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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 4.[1-3] Crystal Structure and Molecular Geometry of $HOs_3Re(CO)_{15}$, a Rhomboidal Metal Cluster Species

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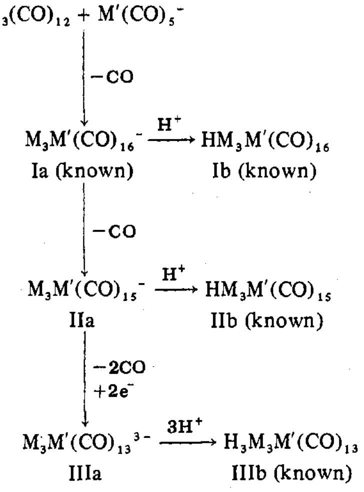
Pentadecacarbonylhydridotriosmiumrhenium, $HOs_3Re(CO)_{15}$, previously synthesized by Knight and Mays, has been examined by a single-crystal x-ray structural analysis. The species crystallizes in the centrosymmetric monoclinic space group $I2/m$ [No. 12] with $a = 10.557$ (2) Å, $b = 10.481$ (2) Å, $c = 10.144$ (2) Å, $\beta = 102.14$ (1) °, $V = 1097.3$ Å^3, and ρ(calcd) = 3.56 g cm^{-3} for mol wt 1177.96 and $Z = 2$. Data complete to $2\theta = 40°$ were collected on a Syntex $P2_1$ diffractometer using Mo Kα radiation. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques using the Syntex XTL structure-solving system. All nonhydrogen atoms were located, final discrepancy indices being $R_F = 3.1\%$ and $R_{wF} = 3.2\%$ for the 554 symmetry-independent data. The molecule contains a planar triangulated rhombus of metal atoms [situated on a site of crystallographic C_{2h} ($2/m$) symmetry] and is subject to a fourfold disorder which principally affects the bridgehead metal atoms and their associated equatorial ligands. The observed pattern is consistent with the bridgehead sites being occupied by $Re(CO)_4$ and $Os(CO)_3H$ moieties which are mutually linked (M–M = 2.944 (1) Å) and which are bridged by two $Os(CO)_4$ systems (M–Os = 2.957 (1) Å). The hydride ligand occupies an equatorial coordination site on the bridgehead osmium atom.

Introduction

The reaction of neutral trimetallic dodecacarbonyls [$M_3(CO)_{12}$; M = Fe, Ru, Os] with pentacarbonylmetalate anions [$M'(CO)_5^-$; M′ = Mn, Re] has been studied by Knight and Mays.[4] Separation of the resulting heteronuclear anionic products was not always possible. [Knight and Mays[4] stated that "...all the reactions...give rise to complex mixtures of anionic species in solution which are often exceedingly difficult to separate and crystallize in pure condition".] Of the possible tetranuclear anionic species only [$Ru_3Re(CO)_{16}^-$] was prepared in analytically pure condition. Acidification of the reaction mixtures has, however, led to the obtention of such neutral hydridic species as $HOs_3Re(CO)_{16}$, $HOs_3Re(CO)_{15}$, and $H_3Os_3Re(CO)_{13}$. The known anionic and hydridic species may be interrelated (at least formally) via Scheme I. On the basis of application of the "18-electron rule", possible cluster geometries include the following: either a square or a "methylcyclopropane"[5] skeleton for the 64-electron[6] clusters Ia and Ib, a planar triangulated rhombus [previously found in $Re_4(CO)_{16}^{2-}$ by Churchill and Bau[7]] for the 62-electron[6] clusters IIa and IIb, and a tetrahedral arrangement for the 60-electron[6] species IIIa and IIIb.

Scheme I



$$\begin{tikzcd}
M_3(CO)_{12} + M'(CO)_5^- \arrow[d, "-CO"] & \\
M_3M'(CO)_{16}^- \arrow[r, "H^+"] & HM_3M'(CO)_{16} \\
\text{Ia (known)} \arrow[d, "-CO"] & \text{Ib (known)} \\
M_3M'(CO)_{15}^- \arrow[r, "H^+"] & HM_3M'(CO)_{15} \\
\text{IIa} \arrow[d, "\begin{matrix}-2CO\\+2e^-\end{matrix}"] & \text{IIb (known)} \\
M_3M'(CO)_{13}^{3-} \arrow[r, "3H^+"] & H_3M_3M'(CO)_{13} \\
\text{IIIa} & \text{IIIb (known)}
\end{tikzcd}$$

We have now undertaken a single-crystal x-ray structural analysis of $HOs_3Re(CO)_{15}$ (IIb, M = Os, M′ = Re) with a view toward determining the gross molecular geometry and (possibly) the location of the hydride ligand.

