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Structural studies on polynuclear osmium carbonyl hydrides

XXXIV *. Elucidation of the molecular structure from a crystal structure of disordered $(\mu\text{-H})_5Os_3Re(CO)_{12}$

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Abstract

The complex $(\mu\text{-H})_5Os_3Re(CO)_{12}$ crystallizes in the centrosymmetric hexagonal space group $P6_3/m$ (C_{6h}^2; No. 176) with a 19.087(5), c 10.963(1) Å, V 3459(3) Å^3, and $Z = 6$. Diffraction data were collected on a Syntex P2_1 automated four-circle diffractometer (Mo-K_α radiation, $2\theta = 4.5$–$45.0°$) and the structure was refined to $R_F = 7.9\%$ for all 1480 unique reflections ($R_F = 5.4\%$ for those 1007 data with $|F_o| > 6\sigma(|F_o|)$). The molecule contains a tetrahedral core of metal atoms each associated with three terminal carbonyl ligands. It is bisected by a crystallographic mirror plane. Although the hydride ligands were not located, a consideration of metal–metal distances allows the distinction between osmium and rhenium atoms and suggests that the structure is subject to a subtle form of two-fold disorder.

Introduction

We have previously reported the results of single-crystal X-ray diffraction studies on the "spiked" osmium-rhenium clusters $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ [6,7] and $(\mu\text{-H})Os_3Re(CO)_{15}(NCMe)$ [8,9]. These have the planar core geometry shown in **1** and **2**, respectively.

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* For previous parts, see ref. 1–5.

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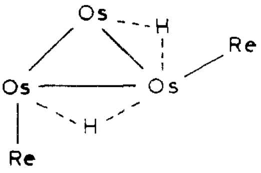
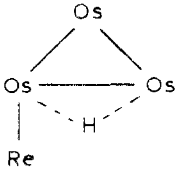


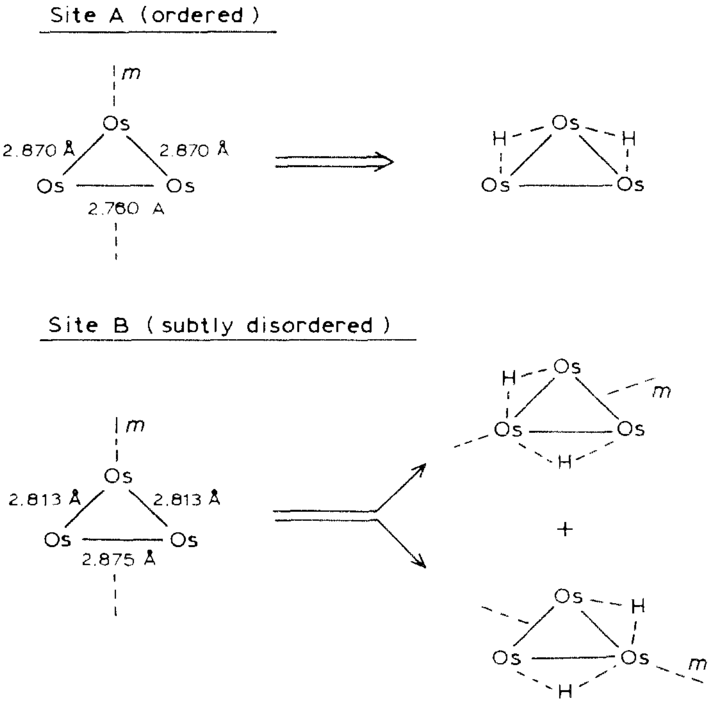
(1)



(2)

It has been shown [8] that treatment of $(\mu\text{-H})Os_3Re(CO)_{15}(NCMe)$ in acetonitrile with H_2 and trimethylamine *N*-oxide dihydrate leads to $(\mu\text{-H})_5Os_3Re(CO)_{12}$ in good yield (> 70%). This complex has been characterized by mass spectrometry, infra-red spectroscopy and ^{1}H NMR and a very brief report of the crystal structure (at an intermediate stage of refinement) has appeared [8]. We now report the details of the crystal structure of $(\mu\text{-H})_5Os_3Re(CO)_{12}$ and of our treatment of a rather subtle disorder problem.

Metal carbonyl clusters show a penchant for disorder, particularly when the exterior polyhedron defined by the oxygen atoms of the carbonyl groups possesses higher symmetry (usually augmented by an inversion center) than the interior metal atom cluster. This occurs particularly for triangular and tetrahedral metal cluster derivatives, e.g. $Fe_3(CO)_{10}(\mu\text{-CO})_2$ [10–12], $Co_4(CO)_9(\mu\text{-CO})_3$ [10,13–14], $Rh_4(CO)_9(\mu\text{-CO})_3$ [13,15], $Ir_4(CO)_{12}$ [16] and $Os_3(CO)_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$ [17]; the trigonal-bipyramidal cluster $Bi_2Fe_3(CO)_9$ [18] exhibits a related form of disorder.



