Organometallics **1993,** *12,* 951-954

Partial Oxidation of the Triosmium Cluster Complex $Os_3(CO)_{10}[\mu\text{-}(SCH_2CMe_2CH_2)_3]$ with Ferrocenium Ion

Richard D. Adams,* Michael P. Pompeo, and John H. Yamamoto

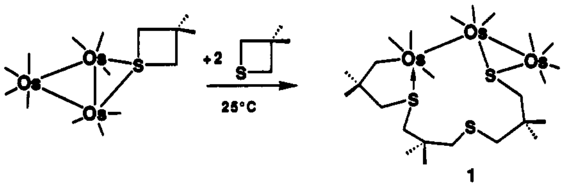
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received March 26, 1992

Summary: The complex $Os_3(CO)_{10}[\mu\text{-}(SCH_2CMe_2CH_2)_3]$, 1, was found to react with $[Cp_2Fe]^+$ at 25 °C in the presence of acetic anhydride to yield the new complex $Os_3(CO)_9(O_2CCH_3)_2[\mu\text{-}SCH_2CMe_2CH_2)_3]$, 2, by decarbonylation and a selective oxidation of one of the osmium atoms of the cluster. Two acetate ligands became coordinated to that metal atom. Treatment of 2 with carbon monoxide at 75 °C resulted in the removal of the oxidized osmium fragment from the cluster to produce the dinuclear complex $Os_2(CO)_5[\mu\text{-}\eta^2\text{-}O{=}C(SCH_2CMe_2CH_2)_3]$, 3. Both 2 and 3 were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analysis. Crystallographic data: 2, space group $P2_1/n$, a = 13.474(2) Å, b = 23.059(4) Å, c = 16.022(3) Å, β = 98.92(1)°, Z = 4, 3293 reflections, R = 0.035; 3, space group $P\bar{1}$, a = 13.813(2) Å, b = 15.776(3) Å, c = 13.306(3) Å, α = 107.68(2)°, β = 99.94(2)°, γ = 79.27(2)°, Z = 4, 4529 reflections, R = 0.025.

Introduction

In recent studies we have shown that bridging coordination of thietanes activates these molecules toward nucleophilic ring-opening addition reactions.[1,2] We have also found an example of a cluster-assisted ring-opening oligomerization of 3,3-dimethylthietane (3,3-DMT) to yield the complex $Os_3(CO)_{10}[\mu\text{-}(SCH_2CMe_2CH_2)_3]$, 1 (eq 1), containing an unusual 11-osmio-2,2,6,6,10,10-hexamethyl-4,8-dithiaundecanethiolato ligand that appears to proceed by this same mechanism.[3]



(1)

1

In an effort to remove the ligand from this complex, we investigated the thermal transformations of 1 by mild heating and its reaction with carbon monoxide at elevated temperature and pressure.[3] The thiolato ligand was found to be very stable but could be carbonylated at the C-terminus to produce an acyl grouping that bridges two of the metal atoms of a triosmium cluster.

It is well established that oxidation can promote ligand elimination in metal complexes.[4] Accordingly, we have investigated the reaction of 1 with the mild oxidant ferrocenium ion. With an excess of this oxidant the complex is completely degraded and the ligand could not be recovered. However, with a limited amount of oxidant, a partially oxidized complex $Os_3(CO)_9(O_2CCH_3)_2[\mu\text{-}(SCH_2CMe_2CH_2)_3]$, 2, was formed. This complex was isolated and structurally characterized. It was subsequently degraded further by treatment with carbon monoxide to yield to the diosmium complex $Os_2(CO)_5[\mu\text{-}\eta^2\text{-}O{=}C(SCH_2CMe_2CH_2)_3]$, 3. Compound 3 was also characterized crystallographically. The results of this study are reported here.

