Organometallics 1988, *7*, 963–969

Hz, CO); IR ν(CO) 2020 (m), 2005 (w), 1975 (m), 1880 (s) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 842 (M – CO, 2), 702 (M – 6CO, 45), 442 (100). Anal. Calcd for $C_{37}H_{28}FeO_6P_2W$: C, 51.09; H, 3.24. Found: C, 51.02; H, 3.32.

20b: ^{1}H NMR (C_6D_6) δ 4.0 (s, 5 H, Cp), 5.08–6.20 (m, 3 H, vinyl), 6.94–8.0 (m, 20 H, Ph); ^{31}P NMR δ (P_A) 20.31 ($^1J(^{31}P-^{183}W)$ = 224.61 Hz), δ (P_B) –16.8 ($^1J(^{31}P-^{183}W)$ = 200.19 Hz), $^2J(P_A-P_B)$ = 26.86 Hz; ^{13}C NMR (C_6D_6) δ 87.33 (Cp), 122.52 (s, CH_2), 143.58 (d, ^1J(C–P) = 8.0 Hz, HCP), 205–206 (m, $(CO)_4$), 213.05 (d, ^2J(C–P) = 16.39 Hz, CO), 214.64 (d, ^2J(C–P) = 14.94 Hz, CO); IR ν(CO) 2022 (m), 2005 (w), 1980 (m), 1910 (s), 1890 (s) cm^{-1}.

Synthesis of [η^1-[(MeO)$_3$P]W(CO)$_4$P(Ph)(CH=CH$_2$)]Fe(CO)$_2$Cp (21). A solution of 0.6 g (1 mmol) of **6a** and 0.12 g of $P(OMe)_3$ (1 mmol) in 25 mL of toluene was heated at 60 °C for 1.5 h. Addition of hexane precipitated red crystals that were recrystallized from hexane/toluene (90:10) to give **21** (0.5 g, 68%): mp 156 °C dec; ^{1}H NMr δ 3.40 (d, ^3J(H–P) = 11.0 Hz, 9 H, OCH_3), 4.69 (d, ^3J(H–P) = 1.5 Hz, 5 H, Cp), 5.32–6.99 (m, ABCX, 3 H, vinyl), 7.18–7.77 (m, 5 H, Ph); ^{31}P NMR δ 139.20 ($^1J(^{31}P-^{183}W)$ = 373.5 Hz), –14.4 ($^1J(^{31}P-^{183}W)$ = 212.4 Hz) ($^2J(P_A-P_B)$ = 31.7 Hz); ^{13}C NMR δ 51.2 (d, ^2J(C–P) = 3.7 Hz, OCH_3), 87.3 (s, Cp), 121.7 (s, CH_2=), 143.4 (d, ^1J(C–P) = 12.2 Hz, PCH), 201.205 (m, COW), 213.10 (d, ^2J(C–P) = 15.87 Hz, CO), 213.85 (d, ^2J(C–P) = 14.65 Hz, CO); IR ν(CO) 2022 (m), 2010 (m), 1978 (m), 1925–1890 (sh, s); MS (^{184}W), *m/z* (relative intensity) 678 (M – 2CO + 2H, 85), 566 (M – 6CO + 2H, 100). Anal. Calcd for $C_{22}H_{22}FeO_9P_2W$: C, 36.09; H, 3.03; Fe, 7.63; P, 8.46. Found: C, 36.31; H, 2.69; Fe, 7.28; P, 8.41.

Synthesis of (CO)$_5$W[P(Ph)(CH=CHPh)I] (24). A solution of 0.68 g (1 mmol) of **6a** was stirred for 10 min at room temperature in 25 mL of CH_2Cl_2 with 0.25 g (1 mmol) of I_2. The solvent was removed, and the residue was chromatographed rapidly on a short column (eluent toluene), yielding a red-orange oil (180 mg, 27%) which was not pure enough to give correct elemental analysis: ^{1}H NMR δ 6.96–7.35 (m, ABX, 2 H, vinyl), 7.39–7.79 (m, 10 H, Ph); ^{31}P NMR δ 12.7 ($^1J(^{31}P-^{183}W)$ = 271.0 Hz); ^{13}C NMR δ 125.28 (d, ^2J(C–P) = 28.36 Hz, CH_2=); 147.31 (d, ^1J(C–P) = 13.2 Hz, CHP), 196.88 (d, ^2J(C–P) = 7.0 Hz, cis CO), 199.5 (d, ^2J(C–P) = 28.4 Hz, trans CO); IR ν(CO) 2070 (w), 1955 (vs), 1948 (vs) cm^{-1}; MS (^{184}W), *m/z* (relative intensity) 662 (M, 22), 535 (M – I, 65), 395 (M – (I + 5CO), 100).

Registry No. **1a**, 101078-12-0; **1b**, 101078-13-1; **1c**, 112712-67-1; **1d**, 99331-07-4; **1e**, 112712-68-2; **2a**, 101078-19-7; **2b**, 101078-20-0; **2c**, 112712-69-3; **2d**, 99331-09-6; **2e**, 112712-70-6; **4a**, 112712-71-7; **4b**, 101078-16-4; **4c**, 112712-73-9; **4d**, 112712-74-0; **4e**, 112712-75-1; **5a**, 112712-76-2; **6a**, 101144-76-7; **6a′**, 112712-84-2; **6b**, 101078-17-5; **6b′**, 101078-18-6; **6c**, 112712-85-3; **6d**, 112712-86-4; **6d′**, 112791-08-9; **6**, 112712-87-5; **6e′**, 112863-66-8; **7**, 112712-89-7; **8**, 112712-90-0; **9**, 112712-91-1; **10**, 112712-77-3; **11**, 112712-78-4; **12**, 112712-79-5; **13**, 112739-91-0; **14**, 112712-88-6; **15**, 112712-92-2; **16**, 112712-80-8; **17**, 112712-81-9; **18**, 112739-92-1; **19**, 112712-82-0; **20a**, 112739-93-2; **20b**, 112835-50-4; **21**, 112739-94-3; **24**, 112712-83-1; $W(CO)_5$·THF, 36477-75-5; $[CpFe(CO)_2]_2$, 12154-95-9; $(CO)_5WP(H)(Ph)CH{=}CH_2$, 101078-14-2; $BrCpFe(CO)_2$, 12078-20-5; $Fe_2(CO)_9$, 15321-51-4; $BrMgCH{=}CH_2$, 1826-67-1; BrMgCH=CHPh, 30094-01-0; $PhPCl(NEt_2)$, 4073-31-8; $MePCl(NEt_2)$, 40467-94-5; Et_2NPCl_2, 1069-08-5; t-$BuPCl_2$, 25979-07-1.

