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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 7.[1-6] Crystal Structure and Molecular Geometry of $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$

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The complex di-μ-hydrido-icosacarbonyltriosmiumdirhenium(3*Os–Os*,2*Os–Re*), $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$, previously prepared from $Os_3(CO)_{10}(c\text{-}C_8H_{14})_2$ and $HRe(CO)_5$, has been studied by a complete three-dimensional single-crystal X-ray structural analysis. The complex crystallizes in the noncentrosymmetric monoclinic space group *Cc* with $a = 9.2480$ (16) Å, $b = 23.010$ (4) Å, $c = 29.665$ (5) Å, $\beta = 104.589$ (13)°, $V = 6109.0$ (17) Å^3, and ρ(calcd) = 3.273 g cm^{-3} for mol wt 1505.2 and $Z = 8$. Diffraction data were collected with a Syntex $P2_1$ diffractometer using an ω-scan collection mode; the structure was solved and refined to $R_F = 5.7\%$ for those 2913 data with $F_o > 2\sigma(F_o)$ and $4° < 2\theta < 40°$ (Mo Kα radiation). All atoms other than the hydrogen atoms were located. The crystallographic asymmetric unit consists of two independent molecules of $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ which are related to each other by a *local* pseudo-inversion center at a general position in the unit cell. The two molecules have identical connectivities, and their bond lengths and bond angles are equivalent. The core of the molecule consists of a triangle of osmium atoms with the two rhenium atoms bonded in C_3-related equatorial sites on two of the osmium atoms. Each rhenium atom bears five carbonyl groups, the osmium atoms which are linked to rhenium each bear three carbonyl groups, and the third osmium atom bears four carbonyl groups. The Os–Re bond lengths range from 2.942 (3) to 2.983 (3) Å; Os–Os distances break down into two distinct groups—those believed to be bridged by single μ-hydride ligands, which range in length from 3.059 (3) to 3.084 (2) Å, and normal (nonbridged) Os–Os bonds, which have values of 2.876 (3) and 2.880 (3) Å.

Introduction

Shapley and co-workers have shown[7] that heteronuclear metal carbonyl hydride clusters can be prepared selectively by the reaction of a monomeric metal carbonyl hydride with a species $M_x(CO)_yS_z$, in which S is a labile two-electron donor ligand.

In particular, the reaction of the dicyclooctene complex $Os_3(CO)_{10}(c\text{-}C_8H_{14})_2$ with excess $HRe(CO)_5$ yields $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$, as indicated by eq 1.

$$Os_3(CO)_{10}(c\text{-}C_8H_{14})_2 + 2HRe(CO)_5 \rightarrow (\mu\text{-H})_2Os_3Re_2(CO)_{20} + 2(c\text{-}C_8H_{14}) \quad (1)$$

We have now completed a full three-dimensional X-ray diffraction study of $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$; our results are presented below.

Experimental Section

A small sample of $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ was supplied to us by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. Crystals of this complex were a clear yellow color with a platelike habit but exhibited extensive twinning. The only crystal of satisfactory quality was carefully cleaved into two unequal pieces, which were then each mounted on a glass fiber (in the air) using G.E. varnish. Precession photographs confirmed the quality of these crystals and indicated $2/m$ Laue symmetry. The systematic absences *hkl* for $h + k = 2n + 1$ and *h*0*l* for $l = 2n + 1$ are consistent with the centrosymmetric space group $C2/c$ [C_{2h}^6; No. 15] or with the corresponding noncentrosymmetric space group *Cc* [C_s^4; No. 9]. The latter, noncentrosymmetric, space group was later confirmed by the successful solution and refinement of the crystal structure.

A complete set of diffraction data (Syntex $P2_1$ diffractometer; Mo Kα radiation) was initially collected on the larger and apparently more desirable of the two fragments described above. The structure was solved using this data set (via Patterson and difference-Fourier techniques) and was refined via least-squares techniques, yielding the results given in our preliminary report.[7] However, the absorption corrections for the intensities of reflections in this data set varied by a factor of 10; further, the resulting anisotropic thermal parameters of the rhenium and osmium atoms defined ellipsoids which closely resembled a set of parallel pancakes, thereby indicating that the applied absorption correction was not satisfactory. (The linear absorption coefficient for the compound is $\mu = 205.4$ cm^{-1} for Mo Kα radiation.) We therefore concluded that a better data set was essential. We investigated the other (smaller) portion of the cleaved crystal and ascertained that it had a significantly lower variation in transmission factor than did the initial crystal. We therefore collected a second data set, the results of which appear below.

Table I. Experimental Data for the X-ray Diffraction Study of $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$

(A) Crystal Parameters at 25 °C[a]

crystal system: monoclinic
space group: *Cc* [C_s^4; No. 9]
$a = 9.2480$ (16) Å
$b = 23.010$ (4) Å
$c = 29.665$ (5) Å
$\beta = 104.589$ (13)°
$V = 6109.0$ (17) Å
$Z = 8$
mol wt = 1505.2
ρ(calcd) = 3.273 g cm^{-3}
$\mu = 205.4$ cm^{-1}

(B) Measurement of Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda}$ 0.710 73 Å)
monochromator: highly oriented graphite ($2\theta = 12.2°$); equatorial mode
reflections measd: $+h,+k,\pm l$
2θ range: $4° \rightarrow 40°$
scan type: ω(crystal)–stationary counter
scan speed: 2.0°/min
scan width: $[\omega - 0.45]° \rightarrow [\omega + 0.45]°$
background measurement: stationary crystal and counter at positions offset by ± 0.60° in ω from the peak center, measured for 1/8 of the scan time at each position
standard reflections: 0,16,5; 4,0,$\overline{20}$; 602; measured after each 47 reflections; there was no apparent decay in intensity
reflections collected: 3082, excluding standards

[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo $K\bar{\alpha}$ components of 24 reflections with 2θ between 24 and 30°. Reflections used were $\{0,16,\bar{5}\}$, $\{60\bar{2}\}$, $\{2,8,\overline{17}\}$, $\{2,2,14\}$, $\{4,0,\overline{20}\}$, $\{4,10,5\}$, and $\{5,7,\overline{15}\}$.

The approximate dimensions of this second crystal were 0.13 mm × 0.19 mm × 0.32 mm. The crystal was shaped somewhat like a cold chisel. It was mounted on our Syntex $P2_1$ diffractometer with its extended direction approximately parallel to the spindle axis (ϕ). Details of the data collection are given in Table I. (The $+h,+k,+l$ and $+h,+k,-l$ data were measured.)

