Contribution from the Department of Chemistry and Biochemistry,
University of South Carolina, Columbia, South Carolina 29208

Coordination of Trialkoxysilyl Ligands in Triosmium Cluster Complexes. Complexes with Edge and Triply Bridging Trialkoxysilyl Ligands

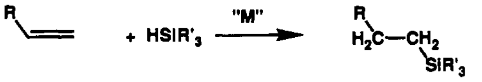
Richard D. Adams,* Jeffrey E. Cortopassi, and Michael P. Pompeo

Received January 17, 1992

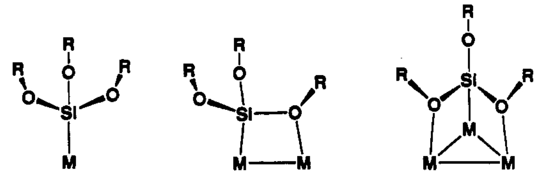
The reactions of $Os_3(CO)_{10}(NCMe)_2$ and $Os_3(CO)_{11}(NCMe)$ with the silanes $HSi(OR)_3$, R = Et and Me, yielded the new complexes $Os_3(CO)_{10}(NCMe)[Si(OR)_3](\mu\text{-}H)$, R = Et and Me (**1a**,**b**), and $Os_3(CO)_{11}[Si(OR)_3](\mu\text{-}H)$, R = Et and Me (**2a**,**b**), respectively. When compounds **1a**,**b** were heated to reflux in hexane solvent, two products $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}Si(OR)_3](\mu\text{-}H)$ (**3a**,**b**; R = Et, Me) and $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}Si(OR)_3](\mu\text{-}H)$ (**4a**,**b**; R = Et, Me) were formed by loss of NCMe and NCMe plus CO, respectively. Compounds **1a**, **3b**, and **4a** were characterized by single-crystal X-ray diffraction analyses. Compound **1a** contains a terminally coordinated $Si(OEt)_3$ ligand in an equatorial coordination site of a triosmium cluster. Compound **3b** contains a bridging $\eta^2\text{-}Si(OMe)_3$ ligand occupying diaxial sites in the triosmium cluster, and compound **4a** contains the first example of a triply bridging $\eta^3\text{-}Si(OEt)_3$ ligand coordinated to the face of the cluster through the silicon atom and the oxygen atoms of two of the OEt groups. Compound **3b** exhibits an unusual dynamical behavior in which the $Si(OMe)_3$ ligand rocks back and forth between two edges of the cluster in a process that averages the bridging OMe group with only one of the uncoordinated OMe groups. Crystal data: for **1a**, space group $P\bar{1}$, $a = 16.630$ (5) Å, $b = 20.062$ (7) Å, $c = 9.501$ (2) Å, $\alpha = 101.04$ (3)°, $\beta = 103.22$ (2)°, $\gamma = 106.26$, $Z = 4$, 3603 reflections, $R = 0.051$; for **3b**, space group *Pbca*, $a = 15.573$ (2) Å, $b = 18.597$ (4) Å, $c = 14.952$ (2) Å, $Z = 8$, 2252 reflections, $R = 0.038$; for **4a**, space group $P2_1/n$, $a = 9.504$ (2) Å, $b = 18.856$ (8) Å, $c = 13.776$ (3) Å, $\beta = 94.37$ (2)°, $Z = 4$, 1955 reflections, $R = 0.047$.

Introduction

Complexes containing alkoxysilyl ligands are readily obtained from the reactions of alkoxysilanes with metal complexes.[1] Such complexes are often intermediates in metal-catalyzed hydrosilation reactions, (e.g. eq 1).[1,2] In most cases trialkoxysilyl groups coordinate to metal atoms in the conventional η^1-mode (A) that is commonly found for trialkyl- and triarylsilyl groups. Recently, Braunstein and co-workers have reported the first examples of bridging η^2-siloxyl ligands (B) in binuclear metal complexes in which the oxygen atom of one of the alkoxy groups is coordinated to one of the metal atoms.[3] We have now found that trialkoxysilyl ligands may serve as a triply bridging η^3 ligands (C) in trinuclear metal complexes by using the oxygen atoms from two of the alkoxy groups attached to silicon. The results of our study of the coordination of $Si(OR)_3$ groups, R = Et and Me, to a triosmium cluster are given here. A preliminary report of this work has been published.[4]



(1)



η^1 $\mu\text{-}\eta^2$ $\mu_3\text{-}\eta^3$

A B C

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere unless specified otherwise. Reagent grade solvents were dried over 4-Å molecular sieves. $Os_3(CO)_{11}NCMe$[5] and $Os_3(CO)_{10}(NCMe)_2$[6] were prepared by the published procedures. All other reagents were purchased from Aldrich and were used as received. Trimethylamine *N*-oxide dihydrate was dehydrated by using a Dean–Stark apparatus with benzene as the solvent prior to use. UV irradiation experiments were performed using a 1000-W external medium-pressure mercury lamp on reaction solutions contained in Pyrex glassware. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. NMR spectra were run on either a Bruker AM-300 or AM-500 spectrometer operating at 300 or 500 MHz, respectively. Variable-temperature experiments were performed on a Bruker AM-500 instrument operating at 500 MHz for ^1H and 125.7 MHz for ^{13}C. Spectra below 25 °C were recorded in acetone-d_6. Spectra above 25 °C were recorded in $CDCl_3$ solvent. Temperatures below 22 °C were calibrated with a standard sample consisting of 4% CH_3OH in CD_3OD. Temperatures above 22 °C were calibrated with a standard sample consisting of 80% ethylene glycol in DMSO-d_6. Mass spectra were obtained on a VG Model 70 SQ spectrometer. Thin-layer chromatographic separations were performed in air on Whatman or Analtech 0.25-mm silica gel 60-Å F_{254} plates. Silica gel (70–230 mesh, 60 Å) for column chromatography was purchased from Aldrich. Elemental analyses were performed either by Desert Analytics, Tucson, AZ, or by Oneida Research Services, Whitesboro, NY.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with Trialkoxysilanes. To a 100 mL round-bottom flask was added 103.9 mg (0.111 mmol) of $Os_3(CO)_{10}(NCMe)_2$ in 60 mL of methylene chloride. This solution was then charged with 61.7 μL (0.334 mmol) of triethoxysilane and allowed to stir for 1 h at 25 °C. The volatiles were removed in vacuo, and the residue was separated by TLC using a 3/2 (v/v) methylene chloride/hexane solvent mixture as the eluent to yield in order of elution a minor yellow product, $Os_3(CO)_{11}[Si(OEt)_3](\mu\text{-}H)$ (**2a**) (ca. 5 mg), and yellow $Os_3(CO)_{10}(NCMe)[Si(OEt)_3](\mu\text{-}H)$ (**1a**) (98.8 mg, 84% yield). The compounds $Os_3(CO)_{10}(NCMe)[Si(OMe)_3](\mu\text{-}H)$ (**1b**) (71% yield) and $Os_3(CO)_{11}[Si(OMe)_3](\mu\text{-}H)$ (**2b**) (a trace) were made in a similar manner from $Os_3(CO)_{10}(NCMe)_2$ (59.4 mg) and 0.010 g (0.082 mmol) of trimethoxysilane. Analytical and spectral data are as follows. IR [ν(CO) (cm^{-1})] in hexane: For **1a**, 2103 (m), 2065 (vs), 2041 (vs), 2021 (vs), 2008 (s), 2000 (vs), 1988 (vs), 1976 (m); for **1b**, 2104 (m), 2066 (vs), 2042 (vs), 2022 (vs), 2009 (s), 2001 (vs), 1989 (vs), 1977 (m). ^1H NMR (δ in $CDCl_3$): For **1a**, 3.89 (q, OCH_2), 6 H), 2.57 (s, $NCCH_3$, 3 H), 1.27 (t, CH_2CH_3, 9 H), −16.40 (s, *Os–H*, 1 H); for **1b**, 3.61 (s, OCH_3, 9 H), 2.59 (s, $NCCH_3$, 3 H), −16.57 (s, *Os–H*, 1 H). Anal. Calcd (found) for **1a**: C, 20.5 (20.6); H, 1.81 (1.77); N, 1.33 (1.32).