Clusters Containing Carbene Ligands. 3. The Transformations of a (Dimethylamino)methyl Ligand in a Triosmium Cluster. The Synthesis and Structural Characterizations of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$, $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$, and $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$

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Received September 24, 1987

The reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $CH_2(NMe_2)_2$ at 25 °C has yielded the compound $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (**1**, 32%). Compound **1** was characterized by X-ray diffraction methods: space group $P2_1/n$, a = 9.396 (4) Å, b = 14.362 (9) Å, c = 15.175 (8) Å, β = 105.57 (3)°, V = 1972 (1) Å^3, Z = 4. The structure was solved by direct methods and was refined (1706 reflections) to the final values of the residuals R = 0.032 and R_w = 0.033. The molecule contains a triangular cluster of three osmium atoms with a (dimethylamino)methyl ligand bridging an edge of the cluster, C–N = 1.53 (2) Å. At 98 °C **1** was converted into two products, $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$ (**2**, 28%) and $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (**3**, 60%). Both products were characterized by X-ray diffraction methods. For **2**: space group $P2_12_12_1$, a = 13.769 (6) Å, b = 14.841 (8) Å, c = 9.058 (3) Å, V = 1851 (1) Å^3, Z = 4. The structure was solved by direct methods and was refined (1362 reflections) to the final values of the residuals R = 0.054 and R_w = 0.054. Compound **2** contains a triangular cluster of three osmium atoms with a triply bridging η^2-(dimethylamino)carbene ligand, $HC(NMe_2)$, C–N = 1.40 (5) Å. For **3**: space group $P\bar{1}$, a = 9.147 (2) Å, b = 13.036 (2) Å, c = 8.969 (2) Å, α = 104.42 (2)°, β = 109.13 (2)°, γ = 90.07 (2)°, V = 974.5 (8) Å, Z = 2. The structure was solved by the heavy-atom method and was refined (2649 reflections) to the final values of the residuals R = 0.042 and R_w = 0.048. Compound **3** consists of a triangular cluster of three osmium atoms with a (dimethylamino)carbyne ligand bridging one edge, C=N = 1.28 (2) Å. Compound **2** can be converted to **3** at 125 °C under 1 atm of CO, but not under the conditions of its formation from **1**. Two routes to **3** that involve multicenter metal C–H activation processes have been proposed.

Introduction

The ability of transition-metal cluster compounds to produce unusual ligand transformations by multicenter activation processes has been a subject of great interest.[1-3] In our recent studies, we have been investigating the coordination behavior and reactivity of heteroatom-substi-

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tuted derivatives of methyl, CH_2X (X = S, NR_2), and methylene, CHX (X = S, NR_2), groups in triosmium clusters.[4-10] We have shown that multicenter coordination plays an integral role in a variety of unusual intramolecular C–H activation processes.

We have recently discovered that bis(dialkylamino)methane compounds are effective reagents for the introduction of secondary (dialkylamino)carbene ligands into osmium carbonyl clusters.[8] We have now examined the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $CH_2(NMe)_2$. This reaction yields initially the new compound $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1) which can be transformed into the compounds $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$ (2) and $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (3) through a sequence of C–H activation processes in the (dimethylamino)methyl group. The results of these studies are reported herein.

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere, unless otherwise specified. Reagent grade solvents were dried over molecular sieves and were deoxygenated by purging with nitrogen prior to use. The compound $Os_3(CO)_{10}(\mu\text{-}H)_2$ was prepared by the published procedure.[12] $CH_2(NMe)_2$ and CP grade CO gas were purchased from Aldrich Chemical and Linde Corp., respectively, and were used without further purification. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. A Brüker AM-300 FT-NMR was used to obtain ^1H NMR spectra. Low-temperature ^1H NMR spectra were recorded on an IBM NR-80 FT-NMR spectrometer. TLC separations were performed in air on plates of 0.25-mm Kieselgel 60 F_{254} obtained from E. Merck, West Germany. Elemental microanalyses were performed by Desert Analytics, Tucson, AZ.

Preparation of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1). To a solution of $Os_3(CO)_{10}(\mu\text{-}H)_2$ (25 mg, 0.029 mmol) in CH_2Cl_2 (20 mL) was added an excess of $CH_2(NMe_2)_2$ (20 μL). The reaction mixture was allowed to stir at room temperature for 45 min and was then filtered through a silica gel plug by using CH_2Cl_2 as the eluent. The solvent was removed in vacuo, and the residue was dissolved in a minimum quantity of CH_2Cl_2 and applied to silica gel TLC plates. Elution with a CH_2Cl_2/hexane (1/9) solvent mixture separated violet unreacted $Os_3(CO)_{10}(\mu\text{-}H)_2$ (2 mg) from yellow $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1, 8 mg, 32% yield). Several trace (<1 mg) products remained at or near the base line of the plate. These products have not yet been identified. For 1: IR (ν(CO) in hexane) 2101 (w), 2059 (vs), 2045 (s), 2020 (vs), 2000 (w), 1995 (s), 1984 (s), 1978 (w), 1970 (w) cm^{-1}; ^1H NMR (δ in $CDCl_3$) 4.10 (1 H, d (11.5 Hz)), 3.61 (1 H, d (11.5 Hz)), 3.18 (3 H, s), 2.98 (3 H, s), −14.66 (1 H, s). Anal. Calcd for 1: C, 17.15; N, 1.54; H, 0.99. Found: C, 17.25; N, 1.50; H, 1.00.

