Organometallics **1993,** *12,* 4955-4961 4955

Transformations of Thiacyclohexane by a Triosmium Cluster

Richard D. Adams,* Jeffrey E. Cortopassi, John H. Yamamoto, and Wengan Wu

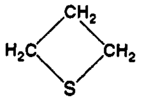
Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208

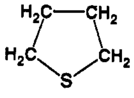
Received August 19, 1993⊗

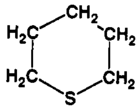
The reactions of thiacyclohexane (TCH) with $Os_3(CO)_{10}(NCMe)_2$, $Os_3(CO)_{11}(NCMe)$, and $Os_3(CO)_{12}$ have been investigated. The reaction of TCH with $Os_3(CO)_{10}(NCMe)_2$ at 25 °C yielded the disubstituted product $Os_3(CO)_{10}(TCH)_2$, **1**, in 86% yield. At 97 °C, compound **1** was transformed into four new compounds: $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH_2CH_2C)(\mu\text{-}H)_2$, **2** (20%), $Os_3(CO)_8(\mu\text{-}SCH_2CH_2CH_2C)[S(CH_2)_5](\mu\text{-}H)_2$, **3** (4%), $Os_3(CO)_{11}(SCH_2CH_2CH_2CH_2CH_2)$, **4** (15%), and $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH_2CH_2CH)(\mu\text{-}H)$, **5** (13%). Compounds **2**, **3**, and **5** were characterized by single crystal X-ray diffraction analysis. These three products were formed by the loss of one TCH ligand. In compounds **5** and **2** the remaining TCH ligand has undergone activation of one and two CH bonds, respectively, α to the sulfur atom and the TCH ligand was transformed into a metalated triply bridging ligand. Compounds **2** and **5** are interconvertible isomers. Compounds **2**, **3**, and **5** were also obtained from the pyrolysis of **4** at 97 °C and from the reaction of $Os_3(CO)_{12}$ with TCH at 125 °C. Crystallographic data for **2**: space group, $P\bar{1}$, $a = 9.2559(9)$ Å, $b = 13.653(1)$ Å, $c = 8.9907(9)$ Å, $\alpha = 92.73(1)°$, $\beta = 112.679(6)°$, $\gamma = 85.475(9)°$, $Z = 2$, 2320 reflections, $R = 0.028$. For **3**: space group $P2_1/n$, $a = 9.060(2)$ Å, $b = 11.823(2)$ Å, $c = 23.024(3)$ Å, $\beta = 95.27(1)°$, $Z = 4$, 1808 reflections, $R = 0.024$. For **5**·C_6H_6: space group $P\bar{1}$, $a = 9.504(2)$ Å, $b = 15.967(3)$ Å, $c = 8.293(2)$ Å, $\alpha = 104.71(1)°$, $\beta = 110.95(1)°$, $\gamma = 83.82(2)°$, $Z = 2$, 2430 reflections, $R = 0.038$.

Introduction

The activation of alkyl- and arylphosphines[1,2] and diphosphines[3] by triosmium cluster complexes has been the subject of numerous studies. Investigations of the reactions of thioethers[4] and thiolates[5] with triosmium cluster complexes have been relatively few. Recently, we have been investigating transformations of saturated heterocycles containing sulfur (i.e. thietanes **A**[6,7] and tetrahydrothiophene **B**[8]) by metal cluster complexes. We have found that bridging coordination of the sulfur atom can promote the cleavage of carbon–sulfur bonds in thietane ligands by nucleophiles.[6] The insertion of metal atoms into the carbon–sulfur bond has also been observed.[7] We have observed similar transformations of tetrahydrothiophene.[8] Tetrahydrothiophene has been studied as a model for catalytic hydrodesulfurization processes.[9,10]


A


B


C

We have now investigated the reactions of thiacyclohexane (TCH) **C** with the triosmium cluster complexes $Os_3(CO)_{10}(NCMe)_2$, $Os_3(CO)_{11}(NCMe)$, and $Os_3(CO)_{12}$. We have found that CH activation reactions at one of the carbon atoms α to the sulfur atom are the dominant transformation, and carbon–sulfur bond cleavage has not occurred in the temperature ranges that we have studied. The results of these studies are reported here.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1993.

(1) Burgess, K. *Polyhedron* **1984,** *3,* 1175.

(2) (a) Deeming, A. J. *J. Organomet. Chem.* **1977,** *128,* 63. (b) Deeming, A. J.; Underhill, J. *J. Chem. Soc., Dalton Trans.* **1973,** 2727. (c) Deeming, A. J.; Kimber, R. E.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973,** 2589. (d) Bradford, C. W.; Nyholm, R. S.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1972,** 87. (e) Bradford, C. W.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R.; Nyholm, R. S. *J. Organomet. Chem.* **1972,** *40,* C70.

(3) (a) Hodge, S. R.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1987,** 931. (b) Clucas, J. A.; Harding, M. M.; Smith, A. K. *J. Chem. Soc., Chem. Commun.* **1985,** 1280. (c) Clucas, J. A.; Foster, D. F.; Harding, M. M.; Smith, A. K. *J. Chem. Soc., Chem. Commun.* **1984,** 949.

(4) (a) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982,** *1,* 235. (b) Boyar, E.; Deeming, A. J.; Henrick, K.; McPartlin, M.; Scott, A. *J. Chem. Soc., Dalton Trans.* **1986,** 1431. (c) Glavee, G. N.; Daniels, L. M.; Angelici, R. *J. Organometallics* **1989,** *8,* 1856.

(5) (a) Adams, R. D.; Yang, L.-W. *J. Am. Chem. Soc.* **1982,** *104,* 4115. (b) Adams, R. D.; Horvath, I. T.; Segmuller, B. E.; Yang, L.-W. *Organometallics* **1983,** *2,* 1301. (c) Adams, R. D.; Horvath, I. T.; Kim, H.-S. *Organometallics* **1984,** *3,* 548.

(6) (a) Adams, R. D. *J. Cluster Sci.* **1992,** *3,* 263. (b) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1991,** *10,* 2539. (c) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992,** *11,* 1460. (d) Adams, R. D.; Pompeo, M. P. *J. Am. Chem. Soc.* **1991,** *113,* 1619. (e) Adams, R. D.; Belinski, J. A. *Organometallics* **1992,** *11,* 2488. (f) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1992,** *11,* 3129. (g) Adams, R. D.; Cortopassi, J. E.; Falloon, S. B. *Organometallics* **1992,** *11,* 3794.

(7) (a) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992,** *11,* 103. (b) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992,** *11,* 2281. (c) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1992,** *11,* 2016. (d) Adams, R. D.; Belinski, J. A.; Schierlmann, J. A. *J. Am. Chem. Soc.* **1991,** *113,* 9004.