Scheme 1. Interpretation of observed Os–Os distances in $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-CCO})$.

A more subtle and insidious form of disorder is possible when the isolated molecule has low symmetry but is only slightly (but necessarily) distorted from a point group of higher symmetry. All or most of the atoms of the molecule overlap upon performing an "approximately-allowed" symmetry operation, but the resulting composite molecular image exhibits unexpected (and inexplicable) features. An excellent example of this is $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^1\text{-CCO})$, a molecule with precise C_s symmetry which is only slightly perturbed from an arrangement of C_{3v} symmetry. An X-ray structural study of this cluster reveals two crystallographically unrelated environments (hereafter termed 'A' and 'B') for molecules in the unit cell; the apparent Os–Os bond lengths in the two independent molecules are not mutually consistent. Molecules on site A lie on a mirror plane coincident with the molecular mirror plane and have the expected Os–Os distances. Molecules on site B have a different pattern of apparent Os–Os distances which can be explained only if we assume that site B represents the composite of two molecular orientations related by a pseudo-C_3^1 and pseudo-C_3^2 operation relative to the crystallographic mirror plane (see Scheme 1). The present study reveals that the observed solid-state structure of $(\mu\text{-H})_5\text{Os}_3\text{Re}(\text{CO})_{12}$ can best be explained by invoking a similar scrambling of M–M and M–(H)–M bonds.

Species with a H_4M_4 core (e.g. $(\mu\text{-H})_4\text{Ru}_4(\text{CO})_{12}$ [20] and its derivatives [20–22], $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{12}$ [38] and its derivatives [23], and $(\mu_3\text{-H})_4\text{Re}_4(\text{CO})_{12}$ [24]) are well known. Metal clusters with five or more bridging hydride ligands are rather rare, examples being $[(\mu\text{-H})_6\text{Re}_4(\text{CO})_{12}{}^{2-}]$ [25,26], $(\mu\text{-H})_6\text{Cu}_6(\text{PPh}_3)_6$ [27] and $(\mu\text{-H})_6\text{Cu}_6[\text{P}(p\text{-tolyl})_3]_6$ [28]. The present $(\mu\text{-H})_5\text{Os}_3\text{Re}(\text{CO})_{12}$ molecule represents a further example of this structural type.

Experimental

Collection of X-ray diffraction data

The crystal chosen for the diffraction study was a very small rectangular parallelepiped with approximate dimensions 0.05 × 0.08 × 0.14 mm^3. It was sealed into a thin-walled glass capillary under an inert atmosphere (Ar), was mounted into a eucentric goniometer and was aligned and centered (with its extended direction parallel with the instrument's ϕ-axis) on a Syntex $P2_1$ automated four-circle diffractometer. All subsequent set-up operations (i.e., determination of the crystal's unit cell dimensions and orientation matrix) and data collection (Mo-K_α radiation, coupled θ(crystal)–2θ(counter) scan technique) were performed as described previously [29]. Details appear in Table 1.

The observed diffraction symmetry (C_{6h}, $6/m$) indicated that the crystal belonged to the hexagonal crystal system. The observed systematic absences ($00l$ for $l = 2n + 1$) are consistent with either the non-centrosymmetric hexagonal space group $P6_3$ (C_6^6; No. 173) or the centrosymmetric space group $P6_3/m$ ($C_{6h}{}^2$; No. 176) [30]. The crystallographic asymmetric unit would be one entire molecule in space group $P6_3$ or one-half of the molecule (i.e., crystallographically-required $C_s(m)$ symmetry) in space group $P6_3/m$. We elected to collect two forms of data (hkl and $hk\bar{l}$) because of the possibility that the crystal belonged to the polar space group $P6_3$. All data were corrected for Lorentz and polarization factors and for the effects of absorption (via interpolation in ϕ and 2θ between a set of ψ-scans of close-to-axial reflections). Absorption was not a serious problem since a very small

Table 1

Experimental data for the X-ray diffraction study of $(\mu\text{-H})_5\text{Os}_3\text{Re(CO)}_{12}$

(A) Crystallographic information

Cryst. system: hexagonal	Formula: $C_{12}H_5O_{12}Os_3Re$
Space group: $P6_3/m$ [$C_{6h}{}^2$: No. 176]	Mol. wt.: 1097.9
a 19.087(5) Å	$Z = 6$
c 10.963(1) Å	D_{calc} 3.16 g cm^{-3}
V 3459(3) Å^3	T 24 °C (297 K)

(B) Conditions for data collection

Diffractometer: Syntex $P2_1$

Radiation: Mo-$K_{\bar{\alpha}}$ ($\bar{\lambda}$ 0.710730 Å)

Monochromator: pyrolytic graphite: equatorial mode with $2\theta(\text{mono}) = 12.160°$: assumed to be 50% perfect/50% ideally mosaic for polarization correction.

