filtration, the resulting mixture was analyzed by ^{1}H NMR spectroscopy: $Cp^*_2Ti(Me)Cl$ (δ 1.78 ppm (Cp*), 0.23 (Me)), the reaction product of $Cp^*_2TiO_2CH$ and $PbCl_2$ is insoluble.

Deuterium Scrambling between Cp^*_2TiEt and $Cp^*_2Ti(Et\text{-}d_5)$. Cp^*_2TiEt (61 mg, 0.17 mmol) and $Cp^*_2Ti(Et\text{-}d_5)$ (60 mg, 0.17 mmol) were dissolved in 2 mL of toluene, and the solution was stirred for 48 h under vacuum. D_2O was condensed into the vessel at −196 °C, and the mixture warmed to room temperature. The evolved ethane was collected with a Toepler pump (0.26 mmol, 77%) and subsequently analyzed with MS (m/e (int (%))): 36 (3.5, C_2D_6), 35 (17.5, C_2D_5H), 34 (55.5, $C_2D_4H_2$), 33 (53, $C_2D_3H_3$).

Scambling in $Cp^*_2Ti^{13}CH_2CH_3$. Cp^*_2TiCl (600 mg, 1.70 mmol) was dissolved in 20 mL of ether, and 6.0 mL of a 0.28 M solution of $CH_3{}^{13}CH_2MgI$ (1.68 mmol) was syringed in. After stirring for 1 h, the volatiles were removed in vacuum and the brown residue was extracted with pentane. After crystallization at −80 °C brown crystals were collected: 364 mg (1.05 mmol, 62%). A sample was dissolved in toluene, and DCl was added. The formed ethane was collected in $CDCl_3$ and analyzed by ^{13}C NMR: 1:1 mixture of $CH_3{}^{13}CH_2D$ and $^{13}CH_3CH_2D$.

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Thermal and Photoassisted Ring Opening of Thietane in a Triosmium Cluster Complex

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UV irradiation of $Os_3(CO)_{11}[S(CH_2)_3]$, **1**, produced decarbonylation and formation of two isomers, $Os_3(CO)_{10}[\mu\text{-}S(CH_2)_2CH_2]$, **2**, and $Os_3(CO)_{10}[\mu\text{-}SCH_2CH{=}CH_2](\mu\text{-}H)$, **3**, by C—S bond cleavage and opening of the thietane ring. Compound **2** contains a thiametallacyclopentane ring system that was formed by insertion of an osmium atom into one of the C–S bonds. Compound **3** contains a 2-propenethiolato ligand and bridging hydride ligand formed by a combination of C–S and C–H bond cleavage at the 3-position of the thietane ligand. When heated to 97 °C, **2** was converted to **3** by a β-elimination reaction and $Os_2(CO)_6[\mu\text{-}SCH_2CH_2CH](\mu\text{-}H)$, **4**, by a fragmentation of the cluster. Compound **4** has only two metal atoms, and these are bridged by the sulfur atom, a hydride ligand, and an alkylidene carbon. Compound **3** was also formed in the reaction of thietane with $Os_3(CO)_{10}(NCMe)_2$ at 25 °C. Compound **2** adds phosphines by opening the cluster to yield the adducts $Os_3(CO)_{10}[\mu\text{-}S(CH_2)_2](L)$ (**5**, L = PPh_3; **6**, L = PMe_2Ph). At 97 °C, **5** and **6** undergo β-elimination involving the metallacycle to yield the complexes $Os_3(CO)_9[\mu\text{-}SCH_2CH{=}CH_2](L)(\mu\text{-}H)$ (**7**, L = PPh_3; **8**, L = PMe_2Ph) which are simply phosphine-substitution derivatives of **2**. Compounds **1**, **2**, **4**, **6**, and **7** were characterized by single-crystal X-ray diffraction analysis. For **1**: space group $P2_1/c$, $a = 9.020$ (2) Å, $b = 11.673$ (3) Å, $c = 19.7000$ (4) Å, $\beta = 94.21$ (2)°, $Z = 4$, 1947 reflections, $R = 0.038$. For **2**: space group $P2_1$, $a = 11.750$ (3) Å, $b = 12.623$ (2) Å, $c = 13.242$ (5) Å, $\beta = 100.79$ (2)°, $Z = 4$, 2423 reflections, $R = 0.055$. For **4**: space group $P\bar{1}$, $a = 8.5830$ (9) Å, $b = 12.999$ (2) Å, $c = 6.4810$ (6) Å, $\alpha = 92.23$ (1)°, $\beta = 110.370$ (8)°, $\gamma = 74.165$ (9)°, $Z = 2$, 1266 reflections, $R = 0.027$. For **6**: space group $P2_1/n$, $a = 10.536$ (2) Å, $b = 18.131$ (3) Å, $c = 14.174$ (2) Å, $\beta = 99.57$ (1)°, $Z = 4$, 2780 reflections, $R = 0.024$. For **7**: space group = $P\bar{1}$, $a = 10.341$ (1) Å, $b = 17.584$ (4) Å, $c = 9.736$ (2) Å, $\alpha = 98.35$ (2)°, $\beta = 93.14$ (1)°, $\gamma = 84.39$ (2)°, $Z = 2$, 3247 reflections, $R = 0.038$.

Introduction

Studies of the coordination and reactivity of organosulfur ligands in metal complexes have attracted much attention recently.[1] The transformations of cyclic thioethers such as thiophenes in organometallic complexes and on metal surfaces have been widely studied in an effort to develop an understanding of the mechanisms of the metal-catalyzed hydrodesulfurization reaction.[2] The cleavage of C–S bonds is a key step in this process. We have been investigating the ring opening of the strained-ring thioethers thiirane[3] **A** and thietane[4–10] **B** and their derivatives by transition-metal carbonyl cluster complexes.


A


B

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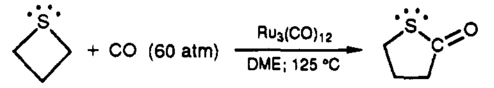
Both of these compounds are readily desulfurized on metal surfaces.[11-13] Alper and co-workers[14] have reported that certain metal cluster complexes can serve as catalyst precursors for the regiospecific ring-opening carbonylation of thietanes to form thiobutyrolactones (eq 1).



(1)

The results of our study of the ring-opening transformations of thietane in triosmium carbonyl cluster complexes are described in this report. A preliminary report of a portion of this work has been published.[4]

Experimental Section

General Data. Reagent-grade solvents were stored over 4-Å molecular sieves. $Os_3(CO)_{11}NCMe$[15] and $Os_3(CO)_{10}(NCMe)_2$[16] were prepared by the published procedures. Thietane (99%, Fluka), PPh_3 (Aldrich), and PMe_2Ph (Aldrich) were used as purchased. Allyl mercaptan (Aldrich) was distilled prior to use. All reactions were performed under a nitrogen atmosphere unless specified otherwise. UV irradiation experiments were performed using a 360-W external high-pressure mercury lamp on reaction solutions in Pyrex glassware. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^1H NMR spectra were run on either a Bruker AM-300 spectrometer or a Bruker AM-500 spectrometer operating at 300 or 500 MHz, respectively. Chromatographic separations were performed in air on Analtech 250-μm F_{254} silica gel HLF Uniplates. Silica gel (70–230 mesh, 60 Å) was used for column chromatography. Mass spectra were obtained on a VG Model 70SQ spectrometer using electron impact ionization. Elemental analyses were performed by either Desert Analytics, Tucson, AZ, or Oneida Research Services, Whitesboro, NY.

Preparation of $Os_3(CO)_{11}[S(CH_2)_3]$, 1. One equivalent of thietane (5.0 μL) was allowed to react with a solution of $Os_3(CO)_{11}(NCMe)$ (60 mg, 0.065 mmol) in 60 mL of CH_2Cl_2 at 25 °C for 1 h. The solvent was removed in vacuo, and the residue was chromatographed by TLC. Elution with a 5/1 (v/v) hexane/CH_2Cl_2 solvent mixture yielded yellow $Os_3(CO)_{11}[S(CH_2)_3]$, 1 (52 mg, 84%). For 1. IR ν(CO) (cm^{-1} in hexane): 2111 (w), 2057 (s), 2036 (s), 2022 (vs), 2010 (m), 2004 (m), 1993 (m), 1977 (m), 1970 (w), 1958 (w). ^1H NMR δ (in $CDCl_3$): 3.65 (t, 4 H, $^3J_{H-H}$ = 7.9 Hz), 2.84 (br s, 2 H). ^1H NMR δ (in CD_2Cl_2 at −43 °C): 3.61 (br m, 4 H), 2.94 (m, 1 H), 2.82 (m, 1 H). Anal. Calcd (Found) for 1: C, 17.65 (17.66); H, 0.63 (0.62).

