (2)
Os2	Os3	2.8640 (9)	N	C2	1.47 (3)
Os3	C32	1.87 (2)	C41	C46	1.37 (2)
Os3	C31	1.90 (2)	C41	C42	1.38 (2)
Os3	C	2.02 (2)	C42	C43	1.39 (2)
Os3	S	2.428 (4)	C43	C44	1.37 (2)
S	C41	1.81 (1)	C44	C45	1.37 (2)
O11	C11	1.19 (2)	C45	C46	1.37 (2)

^{a} Distances are in Å. esd's in the least significant figure are given in parentheses.

was observed at a characteristically high field shift $\delta = -17.24$ ppm.

When the compounds **3a–d** were irradiated under a nitrogen purge, three products were formed as a result of the loss of a CO ligand. The major product was the (dialkylamino)carbyne containing cluster complexes $Os_3(CO)_8(\mu\text{-CNR}'_2)(\mu\text{-SR})(\mu\text{-H})_2$ (**3a**, R = Ph, R' = Me; **3b**, R = C_6F_5, R' = Me; **3c**, R = $p\text{-}C_6H_4Me$, R' = Me; **3d**, R = $p\text{-}C_6H_4Me$, R' = Et). The structure of **3a** was determined by an X-ray crystallographic analysis. Positional parameters for **3a** are listed in Table VI. Interatomic distances and angles are listed in Tables VII and VIII, respectively. Two independent but structurally similar molecules of **3a** were found in the asymmetric crystal unit. An ORTEP drawing of one of these is shown in Figure 2. The structure of **3a** consists of a triangular cluster of three osmium atoms, but the metal–metal bond lengths vary considerably: Os(1)–Os(2) = 2.942 (2) Å [2.933 (1) Å], Os(2)–Os(3) = 2.842 (1) Å [2.850 (1) Å], and Os(1)–Os(3) at 2.791 (1) Å [2.794 (1) Å]. The Os(2)–Os(3) distance is sym-
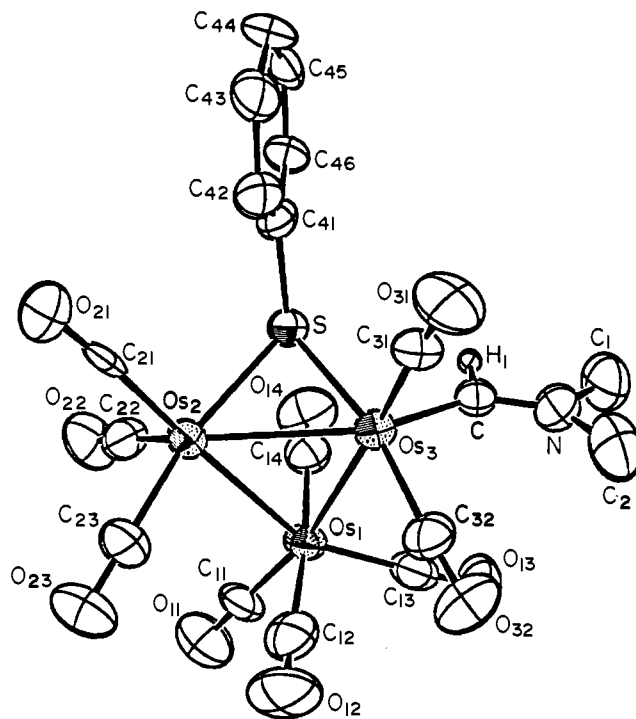
Figure 1. An ORTEP diagram of $Os_3(CO)_9[C(H)NMe_2](\mu\text{-SPh})(\mu\text{-H})$, **2a**, showing 50% probability thermal ellipsoids. The hydrogen atom H(1) is shown with an arbitrarily assigned temperature factor of $B = 1.0$ Å^2.
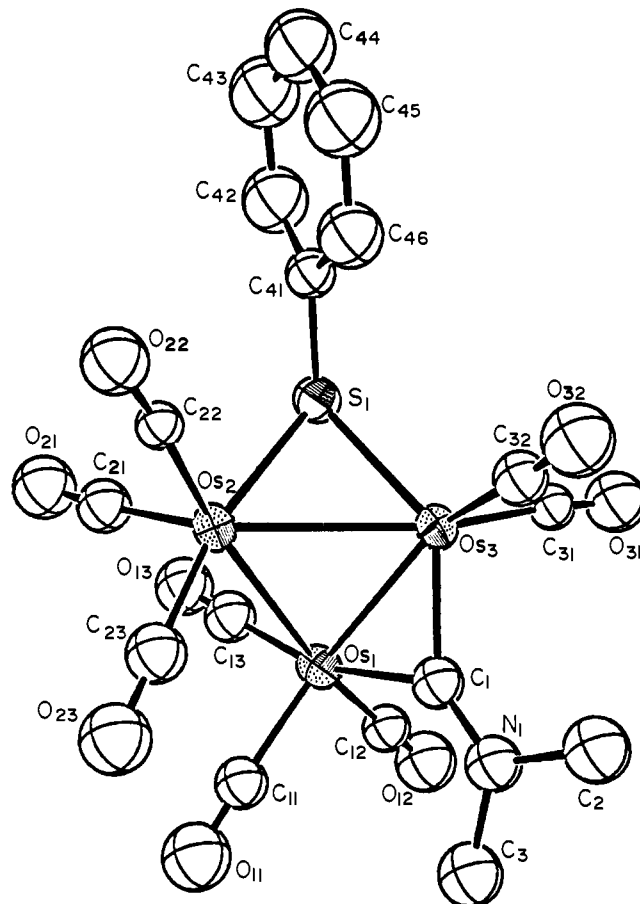
Figure 2. An ORTEP diagram of one of the two crystallographically independent molecules of $Os_3(CO)_8(\mu\text{-C}=NMe_2)(\mu\text{-SPh})(\mu\text{-H})_2$, **3a**, showing 50% probability thermal ellipsoids.

metrically bridged by a benzenethiolato ligand. The Os(1)–Os(3) distance is bridged by a (dimethylamino)carbyne ligand. The carbon atom is bonded in a slightly asymmetric fashion to the

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Table V. Intramolecular Bond Angles for $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}SPh)(\mu\text{-}H)$ (2a)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C11	Os1	C13	106.2 (7)	C21	Os2	Os1	176.9 (4)	C41	S	Os2	114.9 (5)
C11	Os1	C14	91.6 (8)	C22	Os2	S	96.4 (5)	Os3	S	Os2	72.2 (1)
C11	Os1	C12	89.2 (8)	C22	Os2	Os3	136.2 (5)	C	N	C1	124 (2)
C11	Os1	Os2	106.2 (5)	C22	Os2	Os1	86.9 (5)	C	N	C2	123 (2)
C11	Os1	Os3	165.4 (5)	S	Os2	Os3	53.83 (8)	C1	N	C2	113 (1)
C13	Os1	C14	92.6 (7)	S	Os2	Os1	81.73 (8)	N	C	Os3	137 (1)
C13	Os1	C12	93.8 (7)	Os3	Os2	Os1	60.22 (3)	O11	C11	Os1	178 (2)
C13	Os1	Os2	147.6 (5)	C32	Os3	C31	90.9 (7)	O12	C12	Os1	179 (2)
C13	Os1	Os3	87.9 (5)	C32	Os3	C	97.3 (6)	O13	C13	Os1	176 (2)
C14	Os1	C12	173.0 (6)	C32	Os3	S	167.2 (5)	O14	C14	Os1	172 (2)
C14	Os1	Os2	87.7 (4)	C32	Os3	Os2	115.0 (5)	O21	C21	Os2	175 (1)
C14	Os1	Os3	91.9 (5)	C32	Os3	Os1	86.9 (5)	O22	C22	Os2	178 (2)
C12	Os1	Os2	85.4 (4)	C31	Os3	C	93.3 (6)	O23	C23	Os2	179 (2)
C12	Os1	Os3	85.7 (6)	C31	Os3	S	99.8 (4)	O31	C31	Os3	174 (1)
Os2	Os1	Os3	59.77 (2)	C31	Os3	Os2	115.3 (4)	O32	C32	Os3	177 (2)
C23	Os2	C21	91.1 (6)	C31	Os3	Os1	172.9 (5)	C46	C41	C42	120 (1)
C23	Os2	C22	92.1 (8)	C	Os3	S	89.1 (4)	C46	C41	S	116 (1)
C23	Os2	S	168.4 (5)	C	Os3	Os2	135.1 (4)	C42	C41	S	124 (1)
C23	Os2	Os3	114.6 (5)	C	Os3	Os1	93.6 (4)	C41	C42	C43	119 (1)
C23	Os2	Os1	90.9 (5)	S	Os3	Os2	54.0 (1)	C44	C43	C42	120 (1)
C21	Os2	C22	95.4 (6)	S	Os3	Os1	81.7 (1)	C45	C44	C43	120 (1)
C21	Os2	S	95.9 (4)	Os2	Os3	Os1	60.01 (2)	C44	C45	C46	120 (1)
C21	Os2	Os3	116.7 (4)	C41	S	Os3	111.7 (4)	C41	C46	C45	121 (1)