(8) Adams, R. D.; Pompeo, M. P.; Yamamoto, J. H.; Wu, W. *J. Am. Chem. Soc.* **1993,** *115,* 8207–8213.

(9) (a) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986,** *108,* 7204. (b) Kolboe, S. *Can. J. Chem.* **1969,** *47,* 352. (c) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989,** *116,* 11. (d) Lang, J. F.; Masel, R. I. *Surf. Sci.* **1987,** *183,* 44.

(10) Moser, W. R.; Rossetti, G. A.; Gleaves, J. T.; Ebner, J. R. *J. Catal.* **1991,** *127,* 190.

0276-7333/93/2312-4955$04.00/0 © 1993 American Chemical Society

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. Thiacyclohexane $SCH_2CH_2CH_2CH_2CH_2$ (99%) was used as purchased from Aldrich. The compounds $Os_3(CO)_{11}NCMe$[11] and $Os_3(CO)_{10}(NCMe)_2$[12] 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 and 500 MHz, respectively. Chromatographic separations were performed in air on silica gel by using Analtech (0.25 mm) F_{254} uniplates. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with Thiacyclohexane. A 70-mg amount of $Os_3(CO)_{10}(NCMe)_2$ (0.075 mmol) and 30 μL (3.0 mmol) of thiacyclohexane were dissolved in 2 mL of CH_2Cl_2 at 25 °C. After stirring for 3 h at 25 °C, the solvent was removed *in vacuo*. The residue was dissolved in 5 mL of hexane, and the solution was placed in the freezer at −14 °C. After 12 h, a pure orange crystalline product had precipitated. The product was filtered off and washed with cold heptane. This was identified as $Os_3(CO)_{10}(SCH_2CH_2CH_2CH_2CH_2)_2$, **1**. Yield: 50.0 mg, 86%. Analytical and spectral data for **1**: IR νCO (cm^{-1}) in hexane 2088 (w), 2081 (w), 2028 (vs), 2016 (s), 2002 (vs), 1995 (vs), 1984 (m), 1968 (s), 1953 (m), 1944 (w), 1934 (w); ^1H NMR (δ in $CDCl_3$) 2.88 (s, 8H), 1.92 (s, 8H), 1.81 (s, 4H). Anal. Calcd (found) in **1**: C, 22.76 (22.78); H, 1.90 (1.89).

Thermolysis of 1. A 72.0-mg amount of **1** (0.068 mmol) was dissolved in 80 mL of heptane, and then the solution was heated to reflux for 6 h in the presence of a slow purge with nitrogen. The solvent was removed *in vacuo*, and the residue was separated by TLC using a 4/1 hexane/CH_2Cl_2 solvent mixture. The following compounds were isolated in order of elution: $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH_2CH_2C)(\mu\text{-}H)_2$, **2** (13.7 mg, 20%), $Os_3(CO)_8(\mu\text{-}SCH_2CH_2CH_2CH_2C)[S(CH_2)_5](\mu\text{-}H)_2$, **3** (2.5 mg, 4%), $Os_3(CO)_{11}(SCH_2CH_2CH_2CH_2CH_2)$, **4** (11 mg, 15%), $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH_2CH_2CH)(\mu\text{-}H)$, **5** (9.0 mg, 13%), and $Os_3(CO)_{12}$ (6.0 mg, 10%). Analytical and spectral data for **2**: IR νCO (cm^{-1}) in hexane 2091 (m), 2062 (s), 2035 (vs), 2015 (s), 2001 (m), 1991 (m), 1974 (w), 1962 (w); ^1H NMR (δ in $CDCl_3$) 2.75–2.70 (m, 2H), 2.39 (bt, 1H), 2.15 (bd, 1H), 1.99 (m, 3H), 1.87 (bd, 1H), −15.00 (bs, 1H), −17.50 (bs, 1H). Anal. Calcd (found) for **2**: C, 18.20 (18.73), H, 1.11 (1.12). For **3**: IR νCO (cm^{-1}) in hexane 2078 (m), 2044 (vs), 2015 (s), 2000 (s), 1989 (s), 1970 (m), 1944 (w); ^1H NMR (δ in $CDCl_3$) 3.0 (bs, 5H), 2.66 (dt, $J_{H-H} = 3.1$, $J_{H-H} = 15.7$ Hz, 1H), 2.48 (t, $J_{H-H} = 2.8$ Hz, 1H), 2.47 (t, $J_{H-H} = 3.1$ Hz, 1H) 2.1–1.6 (m, 10H), −13.98 (s, 1H), −15.99 (s, 1H). Anal. Calcd for **3**: C, 21.62 (21.79); H, 2.00 (1.90). For **4**: IR νCO (cm^{-1}) in hexane 2109 (w), 2055 (s), 2036 (s), 2012 (vs), 2008 (m), 2003 (m), 1992 (m), 1976 (m), 1965 (w), 1957 (w). ^1H NMR (δ in $CDCl_3$): 2.91 (bs, 4H), 1.98 (bs, 4H), 1.81 (bs, 2H). Anal. Calcd (found) for **4**: C, 19.58 (19.68); H, 1.02 (0.99). For **5**: IR νCO (cm^{-1}) in hexane 2091 (m), 2062 (vs), 2035 (vs), 2015 (s), 2001 (m), 1991 (m), 1974 (w), 1962 (w); ^1H NMR (δ in $CDCl_3$) 3.49 (bd, 0.39H), 3.08 (td, 1H, $J_{H-H} = 12.8$ Hz, $J_{H-H} = 3.3$ Hz), 3.02 (dt, $J_{H-H} = 11.8$ Hz, $J_{H-H} = 3.3$ Hz, $J_{H-H} = 3.2$ Hz, 1H), 2.32 (bd, 0.39H), 2.2–1.8 (m, 3H), 1.59 (q, $J_{H-H} = 12$ Hz, 1H), 1.22 (q, $J_{H-H} = 14$ Hz, 2H), −16.95 (s, 0.39H), −17.12 (d, 1H, $J_{H-H} = 3.2$). Anal. Calcd (found) for **5**: C, 18.10 (18.30); H, 1.10 (1.08).

Interconversions of 2 and 5. Samples (12.5 mg) of **2** and **5** were dissolved in 1 mL of toluene-d_8 in separate NMR tubes. The samples were heated to 70 °C in a constant temperature bath for 24 h. The ratio of **2**/**5** in both samples as determined by observing the hydride resonances in the ^1H NMR spectra was 1/2.

