Organometallics **1987,** *6,* 1717–1727

in Table IVS, a complete listing of bond distances and angles in Table VS, and F_o vs. F_c in Table VIS.

Acknowledgment. This work was supported by the National Science Foundation (Grants CHE-8206153 and CHE-8305235) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. **2**, 80398-83-0; $Cp_2Mo_2(CO)_4[\mu\text{-}C(C_6H_4\text{-}p\text{-}Me)_2]$, 76114-00-6; $(p\text{-}MeC_6H_4)_2CN_2$, 1143-91-5.

Supplementary Material Available: Tables IVS, temperature factors, Table VS, a complete listing of bond distances and angles (4 pages); Table VIS, F_o vs. F_c (11 pages). Ordering information is on any current masthead page.

Transformations of a Methylene Ligand in a Metal Cluster Containing Sulfur. A Model for Sulfur Poisoning in a Molecular Complex

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Received March 26, 1987

The reactions of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ (**1**) with ethylene or cyclohexene sulfides at 80 °C lead to formation of the two new thioformaldehyde complexes $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (**2**, 23–24%) and $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (**3**, 15–18%) in addition to the known compound $Os_3(CO)_9(\mu_3\text{-}S)_2$ (**4**, 7%). Compounds **2** and **3** can be interconverted quantitatively by decarbonylation (80 °C) and carbonylation (85 °C (55 atm of CO)). Compounds **2** and **3** were both characterized by single-crystal X-ray diffraction analyses. Compound **2** consists of an open triangular cluster of three metal atoms with a σ,π-bonded thioformaldehyde ligand bridging the unbonded pair of metal atoms, C–S = 1.77 (2) Å. Compound **3** contains a closed triangular cluster of metal atoms with a triply bridging thioformaldehyde ligand, C–S = 1.82 (3) Å. At 125 °C **3** is decarbonylated and undergoes a C–H activation to form the new compound $Os_3(CO)_9(\mu_3\text{-}SCH)(\mu\text{-}H)$ (**5**) which contains a triply bridging thioformyl ligand: ^1H NMR δ 10.34. **5** reacts with tertiary phosphines by addition of the phosphorus atom to the thioformyl ligand. The compounds $Os_3(CO)_9[\mu_3\text{-}SC(H)PR_3](\mu\text{-}H)$ (**7a**, $PR_3 = PMe_2Ph$; **7b**, $PR_3 = PMePh_2$; **7c**, $PR_3 = PPh_3$) have been prepared. **7b** was characterized by a single-crystal diffraction analysis. **7b** contains a triply bridging $SC(H)PMePh_2$ ligand on a closed triosmium cluster, P–C = 1.82 (2) and S–C = 1.85 (2) Å. When heated, compounds **7** eliminate the PR_3 molecule and regenerate **5**. In the presence of Me_3NO and PPh_3, **5** is decarbonylated and the PPh_3 ligand is added to a metal atom. The product $Os_3(CO)_8(PPh_3)(\mu_3\text{-}SCH)(\mu\text{-}H)$ (**8**) was characterized by a single-crystal X-ray diffraction analysis. The molecule consists of a closed triangular cluster of three osmium atoms with a triply briding thioformyl ligand. The C–S distance (average 1.74 (2) Å) is shorter than those of the thioformaldehyde ligands and indicates a higher degree of C–S unsaturation. Compound **3** reacts with hydrogen to yield $Os_3(CO)_{10}(\mu\text{-}SMe)(\mu\text{-}H)$ (**9**). At 150 °C (1 atm of H_2), **9** eliminates methane and adds H_2 to yield $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**10**). The transformations of the CH_2 ligand in these sulfur-containing complexes are compared with those of the non-sulfur-containing complex $Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}H)_2$.

Introduction

The adverse effects produced by sulfur upon reactions performed by metal catalysts is one of the most important problems faced by the petrochemical industry.[1] In most cases, the mechanisms of sulfur poisoning on heterogeneous catalysts are not clearly understood. The geometric blocking of active sites and surface reconstruction (faceting) are the most widely discussed mechanisms.[1,2] Although the notion of direct chemical interactions between sulfur and adsorbed molecules has been mentioned, very little evidence to demonstrate this has been obtained.[2c] There is now considerable evidence to indicate that the methylene (CH_2) ligand is a key intermediate in the Fischer–Tropsch reaction.[3] This reaction is well-known to be severely inhibited by sulfur contamination of the catalysts.[2]

In our recent studies of the reactions of sulfur-containing osmium carbonyl cluster compounds with alkynes we have observed several examples in which the formation of bonds between the alkyne molecules and the sulfido ligands occurred.[4,5]

To obtain evidence concerning the importance of methylene–sulfur interactions and their effect on transformations of the methylene ligand at multinuclear metal sites, we have now investigated the reactions of ethylene and cyclohexene sulfides with $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ (**1**).

Experimental Section

General Data. Reagent grade solvents were stored over 4-Å molecular sieves. THF was freshly distilled from sodium diphenylketyl before use. $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ (**1**) was prepared by the procedure of Geoffroy.[7] Ethylene sulfide, cyclohexene sulfide, PMe_2Ph, PPh_2Me, and PPh_3 were purchased from Aldrich Chemical Co. The ethylene sulfide was freshly distilled before

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use; the others were used without further purification. Trimethylamine *N*-oxide dihydrate was purchased from Aldrich Chemical Co. and was converted to its anhydrous form by sublimation. Carbon monoxide and hydrogen were purchased from Linde Co. and were used without further purification. All reactions were performed under a nitrogen atmosphere. High-pressure reactions were performed in a 45-mL Parr Model 4713 high-pressure reaction vessel or in an Autoclave Engineers Model APB-300 300-mL magnedrive high-pressure autoclave. IR spectra were recorded on a Nicolet 5 DXB FT-IR spectrometer. NMR spectra were run on IBM NR-80 and Bruker AM-300 spectrometers operating at 80 and 300 MHz, respectively. Mass spectra were run on a Finnigan Model 4521 mass spectrometer by using electron-impact ionization. GC-MS measurements were made on the same instrument by using an SE 54-25 meter capillary column in the GC unit. Chromatographic separations were performed on plates (0.25 mm Kieselgel 60 F_{254}, E. Merck, West Germany) purchased from Bodman Chemicals unless otherwise indicated. Elemental analyses were performed by MicAnal, Tucson, AZ.

Reaction of 1 with Ethylene Sulfide. **1** (20.0 mg, 0.022 mmol) was dissolved in 15 mL of cyclohexane and was heated to reflux. Ethylene sulfide (50 μL, 0.84 mmol) was then added, and the reflux was continued for 25 min. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2, filtered, and chromatographed by TLC using hexane solvent. The following yellow bands were separated in order of elution: $Os_3(CO)_9(\mu_3\text{-}S)_2$,[8] (**4**) (1.4 mg, 7%), $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (**3**) (3.2 mg, 15%), and $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (**2**) (5.0 mg, 24%). Anal. Calcd for $Os_3SO_{11}C_{12}H_2$ (**2**): C, 15.58; H, 0.22. Found: C, 15.64; H, 0.16. Anal. Calcd for $Os_3SO_{10}C_{11}H_2$ (**3**): C, 14.73; H, 0.22. Found: C, 15.04; H, 0.34.

The reaction of cyclohexene sulfide with **1** under similar conditions produced **4** (6%), **3** (18%), and **2** (23%).

Decarbonylation of 2. Compound **2** (15.0 mg, 0.017 mmol) in a 30 mL of cyclohexane solution was refluxed for 75 min. The workup as described above yielded 14.1 mg (97%) of **3**.

Addition of CO to 3. Compound **3** (5.0 mg, 0.006 mmol) in 10 mL of hexane was placed into the 45-mL Parr high-pressure reaction vessel. The reaction with CO was performed at 85 °C/55 atm of CO for 6 h. Workup as described above yielded compound **2** in a quantitative yield.

Preparation of $Os_3(CO)_9(\mu_3\text{-}SCH)(\mu\text{-}H)$ (5). Method A. By Thermolysis of 3. **3** (5.0 mg, 0.006 mmol) dissolved in 10 mL of *n*-octane was refluxed for 2 h. The solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH_2Cl_2 and was chromatographed by TLC with hexane solvent to yield one yellow band, compound **5** (4.6 mg, 95%). Compound **5** was a yellow oil that could not be crystallized.

Method B. By Reaction of $Os_3(CO)_9(\mu_3\text{-}CCO)(\mu\text{-}H)_2$ (6) with Ethylene Sulfide. A 15 mL solution of **6** in octane was obtained by heating 20.0 mg (0.022 mmol) of **1** for 20 min.[9] Ethylene sulfide (15 μL, 0.224 mmol) was then added, and the reaction solution was refluxed for 8 h. Workup as described above yielded 5.7 mg of compound **5** (30%, based on the amount of **1**).

Addition of Phosphines to 5. (a) PMe_2Ph. At 25 °C 15 μL (0.10 mmol) of PMe_2Ph was added to a solution of 8.6 mg (0.010 mmol) of **5** in 15 mL of hexane. The solution was stirred for 1 h. During this time the solution became cloudy. An IR spectrum showed the complete disappearance of **5**. The solvent was removed. The residue was dissolved in $CHCl_2$ and was chromatographed by TLC with a hexane/CH_2Cl_2 (7/3, v/v) solvent mixture. The separation yielded one yellow band identified as $Os_3(CO)_9[\mu_3\text{-}SC(H)PMe_2Ph]H$ (**7a**) (8.1 mg, 81%).

(b) $PMePh_2$. The reaction of **5** with $PMePh_2$ was performed as described in section a. Separation by TLC with a hexane/CH_2Cl_2 (v/v, 7/3) solvent mixture yielded yellow $Os_3(CO)_9[\mu_3\text{-}SC(H)PMePh_2]$ (**7b**) in 74% yield. Anal. Calcd for $Os_3SPO_9C_{23}H_{15}$: C, 25.84; H, 1.40. Found: C, 26.09; H, 1.41.

(c) PPh_3. There was no reaction observed between compound **5** and PPh_3 in hexane at 25 °C in 24 h or in refluxing hexane over 5 h. However, when 10 mg (0.012 mmol) of **5** and 4.5 mg (0.017 mmol) of PPh_3 was dissolved in freshly distilled THF under a N_2 atmosphere and a 50 μL (0.025 mmol/mL) of THF solution of $Na^+[Ph_2CO]^-$[10] was added, a reaction was observed. After the solution was stirred for 30 min at 25 °C, the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and was chromatographed by TLC by using hexane/CH_2Cl_2 (v/v, 4/1) solvent mixture. This yielded 0.8 mg of **5** plus a second yellow band (6.5 mg). The latter was shown to be a mixture of **5** and **7c**. All attempts to obtain **7c** free from **5** were unsuccessful.

Loss of Phosphine from the Compounds 7. Compounds **7a–c** rapidly (10–15 min) eliminate the phosphine ligand when heated to reflux in heptane solution. IR spectra of these reaction solutions indicated they were mixtures of **7** and **5**, but **5** could be recovered in 100% yield by adding a large excess of CH_3I to the hot reaction solutions.

Preparation of $Os_3(CO)_8(PPh_3)(\mu_3\text{-}SCH)(\mu\text{-}H)$ (8). **5** (19 mg, 0.022 mmol) and 6 mg (0.023 mmol) of PPh_3 were dissolved in 20 mL of CH_2Cl_2 under a N_2 atmosphere. Me_3NO (2.5 mg, 0.033 mmol) dissolved in 5 mL of CH_2Cl_2 was added from a dropping funnel. The reaction was monitored by IR spectroscopy, and when absorptions of the starting material had completely disappeared (approximately 20 min), the solution was concentrated and chromatographed by TLC using a hexane/CH_2Cl_2 (v/v, 7/3) solvent mixture. The first yellow band yielded 4.0 mg (17%) of **8** after recrystallization from pentane at −70 °C. Anal. Calcd for $Os_3SPC_{27}H_{17}$: C, 29.40; H, 1.54. Found: C, 29.32; H, 1.24. ^1H NMR spectra of the reaction mixtures showed the presence of a minor second product B (see Table II) which is believed to be an isomer of the major product A.

Reaction of 3 with Hydrogen. **3** (9.0 mg, 0.010 mmol) was refluxed in octane for 40 min while the solution was slowly purged with H_2. The solvent was removed in vacuo, and the residue was chromatographed by TLC with hexane solvent. This yielded 4.1 mg of compound **5** (47%), 3.7 mg of $Os_3(CO)_{10}(\mu\text{-}SMe)(\mu\text{-}H)$ (**9**)[11] (41%), and 0.6 mg of unreacted starting material.

