1530 *Organometallics* **1990**, *9*, 1530–1538

Clusters Containing Carbene Ligands. 9. Reaction of MeC≡CNMe$_2$ with Os$_3$(CO)$_{10}$(μ-H)$_2$

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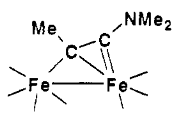
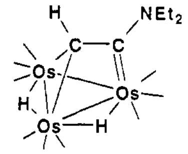
The reaction of Os$_3$(CO)$_{10}$(μ-H)$_2$ with MeC≡CNMe$_2$ at 25 °C yielded the new complex Os$_3$(CO)$_{10}$[μ-C(Me)C(H)NMe$_2$](μ-H) (**1**, 68%) by the addition and insertion of MeC≡CNMe$_2$ into one of the metal–hydrogen bonds. Compound **1** contains a bridging C(Me)C(H)NMe$_2$ ligand that is coordinated only by the methyl-substituted carbon atom. The hydride ligand was shifted to the NMe$_2$-substituted carbon atom. When heated to 68 °C in hexane, **1** isomerized to the new complex Os$_3$(CO)$_{10}$[μ-CH(Me)CNMe$_2$](μ-H) (**2**) by a shift of the hydrogen atom from the NMe$_2$-substituted carbon atom to the methyl-substituted carbon atom. At 68 °C, **2** was slowly decarbonylated to yield the new compound Os$_3$(CO)$_9$(μ_3-MeC$_2$NMe$_2$)(μ-H)$_2$ (**3**), which contains a triply bridging MeC$_2$NMe$_2$ ligand. In a competing reaction **2** simultaneously isomerized to the new compound Os$_3$(CO)$_{10}$[μ-C(Et)N(Me)CH$_2$](μ-H) (**4**), which contains an *N*-methyl-metalated ethyl(dimethylamino)carbene ligand that bridges an edge of the triosmium cluster. When heated to 97 °C for 36 h, **3** isomerized to the new compound Os$_3$(CO)$_9$[η^3-CH(Me)C(H)NMe$_2$](μ-H) (**5**), which exists in solution as a mixture of isomers. One of the isomers was crystallized and characterized structurally. It was shown to contain a triply bridging MeC(H)CNMe$_2$ ligand. The carbon atoms of the alkenyl group are σ–π coordinated to an edge of the cluster, while the nitrogen atom is coordinated to the third metal atom. The ligand has *Z* stereochemistry. On the basis of NMR spectroscopy the other isomer is believed to contain a similarly coordinated ligand having *E* stereochemistry. Compounds **1**–**5** were all characterized by IR, NMR, and single-crystal X-ray diffraction analyses. Crystal data: for **1**, space group $P2_1/c$, a = 8.842 (2) Å, b = 17.275 (8) Å, c = 14.211 (2) Å, β = 101.04 (1)°, Z = 4, 2211 reflections, R = 0.051, R_w = 0.053; for **2**, space group $P2_12_12_1$, a = 11.529 (2) Å, b = 17.829 (3) Å, c = 10.041 (1) Å, Z = 4, 1849 reflections, R = 0.0298 R_w = 0.030; for **3**, space group $P2_1/c$, a = 9.854 (1) Å, b = 15.517 (2) Å, c = 13.188 (2) Å, β = 92.09 (2)°, Z = 4, 2122 reflections, R = 0.037, R_w = 0.040; for **4**, space group $P\bar{1}$, a = 8.866 (2) Å, b = 15.310 (4) Å, c = 8.188 (2) Å, α = 103.12 (2)°, β = 105.38 (2)°, γ = 87.44 (2)°, Z = 2, 2497 reflections, R = 0.044, R_w = 0.050; for **5**, space group $C2/c$, a = 17.241 (2) Å, b = 8.310 (1) Å, c = 26.767 (4) Å, β = 94.10 (1)°, Z = 8, 2298 reflections, R = 0.027, R_w = 0.028.

Introduction

Recent studies of the coordination of ynamine ligands in metal carbonyl cluster complexes have shown that the amine-substituted carbon atom exhibits a substantial degree of carbene-like character.[1-4] This is illustrated by the structures of the complexes Fe$_2$(CO)$_7$(μ-MeC$_2$NEt$_2$) (A),[1a] Os$_3$(CO)$_9$(μ_3-HC$_2$NEt$_2$)(μ-H)$_2$ (B),[2] and Os$_3$(CO)$_9$(μ_3-MeC$_2$NMe$_2$)(μ_3-S) (C).[4] We have observed that this carbene character also influences the reactivity of the complexes. For example, we have shown that C reacts with hydrogen to yield the carbene complex Os$_3$(CO)$_9$[C(Et)NMe$_2$](μ_3-S)(μ-H)$_2$ (D) by a novel 1,1-hydrogenation of the ynamine ligand (eq 1).[5]



A



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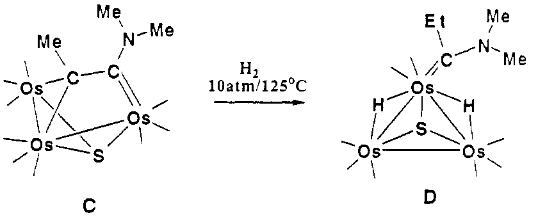

(1)

In this report, the reaction of MeC≡CNMe$_2$ with Os$_3$(CO)$_{10}$(μ-H)$_2$ is described. It was found that MeC≡CNMe$_2$ adds to Os$_3$(CO)$_{10}$(μ-H)$_2$ by an insertion reaction to yield the complex Os$_3$(CO)$_{10}$[μ-MeCC(H)NMe$_2$](μ-H) (**1**). This complex subsequently engages in a variety of isomerization and decarbonylation reactions that involve the partially hydrogenated ynamine ligand. One of the products contains an *N*-methyl-metalated aminocarbene ligand. Compound **1** and four products derived from **1** have been isolated and characterized by single-crystal X-ray diffraction analyses. These complexes are described in this report.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Reagent grade solvents were stored over 4-Å molecular sieves. All chromatographic separations were performed in air on TLC plates (0.25 mm silica gel 60 F$_{254}$). 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. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Os$_3$(CO)$_{10}$(μ-H)$_2$[6] and MeC$_2$NMe$_2$[7] were prepared by the previously reported procedures.

Preparation of Os$_3$(CO)$_{10}$[μ-CMeC(H)NMe$_2$)](μ-H) (1). To a solution of Os$_3$(CO)$_{10}$(μ-H)$_2$ (105 mg, 0.123 mmol) in hexane (60 mL) was added an excess of CH$_3$C≡CNMe$_2$ (50 μL). The reaction mixture was stirred at 25 °C for 1.5 h and was then filtered through a Florisil column with CH$_2$Cl$_2$/hexane (3/7) as eluent. An orange band gave 79 mg (68% yield) of Os$_3$(CO)$_{10}$[μ-CMeC(H)NMe$_2$](μ-H) (**1**). IR and ^{1}H NMR spectra are given in Table I. Anal. Calcd for **1**: C, 19.25; N, 1.50; H, 1.18. Found: C, 19.62; N, 1.48; H, 1.02.

Thermolysis of 1. A solution of **1** (40 mg, 0.0427 mmol) in hexane (50 mL) was refluxed for 2 h. The solvent was removed

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Table I. IR and ^{1}H NMR Spectra of Compounds 1–5

compd	IR, cm^{-1} (in hexane)	^{1}H NMR, δ (in CDCl$_3$)
$Os_3(CO)_{10}(\mu\text{-}C(Me)CHNMe_2)(\mu\text{-}H)$ (1)	2094 m, 2049 vs, 2041 s, 2014 s, 1990 vs, 1979 s, 1968 w	8.21 (1 H, s), 3.10 (6 H, s), 2.83 (3 H, s), –15.01 (1 H, s)
$Os_3(CO)_{10}[\mu\text{-}CH(Me)CN(Me)_2](\mu\text{-}H)$ (2)	2098 m, 2057 vs, 2043 s, 2018 s, 2012 vs, 1997 sh, 1993 s, 1987 s, 1977 s	3.40 (3 H, s), 3.36 (3 H, s), 3.09 (1 H, dq, $J_{H\text{-}H}$ = 7.2, 3.7 Hz), 1.64 (3 H, d, $J_{H\text{-}H}$ = 7.2 Hz), –16.35 (1 H, d, $J_{H\text{-}H}$ = 3.7 Hz)
$Os_3(CO)_9[\mu_3\text{-}C(Me)CN(Me)_2](\mu\text{-}H)_2$ (3)	2099 m, 2070 vs, 2044 vs, 2017 s, 2014 sh, 1997 s, 1982 m, 1976 w, 1967 m	3.45 (6 H, s), 2.86 (3 H, s)^a [3.55 (3 H, s), 3.24 (3 H, s), 2.80 (3 H, s), –16.27 (1 H, s) –17.88 (1 H, s)]^b
$Os_3(CO)_{10}[\mu\text{-}CH_2N(Me)C(Et)](\mu\text{-}H)$ (4)	2099 m, 2059 vs, 2048 vs, 2019 s, 1999 s, 1993 s, 1984 s, 1969 w	4.06 (1 H, d, $^1J_{H\text{-}H}$ = 16.3 Hz, 3.31 (1 H, d, $^1J_{H\text{-}H}$ = 16.3 Hz), 3.32 (3 H, s), 3.28 (1 H, dq, $^1J_{H\text{-}H}$ = 12.7 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz), 3.17 (1 H, dq, $^1J_{H\text{-}H}$ = 12.7 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz, 1.03 (3 H, t, $^3J_{H\text{-}H}$ = 7.7 Hz, –16.34 (1 H, s)
$Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}C(CHMe)N(Me)_2](\mu\text{-}H)$ (5)	2090 m, 2059 s, 2030 vs, 2012 s, 1998 m, 1992 s, 1987 m, 1977 m, 1952 w	*Z* isomer, 4.82 (1 H, q, $J_{H\text{-}H}$ = 6.5 Hz), 2.87 (3 H, s), 2.46 (3 H, s), 2.14 (3 H, d, $J_{H\text{-}H}$ = 6.5 Hz), –13.30 (1 H, s); *E* isomer, 4.05 (1 H, q, $J_{H\text{-}H}$ = 6.0 Hz), 3.15 (3 H, sbr), 2.62 (3 H, sbr), 2.06 (3 H, d, $J_{H\text{-}H}$ = 6.0 Hz), –13.96 (s)

