R_F = 0.051 and R_{wF} = 0.060. Atomic fractional coordinates, thermal parameters, and structure factor tables are included in the supplementary material.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for an instrument grant toward the purchase of the Bruker AM-360 NMR spectrometer. We also thank Dr. Steven P. VanKouwenberg for useful discussions.

Supplementary Material Available: Tables of atomic coordinates, bond angles and distances, and isotropic as well as anisotropic thermal parameters for **1**, **5**, **8**, and **9** (20 pages); tables of observed and calculated structure factors (106 pages). Ordering information is given on any current masthead page.

Clusters Containing Carbene Ligands. 11. Carbene Ligand Transfer. Reaction of $Os_3(CO)_{11}[C(Et)NMe_2]$ with Terminal Alkynes

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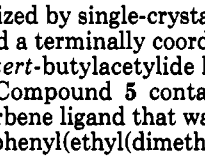
The reaction of $Os_3(CO)_{11}[C(Et)NMe_2]$ (**1**) with Bu^tC_2H in the presence of Me_3NO has yielded the new complex $Os_3(CO)_9[C(Et)NMe_2][\mu_3\text{-}C(H)CBu^t]$ (**3**) in 22% yield and the known complex $Os_3(CO)_{10}[\mu\text{-}H_2CNMeC(Et)](\mu\text{-}H)$ (**2**) in 14% yield. When refluxed in hexane solvent for 1.5 h, compound **3** was converted to the three new complexes $Os_3(CO)_8[C(Et)NMe_2][\mu_3\text{-}CCBu^t](\mu\text{-}H)$ (**4**; 35%), $Os_3(CO)_8[C(Et)N(Me)CH_2][\mu_3\text{-}CHCBu^t](\mu\text{-}H)$ (**5**; 43%), and $Os_3(CO)_9[\mu_3\text{-}Bu^tCC\{C(Et)(NMe_2)\}](\mu\text{-}H)$ (**6a**; 8%). The reaction of **1** with PhC_2H in the presence of Me_3NO yielded $Os_3(CO)_9[\mu_3\text{-}PhC_2C(Et)(NMe_2)](\mu\text{-}H)$ (**6b**; 35%). Compound **5** was converted back to **3** (9%) with the formation of some **4** (7%) by reaction with CO at 68 °C/1 atm. Compound **4** was converted to **6a** (60%) by reaction with CO at 102 °C/1000 psi, but no **6a** could be obtained from **4** under the original reaction conditions. The phenyl derivative **6b** was also obtained in 35% yield from the reaction of **1** with PhC_2H at 97 °C without addition of Me_3NO. Compounds **3**–**5** and **6b** were characterized by single-crystal X-ray diffraction analysis. Compound **3** contains a triply bridging Bu^tC_2H ligand and a terminally coordinated ethyl(dimethylamino)carbene ligand. Compound **4** contains a triply bridging *tert*-butylacetylide ligand, terminally coordinated ethyl(dimethylamino)carbene, and a hydride ligand. Compound **5** contains a triply bridging Bu^tC_2H ligand, a hydride, and an ethyl(dimethylamino)carbene ligand that was metalated on one of the *N*-methyl groups. Compound **6b** contains a triply bridging phenyl(ethyl(dimethyliminio)methyl)alkyne ligand that was formed by the transfer of the carbene ligand to the alkyne ligand. Crystal data: for **3**, space group $P2_1$, a = 8.648 (3) Å, b = 12.039 (5) Å, c = 12.084 (2) Å, β = 97.18 (2)°, Z = 2, 1748 reflections, R = 0.025; for **4**, space group $P2_1/n$, a = 10.755 (2) Å, b = 14.669 (4) Å, c = 15.841 (3) Å, β = 96.64 (2)°, Z = 4, 2074 reflections, R = 0.030; for **5**, space group $P2_1/n$, a = 8.623 (4) Å, b = 23.836 (4) Å, c = 11.925 (3) Å, β = 99.92 (1)°, Z = 4, 2705 reflections, R = 0.031; for **6b**, space group $P2_1/n$, a = 9.027 (3) Å, b = 16.051 (4) Å, c = 17.769 (3) Å, β = 93.17 (1)°, Z = 4, 1804 reflections, R = 0.035.

Introduction

Recently, there has been a flurry of interest in the use of metal complexes containing carbene ligands as reagents in organic syntheses.[1] Since there are relatively few examples of transition-metal cluster complexes containing carbene ligands,[2] most studies of organic syntheses with these ligands have been concentrated on mononuclear metal carbene complexes.

We have recently reported the first example of a simple carbene derivative of $Os_3(CO)_{12}$, $Os_3(CO)_{11}[C(Et)NMe_2]$ (**1**).[3] An important and characteristic feature of the organic chemistry of metal cluster complexes is their ability to produce multicenter transformations of organic ligands.[4] As a part of our continuing investigations of the chemistry of this and related complexes, we have studied the nature of the reactions of **1** with the terminal alkynes Bu^tC_2H and PhC_2H. These results are reported here. A preliminary report of this work has been published.[3]



1

Experimental Section

General Methods. All reactions were carried out under an atmosphere of nitrogen. Reagent grade solvents were stored over 4-Å molecular sieves. TLC separations were performed in air on Whatman 0.25-mm silica gel 60-Å F_{254} plates. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were taken at 300 MHz on a Bruker AM-300 spectrometer. Phenylacetylene and *tert*-butylacetylene were purchased from Aldrich and were used without further purification. $Os_3(CO)_{11}[C(Et)NMe_2]$ (**1**)[3] and $Os_3(CO)_{10}[\mu\text{-}CH_2N(Me)C(Et)](\mu\text{-}H)$ (**2**)[5] were prepared by the previously reported procedures.

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Table I. IR and ^{1}H NMR Spectra of Compounds 3–6

compd	IR ν(CO), cm^{-1} (in hexane)	^{1}H NMR, δ (in $CDCl_3$)
$Os_3(CO)_9[C(Et)NMe_2][\mu_3\text{-}C(H)CBu^t]$ (**3**)	2047 s, 2036 vs, 2028 vw, 2023 vw, 2008 m, 1994 s, 1982 w, 1966 m, 1942 vw	8.95 (1 H, s, HCC), 3.77 (3 H, s, NMe), 3.55 (3 H, s, NMe), 3.34 (1 H, dq, C*H*H, $^2J_{H\text{-}H}$ = 12.6 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz, 3.27 (1 H, dq, CH*H*, $^2J_{H\text{-}H}$ = 12.6 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz)
$Os_3(CO)_8[C(Et)NMe_2][\mu_3\text{-}CCBu^t](\mu\text{-}H)$ (**4**)	2076 m, 2053 s, 2037 w, 2009 w, sh, 2004 vs, 1994 m, 1981 w, 1974 w, 1968 vs, 1952 w, 1927 m	3.81 (3 H, s, NMe), 3.65 (1 H, dq, C*H*H, $^2J_{H\text{-}H}$ = 12.1 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz), 3.37 (3 H, s, NMe), 3.31 (1 H, dq, CH*H*, $^2J_{H\text{-}H}$ = 12.1 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz), 1.36 (9 H, s, Bu^t), 1.23 (3 H, t, CH_3, $^3J_{H\text{-}H}$ = 7.6 Hz), –23.94 (1 H, s, OsH)
$Os_3(CO)_8[C(Et)N(Me)CH_2][\mu_3\text{-}C(H)CBu^t](\mu\text{-}H)$ (**5**)	2075 s, 2042 vs, 2014 s, 1988 s, 1982 m, 1964 m	9.71 (1 H, d, HCC), 3.18 (3 H, s, NMe), 3.11 (1 H, d, NC*H*H, $^2J_{H\text{-}H}$ = 9.0 Hz), 2.81 (1 H, dq, C*H*H, $^2J_{H\text{-}H}$ = 13.3 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz), 2.74 (1 H, dq, CH*H*, $^2J_{H\text{-}H}$ = 13.3 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz), 2.57 (1 H, d, NCH*H*, $^2J_{H\text{-}H}$ = 9.0 Hz), –20.4 (1 H, s, OsH)
$Os_3(CO)_9[\mu_3\text{-}Bu^tC_2\{C(Et)NMe_2\}](\mu\text{-}H)$ (**6a**)	2079 m, 2049 s, 2024 vw, 2000 s, 1984 m, 1973 w, sh, 1969 s, 1949 w	3.22 (3 H, s, NMe), 3.04 (3 H, s, NMe), 2.88 (2 H, q, $^3J_{H\text{-}H}$ = 7.6 Hz), 1.34 (3 H, t, $^3J_{H\text{-}H}$ = 7.6 Hz), 1.03 (9 H, s, Bu^t), –19.04 (1 H, s, OsH)
$Os_3(CO)_9[\mu_3\text{-}PhC_2\{C(Et)NMe_2\}](\mu\text{-}H)$ (**6b**)	2080 m, 2050 s, 2027 vs, 2003 s, 1986 m, 1975 w, sh, 1968 s, 1948 w	9.20–6.90 (5 H, m, Ph), 3.04 (3 H, s, NMe), 2.91 (1 H, dq, C*H*H, $^2J_{H\text{-}H}$ = 13.4 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz), 2.75 (1 H, dq, CH*H*, $^2J_{H\text{-}H}$ = 13.4 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz), 2.60 (3 H, s, NMe), 1.45 (3 H, t, Me, $^3J_{H\text{-}H}$ = 7.7 hz), –19.52 (1 H, s, OsH)