Reaction of 5 with Hydrogen. **5** (6.0 mg 0.007 mmol) in 8 mL of heptane was placed into the 45-mL Parr high-pressure reaction vessel. The reaction with H_2 was performed at 150 °C/70 atm of H_2 for 14 hrs. Workup described above yielded $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**10**)[12] (4.8 mg, 81%) plus 0.4 mg of $Os_3(CO)_9(\mu_3\text{-}S)_2$.[8,13]

Reaction of 9 with Hydrogen. **9** (10.0 mg, 0.11 mmol) was refluxed in 10 mL of nonane for 5 h in the presence of a slow purge of H_2 through the solution. The usual workup yielded 8.3 mg of compound **10** (87%). The same reaction was performed for GC-MS determination of the evolved gas in the following way. Compound **9** (40 mg, 0.44 mol) dissolved in 10 mL of nonane was placed into a Schlenk tube equipped with a rubber septum for sampling. After evacuation the Schlenk tube was filled with 1 atm of H_2 gas and then heated at 145 °C for 4.5 h while being stirred vigorously. The reaction solution was then cooled to −78 °C. Samples of the gas phase were removed by syringe. The GC-MS spectra recorded at 20 °C showed CH_4 as only hydrocarbon present. After the GC-MS measurements the Schlenk tube was allowed to warm to room temperature. The IR spectrum of the solution showed only unreacted starting material (~60%) and compound **10** (~40%).

Reaction of 5 with a 1/1 CO/H_2 Gas Mixture. Compound **5** (6.0 mg, 0.007 mmol) in 8 mL of heptane was placed into the 45-mL Parr high-pressure reaction vessel, pressurized with 35 atm of CO and 35 atm of H_2, and then heated at 120 °C for 15 h. After cooling, the solvent was removed in vacuo. The residue dissolved in minimum amount of CH_2Cl_2 was chromatographed by TLC with hexane solvent. This yielded 4.5 mg of unreacted starting

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[11] For comparison, authentic $Os_3(CO)_{10}(\mu\text{-}SMe)(\mu\text{-}H)$ (**9**) was prepared from $Os_3(CO)_{12}$ and MeSH by the method of Crooks et al.[12]

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Table I. Crystallographic Data for the Structural Analyses for Compounds 2, 3, 7b, and 8

	2	3	7b	8
(A) Crystal Data				
formula	$Os_3SO_{11}C_{12}H_2$	$Os_3SO_{10}C_{11}H_2$	$Os_3SPO_9C_{23}H_{15}$	$Os_3SPO_8C_{27}H_{17}$
temp, ±3 °C	25	25	25	25
space group	$P2_1/n$, No. 14	*Pnma*, No. 62	$P2_1/c$, No. 14	$P\bar{1}$, No. 2
a, Å	8.262 (2)	13.721 (3)	12.931 (5)	14.430 (5)
b, Å	14.092 (5)	13.899 (5)	14.066 (5)	17.866 (6)
c, Å	16.315 (5)	8.908 (2)	14.894 (7)	12.382 (4)
α, deg	90.0	90.0	90.0	102.14 (2)
β, deg	102.02 (2)	90.0	93.88 (3)	100.92 (3)
γ, deg	90.0	90.0	90.0	104.57 (3)
V, Å^3	1858 (1)	1698.7 (7)	2703 (2)	2920 (2)
M_r	924.8	896.8	1068.9	1102.9
Z	4	4	4	4
ρ_{calcd}, g/cm^3	3.31	3.51	2.63	2.51
(B) Measurement of Intensity Data				
radiation	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)
monochromator	graphite	graphite	graphite	graphite
detector aperture, mm				
horizontal	2.0	2.0	2.0	2.0
vertical	2.0	2.0	2.0	2.0
cryst faces	001, $00\bar{1}$, 010 $0\bar{1}0$, $01\bar{1}$, $0\bar{1}1$	$10\bar{1}$, $\bar{1}01$, 100, 101 $\bar{1}0\bar{1}$, 110, 010, $1\bar{2}0$	100, $\bar{1}00$, $1\bar{2}1$ $02\bar{1}$, 121, $0\bar{1}\bar{1}$	$10\bar{1}$, $\bar{1}01$, $\bar{1}10$ $1\bar{1}0$, 010, $0\bar{1}0$
cryst size, mm	0.10 × 0.27 × 0.24	0.13 × 0.24 × 0.21	0.10 × 0.19 × 0.21	0.14 × 0.28 × 0.32
cryst orientn: directn; deg from ϕ axis	*b*; 6.8°	*a*; 3.4°	[102]; 10.8	[122]; 3.1
reflctns measured	*h*, *k*, ± *l*	-*h*, -*k*, + *l*	*h*, *k*, ± *l*	*h*, ± *k*, ± *l*
max 2 θ, deg	50	50	48	48
scan type	moving crystal–stationary counter	moving crystal–stationary counter	moving crystal–stationary counter	moving crystal–stationary counter
ω-scan width: $(A + 0.347 \tan\theta)^{\circ}$,[a] *A* =	1.10	1.10	1.10	1.10
bkgd at each end of scan, s	9.0 s	9.0 s	$^1/_4$ scan time	$^1/_4$ scan time
ω-scan rate, deg/min	4.0	4.0	2.0	4.0
no. of reflctns measd	3299	1495	5300	9607
data used ($F^2 \geq 3.0\ \sigma\ (F^2)$)	2384	1138	3291	6413[b]
(C) Treatment of Data				
absorptn correctn	applied	applied	applied	applied
coeff cm^{-1}	218.5	238.8	150.9	139.7
grid	12 × 16 × 4	8 × 14 × 8	10 × 10 × 10	12 × 6 × 12
transmissn coeff				
max	0.183	0.136	0.29	0.19
min	0.005	0.072	0.14	0.06
P factor	0.04	0.02	0.02	0.02
final residuals				
R_F	0.044	0.045	0.048	0.043
R_{wF}	0.052	0.047	0.058	0.047
esd of unit wt observn	1.83	2.26	2.09	2.37
largest shift/error value of final cycle	0.03	0.03	0.02	0.30
largest peak in final diff Fourier, e/Å^3	2.29	1.83	2.68	4.84
no. of variables	244	125	174	541

[a] Rigaku software uses a multiple scan technique. If the $I/\sigma(I)$ ratio is less than 10.0, a second scan is made and the results are added to first scan etc. A maximum of three scans was permitted per reflection. [b] $F^2 \geq 5.0\ \sigma\ (F^2)$.

material (75%), 0.5 mg of compound **9** (8%), and 0.6 mg of compound **10** (10%).

Attempted Carbonylation of 9. **9** (25 mg, 0.028 mmol) in 70 mL of octane was placed into the 300-mL autoclave. The autoclave was purged with CO, pressurized to 100 atm with CO, and then heated to 100 °C. After stirring for 24 h, the solution was removed from the autoclave and was concentrated in vacuo. Cooling to −20 °C yielded 1.2 mg (4.7%) of $Os_3(CO)_{12}$. The solution then was chromatographed over a silica gel column with hexane solvent. This yielded 23.5 mg (94%) of unreacted **9**.

Crystallographic Analyses. Yellow crystals of **2** and **3** suitable for diffraction analyses were obtained from solutions in $CHCl_3$/cyclohexane solvent by cooling to −20 °C. Orange single crystals of **7b** were grown from a solution in hexane/CH_2Cl_2 (7/3) solvent by slow evaporation at −20 °C. Orange single crystals of **8** were grown from a solution in pentane solvent by slow evaporation at 25 °C. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo K_α radiation. Unit cells were determined and refined from 25 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. MICROVAX II computer by using the Molecular Structure Corp. TEXSAN structure solving program library. Absorption corrections of a Gaussian integration type were done for each structure. Neutral atom scattering factors were obtained from the standard sources.[14a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[14b] Full-matrix least-squares

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

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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o)^2]^{1/2}/Lp$.

Compound 2 crystallized in the monoclinic crystal system. The space group $P2_1/n$ (a variant of $P2_1/c$) was identified uniquely from the systematic absences observed during the collection of the data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. The two hydrogen atoms were located in chemically reasonable positions in a difference Fourier map. Their scattering contributions were included in the structure factor (SF) calculations, but their positions were not refined.

Compound 3 crystallized in the orthorhombic crystal system. The systematic absences in the data were consistent with either of the space groups, *Pnma* or $Pn2_1a$. The former is centrosymmetric and was therefore chosen for the initial solution attempts. This selection was deemed to be correct by the successful solution and refinement of the structure. This structure was solved by a combination of direct methods and difference Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. The single symmetry independent hydrogen atom was located in a difference Fourier map. Its scattering contributions were included in the SF calculations, but its position was not refined.

Compound **7b** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was identified uniquely from the systematic absences observed in the data. The structure was solved by a combination of Patterson and difference Fourier techniques. All atoms heavier than oxygen were refined with anisotropic thermal parameters. All remaining non-hydrogen atoms were refined with isotropic thermal parameters. The hydrogen atom H(1) was located in a difference Fourier map. The hydrogen atoms on the phenyl rings and the methyl group were calculated by assuming idealized geometries. These hydrogen atoms were included in the SF calculations but were not refined. The hydride ligand was not located and was ignored.

Compound 8 crystallized in the triclinic crystal system. The centrosymmetric 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 Patterson and difference Fourier techniques. Except for the carbon atoms of the phenyl groups, all non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl carbon atoms were refined with isotropic thermal parameters. The structure consists of two symmetry-independent units of the complex. The hydrogen atom on the carbon atom of the thioformyl ligands was located in a difference Fourier map. The positions of the hydrogen atoms on the phenyl rings were calculated by assuming idealized geometries. Contributions to the scattering by these hydrogen atoms were included in the SF calculations, but their positions were not refined. The hydride ligands were not located and were ignored in the structural analysis. The largest peak in the final difference Fourier synthesis was relatively large (4.8e/Å^3), however, it was located close to one of the osmium atoms (1.0 Å) and is believed to be a structurally insignificant residual. The osmium-carbon and carbon-oxygen distances of one carbonyl ligand, Os(3A)-C(33A) and C(33A)-O(33A), were of abnormal lengths, 1.51 (4) and 1.47 (4) Å, respectively. This is believed to be an artifact due to some unidentified systematic error in the diffraction data, possibly that of an imperfect absorption correction because the corresponding bond distances in the other crystallographically independent molecule were normal. Error analyses were calculated from the inverse matrix obtained on the final cycle of refinement for each structure. See supplementary material for the tables of structure factor amplitudes and the values of the anisotropic thermal parameters for compounds **7b** and 8. For compounds 2 and 3 this information was published previously.[6]

Results

From the reaction of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ (1) with C_2H_4S or $C_6H_{10}S$ at 80°C over 25 min, three products were isolated. Two of these are the new compounds $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (2) (24% yield) and $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (3) (15% yield). The third product was the previously known compound $Os_3(CO)_9(\mu_3\text{-}S)_2$ (4) (7% yield).[8,13] Compounds 2 and 3 were analyzed by IR and ^{1}H NMR spectroscopies and by elemental and single-crystal X-ray diffraction analyses. IR and ^{1}H NMR spectra are listed in Table II. Compound 2 showed two resonances in the ^{1}H NMR spectrum at 3.74 and 3.56 ppm that are coupled, $J_{H\text{-}H} = 5.81$ Hz. Compound 3 showed only a singlet at 1.69 ppm.

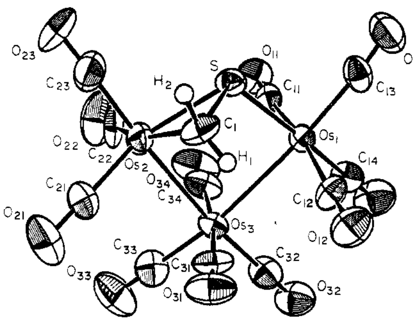

Figure 1. An ORTEP diagram of the molecular structure of $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (2) showing 50% probability thermal ellipsoids. The ellipsoids on the hydrogen atoms have been reduced for clarity.

