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Ring-Opening Oligomerization of 3,3-Dimethylthietane by a Triosmium Cluster Complex

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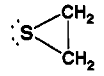
Abstract: The complexes $Os_3(CO)_{11}(SCH_2CMe_2CH_2)$ (**1**) and $Os_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2)$ (**2**) were synthesized by the reactions of 3,3-dimethylthietane (3,3-DMT) with $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$, respectively. Complex **2** was characterized crystallographically and was found to contain an S-coordinated bridging DMT ligand. Compound **2** reacts with 3,3-DMT at 25 °C to yield the complex $Os_3(CO)_{10}[(\mu\text{-}SCH_2CMe_2CH_2)_3]$ (**3**), which contains an 11-osmio-2,2,6,6,10,10-hexamethyl-4,7-dithiaundecanethiolato ligand formed by the ring-opening oligomerization of three 3,3-DMT molecules. Complex **3** was characterized crystallographically and was found to contain a bridging thiolato group and σ-bonded carbon at the termini of the oligomer and one thioether group coordinated to an open cluster. Compound **1** does not oligomerize 3,3-DMT at 25 °C. When heated to 125 °C, **3** eliminated carbon monoxide and was transformed to two isomers $Os_3(CO)_9[(\mu\text{-}SCH_2CMe_2CH_2)_3]$ **4** and **5** that contain closed triosmium clusters. Both also contain the same oligomeric grouping of the three 3,3-DMT ligands as in **3**, but differ in the coordination position of the thiolato bridge. When heated to 120 °C under 650 psi CO, compounds **3** and **5** were converted to $Os_3(CO)_{10}[\mu\text{-}O{=}C(CH_2CMe_2CH_2S)_3]$ (**6**), 68% by carbonylation. The C-terminus of the oligomer is functionalized by a CO group that bridges an open edge of the cluster in a $\mu\text{-}\eta^2\text{–}O{=}C$ bridging mode. Both thioether groups are uncoordinated in **6**. Compound **6** is decarbonylated at 68 °C under nitrogen to yield $Os_3(CO)_9[\mu\text{-}O{=}C(CH_2CMe_2CH_2S)_3]$ (**7**), 46%. Compound **7** is similar to **6** except that one of the thioether groups of the oligomer is coordinated. Crystallographic data. For **2**: space group $P2_1/c$, $a = 14.075$ (3) Å, $b = 22.143$ (4) Å, $c = 14.788$ (3) Å, $\beta = 108.37$ (2)°, $Z = 2$, 3227 reflections, $R = 0.046$. For **3**: space group $P\bar{1}$, $a = 12.025$ (3) Å, $b = 16.596$ (4) Å, $c = 9.738$ (2) Å, $\alpha = 95.84$ (2)°, $\beta = 108\ 76$ (2)°, $\gamma = 79.96$ (2)°, $Z = 2$, 2867 reflections, $R = 0.029$. For **4**: space group $P\bar{1}$, $a = 11.102$ (2) Å, $b = 14.724$ (3) Å, $c = 10.767$ (2) Å, $\alpha = 104.94$ (2)°, $\beta = 99.19$ (1)°, $\gamma = 72.73$ (1)°, $Z = 2$, 3519 reflections, $R = 0.023$. For **5**: space group $P2_1/n$, $a = 15.153$ (3) Å, $b = 24.453$ (7) Å, $c = 10.359$ (2) Å, $\beta = 90.58$ (2)°, $Z = 4$, 2801 reflections, $R = 0.031$. For **6**: space group $P\bar{1}$, $a = 9.909$ (2) Å, $b = 20.642$ (4) Å, $c = 9.283$ (2) Å, $\alpha = 101.30$ (2)°, $\beta = 103.30$ (2)°, $\gamma = 96.92$ (2)°, $Z = 2$, 2568 reflections, $R = 0.048$. For **7**: space group $P2_1/c$, $a = 12.256$ (3) Å, $b = 12.054$ (2) Å, $c = 23.110$ (3) Å, $\beta = 103.53$ (1)°, $Z = 4$, 3049 reflections, $R = 0.033$.

Introduction

The ring opening of heterocycles containing sulfur is of great interest because it is believed to be a key step in the purification of fossil fuels by the process of hydrodesulfurization.[1] In this regard strained ring thioethers, such as thiirane A and thietane B, have attracted attention since the release of ring strain in these molecules should lead to more facile carbon–sulfur bond cleavage processes. Thiiranes and thietanes undergo facile desulfurization on certain metal surfaces.[1b,2] Presently, we are investigating the nature of the ring opening of thiirane and thietanes by metal carbonyl cluster complexes in the hope of establishing the mechanistic features and the importance of metal coordination to this process.[3,4]



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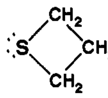

B

We have now discovered a facile ring-opening oligomerization process involving 3,3-dimethylthietane (3,3-DMT) that appears to be promoted by bridging coordination of the DMT ligand. These results are described in this report.

Experimental Section

General Data. Reagent-grade solvents were stored over 4-Å molecular sieves. Octane was distilled from sodium benzophenone ketyl prior to use. The compounds $Os_3(CO)_{11}NCMe$,[5] $Os_3(CO)_{10}(NCMe)_2$,[6] and 3,3-dimethylthietane[7] (DMT) were prepared by the published procedures. All reactions were performed under a nitrogen atmosphere unless specified otherwise. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer. NMR spectra were run on either a Bruker AM-300 or AM-500 spectrometer operating at 300 and 500 MHz, respectively. TLC separations were performed in air on Whatman 0.25-mm silica gel 60-Å F_{254} plates purchased from Curtin Matheson. Florisil (60–100 mesh) was purchased from Fisher Scientific and silica gel (70–230 mesh, 60 Å) was purchased from Aldrich. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of $Os_3(CO)_{11}(NCMe)$ with 3,3-Dimethylthietane. One equivalent (11.0 μL, 0.098 mmol) of 3,3-DMT was allowed to react with $Os_3(CO)_{11}(NCMe)$ (100 mg, 0.109 mmol) in 35 mL of CH_2Cl_2 at 25 °C for 5 h. TLC using a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture yielded yellow $Os_3(CO)_{11}(SCH_2CMe_2CH_2)$ (**1**; 46 mg, 48%). Analytical and spectral data for **1**. IR ν_{CO} (cm^{-1}) in hexane: 2110 (w), 2056 (s), 2036 (s), 2021 (vs), 2010 (m), 2004 (m), 1993 (m), 1977 (m), 1969 (w), 1956 (w). ^{1}H NMR (δ in $CDCl_3$): 3.44 (br, 4 H), 1.35 (s, 6 H). Anal. Calcd: C, 19.59; H, 1.03. Found: C, 20.40; H, 0.98.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with 3,3-Dimethylthietane. 3,3-DMT (16.0 μL, 0.147 mmol) was allowed to react with $Os_3(CO)_{10}(NCMe)_2$ (115 mg, 0.123 mmol) in 25 mL of CH_2Cl_2 at 25 °C for 2 h. The following compounds were separated by TLC using a 9/1 (v/v) hexane/CH_2Cl_2 solvent mixture: **1** (20 mg, 16%) and yellow $Os_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2)$ (**2**; 48 mg, 41%). For **2**. IR ν_{CO} (cm^{-1}) in hexane: 2095 (m), 2038 (sh), 2035 (vs), 2020 (s), 1988 (s), 1969 (m). ^{1}H NMR (δ in $CDCl_3$): 4.04 (s, 2 H), 3.76 (s, 2 H), 1.58 (s, 6 H). Anal. Calcd: C, 18.91; H, 1.06. Found: C, 18.84; H, 0.94.