Eight close-to-axial reflections ($\chi_0 = 90 \pm 15°$) distributed over the range of 2θ values used in data collection were used to correct the intensity data for absorption. These were each measured at 36 positions around their diffraction vectors (from $\psi = 0°$ to $\psi = 350°$, at intervals of 10°). Each reflection was used to define a normalized absorption curve of relative intensity vs. ϕ. These curves were interpolated both in 2θ and in ϕ to provide absorption corrections for the intensity data. The reflections used for the absorption curves were as follows: $20\bar{2}$ ($2\theta = 8.83°$, (maximum intensity)/(minimum intensity) = 3.40), $31\bar{2}$ (13.36°, 2.59), $42\bar{3}$ (18.03°, 2.49), $51\bar{2}$ (22.41°, 2.45), $6\bar{2}\bar{4}$ (26.91°, 2.33), $6\bar{2}\bar{6}$ (26.94°, 2.33), $7\bar{1}\bar{1}$ (31.97°, 2.51), and $80\bar{8}$ (35.85°, 2.31). All were self-consistent in positions of maxima and minima and in general shape of the curve. (There was, as usual, some broadening of the intensity profiles with increasing 2θ.)

The intensity data were not averaged since we knew already that the space group was noncentric. (The $0kl$ and $0k\bar{l}$ reflections are *not* equivalent in the point group C_s which corresponds to space group *Cc*.) Data were converted to unscaled $|F_o|$ values following correction for Lorentz and polarization effects. (The graphite monochromator was mounted in the parallel mode, with $2\theta_{mono} = 12.2°$, and was assumed to be 50% perfect and 50% ideally imperfect in the scattering direction.) A value of $|F_o| = 0.0$ was given to any reflection with $I < 0$.

Refinement was begun[8] using the positional and thermal parameters for all atoms derived from the previous data set. The analytical scattering factors of Cromer and Waber were used throughout the analysis;[9a] both the real and the imaginary components of anomalous dispersion[9b] were included for all nonhydrogen atoms. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights are those in eq 2, and $\sigma(F_o)$ is propagated from $\sigma(I)$ and is based solely upon counting statistics. Reflections with $F_o < 2\sigma(F_o)$ were given zero weight.

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

The "ignorance factor" (p) was initially given a value of 0.015. Discrepancy indices, R_F and R_{wF}, and the "goodness-of-fit" (GOF) are defined in eq 3–5; here NO is the number of observations and NV is the number of variables.

$$R_F = \left[\frac{\sum||F_o| - |F_c||}{\sum|F_o|}\right] \times 100\ (\%) \tag{3}$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} \times 100\ (\%) \tag{4}$$

$$\text{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{(\text{NO} - \text{NV})}\right]^{1/2} \tag{5}$$

The origin of the unit cell was defined by fixing the x and z coordinates of atom Os3A. Full-matrix least-squares refinement of the metal atom positional and anisotropic thermal parameters led to convergence with $R_F = 6.1\%$, $R_{wF} = 6.1\%$, and GOF = 1.95.

A few cycles of full-matrix least-squares refinement of the scale factor, all positional parameters (except x and z for Os3A—vide supra), anisotropic thermal parameters for the metal atoms, and isotropic thermal parameters for carbon and oxygen atoms (409 parameters in all, since there are two molecules in the asymmetric unit) led to $R_F = 6.0\%$ and $R_{wF} = 5.8\%$. However, some of the positional parameters of the light atoms were found to be "oscillating". Since the structure contains a very strong pseudo center of symmetry (which relates the two independent molecules), we concluded that the observed oscillations were the result of correlation of pseudo-centrosymmetrically related parameters on the two molecules. We continued refinement, varying all parameters for one molecule only in a given cycle and then varying all parameters for the other molecule. After two rounds of this, only one carbonyl group (C55B–O55B) was still showing any appreciable shifts. We now fixed most parameters but allowed the refinement of thermal and positional parameters for the metal atoms and C55B and O55B of molecule B. Four cycles of this "forced" refinement led to some damping of the oscillation (final shifts were 0.061 Å for C55B and 0.018 Å for O55B) and to discrepancy indices of $R_F = 6.0\%$ and $R_{wF} = 5.8\%$.

A careful examination of the data set now suggested that a slight correction for secondary extinction was necessary. A least-squares fit to nine reflections with $I > 90\,000$ counts gave a value for k of 2.6×10^{-7} in the approximate Zachariasen correction[10] (see eq 6).

$$F_o^{\text{cor}} = F_o^{\text{uncor}}(1.0 + kI) \tag{6}$$

This correction was applied to all data and the weighting scheme was changed to accommodate a slightly larger "ignorance factor" ($p = 0.02$), so as to reduce the effects of errors in the very strong reflections.

Two cycles of full-matrix least-squares refinement led to convergence with $R_F = 5.8\%$, $R_{wF} = 6.1\%$, and GOF = 1.854 (409 parameters varied against 2913 data with $F > 2\sigma(F)$). At this stage, molecular geometry calculations revealed that the osmium–"axial" oxygen distances varied systematically depending upon the direction of the M→O vector. The average Os*n*A to O*n*1A and Os*n*B to O*n*2B (n = 1–3) was 2.92 [3] Å, while the average Os–O distance on the opposite surface of the triosmium clusters was 3.12 [3] Å.[11] This effect is precisely what is expected if one has refined the "wrong enantiomer" in a polar group using one "asymmetric unit" of data.[12]

We therefore inverted the positional parameters to define the correct enantiomeric structure and refined once more to convergence. The final discrepancy indices were $R_F = 5.7\%$, $R_{wF} = 6.0\%$, and GOF = 1.840. While these agreement factors are only slightly better than for the refinement as the wrong enantiomer, there is a great improvement in the agreement between chemically equivalent bond lengths on opposite sides of the molecule (the previously defined average distances (vide supra) are now 2.98 [1] and 3.04 [4] Å, respectively). Clearly, the inverted structure is the true one for the particular crystal under consideration.

A final difference-Fourier synthesis showed peaks up to 2.28 e Å^{-3} in height; all major peaks were, however, close to the positions of the 10 independent "heavy" atoms [Z(Re) = 75 and Z(Os) = 76]. There was no convincing direct evidence on this map for the positions of the hydride ligands.

A listing of the final values of $|F_o|$, F_c, and $\sigma(F_o)$ is available as supplementary material. Final positional and thermal parameters are collected in Tables II and III.

Discussion

The crystal consists of discrete molecular units of $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$, which are mutually separated by normal van der Waals distances. There are no abnormally short intermolecular contacts.

The complex crystallizes in the noncentrosymmetric space group *Cc* with two crystallographically independent molecules (hereafter referred to as "molecule A" and "molecule B") in the asymmetric unit. There is a strange crystallographic complication in that these two independent molecules are related by a (local) pseudo-inversion center at the *general* position $x = -0.116$, $y = -0.146$, $z = -0.176$. This pseudo-inversion center is close to exact for the metal atoms (atoms Re5A and Re5B deviate from being precisely centrosymmetrically related by 0.07 Å; other equivalent pairs of metal atoms have deviations of less than 0.05 Å). The equivalent sets of carbon or of oxygen atoms deviate by slightly larger distances than do the metal atoms. Nevertheless, the closeness of the approximation of the bimolecular asymmetric unit to an idealized centrosymmetric doublet is astounding. The pseudo-inversion center is, however, a *local* center of symmetry only—not a mislaid crystallographic center of symmetry! (For this to be a true crystallographic center of symmetry it would necessarily be placed in a special position relative to the *c* glide.) This is shown clearly in Figure 1, which illustrates the arrangement of the Os_3Re_2 cores of all $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ molecules within the unit cell.