Experimental Section

General Data. Reagent grade solvents were dried with appropriate drying agents and stored over 4-Å molecular sieves. The compounds $Os_3(CO)_{10}[\mu_3\text{-}(SCH_2CMe_2CH_2)_3]$, 1, and $[Cp_2Fe]^+PF_6^-$ were prepared as described.[3,5] 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 Bruker AM-300 or AM-500 spectrometer operating at 300 or 500 MHz, respectively. Mass spectral analysis was performed on a VG model 70SQ spectrometer using electron impact ionization. Chromatographic separations were performed in air on Analtech silica gel (0.25 mm) F_{254} Uniplates. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Reaction of 1 with $[(Cp)_2Fe]^+$. A solution of $[(Cp)_2Fe]PF_6$ (11.8 mg, 0.036 mmol) in 1 mL of MeCN was added to a CH_2Cl_2 solution (containing 0.5 mL of Ac_2O) of 1 (20.4 mg, 0.0176 mmol). The solution was stirred for 3 h at 25 °C. The solvents were removed in vacuo, and the residue was chromatographed by TLC. Elution with a 3/1 (v/v) hexane/acetone solvent mixture yielded pale yellow $Os_3(CO)_9(O_2CMe)_2[\mu\text{-}(SCH_2CMe_2CH_2)_3]$, 2 (15.8 mg, 71%). Data for 2 are as follows. IR ν(CO) (cm^{-1}) in CH_2Cl_2: 2110, m, 2087, w, 2033, m, 2009, s, 1991, vs, 1973, m (sh), 1960, w (sh), 1634, m, 1613, w, 1366, w, 1309, m. ^1H NMR (δ in CD_2Cl_2 at -57 °C): 3.45-2.20 (m, 12 H), 2.04 (s, 3 H), 2.02 (s, 3 H), 1.37 (s, 3 H), 1.14 (s, 3 H), 1.11 (s, 3 H), 1.08 (s, 3 H), 1.05 (s, 3 H), 1.03 (s, 3 H). Anal. Calcd (found): C, 29.96 (29.44); H, 2.91 (2.98).

Carbonylation of 2. A 50-mL Parr autoclave was charged with a solution of 2 (23.0 mg, 0.018 mmol) in 15 mL of acetone. The vessel was purged twice with CO and then filled to 450 psi and sealed. After the mixture was stirred in an oil bath at 75 °C for 3 h, the vessel was vented and the contents removed. The solvent was removed in vacuo, and the residue was chromatographed by TLC. Elution with pure hexanes separated colorless $Os_2(CO)_5[\mu\text{-}\eta^2\text{-}O{=}C(SCH_2CMe_2CH_2)_3]$, 3 (6.5 mg, 54%, based on amount of 2 consumed), from unreacted 2 (5.5 mg). A small amount (3 mg) of $Os_3(CO)_{12}$ was also obtained. Data for 3 are as follows. IR ν(CO) (cm^{-1}) in hexane: 2085 m, 2051 vs, 2006 vs, 1994 s, 1987 w sh, 1972 m. ^1H NMR (δ in $CDCl_3$): 3.57-2.02 (m, 12 H), 1.19 (s, 3 H), 1.14 (s, 3 H), 1.04 (s, 3 H), 0.99 (s, 3 H), 0.94

---

(1) (a) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1991,** *10,* 2539. (b) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992,** *11,* 1460.

(2) (a) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1992,** *11,* 3129. (b) Adams, R. D.; Belinski, J. A. *Organometallics* **1992,** *11,* 2488. (c) Adams, R. D.; E. Cortopassi, J.; Falloon, S. B. *Organometallics* **1992,** *11,* 3794.

(3) Adams, R. D.; Pompeo, M. P. *J. Am. Chem. Soc.* **1991,** *113,* 1619.

(4) (a) Johnson, M. D. *Acc. Chem. Res.* **1978,** *11,* 57. (b) Lau, W.; Huffman, J. C.; Kochi, J. *Organometallics* **1982,** *1,* 155. (c) Pinhas, A. R.; Herschberger, J. W. *Organometallics* **1990,** *9,* 2840. (d) Tsou, T. T.; Kochi, J. *J. Am. Chem. Soc.* **1978,** *100,* 1634.

(5) Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971,** *10,* 1559.