Description of the Structures of Compounds 2 and 3. An ORTEP drawing of the molecular structure of compound 2 is shown in Figure 1. The crystallographic positional parameters are listed in Table III. Interatomic distances and angles are listed in Tables IV and V, respectively. Compound 2 consists of an open cluster of three osmium atoms with two osmium-osmium bonds, Os(1)-Os(3) = 2.951 (1) Å and Os(2)-Os(3) = 2.948 (1) Å. The Os(1)···Os(2) nonbonding interaction (3.859 (1) Å) is bridged by a thioformaldehyde ligand, $S{=}CH_2$, in a σ, π-bonding mode. The carbon-sulfur bond distance at 1.77 (2) Å is slightly shorter than that of a C-S single bond. The carbon atom is coordinated only to Os(2), Os(2)-C(1) = 2.16 (2) Å, while the sulfur atom is bonded both to Os(1) and Os(2), Os(1)-S = 2.443 (4)Å and Os(2)-S = 2.394 (4) Å. A structurally similar bridging thioformaldehyde ligand was observed previously in the compound $Os_3(CO)_9(PMe_2Ph)(\mu\text{-}SCH_2)(\mu_3\text{-}S)$, C-S = 1.788 (11) Å.[15] A η^2-thioformaldehyde ligand has been structurally characterized in the mononuclear rhenium complex $[CpRe(NO)(PPh_3)(\eta^2\text{-}SCH_2)]^+PF_6^-$.[16] In this complex the C-S distance is slightly shorter, 1.742 (9) Å, than those of bridging thioformaldehyde ligands. Compound 2 contains 11 linear terminal carbonyl ligands distributed as shown in Figure 1. The two hydrogen atoms were located in chemically reasonable positions as shown in Figure 1 and are inequivalent as indicated by the ^{1}H NMR spectrum. If the thioformaldehyde ligand is viewed as a four-electron donor (two σ electrons to Os(1) and two π-C=S electrons to Os(2)), then all the metal atoms obey the EAN rule, but formally both metal-metal bonds are heteropolar, Os(1)→Os(3) and Os(3)→Os(2).

An ORTEP drawing of the molecular structure of 3 is shown in Figure 2. The final positional parameters are listed in Table VI, and the interatomic distances and angles are listed in Tables VII and VIII, respectively. The molecule lies on a crystallographic symmetry plane that passes through the atoms Os(1), C, S, C(12), O(12), C(13), and O(13). The structure of 3 consists of a closed triangular cluster of three osmium atoms, Os(1)-Os(2) = Os-

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[15] Adams, R. D.; Golembeski, N. M.; Seleque, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546.

[16] Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 1056.

Table II. Spectroscopic Data

compound	^{1}H NMR (δ in $CDCl_3$)	IR (ν(CO), cm^{-1} (in hexane))
$Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (2)	3.74 (d, $J_{H\text{-}H}$ = 5.81 Hz, 1 H), 3.56 (d, $J_{H\text{-}H}$ = 5.81 Hz, 1 H)	2126 (w), 2077 (s), 2055 (m), 2049 (s), 2040 (m), 2028 (m), 2011 (w), 1997 (m), 1992 (m), 1976 (m), 1970 (w)
$Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (3)	1.69 (s, 2 H)	2104 (w), 2068 (s), 2056 (s), 2034 (m), 2016 (w), 2002 (m)
$Os_3(CO)_9(\mu_3\text{-}SCH)(\mu\text{-}H)^a$ (5)	10.34 (s, 1 H), –18.49 (s, 1 H)	2104 (w), 2077 (s), 2053 (vs), 2026 (s), 2016 (m), 2009 (s), 1994 (w), 1986 (w)
$Os_3(CO)_9[\mu_3\text{-}SC(H)PMe_2Ph](\mu\text{-}H)^b$ (**7a**)	isomer A: 7.65–7.50 (m, 5 H), 2.89 (q, $J_{H\text{-}H}$ = 4.1 Hz, $J_{P\text{-}H}$ = 7.3 Hz, 1 H), 1.98 (d, $J_{P\text{-}H}$ = 12.7 Hz, 3 H), 1.88 (d, $J_{P\text{-}H}$ = 12.7 Hz, 3 H), –15.72 (q, $J_{P\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 4.1 Hz, 1 H)	2079 (m), 2049 (s), 2022 (s), 2000 (m), 1989 (w), 1983 (w), 1961 (m), 1959 (m), 1940 (vw), 1928 (vw)
	isomer B: 7.72–7.64 (m, 5 H), 3.12 (d, $J_{P\text{-}H}$ = 12.7 Hz, 1 H), 2.03 (d, $J_{P\text{-}H}$ = 12.7 Hz, 3 H), 1.98 (d, $J_{P\text{-}H}$ = 12.7 Hz, 3 H), –14.87 (d, $J_{P\text{-}H}$ = 13 Hz, 1 H)	
$Os_3(CO)_9[\mu_3\text{-}SC(H)PMePh_2](\mu\text{-}H)^{b,c}$ (**7b**)	isomer A: 7.65–7.43 (m, 10 H), 3.27 (q, $J_{H\text{-}H}$ = 3.5 Hz, $J_{P\text{-}H}$ = 7.3 Hz, 1 H), 2.42 (d, $J_{P\text{-}H}$ = 12.7 Hz, 3 H), –15.62 (q, $J_{H\text{-}H}$ = 3.5 Hz, $J_{P\text{-}H}$ = 1.4 Hz, 1 H)	2078 (s), 2048 (vs), 2021 (vs), 1999 (m), 1987 (m), 1983 (w, sh), 1962 (s), 1956 (m, sh), 1941 (w), 1927 (vw)
	isomer B: 7.78–7.65 (m, 10 H), 3.58 (d, $J_{P\text{-}H}$ = 8.4 Hz, 1 H), 2.43 (d, $J_{P\text{-}H}$ = 12.7 Hz, 3 H), –14.83 (d, $J_{P\text{-}H}$ = 12 Hz, 1 H)	
$Os_3(CO)_9[\mu_3\text{-}SC(H)PPh_3](\mu\text{-}H)^d$ (**7c**)	7.65–7.20 (m, 15 H), 3.75 (q, $J_{H\text{-}H}$ = 3.63 Hz, 1 H), –15.28 (dd, $J_{H\text{-}H}$ = 2.18 Hz, 1 H)	2077 (s), 2047 (vs), 2020 (vs), 1996 (m), 1985 (m), 1967 (m), 1938 (w)
$Os_3(CO)_8(PPh_3)(\mu_3\text{-}SCH)(\mu\text{-}H)^e$ (8)	isomer A: 10.23 (dd, $J_{H\text{-}H}$ = 1.40 Hz, 1 H), 7.45–7.20 (m, 15 H), –17.12 (dd, $J_{H\text{-}H}$ = 1.40 Hz, $J_{P\text{-}H}$ = 12.53 Hz, 1 H)	2085 (s), 2050 (vs), 2019 (vs), 2006 (w), 1996 (m), 1983 (m), 1974 (w), 1959 (vw)
	isomer B: 9.86 (dd, J = 1.90 Hz, 1 H), 7.45–7.20 (m, 15 H), –17.42 (dd, $J_{H\text{-}H}$ = 1.90 Hz, $J_{P\text{-}H}$ = 13.08 Hz, 1 H)	

[a] Mass spectrum (70 eV, 90 °C), m/e 868 – 28x, x = 0–9 ($[M]^+ - x$CO). [b] Mixture of isomers. A/B in an approximate 4/1 ratio. [c] Proton-decoupled ^{31}P NMR (δ in $CDCl_3$): 31.27 (s), 29.81 (s). [d] These spectra were obtained from solutions that contained small amounts of **5**. [e] Solution spectra of pure A were obtained from crystals from which the X-ray data crystal was chosen. B is believed to be an isomer of A which could not be obtained free of A.

(1)–Os(2′) = 2.862 (1) Å and Os(2)–Os(2′) = 2.745 (2) Å. The thioformaldehyde ligand serves as a triple bridge with the carbon atom bonded to Os(1), Os(1)–C = 2.14 (3) Å, and the sulfur atom bridging Os(2)–Os(2′), Os(2)–S = 2.415 (6) Å. The C–S distance, 1.82 (3) Å, is slightly longer than that in **2** and more in accord with a formulation as a single bond length. A triply bridging thioformaldehyde ligand was observed in the open cluster $Os_3(CO)_8(PMe_2Ph)(\mu\text{-}SCH_2)(\mu_3\text{-}S)$. The C–S distance in this compound was longer still, 1.869 (6) Å.[15] Compound **3** contains ten carbonyl ligands. Atom Os(1) that contains four carbonyl ligands is sterically crowded, and two of the carbonyl ligands, C(11)–O(11) and C(11′)–C(11′) that lie approximately in the plane of the cluster have adopted semibridging coordination to the adjacent metal atoms, Os(2)···C(11) = 2.572 (2) Å. The single symmetry-independent hydrogen atom was located in a difference Fourier map, C–H = 1.02 Å and H–C–H = 121°, but its position was not refined.

Since compounds **2** and **3** differ in their formulas by only one carbonyl ligand, it was suspected that they could be interconverted easily, and this was confirmed by independent experiments. When heated to 80 °C in cyclohexane solvent, **2** was transformed into **3** quantitatively in 75 min. The transformation of **3** into **2** also occurs quantitatively at 85 °C under 55 atm of CO. However, when heated to 125 °C under a nitrogen atmosphere, **3** was further decarbonylated to form the new compound **5** in 95% yield. Compound **5** is a yellow oil at 25 °C, and all attempts to grow crystals of it were unsuccessful. Compound **5** was characterized by IR and ^{1}H NMR analysis and by structural analyses of two phosphine derivatives (vide infra). Compound **5** showed ^{1}H resonances at –18.49 (1 H) and 10.34 ppm (1 H). The former is indicative of a bridging hydride ligand. The latter is indicative of a thioformyl, HCS, ligand although the downfield shift is not as large as that which has been observed for this ligand in mononuclear metal complexes.[17] Compound **5** appears

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(17) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* 1978, *159*, 73.

Table III. Positional Parameters and B(eq) for $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (2)

atom	x	y	z	B(eq),[a] Å^2
Os(1)	0.795953 (65)	0.367794 (45)	0.361280 (39)	2.72 (3)
Os(2)	0.900650 (83)	0.396152 (50)	0.142885 (45)	3.64 (3)
Os(3)	0.996387 (67)	0.248408 (46)	0.271832 (44)	3.21 (3)
S	0.72716 (47)	0.45805 (28)	0.23081 (26)	3.3 (2)
O(11)	1.0826 (14)	0.50987 (96)	0.41011 (98)	5.6 (7)
O(12)	0.5335 (15)	0.2140 (10)	0.30389 (98)	5.6 (7)
O(13)	0.5665 (17)	0.5077 (11)	0.4265 (11)	6.5 (8)
O(14)	0.9063 (20)	0.2581 (11)	0.5261 (11)	7.3 (8)
O(21)	0.9508 (26)	0.2584 (14)	0.0072 (11)	9 (1)
O(22)	1.2594 (20)	0.4667 (15)	0.1889 (13)	9 (1)
O(23)	0.8087 (22)	0.5577 (12)	0.0205 (11)	8 (1)
O(31)	0.7016 (15)	0.15497 (88)	0.15245 (95)	5.3 (6)
O(32)	1.0436 (18)	0.1018 (11)	0.4118 (11)	6.4 (8)
O(33)	1.2215 (18)	0.1560 (13)	0.1703 (12)	8 (1)
O(34)	1.2937 (16)	0.3669 (11)	0.3584 (13)	8 (1)
C(1)	0.6420 (19)	0.3824 (11)	0.1461 (12)	4.0 (7)
C(11)	0.9823 (18)	0.4567 (12)	0.3903 (11)	3.4 (7)
C(12)	0.6325 (18)	0.2696 (12)	0.3240 (10)	3.5 (7)
C(13)	0.6491 (19)	0.4535 (14)	0.4057 (12)	4.0 (8)
C(14)	0.8660 (19)	0.2994 (13)	0.4611 (10)	3.8 (7)
C(21)	0.9345 (27)	0.3107 (16)	0.0603 (13)	6 (1)
C(22)	1.1272 (22)	0.4390 (16)	0.1728 (11)	5.0 (9)
C(23)	0.8408 (25)	0.4979 (15)	0.0658 (14)	5 (1)
C(31)	0.8061 (21)	0.1904 (11)	0.1969 (14)	4.3 (8)
C(32)	1.0232 (22)	0.1559 (15)	0.3584 (13)	4.8 (9)
C(33)	1.1343 (20)	0.1909 (15)	0.2084 (14)	4.9 (9)
C(34)	1.1790 (20)	0.3255 (14)	0.3279 (14)	5.0 (9)
H(2)	0.5608	0.4258	0.1023	4.0
H(1)	0.5978	0.3286	0.1610	4.0

[a] $B(\text{eq}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\alpha)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\gamma)\beta_{23}]$.