Thermolysis of 1. A solution of 1 (25 mg, 0.0275 mmol) in heptane (25 mL) was refluxed for 20 min. The solvent was removed in vacuo, and the residue was separated by TLC. Elution with a CH_2Cl_2/hexane (1/9) solvent mixture separated colorless $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$ (2, 7.0 mg (28%)) from light yellow $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (3[13] 15.0 mg, (60%)). For 2: IR (ν(CO) in hexane) 2100 (w), 2074 (s), 2047 (vs), 2024 (m), 2004 (s), 1991 (m), 1980 (m), 1965 (w) cm^{-1}; ^1H NMR (300 MHz, δ in $CDCl_3$ at 25 °C) 6.64 (1 H, s), 3.05 (6 H, s); low-temperature ^1H NMR (in toluene-d_8 at 80 MHz, δ at −50 °C) 5.94 (1 H, s), 2.29 (3 H, s), 2.12 (3 H, s), −15.62 (1 H, s), −16.34 (1 H, s). Methyl resonances coalesce at approximately −10 °C to a broad singlet. Hydride resonances coalesce at 8 °C. Anal. Calcd for 2: C, 16.33; N, 1.59; H, 1.02. Found: C, 16.69; N, 1.57; H, 1.08.

Thermolysis of 2 at 98 °C under a CO Atmosphere. A solution of 2 (10 mg, 0.0114 mmol) in heptane (15 mL) was refluxed under a CO atmosphere for 1 h. IR and test TLC analyses showed no evidence for a reaction.

Thermolysis of 2 at 125 °C under a CO Atmosphere. A solution of 2 (10 mg, 0.0114 mmol) in octane (15 mL) was refluxed under a CO atmosphere for 5 h. The solvent was removed in vacuo. The residue was separated by TLC. Elution with a CH_2Cl_2/hexane (1/9) solvent mixture separated: unreacted 2 (5 mg) and 3 (8 mg, 80% yield based on amount of 3 consumed).

Crystallographic Analyses. Yellow crystals of 1 and colorless crystals of 2 were grown by slow evaporation of solvent from hexane solutions at −25 °C. Yellow crystals of 3 were grown by evaporation of solvent from solutions in CH_2Cl_2/hexane solvent mixtures at 23 °C. Data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined from 25 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. MICROVAX II computer, by using the TEXSAN structure solving program library (v 2.0) obtained from Molecular Structure Corp., College Station, TX. Analytical absorption corrections were performed for each structure. Neutral atom scattering factors were calculated by the standard procedures.[14a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[14b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

Compound 1 crystallized in the monoclinic crystal system. The space group, $P2_1/n$, was determined from the systematic absences observed in the data. The positions of the metal atoms were determined by direct methods (MITHRIL). The remaining atoms were located by a series of difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions, including the bridging hydride ligand, were also obtained from difference Fourier synthesis, but only the bridging hydride ligand and the hydrogen atoms bonded to the iminium carbon atom were successfully refined. The contributions of all hydrogen atoms were added to the structure factor calculations.

Compound 2 crystallized in the orthorhombic crystal system, and the acentric space group $P2_12_12_1$ was indicated by the systematic absences in the data. The structure was solved by a combination of direct methods and difference Fourier techniques. Standard reflections monitored after every 150 data reflections showed a 14% decrease during the course of the data collection. A linear rescale correction was applied. Because of the small amount of data, only the metal atoms were refined anisotropically. All hydrogen atom positions were calculated by assuming idealized geometries. Hydrogen atom positions were not refined. Because 2 crystallized in an acentric space group, refinement was also performed on the enantiomer by inverting the coordinates of all the atoms. Refinement upon this enantiomer resulted in the slightly higher weighted residual, $R_w = 0.057$, and indicated that the original choice was correct. Thus, the atomic coordinates were returned to the original enantiomer for the completion of the analysis.

Compound 3 crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of Patterson and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Methyl hydrogen atom positions were calculated by

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

Table I. Crystallographic Data for the Structural Analyses for Compounds 1, 2, and 3

	1	2	3
(A) Crystal Data			
formula	$Os_3O_{10}NC_{13}H_9$	$Os_3O_9C_{12}H_9$	$Os_3O_{10}NC_{13}H_7$
temp, (±3 °C)	23 °C	23 °C	23 °C
space group	$P2_1/n$, No. 14	$P2_12_12_1$, No. 19	$P\bar{1}$, No. 2
a (Å)	9.396 (4)	13.769 (6)	9.147 (2)
b (Å)	14.362 (9)	14.841 (8)	13.036 (2)
c (Å)	15.175 (8)	9.058 (3)	8.969 (2)
α (deg)	90.0	90.0	104.42 (2)
β (deg)	105.57 (3)	90.0	109.13 (2)
γ (deg)	90.0	90.0	90.07 (2)
V (Å^3)	1972 (1)	1851 (1)	974.5 (8)
M_r	909.8	881.8	907.8
Z	4	4	2
ρ_{calcd} (g/cm^3)	3.06	3.16	3.09
(B) Measurement of Intensity Data			
radiatn	Mo Kα		
monochromator	graphite		
detector aperture (mm)			
horizontal	2.0		
vertical	2.0		
cryst faces	01$\bar{2}$, 01$\bar{3}$, $\bar{1}$01 10$\bar{1}$, 010, 0$\bar{1}\bar{1}$	110, $\bar{1}\bar{1}$0, 1$\bar{2}$0, $\bar{1}$10 102, 10$\bar{1}$, $\bar{1}$0$\bar{1}$	001, 01$\bar{2}$, 010, 0$\bar{1}$0 $\bar{2}$01, 21$\bar{2}$, $\bar{1}$10
cryst size (mm)	0.08 × 0.11 × 0.20	0.14 × 0.24 × 0.30	0.06 × 0.19 × 0.32
cryst orientatn			
lattice directn	[010]; 9.2	[001]; 8.1	[201]; 9.3
deg from ϕ axis	4.4°	10.4	7.7
reflctns measd	$+h,+k,\pm l$	$+h,+k,+l$	$+h,\pm k,\pm l$
max 2θ (deg)	43	50	48
scan type	moving crystal–stationary counter		
ω-scan width (A + 0.347 tan θ)°, A =	1.10		
background: time at	$^1/_4$ scan time at each end of scan		
ω-scan rate (deg/min)^a	4.0		
data used ($F^2 \geq 3.0\sigma(F^2)$)	1706	1362	2649
(C) Treatment of Data			
absorptn correctn	analytical	analytical	analytical
coeff (cm^{-1})	204.7	218.1	207.2
transmissn coeff			
max	0.336	0.103	0.184
min	0.108	0.033	0.057
P factor	0.02	0.02	0.02
final residuals			
R_F	0.0322	0.0544	0.0419
R_{wF}	0.0329	0.0541	0.0484
esd. of unit weight observn	1.449	2.226	2.831
largest shift/error value of final cycle	0.05	0.05	0.17
largest peak in final diff Fourier (e/Å^3)	0.96	1.87	2.20
no. of variables	250	117	245

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

assuming idealized geometry. The positions of these atoms were not refined.