^{a} In CD$_2$Cl$_2$. ^{b} In CD$_2$Cl$_2$ at –56 °C.

in vacuo, and the residue was separated by TLC. Elution with a CH_2Cl_2/hexane (1/9) solvent mixture yielded yellow bands of $Os_3(CO)_{10}[\mu\text{-}CH(Me)CNMe_2](\mu\text{-}H)$ (**2**; 13.4 mg (34%)), $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}H)_2$ (**3**; 2.3 mg (6%)), and $Os_3(CO)_{10}(\mu\text{-}EtCN(Me)CH_2](\mu\text{-}H)$ (**4**; 11 mg (28%)). IR and ^{1}H NMR spectra are given in Table I. Anal. Calcd for **2**: C, 19.25; N, 1.50; H, 1.18. Found: C, 19.31; N, 1.60; H, 1.09. Calcd for **4**: C, 19.25; N, 1.50; H, 1.18. Found: C, 19.39; N, 1.45; H, 1.07.

Thermolysis of 2. A solution of **2** (19 mg, 0.0203 mmol) in hexane (40 mL) was refluxed for 36 h. The solvent was removed in vacuo. The residue was dissolved in a minimum quantity of CH_2Cl_2 and transferred to silica gel TLC plates. Elution with a CH_2Cl_2/hexane (1/9) solvent mixture yielded pale yellow **3** (7.9 mg (43% yield)) and **4** (1.2 mg (6%)). Anal. Calcd for **3**: C, 18.52; N, 1.54; H, 1.22. Found: C, 18.65; N, 1.38; H, 1.14.

Thermolysis of 3. (a) A solution of **3** (11.8 mg) in hexane (50 mL) was refluxed for 36 h. The solvent was removed in vacuo, the residue was redissolved in heptane, and this solution was refluxed for an additional 16 h. Separation by TLC with a CH_2Cl_2/hexane (1/9) solvent mixture as eluent yielded yellow $Os_3(CO)_9[\mu\text{-}Me_2NCC(H)Me](\mu\text{-}H)$ (**5**; 1.6 mg (14%)) and unreacted **3** (6.9 mg, 59%). The remainder of the material was uncharacterizable decomposition products. Anal. Calcd for **5**: C, 18.52; N, 1.54; H, 1.22. Found: C, 18.80; N, 1.63; H, 1.11.

(b) A solution of **3** (15.7 mg, 0.0173 mmol) in 40 mL of octane was refluxed for 6 h. The solvent was removed in vacuo, and the residue was separated by TLC as described above. A yellow band identified as $Os_3(CO)_9[\mu_3\text{-}H_2CC_2N(CH_3)_2](\mu\text{-}H)$ (**6**; 13.3 mg (85%)) was separated.

NMR Analysis of the Thermolysis of 2 in a Sealed Tube. A 10-mg amount of compound **2** was dissolved in 1.0 mL of toluene-d_8. The solution was transferred to a 5-mm NMR tube. The solution was degassed by using three freeze–pump–thaw cycles. The tube was sealed and placed in an oil bath at 80 °C. At the end of 4 h, an NMR spectrum showed a hydride resonance at –16.36 ppm that is attributed to compound **4**. Resonances at 2.54 and 2.67 ppm due to the NMe_2 and CMe resonances of compound **3** were also observed. No substantial changes were observed in a spectrum after a period of 6 h of heating at 80 °C. A spectrum taken after heating a total of 13 h showed the presence of compounds **2** and **4** in an approximately 2/1 ratio. The NMe_2 and CMe resonances of **3** had become more pronounced. During the 13-h period, **3** and **4** appeared to be forming from **2** at approximately equal rates.

NMR Analysis of the Thermolysis of 3 in a Sealed Tube. A 9-mg portion of compound **3** was dissolved in 1.0 mL of toluene-d_8. The solution was transferred to a 5-mm NMR tube and degassed as described above. The tube was sealed and placed in an oil bath at 80 °C. At the end of 1 h, a spectrum was taken and resonances at 1.86 and 1.88 ppm corresponding to the C(H)–CH_3 doublet of a species that has been identified as the *Z* isomer of **5** were observed. Resonances at 1.74 and 1.76 ppm, assigned to a C(H)–CH_3 doublet of the *E* isomer of **5**, were also observed. At this time, the *Z*/*E* ratio determined from integration was 1.9/1. After 3 h, the doublets due to the isomers of **5** were more pronounced, and the *Z*/*E* ratio was 4.1/1. At the end of 8 h, the resonances due to *E*- and *Z*-**5** were almost absent and a new resonance at 2.35 ppm and a hydride resonance at –23.5 ppm were present. This compound was subsequently identified as the known compound $Os_3(CO)_9(\mu_3\text{-}C_2Me)(\mu\text{-}H)$ (**7**).[8] There was no evidence for the formation of **4** in this reaction at any time.

NMR Analysis of the Thermolysis of 5 in a Sealed Tube. A 10-mg amount of compound **5** was dissolved in 1.0 mL of toluene-d_8. The solution was transferred to a 5-mm NMR tube and degassed as before. At this time, an NMR spectrum showed a *Z*/*E* ratio of **5** to be ≃3.3. The tube was placed in an oil bath at 80 °C. At the end of 2.5 h, an NMR spectrum showed two new resonances at 2.82 and 3.42 ppm due to compound **3**. At this time, the ratio of compound **3** to compound **5** determined by peak integration was 3.2. After the tube was heated at 80 °C for 24 h, an NMR spectrum showed the relative amount of **3** to **5** was approximately 5. On the basis of the last measurement, the equilibrium value is believed to be 5.0 ± 0.1.

Crystallographic Analyses. Crystals of **1** and **5** suitable for X-ray diffraction analyses were grown from solutions in hexane/CH_2Cl_2 solvent mixtures by slow evaporation of the solvent at 0 °C. Crystals of **2**–**4** were grown from hexane/CH_2Cl_2 solvent mixtures by slow evaporation of solvent at 25 °C. All data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromatized Mo Kα radiation. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table II. All intensity measurements were made by using the standard ω-scan (moving-crystal–stationary-counter) technique. Background measurements were made by a one-fourth additional scan at each end of the scan. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer by using the TEXSAN structure-solving program library (version 2.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[9a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] Full-matrix least-squares refinements minimized the function

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

where

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

$$\sigma(F) = \sigma(F_o^2)/2F_{o,hkl}$$

$$\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)_2]^{1/2}/Lp$$

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

Table II. X-ray Crystallographic Data for Compounds 1–5

	1	2	3	4	5
empirical formula	$Os_3NC_{15}O_{10}H_{11}$	$Os_3NO_{10}C_{15}H_{11}$	$Os_3NO_9C_{14}H_{11}$	$Os_3O_{10}NC_{15}H_{11}$	$Os_3NO_9C_{14}H_{11}$
fw	935.85	935.85	907.84	935.85	907.84
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
lattice params					
a, Å	8.842 (2)	11.529 (2)	9.854 (1)	8.866 (2)	17.241 (2)
b, Å	17.275 (8)	17.829 (3)	15.517 (2)	15.310 (4)	8.310 (1)
c, Å	14.211 (2)	10.041 (1)	13.188 (2)	8.188 (2)	26.767 (4)
α, deg				103.12 (2)	
β, deg	101.04 (1)		92.09 (1)	105.38 (2)	94.10 (1)
γ, deg				87.44 (2)	
V, Å^3	2130 (2)	2063.9 (9)	2015.0 (8)	1043.4 (8)	3825 (1)
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
Z	4	4	4	2	8
D_{calc}, g/cm^3	2.92	3.01	2.99	2.98	3.15
F_{000}	1664	1664	1608	832	3216
temp, °C	23	23	23	23	23
$2\theta_{max}$, deg	46.0	50.0	46.0	46.0	48.0
no. of observns (I>3s(I))	2211	1849	2122	2497	2298
no. of variables	187	265	250	265	247
residuals: R; R_w	0.051; 0.053	0.029; 0.030	0.037; 0.040	0.044; 0.050	0.027; 0.028
goodness of fit indicator	2.36	1.40	1.90	2.89	1.20
max shift in final cycle	0.01	0.02	0.05	0.32	0.10
largest peak in final diff map, e/Å^3	1.55	0.95	1.80	2.68	0.85
abs cor	empirical	empirical	empirical	empirical	empirical
max/min	1.00/0.30	1.00/0.38	1.00/0.30	1.00/0.18	1.00/0.49
scan speed, deg/min	4.0	4.0	4.0	4.0	4.0

Compounds **1** and **3** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely from the systematic absences observed in the data for both compounds. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. For **1** all atoms heavier than carbon were refined with anisotropic thermal parameters. For **3** all of the non-hydrogen atoms were refined with anisotropic thermal parameters. For **1** the positions of the hydrogen atoms on the ligand were calculated by assuming idealized geometries. The hydride ligand was not located and was ignored. For **3** the positions of the hydrogen atoms on the ligand were calculated by assuming idealized geometries. The hydride ligands of **3** were obtained from difference Fourier syntheses and were refined on their coordinates only. The scattering contributions of all other hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

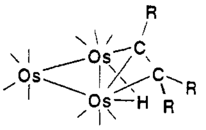
Compound **2** crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was identified on the basis of the systematic absences observed in the data. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the ligand were calculated in idealized positions. The hydride ligand was located in a difference Fourier map, and its positional parameters were satifactorily refined. A test for an enantiomorph was made by inverting the coordinates of all atoms and refining further, but this yielded poorer R factors, $R = 0.034$ and $R_w = 0.037$. Thus, the original enantiomorph was retained.