Reaction of $Os_3(CO)_{11}NCMe$ with Trialkoxysilanes. A 100-mL round-bottom flask containing 49.8 mg (0.054 mmol) of $Os_3(CO)_{11}$-

---

(1) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 25, pp 1479–1526. (c) Dickers, H. M.; Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *J. Organomet. Chem.* **1978**, *161*, 91. (d) Brady, K. A.; Nile, T. A. *J. Organomet. Chem.* **1981**, *206*, 299. (e) Harrod, J. F.; Chalk, A. J. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; John Wiley: New York, 1977. (f) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (g) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253.

(2) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998.

(3) (a) Braunstein, P.; Knorr, M.; Tiripicchio, A.; Tiripicchio Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1361. (b) Braunstein, P.; Knorr, M. *New J. Chem.* **1990**, *14*, 583. (c) Braunstein, P.; Knorr, M.; Piana, H.; Schubert, U. *Organometallics* **1991**, *10*, 828. (d) Braunstein, P.; Knorr, M.; Villarroya, E.; DeCian, A.; Fischer, J. *Organometallics* **1991**, *10*, 3714.

(4) Adams, R. D.; Cortopassi, J. E.; Pompeo, M. P. *Inorg. Chem.* **1991**, *30*, 2960.

(5) Aime, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1809.

(6) Johnson, B. F. G.; Lewis, J.; Pippard, D. *J. Organomet. Chem.* **1978**, *160*, 263; **1981**, *213*, 249.

0020-1669/92/1331-2563$03.00/0

(NCMe) and 50 mL of methylene chloride was charged with 29.9 μL (0.162 mmol) of triethoxysilane. The solution was allowed to stir at 25 °C for 1 h. The volatiles were removed in vacuo, and the residue was separated by TLC using a solvent mixture of 3/2 methylene chloride/hexane to yield 52.2 mg (0.050 mmol, 93% yield) of **2a**. Compound **2b** (56.9 mg, 0.057 mmol, 84% yield) was made in a similar manner from $Os_3(CO)_{11}NCMe$ (65.5 mg, 0.068 mmol) and 0.010 g (0.082 mmol) of trimethoxysilane. Analytical and spectral data are as follows. IR [ν(CO) (cm^{-1})] in hexane: For **2a**, 2135 (m), 2086 (s), 2071 (m), 2053 (vs), 2027 (s), 2014 (s), 2003 (s), 1996 (m), 1990 (sh); for **2b**, 2135 (m), 2086 (s), 2069 (m), 2054 (vs), 2029 (s), 2016 (s), 2004 (s), 1998 (m), 1989 (sh). ^{1}H NMR (δ in $CDCl_3$): For **2a**, 3.87 (q, OCH_2, 6 H), 1.26 (t, CH_2CH_3, 9 H), −18.61 (s, *Os–H*, 1 H); for **2b**, 3.60 (s, OCH_3, 9 H), −18.83 (s, *Os–H*, 1 H). Mass spectral analysis (70 eV, 80 °C): **2a**, m/e for ^{192}Os = 1044 − 28x, x = 0–11 {[M]$^+$ − x(CO)}. Anal. Calcd (found) for **2a**·C_2H_6O: C, 21.5 (21.7); H, 2.09 (1.84).

Thermolysis of 1a in Hexane. A 50-mL solution of hexane containing 47.0 mg (0.045 mmol) of **1a** was heated to reflux for 20 min under a nitrogen purge. The solvent was then removed in vacuo, and the residue was separated first by silica gel TLC using a 3/1 hexane/methylene chloride solvent mixture to elute a yellow band which contained a mixture of two products. This was followed by two yellow bands which contained 6.6 mg (0.006 mmol) of **2a** and 6.6 mg (0.006 mmol) of **1a**. The first yellow band was then separated by TLC on alumina using a 9/2 hexane/methylene chloride solvent mixture to yield in order of elution 9.8 mg (0.010 mmol, 25% yield based on **1a** consumed) of yellow $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}Si(OEt)_3](\mu\text{-}H)$ (**3a**), followed by 10.1 mg (0.010 mmol) of yellow $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}Si(OEt)_3](\mu\text{-}H)$ (**4a**). Analytical and spectral data are as follows. IR [ν(CO) (cm^{-1})] in hexane: For **3a**, 2108 (m), 2063 (vs), 2053 (vs), 2024 (vs), 2020 (s, sh), 2004 (s), 1994 (m), 1988 (s), 1975 (m). ^{1}H NMR (δ in $CDCl_3$ at 25 °C): For **3a**, 3.78 (complex multiplet, OCH_2, 6 H), 1.23 (t, CH_2CH_3, 3 H, $^3J_{H-H}$ = 6.9 Hz), 1.14 (t, CH_2CH_3, 6 H, $^3J_{H-H}$ = 7.1 Hz), −15.33 (s, *Os–H*, 1 H).