Reflections measd: hkl and $hk\bar{l}$ for $2\theta = 4.5\text{–}45.0°$; 3364 reflections collected and merged to 1480 unique data with $I(\text{net}) > 0$ (filename H5RO-034).

Scan conditions: coupled θ(crystal)–2θ(counter) scan from $[2\theta(K_{\alpha_1}) - 1.2]°$ through $[2\theta(K_{\alpha_2}) + 1.2]°$ at 2.0 °/min in 2θ.

Backgrounds: stationary-crystal and stationary counter at the two extremes of the 2θ scan; each for one-half of total scan time.

Standard reflections: 3 approximately mutually orthogonal reflections (610, $1\bar{7}0$, 117) collected after each batch of 97 data points. No significant fluctuations nor decay were observed.

Absorption correction: $\mu(\text{Mo-}K_\alpha)$ 230.5 cm^{-1}; all data were corrected empirically by interpolation (in 2θ and ϕ) between the normalized transmission curves of 4 close-to-axial ψ-scans. (See text.)

crystal was used (vide supra). The variations in transmission factors for the ψ-scans were as follows: $T_{\text{min}}/T_{\text{max}} = 0.867$ for 034 ($2\theta = 16.6°$), 0.929 for 006 ($2\theta = 22.4°$), 0.911 for 117 ($2\theta = 26.5°$) and 0.936 for 008 ($2\theta = 30.0°$).

Data were reduced to unscaled $|F_o|$ values, any reflection with $I(\text{net}) \leqslant 0$ being expunged from the file. Intensity statistics now strongly suggested that the structure was centric (see Table 2). This was confirmed later by the successful solution of the structure in space group $P6_3/m$. The 3364 hkl and $hk\bar{l}$ data were merged to a unique set of 1619 reflections. Only those 1480 data with $I(\text{net}) > 0$ were used in the refinement process. (Averaging statistics were $R(I) = 3.96\%$ and $R_w(I) = 3.91\%$ for 1443 pairs of reflections.)

Table 2

Intensity statistics on diffraction data for $(\mu\text{-H})_5\text{Os}_3\text{Re(CO)}_{12}$

Function	Observed value	Theoretical	
		Centric	Acentric
$\langle \lvert E \rvert \rangle$	0.845	0.798	0.886
$\langle \lvert E \rvert^2 \rangle$	1.013	1.000	1.000
$\langle \lvert \lvert E \rvert^2 - 1 \rvert \rangle$	0.893	0.968	0.736
$\lvert E \rvert > 1.0$ (%)	31.42	31.73	36.79
$\lvert E \rvert > 2.0$ (%)	4.05	4.55	1.89
$\lvert E \rvert > 2.5$ (%)	0.95	1.24	0.19
$\lvert E \rvert > 3.0$ (%)	0.14	0.27	0.01

Solution and refinement of the structure

All calculations were performed on a Syntex XTL system using the SUNY-Buffalo version of the XTL interrogative crystallographic program package. The analytical form of the scattering factors for neutral atoms was corrected for both the real and imaginary components of anomalous dispersion [31]. The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\{\sigma(|F_o|)\}^2 + \{0.015|F_o|\}^2]^{-1}$. Discrepancy indices used below are defined as follows:

$$R_F(\%) = 100\Sigma||F_o| - |F_c||/\Sigma|F_o|$$

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

$$GOF = \left[\Sigma w(|F_o| - |F_c|)^2/(NR - NV)\right]^{1/2}$$

In the last equation, NR is the number of reflections and NV is the number of variables.

