Articles

Promotion of Ring-Opening Nucleophilic Addition to Thietane Ligands by the Bridging Coordination of the Sulfur Atom in the Complexes $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ and $Os_3(CO)_{10}[\mu\text{-}trans\text{-}SC(H)MeCH_2C(H)Me]$

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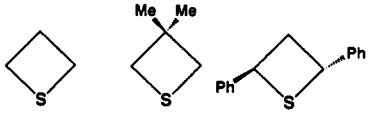
The reaction of $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ (1) with the nucleophiles F^-, Cl^-, Br^-, I^-, EtO^-, Et_2NH, and $(CH_2)_3NH$ at 25 °C yielded after acidification the series of new complexes $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2X](\mu\text{-}H)$ (X = F, **2**, 27%; X = Cl, **3**, 57%; X = Br, **4**, 81%; X = I, **5**, 90%; X = OEt, **6**, 61%; X = NEt_2, **7**, 48%; X = $N(CH_2)_3$, **8**, 68%). Complex **3** was characterized crystallographically and was found to contain a bridging chloroneopentanethiolato ligand formed by the ring-opening addition of chloride to one of the methylene groups of the thietane ligand. Each of the compounds **2–8** contains similarly derived thiolato ligands. The complex $Os_3(CO)_{10}[\mu\text{-}trans\text{-}SC(H)MeCH_2C(H)Me]$ (**9**), an equimolar mixture of the 2*R*,4*R* and 2*S*,4*S* enantiomers, was found to undergo a ring-opening addition of I^- to yield $Os_3(CO)_{10}[\mu\text{-}SC(H)MeCH_2C(H)Me(I)](\mu\text{-}H)$ (**10**), an equimolar mixture of 2*R*,4*S* and 2*S*,4*R* enantiomers formed by an inversion of stereochemistry at the iodine-substituted carbon atom. The stereochemical inversion is consistent with the conventional backside nucleophilic addition mechanism. The reaction of the complex $Os_3(CO)_{11}[SCH_2CMe_2CH_2]$ (**11**) with chloride yielded only the known anion $[Os_3(CO)_{11}Cl]^-$ by ligand displacement. Compounds **3** and **10** were characterized by single-crystal X-ray diffraction analyses. Crystal data: for **3**, space group $P2_1/c$, a = 11.841 (2) Å, b = 14.310 (3) Å, c = 14.642 (3) Å, β = 100.91 (1)°, Z = 4, 2263 reflections, R = 0.036; for **10**, space group $P\bar{1}$, a = 12.534 (2) Å, b = 12.844 (3) Å, c = 7.587 (1) Å, α = 95.62 (2)°, β = 94.62 (1)°, γ = 89.24 (2)°, Z = 2, 2680 reflections, R = 0.029.

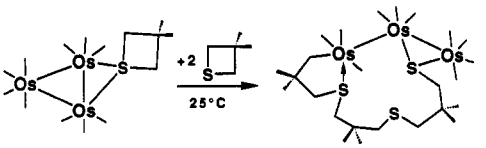
Introduction

The cleavage of carbon–sulfur bonds is a fundamental step in the process of hydrodesulfurization.[1] Recently, we have been investigating the nature of ring-opening transformations of thietane (A) and some of its derivatives (e.g. 3,3-dimethylthietane (B) and *trans*-2,4-diphenylthietane (C)) in metal carbonyl cluster complexes.[2-7]



A B C

We have found that they undergo both thermally[2,3] and photochemically[4,6] induced ring-opening reactions. We have also observed an unusual ring-opening oligomerization of 3,3-dimethylthietane by compound 1 (eq 1).[5] The mechanism of this reaction was proposed to involve a nucleophilic attack of a molecule of 3,3-dimethylthietane on the bridging thietane ligand in 1.



1 (1)

We have now discovered that a variety of nucleophiles will engage in facile ring-opening addition reactions to the bridging 3,3-dimethylthietane ligand in 1. We have established the stereochemical consequences of this ring-opening addition reaction on the carbon center by studying the addition of iodide to the ligand *trans*-2,4-dimethylthietane in the complex $Os_3(CO)_{10}[\mu\text{-}trans\text{-}SC(H)MeCH_2C(H)Me]$. These results are reported here. A preliminary report has been published.[7]

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. Tetrabutylammonium fluoride, tetraethylammonium bromide, tetrabutylammonium iodide, diethylamine (97%), thiophenol (99%), ethyl mercaptan (97%; Aldrich), and tetrapropylammonium chloride and tetraethylammonium chloride (Eastman) were used as purchased. 3,3-Dimethylthietane (3,3-DMT)[8] and racemic *trans*-2,4-dimethylthietane (2,4-DMT)[9] were

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prepared by the published procedures. The latter was separated from its cis isomer by preparative gas chromatography. The syntheses of $Os_3(CO)_{10}[\mu$-3,3-DMT] (1) and $Os_3(CO)_{11}$(3,3-DMT) (11) were described previously,[5] but an improved synthesis of 1 is presented below. Na^+OEt^- in EtOH solution was prepared by the addition of sodium metal to ethanol. Na^+SEt^- was prepared by the reaction of sodium hydride with ethyl mercaptan. All reactions were performed under a nitrogen atmosphere unless specified otherwise. 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, for ^1H and 125.7 MHz for ^{13}C. Chromatographic separations were performed in air on Analtech silica gel (250 μM) F_{254} uniplates. Mass spectra were obtained on a VG Model 70SQ spectrometer using electron impact ionization. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Synthesis of 1. A 15-μL amount of 3,3-dimethylthietane (0.14 mmol) was added via syringe to a solution of $Os_3(CO)_{10}(NCMe)_2$ (125.0 mg, 0.134 mmol) in 30 mL of CH_2Cl_2 at 25 °C. After the mixture was stirred for 1.5 h under a nitrogen purge, the solvent was removed in vacuo, and the residue was chromatographed by TLC. A 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture separated yellow $Os_3(CO)_{11}$(3,3-DMT) (11; 10.8 mg, 8%) from yellow 1 (105.2 mg, 82%). Solid 1 can be stored at −17 °C for weeks.

