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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 10. Molecular Geometry and Comments on the Location of the μ_2-Hydride Ligand in $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)^1$

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The heteronuclear tetrahedral cluster derivative $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$ has been studied by means of a single-crystal X-ray structural analysis. The complex crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ [D_2^4; No. 19] with $a = 9.2707$ (14) Å, $b = 11.8539$ (23) Å, $c = 19.7258$ (33) Å, $V = 2167.7$ (6) Å^3, and $\rho(\text{calcd}) = 3.544$ g cm^{-3} for $Z = 4$ and mol wt 1156.69. Diffraction data were collected with a Syntex $P2_1$ diffractometer and the structure was refined to $R_F = 5.6\%$ and $R_{wF} = 4.6\%$ for those 1446 reflections with $|F_o| > 3\sigma(|F_o|)$ and $4.0° < 2\theta < 45.0°$ [Mo Kα radiation]. The molecule contains a tetrahedral cluster of metal atoms in which the tungsten is coordinated to an $\eta^5\text{-}C_5H_5$ ligand and two terminal carbonyl ligands and in which each osmium is associated with three terminal carbonyl ligands. There is, in addition, a bridging carbonyl ligand across the Os(1)–W(4) bond and a bridging hydride ligand across the Os(2)–Os(3) vector. Consideration of bond lengths and cis M–M–L angles reveal that the bridging hydride ligand lies in, or close to, the Os(1)–Os(2)–Os(3) plane.

Introduction

The heteronuclear metal carbonyl hydride $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$ has previously been prepared by the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $HW(CO)_3(\eta^5\text{-}C_5H_5)$.[2] A single-crystal X-ray structural analysis of $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$ has been undertaken in order to determine the location of the bridging hydride ligand and the overall connectivity within this complex tetranuclear species.

Experimental Section

A. Collection of X-ray Diffraction Data. Dark red transparent crystals of $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$ were supplied to us by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The columnar crystals generally showed a hexagonal cross section and often gave evidence of twinning parallel to the long axis of the crystal. A "house-shaped" crystal of approximate dimensions 0.18 × 0.20 × 0.25 mm was cleaved from one of the columnar crystals. Careful examination under a polarizing microscope gave no evidence of twinning. The crystal was mounted on a glass fiber and sealed into a thin-walled glass capillary tube which was fixed in an aluminum pin and mounted in a eucentric goniometer. Preliminary precession photographs indicated *mmm* (D_{2h}) Laue symmetry (i.e., suggested the orthorhombic crystal class) and confirmed the crystal quality. The crystal was transferred to a Syntex $P2_1$ automated diffractometer and oriented with the a^* axis approximately 8.5° from the spindle axis (ϕ) of the diffractometer. Crystal alignment, determination of the orientation matrix and accurate cell dimensions, and data collection were all carried out as described previously.[3] Details specific to the present analysis are listed in Table I. The systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$ uniquely define the noncentrosymmetric nonpolar space group $P2_12_12_1$ (D_2^4; No. 19).

All crystallographic computations were performed using our Syntex XTL system,[4] which is comprised of (i) and in-house Data General Nova 1200 computer with 24K of 16-bit word memory and with a parallel floating-point processor for 32- and 64-bit arithmetic, (ii) a Diablo moving-head disk unit with a capacity of 1.2 million 16-bit words, (iii) a Versateo electrostatic printer/plotter, and (iv) the XTL conversational crystallographic program package, as modified by our

Table I. X-ray Data for $(\mu$-H)Os$_3$W(CO)$_{12}(\eta^5$-C$_5$H$_5)$

(A) Crystal Parameters at 24 °C^a

crystal system: orthorhombic	$V = 2167.7$ (6) Å^3
space group: $P2_12_12_1$	$Z = 4$
$a = 9.2707$ (14) Å	mol wt 1156.69
$b = 11.8539$ (23) Å	ρ(calcd) = 3.544 g cm^{-3}
$c = 19.7258$ (33) Å	$\mu = 230.1$ cm^{-1}

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kᾱ (λ̄ 0.710 730 Å)
monochromator: graphite, equatorial mode
scan type: coupled θ(crystal)–2θ(counter)
2θ range: 4.0–45.0°
scan speed: 2°/min in 2θ
scan width: $[2\theta$(Mo Kα_1)–1.0]° to $[2\theta$(Mo Kα_2) + 1.0]°
bkgd measurement: stationary crystal, stationary counter at
  beginning and end of each scan–each for one-quarter of the
  scan time
standard reflections: 400, 240, 008; measd after every 97
  reflections; some decrease in intensity (see text)
reflections measd: 1652 unique; 1446 with $|F_o| > 3\sigma(|F_o|)$ were
  used in the least-squares refinement process

^{a} Unit cell parameters were derived from a least-squares fit to
the setting angles of the unresolved Mo Kᾱ components of 24 re-
flections between 20 and 30° in 2θ. Reflections of the forms
{3.4.11}, {058}, {454}, {544}, and {604} were used.

research group at SUNY—Buffalo.

Intensity data were corrected for absorption ($\mu = 230$ cm^{-1}) by
an empirical method. Five relatively intense and close-to-axial re-
flections were measured at 36 positions around their diffraction vectors
(ψ); these measurements were converted to normalized transmission
curves and were used to correct the primary data set as described
previously.[5] The reflections used, their 2θ values, and maximum:
minimum intensity ratios are as follows: $30\bar{1}$, $2\theta = 13.34°$, max/min
=1.835; 400, 17.60°, 1.767; $50\bar{1}$, 22.15°, 1.678; $60\bar{4}$, 27.83°, 1.524;
$90\bar{4}$, 41.18°, 1.475. All curves had maxima and minima occurring
at essentially identical ϕ values and all curves had similar basic shapes;
there was, however, the usual broadening of the intensity profile with
increasing 2θ.