Experimental Section

A. Collection of Data. A small microcrystalline sample (~10 μg) of $HOs_3Re(CO)_{15}$ was supplied to us by Dr. M. J. Mays, of Cambridge University, Cambridge, England, in 1970. Many attempts at recrystallization from various solvents were unsuccessful. Recently we managed to obtain a single crystal by dissolution of the material in boiling acetone followed by slow cooling and evaporation of the solvent.

The crystal thus obtained was an irregularly shaped polyhedron with approximate dimensions of 0.09 mm × 0.13 mm × 0.23 mm. It was sealed into a glass capillary to protect it from possible x-ray-induced sensitivity to air or moisture.

A preliminary set of precession photographs was (erroneously) interpreted in terms of a primitive triclinic cell of approximate volume 563 Å^3.

The crystal was transferred to, and centered on, a Syntex $P2_1$ diffractometer. Determination of the crystal quality, orientation, and unit cell parameters were carried out as described previously.[8] Examination of the computer-generated real space vectors (derived from the angular coordinates of 15 reflections) led to indications of monoclinic symmetry, which were confirmed by the m symmetry observed on a partial-rotation photograph taken about this axis via a Polaroid cassette mounted on the diffractometer. The monoclinic cell finally chosen (for reasons of a convenient β angle) is body centered with $a = 10.557$ (2) Å, $b = 10.481$ (2) Å, $c = 10.144$ (2) Å, and $\beta = 102.14$ (1)°. [These values were determined by refinement against the setting angles of 16 reflections with $2\theta = 24–30°$, based upon λ(Mo K$\bar{\alpha}$) 0.71073 Å.] The calculated density is 3.56 g cm^{-3} for mol wt 1177.96, $V = 1097.3$ Å^3, and $Z = 2$.

The only systematic absences are those due to the body centering, i.e., $h + k + l = 2n + 1$. Possible space groups are therefore $I2$, Im, and $I2/m$.

Intensity data were collected using graphite-monochromatized Mo Kα radiation, the monochromator being in the parallel position and assumed to be 50% perfect in the reflecting direction.[8] A coupled θ(crystal)–2θ(counter) scan technique was used, the scan speed being 2.0°/min in 2θ. The scan was from 1.0° below the Mo Kα_1 peak to 1.0° above the Mo Kα_2 peak. Backgrounds (B_1 and B_2) were measured at the beginning and at the end of the scan with crystal and counter stationary; each measurement was for half of the time taken for the scan.

A full sphere of data was collected out to $2\theta = 25°$ and a hemispherical shell ($\pm h$, $+k$, $\pm l$) was collected for the range $25° < 2\theta \leq 40°$. Three reflections were monitored periodically to check on instrumental and crystal stability. The intensity of these standards decreased uniformly by ~2% over the course of the experiment. No correction was made for this decay.

A total of 1388 data were recorded. These were reduced to net intensities (I) and their esd's, $\sigma(I)$, as shown in eq 1 and 2. Data

$$I = \mathrm{CT} - (B_1 + B_2) \tag{1}$$

$$\sigma(I) = [\mathrm{CT} + B_1 + B_2]^{1/2} \tag{2}$$

were corrected for absorption ($\mu = 229.8$ cm^{-1}) by an empirical method. Several pairs of close-to-axial reflections, distributed over the range of 2θ values used in data-collection, and each of fairly strong intensity (but not so strong as to be susceptible to significant effects due to secondary extinction), were measured at 36 positions around the diffraction vector (from $\psi = 0°$ to $\psi = 350°$, $\Delta\psi = 10°$). Each pair of reflections was used to define a normalized absorption curve vs. ϕ, corrected for ω and χ. The curves bracketing the 2θ value of the reflection under consideration were interpolated both in 2θ and in ϕ to derive the absorption correction for the intensity of that reflection. Reflections used for the absorption curves were $21\bar{1}$ and $\bar{2}\bar{1}1$ ($2\theta = 12.46°$), $41\bar{1}$ and $\bar{4}\bar{1}1$ ($2\theta = 18.05°$), $51\bar{2}$ and $\bar{5}\bar{1}2$ ($2\theta = 24.22°$), and $64\bar{2}$ and $\bar{6}\bar{4}2$ ($2\theta = 28.29°$). All curves were mutually consistent—i.e., maxima and minima were observed at essentially the same values of ϕ, all curves had similar profiles, and had values of approximately 1.67 for (maximum intensity)/(minimum intensity). Data were next averaged according to $2/m$ symmetry to yield 554 unique reflections. The agreement factor for averaging, $R(I)$, defined in eq 3, was 0.045. The esd for an averaged intensity was taken as

$$R(I) = \Sigma \left| |I| - |I_{\mathrm{av}}| \right| / \Sigma |I| \tag{3}$$

the larger of (i) that calculated from counting statistics and (ii) that calculated from scatter from the mean.

