314 *Inorganic Chemistry, Vol. 18, No. 2, 1979* Robert W. Broach and Jack M. Williams

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Interaction of Hydrogen and Hydrocarbons with Transition Metals. Neutron Diffraction Study of Di-μ-hydrido-decacarbonyltriosmium, $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$, Containing a Four-Center, Four-Electron H_2Os_2 Bond

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The low-temperature crystal and molecular structure of $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$ has been determined by neutron diffraction techniques. Lattice parameters at 110 K for the centrosymmetric triclinic space group $P\bar{1}$ are $a = 8.499$ (4) Å, $b = 9.029$ (4) Å, $c = 11.714$ (5) Å, $\alpha = 91.59$ (1)°, $\beta = 98.98$ (2)°, $\gamma = 117.33$ (2)°, and $V = 783.7$ Å^3. The triosmium fragment may be viewed as forming an isosceles triangle with one short and two long metal–metal distances. The short osmium–osmium bond, which is symmetrically bridged by the two hydrogen atoms, has a length of 2.683 (1) Å, while the two long nonbridged bonds have equal lengths of 2.814 (1) and 2.815 (1) Å. The mean osmium–hydrogen bond distance is 1.845 (3) Å. A bonding scheme is presented which supports the formulation of the metal–hydrogen interaction as a four-center, four-electron bond.

Introduction

The triosmium carbonyl hydride complex $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$ is characterized by relatively high reactivity (mild reaction conditions) and a stable triosmium framework. These properties have made possible the isolation of derivatives which may mimic the sorption of alkenes or alkynes on metal surfaces.[1,2] In particular, in the catalytic isomerization and hydrogenation of 1-alkenes to internal alkenes and alkanes by $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$, intermediates have been isolated which may provide insight into the mechanism of these reactions.[3]

The interest in $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$ has led to two independent X-ray diffraction studies.[4] However, in both cases, the hydrogen atoms could not be directly located due to their inherently low X-ray scattering power. An accurate structural determination of $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$ is important in order to provide a basis for comparison with its derivatives and to contribute to the characterization of hydrogen-bridged metal–metal bonds. Consequently, we report here a high-precision neutron diffraction study of $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$.

Data Collection

Large crystals suitable for neutron diffraction data collection were generously supplied by Dr. John R. Shapley and R. Bruce Calvert of the University of Illinois. A well-formed crystal weighing 43 mg and having approximate dimensions of 2.2 × 2.3 × 3.0 mm was sealed in a lead-glass capillary and mounted in an arbitrary orientation on the fully automated[5] Electronics-and-Alloys four-circle diffractometer at the Argonne CP-5 reactor. The sample was cooled and maintained at 110 K throughout the alignment and data collection using a cold N_2 stream.[6] One-half sphere of data was measured for $7° \le 2\theta \le 95°$, using coupled θ–2θ step scans with 0.1° step intervals and scan ranges of 48 steps when $2\theta \le 40°$ and 58 steps when $2\theta > 40°$. Stationary-counter, stationary-crystal backgrounds were measured at the beginning and end of each scan range. Two standard reflections measured after every 80 data reflections, showed a maximum 5% variation in intensities.

The observed integrated intensities were corrected for absorption ($\mu = 0.580$ cm^{-1}), and the minimum and maximum transmission coefficients were 0.867 and 0.908, respectively. The observed structure factors, F_o^2, were calculated as previously described.[8] A total of 3805 data were then sorted and merged[9] under $P\bar{1}$ symmetry to yield 3532 unique data, all of which were used in subsequent calculations.

Hydrogen Atom Location and Refinement.[10] The two hydrogen atoms were located from a difference Fourier map which was phased using the 23 nonhydrogen positional parameters given in an X-ray diffraction study of $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$.[4a] Full-matrix least-squares refinement of the positional and anisotropic temperature factors for all atoms converged, with final discrepancy indices of $R(F_o) = 0.054$, $R(F_o^2) = 0.050$, and $R_w(F_o^2) = 0.077$. In the later stages of refinement the data were corrected for secondary extinction,[11] with a final refined isotropic extinction parameter $g = 0.14\ (1) \times 10^{-4}$. The scale factor was 0.912 (2), and the standard deviation of an observation of unit weight was 0.93. The data to parameter ratio in the final cycles of refinement was 15:1.

Table I. Crystal Parameters for $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$ at 110 K[a,b]

$a = 8.499$ (4) Å	$V = 783.7$ Å^3
$b = 9.029$ (4) Å	$\lambda = 1.142$ (1) Å
$c = 11.714$ (5) Å	space group: $P\bar{1}$ (C_i^1; No. 2)
$\alpha = 91.59$ (1)°	$Z = 2$
$\beta = 98.98$ (2)°	mol wt = 852.7
$\gamma = 117.33$ (2)°	ρ(calcd) = 3.61 g cm^{-3}

[a] Lattice constants were determined from a least-squares fit of the setting angles for 29 carefully centered reflections with $74° < 2\theta < 90°$. [b] The temperature was maintained by a cold N_2 stream.[6]

A final difference Fourier synthesis of nuclear scattering density was virtually featureless. Positional and anisotropic thermal parameters are given in Table II. Interatomic distances and bond angles are given in Tables III and IV. Selected planes and interplanar angles are given in Table V.

