

Clusters Containing Carbene Ligands. 5. The Synthesis, Structural Characterization, and Reactivity of a Triply Bridging (Dimethylamino)carbene Ligand in a Triosmium Cluster Complex

Richard D. Adams* and James E. Babin

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

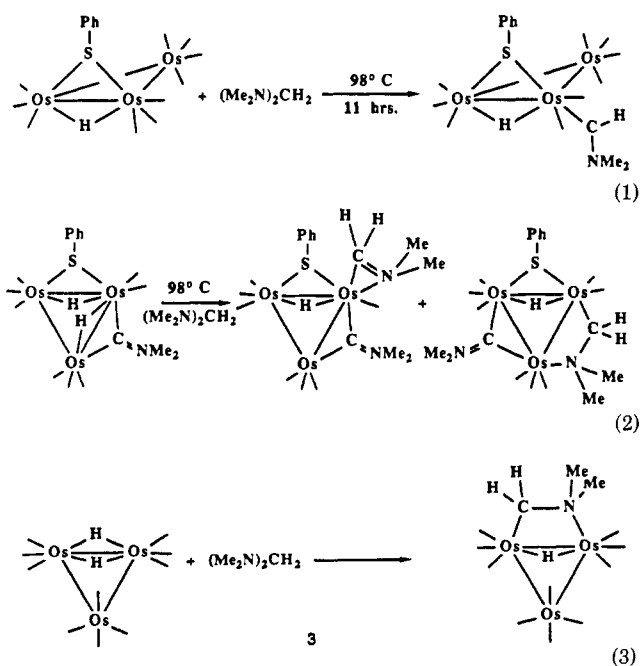
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The reaction of $\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})(\mu\text{-H})$ (1) with $\text{CH}_2(\text{NMe}_2)_2$ at 98 °C has yielded the two isomeric cluster complexes $\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^2\text{-C(H)NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (2, 25%) and $\text{Os}_3(\text{CO})_9[\text{C(H)NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (3, 52%) which contain secondary (dimethylamino)carbene ligands. Compound 2 was transformed to 3 in 60% yield by heating to 98 °C under a CO atmosphere. Compounds 2 and 3 were both characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. For 2: space group $P2_1/n$, $a = 8.878$ (2) Å, $b = 26.287$ (8) Å, $c = 9.243$ (2) Å, $\beta = 115.19$ (1)°, $Z = 4$, $V = 1951.9$ (8) Å³, and $\rho_{\text{calcd}} = 3.09$ g/cm³. The structure was solved by direct methods and was refined (2226 reflections) to the final values of the residuals $R = 0.0381$ and $R_w = 0.0387$. The molecule consists of an open triangular cluster of three metals with a triply bridging η^2 -(dimethylamino)carbene ligand and a methoxy group bridging the nonbonded pair of metal atoms. The carbene C-N distance is very long, 1.54 (2) Å, and can be attributed, in part, to the lack of C-N multiple bonding due to the coordination of the nitrogen lone pair of electrons. For 3: space group $P\bar{1}$, $a = 8.782$ (1) Å, $b = 16.042$ (3) Å, $c = 7.731$ (1) Å, $\alpha = 100.00$ (1)°, $\beta = 109.79$ (1)°, $\gamma = 94.43$ (2)°, $Z = 2$, $V = 998.2$ (6) Å³, and $\rho_{\text{calcd}} = 3.02$ g/cm³. The structure was solved by the heavy-atom method and was refined (2556 reflections) to the final values of the residuals $R = 0.0344$ and $R_w = 0.0341$. The molecule contains a closed triangular cluster of metal atoms with a bridging methoxy group and a terminally coordinated (dimethylamino)carbene ligand, C-N = 1.29 (2) Å. The reaction of $\text{HC}_2\text{CO}_2\text{Me}$ with 2 at 80 °C yielded the product $\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^3\text{-Me}_2\text{NCC(H)CCO}_2\text{Me}](\mu\text{-OMe})$ (4) in 42% yield. Compound 4 was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. For 4: space group $P2_1/c$, $a = 30.68$ (1) Å, $b = 9.638$ (2) Å, $c = 16.659$ (4) Å, $\beta = 91.56$ (2)°, $Z = 4$, $V = 4924$ (2) Å³, and $\rho_{\text{calcd}} = 2.80$ g/cm³. The structure was solved by direct methods and was refined (4030 reflections) to the final values of the residuals $R = 0.0353$ and $R_w = 0.0347$. The molecular structure of 4 consists of an open triangular cluster of metal atoms bridged by a methoxy ligand and a substituted triply bridging dimetallaallyl ligand, $(\text{Me}_2\text{N})\text{CC(H)C}(\text{CO}_2\text{Me})$. The latter was formed by a coupling of the alkyne molecule to the carbene ligand and a cleavage of the hydrogen atom from the carbene ligand.

Introduction

We have recently found that N,N,N',N' -tetraalkyldiaminomethanes are excellent reagents for the introduction of secondary (dialkylamino)carbene ligands into cluster complexes¹⁻³ (eq 1). These reactions are believed to proceed through a series of metal-mediated steps that ultimately lead to the elimination of a formula equivalent of R_2NH from the tetraalkyldiaminomethane molecule, and the initial coordination of an N,N -dialkyliminium ligand to the cluster^{4,5} (eq 2 and 3). Subsequent activation of a C-H bond in the iminium ligand results in the formation of the (dialkylamino)carbene ligand.

An important feature of these transformations is the ability of the metal cluster to support the polynuclear coordinations of the ligands.⁶⁻⁹ To further demonstrate the versatility of metal clusters in promoting unusual ligand transformations through novel polynuclear ligand interactions, we now wish to report the synthesis, structural characterization, and transformational behavior of a new cluster complex, $\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^2\text{-C(H)NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (2), which has been found to contain a η^2 triply bridging (dimethylamino)carbene ligand. In addition, the reactivity



of this ligand toward methyl propiolate will be described. A portion of these results have appeared in a preliminary report.¹⁰

Experimental Section

General Procedures. All reactions were performed under a dry nitrogen atmosphere, unless otherwise specified. Reagent

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grade solvents were dried over molecular sieves and were deoxygenated by purging with nitrogen prior to use. *N,N,N',N'*-tetramethyldiaminomethane and methyl propiolate were purchased from Aldrich Chemical Co. and were used without further purification. $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ was prepared by the published procedure.¹¹ IR spectra were recorded on a Nicolet 5-DXB FT-IR spectrophotometer. A Bruker AM-300 FT-NMR spectrometer was used to obtain ^1H NMR spectra. Low-temperature spectra were recorded on an IBM NR-80 FT-NMR spectrometer. TLC separations were performed in air on plates of 0.25-mm Kieselgel 60 F₂₅₄ obtained from E. Merck, West Germany.

