Clusters Containing Carbene Ligands. 14. Further Studies of the Reactivity of the Carbene Centers in the Dicarbene Cluster Complex $Os_3(CO)_9[\mu_3\text{-}C(Et)N(Me)CH](\mu\text{-}H)_2$ with Diphenylacetylene

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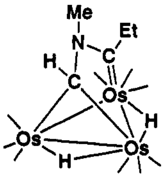
Six products were obtained from the reaction of $Os_3(CO)_9[\mu_3\text{-}C(Et)N(Me)CH](\mu\text{-}H)_2$: (1) with PhC_2Ph at 125 °C. They have been identified as the two previously reported compounds $Os_3(CO)_8[\mu_3\text{-}\eta^2\text{-}C(H)N(Me)C(Et)][\eta^2\text{-}CPhC(H)Ph](\mu\text{-}H)$ (**2**) (3%) and $Os_3(CO)_8\{\mu_3\text{-}C[C(Ph)CH(Ph)]N(Me)C(Et)\}(\mu\text{-}H)_2$ (**3**) (39%) and four new compounds $Os_3(CO)_8\{\mu\text{-}\eta^3\text{-}C[N(Me)C(Et)]C(Ph)C(Ph)\}(\mu\text{-}H)$ (**4**) (4%), $Os_3(CO)_8(\mu_3\text{-}CEt)[\mu\text{-}N(Me)C(H)C(Ph)CPh]$ (**5**) (6%), $Os_3(CO)_8[C(Et)N(Me)CH_2][\mu_3\text{-}C(Ph)C(Ph)](\mu\text{-}H)$ (**6**) (3%), and $Os_3(CO)_7\{\mu_3\text{-}C[C(Ph)CH(Ph)]N(Me)C(Et)\}[\eta^2\text{-}C(Ph)C(H)Ph](\mu\text{-}H)$ (**7**) (3%). Compounds **4**–**7** were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. Compound **4** contains a PhC(Ph)CCN(Me)CEt ligand with the PhC(Ph)CC portion coordinated in di-$\sigma + \pi$ triply bridging mode that is linked to a carbene center through the *N*-methyl group. Compound **5** contains a triply bridging PhC(Ph)CC(H)N(Me) and triply bridging propylidyne ≡CEt ligands. The latter was derived from the terminal carbene grouping in **1** by rupture of the carbene–nitrogen bond. Compound **6** contains a triply bridging PhC≡CPh ligand in the $\mu\text{-}\|$coordination mode and an ethyl(dimethylamino)carbene ligand that is metalated on one of the *N*-methyl groups. Compound **7** is formed in a secondary reaction that involves decarbonylation and the addition and insertion of a second molecule of PhC≡CPh into one of the metal–hydrogen bonds of **3**. Compound **2** is converted to **3** (29%) and **6** (6%) at 125 °C in octane solution. Compound **5** is converted to the new compound $Os_3(CO)_7[\mu\text{-}C(H)C(H)Me][\mu\text{-}N(Me)C(H)C(Ph)CPh]$ (**8**) in 49% yield at 125 °C. Compound **8** was characterized crystallographically and found to contain a σ–π coordinated methyl-substituted vinyl ligand formed by a transformation of the propylidyne ligand in **5**. Crystal data: for **4**, space group $P2_1/n$, $a = 9.773$ (2) Å, $b = 15.822$ (7) Å, $c = 18.687$ (6) Å, $\beta = 103.91$ (2)°, $Z = 4$, 2787 reflections, $R = 0.034$; for **5**, space group Cc, $a = 15.089$ (4) Å, $b = 13.385$ (2) Å, $c = 14.618$ (3) Å, $\beta = 108.78$ (2)°, $Z = 4$, 1711 reflections, $R = 0.031$; for **6**, space group $P2_1/c$, $a = 16.916$ (3) Å, $b = 9.763$ (2) Å, $c = 18.607$ (2) Å, $\beta = 111.82$ (1)°, $Z = 4$, 2388 reflections, $R = 0.029$; for **7**, space group $P2_1/n$, $a = 12.266$ (4) Å, $b = 26.191$ (9) Å, $c = 14.486$ (3) Å, $\beta = 98.64$ (2)°, $Z = 2$, 2735 reflections, $R = 0.039$; for **8**, space group $P\bar{1}$, $a = 11.304$ (2) Å, $b = 14.276$ (2) Å, $c = 9.648$ (2) Å, $\alpha = 101.95$ (1)°, $\beta = 113.99$ (1)°, $\gamma = 71.01$ (1)°, $Z = 2$, 2939 reflections, $R = 0.026$.

Introduction

New procedures for the synthesis of carbene ligands in cluster complexes have produced new opportunities to study the chemistry of these ligands in the multicenter metal environment.[1-9] We have recently reported the preparation and structural characterization of the compound $Os_3(CO)_9[\mu_3\text{-}CEtN(Me)CH](\mu\text{-}H)_2$ (**1**).[8b] The EtCN(Me)CH ligand in **1** contains both bridging and terminal carbene centers. In recent studies we have been trying to identify differences in the reactivity of the two carbene centers in this compound.[10] When activated by treatment with Me_3NO in NCMe, compound **1** engages in facile reactions with diarylalkynes. Insertion reactions involving the hydride ligands followed by coupling of the alkenyl groups to the *bridging* carbene center were observed. In this report we present the results of investigations of the reactions of **1** with diphenylacetylenes at 125 °C.



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Carbene complexes have attracted attention as reagents for use in novel organic syntheses.[11] It is possible that the multicenter environment provided by the cluster complex may provide new pathways to organic products.

Experimental Section

General Methods. 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. ^1H NMR spectra were taken at 300 MHz on a Brüker

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Table I. IR and ^{1}H NMR Spectra of Compounds 4–8

compound	IR: ν(CO), cm^{-1} (hexane)	^{1}H NMR: δ ($CDCl_3$)
$Os_3(CO)_8\{\mu\text{-}\eta^3\text{-}C[N(Me)C(Et)]C(Ph)C(Ph)\}(\mu\text{-}H)$ (4)	2086 m, 2061 m, 2010 m, 1996 vs, 1984 vw, 1979 w	7.60–6.30 (10 H, m, Ph), 2.89 (3 H, s, NMe), 2.31 (1 H, dq, $^2J_{H\text{-}H}$ = 15.8 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, C*H*H), 1.97 (1 H, dq, $^2J_{H\text{-}H}$ = 15.8, $^3J_{H\text{-}H}$ = 7.5 Hz, CH*H*), 1.12 (3 H, t, $^3J_{H\text{-}H}$ = 7.5 Hz, Me), −17.35 (1 H, s, OsH)
$Os_3(CO)_8(\mu_3\text{-}CEt)[\mu\text{-}N(Me)C(H)C(Ph)CPh]$ (5)	2090 m, 2070 vw, 2059 vs, 2026 m, 2020 vw, 2011 vs, 1997 s, 1984 m, 1967 m, 1936 m	7.41–7.20 (10 H, m, Ph), 5.16 (1 H, s, CH), 4.62 (1 H, dq, $^2J_{H\text{-}H}$ = 12.8 Hz, $^3J_{H\text{-}H}$ = 7.3 Hz, C*H*H), 4.35 (1 H, dq, $^2J_{H\text{-}H}$ = 12.8 Hz, $^3J_{H\text{-}H}$ = 7.3 Hz, CH*H*), 2.80 (3 H, s, NMe), 1.58 (3 H, t, $^3J_{H\text{-}H}$ = 7.3 Hz, Me)
$Os_3(CO)_8[C(Et)N(Me)CH_2][\mu_3\text{-}C(Ph)C(Ph)](\mu\text{-}H)$ (6)	2078 s, 2045 vs, 2018 s, 2001 vs, 1986 w, 1976 vw, 1964 m	7.25–6.83 (10 H, m, Ph), 2.44 (1 H, d, $^2J_{H\text{-}H}$ = 9.2 Hz, NC*H*H), 1.89 (1 H, d, $^2J_{H\text{-}H}$ = 9.2 Hz, NCH*H*), 1.80 (2 H, q, CH_2, $^3J_{H\text{-}H}$ = 7.7 Hz), 1.68 (3 H, s, NMe), 0.51 (3 H, t, $^3J_{H\text{-}H}$ = 7.7 Hz, Me), −20.63 (1 H, s, OsH)[a]
$Os_3(CO)_7[\mu_3\text{-}C[C(Ph)CH(Ph)]N(Me)C(Et)\}[\eta^2\text{-}C(Ph)C(H)Ph](\mu\text{-}H)$ (7)	2061 m, 2047 vs, 1992 s, 1986 s, sh, 1982 s, 1955 w, 1930 m	8.20–6.60 (20 H, m, Ph), 5.75 (1 H, s, *H*C(Ph)C(Ph)), 2.92 (1 H, s, *H*C(Ph)C(Ph)C), 2.90 (1 H, dq, $^2J_{H\text{-}H}$ = 12.7 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz, C*H*H), 2.55 (3 H, s, NMe), 2.27 (1 H, dq, $^2J_{H\text{-}H}$ = 12.7 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz, CH*H*), 1.15 (3 H, t, $^3J_{H\text{-}H}$ = 7.7 Hz, Me), −16.90 (1 H, s, OsH)
$Os_3(CO)_7[\mu\text{-}C(H)C(H)Me][\mu\text{-}N(Me)C(H)C(Ph)CPh]$ (8)	2071 m, 2020 s, 2008 vs, 2001 m, 1984 vw, 1962 m, 1942 w	9.73 (1 H, d, $^3J_{H\text{-}H}$ = 12.0 Hz, C═CH), 7.30–6.80 (10 H, m, Ph), 5.87 (1 H, dq, $^3J_{H\text{-}H}$ = 12.0 Hz, $^3J_{H\text{-}H}$ = 5.6 Hz, C*H*Me), 4.79 (1 H, s, CH), 4.03 (3 H, s, NMe), 2.40 (3 H, d, $^3J_{H\text{-}H}$ = 5.6, CH*Me*)

[a] In C_6D_6.

