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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 1. Crystal Structures of the Isomorphous Species $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$. Direct Information on the Role of an Equatorial μ_2-Bridging Hydride Ligand in Perturbing the Arrangement of Carbonyl Ligands in a Triangular Cluster

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Received July 2, 1976 AIC60462V

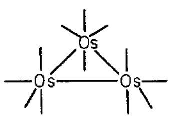
The complex $H_2Os_3(CO)_{11}$, undecacarbonyldihydridotriosmium, has been studied by a single-crystal x-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 8.0744 (16) Å, b = 14.7265 (29) Å, c = 14.7770 (28) Å, β = 101.36 (1)°, and Z = 4. This species is found to be isomorphous with and quasi-isostructural to $Os_3(CO)_{12}$. The structure of $Os_3(CO)_{12}$ [previously reported by Corey and Dahl in 1962] has been completely redetermined; accurate cell dimensions are a = 8.0817 (6) Å, b = 14.7683 (11) Å, c = 14.5773 (11) Å, β = 100.56 (1)°, Z = 4, and space group $P2_1/n$. Data for both complexes were collected with a Picker FACS-1 diffractometer (using Mo Kα radiation) and structural parameters were optimized via full-matrix least-squares refinement. Final discrepancy indices are R_F = 3.68% and R_{wF} = 3.52% for $H_2Os_3(CO)_{11}$ (2259 reflections) and R_F = 3.35% and R_{wF} = 3.62% for $Os_3(CO)_{12}$ (3040 reflections). The effects of the equatorial μ_2-bridging hydride ligand in $H_2Os_3(CO)_{11}$ (relative to the isomorphous species $Os_3(CO)_{12}$) include a lengthening of the bridged osmium–osmium bond and angular redistribution of the equatorial carbonyl ligands.

Introduction

We have been interested in the structural characterization of species with bridging hydride ligands for the last 10 years and have reported structural studies of $Zr(BH_4)_4$,[3] $HRe_2Mn(CO)_{14}$,[4] $[H_2Re_3(CO)_{12}^-]$,[5] $[H_6Re_4(CO)_{12}^{2-}]$,[6] $H_2Ru_6(CO)_{18}$,[7] $H_6Cu_6(PPh_3)_6$,[8] $[C_5Me_5RhCl]_2(\mu\text{-H})(\mu\text{-Cl})$,[9] $[H_2W_2(CO)_8^{2-}]$,[10] $HRu_3(CO)_{10}(C{=}NMe_2)$,[11] and $HOs_3(CO)_{10}(CHCH_2PMe_2Ph)$.[12] The overall structural effects of bridging hydride ligands have been summarized in a recent article.[11b]

We recently reported a preliminary account of the structure of $H_2Os_3(CO)_{11}$[13] and noted that it was isomorphous with $Os_3(CO)_{12}$, a species studied previously by Corey and Dahl.[14]

We have now completed our structural study of $H_2Os_3(CO)_{11}$ and have also carried out an accurate new structural study of $Os_3(CO)_{12}$. Since the two species are isomorphous and close to isostructural, the differences in geometry should be attributable almost entirely to the presence or absence of a μ_2-bridging hydride ligand. [The structures of $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{11}$ are known to be I and II, respectively; we assume that replacement of an axial terminal carbonyl ligand by a hydride ligand will be of little stereochemical consequence.]



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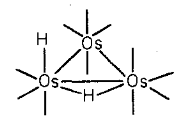


II

Experimental Section

Data Collection for $H_2Os_3(CO)_{11}$. Yellow crystals of $H_2Os_3(CO)_{11}$ were provided by Professor J. R. Shapley of the University of Illinois at Urbana—Champaign. The crystal selected for the diffraction experiment was rod-shaped with ends defined by $(10\bar{1})$ and $(\bar{1}01)$ separated by 0.213 mm and a pentagonal cross section with sides defined cyclically by $(00\bar{1})$, $(0\bar{1}0)$, $(0\bar{2}1)$, (001), and (010). Perpendicular distances of faces from the origin (defined by the point of intersection of $(00\bar{1})$, $(0\bar{1}0)$, and $(\bar{1}01)$) were 0.059 mm for (001), 0.087 mm for (010), 0.213 mm for $(10\bar{1})$, and 0.016 mm for $(0\bar{2}1)$.

The crystal was mounted on a glass fiber on a eucentric goniometer head. Preliminary photographs yielded approximate cell dimensions, indicated C_{2h} Laue symmetry, and revealed the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$ is thereby indicated. The crystal was transferred to a Picker FACS-1 automated diffractometer, was accurately centered, and was oriented with $[10\bar{1}]$ offset by about 4° from coincidence with the ϕ axis. Unit cell measurement and data collection were carried out as described previously;[15] details are given in Table I.

The unit cell parameters obtained for $H_2Os_3(CO)_{11}$ were sufficiently close to those reported by Corey and Dahl[14] for $Os_3(CO)_{12}$ [a = 8.10 (3) Å, b = 14.79 (4) Å, c = 14.64 (4) Å, β = 100° 27′ (20′); space group $P2_1/n$] to cause us considerable concern. However, Professor Shapley assured us that the sample of $H_2Os_3(CO)_{11}$ was pure and well-characterized and we found (later) that more precisely determined unit cell parameters for $Os_3(CO)_{12}$ were significantly different from those of $H_2Os_3(CO)_{11}$. The two compounds are, nevertheless, both isomorphous and (as shown below) quasi-isostructural.

Following data collection, the $H_2Os_3(CO)_{11}$ crystal was realigned with $[10\bar{1}]$ along the ϕ axis. Measurement of the axial $20\bar{2}$ and $50\bar{5}$ reflections via θ–2θ scans at 10° intervals from ϕ = 0 to ϕ = 350° showed variations in intensity of 47.8% and 42.0%, respectively [variation (%) = 100 × (maximum − minimum)/(average)]. These data were corrected for absorption along with the primary data set. Variations were reduced to 13.5% and 9.4%, respectively. [These rather large residual variations arise principally as a result of the difficulty of measuring a highly absorbing small crystal with sufficient precision.]

Data Collection for $Os_3(CO)_{12}$. The crystal selected for data collection was multifaceted with approximate dimensions 0.093 mm × 0.109 mm × 0.204 mm.[16] It was mounted along its extended direction. Measurement of unit cell parameters and data collection proceeded as for $H_2Os_3(CO)_{11}$. Details are given in Table I.

The absorption correction for this crystal was checked by measuring the $33\bar{1}$ reflection at χ = 90 and 10° intervals of ϕ. The observed variation in intensity of 37.8% was reduced to 6.4% following correction for absorption.

Solution of the Structure of $H_2Os_3(CO)_{11}$. Programs used for structure determination were LSHF (full-matrix least-squares refinement and structure factor calculations, by B. G. DeBoer), FORDAP (Fourier synthesis, by A. Zalkin), STAN1 (distances and angles, with esd's, by DeBoer), and ORTEP (thermal ellipsoid plotting program, by C. K. Johnson). All calculations were performed on an IBM 370/158 computer.

