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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 19.[1-3] Crystal Structure of (μ-H)$Os_3Re(CO)_{15}$(NCMe), an Equatorially Metallo-Ligated Triangular Cluster Complex

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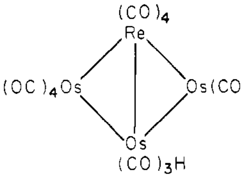
(μ-H)$Os_3Re(CO)_{15}$(NCMe) crystallizes in the noncentrosymmetric monoclinic space group $P2_1$, with a = 9.1326 (12) Å, b = 16.4244 (20) Å, c = 9.4573 (13) Å, β = 114.609 (9)°, V = 1289.7 (3) Å^3, and ρ(calcd) = 3.139 g cm^{-3} for mol wt 1219.0 and Z = 2. Diffraction data were collected on a Syntex P2$_1$ automated four-circle diffractometer using Mo Kα radiation, and the structure was refined to R_F = 3.1% and R_{wF} = 2.5% for all 3376 independent data in the range 4.5° < 2θ < 45°. The molecule contains a triangle of osmium atoms; the Os(1)–Os(2) and Os(2)–Os(3) bond lengths are normal (2.861 (1) and 2.885 (1) Å), while the Os(1)–Os(3) distance is long (3.032 (1) Å) and (taken with the cis-diequatorial angles of Os(1)–Os(3)–C(34) = 116.1 (5)° and Os(3)–Os(1)–Re(4) = 104.84 (2)°) is indicative of an equatorial bridging hydride ligand across this vector. An $Re(CO)_5$ group occupies an equatorial ligand position on Os(1) [Os(1)–Re(4) = 2.959 (1) Å] and an acetonitrile ligand occupies an axial site on Os(3) [Os(3)–N = 2.091 (11) Å].

Introduction

We have previously reported structural studies on the heteronuclear (osmium–rhenium) clusters (H)$Os_3Re(CO)_{15}$,[4] I (synthesized by Knight and Mays[5] as in eq 1), and (μ-H)$_2Os_3Re_2(CO)_{20}$,[6] II (synthesized by Shapley and co-workers[7] as in eq 2, where c-C_8H_{14} = cyclooctene).



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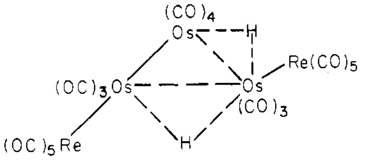

II

$$Os_3(CO)_{12} \xrightarrow[(2)\ H^+]{(1)\ Re(CO)_5^-} (H)Os_3Re(CO)_{15} \qquad (1)$$

$$Os_3(CO)_{10}(c\text{-}C_8H_{14})_2 + 2HRe(CO)_5 \rightarrow (\mu\text{-}H)_2Os_3Re(CO)_{20} + 2(c\text{-}C_8H_{14}) \qquad (2)$$

It has recently been shown[8] that (μ-H)$_2Os_3Re_2(CO)_{20}$ decomposes (by loss of $HRe(CO)_{15}$) upon heating in acetonitrile to yield a tetranuclear species shown below to be (μ-H)$Os_3Re(CO)_{15}$(NCMe). The crystal structure of this new molecule has been determined in a continuing effort to understand the detailed steps possible in conversion of an n-closo cluster to an (n + 1)-closo cluster.

Collection of Diffraction Data and Solution of Crystal Structure

The crystals of the compound are clear yellow with a platelike habit. Several fragments were chipped from a large plate and were examined for quality by means of precession photographs. These preliminary observations established the crsytal class as monoclinic and indicated $P2_1$ or $P2_1/m$ as the possible space groups (absences: $0k0$ for k = $2n$ + 1, only). The former noncentrosymmetric space group was confirmed by the successful solution and refinement of the structure.

Table I. Crystal Data for (μ-H)$Os_3Re(CO)_{15}$(NCMe)

A. Crystal Parameters[a] at 24 °C

cryst system: monoclinic
space group: $P2_1$ [C_2^2; No. 4]
a = 9.1326 (12) Å
b = 16.4244 (20) Å
c = 9.4573 (13) Å
β = 114.609 (9)°
Z = 2
V = 1289.7 (3) Å^3
mol wt = 1219.0
ρ(calcd) = 3.139 g cm^{-3}
μ = 195.6 cm^{-1}

B. Measurement of Intensity Data

diffractometer: Syntex P2$_1$
radiation: Mo Kα ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: highly oriented (pyrolitic) graphite; equatorial mounting geometry
reflctns measd: $-h,+k,\pm l$ and $-h,-k,\pm l$ for 4.5° < 2θ < 45.5°
scan type: coupled θ(cryst)–2θ(counter) at 3° min^{-1} (2θ)
scan range: [2θ(Mo Kα_1) − 0.9]° → [2θ(Mo Kα_2) + 0.9]°
bkgd measmt: stationary crystal–stationary counter, for one-fourth of the time taken for the 2θ scan, at each end of scan
reflctns collected: 3755 total, averaged to 3376 unique reflections under point group C_2
std reflctns: 080, 005, $53\bar{3}$ remeasured every 100 reflections; a 3% decrease in intensity corrected for

[a] Based on a least-squares fit to the centering angles of 24 reflections of the forms {$12\bar{6}$}, {215}, {2,10,2}, {$\bar{1}$,10,2}, {511}, and {$64\bar{2}$}, each with 2θ between 25 and 30°.