$Me_3NO\cdot 2H_2O$ was purchased from Aldrich and was dehydrated by the published procedure before use.[6] Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of 1 with Bu^{t}C≡CH at 25 °C. A CH_2Cl_2 solution (20 mL) containing 90.0 mg (0.0934 mmol) of **1** and 1.0 g of Bu^{t}C≡CH was placed in a dropping funnel and was then added dropwise to a stirred solution containing 22.0 mg of Me_3NO, 1 mL of CH_3CN, and 2 mL of CH_2Cl_2 over a period of 10 min at 25 °C. After the addition, the solvent was removed immediately in vacuo. The residue was then dissolved in a minimal amount of CH_2Cl_2 and chromatographed by TLC with a solvent mixture of CH_2Cl_2/hexane (3/7) as eluent. This yielded, in order of elution, 12.7 mg of **2** (14%), 7.8 mg of unreacted **1**, and 20.5 mg of yellow $Os_3(CO)_9[C(Et)(NMe_2)][\mu_3\text{-}C(H)CBu^t]$ (**3**; 22%). IR and ^{1}H NMR data for **3** are given in Table I. Anal. Calcd for **3**: C, 24.26; H, 2.14; N, 1.41. Found: C, 24.59; H, 2.00; N, 1.45.

Attempted Reaction of 2 with Bu^{t}C≡CH. A CH_2Cl_2 solution (20 mL) containing 13.4 mg (0.0143 mmol) of **2** and 0.23 g of Bu^tC_2H was stirred for 15 min at 25 °C. IR spectra and separation by TLC analyses showed no evidence for a reaction.

Thermolysis of 3. A solution of **3** (20.0 mg, 0.0202 mmol) in hexane (25 mL) was refluxed for 1.5 h. After the solution was cooled, the solvent was removed, and the residue was separated by TLC with a CH_2Cl_2/hexane (1/4) solvent mixture to yield two bands visible under ultraviolet light, 8.3 mg of $Os_3(CO)_8[C(Et)N(Me)CH_2][\mu_3\text{-}C(H)CBu^t](\mu\text{-}H)$ (**5**; 43%) and 6.7 mg of $Os_3(CO)_8[C(Et)NMe_2][\mu_3\text{-}CCBu^t](\mu\text{-}H)$ (**4**; 35%), and two yellow bands, 1.5 mg of $Os_3(CO)_9[\mu_3\text{-}Bu^tCC\{C(Et)(NMe_2)\}](\mu\text{-}H)$ (**6a**; 8%) and 2.0 mg of unreacted **3**. Spectroscopic data for **4**, **5**, and **6a** are given in Table I. The electron impact mass spectrum of **6a** at 160 °C showed the expected parent ion (*m/e* 991) and fragment ions corresponding to the loss of each of nine carbonyl ligands. Anal. Calcd for **4**: C, 23.72; H, 2.20; N, 1.46. Found: C, 24.35; H, 2.18; N, 1.45. Calcd for **5**: C, 23.72; H, 2.20; N, 1.46. Found: C, 23.81; H, 2.02; N, 1.34.

Reaction of 4 with CO under 1 atm. A solution of **4** (17.7 mg, 0.0184 mmol) in 20 mL of hexane was heated to reflux in the presence of a slow purge with CO for 1.5 h. IR and TLC analyses showed no evidence of a reaction.

Reaction of 4 with CO at 1000 psi. A solution of **4** (16.5 mg, 0.0172 mmol) in hexane (15 mL) was placed in a 45-mL stainless steel Parr high-pressure reaction vessel. The vessel was pressurized with CO to 1000 psi and then heated to 102 °C with stirring for 26 h. After the mixture was cooled, it was separated by TLC as described above to yield 0.9 mg of unreacted **4** and 10.3 mg of **6a** (60%).

Reaction of 5 with CO at 1 atm. A solution of **5** (13.7 mg, 0.0142 mmol) in hexane (20 mL) was refluxed and purged with CO for 1.5 h. After the mixture was cooled, the separation by TLC on silica gel as described above yielded 10.9 mg of unreacted **5** (80%), 1.0 mg of **4** (7%), and 1.2 mg of **3** (9%).

Reaction of 1 with PhC≡CH in the Presence of Me_3NO at 25 °C. Over a period of 30 min, a CH_2Cl_2 solution (30 mL) containing 65 mg (0.0674 mmol) of **1** and 0.20 mL of PhC_2H was added dropwise to a solution containing 18.0 mg of Me_3NO, 1 mL of CH_3CN, and 2 mL of CH_2Cl_2 at 25 °C. After addition was completed, the solvent was immediately removed in vacuo. The residue was transferred to TLC plates by dissolving it in a minimal amount of CH_2Cl_2 and separated by elution with a CH_2Cl_2/hexane (3/7) solvent mixture. This yielded in order of elution 7.5 mg of unreacted **1** and 24.0 mg of $Os_3(CO)_9[\mu_3\text{-}PhC_2C(Et)(NMe_2)](\mu\text{-}H)$ (**6b**; 35%). No PhC_2H analogue of **3** was found.

Reaction of 1 with PhC≡CH at 97 °C. A heptane solution (35 mL) containing 12.6 mg (0.0131 mmol) of **1** and 0.20 mL of PhC_2H was heated to reflux for 1.5 h. The solvent was removed in vacuo, and the residue was separated by TLC with a CH_2Cl_2/hexane (1/4) solvent mixture. This yielded 3.3 mg of **2** (27%), 1.2 mg of **1**, and 4.6 mg of **6b** (35%). Spectroscopic data for **6b** are given in Table I. Anal. Calcd for **6b**: C, 26.15; H, 1.68; N, 1.39. Found: C, 26.23; H, 1.65; N, 1.36.

Thermolysis of 3 under 1 atm of ^{13}CO. A 9.5-mg amount of **3** in 15 mL of hexane was placed in a 50-mL Parr high-pressure apparatus equipped with a glass liner. The vessel was evacuated and then filled with CO (99.0% ^{13}C and 9.9% ^{18}O) to 1 atm. The vessel was sealed and heated to 68 °C for 1.5 h. After it was cooled, the product mixture was separated in the usual way to yield 2.6 mg of **5**, 1.8 mg of **6a**, and 2.7 mg of unreacted **3**. Analysis of the product **6a** by IR and mass spectra showed no evidence of the presence of labeled CO in an amount greater than natural abundance.

Crystallographic Analyses. Crystals of **3** and **6b** suitable for X-ray diffraction analyses were grown from solution in hexane/CH_2Cl_2 solvent mixtures by slow evaporation of the solvent at 0 °C. Crystals of **4** were grown from solution in a MeOH/CH_2Cl_2 solvent mixture by slow evaporation of solvent at 0 °C. Crystals of **5** were grown from a hexane/CH_2Cl_2 solvent mixture by slow evaporation of solvent at 25 °C. All 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 data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library obtained from Molecular Structure Corp., The Woodlands, TX.

