Clusters Containing Carbene Ligands. 10. Transformation of an Ynamine into an Aminocarbene Ligand by Unsymmetric Hydrogenation with a Triosmium Cluster Complex

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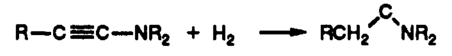
The reaction of ynamine MeC_2NMe_2 with the lightly stabilized cluster complex $Os_3(CO)_9(NCMe)(\mu\text{-}OMe)(\mu\text{-}H)$ (1) at 25 °C yielded the product $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}MeC(H)CNMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (2; 47%). Compound 2 was characterized crystallographically and was shown to consist of an open triosmium cluster with a triply bridging $MeC(H)CNMe_2$ ligand formed by the transfer of the hydride ligand to the methyl-substituted carbon atom of the ynamine. A small amount of $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}MeC(H)CNMe_2](\mu\text{-}OMe)$ (3) was also obtained from this reaction. Compounds 2 and 3 can be interconverted by the addition and elimination of CO. Compound 3 contains an open triosmium cluster with a $MeC(H)CNMe_2$ ligand bridging the two nonbonded metal atoms. Compound 2 was found to react with hydrogen at 80 °C to yield two products, $Os_3(CO)_8[\mu_3\text{-}\eta^3\text{-}MeC(H)CNMe_2](\mu\text{-}OMe)(\mu\text{-}H)(H)$ (4; 35%) and $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}EtCNMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (5; 15%). Compounds 4 and 5 were characterized crystallographically. 4 is similar to 2, but has one less CO ligand and two hydride ligands, one terminal and one bridge. 5 consists of an open cluster with a triply bridging ethyl(dimethylamino)carbene ligand. Compound 4 reacts with PMe_2Ph to yield the complex $Os_3(CO)_8(PMe_2Ph)[\mu_3\text{-}\eta^2\text{-}MeC(H)CNMe_2](\mu\text{-}OMe)(\mu\text{-}H)(H)$ (6; 66%), a simple PMe_2Ph derivative of 4. 4 reacts with pyridine to yield $Os_3(CO)_8(py)[\mu_3\text{-}EtCNMe_2](\mu\text{-}H)$ (7; 17%). Compound 7 was characterized crystallographically and was shown to be a pyridine derivative of 5. When CO was added to 7, it was converted to 5 in 96% yield. When heated to 125 °C, 5 was isomerized to $Os_3(CO)_9[C(Et)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (8) in 55% yield, which contains a closed triosmium cluster with a terminally coordinated ethyl(dimethylamino)carbene ligand. The net result is the unsymmetric hydrogenation of the ynamine, MeC_2NMe_2, to an ethyl(dimethylamino)carbene ligand. Crystal data are as follows: for 2, space group = $P\bar{1}$, a = 9.092 (1) Å, b = 14.751 (2) Å, c = 8.542 (1) Å, α = 97.28 (1)°, β = 115.302 (9)°, γ = 91.33 (1)°, Z = 2, 2450 reflections, R = 0.021; for 3, space group = $P2_1/n$, a = 10.041 (2) Å, b = 15.650 (3) Å, c = 14.135 (3) Å, β = 113.109 (9)°, Z = 4, 2509 reflections, R = 0.024; for 4, space group = $P2_1/c$, a = 17.30 (1) Å, b = 15.165 (6) Å, c = 17.488 (8) Å, β = 117.29 (3)°, Z = 8, 2704 reflections, R = 0.061; for 5, space group = $P2_1/n$, a = 12.354 (2) Å, b = 13.017 (2) Å, c = 13.371 (2) Å, β = 96.10 (1)°, Z = 4, 2143 reflections, R = 0.025; for 6, space group = $P2_1/c$, a = 9.381 (1) Å, b = 11.653 (2) Å, c = 23.815 (8) Å, β = 90.40 (2)°, Z = 4, 2626 reflections, R = 0.037; for 7, space group = $P\bar{1}$, a = 9.498 (1) Å, b = 16.261 (3) Å, c = 8.828 (1) Å, α = 97.72 (2)°, β = 115.82 (3)°, γ = 78.61 (2)°, Z = 2, 2760 reflections, R = 0.022; for 8, space group = $P2_1/n$, a = 7.6725 (9) Å, b = 18.862 (3) Å, c = 15.250 (2) Å, β = 100.15 (1)°, Z = 4, 2426 reflections, R = 0.023.

Introduction

In recent studies, we have discovered the first examples of the formation of aminocarbene ligands by the "unsymmetric" addition of hydrogen to the carbon–carbon triple bond of ynamines (eq 1).[1,2] The reactions are facilitated by and are, to date, unique to metal cluster complexes. In the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with MeC_2NMe_2 to form $Os_3(CO)_{11}[\mu\text{-}C(Et)NMe_2]$, a series of intermediates were isolated and structurally characterized. These complexes showed the importance of multicenter coordination of the partially hydrogenated ynamine ligand and indicated that this was a characteristic feature of the hydrogenation process.[2,3]



$$R{-}C{\equiv}C{-}NR_2 + H_2 \longrightarrow RCH_2{-}\overset{..}{C}{-}NR_2 \quad (1)$$

We have now investigated the reaction of MeC_2NMe_2 with the complex $Os_3(CO)_9(NCMe)(\mu\text{-}OMe)(\mu\text{-}H)$ (1) generated from $Os_3(CO)_{10}(\mu\text{-}OMe)(\mu\text{-}H)$ by reaction with Me_3NO and MeCN. These results have not only shown the importance of multicenter bridging coordinations to the hydrogenation process but also show that cluster rearrangements and an intermolecular proton shift step are involved in this system as well.

Experimental Seciton

General Methods. Although the reaction products are air stable, all of the reactions were performed under an atmosphere of nitrogen. Methylene chloride was freshly distilled from calcium hydride before use. $Os_3(CO)_{10}(\mu\text{-}OMe)(\mu\text{-}H)$ was made by the procedure of Shapley from $Os_3(CO)_{10}(NCMe)_2$ and MeOH.[4] MeC_2NMe_2 was prepared by the published procedure.[5] $Me_3NO{\cdot}2H_2O$ was dehydrated by the published procedure.[6] Reagent grade pyridine was distilled from calcium hydride before use. Technical grade octane was purchased from Phillips Co. and was purified by treatment with sulfuric acid followed by distillation from sodium/benzophenone before use. IR spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM-300 or AM-500 spectrometer operating at 300 or 500 MHz, respectively. Elemental analyses were performed by Desert Analytics, Tucson, AZ. TLC separations were performed in air on Whatman 0.25-mm silica gel 60Å F_{254} plates.

Preparation of $Os_3(CO)_9(\mu\text{-}OMe)(NCMe)(\mu\text{-}H)$ (1). A 200-mg (0.227-mmol) amount of $Os_3(CO)_{10}(\mu\text{-}OMe)(\mu\text{-}H)$ was dissolved in 150 mL of CH_2Cl_2. A 20-mg (0.266-mmol) amount of Me_3NO in 15 mL of NCMe was added dropwise to the solution at 25 °C. The reaction mixture was allowed to stir at 25 °C for 30 min. After this time an IR spectrum of the reaction mixture revealed no remaining starting material. The solution was then passed over a silica gel column. Elution with CH_2Cl_2 gave one

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yellow band. Removal of the solvent in vacuo yielded 190 mg of yellow $Os_3(CO)_9(\mu\text{-OMe})(NCMe)(\mu\text{-H})$ (1; 98%). Analytical and spectral data for 1: IR (ν(CO) (cm^{-1}) in CH_2Cl_2) 2098 (m), 2055 (s), 2012 (vs), 2002 (sh), 1977 (sh), 1932 (w); ^{1}H NMR (δ in $CDCl_3$) 3.67 (s, 3 H), 2.46 (s, 3 H), −11.35 (s, 1 H).

Reaction of 1 with MeC_2NMe_2. A 290-mg (0.324-mmol) amount of 1 was dissolved in 150 mL of CH_2Cl_2. A 50-μL (0.602-mmol) amount of MeC_2NMe_2 was added to the solution via syringe. The reaction mixture was allowed to stir for 24 h at 25 °C. After this time the color of the solution had turned dark orange. The product was separated by column chromatography on silica gel with CH_2Cl_2 solvent. One yellow band was eluted, but a substantial amount of orange material remained on the top of the column. Attempts to elute this material with acetone solvent were unsuccessful. The solvent was removed from the eluate in vacuo, and the dark yellow residue was recrystallized from a 9/1 (v/v) hexane/CH_2Cl_2 solvent mixture at −10 °C. A 104-mg amount of $Os_3(CO)_9(\mu\text{-OMe})[\mu_3\text{-}\eta^2\text{-MeC(H)CNMe}_2]$ (2) was recovered as yellow solid. The yellow precipitate was washed with hexane, and the wash and mother liquor from the recrystallization were combined and evaporated to dryness under a nitrogen purge. The residue was then dissolved in a minimum of CH_2Cl_2, and the solution was chromatographed (TLC) by using a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture, which separated 20.0 mg of $Os_3(CO)_{10}(\mu\text{-OMe})[\mu\text{-Me(H)CCNMe}_2]$ (3) as a yellow band (6.4%) from 40 mg of 2 as a pale yellow band (total yield of 2 was 144 mg, 47%). Analytical and spectral data for 2: IR (ν(CO) (cm^{-1}) in hexane) 2084 (w), 2059 (vs), 2022 (vs), 2002 (vs), 1987 (m), 1981 (sh), 1968 (m), 1951 (w); ^{1}H NMR (δ in $CDCl_3$) 3.88 (s, 3 H), 3.79 (q, 1 H, $^3J_{H-H} = 6.4$ Hz), 3.74 (s, 3 H), 3.65 (s, 3 H), 1.80 (d, 3 H $^3J_{H-H} = 6.4$ Hz). Anal. Calcd: C, 19.21; N, 1.50; H, 1.40. Found: C, 19.55; N, 1.47; H, 1.39. Analytical and spectral data for 3: IR (ν(CO) (cm^{-1}) in hexane) 2090 (w), 2058 (vs), 2036 (s), 2006 (m), 1987 (vs), 1989 (s, sh), 1966 (s), 1959 (w, sh); ^{1}H NMR (δ in $CDCl_3$) 3.88 (s, 3 H), 3.79 (q, 1 H, $^5J_{H-H} = 7.4$ Hz), 3.74 (s, 3 H), 3.65 (s, 3 H), 1.80 (d, 3 H, $^3J_{H-H} = 7.4$ Hz). Anal. Calcd: C, 19.89; N, 1.45, H, 1.35. Found: C, 19.97; N, 1.47; H, 1.29.

Pyrolysis of 3. A 20-mg sample of 3 was dissolved in 50 mL hexane, and the solution was heated to reflux for 20 min. At the end of this time an IR spectrum of the solution revealed quantitative conversion to compound 2. The solvent was removed in vacuo. The yellow residue was dissolved in a minimum of CH_2Cl_2, and the solution was chromatographed by TLC. Elution with a 7/3 (v/v) hexane/CH_2Cl_2 solvent mixture yielded 18 mg of 2 (91%).

Reaction of 2 with Carbon Monoxide. A 20-mg sample of 2 was placed in a 50-mL Parr high-pressure autoclave. A 35-mL volume of CH_2Cl_2 was added to the reactor, and the solution was stirred for 24 h under 30 atm of CO at 25 °C. At the end of this time the solution was concentrated under nitrogen purge to ≈1 mL and chromatographed by TLC. Elution with a 7/3 (v/v) hexane/CH_2Cl_2 solvent mixture separated 4.0 mg of unreacted 2 from 12.0 mg of 3 (57%).

