2.435 (3) Å, slightly shorter than those in the metallacarboranes in this study. The analogy between this species and the boron cages is strengthened by the fact that the three equatorial C–C bond lengths are identical within experimental error [mean value 1.45 (2) Å], suggesting considerable electron delocalization. Moreover, the molecule is isoelectronic, in terms of electrons involved in bonding the Fe_3C_4 skeleton together, with the $FeCoC_2B_3$ and $Co_2C_2B_3$ systems in the present investigation. All three molecules formally contain 16 skeletal valence electrons and thus are $(2n + 2)$-electron cages, in conformity with the well-known structural correlation originated by Wade.[23] A recently reported tetrametallic cluster, $(\eta^5\text{-}C_5H_5)NiRu_3(CO)_8(C_6H_9)$, is also a 7-vertex pentagonal-bipyramidal 16-electron cage, in which two ruthenium atoms occupy the apices while the remaining two metals are in vicinal positions in the equator.[24]

Among the family of 6-vertex nido clusters is $(CO)_5Co_2(C_8H_{12})_2$,[25] whose central core is a Co_2C_4 pyramid with a cobalt in the apex. The Co–Co distance of 2.4738 (7) Å and average framework C–C distance of 1.423 (2) Å compare closely with those in the metallacarboranes reported here. Several other 6-vertex pyramidal clusters contain an Fe_2C_4 core and were derived from an iron carbonyl and a cycloalkyne;[26] each has an apical and a basal iron atom, and the Fe–Fe bond lengths range from 2.46 to 2.54 Å with basal C–C distances around 1.42 Å, closely comparable to the clusters described above. All of these species are formal 16-electron cage systems whose nido geometry is in accord with electron-counting procedures.[23] Such comparisons emphasize the close relationship which exists among the different types of clusters, often overlooked because of their widely varying synthetic origins.

Acknowledgment. This work was supported by the National Science Foundation, Grant CHE 79-09948.

Registry No. $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$, 60569-32-6; $(\eta^5\text{-}C_5H_5)_2CoFe(H)(CH_3)_2C_2B_3H_3$, 64091-68-5.

Supplementary Material Available: Listings of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 16.[1-6] Crystal Structure of $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ and a Comparison of the Hinged $Os(\mu\text{-H})_2Os$, $Os(\mu\text{-H})(\mu\text{-OMe})Os$, and $Os(\mu\text{-OMe})_2Os$ Bridges in Trinuclear $(\mu\text{-H})_n(\mu\text{-OMe})_{2-n}Os_3(CO)_{10}$ (n = 0–2) Complexes

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The complex $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 7.4156 (15) Å, b = 26.932 (11) Å, c = 8.9941 (22) Å, β = 106.325 (18)°, V = 1723.8 (9) Å^3, and ρ(calcd) = 3.40 g cm^{-3} for mol wt = 882.59 and Z = 4. Diffraction data were collected with a Syntex P2$_1$ diffractometer and the structure was solved and refined via a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement techniques. The final discrepancy indices are R_F = 5.1% and R_{wF} = 3.4% for 2243 independent reflections with 3.5° < 2θ < 45° [Mo Kα radiation]. The molecule contains a triangular arrangement of osmium atoms in which atom Os(2) is linked to four terminal carbonyl ligands; atoms Os(1) and Os(3) are each linked to three terminal carbonyl and are bridged by a μ-hydride and a μ-methoxide ligand. The nonbridged osmium–osmium bond lengths (Os(1)–Os(2) = 2.8130 (12) Å, Os(2)–Os(3) = 2.8221 (10) Å) are not distinguishable from the μ-hydrido-μ-methoxy-bridged Os–Os distance (2.8120 (11) Å). Important distances and angles within the $Os(\mu\text{-H})(\mu\text{-OMe})Os$ bridge are as follows: Os(1)–O(B) = 2.112 (9) Å, Os(3)–O(B) = 2.093 (9) Å, Os(1)–O(B)–Os(3) = 83.9 (2)°; Os(1)–H(Os) = 1.93 (11) Å, Os(3)–H(Os) = 1.84 (11) Å, Os(1)–H(Os)–Os(3) = 96 (5)°. The geometry of the $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ molecule is compared to that of the species $(\mu\text{-H})_2Os_3(CO)_{10}$ and $(\mu\text{-OMe})_2Os_3(CO)_{10}$.

Introduction

Some years ago Mason and co-workers provided an interesting comparison of the structural geometry of the species $(\mu\text{-H})_2Os_3(CO)_{10}$, $(\mu\text{-H})(\mu\text{-SEt})Os_3(CO)_{10}$, and $(\mu\text{-OMe})_2Os_3(CO)_{10}$. It was explicitly indicated that "electron deficient" hydrido species were associated with formal metal–metal bonds, whereas the "electron precise" di-μ-methoxy complex required no metal–metal bond.[7-9] The details of the Mason–Mingos symmetry-based model[8] have been challenged by semiquantitative calculations of Teo et al.,[10] but the net formal bond orders of 2 for the $Os(\mu\text{-H})_2Os$ system (**1**) in $(\mu\text{-H})_2Os_3(CO)_{10}$, 1 for the $Os(\mu\text{-H})(\mu\text{-SEt})Os$ system (**2**) in

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(1) For recent parts in this series see ref 2–6.

