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ON THE STRUCTURAL EFFECT OF THE BRIDGING HYDRIDE LIGAND ON A METAL—METAL BOND IN A TRINUCLEAR CLUSTER. THE CRYSTAL AND MOLECULAR STRUCTURES OF (μ-H)(μ-S_2CH)$Os_3(CO)_{10}$ AND (μ-H)(μ-S_2CH)$Os_3(CO)_9[P(CH_3)_2C_6H_5]$

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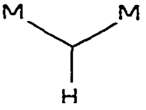
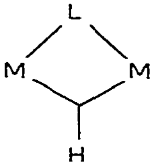
Summary

The crystal and molecular structures of the complexes (μ-H)(μ-S_2CH)$Os_3(CO)_{10}$, III and (μ-H)(μ-S_2CH)$Os_3(CO)_9[P(CH_3)_2C_6H_5]$, IV, are reported. For III: Space group = $P2_1/c$, No. 14, $[C_{2h}^5]$, at —35° C, a = 8.452(2), b = 25.435(12), c = 16.818(5) Å, β = 91.75(3), Z = 8, ρ_{calc} = 3.43 g/cc. For IV: Space group = $P\bar{1}$, No. 2, at —35°C, a = 8.375(3), b = 12.960(4), c = 15.106(4) Å, α = 64.50(2)°, β = 70.22(3)°, γ = 79.20(3)°, Z = 2, ρ_{calc} = 2.48 g/cc. Both compounds contain triangular clusters of osmium atoms and have dithioformato ligands bridging edges of the clusters in axial coordination sites. The dimethylphenylphosphine ligand is bonded to the unique osmium atom in IV in an equatorial coordination site. The hydride ligands were not observed directly but their positions are strongly inferred on the basis of geometrical considerations. In III the hydride and the dithioformato ligands bridge the same metal—metal bond. The Os—Os internuclear distance is 2.973(1) Å. In IV the hydride ligand bridges a metal—metal bond which is adjacent to the one bridged by the dithioformato ligand. The Os—Os distance of the dithioformato bridged bond in IV is only 2.854(1) Å. The much longer dithioformato bridged metal—metal bond in III is thus attributed principally to the presence of the bridging hydride ligand.

Introduction

The nature of metal—metal bonding in the presence of a bridging hydride ligand has been a subject of considerable interest and study [1—3]. Examples


(I)


(II)

now range from those where the metal—metal distance is large (e.g. $[(\mu\text{-H})\{Cr(CO)_5\}_2]^-$,[4]) to those where it is unusually short (e.g. $(\mu\text{-H})_2Os_3(CO)_{10}$, [5,6]). In all known cases, the addition of a single bridging hydride ligand to an unsupported metal—metal bond, I, causes an increase in the metal—metal internuclear distance [7,8]. The metal—metal distance in systems which contain a supplementary bridging ligand L, II, may be longer than, shorter than or equivalent to a normal metal—metal bond distance [9]. However, analysis of these latter systems is fraught with the difficulties of assigning values for the "normal" internuclear distances and trying to unravel the independent effects of L and H. Churchill has made a thorough study of the doubly bridged bond, II, in triosmium cluster compounds by varying the ligand L [9,10]. He has shown that for those molecules the M—M distance is directly influenced by the size of the bridging ligand, L, and he suggested that the effect of the hydride ligand was more important than that of the L ligand in determining the Os—Os distance [9].

It seems like a very straightforward way of analyzing the independent effects of the bridging hydride ligand on the doubly bridged metal—metal bond would be simply to compare the two cases in which the hydride is present and absent. To date very few reports of this comparison have been made. Petersen et al. have compared the structures of the two molecules $(C_5H_5)_2Mo_2(CO)_4(\mu\text{-H})[\mu\text{-P}(CH_3)_2]$, [11] and $(C_5H_5)_2Mo_2(CO)_4[\mu\text{-P}(CH_3)_2]^-$, [12]. It was shown that the protonation of the Mo—Mo bond of the anion resulted in an increase in the Mo—Mo internuclear distance by 0.11 Å [12].

In the course of our recent studies on the reactions of triosmium cluster compounds with CS_2 [13,14] we have prepared the complexes $(\mu\text{-H})(\mu\text{-S}_2CH)Os_3(CO)_{10}$, III, and $(\mu\text{-H})(\mu\text{-S}_2CH)Os_3(CO)_9[P(CH_3)_2C_6H_5]$, IV. Crystal structure analyses of both complexes have been performed and are reported here. Each complex contains a bridging dithioformato ligand and a bridging hydride ligand but the hydrides bridge different metal—metal bonds in the different clusters.

Experimental

The compound $(\mu\text{-H})(\mu\text{-S}_2CH)Os_3(CO)_{10}$ was prepared by the reaction of $(C_6H_8)Os_3(CO)_{10}$ [15a] with KS_2CH [15b] followed by acidification. $(\mu\text{-H})(\mu\text{-S}_2CH)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ was prepared by the reaction of CS_2 with $(\mu\text{-H})_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$, [14]. Details of both preparations will be reported in a forthcoming publication. Orange crystals of both complexes were prepared by cooling hexane solutions to −20°C.

All diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite monochromatized Mo-K_α radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained using the CAD-4 automatic search, center, index and least squares routines.

All calculations were performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. Anomalous dispersion corrections [16a] were added to the neutral atom scattering factors [16b] used for all nonhydrogen atoms. Full-matrix least-squares refinements minimized the function $w(F_{\text{obs}} - F_{\text{calc}})^2$ where the weighting factor $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F^2_{\text{obs}})/2F_{\text{obs}}$ and

TABLE 1

CRYSTALLOGRAPHIC DATA FOR X-RAY DIFFRACTION STUDIES OF $(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_{10}$, III, AND $(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_9[\text{P(CH)}_3\text{C}_6\text{H}_5]$, IV

	III	IV
A) Crystal parameters		
Temperature (°C)	−35	−35
Space group	$P2_1/c$,[C_{2h}^5], No. 14	$P\bar{1}$,[C_i], No. 2
a (Å)	8.452(2)	8.375(3)
b (Å)	25.345(12)	12.960(4)
c (Å)	16.818(5)	15.106(4)
α (°)	—	64.50(2)
β (°)	91.75(3)	70.22(3)
γ (°)	—	79.20(3)
V (Å^3)	3601.1	1390.8
Z	8	2
Mol.wt.	928.86	1039.00
calc (g/cc)	3.43	2.48
B) Measurement of intensity data		
Radiation	Mo-$K_{\bar{\alpha}}$ (0.71073 Å)	
Monochromator	Graphite	
Detector aperture (mm)		
Horizontal: A + Btanθ	A = 3.0	3.0
	B = 1.0	1.0
Vertical:	4.0	4.0
Reflections measured	$+h$, $+k$, $\pm l$	$+h$, $\pm k$, $\pm l$
Max 2θ (°)	46	52
Scan type	moving crystal—stationary counter	
ω Scan width	0.8	0.75
Background	1/4 additional scan at each end of scan	
Scan rate (°/min) (variable)		
Max	10	10
Min	1.25	1.18
No. reflections measured	5449	5368
Data used ($F^2 > 3.0\sigma(F^2)$)	2607	4282
C) Treatment of data		
Absorption coefficient μ(cm^{-1})	227.3	147.8
Grid	14 × 8 × 6	14 × 8 × 6
Transmission coefficient		
Max	0.260	0.360
Min	0.019	0.035
p-factor	0.02	0.01
Final residuals		
R	0.043	0.050
R_w	0.045	0.067
Esd of unit weight	2.07	6.78
Largest shift/error on final cycle	0.34	0.08

$\sigma(F^2_{\text{obs}}) = [\sigma(I_{\text{raw}})^2 + (pF^2_{\text{obs}})^2]^{1/2}/LP$. Crystal data and data collection parameters are listed in Table 1.

