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Isolation, Characterization, and Substitution Reactions of the Trinuclear Triflate Complex $H_2Os_3(CO)_9(O_3SCF_3)_2$. X-ray Crystal Structure of the Mixed Oxy Ligand Cluster $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCH_3)(\eta^1\text{-}O_3SCF_3)$

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The complex $H_2Os_3(CO)_9(O_3SCF_3)_2$ (1) has been prepared from the reaction of $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CH)$ with neat trifluoromethanesulfonic acid. The reaction of 1 with various protonic acids has been studied, and two kinds of product have been obtained. These were (i) replacement of *both* triflate ligands and isolation of the previously reported cluster $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3SO)$ (2) or the new oxy ligand clusters $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CR)(\eta^1\text{-}O_2CR)$ [R = H (6), CF_3 (7)] and (ii) replacement of just *one* triflate ligand and isolation of mixed oxy ligand clusters $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CR)(\eta^1\text{-}O_3SCF_3)$ [R = H (3), CH_3 (4), CF_3 (5)]. Reaction of 1 with MeCN also lead to displacement of both triflate ligands to give $[(\mu\text{-}H)_2Os_3(CO)_9(MeCN)_3][O_3SCF_3]_2$ (8). The new compounds were isolated as crystalline solids and were characterized analytically and spectroscopically; in the case of compound 4, a single-crystal X-ray diffraction study was conducted. $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCH_3)(\eta^1\text{-}O_3SCF_3)$ (4) crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.469$ (3) Å, $b = 20.840$ (9) Å, $c = 12.562$ (4) Å, $\beta = 95.49$ (3)°, $V = 2207$ (2) Å^3, and $Z = 4$. The structure was solved by conventional methods and refined to final agreement factors of $R = 0.033$ and $R_w = 0.043$ for the 3079 unique reflections. The molecule contains a triangular triosmium core in which each osmium atom is linked to three terminal carbonyl ligands. Acetate bridges diaxially the Os(2)–Os(3) edge, and the Os(1)–Os(2) and Os(1)–Os(3) edges are apparently each bridged by a hydride ligand (which was not located directly). The triflate ligand is axially bound to Os(1), on the opposite side of the trimetal plane from the bridging acetate ligand, and displays unusual distances to the coordinated oxygen atom [Os–O = 2.146 (10) Å; S–O = 1.50 (1) Å] suggestive of strong binding. Compound 4 did not react with a variety of possible donor ligands (CO, MeCN, PhCN, THF, and H_2) at 72 °C in 1,2-dichloroethane over 2 h. Under similar conditions, reactions with Cl⁻, I⁻, and $S_2O_3^{2-}$ gave the known clusters $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}X)$ [X = Cl, I] and $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}S)$, respectively. In neat acetic acid at 60 °C, compound 4 formed $Os_2(CO)_6(\mu\text{-}O_2CCH_3)_2$, apparently via $H_2Os_3(CO)_9(O_2CCH_3)_2$.

Introduction

The utility of trifluoromethanesulfonate (O_3SCF_3 or triflate) complexes of the transition metals as synthetic precursors has been thoroughly demonstrated.[1,2] The comparative lability of coordinated triflate commonly leads to mild conditions (often room temperature or slightly above) for ligand substitution reactions, frequently resulting in cleaner reactions, better yields, and molecules not accessible by other routes. Most work to date has concentrated on triflate complexes of mononuclear compounds,[1,2] although dinuclear $(Mo_2(O_3SCF_3)_4)$[3] and tetranuclear $([Cu_4(OH)_4(O_3SCF_3)_2[N(C_5H_4N)_3]_4][O_3SCF_3]_2 \cdot C_3H_6O)$[4] complexes are known as well. We report here the isolation of $H_2Os_3(CO)_9(O_3SCF_3)_2$ (1), a trinuclear triflate compound, and describe some of its reactivity toward substitution of its triflate ligands. These reactions are summarized in Scheme I. So far as we are aware 1 and its derivatives are the only examples of coordinated triflate for any carbonyl cluster compounds.

Substitution of a single triflate ligand in 1 has given complexes that are surprisingly robust toward substitution of the remaining triflate ligand. In the particular case of the mixed oxy ligand cluster $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCH_3)(\eta^1\text{-}O_3SCF_3)$ (4), the structure has been determined by X-ray diffraction and this structural evidence serves to rationalize the relative lack of lability of its coordinated triflate ligand. Given the limited number of triflate complexes known for metal carbonyls, it is worth considering whether triflate is always as weakly bound as is generally supposed.

Experimental Section

The compounds $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CH)$[5] and $(PPN)_2(S_2O_3)$[6] were

Scheme I
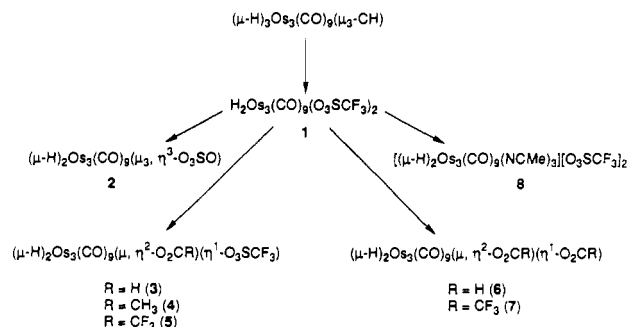
prepared according to the literature methods. $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CH)$ was prepared by the method of St. George.[7a] $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CCF_3)$ and $(\mu\text{-}H)Os_3(CO)_{10}(\mu,\eta^2\text{-}O_2CCH_3)$ were prepared similarly from $Os_3(CO)_{10}(NCCH_3)_2$.[7b,c] H_2SO_4 (Baker, 96.3%), HCO_2H (Aldrich, 97%), F_3CCO_2H (Aldrich, 99%), *n*-pentane (American Burdick and Jackson), $(n\text{-}Bu_4N)OH$ (Aldrich, 40 wt % in water), $(n\text{-}Bu_4N)I$ (Eastman), $(n\text{-}Bu_4N)Cl$ (Eastman), CO (Union Carbide), H_2 (Union Carbide), and cyclohexane (Mallinckrodt) were used as received. F_3CSO_3H (Aldrich) was distilled at reduced pressure. Acetic acid (Mallinckrodt) was distilled from P_4O_{10}, taking a middle cut. Dichloromethane and 1,2-dichloroethane (Baker) were distilled from P_4O_{10}. Acetone (Baker) was distilled from K_2CO_3. Acetonitrile (Mallinckrodt) was distilled from CaH_2. THF and diethyl ether (Baker) were distilled from sodium. H_3PO_4 (Mallinckrodt) saturated with P_4O_{10} (Baker) was prepared by adding P_4O_{10} to H_3PO_4 until excess $P_4O_{10}(s)$ was evident after several days of standing.

Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences. ^1H NMR spectra were obtained on either a Nicolet NT-360 spectrometer (360 MHz) or a GE QE-300 spectrometer (300 MHz) and were referenced to residual proton resonances in the deuterated solvents. ^{19}F NMR spectra were obtained on a Varian EM-390 spectrometer (84.7 MHz) and referenced to external $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCF_3)$ (δ -70.5 vs $CFCl_3$). IR spectra were recorded on either a Perkin-Elmer 281B or a Perkin-Elmer 1750 Fourier transform IR spectrometer and were calibrated with polystyrene film and

(1) For a recent review on coordinated triflate see Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.
(2) E.g. (a) Strope, D.; Shriver, D. F. *Inorg. Chem.* **1974**, *13*, 2652. (b) Black, D. St. C.; Deacon, G. B.; Thomas, N. C. *Polyhedron* **1983**, *2*, 409. (c) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2940. (d) *Inorganic Syntheses*; Shreeve, J. M., Ed.; John Wiley & Sons: New York, 1986; Vol. 24, Chapter 5. (e) Hendry, P.; Sargeson, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 2521. (f) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.* **1989**, *28*, 3001, and references therein.
(3) Abbott, E. H.; Schoenewolf, F.; Backstrom, T. *J. Coord. Chem.* **1974**, *3*, 255.
(4) Dedert, P. L.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 3509.

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(6) Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *31*, 645.
(7) (a) Shapley, J. R.; St. George, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1982**, *21*, 3295. (b) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328. (c) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407.

cyclohexane (2138.5 cm^{-1}). Mass spectra were obtained by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences by using a Varian MAT CH-5 for electron impact, a Varian MAT-731 for field desorption, and a Varian ZAB-SE for fast atom bombardment ionization methods.

The following reactions were carried out customarily under N$_2$ to prevent dilution of the acids with atmospheric water. The starting materials and isolated products are not air sensitive.

H$_2$Os$_3$(CO)$_9$(O$_3$SCF$_3$)$_2$ (1). To (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CH) (200.1 mg, 0.239 mmol) in a round-bottom flask was added neat F$_3$CSO$_3$H (1.0 mL). The solid dissolved slowly with gas evolution and the formation of a yellow solution. This solution was then carefully layered with diethyl ether (ca. 9 mL) and allowed to stand undisturbed at ca. 25 °C. After 60 h, the pale yellow precipitate of **1** was collected, washed with several portions of diethyl ether, and dried in vacuo. Yield: 203.1 mg, 0.181 mmol, 76%.

Anal. Calcd for C$_{11}$H$_2$F$_6$O$_{15}$Os$_3$S$_2$: C, 11.77; H, 0.18; S, 5.71. Found: C, 11.87; H, 0.18; S, 5.65. IR (acetonitrile): ν_{CO} 2149 (m), 2112 (s), 2086 (vs), 2062 (m), 2036 (m), 2017 (m) cm^{-1}. IR (KBr, region from 1400 to 600 cm^{-1}): 1338 (m), 1318 (s), 1302 (vw), 1261 (m, br), 1231 (s), 1215 (vw), 1202 (vs), 1159 (w), 1131 (w), 1033 (m), 1027 (vw), 1000 (s), 983 (m), 697 (w), 644 (vs) cm^{-1}. ^{19}F NMR (acetonitrile): δ −73.6, −73.9, −76.1 (variable intensities, see discussion). MS (field desorption, ^{192}Os, ^{32}S): *m/z* 1128 (M$^+$).

