ligands have also been studied by Burk and co-workers.[22b] The greater steric bulk of substituted Cp ligands would also be expected to increase kinetic stability. Third, substituents which are good π-donors (e.g., OR and NR_2) could be attached to the α-silicon. Of course, heteroatom donors open up the possibility of rearrangements of the silylidene to form complexes in which the multiple bond is to the heteroatom. As with the ligands, greater steric bulk of the substituents would be expected to increase the kinetic stability of silylidenes by lowering the probability of dimerization (or polymerization) and the access to external reagents. This choice of bulky, electron-withdrawing ligands and bulky, π-donor substituents should, on the basis of the present theoretical results, provide a good opportunity for the synthesis of a high-valent transition-metal silylidene complex.

Acknowledgment. This work was supported by grants from the Air Force Office of Scientific Research (Grant No. 90-0052) and the National Science Foundation (Grant No. CHE-8911911).

Supplementary Material Available: A table of GVB-1/TCSCF stationary points for silylidenes (7 pages). Ordering information is given on any current masthead page.

OM920249S

Nucleophilic Ring Opening of a Bridging Thietane Ligand in an Open Tetraosmium Carbonyl Cluster Complex

Richard D. Adams,* Judy A. Belinski, and Michael P. Pompeo

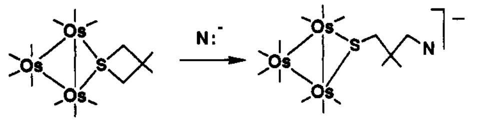
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received April 8, 1992

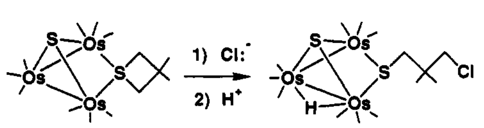
The complex $\mathrm{Os_4(CO)_{12}(\mu\text{-}CO)[\mu\text{-}\overline{SCH_2CMe_2C}H_2]}$ (1) was found to react with bis(triphenylphosphine)nitrogen(1+) chloride, [PPN]Cl, at 25 °C to yield the salt $\mathrm{[PPN][Os_4(\mu\text{-}CO)(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2Cl)}$ (**2**; 43%), in which the chloride ion was added to one of the methylene groups of the $\mathrm{SCH_2CMe_2CH_2}$ ligand in a ring-opening process that involved the cleavage of one of the carbon–sulfur bonds. Compound **2** was converted to the neutral complex $\mathrm{Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)}$ (**3**) by protonation with HCl. Complex **3** was characterized crystallographically and was found to contain a 4-chloro-3,3-dimethylpropanethiolato ligand bridging the wing-tip metal atoms of a butterfly tetrahedron of four metal atoms in the cluster. A hydride ligand bridges one of the edge metal–metal bonds of the cluster. Compound **3** was obtained in good yield (67%) in one step by the reaction of **1** with HCl. At 97 °C, **3** was decarbonylated to form the complex $\mathrm{Os_4(CO)_{12}(\mu_3\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)}$ (**4**; 97%). Compound **4** was also characterized crystallographically and was found to contain a triply bridging 4-chloro-3,3-dimethylpropanethiolato ligand serving as a 5-electron donor. Data for **1**: space group = $P\bar{1}$, a = 10.205 (4) Å, b = 14.399 (2) Å, c = 9.342 (2) Å, α = 92.52 (2)°, β = 108.89 (3)°, γ = 85.82 (2)°, Z = 2, 2678 reflections, R = 0.029. Data for **3**: space group = $P\bar{1}$, a = 20.646 (4) Å, b = 9.610 (1) Å, c = 8.753 (1) Å, α = 116.308 (9)°, β = 102.27 (2)°, γ = 75.12 (1)°, Z = 2, 3186 reflections, R = 0.032. Data for **4**: space group = $P\bar{1}$, a = 10.558 (1) Å, b = 13.673 (2) Å, c = 9.473 (1) Å, α = 94.10 (1)°, β = 91.424 (9)°, γ = 76.08 (1)°, Z = 2, 2421 reflections, R = 0.036.

Introduction

The most important step in the desulfurization of sulfur-containing heterocycles is the cleavage of the carbon–sulfur bonds.[1-3] We have recently shown that bridging coordination of the sulfur atom of thietane ligands in certain triosmium cluster complexes enhances the reactivity of the carbon–sulfur bond to ring-opening cleavage (eqs 1 and 2).[4-6]



(1)



(2)

It was found that the thietane ligand in the closed cluster complex $\mathrm{Os_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2C}H_2]}$ was slightly more susceptible to ring opening than the thietane ligand in the open cluster complex $\mathrm{Os_3(CO)_9[\mu\text{-}\overline{SCH_2CMe_2C}H_2](\mu\text{-}S)}$. We have recently synthesized the tetraosmium complex $\mathrm{Os_4(CO)_{12}(\mu\text{-}CO)[\mu\text{-}\overline{SCH_2CMe_2C}H_2]}$ (1)[7] and have now discovered that the bridging thietane ligand in this com-

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Table I. Crystallographic Data for Diffraction Studies

	compd		
	1	3	4
empirical formula	$Os_4SO_{13}C_{18}H_{10}$	$Os_4ClSO_{13}C_{18}H_{11}$	$Os_4ClSO_{12}C_{17}H_{11}$
M_r	1227.13	1302.65	1235.58
cryst system	triclinic	triclinic	triclinic
lattice params			
a (Å)	10.205 (4)	20.646 (4)	10.558 (1)
b (Å)	14.399 (2)	9.610 (1)	13.673 (2)
c (Å)	9.342 (2)	8.753 (1)	9.473 (1)
α (deg)	92.52 (2)	116.308 (9)	94.10 (1)
β (deg)	108.89 (3)	102.27 (2)	91.424 (9)
γ (deg)	85.82 (2)	75.12 (1)	76.08 (1)
V (Å)^3	1195.0 (1)	1494.8 (4)	1324.0 (3)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z value	2	2	2
D_{calc} (g/cm^3)	3.15	2.89	3.10
μ(Mo Kα) (cm^{-1})	197.2	171.8	193.8
temp (°C)	20	20	20
$2\theta_{max}$ (deg)	45.0	45.0	42.0
no. of observns ($I > 3\sigma(I)$)	2678	3186	2421
no. of variables	325	365	316
residuals: R; R_w	0.029; 0.030	0.032; 0.035	0.036; 0.044
goodness of fit indicator	1.52	1.82	2.48
max shift in final cycle	0.05	0.13	0.00
largest peak in final diff map (e/Å^3)	0.99	1.62	1.00
abs corr	analytical	empirical	analytical

plex also undergoes a ring-opening C–S bond cleavage upon reaction with Cl^- or HCl. The results of these studies are reported here.

