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Neutron and X-Ray Diffraction Studies on Tris(dimethylphenylphosphine)osmium Tetrahydride

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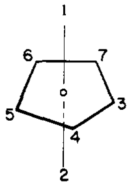
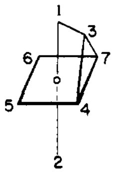
Abstract: The crystal and molecular structure of $H_4Os(PMe_2Ph)_3$ has been investigated by x-ray and neutron diffraction techniques. X-ray data collected at 298 K gave the unit cell parameters a = 11.489 (4) Å, b = 12.441 (4) Å, c = 11.103 (4) Å, α = 90.54 (2)°, β = 124.63 (2)°, γ = 89.93 (2)°, Z = 2 in the triclinic space group $P\bar{1}$. Neutron data collected at 90 K gave the cell parameters a = 11.409 (2) Å, b = 12.388 (2) Å, c = 11.098 (2) Å, α = 90.36 (5)°, β = 125.07 (1)°, and γ = 90.06 (4)°. Refinement against the x-ray data coverged at R = 0.055 and R_w = 0.060 with 3486 reflections with $I \geq 3\theta$. For the neutron study, agreement factors are R = 0.044 and R_w = 0.042 based on 3381 reflections. The complex is a distorted pentagonal bipyramid, the four hydride ligands, osmium, and one phosphorus atom being essentially coplanar. Important distances and angles in the molecule are as follows: Os-H = 1.663 (3), 1.648 (3), 1.644 (3), 1.681 (3) Å; Os-P = 2.317 (2), 2.307 (2), 2.347 (2) Å; H-Os-H = 67.9 (2), 69.4 (2), 70.0 (2)°; P-Os-P = 166.1 (1), 97.0 (1), 96.9 (1)°; H-Os-P(eq) = 73.0 (1), 79.7 (1)°.

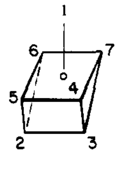
There has been a great amount of interest in transition metal hydrides over the past two decades.[2] The structure of many hydride complexes is elusive because standard spectroscopic methods may fail to give useful information on the disposition of hydride ligands. Infrared spectra may be difficult to interpret and the metal-hydrogen stretching frequency is not always observed. NMR spectra of diamagnetic hydrides give information concerning the stoichiometry of the complex, but structural information is often lost owing to the fluxional nature of many complexes. The NMR of $H_4Os(PMe_2Ph)_3$[3] shows a high-field quartet, due to four equivalent hydrogens coupled to three equivalent phosphorus atoms. Four geometries may be considered for the seven-coordinate $H_4Os(PMe_2Ph)_3$ complex: pentagonal bipyramid (I), face-capped octahedron (II), capped trigonal prism (III), and the piano stool geometry (IV). None of these, or any other, rigid geometry is consistent with the observed NMR spectrum. This complex, as well as many other MH_xL_y hydrides, is fluxional, with the chemically inequivalent protons interchanging at a rate that is rapid on the NMR time scale.



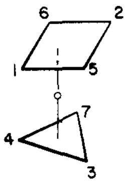
I D_{5h}



II C_{3v}



III C_{2v}



IV C_s

Interest in $H_4Os(PMe_2Ph)_3$ comes not only from its fluxional properties, but also from the fact that seven-coordination is fairly uncommon, especially in complexes of group 8 metals. High coordination numbers are made possible in metal hydride complexes by the ability of the hydride ligand to stabilize high oxidation states and by its modest steric requirements. We report here the structure of $H_4Os(PMe_2Ph)_3$ as determined by single crystal x-ray and neutron diffraction techniques. An x-ray diffraction analysis of the analogous $H_4Os(PEt_2Ph)_3$ was earlier completed by Mason.[4]

Successful location and refinement of hydrogen atom positions by x-ray diffraction has been reported for several second- and third-row transition metal hydrides.[5] The errors in these parameters are often large and probably frequently underestimated. In the present work, results from the x-ray study allowed geometries III and IV to be ruled out as possible structures for $H_4Os(PMe_2Ph)_3$. X-ray data alone were not adequate to distinguish unambiguously between configurations I and II, but I was strongly favored by the fact that the OsP_3 skeleton of the molecule is planar and T-shaped. Neutron data subsequently confirmed I as the correct geometry.