Table II. Reflections Used for Empirical Absorption Correction

2θ, deg	hkl	max/min intens (ψ scan) hkl	max/min intens (ψ scan) $\bar{h}\bar{k}\bar{l}$
14.9	060	2.20	2.26
19.9	080	2.24	2.25
25.4	0,10,1	2.20	2.18
30.0	0,12,0	2.23	2.15
36.4	2,14,$\bar{1}$	1.98	2.08

The crystal used for data collection had a rather irregular shape, approximating to a rectangular parallelepiped of maximum orthogonal dimensions 0.16 × 0.10 × 0.06 mm. It was mounted on a thin glass fiber using GE varnish; the fiber was fixed (with beeswax) into an aluminum pin, which was mounted in a eucentric goniometer and centered optically on our Syntex P2$_1$ automated four-circle diffractometer. Alignment, determination of cell parameters, and data collection proceeded as described previously;[9] details are given in Table I.

All crystallographic computations were performed by using a Syntex XTL structure-determination system, with our locally (SUNYAB)

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(1) (1) Part 18: Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2905–2909.
(2) Part 17: Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1580–1584.
(3) Part 16: Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1980**, *19*, 2391–2395.
(4) Part 4: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1977**, *16*, 2493–2497.
(5) Knight, J.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1022.
(6) Part 7: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 3546–3552.
(7) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064–8065.
(8) Churchill, M. R.; Hollander, F. J.; Lashewycz, R. A.; Pearson, G. A.; Shapley, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 2430–2431.
(9) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

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Table III. Intensity Statistics for (μ-H)$Os_3Re(CO)_{15}$(NCMe)

		theoretical	
	obsd	acentric	centric
$\langle \lvert E\rvert^2\rangle$	1.000	1.000	1.000
$\langle \lvert E\rvert\rangle$	0.891	0.886	0.798
$\langle \lvert E^2 - 1\rvert\rangle$	0.712	0.736	0.968
$\lvert E\rvert > 1.0$, %	38.48	36.79	31.73
$\lvert E\rvert > 2.0$, %	1.30	1.89	4.55
$\lvert E\rvert > 3.0$, %	0.00	0.01	0.27

modified program package.[10] Data were corrected for absorption (μ = 195.6 cm^{-1}) by an empirical method based on a set of ψ scans of reflections[11] near χ = 90 and 270° (see Table II). The curves for the Friedel-related reflections were averaged before use in correcting the data. The profiles of the ψ scans and the positions (in ϕ) of the maxima and minima were self-consistent for all reflections; there was, as usual, some broadening of the profiles with increasing 2θ.

Intensities were next converted to unscaled $|F_o|$ values after correction for Lorentz and polarization effects. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$. Redundant data were averaged to yield 3376 unique data by assuming point group C_2 for diffraction symmetry; $R(I)$ = 1.27% for the 370 data with two contributors. [For comparison, averaging under point group C_{2h} (i.e., space group $P2_1/m$) gives 1758 "unique" reflections and a value of $R(I)$ = 2.48%.] Intensity statistics (see Table III) strongly indicated the noncentrosymmetric space group $P2_1$, and this choice was confirmed by the structure solution (vide infra).

The analytical form of scattering factors[12a] for neutral osmium, rhenium, carbon, oxygen, nitrogen, and hydrogen was corrected for both real ($\Delta f'$) and imaginary components of anomalous dispersion.[12b] The function $\sum w(|F_o| - |F_c|)^2$ was minimized during least-squares refinement. The final weighting scheme was $w = [(\sigma(F_o))^2 + (0.010F_o)^2]^{-1}$ for all reflections; none was rejected.

The analysis was begun by using the C_{2h}-averaged data set; a Patterson map was solved to provide the coordinates of the four heavy-metal atoms. (The y coordinate of Re(4) was fixed at zero.) Three cycles of refinement of positional and isotropic thermal parameters resulted in R_F = 9.7%. A subsequent difference-Fourier synthesis yielded the positions of 16 linear ligands, each of which was treated initially as a carbonyl group. Continued refinement (isotropic thermal parameters for all atoms) led to R_F = 5.3%; the use of anisotropic thermal parameters for metal and oxygen atoms led to R_F = 3.5%. At this stage we discovered that one ligand previously treated as a carbonyl group [C(31)–O(31)] was an acetonitrile ligand. [This was now redefined as N–C(1)–C(2).] Refinement of the corrected structure to convergence ($\Delta/\sigma \leq 0.04$ for all parameters) resulted in the final discrepancy indices R_F = 3.1%, R_{wF} = 2.5%, and GOF = 1.148 for refinement of 243 variables against all 3376 data (none excluded). A final difference-Fourier synthesis showed no peaks greater than 1.1 e/Å^3. No indication was found of the bridging hydride ligand or of the methyl hydrogen atoms in the acetonitrile ligand. The following tests were also made: (1) The coordinates of all atoms were reflected about y = 0 to define the alternative enantiomeric structure. Refinement led to the increased residuals R_F = 3.8% and R_{wF} = 3.2%, indicating that our original choice of crystal chirality was correct. (2) Attempts were made to refine all carbon atoms anisotropically. "Non-positive-definite" tensors resulted for a couple of carbon atoms; these results were discarded.