Table IV. Intramolecular Distances (Å) for $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (2)[a]

Os(1)–C(14)	1.88 (2)	Os(3)–C(31)	1.96 (2)
Os(1)–C(12)	1.94 (2)	S–C(1)	1.77 (2)
Os(1)–C(13)	1.95 (2)	O(11)–C(11)	1.11 (2)
Os(1)–C(11)	1.97 (2)	O(12)–C(12)	1.13 (2)
Os(1)–S	2.443 (4)	O(13)–C(13)	1.12 (2)
Os(1)–Os(3)	2.951 (1)	O(14)–C(14)	1.19 (2)
Os(2)–C(21)	1.87 (2)	O(21)–C(21)	1.17 (2)
Os(2)–C(23)	1.90 (2)	O(22)–C(22)	1.14 (2)
Os(2)–C(22)	1.93 (2)	O(23)–C(23)	1.12 (2)
Os(2)–C(1)	2.16 (2)	O(31)–C(31)	1.12 (2)
Os(2)–S	2.394 (4)	O(32)–C(32)	1.14 (2)
Os(2)–Os(3)	2.948 (1)	O(33)–C(33)	1.15 (2)
Os(3)–C(33)	1.88 (2)	O(34)–C(34)	1.14 (2)
Os(3)–C(32)	1.92 (2)	C(1)–H(1)	0.90
Os(3)–C(34)	1.93 (2)	C(1)–H(2)	1.06

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

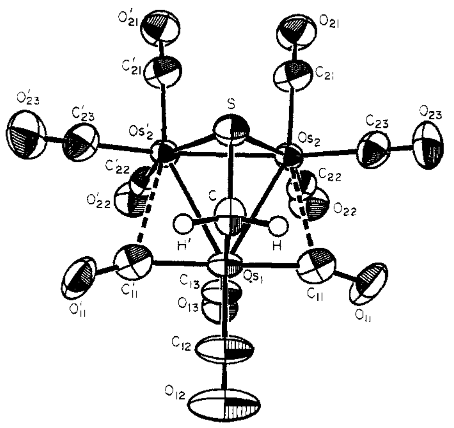

Figure 2. An ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (3) showing 50% probability thermal ellipsoids. The ellipsoids on the hydrogen atoms have been reduced for clarity.

Table V. Intramolecular Bond Angles (deg) for $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (2)[a]

C(14)–Os(1)–C(12)	88.5 (7)	C(33)–Os(3)–Os(2)	90.8 (6)
C(14)–Os(1)–C(13)	95.7 (8)	C(33)–Os(3)–Os(1)	170.8 (6)
C(14)–Os(1)–C(11)	92.0 (7)	C(32)–Os(3)–C(34)	94.3 (9)
C(14)–Os(1)–S	175.6 (5)	C(32)–Os(3)–C(31)	97.6 (8)
C(14)–Os(1)–Os(3)	91.9 (5)	C(32)–Os(3)–Os(2)	170.7 (5)
C(12)–Os(1)–C(13)	96.4 (7)	C(32)–Os(3)–Os(1)	90.8 (6)
C(12)–Os(1)–C(11)	171.6 (7)	C(34)–Os(3)–C(31)	168.1 (9)
C(12)–Os(1)–S	94.5 (5)	C(34)–Os(3)–Os(2)	90.5 (6)
C(12)–Os(1)–Os(3)	82.2 (5)	C(34)–Os(3)–Os(1)	84.8 (5)
C(13)–Os(1)–C(11)	91.9 (7)	C(31)–Os(3)–Os(2)	77.8 (5)
C(13)–Os(1)–S	87.2 (6)	C(31)–Os(3)–Os(1)	95.0 (5)
C(13)–Os(1)–Os(3)	172.3 (6)	Os(2)–Os(3)–Os(1)	81.69 (3)
C(11)–Os(1)–S	84.6 (5)	C(1)–S–Os(2)	60.2 (6)
C(11)–Os(1)–Os(3)	89.4 (5)	C(1)–S–Os(1)	110.4 (6)
S–Os(1)–Os(3)	85.3 (1)	Os(2)–S–Os(1)	105.8 (2)
C(21)–Os(2)–C(23)	94 (1)	H(1)–C(1)–H(2)	116 (2)
C(21)–Os(2)–C(22)	95.8 (9)	H(1)–C(1)–S	114 (2)
C(21)–Os(2)–C(1)	104.9 (8)	H(1)–C(1)–Os(2)	123 (1)
C(21)–Os(2)–S	149.8 (7)	H(2)–C(1)–S	106 (1)
C(21)–Os(2)–Os(3)	90.1 (7)	H(2)–C(1)–Os(2)	115 (1)
C(23)–Os(2)–C(22)	92.1 (9)	S–C(1)–Os(2)	74.3 (6)
C(23)–Os(2)–C(1)	87.8 (7)	O(11)–C(11)–Os(1)	176 (2)
C(23)–Os(2)–S	90.9 (6)	O(12)–C(12)–Os(1)	177 (2)
C(23)–Os(2)–Os(3)	176.0 (6)	O(13)–C(13)–Os(1)	175 (2)
C(22)–Os(2)–C(1)	159.3 (8)	O(14)–C(14)–Os(1)	177 (2)
C(22)–Os(2)–S	113.9 (6)	O(21)–C(21)–Os(2)	178 (2)
C(22)–Os(2)–Os(3)	86.5 (6)	O(22)–C(22)–Os(2)	178 (2)
C(1)–Os(2)–S	45.5 (5)	O(23)–C(23)–Os(2)	179 (2)
C(1)–Os(2)–Os(3)	92.2 (4)	O(31)–C(31)–Os(3)	177 (2)
S–Os(2)–Os(3)	86.3 (1)	O(32)–C(32)–Os(3)	178 (2)
C(33)–Os(3)–C(32)	97.1 (8)	O(33)–C(33)–Os(3)	179 (2)
C(33)–Os(3)–C(34)	90.0 (8)	O(34)–C(34)–Os(3)	175 (2)
C(33)–Os(3)–C(31)	88.6 (8)		

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

Table VI. Positional Parameters and B(eq) for $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (3)

atom	x	y	z	B(eq),[a] Å^2
Os(1)	0.863664 (80)	1/4	0.08860 (12)	3.13 (5)
Os(2)	0.821050 (56)	0.151239 (55)	−0.185629 (81)	3.04 (4)
S	0.96367 (52)	1/4	−0.22443 (75)	3.4 (3)
O(11)	0.8710 (13)	0.0290 (11)	0.1280 (19)	6 (1)
O(12)	0.9606 (17)	1/4	0.3948 (26)	8 (2)
O(13)	0.6566 (14)	1/4	0.2226 (24)	5 (1)
O(21)	0.7638 (13)	0.1366 (11)	−0.5113 (17)	6.1 (9)
O(22)	0.6184 (12)	0.0905 (12)	−0.0738 (18)	6 (1)
O(23)	0.9139 (13)	−0.0473 (11)	−0.2081 (19)	6 (1)
C	0.9999 (18)	1/4	−0.0275 (31)	3 (1)
C(11)	0.8659 (13)	0.1097 (16)	0.0871 (23)	4 (1)
C(12)	0.9257 (26)	1/4	0.2776 (33)	6 (2)
C(13)	0.7334 (19)	1/4	0.1715 (28)	4 (1)
C(21)	0.7896 (16)	0.1436 (16)	−0.3930 (23)	4 (1)
C(22)	0.6891 (15)	0.1130 (15)	−0.1187 (23)	4 (1)
C(23)	0.8763 (15)	0.0268 (16)	−0.1997 (24)	4 (1)
H	1.0347	0.1864	−0.0092	4 (0)

[a] $B(\text{eq}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\alpha)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\gamma)\beta_{23}]$.

to have been formed by an intramolecular C–H activation in the CH_2 group and is formulated as $Os_3(CO)_9(\mu_3\text{-}SCH)(\mu\text{-}H)$. The infrared spectrum of **5** is very similar to the structurally characterized compound $Os_3(CO)_9[\mu_3\text{-}N(Me)CH](\mu\text{-}H)$[18] and is believed to be structurally similar as well. This is further supported by a single-crystal X-ray diffraction analysis of the PPh_3 substitution derivative of **5** (vide infra). It was found that compound **5** could be prepared also by the reaction $Os_3(CO)_9(\mu_3\text{-}CCO)(\mu\text{-}H)_2$[9] (**6**) with C_2H_4S (30% yield).

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[18] Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579.

Table VII. Intramolecular Distances (Å) for $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (3)[a]

Os(1)–C(12)	1.89 (3)	Os(2)–Os(2′)	2.745 (2)
Os(1)–C(13)	1.93 (3)	S–C	1.82 (3)
Os(1)–C(11)	1.95 (2)	O(11)–C(11)	1.18 (2)
Os(1)–C(11′)	1.95 (2)	O(12)–C(12)	1.15 (4)
Os(1)–C	2.14 (3)	O(13)–C(13)	1.15 (3)
Os(1)–Os(2)	2.862 (1)	O(21)–C(21)	1.12 (2)
Os(1)–Os(2′)	2.862 (1)	O(22)–C(22)	1.09 (2)
Os(2)–C(23)	1.89 (2)	O(23)–C(23)	1.15 (2)
Os(2)–C(21)	1.90 (2)	C–H	1.02
Os(2)–C(22)	1.98 (2)	Os(2)–C(11)	2.57 (2)
Os(2)–S	2.415 (6)		

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

Table VIII. Intramolecular Bond Angles (deg) for $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (3)

C(12)–Os(1)–C(13)	94 (1)	C(21)–Os(2)–C(22)	94.0 (8)
C(12)–Os(1)–C(11)	89.9 (6)	C(21)–Os(2)–S	94.4 (6)
C(12)–Os(1)–C(11)	89.9 (6)	C(21)–Os(2)–Os(2′)	93.2 (7)
C(12)–Os(1)–C	92 (1)	C(21)–Os(2)–Os(1)	154.5 (7)
C(12)–Os(1)–Os(2)	148.6 (4)	C(22)–Os(2)–S	159.6 (6)
C(12)–Os(1)–Os(2)	148.6 (4)	C(22)–Os(2)–Os(2′)	105.6 (6)
C(13)–Os(1)–C(11)	91.0 (5)	C(22)–Os(2)–Os(1)	93.3 (6)
C(13)–Os(1)–C(11)	91.0 (5)	S–Os(2)–Os(2′)	55.4 (1)
C(13)–Os(1)–C	173 (1)	S–Os(2)–Os(1)	71.6 (2)
C(13)–Os(1)–Os(2)	97.9 (7)	Os(2)–Os(2)–Os(1)	61.34 (2)
C(13)–Os(1)–Os(2)	97.9 (7)	C–S–Os(2)	94.8 (7)
C(11)–Os(1)–C(11)	178 (1)	C–S–Os(2′)	94.8 (7)
C(11)–Os(1)–C	89.0 (6)	Os(2)–S–Os(2′)	69.3 (2)
C(11)–Os(1)–Os(2)	61.2 (6)	H–C–H′	121
C(11)–Os(1)–Os(2)	118.5 (6)	H–C–S	106
C(11)–Os(1)–C	89.0 (6)	H–C–Os(1)	109
C(11)–Os(1)–Os(2)	118.5 (6)	H–C–S	106
C(11)–Os(1)–Os(2)	61.2 (6)	H–C–Os(1)	109
C–Os(1)–Os(2)	76.4 (6)	S–C–Os(1)	103 (1)
C–Os(1)–Os(2)	76.4 (6)	O(11)–C(11)–Os(1)	162 (2)
Os(2)–Os(1)–Os(2′)	57.31 (4)	O(12)–C(12)–Os(1)	178 (3)
C(23)–Os(2)–C(21)	89 (1)	O(13)–C(13)–Os(1)	179 (2)
C(23)–Os(2)–C(22)	98.1 (9)	O(21)–C(21)–Os(2)	174 (2)
C(23)–Os(2)–S	100.7 (6)	O(22)–C(22)–Os(2)	176 (2)
C(23)–Os(2)–Os(2′)	156.0 (6)	O(23)–C(23)–Os(2)	177 (2)
C(23)–Os(2)–Os(1)	114.4 (7)		

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

Due to our unsuccessful attempts to obtain crystals of **5**, efforts to prepare crystalline derivatives of **5** were undertaken. Surprisingly, compound **5** was found to engage in a facile addition reaction with tertiary phosphines. The new compounds **7a** and **7b** were obtained in 81% and 74% yields from the reaction of **5** with PMe_2Ph and $PMePh_2$, respectively, at 25 °C. Both products contain a hydride ligand as indicated by their ^1H NMR spectra (see Table II), but the resonance attributed to the thioformyl ligand in **5** was shifted back to the region characteristic of the thioformaldehyde ligands, (e.g., 2–4 ppm). In addition, both **7a** and **7b** existed in solution as a mixture of two slowly interconverting isomers in a 4/1 ratio at 25 °C. At higher temperatures the rate of interconversion was increased and became rapid on the NMR time scale. The resonance's coalescence temperature for the methyl groups attached to phosphorus atom was 50 °C for **7b** in toluene-d_8 solvent at 80 MHz. Interestingly, the resonances of the diastereotopic methyl groups of the isomers of **7a** were not averaged by the exchange process. The hydride resonances as well as the thioformyl CH resonances of the isomers also broaden, but fast exchange limits for these resonances could not be obtained due to their larger shift separations and the existence of a slow decomposition process through which the compounds **7a, b** released the phosphine ligand and were converted back into **5**. Resonances due to free phosphine slowly increased in intensity over a period of time. It is significant that resonances of the free phosphine did not average with those of the isomers when the latter were engaged in rapid exchange. When heated in the presence of CH_3I, compounds **7a,b** were reconverted to **5** in quantitative yield.