Analysis of the check reflections showed an essentially linear decay
of intensity vs. reflection number to final values approximately 94%
of the original intensity. The intensities of all reflections were corrected
for this decay.

The absorption- and decay-corrected intensity data were converted
to $|F_o|$ values following correction for Lorentz and polarization effects.
Any reflection with $I \leq 0$ was assigned a value of $|F_o| = 0$. The esd's,
$\sigma(|F_o|)$, were calculated by finite differences from the esd's $\sigma(F^2)$ based
solely on counting statistics.

B. Solution and Refinement of the Structure. The analytical form[6a]
of the scattering factors for *neutral* osmium, tungsten, oxygen, carbon,
and hydrogen were used throughout the analysis: both the real and
imaginary components of anomalous dispersion[6b] were included for
all nonhydrogen atoms. The function minimized during least-squares
refinement was $\sum w(|F_o| - |F_c|)^2$, with w defined in eq 1. The final

$$w = [\{\sigma(|F_o|)\}^2 + \{p|F_o|\}^2]^{-1} \quad (1)$$

value for p (the "ignorance factor") was 0.015. The discrepancy indices
R_F and R_{wF} and the "goodness-of-fit" (GOF) are defined by eq 2–4,
where NO is the number of observations and NV is the number of
variables.

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \right] \times 100 \ (\%) \quad (2)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} \times 100 \ (\%) \quad (3)$$

$$\text{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{(\text{NO} - \text{NV})} \right]^{1/2} \quad (4)$$

A three-dimensional Patterson map was solved to give the positions
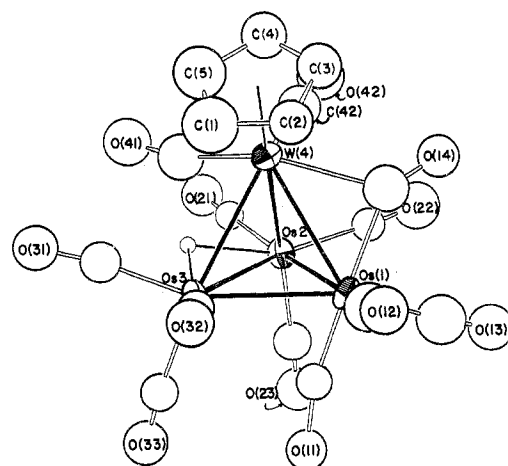of the four heavy atoms. These were all initially assigned the scattering

Figure 1. Labeling of atoms in the $(\mu$-H)Os$_3$W(CO)$_{12}(\eta^5$-C$_5$H$_5)$
molecule. The hydride ligand bridging the Os(2)–Os(3) bond is shown
in its predicted position. [ORTEP-II diagram; 50% probability ellipsoids.]
All carbonyl carbon atoms have the same labels as the oxygens to
which they are attached.

curves for osmium and were refined, using isotropic thermal pa-
rameters, to give $R = 11.8\%$ and $R_{wF} = 12.3\%$. A difference-Fourier
synthesis revealed the positions of 24 of the 29 lighter atoms (carbon
or oxygen atoms) and allowed differentiation of the tungsten atom
from the osmium atoms on the basis of its chemical environment (i.e.,
attached to the η^5-C$_5$H$_5$ ligand).[7] Subsequent cycles of least-squares
refinement, followed by another difference-Fourier synthesis, revealed
the positions of the remaining nonhydrogen atoms. Full-matrix
least-squares refinement of positional and thermal parameters
(anisotropic for metal atoms, isotropic for all other atoms) led to R_F
= 6.7\%, R_{wF} = 4.8\%, and GOF = 1.604. An examination of the
observed and calculated structure factor amplitudes showed evidence
for the effects of secondary extinction. A correction to the data set
was made, using the form shown in eq 5. The extinction coefficient,

$$|F_o|^{\text{cor}} = (1.0 + kI_0)|F_o|^{\text{uncor}} \quad (5)$$

k, was determined to have a value of 9.6×10^{-8} by a least-squares
analysis of $|F_o|$ and $|F_c|$ values for intense reflections. Continued
full-matrix least-squares refinement led to convergence with R_F =
5.6\%, R_{wF} = 4.7\%, and GOF = 1.3645. Since $P2_12_12_1$ is a non-
centrosymmetric space group, it is necessary to refine the structure
in each of the possible enantiomeric crystal forms. Accordingly, we
inverted all atomic coordinates $(x, y, z \rightarrow -x, -y, -z)$ and refined to
convergence once again. The resulting values of R_F = 5.6\%, R_{wF} =
4.6\%, and GOF = 1.3556, although only slightly better than for the
original enantiomer, indicate that the "inverted" structure should be
accepted.

A final difference-Fourier map showed peaks up to 2.3 e/Å^3 in
the vicinity of the heavy atoms.

The residual $\sum w(|F_o| - |F_c|)^2$ showed no unusual variations as a
function of $|F_o|$ or $(\sin \theta)/\lambda$.

Final positional and thermal parameters are collected in Table II.

Results and Discussion

Intramolecular distances and their estimated standard
deviations (esd's) are given in Table III. Interatomic angles
(with esd's) are collected in Table IV. The scheme used for
labeling atoms is shown in Figure 1 and a stereoscopic view
of the molecule is shown in Figure 2.