$(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_{10}$, III

A crystal shaped like an octahedron extended along one of its 2-fold axes having approximate dimensions 0.21 × 0.09 × 0.07 mm was selected and mounted in a thin-walled glass capillary. ω-scan peak widths at half height were in the range 0.20—0.25°. Because crystals of this compound are unstable at room

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TABLE 2

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_{10}$, III

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
Os(1)	0.3687(2)	0.25674(5)	0.11971(8)	[a]	O(16)	1.387(3)	0.0269(8)	0.375(1)	3.8(5)
Os(2)	0.5644(1)	0.17974(5)	0.03204(8)	[a]	O(17)	1.398(2)	−0.1165(8)	0.244(1)	3.4(5)
Os(3)	0.6064(1)	0.29245(5)	0.01040(8)	[a]	O(18)	1.342(3)	0.1007(3)	0.235(1)	4.5(6)
Os(4)	0.8890(1)	0.03670(5)	0.31100(7)	[a]	O(19)	1.315(2)	−0.0423(8)	0.081(1)	3.7(5)
Os(5)	1.1290(1)	−0.04528(5)	0.29716(8)	[a]	O(20)	1.019(3)	0.1108(9)	0.039(1)	4.7(6)
Os(6)	1.0819(1)	0.02879(5)	0.16700(8)	[a]	C(1)	0.321(4)	0.327(1)	0.130(2)	3.6(8)
S(1)	0.157(1)	0.2494(4)	0.0178(6)	[a]	C(2)	0.214(4)	0.230(1)	0.192(2)	3.4(8)
S(2)	0.359(1)	0.1725(4)	−0.0737(6)	[a]	C(3)	0.530(4)	0.260(1)	0.208(2)	2.4(7)
S(3)	0.678(1)	−0.0159(3)	0.2468(6)	[a]	C(4)	0.718(3)	0.170(1)	−0.048(2)	1.8(6)
S(4)	0.871(1)	−0.0214(4)	0.0978(5)	[a]	C(5)	0.729(3)	0.179(1)	0.117(2)	1.8(6)
O(1)	0.276(3)	0.3731(9)	0.131(1)	5.2(6)	C(6)	0.524(4)	0.108(1)	0.051(2)	2.8(7)
O(2)	0.125(3)	0.2131(10)	0.236(2)	6.4(7)	C(7)	0.450(4)	0.290(1)	−0.077(2)	3.7(8)
O(3)	0.609(3)	0.2617(8)	0.258(1)	4.5(5)	C(8)	0.579(4)	0.365(1)	0.020(2)	3.7(8)
O(4)	0.812(3)	0.1642(8)	−0.097(1)	4.1(5)	C(9)	0.765(4)	0.290(1)	−0.066(2)	3.5(7)
O(5)	0.818(3)	0.1773(8)	0.164(1)	3.9(5)	C(10)	0.767(3)	0.293(1)	0.096(2)	2.4(6)
O(6)	0.495(3)	0.0629(8)	0.062(1)	3.9(5)	C(11)	0.826(4)	0.006(1)	0.410(2)	3.2(7)
O(7)	0.361(3)	0.2974(9)	−0.131(1)	4.7(6)	C(12)	0.739(3)	0.093(1)	0.312(2)	2.5(6)
O(8)	0.559(3)	0.4114(8)	0.024(1)	4.5(5)	C(13)	1.047(4)	0.082(1)	0.363(2)	3.4(7)
O(9)	0.873(3)	0.2895(8)	−0.111(1)	4.0(5)	C(14)	0.986(4)	−0.093(1)	0.241(2)	3.4(7)
O(10)	0.860(2)	0.2983(8)	0.147(1)	3.3(5)	C(15)	1.094(4)	−0.078(1)	0.396(2)	2.9(7)

O(11)	0.798(3)	−0.0107(8)	0.468(1)	3.6(5)	C(16)	1.283(4)	0.002(1)	0.344(2)	2.6(7)
O(12)	0.643(3)	0.1245(8)	0.312(1)	4.2(5)	C(17)	1.294(4)	−0.089(1)	0.261(2)	3.2(7)
O(13)	1.135(2)	0.1091(7)	0.392(1)	3.3(5)	C(18)	1.243(3)	0.073(1)	0.214(2)	2.2(6)
O(14)	0.907(3)	−0.1258(8)	0.214(1)	4.5(6)	C(19)	1.232(4)	−0.016(1)	0.114(2)	2.9(7)
O(15)	1.058(2)	−0.0973(7)	0.457(1)	2.9(4)	C(20)	1.048(4)	0.080(1)	0.092(2)	2.5(6)
					C(21)	0.199(4)	0.205(1)	−0.055(2)	4.7(9)
H(1)[b]	0.1079	0.1972	−0.0928	5.0	C(22)	0.720(4)	−0.031(1)	0.155(2)	4.8(9)
H(2)[b]	0.6299	−0.0521	0.1258	5.0					

[a]) Final anisotropic thermal parameters are: [c]

	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Os(1)	1.44(5)	3.12(6)	2.38(6)	0.32(5)	0.12(5)	−0.06(5)
Os(2)	1.43(5)	2.19(5)	2.91(6)	−0.00(5)	0.25(5)	−0.15(5)
Os(3)	1.64(5)	2.29(5)	2.34(6)	0.05(5)	−0.06(5)	0.10(5)
Os(4)	1.79(5)	2.40(5)	1.84(6)	0.09(5)	0.53(5)	−0.34(5)
Os(5)	1.63(5)	2.37(5)	1.76(6)	−0.02(5)	0.15(5)	0.02(5)
Os(6)	1.94(5)	2.58(5)	1.78(6)	0.29(5)	0.47(5)	0.09(5)
S(1)	3.0(4)	5.8(5)	4.2(5)	0.7(4)	0.4(4)	−0.5(5)
S(2)	3.2(4)	5.1(5)	5.4(6)	−0.1(4)	−0.2(4)	−1.4(5)
S(3)	3.1(4)	4.3(4)	3.6(5)	−0.5(4)	1.1(4)	−1.1(4)
S(4)	3.7(5)	5.0(5)	3.1(5)	0.3(4)	0.0(4)	−0.9(4)

[b] Hydrogen atom positions were calculated and not refined. [c] The form of the anisotropic thermal parameter is:

$$\mathrm{Exp}\ -1/4[(B(1,1)h^2a^{*2} + B(2,2)k^2b^{*2} + B(3,3)l^2c^{*2} + B(1,2)hka^*b^* + B(1,3)hla^*c^* + B(2,3)klb^*c^*)].$$

temperature, data were collected at —35 ± 5°C using an Enraf-Nonius model FR-524H low temperature device. Crystal faces were subsequently identified as $(0\bar{1}1)$, $(01\bar{1})$, (011), $(0\bar{1}\bar{1})$, $(1\bar{2}0)$, $(\bar{1}20)$, (120), and $(\bar{1}\bar{2}0)$. The systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$ unambiguously identified the space group $P2_1/c$, No. 14. 5449 reflections (including absences) were collected in the scan range 2θ = 0—46°. From these, 2607 unique data conforming to the relation $F^2 > 3.0\sigma(F^2)$ were obtained and used in the subsequent solution and refinement of the structure. Three standard reflections monitored periodically during the course of data collection showed a 16% decrease in their original intensity. A linear rescale correction was applied to the data. The linear absorption coefficient for III is 227.3 cm^{-1}. An absorption correction was applied using the Gaussian integration method and a grid of 14 × 8 × 6.