Reaction of $Os_3(CO)_{11}(NCMe)$ with Thiacyclohexane. A 50.0-mg amount of $Os_3(CO)_{11}(NCMe)$ (0.05 mmol) was combined with 11.5 μL (0.080 mmol) of thiacyclohexane in 5 mL of dichloromethane. This solution was stirred for 2 h at 25 °C. The product $Os_3(CO)_{11}(SCH_2CH_2CH_2CH_2CH_2)$, **4**, was separated by TLC using a 4/1 hexane/CH_2Cl_2 elution solvent. Yield: 40.0 mg, 80%.

Thermolysis of 4. A 30.0-mg amount of $Os_3(CO)_{11}(SCH_2CH_2CH_2CH_2CH_2)$, **4** (0.030 mmol), was dissolved in 25 mL of heptane, and the solution was heated to reflux for 4 h in the presence of a slow nitrogen purge. Four products separated by TLC were found to be **2** (3.4 mg, 11%), **3** (0.5 mg, 2%), unreacted **4** (1.5 mg), and **5** (3.2mg, 11%). An insoluble solid left at the bottom of the plate was shown to be $Os_3(CO)_{12}$ (15 mg) by IR analysis.

Reaction of $Os_3(CO)_{12}$ with Thiacyclohexane. A 50.0-mg amount of $Os_3(CO)_{12}$ (0.05 mmol) and 28 μL of thiacyclohexane (0.27 mmol) were combined in 15 mL of octane and then heated to reflux for 4 h. Workup by TLC yielded **2** (5.1 mg, 10%), **3** (31.8 mg, 64%), and **5** (4.8 mg, 9%).

Crystallographic Analyses. Crystals of **2** suitable for X-ray diffraction measurements were obtained by slow evaporation of solvent from solutions in a heptane/CH_2Cl_2 solvent mixture at 25 °C. Crystals of **3** were grown from a solution of hexane at 25 °C. Crystals of **5** suitable for X-ray diffraction measurements were obtained by slow evaporation of solvent from solutions in a heptane/CH_2Cl_2/benzene solvent mixture at 25 °C. The crystals used in data collection 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.[13a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[13b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/L_p$.

Compounds **2** and **5** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed in each case by the successful solution and refinement of the structures. The structures where solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the analysis of **2** one of the hydride ligands H(1) was located and refined; the position of the other was calculated by using the energy minimization program HYDEX and Os–H = 1.85 Å. All hydrogen atom positions on the ligands were calculated by assuming idealized geometries, C–H = 0.95 Å. For compound **5** the position of the hydride ligand was found in a difference Fourier synthesis, but its position could not be refined. It was added as a constant contribution without refinement. In the final stages of the analysis half of a formula unit of benzene that had cocrystallized from the crystallization solvent was situated about a center of symmetry. It was added and satisfactorily refined using isotropic thermal parameters. All hydrogen atom positions on the ligand and the benzene of crystallization were calculated by assuming idealized geometries and C–H = 0.95 Å. The contributions of the hydrogen atoms in the calculated positions

---

(11) Johnson, B. F. G.; Lewis, J.; Pippard, D. *J. Organomet. Chem.* **1978**, *160*, 263; **1981**, *213*, 249.

(12) Nicholls, J. N.; Vargas, M. D. *Inorg. Synth.* **1989**, *28*, 232.

(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 I. Crystal Data for Compounds 2, 3, and 5

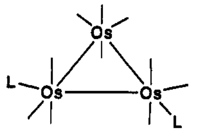
compd	2	3	5
formula	$Os_3SO_9C_{14}H_{10}$	$Os_3S_2O_8C_{18}H_{20}$	$Os_3SO_9C_{14}H_{10}\cdot 0.5C_6H_6$
fw	924.89	999.07	963.94
cryst syst	triclinic	monoclinic	triclinic
Lattice parameters			
a (Å)	9.2559(9)	9.060(2)	9.504(2)
b (Å)	13.653(1)	11.823(2)	15.967(3)
c (Å)	8.9907(9)	23.024(3)	8.293(2)
α (deg)	92.73(1)	90.0	104.71(1)
β (deg)	117.679(6)	95.27(1)	110.95(1)
γ (deg)	85.475(9)	90.0	83.82(2)
V (Å^3)	1002.9(2)	2456(1)	1136.6(8)
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z value	2	4	2
ρ_{calc} (g/cm^3)	3.06	2.70	2.82
μ(MoKα) (cm^{-1})	191.2	157.02	168.8
temp (°C)	20	20	20
$2\theta_{max}$ (deg)	45.0	40.0	44.0
no. of obs ($I > 3\sigma$)	2320	1808	2430
abs cor	empirical	empirical	empirical
residuals: R, R_w	0.028, 0.033	0.024, 0.028	0.038, 0.046
goodness of fit indicator	2.09	1.73	2.71
max shift in final cycle	0.00	0.02	0.00
largest peak in final diff map (e/Å^3)	0.96	0.61	2.02

were added to the structure factor calculations, but their positions were not refined.

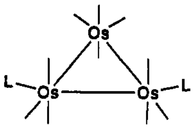
Compound **3** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. One hydride ligand H(1) was located and its position was refined. The other H(2) was not located, and its position was calculated by using the program HYDEX with Os–H = 1.70 Å. All hydrogen atom positions on the ligands were calculated by assuming idealized geometries, C–H = 0.95 Å. Their contributions 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 thiacyclohexane $\overline{SCH_2CH_2CH_2CH_2CH_2}$ (TCH), **C**, at 25 °C yielded the disubstituted complex $Os_3(CO)_{10}(\overline{SCH_2CH_2CH_2CH_2CH_2})_2$, **1**, in 86% yield. An excessive number of IR absorptions together with the observation of two at 2088 (w) and 2081 (w) cm^{-1} in the high frequency region that would be associated with the in-phase stretching of all CO ligands of a single species suggests that compound **1** probably exists in solution as a mixture of two isomers. The two most likely structures are represented by the figures **D** and **E**. Bis(phosphine) substituted clusters $Os_3(CO)_{10}(L)_2$ have been shown to exist in isomeric mixtures like this in solution.[14] The bis(tetrahydrothiophene) (THT) complex $Os_3(CO)_{10}(\overline{SCH_2CH_2CH_2CH_2})_2$ has been shown to possess the structure **D** in the solid state L = ($\overline{SCH_2CH_2CH_2CH_2}$).



