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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 9.[1,2] The Molecular Geometry of (μ-H)₃Os₃W(CO)₁₁(η⁵-C₅H₅) Including Some Comments on the Positions of μ-Hydride Ligands in Tetranuclear Metal Clusters

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The heteronuclear species (μ-H)₃Os₃W(CO)₁₁(η⁵-C₅H₅) has been examined via a single-crystal X-ray diffraction study. This complex crystallizes in the noncentrosymmetric monoclinic space group $P2_1$ [C_2^2; No. 4] with a = 8.385 (2) Å, b = 14.682 (4) Å, c = 8.872 (2) Å, β = 104.60 (2)°, V = 1057.0 (4) Å³, and ρ(calcd) = 3.553 g cm⁻³ for Z = 2 and mol wt 1130.68. Diffraction data were collected with a Syntex $P2_1$ diffractometer and the structure was refined to R_F = 5.4% for 1454 reflections with 3° < 2θ < 45° (Mo Kα radiation). The molecule contains a tetrahedral heterometallic core in which the tungsten atom is coordinated to two carbonyl ligands and an η⁵-cyclopentadienyl ring, while each osmium atom is bonded to three terminal carbonyl ligands. There is evidence that the two carbonyl ligands primarily associated with W(4) act in a "semibridging" capacity and donate electron density to the otherwise electron-poor atom Os(2). There are three normal metal–metal distances [Os(1)–Os(2) = 2.825 (2) Å, Os(2)–Os(3) = 2.827 (2) Å, Os(2)–W(4) = 2.880 (3) Å] and three long (hydride-bridged) metal–metal vectors [Os(1)–Os(3) = 2.941 (2) Å, Os(1)–W(4) = 3.073 (2) Å, Os(3)–W(4) = 3.082 (3) Å]. Careful consideration of metal–metal–ligand angles leads to the conclusion that the three hydride ligands occupy mutually cisoid sites and that the three M–H–M systems lie essentially perpendicular to the Os(1)–Os(3)–W(4) face of the tetrahedron. This arrangement is consistent with ease of interchange of hydride ligands between nonequivalent sites, as indicated previously by ¹H NMR spectroscopy.

Introduction

The heteronuclear metal carbonyl hydride (μ-H)₃Os₃W-(CO)₁₁(η⁵-C₅H₅) can be prepared either by the reaction of Os₃(CO)₁₀(NCMe)₂ with a threefold excess of HW(CO)₃-(η⁵-C₅H₅) or by the action of H₂ on (μ-H)Os₃W(CO)₁₂(η⁵-C₅H₅).[3] A single-crystal X-ray diffraction study of this species was taken in order to determine (i) the overall connectivity of metal atoms and ligands in this cluster complex and (ii) the location of the hydride ligands. (¹H NMR studies showed only a broad singlet at τ 30.50 (intensity 3) along with the η⁵-C₅H₅ resonance at τ 4.25 (intensity 5).[3] The hydride ligands cannot be equivalent and are thus involved in some dynamic process in solution.)

Experimental Section

A small sample of the complex was provided by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The complex forms clear orange tabular crystals. Only one of the crystals provided appeared to be suitable for diffraction work; this was rather large but was trimmed to yield a rather irregular fragment of approximate dimensions 0.36 × 0.33 × 0.30 mm, which was mounted on a glass fiber with quick-setting transparent epoxy resin. Preliminary precession photographs provided approximate cell dimensions and indicated monoclinic (2/m) diffraction symmetry.

The crystal was transferred to our Syntex $P2_1$ automated diffractometer. Crystal alignment, determination of the orientation matrix and accurate cell dimensions, and data collection were all carried out as described previously.[4] Details specific to the present analysis are given in Table I. Two complete asymmetric sets of data were collected, one with indices −h, +k, ±l and a second with indices +h, +k, ±l. The latter set was later discarded (vide infra).

All crystallographic computations were performed using the Syntex XTL system[5] which consists of (i) a Data General Nova 1200 computer with 24K of 16-bit word memory and a parallel floating-point processor for 32- or 64-bit arithmetic, (ii) a Diablo moving-head disk unit with 1.2 million 16-bit words, (iii) a Versetec electrostatic printer/plotter, and (iv) the XTL conversational crystallographic program package as modified by our research group at SUNY at Buffalo.

Data were corrected for absorption (μ = 232.5 cm⁻¹) by an empirical method based upon ψ scans of reflections near χ = 90°.[6] The reflections used for the absorption curves (their 2θ values and maximum:minimum intensity ratios) were as follows: 1̄41̄ (13.52°, 3.47:1), 2̄51̄ (18.47°, 3.32:1), 1̄71̄ (20.97°, 3.17:1), 2̄82̄ (27.24°, 2.91:1), 2̄,10,2̄ (32.10°, 2.85:1), 2̄,12,2̄ (37.27°, 2.72:1). The shapes of the curves and the positions (in φ) of maxima and minima were self-consistent for all of these reflections; there was the usual broadening of the intensity profile with increasing 2θ.

Analysis of the check reflections showed a gradual linear decrease in intensity of approximately 6% over the period of data collection.