Intensities were then reduced to (unscaled) observed structure factor amplitudes by taking the square root of the intensities after correction for Lorentz and polarization factors. Esd's, $\sigma(F)$, were calculated by finite differences as shown in eq 4. If F^2 (or I, from eq 1) was

$$\sigma(F) = [|F^2| + \sigma(F^2)]^{1/2} - |F^2|^{1/2} \tag{4}$$

less than zero, F was set equal to zero after calculation of $\sigma(F)$.

B. Solution and Refinement of the Structure. All calculations were performed using the Syntex XTL Structure Determination System, consisting of the following: an in-house Data General NOVA 1200 computer with 24K of 16-bit word memory; a Diablo disk unit of 1.2 million 16-bit words; and a locally modified version of the XTL conversational crystallographic program package.[9]

The analytical scattering factors compiled by Cromer and Waber[10a] were used throughout the analysis; both real and imaginary components of anomalous dispersion[10b] were included for the metal atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights used are those shown in eq 5, with $p = 0.02$.

$$w = [\sigma^2(F) + (pF)^2]^{-1} \tag{5}$$

Discrepancy indices used below are defined in eq 6 and 7. The

$$R_F = \left[\frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}\right] \times 100\,(\%) \tag{6}$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2}\right]^{1/2} \times 100\,(\%) \tag{7}$$

"goodness-of-fit" (GOF) is defined in eq 8, where NO is the number

$$\mathrm{GOF} = \left[\frac{\Sigma w(|F_o| - |F_c|)}{\mathrm{NO} - \mathrm{NV}}\right]^{1/2} \tag{8}$$

of observations and NV is the number of variables.

The positions of the heavy atoms were determined from a three-dimensional Patterson map. The core of the molecule consisted of a planar, triangulated, rhomboidal framework centered on the point (0, 0, $^1/_2$) and having required C_{2h} ($2/m$) symmetry. Two symmetry-related atoms lay on the twofold axis [at (0, 0.141, $^1/_2$) and (0, −0.141, $^1/_2$)], while another pair of symmetry-related atoms lay in the mirror plane at $y = 0$ [at (0.219, 0, 0.430) and (−0.219, 0, 0.570)]. The analysis was continued with the realization that there was a problem of Os/Re disorder.

A difference-Fourier map phased by the two crystallographically unique heavy atoms (each of which was assigned the scattering factor of neutral osmium for calculation of structure factors) yielded the positions of all carbon and oxygen atoms save for the set of symmetry-related equatorial carbonyl ligands associated with "Os(1)". Refinement of positional and thermal parameters (anisotropic for osmium; otherwise isotropic) for these atoms led to convergence with $R_F = 7.3\%$ A difference-Fourier map now revealed as its strongest features two diffuse peaks corresponding to the "missing" equatorial carbonyl ligand [C(5)–O(5)] on "Os(1)". These atoms were included with full occupancy, leading to $R_F = 4.4\%$ but yielding enormous isotropic thermal parameters for the newly input atoms (viz., B(C(5)) = 20.8 Å^2 and B(O(5)) = 23.8 Å^2). Clearly, as was demanded by the correct stoichiometry for this species, this newly found carbonyl group was only of partial occupancy. Since all other carbonyl ligands were well behaved, we believed the equatorial bridgehead ligands to be three carbonyls and one terminal hydride, statistically disordered. We therefore reinput C(5) and O(5) with occupancies of $^3/_4$. As an insurance measure (immediately to be collected upon) we refined independently the net occupancies for each of these atoms, along with all previously refined parameters. Convergence was reached with $R_F = 3.8\%$, $R_{wF} = 4.1\%$, and GOF = 1.066; the relevant occupancies were, however, 0.65 (6) for C(5) and 0.48 (4) for O(5). A difference-Fourier now showed two remaining features, of height, 1.01 and 1.16 e Å^{-3} consistent either with gross anisotrophy of C(5)–O(5) or with a nearby second possible orientation for an equatorial carbonyl ligand on "Os(1)". We therefore refined the previous model, using anisotropic thermal parameters for all input atoms, leading to $R_F = 3.3\%$, $R_{wF} = 3.5\%$, and GOF = 0.947. Occupancy factors for C(5) and O(5) remained essentially unchanged and a further difference-Fourier synthesis showed the same pattern of residual peaks (now of height 0.75 and 0.91 e Å^{-3}) near "Os(1)".

