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Formation of Butenethiolate by the Ring Opening of Tetrahydrothiophene by a Triosmium Cluster Complex

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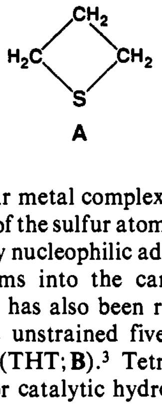
Abstract: The complex $Os_3(CO)_{10}(\overline{SCH_2CH_2CH_2CH_2})_2$ (**1**) was prepared by the reaction of $Os_3(CO)_{10}(NCMe)_2$ with tetrahydrothiophene (THT) at 25 °C. When heated to 97 °C, **1** was transformed into the complex $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}(\overline{SCH_2CH_2CH_2CH})](\mu\text{-}H)$ (**2**) by loss of one THT ligand and the activation of a C–H bond on one of the methylene groups bonded to the sulfur atom. At 125 °C, **2** was decarbonylated and transformed into the new compound $Os_3(CO)_9[\mu\text{-}\eta^3\text{-}S(CH_2)_2CH{=}CH_2](\mu\text{-}H)$ (**3**) by a ring-opening cleavage of one of the C–S bonds. Compound **3** contains a 3-butenethiolate ligand in which the sulfur atom bridges one of the metal–metal bonds and the double bond is π-coordinated to one of the sulfur-bridged metal atoms. An investigation of the transformation of $Os_3(CO)_{10}[\mu\text{-}(\overline{SCH_2CD_2CD_2CH})](\mu\text{-}H)$ (**2**-d_4) into $Os_3(CO)_9[\mu\text{-}\eta^3\text{-}SCH_2CD_2CD{=}CH_2](\mu\text{-}D)$ (**3**-d_4) at 125 °C showed that the hydride ligand was returned to the carbon atom from which it was initially cleaved and deuterium was shifted to the metal atoms. When heated to 205 °C, compound **3** released butene. Complexes **1**–**3** were characterized by single-crystal X-ray diffraction analysis. Crystallographic data: for **1**, space group $P\bar{1}$, $a = 12.412(4)$ Å, $b = 12.658(2)$ Å, $c = 9.355(2)$ Å, $\alpha = 108.86(2)°$, $\beta = 112.04(3)°$, $\gamma = 96.18(2)°$, $Z = 2$, 2681 reflections, $R = 0.029$; for **2**, space group $P2_1/a$, $a = 12.975(2)$ Å, $b = 21.679(8)$ Å, $c = 21.865(4)$ Å, $\beta = 100.87(1)°$, $Z = 12$, 4129 reflections, $R = 0.047$; for **3**, space group *Pbca*, $a = 16.556(4)$ Å, $b = 18.452(3)$ Å, $c = 12.490(3)$ Å, $Z = 8$, 1693 reflections, $R = 0.048$.

Introduction

In recent studies we have been investigating ring-opening transformations of the strained-ring heterocycles thietanes (A) by polynuclear metal complexes. We have found that bridging coordination of the sulfur atom promotes cleavage of the carbon–sulfur bond by nucleophilic addition,[1] and spontaneous insertion of metal atoms into the carbon–sulfur bond has also been observed.[2] It has also been reported that certain nucleophiles will open the unstrained five-membered heterocycle tetrahydrothiophene (THT; **B**).[3] Tetrahydrothiophene has been studied as a model for catalytic hydrodesulfurization processes.[4,5]



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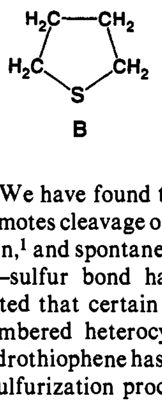

B

We have now discovered a facile ring-opening transformation of THT by a triosmium cluster complex. We have observed both CH activation and carbon-sulfur bond cleavage and have isolated and structurally characterized the first example of a butenethiolate ligand from the ring opening of THT. The results of this study are reported here.

Experimental Section

General Data. Reagent grade solvents were dried by using sodium-benzophenone followed by distillation and were either used immediately or stored over 4-Å molecular sieves. Tetrahydrothiophene (THT) and tetramethylene sulfoxide (96%) were used as purchased from Aldrich. The compounds $Os_3(CO)_{11}NCMe$,[6] $Os_3(CO)_{10}(NCMe)_2$,[7] 2-acetoxytetrahydrothiophene,[8] 3-dihydrothiophene,[9] and tetrahydrothiophene-*3,3,4,4-d*$_4$[10] 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 obtained on Bruker AM-300 and AM-500 spectrometers operating at 300 and 500 MHz, respectively. Chromatographic separations were performed in air on Analtech silica gel (0.25 mm) F_{254} uniplates. Silica gel (70–230 mesh, 60 Å) was purchased from Aldrich. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Synthesis of $Os_3(CO)_{10}(\overline{SCH_2CH_2CH_2CH_2})_2$. $Os_3(CO)_{10}(NCCH_3)_2$ (55.9 mg, 0.060 mmol) was added to a solution of 30 μL (0.34 mmol) of THT in 1 mL of CH_2Cl_2 at 25 °C. After the solution was stirred for 3 h, the solvent was removed *in vacuo* and the residue was redissolved in 5 mL of hexane. This solution was placed in the freezer. After 12 h, an orange crystalline product, $Os_3(CO)_{10}[\overline{SCH_2CH_2CH_2CH_2}]_2$ (**1**), had precipitated (50.0 mg, 86%). The solvent was decanted, and the product was washed with cold hexane and dried. IR δ(CO) (cm^{-1}) in hexane for **1**: 2094 (w), 2033 (vs), 2018 (s), 2002 (w), 1996 (m), 1986 (m), 1966 (m). ^1H NMR (δ; in $CDCl_3$) for **1**: 3.18 (s, br, 8 H), 2.08 (s, br, 8 H). Anal. Calcd (found) for **1**: C, 20.80 (20.95); H, 1.54 (1.40).