Table IX. Positional Parameters and *B*(eq) for $Os_3(CO)_9[\mu_3\text{-}SC(H)PMePh_2]H$ (7b)

atom	*x*	*y*	*z*	*B*(eq),[a] Å²
Os(1)	0.211605 (61)	0.514421 (46)	0.343884 (46)	3.2*
Os(2)	0.376250 (59)	0.646946 (48)	0.335784 (48)	3.0*
Os(3)	0.193415 (59)	0.697569 (45)	0.244803 (47)	3.3*
S	0.32562 (37)	0.59915 (29)	0.18549 (29)	3.3*
P	0.21712 (39)	0.41963 (30)	0.12397 (31)	3.1*
O(11)	0.1365 (13)	0.6055 (11)	0.5139 (10)	5.8*
O(12)	0.0193 (14)	0.3930 (13)	0.3168 (12)	6.9*
O(13)	0.3539 (13)	0.3771 (12)	0.4454 (11)	6.3*
O(21)	0.3500 (13)	0.7291 (12)	0.5205 (11)	6.0*
O(22)	0.5143 (15)	0.8094 (13)	0.2798 (12)	7.0*
O(23)	0.5457 (15)	0.5072 (13)	0.3912 (12)	7.1*
O(31)	0.0994 (13)	0.8075 (11)	0.3962 (11)	5.9*
O(32)	0.2903 (13)	0.8825 (12)	0.1862 (11)	6.1*
O(33)	0.0132 (14)	0.6994 (12)	0.1049 (11)	6.3*
C	0.2831 (13)	0.4797 (11)	0.2198 (11)	2.6*
C(11)	0.1681 (16)	0.5698 (15)	0.4507 (14)	4.2*
C(12)	0.0960 (17)	0.4372 (15)	0.3245 (14)	4.4*
C(13)	0.2999 (15)	0.4295 (14)	0.4049 (13)	3.6*
C(21)	0.3607 (17)	0.6959 (15)	0.4498 (15)	4.8*
C(22)	0.4604 (19)	0.7487 (17)	0.2985 (15)	5.1*
C(23)	0.4804 (16)	0.5599 (14)	0.3707 (13)	3.9*
C(31)	0.1313 (16)	0.7651 (14)	0.3374 (13)	4.0*
C(32)	0.2528 (15)	0.8121 (14)	0.2053 (13)	3.9*
C(33)	0.0804 (15)	0.6987 (13)	0.1549 (13)	3.6*
C(41)	0.2001 (14)	0.2962 (13)	0.1470 (12)	3.3*
C(42)	0.2346 (18)	0.2572 (16)	0.2268 (15)	4.8*
C(43)	0.2104 (20)	0.1585 (18)	0.2423 (17)	6.1*
C(44)	0.1624 (21)	0.1114 (18)	0.1786 (17)	6.1*
C(45)	0.1258 (19)	0.1465 (17)	0.0998 (16)	5.7*
C(46)	0.1477 (17)	0.2419 (15)	0.0823 (14)	4.5*
C(51)	0.2919 (14)	0.4294 (12)	0.0253 (12)	3.1*
C(52)	0.2860 (17)	0.5112 (15)	−0.0239 (14)	4.5*
C(53)	0.3513 (18)	0.5260 (16)	−0.0930 (15)	5.2*
C(54)	0.4176 (19)	0.4592 (17)	−0.1126 (16)	5.4*
C(55)	0.4246 (19)	0.3728 (17)	−0.0653 (16)	5.5*
C(56)	0.3634 (16)	0.3611 (14)	0.0072 (14)	4.3*
C(61)	0.0923 (15)	0.4682 (13)	0.0923 (12)	3.6*
H(1)	0.3510	0.4311	0.2288	5.0

[a] $B(\text{eq}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\alpha)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\gamma)\beta_{23}]$. Atoms with an asterisk were refined with isotropic thermal parameters.

There was no evidence of a reaction between **5** and PPh_3 at 25 °C (24 h) or 68 °C (5 h). However, evidence for the formation of the PPh_3 adduct **7c** was obtained when a solution of sodium diphenylketyl was added to the reaction mixture at 25 °C. Unfortunately, when it was subjected to purification procedures, it was found that **7c** slowly released PPh_3 even at 25 °C, and all attempts to isolate it in a pure form were unsuccessful. Nevertheless, the spectra of **7c** were easily distinguished from **5** in the mixtures of **5** and **7c** and showed clearly that **7c** is an analogue of **7a** and **7b**; see Table II. However, unlike **7a,b**, **7c** did not exist as a mixture of isomers.

Description of the Structure of $Os_3(CO)_9[\mu_3\text{-}SC(H)PMePh_2](\mu\text{-}H)$ (7b). The form of the molecular structure of **7b** was determined by a single-crystal X-ray diffraction analysis. An ORTEP drawing of its structure is shown in Figure 3. Final positional parameters are listed in Table IX. Interatomic distances and angles are listed in Tables X and XI, respectively. It is readily seen that **7b** is a $PMePh_2$ adduct of **5**. The surprising observation is the site of addition. The $PMePh_2$ ligand was added to the carbon atom of the thioformyl ligand. The P–C bond distance of 1.82 (2) Å is typical of a P–C single bond and

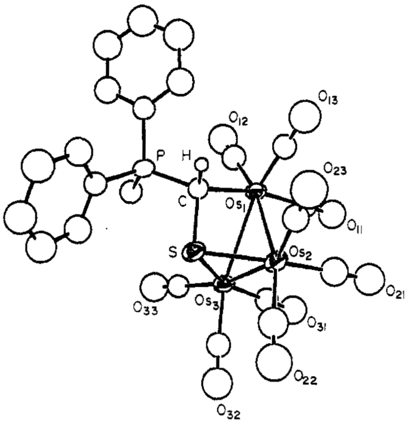

Figure 3. An ORTEP diagram of the molecular structure of $Os_3(CO)_9[\mu_3\text{-}SC(H)PMePh_2](\mu\text{-}H)$ (**7b**) showing 50% probability thermal ellipsoids. The ellipsoid on the hydrogen atom H_1 has been reduced for clarity.

Table X. Intramolecular Distances (Å) for $Os_3(CO)_9[\mu_3\text{-}SC(H)PMePh_2]H$ (7b)[a]

Os(1)–C(13)	1.85 (2)	O(12)–C(12)	1.17 (2)
Os(1)–C(12)	1.85 (2)	O(13)–C(13)	1.16 (2)
Os(1)–C(11)	1.89 (2)	O(21)–C(21)	1.17 (2)
Os(1)–C	2.18 (2)	O(22)–C(22)	1.15 (3)
Os(1)–Os(2)	2.839 (1)	O(23)–C(23)	1.15 (2)
Os(1)–Os(3)	2.970 (1)	O(31)–C(31)	1.16 (2)
Os(2)–C(21)	1.86 (2)	O(32)–C(32)	1.15 (2)
Os(2)–C(23)	1.87 (2)	O(33)–C(33)	1.11 (2)
Os(2)–C(22)	1.90 (2)	C(41)–C(42)	1.36 (3)
Os(2)–S	2.386 (5)	C(41)–C(46)	1.37 (3)
Os(2)–Os(3)	2.739 (2)	C(42)–C(43)	1.44 (3)
Os(3)–C(32)	1.90 (2)	C(43)–C(44)	1.28 (3)
Os(3)–C(31)	1.90 (2)	C(44)–C(45)	1.33 (3)
Os(3)–C(33)	1.91 (2)	C(45)–C(46)	1.40 (3)
Os(3)–S	2.413 (4)	C(51)–C(52)	1.36 (3)
S–C	1.85 (2)	C(51)–C(56)	1.37 (3)
P–C(41)	1.79 (2)	C(52)–C(53)	1.39 (3)
P–C(61)	1.79 (2)	C(53)–C(54)	1.32 (3)
P–C(51)	1.82 (2)	C(54)–C(55)	1.40 (3)
P–C	1.82 (2)	C(55)–C(56)	1.39 (3)
O(11)–C(11)	1.17 (2)	C–H(1)	1.12

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

is experimentally equivalent in length to the three other P–C bond distances to this phosphorus atom. The C–S distance of 1.85 (2) Å is only slightly longer than that observed for the thioformaldehyde ligands in **2** and **3**. The carbon atom C is coordinated only to the metal atom Os(1). The Os(1)–C distance of 2.18 (2) Å is slightly longer than the corresponding distance in **3**. The sulfur atom bridges Os(2) and Os(3). The Os–S distances are very similar to those in **3**. The three metal atoms are arranged in the form of a distorted triangle. The distances Os(1)–Os(2) = 2.839 (1) Å and Os(2)–Os(3) = 2.739 (2) Å are very similar to those in **3**; however, the Os(1)–Os(3) distance at 2.970 (1) Å is much longer (0.108 Å) than that in **3**. It is believed that this elongation is due to the presence of the structurally unobserved bridging hydride ligand at this site.[19] The hydrogen atom on the carbon C was located in a chemically reasonable position, C–H = 1.12 Å, but was not subjected to refinement. The compound contains nine linear terminal carbonyl ligands arranged with three on each metal atom.

Table XI. Intramolecular Bond Angles (deg) for $Os_3(CO)_9[\mu_3\text{-}SC(H)PMePh_2]H$ (7b)[a]