Reaction of 1 with Tetraethylammonium Chloride. A 4.4-mg (0.024-mmol) amount of $[Et_4N]^+Cl^-\cdot H_2O$ dissolved in 1 mL of CH_3CN was added dropwise to a solution of 1 (22.9 mg, 0.024 mmol) in 10 mL of CH_2Cl_2 at 25 °C. This produced an intermediate species that was partially characterized by IR and ^1H NMR spectroscopy. IR (ν(CO), cm^{-1}; in CH_2Cl_2): 2069 w, 2009 s, 1995 vs, 1982 s, 1927 m. ^1H NMR (δ; in CD_2Cl_2): 3.57 (s, 2 H), 3.14 (m, 8 H), 2.37 (s, 2 H), 1.26 (m, 12 H), 1.14 (s, 6 H). This intermediate is believed to be the salt $Os_3(CO)_{10}[\mu$-$SCH_2CMe_2CH_2Cl]^-[Et_4N]^+$. After the reaction mixture was stirred for 1 h, the anion was protonated by the addition of 10 μL of glacial acetic acid. Conversion to a neutral species was indicated by IR and ^1H NMR spectra. The solvent was removed in vacuo and the residue chromatographed by TLC. Elution with a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture separated yellow $Os_3(CO)_{10}[\mu$-$SCH_2CMe_2CH_2Cl](\mu$-H) (3; 13.2 mg, 57%) from yellow $Os_3(CO)_{10}(\mu$-OH)(μ-H)[8] (3.1 mg, 14%). The reactions of the other halide salts and the isolations of the products were performed similarly: reaction of 1 (44.7 mg, 0.047 mmol) with 42.7 μL (0.047 mmol) of $[Bu_4N]^+F^-$ (TBAF, 1.1 M in THF) yielded yellow $Os_3(CO)_{10}[\mu$-$SCH_2CMe_2CH_2F](\mu$-H) (2; 12.2 mg, 27%); reaction of 1 (34.3 mg, 0.036 mmol) with $[Et_4N]^+Br^-$ (7.6 mg, 0.036 mmol) yielded yellow $Os_3(CO)_{10}[\mu$-$SCH_2CMe_2CH_2Br](\mu$-H) (4; 30.1 mg, 81%); reaction of 1 (39.6 mg, 0.041 mmol) with $[Bu_4N]^+I^-$ (15.0 mg, 0.041 mmol) yielded yellow $Os_3(CO)_{10}[\mu$-$SCH_2CMe_2CH_2I](\mu$-H) (5; 40.1 mg, 90%). In the reactions using F^- and Cl^- small amounts of $Os_3(CO)_{10}(\mu$-OH)(μ-H) were observed. Spectral and analytical data for 2–5 are as follows. For 2: IR (ν(CO), cm^{-1}; in hexane) 2110 w, 2069 vs, 2060 s, 2025 vs, 2019 s, 2007 w, 2001 m, 1991 m, 1985 w; ^1H NMR (δ; in $CDCl_3$) 4.22 (d, 2 H, $^2J_{H-F}$ = 47.5 Hz), 2.37 (s, 2 H), 1.08 (d, 6 H, $^4J_{H-F}$ = 1.7 Hz), −17.40 (s, 1 H). Anal. Calcd (found) for 2: C, 18.52 (18.27); H, 1.14 (1.00). For 3: IR (ν(CO), cm^{-1}; in hexane) 2110 m, 2069 vs, 2060 s, 2036 vs, 2019 s, 2007 w, 2001 s, 1991 s, 1984 m; ^1H NMR (δ; in $CDCl_3$) 3.48 (s, 2 H), 2.38 (s, 2 H), 1.14 (s, 6 H), −17.40 (s, 1 H); ^{13}C NMR (δ; in $CDCl_3$) 181.01 (s, *C*O), 180.44 (s, *C*O), 176.36, 176.34 (d, 2 *C*O, J_{C-H} = 2.4 Hz), 174.10 (s, 2 *C*O), 171.06, 171.04 (d, 2 *C*O, J_{C-H} = 2.9 Hz), 169.88, 169.80 (d, 2 *C*O, J_{C-H} = 10 Hz), 64.27 (s, *C*H_2), 53.80 (s, *C*), 39.58 (s, *C*H_2), 24.81 (s, 2 *C*H_3); MS (70 eV, 100 °C; m/z for ^{192}Os 990 − 28x, x = 0–10 {[M]$^+$ − x(CO)}. Anal. Calcd (found) for 3: C, 18.21 (18.10); H, 1.12 (1.01). For 4: IR (ν(CO), cm^{-1}; in hexane) 2110 m, 2069 vs, 2060 s, 2026 vs, 2019 s, 2007 w, 2001 s, 1991 s, 1984 m; ^1H NMR (δ; in $CDCl_3$) 3.41 (s, 2 H), 2.40 (s, 2 H), 1.18 (s, 6 H), −17.40 (s, 1 H). Anal. Calcd (found) for 4: C, 17.43 (17.58); H, 1.07 (1.01). For 5. IR (ν(CO), cm^{-1}; in hexane) 2110 m, 2069 vs, 2060 s, 2026 vs, 2019 s, 2007 w, 2001 s, 1991 s, 1984 m; ^1H NMR (δ; in $CDCl_3$) 3.29 (s, 2 H), 2.39 (s, 2 H), 1.19 (s, 6 H), −17.40 (s, 1 H). Anal. Calcd (found) for 5: C, 16.67 (16.84); H, 1.03 (0.98).

Reaction of 1 with NaOEt. An ethanolic solution of sodium ethoxide (190 μL, 0.036 mmol, 0.19 M solution) was added via syringe to a solution of 1 (33.8 mg, 0.035 mmol) in 25 mL of ethanol at 25 °C. After it was stirred for 1 h at 25 °C, the mixture was separated as described above to yield yellow $Os_3(CO)_{10}[\mu$-$OC_2H_5](\mu$-H)[11] (3.1 mg, 10%) and yellow $Os_3(CO)_{10}[\mu$-$SCH_2CMe_2CH_2OC_2H_5](\mu$-H) (6; 21.0 mg, 60%). For 6: IR (ν(CO), cm^{-1}; in hexane) 2109 w, 2067 s, 2059 m, 2024 s, 2017 m, 2000 m, 1989 m, 1983 w; ^1H NMR (δ; in $CDCl_3$) 3.47 (q, 2 H, $^3J_{H-H}$ = 7 Hz), 3.22 (s, 2 H), 2.37 (s, 2 H), 1.16 (t, 3 H, $^3J_{H-H}$ = 7 Hz), 1.02 (s, 6 H), −17.40 (s, 1 H); MS (70 eV, 100 °C) m/z for ^{192}Os 999 − 28x, x = 0–10 {[M]$^+$ − x(CO)}.