[a] Angles are in deg. esd's in the least significant figure are given in parentheses.

metal atoms with distances of $Os(1)-C(1) = 2.12$ (2) Å [2.10 (2) Å] and $Os(3)-C(1) = 2.00$ (2) Å [2.00 (2) Å]. It is structurally similar to one found in the cluster $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$, 8.[11] The $C(1)-N(1)$ distance of 1.27 (3) Å [1.32 (3) Å] is similar to that in 8, 1.279 (5) Å [1.280 (6) Å]. There are two inequivalent hydride ligands which were not observed crystallographically but were observed in the ^1H NMR spectrum at -13.71 and -15.84 ppm.

Two additional products were obtained from each of the photolysis reactions of 2a, 2c, and 2d. Both of these products appear to be ring metalated isomers with the formulas $Os_3(CO)_8[C(H)NR'_2](\mu_3\text{-}SC_6H_3R)(\mu\text{-}H)_2$ (4a and 5a, R = H, R' = Me; 4c and 5c, R = Me, R' = Me; 4d and 5d, R = Me, R' = Et). This was confirmed for the compound 5d which was separated from 4d in a pure form, crystallized, and analyzed by a single-crystal X-ray diffraction analysis. The ring metalation of 4d was established from its ^1H NMR spectrum which shows aryl proton resonance with a total relative intensity of three and the presence of two hydride ligands. Compounds 4a and 5a and 4c and 5c can be partially separated chromatographically, but they equilibrate in solution and achieve equilibria of 1.65/1.00 and 1.60/1.00 within approximately 30 min at 25 °C. The ^1H NMR spectra of 4a, 5a, 4b, and 5b indicate that they are ring-metalated species analogous to 4d and 5d.

An ORTEP drawing of 5d is shown in Figure 3. Final positional parameters are listed in Table IX. Interatomic distances and angles are listed in Tables X and XI, respectively. The cluster consists of a triangle of osmium atoms with one very long osmium–osmium bond, $Os(1)-Os(3) = 3.034$ (1) Å. The other metal–metal distances are similar to those of 2a, $Os(1)-Os(2) = 2.842$ (1) Å and $Os(2)-Os(3) = 2.882$ (1) Å. A (diethylamino)carbene ligand is bonded to $Os(3)$, $Os(3)-C(1) = 2.03$ (2) Å, and is structurally similar to the carbene ligands in 2a and 7.[4] The carbenoid hydrogen atom $H(1)$ is shown in an idealized position in Figure 3. Its ^1H NMR resonance was observed in the characteristically low-field region, $\delta = 10.42$ ppm. Two inequivalent hydride ligands were detected by ^1H NMR spectroscopy, -14.96 and -15.37 ppm, but were not observed crystallographically. One is believed to bridge the long $Os(1)-Os(3)$ bond. The other is believed to bridge the $Os(2)-Os(3)$ bond on the side of the cluster opposite the sulfur atom. The p-tolyl group has been ortho-metalated and bonded to the third metal atom $Os(1)$ by the ortho ring carbon $C(42)$, $Os(1)-C(42) = 2.15$ (1) Å.

Figure 3. An ORTEP diagram of $Os_3(CO)_8[C(H)NEt_2](\mu_3\text{-}SC_6H_3Me)(\mu\text{-}H)_2$, 5d, showing 50% probability thermal ellipsoids. The hydrogen atom $H(1)$ is shown with an arbitrarily assigned temperature factor of $B = 1.0$ Å^2.
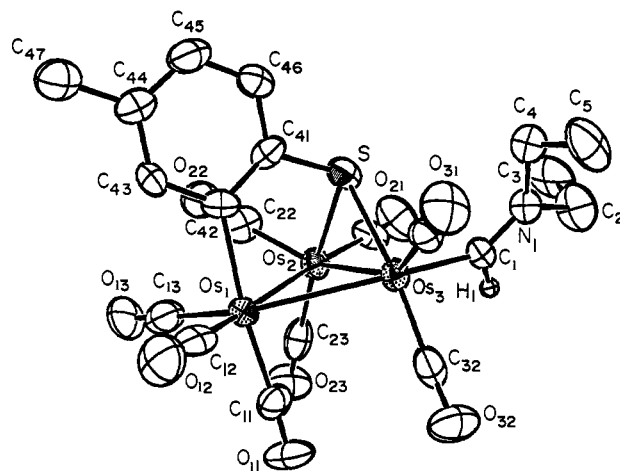
When the compounds 3a–d were heated to reflux in an octane solution for 1 h, the aryl group of the thiolato ligand in each compound was transferred to the carbon atom of the carbyne ligand to yield the aryl(dialkylamino)carbene containing cluster complexes $Os_3(CO)_8[C(R)NR'_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (6a, R = Ph, R' = Me; 6b, R = C_6F_5, R' = Me; 6c, R = $C_6H_4CH_3$, R' = Me; 6d, R = $C_6H_4CH_3$, R' = Et) in good yields. The molecular structure of 6a was determined by an X-ray crystallographic analysis. Positional parameters are listed in Table XII. Interatomic distances and angles are listed in Tables XIII and XIV, respectively. An ORTEP diagram of 6a is shown in Figure 4. The cluster consists of a triangle of osmium atoms capped by a triply bridging sulfido ligand. Two of the osmium–osmium distances are significantly longer than the third, $Os(1)-Os(3) = 2.9225$ (6), $Os(2)-Os(3) = 2.9192$ (7), and $Os(1)-Os(2) = 2.7815$ (7) Å. The long bonds are believed to contain the inequivalent bridging hydride ligands. Similar increases in the metal–metal bond lengths were observed for the hydride bridged bonds in $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$.[12] A phenyl(dimethylamino)carbene ligand is coordinated to $Os(3)$ in a terminal mode. The metal–carbon and carbon–nitrogen bonding distances, $Os(3)-C(1) = 2.07$ (1) and

