Nucleophilic Ring Opening of Bridging Thietanes in Open Triosmium Cluster Complexes

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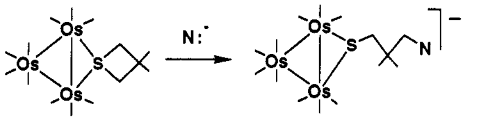
The complexes $\text{Os}_3(\text{CO})_9(\mu_3\text{-S})[\mu\text{-}\overline{\text{SCH}_2\text{CMe}_2\text{C}}\text{H}_2]$ (1) and $\text{Os}_3(\text{CO})_9(\mu_3\text{-S})[\mu\text{-}\overline{\text{SCH}_2\text{CH}_2\text{C}}\text{H}_2]$ (2) were obtained from the reactions of $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ with 3,3-dimethylthietane (DMT) and thietane, respectively, at −42 °C in the presence of Me_3NO. Compound 1 was characterized by a single-crystal X-ray diffraction analysis and was found to contain a DMT group bridging two of the nonbonded metal atoms in the open cluster of three metal atoms by using both lone pairs of electrons on the sulfur atom. Compound 1 reacted with bis(triphenylphosphine)nitrogen(1+) chloride ([PPN]Cl) at 25 °C to yield the salt $[\text{PPN}][\text{Os}_3(\text{CO})_9(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})(\mu_3\text{-S})]$ (3; 76%), in which the chloride ion was added to one of the methylene groups of the DMT ring in a process that caused the ring to open by cleavage of one of the carbon–sulfur bonds. A 4-chloro-3,3-dimethylpropanethiolate ligand bridges the open edge of the anionic triosmium cluster. Compound 3 was converted to the neutral complex $\text{Os}_3(\text{CO})_9[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl}](\mu_3\text{-S})(\mu\text{-H})$ (4) by reaction with HCl at 25 °C. Compound 4 is structurally similar to 3, except that it contains a hydride ligand bridging one of the two metal–metal bonds. Compounds 1 and 2 react with HCl in CH_2Cl_2 solvent to yield the neutral compounds 4 and $\text{Os}_3(\text{CO})_9[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{Cl}](\mu_3\text{-S})(\mu\text{-H})$ (5) in 89% and 90% yields, respectively, in one step. Crystal data for 1: space group $P2_1/c$, a = 9.690 (2) Å, b = 18.813 (4) Å, c = 13.932 (2) Å, β = 109.41 (1)°, Z = 4, 2112 reflections, R = 0.027. Crystal data for 3: space group $P\bar{1}$, a = 17.309 (2) Å, b = 17.768 (2) Å, c = 9.558 (1) Å, α = 104.99 (1)°, β = 103.64 (1)°, γ = 104.04 (1)°, Z = 2, 3825 reflections, R = 0.025. Crystal data for 4: space group $P\bar{1}$, a = 12.500 (2) Å, b = 14.108 (2) Å, c = 6.4657 (6) Å, α = 102.380 (9)°, β = 99.20 (1)°, γ = 86.87 (1)°, Z = 2, 2111 reflections, R = 0.024.

Introduction

The cleavage of carbon–sulfur bonds in sulfur-containing heterocycles is an essential step in the process of desulfurization of these molecules.[1-3] We have recently shown that bridging alkyl-substituted thietane ligands in triosmium cluster complexes exhibit an enhanced tendency to undergo ring-opening addition of nucleophiles (e.g. addition to $\text{Os}_3(\text{CO})_{10}[\mu\text{-}\overline{\text{SCH}_2\text{CMe}_2\text{C}}\text{H}_2]$ in eq 1).[4,5] In



(1)

$\text{Os}_3(\text{CO})_{10}[\mu\text{-}\overline{\text{SCH}_2\text{CMe}_2\text{C}}\text{H}_2]$ the ligand-bridged metal atoms are mutually bonded and the ring opening might have been affected by strain at the sulfur atom caused by the close proximity of the two metal atoms (Os–S–Os = 73.1 (2)°). We have now prepared the new complexes $\text{Os}_3(\text{CO})_9[\mu\text{-}\overline{\text{SCH}_2\text{CMe}_2\text{C}}\text{H}_2](\mu_3\text{-S})$ (1) and $\text{Os}_3(\text{CO})_9[\mu\text{-}\overline{\text{SCH}_2\text{CH}_2\text{C}}\text{H}_2](\mu_3\text{-S})$ (2) from the reactions of $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ with 3,3-dimethylthietane (3,3-DMT) and thietane in which the thietane ligands bridge two metal atoms that are not mutually bonded, and we have studied their ability to undergo nucleophilic ring opening by chloride ion. These results are reported here.

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. The compounds $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$[6] and 3,3-dimethylthietane[7] were prepared by the published procedures. Thietane was purchased from Fluka and was used without further purification. Bis(triphenylphosphine)nitrogen(1+) chloride ([PPN]Cl) was purchased form Aldrich and was used without further purification. Trimethylamine *N*-oxide dihydrate (Aldrich) was dehydrated by using a Dean–Stark apparatus with benzene as the solvent prior to use. All reactions were performed under a nitrogen atmosphere unless specified otherwise. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^{1}H NMR spectra were run on either a Bruker AM-300 or 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 purchased from Aldrich. Mass spectra were obtained on a VG Model 70SQ spectrometer using electron impact ionization. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Preparation of $\text{Os}_3(\text{CO})_9(\overline{\text{SCH}_2\text{CMe}_2\text{C}}\text{H}_2)(\mu_3\text{-S})$. A 147.1-mg amount of $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ (0.167 mmol) and 54 μL (0.498 mmol) of $\text{SCH}_2\text{CMe}_2\text{CH}_2$ were dissolved in 15 mL of CH_2Cl_2, and the mixture was cooled to −42 °C. A solution containing 12.5 mg (0.167 mmol) of Me_3NO in 5 mL of CH_2Cl_2 was added dropwise over a period of 10 min. After addition the solution was warmed to room temperature and the solvent was removed immediately on a rotary evaporator. The residue was dissolved in a minimum amount of dichloromethane and chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (4/1) yielded a yellowish brown band of $\text{Os}_3(\text{CO})_9[\mu\text{-}\overline{\text{SCH}_2\text{CMe}_2\text{C}}\text{H}_2](\mu_3\text{-S})$ (1; 57.3 mg, 36%). Spectral and analytical data for 1: IR (ν(CO) in hexane) 2084 (w), 2062 (vs), 2028 (s), 2003 (s), 1978 (s), 1961 (w), 1949 (w) cm^{-1}; ^{1}H NMR (δ in CDCl_3) 3.79 (s, 4 H), 1.31 (s, 6 H). Anal. Calcd for 1: C, 20.50; H, 1.32. Found: C, 20.04; H, 1.20.

