Ring Opening and Carbonylation of 3,3-Dimethylthietane Ligands in Ruthenium Carbonyl Cluster Complexes

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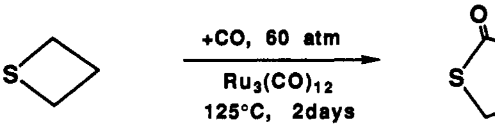
When heated to 97 °C, the complex $Ru_4(CO)_{12}[\mu\text{-}\overline{SCH_2CMe_2C}H_2]_2$ (1) was transformed into two new hexaruthenium cluster complexes, $Ru_6(CO)_{13}(\mu_3\text{-}SCH_2CMe_2CH_2)_4$ (2) and $Ru_6(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2)(\mu_3\text{-}SCH_2CMe_2CH_2)_3[\mu_3\text{-}SCH_2C(Me)(CH_2)CH_2](\mu\text{-}H)$ (3), that contain four and five ring-opened 3,3-dimethylthietane (3,3-DMT) ligands, respectively. In compound **3** one of the ring-opened DMT ligands has also undergone a CH activation on one of the methyl groups. Compound **2** reacts with additional 3,3-DMT at 97 °C to form **3** in 18% yield. When treated with CO at 95 °C (500 psi), compound **2** yielded 4,4-dimethylthiobutyrolactone and $Ru_3(CO)_{12}$. It was also found that the complex $Os_3(CO)_{11}(SCH_2CMe_2CH_2C{=}O)$ (4) yields 4,4-dimethylthiobutyrolactone when treated with CO at 120 °C (1200 psi). Crystal data for **2**: space group $P2_1/n$, $a = 22.652$ (7) Å, $b = 11.712$ (2) Å, $c = 19.965$ (6) Å, $\beta = 115.75$ (2)°, $Z = 4$, 3665 reflections, $R = 0.021$. Crystal data for **3**: space group $P2_1/c$, $a = 17.332$ (8) Å, $b = 14.668$ (9) Å, $c = 19.823$ (9) Å, $\beta = 91.27$ (4)°, $Z = 4$, 1875 reflections, $R = 0.050$.

Introduction

The ring opening of sulfur-containing heterocycles[1] is an essential step in the desulfurization of these molecules and is also one of the key transformations in the purification of fossil fuels by the process of hydrodesulfurization.[2] In order to gain a better understanding of the importance of metal coordination to these processes, we are presently investigating the nature of ring opening of thietanes (thiacyclobutanes) by metal carbonyl cluster complexes.[3-9] We have shown that bridging coordination of the sulfur atom of thietane ligands in a number of cluster complexes of the element osmium produces an activation sufficient to permit opening of the heterocyclic ring by cleavage of one of the carbon–sulfur bonds.

Recently, Alper and co-workers have shown that $Ru_3(CO)_{12}$ and $Co_2(CO)_8/Ru_3(CO)_{12}$ mixtures can serve as catalyst precursors for the carbonylation of thietanes to thiobutyrolactones by insertion of a molecule of CO into one of the carbon–sulfur bonds (eq 1).[10]



(1)

We have now found that when heated to 97 °C the cluster complex $Ru_4(CO)_{12}[\mu\text{-}\overline{SCH_2CMe_2C}H_2]_2$[11] (1) is transformed into two new hexaruthenium cluster complexes, $Ru_6(CO)_{13}(\mu_3\text{-}SCH_2CMe_2CH_2)_4$ (2) and $Ru_6(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2)(\mu_3\text{-}SCH_2CMe_2CH_2)_3[\mu_3\text{-}SCH_2C(Me)(CH_2)CH_2](\mu\text{-}H)$ (3), that contain several ring-opened thietane ligands, and when **2** is heated to 95 °C under CO at 500 psi pressure, 4,4-dimethylthiobutyrolactone and $Ru_3(CO)_{12}$ are produced. We have also found that the thiametallacyclic complex $Os_3(CO)_{11}(SCH_2CMe_2CH_2C{=}O)$[9b] (4) formed by the carbonylation of the thiametallacyclic cluster complex $Os_3(CO)_{11}(SCH_2CMe_2CH_2)$[9b] also yields 4,4-dimethylthiobutyrolactone when treated with CO at 120 °C (1200 psi). The results of these studies are reported here.

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. The compound $Ru_4(CO)_{12}[\mu\text{-}\overline{SCH_2CMe_2C}H_2]_2$[11] (1), $Os_3(CO)_{11}(SCH_2CMe_2CH_2C{=}O)$[9b] (4), and 3,3-dimethylthietane[12] (3,3-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 spectrophotometer. ^1H NMR spectra were run on either a Brüker 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.

Thermolysis of 1. A 14.4-mg amount (0.015 mmol) of **1** was dissolved in 15 mL of heptane, and the solution was then heated to reflux for 30 min. During this time the color changed from orange to brown. The solvent was removed by rotary evaporation. This residue was dissolved in a minimum amount of CH_2Cl_2 and was chromatographed by TLC. Elution with hexane/benzene (7/3) yielded the following bands: 0.5 mg of yellow $Ru_6(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2)(\mu_3\text{-}SCH_2CMe_2CH_2)_3[\mu_3\text{-}SCH_2C(Me)(CH_2)CH_2](\mu\text{-}H)$ (**3**; 4%), 1.9 mg of unreacted **1**, and 6.0 mg of brown $Ru_6(CO)_{13}(\mu_3\text{-}SCH_2CMe_2CH_2)_4$ (**2**; 49%). For **2**: IR (ν(CO) cm^{-1} in hexane) 2052 (w), 2039 (vs), 2035 (vs), 2026 (m), 2004 (m), 2000 (m), 1983 (m), 1978 (m), 1963 (m), 1952 (m), 1779 (w); ^1H NMR (δ in acetone-d_6) 3.50 (d, 1 H, $^2J_{H-H} = 10.5$ Hz), 3.28 (dd, 1 H, $^2J_{H-H} = 11.7$ Hz, $^4J_{H-H} = 2.7$ Hz), 2.90–2.79 (m, 3 H), 2.68–2.61