(μ-H)$_2$Os$_3$(CO)$_9$(μ_3,η^3-O$_3$SO) (2). Compound **1** (7.5 mg, 0.0067 mmol) and neat H$_2$SO$_4$ (0.6 mL) were placed in a round-bottom flask which also contained a Teflon-coated magnetic stir bar. The flask was then placed in a water bath preheated to ca. 60 °C. Stirring effected the slow dissolution of the starting material to give a yellow solution. After 10 min, the flask was removed from the bath and the pale yellow supernatant removed from a small quantity of starting material with the aid of a pipet. Addition of this supernatant to water (4 mL) gave **2** as an exceedingly pale yellow powder. This powder was washed with water (two 4-mL portions), dried in vacuo, and identified by its characteristic infrared spectrum.[8] Yield: 2.6 mg, 0.0028 mmol, 42%.

(μ-H)$_2$Os$_3$(CO)$_9$(μ,η^2-O$_2$CH)(η^1-O$_2$CH) (6). To **1** (36.7 mg, 0.0327 mmol) in a Schlenk tube containing a stir bar and under N$_2$ was added HCO$_2$H (2.0 mL). After the mixture was stirred for ca. 12 h, the yellow solution was concentrated at reduced pressure to approximately half its original volume. Upon addition of the remaining solution to water (5.5 mL) a fluffy light yellow precipitate of **6** resulted. The product was collected, washed with several portions of water, and dried in vacuo. Yield: 21.5 mg, 0.0235 mmol, 72%.

Anal. Calcd for C$_{11}$H$_4$O$_{13}$Os$_3$: C, 14.44; H, 0.44. Found: C, 14.18; H, 0.62. ^{1}H NMR (dichloromethane-*d$_2$*): δ 7.54 (1 H; μ-O$_2$CH), 7.13 (1 H, η^1-O$_2$CH), −12.50 (2 H). MS (field desorption, ^{192}Os): *m/z* 920 (M$^+$).

(μ-H)$_2$Os$_3$(CO)$_9$(μ,η^2-O$_2$CH)(η^1-O$_3$SCF$_3$) (3). Compound **1** (42.6 mg, 0.0379 mmol) was placed in a 12-mL conical centrifuge tube and the tube fitted with a rubber serum stopper. HCO$_2$H (2.0 mL) was added via syringe and the tube vigorously shaken for ca. 3 min. The mixture was then separated by centrifugation and the light yellow supernatant decanted from a yellow solid (**1**) via cannula directly into water (ca. 50 mL). Immediately upon addition of the extract to water, a fine yellow precipitate of crude **3** formed. The above extraction process was repeated five additional times, with each new HCO$_2$H extract being decanted into the common aqueous suspension. Some unreacted **1** remained (11 mg, 0.010 mmol). The crude product was collected on a sintered-glass funnel (medium porosity), washed with water, and then extracted from the frit with dichloromethane. After the solvent was removed, the crude product **3** was dried over NaOH for 12 h. The crude product was extracted with dichloromethane/*n*-pentane (1/1) to give, after removal of the solvent from the extract and drying in vacuo, a moderately pure product (15.2 mg, 0.0149 mmol, 53%). Further purification was effected by recrystallization from dichloromethane/cyclohexane, followed by a *n*-pentane wash and drying in vacuo. Yield: 9.1 mg, 0.0089 mmol, 32%.

Anal. Calcd for C$_{11}$H$_3$F$_3$O$_{14}$Os$_3$S: C, 12.97; H, 0.30. Found: C, 13.09; H, 0.30. ^{1}H NMR (dichloromethane-*d$_2$*): δ 7.574 (1 H), −11.88 (2 H). MS (field desorption, ^{192}Os, ^{32}S): *m/z* 1024 (M$^+$), 875 (M$^+$ − O$_3$SCF$_3$).

(μ-H)$_2$Os$_3$(CO)$_9$(μ,η^2-O$_2$CCH$_3$)(η^1-O$_3$SCF$_3$) (4). To **1** (57.0 mg, 0.0508 mmol) in a Schlenk tube containing a stir bar and under N$_2$ was added acetic acid (4.0 mL). The solid slowly dissolved to give a yellow solution. After about 30 min, a light yellow precipitate of **4** began to form. Stirring of the resulting mixture was continued for another 14 h. The product was then collected on a sintered-glass funnel (medium porosity), washed with *n*-pentane, and dried in vacuo. Yield: 40.0 mg,

0.0387 mmol, 76%. Crystals suitable for X-ray diffraction were grown by slow evaporation of a concentrated acetone solution of **4**.

Anal. Calcd for C$_{12}$H$_5$F$_3$O$_{14}$Os$_3$S: C, 13.96; H, 0.49. Found: C, 14.01; H, 0.44. ^{1}H NMR (dichloromethane-*d$_2$*): δ 1.89 (3 H), −11.80 (1 H). ^{19}F NMR (dichloromethane-*d$_2$*): δ −72.6. MS (field desorption, ^{192}Os, ^{32}S): *m/z* 1038 (M$^+$).

(μ-H)$_2$Os$_3$(CO)$_9$(μ,η^2-O$_2$CCF$_3$)(η^1-O$_3$SCF$_3$) (5). Compound **1** (24.6 mg, 0.0219 mmol) was placed in a 12-mL conical centrifuge tube and the tube fitted with a rubber serum stopper. F$_3$CCO$_2$H (1.0 mL) was added via syringe and the tube shaken vigorously for 3.5 min. The mixture was then separated by centrifugation and the yellow supernatant decanted from unreacted **1** via cannula directly into water (ca. 40 mL). The above extraction was repeated with a second portion of F$_3$CCO$_2$H (1.0 mL) and the resulting supernatant decanted into the common aqueous suspension. Immediately upon addition of the extracts to water, a fine yellow precipitate of crude **5** formed. This precipitate was collected on a sintered-glass funnel (fine porosity), washed with water, and dried in air for ca. 1 h. It was then extracted from the frit with dichloromethane/*n*-pentane (1/1, 30 mL). Hexanes (10 mL) were added to this extract and the resulting solution concentrated to ca. 3 mL. The precipitate thus formed was collected, washed with *n*-pentane (two 3-mL portions), and dried in vacuo. Recrystallization from dichloromethane/*n*-pentane gave 7.9 mg, 0.0073 mmol, 33% of pure **5**.

Anal. Calcd for C$_{12}$H$_2$F$_6$O$_{14}$Os$_3$S: C, 13.26; H, 0.19. Found: C, 13.44; H, 0.33. ^{1}H NMR (dichloromethane-*d$_2$*): δ −11.84. MS (field desorption, ^{192}Os, ^{32}S): *m/z* 1092 (M$^+$).

Attempted Synthesis of H$_2$Os$_3$(CO)$_9$(O$_3$POH) (9) from 1. (Method A). Compound **1** (18.3 mg, 0.0163 mmol) and H$_3$PO$_4$ (0.2 mL, saturated with P$_4$O$_{10}$) were dissolved in acetone (1.0 mL) to give an orange solution. ^{1}H NMR showed no significant signals in the hydride region. No solids were recovered upon dilution of this solution with water.

(Method B). In a solvent-free approach, **1** (32.7 mg, 0.0291 mmol) and H$_3$PO$_4$ (0.5 mL, saturated with P$_4$O$_{10}$) were heated at 60 °C with constant stirring for 45 min. After unreacted and undissolved **1** was collected (21.8 mg, 0.0194 mmol), the H$_3$PO$_4$ phase was diluted with water but no solids were recovered.

[(μ-H)$_2$Os$_3$(CO)$_9$(NCCH$_3$)$_3$]O$_3$SCF$_3$]$_2$ (8). To **1** (48.1 mg, 0.0428 mmol) in a round-bottom flask containing a Teflon-coated magnetic stir bar was added acetonitrile (5 mL) via syringe. The mixture was stirred, and **1** slowly dissolved to give a yellow solution. The reaction was followed to completion by IR or ^{19}F NMR. Complete reaction usually required 12–15 h. When no **1** remained, the volatiles were removed at reduced pressure. The yellow residue was triturated with diethyl ether (5 mL), and **8** formed as a bright yellow powder. This powder was collected, washed with diethyl ether (three 5-mL portions), and dried in vacuo. The product thus obtained was analytically pure. Yield: 42.1 mg, 0.0338 mmol, 79%. In an attempt to grow diffraction quality crystals, it was found that **8** can be recrystallized by adding the minimum amount of methanol dropwise to a diethyl ether suspension of **8** and storing at −15 °C. Quality crystals were not obtained, however.