The structure was solved by use of a Patterson map. Subsequent difference-Fourier syntheses revealed the locations of all non-hydrogen atoms. The hydride ligands were not located directly. Full-matrix least-squares refinement converged with $R_F = 7.9\%$, $R_{wF} = 7.0\%$ and $GOF = 1.79$ for all 1480 reflections ($R_F = 5.4\%$ and

Table 3

Final atomic parameters for $(\mu\text{-H})_5Os_3Re(CO)_{12}$

(A) Positional and isotropic thermal parameters

Atom	x	y	z	B (Å^2)
Os(1)	0.27975(8)	0.32905(8)	0.11480(12)	–
Os(2)	0.40423(11)	0.45785(11)	1/4	–
Re(4)	0.24082(11)	0.44303(11)	1/4	–
C(11)	0.3488(20)	0.2851(20)	0.0965(32)	3.9(7)
O(11)	0.3875(14)	0.2528(15)	0.0906(23)	5.2(6)
C(12)	0.3213(21)	0.3957(22)	−0.0219(35)	4.6(8)
O(12)	0.3450(14)	0.4415(15)	−0.1048(25)	5.3(6)
C(13)	0.1898(29)	0.2455(29)	0.0344(46)	7.7(12)
O(13)	0.1344(21)	0.1969(22)	−0.0156(34)	9.3(9)
C(21)	0.4705(24)	0.4107(25)	1/4	2.4(8)
O(21)	0.5177(23)	0.3899(22)	1/4	5.7(9)
C(22)	0.4606(18)	0.5324(18)	0.1293(30)	3.2(6)
O(22)	0.4940(14)	0.5746(14)	0.0482(24)	5.4(6)
C(41)	0.1267(31)	0.3965(29)	1/4	3.8(10)
O(41)	0.0596(22)	0.3662(20)	1/4	5.0(8)
C(42)	0.2526(19)	0.5154(21)	0.1263(32)	4.1(7)
O(42)	0.2594(14)	0.5604(14)	0.0485(23)	4.9(5)

(B) Anisotropic thermal parameters [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	3.33(7)	3.33(6)	3.04(6)	1.99(5)	−0.33(5)	−0.66(5)
Os(2)	2.53(9)	3.04(9)	2.69(9)	1.74(8)	0	0
Re(4)	2.47(8)	3.04(9)	2.43(8)	1.73(8)	0	0

[a] These enter the expression for F_c in the form: $\exp[-0.25(h^2a^{*2}B_{11} + \ldots 2hka^*b^*B_{12} + \ldots)]$.

$R_{wF} = 6.5\%$ for those 1007 reflections with $|F_o| > 6\sigma(|F_o|)$). A final difference-Fourier synthesis revealed residual peaks of height $\sim 1.2\ e^-/\text{Å}^3$ within 1 Å of the positions of the metal atoms but was otherwise featureless. The structure is thus complete. Final atomic parameters are collected in Table 3.

Discussion

The crystal is composed of discrete molecular units of $(\mu\text{-H})_5Os_3Re(CO)_{12}$ which are separated by normal Van der Waals' distances; there are no abnormally short intermetallic contacts. The overall geometry of the $Os_3Re(CO)_{12}$ portion of the structure is illustrated in Fig. 1. Interatomic distances and angles are collected in Tables 4 and 5.

While the tetrahedral geometry of the metal cluster core and the presence of three terminal carbonyl ligands on each metal atom are unambiguous, there remain the problems of identifying the metal atoms (which is not possible by X-ray diffraction techniques, since their scattering power is very similar with $Z = 75$ for Re and $Z = 76$ for Os) and of ascertaining the locations of the five hydride ligands. A self-consistent argument which yields an answer to these problems can be constructed using the following steps.

(1) The cluster as a whole contains an $M_4(CO)_{12}$ core which has a geometry only slightly distorted from T_d. The $M(CO)_3$ fragments are all regular with OC–M–CO angles of 91.7(15)–96.8(2)°. There are no obvious "holes" in the ligand distribution

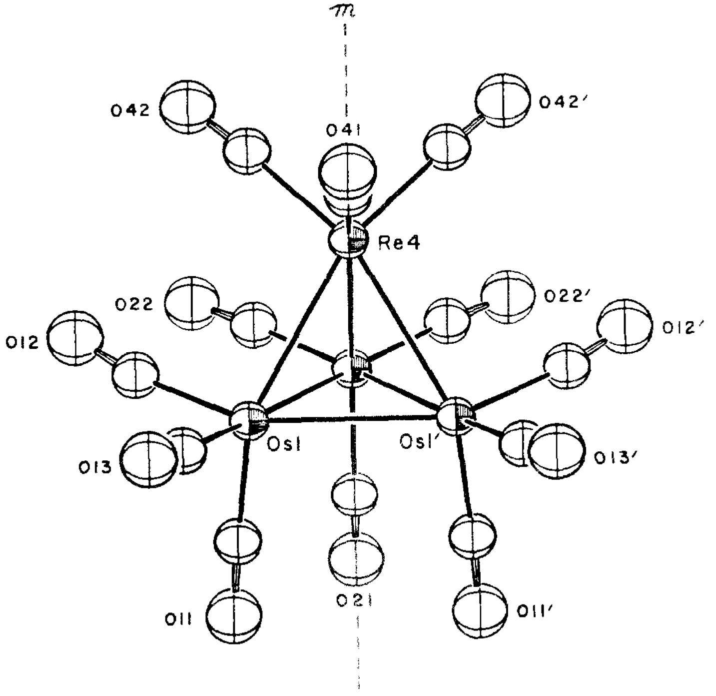


Fig. 1. View of the $Os_3Re(CO)_{12}$ core of the disordered $(\mu\text{-H})_5Os_3Re(CO)_{12}$ molecule. The crystallographic mirror plane is vertical.

