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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 13.[1,2] Molecular Geometry of μ-Bromo-μ-hydrido-decacarbonyltriosmium, $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$, and a Comparison of $Os(\mu\text{-H})(\mu\text{-X})Os$ Bridges

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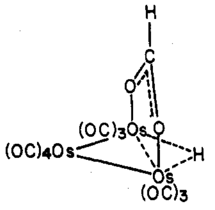
The structure of $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$ has been elucidated by means of a single-crystal X-ray diffraction study. This complex crystallizes in the centrosymetric triclinic space group $P\bar{1}$ [C_i^1; No. 2] with a = 8.5736 (14) Å, b = 14.0277 (22) Å, c = 14.8818 (30) Å, α = 95.606 (15)°, β = 92.801 (15)°, γ = 98.347 (13)°, V = 1758.8 (5) Å^3, and ρ(calcd) = 3.518 g cm^{-3} for mol wt 931.62 and Z = 4. Diffraction data were collected with a Syntex P2$_1$ automated diffractometer using Mo Kα radiation and a coupled θ(crystal)–2θ(counter) scan technique. The structure was solved by conventional techniques and refined to R_F = 5.5% and R_{wF} = 4.4% for all 4614 independent data with $3.5° < 2\theta < 45°$ (R_F = 4.3% and R_{wF} = 4.2% for those 3976 data with $I > 3\sigma(I)$). The crystallographic asymmetric unit consists of two independent molecules of $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$. These molecules contain a triangular arrangement of osmium atoms; for each molecule Os(1) and Os(2) are each associated with three carbonyl ligands, while Os(3) is linked to four such ligands. In molecule A, Os(1) and Os(2) are clearly seen to be bridged by a μ-bromide and a μ-hydride ligand. Osmium–osmium distances in this molecule are Os(1A)–Os(3A) = 2.842 (1), Os(2A)–Os(3A) = 2.844 (1), and Os(1A)–Os(2A) = 2.851 (1) Å. Molecule B appears to suffer from a slight disorder problem, wherein the μ-bromide ligand occupies both possible sites above and below the triosmium plane with relative occupancies of 0.917 (4):0.083 (4). Interatomic parameters for this molecule, while consistent with those for molecule A, are regarded as less reliable.

Introduction

Extensive studies on triangular metal carbonyl cluster complexes (and more condensed cluster systems) have led to the following stereochemical principles:[3-5] (i) a single unsupported equatorial μ-hydride ligand causes the bridged metal–metal distance to be greater than the normal nonbridged metal–metal distance; (ii) M–M–L angles for ligands (L) adjacent to (and in the same plane as) the M–H–M system are abnormally large.

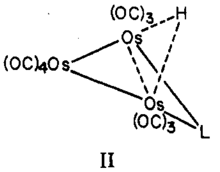
The mean osmium–osmium distance in the trinuclear parent carbonyl, $Os_3(CO)_{12}$, is 2.877 (3) Å.[6] Equatorially μ-hydrido bridged osmium–osmium distances in triangular clusters are 2.989 (1) Å in $(\mu\text{-H})(H)Os_3(CO)_{11}$,[6] 3.019 (1) Å in $(\mu\text{-H})(H)Os_3(CO)_{10}(PPh_3)$,[7] and 3.059 (3)–3.084 (3) Å in $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$.[8]

We have noted previously[4] that, when a μ-hydride ligand is accompanied by another ligand, the resulting dibridged metal–metal distance may be shorter than, longer than, or equivalent to a normal nonbridged metal–metal bond length. An example of the contraction (from its normal value) of an equatorially hydrido-bridged Os–Os distance by a strictly diaxially bridging group occurs in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-O}_2CH)$[9] (I). [Os–(H)–Os = 2.901 (1) and 2.916 (1) Å in two crystallographically independent molecules.]



I

The situation in species with two bridging ligands (one of which is hydride) in the intermediate geometry shown in II



II

is rather less easy to understand but clearly should depend upon the nature of the bridgehead atom (or atoms) on L. Species of this type, which have already been characterized, include those with an $Os(\mu\text{-H})_2Os$ system [Os–Os = 2.681 (1) Å (X-ray diffraction),[10,11] 2.680 (2) Å (combined X-ray/neutron diffraction),[12] and 2.683 (1) Å (neutron diffraction)[13] for $[(\mu\text{-H})_2Os_3(CO)_{10}]$, those with an $Os(\mu\text{-H})(\mu\text{-C})Os$ system [Os–Os = 2.800 (1) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH}_2PMe_2Ph)$,[14] 2.785 (2) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH=NEt}_2)$,[1] and 2.824 (3) Å in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$[15]], and those with an $Os(\mu\text{-H})(\mu\text{-S})Os$ system [Os–Os = 2.863 (2) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SEt})$,[16] 2.867 (1) and

Table I. Data for the X-ray Diffraction Study of $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$

A. Crystal Data

cryst system: triclinic	γ = 98.347 (13)°
space group: $P\bar{1}$ [C_i^1; No. 2]	V = 1758.8 (5) Å^3
a = 8.5736 (14) Å^a	temp 24 °C
b = 14.0277 (22) Å^a	Z = 4
c = 14.8818 (30) Å^a	mol wt 931.62
α = 95.606 (15)°	ρ(calcd) = 3.518 g cm^{-3}
β = 92.801 (15)°	

B. Intensity Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite
reflctns measd: $+h, \pm k, \pm l$
max 2θ: 45.0°
min 2θ: 3.5°
scan type: θ(crystl)–2θ(counter)
scan speed: 2.0°/min
scan range: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]$°
reflctns collected: 4797 total; 4615 independent
std reflctns: $0,\overline{10},0$, $0,\bar{1},\overline{10}$, and $6\bar{1}0$ reflctns measd after every 97 reflctns, their intensities decreasing steadily by 4.8% (av) over the course of data collection
abs coeff: μ = 239.56 cm^{-1}
reflctns used for empirical absorption correction^b (hkl, 2θ, T_{max}/T_{min}): 052, 16.32, 1.48; 154, 20.70, 1.26; 074, 24.57, 1.30; 175, 27.40, 1.21
data averaging: $R(I)$ = 1.92% for 14 reflctns with two or more contributions

^{a} Based upon a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 14 reflections of the forms $\{5,4,\bar{4}\}$, $\{4,4,4\}$, $\{4,\bar{6},3\}$, $\{3,5,\bar{7}\}$, $\{1,9,\bar{5}\}$, $\{1,\bar{9},1\}$, and $\{0,6,\bar{9}\}$, all with 2θ = 25–30°. ^{b} For details of the experimental absorption correction, see: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