The structure was solved by direct methods using the program MULTAN and phases of 205 reflections for which $E_{\min} > 1.66$. The crystal contains two independent molecules in the asymmetric unit. An E-map based on these data provided the coordinates of the six osmium atoms of the two clusters. All remaining nonhydrogen atoms were obtained by a series of least-squares refinements and difference Fourier syntheses. The dithioformato hydrogen atoms were not located crystallographically. Their positions were calculated using idealized geometry. Their contributions were added to the structure factor calculations but their positions were not refined. The hydride ligands were not observed crystallographically and no attempts to place them artificially were made.

Refinement using anisotropic thermal parameters for the osmium and sulfur atoms and isotropic thermal parameters for the remaining nonhydrogen atoms converted to final residuals R = 0.043 and R_w = 0.045. The e.s.d. in an observation of unit weight was 2.07. On the final cycle the largest parameter shift was 0.34 times its e.s.d. The largest residual peaks in a final Fourier synthesis were 2.2—2.4 $e/\text{Å}^3$ and were clustered about the osmium atoms. They are believed to be structurally insignificant. Final fractional atomic coordinates and thermal parameters are listed in Table 2. Final bond distances and angles with errors obtained from the inverse matrix calculated on the final cycle of least-squares refinement are listed in Tables 3 and 4. A table of final structure factor amplitudes is available.*

$(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$, IV

A thick rectangular plate of dimensions 0.08 × 0.14 × 0.40 mm was mounted in a thin-walled glass capillary. ω-scan peak widths at half-height were in the range 0.10—0.15°. Crystals of this compound also shattered at room temperature, so data were collected at —35 ± 5°C. A triclinic cell containing two molecules was selected. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The crystal faces were identified as (011), $(0\bar{1}\bar{1})$, $(00\bar{1})$, (001), (212) and $(\bar{2}\bar{1}\bar{2})$. 5368 reflections were collected in the scan range 2θ = 0—52°, from which 4282 unique data

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* See NAPS document no. 03678 for 31 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only $ 7.75 for photocopies or $ 3.00 for microfiche. Outside the U.S. and Canada add postage of $ 3.00 for photocopy and $ 1.00 for microfiche.

TABLE 3

INTERATOMIC DISTANCES WITH E.S.D.'S FOR $(\mu\text{—H})(\mu\text{—S}_2\text{CH})\ \text{Os}_3(\text{CO})_{10}$, III

Molecule A		Molecule B	
Atoms	Distance (Å)	Atoms	Distance (Å)
Os(1)—Os(2)	2.978(1)	Os(4)—Os(6)	2.968(1)
Os(1)—Os(3)	2.909(1)	Os(4)—Os(5)	2.918(1)
Os(2)—Os(3)	2.903(1)	Os(5)—Os(6)	2.902(1)
Os(1)—S(1)	2.445(7)	Os(4)—S(3)	2.448(7)
Os(1)—C(1)	1.83(2)	Os(4)—C(11)	1.92(2)
Os(1)—C(2)	1.94(3)	Os(4)—C(12)	1.92(2)
Os(1)—C(3)	1.99(2)	Os(4)—C(13)	1.96(2)
Os(2)—S(2)	2.454(7)	Os(6)—S(4)	2.454(7)
Os(2)—C(4)	1.91(2)	Os(6)—C(18)	1.92(2)
Os(2)—C(5)	1.97(2)	Os(6)—C(19)	1.94(2)
Os(2)—C(6)	1.88(2)	Os(6)—C(20)	1.83(2)
Os(3)—C(7)	1.95(3)	Os(5)—C(14)	1.94(2)
Os(3)—C(8)	1.85(2)	Os(5)—C(15)	1.87(2)
Os(3)—C(9)	1.89(2)	Os(5)—C(16)	1.92(2)
Os(3)—C(10)	1.95(2)	Os(5)—C(17)	1.89(2)
S(1)—C(21)	1.71(3)	S(3)—C(22)	1.64(3)
S(2)—C(21)	1.62(3)	S(4)—C(22)	1.64(3)
C(1)—O(1)	1.24(2)	C(11)—O(11)	1.11(2)
C(2)—O(2)	1.15(3)	C(12)—O(12)	1.13(2)
C(3)—O(3)	1.07(2)	C(13)—O(13)	1.10(2)
C(4)—O(4)	1.17(2)	C(14)—O(14)	1.15(2)
C(5)—O(5)	1.08(2)	C(15)—O(15)	1.18(2)
C(6)—O(6)	1.19(2)	C(16)—O(16)	1.18(2)
C(7)—O(7)	1.18(3)	C(17)—O(17)	1.17(2)
C(8)—O(8)	1.10(2)	C(18)—O(18)	1.14(2)
C(9)—O(9)	1.10(3)	C(19)—O(19)	1.13(2)
C(10)—O(10)	1.15(2)	C(20)—O(20)	1.21(2)

conforming to the relation $F^2 > 3.0\sigma(F^2)$ were used in the structure solution and refinement. Three standard reflections monitored periodically during data collection showed only random fluctuations. The linear absorption coefficient for IV is 147.8 cm^{-1}. An absorption correction was applied using the Gaussian integration method and a grid of $14 \times 8 \times 6$.

The structure was solved by the heavy atom method. The hydrogen atoms were not located crystallographically. All hydrogen atom positions, except the hydride ligand, were calculated assuming idealized geometry with three-fold rotational geometry and staggered conformations for the methyl groups. Contributions from hydrogen atom scattering were added to structure factor calculations but the hydrogen atom positions were not refined. Refinement using anisotropic thermal parameters for the osmium, sulfur, and phosphorus atoms and isotropic thermal parameters for the remaining nonhydrogen atoms converged to values for the residuals of $R = 0.050$ and $R_w = 0.067$. The e.s.d. in an observation of unit weight was 6.78. On the final cycle the largest shift was 0.08 times its e.s.d. The largest residual peaks in a final difference Fourier synthesis were 3.9—4.2 $e/\text{Å}^3$ and were clustered closely around the osmium atoms. They are believed to be structurally insignificant. Final fractional atomic coordinates and thermal parameters are listed in Table 5. Final bond distances and angles with errors obtained from the inverse matrix obtained on

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TABLE 4

BOND ANGLES WITH E.S.D.'S FOR $(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_{10}$, III

