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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 12.[1] Molecular Geometry of μ-Chloro-μ-hydrido-decacarbonyltriosmium, $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$, and Characterization of the $Os(\mu\text{-H})(\mu\text{-Cl})Os$ Bridge

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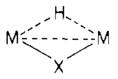
The complex $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$ has been studied via a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 7.8230\ (14)$ Å, $b = 8.8678\ (23)$ Å, $c = 13.6583\ (26)$ Å, $\alpha = 94.829\ (18)°$, $\beta = 103.028\ (15)°$, $\gamma = 110.677\ (18)°$, and $V = 849.6\ (3)$ Å^3. The calculated density is 3.467 g cm^{-3} for $Z = 2$ and mol wt 887.17. Diffraction data were collected on a Syntex $P2_1$ automated four-circle diffractometer by using Mo Kα radiation ($2\theta_{max} = 45.0°$). The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. Final discrepancy indices are $R_F = 3.1\%$ and $R_{wF} = 2.9\%$ for those 2143 data with $F_o > \sigma(F_o)$ and $R_F = 3.4\%$ and $R_{wF} = 2.9\%$ for all 2243 independent data. All nonhydrogen atoms were located, and the hydride ligand was included in its idealized position. The molecule contains a triangular arrangement of osmium atoms. Os(1) and Os(3) are each associated with three carbonyl ligands, while Os(2) is linked to four such ligands. In addition, Os(1) and Os(3) are mutually bridged both by a hydride ligand and by a chloride ligand. Osmium–osmium bond lengths are Os(1)–Os(2) = 2.829 (1) Å and Os(2)–Os(3) = 2.836 (1) Å, while the dibridged osmium–osmium distance is Os(1)–Os(3) = 2.846 (1) Å. A single unsupported bridging hydride ligand normally causes a significant expansion in a metal–metal bond (relative to its value in an analogous nonbridged system). However, in the present case this effect appears to be almost counterbalanced by the presence of the bridging chloride ligand. Osmium–chlorine distances are symmetrical, with Os(1)–Cl = 2.454 (3) Å and Os(3)–Cl = 2.458 (3) Å; the angle Os(3)–Cl–Os(3) is quite acute, with a value of 70.83 (9)°.

Introduction

It has been shown previously that the spanning of an osmium–osmium vector by a single bridging hydride ligand causes an elongation of the vector relative to a normal osmium–osmium single bond. Thus, the mean (normal, nonbridged) Os–Os distance in $Os_3(CO)_{12}$ is 2.877 (3) Å.[2] In contrast to this, the mono-μ_2-hydrido bridged vectors in other molecules containing a triangular Os_3 system are as follows: 2.989 (1) Å, $(\mu\text{-H})(H)Os_3(CO)_{11}$;[2] 3.019 (1) Å, $(\mu\text{-H})(H)Os_3(CO)_{10}(PPh_3)$;[3] 3.059 (3)–3.084 (3) Å, $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$.[4] In tetrahedral clusters the corresponding values are 2.941 (2) Å in $(\mu\text{-H})_3Os_3W(CO)_{11}(\eta^5\text{-}C_5H_5)$[5] and 2.932 (2) Å in $(\mu\text{-H})Os_3W(CO)_{12}(\eta^5\text{-}C_5H_5)$.[6]

When a μ_2-bridging hydride ligand is accompanied by another μ_2-bridging ligand about the same metal–metal vector (see I), the resulting metal–metal distance may be shorter than, longer than, or (fortuitously) equivalent to a nonbridged metal–metal bond.[7,8] In triosmium clusters the best characterized dibridged hydrido species are those with an $Os(\mu\text{-H})_2Os$ system [Os–Os = 2.681 (1) Å in $(\mu\text{-H})_2Os_3(CO)_{10}$],[9] those with an $Os(\mu\text{-H})(\mu\text{-C})Os$ system [Os–Os = 2.800 (1) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH}_2PMe_2Ph)$[10] and 2.785 (2) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH=NEt}_2)$[1]], and those with an $Os(\mu\text{-H})(\mu\text{-S})Os$ system [Os–Os = 2.863 (2) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SEt})$[11]]. We now report the results of an X-ray structural analysis of one of the simplest dibridged hydridotriosmium species, $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$, including the characterization of the $Os(\mu\text{-H})(\mu\text{-Cl})Os$ system in a triangular cluster.



I

Experimental Section

A. Data Collection. Yellow crystals of $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$ were provided by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The crystal selected for the structural analysis was of approximately square cross section (0.16 mm in thickness) and 0.20 mm in length. It was mounted with its longest dimension collinear with the thin glass fiber and set into a eucentric goniometer head.

Preliminary precession photographs revealed no symmetry (except for the Friedel condition); the crystal was assumed to be triclinic. The crystal was transferred to a Syntex $P2_1$ automated diffractometer and was accurately centered.