0276-7333/93/2312-0951$04.00/0

Table I. Crystallographic Data for Compounds 2 and 3

	compd	
	2	3
empirical formula	$Os_3S_3O_{13}C_{28}H_{36}\cdot C_{12}H_{10}$	$Os_2S_3O_6C_{21}H_{30}$
fw	1247.36	855.04
cryst system	monoclinic	triclinic
lattice params		
a (Å)	13.474(2)	13.813(2)
b (Å)	23.059(4)	15.776(3)
c (Å)	16.022(3)	13.306(3)
α (deg)		107.68(2)
β (deg)	98.92(1)	99.94(2)
γ (deg)		79.27(2)
V (Å^3)	4918(1)	2693.4(9)
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z value	4	4
D_{calc} (g/cm^3)	1.68	2.11
μ(Mo Kα) (cm^{-1})	79.04	96.90
temp (°C)	20	20
no. of observns ($I > 3\sigma(I)$)	3293	4529
residuals: R; R_w	0.035; 0.035	0.025; 0.030
goodness of fit indicator	1.63	1.89
final cycle	0.09	0.02
largest peak in final diff map (e/Å^3)	1.12	0.89
abs corr	empirical	empirical

(s, 3 H), 0.74 (s, 3 H). Mass spectral analysis (m/e) (70 eV, 80 °C) for ^{192}Os = 855 − 28x, x = 0–5 {[M$^+$] − x(CO)}.

Crystallographic Analyses. Pale yellow crystals of **2** and **3** were grown by slow evaporation of solvent from heptane/CH$_2$Cl$_2$/benzene solutions at 25 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. 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.[6a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[6b] Full matrix least-squares refinements minimized the function

$$\sum_{hkl} w(|F_o| - |F_c|)^2$$

where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. For both structures all hydrogen atom positions were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

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

Compound **3** crystallized in the triclinic crystal system with two independent molecules in the unit cell. 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.

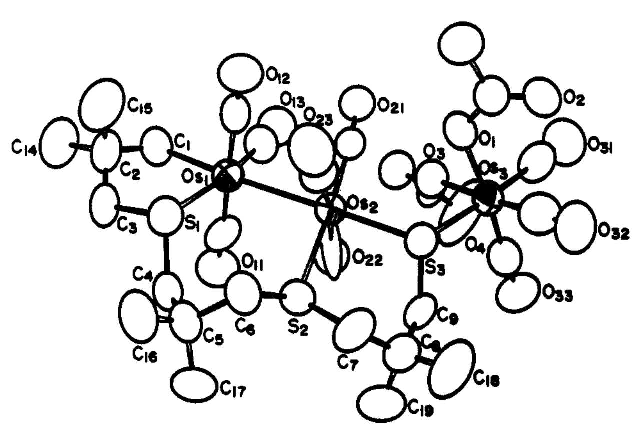
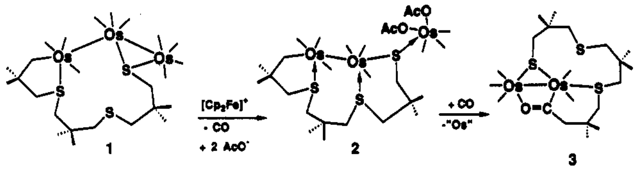


Figure 1. ORTEP drawing of $Os_3(CO)_9(O_2CCH_3)_2[\mu\text{-}(SCH_2CMe_2CH_2)_3]$, **2**, showing 50% probability thermal ellipsoids.

Scheme I



Results and Discussion

Our study of the reaction of **1** with 2 equiv of [(Cp)$_2$Fe]$^+$ in acetic anhydride resulted in decarbonylation and oxidation of one of the osmium atoms of the cluster to form the new complex $Os_3(CO)_9(O_2CCH_3)_2[\mu\text{-}(SCH_2CMe_2CH_2)_3]$, **2**; see Scheme I. Compound **2** was characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected interatomic distances and angles are listed in Tables III and IV. Compound **2** consists of a fragmented cluster of three metal atoms in which only two are mutually bonded (Os(1)–Os(2) = 2.9950(9) Å). Metal atom Os(3) is formally in the +2 oxidation state and contains two acetate ligands that were derived from the acetic anhydride present in the reaction solution. This group is linked to the remainder of the molecule through a coordinate bond to the thiolate sulfur atom S(3). The C-terminus of the ligand is part of a dimethylthiametallacyclopentane ring containing Os(1) (Os(1)–C(1) = 2.18 (1) and Os(1)–S(1) = 2.420(5) Å). A similar group was found in **1**. Complex **2** shows broad resonances in the ^{1}H NMR spectrum at 25 °C due to fluxionality, but at −57 °C all of the expected resonances including six singlets for the methyl groups of the thiolate ligand and one singlet for each methyl group on the two acetate ligands were clearly displayed.

