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Ring opening of 1,3-dithietane-1,1-dioxide by a triosmium cluster[1]

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Abstract

The reaction of the cyclic sulfone, 1,3-dithietane-1,1-dioxide, **1** with $Os_3(CO)_{10}(NCMe)_2$, **2** at 25°C provided the new compound $Os_3(CO)_{10}(\mu\text{-}CH_2SCH_2SO_2)$, **3** in 73% yield. When solutions of **3** in heptane solvent were heated to reflux, they are converted to the compound $Os_2(CO)_6(\mu\text{-}CH_2SCH_2SO_2)$, **4** in 46% yield. Both products were characterized by IR, ^{1}H-NMR and single crystal X-ray diffraction analyses. Compound **3** contains a bridging $SCH_2SO_2CH_2$ ligand formed by an opening of the ring of the sulfone and one edge of the osmium cluster. Compound **4** was formed by the loss of an $Os(CO)_4$ group from **3**. The $SCH_2SO_2CH_2$ ligand in **4** is coordinated in a fashion similar to that in **3**. In both products, one of the oxygen atoms of the sulfone group is coordinated to one of the osmium atoms. In both cases, the S–O bond distance to the coordinated oxygen atom has increased in length and IR spectra of the S–O stretching absorptions show a substantial weakening of the S–O bond. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ring opening; Triosmium cluster; Cyclic sulfone

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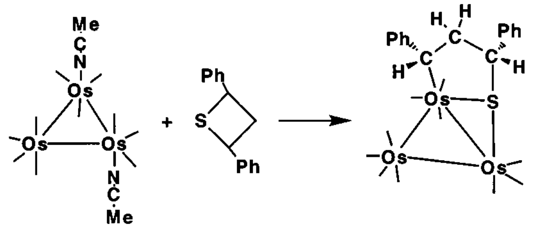
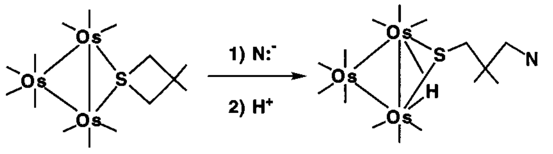
1. Introduction

In recent studies we have shown that thietanes are activated toward opening of their strained four-membered ring when they become coordinated to transition metal atoms [1–3]. In some cases ring opening occurs spontaneously at r.t., e.g.



Methyl substituents tend to retard the spontaneous ring opening process; and in some of these cases we have been able to observe controlled nucleophilic ring opening addition reactions at one of the carbon atoms that is bonded to the coordinated sulfur atom [2], e.g.



By using this mechanism, we have devised the first catalytic procedures for the preparation of a number of trithioether macrocycles [3], e.g.

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[1] Dedicated to Professor Brian Johnson on the occasion of his 60th birthday in recognition of his outstanding contributions to organometallic and inorganic chemistry.

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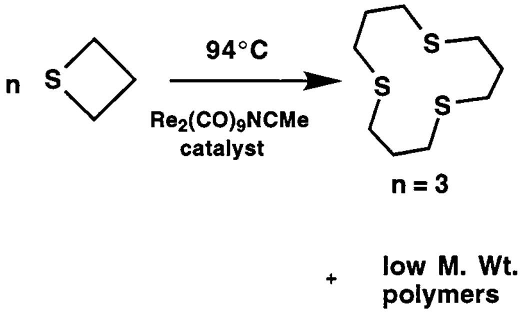
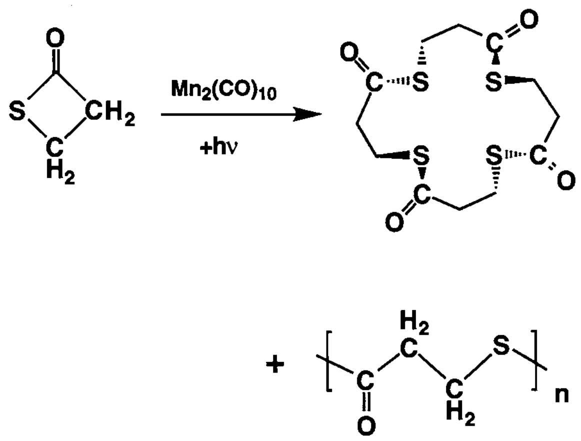
Table 1
Crystal data for compounds **1**, **3** and **4**

Compound	**1**	**3**	**4**
Formula	$S_2O_2C_2H_4$	$Os_3S_2O_{12}C_{12}H_4$	$Os_2S_2O_8C_8H_4$
Formula weight	124.17	974.88	672.63
Crystal system	orthorhombic	monoclinic	triclinic
Lattice parameters:			
a (Å)	8.0506(8)	10.260(3)	11.391(2)
b (Å)	12.6461(14)	14.483(3)	14.204(3)
c (Å)	9.1079(10)	13.752(4)	9.230(2)
α (°)	90.0	90.0	93.96(2)
β (°)	90.0	105.15(2)	107.07(2)
γ (°)	90.0	90.0	99.71(2)
V (Å^3)	927.26(15)	1973(1)	1396.0(6)
Space group	*Pbca* (No. 61)	$P2_1/n$ (No.14)	$P\bar{1}$ (No. 2)
Z	8	4	4
D_{calc} (g cm^{-3})	1.78	3.28	3.20
μ(Mo–K$_\alpha$) (cm^{-1})	9.96	195.36	185.04
Temperature (°C)	20	20	20
$2\theta_{max}$ (°)	52	47	47
Obs. Used ($I > 3\sigma(I)$)	564	2175	2796
Variables	68	263	362
Residuals: R, R_w^a	0.052, 0.066	0.031, 0.030	0.034, 0.036
Goodness-of-fit[a]	2.34	1.55	1.94
Abs. Cor.	Difabs	Difabs	Difabs
Transmission coefficient (min/max)	1.00/0.83	1.00/0.45	1.00/0.60
Max shift/error in final cycle	0.02	0.00	0.00
Largest peak in final diff. map (e Å^{-3})	0.83	1.36	1.38