Results and Discussion

General Description of the Structure. A drawing of the molecular configuration of $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$ is given in Figure 1 (a stereopair is given in Figure 2). As shown in Figure 3, the three osmium atoms form an isosceles triangle with two long, nonbridged Os–Os distances of 2.815 (1) and 2.814 (1) Å and one short, dihydrido-bridged M–M distance of 2.683 (1) Å. These are equivalent within error to the values determined in the X-ray refinement of $(\mu\text{-H})_2\mathrm{Os}_3(\mathrm{CO})_{10}$ by Churchill, Hollander, and Hutchinson[4a] but are longer than those derived in the X-ray refinement by Allen, Mason, and Hitchcock.[4b] The geometry about each osmium atom is approximately octahedral. The entire molecule closely conforms to idealized C_{2v} symmetry with the twofold axis passing through Os(1) and bisecting the Os(2)–Os(3) bond (see Figure 3).

All intramolecular bond lengths and angles are in essential agreement with the two room-temperature X-ray diffraction studies,[4] although the errors derived from the neutron diffraction data are an order of magnitude smaller.[12] The only significant difference in the room-temperature and low-temperature determinations is a slight decrease in the intermolecular nonbonding contacts, which is most apparent in the observed 4% decrease in cell volume at 110 K.

There are no unusually short intermolecular contacts, indicating normal van der Waals separations between molecules. The shortest intermolecular contacts involving the hydrogen

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Table II. Final Positional[a] and Thermal[b] Parameters for $(\mu\text{-H})_2Os_3(CO)_{10}$

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
OS(1)	0.10767(8)	0.31371(7)	0.21157(5)	0.0105(3)	0.0109(3)	0.0137(3)	0.0048(2)	0.0020(2)	0.0003(2)
OS(2)	0.38532(8)	0.23547(8)	0.29851(6)	0.0117(3)	0.0119(3)	0.0153(3)	0.0056(2)	0.0011(2)	-0.0002(2)
OS(3)	0.47563(8)	0.55032(7)	0.25087(5)	0.0111(3)	0.0111(3)	0.0143(3)	0.0032(2)	0.0026(2)	0.0005(2)
H(1)	0.4961(4)	0.3707(3)	0.1904(2)	0.036(1)	0.027(1)	0.030(1)	0.014(1)	0.012(1)	0.002(1)
H(2)	0.4789(3)	0.4429(3)	0.3830(2)	0.034(1)	0.026(1)	0.026(1)	0.013(1)	0.004(1)	0.001(1)
C(11)	0.0120(2)	0.4586(1)	0.1539(1)	0.0200(5)	0.0159(5)	0.0224(5)	0.0110(4)	0.0017(4)	0.0020(4)
C(12)	-0.1189(2)	0.1142(1)	0.2029(1)	0.0156(5)	0.0124(5)	0.0239(5)	0.0026(4)	0.0047(4)	-0.0007(4)
C(13)	0.1281(1)	0.3815(1)	0.3751(1)	0.0151(5)	0.0201(5)	0.0151(5)	0.0076(4)	0.0025(4)	-0.0007(4)
C(14)	0.1444(1)	0.2473(1)	0.0622(1)	0.0173(5)	0.0185(5)	0.0145(5)	0.0091(4)	0.0012(4)	-0.0009(4)
C(21)	0.6064(1)	0.2313(1)	0.3608(1)	0.0141(5)	0.0203(5)	0.0204(5)	0.0095(4)	0.0017(4)	-0.0002(4)
C(22)	0.2572(1)	0.1108(1)	0.4127(1)	0.0149(5)	0.0172(5)	0.0230(5)	0.0071(4)	0.0038(4)	0.0037(4)
C(23)	0.2913(2)	0.0345(1)	0.1954(1)	0.0226(6)	0.0146(5)	0.0244(6)	0.0090(4)	-0.0024(4)	-0.0046(4)
C(31)	0.7371(1)	0.6763(1)	0.2842(1)	0.0126(5)	0.0187(5)	0.0203(5)	0.0033(4)	0.0023(4)	-0.0003(4)
C(32)	0.4360(2)	0.7185(1)	0.3220(1)	0.0213(5)	0.0137(5)	0.0184(5)	0.0085(4)	0.0033(4)	0.0010(4)
C(33)	0.4460(2)	0.6352(1)	0.1066(1)	0.0180(5)	0.0181(5)	0.0159(5)	0.0047(4)	0.0031(4)	0.0025(4)
O(11)	-0.0454(2)	0.5449(2)	0.1200(1)	0.0391(9)	0.0285(7)	0.0342(8)	0.0254(7)	0.0011(6)	0.0035(6)
O(12)	-0.2578(2)	0.0017(2)	0.1964(1)	0.0211(7)	0.0173(6)	0.0423(9)	-0.0021(6)	0.0094(6)	-0.0027(6)
O(13)	0.1428(2)	0.4223(2)	0.4714(1)	0.0236(7)	0.0350(7)	0.0170(6)	0.0127(6)	0.0025(5)	-0.0043(5)
O(14)	0.1669(2)	0.2056(2)	-0.0245(1)	0.0301(7)	0.0340(7)	0.0161(6)	0.0194(6)	0.0029(5)	-0.0025(5)
O(21)	0.7338(2)	0.2241(2)	0.3995(1)	0.0171(6)	0.0363(8)	0.0318(7)	0.0167(6)	0.0006(5)	0.0000(6)
O(22)	0.1845(2)	0.0427(2)	0.4844(1)	0.0224(7)	0.0294(7)	0.0290(7)	0.0092(6)	0.0100(6)	0.0121(6)
O(23)	0.2399(2)	-0.0817(2)	0.1301(1)	0.0414(9)	0.0220(7)	0.0343(8)	0.0148(7)	-0.0087(7)	-0.0125(6)
O(31)	0.8895(2)	0.7534(2)	0.3013(1)	0.0129(6)	0.0312(7)	0.0294(7)	0.0028(6)	0.0026(5)	-0.0012(6)
O(32)	0.4099(2)	0.8173(2)	0.3667(1)	0.0360(8)	0.0225(6)	0.0273(7)	0.0189(6)	0.0066(6)	-0.0004(5)
O(33)	0.4255(2)	0.6837(2)	0.0193(1)	0.0313(8)	0.0325(7)	0.0188(7)	0.0110(6)	0.0035(6)	0.0089(6)