Error analyses for each structure were calculated from the inverse matrix obtained on the final cycle of refinement. See supplementary material for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters.

Results

Treatment of the cluster $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $CH_2(NMe_2)_2$ resulted in the formation of the new compound $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1) in 32% yield. Compound 1 was characterized by IR, ^1H NMR, and single-crystal X-ray difraction analyses.

An ORTEP drawing of 1 is shown in Figure 1. Selected interatomic distances and angles are listed in Table II. The structure of 1 consists of a triangular cluster of three osmium atoms. The three metal–metal bonds have nearly equal lengths, 2.889 (2), 2.913 (2), and 2.890 (1) Å, and are similar to those in $Os_3(CO)_{12}$, 2.877 (3) Å.[10] The Os(2)–Os(3) bond is bridged by μ-η^2-dimethyliminium ligand, H_2CNMe_2, Os(2)–C = 2.19 (2) Å and Os(3)–N = 2.21 (1) Å. The C–N distance of 1.53 (2) Å is slightly longer than that of a carbon–nitrogen single bond (e.g., C(1)–N and C(2)–N = 1.49 (2) Å). In this form the ligand could also be viewed as a bridging (dimethylamino)methyl ligand. A

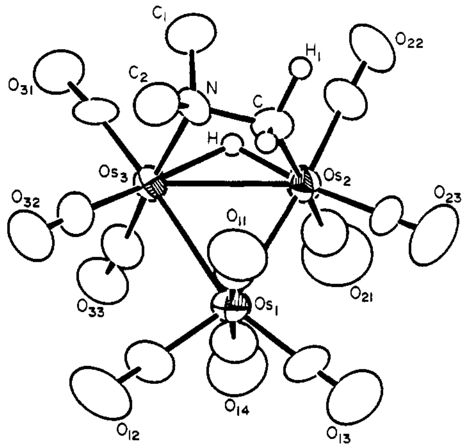

Figure 1. An ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1) showing 50% probability thermal ellipsoids.

Table II. Selected Distances (Å) and Angles (deg) for $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (1)[a]

(A) Intramolecular Distances

atom	atom	dist	atom	atom	dist
Os1	C13	1.86 (2)	Os2	C	2.19 (2)
Os1	C12	1.92 (2)	Os2	Os3	2.890 (1)
Os1	C14	1.94 (2)	Os3	C31	1.87 (2)
Os1	C11	1.96 (2)	Os3	C33	1.88 (2)
Os1	Os2	2.889 (2)	Os3	C32	1.91 (2)
Os1	Os3	2.913 (2)	Os3	N	2.21 (1)
Os2	C23	1.88 (2)	N	C1	1.49 (2)
Os2	C22	1.90 (2)	N	C2	1.49 (2)
Os2	C21	1.97 (2)	N	C	1.53 (2)
			O	C	1.14 (2)[b]

(B) Intramolecular Bond Angles

atom	atom	atom	angle	atom	atom	atom	angle
C13	Os1	Os2	101.7 (6)	Os1	Os2	Os3	60.55 (4)
C13	Os1	Os3	161.4 (6)	C31	Os3	N	89.2 (6)
C12	Os1	Os2	155.1 (6)	C31	Os3	Os2	121.6 (6)
C12	Os1	Os3	95.7 (6)	C31	Os3	Os1	173.1 (5)
C14	Os1	Os2	85.4 (6)	C33	Os3	N	173.7 (6)
C14	Os1	Os3	90.6 (6)	C33	Os3	Os2	103.2 (5)
C11	Os1	Os2	93.1 (6)	C33	Os3	Os1	81.7 (5)
C11	Os1	Os3	91.6 (5)	C32	Os3	N	94.3 (7)
Os2	Os1	Os3	59.74 (3)	C32	Os3	Os2	140.3 (6)
C23	Os2	C	90.4 (8)	C32	Os3	Os1	87.2 (5)
C23	Os2	Os1	87.7 (6)	N	Os3	Os2	71.2 (3)
C23	Os2	Os3	142.7 (6)	N	Os3	Os1	97.5 (4)
C22	Os2	C	87.1 (8)	Os2	Os3	Os1	59.71 (4)
C22	Os2	Os1	174.9 (6)	C1	N	C2	107 (1)
C22	Os2	Os3	115.5 (6)	C1	N	C	107 (1)
C21	Os2	C	174.6 (8)	C1	N	Os3	110 (1)
C21	Os2	Os1	92.6 (7)	C2	N	C	112 (1)
C21	Os2	Os3	104.9 (6)	C2	N	Os3	115 (1)
C	Os2	Os1	88.4 (5)	C	N	Os3	106 (1)
C	Os2	Os3	71.0 (5)	N	C	Os2	107 (1)
				O	C	Os	175 (2)[b]

[a] Estimated standard deviations in the least significant figure are given in parentheses. [b] Average value.

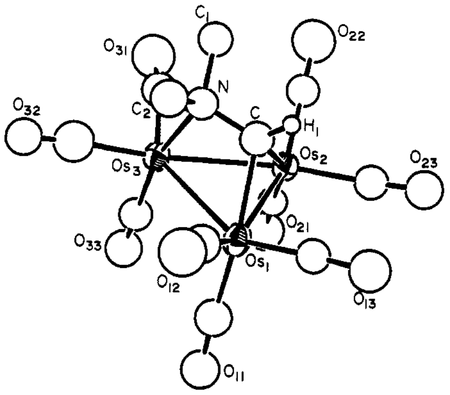

Figure 2. An ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$ (**2**) showing 50% probability thermal ellipsoids.