Interatomic distances and their estimated standard deviations (esd's) are collected in Table IV; selected intramolecular angles, with their esd's, are listed in Table V.

The overall geometry of the $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ molecules (including the scheme used for labeling atoms) and stereoscopic views of the molecules are shown in Figures 2 and 3.

The metal core consists of a triangle of osmium atoms with rhenium atoms linked to two equatorial sites (related to each other by a C_3 rotation) on adjacent osmium atoms. (We note here that osmium and rhenium atoms have been assigned locations that are chemically sensible and are in keeping with the stated identity of the metal atom, with the method of synthesis, and with bond length considerations (vide infra). No attempt was made to differentiate between rhenium and osmium via refinement of crystallographic occupancies or switching of scattering factors, nor do we believe that such

Table II. Positional Parameters and Isotropic Thermal Parameters for $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$

	x	y	z	B, Å^2		x	y	z	B, Å^2
(A) Molecule A					(B) Molecule B				
Os1A	−0.19549 (29)	−0.02526 (10)	−0.03777 (7)		Os1B	−0.03561 (28)	−0.26644 (10)	−0.31401 (7)	
Os2A	−0.31484 (26)	−0.14860 (10)	−0.06078 (7)		Os2B	0.08381 (28)	−0.14290 (9)	−0.29095 (7)	
Os3A	0	−0.12014 (10)	0		Os3B	−0.23138 (28)	−0.17089 (11)	−0.35040 (8)	
Re4A	−0.43549 (30)	0.04974 (10)	−0.09232 (8)		Re4B	0.20131 (29)	−0.34133 (10)	−0.25864 (8)	
Re5A	−0.32452 (29)	−0.27820 (11)	−0.06231 (9)		Re5B	0.09099 (30)	−0.01391 (10)	−0.29185 (8)	
C11A	−0.118 (6)	−0.0241 (25)	−0.0890 (19)	3.7 (13)	C11B	−0.117 (6)	−0.2694 (25)	−0.2648 (18)	3.4 (12)
C12A	−0.304 (6)	−0.0245 (22)	0.0087 (16)	2.6 (11)	C12B	0.039 (7)	−0.2684 (26)	−0.3596 (18)	3.9 (13)
C13A	−0.091 (8)	0.0337 (33)	−0.0129 (23)	6.0 (17)	C13B	−0.144 (6)	−0.3228 (25)	−0.3421 (18)	3.2 (11)
C21A	−0.260 (6)	−0.1536 (23)	−0.1137 (16)	2.8 (11)	C21B	0.020 (6)	−0.1386 (25)	−0.2393 (18)	3.5 (12)
C22A	−0.409 (6)	−0.1518 (25)	−0.0133 (19)	3.8 (12)	C22B	0.142 (6)	−0.1406 (22)	−0.3431 (16)	2.6 (10)
C23A	−0.502 (7)	−0.1506 (27)	−0.0978 (20)	4.4 (13)	C23B	0.288 (9)	−0.1388 (33)	−0.2505 (25)	6.2 (17)
C31A	0.043 (5)	−0.1199 (19)	−0.0532 (14)	1.3 (9)	C31B	−0.297 (5)	−0.1656 (21)	−0.2955 (16)	2.1 (10)
C32A	−0.090 (6)	−0.1142 (24)	0.0495 (18)	3.3 (12)	C32B	−0.164 (7)	−0.1783 (28)	−0.4051 (20)	4.6 (14)
C33A	0.107 (9)	−0.1760 (38)	0.0247 (26)	7.9 (21)	C33B	−0.368 (8)	−0.1155 (34)	−0.3779 (24)	5.9 (16)
C34A	0.120 (8)	−0.0700 (31)	0.0215 (21)	5.3 (15)	C34B	−0.376 (8)	−0.2303 (33)	−0.3688 (23)	5.8 (16)
C41A	−0.586 (7)	0.0949 (26)	−0.1282 (19)	3.7 (12)	C41B	0.350 (8)	−0.3839 (31)	−0.2232 (22)	5.4 (15)
C42A	−0.440 (7)	−0.0038 (26)	−0.1454 (19)	3.7 (12)	C42B	0.195 (6)	−0.2898 (26)	−0.2065 (19)	3.8 (12)
C43A	−0.273 (7)	0.0958 (29)	−0.1073 (20)	4.5 (14)	C43B	0.043 (7)	−0.3922 (28)	−0.2473 (19)	4.3 (13)
C44A	−0.422 (7)	0.0965 (27)	−0.0361 (20)	4.5 (14)	C44B	0.182 (9)	−0.3846 (35)	−0.3171 (26)	6.7 (19)
C45A	−0.579 (7)	−0.0072 (28)	−0.0733 (20)	4.3 (13)	C45B	0.349 (9)	−0.2913 (34)	−0.2756 (24)	6.7 (18)
C51A	−0.341 (6)	−0.3573 (24)	−0.0669 (17)	3.0 (11)	C51B	0.087 (9)	0.0649 (33)	−0.2936 (23)	5.9 (15)
C52A	−0.134 (6)	−0.2747 (21)	−0.0731 (16)	2.1 (10)	C52B	−0.109 (7)	−0.0166 (27)	−0.2800 (19)	3.9 (12)
C53A	−0.412 (7)	−0.2731 (29)	−0.1322 (22)	5.1 (15)	C53B	0.161 (8)	−0.0155 (29)	−0.2248 (23)	5.6 (15)
C54A	−0.526 (7)	−0.2745 (25)	−0.0518 (18)	3.5 (12)	C54B	0.299 (8)	−0.0215 (30)	−0.2991 (22)	5.4 (16)
C55A	−0.238 (8)	−0.2798 (30)	0.0059 (23)	5.6 (16)	C55B	0.011 (11)	−0.0210 (43)	−0.3601 (34)	9.9 (26)
O11A	−0.076 (6)	−0.0200 (23)	−0.1219 (18)	7.6 (13)	O11B	−0.164 (5)	−0.2734 (18)	−0.2306 (13)	4.8 (9)
O12A	−0.372 (5)	−0.0228 (18)	0.0385 (13)	5.0 (9)	O12B	0.132 (5)	−0.2702 (19)	−0.3866 (13)	5.2 (10)
O13A	−0.026 (5)	0.0789 (21)	0.0039 (14)	6.1 (11)	O13B	−0.207 (5)	−0.3691 (21)	−0.3595 (14)	6.1 (11)
O21A	−0.210 (5)	−0.1617 (18)	−0.1475 (14)	5.3 (10)	O21B	−0.017 (6)	−0.1271 (23)	−0.2029 (17)	7.8 (13)
O22A	−0.451 (5)	−0.1566 (20)	0.0214 (15)	6.4 (11)	O22B	0.226 (6)	−0.1348 (25)	−0.3703 (18)	8.5 (14)
O23A	−0.622 (5)	−0.1528 (20)	−0.1208 (15)	5.7 (10)	O23B	0.399 (6)	−0.1403 (22)	−0.2226 (17)	6.9 (12)
O31A	0.103 (5)	−0.1244 (19)	−0.0874 (14)	5.6 (10)	O31B	−0.336 (5)	−0.1578 (20)	−0.2616 (15)	6.0 (11)
O32A	−0.124 (4)	−0.1153 (18)	0.0865 (13)	4.8 (9)	O32B	−0.100 (5)	−0.1793 (18)	−0.4327 (14)	5.1 (9)
O33A	0.197 (6)	−0.2239 (25)	0.0362 (18)	8.2 (14)	O33B	−0.437 (7)	−0.0696 (28)	−0.3931 (19)	9.4 (15)
O34A	0.222 (6)	−0.0260 (25)	0.0386 (17)	8.0 (13)	O34B	−0.448 (5)	−0.2711 (19)	−0.3812 (13)	5.0 (9)
O41A	−0.685 (6)	0.1237 (22)	−0.1536 (16)	6.8 (11)	O41B	0.452 (5)	−0.4149 (18)	−0.2003 (13)	5.1 (9)
O42A	−0.431 (5)	−0.0338 (18)	−0.1764 (14)	4.9 (9)	O42B	0.188 (5)	−0.2589 (20)	−0.1770 (15)	5.8 (10)
O43A	−0.191 (6)	0.1264 (23)	−0.1153 (16)	7.1 (12)	O43B	−0.054 (4)	−0.4141 (17)	−0.2357 (12)	4.1 (8)
O44A	−0.412 (5)	0.1242 (21)	−0.0040 (16)	6.6 (11)	O44B	0.157 (5)	−0.4120 (19)	−0.3506 (14)	5.2 (10)
O45A	−0.652 (6)	−0.0338 (21)	−0.0596 (15)	6.4 (11)	O45B	0.434 (6)	−0.2566 (24)	−0.2882 (17)	7.8 (13)
O51A	−0.331 (5)	−0.4107 (21)	−0.0647 (15)	6.5 (11)	O51B	0.085 (6)	0.1170 (23)	−0.2954 (17)	7.4 (12)
O52A	−0.004 (6)	−0.2696 (22)	−0.0788 (16)	7.2 (12)	O52B	−0.225 (5)	−0.0198 (18)	−0.2780 (13)	4.9 (9)
O53A	−0.434 (6)	−0.2695 (22)	−0.1707 (17)	7.2 (12)	O53B	0.227 (5)	−0.0168 (20)	−0.1854 (15)	6.2 (11)
O54A	−0.643 (5)	−0.2700 (17)	−0.0466 (12)	4.5 (9)	O54B	0.408 (8)	−0.0227 (28)	−0.3093 (20)	9.5 (16)
O55A	−0.177 (6)	−0.2836 (42)	0.0448 (18)	8.0 (13)	O55B	−0.028 (6)	−0.0234 (21)	−0.3976 (17)	6.4 (12)