[a] $R = \Sigma_{hkl}(||F_o| - |F_c||)/\Sigma_{hkl}|F_o|$; $R_w = \left[\Sigma_{hkl} w(|F_o| - |F_c|)^2/\Sigma_{hkl} wF_o^2\right]^{1/2}$, $w = 1/\sigma^2(F_o)$; GOF $= \left[\Sigma_{hkl} w(|F_o| - |F_c|)^2/(n_{data} - n_{vari})\right]^{1/2}$.



We have also shown that β-propiothiolactones can be opened catalytically in the presence of metal carbonyls radicals to yield macrocycles and polymers [4],



In a continuation of our studies of the reactions of thietanes with polynuclear metal carbonyls, we have investigated the reaction of 1,3-dithietane-1,1-dioxide, $\overline{\mathrm{CH_2SCH_2SO_2}}$, **1** with $Os_3(CO)_{10}(NCMe)_2$, **2**. This reaction proceeds with displacement of the two NCMe ligands and the addition and spontaneous opening of the dithietane ring of **1**. These results are reported here.

2. Experimental

2.1. General data

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. Reagent grade solvents were appropriately dried before use. IR spectra were recorded on a Nicolet 5DXBO FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker AM-400 NMR spectrometer operating at 400 MHz. 1,3-dithietane-1,1-dioxide, $\overline{\mathrm{CH_2SCH_2SO_2}}$, **1** [5] and $Os_3(CO)_{10}(NCMe)_2$, **2** [6] were prepared according to the published procedures. Product isolations were performed by TLC in air on Analtech 0.25 and 0.50 mm silica gel, 60 Å F_{254} plates. Elemental analysis were performed by Oneida Research Services, Whitesboro, NY.

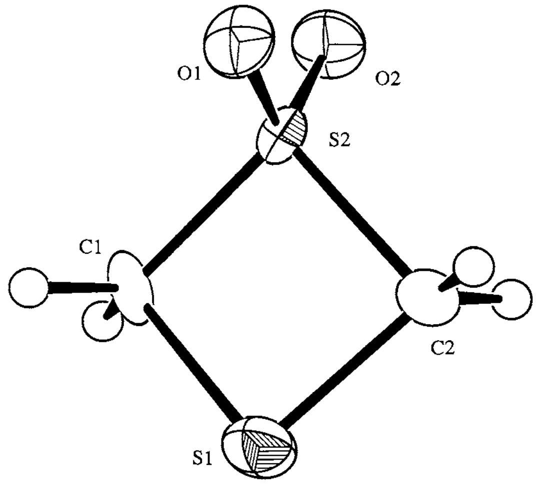


Fig. 1. An ORTEP diagram of the molecular structure of $CH_2SCH_2SO_2$ showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°) are: S(1)–C(1) = 1.83(1), S(1)–C(2) = 1.82(1), S(2)–C(1) = 1.77(1), S(2)–C(2) = 1.81(2), S(2)–O(1) = 1.439(3), S(2)–O(2) = 1.433(2); C(1)–S(1)–C(2) = 86.1(3), C(1)–S(2)–C(2) = 88.4(2), S(1)–C(1)–S(2) = 91.8(6), S(1)–C(2)–S(2) = 91.0(7), O(1)–S(2)–O(2) = 117.7(2).

2.2. Synthesis of $Os_3(CO)_{10}(\mu\text{-}CH_2SCH_2SO_2)$ 3

A 20.0-mg amount (0.0210 mmol) of **2** was dissolved 15 ml of CH_2Cl_2 in a 25 ml 3-neck round-bottom flask equipped with a stir bar, reflux condenser and a nitrogen inlet. Compound **1** (4.00 mg, 0.032mmol) was then added, and the solution was stirred at 25°C for 12 h. The solvent was removed in vacuo and the residue was separated by TLC using a CH_2Cl_2/hexane (1/1) mixture. This yielded a yellow band consisting of 15.3 mg (0.0157 mmol) of $Os_3(CO)_{10}(\mu\text{-}SCH_2SO_2CH_2)$, **3** (73%). Spectral data for **3**: IR (cm^{-1}, in CCl_4): 2104 (m), 2072 (vs), 2051 (s), 2021 (vs), 2006 (s), 1995 (m), 1992 (m), 1976 (m), 1375 (vw), 1272 (m), 1167 (vw), 1113 (vw), 1047 (vw), 1025 (w). ^{1}H-NMR (δ in $CDCl_3$): 4.13 (m, 2H), 3.34 (d, 1H, $^2J_{HH} = 13.9$ Hz), 3.10 (ddd, 1H, $^2J_{HH} = 13.9$ Hz, $^4J_{HH} = 3.0$ Hz, $^4J_{HH} = 1.0$ Hz). Anal. Calc. (found): C, 14.78 (14.86); H, 0.41 (0.86).