Table III. Selected Distances (Å) and Angles (deg) for $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$ (2)[a]

(A) Intramolecular Distances

atom	atom	dist	atom	atom	dist
Os1	C13	1.76 (4)	Os2	C	2.16 (4)
Os1	C11	1.80 (5)	Os2	Os3	2.775 (2)
Os1	C12	1.97 (5)	Os3	C33	1.84 (4)
Os1	C	2.20 (4)	Os3	C31	1.87 (5)
Os1	Os2	2.822 (3)	Os3	C32	1.90 (6)
Os1	Os3	2.977 (2)	Os3	N	2.20 (3)
Os2	C22	1.79 (4)	N	C2	1.39 (5)
Os2	C21	1.86 (4)	N	C	1.40 (5)
Os2	C23	1.89 (4)	N	C1	1.46 (5)
			O	C	1.18 (5)[b]

(B) Intramolecular Bond Angles

atom	atom	atom	angle	atom	atom	atom	angle
C13	Os1	C	92 (2)	Os3	Os2	Os1	64.24 (6)
C13	Os1	Os2	92 (1)	C33	Os3	N	166 (2)
C13	Os1	Os3	147 (1)	C33	Os3	Os2	95 (1)
C11	Os1	C	162 (2)	C33	Os3	Os1	97 (1)
C11	Os1	Os2	116 (1)	C31	Os3	N	93 (2)
C11	Os1	Os3	105 (2)	C31	Os3	Os2	86 (1)
C12	Os1	C	100 (2)	C31	Os3	Os1	143 (1)
C12	Os1	Os2	149 (1)	C32	Os3	N	94 (2)
C12	Os1	Os3	109 (2)	C32	Os3	Os2	168 (2)
C	Os1	Os2	49 (1)	C32	Os3	Os1	117 (2)
C	Os1	Os3	60 (1)	N	Os3	Os2	74.3 (9)
Os2	Os1	Os3	57.12 (6)	N	Os3	Os1	69 (1)
C22	Os2	C	99 (2)	Os2	Os3	Os1	58.64 (6)
C22	Os2	Os3	102 (1)	C2	N	C	121 (4)
C22	Os2	Os1	149 (1)	C2	N	C1	104 (4)
C21	Os2	C	154 (2)	C2	N	Os3	118 (3)
C21	Os2	Os3	92 (1)	C	N	C1	109 (3)
C21	Os2	Os1	113 (1)	C	N	Os3	92 (3)
C23	Os2	C	101 (2)	C1	N	Os3	113 (3)
C23	Os2	Os3	162 (1)	N	C	Os2	115 (3)
C23	Os2	Os1	99 (1)	N	C	Os1	112 (3)
C	Os2	Os3	64 (1)	Os2	C	Os1	81 (1)
C	Os2	Os1	50 (1)	O	C	Os	174 (5)[b]

[a] Estimated standard deviations in the least significant figure are given in parentheses. [b] Average value.

long C–N bond, 1.50 (2) Å, was observed for a similarly coordinated (dimethylamino)methyl ligand in the compound $Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}SPh)(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (**4**).[11] The hydride ligand was located crystallographically and found to bridge the Os(2)–Os(3) bond, Os(2)–H = 1.6 (2) Å and Os(3)–H = 1.8 (2) Å. Interestingly, the C–N vector is not parallel to the Os(2)–Os(3) vector. The (dimethylamino)methyl ligand is twisted such that the methylene group is shifted toward the metal atom Os(3). The magnitude of this shift is reflected by the angles Os(1)–Os(2)–C = 88.4 (5)° and Os(1)–Os(3)–N = 97.5 (4)°. The explanation for this twisting effect may be simply the differences in steric repulsions between the substituents on the carbon, C, and the nitrogen, N, with the carbonyl ligand C(11)–O(11).

When compound **1** was refluxed in heptane solvent for 30 min, two products $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$ (**2**, 28%) and $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (**3**, 60%) were formed. Compound **3** was obtained previously in very low yield, from the reaction of $Os_3(CO)_{12}$ with NMe_3 at 170 °C.[13] It was identified by its characteristic IR and ^1H NMR spectra. Compounds **2** and **3** were also characterized by X-ray crystallographic analyses. Compound **2** was converted into **3** (80% yield) in refluxing octane solvent under a CO atmosphere.

An ORTEP drawing of **2** is shown in Figure 2. Selected interatomic distances and angles are listed in Table III. The structure of **2** consists of a triangular cluster of three osmium atoms. The metal–metal bond distances in **2** span a wide range, Os(1)–Os(2) = 2.822 (3) Å, Os(1)–Os(3) = 2.977 (2) Å, and Os(2)–Os(3) = 2.775 (2) Å. This variation can be attributed, in part, to the presence of two hydride ligands. It is well-known that bridging hydride ligands produce a lengthening effect on metal–metal bonds. Thus, it is believed that one hydride ligand bridges the very long Os(1)–Os(3) bond. The other ligand probably bridges the Os(1)–Os(2) bond, since this bond is inequivalent to the Os(1)–Os(3) bond. The Os(1)–Os(2) bond is not elongated due to the bond contraction effect that is produced by the bridging carbon atom of the carbene ligand.[15]

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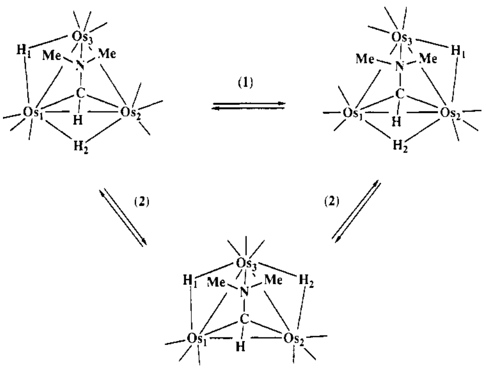
(15) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843.

Scheme I



Although they were not observed crystallographically, the existence of the hydride ligands was established by the observation of two high-field resonances, δ −15.62 and −16.34, in the ^{1}H NMR spectrum recorded at −50 °C. These hydride ligands undergo a dynamic exchange that results in a broadening and coalescence of the resonances, T_c = 8 °C and ΔG^*_{284K} = 15.2 kcal/mol. They appear as a broad singlet at −15.89 ppm at 25°C. The resonances of the methyl groups are also averaged: at −50 °C, δ 2.29 and 2.12, T_c = −10 °C; at 25 °C, δ 2.38, ΔG^* = 14.5_{263K} kcal/mol. However, an analysis of the line shapes in the exchanged broadened regions revealed that the rates of exchange of the methyl group resonances were approximately three times that of the exchange of the hydride ligands and indicates that two exchange processes are operative. It is believed that both processes involve a shifting of the hydride ligands, as shown in Scheme I. The fastest process (1) involves a shifting of the hydride ligand H_1 from the Os(1)–Os(3) bond to Os(2)–Os(3) bond and back. This process leads to an averaging of the methyl group environments but does not lead to an averaging of the hydride ligands. The second process (2) involves a shifting of the hydride ligand H_2 from the Os(1)–Os(2) bond to the Os(2)–Os(3) bond and subsequently a shifting of H_1 from the Os(1)–Os(3) bond to the Os(1)–Os(2) bond. This process results in exchange of both the hydride ligands and the methyl groups. Similar exchange processes were also observed for the structurally related cluster $Os_3(CO)_9(\mu_3\text{-}C{=}CH_2)(\mu\text{-}H)_2$.[16]