Preparation of $\text{Os}_3(\text{CO})_9(\overline{\text{SCH}_2\text{CH}_2\text{C}}\text{H}_2)(\mu_3\text{-S})$. A 28.8-mg amount of $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ (0.033 mmol) and 7.2 μL of thietane ($\text{SCH}_2\text{CH}_2\text{CH}_2$; 0.098 mmol) were dissolved in 15 mL of CH_2Cl_2, and the mixture was cooled to −42 °C. A solution containing 2.5 mg (0.033 mmol) of Me_3NO in 5 mL of CH_2Cl_2 was added dropwise over a period of 10 min. The solution was then warmed to room temperature, and the solvent was removed on a rotary evaporator. The product was purified by simple recrystallization from a

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[1] (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394. (c) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11. (d) Prins, R.; De Beer, V. H. H.; Somorjai, G. A. *Catal. Rev.—Sci. Eng.* **1989**, *31*, 1.

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Table I. Crystallographic Data for Diffraction Studies

	1	3	4
empirical formula	$Os_3S_2O_9C_{17}H_{13}$	$Os_3ClS_2P_2O_9NC_{50}H_{40}$	$Os_3ClS_2O_9C_{14}H_{11}$
mol wt	996.00	1530.99	993.41
cryst syst	monoclinic	triclinic	triclinic
lattice params			
a, Å	9.690 (2)	17.309 (2)	12.500 (2)
b, Å	18.813 (4)	17.768 (2)	14.108 (2)
c, Å	13.932 (2)	9.558 (1)	6.4657 (6)
α, deg		104.99 (1)	102.380 (9)
β, deg	109.41 (1)	103.64 (1)	99.20 (1)
γ, deg		104.04 (1)	86.87 (1)
V, Å^3	2395.4 (8)	2611.1 (7)	1099.2 (2)
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	4	2	2
D_{calc}, g/cm^3	2.76	1.95	3.00
$F(000)$	1788	1452	888
μ(Mo Kα), cm^{-1}	161.0	75.3	176.6
temp, °C	20	20	20
$2\theta_{max}$, deg	42.0	40.0	42.0
no. of observns ($I > 3\sigma(I)$)	2112	3825	2111
no. of variables	280	613	265
residuals: R; R_w	0.027; 0.032	0.025; 0.055	0.024; 0.029
goodness-of-fit indicator	1.72	1.22	1.75
max shift in final cycle	0.00	0.03	0.10
largest peak in final diff map, e/Å^3	0.65	0.62	0.84
abs cor	empirical	empirical	empirical

CH_2Cl_2/hexane mixture. Yellow crystals of $Os_3(CO)_9[\mu\text{-}\overline{SCH_2CH_2CH_2}](\mu_3\text{-}S)$ (2; 10.0 mg, 33%) were collected. Spectral and analytical data for 2: IR (ν(CO) in hexane) 2085 (w), 2063 (vs), 2029 (s), 2005 (s), 1980 (s), 1963 (w), 1950 (w) cm^{-1}; ^{1}H NMR (δ in $CDCl_3$ at −57 °C) 3.91 (t, ^3J = 7.8 Hz, 2 H), 3.88 (t, ^3J = 7.8 Hz, 2 H), 2.46 (q, ^3J = 7.8 Hz, 2 H). Anal. Calcd for 2: C, 15.52; H, 0.65. Found: C, 16.01; H. 0.59.

Reaction of 1 with [PPN]Cl. A 28.8-mg (0.030-mmol) amount of 1 and 20.6 g (0.036 mmol) of [PPN]Cl were dissolved in 20 mL of CH_2Cl_2. After the mixture was stirred at room temperature for 4 h, the solvent was removed via rotary evaporation. The residue was purified by recrystallization from methanol at −20 °C to yield 35.2 mg of yellow $[Os_3(CO)_9(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu_3\text{-}S)]$PPN (3; 76%). Spectral and analytical data for 3: IR (ν(CO) in CH_2Cl_2) 2104 (w), 2067 (w), 2059 (w), 2032 (vs), 1989 (s), 1963 (s), 1947 (sh), 1910 (w, br) cm^{-1}. ^{1}H NMR (δ in $CDCl_3$) 7.65–7.40 (m, 30 H), 3.29 (s, 2 H), 3.13 (s, 2 H), 0.90 (s, 6 H). Anal. Calcd for 3: C, 39.23; H, 2.63; N, 0.91. Found: C, 38.72; H, 2.28; N, 0.61.

Reaction of 1 with HCl. An 11.7-mg (0.012-mmol) amount of 1 was dissolved in 20 mL of CH_2Cl_2, and 10 μL of concentrated HCl was added. The solution was stirred at 25 °C for 10 min. During this time the color changed from bright yellow to nearly colorless. The solvent was removed, and the product was separated by TLC using a hexane/CH_2Cl_2 (9/1) solvent mixture to yield 10.8 mg of $Os_3(CO)_9(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu_3\text{-}S)(\mu\text{-}H)$ (4; 89%). Spectral and analytical data for 4: IR (ν(CO) in hexane) 2112 (m), 2081 (vs), 2051 (vs), 2031 (m), 2010 (s), 1990 (s), 1983 (m), 1976 (m) cm^{-1}; ^{1}H NMR (δ in $CDCl_3$ at −47 °C) major isomer 3.50 (d, ^2J = 13.2 Hz, 1 H), 3.38 (d, ^2J = 11.0 Hz, 1 H), 3.17 (d, ^2J = 11.0 Hz, 1 H), 3.00 (d, ^2J = 13.2 Hz, 1 H), 0.96 (s, 3 H), 0.90 (s, 3 H), −14.61 (s, 1 H), minor isomer 3.45 (d, ^2J = 11.0 Hz, 1 H), 3.19 (d, ^2J = 11.0 Hz, 1 H), 2.81 (d, ^2J = 13.6 Hz, 1 H), 2.33 (d, ^2J = 13.6 Hz, 1 H), 0.88 (s, 3 H), 0.86 (s, 3 H), −15.0 (s, 1 H), major/minor ratio 3.8. Anal. Calcd for 4: C, 16.93; H, 1.12. Found: C, 16.95; H, 0.98.