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Thermolysis of 1. A 21.0-mg amount of **1** (0.020 mmol) in 66 mL of cyclohexane was heated to reflux for 1 h. The solvent was removed *in vacuo*, and the residue was separated by TLC using a hexane/CH_2Cl_2 4/1 solvent mixture. This yielded the following compounds in order of elution: bright yellow $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}(\overline{\mathrm{SCH_2CH_2CH_2CH}})](\mu\text{-H})$ (**2**) (5.0 mg, 24%) and $Os_3(CO)_{11}(\overline{\mathrm{SCH_2CH_2CH_2CH_2}})$ (3.1 mg, 14%). A small amount (5 mg) of $Os_3(CO)_{12}$ was also obtained. IR $\nu(CO)$ (cm^{-1}) for **2**: in hexane, 2104 (m), 2063 (vs), 2050 (s), 2024 (s), 2005 (s), 1991 (m), 1982 (w), 1973 (w); in CH_2Cl_2, 2103 (m), 2062 (vs), 2047 (s), 2019 (s), 2002 (s), 1988 (m), 1966 (w). ^1H NMR (δ; in C_6D_6) for **2**: 3.01 (dt, 1 H, J_{H-H} = 6.7 Hz, J_{H-H} = 2.2 Hz), 1.95 (dt, 1 H, J_{H-H} = 11.7 Hz, J_{H-H} = 6.3 Hz), 1.88 (dt, 1 H, J_{H-H} = 11.7 Hz, J_{H-H} = 6.3 Hz), 1.80 (m, 1 H), 1.72 (m, 1 H), 1.46 (m, 1 H), 0.91 (m, 1 H), −16.57 (m, 1 H, J_{H-H} = 2.2 Hz). ^1H NMR (δ; in $CDCl_3$) for **2**: 3.24 (dt, 1 H, J_{H-H} = 6.7 Hz, J_{H-H} = 2.2 Hz), 2.90 (dt, 1 H, J_{H-H} = 11.7 Hz, J_{H-H} = 6.3 Hz), 2.71 (dt, 1 H, J_{H-H} = 11.7 Hz, J_{H-H} = 6.3 Hz), 2.42 (m, 1 H), 2.22 (m, 2 H), 1.80 (m, 1 H), −16.57 (m, 1 H, J_{H-H} = 2.2 Hz). Anal. Calcd (found) for **2**: C, 17.91 (18.06); H, 0.86 (0.95).

Thermolysis of 2. A solution of **2** (12.0 mg, 0.013 mmol) in 20 mL of octane was heated to 125 °C for 1 h. The solvent was removed *in vacuo*, and the residue was separated by TLC. Elution with a 4/1 (v/v) hexane/CH_2Cl_2 solvent mixture yielded yellow $Os_3(CO)_9[\mu\text{-}\eta^3\text{-S}(CH_2)_2\text{-}CH{=}CH_2](\mu\text{-H})$ (**3**) (7.3 mg, 61%) and a small amount (5 mg) of $Os_3(CO)_{12}$. IR $\nu(CO)$ (cm^{-1}) in hexane for **3**: 2103 (m), 2060 (s), 2024 (vs), 2017 (s), 1991 (w), 1982 (m), 1966 (m). ^1H NMR (δ; in $CDCl_3$) for **3**: 4.28 (dd, 1 H, J_{H-H} = 12.2 Hz, J_{H-H} = 8.7 Hz, J_{H-H} = 2.1 Hz), 3.64 (d, 1 H, J_{H-H} = 8.7 Hz), 2.56 (d, 1 H, J_{H-H} = 12.2 Hz), 2.26 (d, 1 H, J_{H-H} = 9.3 Hz), 1.60–1.70 (m, 3 H), −17.28 (m, 1 H). Anal. Calcd (found) for **3**: C, 17.14 (17.06); H, 0.88 (0.83).

Reaction of $Os_3(CO)_{10}(\mu\text{-H})_2$ with 2,3-Dihydrothiophene.[11] A 300-μL amount of 2,3-dihydrothiophene (3.5 mmol) was added by syringe to a solution containing 150 mg of $Os_3(CO)_{10}(\mu\text{-H})_2$ (0.170 mmol) in 30 mL of hexane at 25 °C. The solution was stirred for 48 h, during which time the color gradually changed from purple to brown. A yellow-brown precipitate (approximately 20 mg) also formed that was shown to be predominantly $Os_3(CO)_{12}$ by IR analysis. The mother liquor was separated from the precipitate by a cannula and concentrated *in vacuo*. TLC of the residue using a pure hexane solvent separated unreacted $Os_3(CO)_{10}(\mu\text{-H})_2$ (10 mg) from yellow **2** (38.1 mg, 28% based on the amount of $Os_3(CO)_{10}(\mu\text{-H})_2$ consumed). The compound **2** produced in this way was spectroscopically identical to that obtained by the thermal transformation of **1**.

Preparation of 1-d_8. An 81-mg amount of $Os_3(CO)_{10}(NCMe)_2$ (0.087 mmol) was added to a solution containing 40 μL (0.434 mmol) of tetrahydrothiophene-*3,3,4,4*-d_4 in 1 mL of CH_2Cl_2 at 25 °C. After the solution was stirred for 3 h, the solvent was removed *in vacuo*. The residue was dissolved in hexane, and the solution was cooled to 0 °C. After 12 h, an orange crystalline product, $Os_3(CO)_{10}[\overline{\mathrm{SCH_2CD_2CD_2CH_2}}]_2$ (**1**-d_8) (69 mg, 85%), had precipitated. The product was washed with cold heptane (3 × 1 mL) and dried *in vacuo*. IR $\nu(CO)$ (cm^{-1}) in hexane for **1**-d_8: 2094 (w), 2033 (vs), 2018 (s), 2002 (w), 1996 (m), 1986 (m), 1966 (m). ^1H NMR (δ; in $CDCl_3$) for **1**-d_8: 3.16 (s, br, 8 H).

Synthesis of 2-d_4. A 32.7-mg amount of **1**-d_8 (0.032 mmol) in 40 mL of cyclohexane was heated to reflux for 1 h. The solvent was removed *in vacuo*, and the residue was chromatographed by TLC using a hexane/CH_2Cl_2 9/1 solvent mixture. The following compounds were separated in order of elution: bright yellow $Os_3(CO)_{10}[\mu\text{-}\overline{\mathrm{SCH_2CD_2CD_2CH}}](\mu\text{-H})$ (**2**-d_4) (6.6 mg, 20%) and $Os_3(CO)_{11}[\overline{\mathrm{SCH_2CD_2CD_2CH_2}}]$ (11 mg, 34%). IR $\nu(CO)$ (cm^{-1}) in hexane for **2**-d_4: 2104 (m), 2063 (vs), 2050 (s), 2024 (s), 2005 (s), 1991 (m), 1982 (w), 1973 (w). ^1H NMR (δ; in $CDCl_3$) for **2**-d_4: 3.25 (d, 1 H, J_{H-H} = 2.2 Hz), 2.88 (d, 1 H, J_{H-H} = 11.7 Hz), 2.70 (d, 1 H, J_{H-H} = 11.7 Hz), −16.47 (d, 1 H, J_{H-H} = 2.2 Hz).