Treatment of **2** with CO (450 psi/75 °C) resulted in the removal of the acetate containing osmium fragment from the complex and an insertion of a CO moiety into the metal–carbon bond at the C-terminus of the thiolate ligand to form an acyl group in the new complex $Os_2(CO)_5[\mu\text{-}\eta^2\text{-}O{=}C(SCH_2CMe_2CH_2)_3]$, **3**. Compound **3** was characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 2. The crystal of **2** contains two symmetry-independent but structurally similar molecules. Final atomic positional parameters and selected interatomic

---

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

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

atom	*x*	*y*	*z*	*B*(eq)
Os(1)	0.859497(05)	0.04932(03)	0.26621(04)	5.31(3)
Os(2)	0.70320(05)	0.13488(03)	0.30871(04)	4.95(3)
Os(3)	0.40506(05)	0.18664(03)	0.25083(05)	5.62(4)
S(1)	0.9960(03)	0.08010(18)	0.3690(03)	6.3(2)
S(2)	0.8252(03)	0.21244(17)	0.3483(03)	5.9(2)
S(3)	0.5739(03)	0.20635(17)	0.3240(03)	5.8(2)
O(1)	0.4266(08)	0.1135(05)	0.3245(07)	6.8(6)
O(2)	0.2871(09)	0.1218(05)	0.3816(09)	9.5(8)
O(3)	0.4657(08)	0.1329(05)	0.1702(07)	6.4(6)
O(4)	0.4012(15)	0.1745(08)	0.0547(09)	16(1)
O(11)	0.9336(10)	0.1268(06)	0.1369(08)	9.6(9)
O(12)	0.7753(10)	−0.0250(05)	0.4009(09)	9.6(9)
O(13)	0.7079(10)	−0.0059(05)	0.1263(09)	9.1(8)
O(21)	0.5693(08)	0.0306(05)	0.2649(08)	7.6(7)
O(22)	0.7044(08)	0.1666(05)	0.1257(08)	7.5(7)
O(23)	0.7266(09)	0.0950(06)	0.4915(08)	9.3(8)
O(31)	0.1918(11)	0.1548(07)	0.1738(10)	11(1)
O(32)	0.3310(10)	0.2599(06)	0.3852(10)	10(1)
O(33)	0.3880(10)	0.2931(06)	0.1397(08)	8.7(8)
C(1)	0.9624(12)	−0.0181(07)	0.2456(11)	7(1)
C(2)	1.0574(13)	−0.0232(08)	0.3087(13)	7(1)
C(3)	1.0952(12)	0.0369(08)	0.3329(13)	8(1)
C(4)	1.0412(11)	0.1528(06)	0.3500(10)	5.7(8)
C(5)	1.0294(11)	0.1960(07)	0.4213(11)	6(1)
C(6)	0.9197(11)	0.1933(07)	0.4371(09)	6.1(9)
C(7)	0.7625(13)	0.2689(07)	0.4027(12)	8(1)
C(8)	0.6909(14)	0.3073(08)	0.3465(12)	7(1)
C(9)	0.6167(12)	0.2737(07)	0.2812(12)	7(1)
C(11)	0.9009(14)	0.0979(07)	0.1850(11)	7(1)
C(12)	0.8059(12)	0.0031(08)	0.3504(12)	7(1)
C(13)	0.7600(13)	0.0162(08)	0.1810(11)	7(1)
C(14)	1.1383(14)	−0.0597(08)	0.2799(13)	10(1)
C(15)	1.0319(16)	−0.0544(09)	0.3916(14)	11(1)
C(16)	1.0971(13)	0.1805(08)	0.5020(13)	9(1)
C(17)	1.0553(13)	0.2559(07)	0.3902(12)	8(1)
C(18)	0.6329(16)	0.3418(09)	0.4026(14)	11(1)
C(19)	0.7507(16)	0.3471(08)	0.2935(16)	11(1)
C(21)	0.6151(12)	0.0721(07)	0.2787(11)	6(1)
C(22)	0.7103(13)	0.1624(11)	0.2007(13)	12(2)
C(23)	0.7174(13)	0.1098(07)	0.4215(11)	6(1)
C(31)	0.2709(15)	0.1663(08)	0.2043(11)	7(1)
C(32)	0.3580(14)	0.2296(08)	0.3321(12)	7(1)
C(33)	0.3976(13)	0.2507(08)	0.1801(12)	7(1)
C(41)	0.3657(15)	0.0982(08)	0.3728(13)	7(1)
C(43)	0.3960(15)	0.0423(09)	0.4227(14)	11(1)
C(43)	0.4513(14)	0.1360(08)	0.0931(14)	7(1)
C(44)	0.4894(13)	0.0910(08)	0.0394(11)	8(1)

