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lution, the rate constants were evaluated at 428 nm.

For the slow decompositions of neopentylcobinamide and protonated base-off neopentylcobalamin at room temperature, solutions were stored in the dark, and at appropriate times, spectra of aliquots were recorded before and after photolysis. First-order rate constants were determined from the slopes of ln $[1 - (A_t/A_{h\nu})]$ vs. time, where A_t is the absorbance at time t and $A_{h\nu}$ is the corresponding absorbance after photolysis, measured at the wavelength of the cobalt(III) corrin γ-band.

The anaerobic decomposition of isobutylcobalamin was followed under an atmosphere of argon and produced vitamin B_{12s}, which more slowly was oxidized by protons to vitamin B_{12r}. The first-order rate constant was determined at 540 nm, a vitamin B_{12s}–vitamin B_{12r} isosbestic point.

Hydrocarbon Product Analysis. In typical experiments, 0.1 mL of a solution of the organocobalamin in 0.1 M H_3PO_4 was injected into a serum capped vial of 38-mL capacity which contained 5 mL of the buffered reaction solvent. For anaerobic conditions, both of the solutions were first rigorously deaerated with argon. After completion of the reactions, hydrocarbons in the gas phase were analyzed by GLPC. The identities and yields of products were determined by comparison with standards.

Carbonylic Product Identification. In the terminal solutions from aerobic decompositions of 25-mg samples of the cobalamins, carbonylic reaction products were converted into the 2,4-dinitrophenylhydrazones by adding 5 mL of a saturated (ca. 4 mg/mL) solution of 2,4-dinitrophenylhydrazine in 2 N HCl. The derivatized products were extracted into hexane and identified against standards by thin-layer chromatography on silica gel, using 1:1 hexanes/diethyl ether as the eluant for the products from neopentylcobalamin and benzene for benzaldehyde/DNPH from benzylcobalamin.

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Aspects of the Hydrogenation of Carbon Disulfide by Transition-Metal Cluster Compounds. The Reactions of Carbon Disulfide with Hydridotriosmium–Carbonyl Clusters

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Abstract: The reactions of CS_2 with $H_2Os_3(CO)_{10}$ (Ia) and $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (Ib) are reported. Both clusters react with CS_2 to produce dicluster complexes of formula $(\mu\text{-}S_2CH_2)[HOs_3(CO)_9L]_2$ (L = CO, IIa; L = $P(CH_3)_2C_6H_5$, IIb). IIa was analyzed crystallographically: space group $P\bar{1}$, a = 10.093 (3) Å, b = 13.289 (2) Å, c = 13.865 (3) Å, α = 84.53 (2)°, β = 75.44 (2)°, γ = 88.24 (2)°, Z = 2, ρ_{calcd} = 3.30 g/cm^3. For 3795 reflections ($F^2 \geq 3\sigma(F)^2$) R = 0.048 and R_w = 0.055. IIa contains a methanedithiolato ligand linking two triosmium clusters. The C–S distances at 1.85 Å are typical of carbon–sulfur single bonds. The S–C–S angle at 104.4 (7)° is approximately tetrahedral. In the formation of IIa two cluster complexes have reacted with a single molecule of CS_2 and each has transferred one hydride ligand to the carbon atom. A dithioformato complex $(\mu\text{-}S_2CH)HOs_3(CO)_9[P(CH_3)_2C_6H_5]$ (IIIb) and a thioformaldehyde complex $(\mu\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IVb) were also isolated from the reaction of Ib with CS_2. IVb has been analyzed crystallographically: space group $P2_1/c$, a = 10.001 (2) Å, b = 13.523 (3) Å, c = 18.660 (5) Å, β = 91.26 (2)°, Z = 4, ρ_{calcd} = 2.74 g/cm^3. For 3404 reflections ($F^2 \geq 3.0\sigma(F)^2$) R = 0.058 and R_w = 0.067. IVb contains a thioformaldehyde ligand which is π bonded to one osmium atom C–S = 1.79 (1) Å while the sulfur atom simultaneously serves as a bridge across two osmium atoms. It also contains a triply-bridging inorganic sulfide ligand in a cluster of three osmium atoms which has only one osmium–osmium bond. When heated, both IIIb and IVb decarbonylate to form the complex $(\mu_3\text{-}\eta^2\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_8[P(CH_3)_2C_6H_5]$ (Vb). Vb was also analyzed crystallographically: space group $P\bar{1}$, at −35 °C, a = 9.103 (4) Å, b = 11.722 (4) Å, c = 11.819 (2) Å, α = 71.87 (2)°, β = 79.66 (2), γ = 82.20 (3)°, Z = 2, ρ_{calcd} = 2.86 g/cm^3. For 3668 reflections ($F^2 \geq 3.0\sigma(F)^2$) R = 0.037 and R_w = 0.041. Vb contains a triply-bridging thioformaldehyde ligand with the sulfur atom directly bridging two osmium atoms and the carbon atom bonded solely to the third. The C–S distance is 1.869 (6) Å. Vb also contains a triply-bridging inorganic sulfide ligand, but unlike IVb the cluster has two osmium–osmium bonds. Mechanisms for the formation of all products are proposed and discussed. It was shown that dithioformato cluster complexes are not intermediates in the formation of IIa and IIb as demonstrated by the inability of the complexes $(\mu\text{-}S_2CH)HOs_3(CO)_{10}$ (IIIa), prepared by an independent method, and IIIb to be converted into the dicluster complexes.

Introduction

There has been much interest in transition-metal cluster compounds as a possible source for a new class of homogeneous catalysts.[1] Polynuclear coordination[2] and metal–metal bond cleavage[3] and formation[4] processes may serve as new means for the activation of small molecules. We are attempting to define the roles of these processes in the cluster-assisted hydrogenations of small unsaturated molecules.

Our earlier study of the $H_2Os_3(CO)_{10}$–isocyanide system provided insight into the roles of multiple coordination and isocyanide insertion in the cluster-catalyzed hydrogenation of isocyanide molecules.[5] We have now undertaken a study of the interaction of osmium hydride clusters with heterocumulenes[6] X = C = Y (X,Y = O, S, or NR) with the hope that they might provide some

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insight into the nature of the heterogeneously catalyzed hydrogenation of carbon dioxide.[7] We report here the details of the reactions of carbon disulfide with $(\mu\text{-H})_2Os_3(CO)_{10}$ and $(\mu\text{-H})_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$. Preliminary reports of this work have appeared.[8]

Experimental Section

General Remarks. Although the cluster complexes were generally air stable, reactions were routinely performed under a prepurified nitrogen atmosphere. Solvents were purified by distillation from sodium benzophenone (hexane, toluene, and THF) or by storage over 4-Å molecular sieves and purging with nitrogen through a gas dispersion tube. Carbon disulfide was purified by passage over activated alumina, distillation under nitrogen, and subsequent vacuum distillation directly into the reaction flask. Osmium carbonyl was obtained commercially (Strem) or prepared from OsO_4.[9] Dimethylphenylphosphine (Strem) was distilled in vacuo and stored under nitrogen. Alumina for chromatography was Baker acid-washed aluminum oxide deactivated with water, 6% by weight. Potassium dithioformate,[10] $H_2Os_3(CO)_{10}$,[11a] $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$,[11b] and $(\eta^4\text{-}C_6H_8)Os_3(CO)_{10}$[12] were prepared by published methods. Other reagents were used as received from commercial sources.

Elemental analyses were performed by Midwest Microlab, Ltd. Melting points were determined in evacuated capillaries by using a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 273B spectrometer. Fourier transform ^1H NMR spectra were obtained at 270 MHz on a Bruker HX270. Field-desorption mass spectra were obtained at the MIT mass spectrometry facility. Dynamical NMR analyses were made by standard procedures.[13]

Reaction of $H_2Os_3(CO)_{10}$ with CS_2. Carbon disulfide (ca. 80 mL) was distilled onto $H_2Os_3(CO)_{10}$ (0.200 g, 0.234 mmol), and the solution was heated to reflux for 28 h. After removal of the CS_2 in vacuo, the residue was extracted with benzene to give a yellow-orange solution and an intractable brown residue. The solution was applied to an alumina column (acid washed, 6% H_2O), and a single yellow band was eluted with benzene. The solvent was removed in vacuo. The residue was extracted with toluene and concentrated. Cooling to −20 °C overnight gave 0.101 g (0.057 mmol, 48% yield) of $(\mu\text{-}CH_2S_2)[HOs_3(CO)_{10}]_2$ (IIa) as a yellow powder.

Preparation of $H(\mu\text{-}S_2CH)Os_3(CO)_{10}$ (IIIa). A mixture of $(\eta^4\text{-}C_6H_8)Os_3(CO)_{10}$ (271 mg, 0.291 mmol), KS_2CH (153 mg, 1.32 mmol), and THF (50 mL) was heated to reflux for 25 min. After the solution was cooled to 0 °C with an ice bath, CF_3COOH (0.15 mL, 1.95 mmol) was added to the deep orange solution by syringe. After 10 min at 0 °C, the orange-yellow solution was warmed to room temperature and reduced to dryness in vacuo. The solid was extracted with benzene (3 × 3 mL), and the extracts were reduced in volume and chromographed on alumina. Hexane eluted a yellow-orange band which was reduced to dryness. Recrystallization from pentane at −20 °C gave 172 mg (64% yield) of $H(\mu\text{-}S_2CH)Os_3(CO)_{10}$ as orange crystals. The supernatant contained a mixture of $H(\mu\text{-}S_2CH)Os_3(CO)_{10}$ and $H_2(\mu_3\text{-S})Os_3(CO)_9$.[14]

Reaction of $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ with CS_2. (a) In Dilute Solution. Carbon disulfide (ca. 25 mL) was distilled onto $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (0.120 g, 0.125 mmol), and the solution was refluxed for 2 h. After removal of the CS_2 in vacuo, the residue was dissolved in a minimum of benzene and applied to an alumina column. Elution with hexane/benzene (5/1) separated two yellow bands. The first band was reduced to dryness and crystallized from hexane at −20 °C to give $(\mu_3\text{-S})(\mu_2\text{-}CH_2S)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IVb, 0.021 g, 0.020 mmol, 16%) as yellow crystals. The second band was eluted with hexane/benzene (1/1) reduced to dryness and fractionally crystallized from toluene/hexane at −20 °C to give $(\mu\text{-H})(\mu\text{-}S_2CH)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IIIb, 0.011 g, 0.010 mmol, 9%) as orange crystals.