Reaction of 2 with 3,3-Dimethylthietane. When a solution of **2** (30 mg, 0.031 mmol) in 25 mL of CH_2Cl_2 was allowed to react with a 10-fold excess of 3,3-DMT (32 μL) at 25 °C for 14 h, orange $Os_3(CO)_{10}[(\mu\text{-}SCH_2CMe_2CH_2)_3]$ (**3**; 18 mg, 49%) was obtained along with a small amount of **1** (4 mg) after separation by TLC using a 9/1 (v/v) hexane/CH_2Cl_2 solvent mixture. For **3**. IR ν_{CO} (cm^{-1}) in hexane: 2105 (m), 2056 (vs), 2024 (s), 2001 (s), 1987 (s), 1975 (w), 1960 (m), 1953 (m), 1940 (m). ^{1}H NMR (δ in $CDCl_3$): 3.44–2.08 (m, 12 H), 1.33 (s, 3 H), 1.26 (s, 3 H), 1.17 (s, 3 H), 1.10 (s, 3 H), 1.05 (s, 3 H), 0.89 (s, 3 H).

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Table 1. Crystallographic Data for Diffraction Studies

compound	**2**	**3**	**4**	**5**	**6**	**7**
empirical formula	$Os_3SO_{10}C_{15}H_{10}$	$Os_3S_3O_{10}C_{25}H_{30}\cdot 0.5C_6H_6$	$Os_3S_3O_9C_{24}H_{30}$	$Os_3S_3O_9C_{24}H_{30}\cdot C_6H_{14}$	$Os_3SO_{11}C_{26}H_{30}$	$Os_3S_3O_{10}C_{25}H_{30}$
fw	952.90	1196.34	1129.28	1215.45	1121.18	1157.29
cryst syst	monoclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic
lattice params						
a, Å	14.075 (3)	12.025 (3)	11.102 (2)	15.153 (3)	9.909 (2)	12.256 (3)
b, Å	22.143 (4)	16.596 (4)	14.724 (3)	24.453 (7)	20.642 (4)	12.054 (2)
c, Å	14.778 (3)	9.738 (2)	10.767 (2)	10.359 (2)	9.283 (2)	23.110 (3)
α, deg		95.84 (2)	104.94 (2)		101.30 (2)	
β, deg	108.37 (2)	108.76 (2)	99.19 (1)	90.58 (2)	103.30 (2)	103.53 (1)
γ, deg		79.96 (2)	72.73 (1)		96.92 (2)	
V, Å^3	4371 (3)	1810 (1)	1617 (1)	3838 (2)	1784 (1)	3319 (1)
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Z value	8	2	2	4	2	4
D_{calc}, g/cm^3	2.90	2.19	2.32	2.10	2.09	2.32
$F000$	3392	1114	1044	2288	1036	2144
μ(Mo Kα), cm^{-1}	175.55	107.29	119.98	101.18	107.68	116.96
temp, °C	23	23	23	23	23	23
$2\theta_{max}$, deg	40.0	43.0	45.0	40.0	40.0	42.0
no. of observns ($I > 3\sigma(I)$)	3227	2867	3519	2801	2568	3049
no. of variables	373	382	352	376	258	370
residuals: R; R_w	0.046; 0.049	0.029; 0.028	0.023; 0.025	0.031; 0.032	0.048; 0.050	0.033; 0.036
goodness of fit indicator	2.65	1.14	1.35	1.52	2.30	2.07
max shift in final cycle	0.05	0.12	0.00	0.10	0.04	0.03
largest peak in final diff map, e/Å^3	1.56	0.60	0.50	0.90	1.88	1.98
abs corr	analytical	empirical	empirical	empirical	analytical	empirical

Anal. Calcd for **3**$\cdot{}^1/_2C_6H_6$: C, 29.06; H, 3.13. Found: C, 28.81; H, 2.81.

Attempted Reaction of 1 with 3,3-Dimethylthietane. A solution of **1** (10 mg, 0.01 mmol) and a 10-fold excess of 3,3-DMT (10 μL) were allowed to react for 12 h at 25 °C. There was no evidence for a reaction by IR analysis of the mixture and all of compound **1** was recovered by TLC.

Pyrolysis of 3 under CO (1 atm). A solution of **3** (40 mg, 0.035 mmol) in 40 mL of octane was heated to reflux for 2 h under a slow carbon monoxide purge. Two products of the same formula but different structure were obtained and were separated by TLC using a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture in order of elution: orange $Os_3(CO)_9[(\mu\text{-}SCH_2CMe_2CH_2)_3]$ (**4**; 14 mg, 36%) and yellow $Os_3(CO)_9[(\mu\text{-}SCH_2CMe_2CH_2)_3)]$ **5** (11 mg, 28%). For **4**. IR ν_{CO} (cm^{-1}) in hexane: 2086 (s), 2046 (vs), 2009 (vs), 1997 (s), 1989 (s), 1963 (s), 1927 (m). ^{1}H NMR (δ in $CDCl_3$): 3.85–2.04 (m, 12 H), 1.35 (s, 3 H), 1.32 (s, 3 H), 1.23 (s, 3 H), 1.19 (s, 3 H), 1.18 (s, 3 H), 1.01 (s, 3 H). Anal. Calcd: C, 25.53; H, 2.68. Found: C, 25.80; H, 2.64. For **5**. IR ν_{CO} (cm^{-1}) in hexane: 2096 (m), 2078 (m), 2054 (s), 2036 (vs), 2025 (s), 2016 (vs), 2000 (s), 1981 (s), 1973 (m), 1960 (w), 1940 (m). ^{1}H NMR (δ in $CDCl_3$): 3.70–1.81 (m, 12 H), 1.42 (s, 3 H), 1.12 (s, 3 H), 0.95 (s, 9 H), 0.86 (s, 3 H). Anal. Calcd: C, 25.53; H, 2.68. Found: C, 25.72; H, 2.65.

Isomerization of 5 to 4. When an octane solution of **5** (10 mg, 0.009 mmol) was heated to reflux under an atmosphere of carbon monoxide for 4 h, 5 mg of **4** (71% based on amount of **5** consumed) had formed.

Reaction of 3 with CO. A solution of **3** (50 mg, 0.043 mmol) in 15 mL of octane was placed in a 50-mL Parr high-pressure autoclave, pressurized to 650 psi with carbon monoxide, sealed, and heated to 120 °C for 6 h. The vessel was cooled and vented. The solvent was removed in vacuo and the residue was chromatographed by TLC. Elution with a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture yielded colorless $Os_3(CO)_{10}[\mu_3\text{-}O{=}C(CH_2CMe_2CH_2S)_3]$ (**6**; 35 mg, 68%) as the only product. For **6**. IR ν_{CO} (cm^{-1}) in hexane: 2101 (m), 2066 (vs), 2051 (m), 2019 (s), 2009 (s), 2003 (m), 1999 (sh), 1988 (m), 1973 (m). ^{1}H NMR (δ in $CDCl_3$): 3.93–1.93 (m, 12 H), 1.12 (s, 3 H), 1.09 (s, 3 H), 1.08 (s, 3 H), 1.03 (s, 3 H), 0.98 (s, 3 H), 0.97 (s, 3 H). Anal. Calcd: C, 26.35; H, 2.55. Found: C, 26.72; H, 2.51.

Reaction of 5 with CO. A solution of **5** (20 mg, 0.017 mmol) in 10 mL of octane was placed in a 50-mL Parr high-pressure autoclave, pressurized to 600 psi with carbon monoxide, sealed, and heated to 120 °C for 10 h. The vessel was cooled and vented. TLC yielded **6** (14 mg, 67%) as the only product.