UV Irradiation of 1. In a typical reaction, 80.0 mg (0.084 mmol) of 1 dissolved in 80 mL of hexane was irradiated for 2 h at 25 °C. The color of the solution changed from yellow to orange/red. The solvent was removed in vacuo, and the unreacted 1 (10 mg) was separated by TLC using hexane as the eluent from a red band that was determined to be a mixture of two products, red $Os_3(CO)_{10}[\mu\text{-}S(CH_2)_3]$, 2, and yellow $Os_3(CO)_{10}[\mu\text{-}SCH_2CH{=}CH_2](\mu\text{-}H)$, 3 (20.0 mg combined total). A ^1H NMR spectrum of this mixture at −43 °C indicated that it contained complex 3 in the amount of 23% based on NMR integrations. A small amount of $Os_3(CO)_{12}$ was also obtained from the reaction. Efforts to separate the isomers in a pure form by chromatography were unsuccessful. However, we were able to separate 3 from 2 by removal of the 3 through repeated fractional crystallizations from the mixture. Both 2 and 3 can be obtained in a pure crystalline form by this procedure. Yields based on the amount of 1 consumed are as follows: 2 (15.4 mg, 23%), 3 (4.6 mg, 7%). For 2. IR ν(CO) (cm^{-1} in hexane): 2107 (w), 2059 (s), 2048 (w), 2021 (vs), 2000 (m), 1989 (sh), 1987 (m), 1945 (w). ^1H NMR δ (in $CDCl_3$ at 25 °C): 3.36 (br m, 1 H), 3.21 (br m, 1 H), 2.60 (br m, 1 H), 2.23 (br m, 1 H). 1.91 (br m, 1 H), 1.59 (br m, 1 H). ^1H NMR δ (in CD_2Cl_2 at −43 °C): 3.30 (m, 1 H), 3.15 (m, 1 H), 2.63 (m, 1 H), 2.18 (m, 1 H), 1.81 (m, 1 H), 1.63 (m, 1 H). Mass spectral analysis m/z (70 eV, 100 °C): for $^{192}Os = 925 - 28x$, $x = 0\text{–}10$ $\{[M]^+ - x(CO)\}$. For 3. IR ν(CO) (cm^{-1} in hexane): 2109 (w), 2068 (vs), 2060 (s), 2025 (vs), 2019 (s), 2000 (m), 1990 (m), 1985 (w). ^1H NMR δ (in $CDCl_3$): 5.81 (ddt, 1 H, $^3J_{H-H}$ = 17.1, 9.8, 6.9 Hz), 5.27 (dd, 2 H, $^3J_{H-H}$ = 17.1, 9.8 Hz), 3.03 (d, 2 H, $^3J_{H-H}$ = 6.9 Hz), −17.44 (s, 1 H). Anal. Calcd (Found) for 3: C, 16.88 (17.14); H, 0.65 (0.58).

Thermolysis of 2. A solution of crystalline 2 (11.5 mg, 0.0124 mmol) in 10 mL of heptane was heated to 97 °C for 1 h. The solvent was removed in vacuo and the residue chromatographed by TLC. Elution with hexanes separated colorless $Os_2(CO)_6[\mu\text{-}SCH_2CH_2CH](\mu\text{-}H)$, 4 (4.0 mg, 51%), from yellow 3 (2.7 mg, 24%). $Os_3(CO)_{12}$ (1.7 mg) was also obtained. For 4. IR ν(CO) (cm^{-1} in hexane): 2094 (w), 2073 (s), 2011 (vs), 2004 (s). ^1H NMR δ (in $CDCl_3$): 5.38 (t, 1 H, $^3J_{H-H}$ = 3.0 Hz), 3.22 (dt, 2 H, $^3J_{H-H}$ = 3.0, 5.9 Hz), 2.75 (t, 2 H, $^3J_{H-H}$ = 5.9 Hz), −14.45 (s, 1 H). ^{13}C NMR δ (in $CDCl_3$): 174.28 (d, 2 *C*O, $^2J_{C-H1}$ = 3 Hz), 172.09 (d, 2 *C*O, $^2J_{C-H1}$ = 3 Hz), 171.85 (d, 2 *C*O, $^2J_{C-H1}$ = 9 Hz), 57.09 (d, *C*H, $^1J_{C-H}$ = 146, $^2J_{C-H1}$ = 3 Hz), 46.17 (d, *C*H_2, $^1J_{C-H}$ = 130, $^3J_{C-H1}$ = 2 Hz), 38.66 (d, *C*H_2, $^1J_{C-H}$ = 141, $^4J_{C-H1}$ = 1 Hz). All ^{13}C NMR experiments were performed at ambient temperature on a Bruker AM-500 spectrometer operating at 125.7 MHz. For normal decoupled experiments, a standard decoupler offset value was used, resulting in the observation of C–H coupling to the hydride ligand. A gated decoupling sequence was employed to ascertain coupling constants to the aliphatic protons. For comparison, the ^{13}C spectrum of the trinuclear alkylidene complex $Os_3(CO)_9[\mu\text{-}SCH_2CMe_2CH](\mu\text{-}H)$[5] is reported here ($\delta$ in $CDCl_3$): 132.91 (d, *C*H, J_{C-H1} = 2.3 Hz), 62.89 (s, *C*H_2), 50.75 (d, *C*Me_2, J_{C-H1} = 2.3 Hz), 33.76 (s, *C*H_3), 33.35 (s, *C*H_3).

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with $CH_2{=}CHCH_2SH$. One equivalent of allyl mercaptan (8.0 μL) was allowed to react with $Os_3(CO)_{10}(NCMe)_2$ (100 mg, 0.110 mmol) in 80 mL of CH_2Cl_2 at 25 °C for 2 h. The solvent was removed in vacuo and the residue chromatographed by TLC. Elution with hexanes yielded yellow 3 (75 mg, 76%).

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with Thietane. An excess of thietane (7 μL) was allowed to react with a solution of $Os_3(CO)_{10}(NCMe)_2$ (30.8 mg, 0.033 mmol) in 15 mL of CH_2Cl_2 at 25 °C for 2 h. The solvent was removed in vacuo, and the residue was chromatographed by TLC to separate yellow 1 (4.9 mg, 16%) from 3 (11.1 mg, 36%). At no time during the reaction did the yellow color of the solution change.

Addition of Phosphines to 2. (a) PPh_3. Triphenylphosphine (10.0 mg, 0.038 mmol) dissolved in 3 mL of hexane was added to a solution of 2 (11.5 mg, 0.012 mmol) in 10 mL of hexane. After the solution was stirred for 18 h at 25 °C, the color had changed from red to bright yellow. 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 yielded yellow $Os_3(CO)_{10}[\mu\text{-}S(CH_2)_2CH_2](PPh_3)$, 5 (4.8 mg, 33%). IR ν(CO) (cm^{-1} in hexane): 2099 (w), 2062 (m), 2038 (s), 2013 (vs), 2003 (m), 1995 (s), 1980 (m), 1975 (w), 1961 (w). ^1H NMR δ (in $CDCl_3$): 7.48–7.38 (m, 15 H), 2.24 (t, 2 H, $^3J_{H-H}$ = 6.4 Hz), 1.19 (t, 2 H, $^3J_{H-H}$ = 5.4 Hz), 1.16 (dt, 2 H, $^3J_{H-H}$ = 6.4, 5.4 Hz). Anal. Calcd (Found) for 5: C, 31.36 (32.12); H, 1.78 (1.58).

(b) PMe_2Ph. Dimethylphenylphosphine (7.0 μL, 0.050 mmol) was added via syringe to a solution of 2 (13.3 mg, 0.014 mmol) in 10 mL of hexane. After the solution was stirred for 1 h at 25 °C, the color had changed from red to yellow. 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 yielded golden yellow $Os_3(CO)_{10}[\mu\text{-}S(CH_2)_2CH_2](PMe_2Ph)$, 6 (9.3 mg, 61%). IR ν(CO) (cm^{-1} in hexane): 2098 (w), 2060 (m), 2036 (m), 2011 (s), 1999 (sh), 1994 (m), 1979 (m), 1974 (m), 1960 (w). ^1H NMR δ (in $CDCl_3$): 7.54–7.44 (m, 5 H), 2.29 (t, 2 H, $^3J_{H-H}$ = 6.6 Hz), 2.17 (d, 6 H, $^2J_{H-P}$ = 9.7 Hz), 1.69 (t, 2 H, $^3J_{H-H}$ = 5.8 Hz), 1.32 (dt, 2 H, $^3J_{H-H}$ = 6.6, 5.8 Hz). Anal. Calcd (Found) for 6: C, 23.73 (23.88); H, 1.61 (1.55).

Attempted Addition of PMe_2Ph to 3. No reaction was observed after 12 h when an excess of dimethylphenylphosphine

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Table I. Crystallographic Data for Compounds 1, 2, 4, 6, and 7

compound	1	2	4	6	7
empirical formula	$Os_3SO_{11}C_{14}H_6$	$Os_3SO_{10}C_{13}H_6$	$Os_2SO_6C_9H_6$	$Os_3SPO_{10}C_{21}H_{17}$	$Os_3SPO_9C_{31}H_{23}Cl_2$
molec wt	952.85	924.84	622.60	1062.99	1244.06
crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
lattice params					
a, Å	9.020 (2)	11.750 (3)	8.5830 (9)	10.536 (2)	10.341 (1)
b, Å	11.673 (3)	12.623 (2)	12.999 (2)	18.131 (3)	17.584 (4)
c, Å	19.7000 (4)	13.242 (5)	6.4810 (6)	14.174 (2)	9.736 (2)
α, deg	90.0	90.0	92.23 (1)	90.0	98.35 (2)
β, deg	94.21 (2)	100.79 (2)	110.370 (8)	99.57 (1)	93.14 (1)
γ, deg	90.0	90.0	74.165 (9)	90.0	84.39 (2)
V, Å^3	2068.8 (9)	1929.3 (9)	650.9 (1)	2670 (1)	1742 (1)
space group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z	4	4	2	4	2
D_{calc}, g/cm^3	3.06	3.18	3.18	2.64	2.37
μ(Mo Kα), cm^{-1}	185.49	198.80	196.90	144.40	112.34
temp, °C	20	20	20	20	20
$2\theta_{max}$, deg	45.0	45.0	42.0	45.0	44.0
no. of obsvns ($I > 3\sigma(I)$)	1947	2423	1266	2780	3247
no. of variables	262	355	161	325	400
residuals: R, R_w	0.038, 0.043	0.055, 0.057	0.027, 0.033	0.024, 0.026	0.038, 0.043
GOF	1.50	2.77	2.28	1.32	1.96
max shift in final cycle	0.11	0.22	0.12	0.01	0.11
largest peak in final diff map, $e^-/Å^3$	1.12	3.52	1.31	0.59	2.74
abs corr	analytical	analytical	analytical	empirical	empirical

was mixed with a hexane solution of 3 at 25 °C, and all of the 3 was recovered by TLC.