AM-300 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)N(Me)C(Et)](\mu\text{-}H)_2$ (1) was prepared by the previously reported procedure.[8b]

Reaction of 1 with PhC≡CPh at 125 °C. 1 (126 mg, 0.139mmol) and PhC_2Ph (120 mg, 0.72 mmol) were dissolved in 50 mL of octane in a 100-mL three-necked round-bottomed flask. The solution was heated to reflux for a period of 3 h. After cooling, the solvent was removed in vacuo. The residue was dissolved in a minimal amount CH_2Cl_2 and was chromatographed by TLC. Elution with a CH_2Cl_2/hexane (2/8) solvent mixture yielded the following compounds in the order of elution: 21.0 mg of unreacted 1, 8.1 mg of yellow $Os_3(CO)_8(\mu_3\text{-}CEt)[\mu\text{-}N(Me)C(H)C(Ph)CPh]$ (5) (6%), 57.6 mg of yellow $Os_3(CO)_8\{\mu_3\text{-}C[C(Ph)CH(Ph)]N(Me)C(Et)\}(\mu\text{-}H)_2$ (3) (39%), 5.5 mg of yellow $Os_3(CO)_8\{\mu\text{-}\eta^3\text{-}C[N(Me)C(Et)]C(Ph)C(Ph)\}(\mu\text{-}H)$ (4) (4%), 4.7 mg of orange $Os_3(CO)_8[\mu_3\text{-}\eta^2\text{-}C(H)N(Me)C(Et)][\eta^2\text{-}C(Ph)C(H)Ph](\mu\text{-}H)$ (2) (3%), 3.8 mg of yellow $Os_3(CO)_8[C(Et)N(Me)CH_2][\mu_3\text{-}C(Ph)C(Ph)](\mu\text{-}H)$ (6) (3%), 5.2 mg of orange $Os_3(CO)_7\{\mu_3\text{-}C[C(Ph)CH(Ph)]N(Me)C(Et)\}[\eta^2\text{-}C(Ph)C(H)Ph](\mu\text{-}H)$ (7) (3%), and a few uncharacterizable trace products. Spectral data of 4–7 are listed in Table I. Anal. Calcd (Found) for 4: C, 30.71 (30.96); H, 1.81 (1.69); N, 1.33 (1.45). For 5: C, 30.71 (31.46); H, 1.81 (1.75); N, 1.33 (1.19). For 6: C, 30.65 (30.84); H, 2.00 (1.79); N, 1.32 (1.27). For 7: C, 39.76 (39.84); H, 2.59 (2.34); N, 1.16 (1.00).

Thermolysis of 2 at 125 °C. In a 50-mL round-bottomed flask was refluxed a solution of 2 (11.4 mg, 0.0108 mmol) in 20 mL of octane for 3 h. After cooling, the solvent was removed and the residue was separated by TLC as described above to yield 3.3 mg of 3 (29%) and 0.7 mg of 6 (6%).

Reaction of 3 with PhC≡CPh. In a 50-mL round-bottomed flask was refluxed a solution of 3 (27.6 mg, 0.0261 mmol) and 30 mg of PhC_2Ph in 20 mL of octane for 3 h. Separation of products by TLC yielded in order to elution 15.8 mg of unreacted 3, 7.3 mg of 7 (21%), and traces of a few uncharacterizable decomposition products.

Thermolysis of 3 at 125 °C. A solution (25 mL) containing 3 (20.7 mg, 0.0196 mmol) was heated to reflux for 3 h. Analysis of the solution by IR spectroscopy and TLC showed no evidence for a reaction.

Thermolysis of 4 at 125 °C. An octane solution (20 mL) of 4 (7.5 mg, 0.00710 mmol) was refluxed for 4 h. After the solution was cooled and solvent was evaporated, the residue was separated by TLC as described above to yield 1.1 mg of unknown yellow compound X, 1.0 mg of 8 (14%), and 3.2 mg of unreacted 4. The IR spectrum of X shows absorptions at 2089 m, 2065 w, 2035 s, 2011 vs, sh, 2009 vs, 1994 vw, 1971 m, and 1960 w cm^{-1}.

Thermolysis of 5 at 125 °C. An octane solution (20 mL) containing 13.3 mg of 5 was refluxed for 3 h. After the solution was cooled and solvent was removed in vacuo, the residue was separated by TLC in usual way to yield 6.5 mg of yellow $Os_3(CO)_7[\mu\text{-}C(H)C(H)Me]C(Et)][\mu\text{-}N(Me)C(H)C(Ph)CPh]$ (8) (49%) and traces of a few uncharacterizable decomposition products. Spectral data of 8 are listed in Table I. Anal. Calcd (Found) for 8: C, 30.38 (30.50); H, 1.86 (1.65); N, 1.36 (1.32).

Thermolysis of 6 at 125 °C. A solution of 6 (5.5 mg) was refluxed for 3 h. IR and TLC separation analyses of solution mixture showed no evidence for a reaction. A 4.0-mg portion of 6 was recovered after workup.

Crystallographic Analyses. Crystals of 4 suitable for X-ray diffraction analyses were grown from solution in hexane/CH_2Cl_2 solvent mixtures by slow evaporation of the solvent at 25 °C. Crystals of 5 and 8 were grown from a $MeOH/CH_2Cl_2$ solvent mixture by slow evaporation of solvent at 0 °C. Crystals of 6 were grown from a pure hexane solvent by slow evaporation of solvent at 25 °C. Crystals of 7 were grown from a benzene/heptane 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 (Version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz–polarization (*Lp*) corrections were applied. Neutral atom scattering factors were calculated by the standard procedures.[12a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[12b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net}^2)^2]^{1/2}/Lp$.

Compounds 4, 6, and 7 crystallized in the monoclinic crystal system. The space groups $P2_1/c$ and $P2_1/n$ were 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 6 all of non-hydrogen atoms were refined with anisotropic thermal parameters. For 7 only all metal atoms and carbon and oxygen atoms of carbonyl ligands were refined with anisotropic thermal parameters. For 4, 6, and 7 the positions of hydrogen atoms on the ligands were calculated by assuming idealized geometries. For compound 4 two significant residuals that were approximately 3 Å from each other and also 3 Å from atom Os(3) were observed in a difference Fourier map after the complete

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(12) (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.

Table II. Crystallographic Data for Compounds 4–8

	4	5	6
empirical formula	$Os_3O_8NC_{27}H_{19}$	$Os_3O_8NC_{27}H_{19}$	$Os_3O_8NC_{27}H_{21}$
formula weight	1056.05	1056.05	1058.06
crystal system	monoclinic	monoclinic	monoclinic
lattice parameters			
a (Å)	9.773 (2)	15.089 (4)	16.916 (3)
b (Å)	15.822 (7)	13.385 (2)	9.763 (2)
c (Å)	18.687 (6)	14.618 (3)	18.607 (2)
α (deg)			
β (deg)	103.91 (2)	108.78 (2)	111.82 (1)
γ (deg)			
V (Å^3)	2805 (3)	2795 (2)	2852.9 (8)
space group	$P2_1/n$ (No. 14)	*Cc* (No. 9)	$P2_1/c$ (No. 14)
Z	4	4	4
D_{calc}, g/cm^3	2.50	2.51	2.46
$\mu_{(Mo\ K\alpha)}$, cm^{-1}	136.19	136.64	133.89
temp (°C)	20	20	20
$2\theta_{max}$ (deg)	44.0	46.0	42.0
no. of observns ($I > 3\sigma(I)$)	2787	1711	2388
no. of variables	370	250	352
residuals: R, R_w	0.034, 0.037	0.031, 0.030	0.029, 0.029
goodness of fit indicator	1.73	1.22	1.29
max shift in final cycle	0.01	0.01	0.00
largest peak in final diff map, e$^-$/Å^3	1.03	0.96	1.41
abs corr	empirical	analytical	empirical
max/min	1.00/0.46	0.42/0.32	1.00/0.25
scan speed, deg/min	4.0	4.0	4.0

	7	8
empirical formula	$Os_3O_7NC_{40}H_{31}\cdot C_7H_{16}$	$Os_3O_7NC_{26}H_{19}$
formula weight	1308.49	1028.04
crystal system	monoclinic	triclinic
lattice parameters:		
a (Å)	12.266 (4)	11.304 (2)
b (Å)	26.191 (9)	14.276 (2)
c (Å)	14.486 (3)	9.648 (2)
α (deg)		101.95 (1)
β (deg)	98.64 (2)	113.99 (1)
γ (deg)		71.01 (1)
V (Å^3)	4601 (4)	1340.0 (4)
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z	4	2
D_{calc}, g/cm^3	1.89	2.55
$\mu_{(Mo\ K\alpha)}$, cm^{-1}	83.20	142.46
temp (°C)	20	20
$2\theta_{max}$ (deg)	40.0	44.0
no. of observns ($I > 3\sigma(I)$)	2735	2939
no. of variables	322	346
residuals: R, R_w	0.039, 0.040	0.026, 0.031
goodness of fit indicator	1.39	1.89
max shift in final cycle	0.05	0.05
largest peak in final diff map, e$^-$/Å^3	0.83	0.78
abs corr	empirical	empirical
max/min	1.00/0.47	1.00/0.31
scan speed, deg/min	4.0	4.0

molecule had been refined. It was suspected that these were due to the metal atoms from a small component of a disordered cluster. Occupancy refinement upon these residuals assigned as osmium atoms Os(1A) and Os(2A) indicated a 6.5% disorder component. This model was included on the final cycles of least-squares refinement. Due to the lower quality of the structure caused by the disorder, the hydride ligand of 4 was not located. For compound 6, the hydride ligand was located but it could not be refined. The hydride ligands of 7 were obtained from difference Fourier syntheses and were refined on their positional parameters. The scattering contributions of the other hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

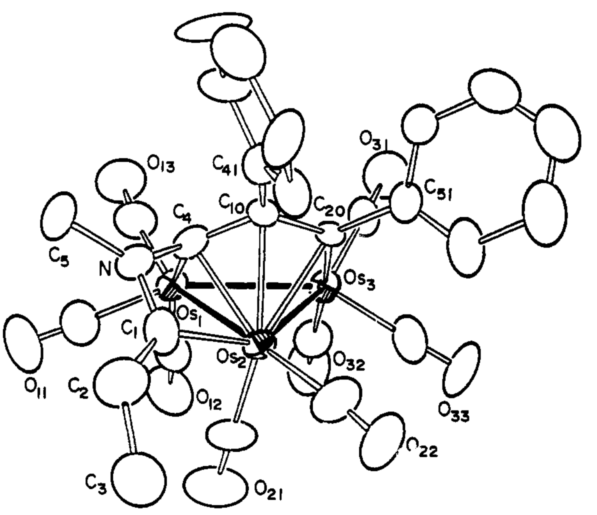

Figure 1. ORTEP diagram of $Os_3(CO)_8\{\mu\text{-}\eta^3\text{-}C[N(Me)C(Et)]C(Ph)C(Ph)\}(\mu\text{-}H)$ (4) showing 50% probability thermal ellipsoids.