Table 2
Positional parameters and U_{eq} for **1**

Atom	x	y	z	U_{eq}
S(1)	0.3134(2)	0.1236(1)	0.2224(1)	3.33(3)
S(2)	0.2500(1)	0.1250(3)	0.5012(1)	1.77(3)
O(1)	0.4007(4)	0.1298(7)	0.5859(3)	3.12(8)
O(2)	0.0957(4)	0.1223(7)	0.5795(3)	3.11(8)
C(1)	0.2609(8)	0.0260(3)	0.364(1)	1.9(2)
C(2)	0.2540(8)	0.223(1)	0.357(2)	3.0(3)
H(1)	0.15(1)	−0.017(6)	0.332(8)	5.0000
H(2)	0.36(1)	−0.020(5)	0.365(7)	5.0000
H(3)	0.34(1)	0.272(6)	0.386(8)	5.0000
H(4)	0.13(1)	0.251(5)	0.354(8)	5.0000

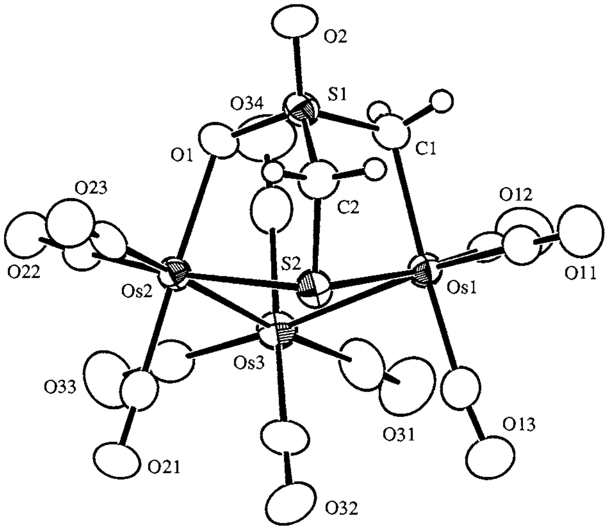


Fig. 2. An ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu\text{-}CH_2SCH_2SO_2)$, **3** showing 50% probability thermal ellipsoids.

2.3. Synthesis of $Os_2(CO)_6(\mu\text{-}SCH_2SO_2CH_2)$ 4

A 20.0-mg amount (0.0205 mmol) of **3** was dissolved in 15 ml heptane in a 25 ml 3-neck round-bottom flask equipped with a stir bar, reflux condenser and a nitrogen inlet. The solution was heated to reflux for 90 min. After this period, the volatiles were removed in vacuo and the residue was separated by TLC using a 1/2 CH_2Cl_2/hexane solvent mixture to yield 6.3 mg (0.0093 mmol) of yellow $Os_2(CO)_6(\mu\text{-}SCH_2SO_2CH_2)$, 4 (46%). Spectral data for **4**: IR (cm^{-1} in CCl_4): 2091 (s), 2055 (vs), 2007 (vs), 2004 (s), 1981 (s), 1368 (vw), 1275 (m), 1170 (w), 1116 (vw), 1025 (w). ^{1}H-NMR (δ in $CDCl_3$): 3.26 (dd, 1H, $^2J_{HH} = 13.3$ Hz, $^4J_{HH} = 3.4$ Hz), 3.11 (d, 1H, $^2J_{HH} = 13.3$ Hz), 2.19 (d, 1H, $^2J_{HH} = 13.8$ Hz), 1.99 (dd, 1H, $^2J_{HH} = 13.8$ Hz, $^4J_{HH} = 3.4$ Hz). Anal. Calc. (found): C, 14.29 (14.36); H, 0.60 (0.47).

2.4. Crystallographic analysis

Colorless crystals of **1** suitable for diffraction analysis were grown from solutions in acetone solvent by cooling to −14°C. Light-yellow crystals of **3** and yellow crystals **4** suitable for diffraction analysis were grown from solutions in 2/1 hexane/CH_2Cl_2 solvent mixtures by slow evaporation of solvent at 25°C. The crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements were performed on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo–K_α radiation. The unit cells of the crystals were determined and refined from

15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a SGI Indigo2 computer by using the TEXSAN motif structure solving program library obtained from Molecular Structure, The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures ([7]a) and anomalous dispersion corrections were applied to all non-hydrogen atoms ([7]b). Lorentz polarization (L_p) and absorption corrections were applied to the data for each analysis. Full-matrix least-squares refinements minimized the function: $\Sigma_{hkl}\, w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(F_o{}^2)/2F_o$ and $\sigma(F_o{}^2) = [\sigma(I_{raw})2 + (0.02I_{net})^2]^{1/2}/L_p$.

Compound **1** crystallized in the orthorhombic crystal system. The space group *Pbca* was identified uniquely on the basis of the patterns of systematic absences observed during the collection of the intensity data. The structure was solved by direct methods (MITHRIL). All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were refined on their positional parameters with fixed isotropic *U* values of 5.0 Å^2.