Preparation of $\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})(\mu\text{-H})$ (1). To a CH_2Cl_2 solution (100 mL) containing $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ (300 mg, 0.322 mmol) was added 10 mL of MeOH. The solution was allowed to stir at room temperature for 1 h. The solvent was removed in vacuo, and the residue was passed through a silica gel column using hexane as the eluent. A yellow band was collected and identified as $\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})(\mu\text{-H})$ (1) (165 mg (55% yield)) by its characteristic IR and ^1H NMR spectra.¹²

Reaction of 1 with $\text{CH}_2(\text{NMe}_2)_2$. An excess of $\text{CH}_2(\text{NMe}_2)_2$ (1 mL) was added to a heptane solution of compound 1 (100 mg, 0.113 mmol), and the mixture was then heated to reflux for 6 h. After cooling, 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 40:60 CH_2Cl_2 /hexane solvent mixture separated in order of elution: unreacted 1 (40 mg) and the two isomeric compounds, yellow $\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^2\text{-C}(\text{H})\text{NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (2) (15 mg (25% yield based on amount of 1 consumed)) and yellow $\text{Os}_3(\text{CO})_9[\text{C}(\text{H})\text{NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (3) (31 mg (52% yield based on amount of 1 consumed)). IR ($\nu(\text{CO})$ in hexane solvent) for 2: 2095 (m), 2071 (s), 2038 (s), 2011 (s), 1995 (vs), 1978 (m), 1970 (m), 1959 (w), 1935 (vw) cm^{-1} . IR ($\nu(\text{CO})$ in hexane solvent) for 3: 2092 (m), 2051 (s), 2011 (vs), 2003 (m), 1996 (s), 1989 (m), 1982 (w), 1964 (m), 1937 (m) cm^{-1} . ^1H NMR (δ in CDCl_3 solvent) for 2: 7.62 (d, $J_{\text{H-H}} = 1.38$ Hz, 1 H), 4.01 (s, 3 H), 3.65 (s, 3 H), 3.03 (s, 3 H), -11.37 (d, $J_{\text{H-H}} = 1.38$ Hz, 1 H). ^1H NMR (δ in CDCl_3 solvent) for 3: 10.88 (s, 1H), 3.99 (s, 3H), 3.61 (s, 3 H), 3.57 (s, 3 H), -12.92 (s, 1 H). Anal. Calcd for 2: C, 17.11; H, 1.22; N, 1.54. Found: C, 17.22; H, 1.24; N, 1.55. Calcd for 3: C, 17.11; H, 1.22; N, 1.54. Found: C, 17.27; H, 1.24; N, 1.59.

Thermolysis of 2 under a CO Atmosphere. A heptane solution (30 mL) of 2 (20 mg, 0.022 mmol) was refluxed under a constant purge with CO for 4 h. The solvent was removed in vacuo, and the residue was transferred to silica gel TLC plates in a minimum quantity of CH_2Cl_2 . Elution with a 40:60 CH_2Cl_2 /hexane solvent mixture yielded 3 (12 mg (60%)).

Reaction of 2 with Methyl Propiolate. An excess of methyl propiolate (10 μL) was added to a cyclohexane solution (40 mL) of 2 (30 mg, 0.033 mmol). The solution was refluxed for 40 min, and after cooling, the solvent was removed in vacuo. The residue was dissolved in a minimum quantity of CH_2Cl_2 and applied to silica gel TLC plates. Elution with a 50:50 CH_2Cl_2 /hexane solvent mixture separated unreacted 2 (4 mg) from $\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^3\text{-Me}_2\text{NCC}(\text{H})\text{CCO}_2\text{Me}](\mu\text{-OMe})$ (4) (12 mg (42%)). IR ($\nu(\text{CO})$ in hexane solvent) for 4: 2090 (m), 2063 (m), 2036 (vs), 2008 (m), 1995 (m), 1980 (s), 1972 (vw), 1963 (w), 1703 (vw) cm^{-1} . ^1H NMR (δ in CD_2Cl_2 solvent) for 4: 6.81 (s, 1 H), 3.82 (s, 3 H), 3.65 (br s, 3 H), 3.54 (br s, 3 H), 3.32 (s, 3 H). ^1H NMR (δ in CD_2Cl_2 solvent at 80 MHz) at -45°C for 4: 6.73 (s, 1 H), 3.78 (s, 3 H), 3.64 (s, 3 H), 3.50 (s, 3 H), 3.29 (s, 3 H), 3.50 (s, 3 H), 3.29 (s, 3 H). Anal. Calcd for 4: C, 20.53; H, 1.32; N, 1.41. Found: C, 20.94; H, 1.20; N, 1.56.

Reaction of 3 with Methyl Propiolate. An excess of methyl propiolate (10 μL) was added to a cyclohexane solution (40 mL) of 3 (30 mg, 0.033 mmol). The solution was refluxed for 4 h. IR and test TLC showed no evidence of a reaction. Similarly, in a refluxing heptane solution no 4 was formed; however, some decomposition of the starting material was observed.

Crystallographic Analyses. Yellow crystals of 2 and 4 were grown by slow evaporation of solvent from CH_2Cl_2 /hexane so-

lutions at -25°C . Yellow crystals of 3 were grown by slow evaporation of solvent from CH_2Cl_2 /hexane solutions 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 $K\alpha$ 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 I. All data processing was performed on a Digital Equipment Corp. MICRO-VAX II computer by using the TEXSAN structure solving program library obtained from Molecular Structure Corp., College Station, TX. Absorption corrections of a Gaussian integration type were performed for all structures. Neutral atom scattering factors were obtained from the standard sources.^{13a} Anomalous dispersion corrections were applied to all non-hydrogen atoms.^{13b} Full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F)^2$, $\sigma(F)^2 = \sigma(F_o)^2/2F_o$, and $\sigma(F_o)^2 = [\sigma(I_{\text{raw}})^2 + (PF_o)^2]^{1/2}/Lp$.

Compound 2 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was determined from systematic absences observed during the data collection. The positions of the metal atoms were determined by direct methods (MITHRIL). The remaining non-hydrogen atoms were located in a series of difference Fourier syntheses. All non-hydrogen atoms were refined by using anisotropic thermal parameters. The position of the bridging hydride ligand was obtained from a difference Fourier synthesis and was successfully refined. The carbenoid hydrogen atom was also located from a difference Fourier map, but its position was not refined. All other hydrogen atom positions were calculated by assuming idealized tetrahedral geometry. The contributions of these hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound 3 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 was solved by a combination of Patterson and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. The bridging hydride ligand was located from a difference map, and its position was successfully refined. The hydrogen atom of the carbene ligand was also located but was not refined. Methyl hydrogen atom positions were calculated by assuming idealized geometry. The positions of these atoms were not refined.

Compound 4 crystallized in the monoclinic crystal system, and the space group $P2_1/c$ was determined from systematic absences observed in the data. The structure was solved by a combination of direct methods and difference Fourier techniques. Only atoms larger than oxygen were refined anisotropically. Hydrogen atom positions were calculated by assuming idealized tetrahedral geometry. The contributions of these atoms were added to the structure factor calculations, but their positions were not refined. In the final stages of refinement 1 mol of CH_2Cl_2 was found to have cocrystallized with the 2 mol of 4 observed in the asymmetric unit. It was refined without difficulty.