Attempted Reaction of 1 with Et_2NH. A 21.6-mg (0.023-mmol) amount of 1 and 2.5 μL (0.047 mmol) of Et_2NH were dissolved in 20 mL of CH_2Cl_2. After the mixture was stirred at room temperature for 2 days, IR spectroscopy indicated no reaction had taken place; 20.8 mg (0.022 mmol) of 1 was recovered.

Attempted Reaction of 1 with CH_3COOH. A 16.4-mg (0.017-mmol) amount of 1 and 15 μL of CH_3COOH were dissolved in 20 mL of CH_3CN. After the mixture was stirred at room temperature for 24 h, IR spectroscopy indicated no reaction had taken place; 16.0 mg (0.017) mmol) of 1 was recovered.

Reaction of 3 with HCl. A 7.8-mg (0.0051-mmol) amount of 3 was dissolved in 20 mL of CH_2Cl_2. A 10-μL amount of concentrated HCl was added. The color immediately changed from yellow to nearly colorless. After removal of the solvent, the product was separated by TLC using a hexane/CH_2Cl_2 (4/1) solvent mixture to yield 4 (5.0 mg, 99%).

Reaction of 2 with HCl. A 9.5-mg (0.010-mmol) amount of 2 was dissolved in 20 mL of CH_2Cl_2. A 10-μL amount of concentrated HCl was added. Within a few minutes the color changed from yellow to nearly colorless. The solvent was removed on a rotary evaporator. The product was purified by TLC on silica gel by using a hexane/CH_2Cl_2 (7/3) solvent mixture to yield 8.9 mg of $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu_3\text{-}S)(\mu\text{-}H)$ (5; 90%). Spectral and analytical data for 5: IR (ν(CO) in hexane) 2112 (m), 2081 (vs), 2052 (vs), 2031 (m), 2028 (m), 2011 (s), 1992 (m), 1984 (m), 1979 (m) cm^{-1}; ^{1}H NMR (δ in $CDCl_3$ at −47 °C) major isomer 3.6 (dt, ^2J = 11.2 Hz, ^3J = 5.6 Hz, 1 H), 3.57 (dt, ^2J = 11.2 Hz, ^3J = 5.6 Hz, 1 H), 3.14 (dt, ^2J = 12.3 Hz, ^3J = 7.5 Hz, 1 H), 2.94 (dt, ^2J = 12.4 Hz, ^3J = 7.5 Hz, 1 H), 1.79 (q, ^3J = 6.8 Hz, 2 H), −14.78 (s, 1 H), minor isomer 3.54–3.52 (m, 2 H), 2.72 (dt, ^3J = 12.3 Hz, ^2J = 7.6 Hz, 1 H), 2.28–2.23 (m, 1 H), 1.67–1.63 (m, 1 H), −15.09 (s, 1 H), major/minor ratio 2.4. Anal. Calcd for 5: C, 14.93; H, 0.73. Found: C, 17.60; H, 0.72.

Crystallographic Analyses. Yellow crystals of 1 were grown by slow evaporation of solvent from solution in a benzene solvent mixture at 5 °C. Light yellow crystals of 3 were grown from a solution in methanol solvent at −10 °C. Yellow crystals of 4 were grown by slow evaporation of solvent from solution in a benzene solvent mixture at 5 °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. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of these 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] Lorentz-polarization (Lp) and absorption corrections were applied in each analysis. Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. For each analysis the

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[8] (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.

Table II. Positional Parameters and *B*(eq) Values for 1

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.57302 (6)	0.24339 (3)	0.48709 (5)	2.99 (3)
Os(2)	0.19356 (5)	0.18903 (3)	0.42217 (4)	2.80 (3)
Os(3)	0.42933 (6)	0.12184 (3)	0.38325 (4)	2.97 (3)
S(1)	0.4305 (4)	0.1576 (2)	0.5464 (3)	3.3 (2)
S(2)	0.3334 (4)	0.2866 (2)	0.3995 (3)	2.8 (2)
O(11)	0.846 (1)	0.1600 (7)	0.603 (1)	6.6 (6)
O(12)	0.703 (1)	0.2900 (8)	0.328 (1)	6.9 (7)
O(13)	0.651 (1)	0.3682 (7)	0.635 (1)	6.6 (7)
O(21)	−0.046 (1)	0.1979 (7)	0.2147 (9)	5.9 (6)
O(22)	0.029 (1)	0.2702 (8)	0.539 (1)	7.2 (8)
O(23)	0.071 (1)	0.0448 (8)	0.448 (1)	7.2 (7)
O(31)	0.346 (1)	0.1656 (7)	0.162 (1)	5.8 (6)
O(32)	0.725 (1)	0.063 (1)	0.399 (1)	9.1 (8)
O(33)	0.288 (1)	−0.0234 (7)	0.346 (1)	7.3 (7)
C(1)	0.283 (2)	0.3780 (8)	0.419 (1)	3.9 (7)
C(2)	0.292 (1)	0.4017 (9)	0.314 (1)	3.8 (7)
C(3)	0.294 (2)	0.3265 (9)	0.273 (1)	3.9 (7)
C(4)	0.433 (2)	0.440 (1)	0.325 (1)	5.5 (9)
C(5)	0.162 (2)	0.445 (1)	0.250 (1)	5.5 (9)
C(11)	0.749 (2)	0.192 (1)	0.558 (1)	4.3 (8)
C(12)	0.657 (2)	0.274 (1)	0.391 (1)	4.4 (8)
C(13)	0.623 (1)	0.321 (1)	0.580 (1)	4.5 (8)
C(21)	0.043 (2)	0.1975 (9)	0.290 (1)	4.0 (8)
C(22)	0.094 (2)	0.2403 (9)	0.496 (1)	3.9 (8)
C(23)	0.116 (2)	0.100 (1)	0.441 (1)	4.5 (8)
C(31)	0.379 (1)	0.1482 (9)	0.246 (1)	3.5 (7)
C(32)	0.613 (2)	0.085 (1)	0.395 (1)	5.3 (9)
C(33)	0.338 (2)	0.033 (1)	0.361 (1)	4.8 (8)
C(101)	−0.075 (3)	0.058 (1)	0.015 (2)	8 (1)
C(102)	0.042 (3)	0.037 (2)	0.091 (2)	8 (1)
C(103)	0.111 (2)	−0.022 (2)	0.075 (2)	9 (2)

positions of all hydrogen atoms on the ligand were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound 1 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All remaining non-hydrogen atoms were subsequently obtained from difference Fourier syntheses and were refined with anisotropic thermal parameters. In the final stages of the analysis a molecule of benzene from the crystallization solvent located about a center of symmetry was found. It was included in the analysis and satisfactorily refined.