Decarbonylation of 6. A solution of **6** (15 mg, 0.013 mmol) in 15 mL of hexane was heated to reflux for 5 h. The solvent was removed in vacuo and the residue chromatographed by TLC. Elution with a 9/1 (v/v) hexane/CH_2Cl_2 solvent mixture separated 4 mg of unreacted **6** from pale yellow $Os_3(CO)_9[\mu_3\text{-}CO(CH_2CMe_2CH_2S)_3]$ (**7**; 5 mg, 46% based on amount of **6** consumed). For **7**. IR ν_{CO} (cm^{-1}) in hexane: 2901 (m), 2051 (s), 2014 (m), 2004 (vs), 1990 (w), 1982 (w), 1969 (m), 1941 (w). ^{1}H NMR (δ in $CDCl_3$): 3.82–2.01 (m, 12 H), 1.25 (s, 3 H), 1.22 (s, 3 H), 1.12 (s, 3 H), 1.06 (s, 3 H), 1.03 (s, 3 H), 0.85 (s, 3 H). Anal. Calcd: C, 25.95; H, 2.61. Found: C, 26.02; H, 2.55.

Crystallographic Analyses. Yellow crystals of **2** were grown by cooling a concentrated hexane/CH_2Cl_2 (4/1) solution to 0 °C under a nitrogen atmosphere. Orange crystals of **3** were grown by slow evaporation of a benzene/heptane (1/1) solution at 25 °C and were subsequently found to contain 0.5 equiv of a benzene molecule of crystallization. Orange crystals of **4** were grown by slow evaporation of a hexane solution at 25 °C. Yellow crystals of **5** were grown by slow evaporation of a hexane solution at 25 °C and were subsequently found to contain 1 equiv of a hexane molecule of crystallization. Colorless crystals of **6** were grown by slow evaporation of a hexane/CH_2Cl_2 (4/1) solution at 25 °C. Light yellow crystals of **7** were grown by slow evaporation of a hexane solution 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 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.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] 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

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

Compound **2** crystallized in the monoclinic crystal system with two symmetry-independent molecules in the asymmetric crystal unit. The space group $P2_1/c$ was identified uniquely based on the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Due to the large size of the structure, only atoms larger than carbon were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated by assuming idealized geometries and the C–H distances equal to 0.95 Å. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compounds **3** and **4** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of each structure. The coordinates of the heavy atoms were obtained by direct methods (MITHRIL). All

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

Table II. Intramolecular Distances for **2**

atom	atom	distance[a]	atom	atom	distance[a]
Os(1)	C(13)	1.89 (3)	Os(3)	C(34)	1.89 (3)
Os(1)	C(12)	1.94 (3)	Os(3)	C(32)	1.92 (3)
Os(1)	C(11)	1.96 (3)	Os(3)	C(31)	1.97 (3)
Os(1)	S(1)	2.320 (6)	Os(3)	C(33)	1.97 (3)
Os(1)	Os(2)	2.764 (2)	S(1)	C(3)	1.82 (3)
Os(1)	Os(3)	2.896 (2)	S(1)	C(1)	1.87 (2)
Os(2)	C(21)	1.92 (3)	O	C(av)	1.13 (3)
Os(2)	C(22)	1.92 (3)	C(1)	C(2)	1.52 (3)
Os(2)	C(23)	2.01 (3)	C(2)	C(4)	1.48 (4)
Os(2)	S(1)	2.322 (7)	C(2)	C(5)	1.51 (4)
Os(2)	Os(3)	2.871 (2)	C(2)	C(3)	1.54 (4)

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

remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stages of refinement of compound **3**, 0.5 equiv of benzene was located about a center of symmetry. It was satisfactorily refined with isotropic thermal parameters. The positions of all hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

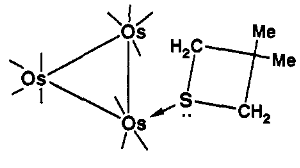
Compound **5** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely based on the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stages of refinement 1 equiv of hexane of crystallization was located in the lattice. The carbon atoms of this molecule were refined with isotropic thermal parameters. All hydrogen atom positions, except those of the hexane molecule, were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined. The hydrogen atoms of the hexane molecule were ignored.

Compound **6** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed as correct by the successful solution and refinement of the structure. The coordinates of the heavy atoms were obtained by direct methods (MITHRIL). All remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses. All atoms larger than carbon were refined with anisotropic thermal parameters. The positions of all hydrogen atoms were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **7** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was determined uniquely from the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Results

The reactions of $Os_3(CO)_{11}NCMe$ and $Os_3(CO)_{10}(NCMe)_2$ with 3,3-DMT have yielded the complexes $Os_3(CO)_{11}[S(CH_2)_2CMe_2]$ (**1**) and $Os_3(CO)_{10}[\mu\text{-}S(CH_2)_2CMe_2]$ (**2**) in yields of 43% and 41%, respectively. Small amounts of **1** obtained from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 3,3-DMT are believed to be due to the presence of $Os_3(CO)_{11}NCMe$ impurity in the $Os_3(CO)_{10}(NCMe)_2$. The IR spectrum of **1** is virtually identical with that of $Os_3(CO)_{11}[S(CH_2)_3]$ (**1a**), which we have synthesized and structurally characterized previously.[3b] Thus, we feel that **1** and **1a** are structurally similar to the thietane ligand occupying an equatorial coordination site in the triosmium cluster.



1

Compound **2** was characterized crystallographically and an ORTEP drawing of its molecular structure is shown in Figure 1.

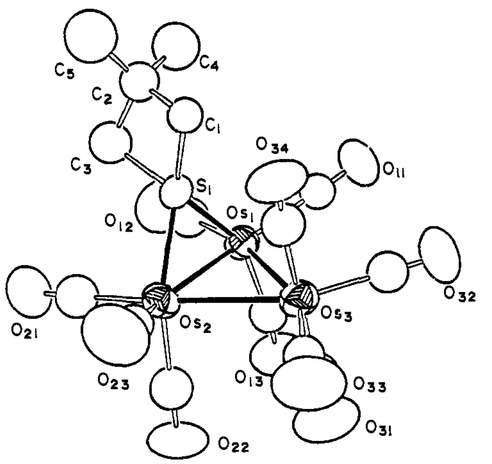


Figure 1. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ (**2**) showing 50% probability thermal ellipsoids.

Table III. Intramolecular Bond Angles for **2**

atom	atom	atom	angle[a]
C(13)	Os(1)	S(1)	151.9 (8)
C(13)	Os(1)	Os(1)	99.1 (8)
C(13)	Os(1)	Os(3)	88.0 (8)
C(12)	Os(1)	S(1)	90.8 (8)
C(12)	Os(1)	Os(2)	106.0 (8)
C(12)	Os(1)	Os(3)	166.7 (8)
C(11)	Os(1)	S(1)	110.4 (7)
C(11)	Os(1)	Os(2)	149.4 (7)
C(11)	Os(1)	Os(3)	93.8 (7)
S(1)	Os(1)	Os(2)	53.5 (2)
S(1)	Os(1)	Os(3)	83.2 (2)
Os(2)	Os(1)	Os(3)	60.91 (4)
C(21)	Os(2)	S(1)	91 (1)
C(21)	Os(2)	Os(1)	104.9 (9)
C(21)	Os(2)	Os(3)	166.2 (9)
C(22)	Os(2)	S(1)	152.3 (9)
C(22)	Os(2)	Os(1)	99.6 (9)
C(22)	Os(2)	Os(3)	87.9 (9)
C(23)	Os(2)	S(1)	111.6 (7)
C(23)	Os(2)	Os(1)	150.8 (7)
C(23)	Os(2)	Os(3)	93.9 (7)
S(1)	Os(2)	Os(1)	53.4 (2)
S(1)	Os(2)	Os(3)	83.7 (2)
Os(1)	Os(2)	Os(3)	61.81 (4)
Os(2)	Os(3)	Os(1)	57.28 (4)
C(3)	S(1)	C(1)	76 (1)
C(3)	S(1)	Os(1)	76 (1)
C(3)	S(1)	Os(2)	122 (1)
C(1)	S(1)	Os(1)	132.1 (8)
C(1)	S(1)	Os(2)	140.1 (8)
Os(1)	S(1)	Os(2)	73.1 (2)
C(2)	C(1)	S(1)	91 (1)
C(1)	C(2)	C(3)	96 (2)
C(2)	C(3)	S(1)	92 (2)
O	C	Os(av)	176 (2)