D



E

The reaction of $Os_3(CO)_{11}(NCMe)$ with TCH yielded only the product $Os_3(CO)_{11}(\overline{SCH_2CH_2CH_2CH_2CH_2})$, **4**, in 80% yield. A strong similarity of its IR spectrum to that of the complex $Os_3(CO)_{11}(\overline{SCH_2CH_2CH_2})$ that has been crystallographically characterized indicates that the structures are similar and the TCH ligand lies in an equatorial coordination site.[7b]

When compound **1** was pyrolyzed in heptane solvent at 97 °C, three new compounds were formed $Os_3(CO)_9(\mu\text{-}\overline{SCH_2CH_2CH_2CH_2C})(\mu\text{-}H)_2$, **2** (20% yield), $Os_3(CO)_8(\mu\text{-}\overline{SCH_2CH_2CH_2CH_2C})[S(CH_2)_5](\mu\text{-}H)_2$, **3** (4%), and $Os_3(CO)_9(\mu\text{-}\overline{SCH_2CH_2CH_2CH_2CH})(\mu\text{-}H)$, **5** (13%) together with some **4** (15%) and $Os_3(CO)_{12}$. Compounds **2**, **3**, and **5** were also obtained from the pyrolysis of **4** at 97 °C, but the yields were lower, 11%, 2%, and 11%, respectively. Compounds **2** (10%), **3** (64%), and **5** (9%) were obtained from the reaction of $Os_3(CO)_{12}$ with TCH in an octane solution at reflux (125 °C) for 4 h.

In order to establish the details of their molecular structures compounds **2**, **3**, and **5** were investigated by single crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **2** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected bond distances and angles are listed in Tables III and IV, respectively. Complex **2** contains a triangular triosmium cluster with three linear terminal carbonyl ligands on each metal atom. There are two bridging hydride ligands, as determined by ^1H NMR spectroscopy, δ = −15.00, −17.50 ppm. The position of one of these H(1) was located and refined in the structural analysis; the position of the other was calculated. The complex contains one thiacyclohexane ligand that has been doubly metalated at one of the carbon atoms α to the sulfur atom. This carbon atom C(5) can be viewed as a carbene center and it bridges the two metal atoms Os(1) and Os(2), Os(1)–C(5) = 2.17(1) Å and Os(2)–C(5) = 2.16(1) Å. The sulfur atom is terminally coordinated to the third metal atom Os(3). The Os(3)–S distance of 2.396(3) Å is similar to those found for the Os–S distances to the terminally coordinated thietane 2.375(5) Å[7b] and tetrahydrothiophene

---

(14) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir, S. E.; Manning, P. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1037.

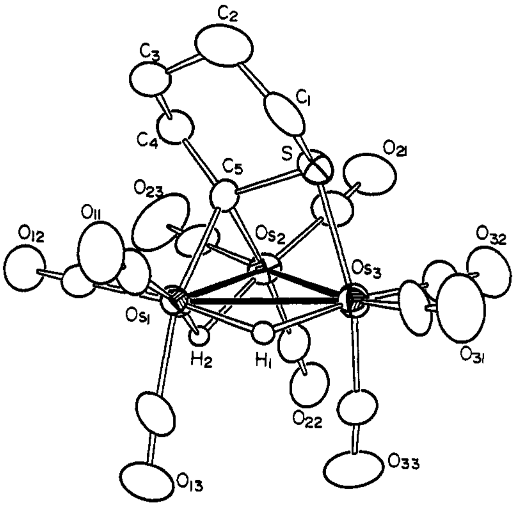


Figure 1. ORTEP diagram of the molecular structure of $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH_2CH_2C)(\mu\text{-}H)_2$, **2**, showing 50% probability thermal ellipsoids.

Table II. Positional Parameters and *B*(eq) for 2

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Os(1)	0.71018(05)	0.34958(03)	0.81668(05)	2.37(2)
Os(2)	0.59145(05)	0.25984(04)	1.01163(06)	2.65(2)
Os(3)	0.93620(05)	0.25019(04)	1.13943(06)	2.51(2)
S	0.8250(03)	0.1205(02)	0.9374(04)	2.9(1)
O(11)	0.8807(10)	0.3303(08)	0.5970(11)	4.7(4)
O(12)	0.3816(10)	0.4011(07)	0.5154(12)	4.9(4)
O(13)	0.8041(11)	0.5625(08)	0.9273(13)	5.4(5)
O(21)	0.5951(15)	0.0639(09)	1.1596(14)	6.6(6)
O(22)	0.5732(11)	0.3855(08)	1.2957(12)	5.7(5)
O(23)	0.2249(12)	0.2620(12)	0.7825(15)	9.5(8)
O(31)	1.2919(11)	0.2135(08)	1.2052(12)	5.5(5)
O(32)	0.9728(12)	0.1307(08)	1.4342(12)	5.5(5)
O(33)	0.9688(13)	0.4446(08)	1.3301(13)	6.3(5)
C(1)	0.9093(15)	0.0952(09)	0.7933(16)	3.6(5)
C(2)	0.7728(17)	0.0489(10)	0.6343(18)	4.5(6)
C(3)	0.6164(15)	0.1154(09)	0.5469(15)	3.6(5)
C(4)	0.5350(13)	0.1454(09)	0.6551(14)	3.1(5)
C(5)	0.6487(11)	0.1993(08)	0.8169(12)	2.4(4)
C(11)	0.8175(14)	0.3360(09)	0.6801(15)	3.4(5)
C(12)	0.5051(15)	0.3824(09)	0.6291(15)	3.2(5)
C(13)	0.7676(15)	0.4852(11)	0.8816(17)	3.9(6)
C(21)	0.5966(15)	0.1368(11)	1.1073(17)	3.9(6)
C(22)	0.5801(13)	0.3383(10)	1.1913(16)	3.5(5)
C(23)	0.3622(15)	0.2640(11)	0.8700(17)	4.2(6)
C(31)	1.1591(15)	0.2314(10)	1.1791(16)	3.7(6)
C(32)	0.9574(14)	0.1748(10)	1.3238(17)	3.7(6)
C(33)	0.9613(15)	0.3703(11)	1.2656(16)	3.7(6)
H(1)	0.924(10)	0.335(07)	0.975(11)	2(2)
H(2)	0.5958	0.3828	0.9365	4.0

Table III. Intramolecular Distances for 2[a]

Os(1)–Os(2)	2.8263(7)	Os(2)–H(2)	1.85
Os(1)–Os(3)	2.9876(7)	Os(3)–S	2.396(3)
Os(1)–C(5)	2.17(1)	Os(3)–C(31)	1.92(1)
Os(1)–C(11)	1.90(1)	Os(3)–C(32)	1.92(1)
Os(1)–C(12)	1.90(1)	Os(3)–C(33)	1.92(1)
Os(1)–C(13)	1.95(1)	Os(3)–H(1)	1.9(1)
Os(1)–H(1)	1.83(8)	S–C(1)	1.81(1)
Os(1)–H(2)	1.85	S–C(5)	1.79(1)
Os(2)–Os(3)	2.8393(6)	C(1)–C(2)	1.55(2)
Os(2)–C(5)	2.16(1)	C(2)–C(3)	1.53(2)
Os(2)–C(21)	1.91(2)	C(3)–C(4)	1.51(2)
Os(2)–C(22)	1.93(1)	C(4)–C(5)	1.54(1)
Os(2)–C(23)	1.90(1)	O–C(av)	1.14(2)