Compound 3 crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by 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.

Compound 4 crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by 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 parametes. The hydride ligand was located and refined crystallographically.

Results

Treatment of the complex $Os_3(CO)_{10}(\mu_3\text{-}S)$ with 3,3-dimethylthietane (DMT) or thietane ($\overline{SCH_2CH_2CH_2}$) at −42 °C in the presence of Me_3NO yielded the complexes $Os_3(CO)_9[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu_3\text{-}S)$ (1) and $Os_3(CO)_9[\mu\text{-}\overline{SCH_2CH_2CH_2}](\mu_3\text{-}S)$ (2), respectively, by decarbonylation of the cluster and the addition of one thietane ligand. The molecular structure of these complexes was established by a single-crystal X-ray diffraction analysis of compound 1. An ORTEP drawing of the molecular structure of 1 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 an open triangular cluster of three metal atoms with three terminal carbonyl ligands coordinated to each metal atom. The three metal atoms are bridged by the triply bridging sulfido ligand S(1), while the open edge of the cluster is bridged by the sulfur atom of the DMT ligand. The Os–S distances to the thietane sulfur atom in 1 (2.379 (3) and

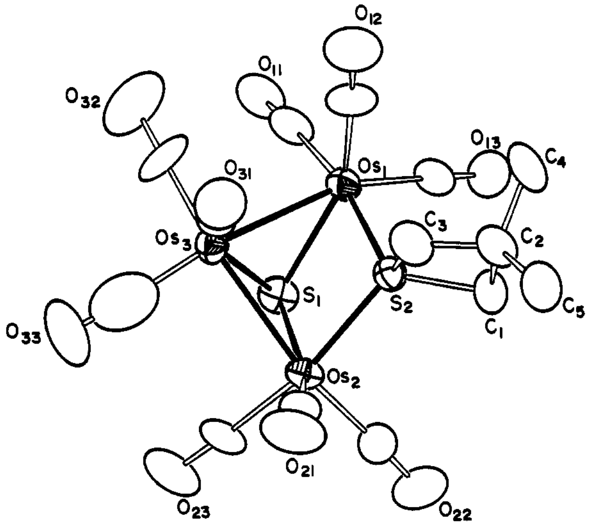

Figure 1. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}S)[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$ (1), showing 50% probability thermal ellipsoids.

Table III. Intramolecular Distances for 1[a]

Os(1)–Os(3)	2.815 (1)	Os(2)–C(22)	1.90 (2)
Os(1)–Os(2)	3.629 (1)	Os(2)–C(23)	1.89 (2)
Os(1)–S(1)	2.440 (4)	Os(3)–S(1)	2.366 (4)
Os(1)–S(2)	2.379 (3)	Os(3)–C(31)	1.88 (2)
Os(1)–C(11)	1.93 (2)	Os(3)–C(32)	1.86 (1)
Os(1)–C(12)	1.87 (2)	Os(3)–C(33)	1.87 (2)
Os(1)–C(13)	1.91 (2)	S(2)–C(1)	1.83 (2)
Os(2)–Os(3)	2.8168 (9)	S(2)–C(3)	1.84 (1)
Os(2)–S(1)	2.444 (3)	C(1)–C(2)	1.55 (2)
Os(2)–S(2)	2.365 (4)	C(2)–C(3)	1.53 (2)
Os(2)–C(21)	1.94 (2)	O–C (av)	1.14 (2)

[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]

Os(3)–Os(1)–S(1)	53.0 (1)	Os(1)–Os(3)–S(1)	55.4 (1)
Os(3)–Os(1)–S(2)	77.4 (1)	Os(1)–Os(3)–C(31)	103.1 (5)
Os(3)–Os(1)–C(11)	93.2 (5)	Os(1)–Os(3)–C(32)	88.0 (6)
Os(3)–Os(1)–C(12)	98.2 (6)	Os(1)–Os(3)–C(33)	159.8 (5)
Os(3)–Os(1)–C(13)	160.7 (5)	Os(2)–Os(3)–S(1)	55.46 (8)
S(1)–Os(1)–S(2)	80.5 (1)	Os(2)–Os(3)–C(31)	97.2 (4)
S(1)–Os(1)–C(11)	89.7 (5)	Os(2)–Os(3)–C(32)	163.8 (5)
S(1)–Os(1)–C(12)	151.1 (6)	Os(2)–Os(3)–C(33)	93.6 (6)
S(1)–Os(1)–C(13)	108.9 (5)	S(1)–Os(3)–C(31)	145.1 (5)
S(2)–Os(1)–C(11)	169.2 (5)	S(1)–Os(3)–C(32)	108.6 (5)
S(2)–Os(1)–C(12)	96.2 (5)	S(1)–Os(3)–C(33)	105.3 (5)
S(2)–Os(1)–C(13)	94.1 (5)	Os(1)–S(1)–Os(2)	96.0 (1)
Os(3)–Os(2)–S(1)	52.9 (1)	Os(1)–S(1)–Os(3)	71.7 (1)
Os(3)–Os(2)–S(2)	77.60 (9)	Os(2)–S(1)–Os(3)	71.7 (1)
Os(3)–Os(2)–C(21)	104.7 (4)	Os(1)–S(2)–Os(2)	99.8 (1)
Os(3)–Os(2)–C(22)	157.9 (4)	Os(1)–S(2)–C(1)	120.5 (5)
Os(3)–Os(2)–C(23)	90.8 (5)	Os(1)–S(2)–C(3)	119.2 (5)
S(1)–Os(2)–S(2)	80.6 (1)	Os(2)–S(2)–C(1)	121.2 (5)
S(1)–Os(2)–C(21)	157.6 (5)	Os(2)–S(2)–C(3)	120.0 (5)
S(1)–Os(2)–C(22)	105.5 (5)	C(1)–S(2)–C(3)	77.1 (7)
S(1)–Os(2)–C(23)	90.7 (5)	S(2)–C(1)–C(2)	92 (1)
S(2)–Os(2)–C(21)	95.2 (5)	C(1)–C(2)–C(3)	96 (1)
S(2)–Os(2)–C(22)	95.5 (5)	S(2)–C(3)–C(2)	92 (1)
S(2)–Os(2)–C(23)	168.2 (5)	Os–C–O (av)	177 (2)
Os(1)–Os(3)–Os(2)	80.26 (3)		

