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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 3.[1,2] Crystal Structure and Molecular Geometry of $H_2Os_3(CO)_{10}(PPh_3)$, Including Direct Location of Both Terminal and μ_2-Bridging Hydride Ligands

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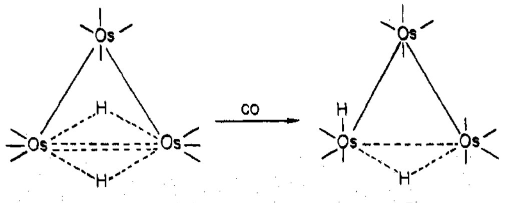
The complex decacarbonyl(triphenylphosphine)dihydridotriosmium, $H_2Os_3(CO)_{10}(PPh_3)$, prepared previously by Shapley and Keister from the reaction of the "unsaturated" species $H_2Os_3(CO)_{10}$ with PPh_3, has been subjected to a single-crystal x-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 9.126 (2) Å, b = 13.334 (2) Å, c = 25.106 (4) Å, β = 103.45 (1) °, and V = 2971 (1) Å^3. Observed and calculated densities are (respectively) 2.51 (2) and 2.493 g cm^{-3} for Z = 4 and mol wt 1115.0. Diffraction data were collected with a Picker FACS-1 diffractometer using Mo Kα radiation ($2\theta_{max}$ = 48°). The structure was solved by a combination of Patterson, Fourier, and least-squares refinement (403 parameters) techniques. Final discrepancy indices are R_F = 4.38% and R_{wF} = 3.27% for the 4698 independent data (none rejected). All atoms, including both bridging and terminal hydride ligands, were located. The osmium atoms form a triangular array, each being linked to four terminal ligands, two axial and two equatorial. The triphenylphosphine ligand occupies an equatorial site on Os(1), while the terminal hydride ligand occupies an axial site on Os(2). Os(1) and Os(2) are further bridged by a μ_2-hydrido ligand which lies in the plane of the three osmium atoms. Osmium–osmium distances are Os(1)–Os(2) = 3.0185 (6) Å, Os(1)–Os(3) = 2.9170 (5) Å, and Os(2)–Os(3) = 2.8645 (7) Å. The bond lengthening effect of an unsupported bridging hydride ligand is both confirmed and rendered quantitative.

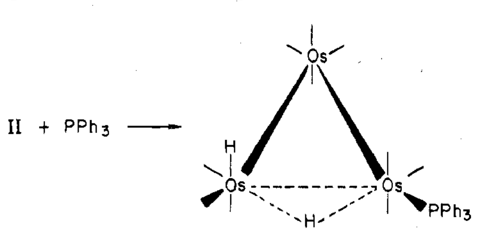
Introduction

We have recently reported[1] the structure of $H_2Os_3(CO)_{11}$ (I) which was synthesized[5] from $H_2Os_3(CO)_{10}$ (II)[6] and CO (see eq 1). The crystallographic analysis was, however, marred by a disorder (approximately 64%:36%) of the terminal hydride ligand and the axial carbonyl group on the same osmium atom. Furthermore, the analysis gave no information on the site taken up by the newly arrived carbonyl ligand.



II I (1)

We have now undertaken a single-crystal x-ray diffraction study of the related species $H_2Os_3(CO)_{10}(PPh_3)$, synthesized[5] as in eq 2, and found this species to be ordered with the incoming triphenylphosphine ligand occupying an equatorial site. Our results are reported below.



III (2)

Experimental Section

Yellow crystals of $H_2Os_3(CO)_{10}(PPh_3)$ were kindly supplied by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The crystal selected for the structural analysis approximated to a triangular prism of maximum orthogonal dimensions 0.51 mm × 0.19 mm × 0.17 mm, the "prism" faces being approximated by (034), (0$\bar{3}$4), and "($\bar{1}$,0,$\overline{27}$)" and clipped slightly by smaller (0$\bar{3}\bar{4}$) and (03$\bar{4}$) faces. One end was formed by (110), (1$\bar{1}$0), and "(9,0,26)" faces; the other by ($\bar{1}$10) and ($\bar{1}\bar{1}$0). Perpendicular distances (in mm) of faces from the point of intersection of (034), (0$\bar{3}$4), and "(9,0,26)" were 0.170 for "($\bar{1}$,0,$\overline{27}$)", 0.151 for (0$\bar{3}$4), 0.155 for (0$\bar{3}\bar{4}$), 0.198 for ($\bar{1}$,±1,0), and 0.150 for (1,±1,0).

The crystal was mounted on a glass fiber on a eucentric goniometer. The material is air stable indefinitely but slowly decomposes upon exposure to x rays.

Preliminary photographic data yielded approximate cell dimensions, indicated C_{2h} Laue symmetry, and revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ is thereby indicated. The crystal was transferred to a Picker FACS-1 automated diffractometer, was accurately centered, and (to avoid the possible problems of multiple-diffraction) was oriented with [20$\bar{3}$] offset by ~4.9° from coincidence with the ϕ axis. Unit cell measurement and data collection were carried out as described previously;[7] details are given in Table I.

Following data collection, the $H_2Os_3(CO)_{10}(PPh_3)$ crystal was realigned with [10$\bar{2}$] coincident with the ϕ axis. Measurement of the axial 10$\bar{2}$ and 20$\bar{4}$ reflections via θ–2θ scans at 10° intervals from ϕ = 0° to ϕ = 350° showed variations of 33.0% and 31.1%, respectively. [Variation (%) = 100 × (maximum − minimum)/average.] These "ϕ-scan" data were corrected for absorption along with the primary data set. Variations were thereby reduced to the very acceptable values of 1.5% and 4.4%, respectively.

Solution and Refinement of the Structure

Programs used during the course of the 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;[8a] $\Delta f'$ and $\Delta f''$ were included for all atoms, using the values of Cromer and Liberman.[8b]

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 in eq 3 and 4. The "goodness-of-fit" (GOF) is defined in eq 5, where m is the number of observations and n is the number of variables.

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

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

$$\mathrm{GOF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{m - n}\right]^{1/2} \tag{5}$$

The structural analysis was begun using data which had yet to be corrected for absorption. The positions of the three independent osmium atoms were quickly and unambiguously determined from a three-dimensional Patterson map. Refinement of the scale factor and positional and anisotropic thermal parameters for the osmium atoms (28 parameters in all) converged with $R_F = 17.7\%$ and $R_{wF} = 24.2\%$. A difference-Fourier synthesis led to location of all 39 remaining nonhydrogen atoms. A structure factor calculation based upon the unrefined coordinates, with all isotropic thermal parameters set at 3.5 Å^2, yielded $R_F = 11.2\%$ and $R_{wF} = 11.7\%$. Refinement of the scale factor, all positional parameters for nonhydrogen atoms, anisotropic thermal parameters for osmium atoms, and isotropic thermal parameters for all phosphorus, carbon, and oxygen atoms (184 parameters in all) led to convergence with $R_F = 6.38\%$ and $R_{wF} = 6.48\%$.