The crystal structure consists of isolated molecules of (μ-
H)Os$_3$W(CO)$_{12}(\eta^5$-C$_5$H$_5)$ which are in an approximately cubic
close packed arrangement and mutually separated by normal
van der Waals distances (cf. Table V).

Each molecule contains a tetrahedral core of metal
atoms—three osmium and one tungsten. Each osmium atom
is in coordination to three terminal carbonyl ligands, while the
tungsten atom is coordinated to two terminal carbonyl ligands
and an η^5-cyclopentadienyl ring. A 12th carbonyl ligand,
C(14)–O(14), bridges the Os(1)–W(4) bond. The hydride

Table II. Final Positional and Thermal Parameters for $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$

(A) Positional and Isotropic Thermal Parameters

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Os1	−0.17436 (21)	−0.12915 (14)	−0.14771 (9)		C1	−0.577 (7)	−0.101 (6)	−0.0364 (30)	7.5 (16)
Os2	−0.17354 (21)	0.10354 (14)	−0.16691 (8)		C2	−0.461 (6)	−0.157 (4)	−0.0052 (24)	4.5 (11)
Os3	−0.42174 (17)	−0.03512 (15)	−0.20625 (8)		C3	−0.396 (6)	−0.078 (4)	0.0416 (24)	4.9 (12)
W4	−0.36490 (16)	0.00734 (17)	−0.06349 (8)		C4	−0.468 (5)	0.015 (5)	0.0423 (24)	5.2 (12)
O11	−0.147 (3)	−0.1751 (24)	−0.2981 (15)	4.4 (7)	C5	−0.579 (6)	−0.007 (5)	−0.0062 (28)	6.8 (14)
O12	−0.275 (4)	−0.3639 (30)	−0.1117 (16)	5.2 (8)	C11	−0.177 (5)	−0.152 (4)	−0.2353 (20)	3.4 (9)
O13	0.152 (4)	−0.1617 (31)	−0.1371 (18)	5.9 (8)	C12	−0.234 (7)	−0.275 (5)	−0.1289 (29)	5.8 (14)
O14	−0.070 (4)	−0.0838 (26)	−0.0026 (16)	4.7 (8)	C13	0.039 (7)	−0.154 (5)	−0.1441 (32)	6.9 (16)
O21	−0.227 (4)	0.3620 (31)	−0.1730 (17)	5.8 (9)	C14	−0.152 (6)	−0.084 (5)	−0.0470 (26)	5.7 (13)
O22	0.106 (4)	0.1261 (34)	−0.0836 (18)	7.0 (10)	C21	−0.211 (4)	0.265 (4)	−0.1702 (21)	2.6 (8)
O23	−0.015 (4)	0.0846 (29)	−0.2987 (18)	5.7 (8)	C22	0.005 (5)	0.115 (4)	−0.1157 (21)	3.4 (9)
O31	−0.708 (4)	0.0826 (28)	−0.2213 (16)	5.3 (8)	C23	−0.070 (6)	0.092 (4)	−0.2509 (25)	4.5 (11)
O32	−0.565 (4)	−0.2634 (27)	−0.1859 (16)	5.0 (8)	C31	−0.589 (5)	0.045 (4)	−0.2119 (24)	4.4 (10)
O33	−0.395 (3)	−0.0400 (29)	−0.3587 (17)	5.4 (8)	C32	−0.505 (5)	−0.176 (4)	−0.1891 (21)	3.1 (9)
O41	−0.528 (4)	0.2221 (33)	−0.1205 (18)	6.5 (10)	C33	−0.412 (5)	−0.041 (4)	−0.3055 (23)	3.8 (10)
O42	−0.189 (5)	0.1951 (32)	0.0044 (19)	6.9 (10)	C41	−0.454 (6)	0.140 (5)	−0.1077 (28)	5.9 (14)
					C42	−0.259 (6)	0.122 (5)	−0.0237 (26)	5.3 (13)

(B) Anisotropic Thermal Parameters $(\text{Å}^2)^a$ for the Metal Atoms

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os1	1.44 (8)	2.08 (8)	3.26 (8)	0.13 (7)	0.14 (7)	−0.04 (7)
Os2	1.95 (8)	2.22 (7)	2.77 (7)	−0.53 (7)	−0.20 (7)	0.17 (7)
Os3	1.65 (7)	2.74 (8)	2.71 (8)	−0.24 (7)	−0.45 (6)	0.21 (7)
W4	2.28 (7)	2.80 (8)	2.39 (7)	0.23 (7)	0.38 (6)	−0.21 (7)

^{a} The anisotropic thermal parameter enters the equation for F_c in the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

Table III. Selected Intramolecular Distances (Å) for $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)^a$

(A) Metal-Metal Distances

Os(1)–Os(2)	2.784 (2)	Os(1)–W(4)	2.915 (2)
Os(1)–Os(3)	2.799 (2)	Os(2)–W(4)	2.934 (2)
Os(2)–Os(3)	2.932 (2)	Os(3)–W(4)	2.909 (2)