Reaction of 1 with EtOH. A solution of 1 (20.6 mg, 0.022 mmol) in 25 mL of ethanol was stirred at 25 °C for 19 h. Treatment as above separated yellow $Os_3(CO)_{10}[\mu$-OEt](μ-H) (1.9 mg, 10%) from yellow 6 (12.3 mg, 57%).

Reaction of 1 with NaSEt. Solid sodium ethanethiolate (4.0 mg, 0.05 mmol) was added to a solution of 1 (20.5 mg, 0.022 mmol) in 20 mL of CH_2Cl_2 at 25 °C. After the mixture was stirred for 12 h, treatment as above yielded yellow $Os_3(CO)_{10}[\mu$-SEt](μ-H)[12] (17.2 mg, 87%).

Reaction of 1 with EtSH. Ethyl mercaptan (0.7 μL, 0.012 mmol) was added via syringe to a solution of 1 (10.4 mg, 0.011 mmol) in 5 mL of CH_2Cl_2 at 25 °C. After the mixture was stirred for 12 h, treatment as above yielded yellow $Os_3(CO)_{10}(\mu$-SEt)(μ-H)[12] (7.3 mg, 72%).

Reaction of 1 with PhSH. Thiophenol (5 μL, 0.05 mmol) was added via syringe to a solution of 1 (43.5 mg, 0.045 mmol) in 20 mL of CH_2Cl_2 at 25 °C. After the mixture was stirred for 1.5 h, treatment as above yielded yellow $Os_3(CO)_{10}(\mu$-SPh)(μ-H)[12] (35.0 mg, 81%).

Reaction of 1 with Et_2NH. Diethylamine (2 μL, 0.03 mmol) was added via syringe to a solution of 1 (25.2 mg, 0.027 mmol) in 12 mL of CH_2Cl_2 at 25 °C. After the mixture was stirred for 12 h, a TLC separation using a 2/1 (v/v) hexane/acetone solvent mixture yielded yellow $Os_3(CO)_{10}[\mu$-$SCH_2CMe_2CH_2NEt_2](\mu$-H) (7; 13.2 mg, 48%). For 7: IR (ν(CO), cm^{-1}; in hexane) 2109 w, 2067 s, 2059 m, 2024 s, 2018 m, 1999 m, 1989 m, 1983 w; ^1H NMR (δ; in $CDCl_3$) 2.51 (q, 4 H, $^3J_{H-H}$ = 7 Hz), 2.40 (s, 2 H), 2.28 (s, 2 H), 0.96 (s, 6 H), 0.94 (t, 6 H, $^3J_{H-H}$ = 7 Hz), −17.37 (s, 1 H); MS (70 eV, 160 °C) m/z for ^{192}Os 1026 − 28x, x = 0–10 {[M]$^+$ − x(CO)}.

Reaction of 1 with $(CH_2)_3NH$. Azetidine, $(CH_2)_3NH$ (1.5 μL, 0.027 mmol), was allowed to react with 1 (25.5 mg, 0.026 mmol) in 10 mL of CH_2Cl_2 at 25 °C for 18 h. After removal of the solvent, the product was separated by TLC using a 2/1 (v/v) hexane/acetone solvent mixture to yield yellow $Os_3(CO)_{10}[\mu$-$SCH_2CMe_2CH_2N(CH_2)_3](\mu$-H) (8; 18.3 mg, 68%). For 8: IR (ν(CO), cm^{-1}; in hexane) 2109 w, 2067 s, 2059 m, 2024 s, 2017 m, 1999 m, 1989 m, 1983 w; ^1H NMR (δ; in $CDCl_3$) 3.26 (s, br, 4 H), 2.34 (s, 4 H), 2.03 (t, 2 H, $^3J_{H-H}$ = 6.4 Hz), 0.97 (s, 6 H), −17.39 (s, 1 H); MS (70 eV, 160 °C) m/z for ^{192}Os 1010 − 28x, x = 0–10 {[M]$^+$ − x(CO)}. Anal. Calcd (found) for 8: C, 21.41 (21.48); N, 1.38 (1.28); H, 1.69 (1.59).

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with *trans*-2,4-DMT. *trans*-2,4-Dimethylthietane (approximately 0.06 mmol in 2 mL of CH_2Cl_2) was allowed to react with $Os_3(CO)_{10}(NCMe)_2$ (50.2 mg, 0.054 mmol) in 20 mL of CH_2Cl_2 at 25 °C for 2.5 h. The solvent was removed in vacuo, and the residue was chromatographed by TLC. A 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture yielded yellow $Os_3(CO)_{10}[\mu$-*trans*-$\overline{SC(H)MeCH_2C(H)Me}]$ (9; 23.3 mg, 45%). For 9: IR (ν(CO), cm^{-1}; in hexane) 2093 w, 2036 vs, 2018 m, 1986 m, 1968 m; ^1H NMR (δ; in $CDCl_3$) 4.54 (ddq, 1 H, $^3J_{H-H}$ = 5.6, 8.5 Hz, $^3J_{H-CH_3}$ = 6.8 Hz, $^4J_{H-H}$ = 1.2 Hz), 4.04 (ddq, 1 H, $^3J_{H-H}$ = 7.9, 8.4 Hz, $^3J_{H-CH_3}$ = 7.0 Hz, $^4J_{H-H}$ = 1.1 Hz), 3.05 (ddd, 1 H, $^2J_{H-H}$ = 12.1 Hz, $^3J_{H-H}$ = 7.9, 8.4 Hz), 2.96 (ddd, 1 H, $^2J_{H-H}$ = 12.2

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Hz, $^3J_{H-H}$ = 5.6, 8.5 Hz), 1.58 (d, 3 H, $^3J_{H-H}$ = 7.0 Hz), 1.53 (d, 3 H, $^3J_{H-H}$ = 6.8 Hz).