Compound 5 crystallized in the monoclinic crystal system. The systematic absences observed in the data were consistent with both space groups *C*2/*c* and *Cc*. *Z* was calculated to be approximately 4, so the noncentric space group *Cc* was assumed. This was confirmed by the successful solution and refinement of a structure containing one asymmetric molecule in the asymmetric crystal unit. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms except carbon atoms of carbonyl ligands and phenyl groups were refined with anisotropic thermal parameters. All hydrogen atoms on the ligands were calculated by assuming idealized geometries. The contributions of all hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound 8 crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The coordinates of the heavy atoms were obtained by direct methods (MITHRIL). All remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries and employing observed positions whenever possible. Contributions of all of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Results

Six products were obtained from the reaction of $Os_3(CO)_9[\mu_3\text{-}C(Et)NMe(CH)](\mu\text{-}H)_2$ (1) with PhC_2Ph at 125 °C. They have been identified as $Os_3(CO)_8[\mu_3\text{-}\eta^2\text{-}C(H)N(Me)C(Et)][\eta^2\text{-}CPhC(H)Ph](\mu\text{-}H)$ (2) (3%), $Os_3(CO)_8\{\mu_3\text{-}C[C(Ph)CH(Ph)]N(Me)\text{-}C(Et)\}(\mu\text{-}H)_2$ (3) (39%), $Os_3(CO)_8\{\mu\text{-}\eta^3\text{-}C[N(Me)C(Et)]C(Ph)C(Ph)\}(\mu\text{-}H)$ (4) (4%), $Os_3(CO)_8(\mu_3\text{-}CEt)[\mu\text{-}N(Me)C(H)C(Ph)CPh]$ (5) (6%), $Os_3(CO)_8[C(Et)N(Me)CH_2][\mu_3\text{-}C(Ph)C(Ph)](\mu\text{-}H)$ (6) (3%), and $Os_3(CO)_7\{\mu_3\text{-}C[C(Ph)CH(Ph)]N(Me)C(Et)\}[\eta^2\text{-}C(Ph)\text{-}C(H)Ph](\mu\text{-}H)$, (7) (3%). Compounds 2 and 3 were obtained previously from the reaction of the lightly stabilized derivative of 1, $Os_3(CO)_8(NCMe)[\mu_3\text{-}C(Et)NMe(CH)](\mu\text{-}H)_2$, with PhC_2Ph.[10] Compound 2 is known to be converted to 3 by a coupling of the σ–π coordinated diphenylvinyl ligand to the bridging carbene carbon and a shift of the hydrogen atom from the bridging carbene carbon to the metal atoms.[10] This transformation occurs under milder conditions (97 °C) than those used here. At 125 °C compound 3 is still the principal product obtained from 2, but a small amount of 6 (6%) was also obtained. Compounds 4–7 are new and were characterized by a combination of IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses.

An ORTEP drawing of the molecular structure of 4 is shown in Figure 1. Final atomic positional parameters are listed in Table III. Selected interatomic distances and angles are listed in Tables IV and V. The molecule consists of a triangular cluster of three osmium atoms bridged by a PhC(Ph)CCN(Me)CEt ligand. The PhC(Ph)CC

Table III. Positional Parameters and *B*(eq) Values (Å^2) for 4

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.28919 (06)	0.16970 (04)	0.38542 (03)	2.44 (3)
Os(1A)	0.2909 (09)	0.0819 (06)	0.3876 (05)	3.0 (4)
Os(2)	0.17692 (06)	0.02781 (04)	0.29579 (03)	2.25 (3)
Os(2A)	0.1782 (10)	0.2243 (05)	0.3010 (06)	2.9 (4)
Os(3)	−0.01261 (06)	0.12608 (04)	0.35262 (03)	2.59 (3)
O(11)	0.5971 (13)	0.1240 (08)	0.4031 (07)	5.6 (6)
O(12)	0.3247 (14)	0.1154 (09)	0.5477 (07)	6.5 (7)
O(13)	0.3303 (15)	0.3561 (08)	0.4208 (08)	7.0 (7)
O(21)	0.2986 (16)	−0.0683 (09)	0.4386 (08)	7.7 (8)
O(22)	0.0463 (12)	−0.1352 (07)	0.2220 (08)	5.7 (6)
O(31)	−0.2264 (13)	0.2685 (08)	0.3314 (09)	6.8 (7)
O(32)	0.0043 (14)	0.1078 (09)	0.5187 (06)	7.0 (8)
O(33)	−0.2224 (13)	−0.0200 (08)	0.3280 (07)	6.1 (7)
N	0.3696 (12)	0.1130 (07)	0.2468 (06)	2.7 (5)
C(1)	0.3536 (14)	0.0322 (10)	0.2532 (08)	3.2 (7)
C(2)	0.4424 (18)	−0.0330 (10)	0.2267 (11)	5.1 (9)
C(3)	0.4493 (18)	−0.1175 (10)	0.2599 (11)	5.1 (9)
C(4)	0.2560 (15)	0.1496 (08)	0.2738 (08)	3.0 (7)
C(5)	0.4817 (16)	0.1558 (10)	0.2185 (10)	4.4 (8)
C(10)	0.1245 (14)	0.1397 (08)	0.2164 (07)	2.3 (6)
C(11)	0.4840 (18)	0.1390 (11)	0.3970 (08)	3.8 (8)
C(12)	0.3058 (17)	0.1374 (11)	0.4878 (11)	4.5 (9)
C(13)	0.3232 (19)	0.2855 (11)	0.4097 (10)	4.8 (9)
C(20)	−0.0005 (13)	0.1223 (08)	0.2405 (07)	2.0 (5)
C(21)	0.2534 (19)	−0.0325 (10)	0.3850 (11)	4.9 (9)
C(22)	0.0903 (18)	−0.0723 (10)	0.2483 (09)	4.2 (8)
C(31)	−0.1461 (16)	0.2132 (11)	0.3409 (09)	4.0 (8)
C(32)	0.0000 (18)	0.1146 (10)	0.4572 (11)	4.6 (9)
C(33)	−0.1450 (17)	0.0326 (12)	0.3370 (09)	4.1 (8)
C(41)	0.1339 (14)	0.1410 (08)	0.1384 (07)	2.6 (6)
C(42)	0.1666 (17)	0.2169 (10)	0.1095 (08)	3.9 (8)
C(43)	0.186 (02)	0.2214 (10)	0.0402 (10)	5 (1)
C(44)	0.1802 (16)	0.1470 (11)	−0.0031 (09)	4.3 (8)
C(45)	0.1432 (15)	0.0733 (10)	0.0232 (08)	3.5 (7)
C(46)	0.1207 (14)	0.0701 (09)	0.0945 (09)	3.4 (7)
C(51)	−0.1320 (14)	0.1136 (09)	0.1808 (08)	2.8 (6)
C(52)	−0.1911 (16)	0.1857 (10)	0.1434 (09)	4.2 (8)
C(53)	−0.312 (02)	0.1763 (14)	0.0862 (11)	6 (1)
C(54)	−0.3754 (19)	0.1012 (15)	0.0677 (10)	6 (1)
C(55)	−0.3191 (18)	0.0300 (12)	0.1035 (10)	5 (1)
C(56)	−0.1948 (16)	0.0352 (10)	0.1599 (09)	4.0 (8)

Table IV. Intramolecular Distances for 4[a]

Os(1)–Os(2)	2.858 (1)	Os(3)–C(20)	2.13 (1)
Os(1)–Os(3)	2.947 (1)	Os(3)–C(31)	1.87 (2)
Os(1)–C(4)	2.06 (2)	Os(3)–C(32)	1.94 (2)
Os(1)–C(11)	1.93 (2)	Os(3)–C(33)	1.94 (2)
Os(1)–C(12)	1.95 (2)	N–C(1)	1.30 (2)
Os(1)–C(13)	1.90 (2)	N–C(4)	1.45 (2)
Os(1A)–Os(3)	2.964 (9)	N–C(5)	1.49 (2)
Os(1A)–Os(2A)	2.84 (1)	C(1)–C(2)	1.51 (2)
Os(2)–Os(3)	2.815 (1)	C(2)–C(3)	1.47 (2)
Os(2)–C(1)	2.07 (1)	C(4)–C(10)	1.47 (2)
Os(2)–C(4)	2.15 (1)	C(10)–C(20)	1.43 (2)
Os(2)–C(10)	2.29 (1)	C(10)–C(41)	1.48 (2)
Os(2)–C(20)	2.33 (1)	C(20)–C(51)	1.49 (2)
Os(2)–C(21)	1.91 (2)	O–C(av)	1.14 (2)
Os(2)–C(22)	1.91 (2)	C(Ph)–C(av)	1.39 (2)
Os(2A)–Os(3)	2.773 (9)		

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

portion of this ligand exhibits a di-$\sigma + \pi$ triply bridging mode of coordination analogous to that observed for the substituted dimetalloallyl ligands found in the complexes $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}MeCC(H)CEt)(\mu\text{-}H)$,[13a] $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}CMeCMeCR)(\mu\text{-}H)$ (R = Me, OMe, SEt),[13b] and $Mo_2Ru(CO)_2Cp[\mu\text{-}\eta^3\text{-}PhCC(H)CPh][\mu\text{-}\eta^3\text{-}HCC(Ph(CH](\mu_3\text{-}S)$.[14]

Table V. Intramolecular Bond Angles for 4[a]