Thermolysis of 1b in Hexane. A hexane solution (75 mL) containing 41.6 mg (0.041 mmol) of **1b** was heated to reflux for 45 min. The solvent was removed in vacuo, and the residue was separated by silica gel TLC using a 7/3 hexane/methylene chloride solvent mixture eluent to yield in order of elution a small amount of **4b** (0.4 mg) followed by **3b** (13.9 mg, 0.014 mmol, 34% yield). Analytical and spectra data for **3b** are as follows. IR [ν(CO) (cm^{-1})] in hexane: 2109 (m), 2064 (vs), 2054 (vs), 2026 (vs), 2018 (s, sh), 2006 (s), 1996 (m), 1990 (s), 1978 (m). ^{1}H NMR (δ in $CDCl_3$, at 25 °C): 3.55 (s, OCH_3, 3 H), 3.52 (br s, OCH_3, 6 H), −15.38 (s, *Os–H*, 1 H). ^{1}H NMR (δ in CD_2Cl_2, at −43 °C): 3.61 (s, OCH_3, 3 H), 3.458 (s, OCH_3, 3 H), 3.455 (s, OCH_3, 3 H), −15.36 (s, *Os–H*, 1 H). ^{1}H NMR (δ in acetone-d_6, at −40 °C): 3.80 (s, 3 H), 3.53 (s, 3 H), 3.49 (s, 3 H), −15.31 (s, 1 H). ^{13}C NMR (δ in acetone-d_6, at −40 °C): 183.1, 181.8, 180.0, 178.1, 177.6, 176.7, 175.4, 174.9, 174.5, 173.7 (s, 10 CO), 63.8 (s, OCH_3), 51.5 (s, OCH_3), 49.8 (s, OCH_3). At −20 °C, all but two carbonyl resonances (δ = 183.1, 181.8 ppm) were broadened significantly. The methyl resonances at 63.7 and 51.4 ppm were broadened similarly. At 22 °C, only two carbonyl resonances located at 182.3 and 181.4 ppm and one methyl resonance shifted to 50.8 ppm were observed. At 45 °C, the methyl resonance appeared as a broad singlet at 50.7 ppm, $\Delta\nu_{1/2} \approx 9$ Hz. The carbonyl resonances at 182.3 and 181.4 ppm were still observed. Spectra at higher temperatures were precluded due to decomposition to **2b** and **4b**. At −20 °C the resonances of the protons of the methyl groups at 3.79 and 3.51 ppm were broadened and shifted closer together. At −3 °C their resonances are very broad, while the other methyl signal at 3.56 ppm remained sharp. At 13 °C, the broad methyl resonances had disappeared into the baseline. At 22 °C they had re-formed as one broad peak at 3.65 ppm. This resonance sharpened considerably and moved to 3.55 ppm upon warming to 28 °C. The other methyl signal was shifted to 3.52 ppm. At 39 °C the resonance at 3.52 ppm showed considerable broadening which continued until it coalesced at 42 °C with the broad average of the other two resonances. Anal. Calcd (found) for **3b**: C, 16.5 (16.8); H, 1.07 (1.11).

Thermolysis of 1a,b in Heptane. A 75-mL solution of heptane containing 47.6 mg (0.045 mmol) of **1a** was heated to reflux for 20 min under a nitrogen purge. The volatiles were removed in vacuo, and the residue was separated by TLC using a 7/3 hexane/methylene chloride solvent mixture as the eluent to yield in order of elution 25.9 mg of yellow $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}Si(OEt)_3](\mu\text{-}H)$ (**4a**) (62% yield based on **1a** consumed) and 3.4 mg of unreacted **1a**. The ^{1}H NMR spectrum of **4a** shows that it exists as a mixture of two isomers in solution. To determine which resonances correspond to the structure found in the solid state, crystals of **4a** were dissolved in CD_2Cl_2 in a NMR tube at −78 °C. The sample was transferred without warming to the NMR spectrometer which had been precooled to −69 °C, and the spectrum was recorded. Additional spectra were also taken as the temperature was raised at 10° intervals to 25 °C. Compound **4b** (7.6 mg, 0.008 mmol) was prepared in a similar manner in 50% yield from **1b** (16.2 mg, 0.016 mmol). Analytical and spectral data are as follows. IR [ν(CO) (cm^{-1})] in hexane: For **4a**, 2090 (s), 2062 (vs), 2052 (vs), 2032 (vs), 2021 (s), 2012 (vs), 2007 (vs), 1991 (vs), 1976 (m), 1968 (m), 1956 (m), 1944 (m); for **4b**, 2092 (s), 2064 (vs), 2055 (vs), 2035 (vs), 2024 (s), 2013 (vs), 2009 (vs), 1994 (vs), 1979 (m), 1970 (m), 1958 (m), 1947 (m). ^{1}H NMR (δ in CD_2Cl_2 at 25 °C): For **4a**, 4.03 (dq, CH_2, 2 H, $^2J_{H-H}$ = 10.6 Hz, $^3J_{H-H}$ = 7.0 Hz, b), 3.93 (dq, CH_2, 1 H, $^2J_{H-H}$ = 10.5 Hz, $^3J_{H-H}$ = 7.1 Hz, a), 3.74 (dq, CH_2, 1 H, $^2J_{H-H}$ = 10.4 Hz, $^3J_{H-H}$ = 7.1 Hz, a), 3.68 (q, CH_2, 2 H, $^3J_{H-H}$ = 6.9 Hz, b), 3.64 (complex multiplet, CH_2, 3 H, a), 3.28 (dq, CH_2, 2 H, $^2J_{H-H}$ = 10.7 Hz, $^3J_{H-H}$ = 7.0 Hz, b), 3.25 (unresolved dq, CH_2, 1 H, a), 1.15 (t, CH_3, 3 H, $^3J_{H-H}$ = 7.1 Hz, b), 1.14 (t, CH_3, 3 H, $^3J_{H-H}$ = 7.1 Hz, a), 1.08 (t, CH_3, 3 H, $^3J_{H-H}$ = 6.9 Hz, a), 1.07 (t, CH_3, 3 H, $^3J_{H-H}$ = 6.8 Hz, a), 1.06 (t, CH_3, 6 H, $^3J_{H-H}$ = 7.1 Hz, b), −9.61 (s, *Os–H*, 1 H, b), −13.38 (s, *Os–H*, 1 H, a). From the low temperature study it was established that isomer a is found in the solid state. Compound **4b** also exists as a mixture of isomers in solution. ^{1}H NMR (δ) for **4b**: 3.52 (s, CH_3, 3 H, a), 3.50 (s, CH_3, 6 H, b), 3.37 (s, CH_3, 3 H, b), 3.35 (s, CH_3, 3 H, a), 3.30 (s, CH_3, 3 H, a), −9.33 (s, *Os–H*, 1 H, b), −13.29 (s, *Os–H*, 1 H, a). Anal. Calcd (found) for **4a**: C, 18.3 (18.6); H, 1.63 (1.60).

Conversions of 3a,b to 4a,b. A 15-mL heptane solution containing 4.1 mg (0.004 mmol) of **3a** was heated to reflux for 5 min under a nitrogen purge. The volatiles were removed in vacuo, and the residue was separated by TLC using a 7/3 hexane/methylene chloride solvent mixture to yield only 2.1 mg (50% yield) of **4a**. Similarly, compound **3b** (7.8 mg) was converted to **4b** in 44% yield (3.2 mg, 0.003 mmol) after 10 min of reflux with only a trace of starting material remaining (0.4 mg).

Reaction of 1a,b with CO. A solution containing 29.8 mg (0.028 mmol) of **1a** in 50 mL of methylene chloride was slowly purged with CO for 7 h at 25 °C. The volatiles were removed in vacuo, and the residue was separated by TLC using a 3/2 methylene chloride/hexane solvent mixture to yield in order of elution 22.9 mg of **2a** (0.022 mmol, 92% yield based on **1a** consumed) and 4.5 mg of unreacted **1a**. Compound **1b** (38.6 mg, 0.038 mmol) was transformed to **2b** in a similar manner (28.5 mg, 75% yield).