Compound **4** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Both of these structures were solved by combinations of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the alkyl groups were calculated by assuming idealized geometries. The position of the hydride ligand and the hydrogen atom H(41) were obtained from difference Fourier syntheses. Only the positions of the latter two hydrogen atoms were refined. The contributions of all of the hydrogen atoms were added to the structure factor calculations.

Compound **5** crystallized in the monoclinic crystal system. The systematic absences observed in the data were consistent with both of the space groups $C2/c$ and Cc. Since $Z = 8$, the centrosymmetric space group was assumed. This was confirmed by the successful solution and refinement of the structure. This structure was solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All of the non-hydrogen atoms were refined by using anisotropic thermal parameters. The hydride ligand was located in a difference Fourier synthesis. Its position was satisfactorily refined. The positions of the remaining hydrogen atoms were calculated by assuming idealized geometries and employing observed positions whenever possible. The contributions of these hydrogen atoms were added to the structure factor calculations. See the supplementary material for tables of structure factor amplitudes, hydrogen atom positional parameters, and anisotropic thermal parameters for all of the structural analyses.

Results and Discussion

The reactions of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with ethyne and alkyl- and aryl-substituted alkynes are known to proceed by a combination of addition and insertion to yield the complexes E, which contain a σ–π bridging alkenyl ligand.[10]



E

The reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $MeC{\equiv}CNMe_2$ proceeds smoothly at 25 °C to give the compound $Os_3(CO)_{10}[\mu\text{-}C(Me)C(H)NMe_2](\mu\text{-}H)$ (**1**) in 68% yield. IR and ^1H NMR spectra of **1** are given in Table I. Compound **1** was also characterized by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **1** is shown in Figure 1. Final atomic positional parameters are listed in Table III. Selected interatomic bond distances and angles are listed in Tables IV and V, respectively. The molecule consists of a triangular cluster of three osmium atoms with 10 linear terminal carbonyl ligands distributed as shown in Figure 1. The most inter-

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Table III. Positional Parameters and B(eq) Values for 1

atom	x	y	z	B(eq), Å^2
Os(1)	0.41121 (12)	0.17816 (6)	0.79693 (6)	3.72 (4)
Os(2)	0.21619 (11)	0.06548 (6)	0.84660 (6)	3.32 (4)
Os(3)	0.38853 (13)	0.03332 (6)	0.69633 (6)	3.79 (5)
O(11)	0.406 (3)	0.2700 (14)	0.6149 (13)	9 (1)
O(12)	0.464 (3)	0.3182 (13)	0.9274 (15)	10 (1)
O(13)	0.759 (2)	0.1456 (16)	0.8312 (17)	9 (1)
O(21)	0.348 (2)	−0.0829 (11)	0.9492 (13)	7 (1)
O(22)	−0.061 (3)	−0.0154 (11)	0.7276 (14)	7 (1)
O(23)	0.057 (3)	0.0962 (12)	1.0124 (13)	8 (1)
O(31)	0.254 (3)	−0.1266 (14)	0.6468 (16)	9 (1)
O(32)	0.637 (3)	−0.0258 (14)	0.8661 (13)	8 (1)
O(33)	0.175 (3)	0.0999 (17)	0.5190 (13)	11 (2)
O(34)	0.643 (2)	0.0444 (13)	0.5784 (12)	8 (1)
N	−0.044 (3)	0.2296 (13)	0.6550 (14)	6 (1)
C(1)	0.065 (3)	0.1815 (14)	0.6994 (15)	3.8 (5)
C(2)	0.158 (3)	0.1846 (14)	0.7913 (14)	3.7 (5)
C(3)	0.115 (3)	0.2417 (16)	0.8670 (17)	5.1 (6)
C(4)	−0.095 (5)	0.296 (3)	0.692 (3)	11 (1)
C(5)	−0.129 (4)	0.2077 (20)	0.562 (2)	7.7 (8)
C(11)	0.406 (3)	0.2361 (16)	0.6824 (17)	4.7 (5)
C(12)	0.445 (3)	0.2643 (18)	0.8814 (19)	5.6 (6)
C(13)	0.633 (4)	0.1559 (18)	0.8184 (19)	5.8 (7)
C(21)	0.304 (3)	−0.0271 (15)	0.9102 (15)	3.7 (5)
C(22)	0.042 (3)	0.0162 (15)	0.7760 (16)	4.0 (5)
C(23)	0.120 (3)	0.0849 (15)	0.9506 (16)	4.4 (5)
C(31)	0.301 (3)	−0.0662 (18)	0.6669 (17)	5.1 (6)
C(32)	0.536 (3)	−0.0058 (16)	0.8046 (17)	4.7 (5)
C(33)	0.248 (4)	0.0820 (19)	0.590 (2)	6.5 (7)
C(34)	0.545 (3)	0.0398 (15)	0.6219 (16)	4.4 (5)

Table IV. Intramolecular Distances for 1[a]

Os(1)–C(12)	1.90 (3)	Os(3)–C(31)	1.90 (3)
Os(1)–C(11)	1.91 (3)	Os(3)–C(34)	1.90 (3)
Os(1)–C(13)	1.97 (3)	Os(3)–C(32)	1.94 (3)
Os(1)–C(2)	2.23 (2)	Os(3)–C(33)	1.95 (3)
Os(1)–Os(2)	2.780 (2)	O–C (av)	1.14 (3)
Os(1)–Os(3)	2.870 (2)	N–C(1)	1.34 (3)
Os(2)–C(22)	1.87 (3)	N–C(4)	1.38 (4)
Os(2)–C(23)	1.87 (2)	N–C(5)	1.44 (3)
Os(2)–C(21)	1.93 (3)	C(1)–C(2)	1.40 (3)
Os(2)–C(2)	2.23 (2)	C(2)–C(3)	1.56 (3)
Os(2)–Os(3)	2.905 (1)		

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

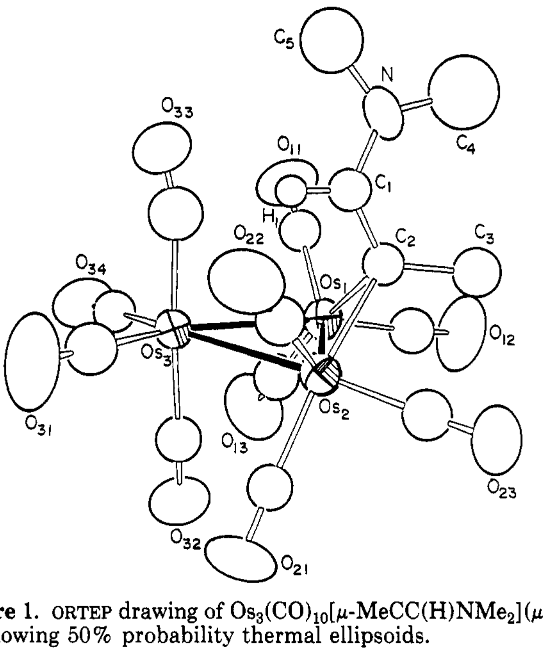


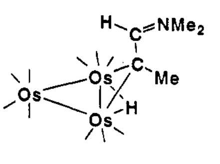
Figure 1. ORTEP drawing of $Os_3(CO)_{10}[\mu\text{-}MeCC(H)NMe_2](\mu\text{-}H)$ (1) showing 50% probability thermal ellipsoids.

Table V. Intramolecular Bond Angles for 1[a]

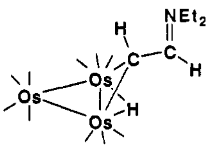
C(12)–Os(1)–C(2)	91 (1)	C(31)–Os(3)–Os(1)	152.4 (8)
C(12)–Os(1)–Os(2)	114.8 (8)	C(31)–Os(3)–Os(2)	95.0 (8)
C(12)–Os(1)–Os(3)	170.2 (8)	C(34)–Os(3)–Os(1)	103.7 (8)
C(11)–Os(1)–C(2)	95 (1)	C(34)–Os(3)–Os(2)	159.9 (7)
C(11)–Os(1)–Os(2)	132.2 (8)	C(32)–Os(3)–Os(1)	86.3 (8)
C(11)–Os(1)–Os(3)	92.6 (8)	C(32)–Os(3)–Os(2)	81.3 (7)
C(13)–Os(1)–C(2)	169 (1)	C(33)–Os(3)–Os(1)	89 (1)
C(13)–Os(1)–Os(2)	118.2 (9)	C(33)–Os(3)–Os(2)	98.2 (9)
C(13)–Os(1)–Os(3)	83.1 (9)	Os(1)–Os(3)–Os(2)	57.55 (3)
C(2)–Os(1)–Os(2)	51.4 (6)	C(1)–N–C(4)	127 (3)
C(2)–Os(1)–Os(3)	93.0 (6)	C(1)–N–C(5)	118 (2)
Os(2)–Os(1)–Os(3)	61.86 (4)	C(4)–N–C(5)	115 (3)
C(22)–Os(2)–C(2)	97 (1)	H(1)–C(1)–N	113.38
C(22)–Os(2)–Os(1)	131.9 (7)	H(1)–C(1)–C(2)	115.64
C(22)–Os(2)–Os(3)	90.6 (7)	N–C(1)–C(2)	131 (2)
C(23)–Os(2)–C(2)	90 (1)	C(1)–C(2)–C(3)	119 (2)
C(23)–Os(2)–Os(1)	118.3 (8)	C(1)–C(2)–Os(2)	110 (2)
C(23)–Os(2)–Os(3)	175.4 (8)	C(1)–C(2)–Os(1)	116 (2)
C(21)–Os(2)–C(2)	168 (1)	C(3)–C(2)–Os(2)	114 (1)
C(21)–Os(2)–Os(1)	119.2 (7)	C(3)–C(2)–Os(1)	112 (2)
C(21)–Os(2)–Os(3)	88.0 (6)	Os(2)–C(2)–Os(1)	77.2 (8)
C(2)–Os(2)–Os(1)	51.4 (6)	O(33)–C(33)–Os(3)	168 (3)
C(2)–Os(2)–Os(3)	92.0 (5)	O–C–Os (av)	177 (3)
Os(1)–Os(2)–Os(3)	60.59 (4)		