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. Compound **1**[7] and 3,3-dimethylthietane[8] were prepared by the published procedures. Bis(triphenylphosphine)nitrogen(1+) chloride, [PPN]Cl, was purchased form Aldrich and was used without further purification. All reactions were performed under a nitrogen atmosphere unless specified otherwise. Yields are calculated on the basis of the the amount of starting cluster consumed in the reaction. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^1H 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. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reaction of 1 with [PPN]Cl. A 32.9-mg amount (0.027 mmol) of **1** and a 23.4-mg amount (0.041 mmol) of [PPN]Cl were dissolved in 20 mL of CH_2Cl_2. After the mixture was stirred at 25 °C for $5^1/_4$ h, the solvent was removed via rotary evaporation. The residue was purified by recrystallization from methanol at 5 °C to yield 20.7 mg of red $[Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2Cl)]PPN$ (**2**; 43%). Data for **2**: IR (ν(CO) in CH_2Cl_2) 2067 (w), 2027 (vs), 2008 (s), 1998 (s), 1962 (br, m), 1933 (br, w) cm^{-1}; ^1H NMR (δ in $CDCl_3$) 7.67–7.40 (m, 30 H), 3.67 (s, 2 H), 3.57 (s, 2 H), 1.19 (s, 6 H). Anal. Calcd for **2**: C, 36.01; H, 2.24; N, 0.78. Found: C, 36.22; H, 2.19; N, 0.76.

Reaction of 2 with HCl. A 23.0-mg amount (0.013 mmol) of **2** was dissolved in 20 mL of CH_2Cl_2, and 10 μL of cconcentrated HCl was added. The solution was stirred at 25 °C for 5 min. During this time the color changed from brown to yellow. The solvent was removed, and the product was separated by TLC using a 9/1 hexane/CH_2Cl_2 solvent mixture to yield 14.8 mg of **3** (92%). Data for **3**: IR (ν(CO) in hexane) 2105 (w), 2076 (vs), 2057 (s), 2051 (s), 2021 (m), 2013 (m), 2005 (m), 1993 (w) cm^{-1}; ^1H NMR (δ in $CDCl_3$ at −47 °C) major isomer 3.47 (d, ^2J = 11.1 Hz, 1 H), 3.39 (d, ^2J = 11.1 Hz, 1 H), 3.24 (d, ^2J = 13.7 Hz, 1 H), 3.08 (d, ^2J = 13.7 Hz, 1 H), 1.05 (s, 3 H), 1.03 (s, 3 H), −16.63 (s, 1 H), minor isomer 3.58 (d, ^2J = 11.4 Hz, 1 H), 3.51 (d, ^2J = 11.4 Hz, 1 H), 2.92 (d, ^2J = 13.9 Hz, 1 H), 2.82 (d, ^2J = 13.9 Hz, 1 H), 1.06 (s, 3 H), 1.04 (s, 3 H), −17.61 (s, 1 H). Ratio major/minor − 1.1/1. Anal. Calcd for **3**: C, 19.36; H, 1.08. Found: C, 19.45; H, 0.93.

Reaction of 1 with HCl. A 10.0-mg amount (0.008 mmol) of **1** was dissolved in 20 mL of CH_2Cl_2, and 20 μL of concentrated HCl was added. The solution was stirred at 25 °C for 12.5 h. During this time the color changed from red to yellow. The solvent was removed, and the reaction mixture was separated by TLC using a 9/1 hexane/CH_2Cl_2 solvent mixture to yield 4.7 mg of $Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$ (**3**; 67%) and 3.2 mg of unreacted **1**.

Thermolysis of 3. A 12.2-mg amount (0.010 mmol) of **3** was dissolved in 20 mL of heptane. The solution was heated to reflux for 10 min. During this time the color changed from yellow to red. The solvent was removed, and the reaction mixture was separated by TLC using a 9/1 hexane/CH_2Cl_2 solvent mixture to yield 1.3 mg of unreacted **3** and 10.3 mg of $Os_4(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$ (**4**; 97%). Data for **4**: IR (ν(CO) in hexane) 2101 (w), 2073 (vs), 2042 (s), 2031 (vs), 2025 (sh, m), 2005 (m), 1982 (m), 1971 (w) cm^{-1}; ^1H NMR (δ in $CDCl_3$ at −50 °C) 3.66 (d, ^2J = 11.6 Hz, 1 H), 3.65 (d, ^2J = 13.3 Hz, 1 H), 3.41 (d, ^2J = 11.6 Hz, 1 H), 2.79 (d, ^2J = 13.3 Hz, 1 H), 1.33 (s, 3 H), 1.14 (s, 3 H), −17.37 (s, 1 H). Anal. Calcd for **4**: C, 17.11; H, 0.88. Found: C, 16.61; H, 0.80.