Reactions of 2a,b with (Me)$_3$NO and MeCN. A 10-mL solution of acetonitrile containing 3.0 mg (0.027 mmol) of trimethylamine *N*-oxide was added dropwise to a 60-mL solution of methylene chloride and acetonitrile (5/1) containing 23.3 mg (0.022 mmol) of **2a**. The solution was allowed to stir for 1 h at 25 °C. The volatiles were removed in vacuo, and the residue was separated by TLC using a 3/2 methylene chloride/hexane solvent mixture to yield 3.5 mg of unreacted **2a** and 14.8 mg of **1a** (75% yield based on the amount of **2a** consumed). Compound **2b** (26.0 mg, 0.026 mmol) was transformed to **1b** (18.7 mg, 75% yield) in a similar manner with trimethylamine *N*-oxide.

Photolysis of 2a,b. A 24.7-mg (0.024-mmol) amount of **2a** in a solution of 50 mL of hexane was irradiated for 45 min at 25 °C. The volatiles were removed in vacuo, and the residue was separated by TLC with a 7/3 hexane/methylene chloride solvent mixture. The only product isolated was **4a** (11.9 mg, 50% yield). Compound **2b** (63.0 mg, 0.063 mmol) was irradiated in a similar manner to yield **4b** (26.8 mg, 44%).

Thermolysis of 2a,b in Heptane. A 13.6-mg (0.013-mmol) sample of **2a** in a solution of 50 mL of heptane was heated to reflux for 90 min. The volatiles were removed in vacuo, and the residue was separated by TLC with a 7/3 hexane/methylene chloride solvent mixture. The only product isolated was **4a** (4.9 mg, 37%). Compound **2b** (14.7 mg, 0.015 mmol) yielded **4b** (4.5 mg, 32%) in a similar manner.

Reaction of 4a,b with CO. A 48.0-mg (0.049-mmol) amount of **4a** in a solution of 75 mL of hexane was heated to reflux in the presence of a slow CO purge for 4 h. The solvent was removed in vacuo, and the residue was separated by TLC with a hexane/methylene chloride 1/1 solvent mixture to yield in order of elution 8.9 mg of unreacted **4a** and 31.1 mg of **2a** (77% yield based on reacted **4a**). There was no evidence of the formation of **3a**. Compound **4b** (20.3 mg) yielded **2b** (15.0 mg, 71%) in a similar manner, and there was no evidence of the formation of **3b**.

Crystallographic Analyses. Yellow crystals of **1a** were grown by slow evaporation of a methylene chloride/light petroleum ether solution at 25 °C. Yellow crystals of **3b** were grown by slow evaporation of solvent from a methylene chloride/hexane solution at −15 °C. Yellow crystals of **4a** were grown by slow evaporation of solvent at 25 °C from a solution in hexane. All 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 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library obtained

Table I. Crystal Data for Compounds **1a**, **3b**, and **4a**

	compd		
	1a	**3b**	**4a**
formula	$Os_3SiO_{13}NC_{18}H_{19}$	$Os_3SiO_{13}C_{13}H_{10}$	$Os_3SiO_{12}C_{15}H_{16}$
fw	1056.03	972.90	986.97
cryst syst	triclinic	orthorhombic	monoclinic
cell params			
a, Å	16.630 (5)	15.573 (2)	9.504 (2)
b, Å	20.062 (7)	18.579 (4)	18.856 (8)
c, Å	9.501 (2)	14.952 (2)	13.776 (3)
α, deg	101.04 (3)	90.00	90.00
β, deg	103.22 (2)	90.00	94.37 (2)
γ, deg	106.26 (3)	90.00	90.00
V, Å^3	2850 (4)	4330 (1)	2462 (1)
space group	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)	$P2_1/n$ (No. 14)
Z	4	8	4
ρ_{calc}, g/cm^3	2.46	2.98	2.66
μ(Mo, Kα), cm^{-1}	134.5	176.9	155.6
temp, °C	20	20	20
no. of observns ($I > 3\sigma(I)$)	3603	2252	1955
no. of variables	439	275	249
residuals:[a] R, R_w	0.051, 0.052	0.038, 0.040	0.047, 0.047

[a] $R = \sum_{hkl}(||F_o| - |F_c||)/\sum_{hkl}|F_o|$; $R_w = (\sum_{hkl}w(|F_o| - |F_c|)^2/\sum_{hkl}w|F_o|^2)^{1/2}$.

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 $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net}^2)]^{1/2}/Lp$.

Compound **1a** crystallized in the triclinic crystal system with two symmetry-independent molecules in the asymmetric crystal unit. 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 direct methods (MITHRIL) and difference Fourier syntheses. Due to the large size of the structure only atoms larger than carbon were refined with anisotropic thermal parameters. The alkoxy oxygen atoms were refined isotropically. The hydride ligand in each complex was located in a difference Fourier synthesis but could not be well refined. These ligands were thus added as fixed contributions only. All other hydrogen atoms were ignored.

Compound **3b** crystallized in the orthorhombic crystal system. The space group $Pbca$ 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 hydride ligand was located and satisfactorily refined. All other hydrogen atom positions were calculated by assuming idealized geometries and were added to the structure factor calculations as fixed contributions.

Compound **4a** 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 atoms larger than carbon plus the carbonyl carbon atoms were refined with anisotropic thermal parameters. All three ethyl groups exhibited extensive disorder, and efforts to devise a satisfactory disorder model were not successful. Carbon C(6) could not be refined to a credible position and was finally added as a fixed contribution in the position observed in a difference Fourier synthesis. The hydride ligand was located and satisfactorily refined. All other hydrogen atom positions were calculated by assuming idealized geometries and were added to the structure factor calculations as fixed contributions.

Results and Discussion

The reactions of $Os_3(CO)_{10}(NCMe)_2$ and $Os_3(CO)_{11}(NCMe)$ with the silanes $HSi(OR)_3$, R = Et and Me, yielded the new complexes $Os_3(CO)_{10}(NCMe)[Si(OR)_3](\mu\text{-H})$, R = Et and Me (**1a,b**), and $Os_3(CO)_{11}[Si(OR)_3](\mu\text{-H})$, R = Et and Me (**2a,b**), respectively, in good yields by displacement of a NCMe ligand

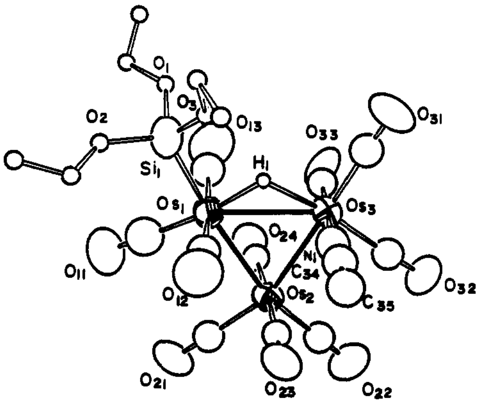


Figure 1. ORTEP diagram of $Os_3(CO)_{10}(NCMe)[Si(OEt)_3](\mu\text{-H})$ (**1a**), showing 40% probability thermal ellipsoids.