Analytical scattering factors for neutral osmium, carbon, and oxygen were taken from the compilation of Cromer and Mann;[17] $\Delta f'$ and $\Delta f''$ were included for all atoms, using the values of Cromer and Liberman.[18]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}$. Discrepancy indices used below are defined as

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

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

The similar cell dimensions and identical space group of $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$ led us to assume that the species were quasi-isostructural and that the osmium atoms would be located at approximately the same positions in each species. We therefore took the coordinates of the osmium atoms from Corey and Dahl's determination of $Os_3(CO)_{12}$,[14] along with a scale factor and isotropic thermal parameter from a Wilson plot of the $H_2Os_3(CO)_{11}$ data. Refinement of the scale factor and positional and anisotropic thermal parameters for the three osmium atoms converged with $R_F = 11.3\%$ and $R_{wF} = 14.9\%$. A difference-Fourier map revealed the presence of, apparently, 12 (not 11!) carbonyl ligands. The carbonyl ligand defined by atoms C(22) and O(22) was the weakest, peak heights being only 2.88 and 2.32 e $Å^{-3}$, respectively. We now included all 12 carbonyl groups in the model, using isotropic thermal parameters for carbon and oxygen atoms. Three cycles of full-matrix least-squares refinement led to convergence with $R_F = 4.97\%$ and $R_{wF} = 5.29\%$. However, the thermal parameters of C(22) and O(22) were outrageously high, with values of 14.9 and 23.3 $Å^2$, respectively. Following removal of these two atoms from the model, four cycles of refinement led to convergence with little improvement in the discrepancy indices ($R_F = 4.85\%$ and $R_{wF} = 5.27\%$). A difference-Fourier map revealed peaks of height 2.65 and 2.49 e $Å^{-3}$ at the positions previously occupied by C(22) and O(22). Clearly this ligand was present, but only with partial occupancy. A careful study of thermal parameters for all other carbon and oxygen atoms indicated that the ligand defined by C(21) and O(21) [which is trans to C(22)–O(22)] was also only of partial occupancy. Ligands C(21)–O(21) and C(22)–O(22) were now input with coupled occupancies of α and $(1 - \alpha)$, respectively, with α initially being assigned a value of 0.65. (The ratio of peak heights of C(21)–O(21) vs. C(22)–O(22) was approximately 0.65:0.35.) A structure factor calculation based on this model showed discrepancy indices of $R_F = 4.49\%$ and $R_{wF} = 4.50\%$ even before refinement, indicating a valid improvement. Continued least-squares refinement with anisotropic thermal parameters for all osmium, oxygen, and carbon atoms and with a secondary extinction correction led to final convergence with $(\Delta/\sigma)_{max} = 0.014$ and with $R_F = 3.68\%$ and $R_{wF} = 3.52\%$ for all 2259 data (none rejected). The "goodness-of-fit", given by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 0.975 where m, the number of observations, was 2259 and n, the number of variables, was 246, yielding an observation-to-variable ratio of 9.18:1.

A final difference-Fourier synthesis had a maximum peak height of 0.88 e $Å^{-3}$. Neither the bridging hydride ligand nor the terminal hydride ligand (vide infra) could be located unambiguously either on this map or on any of a series of other maps which were calculated from data with successively restricted $(\sin\theta)/\lambda$ values.

The final value for the secondary extinction coefficient (c) was 5.4 (21) × 10^{-7} mm^{-1} e^{-2}, where the corrected calculated structure factor ($F_{c,cor}$) is given by[19] $F_{c,cor} = F_{c,uncor}(1 + c\beta F^2_{c,uncor})^{-1/4}$ and

$$\beta = \left[\frac{1 + \cos^4 2\theta}{(\sin 2\theta)(1 + \cos^2 2\theta)}\right]\left(\frac{-d \ln \bar{T}}{d\mu}\right)$$

The maximum extinction correction was for the 002 reflection for which $R^2_{c,cor}/F^2_{c,uncor} = 0.923$.

Refinement of the Structure of $Os_3(CO)_{12}$. A structural study of $Os_3(CO)_{12}$ was reported by Corey and Dahl in 1962.[14] The precision of the study was in keeping with prevailing standards (viz., visual estimation of film data, $R_F = 12.4\%$ for 1873 data) but not sufficient to allow an accurate comparison of the molecular geometry of $Os_3(CO)_{12}$ with that of $H_2Os_3(CO)_{11}$.

Refinement began, using a scale factor and overall isotropic thermal parameter from a Wilson plot of our new data set, in conjunction with the positional coordinates of all atoms from the previous study. Refinement proceeded smoothly; the last few cycles included refinement of the scale factor, positional and anisotropic thermal parameters for all 27 atoms, and a secondary extinction parameter. Convergence ($(\Delta/\sigma)_{max} = 0.044$) was reached with $R_F = 3.35\%$, $R_{wF} = 3.62\%$, and a "goodness-of-fit" of 0.983. The number of observations was 3040 (none rejected) and the number of parameters refined was 245. The observations-to-parameter ratio was 12.41:1.

Table I. Experimental Data for the X-Ray Diffraction Studies of $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$

(A) Crystal Parameters

Compd	$H_2Os_3(CO)_{11}$[a]	$Os_3(CO)_{12}$[b]
Temp, °C	21.1 (3)	20.8 (3)
a, A	8.0744 (16)	8.0817 (6)
b, A	14.7265 (29)	14.7683 (11)
c, A	14.7770 (28)	14.5773 (11)
cos β	−0.1970 (2)	−0.1832 (1)
β, deg	101.36 (1)	100.56 (1)
V, A^3	1722.7 (6)	1710.41 (23)
Space group	$P2_1/n$[c]	$P2_1/n$[c]
Z	4	4
Mol wt	880.73	906.73
ρ(calcd), g cm^{-3}	3.396	3.521

(B) Measurement of Intensity Data

Radiation: Mo Kα
Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators: Cu foil; used if $I > 10^4$ counts/s
Takeoff angle: 3.0°
Detector aperture: 3 mm wide (in 2θ) × 4 mm high (in χ)
Crystal–detector distance: 330 mm
Crystal orientation: for $H_2Os_3(CO)_{11}$, ϕ axis ~4.0° from $[10\bar{1}]$; for $Os_3(CO)_{12}$, ϕ axis ~1.0° from $[22\bar{1}]$
Reflections measd: for $H_2Os_3(CO)_{11}$, $+h,\pm k,\pm l$ for $2\theta \leqslant 30°$ and $+h,+k,\pm l$ for $30° < 2\theta \leqslant 45°$;[d] for $Os_3(CO)_{12}$, $+h,+k,\pm l$ for $0° < 2\theta \leqslant 50°$
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 1.0°/min
Scan length: $\Delta(2\theta) = (W + 0.692 \tan\theta)°$ starting $(W/2)°$ below the Mo $K\alpha_1$ peak; for $H_2Os_3(CO)_{11}$, $W = 1.00°$; for $Os_3(CO)_{12}$, $W = 0.80°$
Background measurement: stationary crystal–stationary counter; 20 s each at beginning and end of 2θ scan
Std reflections: three remeasured after every 47 reflections; rms deviations (after application of an anisotropic linear decay correction)[e] for $H_2Os_3(CO)_{11}$ were 0.70% for 213, 1.64% for 020, and 0.88% for $20\bar{4}$; for $Os_3(CO)_{12}$ they were 0.71% for 303, 0.76% for 020, and 0.54% for $20\bar{4}$
Reflections collected: for $H_2Os_3(CO)_{11}$, 2259 independent measurements, plus 826 duplicate or equivalent measurements (averaged into primary data set) and 181 systematic absences; for $Os_3(CO)_{12}$, 3041 independent measurements, 18 duplicates, and 139 systematic absences