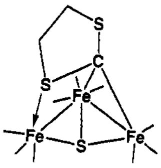
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table IV. Intramolecular Bond Angles for 2[a]

Os(2)–Os(1)–Os(3)	58.39(2)	C(2)–C(3)–C(4)	114(1)
Os(1)–Os(2)–Os(3)	63.65(2)	C(3)–C(4)–C(5)	112(1)
Os(1)–Os(3)–Os(2)	57.96(2)	Os(1)–C(5)–Os(2)	81.4(4)
Os(1)–Os(3)–S	74.40(7)	Os(1)–C(5)–S	112.0(5)
Os(2)–Os(3)–S	70.73(7)	Os(1)–C(5)–C(4)	122.3(7)
Os(3)–S–C(1)	117.3(4)	Os(2)–C(5)–S	100.7(5)
Os(3)–S–C(5)	89.8(4)	Os(2)–C(5)–C(4)	127.4(7)
C(1)–S–C(5)	102.1(5)	S–C(5)–C(4)	109.4(8)
S–C(1)–C(2)	106.1(8)	Os–C(av)–O	178(1)
C(1)–C(2)–C(3)	114(1)		

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

ligands 2.404(4) Å[8] in the compounds $Os_3(CO)_{11}(SCH_2CH_2CH_2)$ and $Os_3(CO)_{10}(SCH_2CH_2CH_2CH_2)_2$. The carbon–sulfur distances are very similar, but the C–S distance to the carbene carbon atom is slightly shorter than the other, C(5)–S = 1.79(1) Å and C(1)–S = 1.81(1) Å. It is known that the C–S distances for thiolate substituted terminal carbenes are significantly shorter than normal C–S single bonds.[15] The carbene–sulfur distance has essentially a normal single bond value when the carbene carbon bridges two metal atoms, as found in the complex $Cp_2Fe_2(CO)_3[\mu\text{-}C(H)SMe)]$, but even in this complex the carbene C–S distance is slightly shorter than the S–C distance to the methyl group, 1.785(9) Å vs 1.804(15) Å.[16] The triiron complex $Fe_3(CO)_9[\mu_3\text{-}CS(CH_2)_2S](\mu_3\text{-}S)$, **6**, contains a triply bridging thiocarbene center similar to that in **2** where the carbene carbon bridges two metal atoms and the sulfur atom is coordinated to the third.[17] In this compound too the C–S distance between the carbene carbon and the coordinated sulfur atom is slightly shorter than the S–C distance between the coordinated sulfur atom and the methylene group, 1.793(4) Å vs 1.825(5) Å. If the shortness of the C–S bond is an indicator of bond strength, this factor could make it more difficult to cleave the carbon–sulfur bond when the carbon atom is transformed into a carbene. At elevated temperatures the hydride resonances in **2** were observed to broaden and merge into a single resonance, T_c = 80 °C, indicating that they are rapidly exchanging sites on the NMR time scale in solution.



6

An ORTEP diagram of the molecular structure of **3** is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected bond distances and angles are listed in Tables VI and VII, respectively. Compound **3** contains two TCH ligands. One of these is an unmodified terminally coordinated ligand that is bonded to the metal Os(1) in an axial position Os(1)–S(1) = 2.446(3) Å. The other TCH has been dimetalated in a fashion analogous

---

(15) Schubert, U. In *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissel, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, 1983.

(16) Schroeder, N. C.; Funchess, R.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1989**, *8*, 521.

(17) Kruger, G. J.; Linford, L.; Raubenheimer, H. G.; Chalmers, A. A. *J. Organomet. Chem.* **1984**, *262*, 69.

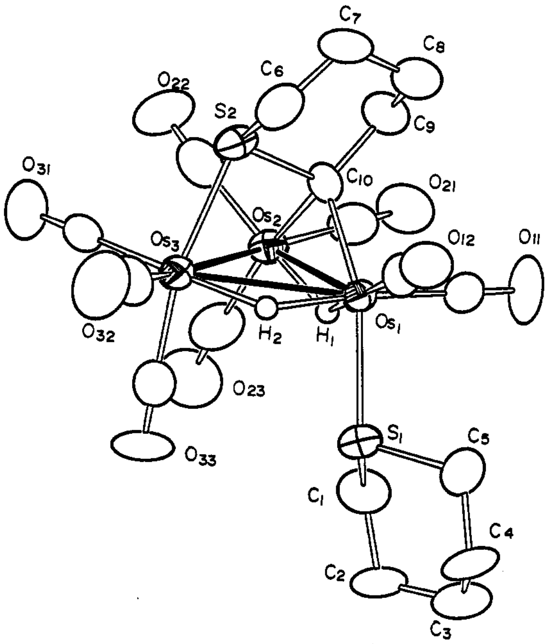


Figure 2. ORTEP diagram of the molecular structure of $\mathrm{Os_3(CO)_8(\mu\text{-}\overline{SCH_2CH_2CH_2CH_2C})[S(CH_2)_5](\mu\text{-}H)_2}$, **3**, showing 50% probability thermal ellipsoids.