(2) Part 15, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$: Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Keister, J. B. *Inorg. Chem.* **1980**, *19*, 1272–1277.

(3) Part 14, $(\mu\text{-H})_4Os_4(CO)_{11}(CNMe)$: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1980**, *19*, 306–310.

(4) Part 13, $(\mu\text{-H})(\mu\text{-Br})Os_3(CO)_{10}$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 3261–3267.

(5) Part 12, $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 1926–1930.

(6) Part 11, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH=NEt}_2)$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 848–853.

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0020-1669/80/1319-2391$01.00/0

Table I. Experimental Data for the X-ray Diffraction Study

(A) Crystal Parameters[a] at 24 °C

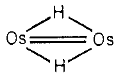
cryst system: monoclinic
space group: $P2_1/n$[b]
$a = 7.4156\ (15)$ Å
$b = 26.932\ (11)$ Å
$c = 8.9941\ (22)$ Å
$\beta = 106.325\ (18)°$
$V = 1723.8\ (9)$ Å^3
$Z = 4$
mol wt = 882.59
ρ(calcd) = 3.40 g cm^{-3}

(B) Measurement of Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite, equatorial
reflctns measd: $+h, +k, \pm l$
2θ range: 3.5–45.0°
scan type: ω
scan speed: 1.50°/min
scan range: 0.9° (0.6° offset from center for bkgd)
reflctns collected: 2932 total, yielding 2243 independent
standards: 3 every 47 reflections; no significant changes in intensity were observed
abs coeff: 234.2 cm^{-1}

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo Kα component of 15 reflections with 2θ between 20 and 30°. [b] Nonstandard setting of space group $P2_1/c$ [C_{2h}^5; No. 14] having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.

$(\mu\text{-H})(\mu\text{-SEt})Os_3(CO)_{10}$, and 0 for the $Os(\mu\text{-OMe})_2Os$ core (3) in $(\mu\text{-OMe})_2Os_3(CO)_{10}$ are common to the two models.



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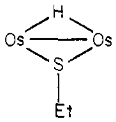
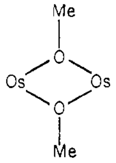


2



3

We have recently reported structural studies on several complexes of the type $(\mu\text{-H})(\mu\text{-L})Os_3(CO)_{10}$ (L = some uninegatively charged ligand) and have shown that the osmium–osmium distance in the $Os(\mu\text{-H})(\mu\text{-L})Os$ system is dependent (at least to some extent) on the nature of the bridgehead atom (X) on the ligand L. Molecules with $Os(\mu\text{-H})(\mu\text{-C})Os$,[6,11] $Os(\mu\text{-H})(\mu\text{-N})Os$,[2] $Os(\mu\text{-H})(\mu\text{-S})Os$,[9,12] $Os(\mu\text{-H})(\mu\text{-Cl})Os$,[5] and $Os(\mu\text{-H})(\mu\text{-Br})Os$[4] systems have been examined either by our research group or by others.

We have now completed a structural study of the simple species $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$. This provides an opportunity to study an $(\mu\text{-H})(\mu\text{-L})Os_3(CO)_{10}$ species containing an $Os(\mu\text{-H})(\mu\text{-O})Os$ bridge. More importantly, however, this study provides the final link so that valid metric comparisons may be made for the series $(\mu\text{-H})_n(\mu\text{-OMe})_{2-n}Os_3(CO)_{10}$ (n = 0–2).

Experimental Section

A. Data Collection. Yellow crystals of $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ were provided by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. Crystals suitable for analysis were obtained by recrystallization from methanol. The crystal selected for the diffraction experiments was of approximately square cross section, 0.09 mm in thickness and 0.13 mm in length. It was mounted with its longest dimension approximately collinear with the thin glass fiber to which it was glued. The fiber was set into a eucentric goniometer head which was transferred to a Syntex P2$_1$ automated diffractometer. Refinement of unit cell parameters, determination of the orientation matrix, and data collection were all carried out as described in an earlier publication;[13] details pertinent to the present investigation appear in Table I.