Table I. Final Positional Parameters[a] for $HOs_3Re(CO)_{15}$ with Esd's[b]

Atom	Occupancy[d]	x	y	z	B, Å^2
M(1)[c]	$^1/_2$	0	0.14047 (7)	$^1/_2$	
Os(2)	$^1/_2$	0.21960 (7)	0	0.42974 (8)	
C(1)	$^1/_2$	0.1280 (19)	0	0.2471 (25)	
O(1)	$^1/_2$	0.0807 (19)	0	0.1300 (23)	
C(2)	$^1/_2$	0.3112 (21)	0	0.6140 (29)	
O(2)	$^1/_2$	0.3745 (20)	0	0.7244 (23)	
C(3)	1	0.3291 (15)	0.1307 (14)	0.3880 (17)	
O(3)	1	0.3970 (14)	0.2062 (15)	0.3629 (16)	
C(4)	1	0.0887 (16)	0.1397 (12)	0.6849 (19)	
O(4)	1	0.1467 (12)	0.1508 (10)	0.7950 (14)	
C(5A)	$^1/_2$	0.1125 (26)	0.2772 (24)	0.4535 (28)	3.5 (5)
O(5A)	$^1/_2$	0.1729 (23)	0.3671 (18)	0.4336 (27)	5.5 (5)
C(5B)	$^1/_4$	0.0467 (55)	0.2970 (50)	0.4924 (70)	4.7 (14)
O(5B)	$^1/_4$	0.0870 (54)	0.4130 (49)	0.4741 (61)	9.7 (15)

[a] These are based upon space group $I2/m$ which has the eight equipoints $\pm(x, \pm y, z)$ and $\pm(^1/_2 \pm x, ^1/_2 \pm y, ^1/_2 + z)$ and is a nonstandard setting of $C2/m$ [$C_{2h}{}^3$; No. 12]. [b] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. They were calculated from the inverse of the final least-squares matrix. [c] M(1) is a composite $^1/_2$ Re–$^1/_2$ Os atom. [d] Occupancies are those for input to a structure factor calculation based upon all eight equipoints of the space group $I2/m$.

These observations could be fully explained in terms of a fourfold disorder of two distinct equatorial carbonyl positions—one (C(5A)–O(5A)) of occupancy $^1/_2$ and the second (C(5B)–O(5B)) of occupancy $^1/_4$.

To test this hypothesis we calculated the position for C(5B) based upon the observed position of O(5B) and assumption of a linear "Os(1)"–C(5B)–O(5B) system. Continued refinement of all appropriate positional-and-thermal parameters (with C(5A), O(5A), C(5B), and O(5B) constrained to be isotropic and with the occupancies of C(5B) and O(5B) fixed at $^1/_4$) led to $R_F = 3.1\%$, $R_{wF} = 3.2\%$, and GOF = 0.866. The resulting refined occupancies for C(5A) and O(5A) were 0.49 (4) and 0.54 (4), thereby confirming our hypothesis.

Finally, we fixed all occupancies at their idealized values and refined the model to convergence [$(\Delta/\sigma)_{\max} = 0.01$], leading to $R_F = 3.1\%$, $R_{wF} = 3.2\%$, and GOF = 0.865. A final difference-Fourier synthesis showed no structurally significant features ($\rho(\max) = 0.67$ e Å^{-3}) and the analysis was declared complete. There was no evidence suggestive of secondary extinction.

Intuitive dissatisfaction with our fourfold disordered model led to careful investigation of models in the related noncentrosymmetric space groups Im and $I2$ (each of which still requires at least twofold disorder of the molecule). Exhaustive attempts, over several months, yielded no preferable alternative solution.

Final positional parameters are listed in Table I; anisotropic thermal parameters are collected in Table II.

Discussion

An overall view of the disordered structure, as resulting from refinement, is shown in Figure 1. This structure is centered

Table II. Anisotropic Thermal Parameters[a] for $HOs_3Re(CO)_{15}$ with Esd's[b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
M(1)	2.94 (5)	4.28 (5)	2.90 (5)	0	−0.03 (3)	0
Os(2)	2.36 (4)	3.68 (4)	2.82 (5)	0	0.25 (3)	0
C(1)	3.3 (10)	4.1 (10)	3.7 (13)	0	0.4 (10)	0
O(1)	5.9 (10)	10.8 (13)	5.4 (13)	0	1.4 (10)	0
C(2)	2.7 (11)	2.9 (9)	6.5 (16)	0	1.5 (11)	0
O(2)	5.4 (11)	9.3 (12)	5.0 (12)	0	−0.7 (10)	0
C(3)	3.7 (8)	6.0 (9)	4.3 (10)	−1.8 (7)	−0.6 (7)	1.8 (6)
O(3)	6.7 (7)	10.1 (9)	9.2 (11)	−2.1 (7)	−0.1 (7)	4.8 (7)
C(4)	4.1 (8)	4.5 (8)	2.6 (10)	0.1 (5)	0.8 (8)	−0.1 (6)
O(4)	4.8 (6)	6.6 (7)	4.0 (9)	−0.4 (4)	0.3 (7)	−1.5 (5)

[a] In units of Å². These enter the equation for the calculated structure factor in the form $\exp[-0.25(a^{*2}h^2B_{11} + b^{*2}k^2B_{22} + c^{*2}l^2B_{33} + 2a^*b^*hkB_{12} + 2a^*c^*hlB_{13} + 2b^*c^*klB_{23})]$. [b] See footnote *b* to Table I.