Table 4

Interatomic distances (Å) for $(\mu\text{-H})_5\text{Os}_3\text{Re(CO)}_{12}$

(A) Metal – metal distances			
Os(1)–Os(1′)	2.964(2)	Os(1)–Re(4)	3.016(2)
Os(1)–Os(2)	2.836(2)	Os(1′)–Re(4)	3.016(2)
Os(1′)–Os(2)	2.836(2)	Os(2)–Re(4)	2.987(3)
(B) Metal – carbon distances			
Os(1)–C(11)	1.89(4)	Os(2)–C(21)	1.88(5)
Os(1)–C(12)	1.87(4)	Os(2)–C(22)	1.85(3)
Os(1)–C(13)	1.88(5)	Os(2)–C(22′)	1.85(3)
Os(1′)–C(11′)	1.89(4)	Re(4)–C(41)	1.90(6)
Os(1′)–C(12′)	1.87(4)	Re(4)–C(42)	1.87(4)
Os(1′)–C(13′)	1.88(5)	Re(4)–C(42′)	1.87(4)
(C) Carbon – oxygen distances			
C(11)–O(11)	1.18(5)	C(21)–O(21)	1.15(7)
C(12)–O(12)	1.18(5)	C(22)–O(22)	1.15(4)
C(13)–O(13)	1.14(7)	C(22′)–O(22′)	1.15(4)
C(11′)–O(11′)	1.18(5)	C(41)–O(41)	1.11(8)
C(12′)–O(12′)	1.18(5)	C(42)–O(42)	1.17(4)
C(13′)–O(13′)	1.14(7)	C(42′)–O(42′)	1.17(4)

about the cluster, so terminal hydride ligands (as observed in $(\mu\text{-H})\text{HOs}_3\text{(CO)}_{11}$ [32] and $(\mu\text{-H})\text{HOs}_3\text{(CO)}_{10}\text{(PPh}_3)$ [33]) are not present. Furthermore, terminal hydride ligands are very uncommon on clusters involving third row transition metal atoms. The hydride ligands could, in principle, be in some combination of μ-, μ_3- or μ_4-locations. With five such ligands, by far the most probable structure involves five μ-hydride ligands bridging five of the six edges of the M_4 tetrahedron. (The $(\mu\text{-H})_6\text{Re}_4\text{(CO)}_{12}{}^{2-}$ anion has six such μ-hydride ligands about each of the edges of the Re_4 tetrahedron [25–26].) Note that the presence of two bridging hydride ligands on any one edge would give rise to a substantial shortening (rather than lengthening) of the bond relative to a non-bridged metal–metal bond.

(2) Metal–metal distances in the cluster show a substantial variation (from 2.836(2) through 3.016(2) Å). We can be assured that the metal atoms are not completely scrambled and that the relative lengths of the metal–metal bonds may be used in arguments concerning the identity of the individual metal atoms.

(3) In the absence of any other bridging ligands, a μ-hydrido-bridged M–M bond is always longer than the corresponding non-bridged M–M bond [34–36]. Thus, in the tetrahedral cluster $(\mu\text{-H})_4\text{Os}_4\text{(CO)}_{11}\text{(CNMe)}$ the Os–(H)–Os distances are 2.956(1)–2.971(1) Å and are ~ 0.14 Å longer than the non-bridged Os–Os bonds of 2.822(1) Å [37]. Similar results are forthcoming from other molecules (see references in [36]). Although tetrahedral Re_4 clusters are substantially less common than tetrahedral Os_4 clusters, there have been two studies of $(\mu\text{-H})_6\text{Re}_4\text{(CO)}_{12}{}^{2-}$ derivatives. In $[\text{AsPh}_4{}^+]_2[(\mu\text{-H})_6\text{Re}_4\text{(CO)}_{12}{}^{2-}]$, the Re–(H)–Re distances average 3.160(7) Å [25], while in $[\text{NMe}_3\text{Bz}^+]_2[(\mu\text{-H})_6\text{Re}_4\text{(CO)}_{12}{}^{2-}]$, they average 3.157(6) Å [26]. In general, then, we can assume that intermetallic distances in the present structure will differ such that Os–(H)–Os > Os–Os and Os–(H)–Re > Os–Re.