Synthesis of 3-d_4. A 3.2-mg amount of **2**-d_4 (0.003 mmol) in 35 mL of octane was heated to reflux until its CO absorptions were no longer observed in the IR spectrum of the solution (approximately 40 min). The solvent was removed *in vacuo*, and the residue was separated by TLC to yield yellow **3**-d_4 (2.0 mg, 62%). IR $\nu(CO)$ (cm^{-1}) in hexane for **3**-d_4: 2103 (m), 2060 (s), 2024 (vs), 2017 (s), 1991 (w), 1982 (m), 1966 (m). ^1H NMR (δ; in $CDCl_3$) for **3**-d_4: 4.28 (s, 0.10–0.15 H), 3.64 (s, 0.85–0.90 *H*), 2.56 (s, 0.85–0.90 H), 1.69 (d, 1 H, J_{H-H} = 13.9 Hz), 1.60 (d, 1 H, J_{H-H} = 13.9 Hz), −17.28 (s, 0.10–0.15 H).

Table I. Crystallographic Data for Compounds **1–3**

	1	**2**	**3**
empirical formula	$Os_3S_2O_{10}C_{18}H_{16}$	$Os_3SO_{10}C_{14}H_8$	$Os_3SO_9C_{13}H_8$
fw	1027.04	938.87	910.86
crystal system	triclinic	monoclinic	orthorhombic
lattice params			
a (Å)	12.412(4)	12.975(2)	16.556(4)
b (Å)	12.658(2)	21.679(8)	18.452(3)
c (Å)	9.355(2)	21.865(4)	12.490(3)
α (deg)	108.86(2)	90.0	90.0
β (deg)	112.04(3)	100.87(1)	90.0
γ (deg)	96.18(2)	90.0	90.0
V ($Å^3$)	1245(1)	6040(5)	3815(3)
space group (No.)	$P\bar{1}$ (2)	$P2_1/a$ (14)	*Pbca* (61)
Z value	2	12	8
D_{calc} (g/cm^3)	2.74	3.10	3.17
μ(Mo Kα) (cm^{-1})	155.0	190.5	201.0
temp (°C)	20	20	20
$2\theta_{max}$ (deg)	44.0	40.0	43.0
no. of observns ($I > 3\sigma(I)$)	2681	4129	1693
no. of variables	298	557	170
residuals: *R*, R_w	0.029, 0.035	0.047, 0.047	0.048, 0.052
goodness of fit indicator	1.30	2.05	2.31
max shift in final cycle	0.07	0.03	0.07
largest peak in final diff map ($e/Å^3$)	1.30	2.04	3.24
abs corr	empirical	empirical	empirical

Thermolysis of 3. A 2.0-mg amount of **3** was placed into a 3-in. glass capillary. The capillary was placed under vacuum for 30 min and then sealed by flame. The capillary was then placed into a melting point apparatus at 205 °C for 3.25 h. The gas formed from this reaction was shown by mass spectroscopy to be butene (M^+ = 56 amu). The remaining solid black residue was extracted with CH_2Cl_2 and separated by TLC with hexane solvent. The only cluster complex that was found was shown to be the known compound $Os_3(CO)_9(\mu_3\text{-S})(\mu\text{-H})_2$ (0.3 mg, 15%) by IR analysis.

Crystallographic Analyses. Yellow crystals of **1** suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from solutions in hexane solvent by cooling to 0 °C. Yellow crystals of **2** and **3** were grown by slow evaporation of solvent from hexane/CH_2Cl_2 solutions. All crystals used for diffraction measurements 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. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures.[12a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[12b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compound **1** 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 structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated by assuming idealized geometries and a C–H distance of 0.95 Å. The scattering contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

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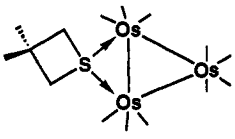
(12) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

Compound **2** crystallized in the monoclinic crystal system. The space group $P2_1/a$ 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 atoms heavier than carbon were refined with anisotropic thermal parameters. All carbon atoms were refined with isotropic thermal parameters. Compound **2** crystallized with three independent molecules in the asymmetric crystallographic unit. The metal-coordinated carbon and sulfur atoms of the activated tetrahydrothiophene ligand were disordered in all three molecules. Occupancy refinement was performed on these atoms in each case. The hydride ligands were not located in this analysis, and due to the disorder problem all hydrogen atom positions on the ligands were ignored.

Compound **3** crystallized in the orthorhombic crystal system. The space group *Pbca* was established 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. All hydrogen atom positions were calculated by assuming idealized geometries. The scattering contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Results and Discussion

The reaction of $Os_3(CO)_{10}(NCMe)_2$ with tetrahydrothiophene (**B**), ($SCH_2CH_2CH_2CH_2$) or THT, at 25 °C yielded the complex $Os_3(CO)_{10}(SCH_2CH_2CH_2CH_2)_2$ (**1**) in 85% yield. A small amount of the complex $Os_3(CO)_{11}(SCH_2CH_2CH_2CH_2)$ (9% yield) was also obtained. Although it is well established that the reaction of $Os_3(CO)_{10}(NCMe)_2$ with two-electron donors leads to the formation of disubstituted complexes,[13] we have observed previously that the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 3,3-dimethylthietane yields only the monothietane complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ (**4**) in which the thietane serves as a bridging ligand donating four electrons.[1d]



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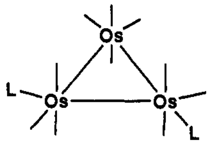
In order to establish the details of the molecular structure of **1**, a single-crystal X-ray diffraction analysis was performed; an ORTEP diagram of the molecule is shown in Figure 1, and selected bond distances and angles are listed in Tables II and III, respectively. Complex **1** contains a triangular triosmium cluster with ten linear terminal carbonyl ligands. The two THT ligands occupy "equatorial" coordination sites on different metal atoms with the sulfur atoms trans to two different metal–metal bonds (see structure **C**). These metal–metal bonds are slightly shorter than the third, Os(1)–Os(2) = 2.8559(9) Å and Os(2)–Os(3) = 2.8598(8) Å vs Os(1)–Os(3) = 2.8976(9) Å. It has been observed previously that metal–metal bonds positioned trans to strong σ-donor ligands exhibit bond contraction effects.[14] This structure of **1** differs from the bis(tertiary phosphine)-substituted cluster complexes $M_3(CO)_{10}L_2$ (M = Ru, Os), where the bulky phosphine ligands were found to lie in equatorial sites with both ligands trans to the same metal–metal bond (see structure **D**).[15] The thietane ligand in the monosubstitution complex $Os_3(CO)_{11}(SCH_2$-