Table II. Positional Parameters and B(eq) Values for Selected Atoms for One of the Two Independent Molecules of **1a** in the Crystal

atom	x	y	z	B(eq), Å^2
Os(1)	0.29508 (08)	0.24077 (08)	0.49591 (15)	6.14 (6)
Os(2)	0.15464 (08)	0.11366 (07)	0.29429 (14)	5.68 (5)
Os(3)	0.21354 (08)	0.11479 (07)	0.60552 (14)	5.60 (5)
Si(1)	0.3935 (07)	0.3440 (06)	0.6935 (13)	8.2 (5)
O(1)	0.493 (02)	0.3442 (18)	0.759 (03)	13.4 (9)
O(2)	0.411 (02)	0.423 (02)	0.659 (04)	17 (1)
O(3)	0.3577 (20)	0.3474 (19)	0.846 (04)	15 (1)
N(1)	0.1231 (14)	0.1630 (14)	0.662 (02)	6 (1)
C(101)	0.574 (06)	0.378 (05)	0.734 (10)	27 (3)
C(102)	0.632 (04)	0.382 (04)	0.854 (08)	21 (2)
C(201)	0.366 (06)	0.455 (06)	0.610 (11)	28 (3)
C(202)	0.403 (04)	0.526 (04)	0.632 (08)	21 (2)
C(301)	0.365 (04)	0.401 (04)	0.980 (07)	19 (2)
C(302)	0.281 (04)	0.391 (03)	0.975 (07)	18 (2)

Table III. Intramolecular Distances for **1a**[a]

Os(1)–Os(2)	2.894 (3)	Si(1)–O(3)	1.69 (3)
Os(1)–Os(3)	3.008 (2)	O(Si)–C(av)	1.4 (1)
Os(1)–Si(1)	2.39 (1)	O–C(av)	1.14 (3)
Os(1)–H(1)	1.84	N(1)–C(34)	1.15 (3)
Os(2)–Os(3)	2.888 (2)	C(34)–C(35)	1.45 (4)
Os(3)–N(1)	2.11 (2)	C(101)–C(102)	1.29 (9)
Si(1)–O(1)	1.63 (3)	C(201)–C(202)	1.3 (1)
Si(1)–O(2)	1.64 (4)	C(301)–C(302)	1.35 (7)

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

---

(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.

(8) (a) Teller, R. G.; Bau, R. *Struct. Bonding* **1981**, *44*, 1. (b) Churchill, M. R. In *Transition Metal Hydrides*; Advances in Chemistry Series No. 167; Bau, R., Ed.; American Chemical Society: Washington, DC, 1978.

Table IV. Intramolecular Bond Angles for **1a**[a]

Os(2)–Os(1)–Os(3)	58.56 (5)	Os(1)–Si(1)–O(1)	116 (1)
Os(2)–Os(1)–Si(1)	169.0 (3)	Os(1)–Si(1)–O(2)	117 (1)
Os(3)–Os(1)–Si(1)	113.5 (3)	Os(1)–Si(1)–O(3)	109 (1)
Os(1)–Os(2)–Os(3)	62.68 (5)	O–Si–O(av)	104 (2)
Os(1)–Os(3)–Os(2)	58.75 (5)	Si–O–C(av)	138 (6)
Os(1)–Os(3)–N(1)	90.4 (6)	Os–C–O(av)	176 (3)
Os(2)–Os(3)–N(1)	92.1 (5)	O–C–C(av)	111 (9)

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

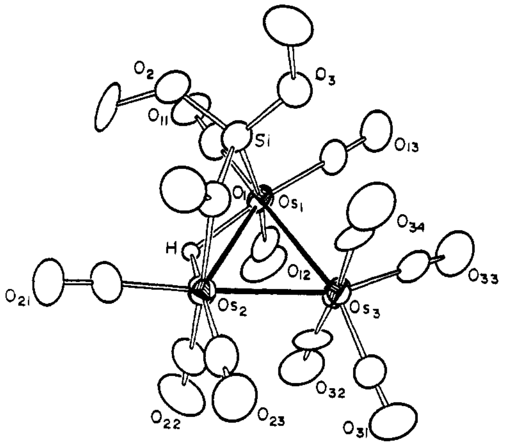


Figure 2. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}Si(OMe)_3](\mu\text{-}H)$ (**3b**), showing 40% probability thermal ellipsoids.

and the oxidative-addition of the silane SiH bond to the cluster. Interestingly, for $Os_3(CO)_{10}(NCMe)_2$ only one of the two NCMe ligands was displaced in the room-temperature reaction. All products were characterized by IR and ^1H NMR spectroscopy. Compound **1a** was also characterized by a single-crystal X-ray diffraction analysis. The crystal contains two independent but structurally similar molecules in the asymmetric crystal unit. An ORTEP drawing of the molecular structure of one of these is shown in Figure 1. Selected atomic positional parameters for one of the two molecules are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. The molecule consists of a closed triangular cluster of three osmium atoms with nine linear terminal carbonyl ligands distributed about the cluster as shown in Figure 1. There is a linear NCMe ligand coordinated to atom Os(3) in an axial site and a terminally coordinated η^1-$Si(OEt)_3$ ligand bonded to Os(1) in an equatorial site. None of the ligands exhibit any unusual distortions. The SiO_3 grouping is structurally similar to the η^1-$Si(OMe)_3$ group observed in the complex $Fe(CO)_3\{Si(OMe)_3\}(\mu\text{-dppm})Cu(AsPh_3)$.[3b] The Os–Si distance, 2.39 (1) Å, is slightly shorter than that found for arylsilanes, 2.455 (2) Å in $Os_3(CO)_{10}(SiHPh_2)(\mu\text{-}H)_2(H)$[9] and 2.429 (2) Å in $Os_3(CO)_9(SiPh_3)_3(\mu\text{-}H)_3$,[10] but is similar to Os–Si distances observed for trichlorosilyl groups bonded to osmium (e.g. 2.389 (12), 2.394 (14), and 2.367 (13) Å in $Os_3(CO)_9(SiCl_3)_3(\mu\text{-}H)_3$[11] and 2.377 (3) Å in $Os_3(CO)_{12}(SiCl_3)_2$).[11] There is a hydride ligand bridging the Os(1)–Os(3) bond ($\delta = -16.40$ ppm), which produces the usual lengthening effect of about 0.1 Å upon the metal–metal bond distance.[8]

Compounds **2a,b** were obtained in good yields from the reactions of $Os_3(CO)_{11}NCMe$ with the appropriate silanes, and their formation in small amounts in the reactions of $Os_3(CO)_{10}(NCMe)_2$ with the silanes could have been due to the presence of small amounts of $Os_3(CO)_{11}NCMe$ impurity in the $Os_3(CO)_{10}(NCMe)_2$.