Molecule A		Molecule B [a]	
Atoms	Angle (°)	Atoms	Angle (°C)
Os(1)—Os(2)—Os(3)	59.27(3)	Os(4)—Os(6)—Os(5)	59.62(3)
Os(2)—Os(1)—Os(3)	59.08(3)	Os(5)—Os(4)—Os(6)	59.07(3)
Os(1)—Os(3)—Os(2)	61.65(3)	Os(4)—Os(5)—Os(6)	61.31(3)
Os(2)—Os(1)—S(1)	90.5(2)	Os(4)—Os(6)—S(4)	90.7(2)
Os(2)—Os(1)—C(1)	144.3(8)	Os(4)—Os(6)—C(19)	142.8(6)
Os(2)—Os(1)—C(2)	118.4(6)	Os(4)—Os(6)—C(20)	115.8(7)
Os(2)—Os(1)—C(3)	91.0(6)	Os(4)—Os(6)—C(18)	91.6(6)
Os(3)—Os(1)—S(1)	94.9(2)	Os(5)—Os(6)—S(4)	95.9(2)
Os(3)—Os(1)—C(1)	85.4(8)	Os(5)—Os(6)—C(19)	83.7(6)
Os(3)—Os(1)—C(2)	177.4(6)	Os(5)—Os(6)—C(20)	174.4(7)
Os(3)—Os(1)—C(3)	89.5(6)	Os(5)—Os(6)—C(18)	89.4(6)
S(1)—Os(1)—C(1)	89.1(8)	S(4)—Os(6)—C(19)	87.5(7)
S(1)—Os(1)—C(2)	85.5(7)	S(4)—Os(6)—C(20)	87.1(7)
S(1)—Os(1)—C(3)	175.5(6)	S(4)—Os(6)—C(18)	174.7(6)
C(1)—Os(1)—C(2)	97.2(10)	C(19)—Os(6)—C(20)	101.2(9)
C(1)—Os(1)—C(3)	92.2(9)	C(19)—Os(6)—C(18)	93.6(9)
C(2)—Os(1)—C(3)	90.0(9)	C(20)—Os(6)—C(18)	87.6(9)
Os(1)—Os(2)—S(2)	90.9(2)	Os(6)—Os(4)—S(3)	90.8(2)
Os(1)—Os(2)—C(4)	146.0(6)	Os(6)—Os(4)—C(11)	148.2(7)
Os(1)—Os(2)—C(5)	92.0(6)	Os(6)—Os(4)—C(13)	91.3(7)
Os(1)—Os(2)—C(6)	116.3(7)	Os(6)—Os(4)—C(12)	115.7(6)
Os(3)—Os(2)—S(2)	93.9(2)	Os(5)—Os(4)—S(3)	94.3(2)
Os(3)—Os(2)—C(4)	86.9(6)	Os(5)—Os(4)—C(11)	89.4(7)
Os(3)—Os(2)—C(5)	90.5(6)	Os(5)—Os(4)—C(13)	89.4(7)
Os(3)—Os(2)—C(6)	175.5(7)	Os(5)—Os(4)—C(12)	174.7(6)
S(2)—Os(2)—C(4)	87.7(6)	S(3)—Os(4)—C(11)	86.7(7)
S(2)—Os(2)—C(5)	175.5(6)	S(3)—Os(4)—C(13)	176.3(7)
S(2)—Os(2)—C(6)	85.7(7)	S(3)—Os(4)—C(12)	86.5(6)
C(4)—Os(2)—C(5)	91.8(8)	C(11)—Os(4)—C(13)	93.1(10)
C(4)—Os(2)—C(6)	97.6(9)	C(11)—Os(4)—C(12)	95.8(9)
C(5)—Os(2)—C(6)	89.9(9)	C(13)—Os(4)—C(12)	89.8(9)
Os(1)—Os(3)—C(7)	90.1(7)	Os(6)—Os(5)—C(14)	88.1(7)
Os(1)—Os(3)—C(8)	99.4(8)	Os(6)—Os(5)—C(17)	102.9(7)
Os(1)—Os(3)—C(9)	160.2(7)	Os(6)—Os(5)—C(15)	157.7(7)
Os(1)—Os(3)—C(10)	90.7(6)	Os(6)—Os(5)—C(16)	88.8(6)
Os(2)—Os(3)—C(7)	89.0(7)	Os(4)—Os(5)—C(14)	93.6(7)
Os(2)—Os(3)—C(8)	161.0(8)	Os(4)—Os(5)—C(17)	164.2(7)
Os(2)—Os(3)—C(9)	98.6(7)	Os(4)—Os(5)—C(15)	96.4(7)
Os(2)—Os(3)—C(10)	89.7(6)	Os(4)—Os(5)—C(16)	89.2(6)
C(7)—Os(3)—C(8)	90.5(10)	C(14)—Os(5)—C(17)	85.9(9)
C(7)—Os(3)—C(9)	88.1(10)	C(14)—Os(5)—C(15)	92.7(9)
C(7)—Os(3)—C(10)	178.0(9)	C(14)—Os(5)—C(16)	174.3(10)
C(8)—Os(3)—C(9)	100.4(10)	C(17)—Os(5)—C(15)	99.4(10)
C(8)—Os(3)—C(10)	91.3(9)	C(17)—Os(5)—C(16)	90.1(9)
C(9)—Os(3)—C(10)	90.6(9)	C(16)—Os(5)—C(15)	92.0(9)
Os(1)—S(1)—C(21)	112.8(9)	Os(6)—S(4)—C(22)	111.5(9)
Os(2)—S(2)—C(21)	113.2(10)	Os(4)—S(3)—C(22)	111.8(10)
S(1)—C(21)—S(2)	132.0(16)	S(3)—C(22)—S(4)	131.1(17)
Os(1)—C(1)—O(1)	173(2)	Os(6)—C(19)—O(19)	177(2)
Os(1)—C(2)—O(2)	178(2)	Os(6)—C(20)—O(20)	174(2)
Os(1)—C(3)—O(3)	176(2)	Os(6)—C(18)—O(18)	174(2)
Os(2)—C(4)—O(4)	179(2)	Os(4)—C(11)—O(11)	176(2)
Os(2)—C(5)—O(5)	177(2)	Os(4)—C(13)—O(13)	178(2)
Os(2)—C(6)—O(6)	178(2)	Os(4)—C(12)—O(12)	175(2)
Os(3)—C(7)—O(7)	169(2)	Os(5)—C(14)—O(14)	172(2)
Os(3)—C(8)—O(8)	178(2)	Os(5)—C(17)—O(17)	176(2)
Os(3)—C(9)—O(9)	176(2)	Os(5)—C(15)—O(15)	174(2)
Os(3)—C(10)—O(10)	173(2)	Os(5)—C(16)—O(16)	172(2)

[a] The listing of angles for molecule B has been arranged so that they are directly comparable to the corresponding angles for molecule A.