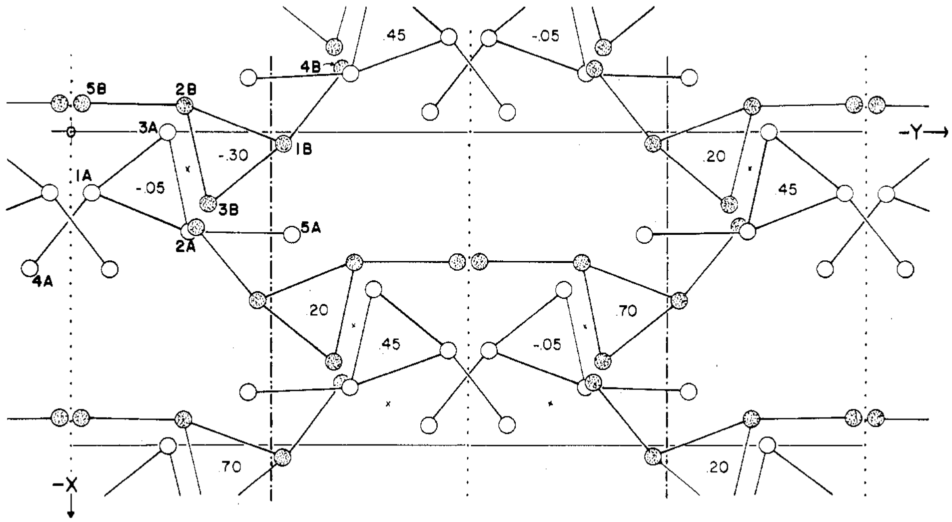


Figure 1. Relative locations of Os_3Re_2 cores of the $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ molecules within the unit cell, as viewed down "c". Molecule A and those molecules related to it are shown with metal atoms as hollow circles; molecules of type B are shown with their metal atoms as bespeckled circles. The numbers given within the triosmium rings indicate the z coordinates of the centroids of those rings. Some of the local (noncrystallographic) centers of symmetry are designated by saltires (×).

Table III. Anisotropic Thermal Parameters[a] for the Metal Atoms in the $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ Molecule

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os1A	3.48 (12)	2.68 (12)	2.29 (10)	0.03 (10)	0.33 (8)	−0.08 (8)
Os2A	3.21 (12)	2.57 (12)	2.66 (10)	0.00 (10)	0.81 (8)	−0.02 (9)
Os3A	3.49 (12)	2.82 (12)	2.94 (11)	0.37 (11)	0.09 (9)	0.09 (9)
Re4A	4.01 (13)	2.48 (12)	3.00 (10)	0.24 (11)	0.07 (9)	−0.05 (9)
Re5A	3.39 (12)	2.74 (12)	3.98 (11)	−0.38 (11)	0.87 (9)	−0.49 (9)
Os1B	3.74 (13)	2.50 (12)	2.71 (10)	−0.45 (10)	0.37 (9)	−0.04 (9)
Os2B	3.09 (11)	2.51 (11)	2.61 (10)	−0.35 (10)	0.63 (8)	−0.32 (9)
Os3B	3.45 (12)	3.27 (12)	2.73 (10)	−0.55 (11)	−0.04 (9)	0.07 (9)
Re4B	3.89 (13)	2.41 (12)	3.23 (10)	0.03 (11)	0.48 (9)	−0.05 (9)
Re5B	3.35 (12)	2.56 (12)	4.10 (12)	−0.22 (11)	0.86 (9)	−0.32 (10)