Table III. Intramolecular Distances for 2[a]

Os(1)–Os(2)	2.9950(9)	S(1)–C(3)	1.83(2)
Os(1)–S(1)	2.420(5)	S(1)–C(4)	1.82(1)
Os(1)–C(1)	2.18(1)	S(2)–C(6)	1.81(2)
Os(1)–C(11)	1.89(2)	S(2)–C(7)	1.84(2)
Os(1)–C(12)	1.92(2)	S(3)–C(9)	1.83(2)
Os(1)–C(13)	1.88(2)	O(1)–C(41)	1.26(2)
Os(2)–S(2)	2.445(4)	O(2)–C(41)	1.22(2)
Os(2)–S(3)	2.438(4)	O(3)–C(43)	1.22(2)
Os(2)–C(21)	1.89(2)	O(4)–C(43)	1.22(2)
Os(2)–C(22)	1.86(2)	O–C(av)	1.15(2)
Os(2)–C(23)	1.88(2)	C(1)–C(2)	1.51(2)
Os(3)–S(3)	2.435(4)	C(2)–C(3)	1.51(2)
Os(3)–O(1)	2.05(1)	C(4)–C(5)	1.54(2)
Os(3)–O(3)	2.05(1)	C(5)–C(6)	1.54(2)
Os(3)–C(31)	1.90(2)	C(7)–C(8)	1.50(2)
Os(3)–C(32)	1.83(2)	C(8)–C(9)	1.54(2)
Os(3)–C(33)	1.85(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)–S(1)	98.3(1)	C(6)–S(2)–C(7)	96.8(8)
Os(2)–Os(1)–C(1)	174.4(4)	Os(2)–S(3)–Os(3)	117.0(2)
S(1)–Os(1)–C(1)	80.9(5)	Os(2)–S(3)–C(9)	105.4(5)
Os(1)–Os(2)–S(2)	94.9(1)	Os(3)–S(3)–C(9)	107.7(6)
Os(1)–Os(2)–S(3)	172.7(1)	Os(3)–O(1)–C(41)	122(1)
S(2)–Os(2)–S(3)	86.7(1)	Os(3)–O(3)–C(43)	126(1)
S(3)–Os(3)–O(1)	80.7(3)	Os(1)–C(1)–C(2)	118(1)
S(3)–Os(3)–O(3)	89.0(3)	S(1)–C(3)–C(2)	110(1)
O(1)–Os(3)–O(3)	80.3(4)	S(1)–C(4)–C(5)	113(1)
Os(1)–S(1)–C(3)	99.2(6)	S(2)–C(6)–C(5)	116(1)
Os(1)–S(1)–C(4)	113.8(5)	S(2)–C(7)–C(8)	116(1)
C(3)–S(1)–C(4)	99.7(8)	S(3)–C(9)–C(8)	113(1)
Os(2)–S(2)–C(6)	112.8(5)	Os–C–O(av)	177(2)
Os(2)–S(2)–C(7)	107.5(6)		

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

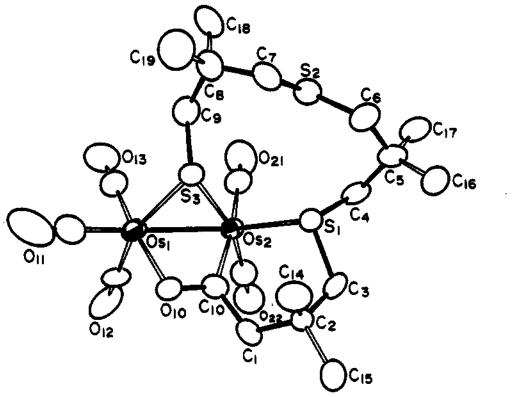


Figure 2. ORTEP diagram of $Os_2(CO)_5[\mu\text{-}\eta^2\text{-}O{=}C(SCH_2CMe_2CH_2)_3]$, **3**, showing 50% probability thermal ellipsoids.