Table I. Experimental Data for the X-ray Diffraction Study of $(\mu\text{-H})_3\text{Os}_3\text{W(CO)}_{11}(\eta^5\text{-C}_5\text{H}_5)$

(A) Crystal Parameters at 25 °C[a]

crystal system: monoclinic	$V = 1057.0$ (4) A³
space group: $P2_1$ [$C_2{}^2$; No. 4]	$Z = 2$
$a = 8.385$ (2) A	mol wt = 1130.68
$b = 14.682$ (4) A	ρ(calcd) = 3.553 g cm⁻³
$c = 8.872$ (2) A	μ(Mo Kα) = 232.5 cm⁻¹
$\beta = 104.60$ (2)°	

(B) Measurement of Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda}$ 0.710 73 A)
monochromator: highly oriented graphite, equatorial mode
($2\theta_{\text{mono}} = 12.2°$)
reflections measd: $\pm h, +k, \pm l$
2θ range: 3–45°
scan type: θ(crystal)–2θ(counter)
scan width: $[2\theta(\text{K}\alpha_1) - 1.1]°$ to $[2\theta(\text{K}\alpha_2) + 1.1]°$
scan speed: 2.5°/min (in 2θ)
bkgd measurement: stationary crystal and counter at beginning
and end of 2θ scan, each for one-eighth of the scan time
standard reflections: three remeasured after each 47 reflections
(005, $\bar{5}$01, 080); linear decay of ca. 6% was observed over the
period of data collection (see text above)

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with $2\theta = 29.5 \pm 0.5°$. Reflections used were {084}, {235}, {23$\bar{6}$}, {390}, {512} and {56$\bar{1}$}.

Table II. Statistics for Intensity Distribution for Diffraction Data of $(\mu\text{-H})_3\text{Os}_3\text{W(CO)}_{11}(\eta^5\text{-C}_5\text{H}_5)$

	obsd	theoretical[a]	
		acentric	centric
$\langle |E|^2 \rangle$	1.000	1.000	1.000
$\langle |E| \rangle$	0.871	0.886	0.798
$\langle |E^2 - 1| \rangle$	0.777	0.736	0.968
$|E| > 1.0, \%$	37.69	36.79	31.73
$|E| > 2.0, \%$	1.65	1.89	4.55
$|E| > 3.0, \%$	0.00	0.01	0.27

[a] See I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, 19, 713 (1965).

Superimposed on this gradual decay, toward the end of the second half of the data collection, was a sudden drop to 70–80% of the original intensity; this persisted through several measurements of the standards and then the intensities returned to the extrapolated line for the gradual decay. (This errant effect was later deduced to be a preliminary symptom of catastrophic failure of the transformer of the X-ray generator.) Initially, only reflections in the anomalous region (~300 in number) were eliminated from the data set and the remaining data were averaged ($R(I) = 5.97\%$ for all averaged pairs of reflections). Later, however, we discovered that the presence of both averaged and nonaveraged data led to a bias in the weighting scheme in favor of the nonaveraged data. For the final analysis, therefore, we used only the first unique portion of the data set (i.e., $-h, +k, \pm l$).

Intensities were converted to unscaled $|F_0|$ values after correction for decay and for Lorentz and polarization effects. Any reflection with $I < 0$ was assigned $|F_0| = 0$; estimated standard deviations (esd's), $\sigma(F_0)$, were calculated from $F_0{}^2$ and $\sigma(F_0{}^2)$ by finite differences.

An examination of the entire data set revealed the systematic absences $k = 2n + 1$ for $0k0$ (only). This is consistent with the centrosymmetric monoclinic space group $P2_1/m$ [$C_{2h}{}^2$; No. 11] or the related noncentrosymmetric space group $P2_1$ [$C_2{}^2$; No. 4]. Intensity statistics (Table II) strongly suggested that the noncentrosymmetric space group $P2_1$ was appropriate; this was confirmed by the successful solution and refinement of the structure.

The analytical form[7a] of the scattering factors for neutral tungsten, osmium, carbon, and oxygen were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[7b] The function $\sum w(|F_0| - |F_c|)^2$ was minimized during least-squares refinement. The final weighting scheme gave zero weight to reflections with $F_0 < 3\sigma(F_0)$ and weights as defined in eq 1 for other reflections.

$$w = [\{\sigma(F_0)\}^2 + \{0.02(F_0)\}^2]^{-1} \qquad (1)$$

The discrepancy indices R_F and R_{wF} and the "goodness-of-fit" (GOF) are defined in eq 2–4.

$$R_F = \left[\frac{\sum ||F_0| - |F_c||}{\sum |F_0|} \right] \times 100 \ (\%) \qquad (2)$$

$$R_{wF} = \left[\frac{\sum w(|F_0| - |F_c|)^2}{\sum w|F_0|^2} \right]^{1/2} \times 100 \ (\%) \qquad (3)$$

$$\text{GOF} = \left[\frac{\sum w(|F_0| - |F_c|)^2}{\text{NO} - \text{NV}} \right]^{1/2} \qquad (4)$$

The analysis was begun using the "averaged" data set. The positions of the four metal atoms were determined from a Patterson map. Refinement of positional and isotropic thermal parameters for these atoms (assuming each to be osmium) led to $R_F = 11.7\%$. (Throughout all cycles of refinement the y coordinate of Os(1) was fixed at zero to define the origin of the unit cell.) The subsequent difference-Fourier map yielded the locations of the 27 remaining nonhydrogen atoms and allowed the differentiation of the tungsten atom from the osmium atoms on the basis of its chemical environment (i.e., W is attached to the $\eta^5\text{-C}_5\text{H}_5$ ligand). Continued least-squares refinement of positional parameters, anisotropic thermal parameters for the metal atoms, and isotropic thermal parameters for carbon and oxygen atoms led to convergence with $R_F = 6.2\%$.