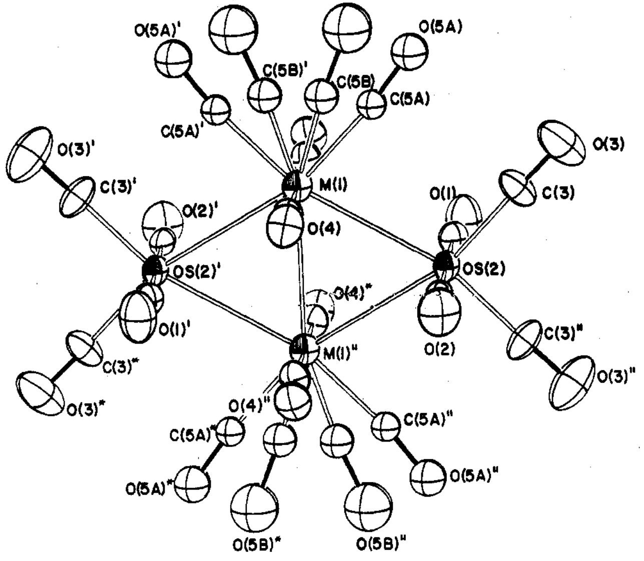


Figure 1. The gross disordered structure of $HOs_3Re(CO)_{15}$. This structure is the composite of four overlapping molecular images (cf. Scheme II). The labeling of atoms is indicated. Superscripts indicate the following transformations relative to the basic asymmetric unit defined in Table I: ′ = C_2, ″ = σ, and * = *i* [ORTEP-II diagram; 50% probability envelopes are shown for the thermal vibration ellipsoids]. Note that C(5A)–O(5A) has 50% occupancy and C(5B)–O(5B) has 25% occupancy.

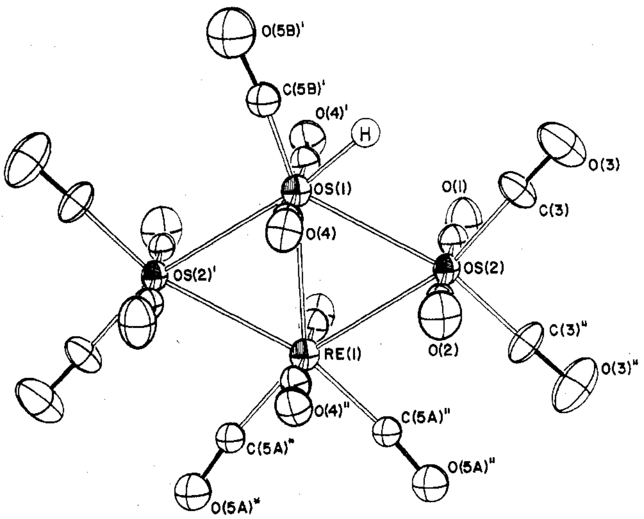


Figure 2. The ordered structure for the $HOs_3Re(CO)_{15}$ molecule, with the hydride ligand shown in its presumed position.

on a site of crystallographic C_{2h} ($2/m$) symmetry and is, in fact, very little perturbed from the higher D_{2h} ($2/mmm$) symmetry. In can quickly be seen (by inspection of the atomic vibration ellipsoids and the magnitude of the appropriate thermal parameters, inter alia) that the exterior $Os(CO)_4$ fragments associated with Os(2) and the symmetry-related Os(2)′ are clearly and cleanly defined, as are the *axial* terminal carbonyl groups [C(4)–O(4) etc.] on M(1) and M(1)″. In contrast to this, there is severe disorder of the *equatorial* ligands on M(1) and M(1)″. However, the observed disordered structure can be explained and the geometry of the ordered $HOs_3Re(CO)_{15}$ molecule can be elucidated via the following considerations.

(1) The observed metal–metal distances [M(1)–M(1)″ = 2.944 (1) Å and M(1)–Os(2) = M(1)″–Os(2) = M(1)–Os(2)′ = M(1)″–Os(2)′ = 2.957 (1) Å] are consistent with their being normal metal–metal single σ bonds. For comparison we note that the average osmium–osmium distance is 2.877 Å in $Os_3(CO)_{12}$[1] and the average rhenium–rhenium distance is 2.989 Å in $Re_4(CO)_{16}^{2-}$,[7] the predicted osmium–rhenium distance therefore being 2.933 Å. If the hydride ligand were in a μ_2-bridging site (or even a μ_3-bridging site), the hydrido-bridged metal–metal vector would be expanded significantly [by some 0.10–0.15 Å][11] from its normal value. This was not observed, nor were there any abnormally high thermal parameters associated with the metal atoms. In addition, a μ_2-bridging hydride ligand would necessitate disorder of the equatorial carbonyl groups on Os(2). This, again, was not observed. We conclude, therefore, that the hydride ligand (which was not located directly in the study) occupies a *terminal*, rather than a *bridging*, site.