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(m, 3 H), 2.51–2.45 (m, 3 H), 2.41–2.34 (m, 4 H), 2.16 (dd, 1 H, $^2J_{H-H}$ = 10.5 Hz, $^4J_{H-H}$ = 2.8 Hz), 1.47 (s, 3 H), 1.41 (s, 3 H), 1.40 (s, 3 H), 1.37 (s, 6 H), 1.34 (s, 3 H), 1.26 (s, 3 H), 1.24 (s, 3 H). Anal. Calcd: C, 30.57; H, 3.47. Found: C, 30.27; H, 3.19. For **3**: IR (ν(CO) cm^{-1} in hexane) 2054 (w), 2041 (vs), 2037 (vs), 2030 (s), 2016 (m), 1990 (m), 1974 (sh), 1971 (s), 1961 (m), 1931 (w), 1917 (w); ^{1}H NMR (δ in CDCl$_3$) 3.13 (d, 1 H, $^2J_{H-H}$ = 10.9 Hz), 2.93 (d, 1 H, $^2J_{H-H}$ = 10.9 Hz), 2.78 (d, 1 H, $^2J_{H-H}$ = 10.9 Hz), 2.65 (d, 1 H, $^2J_{H-H}$ = 10.9 Hz), 2.52–2.03 (m, 16 H), 1.39 (s, 3 H), 1.35 (s, 6 H), 1.30 (s, 3 H), 1.25 (s, 3 H), 1.24 (s, 3 H), 1.21 (s, 3 H), 1.20 (s, 3 H), 1.05 (s, 3 H), −12.34 (s, 1 H). Anal. Calcd: C, 28.74; H, 2.92. Found: C, 27.64; H, 2.82.

Conversion of 2 to 3. A 16.9-mg amount (0.012 mmol) of **2** was dissolved in 15 mL of heptane. A 6-μL amount (0.055 mmol) of 3,3-DMT was added. The solution was heated to reflux for 20 min. The solvent was removed and the residue dissolved in a minimum amount of dichloromethane and chromatographed by TLC on silica gel. Elution with a hexane/CH$_2$Cl$_2$ (9/1) solvent mixture yielded 3.2 mg of **3** (18%).

Carbonylation of 2. A solution of **2** (25.2 mg, 0.020 mmol) in 2.0 mL of toluene-d_8 was placed in a 50-mL Parr high-pressure reactor. The vessel was sealed, pressurized to 500 psi with carbon monoxide, and heated to 95 °C in an oil bath. After 18 h the vessel was cooled and opened. A ^{1}H NMR spectrum and a GC/MS spectrum were obtained from this reaction solution. Both spectra showed evidence for 4,4-dimethylthiobutyrolactone: ^{1}H NMR (δ in C$_6$D$_5$CD$_3$) 2.41 (s, 2 H), 1.75 (s, 2 H), 0.67 (s, 6 H); Mass spectrum (123 °C) m/z [M]$^+$ 130. The solvent was then removed and the residue chromatographed by TLC. Elution with hexane/CH$_2$Cl$_2$ (8/2) solvent mixture yielded 20.1 mg of Ru$_3$(CO)$_{12}$ (80%).

Carbonylation of 4. A solution of **4** (19.8 mg, 0.020 mmol) in 2 mL of toluene-d_8 was placed in a 50-mL Parr autoclave. The vessel was sealed, pressurized to 1200 psi with carbon monoxide, and heated to 120 °C in an oil bath. After 16 h the vessel was cooled and opened. A carefully measured amount of CH$_2$Cl$_2$ was added to the reaction solution, and a ^{1}H NMR spectrum of the entire solution was recorded. The ratio of CH$_2$Cl$_2$ to 4,4-dimethylthiobutryolactone was determined by peak integration. This showed the yield of 4,4-dimethylthiobutyrolactone to be 63%. The solvent was then removed in vacuo, and the residue was chromatographed by TLC. Elution with hexane/CH$_2$Cl$_2$ (9/1) solvent mixture yielded 4.6 mg of colorless Os$_2$(CO)$_6$(μ-SCH$_2$C(Me)(CH$_2$)CH$_2$)(μ-H) (**5**; 24%) and 11.0 mg of Os$_3$(CO)$_{12}$ (62%).

Attempted Catalytic Carbonylation of 3,3-Dimethylthietane with 5. A solution of **5** (19.9 mg, 0.031 mmol) and 33 μL (0.030 mmol) of 3,3-DMT in 2 mL of toluene-d_8 was placed in a 50-mL Parr autoclave. The vessel was sealed, pressurized to 1200 psi with carbon monoxide, and heated to 120 °C in an oil bath. After 24 h the bomb was cooled and vented. A ^{1}H NMR spectrum was immediately taken of the solution and revealed only a trace amount of 4,4-dimethylbutyrolactone in relation to 3,3-DMT. The solvent was removed and the residue chromatographed by TLC. Elution with a hexane/CH$_2$Cl$_2$ (9/1) solvent mixture yielded 5.4 mg of unreacted **5**.

Attempted Catalytic Carbonylation of 3,3-Dimethylthietane with Os$_3$(CO)$_{12}$. A solution of Os$_3$(CO)$_{12}$ (18.2 mg, 0.020 mmol) and 3,3-DMT (22 μL, 0.20 mmol) in 2 mL of toluene-d_8 was placed in a 50-mL Parr autoclave. The vessel was sealed, pressurized to 1200 psi with carbon monoxide, and heated to 120 °C in an oil bath. After 2 days the bomb was cooled and vented. A ^{1}H NMR spectrum of the reaction solution showed only free 3,3-DMT and no 4,4-dimethylthiobutyrolactone. The solvent was removed and the residue chromatographed by TLC. Elution with a hexane/CH$_2$Cl$_2$ (7/3) solvent mixture yielded 16.6 mg of unreacted Os$_3$(CO)$_{12}$.