Analysis of the residuals led at this point to our rejection of the latter half of the doubly redundant data set in toto and to rereduction of the data with $h \leq 0$ (vide supra). Refinement on the revised data set with the same parameters varied yielded $R_F = 5.5\%$, $R_{wF} = 7.5\%$, and GOF = 3.13. Inspection of the data now suggested that they were affected slightly by secondary extinction. A correction to the data set was made using the form shown in eq 5. Here, g was

$$F_0{}^{\text{cor}} = F_0{}^{\text{uncor}}(1.0 + gI_0) \qquad (5)$$

determined (by least-squares analysis of F_0 and $|F_c|$ values for intense reflections) to have a value of 8.65×10^{-8}. Three more cycles of least-squares refinement as before yielded the final agreement factors $R_F = 5.4\%$, $R_{wF} = 7.5\%$, and GOF = 3.10 for 144 parameters refined against the 1433 data with $F_0 > 3\sigma(F_0)$ (i.e., NO:NV = 9.95:1). The corresponding R values for all 1454 unique data were identical—$R_F = 5.4\%$ and $R_{wF} = 7.5\%$.

Inversion of the structure and refinement of all parameters in the other enantiomeric form led to convergence with increased residuals ($R_F = 5.9\%$ and $R_{wF} = 8.0\%$) indicating that our original choice of crystal chirality was correct. The refinement of anisotropic thermal parameters for the oxygen atoms led only to marginal improvement in the discrepancy indices ($R_F = 5.3\%$ and $R_{wF} = 7.3\%$—a decrease insufficient to justify the incorporation of an additional 55 parameters into the model); these results were discarded.

The largest peaks on a final difference-Fourier map were all close to the positions of the metal atoms; no features were observed at, or near, the positions where hydride ligands or hydrogen atoms of the cyclopentadienyl ring were expected.

The residual $\sum w(|F_0| - |F_c|)^2$ showed no significant dependency on $|F_0|$ or on $(\sin \theta)/\lambda$ but did show a slight systematic variation as a function of $|h|$. Our explanation of this is as follows. Reflections of high $|h|$, where the residual is systematically increased, were measured near diffractometer angle $\chi = 0°$, where the empirical absorption correction is expected to be the least satisfactory. There is no reliable way of correcting for this slight systematic problem in the present case where our crystal is of irregular shape and the use of an analytical absorption correction is not possible. Indeed, with $\mu = 232.5$ cm⁻¹ and $\mu R_{\text{av}} = 3.84$ for the sole available crystal, problems of this nature are close to inevitable.

Final positional and thermal parameters are collected in Table III.

Results and Discussion

Intramolecular distances and their esd's are given in Table IV; interatomic angles and their esd's are listed in Table V. The scheme used for labeling the atoms is shown in Figure 1; a stereoscopic view of the molecule is shown in Figure 2.

Table III. Final Positional and Thermal Parameters for $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$

(A) Positional and Isotropic Thermal Parameters

atom	x	y	z	B, Å^2
Os1	0.41883 (18)	0	0.10691 (16)	
Os2	0.63130 (18)	0.14955 (15)	0.10835 (16)	
Os3	0.47646 (19)	0.13723 (16)	0.35622 (17)	
W4	0.76206 (19)	0.01011 (16)	0.33393 (17)	
O11	0.124 (5)	0.097 (3)	−0.106 (4)	3.8 (7)
O12	0.215 (5)	−0.166 (3)	0.157 (5)	5.6 (10)
O13	0.532 (4)	−0.078 (3)	−0.169 (4)	3.9 (7)
O21	0.352 (5)	0.265 (3)	−0.091 (4)	4.1 (8)
O22	0.846 (5)	0.318 (2)	0.206 (4)	3.9 (7)
O23	0.750 (5)	0.114 (3)	−0.190 (4)	4.2 (8)
O31	0.191 (5)	0.257 (3)	0.178 (4)	4.3 (8)
O32	0.676 (6)	0.300 (3)	0.497 (5)	5.9 (10)
O33	0.344 (6)	0.094 (3)	0.631 (5)	5.6 (10)
O41	0.923 (5)	−0.030 (3)	0.053 (5)	5.6 (10)
O42	1.005 (5)	0.175 (3)	0.422 (4)	4.2 (8)
C1	0.995 (5)	−0.062 (3)	0.471 (5)	2.0 (8)
C2	0.892 (6)	−0.130 (4)	0.384 (6)	3.0 (9)
C3	0.752 (6)	−0.138 (4)	0.441 (6)	3.3 (10)
C4	0.780 (7)	−0.066 (4)	0.562 (6)	3.7 (10)
C5	0.920 (6)	−0.024 (4)	0.576 (6)	3.3 (10)
C11	0.235 (5)	0.062 (3)	−0.022 (5)	2.1 (8)
C12	0.293 (6)	−0.102 (3)	0.140 (5)	2.5 (8)
C13	0.479 (6)	−0.043 (4)	−0.068 (5)	2.9 (9)
C21	0.449 (5)	0.216 (3)	−0.015 (5)	1.7 (7)
C22	0.763 (6)	0.256 (3)	0.170 (5)	2.2 (8)
C23	0.712 (7)	0.123 (4)	−0.071 (6)	4.1 (11)
C31	0.299 (6)	0.211 (3)	0.252 (5)	2.7 (9)
C32	0.620 (6)	0.237 (4)	0.443 (6)	3.4 (10)
C33	0.404 (7)	0.110 (4)	0.534 (7)	4.2 (12)
C41	0.824 (7)	−0.003 (5)	0.142 (6)	4.5 (12)
C42	0.908 (6)	0.122 (3)	0.385 (5)	2.1 (8)

(B) Anisotropic Thermal Parameters for the Metal Atoms^a

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os1	2.06 (7)	1.65 (7)	1.40 (6)	−0.15 (6)	1.21 (5)	−0.19 (6)
Os2	2.04 (7)	1.59 (7)	1.41 (6)	0.05 (6)	1.24 (5)	0.25 (6)
Os3	2.36 (7)	1.97 (8)	1.39 (7)	0.15 (7)	1.38 (5)	−0.30 (6)
W4	2.04 (7)	1.73 (7)	1.61 (7)	0.23 (6)	1.08 (5)	0.27 (6)

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

Hydride ligands are shown in their deduced positions (vide infra); they were not located directly from the structural analysis.