(4) From studies on the cluster complexes $(\mu\text{-H})_2\text{Os}_3\text{Re}_2\text{(CO)}_{20}$ [6,7] and $(\mu\text{-H})\text{Os}_3\text{Re(CO)}_{15}\text{(NCMe)}$ [8,9] we find that Os–Re distances are longer than Os–Os

Table 5

Interatomic angles (°) for $(\mu\text{-H})_5Os_3Re(CO)_{12}$

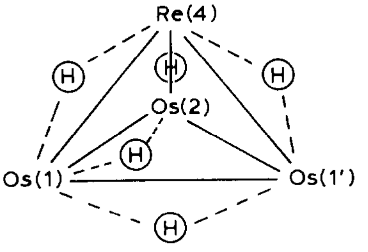
(A) Metal-metal-metal angles			
Os(1′)-Os(1)-Os(2)	58.49(5)	Os(1)-Os(1′)-Os(2)	58.49(5)
Os(2)-Os(1)-Re(4)	61.30(6)	Os(1)-Os(1′)-Re(4)	60.57(5)
Os(1′)-Os(1)-Re(4)	60.57(5)	Os(2)-Os(1′)-Re(4)	61.30(6)
Os(1)-Os(2)-Os(1′)	63.01(6)	Os(1)-Re(4)-Os(1′)	58.87(5)
Os(1)-Os(2)-Re(4)	62.32(6)	Os(1)-Re(4)-Os(2)	56.38(5)
Os(1′)-Os(2)-Re(4)	62.32(6)	Os(1′)-Re(4)-Os(2)	56.38(5)
(B) Metal-metal-carbon angles			
Os(1′)-Os(1)-C(11)	96.1(11)	Os(1)-Os(1′)-C(11′)	96.1(11)
Os(1′)-Os(1)-C(12)	143.4(12)	Os(1)-Os(1′)-C(12′)	143.4(12)
Os(1′)-Os(1)-C(13)	118.0(16)	Os(1)-Os(1′)-C(13′)	118.0(16)
Os(2)-Os(1)-C(11)	88.4(11)	Os(2)-Os(1′)-C(11′)	88.4(11)
Os(2)-Os(1)-C(12)	86.7(12)	Os(2)-Os(1′)-C(12′)	86.7(12)
Os(2)-Os(1)-C(13)	174.2(16)	Os(2)-Os(1′)-C(13′)	174.2(16)
Re(4)-Os(1)-C(11)	148.1(11)	Re(4)-Os(1′)-C(11′)	148.1(11)
Re(4)-Os(1)-C(12)	94.4(12)	Re(4)-Os(1′)-C(12′)	94.4(12)
Re(4)-Os(1)-C(13)	113.1(16)	Re(4)-Os(1′)-C(13′)	113.1(16)
Os(1)-Os(2)-C(21)	93.3(12)	Os(1)-Re(4)-C(41)	107.6(14)
Os(1)-Os(2)-C(22)	101.9(10)	Os(1)-Re(4)-C(42)	101.2(11)
Os(1)-Os(2)-C(22′)	163.0(10)	Os(1)-Re(4)-C(42′)	155.3(11)
Os(1′)-Os(2)-C(21)	93.3(12)	Os(1′)-Re(4)-C(41)	107.6(14)
Os(1′)-Os(2)-C(22)	163.0(10)	Os(1′)-Re(4)-C(42)	155.3(11)
Os(1′)-Os(2)-C(22′)	101.9(10)	Os(1′)-Re(4)-C(42′)	101.2(11)
Re(4)-Os(2)-C(21)	150.9(12)	Os(2)-Re(4)-C(41)	160.8(14)
Re(4)-Os(2)-C(22)	104.5(10)	Os(2)-Re(4)-C(42)	101.3(11)
Re(4)-Os(2)-C(22′)	104.5(10)	Os(2)-Re(4)-C(42′)	101.3(11)
(C) Carbon-metal-carbon angles			
C(11)-Os(1)-C(12)	93.7(17)	C(21)-Os(2)-C(22)	95.6(16)
C(11)-Os(1)-C(13)	96.8(20)	C(21)-Os(2)-C(22′)	95.6(16)
C(12)-Os(1)-C(13)	95.6(21)	C(22)-Os(2)-C(22′)	91.7(15)
C(11′)-Os(1′)-C(12′)	93.7(17)	C(41)-Re(4)-C(42)	91.8(18)
C(11′)-Os(1′)-C(13′)	96.8(20)	C(41)-Re(4)-C(42′)	91.8(18)
C(12′)-Os(1′)-C(13′)	95.6(21)	C(42)-Re(4)-C(42′)	93.1(16)
(D) Metal-carbon-oxygen angles			
Os(1)-C(11)-O(11)	174.8(32)	Os(2)-C(21)-O(21)	173.0(35)
Os(1)-C(12)-O(12)	174.6(34)	Os(2)-C(22)-O(22)	175.2(30)
Os(1)-C(13)-O(13)	177.4(48)	Os(2)-C(22′)-O(22′)	175.2(30)
Os(1′)-C(11′)-O(11′)	174.8(32)	Re(4)-C(41)-O(41)	177.1(42)
Os(1′)-C(12′)-O(12′)	174.6(34)	Re(4)-C(42)-O(42)	179.5(32)
Os(1′)-C(13′)-O(13′)	177.4(48)	Re(4)-C(42′)-O(42′)	179.5(32)