Anal. Calcd for C$_{17}$H$_{11}$F$_6$N$_3$O$_{15}$Os$_3$S$_2$: C, 16.39; H, 0.89; N, 3.37; S, 5.15. Found: C, 16.26; H, 0.99; N, 3.22; S, 5.19. ^{1}H NMR (acetone-*d$_6$*, −30 °C): (isomer II) δ 2.84 (3 H), 2.79 (3 H), 2.73 (3 H), −14.36 (1 H), −14.53 (1 H); (isomer I) δ 2.82 (6 H), 2.67 (3 H), −14.39 (2 H). ^{13}C NMR ($\{^1$H$\}$, acetone-*d$_6$*, −30 °C): (isomer II) δ 174.41 (1 C), 173.60 (1 C), 172.70 (1 C), 172.55 (1 C), 169.18 (1 C), 168.78 (1 C), 165.28 (1 C), 160.99 (1 C), 160.85 (1 C). ^{19}F NMR (acetonitrile): δ −76.1. IR (acetonitrile): ν_{CO} 2154 (mw), 2116 (s), 2092 (vs), 2075 (m), 2046 (m), 2026 (m) cm^{-1}. IR (KBr): ν_{SO}, 1270 (vs, br), 1032 (vs) cm^{-1}; ν_{CF}, 1226 (s), 1158 (s) cm^{-1}. MS (fast atom bombardment, positive ion, ^{192}Os, ^{32}S): *m/z* 1102 (M$^+$ − O$_3$SCF$_3$), 1074 (M$^+$ − O$_3$SCF$_3$ − CO), 1102 − 41*x* (M$^+$ − O$_3$SCF$_3$ − *x*H$_3$CCN, *x* = 1–3), 1074 − 41*x* (M$^+$ − O$_3$SCF$_3$ − CO − *x*H$_3$CCN, *x* = 1–3), 1046 − 41*x* (M$^+$ − O$_3$SCF$_3$ − 2CO − *x*H$_3$CCN, *x* = 1–2), and other unassigned peaks.

Metathesis of 8. Compound **8** (19.0 mg, 0.0152 mmol) was dissolved in acetonitrile (1 mL) and a solution of (*n*-Bu$_4$N)(PF$_6$) (ca. 50 mg) in acetonitrile (1 mL) added with thorough mixing. After the resulting solution was concentrated to ca. 0.2 mL, diethyl ether (5 mL) was added to give a yellow precipitate. This was collected, washed with diethyl ether/dichloromethane (1/1) (two 10-mL portions), and dried in vacuo. This material was treated twice more with (Bu$_4$N)(PF$_6$) (50–100 mg portions) as described above. After a final wash (five 9-mL portions of diethyl ether/dichloromethane (1/1)), the bright yellow solid of [(μ-H)$_2$Os$_3$(CO)$_9$(NCCH$_3$)$_3$][PF$_6$]$_2$ was collected and dried in vacuo. Yield: 10.5 mg, 0.0085 mmol, 56%.

IR (acetonitrile): ν_{CO} 2154 (mw), 2116 (s), 2093 (vs), 2073 (m), 2046 (m), 2027 (m) cm^{-1}. IR (KBr): ν_{PF} 848 (vs) cm^{-1}.

(μ-H)$_2$Os$_3$(CO)$_9$(μ,η^2-O$_2$CCF$_3$)(η^1-O$_2$CCF$_3$) (7). To (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CH) (78.6 mg, 0.0937 mmol) in a round-bottom flask containing a stir bar and fitted with a condenser was added F$_3$CCO$_2$H (ca.

(8) Keiter, R. L.; Strickland, D. S.; Wilson, S. R.; Shapley, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 3846.

5 mL). The reaction mixture was stirred and heated at 75 °C. The $(\mu$-H$)_3$Os$_3$(CO)$_9(\mu_3$-CH$)$ slowly dissolved to give a yellow solution. After 1.5 h, the reaction solution was cooled to room temperature, and the volatiles were removed at reduced pressure. The sticky yellow residue was extracted with dichloromethane, the solution was then evaporated, and the resulting residue was dissolved in acetone. This acetone solution was added to water, which gave an exceedingly fine yellow precipitate of crude **7**, most of which did not settle upon centrifugation. After the crude product that did settle out was recovered, the turbid supernatant was extracted with several portions of dichloromethane. These extracts were combined and concentrated to dryness. The yellow residue was dissolved in acetone. Upon dilution of this acetone solution with water, more crude product precipitated. It was collected by centrifugation, washed with water, and dried in vacuo. The combined crude products were recrystallized from dichloromethane/*n*-pentane at -15 °C to give yellow crystals of **7**. Yield: 57.5 mg, 0.0547 mmol, 58%.

Anal. Calcd for C$_{13}$H$_2$F$_6$O$_{13}$Os$_3$: C, 14.86; H, 0.19. Found: C, 14.82; H, 0.22. ^{1}H NMR (dichloromethane-d_2): δ -12.29. ^{19}F NMR (dichloromethane): δ 70.6 (two resonances). MS (field desorption, ^{192}Os): m/z 1056 (M$^+$).

Reaction of H$_2$Os$_3$(CO)$_9$(O$_3$SCF$_3$)$_2$ (1) with F$_3$CCO$_2$H. To **1** (6.4 mg, 0.0057 mmol) was added F$_3$CCO$_2$H (0.44 mL). After 23 h at ca. 25 °C, the yellow reaction solution was added to water. The pale yellow precipitate was collected, washed with water, and dried in vacuo. It was identified as $(\mu$-H$)_2$Os$_3$(CO)$_9(\mu,\eta^2$-O$_2$CCF$_3)(\eta^1$-O$_2$CCF$_3$) (7) by IR. Yield: 2.6 mg, 0.0025 mmol, 43%.

Reaction of $(\mu$-H$)_2$Os$_3$(CO)$_9(\mu,\eta^2$-O$_2$CCH$_3)(\eta^1$-O$_3$SCF$_3$) (4) with Acetic Acid. Compound **4** (22.6 mg, 0.0219 mmol) and acetic acid (1.5 mL) were placed in a round-bottom flask under N$_2$, and the resulting mixture was heated at 75 °C for 5 min, whereupon a light yellow solution resulted. After the flask was cooled to room temperature, unreacted **4** that had precipitated was filtered off, and water (5 mL) was added to the acetic acid solution. The resulting solids were collected, washed with water, and dried in vacuo.

IR (cyclohexane): ν_{CO} 2124 (w), 2099 (m), 2069 (s), 2019 (vs), 2000 (m) cm^{-1} in addition to weaker bands for **4**. MS (field desorption, ^{192}Os): 1038 (M$^+$ for **4**), 948 (M$^+$ for H$_2$Os$_3$(CO)$_9$(O$_2$CCH$_3$)$_2$), 670 (M$^+$ for Os$_2$(CO)$_6(\mu$-O$_2$CCH$_3$)$_2$).

A longer reaction time of **4** with acetic acid at 75 °C (52 min) completely consumed the starting cluster and gave a solid (after water quench) for which the following spectra were obtained: ^{1}H NMR (dichloromethane-d_2): δ 2.076 (Os$_2$(CO)$_6(\mu$-O$_2$CCH$_3$)$_2$); 1.848 (3 H), 1.805 (3 H), -12.455 (2 H) (H$_2$Os$_3$(CO)$_9$(O$_2$CCH$_3$)$_2$). IR (cyclohexane): ν_{CO} 2124 (w), 2099 (m), 2070 (s), 2065 (s), 2021 (s), 2014 (s), 2000 (vs), 1998 (w) cm^{-1}1. MS (field desorption, ^{192}Os): m/z 948 (M$^+$ for H$_2$Os$_3$(CO)$_9$(O$_2$CCH$_3$)$_2$), 670 (M$^+$ for Os$_2$(CO)$_6(\mu$-O$_2$CCH$_3$)$_2$. Attempts to isolate the cluster H$_2$Os$_3$(CO)$_9$(O$_2$CCH$_3$)$_2$ in pure form were unsuccessful.

Os$_2$(CO)$_6(\mu$-O$_2$CCH$_3$)$_2$. Compound **4** (11.7 mg, 0.0113 mmol) was placed in a 15-mL conical centrifuge tube under N$_2$. Acetic acid (0.5 mL) was added and the resulting mixture stirred at 60 °C for 13.5 h, after which time a yellow solution remained. After the volatiles were removed at reduced pressure, the residue was taken up in dichloromethane, loaded onto a TLC plate, and eluted with dichloromethane. The colorless mobile band of Os$_2$(CO)$_6(\mu$-O$_2$CCH$_3$)$_2$ was recovered and identified by IR[9a] and FD MS. Yield: 4.2 mg, 0.0063 mmol, 56%.

IR (cyclohexane): ν_{CO} 2099 (m), 2064 (vs), 2014 (s), 2001 (vs), 1998 (m), 1976 (vw) cm^{-1}. MS (field desorption, ^{192}Os): m/z 670 (M$^+$), 642 (M$^+$ $-$ CO).

Attempted Reactions of 4 with CO, H$_2$, (n-Bu$_4$N)(O$_3$SCF$_3$), THF, MeCN, and PhCN. The interaction of **4** with each of these substrates was carried out under comparable conditions and was monitored by IR spectroscopy (carbonyl region). The cluster **4** was dissolved in dry 1,2-dichloroethane in a round-bottom flask fitted with a condenser and under a nitrogen atmosphere. In the cases of CO and H$_2$, the gases were admitted slowly and continuously via an immersed dispersion tube. (n-Bu$_4$N)(O$_3$SCF$_3$) (ca. 4 equiv) was added as a solid. For the THF, MeCN, and PhCN reactions, the relevant quantities were 2.5–3 mg of the cluster **4**, 3–5 mL of 1,2-dichloroethane, and 10–30 μL of ligand. After introduction of the substrates, the reaction flasks were placed in an oil bath maintained at 72 °C. After 2 h, no reaction was observed by IR in any instance.

Reaction of 4 with (PPN)Cl. Compound **4** (13.2 mg, 0.0128 mmol) and (PPN)Cl (13.1 mg, 0.0241 mmol) were dissolved in dry 1,2-dichloroethane (3.0 mL) and the resulting solution was heated with an oil bath maintained at 67 °C. Progress of the reaction was followed by

analytical TLC (SiO$_2$/cyclohexane). When no further reaction was evident (2.5 h), the solvent was removed and the resulting residue subjected to preparative TLC (SiO$_2$/hexanes). A single mobile yellow band (R_f = 0.47) was observed and, after recovery, it was identified as the previously reported $(\mu$-H$)$Os$_3$(CO)$_{10}(\mu$-Cl$)$ by IR (carbonyl region).[10] Yield: 3.6 mg, 0.0041 mmol, 32%.