(b) In Concentrated Solution. Carbon disulfide (1 mL) and dichloromethane (1 mL) were added to $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (0.205 g, 0.213 mmol), and the solution was stirred for 30 h at room temperature. The resulting deep orange-red solution and a small quantity of orange-brown precipitate were chromatographed as in part a to give $(\mu_3\text{-S})(\mu_2\text{-}SCH_2)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IVb, 33 mg, 0.032 mmol, 15%) and a second band which was reduced in vacuo to 71.6 mg of a deep yellow solid. NMR analysis showed that this solid was a mixture of $H(\mu\text{-}S_2CH)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IIIb, ca. 14% yield) and $(\mu\text{-}S_2CH_2)\{HOs_3(CO)_9[P(CH_3)_2C_6H_5]\}_2$ (IIb, ca. 21% yield). This mixture was dissolved in heptane (15 mL) and heated to reflux for 5 h. Chromatography on alumina (acid washed, 2.5% H_2O) gave two yellow bands. The first band, eluted with hexane/benzene (4/1), contained a small amount of $(\eta_3\text{-S})(\mu_3\text{-}SCH_2)Os_3(CO)_8[P(CH_3)_2C_6H_5]$ (Vb). The second band was reduced to dryness in vacuo to give $(\mu\text{-}S_2CH_2)\{HOs_3(CO)_9[P(CH_3)_2C_6H_5]\}_2$ (IIb, 28 mg, 0.014 mmol, 14%) as a deep yellow powder. Anal. Calcd for $(C_{35}H_{26}O_{18}P_2Os_6S_2)$: H, S, and C, 21.00. Found H, S, and C, 21.69.

(c) Monitored by NMR. Chloroform-*d*, (0.40 mL) and carbon disulfide (0.15 mL) were added by syringe to a septum capped, nitrogen-filled NMR tube containing 100 mg (0.117 mmol) of $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$. The reaction was monitored by periodically recording the NMR spectrum of the reaction mixture as described in the Results section.

Attempted Coupling Reactions of $H_2Os_3(CO)_9(L)$ and $H(\mu\text{-}S_2CH)Os_3(CO)_9(L)$ ($L = CO, P(CH_3)_2C_6H_5$). All reactions were conducted similarly. In a typical reaction, $H_2Os_3(CO)_{10}$ (45.7 mg, 0.054 mmol) and $H(S_2CH)Os_3(CO)_{10}$ (50.3 mg, 0.054 mmol) were heated for 19 h in refluxing hexane. The solvent was removed in vacuo, and an NMR spectrum was taken of the crude reaction mixture in $CDCl_3$. Most of the $H_2Os_3(CO)_{10}$ and a small amount of the $H(\mu\text{-}S_2CH)Os_3(CO)_{10}$ remained. In addition, two new AB quartets at δ 3.92 and 3.69 were observed, but no trace of $(\mu\text{-}S_2CH_2)[HOs_3(CO)_{10}]_2$ could be detected. The new complexes could not be isolated by chromatography on alumina.

Thermolysis of $(\mu_3\text{-S})(\mu_2\text{-}SCH_2)Os_3(CO)_9[P(CH_3)_2C_6H_5]$. The title complex (0.060 g, 0.058 mmol) was dissolved in hexane (100 mL) and heated to reflux for 6 h. The solvent was removed in vacuo, and the yellow residue was chromatographed on alumina. Hexane/benzene (1/1) eluted a single yellow band which was reduced to dryness and crystallized from pentane at −20 °C to give yellow crystals of $(\mu_3\text{-S})(\mu_3\text{-}SCH_2)Os_3(CO)_8[P(CH_3)_2C_6H_5]$ (Vb, 44 mg, 0.043 mmol, 74%).

Thermolysis of $H(\mu\text{-}S_2CH)Os_3(CO)_9[P(CH_3)_2C_6H_5]$. The title complex (0.072 g, 0.069 mmol) was dissolved in heptane (20 mL) and heated to reflux for 15 h. The solvent was removed in vacuo, and the residue was chromatographed on alumina to give a single yellow band, eluted with hexane/benzene (4/1). This band was reduced to dyrness in vacuo and crystallized from pentane at −20 °C to give yellow crystals of $(\mu_3\text{-S})(\mu_3\text{-}SCH_2)Os_3(CO)_8[P(CH_3)_2C_6H_5]$ (Vb, 32 mg, 0.032 mmol, 46%).

Crystallographic Analyses. Crystals of IIa suitable for diffraction analyses were obtained by slow crystallization from toluene solutions at −20 °C. Crystals of IVb and Vb were obtained from hexane solutions cooled to −20 °C. All crystals were mounted in thin-walled glass capillaries. All diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo $K\bar{\alpha}$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. The space groups were determined from the systematic absences observed during data collection. In the triclinic cases the space group $P\bar{1}$ was assumed. These were confirmed by the successful solution and refinement of the structures. Crystal data and data collections parameters are listed in Table II. All data processing were performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. Absorption corrections of a Gaussian integration type were done for all structures. Neutral atom scattering factors were calculated by the standard procedures.[15a] Anomalous dispersion corrections were applied to all nonhydrogen atoms.[15b] All structures were solved by a combination of Patterson and difference Fourier techniques. Hydrogen atom positions were obtained either from difference Fourier syntheses or calculated on the basis of geometric considerations. Hydrogen atom contributions were included in structure factor calculations, but their positions were not

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

Table I. Spectroscopic and Physical Data

compd	mp, °C	^{1}H NMR, δ	IR, cm^{-1} (±3 cm^{-1})
IIa, $H_2CS_2[HOs_3(CO)_{10}]_2$	213–215	2.92 (2 H), −17.46 (2 H)[a]	2105 w, 2075 s, 2065 w, sh, 2025 s, 2015 m, 2000 w, sh[b]
IIb, (μ-H_2CS_2){$HOs_3(CO)_9$-[$P(CH_3)_2C_6H_5$]}$_2$	100–103	isomer A: 7.47 (m, 5 H), 2.89 (s, 1 H), 2.19 (d, $^2J_{P-H}$ = 2.4 Hz, 3 H), 2.15 (d, $^2J_{P-H}$ = 2.4 Hz, 3 H), −17.19 (br s, 1 H) isomer B: 7.47 (m, 5 H), 2.88 (s, 1 H), 2.32 (d, $^2J_{P-H}$ = 9.8 Hz, 6 H), −17.13 (s, 1 H)[e]	2075 w, 2055 vs, 2020 m, 2000 s, 1990 s, 1955 w[d]
IIIa, (μ-H)(μ-S_2CH)$Os_3(CO)_9$-[$P(CH_3)_2C_6H_5$]	127–129	13.17 (s, 1 H), 7.53 (m, 5 H), 2.30 (d, 6 H, J_{P-H} = 12.20 Hz), −16.07 (d, 1 H, J_{P-H} = 12.21 Hz)[c]	2090 m, 2080 w, sh, 2060 s, br, 2035 s, 2010 s, 2000 m, sh, 1990 m, sh[d]
IIIb, (μ-H)(μ-S_2CH)$Os_3(CO)_{10}$	165–166	12.15 (s, 1 H), −14.92 (s, 1H)[c]	2100 w, 2060 sh, 2055 s, 2025 sh, 2020 m, 2010 s, 1980 w, 1975 w[d]
IVb, (μ-SCH_2)(μ_3-S)$Os_3(CO)_9$-[$P(CH_3)_2C_6H_5$]	124.8–125.5	isomer A: 7.7 (m, 5 H), 3.60 (d, 1 H), 3.44 (d, 1 H, J_{H-H} = 5.13 Hz), 2.47 (d, 3 H, J_{P-H} = 9.3 Hz) isomer B: 7.7 (m, 5 H), 3.63 (d, 1 H), 3.57 (d, 1 H, J_{H-H} = 5.13 Hz), 2.30 (d, 6 H, J_{P-H} = 9.45 Hz)[c,f]	2085 w, 2070 s, 2045 s, 2002 s, 1997 s, 1980 s, 1975 m, sh[d]
Vb, (μ_3-SCH_2)(μ_3-S)$Os_3(CO)_8$-[$P(CH_3)_2C_6H_5$]	163.5–165.0	isomer A: 7.07 (m 5 H), 2.14 (d, 1 H, J_{H-H} = 11.36 Hz), 1.50 (d, 3 H), 1.46 (3 H, J_{P-H} = 10.99 Hz) isomer B: 7.07 (m, 5 H), 2.71 (q, 1 H), 1.33 (q, 1 H, J_{H-H} = 12.3 Hz, $^2J_{P-H}$ = 4.03 Hz), 1.63 (d, 3 H), 1.59 (d, 3 H, J_{P-H} = 9.53 Hz)[c,f]	2085 m, 2052 s, 2025 m, 2012 s, 1980 m, br[a]

[a] Acetone-d_6. [b] CCl_4. [c] $CDCl_3$. [d] Hexane. [e] Toluene-d_8. [f] Isomer A corresponds to solid-state structure.

refined. 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$. All atoms heavier than oxygen were refined with anisotropic temperature factors. All other atoms were refined with isotropic temperature factors only. Final fractional atomic coordinates and structure factor amplitudes are available for all structures (see supplementary material). Interatomic distances and angles with errors obtained from the inverse matrix calculated on the final cycle of least-squares refinement are listed in Tables III–VII.