C(13)–Os(1)–C(12)	99.4 (9)	C(33)–Os(3)–Os(1)	112.7 (6)
C(13)–Os(1)–C(11)	93.5 (8)	S–Os(3)–Os(2)	54.7 (1)
C(13)–Os(1)–C	89.4 (7)	S–Os(3)–Os(1)	69.5 (1)
C(13)–Os(1)–Os(2)	90.3 (6)	Os(2)–Os(3)–Os(1)	59.47 (3)
C(13)–Os(1)–Os(3)	146.1 (6)	C–S–Os(2)	93.7 (5)
C(12)–Os(1)–C(11)	95.1 (9)	C–S–Os(3)	100.9 (5)
C(12)–Os(1)–C	96.9 (8)	Os(2)–S–Os(3)	69.6 (1)
C(12)–Os(1)–Os(2)	167.7 (6)	C(41)–P–C(61)	107.5 (9)
C(12)–Os(1)–Os(3)	113.2 (6)	C(41)–P–C(51)	107.9 (8)
C(11)–Os(1)–C	167.0 (8)	C(41)–P–C	111.0 (8)
C(11)–Os(1)–Os(2)	91.8 (6)	C(61)–P–C(51)	106.1 (8)
C(11)–Os(1)–Os(3)	92.4 (6)	C(61)–P–C	113.4 (8)
C–Os(1)–Os(2)	75.4 (4)	C(51)–P–C	110.6 (8)
C–Os(1)–Os(3)	78.3 (4)	P–C–S	109.7 (8)
Os(2)–Os(1)–Os(3)	56.20 (3)	P–C–Os(1)	124.5 (9)
C(21)–Os(2)–C(23)	96.3 (9)	S–C–Os(1)	100.5 (7)
C(21)–Os(2)–C(22)	95 (1)	O(11)–C(11)–Os(1)	176 (2)
C(21)–Os(2)–S	157.4 (7)	O(12)–C(12)–Os(1)	175 (2)
C(21)–Os(2)–Os(3)	102.3 (7)	O(13)–C(13)–Os(1)	178 (2)
C(21)–Os(2)–Os(1)	94.4 (7)	O(21)–C(21)–Os(2)	178 (2)
C(23)–Os(2)–C(22)	99 (1)	O(22)–C(22)–Os(2)	177 (2)
C(23)–Os(2)–S	102.9 (6)	O(23)–C(23)–Os(2)	179 (2)
C(23)–Os(2)–Os(3)	152.9 (6)	O(31)–C(31)–Os(3)	176 (2)
C(23)–Os(2)–Os(1)	95.0 (6)	O(32)–C(32)–Os(3)	176 (2)
C(22)–Os(2)–S	93.7 (7)	O(33)–C(33)–Os(3)	178 (2)
C(22)–Os(2)–Os(3)	98.7 (7)	O(42)–C(41)–C(46)	120 (2)
C(22)–Os(2)–Os(1)	162.1 (7)	C(42)–C(41)–P	122 (2)
S–Os(2)–Os(3)	55.7 (1)	C(46)–C(41)–P	118 (1)
S–Os(2)–Os(1)	72.3 (1)	C(41)–C(42)–C(43)	118 (2)
Os(3)–Os(2)–Os(1)	64.33 (3)	C(44)–C(43)–C(42)	119 (2)
C(32)–Os(3)–C(31)	90.0 (8)	C(43)–C(44)–C(45)	126 (3)
C(32)–Os(3)–C(33)	94.7 (8)	C(44)–C(45)–C(46)	117 (2)
C(32)–Os(3)–S	93.6 (6)	C(41)–C(46)–C(45)	120 (2)
C(32)–Os(3)–Os(2)	91.2 (6)	C(52)–C(51)–C(56)	120 (2)
C(32)–Os(3)–Os(1)	150.6 (6)	C(52)–C(51)–P	119 (1)
C(31)–Os(3)–C(33)	99.4 (8)	C(56)–C(51)–P	121 (1)
C(31)–Os(3)–S	154.0 (6)	C(51)–C(52)–C(53)	121 (2)
C(31)–Os(3)–Os(2)	99.5 (6)	C(54)–C(53)–C(52)	120 (2)
C(31)–Os(3)–Os(1)	95.5 (6)	C(53)–C(54)–C(55)	122 (2)
C(33)–Os(3)–S	106.0 (6)	C(56)–C(55)–C(54)	118 (2)
C(33)–Os(3)–Os(2)	160.2 (6)	O(51)–C(56)–C(55)	120 (2)

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

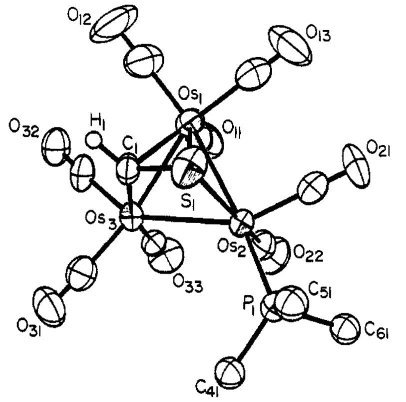

Figure 4. An ORTEP diagram of molecule A of $Os_3(CO)_8(PPh_3)(\mu_3\text{-}SCH)(\mu\text{-}H)$ (**8**) showing 50% probability ellipsoids. The ellipsoid on the hydrogen atom H_1 has been reduced for clarity.

When solutions of **5** and PPh_3 were treated with Me_3NO at 25 °C, **7c** was not formed, but instead the new compound **8** was formed in 17% yield. The ^1H NMR spectrum of **8** showed resonances at 10.23 (d, 1 H, J_{H-H} = 1.45 Hz) and −17.12 ppm (dd, 1 H, J_{H-H} = 1.45 Hz, J_{P-H} = 12.53 Hz) in addition to the resonances of the phenyl groups, 7.20–7.45 ppm (15 H). The very low-field resonance is nearly identical with that in **5** and indicates that the thioformyl ligand was not modified in **8**. This was confirmed by an X-ray structural analysis.

Description of the Structure of $Os_3(CO)_8(PPh_3)(\mu_3\text{-}SCH)(\mu\text{-}H)$ (8). Compound **8** crystallizes with

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[19] (a) Churchill, M. R. *Adv. Chem. Ser.* **1978**, *No. 167*, 36. (b) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

Table XII. Positional Parameters and *B*(eq) for $Os_3(CO)_8(PPh_3)(\mu_3\text{-}SCH)(\mu\text{-}H)$ (8)

atom	*x*	*y*	*z*	*B*(eq),[a] Å²	atom	*x*	*y*	*z*	*B*(eq),[a] Å²
Os(1A)	0.224134 (56)	−0.028217 (43)	0.080840 (58)	4.01 (3)	C(32B)	0.0878 (14)	0.3584 (11)	0.1878 (16)	5.0 (7)
Os(1B)	0.276877 (57)	0.497476 (41)	0.390386 (57)	4.09 (3)	C(33A)	0.4322 (31)	0.1974 (16)	0.1187 (17)	11 (2)
Os(2A)	0.235411 (46)	0.019763 (36)	−0.117387 (50)	2.83 (2)	C(33B)	0.1439 (13)	0.2644 (11)	0.3273 (13)	4.2 (6)
Os(2B)	0.245211 (49)	0.437325 (37)	0.575621 (51)	3.19 (2)	C(41A)	0.3407 (12)	−0.05443 (88)	−0.3359 (13)	3.4 (3)*
Os(3A)	0.338816 (56)	0.130944 (47)	0.106446 (57)	3.71 (3)	C(41B)	0.0704 (12)	0.35314 (88)	0.7198 (13)	3.5 (3)*
Os(3B)	0.108780 (49)	0.365089 (38)	0.347743 (53)	3.26 (2)	C(42)A)	0.4021 (16)	−0.0452 (12)	−0.4049 (18)	6.2 (5)*
S(1A)	0.34295 (34)	−0.04470 (27)	−0.02738 (36)	4.2 (2)	C(42B)	−0.0082 (13)	0.35245 (98)	0.6354 (14)	4.3 (4)*
S(1B)	0.18753 (42)	0.54330 (27)	0.52338 (40)	5.2 (2)	C(43A)	0.4304 (19)	−0.1115 (15)	−0.4577 (21)	7.9 (6)*
P(1A)	0.30047 (30)	0.03051 (23)	−0.27368 (32)	2.9 (1)	C(43B)	−0.1028 (15)	0.3013 (11)	0.6200 (16)	5.5 (4)*
P(1B)	0.18870 (33)	0.42799 (25)	0.73882 (34)	3.4 (1)	C(44A)	0.3935 (16)	−0.1851 (12)	−0.4381 (17)	6.0 (5)*
O(11A)	0.0735 (10)	0.05646 (81)	0.1324 (12)	6.6 (6)	C(44B)	−0.1180 (17)	0.2516 (12)	0.6879 (18)	6.5 (5)*
O(11B)	0.3530 (11)	0.36151 (94)	0.2884 (14)	7.4 (7)	C(45A)	0.3363 (14)	−0.1946 (10)	−0.3675 (15)	4.6 (4)*
O(12A)	0.0592 (13)	−0.18568 (82)	−0.0400 (15)	8.3 (7)	C(45B)	−0.0429 (18)	0.2503 (13)	0.7712 (19)	6.9 (5)*
O(12B)	0.2575 (16)	0.57026 (99)	0.1898 (13)	11 (1)	C(46A)	0.3068 (13)	−0.13011 (95)	−0.3163 (14)	4.0 (3)*
O(13A)	0.2877 (12)	−0.0697 (11)	0.3031 (13)	9.2 (8)	C(46B)	0.0547 (15)	0.3019 (12)	0.7874 (17)	5.7 (4)*
O(13B)	0.4818 (15)	0.6175 (12)	0.5080 (17)	12 (1)	C(51A)	0.4111 (11)	0.11528 (85)	−0.2493 (12)	3.2 (3)*
O(21A)	0.0864 (10)	0.11054 (81)	−0.1566 (11)	6.4 (6)	C(51B)	0.1727 (12)	0.52054 (93)	0.8215 (13)	3.8 (3)*
O(21B)	0.4467 (11)	0.5448 (10)	0.7262 (13)	8.5 (7)	C(52A)	0.4213 (12)	0.16589 (94)	−0.3188 (14)	3.9 (3)*
O(22A)	0.07243 (93)	−0.13112 (76)	−0.2608 (12)	5.7 (5)	C(52B)	0.2267 (14)	0.5944 (11)	0.8175 (16)	5.0 (4)*
O(22B)	0.3238 (10)	0.29349 (83)	0.5524 (11)	6.4 (6)	C(53A)	0.5076 (14)	0.2290 (10)	−0.2936 (15)	4.9 (4)*
O(31A)	0.3636 (12)	0.1666 (10)	0.3626 (11)	8.3 (7)	C(53B)	0.2221 (16)	0.6644 (12)	0.8901 (18)	6.1 (5)*
O(31B)	−0.1084 (10)	0.29054 (90)	0.3309 (13)	6.7 (6)	C(54A)	0.5852 (14)	0.2401 (11)	−0.2031 (16)	5.2 (4)*
O(32A)	0.2044 (11)	0.23908 (82)	0.0745 (12)	7.0 (6)	C(54B)	0.1635 (16)	0.6572 (12)	0.9630 (18)	6.1 (5)*
O(32B)	0.07856 (96)	0.35814 (76)	0.0961 (10)	5.5 (5)	C(55A)	0.5751 (14)	0.1871 (11)	−0.1373 (16)	5.3 (4)*
O(33A)	0.5305 (14)	0.25387 (95)	0.1351 (14)	8.3 (8)	C(55B)	0.1103 (18)	0.5875 (14)	0.9671 (20)	7.4 (6)*
O(33B)	0.1658 (11)	0.20835 (75)	0.3154 (12)	6.4 (6)	C(56A)	0.4891 (12)	0.12638 (92)	−0.1562 (13)	3.8 (3)*
C(1A)	0.3842 (14)	0.03033 (93)	0.1038 (12)	4.4 (6)	C(56B)	0.1131 (16)	0.5158 (12)	0.8957 (18)	6.0 (5)*
C(1B)	0.1196 (12)	0.48550 (88)	0.3893 (13)	3.6 (6)	C(61A)	0.2120 (12)	0.03776 (90)	−0.3956 (13)	3.6 (3)*
C(11A)	0.1313 (13)	0.0264 (10)	0.1208 (14)	4.0 (6)	C(61B)	0.2750 (12)	0.40607 (92)	0.8466 (13)	3.7 (3)*
C(11B)	0.3225 (14)	0.4119 (11)	0.3272 (17)	5.2 (7)	C(62A)	0.1819 (13)	0.1062 (10)	−0.3798 (15)	4.6 (4)*
C(12A)	0.1182 (16)	−0.1292 (12)	0.0066 (17)	4.9 (8)	C(62B)	0.2992 (14)	0.3349 (10)	0.8214 (15)	4.9 (4)*
C(12B)	0.2667 (17)	0.5426 (12)	0.2660 (17)	6.3 (9)	C(63A)	0.1145 (16)	0.1135 (12)	−0.4729 (18)	6.1 (5)*
C(13A)	0.2591 (15)	−0.0584 (14)	0.2142 (18)	6 (1)	C(63B)	0.3658 (15)	0.3175 (11)	0.9010 (16)	5.4 (4)*
C(13B)	0.4078 (18)	0.5721 (14)	0.4638 (17)	6 (1)	C(64A)	0.0805 (16)	0.0524 (12)	−0.5729 (18)	6.1 (5)*
C(21A)	0.1440 (13)	0.07761 (99)	−0.1433 (14)	4.2 (7)	C(64B)	0.4128 (16)	0.3730 (13)	1.0047 (18)	6.4 (5)*
C(21B)	0.3727 (16)	0.5031 (12)	0.6688 (15)	5.3 (8)	C(65A)	0.1069 (16)	−0.0128 (12)	−0.5855 (17)	6.1 (5)*
C(22A)	0.1358 (13)	−0.0761 (11)	−0.2061 (15)	3.8 (6)	C(65B)	0.3909 (17)	0.4440 (13)	1.0305 (18)	6.7 (5)*
C(22B)	0.2936 (13)	0.3467 (10)	0.5617 (15)	4.3 (6)	C(66A)	0.1745 (13)	−0.0230 (10)	−0.4962 (15)	4.6 (4)*
C(31A)	0.3549 (14)	0.1554 (12)	0.2691 (16)	5.5 (8)	C(66B)	0.3230 (14)	0.4604 (10)	0.9508 (15)	4.9 (4)*
C(31B)	−0.0268 (16)	0.3171 (11)	0.3389 (15)	4.6 (7)	H(1A)	0.4424	0.0350	0.1704	4.0
C(32A)	0.2570 (15)	0.20219 (99)	0.0895 (15)	4.8 (7)	H(1B)	0.0920	0.5195	0.3377	4.0