Reaction of 2 with Hydrogen. A 200-mg (0.213-mmol) amount of 2 was dissolved in 150 mL of cyclohexane. The solution was heated to reflux for 12.5 h under a slow H_2 purge. At this time an IR spectrum of the reaction mixture revealed that nearly all of the starting material had reacted. The solvent was removed in vacuo, and the yellow residue was chromatographed by TLC with a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture. This separated the following compounds in order of elution: trace amounts of $Os_3(CO)_{10}(\mu\text{-H})_2$ and $Os_3(CO)_{10}(\mu\text{-OMe})(\mu\text{-H})$, 30 mg of $Os_3(CO)_9(\mu\text{-OMe})[\mu_3\text{-}\eta^2\text{-MeCH}_2\text{CNMe}_2](\mu\text{-H})$, 5 as a UV band (15%), and 60 mg of $Os_3(CO)_8[\mu\text{-OMe})[\mu_3\text{-}\eta^2\text{-MeC(H)CNMe}_2](\mu\text{-H})(H)$ (4) as a UV band (35%). Analytical and spectral data for 4: IR (ν(CO) (cm^{-1}) in hexane) 2084 (m), 2045 (vs), 2028 (vs), 2002 (vs), 1986 (s), 1978, (w, sh), 1966 (vs), 1990 (w, sh); ^{1}H NMR (δ in $CDCl_3$) 7.43 (q, 1 H, $^3J_{H-H} = 6.5$ Hz), 3.91 (s, 3 H), 3.41 (s, 3 H), 2.95 (s, 3 H), 1.98 (d, 3 H, $^3J_{H-H} = 6.5$ Hz), −6.54 (s, 1 H), −11.37 (s, 1 H). Anal. Calcd: C, 18.45; N, 1.54; H, 1.65. Found: C, 18.52; N, 1.53; H, 1.57. Analytical and spectral data for 5: IR (ν(CO) (cm^{-1}) in hexane) 2090 (s), 2069 (vs), 2036 (vs), 2008 (vs), 1993 (vs), 1974 (s), 1968 (sh), 1956 (m); ^{1}H NMR (δ in $CDCl_3$) 3.97 (s, 3 H), 3.72 (dq, 1 H, $^2J_{H-H} = 16.1$ Hz, $^3J_{H-H} = 7.1$ Hz), 3.64 (s, 3 H), 3.27 (s, 3 H), 2.54 (dq, 1 H, $^2J_{H-H} = 16.1$ Hz, $^3J_{H-H} = 7.7$ Hz), 1.41 (t, 3 H, $^3J_{H-H} = 7.5$ Hz), −10.85 (s, 1 H). Anal. Calcd: C, 19.18; N, 1.50; H, 1.60. Found: C, 19.14; N, 1.56; H, 1.43.

Reaction of 4 with Carbon Monoxide. A 15-mg (0.016-mmol) amount of 4 was dissolved in 25 mL of hexane. The solution was heated to reflux (69 °C) for 2 h under a slow CO purge. At this time, an IR spectrum of the solution indicated complete conversion to $Os_3(CO)_{10}(\mu\text{-OMe})(\mu\text{-H})$. The solvent was removed in vacuo. The yellow residue was dissolved in a minimum of CH_2Cl_2, and the solution was chromatographed by TLC. Elution with a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture yielded 11.0 mg (78%) of yellow $Os_3(CO)_{10}(\mu\text{-OMe})(\mu\text{-H})$.

NMR Analysis of the Reaction of 4 with Carbon Monoxide. A 10-mg sample of 4 was dissolved in 0.5 mL of toluene-d_8. The solution was transferred to a 5-mm NMR tube and degassed by using three freeze–pump–thaw cycles. The NMR tube was then filled with CO, sealed, and allowed to stand at 25 °C for 72 h. During this time the reaction was monitored by ^{1}H NMR spectra taken at 12-h intervals. At no time were resonances other than those due to 4 observed. The NMR tube was then placed in an oil bath at 90 °C. ^{1}H NMR spectra were taken at 15-min intervals and showed only the slow disappearance of the hydride resonances due to 4 and the formation and growth of the new hydride resonance due to $Os_3(CO)_{10}(\mu\text{-OMe})(\mu\text{-H})$. At the end of 1.5 h, the hydride resonances due to 4 had completely disappeared. At no time was the hydride resonance due to 5 observed. The NMR tube was opened, and the solvent was removed in vacuo. Workup of the yellow residue by TLC yielded 7.0 mg (80%) of $Os_3(CO)_{10}(\mu\text{-OMe})(\mu\text{-H})$.

Reaction of 4 with Dimethylphenylphosphine. A 46-mg (0.050-mmol) amount of 4 was dissolved in 35 mL of CH_2Cl_2. A 0.8-μL (0.056-mmol) amount of PMe_2Ph was added to the solution via syringe. The solution was heated to reflux for 1 h, at which time an IR spectrum of the reaction mixture revealed that only a trace amount of compound 4 remained. The solvent was removed in vacuo and the orange/yellow residue was dissolved in a minimum of CH_2Cl_2. TLC using a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture separated 5 mg of unreacted 4 from 30 mg of pale orange $Os_3(CO)_7(\mu\text{-OMe})(PMe_2Ph)[\mu_3\text{-}\eta^2\text{-MeC(H)CNMe}_2](\mu\text{-H})(H)$ (6; 66%). Analytical and spectral data for 6: IR (ν(CO) (cm^{-1}) in hexane) 2059 (s), 2023 (vs), 2002 (m, sh), 1995 (s), 1984 (s), 1967 (s), 1967 (s), 1954 (m), 1954 (w); ^{1}H NMR (δ in $CDCl_3$) 7.47–7.43 (m, 5 H), 7.24 (q, 1 H $^3J_{H-H} = 7.8$ Hz), 4.02 (s, 3 H), 2.79 (s, 3 H), 2.62 (s, 3 H), 1.85 (dd, 6 H, $^3J_{P-H} = 6.2$ Hz), 1.70 (d, 3 H, $^3J_{H-H} = 7.8$ Hz), −6.07 (s, 1 H), −11.38 (s, 1 H). Anal. Calcd: C, 18.45; N, 1.54; H, 1.65. Found: C, 18.52, N, 1.53; H, 1.57.

Reaction of 4 with Pyridine. A 35-mg (0.038-mmol) amount of 4 was dissolved in 50 mL of hexane. A 100-μL volume of pyridine was added to the solution via syringe. The solution was heated to reflux for 5 h, slowly changing from colorless to yellow. At this time an IR spectrum of the reaction mixture revealed that no starting material remained. The solvent was removed in vacuo. The yellow residue was dissolved in a minimum of CH_2Cl_2, and the solution was chromatographed by TLC. Elution with a 7/3 (v/v) hexane/CH_2Cl_2 solvent mixture separated 1.0 mg of unreacted 4 as a UV band from 6.0 mg of pale yellow $Os_3(CO)_8(C_5H_5N)(\mu\text{-OMe})[\mu_3\text{-}\eta^2\text{-(Et)CNMe}_2](\mu\text{-H})$ (7; 17%). Analytical and spectral data for 7: IR (ν(CO) (cm^{-1}) in hexane) 2070 (m), 2030 (vs), 2002 (s), 1985 (vs), 1959 (m), 1953 (w, sh), 1931 (m); ^{1}H NMR (δ in $CDCl_3$) 9.0–9.1 (m, 2 H), 7.8–8.0 (m, 1 H), 7.4–7.6 (m, 2 H), 3.72 (dq, 1 H, $^2J_{H-H} = 16.0$ Hz, $^3J_{H-H} = 6.7$ Hz), 3.58 (s, 3 H), 3.50 (s, 3 H), 3.31 (s, 3 H), 2.41 (dq, 1 H, $^2J_{H-H} = 16.0$ Hz, $^3J = 7.8$ Hz), 1.32 (t, 3 H, $^3J = 7.3$ Hz), −9.77 (s, 1 H). Anal. Calcd: C, 23.03; N, 2.83; H, 2.03. Found: C, 23.01; N, 2.83; H, 1.92.

Reaction of 7 with Carbon Monoxide. A 20-mg (0.020-mmol) amount of 7 was dissolved in 35 mL of hexane. The solution was heated to reflux under a slow CO purge for 30 min. At this time an IR spectrum of the reaction mixture indicated complete conversion to compound 5. The solvent was removed in vacuo. The yellow residue was dissolved in a minimum of CH_2Cl_2, and the solution was chromatographed by TLC. Elution with a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture yielded 18 mg of 5 (96%).

Pyrolysis of 5 under a CO Atmosphere. A 46-mg (0.050-mmol) amount of 5 was dissolved in 65 mL of octane. The solution was heated to reflux under a slow CO purge for 5 h. The solvent was removed in vacuo. The yellow residue was taken up in a

Table I. Crystallographic Data for Diffraction Studies

	compound						
	2	**3**	**4**	**5**	**6**	**7**	**8**
empirical formula	$Os_3O_{10}NC_{15}H_{13}$	$Os_3O_{11}NC_{16}H_{13}$	$Os_3O_9NC_{14}H_{15}$	$Os_3O_9NC_{15}H_{15}$	$Os_3P_1O_8NC_{21}H_{26}$	$Os_3N_2C_{10}O_9H_{20}$	$Os_3O_{10}NC_{15}H_{16}$
fw	937.87	965.88	912.88	939.88	1022.01	990.97	941.90
cryst system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
lattice params							
a, Å	9.092 (1)	10.041 (2)	17.30 (1)	12.354 (2)	9.381 (1)	9.498 (1)	7.6725 (9)
b, Å	14.751	15.650 (3)	15.165 (6)	13.017 (2)	11.653 (2)	16.261 (3)	18.862 (3)
c, Å	8.542 (1)	14.135 (3)	17.488 (8)	13.371 (2)	23.815 (8)	8.828 (1)	15.250 (2)
α, deg	97.28 (1)					97.72 (2)	
β, deg	115.302 (9)	113.109 (9)	117.29 (3)	96.10 (1)	90.40 (2)	115.82 (3)	100.15 (1)
γ, deg	91.33 (1)					78.61 (2)	
V, Å^3	1023.6 (3)	2220 (1)	4077.3 (9)	2138.1 (5)	2603 (2)	1201.4 (8)	2172 (1)
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Z	2	4	8	4	4	2	4
D_{calc}, g/cm^3	3.04	2.89	2.97	2.92	2.62	2.74	2.88
μ(Mo Kα), cm^{-1}	186.44	171.98	187.15	178.51	147.25	158.90	175.71
radiation	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
abs corr	analytical	empirical	analytical	analytical	empirical	analytical	empirical
temp, °C	23	23	23	23	23	23	23
$2\theta max$, deg	46.0	46.0	42.0	45.0	45.0	45.0	45.0
no. of observns ($I > 3\sigma(I)$)	2450	2509	2704	2143	2626	2760	2426
no. of variables	262	283	271	265	315	302	266
residuals: *R*; R_w	0.021; 0.023	0.024; 0.025	0.061; 0.068	0.025; 0.026	0.037; 0.041	0.022; 0.024	0.023; 0.026
goodness of fit indicator	1.23	1.24	2.74	1.21	1.81	1.49	1.51
max shift in final cycle	0.01	0.80	1.38	0.16	0.30	0.25	0.13
largest peak in final diff map, e Å^3	1.08	0.62	2.15	0.70	1.13	0.95	0.72

minimum of CH_2Cl_2 and was chromatographed by TLC using a 7/3 (v/v) hexane/CH_2Cl_2 solvent mixture. This separated the following compounds in order of elution: 9.0 mg of $Os_3(CH)_{10}(\mu\text{-OMe})(\mu\text{-H})$, 10.0 mg of unreacted **5**, and 26 mg of yellow $Os_3(CO)_9(\mu\text{-OMe})[(Et)CNMe_2](\mu\text{-H})$ (**8**; 55%). Analytical and spectral data for **8**: IR (ν(CO) (cm^{-1}) in hexane) 2090 (s), 2049 (vs), 2011 (vs), 1995 (vs), 1958 (s), 1930 (s); ^{1}H NMR (δ in $CDCl_3$) 4.07 (s, 3 H), 3.64 (s, 3 H), 3.52 (dq, 1 H, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 7.5 Hz), 3.47 (s, 3 H), 2.82 (dq, 1 H, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 7.5 Hz), 1.15 (t, 3 H, $^3J_{H-H}$ = 7.5 Hz), −13.30 (s, 1 H). Anal. Calcd: C, 19.84; N, 1.75; N, 1.65. Found: C, 19.40; N, 1.58; H, 1.54.