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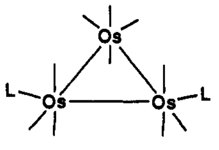

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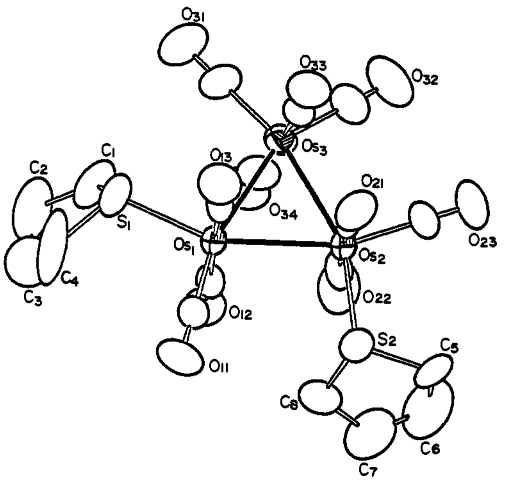

Figure 1. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(SCH_2CH_2CH_2CH_2)_2$ (**1**) showing 50% probability thermal ellipsoids.

Table II. Intramolecular Distances for **1**[a]

Os(1)–Os(2)	2.8559(9)	Os(3)–C(33)	1.95(2)
Os(1)–Os(3)	2.8976(9)	Os(3)–C(34)	1.91(2)
Os(1)–S(1)	2.404(4)	S(1)–C(1)	1.79(2)
Os(1)–C(11)	1.88(1)	S(1)–C(4)	1.82(3)
Os(1)–C(12)	1.92(1)	S(2)–C(5)	1.82(2)
Os(1)–C(13)	1.93(1)	S(2)–C(8)	1.79(1)
Os(2)–Os(3)	2.8598(8)	O–C(av)	1.15(1)
Os(2)–S(2)	2.404(3)	C(1)–C(2)	1.48(3)
Os(2)–C(21)	1.92(1)	C(2)–C(3)	1.41(3)
Os(2)–C(22)	1.93(1)	C(3)–C(4)	1.53(3)
Os(2)–C(23)	1.87(1)	C(5)–C(6)	1.40(3)
Os(3)–C(31)	1.88(2)	C(6)–C(7)	1.41(3)
Os(3)–C(32)	1.90(2)	C(7)–C(8)	1.52(3)

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

Table III. Intramolecular Bond Angles for **1**[a]

Os(2)–Os(1)–Os(3)	59.61(2)	Os(1)–Os(3)–Os(2)	59.47(2)
Os(2)–Os(1)–S(1)	154.7(1)	Os(1)–Os(3)–C(31)	102.8(5)
Os(2)–Os(1)–C(11)	103.9(4)	Os(1)–Os(3)–C(32)	152.8(5)
Os(2)–Os(1)–C(12)	87.2(4)	Os(1)–Os(3)–C(33)	91.3(3)
Os(2)–Os(1)–C(13)	91.1(4)	Os(1)–Os(3)–C(34)	82.9(4)
Os(3)–Os(1)–S(1)	95.1(1)	Os(2)–Os(3)–C(31)	161.5(5)
Os(3)–Os(1)–C(11)	162.8(4)	Os(2)–Os(3)–C(32)	94.7(5)
Os(3)–Os(1)–C(12)	95.3(4)	Os(2)–Os(3)–C(33)	85.0(4)
Os(3)–Os(1)–C(13)	87.5(4)	Os(2)–Os(3)–C(34)	92.3(4)
S(1)–Os(1)–C(11)	101.4(4)	Os(1)–S(1)–C(1)	113.3(6)
S(1)–Os(1)–C(12)	94.5(4)	Os(1)–S(1)–C(4)	112.6(7)
S(1)–Os(1)–C(13)	88.8(4)	C(1)–S(1)–C(4)	93(1)
Os(1)–Os(2)–Os(3)	60.92(2)	Os(2)–S(2)–C(5)	110.3(5)
Os(1)–Os(2)–S(2)	96.85(9)	Os(2)–S(2)–C(8)	112.1(5)
Os(1)–Os(2)–C(21)	87.9(3)	C(5)–S(2)–C(8)	94.3(8)
Os(1)–Os(2)–C(22)	92.8(4)	S(1)–C(1)–C(2)	106(1)
Os(1)–Os(2)–C(23)	159.8(4)	C(1)–C(2)–C(3)	108(2)
Os(3)–Os(2)–S(2)	157.76(9)	C(2)–C(3)–C(4)	107(2)
Os(3)–Os(2)–C(21)	94.0(3)	S(1)–C(4)–C(3)	104(2)
Os(3)–Os(2)–C(22)	88.0(4)	S(2)–C(5)–C(6)	106(1)
Os(3)–Os(2)–C(23)	99.0(4)	C(5)–C(6)–C(7)	117(2)
S(2)–Os(2)–C(21)	85.2(4)	C(6)–C(7)–C(8)	110(2)
S(2)–Os(2)–C(22)	92.7(4)	S(2)–C(8)–C(7)	107(1)
S(2)–Os(2)–C(23)	103.2(4)	Os–C–O(av)	176(1)

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

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(14) Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L.-Y. *Organometallics* **1983**, *2*, 144.

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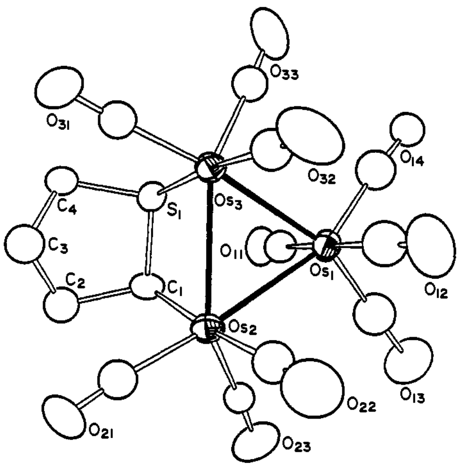


Figure 2. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}[\mu$-η^2-$(\overline{SCH_2CH_2CH_2CH})](\mu$-H) (**2**) showing 50% probability thermal ellipsoids.