Diffraction data were reduced to net intensities and their estimated standard deviations ($\sigma_c(I)$). An empirical absorption correction was applied to all data. The intensities of six close-to-axial reflections distributed over the 2θ range used in the data set, and each of fairly high intensity, were measured at 10° intervals around the diffraction vector from $\Psi = 0$ to $\Psi = 360°$. Each reflection defined an absorption curve of intensity vs. ϕ, corrected for ω and χ. The curve(s) bracketing the Bragg angle (2θ) of the intensity datum was interpolated in ϕ (and in 2θ, where appropriate) to correct that reflection for absorption. Reflections used for the absorption curves were $0\bar{3}1$ ($2\theta = 6.55°$), $06\bar{2}$ (13.12°), $0\bar{4}3$ (15.44°), $08\bar{3}$ (18.70°), $0,10,\bar{4}$ (24.36°), and $1,16,\bar{5}$ (33.6°). The values of (maximum intensity)/(minimum intensity) for the six curves were respectively 2.32, 2.10, 2.09, 1.96, 1.95, and 1.73. The curves were all internally consistent, with similar profiles and maxima and minima at common values of ϕ.

Data were then averaged, corrected for Lorentz and polarization factors, converted to $|F_o|$ values, and placed on an approximate absolute scale via a Wilson plot. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$.

B. Solution and Refinement of the Structure. All subsequent calculations were performed on the CDC 6600-Cyber 173 at State University of New York at Buffalo. Programs used during the structural analysis were the following: LSHF (full-matrix least-squares refinement and structure factor calculations, by B. G. DeBoer), JIMDAP (Fourier synthesis, derived from A. Zalkin's FORDAP by J. A. Ibers), STAN1 (distances and angles with esd's, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), HAITCH (hydrogen atom position calculations), and ORTEP II (thermal ellipsoid plotting program, by C. K. Johnson).

Analytical scattering factors for neutral atoms from a compilation by Cromer and Mann[14a] were used along with both real, $\Delta f'$, and imaginary, $\Delta f''$, correction factors for anomalous dispersion which were taken from a listing by Cromer and Liberman.[14b]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weighting scheme was derived from counting statistics and the ignorance factor, p, was set at a value of 0.04.

The positions of the three osmium atoms were obtained from a Patterson synthesis. Refinement of the scale factor and positional and isotropic thermal parameters of the three osmium atoms led to $R_F = 0.139$ and $R_{wF} = 0.159$. The positions of all remaining nonhydrogen atoms were then obtained from a difference-Fourier calculation. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all 25 atoms converged with R = 5.13% and R_{wF} = 3.89%. A difference-Fourier synthesis based on all data failed to provide any useful information about the bridging hydride ligand. However, a ΔF calculation using only those data with $0 < (\sin\theta)/\lambda < 0.30$ Å^{-1} showed a peak of height 0.36 e Å^{-3} close to the position where a μ-bridging hydride was to be expected. Neither calculation yielded any indication of the hydrogen atoms of the bridging OCH_3 moiety. The hydride was included in the model and refined with its isotropic thermal parameter fixed at 2.5 Å^2. The methyl hydrogen atom positions were calculated by assuming an idealized geometry such that one hydrogen atom was staggered with respect to Os(2) and d(C–H) = 0.95 Å.[15] With isotropic thermal parameters fixed at 6.0 Å^2, these hydrogen atoms were refined such that their positional shifts were coupled to those of the carbon atom to which they were attached. Refinement proceeded to convergence with R_F = 5.1%, R_{wF} = 3.4%, and GOF = 1.108.

There was no evidence of secondary extinction. The function $\sum w(|F_o| - |F_c|)^2$ displayed no appreciable dependence upon $(\sin\theta)/\lambda$, $|F_o|$, or Miller indices. The weighting scheme is thus acceptable. A final difference-Fourier synthesis revealed no regions of significant electron density.

Final positional and thermal parameters are listed in Tables II and III.

Description of the Structure

The crystal consists of discrete ordered units of $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ which are separated by normal van der

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(11) Part 2, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH_2PPhMe_2})$: Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 1141–1146.

(12) $[(\mu\text{-H})Os_3(CO)_{10}]_2(\mu\text{-SCH_2S-}\mu)$: Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 1306–1307.

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Table II. Positional and Isotropic Thermal Parameters for $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$[a]