Table V. Positional Parameters and *B*(eq) Values for Selected Atoms in the Crystal of **3b**

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.71853 (04)	0.13638 (04)	0.67916 (04)	2.49 (3)
Os(2)	0.69391 (04)	0.08462 (04)	0.86367 (04)	2.67 (3)
Os(3)	0.57990 (04)	0.18938 (04)	0.79217 (05)	2.99 (3)
Si	0.6583 (03)	0.0171 (03)	0.6708 (03)	2.9 (2)
O(1)	0.6333 (06)	0.0022 (06)	0.7806 (07)	2.9 (5)
O(2)	0.7221 (07)	−0.0493 (07)	0.6427 (08)	3.6 (6)
O(3)	0.5735 (06)	0.0027 (07)	0.6129 (08)	3.6 (6)
C(1)	0.5980 (12)	−0.0651 (11)	0.8180 (13)	4 (1)
C(2)	0.7989 (11)	−0.0696 (11)	0.6878 (15)	5 (1)
C(3)	0.5409 (13)	−0.0652 (14)	0.5801 (14)	6 (1)

Table VI. Intramolecular Distances for **3b**[a]

Os(1)–Os(2)	2.947 (1)	Os(3)–C(31)	1.91 (2)
Os(1)–Os(3)	2.9134 (9)	Os(3)–C(32)	1.93 (2)
Os(1)–Si	2.412 (5)	Os(3)–C(33)	1.95 (2)
Os(1)–C(11)	1.89 (2)	Os(3)–C(34)	1.95 (2)
Os(1)–C(12)	1.95 (2)	Si–O(1)	1.71 (1)
Os(1)–C(13)	1.90 (2)	Si–O(2)	1.64 (1)
Os(2)–Os(3)	2.844 (1)	Si–O(3)	1.60 (1)
Os(2)–O(1)	2.19 (1)	O(1)–C(1)	1.48 (2)
Os(2)–C(21)	1.93 (2)	O(2)–C(2)	1.42 (2)
Os(2)–C(22)	1.85 (2)	O(3)–C(3)	1.45 (2)
Os(2)–C(23)	1.91 (2)	O–C(av)	1.13 (2)

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

Table VII. Intramolecular Bond Angles for **3b**[a]

Os(2)–Os(1)–Os(3)	58.07 (2)	O(1)–Si–O(2)	105.1 (6)
Os(2)–Os(1)–Si	72.4 (1)	O(1)–Si–O(3)	107.7 (6)
Os(3)–Os(1)–Si	93.0 (1)	O(2)–Si–O(3)	103.6 (7)
Os(1)–Os(2)–Os(3)	60.37 (2)	Os(2)–O(1)–Si	109.5 (5)
Os(1)–Os(2)–O(1)	75.7 (3)	Os(2)–O(1)–C(1)	123 (1)
Os(3)–Os(2)–O(1)	89.9 (3)	Si–O(1)–C(1)	126 (1)
Os(1)–Os(3)–Os(2)	61.56 (3)	Si–O(2)–C(2)	126 (1)
Os(1)–Si–O(1)	100.8 (4)	Si–O(3)–C(3)	128 (1)
Os(1)–Si–O(2)	118.0 (5)	Os–C–O(av)	176 (2)
Os(1)–Si–O(3)	120.2 (5)		

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

When compounds **1a,b** were heated to reflux in hexane solvent, two products $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}Si(OR)_3](\mu\text{-}H)$ (**3a,b**; R = Et, Me) and $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}Si(OR)_3](\mu\text{-}H)$ (**4a,b**; R = Et, Me) were formed by loss of NCMe and NCMe plus CO, respectively. Compound **3a** was relatively unstable and spontaneously transformed to **4a** by loss of CO even at 25 °C. It was characterized only spectroscopically. Compound **3b** was more stable and was characterized crystallographically and by variable-temperature NMR. An ORTEP drawing of **3b** is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. This compound also consists of a closed triangular cluster of three osmium atoms with 10 linear terminal carbonyl ligands distributed as shown in Figure 2. The most interesting ligand is a μ-η^2-siloxyl group that bridges the Os(1)–Os(2) edge of the cluster in axial coordination sites. The oxygen atom O(1) of one of the methoxyl substituents is coordinated to Os(2), Os(2)–O(1) = 2.19 (1) Å, and the silicon atom is coordinated to Os(1) with an Os–Si distance similar to that in **1a**, Os(1)–Si = 2.412 (5) Å. The Si–O(1) distance, 1.71 (1) Å, is significantly longer than the Si–O distances to the methoxyl groups that are not coordinated, 1.64 (1) and 1.60 (1) Å. Lengthening of the Si–O bond has been observed for other μ–η^2-bridging ligands[2c–d] although the effect is not always large.[3a] A hydride ligand (located and refined, $\delta = -15.38$ ppm) also bridges the Os(1)–Os(2) bond.

Only two resonances are observed for the methyl groups at δ = 3.55 (6 H) and 3.52 (3 H) at 25 °C in $CDCl_3$ solvent, but the resonance at 3.55 ppm shows significant broadening. The existence of a dynamical process was confirmed by a variable-temperature study in acetone-d_6 solvent. At −31 °C the spectrum shows three singlets of equal intensity at 3.80, 3.54, and 3.50 ppm. As the temperature is raised, two of these resonances at 3.80 and 3.50

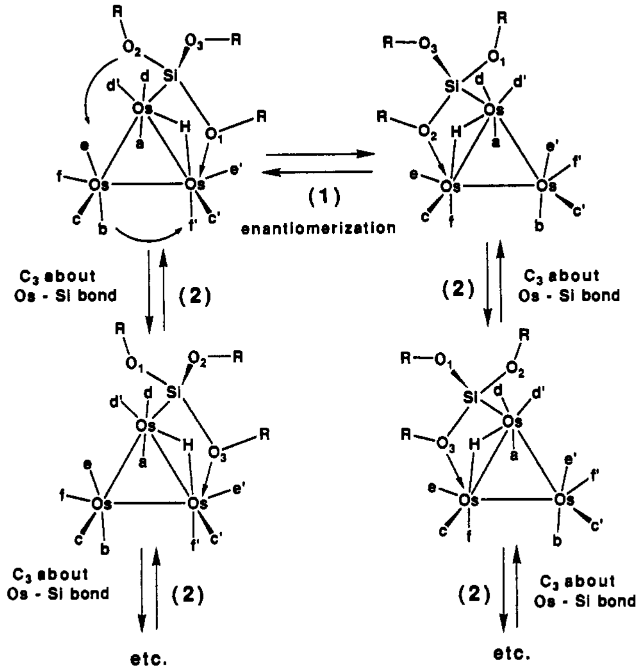
---

(9) Einstein, F. W. B.; Pomeroy, R. K.; Willis, A. C. *J. Organomet. Chem.* **1986**, *311*, 257.