The molecule contains a tetrahedral cluster of metal atoms—three osmium atoms and one tungsten atom. Each osmium atom is linked to three terminal carbonyl ligands, while the tungsten atom is coordinated to two terminal (or, possibly, "semibridging") carbonyl ligands and a η^5-cyclopentadienyl ring. (The differentiation between osmium and tungsten atoms was made initially on the basis of the method of synthesis of the compound; it is confirmed by consideration of bond lengths within the cluster. No attempt was made to distinguish between osmium ($Z = 76$) and tungsten ($Z = 74$) by such crystallographic techniques as refining occupancies of the metal atoms with common scattering factors or testing the four ordered permutations of the three osmium atoms and one tungsten atom. We do not believe that such tests would be useful or definitive.)

Metal–metal distances in the present molecule may be divided into the following four sets. (Note that the use of the words "short" and "long" are used below in a local comparative sense only; these words should not be considered here as being used in any more significant *general* context.)

(a) Short osmium–osmium bonds. The Os(1)–Os(2) and Os(2)–Os(3) linkages are 2.825 (2) and 2.827 (2) Å in length, respectively. These distances are consistent with normal osmium–osmium single-bond lengths. The average Os–Os

Table IV. Selected Interatomic Distances (Å) for the $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$ Molecule

(A) Metal–Metal Distances

Os(1)–Os(2)	2.825 (2)	Os(2)–Os(3)	2.827 (2)
Os(1)–Os(3)	2.941 (2)	Os(2)–W(4)	2.880 (3)
Os(1)–W(4)	3.073 (2)	Os(3)–W(4)	3.082 (3)

(B) Metal–Carbonyl Distances

Os(1)–C(11)	1.91 (4)	Os(1)···O(11)	3.06 (4)
Os(1)–C(12)	1.90 (5)	Os(1)···O(12)	3.07 (5)
Os(1)–C(13)	1.86 (5)	Os(1)···O(13)	3.06 (4)
Os(2)–C(21)	1.91 (4)	Os(2)···O(21)	3.06 (4)
Os(2)–C(22)	1.91 (5)	Os(2)···O(22)	3.05 (4)
Os(2)–C(23)	1.93 (6)	Os(2)···O(23)	3.10 (4)
Os(3)–C(31)	1.90 (5)	Os(3)···O(31)	3.07 (4)
Os(3)–C(32)	1.93 (6)	Os(3)···O(32)	3.00 (4)
Os(3)–C(33)	1.87 (6)	Os(3)···O(33)	2.98 (5)
Os–C(av)	1.90 [2]^b	Os···O(av)	3.05 [4]^b

(C) Distances Involving the η^5-C$_5$H$_5$ Ligand

W(4)–C(1)	2.29 (4)	C(1)–C(2)	1.41 (7)
W(4)–C(2)	2.32 (6)	C(2)–C(3)	1.40 (8)
W(4)–C(3)	2.39 (6)	C(3)–C(4)	1.48 (8)
W(4)–C(4)	2.29 (5)	C(4)–C(5)	1.31 (8)
W(4)–C(5)	2.28 (5)	C(5)–C(1)	1.38 (7)
W(4)···Cp^a	1.986		

(D) Carbon–Oxygen Distances

C(11)–O(11)	1.15 (6)	C(23)–O(23)	1.18 (7)
C(12)–O(12)	1.18 (7)	C(31)–O(31)	1.18 (6)
C(13)–O(13)	1.21 (6)	C(32)–O(32)	1.09 (7)
C(21)–O(21)	1.17 (6)	C(33)–O(33)	1.12 (8)
C(22)–O(22)	1.14 (6)		

(E) "Semibridging" (?) Carbonyl Distances

W(4)–C(41)	1.91 (6)	W(4)···O(41)	3.18 (4)
Os(2)···C(41)	2.73 (6)	C(41)–O(41)	1.34 (7)
W(4)–C(42)	2.03 (5)	W(4)···O(42)	3.13 (4)
Os(2)···C(42)	2.95 (4)	C(42)–O(42)	1.11 (6)

^{a} Cp is the centroid of the η^5-C$_5$H$_5$ system. ^{b} The esd of the average value is calculated using the "scatter formula" $\sigma(\text{av}) = [\Sigma_n(d_i - \bar{d})^2/(n - 1)]^{1/2}$. It thus represents an external estimate of the esd on the individual bond length. Here d_i is the ith and $\bar{d}$ is the average of n equivalent distances.
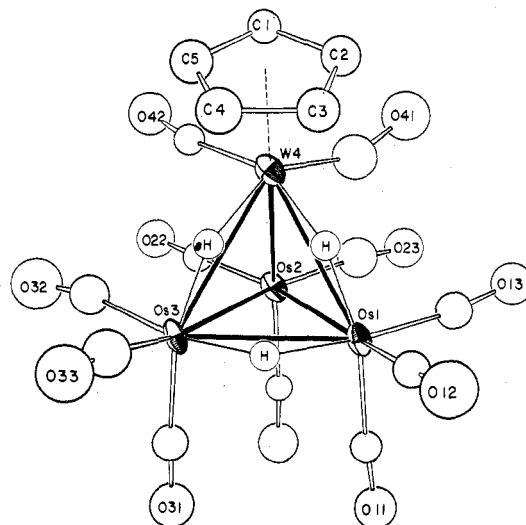