atom	x	y	z	B_{iso}, Å^2
Os(1)	0.20961 (7)	0.10267 (2)	0.12931 (6)	
Os(2)	0.53713 (7)	0.15964 (2)	0.24474 (6)	
Os(3)	0.33329 (7)	0.12573 (2)	0.44677 (7)	
O(B)	0.3395 (12)	0.0595 (3)	0.3264 (10)	
C(1)	0.2480 (24)	0.0143 (6)	0.3567 (20)	
H(Os)	0.118 (15)	0.134 (4)	0.287 (13)	2.50
C(11)	0.1138 (21)	0.1527 (6)	−0.0191 (17)	
O(11)	0.0608 (19)	0.1830 (5)	−0.1089 (15)	
C(12)	−0.0225 (22)	0.0659 (6)	0.0663 (18)	
O(12)	−0.1598 (14)	0.0450 (4)	0.0153 (14)	
C(13)	0.3257 (20)	0.0710 (5)	−0.0050 (17)	
O(13)	0.3968 (15)	0.0518 (5)	−0.0905 (13)	
C(21)	0.5822 (22)	0.1682 (6)	0.0484 (19)	
O(21)	0.6065 (20)	0.1732 (5)	−0.0725 (15)	
C(22)	0.3659 (19)	0.2164 (5)	0.2195 (16)	
O(22)	0.2634 (15)	0.2481 (4)	0.2102 (14)	
C(23)	0.7477 (20)	0.1948 (6)	0.3671 (18)	
O(23)	0.8782 (16)	0.2159 (5)	0.4343 (17)	
C(24)	0.6633 (19)	0.0959 (6)	0.2929 (18)	
O(24)	0.7417 (14)	0.0593 (5)	0.3210 (13)	
C(31)	0.3189 (21)	0.1914 (6)	0.5229 (18)	
O(31)	0.3120 (16)	0.2287 (4)	0.5752 (14)	
C(32)	0.1671 (21)	0.1006 (6)	0.5578 (18)	
O(32)	0.0750 (16)	0.0869 (5)	0.6320 (14)	
C(33)	0.5664 (19)	0.1171 (5)	0.6012 (16)	
O(33)	0.7058 (14)	0.1105 (4)	0.6934 (13)	
H(1)[b]	0.1496	−0.0048	0.3765	6.00
H(2)[b]	0.3567	0.0121	0.4428	6.00
H(3)[b]	0.2761	0.0019	0.2668	6.00

[a] Esd's are right adjusted to the least significant figure of the preceding number. [b] These hydrogen atoms are in their calculated positions.

Waals distances. Figure 1 indicates the atomic labeling scheme. Interatomic distances and their estimated standard deviations (esd's) are collected in Table IV; interatomic angles (with their esd's) are listed in Table V, while principal molecular planes are given in Table VI.

The $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ molecule has approximate C_s symmetry in the solid state. The triosmium core defines a close-to-equilateral triangle. One osmium atom [Os(2)] is linked to four terminal carbonyl ligands, while the other two osmium atoms [Os(1) and Os(3)] are each associated with three terminal carbonyl ligands and are mutually bridged via a hydride ligand [H(Os)] and a methoxide ligand [centered on O(B)].

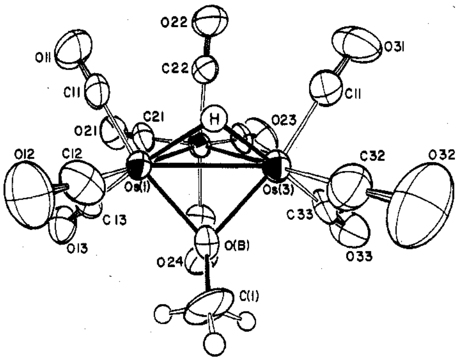

Figure 1. Labeling of atoms within the $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ molecule [ORTEP II diagram; 50% ellipsoids].

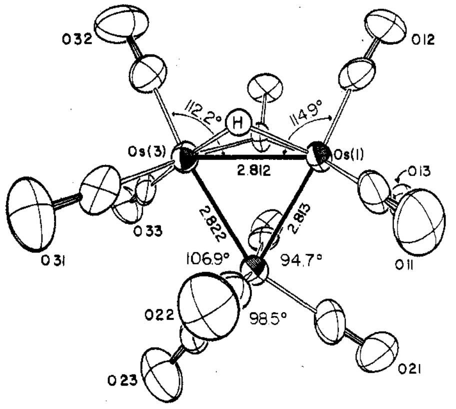

Figure 2. Distances and angles within the equatorial plane of the $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ molecule.