Reaction of 4 with CO. A 9.1-mg amount (0.0074 mmol) of **4** was dissolved in 20 mL of CH_2Cl_2. A slow purge of CO through the solution was performed for 7.5 h. During this time the color changed from red to yellow. The solvent was removed, and the product was separated by TLC using a 9/1 hexane/CH_2Cl_2 solvent mixture to yield 4.2 mg of $Os_3(CO)_{10}(SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$[1] (**5**; 70%), 1.7 mg of **3**, 22%, and 1.4 mg of unreacted **4**.

Reaction of 3 with CO. A 6.7-mg amount (0.0053 mmol) of **3** was dissolved in 20 mL of CH_2Cl_2. The solution was purged with CO for 13 h. The solvent was removed, and the product was separated by TLC using a 9/1 hexane/CH_2Cl_2 solvent mixture to yield 2.7 mg of $Os_3(CO)_{10}(SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$[4] (**5**; 62%) and 2.5 mg of unreacted **3**.

Crystallographic Analyses. Red crystals of **1** were grown by slow evaporation of a solution in a 4/1 hexane/CH_2Cl_2 solvent mixture at 25 °C. Red crystals of **3** were grown from solution in benzene solvent at 5 °C. Dark red crystals of **4** were grown from a solution in Et_2O solvent at 5 °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. 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.

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Table II. Positional Parameters and B(eq) Values (Å^2) for 1

atom	x	y	z	B(eq)
Os(1)	0.764651 (05)	0.25802 (04)	0.21308 (06)	3.58 (2)
Os(2)	0.89446 (05)	0.14141 (04)	0.30459 (06)	3.44 (2)
Os(3)	0.74035 (06)	0.16277 (04)	−0.00949 (06)	3.98 (3)
Os(4)	0.79653 (05)	0.35293 (04)	0.06487 (05)	3.21 (2)
S(1)	0.9806 (03)	0.2830 (02)	0.2619 (03)	3.2 (1)
O(11)	0.7680 (11)	0.3683 (09)	0.5013 (13)	6.5 (6)
O(12)	0.3924 (12)	0.3938 (10)	0.0995 (13)	7.4 (7)
O(13)	0.4198 (11)	0.1914 (09)	−0.0912 (12)	7.0 (6)
O(14)	0.5024 (12)	0.1257 (09)	0.3551 (12)	6.8 (7)
O(21)	0.9664 (11)	0.1757 (09)	0.6430 (11)	6.4 (6)
O(22)	1.1551 (12)	0.0180 (08)	0.3142 (12)	6.4 (6)
O(23)	0.7258 (13)	−0.0222 (09)	0.3005 (12)	7.2 (7)
O(31)	0.6560 (10)	0.2137 (10)	−0.3396 (11)	7.6 (7)
O(32)	0.6677 (14)	−0.0397 (10)	−0.0604 (15)	8.6 (8)
O(33)	1.0372 (12)	0.1202 (10)	−0.0177 (12)	6.9 (7)
O(41)	0.9678 (13)	0.3973 (11)	−0.1326 (13)	8.7 (8)
O(42)	0.8003 (10)	0.5374 (08)	0.2378 (12)	5.3 (5)
O(43)	0.5250 (11)	0.4052 (09)	−0.1794 (12)	7.2 (6)
C(1)	1.0689 (13)	0.3576 (10)	0.4266 (14)	4.4 (6)
C(2)	1.2153 (13)	0.3236 (12)	0.4200 (15)	4.6 (7)
C(3)	1.1601 (12)	0.2786 (11)	0.2600 (15)	4.3 (7)
C(4)	1.2799 (14)	0.2472 (13)	0.5354 (17)	6.0 (8)
C(5)	1.3067 (15)	0.4020 (13)	0.4324 (19)	6.2 (9)
C(11)	0.7229 (13)	0.3280 (11)	0.3931 (17)	4.4 (7)
C(12)	0.4918 (16)	0.3452 (12)	0.1418 (16)	4.8 (7)
C(13)	0.5370 (16)	0.1920 (12)	−0.0225 (15)	5.0 (7)
C(14)	0.5549 (14)	0.1738 (11)	0.2982 (15)	4.4 (7)
C(21)	0.9386 (13)	0.1617 (11)	0.5145 (17)	4.6 (7)
C(22)	1.0567 (17)	0.0628 (11)	0.3111 (15)	4.5 (7)
C(23)	0.7904 (17)	0.0397 (11)	0.3012 (17)	5.2 (8)
C(31)	0.6860 (13)	0.1940 (12)	−0.2166 (15)	4.6 (7)
C(32)	0.6972 (17)	0.0352 (12)	−0.0396 (17)	5.2 (8)
C(33)	0.9310 (18)	0.1382 (12)	−0.0056 (15)	5.3 (8)
C(41)	0.9048 (15)	0.3805 (11)	−0.0572 (16)	4.8 (7)
C(42)	0.8003 (12)	0.4694 (10)	0.1696 (15)	3.5 (6)
C(43)	0.6283 (15)	0.3850 (11)	−0.0873 (15)	4.7 (7)

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.[9a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] Lorentz–polarization (Lp) and absorption corrections were applied in each analysis. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_0| - |F_c|)^2$, 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 positions of all hydrogen atoms on the ligands 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 triclinic crystal system. The 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 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. The hydride ligand was located and refined. In the final stages of the analysis, a molecule of benzene from the crystallization solvent was located about a center of symmetry. It was included in the analysis and satisfactorily refined.

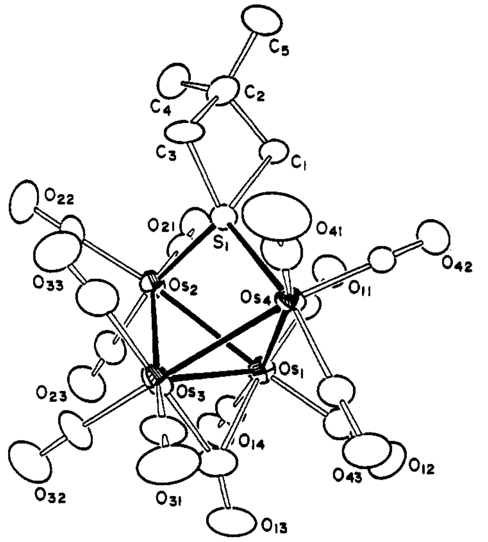

Figure 1. ORTEP diagram of $Os_4(CO)_{13}[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$ (1), showing 50% probability thermal ellipsoids.