Thermolysis of 5 and 6. A solution of 5 (5.0 mg, 0.04 mmol) in 15 mL of heptane was heated to 97 °C for 1 h. The solvent was removed in vacuo, and the residue was chromatographed by TLC with hexane to yield yellow $Os_3(CO)_9[\mu\text{-}SCH_2CH{=}CH_2](PPh_3)(\mu\text{-}H)$, 7 (4.5 mg, 92%). For 7: IR ν(CO) (cm^{-1} in hexane): 2095 (m), 2054 (s), 2018 (vs), 2013 (s), 2006 (m), 1993 (w), 1981 (m), 1975 (m), 1958 (w). ^{1}H NMR δ (in $CDCl_3$): 7.51–7.40 (m, 15 H), 5.50 (m, 1 H), 4.93 (d, 1 H, $^3J_{H-H}$ = 10.1 Hz), 4.71 (d, 1 H, $^3J_{H-H}$ = 17.0 Hz), 2.71 (dd, 1 H, $^2J_{H-H}$ = 13.1, $^3J_{H-H}$ = 5.8 Hz), 1.47 (dd, 1 H, $^2J_{H-H}$ = 13.1, $^3J_{H-H}$ = 7.9 Hz), –16.48 (d, 1 H, J_{P-H} = 6.0 Hz). Mass spectral analysis m/z (70 eV): for ^{192}Os = 1160 – 28x, x = 0–9 {[M]$^+$ – x(CO)}. By a similar treatment, 6 was converted to yellow $Os_3(CO)_9[\mu\text{-}SCH_2CH{=}CH_2](PMe_2Ph)(\mu\text{-}H)$, 8, in 60% yield. For 8: IR ν(CO) (cm^{-1} in hexane): 2091 (m), 2051 (s), 2014 (vs), 2000 (m), 1989 (m), 1967 (m), 1947 (w), 1943 (w). ^{1}H NMR δ (in $CDCl_3$): 7.53–7.35 (m, 5 H), 5.72 (m, 1 H), 5.15 (dd, 2 H, $^3J_{H-H}$ = 16.3, 9.5 Hz), 2.81 (dd, 1 H, $^2J_{H-H}$ = 12.7 Hz, $^3J_{H-H}$ = 6.6 Hz), 2.55 (dd, 1 H, $^2J_{H-H}$ = 12.7, $^3J_{H-H}$ = 7.6 Hz), 2.29 (d, 3 H, J_{P-H} = 10 Hz), 2.26 (d, 3 H, J_{P-H} = 10 Hz), –17.03 (d, 1 H, J_{P-H} = 25.6 Hz). Mass spectral analysis m/z (70 eV): for ^{192}Os = 1036 – 28x, x = 0–9 {[M]$^+$ – x(CO)}.

Crystallographic Analyses. Yellow crystals of 1 were grown by slow evaporation of solvent from a solution in hexane at 25 °C. Red crystals of 2 were grown from a hexane/CH_2Cl_2 solvent mixture at –11 °C. Colorless crystals of 4 were grown from a solution by slow evaporation of a hexane/CH_2Cl_2 solvent mixture at 25 °C. Orange crystals of 6 were grown from a solution by slow evaporation of a hexane/CH_2Cl_2 solvent mixture at 25 °C. Yellow crystals of 8 were grown from a solution by slow evaporation of a hexane/CH_2Cl_2 solvent mixture at 0 °C. All data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[17a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[17b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net}^2)]^{1/2}/\text{Lp}$.

Compound 1 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was established on the basis of the systematic absences observed in the data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound 2 crystallized in the monoclinic crystal system. The systematic absences in the data were consistent with both of the space groups $P2_1/m$ and $P2_1$. However, all attempts to solve the structure in the centric space group $P2_1/m$ were unsuccessful. The noncentric space group $P2_1$ was then assumed and confirmed by a 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 positions of the remaining hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. The residuals in the final difference Fourier synthesis were structurally insignificant.

Compound 4 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 its positional parameters were satisfactorily refined. The positions of the remaining hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound 6 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established on the basis of the systematic absences in the data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added

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

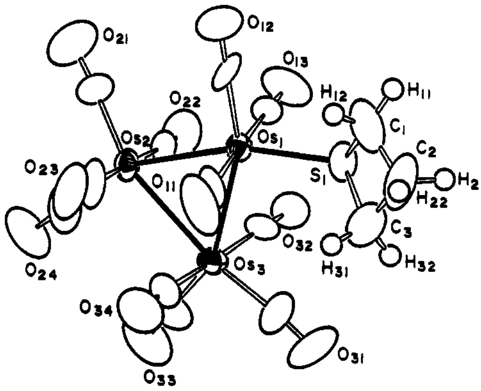

Figure 1. ORTEP diagram of $Os_3(CO)_{11}[S(CH_2)_3]$, 1, showing 50% probability thermal ellipsoids.

Table II. Positional Parameters and *B*(eq) Values (Å^2) for $Os_3(CO)_{11}[S(CH_2)_3]$, 1

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.81937 (8)	0.17609 (7)	0.34471 (3)	2.64 (3)
Os(2)	0.75833 (9)	0.41112 (7)	0.37020 (4)	3.12 (3)
Os(3)	0.53804 (8)	0.23961 (7)	0.39481 (3)	3.10 (3)
S(1)	0.7750 (6)	−0.0208 (4)	0.3205 (2)	4.0 (2)
O(11)	0.924 (2)	0.1131 (14)	0.4918 (7)	8 (1)
O(12)	1.1417 (17)	0.1906 (17)	0.3120 (9)	8 (1)
O(13)	0.7304 (17)	0.2176 (17)	0.1928 (7)	7 (1)
O(21)	1.027 (2)	0.5290 (18)	0.3199 (9)	9 (1)
O(22)	0.5954 (18)	0.4449 (15)	0.2293 (8)	7 (1)
O(23)	0.9357 (19)	0.3768 (13)	0.5083 (8)	7 (1)
O(24)	0.595 (3)	0.6167 (15)	0.4245 (9)	9 (1)
O(31)	0.378 (2)	0.021 (2)	0.4266 (9)	10 (1)
O(32)	0.4273 (15)	0.2165 (14)	0.2444 (7)	5.5 (8)
O(33)	0.291 (2)	0.4087 (19)	0.4189 (10)	10 (1)
O(34)	0.6659 (19)	0.2413 (18)	0.5451 (7)	8 (1)
C(1)	0.939 (3)	−0.113 (2)	0.3390 (12)	7 (1)
C(2)	0.849 (3)	−0.198 (2)	0.3727 (12)	7 (1)
C(3)	0.726 (3)	−0.118 (2)	0.3881 (11)	6 (1)
C(11)	0.877 (2)	0.1415 (19)	0.4396 (10)	4 (1)
C(12)	1.017 (2)	0.1858 (19)	0.3251 (12)	5 (1)
C(13)	0.7593 (20)	0.2076 (15)	0.2499 (10)	3.2 (9)
C(21)	0.925 (3)	0.480 (2)	0.3384 (9)	6 (1)
C(22)	0.653 (2)	0.4285 (16)	0.2810 (10)	4 (1)
C(23)	0.868 (3)	0.3852 (16)	0.4592 (10)	6 (1)
C(24)	0.657 (3)	0.539 (2)	0.4050 (12)	6 (1)
C(31)	0.438 (3)	0.102 (2)	0.4115 (11)	7 (1)
C(32)	0.4755 (19)	0.2236 (19)	0.3001 (10)	4 (1)
C(33)	0.386 (2)	0.349 (3)	0.4114 (12)	7 (1)
C(34)	0.624 (2)	0.2433 (18)	0.4910 (10)	4 (1)

to the structure factor calculations, but their positions were not refined.

Compound 7 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 anistropic thermal parameters. The hydride ligand was located and its positional parameters were successfully refined. The positions of all other hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. In the final stages of the refinement, a CH_2Cl_2 molecule of crystallization was located in a difference Fourier synthesis. It was added to the analysis and was successfully refined.

Results and Discussion

$Os_3(CO)_{11}[S(CH_2)_3]$, 1, was obtained in 84% yield from the reaction of $Os_3(CO)_{11}(NCMe)$ and thietane at 25 °C. Compound 1 was characterized crystallographically, and an ORTEP drawing of its molecular structure 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 three osmium atoms. The ligand occupies an equatorial coordination site in the cluster. The osmium–osmium bond trans to the thietane ligand is slightly shorter than the other two osmium–osmium bonds, Os(1)–Os(2) = 2.850 (1) Å vs Os(1)–Os(3) = 2.887 (1) Å and Os(2)–Os(3) = 2.887 (1) Å, but all three distances are similar to those found in $Os_3(CO)_{12}$, 2.877 (3) Å.[18] The structure of the thietane ligand does not differ significantly from that reported from an analysis of the free molecule in the gas phase.[19] The ligand is nonplanar with a dihedral angle of 28°. The ^1H NMR spectrum of 1 at 25 °C is not consistent with the structure found in the crystal. The α-positioned CH_2 protons appear as a triplet at 3.65 ppm, while the β-CH_2 protons appear as a broad singlet at 2.84 ppm. However, at −43 °C, the resonance at 2.84 ppm is separated into two multiplets and the resonance at 3.65 appears as a broad multiplet. The temperature-dependent changes are indicative of a dynamical process that probably involves a simple intramolecular inversion of configuration at the pyramidal sulfur atom. Inversions at sulfur in similarly coordinated thioethers have been observed previously.[20]