Table I. Crystallographic Data for Compounds 2 and 3

	2	3
empirical formula	Ru$_6$S$_4$O$_{13}$C$_{33}$H$_{40}$	Ru$_6$S$_5$O$_{12}$C$_{37}$H$_{50}$
MW	1379.33	1453.51
crystal system	monoclinic	monoclinic
lattice params		
a (Å)	22.652 (7)	17.361 (3)
b (Å)	11.712 (2)	14.677 (4)
c (Å)	19.965 (6)	19.829 (5)
α (deg)	90	90
β (deg)	115.75 (2)	91.32 (2)
γ (deg)	90	90
V (Å^3)	4771 (5)	5051 (3)
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
Z	4	4
D_{calc} (g/cm^3)	1.92	1.92
μ(Mo, Kα) (cm^{-1})	20.4	19.7
temp (°C)	20	20
$2\theta_{max}$ (deg)	40.0	40.0
no. of obsd data ($I > 3\sigma(I)$)	3665	3531
no. of variables	532	545
residuals: R, R_w	0.021; 0.022	0.029; 0.031
goodness of fit indicator	1.17	1.39
max shift in final cycle	0.05	0.04
largest peak in final diff map (e$^-$/Å^3)	0.28	1.56
abs corr	empirical	empirical

Crystallographic Analyses. Brown crystals of **2** and yellow crystals of **3** were grown by cooling concentrated solutions in hexane/CH$_2$Cl$_2$ solvent mixtures to −20 °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-monochromated 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.[13a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[13b] 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 positions of all hydrogen atoms on the ligands were calculated by assuming idealized geometries with C–H distance of 0.95 Å. Their contributions were added to the structure factor calculations without refinement.

Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stages of refinement, a molecule of hexane cocrystallized in the lattice was observed located about a center of symmetry. The carbon atoms of this molecule were refined satisfactorily with isotropic thermal parameters. The hydrogen atoms of the hexane molecule were ignored.

Compound **3** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely on the basis of the systematic absences observed during the collection of the data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stages of refinement a molecule of hexane cocrystallized in the lattice was observed located about a center of symmetry. The carbon atoms of this molecule were refined satisfactorily with isotropic thermal parameters. The hydride ligand was located and refined with an isotropic thermal parameter. The hydrogen

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(13) (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. Positional Parameters and *B*(eq) Values for 2

atom	*x*	*y*	*z*	*B*(eq) (Å²)
Ru(1)	0.01579 (2)	0.16732 (4)	0.17900 (3)	2.39 (2)
Ru(2)	0.12451 (2)	0.11588 (4)	0.31634 (3)	2.61 (2)
Ru(3)	−0.10941 (2)	0.08131 (4)	0.07598 (3)	2.55 (2)
Ru(4)	−0.09202 (2)	0.15025 (4)	0.22985 (3)	2.45 (2)
Ru(5)	−0.00367 (2)	−0.17807 (4)	0.23626 (3)	2.23 (2)
Ru(6)	−0.14135 (2)	−0.20275 (4)	0.18127 (3)	2.74 (2)
S(1)	−0.07661 (7)	−0.0488 (1)	0.26201 (8)	2.49 (6)
S(2)	0.05796 (7)	−0.0226 (1)	0.22469 (8)	2.31 (6)
S(3)	0.02271 (7)	0.1896 (1)	0.30374 (8)	2.69 (6)
S(4)	−0.08882 (7)	−0.1209 (1)	0.11258 (8)	2.43 (6)
O(11)	0.1350 (2)	0.2246 (5)	0.1543 (3)	5.6 (3)
O(12)	−0.0225 (3)	0.4131 (4)	0.1359 (3)	5.7 (3)
O(13)	−0.0109 (2)	0.1223 (4)	0.0186 (2)	4.3 (2)
O(26)	0.2467 (2)	0.0632 (5)	0.2982 (3)	6.3 (3)
O(27)	0.1878 (2)	0.0154 (5)	0.4691 (3)	5.7 (3)
O(31)	−0.1686 (3)	0.3134 (4)	0.0261 (3)	5.9 (3)
O(32)	−0.1909 (2)	0.0121 (4)	−0.0841 (3)	4.7 (2)
O(46)	−0.2346 (2)	0.1037 (4)	0.1340 (3)	5.1 (2)
O(47)	−0.1333 (2)	0.3968 (4)	0.2093 (3)	5.8 (3)
O(56)	−0.0341 (2)	−0.4215 (4)	0.2575 (3)	4.7 (2)
O(57)	0.0918 (2)	−0.2081 (4)	0.3973 (3)	5.0 (2)
O(66)	−0.1739 (3)	−0.3462 (5)	0.2853 (3)	7.2 (3)
O(67)	−0.2836 (2)	−0.1466 (5)	0.1081 (3)	6.7 (3)
C(11)	0.0944 (3)	0.1993 (6)	0.1706 (4)	3.7 (3)
C(12)	−0.0099 (3)	0.3184 (6)	0.1521 (4)	3.9 (3)
C(13)	−0.0284 (3)	0.1211 (5)	0.0667 (4)	3.0 (3)
C(21)	0.1574 (3)	0.2820 (5)	0.3599 (4)	3.9 (3)
C(22)	0.1166 (3)	0.3419 (6)	0.3933 (4)	4.1 (3)
C(23)	0.1277 (4)	0.2888 (7)	0.4679 (4)	5.8 (4)
C(24)	0.1354 (4)	0.4681 (7)	0.4059 (50	6.3 (4)
C(25)	0.0442 (3)	0.3360 (5)	0.3401 (4)	3.7 (3)
C(26)	0.2008 (3)	0.0857 (6)	0.3066 (3)	3.6 (3)
C(27)	0.1638 (3)	0.0539 (6)	0.4101 (4)	3.6 (3)
C(31)	−0.1440 (3)	0.2265 (6)	0.0463 (4)	3.8 (3)
C(32)	−0.1617 (3)	0.0334 (5)	−0.0219 (4)	3.1 (3)
C(41)	−0.1116 (3)	0.1579 (6)	0.3270 (3)	3.6 (3)
C(42)	−0.1144 (3)	0.0432 (6)	0.3633 (3)	3.5 (3)
C(43)	−0.0951 (4)	0.0640 (6)	0.4461 (4)	5.2 (4)
C(44)	−0.1834 (3)	−0.0075 (6)	0.3284 (4)	5.0 (4)
C(45)	−0.0653 (3)	−0.0404 (5)	0.3583 (3)	3.3 (3)
C(46)	−0.1793 (3)	0.1198 (5)	0.1690 (4)	3.1 (3)
C(47)	−0.1146 (3)	0.3064 (6)	0.2160 (4)	3.7 (3)
C(51)	0.0543 (3)	−0.2738 (5)	0.1934 (3)	3.0 (3)
C(52)	0.1138 (3)	−0.2117 (5)	0.1931 (3)	2.9 (3)
C(53)	0.1305 (3)	−0.2688 (6)	0.1340 (4)	4.4 (3)
C(54)	0.1721 (3)	−0.2181 (6)	0.2686 (3)	4.0 (3)
C(55)	0.0942 (3)	−0.0894 (5)	0.1686 (3)	2.7 (3)
C(56)	−0.0322 (3)	−0.3272 (6)	0.2446 (3)	3.1 (3)
C(57)	0.0564 (3)	−0.1976 (5)	0.3355 (4)	3.0 (3)
C(61)	−0.1630 (3)	−0.3383 (5)	0.1004 (3)	3.6 (3)
C(62)	−0.1659 (3)	−0.2993 (5)	0.0258 (3)	3.4 (3)
C(63)	−0.1632 (4)	−0.4047 (6)	−0.0192 (4)	4.9 (3)
C(64)	−0.2284 (3)	−0.2322 (6)	−0.0197 (4)	4.5 (3)
C(65)	−0.1057 (3)	−0.2259 (5)	0.0387 (3)	3.0 (3)
C(66)	−0.1617 (3)	−0.2909 (6)	0.2464 (4)	4.2 (3)
C(67)	−0.2284 (4)	−0.1665 (6)	0.1346 (4)	4.1 (3)