A survey of $\sum w(|F_o| - |F_c|)^2$ values showed no significant fluctuations as a function of $|F_o|$, (sin θ)/λ, identity or parity of Miller indices, or sequence number. The weighting scheme is thus satisfactory.

Final positional and thermal parameters are reported in Table IV.

The Molecular Structure

The crystal is composed of individual (μ-H)$Os_3Re(CO)_{15}$(NCMe) molecules, which are mutually separated by normal van der Waals distances. (The two closest intermolecular contacts are O(24)···O(45)′ = 2.89 (2) Å and O(33)···O(42)′ = 2.99 (2) Å. All other contacts are >3.00 Å. See Table V.

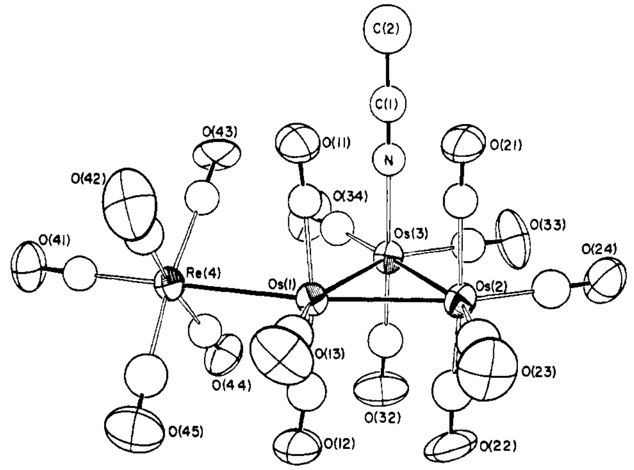

Figure 1. Labeling of atoms and geometry of the (μ-H)$Os_3Re(CO)_{15}$(NCMe) molecule (ORTEP-II diagram).

The geometry of the (μ-H)$Os_3Re(CO)_{15}$(NCMe) molecule and the atomic numbering scheme are shown in Figure 1; a stereoscopic view of the molecule is presented as Figure 2. Interatomic distances and their estimated standard deviations (esd's) are collected in Table VI. Selected interatomic angles (and esd's) are collected in Table VII.

The molecular core consists of a triangular array of osmium atoms with a rhenium atom bound to one of the equatorial coordination sites of an osmium atom. The osmium–rhenium bond length (Os(1)–Re(4) = 2.959 (1) Å) is comparable to that found previously[6] in (μ-H)$Os_3Re_2(CO)_{20}$. The Os(1)–Os(2) and Os(2)–Os(3) distances of 2.861 (1) and 2.885 (1) Å average 2.873 Å—in good agreement with the mean value of 2.877 (3) Å found for the osmium–osmium linkages in the parent triosmium dodecacarbonyl[13] and indicative of normal nonbridged Os–Os bonds. The third osmium–osmium distance, Os(1)–Os(3) = 3.032 (1) Å, is 0.159 Å longer than the average of the other two Os–Os distances and is comparable to the mean of 3.070 Å for μ-hydrido-bridged osmium–osmium vectors in (μ-H)$_2Os_3Re_2(CO)_{20}$[6] and to other simple μ-hydrido-bridged Os–Os bonds (e.g., 2.989 (1) Å in (μ-H)(H)$Os_3(CO)_{11}$[13] and 3.0185 (6) Å in (μ-H)(H)$Os_3(CO)_{10}(PPh_3)$[14]). Consideration of diequatorial angles about osmium atoms (see Figure 3) confirms the assignment of the location of the bridging hydride ligand.[15],[16] The two diequatorial angles adjacent to the Os(1)–Os(3) bond are Os(1)–Os(3)–C(34) = 116.1 (5)° and Os(3)–Os(1)–Re(4) = 104.84 (2)°. These are closely similar to the analogous angles in the (μ-H)$_2Os_3Re_2(CO)_{20}$ molecule (average Os–Os–C = 117.4° and average Os–Os–Re = 103.7°[6]) and are the largest diequatorial angles within the molecular framework. (It should be noted that the diequatorial Os–Os–CO angles in $Os_3(CO)_{12}$ average 98.2°.[13]) As in the (μ-H)$_2Os_3Re_2(CO)_{20}$ structure, it appears that the Os–Os–Re angle is increased less than the Os–Os–CO angle due to a combination of mass and steric bulk.