(10) Willis, A. C.; Einstein, F. W. B.; Ramadan, R. M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 935.

(11) Willis, A. C.; van Buuren, G. N.; Pomeroy, R. K.; Einstein, F. W. B. *Inorg. Chem.* **1983**, *22*, 1162.

Scheme I



ppm broaden and coalesce (coalescence at +13 °C, ΔG^*_{286} = 16.3 kcal/mol) and re-form as a broad singlet at 25 °C. Interestingly, at higher temperatures the third singlet broadens and coalesces (coalescence at +42 °C, ΔG^*_{315} = 17.2 kcal/mol) with the average of the previous two. The resonances of the carbon atoms of the methyl resonances show a similar averaging behavior. At −31 °C the spectrum shows three singlets of equal intensity at 63.78, 51.44, and 50.09 ppm. Braunstein has observed that the carbon resonance of the bridging OMe group lies at approximately 10 ppm to a lower field shift value than the uncoordinated OMe groups in the complex $FeRh(CO)_4(\mu\text{-dppm})[\mu\text{-Si(OMe)}_3]$.[2b] Accordingly, we assign the resonance at 63.78 ppm in **3b** to the bridging OMe grouping. Two of the resonances 63.78 and 51.44 ppm are significantly broadened at −20 °C and have collapsed into the baseline at 0 °C. We were unable achieve temperatures high enough to observe the position of the averaged resonance. At 45 °C, the remaining methyl resonance was significantly broadened, $\Delta\nu_{1/2} \approx 9$ Hz. At temperatures greater than 50 °C, the compound decomposed at a significant rate to a mixture of **2b** and **4b**.

The resonances of the carbonyl ligands also exhibited dynamical changes. At −40 °C the resonances of all 10 carbonyl ligands were observed as sharp singlets: 183.1, 181.8, 180.0, 178.1, 177.6, 176.7, 175.4, 174.9, 174.5, and 173.7 ppm. At −20 °C, all but two carbonyl resonances (δ = 183.1, 181.8 ppm) were broadened significantly. At 22 °C, the eight broad resonances had disappeared into the baseline while the two remaining resonances were sharp at 182.3 and 181.4 ppm. Due to decomposition it was not possible to record spectra of **3b** at temperatures high enough to observe the expected averaged resonances.

From the ^1H NMR spectra it is clear that two dynamical processes are operative in this molecule on the NMR time scale. The lowest energy process is one that averages only two of the methoxyl groups of the $Si(OMe)_3$ ligand. This process was also observed in the ^{13}C NMR spectra of these groupings. Curiously, on the basis of the ^{13}C NMR chemical shift positions, the two groupings involved in the process appear to be the bridging methoxyl group and one of the uncoordinated methoxyl groups. The ^{13}C NMR resonances of the carbonyl ligands also show the existence of a dynamical process of similar energy that involves exchange of sites of only eight of the ten carbonyl ligands. A mechanism that would explain these observations is the enantiomerization process 1 shown on the top of Scheme I. In this mechanism the $Si(OMe)_3$ ligand rocks back and forth between two edges of the cluster in a process that averages the bridging OMe group with only one of the uncoordinated OMe groups. The uncoordinated methoxyl group becomes coordinated to the metal atom of the $Os(CO)_4$ group, and the methoxyl group that is coordinated is released. Simultaneously, one of the carbonyl ligands (b) on the $Os(CO)_4$ group is shifted to a corresponding site on the osmium atom from which the bridging methoxyl group was released to form a new $Os(CO)_4$ grouping and the hydride ligand is shifted to the metal–metal bond that contains the newly formed bridging Si–O grouping. The environments of the CO groups a and b, the hydride ligand, and the remaining uncoordinated methoxyl group are "formally" unchanged.[12] The exchange of CO ligands between metal atoms in osmium carbonyl cluster complexes is a well-established phenomena.[13] All of the remaining carbonyl ligands undergo a pairwise exchange: c–c′, d–d′, e–e′, and f–f′. This process is consistent with the spectral changes observed in the carbonyl region.

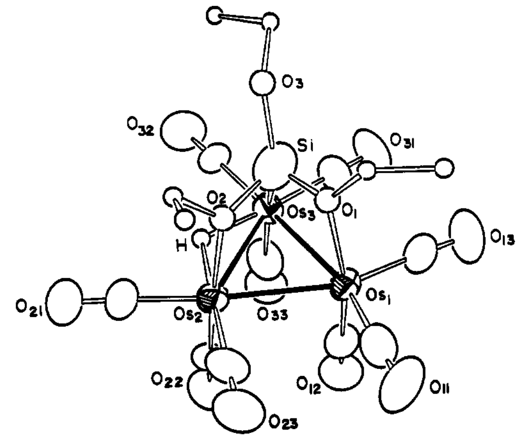


Figure 3. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-Si(OEt)}_3](\mu\text{-H})$ (**4a**), showing 40% probability thermal ellipsoids.

Table VIII. Positional Parameters and B(eq) Values for Selected Atoms in the Crystal of **4b**

atom	x	y	z	B(eq), Å^2
Os(1)	0.33574 (11)	0.20412 (06)	0.14499 (07)	5.77 (6)
Os(2)	0.26022 (10)	0.19933 (06)	0.34104 (07)	5.74 (6)
Os(3)	0.54997 (10)	0.16671 (07)	0.28847 (07)	5.97 (6)
Si	0.4036 (14)	0.0703 (07)	0.2546 (08)	12.1 (8)
O(1)	0.3081 (14)	0.0862 (07)	0.1679 (11)	5.1 (8)
O(2)	0.233 (02)	0.0874 (10)	0.3116 (18)	12 (1)
O(3)	0.447 (04)	−0.0201 (15)	0.273 (02)	18 (3)
C(1)	0.240 (04)	0.032 (02)	0.107 (03)	12 (1)
C(2)	0.224 (05)	0.025 (03)	0.003 (03)	19 (2)
C(3)	0.151 (08)	0.039 (04)	0.362 (05)	22 (3)
C(4)	0.047 (09)	0.034 (05)	0.328 (06)	31 (4)
C(5)	0.566 (06)	−0.065 (03)	0.272 (04)	19 (2)
C(6)	0.6930	−0.0522	0.3770	20.0

At temperatures slightly above 25 °C, the third methyl resonance broadens and merges with the average of the first two. This can be explained by pseudo-3-fold rotation of the SiO_3 group about the Si–Os bond, pathway 2. The bridging methoxyl group is sequentially replaced with each of the uncoordinated methoxyl groups. This process leads to the averaging of all three methoxyl groups but does not cause any additional exchanges among the carbonyl ligands. Braunstein has observed similar processes for $\mu\text{-}\eta^2$-ligands in binuclear metal complexes.[3a,c,d]

Compounds **3a,b** were rapidly decarbonylated at 97 °C (5–10 min) to yield the new compounds **4a,b**, respectively. Compound **4a** was also characterized crystallographically, and an ORTEP drawing of its structure is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected interatomic distances and angles are listed in Tables IX and X. This

---

(12) In fact the environments of these ligands are changed, but the magnetic environment in this enantiomer is isochronous to that of the first enantiomer.