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Table VI. Positional Parameters and *B*(eq) for Os₃(CO)₈(μ-CNMe₂)(μ-SPh)(μ-H)₂ (**3a**)

atom	x	y	z	B(eq)
Os1A	0.04430 (11)	0.184159 (33)	0.17710 (15)	3.72 (4)
Os1B	0.81234 (10)	0.326816 (31)	0.49156 (13)	2.98 (4)
Os2A	0.05216 (12)	0.095696 (34)	0.24264 (16)	4.15 (5)
Os2B	0.509585 (97)	0.345947 (29)	0.37199 (13)	2.76 (4)
Os3A	0.31230 (11)	0.151480 (31)	0.27114 (14)	3.45 (4)
Os3B	0.753591 (96)	0.408173 (29)	0.43085 (12)	2.70 (4)
S1A	0.21887 (73)	0.11710 (22)	0.52049 (94)	4.2 (3)
S1B	0.60741 (63)	0.38651 (19)	0.14220 (77)	3.0 (2)
O11A	−0.2104 (27)	0.17130 (78)	−0.1327 (33)	7.7 (6)
O11B	0.7461 (22)	0.26225 (68)	0.7638 (28)	6.2 (5)
O12A	0.0793 (24)	0.27839 (75)	0.1482 (30)	6.8 (5)
O12B	1.1332 (23)	0.31732 (68)	0.5808 (28)	6.3 (5)
O13A	−0.1611 (27)	0.18298 (78)	0.4558 (33)	7.8 (6)
O13B	0.7399 (22)	0.26704 (66)	0.1671 (28)	5.8 (5)
O21A	−0.2097 (26)	0.08500 (76)	0.4412 (32)	7.5 (6)
O21B	0.4070 (22)	0.27328 (65)	0.1082 (27)	5.7 (5)
O22A	0.1214 (28)	0.00654 (88)	0.2600 (36)	8.6 (7)
O22B	0.2135 (18)	0.37795 (55)	0.3056 (23)	4.3 (4)
O23A	−0.1172 (27)	0.08444 (80)	−0.1372 (35)	8.2 (6)
O23B	0.4544 (21)	0.30167 (62)	0.7021 (27)	5.4 (4)
O31A	0.5389 (22)	0.21993 (65)	0.4409 (27)	5.8 (5)
O31B	1.0321 (21)	0.45814 (61)	0.3708 (25)	5.3 (4)
O32A	0.5514 (26)	0.10793 (77)	0.1515 (32)	7.7 (6)
O32B	0.6556 (19)	0.48675 (62)	0.5516 (25)	5.2 (4)
N1A	0.2697 (22)	0.19301 (66)	−0.0892 (28)	4.0 (4)
N1B	0.8894 (21)	0.38949 (64)	0.8206 (27)	3.7 (4)
C1A	0.2274 (25)	0.17903 (76)	0.0502 (32)	3.4 (5)
C1B	0.8373 (24)	0.38024 (75)	0.6523 (31)	3.3 (5)
C2A	0.4203 (29)	0.43256 (90)	0.8906 (37)	4.7 (6)
C2B	0.8954 (29)	0.43256 (90)	0.8906 (37)	4.7 (6)
C3A	0.1783 (31)	0.21430 (93)	−0.2313 (39)	5.1 (6)
C3B	0.9491 (30)	0.35911 (92)	0.9506 (38)	5.0 (6)
C11A	−0.1146 (33)	0.17687 (98)	−0.0103 (42)	5.5 (7)
C11B	0.7652 (26)	0.28626 (81)	0.6616 (33)	3.7 (5)
C12A	0.0598 (35)	0.2425 (11)	0.1579 (45)	6.2 (7)
C12B	1.0084 (26)	0.32067 (78)	0.5481 (32)	3.6 (5)
C13A	−0.0786 (37)	0.1813 (11)	0.3542 (47)	6.6 (8)
C13B	0.7650 (28)	0.28858 (86)	0.2922 (36)	4.2 (5)
C21A	−0.1169 (36)	0.0895 (11)	0.3638 (44)	6.2 (7)
C21B	0.4482 (27)	0.29935 (83)	0.2125 (34)	3.9 (5)
C22A	0.0922 (32)	0.0394 (10)	0.2669 (41)	5.5 (7)
C22B	0.3256 (21)	0.36773 (65)	0.3291 (27)	2.3 (4)
C23A	−0.0551 (35)	0.0873 (10)	0.0073 (45)	6.0 (7)
C23B	0.4776 (27)	0.31834 (83)	0.5727 (35)	4.1 (5)
C31A	0.4466 (28)	0.19442 (86)	0.3762 (35)	4.3 (5)
C31B	0.9246 (24)	0.44043 (71)	0.3886 (29)	2.8 (4)
C32A	0.4591 (34)	0.1245 (10)	0.2217 (43)	6.0 (7)
C32B	0.6943 (24)	0.45698 (77)	0.5096 (31)	3.2 (5)
C41A	0.3108 (27)	0.07477 (83)	0.6099 (35)	4.1 (5)
C41B	0.4748 (23)	0.41821 (72)	0.0383 (30)	3.0 (4)
C42A	0.2358 (37)	0.0484 (11)	0.7128 (46)	6.6 (8)
C42B	0.4339 (33)	0.4144 (10)	−0.1469 (42)	5.7 (7)
C43A	0.3035 (38)	0.0148 (12)	0.7917 (47)	7.0 (8)
C43B	0.3276 (34)	0.4377 (11)	−0.2375 (43)	6.1 (7)
C44A	0.4477 (39)	0.0100 (12)	0.7730 (48)	7.1 (9)
C44B	0.2761 (32)	0.46722 (97)	−0.1501 (41)	5.4 (7)
C45A	0.5188 (41)	0.0369 (12)	0.6778 (51)	8 (1)
C45B	0.3187 (33)	0.4720 (10)	0.0311 (43)	5.8 (7)
C46A	0.4499 (35)	0.0701 (11)	0.6005 (44)	6.2 (7)
C46B	0.4206 (29)	0.44896 (39)	0.1203 (36)	4.7 (6)

Table VII. Intramolecular Distances for Os₃(CO)₈(C=NMe₂)(SPh)(H)₂ (**3a**)[a]

atom	atom	distance	atom	atom	distance
Os1A	C11A	1.86 (3)	O11A	C11A	1.17 (3)
Os1A	C12A	1.91 (4)	O12A	C12A	1.17 (4)
Os1A	C13A	1.91 (4)	O12B	C12B	1.16 (3)
Os1A	C1A	2.12 (2)	O13B	C13B	1.16 (3)
Os1A	Os3A	2.791 (1)	O13A	C13A	1.19 (4)
Os1A	Os2A	2.942 (2)	O21B	C21B	1.15 (3)
Os1B	C12B	1.83 (2)	O21A	C21A	1.12 (3)
Os1B	C13B	1.93 (3)	O22B	C22B	1.11 (2)
Os1B	C11B	1.93 (3)	O22A	C22A	1.14 (4)
Os1B	C1B	2.10 (2)	O23A	C23A	1.15 (4)
Os1B	Os3B	2.794 (1)	O23B	C23B	1.17 (3)
Os1B	Os2B	2.933 (1)	O31B	C31B	1.13 (2)
Os2A	C23A	1.90 (3)	O31A	C31A	1.17 (3)
Os2A	C22A	1.92 (4)	O32A	C32A	1.25 (4)
Os2A	C21A	1.95 (3)	O32B	C32B	1.14 (3)
Os2A	S1A	2.452 (7)	N1B	C1B	1.32 (3)
Os2A	Os3A	2.842 (1)	N1B	C3B	1.49 (3)
Os2B	C23B	1.84 (3)	N1B	C2B	1.49 (3)
Os2B	C22B	1.90 (2)	N1A	C1A	1.27 (3)
Os2B	C21B	1.92 (3)	N1A	C3A	1.48 (3)
Os2B	S1B	2.447 (6)	N1A	C2A	1.51 (3)
Os2B	Os3B	2.850 (1)	C41B	C46B	1.37 (3)
Os3B	C32B	1.87 (3)	C41B	C42B	1.40 (4)
Os3B	C31B	1.89 (2)	C41A	C46A	1.33 (4)
Os3B	C1B	2.00 (2)	C41A	C42A	1.38 (4)
Os3B	S1B	2.440 (6)	C42B	C43B	1.40 (4)
Os3A	C32A	1.79 (3)	C42A	C43A	1.41 (5)
Os3A	C31A	1.85 (3)	C43A	C44A	1.40 (5)
Os3A	C1A	2.00 (2)	C43B	C44B	1.34 (4)
Os3A	S1A	2.456 (7)	C44A	C45A	1.34 (5)
S1B	C41B	1.78 (2)	C44B	C45B	1.38 (4)
S1A	C41A	1.78 (3)	C45A	C46A	1.40 (5)
O11B	C11B	1.13 (3)	C45B	C46B	1.36 (4)