The osmium–carbonyl bond distances appear to be normal, averaging 1.926 [33] Å. That trans to the acetonitrile is (as might be expected) the shortest (Os(3)–C(32) = 1.883 (16) Å) and is excluded from subsequent statistics for chemical reasons. The average Os–CO (axial) distance of 1.948 [30] Å is slightly longer than the average Os–CO (equat) distance

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[10] The system has been described previously. See: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1978**, *17*, 1291–1295.

[11] This technique has been described in detail. See: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957–1962.

[12] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4: (a) pp 99–101; (b) pp 149–150.

[13] Part 1: Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878–884.

[14] Part 3: Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 2397–2403.

[15] Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843–1853. (See discussion on pp 1848–1852.)

[16] Churchill, M. R. *Adv. Chem. Ser.* **1978**, *No. 167*, 36–60.

Table IV. Final Atomic Parameters with Esd's for (μ-H)$Os_3Re(CO)_{15}$(NCMe)

A. Positional and Isotropic Thermal Parameters

atom	x	y	z	atom	x	y	z	B, Å^2
Os1	0.13634 (6)	0.14020 (4)	0.30855 (6)	C11	0.1511 (16)	0.2078 (9)	0.1450 (16)	3.2 (3)
Os2	0.23841 (7)	0.26647 (5)	0.53770 (6)	C12	0.1147 (20)	0.0618 (10)	0.4509 (19)	4.8 (3)
Os3	0.48920 (7)	0.16612 (5)	0.51938 (6)	C13	−0.0877 (18)	0.1584 (9)	0.2236 (16)	4.4 (3)
Re4	0.13197 (7)	0	0.11039 (6)	C21	0.2557 (17)	0.3388 (9)	0.3771 (17)	3.3 (3)
O11	0.1540 (14)	0.2449 (6)	0.0455 (12)	C22	0.2255 (20)	0.1881 (10)	0.6824 (19)	5.1 (4)
O12	0.0901 (16)	0.0112 (8)	0.5251 (14)	C23	0.0218 (22)	0.3037 (10)	0.4930 (19)	5.0 (4)
O13	−0.2229 (12)	0.1687 (8)	0.1673 (15)	C24	0.3679 (19)	0.3393 (9)	0.6972 (18)	4.5 (3)
O21	0.2586 (15)	0.3829 (6)	0.2879 (12)	C32	0.4793 (19)	0.0920 (10)	0.6672 (19)	4.4 (3)
O22	0.2083 (17)	0.1450 (8)	0.7713 (15)	C33	0.6419 (19)	0.2298 (9)	0.6829 (18)	4.2 (3)
O23	−0.1038 (14)	0.3210 (9)	0.4683 (16)	C34	0.6411 (21)	0.0957 (10)	0.4819 (18)	4.4 (3)
O24	0.4458 (15)	0.3848 (8)	0.7903 (14)	C41	0.1287 (17)	−0.0905 (9)	−0.0203 (16)	3.7 (3)
O32	0.4728 (17)	0.0441 (8)	0.7524 (15)	C42	−0.0173 (19)	0.0627 (9)	−0.0705 (18)	4.5 (3)
O33	0.7373 (14)	0.2647 (8)	0.7818 (14)	C43	0.3265 (19)	0.0531 (9)	0.0967 (17)	3.9 (3)
O34	0.7263 (14)	0.0529 (8)	0.4641 (13)	C44	0.2796 (18)	−0.0500 (9)	0.3122 (18)	3.9 (3)
O41	0.1292 (14)	−0.1431 (7)	−0.0977 (13)	C45	−0.0593 (23)	−0.0424 (10)	0.1405 (20)	5.4 (4)
O42	−0.1063 (16)	0.1010 (7)	−0.1719 (15)	N	0.5056 (13)	0.2446 (7)	0.3525 (13)	3.6 (2)
O43	0.4336 (13)	0.0776 (8)	0.0898 (13)	C1	0.5209 (18)	0.2848 (9)	0.2623 (18)	4.3 (3)
O44	0.3654 (13)	−0.0786 (7)	0.4261 (11)	C2	0.5348 (23)	0.3393 (12)	0.1433 (22)	7.1 (5)
O45	−0.1704 (17)	−0.0627 (11)	0.1579 (20)					