Table III. Anisotropic Thermal Parameters[a] with Esd's for $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	2.79 (3)	2.78 (3)	2.37 (3)	−0.13 (2)	0.26 (2)	−0.10 (2)
Os(2)	2.90 (3)	2.98 (3)	2.93 (3)	−0.35 (2)	0.82 (2)	−0.35 (2)
Os(3)	2.65 (3)	3.51 (3)	2.39 (3)	0.19 (2)	0.58 (2)	−0.30 (2)
O(B)	3.59 (43)	3.33 (49)	1.96 (41)	−0.15 (37)	0.29 (34)	−0.57 (36)
C(1)	6.91 (101)	4.01 (88)	4.97 (97)	−1.90 (76)	1.68 (81)	2.61 (75)
C(11)	4.32 (79)	3.77 (84)	3.04 (77)	−0.59 (66)	−0.10 (62)	−0.74 (69)
O(11)	8.52 (82)	5.51 (72)	5.16 (77)	0.79 (63)	−0.45 (60)	1.97 (61)
C(12)	4.91 (89)	3.80 (83)	4.60 (88)	−0.36 (72)	2.80 (74)	−0.52 (70)
O(12)	4.19 (57)	6.39 (72)	5.99 (71)	−2.54 (54)	1.13 (52)	−1.30 (57)
C(13)	4.44 (79)	2.34 (70)	3.71 (79)	−1.10 (60)	0.58 (65)	−0.16 (61)
O(13)	5.12 (60)	7.20 (77)	3.95 (60)	0.45 (55)	1.16 (50)	−0.95 (55)
C(21)	4.86 (85)	5.68 (104)	3.86 (91)	−0.03 (73)	1.36 (72)	−1.47 (77)
O(21)	10.42 (97)	6.18 (78)	5.47 (75)	−2.02 (66)	4.23 (70)	0.35 (61)
C(22)	3.08 (65)	3.29 (75)	3.34 (73)	−0.32 (55)	0.63 (54)	−0.14 (57)
O(22)	5.44 (64)	4.08 (62)	5.63 (69)	0.96 (52)	0.63 (52)	−0.04 (51)
C(23)	3.58 (77)	5.19 (94)	3.96 (83)	−1.18 (69)	1.48 (64)	−1.80 (71)
O(23)	4.69 (64)	7.65 (83)	9.81 (98)	−1.65 (60)	2.38 (65)	−4.47 (74)
C(24)	2.62 (68)	3.83 (84)	4.74 (86)	0.13 (63)	1.92 (61)	0.10 (68)
O(24)	4.33 (56)	6.89 (78)	5.60 (69)	2.83 (54)	2.06 (49)	1.66 (57)
C(31)	4.72 (84)	5.16 (99)	3.21 (81)	1.19 (75)	1.41 (65)	−0.02 (73)
O(31)	5.63 (65)	5.77 (74)	6.13 (74)	1.95 (56)	−0.11 (53)	−2.91 (62)
C(32)	4.06 (76)	5.10 (91)	3.14 (74)	0.88 (70)	0.99 (63)	0.66 (70)
O(32)	5.67 (68)	10.71 (107)	5.20 (70)	−1.12 (64)	2.69 (57)	2.01 (66)
C(33)	3.29 (74)	4.38 (83)	2.55 (71)	0.21 (62)	1.07 (61)	−1.41 (61)
O(33)	4.15 (56)	5.63 (69)	4.61 (61)	0.19 (49)	−0.88 (49)	−1.18 (51)

[a] The anisotropic thermal parameters have units of Å^2 and enter the expression for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

Table IV. Interatomic Distances (in Å) for $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$ with Esd's

(A) Osmium-Osmium Distances			
Os(1)-Os(2)	2.8130 (12)	Os(1)-Os(3)	2.8120 (11)
Os(2)-Os(3)	2.8221 (10)		
(B) Osmium-(Bridging Ligand) Distances			
Os(1)-O(B)	2.112 (9)	Os(1)-H(Os)	1.93 (11)
Os(3)-O(B)	2.093 (9)	Os(3)-H(Os)	1.84 (11)
(C) Osmium-Carbonyl Distances			
Os(1)-C(11)	1.889 (16)	Os(2)-C(23)	1.892 (15)
Os(1)-C(12)	1.928 (16)	Os(2)-C(24)	1.944 (15)
Os(1)-C(13)	1.874 (16)	Os(3)-C(31)	1.911 (17)
Os(2)-C(21)	1.901 (17)	Os(3)-C(32)	1.915 (15)
Os(2)-C(22)	1.960 (15)	Os(3)-C(33)	1.903 (14)
(D) Carbon-Oxygen Distances in Carbonyl Ligand			
C(11)-O(11)	1.138 (17)	C(23)-O(23)	1.139 (16)
C(12)-O(12)	1.142 (17)	C(24)-O(24)	1.137 (16)
C(13)-O(13)	1.168 (16)	C(31)-O(31)	1.115 (17)
C(21)-O(21)	1.160 (18)	C(32)-O(32)	1.142 (16)
C(22)-O(22)	1.130 (15)	C(33)-O(33)	1.143 (15)
(E) Methoxide Carbon-Oxygen Distances			
C(1)-O(B)	1.456 (16)		

Table V. Interatomic Angles (in Deg) for $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$, with Esd's