The unit cell parameters and the orientation matrix were determined and refined as described in detail previously.[12] The crystal quality was checked via a series of θ–2θ and ω scans of reflections along the principal reciprocal axes and was found to be satisfactory. Collection of intensity data was then carried out as described previously;[12] details are given in Table I.

Diffraction data were reduced to net intensities (I) and their estimated standard deviations ($\sigma_c(I)$). The ratio of time taken for the main scan relative to the total time for background measurement, τ, was 1.50.

All data were corrected for the effects of absorption [μ(Mo Kα) = 226.03 cm^{-1}] by an empirical method. Several close-to-axial reflections (χ_o = 273–292°) distributed over the 2θ range used in data collection and each of fairly high intensity ($I/\sigma(I) > 75$) were measured at 10° intervals of ψ (the diffraction vector) from 0 to 360°. Each reflection was used to define a normalized absorption curve vs. ϕ, corrected for ω and χ. The angle ϕ_c (ϕ corrected for both χ and ω) was calculated for the data reflection, and the two normalized absorption curves bracketing the 2θ value were interpolated both in 2θ and in ϕ_c to derive the absorption correction. The reflections used were all mutually consistent, with similar profiles and with maxima and minima at common values; they are listed in Table I.

The check reflections were examined (no significant decay was detected) and deleted. The data were averaged according to $\bar{1}$ symmetry, yielding a unique data set of 2243 independent reflections. Intensities were then corrected for Lorentz and polarization factors.

B. Solution and Refinement of the Structure. All calculations were performed with the Syntex XTL structure determination system consisting of an in-house Data General Nova 1200 computer with 24K of 16-bit words, a Diablo disk unit of 1.2 million 16-bit words, and a locally modified version of the XTL conversational crystallographic program package. The atomic scattering factors of Cromer and Waber[13a] were used for neutral osmium, chlorine, oxygen, carbon and hydrogen throughout the analysis. Both real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms by using the values of Cromer and Liberman.[13b]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weights used were obtained from counting statistics, modified by the "ignorance factor", p, set at a value of 0.010.

The positions of the osmium atoms were found from a sharpened Patterson synthesis. Full-matrix least-squares refinement of the scale factor along with the positional and isotropic thermal parameters for

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Table I. Data for the X-ray Diffraction Study of $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$

(A) Crystal Data

crystal system: triclinic
space group: $P\bar{1}$ [C_i^1; No. 2]
$V = 849.6$ (3) Å^3
$T = 23$ °C
$Z = 2$
mol wt 887.17
ρ(calcd) = 3.467 g cm^{-3}
$a = 7.8230$ (14) Å[a]
$b = 8.8678$ (23) Å[a]
$c = 13.6583$ (26) Å[a]
$\alpha = 94.829$ (18)°
$\beta = 103.028$ (15)°
$\gamma = 110.677$ (18)°

(B) Intensity Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite
rflctns measd: $-h$, $\pm k$, $\pm l$
max 2θ: 45.0°
min 2θ: 3.0°
scan type: θ(cryst)–2θ(counter)
scan speed: 2.0°/min
scan range: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]°$
rflctns collected: 2519 total, 2243 independent
std rflctns: 3 measd every 97 rflctns; there was no significant decay
abs coeff: $\mu = 226.03$ cm^{-1}
rflctns used for empirical abs cor (hkl, 2θ, T_{max}/T_{min}): $0\bar{2}0$, 9.97, 1.38; $0\bar{3}1$, 14.74, 1.35; $0\bar{4}2$, 22.04, 1.33; $0\bar{5}1$, 24.72, 1.32; $1\bar{6}1$, 28.21, 1.30; $1\bar{7}1$, 33.24, 1.24
data averaging: $R(I) = 1.58\%$ for 196 rflctns with two or more contributors

[a] Based upon a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 24 reflections of the forms $\{0,\bar{5},3\}$, $\{0,2,\bar{8}\}$, $\{1,\bar{4},\bar{5}\}$, $\{1,0,7\}$, $\{2,\bar{1},\bar{7}\}$, $\{3,\bar{3},6\}$, $\{3,1,\bar{8}\}$, $\{4,1,\bar{1}\}$, $\{4,\bar{4},4\}$, $\{4,\bar{2},\bar{4}\}$, $\{5,\bar{4},1\}$, $\{5,\bar{2},5\}$, all with 2θ = 22–30°. As has been pointed out elsewhere (see *b*), cell parameters should be looked upon as "instrumental cell parameters" since they may be affected by systematic errors (e.g., imperfections in the diffractometer per se, alignment errors of the diffractometer, and errors in centering the crystal precisely). Similarly, the esd's of these parameters are estimates of precision rather than of absolute accuracy (see *c*). [b] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197. [c] Simon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 2164, especially footnote 28.

the three independent osmium atoms led to $R_F = 13.4\%$ and $R_{wF} = 17.4\%$. A difference-Fourier synthesis at this point revealed the positions of all remaining nonhydrogen atoms. Full-matrix least-squares refinement of positional and isotropic thermal parameters for all nonhydrogen atoms and anisotropic thermal parameters for the osmium atoms gave $R_F = 3.9\%$, $R_{wF} = 3.9\%$, and GOF = 2.1786. Continued refinement, with anisotropic thermal parameters for all nonhydrogen atoms, led to $R_F = 3.5\%$, $R_{wF} = 3.5\%$, and GOF = 1.9818 by using only those 2143 reflections with $F_o > \sigma(F_o)$. $R_F = 3.8\%$ and $R_{wF} = 3.8\%$ for all data.