Compound **3** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established on the basis of the patterns of systematic absences observed in the data. Compound **4** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structures of both metal complexes were solved by a combination of direct methods (SIR92) and difference Fourier syntheses. Compound **4** crystallized with two complete independent molecules in the asymmetric crystal unit. For both of these analyses, all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms for both complexes were calculated by assuming idealized tetrahedral geometries at the carbon atoms with C–H distances of 0.95 Å. The scattering contributions of the hydrogen atoms were included in the structure factor calculations, but their positions were not refined.

3. Results and discussion

1,3-Dithietane-1,1-dioxide, **1** reacts with $Os_3(CO)_{10}(NCMe)_2$, **2** at 25°C to yield the new compound $Os_3(CO)_{10}(\mu\text{-}CH_2SCH_2SO_2)$, **3** in 73% yield. When solutions of **3** in heptane solvent are heated to reflux for 90 min, they are converted to the compound $Os_2(CO)_6(\mu\text{-}CH_2SCH_2SO_2)$, **4** in 46% yield. Both products were characterized by a combination of IR, ^{1}H-NMR and single crystal X-ray diffraction analyses. In addition, since the starting material **1** has not yet been characterized by a single crystal X-ray analysis, we have

Table 3
Positional parameters and U_{eq} for **3**

Atom	*x*	*y*	*z*	U_{eq}
Os(1)	0.62013(6)	0.21411(4)	1.01566(4)	2.66(1)
Os(2)	0.91937(6)	0.32936(4)	0.94658(4)	2.42(1)
Os(3)	0.91161(6)	0.17061(4)	1.07378(4)	2.99(1)
S(1)	0.6911(4)	0.4360(2)	1.0269(3)	2.71(8)
S(2)	0.6811(3)	0.2956(3)	0.8769(2)	2.73(8)
O(1)	0.8398(9)	0.4221(6)	1.0425(6)	3.2(2)
O(2)	0.657(1)	0.5282(7)	1.0486(7)	3.8(3)
O(11)	0.317(1)	0.2411(9)	0.9349(9)	5.8(4)
O(12)	0.610(1)	0.1291(8)	1.2178(8)	6.4(4)
O(13)	0.582(1)	0.0236(8)	0.9190(9)	5.7(4)
O(21)	1.017(1)	0.2029(7)	0.8054(9)	5.4(3)
O(22)	1.201(1)	0.3622(8)	1.0822(8)	4.5(3)
O(23)	0.918(1)	0.4911(8)	0.8002(7)	4.6(3)
O(31)	0.861(1)	0.0054(8)	1.1957(9)	6.6(4)
O(32)	0.859(1)	0.0611(8)	0.8773(9)	5.8(4)
O(33)	1.220(1)	0.1487(9)	1.127(1)	6.3(4)
O(34)	0.922(1)	0.3186(8)	1.2377(8)	5.4(3)
C(1)	0.627(1)	0.3508(9)	1.0872(9)	2.8(3)
C(2)	0.618(1)	0.408(1)	0.899(1)	3.3(3)
C(11)	0.429(2)	0.233(1)	0.963(1)	3.8(4)
C(12)	0.613(2)	0.161(1)	1.140(1)	3.8(4)
C(13)	0.604(2)	0.096(1)	0.955(1)	3.7(4)
C(21)	0.980(2)	0.250(1)	0.860(1)	3.5(4)
C(22)	1.095(2)	0.348(1)	1.029(1)	2.8(4)
C(23)	0.919(2)	0.432(1)	0.855(1)	3.6(4)
C(31)	0.876(2)	0.066(1)	1.152(1)	5.0(5)
C(32)	0.877(2)	0.104(1)	0.949(1)	3.6(4)
C(33)	1.103(2)	0.159(1)	1.103(1)	4.2(4)
C(34)	0.916(2)	0.262(1)	1.178(1)	3.7(4)

Table 4
Intramolecular distances for **3**

Atom	Atom	Distance	Atom	Atom	Distance
Os(1)	Os(3)	2.955(1)	S(1)	O(1)	1.50(1)
Os(1)	S(2)	2.459(3)	S(1)	O(2)	1.43(1)
Os(1)	C(1)	2.20(1)	S(1)	C(1)	1.71(1)
Os(1)	C(11)	1.92(2)	S(1)	C(2)	1.77(1)
Os(1)	C(12)	1.89(2)	S(2)	C(2)	1.81(1)
Os(1)	C(13)	1.89(2)	O(11)	C(11)	1.12(2)
Os(2)	Os(3)	2.9026(7)	O(12)	C(12)	1.17(2)
Os(2)	S(2)	2.432(4)	O(13)	C(13)	1.16(2)
Os(2)	O(1)	2.185(8)	O(21)	C(21)	1.14(1)
Os(2)	C(21)	1.88(1)	O(22)	C(22)	1.16(2)
Os(2)	C(22)	1.88(2)	O(23)	C(23)	1.13(2)
Os(2)	C(23)	1.95(2)	O(31)	C(31)	1.10(2)
Os(3)	C(31)	1.95(2)	O(32)	C(32)	1.14(2)
Os(3)	C(32)	1.92(2)	O(33)	C(33)	1.17(2)
Os(3)	C(33)	1.90(2)	O(34)	C(34)	1.15(2)
Os(3)	C(34)	1.94(2)			

Distances are in Å; estimated S.D. in the least significant figure are given in parentheses.