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[a] X, Y and Z are fractional coordinates.

[b] Anisotropic temperature factors of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \cdots + 2a^*b^*U_{12}hk + \cdots)]$.

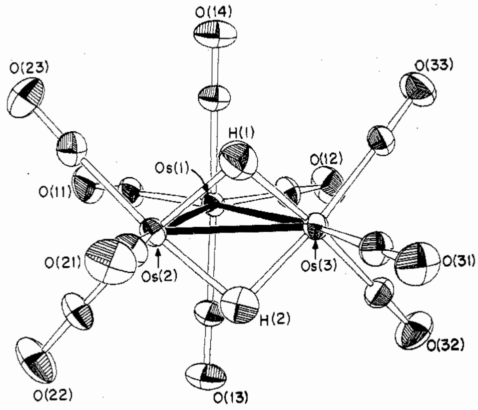


Figure 1. Drawing of the molecular configuration of $(\mu\text{-H})_2Os_3(CO)_{10}$ determined by neutron diffraction at 110 K showing the atom labeling scheme (carbon atoms in each carbonyl ligand carry the same atom label number as the oxygen atom). The ellipsoids of thermal motion for all atoms are scaled to enclose 50% probability. The two hydrogen atoms were found to symmetrically bridge the Os(2)–Os(3) bond with an average osmium–hydrogen bond distance of 1.845 (3) Å.

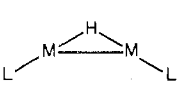
Table III. Interatomic Distances (Å) for $(\mu\text{-H})_2Os_3(CO)_{10}$[a,b]

(A) Metal–Metal Distances			
Os(1)–Os(2)	2.815 (1)	Os(2)–Os(3)	2.683 (1)
Os(1)–Os(3)	2.814 (1)		
	2.814 (1)		
(B) Metal–Hydrogen and Hydrogen–Hydrogen Distances			
Os(2)–H(1)	1.840 (3)	H(1)···H(2)	2.376 (3)
Os(3)–H(1)	1.843 (3)		
Os(2)–H(2)	1.845 (3)		
Os(3)–H(2)	1.852 (3)		
	1.845 (3)		
(C) Metal–Carbon and Carbon–Oxygen Distances			
Os(1)–C(11)	1.920 (1)	C(11)–O(11)	1.143 (2)
Os(1)–C(12)	1.926 (1)	C(12)–O(12)	1.139 (2)
	1.923 (3)		1.141 (2)
Os(1)–C(13)	1.951 (1)	C(13)–O(13)	1.147 (2)
Os(1)–C(14)	1.950 (1)	C(14)–O(14)	1.146 (2)
	1.950 (1)		1.146 (1)
Os(2)–C(21)	1.924 (1)	C(21)–O(21)	1.138 (2)
Os(3)–C(31)	1.941 (1)	C(31)–O(31)	1.134 (2)
	1.932 (8)		1.136 (2)
Os(2)–C(22)	1.912 (1)	C(22)–O(22)	1.142 (2)
Os(2)–C(23)	1.907 (1)	C(23)–O(23)	1.143 (2)
Os(3)–C(32)	1.898 (1)	C(32)–O(32)	1.144 (2)
Os(3)–C(33)	1.904 (1)	C(33)–O(33)	1.144 (2)
	1.905 (3)		1.143 (1)

[a] Eds's of the last significant figure were calculated from the variance–covariance matrix using the Busing–Martin–Levy program ORFFE3. [b] Error estimates of the precision of the average value, $\bar{d}$, were calculated from the equation $[\Sigma_n(\bar{d} - d)^2/(n^2 - n)]^{1/2}$.

atoms are 2.73 Å [H(1)···O(33)], 2.81 Å [H(1)···H(2)], and 3.05 Å [H(2)···O(13)]. Aspects of the metal–carbonyl bonding, which are summarized in Tables III and IV, are discussed in detail in the X-ray studies.[4]