Results

The Reactions of CS_2 with (μ-H)$_2Os_3(CO)_9$(L) (L = CO or $P(CH_3)_2(C_6H_5)$). A solution of $H_2Os_3(CO)_{10}$ (Ia) in refluxing carbon disulfide changes from purple to yellow-orange over a period of 19–34 h. The major product (isolated in about 49% yield after chromatographic workup) has been characterized as (μ_2-H_2CS_2)[$HOs_3(CO)_{10}$]$_2$ (IIa) on the basis of its infrared and ^{1}H NMR spectra, field-desorption mass spectrum (parent ion m/e 1780 for ^{190}Os) and an X-ray crystallographic analysis. An ORTEP diagram of IIa is shown in Figure 1. The most important feature of IIa to note at this time is the presence of *two* (μ-H)$Os_3(CO)_{10}$ moieties linked by a methanedithiolate group. The infrared spectrum in the carbonyl region shows absorptions at 2105 (w), 2075 (s), 2065 (w, sh), 2025 (s), 2015 (m), 2000 (w, sh) and 1990 (w) cm^{-1} CCl_4 solvent. This is very similar to the spectra of the molecules (μ-H)(μ-SR)$Os_3(CO)_{10}$[16] (R = C_2H_5, C_6H_5, and C_4H_9) and indicates that there is little or no vibrational coupling of the carbonyl ligands between the two clusters. The ^{1}H NMR spectrum of IIa shows resonances at δ 2.92 and −17.46 of approximately equal intensity. These can be assigned to the two hydrogen atoms of the methylene group and the two equivalent hydride ligands, one on each cluster, respectively. Complete ^{1}H NMR spectra of all complexes reported here are listed in Table I. Since the general pattern of reactivity of mononuclear metal hydrides with CS_2 is insertion to form chelating dithioformate ligands, this result was both novel and unexpected. An NMR analysis of a reaction mixture of a preparation of Ia showed only traces of other products, which could not be isolated in a pure form. In an effort to gain further insight into the mechanism of this unusual reaction, we next studied the reaction of the phosphine derivative (μ-H)$_2Os_3(CO)_9$[$P(CH_3)_2C_6H_5$] (Ib) with CS_2.

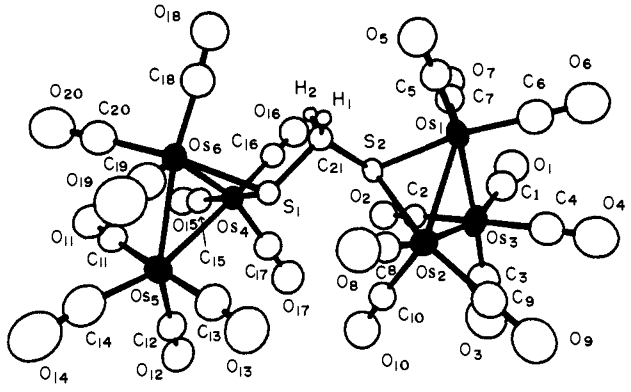

Figure 1. An ORTEP diagram of (μ-S_2CH_2)[$HOs_3(CO)_{10}$]$_2$ (IIa) showing 50% probability ellipsoids for all nonhydrogen atoms.

To our suprise, the result of the reaction of Ib with CS_2 was markedly different. Depending upon the initial concentration of Ib, varying yields of three major products were obtained. At relatively high cluster concentrations (ca. 0.1 M), one product (14% yield) was the methanedithiolato-bridged dicluster complex (μ-H_2CS_2){$HOs_3(CO)_9$[$P(CH_3)_2C_6H_5$]}$_2$ (IIb), which is simply a phosphine-substituted derivative of IIa. Although we were not able to obtain crystals of this complex suitable for X-ray analysis, its formulation was confirmed by elemental analysis, infrared and ^{1}H NMR spectra, and the observation of a molecular ion and isotope pattern consistent with the presence of six osmium atoms in its field-desorption mass spectrum (m/e 2000 for ^{190}Os).

The ^{1}H NMR spectrum of IIb indicated the presence of isomers in solution, presumably with different relative positions of the phosphine ligands. Curiously, very little of this product was obtained when the initial concentration of Ib was less than about 10^{-3} M in the reaction mixtures.

Under either dilute or concentrated reaction conditions, the complex (μ-H)(μ-S_2CH)$Os_3(CO)_9$[$P(CH_3)_2C_6H_5$] (IIIb) was obtained in 9–15% yield. It was characterized spectroscopically and by an X-ray crystallographic analysis, details of which have been published elsewhere.[17] Figure 2, a diagram of its structure,

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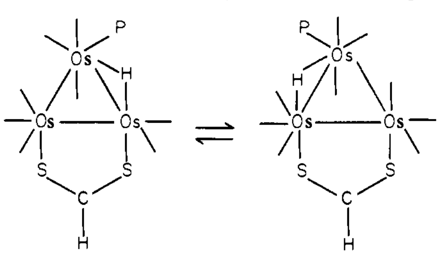
[16] Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1969**, 797.

Table II

	IIa	IVb	Vb
	(A) Crystallographic Data for X-ray Diffraction Studies		
formula	$C_{21}H_4O_{20}Os_6S_2$	$C_{18}H_{13}O_9Os_3PS_2$	$C_{17}H_{14}O_8Os_3PS_2$
temp (±5 °C)	27	27	−35
space group	$P\bar{1}$, No. 2, [C_i]	$P2_1/c$, No. 14, [C_{2h}^5]	$P\bar{1}$, No. 2, [C_i]
a, Å	10.093 (3)	10.001 (2)	9.103 (4)
b, Å	13.289 (2)	13.523 (3)	11.722 (4)
c, Å	13.865 (3)	18.660 (5)	11.819 (2)
α, deg	84.53 (2)	90.0	71.87 (2)
β, deg	75.44 (2)	91.26 (2)	79.66 (2)
γ, deg	88.24 (2)	90.0	82.20 (3)
V, Å^3	1791.7 (10)	2522.9 (14)	1174.7 (8)
mol wt	1781.6	1039.0	1012.0
Z	2	4	2
ρ_{calcd}, g/cm^3	3.30	2.74	2.86
	(B) Measurement of Intensity Data		
radiation		Mo K$\bar{\alpha}$ (0.710 73 Å)	
monochromator		graphite	
detector aperture, mm			
horizontal ($A + B \tan \theta$)			
A	3.0	3.0	2.6
B	1.0	1.0	1.2
vertical	4.0	4.0	4.0
cryst size, mm	$02\bar{1}$, $0\bar{2}1$, $\bar{4}\bar{1}\bar{1}$ 411, $\bar{1}\bar{3}4$, 134	$\bar{2}01$, $20\bar{1}$, 043 $0\bar{4}\bar{3}$, 001, $00\bar{1}$	010, $0\bar{1}0$, 001, $00\bar{1}$ 211, $2\bar{1}\bar{1}$, $\bar{1}\bar{1}2$, $\bar{1}00$
cryst size, mm	0.10 × 0.22 × 0.10	0.28 × 0.24 × 0.36	0.04 × 0.26 × 0.03
cryst orientatn: directn, deg from ϕ axis	normal to 011, 9.0°	normal to 012, 12°	normal to 100, 15°
reflctn measd	$+h,\pm k,\pm l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$
max 2θ	48°	51°	52°
scan type		moving crystal–stationary counter	
ω-scan width	1.0°	0.8°	0.8°
bkgd		$^1/_4$ additional scan at each end of scan	
ω-scan rate			
max, deg/min	10.0	6.7	10.0
min, deg/min	1.5	1.3	1.3
no. reflctns measd	5543	5089	4546
data used ($F^2 \geqslant 3.0\sigma(F)^2$)	3795	3404	3668
	(C) Treatment of Data		
absn coeff μ, cm^{-1}	227.2	162.9	174.9
grid	12 × 6 × 12	8 × 10 × 8	14 × 4 × 12
transmission coeff			
max	0.134	0.110	0.536
min	0.026	0.040	0.044
P factor	0.01	0.015	0.01
final residuals			
R	0.048	0.058	0.037
R_w	0.055	0.067	0.041
Esd of unit wt	2.99	4.56	4.15
largest shift/error value on final cycle	0.18	0.02	0.01

shows the presence of a bridging dithioformato ligand S(1)–C(10)–S(2) in a diaxial coordination site. At room temperature the ^{1}H NMR spectrum of IIIb shows resonances of δ 13.17 (s, 1 H) and −16.07 (d, 1 H, J_{PH} = 12.2 Hz) which are characteristic of the proton on the dithioformato ligand and the hydride ligand, respectively. There is a doublet at δ 2.30 (6 H, $^2J_{PH}$ = 12.2 Hz) and a multiplet at δ 7.53 (5 H) which are due to the methyl and phenyl groups of the dimethylphenylphosphine ligand. However, according to the solid-state structure the methyl groups on the phosphine ligand are inequivalent since the dithioformato ligand lies on one side of the Os_3 plane. A dynamic averaging process was suspected and confirmed by variable-temperature studies. At −55 °C the methyl groups of the phosphine ligand appear as two doublets δ 2.65 ($^2J_{PH}$ = 11.0 Hz) and δ 2.59 ($^2J_{PH}$ = 11.0 Hz). As the temperature is raised, the doublets broaden, coalesce (2 °C), and eventually reform as the single sharp doublet observed at room temperature. Line-shape analyses[13a] of the exchange-broadened spectra produced exchange rates that obeyed the Arrhenius and Eyring equations and yielded the activation parameters E_a = 16.2 ± 0.5 kcal/mol, log A = 14.2, $\Delta H^{\ddagger}$ = 15.7 ± 0.5 kcal/mol, $\Delta S^{\ddagger}$ = 4.6 eu, and $\Delta G_{298}{}^{\ddagger}$ = 14.3 ± 0.5 kcal. A rearrangement process which accounts for the observed averaging of the methyl groups is shown in eq 1. In the overall process both



(1)

the hydride ligand and phosphine ligand must change sites. The hydride moves to a different metal–metal bond while the phosphine ligand simply changes coordination sites on the same osmium atom. High mobility of hydride ligands in cluster complexes has been observed previously.[18] The observation of coupling between the phosphine and hydride ligand in the fast exchange region

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

(18) (a) Churchill, M. R.; Lashewycz, R. A.; Shapley, J. R.; Richter, S. I. *Inorg. Chem.* **1980**, *19*, 1277. (b) Shapley, J. R.; Richter, S. I.; Churchill, M. R.; Lashewycz, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 7384.

(19) Robinson, S. D.; Sahajpal, A. *J. Organomet. Chem.* **1975**, *99*, C65.