At this point all data were corrected for the effects of absorption; those 17 data with $(\sin\theta)/\lambda \leq 0.086$ were found to be in need of a "β-filter correction" and were corrected graphically as described previously.[7] Continued refinement (184 parameters, as above) converged with $R_F = 5.54\%$ and $R_{wF} = 5.82\%$. A difference-Fourier synthesis now indicated that anisotropic thermal parameters were required for nonhydrogen atoms. These were introduced. Due to the large number of parameters now involved (379—9 from each of 42 atoms + the scale factor), full-matrix least-squares refinement was no longer possible. Each "cycle" now consisted of two steps: (1) parameters for all atoms other than those of carbon atoms of the phenyl rings were refined and (2) parameters for all atoms other than those in carbonyl ligands were refined. Three such cycles led to convergence with $R_F = 4.95\%$ and $R_{wF} = 5.23\%$ (or $R_F = 4.88\%$ and $R_{wF} = 4.05\%$ upon rejection of the reflections 024, 031, and 121). We now carefully remeasured the intensities of the ten reflections for which the disagreement between $|F_o|$ and $|F_c|$ was more than 6.0σ. These data were scaled by remeasuring the standards also. The three reflections listed above *had* originally been mismeasured (due, apparently, to dropped digits on a teletype output!). Continued refinement (3 more "cycles") using the corrected data led to $R_F = 4.61\%$ and $R_{wF} = 3.68\%$. At this stage we attempted systematically to locate all hydrogen atoms. Three difference-Fourier syntheses were run, based on different $(\sin\theta)/\lambda$ cutoffs of data.[9]

Table I. Experimental Data for the X-Ray Diffraction Study of $H_2Os_3(CO)_{10}(PPh_3)$

(A) Crystal Parameters[a] at 20 °C

Crystal system: monoclinic
$a = 9.1256\ (18)$ Å
$b = 13.3342\ (24)$ Å
$c = 25.1056\ (40)$ Å
$\beta = 103.45\ (1)°$
$V = 2971.1\ (10)$ Å^3

Space group: $P2_1/c$ (C_{2h}^5; No. 14)
$Z = 4$
Mol wt 1115.0
ρ(calcd) = 2.493 g cm^{-3}
ρ(obsd)[b] = 2.51(2) g cm^{-3}

(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(peak) > 10^4 counts/s
Takeoff angle: 3.0°
Detector aperture: 6.3 mm × 6.3 mm
Crystal–detector distance: 330 mm
Crystal orientation: ϕ axis = 4.9° from $20\bar{3}$
Reflections measd: $+h, +k, \pm l$
Maximum 2θ: 48°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: 1.0°/min for $2\theta \leqslant 35°$, 2°/min for $35° < 2\theta \leqslant 48°$
Scan length: $\Delta(2\theta) = (0.90 + 0.692 \tan\theta)°$, starting 0.45° below the Mo Kα_1 peak
Background measurement: Stationary crystal, stationary counter; 20 s each at beginning and end of 2θ scan for $2\theta \leqslant 35°$; 10 s each for $35° < 2\theta \leqslant 48°$
Std reflections: three remeasured after every 48 reflections; rms deviations (after application of an anisotropic linear decay correction)[c] were 1.3% for 060, 1.2% for $31\bar{1}$, and 1.4% for 004
Reflections collected: 4698 independent measurements and 237 systematic absences

(C) Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 7, using an "ignorance factor" of $p = 0.03$
Absorption coeff: $\mu = 129.2$ cm^{-1}; maximum and minimum transmission factors[d] were 0.205 and 0.293, respectively

[a] Unit cell parameters are from a least-squares fit to the setting angles of the Mo Kα_1 peaks (λ 0.709 300 Å) of 12 reflections with $2\theta = 45$–$52°$). [b] The density was measured by neutral buoyancy in a mixture of *sym*-tetrabromoethane and carbon tetrachloride. [c] Data reduction and analysis, including decay correction, were performed using the Fortran IV program RDUS2, by B. G. DeBoer. In the course of data collection, the standard reflections declined to 82%, 82%, and 88% of their initial intensities for 060, $31\bar{1}$, and 004, respectively. [d] Absorption corrections were applied using the program DRABZ, by B. G. DeBoer.

(1) All 4698 data were used. The largest peak, of height 1.26 e Å^{-3}, was ~0.8 Å from Os(2) in the orientation expected for the *terminal* hydride ligand; peak 7 (height 0.86 e Å^{-3}) was consistent with the position for a bridging hydride ligand. Peaks 2–6 were all close to the osmium atoms. Little useful information was obtained from this map.

(2) Those 1072 data with $(\sin\theta)/\lambda \leq 0.35$ were used. The highest peak (0.57 e Å^{-3}) corresponded to the terminal hydride ligand; the second highest peak (0.48 e Å^{-3}) corresponded to the bridging hydride ligand. Peaks 3–15 (heights 0.37–0.23 e Å^{-3}) consisted of 10 correctly positioned phenyl hydrogens and 3 "background features".

(3) Those 672 data with $(\sin\theta)/\lambda \leq 0.30$ were used. The highest and second highest peaks (0.48 and 0.42 e Å^{-3}) corresponded, respectively, to the terminal and bridging hydride ligands, 10 of the phenyl hydrogens appeared in peaks 3–16 (height 0.28–0.20 e Å^{-3}) and the remaining 5 appeared in peaks 17–33 (height 0.19–0.13 e Å^{-3}).

The hydride ligands were thus clearly located and the hydrogens of the phenyl groups were at least "indicated". We continued refinement with H(T) and H(B) in their observed positions and with all phenyl hydrogens assigned calculated positions (d(C–H) = 0.95 Å[10] with C→H vectors fanning out from the centroid of the aromatic ring). Positional and isotropic thermal parameters of the hydride ligands were refined, as were the isotropic thermal parameters of the phenyl hydrogens. [Positional changes of these latter atoms were, however, coupled to those of their attached carbon atoms—i.e., we treated each C–H system as a rigid nonrotating group.] A secondary extinction correction was also included in the refinement at this point. Continued refinement (403 parameters in all), in two "blocks" as before, led to final convergence in four "cycles" with $R_F = 4.383\%$, $R_{wF} = 3.274\%$, and GOF = 0.962. A final cycle of refinement of all positional parameters (for use in determining a full positional correlation matrix) showed no changes in discrepancy indices. The function $\sum w(|F_o| - |F_c|)^2$ showed no systematic variations as a function of $|F_o|$ or $(\sin\theta)/\lambda$. The weighting scheme was thus declared satisfactory.

A difference-Fourier synthesis based upon all data showed maxima and minima of +1.21 and −0.83 e Å^{-3}, both close to osmium positions. The analysis is thus both correct and complete. The structure was now refined to convergence with H(T) and H(B) both omitted, leading to $R_F = 4.446\%$ and $R_{wF} = 3.400\%$. Application of the Hamilton R-factor ratio test[11] shows that the improvement in R_{wF} (by a factor of 1.038), on incorporating the hydride ligands, is meaningful at a level of confidence far greater than 99.5%.

Finally, with H(T) and H(B) both omitted from the structure factor calculation, we calculated a difference-Fourier synthesis based on the 672 data with $(\sin\theta)/\lambda \leq 0.30$. The atoms H(T) and H(B) had peak heights of 0.49 and 0.44 e Å^{-3}. The appearance of these features is illustrated in Figure 1.