[a] Distances are in Å. esd's in the least significant figure are given in parentheses.
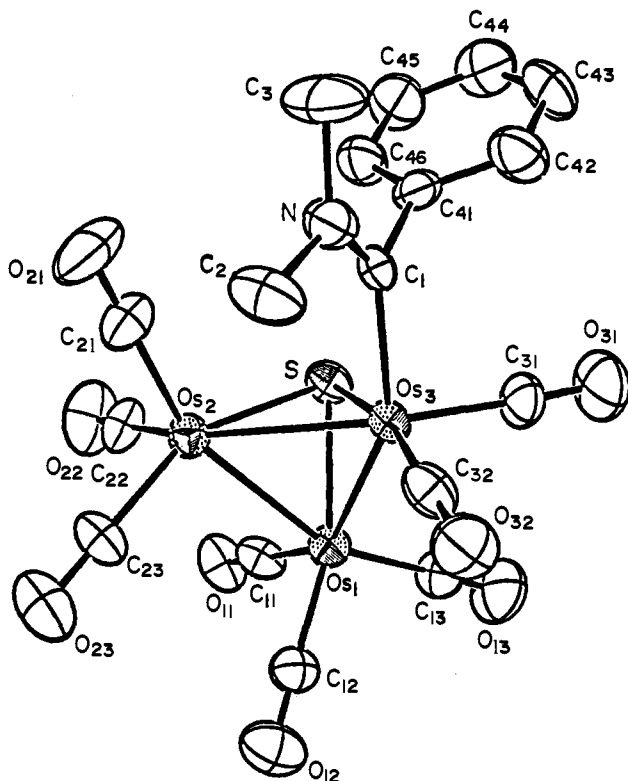
Figure 4. An ORTEP diagram of Os₃(CO)₈[C(Ph)NMe₂](μ₃-S)(μ-H)₂, **6a**, showing 50% probability thermal ellipsoids.

C(1)–N = 1.34 (1) Å, are both slightly longer than those observed in the compounds **2a**, **5a**, and **7**, vide supra.

To determine if the shift of the aryl group from the sulfido ligand to the carbyne carbon atom occurred by an intermolecular or intramolecular process a crossover experiment which consisted of transforming a mixture of the carbyne cluster complexes **3a** and **3d** into the aryl carbene cluster complexes **6** was performed. The results of this experiment showed the formation of only the two aryl carbene cluster compounds **6a** and **6d** in the yields 57% and 43%, respectively. There was no evidence for the product **6c** which was prepared independently or Os₃(CO)₈[C(Ph)-NEt₂](μ₃-S)(μ-H)₂ which we have not attempted to prepare independently.

Discussion

To date there have been very few reports of metal–carbonyl cluster complexes that contain heteronuclear carbene ligands.[4,13]

Table VIII. Intramolecular Bond Angles for $Os_3(CO)_8(C{=}NMe_2)(\mu\text{-}SPh)(\mu\text{-}H)_2$ (3a)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C11A	Os1A	C12A	92 (1)	C23B	Os2B	S1B	167.2 (8)	C41A	S1A	Os2A	110 (1)
C11A	Os1A	C13A	93 (1)	C23B	Os2B	Os3B	114.0 (8)	C41A	S1A	Os3A	116.2 (9)
C11A	Os1A	C1A	103 (1)	C23B	Os2B	Os1B	82.7 (8)	Os2A	S1A	Os3A	70.8 (2)
C11A	Os1A	Os3A	136 (1)	C22B	Os2B	C21B	95 (1)	C1B	N1B	C3B	123 (2)
C11A	Os1A	Os2A	95 (1)	C22B	Os2B	S1B	94.0 (6)	C1B	N1B	C2B	121 (2)
C12A	Os1A	C13A	96 (1)	C22B	Os2B	S1B	94.0 (6)	C3B	N1B	C2B	116 (2)
C12A	Os1A	C1A	93 (1)	C22B	Os2B	Os3B	112.9 (6)	C1A	N1A	C3A	125 (2)
C12A	Os1A	Os3A	115 (1)	C22B	Os2B	Os1B	168.0 (6)	C1A	N1A	C2A	123 (2)
C12A	Os1A	Os2A	173 (1)	C21B	Os2B	S1B	91.9 (8)	C3A	N1A	C2A	112 (2)
C13A	Os1A	C1A	161 (1)	C21B	Os2B	Os3B	135.6 (7)	N1B	C1B	Os3B	139 (2)
C13A	Os1A	Os3A	116 (1)	C21B	Os2B	Os1B	96.7 (7)	N1B	C1B	Os1B	135 (2)
C13A	Os1A	Os2A	84 (1)	S1B	Os2B	Os3B	54.2 (1)	Os3B	C1B	Os1B	86 (1)
C1A	Os1A	Os3A	45.5 (6)	S1B	Os2B	Os1B	86.1 (1)	N1A	C1A	Os3A	138 (2)
C1A	Os1A	Os2A	85.4 (7)	Os3B	Os2B	Os1B	57.76 (3)	N1A	C1A	Os1A	136 (2)
Os3A	Os1A	Os2A	59.38 (4)	C32B	Os3B	C31B	87 (1)	Os3A	C1A	Os1A	85 (1)
C12B	Os1B	C13B	98 (1)	C32B	Os3B	C1B	105 (1)	O11B	C11B	Os1B	176 (2)
C12B	Os1B	C11B	92 (1)	C32B	Os3B	S1B	110.2 (7)	O11A	C11A	Os1A	177 (3)
C12B	Os1B	C1B	92 (1)	C32B	Os3B	Os1B	149.7 (7)	O12A	C12A	Os1A	176 (3)
C12B	Os1B	Os3B	113.9 (8)	C32B	Os3B	Os2B	109.7 (7)	O12B	C12B	Os1B	178 (2)
C12B	Os1B	Os2B	172.3 (8)	C31B	Os3B	C1B	100 (1)	O13B	C13B	Os1B	177 (2)
C13B	Os1B	C11B	94 (1)	C31B	Os3B	S1B	107.4 (7)	O13A	C13A	Os1A	173 (3)
C13B	Os1B	C1B	163 (1)	C31B	Os3B	Os1B	110.0 (7)	O21B	C21B	Os2B	175 (2)
C13B	Os1B	Os3B	117.5 (8)	C31B	Os3B	Os2B	158.4 (7)	O21A	C21A	Os2A	176 (3)
C13B	Os1B	Os2B	83.0 (8)	C1B	Os3B	S1B	136.2 (7)	O22B	C22B	Os2B	175 (2)
C11B	Os1B	C1B	99 (1)	C1B	Os3B	Os1B	48.5 (7)	O22A	C22A	Os2A	171 (3)
C11B	Os1B	Os3B	134.3 (7)	C1B	Os3B	Os2B	89.8 (7)	O23A	C23A	Os2A	176 (3)
C11B	Os1B	Os2B	96.0 (7)	S1B	Os3B	Os1B	89.4 (1)	O23B	C23B	Os2B	178 (2)
C1B	Os1B	Os3B	45.6 (6)	S1B	Os3B	Os2B	54.4 (1)	O31B	C31B	Os3B	176 (2)
C1B	Os1B	Os2B	85.7 (6)	Os1B	Os3B	Os2B	62.60 (3)	O31A	C31A	Os3A	175 (2)
Os3B	Os1B	Os2B	59.64 (3)	C32A	Os3A	C31A	91 (1)	O32A	C32A	Os3A	167 (3)
C23A	Os2A	C22A	94 (1)	C32A	Os3A	C1A	108 (1)	O32B	C32B	Os3B	178 (2)
C23A	Os2A	C21A	97 (1)	C32A	Os3A	S1A	108 (1)	C46B	C41B	C42B	117 (2)
C23A	Os2A	S1A	169 (1)	C32A	Os3A	Os1A	153 (1)	C46B	C41B	S1B	126 (2)
C23A	Os2A	Os3A	114 (1)	C32A	Os3A	Os2A	109 (1)	C42B	C41B	S1B	117 (2)
C23A	Os2A	Os1A	86 (1)	C31A	Os3A	C1A	99 (1)	C46A	C41A	C42A	119 (3)
C22A	Os2A	C21A	95 (1)	C31A	Os3A	S1A	104.6 (8)	C46A	C41A	S1A	124 (2)
C22A	Os2A	S1A	93 (1)	C31A	Os3A	Os1A	106.2 (8)	C42A	C41A	S1A	116 (2)
C22A	Os2A	Os3A	112.7 (9)	C31A	Os3A	Os2A	154.3 (8)	C43B	C42B	C41B	120 (3)
C22A	Os2A	Os1A	169 (1)	C1A	Os3A	S1A	136.7 (7)	C41A	C42A	C43A	119 (3)
C21A	Os2A	S1A	91 (1)	C1A	Os3A	Os1A	49.1 (7)	C44A	C43A	C42A	120 (3)
C21A	Os2A	Os3A	135 (1)	C1A	Os3A	Os2A	90.4 (7)	C44B	C43B	C42B	120 (3)
C21A	Os2A	Os1A	96 (1)	S1A	Os3A	Os1A	89.2 (2)	C45A	C44A	C43A	120 (4)
S1A	Os2A	Os3A	54.7 (2)	S1A	Os3A	Os2A	54.5 (2)	C43B	C44B	C45B	120 (3)
S1A	Os2A	Os1A	85.9 (2)	Os1A	Os3A	Os2A	62.96 (4)	C44A	C45A	C46A	120 (4)
Os3A	Os2A	Os1A	57.66 (3)	C41B	S1B	Os3B	118.9 (8)	C45B	C46B	C41B	122 (3)
C23B	Os2B	C22B	96 (1)	C41B	S1B	Os2B	110.0 (8)	C41A	C46A	C45A	122 (3)
C23B	Os2B	C21B	95 (1)	Os3B	S1B	Os2B	71.4 (2)				