Table III. Intramolecular Distances for 1[a]

Os(1)–C(11)	1.89 (2)	Os(3)–C(32)	1.91 (2)
Os(1)–C(12)	1.90 (2)	Os(3)–C(33)	1.94 (2)
Os(1)–C(14)	1.93 (2)	Os(3)–C(13)	2.05 (2)
Os(1)–C(13)	2.32 (1)	Os(3)–Os(4)	2.848 (1)
Os(1)–Os(3)	2.823 (1)	Os(4)–C(43)	1.88 (1)
Os(1)–Os(4)	2.824 (1)	Os(4)–C(41)	1.90 (1)
Os(1)–Os(2)	2.839 (1)	Os(4)–C(42)	1.90 (2)
Os(2)–Os(4)	3.741 (1)	Os(4)–S(1)	2.362 (3)
Os(2)–C(23)	1.86 (2)	S(1)–C(3)	1.83 (1)
Os(2)–C(21)	1.88 (2)	S(1)–C(1)	1.85 (1)
Os(2)–C(22)	1.92 (2)	C(1)–C(2)	1.56 (2)
Os(2)–S(1)	2.376 (4)	C(2)–C(3)	1.55 (2)
Os(2)–Os(3)	2.863 (1)	O–C(av)	1.14 (2)
Os(3)–C(31)	1.90 (1)		

[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)–Os(4)	60.59 (2)	C(42)–Os(4)–S(1)	93.8 (4)
Os(3)–Os(1)–Os(2)	60.76 (3)	S(1)–Os(4)–Os(1)	79.49 (8)
Os(4)–Os(1)–Os(2)	82.71 (3)	S(1)–Os(4)–Os(3)	81.24 (9)
C(23)–Os(2)–S(1)	166.6 (4)	Os(1)–Os(4)–Os(3)	59.69 (2)
C(21)–Os(2)–S(1)	94.8 (5)	C(3)–S(1)–C(1)	76.5 (6)
C(22)–Os(2)–S(1)	96.7 (5)	C(3)–S(1)–Os(4)	121.3 (5)
S(1)–Os(2)–Os(1)	78.95 (8)	C(3)–S(1)–Os(2)	117.3 (5)
S(1)–Os(2)–Os(3)	80.68 (7)	C(1)–S(1)–Os(4)	117.6 (5)
Os(1)–Os(2)–Os(3)	59.34 (3)	C(1)–S(1)–Os(2)	119.0 (5)
Os(1)–Os(3)–Os(4)	59.72 (2)	Os(4)–S(1)–Os(2)	104.3 (1)
Os(1)–Os(3)–Os(2)	59.90 (3)	C(2)–C(1)–S(1)	92.4 (8)
Os(4)–Os(3)–Os(2)	81.85 (3)	C(3)–C(2)–C(1)	95 (1)
C(43)–Os(4)–S(1)	166.8 (4)	C(2)–C(3)–S(1)	93.4 (8)
C(41)–Os(4)–S(1)	96.4 (4)	O–C(av)–Os	178 (1)

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

Compound 4 crystallized in the triclinic crystal system. The 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. The hydride ligand was located but could not be refined and was included in the final analysis only as a fixed contribution.

Results and Discussion

To be certain about the coordination of the thietane ligand in the complex 1, a single-crystal X-ray diffraction analysis of it was performed. An ORTEP drawing 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 a butterfly cluster of four metal atoms bridged at the wing-tip metal atoms by the sulfur atom of the

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(9) (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.

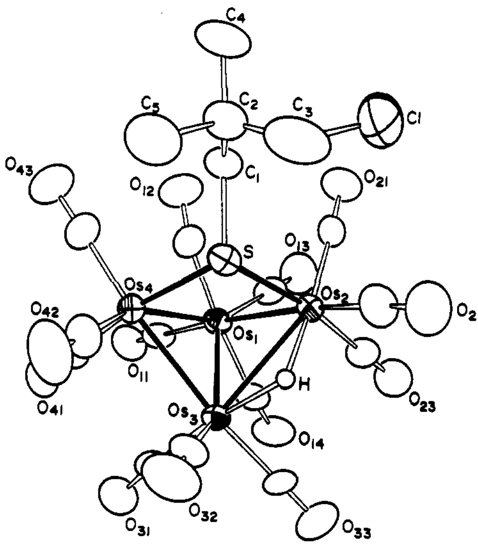
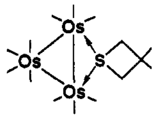
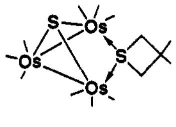


Figure 2. ORTEP diagram of $Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$ (3), showing 50% probability thermal ellipsoids.