(C) Treatment of Intensity Data

Conversion[e] $|F_o|$ and $\sigma(|F_o|)$: as in ref 15, using "ignorance factors" of $p = 0.04$
Absorption correction: for $H_2Os_3(CO)_{11}$, $\mu = 221.5$ cm^{-1} and the maximum and minimum transmission factors[f] were 0.307 and 0.166, respectively; for $Os_3(CO)_{12}$, $\mu = 223.2$ cm^{-1} and the maximum and minimum transmission factors were 0.196 and 0.117, respectively; crystal shapes are described in text

[a] Unit cell parameters are from a least-squares fit to the setting angles of the resolved Mo $K\alpha_1$ peaks of 12 reflections in the 2θ range 37–43° and widely dispersed in reciprocal space. The maximum and root-mean-square angular disagreements were 0.037 and 0.018°, respectively (λ(Mo $K\alpha_1$) 0.709 30 A). [b] As in footnote *a*, except $2\theta = 41.8$–$49.1°$ and the maximum and rms disagreements were 0.019 and 0.008°. These values are in agreement with, but more precise than, those reported by Corey and Dahl[14] from film measurements. [c] $P2_1/n$ is a nonstandard setting of $P2_1/c$ [C_{2h}^5; No. 14] having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$. [d] Averaging of the two forms of data (hkl; $h, -k, l$) collected from the $H_2Os_3(CO)_{11}$ crystal for $2\theta \leqslant 30°$ gave $R(F^2)$ and $R(wF^2)$ values of 2.04% and 4.59%, respectively. Prior to application of the absorption correction, these were 4.40% and 6.04%, respectively. [e] Data reduction and analysis, including decay correction, were performed using the Fortran IV program RDUS2, by B. G. DeBoer. [f] Absorption corrections and secondary extinction coefficients were calculated by the program DRABZ, by B. G. DeBoer.

Secondary extinction was significant, the final value for c (vide supra) being 1.30 (5) × 10^{-5} mm^{-1} e^{-2}; maximum corrections were

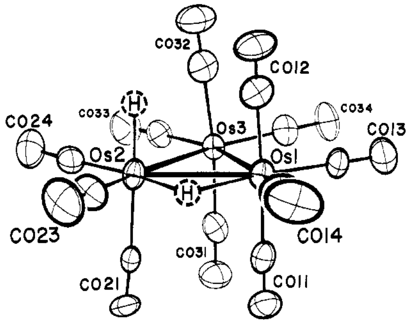


Figure 1. General view of an $H_2Os_3(CO)_{11}$ molecule with probable positions of hydrogen atoms shown as broken circles (ORTEP diagram, 30% probability ellipsoids).

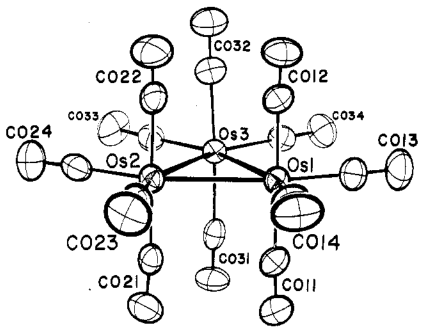


Figure 2. Molecular geometry of $Os_3(CO)_{12}$ (ORTEP diagram, 50% ellipsoids).

$F^2_{c,cor}/F^2_{c,uncor}$ = 0.623 for 002, 0.647 for 20$\bar{4}$, 0.695 for 11$\bar{2}$.

A final difference-Fourier map showed peaks of height 0.99 → 0.83 e Å^{-3} and troughs of depth −1.22 → −0.92 e Å^{-3} close to the positions of the osmium atoms. All other features were smaller than these.

Positional parameters for $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$ are shown in Table II; anisotropic thermal parameters are listed in Table III.

Results and Discussion

General views of $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$ appear in Figures 1 and 2, respectively. Interatomic distances for the two species are shown Table IV, while interatomic angles are collected in Table V.

The structure determined for $Os_3(CO)_{12}$ is completely in accord with that previously published by Corey and Dahl;[14] the only difference is that esd's of parameters in the present determination are reduced to approximately one-tenth of the previous values. The $Os_3(CO)_{12}$ molecule has approximate D_{3h} symmetry (broken by a minor rotation of the $(CO)_4$ groups such that equatorial carbonyl ligands are displaced alternately above and below the Os_3 plane; see Table VI(B)) with an average Os–Os distance of 2.8771 [27] Å.[20] The average Os–CO(axial) bond length is 1.946 [6] Å, i.e., some 0.034 ± 0.009 Å (or 3.8σ) longer than the average Os–CO (equatorial) distance of 1.912 [7] Å; carbon–oxygen distances show the reverse pattern, but at a much lower level of significance, with C–O(axial) = 1.134 [8] Å and C–O(equatorial) = 1.145 [5] Å, for a difference of −0.011 ± 0.009 Å. This overall pattern is expected since competition for back-donated electron density is severe for mutually trans carbonyl ligands and close to minimal for carbonyl ligands trans to a simple metal–metal σ bond. [Somewhat surprisingly, Mason and Rae[21] reported that in $Ru_3(CO)_{12}$ the Ru–CO(axial) bonds average 1.89 (2) Å as opposed to an average Ru–CO(equatorial) distance of 1.93 (2) Å. However, despite being done fairly recently (1968), this crystallographic analysis is not of the highest precision and the problem could bear reinvestigation.]

Table II. Final Positional Parameters with Esd's[a] for $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$