atoms of the hexane molecule were ignored.

Results

Two new hexaruthenium cluster complexes were obtained by heating the complex $Ru_4(CO)_{12}[\mu\text{-}SCH_2CMe_2CH_2]_2$ (1) to 97 °C. The principal product (49% yield) was identified as $Ru_6(CO)_{13}(\mu_3\text{-}SCH_2Me_2CH_2)_4$ (2). The minor product (4% yield) was identified as $Ru_6(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2)(\mu_3\text{-}SCH_2CMe_2CH_2)_3[\mu_3\text{-}SCH_2C(Me)(CH_2)CH_2](\mu\text{-}H)$ (3). 2 was transformed to 3 in 18% yield by reaction with an additional amount of 3,3-dimethylthietane at 97 °C. Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure 2 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 six metal atoms are divided into groups of four and two. The metal atoms of the group of four Ru(1)–Ru(4) are arranged in the form of the "spiked" triangle. The group of two, Ru(5) and Ru(6), has two bridging thiolato sulfur atoms that were derived from two ring-opened 3,3-dimethylthietane molecules. These sulfur atoms also bridge to the group of four ruthenium atoms. In a similar manner, the thiolato sulfur, S(2), bridges the Ru(1)–Ru(2) bond of the group of four, but also extends to the group of two through a bond to Ru(5). The three sulfur atoms are the

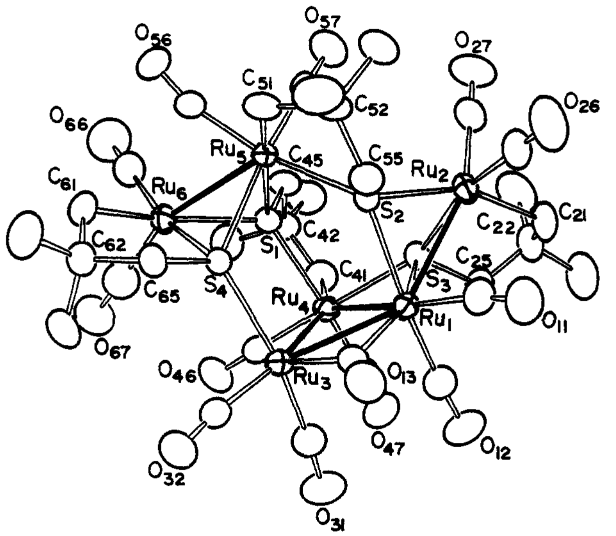


Figure 1. ORTEP diagram of $Ru_6(CO)_{13}(\mu_3\text{-}SCH_2CMe_2CH_2)_4$ (2) showing 50% probability thermal ellipsoids.