A difference Fourier synthesis based upon all data showed maxima of 0.98 e Å^{-3} close to the osmium positions. A difference Fourier synthesis based upon only those reflections with $(\sin\theta)/\lambda < 0.30$ Å^{-1} provided no useful information. The bridging hydride ligand could not be located unambiguously.

Careful comparison of observed and calculated structure factor amplitudes indicated that a correction for secondary extinction was necessary. The value for the secondary extinction parameter (k) used was 4.554×10^{-7}. $F_{o,cor}$, the corrected observed structure factor, and $\sigma(F_{o,cor})$ are given by eq 1 and 2, respectively.

$$F_{o,cor} = F_o(1.0 + kI_{obsd}) \qquad (1)$$

$$\sigma(F_{o,cor}) = \sigma(F_o)(1.0 + kI_{obsd}) \qquad (2)$$

Continued refinement led to convergence with $R_F = 3.2\%$, $R_{wF} = 3.0\%$, and GOF = 1.6941 for the 2143 reflections with $F_o > \sigma(F_o)$. $R_F = 3.5\%$ and $R_{wF} = 3.0\%$ for all data.

Another attempt was made to locate the hydride ligand, but a difference Fourier map based only on those data with $(\sin\theta)/\lambda < 0.30$ Å^{-1} showed only maxima up to 0.62 e Å^{-3} close to the osmium atoms.

The idealized position of the hydride ligand was calculated. First, we determined the point of intersection of the pair of vectors C(13)→Os(1) and C(32)→Os(3). Then, we moved the "hydrogen atom" along a vector from this calculated position toward the center of the Os(1)–Os(3) bond until the Os–"H" distances were 1.85 Å. The hydride ligand was included in our model in this fixed position. The resulting discrepancy indices were $R_F = 3.1\%$, $R_{wF} = 2.9\%$, and GOF = 1.6602 for the 2143 reflections with $F_o > \sigma(F_o)$ [for all data, $R_F = 3.4\%$ and $R_{wF} = 2.9\%$], showing a significant improvement upon incorporation of the hydride ligand into the model.

A final difference Fourier synthesis based on all data had peaks of height 0.98–0.74 e Å^{-3} in the vicinity of the osmium atoms; all other peaks were less than 0.68 e Å^{-3} in height.

The average value of $\sum w(|F_o| - |F_c|)^2$ showed no major variations as a function of $|F_o|$, $(\sin\theta)/\lambda$, identity or parity of Miller indices, or sequence number. The weighting scheme is therefore acceptable. The final NO:NV ratio was 2143:217 or approximately 9.9:1.

The final positional and thermal parameters are listed in Tables II and III.

Table II. Final Positional Parameters for $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$

atom	x	y	z
Os(1)	0.09399 (6)	0.27875 (5)	0.19077 (3)
Os(2)	0.37925 (6)	0.17830 (5)	0.29555 (3)
Os(3)	−0.00625 (6)	−0.04212 (5)	0.23835 (3)
Cl	−0.0710 (4)	0.1819 (4)	0.32001 (27)
O(11)	0.3111 (14)	0.3590 (13)	0.0322 (7)
O(12)	−0.2483 (14)	0.3426 (13)	0.0714 (8)
O(13)	0.3049 (16)	0.6185 (13)	0.3177 (9)
O(21)	0.3250 (14)	0.3184 (14)	0.4969 (7)
O(22)	0.5664 (13)	−0.0345 (11)	0.4030 (7)
O(23)	0.3881 (15)	0.0389 (12)	0.0826 (7)
O(24)	0.7263 (14)	0.4847 (11)	0.3076 (8)
O(31)	0.0914 (14)	−0.2886 (11)	0.1200 (7)
O(32)	0.0698 (15)	−0.1867 (13)	0.4305 (8)
O(33)	−0.4343 (14)	−0.2482 (14)	0.1631 (8)
C(11)	0.2283 (17)	0.3305 (15)	0.0918 (9)
C(12)	−0.1260 (18)	0.3149 (15)	0.1141 (10)
C(13)	0.2316 (19)	0.4962 (18)	0.2671 (10)
C(21)	0.3402 (16)	0.2662 (14)	0.4231 (10)
C(22)	0.4971 (16)	0.0432 (15)	0.3635 (9)
C(23)	0.3845 (16)	0.0896 (14)	0.1623 (10)
C(24)	0.5976 (15)	0.3708 (15)	0.3062 (10)
C(31)	0.0560 (18)	−0.1939 (17)	0.1645 (10)
C(32)	0.0439 (17)	−0.1338 (16)	0.3569 (10)
C(33)	−0.2808 (19)	−0.1729 (17)	0.1889 (10)
H_b[a]	−0.040	0.063	0.128

[a] The bridging hydrogen atom is in its calculated position (see text). It was assigned an isotropic thermal parameter of $B = 2.0$ Å^2.