Figure 1. Labeling of atoms in the $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$ molecule. Each carbonyl carbon has the same number as its attached oxygen atom. Hydride ligands are shown in their predicted positions (see text) as spheres of arbitrary radius located 1.6 Å from each of the bridged metal atoms (ORTEPII diagram; 50% probability ellipsoids for all nonhydrogen atoms). Note the approximate $C_s(m)$ symmetry of the molecule.

distance in $Os_3(CO)_{12}$ is 2.877 (3) Å;^{8} however, comparisons of bond lengths in $Ru_3(CO)_{12}$ (Ru–Ru(av) = 2.854 (5) Å^9) with normal unbridged Ru–Ru distances in tetrahedral clusters [2.791 (7) Å (av) in $(\mu\text{-H})_4Ru_4(CO)_{10}$(diphos),^{10,11} 2.786 (1)
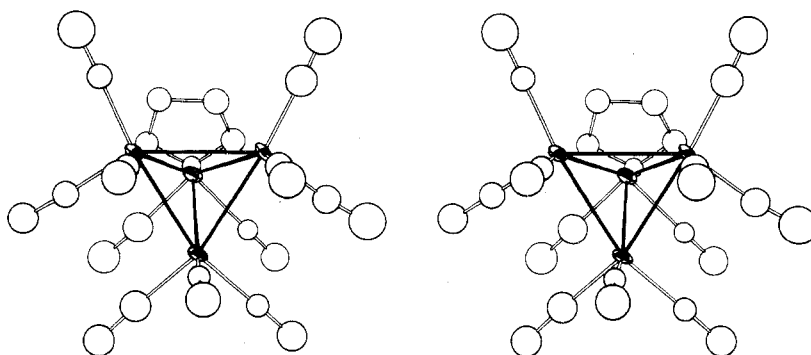
Figure 2. Stereoscopic view of the $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$ molecule.

Table V. Selected Interatomic Angles (deg) for $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$

(A) Intermetallic Angles

Os(2)–Os(1)–Os(3)	58.68 (6)	Os(1)–Os(3)–Os(2)	58.62 (6)
Os(2)–Os(1)–W(4)	58.27 (6)	Os(1)–Os(3)–W(4)	61.30 (6)
Os(3)–Os(1)–W(4)	61.61 (6)	Os(2)–Os(3)–W(4)	58.14 (6)
Os(1)–Os(2)–Os(3)	62.69 (6)	Os(1)–W(4)–Os(2)	56.57 (5)
Os(1)–Os(2)–W(4)	65.16 (6)	Os(1)–W(4)–Os(3)	57.09 (5)
Os(3)–Os(2)–W(4)	65.35 (7)	Os(2)–W(4)–Os(3)	56.50 (6)

(B) M–M–CO Angles

Os(2)–Os(1)–C(11)	92.4 (13)	Os(1)–Os(3)–C(31)	93.7 (15)
Os(3)–Os(1)–C(11)	94.2 (13)	Os(2)–Os(3)–C(31)	92.3 (15)
W(4)–Os(1)–C(11)	148.3 (13)	W(4)–Os(3)–C(31)	147.8 (15)
Os(2)–Os(1)–C(12)	170.9 (14)	Os(1)–Os(3)–C(32)	142.0 (16)
Os(3)–Os(1)–C(12)	114.6 (14)	Os(2)–Os(3)–C(32)	84.2 (16)
W(4)–Os(1)–C(12)	113.8 (14)	W(4)–Os(3)–C(32)	93.7 (16)
Os(2)–Os(1)–C(13)	88.0 (15)	Os(1)–Os(3)–C(33)	117.4 (19)
Os(3)–Os(1)–C(13)	146.5 (15)	Os(2)–Os(3)–C(33)	168.4 (19)
W(4)–Os(1)–C(13)	99.1 (15)	W(4)–Os(3)–C(33)	110.3 (19)
Os(1)–Os(2)–C(21)	89.0 (12)	Os(1)–W(4)–C(41)	80.3 (18)
Os(3)–Os(2)–C(21)	91.2 (12)	Os(2)–W(4)–C(41)	66.0 (18)
W(4)–Os(2)–C(21)	150.7 (12)	Os(3)–W(4)–C(41)	120.5 (18)
Os(1)–Os(2)–C(22)	162.8 (14)	Os(1)–W(4)–C(42)	126.6 (13)
Os(3)–Os(2)–C(22)	100.2 (14)	Os(2)–W(4)–C(42)	71.4 (13)
W(4)–Os(2)–C(22)	106.8 (14)	Os(3)–W(4)–C(42)	86.0 (13)
Os(1)–Os(2)–C(23)	100.9 (17)	Os(1)–W(4)–Cp	126.6
Os(3)–Os(2)–C(23)	163.4 (17)	Os(2)–W(4)–Cp	175.9
W(4)–Os(2)–C(23)	106.2 (17)	Os(3)–W(4)–Cp	126.7

(C) Carbon–Metal–Carbon Angles

C(12)–Os(1)–C(11)	94.3 (19)	C(32)–Os(3)–C(31)	95.4 (22)
C(13)–Os(1)–C(11)	90.7 (20)	C(33)–Os(3)–C(31)	98.9 (24)
C(13)–Os(1)–C(12)	98.0 (20)	C(33)–Os(3)–C(32)	97.4 (25)
C(22)–Os(2)–C(21)	94.0 (18)	C(41)–W(4)–C(42)	89.7 (22)
C(23)–Os(2)–C(21)	91.6 (21)	C(41)–W(4)–Cp	111.5
C(23)–Os(2)–C(22)	96.0 (22)	C(42)–W(4)–Cp	105.8