The most interesting ligand is the triply bridging C,N-η^2-(dimethylamino)carbene ligand. The carbon atom is bonded to two metal atoms, Os(1)–C = 2.20 (4) Å and Os(2)–C = 2.16 (4) Å, while the nitrogen atom is bonded to the third, Os(3)–N = 2.20 (3) Å. These distances are similar to those found for the triply bridging carbene ligand in the complex $Os_3(CO)_9(\mu\text{-}OMe)[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)$ (**5**), Os–C = 2.11 (2) and 2.15 (2) Å and Os–N = 2.15 (1) Å.[9] However, the carbon–nitrogen distance in **2**, C–N = 1.40 (5) Å, is significantly shorter than that in **5**, C–N = 1.54 (2) Å. The carbene hydrogen atom H(1) was located crystallographically. It displays a ^{1}H NMR shift (δ 6.64) similar to that of the hydrogen atom on the triply bridging carbene ligand in **5**.

An ORTEP drawing of **3** is shown in Figure 3. Selected interatomic distances and angles are listed in Table IV. The structural parameters of **3** were found to be very similar to those of its ruthenium analogue, $Ru_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (**6**), which has also been structurally characterized.[15] The (dimethylamino)carbyne ligand symmetrically bridges one edge of the triangular cluster, Os(1)–C = 2.05 (1) Å and Os(2)–C = 2.05 (2) Å. The short C–N distance, C–N = 1.28 (2) Å, indicates the existence of C–N multiple bonding. The hydride ligand was not observed crystallographically. It is believed to bridge the Os(1)–Os(2) bond in a manner similar to that in **6**.

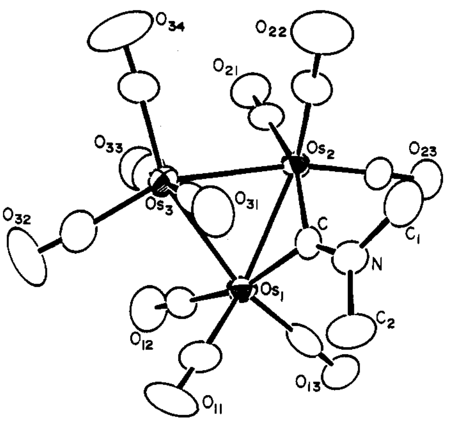


Figure 3. An ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (**3**) showing 50% probability thermal ellipsoids.

Table IV. Selected Distances (Å) and Angles (deg) for $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (3)[a]

(A) Intramolecular Distances

atom	atom	dist	atom	atom	dist
Os1	C13	1.88 (2)	Os2	C	2.05 (2)
Os1	C11	1.91 (2)	Os2	Os3	2.860 (1)
Os1	C12	1.96 (2)	Os3	C31	1.91 (2)
Os1	C	2.06 (1)	Os3	C34	1.92 (2)
Os1	Os2	2.820 (1)	Os3	C33	1.93 (2)
Os1	Os3	2.8570 (9)	Os3	C32	1.94 (2)
Os2	C22	1.87 (2)	N	C	1.28 (2)
Os2	C23	1.91 (2)	N	C2	1.46 (2)
Os2	C21	1.95 (2)	N	C1	1.49 (2)
			O	C	1.13 (2)[b]

(B) Intramolecular Bond Angles

atom	atom	atom	angle	atom	atom	atom	angle
C13	Os1	C	94.0 (6)	C21	Os2	Os3	92.5 (5)
C13	Os1	Os2	106.0 (4)	C	Os2	Os1	46.7 (4)
C13	Os1	Os3	166.5 (4)	C	Os2	Os3	76.9 (4)
C11	Os1	C	101.7 (7)	Os1	Os2	Os3	60.40 (2)
C11	Os1	Os2	140.7 (5)	C31	Os3	Os1	86.4 (5)
C11	Os1	Os3	94.0 (5)	C31	Os3	Os2	89.8 (5)
C12	Os1	C	162.4 (7)	C34	Os3	Os1	159.2 (5)
C12	Os1	Os2	116.5 (5)	C34	Os3	Os2	100.1 (5)
C12	Os1	Os3	89.9 (5)	C33	Os3	Os1	86.3 (5)
C	Os1	Os2	46.7 (4)	C33	Os3	Os2	84.0 (5)
C	Os1	Os3	76.9 (4)	C32	Os3	Os1	96.6 (5)
Os2	Os1	Os3	60.50 (2)	C32	Os3	Os2	155.5 (5)
C22	Os2	C	101.7 (7)	Os1	Os3	Os2	59.10 (2)
C22	Os2	Os1	139.2 (6)	C	N	C2	123 (1)
C22	Os2	Os3	91.4 (6)	C	N	C1	124 (1)
C23	Os2	C	93.2 (6)	C2	N	C1	113 (1)
C23	Os2	Os1	107.6 (5)	N	C	Os2	135 (1)
C23	Os2	Os3	167.8 (5)	N	C	Os1	138 (1)
C21	Os2	C	162.7 (6)	Os2	C	Os1	86.7 (6)
C21	Os2	Os1	116.2 (5)	O	C	Os	177 (2)[b]

[a] Estimated standard deviations in the least significant figure are given in parentheses. [b] Average value.