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

Selected interatomic distances and angles are listed in Tables II and III. Although a few complexes containing bridging thioether ligands have been reported,[9] we are not aware of any previous structural characterizations of complexes containing bridging thietane ligands. Compound **2** crystallizes with two symmetry-independent molecules in the asymmetric crystal unit. Both molecules are structurally similar and consist of a triangular cluster of three metal atoms with 10 linear terminal carbonyl ligands. One edge of the cluster is bridged by the sulfur atom of the

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(9) (a) Rossi, S.; Persiainen, J.; Ahlgren, M.; Pakkanen, T. A. *Organometallics* **1990**, *9*, 475. (b) Boorman, P. M.; Moynihan, K. J.; Richardson, J. F. *Inorg. Chem.* **1988**, *27*, 3207. (c) Sales, D. L.; Stokes, J.; Woodward, P. *J. Chem. Soc. A* **1968**, 1852. (d) Paulus, E. F.; Fritz, H. P.; Schwarhans, K. E. *J. Organomet. Chem.* **1968**, *11*, 647.

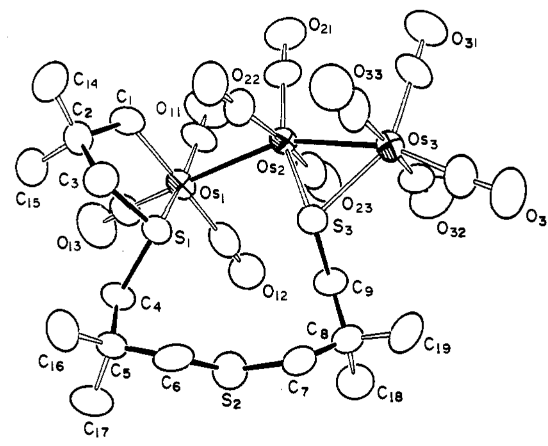

Figure 2. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}(SCH_2CMe_2CH_2)_3]$ (**3**) showing 50% probability thermal ellipsoids.

Table IV. Intramolecular Distances for **3**

atom	atom	distance[a]	atom	atom	distance[a]
Os(1)	C(13)	1.88 (1)	Os(3)	C(34)	1.91 (2)
Os(1)	C(11)	1.89 (1)	Os(3)	C(33)	1.95 (2)
Os(1)	C(12)	1.94 (2)	Os(3)	C(32)	1.97 (2)
Os(1)	C(1)	2.18 (1)	Os(3)	S(3)	2.424 (4)
Os(1)	S(1)	2.419 (3)	S(1)	C(4)	1.82 (1)
Os(1)	Os(2)	2.967 (2)	S(1)	C(3)	1.82 (1)
Os(2)	C(21)	1.86 (1)	S(2)	S(6)	1.79 (1)
Os(2)	C(22)	1.91 (2)	S(2)	C(7)	1.83 (1)
Os(2)	C(23)	1.93 (2)	S(3)	C(9)	1.83 (1)
Os(2)	S(3)	2.408 (3)	O	C(av)	1.14 (2)
Os(2)	Os(3)	2.851 (2)	C	C(av)	1.53 (2)
Os(3)	C(31)	1.91 (2)			

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

Table V. Intramolecular Bond Angles for **3**

atom	atom	atom	angle[a]
C(13)	Os(1)	Os(2)	172.9 (4)
C(11)	Os(1)	C(1)	86.6 (6)
C(11)	Os(1)	S(1)	163.8 (4)
C(11)	Os(1)	Os(2)	80.9 (4)
C(12)	Os(1)	C(1)	177.4 (5)
C(12)	Os(1)	S(1)	96.1 (4)
C(12)	Os(1)	Os(2)	85.5 (4)
C(1)	Os(1)	S(1)	81.5 (3)
C(1)	Os(1)	Os(2)	95.4 (3)
S(1)	Os(1)	Os(2)	89.20 (9)
C(21)	Os(2)	Os(3)	106.5 (4)
C(21)	Os(2)	Os(1)	100.4 (4)
C(22)	Os(2)	Os(3)	93.4 (4)
C(22)	Os(2)	Os(1)	86.0 (4)
C(23)	Os(2)	Os(3)	96.4 (4)
C(23)	Os(2)	Os(1)	84.8 (4)
S(3)	Os(2)	Os(3)	54.09 (9)
S(3)	Os(2)	Os(1)	99.0 (1)
Os(3)	Os(2)	Os(1)	153.08 (3)
C(31)	Os(3)	Os(2)	93.6 (5)
C(34)	Os(3)	Os(2)	161.5 (5)
C(33)	Os(3)	Os(2)	89.8 (4)
C(32)	Os(3)	Os(2)	86.4 (5)
S(3)	Os(3)	Os(2)	53.58 (9)
C(4)	S(1)	Os(1)	110.2 (4)
C(3)	S(1)	Os(1)	101.9 (4)
C(9)	S(3)	Os(2)	113.5 (5)
C(9)	S(3)	Os(3)	113.5 (5)
Os(2)	S(3)	Os(3)	72.3 (1)
O	C(av)	Os	177.0 (2)

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

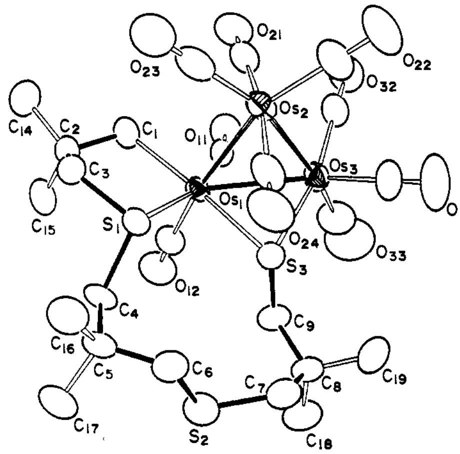

Figure 3. ORTEP diagram of $Os_3(CO)_9[\mu\text{-}(SCH_2CMe_2CH_2)_3]$ (**4**) showing 50% probability thermal ellipsoids.

3,3-DMT ligand and this metal–metal bond is significantly shorter, 2.764 (2) Å [2.776 (2) Å], than the unbridged metal–metal bonds, 2.896 (2) Å [2.858 (2) Å] and 2.871 (2) Å [2.890 (2) Å]. The latter are very similar to the Os–Os distances found in $Os_3(CO)_{12}$, 2.878 (3) Å.[10] The metal–sulfur distances, 2.310 (6)–2.322 (7) Å, are shorter than the metal–sulfur distances found for bridging thiolato ligands in triosmium cluster complexes, which usually lie in the range 2.40–2.46 Å.[11] They are also shorter than the Os–S distance of 2.375 (5) Å to the terminally coordinated thietane ligand in **1a**.[3] The C–S distances 1.79 (2) Å are similar to those in **1a** [1.83 (2) Å and 1.85 (2) Å] and are typical of C–S single bonds. The thietane ring in **1** is slightly less puckered than the thietane ring in **1a**.[3] The dihedral angles are 20.6° and 28.0°, respectively.