The final value of the secondary extinction coefficient (c) was 1.88 (13) × 10^{-6} mm^{-1} e^{-2}. This variable enters the expression for the corrected calculated structure factor ($F_{c,cor}$) as shown in eq 6, where

$$F_{c,\mathrm{cor}} = F_{c,\mathrm{uncor}}(1.0 + c\beta F^2{}_{c,\mathrm{uncor}})^{-1/4} \tag{6}$$

β is defined by eq 7.[12]

$$\beta = \left[\frac{1.0 + \cos^4 2\theta}{(\sin 2\theta)(1.0 + \cos^2 2\theta)}\right]\left(\frac{-\mathrm{d}\ln T}{\mathrm{d}\mu}\right) \tag{7}$$

Final positional parameters are collected in Table II; anisotropic thermal parameters are listed in Table III. A list of observed and

Table II. Final Positional Parameters with Esd's[a] for $H_2Os_3(CO)_{10}(PPh_3)$

Atom	*x*	*y*	*z*	*B*,[b] Å^2
Os(1)	0.24387 (3)	0.17643 (2)	0.116519 (12)	3.283
Os(2)	0.39383 (3)	−0.00193 (2)	0.180883 (13)	3.581
Os(3)	0.07277 (3)	0.00621 (2)	0.142884 (13)	3.499
P	0.37566 (21)	0.31094 (13)	0.08724 (8)	3.39
C(11)	0.2440 (8)	0.2378 (5)	0.1849 (3)	3.9
O(11)	0.2466 (7)	0.2741 (4)	0.2264 (2)	5.4
C(12)	0.2644 (10)	0.1000 (6)	0.0527 (4)	5.4
O(12)	0.2824 (9)	0.0592 (5)	0.0154 (3)	8.3
C(13)	0.0556 (9)	0.2320 (6)	0.0808 (3)	4.6
O(13)	−0.0584 (7)	0.2644 (5)	0.0594 (2)	6.5
C(21)	0.3938 (8)	0.0552 (6)	0.2530 (3)	4.0
O(21)	0.4017 (7)	0.0867 (5)	0.2955 (2)	6.0
C(23)	0.6050 (10)	−0.0064 (5)	0.1953 (4)	4.8
O(23)	0.7343 (7)	−0.0096 (5)	0.2062 (3)	7.1
C(24)	0.3783 (9)	−0.1358 (6)	0.2002 (3)	5.0
O(24)	0.3666 (7)	−0.2194 (4)	0.2093 (3)	6.8
C(31)	0.0666 (8)	0.0733 (5)	0.2119 (3)	3.9
O(31)	0.0587 (6)	0.1074 (4)	0.2523 (2)	5.3
C(32)	0.1062 (9)	−0.0651 (6)	0.0797 (4)	5.0
O(32)	0.1146 (8)	−0.1140 (5)	0.0428 (3)	7.1
C(33)	0.0204 (9)	−0.1147 (6)	0.1724 (3)	4.5
O(33)	−0.0123 (7)	−0.1878 (4)	0.1900 (2)	6.6
C(34)	−0.1262 (9)	0.0503 (6)	0.1068 (3)	4.7
O(34)	−0.2445 (6)	0.0749 (5)	0.0869 (2)	6.2
C(1a)	0.3831 (9)	0.2930 (5)	0.0154 (3)	3.9
C(2a)	0.5112 (10)	0.2630 (9)	0.0017 (4)	6.9
C(3a)	0.5113 (12)	0.2421 (10)	−0.0535 (4)	8.8
C(4a)	0.3822 (12)	0.2483 (8)	−0.0918 (4)	7.2
C(5a)	0.2560 (10)	0.2778 (7)	−0.0785 (3)	6.0
C(6a)	0.2513 (10)	0.2984 (6)	−0.0262 (3)	5.2
C(1b)	0.5706 (8)	0.3389 (5)	0.1206 (3)	3.5
C(2b)	0.6396 (9)	0.4245 (6)	0.1078 (4)	5.5
C(3b)	0.7883 (9)	0.4464 (7)	0.1325 (4)	5.6
C(4b)	0.8664 (9)	0.3829 (6)	0.1712 (4)	5.4
C(5b)	0.8011 (10)	0.2988 (6)	0.1852 (4)	5.8
C(6b)	0.6537 (9)	0.2757 (6)	0.1601 (3)	4.6
C(1c)	0.2873 (8)	0.4339 (5)	0.0904 (3)	3.5
C(2c)	0.2675 (10)	0.4663 (6)	0.1402 (3)	5.4
C(3c)	0.2060 (9)	0.5592 (6)	0.1456 (4)	5.7
C(4c)	0.1622 (10)	0.6182 (7)	0.1014 (4)	6.9
C(5c)	0.1814 (13)	0.5888 (7)	0.0528 (4)	9.2
C(6c)	0.2453 (12)	0.4964 (6)	0.0472 (4)	6.7
H(T)	0.3834 (75)	−0.0351 (49)	0.1223 (27)	5.1 (16)
H(B)	0.4210 (62)	0.1335 (42)	0.1507 (22)	3.5 (13)
H(2a)	0.6006	0.2576	0.0299	8.1 (25)
H(3a)	0.6017	0.2223	−0.0632	15.6 (51)
H(4a)	0.3819	0.2329	−0.1288	7.2 (27)
H(5a)	0.1665	0.2831	−0.1067	4.3 (19)
H(6a)	0.1598	0.3180	−0.0173	2.7 (15)
H(2b)	0.5836	0.4688	0.0811	4.2 (17)
H(3b)	0.8352	0.5050	0.1229	7.0 (28)
H(4b)	0.9682	0.3975	0.1886	2.5 (14)
H(5b)	0.8574	0.2551	0.2123	6.2 (21)
H(6b)	0.6083	0.2165	0.1700	5.1 (21)
H(2c)	0.2977	0.4236	0.1711	12.1 (34)
H(3c)	0.1931	0.5814	0.1802	16.4 (47)
H(4c)	0.1186	0.6819	0.1050	6.2 (20)
H(5c)	0.1506	0.6322	0.0223	5.8 (22)
H(6c)	0.2588	0.4748	0.0126	8.0 (34)

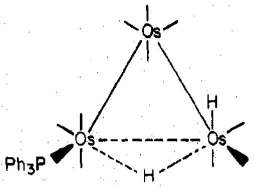
[a] Esd's (estimated standard deviations), right-adjusted to the last digit of the preceding number, are shown in parentheses. They are calculated from the inverse of the least-squares matrix for the last cycle in which that particular parameter was refined. [b] For nonhydrogen atoms, so-called "equivalent" isotropic thermal parameters are listed. For anisotropic thermal parameters see Table III.

calculated structure factor amplitudes is available as supplementary material.

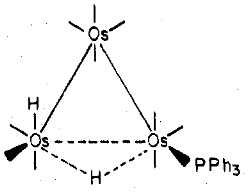
Results and Discussion

The crystal consists of discrete molecular units of $H_2Os_3(CO)_{10}(PPh_3)$ which are mutually separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. The geometry of the $H_2Os_3(CO)_{10}(PPh_3)$ molecule and the system used for labeling atoms are shown in Figures 2 and 3. Interatomic distances and their estimated standard deviations (esd's) are collected in Table IV; bond angles, with esd's, are compiled in Table V.