Table III. Intramolecular Distances for 2[a]

Ru(1)–Ru(2)	2.842 (1)	Ru(3)–C(32)	1.877 (7)	Ru(6)–C(66)	1.867 (8)
Ru(1)–Ru(3)	2.867 (1)	Ru(4)–S(1)	2.403 (2)	Ru(6)–C(67)	1.828 (7)
Ru(1)–Ru(4)	3.031 (1)	Ru(4)–S(3)	2.411 (2)	S(1)–C(45)	1.828 (6)
Ru(1)–S(2)	2.436 (2)	Ru(4)–C(41)	2.171 (6)	S(2)–C(55)	1.828 (6)
Ru(1)–S(3)	2.440 (2)	Ru(4)–C(46)	1.850 (7)	S(3)–C(25)	1.843 (6)
Ru(1)–C(11)	1.897 (7)	Ru(4)–C(47)	1.887 (7)	S(4)–C(65)	1.828 (6)
Ru(1)–C(12)	1.867 (8)	Ru(5)–Ru(6)	2.835 (1)	C(21)–C(22)	1.524 (9)
Ru(1)–C(13)	2.091 (6)	Ru(5)–S(1)	2.454 (2)	C(22)–C(25)	1.519 (8)
Ru(2)–S(2)	2.419 (2)	Ru(5)–S(2)	2.366 (2)	C(41)–C(42)	1.541 (9)
Ru(2)–S(3)	2.371 (2)	Ru(5)–S(4)	2.475 (2)	C(42)–C(45)	1.518 (8)
Ru(2)–C(21)	2.129 (6)	Ru(5)–C(51)	2.166 (6)	C(51)–C(52)	1.534 (8)
Ru(2)–C(26)	1.855 (7)	Ru(5)–C(56)	1.894 (7)	C(52)–C(55)	1.517 (8)
Ru(2)–C(27)	1.838 (7)	Ru(5)–C(57)	1.867 (7)	C(61)–C(62)	1.533 (8)
Ru(3)–S(4)	2.462 (2)	Ru(6)–S(1)	2.438 (2)	C(62)–C(65)	1.535 (8)
Ru(3)–C(13)	1.979 (7)	Ru(6)–S(4)	2.374 (2)	O–C(AV)	1.149 (7)
Ru(3)–C(31)	1.858 (7)	Ru(6)–C(61)	2.163 (6)		

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

Table IV. Intramolecular Bond Angles for 2[a]

Ru(2)–Ru(1)–Ru(3)	142.19 (3)	Ru(5)–Ru(6)–S(1)	54.85 (4)
Ru(2)–Ru(1)–S(2)	53.90 (4)	Ru(5)–Ru(6)–S(4)	55.90 (4)
Ru(2)–Ru(1)–S(3)	52.67 (4)	S(1)–Ru(6)–S(4)	76.99 (5)
Ru(3)–Ru(1)–S(2)	93.02 (4)	Ru(4)–S(1)–Ru(5)	125.12 (6)
Ru(3)–Ru(1)–S(3)	112.00 (5)	Ru(4)–S(1)–Ru(6)	124.39 (6)
S(2)–Ru(1)–S(3)	82.80 (5)	Ru(5)–S(1)–Ru(6)	70.84 (5)
Ru(1)–Ru(2)–S(2)	54.44 (4)	Ru(1)–S(2)–Ru(2)	71.66 (5)
Ru(1)–Ru(2)–S(3)	54.93 (4)	Ru(1)–S(2)–Ru(5)	125.96 (6)
S(2)–Ru(2)–S(3)	84.62 (6)	Ru(2)–S(2)–Ru(5)	129.96 (7)
Ru(1)–Ru(3)–S(4)	97.14 (4)	Ru(1)–S(3)–Ru(2)	72.40 (5)
S(1)–Ru(4)–S(3)	91.68 (5)	Ru(1)–S(3)–Ru(4)	77.34 (5)
Ru(6)–Ru(5)–S(1)	54.32 (4)	Ru(2)–S(3)–Ru(4)	137.34 (7)
Ru(6)–Ru(5)–S(2)	129.57 (4)	Ru(3)–S(4)–Ru(5)	121.42 (6)
Ru(6)–Ru(5)–S(4)	52.56 (4)	Ru(3)–S(4)–Ru(6)	118.82 (6)
S(1)–Ru(5)–S(2)	91.44 (6)	Ru(5)–S(4)–Ru(6)	71.54 (5)
S(1)–Ru(5)–S(4)	74.83 (5)	Ru(1)–C(13)–Ru(3)	89.5 (3)
S(2)–Ru(5)–S(4)	86.07 (5)		