Reaction of 4 with (n-Bu$_4$N)I. Compound **4** (15.6 mg, 0.0151 mmol) and (n-Bu$_4$N)I (9.2 mg, 0.026 mmol) were dissolved in dry 1,2-dichloroethane (25 mL), and the resulting solution was heated with an oil bath maintained at 72 °C. The reaction was followed by IR (carbonyl region) until bands for the starting cluster were no longer evident (2 h). The solvent was then removed and the resulting residue subjected to preparative TLC (SiO$_2$/(hexanes/dichloromethane (10/1))). The predominant mobile yellow band (R_f = 0.67) was recovered and identified as the previously reported $(\mu$-H$)$Os$_3$(CO)$_{10}(\mu$-I$)$[10] by IR (carbonyl region) and FD MS. Yield: 2.6 mg, 0.0027 mmol, 18%.

Reaction of 4 with (PPN)$_2$(S$_2$O$_3$). Compound **4** (12.6 mg, 0.0122 mmol) and (PPN)$_2$(S$_2$O$_3$) (15.6 mg, 0.0131 mmol) were dissolved in 1,2-dichloroethane (10 mL), and the resulting solution was placed in an oil bath maintained at 72 °C. Progress of the reaction was followed by IR; after nearly 4 h, the bands for the starting cluster **4** were only weakly evident. At this point, the solution was cooled to room temperature and the volatiles were removed at reduced pressure. TLC separation of the residue (SiO$_2$/dichloromethane) gave a mobile yellow band that was recovered and identified as the known cluster $(\mu$-H$)_2$Os$_3$(CO)$_9(\mu_3$-S$)$ by comparison of its IR spectrum (ν_{CO} region) with literature values.[11,12] Yield: ca. 5 mg, 50%.

$(\mu$-H$)$Os$_3$(CO)$_{11}(\eta^1$-O$_2$CCF$_3$) and $(\mu$-H$)$Os$_3$(CO)$_{10}(\mu,\eta^2$-O$_2$CCF$_3$). Os$_3$(CO)$_{11}$(NCCH$_3$) (257 mg, 0.279 mmol) in dichloromethane was treated with Me$_3$NO (22 mg, 0.293 mmol) (added as an acetonitrile solution). After 1 h, the reaction solution was evaporated to dryness leaving Os$_3$(CO)$_{10}$(NCCH$_3$)$_2$. Dry cyclohexane solvent (ca. 85 mL) and F$_3$CCO$_2$H (0.4 mL) were then added, and the reaction mixture was stirred and heated under reflux for 2 h. After cooling, the volatiles were removed by rotary evaporation and the resulting yellow residue was subjected to column chromatography (SiO$_2$). The major yellow band that eluted with n-pentane was collected and purified by recrystallization from n-pentane/dichloromethane at -15 °C to give $(\mu$-H$)$Os$_3$(CO)$_{10}$-$(\mu,\eta^2$-O$_2$CCF$_3$) (94.5 mg, 0.0980 mmol, 35%). A second yellow band was eluted with dichloromethane; the material in this band was purified further by preparative TLC (SiO$_2$/dichloromethane, R_f = 0.5), followed by recrystallization from n-pentane/dichloromethane, to give $(\mu$-H$)$-Os$_3$(CO)$_{11}(\eta^1$-O$_2$CCF$_3$) as a bright yellow crystalline material. Yield: 22.6 mg, 0.0228 mmol, 8.2%. Direct reaction of Os$_3$(CO)$_{11}$(NCCH$_3$) (51.3 mg, 0.0558 mmol) with F$_3$CCO$_2$H (0.28 mL) in cyclohexane (ca, 20 mL) at 72 °C for 50 min gave $(\mu$-H$)$Os$_3$(CO)$_{11}(\eta^1$-O$_2$CCF$_3$) in better yield (26.7 mg, 0.0269 mmol, 48%), along with an undetermined quantity of $(\mu$-H$)$Os$_3$(CO)$_{10}(\mu,\eta^2$-O$_2$CCF$_3$).

Characterization data for $(\mu$-H$)$Os$_3$(CO)$_{11}(\eta^1$-O$_2$CCF$_3$). Anal. Calcd for C$_{13}$HF$_3$O$_{13}$Os$_3$: C, 15.73; H, 0.10; N, 0.0. Found: C, 15.71; H, 0.29; N, 0.0. ^{1}H NMR (dichloromethane-d_2): δ -15.29. ^{19}F NMR (dichloromethane): δ -71.1. MS (field desorption, ^{192}Os): m/z 998 (M$^+$).

(n-Bu$_4$N)(O$_3$SCF$_3$). F$_3$CSO$_3$H (0.3 mL) in water (ca. 15 mL) was titrated to the phenolphthalein end point with (n-Bu$_4$N)OH (ca. 20 mL of a 0.15 N aqueous solution). The fluffy white precipitate of (n-Bu$_4$N)(O$_3$SCF$_3$) that resulted was collected, washed with cold water, and dried in vacuo.

Anal. Calcd for C$_{17}$H$_{36}$F$_3$NO$_3$S: C, 52.15; H, 9.27; N, 3.58; S, 8.19. Found: C, 52.33; H, 9.40; N, 3.58; S, 8.25. ^{19}F NMR (acetonitrile): δ -76.1.

Collection of X-ray Diffraction Data for $(\mu$-H$)_2$Os$_3$(CO)$_9(\mu,\eta^2$-O$_2$CCH$_3)(\eta^1$-O$_3$SCF$_3$) (4). A yellow, translucent, tabular crystal (approximate dimensions 0.1 $\times$ 0.2 $\times$ 0.4 mm) with well-developed faces was used for the data collection. There were several visible flaws in the crystal; however, the sample uniformly extinguished plane-polarized light. The sample was mounted with epoxy to a thin glass fiber with the (231) scattering planes roughly normal to the spindle axis. Data were collected with a Syntex P2$_1$ automated four-circle diffractometer; details are given in Table I. Questionable reflections deleted were as follows: two reflections had imbalanced background counts, two peaks were poorly centered, and three peaks flooded the scintillation counter. No problems were encountered collecting the data and there was no change in the appearance of the sample during the experiment. No Ψ-scans were

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Table I. Crystallographic Data for
$(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCH_3)(\eta^1\text{-}O_3SCF_3)$ (4)

$Os_3C_{12}F_3H_5O_{14}S$	fw = 1032.82
a = 8.469 (3) Å	$P2_1/n$ (No. 14), monoclinic
b = 20.840 (9) Å	T = 25 °C
c = 12.562 (4) Å	λ (Mo Kα) = 0.71073 Å
β = 95.49° (3)	ρ_{calcd} = 3.108 g cm^{-3}
V = 2207 (2) Å^3	μ = 174.28 cm^{-1} (numerical cor)
Z = 4	transm factors = 0.282–0.052
$R(F_o)$ = 0.033	$R_2(F_o)$ = 0.043

Table II. Final Positional Parameters for
$(\mu\text{-}H)_2Os_3(CO)_9)(\mu,\eta_2\text{-}O_2CCH_3)(\eta^1\text{-}O_3SCF_3)$ (4)

	x/a	y/b	z/c
Os1	0.99381 (7)	0.17809 (3)	0.65907 (5)
Os2	0.77390 (7)	0.13380 (3)	0.82505 (5)
Os3	0.75841 (7)	0.06379 (3)	0.63678 (5)
S	0.8021 (5)	0.2946 (2)	0.5281 (3)
F1	0.612 (2)	0.3470 (6)	0.655 (1)
F2	0.852 (2)	0.3519 (7)	0.712 (1)
D3	0.764 (1)	0.4129 (5)	0.587 (1)
O11	1.271 (1)	0.1003 (6)	0.7560 (9)
O12	1.172 (2)	0.2963 (6)	0.746 (1)
O13	1.142 (2)	0.1757 (7)	0.4437 (9)
O21	0.534 (1)	0.0486 (6)	0.9228 (10)
O22	0.504 (2)	0.2231 (6)	0.744 (1)
O23	0.838 (2)	0.2110 (7)	1.036 (1)
O31	0.505 (2)	0.1437 (7)	0.518 (1)
O32	0.807 (2)	−0.0229 (7)	0.445 (1)
O33	0.496 (1)	−0.0231 (7)	0.706 (1)
O41	0.796 (1)	0.23337 (5)	0.5918 (8)
O42	0.958 (1)	0.3097 (6)	0.503 (1)
O43	0.677 (1)	0.2971 (6)	0.4444 (9)
O52	0.955 (1)	0.0677 (5)	0.8755 (8)
O53	0.936 (1)	0.0079 (5)	0.7243 (8)
C11	1.164 (2)	0.1285 (8)	0.723 (1)
C12	1.106 (2)	0.2537 (8)	0.716 (1)
C13	1.090 (2)	0.1791 (9)	0.523 (2)
C21	0.623 (2)	0.0796 (9)	0.887 (1)
C22	0.607 (2)	0.1896 (8)	0.775 (1)
C23	0.823 (2)	0.1815 (8)	0.959 (1)
C31	0.601 (2)	0.1144 (8)	0.562 (1)
C31	0.790 (2)	0.0118 (8)	0.514 (2)
C33	0.595 (2)	0.0095 (9)	0.683 (1)
C41	0.756 (2)	0.3567 (9)	0.623 (2)
C51	0.993 (2)	0.0189 (7)	0.818 (1)
C52	1.124 (2)	−0.0249 (8)	0.867 (1)

collected. The 3079 unique reflections (R_i = 0.057, 2350 observed, $I > 2.58\sigma(I)$) were corrected for Lorentz and polarization effects, anomalous dispersion, crystal decay (<3%), and extinction. A numerical absorption correction was applied; maximum and minimum transmission factors were 0.282 and 0.052, respectively.