Discussion

The reaction of the unsaturated cluster $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $CH_2(NMe_2)_2$ yielded the new compound $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (**1**). To date, the only other complex which contains a (dimethylamino)methyl ligand of this type is $Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}SPh)(\mu\text{-}\eta^2\text{-}H_2CNMe_2)(\mu\text{-}H)$ (**4**).[11] The complexes $Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}SPh)(\eta^2\text{-}$

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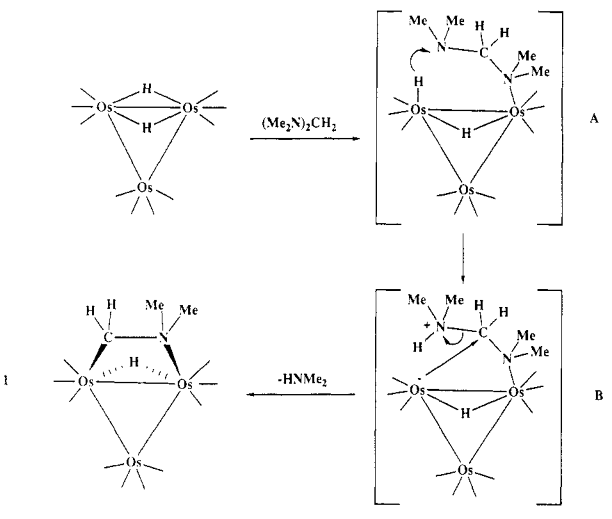
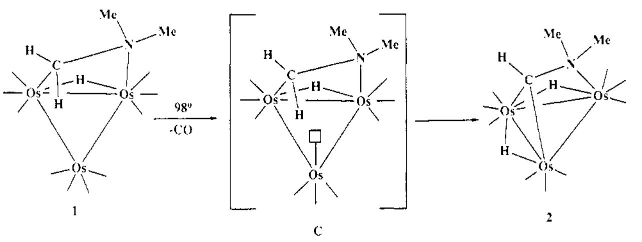
[16] Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415.

Scheme II



Scheme III



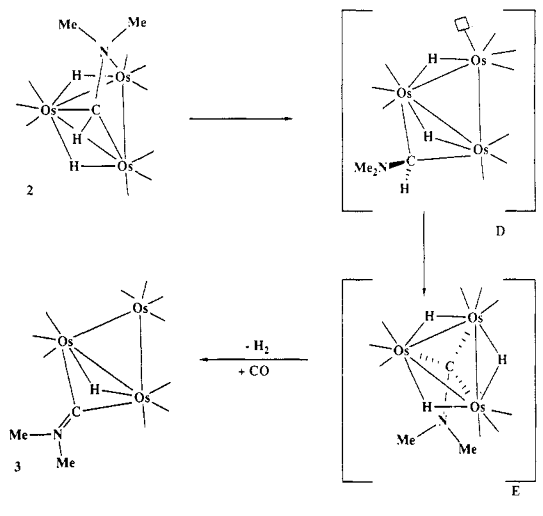
$H_2CNMe_2)(\mu\text{-}H)$ (**5**), an isomer of **4**, and $Os_3(CO)_8(\mu\text{-}H(Ph)CNMe_2)(\mu_3\text{-}S)(\mu\text{-}H)$ (**7**)[16] contain *iminium* ligands that are π-complexed to a *single* metal atom.

The pathway for the formation of 1 has not yet been determined; however, it is possible to speculate on the nature of possible intermediates. $Os_3(CO)_{10}(\mu\text{-}H)_2$ reacts quickly with Lewis bases to yield adducts of the type $Os_3(CO)_{10}(L)(\mu\text{-}H)H$ (L = CO, Pr_3, CNR, NCR).[17] In the present case, we would expect that the diamine reagent would react in a similar manner to yield an intermediate such as $Os_3(CO)_{10}(Me_2NCH_2NMe_2)(\mu\text{-}H)H$ (A, Scheme II). This intermediate could then undergo a proton transfer to the uncoordinated nitrogen atom to yield the zwitterionic intermediate **B**, which could expel dimethylamine and form 1. Dimethylamine was not detected in this reaction, but this could have been overlooked by the small scale of the reaction.

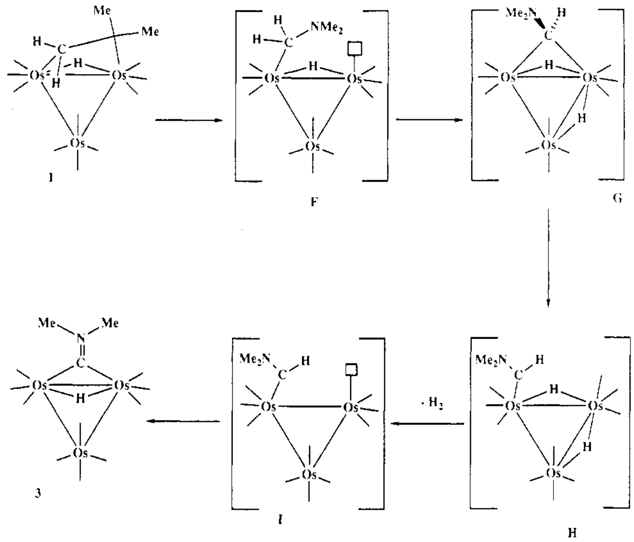
Compound 1 was transformed thermally into the compounds $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)_2$ (**2**) and $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ (**3**). Compound 2 contains a triply bridging (dimethylamino)carbene ligand. Triply bridging alkoxy-[18] and phosphinocarbenes[19] have been reported previously.

The transformation of 1 to 2 is believed to occur by an initial dissociation of a CO ligand from the $Os(CO)_4$ group in the cluster; see C, Scheme III. This would be followed by an intramolecular oxidative addition of one of the C–H bonds of the methylene group at the vacant site on this metal atom. The fact that the methylene group in 1 is

Scheme IV



Scheme V



leaning toward the third metal atom of the cluster (vide supra) should facilitate this process.

The transformation of 2 to 3 requires a cleavage of the C–H bond of the carbene ligand, the elimination of H_2, and the addition of one CO ligand. A possible mechanism is shown in Scheme IV. Cleavage of the Os–N bond in 2 would generate a vacant site on one metal atom and a C-coordinated edge-bridging carbene ligand on the two other metal atoms, D. Unfortunately, at this point the C–H bond is directed away from the third metal atom. It could achieve a favorable orientation by allowing the bridging carbene ligand to "roll" about the Os–Os bond to the opposite face of the cluster. This would require a shift of the bridging hydride ligand to another site. This should be facile since the ^1H NMR spectra of 2 show that migration of the hydride ligands about the cluster are rapid. Once suitably positioned, the carbene C–H bond could be cleaved by oxidative addition at the vacant site to yield an intermediate such as, E, containing three hydride ligands and a triply bridging (dimethylamino)carbyne ligand. Keister has prepared a series of complexes, $M_3(CO)_9(\mu_3\text{-}COMe)(\mu_3\text{-}H)_3$ (**8**, M = Fe, Ru, Os).[20] The elimination of H_2 from E and the addition of CO would yield 3. Keister

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[17] Adams, R. D.; Babin, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 6872.