(A) Osmium-Osmium-Osmium Angles			
Os(2)-Os(1)-Os(3)	60.23 (3)	Os(1)-Os(3)-Os(2)	59.90 (3)
Os(1)-Os(2)-Os(3)	59.87 (3)		
(B) Angles Involving the Bridging Ligands			
Os(1)-H(Os)-Os(3)	96 (5)	Os(1)-O(B)-Os(3)	83.9 (2)
Os(1)-Os(3)-H(Os)	43 (3)	Os(1)-Os(3)-O(B)	48.3 (2)
Os(3)-Os(1)-H(Os)	40 (3)	Os(3)-Os(1)-O(B)	47.8 (2)
O(B)-Os(1)-H(Os)	78 (3)	O(B)-Os(3)-H(Os)	81 (3)
Os(2)-Os(1)-H(Os)	86 (3)	Os(2)-Os(1)-O(B)	81.2 (2)
Os(2)-Os(3)-H(Os)	88 (3)	Os(2)-Os(3)-O(B)	81.3 (2)
C(13)-Os(1)-H(Os)	173 (5)	C(11)-Os(1)-O(B)	167.9 (5)
C(33)-Os(3)-H(Os)	176 (3)	C(31)-Os(3)-O(B)	170.3 (5)
(C) Osmium-Osmium-Carbonyl Angles			
Os(2)-Os(1)-C(11)	89.2 (4)	Os(1)-Os(3)-C(31)	122.2 (5)
Os(2)-Os(1)-C(12)	174.6 (4)	Os(1)-Os(3)-C(32)	112.2 (5)
Os(2)-Os(1)-C(13)	88.9 (4)	Os(1)-Os(3)-C(33)	133.2 (4)
Os(3)-Os(1)-C(11)	120.7 (4)	Os(2)-Os(3)-C(31)	91.4 (4)
Os(3)-Os(1)-C(12)	114.9 (4)	Os(2)-Os(3)-C(32)	171.9 (5)
Os(3)-Os(1)-C(13)	132.6 (4)	Os(2)-Os(3)-C(33)	88.2 (4)
Os(1)-Os(2)-C(21)	94.7 (5)	Os(3)-Os(2)-C(21)	154.6 (5)
Os(1)-Os(2)-C(22)	85.4 (4)	Os(3)-Os(2)-C(22)	83.1 (4)
Os(1)-Os(2)-C(23)	166.7 (5)	Os(3)-Os(2)-C(23)	106.9 (5)
Os(1)-Os(2)-C(24)	85.0 (4)	Os(3)-Os(2)-C(24)	83.2 (4)
(D) Carbonyl-Osmium-Carbonyl Angles			
C(11)-Os(1)-C(12)	91.8 (7)	C(31)-Os(3)-C(32)	91.8 (7)
C(11)-Os(1)-C(13)	91.1 (6)	C(31)-Os(3)-C(33)	89.0 (6)
C(12)-Os(1)-C(13)	96.4 (6)	C(32)-Os(3)-C(33)	99.3 (6)
C(21)-Os(2)-C(22)	94.3 (7)	C(22)-Os(2)-C(23)	94.5 (6)
C(21)-Os(2)-C(23)	98.5 (7)	C(22)-Os(2)-C(24)	166.0 (6)
C(21)-Os(2)-C(24)	96.6 (7)	C(23)-Os(2)-C(24)	92.6 (7)
(E) Osmium-Carbon-Oxygen (Carbonyl) Angles			
Os(1)-C(11)-O(11)	178.2 (11)	Os(2)-C(23)-O(23)	176.4 (19)
Os(1)-C(12)-O(12)	173.7 (16)	Os(2)-C(24)-O(24)	178.0 (10)
Os(1)-C(13)-O(13)	179.0 (09)	Os(3)-C(31)-O(31)	176.2 (20)
Os(2)-C(21)-O(21)	178.8 (10)	Os(3)-C(32)-O(32)	175.8 (19)
Os(2)-C(22)-O(22)	176.6 (17)	Os(3)-C(33)-O(33)	178.1 (10)
(F) Osmium-Carbon-Oxygen (Methoxide) Angles			
Os(1)-O(B)-C(1)	119.4 (8)	Os(3)-O(B)-C(1)	122.5 (9)

Table VI. Pertinent Least-Squares Planes[a] and Deviations of Atoms Therefrom and Plane Angles

(A) Os(1)-Os(2)-Os(3) Plane			
$-0.5222X + 0.8362Y - 0.1677Z = 1.4841$			
Os(1)*	0.000	C(21)	−0.042 (17)
Os(2)*	0.000	O(21)	−0.049 (14)
Os(3)*	0.000	C(23)	−0.039 (16)
O(B)	−1.500 (9)	O(23)	−0.078 (14)
H(Os)	1.05 (11)	C(32)	0.191 (16)
C(11)	1.516 (16)	O(32)	0.230 (13)
O(11)	2.415 (13)	C(13)	−1.146 (15)
C(22)	1.946 (14)	O(13)	−1.843 (12)
O(22)	3.057 (12)	C(24)	−1.929 (15)
C(31)	1.652 (16)	O(24)	−3.061 (12)
O(31)	2.512 (12)	C(33)	−1.117 (15)
C(12)	0.079 (16)	O(33)	−1.816 (11)
O(12)	0.145 (12)		
(B) Os(1)-Os(3)-H(Os) Plane			
$0.4251X + 0.8788Y - 0.2169Z = 2.7097$			
Os(1)*	0.0000	C(11)	1.319 (16)
Os(3)*	0.000	O(11)	2.134 (13)
H(Os)*	0.000	C(31)	1.285 (16)
O(B)	−1.193 (9)	O(31)	1.991 (12)
Os(2)	2.0404 (6)		
(C) Os(1)-Os(3)-O(B) Plane			
$0.9647X + 0.2452Y - 0.0959Z = 1.7551$			
Os(1)*	0.000	C(13)	1.060 (15)
Os(3)*	0.000	O(13)	1.721 (12)
O(B)*	0.000	C(33)	1.106 (15)
H(Os)	−0.96 (11)	O(33)	1.759 (11)
Os(2)	2.3421 (6)		
(D) Dihedral Angles, Deg			
plane A-plane B	123.32	plane B-plane C	130.26
plane A-plane C	106.42		