Error analyses for each structure were calculated from the inverse matrix obtained on the final cycle of refinement. See supplementary material for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters for compound 4. For compounds 2 and 3 this information was published previously.¹⁰

Results

Reaction of the cluster $\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})(\mu\text{-H})$ (1) with an excess of *N,N,N',N'*-tetramethyldiaminomethane in refluxing heptane yielded the two isomeric products $\text{Os}_3(\text{CO})_9[\mu_3\text{-}\eta^2\text{-C}(\text{H})\text{NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (2) and $\text{Os}_3(\text{CO})_9[\text{C}(\text{H})\text{NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (3) in 25% and 52% yields, respectively. When a heptane solution of 2 was heated to reflux under a CO atmosphere for 4 h, it was converted to compound 3 in 60% yield. Both compounds were

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

Table I. Crystallographic Data for Diffraction Studies

	2	3	4
(A) Crystal Data			
formula	Os ₃ O ₁₀ NC ₁₃ H ₁₁	Os ₃ O ₁₀ NC ₁₃ H ₁₁	Os ₃ O ₁₀ NC ₁₇ H ₁₄ ·0.5CH ₂ Cl ₂
temp (±3 °C)		25	
space group	<i>P</i> 2 ₁ / <i>n</i> , No. 14	<i>P</i> 1̄, No. 2	<i>P</i> 2 ₁ / <i>c</i> , No. 14
<i>a</i> , Å	8.878 (2)	8.782 (1)	30.681 (9)
<i>b</i> , Å	26.287 (8)	16.042 (3)	9.638 (2)
<i>c</i> , Å	9.243 (2)	7.731 (1)	16.659 (4)
α, deg	90.0	100.00 (1)	90.0
β, deg	115.19 (1)	109.79 (1)	91.56 (2)
γ, deg	90.0	93.43 (1)	90.0
<i>V</i> , Å ³	1951.9 (8)	998.2 (6)	4924 (2)
<i>M_r</i>	911.6	911.6	2076.7
<i>Z</i>	4	2	8
ρ, g·cm ³	3.09	3.02	2.80
(B) Measurement of Intensity Data			
radiatn		Mo Kα (0.71073 Å ⁻¹)	
monochromator		graphite	
detector aperture, mm			
horizontal		2.0	
vertical		2.0	
cryst faces	010, 010, 100, 211, 001, 001	010, 010, 100, 100, 001, 101, 021	001, 001, 100, 100, 210, 010
cryst size, mm	0.07, 0.15, 0.17	0.03, 0.25, 0.22	0.05, 0.12, 0.40
crystal orientation direction; deg from Φ axis	[110]; 0.5	[120]; 2.7	[100]; 0.2
reflectns measd	+ <i>h</i> , + <i>k</i> , ± <i>l</i>	+ <i>h</i> , ± <i>k</i> , ± <i>l</i>	+ <i>h</i> , + <i>k</i> , ± <i>l</i>
max 2θ, deg	48	48	43
ω-scan width, deg		1.1	
scan type		moving crystal-stationary counter	
bkgd (count time at each end of scan)		1/4 scan	
ω-scan rate, deg/min		4.0	
no. of reflectns measd	3382	3381	6419
no. of data used (<i>F</i> ² > 3.0σ(<i>F</i>) ²)	2226	2556	4030
(C) Treatment of Data			
abs corr	analytical	numerical	analytical
abs coeff, cm ⁻¹	206.9	202.3	165.3
grid		12 × 4 × 20	
transmissns coeff			
max	0.269	0.512	0.44
min	0.129	0.022	0.17
<i>P</i> factor	0.02	0.02	0.02
final residuals			
<i>R_F</i>	0.0381	0.0344	0.0353
<i>R_{wF}</i>	0.0387	0.0341	0.0347
esd of unit wt observn	1.487	1.792	1.371
largest shift/error value of final cycle	0.705	0.11	0.02
largest peak in final diff Fourier	1.81	1.58	1.32
no. of variables	247	252	307

^aRigaku software uses a multiple-scan technique. If the *I*/σ(*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.

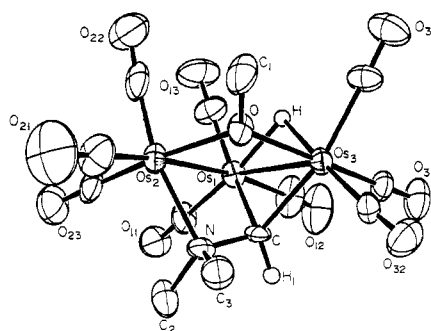


Figure 1. An ORTEP diagram of Os₃(CO)₉[μ₃-η²-C(H)NMe₂](μ-OMe)(μ-H) (2) showing 50% probability thermal ellipsoids.

characterized by IR and ¹H NMR spectroscopies and by single-crystal X-ray diffraction analyses.

An ORTEP drawing of compound 2 is shown in Figure 1. Interatomic distances and angles are listed in Tables II and III, respectively. The structure consists of a triangular cluster of three osmium atoms with only two metal-metal bonds. The Os(1)–Os(3) bond at 2.873 (1) Å is similar to

Table II. Intramolecular Distances (Å) for Os₃(CO)₉[μ₃-η²-C(H)NMe₂](μ-OMe)(μ-H) (2)

Os(1)–C(11)	1.85 (2)	Os(3)–C(31)	1.89 (2)
Os(1)–C(13)	1.91 (2)	Os(3)–C(32)	1.91 (2)
Os(1)–C(12)	1.94 (2)	Os(3)–C(33)	1.97 (2)
Os(1)–C	2.11 (2)	Os(3)–O	2.07 (1)
Os(1)–H	1.8 (1)	Os(3)–C	2.14 (2)
Os(1)–Os(2)	2.793 (1)	Os(3)–H	2.0 (1)
Os(1)–Os(3)	2.873 (1)	O–C(1)	1.44 (2)
Os(2)–C(22)	1.81 (3)	N–C(3)	1.47 (2)
Os(2)–C(23)	1.88 (2)	N–C(2)	1.49 (2)
Os(2)–C(21)	1.95 (2)	N–C	1.54 (2)
Os(2)–O	2.10 (1)	O–C(av)	1.14 (2)
Os(2)–N	2.15 (1)		

^aEstimated standard deviations in the least significant figure are given in parentheses.

that in Os₃(CO)₁₂, 2.877 (3) Å¹⁴. The Os(1)–Os(2) bond distance, 2.793 (1) Å, is significantly shorter. The non-bonding osmium–osmium distance, Os(2)⋯Os(3) = 3.492 (1) Å, is bridged by a methoxide ligand. The osmium–

Table III. Intramolecular Bond Angles (deg) for $\text{Os}_3(\text{CO})_9[\mu_3-\eta^2\text{-C(H)NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (2)^a