[18] (a) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145. (b) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313. (c) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579.

[19] Boyar, E.; Deeming, A. J.; Arce, A. J.; DeSanctis, Y. *J. Organomet. Chem.* **1984**, *276*, C45.

[20] (a) Lavigne, G.; Bonnet, J. J. *Inorg. Chem.* **1981**, *20*, 2713. (b) Deeming, A. J. *J. Organomet. Chem.* **1977**, *128*, 63.

has shown that the compounds 8 eliminate H_2 and add CO under mild conditions.

Although 2 can be converted into 3 at 125 °C, it was observed that significant amounts of 3 were also formed in the original preparation of 2 (98 °C). We have not been able to transform 2 to 3 at these milder conditions. Thus, we have considered the possibility of a route from 1 to 3 that does not involve a CO dissociative step (Scheme V). Cleavage of the Os–N bond in 1 would yield a terminally coordinated (dimethylamino)methyl ligand with a vacant site on the neighboring metal atom, F. C–H activation of the methylene group would yield intermediate G containing a C-coordinated bridging carbene ligand and ten carbonyl ligands. However, except for those complexes that contain dihapto triply bridging aminocarbene ligands,[9] in all examples of cluster complexes containing (dialkylamino)carbene ligands, the carbene ligands are found to adopt terminal bonding modes.[4,5,7-9] This may be due to the strong tendency of the lone pair of electrons on the nitrogen atom to donate to the carbene carbon atom and thus prevent the formation of the second metal–carbon bond. Accordingly, it seems likely that the intermediate G would convert to an isomer like H having a terminally coordinated carbene ligand. Loss of H_2 from H could generate a vacant site on the metal atom adjacent to the carbene ligand, I, and a subsequent α-CH activation of the carbene C–H bond would lead directly to the product 3. Binuclear α-CH activations in secondary (dialkylamino)carbene ligands have been observed previously.[8]

Several years ago, Deeming reported that compound 3 was obtained in a low yield from the reaction of $Os_3(CO)_{12}$ and NMe_3 at high temperature.[13] The compounds 1 and 2 that were prepared under the much milder conditions reported here now appear to provide the first evidence of a rational pathway for this reaction.

The transformation behavior of the (dimethylamino)methyl ligand in this series of triosmium cluster complexes shows similarities to the transformation of the methyl group in the $Os_3(CO)_{10}(\mu\text{-}CH_3)(\mu\text{-}H)$, $Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}H)_2$, and $Os_3(CO)_9(\mu_3\text{-}CH)(\mu\text{-}H)_3$ series studied by Shapley.[21] The C–H activation processes are based upon multicenter interactions of the ligand with the triosmium group. It is expected that these processes will be general in nature. Similar transformations have been observed for bridging thioformaldehyde ligands in triosmium clusters.[22] The ability of cluster complexes to produce novel ligand transformations and catalysis is proving to be an intrinsic feature of their chemistry.

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. We wish to thank Johnson-Matthey Inc. for a loan of osmium tetraoxide. The Brüker AM-300 NMR spectrometer was purchased with funds from the National Science Foundation under Grant No. CHE-8411172.

Registry No. 1, 112839-61-9; 2, 112839-62-0; 3, 63373-87-5; $Os_3(CO)_{10}(\mu\text{-}H)_2$, 41766-80-7; $CH_2(NMe_2)_2$, 51-80-9.

Supplementary Material Available: Tables of positional parameters and anisotropic thermal parameters for compounds 1, 2, and 3 (9 pages); listings of structure factor amplitudes for compounds 1, 2, and 3 (40 pages). Ordering information is given on any current masthead page.

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(21) Keister, J. B.; Payne, M. W.; Muscatella, M. J. *Organometallics* 1986, *2*, 219.

(22) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* 1977, *99*, 5226.

(23) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* 1987, *6*, 1717.

Polynuclear Acetylides. Synthesis, Spectroscopic Features, and Structural Systematics for a Complete Triad of μ_2-η^2-Complexes: $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (M = Fe, Ru, Os)

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Received September 25, 1987

The synthesis of the triad of phosphido-bridged, acetylide-bridged dimetallic carbonyls $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C_2R)(\mu\text{-}PPh_2)$ (**1**, M = Fe; **2**, M = Ru; **3**, M = Os; **a**, R = Ph, **b**, R = *t*-Bu, **c**, R = *i*-Pr) is described. The molecules **1**, **2**, and **3** were prepared via pyrolysis of $M_3(CO)_{11}(Ph_2PC{\equiv}CR)$ which initiates metal metal bond cleavage and oxidative addition of the P–C(acetylide) bond across a metal–metal edge. Compounds **1b**, **2b**, and **3b** have been structurally characterized by single-crystal X-ray analysis. Crystals of **1–3b** are monoclinic of space group $P2_1/n$ with unit cell dimensions. **1b**: a = 15.140 (3) Å, b = 10.559 (2) Å, c = 16.659 (3) Å, β = 110.61 (1)°. **2b**: a = 12.549 (1) Å, b = 14.528 (2) Å, c = 14.266 (1) Å, β = 92.95 (1)°. **3b**: a = 15.357 (2) Å, b = 10.604 (2) Å, c = 16.969 (2) Å, β = 111.56 (1)°. The structures were solved and refined to the following R and R_w values: **1b**, R = 0.028, R_w = 0.031 on 3071 observed ($I \geq 3\sigma(I)$) data; **2b**, R = 0.028, R_w = 0.030 on 4349 observed ($I \geq 3\sigma(I)$) data; **3b**, R = 0.035, R_w = 0.040 on 2734 observed ($I \geq 3\sigma(I)$) data. The three molecules are isostructural with a metal–metal bond supported by a phosphido bridge and a σ–π bound acetylide ligand. In solution all three compounds are fluxional via processes of acetylide σ–π interchange and $M(CO)_3$ trigonal rotation. Changes in structural parameters down the triad are discussed.

As a carbon ligand isoelectronic with both CO and CN^-, organometallic complexes of the acetylide anion $HC{\equiv}C^-$ have been known for decades.[1] In fact, acetylides are virtually unrivaled among unsaturated hydrocarbyls in