[a] Angles are in deg. esd's in the least significant figure are given in parentheses.

We have recently reported that trimethylamine reacts with the sulfido–osmium cluster complex $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ by the activation of two C–H bonds in one of the methyl groups to yield the carbene containing cluster complex 7.[4] In these studies we have described the synthesis, structural characterizations, and chemistry of the new series of carbene containing cluster complexes $Os_3(CO)_9[C(H)NR'_2](\mu\text{-}SR)(\mu\text{-}H)$ (2a–d) from the reaction of the complexes $Os_3(CO)_{10}(\mu\text{-}SR)(\mu\text{-}H)$, 1a–c with the bis(dialkylamino)methanes, $CH_2(NR'_2)_2$, R′ = Me, Et. The overall reaction involves the substitution of a carbonyl ligand by a (dialkylamino)carbene ligand. The exact pathway for this transformation has not been determined but would seem to involve one C–H activation on the central methylene group and the cleavage of one of the dialkylamino groups from the diaminomethane molecule.

When the compounds 2a–d were photolyzed under a nitrogen purge, three types of products were formed in nearly equal amounts. One type was the (dialkylamino)carbyne cluster complexes $Os_3(CO)_8(CNR'_2)(\mu\text{-}SR)(\mu\text{-}H)_2$ (3a–d). These products are believed to be formed by an α-CH activation of the carbene ligand which is facilitated by a photoinduced decarbonylation reaction. It is believed that the decarbonylation occurs at the CO-rich $Os(CO)_4$ group which is adjacent to the coordination site of the carbene ligand as illustrated by intermediate A in Scheme I. An oxidative addition of the C–H bond then occurs at the vacant site and leads to the formation of the carbyne ligand and a new hydride ligand. Cluster complexes containing (dialkylamino)carbyne ligands have been prepared previously by other methods.[14] Fischer[15] has reported the formation of aminocarbyne ligands from the mononuclear metal complexes $Cr(CO)_5[C(X)NEt_2]$ by the activation of C–X bonds, but these transformations have, so far, been limited to cases where X = Cl, Br, I, SnPh₃,

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Scheme I
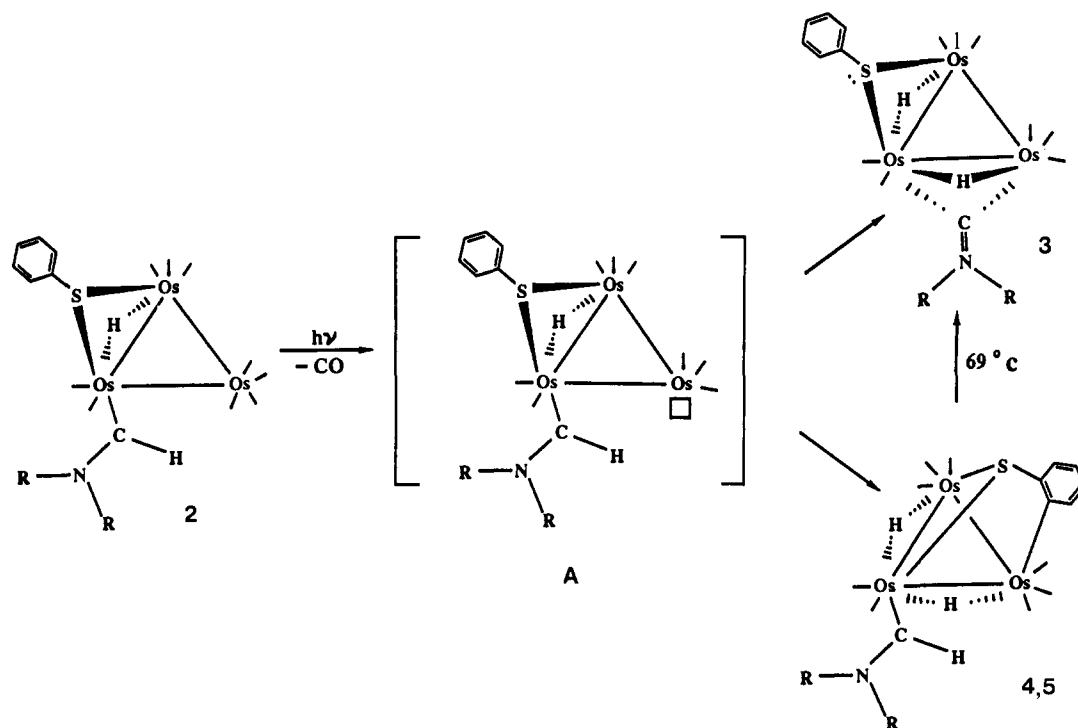
Table IX. Positional Parameters and B(eq) for $Os_3(CO)_8[C(H)NEt_2](\mu_3\text{-}SC_6H_3Me)(\mu\text{-}H)_2$ **(5d)**