Table III. Interatomic Distances (Å) with Esds for (μ-S_2CH_2)-$[HOs_2(CO)_{10}]_2$ (IIa)

Os(1)–Os(2)	2.863 (1)	Os(6)–C(18)	1.90 (2)
Os(1)–Os(3)	2.873 (1)	Os(6)–C(19)	1.86 (2)
Os(2)–Os(3)	2.854 (1)	Os(6)–C(20)	1.87 (2)
Os(4)–Os(5)	2.876 (1)	S(1)–C(21)	1.85 (1)
Os(4)–Os(6)	2.873 (1)	S(2)–C(21)	1.85 (2)
Os(5)–Os(6)	2.872 (1)	C(1)–O(1)	1.21 (2)
Os(1)–S(2)	2.413 (3)	C(2)–O(2)	1.18 (2)
Os(1)–C(5)	1.89 (2)	C(3)–O(3)	1.20 (2)
Os(1)–C(6)	1.87 (2)	C(4)–O(4)	1.14 (2)
Os(1)–C(7)	1.89 (2)	C(5)–O(5)	1.16 (2)
Os(2)–S(2)	2.429 (4)	C(6)–O(6)	1.18 (2)
Os(2)–C(8)	1.90 (2)	C(7)–O(7)	1.16 (2)
Os(2)–C(9)	1.88 (2)	C(8)–O(8)	1.13 (2)
Os(2)–C(10)	1.90 (2)	C(9)–O(9)	1.16 (2)
Os(3)–C(1)	1.86 (2)	C(10)–O(10)	1.16 (2)
Os(3)–C(2)	1.93 (2)	C(11)–O(11)	1.13 (2)
Os(3)–C(3)	1.85 (2)	C(12)–O(12)	1.10 (2)
Os(3)–C(4)	1.94 (2)	C(13)–O(13)	1.16 (2)
Os(4)–S(1)	2.416 (4)	C(14)–O(14)	1.11 (2)
Os(4)–C(15)	1.89 (2)	C(15)–O(15)	1.16 (2)
Os(4)–C(16)	1.84 (2)	C(16)–O(16)	1.21 (2)
Os(4)–C(17)	1.85 (2)	C(17)–O(17)	1.19 (2)
Os(5)–C(11)	1.94 (2)	C(18)–O(18)	1.16 (2)
Os(5)–C(12)	1.96 (2)	C(19)–O(19)	1.18 (2)
Os(5)–C(13)	1.95 (2)	C(20)–O(20)	1.16 (2)
Os(5)–C(14)	1.92 (2)	C(21)–H(1)[a]	1.09[a]
Os(6)–S(1)	2.409 (4)	C(21)–H(2)[a]	1.00[a]

[a] Hydrogen atom positions were not refined.

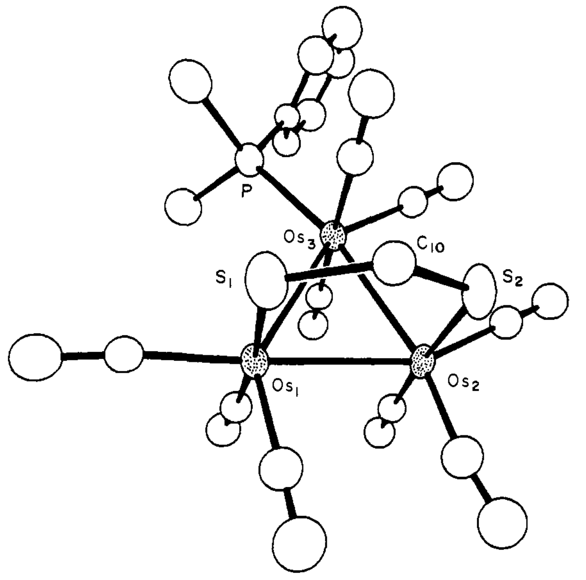

Figure 2. An ORTEP diagram of (μ-H)(μ-S_2CH)$Os_3(CO)_9$[P-$(CH_3)_2C_6H_5$] (IIIb) showing 50% probability ellipsoids.

Table IV. Bond Angles (Deg) with Esds for (μ-S_2CH)-$[HOs_3(CO)_{10}]_2$ (IIa)

Os(1)–Os(2)–Os(3)	60.34 (2)	C(15)–Os(4)–C(17)	91.9 (8)
Os(2)–Os(1)–Os(3)	59.67 (2)	Os(4)–Os(6)–S(1)	53.57 (9)
Os(1)–Os(3)–Os(2)	59.99 (2)	Os(4)–Os(6)–C(18)	112.1 (6)
Os(4)–Os(5)–Os(6)	59.98 (2)	Os(4)–Os(6)–C(19)	136.5 (5)
Os(5)–Os(4)–Os(6)	59.95 (2)	Os(4)–Os(6)–C(20)	116.4 (6)
Os(4)–Os(6)–Os(5)	60.08 (2)	Os(5)–Os(6)–S(1)	78.37 (8)
Os(2)–Os(1)–S(2)	54.01 (8)	Os(5)–Os(6)–C(18)	171.2 (6)
Os(2)–Os(1)–C(5)	108.9 (5)	Os(5)–Os(6)–C(19)	87.4 (5)
Os(2)–Os(1)–C(6)	116.0 (5)	Os(5)–Os(6)–C(20)	93.2 (5)
Os(2)–Os(1)–C(7)	138.6 (5)	S(1)–Os(6)–C(18)	93.7 (5)
Os(3)–Os(1)–S(2)	79.50 (9)	S(1)–Os(6)–C(19)	94.6 (5)
Os(3)–Os(1)–C(5)	168.6 (4)	S(1)–Os(6)–C(20)	169.2 (5)
Os(3)–Os(1)–C(6)	92.8 (6)	C(18)–Os(6)–C(19)	97.2 (7)
Os(3)–Os(1)–C(7)	91.8 (6)	C(19)–Os(6)–C(20)	91.7 (8)
S(2)–Os(1)–C(5)	92.8 (5)	C(18)–Os(6)–C(20)	94.2 (7)
S(2)–Os(1)–C(6)	169.6 (6)	Os(4)–Os(5)–C(11)	86.0 (4)
S(2)–Os(1)–C(7)	94.4 (5)	Os(4)–Os(5)–C(12)	99.0 (5)
C(5)–Os(1)–C(6)	93.8 (7)	Os(4)–Os(5)–C(13)	92.6 (5)
C(6)–Os(1)–C(7)	92.8 (8)	Os(4)–Os(5)–C(14)	159.5 (6)
C(5)–Os(1)–C(7)	97.3 (7)	Os(6)–Os(5)–C(11)	87.9 (4)
Os(1)–Os(2)–S(2)	53.49 (7)	Os(6)–Os(5)–C(12)	158.9 (5)
Os(1)–Os(2)–C(8)	109.6 (4)	Os(6)–Os(5)–C(13)	88.9 (5)
Os(1)–Os(2)–C(9)	113.9 (5)	Os(6)–Os(5)–C(14)	100.1 (6)
Os(1)–Os(2)–C(10)	139.9 (4)	C(11)–Os(5)–C(12)	92.6 (7)
Os(3)–Os(2)–S(2)	79.63 (9)	C(11)–Os(5)–C(13)	176.8 (7)
Os(3)–Os(2)–C(8)	169.2 (4)	C(11)–Os(5)–C(14)	88.9 (8)
Os(3)–Os(2)–C(9)	88.6 (5)	C(12)–Os(5)–C(13)	90.4 (7)
Os(3)–Os(2)–C(10)	94.3 (5)	C(12)–Os(5)–C(14)	101.0 (7)
S(2)–Os(2)–C(8)	97.6 (4)	C(13)–Os(5)–C(14)	91.4 (8)
S(2)–Os(2)–C(9)	166.0 (5)	Os(1)–S(2)–Os(2)	72.5 (1)
S(2)–Os(2)–C(10)	94.2 (4)	Os(1)–S(2)–C(21)	110.8 (4)
C(8)–Os(2)–C(9)	92.6 (7)	Os(2)–S(2)–C(21)	111.0 (4)
C(9)–Os(2)–C(10)	94.2 (6)	Os(4)–S(1)–Os(6)	73.1 (1)
C(8)–Os(2)–C(10)	96.4 (6)	Os(4)–S(1)–C(21)	111.4 (4)
Os(1)–Os(3)–C(1)	95.4 (6)	Os(6)–S(1)–C(21)	113.2 (5)
Os(1)–Os(3)–C(2)	94.4 (5)	Os(3)–C(1)–O(1)	171 (2)
Os(1)–Os(3)–C(3)	164.0 (7)	Os(3)–C(2)–O(2)	171 (1)
Os(1)–Os(3)–C(4)	83.3 (6)	Os(3)–C(3)–O(3)	174 (2)
Os(2)–Os(3)–C(1)	155.4 (6)	Os(3)–C(4)–O(4)	176 (2)
Os(2)–Os(3)–C(2)	87.6 (5)	Os(1)–C(5)–O(5)	174 (1)
Os(2)–Os(3)–C(3)	104.7 (7)	Os(1)–C(6)–O(6)	178 (2)
Os(2)–Os(3)–C(4)	87.4 (6)	Os(1)–C(7)–O(7)	173 (2)
C(1)–Os(3)–C(2)	96.2 (8)	Os(2)–C(8)–O(8)	177 (1)
C(1)–Os(3)–C(3)	99.6 (9)	Os(2)–C(9)–O(9)	179 (1)
C(1)–Os(3)–C(4)	88.4 (8)	Os(2)–C(10)–O(10)	174 (1)
C(2)–Os(3)–C(3)	89.5 (8)	Os(5)–C(11)–O(11)	178 (1)
C(2)–Os(3)–C(4)	175.0 (7)	Os(5)–C(12)–O(12)	179 (1)
C(3)–Os(3)–C(4)	91.6 (8)	Os(5)–C(13)–O(13)	174 (2)
Os(6)–Os(4)–S(1)	53.33 (9)	Os(5)–C(14)–O(14)	173 (2)
Os(6)–Os(4)–C(15)	114.3 (5)	Os(4)–C(15)–O(15)	177 (2)
Os(6)–Os(4)–C(16)	111.4 (5)	Os(4)–C(16)–O(16)	174 (1)
Os(6)–Os(4)–C(17)	141.0 (6)	Os(4)–C(17)–O(17)	175 (2)
Os(5)–Os(4)–S(1)	78.19 (8)	Os(6)–C(18)–O(18)	176 (2)
Os(5)–Os(4)–C(15)	91.7 (5)	Os(6)–C(19)–O(19)	179 (2)
Os(5)–Os(4)–C(16)	170.8 (5)	Os(6)–C(20)–O(20)	176 (2)
Os(5)–Os(4)–C(17)	92.6 (6)	S(1)–C(21)–S(2)	104.4 (7)
S(1)–Os(4)–C(15)	166.9 (5)	S(1)–C(21)–H(1)[a]	103
S(1)–Os(4)–C(16)	94.0 (5)	S(1)–C(21)–H(2)[a]	109
S(1)–Os(4)–C(17)	96.9 (6)	S(2)–C(21)–H(1)[a]	125
C(15)–Os(4)–C(16)	95.3 (7)	S(2)–C(21)–H(2)[a]	99
C(16)–Os(4)–C(17)	93.2 (7)	H(1)–C(21)–H(2)[a]	115

[a] Hydrogen atom positions were not refined.

indicates that neither the phosphine nor hydride ligands dissociate from the cluster in the course of the exchange process. An alternative mechanism in which the dithioformato ligand moves from a diaxial position on one side of the Os_3 plane to a diaxial position on the other side of the Os_3 plane is considered unlikely.