(D) Metal–Carbon–Oxygen Angles

Os(1)–C(11)–O(11)	176.1 (39)	Os(3)–C(31)–O(31)	175.9 (43)
Os(1)–C(12)–O(12)	178.4 (42)	Os(3)–C(32)–O(32)	167.4 (51)
Os(1)–C(13)–O(13)	171.5 (43)	Os(3)–C(33)–O(33)	172.5 (55)
Os(2)–C(21)–O(21)	171.8 (37)	W(4)–C(41)–O(41)	154.2 (47)
Os(2)–C(22)–O(22)	178.4 (41)	Os(2)···C(41)–O(41)	128.1 (40)
Os(2)–C(23)–O(23)	172.7 (49)	W(4)–C(42)–O(42)	170.0 (41)
		Os(2)···C(42)–O(42)	121.1 (35)

(E) Carbon–Carbon–Carbon Angles

C(5)–C(1)–C(2)	110.3 (42)	C(3)–C(4)–C(5)	113.0 (49)
C(1)–C(2)–C(3)	108.1 (45)	C(4)–C(5)–C(1)	106.4 (47)
C(2)–C(3)–C(4)	102.1 (45)		

Å in $(\mu\text{-H})_4Ru_4(CO)_{12}$,[12] 2.772 (2) Å in $(\mu\text{-H})_4Ru_4(CO)_{10}$-$(PPh_3)_2$,[12] 2.76 Å in $(\mu\text{-H})_4Ru_4(CO)_{11}P(OMe)_3$[13]] suggest that normal metal–metal distances in tetrahedral clusters are some 0.06–0.09 Å shorter than those in triangular clusters.

(b) A long osmium–osmium bond. The Os(1)–Os(3) distance of 2.941 (2) Å is 0.115 Å longer than the average "short" osmium–osmium bond length of 2.826 Å. As such, the Os(1)–Os(3) vector is designated as a site for a bridging hydride ligand. We note here that the following Os···Os distances have been observed in association with single un-

supported μ-hydride ligands in *triangular* clusters: 2.989 (1) Å in $(\mu\text{-H})(H)Os_3(CO)_{11}$,[8] 3.019 (1) Å in $(\mu\text{-H})(H)Os_3\text{-}(CO)_{10}(PPh_3)$,[14] 3.007 (1) Å in $(\mu\text{-H})Os_3(CO)_8[\overline{C(O-)C\text{-}(CHMe-)CHCHCEt}]$,[15,16] 3.059 (3)–3.084 (2) Å in $(\mu\text{-}H)_2Os_3Re_2(CO)_{20}$,[1,17] and 2.965 (1) Å in $(\mu\text{-H})Os_3(CO)_9\text{-}[\overline{-CHC(=O)CH=CEtC(=CHMe)}]$.[2]

(c) A short osmium–tungsten bond, Os(2)–W(4) = 2.880 (3) Å. This appears to be the first reported osmium–tungsten bond length; it can therefore be compared only with the "long" osmium–tungsten distances in set (d).

(d) Long osmium–tungsten distances. The Os(1)–W(4) and Os(3)–W(4) distances are 3.073 (2) and 3.082 (3) Å, respectively. The average distance of 3.078 (6) Å is 0.198 Å longer than the "short" distance of 2.880 (3) Å. These two vectors are assigned as the locations of the remaining two bridging hydride ligands, by analogy with other systems containing single unsupported μ-bridging-hydride ligands.[18,19]

The overall tetranuclear core of the $(\mu\text{-H})_3Os_3W(CO)_{11}\text{-}(\eta^5\text{-}C_5H_5)$ molecule contains three "short" metal–metal bonds (which we believe to be normal metal–metal σ bonds) and three "long" metal–metal vectors (which we believe to be participating in closed two-electron, three-center $M(\mu\text{-H})M$ systems). While this argument, based solely upon metal–metal distances, uniquely identifies the three hydride-bridged metal–metal vectors, it does not, however, uniquely define the *positions* of the three hydride ligands. The reason for this is that (in a tetrahedral M_4 cluster) the M–H–M plane can occur at various angles relative to the M–M–M planes. Cases of interest in the present discussion are as follows.

(a) The case where an M_1–H–M_2 plane bisects the exterior angle between M_1–M_3–M_2 and M_1–M_4–M_2 tetrahedral faces meeting at the common M_1–M_2 edge (see I).