Atom	x	y	z	B,[b] Å^2
		(A) $H_2Os_3(CO)_{11}$		
Os(1)	0.429 67 (5)	−0.039 26 (3)	0.212 95 (3)	3.83
Os(2)	0.440 89 (6)	0.163 10 (3)	0.200 09 (3)	4.07
Os(3)	0.689 65 (5)	0.068 01 (3)	0.330 08 (3)	3.40
C(11)	0.576 1 (16)	−0.045 2 (7)	0.120 0 (10)	4.5
O(11)	0.653 0 (13)	−0.051 0 (6)	0.065 3 (6)	6.0
C(12)	0.289 0 (16)	−0.026 2 (9)	0.306 9 (9)	5.2
O(12)	0.205 9 (12)	−0.021 5 (8)	0.359 2 (8)	7.5
C(13)	0.527 7 (16)	−0.145 4 (8)	0.271 2 (9)	5.0
O(13)	0.588 0 (13)	−0.209 9 (7)	0.307 4 (7)	7.7
C(14)	0.247 4 (20)	−0.092 5 (13)	0.130 6 (11)	7.9
O(14)	0.133 6 (17)	−0.124 6 (11)	0.083 7 (9)	12.2
C(21)[c]	0.585 6 (21)	0.162 9 (9)	0.102 4 (11)	3.1
O(21)[c]	0.666 4 (16)	0.169 3 (8)	0.049 7 (8)	4.7
C(22)[c]	0.280 7 (37)	0.170 7 (14)	0.294 5 (18)	2.7
O(22)[c]	0.190 5 (32)	0.180 9 (17)	0.344 5 (17)	5.8
C(23)	0.259 6 (16)	0.209 6 (10)	0.110 7 (10)	6.1
O(23)	0.152 3 (15)	0.239 3 (9)	0.059 0 (9)	10.7
C(24)	0.529 0 (16)	0.274 2 (9)	0.242 2 (9)	5.4
O(24)	0.585 2 (14)	0.344 2 (7)	0.272 0 (8)	7.8
C(31)	0.827 8 (16)	0.061 1 (7)	0.237 8 (9)	4.8
O(31)	0.916 5 (12)	0.059 5 (6)	0.186 5 (7)	6.4
C(32)	0.536 1 (17)	0.088 6 (9)	0.416 1 (10)	5.7
O(32)	0.456 6 (14)	0.102 2 (8)	0.469 6 (8)	8.1
C(33)	0.819 2 (15)	0.168 9 (8)	0.382 8 (8)	4.8
O(33)	0.897 4 (13)	0.230 9 (7)	0.412 9 (7)	7.5
C(34)	0.812 6 (15)	−0.027 9 (8)	0.403 2 (9)	4.9
O(34)	0.884 9 (12)	−0.084 3 (6)	0.445 0 (7)	6.8
		(B) $Os_3(CO)_{12}$		
Os(1)	0.441 82 (4)	−0.024 44 (2)	0.222 39 (2)	2.26
Os(2)	0.441 62 (4)	0.170 11 (2)	0.206 54 (2)	2.37
Os(3)	0.696 45 (4)	0.080 84 (2)	0.339 17 (2)	2.12
C(11)	0.582 5 (12)	−0.031 2 (7)	0.127 9 (6)	2.9
O(11)	0.661 3 (10)	−0.040 4 (5)	0.070 7 (5)	4.3
C(12)	0.302 6 (12)	−0.016 2 (7)	0.317 6 (6)	2.9
O(12)	0.216 6 (9)	−0.016 1 (6)	0.370 3 (5)	4.3
C(13)	0.517 4 (14)	−0.140 8 (7)	0.267 4 (7)	3.5
O(13)	0.569 3 (11)	−0.210 2 (6)	0.297 6 (6)	5.1
C(14)	0.243 2 (13)	−0.052 1 (8)	0.129 7 (7)	3.6
O(14)	0.127 8 (10)	−0.066 8 (7)	0.075 0 (6)	5.5
C(21)	0.584 9 (12)	0.161 7 (6)	0.114 4 (6)	2.8
O(21)	0.669 2 (11)	0.163 8 (5)	0.058 4 (5)	4.5
C(22)	0.296 0 (13)	0.177 5 (7)	0.298 6 (7)	3.3
O(22)	0.205 2 (11)	0.185 1 (7)	0.348 7 (6)	5.8
C(23)	0.252 3 (13)	0.185 6 (7)	0.108 3 (7)	3.5
O(23)	0.136 3 (10)	0.196 2 (7)	0.050 5 (6)	5.5
C(24)	0.517 0 (12)	0.289 3 (7)	0.237 4 (7)	3.2
O(24)	0.565 6 (11)	0.361 2 (6)	0.257 0 (6)	5.3
C(31)	0.841 2 (12)	0.070 7 (6)	0.244 2 (7)	2.7
O(31)	0.931 4 (9)	0.068 1 (5)	0.196 1 (5)	3.7
C(32)	0.554 2 (11)	0.097 1 (7)	0.431 8 (6)	2.8
O(32)	0.480 1 (9)	0.105 7 (5)	0.490 6 (5)	4.3
C(33)	0.824 0 (12)	0.183 7 (7)	0.391 6 (6)	3.1
O(33)	0.896 5 (10)	0.244 6 (5)	0.424 4 (6)	4.7
C(34)	0.810 3 (12)	−0.019 3 (7)	0.406 3 (6)	2.9
O(34)	0.879 2 (10)	−0.079 1 (5)	0.445 9 (5)	4.4

[a] Esd's (estimated standard deviations) are shown in parentheses and are right-adjusted to the last digit of the preceding number. They are derived from the inverse of the least-squares matrix calculated in the final cycle of refinement. [b] These are the so-called "equivalent" isotropic thermal parameters. They are equal to one-third of the trace of the (orthogonalized) anisotropic thermal tensors. [c] These atoms were assigned fractional occupancies as a model for the disordered carbonyl ligand. Atoms C(21) and O(21) were assigned occupancies of α, and atoms C(22) and O(22), occupancies of $(1-\alpha)$; α was least-squares refined to a final value of 0.638 (11) $[1-\alpha = 0.362]$.

We now turn our attention to the molecular geometry of $H_2Os_3(CO)_{11}$. The $Os_3(CO)_{11}$ portion of this molecule has been located directly by x-ray structural analysis. There are two orientations of the molecule in the crystallographic site—one of 63.8% occupancy (shown in Figure 1) and one of 36.2% occupancy, in which the suggested terminal hydrogen site of Figure 1 is replaced by the ligand C(22)–O(22) and