atom	x	y	z	B(eq)	esd's
Os1	0.993525 (56)	0.423126 (43)	0.256844 (47)	3.3	(3)
Os2	0.767247 (60)	0.382976 (46)	0.150562 (47)	3.3	(3)
Os3	0.817302 (57)	0.420074 (44)	0.356536 (45)	3.4	(3)
S	0.79488 (37)	0.26905 (29)	0.27973 (30)	3.6	(2)
O11	0.9438 (11)	0.63133 (77)	0.22091 (96)	4.9	(6)
O12	1.2311 (12)	0.45199 (98)	0.3949 (10)	5.5	(6)
O13	1.0490 (13)	0.39864 (94)	0.0686 (11)	8.0	(7)
O21	0.5154 (12)	0.3430 (11)	0.0678 (11)	6.4	(8)
O22	0.8405 (12)	0.24935 (87)	0.02032 (93)	5.8	(6)
O23	0.7558 (12)	0.55433 (90)	0.02210 (86)	5.9	(6)
O31	0.9167 (12)	0.35028 (91)	0.56434 (87)	6.1	(6)
O32	0.8375 (12)	0.62371 (89)	0.42029 (95)	5.1	(7)
N1	0.5933 (13)	0.37045 (94)	0.3892 (10)	4.9	(7)
C1	0.6565 (14)	0.4194 (11)	0.3537 (12)	4.8	(7)
C2	0.4755 (16)	0.3883 (16)	0.3690 (18)	7.0	(1)
C3	0.4064 (17)	0.3358 (16)	0.2791 (20)	8.6	(1)
C4	0.6356 (17)	0.2899 (12)	0.4544 (14)	6.1	(1)
C5	0.6565 (19)	0.3118 (15)	0.5612 (13)	5.4	(1)
C11	0.9601 (15)	0.5538 (12)	0.2355 (12)	3.9	(8)
C12	1.1402 (20)	0.4412 (11)	0.3428 (12)	5.8	(8)
C13	1.0332 (18)	0.4084 (12)	0.1380 (15)	6.0	(1)
C21	0.6047 (17)	0.3587 (12)	0.0982 (12)	3.8	(8)
C22	0.8150 (17)	0.3012 (13)	0.0699 (12)	4.3	(8)
C23	0.7606 (16)	0.4900 (14)	0.0694 (12)	4.7	(9)
C31	0.8776 (13)	0.3771 (11)	0.4853 (12)	3.4	(7)
C32	0.8301 (15)	0.5473 (14)	0.3948 (12)	3.8	(8)
C41	0.9304 (13)	0.22226 (10)	0.2990 (11)	3.0	(7)
C42	1.0137 (14)	0.2768 (10)	0.2856 (11)	3.4	(7)
C43	1.1153 (14)	0.2289 (11)	0.2938 (12)	4.3	(8)
C44	1.1306 (15)	0.1353 (11)	0.3164 (11)	3.7	(8)
C45	1.0485 (18)	0.0854 (11)	0.3349 (13)	5.3	(8)
C46	0.9469 (14)	0.1294 (11)	0.3246 (11)	3.2	(7)
C47	1.2372 (18)	0.0891 (12)	0.3226 (13)	5.2	(9)

Table X. Intramolecular Distances for $Os_3(CO)_8[C(H)NEt_2](\mu_3\text{-}SC_6H_3Me)(\mu\text{-}H)_2$ **(5d)**[a]

atom	atom	distance	atom	atom	distance
Os1	C12	1.89 (2)	O13	C13	1.09 (2)
Os1	C11	1.93 (2)	O21	C21	1.10 (2)
Os1	C13	1.95 (2)	O22	C22	1.15 (2)
Os1	C42	2.15 (1)	O23	C23	1.14 (2)
Os1	Os2	2.842 (1)	O31	C31	1.15 (2)
Os1	Os3	3.034 (1)	O32	C32	1.16 (2)
Os2	C22	1.89 (2)	N1	C1	1.29 (2)
Os2	C23	1.92 (2)	N1	C2	1.45 (2)
Os2	C21	1.99 (2)	N1	C4	1.48 (2)
Os2	S	2.423 (4)	C2	C3	1.51 (3)
Os2	Os3	2.8823 (9)	C4	C5	1.51 (2)
Os3	C31	1.87 (2)	C41	C42	1.38 (2)
Os3	C32	1.91 (2)	C41	C46	1.39 (2)
Os3	C1	2.03 (2)	C42	C43	1.44 (2)
Os3	S	2.417 (4)	C43	C44	1.39 (2)
S	C41	1.78 (2)	C44	C45	1.36 (2)
O11	C11	1.14 (2)	C44	C47	1.48 (3)
O12	C12	1.17 (2)	C45	C46	1.40 (2)

[a] Distances are in Å. esd's in the least significant figure are given in parentheses.

SeC_6H_4R, $PbPh_3$, $TePh$. The conversion of **2a–d** to **3a–d** is the *first example of a binuclear intramolecular transformation involving heteroatom-substituted carbene–carbyne ligands.*

Also formed in the photolysis of **2a, 2c,** and **2d** are two isomeric carbene cluster complexes in which the aryl group of the thiolato ligand has become orthometalated, $Os_3(CO)_8[C(H)NR'_2](\mu\text{-}SC_6H_3R)(\mu\text{-}H)_2$, **4a, 4c, 4d** and **5a, 5c, 5d.** Interestingly, if these

compounds are refluxed in hexane solvent, they are converted to **3a, 3c,** and **3d,** respectively. Although this observation suggests that the orthometalated species may be intermediates in the formation of the carbyne containing clusters, the synthesis and transformation of the perfluorothiolato complex **2b** into Os_3-$(CO)_8(\mu\text{-}CNMe_2)(\mu\text{-}SC_6F_5)(\mu\text{-}H)_2$, **3b,** indicates that the orthometalation step is not necessary. In **2b** both ortho carbon atoms of the aryl ring contain fluorine substituents. C–F bonds are not known to undergo metalation, and indeed **2b** does not yield any orthometalation products, but it is converted into **3b** in good yield. In the other reactions, the orthometalated products are formed evidently by an independent competing reaction which serves as an alternative means for the molecule to relieve the unsaturation brought about by the loss of the CO ligand (Scheme I). Their conversion into the carbyne complexes could proceed by a conversion back into the intermediate A.