Bridging Hydride Ligands. The unique features of this study deal with the metal–hydrogen interactions in $(\mu\text{-H})_2Os_3(CO)_{10}$. Shown in Figure 4 is the $(\mu\text{-H})_2Os_2(CO)_4$ fragment which is composed of two edge-bridged $OsH_2(CO)_2$ planes. The entire fragment is nonplanar and is folded along the H···H vector with a dihedral angle of 137.6° between the two $OsH_2(CO)_2$ planes. Both hydrogen atoms symmetrically bridge the Os(2)–Os(3) bond with the largest amplitude of thermal vibration perpendicular to the metal–metal bond. The four separate osmium–hydrogen bond lengths are essentially equivalent with a mean value of 1.845 (3) Å, which may be compared with the average Os–H (bridging) bond distance of 1.820 Å in the neutron diffraction study of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$[13a] and of 1.87 Å in the X-ray diffraction study of $(\mu\text{-H})HOs_3(CO)_{10}(PPh_3)$.[13b] All of these distances are approximately 0.2 Å longer than the Os–H (terminal) bond distances of 1.644 (3)–1.681 (3) Å in $H_4Os(PMe_2Ph)_3$.[14] As illustrated in Figure 3, the H–Os–H angles are slightly acute while the Os–H–Os angles are slightly obtuse. Although it can be difficult to distinguish between a single-minimum and a double-minimum potential well in M–H–M systems from structural data alone,[15,16b] the size, shape, and orientations of the hydrogen thermal ellipsoids and the equivalency of the four osmium–hydrogen bond distances in $(\mu\text{-H})_2Os_3(CO)_{10}$ point



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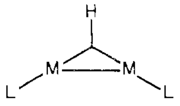

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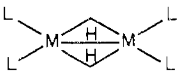


III

clearly to single-minimum potential wells for both bridging hydrogen atoms in the solid state at 110 K.

Comparison with Other M–H–M Bridged Systems. To a first approximation bridging hydrogen positions are often predicted to lie at the intersection of two ligand–metal vectors, i.e., to occupy regular metal coordination sites of type I.[17] Recent neutron diffraction studies of $(\mu\text{-H})W_2(CO)_9(NO)$[18] and the $[(\mu\text{-H})Cr_2(CO)_{10}]^-$ monoanion[19] indicate that the bridging hydrogen atoms in these compounds are displaced from the predicted positions with the ligand–metal vectors pointing toward the center of the MHM triangle. By analogy with B–H–B bridge bonding concepts, these results have been interpreted as evidence for a closed three-center electron-pair interaction of type II, in which there is appreciable metal–metal overlap. In direct contrast to these monobridged species, the two hydrogen atoms in the dibridged $(\mu\text{-H})_2Os_3(CO)_{10}$ compound are displaced *toward* the metal–metal vector in positions represented by type III. Thus, the predicted Os(2)–H(1)–Os(3) and Os(2)–H(2)–Os(3) angles based on a type I model are 81.4 and 80.1°, while the observed angles are 95.5 (1) and 93.1 (1)°.

The reason for this inward displacement is not readily apparent. If the hydrogen atoms were forced inward due to steric crowding from adjacent carbonyl ligands, then we would expect to observe acute H–Os–CO(cis) angles and obtuse CO–Os–CO angles within the folded $H_2Os_2(CO)_4$ moiety. However, as shown in Figure 3, the opposite case exists here. Furthermore, the possibility of an attractive H···H interaction is not likely in view of the long H···H distance of 2.376 (3) Å. Therefore, it is our opinion that the geometry of the Os_2H_2 moiety is due to the constraints of the Os–Os and Os–H bond distances. That is, the hydrogen atoms adopt positions in which nuclear repulsive forces, metal–metal overlap, and metal–hydrogen overlap are most favorably balanced. Churchill, Hollander, and Hutchinson[4a] estimate the Os–H (bridging) distance would be approximately 2.05 Å if the hydrogen atoms in $(\mu\text{-H})_2Os_3(CO)_{10}$ were in positions corresponding to I above. However, as they have observed, this distance is unreasonably long when compared with other metal–hydrogen (bridging) distances[13–19] and would result in a significant decrease in the metal–hydrogen orbital overlap. Clearly, on the basis of coordination geometries for the nonhydrogen ligands alone, and without accurate metal–hydrogen distances from neutron diffraction studies, it is difficult to correctly predict the geometry of M–H–M systems.

The Four-Center, Four-Electron Bond. In the three structural studies of compounds with two μ-hydrido ligands bridging a pair of metal atoms $[(\mu\text{-H})_2Os_3(CO)_{10}$, $(\mu\text{-H})_2Re_2(CO)_8$,[16a] and $(\mu\text{-H})_2W_2(CO)_8{}^{2-}$ [16b]], the bridged metal–metal distances are all less than metal–metal single-bond distances. Churchill, DeBoer, and Rotella[20] have suggested that bis(μ-hydrido)-bridged species can be considered doubly protonated double bonds.