0020-1669/79/1318-3261$01.00/0

Table II. Final Positional Parameters for $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$

atom	x	y	z	B, Å^2
Os(1A)	0.29220 (8)	0.65134 (5)	0.09214 (5)	
Os(2A)	0.54265 (8)	0.68912 (5)	0.23002 (5)	
Os(3A)	0.54484 (8)	0.80488 (5)	0.08339 (5)	
Os(1B)	0.08446 (8)	0.10788 (5)	0.31420 (5)	
Os(2B)	−0.10124 (8)	0.20827 (5)	0.43664 (5)	
Os(3B)	0.12492 (9)	0.31310 (5)	0.33596 (5)	
Br(A)	0.25864 (21)	0.72156 (14)	0.25648 (13)	
Br(B1)	−0.21454 (20)	0.10953 (13)	0.28591 (12)	
Br(B2)	0.0541 (27)	0.0825 (17)	0.4697 (16)	3.6 (5)
O(11A)	0.0495 (16)	0.4742 (10)	0.1153 (10)	
O(12A)	0.0664 (18)	0.7709 (10)	0.0097 (12)	
O(13A)	0.3611 (17)	0.5606 (10)	−0.0883 (9)	
O(21A)	0.5121 (21)	0.5349 (12)	0.3621 (11)	
O(22A)	0.6844 (18)	0.8605 (10)	0.3650 (10)	
O(23A)	0.8660 (17)	0.6440 (13)	0.1781 (11)	
O(31A)	0.4394 (23)	0.8803 (14)	−0.0898 (12)	
O(32A)	0.8608 (18)	0.9388 (13)	0.1143 (12)	
O(33A)	0.7099 (16)	0.6495 (12)	−0.0150 (10)	
O(34A)	0.3768 (20)	0.9438 (11)	0.2029 (13)	
O(11B)	0.0218 (16)	−0.1121 (9)	0.3064 (12)	
O(12B)	0.1614 (19)	0.1149 (12)	0.1186 (10)	
O(13B)	0.4314 (17)	0.1208 (14)	0.3739 (13)	
O(21B)	−0.3319 (19)	0.0763 (14)	0.5400 (11)	
O(22B)	−0.3049 (21)	0.3687 (13)	0.4202 (15)	
O(23B)	0.0778 (16)	0.3082 (11)	0.6079 (9)	
O(31B)	0.3894 (23)	0.3475 (17)	0.2078 (11)	
O(32B)	0.0926 (30)	0.5213 (13)	0.4032 (15)	
O(33B)	0.3639 (17)	0.3006 (12)	0.4900 (10)	
O(34B)	−0.1407 (20)	0.3058 (13)	0.1873 (12)	
C(11A)	0.1398 (23)	0.5409 (14)	0.1099 (13)	3.4 (4)
C(12A)	0.1510 (23)	0.7259 (14)	0.0371 (13)	3.6 (4)
C(13A)	0.3357 (21)	0.5949 (13)	−0.0198 (13)	3.1 (4)
C(21A)	0.5180 (22)	0.5914 (14)	0.3150 (13)	3.2 (4)
C(22A)	0.6358 (21)	0.7959 (14)	0.3135 (13)	3.2 (4)
C(23A)	0.7415 (27)	0.6610 (16)	0.1956 (15)	4.7 (5)
C(31A)	0.4780 (28)	0.8514 (17)	−0.0264 (17)	5.4 (5)
C(32A)	0.7466 (24)	0.8905 (14)	0.1062 (13)	3.4 (4)
C(33A)	0.6469 (22)	0.7065 (13)	0.0206 (13)	3.1 (4)
C(34A)	0.4330 (24)	0.8874 (15)	0.1574 (14)	4.2 (4)
C(11B)	0.0400 (21)	−0.0313 (14)	0.3100 (12)	3.1 (4)
C(12B)	0.1335 (24)	0.1109 (14)	0.1909 (15)	3.9 (4)
C(13B)	0.3019 (30)	0.1176 (17)	0.3539 (16)	5.6 (5)
C(21B)	−0.2412 (25)	0.1233 (15)	0.4984 (14)	4.2 (4)
C(22B)	−0.2262 (28)	0.3123 (17)	0.4282 (15)	5.0 (5)
C(23B)	0.0065 (23)	0.2699 (14)	0.5424 (14)	3.5 (4)
C(31B)	0.2923 (25)	0.3322 (15)	0.2524 (15)	4.2 (4)
C(32B)	0.1028 (29)	0.4459 (19)	0.3769 (17)	5.8 (5)
C(33B)	0.2711 (24)	0.3042 (14)	0.4314 (14)	3.7 (4)
C(34B)	−0.0444 (27)	0.3078 (16)	0.2428 (16)	4.7 (5)
H(A)	0.447 (16)	0.571 (10)	0.145 (9)	2.5