[a] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Interatomic Distances (Å) and Esd's for $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$[a,b]

	molecule A	molecule B
(A) Metal-Metal Distances		
Os1-Os2	3.059 (3)	3.064 (3)
Os1-Os3	2.876 (3)	2.880 (3)
Os1-Re4	2.952 (3)	2.942 (3)
Os2-Os3	3.084 (2)	3.071 (4)
Os2-Re5	2.983 (3)	2.969 (3)
av Os-(H)-Os	3.070 [11][b]	
av Os-Os	2.878	
av Os-Re	2.962 [18]	
(B) Metal-Oxygen Distances		
Os1-O11	2.98 (5)	3.01 (4)
Os1-O12	3.11 (4)	2.96 (4)
Os1-O13	2.96 (5)	2.97 (5)
Os2-O21	2.98 (4)	3.01 (5)
Os2-O22	3.02 (5)	2.98 (6)
Os2-O23	2.95 (5)	3.10 (5)
Os3-O31	2.98 (4)	3.04 (4)
Os3-O32	3.07 (4)	3.00 (4)
Os3-O33	3.03 (6)	3.07 (6)
Os3-O34	3.00 (6)	3.04 (4)
Re4-O41	3.07 (5)	3.04 (4)
Re4-O42	3.16 (4)	3.10 (4)
Re4-O43	3.08 (5)	3.11 (4)
Re4-O44	3.09 (5)	3.11 (4)
Re4-O45	3.10 (5)	3.18 (6)
Re5-O51	3.05 (5)	3.01 (5)
Re5-O52	3.13 (6)	3.06 (5)
Re5-O53	3.12 (5)	3.09 (4)
Re5-O54	3.10 (4)	3.11 (7)
Re5-O55	3.13 (5)	3.06 (5)
av Os-O	3.01 [5][b]	
av Re-O(trans)	3.04 [3]	
av Re-O(cis)	3.11 [3]	
(C) Metal-Carbon Distances		
Os1-C11	1.84 (6)	1.80 (6)
Os1-C12	1.90 (5)	1.67 (6)
Os1-C13	1.72 (7)	1.72 (6)
Os2-C21	1.77 (5)	1.78 (5)
Os2-C22	1.84 (6)	1.76 (5)
Os2-C23	1.80 (6)	1.97 (8)
Os3-C31	1.72 (4)	1.88 (5)
(C) *Continued*		
Os3-C32	1.87 (5)	1.89 (6)
Os3-C33	1.67 (9)	1.84 (8)
Os3-C34	1.62 (7)	1.89 (8)
Re4-C41	1.84 (6)	1.80 (7)
Re4-C42	1.99 (6)	1.96 (6)
Re4-C43	1.98 (7)	1.97 (6)
Re4-C44	1.96 (6)	1.97 (8)
Re4-C45	2.04 (7)	1.94 (8)
Re5-C51	1.83 (6)	1.82 (8)
Re5-C52	1.87 (5)	1.97 (7)
Re5-C53	2.03 (6)	1.93 (6)
Re5-C54	1.96 (6)	1.99 (8)
Re5-C55	1.98 (7)	1.98 (9)
av Os-C	1.80 [9][b]	
av Re-C(trans)	1.82 [2]	
av Re-C(cis)	1.97 [4]	
(D) Carbon-Oxygen Distances		
C11-O11	1.14 (8)	1.20 (7)
C12-O12	1.21 (6)	1.32 (7)
C13-O13	1.24 (9)	1.26 (7)
C21-O21	1.22 (7)	1.24 (7)
C22-O22	1.19 (7)	1.26 (7)
C23-O23	1.14 (8)	1.15 (9)
C31-O31	1.28 (6)	1.16 (6)
C32-O32	1.22 (6)	1.12 (8)
C33-O33	1.37 (10)	1.26 (10)
C34-O34	1.39 (9)	1.16 (9)
C41-O41	1.22 (8)	1.24 (8)
C42-O42	1.17 (7)	1.14 (7)
C43-O43	1.10 (9)	1.16 (8)
C44-O44	1.13 (8)	1.15 (9)
C45-O45	1.06 (8)	1.24 (10)
C51-O51	1.23 (7)	1.20 (9)
C52-O52	1.26 (8)	1.10 (8)
C53-O53	1.10 (8)	1.17 (8)
C54-O54	1.14 (8)	1.13 (11)
C55-O55	1.16 (8)	1.08 (11)
av C-O (on Os)	1.23 [7]	
av C-O (on Re)	1.16 [6]	
av C-O	1.19 [7]	

[a] Esd's are given in parentheses right-justified to the least significant digits of the distance as calculated from the esd's of the positional parameters not including the effects of correlation. [b] Esd's of the average values, given in square brackets, are calculated by the expression esd $= [(\Sigma(\bar{d} - d_i)^2)/(n-1)]^{1/2}$, where n is the number of terms averaged.

tests would be meaningful, with $Z(\mathrm{Re}) = 75$ and $Z(\mathrm{Os}) = 76$. There is, however, no reasonable doubt as to the correct identity of each metal atom.)

The four independent osmium–rhenium bond distances are Os1A–Re4A = 2.952 (3) Å, Os2A–Re5A = 2.983 (3) Å, Os1B–Re4B = 2.942 (3) Å, and Os2B–Re5B = 2.969 (3) Å. The mean value of the four independent osmium–rhenium distances is 2.962 [18] Å.[11] This value is in keeping with the predicted osmium–rhenium single-bond length of ~2.95 Å, derived from the mean Os–Os bond length of 2.877 [3] Å in $Os_3(CO)_{12}$[1] and the Re–Re bond length of ~3.02 Å in $Re_2(CO)_{10}$.[13]

The Os1A–Os3A and Os1B–Os3B bond lengths [2.876 (3) and 2.880 (3) Å, respectively] are indistinguishable from the mean Os–Os bond length of 2.877 [3] Å in $Os_3(CO)_{12}$ and are therefore clearly identified as normal nonbridged Os–Os single bonds. In contrast to this, the remaining four osmium–osmium vectors are each greater than 3.05 Å in length, individual distances being Os1A–Os2A = 3.059 (3) Å, Os2A–Os3A = 3.084 (2) Å, Os1B–Os2B = 3.064 (3) Å, and