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

atom	*x*	*y*	*z*	*B*(eq)
Os(1A)	0.37936(03)	0.19819(03)	0.34898(03)	2.91(2)
Os(2A)	0.35118(03)	0.31621(02)	0.54129(03)	2.41(2)
S(1A)	0.41987(18)	0.33194(16)	0.72211(18)	2.7(1)
S(2A)	0.2531(02)	0.20916(18)	0.7591(02)	3.8(1)
S(3A)	0.38695(19)	0.15343(16)	0.50760(19)	2.9(1)
O(10A)	0.5191(05)	0.2427(04)	0.4265(05)	3.3(3)
O(11A)	0.4850(06)	0.0283(05)	0.2015(06)	5.6(4)
O(12A)	0.3477(07)	0.3253(06)	0.2116(07)	6.4(5)
O(13A)	0.1725(07)	0.1561(07)	0.2615(07)	7.5(6)
O(21A)	0.1280(06)	0.3371(05)	0.5516(06)	5.3(4)
O(22A)	0.3150(06)	0.5026(05)	0.5154(06)	5.1(4)
C(1A)	0.5701(07)	0.3641(06)	0.5670(08)	3.2(5)
C(2A)	0.5990(07)	0.3678(06)	0.6845(07)	2.9(5)
C(3A)	0.5140(07)	0.4072(06)	0.7509(07)	3.1(5)
C(4A)	0.3329(07)	0.3913(06)	0.8159(07)	3.0(4)
C(5A)	0.3394(07)	0.3533(07)	0.9096(07)	3.4(5)
C(6A)	0.3470(08)	0.2506(07)	0.8711(07)	4.0(5)
C(7A)	0.3234(07)	0.1028(07)	0.6988(09)	3.9(5)
C(8A)	0.2808(08)	0.0534(06)	0.5856(09)	3.9(5)
C(9A)	0.2728(08)	0.1083(07)	0.5068(08)	3.9(5)
C(10A)	0.4938(07)	0.3037(06)	0.5084(07)	2.6(4)
C(11A)	0.4463(08)	0.0913(08)	0.2542(08)	3.5(5)
C(12A)	0.3622(08)	0.2777(08)	0.2639(09)	4.2(6)
C(13A)	0.2506(09)	0.1720(08)	0.2947(09)	4.5(6)
C(14A)	0.6483(08)	0.2765(07)	0.6944(08)	4.1(5)
C(15A)	0.6777(08)	0.4342(08)	0.7287(08)	4.5(6)
C(16A)	0.4318(08)	0.3736(08)	0.9884(08)	4.6(6)
C(17A)	0.2452(08)	0.3936(07)	0.9634(08)	4.2(5)
C(18A)	0.1749(09)	0.0356(07)	0.5862(10)	5.4(6)
C(19A)	0.3456(09)	−0.0352(07)	0.5489(10)	5.6(6)
C(21A)	0.2113(09)	0.3262(06)	0.5496(08)	3.3(5)
C(22A)	0.3283(07)	0.4325(07)	0.5271(08)	3.2(5)

distances and angles for one of these molecules (A) are listed in Tables V–VII. A listing of the values for the second molecule is included with the supplementary material accompanying this report. The complex contains two mutually bonded osmium atoms, Os(1)–Os(2) = 2.7102(8) Å [2.7059(8) Å], that are bridged by groups at both terminii of the ligand: a bridging sulfur atom S(1) and a μ-η^2-coordinated acyl group, with Os(1A)–O(10A) = 2.159(6) Å [2.152(6) Å] and Os(2A)–C(10A) = 2.05(1) Å [2.07(1) Å]. The C–O bond distance in the acyl group,

Table VI. Intramolecular Distances for 3[a]