(B) Metal-(Terminal Carbonyl) Distances

Os(1)–C(11)	1.75 (4)	Os(1)···O(11)	3.03 (3)
Os(1)–C(12)	1.85 (6)	Os(1)···O(12)	3.02 (4)
Os(1)–C(13)	2.00 (7)	Os(1)···O(13)	3.06 (4)
Os(2)–C(21)	1.94 (4)	Os(2)···O(21)	3.11 (4)
Os(2)–C(22)	1.95 (4)	Os(2)···O(22)	3.08 (4)
Os(2)–C(23)	1.92 (5)	Os(2)···O(23)	2.99 (4)
Os(3)–C(31)	1.82 (5)	Os(3)···O(31)	3.02 (3)
Os(3)–C(32)	1.87 (4)	Os(3)···O(32)	3.04 (3)
Os(3)–C(33)	1.96 (4)	Os(3)···O(33)	3.02 (3)
W(4)–C(41)	1.98 (6)	W(4)···O(41)	3.17 (4)
W(4)–C(42)	1.85 (6)	W(4)···O(42)	3.07 (4)

(C) Metal-(Bridging Carbonyl) Distances

Os(1)–C(14)	2.07 (5)	Os(1)···O(14)	3.07 (3)
W(4)–C(14)	2.27 (6)	W(4)···O(14)	3.17 (3)

(D) Distances Involving the $\eta^5\text{-}C_5H_5$ Ligand

W(4)–C(1)	2.41 (7)	C(1)–C(2)	1.40 (8)
W(4)–C(2)	2.44 (5)	C(2)–C(3)	1.45 (7)
W(4)–C(3)	2.32 (5)	C(3)–C(4)	1.29 (8)
W(4)–C(4)	2.30 (5)	C(4)–C(5)	1.43 (8)
W(4)–C(5)	2.29 (6)	C(5)–C(1)	1.26 (9)
W(4)···Cp^b	2.04		

(E) Terminal Carbon-Oxygen Distances

C(11)–O(11)	1.30 (5)	C(31)–O(31)	1.21 (6)
C(12)–O(12)	1.18 (6)	C(32)–O(32)	1.18 (6)
C(13)–O(13)	1.06 (8)	C(33)–O(33)	1.06 (6)
C(21)–O(21)	1.17 (6)	C(41)–O(41)	1.22 (7)
C(22)–O(22)	1.17 (6)	C(42)–O(42)	1.22 (7)
C(23)–O(23)	1.07 (6)		

(F) Bridging Carbon-Oxygen Distance

C(14)–O(14)	1.16 (6)

(G) Other Close Metal···Carbon Contacts

Os(2)···C(41)	2.88 (6)	Os(3)···C(11)	2.72 (5)
Os(3)···C(41)	2.86 (6)		

^{a} Esd's are shown in parentheses right justified to the least significant digit(s). ^{b} Cp represents the centroid of the η^5-cyclopentadienyl system.

ligand was not located unambiguously from the crystallographic analysis, but its position (i.e., bridging the Os(2)–Os(3) vector) can be inferred by detailed considerations of the molecular geometry (vide infra).

The metal–metal distances within the present molecule may be partitioned into three distinct sets, as follows.

(1) Normal Osmium–Osmium Bonds. The Os(1)–Os(2) and Os(1)–Os(3) linkages are, respectively, 2.784 (2) and 2.799 (2) Å [average 2.792 Å] in length. These appear to be normal osmium–osmium single-bond lengths for a tetrahedral cluster—we note that the non-hydrido-bridged Os–Os linkages in $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)^{1,2}$ average 2.826 (2) Å in length. These distances in the tetrahedral metal clusters are, however, all shorter than those observed for normal osmium–osmium distances in the "two-dimensional" trinuclear triangular frameworks (viz., Os–Os = 2.877 (3) Å in Os_3-$(CO)_{12}$).[8]

(2) A "Long" Osmium–Osmium Bond. The Os(2)–Os(3) distance of 2.932 (2) Å is some 0.14 Å longer than the average "normal" osmium–osmium bond length of 2.792 Å in (1) above. As such, this linkage is clearly identified as that bridged by a single, unsupported μ_2-hydride ligand (cf. ref 9). The μ_2-hydrido-bridged osmium–osmium distance in $(\mu\text{-}H)_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$ is 2.941 (2) Å.[1,2]

(3) Osmium–Tungsten Bonds. The appropriate distances are Os(1)–W(4) = 2.915 (2) Å, Os(2)–W(4) = 2.934 (2) Å, and Os(3)–W(4) = 2.909 (2) Å, the average being 2.919 (13) Å. It is noteworthy that the carbonyl bridged Os(1)–W(4) bond is not the shortest of the three linkages.

The bridging carbonyl ligand [C(14)–O(14)] is bonded to the tetrahedral metal cluster via the linkages Os(1)–C(14) = 2.07 (5) Å and W(4)–C(14) = 2.27 (7) Å. At first glance this appears to indicate that C(14)–O(14) is a typical asymmetric (or "semibridging") carbonyl group. Further considerations fail to confirm this hypothesis. The following points should be noted.