Table V. Selected Interatomic Angles (deg) and Their Esd's for $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$

	molecule A	molecule B
(A) Angles in the Os_3Re_2 Plane		
Os2-Os1-Os3	62.53 (7)	62.14 (8)
Os2-Os1-Re4	103.93 (10)	104.06 (10)
Os3-Os1-C13	101.7 (24)	99.2 (19)
Re4-Os1-C13	92.1 (24)	95.1 (19)
Os1-Os2-Os3	55.82 (6)	55.99 (8)
Os1-Os2-C23	113.4 (20)	114.7 (22)
Os3-Os2-Re5	103.97 (9)	102.98 (10)
Re5-Os2-C23	86.8 (20)	86.4 (22)
Os1-Os3-Os2	61.65 (7)	61.88 (8)
Os1-Os3-C34	85.0 (24)	83.6 (22)
Os2-Os3-C33	117.4 (29)	124.0 (23)
C33-Os3-C34	96.0 (38)	90.8 (32)
Os1-Re4-C41	178.0 (18)	177.1 (22)
Os2-Re5-C51	176.0 (17)	177.8 (24)
(B) Out-of-Plane Angles		
C11-Os1-Os2	91.4 (18)	93.1 (18)
C11-Os1-Os3	89.7 (18)	88.9 (18)
C11-Os1-Re4	86.3 (18)	86.0 (18)
C11-Os1-C13	92.8 (30)	93.1 (26)
C12-Os1-Os2	86.8 (15)	90.4 (20)
C12-Os1-Os3	96.8 (15)	93.9 (20)
C12-Os1-Re4	86.1 (15)	91.9 (20)
C12-Os1-C13	91.3 (29)	84.1 (27)
C12-Os1-C11	171.5 (24)	176.3 (27)
C21-Os2-Os1	95.2 (17)	93.7 (18)
C21-Os2-Os3	95.4 (17)	91.9 (18)
C21-Os2-Re5	86.3 (17)	88.0 (18)
C21-Os2-C23	84.4 (26)	87.0 (29)
C22-Os2-Os1	94.6 (18)	90.3 (16)
C22-Os2-Os3	96.9 (18)	87.7 (16)
C22-Os2-Re5	87.4 (18)	87.1 (16)
C22-Os2-C23	84.1 (27)	94.2 (28)
C22-Os2-C21	167.1 (24)	174.8 (24)
C31-Os3-Os1	84.8 (15)	91.9 (15)
C31-Os3-Os2	82.5 (15)	87.3 (15)
C31-Os3-C33	98.9 (32)	90.2 (27)
C31-Os3-C34	93.6 (28)	86.6 (26)
C32-Os3-Os1	83.7 (17)	86.5 (19)
C32-Os3-Os2	86.2 (17)	92.3 (19)
C32-Os3-C33	92.4 (33)	91.2 (30)
C32-Os3-C34	92.0 (29)	92.8 (29)
C32-Os3-C31	166.7 (22)	178.4 (24)
Os1-Re4-C42	86.3 (17)	85.5 (17)
Os1-Re4-C43	85.9 (19)	87.9 (18)
Os1-Re4-C44	88.6 (18)	85.1 (23)
Os1-Re4-C45	85.6 (18)	88.9 (23)
Os2-Re5-C52	86.2 (15)	86.7 (18)
Os2-Re5-C53	87.7 (19)	88.5 (21)
Os2-Re5-C54	88.9 (17)	86.5 (20)
Os2-Re5-C55	90.0 (20)	85.6 (29)
av Os-Re-C(cis)	87.1 [15]	

Table VI. Important Least-Squares Planes for $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$

atom	dev, Å	atom	dev, Å
Plane A: $0.6051X - 0.0227Y - 0.7958Z - 0.0187 = 0^b$			
Os1A[a]	−0.066 (2)	C33A	−0.00 (8)
Os2A[a]	−0.039 (2)	C34A	0.10 (6)
Os3A[a]	0.044 (2)	O13A	−0.32 (4)
Re4A[a]	0.045 (3)	O23A	−0.11 (5)
Re5A[a]	0.017 (3)	O33A	0.21 (5)
C13A	−0.19 (7)	O34A	0.18 (5)
C23A	−0.07 (6)		
Plane B: $0.5977X - 0.0336Y - 0.8010Z - 8.5362 = 0^b$			
Os1B[a]	0.097 (2)	C33B	−0.10 (7)
Os2B[a]	0.028 (2)	C34B	−0.31 (7)
Os3B[a]	−0.060 (2)	O13B	0.48 (4)
Re4B[a]	−0.057 (2)	O23B	−0.11 (5)
Re5B[a]	−0.008 (3)	O33B	−0.10 (6)
C13B	0.31 (5)	O34B	−0.33 (4)
C23B	0.04 (7)		

dihedral angle: plane A-plane B = 0.81°

[a] Planes are calculated using these atoms. [b] The equations to the planes are in orthonormal coordinates.

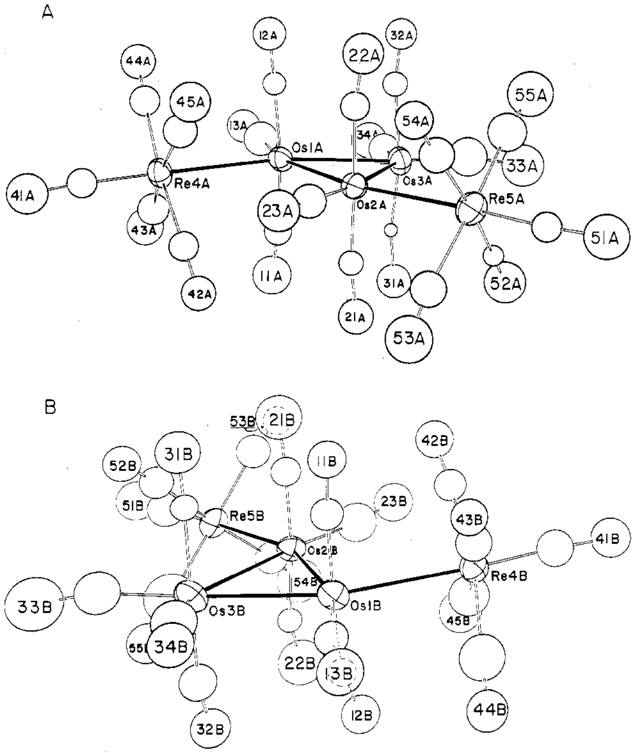


Figure 2. Labeling of atoms in the $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ molecules: (A) molecule A; (b) molecule B. (ORTEP-II diagrams, 50% probability contours shown for the vibration ellipsoids.)

Os2B–Os3B = 3.071 (4) Å. These expanded osmium–osmium distances are consistent with their each being bridged by single μ-bridging hydride ligands, lying in the triosmium plane.[14,15] [Simple μ-hydrido-bridged osmium–osmium bond lengths in other molecules are 2.989 (1) Å (for $(\mu\text{-H})(H)Os_3(CO)_{11}$[1]), 3.019 (1) Å (for $(\mu\text{-H})(H)Os_3(CO)_{10}(PPh_3)$[3]), and 3.007 (1) Å (for $(\mu\text{-H})Os_3(CO)_8[C(O-)C(CHMe-)CHCHCEt]$[6]).]