B. Anisotropic Thermal Parameters[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os1	2.555 (25)	2.953 (25)	3.345 (24)	0.094 (21)	1.200 (21)	−0.112 (20)
Os2	3.552 (27)	3.400 (26)	3.251 (26)	0.355 (24)	1.628 (22)	−0.234 (22)
Os3	2.673 (24)	3.347 (27)	2.775 (23)	0.404 (20)	0.588 (20)	0.027 (20)
Re4	2.500 (24)	2.987 (25)	3.040 (25)	0.063 (21)	0.817 (20)	−0.124 (21)
O11	6.5 (6)	5.2 (6)	3.7 (5)	−0.8 (5)	1.1 (5)	1.2 (4)
O12	8.6 (8)	5.7 (7)	6.4 (6)	−0.5 (6)	4.4 (6)	1.4 (5)
O13	2.7 (5)	7.6 (7)	10.7 (8)	0.9 (5)	2.1 (5)	0.8 (7)
O21	8.4 (7)	4.0 (5)	4.5 (5)	0.9 (5)	3.3 (5)	1.3 (4)
O22	12.7 (10)	6.9 (7)	7.8 (7)	0.5 (8)	8.2 (7)	1.8 (6)
O23	3.4 (6)	9.7 (9)	9.6 (8)	1.9 (6)	2.6 (6)	−0.7 (7)
O24	5.4 (6)	9.1 (8)	6.1 (6)	−2.8 (5)	3.0 (5)	−3.1 (6)
O32	7.9 (8)	8.0 (8)	6.6 (7)	1.2 (7)	3.6 (6)	3.9 (6)
O33	6.0 (6)	5.7 (6)	7.5 (7)	−0.5 (6)	−1.0 (6)	−2.4 (6)
O34	4.8 (6)	9.7 (9)	6.0 (7)	2.7 (6)	1.0 (5)	−0.5 (6)
O41	5.6 (6)	5.1 (6)	6.4 (6)	0.5 (5)	2.4 (5)	−2.2 (5)
O42	7.2 (8)	7.0 (7)	6.4 (7)	2.2 (6)	−2.0 (6)	1.2 (6)
O43	3.2 (5)	10.2 (8)	5.9 (6)	−2.5 (5)	3.0 (5)	0.1 (6)
O44	6.4 (6)	5.7 (6)	3.4 (5)	1.7 (5)	1.4 (5)	0.8 (4)
O45	7.0 (8)	14.2 (13)	13.0 (12)	−4.8 (8)	7.1 (8)	−3.3 (10)

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^*B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

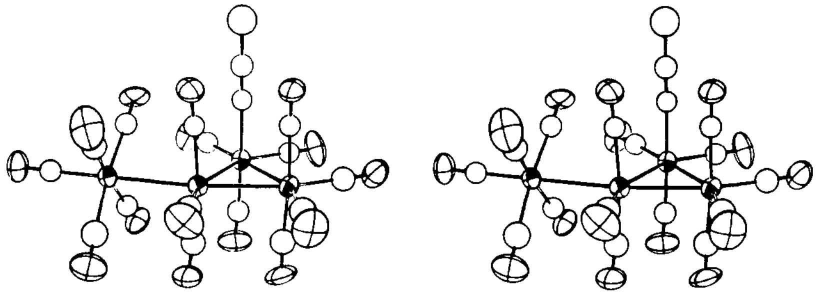

Figure 2. Stereoscopic view of the (μ-H)$Os_3Re(CO)_{15}$(NCMe) molecule.

of 1.917 [27] Å. This is expected as a result of the greater competition for π-electron density between mutually axial ligands and follows similar results for $Os_3(CO)_{12}$ (1.946 [6] vs. 1.912 [7] Å),[13] (μ-H)(H)$Os_3(CO)_{11}$ (1.961 [12] vs. 1.889 [11] Å,[13] (μ-H)(H)$Os_3(CO)_{10}(PPh_3)$ (1.935 [12] vs. 1.888 [10] Å),[14] and $Ru_3(CO)_{12}$ (1.942 [4] vs. 1.921 [5] Å).[17]

The equatorial rhenium-carbonyl linkages average 2.003 [22] Å; these are each longer than the axial distance, Re(4)–C(41) = 1.926 (15) Å. Again, these differences derive from the greater competition between mutually trans (i.e., *equatorial*) CO ligands on the rhenium atom. The $Re(CO)_5$ group takes up a staggered configuration with respect to the ligands on Os(1), the two groups being rotated by 47.2° from a perfectly eclipsed conformation. (This angle is calculated as the mean of the angles between equatorial Re–C vectors and the triosmium plane.)

The acetonitrile ligand takes up an ordered, well-defined location in an axial position on Os(3), i.e., adjacent to the bridging hydride ligand. The acetonitrile ligand is linear (∠Os(3)–N–C(1) = 176.5 (12)°, ∠N–C(1)–C(2) = 177.6 (18)°); bond lengths within this system are Os(3)–N = 2.091

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(17) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655–2659.