When the compounds **3a–d** were heated to reflux in octane solutions, the aryl group of the thiolato ligand was shifted to the carbon atom of the carbyne ligand. This resulted in the formation

Table XI. Intramolecular Bond Angles for $Os_3(CO)_8[C(H)NEt_2](\mu_3\text{-}SC_6H_3Me)(\mu\text{-}H)_2$ (**5d**)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C12	Os1	C11	95.1 (7)	C21	Os2	Os1	170.1 (5)	C2	N1	C4	114 (2)
C12	Os1	C13	96.3 (8)	C21	Os2	Os3	106.1 (5)	N1	C1	Os3	138 (1)
C12	Os1	C42	88.8 (6)	S	Os2	Os1	81.7 (1)	N1	C1	Os3	138 (1)
C12	Os1	Os2	171.8 (5)	S	Os2	Os3	53.4 (1)	N1	C2	C3	111 (2)
C12	Os1	Os3	114.4 (5)	Os1	Os2	Os3	64.00 (2)	N1	C4	C5	113 (2)
C11	Os1	C13	94.1 (7)	C31	Os3	C32	93.6 (7)	O11	C11	Os1	177 (2)
C11	Os1	C42	173.3 (7)	C31	Os3	C1	95.8 (7)	O12	C12	Os1	179 (2)
C11	Os1	Os2	88.9 (5)	C31	Os3	S	96.1 (5)	O13	C13	Os1	176 (2)
C11	Os1	Os3	86.1 (5)	C31	Os3	Os2	147.7 (5)	O21	C21	Os2	178 (2)
C13	Os1	C42	90.8 (7)	C31	Os3	Os1	110.5 (5)	O22	C22	Os2	177 (2)
C13	Os1	Os2	90.5 (6)	C32	Os3	C1	90.0 (7)	O23	C23	Os2	179 (2)
C13	Os1	Os3	149.2 (6)	C32	Os3	S	170.1 (5)	O31	C31	Os3	179 (2)
C42	Os1	Os2	86.6 (4)	C32	So3	Os2	116.5 (5)	O32	C32	Os3	178 (2)
C42	Os1	Os3	87.3 (5)	C32	Os3	Os1	96.7 (5)	C42	C41	C46	122 (2)
Os2	Os1	Os3	58.64 (2)	C1	Os3	S	91.1 (5)	C42	C41	S	121 (1)
C22	Os2	C23	94.8 (7)	C1	Os3	Os2	95.6 (5)	C46	C41	S	117 (1)
C22	Os2	C21	99.2 (8)	C1	Os3	Os1	152.3 (5)	C41	C42	C43	115 (1)
C22	Os2	S	93.3 (5)	S	Os3	Os2	53.6 (1)	C41	C42	Os1	122 (1)
C22	Os2	Os1	89.3 (6)	S	Os3	Os1	77.9 (1)	C43	C42	Os1	122 (1)
C22	Os2	Os3	138.1 (5)	Os2	Os3	Os1	57.35 (2)	C44	C43	C42	123 (2)
C23	Os2	C21	94.4 (7)	C41	S	Os3	107.7 (5)	C45	C44	C43	120 (2)
C23	Os2	S	168.4 (5)	C41	S	Os2	105.3 (6)	C45	C44	C47	120 (2)
C23	Os2	Os1	90.1 (6)	Os3	S	Os2	73.1 (1)	C43	C44	C47	120 (2)
C23	Os2	Os3	115.6 (5)	C1	N1	C2	124 (2)	C44	C45	C46	119 (2)
C21	Os2	S	92.6 (5)	C1	N1	C4	122 (2)	C41	C46	C45	121 (2)

[a] Angles are in deg. esd's in the least significant figure are given in parentheses.

Table XII. Positional Parameters and $B(eq)$ for $Os_3(CO)_8[C(Ph)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**6a**)

atom	x	y	z	$B(eq)$
Os1	0.864810 (51)	0.817394 (42)	0.914958 (13)	2.57 (2)
Os2	1.182854 (50)	0.689832 (44)	0.931867 (13)	2.55 (2)
Os3	0.945263 (49)	0.554099 (41)	0.866437 (12)	2.28 (2)
S	1.07148 (35)	0.79807 (28)	0.866092 (86)	3.0 (1)
O11	0.9890 (12)	1.10718 (81)	0.95822 (27)	4.8 (4)
O12	0.7017 (12)	0.72031 (92)	0.99273 (30)	5.1 (4)
O13	0.5524 (12)	0.9484 (12)	0.86412 (36)	6.8 (6)
O21	1.4926 (11)	0.5112 (10)	0.91648 (37)	6.3 (5)
O22	1.3726 (12)	0.97516 (96)	0.96080 (35)	6.5 (5)
O23	1.1532 (12)	0.59313 (93)	1.02237 (28)	5.4 (5)
O31	0.7198 (12)	0.6034 (11)	0.78453 (31)	6.1 (5)
O32	0.7545 (11)	0.27386 (83)	0.88678 (27)	4.2 (4)
N	1.2164 (11)	0.32919 (95)	0.84419 (28)	3.2 (4)
C1	1.1274 (12)	0.4533 (10)	0.83434 (29)	2.4 (4)
C2	1.1992 (16)	0.2376 (13)	0.88335 (39)	4.1 (5)
C3	1.3397 (18)	0.2645 (15)	0.81932 (47)	5.5 (7)
C11	0.9403 (16)	0.9989 (13)	0.94175 (39)	3.8 (5)
C12	0.7629 (14)	0.7574 (12)	0.96388 (38)	3.3 (5)
C13	0.6689 (16)	0.8966 (12)	0.88248 (41)	4.0 (5)
C21	1.3782 (14)	0.5803 (12)	0.92167 (41)	3.8 (5)
C22	1.3025 (14)	0.8673 (13)	0.95126 (41)	3.8 (5)
C23	1.1657 (15)	0.6283 (12)	0.98819 (35)	3.5 (5)
C31	0.8042 (14)	0.5839 (12)	0.81627 (36)	3.5 (5)
C32	0.8372 (15)	0.3774 (12)	0.87928 (35)	3.3 (5)
C41	1.1744 (12)	0.5255 (12)	0.79551 (34)	3.0 (4)
C42	1.0907 (17)	0.4862 (14)	0.75602 (39)	4.4 (6)
C43	1.1314 (19)	0.5558 (19)	0.71996 (38)	5.8 (7)
C44	1.2507 (18)	0.6718 (17)	0.72240 (45)	5.4 (7)
C45	1.3300 (17)	0.7118 (15)	0.76127 (43)	4.8 (6)
C46	1.2908 (15)	0.6395 (13)	0.79679 (38)	3.9 (5)

Table XIII. Intramolecular Distances for $Os_3(CO)_8[C(Ph)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**6a**)[a]

atom	atom	distance	atom	atom	distance
Os1	C11	1.90 (1)	O13	C13	1.14 (1)
Os1	C12	1.91 (1)	O21	C21	1.13 (1)
Os1	C13	1.91 (1)	O22	C22	1.14 (1)
Os1	S	2.395 (3)	O23	C23	1.15 (1)
Os1	Os2	2.7815 (7)	O31	C31	1.16 (1)
Os1	Os3	2.9225 (6)	O32	C32	1.18 (1)
Os2	C23	1.89 (1)	N	C1	1.34 (1)
Os2	C21	1.90 (1)	N	C3	1.45 (1)
Os2	C22	1.92 (1)	N	C2	1.51 (1)
Os2	S	2.385 (3)	C1	C41	1.48 (1)
Os2	Os3	2.9192 (7)	C41	C46	1.38 (1)
Os3	C32	1.87 (1)	C41	C42	1.40 (2)
Os3	C31	1.87 (1)	C42	C43	1.37 (2)
Os3	C1	2.07 (1)	C43	C44	1.40 (2)
Os3	S	2.401 (3)	C44	C45	1.37 (2)
O11	C11	1.15 (1)	C45	C46	1.37 (2)
O12	C12	1.14 (1)			

[a] Distances are in Å. esd's in the least significant figure are given in parentheses.

of **3a** and **3d** was transformed into the products **6a** and **6d** only indicates that it is an intramolecular process.