The $H_2Os_3(CO)_{10}(PPh_3)$ molecule is closely related both to $H_2Os_3(CO)_{11}$[1] and to $Os_3(CO)_{12}$.[1] The three osmium atoms define a triangular cluster of metal atoms. Each osmium atom is associated with four terminal ligands—Os(1) with three carbonyl and one triphenylphosphine ligand, Os(2) with three carbonyl and one terminal hydride ligand [H(T)], and Os(3) with four carbonyl ligands; in addition, the Os(1)–Os(2) vector is bridged by a μ_2-bridging hydride ligand [H(B)]. The $H_2Os_3(CO)_{10}(PPh_3)$ molecule contains no improper rotation axis (S_n). The molecule is therefore chiral. However, the crystal consists of an ordered racemic array of the enantiomers IV and V by virtue of crystallographic S_2 ($\bar{1}$) and *c*-glide operations. The triphenylphosphine ligand takes up the *equatorial* site on Os(1) adjacent to the bridging hydride ligand. (Equatorial sites are, of course, less sterically crowded than axial sites on a trinuclear species of quasi-D_{3h} symmetry.) The terminal hydride ligand occupies an axial site on Os(2).



IV



V

As outlined above, and as indicated specifically in Figure 1, both terminal and bridging hydride ligands were located directly from the structural study. The osmium–(terminal hydride) distance, Os(2)–H(T), was determined as 1.52 (7) Å. On the basis of realistic estimates of covalent radii [r(Os) = 1.44 Å, from Os–Os (average) = 2.877 (3) Å in $Os_3(CO)_{12}$;[1] r(H) = 0.30 Å[13]] one predicts an Os–H distance of 1.74 Å. The observed contraction of ~0.22 Å from this value unfortunately represents a difference of only about 3σ and could be due to (i) statistical deviations, (ii) noncoincidence of the hydrogen nucleus with the centroid of electron density of the hydrogen atom, or (iii) some combination of (i) and (ii).

We note here that a neutron-diffraction study of $H_4Os(PMe_2Ph)_3$[14] yields Os–H(terminal) bond lengths of 1.644 (3), 1.648 (3), 1.663 (3), and 1.681 (3) Å.

The μ_2-bridging hydride ligand, H(B), is associated with the distances Os(1)–H(B) = 1.74 (6) Å and Os(2)–H(B) = 2.00 (6) Å [average 1.87 Å] and an Os(1)–H(B)–Os(2) angle of 107.5 (28)°.

The effect of the μ_2-bridging hydride on osmium–osmium distances and upon interligand angles within the $H_2Os_3(CO)_{10}(PPh_3)$ molecule can be seen in Figure 4. Comparisons with our previous determination of $H_2Os_3(CO)_{11}$[1] are also pertinent. Specific points are as follows.

(i) The μ_2-hydrido-bridged osmium–osmium vector, Os(1)–Os(2), is 3.0185 (6) Å in length and is expanded by 0.1277 Å relative to the average nonbridged osmium–osmium bond length of 2.8908 Å in this molecule and by 0.1414 Å relative to the average osmium–osmium bond length of 2.8771 [27] Å[15] in $Os_3(CO)_{12}$.[1] [Analogous osmium–osmium distances within the $H_2Os_3(CO)_{11}$ molecule are Os–Os (average) = 2.8835 Å and Os–(H)–Os = 2.9886 (9) Å; Δ = 0.1051 Å.][1]

(ii) Equatorial ligands in positions adjacent to H(B) are repelled from the position of H(B). Thus, the angles Os(2)–Os(1)–P = 124.25 (5)° and Os(1)–Os(2)–C(23) = 116.4 (2)° are each more than 16° larger than any other equatorial cis Os–Os–CO angle in the molecule [the range of other such angles is 86.4 (2)–99.8 (2°)].

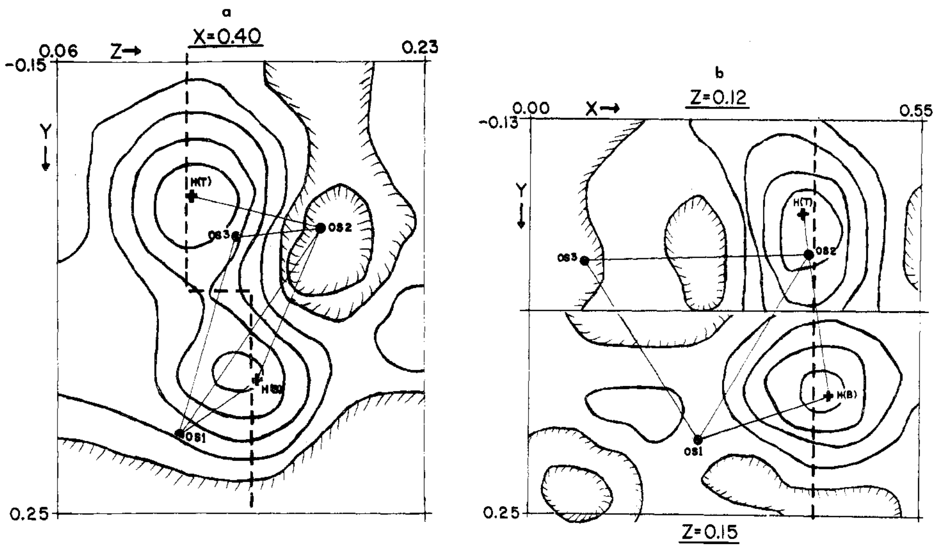


Figure 1. Sections of a difference-Fourier synthesis calculated from structure factors based upon the final parameters of all atoms except H(T) and H(B), using the 672 data for which $(\sin\theta)/\lambda \leq 0.30$. The contour interval is 0.10 e $Å^{-3}$, zero and negative contours being hachured. Final positions of osmium atoms and hydride ligands, as obtained from least-squares refinement using the entire data set, are marked with circles and crosses, respectively. The heavy dashed line marks the intersection of the two maps. (a) The section at $x = 0.40$ is shown. (b) The top half of this diagram is the $z = 0.12$ section and the bottom half is the $z = 0.15$ section. The y axis is continuous and runs vertically.