When **2** was allowed to react with an excess of 3,3-DMT at 25 °C, the product $Os_3(CO)_{10}[(\mu\text{-}SCH_2CMe_2CH_2)_3]$ (**3**) was obtained in 49% yield. Compound **3** was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **3** is shown in Figure 2. Selected interatomic distances and angles are listed in Tables IV and V. The molecule consists of an open triosmium cluster with only two metal–metal bonds, Os(1)–Os(2) = 2.967 (2) Å and Os(2)–Os(3) = 2.851 (2) Å. The shorter length of the latter may be attributed to the presence of a bridging sulfur atom of a thiolato grouping. The thiolato grouping is one terminus of an 11-osmio-2,2,6,6,10,10-hexamethyl-4,7-dithiaundecanethiolato ligand that bridges the Os(2)–Os(3) bond. The C-terminus of the ligand is metalated at Os(1), Os(1)–C(1) = 2.18 (1) Å. The Os–S bond lengths to the thiolato sulfur atom, 2.408 (3) and 2.424 (4) Å, lie in the expected range for thiolato ligands coordinated to osmium and are slightly longer than the Os–S distances observed in **1**, vide supra. The ligand has two thioether groups, S(1) and S(2). S(1) is coordinated to Os(1), Os(1)–S(1) = 2.419 (3) Å and together with Os(1) and the three carbon atoms at the C-terminus it forms a metallathiacyclopentane ring. The ^1H NMR spectrum shows six singlets in the methyl region, which is consistent with the presence of six inequivalent methyl groups as indicated by the structural analysis. As expected, the methylene region of the spectrum is complex. The molecule contains 10 linear terminal carbonyl ligands. Interestingly, compound **1** was found *not* to react with 3,3-DMT under conditions similar to those of **2**.

When compound **3** was heated to reflux in an octane solution under a CO atmosphere, it was decarbonylated and transformed into two isomers, $Os_3(CO)_9[(\mu\text{-}SCH_2CMe_2CH_2)_3]$ **4**, 36%, and **5**, 28%. When heated to reflux in an octane solution, compound **5** was converted to **4** in 71% yield in 4 h. Compounds **4** and **5** were both characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses.

An ORTEP drawing of the molecular structure of **4** is shown in Figure 3. Selected interatomic distances and angles are listed in Tables VI and VII. Compound **4** consists of a closed triangular

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

Table VI. Intramolecular Distances for **4**

atom	atom	distance[a]	atom	atom	distance[a]
Os(1)	Os(2)	2.9401 (8)	Os(3)	C(32)	1.92 (1)
Os(1)	Os(3)	2.8309 (6)	Os(3)	C(33)	1.91 (1)
Os(1)	S(1)	2.427 (2)	S(1)	C(3)	1.818 (8)
Os(1)	S(3)	2.443 (2)	S(1)	C(4)	1.839 (7)
Os(1)	C(1)	2.188 (8)	S(2)	C(6)	1.816 (8)
Os(1)	C(11)	1.879 (8)	S(2)	C(7)	1.82 (1)
Os(1)	C(12)	1.876 (9)	S(3)	C(9)	1.820 (8)
Os(2)	Os(3)	2.8341 (7)	O	C(av)	1.14 (1)
Os(2)	C(22)	1.91 (1)	C(4)	C(5)	1.54 (1)
Os(2)	C(23)	1.91 (1)	C(5)	C(6)	1.54 (1)
Os(2)	C(24)	1.96 (1)	C(7)	C(8)	1.54 (1)
Os(3)	S(3)	2.371 (2)	C(8)	C(9)	1.54 (1)
Os(3)	C(31)	1.88 (1)			

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

Table VII. Intramolecular Bond Angles for **4**

atom	atom	atom	angle[a]
Os(2)	Os(1)	Os(3)	58.79 (2)
Os(2)	Os(1)	S(1)	87.11 (5)
Os(2)	Os(1)	S(3)	79.83 (5)
Os(2)	Os(1)	C(1)	93.7 (2)
Os(3)	Os(1)	S(1)	126.63 (5)
Os(3)	Os(1)	S(3)	52.81 (5)
Os(3)	Os(1)	C(1)	135.0 (2)
S(1)	Os(1)	S(3)	83.94 (7)
S(1)	Os(1)	C(1)	81.3 (2)
S(1)	Os(1)	C(11)	162.5 (2)
S(1)	Os(1)	C(12)	95.7 (2)
S(3)	Os(1)	C(1)	164.2 (2)
S(3)	Os(1)	C(11)	113.3 (2)
S(3)	Os(1)	C(12)	94.0 (3)
C(1)	Os(1)	C(11)	81.3 (3)
C(1)	Os(1)	C(12)	93.1 (3)
Os(1)	Os(2)	Os(3)	58.68 (2)
Os(1)	Os(3)	Os(2)	62.53 (2)
Os(1)	Os(3)	S(3)	55.17 (5)
Os(2)	Os(3)	S(3)	83.26 (5)
S(3)	Os(3)	C(31)	96.1 (3)
S(3)	Os(3)	C(32)	167.3 (3)
S(3)	Os(3)	C(33)	95.0 (3)
Os(1)	S(1)	C(3)	101.2 (2)
Os(1)	S(1)	C(4)	114.6 (2)
C(3)	S(1)	C(4)	103.2 (4)
C(6)	S(2)	C(7)	100.6 (4)
Os(1)	S(3)	Os(3)	72.03 (6)
Os(1)	S(3)	C(9)	112.0 (3)
Os(3)	S(3)	C(9)	112.4 (3)
Os(1)	C(1)	C(2)	115.7 (5)
C(1)	C(2)	C(3)	109.0 (7)
S(1)	C(3)	C(2)	112.9 (5)
S(1)	C(4)	C(5)	112.7 (5)
C(4)	C(5)	C(6)	110.7 (6)
S(2)	C(6)	C(5)	112.9 (6)
S(2)	C(7)	C(8)	113.9 (6)
C(7)	C(8)	C(9)	111.7 (7)
S(3)	C(9)	C(8)	112.3 (6)
Os	C	O(av)	176 (1)

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

cluster of three osmium atoms with nine linear terminal carbonyl ligands distributed about the cluster as shown in Figure 3. Compound **4** also contains an 11-osmio-2,2,6,6,10,10-hexamethyl-4,7-dithiaundecanethiolato ligand similar to that in **3**. The thiolato sulfur atom S(3) bridges the Os(1)–Os(3) bond adjacent to the C-terminus. The thioether sulfur atom S(1) is coordinated to Os(1), Os(1)–S(1) = 2.427 (2) Å, and forms a metallathiacyclopentane grouping similar to that in **3**. As in **3**, the thioether group S(2) is uncoordinated. The ^{1}H NMR spectrum of this compound also exhibits six singlets in the methyl region as expected on the basis of the structural analyses.

An ORTEP drawing of **5** is shown in Figure 4. Selected interatomic distances and angles are listed in Tables VIII and IX.