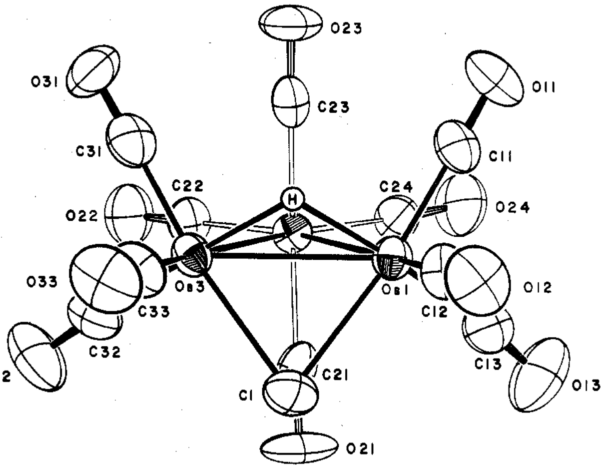

Figure 1. Labeling of atoms in the $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$ molecule, with the hydride ligand shown in its idealized (calculated) position (ORTEP-II diagram).

Results and Discussion

The crystal consists of discrete ordered units of $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$, which are mutually separated by normal van der Waals distances. Figure 1 shows the system used for numbering atoms while Figure 2 presents a stereoscopic view

Table III. Anisotropic Thermal Parameters[a] (Å^2) for $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	2.671 (22)	2.658 (21)	2.818 (22)	1.074 (17)	0.534 (16)	0.614 (16)
Os(2)	2.182 (20)	2.535 (21)	2.623 (21)	0.829 (16)	0.587 (15)	0.334 (16)
Os(3)	2.389 (21)	2.704 (22)	2.725 (22)	0.555 (17)	0.633 (16)	0.602 (17)
Cl	3.62 (14)	5.02 (17)	3.92 (15)	2.05 (13)	1.55 (12)	0.89 (13)
O(11)	6.2 (6)	7.0 (6)	4.2 (5)	2.4 (5)	2.5 (4)	2.8 (4)
O(12)	4.4 (5)	8.0 (7)	6.4 (6)	3.3 (5)	0.6 (4)	2.7 (5)
O(13)	7.3 (7)	3.9 (5)	7.4 (7)	1.7 (5)	−1.0 (5)	−1.0 (5)
O(21)	6.4 (6)	8.7 (7)	2.3 (4)	4.0 (5)	1.2 (4)	−1.2 (4)
O(22)	4.9 (5)	4.7 (5)	5.5 (5)	2.3 (4)	0.9 (4)	1.9 (4)
O(23)	7.7 (6)	5.5 (5)	3.9 (5)	1.9 (5)	3.3 (4)	−0.5 (4)
O(24)	5.0 (5)	3.2 (4)	7.4 (6)	−0.6 (4)	1.9 (5)	−0.0 (4)
O(31)	6.8 (6)	3.9 (5)	5.1 (5)	2.9 (4)	1.5 (4)	−0.0 (4)
O(32)	7.0 (6)	7.1 (6)	4.3 (5)	1.1 (5)	1.0 (5)	2.8 (5)
O(33)	2.8 (5)	7.7 (7)	6.5 (6)	0.0 (5)	0.5 (4)	0.6 (5)
C(11)	3.5 (6)	4.0 (6)	2.9 (6)	1.2 (5)	0.2 (5)	1.3 (5)
C(12)	3.1 (6)	3.6 (6)	4.2 (7)	1.0 (5)	0.4 (5)	1.0 (5)
C(13)	4.6 (7)	4.8 (8)	3.2 (6)	2.5 (6)	0.4 (5)	1.2 (6)
C(21)	2.6 (5)	2.7 (5)	4.9 (7)	1.4 (4)	0.0 (5)	0.6 (5)
C(22)	2.8 (6)	3.4 (6)	3.8 (6)	1.4 (5)	0.7 (5)	1.0 (5)
C(23)	2.6 (5)	2.8 (5)	4.3 (7)	0.9 (4)	0.9 (5)	1.4 (5)
C(24)	2.8 (6)	3.0 (6)	4.8 (7)	0.8 (5)	1.8 (5)	0.5 (5)
C(31)	4.2 (7)	4.5 (7)	3.0 (6)	1.4 (6)	0.2 (5)	1.1 (5)
C(32)	3.5 (6)	4.5 (7)	3.2 (6)	0.1 (5)	1.0 (5)	0.2 (5)
C(33)	2.6 (5)	5.2 (7)	4.2 (7)	0.7 (6)	0.7 (5)	1.2 (6)