Crystallographic Analyses. Crystals of compounds **2**–**8** suitable for diffraction analyses were grown by slow evaporation of hexane/CH_2Cl_2 solutions at −10 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. MICROVAX II or VAXstation 3520 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[7a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[7b] Full-matrix least-squares refinements minimized the function

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

where

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

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

Compound **2** 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. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **3** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **4** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was determined uniquely from the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. In the course of the refinement, three large residuals were observed in the region of the metal atoms of both of the crystallographically independent molecules of the complex in the unit cell. These were attributed to a disorder component of a second complete cluster. The metal atoms of the disordered component were included in the refinement and converged at 11% occupancy. Thus, only the metal atoms of the disordered clusters were located. Only the metal atoms were refined with anisotropic thermal parameters. The hydrogen atom positions of the major component of the disorder were calculated by using idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **5** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The bridging hydride ligand was located crystallographically and was successfully refined with an isotropic thermal parameter. All other hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **6** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was determined uniquely from the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and

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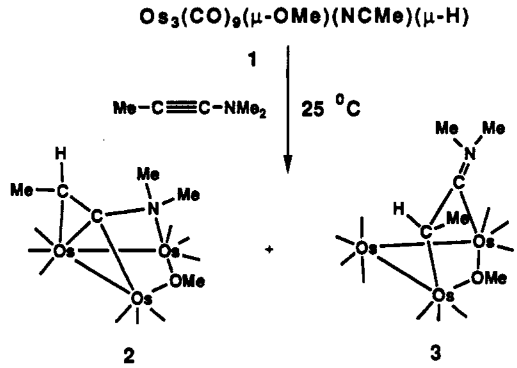
[7] (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

Scheme I



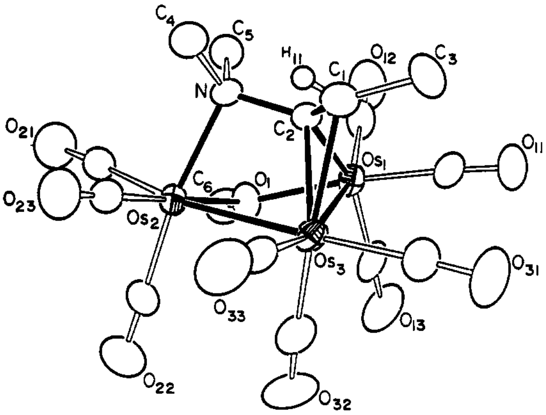


Figure 1. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}MeC(H)CNMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (2), showing 50% probability thermal ellipsoids.

difference Fourier syntheses. Both the terminal and bridging hydride ligands were located crystallographically and successfully refined. All other hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound 7 crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed as correct 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 bridging hydride ligand was located crystallographically and was successfully refined. The positions of all other hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound 8 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was determined uniquely from the systematic absences observed during the collection of data. The structure was solved by a combination of direct method (MITHRIL) and difference Fourier syntheses. The bridging hydride ligand was located crystallographically and was successfully refined. All remaining hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Results

Since $Os_3(CO)_{10}(\mu\text{-}OMe)(\mu\text{-}H)$ is relatively unreactive, an activated form $Os_3(CO)_9(NCMe)(\mu\text{-}OMe)(\mu\text{-}H)$ (1) was synthesized by treatment with Me_3NO and NCMe. The site of ligation of the NCMe ligand in 1 was not established. The reaction of 1 with MeC_2NMe_2 at 25 °C yielded the product $Os_3(CO)_9(\mu\text{-}OMe)[\mu_3\text{-}\eta^3\text{-}MeC(H)CNMe_2]$ (2) in 47% yield, along with a minor amount (6% yield) of the complex $Os_3(CO)_{10}(\mu\text{-}OMe)[\mu\text{-}MeC(H)CNMe_2]$ (3) (Scheme I).

Table II. Positional Parameters and B(eq) for 2

atom	x	y	z	B(eq), Å^2
Os(1)	0.46098 (4)	0.20795 (3)	0.74849 (4)	2.33 (1)
Os(2)	0.88501 (4)	0.22751 (2)	0.89163 (4)	2.14 (1)
Os(3)	0.63774 (4)	0.30640 (2)	0.61913 (4)	2.26 (1)
O(1)	0.6817 (6)	0.1433 (4)	0.8555 (7)	2.8 (2)
O(11)	0.1392 (8)	0.2849 (6)	0.5545 (9)	4.8 (3)
O(12)	0.3354 (8)	0.1576 (7)	1.007 (1)	6.1 (4)
O(13)	0.325 (1)	0.0367 (6)	0.468 (1)	5.7 (3)
O(21)	1.123 (1)	0.1538 (6)	1.217 (1)	5.7 (3)
O(22)	0.9820 (9)	0.0978 (6)	0.653 (1)	5.8 (3)
O(23)	1.1522 (8)	0.3647 (5)	0.9240 (9)	4.1 (3)
O(31)	0.3282 (9)	0.3602 (6)	0.330 (1)	5.7 (3)
O(32)	0.639 (1)	0.1377 (6)	0.3738 (9)	5.3 (3)
O(33)	0.8844 (8)	0.4368 (5)	0.5805 (9)	4.7 (3)
N	0.7802 (8)	0.3196 (5)	1.0274 (8)	2.3 (2)
C(1)	0.598 (1)	0.4153 (6)	0.819 (1)	3.0 (3)
C(2)	0.618 (1)	0.3288 (6)	0.876 (1)	2.3 (3)
C(3)	0.444 (1)	0.4625 (7)	0.752 (1)	4.0 (4)
C(4)	0.886 (1)	0.4056 (7)	1.117 (1)	3.5 (3)
C(5)	0.759 (1)	0.2810 (7)	1.165 (1)	3.2 (3)
C(6)	0.694 (1)	0.0579 (7)	0.921 (1)	3.7 (4)
C(11)	0.266 (1)	0.2589 (7)	0.632 (1)	3.0 (3)
C(12)	0.383 (1)	0.1728 (7)	0.911 (1)	3.3 (4)
C(13)	0.373 (1)	0.0993 (8)	0.574 (1)	3.4 (4)
C(21)	1.029 (1)	0.1803 (7)	1.098 (1)	3.2 (4)
C(22)	0.943 (1)	0.1465 (7)	0.741 (1)	3.4 (4)
C(23)	1.050 (1)	0.3130 (7)	0.912 (1)	2.9 (3)
C(31)	0.444 (1)	0.3413 (7)	0.440 (1)	3.5 (4)
C(32)	0.542 (1)	0.1987 (7)	0.467 (1)	3.3 (4)
C(33)	0.793 (1)	0.3860 (7)	0.595 (1)	3.0 (3)

Table III. Intramolecular Distances for 2[a]

Os(1)–Os(3)	2.7801 (5)	Os(3)–C(1)	2.343 (9)
Os(1)–Os(2)	3.5030 (7)	Os(3)–C(2)	2.260 (7)
Os(1)–O(1)	2.124 (5)	Os(3)–C(31)	1.91 (1)
Os(1)–C(2)	2.113 (9)	Os(3)–C(32)	1.93 (1)
Os(1)–C(1)	1.858 (9)	Os(3)–C(33)	1.91 (1)
Os(1)–C(12)	1.924 (9)	O(1)–C(6)	1.43 (1)
Os(1)–C(13)	1.93 (1)	O–C(av)	1.14 (1)
Os(2)–Os(3)	2.8570 (6)	N–C(2)	1.51 (1)
Os(2)–O(1)	2.089 (5)	N–C(4)	1.48 (1)
Os(2)–N	2.169 (6)	N–C(5)	1.50 (1)
Os(2)–C(21)	1.92 (1)	C(1)–C(2)	1.41 (1)
Os(2)–C(22)	1.90 (1)	C(1)–C(3)	1.50 (1)
Os(2)–C(23)	1.87 (1)		

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

Table IV. Intramolecular Bond Angles for 2[a]

Os(3)–Os(1)–O(1)	82.1 (1)	Os(2)–Os(3)–C(33)	93.0 (2)
Os(3)–Os(1)–C(2)	52.9 (2)	C(1)–Os(3)–C(2)	35.6 (3)
Os(3)–Os(1)–C(11)	95.6 (3)	Os(1)–O(1)–Os(2)	112.5 (3)
Os(3)–Os(1)–C(12)	159.2 (3)	Os(1)–O(1)–C(6)	123.7 (5)
Os(3)–Os(1)–C(13)	102.7 (3)	Os(2)–O(1)–C(6)	123.2 (5)
Os(3)–Os(2)–O(1)	80.0 (1)	Os(2)–N–C(2)	99.6 (4)
Os(3)–Os(2)–N	75.8 (2)	Os(2)–N–C(4)	112.2 (5)
Os(3)–Os(2)–C(21)	169.9 (2)	Os(2)–N–C(5)	114.8 (5)
Os(3)–Os(2)–C(22)	95.6 (3)	C(2)–N–C(4)	116.3 (7)
Os(3)–Os(2)–C(23)	93.0 (3)	C(2)–N–C(5)	108.7 (6)
O(1)–Os(2)–N	80.2 (2)	C(4)–N–C(5)	105.6 (6)
Os(1)–Os(3)–Os(2)	76.83 (2)	Os(3)–C(1)–C(2)	69.0 (5)
Os(1)–Os(3)–C(1)	75.6 (2)	Os(3)–C(1)–C(3)	117.4 (6)
Os(1)–Os(3)–C(2)	48.2 (2)	C(2)–C(1)–C(3)	126.8 (8)
Os(1)–Os(3)–C(31)	92.4 (3)	Os(1)–C(2)–Os(3)	78.9 (3)
Os(1)–Os(3)–C(32)	91.7 (3)	Os(1)–C(2)–N	117.3 (6)
Os(1)–Os(3)–C(33)	164.7 (2)	Os(1)–C(2)–C(1)	126.3 (6)
Os(2)–Os(3)–C(1)	92.6 (2)	Os(3)–C(2)–N	110.8 (4)
Os(2)–Os(3)–C(2)	66.3 (2)	Os(3)–C(2)–C(1)	75.4 (4)
Os(2)–Os(3)–C(31)	168.7 (3)	N–C(2)–C(1)	115.7 (7)
Os(2)–Os(3)–C(32)	85.0 (3)	O–C–Os(av)	177 (1)

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

Compound 2 was characterized by IR and ^1H NMR spectroscopy and by single-crystal X-ray diffraction

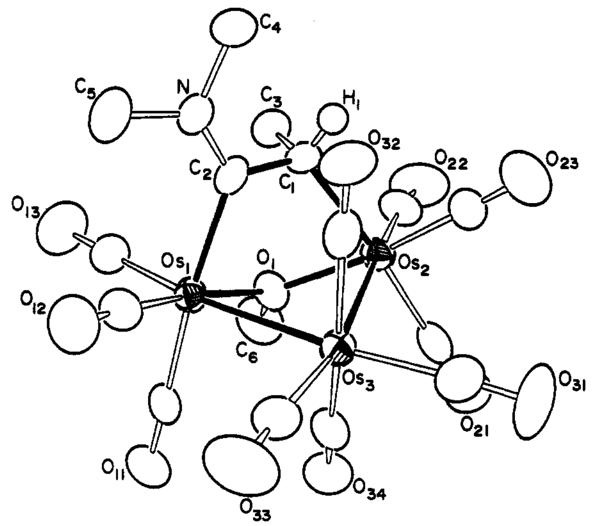
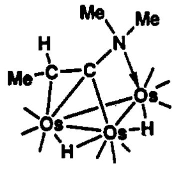


Figure 2. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}MeC(H)CNMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (**3**), showing 50% probability thermal ellipsoids.

analysis. An ORTEP drawing of compound **2** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV, respectively. The molecule consists of a triangular cluster of osmium atoms with two metal-metal bonds. The Os(1)–Os(2) bond distance of 2.7801 (6) Å is significantly shorter than the Os(1)–Os(3) distance of 2.8570 (7) Å. The osmium atoms, Os(1) and Os(2), are not mutually bonded (3.5030 (7) Å) but are bridged by a methoxide ligand. The osmium–oxygen bond distances, Os(1)–O(1) = 2.124 (5) Å and Os(2)–O(1) = 2.089 (5) Å, are similar to the corresponding distances in the cluster complexes $Os_3(CO)_{10}(\mu\text{-}OMe)(\mu\text{-}H)$,[8] $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$,[8] $Os_3(CO)_9[C(H)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$,[9] and $Os_3(CO)_{10}(\mu\text{-}OMe)_2$.[10] The most interesting ligand is the triply bridging σ-π-(dimethylamino)alkenyl ligand that was formed by the transfer of the hydride ligand to the methyl-substituted carbon atom of the ynamine molecule. The ligand is very similar to the (dimethylamino)alkenyl ligand found in the complex $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}Me_2NCC(H)Me](\mu\text{-}H)_2$ (**9**).