Table IV. Selected Intramolecular Distances for Molecule A of **2**[a]

Os(1)–Os(2)	2.905(2)	Os(3)–S(1)	2.37(1)
Os(1)–Os(3)	2.907(2)	Os(3)–C(31)	1.91(3)
Os(1)–C(11)	1.90(4)	Os(3)–C(32)	1.91(4)
Os(1)–C(12)	1.92(5)	Os(3)–C(33)	1.88(4)
Os(1)–C(13)	1.95(4)	S(1)–C(1)	1.81(2)
Os(1)–C(14)	1.88(3)	S(1)–C(4)	1.78(3)
Os(2)–Os(3)	2.928(2)	C(1)–C(2)	1.70(3)
Os(2)–C(1)	2.33(2)	O–C(av)	1.14(4)
Os(2)–C(21)	1.89(3)	C(1)–C(2)	1.70(3)
Os(2)–C(22)	1.92(4)	C(2)–C(3)	1.52(4)
Os(2)–C(23)	1.85(3)	C(3)–C(4)	1.53(4)

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

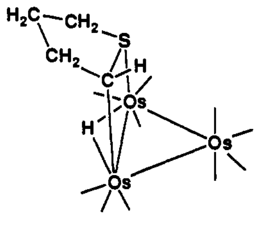
Table V. Selected Intramolecular Bond Angles for Molecule A of **2**[a]

Os(2)–Os(1)–Os(3)	60.50(4)	Os(1)–Os(3)–C(32)	91.0(9)
Os(2)–Os(1)–C(11)	91(1)	Os(1)–Os(3)–C(33)	88.7(3)
Os(2)–Os(1)–C(12)	91(1)	Os(2)–Os(3)–S(1)	75.6(2)
Os(2)–Os(1)–C(13)	102(1)	Os(2)–Os(3)–C(31)	114(1)
Os(2)–Os(1)–C(14)	158.4(8)	Os(2)–Os(3)–C(32)	99(1)
Os(3)–Os(1)–C(11)	95.7(9)	Os(2)–Os(3)–C(33)	146.7(8)
Os(3)–Os(1)–C(12)	85(1)	S(1)–Os(3)–C(31)	92(1)
Os(3)–Os(1)–C(13)	162(1)	S(1)–Os(3)–C(32)	174(1)
Os(3)–Os(1)–C(14)	98.1(8)	S(1)–Os(3)–C(33)	93(1)
Os(1)–Os(2)–Os(3)	59.78(4)	Os(3)–S(1)–C(1)	103.5(7)
Os(1)–Os(2)–C(1)	87.5(4)	Os(3)–S(1)–C(4)	113(1)
Os(1)–Os(2)–C(21)	174.4(9)	C(1)–S(1)–C(4)	97(1)
Os(1)–Os(2)–C(22)	88(1)	Os(2)–C(1)–S(1)	104.0(7)
Os(1)–Os(2)–C(23)	87.1(9)	Os(2)–C(1)–C(2)	112(1)
Os(3)–Os(2)–C(1)	76.7(3)	S(1)–C(1)–C(2)	105(1)
Os(3)–Os(2)–C(21)	114.6(9)	Os(2)–C(1)–S(1)	104.0(3)
Os(3)–Os(2)–C(22)	100(1)	Os(2)–C(1)–C(2)	112(1)
Os(3)–Os(2)–C(23)	143(1)	S(1)–C(1)–C(2)	105(1)
Os(1)–Os(3)–Os(2)	59.72(4)	C(2)–C(3)–C(4)	108(2)
Os(1)–Os(3)–S(1)	84.8(2)	S(1)–C(4)–C(3)	106(2)
Os(1)–Os(3)–C(31)	173.8(9)	Os–C–O(av)	175(3)

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

$\overline{CH_2}CH_2$) was also found coordinated in an equatorial site.[2b] The THT ligands exhibit no unusual distortions, and the Os–S bond distances are also normal, 2.404(4) Å.[2b]

When compound **1** was heated to reflux in cyclohexane solvent for 1 h, the compound $Os_3(CO)_{10}[\mu$-η^2-$(\overline{SCH_2CH_2CH_2CH})](\mu$-H) (**2**) was obtained in 24% yield together with a small amount of $Os_3(CO)_{11}(\overline{SCH_2CH_2CH_2CH_2})$ (14% yield) and a small amount of $Os_3(CO)_{12}$. Compound **2** was characterized by a combination of IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. The complex crystallizes with three independent molecules in the asymmetric crystal unit, and all three molecules are structurally similar. An ORTEP diagram of the molecular structure of one of these is shown in Figure 2, and selected bond distances and angles are listed in Tables IV and V, respectively. Complex **2** also contains a triangular triosmium cluster with ten linear terminal carbonyl ligands, but it has only one THT ligand, which has been transformed into a metalated bridging ligand and a hydride ligand by the activation of one of the CH bonds on one of the methylene groups α to the sulfur atom. This metalated THT ligand bridges an edge of the cluster in a diaxial coordination with the sulfur atom bonded to one metal, Os(3), and the carbon, C(1), coordinated to the other Os(2). A similarly coordinated metalated THT ligand was found in the complex $Os_3(CO)_9(PPh_3)[\mu$-η^2-$(\overline{SCH_2CH_2CH_2CH})](\mu$-H) (**5**), which was obtained from the reaction of $Os_3(CO)_{10}(\mu$-$H)_2$ with 2,3-dihydrothiophene.[11] The bonding and coordination modes of the metalated THT ligands in **2** and **5** are not significantly different. There are some differences in the metal–metal bonding between **2** and **5** due to differences in the locations of the bridging hydride ligands. Although the hydride ligands were not located directly in either of the structural analyses, the hydride ligand in **5** appears to bridge one of the metal–metal bonds that is located adjacent to



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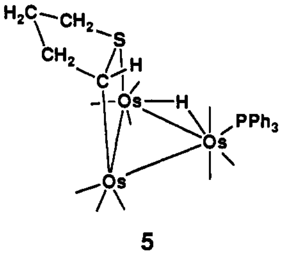

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the bridging THT ligand and the phosphine ligand, while the hydride ligand in **2** appears to bridge the same metal–metal bond as the bridging THT ligand. It is well established that the presence of a bridging hydride ligand will affect the length of the associated metal–metal bonds.[16] Accordingly, the differences in the lengths of the metal–metal bonds between **2** and **5** can be attributed to the different locations of the hydride ligands.