On the basis of the simple qualitative LCAO molecular orbital treatment for $(\mu\text{-H})_2Os_3(CO)_{10}$ presented here (vide infra), we prefer to describe the Os_2H_2 moiety in terms of a four-center, four-electron bond. A total of 46 electrons (8 from each osmium atom, 2 from each carbonyl ligand, and 1 from each hydrogen atom) must be accounted for in the cluster bonding. Three atomic orbitals on each osmium atom are assumed to form nine nonbonding (or weakly bonding and antibonding) molecular orbitals under C_{2v} symmetry which are all fully occupied. Using the remaining six atomic orbitals on each osmium atom we may then construct six hybridized sp^3d^2 octahedral atomic orbitals at each metal atom. Although this formalism is in agreement with the approximately octahedral coordination about each Os atom, it is adopted for conceptual purposes only, since in this way metal–carbonyl, metal–metal, and metal–hydrogen interactions are conveniently separated. Ten of these eighteen orbitals are used for metal–carbonyl σ bonding [four on Os(1) and three each on Os(2) and Os(3)]. Linear combinations of the two remaining hybridized orbitals on Os(1), with one hybridized orbital from each of Os(2) and Os(3), form metal–metal bonding and antibonding combinations. Filling the bonding combinations only gives formal bond orders of 1 for the two long edges of the osmium triangle. The observed mean length of 2.814 (1) Å for these two distances is at the lower end of the range of 2.819 (1)–2.917 (1) Å observed for single-bond metal–metal distances in other triosmium clusters[21,22] and is therefore consistent with the predicted bond order of 1.

Table IV. Interatomic Angles (deg) for $(\mu\text{-H})_2Os_3(CO)_{10}$

(A) Osmium–Osmium–Osmium Angles			
Os(1)–Os(2)–Os(3)	61.51 (2)	Os(2)–Os(1)–Os(3)	56.93 (4)
Os(1)–Os(3)–Os(2)	61.56 (2)		
(B) Osmium–Osmium–Hydrogen Angles			
Os(1)–Os(2)–H(1)	82.34 (9)	Os(2)–Os(3)–H(1)	43.18 (8)
Os(1)–Os(2)–H(2)	81.89 (8)	Os(2)–Os(3)–H(2)	43.36 (7)
Os(1)–Os(3)–H(1)	82.32 (9)	Os(3)–Os(2)–H(1)	43.28 (8)
Os(1)–Os(3)–H(2)	81.80 (8)	Os(3)–Os(2)–H(2)	43.58 (8)
(C) Osmium–Hydrogen–Osmium Angles			
Os(2)–H(1)–Os(3)	95.54 (12)	Os(2)–H(2)–Os(3)	93.06 (11)
(D) Hydrogen–Osmium–Hydrogen Angles			
H(1)–Os(2)–H(2)	80.32 (11)	H(1)–Os(3)–H(2)	80.03 (11)
(E) Hydrogen–Osmium–Carbon Angles			
H(1)–Os(2)–C(21)	90.00 (9)	H(1)–Os(2)–C(23)	93.40 (9)
H(1)–Os(3)–C(31)	88.32 (9)	H(1)–Os(3)–C(33)	96.22 (9)
H(2)–Os(2)–C(21)	87.96 (9)	H(2)–Os(2)–C(22)	95.52 (9)
H(2)–Os(3)–C(31)	90.62 (9)	H(2)–Os(3)–C(32)	95.34 (9)
H(1)–Os(2)–C(22)	173.41 (9)		
H(1)–Os(3)–C(32)	173.76 (9)		
H(2)–Os(2)–C(23)	173.31 (9)		
H(2)–Os(3)–C(33)	172.78 (9)		
(F) Osmium–Osmium–Carbon Angles			
Os(2)–Os(1)–C(11)	154.68 (5)	Os(2)–Os(1)–C(12)	107.80 (4)
Os(3)–Os(1)–C(12)	164.69 (5)	Os(3)–Os(1)–C(11)	97.75 (4)
Os(2)–Os(1)–C(13)	83.65 (4)	Os(1)–Os(2)–C(22)	92.05 (4)
Os(2)–Os(1)–C(14)	82.62 (4)	Os(1)–Os(2)–C(23)	95.04 (4)
Os(3)–Os(1)–C(13)	83.57 (4)	Os(1)–Os(3)–C(32)	92.93 (4)
Os(3)–Os(1)–C(14)	85.96 (4)	Os(1)–Os(3)–C(33)	91.61 (4)
Os(1)–Os(2)–C(21)	168.16 (5)	Os(2)–Os(3)–C(31)	107.35 (5)
Os(1)–Os(3)–C(31)	168.83 (5)	Os(3)–Os(2)–C(21)	106.81 (4)
Os(2)–Os(3)–C(32)	130.78 (5)		
Os(2)–Os(3)–C(33)	130.42 (5)		
Os(3)–Os(2)–C(22)	130.65 (5)		
Os(3)–Os(2)–C(23)	129.77 (5)		
(G) Carbon–Osmium–Carbon Angles			
C(11)–Os(1)–C(12)	97.52 (6)	C(13)–Os(1)–C(14)	165.81 (6)
C(11)–Os(1)–C(13)	94.70 (5)	C(21)–Os(2)–C(22)	94.98 (5)
C(11)–Os(1)–C(14)	96.18 (5)	C(21)–Os(2)–C(23)	94.41 (6)
C(12)–Os(1)–C(13)	94.12 (5)	C(31)–Os(3)–C(32)	95.95 (5)
C(12)–Os(1)–C(14)	93.46 (5)	C(31)–Os(3)–C(33)	95.47 (5)
C(22)–Os(2)–C(23)	90.51 (6)		
C(32)–Os(3)–C(33)	87.92 (5)		
(H) Osmium–Carbon–Oxygen Angles			
Os(1)–C(11)–O(11)	179.6 (1)	Os(2)–C(21)–O(21)	177.6 (1)
Os(1)–C(12)–O(12)	176.1 (1)	Os(3)–C(31)–O(31)	177.8 (1)
Os(1)–C(13)–O(13)	179.0 (1)	Os(2)–C(22)–O(22)	177.0 (1)
Os(1)–C(14)–O(14)	178.4 (1)	Os(2)–C(23)–O(23)	176.8 (1)
		Os(3)–C(32)–O(32)	178.4 (1)
		Os(3)–C(33)–O(33)	178.9 (1)