9

As in **9**, the CC(H)Me alkenyl grouping in **2** adopts the normal σ-π coordination mode bridging the two metal atoms Os(1) and Os(3). The metal–alkenyl carbon bonds, Os(1)–C(2) = 2.113 (9) Å, Os(3)–C(2) = 2.260 (7) Å, and Os(3)–C(1) = 2.343 (9) Å, are similar to the corresponding distances found in **9**, 2.13 (1), 2.27 (1), and 2.42 (1) Å. The nitrogen atom is coordinated to the third metal atom, Os(2)–N = 2.169 (5) Å. This distance is also similar to the corresponding distance found in **9** of 2.18 (1) Å. The C(2)–N distance of 1.51 (1) Å is consistent with a carbon–nitrogen single bond. The C(1)–C(2) distance of 1.48 (2) Å is only slightly longer than the corresponding distance of 1.42 (2) Å found in **9**. The alkenyl ligand in **2** adopts a Z stereochemistry. No evidence for an E isomer was obtained from the ^1H NMR spectrum of **2**, in contrast to **9**, which showed the presence of both E and Z isomers.[2]

Table V. Positional Parameters and B(eq) for 3

atom	x	y	z	B(eq), Å^2
Os(1)	0.26798 (04)	0.15743 (02)	0.14556 (03)	2.47 (2)
Os(2)	0.26199 (04)	0.34073 (02)	0.01514 (03)	2.60 (2)
Os(3)	0.03698 (04)	0.26599 (02)	0.11291 (03)	2.55 (2)
O(1)	0.3732 (06)	0.2723 (04)	0.1178 (04)	3.1 (3)
O(11)	0.2710 (08)	0.1952 (05)	0.3615 (05)	4.4 (4)
O(12)	0.0750 (08)	0.0169 (05)	0.1906 (06)	4.9 (4)
O(13)	0.5051 (09)	0.0379 (06)	0.1545 (07)	6.8 (5)
O(21)	0.2089 (09)	0.5042 (05)	0.1299 (06)	5.3 (4)
O(22)	0.4879 (10)	0.4309 (06)	−0.0826 (06)	7.2 (6)
O(23)	0.0725 (09)	0.3949 (06)	−0.1433 (06)	5.9 (5)
O(31)	−0.1554 (10)	0.4123 (06)	0.0675 (07)	7.3 (6)
O(32)	−0.0211 (07)	0.1747 (05)	−0.0763 (05)	4.5 (4)
O(33)	−0.1597 (09)	0.1595 (06)	0.2252 ()6)	6.2 (5)
O(34)	0.1703 (08)	0.3658 (05)	0.2789 (05)	4.7 (4)
N	0.2379 (08)	0.0745 (05)	−0.0535 (06)	3.2 (4)
C(1)	0.3074 (10)	0.2214 (06)	−0.0565 (07)	2.7 (4)
C(2)	0.2642 (09)	0.1436 (06)	−0.0042 (07)	2.8 (5)
C(3)	0.4564 (11)	0.2094 (07)	−0.0711 (07)	3.7 (5)
C(4)	0.2302 (10)	0.0729 (07)	−0.1596 (07)	3.8 (5)
C(5)	0.2115 (13)	−0.0094 (07)	−0.0161 (09)	5.0 (6)
C(6)	0.4804 (12)	0.3056 (08)	0.1732 (09)	5.5 (7)
C(11)	0.2709 (10)	0.1828 (06)	0.2817 (07)	2.9 (5)
C(12)	0.1495 (11)	0.0686 (07)	0.1710 (07)	3.3 (5)
C(13)	0.4205 (11)	0.0863 (07)	0.1530 (07)	3.6 (5)
C(21)	0.2277 (11)	0.4432 (07)	0.0885 (07)	3.5 (5)
C(22)	0.4101 (12)	0.3935 (07)	−0.0449 (07)	4.2 (6)
C(23)	0.1454 (11)	0.3758 (07)	−0.0825 (07)	3.5 (5)
C(31)	−0.0813 (11)	0.3584 (07)	0.0823 (08)	3.9 (6)
C(32)	0.0004 (11)	0.2069 (06)	−0.0059 (08)	3.5 (5)
C(33)	−0.0829 (11)	0.1970 (07)	0.1853 (07)	3.5 (5)
C(34)	0.1210 (11)	0.3272 (07)	0.2174 (08)	3.4 (5)
H(1)	0.272 (10)	0.225 (07)	−0.114 (07)	5.0

Table VI. Intramolecular Distances for 3[a]

Os(1)–Os(3)	2.9009 (7)	Os(2)–C(23)	1.87 (1)
Os(1)–Os(2)	3.4091 (7)	Os(3)–C(31)	1.91 (1)
Os(1)–O(1)	2.128 (7)	Os(3)–C(32)	1.94 (1)
Os(1)–C(2)	2.13 (1)	Os(3)–C(33)	1.93 (1)
Os(1)–C(11)	1.96 (1)	Os(3)–C(34)	1.93 (1)
Os(1)–C(12)	1.87 (1)	O(1)–C(6)	1.41 (1)
Os(1)–C(13)	1.89 (1)	O–C(av)	1.14 (1)
Os(2)–Os(3)	2.9276 (8)	N–C(2)	1.31 (1)
Os(2)–O(1)	2.098 (6)	N–C(4)	1.50 (1)
Os(2)–C(1)	2.18 (1)	N–C(5)	1.44 (1)
Os(2)–C(21)	1.95 (1)	C(1)–C(2)	1.50 (1)
Os(2)–C(22)	1.92 (1)	C(1)–C(3)	1.53 (1)

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

The reaction of **1** with MeC_2NMe_2 also yielded a small amount of $Os_3(CO)_{10}(\mu\text{-}OMe)[\mu\text{-}MeC(H)CNMe_2]$ (**3**). Compound **3** was characterized by IR and ^1H NMR spectroscopy and by single-crystal X-ray diffraction analysis. An ORTEP drawing of compound **3** is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected interatomic bond distances and angles are listed in Tables VI and VII, respectively. The molecule consists of an open triangular cluster of three osmium atoms with 10 linear terminal carbonyl ligands distributed among the metal atoms, as shown in Figure 2. There are two osmium–osmium bonds, Os(1)–Os(3) = 2.9009 (7) Å and Os(2)–Os(3) = 2.9276 (8) Å, and one nonbonding osmium–osmium distance, Os(1)–Os(2) = 3.4091 (7) Å. As in **2**, this nonbonding distance is bridged by the methoxide ligand. The most interesting ligand is the $MeC(H)NMe_2$ group, which bridges the nonbonding Os(1)–Os(2) distance. The ligand is best viewed as an NMe_2-substituted alkenyl ligand, but unlike the ligand in **2**, the NMe_2-substituted carbon atom is coordinated only to one metal atom Os(1), Os(1)–C(2) = 2.13 (1) Å, and the

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(9) Adams, R. D.; Babin, J. E. *Organometallics* **1987**, *6*, 1364.

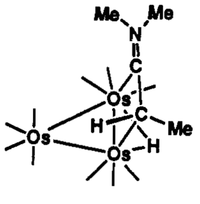
(10) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *140*, 297.

Table VII. Intramolecular Bond Angles for 3[a]

C(12)–Os(1)–C(2)	97.1 (4)	C(33)–Os(3)–Os(1)	95.5 (3)
C(12)–Os(1)–Os(3)	87.5 (3)	C(33)–Os(3)–Os(2)	167.1 (3)
C(13)–Os(1)–C(2)	89.2 (4)	C(34)–Os(3)–Os(1)	80.8 (3)
C(13)–Os(1)–Os(3)	174.0 (3)	C(34)–Os(3)–Os(2)	80.6 (3)
C(11)–Os(1)–C(2)	174.2 (4)	C(32)–Os(3)–Os(1)	89.3 (3)
C(11)–Os(1)–Os(3)	91.5 (3)	C(32)–Os(3)–Os(2)	84.9 (3)
C(2)–Os(1)–O(1)	84.1 (3)	Os(1)–Os(3)–Os(2)	71.60 (2)
C(2)–Os(1)–Os(3)	84.9 (2)	C(6)–O(1)–Os(2)	125.3 (7)
O(1)–Os(1)–Os(3)	82.2 (2)	C(6)–O(1)–Os(1)	125.7 (6)
C(23)–Os(2)–C(1)	92.5 (4)	Os(2)–O(1)–Os(1)	107.6 (3)
C(23)–Os(2)–Os(3)	89.5 (3)	C(2)–N–C(5)	126.3 (9)
C(22)–Os(2)–C(1)	89.3 (4)	C(2)–N–C(4)	123.4 (9)
C(22)–Os(2)–Os(3)	177.5 (3)	C(5)–N–C(4)	110.3 (8)
C(21)–Os(2)–C(1)	175.3 (4)	C(2)–C(1)–C(3)	105.5 (8)
C(21)–Os(2)–Os(3)	85.8 (3)	C(2)–C(1)–Os(2)	113.6 (6)
O(1)–Os(2)–C(1)	76.7 (3)	C(3)–C(1)–Os(2)	112.8 (7)
O(1)–Os(2)–Os(3)	82.6 (2)	N–C(2)–C(1)	117.8 (9)
C(1)–Os(2)–Os(3)	93.0 (3)	N–C(2)–Os(1)	127.7 (7)
C(31)–Os(3)–Os(1)	165.2 (3)	C(1)–C(2)–Os(1)	114.3 (6)
C(31)–Os(3)–Os(2)	94.2 (3)	O–C(av)–Os	176 (2)

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

nitrogen atom is not coordinated. This complex is very similar to the complex $Os_3(CO)_{10}[\mu\text{-}MeC(H)CNMe_2](\mu\text{-}H)$ (**10**).[2] The nitrogen atom in **3** is planar, and the short C(2)–N distance of 1.31 (1) Å (1.35 (2) Å for **10**) is indicative of partial multiple C–N bonding. The observation of two *N*-methyl resonances in the ^1H NMR spectrum indicates the existence of a significantly hindered rotation about the C(1)–N bond. The C(1)–C(2) distance of 1.50 (1) Å is identical with the corresponding distance found in **10**. The formation is compound **3** from the reaction of **1** plus ynamine must also involve a CO addition. It was subsequently discovered that compounds **2** and **3** could be interconverted in good yields by CO addition and elimination reactions (see Scheme I).



10

The reaction of **2** with hydrogen (1 atm) at 80 °C yielded two new compounds $Os_3(CO)_8(\mu\text{-}OMe)[\mu_3\text{-}\eta^2\text{-}MeC(H)CNMe_2](\mu\text{-}H)(H)$ (**4**) and $Os_3(CO)_9(\mu\text{-}OMe)[\mu_3\text{-}\eta^2\text{-}(Et)CNMe_2](\mu\text{-}H)$ (**5**) in 38% and 15% yields, respectively. Compounds **4** and **5** were both characterized by IR and ^1H NMR spectroscopy and single-crystal X-ray diffraction analyses. Compound **4** crystallized with two independent molecules in the unit cell, but due to disorder a good refinement was not obtained. The dimethylphenylphosphine derivative of **4** was subsequently prepared, and a high-quality structural analysis of this compound was obtained; see below. Therefore, the structural features of compound **4** will be discussed only briefly. Both independent molecules in the crystal of **4** are structurally similar. An ORTEP drawing of one of these (molecule B) is shown in Figure 3. Selected interatomic bond distances and bond angles for both molecules are listed in Tables VIII and IX, respectively. The molecule consists of an open cluster of three osmium atoms with eight linear terminal carbonyl ligands. The NMe_2-substituted alkenyl ligand exhibits the normal σ-π coordination to two metal atoms, and the nitrogen atom is coordinated to the third metal atom, Os(2)–N(1) = 2.11(3) Å. Two resonances were observed in the hydride region of the ^1H NMR spectrum at –6.54 and –11.37 ppm. The resonance at –6.54 ppm is characteristic of a terminal hydride ligand, and its position is clearly indicated by the "vacant" coordination site trans to C(1) and Os(1). The resonance at –11.37 ppm is attributed to a bridging hydride ligand that is believed to bridge the long osmium–osmium distance, Os(1)–Os(3) = 2.911 (5) Å. Although the distances are not precise, the Os(1)–alkenyl carbon distances, Os(1)–C(1) = 2.53 (4) Å and Os(1)–C(2) = 2.30 (3) Å, are significantly longer than those found in **2**, 2.260 (7) and 2.113 (9) Å. This was further confirmed by the structure of **6**; see below. The bond lengthening might be due to a *trans influence* of the terminal hydride ligand on Os(1). Metal–ligand bonds trans to terminal

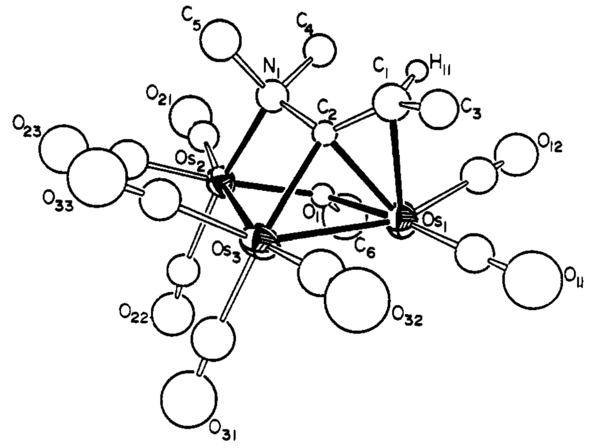


Figure 3. ORTEP diagram of $Os_3(CO)_8[\mu_3\text{-}\eta^3\text{-}MeC(H)CNMe_2](\mu\text{-}OMe)(\mu\text{-}H)(H)$ (**4**) (molecule B), showing 50% probability thermal ellipsoids.