Table 5
Intramolecular bond angles for **3**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Os(3)	Os(1)	S(2)	82.40(8)	Os(2)	S(2)	C(2)	96.9(5)
Os(3)	Os(1)	C(1)	99.0(4)	Os(2)	O(1)	S(1)	121.6(5)
S(2)	Os(1)	C(1)	86.0(4)	Os(1)	C(1)	S(1)	113.9(7)
Os(3)	Os(2)	S(2)	83.97(9)	S(1)	C(2)	S(2)	106.9(7)
Os(3)	Os(2)	O(1)	92.8(2)	Os(1)	C(11)	O(11)	177(2)
S(2)	Os(2)	O(1)	82.3(2)	Os(1)	C(12)	O(12)	179(1)
Os(1)	Os(3)	Os(2)	81.56(2)	Os(1)	C(13)	O(13)	173(2)
O(1)	S(1)	O(2)	113.0(6)	Os(2)	C(21)	O(21)	179(1)
O(1)	S(1)	C(1)	109.8(6)	Os(2)	C(22)	O(22)	177(1)
O(1)	S(1)	C(2)	105.4(7)	Os(2)	C(23)	O(23)	179(1)
O(2)	S(1)	C(1)	115.3(7)	Os(3)	C(31)	O(31)	177(2)
O(2)	S(1)	C(2)	110.7(6)	Os(3)	C(32)	O(32)	177(1)
C(1)	S(1)	C(2)	101.7(7)	Os(3)	C(33)	O(33)	175(2)
Os(1)	S(2)	Os(2)	102.9(1)	Os(3)	C(34)	O(34)	177(1)
Os(1)	S(2)	C(2)	97.4(5)				

Angles are in °; estimated S.D. in the least significant figure are given in parentheses.

performed that analysis as well for comparative purposes.

An ORTEP drawing of the molecular structure of **1** as found in the solid state is shown in Fig. 1. Final atomic positional parameters are listed in Table 2. As expected, the molecule consists of a four-membered dithietane ring. There is slight puckering of the ring which results in a C–S–C/C–S–C dihedral angle of 163.0°. This value is slightly larger than those of the simple substituted thietane-1,1-dioxides: 3-chlorothietane-1,1-dioxide, **5**; 170.6° [8] and 3-hydroxythietane-1,1-dioxide, **6**, 172.3° [9], but is similar to that of the 3-acetoxythietane-1,1-dioxide, **7**, 162.1° [10]. 1,3-Dithietane-1,1,3,3-tetraoxide, **8** is planar, while 1,3-dithietane-1-oxide is puckered with a dihedral angle of 140.7° in the gas phase ([5]a). The C–S distances to the thioether sulfur S(1), S(1)–C(1) = 1.83(1) Å, S(1)–C(2) = 1.82(1) Å appear to be slightly longer than those to the sulfone sulfur S(2), S(2)–C(1) = 1.77(1) Å, S(2)–C(2) = 1.81 (2) Å, but the difference is not significant by the 3σ criterion. The C–S distances in **5**–**7** lie in the narrow range 1.782–1.791 Å, while those in **8** are 1.813(2) and 1.804(2) Å, respectively. The S–O distances: S(2)–O(1) = 1.439(3) Å, and S(2)–O(2) = 1.433(2) Å are not significantly different from those in **5**–**8**.

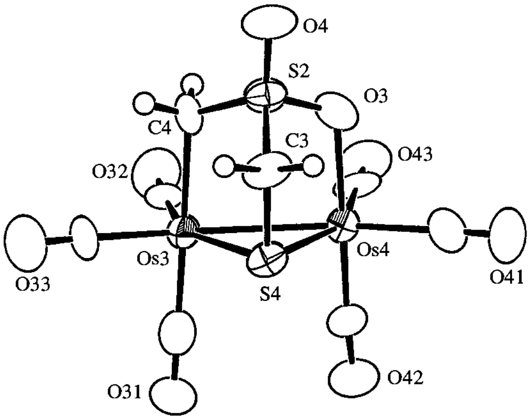
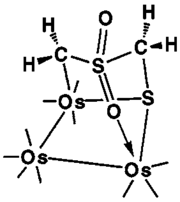


Fig. 3. An ORTEP diagram of the molecular structure of $\mathrm{Os_2(CO)_6(\mu\text{-}CH_2SCH_2SO_2)}$, **4** showing 50% probability thermal ellipsoids.