Reaction of 9 with Tetrabutylammonium Iodide. $[Bu_4N]^+I^-$ (14.4 mg, 0.039 mmol) dissolved in 2 mL of CH_2Cl_2 was added dropwise to a solution of **9** (37.3 mg, 0.039 mmol) in 10 mL of CH_2Cl_2 at 25 °C. After it was stirred for 45 min, the solution was acidified with acetic acid and the solvent was removed in vacuo. The major product, yellow (2*R*,4*S*)-$Os_3(CO)_{10}[\mu$-SC(H)MeC(H)$_2$C(H)(Me)I](μ-H) (**10**; 24.1 mg, 57%), was separated by TLC from a small amount of yellow $Os_3(CO)_{11}$[2,4-DMT] (2.3 mg). For **10**: IR (ν(CO), cm^{-1}; in hexane) 2110 w, 2069 vs, 2060 s, 2025 vs, 2019 s, 2001 s, 1991 m, 1985 w; ^{1}H NMR (δ; in $CDCl_3$) 4.01 (ddq, 1 H, $^3J_{H-H}$ = 11.7, 3.2 Hz, $^3J_{H-CH_3}$ = 6.7 Hz), 2.11 (m, 1 H, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 11.7, 3.6 Hz), 1.98 (d, 3 H, $^3J_{H-H}$ = 6.7 Hz), 1.91 (ddq, 1 H, $^3J_{H-H}$ = 10.7, 3.5 Hz, $^3J_{H-CH_3}$ = 6.6 Hz), 1.42 (m, 1 H, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 10.7, 3.6 Hz), 1.24 (d, 3 H, $^3J_{H-H}$ = 6.6 Hz), −17.56 (s, 1 H). Anal. Calcd (found) for **10**: C, 16.67 (16.90); H, 1.02 (0.95). For $Os_3(CO)_{11}$[SC(H)MeCH$_2$C(H)Me]: IR (ν(CO), cm^{-1}; in hexane) 2110 m, 2056 s, 2037 m, 2021 vs, 2002 m, 1993 m, 1979 m, 1966 w, 1956 w.

Reaction of $Os_3(CO)_{11}$(3,3-DMT) with Tetraethylammonium Chloride. A 7.0-mg (0.04-mmol) amount of $[Et_4N]^+Cl^-\cdot H_2O$ dissolved in 0.5 mL of CD_3CN was added to a solution of $Os_3(CO)_{11}$[3,3-DMT] (**11**; 35 mg, 0.036 mmol) in 1 mL of CD_2Cl_2 at 25 °C. The reaction solution was transferred to a 5-mm NMR tube, and the process was followed by ^{1}H NMR spectroscopy. No formation of a ring-opened thiolate species was detected. Only free 3,3-DMT was observed by NMR. Approximately 10 mg of $Os_3(CO)_{11}(NCCD_3)$ (identified by IR) precipitated from the solution.

Reaction of $Os_3(CO)_{11}$(3,3-DMT) with Tetrapropylammonium Chloride. A 3.3-mg (0.015-mmol) amount of $[Pr_4N]^+Cl^-$ dissolved in 0.5 mL of CH_2Cl_2 was added to a solution of $Os_3(CO)_{11}$(3,3-DMT) (**11**; 15 mg, 0.015 mmol) in 10 mL of CH_2Cl_2 at 25 °C. After the mixture was stirred for 22 h, the solvent was reduced in volume and the residue was chromatographed by TLC using a 1/1 (v/v) CH_2Cl_2/THF solvent mixture. This yielded the known anion $[Os_3(CO)_{11}Cl]^-$, identified by IR spectroscopy.[13]

Crystallographic Analyses. Yellow crystals of **3** were grown by slow evaporation of solvent from a 4/1 hexane/CH_2Cl_2 solvent mixture at −14 °C. Yellow crystals of (2*R*,4*S*)-**10** were grown by slow evaporation of solvent from a 1/1 heptane/benzene solvent mixture at 25 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and the 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 (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[14a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[14b] Lorentz–polarization (Lp) and absorption corrections were applied in each analysis. 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 **3** crystallized in the monoclinic crystal system. The space group $P2_1/c$ 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 except those of the chloroneopentanethiolato ligand were refined with anisotropic thermal parameters. The chloromethyl group was disordered among the three sites adjacent to atom C(2). Occupancy refinement of the chlorine disorder was satisfactorily achieved. All hydrogen atom positions were calculated by assuming idealized geometries. These contributions were added to the structure factor calculations, but their positions were not refined. The hydride ligand was located in a difference Fourier synthesis in a chemically reasonable position but could not be adequately refined.

Compound **10** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydride ligand was located and successfully refined using an isotropic thermal parameter. All other hydrogen atom positions were either located or calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Table I. Crystallographic Data for Diffraction Studies

	3	**10**
empirical formula	$Os_3ClSO_{10}C_{15}H_{11}$	$Os_3ISO_{10}C_{15}H_{11}$
mw	989.36	1080.80
cryst syst	monoclinic	triclinic
lattice params		
a, Å	11.841 (2)	12.534 (2)
b, Å	14.310 (3)	12.844 (3)
c, Å	14.642 (3)	7.587 (1)
α, deg		95.62 (2)
β, deg	110.91 (1)	95.04 (2)
γ, deg		89.24 (2)
V, Å^3	2317.6 (8)	1211.6 (7)
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Z value	4	2
D_{calc}, g/cm^3	2.84	2.96
F_{000}	1768	956
μ(Mo Kα), cm^{-1}	166.7	171.0
temp, °C	20	20
$2\theta_{max}$, deg	43.0	44.0
no. of observns ($I > 3\sigma(I)$)	2363	2680
no. of variables	274	275
residuals: R, R_w	0.036, 0.041	0.029, 0.034
goodness-of-fit indicator	2.25	1.27
max shift in final cycle	0.02	0.04
largest peak in final diff map, e/Å^3	1.21	0.89
abs cor	empirical	empirical

Results

The reactions of $Os_3(CO)_{10}(\mu$-3,3-DMT) (**1**) at 25 °C with a series of nucleophiles produced after acidification the new complexes $Os_3(CO)_{10}(\mu$-SCH$_2$CMe$_2$CH$_2$X)(μ-H) (X = F, **2**, 27%; X = Cl, **3**, 57%; X = Br, **4**, 81%; X = I, **5**, 90%; X = OEt, **6**, 61%; X = NEt$_2$, **7**, 48%; X = N(CH$_2$)$_3$, **8**, 68%). In the preparations of **2**–**5**, intermediates attributed to anionic species of the form $Os_3(CO)_{10}(\mu$-SCH$_2$CMe$_2$CH$_2$X)$^-$ were detected by IR spectroscopy prior to protonation with acetic acid. The anion of **3** was characterized in situ by both IR and ^{1}H NMR spectroscopy. However, all attempts to isolate the anionic species in a crystalline form were unsuccessful. For the reactions of **1** with the secondary amines NEt$_2$H and N(CH$_2$)$_3$H, the hydrogen atom bonded to the nitrogen atom was transferred to the cluster. No acidificiation was performed in the reactions with the amines. In the preparation of the fluoride derivative **2** significant amounts of the side product $Os_3(CO)_{10}(\mu$-OH)(μ-H) (28% yield) were formed from the reaction with H_2O in the TBAF reagent. The structure of **2** was confirmed by its ^{1}H NMR spectrum, which displays fluorine coupling to the hydrogen atoms on the adjacent methylene group (d, 2 H, $^2J_{F-H}$ = 47.5 Hz) on the fluoroneopentanethiolato ligand. Some $Os_3(CO)_{10}(\mu$-OH)(μ-H) was also formed in the preparation of the chloride derivative **3**, possibly due to the H_2O of hydration in the $Et_4NCl\cdot H_2O$ that was used. It is noteworthy that the yield of the