Table VIII. Intramolecular Distances for **5**

atom	atom	distance[a]	atom	atom	distance[a]
Os(1)	Os(2)	2.965 (1)	Os(3)	C(32)	1.92 (2)
Os(1)	Os(3)	3.022 (1)	Os(3)	C(33)	1.83 (2)
Os(1)	S(1)	2.500 (4)	S(1)	C(3)	1.83 (1)
Os(1)	C(1)	2.20 (1)	S(1)	C(4)	1.83 (1)
Os(1)	C(11)	1.93 (2)	S(2)	C(9)	1.86 (1)
Os(1)	C(12)	1.94 (2)	S(3)	C(6)	1.82 (2)
Os(1)	C(13)	1.92 (2)	S(3)	C(7)	1.80 (2)
Os(2)	Os(3)	2.689 (1)	O	C(av)	1.14 (2)
Os(2)	S(2)	2.391 (4)	C(1)	C(2)	1.54 (2)
Os(2)	C(21)	1.93 (2)	C(2)	C(3)	1.52 (2)
Os(2)	C(22)	1.90 (2)	C(4)	C(5)	1.55 (2)
Os(2)	C(23)	1.84 (2)	C(5)	C(6)	1.52 (2)
Os(3)	S(2)	2.383 (4)	C(7)	C(8)	1.52 (2)
Os(3)	C(31)	1.94 (2)	C(8)	C(9)	1.53 (2)

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

Table IX. Intramolecular Bond Angles for **5**

atom	atom	atom	angle[a]
Os(2)	Os(1)	Os(3)	53.36 (2)
Os(2)	Os(1)	S(1)	95.64 (8)
Os(2)	Os(1)	C(1)	154.1 (4)
Os(3)	Os(1)	S(1)	104.05 (9)
Os(3)	Os(1)	C(1)	152.5 (4)
S(1)	Os(1)	C(1)	80.8 (4)
S(1)	Os(1)	C(11)	167.5 (4)
S(1)	Os(1)	C(12)	90.7 (4)
S(1)	Os(1)	C(13)	86.9 (5)
Os(1)	Os(2)	Os(3)	64.40 (3)
Os(1)	Os(2)	S(2)	76.64 (9)
Os(3)	Os(2)	S(2)	55.6 (1)
S(2)	Os(2)	C(21)	157.1 (5)
S(2)	Os(2)	C(22)	95.2 (5)
S(2)	Os(2)	C(23)	103.5 (5)
Os(1)	Os(3)	Os(2)	62.23 (3)
Os(1)	Os(3)	S(2)	75.6 (1)
Os(2)	Os(3)	S(2)	55.9 (1)
S(2)	Os(3)	C(31)	151.8 (5)
S(2)	Os(3)	C(32)	105.9 (5)
S(2)	Os(3)	C(33)	95.2 (5)
Os(1)	S(1)	C(3)	98.0 (5)
Os(1)	S(1)	C(4)	112.2 (4)
C(3)	S(1)	C(4)	100.0 (7)
Os(2)	S(2)	Os(3)	68.5 (1)
Os(2)	S(2)	C(9)	110.6 (5)
Os(3)	S(2)	C(9)	115.5 (5)
C(6)	S(3)	C(7)	100.9 (7)
Os(1)	C(1)	C(2)	116.5 (9)
C(1)	C(2)	C(3)	108 (1)
S(1)	C(3)	C(2)	110 (1)
S(1)	C(4)	C(5)	116 (1)
C(4)	C(5)	C(6)	114 (1)
S(3)	C(6)	C(5)	114 (1)
S(3)	C(7)	C(8)	114 (1)
C(7)	C(8)	C(9)	111 (1)
S(2)	C(9)	C(8)	113 (1)
Os	C	O(av)	177 (1)

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

Like **4**, this compound also consists of a closed triangular cluster of three osmium atoms with nine linear terminal carbonyl ligands, three on each metal atom. Compound **5** also contains an 11-osmio-2,2,6,6,10,10-hexamethyl-4,7-dithiaundecanethiolato ligand, but unlike that in **4**, the thiolate sulfur atom S(3) bridges the Os(2)–Os(3) bond that is remote from the C-terminus. The Os(2)–Os(3) bond length at 2.689 (1) Å is much shorter than the Os(1)–Os(2) and Os(1) and Os(3) bond lengths of 2.965 (1) and 3.022 (1) Å and can be attributed at least in part to the presence of the bridging sulfur atom. As in **3** and **4**, the thioether group S(1) is coordinated, Os(1)–S(1) = 2.500 (4) Å, and forms a metallathiacyclopentane ring with the metal atom Os(1) and the last three carbon atoms of the chain. The ^{1}H NMR spectrum of **5** shows four methyl resonances in a 1,1,3,1 intensity ratio, which

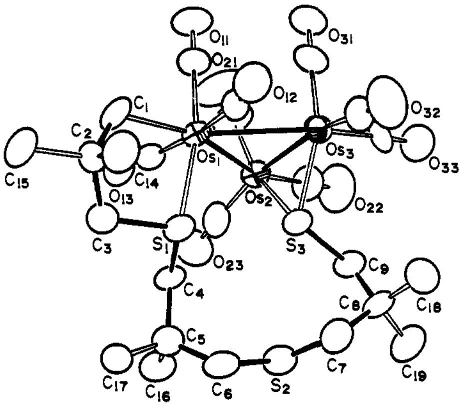

Figure 4. ORTEP diagram of $Os_3(CO)_9[\mu\text{-}(SCH_2CMe_2CH_2)_3]$ (**5**) showing 50% probability thermal ellipsoids.

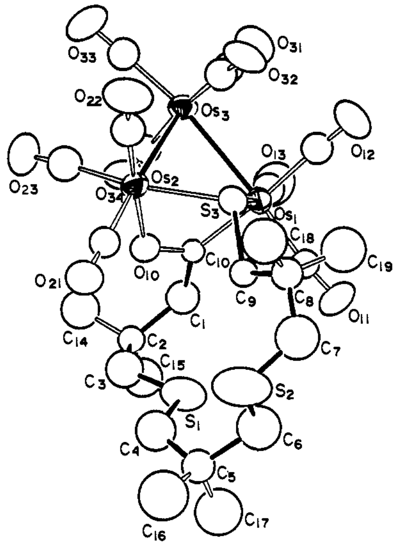

Figure 5. ORTEP diagram of $Os_3(CO)_{10}[\mu\text{-}O{=}C(SCH_2CMe_2CH_2)_3]$ (**6**) showing 50% probability thermal ellipsoids.

Table X. Intramolecular Distances for **6**

atom	atom	distance[a]	atom	atom	distance[a]
Os(1)	Os(3)	2.907 (1)	S(1)	C(3)	1.73 (3)
Os(1)	S(3)	2.431 (6)	S(1)	C(4)	1.75 (3)
Os(1)	C(10)	2.03 (2)	S(2)	C(6)	1.62 (4)
Os(1)	C(11)	1.89 (2)	S(2)	C(7)	1.74 (4)
Os(1)	C(12)	1.93 (3)	S(3)	C(9)	1.85 (2)
Os(1)	C(13)	1.93 (3)	O(10)	C(10)	1.33 (2)
Os(2)	Os(3)	2.904 (2)	O	C(av)	1.16 (2)
Os(2)	S(3)	2.397 (6)	C(1)	C(2)	1.61 (3)
Os(2)	O(10)	2.09 (2)	C(1)	C(10)	1.51 (3)
Os(2)	C(21)	1.92 (3)	C(2)	C(3)	1.51 (3)
Os(2)	C(22)	1.87 (3)	C(4)	C(5)	1.53 (4)
Os(2)	C(23)	1.90 (3)	C(5)	C(6)	1.74 (5)
Os(3)	C(31)	1.90 (3)	C(7)	C(8)	1.53 (4)
Os(3)	C(32)	1.91 (3)	C(8)	C(9)	1.57 (3)
Os(3)	C(33)	1.92 (3)	Os(1)	Os(2)	3.514 (1)
Os(3)	C(34)	1.91 (3)			