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

esting ligand is the $MeCC(H)NMe_2$ group, which symmetrically bridges the Os(1)–Os(2) bond through the carbon atom C(2). This ligand was formed by the insertion of the MeC_2NMe_2 molecule into a metal–hydrogen bond, which leads to the transfer of the hydride ligand to the Me_2N-substituted carbon atom C(1). The C(1)–N distance of 1.34 (3) Å is indicative of a partial multiple-bonding interaction formed by the donation of the lone pair of electrons on the nitrogen atom to C(1). In accord with this, the nitrogen atom exhibits a planar geometry. Separate resonances for the two *N*-methyl groups indicate that there is a hindered rotation about the C(1)–N bond that is slow on the NMR time scale. The C(1)–C(2) distance of 1.40 (3) Å is also short and indicates that some degree of multiple bonding exists between these atoms also. This ligand is structurally similar to the $HCC(H)NEt_2$ ligand found in the complex $Os_3(CO)_{10}[\mu\text{-}C(H)C(H)NEt_2](\mu\text{-}H)$ (8) reported by Shapley et al.,[11] except that it exhibits a syn conformation with respect to the cluster instead of the anti conformation found in 8. Compound 1 contains one bridging hydride ligand; $\delta = -15.01$ ppm. This is believed to bridge the Os(1)–Os(2) bond similar to the bridge in 8, but it was not located in the structural analysis.



1



8

When 1 was heated to reflux in hexane solvent for 2 h, the three new products $Os_3(CO)_{10}[\mu\text{-}Me(H)CCNMe_2](\mu\text{-}H)$ (2), $Os_3(CO)_9[\mu_3\text{-}MeC_2NMe_2](\mu\text{-}H)_2$ (3), and $Os_3(CO)_{10}[\mu\text{-}EtCN(Me)CH_2](\mu\text{-}H)$ (4) were obtained in yields of 34%, 6%, and 28%, respectively. Compounds 1, 2, and 4 are isomers. Compound 3 is a decarbonylation product. Each of the products 2–4 was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses.

An ORTEP drawing of the molecular structure of 2 is shown in Figure 2. Final atomic positional parameters are listed in Table VI. Selected interatomic distances and

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[11] (a) Shapley, J. R.; Tachikawa, M.; Churchill, M. R.; Lashewycz, R. A. *J. Organomet. Chem.* 1978, *162*, C39. (b) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* 1979, *18*, 848.

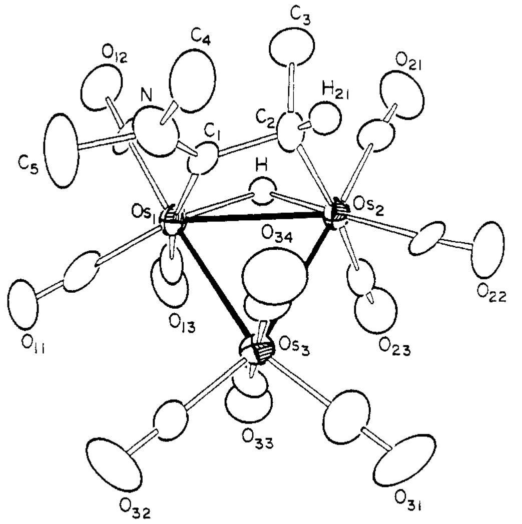

Figure 2. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}CH(Me)CNMe_2](\mu\text{-}H)$ (**2**) showing 50% probability thermal ellipsoids.

Table VI. Positional Parameters and *B*(eq) Values for 2

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.51918 (5)	0.19840 (4)	0.38486 (7)	2.14 (3)
Os(2)	0.37644 (6)	0.06533 (4)	0.42500 (7)	2.12 (3)
Os(3)	0.62656 (6)	0.05207 (4)	0.40394 (7)	2.57 (3)
O(11)	0.7586 (11)	0.2575 (9)	0.3158 (18)	5.3 (8)
O(12)	0.3913 (14)	0.3438 (8)	0.3321 (19)	6.0 (9)
O(13)	0.5488 (12)	0.2408 (10)	0.6790 (15)	5.3 (8)
O(21)	0.1200 (12)	0.0902 (10)	0.4801 (16)	5.4 (8)
O(22)	0.3544 (13)	−0.0958 (8)	0.3274 (17)	5.2 (8)
O(23)	0.4054 (14)	0.0260 (10)	0.7224 (14)	5.4 (8)
O(31)	0.6456 (18)	−0.1123 (10)	0.473 (2)	8 (1)
O(32)	0.8780 (11)	0.0906 (11)	0.3361 (17)	7 (1)
O(33)	0.6557 (12)	0.0873 (10)	0.7009 (15)	5.1 (8)
O(34)	0.5885 (13)	0.0138 (9)	0.1082 (17)	5.4 (8)
N	0.4968 (14)	0.1742 (9)	0.0765 (14)	4.1 (7)
C(1)	0.4628 (13)	0.1577 (9)	0.2019 (15)	1.9 (7)
C(2)	0.3621 (15)	0.1045 (10)	0.2146 (17)	2.6 (7)
C(1)	0.4628 (13)	0.1577 (9)	0.2019 (15)	1.9 (7)
C(2)	0.3621 (15)	0.1045 (10)	0.2146 (17)	2.6 (7)
C(3)	0.2502 (15)	0.1472 (12)	0.189 (2)	4 (1)
C(4)	0.4514 (20)	0.1360 (13)	−0.0420 (19)	5 (1)
C(5)	0.589 (2)	0.2301 (15)	0.051 (2)	6 (1)
C(11)	0.6676 (19)	0.2339 (10)	0.338 (2)	4 (1)
C(12)	0.4397 (15)	0.2904 (9)	0.3532 (17)	2.7 (8)
C(13)	0.5406 (15)	0.2238 (10)	0.5735 (19)	3.1 (8)
C(21)	0.2162 (15)	0.0830 (10)	0.4549 (16)	2.6 (7)
C(22)	0.3636 (15)	−0.0344 (10)	0.374 (2)	3.5 (9)
C(23)	0.3970 (14)	0.0411 (11)	0.611 (2)	3.4 (8)
C(31)	0.640 (2)	−0.0503 (13)	0.439 (3)	5 (1)
C(32)	0.7831 (15)	0.0761 (11)	0.3652 (20)	3.5 (8)
C(33)	0.6431 (13)	0.0774 (12)	0.5898 (19)	3.3 (8)
C(34)	0.5989 (16)	0.0294 (11)	0.217 (2)	3.3 (9)
H	0.373 (13)	0.166 (10)	0.507 (17)	4.0

Table VII. Intramolecular Distances for 2[a]

Os(1)–C(11)	1.88 (2)	Os(2)–Os(3)	2.901 (1)
Os(1)–C(12)	1.91 (2)	Os(3)–C(31)	1.87 (2)
Os(1)–C(13)	1.96 (2)	Os(3)–C(32)	1.89 (2)
Os(1)–C(1)	2.08 (2)	Os(3)–C(33)	1.93 (2)
Os(1)–H	2.2 (2)	Os(3)–C(34)	1.95 (2)
Os(1)–Os(3)	2.894 (1)	N–C(1)	1.35 (2)
Os(1)–Os(2)	2.916 (1)	N–C(4)	1.47 (2)
Os(2)–C(22)	1.86 (2)	N–C(5)	1.48 (2)
Os(2)–C(21)	1.90 (2)	C(1)–C(2)	1.50 (2)
Os(2)–C(23)	1.93 (2)	C(2)–C(3)	1.52 (2)
Os(2)–C(2)	2.23 (2)	O–C (av)	1.14 (3)
Os(2)–H	2.0 (2)		

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

Table VIII. Intramolecular Bond Angles for 2[a]

C(11)–Os(1)–C(1)	100.5 (8)	C(2)–Os(2)–Os(1)	69.9 (4)
C(11)–Os(1)–Os(3)	86.0 (5)	Os(3)–Os(2)–Os(1)	59.68 (2)
C(11)–Os(1)–Os(2)	145.2 (5)	C(31)–Os(3)–Os(1)	158.4 (7)
C(12)–Os(1)–C(1)	90.2 (7)	C(31)–Os(3)–Os(2)	98.6 (7)
C(12)–Os(1)–Os(3)	173.1 (5)	C(32)–Os(3)–Os(1)	101.0 (6)
C(12)–Os(1)–Os(2)	116.9 (5)	C(32)–Os(3)–Os(2)	160.6 (6)
C(13)–Os(1)–C(1)	166.4 (6)	C(33)–Os(3)–Os(1)	84.0 (6)
C(13)–Os(1)–Os(3)	95.2 (6)	C(33)–Os(3)–Os(2)	90.5 (4)
C(13)–Os(1)–Os(2)	97.2 (5)	C(34)–Os(3)–Os(1)	93.0 (6)
C(1)–Os(1)–Os(3)	83.0 (4)	C(34)–Os(3)–Os(2)	85.7 (5)
C(1)–Os(1)–Os(2)	70.2 (4)	Os(1)–Os(3)–Os(2)	60.41 (2)
Os(3)–Os(1)–Os(2)	59.91 (2)	C(1)–N–C(4)	123 (2)
C(22)–Os(2)–C(2)	91.9 (8)	C(1)–N–C(5)	121 (2)
C(22)–Os(2)–Os(3)	88.9 (5)	C(4)–N–C(5)	115 (2)
C(22)–Os(2)–Os(1)	141.9 (6)	N–C(11)–C(2)	116 (1)
C(21)–Os(2)–C(2)	91.5 (7)	N–C(1)–Os(1)	131 (1)
C(21)–Os(2)–Os(3)	173.0 (5)	C(2)–C(1)–Os(1)	113 (1)
C(21)–Os(2)–Os(1)	115.8 (6)	C(1)–C(2)–C(3)	109 (1)
C(23)–Os(2)–C(2)	174.0 (7)	C(1)–C(2)–Os(2)	103 (1)
C(23)–Os(2)–Os(3)	86.0 (5)	C(3)–C(2)–Os(2)	112 (1)
C(23)–Os(2)–Os(1)	104.2 (5)	O–C–Os (av)	176 (2)
C(2)–Os(2)–Os(3)	91.7 (4)	Os(1)–H–Os(2)	90 (6)