(1) The average intermetallic distances found in this structure (Os–Os(normal) = 2.792 Å (average), Os–W = 2.919 Å (average)) suggest covalent radii of 1.396 Å for osmium and 1.523 Å for tungsten—i.e., r(W) is some 0.127
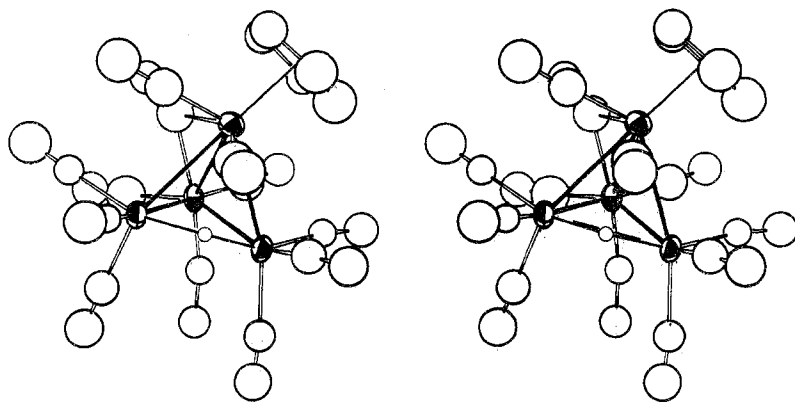
Figure 2. Stereoscopic view of the $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$ molecule.
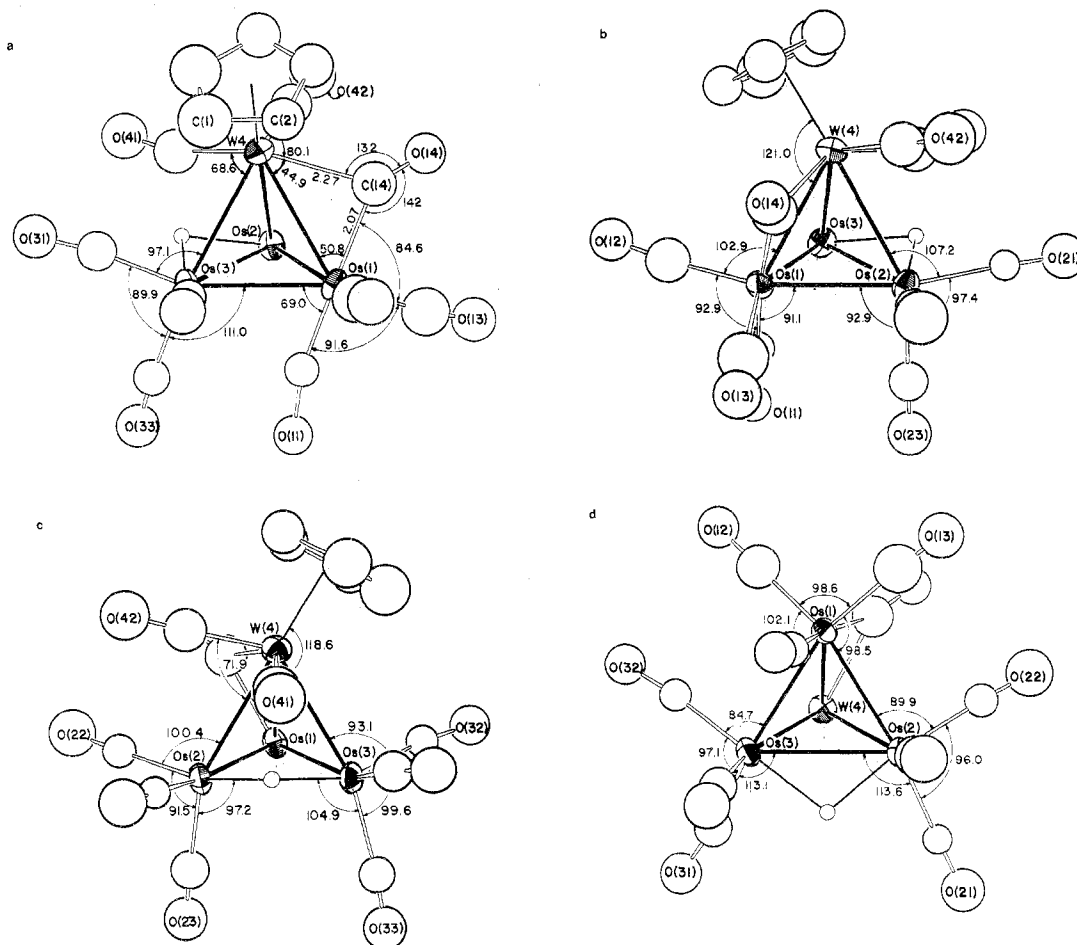

Figure 3. Projections of the molecule onto each of the four faces of the Os_3W core. Ligands attached to the rear metal atom are eliminated for clarity in each view. (a) Projection onto the $Os(1)-Os(3)-W(4)$ face, showing the geometry about the bridging carbonyl ligand, $C(14)-O(14)$. Distances are in Å and angles are in degrees. (b) Projection onto the $Os(1)-Os(2)-W(4)$ plane. (c) Projection onto the $Os(2)-Os(3)-W(4)$ plane. (d) Projection onto the $Os(1)-Os(2)-Os(3)$ plane. Note the large cis Os–Os–CO angles, revealing the location of the μ_2-hydride ligand.

Å *greater* than r(Os) in this tetrahedral cluster. One might expect, therefore, that for an *electronically symmetrical*[10] bridging carbonyl between an osmium and a tungsten atom, the W–CO distance should be greater (by up to ~0.127 Å) than the Os–CO distance. The observed difference between W–CO and OS–CO distances is 0.20 Å—i.e., it is within 0.07 Å (less than 1.0σ!) of being *electronically symmetrical*.[10]

(2) A careful survey of the geometry of the $Os(1)-[C(14)-O(14)]-W(4)$ system (see Figure 3a,b) shows the carbonyl group to more closely resemble a normal bridging carbonyl ligand than a "semibridging" ligand. Thus the angles $Os(1)-C(14)-O(14) = 142.4 (43)°$ and $W(4)-C(14)-O(14) = 132.4 (41)°$ differ by only 10.0°.