Table III. Final Anisotropic Thermal Parameters[a,b] for $H_2Os_3(CO)_{10}(PPh_3)$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[c]
Os(1)	3.744 (15)	2.832 (13)	3.228 (14)	0.010 (11)	0.720 (10)	0.129 (11)	0.188, 0.203, 0.219
Os(2)	3.410 (15)	3.134 (15)	4.267 (16)	0.461 (11)	1.029 (12)	0.294 (11)	0.188, 0.213, 0.235
Os(3)	3.382 (15)	3.177 (15)	3.893 (16)	−0.148 (11)	0.754 (12)	−0.066 (11)	0.198, 0.209, 0.223
P	3.54 (9)	3.17 (8)	3.17 (8)	0.15 (7)	0.63 (7)	0.39 (7)	0.190, 0.213, 0.218
C(11)	4.2 (4)	3.4 (4)	3.7 (4)	−0.5 (3)	0.2 (3)	−0.1 (13)	0.19, 0.21, 0.25
O(11)	7.9 (4)	4.4 (3)	4.2 (3)	−0.2 (3)	1.7 (3)	−0.3 (2)	0.22, 0.24, 0.32
C(12)	7.5 (6)	4.1 (4)	4.7 (5)	−0.4 (4)	1.5 (4)	−0.3 (4)	0.22, 0.24, 0.31
O(12)	14.6 (6)	5.8 (4)	5.3 (4)	−2.5 (4)	3.8 (4)	−1.9 (3)	0.21, 0.28, 0.44
C(13)	4.3 (4)	4.7 (4)	4.5 (4)	−0.8 (4)	0.6 (4)	0.4 (3)	0.22, 0.23, 0.27
O(13)	4.9 (3)	7.6 (4)	6.3 (4)	1.0 (3)	−0.2 (3)	2.0 (3)	0.21, 0.30, 0.34
C(21)	3.4 (4)	4.3 (4)	4.0 (4)	0.1 (3)	0.4 (3)	0.5 (3)	0.20, 0.22, 0.25
O(21)	6.4 (4)	7.6 (4)	3.9 (3)	0.8 (3)	0.8 (3)	−0.4 (3)	0.22, 0.28, 0.32
C(23)	4.8 (5)	4.7 (4)	5.6 (5)	0.4 (4)	2.5 (4)	1.2 (3)	0.20, 0.23, 0.30
O(23)	3.9 (3)	8.9 (4)	8.9 (4)	1.0 (3)	2.5 (3)	2.2 (3)	0.21, 0.29, 0.38
C(24)	4.6 (4)	3.9 (4)	6.4 (5)	0.5 (3)	1.5 (4)	1.2 (4)	0.21, 0.24, 0.30
O(24)	8.8 (4)	3.9 (3)	8.5 (4)	0.6 (3)	2.6 (3)	1.1 (3)	0.22, 0.31, 0.34
C(31)	3.1 (4)	3.2 (4)	5.2 (5)	−0.4 (3)	0.4 (3)	0.3 (3)	0.19, 0.21, 0.27
O(31)	6.2 (3)	5.3 (3)	4.6 (3)	−0.3 (2)	1.7 (3)	−1.1 (2)	0.22, 0.27, 0.29
C(32)	4.2 (4)	4.7 (4)	6.3 (5)	0.0 (3)	1.5 (4)	0.4 (4)	0.23, 0.24, 0.29
O(32)	8.7 (4)	6.6 (4)	6.5 (4)	−1.0 (3)	2.6 (3)	−3.1 (3)	0.21, 0.32, 0.36
C(33)	4.7 (4)	4.7 (4)	3.8 (1)	−0.4 (4)	0.7 (3)	−0.1 (3)	0.22, 0.24, 0.26
O(33)	8.1 (4)	5.1 (3)	6.0 (3)	−2.3 (3)	0.4 (3)	0.5 (3)	0.22, 0.27, 0.36
C(34)	4.6 (5)	4.4 (4)	5.0 (5)	−0.2 (4)	0.8 (4)	−0.1 (3)	0.23, 0.24, 0.26
O(34)	4.7 (3)	7.5 (4)	5.9 (3)	1.2 (3)	−0.1 (3)	−0.1 (3)	0.22, 0.29, 0.33
C(1a)	4.5 (4)	3.8 (4)	3.4 (4)	−0.7 (3)	1.1 (3)	0.7 (3)	0.18, 0.22, 0.25
C(2a)	4.7 (5)	10.8 (8)	5.3 (5)	1.7 (5)	1.5 (4)	−1.1 (5)	0.22, 0.26, 0.38
C(3a)	7.3 (7)	12.9 (9)	6.9 (7)	1.0 (6)	2.7 (6)	−3.3 (7)	0.23, 0.31, 0.43
C(4a)	9.8 (8)	8.1 (6)	3.4 (5)	−1.1 (6)	0.9 (5)	−1.1 (4)	0.20, 0.32, 0.36
C(5a)	6.6 (6)	7.5 (6)	3.4 (5)	0.0 (5)	0.1 (4)	−0.3 (4)	0.20, 0.30, 0.31
C(6a)	4.6 (5)	7.0 (5)	4.2 (4)	−0.5 (4)	1.1 (4)	−0.7 (4)	0.23, 0.24, 0.30
C(1b)	3.9 (4)	3.1 (3)	3.2 (3)	0.4 (3)	−0.1 (3)	−0.2 (3)	0.19, 0.19, 0.25
C(2b)	3.9 (4)	4.6 (4)	7.3 (5)	−0.4 (4)	−0.5 (4)	1.5 (4)	0.21, 0.22, 0.34
C(3b)	4.1 (5)	5.2 (5)	8.0 (6)	−0.8 (4)	2.2 (4)	0.6 (4)	0.20, 0.27, 0.32
C(4b)	3.5 (4)	5.1 (5)	6.9 (5)	0.0 (4)	0.0 (4)	−1.1 (4)	0.20, 0.24, 0.32
C(5b)	5.2 (5)	5.5 (5)	5.8 (5)	0.8 (4)	−0.7 (4)	0.2 (4)	0.22, 0.27, 0.32
C(6b)	4.7 (5)	4.2 (4)	4.3 (4)	0.3 (4)	−0.4 (3)	0.3 (3)	0.20, 0.23, 0.28
C(1c)	3.6 (4)	3.2 (3)	3.5 (4)	0.5 (3)	0.3 (3)	0.4 (3)	0.18, 0.22, 0.23
C(2c)	8.0 (6)	3.4 (4)	4.8 (5)	−0.7 (4)	1.9 (4)	−0.2 (4)	0.20, 0.24, 0.32
C(3c)	6.2 (5)	3.6 (4)	7.5 (6)	1.1 (4)	2.0 (5)	−0.4 (4)	0.20, 0.29, 0.31
C(4c)	5.6 (5)	4.7 (5)	9.9 (8)	2.5 (4)	0.6 (5)	−0.9 (5)	0.18, 0.30, 0.38
C(5c)	14.5 (10)	5.7 (6)	5.6 (6)	4.8 (6)	−1.3 (6)	−0.2 (5)	0.21, 0.26, 0.49
C(6c)	8.6 (7)	6.1 (6)	5.0 (5)	2.8 (5)	0.9 (5)	0.3 (4)	0.23, 0.26, 0.37

[a] These are in units of $Å^2$ and enter the structure factor equation in the form $\exp[-0.25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$. [b] See footnote *a* to Table II. [c] These are the rms amplitudes of vibration (in Å) along the principal axes of the thermal-motion tensor. For orientations, see the figures.

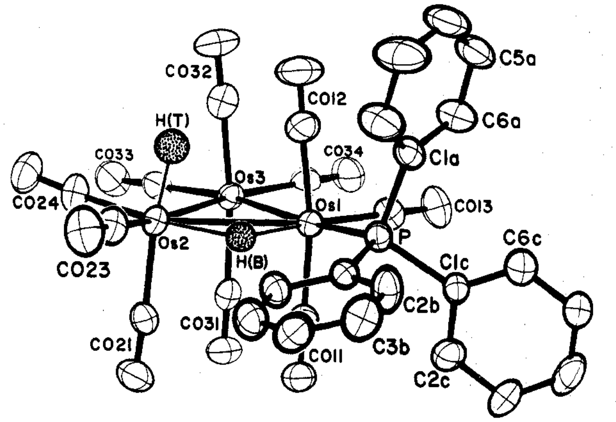


Figure 2. The $H_2Os_3(CO)_{10}(PPh_3)$ molecule, viewed from a direction 75° from the normal to the triosmium plane. [ORTEP diagram, 30% ellipsoids; hydride ligands strippled]. Please note that (for ease of comparison with figures in our previous publications—see ref 1 and 2) the molecule illustrated here and in Figure 3 is that related to the molecule described in the list of atomic positions (Table II) by crystallographic $\bar{1}$ or *c*-glide operations.