The third product of the reaction of CS_2 with Ib was the most unusual of all. The complex (μ_3-S)(μ_2-SCH_2)$Os_3(CO)_9$[P-$(CH_3)_2C_6H_5$] (IVb) formed in about 15% yield, was characterized spectroscopically and crystallographically. An ORTEP diagram of its molecular structure is shown in Figure 3. The two-atom group C(10)–S(1) is believed to be part of a thioformaldehyde ligand. This is supported by its ^1H NMR spectrum which shows AB quartet resonance patterns δ 3.60 (d, 1 H) and 3.44 (d, 1 H, J_{H-H} = 5.13 Hz) and δ 3.63 (d, 1 H) and 3.57 (d, 1 H, J_{H-H} = 5.13 Hz) which are attributed to inequivalent protons of the thioformaldehyde ligand. The presence of two AB quartets and a doubling of the number of expected methyl resonances from the phosphine ligand suggested that IVb exists as a mixture of isomers in solution. This was confirmed by dissolving crystals of IVb in acetone-d_6 at −78 °C and recording an NMR spectrum at that temperature. Only a single isomer (A), presumably having the structure which was observed crystallographically, was evident. As the temperature of the solution was gradually increased above −50 °C, a second isomer (B) became apparent. After 20 min at −5 °C, the relative concentrations of the two isomers approached the equilibrium ratio.

The exact structural differences between these isomers are not known, but the placement of the phosphine ligand in a different coordination position on the osmium atom to which it is attached (see Figure 3) would seem to be the most plausible explanation.

Table V. Interatomic Distances (Å) with Esds for $(\mu\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IVb)

Os(1)···Os(2)	3.780 (1)	C(10)–S(1)	1.788 (11)
Os(1)–Os(3)	2.855 (1)	P–C(17)	1.833 (11)
Os(2)···Os(3)	4.033 (1)	P–C(18)	1.783 (12)
Os(1)–S(1)	2.482 (3)	P–C(11)	1.827 (11)
Os(1)–S(2)	2.437 (3)	C(11)–C(12)	1.424 (15)
Os(1)–C(1)	1.932 (13)	C(12)–C(13)	1.407 (16)
Os(1)–C(2)	1.845 (14)	C(13)–C(14)	1.344 (17)
Os(1)–C(3)	1.876 (13)	C(14)–C(15)	1.318 (16)
Os(2)–S(1)	2.416 (3)	C(15)–C(16)	1.414 (16)
Os(2)–S(2)	2.494 (3)	C(16)–C(11)	1.358 (15)
Os(2)–C(4)	1.902 (4)	C(1)–O(1)	1.160 (14)
Os(2)–C(5)	1.982 (12)	C(2)–O(2)	1.187 (14)
Os(2)–C(6)	1.884 (12)	C(3)–O(3)	1.161 (13)
Os(2)–C(10)	2.114 (10)	C(4)–O(4)	1.139 (13)
Os(3)–S(2)	2.463 (3)	C(5)–O(5)	1.130 (12)
Os(3)–P	2.352 (3)	C(6)–O(6)	1.160 (13)
Os(3)–C(7)	1.947 (13)	C(7)–O(7)	1.151 (13)
Os(3)–C(8)	1.878 (11)	C(8)–O(8)	1.174 (12)
Os(3)–C(9)	1.939 (12)	C(9)–O(9)	1.158 (13)

Table VI. Interatomic Angles (Deg) with Esds for $(\mu\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IVb)

Os(3)–Os(1)–S(1)	96.79 (6)	S(2)–Os(3)–C(9)	84.5 (3)
Os(3)–Os(1)–S(2)	54.78 (6)	P–Os(3)–C(7)	87.3 (4)
Os(3)–Os(1)–C(1)	160.3 (4)	P–Os(3)–C(8)	94.0 (3)
Os(3)–Os(1)–C(2)	105.9 (4)	P–Os(3)–C(9)	89.3 (3)
Os(3)–Os(1)–C(3)	83.8 (4)	C(7)–Os(3)–C(8)	93.1 (5)
S(1)–Os(1)–S(2)	79.4 (1)	C(7)–Os(3)–C(9)	173.3 (5)
S(1)–Os(1)–C(1)	87.9 (4)	C(8)–Os(3)–C(9)	92.8 (5)
S(1)–Os(1)–C(2)	93.6 (4)	Os(1)–S(1)–Os(2)	101.0 (1)
S(1)–Os(1)–C(3)	176.7 (4)	Os(1)–S(1)–C(10)	101.6 (4)
S(2)–Os(1)–C(1)	107.8 (4)	Os(2)–S(1)–C(10)	58.1 (3)
S(2)–Os(1)–C(2)	157.7 (4)	Os(2)–C(10)–S(1)	76.0 (4)
S(2)–Os(1)–C(3)	98.5 (4)	Os(1)–S(2)–Os(2)	100.1 (1)
C(1)–Os(1)–C(2)	92.9 (5)	Os(1)–S(2)–Os(3)	71.27 (7)
C(1)–Os(1)–C(3)	90.5 (5)	Os(2)–S(2)–Os(3)	108.9 (1)
C(2)–Os(1)–C(3)	89.3 (5)	Os(3)–P–C(17)	114.4 (4)
S(1)–Os(2)–S(2)	79.5 (1)	Os(3)–P–C(18)	117.0 (4)
S(1)–Os(2)–C(4)	147.9 (4)	Os(3)–P–C(11)	113.7 (3)
S(1)–Os(2)–C(5)	117.2 (3)	C(17)–P–C(18)	100.7 (5)
S(1)–Os(2)–C(6)	97.0 (3)	C(17)–P–C(11)	104.1 (5)
S(1)–Os(2)–C(10)	45.9 (3)	C(18)–P–C(11)	105.4 (5)
S(2)–Os(2)–C(4)	94.1 (4)	P–C(11)–C(12)	117.4 (8)
S(2)–Os(2)–C(5)	88.1 (3)	P–C(11)–C(16)	123.5 (9)
S(2)–Os(2)–C(6)	175.1 (3)	C(16)–C(11)–C(12)	118.9 (10)
S(2)–Os(2)–C(10)	87.9 (3)	C(11)–C(12)–C(13)	120.9 (11)
C(4)–Os(2)–C(5)	93.7 (5)	C(12)–C(13)–C(14)	116.4 (12)
C(4)–Os(2)–C(6)	90.7 (5)	C(13)–C(14)–C(15)	124.4 (13)
C(4)–Os(2)–C(10)	103.0 (5)	C(14)–C(15)–C(16)	120.8 (12)
C(5)–Os(2)–C(6)	90.5 (5)	C(15)–C(16)–C(11)	118.4 (11)
C(5)–Os(2)–C(10)	163.1 (4)	Os(1)–C(1)–O(1)	169.8 (12)
C(6)–Os(2)–C(10)	92.0 (4)	Os(1)–C(2)–O(2)	168.5 (12)
Os(1)–Os(3)–S(2)	53.94 (6)	Os(1)–C(3)–O(3)	178.0 (12)
Os(1)–Os(3)–P	106.79 (6)	Os(2)–C(4)–O(4)	174.0 (12)
Os(1)–Os(3)–C(7)	81.8 (4)	Os(2)–C(5)–O(5)	173.2 (11)
Os(1)–Os(3)–C(8)	158.3 (3)	Os(2)–C(6)–O(6)	172.1 (10)
Os(1)–Os(3)–C(9)	93.6 (3)	Os(3)–C(7)–O(7)	174.1 (10)
S(2)–Os(3)–P	159.1 (1)	Os(3)–C(8)–O(8)	176.2 (10)
S(2)–Os(3)–C(7)	96.7 (4)	Os(3)–C(9)–O(9)	172.2 (10)
S(2)–Os(3)–C(8)	106.2 (3)		

Table VII. Bond Distances (Å) for $(\mu_3\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_8[P(CH_3)_2C_6H_5]$ (Vb)

Os(1)–Os(2)	2.849 (1)	P–C(18)	1.815 (6)
Os(1)–Os(3)	2.838 (1)	P–C(11)	1.815 (6)
Os(1)–S(1)	2.447 (1)	C(11)–C(12)	1.394 (8)
Os(1)–S(2)	2.446 (1)	C(12)–C(13)	1.384 (11)
Os(1)–C(1)	1.915 (6)	C(13)–C(14)	1.376 (10)
Os(1)–C(2)	1.900 (7)	C(14)–C(15)	1.351 (10)
Os(1)–C(3)	1.876 (6)	C(15)–C(16)	1.394 (11)
Os(2)–S(2)	2.395 (2)	C(16)–C(11)	1.387 (9)
Os(2)–C(4)	1.883 (7)	C(1)–O(1)	1.146 (6)
Os(2)–C(5)	1.894 (7)	C(2)–O(2)	1.175 (8)
Os(2)–C(6)	1.933 (5)	C(3)–O(3)	1.175 (7)
Os(2)–C(10)	2.144 (5)	C(4)–O(4)	1.152 (8)
Os(3)–S(1)	2.395 (1)	C(5)–O(5)	1.165 (8)
Os(3)–S(2)	2.382 (1)	C(6)–O(6)	1.154 (6)
Os(3)–P	2.307 (2)	C(7)–O(7)	1.145 (7)
Os(3)–C(7)	1.913 (6)	C(8)–O(8)	1.183 (7)
Os(3)–C(8)	1.871 (6)	C(10)–H(101)[a]	0.83
C(10)–S(1)	1.869 (6)	C(10)–H(102)[a]	0.96
P–C(17)	1.823 (8)		

[a] Hydrogen atom positions were not refined.