(13) Zuffa, J. L.; Kivi, S. J.; Gladfelter, W. *Inorg. Chem.* **1989**, *28*, 1888.
(14) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 22B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

Table II. Positional Parameters and *B*(eq) Values for 3

atom	*x*	*y*	*z*	*B*(eq), Å^2	occ
Os(1)	0.26426 (06)	0.13308 (04)	0.28683 (05)	2.90 (3)	
Os(2)	0.12590 (06)	0.15255 (05)	0.41010 (05)	3.17 (3)	
Os(3)	0.17815 (06)	0.31271 (05)	0.31607 (05)	2.97 (3)	
Cl(1A)	0.6155 (12)	0.4183 (11)	0.5374 (10)	10.2 (8)	0.56
Cl(1B)	0.694 (03)	0.316 (03)	0.278 (03)	11 (2)	0.20
Cl(1C)	0.657 (03)	0.153 (02)	0.357 (03)	10 (2)	0.24
S(1)	0.3802 (04)	0.2543 (03)	0.3949 (03)	3.1 (2)	
O(11)	0.4122 (15)	0.1290 (11)	0.1543 (12)	7.5 (8)	
O(12)	0.3916 (17)	−0.0315 (11)	0.4114 (13)	9 (1)	
O(13)	0.0720 (14)	0.0109 (10)	0.1466 (11)	6.6 (7)	
O(21)	−0.0995 (13)	0.1269 (12)	0.2217 (12)	7.7 (8)	
O(22)	−0.0112 (13)	0.2574 (10)	0.5197 (10)	5.8 (7)	
O(23)	0.3609 (13)	0.1623 (10)	0.5864 (10)	5.9 (7)	
O(24)	0.1049 (15)	−0.0486 (10)	0.4705 (12)	7.1 (8)	
O(31)	−0.0896 (14)	0.3428 (10)	0.2099 (11)	7.2 (8)	
O(32)	0.2446 (15)	0.4699 (10)	0.2042 (10)	7.1 (8)	
O(33)	0.1772 (13)	0.4310 (09)	0.4876 (09)	5.6 (7)	
C(1)	0.4847 (15)	0.3128 (12)	0.3487 (13)	4.0 (8)	
C(2)	0.6204 (16)	0.3008 (17)	0.4141 (17)	6 (1)	
C(3)	0.651 (04)	0.321 (03)	0.512 (03)	14 (1)	
C(4)	0.691 (02)	0.3566 (16)	0.3649 (17)	6.7 (6)	
C(5)	0.652 (05)	0.193 (04)	0.408 (04)	17 (2)	
C(11)	0.3546 (17)	0.1333 (13)	0.2051 (13)	4.4 (9)	
C(12)	0.3470 (17)	0.0288 (13)	0.3625 (14)	4.6 (9)	
C(13)	0.1424 (18)	0.0558 (13)	0.1982 (13)	4.2 (8)	
C(21)	−0.0192 (19)	0.1374 (14)	0.2887 (16)	5 (1)	
C(22)	0.0375 (17)	0.2177 (13)	0.4778 (13)	4.1 (8)	
C(23)	0.2781 (18)	0.1621 (12)	0.5195 (13)	3.9 (8)	
C(24)	0.1093 (19)	0.0270 (14)	0.4472 (13)	5 (1)	
C(31)	0.0112 (17)	0.3296 (12)	0.2505 (14)	4.3 (8)	
C(32)	0.2203 (17)	0.4096 (13)	0.2457 (12)	4.1 (8)	
C(33)	0.1764 (15)	0.3895 (12)	0.4249 (13)	3.5 (7)	

Table III. Intramolecular Distances for 3[a]

Os(1)–Os(2)	2.851 (1)	Os(3)–C(31)	1.88 (2)
Os(1)–Os(3)	2.853 (1)	Os(3)–C(32)	1.90 (2)
Os(1)–S(1)	2.418 (4)	Os(3)–C(33)	1.94 (2)
Os(1)–C(11)	1.87 (2)	Os(3)–H	1.74
Os(1)–C(12)	1.91 (2)	Cl(1A)–C(3)	1.54 (4)
Os(1)–C(13)	1.91 (2)	Cl(1B)–C(4)	1.42 (4)
Os(1)–H	1.64	Cl(1C)–C(5)	0.96 (5)
Os(2)–Os(3)	2.853 (1)	S(1)–C(1)	1.81 (2)
Os(2)–C(21)	1.99 (2)	O–C (av)	1.14 (2)
Os(2)–C(22)	1.92 (2)	C(1)–C(2)	1.56 (2)
Os(2)–C(23)	1.94 (2)	C(2)–C(3)	1.38 (4)
Os(2)–C(24)	1.91 (2)	C(2)–C(4)	1.51 (3)
Os(3)–S(1)	2.404 (4)	C(2)–C(5)	1.59 (5)

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

halogen-containing products increased progressively in the order F < Cl < Br < I.

Complex **6** was formed both by the reaction of **1** with Na^+OEt^- in ethanol (1 h) and by stirring solutions of **1** in ethanol at 25 °C (19 h). A small amount of $Os_3(CO)_{10}(\mu$-OEt)(μ-H)[11] was also isolated from the latter reaction. In contrast, the reactions of the analogous thiol EtSH and thiolate Na^+SEt^- with **1** resulted only in displacement of the thietane ligand and formation of $Os_3(CO)_{10}(\mu$-SEt)(μ-H).[10]

Compounds **2**–**8** were characterized by IR and ^{1}H NMR spectroscopy. Compound **3** was also characterized by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **3** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. The molecule consists of a triangular cluster of 3 osmium atoms with 10 linear carbonyl ligands. One edge of the triangle, Os(1)–Os(3), is bridged by a chloroneopentanethiolato ligand and a hydride ligand (δ −17.40 ppm). The metal–sulfur distances (2.418 (4) and 2.404 (4) Å) are similar to the metal–sulfur distances (2.40–2.46 Å) normally found for bridging thiolato ligands in osmium cluster complexes.[15] The C(1)–S(1) distance (1.81 (2) Å) is typical of a C–S single bond. The chloromethyl group was disordered unequally among the three sites of the methyl groups on atom C(2). The Cl–C(3) bond distance is 1.54 (4) Å.