[a] $B(\text{eq}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\alpha)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\gamma)\beta_{23}]$. Atoms were refined with isotropic thermal parameters.

two symmetry-independent molecules in the asymmetric crystallographic unit. The two molecules were found to be structurally similar. An ORTEP drawing of molecule A is shown in Figure 4. Final positional parameters are listed in Table XII. Interatomic distances and angles are listed in Tables XIII and XIV, respectively. The molecule consists of a triangular cluster of three osmium atoms with a triply bridging thioformyl ligand on the triangular face. The carbon atom C(1) bridges the Os(1)–Os(3) bond while the sulfur atom bridges the Os(1)–Os(2) bond. These metal–metal bond distances are very similar in both molecules, 2.784 (1)–2.825 (2) Å. However, the Os(2)–Os(3) distance is considerably longer than the others, 2.912 (2) and 2.931 (2) Å. This elongation effect suggests that the structurally unobserved bridging hydride ligand is located across this bond.[19] The osmium–sulfur distances are of equal length, 2.400 (4)–2.411 (6) Å and are very similar to those in **2**, **3**, and **7b**. The Os(1)–C(1) distance, 2.22 (2) Å, is considerably longer than the Os(3)–C(1) distance, 2.06 (1) Å. Similar distances and inequivalence were observed for Os–C bonding in the complex $Os_3(CO)_9[\mu_3\text{-}N(Ph)\text{-}CH](\mu\text{-}H)$ which contains a triply bridging formimidoyl ligand in a coordination mode similar to the thioformyl ligand in **8**.[18] The C–S distances in molecules A and B of **8** are slightly different, 1.76 (2) and 1.71 (2) Å. There seems to be no chemical basis for this variation. Therefore, it is believed that the average value, 1.74 (2) Å, is of greater accuracy. There are no reported examples of bridging thioformyl ligands for the purposes of comparison. Perhaps the closest related ligand species is that of a triply bridging methylthioacyl group that was found in the complex $Fe_2W(CO)_8(C_5H_5)(\mu_3\text{-}SCCH_3)$. The C–S distance in this complex is 1.755 (8) Å.[20] Roper has characterized a η^2-thioacyl ligand in the mononuclear osmium complex $Os(CO)(PPh_3)_2[\eta^2\text{-}C(S)(p\text{-tol})](O_2CCF_3)$ (tol = tolyl), which showed a C–S distance of 1.76 (4) Å.[17] The C–S distance in **8** is shorter than the C–S distances in **2**, **3**, and **7b** and is indicative of a higher degree of unsaturation. The hydrogen atom on the thioformyl carbon atom was located in a difference Fourier map, C–H = 1.03 and 1.06 Å. The molecule has eight linear terminal carbonyl ligands distributed as shown in Figure 4. The PPh_3 ligand is attached to the sulfur-coordinated metal atom Os(2).

Hydrogenation of Compounds 3 and 5. When heated to reflux in octane solvent under 1 atm of hydrogen, compound **3** was transformed into $Os_3(CO)_{10}(\mu\text{-}SMe)(\mu\text{-}H)$ (**9**) in 41% yield. However, at this temperature the transformation of **3** and **5** also occurs and a 47% yield of **5** was obtained. It is believed that **9** was formed from **3** and not from **5** since **5** could not be converted into **9** under these conditions. Under more forcing conditions (120 °C/70 atm, 1/1 CO/H_2), small amounts of **9** (8% yield) were obtained from solutions of **5**.

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Table XIII. Intramolecular Distances (Å) for $Os_3(CO)_8(PPh_3)(\mu_3\text{-}SCH)(\mu\text{-}H)$ (8)[a]

Os(1A)–C(13A)	1.86 (2)	Os(3B)–C(32B)	1.92 (2)
Os(1A)–C(11A)	1.92 (2)	Os(3B)–C(33B)	1.97 (2)
Os(1A)–C(12A)	1.95 (2)	Os(3B)–C(1B)	2.06 (1)
Os(1A)–C(1A)	2.22 (2)	S(1A)–C(1A)	1.76 (2)
Os(1A)-S(1A)	2.404 (5)	S(1B)–C(1B)	1.71 (2)
Os(1A)–Os(2A)	2.784 (1)	P(1A)–C(51A)	1.83 (2)
Os(1A)–Os(3A)	2.825 (2)	P(1A)–C(41A)	1.83 (2)
Os(1B)–C(12B)	1.88 (2)	P(1A)–C(61A)	1.83 (2)
Os(1B)–C(11B)	1.89 (2)	P(1B)–C(61B)	1.82 (2)
Os(1B)–C(13B)	1.94 (2)	P(1B)–C(41B)	1.82 (2)
Os(1B)–C(1B)	2.22 (2)	P(1B)–C(51B)	1.85 (2)
Os(1B)–S(1B)	2.411 (6)	O(11A)–C(11A)	1.11 (2)
Os(1B)–Os(2B)	2.795 (1)	O(11B)–C(11B)	1.15 (2)
Os(1B)–Os(3B)	2.804 (2)	O(12A)–C(12A)	1.10 (2)
Os(2A)–C(21A)	1.89 (2)	O(12B)–C(12B)	1.16 (2)
Os(2A)–C(22A)	1.89 (2)	O(13A)–C(13A)	1.18 (2)
Os(2A)–P(1A)	2.328 (4)	O(13B)–C(13B	1.12 (2)
Os(2A)–S(1A)	2.400 (4)	O(21A)–C(21A)	1.14 (2)
Os(2A)–Os(3A)	2.912 (2)	O(21B)–C(21B)	1.14 (2)
Os(2B)–C(21B)	1.91 (2)	O(22A)–C(22A)	1.14 (2)
Os(2B)–C(22B)	1.91 (2)	O(22B)–C(22B)	1.13 (2)
Os(2B)–P(1B)	2.340 (4)	O(31A)–C(31A)	1.11 (2)
Os(2B)–S(1B)	2.408 (4)	O(31B)–C(31B)	1.13 (2)
Os(2B)–Os(3B)	2.931 (2)	O(32A)–C(32A)	1.14 (2)
Os(3A)–C(33A)	1.51 (4)	O(32B)–C(32B)	1.12 (2)
Os(3A)–C(31A)	1.92 (2)	O(33A)–C(33A)	1.47 (4)
Os(3A)–C(32A)	1.96 (2)	O(33B)–C(33B)	1.11 (2)
Os(3A)–C(1A)	2.06 (1)	C(1A)–H(1A)	1.03
Os(3B)–C(31B)	1.90 (2)	C(1B)–H(1B)	1.06

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

The reaction of **9** with hydrogen (150 °C/1 atm) gave a good yield of $Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)_2$ (**10**)[21] and methane. The latter was identified by a GC–MS analysis. The reductive elimination of methane from **9** could not be effected by treatment of **9** with CO at 100 °C/100 atm.

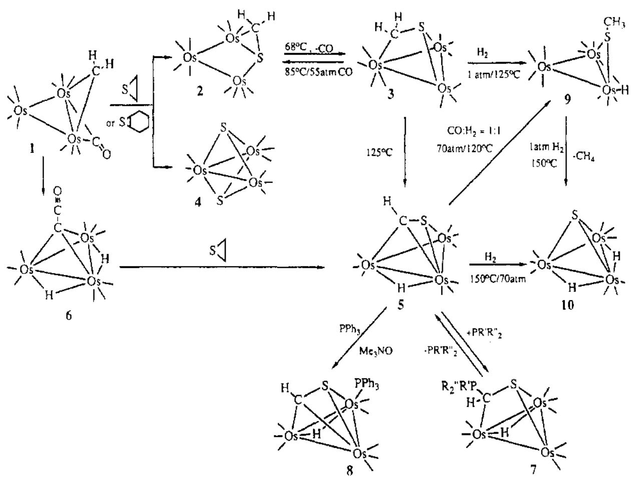
Discussion

Since the first report in 1977,[22] thioformaldehyde ligands have been prepared by a variety of methods including hydrogenation of thiocarbonyl ligands,[17] hydrogenation and fragmentation of CS_2,[15] reactions of diazomethane with sulfido metal complexes,[23] reactions of NaSH with iodomethyl iodo metal complexes,[24] and reaction of an episulfide with a methylene-containing metal complex.[16]

Geoffroy has shown that compound **1** readily engages in an addition reaction with CO to induce a coupling of the methylene ligand to a carbonyl ligand and form the complex $Os_3(CO)_{12}(\mu\text{-}CH_2C{=}O)$ that contains a bridging ketene ligand.[25] With anions **1** engages in a CO substitution reaction.[26] More recently, **1** has been shown to add unsaturated transition-metal fragments.[27]

In this work it has been shown that **1** will accept a sulfur atom from an organic episulfide to yield complexes **2** and **3** in which the sulfur atom has been added to the methylene ligand to form a thioformaldehyde ligand. Compound **3** was formed from **2** by a loss of one CO ligand. Gladysz has shown that the sulfur can be transferred from cyclohexene sulfide to the methylene ligand in the mononuclear rhenium complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)^+$ to yield the complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)^+$ that contains a π-bonded thioformaldehyde ligand.[16]

Scheme I



At 125 °C **3** is decarbonylated in a process that also induces the activation of one of the C–H bonds in the CH_2 group and yields complex **5** that contains the first example of a thioformyl ligand in a cluster complex; see Scheme I. Similar C–H activation processes have been observed in the methylene ligands in complexes **1**[9] and $Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}H)_2$ (**10**)[28] under similar conditions. The implication is that even though the methylene group in **3** is bonded to a sulfur atom, the C–H activation barrier is not significantly different from those examples where the sulfur is not present. Interestingly, **5** could also be made in a good yield by the transfer of sulfur from ethylene sulfide to **6**. In this reaction a hydride ligand is shifted from the metal atoms to the carbon atom.

In our attempts to obtain a phosphine ligand derivative of **5**, compounds **7a–c** were obtained in which it was found that the phosphine ligand had been added to the complex at the carbon atom of the thioformyl ligand. The length of the new P–C bond is normal yet the bond is readily cleaved to release the phosphine molecule and regenerate **5**. Except for **7c**, ¹H NMR spectra of **7a,b** and ³¹P NMR spectra of **7b** indicate that the compounds exist in solution as a mixture of two isomers that can be interconverted rapidly on the NMR time scale at temperatures slightly above 25 °C. Two types of isomerism are readily available to the compounds **7a,b**. Energetically similar structural isomers could be formed by positoning the hydride ligand on bridging sites across different metal–metal bonds. Alternatively, rotational conformers formed by different rotational configurations about the thioformyl carbon–phosphorus bond should be possible. While it would seem that conformational interconversions should be rapid on the NMR time scale at all routinely available temperatures, in fact, inspection of models of **7b** shows that extremely unfavorable steric interactions between the phenyl rings and the carbonyls C(12)–O(12) and C(33)–O(33) would occur during rotational transformations about the P–C bond. The absence of isomer formation in compound **7c** leads us to favor the conformational explanation over that of the hydride ligand positional isomers.