Table III. Final Anisotropic Thermal Parameters[a] for $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1A)	1.571 (29)	2.480 (32)	2.688 (34)	0.249 (24)	0.132 (24)	0.194 (25)
Os(2A)	1.964 (31)	2.791 (34)	2.259 (32)	0.540 (25)	0.025 (24)	0.035 (25)
Os(3A)	2.296 (32)	2.475 (33)	2.601 (34)	−0.002 (25)	0.370 (25)	0.199 (25)
Os(1B)	1.766 (30)	2.564 (33)	2.693 (34)	0.332 (24)	0.197 (24)	0.263 (25)
Os(2B)	2.048 (31)	2.772 (34)	2.364 (33)	0.477 (25)	0.327 (25)	0.355 (25)
Os(3B)	3.67 (4)	2.470 (34)	2.659 (35)	−0.456 (28)	0.582 (28)	0.351 (27)
Br(A)	2.71 (8)	4.32 (10)	3.54 (9)	0.80 (7)	1.27 (7)	−0.09 (7)
Br(B1)	1.50 (8)	3.23 (9)	2.72 (9)	0.15 (6)	−0.35 (6)	−0.03 (7)
O(11A)	3.7 (7)	3.9 (7)	7.7 (10)	−1.0 (6)	0.9 (7)	1.0 (6)
O(12A)	5.0 (8)	4.2 (8)	10.0 (12)	1.4 (6)	−2.1 (8)	2.1 (8)
O(13A)	6.3 (9)	4.2 (7)	4.0 (7)	0.0 (6)	0.9 (6)	−0.1 (6)
O(21A)	9.5 (12)	5.5 (9)	6.3 (10)	−0.7 (8)	−1.8 (8)	3.8 (8)
O(22A)	5.7 (9)	4.1 (7)	6.1 (9)	−0.4 (6)	−0.6 (7)	−1.6 (7)
O(23A)	3.5 (7)	10.0 (12)	7.1 (10)	2.5 (7)	0.1 (7)	−2.3 (8)
O(31A)	9.1 (12)	9.7 (13)	6.2 (10)	−0.8 (10)	−2.1 (9)	4.6 (9)
O(32A)	4.3 (8)	8.8 (11)	7.7 (11)	−4.0 (8)	1.1 (7)	−2.9 (9)
O(33A)	3.8 (7)	7.4 (10)	5.5 (8)	0.7 (7)	1.2 (6)	−1.9 (7)
O(34A)	7.6 (11)	4.0 (8)	10.8 (13)	1.6 (7)	4.0 (10)	0.4 (8)
O(11B)	4.1 (7)	2.2 (6)	10.6 (12)	0.3 (5)	0.7 (7)	0.8 (7)
O(12B)	7.5 (10)	7.8 (10)	3.4 (8)	0.3 (8)	2.1 (7)	0.5 (7)
O(13B)	2.1 (7)	10.6 (13)	11.5 (14)	1.5 (8)	−2.6 (8)	0.8 (10)
O(21B)	5.7 (9)	11.7 (14)	6.4 (10)	−0.7 (9)	2.5 (8)	4.5 (10)
O(22B)	6.6 (10)	6.7 (10)	14.2 (16)	4.9 (9)	3.0 (10)	2.8 (10)
O(23B)	4.0 (7)	6.6 (9)	3.3 (7)	0.3 (6)	0.2 (5)	−0.7 (6)
O(31B)	8.7 (12)	16.2 (18)	3.9 (8)	−5.4 (12)	3.5 (8)	0.3 (10)
O(32B)	16.9 (20)	3.2 (9)	11.8 (15)	2.3 (10)	3.1 (14)	−0.3 (9)
O(33B)	4.4 (8)	8.1 (10)	5.0 (8)	−0.2 (7)	−0.2 (7)	0.4 (7)
O(34B)	6.7 (10)	7.9 (11)	7.8 (11)	−0.5 (8)	−2.2 (9)	4.1 (9)

[a] The anisotropic thermal parameters are in the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

2.871 (1) Å in $[(\mu\text{-H})Os_3(CO)_{10}]_2(SCH_2S)$,[17] and 2.842 (1) Å in $(\mu\text{-H})Os_3(CO)_9(C_2H_4)(\mu\text{-SMe})$[18]].

We have previously reported the results of a structural investigation of the simplest of the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-X})$ (X $\neq$ H) species, $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$.[2] We have now undertaken a study of the related species $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$ with the expectation of determining the relationship between osmium–osmium distance and size of the bridgehead atom X. Our results appear below.

Experimental Section

A. Collection of Diffraction Data. A sample of $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$ was supplied by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The crystal selected for the structural analysis was a parallelepiped of approximate dimensions 0.14 × 0.20 × 0.22 mm. It was mounted on a thin glass fiber by using GE varnish and was fixed with beeswax, into a eucentric goniometer head.

The crystal was transferred to a Syntex P2$_1$ four-circle diffractometer and was accurately centered. Determination of preliminary unit cell parameters and the orientation matrix were carried out as described previously.[19] The crystal quality was checked via a series of θ–2θ and ω scans of reflections along the principal axes and was found to be satisfactory. Collection of intensity data was then carried out as described previously;[19] details are given in Table I.

Diffraction data were reduced to net intensities (I) and their esd's ($\sigma_c(I)$). The ratio of time taken for the main scan relative to the total time for background measurement, τ, was 2.0.

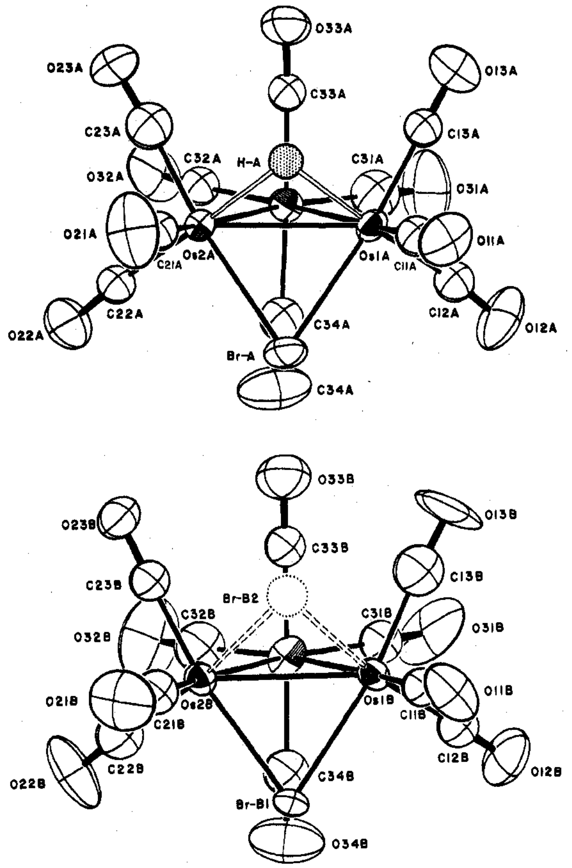


Figure 1. Labeling of atoms in the (μ-H)(μ-Br)$Os_3(CO)_{10}$ molecules (ORTEP-II diagrams): top, molecule A, with the bridging hydride ligand stippled; bottom, molecule B, with the minor component of the disordered bromide ligand shown as a dotted circle.