In addition to indicating the molecular geometry of $H_4Os(PMe_2Ph)_3$, the neutron diffraction study has made possible an accurate determination of the metal-hydrogen bond lengths. Precise knowledge of metal-hydrogen distances, although generally difficult to obtain, potentially offers more information concerning the covalent radius of the metal than do the lengths of other bonds. Interpretation of M-H bond distances is facilitated by the very simplicity of the hydride ligand, which is not able to participate in π bonding.

Experimental Section

X-Ray Diffraction. Tris(dimethylphenylphosphine)osmium tetrahydride was made by the published procedure[3] and crystallized from absolute ethanol. A crystal with approximate dimensions 0.2 × 0.25 × 0.06 mm was mounted along its $1\bar{1}0$ axis on a glass fiber. Preliminary precession photographs showed no systematic extinctions or symmetry of the diffraction pattern other than the center of inversion. Density measurements in aqueous zinc iodide agree well with the density calculated for two molecules per unit cell (ρ_{obsd} = 1.51, ρ_{calcd} = 1.55 g/cm^3 for $OsC_{24}H_{37}P_3$), thus suggesting the space group to be $P\bar{1}$. Successful solution of the structure confirmed the correctness of this space group.

Data were collected at room temperature on an automatic Nonius

Table I. Final Atomic Parameters[a] of $H_4Os(PMe_2Ph)_3$

A. Results from the Neutron Diffraction Analysis

Atom	10^5x	10^5y	10^5z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Os	15015 (9)	27753 (7)	13899 (10)	26 (1)	12 (1)	28 (1)	1 (1)	16 (1)	3 (1)
P(1)	19704 (20)	36292 (16)	−1434 (22)	35 (3)	13 (1)	32 (3)	−1 (2)	18 (2)	0 (2)
P(2)	4779 (20)	20708 (17)	25029 (22)	26 (2)	22 (2)	35 (3)	0 (2)	19 (2)	2 (2)
P(3)	38369 (20)	21647 (16)	31290 (21)	28 (2)	18 (2)	32 (3)	2 (2)	15 (2)	6 (2)
C(11)	29469 (17)	49180 (13)	5294 (18)	54 (2)	13 (1)	48 (2)	−3 (1)	32 (3)	1 (1)
C(12)	3853 (17)	40528 (14)	−19285 (18)	41 (2)	26 (1)	37 (2)	6 (1)	16 (2)	7 (1)
C(13)	29273 (16)	28869 (12)	−7813 (17)	37 (2)	17 (1)	32 (2)	−2 (1)	21 (2)	0 (1)
C(14)	27367 (17)	17626 (13)	−9687 (18)	53 (2)	19 (1)	45 (2)	−5 (1)	31 (2)	−7 (1)
C(15)	34695 (18)	11558 (14)	−14053 (19)	73 (3)	20 (1)	67 (3)	−4 (1)	51 (2)	−10 (2)
C(16)	43927 (19)	16663 (14)	−16733 (20)	68 (2)	28 (1)	63 (3)	−1 (1)	48 (2)	−8 (2)