Interestingly, compound **2** was also reported to be a product of the reaction of $Os_3(CO)_{10}(\mu$-$H)_2$ with 2,3-dihydrothiophene.[11] However, our IR and ^{1}H NMR spectra [δ (in C_6D_6): 3.01 (dt, 1 H, J_{H-H} = 6.7 Hz, J_{H-H} = 2.2 Hz), 1.95 (dt, 1 H, J_{H-H} = 11.7 Hz, J_{H-H} = 6.3 Hz), 1.88 (dt, 1 H, J_{H-H} = 11.7 Hz, J_{H-H} = 6.3 Hz), 1.80 (m, 1 H), 1.72 (m, 1 H), 1.46 (m, 1 H), 0.91 (m, 1 H), −16.57 (m, 1 H, J_{H-H} = 2.2 Hz)] are substantially different from those previously reported.[11] Accordingly, we have repeated the reaction of $Os_3(CO)_{10}(\mu$-$H)_2$ with 2,3-dihydrothiophene under conditions similar to those of the previous report. We have indeed obtained **2** from this reaction, but it is not the "sparingly soluble" yellow powder that was described. Instead, it is a hexane-soluble product that is readily isolated by TLC and is spectroscopically identical to the product obtained from the thermal transformation of **1**. We also observed the formation of a sparingly soluble yellow precipitate in this reaction, but our IR analysis indicated that this material is predominantly $Os_3(CO)_{12}$.

When a solution of **2** in octane was heated to reflux (125 °C) for 1 h, the new compound $Os_3(CO)_9[\mu$-η^3-$S(CH_2)_2CH{=}CH_2]$(μ-H) (**3**) was obtained in 61% yield. Compound **3** was characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **3** is shown in Figure 3, and selected bond distances and angles are listed in Tables VI and VII, respectively. Complex **3** contains a triangular triosmium cluster with nine linear terminal carbonyl ligands. The most interesting ligand is a 3-butenethiolate ligand

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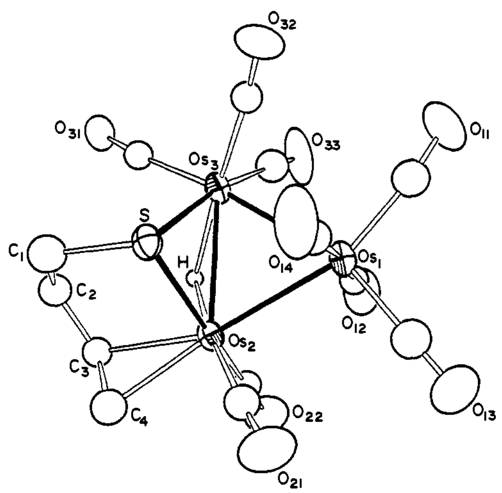


Figure 3. ORTEP diagram of the molecular structure of $Os_3(CO)_9[\mu\text{-}\eta^3\text{-}S(CH_2)_2CH{=}CH_2](\mu\text{-}H)$ (**3**) showing 50% probability thermal ellipsoids.

Table VI. Intramolecular Distances for **3**[a]

Os(1)–Os(2)	2.829(2)	Os(2)–C(22)	1.85(3)
Os(1)–Os(3)	2.847(2)	Os(3)–S(1)	2.419(7)
Os(1)–C(11)	1.89(3)	Os(3)–C(31)	1.89(3)
Os(1)–C(12)	1.89(3)	Os(3)–C(32)	1.96(3)
Os(1)–C(13)	1.92(3)	Os(3)–C(33)	1.91(3)
Os(1)–C(14)	1.95(3)	S(1)–C(1)	1.84(3)
Os(2)–Os(3)	2.850(2)	C(1)–C(2)	1.53(4)
Os(2)–S(1)	2.396(6)	C(2)–C(3)	1.44(3)
Os(2)–C(3)	2.30(3)	C(3)–C(4)	1.35(3)
Os(2)–C(4)	2.26(3)	O–C(av)	1.14(3)
Os(2)–C(21)	1.85(3)		

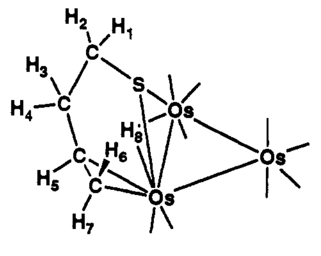
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table VII. Intramolecular Bond Angles for **3**[a]

Os(2)–Os(1)–Os(3)	60.27(4)	C(3)–Os(2)–C(22)	92(1)
Os(2)–Os(1)–C(11)	158.8(9)	C(4)–Os(2)–C(21)	81(1)
Os(2)–Os(1)–C(12)	83.1(9)	C(4)–Os(2)–C(22)	92(1)
Os(2)–Os(1)–C(13)	101(1)	Os(1)–Os(3)–Os(2)	59.55(4)
Os(2)–Os(1)–C(14)	89.8(8)	Os(1)–Os(3)–S(1)	83.2(2)
Os(3)–Os(1)–C(11)	98.6(9)	Os(1)–Os(3)–C(31)	173.6(8)
Os(3)–Os(1)–C(12)	85.0(8)	Os(1)–Os(3)–C(32)	88.2(8)
Os(3)–Os(1)–C(13)	161(1)	Os(1)–Os(3)–C(33)	89(1)
Os(3)–Os(1)–C(14)	90.2(8)	Os(2)–Os(3)–S(1)	53.3(2)
Os(1)–Os(2)–Os(3)	60.19(4)	Os(2)–Os(3)–C(31)	114.3(8)
Os(1)–Os(2)–S(1)	84.0(2)	Os(2)–Os(3)–C(32)	135.2(7)
Os(1)–Os(2)–C(3)	158.5(6)	Os(2)–Os(3)–C(33)	117.4(9)
Os(1)–Os(2)–C(4)	161.6(7)	S(1)–Os(3)–C(31)	94.1(8)
Os(1)–Os(2)–C(21)	83(1)	S(1)–Os(3)–C(32)	95.9(8)
Os(1)–Os(2)–C(22)	97.9(9)	S(1)–Os(3)–C(33)	170.4(9)
Os(3)–Os(2)–S(1)	54.1(2)	Os(2)–S(1)–Os(3)	72.6(2)
Os(3)–Os(2)–C(3)	98.3(6)	Os(2)–S(1)–C(1)	103(1)
Os(3)–Os(2)–C(4)	128.3(7)	Os(3)–S(1)–C(1)	110(1)
Os(3)–Os(2)–C(21)	133.2(9)	S(1)–C(1)–C(2)	109(2)
Os(3)–Os(2)–C(22)	115.7(8)	C(1)–C(2)–C(3)	117(2)
S(1)–Os(2)–C(3)	82.0(6)	Os(2)–C(3)–C(2)	109(2)
S(1)–Os(2)–C(4)	89.8(7)	Os(2)–C(3)–C(4)	71(2)
S(1)–Os(2)–C(21)	97.5(8)	C(2)–C(3)–C(4)	128(3)
S(1)–Os(2)–C(22)	166.8(8)	Os(2)–C(4)–C(3)	74(2)
C(3)–Os(2)–C(4)	34.5(9)	Os–C–O(av)	176(3)
C(3)–Os(2)–C(21)	115(1)		