[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)
Ru(1)	0.27290 (6)	0.18162 (7)	0.63864 (5)	2.47 (6)
Ru(2)	0.20096 (6)	0.28037 (7)	0.75104 (5)	2.54 (6)
Ru(3)	0.37456 (6)	0.08634 (7)	0.82708 (5)	2.58 (6)
Ru(4)	0.13993 (6)	−0.00720 (7)	0.76159 (5)	2.52 (5)
Ru(5)	0.33201 (6)	−0.00804 (7)	0.62147 (5)	2.81 (6)
Ru(6)	0.23444 (6)	−0.16109 (7)	0.79259 (5)	2.92 (6)
S(1)	0.2269 (2)	−0.0865 (2)	0.6862 (2)	2.7 (2)
S(2)	0.2596 (2)	−0.0067 (2)	0.8324 (2)	2.6 (2)
S(3)	0.2872 (2)	0.2180 (2)	0.8385 (2)	2.7 (2)
S(4)	0.1632 (2)	0.1349 (2)	0.7054 (2)	2.4 (2)
S(5)	0.3663 (2)	0.1016 (2)	0.7038 (2)	2.7 (2)
O(16)	0.3541 (6)	0.3531 (7)	0.6817 (5)	4.7 (6)
O(17)	0.1737 (6)	0.2633 (7)	0.5260 (5)	5.2 (6)
O(26)	0.0778 (6)	0.3043 (7)	0.8513 (5)	5.9 (7)
O(27)	0.1151 (6)	0.4071 (7)	0.6567 (5)	5.2 (6)
O(36)	0.5218 (7)	0.1837 (8)	0.8578 (6)	7.5 (7)
O(37)	0.4762 (6)	−0.0782 (7)	0.8232 (6)	6.6 (7)
O(46)	0.0435 (6)	−0.1656 (7)	0.8053 (5)	5.2 (6)
O(47)	0.0515 (6)	0.1008 (7)	0.8638 (6)	6.3 (7)
O(56)	0.4568 (6)	−0.1338 (7)	0.6686 (6)	7.1 (7)
O(57)	0.2967 (7)	−0.1156 (7)	0.4938 (5)	6.6 (7)
O(66)	0.1912 (6)	−0.2535 (8)	0.9224 (6)	6.9 (7)
O(68)	0.3803 (6)	−0.2648 (7)	0.7970 (5)	5.7 (6)
C(16)	0.3095 (8)	0.293 (1)	0.6762 (6)	3.0 (8)
C(17)	0.2097 (7)	0.2328 (9)	0.5692 (7)	3.1 (8)
C(21)	0.2458 (7)	0.4108 (8)	0.7866 (6)	3.3 (7)
C(22)	0.2975 (8)	0.4059 (8)	0.8519 (7)	3.2 (8)
C(23)	0.3511 (8)	0.4876 (9)	0.8528 (7)	4.8 (8)
C(24)	0.2463 (8)	0.408 (1)	0.9144 (6)	4.2 (8)
C(25)	0.3456 (7)	0.3202 (9)	0.8507 (6)	3.3 (7)
C(26)	0.1255 (8)	0.2949 (9)	0.8143 (7)	3.1 (8)
C(27)	0.1461 (7)	0.355 (1)	0.6898 (7)	3.0 (7)
C(31)	0.3702 (8)	0.075 (1)	0.9371 (6)	4.0 (8)
C(32)	0.3160 (8)	0.0041 (9)	0.9630 (6)	3.1 (7)
C(33)	0.2963 (8)	0.031 (1)	1.0364 (7)	4.8 (9)
C(34)	0.3506 (8)	−0.090 (1)	0.9624 (7)	4.3 (8)
C(35)	0.2406 (7)	0.0077 (9)	0.9219 (6)	3.3 (7)
C(36)	0.4645 (9)	0.152 (1)	0.8416 (7)	4.5 (9)
C(37)	0.4365 (8)	−0.016 (1)	0.8246 (7)	3.7 (8)
C(41)	0.0394 (6)	−0.0097 (8)	0.6951 (6)	2.9 (7)
C(42)	0.0381 (7)	0.0613 (9)	0.6380 (7)	3.2 (8)
C(43)	0.0830 (8)	0.0292 (9)	0.5762 (7)	4.4 (8)
C(44)	−0.0460 (8)	0.077 (1)	0.6137 (7)	4.9 (9)
C(45)	0.0689 (6)	0.1500 (8)	0.6652 (6)	2.7 (7)
C(46)	0.0893 (8)	−0.112 (1)	0.7916 (7)	3.7 (8)
C(47)	0.0840 (8)	0.059 (1)	0.8246 (7)	3.5 (8)
C(51)	0.4235 (7)	0.053 (1)	0.5662 (6)	4.1 (8)
C(52)	0.4389 (7)	0.1513 (8)	0.5917 (6)	2.9 (7)
C(53)	0.3688 (7)	0.2103 (8)	0.5753 (6)	3.3 (7)
C(54)	0.5108 (7)	0.189 (1)	0.5560 (6)	4.2 (8)
C(55)	0.4538 (6)	0.1476 (8)	0.6675 (6)	3.0 (7)
C(56)	0.4047 (8)	−0.090 (1)	0.6500 (7)	4.2 (9)
C(57)	0.3074 (8)	−0.0759 (9)	0.5419 (8)	3.6 (8)
C(61)	0.1856 (7)	−0.2752 (8)	0.7371 (7)	3.9 (8)
C(62)	0.1981 (8)	−0.270 (1)	0.6607 (7)	3.8 (8)
C(63)	0.1438 (8)	−0.338 (1)	0.6252 (8)	5.5 (9)
C(64)	0.2791 (8)	−0.294 (1)	0.6441 (7)	4.6 (8)
C(65)	0.1754 (7)	−0.174 (1)	0.6365 (6)	3.5 (7)
C(66)	0.2093 (8)	−0.217 (1)	0.8753 (8)	4.3 (9)
C(68)	0.3229 (8)	−0.224 (1)	0.7947 (7)	3.9 (8)

only links between the two groups. The fourth sulfur atom, S(3), is also part of a triply briding thiolato group derived from a ring-opened dimethylthietane molecule, but it is coordinated to three metal atoms, Ru(1), Ru(2), and Ru(4), all in the group of four. Each of the ring-opened dimethylthietane ligands can be described as a thiaruthenacyclopentane ring formed by the insertion of a ruthenium atom into one of the C–S bonds of a thietane molecule; see Figure 1. Similar thiametallacycles were found in the complexes $Os_3(CO)_{11}(\mu\text{-}SCH_2CMe_2CH_2)$[9] and $Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2)$.[7b] Each metal atom has two linear terminal carbonyl ligands, but there is also one carbonyl ligand bridging the Ru(1)–Ru(3) bond, (ν(CO) 1779 cm^{-1}).

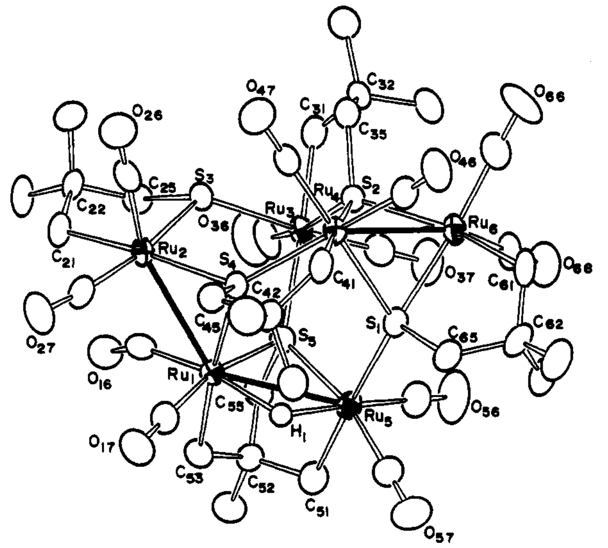


Figure 2. ORTEP diagram of $Ru_6(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2)(\mu_3\text{-}SCH_2CMe_2CH_2)_3(\mu_3\text{-}SCH_2C(Me)(CH_2)CH_2\text{-}(\mu\text{-}H)$ (3) showing 50% probability thermal ellipsoids.