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

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Os(1)	0.41702(05)	0.21802(04)	0.31630(02)	2.51(2)
Os(2)	0.68576(05)	0.13018(04)	0.37046(02)	2.84(3)
Os(3)	0.66429(05)	0.37041(04)	0.36256(02)	2.78(3)
S(1)	0.4253(03)	0.2632(02)	0.21300(14)	3.1(1)
S(2)	0.5447(04)	0.3065(03)	0.44516(14)	3.3(1)
O(11)	0.2539(11)	−0.0026(07)	0.2948(05)	6.5(6)
O(12)	0.1340(10)	0.3462(08)	0.3223(04)	5.0(5)
O(21)	0.6031(13)	−0.1185(09)	0.3786(05)	6.8(6)
O(22)	0.8778(13)	0.1223(09)	0.4872(05)	6.3(6)
O(23)	0.9412(12)	0.1043(09)	0.2919(05)	7.6(7)
O(31)	0.9607(12)	0.3868(08)	0.4354(05)	6.1(6)
O(32)	0.5833(12)	0.6223(09)	0.3611(05)	7.0(6)
O(33)	0.8067(12)	0.3693(09)	0.2473(04)	6.2(6)
C(1)	0.5368(15)	0.1590(10)	0.1792(06)	4.4(7)
C(2)	0.5191(15)	0.1772(11)	0.1126(05)	4.3(7)
C(3)	0.3605(20)	0.1582(11)	0.0857(06)	5.7(8)
C(4)	0.2516(17)	0.2383(12)	0.1094(06)	5.2(8)
C(5)	0.2456(13)	0.2269(10)	0.1745(06)	4.2(7)
C(6)	0.3701(14)	0.3714(10)	0.4596(06)	4.2(7)
C(7)	0.2852(14)	0.2877(13)	0.4918(06)	5.0(8)
C(8)	0.2494(15)	0.1743(11)	0.4595(06)	4.7(7)
C(9)	0.3908(15)	0.1107(10)	0.4435(06)	4.4(7)
C(10)	0.4827(12)	0.1822(09)	0.4038(05)	2.9(6)
C(11)	0.3131(14)	0.0822(12)	0.3024(06)	3.8(7)
C(12)	0.2405(14)	0.2956(10)	0.3211(06)	3.2(6)
C(21)	0.6375(16)	−0.0255(13)	0.3751(06)	4.5(7)
C(22)	0.8079(16)	0.1291(11)	0.4439(08)	4.4(8)
C(23)	0.8497(17)	0.1143(11)	0.3234(07)	4.8(8)
C(31)	0.8499(16)	0.3793(11)	0.4082(06)	3.8(7)
C(32)	0.6132(15)	0.5272(12)	0.3614(06)	4.6(8)
C(33)	0.7557(15)	0.3711(10)	0.2889(07)	4.1(7)
H(1)	0.565(10)	0.144(07)	0.313(04)	3.0
H(2)	0.5011	0.3466	0.3218	3.0

to that found for the TCH ligand in compound **2**, and the Os–S distance is identical to that observed in **2**, Os(3)–S = 2.396(3) Å. There is no significant difference between and carbon–sulfur distances in the modified and unmodified TCH ligands in **3**: C(6)–S(2) = 1.82(1) Å, C(10)–S(2) = 1.81(1) Å, C(1)–S(1) = 1.81(1) Å, and C(5)–S(1) = 1.83(1) Å or with those in the modified TCH ligand in **2**. Interestingly, the Os–C distances to the bridging carbene carbon, C(10), are significantly different, Os(1)–C(10) = 2.09(1) Å and Os(2)–C(10) = 2.15(1) Å with the short distance lying *trans* to the sulfur atom of the unmodified TCH ligand. This could be explained by a weaker structural *trans* effect of the TCH ligand compared to that of CO. Compound **3** also contains two hydride ligands, δ = −13.98 and −15.99 ppm, that occupy bridging positions similar to those found in **2**. Note that the hydride ligands are both bonded to the metal Os(1) that contains the unmodified TCH ligand. The tendency of hydride ligands to lie close to strongly donating ligands in osmium clusters has been observed previously.[4c,18]

Table VI. Intramolecular Distances for 3[a]

Os(1)–Os(2)	2.8290(8)	Os(3)–C(32)	1.91(1)
Os(1)–Os(3)	2.9934(8)	Os(3)–C(33)	1.96(2)
Os(1)–S(1)	2.446(3)	Os(3)–H(2)	1.70
Os(1)–C(10)	2.09(1)	S(1)–C(1)	1.81(1)
Os(1)–C(11)	1.87(1)	S(1)–C(5)	1.83(1)
Os(1)–C(12)	1.86(1)	S(2)–C(6)	1.82(1)
Os(1)–H(1)	1.61(9)	S(2)–C(10)	1.81(1)
Os(1)–H(2)	1.70	O–C(av)	1.14(1)
Os(2)–Os(3)	2.8516(7)	C(1)–C(2)	1.54(2)
Os(2)–C(10)	2.15(1)	C(2)–C(3)	1.53(2)
Os(2)–C(21)	1.90(2)	C(3)–C(4)	1.50(2)
Os(2)–C(22)	1.93(2)	C(4)–C(5)	1.51(2)
Os(2)–C(23)	1.93(2)	C(6)–C(7)	1.49(2)
Os(2)–H(1)	1.7(1)	C(7)–C(8)	1.55(2)
Os(3)–S(2)	2.396(3)	C(8)–C(9)	1.56(2)
Os(3)–C(31)	1.90(2)	C(9)–C(10)	1.54(2)

[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)	58.57(2)	C(6)–S(2)–C(10)	101.9(5)
Os(2)–Os(1)–S(1)	114.01(8)	S(1)–C(1)–C(2)	108.7(9)
Os(2)–Os(1)–C(10)	49.0(3)	C(1)–C(2)–C(3)	113(1)
Os(3)–Os(1)–S(1)	97.23(7)	C(2)–C(3)–C(4)	113(1)
Os(3)–Os(1)–C(10)	69.0(3)	C(3)–C(4)–C(5)	113(1)
S(1)–Os(1)–C(10)	161.8(3)	S(1)–C(5)–C(4)	110(1)
Os(1)–Os(2)–Os(3)	63.60(2)	S(2)–C(6)–C(7)	108.0(9)
Os(1)–Os(2)–C(10)	47.3(3)	C(6)–C(7)–C(8)	115(1)
Os(3)–Os(2)–C(10)	71.4(3)	C(7)–C(8)–C(9)	113(1)
Os(1)–Os(3)–Os(2)	57.83(2)	C(8)–C(9)–C(10)	112(1)
Os(1)–Os(3)–S(2)	73.41(8)	Os(1)–C(10)–Os(2)	83.8(4)
Os(2)–Os(3)–S(2)	70.65(7)	Os(1)–C(10)–S(2)	112.9(5)
Os(1)–S(1)–C(1)	109.7(5)	Os(1)–C(10)–C(9)	124.1(8)
Os(1)–S(1)–C(5)	108.3(4)	Os(2)–C(10)–S(2)	100.7(5)
C(1)–S(1)–C(5)	98.0(6)	Os(2)–C(10)–C(9)	125.5(8)
Os(3)–S(2)–C(6)	118.5(5)	S(2)–C(10)–C(9)	106.9(8)
Os(3)–S(2)–C(10)	88.8(4)	Os–C–O(av)	177(1)

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

An ORTEP diagram of the molecular structure of **5** is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected bond distances and angles are listed in Tables IX and X, respectively. Compound **5** contains a triangular triosmium cluster with nine linear terminal carbonyl ligands, three on each metal atom. The complex contains only one thiacyclohexane ligand and it has been metalated only once at one of the carbon atoms α to the sulfur atom. This carbon atom C(5) can be viewed as an alkyl center and it occupies an axial site on Os(2), Os(2)–C(5) = 2.18(2) Å. The sulfur atom is a bridge across the Os(1)–Os(3) bond and the Os–S distances, Os(1)–S = 2.315(4) Å and Os(3)–S = 2.344(4) Å, are significantly shorter than those to the terminally coordinated ligands described above and also shorter than the Os–S distances typically observed for bridging thiolate

---

(18) Adams, R. D.; Selegue, J. P. *J. Organomet. Chem.* **1980**, *195*, 223.