(13) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437 and references therein.

Table IX. Intramolecular Distances for **4a**[a]

Os(1)–Os(2)	2.848 (2)	Os(3)–C(32)	1.88 (3)
Os(1)–Os(3)	2.817 (2)	Os(3)–C(33)	1.93 (3)
Os(1)–O(1)	2.26 (1)	Os(3)–H	1.7 (1)
Os(1)–C(11)	1.93 (4)	Si–O(1)	1.47 (2)
Os(1)–C(12)	1.90 (3)	Si–O(2)	1.88 (2)
Os(1)–C(13)	1.85 (3)	Si–O(3)	1.77 (3)
Os(2)–Os(3)	2.965 (1)	O(1)–C(1)	1.44 (4)
Os(2)–O(2)	2.16 (2)	O(2)–C(3)	1.41 (7)
Os(2)–C(21)	1.89 (3)	O(3)–C(5)	1.42 (5)
Os(2)–C(22)	1.90 (3)	O–C(av)	1.14 (3)
Os(2)–C(23)	1.93 (3)	C(1)–C(2)	1.44 (5)
Os(2)–H	1.9 (2)	C(3)–C(4)	1.08 (9)
Os(3)–Si	2.32 (1)	C(5)–C(6)	1.82 (5)
Os(3)–C(31)	1.88 (3)		

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

Scheme II

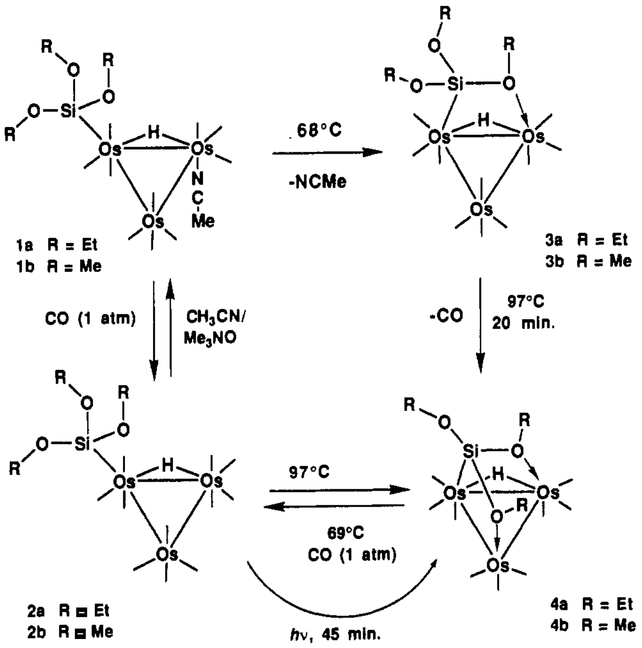


Table X. Intramolecular Bond Angles for **4a**[a]

Os(2)–Os(1)–Os(3)	63.11 (4)	Os(3)–Si–O(1)	109.1 (8)
Os(2)–Os(1)–O(1)	78.3 (4)	Os(3)–Si–O(2)	107.8 (8)
Os(3)–Os(1)–O(1)	75.0 (3)	Os(3)–Si–O(3)	127 (1)
O(1)–Os(1)–C(11)	95 (1)	O(1)–Si–O(2)	79 (1)
O(1)–Os(1)–C(12)	167 (1)	O(1)–Si–O(3)	116 (1)
O(1)–Os(1)–C(13)	93 (1)	O(2)–Si–O(3)	108 (1)
Os(1)–Os(2)–Os(3)	57.93 (4)	Os(1)–O(1)–Si	104.0 (9)
Os(1)–Os(2)–O(2)	83.6 (6)	Os(1)–O(1)–C(1)	132 (2)
Os(3)–Os(2)–O(2)	81.4 (6)	Si–O(1)–C(1)	123 (2)
O(2)–Os(2)–C(21)	94 (1)	Os(2)–O(2)–Si	99 (1)
O(2)–Os(2)–C(22)	176 (1)	Os(2)–O(2)–C(3)	127 (3)
O(2)–Os(2)–C(23)	91 (1)	Si–O(2)–C(3)	128 (3)
Os(1)–Os(3)–Os(2)	58.96 (4)	Si–O(3)–C(5)	140 (3)
Os(1)–Os(3)–Si	70.4 (3)	Os–C–O(av)	177 (3)
Os(2)–Os(3)–Si	69.9 (3)		

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

compound consists of a triosmium cluster with a triply bridging η^3-Si(OEt)$_3$ ligand that is coordinated across the face of the cluster through the silicon atom and the oxygen atoms of two of the OEt groups. The silicon atom is coordinated to Os(3), Os(3)–Si = 2.32 (1) Å. The Os–O distances, Os(1)–O(1) = 2.26 (1) and Os(2)–O(2) = 2.16 (1) Å, are similar to that observed in **3b**, but the Si–O and other metrical parameters associated with the Si(OEt)$_3$ ligand are of questionable accuracy due to the existence of considerable unresolvable disorder of the ethyl groups. There is one bridging hydride ligand which spans the elongated Os(2)–Os(3) bond. In solution the complex exists as a mixture of two isomers in which the hydride ligand is believed to bridge different metal–metal bonds of the cluster. Compounds **4a,b** react with CO (69 °C/1 atm) to yield components **2a,b**, respectively, in good yields by displacement of the coordinated oxygen atoms of both alkoxy ligands. When irradiated (UV) or heated to 97 °C, compounds **2a,b** were decarbonylated and converted back to **4a,b** although the yields were generally less than 50%.

The results of this study are summarized in Scheme II. Ligand elimination from compounds **1a,b** and **2a,b** yielded the complexes **3a,b** and **4a,b**, which contain μ-η^2-Si(OR)$_3$ and μ_3-η^3-Si(OR)$_3$ ligands, respectively. Compounds **3a,b** can be converted to **4a,b**, but the reverse is not achieved. Addition of CO transformed **4a,b** back to **2a,b**. These studies extend further the pioneering studies of Braunstein on the bridging coordination of Si(OR)$_3$ ligands.[3] It is likely that additional examples will be found in other cluster complexes. The importance of the bridging coordination mode for Si(OR)$_3$ ligands may even extend to very large metal clusters and colloidal-sized particles which have been shown to be formed in the reactions of some hydrosilation catalysts.[2,14]

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE-8919786).

Supplementary Material Available: Complete listings of positional parameters and anisotropic thermal parameters for all of the structural analyses and tables of bond distance and angles for **1a** and bond angles for **3b** (21 pages); a listing of structure factor amplitudes for **3b** (16 pages). Ordering information is given on any current masthead page. Structure factor tables for **1a** and **4a** were deposited previously.[4]

---

(14) (a) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228. (b) Lewis, L. N.; Lewis, N. *Chem. Mater.* **1989**, *1*, 106.