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Table II. Crystallographic Data for Compounds 3-5 and 6b

	3	4	5	6b
empirical formula	$Os_3O_9NC_{20}H_{21}$	$Os_3O_8NC_{19}H_{21}$	$Os_3O_8NC_{19}H_{21}$	$Os_3O_9NC_{22}H_{18}$
fw	989.99	961.98	961.98	1010.98
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
lattice params				
a, Å	8.648 (3)	10.755 (2)	8.623 (1)	9.027 (3)
b, Å	12.039 (5)	14.669 (4)	23.836 (4)	16.051 (4)
c, Å	12.084 (2)	15.841 (3)	11.925 (1)	17.769 (3)
β, deg	97.18 (2)	96.64 (2)	99.92 (1)	93.17 (2)
V, Å^3	1248 (1)	2482.3 (9)	2414.2 (7)	2571 (2)
space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z	2	4	4	4
D_{calc}, g/cm^3	2.63	2.57	2.65	2.61
F_{000}	896	1736	1736	1828
μ(Mo Kα), cm^{-1}	152.93	153.74	158.08	148.55
temp, °C	20	20	20	20
$2\theta_{max}$, deg	46.0	43.0	46.0	40.0
no. of observns ($I > 3\sigma(I)$)	1748	2074	2705	1804
no. of variables	297	283	286	156
residuals: R, R_w	0.025, 0.028	0.030, 0.032	0.031, 0.033	0.035, 0.036
goodness-of-fit indicator	1.64	1.40	1.66	1.35
max shift in final cycle	0.01	0.05	0.04	0.01
largest peak in final diff map, e/Å^3	0.78	0.71	1.48	1.08
abs cor	empirical	empirical	empirical	empirical
max/min	1.00/0.42	1.00/0.76	1.00/0.31	1.00/0.59
scan speed, deg/min	4.0	4.0	4.0	4.0

Lorentz-polarization (Lp) and empirical absorption corrections were applied to the data in each analysis. Neutral atom scattering factors were calculated by the standard procedures.[7a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[7b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net}^2)^2]^{1/2}/Lp$.

Compound **3** crystallized in the monoclinic crystal system. The space group $P2_1$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens on the ligands were calculated by assuming idealized geometries. A test for an enantiomorph was made by inverting the coordinates of all atoms and refining again; however, this did not produce an improvement in the R factors. Thus, the original configuration was retained. The contributions of all of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compounds **4**, **5**, and **6b** crystallized in the monoclinic crystal system. In each case the space group $P2_1/c$ was determined uniquely from the systematic absences observed during the collection of data. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. For **4** and **5** all of the non-hydrogen atoms were refined with anisotropic thermal parameters. For **6b** only, all metal atoms were refined with anisotropic thermal parameters. For **4**, **5**, and **6b** the positions of hydrogen atoms on the ligands were calculated by assuming idealized geometries. The hydride ligands of **4** and **5** were obtained from difference Fourier syntheses and were refined on their coordinates only. For **6b** the hydride ligand was located but was not refined. The scattering contributions of all other hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

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

atom	x	y	z	B(eq), Å^2
Os(1)	0.84642 (08)	0.0608	0.39413 (05)	2.40 (3)
Os(2)	0.92495 (08)	0.18738 (08)	0.20855 (06)	2.69 (3)
Os(3)	0.86831 (08)	−0.03605 (08)	0.18884 (06)	2.71 (3)
O(11)	1.1771 (16)	0.0846 (14)	0.5214 (13)	5.7 (8)
O(12)	0.893 (02)	−0.1806 (14)	0.4598 (13)	7 (1)
O(13)	0.7631 (19)	0.3122 (13)	0.4098 (12)	5.3 (8)
O(21)	1.0530 (16)	0.1773 (14)	−0.0134 (11)	5.1 (7)
O(22)	0.810 (02)	0.4268 (14)	0.1797 (19)	8 (1)
O(23)	1.2533 (19)	0.2447 (19)	0.3256 (14)	8 (1)
O(31)	0.8564 (19)	−0.0691 (12)	−0.0600 (12)	5.7 (8)
O(32)	1.2176 (18)	−0.0899 (16)	0.2386 (15)	7 (1)
O(33)	0.7207 (19)	−0.2569 (14)	0.2193 (12)	5.6 (8)
N	0.6011 (19)	0.0101 (15)	0.5502 (13)	4.5 (8)
C(1)	0.717 (02)	0.0727 (18)	0.5318 (13)	3.4 (8)
C(2)	0.772 (03)	0.1539 (19)	0.6251 (17)	5 (1)
C(3)	0.884 (03)	0.103 (03)	0.7119 (19)	8 (2)
C(4)	0.525 (02)	0.008 (03)	0.652 (02)	7 (1)
C(5)	0.529 (02)	−0.072 (02)	0.4741 (18)	5 (1)
C(6)	0.6686 (18)	0.0524 (14)	0.2471 (12)	2.4 (7)
C(7)	0.7013 (18)	0.1157 (15)	0.1674 (15)	3.3 (8)
C(8)	0.577 (02)	0.1450 (16)	0.0670 (13)	3.3 (8)
C(10)	0.642 (02)	0.187 (02)	−0.0348 (15)	5 (1)
C(11)	1.048 (02)	0.0821 (18)	0.4751 (15)	4.0 (9)
C(12)	0.875 (02)	−0.0883 (17)	0.4291 (16)	3.5 (9)
C(13)	0.807 (02)	0.2247 (15)	0.3820 (14)	3.4 (9)
C(20)	0.475 (03)	0.234 (02)	0.1092 (19)	6 (1)
C(21)	1.0015 (19)	0.1810 (17)	0.0713 (15)	3.5 (8)
C(22)	0.856 (03)	0.3376 (19)	0.194 (02)	5 (1)
C(23)	1.126 (02)	0.2245 (20)	0.2800 (15)	4 (1)
C(30)	0.477 (02)	0.0430 (19)	0.0301 (19)	5 (1)
C(31)	0.858 (02)	−0.0537 (16)	0.0388 (16)	4 (1)
C(32)	1.089 (03)	−0.0730 (20)	0.2218 (19)	5 (1)
C(33)	0.776 (02)	−0.1708 (16)	0.2058 (15)	3.5 (8)

Results

When a solution of **1** and Bu^tC_2H was slowly added to a solution of CH_2Cl_2 and MeCN containing Me_3NO, compound **1** was decarbonylated and *tert*-butylacetylene was added to the cluster to form the new acetylene/carbene cluster complex $Os_3(CO)_9[C(Et)NMe_2][\mu_3\text{-}C(H)CBu^t]$ (**3**) in 22% yield. In a competing process, compound **2** was formed in 14% yield by a decarbonylation and intramolecular metalation of one of the *N*-methyl groups of the carbene ligand, the reverse of the process by which **1** was prepared.[3] Compound **3** was characterized by IR and ^1H NMR spectroscopy and by a single-crystal X-ray diffraction analysis. An ORTEP drawing of **3** is shown in Figure 1. Final atomic positional parameters are listed in Table III. Selected bond distances and angles are listed in Tables IV and V. The molecule consists of a closed triangular cluster of three metal atoms with a triply bridging Bu^tC_2H ligand. The Os-Os bond distances are normal. The alkyne has adopted the μ_3-$\|$ bridging coordination that is commonly observed for 48-electron trimetallic cluster

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

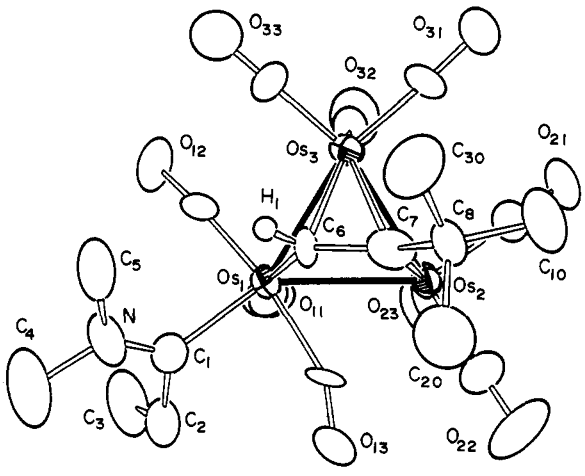

Figure 1. ORTEP diagram of $Os_3(CO)_9[C(Et)(NMe_2)][\mu_3\text{-}C(H)\text{-}CBu^t]$ (3) showing 50% probability thermal ellipsoids.