Table III. Final Anisotropic Thermal Parameters[a,b] for $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[c]
				(A) $H_2Os_3(CO)_{11}$			
Os(1)	3.34 (2)	3.46 (2)	4.34 (2)	−0.30 (2)	−0.09 (2)	−0.34 (2)	0.187, 0.216, 0.253
Os(2)	3.77 (2)	3.30 (2)	4.70 (3)	0.72 (2)	−0.23 (2)	0.21 (2)	0.181, 0.223, 0.268
Os(3)	3.08 (2)	3.26 (2)	3.52 (2)	−0.08 (2)	−0.18 (2)	0.03 (2)	0.181, 0.203, 0.235
C(11)	4.5 (6)	3.5 (5)	5.0 (7)	0.1 (5)	−0.2 (5)	−0.5 (5)	0.21, 0.22, 0.28
O(11)	7.2 (6)	6.4 (5)	4.8 (5)	−0.4 (4)	1.8 (5)	−1.0 (4)	0.23, 0.29, 0.31
C(12)	3.4 (6)	5.9 (7)	5.7 (7)	−1.6 (5)	−0.3 (5)	−1.7 (6)	0.16, 0.27, 0.31
O(12)	5.4 (5)	9.8 (7)	8.2 (6)	−1.1 (5)	3.2 (5)	−2.1 (5)	0.22, 0.30, 0.38
C(13)	5.8 (7)	3.2 (5)	6.4 (7)	1.2 (5)	2.2 (6)	0.6 (5)	0.19, 0.25, 0.30
O(13)	9.1 (7)	5.4 (5)	9.1 (7)	1.0 (5)	2.9 (5)	1.7 (5)	0.24, 0.31, 0.37
C(14)	5.5 (8)	11.5 (12)	5.5 (8)	−0.6 (8)	−1.8 (7)	−0.8 (8)	0.19, 0.34, 0.38
O(14)	9.7 (8)	18.1 (13)	7.5 (7)	−6.1 (9)	−1.4 (6)	−2.3 (7)	0.22, 0.38, 0.52
C(21)[d]	3.4 (8)	2.3 (7)	3.1 (8)	0.2 (6)	−0.2 (7)	−0.2 (6)	0.17, 0.18, 0.23
O(21)[d]	5.2 (7)	5.5 (7)	3.7 (6)	0.5 (5)	2.0 (5)	−0.7 (5)	0.18, 0.26, 0.27
C(22)[d]	4.4 (15)	0.4 (9)	2.5 (12)	0.4 (9)	−1.0 (11)	0.2 (8)	0.06, 0.15, 0.27
O(22)[d]	6.8 (15)	5.5 (13)	5.3 (13)	0.1 (11)	1.8 (12)	−0.9 (10)	0.23, 0.28, 0.30
C(23)	3.6 (6)	7.8 (9)	6.6 (8)	0.9 (6)	−0.1 (6)	2.0 (7)	0.19, 0.28, 0.34
O(23)	7.8 (7)	12.1 (9)	11.4 (9)	3.7 (6)	−0.4 (6)	4.8 (7)	0.22, 0.39, 0.46
C(24)	5.6 (7)	5.0 (7)	6.5 (8)	0.8 (6)	3.0 (6)	1.1 (6)	0.22, 0.24, 0.32
O(24)	8.3 (7)	5.0 (5)	10.2 (7)	−0.4 (5)	1.9 (5)	0.0 (5)	0.25, 0.32, 0.36
C(31)	4.8 (6)	4.0 (6)	5.0 (7)	−1.9 (5)	−0.3 (6)	0.0 (5)	0.17, 0.24, 0.30
O(31)	5.6 (5)	7.4 (6)	6.7 (5)	−0.5 (4)	2.5 (5)	−0.1 (4)	0.23, 0.30, 0.31
C(32)	4.6 (7)	5.5 (7)	6.8 (8)	−2.1 (5)	0.4 (6)	−1.0 (6)	0.19, 0.30, 0.31
O(32)	8.3 (6)	9.1 (7)	8.0 (6)	−2.3 (5)	4.4 (6)	−2.5 (5)	0.24, 0.29, 0.41
C(33)	4.6 (6)	4.6 (6)	5.1 (6)	−0.7 (5)	0.7 (5)	0.3 (5)	0.22, 0.25, 0.27
O(33)	8.7 (6)	5.8 (5)	7.5 (6)	−3.4 (5)	0.3 (5)	−1.2 (4)	0.20, 0.32, 0.38
C(34)	3.6 (6)	4.6 (6)	6.4 (7)	−0.8 (5)	0.4 (5)	0.2 (5)	0.20, 0.25, 0.29
O(34)	6.3 (5)	5.2 (5)	8.0 (6)	1.0 (4)	−1.3 (5)	2.5 (4)	0.19, 0.29, 0.37
				(B) $Os_3(CO)_{12}$			
Os(1)	2.199 (17)	2.240 (16)	2.279 (16)	−0.260 (11)	0.264 (11)	−0.132 (11)	0.155, 0.174, 0.178
Os(2)	2.243 (17)	2.268 (16)	2.550 (16)	0.303 (11)	0.326 (11)	0.311 (11)	0.154, 0.177, 0.187
Os(3)	1.921 (15)	2.263 (16)	2.086 (15)	−0.094 (11)	0.140 (11)	−0.014 (10)	0.150, 0.168, 0.172
C(11)	2.6 (4)	3.1 (4)	2.9 (4)	0.1 (3)	0.0 (3)	−0.7 (3)	0.16, 0.19, 0.22
O(11)	4.9 (4)	4.2 (4)	4.3 (4)	0.1 (3)	1.8 (3)	−0.6 (3)	0.20, 0.24, 0.26
C(12)	2.6 (4)	3.2 (4)	2.8 (4)	−0.1 (3)	0.2 (3)	−0.6 (3)	0.17, 0.19, 0.22
O(12)	3.5 (3)	5.8 (5)	3.8 (3)	−0.9 (3)	1.3 (3)	−0.5 (3)	0.19, 0.22, 0.28
C(13)	3.9 (5)	2.8 (5)	3.9 (5)	−1.1 (4)	0.6 (4)	−0.7 (4)	0.16, 0.22, 0.24
O(13)	6.1 (5)	3.1 (4)	5.7 (4)	1.1 (3)	0.4 (4)	0.6 (3)	0.18, 0.27, 0.30
C(14)	2.7 (4)	4.5 (5)	3.5 (4)	0.4 (4)	0.5 (4)	−0.6 (4)	0.18, 0.20, 0.25
O(14)	3.3 (4)	8.9 (6)	4.1 (4)	−1.2 (4)	−0.1 (3)	−1.8 (4)	0.18, 0.24, 0.35
C(21)	3.2 (4)	2.2 (4)	2.7 (4)	0.5 (3)	0.0 (3)	0.2 (3)	0.15, 0.18, 0.22
O(21)	4.9 (4)	4.9 (4)	4.2 (4)	1.0 (3)	1.8 (3)	1.3 (3)	0.20, 0.22, 0.29
C(22)	3.8 (5)	2.6 (4)	3.4 (4)	0.9 (4)	0.5 (4)	0.3 (3)	0.16, 0.21, 0.23
O(22)	5.7 (5)	6.7 (5)	5.6 (4)	2.9 (4)	2.7 (4)	1.3 (4)	0.19, 0.25, 0.35
C(23)	3.4 (5)	3.3 (5)	3.9 (5)	0.9 (4)	0.4 (4)	1.0 (4)	0.16, 0.22, 0.24
O(23)	3.6 (4)	7.5 (5)	4.7 (4)	0.6 (4)	−0.9 (3)	1.2 (4)	0.18, 0.28, 0.32
C(24)	3.2 (4)	3.5 (5)	3.0 (4)	0.1 (4)	1.0 (3)	0.5 (3)	0.17, 0.20, 0.22
O(24)	6.4 (5)	3.2 (4)	6.4 (5)	−1.0 (3)	1.4 (4)	−0.3 (3)	0.19, 0.28, 0.30
C(31)	2.6 (4)	1.9 (4)	3.1 (4)	0.3 (3)	−0.5 (3)	−0.1 (3)	0.15, 0.16, 0.23
O(31)	2.8 (3)	5.1 (4)	3.4 (3)	0.3 (3)	1.5 (3)	0.3 (3)	0.16, 0.22, 0.26
C(32)	1.6 (3)	3.8 (5)	2.8 (4)	0.2 (3)	0.0 (3)	−0.3 (3)	0.14, 0.19, 0.22
O(32)	3.8 (3)	5.4 (4)	3.9 (3)	−0.2 (3)	1.4 (3)	−0.5 (3)	0.19, 0.23, 0.27
C(33)	3.5 (5)	2.9 (4)	2.7 (4)	0.0 (4)	0.4 (3)	0.1 (3)	0.18, 0.19, 0.21
O(33)	4.0 (4)	4.3 (4)	5.6 (4)	−1.9 (3)	0.5 (3)	−1.9 (3)	0.15, 0.26, 0.30
C(34)	2.8 (4)	3.2 (4)	2.4 (4)	−0.3 (3)	0.2 (3)	−0.1 (3)	0.17, 0.19, 0.21
O(34)	5.0 (4)	3.8 (4)	4.1 (4)	1.1 (3)	0.1 (3)	1.3 (3)	0.17, 0.26, 0.27

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of $Å^2$. They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] See footnote *a* to Table II. [c] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see figures. [d] See footnote *c* to Table II.

in which C(21)–O(21) is absent. Reasonable stereochemistry about each osmium atom can be obtained only by assigning a terminal hydride ligand to the site trans to C(21)–O(21) (as shown in Figure 1) or trans to C(22)–O(22) for the minor orientational component. It is worth noting that the thermal parameters for C(22) are unrealistic—this is probably a result of hydrogen atom contributions not being included in the analysis; C(22) occupies a site which represents the composite of 36.2% occupancy of carbon (approximately 2.2 e) from a carbonyl ligand and 63.8% occupancy of hydrogen (0.6 e) from a hydride ligand, but only the carbon atom contribution was included in the computation; the observed thermal parameters are therefore reduced from their true values. The bridging hydride ligand can be assigned a site in the equatorial plane, displaced outward from the Os(1)–Os(2) vector and at, or near, the point of intersection of imaginary lines C(24)→Os(2) and C(13)→Os(1).

The effects of this equatorial μ_2-bridging hydride ligand can be assessed in detail by comparing the geometry of the equatorial $Os_3(CO)_6$ fragments in $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{11}$. [Note that there are no major differences in the geometry of the *axial* ligands of $Os_3(CO)_{12}$ vs. $H_2Os_3(CO)_{11}$.