C(11)–Os(1)–C(13)	94 (1)	C(23)–Os(2)–C(21)	92.4 (8)	C(33)–Os(3)–O	90.1 (6)
C(11)–Os(1)–C(12)	90.9 (9)	C(23)–Os(2)–O	174.7 (6)	C(33)–Os(3)–C	166.2 (7)
C(11)–Os(1)–C	99.0 (8)	C(23)–Os(2)–N	97.3 (7)	C(33)–Os(3)–Os(1)	121.0 (5)
C(11)–Os(1)–Os(2)	93.9 (6)	C(23)–Os(2)–Os(1)	91.8 (5)	O–Os(3)–C	82.0 (5)
C(11)–Os(1)–Os(3)	147.0 (6)	C(21)–Os(2)–O	91.7 (7)	O–Os(3)–Os(1)	82.1 (3)
C(13)–Os(1)–C(12)	100 (1)	C(21)–Os(2)–N	97.5 (7)	C–Os(3)–Os(1)	46.9 (4)
C(13)–Os(1)–C	160.2 (7)	C(21)–Os(2)–Os(1)	170.8 (6)	C(1)–O–Os(3)	123 (1)
C(13)–Os(1)–Os(2)	96.1 (6)	O–Os(2)–N	78.8 (5)	C(1)–O–Os(2)	121 (1)
C(13)–Os(1)–Os(3)	117.9 (7)	O–Os(2)–Os(1)	83.7 (3)	Os(3)–O–Os(2)	113.7 (5)
C(12)–Os(1)–C	94.9 (8)	N–Os(2)–Os(1)	73.8 (3)	C(3)–N–C(2)	105 (1)
C(12)–Os(1)–Os(2)	163.1 (7)	C(31)–Os(3)–C(32)	88.0 (8)	C(3)–N–C	114 (1)
C(12)–Os(1)–Os(3)	91.2 (6)	C(31)–Os(3)–C(33)	90.8 (8)	C(3)–N–Os(2)	116 (1)
C–Os(1)–Os(2)	68.4 (4)	C(31)–Os(3)–O	174.8 (6)	C(2)–N–C	110 (1)
C–Os(1)–Os(3)	48.0 (4)	C(31)–Os(3)–C	96.1 (7)	C(2)–N–Os(2)	114 (1)
Os(2)–Os(1)–Os(3)	76.08 (3)	C(31)–Os(3)–Os(1)	93.0 (5)	C–N–Os(2)	97.7 (9)
C(22)–Os(2)–C(23)	89.5 (9)	C(32)–Os(3)–C(33)	95.7 (8)	N–C–Os(1)	110 (1)
C(22)–Os(2)–C(21)	95.5 (9)	C(32)–Os(3)–O	97.0 (6)	N–C–Os(3)	116 (1)
C(22)–Os(2)–O	93.5 (7)	C(32)–Os(3)–C	96.5 (7)	Os(1)–C–Os(3)	85.0 (6)
C(22)–Os(2)–N	165.0 (7)	C(32)–Os(3)–Os(1)	143.3 (5)	O–C(av)–Os	177 (2)
C(22)–Os(2)–Os(1)	92.7 (6)				

^a Estimated standard deviations in the least significant figure are given in parentheses.

oxygen bonding distances, Os(2)–O = 2.10 (1) Å and Os(3)–O = 2.07 (1) Å, are similar to the corresponding distances in the clusters $\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})(\mu\text{-H})$ ¹⁵ and $\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})_2$ (5).¹⁶ The most interesting ligand in the cluster is a η^2 triply bridging secondary (dimethylamino)carbene ligand, C(H)NMe₂. The carbene carbon atom bridges the Os(1)–Os(3) distance in a symmetric fashion, Os(1)–C = 2.11 (2) Å and Os(3)–C = 2.15 (2) Å. These distances are similar to the Os–C distance, 2.20 (4) and 2.16 (4) Å, observed for the triply bridging (dimethylamino)carbene ligand found in the complex $\text{Os}_3(\text{C-O})_9[\mu_3-\eta^2\text{-C(H)NMe}_2](\mu\text{-H})_2$ (6).⁵ The nitrogen atom of the carbene ligand is coordinated to the third metal atom, Os(2)–N = 2.15(1) Å. An interesting feature of this ligand is the unusually long carbon–nitrogen bonding distance, C–N = 1.54 (2) Å. It is significantly longer than the typical bonding distance of a terminal aminocarbene ligand, C–N = 1.30 Å,^{2,17} and even longer than the C–N single bond lengths to the methyl groups, C(2)–N = 1.49 (2) Å and C(3)–N = 1.47 (2) Å. The carbene C–N distance observed in 6 was 1.46 (5) Å. The reason for the excessive bond lengthening must be related to the polynuclear coordination of the ligand and possibly to the fact that 2 contains an open cluster while the cluster in 6 was closed. The carbene hydrogen atom was located crystallographically, C–H = 1.02 Å, but its position was not refined. Its signal in the ¹H NMR spectrum appears at 7.62 ppm, a value typical of previously observed doubly bridging secondary carbene ligands¹⁸ and similar to the value of 6.64 ppm found for the hydrogen atom of the triply bridging carbene ligand in 6. The hydride ligand, also located crystallographically, bridges the Os(1)–Os(3) bond, Os(1)–H = 1.8 (1) Å and Os(3)–H = 2.0 (1) Å. It shows a characteristically high-field shift, δ –11.37, in the ¹H NMR spectrum.

An ORTEP drawing of compound 3 is shown in Figure 2. Interatomic distances and angles are listed in Tables IV and V, respectively. The molecular structure of compound 3 is similar to that of the analogous benzenethiolato cluster complex $\text{Os}_3(\text{CO})_9[\text{C(H)NMe}_2](\mu\text{-SPh})(\mu\text{-H})$ (7).² The

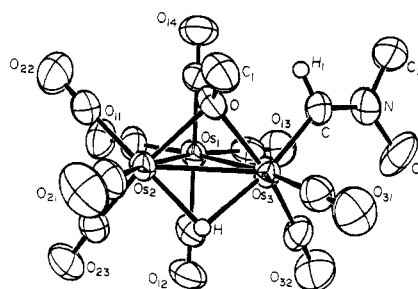


Figure 2. An ORTEP diagram of $\text{Os}_3(\text{CO})_9[\text{C(H)NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (3) showing 50% probability thermal ellipsoids.