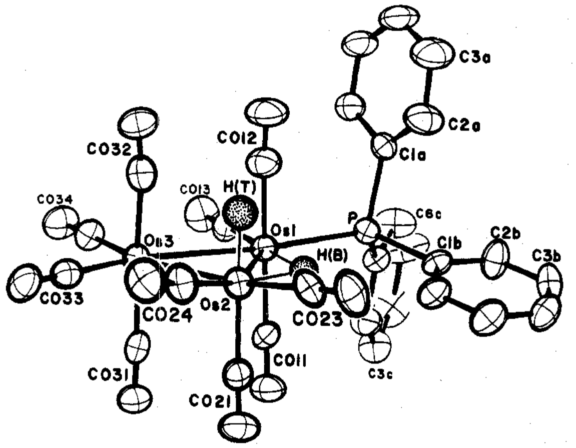


Figure 3. Another view of the $H_2Os_3(CO)_{10}(PPh_3)$ molecule.

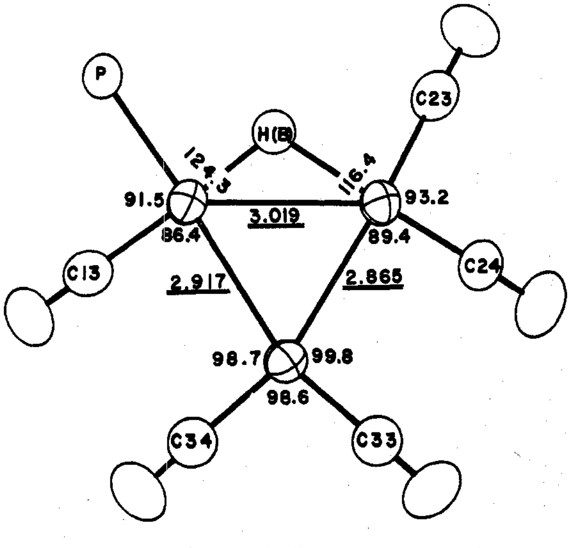


Figure 4. Distribution of equatorial ligands in the $H_2Os_3(CO)_{10}(PPh_3)$ molecule. Interatomic distances are in Å and are underlined. All other numerical values are angles (in degrees).

Table IV. Interatomic Distances (Å), with Esd's,[a] for $H_2Os_3(CO)_{10}(PPh_3)$

(A) Osmium-Osmium, Osmium-Phosphorus, and Osmium-Hydrogen			
Os(1)-Os(2)	3.0185 (6)	Os(1)-H(B)	1.74 (6)
Os(1)-Os(3)	2.9170 (5)	Os(2)-H(B)	2.00 (6)
Os(2)-Os(3)	2.8645 (7)	Os(2)-H(T)	1.52 (7)
Os(1)-P	2.370 (2)		
(B) Osmium-Carbon (Axial)			
Os(1)-C(11)	1.902 (8)	Os(3)-C(31)	1.961 (8)
Os(1)-C(12)	1.943 (9)	Os(3)-C(32)	1.933 (9)
Os(2)-C(21)	1.965 (8)		
(C) Osmium-Carbon (Equatorial)			
Os(1)-C(13)	1.894 (8)	Os(3)-C(33)	1.883 (8)
Os(2)-C(23)	1.878 (9)	Os(3)-C(34)	1.923 (8)
Os(2)-C(24)	1.864 (8)		
(D) Carbon-Oxygen (Axial)			
C(11)-O(11)	1.144 (8)	C(31)-O(31)	1.130 (8)
C(12)-O(12)	1.129 (9)	C(32)-O(32)	1.150 (9)
C(21)-O(21)	1.131 (8)		
(E) Carbon-Oxygen (Equatorial)			
C(13)-O(13)	1.139 (8)	C(33)-O(33)	1.137 (8)
C(23)-O(23)	1.148 (9)	C(34)-O(34)	1.127 (8)
C(24)-O(24)	1.147 (8)		
(F) Phosphorus-Carbon			
P-C(1a)	1.837 (7)	P-C(1c)	1.838 (7)
P-C(1b)	1.820 (7)		
(G) C-C (Phenyl)			
C(1a)-C(2a)	1.354 (10)	C(4a)-C(5a)	1.331 (12)
C(2a)-C(3a)	1.414 (12)	C(5a)-C(6a)	1.353 (10)
C(3a)-C(4a)	1.338 (13)	C(6a)-C(1a)	1.399 (10)
C(1b)-C(2b)	1.377 (10)	C(4b)-C(5b)	1.355 (11)
C(2b)-C(3b)	1.385 (11)	C(5b)-C(6b)	1.381 (11)
C(3b)-C(4b)	1.359 (11)	C(6b)-C(1b)	1.386 (9)
C(1c)-C(2c)	1.373 (10)	C(4c)-C(5c)	1.331 (12)
C(2c)-C(3c)	1.379 (11)	C(5c)-C(6c)	1.384 (11)
C(3c)-C(4c)	1.343 (12)	C(6c)-C(1c)	1.350 (10)

[a] Esd's (see footnote *a* to Table II) were calculated from the full covariance matrix generated in the final cycle of least-squares refinement, plus contributions from the uncertainties in the unit cell parameters, using the program STAN1. No corrections for the systematic errors due to thermal motion have been applied.

(iii) The cis-diequatorial angles P–Os(1)–C(13) = 91.5 (2)° and C(23)–Os(2)–C(24) = 93.2 (3)° are each contracted significantly relative to the C(33)–Os(3)–C(34) angle of 98.6 (3)°, providing further evidence of the net compressional effect of H(B) on other angles within the equatorial plane.

(iv) The compression of equatorial angles propagates even further around the Os_3 ring, causing the pair of angles Os(3)–Os(1)–C(13) and Os(3)–Os(2)–C(24) [86.4 (2) and 89.4 (2)°] to be contracted by some 10° relative to the corresponding pair of Os–Os–CO(cis) angles associated with Os(3)—viz., Os(1)–Os(3)–C(34) = 98.7 (2)° and Os(2)–Os(3)–C(33) = 99.8 (2)°.

Least-squares planes in $H_2Os_3(CO)_{10}(PPh_3)$ are given in Table VI. As can be seen from plane I, most of the equatorial ligands are slightly displaced from the Os_3 plane. This presumably results from the presence of the (small) axial hydride ligand, H(T), since most equatorial ligands are displaced in the direction of this atom to accommodate the extra "space" in the coordination surface. The greatest deviations of equatorial ligands from this plane are 0.596 (6) Å for O(24), 0.328 (8) Å for C(24), 0.330 (7) Å for O(23), 0.231 (8) Å for C(23), and 0.181 (2) Å for P. The bridging hydride ligand lies –0.07 (6) Å from the Os_3 plane—i.e., is coplanar with the triosmium triangle, within the limits of experimental error.

The mutually trans axial osmium–carbonyl distances range from 1.902 (8) Å to 1.961 (8) Å, averaging 1.935 [12] Å;[15] equatorial osmium–carbonyl distances range from 1.864 (8) to 1.923 (8) Å, averaging 1.888 [10] Å. The difference {Os–Co(ax)} – {Os–CO(eq)} = +0.047 ± 0.016 Å is the result

Table V. Interatomic Angles (deg), with Esd's,[a] for $H_2Os_3(CO)_{10}(PPh_3)$.