Table IV. Interatomic Distances (Å) with Esd's[a] for $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$

Atoms	Dist in $H_2Os_3(CO)_{11}$	Dist in $Os_3(CO)_{12}$
(A) Osmium–Osmium		
Os(1)–Os(2)	2.9886 (9)	2.8824 (5)
Os(1)–Os(3)	2.9097 (7)	2.8752 (5)
Os(2)–Os(3)	2.8574 (7)	2.8737 (5)
Average^b		2.8771 [27]
(B) Osmium–Carbon (Axial)		
Os(1)–C(11)	1.983 (15)	1.943 (10)
Os(1)–C(12)	1.968 (15)	1.944 (10)
Os(2)–C(21)	2.028 (18)^c	1.931 (10)
Os(2)–C(22)	2.084 (32)^c	1.943 (10)
Os(3)–C(31)	1.926 (15)	1.975 (10)
Os(3)–C(32)	1.966 (16)	1.942 (9)
Average	1.961 [12]	1.946 [6]
(C) Osmium–Carbon (Equatorial)		
Os(1)–C(13)	1.882 (12)	1.900 (11)
Os(1)–C(14)	1.886 (16)	1.943 (11)
Os(2)–C(23)	1.896 (13)	1.909 (10)
Os(2)–C(24)	1.843 (15)	1.889 (11)
Os(3)–C(33)	1.894 (13)	1.914 (10)
Os(3)–C(34)	1.930 (13)	1.914 (10)
Average	1.889 [11]	1.912 [7]
(D) Carbon–Oxygen (Axial)		
C(11)–O(11)	1.114 (14)	1.146 (11)
C(12)–O(12)	1.122 (14)	1.126 (11)
C(21)–O(21)	1.114 (18)^c	1.156 (11)
C(22)–O(22)	1.145 (33)^c	1.132 (12)
C(31)–O(31)	1.142 (15)	1.101 (12)
C(32)–O(32)	1.131 (15)	1.140 (11)
Average	1.127 [7]	1.134 [8]
(E) Carbon–Oxygen (Equatorial)		
C(13)–O(13)	1.150 (14)	1.163 (13)
C(14)–O(14)	1.139 (17)	1.131 (12)
C(23)–O(23)	1.124 (14)	1.150 (12)
C(24)–O(24)	1.175 (15)	1.150 (13)
C(33)–O(33)	1.150 (13)	1.132 (12)
C(34)–O(34)	1.127 (14)	1.142 (11)
Average	1.144 [8]	1.145 [5]
(F) Carbon–Carbon (Axial, Nonbonding)		
C(11)–C(21)	3.078 (18)^c	2.856 (13)
C(11)–C(31)	2.867 (15)	2.866 (12)
C(21)–C(31)	2.922 (18)^c	2.871 (12)
C(12)–C(22)	2.906 (25)^c	2.874 (14)
C(12)–C(32)	2.860 (15)	2.910 (12)
C(22)–C(32)	2.735 (26)^c	2.837 (13)
Average		2.869 [10]
(G) Oxygen–Oxygen (Axial, Nonbonding)		
O(11)–O(21)	3.257 (16)^c	3.023 (11)
O(11)–O(31)	2.979 (12)	3.035 (11)
O(21)–O(31)	3.028 (15)^c	2.994 (10)
O(12)–O(22)	2.989 (27)^c	2.988 (13)
O(12)–O(32)	2.963 (14)	3.079 (11)
O(22)–O(32)	2.795 (26)^c	2.985 (11)
Average		3.017 [15]

[a] Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. Their calculation, using the Fortran IV program STAN1 by B. G. DeBoer, included the effects of uncertainties in unit cell parameters, as well as all correlation coefficients. No corrections have been applied for the effects of thermal motion. [b] Error estimates shown in brackets for average distances, $\bar{d}$, are the exterior estimates of the precision of the average value given by $[\Sigma_n(\bar{d} - d)^2/(n^2 - n)]^{1/2}$. [c] These distances involve atoms of the disordered carbonyl ligand. They were *not* included in the calculations of average values.

We conclude, therefore, that the terminal hydride ligand in $H_2Os_3(CO)_{11}$ has essentially the same stereochemical influence as the corresponding terminal carbonyl ligand in $Os_3(CO)_{12}$ and that *all structural dissimilarities between $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{11}$ arise from the presence or absence of a μ_2-bridging hydride ligand in the equatorial plane.*]

Table V. Interatomic Angles (deg) in $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$

Atoms	Angles in $H_2Os_3(CO)_{11}$	Angles in $Os_3(CO)_{12}$
(A) Within the Os_3 Triangle		
Os(2)–Os(1)–Os(3)	57.93 (2)^a	59.88 (1)
Os(1)–Os(2)–Os(3)	59.65 (1)	59.93 (1)
Os(1)–Os(3)–Os(2)	62.42 (2)	60.18 (1)
(B) Os–Os–CO(equatorial)		
Os(2)–Os(1)–C(14)	113.8 (6)	99.5 (4)
Os(1)–Os(2)–C(23)	112.0 (5)	99.7 (3)
Os(3)–Os(1)–C(13)	89.4 (4)	97.8 (3)
Os(3)–Os(2)–C(24)	92.0 (4)	96.1 (3)
Os(1)–Os(3)–C(34)	99.6 (4)	96.3 (3)
Os(2)–Os(3)–C(33)	98.6 (4)	99.9 (3)
(C) OC–Os–CO(equatorial)		
C(13)–Os(1)–C(14)	98.9 (7)	102.8 (5)
C(23)–Os(2)–C(24)	96.3 (6)	104.2 (4)
C(33)–Os(3)–C(34)	99.4 (5)	103.6 (4)
(D) Os–Os–CO(axial)		
Os(2)–Os(1)–C(11)	88.3 (3)	89.2 (3)
Os(3)–Os(1)–C(11)	88.7 (3)	90.0 (3)
Os(2)–Os(1)–C(12)	88.7 (4)	90.2 (3)
Os(3)–Os(1)–C(12)	88.7 (3)	89.3 (3)
Os(1)–Os(2)–C(21)	94.2 (4)^b	90.0 (3)
Os(3)–Os(2)–C(21)	92.9 (4)^b	89.5 (3)
Os(1)–Os(2)–C(22)	88.9 (6)^b	89.6 (3)
Os(3)–Os(2)–C(22)	91.3 (6)	90.7 (3)
Os(1)–Os(3)–C(31)	90.1 (3)	89.7 (3)
Os(2)–Os(3)–C(31)	88.8 (4)	90.4 (3)
Os(1)–Os(3)–C(32)	89.7 (4)	91.6 (3)
Os(2)–Os(3)–C(32)	84.8 (4)	88.2 (3)
(E) OC–Os–CO(axial-equatorial)		
C(11)–Os(1)–C(13)	91.5 (5)	90.3 (4)
C(11)–Os(1)–C(14)	91.7 (6)	90.7 (4)
C(12)–Os(1)–C(13)	90.4 (5)	90.1 (4)
C(12)–Os(1)–C(14)	90.6 (6)	89.8 (4)
C(21)–Os(2)–C(23)	88.8 (6)	89.2 (4)
C(21)–Os(2)–C(24)	90.2 (5)	91.0 (4)
C(22)–Os(2)–C(23)	87.2 (8)	90.5 (4)
C(22)–Os(2)–C(24)	88.6 (7)	89.6 (4)
C(31)–Os(3)–C(33)	89.0 (5)	89.7 (4)
C(31)–Os(3)–C(34)	93.9 (5)	90.5 (4)
C(32)–Os(3)–C(33)	88.9 (5)	88.2 (4)
C(32)–Os(3)–C(34)	94.1 (6)	91.7 (4)
(F) OC–Os–CO(axial-axial)		
C(11)–Os(1)–C(12)	176.7 (5)	179.2 (6)
C(21)–Os(2)–C(22)	175.6 (8)^b	179.4 (3)
C(31)–Os(3)–C(32)	172.9 (6)	177.2 (4)
(G) Os-C–O(axial)		
Os(1)–C(11)–O(11)	176.8 (13)	175.8 (10)
Os(1)–C(12)–O(12)	177.6 (17)	175.6 (10)
Os(2)–C(21)–O(21)	175.0 (15)^b	174.7 (9)
Os(2)–C(22)–O(22)	175.3 (32)^b	175.9 (10)
Os(3)–C(31)–O(31)	176.2 (13)	174.5 (9)
Os(3)–C(32)–O(32)	175.6 (14)	175.4 (9)
(H) Os-C–O(equatorial)		
Os(1)–C(13)–O(13)	179.5 (7)	176.9 (12)
Os(1)–C(14)–O(14)	177.1 (13)	178.7 (8)
Os(2)–C(23)–O(23)	178.1 (12)	178.3 (8)
Os(2)–C(24)–O(24)	177.8 (10)	178.8 (7)
Os(3)–C(33)–O(33)	178.5 (8)	178.1 (13)
Os(3)–C(34)–O(34)	179.2 (8)	179.4 (6)