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

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.28217 (3)	0.22847 (3)	0.40783 (4)	3.07 (2)
Os(2)	0.39885 (3)	0.35035 (3)	0.35520 (5)	3.28 (2)
Os(3)	0.26586 (3)	0.14153 (2)	0.10074 (4)	2.76 (2)
Cl	0.6419 (3)	0.2953 (3)	0.2327 (4)	9.2 (2)
S	0.2517 (2)	0.2846 (2)	0.2095 (3)	3.1 (1)
S(2)	0.4160 (2)	0.2281 (2)	0.1939 (3)	3.2 (1)
P(1)	0.9140 (2)	0.2475 (2)	0.0773 (3)	3.0 (1)
P(2)	0.8124 (2)	0.3055 (2)	−0.1387 (3)	2.8 (1)
O(11)	0.3172 (7)	0.3453 (6)	0.727 (1)	9.3 (5)
O(12)	0.1144 (6)	0.1330 (6)	0.421 (1)	6.8 (4)
O(13)	0.3862 (6)	0.1235 (6)	0.498 (1)	7.0 (4)
O(21)	0.4659 (6)	0.4619 (5)	0.188 (1)	7.1 (4)
O(22)	0.5604 (6)	0.3758 (6)	0.600 (1)	7.6 (4)
O(23)	0.3539 (5)	0.4843 (5)	0.558 (1)	6.0 (3)
O(31)	0.0806 (5)	0.0686 (5)	0.0513 (9)	5.7 (3)
O(32)	0.3114 (6)	−0.0025 (5)	0.112 (1)	6.3 (4)
O(33)	0.2393 (5)	0.1367 (5)	−0.2333 (9)	5.5 (3)
N	0.8402 (5)	0.2788 (5)	0.0053 (8)	3.1 (3)
C(1)	0.4542 (7)	0.2567 (7)	0.044 (1)	4.4 (4)
C(2)	0.5041 (8)	0.2050 (9)	−0.022 (1)	5.9 (6)
C(3)	0.568 (1)	0.193 (1)	0.087 (2)	8.5 (7)
C(4)	0.4488 (9)	0.107 (1)	−0.114 (2)	9.5 (7)
C(5)	0.5384 (8)	0.240 (1)	−0.132 (1)	7.9 (7)
C(11)	0.3019 (9)	0.3012 (8)	0.601 (2)	5.8 (6)
C(12)	0.1772 (8)	0.1651 (7)	0.407 (1)	4.4 (5)
C(13)	0.3464 (8)	0.1647 (7)	0.468 (1)	4.5 (5)
C(21)	0.4400 (7)	0.4189 (7)	0.247 (1)	4.6 (5)
C(22)	0.4995 (8)	0.3662 (7)	0.509 (1)	4.5 (5)
C(23)	0.3722 (7)	0.4332 (7)	0.480 (1)	4.3 (4)
C(31)	0.1505 (8)	0.0992 (6)	0.069 (1)	3.7 (4)
C(32)	0.2930 (7)	0.0549 (7)	0.104 (1)	4.3 (4)
C(33)	0.2518 (6)	0.1436 (6)	−0.106 (1)	3.7 (4)

Table VI. Intramolecular Distances for 3[a]

Os(1)–Os(2)	2.8182 (7)	S(2)–C(1)	1.85 (1)
Os(1)–Os(3)	2.8126 (7)	P(1)–N	1.594 (8)
Os(1)–S	2.372 (3)	P(2)–N	1.577 (7)
Os(2)–S	2.415 (3)	C(1)–C(2)	1.53 (2)
Os(2)–S(2)	2.445 (3)	C(2)–C(3)	1.42 (2)
Os(3)–S	2.422 (3)	C(Ph)–C (av)	1.39 (1)
Os(3)–S(2)	2.442 (3)	P–C (av)	1.79 (1)
Cl–C(3)	1.90 (2)	O–C (av)	1.15 (1)

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

2.365 (4) Å) are significantly longer than those found in the complex Os$_3$(CO)$_{10}$[μ-$\overline{\text{SCH}_2\text{CMe}_2\text{CH}_2}$] (6) (2.320 (6) and 2.322 (7) Å), where the sulfur-bridged metal atoms are bonded to one another.[5] Since the thietane-bridged metal atoms are not bonded (Os(1)···Os(2) = 3.629 (1) Å), the Os–S–Os angle at the sulfur atom is much larger than that in 6 (99.8 (1) vs 73.1 (2)°). The thietane ring is slightly puckered; the C–S–C, C–C–C dihedral angle is 18.3°, very similar to that in 6 (20.6°). The S–C distances in 1 and 6 are not significantly different.

Compound 1 underwent a ring-opening addition of Cl$^-$ upon reaction with [PPN]Cl in CH$_2$Cl$_2$ solvent at 25 °C to yield the anionic cluster complex [Os$_3$(CO)$_9$(μ-SCH$_2$CMe$_2$CH$_2$Cl)(μ_3-S)]$^-$ (anion of 3) in 76% yield. The structure of the cluster of 3 was established in the form of the [PPN]$^+$ salt by X-ray diffraction analysis, and an ORTEP drawing of the molecular structure of the anionic cluster of 3 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. Like 1, the molecule contains a sulfur-bridged open triangular cluster of three metal atoms with nine terminal carbonyl ligands. A SCH$_2$CMe$_2$CH$_2$Cl ligand bridges the open edge of the cluster by the sulfur atom S(2), and the Os–S(2) distances are significantly longer than those in 1 (2.422 (3) and 2.442 (2) Å). The chlorine atom is bonded to the carbon C(3) (C(3)–Cl = 1.90 (2) Å). Except for the disposition of the CH$_2$Cl group, the cluster contains virtual mirror symmetry. There are no unusually short contacts between the anionic cluster and the PPN cation. The cation has adopted a bent structure at the nitrogen atom (P–N–P = 136.6 (5)°).