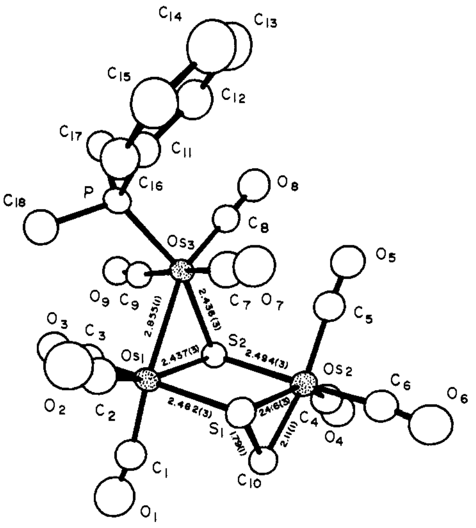

Figure 3. An ORTEP diagram of $(\mu\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IVb) showing 50% probability ellipsoids.

Since the reaction of Ib with carbon disulfide proceeds at a moderate rate at ambient temperature, it could be monitored conveniently by ^1H NMR spectroscopy. Initially, a 0.2 M solution of $(\mu\text{-H})_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$, (Ib) in ca. 3:1 $CDCl_3/CS_2$ showed resonances characteristic of this starting material alone. After about 10 min, new resonances appeared at δ 13.93 (s) and −15.69 (d, J_{PH} = 12.21 Hz). Although these signals are characteristic of dithioformato and hydride ligands, respectively, they *do not* correspond to the complex IIIb characterized crystallographically. After approximately 30 min, the methanedithiolato and hydride signals of IIb became apparent. Minor signals at ca. δ −10 and −20 appeared after about 1 h and persisted throughout the reaction. Signals due to both the isolated dithioformate complex IIIb and the thioformaldehyde complex IVb were evident after 2 h. The gradual appearance of these two species corresponded closely to a gradual *disappearance* of the dithioformate species (δ 13.93, −15.69). After about 4 h, the starting hydride Ib had been completely consumed. The principal species in solution after about 12 h were IIb, IIIb, and IVb, and the dithioformate intermediate is gone. The solution remained homogeneous throughout the course of the reaction. Under more dilute conditions (ca. 0.02 M Ib), the results were similar except that the reaction proceeded more slowly; far less of the methanedithiolato complex IIb was formed, and the trace side products (with ca. δ −10, −20) were not observed.

The isolation of IIIb suggested that such species might be intermediates in the formation of the dicluster complexes IIa and IIb. We have found, however, that IIIb was unreactive toward both Ia and Ib. In addition we prepared the complex IIIa through an independent route (eq 2) and found that it was unreactive

$$(\eta^4\text{-}C_6H_8)Os_3(CO)_{10} \xrightarrow[(2)\ CF_3CO_2H]{(1)\ KS_2CH} \underset{\text{IIIa}}{(\mu\text{-H})(\mu\text{-}S_2CH)Os_3(CO)_{10}} \tag{2}$$

toward Ia. In particular, NMR analysis of an equimolar mixture of Ia and IIIa after 19 h in refluxing hexane merely showed that IIIa had decomposed. No trace of IIa was detected. IIIa has been analyzed crystallographically and confirmed to have the indicated structure.[17]

Thermolyses of $(\mu\text{-H})(\mu\text{-}S_2CH)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IIIb) and $(\mu_3\text{-}S)(\mu\text{-}SCH_2)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (IVb). The complex

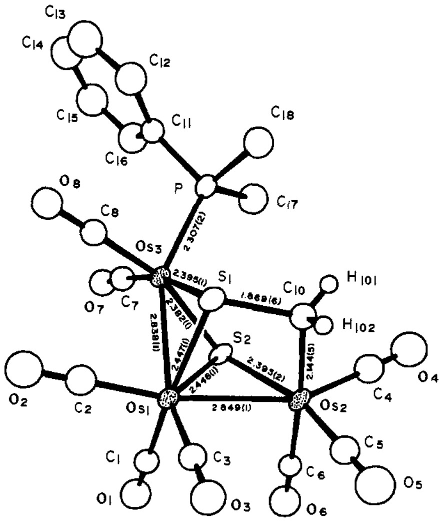

Figure 4. An ORTEP diagram of $(\mu_3\text{-}\eta^2\text{-SCH}_2)(\mu_3\text{-S})\text{Os}_3(\text{CO})_8[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (Vb) showing 50% probability ellipsoids for all nonhydrogen atoms.

IVb readily lost 1 mol of carbon monoxide when heated in refluxing hexane and formed the new complex $(\mu_3\text{-CH}_2\text{S})(\mu_3\text{-S})\text{Os}_3(\text{CO})_8[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (Vb) in 74% yield. This complex was characterized spectroscopically and crystallographically. Its molecular structure is shown in Figure 4. Inorganic sulfide and thioformaldehyde ligands are present, but the latter is a triply bridging ligand. Under slightly more forcing conditions (refluxing heptane, 15 h) the dithioformate complex IIIb was also converted into the thioformaldehyde complex Vb (46% yield).

The ^{1}H NMR spectrum of Vb showed resonances which can be attributed to two thioformaldehyde ligands with each containing inequivalent protons. As with IVb, Vb also exists in solution as a mixture of two isomers. In isomer Vb A the methylene resonances appear in an AB quartet (Table I) while in isomer Vb B they appear in an ABX pattern due to coupling to the phosphorus atom. The interconvertibility of the two isomers was established by a spin saturation transfer experiment[13b] performed at 57 °C in toluene-d_8. Irradiation of the upfield doublet of Vb A caused the upfield multiplet of Vb B to disappear into the base line and the downfield doublet of Vb A to collapse to a singlet. Similarly, irradiation of the downfield multiplet of Vb B caused the downfield doublet of Vb A to disappear and the upfield multiplet of Vb B to collapse to a doublet. Furthermore, when the sample was warmed to 90 °C, reversible broadening of the resonances was observed, but signal averaging was not obtained.

Further thermolysis of thioformaldehyde complex Vb in refluxing octane produced only uncharacterizable decomposition products probably resulting from cluster fragmentation. However, complex Vb does undergo some interesting transformations with various electrophiles and nucleophiles which will be reported in a separate publication.[20]

Description of the Structures

$(\mu\text{-S}_2\text{CH}_2)[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}]_2$ (IIa). We were not completely satisfied with the final refinement of our original X-ray structural analysis of IIa.[8a] We thus redetermined the structure by using a new and presumably better quality crystal. The second analysis gave a significantly improved refinement and what we feel are considerably improved structural parameters. Details of the molecular structure of IIa (based on the second determination) are reported for the first time here. Crystals of IIa consist of discrete moleculers of $(\mu\text{-S}_2\text{CH}_2)[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}]_2$. The shortest intermolecular contacts were between carbonyl oxygen atoms in the range 2.9–3.1 Å.

The molecular structure of IIa is shown in Figure 1. The gross molecular structure is the same as that obtained from the original determination. Overall, the molecule contains two triosmium clusters linked by a $\mu\text{-S}_2\text{CH}_2$ ligand. Each cluster consists of an approximately equilateral triangle of three osmium atoms. The six independent Os–Os bond distances span the small range 2.854–2.876 Å. These are similar to the Os–Os distances 2.842–2.863 Å found in $(\mu\text{-H})(\mu\text{-SC}_2\text{H}_5)\text{Os}_3(\text{CO})_{10}$[21] and 2.842–2.852 Å found in $(\mu\text{-H})(\mu\text{-SCH}_3)\text{Os}_3(\text{CO})_9(\text{C}_2\text{H}_4)$.[22] Complete lists of interatomic bond distances and angles are given in Tables III and IV. Each cluster contains a single sulfur atom bridging an edge of the cluster. The Os–S distances range from 2.409 to 2.429 Å. These are similar to the Os–S distances of 2.39–2.41 Å found in $(\mu\text{-H})(\mu\text{-SC}_2\text{H}_5)\text{Os}_3(\text{CO})_{10}$[21] and 2.402 (7) Å found in $(\mu\text{-H})(\mu\text{-SCH}_3)\text{Os}_3(\text{CO})_9(\text{C}_2\text{H}_4)$.[22] A metal–hydride ligand (not observed crystallogrpahically) is believed to occupy a bridging position across the sulfur bridged metal–metal bond on the opposite side of each Os_3 plane. The stereochemical influences of the hydride ligands are shown by the presence of large cavities circumscribed by the carbonyl groups C(5)–O(5), C(6)–O(6), C(9)–O(9), and C(8)–O(8) in cluster Os(1)–Os(2)–Os(3) and C(15)–O(15), C(16)–O(16), C(18)–O(18), and C(20)–O(20) in cluster Os(4)–Os(5)–Os(6). Hydride ligands have been observed in similar positions in structurally related molecules.[24] The overall geometry of each $(\mu\text{-S})(\mu\text{-H})\text{Os}_3(\text{CO})_{10}$ unit is very similar to that of the molecule $(\mu\text{-H})(\mu\text{-SC}_2\text{H}_5)\text{Os}_3(\text{CO})_{10}$.[22]

The most interesting feature of IIa is that the two sulfur atoms are joined by a methylene group. The C–S distances both of 1.85 Å are very similar to C–S single bond distances 1.80–1.82 Å that have been observed in several thioalkanes[24] and the distance 1.89 (4) Å found in $(\mu\text{-SC}_2\text{H}_5)(\mu\text{-H})\text{Os}_3(\text{CO})_{10}$.[21] The two hydrogen atoms were tentatively identified in a difference Fourier synthesis and are shown in those positions in the figure. The geometry of the two hydrogen atoms and two sulfur atoms about the carbon C(21) is approximately tetrahedral, with the angle S(1)–C–S(2) equal to 104.4 (7)°.

$(\mu\text{-}\eta^2\text{-SCH}_2)(\mu_3\text{-S})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (IVb). Crystals of IVb consist of discrete molecules of $(\mu\text{-}\eta^2\text{-SCH}_2)(\mu_3\text{-S})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$. The shortest intermolecular contacts were between carbonyl oxygen atoms at 3.1–3.2 Å.