A consideration of angles between equatorial substituents around the triosmium clusters confirms that the Os1–Os2 and Os2–Os3 bonds are those bridged by hydride ligands. Thus, as shown in Figure 4, equatorial angles adjacent to the Os1A–Os2A bond are Os2A–Os1A–Re4A = 103.93 (10)° and Os1A–Os2A–C23A = 113.4 (20)°, while those adjacent to Os2A–Os3A are Re5A–Os2A–Os3A = 103.97 (9)° and Os2A–Os3A–C33A = 117.4 (3)°. In "molecule B", equatorial angles adjacent to the Os1B–Os2B bond are Os2B–Os1B–Re4B = 104.06 (10)° and Os1B–Os2B–C23B = 114.7 (22)°, while those adjacent to the Os2B–Os3B bond are Os3B–Os2B–Re5B = 102.98 (10)° and Os2B–Os3B–C33B = 124.0 (23)°.

Each of these angles is larger than the normal cis-equatorial Os–Os–L angle expected in the absence of an equatorial μ-bridging hydride ligand (cf. Os–Os–CO(equ, cis) = 98.2° (average) in $Os_3(CO)_{12}$[1]). It is apparent, however, that the great mass and steric bulk of the two $Re(CO)_5$ substituents also have significant effects on interligand angles in the equatorial plane around the triosmium cluster. Thus, Os–Os–Re angles increase to only ~102–103° adjacent to the μ-hydride ligands, while Os–Os–CO angles increase by a substantially greater amount (to ~113–124°).

Individual osmium–carbon distances range from 1.62 (7) to 1.90 (5) Å in molecule A and from 1.67 (6) to 1.97 (8) Å in molecule B; the average of the 20 independent measure-

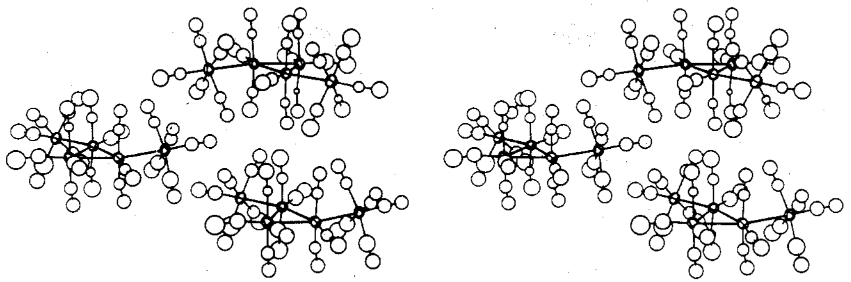


Figure 3. Stereoscopic view of a portion of the crystal structure. The two lower molecules are of type B (molecule B and its symmetry-related image generated via a *C*-centering operation of the space group); the upper molecule is molecule A and is related to the lower molecules by two of the pseudo-inversion centers present in the structure (cf. Figure 1).

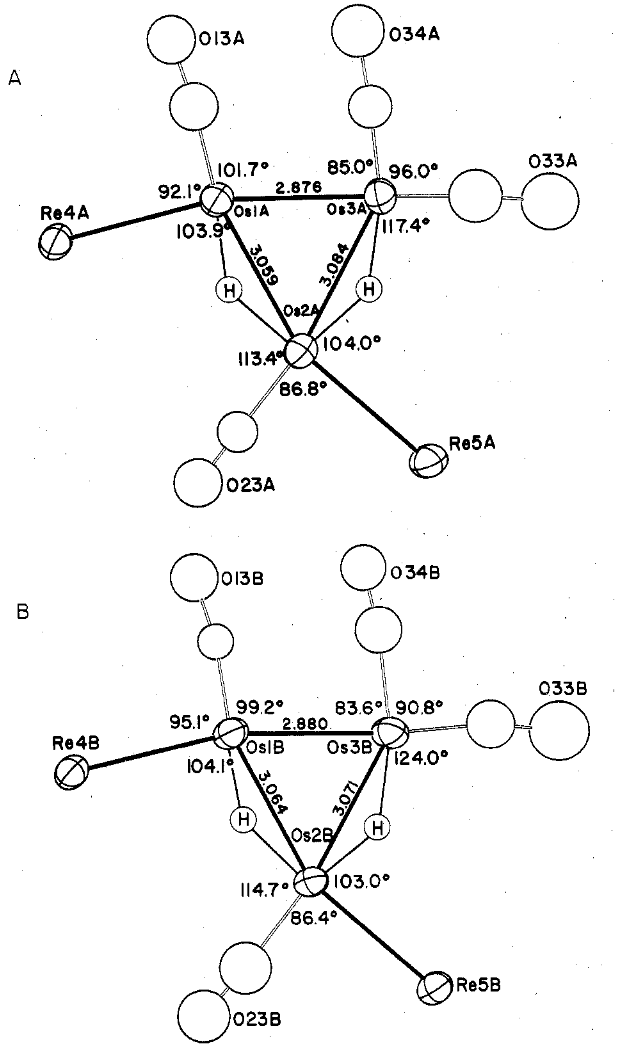


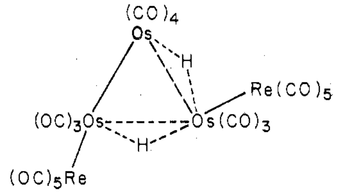
Figure 4. Equatorial distances and angles in the $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ molecules: (A) molecule A; (B) molecule B. (The hydride ligands were not located directly from the X-ray structural analysis and are shown in their presumed positions.)

ments is 1.80 [9] Å. Rhenium–carbon distances vary from 1.83 (6) to 2.04 (7) Å on molecule A and from 1.80 (7) to 1.99 (8) Å on molecule B, the average values being Re–CO(trans) = 1.82 [2] Å and Re–CO(cis) = 1.97 [4] Å. Metal···oxygen distances are, understandably, subject to smaller esd's. Osmium···oxygen distances vary from 2.95 (5) to 3.11 (4) Å in molecule A and from 2.96 (4) to 3.10 (5) Å in molecule B (overall average = 3.01 [5] Å); rhenium···oxygen distances average 3.04 [3] Å for Re···O(trans) and 3.11 [3] Å for Re···O(cis). We note, at this point, that esd's on metal–carbon, metal···oxygen, and carbon–oxygen distances are rather large. However, we believe this to be almost inevitable in the present structural study where we have the following technical problems: (a) ten independent third-row transition-metal atoms in the crystallographic asymmetric unit, (b) a noncentrosymmetric space group, (c) strong pseudosymmetry in the asymmetric unit, and (d) an alarmingly high absorption coefficient coupled with virtually no freedom of choice in selecting a crystal for the diffraction study.

Ligands within the central $Os_3(CO)_{10}L_2$ framework of the molecule take up positions which are in the customary eclipsed configuration relative to each of the osmium–osmium vectors. In contrast to this, the equatorial carbonyl ligands on each rhenium atom are in a staggered configuration relative to the appropriate ligands on the attached osmium atom. [Rotations of $Re(CO)_5$ groups about their Re–Os vectors are 49 [2], 52 [2], 46 [5], and 44 [2]° from the eclipsed configuration for Re4A, Re4B, Re5A, and Re5B, respectively.] This effect is expected (on the basis of simple steric arguments) because interaction between equatorial carbonyl ligands on adjacent osmium and rhenium atoms is minimized in the staggered rotational conformation. It should be noted that the average Os–Re–C(cis) angle is reduced to 87.1°—an effect general for $XM(CO)_5$ species (X = a non-π-bonding ligand; M = Mn, Tc, Re).