Table IV. Intramolecular Distances for 3[a]

Os(1)-Os(2)	2.863 (1)	Os(3)-C(31)	1.82 (2)
Os(1)-Os(3)	2.769 (1)	Os(3)-C(32)	1.95 (3)
Os(1)-C(1)	2.12 (2)	Os(3)-C(33)	1.83 (2)
Os(1)-C(6)	2.12 (1)	N-C(1)	1.30 (2)
Os(1)-C(11)	1.91 (2)	N-C(4)	1.47 (3)
Os(1)-C(12)	1.85 (2)	N-C(5)	1.44 (3)
Os(1)-C(13)	2.00 (2)	C(1)-C(2)	1.52 (3)
Os(2)-Os(3)	2.739 (2)	C(2)-C(3)	1.48 (4)
Os(2)-C(7)	2.12 (2)	C(6)-C(7)	1.38 (2)
Os(2)-C(21)	1.86 (2)	C(7)-C(8)	1.56 (2)
Os(2)-C(22)	1.91 (2)	C(8)-C(10)	1.50 (3)
Os(2)-C(23)	1.90 (2)	C(8)-C(20)	1.52 (3)
Os(3)-C(6)	2.27 (2)	C(8)-C(30)	1.53 (3)
Os(3)-C(7)	2.32 (2)	C-O (av)	1.17 (2)
		Os(2)···C(13)	2.48 (2)

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

Table V. Intramolecular Bond Angles for 3[a]

Os(2)-Os(1)-Os(3)	58.18 (3)	C(6)-Os(3)-C(33)	90.8 (8)
Os(2)-Os(1)-C(1)	141.1 (6)	C(7)-Os(3)-C(31)	91.7 (7)
Os(2)-Os(1)-C(6)	68.5 (4)	C(7)-Os(3)-C(32)	141.3 (8)
Os(3)-Os(1)-C(1)	146.4 (5)	C(7)-Os(3)-C(33)	115.9 (8)
Os(3)-Os(1)-C(6)	53.4 (4)	C(1)-N-C(4)	126 (2)
C(1)-Os(1)-C(6)	102.4 (6)	C(1)-N-C(5)	125 (2)
C(1)-Os(1)-C(11)	97.2 (7)	C(4)-N-C(5)	109 (2)
C(1)-Os(1)-C(12)	87.5 (8)	Os(1)-C(1)-N	126 (1)
C(1)-Os(1)-C(13)	83.7 (8)	Os(1)-C(1)-C(2)	119 (1)
Os(1)-Os(2)-Os(3)	59.19 (3)	N-C(1)-C(2)	115 (2)
Os(1)-Os(2)-C(7)	70.6 (5)	C(1)-C(2)-C(3)	112 (2)
Os(3)-Os(2)-C(7)	55.4 (5)	Os(1)-C(6)-Os(3)	78.2 (5)
C(7)-Os(2)-C(21)	100.9 (7)	Os(1)-C(6)-C(7)	113 (1)
C(7)-Os(2)-C(22)	95.7 (9)	Os(3)-C(6)-C(7)	75 (1)
C(7)-Os(2)-C(23)	164.0 (8)	C(7)-C(6)-H(1)	124.71
Os(1)-Os(3)-Os(2)	62.63 (3)	Os(2)-C(7)-Os(3)	76.0 (5)
Os(1)-Os(3)-C(6)	48.4 (4)	Os(2)-C(7)-C(6)	108 (1)
Os(1)-Os(3)-C(7)	70.0 (4)	Os(2)-C(7)-C(8)	128 (1)
Os(2)-Os(3)-C(6)	69.1 (4)	Os(3)-C(7)-C(6)	70 (1)
Os(2)-Os(3)-C(7)	48.6 (4)	Os(3)-C(7)-C(8)	129 (1)
C(6)-Os(3)-C(7)	35.0 (6)	C(6)-C(7)-C(8)	123 (1)
C(6)-Os(3)-C(31)	118.3 (7)	Os(1)-C(13)-O(13)	156 (2)
C(6)-Os(3)-C(32)	143.3 (8)	Os-C-O (av)	177 (2)

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

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.58129 (06)	0.31820 (04)	0.24647 (04)	3.83 (3)
Os(2)	0.42109 (06)	0.37585 (04)	0.36883 (04)	3.52 (3)
Os(3)	0.32108 (6)	0.26893 (05)	0.22810 (04)	4.09 (3)
O(11)	0.6956 (16)	0.1936 (10)	0.1252 (09)	9 (1)
O(12)	0.5693 (16)	0.4845 (10)	0.1288 (10)	10 (1)
O(21)	0.4767 (14)	0.5675 (10)	0.3130 (10)	9 (1)
O(22)	0.6300 (12)	0.3714 (10)	0.5138 (08)	7.6 (8)
O(23)	0.2086 (12)	0.4245 (09)	0.4751 (08)	6.4 (7)
O(31)	0.3575 (13)	0.0884 (10)	0.1416 (09)	8.4 (8)
O(32)	0.0377 (12)	0.2595 (09)	0.2328 (09)	7.8 (8)
O(33)	0.3135 (15)	0.3725 (11)	0.0606 (09)	9 (1)
N	0.8241 (14)	0.2971 (13)	0.3641 (10)	6 (1)
C(1)	0.7469 (15)	0.3554 (13)	0.3174 (12)	5 (1)
C(2)	0.7848 (15)	0.4523 (13)	0.3204 (13)	6 (1)
C(3)	0.8754 (19)	0.4722 (13)	0.2575 (15)	8 (1)
C(4)	0.9304 (17)	0.3246 (17)	0.4212 (14)	9 (1)
C(5)	0.8051 (17)	0.2011 (15)	0.3597 (13)	7 (1)
C(6)	0.4892 (14)	0.2433 (10)	0.3228 (09)	3.5 (7)
C(7)	0.3890 (14)	0.2250 (10)	0.3575 (10)	3.7 (8)
C(8)	0.3512 (15)	0.1535 (10)	0.4210 (11)	4.3 (8)
C(10)	0.2169 (17)	0.1619 (12)	0.4351 (12)	6 (1)
C(11)	0.6484 (19)	0.2417 (11)	0.1691 (11)	6 (1)
C(12)	0.5808 (10)	0.4198 (13)	0.1730 (12)	6 (1)
C(20)	0.430 (02)	0.1623 (15)	0.5059 (13)	8 (1)
C(21)	0.4594 (19)	0.4937 (13)	0.3358 (12)	6 (1)
C(22)	0.5490 (18)	0.3745 (12)	0.4589 (10)	5 (1)
C(23)	0.2862 (17)	0.4056 (10)	0.4374 (11)	4.4 (9)
C(30)	0.3688 (18)	0.0584 (11)	0.3832 (15)	8 (1)
C(31)	0.3447 (17)	0.1588 (13)	0.1734 (11)	6 (1)
C(32)	0.1431 (17)	0.2602 (13)	0.2312 (13)	6 (1)
C(33)	0.3178 (20)	0.3344 (13)	0.1242 (12)	7 (1)

complexes containing these ligands.[8] The alkyne hydrogen atom on C(6) was located in a difference Fourier synthesis but could not be refined. It exhibits the characteristic low-field resonance shift (δ = 8.95 ppm) of coordinated terminal alkynes.[8a] Each metal contains three carbonyl ligands, but Os(1) also contains the terminally coordinated ethyl(dimethylamino)carbene ligand. The Os(1)-C(1) distance to the carbene carbon atom of 2.12 (2) Å is similar to that found for other osmium carbene cluster complexes.[9] Os(1) is unique since it contains four terminally coordinated ligands. This may explain why one of the carbonyl ligands, C(13)-O(13), has adopted a weak semibridging interaction to the neighboring metal Os(2) (Os(2)···C(13) = 2.48 (2) Å, Os(1)-C(13)-O(13) = 156 (2)°). Semibridging CO ligands have been observed in a number of other complexes containing μ_3-alkyne ligands.[10] Compound 3 is chiral and by chance also crystallized in the chiral space group $P2_1$. As a result, the hydrogen atoms on the prochiral CH_2 group of the carbene ligand are diastereotopic. This inequivalence is observed in the ^1H NMR spectrum of 3, where the CH_2 hydrogen atoms appear as an AB quartet (δ = 3.34 and 3.27 ppm; $J_{H\text{-}H}$ = 12.6 Hz) with each resonance split further into quartets ($J_{H\text{-}H}$ = 7.6 Hz) due to coupling to the methyl group. The *N*-methyl groups are observed as separate resonances (δ = 3.77 and 3.55 ppm), which indicates that rotation about the carbene C-N bond is slow on the NMR time scale. This is also supported by the short C(1)-N distance of 1.30 (2) Å that is indicative of C-N multiple-bond character.[11]

When refluxed in hexane solvent for $1^1/_2$ h, compound 3 was converted to the three new complexes $Os_3(CO)_8[C\text{-}$

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Table VII. Intramolecular Distances for 4[a]