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

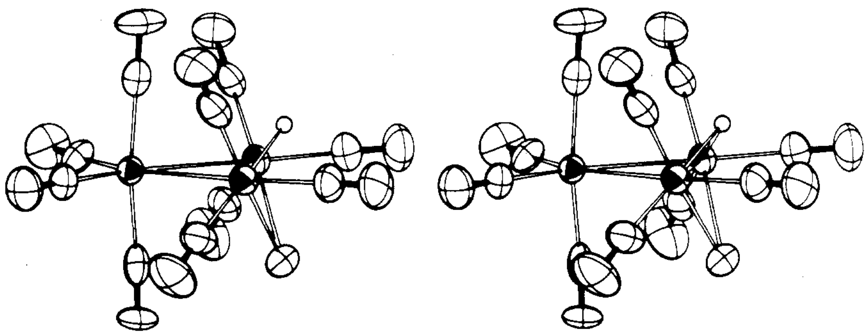

Figure 2. Stereoscopic view of the $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$ molecule.

of the molecule. Interatomic distances and their estimated standard deviations (esd's) are shown in Table IV; interatomic angles are listed in Table V, while important least-squares planes are collected in Table VI.

The molecule has approximate C_s (m) symmetry and is based upon a triangular arrangement of osmium atoms, one of which [Os(2)] is associated with four terminal carbonyl ligands and two of which [Os(1) and Os(3)] are linked to three terminal carbonyl ligands and are mutually bridged by a hydride and a chloride ligand.

The triosmium cluster defines a triangle in which the doubly bridged Os(1)–Os(3) vector is 2.846 (1) Å in length and the nonbridged osmium–osmium distances are Os(1)–Os(2) = 2.829 (1) Å and Os(2)–Os(3) = 2.836 (1) Å (average = 2.833 [5] Å[14]). The following points should be noted.

(1) The μ-hydrido-μ-chloro-bridged osmium–osmium vector is only slightly longer than the nonbridged Os–Os bonds. A survey of molecules based upon the $(\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10}$ system indicates that there is at least a qualitative relationship between the covalent radius[15] of the bridgehead atom X and the observed dibridged Os–Os distance (see Table VII). There is, however, no clear demarkation as to whether or not the dibridged vector will be longer or shorter than a nonbridged Os–Os bond.

(2) The nonbridged Os–Os bonds in $(\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10}$ species can vary significantly from the "normal" Os–Os bond length of 2.877 [3] Å found in $Os_3(CO)_{12}$. These variations, shown in Table VII, are puzzling, since no simple correlation with the nature of X is yet apparent to us. Further investigations are underway in an attempt to understand these variations.

Table IV. Interatomic Distances (Å) with Esd's for $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$

	(A) Osmium-Osmium		
Os(1)-Os(2)	2.829 (1)	Os(1)-Os(3)	2.846 (1)
Os(2)-Os(3)	2.836 (1)		
	(B) Osmium-Bridging Ligand		
Os(1)-Cl	2.454 (3)	Os(3)-Cl	2.458 (3)
	(C) Osmium-Carbon		
Os(1)-C(11)	1.882 (13)	Os(2)-C(23)	1.936 (13)
Os(1)-C(12)	1.948 (15)	Os(2)-C(24)	1.908 (13)
Os(1)-C(13)	1.911 (15)	Os(3)-C(31)	1.877 (14)
Os(2)-C(21)	1.979 (14)	Os(3)-C(32)	1.897 (13)
Os(2)-C(22)	1.930 (13)	Os(3)-C(33)	1.967 (15)
	(D) Carbon-Oxygen		
C(11)-O(11)	1.142 (17)	C(23)-O(23)	1.151 (16)
C(12)-O(12)	1.119 (18)	C(24)-O(24)	1.142 (17)
C(13)-O(13)	1.113 (18)	C(31)-O(31)	1.142 (18)
C(21)-O(21)	1.122 (17)	C(32)-O(32)	1.151 (17)
C(22)-O(22)	1.120 (16)	C(33)-O(33)	1.102 (19)

The bridging chloride ligand is bound to the triosmium cluster via the bonds Os(1)–Cl = 2.454 (3) Å and Os(3)–Cl = 2.458 (3) Å; the Os(1)–Cl–Os(3) angle is quite acute, with a value of 70.83 (9)°. [We have previously reported the detailed structures of the *dinuclear* μ-hydrido-μ-chloro species $[(\eta^5\text{-}C_5Me_5)RhCl]_2(\mu\text{-H})(\mu\text{-Cl})$[16] and $[(\eta^5\text{-}C_5Me_5)IrCl]_2(\mu\text{-}$

Table V. Interatomic Angles (deg) with Esd's, for $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$