The cleavage of an aryl(dialkylamino)carbene ligand and a sulfido ligand in the complexes $Os_3(CO)_8[C(R)NR'_2](\mu_3\text{-}S)(\mu\text{-}H)_2$, **6a–d**. The cleavage of the phenyl group from the sulfur atom in **1a** was found to be an effective method for the synthesis of sulfido–osmium clusters.[16] The cleavage of the phenyl groups from phenyl-containing phosphine ligands is a well-established mode of decomposition in metal complexes.[17]

A key question regarding this transformation is whether it proceeds by a dissociative, intermolecular process or by an intramolecular one. The crossover experiment in which a mixture

Mechanisms that involve orthometalated intermediates can be envisioned, but the transformation of the perfluorophenyl derivative **3b** into **6b** would seem to rule out such a pathway for this complex. A sigmatropic process such as that shown in Scheme II could be a viable mechanism for all the complexes. By this mechanism the aryl group would be transferred to the osmium atom that is not bonded to the sulfur atom. A precedent for the activation and cleavage of a heteroatom–carbon σ bond of a bridging ligand by the third metal atom in a trinuclear cluster complex was established by Carty in his studies of the unsaturated cluster complex $Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}H)$.[18] Nyholm and Mason characterized structurally a σ-bonded phenyl group in the complex $Os_3(CO)_8(Ph)(\mu\text{-}PPh_2)(\mu_3\text{-}P(Ph)C_6H_4)$ which was obtained from the reaction of $Os_3(CO)_{12}$ with PPh_3.[19] Two possible intermediates are shown by the structures B and C. In both intermediates all the metal atoms have 18 electron configurations. Structure

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Table XIV. Intramolecular Bond Angles for $Os_3(CO)_8[C(Ph)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (6a)[a]

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C11	Os1	C12	91.0 (5)	C22	Os2	S	94.1 (4)	Os1	S	Os3	75.08 (8)
C11	Os1	C13	97.3 (5)	C22	Os2	Os1	97.8 (3)	C1	N	C3	125 (1)
C11	Os1	S	98.3 (4)	C22	Os2	Os3	146.5 (4)	C1	N	C2	123.3 (9)
C11	Os1	Os2	91.4 (4)	S	Os2	Os1	54.59 (7)	C3	N	C2	111.3 (9)
C11	Os1	Os3	147.8 (4)	S	Os2	Os3	52.67 (6)	N	C1	C41	112.3 (8)
C12	Os1	C13	98.4 (5)	Os1	Os2	Os3	61.63 (2)	N	C1	Os3	129.0 (7)
C12	Os1	S	153.4 (3)	C32	Os3	C31	93.3 (5)	C41	C1	Os3	118.6 (7)
C12	Os1	Os2	101.0 (3)	C32	Os3	C1	96.2 (4)	O11	C11	Os1	179 (1)
C12	Os1	Os3	110.0 (3)	C32	Os3	S	166.7 (3)	O12	C12	Os1	179 (1)
C13	Os1	S	104.9 (4)	C32	Os3	Os2	118.4 (3)	O13	C13	Os1	177 (1)
C13	Os1	Os2	158.6 (4)	C32	Os3	Os1	115.5 (3)	O21	C21	Os2	178 (1)
C13	Os1	Os3	103.1 (4)	C31	Os3	C1	91.8 (4)	O22	C22	Os2	177 (1)
S	Os1	Os2	54.23 (7)	C31	Os3	S	94.6 (3)	O23	C23	Os2	179 (1)
S	Os1	Os3	52.55 (6)	C31	Os3	Os2	146.4 (3)	O31	C31	Os3	178 (1)
Os2	Os1	Os3	61.51 (2)	C31	Os3	Os1	100.9 (3)	O32	C32	Os3	173 (1)
C23	Os2	C21	99.2 (5)	C1	Os3	S	94.2 (3)	C46	C41	C42	118 (1)
C23	Os2	C22	91.2 (5)	C1	Os3	Os2	95.4 (2)	C46	C41	C1	122 (1)
C23	Os2	S	152.7 (4)	C1	Os3	Os1	144.8 (2)	C42	C41	C1	120 (1)
C23	Os2	Os1	98.1 (4)	S	Os3	Os2	52.15 (7)	C43	C42	C41	120 (1)
C23	Os2	Os3	116.4 (4)	S	Os3	Os1	52.37 (6)	C42	C43	C44	121 (1)
C21	Os2	C22	95.2 (5)	Os2	Os3	Os1	56.87 (2)	C45	C44	C43	119 (1)
C21	Os2	S	107.0 (4)	Os2	S	Os1	71.17 (7)	C46	C45	C44	120 (1)
C21	Os2	Os1	158.1 (4)	Os2	S	Os3	75.18 (7)	C45	C46	C41	123 (1)
C21	Os2	Os3	98.4 (3)								

[a] Angles are in deg. esd's in the least significant figure are given in parentheses.

Scheme II
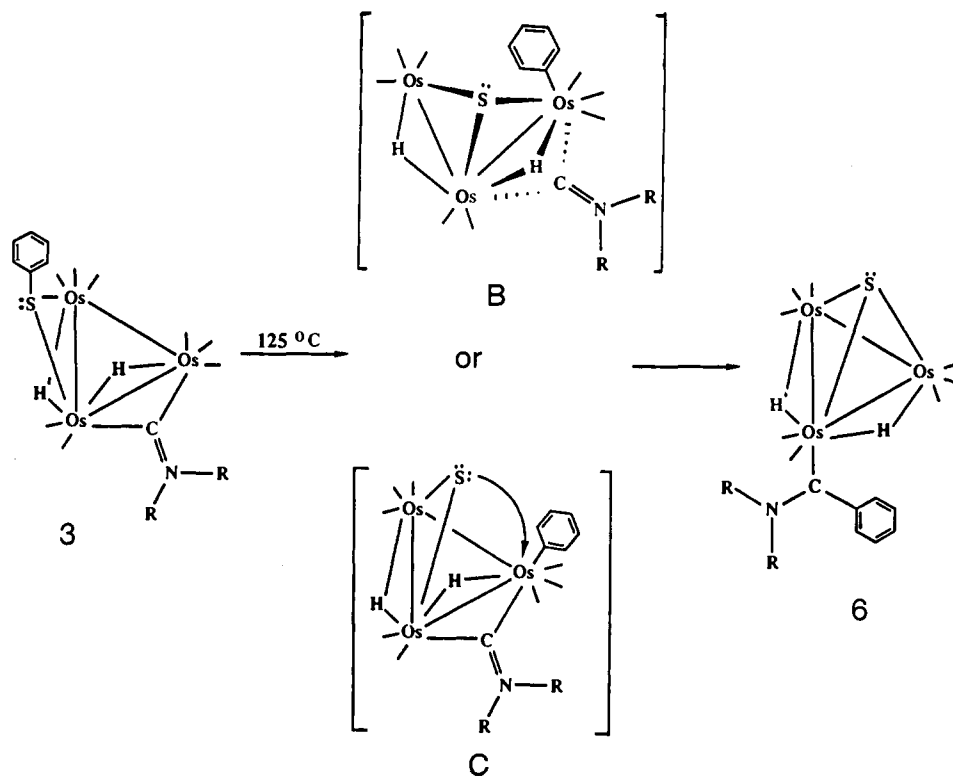
B has only two metal–metal bonds. The formation of a third metal–metal bond could be the driving force for an intramolecular reductive elimination process that leads to the formation of a carbon–carbon bond between the phenyl group and the carbyne carbon atom and results in the formation of the phenyl(dialkylamino)carbene ligand. In structure C the sulfur atom bridges only an edge of the cluster. From this intermediate the formation of a third metal–sulfur bond could be the driving force for the formation of the carbene ligand in a manner similar to that described from intermediate B. All the metal atoms in the proposed intermediate B contain 18 stable electron configurations. An intramolecular nucleophilic attack of the edge-bridging sulfido ligand upon the third metal atom could induce a reductive elimination of the phenyl group bond carbyne carbon atom to form the phenyl(dialkylamino)carbene ligand in a terminal site and the triply bridging sulfido ligand.