(b) Cases where the M_1–H–M_2 plane is coplanar with one of the two triangular tetrahedral faces meeting at the M_1–M_2 edge—either with M_1–M_3–M_2 (as in II) or with M_1–M_4–M_2 (as in III).
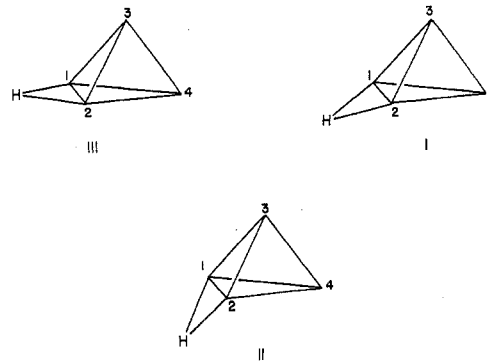
(c) Cases where the M_1–H–M_2 plane is perpendicular to either the M_1–M_3–M_2 or the M_1–M_4–M_2 plane. These cases
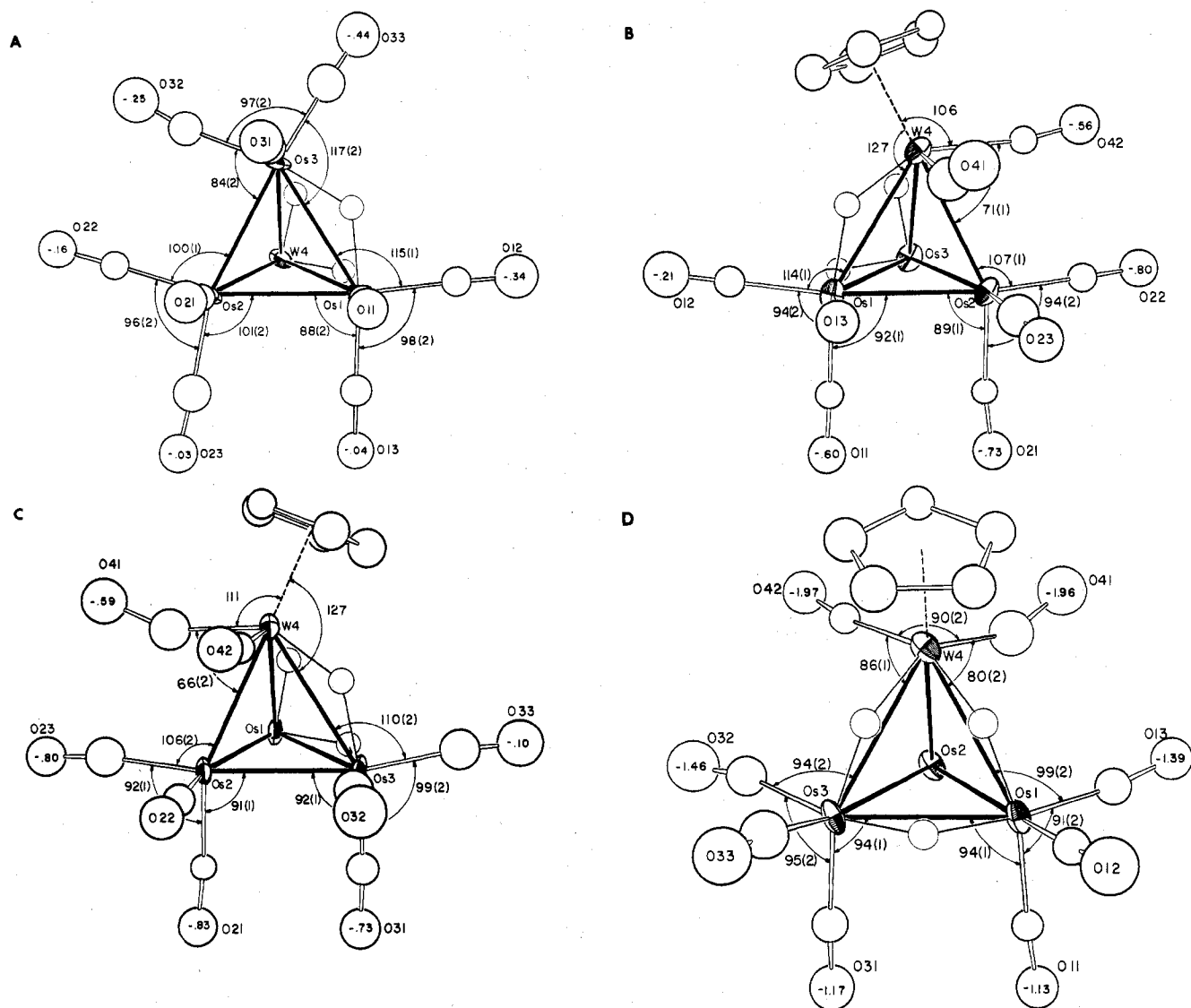
Figure 3. Projections of the molecule onto each of the four faces of the Os$_3$W tetrahedral core: (A) projection onto the Os(1)–Os(2)–Os(3) plane, (B) projection onto the Os(1)–Os(2)–W(4) plane, (C) projection onto the Os(2)–Os(3)–W(4) plane, (D) projection onto the Os(1)–Os(3)–W(4) plane; note the three out-of-plane (i.e., axial–axial) bridging hydride ligands. Ligands attached to the rear metal atom are eliminated for clarity in each view. In-plane M–M–C and C–M–C angles are given and deviations (Å) of appropriate oxygen atoms from the planes are indicated.

cannot be differentiated in our arguments below from III and II (respectively) in case (b) above.

Even when the hydride ligands cannot be located directly (as in the present case), it is possible to identify their approximate positions by the following observation. *We expect to see abnormally large M–M–L angles for ligands* (L) *adjacent to, and in the same plane as, the M–H–M system.* In contradistinction to this, we expect normal M–M–L angles for ligands adjacent to but lying essentially perpendicular to the M–H–M system.

Figure 3A–D shows the geometry of ligands relative to the four M–M–M faces of the tetrahedral cluster. Clearly, ligands do not all lie *precisely* in one or other of these planes. Nevertheless, the M–M–CO angles break down cleanly into two groups—large M–M–CO angles (110–117°, average 114°) coplanar with (and adjacent to) the M–H–M linkages and smaller or "normal" M–M–CO angles (66–107°, average 91°) which are not coplanar with and adjacent to the M–H–M linkages.

In Figure 3A we observe the large in-plane M–M–L angles Os(1)–Os(3)–C(33) = 117 (2)° and Os(3)–Os(1)–C(12) = 115 (1)°; clearly, H(13), the bridging hydride between Os(1)

and Os(3), lies essentially in the Os(1)–Os(2)–Os(3) plane. In Figure 3B, the W(4)–Os(1)–C(12) angle is 114 (1)° and the Os(1)–W(4)–Cp angle is 127° while all other in-plane M–M–L angles are normal. Clearly, H(14), the hydride ligand bridging Os(1) and W(4), lies essentially in the Os(1)–Os(2)–W(4) plane. In Figure 3C, the W(4)–Os(3)–C(33) angle is 110 (2)° while the Os(3)–W(4)–Cp angle is 127°. H(34), the hydride ligand bridging Os(3) and W(4), therefore lies in, or close to, the Os(2)–Os(3)–W(4) plane. Finally, in Figure 3D we find that there are *no* anomalously large in-plane M–M–L angles. Thus, there are no bridging hydride ligands lying in the Os(1)–Os(3)–W(4) plane—all three μ-hydrides are essentially perpendicular to this plane and do not affect equatorial angles around the Os(1)–Os(3)–W(4) triangle.