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

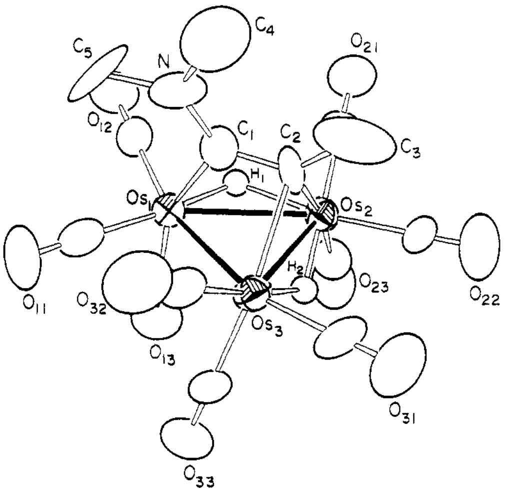

Figure 3. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}H)_2$ (**3**) showing 50% probability thermal ellipsoids.

angles are listed in Tables VII and VIII. Compound **2** consists of a triangular cluster of three osmium atoms with 10 linear terminal carbonyl ligands. The most interesting ligand is the Me(H)CC(NMe_2) group, which bridges the Os(1)–Os(2) bond. This ligand could be viewed as an NMe_2-substituted alkenyl group, but unlike alkyl- and aryl-substituted alkenyl ligands that coordinate in the σ–π fashion[11] (E), the NMe_2-substituted carbon atom is coordinated solely to Os(1); Os(1)–C(1) = 2.08 (2) Å. The nitrogen atom is planar, and the short C(1)–N distance of 1.35 (2) Å is indicative of partial multiple bonding. The observation of two *N*-methyl resonances in the ^{1}H NMR spectrum, 3.36 and 3.40 ppm, indicates the existence of a significantly hindered rotation about the C(1)–N bond. The C(1)–C(2) bond length of 1.50 (2) Å is typical of a C–C single bond. Compound **2** contains one hydride ligand, with a ^{1}H NMR resonance at −16.35 ppm (located and refined crystallographically), which bridges the Os(1)–Os(2) bond.

An ORTEP drawing of **3** is shown in Figure 3. Final atomic positional parameters are listed in Table IX. Selected interatomic distances and angles are listed in Tables X and XI. Compound **3** consists of a triangular cluster of three osmium atoms. Each metal atom contains three linear terminal carbonyl ligands. A triply bridging ynamine ligand, $MeC{\equiv}CNMe_2$, occupies one triangular face of the cluster. Two hydride ligands, with δ = −16.27

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

atom	x	y	z	B(eq), Å^2
Os(1)	0.76994 (7)	−0.09088 (4)	0.63392 (5)	3.43 (3)
Os(2)	0.82277 (6)	0.07452 (4)	0.73832 (5)	3.35 (3)
Os(3)	0.81555 (7)	−0.08388 (5)	0.84329 (5)	3.43 (3)
O(11)	0.7358 (18)	−0.2845 (9)	0.6437 (14)	8 (1)
O(12)	0.6303 (17)	−0.0634 (11)	0.4253 (12)	8 (1)
O(13)	1.0688 (15)	−0.1067 (11)	0.5750 (12)	8 (1)
O(21)	0.6446 (15)	0.2017 (10)	0.6192 (12)	7 (1)
O(22)	0.8567 (20)	0.1942 (10)	0.9214 (14)	9 (1)
O(23)	1.0947 (15)	0.1353 (9)	0.6560 (13)	8 (1)
O(31)	0.8391 (16)	−0.0246 (11)	1.0615 (11)	7 (1)
O(32)	0.6393 (15)	−0.2377 (10)	0.8930 (13)	8 (1)
O(33)	1.0795 (14)	−0.1866 (9)	0.8347 (12)	6.7 (8)
N	0.4742 (13)	−0.0889 (10)	0.7077 (11)	4.8 (8)
C(1)	0.6032 (17)	−0.0520 (11)	0.7234 (13)	4.1 (9)
C(2)	0.6437 (19)	0.0045 (9)	0.7953 (12)	3.4 (8)
C(3)	0.567 (2)	0.0485 (16)	0.8689 (20)	8 (1)
C(4)	0.361 (2)	−0.0660 (18)	0.7739 (20)	9 (2)
C(5)	0.438 (2)	−0.1551 (18)	0.6397 (18)	8 (1)
C(11)	0.7457 (19)	−0.2099 (14)	0.6415 (13)	5 (1)
C(12)	0.6873 (20)	−0.0730 (13)	0.5027 (16)	5 (1)
C(13)	0.961 (2)	−0.1044 (13)	0.5979 (16)	6 (1)
C(21)	0.7097 (18)	0.1542 (12)	0.6631 (14)	4 (1)
C(22)	0.8426 (19)	0.1491 (12)	0.8549 (14)	4 (1)
C(23)	0.995 (2)	0.1156 (12)	0.6885 (16)	5 (1)
C(31)	0.8301 (18)	−0.0481 (14)	0.9813 (14)	5 (1)
C(32)	0.7066 (19)	−0.1818 (13)	0.8742 (14)	4 (1)
C(33)	0.9830 (20)	−0.1498 (12)	0.8380 (13)	4 (1)
H(1)	0.783 (13)	0.014 (8)	0.619 (9)	3.0
H(2)	0.915 (13)	0.011 (8)	0.795 (9)	3.0

Table X. Intramolecular Distances for 3[a]

Os(1)–C(11)	1.87 (2)	Os(2)–Os(3)	2.823 (1)
Os(1)–C(12)	1.91 (2)	Os(3)–C(31)	1.90 (2)
Os(1)–C(13)	1.97 (2)	Os(3)–C(32)	1.91 (2)
Os(1)–C(1)	2.14 (1)	Os(3)–C(33)	1.94 (2)
Os(1)–H(1)	1.6 (1)	Os(3)–C(2)	2.25 (2)
Os(1)–Os(3)	2.783 (1)	Os(3)–C(1)	2.62 (2)
Os(1)–Os(2)	2.950 (1)	Os(3)–H(2)	1.9 (1)
Os(2)–C(21)	1.92 (2)	N–C(5)	1.40 (3)
Os(2)–C(22)	1.93 (2)	N–C(1)	1.40 (2)
Os(2)–C(23)	1.95 (2)	N–C(4)	1.48 (2)
Os(2)–C(2)	2.23 (2)	C(1)–C(2)	1.34 (2)
Os(2)–C(1)	2.92 (2)	C(2)–C(3)	1.43 (3)
Os(2)–H(1)	1.9 (1)	O–C (av)	1.13 (2)
Os(2)–H(2)	1.5 (1)		

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

Table XI. Intramolecular Bond Angles for 3[a]

C(11)–Os(1)–C(1)	98.4 (7)	C(31)–Os(3)–Os(2)	102.3 (6)
C(11)–Os(1)–Os(3)	90.1 (5)	C(32)–Os(3)–C(33)	94.2 (8)
C(11)–Os(1)–Os(2)	149.0 (5)	C(32)–Os(3)–C(2)	97.0 (7)
C(12)–Os(1)–C(1)	98.5 (8)	C(32)–Os(3)–Os(1)	96.3 (5)
C(12)–Os(1)–Os(3)	160.6 (6)	C(32)–Os(3)–Os(2)	145.1 (5)
C(12)–Os(1)–Os(2)	111.1 (6)	C(33)–Os(3)–C(2)	160.2 (6)
C(13)–Os(1)–C(1)	157.0 (8)	C(33)–Os(3)–Os(1)	92.9 (5)
C(13)–Os(1)–Os(3)	97.0 (6)	C(33)–Os(3)–Os(2)	113.8 (5)
C(13)–Os(1)–Os(2)	92.9 (6)	C(2)–Os(3)–Os(1)	69.7 (4)
C(1)–Os(1)–Os(3)	62.7 (5)	C(2)–Os(3)–Os(2)	50.5 (4)
C(1)–Os(1)–Os(2)	67.9 (5)	Os(1)–Os(3)–Os(2)	63.49 (3)
Os(3)–Os(1)–Os(2)	58.92 (2)	C(5)–N–C(1)	127 (2)
C(21)–Os(2)–C(2)	92.1 (7)	C(5)–N–C(4)	112 (2)
C(21)–Os(2)–Os(3)	142.3 (5)	C(1)–N–C(4)	121 (2)
C(21)–Os(2)–Os(1)	103.3 (6)	C(2)–C(1)–N	128 (1)
C(22)–Os(2)–C(2)	94.7 (7)	C(2)–C(1)–Os(1)	111 (1)
C(22)–Os(2)–Os(3)	97.8 (6)	N–C(1)–Os(1)	121 (1)
C(22)–Os(2)–Os(1)	154.9 (6)	C(1)–C(2)–C(3)	130 (2)
C(23)–Os(2)–C(2)	169.7 (7)	C(1)–C(2)–Os(2)	107 (1)
C(23)–Os(2)–Os(3)	119.2 (6)	C(1)–C(2)–Os(3)	90 (1)
C(23)–Os(2)–Os(1)	105.6 (6)	C(3)–C(2)–Os(2)	116 (1)
C(2)–Os(2)–Os(3)	51.3 (4)	C(3)–C(2)–Os(3)	121 (1)
C(2)–Os(2)–Os(1)	66.7 (4)	Os(2)–C(2)–Os(3)	78.2 (6)
Os(3)–Os(2)–Os(1)	57.60 (3)	O–C–Os (av)	177 (2)
C(31)–Os(3)–C(2)	96.9 (7)	Os(1)–H(1)–Os(2)	115 (7)
C(31)–Os(3)–Os(1)	164.5 (6)	Os(2)–H(2)–Os(3)	111 (7)