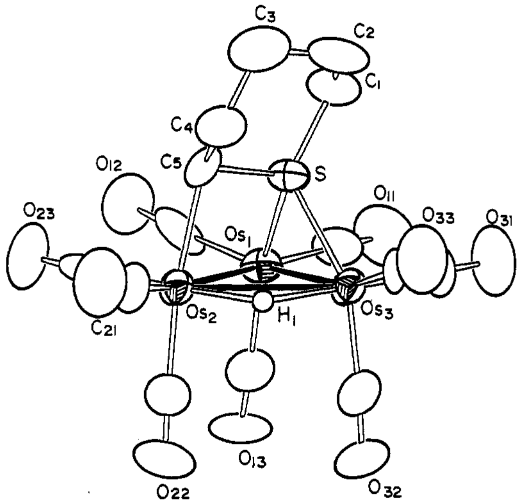


Figure 3. ORTEP diagram of the molecular structure of $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH_2CH_2CH)(\mu\text{-}H)$, **5**, showing 50% probability thermal ellipsoids.

Table VIII. Positional Parameters and *B*(eq) for 5

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Os(1)	0.36143(08)	0.33297(05)	0.56220(09)	3.22(3)
Os(2)	0.39952(08)	0.18779(04)	0.71553(09)	3.00(3)
Os(3)	0.24059(08)	0.34970(04)	0.83078(08)	3.09(3)
S	0.1351(05)	0.2781(03)	0.5316(05)	3.3(2)
O(11)	0.2577(20)	0.5041(12)	0.446(02)	8.3(9)
O(12)	0.4342(18)	0.2311(10)	0.2363(18)	6.6(7)
O(13)	0.6800(16)	0.3932(10)	0.7935(19)	6.4(7)
O(21)	0.3701(19)	0.0328(10)	0.854(02)	7.0(8)
O(22)	0.7055(17)	0.2454(11)	0.996(02)	8.1(8)
O(23)	0.5358(19)	0.0822(10)	0.444(02)	7.1(8)
O(31)	0.108(02)	0.5257(11)	0.776(02)	9(1)
O(32)	0.5143(17)	0.4246(10)	1.147(02)	7.4(7)
O(33)	0.0412(19)	0.3212(11)	1.030(02)	7.8(8)
C(1)	–0.055(02)	0.2916(15)	0.395(02)	6(1)
C(2)	–0.152(02)	0.242(02)	0.445(03)	8(1)
C(3)	–0.111(02)	0.1449(18)	0.431(03)	7(1)
C(4)	0.047(02)	0.1297(12)	0.563(02)	4.7(8)
C(5)	0.1712(19)	0.1667(11)	0.524(02)	3.6(7)
C(11)	0.297(02)	0.4384(14)	0.488(02)	4.6(8)
C(12)	0.4106(18)	0.2714(13)	0.370(03)	4.7(8)
C(13)	0.564(02)	0.3736(13)	0.712(03)	4.7(9)
C(21)	0.384(02)	0.0940(13)	0.811(03)	4.7(8)
C(22)	0.593(02)	0.2238(13)	0.887(03)	5.1(9)
C(23)	0.4853(19)	0.1236(12)	0.552(03)	4.3(8)
C(31)	0.160(02)	0.4592(12)	0.799(03)	4.8(8)
C(32)	0.406(02)	0.3971(12)	1.030(03)	4.8(8)
C(33)	0.119(02)	0.3347(13)	0.954(02)	5.2(8)

Table IX. Intramolecular Distances for 5[a]

Os(1)–Os(2)	2.848(1)	Os(3)–S	2.344(4)
Os(1)–Os(3)	2.795(1)	Os(3)–C(31)	1.88(2)
Os(1)–S	2.315(4)	Os(3)–C(32)	1.88(2)
Os(1)–C(11)	1.90(2)	Os(3)–C(33)	1.86(2)
Os(1)–C(12)	1.84(2)	Os(3)–H(1)	1.81
Os(1)–C(13)	1.95(2)	S–C(1)	1.78(2)
Os(2)–Os(3)	2.969(1)	S–C(5)	1.76(2)
Os(2)–C(5)	2.18(2)	O–C(av)	1.15(2)
Os(2)–C(21)	1.91(2)	C(1)–C(2)	1.50(3)
Os(2)–C(22)	1.92(2)	C(2)–C(3)	1.54(4)
Os(2)–C(23)	1.86(2)	C(3)–C(4)	1.55(3)
Os(2)–H(1)	1.76	C(4)–C(5)	1.54(2)

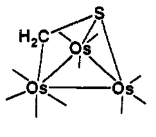
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table X. Intramolecular Bond Angles for 5[a]

Os(2)–Os(1)–Os(3)	63.48(3)	Os(3)–S–C(1)	124.7(7)
Os(2)–Os(1)–S	67.0(1)	Os(3)–S–C(5)	105.9(5)
Os(3)–Os(1)–S	53.6(1)	C(1)–S–C(5)	108(1)
Os(1)–Os(2)–Os(3)	57.39(3)	S–C(1)–C(2)	107(1)
Os(1)–Os(2)–C(5)	79.5(5)	C(1)–C(2)–C(3)	115(2)
Os(3)–Os(2)–C(5)	78.0(4)	C(2)–C(3)–C(4)	112(2)
Os(1)–Os(3)–Os(2)	59.12(3)	C(3)–C(4)–C(5)	111(2)
Os(1)–Os(3)–S	52.7(1)	Os(2)–C(5)–S	93.3(7)
Os(2)–Os(3)–S	64.5(1)	Os(2)–C(5)–C(4)	122(1)
Os(1)–S–Os(3)	73.7(1)	S–C(5)–C(4)	109(1)
Os(1)–S–C(1)	133.4(8)	Os–C–O(av)	177(2)
Os(1)–S–C(5)	105.2(6)		

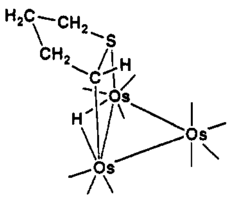
[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

ligands, 2.40–2.43 Å.[6c,19] The compound $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$, **7**,contains a triply thioformaldehyde ligand with sulfur bridging two metal atoms and has probably the closest coordination resemblance to the metalated TCH ligand in **5** and it too has Os–S distances, 2.415(6) Å, that are significantly longer than those found in **5**.[20]