Table V. Nonbonded Contacts Less Than 3.25 Å[a]

O12	O23 (20–11)	3.13 (2)	O33	O41 (2101)	3.11 (2)
O12	O34 (1–100)	3.20 (2)	O33	O42 (1101)	2.99 (2)
O22	O42 (1001)	3.22 (2)	O33	O44 (2101)	3.14 (2)
O22	O43 (1001)	3.06 (2)	O33	C41 (2101)	3.15 (2)
O22	C43 (1001)	3.19 (2)	O33	C44 (2101)	3.16 (2)
O23	C1 (1–100)	3.21 (2)	O34	O42 (1101)	3.23 (2)
O24	O44 (2101)	3.24 (2)	O42	C33 (1–10–1)	3.00 (2)
O24	O45 (2001)	2.89 (2)	O42	C34 (1–10–1)	3.12 (2)
O24	C44 (2101)	3.22 (2)	O45	C24 (20–11)	3.13 (2)
O24	C2 (1001)	3.18 (2)			

[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*. Transformation code for first digit: 1 = *x*, *y*, *z*; 2 = −*x*, ½ + *y*, −*z*.

Table VI. Interatomic Distances (Å) for $(\mu\text{-H})Os_3Re(CO)_{15}(NCMe)$

(A) "Normal" Metal–Metal Distances

Os(1)–Os(2)	2.861 (1)	Os(1)–Re(4)	2.959 (1)
Os(2)–Os(3)	2.885 (1)		

(B) "Long" Metal–Metal Distance

Os(1)–Os(3)	3.032 (1)

(C) Metal–Ligand Bond Lengths

Os(1)–C(11)	1.954 (14)	Os(3)–C(32)	1.883 (16)
Os(1)–C(12)	1.932 (17)	Os(3)–C(33)	1.906 (16)
Os(1)–C(13)	1.885 (17)	Os(3)–C(34)	1.948 (19)
Os(2)–C(21)	1.986 (15)	Re(4)–C(41)	1.926 (15)
Os(2)–C(22)	1.918 (17)	Re(4)–C(42)	1.977 (16)
Os(2)–C(23)	1.941 (20)	Re(4)–C(43)	2.031 (18)
Os(2)–C(24)	1.903 (16)	Re(4)–C(44)	1.998 (16)
Os(3)–N	2.091 (11)	Re(4)–C(45)	2.007 (21)

av Os–C	1.926 [33][a]	excluding C(32)
Os–C(axial)	1.948 [30]	
Os–C (equat)	1.917 [27]	
Re–C (equat)	2.003 [22]	

(D) Metal···Oxygen Distances

Os(1)···O(11)	3.083 (11)	Os(3)···O(33)	3.038 (13)
Os(1)···O(12)	3.095 (13)	Os(3)···O(34)	3.060 (14)
Os(1)···O(13)	3.019 (13)	Re(4)···O(41)	3.060 (11)
Os(2)...O(21)	3.104 (11)	Re(4)...O(42)	3.126 (13)
Os(2)...O(22)	3.073 (14)	Re(4)...O(43)	3.114 (13)
Os(2)...O(23)	3.048 (14)	Re(4)···O(44)	3.135 (10)
Os(2)···O(24)	3.050 (13)	Re(4)···O(45)	3.150 (18)
Os(3)···O(32)	3.029 (14)		

av Os···O	3.060 [28][a]	excluding O(32)
Os···O (axial)	3.089 [14]	
Os···O(equat)	3.043 [16]	
Re···O (equat)	3.131 [15]	

(E) Carbon–Oxygen Bond Lengths

C(11)–O(11)	1.131 (18)	C(33)–O(33)	1.132 (20)
C(12)–O(12)	1.167 (22)	C(34)–O(34)	1.112 (23)
C(13)–O(13)	1.135 (21)	C(41)–O(41)	1.134 (19)
C(21)–O(21)	1.120 (18)	C(42)–O(42)	1.150 (20)
C(22)–O(22)	1.158 (22)	C(43)–O(43)	1.085 (22)
C(23)–O(23)	1.108 (25)	C(44)–O(44)	1.137 (19)
C(24)–O(24)	1.148 (20)	C(45)–O(45)	1.144 (28)
C(32)–O(32)	1.147 (21)		

av C–O 1.134 [21][a]

(F) Bond Lengths in Acetonitrile Ligand

N–C(1)	1.133 (20)	C(1)–C(2)	1.483 (25)

[a] Errors associated with the average values, shown in square brackets, calculated by using the following expression, where $\bar{\chi}$ is the average value and χ_i is the *i*th of *N* equivalent values: $\sigma = [\Sigma_N(\bar{\chi} - \chi_i)^2/(N-1)]^{1/2}$.

(11) Å, N–C(1) = 1.133 (20) Å, and C(1)C(2) = 1.483 (25) Å.