Os(2)–Os(1)–Os(3)	57.99 (2)	Os(2)–C(1)–C(2)	135 (1)
Os(1)–Os(2)–Os(3)	62.59 (3)	N–C(1)–C(2)	124 (1)
Os(1)–Os(2)–C(1)	87.8 (4)	C(1)–C(2)–C(3)	117 (1)
Os(1)–Os(2)–C(10)	76.5 (3)	Os(1)–C(4)–Os(2)	85.5 (5)
Os(3)–Os(2)–C(1)	144.3 (4)	Os(1)–C(4)–N	118 (1)
Os(3)–Os(2)–C(4)	82.9 (4)	Os(1)–C(4)–C(10)	131 (1)
Os(3)–Os(2)–C(10)	75.7 (3)	Os(2)–C(4)–N	92.8 (8)
C(1)–Os(2)–C(4)	61.7 (6)	Os(2)–C(4)–C(10)	75.7 (7)
C(1)–Os(2)–C(10)	78.6 (5)	N–C(4)–C(10)	108 (1)
C(1)–Os(2)–C(20)	114.1 (5)	Os(2)–C(10)–C(4)	65.8 (7)
C(1)–Os(2)–C(21)	99.5 (7)	Os(2)–C(10)–C(20)	73.8 (7)
C(1)–Os(2)–C(22)	99.6 (6)	C(4)–C(10)–C(20)	117 (1)
Os(1)–Os(3)–Os(2)	59.42 (3)	Os(2)–C(20)–Os(3)	78.1 (4)
C(1)–N–C(4)	104 (1)	Os(2)–C(20)–C(10)	70.2 (7)
C(1)–N–C(5)	127 (1)	Os(3)–C(20)–C(10)	124 (1)
C(4)–N–C(5)	129 (1)	Os–C(av)–O	177 (2)
Os(2)–C(1)–N	101 (1)	C–C(av)–C(Ph)	120 (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 (Å^2) for 5

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.1623	0.03251 (07)	0.2046	3.36 (4)
Os(2)	0.06282 (09)	0.18026 (07)	0.07819 (09)	3.02 (4)
Os(3)	0.14579 (09)	0.26736 (07)	0.25668 (09)	2.91 (4)
O(11)	0.2291 (15)	−0.0472 (15)	0.4091 (14)	6 (1)
O(12)	0.2997 (17)	−0.096 (02)	0.1343 (18)	11 (2)
O(13)	0.0256 (17)	−0.1464 (20)	0.126 (02)	12 (2)
O(21)	−0.1432 (11)	0.2304 (13)	0.0169 (13)	4.8 (8)
O(22)	0.0170 (18)	0.055 (03)	−0.099 (02)	15 (2)
O(31)	0.2843 (16)	0.4369 (15)	0.3383 (15)	7 (1)
O(32)	0.1632 (13)	0.1687 (13)	0.4526 (12)	4.8 (8)
O(33)	−0.0117 (15)	0.4027 (19)	0.2765 (13)	8 (1)
N	0.2427 (12)	0.1699 (13)	0.2231 (12)	3.1 (7)
C(1)	0.0652 (18)	0.1340 (20)	0.210 (02)	5 (1)
C(2)	−0.0247 (17)	0.115 (02)	0.2431 (18)	5 (1)
C(3)	−0.089 (02)	0.033 (03)	0.198 (02)	7 (2)
C(4)	0.2259 (15)	0.1773 (15)	0.1219 (15)	3 (1)
C(5)	0.3429 (16)	0.1709 (20)	0.2807 (17)	4 (1)
C(10)	0.1892 (15)	0.2659 (17)	0.0708 (15)	3.0 (9)
C(11)	0.2033 (17)	−0.0197 (19)	0.3281 (18)	4.0 (5)
C(12)	0.253 (02)	−0.051 (02)	0.161 (02)	5.9 (7)
C(13)	0.077 (03)	−0.077 (03)	0.162 (03)	9 (1)
C(20)	0.1319 (16)	0.3221 (19)	0.1110 (15)	3 (1)
C(21)	−0.0606 (16)	0.2122 (16)	0.0400 (15)	3.2 (4)
C(22)	0.033 (02)	0.100 (02)	−0.029 (02)	6.4 (7)
C(31)	0.2318 (17)	0.3723 (20)	0.3089 (18)	4.0 (5)
C(32)	0.1599 (17)	0.2062 (19)	0.3810 (18)	3.8 (5)
C(33)	0.0492 (20)	0.349 (02)	0.268 (02)	4.9 (6)
C(101)	0.2083 (15)	0.2889 (16)	−0.0213 (15)	3.1 (4)
C(102)	0.1384 (17)	0.3148 (19)	−0.1054 (17)	4.1 (5)
C(103)	0.156 (02)	0.333 (02)	−0.189 (02)	6.4 (7)
C(104)	0.243 (02)	0.321 (02)	−0.192 (02)	6.5 (7)
C(105)	0.3170 (19)	0.300 (02)	−0.111 (02)	5.9 (7)
C(106)	0.2978 (17)	0.2838 (18)	−0.0234 (17)	4.2 (5)
C(201)	0.0994 (16)	0.4259 (17)	0.0777 (16)	3.5 (5)
C(202)	0.0072 (18)	0.4580 (19)	0.0597 (18)	4.4 (5)
C(203)	−0.0177 (19)	0.559 (02)	0.0327 (19)	5.0 (6)
C(204)	0.0502 (20)	0.626 (02)	0.0284 (19)	5.4 (6)
C(205)	0.1384 (18)	0.595 (02)	0.0443 (19)	5.0 (6)
C(206)	0.1639 (17)	0.4999 (19)	0.0739 (17)	4.2 (5)

Carbon C(1) is a carbene center that is linked to the PhC(Ph)CC grouping through the *N*-methyl group. The nitrogen atom is planar as expected for such heteroatomic groupings bonded to carbene centers.[15] The Os(2)–C(1) distance of 2.07 (1) Å is similar to that found in other osmium carbonyl cluster complexes containing carbene

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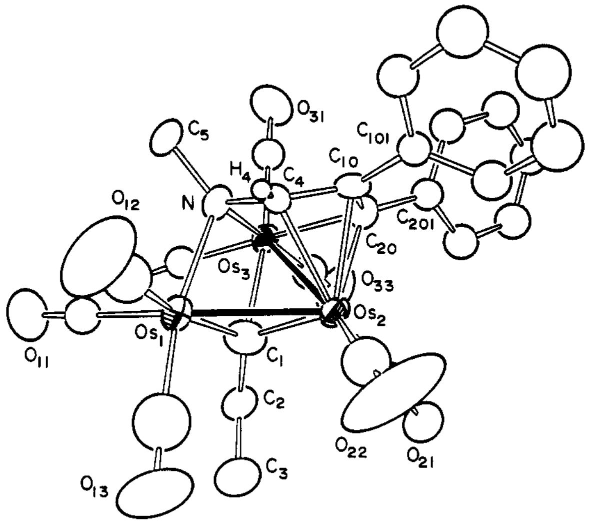

Figure 2. ORTEP diagram of $Os_3(CO)_8\{\mu_3\text{-CEt})[\mu\text{-N(Me)C(H)C(Ph)CPh}]$ (**5**) showing 50% probability thermal ellipsoids.

Table VII. Intramolecular Distances for 5[a]

Os(1)–Os(2)	2.792 (1)	Os(3)–C(1)	2.14 (3)
Os(1)–N	2.17 (2)	Os(3)–C(20)	2.20 (2)
Os(1)–C(1)	2.02 (3)	Os(3)–C(31)	1.90 (3)
Os(1)–C(11)	1.85 (3)	Os(3)–C(32)	1.94 (3)
Os(1)–C(12)	2.02 (3)	Os(3)–C(33)	1.87 (3)
Os(1)–C(13)	1.92 (4)	N–C(4)	1.42 (3)
Os(2)–Os(3)	2.763 (1)	N–C(5)	1.47 (3)
Os(2)–C(1)	2.01 (3)	C(1)–C(2)	1.60 (3)
Os(2)–C(4)	2.34 (2)	C(2)–C(3)	1.47 (4)
Os(2)–C(10)	2.26 (2)	C(4)–C(10)	1.42 (3)
Os(2)–C(20)	2.15 (2)	C(10)–C(20)	1.41 (3)
Os(2)–C(21)	1.82 (2)	C(Ph)–C(av)	1.38 (3)
Os(2)–C(22)	1.83 (3)	Os(1)–C(4)	2.62 (3)
Os(3)–N	2.13 (2)	Os(1)–Os(3)	3.263 (1)

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

ligands.[1,2,4-10] The metal–metal interactions are short enough, 2.815 (1)–2.947 (1) Å, to imply the existence of three metal–metal bonds. The long Os(1)–Os(3) bond is believed to contain the bridging hydride ligand, $\delta = -17.35$ ppm, which was not located crystallographically and is therefore not shown in the figure. The allyl grouping donates 5 electrons to the cluster and the carbene 2. Thus, the cluster contains 48 valence electrons, as expected for an electron-precise trinuclear metal cluster containing three metal–metal bonds.

Table VIII. Intramolecular Bond Angles for 5[a]

Os(2)–Os(1)–N	69.0 (4)	Os(1)–N–C(4)	91 (1)
Os(2)–Os(1)–C(1)	46.1 (8)	Os(3)–N–C(4)	107 (1)
N–Os(1)–C(1)	79.0 (9)	C(4)–N–C(5)	114 (2)
Os(1)–Os(2)–Os(3)	71.94 (4)	Os(1)–C(1)–Os(2)	88 (1)
Os(1)–Os(2)–C(4)	60.8 (5)	Os(1)–C(1)–Os(3)	103 (1)
Os(1)–Os(2)–C(10)	96.2 (6)	Os(2)–C(1)–Os(3)	83 (1)
Os(1)–Os(2)–C(20)	111.1 (6)	C(1)–C(2)–C(3)	119 (2)
C(1)–Os(2)–C(4)	92.3 (9)	Os(2)–C(4)–N	96 (1)
C(1)–Os(2)–C(10)	117 (1)	Os(2)–C(4)–C(10)	69 (1)
C(1)–Os(2)–C(20)	102 (1)	N–C(4)–C(10)	121 (2)
C(10)–Os(2)–C(20)	37.3 (8)	Os(2)–C(10)–C(4)	75 (1)
Os(2)–Os(3)–N	70.1 (4)	Os(2)–C(10)–C(20)	67 (1)
N–Os(3)–C(1)	77.2 (8)	C(4)–C(10)–C(20)	115 (2)
N–Os(3)–C(20)	80.8 (7)	Os–C(av)–O	176 (3)
C(1)–Os(3)–C(20)	96 (1)	C(Ph)–C(av)–C	120 (3)
Os(1)–N–Os(3)	98.6 (7)		