Table VIII. Intramolecular Distances for 4[a]

Os(1B)–Os(3B)	2.911 (5)	Os(2A)–C(22A)	1.98 (6)
Os(1B)–O(1B)	2.11 (2)	Os(2A)–C(23A)	1.85 (4)
Os(1B)–C(2B)	2.30 (3)	Os(3B)–C(2B)	2.21 (4)
Os(1B)–C(11B)	1.85 (4)	Os(3B)–C(31B)	1.89 (6)
Os(1B)–C(12B)	1.99 (6)	Os(3B)–C(32B)	1.83 (5)
Os(1A)–Os(3A)	2.909 (5)	Os(3B)–C(33B)	1.94 (5)
Os(1A)–O(1A)	2.11 (3)	Os(3A)–C(2A)	1.72 (6)
Os(1A)–C(2A)	2.23 (5)	Os(3A)–C(31A)	1.85 (7)
Os(1A)–C(11A)	1.82 (4)	Os(3A)–C(32A)	1.84 (4)
Os(1A)–C(12A)	2.00 (6)	Os(3A)–C(33A)	1.93 (5)
Os(2B)–Os(3B)	2.801 (6)	O(1A)–C(6A)	1.43 (5)
Os(2B)–O(1B)	2.02 (3)	O(1B)–C(6B)	1.39 (6)
Os(2B)–N(1B)	2.11 (3)	N(1B)–C(2B)	1.54 (5)
Os(2B)–C(21B)	1.95 (4)	N(1A)–C(2A)	1.76 (6)
Os(2B)–C(22B)	1.92 (4)	C(1A)–C(2A)	1.61 (7)
Os(2B)–C(23B)	1.82 (6)	C(1A)–C(3A)	1.37 (7)
Os(2A)–Os(3A)	2.801 (6)	C(1B)–C(2B)	1.31 (6)
Os(2A)–O(1A)	2.12 (3)	C(1B)–C(3B)	1.44 (6)
Os(2A)–N(1A)	2.18 (4)	O–C(av)	1.14 (6)
Os(2A)–C(21A)	1.93 (6)		

[a] Two symmetry-independent molecules in the crystal are labeled as A and B accordingly. Distances are in angstroms.

Table IX. Intramolecular Bond Angles for 4[a]

Os(3B)–Os(1B)–O(1B)	79.1 (8)	Os(1B)–C(2B)–Os(3B)	80 (1)
Os(3B)–Os(1B)–C(2B)	48 (1)	Os(1B)–C(2B)–N(1B)	114 (2)
O(1B)–Os(1B)–C(2B)	77 (1)	Os(1B)–C(2B)–C(1B)	84 (3)
Os(3A)–Os(1A)–O(1A)	81.8 (9)	Os(3B)–C(2B)–N(1B)	103 (2)
Os(3A)–Os(1A)–C(2A)	36 (1)	Os(3B)–C(2B)–C(1B)	131 (3)
O(1A)–Os(1A)–C(2A)	79 (1)	Os(1A)–C(2A)–Os(3A)	94 (2)
Os(3A)–Os(2A)–O(1A)	84.4 (7)	Os(1A)–C(2A)–N(1A)	108 (3)
Os(3A)–Os(2A)–N(1A)	73.6 (9)	Os(1A)–C(2A)–C(1A)	78 (3)
Os(1B)–Os(3B)–Os(2B)	77.0 (1)	Os(3A)–C(2A)–N(1A)	121 (3)
Os(1B)–Os(3B)–C(2B)	51 (1)	Os(3A)–C(2A)–C(1A)	145 (3)
Os(2B)–Os(3B)–C(2B)	69.9 (8)		

[a] Two symmetry-independent molecules in the crystal are labeled as A and B accordingly. Angles are in degrees.

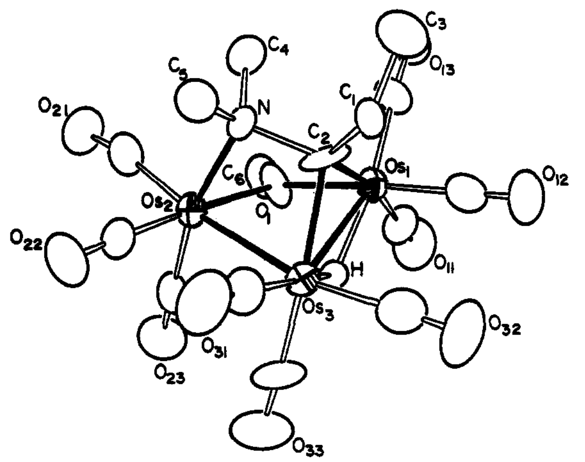


Figure 4. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}EtCNMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (5), showing 50% probability thermal ellipsoids.

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.54213 (04)	0.13107 (04)	0.21414 (04)	2.88 (2)
Os(2)	0.36821 (04)	0.30878 (04)	0.31060 (04)	3.02 (2)
Os(3)	0.36169 (04)	0.24248 (04)	0.11229 (04)	2.75 (2)
O(1)	0.4708 (06)	0.1782 (06)	0.3383 (06)	3.2 (4)
O(11)	0.5079 (09)	−0.0940 (07)	0.2802 (09)	6.9 (6)
O(12)	0.6274 (08)	0.0660 (07)	0.0194 (08)	5.8 (5)
O(13)	0.7771 (08)	0.1408 (07)	0.3080 (08)	5.6 (5)
O(21)	0.3940 (08)	0.4014 (09)	0.5231 (08)	7.0 (6)
O(22)	0.2252 (07)	0.4901 (08)	0.2423 (09)	6.1 (6)
O(23)	0.1621 (08)	0.1907 (08)	0.3443 (08)	6.3 (6)
O(31)	0.2771 (09)	0.4456 (07)	0.0245 (08)	6.3 (6)
O(32)	0.4049 (10)	0.1674 (09)	−0.0980 (08)	7.1 (6)
O(33)	0.1333 (08)	0.1459 (09)	0.1079 (08)	6.8 (6)
N	0.5157 (07)	0.3650 (07)	0.2559 (07)	2.9 (4)
C(1)	0.5983 (09)	0.3266 (10)	0.0917 (10	3.8 (6)
C(2)	0.5297 (09)	0.2880 (08)	0.1626 (09)	3.2 (5)
C(3)	0.7210 (11)	0.3407 (10)	0.1151 (12)	5.3 (8)
C(4)	0.6120 (10)	0.3641 (10)	0.3337 (10)	4.1 (6)
C(5)	0.5034 (10)	0.4752 (09)	0.2196 (12)	4.6 (7)
C(6)	0.4789 (11)	0.1288 (11)	0.4317 (11)	5.1 (7)
C(11)	0.5118 (11)	−0.0141 (10)	0.2559 (10)	4.2 (7)
C(12)	0.5953 (10)	0.0894 (09)	0.0935 (11)	3.9 (7)
C(13)	0.6865 (10)	0.1383 (10)	0.2757 (11)	4.2 (7)
C(21)	0.3948 (11)	0.3647 (11)	0.4455 (12)	4.7 (7)
C(22)	0.2813 (10)	0.4204 (10)	0.2681 (1))	3.9 (6)
C(23)	0.2376 (11)	0.2339 (11)	0.3323 (10)	4.3 (7)
C(31)	0.3104 (10)	0.3704 (11)	0.0584 (10)	4.0 (7)
C(32)	0.3914 (11)	0.1946 (10)	−0.0199 (12)	4.5 (7)
C(33)	0.2201 (11)	0.1824 (11)	0.1065 (10)	4.3 (7)
H	0.391 (07)	0.142 (07)	0.166 (07)	3.0

hydride ligands are known to be longer than bonds cis to terminal hydride ligands.[11]

An ORTEP drawing of 5 is shown in Figure 4. Final atomic positional parameters are listed in Table X. Selected interatomic bond distances and bond angles are listed in Tables XI and XII, respectively. The molecule consists of an open triangular cluster of three osmium atoms with nine linear terminal carbonyl ligands distributed as shown in Figure 4. The $MeCH_2CNMe_2$ ligand in this molecule can be viewed as a dihapto triplybridging ethyl(dimethylamino)carbene ligand with C(2) as the carbene carbon atom. The two recently reported complexes $Os_3(CO)_9[\mu_3\text{-}C(H)NMe_2](\mu\text{-}H)_2$ (11)[12] and $Os_3(CO)_9(\mu\text{-}OMe)[\mu_3\text{-}\eta^2\text{-}C(H)NMe_2](\mu\text{-}H)$ (12)[9] contain the first examples of a triply bridging aminocarbene ligand. Compound 5 is most similar to 12 and differs only by the presence of an ethyl group on the carbene carbon C(2) instead of a hydrogen atom. Structurally, the molecules are also very similar. The osmium–osmium bonding distances in 5 are Os(1)–Os(3) = 2.8778 (7) Å and Os(2)–Os(3) = 2.7816 (8) Å. The corresponding distances found in 12 are 2.873 (1) and 2.793 (1) Å. The nonbonding osmium–osmium distance, Os(2)–Os(3) = 3.4958 (7) Å, is bridged by the methoxide ligand. The carbene carbon atom, C(2), bridges the Os(1)–Os(3) bond symmetrically, Os(1)–C(2) = 2.16 (1) Å and Os(3)–C(2) = 2.19 (1) Å. The nitrogen atom is coordinated to the third metal atom, Os(2)–N = 2.16 (1) Å. This distance is similar to the corresponding distance found in 12, 2.15 (1) Å. The coordination of the nitrogen atom produces a significant lengthening of the carbene carbon–nitrogen bond distance, 1.62 (1) Å. In terminally coordinated aminocarbene ligands, the C–N bond distance is usually much shorter, 1.30–1.35 Å.[9,13] The C(2)–N distance is even longer than the C–N single-bond distances to the methyl groups, C(4)–N = 1.49 (2) Å and C(5)–N = 1.52(1) Å. A relatively long C–N distance 1.54 (2) Å was also found in compound 12. The hydride ligand (δ = −10.83 ppm), which bridges the longest osmium–osmium distance, Os(1)–Os(3), was located and successfully refined crystallographically, Os(1)–H = 1.92 (9) Å and Os(3)–H = 1.5 (1) Å.

The close similarities of 4 and 5 suggested that 4 is most probably a precursor to 5. However, our initial attempts to add CO to 4 (1 atm of CO) in hydrocarbon solvent resulted not in the formation of compound 5 but yielded instead the complex $Os_3(CO)_{10}(\mu\text{-}OMe)(\mu\text{-}H)$ in 80% yield. The fate of the missing $MeC(H)CNMe_2$ ligand is unknown.

Table XI. Intramolecular Distances for 5[a]

Os(1)–Os(3)	2.8778 (7)	Os(2)–C(23)	1.93 (2)
Os(1)–Os(2)	3.4958 (7)	Os(3)–C(2)	2.19 (1)
Os(1)–H	1.92 (9)	Os(3)–C(31)	1.90 (1)
Os(1)–O(1)	2.054 (7)	Os(3)–C(32)	1.95 (2)
Os(1)–C(2)	2.16 (1)	Os(3)–C(33)	1.91 (1)
Os(1)–C(11)	2.00 (1)	Os(3)–H	1.5 (1)
Os(1)–C(12)	1.88 (1)	O(1)–C(6)	1.40 (2)
Os(1)–C(13)	1.89 (1)	O–C(av)	1.14 (2)
Os(2)–Os(3)	2.7816 (8)	N–C(2)	1.62 (1)
Os(2)–O(1)	2.129 (7)	N–C(4)	1.49 (2)
Os(2)–N	2.161 (9)	N–C(5)	1.52 (1)
Os(2)–C(21)	1.94 (2)	C(1)–C(2)	1.43 (2)
Os(2)–C(22)	1.86 (1)	C(1)–C(3)	1.53 (2)

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

Table XII. Intramolecular Bond Angles for 5[a]

Os(3)–Os(1)–O(1)	81.6 (2)	Os(2)–Os(3)–C(2)	72.2 (3)
Os(3)–Os(1)–C(2)	49.2 (3)	Os(2)–Os(3)–C(31)	93.7 (4)
Os(3)–Os(1)–C(11)	118.7 (4)	Os(2)–Os(3)–C(32)	167.5 (4)
Os(3)–Os(1)–C(12)	93.6 (4)	Os(2)–Os(3)–C(33)	95.7 (4)
Os(3)–Os(1)–C(13)	146.2 (4)	Os(1)–O(1)–Os(2)	113.4 (3)
Os(3)–Os(2)–O(1)	82.8 (2)	Os(1)–O(1)–C(6)	126.0 (7)
Os(3)–Os(2)–N	73.9 (2)	Os(2)–O(1)–C(6)	120.5 (7)
Os(3)–Os(2)–C(21)	170.9 (4)	C(2)–C(1)–C(3)	124 (1)
Os(3)–Os(2)–C(22)	89.7 (4)	Os(1)–C(2)–Os(3)	82.8 (3)
Os(3)–Os(2)–C(23)	92.7 (4)	Os(1)–C(2)–N	110.4 (7)
O(1)–Os(2)–N	79.7 (3)	Os(3)–C(2)–N	103.1 (7)
Os(1)–Os(3)–Os(2)	76.28 (2)	Os(3)–C(2)–C(1)	120.0 (9)
Os(1)–Os(3)–C(2)	48.0 (3)	N–C(2)–C(1)	114.3 (8)
Os(1)–Os(3)–C(31)	146.4 (4)	O–C–Os(av)	177 (1)
Os(1)–Os(3)–C(32)	93.3 (4)	Os(1)–H–Os(3)	113 (5)
Os(1)–Os(3)–C(33)	118.2 (4)		

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

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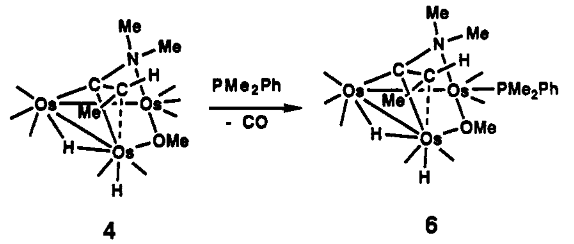
(13) Schubert, U. In *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissel, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, Germany, 1983.