Table III. Intramolecular Distances for 1[a]

atom	atom	distance	atom	atom	distance
Os(1)	C(12)	1.86 (2)	Os(2)	Os(3)	2.887 (1)
Os(1)	C(13)	1.94 (2)	Os(3)	C(31)	1.88 (3)
Os(1)	C(11)	1.95 (2)	Os(3)	C(33)	1.91 (3)
Os(1)	S(1)	2.375 (5)	Os(3)	C(32)	1.92 (2)
Os(1)	Os(2)	2.850 (1)	Os(3)	C(34)	2.00 (2)
Os(1)	Os(3)	2.887 (1)	S(1)	C(3)	1.83 (2)
Os(2)	C(21)	1.86 (2)	S(1)	C(1)	1.85 (2)
Os(2)	C(24)	1.90 (3)	O	C(av)	1.14 (2)
Os(2)	C(22)	1.95 (2)	C(1)	C(2)	1.47 (3)
Os(2)	C(23)	1.97 (2)	C(2)	C(3)	1.50 (3)

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

Table IV. Intramolecular Bond Angles for 1[a]

atom	atom	atom	angle	atom	atom	atom	angle
C(12)	Os(1)	S(1)	99.6 (7)	C(23)	Os(2)	Os(3)	92.9 (6)
C(12)	Os(1)	Os(2)	100.3 (7)	Os(1)	Os(2)	Os(3)	60.41 (3)
C(12)	Os(1)	Os(3)	159.7 (7)	C(31)	Os(3)	Os(1)	106.7 (8)
C(13)	Os(1)	S(1)	87.6 (6)	C(31)	Os(3)	Os(2)	165.0 (9)
C(13)	Os(1)	Os(2)	86.8 (5)	C(33)	Os(3)	Os(1)	152.5 (9)
C(13)	Os(1)	Os(3)	95.2 (5)	C(33)	Os(3)	Os(2)	94.5 (9)
C(11)	Os(1)	S(1)	91.2 (6)	C(32)	Os(3)	Os(1)	81.1 (5)
C(11)	Os(1)	Os(2)	94.1 (6)	C(32)	Os(3)	Os(2)	93.5 (6)
C(11)	Os(1)	Os(3)	84.4 (6)	C(34)	Os(3)	Os(1)	92.2 (5)
S(1)	Os(1)	Os(2)	159.2 (1)	C(34)	Os(3)	Os(2)	85.4 (6)
S(1)	Os(1)	Os(3)	100.3 (1)	Os(1)	Os(3)	Os(2)	59.16 (3)
Os(2)	Os(1)	Os(3)	60.42 (3)	C(3)	S(1)	C(1)	74 (1)
C(21)	Os(2)	Os(1)	100.8 (9)	C(3)	S(1)	Os(1)	119.8 (8)
C(21)	Os(2)	Os(3)	160.6 (8)	C(1)	S(1)	Os(1)	113.8 (9)
C(24)	Os(2)	Os(1)	157.3 (8)	C(2)	C(1)	S(1)	91 (2)
C(24)	Os(2)	Os(3)	97.4 (8)	C(1)	C(2)	C(3)	97 (2)
C(22)	Os(2)	Os(1)	91.7 (6)	C(2)	C(3)	S(1)	91 (2)
C(22)	Os(2)	Os(3)	85.8 (5)	O	C	Os(av)	176 (2)
C(23)	Os(2)	Os(1)	85.3 (6)				

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

When subjected to UV–vis irradiation, compound 1 underwent decarbonylation with insertion of one of the metal atoms into one of the C–S bonds of the thietane ligand to yield 2 as the principal product. A small amount of the propenethiolate complex 3 was also formed (see Scheme I). We were unable to separate the two products

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(18) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.
(19) Karakida, K.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1691.
(20) Abel, E. W.; Bhargava, S. K.; Orrell, K. G. *Prog. Inorg. Chem.* **1984**, *32*, 1.

Scheme I

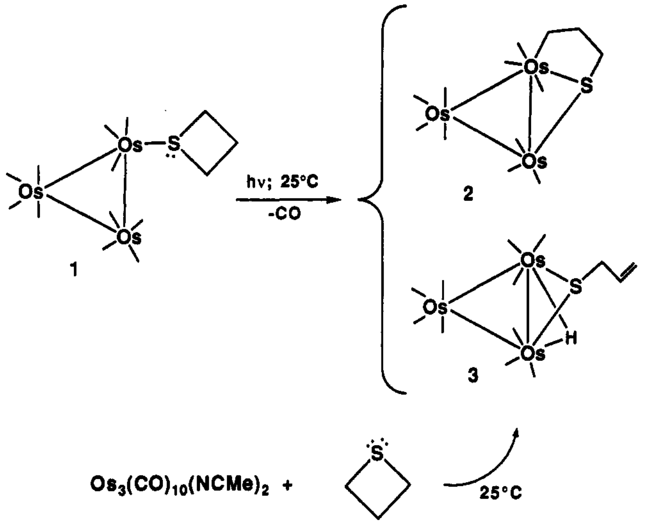

Table V. Positional Parameters and B(eq) Values (Å^2) for 2

atom	x	y	z	B(eq)
Os(1A)	0.640 70 (17)	0.265 7	0.408 48 (14)	3.24 (8)
Os(1B)	0.310 69 (16)	0.374 3	0.952 49 (14)	2.92 (8)
Os(2A)	0.880 91 (15)	0.303 58 (18)	0.431 07 (13)	2.78 (7)
Os(2B)	0.271 59 (16)	0.155 13 (16)	0.968 84 (14)	2.70 (7)
Os(3A)	0.743 62 (18)	0.414 46 (16)	0.555 70 (14)	3.19 (8)
Os(3B)	0.135 57 (15)	0.306 46 (17)	1.057 77 (13)	2.69 (7)
S(1A)	0.6883 (12)	0.2405 (10)	0.5913 (9)	3.7 (6)
S(1B)	0.3227 (10)	0.3759 (10)	1.1339 (9)	3.4 (5)
O(11A)	0.623 (4)	0.348 (4)	0.186 (3)	7 (2)
O(11B)	0.241 (4)	0.345 (3)	0.726 (3)	8 (3)
O(12A)	0.676 (4)	0.052 (4)	0.340 (4)	8 (3)
O(12B)	0.566 (3)	0.347 (4)	0.951 (3)	8 (3)
O(13A)	0.382 (4)	0.253 (4)	0.390 (3)	7 (2)
O(13B)	0.324 (4)	0.619 (3)	0.929 (4)	8 (3)
O(21A)	0.912 (4)	0.175 (4)	0.245 (4)	9 (3)
O(21B)	0.462 (3)	0.147 (3)	1.163 (2)	5 (2)
O(22A)	1.128 (3)	0.390 (3)	0.500 (3)	5 (2)
O(22B)	0.186 (3)	−0.051 (3)	1.022 (3)	6 (2)
O(23A)	0.936 (3)	0.119 (3)	0.580 (3)	5 (2)
O(23B)	0.439 (4)	0.096 (3)	0.826 (3)	7 (2)
O(24A)	0.819 (3)	0.504 (3)	0.297 (3)	6 (2)
O(24B)	0.064 (3)	0.183 (3)	0.797 (3)	7 (2)
O(31B)	0.049 (3)	0.508 (2)	0.930 (3)	5 (2)
O(32A)	0.965 (4)	0.397 (4)	0.728 (3)	9 (3)
C(31B)	0.096 (4)	0.438 (4)	0.971 (3)	4 (1)
C(32A)	0.885 (6)	0.403 (5)	0.665 (5)	6 (1)
C(32B)	−0.015 (5)	0.254 (4)	0.997 (4)	4 (1)
C(33A)	0.598 (5)	0.458 (4)	0.468 (4)	4 (1)
C(33B)	0.153 (5)	0.202 (4)	1.161 (4)	5 (1)

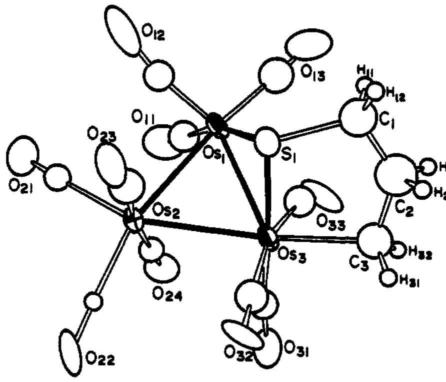

Figure 2. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}S(CH)_2CH_2]$, 2, showing 50% probability thermal ellipsoids.

Table VI. Intramolecular Distances for 2[a]

atom	atom	distance	atom	atom	distance
Os(1A)	Os(2A)	2.823 (3)	Os(2B)	C(23B)	1.96 (6)
Os(1A)	Os(3A)	2.812 (2)	Os(2B)	C(24B)	1.93 (4)
Os(1A)	S(1A)	2.40 (1)	Os(3A)	S(1A)	2.36 (1)
Os(1A)	C(11A)	1.99 (5)	Os(3A)	C(3A)	2.25 (6)
Os(1A)	C(12A)	1.70 (5)	Os(3A)	C(31A)	1.80 (4)
Os(1A)	C(13A)	1.87 (6)	Os(3A)	C(32A)	2.00 (6)
Os(1B)	Os(2B)	2.820 (2)	Os(3A)	C(33A)	1.96 (5)
Os(1B)	Os(3B)	2.826 (3)	Os(3B)	S(1B)	2.41 (1)
Os(1B)	S(1B)	2.38 (1)	Os(3B)	C(3B)	2.25 (6)
Os(1B)	C(11B)	1.83 (5)	Os(3B)	C(31B)	2.02 (5)
Os(1B)	C(12B)	1.90 (6)	Os(3B)	C(32B)	1.92 (6)
Os(1B)	C(13B)	1.98 (6)	Os(3B)	C(33B)	1.88 (5)
Os(2A)	Os(3A)	2.878 (3)	S(1A)	C(1A)	1.86 (7)
Os(2A)	C(21A)	2.01 (6)	S(1B)	C(1B)	1.82 (6)
Os(2A)	C(22A)	1.94 (5)	O	CA(av)	1.14 (6)
Os(2A)	C(23A)	1.87 (4)	O	CB(av)	1.14 (6)
Os(2A)	C(24A)	1.94 (5)	C(1A)	C(2A)	1.4 (1)
Os(2B)	Os(3B)	2.880 (3)	C(1B)	C(2B)	1.55 (9)
Os(2B)	C(21B)	1.95 (4)	C(2A)	C(3A)	1.5 (1)
Os(2B)	C(22B)	1.69 (3)	C(2B)	C(3B)	1.42 (8)