(A) Osmium–Osmium–Osmium			
Os(2)–Os(1)–Os(3)	59.98 (2)	Os(1)–Os(3)–Os(2)	59.71 (2)
Os(1)–Os(2)–Os(3)	60.32 (2)		
(B) Angles Involving the Bridging Chloride			
Os(1)–Cl–Os(3)	70.83 (9)		
Cl–Os(1)–Os(3)	54.65 (8)	Cl–Os(1)–Os(2)	86.32 (8)
Cl–Os(3)–Os(1)	54.52 (8)	Cl–Os(3)–Os(2)	86.08 (8)
Cl–Os(1)–C(11)	173.0 (4)	Cl–Os(3)–C(31)	172.3 (4)
Cl–Os(1)–C(12)	90.2 (4)	Cl–Os(3)–C(32)	96.6 (4)
Cl–Os(1)–C(13)	94.1 (5)	Cl–Os(3)–C(33)	89.8 (4)
(C) Osmium–Osmium–Carbonyl			
Os(2)–Os(1)–C(11)	88.3 (4)	Os(1)–Os(3)–C(31)	117.8 (4)
Os(2)–Os(1)–C(12)	171.8 (4)	Os(1)–Os(3)–C(32)	136.1 (4)
Os(2)–Os(1)–C(13)	90.3 (4)	Os(1)–Os(3)–C(33)	112.7 (4)
Os(3)–Os(1)–C(11)	118.6 (4)	Os(2)–Os(3)–C(31)	90.0 (4)
Os(3)–Os(1)–C(12)	112.1 (4)	Os(2)–Os(3)–C(32)	89.2 (4)
Os(3)–Os(1)–C(13)	135.3 (4)	Os(2)–Os(3)–C(33)	172.4 (4)
Os(1)–Os(2)–C(21)	86.6 (4)	Os(3)–Os(2)–C(21)	88.7 (4)
Os(1)–Os(2)–C(22)	160.1 (4)	Os(3)–Os(2)–C(22)	99.8 (4)
Os(1)–Os(2)–C(23)	86.6 (4)	Os(3)–Os(2)–C(23)	85.4 (4)
Os(1)–Os(2)–C(24)	99.3 (4)	Os(3)–Os(2)–C(24)	159.5 (4)
(D) Carbonyl–Osmium–Carbonyl			
C(11)–Os(1)–C(12)	94.5 (6)	C(31)–Os(3)–C(32)	89.9 (6)
C(11)–Os(1)–C(13)	90.4 (6)	C(31)–Os(3)–C(33)	93.3 (6)
C(12)–Os(1)–C(13)	97.4 (6)	C(32)–Os(3)–C(33)	97.6 (6)
C(21)–Os(2)–C(22)	92.5 (5)	C(22)–Os(2)–C(23)	92.9 (5)
C(21)–Os(2)–C(23)	172.6 (5)	C(22)–Os(2)–C(24)	100.6 (6)
C(21)–Os(2)–C(24)	92.2 (6)	C(23)–Os(2)–C(24)	91.8 (6)
(E) Osmium–Carbon–Oxygen			
Os(1)–C(11)–O(11)	178.5 (12)	Os(3)–C(31)–O(31)	178.8 (12)
Os(1)–C(12)–O(12)	177.1 (12)	Os(3)–C(32)–O(32)	177.2 (12)
Os(1)–C(13)–O(13)	174.2 (14)	Os(3)–C(33)–O(33)	178.3 (13)
Os(2)–C(21)–O(21)	177.5 (12)	Os(2)–C(23)–O(23)	179.1 (11)
Os(2)–C(22)–O(22)	179.6 (12)	Os(2)–C(24)–O(24)	176.8 (12)

Table VI. Selected Planes and Deviations (Å) of Atoms Therefrom[a]

Plane I: $-0.4495X + 0.1842Y + 0.8741Z = 2.8505$[c]			
Os(1)*	0.000	C(22)	−0.031 (12)
Os(2)*	0.000	O(22)	−0.048 (10)
Os(3)*	0.000	C(24)	0.071 (13)
H_b[b]	0.94	O(24)	0.172 (11)
Cl	−1.897 (3)	C(33)	0.031 (14)
C(11)	1.545 (12)	O(33)	0.032 (11)
O(11)	2.491 (10)	C(13)	−1.100 (14)
C(23)	1.930 (13)	O(13)	−1.828 (12)
O(23)	3.077 (10)	C(21)	−1.980 (14)
C(31)	1.579 (13)	O(21)	−3.096 (09)
O(31)	2.533 (10)	C(32)	−1.023 (14)
C(12)	0.070 (13)	O(32)	−1.687 (11)
O(12)	0.087 (11)		
Plane II: $0.7029X + 0.1735Y + 0.6898Z = 1.5353$[c]			
Os(1)*	0.000	C(11)	−0.061 (13)
Os(3)*	0.000	O(11)	−0.110 (11)
Cl*	0.000	C(31)	0.019 (14)
H_b[b]	0.98	O(31)	0.039 (11)
Plane I–Plane II	108.61°		

[a] Atoms marked with asterisks were used in calculating the planes. [b] H_b is in its calculated position (see text). [c] Equations for the planes are in orthonormalized (Å) coordinates.