(2) On the basis of (a) the known stoichiometry of the molecule, (b) the recognition of ordered exterior $Os(CO)_4$ fragments and a total of four ordered terminal carbonyl groups on M(1) and M(1)″, and (c) the carefully investigated occupancies of C(5A)–O(5B) and C(5B)–O(5B) systems, we conclude that the [M(1)–M(1)″–(equatorial ligands)] fragment has a net composition of $HOsRe(CO)_3$.

(3) Assuming that each metal atom in the $HOs_3Re(CO)_{15}$ molecule independently acquires the "noble gas configuration", then the bridgehead positions in the triangulated rhombus must be occupied be $Re(CO)_4$ and $HOs(CO)_3$ moieties—each of which is a "15-electron" system.

(4) The half-occupancy of the ligand C(5A)–O(5A) taken in conjunction with the interligand angle C(5A)–M(1)–C(5A)′ = 87.3 (11)° leads to this ligand being formally associated with the $Re(CO)_4$ group.

(5) The one-fourth occupancy of C(5B)–O(5B), coupled with the overly acute angles C(5B)–M(1)–C(5A) = 26.8 (22)°, C(5B)–M(1)–C(5B)′ = 34.9 (29)°, and C(5B)–M(1)–C(5A)′ = 60.8 (22)°, indicates that C(5B)–O(5B) is the sole equatorial carbonyl group on a bridgehead atom of the isolated molecule; it can thus be unequivocally assigned to an $HOs(CO)_3$ moiety.

(6) The noncoincidence of the ligands C(5B)–O(5B) and C(5A)–O(5A) is a result of the lesser stereochemical bulk (~7 Å³) of a hydride vis à vis a carbonyl ligand (~45 Å³).[12] While it is now generally accepted that a terminal hydride ligand occupies a regular stereochemical site,[12] there are cases where steric factors cause severe distortions from a regular ML_n geometry. Thus the group 5 ligands in both $HRh(Ph_3P)_4$[13] and $HRh(Ph_3P)_3(Ph_3As)$[14] take up idealized tetrahedral sites rather than trigonal-bipyramidal sites around the rhodium atoms; a similar, but less drastic, displacement of equatorial ligands toward the hydride position occurs in β-$HMn(CO)_5$.[15]

Figure 2 shows a view of the ordered $HOs_3Re(CO)_{15}$ molecule as deduced from these considerations. The hydride ligand is shown in its probable position—bisecting the equatorial Os(2)–Os(1)–C(5B)′ angle.

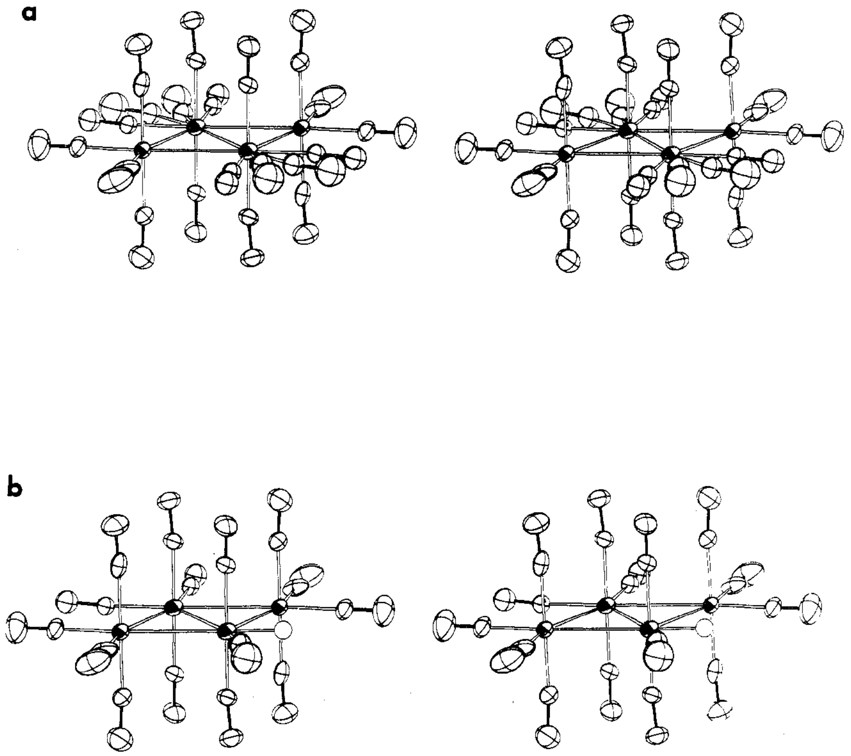


Figure 3. General stereoscopic views: (a) the overall disordered structure; (b) an isolated $HOs_3Re(CO)_{15}$ molecule.