The molecular structure of IVb is shown in Figure 3. Complete lists of interatomic distances and angles are given in Tables V and VI. The molecule contains three osmium atoms, only two of which are mutually bonded, Os(1)–Os(3) = 2.855 (1) Å. The Os(1)···Os(2) and Os(2)···Os(3) distances at 3.780 (1) and 4.033 (1) Å, respectively, are approximately 1 Å longer than normal osmium–osmium bonds (e.g., in $\text{Os}_3(\text{CO})_{12}$,[25] Os–Os = 2.877 (3) Å) and imply little or no direct metal–metal bonding. Each osmium atom contains three linear terminal carbonyl groups while Os(3) also contains a dimethylphenylphosphine ligand.

The molecule is held together by bridging inorganic sulfide and thioformaldehyde ligands. The inorganic sulfide ligand, S(2) is bonded to all three osmium atoms. The Os–S bond distances to the mutually bonded metal atoms Os(1) and Os(3) are 2.437 (3) and 2.436 (3) Å. These distances are similar to the Os–S distances observed in the compounds $(\mu\text{-H})_2(\mu_3\text{-S})\text{Os}_3(\text{CO})_9$,[26] 2.382–2.395 Å, $[\text{PPN}]^+[(\mu\text{-H})(\mu_3\text{-S})\text{Os}_3(\text{CO})_9]^-$,[27] 2.369–2.401 Å, and $(\mu\text{-H})_2(\mu_3\text{-S})_2\text{Os}_3(\text{CO})_7(\text{CS})$,[28] 2.373–2.464 Å. The Os(2)–S(2)

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Table VIII. Bond Angles (Deg) for $(\mu_3\text{-SCH}_2)(\mu_3\text{-S})\text{Os}_3(\text{CO})_8[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (Vb)

Os(2)-Os(1)-Os(3)	91.11 (1)	S(1)-Os(3)-P	101.64 (5)
Os(2)-Os(1)-S(1)	71.81 (4)	S(1)-Os(3)-S(2)	84.29 (5)
Os(2)-Os(1)-S(2)	53.13 (4)	S(1)-Os(3)-C(7)	167.7 (2)
Os(2)-Os(1)-C(1)	98.1 (2)	S(1)-Os(3)-C(8)	89.9 (2)
Os(2)-Os(1)-C(2)	167.3 (2)	S(2)-Os(3)-P	108.62 (5)
Os(2)-Os(1)-C(3)	82.0 (2)	S(2)-Os(3)-C(7)	88.7 (2)
Os(3)-Os(1)-S(1)	53.25 (4)	S(2)-Os(3)-C(8)	160.5 (2)
Os(3)-Os(1)-S(2)	52.96 (3)	P-Os(3)-C(7)	90.1 (2)
Os(3)-Os(1)-C(1)	121.1 (2)	P-Os(3)-C(8)	90.7 (2)
Os(3)-Os(1)-C(2)	80.6 (2)	C(7)-Os(3)-C(8)	93.5 (3)
Os(3)-Os(1)-C(3)	146.2 (2)	Os(2)-C(10)-S(1)	107.2 (3)
S(1)-Os(1)-S(2)	81.85 (5)	Os(1)-S(1)-C(10)	97.3 (2)
S(1)-Os(1)-C(1)	170.1 (2)	Os(3)-S(1)-C(10)	109.1 (2)
S(1)-Os(1)-C(2)	92.5 (2)	Os(3)-P-C(17)	113.7 (2)
S(1)-Os(1)-C(3)	93.1 (2)	Os(3)-P-C(18)	115.1 (2)
S(2)-Os(1)-C(1)	88.3 (2)	Os(3)-P-C(11)	113.2 (2)
S(2)-Os(1)-C(2)	125.5 (2)	C(17)-P-C(18)	102.7 (3)
S(2)-Os(1)-C(3)	134.7 (2)	C(17)-P-C(11)	106.2 (3)
C(1)-Os(1)-C(2)	94.4 (3)	C(18)-P-C(11)	104.8 (3)
C(1)-Os(1)-C(3)	92.7 (3)	P-C(11)-C(12)	121.3 (5)
C(2)-Os(1)-C(3)	99.5 (3)	P-C(11)-C(16)	121.0 (5)
Os(1)-Os(2)-C(10)	80.3 (1)	C(12)-C(11)-C(16)	117.6 (6)
Os(1)-Os(2)-S(2)	54.76 (4)	C(11)-C(12)-C(13)	120.7 (7)
Os(1)-Os(2)-C(4)	155.2 (2)	C(12)-C(13)-C(14)	120.7 (7)
Os(1)-Os(2)-C(5)	104.7 (2)	C(13)-C(14)-C(15)	119.0 (8)
Os(1)-Os(2)-C(6)	95.0 (2)	C(14)-C(15)-C(16)	121.4 (8)
S(2)-Os(2)-C(10)	85.6 (2)	C(15)-C(16)-C(11)	120.3 (6)
S(2)-Os(2)-C(4)	103.5 (2)	Os(1)-C(1)-O(1)	176.5 (6)
S(2)-Os(2)-C(5)	159.4 (2)	Os(1)-C(2)-O(2)	177.6 (6)
S(2)-Os(2)-C(6)	88.5 (2)	Os(1)-C(3)-O(3)	177.2 (5)
C(10)-Os(2)-C(4)	88.1 (2)	Os(2)-C(4)-O(4)	178.4 (7)
C(10)-Os(2)-C(5)	88.9 (2)	Os(2)-C(5)-O(5)	177.4 (6)
C(10)-Os(2)-C(6)	175.3 (2)	Os(2)-C(6)-O(6)	179.4 (5)
C(4)-Os(2)-C(5)	96.9 (3)	Os(3)-C(7)-O(7)	175.8 (6)
C(4)-Os(2)-C(6)	96.1 (3)	Os(3)-C(8)-O(8)	178.1 (5)
C(5)-Os(2)-C(6)	92.6 (2)	Os(2)-C(10)-H(101)[a]	132
Os(1)-S(1)-Os(3)	71.76 (4)	Os(2)-C(10)-H(102)[a]	110
Os(1)-S(2)-Os(2)	72.11 (4)	H(101)-C(10)-H(102)[a]	81
Os(1)-S(2)-Os(3)	72.01 (4)	S(1)-C(10)-H(101)[a]	116
Os(2)-S(2)-Os(3)	116.42 (5)	S(1)-C(10)-H(102)[a]	100
Os(1)-Os(3)-P	149.61 (4)		
Os(1)-Os(3)-S(1)	54.98 (3)		
Os(1)-Os(3)-S(2)	55.03 (4)		
Os(1)-Os(3)-C(7)	112.8 (2)		
Os(1)-Os(3)-C(8)	106.8 (2)		

[a] Hydrogen atom positions were not refined.

distance at 2.494 (3) Å is significantly longer than the other two. The two atom group, C(10)–S(1), belongs to a thioformaldehyde ligand. The hydrogen atoms on C(10) were not observed crystallographically but were confirmed spectroscopically (vide supra). As far as we know this is the first crystallographic characterization of a thioformaldehyde ligand.[29] The bonding can be described as a π bond to the metal atom Os(2), Os(2)–S(1) = 2.416 (3) Å and Os(2)–C(10) = 2.11 (1) Å, while the sulfur atom simultaneously serves as a bridge between Os(1) and Os(2), Os(1)–S(1) = 2.482 (3) Å. The C(10)–S(1) distance, 1.79 (1) Å, is considerably longer than the carbon–sulfur double bond (1.599 (7) Å) found in tetramethylcyclobutane-1,3-dithione[31] and only slightly shorter than a carbon–sulfur single bond, 1.80–1.82 Å.[24] A similar ligand arrangement was recently reported by Alper,[32] for a thiocamphor adduct of $(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ which contains a bridging η^2-thioketonic group. In that complex the C–S bond distance is 1.769 (6) Å.

$(\mu_3\text{-}\eta^2\text{-SCH}_2)(\mu_3\text{-S})\text{Os}_3(\text{CO})_8[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (Vb). Crystals of Vb consist of discrete molecules of $(\mu_3\text{-}\eta^2\text{-SCH}_2)(\mu_3\text{-S})\text{Os}_3(\text{CO})_8[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$. The shortest intermolecular contacts were between carbonyl oxygen atoms at 3.0–3.2 Å.

The molecular structure of Vb is shown in Figure 4. Interatomic bond distances and angles are listed in Tables VII and VIII. The molecule contains three osmium atoms with two osmium–osmium bonds, Os(1)–Os(2) = 2.849 (1) Å and Os(1)–Os(3) = 2.838 (1) Å. The long Os(2)···Os(3) distance of 4.061 (1) Å precludes any signficant metal–metal bonding. The molecule contains eight terminal carbonyl groups distributed such that Os(1) and Os(2) have three each and Os(3) has two. A dimethylphenylphosphine ligand is also coordinated to Os(3). There is a triply-bridging inorganic sulfide ligand with bonding distances to the metal atoms ranging from 2.382 to 2.446 Å.

The most interesting ligand is a triply-bridging thioformaldehyde group. Its sulfur atom S(1) bridges the Os(1)–Os(3) metal–metal bond while its carbon atom alone is bonded to the third osmium atom Os(2), Os(2)–C(10) = 2.144 (5) Å. The C(10)–S(1) distance at 1.869 (6) Å indicates that the C(10)–S(1) interaction is best described as a single bond. The hydrogen atoms bonded to C(10) were located in an electron density map.

Discussion

The reactions of Ia and Ib (in the higher concentration ranges) with CS_2 produced the dicluster complexes IIa and IIb, respectively, both of which contain a S_2CH_2 ligand linking two triosmium cluster groupings. They were evidently formed by the reaction of 2 mol of the cluster complexes with 1 mol of CS_2. Two hydride ligands, presumably one from each cluster, have been transferred to the carbon atom of the CS_2 molecule, thus reducing it to a

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(29) A thioformaldehyde ligand bonded to a single osmium atom was recently reported by Collins and Roper.[30]

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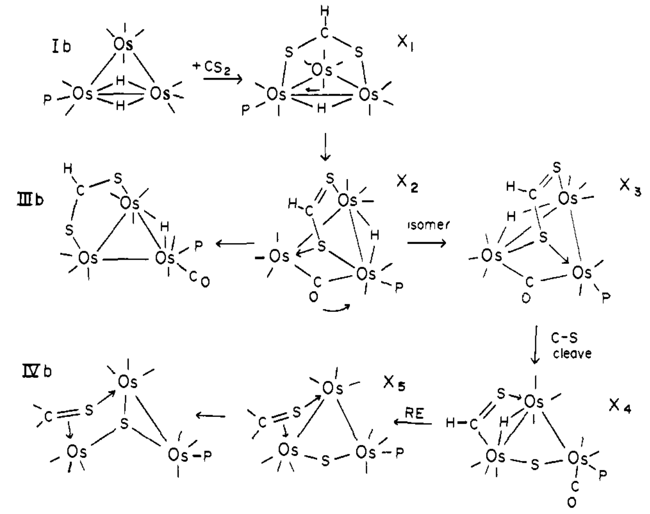
Scheme I



methylene group. One sulfur atom occupies a bridging position in each triosmium cluster unit.