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

in which the sulfur ligand bridges an edge of the cluster and the C–C double bond is coordinated to one of the sulfur-coordinated metal atoms, Os(2)–C(3) = 2.30(3) Å, Os(2)–C(4) = 2.26(3) Å and C(3)–C(4) = 1.35(3) Å. The hydride ligand bridges the same metal–metal bond as the sulfur atom but lies on the other side of the cluster, $\delta = -17.28$ ppm. The ^1H NMR spectrum of **3** with assignments according to the structure shown below is consistent with this formulation: δ 4.28 (dd, H_5, $J_{H-H} = 12.2$ Hz, $J_{H-H} = 8.7$ Hz, $J_{H-H} = 2.1$ Hz), 3.64 (d, H_7, $J_{H-H} = 8.7$ Hz), 2.56 (d, H_6, $J_{H-H} = 12.2$ Hz), 2.26 (d, H_4, $J_{H-H} = 9.3$ Hz), 1.60–1.70 (m, $H_1 + H_2 + H_3$).



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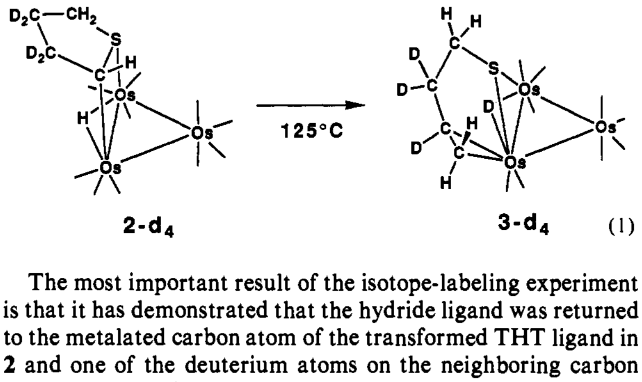
To obtain some information about the mechanism of the transformation of **2** to **3**, the compound $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}(\overline{SCH_2CD_2CD_2CH})](\mu\text{-}H)$ (**2**-d_4) was prepared and converted to **3**-d_4 by heating to 125 °C. The distribution of hydrogen in the product was established by a combination of ^1H NMR and ^2H NMR spectroscopies: H_5, 0.10–0.15 H; H_7, 0.85–0.90 H; H_6, 0.85–0.90 H; H_4, 0 H; H_3, 0 H; H_2, 1 H; H_1, 1 H; H_8, 0.10–0.15 H. The presence of noninteger amounts of hydrogen at some of the positions indicates that the transformation is probably not 100% specific, but since the values do not differ greatly from integers, it is clear that there is considerable selectivity in this transformation. Ignoring the slight differences from integer values, the transformation of **2**-d_4 to **3**-d_4 would be represented by the structures shown in eq 1.

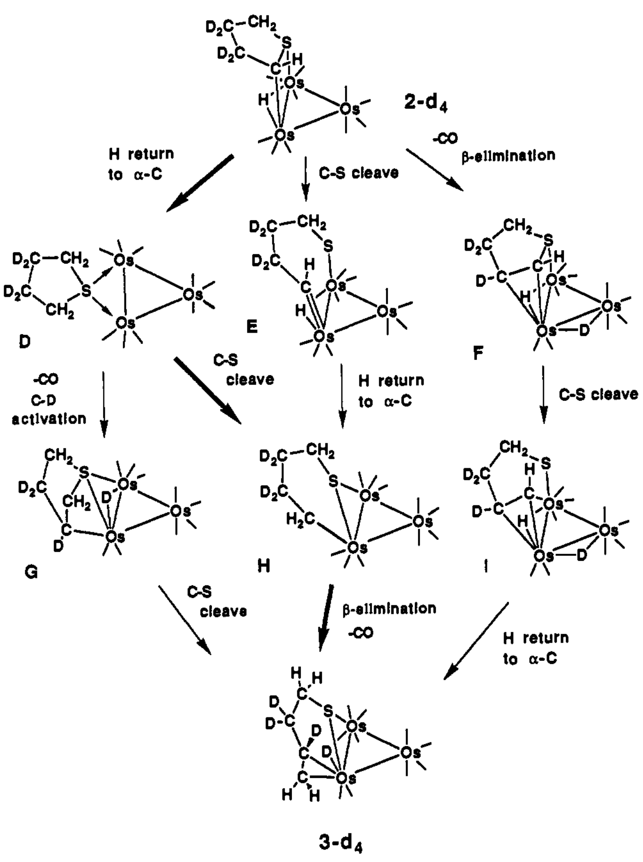


2-d4 **3-d4** (1)

The most important result of the isotope-labeling experiment is that it has demonstrated that the hydride ligand was returned to the metalated carbon atom of the transformed THT ligand in **2** and one of the deuterium atoms on the neighboring carbon atom was shifted to the cluster. All mechanisms that do not include these findings are therefore ruled out. However, there are still a number of mechanisms by which *this* transformation could have occurred. Several possibilities will be discussed and certainly others could be imagined, but the space available in this report does not permit an elaboration upon every conceivable possibility. We will also point out at the outset that this isotope-labeling experiment does not allow one to distinguish among these possibilities since they all meet the requirements of that experiment. In stating our preference among these possibilities, we will draw on examples of established transformations for related cyclic thioethers, particularly those of the four-membered heterocycles thietanes.

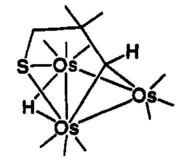
We have analyzed the transformation in terms of a minimum of three basic steps: (1) the hydride ligand in **2** must be returned preferentially to the α-carbon atom of the metalated THT ligand, (2) one carbon–sulfur bond is cleaved, and (3) a CO ligand is eliminated, and one of the deuterium atoms on one of the β-carbon atoms of the THT ligand is shifted to the metal atoms (a β-elimination). The two components of the third step are probably correlated in that the loss of CO probably precedes the activation of the C–D bond on the β-carbon atom by providing a vacant coordination site. The difficult question is, What is the order of

Scheme I



occurrence of these steps? This will be discussed in terms of three mechanisms shown in Scheme I.