(3) The usual purpose of a semibridging carbonyl group in an asymmetric molecule is to transfer electron density from an electron-rich to an electron-poor metal atom. In the present molecule, using conventional electron counting[11] (and assuming a *symmetrical* carbonyl bridge), one finds that W(4) has 19 electrons, Os(1) has 18 electrons, and Os(2) and Os(3) each have $17^1/_2$ electrons; there is, then, no necessity for a semibridging carbonyl ligand bond to transfer electron density from Os(1) to W(4).

(4) Despite our comments in (1)–(3), it should be remembered that there is probably an entire spectrum of available geometries for a carbonyl ligand, including all possibilities between "perfectly terminal" and "perfectly

Table IV. Interatomic Angles (deg) for
$(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$

(A) Angles within the Os₃W Tetrahedron

Os(2)–Os(1)–Os(3)	63.36 (6)	Os(1)–Os(3)–Os(2)	58.07 (6)
Os(2)–Os(1)–W(4)	61.92 (6)	Os(1)–Os(3)–W(4)	61.39 (6)
Os(3)–Os(1)–W(4)	61.16 (6)	Os(2)–Os(3)–W(4)	60.31 (6)
Os(1)–Os(2)–Os(3)	58.57 (6)	Os(1)–W(4)–Os(2)	56.85 (6)
Os(1)–Os(2)–W(4)	61.23 (6)	Os(1)–W(4)–Os(3)	57.46 (6)
Os(3)–Os(2)–W(4)	59.45 (6)	Os(2)–W(4)–Os(3)	60.24 (6)

(B) Transoid M–M–C Angles

Os(2)–Os(1)–C(12)	162.3 (18)	Os(1)–Os(3)–C(31)	158.5 (15)
Os(3)–Os(1)–C(13)	152.0 (19)	Os(2)–Os(3)–C(32)	140.9 (13)
W(4)–Os(1)–C(11)	129.8 (14)	W(4)–Os(3)–C(33)	164.6 (13)
Os(1)–Os(2)–C(21)	168.0 (12)	Os(1)–W(4)–C(41)	116.3 (17)
Os(3)–Os(2)–C(22)	147.5 (13)	Os(2)–W(4)–Cp	177.8
W(4)–Os(2)–C(23)	151.2 (15)	Os(3)–W(4)–C(42)	129.3 (17)

(C) Cisoid M–M–C Angles

Os(2)–Os(1)–C(11)	91.1 (14)	Os(1)–Os(3)–C(32)	84.7 (13)
Os(2)–Os(1)–C(13)	98.5 (19)	Os(1)–Os(3)–C(33)	111.0 (13)
Os(2)–Os(1)–C(14)	82.8 (15)	Os(2)–Os(3)–C(31)	113.1 (15)
Os(3)–Os(1)–C(11)	69.0 (14)	Os(2)–Os(3)–C(33)	104.4 (13)
Os(3)–Os(1)–C(12)	102.1 (18)	W(4)–Os(3)–C(31)	97.1 (15)
Os(3)–Os(1)–C(14)	112.0 (15)	W(4)–Os(3)–C(32)	93.1 (13)
W(4)–Os(1)–C(12)	102.9 (18)	Os(1)–W(4)–C(14)	44.9 (14)
W(4)–Os(1)–C(13)	131.3 (19)	Os(1)–W(4)–C(42)	109.1 (17)
W(4)–Os(1)–C(14)	50.8 (15)	Os(1)–W(4)–Cp	121.0
Os(1)–Os(2)–C(22)	89.9 (13)	Os(2)–W(4)–C(14)	76.1 (14)
Os(1)–Os(2)–C(23)	92.9 (15)	Os(2)–W(4)–C(41)	68.7 (17)
Os(3)–Os(2)–C(21)	113.6 (12)	Os(2)–W(4)–C(42)	71.9 (17)
Os(3)–Os(2)–C(23)	97.2 (15)	Os(3)–W(4)–C(14)	102.3 (14)
W(4)–Os(2)–C(21)	107.2 (12)	Os(3)–W(4)–C(41)	68.6 (17)
W(4)–Os(2)–C(22)	100.4 (13)	Os(3)–W(4)–Cp	118.6

(D) C–M–C Angles

C(11)–Os(1)–C(12)	92.9 (23)	C(31)–Os(3)–C(32)	97.1 (20)
C(11)–Os(1)–C(13)	91.6 (24)	C(31)–Os(3)–C(33)	89.9 (20)
C(11)–Os(1)–C(14)	172.2 (21)	C(32)–Os(3)–C(33)	99.6 (19)
C(12)–Os(1)–C(13)	98.6 (26)	C(41)–W(4)–C(42)	79.9 (24)
C(12)–Os(1)–C(14)	94.5 (24)	C(41)–W(4)–C(14)	143.5 (22)
C(13)–Os(1)–C(14)	84.6 (24)	C(41)–W(4)–Cp	112.9
C(21)–Os(2)–C(22)	96.0 (18)	C(42)–W(4)–C(14)	80.1 (22)
C(21)–Os(2)–C(23)	97.4 (19)	C(42)–W(4)–Cp	109.8
C(22)–Os(2)–C(23)	91.5 (20)	C(14)–W(4)–Cp	102.5

(E) M–C–O Angles

Os(1)–C(11)–O(11)	166.2 (36)	Os(2)–C(23)–O(23)	178.0 (46)
Os(1)–C(12)–O(12)	174.5 (50)	Os(3)–C(31)–O(31)	169.3 (40)
Os(1)–C(13)–O(13)	173.5 (58)	Os(3)–C(32)–O(32)	171.8 (38)
Os(1)–C(14)–O(14)	142.4 (43)	Os(3)–C(33)–O(33)	173.6 (42)
W(4)–C(14)–O(14)	132.4 (41)	W(4)–C(41)–O(41)	164.2 (47)
Os(2)–C(21)–O(21)	176.7 (37)	W(4)–C(42)–O(42)	177.8 (47)
Os(2)–C(22)–O(22)	175.8 (41)		

μ_2-bridging". The present geometry is close to "perfectly μ_2-bridging" but might be displaced slightly along the reaction coordinate toward "perfectly terminal". Regretably, the esd's on bond lengths and angles are rather large and we can impose no fine limits on our description of this feature.