Typically, mononuclear metal hydride complexes react with CS_2 to form complexes containing dithioformato ligands by transferring one hydride ligand to the CS_2 molecule.[33] The transfer of two hydrides is heretofore unprecedented. It is certainly due in part to the fact that two clusters have engaged in reaction with a single CS_2 molecule. However, this might also have been influenced by the tendency of the sulfur atoms to favor bridging positions in the cluster units.

In addition to IIb, the products IIIb and IVb were also obtained from the reaction of Ib with CS_2. The molecular structure of IIIb, described in detail elsewhere,[17] is illustrated in Figure 2. Briefly, the molecule contains a dithioformato ligand bridging an edge of a single triosmium cluster in a diaxial coordination position. A hydride ligand bridges an adjacent edge of the cluster next to the phosphine ligand, which is itself attached to the third osmium atom. It is significant that each osmium atom contains three terminal carbonyl ligands. This feature contrasts with the structure of Ib[34] which is shown schematically in the first row of Scheme I. In Ib the distribution of carbonyl ligands among the three osmium atoms is 4,3,2 and is analogous to the related molecules $(\mu\text{-H})_2Os_3(CO)_9[P(C_6H_5)_3]$[35] and $(\mu\text{-H})_2Os_3(CO)_9(CNCH_3)$.[36] Apparently, IIIb was formed by the reaction of 1 mol of Ib with 1 mol of CS_2 in a process which involved a carbonyl shift between a pair of metal atoms in addition to a hydride transfer to the carbon atom of the CS_2 molecule. A mechanism for the formation of IIIb is shown in Scheme I. An intermediate X_1, containing a dithioformato ligand bridging the same osmium–osmium bond that originally contained the two bridging hydride ligands in Ib, could be formed initially. The distribution of carbonyl ligands in X_1 would be the same as that in Ib, that is, 4,3,2. X_1 then undergoes a slow isomerization wherein the sulfur atom on the osmium atom containing the phosphorus ligand moves into a bridging position. A carbonyl ligand on the opposite side of the cluster, on the osmium atom containing four carbonyl groups, simultaneously moves into a bridging position across the same pair of osmium atoms as the bridging sulfur atom. A transient species such as X_2 can be envisaged. Interestingly, if the bridging sulfur atom serves as a three electron donor, the osmium–osmium bond must formally be cleaved if the metal atoms are not to exceed 18-electron configurations. A few complexes having carbonyl ligands bridging nonbonded metal atoms have been isolated,[37] and intermediates of this type have been detected spectroscopically.[38] The formation of IIIb is completed by shifting the sulfur atom to a terminal position on the osmium atom that originally contained four carbonyl ligands, shifting the bridging carbonyl ligand to a terminal position on the osmium atom containing the phosphine ligand, and reforming the metal–metal bond.

Since the intermediate X_1 is structurally and presumably enegetically very similar to IIIb, one might expect to be able to detect it experimentally. Indeed, when this reaction was followed by ^1H NMR spectroscopy, an intermediate containing a dithioformato proton resonance (δ 13.93) and a bridging hydride ligand (δ −15.69) was observed. We believe that this intermediate was X_1.[39]

Each osmium atom in IVb also contains three carbonyl ligands, and IVb was also formed subsequent to the intermediate assigned by us as X_1. This evidence has led us to consider a relationship between the mechanisms for the formation of IIIb and IVb.

A possible route to IVb is also shown in Scheme I. The isomerization $X_2 \rightarrow X_3$ simply moves the bridging hydride ligand to the other osmium–osmium bond. Facile hydride shifts have been observed in other cluster complexes[17] and are also strongly implicated in the dynamical behavior of IIIb (vide supra). The conversion of X_3 to X_4 would involve a cleavage of the carbon–sulfur bond at the bridging sulfur atom and a shift of the dithioformato carbon atom to the osmium atom containing the bridging hydride ligand. This would place a μ-η^2-thioformyl ligand and a bridging hydride ligand across the same osmium–osmium bond. It would also complete the carbonyl shift, irreversibly cleave the osmium–osmium bond, and create a bridging inorganic sulfide ligand. Each metal atom in X_4 would have an 18-electron configuration. Reductive elimination of a C–H bond, $X_4 \rightarrow X_5$, would produce a bridging thioformaldehyde ligand. The final step could be a nucleophilic attack of the inorganic sulfide ligand on the third osmium atom $X_5 \rightarrow$ IVb. This would produce the triply-bridging sulfide ligand and cleave the osmium–osmium bond bridged by the thioformaldehyde ligand. It is difficult to assess the relative stability of the various intermediates X_2 through X_5. Some might be transition states only. Indeed, the sequence of steps might be different from those shown in Scheme I. For example, the nulceophilic attack of the sulfide ligand on the third osmium atom, $X_5 \rightarrow$ IVb, might precede and even promote the reductive elimination, $X_4 \rightarrow X_5$, or the hydride shift might follow the C–S cleavage. We do, however, believe that the steps shown provide a basis for understanding the types of atomic rearrangements which do occur. Interestingly, this mechanism includes an intermediate X_2 which is common to the formation of both IIIb and IVb. Thus, in principle, IIIb and IVb should be interconvertible. Evidence supporting this notion was provided by the transformation of IIIb into Vb which itself is a simple decarbonylation product of IVb.

Mechanisms which cannot be excluded at this time are intermolecular processes, cluster fragmentation processes involving mononuclear fragments, and processes involving the intermediacy of thiocarbonyl ligands.[28,41] However, we currently have no evidence implicating such processes and have not chosen to invoke them at this time.

As implied by Scheme I, IVb was evidently formed through the reaction of 1 mol of CS_2 with 1 mol of Ib. An important result, regardless of the mechanism, is that in order for the cluster to hydrogenate and fragment the CS_2 molecule in the observed way, two of the metal–metal bonds had to be cleaved. This may be a feature of potential value in some forms of cluster catalyses but will require the presence of inert supportive ligands such as the triply-bridging inorganic sulfide ligand in this case, which can

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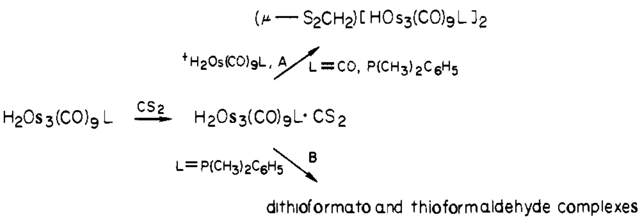
Scheme II



maintain the proximity of the mononuclear fragments after the metal–metal bonds have been cleaved.

When heated, IVb was readily decarbonylated and transformed into Vb. The expelled carbonyl ligand apparently emanated from osmium Os(3) (see Figure 3) which also contained the phosphine ligand. Vb was then formed through a rearrangement in which the sulfur atom of the thioformaldehyde ligand was shifted from a bridging position across the atoms Os(1) and Os(2) to a bridging position across atoms Os(1) and Os(3). The carbon atom C(10) simply remained bonded to Os(2). This rearrangement formally shifted the electron deficiency (created by the loss of CO ligand) from Os(3) to Os(2). The electron deficiency was then removed through the formation of a metal–metal bond between osmium atoms Os(1) and Os(2).

Complexes containing dithioformato ligands were seriously considered as intermediates in the formation of the dicluster complexes. However, we have found that the complex IIIa prepared independently will not react with Ia to form IIa, and IIIb will not react with Ib to form IIb. We have thus ruled out such species as intermediates in this process.

A mechanism which accounts for the formation of the dicluster complexes and also allows for the formation of the dithioformato and thioformaldehyde complexes is shown in Scheme II. CS_2 initially reacts with a molecule I to form an adduct. Adducts of Ia with a variety of other small molecules have been characterized.[5,11b,42] Such a coordinated CS_2 ligand would probably bond in a η^2 manner involving the carbon atom and one sulfur atom. This bonding form has been well characterized in mononuclear metal complexes.[31] It is known that the uncoordinated sulfur atoms in such complexes are very nucleophilic.[41a,43] A second cluster of I could then react with the adduct at the uncoordinated sulfur atom. This could be followed by a rapid transfer of two hydrogen atoms, presumably one from each cluster, and formation of the S_2CH_2 ligand in the products II, route A. Alternatively, the dithioformato and thioformaldehyde complexes IIIb and IVb could be formed through a unimolecular process (Scheme I) in which hydrogen atoms are transferred to the carbon atom of the CS_2 ligand in the adduct, route B. This scheme could also account for the concentration dependent formation of IIb. When the concentration of Ib is low, the adduct decomposes unimolecularly and the yield of IIb is very low. When the concentration of Ib is high, the bimolecular process A becomes important and the yields of IIb are increased.

Summary

The cluster hydride complexes I react with CS_2 to form dicluster complexes II containing methanedithiolato ligands linking the two clusters. The transfer of two hydride ligands to the carbon atom of the CS_2 molecule is an important step beyond that normally achieved with mononuclear metal hydride complexes where generally only one hydride ligand is transferred. This greater reduction may be influenced by the tendency of the sulfur atoms to favor bridging positions in the clusters.

Monocluster complexes containing dithioformato and thioformaldehyde ligands have also be characterized. In these complexes the cleavage of metal–metal bonds evidently played a key role in the hydrogenation and fragmentation of the CS_2 molecule.

In the summary, both polynuclear coordination and metal–metal bond cleavage processes are clearly involved in the cluster-assisted hydrogenation of CS_2. It seems reasonable to expect that such processes could play an important role in other types of cluster reactions and probably in cluster catalysis in general.

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Supplementary Material Available: Final fractional atomic coordinates, thermal parameters, and structure factor amplitudes for all three structures (85 pages). Ordering information is given on any current masthead page.

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