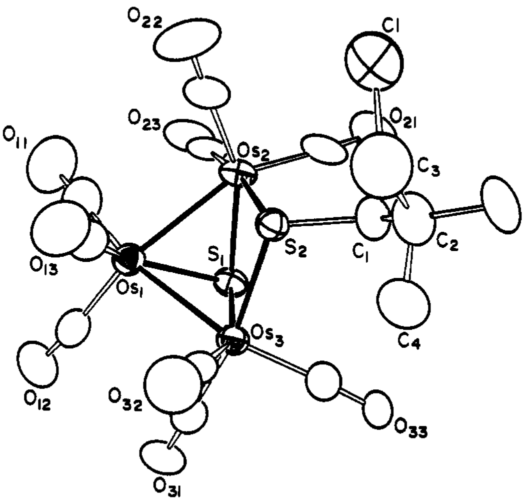

Figure 2. ORTEP diagram of the anionic cluster 3, [Os$_3$(CO)$_9$(μ_3-S)[μ-SCH$_2$CMe$_2$CH$_2$Cl]$^-$, showing 50% probability thermal ellipsoids.

Table VII. Intramolecular Bond Angles for 3[a]

Os(2)–Os(1)–Os(3)	78.42 (2)	Os(1)–Os(3)–S	53.26 (6)
Os(2)–Os(1)–S	54.65 (6)	Os(1)–Os(3)–S(2)	81.21 (6)
Os(2)–Os(1)–C(11)	89.6 (4)	Os(1)–Os(3)–C(31)	87.8 (3)
Os(2)–Os(1)–C(12)	158.5 (3)	Os(1)–Os(3)–C(32)	103.0 (3)
Os(2)–Os(1)–C(13)	102.4 (4)	Os(1)–Os(3)–C(33)	155.8 (3)
Os(3)–Os(1)–S	54.90 (6)	S–Os(3)–S(2)	84.12 (9)
Os(3)–Os(1)–C(11)	167.0 (4)	S–Os(3)–C(31)	90.3 (3)
Os(3)–Os(1)–C(12)	97.8 (3)	S–Os(3)–C(32)	156.0 (3)
Os(3)–Os(1)–C(13)	90.0 (3)	S–Os(3)–C(33)	102.6 (3)
S–Os(1)–C(11)	113.7 (4)	S(2)–Os(3)–C(31)	168.9 (3)
S–Os(1)–C(12)	105.8 (3)	S(2)–Os(3)–C(32)	88.7 (3)
S–Os(1)–C(13)	139.0 (3)	S(2)–Os(3)–C(33)	95.2 (3)
Os(1)–Os(2)–S	53.23 (6)	Os(1)–S–Os(2)	72.12 (7)
Os(1)–Os(2)–S(2)	81.06 (6)	Os(1)–S–Os(3)	71.84 (7)
Os(1)–Os(2)–C(21)	156.8 (3)	Os(2)–S–Os(3)	94.8 (1)
Os(1)–Os(2)–C(22)	101.3 (3)	Os(2)–S(2)–Os(3)	93.5 (1)
Os(1)–Os(2)–C(23)	90.8 (3)	Os(2)–S(2)–C(1)	107.5 (4)
S–Os(2)–S(2)	84.21 (9)	Os(3)–S(2)–C(1)	112.4 (4)
S–Os(2)–C(21)	103.9 (3)	P(1)–N–P(2)	136.6 (5)
S–Os(2)–C(22)	154.5 (3)	S(2)–C(1)–C(2)	114.7 (8)
S–Os(2)–C(23)	89.7 (3)	C(1)–C(2)–C(3)	116 (1)
S(2)–Os(2)–C(21)	94.0 (3)	Cl–C(3)–C(2)	111 (1)
S(2)–Os(2)–C(22)	90.0 (3)	Os–C–O (av)	177 (1)
S(2)–Os(2)–C(23)	171.7 (3)		

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

Compound 3 was converted to the neutral complex Os$_3$(CO)$_9$[μ-SCH$_2$CMe$_2$CH$_2$Cl](μ_3-S)(μ-H) (4) by reaction with HCl at 25 °C. Details of the structure of 4 were also obtained by an X-ray diffraction analysis, and an ORTEP drawing of its structure is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected interatomic distances and angles are listed in Tables IX and X. The structure of this complex is very similar to that of the anion of 3 with the exception of the presence of a bridging hydride ligand (located and refined crystallographically). As expected, the bridging hydride ligand produces a significant elongation on its associated metal–metal bond (Os(2)–Os(3) = 2.9419 (7) Å vs Os(1)–Os(2) = 2.8089 (7) Å).[9] The ^{1}H NMR spectrum of 4 shows two

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(9) Teller, R. G.; Bau, R. *Struct. Bonding* **1981**, *44*, 1.