Scheme II

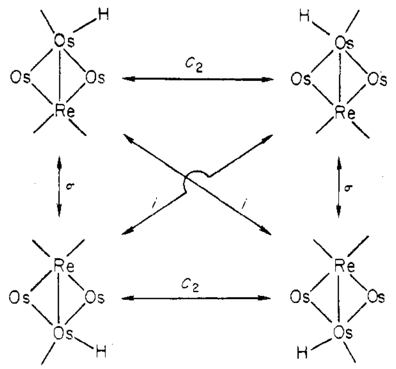


Table III. Interatomic Distances (Å), with Esd's, for $HOs_3Re(CO)_{15}$

(A) Metal-Metal Distances			
M(1)-M(1)″	2.944 (1)	M(1)-Os(2)	2.957 (1)
(B) Metal-Carbon and Metal···Oxygen Distances			
Os(2)-C(1)	1.901 (25)	Os(2)···O(1)	3.085 (23)
Os(2)-C(2)	1.915 (28)	Os(2)···O(2)	3.091 (23)
Os(2)-C(3)	1.897 (15)	Os(2)···O(3)	3.029 (15)
M(1)-C(4)	1.912 (19)	M(1)···O(4)	3.069 (14)
M(1)-C(5A)	1.981 (26)	M(1)···O(5A)	3.153 (22)
M(1)-C(5B)	1.720 (53)	M(1)···O(5B)	3.028 (53)
(C) Carbon-Oxygen Distances			
C(1)-O(1)	1.187 (34)	C(4)-O(4)	1.162 (23)
C(2)-O(2)	1.177 (36)	C(5A)-O(5A)	1.179 (34)
C(3)-O(3)	1.132 (22)	C(5B)-O(5B)	1.313 (75)
(D) C(5A)-O(5A) to C(5B)-O(5B) Distances			
C(5A)···C(5B)	0.893 (67)	O(5A)···O(5B)	1.174 (63)

The nature of the crytallographic disorder is indicated in Scheme II. The observed structure is a composite of these four orientations of the molecule.

Interatomic distances and angles are collected in Tables III, and IV. Stereoscopic views of the disordered and ordered structures are presented in Figure 3.

Table IV. Interatomic Angles (deg), with Esd's, for $HOs_3Re(CO)_{15}$

(A) All Intermetallic Angles			
M(1)-Os(2)-M(1)″	59.71 (2)	Os(2)-M(1)-Os(2)′	120.29 (2)
Os(2)-M(1)-M(1)″	60.14 (2)		
(B) Metal-Metal-Carbon Angles			
M(1)-Os(2)-C(1)	88.3 (6)	M(1)-Os(2)-C(3)	103.9 (5)
M(1)-Os(2)-C(2)	91.4 (6)	M(1)-Os(2)-C(3)″	163.5 (5)
M(1)″-M(1)-C(4)	89.7 (5)	Os(2)-M(1)-C(5B)	102.6 (20)
M(1)″-M(1)-C(5A)	136.3 (8)	Os(2)′-M(1)-C(4)	90.5 (5)
M(1)″-M(1)-C(5B)	162.6 (20)	Os(2)′-M(1)-C(5A)	163.2 (8)
Os(2)-M(1)-C(4)	89.2 (5)	Os(2)′-M(1)-C(5B)	137.1 (20)
Os(2)-M(1)-C(5A)	76.3 (8)		
(C) Carbon-Metal-Carbon Angles			
C(1)-Os(2)-C(2)	179.8 (8)	C(2)-Os(2)-C(3)	90.7 (8)
C(1)-Os(2)-C(3)	89.5 (7)	C(3)-Os(2)-C(3)″	92.4 (7)
C(4)-M(1)-C(4)′	179.5 (7)	C(4)′-M(1)-C(5B)	92.7 (21)
C(4)-M(1)-C(5A)	92.4 (9)	C(5A)-M(1)-C(5A)′	87.3 (11)
C(4)-M(1)-C(5B)	87.8 (21)	C(5A)-M(1)-C(5B)	26.8 (22)
C(4)′-M(1)-C(5A)	88.0 (9)	C(5A)-M(1)-C(5B)′	60.8 (22)
		C(5B)-M(1)-C(5B)′	34.9 (29)
(D) Metal-Carbon-Oxygen Angles			
Os(2)-C(1)-O(1)	174.4 (17)	M(1)-C(4)-O(4)	173.3 (14)
Os(2)-C(2)-O(2)	175.8 (19)	M(1)-C(5A)-O(5A)	172.8 (24)
Os(2)-C(3)-O(3)	178.1 (15)	M(1)-C(5B)-O(5B)	173.4 (53)