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

Table XI. Intramolecular Bond Angles for **6**

atom	atom	atom	angle[a]
Os(3)	Os(1)	S(3)	81.0 (1)
S(3)	Os(1)	C(10)	85.4 (5)
S(3)	Os(1)	C(11)	98.2 (7)
S(3)	Os(1)	C(12)	87.3 (7)
S(3)	Os(1)	C(13)	168.6 (7)
Os(3)	Os(2)	S(3)	81.6 (1)
Os(3)	Os(2)	O(10)	88.6 (4)
S(3)	Os(2)	O(10)	85.7 (4)
S(3)	Os(2)	C(21)	96.5 (7)
S(3)	Os(2)	C(22)	91.5 (9)
S(3)	Os(2)	C(23)	166.7 (9)
O(10)	Os(2)	C(21)	88.6 (8)
O(10)	Os(2)	C(22)	177 (1)
O(10)	Os(2)	C(23)	92 (1)
Os(1)	Os(3)	Os(2)	74.42 (4)
C(3)	S(1)	C(4)	104 (2)
C(6)	S(2)	C(7)	99 (2)
Os(1)	S(3)	Os(2)	93.4 (2)
Os(1)	S(3)	C(9)	109.0 (7)
Os(2)	S(3)	C(9)	110.3 (7)
Os(2)	O(10)	C(10)	120 (1)
C(2)	C(1)	C(10)	128 (2)
C(1)	C(2)	C(3)	110 (2)
S(1)	C(3)	C(2)	119 (2)
S(1)	C(4)	C(5)	117 (2)
C(4)	C(5)	C(6)	112 (2)
S(2)	C(6)	C(5)	108 (2)
S(2)	C(7)	C(8)	123 (3)
C(7)	C(8)	C(9)	106 (2)
S(3)	C(9)	C(8)	112 (2)
Os(1)	C(10)	O(10)	124 (1)
Os(1)	C(10)	C(1)	132 (2)
O(10)	C(10)	C(1)	104 (2)
Os	C	O(av)	176 (2)

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

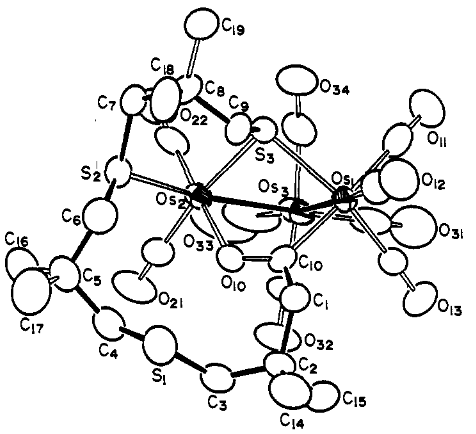

Figure 6. ORTEP drawing of $Os_3(CO)_9[\mu\text{-}O{=}C(SCH_2CMe_2CH_2)_3]$ (**7**) showing 50% probability thermal ellipsoids.

suggests the existence of some accidental degeneracies.

Compounds **3** and **5** both react with CO at 120 °C (650 psi) to yield the new product $Os_3(CO)_{10}[\mu\text{-}O{=}C(CH_2CMe_2CH_2S)_3]$ (**6**) in approximately the same yield, 68%. Compound **6** was also characterized crystallographically and an ORTEP drawing of its structure is shown in Figure 5. Selected interatomic distances and angles are listed in Tables X and XI. This compound consists of an open triosmium cluster. Metal atoms Os(1) and Os(2) are not mutually bonded, Os(1)–Os(2) = 3.514 (1) Å, but they are linked by two bridging groups: (1) the thiolato terminus S(3), and (2) the keto terminus of the 12-oxo,12-osmio-2,2,6,6,10,10-hexamethyl-4,7-dithiadodecanethiolato ligand. The keto function bridges in the well-known $\mu\text{-}\eta_2$ mode with the carbon atom coordinated to Os(1), Os(1)–C(10) = 2.03 (2) Å and the oxygen atom coordinated to Os(2), Os(2)–O(10) = 2.09 (2) Å.[12] The C–O bond has some multiple bond character, C(10)–O(10) = 1.33 (2) Å. The Os–S distances to the thiolato sulfur atom are similar to those in **3**, **4**, and **5**. In **6**, both thioether groups, S(1) and S(2), are uncoordinated.

When a solution of **6** in hexane solvent was heated to reflux for 5 h, the decarbonylation product $Os_3(CO)_9[\mu\text{-}O{=}C(CH_2CMe_2CH_2S)_3]$ (**7**) was obtained in 46% yield. Compound **7** was characterized by a single-crystal X-ray diffraction analysis. An ORTEP diagram of **7** is shown in Figure 6. Selected interatomic

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(12) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

Table XII. Intramolecular Distances for **7**

atom	atom	distance[a]	atom	atom	distance[a]
Os(1)	C(12)	1.87 (2)	S(1)	C(4)	1.79 (1)
Os(1)	C(13)	1.89 (1)	S(1)	C(3)	1.82 (1)
Os(1)	C(11)	1.99 (2)	S(2)	C(6)	1.81 (1)
Os(1)	C(10)	2.11 (1)	S(2)	C(7)	1.81 (1)
Os(1)	S(3)	2.451 (3)	S(3)	C(9)	1.84 (1)
Os(1)	Os(3)	2.903 (1)	O(10)	C(10)	1.24 (1)
Os(2)	C(21)	1.86 (2)	O	C(av)	1.14 (3)
Os(2)	C(22)	1.86 (2)	C(1)	C(10)	1.52 (2)
Os(2)	O(10)	2.124 (8)	C(1)	C(2)	1.55 (2)
Os(2)	S(2)	2.417 (3)	C(2)	C(3)	1.51 (2)
Os(2)	S(3)	2.431 (3)	C(4)	C(5)	1.57 (2)
Os(2)	Os(3)	2.8384 (8)	C(5)	C(6)	1.57 (2)
Os(3)	C(33)	1.87 (2)	C(7)	C(8)	1.55 (2)
Os(3)	C(31)	1.91 (2)	C(8)	C(9)	1.50 (2)
Os(3)	C(32)	1.92 (1)	Os(1)	Os(2)	3.513 (1)
Os(3)	C(34)	1.93 (1)			

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

Table XIII. Intramolecular Bond Angles for **7**

atom	atom	atom	angle[a]
Os(3)	Os(1)	S(3)	81.0 (1)
S(3)	Os(1)	C(10)	85.4 (5)
S(3)	Os(1)	C(11)	98.2 (7)
S(3)	Os(1)	C(12)	87.3 (7)
S(3)	Os(1)	C(13)	168.6 (7)
Os(3)	Os(2)	S(3)	81.6 (1)
Os(3)	Os(2)	O(10)	88.6 (4)
S(3)	Os(2)	O(10)	85.7 (4)
S(3)	Os(2)	C(21)	96.5 (7)
S(3)	Os(2)	C(22)	91.5 (9)
S(3)	Os(2)	C(23)	166.7 (9)
O(10)	Os(2)	C(21)	88.6 (8)
O(10)	Os(2)	C(22)	177 (1)
O(10)	Os(2)	C(23)	92 (1)
Os(1)	Os(3)	Os(2)	74.42 (4)
C(3)	S(1)	C(4)	104 (2)
C(6)	S(2)	C(7)	99 (2)
Os(1)	S(3)	Os(2)	93.4 (2)
Os(1)	S(3)	C(9)	109.0 (7)
Os(2)	S(3)	C(9)	110.3 (7)
Os(2)	O(10)	C(10)	120 (1)
C(2)	C(1)	C(10)	128 (2)
C(1)	C(2)	C(3)	110 (2)
S(1)	C(3)	C(2)	119 (2)
S(1)	C(4)	C(5)	117 (2)
C(4)	C(5)	C(6)	112 (2)
S(2)	C(6)	C(5)	108 (2)
S(2)	C(7)	C(8)	123 (3)
C(7)	C(8)	C(9)	106 (2)
S(3)	C(9)	C(8)	112 (2)
Os(1)	C(10)	O(10)	124 (1)
Os(1)	C(10)	C(1)	132 (2)
O(10)	C(10)	C(1)	104 (2)
Os	C	O(av)	176 (2)