[a] See footnote *a* of Table IV. [b] These angles involve atom(s) of the disordered carbonyl ligand.

The addition of an equatorial μ_2-bridging hydride has the following effects (cf. parts A and B of Figure 3).

(1) It causes elongation of the bridged osmium–osmium vector. Thus, Os(1)–Os(2) in $H_2Os_3(CO)_{11}$ is 2.9886 (9) Å—i.e., 0.1051 Å longer than the average of 2.8835 Å for the nonbridged osmium–osmium bond lengths in this same molecule and 0.1115 Å longer than the average osmium–

Table VI. Important Least-Squares Planes

Atom	Dev, Å	Atom	Dev, Å
(A) $H_2Os_3(CO)_{11}$: Os(1)–Os(2)–Os(3) Plane $0.726\,16X - 0.073\,94Y - 0.683\,54Z = 0.003^a$			
C(13)	−0.010 (13)	C(11)	1.982 (13)
O(13)	−0.021 (11)	O(11)	3.096 (9)
C(14)	−0.020 (17)	C(12)	−1.968 (13)
O(14)	−0.089 (15)	O(12)	−3.089 (11)
C(23)	−0.039 (14)	C(21)	2.022 (15)
O(23)	−0.080 (13)	O(21)	3.123 (13)
C(24)	−0.111 (14)	C(22)	−2.082 (26)
O(24)	−0.215 (11)	O(22)	−3.223 (25)
C(33)	0.017 (12)	C(31)	1.926 (13)
O(33)	0.046 (10)	O(31)	3.065 (10)
C(34)	−0.053 (13)	C(32)	−1.956 (14)
O(34)	−0.070 (10)	O(32)	−3.081 (11)
(B) $Os_3(CO)_{12}$: Os(1)–Os(2)–Os(3) Plane $0.719\,99X - 0.064\,80Y - 0.690\,95Z = -0.035^a$			
C(13)	0.019 (11)	C(11)	1.942 (10)
O(13)	0.030 (8)	O(11)	3.086 (8)
C(14)	−0.034 (11)	C(12)	−1.944 (10)
O(14)	−0.044 (9)	O(12)	−3.067 (8)
C(23)	0.046 (11)	C(21)	1.931 (9)
O(23)	0.044 (9)	O(21)	3.082 (8)
C(24)	−0.041 (10)	C(22)	−1.943 (10)
O(24)	−0.058 (9)	O(22)	−3.071 (9)
C(33)	0.024 (10)	C(31)	1.975 (9)
O(33)	0.000 (8)	O(31)	3.071 (7)
C(34)	−0.036 (10)	C(32)	−1.938 (9)
O(34)	−0.045 (8)	O(32)	−3.074

[a] Equations to planes are expressed in the orthonormal (Å) coordinates X, Y, and Z, which are related to the fractional coordinates x, y, and z by the matrix

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

osmium bond length of 2.8771 [27] Å in $Os_3(CO)_{12}$.

(2) It causes the adjacent equatorial carbonyl ligands to be pushed back relative to their position in $Os_3(CO)_{12}$. Thus, the six equivalent cis Os–Os–CO angles in $Os_3(CO)_{12}$ range from 96.1 (3) to 99.9 (3)° [average 98.2°]; in contrast, the angles Os(2)–Os(1)–C(14) and Os(1)–Os(2)–C(23) are increased to 113.8 (6) and 112.0 (5)° [average 112.9°] in $H_2Os_3(CO)_{11}$. This distortion can be looked at as some combination of (i) van der Waals repulsions between the bridging hydride and the adjacent carbonyl ligands and (ii) an effect necessary to maintain regular octahedral coordination about both Os(1) and Os(2) (ignoring direct Os(1)–Os(2) interaction). This "pushing back" of the equatorial carbonyl ligands propagates on around the Os_3 triangle as follows. (See effects (3)–(6).)

(3) The cis-diequatorial OC–Os–CO angles on atoms Os(1) and Os(2) in $H_2Os_3(CO)_{11}$ are significantly smaller than their counterparts in $Os_3(CO)_{12}$. In $Os_3(CO)_{12}$ these angles range from 102.8 (5) to 104.2 (4)° [average 103.5°] while, in $H_2Os_3(CO)_{11}$, angles C(13)–Os(1)–C(14) and C(23)–Os(2)–C(24) are reduced to 98.9 (7) and 96.3 (6)° [average 97.6°].

(4) The angles Os(3)–Os(1)–C(13) and Os(3)–Os(2)–C(14) are reduced to values of 89.4 (4) and 92.0 (4)° [average 90.8°] in $H_2Os_3(CO)_{11}$, as opposed to the mean cis Os–Os–CO angle of 98.2° (vide supra) in $Os_3(CO)_{12}$.

(5) The cis Os–Os(3)–CO angles in $H_2Os_3(CO)_{11}$ have values of 99.6 (4) and 98.6 (4)° [average 99.1°] which are not significantly different from the mean cis Os–Os–CO angle of 98.2° in $Os_3(CO)_{12}$.

(6) The cis-diequatorial OC–Os(3)–CO angle is reduced from 103.5° (average) in $Os_3(CO)_{12}$ to 99.4 (5)° in $H_2Os_3(CO)_{11}$.

In summary, then, the presence of an equatorial μ_2-bridging hydride ligand in $H_2Os_3(CO)_{11}$ causes the following changes, relative to the $Os_3(CO)_{12}$ structure—a lengthening of the bridged osmium–osmium vector, a gross displacement of the adjacent equatorial carbonyl ligands, and smaller, but significant, compressional distortions of most of the remaining equatorial Os–Os–CO and OC–Os–CO bond angles.