The formation of **7a–c** is believed to have occurred by a direct nucleophilic addition of the phosphorus atom to

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Table XIV. Intramolecular Bond Angles for $Os_3(CO)_8(PPh_3)(\mu_3\text{-}SCH)(\mu\text{-}H)$ (8)[a]

C(13A)–Os(1A)–C(11A)	99.7 (8)	S(1B)–Os(1B)–Os(3B)	76.4 (1)	C(31A)–Os(3A)–C(1A)	92.2 (7)	C(41B)–P(1B)–Os(2B)	117.5 (5)
C(13A)–Os(1A)–C(12A)	93 (1)	Os(2B)–Os(1B)–Os(3B)	63.13 (4)	C(31A)–Os(3A)–Os(1A)	90.4 (7)	C(51B)–P(1B)–Os(2B)	116.0 (5)
C(13A)–Os(1A)–S(1A)	107.9 (6)	C(21A)–Os(2A)–C(22A)	89.3 (7)	C(32A)–Os(3A)–C(1A)	162.8 (7)	S(1A)–C(1A)–Os(3A)	116.2 (7)
C(13A)–Os(1A)–Os(2A)	161.3 (6)	C(21A)–Os(2A)–P(1A)	97.8 (5)	C(32A)–Os(3A)–Os(1A)	112.2 (5)	S(1A)–C(1A)–Os(1A)	73.3 (6)
C(13A)–Os(1A)–Os(3A)	110.1 (7)	C(21A)–Os(2A)–S(1A)	162.4 (5)	C(32A)–Os(3A)–Os(2A)	93.2 (5)	Os(3A)–C(1A)–Os(1A)	82.6 (6)
C(11A)–Os(1A)–C(12A)	91.7 (7)	C(21A)–Os(2A)–Os(1A)	108.7 (5)	C(1A)–Os(3A)–Os(1A)	51.1 (5)	S(1B)–C(1B)–Os(3B)	117.9 (7)
C(11A)–Os(1A)–C(1A)	125.2 (6)	C(21A)–Os(2A)–Os(3A)	92.3 (5)	C(1A)–Os(3A)–Os(2A)	74.4 (4)	S(1B)–C(1B)–Os(1B)	74.3 (6)
C(11A)–Os(1A)–S(1A)	149.0 (5)	C(22A)–Os(2A)–P(1A)	90.9 (5)	Os(1A)–Os(3A)–Os(2A)	58.04 (4)	Os(3B)–C(1B)–Os(1B)	81.6 (6)
C(11A)–Os(1A)–Os(2A)	96.1 (5)	C(22A)–Os(2A)–S(1A)	95.9 (4)	C(31B)–Os(3B)–C(32B)	94.9 (8)	O(11A)–C(11A)–Os(1A)	173 (2)
C(11A)–Os(1A)–Os(3A)	81.2 (5)	C(22A)–Os(2A)–Os(1A)	90.5 (5)	C(31B)–Os(3B)–C(33B)	95.7 (7)	O(11B)–C(11B)–Os(1B)	178 (2)
C(12A)–Os(1A)–C(1A)	142.4 (7)	C(22A)–Os(2A)–Os(3A)	148.7 (5)	C(31B)–Os(3B)–C(1B)	101.4 (7)	O(12A)–C(12A)–Os(1A)	177 (2)
C(12A)–Os(1A)–S(1A)	100.4 (5)	P(1A)–Os(2A)–S(1A)	98.9 (1)	C(31B)–Os(3B)–Os(1B)	153.0 (5)	O(12B)–C(12B)–Os(1B)	178 (2)
C(12A)–Os(1A)–Os(2A)	96.2 (5)	P(1A)–Os(2A)–Os(1A)	153.5 (1)	C(31B)–Os(3B)–Os(2B)	117.6 (5)	O(13A)–C(13A)–Os(1A)	173 (2)
C(12A)–Os(1A)–Os(3A)	156.4 (5)	P(1A)–Os(2A)–Os(3A)	119.8 (1)	C(32B)–Os(3B)–C(33B)	92.1 (7)	O(13B)–C(13B)–Os(1B)	177 (2)
C(1A)–Os(1A)–S(1A)	44.6 (4)	S(1A)–Os(2A)–Os(1A)	54.7 (1)	C(32B)–Os(3B)–C(1B)	92.3 (7)	O(21A)–C(21A)–Os(2A)	177 (2)
C(1A)–Os(1A)–Os(2A)	75.1 (4)	S(1A)–Os(2A)–Os(3A)	74.7 (1)	C(32B)–Os(3B)–Os(1B)	88.6 (6)	O(21B)–C(21B)–Os(2B)	177 (2)
C(1A)–Os(1A)–Os(3A)	46.3 (4)	Os(1A)–Os(2A)–Os(3A)	59.41 (4)	C(32B)–Os(3B)–Os(2B)	146.2 (6)	O(22A)–C(22A)–Os(2A)	176 (1)
S(1A)–Os(1A)–Os(2A)	54.5 (1)	C(21B)–Os(2B)–C(22B)	88.9 (8)	C(33B)–Os(3B)–C(1B)	161.9 (6)	O(22B)–C(22B)–Os(2B)	179 (2)
S(1A)–Os(1A)–Os(3A)	76.3 (1)	C(21B)–Os(2B)–P(1B)	90.4 (5)	C(33B)–Os(3B)–Os(1B)	110.9 (5)	O(31A)–C(31A)–Os(3A)	177 (2)
Os(2A)–Os(1A)–Os(3A)	62.55 (4)	C(21B)–Os(2B)–S(1B)	97.2 (6)	C(33B)–Os(3B)–Os(2B)	93.5 (5)	O(31B)–C(31B)–Os(3B)	177 (2)
C(12B)–Os(1B)–C(11B)	98.1 (9)	C(21B)–Os(2B)–Os(1B)	91.8 (5)	C(1B)–Os(3B)–Os(1B)	51.7 (5)	O(32A)–C(32A)–Os(3A)	175 (2)
C(12B)–Os(1B)–C(13B)	91.3 (8)	C(21B)–Os(2B)–Os(3B)	149.0 (5)	C(1B)–Os(3B)–Os(2B)	73.4 (4)	O(32B)–C(32B)–Os(3B)	177 (2)
C(12B)–Os(1B)–C(1B)	91.3 (8)	C(22B)–Os(2B)–P(1B)	97.2 (5)	Os(1B)–Os(3B)–Os(2B)	58.29 (4)	O(33A)–C(33A)–Os(3A)	172 (2)
C(12B)–Os(1B)–S(1B)	112.6 (7)	C(22B)–Os(2B)–S(1B)	159.5 (5)	C(1A)–S(1A)–Os(2A)	94.3 (5)	O(33B)–C(33B)–Os(3B)	178 (2)
C(12B)–Os(1B)–Os(2B)	165.3 (7)	C(22B)–Os(2B)–Os(1B)	105.8 (5)	C(1A)–S(1A)–Os(1A)	62.1 (7)	C(42A)–C(41A)–P(1A)	120 (1)
C(12B)–Os(1B)–Os(3B)	109.2 (7)	C(22B)–Os(2B)–Os(3B)	90.7 (5)	Os(2A)–S(1A)–Os(1A)	70.8 (1)	C(46A)–C(41A)–P(1A)	122 (1)
C(11B)–Os(1B)–C(13B)	95.0 (9)	P(1B)–Os(2B)–S(1B)	102.3 (2)	C(1B)–S(1B)–Os(2B)	94.5 (5)	C(46B)–C(41B)–P(1B)	124 (1)
C(11B)–Os(1B)–C(1B)	124.3 (7)	P(1B)–Os(2B)–Os(1B)	156.9 (1)	C(1B)–S(1B)–Os(1B)	62.6 (6)	C(42B)–C(41B)–P(1B)	117 (1)
C(11B)–Os(1B)–S(1B)	145.3 (6)	P(1B)–Os(2B)–Os(3B)	120.3 (1)	Os(2B)–S(1B)–Os(1B)	70.9 (1)	C(52A)–C(51A)–P(1A)	124 (1)
C(11B)–Os(1B)–Os(2B)	92.6 (6)	S(1B)–Os(2B)–Os(1B)	54.6 (1)	C(51A)–P(1A)–C(41A)	101.6 (7)	C(56A)–C(51A)–P(1A)	117 (1)
C(11B)–Os(1B)–Os(3B)	78.7 (6)	S(1B)–Os(2B)–Os(3B)	74.0 (1)	C(51A)–P(1A)–C(61A)	104.9 (7)	C(52B)–C(51B)–P(1B)	121 (1)
C(13B)–Os(1B)–C(1B)	139.7 (8)	Os(1B)–Os(2B)–Os(3B)	58.58 (3)	C(51A)–P(1A)–Os(2A)	116.6 (5)	C(56B)–C(51B)–P(1B)	120 (1)
C(13B)–Os(1B)–S(1B)	99.7 (7)	C(33A)–Os(3A)–C(31A)	92 (1)	C(41A)–P(1A)–C(61A)	103.1 (7)	C(66B)–C(61B)–P(1B)	122 (1)
C(13B)–Os(1B)–Os(2B)	97.7 (5)	C(33A)–Os(3A)–C(32A)	92 (1)	C(41A)–P(1A)–Os(2A)	115.6 (5)	C(62B)–C(61B)–P(1B)	120 (1)
C(13B)–Os(1B)–Os(3B)	159.2 (5)	C(33A)–Os(3A)–C(1A)	105 (1)	C(61A)–P(1A)–Os(2A)	113.4 (5)	C(66A)–C(61A)–P(1A)	122 (1)
C(1B)–Os(1B)–S(1B)	43.2 (4)	C(33A)–Os(3A)–Os(1A)	155.7 (8)	C(61B)–P(1B)–C(41B)	104.4 (7)	C(62A)–C(61A)–P(1A)	116 (1)
C(1B)–Os(1B)–Os(2B)	74.3 (4)	C(33A)–Os(3A)–Os(2A)	119.4 (7)	C(61B)–P(1B)–C(51B)	101.6 (7)		
C(1B)–Os(1B)–Os(3B)	46.7 (4)	C(31A)–Os(3A)–C(32A)	92.2 (7)	C(61B)–P(1B)–Os(2B)	112.9 (6)		
S(1B)–Os(1B)–Os(2B)	54.5 (1)			C(41B)–P(1B)–C(51B)	102.6 (7)		

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

the thioformyl carbon atom. While nucleophilic additions to hydrocarbon ligands in cluster complexes are not commonly observed,[29] some interesting examples of these have been reported recently. Casey has shown that CO and NMe_3 will add to the alkylidyne ligand in $Fe_2(CO)_3(\eta\text{-}C_5H_5)_2(\mu\text{-}CH)^+$.[30] Carty has observed the addition of isocyanides to the acetylide ligand in $Ru_3(CO)_9(\mu_3\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}H)$,[31] and PMe_2Ph has been added to the organic ligands in $Os_3(CO)_{10}(\mu\text{-}C_2H_3)(\mu\text{-}H)$,[32] $Os_3(CO)_9(\mu_3\text{-}C{\equiv}CR)(\mu\text{-}H)$,[33] and $Os_3(CO)_9(\mu_3\text{-}MeC{=}C{=}CH_2)(\mu\text{-}H)$.[33]

The addition of hydrogen to **3** and hydrogen plus CO to **5** yielded the (methanethiolato)triosmium cluster complex **9**. The reductive elimination of methane from **9** could not be induced by reaction with CO at 100 °C/100 atm of CO. This contrasts greatly to the sulfur-free osmium cluster $Os_3(CO)_{10}(\mu\text{-}CH_3)(\mu\text{-}H)$ (**11**) which eliminates methane readily at 25 °C in the presence of PMe_2Ph.[28] The important difference between **9** and **11** is that the methyl group in **9** is not bonded to any of the metal atoms, while in **11** it is. The important consequence is that methane elimination is severely inhibited in **9** but is facile in **11**. This difference could be regarded as an example of a *sulfur inhibition or poisoning of a methane formation reaction on a molecular scale* and is directly related to the cleavage of the carbon–sulfur bond. Under more forcing conditions, 150 °C/1 atm of H_2 methane was eliminated from **9** to yield the sulfido cluster **10**.

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. We wish to thank Johnson Matthey Inc. for a loan of osmium tetraoxide. NMR measurements were made on a Brüker AM-300 spectrometer purchased with funds from the National Science Foundation under Grant CHE-8411172.

Registry No. 1, 77208-32-3; **2**, 104034-05-1; **3**, 104034-06-2; **4**, 72282-40-7; **5**, 108742-94-5; **6**, 83585-34-6; **7a**, 108711-85-9; **7b**, 108711-87-1; **7c**, 108711-88-2; **8** (isomer 1), 108711-86-0; **8** (isomer 2), 108813-06-5; **9**, 68796-14-5; **10**, 38979-82-7; PMe_2Ph, 672-66-2; $PMePh_2$, 1486-28-8; PPh_3, 603-35-0; ethylene sulfide, 420-12-2; cyclohexene sulfide, 286-28-2.

Supplementary Material Available: Tables of anisotropic thermal parameters (*U* values) and calculated hydrogen atom positional parameters for compounds **7b** and **8** (4 pages); listings of structure factor amplitudes for **7b** and **8** (66 pages). Ordering information is given on any current masthead page.

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