[a] Equations of planes are expressed in orthonormal (Å) coordinates. Atoms marked with asterisks were assigned unit weight, all others were given zero weight.

The nonbridged osmium–osmium distances, Os(1)–Os(2) = 2.8130 (12) Å and Os(2)–Os(3) = 2.8221 (10) Å [average = 2.8176 [64] Å[16]], are *not* statistically distinguishable from the μ-hydrido-μ-methoxy-bridged Os(1)–Os(3) distance of 2.8120 (11) Å.

The bridging hydride ligand is linked to the cluster by "X-ray determined" bond distances of Os(1)–H(Os) = 1.93 (11) Å and Os(3)–H(Os) = 1.84 (11) Å [average = 1.88 [6] Å[16]], the angle Os(1)–H(Os)–Os(3) being 96 (5)°. While it has been argued that "X-ray determined" M–H distances in bridging transition-metal hydrides should be systematically shorter than the "neutron determined" *internuclear* distances[17] (as in demonstrably the case with C–H and N–H bonds[15]), the esd's on M–H distances are usually sufficiently large as to reduce this potential problem to only secondary significance. Analogous Os–(μ-H) distances from neutron diffraction studies of $(\mu\text{-H})_2Os_3(CO)_{10}$,[18] $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$,[19] and $(\mu\text{-H})Os_3(CO)_{10}(\sigma,\pi\text{-C}_2H_3)$[20] range from 1.754 (8) to 1.883 (9) Å.

The methoxide ligand also forms a symmetrical bridge across the Os(1)–Os(3) vector, the individual osmium–oxygen distances being Os(1)–O(B) = 2.112 (9) Å and Os(3)–O(B) = 2.093 (9) Å [average = 2.103 [13] Å], while the Os(1)–O(B)–Os(3) angle is rather acute, having a value of 83.9 (2)°.

The carbonyl ligands on Os(1) and Os(2) are in three different chemical environments. The osmium–carbonyl bond lengths trans to Os(2) are the longest—Os(1)–C(12) = 1.928 (16) Å and Os(3)–C(32) = 1.915 (15) Å [average = 1.922 [8] Å]; those trans to the methoxide ligand are of intermediate bond length—Os(1)–C(11) = 1.889 (16) Å and Os(3)–C(31) = 1.911 (17) Å [average = 1.900 [15] Å]; and those trans to the bridging hydride ligand are the shortest—Os(1)–C(13) = 1.874 (16) Å and Os(3)–C(33) = 1.903 (14) Å [average = 1.889 [22] Å]. The differences in average values here are,

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(16) The esd's of average values are enclosed in brackets and are calculated via the scatter formula, $\sigma = [\sum_N (d_i - \bar{d})^2/(N-1)]^{1/2}$. Here d_i is the *i*th and $\bar{d}$ is the mean of *N* equivalent values.

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Table VII. Summary of Data from Structural Studies on $(\mu\text{-H})_2Os_3(CO)_{10}$

	neutron[a]	combined neutron/X-ray[b]	X-ray (Churchill et al.)[c]	X-ray (Mason et al.)[d]	av[e]
bridged Os-Os, Å	2.683 (1)	2.680 (2)	2.681 (1)	2.670 (1)	2.682 (1)
Os-Os, Å	2.814 (1)	2.812 (2)	2.812 (1)	2.804 (1)	2.815 (1)
	2.815 (1)	2.818 (2)	2.817 (1)	2.813 (1)	
Os-H-Os, deg	93.06 (11)				
	95.54 (12)				
Os-H-Os (av), deg	94.30 (177)	92.9 (2)			94.3 (18)
Os-H, Å	1.840 (3)				
	1.843 (3)				
	1.845 (3)				
	1.852 (3)				
Os-H (av), Å	1.845 (3)	1.850 (5)			1.845 (3)

[a] See ref 18. [b] See ref 20. [c] See ref 21. [d] See ref 9. [e] Average is either the most precise value or the average of two or more equally precise values.

however, marginal when compared to their esd's.