An ORTEP drawing of the molecular structure of **3** as found in the solid state is shown in Fig. 2. Final atomic positional parameters are listed in Table 3. Selected interatomic distances and angles are listed in Tables 4 and 5. This molecule consists of an open triosmium cluster with a thiolate sulfur bridging the two non-bonded osmium atoms: Os(1)···Os(2) = 3.826(1) Å, Os(1)–S(2) = 2.459(3) Å and Os(2)–S(2) = 2.432(4) Å. This compound is similar to the compound $\mathrm{Os_3(CO)_{11}(\mu\text{-}SCH_2CMe_2CH_2)}$, **9**, formed by the ring opening of the dimethylthietane ligand in the compound $\mathrm{Os_3(CO)_{10}(\mu\text{-}\overline{SCH_2CMe_2CH_2})}$ and the addition of CO ([2]e) except that **3** has one less CO ligand. In place of this CO ligand in **9**, one of the sulfone oxygen atoms is coordinated to the osmium atom Os(2), Os(2)–O(1) = 2.185(8) Å. The S–O bond distance to the coordinated oxygen atom has increased to 1.50(1) Å, while the uncoordinated S–O bond distance has remained essentially unchanged, S(1)–O(2) = 1.43(1) Å. The C–S distance C(1)–S(1) to the sulfone sulfur has shortened to 1.71(1) Å, while the others have not changed significantly, except for the C–S bond that was cleaved, S(2)–C(1).

Table 6
Positional parameters and U_{eq} for **4**

Atom	x	y	z	U_{eq}
Os(1)	0.97129(7)	0.33548(5)	0.72872(8)	2.73(2)
Os(2)	0.95530(7)	0.13642(5)	0.70654(8)	2.72(2)
Os(3)	0.49487(7)	0.33774(5)	0.22452(8)	2.77(2)
Os(4)	0.39456(7)	0.21008(5)	0.39385(8)	2.55(2)
S(1)	1.0246(4)	0.2445(3)	0.9416(5)	3.0(1)
S(2)	0.3812(4)	0.1196(3)	0.0684(5)	3.3(1)
S(3)	0.7538(4)	0.2111(3)	0.8317(5)	3.2(1)
S(4)	0.5883(4)	0.2097(3)	0.3351(5)	3.1(1)
O(1)	0.638(1)	0.1965(3)	0.868(1)	4.5(4)
O(2)	0.780(1)	0.307(1)	0.746(2)	6.5(5)
O(3)	0.310(1)	0.1105(3)	0.188(1)	3.8(3)
O(4)	0.331(1)	0.0425(3)	−0.057(1)	4.9(4)
O(11)	0.997(2)	0.545(1)	0.845(2)	7.0(5)
O(12)	0.878(1)	0.357(1)	0.391(2)	6.7(5)
O(13)	1.244(1)	0.380(1)	0.724(2)	6.3(5)
O(21)	0.971(1)	−0.0607(9)	0.814(2)	5.9(4)
O(22)	0.843(1)	0.094(1)	0.365(2)	5.5(4)
O(23)	1.212(1)	0.155(1)	0.666(1)	4.7(4)
O(31)	0.650(1)	0.484(1)	0.498(2)	5.2(4)
O(32)	0.278(1)	0.4434(9)	0.143(2)	5.7(4)
O(33)	0.668(2)	0.417(1)	0.048(2)	8.0(6)
O(41)	0.386(1)	0.0364(9)	0.576(2)	5.4(4)
O(42)	0.498(1)	0.3511(9)	0.680(1)	4.2(3)
O(43)	0.147(1)	0.271(1)	0.359(1)	4.9(4)
C(1)	0.885(2)	0.227(1)	0.999(2)	3.8(5)
C(2)	0.771(1)	0.1246(9)	0.735(2)	1.2(3)
C(3)	0.536(2)	0.116(1)	0.175(2)	3.3(5)
C(4)	0.390(1)	0.233(1)	0.028(2)	2.6(4)
C(11)	0.985(2)	0.469(1)	0.803(2)	4.0(5)
C(12)	0.911(2)	0.349(1)	0.521(3)	4.5(6)
C(13)	1.143(2)	0.363(1)	0.724(2)	4.3(5)
C(21)	0.959(2)	0.011(1)	0.771(2)	4.0(5)
C(22)	0.884(2)	0.109(1)	0.499(2)	4.3(5)
C(23)	1.115(2)	0.149(1)	0.682(2)	3.5(5)
C(31)	0.587(2)	0.429(1)	0.394(2)	3.5(5)
C(32)	0.362(2)	0.406(1)	0.173(2)	3.3(4)
C(33)	0.601(2)	0.388(1)	0.112(2)	4.9(6)
C(41)	0.385(2)	0.100(1)	0.508(2)	3.6(5)
C(42)	0.464(1)	0.298(1)	0.568(2)	2.6(4)
C(43)	0.241(2)	0.246(1)	0.371(2)	3.1(4)
H(1)	0.8816	0.1713	1.0519	4.1630
H(2)	0.8868	0.2810	1.0674	4.1630
H(3)	0.7111	0.1159	0.6408	3.1087
H(4)	0.7581	0.0705	0.7898	3.1087
H(5)	0.5357	0.0541	0.2102	4.1488
H(6)	0.5868	0.1236	0.1108	4.1488
H(7)	0.3076	0.2460	−0.0036	3.0017
H(8)	0.4287	0.2419	−0.0466	3.0017



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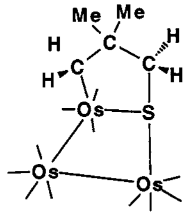
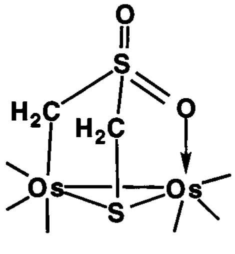


9

All four hydrogen atoms in **3** are inequivalent. The ^{1}H-NMR spectrum of the osmium bound methylene group shows two doublets at 3.34 and 3.10 ppm with *gem*-coupling of 13.9 Hz. Interestingly, the resonance at 3.10 ppm also shows long range coupling through the SO_2 group to both protons on the second methylene group, $^4J_{HH} = 3.0$ Hz and $^4J_{HH} = 1.0$ Hz. The two protons of the second methylene group are nearly isochronous and appear as a complex second order multiplet at 4.13 ppm.