Os(1)–Os(2)	2.866 (1)	Os(3)–C(7)	2.19 (2)
Os(1)–Os(3)	2.872 (1)	Os(3)–C(31)	1.86 (2)
Os(1)–C(1)	2.07 (2)	Os(3)–C(32)	1.92 (2)
Os(1)–C(6)	1.98 (2)	Os(3)–C(33)	1.90 (2)
Os(1)–C(11)	1.87 (2)	Os(3)–H	1.8 (1)
Os(1)–C(12)	1.89 (2)	N–C(1)	1.35 (2)
Os(2)–Os(3)	2.834 (1)	N–C(4)	1.43 (2)
Os(2)–C(6)	2.23 (2)	N–C(5)	1.42 (2)
Os(2)–C(7)	2.24 (1)	C(1)–C(2)	1.48 (2)
Os(2)–C(21)	1.87 (2)	C(2)–C(3)	1.50 (2)
Os(2)–C(22)	1.86 (2)	C(6)–C(7)	1.29 (2)
Os(2)–C(23)	1.96 (2)	C(7)–C(8)	1.54 (2)
Os(2)–H	1.7 (1)	C–O(av)	1.15 (2)
Os(3)–C(6)	2.24 (1)		

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

Table VIII. Intramolecular Bond Angles for 4[a]

Os(2)–Os(1)–Os(3)	59.19 (3)	C(6)–Os(3)–C(32)	134.3 (7)
Os(2)–Os(1)–C(1)	95.9 (4)	C(6)–Os(3)–C(33)	126.6 (8)
Os(2)–Os(1)–C(6)	50.9 (4)	C(7)–Os(3)–C(32)	100.4 (7)
Os(3)–Os(1)–C(1)	152.9 (5)	C(7)–Os(3)–C(33)	158.2 (7)
Os(3)–Os(1)–C(6)	51.2 (4)	C(1)–N–C(4)	124 (2)
C(1)–Os(1)–C(6)	105.9 (7)	C(1)–N–C(5)	122 (2)
C(1)–Os(1)–C(11)	98.1 (7)	C(4)–N–C(5)	114 (2)
C(1)–Os(1)–C(12)	93.9 (9)	Os(1)–C(1)–N	125 (1)
C(6)–Os(1)–C(11)	109.0 (7)	Os(1)–C(1)–C(2)	119 (2)
C(6)–Os(1)–C(12)	147.9 (7)	N–C(1)–C(2)	116 (2)
Os(1)–Os(2)–Os(3)	60.52 (3)	C(1)–C(2)–C(3)	111 (2)
Os(1)–Os(2)–C(6)	43.6 (4)	Os(1)–C(6)–Os(2)	85.6 (5)
Os(1)–Os(2)–C(7)	75.8 (4)	Os(1)–C(6)–Os(3)	85.4 (5)
Os(3)–Os(2)–C(6)	50.9 (3)	Os(1)–C(6)–C(7)	151 (1)
Os(3)–Os(2)–C(7)	49.5 (4)	Os(2)–C(6)–Os(3)	78.6 (5)
C(6)–Os(2)–C(7)	33.6 (5)	Os(2)–C(6)–C(7)	74 (1)
C(6)–Os(2)–C(22)	90.0 (6)	Os(3)–C(6)–C(7)	71 (1)
C(6)–Os(2)–C(23)	131.9 (6)	Os(2)–C(7)–Os(3)	79.4 (5)
C(7)–Os(2)–C(22)	98.3 (6)	Os(2)–C(7)–C(6)	73 (1)
C(7)–Os(2)–C(23)	98.5 (6)	Os(2)–C(7)–C(8)	132 (1)
Os(1)–Os(3)–Os(2)	60.29 (3)	Os(3)–C(7)–C(6)	75 (1)
Os(1)–Os(3)–C(6)	43.5 (4)	Os(3)–C(7)–C(8)	137 (1)
Os(1)–Os(3)–C(7)	76.4 (4)	C(6)–C(7)–C(8)	136 (1)
Os(2)–Os(3)–C(6)	50.5 (4)	Os–C–O (av)	177 (2)
Os(2)–Os(3)–C(7)	51.1 (4)	Os–H–Os	106 (4)
C(6)–Os(3)–C(7)	33.9 (5)		

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

(Et)NMe$_2$][μ_3-CCBu^t](μ-H) (**4**; 35%), Os$_3$(CO)$_8$[C(Et)N(Me)CH$_2$][μ_3-CHCBu^t](μ-H) (**5**; 43%), and Os$_3$(CO)$_9$[μ_3-Bu^{t}CC{C(Et)(NMe$_2$)}](μ-H) (**6a**; 8%). Compounds **4** and **5** were characterized by IR and ^{1}H NMR spectroscopy and crystal structure analyses. The structure of **6a** was established by a comparison with the related compound **6b** obtained from the reaction of **1** with PhC≡CH. This is described below.

The molecular structure of **4** is shown in Figure 2. Final crystallographic atomic coordinates are listed in Table VI. Selected bond distances and angles are listed in Tables VII and VIII. The molecule consists of a triosmium cluster with three metal–metal bonds. There is a triply bridging *tert*-butylacetylide ligand in the μ-$\perp$ coordination mode that is commonly found when these ligands serve as five-electron donors.[8] The coordination of this ligand is very similar to that observed in the related molecule Ru$_3$(CO)$_9$(μ-C$_2$Bu^t)(μ-H).[12] There is a terminally coordinated carbene ligand on Os(1) (Os(1)–C(1) = 2.07 (2) Å), and a bridging hydride ligand (located and refined; δ = −23.94 ppm) lies across the Os(2)–Os(3) bond. As in **3**, complex

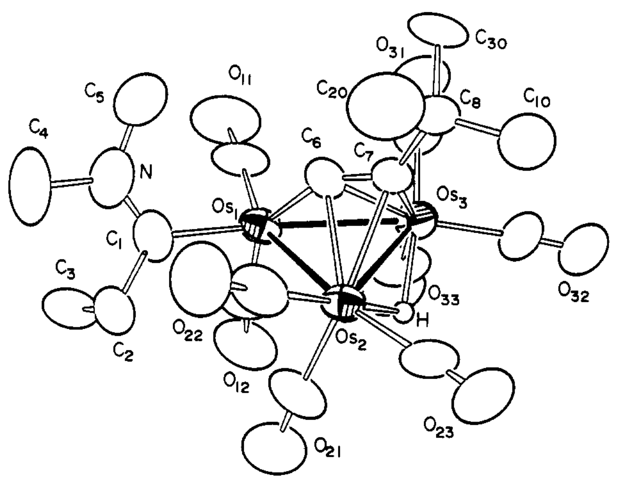

Figure 2. ORTEP diagram of Os$_3$(CO)$_8$[C(Et)NMe$_2$][μ_3-CCBu^t](μ-H) (**4**) showing 50% probability thermal ellipsoids.

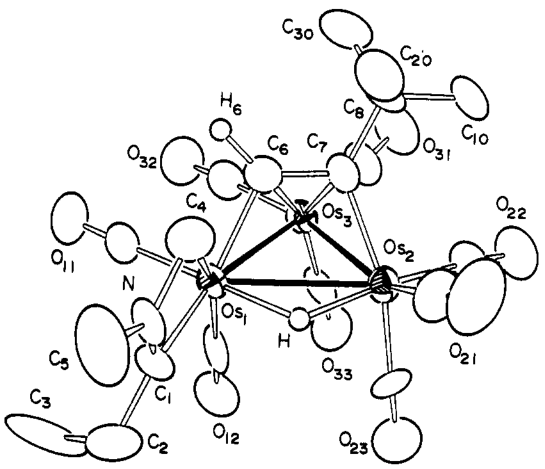

Figure 3. ORTEP diagram of Os$_3$(CO)$_8$[C(Et)N(Me)CH$_2$][μ_3-C(H)CBu^t](μ-H) (**5**) showing 50% probability thermal ellipsoids.