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

Table VII. Intramolecular Bond Angles for 2[a]

atom	atom	atom	angle	atom	atom	atom	angle
Os(2A)	Os(1A)	Os(3A)	61.42 (7)	Os(2B)	Os(3B)	S(1B)	83.1 (3)
Os(2A)	Os(1A)	S(1A)	82.9 (3)	Os(2B)	Os(3B)	C(3B)	161 (1)
Os(3A)	Os(1A)	S(1A)	53.2 (3)	S(1B)	Os(3B)	C(3B)	81 (1)
Os(2B)	Os(1B)	Os(3B)	61.35 (6)	Os(1A)	S(1A)	Os(3A)	72.4 (3)
Os(2B)	Os(1B)	S(1B)	84.9 (3)	Os(1A)	S(1A)	C(1A)	113 (2)
Os(3B)	Os(1B)	S(1B)	54.2 (3)	Os(3A)	S(1A)	C(1A)	102 (2)
Os(1A)	Os(2A)	Os(3A)	59.10 (6)	Os(1B)	S(1B)	Os(3B)	72.4 (3)
Os(1B)	Os(2B)	Os(3B)	59.43 (6)	Os(1B)	S(1B)	C(1B)	113 (2)
Os(1A)	Os(3A)	Os(2A)	59.48 (7)	Os(3B)	S(1B)	C(1B)	98 (2)
Os(1A)	Os(3A)	S(1A)	54.5 (3)	S(1A)	C(1A)	C(2A)	109 (7)
Os(1A)	Os(3A)	C(3A)	118 (1)	S(1B)	C(1B)	C(2B)	102 (4)
Os(2A)	Os(3A)	S(1A)	82.4 (3)	C(1A)	C(2A)	C(3A)	131 (9)
Os(2A)	Os(3A)	C(3A)	163 (1)	C(1B)	C(2B)	C(3B)	115 (6)
S(1A)	Os(3A)	C(3A)	84 (2)	Os(3A)	C(3A)	C(2A)	108 (5)
Os(1B)	Os(3B)	Os(2B)	59.22 (6)	Os(3B)	C(3B)	C(2B)	111 (5)
Os(1B)	Os(3B)	S(1B)	53.4 (3)	Os(A)	C	O(av)	174 (5)
Os(1B)	Os(3B)	C(3B)	118 (1)	Os(B)	C	O(av)	172 (5)

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

by TLC. An ^{1}H NMR analysis of the mixture showed it to contain compound **3** in the amount of 23% of the total. By repeated fractional crystallization, it was possible to remove the **3** and leave **2** in pure crystalline form. Compound **2** was characterized by a crystal structure analysis. The unit cell of **2** was found to contain two independent molecules in the asymmetric unit. Both molecules are structurally similar, and an ORTEP drawing of one of these, molecule A, is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected interatomic distances and angles are listed in Tables VI and VII. The molecule contains a triangular cluster of 3 metal atoms with 10 carbonyl ligands. One of the CO ligands, C(33)–O(33), is a semibridging ligand to Os(1), Os(3)–C(33)–O(33) = 162 (4)°, Os(1)···C(33) = 2.63 (1) Å. Compound **2** contains a thiametallacyclopentane ring formed by the insertion of one of the metal atoms into one of the carbon–sulfur bonds of the thietane ligand. The sulfur atom S(1) bridges the Os(1)–Os(3) bond, while carbon atom C(3) is coordinated solely to Os(3), Os(3)–C(3) = 2.25 (6) Å. The osmium–osmium bond, Os(2)–Os(3), trans to the σ-coordinated methylene group is significantly longer, 2.878 (3) Å [2.880 (3) Å], than the other two metal–metal bonds, 2.823 (3) Å [2.820 (2) Å] and 2.812 (2) Å [2.826 (3) Å]. Compound **2** is structurally very similar to its diphenyl derivative $Os_3[CO)_{10}[\mu\text{-}SCPh(H)CH_2CPh(H)]$ that was structurally characterized recently.[10]

Compound **2** is also dynamically active on the NMR time scale. The ^{1}H NMR resonances of **2** are broad with

Table VIII. Positional Parameters and *B*(eq) Values (Å^2) for 4

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.651 01 (7)	0.153 60 (3)	0.937 55 (8)	2.62 (3)
Os(2)	0.329 58 (7)	0.306 08 (4)	0.792 80 (8)	2.74 (3)
S(1)	0.5968 (5)	0.3396 (3)	1.0310 (6)	3.8 (2)
O(11)	0.7877 (16)	0.0536 (9)	1.4154 (18)	5.9 (7)
O(12)	0.6294 (16)	−0.0563 (8)	0.7203 (18)	5.6 (7)
O(13)	1.0065 (14)	0.1320 (8)	0.9138 (18)	4.9 (6)
O(21)	0.0599 (15)	0.2119 (9)	0.4608 (19)	5.7 (7)
O(22)	0.1348 (17)	0.3617 (10)	1.1193 (19)	6.5 (8)
O(23)	0.1755 (13)	0.5219 (8)	0.5417 (19)	5.3 (6)
C(1)	0.6576 (20)	0.3916 (10)	0.826 (2)	4.0 (8)
C(2)	0.6077 (19)	0.3356 (10)	0.615 (2)	3.6 (7)
C(3)	0.5144 (15)	0.2493 (8)	0.6093 (18)	1.9 (2)
C(11)	0.7373 (19)	0.0906 (10)	1.244 (3)	3.6 (8)
C(12)	0.6373 (17)	0.0207 (11)	0.804 (2)	3.3 (7)
C(13)	0.879 (2)	0.1376 (10)	0.926 (2)	3.4 (7)
C(21)	0.157 (2)	0.2470 (10)	0.585 (3)	4.1 (8)
C(22)	0.2102 (20)	0.3400 (11)	1.006 (3)	3.9 (8)
C(23)	0.2340 (17)	0.4415 (11)	0.637 (2)	3.3 (7)

little fine structure at room temperature. However, at −43 °C, sharp resonances with complex fine structure were observed for each of the six inequivalent methylene protons. The combination of red color, difficulty in the separation of 2 and 3, and the lack of readily identifiable resonances in ^{1}H NMR spectrum of 2 at room temperature led us to believe initially[4] that compound 2 was the red tetraosmium cluster complex $Os_4(CO)_{12}(\mu_3\text{-}S)$.[21]

When solutions of 2 were heated to 97 °C, compounds 3 and 4 were obtained in yields of 24% and 51%, respectively. This transformation could account for the formation of 3 in the photolytic reaction. Compound 3 was characterized by IR and ^{1}H NMR spectroscopy and by an independent synthesis from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with allyl mercaptan, $CH_2{=}CHCH_2SH$. The transformation of 2 to 3 involves a β-elimination reaction at C(2) in the metallacycle. We have shown that the thermal isomerization of the thiametallacyclic complex $Os_3(CO)_{10}[\mu\text{-}SCPh(H)CH_2CPh(H)]$ leads to the related 1,3-diphenylpropenethiolato derivative of 3 by a similar β-elimination reaction.[10]

Compound 3 was also obtained directly from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with thietane at 25 °C. Curiously, in this reaction there was no evidence for the formation of the metallacyclic complex 2 or the dinuclear species 4. The reaction of $Os_3(CO)_{10}(NCMe)_2$ with thietane may have proceeded by formation of a complex having a sulfur-bridged thietane ligand such as $Os_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2]$ through displacement of both NCMe ligands and then undergone rapid C–S and C–H bond cleavages to yield 3. The compound $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ has been shown to have a sulfur-bridged dimethylthietane ligand, and it has also been shown that the bridging coordination does enhance C–S bond cleavage reactions in the thietane ligand.[7,8] We were unable to obtain either 2 or 3 by thermal decarbonylation of 1. This is due in part to simple decomplexation of the thietane ligand at elevated temperatures.

The diosmium product $Os_2(CO)_6[\mu\text{-}S(CH_2)_2CH](\mu\text{-}H)$, 4, was also characterized crystallographically. An ORTEP drawing of its molecular structure is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected interatomic distances and angles are listed in Tables IX and X. The molecule consists of two mutually bonded osmium atoms, Os(1)–Os(2) = 2.7891 (8) Å. Each metal atom contains three linear terminal carbonyl ligands.

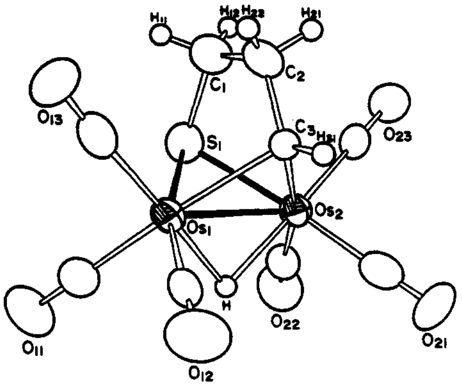

Figure 3. ORTEP diagram of $Os_2(CO)_6[\mu\text{-}S(CH)_2CH](\mu\text{-}H)$, 4, showing 50% probability thermal ellipsoids.