Compound **4** crystallizes with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar and an ORTEP drawing of one of them is shown in Fig. 3. Final atomic positional parameters are listed in Table 6. Selected interatomic distances and angles are listed in Tables 7 and 8. Compound **4** is similar to the compound $Os_2(CO)_6(\mu\text{-}\overline{S(CH_2)_3C}Me)$ **10**, that was formed from $Os_3(CO)_{10}(\mu\text{-}\overline{SCH_2CMe_2CH_2})$ by heating in the absence of CO ([2]e).



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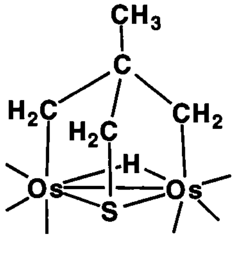

10

There are only two osmium atoms in **10** with an osmium–osmium bond distance Os(1)–Os(2) = 2.7918(9) Å [Os(3)–Os(4) = 2.7886(9) Å]. This distance is significantly shorter than the hydride bridged osmium–osmium bond in **10**, 2.9576(9) Å. Bridging hydride ligands are well-known to produce elongation of metal–metal bonds [11]. The sulfone ligand is very similar to that in **3**. The thiolate sulfur atom bridges the two osmium atoms: Os(1)–S(1) = 2.411(4) Å and Os(2)–S(1) = 2.411 (5) Å [Os(3)–S(4) = 2.399(4) Å and Os(4)–S(4) = 2.422(4) Å], and one of the sulfone oxygen atoms is coordinated to one of the osmium atoms, Os(1)–O(2) = 2.21(1) Å [Os(4)–O(3) = 2.15(1) Å]. As in **3**, the coordinated S–O bond is significantly longer than the uncoordinated one, S(3)–O(2) = 1.65(1) Å [S(2)–O(3) = 1.55(1) Å] versus S(3)–O(1) = 1.44(1) Å [S(2)–O(4) = 1.45(1) Å]. The ^{1}H-NMR spectrum of **4** exhibits two AB quartets as expected on the basis of the solid state structure, $\delta = 3.26$ (dd, $^2J_{HH} = 13.3$ Hz), 3.11 (d, $^2J_{HH} = 13.3$ Hz), 2.19 (d, $^2J_{HH} = 13.8$ Hz). 1.99 (dd, 1H, $^2J_{HH} = 13$ 8 Hz). The first and last of these resonances shows a long range coupling between the methylene groups, $^4J_{HH} = 3.4$ Hz, similar to that found in **3**.

IR spectra of **1**, **3** and **4** were recorded in the S–O stretching region to determine if the coordination and

Table 7
Intramolecular bond distances for **4**

Atom	Atom	Distance	Atom	Atom	Distance
Os(1)	Os(2)	2.7918(9)	Os(3)	C(33)	1.89(2)
Os(1)	S(1)	2.411(4)	Os(4)	S(4)	2.422(4)
Os(1)	O(2)	2.21(1)	Os(4)	O(3)	2.15(1)
Os(1)	C(11)	1.93(2)	Os(4)	C(41)	1.95(2)
Os(1)	C(12)	1.87(2)	Os(4)	C(42)	1.84(2)
Os(1)	C(13)	1.94(2)	Os(4)	C(43)	1.86(2)
Os(2)	S(1)	2.411(5)	S(1)	C(1)	1.80(2)
Os(2)	C(2)	2.17(1)	S(2)	O(3)	1.55(1)
Os(2)	C(21)	1.93(2)	S(2)	O(4)	1.45(1)
Os(2)	C(22)	1.83(2)	S(2)	C(3)	1.76(2)
Os(2)	C(23)	1.88(2)	S(2)	C(4)	1.67(1)
Os(3)	Os(4)	2.7886(9)	S(3)	O(1)	1.44(1)
Os(3)	S(4)	2.399(4)	S(3)	O(2)	1.65(1)
Os(3)	C(4)	2.17(2)	S(3)	C(1)	1.78(2)
Os(3)	C(31)	1.88(2)	S(3)	C(2)	1.55(1)
Os(3)	C(32)	1.90(2)	S(4)	C(3)	1.81(2)
			O	C(av)	1.14(2)

Distances are in Å; estimated S.D. in the least significant figure are given in parentheses.