Table XIII. Positional Parameters and *B*(eq) for 6

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.65587 (07)	0.18230 (05)	0.46977 (03)	2.66 (3)
Os(2)	0.78485 (07)	0.34315 (05)	0.35243 (03)	2.47 (3)
Os(3)	0.94705 (07)	0.22362 (05)	0.43310 (03)	2.52 (3)
P	0.6381 (05)	0.4712 (04)	0.2973 (02)	3.3 (2)
O(1)	0.6070 (11)	0.2586 (08)	0.3898 (05)	2.8 (5)
O(11)	0.7194 (15)	0.0316 (13)	0.5689 (08)	6 (1)
O(12)	0.3592 (17)	0.2222 (13)	0.5110 (07)	6 (1)
O(21)	1.0523 (16)	0.4561 (12)	0.3111 (06)	5.0 (8)
O(22)	0.8110 (18)	0.1736 (13)	0.2592 (07)	7 (1)
O(31)	1.0812 (15)	0.1022 (11)	0.5352 (07)	5.0 (8)
O(32)	1.0413 (17)	0.0499 (14)	0.3446 (07)	7 (1)
O(33)	1.2096 (13)	0.3716 (11)	0.4168 (06)	4.4 (7)
N	0.7618 (13)	0.4352 (10)	0.4326 (05)	2.1 (6)
C(1)	0.7481 (18)	0.3471 (16)	0.5296 (08)	4 (1)
C(2)	0.8094 (17)	0.3425 (13)	0.4732 (07)	2.6 (8)
C(3)	0.814 (02)	0.3011 (16)	0.5799 (08)	4 (1)
C(4)	0.8607 (16)	0.5316 (12)	0.4391 (08)	2.6 (8)
C(5)	0.6151 (20)	0.4857 (15)	0.4412 (09)	4 (1)
C(6)	0.5157 (20)	0.1878 (17)	0.3558 (09)	4 (1)
C(7)	0.446 (02)	0.463 (02)	0.3010 (11)	6 (1)
C(8)	0.673 (02)	0.4544 (17)	0.2233 (08)	5 (1)
C(11)	0.6964 (19)	0.0904 (13)	0.5310 (08)	3 (1)
C(12)	0.4737 (19)	0.2078 (14)	0.4949 (08)	3.1 (9)
C(21)	0.949 (02)	0.4134 (16)	0.3279 (08)	3 (1)
C(22)	0.8024 (19)	0.2387 (16)	0.2941 (08)	3.3 (9)
C(31)	1.0284 (18)	0.1469 (14)	0.4974 (08)	3.0 (9)
C(32)	1.007 (02)	0.1140 (16)	0.3775 (09)	4 (1)
C(33)	1.1118 (18)	0.3178 (15)	0.4214 (07)	3.0 (9)
C(40)	0.6735 (19)	0.6236 (14)	0.3075 (08)	3.3 (9)
C(41)	0.575 (02)	0.6944 (18)	0.3351 (09)	5 (1)
C(42)	0.609 (03)	0.8065 (19)	0.3508 (10)	5 (1)
C(43)	0.735 (03)	0.8490 (18)	0.3362 (13)	7 (2)
C(44)	0.842 (03)	0.782 (02)	0.3080 (11)	7 (1)
C(45)	0.805 (02)	0.6699 (16)	0.2935 (09)	5 (1)
H(1)	0.581 (15)	0.076 (11)	0.431 (06)	2.9 (8)
H(2)	0.797 (16)	0.165 (12)	0.441 (07)	3.9 (8)

This reaction was followed by ^{1}H NMR spectroscopy in a sealed NMR tube in toluene-d_8 solvent. These spectra showed only a smooth transformation of 4 to $Os_3(CO)_{10}(\mu\text{-}OMe)(\mu\text{-}H)$. At no time during the reaction was the hydride resonance due to compound 5 observed.

The reactions of 4 with other nucleophiles were subsequently investigated. Interestingly, the reaction of 4 with dimethylphenylphosphine did not result in hydrogen transfer to the ligand but instead yielded the phosphine-substituted derivative $Os_3(CO)_7(\mu\text{-}OMe)[\mu_3\text{-}\eta^2\text{-}MeC(H)CNMe_2](PMe_2Ph)(\mu\text{-}H)(H)$ (6) as the only product (eq 2).



4 6 (2)

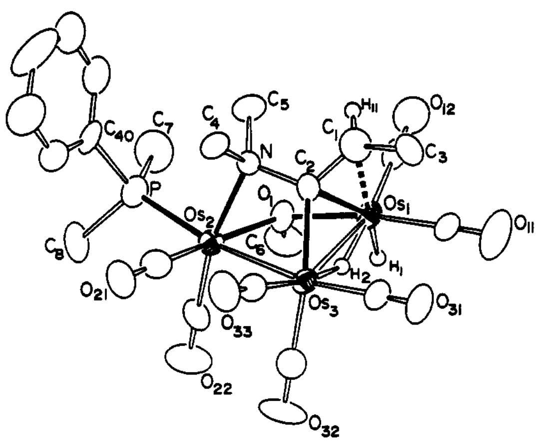


Figure 5. ORTEP diagram of $Os_3(CO)_8(PMe_2Ph)[\mu_3\text{-}\eta^3\text{-}MeC(H)CNMe_2](\mu\text{-}OMe)(\mu\text{-}H)(H)$ (6), showing 50% probability thermal ellipsoids.

Table XIV. Intramolecular Distances for 6[a]

Os(1)–Os(3)	2.914 (1)	Os(3)–C(31)	1.93 (2)
Os(1)–Os(2)	3.583 (1)	Os(3)–C(32)	1.93 (2)
Os(1)–O(1)	2.15 (1)	Os(3)–C(33)	1.92 (2)
Os(1)–C(2)	2.36 (2)	Os(3)–H(2)	1.6 (1)
Os(1)–C(11)	1.85 (2)	P–C(7)	1.81 (2)
Os(1)–C(12)	1.84 (2)	P–C(8)	1.81 (2)
Os(1)–H(1)	1.7 (1)	P–C(40)	1.82 (2)
Os(1)–H(2)	1.5 (2)	O–C(av)	1.14 (2)
Os(2)–Os(3)	2.812 (1)	O(1)–C(6)	1.43 (2)
Os(2)–P	2.412 (5)	N–C(2)	1.51 (2)
Os(2)–O(1)	2.14 (1)	N–C(4)	1.47 (2)
Os(2)–N	2.20 (1)	N–C(5)	1.51 (2)
Os(2)–C(21)	1.84 (2)	C(1)–C(2)	1.41 (2)
Os(2)–C(22)	1.86 (2)	C(1)–C(3)	1.50 (2)
Os(3)–C(2)	2.13 (2)		

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

Table XV. Intramolecular Bond Angles for 6[a]

Os(3)–Os(1)–C(2)	46.1 (4)	Os(2)–Os(3)–C(2)	69.9 (4)
Os(3)–Os(1)–C(11)	98.3 (6)	Os(2)–Os(3)–C(31)	169.3 (5)
Os(3)–Os(1)–C(12)	161.1 (5)	Os(2)–Os(3)–C(32)	91.1 (6)
Os(3)–Os(1)–H(1)	110 (5)	Os(2)–Os(3)–C(33)	92.9 (5)
O(1)–Os(1)–C(2)	80.2 (5)	C(32)–Os(3)–C(33)	92.3 (8)
O(1)–Os(1)–C(11)	168.9 (6)	Os(1)–O(1)–Os(3)	113.4 (5)
O(1)–Os(1)–C(12)	91.6 (6)	Os(1)–O(1)–C(6)	113 (1)
O(1)–Os(1)–H(1)	74 (5)	Os(2)–O(1)–C(6)	120 (1)
C(2)–Os(1)–H(1)	148 (5)	Os(2)–N–C(2)	100.2 (9)
C(11)–Os(1)–H(1)	95 (5)	Os(2)–N–C(4)	114 (1)
C(12)–Os(1)–H(1)	85 (5)	Os(2)–N–C(5)	114 (1)
Os(3)–Os(2)–P	169.2 (1)	C(2)–C(1)–C(3)	126 (2)
Os(3)–Os(2)–N	72.8 (3)	Os(1)–C(2)–Os(3)	80.9 (5)
Os(3)–Os(2)–C(21)	89.2 (5)	Os(1)–C(2)–N	111 (1)
Os(3)–Os(2)–C(22)	97.8 (6)	Os(1)–C(2)–C(1)	79 (1)
Os(1)–Os(3)–Os(2)	77.45 (3)	Os(3)–C(2)–N	111 (1)
Os(1)–Os(3)–C(31)	93.0 (5)	Os(3)–C(2)–C(1)	133 (1)
Os(1)–Os(3)–C(32)	112.1 (6)	N–C(2)–C(1)	116 (1)
Os(1)–Os(3)–C(33)	153.7 (5)	Os–C–O(av)	178 (2)

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

Compound 6 was characterized by IR and ^{1}H NMR spectroscopy and by single-crystal X-ray diffraction analysis. An ORTEP drawing of its molecular structure is shown in Figure 5. Final atomic positional parameters are listed in Table XIII. Selected interatomic bond distances and bond angles are listed in Tables XIV and XV, respectively. The structure of the molecule is very similar to that of 4, with the exception of the presence of a dimethylphenylphosphine ligand coordinated to Os(2). The nonbonding osmium–osmium distance, Os(1)–Os(2) = 3.583 (1) Å, is once again bridged by the methoxide ligand. Due to the high quality of the structure both of the hydride ligands were located crystallographically and successfully refined. The hydride resonances were observed in the ^{1}H NMR spectrum at −6.07 ppm (terminal) and −11.38 ppm (bridge). Hydride H(2) bridges the Os(1)–Os(3) bond, Os(1)–H(2) = 1.5 (2) Å and Os(3)–H(2) = 1.6 (1) Å, and as a result, the Os(1)–Os(3) distance of 2.914 (1) Å is significantly longer than the Os(2)–Os(3) distance of 2.812 (1) Å. The terminal hydride ligand is bonded to Os(1), Os(1)–H(1) = 1.7 (1) Å, and occupies the coordination site trans to the methyl-substituted alkenyl carbon atom C(1), as anticipated for 4. The *trans influence* of the terminal hydride ligand is clearly seen in the long Os(1)–C(1) distance of 2.50 (2) Å, which is substantially longer than the