Os(1A)–Os(2A)	2.7102(8)	S(2A)–C(6A)	1.84(1)
Os(1A)–S(3A)	2.401(3)	S(2A)–C(7A)	1.80(1)
Os(1A)–O(10A)	2.159(6)	S(3A)–C(9A)	1.84(1)
Os(1A)–C(11A)	1.95(1)	O(10A)–C(10A)	1.27(1)
Os(1A)–C(12A)	1.89(1)	O–C(av)	1.14(1)
Os(1A)–C(13A)	1.87(1)	C(1A)–C(2A)	1.53(1)
Os(2A)–S(1A)	2.385(2)	C(1A)–C(10A)	1.51(1)
Os(2A)–S(3A)	2.438(3)	C(2A)–C(3A)	1.52(1)
Os(2A)–C(10A)	2.05(1)	C(4A)–C(5A)	1.52(1)
Os(2A)–C(21A)	1.93(1)	C(5A)–C(6A)	1.53(1)
Os(2A)–C(22A)	1.86(1)	C(7A)–C(8A)	1.54(1)
S(1A)–C(3A)	1.84(1)	C(8A)–C(9A)	1.53(1)
S(1A)–C(4A)	1.808(9)		

[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(2A)–Os(1A)–S(3A)	56.59(6)	Os(1A)–S(3A)–Os(2A)	68.11(7)
Os(2A)–Os(1A)–O(10A)	71.0(2)	Os(1A)–S(3A)–C(9A)	110.3(4)
S(3A)–Os(1A)–O(10A)	82.3(2)	Os(2A)–S(3A)–C(9A)	109.7(3)
Os(1A)–Os(2A)–S(1A)	137.29(6)	Os(1A)–O(10A)–C(10A)	102.5(6)
Os(1A)–Os(2A)–S(3A)	55.30(6)	C(2A)–C(1A)–C(10A)	115.0(8)
Os(1A)–Os(2A)–C(10A)	68.3(3)	C(4A)–C(5A)–C(6A)	110.3(8)
S(1A)–Os(2A)–S(3A)	89.00(8)	C(7A)–C(8A)–C(9A)	112.5(8)
S(1A)–Os(2A)–C(10A)	87.0(3)	Os(2A)–C(10A)–O(10A)	117.4(6)
S(3A)–Os(2A)–C(10A)	83.8(3)	Os(2A)–C(10A)–C(1A)	126.7(7)
Os(2A)–S(1A)–C(3A)	106.2(3)	O(10A)–C(10A)–C(1A)	115.8(8)
Os(2A)–S(1A)–C(4A)	113.5(3)	Os(1A)–C–O(av)	177(1)
C(3A)–S(1A)–C(4A)	103.4(4)	Os(2A)–C–O(av)	176(1)
C(6A)–S(2A)–C(7A)	98.1(5)		

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

1.27(1) Å [1.25(1) Å], is similar to that found for other complexes.[3,7] All of the resonances expected for this complex were observed in the ^{1}H NMR spectrum of **3** at 25 °C. The bridging acyl group was formed by a CO insertion reaction at the C-terminus of the thiolato ligand. A similar CO insertion reaction was observed in the carbonylation of compound **1** to produce $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}O{=}C(SCH_2CMe_2CH_2)_3]$.[3] Carbon monoxide reagent is necessary for the transformation of **2** to **3**, since it was observed that thermolysis of **2** in the absence of CO does not produce **3**. Carbon monoxide has been used before to "extract" metal atoms from clusters.[8] The fate of the acetate-containing osmium fragment has not been established. It may have been converted to $Os_3(CO)_{12}$, which was also isolated in small amounts from the carbonylation reaction.

It is well-known that the removal of electrons from complexes containing metal–metal bonds can lead to cleavage of these bonds.[9] These reactions can be influenced by the presence of ligands in the reaction medium or donor solvents. By using a limited amount of oxidant in the presence of a suitable ligand (acetate), we have been able to demonstrate a partial degradation of the triosmium cluster of **1**. With an excess of $[Cp_2Fe]^+$ the cluster was decomposed completely. Unfortunately, we were not able to recover the thiolate ligand, which might also have been transformed by the oxidant.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Complete listings of positional parameters, bond distances and angles, and anisotropic thermal parameters for both structural analyses (23 pages). Ordering information is given on any current masthead page.

OM9201728

---

[7] Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 5926.

[8] Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

[9] Meyer, T. J. *Prog. Inorg. Chem.* **1975**, *19*, 1.