Scheme I

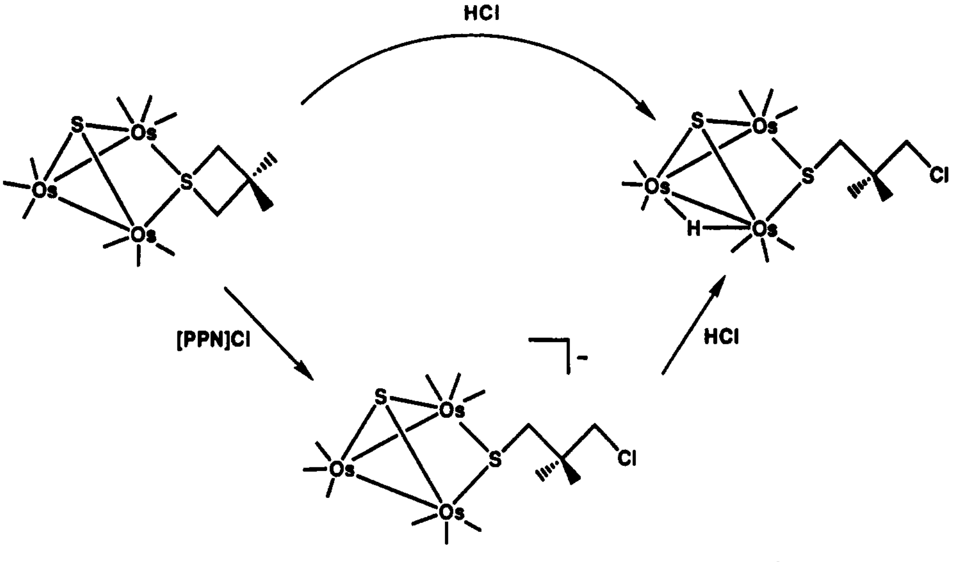


Table VIII. Positional Parameters and B(eq) Values for 4

atom	x	y	z	B(eq), Å^2
Os(1)	0.21436 (4)	0.13092 (3)	0.13993 (7)	2.01 (2)
Os(2)	0.05899 (4)	0.27806 (3)	0.24061 (7)	2.14 (2)
Os(3)	0.26560 (4)	0.38077 (3)	0.35096 (7)	2.07 (2)
Cl	0.7016 (3)	0.2870 (3)	0.3177 (7)	5.6 (2)
S(1)	0.3385 (2)	0.2269 (2)	0.4340 (5)	2.3 (1)
S(2)	0.1883 (2)	0.2805 (2)	0.0085 (5)	2.3 (1)
O(11)	0.0495 (7)	0.0139 (7)	−0.201 (1)	4.0 (4)
O(12)	0.3869 (8)	0.0168 (7)	−0.100 (2)	5.0 (5)
O(13)	0.1938 (8)	0.0043 (7)	0.455 (1)	4.2 (4)
O(21)	−0.0123 (9)	0.2002 (8)	0.596 (2)	6.0 (5)
O(22)	−0.1284 (7)	0.1698 (7)	−0.058 (1)	4.3 (4)
O(23)	−0.0798 (8)	0.4637 (8)	0.273 (2)	5.4 (5)
O(31)	0.1484 (8)	0.5613 (7)	0.228 (2)	5.1 (5)
O(32)	0.3190 (7)	0.4817 (6)	0.818 (1)	3.8 (4)
O(33)	0.4707 (8)	0.4307 (7)	0.207 (2)	4.5 (5)
C(1)	0.476 (1)	0.2016 (9)	0.377 (2)	3.2 (5)
C(2)	0.567 (1)	0.2222 (8)	0.565 (2)	2.7 (5)
C(3)	0.677 (1)	0.204 (1)	0.479 (2)	4.2 (6)
C(4)	0.563 (1)	0.150 (1)	0.706 (3)	5.6 (8)
C(5)	0.560 (1)	0.325 (1)	0.696 (2)	3.7 (6)
C(11)	0.110 (1)	0.0610 (8)	−0.077 (2)	2.5 (5)
C(12)	0.325 (1)	0.0625 (9)	−0.001 (2)	3.4 (6)
C(13)	0.1999 (9)	0.0491 (8)	0.331 (2)	2.1 (5)
C(21)	0.015 (1)	0.231 (1)	0.464 (2)	3.3 (6)
C(22)	−0.057 (1)	0.209 (1)	0.044 (2)	3.0 (5)
C(23)	−0.027 (1)	0.394 (1)	0.259 (2)	4.0 (6)
C(31)	0.192 (1)	0.495 (1)	0.273 (2)	3.4 (6)
C(32)	0.302 (1)	0.4458 (8)	0.642 (2)	2.5 (5)
C(33)	0.395 (1)	0.4132 (8)	0.261 (2)	2.5 (5)

Table IX. Intramolecular Distances for 4[a]

Os(1)–Os(2)	2.8089 (7)	Os(2)–C(23)	1.90 (1)
Os(1)–Os(3)	3.550 (1)	Os(3)–S(1)	2.441 (3)
Os(2)–H(1)	2.0 (1)	Os(3)–S(2)	2.441 (3)
Os(3)–H(1)	1.9 (1)	Os(3)–C(31)	1.94 (1)
Os(1)–S(1)	2.458 (3)	Os(3)–C(32)	1.90 (1)
Os(1)–S(2)	2.426 (3)	Os(3)–C(33)	1.91 (1)
Os(1)–C(11)	1.90 (1)	Cl–C(3)	1.80 (1)
Os(1)–C(12)	1.88 (1)	S(1)–C(1)	1.82 (1)
Os(1)–C(13)	1.90 (1)	C(1)–C(2)	1.52 (2)
Os(2)–Os(3)	2.9419 (7)	C(2)–C(3)	1.55 (2)
Os(2)–S(2)	2.381 (3)	O–C (ave)	1.14 (1)
Os(2)–C(21)	1.88 (1)	Os(2)–H(1)	2.0 (1)
Os(2)–C(22)	1.92 (1)	Os(3)–H(1)	1.9 (1)

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

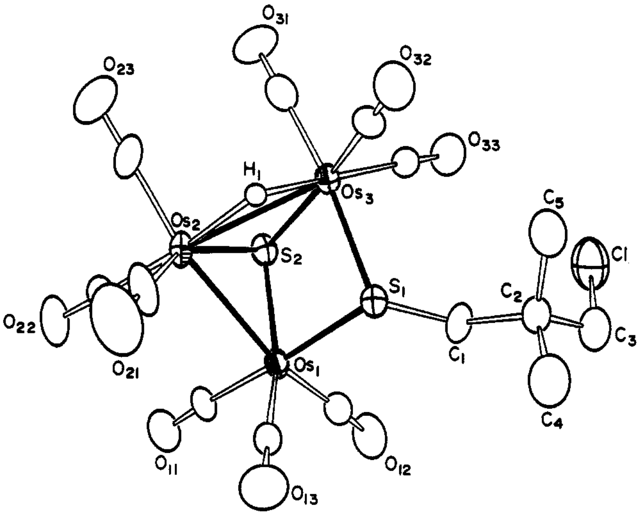


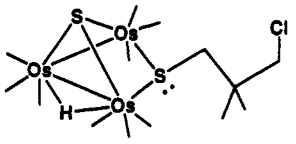
Figure 3. ORTEP diagram of $Os_3(CO)_9[\mu$-$SCH_2CMe_2CH_2Cl](\mu_3$-$S)(\mu$-$H)$ (4), showing 50% probability thermal ellipsoids.