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.21359 (06)	0.54995 (02)	0.29551 (04)	2.60 (2)
Os(2)	0.03555 (06)	0.60976 (02)	0.08920 (04)	2.87 (2)
Os(3)	0.07091 (06)	0.65748 (02)	0.30221 (04)	2.81 (2)
O(11)	0.3906 (13)	0.5473 (05)	0.5364 (09)	5.6 (5)
O(12)	−0.1032 (11)	0.5157 (05)	0.3632 (09)	5.6 (6)
O(21)	0.1588 (13)	0.5794 (06)	−0.1272 (09)	7.3 (7)
O(22)	−0.1664 (12)	0.7056 (05)	−0.0159 (10)	6.2 (6)
O(23)	−0.2657 (13)	0.5402 (05)	0.0628 (10)	6.6 (6)
O(31)	0.0035 (15)	0.7809 (05)	0.2621 (10)	6.8 (6)
O(32)	0.1985 (14)	0.6719 (05)	0.5567 (09)	6.7 (6)
O(33)	−0.2744 (11)	0.6329 (05)	0.3121 (09)	5.5 (5)
N	−0.3892 (13)	0.4702 (04)	0.2263 (09)	3.4 (5)
C(1)	0.2599 (16)	0.4662 (05)	0.2670 (10)	3.2 (6)
C(2)	0.1959 (18)	0.4104 (06)	0.2931 (13)	5.0 (7)
C(3)	0.216 (03)	0.3983 (07)	0.4126 (17)	10 (1)
C(4)	0.4232 (15)	0.5314 (06)	0.2250 (12)	4.0 (7)
C(5)	0.495 (02)	0.4273 (08)	0.1911 (14)	6 (1)
C(6)	0.2990 (14)	0.6301 (06)	0.2697 (11)	3.2 (6)
C(7)	0.2313 (13)	0.6561 (05)	0.1662 (10)	3.0 (5)
C(8)	0.3232 (15)	0.7042 (05)	0.1181 (11)	3.5 (6)
C(10)	0.2193 (18)	0.7387 (06)	0.0276 (12)	5.0 (7)
C(11)	0.3211 (15)	0.5475 (06)	0.4455 (12)	3.4 (6)
C(12)	0.0155 (18)	0.5330 (06)	0.3421 (11)	3.9 (6)
C(20)	0.4504 (17)	0.6759 (07)	0.0626 (12)	5.0 (7)
C(21)	0.1094 (16)	0.5884 (07)	−0.0452 (12)	4.6 (7)
C(22)	−0.0841 (16)	0.6703 (06)	0.0224 (12)	3.9 (7)
C(23)	−0.1506 (16)	0.5659 (06)	0.0731 (11)	4.0 (6)
C(30)	0.4078 (19)	0.7435 (07)	0.2142 (14)	6.0 (9)
C(31)	0.0243 (19)	0.7324 (06)	0.2747 (12)	4.7 (7)
C(32)	0.1511 (17)	0.6675 (06)	0.4608 (12)	4.1 (7)
C(33)	−0.1433 (18)	0.6431 (05)	0.3108 (11)	3.8 (6)

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Table X. Intramolecular Distances for 5[a]

Os(1)–Os(2)	3.0231 (8)	Os(3)–C(6)	2.17 (1)
Os(1)–Os(3)	2.8501 (8)	Os(3)–C(7)	2.31 (1)
Os(1)–C(1)	2.08 (1)	Os(3)–C(31)	1.85 (1)
Os(1)–C(4)	2.17 (1)	Os(3)–C(32)	1.91 (1)
Os(1)–C(6)	2.09 (1)	Os(3)–C(33)	1.90 (2)
Os(1)–C(11)	1.87 (1)	N–C(1)	1.29 (1)
Os(1)–C(12)	1.93 (1)	N–C(4)	1.49 (2)
Os(1)–H	1.9 (1)	N–C(5)	1.48 (2)
Os(2)–Os(3)	2.7517 (8)	C(1)–C(2)	1.49 (2)
Os(2)–C(7)	2.09 (1)	C(2)–C(3)	1.44 (2)
Os(2)–C(21)	1.89 (1)	C(6)–C(7)	1.41 (2)
Os(2)–C(22)	1.87 (1)	C(7)–C(8)	1.56 (2)
Os(2)–C(23)	1.90 (1)	C–O (av)	1.16 (2)
Os(2)–H	1.8 (1)		

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

Table XI. Intramolecular Bond Angles for 5[a]

Os(2)–Os(1)–Os(3)	55.78 (2)	Os(1)–Os(3)–C(6)	46.8 (4)
Os(2)–Os(1)–C(1)	113.9 (3)	Os(1)–Os(3)–C(7)	69.7 (3)
Os(2)–Os(1)–C(4)	97.0 (4)	Os(2)–Os(3)–C(6)	70.8 (3)
Os(2)–Os(1)–C(6)	65.9 (4)	Os(2)–Os(3)–C(7)	47.9 (3)
Os(2)–Os(1)–C(11)	153.2 (4)	C(6)–Os(3)–C(7)	36.7 (4)
Os(2)–Os(1)–C(12)	89.0 (4)	C(1)–N–C(4)	105 (1)
Os(3)–Os(1)–C(1)	165.0 (4)	C(1)–N–C(5)	132 (1)
Os(3)–Os(1)–C(4)	126.0 (4)	C(4)–N–C(5)	123 (1)
Os(3)–Os(1)–C(6)	49.2 (3)	Os(1)–C(1)–N	101.2 (8)
Os(3)–Os(1)–C(11)	98.4 (4)	Os(1)–C(1)–C(2)	137 (1)
Os(3)–Os(1)–C(12)	76.8 (4)	N–C(1)–C(2)	121 (1)
C(1)–Os(1)–C(4)	62.8 (5)	C(1)–C(2)–C(3)	114 (1)
C(1)–Os(1)–C(6)	140.6 (5)	Os(1)–C(4)–N	91.0 (7)
C(1)–Os(1)–C(11)	92.8 (5)	Os(1)–C(6)–Os(3)	84.0 (4)
C(1)–Os(1)–C(12)	92.9 (5)	Os(1)–C(6)–C(7)	115 (1)
C(4)–Os(1)–C(6)	77.9 (5)	Os(3)–C(6)–C(7)	76.9 (7)
C(4)–Os(1)–C(11)	93.2 (5)	Os(2)–C(7)–Os(3)	77.3 (4)
C(4)–Os(1)–C(12)	155.4 (6)	Os(2)–C(7)–C(6)	109.5 (9)
C(6)–Os(1)–C(11)	92.3 (6)	Os(2)–C(7)–C(8)	130.5 (9)
C(6)–Os(1)–C(12)	125.9 (5)	Os(3)–C(7)–C(6)	66.4 (6)
C(11)–Os(1)–C(12)	92.0 (5)	Os(3)–C(7)–C(8)	130.8 (9)
Os(1)–Os(2)–Os(3)	58.92 (2)	C(6)–C(7)–C(8)	119 (1)
Os(1)–Os(2)–C(7)	68.5 (3)	Os–C–O (av)	176 (1)
Os(3)–Os(2)–C(7)	54.8 (3)	Os(1)–H–Os(2)	110 (4)
Os(1)–Os(3)–Os(2)	65.30 (2)		

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

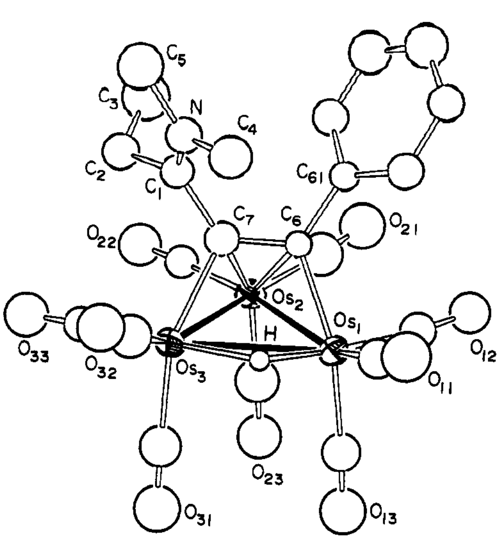

Figure 4. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}PhC_2C(Et)(NMe_2)](\mu\text{-}H)$ (**6b**) showing 50% probability thermal ellipsoids.