Table VI. Intramolecular Distances for 3[a]

Ru(1)–Ru(2)	2.958 (2)	Ru(4)–S(1)	2.444 (3)	S(4)–C(45)	1.82 (1)
Ru(1)–Ru(5)	2.989 (2)	Ru(4)–S(2)	2.480 (3)	S(5)–C(55)	1.83 (1)
Ru(1)–S(4)	2.442 (3)	Ru(4)–S(4)	2.404 (3)	C(21)–C(22)	1.56 (2)
Ru(1)–S(5)	2.362 (3)	Ru(4)–C(41)	2.16 (1)	C(22)–C(25)	1.51 (2)
Ru(1)–C(53)	2.15 (1)	Ru(5)–S(1)	2.532 (3)	C(31)–C(32)	1.50 (2)
Ru(2)–S(3)	2.443 (3)	Ru(5)–S(5)	2.357 (3)	C(32)–C(35)	1.53 (2)
Ru(2)–S(4)	2.404 (3)	Ru(5)–C(51)	2.14 (1)	C(41)–C(42)	1.54 (2)
Ru(2)–C(21)	2.18 (1)	Ru(6)–S(1)	2.379 (3)	C(42)–C(45)	1.50 (2)
Ru(3)–S(2)	2.423 (3)	Ru(6)–S(2)	2.435 (3)	C(51)–C(52)	1.55 (2)
Ru(3)–S(3)	2.470 (3)	Ru(6)–C(61)	2.17 (1)	C(52)–C(55)	1.52 (2)
Ru(3)–S(5)	2.457 (3)	S(1)–C(65)	1.84 (1)	C(61)–C(62)	1.54 (2)
Ru(3)–C(31)	2.19 (1)	S(2)–C(35)	1.82 (1)	C(62)–C(65)	1.54 (2)
Ru(4)–Ru(6)	2.850 (2)	S(3)–C(25)	1.82 (1)	O–C(AVE)	1.14 (1)

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

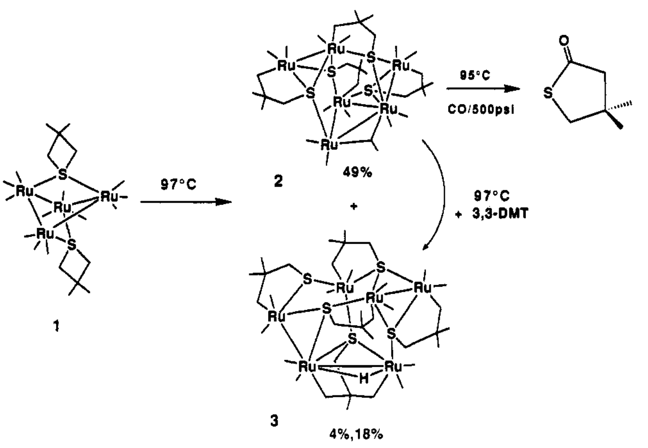
Table VII. Intramolecular Bond Angles for 3[a]

Ru(2)–Ru(1)–Ru(5)	133.92 (5)	Ru(1)–Ru(5)–S(5)	50.78 (8)
Ru(2)–Ru(1)–S(4)	51.79 (8)	S(1)–Ru(5)–S(5)	97.6 (1)
Ru(2)–Ru(1)–S(5)	97.35 (9)	Ru(4)–Ru(6)–S(1)	54.83 (8)
Ru(5)–Ru(1)–S(4)	94.24 (8)	Ru(4)–Ru(6)–S(2)	55.30 (8)
Ru(5)–Ru(1)–S(5)	50.64 (8)	S(1)–Ru(6)–S(2)	82.2 (1)
S(4)–Ru(1)–S(5)	95.6 (1)	Ru(4)–S(1)–Ru(5)	123.8 (1)
Ru(1)–Ru(2)–S(3)	95.12 (9)	Ru(4)–S(1)–Ru(6)	72.4 (1)
Ru(1)–Ru(2)–S(4)	52.96 (8)	Ru(5)–S(1)–Ru(6)	129.3 (1)
S(3)–Ru(2)–S(4)	95.3 (1)	Ru(3)–S(2)–Ru(4)	131.1 (1)
S(2)–Ru(3)–S(3)	85.9 (1)	Ru(3)–S(2)–Ru(6)	130.7 (1)
S(2)–Ru(3)–S(5)	93.7 (1)	Ru(4)–S(2)–Ru(6)	70.9 (1)
S(3)–Ru(3)–S(5)	89.9 (1)	Ru(2)–S(3)–Ru(3)	126.5 (1)
Ru(6)–Ru(4)–S(1)	52.73 (8)	Ru(1)–S(4)–Ru(2)	75.2 (1)
Ru(6)–Ru(4)–S(2)	53.82 (8)	Ru(1)–S(4)–Ru(4)	129.6 (1)
Ru(6)–Ru(4)–S(4)	133.28 (9)	Ru(2)–S(4)–Ru(4)	130.0 (1)
S(1)–Ru(4)–S(2)	80.0 (1)	Ru(1)–S(5)–Ru(3)	127.8 (1)
S(1)–Ru(4)–S(4)	90.9 (1)	Ru(1)–S(5)–Ru(5)	78.6 (1)
S(2)–Ru(4)–S(4)	96.5 (1)	Ru(3)–S(5)–Ru(5)	129.4 (1)
Ru(1)–Ru(5)–S(1)	96.47 (8)	Ru–C–O(AV)	176 (1)