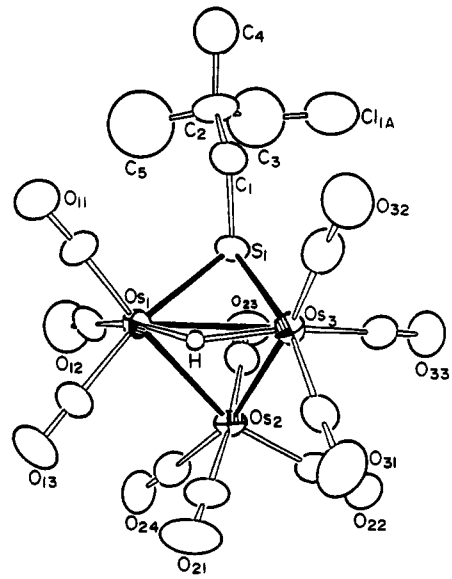


Figure 1. ORTEP diagram of $Os_3(CO)_{10}[\mu$-$SCH_2C(Me)_2CH_2Cl](\mu$-H) (**3**) showing 50% probability thermal ellipsoids.

Table IV. Intramolecular Bond Angles for 3[a]

Os(2)–Os(1)–Os(3)	60.01 (2)	C(1)–C(2)–C(3)	117 (2)
Os(2)–Os(1)–S(1)	80.6 (1)	C(1)–C(2)–C(4)	106 (2)
Os(3)–Os(1)–S(1)	53.5 (1)	C(1)–C(2)–C(5)	107 (2)
Os(1)–Os(2)–Os(3)	60.03 (2)	C(3)–C(2)–C(4)	114 (2)
Os(1)–Os(3)–Os(2)	59.96 (3)	C(3)–C(2)–C(5)	106 (3)
Os(1)–Os(3)–S(1)	54.0 (1)	C(4)–C(2)–C(5)	108 (3)
Os(2)–Os(3)–S(1)	80.8 (1)	Cl(1A)–C(3)–C(2)	116 (3)
Os(1)–S(1)–Os(3)	72.6 (1)	Cl(1B)–C(4)–C(2)	114 (2)
Os(1)–S(1)–C(1)	113.0 (6)	Cl(1C)–C(5)–C(2)	135 (6)
Os(3)–S(1)–C(1)	110.8 (5)	Os–C–O (av)	177 (2)
S(1)–C(1)–C(2)	114 (1)		

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

To obtain information concerning the mechanism of the ring-opening addition reaction, the complex $Os_3(CO)_{10}$(μ-*trans*-SC(H)MeCH$_2$C(H)Me) (**9**), containing a bridging *trans*-2,4-DMT ligand, was prepared. The reaction of **9** with $[Bu_4N]^+I^-$ followed by acidification yielded the ring-opened addition product $Os_3(CO)_{10}[\mu$-(2*R*,4*S*)-SC(H)MeCH$_2$C(H)(Me)I](μ-H) (**10**). The stereochemistry at the carbon centers of the 3-iodo-1-methylbutanethiolato ligand in compound **10** was established by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of $Os_3(CO)_{10}[\mu$-(2*R*,4*S*)-SC(H)MeCH$_2$C(H)(Me)I](μ-H) (**10**) is shown in Figure 2. Since the space group is a centrosymmetric one, the crystal actually contains an equimolar mixture of the two enantiomers $Os_3(CO)_{10}[\mu$-(2*R*,4*S*)-SC(H)MeCH$_2$C(H)(Me)I](μ-H) and $Os_3(CO)_{10}[\mu$-(2*S*,4*R*)-SC(H)MeCH$_2$C(H)(Me)I](μ-H). Final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. The molecule consists of a triangular cluster of 3 osmium atoms with 10 linear carbonyl ligands analogous to that of **3**. One edge of the triangle, Os(1)–Os(3), is bridged by the sulfur atom of the thiolato ligand and a hydride ligand (δ −17.56 ppm). The latter was located

(15) Adams, R. D.; Babin, J. E.; Kim, H. S. *J. Am. Chem. Soc.* **1987**, *109*, 1414.

Table V. Positional Parameters and *B*(eq) Values for 10

atom	*x*	*y*	*z*	*B*(eq), Å²
Os(1)	0.36474 (03)	0.27541 (03)	1.17915 (06)	2.71 (2)
Os(2)	0.27828 (04)	0.14963 (03)	0.86991 (06)	2.97 (2)
Os(3)	0.14560 (03)	0.21123 (03)	1.15074 (06)	2.71 (2)
I(1)	0.25565 (08)	0.63845 (08)	1.68602 (13)	5.70 (5)
S(1)	0.2103 (02)	0.3826 (02)	1.1099 (04)	2.9 (1)
O(11)	0.5318 (08)	0.1079 (08)	1.2476 (13)	5.6 (5)
O(12)	0.5117 (08)	0.3802 (08)	0.9497 (14)	6.3 (5)
O(13)	0.4399 (07)	0.3971 (08)	1.5322 (12)	5.4 (5)
O(21)	0.3440 (08)	−0.0382 (08)	1.0779 (14)	5.9 (5)
O(22)	0.1174 (09)	0.0170 (09)	0.6238 (16)	7.7 (6)
O(23)	0.4689 (08)	0.1247 (08)	0.6425 (14)	6.3 (5)
O(24)	0.2182 (09)	0.3482 (07)	0.6895 (12)	5.9 (5)
O(31)	0.1051 (09)	−0.0202 (07)	1.1714 (15)	6.7 (6)
O(32)	−0.0483 (08)	0.2399 (08)	0.8934 (15)	6.6 (5)
O(33)	0.0256 (07)	0.2590 (08)	1.4844 (13)	5.7 (5)
C(1)	0.1801 (09)	0.4805 (08)	1.2952 (15)	3.2 (5)
C(2)	0.2511 (09)	0.5743 (09)	1.2856 (16)	3.6 (5)
C(3)	0.2285 (09)	0.6701 (09)	1.4085 (16)	3.9 (5)
C(4)	0.0604 (09)	0.5060 (09)	1.2688 (18)	4.1 (6)
C(5)	0.2959 (10)	0.7649 (10)	1.3798 (20)	5.1 (6)
C(11)	0.4681 (10)	0.1709 (10)	1.2204 (15)	3.7 (6)
C(12)	0.4565 (10)	0.3416 (10)	1.0349 (18)	4.3 (6)
C(13)	0.4079 (09)	0.3528 (09)	1.4016 (16)	3.4 (5)
C(21)	0.3202 (10)	0.0305 (10)	1.0036 (18)	4.2 (6)
C(22)	0.1750 (11)	0.0662 (10)	0.7178 (18)	4.5 (6)
C(23)	0.3993 (11)	0.1333 (09)	0.7303 (19)	4.4 (6)
C(24)	0.2392 (10)	0.2772 (10)	0.7623 (15)	3.8 (6)
C(31)	0.1213 (10)	0.0647 (11)	1.1617 (18)	4.3 (6)
C(32)	0.0231 (10)	0.2262 (09)	0.9893 (18)	4.0 (6)
C(33)	0.0739 (09)	0.2462 (09)	1.3584 (17)	3.5 (5)
H	0.284 (07)	0.198 (07)	1.286 (12)	3 (2)