H)(μ-Cl);[17] the angles at the bridging chloride ligands here are Rh–Cl–Rh = 73.20 (6)° and Ir–Cl–Ir = 72.65 (8)°. This suggests that the M(μ-H)(μ-X)M system in trinuclear $(\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10}$ species will behave in essentially the same manner as in the binuclear $[(\eta^5\text{-}C_5Me_5)MX]_2(\mu\text{-H})(\mu\text{-X})$ species (M = Rh, Ir). We had previously[8] expressed concern over the additional restraints that might result from the presence of the $-Os(CO)_4-$ group which acts, essentially, as a third bridge across the Os(μ-H)(μ-X)Os system in $(\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10}$ species. Apparently this exerts no *important* restraints, at least until the osmium atoms in question are bridged by *two large atoms*, i.e., possibly in certain $(\mu\text{-X})_2Os_3(CO)_{10}$ species (X ≠ H)].

Table VII. Dibridged and Nonbridged Osmium–Osmium Distances in Selected Molecules with a $(\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10}$ Skeleton

molecule	X	r(X),[15] Å	dibridged Os–Os dist, Å	nonbridged Os–Os dist, Å
$(\mu\text{-H})_2Os_3(CO)_{10}$[9]	H	~0.30[a]	2.681 (1)	2.812 (1) 2.817 (1)
$(\mu\text{-H})Os_3(CO)_{10}$-$(\mu\text{-CHCH=NEt}_2)$[1]	C	0.77	2.785 (2)	2.866 (2) 2.870 (2)
$(\mu\text{-H})Os_3(CO)_{10}$-$(\mu\text{-CHCH}_2PMe_2Ph)$[10]	C	0.77	2.800 (1)	2.869 (1) 2.873 (1)
$(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$	Cl	0.99	2.846 (1)	2.829 (1) 2.836 (1)
$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SEt})$[11]	S	1.04	2.863 (2)	2.842 (2) 2.856 (2)

[a] See ref 15, Table 7-4, p 226.

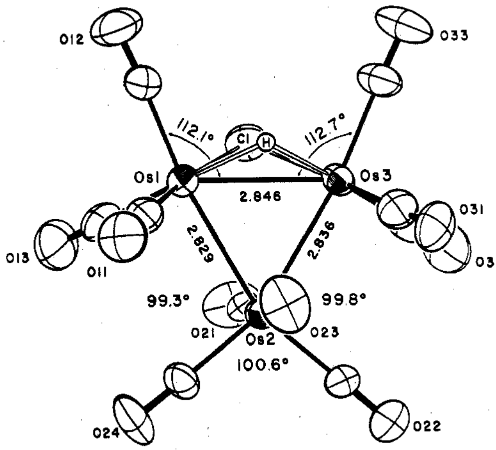

Figure 3. Distances (Å) and angles in the triosmium plane. The molecule is rotated from the triosmium plane by 5° about the vertical axis (midpoint of Os(1)–Os(3)→Os(2)).

Within the $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$ molecule, the chloride ligand makes the angles Cl–Os(1)–Os(2) = 86.32 (8)° and Cl–Os(3)–Os(2) = 86.08° with the triosmium cluster. It is approximately trans to the ligands C(11)–O(11) and C(31)–O(31) [∠Cl–Os(1)–C(11) = 173.0 (4)° and ∠Cl–Os(3)–C(31) = 172.3 (4)°]. The semiaxial carbonyl groups adjacent to the bridging chloride ligand are slightly displaced from their idealized positions. Thus, the angles Cl–Os(1)–C(13) = 94.1 (15)° and Cl–Os(3)–C(32) = 96.6 (4)° are some 4–6° larger than the truly equatorial carbonyl ligands adjacent to the chloride ligand, viz., Cl–Os(1)–C(12) = 90.2 (4)° and Cl–Os(3)–C(33) = 89.8 (4)°.

Figure 3 shows the $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$ molecule projected approximately onto its triosmium plane. The equatorial Os–Os–CO angles based on the doubly bridged Os(1)–Os(3) bond are Os(1)–Os(3)–C(33) = 112.7 (4)° and Os(3)–Os(1)–C(12) = 112.1 (4)°. In contrast to this, the angles Os(1)–Os(2)–C(24) and Os(3)–Os(2)–C(22) are 99.3 (4) and 99.8 (4)°, respectively.