In the first step, a return of the hydride to the α-carbon of the metalated THT ligand is appealing because it could produce the species **D** that is very similar to the known complex **4**.[1d] Alternatively, cleavage of the C–S bond in the first step would yield an alkylidene–thiolate ligand, such as **E**. Other structures could be proposed for **E**, and we have prepared one alkylidene–thiolate ligand triosmium complex, $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}SCH_2CMe_2CH](\mu\text{-}H)$ (**6**), by the decarbonylation of **4**, although **6** has both



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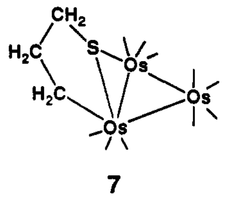
bridging alkylidene and bridging thiolato groups.[2c] A third alternative would be to produce the C–D activation. This might yield a species such as **F** containing a bridging 2,3-dihydrothiophene ligand. A potential problem with **F** and any other species containing both hydrogen and deuterium on the metals at the same time is that, in some subsequent step, the hydrogen atom would have to be shifted back to the α-carbon of the ligand with a higher selectivity than that of the deuterium atom. This could occur if a large kinetic isotope effect were operative, and some examples of large kinetic isotope effects for metal to ligand hydrogen transfers were reported recently.[17]

In the second step, a combination of CO loss and C–D activation could transform **D** to a species such as **G**. There is no precedent for such a structure, and it seems that it would contain considerable strain around the coordination sites of the metalated THT ligand. Alternatively, a C–S bond cleavage (i.e. insertion of one of the metal atoms into one of the C–S bonds) could transform **D** to a thiametallacyclic complex such as H. This structure is very appealing since we have already isolated several similar thiametallacyclic complexes from ring-opening transformations in the reactions of thietanes with triosmium cluster complexes (e.g. $Os_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2]$ (**7**)[2b] and $Os_3(CO)_{10}[\mu\text{-}SCPh(H)CH_2CPh(H)]$ (**8**)[2a]). Furthermore, we have shown that **4**



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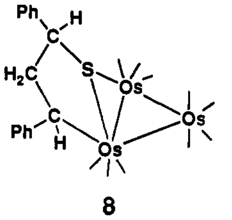

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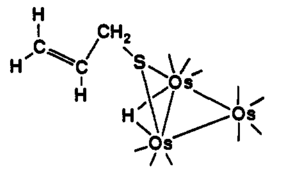
can be ring-opened by photochemical stimulation to yield an analogous species.[2c] Species **H** is also accessible from intermediate **E** by a simple rearrangement. C–S bond cleavage (insertion of one of the metal atoms into one of the C–S bonds) in **F** could lead to an alkylidene–thiolate complex such as **I**.

In the third step, each of the possibilities **G**–**I** could be transformed to the final product **3**-d_4. A simple C–S bond cleavage in **G** would lead to **3**-d_4 directly. A combination of decarbonylation and β-elimination could transform **H** to **3**-d_4. There is precedent for transformations like this one. For example, by mild heating, both compounds **7** and **8** are transformed into complexes containing alkenethiolato ligands, **9**[2b] and **10**.[2a] Decarbonylation



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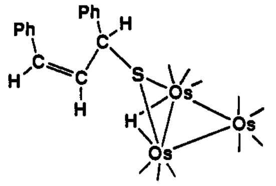

10

does not occur, and the olefinic group at the terminus of the hydrocarbon chain is not coordinated in compounds **9** and **10**.

The transformation of **I** to **3**-d_4 is conceivable, but as mentioned above, it would have to occur with a high selectivity for hydrogen transfer. This seems unlikely, but large kinetic isotope effects have been observed for metal to ligand hydrogen transfers and could account for the large preference for hydrogen transfer.

Our conclusion is that the pathway indicated by the heavy arrows in Scheme I is the most plausible in view of the existence of species analogous to **D** and **H** and the previous examples of transformations related to the transformations of **D** to **H** and **H** to **3**. This also implies that the CH activation step that yielded **2** is probably of little importance to the ring-opening transformation of THT, step **D** to **H**. Note: this mechanism alone does not explain the presence of the small amounts of hydrogen in sites H_5 and H_8 and the small amounts of deuterium that were observed in sites H_4 and H_6. Extended heating of **3**-d_4 did not produce any changes in the distribution, so we feel that this result is not due to hydrogen rearrangements after **3**-d_4 was formed. Perhaps, other slightly less favorable mechanisms for the transformation of **2**-d_4 to **3**-d_4 are responsible for this observation.

When a sample of **3** was heated to 205 °C, the cluster complex was decomposed, and the organic compound butene was formed as detected by mass spectrometry. On the basis of mass spectrometry alone, it was not possible for us to establish which of the butenes were formed or if it was a mixture of isomers.

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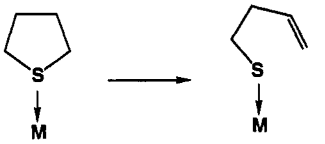
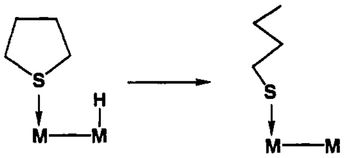
[17] (a) Anslyn, E. V.; Green, M.; Nicola, G.; Rosenberg, E. *Organometallics* **1991**, *10*, 2600. (b) Rosenberg, E.; Freeman, C. Z.; Hardcastle, K.; Yoo, Y. J.; Milone, L.; Gobetto. *J. Cluster Sci.* **1992**, *3*, 439.

Relationship to Proposed THT Hydrodesulfurization Mechanisms. THT has been studied as a model substrate for hydrodesulfurization processes.[4,5] The ring opening of THT by transition metal catalysts has been proposed to proceed via both butenethiolate intermediates (eq 2)[4c,5] and butanethiolate intermediates (eq 3).[4a] The latter path, of course, requires the addition of hydrogen, presumably "surface" hydrogen, from the catalyst. Our cluster complex has no hydrogen on the metals, and thus the latter alternative is effectively ruled out. These proposals are based largely on product analyses and lack much mechanistic detail. We have, however, now demonstrated the viability of the first process to occur under very mild conditions (125 °C) in this model system through the preparation and structural characterization of the first butenethiolato complex (3) derived from the molecule tetrahydrothiophene.



(2)



(3)

A number of intermediates may have been traversed en route to the butenethiolate species. By using selective isotopic labeling, we have been able to monitor the locations of the hydrogen atoms through the course of the reaction. On the basis of the present results and those of our previous studies with THT and thietanes, we think that a strong case can be made for the involvement of thiametallacyclic species such as **H** formed by a carbon–sulfur bond cleavage in a THT ligand in a *bridging* coordination mode. The coordination of the sulfur atom to two metal atoms may be of considerable importance. The olefinic grouping is believed to be formed from a thiametallacyclic species by the classic β-hydride elimination reaction.[18]

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 non-hydrogen and hydrogen atom positional parameters and anisotropic thermal parameters (14 pages); tables of structure factor amplitudes (59 pages). Ordering information is given on any current masthead page.

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(18) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 383.