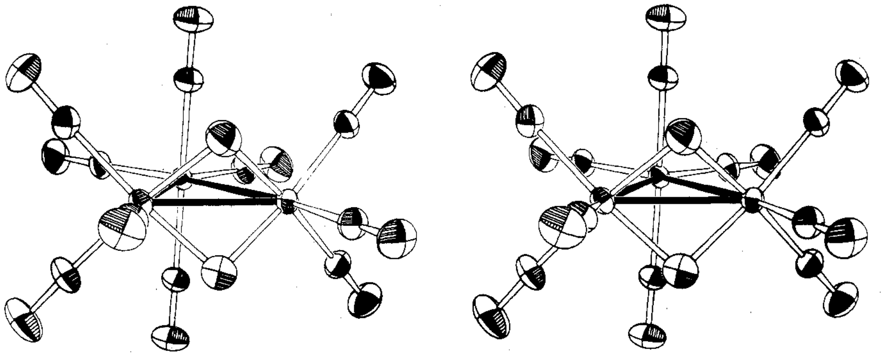
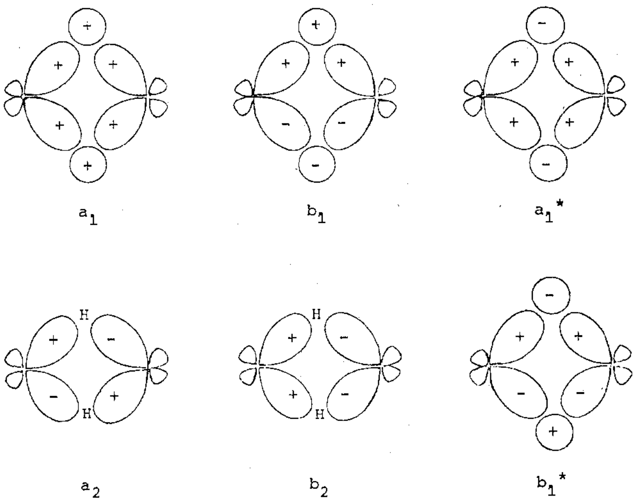


Figure 2. Stereoscopic drawing of the molecular configuration of $(\mu\text{-H})_2Os_3(CO)_{10}$. The geometry about each osmium atom is approximately octahedral. The entire molecule closely conforms to idealized C_{2v} symmetry.

Chart I



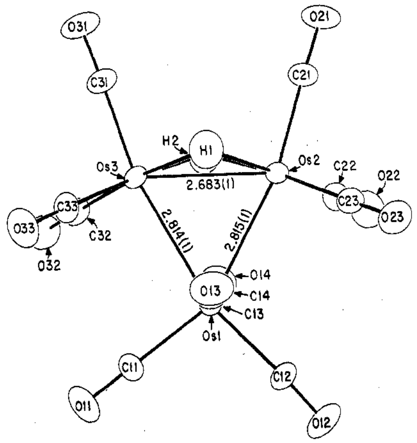


Figure 3. View of the $(\mu\text{-H})_2Os_3(CO)_{10}$ molecule normal to the triosmium plane showing the isosceles triangle of osmium atoms with one short and two long bond distances.

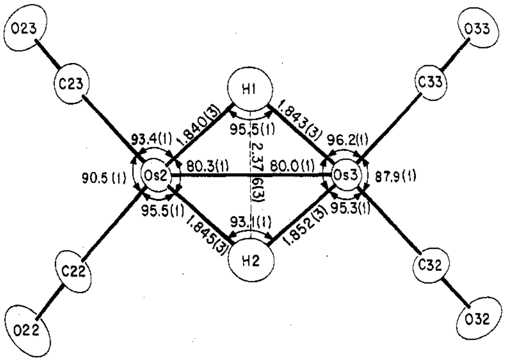


Figure 4. The $(\mu\text{-H})_2Os_2(CO)_4$ fragment of $(\mu\text{-H})_2Os_3(CO)_{10}$. The fragment is folded along the H···H vector with a dihedral angle of 137.6° between the two $H_2Os(CO)_2$ square planes. The positions of two hydrogen atoms are displaced from the intersection of the trans-CO-metal vectors *toward* the metal–metal bond.

The four remaining octahedral hybrids on Os(2) and Os(3) are directed toward the two bridging hydrogen atoms. Linear combination under C_{2v} symmetry of these four orbitals and the two H 1s orbitals produces the set of six four-center molecular orbitals shown in Chart I.[23]

The a_1 and b_1 molecular orbitals are filled with the remaining four cluster electrons forming a four-center, four-electron bond. Since both orbitals are metal–metal bonding, this accounts for the short Os(2)–Os(3) bond distance of 2.683 (1) Å.