Solution and Refinement of the Structure of $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCH_3)(\eta^1\text{-}O_3SCF_3)$ **(4).** The structure was solved by direct methods (SHELX); correct positions for the osmium atoms were deduced from an E map. A weighted difference Fourier synthesis revealed positions for 26 additional non-hydrogen atoms, and subsequent least-squares difference Fourier calculations located the remaining non-hydrogen atoms. Contributions from hydrogen atoms were not included in the calculated structure factors. In the final cycle of least squares, non-hydrogen atoms with anisotropic thermal coefficients and an isotropic extinction parameter were refined. Successful convergence was indicated by the maximum shift/error for the last cycle. The final difference Fourier map had no

significant features; the highest peaks were in the vicinity of the osmium atoms. A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors. Final positional parameters are collected in Table II.

Results

The preparation and substitution chemistry of **1** are summarized in Scheme I. Spectroscopic data for **1** and its derivatives are presented in Tables III and IV. A structure study was undertaken for **4**, whose results are given in Table V and Figures 2 and 3. Compound **4** was found to be surprisingly robust toward substitution of its remaining triflate ligand.

Discussion

Reaction of $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CH)$ **with Trifluoromethanesulfonic and Trifluoroacetic Acids.** Dissolution of $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CH)$ in neat F_3CSO_3H results in gas evolution (presumably methane) and the formation of a yellow solution. Keiter et al.[8] used this solution to prepare $H_2Os_3(CO)_9(O_3POH)$ via addition of H_3PO_4 saturated with P_4O_{10} and subsequent precipitation of the product with water. We have found that careful layering of this solution with anhydrous diethyl ether followed by several days standing gives $H_2Os_3(CO)_9(O_3SCF_3)_2$ (**1**) as a yellow crystalline solid. Analogously, the trifluoroacetate complex $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCF_3)(\eta^1\text{-}O_2CCF_3)$ (**7**) is prepared from direct reaction of $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CH)$ and neat trifluoroacetic acid.

Reactions of 1 with Acids. Reaction of **1** with neat sulfuric acid at ca. 60 °C gave $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3,\eta^3\text{-}O_3SO)$ (**2**), first reported by Keiter et al.[8] However, attempts to prepare the analogous hydrogen phosphate cluster, $H_2Os_3(CO)_9(O_3POH)$ (**8**),[8] from **1** were unsuccessful. Reaction of **1** with neat carboxylic acids (HCO_2H, H_3CCO_2H, and F_3CCO_2H) at ca. 25 °C resulted in facile substitution of one triflate group. In the reaction of **1** with acetic acid, the monosubstituted cluster $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCH_3)(\eta^1\text{-}O_3SCF_3)$ (**4**) precipitated directly from the reaction solution in good yield (76%) and purity. The analogous formate and trifluoroacetate complexes, $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CH)(\eta^1\text{-}O_3SCF_3)$ (**3**) and $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCF_3)(\eta^1\text{-}O_3SCF_3)$ (**5**), were also prepared from **1**, but they did not precipitate from their respective reaction media (i.e. the appropriate neat acid) until after dilution with water. Reaction times for these monosubstituted derivatives were quite short (<5 min for **3** and **5** and ca. 30 min for **4**).

Extended reaction of **1** with HCO_2H or F_3CCO_2H resulted in substitution of both triflate ligands, generating the bis(carboxylate) derivatives $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CH)(\eta^1\text{-}O_2CH)$ (**6**) and $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCF_3)(\eta^1\text{-}O_2CCF_3)$ (**7**). At slightly elevated temperatures (60 °C), **4** reacts with acetic acid to give a reasonable yield (56%) of the previously reported dimer, $Os_2(CO)_6(\mu\text{-}O_2CCH_3)_2$.[9] Evidence (FD MS, IR, ^1H NMR) for formation of the intact cluster substitution product, $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}O_2CCH_3)(\eta^1\text{-}O_2CCH_3)$ (analogous to **6** and **7**), was obtained, but conditions were not found where it could be isolated in pure form.

Characterization of 3, 4, 5, 6, and 7. Compounds **3, 4, 5, 6,** and **7**, not surprisingly, have many common spectral features. Each shows a singlet in the hydride region of the ^1H NMR spectrum near δ −12. This value appears to be indicative of hydrides in nonacarbonyl clusters of the general formulations $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3,\eta^3\text{-}X)$ or $(\mu\text{-}H)_2Os_3(CO)_9(\mu,\eta^2\text{-}X)(\eta^1\text{-}X')$ (where X and X' are oxy ligands). In contrast, hydride ligands

Table III. Carbonyl Region IR Spectra for Oxy Ligand Substituted Clusters

| compound	$\nu_{CO},^a$ cm^{-1}					
$H_2Os_3(CO)_9(O_3SCF_3)_2$ (**1**)	2148 (m)	2118 (s)	2091 (vs)	2060 (m)	2046 (m)	2035 (m)
$H_2Os_3(CO)_9(O_2CCF_3)(O_3SCF_3)$ (**5**)	2146 (mw)	2113 (s)	2087 (vs)	2046 (mw)	2032 (m)	2019 (mw)
$H_2Os_3(CO)_9(O_2CH)(O_3SCF_3)$ (**3**)	2144 (mw)	2109 (s)	2082 (vs)	2046 (mw)	2025 (m)	2012 (sh)
$H_2Os_3(CO)_9(O_2CCH_3)(O_3SCF_3)$ (**4**)	2142 (mw)	2107 (s)	2081 (vs)	2046 (mw)	2023 (m)	2011 (sh)
$H_2Os_3(CO)_9(O_3SO)$ (**2**)	2141 (m)	2108 (s)	2080 (vs)	2048 (s)	2038 (m)	2010 (m)
$H_2Os_3(CO)_9(O_2CCF_3)_2$ (**7**)	2139 (m)	2110 (s)	2082 (vs)	2034 (s)	2015 (m)	2004 (w)
$H_2Os_3(CO)_9(O_3POH)$	2134 (m)	2102 (s)	2074 (vs)	2038 (s)		2002 (m)
$H_2Os_3(CO)_9(O_2CH)_2$ (**6**)	2128 (mw)	2102 (m)	2073 (s)	2026 (vs)		2004 (mw)

^{a} For dichloromethane solutions.

Table IV. Oxy Ligand IR Data for Triosmium Carboxylate and Triflate Derivatives[a]

compound	O₃SCF₃ νSO			νCF		η¹-O₂CR νCOO		η²-O₂CR νCOO	
(μ-H)Os₃(CO)₁₁(η¹-O₂CCF₃)				1207 1148	1191	1694	1413		
(μ-H)Os₃(CO)₁₀(μ,η²-O₂CH)								1576	1362
(μ-H)Os₃(CO)₁₀(μ,η²-O₂CCH₃)								1546	1447
(μ-H)Os₃(CO)₁₀(μ,η³-O₂CCF₃)				1211 1174	1202			1649	1469
(μ-H)₂Os₃(CO)₉(μ,η²-O₂CH)(η¹-O₂CH) (6)						1632	1276	1570	1357
(μ-H)₂Os₃(CO)₉(μ,η²-O₂CCF₃)(η¹-O₂CCF₃) (7)				1225 1188 1150	1204 1164	1695	1406	1645	1472
(μ-H)₂Os₃(CO)₉(μ,η²-O₂CH)(η¹-O₃SCF₃) (3)	1336	1209	993	1233 1165	1180			1572	1363
(μ-H)₂Os₃(CO)₉(μ,η²-O₂CCH₃)(η¹-O₃SCF₃) (4)	1343	1202	995	1232 1164	1185			1552	1449
(μ-H)₂Os₃(CO)₉(μ,η²-O₂CCF₃)(η¹-O₃SCF₃) (5)	1337	1204	981	1236 1212 1164	1225 1187			1643	1471
Co(py)₄(η¹-O₃SCF₃)₂[b]	1310	1240	1040	1230	1170				

[a] Dispersed in KBr. [b] Reference 15.

Table V. Comparative Bond Lengths (Å) and Bond Angles (deg) for Structurally Characterized Transition-Metal η¹-Triflate Complexes

compound	M—OTf	MO—S	S=O (av)	S—C	M—O—S
(C₅Me₅)Fe(CO)₂(OTf)[a]	2.007 (3)	1.454 (3)	1.410 (4)	1.805 (6)	133.2 (2)
Me₂Au(OH₂)(OTf)[b]	2.201 (6)	1.456 (6)	1.439 (4)	1.816 (9)	128.7 (4)
Cp₂Zr(OTf)₂(THF)[c]	2.219 (6)	1.455 (7)	1.402 (13)	1.782 (19)	155.2 (5)
Pd(Et₂N(CH₂)₂C(O))(NHEt₂)(OTf)[d]	2.271 (7)	1.441 (8)	1.423 (7)	1.805 (12)	150.5 (4)
(μ-H)₂Os₃(CO)₉(μ,η²-O₂CCH₃)(OTf)[e]	2.146 (10)	1.50 (1)	1.42 (1)	1.82 (2)	126.7 (6)

[a] Reference 30. [b] Reference 31. [c] Reference 32. [d] Reference 33. [e] This work.
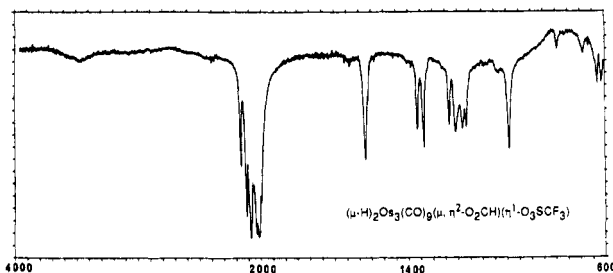
Figure 1. IR spectrum of (μ-H)₂Os₃(CO)₉(μ,η²-O₂CH)(η¹-O₃SCF₃) (3) dispersed in KBr.

in decacarbonyl clusters of formulation (μ-H)Os₃(CO)₁₀(μ,η²-X) exhibit a resonance near δ −10 (e.g., X = O₂CH, O₂CCH₃; δ = −10.28, −10.42).[7b] Compounds 3–7 have similar solution IR spectral patterns (carbonyl region) (see Table III) suggesting that they are isostructural. Values of the carbonyl stretching frequencies follow a trend toward higher energy as the basicity of the oxy ligands decreases.