7

The carbon–sulfur distances are similar to those observed in the TCH ligands described above, C(1)–S = 1.78(2) Å and C(5)–S = 1.76(1) Å. Compound **5** contains one hydride ligand. It was located in a credible position in a difference Fourier synthesis, but its position could not be refined. As expected, the hydride ligand produces a lengthening in the associated metal–metal bond, Os(2)–Os(3) = 2.969(1) Å vs Os(1)–Os(2) = 2.848(1) Å and Os(1)–Os(3) = 2.795(1) Å.[21] The ^1H NMR spectrum of **5** in the hydride region shows two resonances at $\delta = -16.95$ (s) and -17.12 (d, $J_{H-H} = 3.2$) ppm in a ratio of 0.39/1, which idicates the compound exists in solution as a mixture of isomers. One hydride ligand shows long range coupling to the resonance at 3.02 ppm. This isomer probably represents the isomer found in the solid state and the coupling, $J_{H-H} = 3.2$, is to the single hydrogen atom on C(5). A similar coupling was observed for the complex $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}(SCH_2CH_2CH_2CH)](\mu\text{-}H)$, **8**, obtained from the pyrolysis of $Os_3(CO)_{10}[(SCH_2CH_2CH_2CH_2)]_2$ which



8

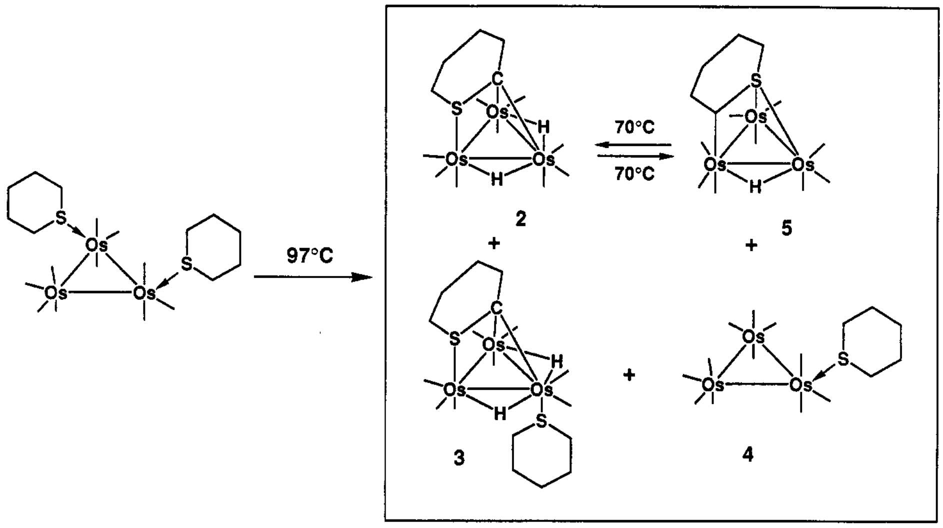
---

(19) (a) Adams, R. D.; Babin, J. E.; Kim, H. S. *Organometallics* **1987**, *6*, 749. (b) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* 1977, *140*, 297. (c) Johnson, B. F. G.; Lewis, J.; Pipard, D.; Raithby, P. R. *Acta Crystallogr.* **1980**, *B36*, 703. (d) Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Uden, G. *Acta Crystallogr.* **1983**, *C39*, 1200. (e) Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Uden, G. *Acta Crystallogr.* **1983**, *C39*, 1203. (f) Adams, R. D.; Golembeski, N.; Selegue, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546.

(20) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1987**, *6*, 1717.

(21) (a) Teller, R. G.; Bau, R. *Struct. Bonding* **1981**, *44*, 1. (b) Bau, R., Ed. *Transition Metal Hydrides*; ACS Advances in Chemistry Series No. 167; American Chemical Society: Washington, DC, 1978.

Scheme I



contains a metalated tetrahydrothiophene ligand bridging the edge of the cluster.[8] The other isomer is probably formed by a repositioning of the hydride ligand to a bridging position across one of the other metal–metal bonds. It was found that the two hydride resonances broaden and merge into a single resonance at higher temperatures, $T_c = 50$ °C, indicating the isomers are rapidly interconverting on the NMR time scale at slightly elevated temperatures in solution. Dynamic hydride shifting has been observed in similar trinuclear metal cluster complexes.[22]

Although they can be isolated in pure forms, compounds **2** and **5** are isomers and they can be isomerized if heated. The equilibrium ratio of **2**/**5** was found to be 1/2 by heating separate samples of **2** and **5** to 70 °C for 24 h.

A summary of the results of this study is presented in Scheme I. As expected, the disubstituted TCH compound **1** and the monosubstituted TCH compound **4** were formed in good yields by replacement of the NCMe ligand in the reactions of TCH with $Os_3(CO)_{10}(NCMe)_2$ and $Os_3(CO)_{11}(NCMe)$ at 25 °C.[14] When heated, these compounds lose two ligands to form the complexes **2**, **3**, and **5** which contain a TCH ligand that has been metalated by CH activation at one of the carbon atoms α to the sulfur atom. In compound **5** the sulfur atom has adopted a bridging position and serves as a four electron donor, thus only a single CH activation has occurred. However, in compounds **2** and **3** the sulfur atom occupies a terminal position, serving as a two electron donor, and thus a double CH activation has occurred at the α carbon atom.

Our previous studies of the bis(tetrahydrothiophene) complex $Os_3(CO)_{10}[(\overline{SCH_2CH_2CH_2CH_2})]_2$ showed that its pyrolysis at 125 °C produced the loss of only one ligand (one of the $(\overline{SCH_2CH_2CH_2CH_2})$ ligands) and a single CH activation to yield complex **8** that contains an edge bridging $(\overline{SCH_2CH_2CH_2CH})$ ligand. The decarbonylation of **8** did not lead to triply bridging ligands, but instead resulted in a carbon–sulfur bond cleavage with an opening of the heterocyclic ring.[8] Carbon–sulfur bond cleavage has not yet been observed in our studies of the transformations of the six membered heterocycle TCH. Interestingly, Wiegand et al. have observed that ring opening of TCH on molybdenum surfaces is considerably more difficult than that of the smaller saturated ring thioethers and is the rate limiting step in its thermal decomposition.[23]

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 (9 pages). Ordering information is given on any current masthead page.

OM930580R

---

(22) Farrugia, L. J.; Rae, S. E. *Organometallics* **1992**, *11*, 196.

(23) Wiegand, B. C.; Friend, C. M.; Roberts, J. T. *Langmuir* **1989**, *5*, 1292.