Table VI. Intramolecular Distances for 10[a]

Os(1)–Os(2)	2.8608 (8)	Os(3)–S(1)	2.412 (3)
Os(1)–Os(3)	2.8637 (7)	Os(3)–C(31)	1.92 (1)
Os(1)–S(1)	2.413 (3)	Os(3)–C(32)	1.91 (1)
Os(1)–C(11)	1.88 (1)	Os(3)–C(33)	1.89 (1)
Os(1)–C(12)	1.91 (1)	I(1)–C(3)	2.18 (1)
Os(1)–C(13)	1.91 (1)	S(1)–C(1)	1.85 (1)
Os(1)–H	1.73 (9)	O–C (av)	1.14 (1)
Os(2)–Os(3)	2.8524 (7)	C(1)–C(2)	1.52 (1)
Os(2)–C(21)	1.96 (1)	C(1)–C(4)	1.53 (2)
Os(2)–C(22)	1.93 (1)	C(2)–C(3)	1.51 (2)
Os(2)–C(23)	1.92 (1)	C(3)–C(5)	1.53 (2)
Os(2)–C(24)	1.94 (1)	Os(3)–H	1.96 (9)

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

Table VII. Intramolecular Bond Angles for 10[a]

Os(2)–Os(1)–Os(3)	59.77 (2)	Os(1)–S(1)–Os(3)	72.80 (8)
Os(2)–Os(1)–S(1)	82.09 (7)	S(1)–C(1)–C(2)	107.0 (7)
Os(3)–Os(1)–S(1)	53.58 (6)	S(1)–C(1)–C(4)	106.7 (8)
S(1)–Os(1)–C(11)	169.4 (4)	C(2)–C(1)–C(4)	113 (1)
S(1)–Os(1)–C(12)	95.1 (4)	C(1)–C(2)–C(3)	116 (1)
S(1)–Os(1)–C(13)	95.8 (3)	I(1)–C(3)–C(2)	111.0 (8)
Os(1)–Os(2)–Os(3)	60.16 (2)	I(1)–C(3)–C(5)	108.5 (8)
Os(1)–Os(3)–Os(2)	60.06 (2)	C(2)–C(3)–C(5)	113 (1)
Os(1)–Os(3)–S(1)	53.62 (7)	Os–C–O (av)	177 (1)
Os(2)–Os(3)–S(1)	82.29 (7)	Os(1)–H–Os(3)	102 (5)

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

and refined in the structural analysis. It contains no unusual distortions (S(1)–C(1) = 1.85 (1) Å and C(3)–I(1) = 2.18 (1) Å). Overall, the structure is very similar to that of **3** with the exception of the positions of the methyl groups on the thiolato ligand.

When $[Pr_4N]^+Cl^-$ was allowed to react with the complex $Os_3(CO)_{11}$[3,3-DMT] (**11**) in CH_2Cl_2 solvent for 22 h at 25 °C, the principal product was the known anion $[Os_3(CO)_{11}Cl]^-$[9] obtained by displacement of the DMT ligand with chloride. When **11** was allowed to react with $[Et_4N]^+Cl^-$ in the presence of CD_3CN, the complex $Os_3(CO)_{11}(NCCD_3)$ was formed.

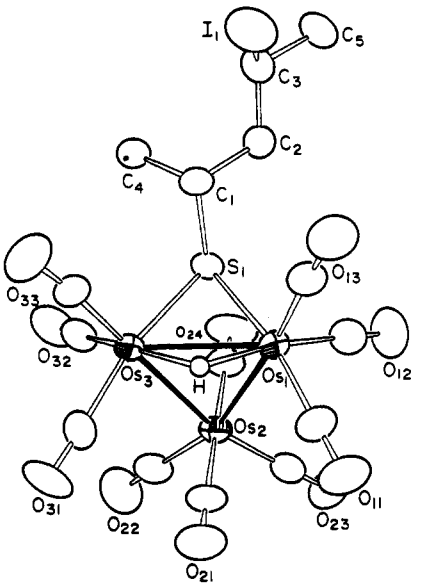
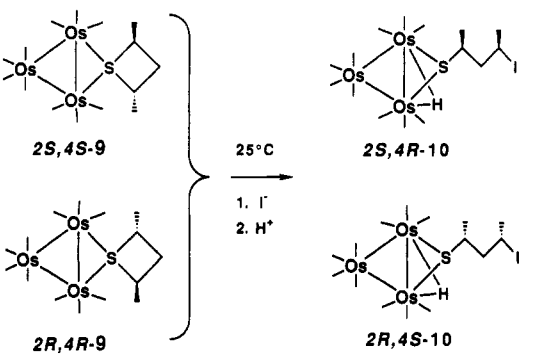


Figure 2. ORTEP diagram of $Os_3(CO)_{10}[\mu$-(2*R*,4*S*)-SC(H)-MeCH$_2$C(H)Me(I)$](\mu$-H) (**10**) showing 50% probability thermal ellipsoids.