The qualitative bonding model presented here is consistent with the observed structural parameters. Mason and Mingos[24] have derived a qualitative bonding model for mono- and dihydrido-bridged metal–metal bonds for which the metal–metal bonding orbitals in $(\mu\text{-H})_2Os_3(CO)_{10}$ are predicted to be of σ- and π-type symmetry. In this scheme, some metal–metal bonding electron density is localized directly between the two metals,[25] which is possibly a more accurate prediction of the actual location of the bonding electrons in view of the short Os–Os distance. The true directional nature of the orbitals involved in the metal–metal bonding could be more clearly ascertained from a more quantitative molecular orbital calculation.

Reaction Mechanisms. It is worthwhile to consider possible reaction mechanisms for $(\mu\text{-H})_2Os_3(CO)_{10}$ based on the above bonding model. Much of the chemistry of the triosmium compound is dominated by nucleophilic addition of two-electron-donor ligands,[3,27] which should depend on the nature of the lowest unoccupied molecular orbital (LUMO). Although the simple treatment described here cannot unambiguously assign this orbital, it is not unreasonable to assume the LUMO will be one of the unoccupied Os_2H_2 four-center molecular orbitals. If this is true, then nucleophilic addition will place two electrons in either the metal–hydrogen nonbonding a_2 or b_2 orbitals or the metal–hydrogen antibonding a_1* or b_1* orbitals. In either case the M–H–M bridge will be destabilized and at least one hydrogen may become ter-

Table V. Mean Planes and Interplanar Angles for $(\mu\text{-H})_2Os_3(CO)_{10}$

(A) Planes[a] and Perpendicular Distances (Å) of Selected Atoms from These Planes

1. Plane through Os(1), Os(2), and Os(3)

$$0.3284X - 0.1405Y - 0.9340Z + 2.8399 = 0$$

H(1)	1.18	H(2)	−1.20
C(11)	0.02	O(11)	0.02
C(12)	−0.04	O(12)	−0.07
C(13)	−1.94	O(13)	−3.07
C(14)	1.93	O(14)	3.07
C(21)	−0.07	O(21)	−0.13
C(22)	−1.32	O(22)	−2.15
C(23)	1.39	O(23)	2.26
C(31)	0.05	O(31)	0.09
C(32)	−1.32	O(32)	−2.14
C(33)	1.32	O(33)	2.11

2. Plane through Os(2), Os(3), and H(1)

$$-0.7523X - 0.2591Y - 0.6057Z + 3.7856 = 0$$

Os(1)	2.31	H(2)	−0.83
C(21)	−1.74	O(21)	−2.77
C(22)	0.09	O(22)	0.11
C(23)	0.93	O(23)	1.48
C(31)	−1.72	O(31)	−2.70
C(32)	0.05	O(32)	0.09
C(33)	1.04	O(33)	1.67

3. Plane through Os(2), Os(3), and H(2)

$$0.9858X + 0.1633Y - 0.0392Z - 1.8383 = 0$$

Os(1)	−2.33	H(1)	0.82
C(21)	1.71	O(21)	2.70
C(22)	−1.01	O(22)	−1.61
C(23)	0.02	O(23)	0.08
C(31)	1.76	O(31)	2.78
C(32)	−0.97	O(32)	−1.58
C(33)	−0.13	O(33)	−0.22

4. Plane through H(1), H(2), Os(2), C(22), and C(23)

$$-0.9199X + 0.1289Y - 0.3704Z + 2.6397 = 0$$

H(1)	0.04	Os(1)	2.74
H(2)	−0.01	Os(3)	0.90
Os(2)	−0.05	C(21)	−1.97
C(22)	0.03	O(22)	0.07
C(23)	−0.01	O(23)	0.01

5. Plane through H(1), H(2), Os(3), C(32), and C(33)

$$-0.8044X - 0.5623Y - 0.1919Z + 3.8283 = 0$$

H(1)	0.00	Os(1)	2.72
H(2)	0.03	Os(2)	0.92
Os(3)	−0.07	C(31)	−2.01
C(32)	0.00	O(32)	0.06
C(33)	0.03	O(33)	0.12

(B) Angles (deg) between Normals to the Planes

	plane				
plane	1	2	3	4	5
1		69.2	70.3	88.5	89.7
2			40.5	28.0	29.9
3				29.4	28.7
4					42.4

[a] The equations of the planes are given in an orthogonal angstrom coordinate system (X, Y, Z) which is related to the fractional unit cell coordinate system (x, y, z) as follows: $X = xa + yb \cos\gamma + zc \cos\beta$, $Y = yb \sin\gamma + zc \cos\mu$, $Z = zc \cos\sigma$, where $\cos\mu = (\cos\alpha - \cos\beta \cos\gamma)/\sin\gamma$ and $\cos\sigma = (1 - \cos^2\beta - \cos^2\mu)^{1/2}$; all atoms are assigned unit weights.

minally bonded. Shapley, Churchill, and co-workers[13b,27] have shown that adducts of $(\mu\text{-H})_2Os_3(CO)_{10}$, namely, $H_2Os_3(CO)_{10}L$ (L = CO, CNMe, PPh_3, PMe_2Ph, $AsMe_2Ph$), each contain one terminal and one bridged hydride ligand in the solid state. Although the structures are fluxional in solution, undergoing mutual exchange of bridging and terminal positions, with a proposed intermediate containing two terminally bound hydrogen atoms,[27] the solid-state structures are in agreement with our bonding model.