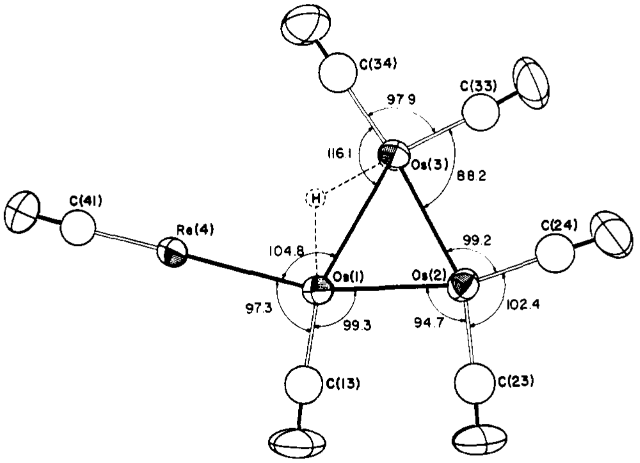
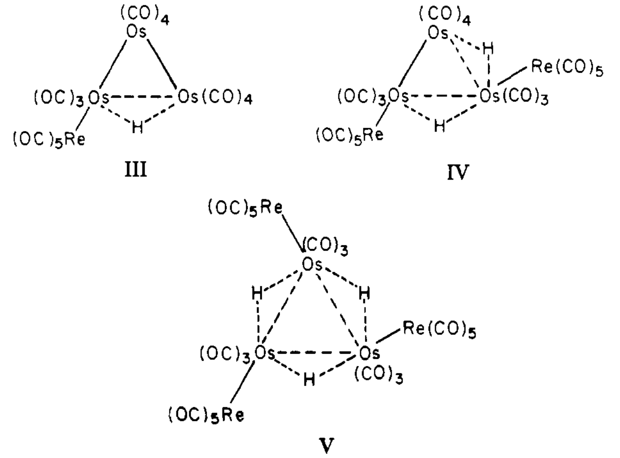


Figure 3. Angles within the equatorial plane of the triosmium cluster, showing the probable location of the hydride ligand.

Chart I

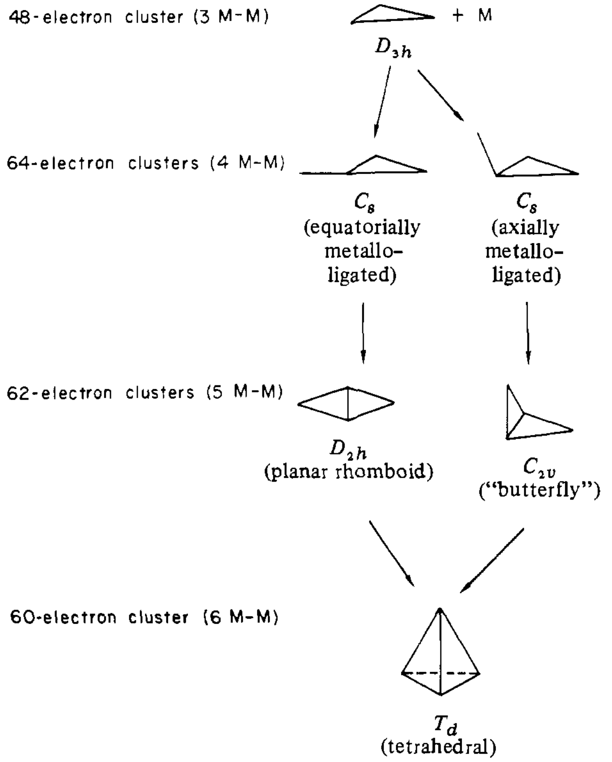


III

IV

V

Scheme I



The $(\mu\text{-H})Os_3Re(CO)_{15}(NCMe)$ molecule is formally related to $(\mu\text{-H})Os_3Re(CO)_{16}$ (III), the first member of the series of "equatorially metallo-ligated" or "equatorially spiked" triangular clusters or stoichiometry $(\mu\text{-H})_nOs_3Re_n(CO)_{12+4n}$