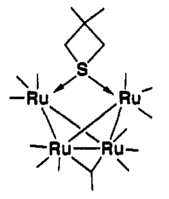
3,3-dimethylthietane ligand. The Os–S distances of 2.376 (4) and 2.362 (3) Å in 1 are longer than those found in the complex $Os_3(CO)_{10}[\overline{\mu\text{-}SCH_2CMe_2CH_2}]$ (6), 2.320 (6) and 2.322 (7) Å, where the sulfur-bridged metal atoms are bonded to one another, but they are quite similar to the Os–S distances found in the complex $Os_3(CO)_9(\mu\text{-}SCH_2CMe_2CH_2)(\mu_3\text{-}S)$ (7), 2.379 (3) and 2.365 (4) Å, where the sulfur-bridged metal atoms are not mutually bonded. Since the thietane-bridged metal atoms are not bonded, Os(2)⋯Os(4) = 3.741 (1) Å, the Os–S–Os angle at the sulfur atom is quite large, 104.3 (1)°. This angle is similar to that in 7, 99.8 (1)°, but much larger than that in 6, 73.1 (2)°. The thietane ring is slightly puckered; the C–S–C, C–C–C dihedral angle is 18.2°, which is similar to that in 6 and 7, 20.6 and 18.3°, respectively. The S–C distances do not differ significantly in 1, 6, and 7. The molecule contains a semibridging carbonyl ligand, C(13)–O(13), between the hinge metal atoms, Os(1)–C(13) = 2.32 (1) Å and Os(3)–C(13) = 2.05 (2) Å. Compound 1 is structurally very similar to the complex $Ru_4(CO)_{12}(\mu\text{-}CO)(\mu\text{-}SCH_2CMe_2CH_2)$ (8) that was reported recently except that in 8 the bridging carbonyl ligand was much more symmetrically positioned than the one in 1.[10]



6



7



8

Compound 1 was found to add Cl^- when treated with [PPN]Cl in CH_2Cl_2 at 25 °C to yield the anionic cluster complex $[Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2Cl)]PPN$ (2) in 43% yield. Compound 2 was characterized by ^1H NMR, IR, and elemental analysis. The observation of two resonances for the methylene groups suggested that the addition had occurred at the thietane ligand to yield a 3-chloro-2,2-dimethylpropanethiolato ligand as observed for other related complexes.[2] This was confirmed by an X-ray crystal structure analysis of the neutral complex 3 that was obtained from reaction of 2 with HCl at 25 °C. An ORTEP drawing of the molecular structure 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. This molecule consists of a butterfly cluster of four metal atoms bridged on the wing-tip metal atoms by the sulfur of a 3-chloro-2,2-dimethylpropanethiolato ligand. Each of the wing-tip metal atoms has three terminally bound carbonyl ligands. The bridging hydride ligand is located across the elongated metal–metal bond, Os(2)–Os(3) = 2.959 (1) Å. One hinge metal atom Os(1) has four terminal CO ligands, while the other Os(3) has only three. The ^1H NMR spectrum of 3 shows only broad resonances at room temperature; however, at −47 °C two

Table V. Positional Parameters and B(eq) Values (Å^2) for 3

atom	x	y	z	B(eq)
Os(1)	0.38942 (3)	0.25686 (6)	0.90177 (7)	2.70 (3)
Os(2)	0.29716 (3)	0.14712 (6)	0.59780 (6)	2.74 (3)
Os(3)	0.32624 (3)	0.47466 (6)	0.75499 (6)	2.50 (3)
Os(4)	0.26507 (3)	0.47338 (6)	1.01765 (6)	2.71 (3)
Cl	0.1137 (3)	−0.0733 (7)	0.4690 (6)	8.3 (4)
S	0.2051 (2)	0.2856 (4)	0.7761 (4)	3.0 (2)
O(11)	0.4830 (7)	0.409 (1)	1.228 (1)	5.2 (6)
O(12)	0.3181 (7)	0.131 (1)	1.077 (1)	5.5 (7)
O(13)	0.4762 (8)	−0.073 (1)	0.790 (2)	6.9 (8)
O(14)	0.4871 (6)	0.292 (1)	0.705 (2)	5.2 (6)
O(21)	0.3137 (7)	−0.159 (1)	0.642 (1)	5.4 (7)
O(22)	0.1985 (8)	0.068 (2)	0.268 (2)	7.3 (8)
O(23)	0.4133 (7)	0.026 (1)	0.384 (1)	5.5 (6)
O(31)	0.3962 (7)	0.749 (1)	0.994 (1)	5.6 (7)
O(32)	0.2021 (7)	0.705 (1)	0.704 (2)	6.4 (7)
O(33)	0.3827 (7)	0.444 (1)	0.446 (1)	6.1 (7)
O(41)	0.3524 (7)	0.704 (1)	1.282 (1)	5.2 (6)
O(42)	0.1448 (8)	0.735 (1)	1.022 (2)	7.0 (7)
O(43)	0.2152 (7)	0.429 (2)	1.296 (1)	6.4 (8)
C(1)	0.1725 (8)	0.156 (2)	0.838 (2)	3.4 (7)
C(2)	0.0963 (8)	0.167 (2)	0.793 (2)	3.8 (7)
C(3)	0.075 (1)	0.125 (2)	0.600 (3)	6 (1)
C(4)	0.078 (1)	0.057 (2)	0.852 (2)	6 (1)
C(5)	0.061 (1)	0.334 (2)	0.892 (3)	8 (1)
C(11)	0.4467 (8)	0.357 (2)	1.109 (2)	3.7 (8)
C(12)	0.3374 (9)	0.196 (2)	1.016 (2)	3.7 (8)
C(13)	0.4447 (8)	0.050 (2)	0.832 (2)	3.6 (8)
C(14)	0.4413 (9)	0.297 (2)	0.767 (2)	3.6 (8)
C(21)	0.3081 (8)	−0.044 (2)	0.621 (2)	3.3 (7)
C(22)	0.231 (1)	0.101 (2)	0.397 (2)	4.7 (9)
C(23)	0.3717 (9)	0.070 (2)	0.468 (2)	3.4 (7)
C(31)	0.3694 (8)	0.645 (1)	0.909 (2)	3.2 (7)
C(32)	0.2483 (9)	0.617 (2)	0.726 (2)	3.6 (8)
C(33)	0.3634 (9)	0.454 (2)	0.562 (2)	3.6 (8)
C(41)	0.3203 (8)	0.616 (2)	1.183 (2)	3.3 (7)
C(42)	0.190 (1)	0.639 (2)	1.018 (2)	4.4 (9)
C(43)	0.235 (1)	0.443 (2)	1.191 (2)	4.4 (9)
C(100)	−0.059 (3)	0.46 (2)	0.47 (2)	15 (4)
C(101)	−0.019 (6)	0.381 (5)	0.371 (6)	11 (3)
C(102)	0.043 (5)	0.42 (1)	0.39 (1)	14 (4)