Scheme I



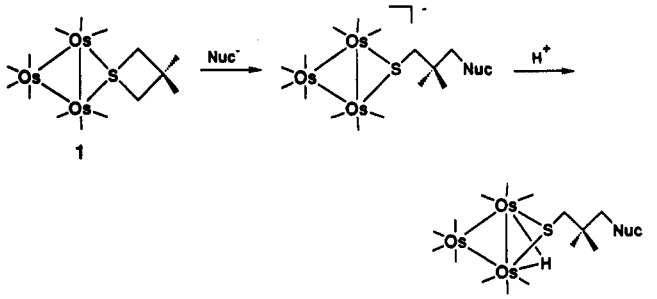
To rule out the possibility of a ring-opening reaction of the free molecule 3,3-DMT by halide, a mixture of 3,3-DMT and $[Et_4N]^+Cl^-$ (dissolved in a minimum of CD_3CN) was placed in an NMR tube in CD_2Cl_2 solution and observed for 48 h at 25 °C. There was no evidence of a reaction.

Discussion

The ring-opening addition of nucleophiles to the bridging dimethylthietane ligands in **1** and **9** has involved the cleavage of a C–S bond and the addition of a nucleophile to one of the α-methylene carbon atoms on the ring. Compound **9** was made from a racemic mixture of (*R*,*R*)-2,4-DMT and (*S*,*S*)-2,4-DMT and thus contains an equimolar mixture of these two enantiomers of the ligand. A ^1H NMR analysis of the mixture formed from the reaction of **9** with I^- shows that an equimolar mixture of enantiomers of only one of the two possible diastereomers of **10** was formed. The stereochemical configuration at the iodine-substituted carbon atom was shown via an X-ray crystallographic analysis to be the inverse of that in the starting material (see Scheme I). A backside S_N2 nucleophilic displacement of sulfur by iodine is the mechanism most consistent with this result.

In the reaction with chloride ion, there was spectroscopic evidence for the existence of an intermediate species. The low frequencies of the absorptions of the CO ligands are consistent with it being negatively charged. For all halide reactions, addition of H^+ produced the neutral hydride-

Scheme II



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containing products in fair to good yields (see Scheme II).

It is noteworthy that the reaction of $[R_4N]^+Cl^-$ in CH_2Cl_2 with **11** yielded only the anion $[Os_3(CO)_{11}Cl]^-$ by nucleophilic displacement of the DMT ligand. When this reaction was performed in CD_3CN, the complex $Os_3(CO)_{11}(NCCD_3)$ was formed. In these reactions there was no evidence for a ring-opening addition reaction.

The greater tendency of the *bridging* thietane ligand to undergo ring opening can be attributed to the combination of Lewis acid effects of the two metal atoms acting to withdraw electron density from the sulfur atom and in turn from the adjacent carbon atoms. Consequently, the carbon atoms in **1** and **9** are more susceptible to nucleophilic attack than those in **11**. Also, the ring-opening reaction in **1** and **9** is significantly faster than the ligand displacement reaction of **11**.

Roundhill et al. have shown that the C–S bonds of thioethers in mononuclear complexes can also be cleaved by the addition of nucleophiles to the carbon center.[16] Kinetic studies of those reactions were consistent with a nucleophilic attack mechanism. Angelici and co-workers[17] have reported that the addition of the nucleophiles MeO^-, MeS^-, EtS^-, i-PrS^-, and $CH(CO_2Me)_2^-$ to the thiophene ligand in the mononuclear complex $[CpRu(\eta\text{-}C_4H_4S)]^+$ produces C–S bond cleavage to give ring-opened products. A mechanism of direct attack of the nucleophile at the ring carbon atom was proposed.

Studies have indicated that thietane rings can be opened by a variety of other mechanisms. For example, Yamamoto et al. have reported that the reaction of $Pd_2(\mu\text{-}Cl)_2Cl_2(PMe_3)_2$ with thietane yields the product $Pd_2(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}Cl)Cl_2(PMe_3)_2$ by a ring-opening addition of chloride to the thietane. However, in this case a mechanism involving the oxidative addition of a C–S bond followed by reductive elimination of a C–Cl bond was proposed.[18] A C–S bond homolysis mechanism was indicated for the ring-opening addition of *trans*-2,4-diphenylthietane to $Os_3(CO)_{10}(NCMe)_2$, which yielded the two isomers $Os_3(CO)_{10}[\mu\text{-}cis\text{-}SC(H)PhCH_2C(H)Ph]$ and $Os_3(CO)_{10}[\mu\text{-}trans\text{-}SC(H)PhCH_2C(H)Ph]$ by a loss of stereochemistry at the carbon atom involved in the C–S cleavage.[3] $Os_3(CO)_{11}(\overline{SCH_2CH_2CH_2})$ and $Re(CO)_8(\overline{SCH_2CMe_2CH_2})^2$ both undergo photoinduced ring opening of their thietane ligands.[4,6] The diversity of mechanism found for the ring-opening reactions of thietanes in metal cluster complexes may extend to metal surfaces.[19]

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Registry No. **1**, 129570-97-4; **2**, 139408-17-6; **3**, 135005-42-4; **4**, 139408-18-7; **5**, 139408-19-8; **6**, 139408-20-1; **7**, 139408-21-2; **8**, 139408-22-3; **9**, 139408-23-4; **10**, 139408-24-5; **11**, 132126-43-3; **B**, 13188-85-7; *trans*-2,4-DMT, 23291-51-2; $Os_3(CO)_{10}(NCMe)_2$, 61817-93-4; $[Et_4N]^+Cl^-$, 56-34-8; $[Bu_4N]^+F^-$, 429-41-4; $[Et_4N]^+Br^-$, 71-91-0; $[Bu_4N]^+I^-$, 311-28-4; NaOEt, 141-52-6; EtOH, 64-17-5; $Os_3(CO)_{10}[\mu\text{-}OEt](\mu\text{-}H)$, 64489-41-4; NaSEt, 811-51-8; $Os_3(CO)_{10}[\mu\text{-}SEt](\mu\text{-}H)$, 23733-18-8; EtSH, 75-08-1; PhSH, 108-98-5; $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$, 23733-19-9; Et_2NH, 109-89-7; $\overline{CH_2CH_2CH_2NH}$, 765-30-0; $[Os_3(CO)_{11}Cl]^-$, 119909-82-9; $[Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2Cl]]^-[Et_4N]^+$, 135005-41-3.

Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for **3** and **10** (8 pages); tables of structure factors (35 pages). Ordering information is given on any current masthead page.

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