Table XVI. Positional Parameters and B(eq) for 7

atom	x	y	z	B(eq), Å^2
Os(1)	0.15714 (03)	0.34564 (02)	0.29550 (03)	2.54 (1)
Os(2)	0.22947 (04)	0.14765 (02)	0.11354 (04)	3.01 (2)
Os(3)	0.35097 (04)	0.19523 (02)	0.45776 (04)	2.79 (1)
O(1)	0.1814 (06)	0.2789 (03)	0.0854 (06)	2.9 (2)
O(11)	−0.1611 (07)	0.4474 (04)	0.0985 (07)	5.2 (3)
O(12)	0.1379 (08)	0.4329 (04)	0.6088 (07)	5.3 (3)
O(21)	0.5475 (09)	0.1314 (06)	0.1010 (10)	7.1 (5)
O(22)	0.0616 (09)	0.0885 (05)	−0.2598 (08)	6.6 (4)
O(23)	0.3068 (08)	−0.0348 (05)	0.1952 (08)	5.5 (3)
O(31)	0.7010 (08)	0.1557 (05)	0.5189 (10)	6.8 (4)
O(32)	0.3380 (08)	0.0294 (05)	0.5740 (09)	6.0 (4)
O(33)	0.4336 (08)	0.2706 (05)	0.8160 (08)	5.7 (4)
N(1)	0.0271 (07)	0.1784 (04)	0.1792 (07)	3.0 (3)
N(2)	0.2980 (07)	0.4338 (04)	0.2684 (07)	3.2 (3)
C(1)	0.0066 (10)	0.2440 (06)	0.4521 (10)	3.6 (4)
C(2)	0.0939 (08)	0.2385 (05)	0.3391 (08)	2.8 (3)
C(3)	−0.1588 (11)	0.2939 (07)	0.3923 (12)	4.8 (5)
C(4)	−0.1204 (09)	0.2194 (06)	0.0379 (09)	3.8 (4)
C(5)	−0.0196 (10)	0.1026 (06)	0.2109 (11)	4.0 (4)
C(6)	0.1163 (10)	0.3142 (06)	−0.0765 (09)	4.1 (4)
C(11)	−0.0380 (10)	0.4088 (06)	0.1719 (09)	3.7 (4)
C(12)	0.1466 (09)	0.3992 (05)	0.4865 (10)	3.3 (4)
C(21)	0.4284 (11)	0.1372 (07)	0.1043 (11)	4.7 (5)
C(22)	0.1106 (11)	0.1189 (06)	−0.1260 (11)	4.3 (4)
C(23)	0.2792 (10)	0.0349 (07)	0.1660 (10)	3.9 (4)
C(31)	0.5704 (11)	0.1680 (06)	0.4942 (10)	4.4 (4)
C(32)	0.3406 (10)	0.0903 (06)	0.5237 (10)	3.9 (4)
C(33)	0.3947 (10)	0.2447 (06)	0.6788 (10)	3.8 (4)
C(40)	0.4089 (10)	0.4045 (06)	0.2116 (10)	4.1 (4)
C(41)	0.5006 (10)	0.4558 (08)	0.1949 (11)	5.0 (5)
C(42)	0.4796 (12)	0.5399 (07)	0.2441 (12)	5.4 (5)
C(43)	0.3693 (12)	0.5695 (07)	0.3054 (11)	5.0 (5)
C(44)	0.2796 (11)	0.5163 (06)	0.3154 (10)	4.2 (4)
H(1)	0.350 (12)	0.280 (07)	0.388 (12)	8.3 (8)

corresponding distance of 2.343 (9) Å found in compound 2 and is similar to the corresponding distance of 2.53 (4) Å found in 4. The Os(2)–N and C(1)–C(2) distances of 2.20 (1) and 1.41 (2) Å are also similar to the corresponding distances found in 2.

In contrast to the reactions of 4 with CO and PMe_2Ph, the reaction of 4 with pyridine in a refluxing hexane solution yielded the new complex $Os_3(CO)_8(py)(\mu\text{-}OMe)[\mu_3\text{-}\eta^2\text{-}(Et)CNMe_2](\mu\text{-}H)$ (7) in 17% yield. Compound 7 was characterized by IR and ^1H NMR spectroscopy and by single-crystal X-ray diffraction analysis. An ORTEP diagram of compound 7 is shown in Figure 6. Final atomic positional parameters are listed in Table XVI. Selected interatomic bond distances and bond angles are listed in Tables XVII and XVIII, respectively. Compound 7 is a pyridine-substituted derivative of compound 5 and contains a triply bridging aminocarbene ligand. The carbene carbon, C(2), bridges the Os(1)–Os(3) bond fairly symmetrically, Os(1)–C(2) = 2.098 (8) Å and Os(3)–C(2) = 2.199 (7) Å. The nitrogen atom is coordinated to the third metal atom, Os(2)–N(1) = 2.189 (6) Å, as in 5. The hydrogen atoms on C(1) are diastereotopic and show the expected geminal coupling to each other as well as to the methyl group, $^2J_{H-H}$ = 16.0 Hz and $^3J_{H-H}$ = 6.7 and 7.6 Hz. The Os(1)–Os(3) bond of 2.879 (8) Å is substantially longer than the Os(2)–Os(3) distance of 2.7986 (7) Å, Os(1)–H(1) = 1.8 (1) Å and Os(3)–H(1) = 1.6 (1) Å. The nonbonded pair of atoms Os(1)–Os(2) = 3.481 (1) Å is bridged by the methoxide ligand. The pyridine ligand occupies the coordination site that was formerly occupied by the terminal hydride ligand on Os(1), Os(1)–N(2) = 2.243 (7) Å. When 7 was allowed to react with 1 atm of CO at 68 °C, compound 5 was obtained in 96% yield.

When 5 was heated to 125 °C in octane solvent under an atmosphere of CO, it was isomerized to the new compound $Os_3(CO)_9[C(Et)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (8) in 55% yield. Compound 8 was characterized by IR and ^1H NMR spectroscopy and by single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of 8 is shown in Figure 7. Final atomic positional parameters are listed in Table XIX. Selected interatomic bond distances and bond angles are listed in Tables XX and XXI, respectively. Compound 8 is very similar to the carbene complex $Os_3(CO)_9(\mu\text{-}OMe)[(H)CNMe_2](\mu\text{-}H)$ (13) reported previously.[9] The molecule contains a triangular cluster of

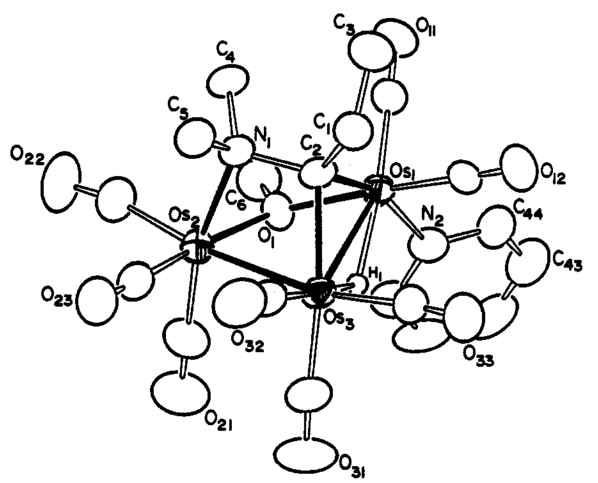


Figure 6. ORTEP drawing of $Os_3(CO)_8(py)[\mu_3\text{-}EtCNMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (7), showing 50% probability thermal ellipsoids.

Table XVII. Intramolecular Distances for 7[a]

Os(1)–Os(3)	2.8791 (8)	Os(3)–C(31)	1.93 (1)
Os(1)–Os(2)	3.481 (1)	Os(3)–C(32)	1.91 (1)
Os(1)–O(1)	2.098 (5)	Os(3)–C(33)	1.906 (9)
Os(1)–N(2)	2.243 (7)	Os(1)–Os(2)	3.481 (1)
Os(1)–C(2)	2.098 (8)	Os(1)–H(1)	1.8 (1)
Os(1)–C(11)	1.863 (9)	Os(3)–H(1)	1.6 (1)
Os(1)–C(12)	1.825 (8)	O(1)–C(6)	1.438 (9)
Os(2)–Os(3)	2.7986 (7)	O–C(av)	1.15 (1)
Os(2)–O(1)	2.117 (5)	N(1)–C(2)	1.55 (1)
Os(2)–N(1)	2.189 (6)	N(2)–C(40)	1.34 (1)
Os(2)–C(21)	1.90 (1)	N(2)–C(44)	1.35 (1)
Os(2)–C(22)	1.957 (9)	C(1)–C(2)	1.53 (1)
Os(2)–C(23)	1.87 (1)	C(1)–C(3)	1.51 (1)
Os(3)–C(2)	2.199 (7)		

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

Table XVIII. Intramolecular Bond Angles for 7[a]

Os(3)–Os(1)–O(1)	81.8 (1)	Os(2)–Os(3)–C(33)	168.0 (3)
Os(3)–Os(1)–N(2)	112.9 (2)	Os(1)–O(1)–Os(2)	111.3 (2)
Os(3)–Os(1)–C(2)	49.4 (2)	Os(1)–O(1)–C(6)	122.5 (5)
Os(3)–Os(1)–C(11)	152.2 (3)	Os(2)–O(1)–C(6)	122.4 (5)
Os(3)–Os(1)–C(12)	94.8 (2)	Os(2)–N(1)–C(2)	100.7 (4)
O(1)–Os(1)–N(2)	85.1 (2)	Os(2)–N(1)–C(4)	112.2 (5)
O(1)–Os(1)–C(2)	87.4 (2)	Os(2)–N(1)–C(5)	112.5 (5)
N(2)–Os(1)–C(2)	161.7 (3)	C(2)–N(1)–C(4)	113.9 (6)
Os(3)–Os(2)–O(1)	83.5 (1)	C(2)–N(1)–C(5)	113.4 (6)
Os(3)–Os(2)–N(1)	73.5 (1)	C(4)–N(1)–C(5)	104.6 (6)
Os(3)–Os(2)–C(21)	93.6 (3)	Os(1)–N(2)–C(40)	120.0 (6)
Os(3)–Os(2)–C(22)	170.6 (3)	Os(1)–N(2)–C(44)	121.8 (6)
Os(3)–Os(2)–C(23)	89.7 (2)	C(2)–C(1)–C(3)	117.9 (7)
O(1)–Os(2)–N(1)	81.3 (2)	Os(1)–C(2)–Os(3)	84.1 (3)
Os(1)–Os(3)–Os(2)	75.61 (2)	Os(1)–C(2)–N(1)	113.8 (4)
Os(1)–Os(3)–C(2)	46.5 (2)	Os(1)–C(2)–C(1)	119.9 (6)
Os(1)–Os(3)–C(31)	120.8 (3)	Os(3)–C(2)–N(1)	106.1 (5)
Os(1)–Os(3)–C(32)	142.6 (2)	Os(3)–C(2)–C(1)	116.3 (5)
Os(1)–Os(3)–C(33)	93.6 (3)	N(1)–C(2)–C(1)	112.8 (6)
Os(2)–Os(3)–C(2)	70.0 (2)	Os–C–O(av)	176.0 (8)
Os(2)–Os(3)–C(31)	95.2 (3)	Os(3)–H(1)–Os(1)	115 (6)
Os(2)–Os(3)–C(32)	94.3 (3)		

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

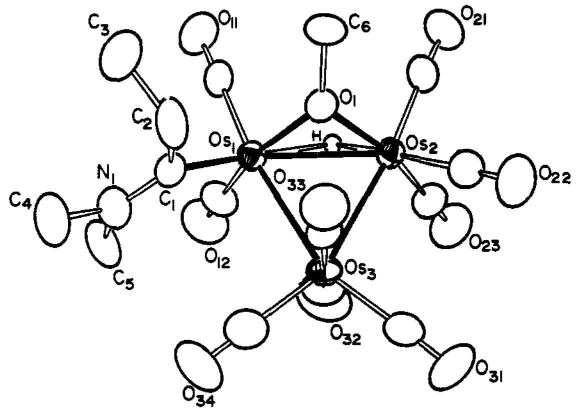


Figure 7. ORTEP diagram of $Os_3(CO)_9[C(Et)NMe_2](\mu\text{-}OMe)(\mu\text{-}H)$ (8), showing 50% probability thermal ellipsoids.