Table IV. Interatomic Distances (A) with Esd's for (μ-H)(μ-Br)$Os_3(CO)_{10}$

	molecule A	molecule B
A. Osmium-Osmium Distances		
Os(1)-Os(2)	2.851 (1)	2.876 (1)
Os(2)-Os(3)	2.844 (1)	2.838 (1)
Os(1)-Os(3)	2.842 (1)	2.834 (1)
B. Osmium-Bridging Ligand Distances		
Os(1)-Br	2.591 (2)	2.581 (2)
Os(2)-Br	2.583 (2)	2.585 (2)
Os(1)-Br(B2)		2.396 (23)
Os(2)-Br(B2)		2.432 (24)
Os(1)-H(A)	2.03 (14)	
Os(2)-H(A)	2.03 (14)	
C. Osmium-Carbon Distances		
Os(1)-C(11)	1.924 (20)	1.928 (20)
Os(1)-C(12)	1.915 (20)	1.905 (22)
Os(1)-C(13)	1.852 (19)	1.909 (26)
Os(2)-C(21)	1.950 (19)	1.900 (21)
Os(2)-C(22)	1.902 (19)	1.942 (24)
Os(2)-C(23)	1.888 (23)	1.854 (20)
Os(3)-C(31)	1.910 (25)	1.951 (22)
Os(3)-C(32)	1.952 (20)	1.942 (27)
Os(3)-C(33)	1.929 (19)	1.874 (21)
Os(3)-C(34)	1.910 (21)	1.946 (23)
D. Carbon-Oxygen Distances		
C(11)-O(11)	1.137 (24)	1.118 (24)
C(12)-O(12)	1.116 (25)	1.119 (26)
C(13)-O(13)	1.130 (24)	1.129 (30)
C(21)-O(21)	1.106 (25)	1.183 (28)
C(22)-O(22)	1.143 (24)	1.123 (30)
C(23)-O(23)	1.164 (28)	1.165 (24)
C(31)-O(31)	1.118 (31)	1.100 (29)
C(32)-O(32)	1.100 (26)	1.109 (33)
C(33)-O(33)	1.133 (24)	1.160 (26)
C(34)-O(34)	1.163 (27)	1.135 (29)

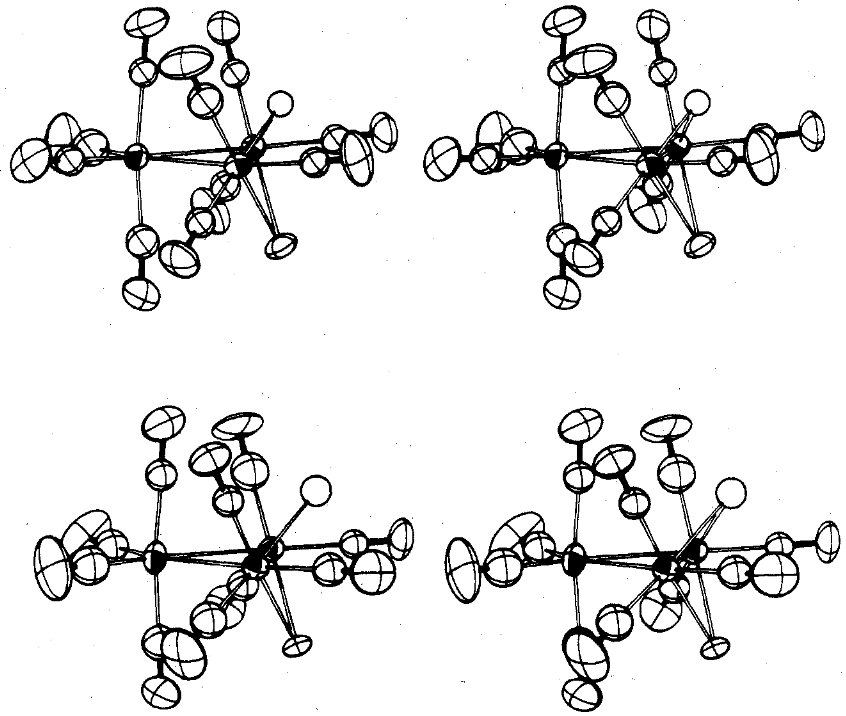


Figure 2. Stereoscopic views of (μ-H)(μ-Br)$Os_3(CO)_{10}$: top, molecule A; bottom, molecule B.

All data were corrected for the effects of absorption [μ(Mo Kα) = 239.56 cm^{-1}] by an empirical method. Several close-to-axial reflections (χ_0 = 272–288°) distributed over the 2θ range used in data collection, each of fairly high intensity ($I/\sigma(I) > 75$), were measured at 10° intervals around the diffraction vector (ψ) from 0 to 350°. Each reflection was used to define a normalized absorption curve vs. ϕ, which was corrected for ω and χ. The two curves bracketing the 2θ values of the reflection under consideration were interpolated both in 2θ and

Table V

Interatomic Angles[a] for Molecules A and B in $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$

	molecule A	molecule B
A. Os-Os-Os Angles		
Os(2)-Os(1)-Os(3)	59.94 (2)	59.60 (2)
Os(1)-Os(2)-Os(3)	59.87 (2)	59.46 (2)
Os(1)-Os(3)-Os(2)	60.20 (2)	60.94 (2)
B. Osmium-Osmium-Carbonyl Angles		
Os(2)-Os(1)-C(11)	112.5 (6)	113.9 (6)
Os(2)-Os(1)-C(12)	135.9 (6)	136.3 (6)
Os(2)-Os(1)-C(13)	117.5 (6)	114.5 (7)
Os(3)-Os(1)-C(11)	172.1 (6)	173.5 (6)
Os(3)-Os(1)-C(12)	89.4 (6)	89.6 (6)
Os(3)-Os(1)-C(13)	90.3 (6)	87.5 (7)
Os(1)-Os(2)-C(21)	110.6 (6)	113.0 (6)
Os(1)-Os(2)-C(22)	136.8 (6)	134.7 (7)
Os(1)-Os(2)-C(23)	116.2 (7)	115.5 (6)
Os(3)-Os(2)-C(21)	169.5 (6)	172.4 (6)
Os(3)-Os(2)-C(22)	92.6 (6)	87.5 (7)
Os(3)-Os(2)-C(23)	86.9 (7)	89.1 (6)
Os(1)-Os(3)-C(31)	99.2 (7)	96.1 (6)
Os(1)-Os(3)-C(32)	162.5 (6)	162.3 (8)
Os(1)-Os(3)-C(33)	84.7 (6)	85.4 (6)
Os(1)-Os(3)-C(34)	88.6 (6)	88.8 (7)
Os(2)-Os(3)-C(31)	159.4 (7)	157.1 (6)
Os(2)-Os(3)-C(32)	102.7 (6)	101.4 (8)
Os(2)-Os(3)-C(33)	85.4 (6)	85.9 (6)
Os(2)-Os(3)-C(34)	86.3 (6)	86.9 (7)