Table XII. Positional Parameters and B(eq) Values for 6b

atom	x	y	z	B(eq), Å^2
Os(1)	0.10695 (09)	0.14685 (05)	0.51983 (05)	2.38 (4)
Os(2)	0.38113 (09)	0.22258 (05)	0.54604 (05)	2.36 (4)
Os(3)	0.16945 (09)	0.31922 (05)	0.46784 (05)	2.39 (4)
O(11)	−0.2189 (19)	0.1213 (10)	0.5382 (09)	5.7 (4)
O(12)	0.2073 (16)	−0.0043 (09)	0.6092 (08)	4.4 (3)
O(13)	0.1424 (18)	0.0598 (10)	0.3681 (09)	5.4 (4)
O(21)	0.5290 (19)	0.1038 (11)	0.6610 (10)	5.9 (4)
O(22)	0.6536 (18)	0.3341 (10)	0.5558 (09)	5.2 (4)
O(23)	0.4766 (18)	0.1333 (10)	0.4065 (09)	5.4 (4)
O(31)	0.1785 (18)	0.2603 (10)	0.3029 (10)	5.5 (4)
O(32)	−0.0983 (18)	0.4337 (10)	0.4579 (09)	5.3 (4)
O(33)	0.3819 (18)	0.4620 (10)	0.4417 (09)	5.1 (4)
N	0.0985 (18)	0.4037 (10)	0.6696 (09)	3.2 (4)
C(1)	0.214 (02)	0.3808 (12)	0.6354 (11)	2.8 (4)
C(2)	0.354 (02)	0.4338 (13)	0.6372 (12)	3.6 (5)
C(3)	0.456 (03)	0.4187 (16)	0.7032 (15)	6.1 (7)
C(4)	−0.047 (03)	0.3640 (14)	0.6622 (13)	4.5 (5)
C(5)	0.098 (03)	0.4784 (15)	0.7178 (14)	5.1 (6)
C(6)	0.1695 (19)	0.2229 (11)	0.6102 (10)	1.8 (4)
C(7)	0.207 (02)	0.3034 (13)	0.5873 (11)	3.2 (5)
C(11)	−0.096 (03)	0.1296 (13)	0.5275 (12)	3.7 (5)
C(12)	0.164 (02)	0.0533 (13)	0.5712 (12)	3.4 (5)
C(13)	0.123 (02)	0.0910 (14)	0.4245 (13)	3.8 (5)
C(21)	0.466 (03)	0.1477 (16)	0.6146 (15)	5.3 (6)
C(22)	0.543 (02)	0.2930 (12)	0.5536 (11)	3.0 (4)
C(23)	0.442 (03)	0.1664 (15)	0.4626 (14)	5.4 (6)
C(31)	0.177 (03)	0.2837 (14)	0.3641 (14)	4.4 (5)
C(32)	0.006 (03)	0.3860 (14)	0.4600 (13)	4.4 (5)
C(33)	0.301 (02)	0.4077 (13)	0.4528 (11)	3.0 (4)
C(61)	0.162 (02)	0.2037 (11)	0.6929 (10)	2.2 (4)
C(62)	0.271 (02)	0.2294 (13)	0.7485 (12)	3.3 (5)
C(63)	0.249 (03)	0.2172 (14)	0.8245 (13)	4.6 (5)
C(64)	0.136 (03)	0.1757 (15)	0.8468 (13)	4.8 (6)
C(65)	0.035 (02)	0.1457 (13)	0.7965 (12)	3.2 (5)
C(66)	0.044 (02)	0.1582 (12)	0.7168 (12)	3.3 (5)

4 is also chiral and the methylene protons on the ethyl group show their expected inequivalence in the ^1H NMR spectrum.

The molecular structure of 5 is shown in Figure 3. Final atomic positional parameters are listed in Table IX. Selected bond distances and angles are listed in Tables X and XI. This molecule consists of a triosmium cluster with three osmium–osmium bonds. A hydride ligand (located and refined; $\delta = -20.4$ ppm) bridges the Os(1)–Os(2) bond and causes it to lengthen considerably (Os(1)–Os(2) = 3.0231 (8) Å). The metal–metal bond-lengthening effects of bridging hydride ligands are well-known.[13] A bridging Bu^tC_2H ligand is coordinated in a μ_3-$\|$ mode similar to that found in **3**, and its hydrogen atom H(6) (also located and refined) exhibits a characteristic low-field resonance shift ($\delta = 9.71$ ppm) similar to that in **3**. An *N*-methyl metalated aminocarbene ligand is coordinated to Os(1) and becomes a chelate as a result of the metalation. A similar chelating, metalated aminocarbene ligand was found in the complex $Os_3(CO)_8[C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)$ (**7**).[9] The osmium to carbene carbon bond distance of 2.08 (1) Å is similar to that observed in **3**, **4**, and **7** and indicates that the metalation process does not significantly affect that bonding. The Os–C distance to the CH_2 group C(4) is significantly longer (2.17 (1) Å) but is very similar to that found 7 (2.16 (1) Å). Complex **5** is chiral, and the inequivalence of the hydrogen atoms on both of the prochiral methylene groups, C(2) and C(4), is seen in its ^1H NMR spectrum (see Table I).

The only product obtained from the reaction of **1** with HC≡CPh in the presence of Me_3NO was $Os_3(CO)_9[\mu_3\text{-}PhC_2C(Et)(NMe_2)](\mu\text{-}H)$ (**6b**; 35%), the phenyl-substituted analogue of **6a**. No evidence for the phenyl-substituted analogues of **3**–**5** was obtained in this reaction. The very close similarities of the IR and ^1H NMR spectra of **6a**,**b** indicate that the compounds are structurally similar, but

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[13] Churchill, M. R. In *Transition Metal Hydrides*; Bau, R. Ed.; Advances in Chemistry Series 167; American Chemical Society: Washington, DC, 1978.

Table XIII. Intramolecular Distances for 6b[a]

Os(1)-Os(2)	2.774 (1)	Os(3)-C(31)	1.93 (2)
Os(1)-Os(3)	2.981 (1)	Os(3)-C(32)	1.82 (2)
Os(1)-C(6)	2.07 (2)	Os(3)-C(33)	1.88 (2)
Os(1)-C(11)	1.86 (2)	Os(3)-H	1.83
Os(1)-C(12)	1.82 (2)	N-C(1)	1.29 (2)
Os(1)-C(13)	1.93 (2)	N-C(4)	1.46 (3)
Os(1)-H	1.64	N-C(5)	1.47 (3)
Os(2)-Os(3)	2.774 (1)	C(1)-C(2)	1.53 (3)
Os(2)-C(6)	2.28 (2)	C(1)-C(7)	1.51 (3)
Os(2)-C(7)	2.20 (2)	C(2)-C(3)	1.47 (3)
Os(2)-C(21)	1.85 (3)	C(6)-C(7)	1.40 (2)
Os(2)-C(22)	1.84 (2)	C(6)-C(61)	1.51 (2)
Os(2)-C(23)	1.85 (3)	O-C (av)	1.18 (2)
Os(3)-C(7)	2.15 (2)	C(Ph)-C (av)	1.38 (2)

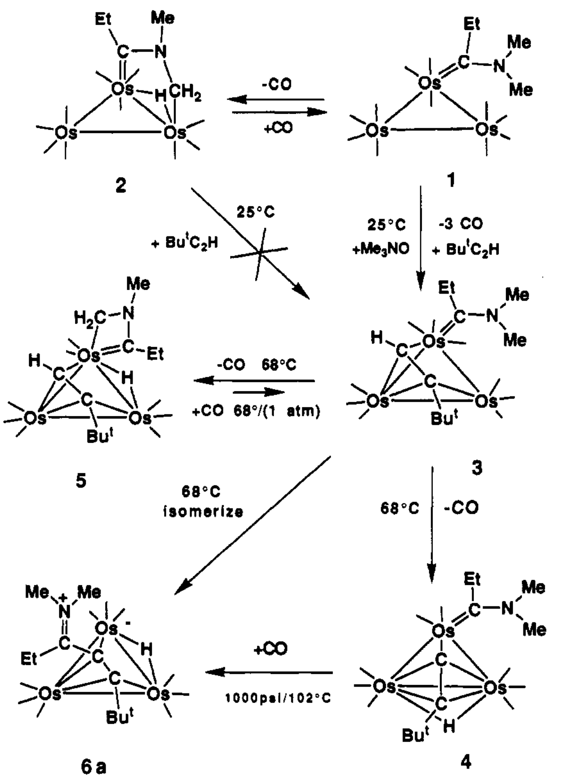
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table XIV. Intramolecular Bond Angles for 6b[a]