Table VII. Interatomic Angles (Deg) for $(\mu\text{-H})Os_3Re(CO)_{15}(NCMe)$

(A) M-M-M Angles			
Os(2)-Os(1)-Os(3)	58.54 (2)	Os(2)-Os(1)-Re(4)	163.38 (3)
Os(1)-Os(2)-Os(3)	63.69 (2)	Os(3)-Os(1)-Re(4)	104.84 (2)
Os(1)-Os(3)-Os(2)	57.77 (2)		
(B) Other Equatorial Angles			
Re(4)-Os(1)-C(13)	97.3 (5)	Os(2)-Os(3)-C(33)	88.2 (5)
Os(2)-Os(1)-C(13)	99.3 (5)	C(33)-Os(3)-C(34)	97.9 (7)
Os(1)-Os(2)-C(23)	94.7 (5)	Os(1)-Os(3)-C(34)	116.1 (5)
C(23)-Os(2)-C(24)	102.4 (7)	Os(1)-Re(4)-C(41)	179.4 (5)
Os(3)-Os(2)-C(24)	99.2 (5)		
(C) Axial M-M-C and M-M-N Angles			
Os(2)-Os(1)-C(11)	94.6 (4)	Os(3)-Os(2)-C(22)	86.9 (5)
Os(2)-Os(1)-C(12)	92.9 (5)	Os(1)-Os(3)-N	88.9 (3)
Os(3)-Os(1)-C(11)	92.1 (4)	Os(1)-Os(3)-C(32)	91.8 (5)
Os(3)-Os(1)-C(12)	91.4 (5)	Os(2)-Os(3)-N	90.1 (3)
Re(4)-Os(1)-C(11)	85.8 (4)	Os(2)-Os(3)-C(32)	92.3 (5)
Re(4)-Os(1)-C(12)	86.8 (5)	Os(1)-Re(4)-C(42)	88.0 (5)
Os(1)-Os(2)-C(21)	87.6 (4)	Os(1)-Re(4)-C(43)	85.7 (4)
Os(1)-Os(2)-C(22)	87.5 (5)	Os(1)-Re(4)-C(44)	83.6 (5)
Os(3)-Os(2)-C(21)	88.7 (4)	Os(1)-Re(4)-C(45)	87.9 (5)
(D) C-M-C and C-M-N Angles			
C(11)-Os(1)-C(12)	172.5 (7)	C(32)-Os(3)-C(34)	90.6 (7)
C(11)-Os(1)-C(13)	89.6 (6)	C(41)-Re(4)-C(42)	91.5 (7)
C(12)-Os(1)-C(13)	89.7 (7)	C(41)-Re(4)-C(43)	94.1 (7)
C(21)-Os(2)-C(22)	174.5 (7)	C(41)-Re(4)-C(44)	96.8 (7)
C(21)-Os(2)-C(23)	92.5 (7)	C(41)-Re(4)-C(45)	92.4 (7)
C(21)-Os(2)-C(24)	90.5 (7)	C(42)-Re(4)-C(43)	91.6 (7)
C(22)-Os(2)-C(23)	90.4 (8)	C(42)-Re(4)-C(44)	171.6 (7)
C(22)-Os(2)-C(24)	93.4 (7)	C(42)-Re(4)-C(45)	88.6 (7)
N-Os(3)-C(32)	177.6 (6)	C(43)-Re(4)-C(44)	88.7 (6)
N-Os(3)-C(33)	90.9 (6)	C(43)-Re(4)-C(45)	173.6 (7)
N-Os(3)-C(34)	87.0 (6)	C(44)-Re(4)-C(45)	90.2 (7)
C(32)-Os(3)-C(33)	89.8 (7)		
(E) M-C-O Angles			
Os(1)-C(11)-O(11)	176.9 (13)	Os(3)-C(33)-O(33)	176.9 (15)
Os(1)-C(12)-O(12)	173.7 (15)	Os(3)-C(34)-O(34)	177.0 (16)
Os(1)-C(13)-O(13)	177.6 (14)	Re(4)-C(41)-O(41)	178.6 (14)
Os(2)-C(21)-O(21)	175.5 (14)	Re(4)-C(42)-O(42)	177.2 (15)
Os(2)-C(22)-O(22)	174.2 (16)	Re(4)-C(43)-O(43)	176.4 (14)
Os(2)-C(23)-O(23)	176.5 (16)	Re(4)-C(44)-O(44)	179.0 (14)
Os(2)-C(24)-O(24)	178.2 (15)	Re(4)-C(45)-O(45)	176.7 (17)
Os(3)-C(32)-O(32)	176.8 (15)		
(F) Angles in Acetonitrile Ligand			
Os(3)-N-C(1)	176.5 (12)	N-C(1)-C(2)	177.6 (18)

(see Chart I). The second member of this series, $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$, IV, has been characterized previously.[6]

Attempts to convert $(\mu\text{-H})Os_3Re(CO)_{15}(NCMe)$ (a species with formally *four* metal–metal bonds) to $HOs_3Re(CO)_{15}$ (with *five* metal–metal bonds) have not met with success.[8]

Conversion of a triangular cluster directly to a tetrahedral cluster (by attack of some metal-containing fragment) is a common occurrence.[18-20] This could, in principle, occur either by direct attack of the incoming fragment on the triangular face *or* via a stepwise process involving the tetranuclear shapes shown in Scheme I.

Despite the pleasing simplicity of this scheme, the only transformations between metallo-ligated (4 M–M) and more condensed clusters of which we are aware both involve closure of (4 M–M) metallo-ligated clusters to (6 M–M) tetrahedral clusters. The two reactions are shown in eq 3[21] and 4.[8]

$$[(\mu\text{-H}_3)HRe_4(CO)_{15}{}^{2-}] \rightarrow [(\mu\text{-H})_4Re_4(CO)_{13}{}^{2-}] + \text{other products} \quad (3)$$

$$(\mu\text{-H})Os_3Re(CO)_{15}(NCMe) \xrightarrow{\Delta, H_2} (\mu\text{-H})_5Os_3Re(CO)_{12} \quad (4)$$

Further studies on these systems are in progress and will be reported later.

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Registry No. $(\mu\text{-H})Os_3Re(CO)_{15}(NCMe)$, 79255-11-1.

Supplementary Material Available: Listings of data-processing formulas and observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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