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

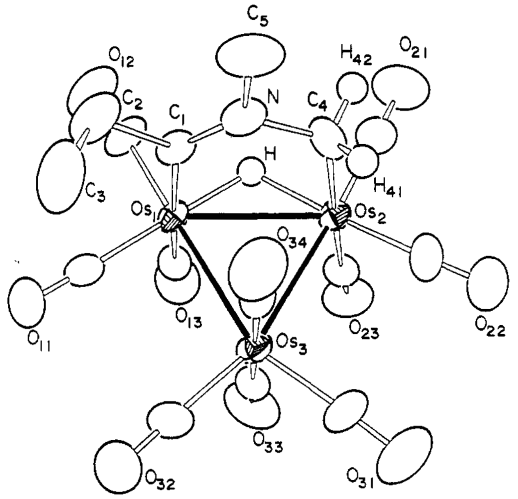

Figure 4. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}C(Et)N(Me)CH_2](\mu\text{-}H)$ (4) showing 50% probability thermal ellipsoids.

and −17.88 ppm at −56 °C, located and refined crystallographically, bridge the Os(1)–Os(2) and Os(2)–Os(3) edges of the cluster. H(1) causes a significant, but not unusual, lengthening of the Os(1)–Os(2) bond (2.950 (1) Å).[12] The hydride bond-lengthening effect is not as large on the Os(2)–Os(3) bond (2.823 (1) Å) due to the contraction effect of the single-atom bridge C(2). The Os(1)–Os(3) bond has no bridging hydride ligand and is the shortest (2.783 (1) Å).

The bridging $MeC{\equiv}CNMe_2$ ligand coordinates in a distorted form of the "slipped" μ-⊥ bonding mode that was first observed in compound B.[2,13] A twist away from the μ-⊥ mode is indicated by the inequality of the nonbonding distances, Os(3)···C(1) = 2.62 (2) Å and Os(2)···C(1) = 2.92 (2) Å. C(1) is coordinated strongly only to the metal atom Os(1) (Os(1)–C(1) = 2.14 (1) Å). C(2) is bonded equally to Os(2) and Os(3) (Os(2)–C(2) = 2.23 (2) Å and Os(2)–C(2) = 2.25 (2) Å). The nitrogen atom is planar, but the C(1)–N distance of 1.40 (2) Å is slightly longer than that in B (1.33 (2),[2a] 1.307 (18) Å[2b]) and implies that the C–N bond in 3 is slightly weaker. In further support of this, compound 3 exhibits a rotation about the C(1)–N bond that is rapid on the ^1H NMR time scale at 25 °C, whereas B exhibited a hindered rotation about this C–N bond even at 102 °C. The hydride ligands in 3 undergo exchange at an intermediate rate, and their NMR resonances are collapsed in the base line at 25 °C. At reduced temperatures rotation about the C–N bond and hydride ligand exchange are slowed and separate resonances were observed for the *N*-methyl groups and the inequivalent hydride ligands at −56 °C (see Table I).

An ORTEP drawing of the molecular structure of 4 is shown in Figure 4. Final atomic positional parameters are listed in Table XII. Selected interatomic distances and angles are listed in Tables XIII and XIV. The molecule consists of a triangular cluster of three osmium atoms with 10 linear terminal carbonyl ligands. There is one bridging hydride ligand (δ = −16.34 ppm), which was located and refined crystallographically. It bridges the Os(1)–Os(2) bond. An $EtCN(Me)CH_2$ ligand also bridges the Os(1)–Os(2) bond. It is coordinated to Os(1) by the

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

(13) Nomikou, Z.; Halet, J. F.; Hoffmann, R.; Tanner, J. T.; Adams, R. D. *Organometallics* **1990**, *9*, 588.

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.22660 (8)	0.32650 (4)	0.41183 (9)	2.29 (3)
Os(2)	0.13682 (8)	0.13863 (4)	0.27037 (9)	2.42 (3)
Os(3)	−0.04445 (8)	0.25557 (4)	0.47909 (9)	2.64 (3)
O(11)	0.1599 (17)	0.4982 (9)	0.6513 (19)	4.7 (6)
O(12)	0.5188 (19)	0.4042 (11)	0.366 (2)	6.3 (8)
O(13)	0.0356 (19)	0.3799 (10)	0.0794 (19)	5.4 (7)
O(21)	0.341 (2)	0.0255 (12)	0.058 (2)	6.9 (8)
O(22)	−0.0457 (18)	−0.0161 9)	0.302 (2)	5.2 (7)
O(23)	−0.1057 (17)	0.1589 (10)	−0.0617 (18)	5.1 (7)
O(31)	−0.290 (2)	0.1165 (12)	0.453 (2)	7.7 (9)
O(32)	−0.1591 (18)	0.4184 (10)	0.697 (2)	5.5 (7)
O(33)	−0.2507 (19)	0.3065 (11)	0.1495 (19)	6.0 (7)
O(34)	0.1656 (18)	0.2039 (9)	0.8101 (18)	4.7 (6)
N	0.4044 (17)	0.1971 (10)	0.628 (2)	3.4 (6)
C(1)	0.3796 (19)	0.2817 (11)	0.620 (2)	2.4 (6)
C(2)	0.479 (2)	0.3478 (14)	0.773 (3)	4.2 (9)
C(3)	0.405 (3)	0.3749 (14)	0.925 (3)	5 (1)
C(4)	0.317 (2)	0.1173 (11)	0.496 (2)	3.2 (7)
C(5)	0.514 (2)	0.1657 (15)	0.767 (3)	5 (1)
C(11)	0.1826 (19)	0.4332 (12)	0.561 (2)	2.6 (7)
C(12)	0.409 (2)	0.3704 (13)	0.379 (2)	3.6 (8)
C(13)	0.099 (2)	0.3631 (11)	0.208 (3)	3.2 (7)
C(21)	0.262 (2)	0.0685 (13)	0.141 (3)	3.8 (8)
C(22)	0.023 (2)	0.0441 (12)	0.290 (2)	3.5 (8)
C(23)	−0.019 (2)	0.1543 (11)	0.061 (2)	2.9 (7)
C(31)	−0.194 (2)	0.1688 (13)	0.461 (3)	4.1 (8)
C(32)	−0.115 (2)	0.3573 (13)	0.616 (2)	3.1 (7)
C(33)	−0.172 (2)	0.2878 (12)	0.267 (3)	3.6 (8)
C(34)	0.094 (2)	0.2210 (11)	0.687 (3)	3.2 (7)
H	0.268 (18)	0.228 (9)	0.30 (2)	3.0

Table XIII. Intramolecular Distances for 4[a]

Os(1)–H	1.7 (1)	Os(2)–Os(3)	2.919 (1)
Os(1)–C(12)	1.89 (2)	Os(3)–C(31)	1.87 (2)
Os(1)–C(11)	1.90 (2)	Os(3)–C(32)	1.89 (2)
Os(1)–C(13)	1.94 (2)	Os(3)–C(33)	1.96 (2)
Os(1)–C(1)	2.11 (2)	Os(3)–C(34)	1.98 (2)
Os(1)–Os(2)	2.907 (1)	N–C(1)	1.32 (2)
Os(1)–Os(3)	2.909 (1)	N–C(5)	1.45 (2)
Os(2)–H	1.8 (1)	N–C(4)	1.52 (2)
Os(2)–C(22)	1.86 (2)	C(1)–C(2)	1.51 (2)
Os(2)–C(21)	1.87 (2)	C(2)–C(3)	1.53 (3)
Os(2)–C(23)	1.95 (2)	O–C (av)	1.15 (2)
Os(2)–C(4)	2.17 (2)		

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

Table XIV Intramolecular Bond Angles for 4[a]