Table VI. Intramolecular Distances for 3[a]

Os(1)–Os(2)	2.865 (1)	Os(3)–C(31)	1.89 (2)
Os(1)–Os(3)	2.8288 (8)	Os(3)–C(32)	1.88 (2)
Os(1)–Os(4)	2.906 (1)	Os(3)–C(33)	1.92 (1)
Os(2)–Os(4)	3.678 (1)	Os(4)–S	2.431 (4)
Os(1)–C(11)	1.94 (2)	Os(4)–C(12)	2.69 (2)
Os(1)–C(12)	1.95 (2)	Os(4)–C(41)	1.90 (2)
Os(1)–C(13)	1.92 (2)	Os(4)–C(42)	1.92 (2)
Os(1)–C(14)	1.96 (2)	Os(4)–C(43)	1.91 (2)
Os(2)–Os(3)	2.9902 (9)	Cl–C(3)	1.80 (2)
Os(2)–S	2.437 (4)	S–C(1)	1.86 (1)
Os(2)–C(21)	1.88 (2)	C(1)–C(2)	1.53 (2)
Os(2)–C(22)	1.94 (2)	C(2)–C(3)	1.54 (2)
Os(2)–C(23)	1.90 (2)	Os(2)–H	1.7 (1)
Os(3)–C(14)	2.56 (2)	Os(3)–H	1.8 (1)
Os(3)–Os(4)	2.8545 (9)	O–C(av)	1.15 (2)

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

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(10) Adams, R. D.; Belinski, J. A. *J. Cluster Sci.* **1990**, *1*, 319.

Table VII. Intramolecular Bond Angles for 3[a]

Os(2)–Os(1)–Os(3)	63.35 (2)	Os(1)–Os(3)–C(32)	147.2 (5)
Os(2)–Os(1)–Os(4)	79.19 (3)	Os(1)–Os(3)–C(33)	116.7 (5)
Os(2)–Os(1)–C(11)	172.9 (5)	Os(2)–Os(3)–Os(4)	77.96 (2)
Os(2)–Os(1)–C(12)	88.5 (4)	Os(2)–Os(3)–C(31)	157.0 (4)
Os(2)–Os(1)–C(13)	90.3 (5)	Os(2)–Os(3)–C(32)	109.9 (4)
Os(2)–Os(1)–C(14)	87.5 (4)	Os(2)–Os(3)–C(33)	95.7 (4)
Os(3)–Os(1)–Os(4)	59.69 (2)	Os(4)–Os(3)–C(31)	93.4 (4)
Os(3)–Os(1)–C(11)	109.8 (5)	Os(4)–Os(3)–C(32)	86.6 (5)
Os(3)–Os(1)–C(12)	120.1 (5)	Os(4)–Os(3)–C(33)	173.5 (4)
Os(3)–Os(1)–C(13)	137.7 (4)	Os(1)–Os(4)–Os(3)	58.82 (2)
Os(3)–Os(1)–C(14)	61.5 (5)	Os(1)–Os(4)–S	87.4 (1)
Os(4)–Os(1)–C(11)	95.8 (5)	Os(3)–Os(4)–S	83.20 (9)
Os(4)–Os(1)–C(12)	63.9 (5)	Os(2)–S–Os(4)	98.1 (1)
Os(4)–Os(1)–C(13)	151.2 (5)	Os(2)–S–C(1)	113.7 (5)
Os(4)–Os(1)–C(14)	119.3 (5)	Os(4)–S–C(1)	112.7 (5)
Os(1)–Os(2)–Os(3)	57.73 (2)	S–C(1)–C(2)	112 (1)
Os(1)–Os(2)–S	88.22 (9)	C(1)–C(2)–C(3)	112 (1)
Os(3)–Os(2)–S	80.26 (8)	Cl–C(3)–C(2)	112 (1)
Os(1)–Os(3)–Os(2)	58.92 (2)	Os(1)–C(12)–O(12)	164 (1)
Os(1)–Os(3)–Os(4)	61.50 (2)	Os(1)–C(14)–O(14)	160 (1)
Os(1)–Os(3)–C(31)	98.2 (4)	Os–C–O(av)	177 (2)

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

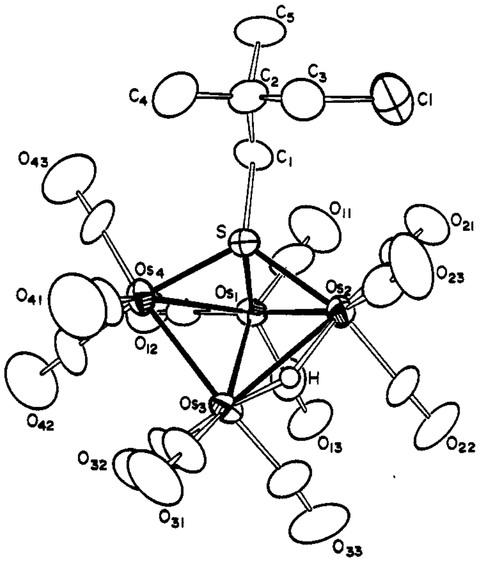
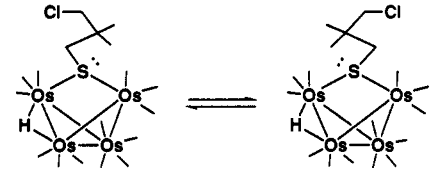


Figure 3. ORTEP diagram of $Os_4(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$ (4), showing 50% probability thermal ellipsoids.