There is some evidence for electron redistribution in the molecule via a bifurcated weakly "semibridging" interaction of C(41)–O(41) with both Os(2) and Os(3) [Os(2)···C(41) = 2.86 (6) Å and Os(3)···C(41) = 2.88 (6) Å]. The bending of the W(4)–C(41)–O(41) system (angle 164.2 (47)°), such that O(41) is displaced further from the Os(2)–Os(3) vector than it would be in a linear W–C–O system, is shown in Figure 3a,c. The Os(1)–C(11)–O(11) system is also slightly bent (angle 166.2 (36)°) and is oriented such as to allow interaction of C(11) with Os(3) [Os(3)···C(11) = 2.72 (5) Å]. This feature of the structure is shown clearly in Figure 3a and is associated also with the very small value of 69.0 (14)° for the angle Os(3)–Os(1)–C(11). However, while the systems W(4)–C(41)–O(41) and Os(1)–C(11)–O(11) are the most bent of the "terminal" carbonyl ligands, the structure is so sterically crowded that it is difficult to assess whether these distortions are a result of attempted electron redistribution via

"semibridging" carbonyl groups or result simply from interligand repulsions. It is probable that each of these effects contributes to the overall geometry.

The hydride ligand was not located unambiguously in this structural study. However, bond length considerations (vide supra) lead to the conclusion that it occupies a bridging position about the Os(2)–Os(3) vector. The remaining question is: what is the *orientation* of the hydride ligand about this vector? The three obvious symmetrical cases are as follows: (1) The hydride ligand lies in, or close to, the Os(1)–Os(2)–Os(3) plane (see I).

(2) The hydride ligand lies in, or close to, the Os(2)–Os(3)–W(4) plane (see II).

(3) The hydride ligand occupies a position intermediate between I and II such that the Os(2)–H–Os(3) plane acts as an external bisector of the Os(1)–Os(2)–Os(3) and Os(2)–Os(3)–W(4) planes (see III).

I

II

III
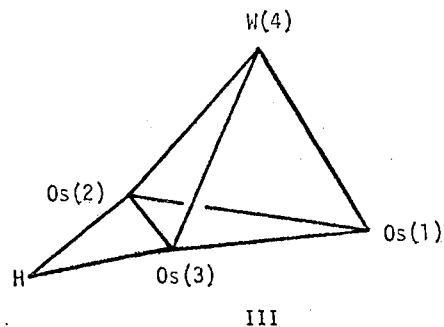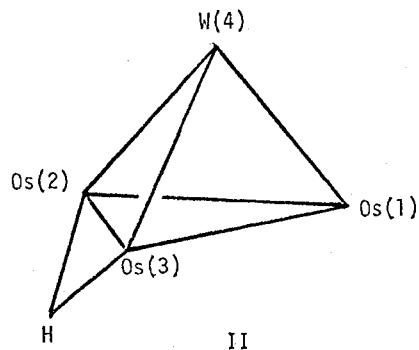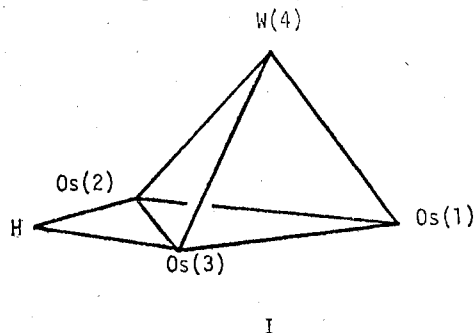
We can distinguish between these possibilities by using the following well-established principle[9,12]—*abnormally large M–M–L angles should be observed for ligands (L) adjacent to, and in the same plane as, a simple unsupported M–(μ_2-H)–M system.*

Figure 3c,d shows the distribution of ligands in the Os(2)–Os(3)–W(4) and Os(1)–Os(2)–Os(3) planes. The larger and more symmetrical M–M–L angles, Os(3)–Os(2)–C(21) = 113.6 (12)° and Os(2)–Os(3)–C(31) = 113.1 (15)°, shown in Figure 3d clearly indicate that the bridging

Table V. Intermolecular Contacts <3.25 Å for (μ-H)Os₃W(CO)₁₂(η^5-C₅H₅)

contact	symmetry operation[a]	distance, Å
O(11)···O(31)	3 –1 –1 –1	3.19 (4)
O(13)···O(32)	1 1 0 0	3.04 (5)
O(14)···O(33)	4 –1 0 0	3.21 (5)
O(14)···C(2)	2 0 –1 0	3.24 (6)
O(22)···O(42)	2 0 0 0	3.25 (6)
O(23)···O(31)	1 1 0 0	3.23 (5)
O(23)···C(12)	3 0 0 –1	3.19 (7)
O(31)···O(11)	3 –1 0 –1	3.19 (4)
O(31)···O(23)	1 –1 0 0	3.23 (5)
O(32)···O(13)	1 –1 0 0	3.04 (5)
O(33)···O(14)	4 –1 0 –1	3.21 (5)
O(33)···O(41)	3 –1 –1 –1	2.94 (5)
O(41)···O(33)	3 –1 0 –1	2.94 (5)
O(41)···O(42)	2 –1 0 0	2.90 (6)
O(41)···C(33)	3 –1 0 –1	3.21 (6)
O(42)···O(41)	2 0 0 0	2.90 (6)
C(2)···O(14)	2 –1 –1 0	3.24 (6)
C(12)···O(23)	3 0 –1 –1	3.19 (7)
C(33)···O(41)	3 –1 –1 –1	3.21 (6)