The coordination modes of the ligands in 3, 4, 5, 6, and 7 can be assigned with reasonable certainty from their IR spectra in the region 1700–900 cm⁻¹ (see Table IV and Figure 1 for a representative IR spectrum). Agreement between the asymmetric and symmetric carboxylate stretching vibrations in 3, 4, and 5 with those observed in the respective (μ-H)Os₃(CO)₁₀(μ,η²-carboxylate) derivatives is excellent. Since both (μ-H)Os₃-(CO)₁₀(μ,η²-O₂CH)[7a] and (μ-H)Os₃(CO)₁₀(μ,η²-O₂CCH₃)[13] have been structurally characterized, the carboxylate moieties in 3, 4, and 5 can be safely assigned as bridging, bidentate.[14] Splitting of the triflate S–O stretches from the two-band pattern of the free ion (1280 and 1035 cm⁻¹)[15] to the three-band pattern seen in 3, 4, and 5 is consistent with a reduction in symmetry of the triflate group from C₃ᵥ (free ion) to Cₛ upon unidentate coordination.

Compound 6 shows four bands in the νCOO region, of which two (1570 and 1357 cm⁻¹) are readily assigned to the expected bihapto formate group. Bands at 1632 and 1276 cm⁻¹ can be assigned to a monohapto formate.[16] A shift of the asymmetric νCOO to higher energy and the symmetric νCOO to lower energy compared to values for η²-carboxylate coordination is characteristic of η¹-carboxylate coordination.[17] Similarly, for 7, the four principal bands observed in the νCOO region can be assigned to one bihapto F₃CCO₂ moiety (1645 and 1472 cm⁻¹) and one monohapto F₃C-CO₂ group (1695 and 1406 cm⁻¹).[18] These values agree well with those for F₃CCO₂ groups in (μ-H)Os₃(CO)₁₀(μ,η²-O₂CCF₃) (1649 and 1469 cm⁻¹) and (μ-H)Os₃(CO)₁₁(η¹-O₂CCF₃) (1694 and 1413 cm⁻¹) (see also Table IV).

Although the spectroscopic data suggest that 3, 4, 5, 6, and 7 are isostructural, they do not establish whether the oxy ligands adopt a cis or trans configuration. A diffraction study was therefore carried out on 4 to answer the cis/trans question.

X-ray Crystal Structure of (μ-H)₂Os₃(CO)₉(μ,η²-O₂CCH₃)(η¹-O₃SCF₃). The structure of 4 (see Figure 2) shows the acetate and triflate ligands in the trans axial configuration with each of the three ligating oxygen atoms bound to a separate metal center. As was suggested by the vibrational data, the acetate adopts an η² coordination mode and the triflate η¹. The hydrides, though not located directly, can be safely assumed to bridge the Os(1)–Os(2) and Os(1)–Os(3) edges. In general, M–M distances are increased when bridging by H occurs.[19] In 4, the Os(1)–Os(2)

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(14) (μ-H)Os₃(CO)₁₀(μ,η²-O₂CCF₃) is isostructural with the formate and acetate derivatives on the basis of spectroscopic evidence. See ref 7b.
(15) Byington, A. R.; Bull, W. E. *Inorg. Chim. Acta* **1977**, *21*, 239.

(16) Brower, D. C.; Winston, P. B.; Tonker, T. L.; Templeton, J. L. *Inorg. Chem.* **1986**, *25*, 2883 have reported the mononuclear complex Mo-(CO)₂(PEt₃)₂(O₂CH)₂ which contains both a chelating bidentate and a unidentate formate ligand.
(17) (a) Deacon, G. B.; Phillips. R. J. *Coord. Chem. Rev.* **1980**, *33*, 227. (b) Deacon, G. B.; Huber, F.; Phillips, R. J. *Inorg. Chim. Acta* **1985**, *104*, 41.
(18) Colbran, S. B.; Irele, P. T.; Johnson, B. F. G.; Kaye, P. T.; Lewis, J.; Raithby, P. *J. Chem. Soc., Dalton Trans.* **1989**, 2033, have recently reported the structure of (μ-H)₂Os₃(CO)₉(μ-PPh₂)(η¹-O₂CCF₃), an osmium cluster containing a unidentate O₂CCF₃ ligand.
(19) In the triosmium system see, for example: (a) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145. (b) Calvert, R. B.; Shapley, J. R.; Shultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6240.
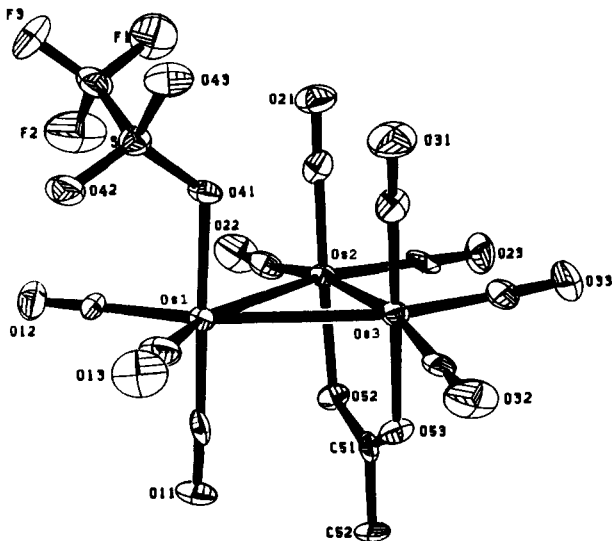
Figure 2. ORTEP diagram showing labeling of non-hydrogen atoms and the molecular geometry for (μ-H)$_2$Os$_3$(CO)$_9$(μ,η^2-O$_2$CCH$_3$)(η^1-O$_3$SCF$_3$) (**4**): osmium–osmium distances (Å) Os(1)–Os(3) 3.1016 (9), Os(1)–Os(2) 3.0677 (9), Os(2)–Os(3) 2.7713 (9); osmium–oxygen distances (Å) Os(2)–O(52) 2.11 (1), Os(3)–O(53) 2.12 (1), Os(1)–O(41) 2.146 (10); distances within triflate ligand (Å) S–O(41) 1.50 (1), S–O(42) 1.42 (1), S–O(43) 1.42 (1), S–C(41) 1.82 (2); distances within acetate ligand (Å) C(51)–O(52) 1.31 (2), C(51)–O(53) 1.25 (2), C(51)–C(52) 1.52 (2); Important triflate and acetate ligand angles (deg): Os(1)–O(41)–S 126.7 (6), O(41)–S–C(41) 103.4 (8), O(41)–S–O(42) 112.7 (7), O(41)–S–O(43) 111.3 (7), Os(2)–O(52)–C(51) 123.4 (9), Os(3)–O(53)–C(51) 125.4 (9), O(52)–C(51)–O(53) 125 (1).

Figure 3. Diagram of the triosmium plane and equatorial carbonyls for (μ-H)$_2$Os$_3$(CO)$_9$(μ,η^2-O$_2$CCH$_3$)(η^1-O$_3$SCF$_3$) (**4**). Bridging hydrogens indicated for the Os(1)–Os(2) and Os(1)–Os(3) edges. Os–Os distances are given in the caption for Figure 2.

and Os(1)–Os(3) distances are quite long (3.0677 (9) and 3.1016 (9) Å, respectively), compared to Os(2)–Os(3) (2.7713 (9) Å), and beyond the range normally found for unsupported Os–Os bonds in triosmium carbonyl cluster compounds. Further, the in-plane carbonyls (see Figure 3) are splayed away from the hydride-bridged metal edges as evidenced by, for example, the large Os(2)–Os(1)–C(12) and Os(3)–Os(1)–C(13) angles (107.5 (5)° and 104.2 (5)°, respectively) and the small C(12)–Os(1)–C(13) angle (94.9 (7)°).[20]

Important bond distances and angles relating to the acetate ligand in **4** are similar to those reported for acetate in (μ-H)·Os$_3$(CO)$_{10}$(μ,η^2-O$_2$CCH$_3$) (**10**).[13] For **4** and **10** respectively, the average Os–O distances are 2.11 (1) and 2.13 (1) Å, and the average C–O distances are 1.28 (2) and 1.25 (2) Å. These data (slightly shorter Os–O bonds and slightly longer C–O bonds for **4**) suggest that the acetate ligand may be bound more tightly in **4** than in **10**. However, given the estimated standard deviations and the small differences in bond lengths, these differences are only marginally significant. Other similar structural features for **4** and **10** include the average Os–O–C angles (124.4 (9)° and 124.5 (7)°), the C–C distances (1.52 (2) and 1.52 (4) Å), and the O–C–O angles (125 (1)° and 127.6 (7)°). The only significant difference is the acetate-bridged Os–Os distance (2.7713 (9) Å versus 2.875 (3) Å); this difference is no doubt a result of the additional influence of a concomitant hydride bridge in **10**, an influence absent in **4**. The slight difference in O–C–O angles (bite angles) is probably related to the increased Os–Os distance, a larger bite angle being required for efficient acetate coordination to the longer Os–Os edge in **10**.