The carbonyl ligands on Os(2) belong to two sets, with the mutually trans *axial* carbonyl groups being associated with longer Os–CO distances then the mutual cis *equatorial* carbonyl groups: Os(2)–C(22) = 1.960 (15) Å and Os(2)–C(24) = 1.944 (15) Å [average Os–CO(trans) = 1.952 [11] Å] as compared to Os(2)–C(21) = 1.901 (17) Å and Os(2)–C(23) = 1.892 (15) Å [average Os–CO(cis) = 1.897 [6] Å].

Carbon–oxygen distances and Os–C–O angles lie in the expected ranges [C–O = 1.115 (17)–1.168 (16) Å; Os–C–O = 173.7 (16)–179.0 (9) Å].

The molecule is shown projected onto its triosmium plane in Figure 2. Noteworthy are the large diequatorial angles Os(3)–Os(1)–C(12) = 114.9 (4)° and Os(1)–Os(3)–C(32) = 112.2 (5)° adjacent to the $Os(\mu\text{-H})(\mu\text{-OMe})Os$ bridge; the analogous diequatorial angles on Os(2) are smaller but somewhat inequivalent, with individual values of Os(1)–Os(2)–C(21) = 94.7 (5)° and Os(3)–Os(2)–C(23) = 106.9 (5)°. [A similar inequivalence was observed in structural studies of $(\mu\text{-H})_2Os_3(CO)_{10}$.][9,18,20,21]

Comparison of $(\mu\text{-H})_2Os_3(CO)_{10}$, $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$, and $(\mu\text{-OMe})_2Os_3(CO)_{10}$. The present structural analysis completes the investigation of $(\mu\text{-H})_n(\mu\text{-OMe})_{2-n}Os_3(CO)_{10}$ (n = 0–2) complexes. The structure of $(\mu\text{-H})_2Os_3(CO)_{10}$ was first reported by Mason and co-workers in 1971,[7] but full details did not appear until 1977.[9] Meanwhile, an independent X-ray study had been undertaken by Churchill et al.,[21] a combined X-ray/neutron diffraction study was undertaken by Sheldrick et al.,[20] and a low-temperature neutron diffraction study was performed by Broach and Williams.[18] Parameters of consequence from these studies are summarized in Table VII.

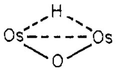
Important bond distances and angles within the species $(\mu\text{-H})_2Os_3(CO)_{10}$, $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$, and $(\mu\text{-OMe})_2Os_3(CO)_{10}$[9] are compared in Table VIII. Our results in all ways agree with the summary of Mason et al.[7-9] (see Introduction) but more *quantitative* significance can be attached to the present set of data.

Table VIII. Distances and Angles within the Complexes $(\mu\text{-H})_2Os_3(CO)_{10}$, $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$, and $(\mu\text{-OMe})_2Os_3(CO)_{10}$

	$(\mu\text{-H})_2$ complex[a]	$(\mu\text{-H})(\mu\text{-OMe})$ complex[b]	$(\mu\text{-OMe})_2$ complex[c]
bridged Os–Os, Å	2.682 (1)	2.812 (1)	3.078 (3)
nonbridged Os–Os (av), Å	2.815 (1)	2.817 [6]	2.819 [6]
Os–H–Os, deg	94.3 (18)	96 (5)	
Os–O–Os, deg		83.9 (2)	95.1 [9]
Os–H, Å	1.845 (3)	1.88 [6]	
Os–O, Å		2.103 [13]	2.09 [2]

[a] From last column of Table VII. [b] This work. [c] From ref 9.

The following points are noteworthy. (1) The dibridged osmium–osmium distances increase from 2.682 (1) Å in the $(\mu\text{-H})_2$ complex to 2.812 (1) Å in the $(\mu\text{-H})(\mu\text{-OMe})$ and 3.078 (3) Å in the $(\mu\text{-OMe})_2$ species. (2) The nonbridged osmium–osmium distances remain essentially unchanged. (3) The Os–H–Os angles appear similar with values of 94.3° for the $(\mu\text{-H})_2$ complex and 96 (5)° for the $(\mu\text{-H})(\mu\text{-OMe})$ complex; this latter value is, of course, of limited precision. (4) The Os–O–Os angles change substantially, with values of 83.9 (2)° for the $(\mu\text{-H})(\mu\text{-OMe})$ complex and 95.1 [9]° for the $(\mu\text{-OMe})_2$ complex. The former, acute, value is symptomatic of the presence of metal–metal bonding (see 4) and the latter is consistent with no metal–metal bonding in the $(\mu\text{-OMe})_2$ complex (see 3). (5) Os–H and Os–O distances are self-consistent throughout the series.



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Registry No. $(\mu\text{-H})(\mu\text{-OMe})Os_3(CO)_{10}$, 12388-57-7.

Supplementary Material Available: A listing of data-processing formulas and observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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