Table IX. Intramolecular Distances for 4[a]

atom	atom	distance	atom	atom	distance
Os(1)	Os(2)	2.7891 (8)	Os(2)	C(21)	1.94 (2)
Os(1)	S(1)	2.429 (3)	Os(2)	C(22)	1.96 (2)
Os(1)	C(3)	2.26 (1)	Os(2)	C(23)	1.89 (1)
Os(1)	C(11)	1.98 (2)	Os(2)	H	2.0 (1)
Os(1)	C(12)	1.92 (1)	S(1)	C(1)	1.80 (1)
Os(1)	C(13)	1.94 (2)	O	C(av)	1.12 (2)
Os(1)	H	1.8 (1)	C(1)	C(2)	1.50 (2)
Os(2)	S(1)	2.421 (4)	C(2)	C(3)	1.54 (2)
Os(2)	C(3)	2.25 (1)			

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

Table X. Intramolecular Bond Angles for 4[a]

atom	atom	atom	angle	atom	atom	atom	angle
Os(2)	Os(1)	S(1)	54.8 (1)	Os(1)	Os(2)	H	40 (3)
Os(2)	Os(1)	C(3)	51.7 (3)	S(1)	Os(2)	C(3)	75.5 (3)
Os(2)	Os(1)	C(11)	117.5 (4)	S(1)	Os(2)	C(21)	164.9 (4)
Os(2)	Os(1)	C(12)	111.0 (4)	S(1)	Os(2)	C(22)	95.7 (4)
Os(2)	Os(1)	C(13)	137.1 (4)	S(1)	Os(2)	C(23)	96.4 (4)
Os(2)	Os(1)	H	46 (3)	S(1)	Os(2)	H	82 (3)
S(1)	Os(1)	C(3)	75.2 (3)	C(3)	Os(2)	H	83 (3)
S(1)	Os(1)	C(11)	96.4 (4)	C(21)	Os(2)	H	88 (3)
S(1)	Os(1)	C(12)	165.1 (4)	C(22)	Os(2)	H	88 (3)
S(1)	Os(1)	C(13)	96.8 (4)	C(23)	Os(2)	H	176 (3)
S(1)	Os(1)	H	87 (3)	Os(1)	S(1)	Os(2)	70.2 (1)
C(3)	Os(1)	H	88 (3)	Os(1)	S(1)	C(1)	98.3 (4)
C(11)	Os(1)	H	84 (3)	Os(2)	S(1)	C(1)	99.0 (5)
C(12)	Os(1)	H	84 (3)	S(1)	C(1)	C(2)	111 (1)
C(13)	Os(1)	H	176 (3)	C(1)	C(2)	C(3)	117 (1)
Os(1)	Os(2)	S(1)	55.02 (8)	Os(1)	C(3)	Os(2)	76.3 (3)
Os(1)	Os(2)	C(3)	52.0 (3)	Os(1)	C(3)	C(2)	106.4 (7)
Os(1)	Os(2)	C(21)	110.6 (4)	Os(2)	C(3)	C(2)	108.2 (7)
Os(1)	Os(2)	C(22)	116.3 (4)	Os	C	O(av)	178 (1)
Os(1)	Os(2)	C(23)	136.8 (4)				

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

The metal atoms are symmetrically bridged by a sulfur atom S(1), a hydride ligand H(1) (located and refined cystallographically, δ = 14.45 ppm), and an alkylidene carbon atom C(3), Os(1)–C(3) = 2.26 (1) Å, Os(2)–C(3) = 2.25 (1) Å. The hydrogen atom on the alkylidene carbon exhibits a low field shift (δ = 5.38 ppm).[22] The ^{13}C NMR spectrum of 4 exhibits resonances at 38.66, 46.17, and 57.09 ppm, one for each carbon of the SCH_2CH_2CH ligand. The signal at 57.09 appeared as a doublet ($^1J_{C-H}$ = 145.5 Hz) in the proton-coupled ^{13}C NMR spectrum and was assigned to the alkylidene carbon C(3). The other two resonances are seen as triplets in the proton-coupled spec-

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(21) Adams, R. D.; Foust, D. F.; Mathur, P. *Organometallics* **1983**, *2*, 990.

(22) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

Table XI. Positional Parameters and B(eq) Values (Å^2) for 6

atom	x	y	z	B(eq)
Os(1)	0.912 65 (4)	0.137 58 (2)	0.597 53 (3)	2.26 (2)
Os(2)	0.661 67 (4)	0.179 95 (2)	0.485 56 (3)	2.43 (2)
Os(3)	0.759 68 (4)	0.101 52 (2)	0.748 29 (3)	2.09 (2)
S(1)	0.5976 (2)	0.096 44 (14)	0.603 27 (17)	2.4 (1)
P(1)	0.6314 (3)	0.065 72 (15)	0.861 78 (20)	2.7 (1)
O(11)	1.1649 (8)	0.0790 (5)	0.7080 (6)	5.5 (5)
O(12)	0.9362 (8)	0.2925 (5)	0.6888 (6)	4.9 (4)
O(13)	0.8395 (8)	−0.0134 (4)	0.5054 (6)	4.4 (4)
O(14)	1.0083 (8)	0.1855 (5)	0.4166 (6)	5.3 (4)
O(21)	0.6261 (10)	0.0508 (5)	0.3448 (6)	6.1 (5)
O(22)	0.7314 (9)	0.2727 (5)	0.3248 (6)	5.7 (5)
O(23)	0.6504 (9)	0.3261 (5)	0.5911 (6)	5.6 (5)
O(31)	0.8194 (9)	−0.0611 (5)	0.7111 (6)	5.8 (5)
O(32)	1.0044 (8)	0.1135 (4)	0.8938 (6)	4.7 (4)
O(33)	0.6803 (8)	0.2613 (4)	0.7806 (6)	4.5 (4)
C(1)	0.4342 (9)	0.1329 (6)	0.6056 (8)	3.5 (5)
C(2)	0.3787 (10)	0.1430 (7)	0.4991 (8)	3.9 (5)
C(3)	0.4530 (10)	0.1981 (6)	0.4487 (8)	3.8 (5)
C(11)	1.0710 (11)	0.1009 (6)	0.6701 (8)	3.3 (5)
C(12)	0.9252 (10)	0.2351 (6)	0.6569 (8)	3.3 (5)
C(13)	0.8627 (10)	0.0427 (6)	0.5398 (7)	3.0 (5)
C(14)	0.9704 (10)	0.1677 (6)	0.4851 (9)	3.6 (5)
C(21)	0.6426 (11)	0.0979 (7)	0.3996 (8)	3.5 (5)
C(22)	0.7052 (10)	0.2380 (6)	0.3869 (8)	3.2 (5)
C(23)	0.660 3 (10)	0.269 5 (6)	0.557 7 (7)	2.9 (5)
C(31)	0.797 6 (11)	−0.000 5 (6)	0.723 3 (8)	3.4 (5)
C(32)	0.9121 (11)	0.1092 (5)	0.8396 (8)	2.9 (5)
C(33)	0.7147 (10)	0.2030 (6)	0.7669 (8)	3.1 (5)
C(41)	0.7053 (10)	0.0894 (6)	0.9834 (7)	3.0 (5)
C(42)	0.7888 (15)	0.0450 (8)	1.0388 (10)	5.9 (7)
C(43)	0.8495 (16)	0.0655 (9)	1.1273 (11)	7.2 (9)
C(44)	0.8264 (17)	0.1338 (10)	1.1633 (10)	6.6 (9)
C(45)	0.7451 (15)	0.1778 (9)	1.1099 (10)	5.8 (8)
C(46)	0.6820 (12)	0.1585 (7)	1.0211 (9)	4.6 (6)
C(47)	0.4713 (11)	0.1062 (8)	0.8511 (9)	5.0 (6)
C(48)	0.6001 (14)	−0.0323 (6)	0.8676 (9)	5.1 (6)

trum. The resonances of the carbonyl carbons were observed at 174.28 (d, 2 *C*O, $^2J_{\text{C-H1}}$ = 3.0 Hz), 172.09 (d, 2 *C*O, $^2J_{\text{C-H1}}$ = 3.0 Hz), and 171.85 (d, 2 *C*O, $^2J_{\text{C-H1}}$ = 9.0 Hz) with suitable couplings to the hydride ligand.

This molecule was apparently formed by the loss of an $Os(CO)_4$ fragment from 2 and CH activation on the carbon atom that was σ-bonded to the metal atom. The formation of $Os_3(CO)_{12}$ in this reaction can account for the fate of the $Os(CO)_4$ group that was expelled. Compound 4 was not obtained from the irradiation of 2 or from the thermolysis of 3. The related metallacyclic complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ has also been shown to undergo α-CH activation at 97 °C to form the triosmium complex $Os_3(CO)_9[\mu\text{-}SCH_2CMe_2CH](\mu\text{-}H)$ that contains a bridging alkylidenethiolato ligand and a structurally different diosmium complex $Os_2(CO)_6[\mu\text{-}SCH_2CMe(CH_2)_2](\mu\text{-}H)$ formed by cluster fragmentation and CH activation on one of the methyl groups.[5] In contrast to 4, the ^{13}C resonance for the alkylidene carbon in $Os_3(CO)_9[\mu\text{-}SCH_2CMe_2CH](\mu\text{-}H)$ is observed much further downfield (δ = 132.9 ppm).

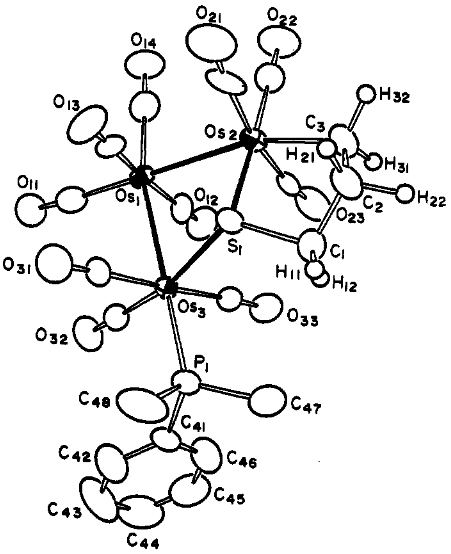

Figure 4. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}S(CH_2)_2CH_2](PMe_2Ph)$, 6, showing 50% probability thermal ellipsoids.