sharp hydride resonances were observed at $\delta = -16.63$ ppm and $\delta = -17.61$ ppm in a ratio of 1.1/1, respectively. This indicates that 3 exists as a mixture of two isomers that are interconverting at an intermediate rate on the NMR time scale at room temperature. It is suspected that the isomers are formed by interconversions at the pyramidal sulfur atom (eq 3), although other dynamical processes such as



(3)

3

the shift of the hydride back and forth between different metal–metal bonds cannot be ruled out and could be occurring in addition. Similar sulfur inversion processes have been observed in related compounds.[11]

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

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.13287 (7)	0.32578 (6)	0.22112 (9)	2.86 (4)
Os(2)	0.33669 (8)	0.31825 (6)	0.02779 (8)	2.88 (5)
Os(3)	0.17911 (7)	0.16561 (6)	0.00831 (9)	3.06 (5)
Os(4)	0.25683 (7)	0.12333 (6)	0.28645 (9)	3.05 (5)
Cl	0.6510 (7)	0.3950 (6)	0.2501 (9)	7.6 (5)
S	0.3562 (4)	0.2559 (4)	0.2562 (5)	2.7 (3)
O(11)	0.122 (2)	0.532 (2)	0.377 (3)	9 (2)
O(12)	−0.047 (1)	0.273 (1)	0.435 (2)	6 (1)
O(13)	−0.078 (2)	0.410 (1)	0.006 (2)	7 (1)
O(21)	0.353 (2)	0.531 (1)	0.132 (2)	6 (1)
O(22)	0.208 (2)	0.403 (2)	−0.241 (2)	8 (1)
O(23)	0.613 (2)	0.255 (1)	−0.087 (2)	7 (1)
O(31)	0.313 (2)	−0.039 (1)	0.120 (2)	7 (1)
O(32)	−0.076 (2)	0.115 (2)	0.073 (2)	8 (1)
O(33)	0.043 (2)	0.245 (2)	−0.262 (2)	8 (1)
O(41)	0.461 (2)	−0.060 (1)	0.185 (2)	7 (1)
O(42)	0.058 (2)	−0.003 (2)	0.316 (2)	10 (2)
O(43)	0.308 (2)	0.120 (2)	0.606 (2)	8 (1)
C(1)	0.432 (2)	0.318 (2)	0.406 (2)	4 (1)
C(2)	0.577 (2)	0.273 (2)	0.432 (2)	4 (1)
C(3)	0.661 (2)	0.273 (2)	0.307 (2)	4 (1)
C(4)	0.605 (2)	0.163 (2)	0.465 (3)	5 (2)
C(5)	0.616 (2)	0.338 (2)	0.554 (3)	6 (2)
C(11)	0.123 (2)	0.454 (2)	0.317 (3)	5 (1)
C(12)	0.026 (2)	0.288 (2)	0.354 (2)	4 (1)
C(13)	−0.001 (2)	0.381 (2)	0.092 (3)	5 (1)
C(21)	0.349 (2)	0.454 (2)	0.095 (2)	4 (1)
C(22)	0.255 (2)	0.371 (2)	−0.148 (2)	5 (1)
C(23)	0.509 (2)	0.281 (2)	−0.046 (2)	4 (1)
C(31)	0.260 (2)	0.037 (2)	−0.073 (2)	4 (1)
C(32)	0.021 (2)	0.129 (2)	0.051 (3)	5 (2)
C(33)	0.097 (2)	0.221 (2)	−0.163 (3)	5 (2)
C(41)	0.386 (2)	0.010 (2)	0.222 (3)	4 (1)
C(42)	0.131 (2)	0.042 (2)	0.303 (3)	5 (2)
C(43)	0.289 (2)	0.124 (2)	0.485 (3)	5 (1)

Table IX. Intramolecular Distances for 4[a]

Os(1)–Os(2)	2.839 (1)	Os(3)–C(32)	1.92 (2)
Os(1)–Os(3)	2.829 (1)	Os(3)–C(33)	1.94 (3)
Os(1)–Os(4)	2.867 (1)	Os(3)–S	3.318 (5)
Os(2)–Os(4)	3.992 (1)	Os(4)–S	2.339 (5)
Os(1)–S	2.346 (5)	Os(4)–C(41)	1.87 (2)
Os(1)–C(11)	1.90 (3)	Os(4)–C(42)	1.93 (2)
Os(1)–C(12)	1.89 (2)	Os(4)–C(43)	1.90 (2)
Os(1)–C(13)	1.90 (3)	Cl–C(3)	1.77 (2)
Os(2)–Os(3)	2.959 (1)	S–C(1)	1.86 (2)
Os(2)–S	2.368 (5)	C(1)–C(2)	1.53 (3)
Os(2)–C(21)	1.96 (3)	C(2)–C(3)	1.50 (3)
Os(2)–C(22)	1.95 (2)	Os(2)–H	2.0 (1)
Os(2)–C(23)	1.90 (2)	Os(3)–H	2.0 (1)
Os(3)–Os(4)	2.799 (1)	O–C(av)	1.13 (3)
Os(3)–C(31)	1.88 (2)		

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

Compound 3 was also obtained in a good yield, 67%, in one step by the addition of HCl to solutions of 1.

At 97 °C complex 3 was decarbonylated and transformed into the new cluster complex $Os_4(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$ (4) in 97% yield. The structure of 4 was established by X-ray diffraction analysis, and 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. Like 3, this molecule consists of a butterfly cluster of four metal atoms, but each metal atom contains only three carbonyl ligands. Thus, the CO ligand that was eliminated came from the CO-rich $Os(CO)_4$ group in 3. To accommodate the loss of the two electrons from the expelled CO group, the thiolate ligand has adopted a triply bridging coordination by donating its lone pair of electrons to that hinge metal atom. Thus, the

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[11] Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 235.