	molecule A	molecule B
C. Carbonyl-Osmium-Carbonyl Angles		
C(11)-Os(1)-C(12)	98.1 (8)	96.1 (8)
C(11)-Os(1)-C(13)	91.8 (8)	95.4 (9)
C(12)-Os(1)-C(13)	91.4 (8)	92.2 (10)
C(21)-Os(2)-C(22)	97.8 (8)	99.4 (9)
C(21)-Os(2)-C(23)	94.2 (9)	93.7 (9)
C(22)-Os(2)-C(23)	92.4 (9)	91.8 (9)
C(31)-Os(3)-C(32)	97.8 (9)	101.5 (10)
C(31)-Os(3)-C(33)	92.9 (9)	91.6 (9)
C(31)-Os(3)-C(34)	93.8 (10)	94.1 (9)
C(32)-Os(3)-C(33)	90.7 (8)	93.5 (10)
C(32)-Os(3)-C(34)	94.0 (9)	90.5 (10)
C(33)-Os(3)-C(34)	171.2 (8)	172.3 (9)
D. Osmium-Carbon-Oxygen Angles		
Os(1)-C(11)-O(11)	176.2 (17)	176.5 (17)
Os(1)-C(12)-O(12)	176.1 (18)	178.3 (19)
Os(1)-C(13)-O(13)	179.4 (17)	176.9 (22)
Os(2)-C(21)-O(21)	176.1 (18)	175.1 (19)
Os(2)-C(22)-O(22)	176.6 (17)	175.9 (21)
Os(2)-C(23)-O(23)	177.2 (20)	178.2 (17)
Os(3)-C(31)-O(31)	178.7 (22)	176.3 (20)
Os(3)-C(32)-O(32)	176.4 (18)	177.5 (24)
Os(3)-C(33)-O(33)	178.4 (17)	178.4 (18)
Os(3)-C(34)-O(34)	173.9 (19)	178.4 (20)

Angles[a] Involving the Bridging Ligands for $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$

Os(1A)-Br(A)-Os(2A)	66.87 (5)	Os(1B)-Br(B1)-Os(2B)	67.65 (5)
Br(A)-Os(1A)-Os(2A)	56.43 (5)	Br(B1)-Os(1B)-Os(2B)	56.24 (4)
Br(A)-Os(1A)-Os(3A)	88.47 (5)	Br(B1)-Os(1B)-Os(3B)	87.84 (5)
Br(A)-Os(2A)-Os(1A)	56.70 (5)	Br(B1)-Os(2B)-Os(1B)	56.11 (4)
Br(A)-Os(2A)-Os(3A)	88.58 (5)	Br(B1)-Os(2B)-Os(3B)	87.67 (5)
Br(A)-Os(1A)-C(11A)	88.6 (6)	Br(B1)-Os(1B)-C(11B)	88.4 (6)
Br(A)-Os(1A)-C(12A)	95.2 (6)	Br(B1)-Os(1B)-C(12B)	95.9 (6)
Br(A)-Os(1A)-C(13A)	173.3 (6)	Br(B1)-Os(1B)-C(13B)	170.7 (7)
Br(A)-Os(2A)-C(21A)	89.2 (6)	Br(B1)-Os(2B)-C(21B)	88.6 (6)
Br(A)-Os(2A)-C(22A)	93.2 (6)	Br(B1)-Os(2B)-C(22B)	96.0 (7)
Br(A)-Os(2A)-C(23A)	172.9 (7)	Br(B1)-Os(2B)-C(23B)	171.4 (6)
Os(1A)-H(A)-Os(2A)	89 (6)	Os(1B)-Br(B2)-Os(2B)	73.1 (7)
H(A)-Os(1A)-Os(2A)	45 (4)	Br(B2)-Os(1B)-Os(2B)	54.0 (6)
H(A)-Os(1A)-Os(3A)	90 (4)	Br(B2)-Os(1B)-Os(3B)	97.7 (6)
H(A)-Os(2A)-Os(1A)	45 (4)	Br(B2)-Os(2B)-Os(1B)	52.9 (6)
H(A)-Os(2A)-Os(3A)	90 (4)	Br(B2)-Os(2B)-Os(3B)	96.8 (6)
H(A)-Os(1A)-C(11A)	83 (4)	Br(B2)-Os(1B)-C(11B)	77.1 (8)
H(A)-Os(1A)-C(12A)	177 (4)	Br(B2)-Os(1B)-C(12B)	169.6 (8)
H(A)-Os(1A)-C(13A)	86 (4)	Br(B2)-Os(1B)-C(13B)	80.9 (9)
H(A)-Os(2A)-C(21A)	80 (4)	Br(B2)-Os(2B)-C(21B)	76.7 (8)
H(A)-Os(2A)-C(22A)	178 (4)	Br(B2)-Os(2B)-C(22B)	172.1 (9)
H(A)-Os(2A)-C(23A)	87 (4)	Br(B2)-Os(2B)-C(23B)	81.7 (8)
Br(A)-Os(1A)-H(A)	88 (4)	Br(B1)-Os(1B)-Br(B2)	91.7 (6)
Br(A)-Os(2A)-H(A)	88 (4)	Br(B1)-Os(2B)-Br(B2)	90.8 (6)

[a] In degrees with esd's.

in (corrected) ϕ to derive the absorption correction. All curves were mutually consistent, with similar profiles and with maxima and minima observed at common values; they are listed in Table I. The data were averaged according to $\bar{1}$ symmetry, yielding a unique set of 4615 independent reflections.

Intensities were then corrected for Lorentz and polarization factors.

B. Solution and Refinement of the Structure. All calculations were performed by using an in-house Syntex XTL structure determination system consisting of the following: a Data General Nova 1200 computer with 24K of 16-bit words, a Diablo disk unit of 1.2 million 16-bit words, and a locally modified version of the XTL conversational crystallographic program package.

The analytical atomic scattering factors compiled by Cromer and Waber[20a] were used for neutral osmium, bromine, oxygen, carbon, and hydrogen throughout the analysis; both real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomolous dispersion were included for all nonhydrogen atoms.[20b]

The function minimized during least-squares refinement was $\sum w\cdot(|F_o| - |F_c|)^2$. The weights used were obtained from counting statistics, modified by the "ignorance factor", p, set at a value of 0.015.

The positions of the osmium atoms were determined from a three-dimensional Patterson synthesis. Least-squares refinement of the positional and isotropic thermal parameters of the osmium atoms coverged with $R_F = 22.8\%$. A difference-Fourier synthesis revealed the positions of the bridging bromide ligands.