In contrast, the triflate ligand shows notable differences with other structurally characterized η^1-triflate complexes, one being the decidedly long S–O$_{Os}$ distance (see Table V). All previous values for this bond length (S–O$_M$) fall in the range 1.441–1.456 Å, whereas for **4** it is 1.50 (1) Å. In addition, the M–O–S angle, at 126.7 (6)°, is smaller than that found in any other complex, though this angle does not correlate with the S–O$_M$ distance. The
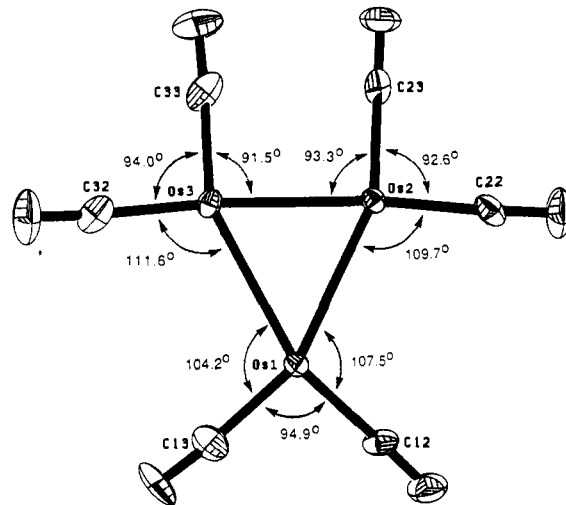
length of the S–O$_{Os}$ bond may indicate a substantial reduction in the S–O$_{Os}$ bond order and, hence, a stronger Os–O bond. Though the Os–O bond length (2.146 Å) in **4** does not support this contention, this length is, at worst, marginally longer than "normal" (cf. Os–O$_{acetate}$ bond lengths above and Os–O distances ranging from 2.11 to 2.14 Å in (μ-H)$_2$Os$_3$(CO)$_9$(μ_3,η^3-O$_3$SO)[8] and 2.149 (21) Å for (μ-H)$_2$Os$_3$(CO)$_9$(μ-PPh$_2$)(η^1-O$_2$CCF$_3$)[18]).

The structure of **4** is reminiscent of that found for (μ-H)$_2$Os$_3$(CO)$_9$(μ_3,η^3-O$_3$SO). Both are nonacarbonyltriosmium clusters containing two symmetrically disposed bridging hydrides and oxy ligands, axially disposed, ligating through three atoms to separate metal centers. In (μ-H)$_2$Os$_3$(CO)$_9$(μ_3,η^3-O$_3$SO), the ligating atoms are constrained, of course, to be cis, but in **4** they adopt the less sterically demanding trans geometry. In either case, cis or trans, they have the same approximate molecular symmetry: C_s. It is, therefore, not surprising that they have similar IR spectra (see Table III).

Reactivity of (μ-H)$_2$Os$_3$(CO)$_9$(μ,η^1-O$_2$CCH$_3$)(η^1-O$_3$SCF$_3$). Compound **4** shows comparative inertness toward further substitution chemistry, consistent with the structural data discussed above for the triflate ligand. No reaction of **4** is observed with H$_2$, CO, THF, MeCN, PhCN, or (n-Bu$_4$N)(O$_3$SCF$_3$) at 72 °C over 2 h. In contrast, the well-studied mononuclear carbonyl triflate complexes M(CO)$_5$(O$_3$SCF$_3$) (M = Mn, Re) undergo rapid substitution of triflate by MeCN in dichloromethane at 26 °C; this occurs via an associative mechanism.[21] The Mn derivative was also found to react with THF under these conditions, but the Re analogue was stable toward substitution even in neat THF.
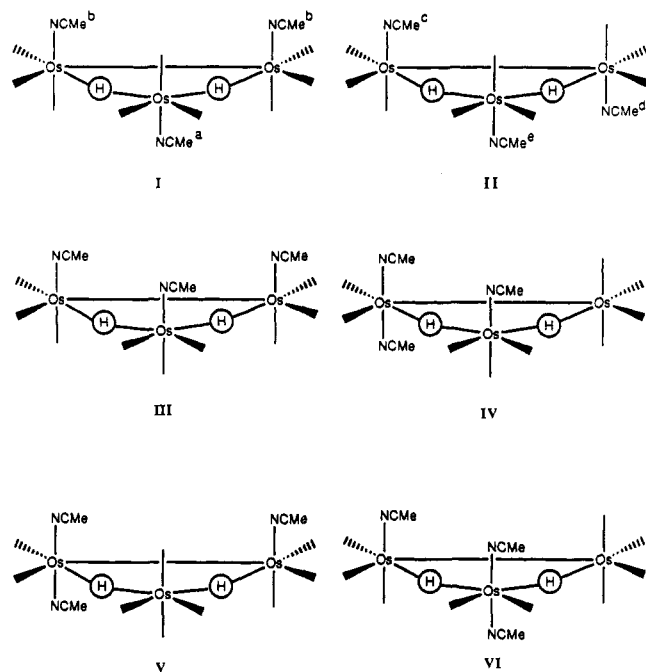
An elevated temperature (75 °C) is required to affect reaction of **4** with acetic acid to produce the bis(acetate) derivative (μ-H)$_2$Os$_3$(CO)$_9$(μ,η^2-O$_2$CCH$_3$)(η^1-O$_2$CCH$_3$); however this cluster could not be isolated in pure form. Another product of this reaction was the known dimer Os$_2$(CO)$_6$(μ-O$_2$CCH$_3$)$_2$. This dimer is formed via **4** under much milder conditions (60 °C, 13.5 h) than its synthesis from Os$_3$(CO)$_{12}$ (185 °C, 5 h).[9a] The presence of two unsupported hydride bridged Os–Os edges in **4** apparently destabilizes its cluster framework allowing fragmentation to lower nuclearity products. A similar destabilization has been observed for [HOs$_3$(CO)$_{12}$]$^+$, which is generated in neat sulfuric acid and, on the basis of ^{1}H NMR evidence, contains a bridging hydride ligand.[22] Upon being heated (100 °C), [HOs$_3$(CO)$_{12}$]$^+$ was reported to fragment to lower nuclearity products such as HOs(CO)$_5^+$.

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Scheme II

I

II

III

IV

V

VI

Figure 4. Variable temperature ^{1}H NMR spectra for $[(\mu\text{-H})_2\text{Os}_3\text{-}(\text{CO})_9(\text{NCCH}_3)_3]^{2+}$ in acetone-d_6: upper panel, hydride region; lower panel, nitrile ligands.

Compound **4** reacts readily with the more nucleophilic halide anions (Cl⁻ and I⁻); the isolable products $((\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-Cl})$ and $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-I})$, respectively), however, result from displacement of both triflate and acetate, as well as scavenging of CO. The cluster $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-I})$ has reportedly been prepared (though not isolated) by thermolysis of $(\mu\text{-H})\text{Os}_3\text{-}(\text{CO})_{10}(\mu\text{-I})$ in *n*-octane solution,[7c] but, owing to the complexity of the solution IR spectrum (ν_{CO} region), we were unable to confirm the presence of this compound in the reaction of **4** with iodide. Reaction of **4** with thiosulfate gave the cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-S})$, perhaps as a result of acid-induced decomposition of $\text{S}_2\text{O}_3^{2-}$ after coordination to the metal framework. This type of decomposition was reported for coordinated thiosulfate in $\text{Cp}_2\text{M}(\text{S}_2\text{O}_3)$ (M = Mo, W) complexes upon reaction with HBr, ultimately giving a species of formula Cp_2MSBr_2.[23]

Reaction of 1 with Acetonitrile. Reaction of **1** with neat acetonitrile proceeded smoothly at room temperature with substitution of the two coordinated triflate ligands by three acetonitrile ligands to give the cluster $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{NCCH}_3)_3][\text{O}_3\text{SCF}_3]_2$ (**8**). During the course of the reaction, IR bands (ν_{CO} region) for **1** (2149 (m), 2112 (s), 2086 (vs), 2062 (m), 2036 (m), 2017 (m) cm⁻¹) disappeared and were replaced by those for **8** (2154 (mw), 2116 (s), 2092 (vs), 2075 (m), 2046 (m), 2026 cm⁻¹). The reaction was complete after 12–15 h. The product **8** was isolated by removing the volatiles at reduced pressure and triturating the resulting yellow residue with diethyl ether. The isolated yield was 79%.

Characterization of 8. The positive ion fast atom bombardment mass spectrum of **8** was obtained and the highest observed multiplet corresponds to a $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{-}(\text{NCCH}_3)_3][\text{O}_3\text{SCF}_3]^+$ fragment (1102, ^{192}Os). Multiplets resulting from successive loss of three acetonitrile ligands from the 1102 amu parent ion were observed, in addition to ones assignable to CO loss or combinations of CO and NCCH₃ loss. The elemental analysis clearly indicated the presence of two triflate counteranions.