Table X. Intramolecular Bond Angles for 4[a]

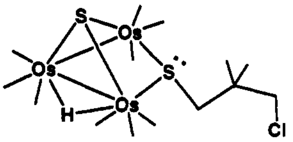
Os(2)–Os(1)–S(1)	86.18 (7)	S(2)–Os(2)–C(23)	109.1 (4)
Os(2)–Os(1)–S(2)	53.51 (7)	Os(2)–Os(3)–S(1)	83.59 (7)
Os(2)–Os(1)–C(11)	90.1 (4)	Os(2)–Os(3)–S(2)	51.49 (7)
Os(2)–Os(1)–C(12)	158.1 (4)	Os(2)–Os(3)–C(31)	89.7 (4)
Os(2)–Os(1)–C(13)	102.2 (3)	Os(2)–Os(3)–C(32)	116.0 (3)
S(1)–Os(1)–S(2)	84.3 (1)	Os(2)–Os(3)–C(33)	148.2 (3)
S(1)–Os(1)–C(11)	175.9 (4)	S(1)–Os(3)–S(2)	84.4 (1)
S(1)–Os(1)–C(12)	95.1 (3)	S(1)–Os(3)–C(31)	173.2 (4)
S(1)–Os(1)–C(13)	86.9 (3)	S(1)–Os(3)–C(32)	91.5 (4)
S(2)–Os(1)–C(11)	94.9 (4)	S(1)–Os(3)–C(33)	94.7 (3)
S(2)–Os(1)–C(12)	104.7 (4)	S(2)–Os(3)–C(31)	90.9 (4)
S(2)–Os(1)–C(13)	154.6 (3)	S(2)–Os(3)–C(32)	167.2 (3)
Os(1)–Os(2)–Os(3)	76.20 (2)	S(2)–Os(3)–C(33)	96.7 (4)
Os(1)–Os(2)–S(2)	54.99 (7)	Os(1)–S(1)–Os(3)	92.9 (1)
Os(1)–Os(2)–C(21)	96.6 (4)	Os(1)–S(1)–C(1)	108.3 (4)
Os(1)–Os(2)–C(22)	94.0 (4)	Os(3)–S(1)–C(1)	112.5 (4)
Os(1)–Os(2)–C(23)	164.1 (4)	Os(1)–S(2)–Os(2)	71.50 (8)
Os(3)–Os(2)–S(2)	53.33 (7)	Os(1)–S(2)–Os(3)	93.7 (1)
Os(3)–Os(2)–C(21)	115.5 (4)	Os(2)–S(2)–Os(3)	75.18 (8)
Os(3)–Os(2)–C(22)	153.8 (4)	S(1)–C(1)–C(2)	117.0 (9)
Os(3)–Os(2)–C(23)	94.0 (4)	C(1)–C(2)–C(3)	109 (1)
S(2)–Os(2)–C(21)	149.9 (4)	Cl–C(3)–C(2)	114 (1)
S(2)–Os(2)–C(22)	101.0 (4)	Os–C–O (av)	177 (1)

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

hydride resonances (δ −14.61, −15.00 ppm) in a ratio of 3.8/1 indicative of a mixture of two isomers that are not rapidly interconverting on the NMR time scale at room temperature. It is suspected that the isomers are formed by different configurations at the pyramidal sulfur atom, as in structures A and B. Evidence for such isomers has



A



B

been reported for the similar compounds $Os_3(CO)_9[\mu_3\text{-}C_6H_4](\mu\text{-}SR)(\mu\text{-}H)$ (7; R = Me, Pr^i).[10] Although the two hydride resonances are sharp at 25 °C, the resonances of the hydrogen atoms on the thiolate ligand are very broad. This broadening is due to a dynamic process that lies at an intermediate exchange rate at 25 °C. At −47 °C the resonances of the hydrogen atoms on the thiolate ligands of both isomers were sharp and showed the expected inequivalences on the basis of the structure observed in the solid state. The dynamic exchange process is believed to involve a simple shift of the hydrogen atom back and forth between the two metal–metal bonds in each isomer. A similar averaging process was observed in the related compounds 7.[10]

Compound 4 and the related compound $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu_3\text{-}S)(\mu\text{-}H)$ (5) were obtained in good yield (90%) in one step by the addition of aqueous solutions of HCl to solutions of 1 and 2 in CH_2Cl_2, respectively. The reaction of 2 with [PPN]Cl was not clean and therefore was not studied in detail. Attempts were made to produce a ring-opening addition by treatments of 1 with acetic acid and NEt_2H, but no ring opening was observed after 2 days at 25 °C in either case.

Discussion

Me_3NO induces the loss of one CO ligand in the complex $Os_3(CO)_{10}(\mu_3\text{-}S)$ at −42 °C to facilitate the addition of 3,3-DMT or thietane $(\overline{SCH_2CH_2CH_2})$ to yield the complexes $Os_3(CO)_9[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu_3\text{-}S)$ (1) and $Os_3(CO)_9[\mu\text{-}\overline{SCH_2CH_2CH_2}](\mu_3\text{-}S)$ (2), respectively. Interestingly, the thietane ligands adopted bridging coordinations by utilizing both lone pairs of electrons on the sulfur atom. This produced a cleavage of one of the three metal–metal bonds, specifically, the one bridged by the sulfur atom of the thietane ligand.

We demonstrated previously that the bridging thietane ligand in complex 6 undergoes a facile ring-opening addition of nucleophiles under mild conditions (eq 1).[4,5] We have now found that the bridging thietane ligands in 1 and 2 can also be opened with chloride ion under mild conditions (see Scheme I). In complex 6 the sulfur-bridged metal atoms are mutually bonded, but in 1 and 2 they are not. It thus appears that the effect of bonding between the metal atoms is not of major importance in determining the ability of bridging coordination to promote the ring opening of thietanes by nucleophiles.

Interestingly, NEt_2H did not produce a ring-opening addition to 1 during 2 days in solution at 25 °C. This contrasts with the reaction of 6 with NEt_2H, where a good yield of the ring-opened addition product was observed after 12 h at 25 °C. This does indicate that the thietane ligand in 6 is *slightly* more susceptible to ring opening than that in 1. At this time we cannot be sure if the slight difference in reactivity is due to the structural difference in the two cluster complexes (i.e. the presence or absence of the metal–metal bond) or perhaps to an electronic effect produced by the presence of the sulfido ligand in 1.

We previously proposed that the facile ring opening of bridging thietane ligands by nucleophiles can be explained by the removal of electron density from the sulfur atom via the σ-donation of the two lone pairs to the two metal atoms.[4b] To a lesser but still significant amount, electron density will also be withdrawn from the carbon atoms bonded to the sulfur atom, thus making them susceptible to attack by nucleophiles. This activation mechanism should also be operative for the complexes 1 and 2. This idea was also proposed to explain the dealkylation of other sulfur-containing ligands.[11]

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Supplementary Material Available: Tables of hydrogen (and phenyl ring carbon for 3) atom positional parameters and anisotropic thermal parameters for the structural analyses of compounds 1, 3, and 4 (14 pages). Ordering information is given on any current masthead page.

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