distances. A survey of M-M distances in the present structural study reveals that one atom (designated Re(4)) is associated with the three longest bonds in the cluster [Os(1)-Re(4) = Os(1′)-Re(4) = 3.016(2), Os(2)-Re(4) 2.987(3) Å (average Os-Re 3.006 Å) as compared to Os(1)-Os(1′) 2.964(2) and Os(1)-Os(2) = Os(1′)-Os(2) = 2.836(2) Å (average Os-Os 2.879 Å)]. The identity of the rhenium atom is thus established.

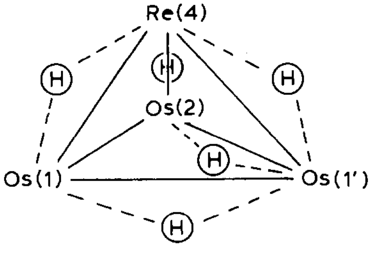
(5) There is no unique "shortest" M-M bond. Therefore an ordered structure is not present. (The two potential ordered structures are that with the Os(1)-Os(1′)

bond unbridged and that with the Os(2)–Re(4) bond unbridged; each of these is, however, associated with a relatively long M–M distance (2.964(2) and 2.987(3) Å, respectively).

(6) The shortest bonds are Os(1)–Os(2) and Os(1′)–Os(2) at 2.836(2) Å. However, only one edge of the M_4 tetrahedron can be unbridged. We therefore interpret this as indicating that the observed structure is composed of equal amounts of structures **3** and **4**, disordered about the crystallographic mirror plane.



(3)



(4)

This interpretation is supported by a survey of the thermal parameters of the metal atoms. Those for Os(2) and Re(4) are significantly lower than those for Os(1) and Os(1′) (see Table 3(B)) as would be expected for a slight displacement of Os(1) and Os(1′) from **3** to **4**. We observe similarly that the thermal parameters for atoms of the carbonyl ligands are larger for C(13)–O(13) and C(13′)–O(13′) than for any other such group and that these are the groups whose vectors extend from the Os(2)–Os(1) and Os(2)–Os(1′) directions.

We can further predict, based upon other μ-hydrido structures [36] that the μ-hydride ligands will be in positions above the M–M bonds such that the M–H–M plane bisects the exterior angle of the tetrahedron.

All other distances and angles in the system are normal (albeit of limited precision) with Os–CO 1.85(3)–1.89(4), Re–CO 1.87(4)–1.90(6) and C≡O 1.11(8)–1.18(5) Å.

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Addendum

One reviewer suggested that the complex studied might have been $(\mu\text{-H})_4Os_4(CO)_{12}$. This suggestion can firmly discounted on the basis of the following facts.

(1) The provenance of the sample is firmly established. It came from the batch on which spectroscopic studies had been performed (see Introduction and ref. 8).

(2) The crystal structure of $(\mu\text{-H})_4Os_4(CO)_{12}$ has been reported [38]. It crystallizes

in the triclinic system, space group $P\bar{1}$, with cell dimensions a 9.811, b 9.893, c 10.240 Å, α 85.56, β 82.71, γ 88.71°, and is isomorphous with $(\mu\text{-H})_4Ru_4(CO)_{12}$ [20].

(3) The pattern of Os–Os distances in $(\mu\text{-H})_4Os_4(CO)_{12}$ is unambiguously that of two non-bridged "short" bonds (2.816(2) and 2.817(2) Å) and four hydrido-bridged "long" bonds (2.962(2), 2.963(2), 2.965(2) and 2.967(2) Å). The present structural study of $(\mu\text{-H})_5Os_3Re(CO)_{12}$ presents a far less well defined pattern.