Continued refinement of positional and isotropic thermal parameters of the six osmium and two bromine atoms led to $R_F = 13.0\%$. The positions of all the carbonyl ligands were now revealed on a difference-Fourier synthesis. Full least-squares refinement of positional and anisotropic thermal parameters for all osmium and bromine atoms as well as positional and isotropic thermal parameters for all oxygen and carbon atoms led to convergence with $R_F = 6.2\%$ and $R_{wF} = 5.3\%$. A careful survey of all data suggested that (i) the $01\bar{2}$ reflection was unreliable and (ii) the data were affected by secondary extinction ($|F_o| < |F_c|$ for intense, low-angle data). The $01\bar{2}$ reflection was removed from the data file, and all data were corrected for secondary extinction

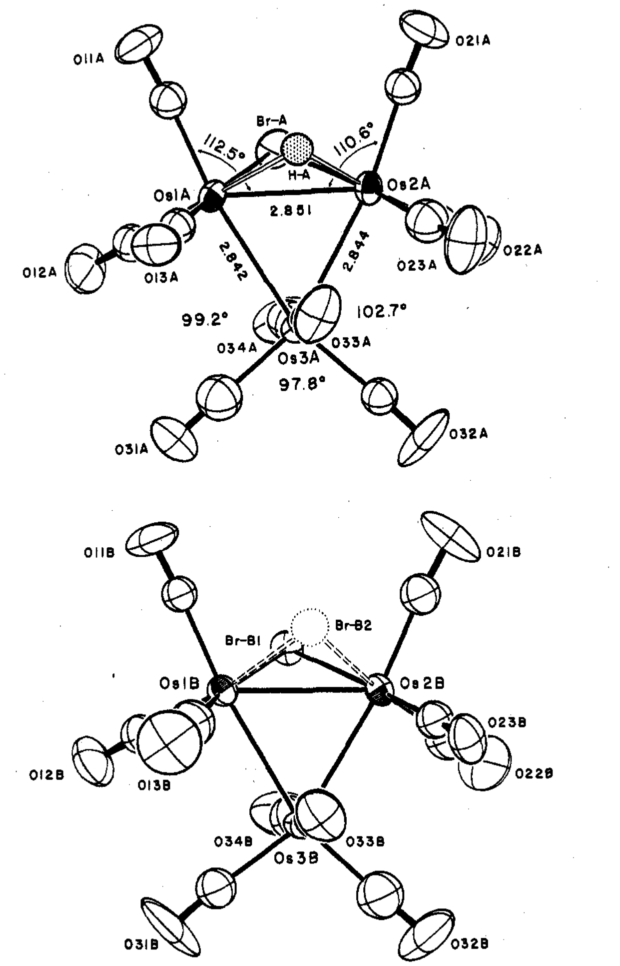


Figure 3. The $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$ molecules shown rotated by 5° (about vertical axis) from their triosmium planes: top, molecule A; bottom, molecule B.

Table VI

Selected Planes and Deviations of Atoms Therefrom

atom	dev, Å	atom	dev, Å
	Molecule A		
Plane IA:	$-0.6290X + 0.5768Y + 0.5212Z = 5.1413$		
Os(1)^a	0.000	C(12)	−1.054 (20)
Os(2)^a	0.000	O(12)	−1.730 (16)
Os(3)^a	0.000	C(22)	−1.094 (19)
H(A)	1.20 (14)	O(22)	−1.806 (15)
Br(A)	−2.025 (2)	C(34)	−1.906 (21)
C(11)	0.076 (20)	O(34)	−3.062 (17)
O(11)	0.168 (14)	C(13)	1.570 (19)
C(21)	0.158 (19)	O(13)	2.523 (14)
O(21)	0.310 (17)	C(23)	1.583 (22)
C(31)	0.004 (25)	O(23)	2.540 (17)
O(31)	−0.012 (19)	C(33)	1.919 (19)
C(32)	0.127 (20)	O(33)	3.047 (15)
O(32)	0.236 (17)		
Plane IIA:	$0.1158X + 0.9596Y - 0.2565Z = 8.3149$		
Os(1)^a	0.000	C(13)	−0.092 (18)
Os(2)^a	0.000	O(13)	−0.146 (14)
Br(A)^a	0.000	C(23)	0.015 (22)
H(A)	−1.18 (14)	O(23)	0.010 (18)
Plane IIIA:	$0.6479X + 0.3462Y - 0.6785Z = 2.8754$		
Os(1)^a	0.000	C(12)	0.084 (20)
Os(2)^a	0.000	O(12)	0.073 (16)
H(A)^a	0.00	C(22)	−0.032 (19)
Br(A)	−1.757 (2)	O(22)	−0.106 (15)
	Molecule B		
Plane IB:	$0.6695X - 0.0639Y + 0.7400Z = 3.5574$		
Os(1)^a	0.000	C(12)	1.026 (21)
Os(2)^a	0.000	O(12)	1.638 (16)
Os(3)^a	0.000	C(22)	1.041 (23)
Br(B1)	2.019 (2)	O(22)	1.704 (20)
Br(B2)	−1.523 (24)	C(34)	1.943 (23)
C(11)	−0.013 (18)	O(34)	3.077 (18)
O(11)	−0.053 (16)	C(13)	−1.645 (25)
C(21)	−0.040 (21)	O(13)	−2.593 (18)
O(21)	−0.063 (17)	C(23)	−1.595 (20)
C(31)	−0.037 (22)	O(23)	−2.610 (13)
O(31)	−0.089 (18)	C(33)	−1.866 (21)
C(32)	−0.006 (25)	O(33)	−3.025 (15)
O(32)	−0.055 (24)		
Plane IIB:	$-0.1011X - 0.8744Y + 0.4746Z = 1.3000$		
Os(1)^a	0.000	C(13)	−0.032 (24)
Os(2)^a	0.000	O(13)	−0.051 (20)
Br(B1)^a	0.000	C(23)	−0.066 (19)
Br(B2)	−1.645 (23)	O(23)	−0.103 (14)
Plane IIIB:	$+0.6885X + 0.6727Y + 0.2712Z = 2.1235$		
Os(1)^a	0.000	C(12)	−0.012 (20)
Os(2)^a	0.000	O(12)	−0.032 (16)
Br(B2)^a	0.000	C(22)	−0.067 (24)
Br(B1)	1.821 (2)	O(22)	−0.030 (18)

Important Dihedral Angles, Deg

plane IA–plane IIA	110.31	plane IA–plane IIIA	124.16
plane IB–plane IIB	109.84	plane IB–plane IIIB	128.22

[a] Atoms used in calculating the planes.

by applying an empirical correction. The value for the secondary extinction parameter (k) used was 4.871×10^{-7}. $F_{o,cor}$, the corrected observed structure factor, and $\sigma(F_{o,cor})$ are given by eq 1 and 2, respectively.

$$F_{o,cor} = F_o(1.0 + kI_o) \tag{1}$$

$$\sigma(F_{o,cor}) = \sigma(F_o)[1.0 + kI_o] \tag{2}$$

Continued refinement of positional and anisotropic thermal parameters for the osmium, bromine, and oxygen atoms and the positional and isotropic thermal parameters for the carbon atoms led to R_F = 5.7% and 4.7%. A difference-Fourier map was now calculated in the hope of finding the positions of the bridging hydride ligands. Instead, we observed a major feature—a peak of height 4.7 e Å^{-3} approximately 2.4 Å from both Os(1B) and Os(2B). After careful consideration we decided that this feature probably resulted from a slight disorder of the bridging bromide ligand about the triosmium plane. This feature was treated as a bromine atom and its occupancy was refined, yielding a value of 0.083 (4) (approximately 2.9 electrons) as opposed to 0.917 (4) for the major site.