Note Added in Proof: Since the submission of this paper a combined X-ray and neutron diffraction structure study of $(\mu\text{-H})_2Os_3(CO)_{10}$ has appeared: A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 723 (1978). Although no coordinates were given, the bond distances etc. agree with the results reported herein.

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Registry No. $(\mu\text{-H})_2Os_3(CO)_{10}$, 41766-80-7.

Supplementary Material Available: A listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(10) The computer programs which were used in performing necessary calculations, with their accession names in the "World List of Crystallographic Computer Programs" (3rd ed.), are as follows: data reduction and absorption correction, DATALIB; data averaging and sort, DATASORT; Fourier summation, FORDAP; least-squares refinement, ORXFLS3; error analysis of distances and angles, ORFFE3; structural drawings, ORTEPII.

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Interaction of Hydrogen and Hydrocarbons with Transition Metals. Neutron Diffraction Study of the Crystal and Molecular Structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$

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The crystal and molecular structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ has been determined by using single-crystal neutron diffraction. The complex crystallizes in the orthorhombic space group $Pn2_1a$ with lattice parameters at 110 K of a = 18.502 (9), b = 10.096 (5), and c = 8.763 (4) Å. The molecule consists of a triangular array of Os atoms with one nonbridged edge (Os–Os = 2.855 (3) Å), one edge bridged by a single hydride (Os–Os = 3.053 (3) Å), and a third edge doubly bridged by a hydride atom and a methylene ligand (Os–Os = 2.824 (3) Å). The complex contains no terminal hydride ligands. The methylene carbon atom has a distorted tetrahedral geometry with an Os–C–Os angle of 82.1 (1)° and a H–C–H angle of 106.0 (8)°.

Introduction

The reaction between diazomethane and $(\mu\text{-H})_2Os_3(CO)_{10}$, the neutron diffraction structure of which is presented in the preceding paper in this issue,[2] yields a product for which the two tautomers $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)$ and $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ exist in equilibrium in solution, based on variable-temperature ^1H and ^{13}C NMR evidence.[3] This was the first direct observation of the interconversion between methyl and methylene ligands. We have previously reported[4] the neutron diffraction structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ using a crystal obtained from the reaction of CH_2N_2 with fully deuterated $(\mu\text{-D})_2Os_3(CO)_{10}$, in which the H/D isotope distribution among the four hydrogen atomic sites was determined. These studies are of particular interest because of the possible relevance of metal cluster complexes as models for catalytically active metal surfaces.[5]

In the neutron diffraction study of partially deuterated $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$,[4] the small size of the crystal coupled with a scattering cancellation from certain hydrogen sites due to a specific H/D isotope ratio resulted in a somewhat imprecise determination of certain hydrogen positions. In fact, the location of one of the hydride ligands could only be inferred from the geometry of the rest of the molecule. A high-precision structural study of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ is important for at least three reasons: (1) Metal–carbene complexes have been postulated as intermediates in many catalytic reaction sequences.[6] Since only two other complexes with bridging methylene ligands have been structurally characterized,[7,8] additional structural data is required in order to provide a better understanding of their structure and bonding. (2) We are afforded the opportunity of comparing the structural parameters of two different bridging hydrido ligands in the same cluster complex. (3) We can accurately compare the neutron diffraction structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ to that of $(\mu\text{-H})_2Os_3(CO)_{10}$[2] and determine which bonding models, if any, correctly predict their geometries. Since we were fortunate in growing large crystals which are fully protonated, we report the results of a single-crystal neutron diffraction study of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ herein.

Experimental Section

Neutron Data Collection. The reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ and CH_2N_2 in methylene chloride slowly yields crystals of the less soluble methylene tautomer at −2 °C.[3] A crystal of the title compound having dimensions 2.1 × 2.1 × 0.9 mm and weighing 14 mg was selected and sealed in a lead-glass capillary. With the crystal mounted in an arbitrary orientation and cooled to ~110 K with a nitrogen cold stream,[9,10] all neutron diffraction data were collected using the computer-controlled diffractometer at the CP-5 reactor at Argonne National Laboratory. The unit cell dimensions (see Table I) were obtained from a least-squares refinement of the angular settings of 14 automatically centered reflections ($40° \leq 2\theta \leq 60°$).

One octant ($+h$, $+k$, $+l$) of neutron data was measured out to $(\sin \theta)/\lambda = 0.62$ Å^{-1} using the θ–2θ step–scan mode with 0.1° steps. The instrumentation and data collection techique have been described elsewhere.[11] A set of F_o^2 values, where F_o is the observed structure factor amplitude, was obtained by applying Lorentz and absorption corrections to the data.[12] Reflections with net intensities less than zero were assigned F_o^2 values of zero. The variance of each F_o^2 was calculated from standard counting statistics with an added factor of $(0.05F_o^2)^2$ based on the 5% maximum variation of two reference reflections which were measured periodically throughout the data collection.

Solution and Refinement of the Structure. Initial nonhydrogen atom positional coordinates were obtained from the neutron structural solution of the partially deuterated compound.[4] The four hydrogen atoms were located on a Fourier map with phases determined from the refined coordinates of the nonhydrogen atoms. In the final stages of least-squares refinement,[13,14] the data were corrected for secondary

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