The IR and ^{19}F NMR spectra for **8** are in accord with the presence of free triflate. For example, bands observed at 1270, 1226, 1158, and 1032 cm⁻¹ compare favorably with those reported for Na(O₃SCF₃) (i.e. 1280 and 1035 cm⁻¹ (ν_{SO}), 1230 and 1168 cm⁻¹ (ν_{CF})).[15] In addition, metathesis of triflate by PF₆⁻ is easily achieved yielding $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{NCCH}_3)_3][\text{PF}_6]_2$. The PF₆

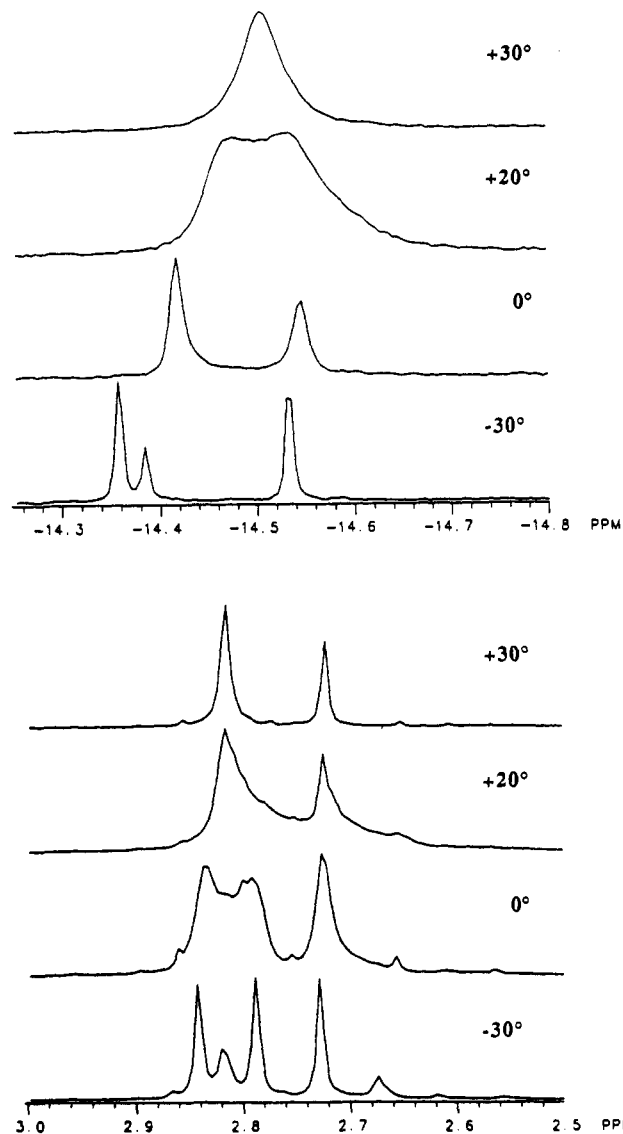salt exhibits a single strong band in the ν_{PF} region at 848 cm⁻¹.[24]

Variable Temperature ^{1}H NMR Studies of 8. Examination of **8** by variable temperature ^{1}H NMR (in acetone-d_6) yielded information on its solution structure and the nature of the dynamic process causing the broad and unsymmetric hydride resonance observed at room temperature. At low temperature (−30 °C), five peaks are observed (see Figure 4) in the nitrile region (δ 2.84, 2.82, 2.79, 2.73, and 2.67) and three in the hydride region (δ −14.36, −14.39, and −14.53). All the nitrile resonances for **8** are downfield of the free ligand (δ 2.03) at values comparable to those for coordinated nitriles in other triosmium clusters.[7c,25,26] Integration indicates that the δ 2.84, 2.79, and 2.73 nitrile resonances and δ −14.36 and −14.53 hydride resonances are of relative intensity 3:3:3:1:1, suggesting a species of low symmetry (C_1).

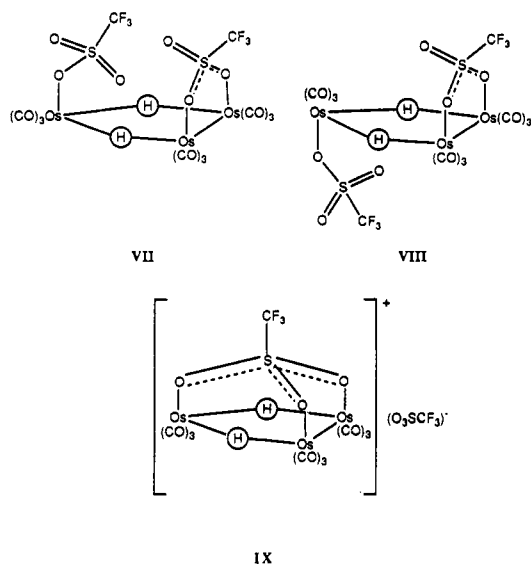(23) Kubas, G. J.; Ryan, R. R. *Inorg. Chem.* **1984**, *23*, 3181.

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(26) Crystallographic studies on Os₃(CO)₁₀(NCCH₃)₂ and $[(\mu\text{-H})\text{Os}_3\text{-}(\text{CO})_{10}(\text{NCCH}_3)_2][\text{Os}(\text{CO})_3\text{Cl}_3]$ indicate axial ligation to be the preferred binding mode for acetonitrile in triosmium carbonyl cluster compounds. See (a) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1982**, 233. (b) Anson, C. E.; Ditzel, E. J.; Fajardo, M.; Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1984**, 2723.

Scheme III

Scheme II shows all the possible isomers (I–VI) of formula [(μ-H)$_2$Os$_3$(CO)$_9$(NCCH$_3$)$_3$]$^{2+}$ assuming (a) only bridging hydrides, and (b) axial acetonitrile coordination.[26] Isomers IV–VI are less likely than I–III since they each contain an unsubstituted Os(CO)$_4$ subunit. This necessitates two strong π-acceptor CO ligands being trans to one another, and such an arrangement is unfavorable on electronic grounds. Also, the ^{13}C NMR spectrum of ^{13}CO enriched **8**, which shows nine equally intense singlets in the CO region assigned to isomer II (C_1 symmetry), shows no evidence for C–C coupling. Such coupling would be expected for the trans CO ligands in a Os(CO)$_4$ subunit and is normally on the order of 33 Hz.[27] The remaining signals in the low temperature ^{1}H NMR spectrum of **8** are of relative intensity 6(δ 2.82):3(δ 2.67):2(δ –14.39). These values are consistent with isomers I and III, both species of approximate C_s symmetry. Isomers I and II can be readily interchanged by hydride migration from adjacent metal–metal edges, and rapid hydride scrambling (on the NMR time scale) should result in only two nitrile resonances and one hydride resonance (relative intensities 6:3:2 respectively) being observed. This is indeed the case for **8** as the +30 °C spectrum shows three signals of relative intensity 6(δ 2.81):3(δ 2.72):2(δ –14.51). This type of dynamic process has been reported in other dihydrido triosmium cluster compounds (e.g. (μ-H)$_2$Os$_3$(CO)$_9$(μ_3-S)[12a] and (μ-H)$_2$Os$_3$(CO)$_9$(μ_3,η^3-O$_3$PPh)[28]). Hydride migration will not interchange isomers II and III. In summary, the variable temperature ^{1}H NMR spectra obtained for **8** are consistent with the presence of two structural isomers, I and II, which are interconverted on the NMR time scale by rapid hydride migration.

Characterization of 1. The formulation of **1** as H$_2$Os$_3$(CO)$_9$-(O$_3$SCF$_3$)$_2$ was based on elemental analysis and the observation of the appropriate molecular ion by FD MS. The IR spectrum

clearly showed coordinated triflate, as evidenced by strong to medium intensity bands attributable to ν_{SO} at 1338, 1318, 1000, and 983 cm^{-1}. Because of the complexity of the spectrum and the absence of a diagnostic difference between ν_{SO} bands for η^1 and η^2 triflate ligands, we cannot, on the basis of the principal ligand vibrations, assign the coordination modes of the triflate ligands. Possible structures for **1** are shown as VII–IX in Scheme III.

The apparent triflate anion bands (e.g. 1261 and 1033 cm^{-1}, cf. ν_{SO} for Na(O$_3$SCF$_3$) at 1280 and 1035 cm^{-1})[15] in the IR spectrum of **1** may result from reaction of a small amount of the cluster with atmospheric water, especially when dispersed (in KBr) and finely divided. A rapid reaction of **1** with water in acetone solution has been observed.[29] The similarity of the pattern for the ν_{CO} bands in the solution IR spectrum of **1** with that for (μ-H)$_2$Os$_3$(CO)$_9$(μ_3,η^3-O$_3$SO) (**2**) and (μ-H)$_2$Os$_3$(CO)$_9$(μ,η^2-O$_2$CCH$_3$)(η^1-O$_3$SCF$_3$) (**4**) (see Table III) suggests similar structures or molecules of similar symmetry (C_s). Though the ν_{CO} values for **1** are shifted to considerably higher energy, this shift is expected given the weak basicity of triflate.

The ^{19}F NMR spectrum of **1** in acetonitrile initially shows three resonances (δ –73.6, –73.9, and –76.1). The signals at δ –73.6 and δ –73.9 are equally intense, while that at δ –76.1 is, initially, much less intense. The δ –73.6 and δ –73.9 resonances are assigned to the two triflate ligands of **1**. The highest field resonance (δ –76.1) is assignable to the uncomplexed triflate anion ((n-Bu$_4$N)(O$_3$SCF$_3$) exhibits this same resonance in acetonitrile). As was mentioned above, **1** reacts slowly with acetonitrile to give **8**.

Compound **1** is insoluble in low polarity solvents such as n-pentane and diethyl ether. It is nearly insoluble in dichloromethane and THF. It is readily soluble in polar solvents such as acetone and nitromethane, but, even though these solvents were carefully dried, evidence for the reaction of **1** with trace amounts of water was noted.

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(29) Compound **1** in dry acetone exhibits carbonyl bands at 2152 (vw), 2137 (w), 2099 (s), 2083 (sh), 2071 (vs), 2051 (m), 2023 (sh), and 2008 (s) cm^{-1}. Upon addition of a small amount of water (1.5 μL/mg cluster) the bands at 2152, 2083, and 2023 cm^{-1} disappear and bands at 2137 (w), 2100 (s), 2071 (vs), 2051 (m), and 2008 cm^{-1} remain. The FD mass spectrum of the solid isolated from this solution was consistent with the formulation H$_2$Os$_3$(CO)$_9$(O$_3$SCF$_3$)(OH) (*m/z* 996 (M$^+$), 846 (M$^+$ – F$_3$CSO$_3$H)). However, the analysis was poor and suggests contamination with triflic acid. Anal. Calcd for C$_{10}$H$_3$F$_3$O$_{13}$Os$_3$S: C, 12.12; H, 0.31; S, 3.24; F, 5.75. Found: C, 13.29; H, 0.76; S, 4.05; F, 7.14.
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