Refinement was continued and convergence was reached with R_F = 5.5% and R_{wF} = 4.5%. In order to find the position of the bridging hydride ligand on molecule A, we calculated a difference-Fourier map by using data with $(\sin \theta)/\lambda < 0.30$ Å^{-1}. A peak approximately 2.0 Å from Os(1A) and 1.8 Å from Os(2A) was found in the position expected for a μ-bridging hydride ligand. The hydride ligand was included in our model; its isotropic thermal parameter was fixed at a value of 2.5 Å.^{2}

Final refinement of all positional parameters, anisotropic thermal parameters for all osmium, oxygen, and bromine atoms, isotropic thermal parameters for all carbon atoms, and the minor disordered component of the bromine on molecule B led to convergence with R_F = 5.5%, R_{wF} = 4.4%, and GOF = 1.5416 for all 4614 independent data. (The 3976 data with $I > 3\sigma(I)$ gave R_F = 4.3%, R_{wF} = 4.2%, and GOF = 1.6165.) The "overdetermination ratio" (i.e., number of observations included in the refinement:number of variables refined) was 13.57:1 (NO = 4614, NO = 340).

A final difference-Fourier synthesis based on all data had no significant features. The average value of $\sum w(|F_o| - |F_c|)^2$ showed no significant systematic variations as a function of $|F_o|$, $(\sin \theta)/\lambda$, identity of parity of Miller indices, or sequence number. The weighting scheme was thus considered to be satisfactory.

The final positional and thermal parameters are collected in Tables II and III.

Results and Discussion

The crystal consists of discrete molecular units of $(\mu\text{-H})(\mu\text{-}$

Br)$Os_3(CO)_{10}$, which are mutually separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with four molecules per unit cell. There are thus two independent molecules in the crystallographic asymmetric unit; these are referred to as "molecule A" and "molecule B" throughout the text. Molecule A is ordered and the bridging hydride ligand associated with this molecule was located and refined successfully. Molecule B appears to be slightly disordered, the observed structure being the composite image of a 91.7 (4)%:8.3 (4)% disorder of the molecule about the triosmium plane. The scheme used for numbering atoms in both molecules is shown in Figure 1, while Figure 2 presents stereoscopic views of the two molecules.

Because of the disorder in molecule B, subsequent discussion will be based largely upon intramolecule parameters from molecule A. Bond lengths within the two molecules are in good agreement (unless otherwise stated below) and dimensions within the two molecules appear side by side in Table IV (interatomic distances, with esd's) and Table V (bond angles, with esd's). Selected planes are shown in Table VI.

The (μ-H)(μ-Br)$Os_3(CO)_{10}$ molecule has approximate C_s symmetry in the crystalline state. It is based upon a triangular arrangement of osmium atoms, one of which [Os(3)] is associated with four terminal carbonyl ligands, while the remaining two osmium atoms [Os(1) and Os(2)] are each linked to three such ligands and are mutually bridged by a hydride and bromide ligand.

The nonbridged osmium–osmium distances in molecule A are Os(1A)–Os(3A) = 2.842 (1) Å and Os(2A)–Os(3A) = 2.844 (1) Å; the average value of 2.843 [1] Å[21] is only 0.008 Å shorter than the μ-hydrido-μ-bromo-bridged Os(1A)–Os(2A) distance of 2.851 (1) Å. [For molecule B, the nonbridged bonds are Os(1B)–Os(3B) = 2.834 (1) Å and Os(2B)–Os(3B) = 2.838 (1) Å. The average value of 2.836 [3] Å is 0.040 Å shorter than the μ-hydrido-μ-bromo-bridged Os–Os distance of 2.876 (1) Å.]

The bridging hydride ligand is bonded to the cluster via the bonds Os(1A)–H(A) = 2.03 (14) Å and Os(2A)–H(A) = 2.03 (14) Å, the Os(1A)–H(A)–Os(2A) angle being 89 (6)°. It should be noted that neutron diffraction studies have shown Os–(μ-H) distances of 1.840 (3)–1.852 (3) Å in (μ-H)$_2Os_3(CO)_{10}$,[13] 1.754 (8)–1.883 (9) Å in (μ-H)$_2Os_3(CO)_{10}$(μ-CH_2),[15] and 1.813 (4)–1.857 (4) Å in (μ-H)$Os_3(CO)_{10}$(σ,π-C_2H_3).[12]

The bromide ligand forms a fairly symmetrical bridge across the Os(1A)–Os(2A) vector, the individual osmium–bromide distances being Os(1A)–Br(A) = 2.591 (2) Å and Os(2A)–Br(A) = 2.583 (2) Å. The angle at the bridging bromide ligand is surprisingly acute—Os(1A)–Br(A)–Os(2A) = 66.87 (5)°. [The corresponding angle for the major component in molecule B is Os(1B)–Br(B1)–Os(2B) = 67.65 (5)°.] These values are both less than that of 70.83 (9)° observed for the Os–Cl–Os bridge in (μ-H)(μ-Cl)$Os_3(CO)_{10}$.[1] This suggests that the hydride ligand (rather than the other bridging ligand) may be dominant in determining the dimensions within the Os(μ-H)(μ-X)Os bridge of (μ-H)$Os_3(CO)_{10}$(μ-L) molecules (see below).

The bridging bromide ligand is approximately trans to two carbonyl ligands, with Br(A)–Os(1A)–C(13A) = 173.3 (6)° and Br(A)–Os(2A)–C(23A) = 172.9 (7)°. The bromide ligand is also adjacent to two equatorial carbonyl ligands (Br(A)–Os(1A)–C(11A) = 88.6 (6)° and Br(A)–Os(2A)–C(21A) = 89.2 (6)°) and to two "semiaxial" carbonyl groups (Br(A)–Os(1A)–C(12A) = 95.2 (6)° and Br(A)–Os(2A)–C(22A) = 93.2 (6)°).