General Considerations

The complex $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ can be depicted as structure I. As such, it joins the species $[H_4Re_4(CO)_{15}{}^{2-}]$ (II)[16] as a member of the general class of metal cluster complexes which have a condensed metal cluster skeleton with one or more further metal atoms in position normally occupied by terminal ligands.



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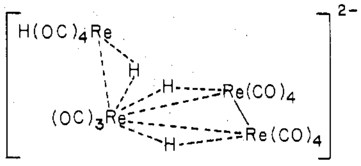
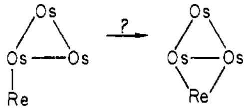


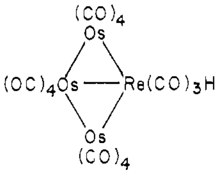
II

One could refer to this class of compound loosely as "metallo-ligated metal clusters" or as "spiked metal clusters".

A problem of general interest, which we are becoming involved with, is—how do such species rearrange upon ligand loss? The pentanuclear species $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ has 80 outer valence electrons associated with the metal atoms and obeys the extended "inert-gas rule" (i.e., the number of outer valence electrons = $18n - 2b$, where n is the number of metal atoms in the cluster and b is the number of metal–metal linkages). It is known[7] to lose a carbonyl ligand to form the species $H_2Os_3Re_2(CO)_{19}$; clearly a sixth metal–metal linkage has been formed; no unambiguous assignment as to its position can be made, although it is probable that further "triangulation" of the metal-atom framework has occurred. Similar problems exist with the closely related tetranuclear species $HOs_3Re(CO)_{16}$ (probably having the skeletal framework III—i.e., an equatorially monospiked triangular cluster or "tetrametallamethylcyclopropane" skeleton) and its conversion, upon carbonyl loss, to an $HOs_3Re(CO)_{15}$ molecule (possibly having the rhomboidal skeleton, IV). It should be noted that the $HOs_3Re(CO)_{15}$ molecule isolated via this decarbonylation reaction is apparently[7] different from the $HOs_3Re(CO)_{15}$ molecule synthesized from $Os_3(CO)_{12}$, $Re(CO)_5^-$, and H^+ (cf. ref 17) and previously shown by us[4] to have structure V. The general problem of possible isomerism based upon metal position is another area which has yet to receive significant attention. Work on these species is continuing and will be reported in subsequent articles.



III IV



V

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Registry No. I, 64885-82-1.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 1: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 878 (1977).
(2) Part 2: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 1141 (1977).
(3) Part 3: M. R. Churchill and B. G. DeBoer, *Inorg Chem.*, **16**, 2397 (1977).
(4) Part 4: M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, **16**, 2493 (1977).
(5) Part 5: M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, **16**, 2697 (1977).
(6) Part 6: M. R. Churchill and R. A. Lashewycz, *Inorg. Chem.*, **17**, 1291 (1978).
(7) J. R. Shapley, G. A. Pearson, M. Tachikawa, G. E. Schmidt, M. R. Churchill, and F. J. Hollander, *J. Am. Chem. Soc.*, **99**, 8064 (1977).
(8) All calculations were performed using the Syntex XTL system, consisting of a Data General Nova 1200 computer (24K memory), a 1.2 million word Diablo disk unit, and a locally modified version of the XTL conversational program package for crystal structure solution.
(9) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 99–101; (b) pp 149–150.
(10) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).
(11) Esd's of average values are shown in square brackets. See footnote *b* of Table IV.
(12) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Crystallogr.*, **20**, 836 (1966).
(13) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).
(14) M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, **15**, 1843 (1976)—see discussion on pp 1848 and 1850–1852.
(15) M. R. Churchill, *Adv. Chem. Ser.* **No. 167**, 36–60 (1978).
(16) V. G. Albano, G. Ciani, M. Freni, and P. Romiti, *J. Organomet. Chem.*, **96**, 259 (1975).
(17) J. Knight and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1022 (1972).

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Four-Coordinate Metal Nitrosyls. 2.[1] Structures of $NiX(NO)(P(C_6H_5)_3)_2$ Complexes[2]

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The crystal and molecular structure of (isothiocyanato)nitrosylbis(triphenylphosphine)nickel, $Ni(NCS)(NO)(P(C_6H_5)_3)_2$, has been determined by single-crystal X-ray diffraction. The complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a = 12.288$ (3) Å, $b = 13.496$ (3) Å, $c = 9.947$ (2) Å, $\alpha = 91.25$ (2)°, $\beta = 86.80$ (2)°, and $\gamma = 95.58$ (2)°. Full-matrix least-squares refinement of the structure based on 4420 unique reflections having $F_o^2 \geq 3\sigma(F_o^2)$ converged with a conventional R factor of 0.065. The structure consists of discrete $Ni(NCS)(NO)(P(C_6H_5)_3)_2$ molecules with pseudotetrahedral coordination geometry about the Ni atom. The P–Ni–P angle is 111.98 (6)°, the N–Ni–N angle is 116.82 (22)°, and the dihedral angle between the P–Ni–P and N–Ni–N planes is 81.73°. The distinctly nonlinear nitrosyl group has an Ni–N–O angle of 161.5 (5)°. The two Ni–P distances of 2.271 (2) and 2.328 (2) Å are significantly different. Chloronitrosylbis(triphenylphosphine)nickel, $NiCl(NO)(P(C_6H_5)_3)_2$, crystallizes in a monoclinic space group (Cc or $C2/c$) with unit cell dimensions of $a = 17.399$ (3) Å, $b = 13.136$ (3) Å, $c = 16.945$ (3) Å, and $\beta = 104.74$ (1)° and four molecules per unit cell. The $NiCl(NO)(P(C_6H_5)_3)_2$ molecules are pseudotetrahedral with an approximate P–Ni–P angle of 121°. The space group could not be unambiguously assigned nor could a satisfactory description of the N, O, and Cl positions be obtained from the several disordered and ordered models which were refined.

Introduction

It has been shown[3-5] that the geometries of $\{MNO\}^7$ and $\{MNO\}^8$ triatomic fragments[6] can be controlled by the stereochemistry of the other ligands coordinated to the metal. The properties of $\{MNO\}^{10}$ complexes should also be sensitive to the stereochemistry about the metal atom, and two limiting possibilities have been proposed[3,7] for four-coordinate complexes containing the $\{MNO\}^{10}$ moiety: (1) pseudotetrahedral geometry with a linear MNO group; (2) square-planar geometry with a strongly bent MNO group. These proposed limiting situations imply that distorted coordination geometries may have intermediate MNO angles.

Several years ago we showed[1] that the $\{NiNO\}^{10}$ complex $Ni(N_3)(NO)(P(C_6H_5)_3)_2$ has distorted tetrahedral coordi-