Our deliberations thus indicate that the hydride ligands take up a mutually cisoid arrangement above the Os(1)–Os(3)–W(4) face of the Os$_3$W tetrahedron. This arrangement of hydride ligands is consistent with the rapid interchange of the hydride ligands between the three observed sites as observed from ^{1}H NMR studies which indicate a broad singlet (τ 30.50) for these three nonequivalent protons in solution.

The molecule has approximate C_s symmetry, as clearly shown in Figure 1. The carbonyl ligand C(41)–O(41) which is associated principally with the tungsten atom [W(4)–C(41) = 1.91 (6) Å; W(4)–C(41)–O(41) = 154.2 (47)°] is oriented such as to suggest a weak interaction also with Os(2) [Os-(2)···C(41) = 2.73 (6) Å; Os(2)···C(41)–O(41) = 128.1 (40)°]. The carbonyl ligand C(42)–O(42) is also associated primarily with the tungsten atom [W(4)–C(42) = 2.03 (5) Å]. This carbonyl ligand is also slightly bent [W(4)–C(42)–O(42) = 170.0 (41)°] and interacts slightly with Os(2) [Os(2)···C(42) = 2.95 (4) Å and Os(2)···C(42)–O(42) = 121.1 (35)°].

Weakly "semibridging" carbonyl ligands often act so as to distribute electron density more evenly around a metal cluster complex.[20,21] (Formal electron counting, assuming *neutral* metal atoms and ligands, gives 19 outer valence electrons at W(4), 18 electrons at Os(1) and Os(3), and 17 electrons at Os(2).) "Semibridging" carbonyl ligands across the W(4)–Os(2) vector are in the appropriate location to effectively donate electron density from W(4) to Os(2).

Registry No. (μ-H)₃Os₃W(CO)₁₁(η⁵-C₅H₅), 68297-92-7.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Molecules with an M₄X₄ Core. 10.[1] Failure of the 1:1:1 Tricyclohexylphosphine–Copper(I)–Chloride Complex to Form a Tetramer. Crystal Structure of Dimeric (Tricyclohexylphosphine)copper(I) Chloride, [(P(cHx)₃)CuCl]₂

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(Tricyclohexylphosphine)copper(I) chloride crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with a = 8.4977 (12) Å, b = 9.2667 (11) Å, c = 13.2797 (18) Å, α = 100.82 (1)°, β = 89.73 (1)°, γ = 113.66 (1)°, V = 937.9 (2) Å³, ρ(obsd) = 1.32, and ρ(calcd) = 1.34 g cm⁻³ for Z = 1 (dimeric molecule). Diffraction data with 4.5° < 2θ < 40.0° (Mo Kα radiation) were collected with a Syntex $P2_1$ automated diffractometer, and the structure was solved via conventional Patterson, Fourier, and least-squares refinement techniques. All atoms (including hydrogens) were located directly, the final discrepancy indices being R_F = 4.9% and R_{wF} = 3.8% for those 1580 reflections with $|F_o| > \sigma(|F_o|)$. The complex exists as the *dimeric* species [(P(cHx)₃)CuCl]₂—in sharp contrast to the *tetrameric* "cubane" or "step" structures found for all previously examined phosphine–copper(I) halide complexes with a 1:1 ratio of monodentate tertiary phosphine to copper(I). The dimeric molecule has precise C_i symmetry. Each copper(I) atom is in trigonal-planar coordination to a phosphine ligand and two bridging chloride ions. Distances and angles within the coordination sphere are as follows: Cu–P = 2.183 (2) Å, Cu–Cl = 2.322 (2) Å, Cu–Cl' = 2.285 (2) Å, ∠P–Cu–Cl = 127.40 (7)°, ∠P–Cu–Cl' = 136.05 (7)°, ∠Cl–Cu–Cl' = 96.56 (7)°. Angles at the bridging chloride ligands are *acute* (∠Cu–Cl–Cu' = 83.44 (7)°) despite the absence of a metal–metal bond (Cu···Cu' = 3.066 (1) Å); this is apparently due to intramolecular chlorine···chlorine repulsions (Cl···Cl' = 3.439 (3) Å).

Introduction

The chemistry of monodentate tertiary phosphine complexes of the copper(I) halides has been surveyed by Lippard and Mayerle.[2] There is a remarkable diversity of stoichiometry, the phosphine-to-copper ratio varying through the range 4:1 in ionic [L₄Cu⁺]X⁻ complexes (L = PR₃, X = Cl, Br, I), 3:1 in L₃CuX complexes, 2:1 in [L₂CuX]₂ and L₂CuX complexes, 3:2 in the asymmetric L₂Cu(μ-X)₂CuL complexes, and 1:1 in [LCuX]₄ complexes. We have previously completed X-ray structural analyses of the tetrameric 1:1 complexes [(PPh₃)CuCl]₄,[3] [(PPh₃)CuBr]₄,[4] [(PPh₃)CuI]₄,[5] [(PEt₃)-CuCl]₄,[6] [(PEt₃)CuBr]₄,[6] [(PEt₃)CuI]₄,[7] and [(PMePh₂)-CuI]₄.[1] It has been established that the "cubane" structure (I) is destabilized relative to the "step" [otherwise termed

I   II