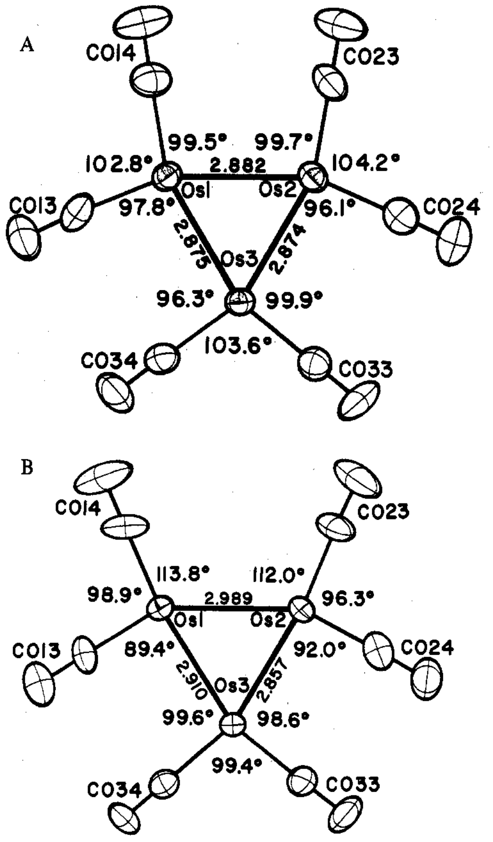
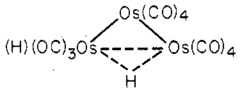


Figure 3. Equatorial distribution of ligands in (A) $Os_3(CO)_{12}$ and (B) $H_2Os_3(CO)_{11}$.

Finally we note that, since the Os–(H)–Os system is a two-electron three-center bond system, the $H_2Os_3(CO)_{11}$ molecule should properly be depicted as in III.



$$\text{(H)(OC)}_3\text{Os}\overset{\text{Os(CO)}_4}{\underset{\text{H}}{\cdots}}\text{Os(CO)}_4$$

III

Acknowledgment. We thank Professor J. R. Shapley for providing samples of both $H_2Os_3(CO)_{11}$ and $Os_3(CO)_{12}$. Time on an IBM 370/158 computer was provided by the Computer Center of the University of Illinois at Chicago Circle. This work was generously supported through a grant from the National Science Foundation (No. CHE76-05564, to M. R. Churchill).

Registry No. $H_2Os_3(CO)_{11}$, 56398-24-4; $Os_3(CO)_{12}$, 15696-40-9.

Supplementary Material Available: Listings of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Bonding of Aromatic Hydrocarbons to Ni(0). Structure of Bistricyclohexylphosphine(1,2-η^2-anthracene)nickel(0)–Toluene

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Received July 8, 1976 AIC60503N

The crystal structure of bistricyclohexylphosphine(1,2-η^2-anthracene)nickel(0)–toluene has been determined from 4743 x-ray data with $I \geq 2\sigma(I)$. The compound crystallizes in the triclinic system with unit cell dimensions a = 9.8620 (9), b = 13.956 (1), c = 19.755 (2) Å, α = 93.398 (8), β = 91.872 (9), and γ = 110.166 (8)°. The crystals have a calculated density of 1.16 g/cm³ for Z = 2 in the space group $P\bar{1}$. The structure was refined by block diagonal least-squares methods with anisotropic temperature factors for all nonhydrogen atoms and isotropic temperature factors for the anthracenic and cyclohexyl hydrogen atoms. The final R value is 0.039. The crystals consist of distinct, monomeric bistricyclohexylphosphine(1,2-η^2-anthracene)nickel(0) molecules, which are separated from the two independent, disordered toluene molecules by van der Waals distances. The bonds formed by the Ni atom are Ni–P(1), 2.227 (1) Å, Ni–P(2), 2.241 (1) Å, Ni–C(1), 2.060 (4) Å, and Ni–C(2), 1.993 (4) Å. The P(1)–Ni–P(2) angle is 118.3 (1)°. The C(1)–C(2) bond of anthracene is lengthened 0.047 (6) Å by coordination. The substituent planes of C(1) and C(2) are bent back 19 (1)° from the Ni atom. The C(1)–C(2) vector is rotated 22.0° out of the plane of Ni, P(1), P(2). The latter as well as other distortions are discussed in terms of the tight packing of ligands about the metal atom. Evidence for partial fixation of single and double bonds in the anthracene moiety is presented. From this observation a model based on a minimized loss of arene resonance energy is formulated and used to predict structures of other 1,2-dihaptoarene transition metal complexes and their relative stabilities.

Introduction

Recently the synthesis of a number of $[(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2]Ni$ (n = 2, 3) and $[(C_6H_{11})_3P]_2Ni$—$(TCP)_2Ni$—complexes of benzene, naphthalene, phenanthrene, anthracene, and tetracene have been reported. The benzene and, to a lesser extent, naphthalene containing compounds react with hydrogen to form a nickel hydride complex. While spectroscopic and potentiometric measurements indicated that the aromatic ligands probably interact with the nickel atom, no detailed structural information could be presented.[1]

Because these compounds belong to a new class of nickel complexes, we were interested in this stereochemistry. Since NMR methods were hindered by the low solubility and dissociation of the compounds,[1] recourse to single-crystal x-ray diffraction techniques was obvious. Attempts to analyze chelate phosphine complexes proved fruitless due to poor crystal quality. Finally good crystals of $(TCP)_2(C_{14}H_{10})Ni$, which contain toluene solvent, were kindly supplied by Dr. Jonas of this institute. We wish to report the results of this x-ray structural investigation.

Experimental Section

A crystal of $(TCP)_2(C_{14}H_{10})Ni\cdot C_6H_5CH_3$ of dimensions 0.325 × 0.15 × 0.225 mm was mounted in a glass capillary under argon. Weissenberg and precession photographs indicated that the crystal belongs to the triclinic system. No higher symmetry was revealed by a reduced cell calculation.[2] The crystal was transferred to an automated CAD-4 diffractometer, which was equipped with a molybdenum source and a graphite monochromator.

An orientation matrix was calculated before data collection from the setting angles of 15 centered reflections. At the end of data collection, precise unit cell constants were obtained by a least-squares technique employing the Bragg angles (Mo K$\bar{\alpha}$ 0.71069 Å) of 89 reflections with 12° < 2θ < 35°. The unit cell dimensions are a = 9.8620 (9),[3] b = 13.956 (1), c = 19.755 (2) Å, α = 93.398 (8), β = 91.872 (9), and γ = 110.166 (8)°. The calculated density is 1.16 g/cm³ for Z = 2. θ scans of several strong reflections indicated that the crystalline quality was satisfactory. One hemisphere (hkl, $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$, 0.5° < 2θ(Mo K$\bar{\alpha}$) < 25.0°) of data was collected by the $\theta/2\theta$ scan technique. Before each intensity measurement a fast scan of the reflection at 20°/min was used to determine the final scanning speed. Moving crystal–moving counter background scans were made by scanning a quarter of the peak width before the start and also after the end of each peak scan. The check reflections 500, 040, and 004 were remeasured after collection of 250 data. These reflections were used to check on the centering and stability of the crystal and diffractometer. The variation of the intensities of the check reflections was less than 7%. A total of 8930 data were collected.

The intensity data were corrected for check reflection fluctuation and reduced to $|F_o|$'s. The fact that no absorption correction (μ = 4.8 cm^{-1}) was applied causes relative errors of less than 5% in the intensities. Multiply measured reflections were averaged to yield 8911 data. Of these, 4734 obeyed the condition $I \geq 2\sigma(I)$ and were considered "observed". Here $I = K[P - 2(BG1 + BG2)]$ and $\sigma(I) = K(P + 4(BG1 + BG2))^{1/2}$, where P is the peak intensity, BG1 and BG2 are the background intensities, and K is a constant which depends on the scanning speed. Each "observed" reflection was assigned a standard deviation $\sigma(|F_o|)$, where $\sigma(|F_o|) = (\sigma^2(I) + (0.04I)^2)^{1/2}/2F$.