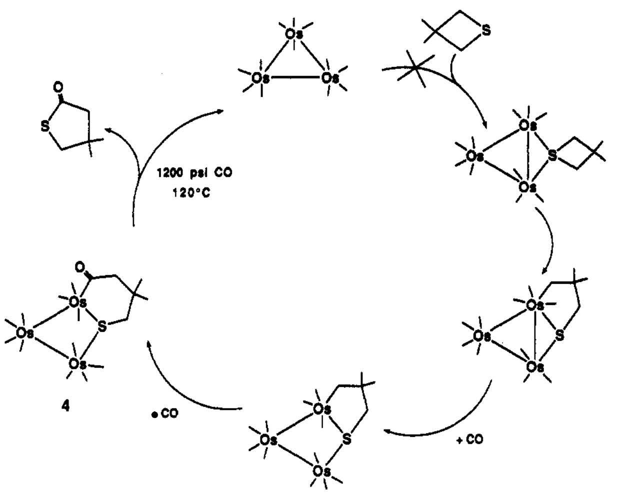
[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

The molecule has no symmetry; thus all eight methyl groups are inequivalent. Seven resonances, one with twice the intensity of the other six (an accidental degeneracy), were observed in the ^{1}H NMR spectrum in the region 1.24–1.47 ppm. The resonances of the eight methylene groups are complex. Each one apparently shows that usual *gem* coupling, but several resonances also exhibit long-range (four bond) coupling of 2–3 Hz. Due to numerous overlaps, it has not been possible for us to make all the assignments definitively.

Scheme I



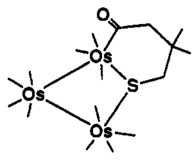
Scheme II



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. In this molecule, the six metal atoms are divided into three groups. One group, Ru(1)–Ru(2)–Ru(5), contains three metal atoms in the form of an open triangular cluster. There is a second group of two, Ru(4)–Ru(6), and the sixth metal atom, Ru(3), is not bonded directly to any other metal atom. As in 2, the cluster is held together by a network of bridging thiolato sulfur atoms derived from ring-opened dimethylthietane ligands. Four of these form simple thiaruthenacyclopentane rings by the insertion of a ruthenium atom into one of the C–S bonds of the thietane as found in 2. The thietane ring containing the sulfur S(5) was opened but also has undergone a CH activation on one of the methyl groups. The hydrogen atom was transferred to the metal atoms to become a bridging hydride ligand, H(1), across the Ru(1)–Ru(5) bond ($\delta = -12.34$ ppm). A similar thiolato ligand was found on the complex $Os_2(CO)_6[\mu\text{-}SCH_2C(Me)(CH_2)CH_2](\mu\text{-}H)$ (5) that was obtained in the dimethylthietane ring opening and fragmentation of the cluster of the complex $Os_3(CO)_{10}[\mu\text{-}\overline{SCH_2CME_2C}H_2]$.[9]

Interestingly, when treated with CO at 95 °C (500 psi), 2 was converted 4,4-dimethylthiobutyrolactone and $Ru_3(CO)_{12}$. The former was characterized by ^{1}H NMR spectroscopy (δ 2.41 (s, 2 H), 1.75 (s, 2 H), 0.67 (s, 6 H) and its mass spectrum (m/z 130). The results of these studies of the ruthenium complexes with thietane are shown in Scheme I.

In previous studies we have made the compound $Os_3(CO)_{11}(\mu\text{-}SCH_2CMe_2CH_2C{=}O)$[9b] (4) by a thietane ring-opening transformation in the compound $Os_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2C}H_2]$ and a subsequent insertion of CO into the osmium–carbon bond of an intermediate containing a thiaosmiacyclopentane ring system. Accordingly, we



4

tested complex 4 to see if it would also yield 4,4-dimethylthiobutyrolactone if carbonylated under forcing conditions. Indeed, when treated with CO at 120 °C (1200 psi), 4.4-dimethylthiobutyrolactone as the free molecule was obtained in 63% yield together with some $Os_2(CO)_6[\mu\text{-}SCH_2C(Me)(CH_2)CH_2](\mu\text{-}H)$ (5; 24%) and $Os_3(CO)_{12}$ (62%). Since it has been shown that $Ru_3(CO)_{12}$ will carbonylate thietanes catalytically to form thiobutyrolactones, we also tested both compound 5 and $Os_3(CO)_{12}$ for catalytic activity, but none was found under the conditions that we used.

Discussion

The formation of the hexaruthenium cluster complexes 2 and 3 with four and five ring opened thietane ligands from the thermal treatment of the tetraruthenium cluster 1 shows that ruthenium carbonyls are very effective in opening the thietane ligands to form thiametallacycles by insertion of a ruthenium atom into one of the carbon–sulfur bonds. However, the change in metal nuclearity indicates that cluster fragmentation and reaggregation processes are also occurring. Although the nuclearity of the clusters when the ring-opening insertion occurred was not established in this study, our previous studies of osmium clusters strongly suggest that complexes having two or more metal atoms are probably involved.

Our observation that complex 2 reacts with CO at moderate temperatures and pressures to yield dimethylthiobutyrolactone suggests that 2 or complexes such as 2 could be involved in the catalytic carbonylation of thietanes to thiolactones as observed by Alper.[10] Our previous studies of the thietane ring opening and carbonylation of $Os_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2C}H_2]$[9] combined the observation reported here that 4 also yields the cyclic thiolactone when treated with CO provide a set of elementary steps for a potential catalytic cycle based on a triosmium system; see Scheme II. All the steps have been confirmed except the one that might seem to be the simpliest of all, the substitution of CO with 3,3-dimethylthietane in $Os_3(CO)_{12}$ under CO at elevated pressures.

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, bond angles, and anisotropic thermal parameters for 2 and 3 (17 pages). Ordering information is given on any current masthead page.

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