Table IV. Intramolecular Distances (Å) for $\text{Os}_3(\text{CO})_9[\text{C(H)NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (3)^a

Os(1)–C(11)	1.91 (2)	Os(2)–H	1.9 (1)
Os(1)–C(13)	1.93 (2)	Os(3)–C(32)	1.86 (2)
Os(1)–C(14)	1.94 (1)	Os(3)–C(31)	1.88 (1)
Os(1)–C(12)	1.96 (1)	Os(3)–C	2.02 (1)
Os(1)–Os(2)	2.8343 (9)	Os(3)–O	2.113 (8)
Os(1)–Os(3)	2.8423 (8)	Os(3)–H	2.0 (1)
Os(2)–C(23)	1.88 (1)	O–C(1)	1.44 (1)
Os(2)–C(22)	1.92 (2)	N–C	1.29 (2)
Os(2)–C(21)	1.93 (1)	N–C(3)	1.46 (2)
Os(2)–O	2.102 (6)	N–C(2)	1.48 (2)
Os(2)–Os(3)	2.7880 (9)	O–C(av)	1.13 (2)

^a Estimated standard deviations in the least significant figure are given in parentheses.

structure consists of a triangle of three osmium atoms with three metal–metal bonds, Os(1)–Os(2) = 2.8343 (9) Å, Os(1)–Os(3) = 2.8423 (9) Å, and Os(2)–Os(3) = 2.7880 (9) Å. All of these are significantly shorter than the corresponding distances found in 7 at 2.8711 (9), 2.877 (1), and 2.8640 (9) Å.² A terminal (dimethylamino)carbene ligand is coordinated to atom Os(3), Os(3)–C = 2.02 (1) Å. The dimensions of this ligand are similar to those found in 7 and other terminally coordinated (dimethylamino)carbene ligands.^{2,17} The carbene hydrogen atom was located in a chemically reasonable position, C–H(1) = 1.00 Å. A bridging hydride ligand was observed across the Os(2)–Os(3) bond, Os(2)–H = 1.9 (1) Å and Os(3)–H = 2.0 (1) Å, and in the ¹H NMR spectrum at δ –12.92.

When compound 2 was treated with an excess of methyl propiolate in refluxing cyclohexane solvent, the addition product $\text{Os}_3(\text{CO})_9[\mu_3-\eta^3\text{-Me}_2\text{NCC(H)CCO}_2\text{Me}](\mu\text{-OMe})$ (4) was obtained in 42% yield. Compound 4 was characterized by IR, ¹H NMR, and a single-crystal X-ray diffraction analysis. Interatomic distances and angles are listed in

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Table V. Intramolecular Bond Angles (deg) for Os₃(CO)₉[C(H)NMe₂](μ-OMe)(μ-H) (3)^a

C(11)–Os(1)–C(13)	104.7 (6)	C(23)–Os(2)–Os(3)	121.8 (4)	C(31)–Os(3)–O	98.1 (5)
C(11)–Os(1)–C(14)	92.5 (6)	C(23)–Os(2)–Os(1)	91.1 (4)	C(31)–Os(3)–Os(2)	113.3 (4)
C(11)–Os(1)–C(12)	95.0 (6)	C(22)–Os(2)–C(21)	96.8 (6)	C(31)–Os(3)–Os(1)	172.7 (4)
C(11)–Os(1)–Os(2)	100.7 (5)	C(22)–Os(2)–O	95.1 (4)	C–Os(3)–O	86.6 (5)
C(11)–Os(1)–Os(3)	159.5 (5)	C(22)–Os(2)–Os(3)	133.3 (4)	C–Os(3)–Os(2)	127.6 (4)
C(13)–Os(1)–C(14)	95.0 (6)	C(22)–Os(2)–Os(1)	88.9 (5)	C–Os(3)–Os(1)	91.3 (4)
C(13)–Os(1)–C(12)	92.5 (6)	C(21)–Os(2)–O	95.1 (4)	O–Os(3)–Os(2)	48.4 (2)
C(13)–Os(1)–Os(2)	154.6 (4)	C(21)–Os(2)–Os(3)	112.6 (4)	O–Os(3)–Os(1)	80.6 (2)
C(13)–Os(1)–Os(3)	95.8 (4)	C(21)–Os(2)–Os(1)	173.3 (4)	Os(2)–Os(3)–Os(1)	60.44 (2)
C(14)–Os(1)–C(12)	167.7 (6)	O–Os(2)–Os(3)	48.7 (2)	C(1)–O–Os(2)	120.3 (7)
C(14)–Os(1)–Os(2)	83.4 (4)	O–Os(2)–Os(1)	80.9 (2)	C(1)–O–Os(3)	122.5 (8)
C(14)–Os(1)–Os(3)	85.0 (4)	Os(3)–Os(2)–Os(1)	60.73 (2)	Os(2)–O–Os(3)	82.8 (3)
C(12)–Os(1)–Os(2)	85.7 (4)	C(32)–Os(3)–C(31)	89.5 (6)	C–N–C(3)	124 (1)
C(12)–Os(1)–Os(3)	84.6 (4)	C(32)–Os(3)–C	100.0 (6)	C–N–C(2)	122 (1)
Os(2)–Os(1)–Os(3)	58.83 (2)	C(32)–Os(3)–O	169.4 (4)	C(3)–N–C(2)	113 (1)
C(23)–Os(2)–C(22)	90.8 (6)	C(32)–Os(3)–Os(2)	121.6 (4)	N–C–Os(3)	137 (1)
C(23)–Os(2)–C(21)	92.3 (5)	C(32)–Os(3)–Os(1)	91.0 (4)	O–C(av)–Os	178 (1)
C(23)–Os(2)–O	170.0 (5)	C(31)–Os(3)–C	95.8 (5)		

^a Estimated standard deviations in the least significant figure are given in parentheses.

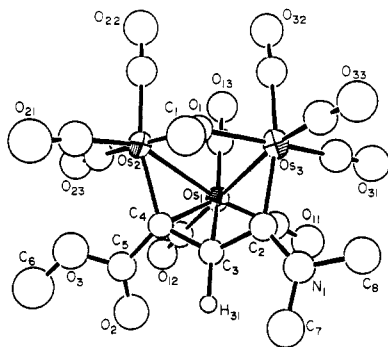


Figure 3. An ORTEP diagram of Os₃(CO)₉[μ₃-η³-Me₂NCC(H)CCO₂Me](μ-OMe) (4) showing 50% probability thermal ellipsoids.

Tables VI and VII, respectively. The crystal contains two independent, but structurally similar, molecules in the asymmetric unit. An ORTEP drawing of one of these is shown in Figure 3. The structure consists of an open triangular cluster of three osmium atoms with two metal-metal bonds, Os(1)–Os(2) = 2.834 (1) Å [2.817 (1) Å] and Os(1)–Os(3) = 2.861 (1) Å [2.855 (1) Å]. These distances are similar to those found in 2 and 5.¹⁶ A methoxide ligand bridges the open osmium–osmium distance, Os(2)–O(1) = 3.404 (1) Å [3.429 (1) Å], Os(2)–O(1) = 2.10 (1) Å [2.09 (1) Å], and Os(3)–O(1) = 2.07 (1) Å [2.10 (1) Å]. The most interesting ligand on the cluster is a dimetallaallyl ligand, (NMe₂)CC(H)C(MeO₂C), which bridges all three metal atoms. Carbon C(4) contains the carbomethoxy group, C(4)–C(5) = 1.47 (2) Å [1.49 (2) Å], and carbon C(2) contains a dimethylamino group, C(2)–N(1) = 1.35 (2) Å [1.34 (2) Å]. C(4) bridges the Os(1)–Os(2) bond, Os(2)–C(4) = 2.09 (2) Å [2.07 (2) Å]. C(3) is coordinated only to Os(1), Os(1)–C(3) = 2.27 (2) Å [2.31 (2) Å]. Examples of triply bridging dimetallaallyl ligands have been reported previously (e.g. Os₃(CO)₉[μ₃-η³-HCC(H)C(OMe)](μ-H)¹⁹ and Ru₃(CO)₉[μ₃-η³-MeCC(H)CET](μ-H)²⁰), but the ligand coordination in these differs from that in 4 because the carbon atoms on each end of the ligand bridge two metal atoms. In 4, however, C(2) is coordinated only to Os(3), Os(3)–C(2) = 2.06 (2) Å [2.09 (1) Å] and Os(1)–C(2) = 2.75 (2) Å [2.73 (2) Å]. This lack of metal-carbon bonding is probably due to a competitive and more efficient π-bonding between the nitrogen atom and