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

Table IX. Positional Parameters and *B*(eq) Values (Å²) for 6

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.25397 (04)	0.24851 (06)	0.34091 (03)	2.51 (2)
Os(2)	0.19672 (04)	0.29508 (06)	0.16875 (03)	2.38 (2)
Os(3)	0.14329 (04)	0.07055 (06)	0.23665 (03)	2.62 (3)
O(11)	0.2705 (08)	0.0681 (12)	0.4782 (06)	5.6 (6)
O(12)	0.4213 (08)	0.3940 (13)	0.4272 (06)	5.4 (6)
O(13)	0.1305 (08)	0.4594 (12)	0.3621 (06)	5.4 (6)
O(21)	0.0175 (08)	0.3808 (12)	0.1564 (06)	5.3 (6)
O(22)	0.1274 (07)	0.2377 (11)	−0.0036 (06)	4.8 (5)
O(31)	0.0250 (08)	−0.0623 (14)	0.0861 (07)	7.0 (7)
O(32)	0.1580 (08)	−0.1807 (13)	0.3377 (07)	6.5 (7)
O(33)	0.0034 (08)	0.1834 (13)	0.2860 (07)	5.7 (6)
N	0.2992 (08)	0.4912 (12)	0.1554 (06)	3.2 (6)
C(1)	0.2208 (10)	0.4962 (15)	0.1485 (07)	3.2 (7)
C(2)	0.1697 (12)	0.6278 (16)	0.1291 (09)	4.6 (8)
C(3)	0.1091 (12)	0.6206 (19)	0.0440 (10)	6 (1)
C(4)	0.3219 (10)	0.3453 (14)	0.1706 (07)	3.3 (7)
C(5)	0.3570 (13)	0.5941 (17)	0.1472 (09)	6 (1)
C(10)	0.2534 (08)	0.0966 (13)	0.2037 (07)	2.3 (6)
C(11)	0.2608 (09)	0.1344 (16)	0.4244 (08)	3.1 (7)
C(12)	0.3573 (11)	0.3430 (16)	0.3932 (08)	3.1 (7)
C(13)	0.1786 (11)	0.3803 (17)	0.3570 (08)	3.5 (7)
C(20)	0.2872 (08)	0.0859 (13)	0.2840 (07)	2.2 (6)
C(21)	0.0848 (11)	0.3354 (15)	0.1639 (08)	3.5 (7)
C(22)	0.1540 (11)	0.2545 (16)	0.0623 (09)	3.8 (7)
C(31)	0.0685 (11)	−0.0107 (18)	0.1427 (10)	4.3 (8)
C(32)	0.1498 (10)	−0.0873 (19)	0.2985 (09)	4.1 (8)
C(33)	0.0554 (09)	0.1397 (16)	0.2671 (08)	3.6 (7)
C(41)	0.2883 (10)	0.0219 (14)	0.1509 (07)	2.8 (6)
C(42)	0.2348 (11)	−0.0341 (14)	0.0807 (08)	4.1 (7)
C(43)	0.2698 (15)	−0.0957 (16)	0.0309 (08)	5.1 (9)
C(44)	0.3569 (15)	−0.0978 (18)	0.0509 (11)	5 (1)
C(45)	0.4047 (13)	−0.0448 (17)	0.1180 (11)	5 (1)
C(46)	0.3764 (11)	0.0148 (16)	0.1686 (09)	4.2 (8)
C(51)	0.3468 (09)	−0.0312 (14)	0.3237 (07)	2.4 (6)
C(52)	0.3300 (10)	−0.1671 (15)	0.3033 (08)	3.1 (7)
C(53)	0.3864 (14)	−0.2684 (17)	0.3404 (11)	5 (1)
C(54)	0.4625 (15)	−0.242 (02)	0.3959 (11)	6 (1)
C(55)	0.4821 (11)	−0.109 (02)	0.4146 (09)	6 (1)
C(56)	0.4261 (12)	−0.0026 (18)	0.3817 (09)	4.6 (8)

An ORTEP drawing of the molecular structure of **5** is shown in Figure 2. Final atomic positional parameters are listed in Table VI. Selected interatomic distances and angles are listed in Tables VII and VIII. This molecule consists of an open cluster of three osmium atoms with a triply bridging PhC(Ph)CC(H)N(Me) ligand and a triply bridging propylidyne ≡CEt ligand. The former can be described as a monometallo-1-(methylamino)-2,3-diphenylallyl ligand in which the PhC(Ph)CC(H) portion is π bonded to Os(2) and the NMe group is coordinated as a bridge between the metal atoms Os(1) and Os(3). Carbons C(4), C(10), and C(20) are π bonded to Os(2) while C(20) is also σ bonded to Os(3); Os(3)–C(20) = 2.20 (2) Å. The nitrogen atom bridges the metal atoms Os(1) and Os(3). There is delocalized unsaturation through the entire C_3N unit. There are only two metal–metal bonds: Os(1)–Os(2) = 2.792 (1) Å and Os(2)–Os(3) = 2.763 (1) Å. The Os–Os and Os–C bond distances to the propylidyne ligand are similar to those found in the bis(alkylidyne)osmium cluster complex $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$.[16] The Os(1)···Os(3) distance, 3.263 (1) Å, is nonbonding. The PhC(Ph)CC(H)N(Me) ligand serves as a 7-electron donor with 4 electrons derived from the C_3 group and 3 from the nitrogen atom, and the propylidyne ligand is a 3-electron donor. When combined with the electrons from the metal atoms and the eight linear terminal carbonyl ligands, there are a total of 50 valence electrons. Thus, with a structure of two metal–metal bonds each metal atom can achieve an 18-electron configuration. This compound appears to have

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[16] Yeh, W. Y.; Shapley, J. R.; Ziller, J. W.; Churchill, M. R. *Organometallics* **1986**, *9*, 1757.

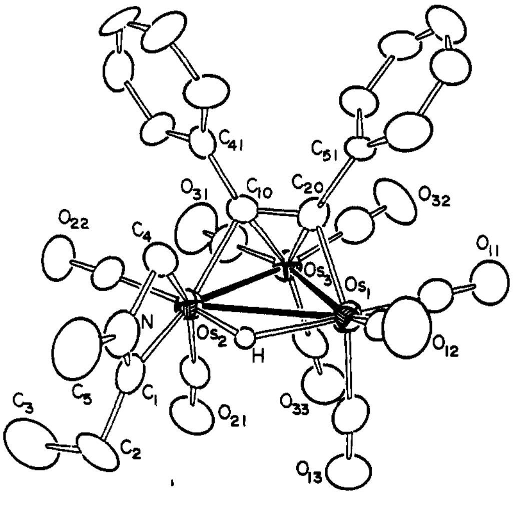

Figure 3. ORTEP diagram of $Os_3(CO)_8[C(Et)N(Me)CH_2][\mu_3\text{-}C(Ph)C(Ph)](\mu\text{-}H)$ (**6**) showing 50% probability thermal ellipsoids.

Table X. Intramolecular Distances for 6[a]

Os(1)–Os(2)	3.0166 (8)	Os(3)–C(20)	2.26 (1)
Os(1)–Os(3)	2.7546 (9)	Os(3)–C(31)	1.91 (2)
Os(1)–C(11)	1.88 (2)	Os(3)–C(32)	1.90 (2)
Os(1)–C(12)	1.90 (2)	Os(3)–C(33)	1.90 (1)
Os(1)–C(13)	1.91 (2)	N–C(1)	1.28 (2)
Os(1)–H	2.09	N–C(4)	1.48 (2)
Os(1)–C(20)	2.10 (1)	N–C(5)	1.45 (2)
Os(2)–Os(3)	2.8403 (8)	C(1)–C(2)	1.52 (2)
Os(2)–C(1)	2.07 (1)	C(2)–C(3)	1.54 (2)
Os(2)–C(4)	2.16 (2)	C(10)–C(20)	1.39 (2)
Os(2)–C(10)	2.15 (1)	C(10)–C(41)	1.51 (2)
Os(2)–C(21)	1.90 (2)	C(20)–C(51)	1.52 (2)
Os(2)–C(22)	1.88 (2)	O–C(av)	1.15 (2)
Os(2)–H	1.69	C(Ph)–C(av)	1.38 (2)
Os(3)–C(10)	2.18 (1)		

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

Table XI. Intramolecular Bond Angles for 6[a]

Os(2)–Os(1)–Os(3)	58.75 (2)	C(1)–Os(2)–C(22)	91.9 (6)
Os(2)–Os(1)–C(11)	149.7 (4)	C(4)–Os(2)–C(10)	82.8 (5)
Os(2)–Os(1)–C(12)	110.0 (4)	C(4)–Os(2)–C(21)	154.9 (6)
Os(2)–Os(1)–C(13)	95.4 (4)	C(4)–Os(2)–C(22)	93.2 (6)
Os(2)–Os(1)–C(20)	67.6 (3)	Os(1)–Os(3)–Os(2)	65.23 (2)
Os(3)–Os(1)–C(11)	91.4 (4)	Os(1)–Os(3)–C(10)	72.3 (3)
Os(3)–Os(1)–C(12)	157.6 (4)	Os(1)–Os(3)–C(31)	162.3 (5)
Os(3)–Os(1)–C(13)	102.5 (5)	Os(1)–Os(3)–C(32)	102.4 (5)
Os(3)–Os(1)–C(20)	53.6 (3)	Os(1)–Os(3)–C(33)	88.2 (5)
C(13)–Os(1)–C(20)	155.2 (6)	Os(2)–Os(3)–C(31)	97.2 (5)
Os(1)–Os(2)–Os(3)	56.01 (2)	Os(2)–Os(3)–C(32)	159.7 (4)
Os(1)–Os(2)–C(1)	109.2 (3)	Os(2)–Os(3)–C(33)	105.8 (4)
Os(1)–Os(2)–C(4)	95.2 (3)	C(1)–N–C(4)	104 (1)
Os(1)–Os(2)–C(10)	67.2 (3)	C(1)–N–C(5)	132 (1)
Os(1)–Os(2)–C(21)	90.1 (4)	C(4)–N–C(5)	123 (1)
Os(1)–Os(2)–C(22)	158.8 (5)	Os(2)–C(1)–N	102 (1)
Os(3)–Os(2)–C(1)	158.5 (3)	Os(2)–C(1)–C(2)	136 (1)
Os(3)–Os(2)–C(4)	129.8 (4)	N–C(1)–C(2)	122 (1)
Os(3)–Os(2)–C(10)	49.5 (3)	C(1)–C(2)–C(3)	108 (1)
Os(3)–Os(2)–C(21)	72.8 (4)	Os(2)–C(4)–N	91.8 (9)
Os(3)–Os(2)–C(22)	104.1 (5)	Os(2)–H–Os(1)	105.62
C(1)–Os(2)–C(4)	61.9 (6)	Os–C(av)–O	176 (1)
C(1)–Os(2)–C(10)	144.5 (6)	C(Ph)–C(av)–C	120 (2)
C(1)–Os(2)–C(21)	93.2 (6)		

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

been derived from 4 by the cleavage of the carbene carbon to nitrogen bond. We have not been able to confirm this transformation, but we have observed that both 4 and 5 can be converted to compound 8 at 125 °C (see below) which suggests that a 4–5 transformation may be involved.