Table XIX. Positional Parameters and *B*(eq) for 8

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.69912 (05)	0.15254 (02)	0.33015 (02)	2.57 (2)
Os(2)	0.66250 (05)	0.03374 (02)	0.21788 (02)	2.71 (2)
Os(3)	0.36909 (05)	0.12573 (02)	0.21482 (02)	2.79 (2)
O(1)	0.6666 (08)	0.0411 (03)	0.3566 (04)	2.9 (3)
O(11)	1.0671 (11)	0.1630 (05)	0.4415 (06)	5.8 (4)
O(12)	0.7572 (12)	0.2891 (05)	0.2388 (06)	6.6 (5)
O(21)	1.0016 (11)	−0.0540 (05)	0.2312 (06)	6.3 (5)
O(22)	0.4026 (12)	−0.0906 (05)	0.1832 (06)	5.9 (4)
O(23)	0.6505 (12)	0.0578 (05)	0.0213 (05)	6.1 (5)
O(31)	0.0955 (12)	0.0510 (05)	0.0739 (06)	6.9 (5)
O(32)	0.5204 (13)	0.2127 (05)	0.0750 (06)	7.3 (5)
O(33)	0.2807 (10)	0.0316 (04)	0.3666 (05)	4.6 (4)
O(34)	0.1565 (12)	0.2475 (05)	0.2753 (06)	6.2 (5)
N(1)	0.5132 (12)	0.2512 (05)	0.4470 (06)	4.2 (4)
C(1)	0.5713 (13)	0.1879 (05)	0.4324 (06)	3.0 (4)
C(2)	0.5527 (15)	0.1319 (05)	0.5016 (07)	4.1 (5)
C(3)	0.694 (02)	0.1413 (07)	0.5852 (08)	6.6 (7)
C(4)	0.4137 (17)	0.2681 (07)	0.5196 (08)	5.7 (7)
C(5)	0.535 (02)	0.3137 (06)	0.3934 (08)	6.2 (7)
C(6)	0.7987 (15)	0.0006 (06)	0.4142 (07)	4.4 (5)
C(11)	0.9267 (14)	0.1583 (05)	0.3991 (07)	3.3 (5)
C(12)	0.7302 (15)	0.2388 (06)	0.2766 (07)	4.0 (5)
C(21)	0.8749 (16)	−0.0208 (06)	0.2287 (07)	3.8 (5)
C(22)	0.5016 (14)	−0.0446 (06)	0.1975 (07)	3.6 (5)
C(23)	0.6536 (14)	0.0490 (06)	0.0942 (07)	4.0 (5)
C(31)	0.1996 (15)	0.0784 (06)	0.1268 (08)	4.1 (5)
C(32)	0.4661 (15)	0.1811 (07)	0.1282 (08)	4.5 (6)
C(33)	0.3165 (13	0.0672 (06)	0.3099 (06)	3.2 (4)
C(34)	0.2392 (15)	0.2031 (06)	0.2528 (07)	4.0 (5)
H	0.810 (11)	0.106 (05)	0.227 (05)	4 (1)

Table XX. Intramolecular Distances for 8[a]

Os(1)–Os(2)	2.8040 (6)	Os(2)–H	1.76 (9)
Os(1)–Os(3)	2.8620 (7)	Os(3)–C(31)	1.92 (1)
Os(1)–O(1)	2.162 (6)	Os(3)–C(32)	1.93 (1)
Os(1)–C(1)	2.09 (1)	Os(3)–C(33)	1.92 (1)
Os(1)–C(11)	1.88 (1)	Os(3)–C(34)	1.91 (1)
Os(1)–C(12)	1.85 (1)	O(1)–C(6)	1.44 (1)
Os(1)–H	2.12 (8)	O–C(av)	1.15 (1)
Os(2)–Os(3)	2.8361 (6)	N(1)–C(1)	1.31 (1)
Os(2)–O(1)	2.115 (6)	N(1)–C(4)	1.49 (1)
Os(2)–C(21)	1.91 (1)	N(1)–C(5)	1.46 (1)
Os(2)–C(22)	1.92 (1)	C(1)–C(2)	1.52 (1)
Os(2)–C(23)	1.90 (1)	C(2)–C(3)	1.53 (2)

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

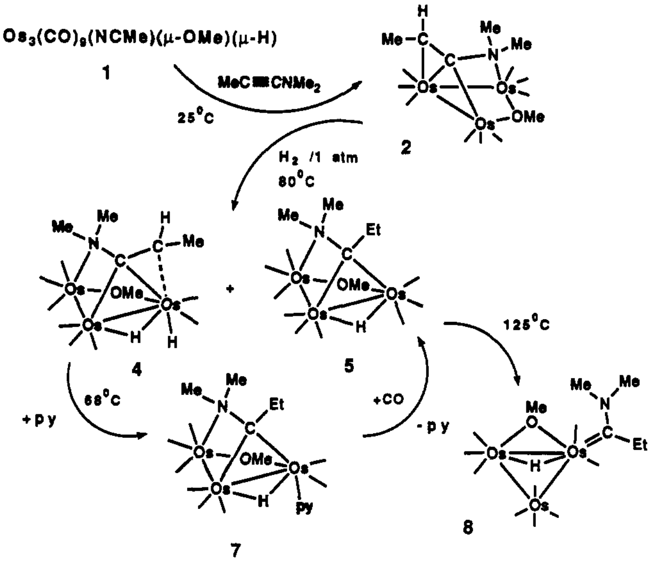
three osmium atoms with three metal–metal bonds, Os(1)–Os(2) = 2.8039 (7) Å, Os(1)–Os(3) = 2.8619 (7) Å, and Os(2)–Os(3) = 2.8362 (6) Å. The Os(1)–Os(2) bond is bridged by the methoxide ligand. The hydride ligand, which bridges the Os(1)–Os(2) bond, was located and refined crystallographically, $\delta = -13.30$ ppm. The metal–carbene carbon distance, Os(1)–C(1) = 2.09 (1) Å, is similar to the corresponding distance found in 13, 2.02 (1) Å. The short C(1)–N distance of 1.31 (1) Å is indicative of multiple bonding between these atoms.[13] The isomerization of 5 to 8 occurred by the formation of a metal–metal bond between Os(1) and Os(2) and a cleavage of the Os–N and one of the Os–C bonds to the carbene carbon that resulted in a shift of the carbene ligand to a terminal coordination mode.

Table XXI. Intramolecular Bond Angles for 8[a]

Os(2)–Os(1)–Os(3)	60.06 (1)	Os(1)–Os(3)–Os(2)	58.95 (2)
oS(2)–Os(1)–O(1)	48.3 (2)	Os(1)–Os(3)–C(31)	158.5 (3)
Os(2)–Os(1)–C(1)	134.4 (3)	Os(1)–Os(3)–C(32)	85.3 (3)
Os(2)–Os(1)–C(11)	111.8 (3)	Os(1)–Os(3)–C(33)	85.3 (3)
Os(2)–Os(1)–C(12)	116.1 (3)	Os(1)–Os(3)–C(34)	97.5 (3)
Os(3)–Os(1)–O(1)	79.9 (2)	Os(2)–Os(3)–C(31)	99.5 (3)
Os(3)–Os(1)–C(1)	92.0 (2)	Os(2)–Os(3)–C(32)	86.6 (3)
Os(3)–Os(1)–C(11)	171.9 (3)	Os(2)–Os(3)–C(33)	84.7 (3)
Os(3)–Os(1)–C(12)	93.0 (4)	Os(2)–Os(3)–C(34)	156.3 (3)
Os(1)–Os(2)–Os(3)	60.98 (2)	Os(1)–O(1)–Os(2)	81.9 (2)
Os(1)–Os(2)–O(1)	49.8 (2)	Os(1)–O(1)–C(6)	122.6 (6)
Os(1)–Os(2)–C(21)	112.7 (3)	Os(2)–O(1)–C(6)	117.4 (6)
Os(1)–Os(2)–C(22)	135.0 (3)	C(1)–N(1)–C(4)	124 (1)
Os(1)–Os(2)–C(23)	117.9 (3)	C(1)–N(1)–C(5)	124 (1)
Os(1)–Os(2)–H	49 (3)	C(4)–N(1)–C(5)	112 (1)
Os(3)–Os(2)–O(1)	81.3 (2)	Os(1)–C(1)–N(1)	129.6 (8)
Os(3)–Os(2)–C(21)	173.7 (3)	Os(1)–C(1)–C(2)	114.2 (7)
Os(3)–Os(2)–C(22)	89.0 (3)	N(1)–C(1)–C(2)	116.2 (9)
Os(3)–Os(2)–C(23)	90.1 (3)	C(1)–C(2)–C(3)	111 (1)
Os(3)–Os(2)–H	92 (3)	O–C–Os(av)	177 (1)
Os(2)–H–Os(1)	92 (4)		

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

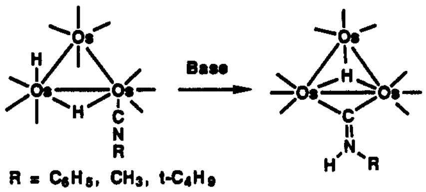
Scheme II



Discussion

Through the isolation of intermediates, we have established many of the details of the mechanism of the unsymmetric hydrogenation of the ynamine $MeC{\equiv}CNMe_2$ by the a methoxy-bridged triosmium cluster to produce an ethyl(dimethylamino)carbene ligand. The results are summarized in Scheme II. The reaction sequence was initiated through the use of the lightly stabilized complex 1. The displacement of the acetonitrile ligand from 1 by the ynamine was accompanied by the transfer of the hydride ligand to the methyl-substituted carbon atom and the formation of a coordinate bond from the nitrogen atom to one of the metal atoms to yield compound 2. The partially hydrogenated triple bond of the ynamine assumed the usual σ-π coordination bridging two metal atoms of the cluster. The coordination of the nitrogen atom to the third osmium atom resulted in the introduction of two additional electrons into the valence shell of the cluster. In order to maintain 18-electron configurations at all three metal atoms, the cluster responded through the cleavage of the metal–metal bond that originally contained the bridging methoxide ligand.

Further hydrogenation of the ynamine was achieved by the reaction of 2 with hydrogen at 80 °C. Interestingly, this reaction yielded two products 4 and 5. Compound 4 was formed by the loss of one CO ligand from 2 and the addition of 1 equiv of H_2. The two hydrogen atoms were identified as hydride ligands, one a bridge and the other a terminal ligand. The partially hydrogenated ynamine ligand repositioned itself on the cluster with the alkenyl grouping π-bonded to one of the methoxy-bridged metal atoms, Os(1), but no hydrogen was added to this ligand. The second product was compound 5. Stoichiometrically, compound 5 was formed simply by the addition of 1 equiv of H_2 to 2. In compound 5, one of the two added hydrogen atoms was identified as a bridging hydride ligand and the other was added to the methyl-substituted carbon atom of the partially hydrogenated ynamine ligand. Mechanistically, we believe complex 4 was an intermediate. The activation of hydrogen by metal complexes is a well-established process.[14] As implied by the formation of 4, the activation of hydrogen by these clusters is also a metal-centered process, probably involving the traditional oxidative-addition mechanism.[14] It remained for us to demonstrate that 4 was a precursor to 5. It seemed that addition of CO accompanied by the formation of a CH bond by the usual reductive elimination process should accomplish this. However, all attempts to form 5 by the addition of CO to 4 in hydrocarbon solvent were unsuccessful and yielded instead only $Os_3(CO)_{10}(\mu\text{-OMe})(\mu\text{-H})$. The transfer of hydrogen from the metal atoms in 4 to the methyl-substituted carbon atom was achieved by the reaction of 4 with pyridine. This yielded the product 7 containing a bridging aminocarbene ligand. Since this reaction was conducted in the absence of CO, a pyridine molecule became coordinated to the metal atom that formerly contained the terminal hydride ligand. The requirement of a nitrogen base to promote the transfer of the hydride ligand from the metal atom to the carbon atom may provide a clue about the mechanism. We have shown previously that strong bases facilitated the transfer of a hydride ligand from a metal atom in the complexes $Os_3(CO)_{10}(CNR)(\mu\text{-H})(H)$, R = Ph, Me, and Bu^t, to the nitrogen atom of the isocyanide ligand to yield the iminyl complexes $Os_3(CO)_{10}[\mu\text{-C}{=}N(H)R](\mu\text{-H})$ (eq 3).[15]



(3)

The rearrangement was interpreted in terms of a base-promoted proton transfer.[15] Likewise, we feel that the base promotion of the hydrogen transfer in 4 to yield 7 also occurs by a proton transfer. We have not identified the base that is responsible for the proton transfer in the original reaction of 2 with hydrogen, but since it is a catalytic process (the base is regenerated after proton transfer), the amount of base involved might have been very small in amount. When exposed to CO, compound 7 was converted to 5 quantitatively, thus completing the 4 to 5 transformation. The failure of the intramolecular reductive elimination mechanism to transform 4 to 5 was unexpected initially. In retrospect, there are two features about the structure of 4 that may have contributed to this. (1) The terminal hydride ligand is positioned trans to the carbon C(1) that must receive it. A trans–cis isomerization barrier would have to be traversed before C–H bond formation could occur. (2) The Os(1)–C(1) bond is unusually long (see above) and presumably weak. If there were no bond between Os(1) and C(1), we would expect the intramolecular reductive elimination barrier to be very large. In 4, the barrier might still be so large that other hydrogen-transfer processes are more favorable.

Throughout the 2 to 5 sequence, the cluster was in an open configuration having only two metal–metal bonds. The completion of the reaction sequence was achieved by heating 5 to 125 °C. At this time, 5 was isomerized to 8 by cleavage of the metal–nitrogen bond, formation of a metal–metal bond between the methoxyl-bridged metal atoms, and a shift of the carbene atom to a terminal coordination site.

These results provide further evidence that the cluster-assisted hydrogenation of ynamines may be a general synthetic route to transition-metal clusters containing (dialkylamino)carbene ligand[1,2] and demonstrate still further the remarkable ability of metal clusters to produce activation and novel transformations of small molecules by utilizing multicenter coordinations and rearrangements.[16]

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Supplementary Material Available: For the structural analyses, tables of hydrogen atom parameters, anisotropic thermal parameters, and positional and isotropic thermal parameters (33 pages); tables of structure factor amplitudes (122 pages). Ordering information is given on any current masthead page.

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