Table VI. Intramolecular Distances (Å) for Os₃(CO)₉[μ₃-η³-Me₂NCC(H)C(CO₂Me)](μ-OMe) (4)^a

Os(1A)–C(13A)	1.86 (2)	Os(3A)–O(1A)	2.07 (1)
Os(1A)–C(11A)	1.87 (2)	Os(3B)–C(31B)	1.83 (2)
Os(1A)–C(12A)	1.90 (2)	Os(3B)–C(33B)	1.87 (2)
Os(1A)–C(4A)	2.21 (2)	Os(3B)–C(32B)	1.92 (2)
Os(1A)–C(3A)	2.27 (2)	Os(3B)–C(2B)	2.09 (1)
Os(1A)–Os(2A)	2.834 (1)	Os(3B)–O(1B)	2.10 (1)
Os(1A)–Os(3A)	2.861 (1)	O(1A)–C(1A)	1.40 (2)
Os(1B)–C(13B)	1.84 (2)	O(1B)–C(1B)	1.42 (2)
Os(1B)–C(11B)	1.88 (2)	O(2A)–C(5A)	1.21 (2)
Os(1B)–C(12B)	1.89 (2)	O(2B)–C(5B)	1.21 (2)
Os(1B)–C(4B)	2.21 (2)	O(3A)–C(5A)	1.34 (2)
Os(1B)–C(3B)	2.31 (2)	O(3A)–C(6A)	1.41 (3)
Os(1B)–Os(2B)	2.817 (1)	O(3B)–C(5B)	1.31 (2)
Os(1B)–Os(3B)	2.855 (1)	O(3B)–C(6B)	1.43 (2)
Os(2A)–C(23A)	1.84 (2)	N(1A)–C(2A)	1.35 (2)
Os(2A)–C(21A)	1.88 (2)	N(1A)–C(7A)	1.44 (2)
Os(2A)–C(22A)	1.91 (2)	N(1A)–C(8A)	1.48 (2)
Os(2A)–C(4A)	2.09 (2)	N(1B)–C(2B)	1.34 (2)
Os(2A)–O(1A)	2.10 (1)	N(1B)–C(7B)	1.45 (2)
Os(2B)–C(23B)	1.84 (2)	N(1B)–C(8B)	1.49 (2)
Os(2B)–C(21B)	1.90 (2)	C(2A)–C(3A)	1.50 (2)
Os(2B)–C(22B)	1.92 (2)	C(2B)–C(3B)	1.49 (2)
Os(2B)–C(4B)	2.07 (2)	C(3A)–C(4A)	1.45 (2)
Os(2B)–O(1B)	2.09 (1)	C(3B)–C(4B)	1.44 (2)
Os(3A)–C(31A)	1.85 (2)	C(4A)–C(5A)	1.47 (2)
Os(3A)–C(33A)	1.87 (2)	C(4B)–C(5B)	1.49 (2)
Os(3A)–C(32A)	1.93 (2)	O–C(A)(av)	1.17 (2)
Os(3A)–C(2A)	2.06 (2)	O–C(B)(av)	1.17 (2)

^a Estimated standard deviations in the least significant figure are given in parentheses.

C(2). The π-character of the carbon–nitrogen bond is indicated by the short C–N distance (see above) and by the observed planarity of the nitrogen atom. Additional support was obtained from the ¹H NMR spectrum. At –45 °C the inequivalent *N*-methyl groups appear as two sharp singlets at 3.64 and 3.50 ppm. As the temperature is raised, these peaks broaden and coalesce, indicating the onset of rapid rotation about the C(2)–N(1) bond. At 25 °C a single sharp resonance is observed at 3.60 ppm. The hindered rotation about the C(2)–N(1) bond is an expected consequence of the pπ-bonding interaction. Similar dynamic processes have been observed for (dialkylamino)carbene ligands.^{21,22} Indeed, atom C(2) could also be viewed as the center of a substituted (dimethylamino)carbene ligand.

Attempts were made to obtain compound 4 from a reaction of 3 with methyl propiolate. However, at 80 °C no reaction was observed, while at 98 °C compound 3 un-

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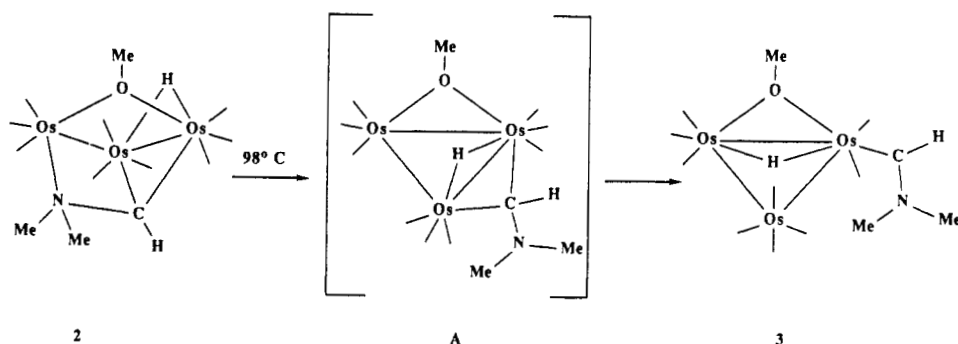
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Table VII. Intramolecular Bond Angles (deg) for $\text{Os}_3(\text{CO})_9[\mu_3-\eta^3\text{-Me}_2\text{NCC(H)C(CO}_2\text{Me)}](\mu\text{-OMe})$ (4)^a