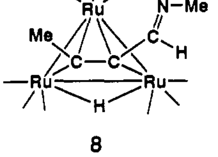
Os(2)-Os(1)-Os(3)	57.51 (3)	Os(1)-Os(3)-C(31)	92.3 (7)
Os(2)-Os(1)-C(6)	53.8 (5)	Os(1)-Os(3)-C(32)	113.8 (7)
Os(2)-Os(1)-C(11)	157.5 (6)	Os(1)-Os(3)-C(33)	151.4 (6)
Os(2)-Os(1)-C(12)	93.0 (7)	Os(2)-Os(3)-C(7)	51.1 (5)
Os(2)-Os(1)-C(13)	103.9 (7)	Os(2)-Os(3)-C(31)	104.6 (7)
Os(3)-Os(1)-C(6)	69.2 (5)	Os(2)-Os(3)-C(32)	154.1 (7)
Os(3)-Os(1)-C(11)	111.3 (6)	Os(2)-Os(3)-C(33)	94.1 (6)
Os(3)-Os(1)-C(12)	150.4 (7)	C(1)-N-C(4)	125 (2)
Os(3)-Os(1)-C(13)	97.7 (7)	C(1)-N-C(5)	122 (2)
Os(1)-Os(2)-Os(3)	65.00 (4)	C(4)-N-C(5)	112 (2)
Os(1)-Os(2)-C(6)	47.2 (4)	N-C(1)-C(2)	122 (2)
Os(1)-Os(2)-C(7)	70.5 (5)	N-C(1)-C(7)	120 (2)
Os(1)-Os(2)-C(21)	99.3 (8)	C(2)-C(1)-C(7)	118 (2)
Os(1)-Os(2)-C(22)	167.3 (6)	C(1)-C(2)-C(3)	114 (2)
Os(1)-Os(2)-C(23)	87.5 (8)	Os(2)-C(6)-C(61)	125 (1)
Os(3)-Os(2)-C(6)	71.1 (4)	C(7)-C(6)-C(61)	120 (2)
Os(3)-Os(2)-C(7)	49.5 (5)	Os(3)-C(7)-C(1)	118 (1)
Os(3)-Os(2)-C(21)	160.7 (8)	Os(3)-C(7)-C(6)	112 (1)
Os(3)-Os(2)-C(22)	102.4 (6)	C(1)-C(7)-C(6)	127 (2)
Os(3)-Os(2)-C(23)	95.7 (8)	Os-C-O (av)	176 (2)
Os(1)-Os(3)-Os(2)	57.49 (3)	C-C(Ph)-C	120 (2)
Os(1)-Os(3)-C(7)	66.8 (5)		

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

Scheme I



only **6b** was characterized by a crystal structure analysis. An ORTEP drawing of the molecular structure of **6b** is shown in Figure 4. Final atomic positional parameters are listed in Table XII. Selected bond distances and angles are listed in Tables XIII and XIV. The molecule consists of a triosmium cluster with three metal–metal bonds. A hydride ligand (located but not refined) bridges the long Os(1)–Os(3) bond (2.981 (1) Å) (δ = −19.52 ppm). The most interesting ligand is a phenyl(ethyl(dimethyliminio)methyl)alkyne that bridges the three metal atoms in the usual μ_3-∥ coordination mode. The compounds **6a,b** are very similar to the ruthenium complex $Ru_3(CO)_9[\mu_3\text{-}MeC_2C(H)(NMe_2)](\mu\text{-}H)$ (**8**), which was obtained from the reaction of $Ru_3(CO)_{12}$ with $MeC{\equiv}CCH_2NMe_2$.[14] The alkyne C–C distance, C(6)–C(7), is normal for such a coordinated alkyne (1.40 (2) Å) and similar to that found in **8** (1.385 (5) Å). The C–C distance to the iminium group (C(1)–C(7) = 1.51 (2) Å) is indicative of a single bond, but the iminium bond length (C(1)–N = 1.29 (2) Å) is that expected for a double bond. Formally, the nitrogen atom is positively charged. Since the molecule is uncharged, a negatively charged center should exist, but this may be delocalized about the three metal atoms of the cluster. Similar zwitterionic character has been proposed for a number of related cluster compounds.[15] This molecule is chiral, and the inequivalence of the hydrogen atoms on the prochiral methylene group, C(2), is observed in the ^1H NMR spectrum (see Table I). Interestingly, the inequivalence of the hydrogen atoms on the methylene group in **6a** was not observed. This could be explained by the existence of a dynamical averaging process produced by a rotation of the alkyne on the face of the cluster. The existence of such processes is well established, but no attempts were made to confirm this by low-temperature NMR measurements in this case.[16] When compound **1** was allowed to react with HC_2Ph at 97 °C, compound **6b** was obtained in 35% yield, and once again no evidence for the phenyl-substituted analogues of **3**–**5** was obtained.



8

When compound **5** was treated with CO (68 °C/1 atm), it was converted back to **3** partially (9% yield). Some **4** was also formed (7% yield), probably by decarbonylation of some of the **3** that was formed. Compound **4** was converted to **6a**, but no **6a** was obtained from the reaction of **4** with CO at 68 °C/1 atm. This latter experiment strongly suggests that **4** is not an intermediate in the formation of **6a** from **3** in the original reaction. In a separate experiment **3** was converted to **6a** in the presence of ^{13}CO, but no

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(14) Aime, S.; Osella, D.; Deeming, A. J.; Arce, A. J.; Hursthouse, M. B.; Dawes, H. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1459.

(15) (a) Cherkas, A. A.; Hadj-Bagheri, N.; Carty, A. J.; Sappa, E.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1990**, *9*, 1887. (b) Cherkas, A. A.; Randall, L. H.; Taylor, N. J.; Mott, G. N.; Yule, J. E.; Guinamant, J. L.; Carty, A. J. *Organometallics* **1990**, *9*, 1677. (c) Aime, S.; Jannon, G.; Osella, D.; Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1987. (d) Henrick, K.; McPartlin, M.; Deeming, A. J.; Hasso, S.; Manning, P. *J. Chem. Soc., Dalton Trans.* **1982**, 899. (e) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *25*, 1.

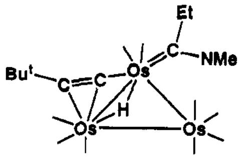
(16) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

evidence was obtained for the incorporation of ^{13}CO in the **6a** that was formed.

Discussion

A summary of the reactions in this study is given in Scheme I. The carbene complex **1** is decarbonylated by Me_3NO, and in the presence of Bu^tC_2H, a Bu^tC_2H ligand is added to the complex to yield compound **3**. In a competing process, the complex undergoes an intramolecular metalation of one of the *N*-methyl groups to yield compound **2**. When heated to 68 °C, compound **3** undergoes a decarbonylation to yield the products **4** and **5** by competing processes. In the formation of **4**, the alkyne ligand was converted into a hydride and acetylide ligand by the cleavage of the alkyne C–H bond. The formation of **5** occurred by a metalation of one of the *N*-methyl groups of the carbene ligand. In the presence of a CO atmosphere, the formation of **5** can be reversed partially, to yield **3** and some **4**.

In a reaction that competes with the formation of **4** and **5**, compound **3** was isomerized to **6a** by a transfer of the carbene ligand to the acetylide. We originally believed that a species such as **4** might be an intermediate in the formation of **6b** from the reaction of **1** with PhC_2H.[3] Our studies of **4** show that it can be converted to **6a** in a good yield. However, the reaction conditions for the transformation of **4** to **6a** are considerably more forcing than those used in the thermal transformation of **3** to **4**, **5**, and **6a**. This indicates that the formation of **6a** does not occur by a mechanism involving the elimination and readdition of CO. This was confirmed by observing the transformation of **3** to **6a** in the presence of ^{13}CO, which took place without the incorporation of any significant amount of ^{13}CO. One possible mechanism would be to cleave the alkyne C–H bond and convert the alkyne to a hydride and an acetylide ligand serving as a three-electron donor bridging two metal atoms such as in the species A. Transfer of the carbene ligand to the acetylide carbon atom could then lead to **6a** without the loss and readdition of CO. In fact, the transformation of **4** to **6a** could also involve an intermediate such as A. The reaction of PhC_2H with $Os_3(CO)_{10}(\mu\text{-}H)_2$ yields the complex $Os_3(CO)_{10}(\mu\text{-}C{\equiv}CPh)(\mu\text{-}H)$, in which the phenylacetylide ligand is proposed to serve as an edge-bridging three-electron donor.[16]



A

The reaction of **1** with PhC_2H either with heating (97 °C) or at 25 °C with Me_3NO activation yielded **6b** without the observed formation of the phenyl-substituted analogues of **3**–**5**. We believe, however, that a species such as **3** and A is probably traversed also in the course of this reaction.

The reaction of terminal alkynes with mononuclear metal carbene complexes usually leads to coupling and annulation products without the cleavage of the alkyne C–H bond.[1]

The ability of clusters to engage in multicenter coordination of alkynes has been shown to result in facile activation of the C–H bonds of terminal alkynes.[8,16] We have now shown that in the presence of a terminally coordinated carbene ligand, a novel form of coupling can occur to give new products.

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Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters for all of the structural analyses (16 pages); tables of structure factor amplitudes (59 pages). Ordering information is given on any current masthead page.