The $HOs_3Re(CO)_{15}$ molecule is pseudo-isoelectronic with the $Re_4(CO)_{16}^{2-}$ ion and has essentially the same connectivity. Each metal atom is associated with four terminal ligands, two of which are axial and two of which are equatorial. Angles between axial ligands on a given metal atom are close to 180° [C(4)-M(1)-C(4)′ = 179.5 (7)° and C(1)-Os(2)-C(2) = 179.8 (8)°] and angles between the axial carbonyl ligands and the metal atom framework are all close to 90° [viz., Os(2)-M(1)-C(4) = 89.2 (5)°, Os(2)′-M(1)-C(4) = 90.5 (5)°, M(1)″-M(1)-C(4) = 89.7 (5)°; M(1)-Os(2)-C(1) = 88.3 (6)°, M(1)-Os(2)-C(2) = 91.4 (6)°]. Thus, unlike the case of the $Re_4(CO)_{16}^{2-}$ ion,[7] the individual $Os(CO)_4$, $Re(CO)_4$, and $Os(CO)_3H$ groups in $HOs_3Re(CO)_{15}$ *do not* suffer a rotation relative to the plane of the four metal atoms.

Osmium–carbonyl distances within the $HOs_3Re(CO)_{15}$ molecule are self-consistent [Os(2)–C(1) = 1.901 (25) Å, Os(2)–C(2) = 1.915 (28) Å, Os(2)–C(3) = 1.897 (15) Å; average 1.904 Å]. There is no significant difference between the bond lengths determined for axial and equatorial sets of osmium–carbonyl vectors and the mean value is in reasonable agreement with the values reported for $Os_3(CO)_{12}$[1] [Os–CO(axial) = 1.946 (6) Å (average) and Os–CO(equatorial) = 1.912 (7) Å (average)]. It should be noted, however, that disorder renders all bond lengths and angles rather imprecise in the current $HOs_3Re(CO)_{15}$ structure.

Distances around M(1) and M(1)″ are, of course, subject to large errors because of the disorder of $Os(CO)_3H$ and $Re(CO)_4$ moieties and the concomitant low occupancies of the C(5A)–O(5A) and C(5B)–O(5B) sites. The resulting metal–carbonyl distances [M(1)–C(4) = 1.912 (19) Å, M(1)–C(5A) = 1.981 (26) Å, and M(1)–C(5B) = 1.720 (53) Å] are, nevertheless, consistent with representing the mean of terminal osmium–carbonyl and rhenium–carbonyl bond lengths.

Finally, we note that the sites of the disordered carbonyl ligands, C(5A)–O(5A) and C(5B)–O(5B), are just far enough apart to be resolved satisfactorily. Separations are 0.893 (67) Å for C(5A)···C(5B) and 1.174 (63) Å for O(5A)···O(5B).

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Supplementary Material Available: Listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

References and Notes

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(6) Assuming the validity of the 18-electron rule, the number of outer valence electrons required for a cluster of N_1 metal atoms mutually linked by a total of N_2 two-electron bonds is given by the expression $(18N_1 - 2N_2)$. A "64-electron" tetranuclear species thus requires four metal–metal bonds, a "62-electron" species requires five metal–metal bonds, and a "60-electron" species requires six metal–metal bonds. See: H. D. Kaesz, *Chem. Br.*, **9**, 344 (1973); P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976)–especially Table VI, p 338.

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Molecular Orbital Theory of Organometallic Compounds. 14. Calculation of the ^{13}C NMR Paramagnetic Shielding in Tricarbonylarenemetals

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^{13}C NMR paramagnetic shielding constants are calculated for the isoelectronic series benzenetricarbonylchromium, cyclopentadienyltricarbonylmanganese, cyclobutadienetricarbonyliron, allyltricarbonylcobalt, and ethylenetricarbonylnickel, using the self-consistent charge and configuration molecular orbital method and the Pople–Karplus equation. Correlation between the observed downfield shifts for the carbonyl ligands and the upfield shifts of the carbon atoms in the hydrocarbon ligands with the calculated σ^p values is noted without the need to consider σ^d. The importance of the various terms in the Pople–Karplus expression is shown.

In previous parts in this series,[1] it was shown that self-consistent charge and configuration molecular orbital theory (SCCCMO method) is successful in correlating a wide range of experimental quantities such as infrared stretching frequencies, force constants, ionization potentials, photoelectron spectra, bond dissociation energies, and, even in cases of very similar transition states, relative reactivities of dissociative carbonyl substitution reactions with theoretical quantities, such as orbital energies and overlap populations.

Although there is an extensive literature concerning the ^{13}C NMR spectra of organometallic complexes,[2] a wide variety of explanations for the nature of the observed shifts has been given and this rather confusing state of affairs is aptly summarized in a recent note by Evans and Norton[3] who quote from one of the first papers in the field[4] that "No convincing explanation of these results within the framework of the current approximate theory has been found" then continue "such pessimism unfortunately is still warranted a decade later".

Following Saika and Slichter[5] the shielding constant of any atom may be divided into the sum of three terms: a diamagnetic term (σ^d), a paramagnetic term (σ^p), and contributions due to electron circulation in distant parts of the molecule (σ') which include effects such as interatomic ring currents. Strictly speaking, both the paramagnetic and diamagnetic terms involve integrals centered not only on the