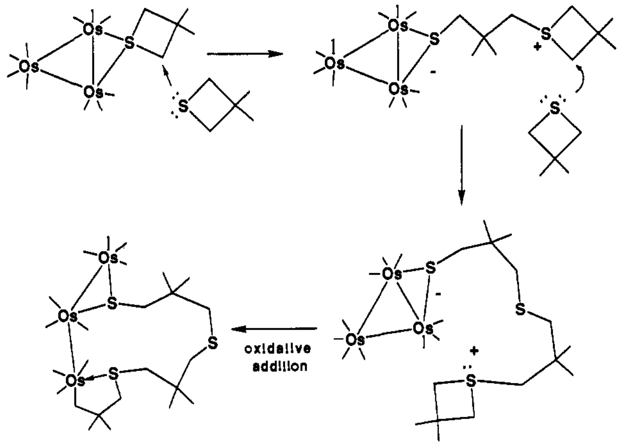
[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

distances and angles are listed in Tables XII and XIII. Like **6**, compound **7** contains an open triosmium cluster with the nonbonded pair of metal atoms, Os(1)–Os(2) = 3.513 (1) Å, bridged by the thiolato terminus and keto terminus of a 12-oxo,12-osmio-2,2,6,6,10,10-hexamethyl-4,7-dithiadodecanethiolato ligand, but unlike **6** the thioether grouping S(2) is coordinated to a metal atom, Os(2)–S(2) = 2.417 (3) Å. All of the metal–metal and metal–ligand bond distances are of normal lengths.

Discussion

The acetonitrile ligands in $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ are readily replaced by 3,3-DMT to yield the new 3,3-DMT complexes **1** and **2**.[4] Compound **2** reacts with 2 equiv of 3,3-DMT to yield compound **3** at 25 °C. No new products were obtained from the reaction of **1** with 3,3-DMT at 25 °C. Compound **3** contains a novel 11-osmio-2,2,6,6,10,10-hexamethyl-4,7-dithiaundecanethiolato ligand that was apparently formed by a ring-opening oligomerization of three 3,3-DMT molecules. It is known that Lewis acid reagents, such as R_3O^+, Me_2SO_4, and BF_3, will initiate the ring-opening polymerization of thietanes.[13] Thus, we believe that the metal centers in **2** acting as Lewis acid centers serve to activate the coordinated 3,3-DMT ligand to a ring-opening nucleophilic attack by a free molecule of 3,3-DMT. This will produce a sulfonium center at the added thietane molecule and a negative charge at the thiolato sulfur of the opened ring. The negative charge will be delocalized into the metal atoms of the cluster; see Scheme I.

Scheme I



The thietanium ring in this intermediate would be susceptible to ring opening by a second molecule of free 3,3-DMT in the usual fashion and produce another thietanium ring, which then undergoes a spontaneous cluster-opening and ring-opening C–S oxidative addition of the thietanium ring and terminates the polymerization process. It is interesting that the coordination of the 3,3-DMT ligand to one metal atom in **1** is not sufficient to initiate the ring-opening reaction. Evidently, it is only by coordination to two metal centers that sufficient Lewis acidity is produced to cause the ring-opening reaction to occur.

We disfavor alternative mechanisms that involve initial intramolecular ring opening of the 3,3-DMT ligand by the cluster since we have shown in another study that such ring-opening processes do not occur for **2** under the very mild conditions observed for this reaction.[4]

When heated to 125 °C, compound **3** is decarbonylated and transformed into two isomeric forms **4** and **5** containing closed triangular clusters. Metal–metal bond formation is a natural consequence of ligand elimination. A simple closure of the cluster of **3** should yield **5** as the first product. Isomerization to **4** most likely occurs by an intramolecular shift of one carbonyl ligand between two metal atoms and a shift of the bridging thiolato group from one metal–metal bond to another; see Scheme II. In support of this, it was found that compound **5** is isomerized to **4** when heated to 125 °C.

It occurred to us that the formation of a C–S bond between the termini of the dithiaundecanethiolato ligand would yield a trithiamacrocycle. The coordination chemistry of polythiamacrocycles has been under active investigation recently.[14] The *gem*-dimethyl effect[15] plus the potential for ligation of the uncoordinated thioether group are two factors that might promote ring closure, but we have not yet obtained any evidence for ring-closure products from the thermal treatments of compounds **3**, **4**, and **5**. Accordingly, we attempted to remove the metal atoms

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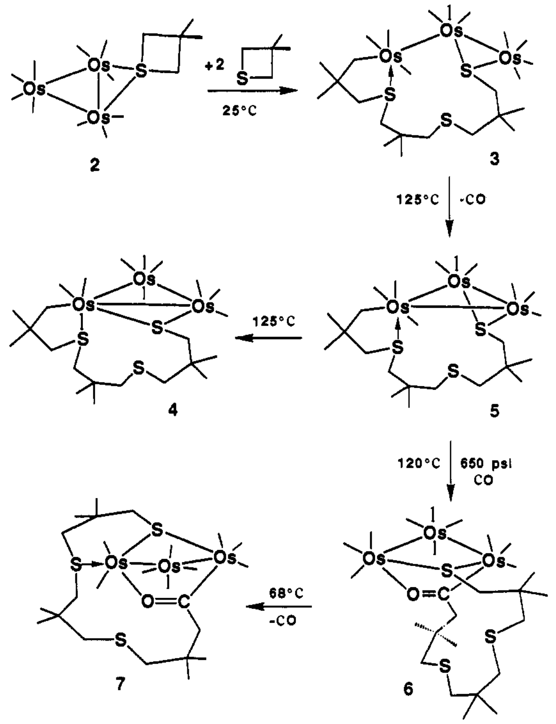
(13) Dittmer, D. C.; Sedergran, T. C. In *Small Ring Heterocycles*, Part 3; Hassner, A., Ed.; Wiley: New York, 1985; Vol. 42, Chapter 5, pp 431–713.

(14) (a) Cooper, S. R.; Rawle, S. C. *Struct. Bonding (Berlin)* **1990**, *72*, 1. (b) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1.

(15) (a) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962. (b) Eliel, E. L.; Allinger, N. L.; Angyll, S. J.; Morrison, *Conformational Analysis*; Interscience: New York, 1965. (c) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, *J. Chem. Soc., Dalton Trans.* **1979**, 1972.

Scheme II



from the ligand by carbonylation with CO at elevated temperature and pressure. The reactions of **3** and **5** with CO at 120 °C, 650 psi CO yielded the product **6**. Two transformations occurred in the formation of **6**. In one of these, the coordinated thioether was replaced by a CO ligand. In the other, a CO group was inserted into the metal–carbon bond at the C-terminus of the ligand. This produced the acyl function, which then assumed a μ-η^2-bridging mode that is commonly observed for these groupings in metal carbonyl cluster complexes.[12] Compound **6** undergoes facile CO elimination (68 °C) to yield the product **7** in which the thioether group proximate to the thiolato grouping is coordinated to the metal atom that contains the oxygen atom. The labilization of metal centers by bridging acyl and carboxamido ligands in metal cluster complexes has been observed previously.[16]

Conclusion

We have observed the first example of a controlled ring-opening oligomerization of 3,3-DMT by a metal complex. The ring opening appears to be promoted by the *bridging* coordination of the 3,3-DMT ligand in complex **2**. The oligomerization is terminated with the coupling of three 3,3-DMT molecules. The oligomer and cluster in these complexes are fairly robust, but the C-terminus of the oligomer can be derivativized with CO. Removal of the oligomer has not yet been achieved, but it is apparent that such removal could lead to the formation of certain trithiamacrocycles or derivatives of the oligomer. Further studies are in progress.

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Supplementary Material Available: Tables of hydrogen atom positional parameters, anisotropic thermal parameters, and nonhydrogen atom positional parameters for complexes **2**–**7** and bond distances and bond angles for the second molecule of complex **2** (50 pages); listing of structure factor amplitudes for all of the structural analyses (124 pages). Ordering information is given on any current masthead page.

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