Table X. Intramolecular Bond Angles for 4

Os(2)–Os(1)–Os(3)	62.95 (3)	Os(1)–Os(3)–C(31)	155.7 (8)
Os(2)–Os(1)–Os(4)	88.79 (3)	Os(1)–Os(3)–C(32)	91.8 (7)
Os(2)–Os(1)–S	53.3 (1)	Os(1)–Os(3)–C(33)	106.6 (7)
Os(2)–Os(1)–C(11)	100.2 (8)	Os(2)–Os(3)–Os(4)	87.74 (3)
Os(2)–Os(1)–C(12)	161.7 (7)	Os(2)–Os(3)–C(31)	116.7 (7)
Os(2)–Os(1)–C(13)	93.8 (7)	Os(2)–Os(3)–C(32)	148.6 (7)
Os(3)–Os(1)–Os(4)	58.85 (3)	Os(2)–Os(3)–C(33)	89.7 (8)
Os(3)–Os(1)–S	79.2 (1)	Os(4)–Os(3)–C(31)	95.8 (8)
Os(3)–Os(1)–C(11)	161.1 (8)	Os(4)–Os(3)–C(32)	86.5 (8)
Os(3)–Os(1)–C(12)	104.8 (7)	Os(4)–Os(3)–C(33)	166.8 (7)
Os(3)–Os(1)–C(13)	81.1 (7)	Os(1)–Os(4)–Os(3)	59.88 (3)
Os(4)–Os(1)–S	52.1 (1)	Os(1)–Os(4)–S	52.4 (1)
Os(4)–Os(1)–C(11)	133.4 (7)	Os(3)–Os(4)–S	79.9 (1)
Os(4)–Os(1)–C(12)	73.0 (7)	Os(1)–S–Os(2)	74.0 (1)
Os(4)–Os(1)–C(13)	133.2 (7)	Os(1)–S–Os(4)	75.5 (1)
S–Os(1)–C(11)	98.1 (7)	Os(1)–S–C(1)	114.7 (7)
S–Os(1)–C(12)	113.1 (6)	Os(2)–S–Os(4)	116.0 (2)
S–Os(1)–C(13)	146.8 (7)	Os(2)–S–C(1)	121.4 (7)
Os(1)–Os(2)–Os(3)	58.36 (3)	Os(4)–S–C(1)	122.3 (7)
Os(1)–Os(2)–S	52.6 (1)	S–C(1)–C(2)	116 (1)
Os(3)–Os(2)–S	76.1 (1)	C(1)–C(2)–C(3)	114 (2)
Os(1)–Os(3)–Os(2)	58.69 (3)	Cl–C(3)–C(2)	113 (2)
Os(1)–Os(3)–Os(4)	61.26 (3)	Os–C–O(av)	176 (2)

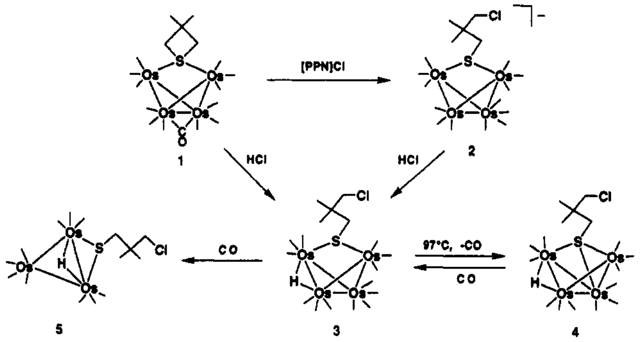
[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

thiolato ligand in 4 serves as a 5-electron donor, and the cluster achieves the 62-electron configuration characteristic of a butterfly tetrahedron. All three Os–S bond distances are similar to each other, Os(1)–S = 2.346 (5) Å, Os(2)–S = 2.368 (5) Å, and Os(4)–s = 2.339 (5) Å, and similar to the Os–S distances observed for the μ_3-SMe ligands in the complex $Os_6(CO)_{12}(\mu\text{-}CNMe_2)_2(\mu_3\text{-}SMe)_2(\mu\text{-}H)_2$.[12] There have been only a few previous examples of the transformation of thiolato ligands between μ_2- and μ_3-bridging sites.[13] The hydride was located crystallographically and was found to bridge the elongated Os(2)–Os(3) bond, 2.959 (1) Å. The ^1H NMR of 4 shows only broad resonances at 25 °C, but at −50 °C all the expected inequivalences were clearly resolved.

When treated with CO at 1 atm/25 °C for 7.5 h, compound 4 was converted partially back to 3 (22%), but the principal product was the known triosmium compound $Os_3(CO)_{10}(\mu_3\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)^4$ (5) evidently formed by a partial degradation of the cluster. In an independent experiment we also observed that 3 was degraded to 5 under similar conditions.

A summary of the results of this study is shown in Scheme I. We have found that the bridging thietane ligand in 1 can be opened by the addition of chloride ion under mild conditions to yield the anionic complex 2. Compound 2 was readily neutralized by protonation that yielded the complex 3 containing a bridging hydride ligand. When heated to 97 °C, 3 was decarbonylated and the thiolato ligand was converted into a triple bridge serving as a 5-electron donor in the complex 4. This decarbonylation was only partially reversible due to the concurrent degradation of 3 by CO.

Scheme I



We have shown previously that complex 6 readily undergoes nucleophilic attack at one of the sulfur bound carbon atoms of the μ-DMT ligand to yield ring-opened species under mild conditions. We have also shown that complex 7 can be opened with chloride ion at 25 °C. The activation of bridging thietane ligands to ring opening by nucleophiles can be explained by the withdrawal of electron density from the sulfur atom via σ-donation of the two lone pairs to the metal atoms. This will also lead to withdrawl of electron density from the carbon atoms bonded to sulfur atom, thus making them susceptible to attack by nucleophiles. Similar mechanisms have been proposed to explain the cleavage of C–S bonds in other sulfur-containing ligands.[14]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Basic Energy Sciences of the U.S. Department of Energy for support of this research.

Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for the structural analyses of compounds 1, 3, and 4 (10 pages). Ordering information is given on any current masthead page.

OM9201932

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