Table XII. Positional Parameters and *B*(eq) Values (Å^2) for 7

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.87190 (07)	0.90835 (03)	0.45641 (06)	3.52 (4)
Os(2)	0.96494 (07)	0.81881 (03)	0.38628 (06)	3.13 (4)
Os(3)	0.94982 (07)	0.90648 (03)	0.27692 (06)	2.95 (4)
O(11)	0.7197 (15)	0.8420 (07)	0.5515 (12)	7 (1)
O(12)	1.0461 (15)	0.9200 (08)	0.6291 (13)	8 (1)
O(13)	0.7747 (15)	1.0104 (07)	0.4951 (12)	7 (1)
O(21)	0.9883 (14)	0.7750 (06)	0.5814 (12)	7 (1)
O(22)	1.0246 (13)	0.7151 (06)	0.3149 (12)	6 (1)
O(31)	0.9565 (13)	0.8641 (06)	0.0844 (11)	6 (1)
O(32)	1.1168 (15)	0.9891 (07)	0.2465 (14)	8 (1)
N	0.7321 (13)	0.8366 (06)	0.3201 (11)	3.2 (4)
C(1)	0.8039 (15)	0.7987 (07)	0.3495 (13)	2.9 (4)
C(2)	0.7543 (17)	0.7464 (08)	0.3545 (15)	4.4 (5)
C(3)	0.732 (02)	0.7232 (09)	0.2558 (18)	6.2 (6)
C(4)	0.7893 (15)	0.8875 (07)	0.3251 (13)	3.0 (4)
C(5)	0.6123 (17)	0.8363 (07)	0.3089 (15)	4.2 (5)
C(10)	0.7656 (15)	0.9172 (07)	0.2401 (13)	2.9 (4)
C(11)	0.7813 (20)	0.8689 (09)	0.5183 (14)	4 (1)
C(12)	0.9805 (19)	0.9156 (09)	0.5667 (17)	5 (1)
C(13)	0.809 (02)	0.9723 (09)	0.4785 (17)	5 (1)
C(20)	0.8184 (15)	0.9658 (07)	0.2427 (13)	2.9 (4)
C(21)	0.9760 (16)	0.7916 (08)	0.5086 (16)	3 (1)
C(22)	1.0071 (17)	0.7568 (08)	0.3360 (15)	4 (1)
C(30)	1.1338 (16)	0.8628 (07)	0.4263 (14)	3.3 (4)
C(31)	0.9518 (17)	0.8798 (08)	0.1593 (15)	4 (1)
C(32)	1.056 (02)	0.9576 (09)	0.2574 (17)	5 (1)
C(40)	1.0940 (16)	0.8611 (07)	0.3300 (13)	3.0 (4)
C(101)	0.6925 (16)	0.8988 (07)	0.1527 (14)	3.4 (4)
C(102)	0.6054 (18)	0.9301 (08)	0.1155 (15)	4.4 (5)
C(103)	0.5305 (18)	0.9140 (08)	0.0383 (15)	4.6 (5)
C(104)	0.543 (02)	0.8688 (10)	0.0041 (18)	6.3 (6)
C(105)	0.6275 (19)	0.8359 (08)	0.0348 (16)	5.0 (5)
C(106)	0.7008 (18)	0.8512 (08)	0.1124 (15)	4.4 (5)
C(201)	0.8097 (17)	1.0022 (08)	0.1644 (15)	4.0 (5)
C(202)	0.8314 (19)	0.9894 (09)	0.0786 (18)	5.7 (6)
C(203)	0.830 (02)	1.0239 (12)	0.002 (02)	8.4 (8)
C(204)	0.803 (02)	1.0726 (11)	0.022 (02)	7.5 (7)
C(205)	0.770 (02)	1.0863 (10)	0.1026 (20)	6.8 (6)
C(206)	0.7802 (19)	1.0508 (09)	0.1759 (17)	5.3 (6)
C(301)	1.2363 (19)	0.8374 (08)	0.4742 (16)	4.8 (5)
C(302)	1.300 (02)	0.8631 (09)	0.5463 (17)	5.6 (6)
C(303)	1.400 (02)	0.8405 (10)	0.5899 (19)	6.9 (7)
C(304)	1.435 (02)	0.7961 (10)	0.5609 (18)	6.2 (6)
C(305)	1.372 (02)	0.7702 (10)	0.4943 (19)	6.6 (6)
C(306)	1.2722 (19)	0.7902 (08)	0.4463 (16)	4.9 (5)
C(401)	1.1671 (16)	0.8453 (07)	0.2647 (14)	3.3 (5)
C(402)	1.1470 (18)	0.8062 (08)	0.2010 (16)	4.6 (5)
C(403)	1.223 (02)	0.7936 (09)	0.1362 (18)	6.0 (6)
C(404)	1.318 (02)	0.8214 (10)	0.1413 (17)	5.9 (6)
C(405)	1.3357 (20)	0.8600 (09)	0.2019 (17)	5.5 (6)
C(406)	1.2666 (19)	0.8725 (08)	0.2649 (16)	5.0 (5)
C(501)	0.056 (04)	0.1651 (17)	0.190 (03)	16 (1)
C(502)	0.166 (04)	0.1311 (17)	0.176 (03)	15 (1)
C(503)	0.276 (05)	0.0965 (20)	0.187 (03)	17 (1)
C(504)	0.355 (06)	0.068 (03)	0.233 (05)	23 (2)
C(505)	0.431 (05)	0.034 (02)	0.257 (04)	20 (2)
C(506)	0.502 (05)	0.007 (03)	0.327 (05)	22 (2)
C(507)	0.492 (04)	−0.0318 (18)	0.377 (03)	15 (1)

An ORTEP drawing of the molecular structure of **6** is shown in Figure 3. Final atomic positional parameters are listed in Tables IX. Selected interatomic distances and angles are listed in Tables X and XI. The molecule consists of a cluster of three osmium atoms. There is a triply bridging PhC≡CPh ligand in the usual μ-‖ coordination mode,[17] and an ethyl(dimethylamino)carbene ligand that is metalated on one of the *N*-methyl groups is coordinated to Os(2). Similar *N*-methyl metalated aminocarbene ligands have been observed in other osmium carbonyl cluster complexes.[2a,b,9] Overall, the molecule is

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[17] (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169.

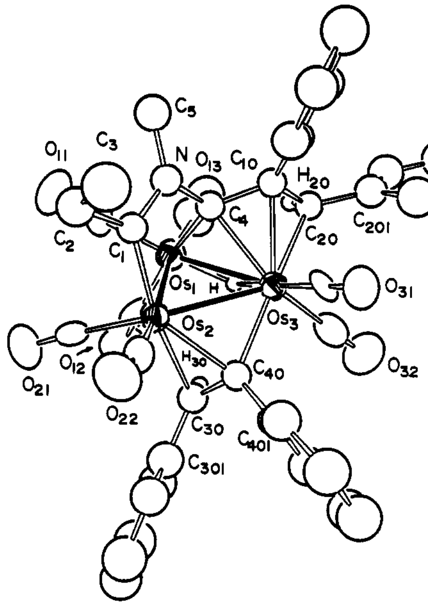


Figure 4. ORTEP diagram of $Os_3(CO)_7[\mu_3\text{-}CC(Ph)C(H)PhN(Me)CEt)][\eta^2\text{-}C(Ph)C(H)Ph](\mu\text{-}H)$ (7) showing 50% probability thermal ellipsoids.

Table XIII. Intramolecular Distances for 7[a]

Os(1)–Os(2)	2.861 (2)	Os(3)–C(32)	1.92 (3)
Os(1)–Os(3)	2.902 (2)	Os(3)–C(40)	2.17 (2)
Os(1)–C(4)	2.09 (2)	Os(3)–H	1.8 (1)
Os(1)–C(11)	1.85 (3)	N–C(1)	1.35 (2)
Os(1)–C(12)	1.93 (2)	N–C(4)	1.50 (2)
Os(1)–C(13)	1.89 (2)	N–C(5)	1.45 (2)
Os(1)–H	1.6 (1)	C(1)–C(2)	1.50 (3)
Os(2)–Os(3)	2.780 (1)	C(2)–C(3)	1.54 (3)
Os(2)–C(1)	2.04 (2)	C(4)–C(10)	1.45 (2)
Os(2)–C(21)	1.90 (2)	C(10)–C(20)	1.43 (2)
Os(2)–C(22)	1.88 (2)	C(10)–C(101)	1.52 (2)
Os(2)–C(30)	2.36 (2)	C(20)–C(201)	1.47 (3)
Os(2)–C(40)	2.19 (2)	C(30)–C(40)	1.41 (2)
Os(3)–C(4)	2.24 (2)	C(30)–C(301)	1.50 (3)
Os(3)–C(10)	2.26 (2)	C(40)–C(401)	1.46 (3)
Os(3)–C(20)	2.24 (2)	O–C(av)	1.14 (2)
Os(3)–C(31)	1.84 (2)	C(Ph)–C(av)	1.38 (3)

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

very similar to its *tert*-butyl analog $Os_3(CO)_8[C(Et)N(Me)CH_2][\mu_3\text{-}C(H)CBu^t](\mu\text{-}H)$.[9] Compound **6** contains a bridging hydride ligand (located but not refined) across the Os(1)–Os(3) bond, $\delta = -20.63$ ppm. The complex contains 48 valence electrons and is electron precise with three metal–metal bonds.