C(12)–Os(1)–C(1)	85.2 (7)	C(4)–Os(2)–Os(1)	84.0 (4)
C(12)–Os(1)–Os(2)	119.6 (6)	C(4)–Os(2)–Os(3)	93.6 (5)
C(12)–Os(1)–Os(3)	176.8 (6)	Os(1)–Os(2)–Os(3)	59.92 (3)
C(11)–Os(1)–C(1)	92.4 (7)	C(31)–Os(3)–Os(1)	156.2 (6)
C(11)–Os(1)–Os(2)	143.7 (5)	C(31)–Os(3)–Os(2)	96.4 (6)
C(11)–Os(1)–Os(3)	83.7 (5)	C(32)–Os(3)–Os(1)	102.4 (6)
C(13)–Os(1)–C(1)	174.9 (7)	C(32)–Os(3)–Os(2)	162.2 (6)
C(13)–Os(1)–Os(2)	93.0 (5)	C(33)–Os(3)–Os(1)	87.9 (6)
C(13)–Os(1)–Os(3)	91.9 (6)	C(33)–Os(3)–Os(2)	88.8 (5)
C(1)–Os(1)–Os(2)	85.5 (4)	C(34)–Os(3)–Os(1)	89.5 (5)
C(1)–Os(1)–Os(3)	91.6 (5)	C(34)–Os(3)–Os(2)	88.1 (5)
Os(2)–Os(1)–Os(3)	60.25 (3)	Os(1)–Os(3)–Os(2)	59.84 (3)
C(22)–Os(2)–C(4)	88.4 (8)	C(1)–N–C(5)	126 (2)
C(22)–Os(2)–Os(1)	144.5 (6)	C(1)–N–C(4)	125 (1)
C(22)–Os(2)–Os(3)	86.2 (6)	C(5)–N–C(4)	109 (1)
C(21)–Os(2)–C(4)	85.1 (7)	N–C(1)–C(2)	114 (2)
C(21)–Os(2)–Os(1)	117.1 (6)	N–C(1)–Os(1)	125 (1)
C(21)–Os(2)–Os(3)	176.9 (6)	C(2)–C(1)–Os(1)	121 (1)
C(23)–Os(2)–C(4)	177.2 (7)	C(1)–C(2)–C(3)	113 (2)
C(23)–Os(2)–Os(1)	97.3 (5)	N–C(4)–Os(2)	120 (1)
C(23)–Os(2)–Os(3)	89.1 (5)	Os(1)–H–Os(2)	115 (9)

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

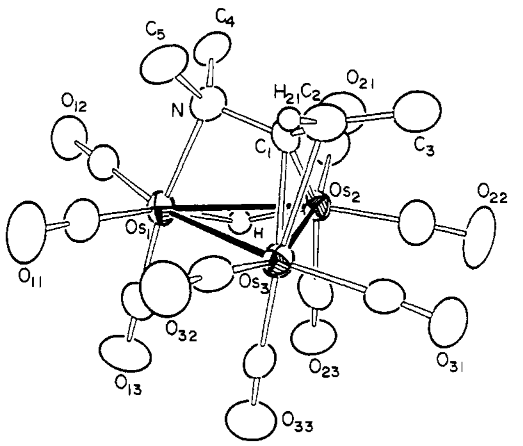
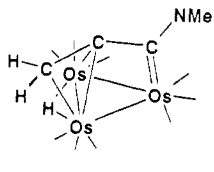


Figure 5. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}Me_2NCC(H)Me](\mu\text{-}H)$ (**5**) showing 50% probability thermal ellipsoids.

carbon atom C(1), which is a carbene center, and to Os(2) by the carbon atom C(4), which is a methylene group. As expected, the Os(1)–C(1) distance is slightly shorter than the Os(2)–C(4) distance (2.11 (2) vs 2.17 (2) Å). The ligand can be viewed as an *N*-methyl-metalated ethyl(dimethylamino)carbene ligand. The nitrogen atom is planar, and the C(1)–N distance is characteristically short (C(1)–N = 1.32 (2) Å), while the C(4)–N distance is characteristic of a C–N single bond length, 1.52 (2) Å. The complex $Os_3(CO)_8[\mu\text{-}C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**9**) one of several products obtained in the reaction of C with hydrogen (eq 1), contains a structurally similar *N*-methyl-metalated ethyl(dimethylamino)carbene ligand.[14] As expected, the diastereotopic hydrogen atoms on both of the methylene groups exhibit separate resonances with appropriate couplings to neighboring hydrogen nuclei (see Table I).

When a heptane solution of **3** was refluxed for 20 h, the new compound $Os_3(CO)_9[\mu_3\text{-}Me_2NCC(H)Me](\mu\text{-}H)$ (**5**) was formed in 14% yield. Approximately half of the original amount of **3** was recovered unchanged. As indicated by ^1H NMR spectroscopy, **5** exists in solution as a mixture of two isomers in a 4/1 ratio. The isomers **5** are also isomers of **3**. When solutions of **5** were heated, **3** was formed. The **3**/**5** equilibrium ratio is approximately 5/1, as determined by ^1H NMR spectroscopy.

When solutions of **3** in octane solvent were heated to reflux for a period of 6 h, the known compound $Os_3(CO)_9[\mu_3\text{-}H_2CC_2NMe_2](\mu\text{-}H)$ (**6**)[3] was formed in 85% yield.



6

Crystals of **5** obtained from the solution mixture were shown to be the *Z* isomer in pure form by a single-crystal X-ray diffraction analysis.

An ORTEP diagram of the molecular structure of *Z*-**5** is shown in Figure 5. Atomic positional parameters are listed in Table XV. Selected interatomic distances and angles are listed in Tables XVI and XVII. The molecule consists of a triangular cluster of three metal atoms with three linear terminal carbonyl ligands attached to each metal atom. The molecule contains a triply bridging η^3-$Me_2NCC(H)Me$ ligand. This ligand is similar to the one found in **2**, except in this case, the nitrogen atom is co-

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(14) Adams, R. D.; Chen, G.; Tanner, J. T.; Yin, J. *Organometallics*, previous article in this issue.

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.31579 (3)	0.47802 (6)	0.655228 (19)	2.43 (2)
Os(2)	0.40312 (3)	0.57439 (6)	0.569186 (18)	2.40 (2)
Os(3)	0.42159 (3)	0.74279 (6)	0.657549 (19)	2.35 (2)
O(11)	0.2706 (6)	0.5761 (13)	0.7591 (4)	5.2 (5)
O(12)	0.1870 (5)	0.2259 (11)	0.6366 (4)	4.4 (5)
O(13)	0.4275 (6)	0.2297 (12)	0.7026 (4)	5.5 (6)
O(21)	0.3307 (6)	0.4539 (14)	0.4690 (4)	6.1 (6)
O(22)	0.5208 (6)	0.8047 (13)	0.5265 (4)	6.0 (6)
O(23)	0.5337 (5)	0.3258 (12)	0.5844 (4)	5.3 (5)
O(31)	0.5452 (5)	0.9918 (12)	0.6383 (4)	5.2 (5)
O(32)	0.3810 (5)	0.8856 (12)	0.7573 (3)	4.4 (5)
O(33)	0.5472 (5)	0.5119 (12)	0.6996 (4)	4.8 (5)
N	0.2523 (5)	0.6684 (11)	0.6140 (4)	3.0 (5)
C(1)	0.3231 (6)	0.7434 (13)	0.5965 (4)	2.6 (5)
C(2)	0.3335 (7)	0.9101 (15)	0.6061 (5)	3.1 (6)
C(3)	0.3717 (7)	1.0254 (15)	0.5719 (6)	4.2 (7)
C(4)	0.1991 (6)	0.6085 (15)	0.5703 (5)	3.4 (6)
C(5)	0.2037 (7)	0.7691 (17)	0.6461 (5)	4.0 (6)
C(11)	0.2862 (7)	0.5419 (15)	0.7189 (5)	3.3 (6)
C(12)	0.2357 (7)	0.3184 (16)	0.6419 (5)	3.3 (6)
C(13)	0.3858 (8)	0.3258 (16)	0.6854 (5)	3.4 (6)
C(21)	0.3582 (7)	0.4967 (17)	0.5070 (5)	3.7 (6)
C(22)	0.4742 (8)	0.7193 (17)	0.5419 (6)	4.3 (7)
C(23)	0.4854 (8)	0.4168 (17)	0.5780 (5)	3.7 (6)
C(31)	0.4988 (7)	0.9002 (16)	0.6436 (5)	3.3 (6)
C(32)	0.3939 (6)	0.8332 (15)	0.7188 (5)	2.9 (6)
C(33)	0.4978 (7)	0.6011 (15)	0.6845 (5)	2.9 (6)
H	0.363 (6)	0.444 (14)	0.600 (5)	5.0

Table XVI Intramolecular Distances for 5[a]

Os(1)–C(11)	1.89 (1)	Os(2)–Os(3)	2.7470 (7)
Os(1)–C(13)	1.89 (1)	Os(3)–C(33)	1.87 (1)
Os(1)–C(12)	1.93 (1)	Os(3)–C(32)	1.90 (1)
Os(1)–N	2.18 (1)	Os(3)–C(31)	1.92 (1)
Os(1)–H	1.8 (1)	Os(3)–C(1)	2.27 (1)
Os(1)–Os(3)	2.8559 (7)	Os(3)–C(2)	2.42 (1)
Os(1)–Os(2)	2.9511 (8)	N–C(1)	1.48 (1)
Os(2)–C(21)	1.90 (1)	N–C(5)	1.50 (2)
Os(2)–C(22)	1.90 (1)	N–C(4)	1.52 (2)
Os(2)–C(23)	1.93 (1)	C(1)–C(2)	1.42 (2)
Os(2)–C(1)	2.13 (1)	C(2)–C(3)	1.51 (2)
Os(2)–H	1.6 (1)	O–C (av)	1.15 (1)

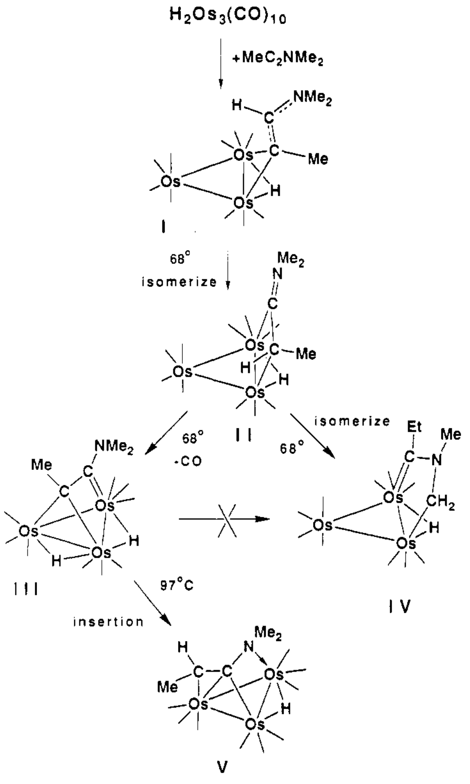
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table XVII. Intramolecular Bond Angles for 5[a]