TABLE 5

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$, IV

Atom	*x/a*	*y/b*	*z/c*	*B*	Atom	*x/a*	*y/b*	*z/c*	*B*
Os(1)	0,01170(8)	0.17454(5)	0,11896(5)	[a]	C(9)	—0,114(2)	0,431(1)	0,161(1)	2,8(3)
Os(2)	—0,28811(8)	0,05938(5)	0,24989(5)	[a]	C(17)	—0,691(3)	0,369(2)	0,267(2)	4.1(5)
Os(3)	—0,25199(8)	0,30255(5)	0,21880(5)	[a]	C(18)	—0,570(3)	0,314(2)	0,438(1)	3,9(4)
S(1)	0,1461(6)	0,0930(4)	0,2580(3)	[a]	C(11)	—0,502(2)	0,532(1)	0,268(1)	2,2(3)
S(2)	—0,1773(6)	—0,0272(4)	0,3969(3)	[a]	C(12)	—0,567(2)	0,616(2)	0,193(1)	3,1(4)
P	—0,5060(6)	0,3814(4)	0,2993(4)	[a]	C(13)	—0,562(3)	0,731(2)	0,169(2)	4,5(5)
O(1)	0,264(2)	0,369(1)	0,0189(10)	4,0(3)	C(14)	—0,485(3)	0,766(2)	0,221(3)	4.7(5)
O(2)	0,256(2)	0,009(1)	0,0335(11)	5,2(4)	C(15)	—0,426(3)	0,685(2)	0,296(2)	5,9(6)
O(3)	—0,121(2)	0,265(1)	—0,0656(9)	3,4(3)	C(16)	—0,433(3)	0,566(2)	0,320(2)	4,2(5)
O(4)	—0,091(2)	—0,123(1)	0,1787(11)	4,8(3)	C(10)	0,023(2)	0,005(1)	0,367(1)	2,6(3)
O(5)	—0,467(2)	0,148(1)	0,0823(9)	3,5(3)	H(1) [b]	0,076	—0,034	0,420	4,0
O(6)	—0,598(2)	—0,078(1)	0,4033(9)	3,6(3)	H(12)	—0,615	0,594	0,154	4.0
O(7)	—0,122(2)	0,226(1)	0,4068(10)	3,8(3)	H(13)	—0,612	0,788	0,117	4,0
O(8)	—0,377(2)	0,399(1)	0,0262(9)	3,4(3)	H(14)	—0,476	0,845	0,204	4,0
O(9)	—0,034(2)	0,509(1)	0,1288(11)	4,6(3)	H(15)	—0,374	0,708	0,333	4,0
C(1)	0,174(2)	0,295(1)	0,057(1)	3,1(4)	H(16)	—0,386	0,510	0,374	4,0
C(2)	0,149(3)	0,072(2)	0,069(2)	4,0(4)	H(171)	—0,674	0,397	0,199	4,0
C(3)	—0,073(2)	0,231(1)	0,005(1)	2,5(3)	H(172)	—0,713	0,286	0,298	4,0
C(4)	—0,168(3)	—0,051(2)	0,204(1)	3,4(4)	H(173)	—0,788	0,403	0,302	4,0
C(5)	—0,394(2)	0,116(1)	0,143(1)	2,6(3)	H(181)	—0,482	0,316	0,463	4,0
C(6)	—0,486(2)	—0,022(1)	0,347(1)	2,4(3)	H(182)	—0,670	0,353	0,465	4,0
C(7)	—0,168(2)	0,248(1)	0,337(1)	2,8(4)	H(183)	—0,595	0,236	0,460	4,0
C(8)	—0,331(2)	0,361(1)	0,098(1)	2,4(3)					

[a] Final anisotropic thermal parameters are: [c]

	B(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Os(1)	1,58(2)	1,92(2)	1,98(2)	—0,14(2)	—0,43(2)	—0,26(2)
Os(2)	1,75(2)	1,65(2)	2,14(2)	—0,026(2)	—0,59(2)	—0,30(2)
Os(3)	1,80(2)	1,60(2)	2,11(2)	—0,07(2)	—0,68(2)	—0,37(2)
S(1)	2,0(2)	4,0(2)	2,5(2)	—0,3(2)	—1,0(1)	0,0(2)
S(2)	2,5(2)	2,8(2)	2,4(2)	—0,4(1)	—1,1(1)	0,1(1)
P	2,3(2)	1,9(2)	2,9(2)	0,0(1)	—0,5(1)	—0,8(1)

[b] All hydrogen atom positions were calculated and were not refined. [c] The form of the anisotropic thermal parameter is:

$$\text{Exp} -1/4[(B(1,1)h^2a^{*2} + B(2,2)k^2b^{*2} + B(3,3)l^2c^{*2} + B(1,2)hka^*b^* + B(1,3)hla^*c^* + B(2,3)klb^*c^*)].$$

TABLE 6

INTERATOMIC DISTANCES WITH E.S.D.'S FOR $(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_9]\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$, IV

Atoms	Distance (Å)	Atoms	Distance (Å)
Os(1)—Os(2)	2.854(1)	P—C(17)	1.827(9)
Os(1)—Os(3)	2.928(1)	P—C(18)	1.807(8)
Os(2)—Os(3)	3.043(1)	P—C(11)	1.803(7)
Os(1)—S(1)	2.424(2)	C(11)—C(12)	1.41(1)
Os(1)—C(1)	1.922(8)	C(12)—C(13)	1.41(1)
Os(1)—C(2)	1.817(9)	C(13)—C(14)	1.42(1)
Os(1)—C(3)	1.909(7)	C(14)—C(15)	1.37(1)
Os(2)—S(2)	2.442(2)	C(15)—C(16)	1.44(1)
Os(2)—C(4)	1.838(9)	C(16)—C(11)	1.37(1)
Os(2)—C(5)	1.893(7)	C(1)—O(1)	1.15(1)
Os(2)—C(6)	1.919(7)	C(2)—O(2)	1.23(1)
Os(3)—P	2.356(2)	C(3)—O(3)	1.15(1)
Os(3)—C(7)	1.943(8)	C(4)—O(4)	1.15(1)
Os(3)—C(8)	1.944(7)	C(5)—O(5)	1.16(1)
Os(3)—C(9)	1.909(7)	C(6)—O(6)	1.15(1)
S(1)—C(10)	1.661(7)	C(7)—O(7)	1.15(1)
S(2)—C(10)	1.666(7)	C(8)—O(8)	1.15(1)
		C(9)—O(9)	1.15(1)

TABLE 7

INTERATOMIC ANGLES WITH E.S.D.'S FOR $(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$, IV