The carbonyl ligands on Os(1A) and Os(2A) are in three different chemical environments. The osmium–carbonyl bond lengths involving the equatorial carbonyl ligands trans to Os(3A) are the longest; Os(1A)–C(11A) = 1.924 (20) Å and Os(2A)–C(21A) = 1.950 (19) Å. The osmium–carbonyl distances for those carbonyls trans to the bridging hydride are somewhat shorter, with Os(1A)–C(12A) = 1.915 (20) Å and Os(2A)–C(22A) = 1.902 (19) Å. The osmium–carbonyl bond lengths trans to the bridging bromide are the shortest, with Os(1A)–C(13A) = 1.852 (19) Å and Os(2A)–C(23A) = 1.888 (23) Å.

The carbonyl groups on Os(3) belong to two sets—axial [C(33A)–O(33A) and C(34A)–O(34A)] or equatorial [C(31A)–O(31A) and C(32A)–O(32A)]—but no clear distinction in osmium–carbonyl bond lengths is possible in the present structural determination.

The carbon–oxygen bond distances range from 1.100 (26) to 1.163 (27) Å in molecule A with an average of 1.131 [22] Å (1.134 [27] Å for molecule B). The Os–C–O systems are all close to linear, with angles in molecule A ranging from 173.9 (19) to 179.4 (17)° [175.1 (19)–178.4 (20)° in molecule B].

A projection of molecule A onto the triosmium plane is shown in Figure 3. As expected, the equatorial Os–Os–CO

Table VII. Dimensions in (μ-H)$Os_3(CO)_{10}$(μ-L) Molecules

				Os–Os, Å		
μ-L	bridgehead atom (X)	r(X),[a] Å	Os–X–Os, deg	bridged	nonbridged	Δ,[b] Å
μ-H[c]	H	~0.30	95.54 (12) 93.06 (11)	2.683 (1)	2.814 (1) 2.815 (1)	−0.132
μ-CHCH=NEt$_2$[1]	C	0.77	80.6 (9)	2.785 (2)	2.866 (2) 2.870 (2)	−0.083
μ-$CH_2CH_2PMe_2Ph$[14]	C	0.77	80.8 (3)	2.800 (1)	2.869 (1) 2.873 (1)	−0.071
μ-Cl[2]	Cl	0.99	70.83 (9)	2.846 (1)	2.829 (1) 2.836 (1)	+0.013
μ-SEt[6]	S	1.04	73.1 (3)	2.863 (2)	2.842 (3) 2.856 (2)	+0.014
μ-SCH_2S-μ[17]	S	1.04		2.867 (1)	2.872 (1) 2.854 (1)	−0.004
				2.871 (1)	2.875 (1) 2.875 (1)	+0.004
μ-Br, molecule A	Br	1.14	66.87 (5)	2.851 (1)	2.842 (1) 2.844 (1)	+0.008
μ-Br, molecule B			67.65 (5)	2.876 (1)	2.838 (1) 2.834 (1)	+0.040

[a] Covalent radii are from: Pauling, L. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Table 7-4, p 226. [b] Δ = (bridged Os–Os distance) − (average nonbridged Os–Os distance). [c] All data for (μ-H)$_2Os_3(CO)_{10}$ are from the neutron diffraction study (see ref 13).

angles based on the doubly bridged Os(1A)–Os(2A) [Os(1A)–Os(2A)–C(21A) = 110.6 (6)° and Os(2A)–Os(1A)–C(11A) = 112.5 (6)°] are some 7–15° larger than those based on the nonbridged osmium–osmium vectors [Os(1A)–Os(3A)–C(31A) = 99.2 (7)° and Os(2A)–Os(3A)–C(32A) = 102.7 (6)°].

In molecule A, atom H(A) lies +1.20 (14) Å from the triosmium plane and Br(A) lies −2.025 (2) Å from this plane. Nearly all of the "equatorial" ligands are displaced out of the triosmium plane toward the hydride ligand, presumably to relieve intramolecular ligand···ligand repulsions. The displacements are quite significant (e.g., +0.310 (17) Å for O(21A), +0.236 (17) Å for O(32A), and +0.168 (14) Å for O(11A)). A similar pattern, though of lesser magnitude, is discernible in the disordered molecule B (see Table VI, plane IB).

Finally, we note that the major component of the disordered bromide ligand on molecule B is associated with normal osmium–bromine distances (Os(1B)–Br(B1) = 2.581 (2) Å and Os(2B)–Br(B1) = 2.585 (2) Å), whereas the minor component is associated with abnormally short osmium–bromine distances (Os(1B)–Br(B2) = 2.396 (23) Å and Os(2B)–Br(B2) = 2.432 (24) Å). This apparent anomaly may be explained in the following way—the "atom" Br(B2) actually represents the composite of 8.3% of a bromide ligand (2.9 electrons) at ~2.6 Å from the osmium atoms and 91.7% of a hydride ligand (0.9 electron) at ~2.0 Å from the osmium atoms.

Os(μ-H)(μ-X)Os Bridges in (μ-H)$Os_3(CO)_{10}$(μ-L) Molecules

The relevant information on these species is compiled in Table VII. We have included only species in which the (μ-H)$Os_3(CO)_{10}$ skeleton is associated with a single additional bridging ligand across the hydrido-bridged osmium–osmium vector; the species (μ-H)$_2Os_3(CO)_{10}$(μ-CH_2)[15] and (μ-H)-$Os_3(CO)_9(C_2H_4)$(μ-SMe)[18] are therefore excluded from consideration.

There are some qualitative trends that are made apparent by Table VII. The most important is that the Os–X–Os angle decreases significantly with increasing radius of X. This suggests that the Os–H–Os system has a more important role than the Os–X–Os system in determining the dibridged Os–Os distance. This distance may well be dictated primarily by the requirement that the osmium atoms each retain an octahedral ligand environment.

The parameter Δ (defined in footnote *b* of Table VII) is decidedly negative for small atoms and becomes slightly positive for larger atoms (r = 0.99–1.14 Å).

To us, the very small difference between Os(μ-H)(μ-X)Os distances in (μ-H)(μ-Br)$Os_3(CO)_{10}$ and (μ-H)(μ-Cl)$Os_3(CO)_{10}$ was an unexpected result. Further studies are in progress to further clarify the quantitative metric trends in this class of molecules.

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Registry No. (μ-H)(μ-Br)$Os_3(CO)_{10}$, 61199-98-2.

Supplementary Material Available: Data-processing formulas and a listing of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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