observed lengthening of the coordinated S–O group produced any effect on the bond strength. The S–O stretching absorptions lie in the region 1000–1400 cm^{-1}, so our spectra were recorded in CCl_4 which is relatively transparent through this region. Compound **1** shows three absorptions at 1357(s), 1200(s) and 1127(m) cm^{-1}. These compare favorably with the absorptions of 1,3-dithietane-1,1,3,3-tetraoxide, **11** which were observed at 1340, 1200 and 1090 cm^{-1}. The first and last of these three have been assigned to asymmetric and symmetric S=O stretching vibrations, respectively [12]. Accordingly, we assign the absorption 1357(s) and 1127(m) cm^{-1} in **1** to the asymmetric and symmetric S=O stretching vibrations, respectively. The spectra of **3** and **4** show several absorptions in this region: at 1375 (vw), 1272 (m), 1167 (vw), 1113 (vw), 1047 (vw), 1025 (w) cm^{-1} for **3**, and at 1368 (vw), 1275 (m), 1170 (vw), 1116 (vw), 1025 (w) cm^{-1} for **4**. The stronger ones, 1272 and 1025 cm^{-1} for **3** and 1275 and 1025 cm^{-1} for **4**, are assigned to the asymmetric and symmetric S=O stretching vibrations, respectively. In both cases, both absorptions have been shifted to lower frequency by 80–100 cm^{-1} relative to those in **1**. We conclude that the coordination of the S=O group does produce a substantial reduction in both S=O stretching vibrations. A reduction in the S=O stretching absorptions was also observed for the sulfone Et_2SO_2 when it was converted into a bridging ligand in the complex anion $[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$ [13].

In summary, we have found that the reaction of **1** with **2** proceeds with displacement of the two NCMe ligands in **2** and the addition of one equivalent of **1** to the cluster with a spontaneous opening of the ring by cleavage of one of the thioether C–S bonds, see Scheme 1. One of the osmium–osmium bonds of the cluster was also cleaved in the formation of the product **3**. When **3** was heated, an $Os(CO)_4$ group was eliminated to form **4**. The fate of the eliminated $Os(CO)_4$ group was not determined. One of the sulfone oxygen atoms was coordinated to one of the osmium atoms in both complexes and this resulted in a substantial weakening of the associated S–O bond.

Acknowledgements

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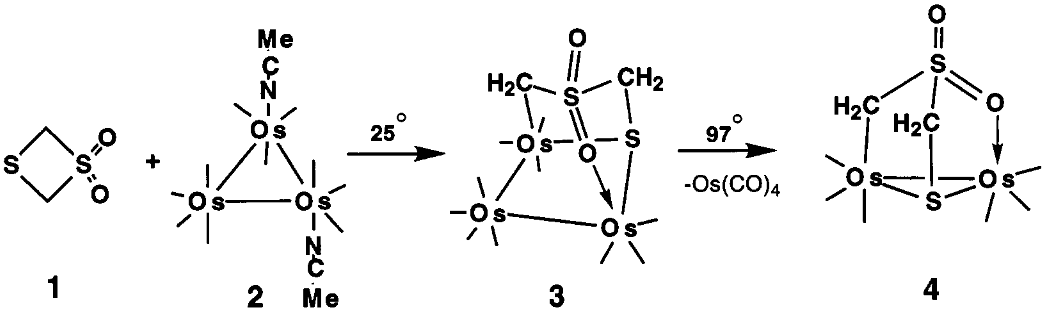
Table 8
Intramolecular bond angles for **4**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Os(2)	Os(1)	S(1)	54.6(1)	O(3)	S(2)	C(4)	106.4(7)
Os(2)	Os(1)	O(2)	86.6(4)	O(4)	S(2)	C(3)	111.2(7)
S(1)	Os(1)	O(2)	85.9(4)	O(4)	S(2)	C(4)	118.0(8)
Os(1)	Os(2)	S(1)	54.6(1)	C(3)	S(2)	C(4)	103.8(8)
Os(1)	Os(2)	C(2)	87.5(3)	O(1)	S(3)	O(2)	115.0(7)
S(1)	Os(2)	C(2)	84.6(4)	O(1)	S(3)	C(1)	111.5(8)
Os(4)	Os(3)	S(4)	55.1(1)	O(1)	S(3)	C(2)	114.6(8)
Os(4)	Os(3)	C(4)	85.8(4)	O(2)	S(3)	C(1)	104.9(9)
S(4)	Os(3)	C(4)	86.8(4)	O(2)	S(3)	C(2)	107.0(7)
Os(3)	Os(4)	S(4)	54.3(1)	C(1)	S(3)	C(2)	102.8(7)
Os(3)	Os(4)	O(3)	88.6(3)	Os(3)	S(4)	Os(4)	70.7(1)
S(4)	Os(4)	O(3)	85.0(3)	Os(3)	S(4)	C(3)	101.9(5)
Os(1)	S(1)	Os(2)	70.8(1)	Os(4)	S(4)	C(3)	100.6(6)
Os(1)	S(1)	C(1)	103.1(5)	S(1)	C(1)	S(3)	107.9(9)
Os(2)	S(1)	C(1)	100.9(6)	S(2)	C(3)	S(4)	108.5(7)
O(3)	S(2)	O(4)	112.7(8)	Os(3)	C(4)	S(2)	112.8(8)
O(3)	S(2)	C(3)	103.3(7)	Os	C	O(av)	177(2)

Angles are in °; estimated S.D. in the least significant figure are given in parentheses.



Scheme 1.

DE-FG05-95ER14548. Tables of positional parameters, bond distances and angles, anisotropic thermal parameters for the structural analysis are available from the authors (RDA).

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