Atoms	Angle (°)	Atoms	Angle (°)
Os(3)—Os(1)—(Os(2)	63.48(1)	Os(2)—Os(3)—P	112.35(4)
Os(1)—Os(2)—Os(3)	59.43(1)	Os(2)—Os(3)—C(7)	91.9(2)
Os(1)—Os(3)—Os(2)	57.08(1)	Os(2)—Os(3)—C(8)	89.6(2)
Os(2)—Os(1)—S(1)	91.60(4)	Os(2)—Os(3)—C(9)	148.9(2)
Os(2)—Os(1)—C(1)	156.5(2)	P—Os(3)—C(7)	92.6(2)
Os(2)—Os(1)—C(2)	103.8(3)	P—Os(3)—C(8)	88.0(2)
Os(2)—Os(1)—C(3)	89.6(2)	P—Os(3)—C(9)	98.7(2)
Os(3)—Os(1)—S(1)	93.83(5)	C(7)—Os(3)—C(8)	178.1(3)
Os(3)—Os(1)—C(1)	93.2(2)	C(7)—Os(3)—C(9)	87.3(3)
Os(3)—Os(1)—C(2)	167.3(3)	C(8)—Os(3)—C(9)	90.8(3)
Os(3)—Os(1)—C(3)	90.3(2)	Os(1)—S(1)—C(10)	113.7(3)
S(1)—Os(1)—C(1)	86.7(2)	Os(2)—S(2)—C(10)	112.4(3)
S(1)—Os(1)—C(2)	87.7(3)	S(1)—C(10)—S(2)	129.9(4)
S(1)—Os(1)—C(3)	175.8(2)	Os(3)—P—C(17)	113.5(3)
C(1)—Os(1)—C(2)	99.5(4)	Os(3)—P—C(18)	114.5(3)
C(1)—Os(1)—C(3)	93.7(3)	Os(3)—P—C(11)	114.3(2)
C(2)—Os(1)—C(3)	88.1(4)	C(17)—P—C(18)	103.4(4)
Os(1)—Os(2)—S(2)	92.16(4)	C(17)—P—C(11)	104.7(4)
Os(1)—Os(2)—C(4)	80.2(2)	C(18)—P—C(11)	105.3(4)
Os(1)—Os(2)—C(5)	94.1(2)	P—C(11)—C(12)	121.3(6)
Os(1)—Os(2)—C(6)	174.8(2)	P—C(11)—C(16)	119.8(6)
Os(3)—Os(2)—S(2)	93.51(5)	C(12)—C(11)—C(16)	117.5(7)
Os(3)—Os(2)—C(4)	139.6(2)	C(11)—C(12)—C(13)	122.8(8)
Os(3)—Os(2)—C(5)	90.5(2)	C(12)—C(13)—C(14)	120.0(8)
Os(3)—Os(2)—C(6)	119.9(2)	C(13)—C(14)—C(15)	118.2(9)
S(2)—Os(2)—C(4)	89.3(2)	C(14)—C(15)—C(16)	120.8(10)
S(2)—Os(2)—C(5)	173.7(2)	C(15)—C(16)—C(11)	121.2(8)
S(2)—Os(2)—C(6)	82.7(2)	Os(1)—C(1)—O(1)	177.9(7)
C(4)—Os(2)—C(5)	90.8(3)	Os(1)—C(2)—O(2)	171.9(8)
C(4)—Os(2)—C(6)	100.5(3)	Os(1)—C(3)—O(3)	177.1(7)
C(5)—Os(2)—C(6)	91.0(3)	Os(2)—C(4)—O(4)	177.4(7)
Os(1)—Os(3)—P	168.33(5)	Os(2)—C(5)—O(5)	176.7(6)
Os(1)—Os(3)—C(7)	92.7(2)	Os(2)—C(6)—O(6)	174.2(6)
Os(1)—Os(3)—C(8)	87.1(2)	Os(3)—C(7)—O(7)	173.8(7)
Os(1)—Os(3)—C(9)	91.9(2)	Os(3)—C(8)—O(8)	177.5(6)
		Os(3)—C(9)—O(9)	177.3(7)

the final cycle of refinement are listed in Tables 6 and 7. A table of final structure factor amplitudes is available *.

Results

Structural analysis of (μ-H)(μ-S_2CH)$Os_3(CO)_{10}$, III

The crystal structure of (μ-H)(μ-S_2CH)$Os_3(CO)_{10}$ contains two crystallographically independent molecules in the asymmetric unit. Figures 1 and 2 show ORTEP diagrams of these molecules [17]. Both molecules have the same basic structural arrangement. This includes a triangular cluster of three osmium atoms, a bridging dithioformato ligand, a bridging hydride ligand and ten linear terminal carbonyl ligands. Bond distances and angles are listed in Tables 3 and 4.

Each cluster forms an isosceles triangle of osmium atoms with one relatively long and two shorter and roughly equivalent osmium—osmium bonds. The shorter bonds range from 2.902—2.918 Å, averaging 2.908(1). This average is slightly longer than the average osmium—osmium bond distances of 2.877(3) Å and 2.897(10) Å found in $Os_3(CO)_{12}$ [18] and $Os_3(CO)_{11}[P(OCH_3)_3]$, [19] respectively. The longer bonds are Os(1)—Os(2) = 2.978(1) Å and Os(4)—Os(6) = 2.968(1) Å, averaging 2.973(1) Å.

We are unaware of any other structural characterizations of the dithioformato ligand in a cluster complex. Here we find that the dithioformato ligand bridges an edge of the cluster in each molecule. The sulfur atoms occupy coordination sites perpendicular to the planes of the Os_3 triangles in what could be called a "diaxial" coordination. The Os—S bond distances average 2.450(7) Å. The carbon—sulfur distances range from 1.62 to 1.71 Å, but the average, 1.65(3) Å, is quite similar to that found for chelating dithioformato ligands in the mononuclear metal complexes $Ru(S_2CH)_2[P(C_6H_5)_3]_2$, C—S, 1.64—1.68 Å, [20] and $Re(S_2CH)(CO)_2[P(C_6H_5)_3]_2$, C—S, 1.64(2) and 1.68(1) Å, [21]. However, the S—C—S angles at 132.0(16)° and 131.1(17)° are significantly larger than those of 115.3(11)° and 113.9(8)° found in the mononuclear ruthenium complex [20] and that of 116.7(1)° found in the mononuclear rhenium complex [21]. This opening of the S—C—S angle in the cluster complex could be due to a decrease in strain relative to the four membered ring which exists when both sulfur atoms are bonded to a single metal atom.

There are ten linear terminal carbonyl groups in each cluster with each unique osmium atom having four carbonyl ligands. The coordination geometry about the osmium atoms is roughly octahedral. Overall, six carbonyl ligands lie in the plane of each Os_3 triangle while the remaining four are essentially perpendicular to it.

The hydride ligand ** was not observed crystallographically, but a significant distortion in the distribution of carbonyl ligands in the equatorial plane of the cluster strongly suggests its true location. For example, the bond angles

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[*] See footnote on p. 228.

[**] The presence of bridging metal hydrides and dithioformate hydrogens in III and IV is supported by their ^1H NMR spectra. For III ($CDCl_3$): δ(OsH) = —14.925s, δ(HCS_2) = 12.15s ppm; for IV ($CDCl_3$): δ(OsH) = —16.07d (J(PH) = 12.21 Hz), δ(HCS_2) = 13.17s ppm. The phosphorus—hydrogen coupling observed in IV suggests that the phosphine and hydride ligands are on the same osmium atom.