(A) Angles within Os_3 Triangle			
Os(2)–Os(1)–Os(3)	57.68 (2)	Os(1)–Os(3)–Os(2)	62.94 (1)
Os(1)–Os(2)–Os(3)	59.38 (1)		
(B) Angles Involving H(T)			
H(T)–Os(2)–Os(1)	78.0 (25)	H(T)–Os(2)–C(21)	173.2 (33)
H(T)–Os(2)–Os(3)	81.9 (25)	H(T)–Os(2)–C(23)	90.5 (25)
H(T)–Os(2)–H(B)	83.2 (29)	H(T)–Os(2)–C(24)	89.0 (25)
(C) Angles Involving H(B)			
Os(1)–H(B)–Os(2)	107.5 (28)	H(B)–Os(1)–C(11)	83.8 (18)
H(B)–Os(1)–Os(2)	39.1 (19)	H(B)–Os(1)–C(12)	88.7 (18)
H(B)–Os(2)–Os(1)	33.4 (16)	H(B)–Os(1)–C(13)	176.1 (31)
H(B)–Os(1)–Os(3)	96.7 (18)	H(B)–Os(2)–C(21)	91.5 (16)
H(B)–Os(2)–Os(3)	92.7 (16)	H(B)–Os(2)–C(23)	83.6 (16)
H(B)–Os(1)–P	85.5 (18)	H(B)–Os(2)–C(24)	171.5 (18)
(D) Os–Os–CO(eq) and Os–Os–P(eq)			
Os(2)–Os(1)–P	124.25 (5)	Os(2)–Os(1)–C(13)	144.1 (2)
Os(1)–Os(2)–C(23)	116.4 (2)	Os(1)–Os(2)–C(24)	147.3 (3)
Os(3)–Os(1)–C(13)	86.4 (2)	Os(3)–Os(1)–P	175.18 (5)
Os(3)–Os(2)–C(24)	89.4 (2)	Os(3)–Os(2)–C(23)	171.9 (3)
Os(1)–Os(3)–C(34)	98.7 (2)	Os(1)–Os(3)–C(33)	162.6 (2)
Os(2)–Os(3)–C(33)	99.8 (2)	Os(2)–Os(3)–C(34)	161.6 (2)
(E) OC(eq)–Os–CO(eq) and OC(eq)–Os–P(eq)			
P–Os(1)–C(13)	91.5 (2)	C(33)–Os(3)–C(34)	98.6 (3)
C(23)–Os(2)–C(24)	93.2 (3)		
(F) Os–Os–CO(ax)			
Os(2)–Os(1)–C(11)	87.2 (2)	Os(1)–Os(3)–C(31)	88.4 (2)
Os(3)–Os(1)–C(11)	91.0 (2)	Os(2)–Os(3)–C(31)	87.7 (2)
Os(2)–Os(1)–C(12)	84.8 (3)	Os(1)–Os(3)–C(32)	90.1 (2)
Os(3)–Os(1)–C(12)	86.5 (2)	Os(2)–Os(3)–C(32)	84.9 (2)
Os(1)–Os(2)–C(21)	95.2 (2)		
Os(3)–Os(2)–C(21)	94.2 (2)		
(G) OC(ax)–Os–CO(eq) and OC(ax)–Os–P(eq)			
C(11)–Os(1)–C(13)	94.0 (3)	C(31)–Os(3)–C(33)	88.9 (3)
C(11)–Os(1)–P	93.5 (2)	C(31)–Os(3)–C(34)	93.4 (3)
C(12)–Os(1)–C(13)	93.7 (4)	C(32)–Os(3)–C(33)	90.3 (3)
C(12)–Os(1)–P	89.3 (2)	C(32)–Os(3)–C(34)	94.3 (3)
C(21)–Os(2)–C(23)	93.1 (3)		
C(21)–Os(2)–C(24)	96.6 (3)		
(H) OC(ax)–Os–OC(ax)			
C(11)–Os(1)–C(12)	171.7 (3)	C(31)–Os(3)–C(32)	172.3 (3)
(I) Os–C–O(ax)			
Os(1)–C(11)–O(11)	178.8 (5)	Os(3)–C(31)–O(31)	176.1 (7)
Os(1)–C(12)–O(12)	176.2 (9)	Os(3)–C(32)–O(32)	173.1 (8)
Os(2)–C(21)–O(21)	176.3 (7)		
(J) Os–C–O (eq)			
Os(1)–C(13)–O(13)	179.2 (5)	Os(3)–C(33)–O(33)	179.5 (5)
Os(2)–C(23)–O(23)	177.4 (10)	Os(3)–C(34)–O(34)	177.8 (9)
Os(2)–C(24)–O(24)	176.4 (9)		
(K) Os–P–C and C–P–C Angles			
Os(1)–P–C(1a)	110.1 (2)	C(1a)–P–C(1b)	102.9 (3)
Os(1)–P–C(1b)	121.7 (2)	C(1b)–P–C(1c)	100.9 (3)
Os(1)–P–C(1c)	113.8 (2)	C(1c)–P–C(1a)	106.0 (3)
(L) P–C–C Angles			
P–C(1a)–C(2a)	121.3 (6)	P–C(1b)–C(6b)	121.2 (6)
P–C(1a)–C(6a)	120.3 (6)	P–C(1c)–C(2c)	118.2 (6)
P–C(1b)–C(2b)	120.9 (5)	P–C(1c)–C(6c)	124.6 (6)
(M) Phenyl C–C–C Angles			
C(6a)–C(1a)–C(2a)	118.0 (7)	C(3a)–C(4a)–C(5a)	120.5 (9)
C(1a)–C(2a)–C(3a)	120.3 (9)	C(4a)–C(5a)–C(6a)	121.9 (9)
C(2a)–C(3a)–C(4a)	119.4 (10)	C(5a)–C(6a)–C(1a)	119.9 (8)
C(6b)–C(1b)–C(2b)	117.8 (7)	C(3b)–C(4b)–C(5b)	120.8 (8)
C(1b)–C(2b)–C(3b)	121.6 (8)	C(4b)–C(5b)–C(6b)	120.5 (8)
C(2b)–C(3b)–C(4b)	119.0 (8)	C(5b)–C(6b)–C(1b)	120.3 (8)
C(6c)–C(1c)–C(2c)	117.6 (7)	C(3c)–C(4c)–C(5c)	120.4 (9)
C(1c)–C(2c)–C(3c)	121.0 (8)	C(4c)–C(5c)–C(6c)	120.3 (10)
C(2c)–C(3c)–C(4c)	119.7 (9)	C(5c)–C(6c)–C(1c)	121.0 (9)

[a] See Footnote *a* to Table IV.