[a] The transformation of the second atom is given by a four-digit code. The first represents the equipoint (see below), while the second through fourth represent the addition (+1) or subtraction (−1) of unit cell vectors a, b, and c. The transformation code is as follows: 1, x, y, z; 2, $^1/_2 + x$, $^1/_2 - y$, $-z$; 3, $-x$, $^1/_2 + y$, $^1/_2 - z$; 4, $^1/_2 - x$, $-y$, $^1/_2 + z$.

hydride ligand lies in, or close to, the Os(1)–Os(2)–Os(3) plane (i.e., case I is indicated).

Finally, we note that a peak corresponding to the predicted position of the bridging hydride ligand was found in the final difference-Fourier map at $x = -0.370$, $y = 0.126$, $z = -0.188$. Attempts to include this atom in the least-squares refinement process were unsuccessful—the positional parameters failed to converge and the isotropic thermal parameter became negative. The hydride ligand is, nevertheless, shown in all of the figures in its predicted position, to add clarity.

References and Notes

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(7) The small percentage difference in scattering between W(0) and Os(0) [Z(W) = 74, Z(Os) = 76, ΔZ = 2 electrons or 2.7% of Z(mean)] makes differentiation between W and Os infeasible solely on the basis of crystallographic techniques.
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(10) The term "electronically symmetrical" is coined in order to describe the situation in an M(μ-CO)M' bridge where the M–CO and M'–CO distances are inequivalent but the M–CO and M'–CO bond orders are equivalent.
(11) Assuming that a cyclopentadienyl group provides five electrons, a terminal carbonyl group provides two electrons, a bridging carbonyl group provides one electron to each metal atom, a bonded metal atom provides one electron, and a bridging hydride ligand shares one electron between the two bridged metal atoms.
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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 11. Crystal Structure and Molecular Geometry of (μ-H)Os₃(CO)₁₀(CHCH=NEt₂), a Species Containing a μ₂-Hydride Ligand and a μ₂-1,3-Dipolar >C⁻HCH=N⁺Et₂ Ligand

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The species (μ-H)Os₃(CO)₁₀(CHCH=NEt₂), previously synthesized by Shapley and co-workers from Os₃(CO)₁₀(NCMe)₂ and triethylamine, has been unambiguously identified and characterized via a full three-dimensional single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 7.676$ (2) Å, $b = 18.392$ (5) Å, $c = 16.026$ (4) Å, $\beta = 97.57$ (2)°, $V = 2243$ (1) Å³, and ρ(calcd) = 2.813 g cm⁻³ for mol wt 949.883 and $Z = 4$. Diffraction data [3.5° ≤ 2θ ≤ 35°; Mo Kα radiation] were collected with a Syntex $P2_1$ automated diffractometer, using graphite-monochromatized radiation. The structure was solved via direct methods (i.e., MULTAN), difference-Fourier techniques, and least-squares refinement techniques, the resulting discrepancy indices being $R_F = 5.03\%$ and $R_{wF} = 4.59\%$ for 1434 independent reflections. The molecule contains a triangular arrangement of osmium atoms. Os(1) and Os(2) are each associated with three carbonyl ligands, while Os(3) is linked to four such ligands. In addition, Os(1) and Os(2) are mutually bridged by a hydride ligand (which was located and refined in the course of the structural analysis) and by a 1,3-dipolar >C⁻HCHN⁺Et₂ ligand. Osmium–osmium bond lengths are Os(1)–Os(2) = 2.785 (2) Å, Os(1)–Os(3) = 2.870 (2) Å, and Os(2)–Os(3) = 2.866 (2) Å. Whereas a single unsupported μ₂-hydrido ligand normally causes a lengthening of its bridged metal–metal vector, this effect is counterbalanced by the (M–M) bond-shortening influence of the >C⁻HCHN⁺Et₂ ligand in the present molecule. Osmium–(μ₂-hydride) distances are Os(1)–H(br) = 1.76 (15) Å and Os(2)–H(br) = 1.82 (17) Å, the angle Os(1)–H(br)–Os(2) being 102 (8)°.

Introduction

We have been interested in polynuclear osmium carbonyl hydride complexes for some time and have previously reported detailed X-ray crystallographic studies of (μ-H)(H)Os₃-(CO)₁₁,[1] (μ-H)Os₃(CO)₁₀(CHCH₂PMe₂Ph),[2] (μ-H)(H)-

Os₃(CO)₁₀(PPh₃),[3] HOs₃Re(CO)₁₅,[4] (μ-H)₂Os₃(CO)₁₀,[5] (μ-H)Os₃(CO)₈[C(O–)C(CHMe–)CHCHCEt],[6] (μ-H)₂-Os₃Re₂(CO)₂₀,[7] (μ-H)Os₃(CO)₉[—CHC(=O)CH=CEtC-(=CHMe)],[8] (μ-H)₃Os₃W(CO)₁₁(η^5-C₅H₅),[9] and (μ-H)-Os₃W(CO)₁₂(η^5-C₅H₅).[10]