Table XII. Intramolecular Distances for 6[a]

atom	atom	distance	atom	atom	distance
Os(1)	C(14)	1.88 (1)	Os(3)	C(33)	1.93 (1)
Os(1)	C(11)	1.93 (1)	Os(3)	C(31)	1.94 (1)
Os(1)	C(13)	1.94 (1)	Os(3)	P(1)	2.358 (3)
Os(1)	C(12)	1.95 (1)	Os(3)	S(1)	2.446 (3)
Os(1)	Os(2)	2.9504 (7)	S(1)	C(1)	1.85 (1)
Os(1)	Os(3)	2.9559 (7)	P(1)	C(48)	1.81 (1)
Os(2)	C(22)	1.87 (1)	P(1)	C(41)	1.82 (1)
Os(2)	C(21)	1.91 (1)	P(1)	C(47)	1.82 (1)
Os(2)	C(23)	1.92 (1)	C(1)	C(2)	1.54 (1)
Os(2)	C(3)	2.20 (1)	C(2)	C(3)	1.52 (1)
Os(2)	S(1)	2.430 (2)	O	C(av)	1.15 (1)
Os(3)	C(32)	1.89 (1)	C(Ph)	C(av)	1.36 (2)

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

Table XIII. Intramolecular Bond Angles for 6[a]

atom	atom	atom	angle	atom	atom	atom	angle
C(14)	Os(1)	Os(2)	81.7 (3)	S(1)	Os(2)	Os(1)	78.16 (6)
C(14)	Os(1)	Os(3)	165.9 (3)	C(32)	Os(3)	P(1)	94.1 (3)
C(11)	Os(1)	Os(2)	174.9 (3)	C(32)	Os(3)	S(1)	166.4 (3)
C(11)	Os(1)	Os(3)	93.8 (3)	C(32)	Os(3)	Os(1)	88.6 (3)
C(13)	Os(1)	Os(2)	81.3 (3)	C(33)	Os(3)	P(1)	89.3 (3)
C(13)	Os(1)	Os(3)	88.1 (3)	C(33)	Os(3)	S(1)	89.9 (3)
C(12)	Os(1)	Os(2)	89.2 (3)	C(33)	Os(3)	Os(1)	93.7 (3)
C(12)	Os(1)	Os(3)	83.9 (3)	C(31)	Os(3)	P(1)	91.2 (3)
Os(2)	Os(1)	Os(3)	84.19 (2)	C(31)	Os(3)	S(1)	87.0 (3)
C(22)	Os(2)	C(3)	95.6 (4)	C(31)	Os(3)	Os(1)	85.7 (3)
C(22)	Os(2)	S(1)	174.9 (3)	P(1)	Os(3)	S(1)	99.42 (9)
C(22)	Os(2)	Os(1)	103.9 (3)	P(1)	Os(3)	Os(1)	175.95 (7)
C(21)	Os(2)	C(3)	88.3 (5)	S(1)	Os(3)	Os(1)	77.82 (6)
C(21)	Os(2)	S(1)	86.6 (3)	C(1)	S(1)	Os(2)	98.9 (3)
C(21)	Os(2)	Os(1)	97.5 (3)	C(1)	S(1)	Os(3)	119.6 (4)
C(23)	Os(2)	C(3)	84.5 (4)	Os(2)	S(1)	Os(3)	108.6 (1)
C(23)	Os(2)	S(1)	97.7 (3)	C(2)	C(1)	S(1)	103.2 (7)
C(23)	Os(2)	Os(1)	91.1 (3)	C(3)	C(2)	C(1)	114 (1)
C(3)	Os(2)	S(1)	82.8 (3)	C(2)	C(3)	Os(2)	111.3 (7)
C(3)	Os(2)	Os(1)	159.8 (3)	O	C	Os(av)	177 (1)

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

Compound 2 reacts with phosphines by a cluster-opening addition process to yield the complexes $Os_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2](L)$ (5, L = PPh_3; 6, L = PMe_2Ph); see Scheme II. Compound 6 was characterized crystallographically, and an ORTEP drawing of its molecular structure is shown in Figure 4. Final atomic positional parameters are listed in Table XI. Selected interatomic distances and angles are listed in Tables XII and XIII. This compound consists of an open triosmium cluster with the sulfur atom S(1) bridging the two nonbonded metal atoms. There are 10 linear terminal carbonyl ligands distributed as shown in Figure 4. The thiametallacyclopentane ring was not significantly different from that in 2, Os(2)–C(3) = 2.20 (1) Å. The dimethylphenylphosphine ligand is coordinated to Os(3). Two complexes that are closely related to 6 are $Os_3(CO)_{11}[\mu\text{-}SCH_2CMe_2CH_2]$[8b] and $Os_3(CO)_{11}[\mu\text{-}SCPh(H)CH_2CPh(H)]$[10] which have dimethyl- and diphenylthiametallacyclopentane rings systems, respectively, in open triosmium cluster complexes. Contrary to our preliminary report, we have found no evidence for

Scheme II

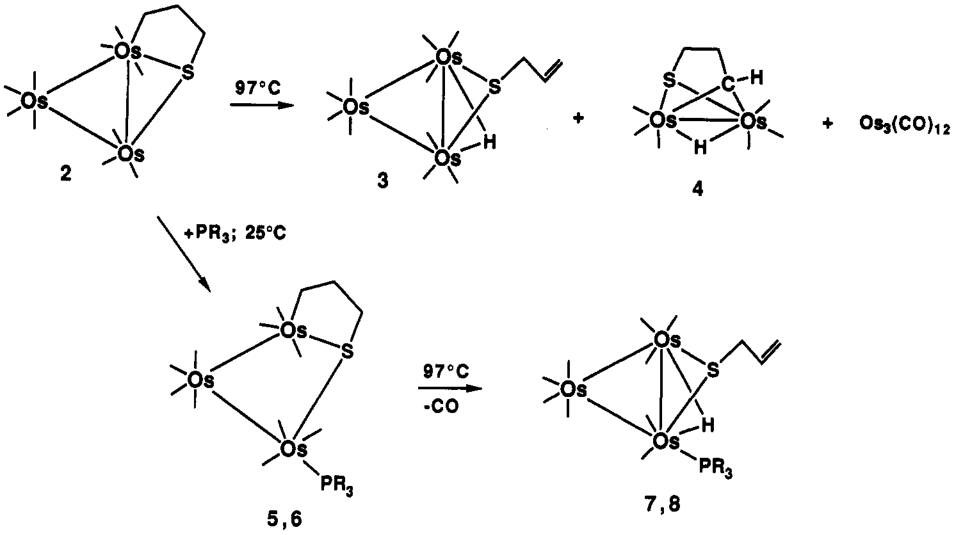

Table XIV. Positional Parameters and *B*(eq) Values (Å²) for 7

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	−0.05242 (6)	0.15001 (4)	0.20843 (7)	4.29 (4)
Os(2)	0.11299 (6)	0.16465 (4)	0.45360 (7)	4.10 (3)
Os(3)	0.12194 (6)	0.27013 (4)	0.25563 (7)	3.45 (3)
S(1)	0.2765 (4)	0.1586 (3)	0.2847 (5)	4.4 (2)
P(1)	0.2717 (4)	0.3633 (3)	0.3126 (4)	3.6 (2)
O(11)	−0.1709 (14)	0.1784 (11)	−0.0756 (15)	9 (1)
O(12)	−0.2486 (12)	0.2671 (8)	0.3662 (13)	6.3 (7)
O(13)	0.1490 (14)	0.0329 (10)	0.0615 (18)	10 (1)
O(14)	−0.1954 (15)	0.0141 (9)	0.2604 (16)	9 (1)
O(21)	0.1320 (14)	−0.0099 (9)	0.4291 (16)	8 (1)
O(22)	−0.1259 (13)	0.1941 (8)	0.6261 (14)	7.4 (8)
O(23)	0.2934 (14)	0.1928 (10)	0.7116 (15)	8 (1)
O(31)	−0.0946 (11)	0.3984 (8)	0.2725 (14)	6.3 (7)
O(32)	0.1225 (13)	0.2666 (9)	−0.0544 (14)	7.0 (8)
C(1)	0.4311 (15)	0.1824 (11)	0.3745 (20)	5 (1)
C(2)	0.499 (2)	0.1127 (13)	0.425 (3)	7 (1)
C(3)	0.555 (3)	0.1104 (16)	0.542 (3)	11 (2)
C(11)	−0.1248 (17)	0.1688 (13)	0.0342 (19)	6 (1)
C(12)	−0.1741 (16)	0.2251 (11)	0.3071 (18)	5 (1)
C(13)	0.0800 (18)	0.0788 (13)	0.120 (2)	7 (1)
C(14)	−0.1420 (18)	0.0655 (13)	0.243 (2)	7 (1)
C(21)	0.1248 (18)	0.0545 (12)	0.441 (2)	6 (1)
C(22)	−0.0342 (17)	0.1823 (10)	0.5614 (18)	5 (1)
C(23)	0.2268 (16)	0.1849 (11)	0.6127 (19)	5 (1)
C(31)	−0.0148 (17)	0.3493 (11)	0.2653 (17)	4.3 (9)
C(32)	0.1270 (16)	0.2681 (11)	0.0642 (20)	5 (1)

the formation of the metallacyclic complexes **5** or **6** from the reaction of **3** with phosphines at 25 °C. It is believed that the previous observation was due entirely to the reaction of phosphines with quantities of **2** in impure solutions of **3**.[4]

At 97 °C, **5** and **6** both underwent decarbonylation and transformation into the propenethiolato complexes $Os_3(CO)_9[\mu\text{-}SCH_2CH{=}CH_2](L)(\mu\text{-}H)$ (**7**, L = PPh_3; **8**, L = PMe_2Ph) via a CH β-elimination process similar to that observed for **2**. It must be noted that the mechanism of this transformation has not yet been established, and it has been shown that β-elimination reactions involving metallacycles in mononuclear metal complexes are energetically unfavorable.[23] The PPh_3 derivative **7** was also characterized structurally, and an ORTEP drawing of its structure is shown in Figure 5. Final atomic positional parameters are listed in Table XIV. Selected interatomic distances and angles are listed in Tables XV and XVI.