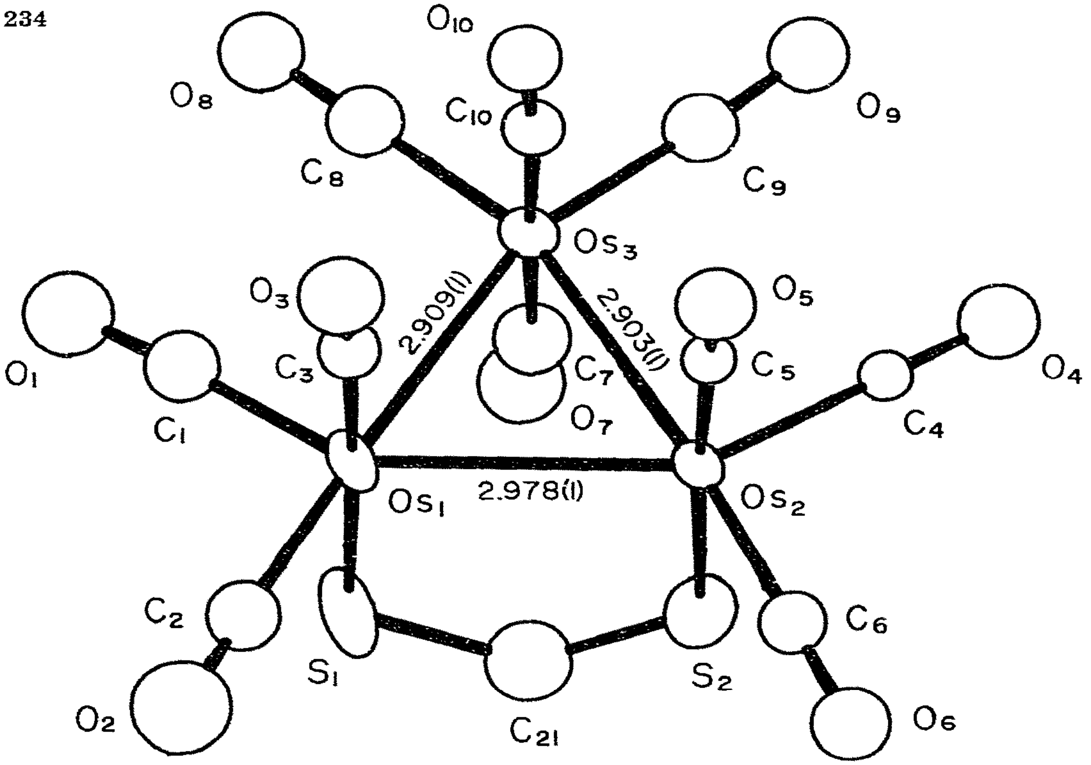


Fig. 1. An ORTEP diagram of one of the two independent molecules of (μ-H)(μ-S_2CH)$Os_3(CO)_{10}$ in the asymmetric crystal unit. Shown with 50% probability ellipsoids.

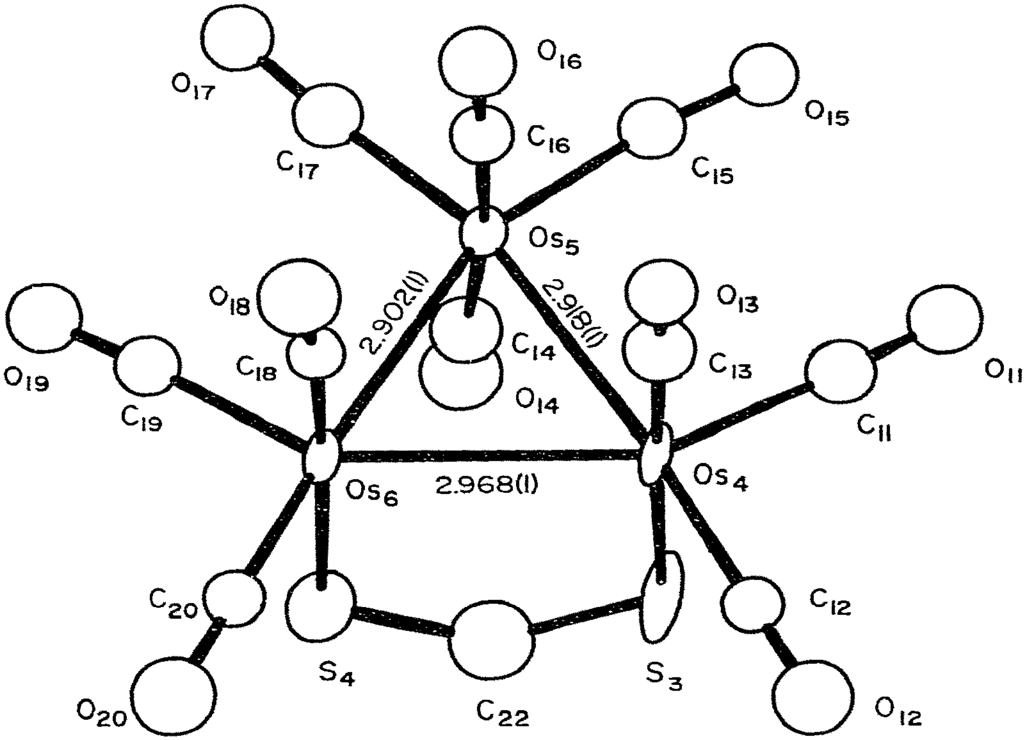


Fig. 2. An ORTEP diagram of the second molecule of (μ-H)(μ-S_2CH)$Os_3(CO)_{10}$ in the asymmetric crystal unit. Shown with 50% probability ellipsoids.

Os(2)—Os(1)—C(2) and Os(1)—Os(2)—C(6) at 118.4(6) and 116.3(7), respectively, are much larger than the analogous angles Os(3)—Os(1)—C(1) and Os(3)—Os(2)—C(4) angles of 85.4(8)° and 86.9(6)°. We attribute this effect to the presence of a bridging hydride ligand which is symmetrically bonded to Os(1) and Os(2) and lies essentially in the equatorial plane of the cluster. A similar distortion was found in the other, symmetry independent molecule in this crystal. Similar distortions have been observed in numerous other cluster complexes containing hydride ligands and these have generally been used as a means of assigning the location of "unobserved" hydride ligands in X-ray crystallographic studies [10]. That this effect is not due to some intrinsic property of the dithioformato ligand is confirmed by the absence of such a distortion at that site in the corresponding complex ($(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$), IV (vide infra).

In the crystal there were no unusually short intermolecular contacts. The shortest contacts were between carbonyl oxygen atoms and were in the range 2.88—2.97 Å.

Structural analysis of $(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$, IV

An ORTEP diagram of the molecular structure of IV is shown in Figure 3

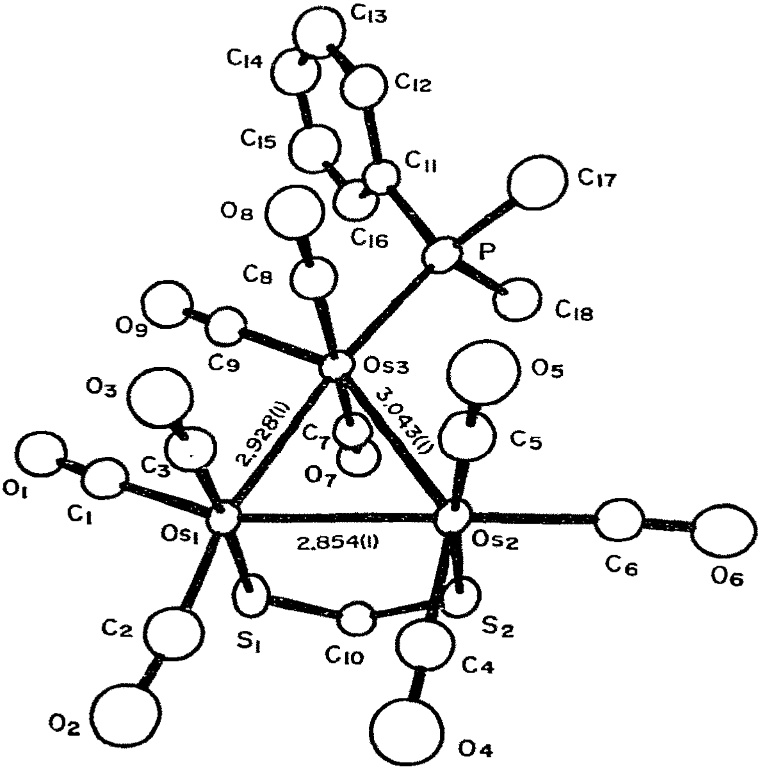


Fig. 3. An ORTEP diagram of $(\mu\text{-H})(\mu\text{-S}_2\text{CH})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ shown with 50% probability ellipsoids.