Table VI. Selected Least-Squares Planes in $H_2Os_3(CO)_{10}(PPh_3)$ and Deviations (in Å) of Atoms Therefrom

Atom	Dist	Atom	Dist
Plane I: Os(1)–Os(2)–Os(3)			
Equation:[a] $0.27365X - 0.44816Y - 0.85104Z = -3.0528$			
Os(1)*	0.000	C(23)	0.231 (8)
Os(2)*	0.000	O(23)	0.330 (7)
Os(3)*	0.000	C(24)	0.328 (8)
P	0.181 (2)	O(24)	0.596 (6)
H(B)	−0.07 (6)	C(33)	−0.070 (8)
H(T)	1.48 (7)	O(33)	−0.107 (6)
C(13)	−0.002 (8)	C(34)	0.047 (8)
O(13)	−0.003 (6)	O(34)	0.049 (6)
Plane II: Phenyl Ring "a"			
Equation: $0.2509X + 0.9561Y - 0.1515Z = 4.524$			
C(1a)*	0.010 (7)	C(5a)*	0.009 (9)
C(2a)*	−0.010 (10)	C(6a)*	−0.010 (8)
C(3a)*	0.009 (12)	P	−0.150 (2)
C(4a)*	−0.009 (10)	Os(1)	−2.3180 (3)
Plane III: Phenyl Ring "b"			
Equation: $0.4876X - 0.5067Y - 0.7110Z = -2.192$			
C(1b)*	0.005 (7)	C(5b)*	−0.005 (9)
C(2b)*	−0.009 (9)	C(6b)*	0.002 (8)
C(3b)*	0.006 (9)	P	−0.001 (2)
C(4b)*	0.001 (8)	Os(1)	−0.2699 (3)
Plane IV: Phenyl Ring "c"			
Equation: $0.8880X + 0.4134Y + 0.2015Z = 4.703$			
C(1c)*	−0.007 (7)	C(5c)*	−0.001 (11)
C(2c)*	−0.002 (9)	C(6c)*	0.009 (10)
C(3c)*	0.010 (9)	P	0.032 (2)
C(4c)*	−0.008 (10)	Os(1)	−1.7852 (3)

[a] Equations are expressed in the orthonormal (Å) coordinate system given by $X = ax + cz \cos\beta$, $Y = by$, and $Z = cz \sin\beta$. Atoms marked with an asterisk were assigned unit weight; all others were given zero weight.

of greater competition for $d_\pi \rightarrow \pi^*(CO)$ back-donation for axial carbonyl ligands than for equatorial carbonyl ligands. Similar results have been observed for $Os_3(CO)_{12}$ [1.946 [6] Å vs. 1.912 [7] Å],[1] $H_2Os_3(CO)_{11}$ [1.961 [12] Å vs. 1.889 [11] Å],[1] and $Ru_3(CO)_{12}$ [1.942 [4] Å vs. 1.921 [5] Å].[16]

The triphenylphosphine ligand has the expected geometry. The Os(1)–P distance is 2.370 (2) Å, Os–P–C angles range from 110.1 (2) to 121.7 (2)°, and C–P–C angles vary from 100.9 (3) to 106.9 (3)°. As noted previously,[17] C–C–C(phenyl) angles at P-bonded carbon atoms are expected to be less than 120°; individual angles in the present molecule are C(6a)–C(1a)–C(2a) = 118.0 (7)°, C(6b)–C(1b)–C(2b) = 117.8 (7)°, and C(6c)–C(1c)–C(2c) = 117.6 (7)°. Each of the phenyl rings is planar within the limits of experimental error, rms deviations from planarity being 0.010 Å for ring "a", 0.006 Å for ring "b", and 0.007 Å for ring "c" (cf. Table VI).

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Registry No. $H_2O_3(CO)_{10}(PPh_3)$, 56093-37-9.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Dichlorobis(1-methylcytosine)palladium(II)

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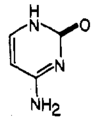
The title complex was synthesized and its structure determined by three-dimensional x-ray crystallography using counter methods. Crystal data for dichlorobis(1-methylcytosine)palladium(II), $Pd(cyt)_2Cl_2$, includes the following: space group $P\bar{1}$; $Z = 1$; $a = 6.831$ (2), $b = 7.377$ (2), $c = 8.824$ (1) Å; $\alpha = 117.94$ (1), $\beta = 105.34$ (2), $\gamma = 90.95$ (2)°; $V = 374$ Å^3; $R = 2.0\%$; 1141 reflections. The palladium atom is located at the inversion center of the cell. The 1-methylcytosine ligands are coordinated via the unsubstituted ring nitrogen atom which has been deprotonated. The ligand environment about the palladium atom is strictly planar, with Cl–Pd–Cl and N–Pd–N linear, due to the crystallographically imposed inversion center. There is a weak intramolecular hydrogen contact, between the palladium and one hydrogen atom of each cytosine group, to complete a very distorted octahedron about the metal. The other amino hydrogen atom of each group is linked to the carbonyl oxygen of an adjacent molecule via a weak hydrogen bond. Thus the crystal structure consists of parallel infinite chains of hydrogen bonded molecules.

Introduction

Most nucleic acid bases including cytosine, **1**, posses more than one basic site where interaction with a proton or a metal ion may take place. Either a proton or a substituent usually occupies the N(1) position so that N(3) and the carbonyl oxygen (O) are the most likely binding sites. The amino group attached to C(4) is not a basic site. Results of single-crystal x-ray diffraction investigations have shown that N(3), O, and chelation between them are possible binding modes for first-row divalent transition metal ions. Three different kinds of Cu(II) complexes have been shown to bind to N(3) of cytosine and also interact with O.[1-4] A similar chelation occurs in a Cu(II) complex to cytidine, **3**, where the N(1) position is substituted with ribose sugar.[5] With cytidine 5′-monophosphate the only base binding is at N(3) for Co(II), Cd(II),[6] and Zn(II).[7] In contrast, base coordination has been found at O(2) and not at N(3) for Mn(II).[8]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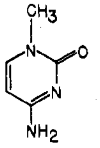
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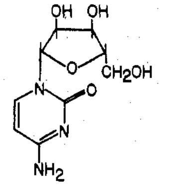
3

As part of a program to investigate the modes of interaction of antitumor Pt(II) complexes with nucleic acids we have undertaken studies of Pt(II) and Pd(II) complexes with nucleic acid bases and nucleosides. Both metal ions form similar diamagnetic tetragonal complexes with an advantage to Pd(II) because it reacts several powers of ten times more rapidly than Pt(II). A comparison has been made of identical complexes of the two metal ions and their interaction with some nucleosides.[9] In this paper we report the crystal structure of a complex of Pd(II) and 1-methylcytosine, **2**. In this ligand the pyrimidine base is substituted at the 1 position as is cytosine upon forming a nucleoside.

Experimental Section

The complex crystallized as small pale yellow prisms from an aqueous solution originally containing 1-methylcytosine and K_2PdCl_4. Every crystal of the sample was examined and the best was chosen for the x-ray study. Crystal data for dichlorobis(1-methylcytosine)palladium(II), $PdCl_2O_2N_6C_{10}H_{14}$, are the following: mol wt 428; pale yellow crystal; space group $P\bar{1}$; $Z = 1$; $a = 6.831$ (2), $b = 7.377$ (2), $c = 8.824$ (1) Å; $\alpha = 117.94$ (1), $\beta = 105.34$ (2), $\gamma = 90.95$ (2)°; $V = 374$ Å^3; $R = 2.0\%$; 1141 reflections; $\rho_{\text{calcd}} = 1.90$, $\rho_{\text{obsd}} = 1.88$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 15.9$ cm^{-1}; crystal dimensions (distances in mm of faces from centroid) (100) 0.03; ($\bar{1}$00) 0.03; (010) 0.075; (0$\bar{1}$0) 0.075; (01$\bar{1}$) 0.05; (0$\bar{1}$1) 0.05.

The Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 48°$. Scan widths (SW) were calculated from the formula $SW = A + B \tan\theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of the peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.60 and 0.30° respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being auto-