Table XIV. Intramolecular Bond Angles for 7[a]

Os(2)–Os(1)–Os(3)	57.68 (3)	C(4)–N–C(5)	118 (1)
Os(2)–Os(1)–C(4)	68.1 (5)	Os(2)–C(1)–N	117 (1)
Os(3)–Os(1)–C(4)	50.2 (6)	Os(2)–C(1)–C(2)	127 (1)
Os(1)–Os(2)–Os(3)	61.91 (4)	N–C(1)–C(2)	116 (2)
Os(1)–Os(2)–C(1)	83.2 (5)	C(1)–C(2)–C(3)	109 (2)
Os(1)–Os(2)–C(30)	84.0 (5)	Os(1)–C(4)–Os(3)	84.1 (6)
Os(1)–Os(2)–C(40)	93.8 (5)	Os(1)–C(4)–N	116 (1)
Os(3)–Os(2)–C(1)	94.9 (5)	Os(1)–C(4)–C(10)	130 (1)
Os(3)–Os(2)–C(30)	73.6 (5)	Os(3)–C(4)–N	127 (1)
Os(3)–Os(2)–C(40)	50.2 (5)	Os(3)–C(4)–C(10)	72 (1)
C(1)–Os(2)–C(30)	165.8 (7)	N–C(4)–C(10)	114 (2)
C(1)–Os(2)–C(40)	139.6 (7)	Os(3)–C(10)–C(4)	71 (1)
Os(1)–Os(3)–Os(2)	60.41 (3)	Os(3)–C(10)–C(20)	71 (1)
Os(1)–Os(3)–C(4)	45.7 (5)	Os(3)–C(10)–C(101)	127 (1)
Os(1)–Os(3)–C(10)	75.9 (5)	C(4)–C(10)–C(20)	115 (2)
Os(1)–Os(3)–C(20)	82.2 (5)	C(4)–C(10)–C(101)	124 (2)
Os(1)–Os(3)–C(40)	93.0 (5)	C(20)–C(10)–C(101)	121 (2)
Os(2)–Os(3)–C(4)	68.0 (5)	Os(3)–C(20)–C(10)	72 (1)
Os(2)–Os(3)–C(10)	102.5 (5)	Os(3)–C(20)–C(201)	126 (1)
Os(2)–Os(3)–C(20)	133.1 (5)	Os(2)–C(30)–C(40)	65 (1)
Os(2)–Os(3)–C(40)	50.6 (5)	Os(2)–C(30)–C(301)	123 (1)
C(4)–Os(3)–C(20)	65.6 (7)	Os(2)–C(40)–Os(3)	79.2 (7)
C(4)–Os(3)–C(31)	109.7 (8)	Os(2)–C(40)–C(30)	79 (1)
C(4)–Os(3)–C(32)	148.0 (9)	Os(2)–C(40)–C(401)	130 (1)
C(4)–Os(3)–C(40)	118.3 (7)	Os(3)–C(40)–C(30)	118 (1)
C(10)–Os(3)–C(40)	152.0 (7)	Os(3)–C(40)–C(401)	118 (1)
C(20)–Os(3)–C(40)	167.9 (7)	Os–C(av)–O	176 (2)
C(1)–N–C(4)	111 (1)	C(Ph)–C(av)–C	120 (2)
C(1)–N–C(5)	129 (2)		

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

Table XV. Positional Parameters and *B*(eq) Values (Å²) for 8

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.37143 (04)	0.26630 (03)	0.14912 (04)	2.80 (2)
Os(2)	0.18379 (04)	0.35387 (03)	0.27371 (04)	2.49 (2)
Os(3)	0.32117 (04)	0.14841 (03)	0.31032 (04)	2.89 (2)
O(11)	0.6314 (10)	0.1557 (07)	0.1024 (12)	7.0 (5)
O(12)	0.3099 (09)	0.3686 (07)	−0.1233 (09)	6.0 (5)
O(21)	0.2166 (10)	0.4531 (06)	0.5933 (09)	6.6 (6)
O(22)	−0.0148 (09)	0.5476 (06)	0.1558 (09)	5.5 (4)
O(31)	0.2519 (11)	−0.0477 (06)	0.2839 (12)	7.8 (6)
O(32)	0.6158 (09)	0.0434 (07)	0.3470 (11)	6.7 (5)
O(33)	0.4024 (10)	0.1848 (07)	0.6558 (09)	6.5 (5)
N	0.2546 (08)	0.1694 (05)	0.0753 (08)	2.9 (4)
C(1)	0.3438 (12)	0.4055 (08)	0.2870 (11)	3.4 (6)
C(2)	0.4782 (12)	0.3601 (09)	0.3592 (13)	4.0 (6)
C(3)	0.5921 (13)	0.3966 (10)	0.3698 (16)	6.4 (8)
C(4)	0.1355 (10)	0.2502 (07)	0.0494 (11)	2.7 (5)
C(5)	0.2540 (12)	0.0893 (08)	−0.0544 (13)	4.7 (6)
C(10)	0.0455 (10)	0.2601 (06)	0.1247 (10)	2.8 (5)
C(11)	0.5339 (11)	0.1954 (08)	0.1243 (13)	4.1 (6)
C(12)	0.3350 (10)	0.3307 (08)	−0.0161 (12)	3.6 (5)
C(20)	0.1132 (10)	0.2264 (07)	0.2729 (11)	3.4 (5)
C(21)	0.2016 (13)	0.4131 (08)	0.4753 (13)	4.6 (6)
C(22)	0.0604 (11)	0.4741 (08)	0.2000 (11)	3.5 (6)
C(31)	0.2771 (12)	0.0256 (10)	0.2915 (14)	5.0 (7)
C(32)	0.5045 (12)	0.0871 (09)	0.3298 (13)	4.4 (6)
C(33)	0.3735 (12)	0.1715 (07)	0.5284 (14)	4.1 (6)
C(101)	−0.1009 (09)	0.2963 (07)	0.0442 (10)	2.9 (5)
C(102)	−0.1574 (11)	0.2557 (08)	−0.1033 (12)	3.9 (6)
C(103)	−0.2942 (11)	0.2865 (09)	−0.1843 (12)	4.6 (6)
C(104)	−0.3754 (11)	0.3552 (09)	−0.1184 (15)	4.9 (6)
C(105)	−0.3242 (11)	0.3978 (08)	0.0277 (14)	4.4 (6)
C(106)	−0.1881 (11)	0.3680 (08)	0.1054 (12)	4.0 (6)
C(201)	0.0385 (10)	0.2111 (07)	0.3596 (11)	3.1 (5)
C(202)	0.0367 (12)	0.2625 (09)	0.4994 (12)	4.6 (7)
C(203)	−0.0287 (13)	0.2414 (09)	0.5781 (12)	5.1 (7)
C(204)	−0.0905 (13)	0.1659 (09)	0.5200 (13)	4.9 (7)
C(205)	−0.0900 (12)	0.1117 (09)	0.3823 (13)	4.9 (7)
C(206)	−0.0265 (12)	0.1357 (08)	0.3011 (12)	4.3 (6)

An ORTEP drawing of the molecular structure of **7** 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. This compound is formed in a secondary reaction that involves decarbonylation and the addition and insertion of a second molecule of PhC≡CPh into one of the metal–hydrogen bonds of **3**. This was confirmed by an independent reaction. Compound **7** consists of a triangular cluster of three mutually bonded osmium atoms with a triply bridging EtCN(Me)CC(Ph)C(H)Ph ligand similar to that observed in the ditolyl analogue **3**, $Os_3(CO)_8\{\mu_3\text{-}C[C(tolyl)CH(tolyl)]N(Me)\text{-}C(Et)\}(\mu\text{-}H)_2$ (**9**),[10] and a σ–π bond diphenylvinyl ligand that bridges the Os(2)–Os(3) bond. The EtCN(Me)CC(Ph)C(H)Ph ligand was formed by the coupling of a PhC≡CPh molecule to the bridging carbene center in **1** and a shift of the carbene hydrogen atom to the metal atoms. The order in which these steps take place is not known. Carbon C(1) is a carbene center, and the Os(1)–C(1) distance 2.04 (2) Å is similar to the corresponding distance found in **9**, 2.11 (1) Å. The three-carbon

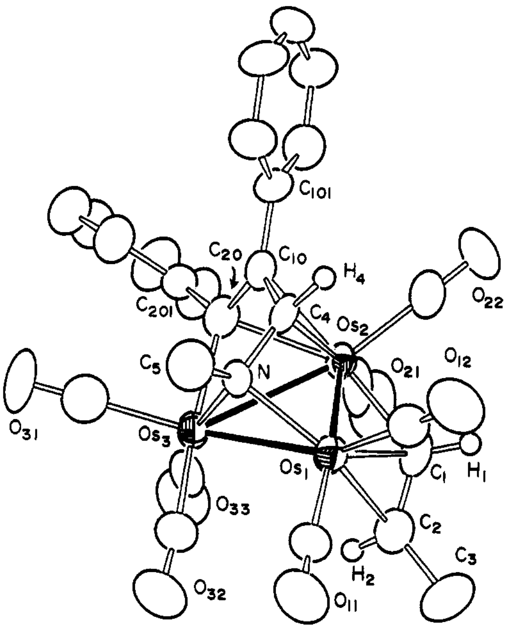


Figure 5. ORTEP diagram of $Os_3(CO)_7[\mu\text{-}C(H)C(H)Me][\mu\text{-}N(Me)C(H)C(Ph)CPh]$ (8) showing 50% probability thermal ellipsoids.