[17]. Bond distances and angles are listed in Tables 6 and 7.

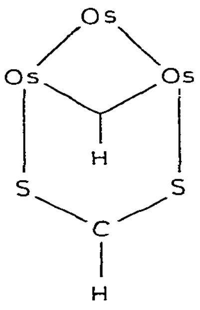
The triangular cluster of three metal atoms contains three significantly different metal—metal separations. The dithioformato ligand bridges the Os(1)—Os(2) bond in a diaxial coordination position. However, unlike III where this metal—metal separation was substantially longer than the others (e.g. 2.973(1) Å), in IV it is substantially shorter, being only 2.854(1) Å. The Os(1)—Os(3) bond is of intermediate length at 2.928(1) Å, which is slightly longer than the corresponding distances in III. This increase could be attributed to the substitution of the phosphine ligand for a carbonyl ligand. A similar increase in the metal—metal bond distances was observed when a trimethylphosphite ligand was substituted for a carbonyl ligand in $Os_3(CO)_{12}$ [19]. The Os(2)—Os(3) bond distance is 3.043(1) Å, substantially longer than the metal—metal bonds found in $Os_3(CO)_{12}$, 2.877(3) Å, [18], $Os_3(CO)_{11}[P(OCH_3)_3]$, 2.897(10) Å [19] and all unbridged metal—metal bonds reported here.

The dithioformato ligand is structurally similar to those found in III. The carbon—sulfur bond distances are 1.661(7) and 1.666(7) Å, and the S—C—S angle is 129.9(4)°. A normal dimethylphenylphosphine ligand is bonded to atom Os(3) in an equatorial coordination site essentially *trans* to the Os(1)—Os(3) bond. The Os(3)—P distance at 2.356(2) Å is similar to that found in other osmium cluster complexes [14]. Nine linear terminal carbonyl ligands are arranged such that each osmium atom contains three. Overall, five lie in the plane of the Os_3 triangle while four are essentially perpendicular to it. The hydride ligand was not observed crystallographically, but we feel its location can be safely inferred from obvious distortions in the molecular structure. We believe the hydride ligand bridges Os(2) and Os(3) in this molecule. The two features which support this are: 1) the long Os(2)—Os(3) separation and 2) the large bond angles Os(3)—Os(2)—C(6) = 119.9(2)° and Os(2)—Os(3)—P = 112.35(4)°. This structural feature of IV contrasts markedly with that of III where the large bond angles were observed along the Os—H—Os bond bridged by the dithioformato ligand.

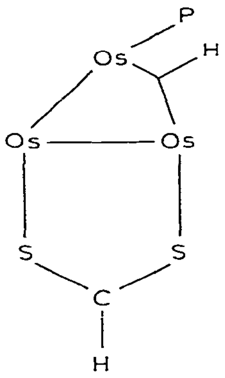
In the crystal there were no unusually short intermolecular contacts. The shortest distances were between carbonyl oxygen atoms and were in the range 2.98—3.00 Å.

Discussion

The gross molecular structures of III and IV are very similar. The principal difference is the relative position of the bridging hydride ligand. In III the



(III)



(IV)

Os—H—Os bond contains the bridging dithioformato ligand while in IV it does not.

The exact reason why the hydride changes position in the different clusters is not clear at this time. However, the bonding of bridging hydride ligands is of a 3-center-2-electron type similar to that of the "electron deficient" boron hydride compounds [1]. Thus, the hydride ligand may prefer to be near a center of higher electron density. The relatively high electron donor ability of the phosphine ligand may serve this purpose. The scope of this phenomenon remains to be seen, but it may be possible to use phosphine ligands to direct a hydride ligand to a specific stereochemical location in a cluster compound.

Because the hydride ligands bridge different edges of the central Os_3 triangle in these clusters, we may by comparison be able to examine the influence of the hydride ligand on the metal—metal interaction. For example, as expected, placement of a hydride ligand along one of the unsupported metal—metal bonds in IV leads to a substantial increase in the length of that bond (e.g., the Os(2)—Os(3) separation is 0.115 Å longer than the Os(1)—Os(3) distance in IV and 0.134 Å longer than the corresponding unbridged bonds in III). Comparison of the dithioformato bridged bonds of III and IV allows a direct assessment of the effect of a bridging hydride ligand on the supported metal—metal bond. In the absence of the hydride ligand, the Os(1)—Os(2) separation in IV is 2.854 Å, whereas in its presence the corresponding separation in III is 2.973(1) Å, an increase of 0.12 Å. This increase is similar to that found when hydrides are added to unsupported metal—metal bonds in clusters. It is also very similar to that observed by Peterson et al. for the $(C_5H_5)_2Mo_2(CO)_4(\mu\text{-}H)[\mu\text{-}P(CH_3)_2]$/ $[(C_5H_5)_2Mo_2(CO)_4\{\mu\text{-}P(CH_3)_2\}]^-$ system [11,12].

The accumulation of results suggests that the addition of a hydride ligand to a metal—metal bond causes the bond length to increase regardless of whether the bond is supported, II, or unsupported, I. Nevertheless, Churchill [9] has reported several examples where supported metal—metal bonds containing hydride ligands are shorter than "normal" metal—metal bonds. We believe a structural analysis if one of these bonds in the absence of a bridging hydride ligand would be most valuable.

Inspection of the osmium—sulfur bond distances suggests that the hydride ligand can also produce a lengthening effect, albeit a much smaller one, on bonds *cis* to it. For example, the osmium—sulfur bonds in III are *cis* to the hydride bridged osmium—osmium bond. The four independent osmium—sulfur bond distances in III range from 2.445—2.454 Å, with the average 2.450(7) Å. In IV, the Os(2)—S(2) bond is *cis* to the hydride bridged metal—metal bond, and the distance is 2.442(2) Å. This is 0.018 Å longer than the Os(1)—S(1) bond (2.424(2) Å) which is not adjacent to the hydride bridged metal—metal bond. Admittedly, the lengthening effect is small and it is desirable to have more examples to confirm it, but this evidence suggests there may be a real effect. Due to the much larger errors in the osmium—carbon bond distances, no systematic influences of the bridging hydride ligand on other bonds could be detected. A large structural *trans* effect of hydride ligands has been thoroughly demonstrated in mononuclear transition metal hydride complexes [22]. These cluster compounds may be providing us with the first opportunity to document a much smaller but significant structural *cis* effect. Of course the *cis* effect of a bridging hydride ligand should be significantly different from a *cis* effect in a mononuclear complex where the hydride ligand would occupy one full coordination site.

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