C(11)–Os(1)–N	95.4 (5)	C(32)–Os(3)–Os(2)	157.8 (3)
C(11)–Os(1)–Os(3)	88.7 (4)	C(32)–Os(3)–Os(1)	97.1 (4)
C(11)–Os(1)–Os(2)	144.4 (4)	C(31)–Os(3)–C(1)	110.6 (5)
C(13)–Os(1)–N	170.1 (4)	C(31)–Os(3)–C(2)	85.0 (5)
C(13)–Os(1)–Os(3)	96.8 (4)	C(31)–Os(3)–Os(2)	102.6 (4)
C(13)–Os(1)–Os(2)	99.8 (4)	C(31)–Os(3)–Os(1)	166.0 (4)
C(12)–Os(1)–N	94.5 (4)	C(1)–Os(3)–C(2)	35.0 (4)
C(12)–Os(1)–Os(3)	168.8 (4)	C(1)–Os(3)–Os(2)	49.2 (3)
C(12)–Os(1)–Os(2)	116.1 (4)	C(1)–Os(3)–Os(1)	62.8 (3)
N–Os(1)–Os(3)	75.4 (2)	C(2)–Os(3)–Os(2)	76.9 (3)
N–Os(1)–Os(2)	71.0 (3)	C(2)–Os(3)–Os(1)	93.2 (3)
Os(3)–Os(1)–Os(2)	56.44 (2)	Os(2)–Os(3)–Os(1)	63.53 (2)
C(21)–Os(2)–C(1)	106.9 (5)	C(1)–N–C(5)	117 (1)
C(21)–Os(2)–Os(3)	160.6 (4)	C(1)–N–C(4)	111 (1)
C(21)–Os(2)–Os(1)	113.2 (4)	C(1)–N–Os(1)	94.1 (6)
C(22)–Os(2)–C(1)	99.5 (5)	C(5)–N–C(4)	107.0 (9)
C(22)–Os(2)—Os(3)	88.3 (5)	C(5)–N–Os(1)	113.4 (8)
C(22)–Os(2)–Os(1)	148.3 (4)	C(4)–N–Os(1)	113.9 (7)
C(23)–Os(2)–C(1)	153.0 (5)	C(2)–C(1)–N	117 (1)
C(23)–Os(2)–Os(3)	101.6 (4)	C(2)–C(1)–Os(2)	128.9 (9)
C(23)–Os(2)–Os(1)	97.6 (4)	C(2)–C(1)–Os(3)	78.1 (7)
C(1)–Os(2)–Os(3)	53.7 (3)	N–C(1)–Os(2)	113.6 (7)
C(1)–Os(2)–Os(1)	62.1 (3)	N–C(1)–Os(3)	111.3 (7)
Os(3)–Os(2)–Os(1)	60.03 (2)	Os(2)–C(1)–Os(3)	77.1 (3)
C(33)–Os(3)–C(1)	138.4 (5)	C(1)–C(2)–C(3)	125 (1)
C(33)–Os(3)–C(2)	167.9 (5)	C(1)–C(2)–Os(3)	66.9 (7)
C(33)–Os(3)–Os(2)	92.6 (4)	C(3)–C(2)–Os(3)	115.3 (8)
C(33)–Os(3)–Os(1)	87.3 (3)	Os(2)–H–Os(1)	125 (7)
C(32)–Os(3)–C(1)	113.6 (4)	O–C–Os (av)	177 (1)
C(32)–Os(3)–C(2)	94.5 (5)		

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

Scheme I



ordinated to one of the metal atoms (Os(1)–N = 2.18 (1) Å) and the alkenyl grouping, C=C(H)Me, exhibits the normal σ–π coordination in bridging the two metal atoms Os(2) and Os(3).[10] The C(1)–N distance (1.48 (1) Å) is significantly longer than that found in **2** (1.35 (2) Å) and is indicative of a C–N single bond. The C(1)–C(2) distance of 1.42 (2) Å is significantly shorter than the corresponding distance in **2** (1.50 (2) Å). This ligand has *Z* stereochemistry, thus the name *Z*-**5** for the complex. The minor isomer observed in solution is believed to contain the alternative *E* stereochemistry of this ligand. This is supported by the similarity of the ^{1}H NMR spectra of the two compounds (see Table I). *Z*-**5** contains one hydride ligand (δ = −13.30 ppm), which was located and refined crystallographically. It bridges the elongated Os(1)–Os(2) bond (Os(1)–Os(2) = 2.9511 (8) Å).

Our experiments show that compound **2** is derived directly from **1** at 68 °C. A sample of **2** was heated in a sealed NMR tube and was shown by ^{1}H NMR spectroscopy to be transformed to **3** and **4** at approximately equal rates at 80 °C. A sample of **3** heated in a sealed tube was transformed to a mixture of two isomers of **5** at 80 °C that exist in equilibrium with **3**. The isomers **5** were converted back partially to **3** when heated to 80 °C. No **4** was obtained from thermolyzed samples of **3**. When heated to 125 °C in octane solvent, **3** was converted in 85% yield to **6**. In contrast, prolonged heating of **3** at 80 °C in toluene-d_8 solvent in the sealed NMR tube eventually yielded **7**. Due to the equilibrium between **3** and **5**, it was not possible to determine if the isomers **5** are intermediates en route to **6** or **7**.

A summary of the results of this study is given in Scheme I. The addition of $MeC{\equiv}CNMe_2$ to $Os_3(CO)_{10}(\mu\text{-}H)_2$ proceeds by an insertion reaction that leads to transfer of one of the hydride ligands to the NMe_2-substituted carbon atom of $MeC{\equiv}CNMe_2$ to yield the kinetic product **1**.

The transformation of **1** to its more stable isomer **2** involves a 1,2-shift of the hydrogen atom from the NMe_2-substituted carbon atom to the methyl-substituted carbon atom, the formation of an Os–C bond to the NMe_2-substituted carbon atom, and the cleavage of one Os–C bond to the bridging methyl-substituted carbon atom. The mechanism of this transformation is unknown, but it is believed that it does *not* involve a metal-centered C–H activation in a decarbonylated intermediate, since such a process would almost certainly lead to **3** and **3** does not react with CO under these conditions to yield **2**.

The decarbonylation of **2** or **3** presumably occurs simply by a loss of CO from the $Os(CO)_4$ group and a CH activation of the methyl-substituted carbon atom at the vacant site. Similar processes are believed to occur in the transformation of osmium clusters E to the alkyne-containing clusters $Os_3(CO)_9(\mu_3\text{-}RC_2R)(\mu\text{-}H)_2$[10a] and the transformation of $Os_3(CO)_{10}(\mu\text{-}Me_2NCH_2)(\mu\text{-}H)$ to $Os_3(CO)_9(\mu_3\text{-}Me_2NCH)(\mu\text{-}H)_2$.[15]

The transformation of **2** to **4** competes with the **2** to **3** transformation. This transformation does not involve a loss of CO; thus, **4** is an isomer of **2**. The formation of **4** presumably occurs by a spontaneous reductive elimination of the hydride ligand and the methyl-substituted carbon atom. This would result in the formation of an ethyl(dimethylamino)carbene ligand and a vacant site on one of the neighboring osmium atoms. One of the *N*-methyl groups then undergoes a C–H activation at the vacant site to yield **4**. The formation of the carbene ligand in **4** represents the second example of the formation of a (dialkylamino)carbene ligand by the *unsymmetrical* hydrogenation of an ynamine ligand.[5,14]

When heated, **3** is transformed to **5**. Compound **5** appears to be a mixture of *E* and *Z* isomers in solution. The *Z* isomer was characterized structurally in the solid state. The transformation of **3** to **5** is an insertion reaction that results in the shift of one hydride ligand to the methyl-substituted carbon atom. Curiously, this is the same carbon atom from which the hydrogen atom was removed when **2** was converted to **3**. One might think that **2** should be readily converted to **5** by the decarbonylation, but it was shown by following the course of the reaction by NMR spectroscopy that this is *not* the favored pathway. Also, it was shown independently that **3** and **5** are interconvertible. An additional step in the transformation of **3** to **5** is the coordination of the nitrogen atom to one of the metal atoms. At this time, it is not known which step, insertion or nitrogen coordination, occurs first, but if the nitrogen coordination step occurred first, it could serve to promote the insertion step. It was not established which of the isomers of **5** is formed initially. In the *Z* isomer, the NMe_2 and Me groups possess a trans stereochemistry; thus, if **3** proceeds to *Z*-**5**, this could be another example of the elusive trans-alkyne insertion that was proposed by Muetterties and others and believed to be facilitated by the presence of adjacent metal centers.[16]

When solutions of **3** were heated to 125 °C for 6 h, 1 equiv of H_2 (not observed) was eliminated and the compound **6** was formed in high yield by CH activation at the *C*-methyl group. Compound **6** was obtained previously by the thermal decarbonylation of $Os_3(CO)_{10}(\mu\text{-}MeC_2NMe_2)$.[3]

When solutions of **3** and **5** in a sealed NMR tube were heated for a prolonged period at 80 °C, significant amounts of compound **7** were formed by the loss of 1 equiv of Me_2NH. This reaction may be simply the reverse of the known addition of amines to acetylide-containing cluster complexes to yield ynamine-containing cluster complexes.[2b] Under these milder conditions, no **6** was formed.

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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 (15 pages); tables of structure factor amplitudes (76 pages). Ordering information is given on any current masthead page.

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