References

1 Part XXXIII. Y. Chi, J.R. Shapley, M.R. Churchill and Y.-J. Li, Inorg. Chem., 25 (1986) 4165.
2 Part XXXII. M.R. Churchill and Y.-J. Li, J. Organomet. Chem., 294 (1985) 367.
3 Part XXXI. M.R. Churchill and Y.-J. Li, J. Organomet. Chem., 291 (1985) 61.
4 Part XXX. W.-Y. Yeh, J.R. Shapley, Y.-J. Li and M.R. Churchill, Organometallics, 4 (1985) 767.
5 Part XXIX. J.T. Park, J.R. Shapley, M.R. Churchill and C. Bueno, Inorg. Chem., 23 (1984) 4476.
6 J.R. Shapley, G.A. Pearson, M. Tachikawa, G.E. Schmidt, M.R. Churchill and F.J. Hollander, J. Am. Chem. Soc., 99 (1977) 8064.
7 M.R. Churchill and F.J. Hollander, Inorg. Chem., 17 (1978) 3546.
8 M.R. Churchill, F.J. Hollander, R.A. Lashewycz, G.A. Pearson and J.R. Shapley, J. Am. Chem. Soc., 103 (1981) 2430.
9 M.R. Churchill and F.J. Hollander, Inorg. Chem., 20 (1981) 4124.
10 C.H. Wei and L.F. Dahl, J. Am. Chem. Soc., 88 (1966) 1821.
11 C.H. Wei and L.F. Dahl, J. Am. Chem. Soc., 91 (1969) 1351.
12 F.A. Cotton and J.M. Troup, J. Am. Chem. Soc., 96 (1974) 4155.
13 C.H. Wei, Inorg. Chem., 8 (1969) 2384.
14 F.H. Carré, F.A. Cotton and B.A. Frenz, Inorg. Chem., 15 (1976) 380.
15 C.H. Wei, G.R. Wilkes and L.F. Dahl, J. Am. Chem. Soc., 89 (1967) 4792.
16 M.R. Churchill and J.P. Hutchinson, Inorg. Chem., 17 (1978) 3528.
17 M.R. Churchill and H.J. Wasserman, Inorg. Chem., 21 (1982) 825.
18 M.R. Churchill, J.C. Fettinger and K.H. Whitmire, J. Organomet. Chem., 284 (1985) 13.
19 J.R. Shapley, D.S. Strickland, G.M. St. George, M.R. Churchill and C. Bueno, Organometallics, 2 (1983) 185.
20 R.D. Wilson, S.M. Wu, R.A. Love and R. Bau, Inorg. Chem., 17 (1978) 1271.
21 M.R. Churchill and R.A. Lashewycz, Inorg. Chem., 17 (1978) 1950.
22 M.R. Churchill, R.A. Lashewycz, J.R. Shapley and S.I. Richter, Inorg. Chem., 19 (1980) 1277.
23 M.R. Churchill and F.J. Hollander, Inorg. Chem., 19 (1980) 306.
24 R.D. Wilson and R. Bau, J. Am. Chem. Soc., 98 (1976) 2434.
25 H.D. Kaesz, B. Fontal, R. Bau, S.W. Kirtley and M.R. Churchill, J. Am. Chem. Soc., 91 (1969) 1021.
26 G. Ciani, A. Sironi and V.G. Albano, J. Organomet. Chem., 136 (1977) 339.
27 M.R. Churchill, S.A. Bezman, J.A. Osborn and J. Wormald, Inorg. Chem., 11 (1972) 1818.
28 D.M. Ho and R. Bau, Inorg. Chim. Acta, 84 (1984) 213.
29 M.R. Churchill, R.A. Lashewycz and F.J. Rotella, Inorg. Chem., 16 (1977) 265.
30 International Tables for X-Ray Crystallography, Vol. 1, Kynoch Press, Birmingham, England (1965), pp. 280 and 283.
31 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, England (1974), pp. 99–101 and 149–150.
32 M.R. Churchill and B.G. De Boer, Inorg. Chem., 16 (1977) 878.
33 M.R. Churchill and B.G. De Boer, Inorg. Chem., 16 (1977) 2397.
34 M.R. Churchill, B.G. De Boer and F.J. Rotella, Inorg. Chem., 15 (1976) 1843.
35 M.R. Churchill, Adv. Chem. Ser., 167 (1978) 36.
36 R.G. Teller and R. Bau, Struct. and Bonding, 44 (1981) 1.
37 M.R. Churchill and F.J. Hollander, Inorg. Chem., 19 (1980) 306.
38 B.F.G. Johnson, J. Lewis, P.R. Raithby and C. Zuccaro, Acta Cryst., Sect. B, B37 (1981) 1728.