C(13A)-Os(1A)-C(4A)	129.5 (7)	C(22A)-Os(2A)-O(1A)	89.9 (6)	C(1B)-O(1B)-Os(2B)	119 (1)
C(13A)-Os(1A)-C(3A)	155.1 (7)	C(22A)-Os(2A)-Os(1A)	111.6 (6)	C(1B)-O(1B)-Os(3B)	120 (1)
C(13A)-Os(1A)-Os(2A)	83.4 (6)	C(4A)-Os(2A)-O(1A)	85.8 (5)	Os(2B)-O(1B)-Os(3B)	110.1 (5)
C(13A)-Os(1A)-Os(3A)	87.1 (5)	C(4A)-Os(2A)-Os(1A)	50.7 (4)	C(5A)-O(3A)-C(6A)	118 (2)
C(11A)-Os(1A)-C(4A)	133.2 (7)	O(1A)-Os(2A)-Os(1A)	86.5 (3)	C(5B)-O(3B)-C(6B)	116 (1)
C(11A)-Os(1A)-C(3A)	97.6 (7)	C(2B)-Os(2B)-C(4B)	94.7 (7)	C(2A)-N(1A)-C(7A)	126 (2)
C(11A)-Os(1A)-Os(2A)	164.7 (5)	C(23B)-Os(2B)-O(1B)	175.5 (6)	C(2A)-N(1A)-C(8A)	123 (2)
C(11A)-Os(1A)-Os(3A)	91.3 (6)	C(23B)-Os(2B)-Os(1B)	89.8 (5)	C(7A)-N(1A)-C(8A)	111 (2)
C(12A)-Os(1A)-C(4A)	87.5 (7)	C(21B)-Os(2B)-C(4B)	105.9 (7)	C(2B)-N(1B)-C(7B)	125 (1)
C(12A)-Os(1A)-C(3A)	101.8 (7)	C(21B)-Os(2B)-O(1B)	92.7 (6)	C(2B)-N(1B)-C(8B)	122 (1)
C(12A)-Os(1A)-Os(2A)	103.1 (5)	C(21B)-Os(2B)-Os(1B)	157.0 (5)	C(7B)-N(1B)-C(8B)	113 (1)
C(12A)-Os(1A)-Os(3A)	173.7 (5)	C(22B)-Os(2B)-C(4B)	158.2 (7)	N(1A)-C(3A)-Os(3A)	112 (2)
C(4A)-Os(1A)-C(3A)	37.6 (5)	C(22B)-Os(2B)-O(1B)	91.3 (6)	N(1A)-C(2A)-Os(3A)	130 (1)
C(4A)-Os(1A)-Os(2A)	46.9 (4)	C(22B)-Os(2B)-Os(1B)	107.3 (6)	C(3A)-C(2A)-Os(3A)	118 (1)
C(4A)-Os(1A)-Os(3A)	86.3 (4)	C(4B)-Os(2B)-O(1B)	84.5 (5)	N(1B)-C(2B)-C(3B)	112 (1)
C(3A)-Os(1A)-Os(2A)	77.4 (4)	C(4B)-Os(2B)-Os(1B)	51.1 (5)	N(1B)-C(2B)-Os(3B)	128 (1)
C(3A)-Os(1A)-Os(3A)	72.4 (4)	O(1B)-Os(2B)-Os(1B)	86.2 (3)	C(3B)-C(2B)-Os(3B)	118 (1)
Os(2A)-Os(1A)-Os(3A)	73.43 (3)	C(31A)-Os(3A)-C(2A)	95.1 (8)	C(4A)-C(3A)-C(2A)	128 (2)
C(13B)-Os(1B)-C(4B)	128.1 (7)	C(31A)-Os(3A)-Os(1A)	175.6 (6)	C(4A)-C(3A)-Os(1A)	69.0 (9)
C(13B)-Os(1B)-C(3B)	153.5 (7)	C(31A)-Os(3A)-Os(1A)	89.9 (6)	C(2A)-C(3A)-Os(1A)	91 (1)
C(13B)-Os(1B)-Os(2B)	81.9 (5)	C(33A)-Os(3A)-C(2A)	100.6 (7)	C(4B)-C(3B)-C(2B)	128 (1)
C(13B)-Os(1B)-Os(3B)	86.3 (5)	C(33A)-Os(3A)-O(1A)	92.0 (6)	C(4B)-C(3B)-Os(1B)	68 (1)
C(11B)-Os(1B)-C(4B)	133.3 (8)	C(33A)-Os(3A)-Os(1A)	166.4 (6)	C(2B)-C(3B)-Os(1B)	89 (1)
C(11B)-Os(1B)-C(3B)	98.9 (8)	C(32A)-Os(3A)-C(2A)	166.2 (7)	C(3A)-C(4A)-C(5A)	109 (2)
C(11B)-Os(1B)-Os(2B)	168.9 (6)	C(32A)-Os(3A)-O(1A)	88.5 (6)	C(3A)-C(4A)-Os(2A)	131 (1)
C(11B)-Os(1B)-Os(3B)	94.6 (6)	C(32A)-Os(3A)-Os(1A)	101.7 (5)	C(3A)-C(4A)-Os(1A)	73 (1)
C(12B)-Os(1B)-C(4B)	91.0 (7)	C(2A)-Os(3A)-O(1A)	85.2 (6)	C(5A)-C(4A)-Os(2A)	120 (1)
C(12B)-Os(1B)-C(3B)	106.2 (6)	C(2A)-Os(3A)-Os(1A)	65.8 (4)	C(5A)-C(4A)-Os(1A)	119 (1)
C(12B)-Os(1B)-Os(2B)	101.7 (5)	O(1A)-Os(3A)-Os(1A)	86.2 (3)	Os(2A)-C(4A)-Os(1A)	82.5 (6)
C(12B)-Os(1B)-Os(3B)	176.0 (5)	C(31B)-Os(3B)-C(2B)	94.1 (7)	C(3B)-C(4B)-C(5B)	111 (1)
C(4B)-Os(1B)-C(3B)	37.0 (5)	C(31B)-Os(3B)-O(1B)	176.3 (7)	C(3B)-C(4B)-Os(2B)	133 (1)
C(4B)-Os(1B)-Os(2B)	46.6 (4)	C(31B)-Os(3B)-Os(1B)	91.7 (6)	C(3B)-C(4B)-Os(1B)	75 (1)
C(4B)-Os(1B)-Os(3B)	85.8 (4)	C(33B)-Os(3B)-C(2B)	102.2 (7)	C(5B)-C(4B)-Os(2B)	116 (1)
C(3B)-Os(1B)-Os(2B)	77.3 (4)	C(33B)-Os(3B)-O(1B)	91.7 (6)	C(5B)-C(4B)-Os(1B)	125 (1)
C(3B)-Os(1B)-Os(3B)	72.5 (4)	C(33B)-Os(3B)-Os(1B)	166.8 (5)	Os(2B)-C(4B)-Os(1B)	82.3 (5)
Os(2B)-Os(1B)-Os(3B)	74.39 (3)	C(32B)-Os(3B)-C(2B)	165.0 (7)	O(2A)-C(5A)-O(3A)	118 (2)
C(23A)-Os(2A)-C(4A)	93.9 (7)	C(32B)-Os(3B)-O(1B)	89.8 (6)	O(2A)-C(5A)-C(4A)	126 (2)
C(23A)-Os(2A)-O(1A)	175.0 (7)	C(32B)-Os(3B)-Os(1B)	100.4 (5)	O(3A)-C(5A)-C(4A)	115 (2)
C(23A)-Os(2A)-Os(1A)	89.5 (6)	C(2B)-Os(3B)-O(1B)	86.2 (5)	O(2B)-C(5B)-O(3B)	122 (2)
C(21A)-Os(2A)-C(22A)	95.5 (8)	C(2B)-Os(3B)-Os(1B)	64.9 (4)	O(2B)-C(5B)-C(4B)	127 (2)
C(21A)-Os(2A)-C(4A)	102.3 (8)	O(1B)-Os(3B)-Os(1B)	85.0 (3)	O(3B)-C(5B)-C(4B)	111 (2)
C(21A)-Os(2A)-O(1A)	94.4 (7)	C(1A)-O(1A)-Os(3A)	123 (1)	O-C(av)-Os(A)	176 (2)
C(21A)-Os(2A)-Os(1A)	152.9 (6)	C(1A)-O(1A)-Os(2A)	121 (1)	O-C(av)-Os(B)	176 (2)
C(22A)-Os(2A)-C(4A)	161.9 (7)	Os(3A)-O(1A)-Os(2A)	109.4 (4)		

^a Estimated standard deviations in the least significant figure are given in parentheses.