Table XV. Intramolecular Distances for 7[a]

atom	atom	distance	atom	atom	distance
Os(1)	C(11)	1.88 (2)	Os(3)	C(31)	1.88 (2)
Os(1)	C(14)	1.91 (2)	Os(3)	P(1)	2.351 (4)
Os(1)	C(13)	1.91 (2)	Os(3)	S(1)	2.445 (4)
Os(1)	C(12)	1.92 (2)	S(1)	C(1)	1.83 (2)
Os(1)	Os(2)	2.855 (1)	P(1)	C(61)	1.82 (1)
Os(1)	Os(3)	2.880 (1)	P(1)	C(51)	1.85 (1)
Os(2)	C(22)	1.87 (2)	P(1)	C(41)	1.85 (2)
Os(2)	C(23)	1.91 (2)	O	C(av)	1.15 (2)
Os(2)	C(21)	1.91 (2)	C(1)	C(2)	1.49 (3)
Os(2)	S(1)	2.407 (4)	C(2)	C(3)	1.25 (3)
Os(2)	Os(3)	2.873 (1)	C(Ph)	C(av)	1.38 (3)
Os(3)	C(32)	1.86 (2)			

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

Table XVI. Intramolecular Bond Angles for 7[a]

atom	atom	atom	angle	atom	atom	atom	angle
C(11)	Os(1)	Os(2)	159.0 (6)	C(32)	Os(3)	C(31)	90.9 (7)
C(11)	Os(1)	Os(3)	99.0 (6)	C(32)	Os(3)	P(1)	95.3 (5)
C(14)	Os(1)	Os(2)	98.8 (6)	C(32)	Os(3)	S(1)	99.6 (6)
C(14)	Os(1)	Os(3)	158.9 (6)	C(32)	Os(3)	Os(2)	139.1 (6)
C(13)	Os(1)	Os(2)	88.3 (6)	C(32)	Os(3)	Os(1)	89.2 (5)
C(13)	Os(1)	Os(3)	91.2 (6)	C(31)	Os(3)	P(1)	89.6 (5)
C(12)	Os(1)	Os(2)	87.4 (5)	C(31)	Os(3)	S(1)	167.6 (5)
C(12)	Os(1)	Os(3)	84.9 (5)	C(31)	Os(3)	Os(2)	114.5 (5)
Os(2)	Os(1)	Os(3)	60.13 (3)	C(31)	Os(3)	Os(1)	93.1 (5)
C(22)	Os(2)	S(1)	168.2 (6)	P(1)	Os(3)	S(1)	96.0 (1)
C(22)	Os(2)	Os(1)	89.4 (5)	P(1)	Os(3)	Os(2)	115.2 (1)
C(22)	Os(2)	Os(3)	114.4 (5)	P(1)	Os(3)	Os(1)	174.7 (1)
C(23)	Os(2)	S(1)	96.0 (5)	S(1)	Os(3)	Os(2)	53.1 (1)
C(23)	Os(2)	Os(1)	173.9 (6)	S(1)	Os(3)	Os(1)	80.4 (1)
C(23)	Os(2)	Os(3)	113.7 (5)	Os(2)	Os(3)	Os(1)	59.51 (3)
C(21)	Os(2)	S(1)	91.9 (5)	C(1)	S(1)	Os(2)	109.2 (6)
C(21)	Os(2)	Os(1)	87.6 (6)	C(1)	S(1)	Os(3)	114.7 (6)
C(21)	Os(2)	Os(3)	134.2 (6)	Os(2)	S(1)	Os(3)	72.6 (1)
S(1)	Os(2)	Os(1)	81.6 (1)	C(2)	C(1)	S(1)	110 (1)
S(1)	Os(2)	Os(3)	54.3 (1)	C(3)	C(2)	C(1)	126 (3)
Os(1)	Os(2)	Os(3)	60.37 (3)	C	O	Os(av)	178 (2)

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

The structure is essentially the same as that proposed for **3** with the exception of a PPh_3 ligand coordinated to Os(3). The molecule consists of a closed triangular cluster of three metal atoms that is bridged on one edge by a hydride ligand (δ = −17.03 ppm) and the sulfur atom of a 2-propenethiolate ligand. There are nine linear terminal carbonyl ligands. The olefinic distance C(2)–C(3) = 1.25

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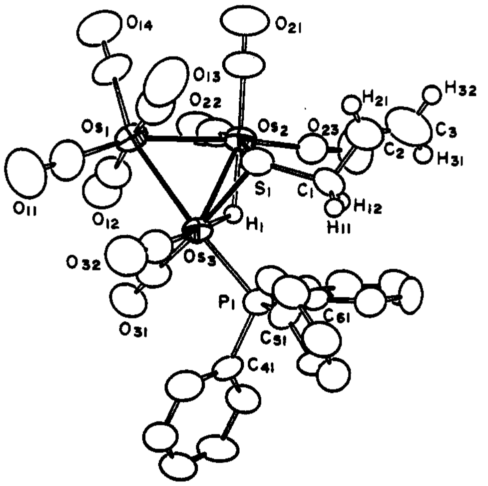

Figure 5. ORTEP diagram of $Os_3(CO)_9[\mu\text{-}SCH_2CH{=}CH_2](PPh_3)(\mu\text{-}H)$, 7, showing 50% probability thermal ellipsoids.

(3) Å is typical of a C–C double bond.

The ring-opening transformation of the thietane ligand in 1 to produce a thiametallacycle is in agreement with the results of our previous studies of triosmium complexes containing alkyl- and aryl-substituted thietane ligands.[5,7,8,10] Interestingly, these reactions seem to differ from the principal transformations of thietane on metal surfaces.[12a] Jensen and co-workers[24] recently observed that thietane undergoes a ring-opening S–C oxidative addition followed by C–Cl reductive elimination in its reaction with $Pd_2(\mu\text{-}Cl)_2Cl_2(PMe_3)_2$ to yield the complex $Pd_2Cl_2(\mu\text{-}Cl)(PMe_3)_2[\mu\text{-}SCH_2CH_2CH_2Cl]$.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for compounds 2, 4, and 8 (9 pages). Ordering information is given on any current masthead page. Supplemental data for compounds 1 and 6 were submitted previously.[4]

OM920029E

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Synthesis and Chemistry of a Molybdenum Carbonyl Phosphinite Complex Containing a Ditopic Macrocyclic Ligand with Chelating Phosphorus-Donor and Crown Ether Characteristics

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The reaction of 1,3-bis(chlorophenylphosphino)propane with triethylene glycol in THF in the presence of NEt_3, using high-dilution conditions, gives a mixture of phosphinite products (as assessed by $^{31}P\{^1H\}$ NMR), one of which is the hybrid phosphinite macrocycle *meso*-11,15-diphenyl-1,4,7,10-tetraoxa-11,15-diphosphacyclopentadecane, $[15]P_2O_4$. This ligand was isolated as its "$Mo(CO)_4P_2$ complex" by reacting the mixture of phosphinite products with $Mo(CO)_4$(norbornadiene) under high-dilution conditions. Chromatographic workup of the products gave the complex *cis*-$Mo(CO)_4\{[15]P_2O_4\}$ in an overall yield of 15–20%. The structure of this complex has been determined by single-crystal X-ray diffraction analysis. Addition of RLi reagents (R = Me, Ph, ^nBu, ^tBu, NEt_2, N^iPr_2) to this complex gives products of the type *fac*-$Mo(CO)_3(RCOLi)\{[15]P_2O_4\}$ in which the Li^+ ion is encapsulated by the five oxygens of the RCO and $[15]P_2O_4$ ligands. The structure of *fac*-$Mo(CO)_3(MeCOLi)\{[15]P_2O_4\}$ has been determined by single-crystal X-ray analysis. A comparison of the relative rate of hydrolysis of $Mo(CO)_3(PhCOLi)P_2$ in wet THF solution to give LiOH + C_6H_6 + *cis*-$Mo(CO)_4P_2$ $\{P_2 = [15]P_2O_4$ and $Ph_2P(OCH_2CH_2)_3OPPh_2\}$ shows that the benzoylate complex in which Li^+ is encapsulated by the $[15]P_2O_4$ ligand is the more inert. The structure of *fac*-$[Mo(CO)_3Br\{[15]P_2O_4\}]Li$ is also reported.

Introduction

A simple approach to the synthesis of heterodinuclear complexes containing low-oxidation-state transition metals and cations of groups 1A and 2A involves the synthesis of ditopic ligands which combine a subunit containing a "soft" binding site with one bearing a "hard" site.[1-8] Of particular relevance are hybrid P-donor crown ether ligands that combine a crown ether or cryptand functionality with one or more P-donor groups and the possible effect(s) that the presence of a proximal class 1A/2A cation may have on the reactivity of ligands coordinated to the transition metal. Recently we have described the synthesis of a range of ditopic α,ω-bis(diphenylphosphinite) polyether ligands and their amino analogues [e.g., $P_2\supset$ = Ph_2POCH_2-

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