The terminal carbonyl ligands on Os(1) and Os(3) are in three different local environments. The longest pair of osmium–carbonyl bond lengths involve the equatorial carbonyl ligands trans to Os(2); Os(1)–C(12) = 1.948 (15) Å and Os(3)–C(33) = 1.967 (15) Å. The semiaxial carbonyl ligands on Os(1) and Os(3) have significantly shorter osmium–carbonyl bond lengths. Individual osmium–carbonyl distances for the carbonyl ligands trans to the bridging chloride are Os(1)–C(11) = 1.882 (13) Å and Os(3)–C(31) = 1.877 (14)

Å; for the carbonyls trans to the bridging hydride, the bond lengths are Os(1)–C(13) = 1.911 (15) Å and Os(3)–C(32) = 1.897 (13) Å. The carbonyl ligands on Os(2) may be grouped as equatorial or axial. The equatorial distances are Os(2)–C(22) = 1.930 (13) Å and Os(2)–C(24) = 1.908 (13) Å (average 1.919 [16] Å), while the axial distances are Os(2)–C(21) = 1.979 (14) Å and Os(2)–C(23) = 1.936 (13) Å (average 1.958 [30] Å). This pattern, while on the borderline of statistical significance in the present complex, is expected as a result of competition for π-electron density between the axial pair of carbonyl groups. A structural study of $Os_3(CO)_{12}$[2] showed the following average bond distances: Os–CO(equatorial) = 1.912 [7] Å and Os–CO(axial) = 1.946 [6] Å.

Finally, we note that carbon–oxygen distances range from 1.102 (19) to 1.151 (16) Å (average 1.130 [17] Å) and that Os–C–O systems are close to linear (range 174.2 (14)–179.6 (12)°).

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Registry No. $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$, 12557-93-6.

Supplementary Material Available: A table of data-processing formulas and a listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Molecular Geometry of $Ta({=}CHCMe_3)_2(mesityl)(PMe_3)_2$, a Bis(alkylidene) Complex of Tantalum with Remarkably Obtuse $Ta{=}C(\alpha){-}C(\beta)$ Angles of 154.0 (6) and 168.9 (6)°

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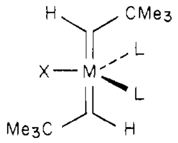
Mesitylbis(neopentylidene)bis(trimethylphosphine)tantalum(V), $Ta({=}CHCMe_3)_2(mesityl)(PMe_3)_2$, previously prepared by Schrock and co-workers, has been subjected to a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15) with a = 17.966 (3) Å, b = 18.217 (4) Å, c = 18.531 (3) Å, β = 97.99 (2)°, V = 6006 (2) Å^3, and Z = 8. Diffraction data were collected with a Syntex $P2_1$ four-circle automated diffractometer by using a coupled θ(crystal)–2θ(counter) scan. The structure was solved by means of Patterson, Fourier, and least-squares refinement techniques. All nonhydrogen atoms were located and refined, the final discrepancy indices being R_F = 5.3% and R_{wF} = 3.7% for all 3946 reflections with $4.5 < 2\theta < 45°$ (Mo Kα radiation). The central tantalum atom is a distorted trigonal-bipyramidal coordination environment, with the phosphine ligands in axial sites (Ta–P(1) = 2.565 (2) Å, Ta–P(2) = 2.569 (2) Å, $\angle$ P(1)–Ta–P(2) = 166.34 (7)°). The three equatorial sites are occupied by an η^1-mesityl ligand (Ta–C(11) = 2.303 (6) Å and two η^1-neopentylidene ligands (Ta–C(1) = 1.932 (7) Å, Ta–C(6) = 1.955 (7) Å). The $Ta{=}C(\alpha){-}C(\beta)$ angles in the two neopentylidene ligands are extraordinarily obtuse for angles at formally sp^2-hybridized carbon atoms and have values of 154.0 (6) and 168.9 (6)°, respectively.

Introduction

Alkylidene,[1] alkylidyne,[1] and benzyne[2] complexes of tantalum have been synthesized by Schrock and co-workers. We have previously reported the results of X-ray structural studies on a tantalum–alkylidene complex $[Ta(\eta^5\text{-}C_5H_5)_2({=}CHCMe_3)Cl]$,[3,4] a tantalum–benzylidyne complex $[Ta(\eta^5\text{-}C_5Me_5)({\equiv}CPh)(PMe_3)_2Cl]$,[5,6] and a tantalum–benzyne complex $[Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2]$.[7]

A series of bis(alkylidene) complexes of tantalum and niobium, of formula $M({=}CHCMe_3)_2(X)L_2$, have recently been reported by Schrock and co-workers.[8] These complexes, as well as certain mono(alkylidene) complexes, have some anomalous physical properties[9] which require explanation, viz., (1) the $^1J_{CH\alpha}$ values are unusually low (ca. 75–100 Hz), and (2) the C–Hα stretches are observed at very low frequencies (ca. 2400–2600 cm^{-1}). In addition to these curiosities, NMR studies did not lead to any umambiguous assignment of the geometry of these molecules; **1** was favored, however. As a result of these problems, we decided to examine one of these species. An attempt to solve the structure of $Nb({=}CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$ was unsuccessful, due to severe disorder problems.[10] Prolonged attempts to find a suitable crystal of $Ta({=}CHCMe_3)_2Cl(PMe_3)_2$ were also unsuccessful, due again (we believe) to disorder and also, possibly, decomposition of the material in the X-ray beam. Finally we investigated the crystal structure of the species $Ta({=}CHCMe_3)_2(mesityl)(PMe_3)_2$ and found it to be suffi-



1