Scheme I



derwent only decomposition. No amount of 4 was observed in either case.

Discussion

The two new carbene-containing cluster complexes, $\text{Os}_3(\text{CO})_9[\mu_3-\eta^2\text{-C(H)NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (2) and $\text{Os}_3(\text{CO})_9[\text{C(H)NMe}_2](\mu\text{-OMe})(\mu\text{-H})$ (3), were synthesized by the reaction of $\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})(\mu\text{-H})$ (1) with $\text{CH}_2(\text{NMe}_2)_2$.

Compound 2 contains a η^2 -triple bridging (dimethylamino)carbene ligand. Only one cluster, $\text{Os}_3(\text{CO})_9[\mu_3-\eta^2\text{-C(H)NMe}_2](\mu\text{-H})_2$ (8), containing a triple bridging dialkylaminocarbene ligand has been reported;⁵ however,

cluster complexes containing triply bridging alkoxy-²³ and phosphino-²⁴⁻²⁶ carbene ligands have been observed previously.

Compounds 2 and 3 are isomers, and 2 may be converted to 3 thermally in refluxing heptane solutions under a carbon monoxide atmosphere. Although the mechanism of this transformation has not been established, the process

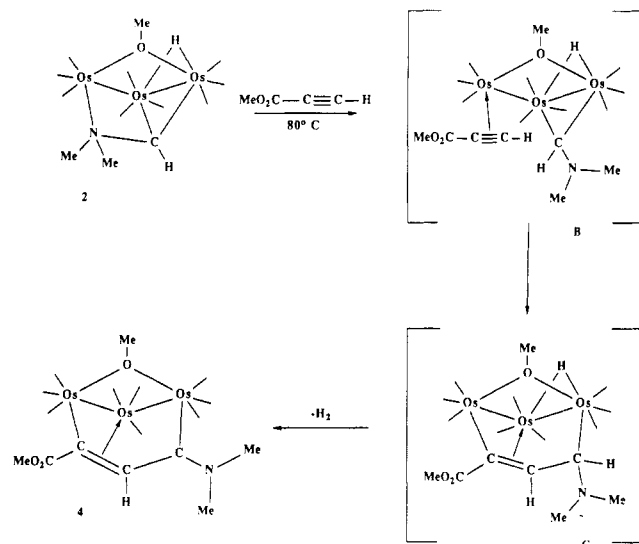
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Scheme II



shown in Scheme I is considered to be very plausible. It is believed that the driving force of the reaction is the bond formation that leads to a closing of the Os(2)⋯Os(3) distance. This would be accompanied by a cleavage of the metal–nitrogen bond and lead to intermediate A, which contains an edge bridging (dimethylamino)carbene ligand. To date no examples of edge-bridging (dimethylamino)carbene ligands have been reported in cluster complexes. This may be due to the importance of the π -bonding between the nitrogen atom and the carbene carbon atom which is more effective in a terminal coordination mode.⁵ Thus, the bridging carbene ligand in A will be transformed to the terminal coordination mode, 3, so that the C–N π -bonding may occur. The transformation of A to 3 must also be accompanied by carbonyl and hydride ligand shifts. The mobility of carbonyl and hydride ligands in transition-metal cluster has been well established.²⁷

The transformation of 2 to 3 indicates that triply bridged aminocarbene ligands could be important intermediates in the formation of the terminal aminocarbene ligands from tetraalkyldiaminomethanes, in general. This is supported by our recent observation of the transformation of the dimethyliminium ligand in Os₃(CO)₁₀(μ_3 - η^2 -H₂CNMe₂)(μ -H) to the triply bridging carbene ligand in compound 8.⁵ In that case, however, the triply bridged carbene ligand could not be transformed to a terminal

carbene ligand. The reactivity of 2 toward the alkyne HC₂CO₂Me was also studied. When 2 was treated with an excess of methyl propiolate, the compound Os₃(CO)₉[μ_3 - η^3 -Me₂NCC(H)CCO₂Me] (4) was obtained. The formation of 4 has involved the formation of a carbon–carbon bond and the elimination of 1 equiv of H₂. One mechanism for such a process is shown in Scheme II.

An initial cleavage of the metal–nitrogen bond and coordination of an acetylene unit could yield the intermediate B. This could bring the carbene carbon atom reasonably close to the alkyne carbon atom and allow carbon–carbon bond formation to occur (e.g. intermediate C). Coupling reactions between alkynes and metal-coordinated carbene ligands are well-known.²⁸ A metal-induced C–H activation at the Me₂N-substituted carbon atom followed by elimination of H₂ would lead directly to compound 4.

Keister has reported the formation of dimetallaallyl ligands from the reaction of the aminocarbene-containing clusters Ru₃(CO)₁₀(μ -CX)(μ -H) (X = OMe, Me, Ph, or (CH₂)₂CMe₃) with alkynes.²⁹ We have observed the activation of the C–H bonds of secondary aminocarbene ligands to yield complexes containing aminocarbene ligands.² Thus, we have considered the possibility that the formation of 4 may have involved intermediates containing (dimethylamino)carbene ligands. However, thermolysis of 2 at 98 °C yielded only the aminocarbene-containing cluster 3, and attempts to obtain 4 from the reaction of 3 with methyl propiolate were unsuccessful. Thus, it is believed that the formation of 4 has involved a direct reaction of 2 with the alkyne as described in Scheme II.

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Registry No. 1, 41766-81-8; 2, 108103-29-3; 3, 108083-01-8; 4, 115796-52-6; Os₃(CO)₁₀(NCMe)₂, 61817-93-4; CH₂(NMe₂)₂, 51-80-9; methyl propiolate, 922-67-8.

Supplementary Material Available: Tables of positional parameters and *B*(eq) for compounds 2–4 and a table of anisotropic thermal parameters for compound 4 (8 pages); a listing of structure factor amplitudes for compound 4 (28 pages). Tables of anisotropic thermal parameters and structure factor amplitudes were published previously for compounds 2 and 3.¹⁰ Ordering information is given on any current masthead page.

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