Table XVI. Intramolecular Distances for 8[a]

Os(1)–Os(2)	2.6893 (7)	Os(3)–C(20)	2.16 (1)
Os(1)–Os(3)	2.8283 (6)	Os(3)–C(31)	1.93 (1)
Os(1)–N	2.045 (7)	Os(3)–C(32)	1.91 (1)
Os(1)–C(1)	2.16 (1)	Os(3)–C(33)	1.93 (1)
Os(1)–C(2)	2.30 (1)	N–C(4)	1.43 (1)
Os(1)–C(11)	1.87 (1)	N–C(5)	1.51 (1)
Os(1)–C(12)	1.84 (1)	C(1)–C(2)	1.38 (2)
Os(2)–Os(3)	2.8562 (7)	C(2)–C(3)	1.50 (2)
Os(2)–C(1)	2.12 (1)	C(4)–C(10)	1.43 (1)
Os(2)–C(4)	2.326 (9)	C(10)–C(20)	1.42 (1)
Os(2)–C(10)	2.25 (1)	C(10)–C(101)	1.47 (1)
Os(2)–C(20)	2.21 (1)	C(20)–C(201)	1.49 (1)
Os(2)–C(21)	1.91 (1)	O–C(av)	1.15 (1)
Os(2)–C(22)	1.88 (1)	C(Ph)–C(av)	1.38 (1)
Os(3)–N	2.132 (8)		

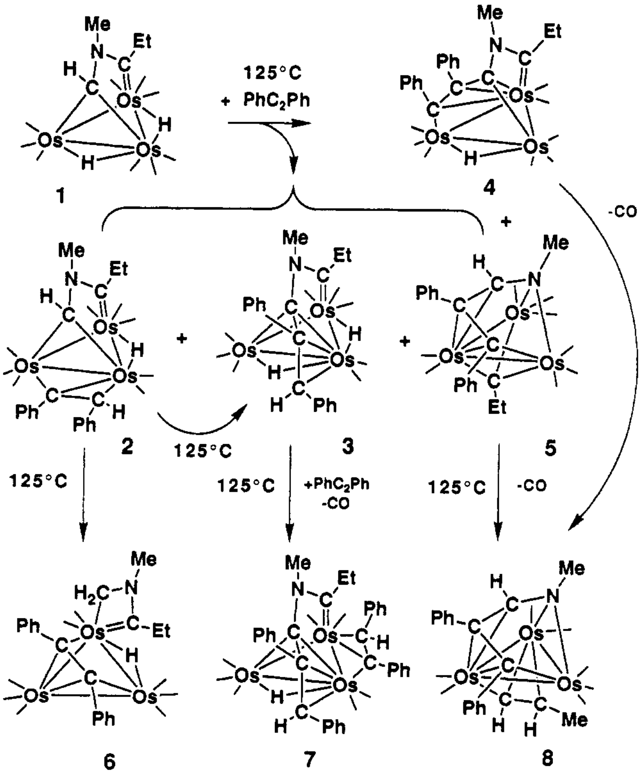
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table XVII. Intramolecular Bond Angles for 8[a]

Os(2)–Os(1)–Os(3)	62.29 (2)	C(4)–Os(2)–C(22)	99.3 (4)
Os(2)–Os(1)–N	77.5 (2)	Os(1)–Os(3)–Os(2)	56.47 (2)
Os(2)–Os(1)–C(1)	50.3 (3)	Os(1)–Os(3)–C(20)	98.5 (3)
Os(2)–Os(1)–C(2)	76.8 (3)	Os(2)–Os(3)–N	72.4 (2)
Os(3)–Os(1)–N	48.7 (2)	N–Os(3)–C(20)	81.4 (3)
Os(3)–Os(1)–C(1)	99.1 (3)	Os(1)–N–Os(3)	85.2 (3)
Os(3)–Os(1)–C(2)	96.3 (3)	Os(1)–N–C(4)	90.9 (5)
N–Os(1)–C(1)	127.7 (3)	Os(1)–N–C(5)	125.1 (7)
N–Os(1)–C(2)	143.7 (4)	Os(3)–N–C(4)	104.3 (6)
C(1)–Os(1)–C(2)	35.8 (4)	Os(3)–N–C(5)	126.8 (6)
C(1)–Os(1)–C(11)	124.0 (4)	C(4)–N–C(5)	116.0 (8)
C(1)–Os(1)–C(12)	91.5 (4)	Os(1)–C(1)–Os(2)	78.0 (3)
C(2)–Os(1)–C(11)	91.7 (5)	Os(1)–C(1)–C(2)	77.8 (7)
C(2)–Os(1)–C(12)	105.6 (4)	Os(2)–C(1)–C(2)	124.7 (8)
Os(1)–Os(2)–Os(3)	61.24 (2)	Os(1)–C(2)–C(1)	66.4 (6)
Os(1)–Os(2)–C(1)	51.7 (3)	Os(1)–C(2)–C(3)	122.8 (8)
Os(1)–Os(2)–C(4)	59.6 (2)	C(1)–C(2)–C(3)	125 (1)
Os(1)–Os(2)–C(10)	94.1 (2)	Os(2)–C(4)–N	103.7 (6)
Os(1)–Os(2)–C(20)	101.4 (3)	Os(2)–C(4)–C(10)	68.7 (5)
Os(3)–Os(2)–C(1)	99.3 (3)	N–C(4)–C(10)	120.4 (8)
Os(3)–Os(2)–C(4)	65.6 (2)	Os(2)–C(10)–C(4)	74.9 (5)
C(1)–Os(2)–C(4)	106.2 (3)	Os(2)–C(10)–C(20)	70.0 (5)
C(1)–Os(2)–C(10)	142.5 (3)	C(4)–C(10)–C(20)	112.6 (9)
C(1)–Os(2)–C(20)	147.8 (4)	Os(2)–C(20)–Os(3)	81.6 (4)
C(1)–Os(2)–C(21)	89.7 (4)	Os(2)–C(20)–C(10)	72.8 (5)
C(1)–Os(2)–C(22)	90.2 (4)	Os(3)–C(20)–C(10)	110.8 (7)
C(4)–Os(2)–C(20)	63.0 (3)	Os–C(av)–O	177 (1)
C(4)–Os(2)–C(21)	162.3 (4)	C(Ph)–C(av)–C	120 (1)

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

Scheme I



group C(4), C(10), and C(20) is π bonded to Os(3) while C(4) bridges to Os(1) as it also did in 1.

When compound 5 was heated to 125 °C for 3 h in an octane solution, it was converted to the new compound $Os_3(CO)_7[\mu\text{-}C(H)C(H)Me]C(Et)][\mu\text{-}N(Me)C(H)C(Ph)CPh]$ (8) in 49% yield. An ORTEP drawing of the molecular structure of 8 is shown in Figure 5. Final atomic positional parameters are listed in Table XV. Selected interatomic distances and angles are listed in Tables XVI and XVII. This compound was formed by the loss of one carbonyl ligand and the transformation of the propylidyne ligand into a methyl-substituted vinyl ligand by the shift of one of the hydrogen atoms on C(2) to C(1). The vinyl ligand is coordinated in the usual σ–π fashion. The triply bridging monometallo-1-(methylamino)-2,3-diphenylallyl, PhC(Ph)CC(H)N(Me), ligand in 8 is not significantly different structurally from that in 5, but since the cluster has only 48 valence electrons, there are three metal–metal single bonds. The Os(1)–Os(2) bond distance is shorter than usual, 2.6893 (7) Å, probably due to the fact that this bond is bridged by two ligands.[18] When compound 4 was heated to 125 °C for 3 h in an octane solution, it was converted to compound 8 in 14% yield.

Discussion

A summary of the results of this study are shown in Scheme I. Compounds 2 and 3 have been obtained previously from the reaction of the lightly stabilized derivative of 1, $Os_3(CO)_8(NCMe)[\mu_3\text{-}C(Et)NMe(CH)](\mu\text{-}H)_2$, with PhC_2Ph under milder conditions. However, the yield of 3 is significantly higher by the method reported here. In addition, the four new products 4–7 were obtained from

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[18] Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1 (see Table III).

the reaction of 1 with PhC_2Ph at 125 °C. Because of their close structural similarity, we expected that 4 might be derived from 3 by elimination of H_2, but our efforts to achieve this transformation independently have not been successful. Likewise, it appears that 5 could be derived from its isomer 4 by a cleavage of a C–N bond and a hydrogen shift. Our efforts to obtain 5 from 4 by thermal treatment at 125 °C have not been successful, but significant amounts of 8 which can also be obtained from 5 under these conditions were obtained. This suggests that a 4–5 transformation may be involved. It does appear that 2 is a precursor to its isomer 6, but the yield of 6 from 2 is not high. When 5 is heated to 125 °C, it is decarbonylated and converted to 8 by a transformation of the propylidyne ligand to a methyl-substituted σ–π coordinated vinyl ligand. This type of transformation is rare but has been observed in other polynuclear metal complexes.[19] The formation of compound 7 is simply the result of addition of another 1 equiv of PhC_2Ph to 3 combined with insertion into a metal–hydrogen bond and decarbonylation. Conceivably, PhC_2Ph could have abstracted H_2 from 3 and thus provide a route to 4, but since no 4 was observed in this reaction, we believe that this possible reaction is not important in this case.

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Registry No. 1, 136131-85-6; 2, 136154-80-8; 3, 136131-88-9; 4, 137823-90-6; 5, 137823-91-7; 6, 137823-92-8; 7, 137823-93-9; 8, 137823-94-0; PhC≡CPh, 501-65-5.

Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters (27 pages); listings of observed and calculated structure factor amplitudes (87 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Reaction Chemistry of the Novel Heterobimetallic Iridium–Platinum Complexes $[(PR_3)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}CH{=}CH_2)Pt(PR'_3)_2]^+[OTf]^-$

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Reactions of Ir(I)–triflate complexes *trans*-$Ir(OTf)(CO)(PR_3)_2$ ($PR_3 = PPh_3$, 1; $PR_3 = PMePh_2$, 2) with Pt^0–π-ethylene complexes $Pt(H_2C{=}CH_2)(PR'_3)_2$ ($PR'_3 = PPh_3$, 3; $(PR'_3)_2 = Ph_2P(CH_2)_3PPh_2$, 4) in CH_3NO_2 result in C–H bond activation and the ready formation of the novel heterobimetallic Ir–Pt complexes $[(PR_3)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}CH{=}CH_2)Pt(PR'_3)_2]^+[OTf]^-$ ($PR_3 = PR'_3 = PPh_3$, 5; $PR_3 = PMePh_2$, $PR'_3 = PPh_3$, 6; $PR_3 = PPh_3$, $(PR'_3)_2 = Ph_2P(CH_2)_3PPh_2$, 7; $PR_3 = PMePh_2$, $(PR'_3)_2 = Ph_2P(CH_2)_3PPh_2$, 8). A definitive structural determination for these heterobimetallic Ir–Pt complexes has been established by an X-ray diffraction study on complex 5 (triclinic, $P\bar{1}$ (No. 2), $a = 13.321$ (1) Å, $b = 15.461$ (2) Å, $c = 17.753$ (2) Å, $\alpha = 90.37$ (1)°, $\beta = 95.47$ (1)°, $\gamma = 100.92$ (1)°, $Z = 2$). Reactivity tests with one of the heterobimetallic complexes 7, using $Ph_2P(CH_2)_3PPh_2$ and acids, have also been conducted.

Introduction

Heterobimetallic complexes containing asymmetric metal–metal bonds[1] have received considerable attention and are of current research interest largely because of their relevance to catalysis.[2] Although a wide variety of heterobimetallic compounds have been prepared and characterized, it is difficult to systematically devise a strategy for the synthesis of particularly desired products. Compared to the well-established organic chemistry, the synthetic chemistry of heterobimetallic complexes is still in its infancy. Therefore, it is not surprising to see in the literature that a large number of reactions leading to the formation of metal–metal-bonded compounds are seren-

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