C(17)	45568 (18)	27825 (14)	−15298 (19)	53 (2)	32 (1)	57 (2)	−4 (1)	40 (2)	−5 (2)
C(18)	38302 (17)	33908 (14)	−10875 (18)	49 (2)	23 (1)	44 (2)	−2 (1)	34 (2)	3 (1)
C(21)	−14773 (17)	18985 (15)	12261 (19)	29 (2)	33 (1)	50 (2)	−3 (1)	19 (2)	2 (1)
C(22)	6220 (17)	28616 (13)	39879 (18)	50 (2)	19 (1)	53 (2)	−1 (1)	34 (2)	−1 (1)
C(23)	9535 (16)	7040 (13)	32663 (17)	33 (2)	19 (1)	37 (2)	−4 (2)	21 (2)	1 (1)
C(24)	12930 (17)	4312 (13)	46571 (17)	41 (2)	23 (1)	34 (2)	2 (1)	24 (2)	6 (1)
C(25)	16228 (17)	−6378 (13)	51512 (18)	48 (2)	26 (1)	40 (2)	2 (1)	19 (2)	8 (1)
C(26)	16085 (17)	−14468 (13)	42690 (18)	41 (2)	22 (1)	42 (2)	0 (1)	17 (2)	8 (1)
C(27)	12761 (17)	−11820 (13)	28810 (18)	58 (2)	16 (1)	46 (2)	−5 (1)	25 (2)	0 (1)
C(28)	9567 (17)	−1192 (13)	23889 (18)	53 (2)	17 (1)	39 (2)	−3 (1)	25 (2)	0 (1)
C(31)	43338 (18)	8378 (14)	28089 (21)	46 (2)	17 (1)	80 (3)	6 (1)	32 (2)	2 (1)
C(32)	43757 (17)	19834 (15)	50222 (18)	40 (2)	40 (2)	41 (2)	−1 (1)	20 (2)	16 (1)
C(33)	52877 (15)	30411 (12)	34364 (17)	27 (2)	17 (1)	36 (2)	0 (1)	19 (2)	1 (1)
C(34)	57913 (16)	38943 (13)	44579 (18)	43 (2)	17 (1)	43 (2)	−2 (1)	30 (2)	−1 (1)
C(35)	68565 (17)	46014 (13)	46774 (18)	42 (2)	21 (1)	50 (2)	−3 (1)	26 (2)	−2 (1)
C(36)	74262 (17)	44632 (14)	38589 (18)	37 (2)	23 (1)	48 (2)	−5 (1)	22 (2)	1 (1)
C(37)	69259 (16)	36237 (13)	28312 (18)	36 (2)	27 (1)	41 (2)	0 (1)	25 (2)	5 (1)
C(38)	58664 (16)	29075 (13)	26231 (17)	36 (2)	17 (1)	32 (2)	0 (1)	19 (2)	1 (1)
H(1)	14181 (38)	15618 (27)	6951 (39)	98 (5)	27 (3)	87 (5)	3 (3)	58 (5)	−9 (3)
H(2)	−883 (36)	25650 (32)	−1466 (37)	58 (5)	68 (4)	55 (5)	−17 (3)	18 (4)	−2 (3)
H(3)	4166 (38)	38009 (30)	9795 (42)	82 (5)	39 (3)	115 (6)	30 (3)	56 (5)	20 (3)
H(4)	23552 (37)	37561 (29)	26679 (39)	81 (5)	41 (3)	78 (5)	−4 (3)	42 (4)	−17 (3)
H(111)	40083 (39)	47925 (31)	15308 (42)	79 (5)	47 (3)	84 (5)	−5 (3)	25 (4)	−3 (3)
H(112)	23355 (42)	−45752 (29)	8035 (46)	122 (6)	29 (3)	149 (7)	0 (3)	95 (6)	−15 (4)
H(113)	30296 (41)	−46687 (29)	−2781 (41)	121 (6)	32 (3)	99 (6)	−15 (3)	70 (5)	−2 (3)
H(121)	2539 (40)	−46075 (33)	17497 (42)	93 (6)	61 (4)	90 (6)	32 (4)	43 (5)	7 (4)
H(122)	2557 (40)	−33458 (31)	25344 (39)	90 (5)	44 (3)	66 (5)	−9 (3)	3 (4)	−4 (3)
H(123)	−6930 (39)	−44658 (32)	25768 (40)	90 (5)	57 (3)	78 (5)	1 (3)	41 (5)	26 (3)
H(211)	−16967 (39)	13259 (33)	3687 (42)	79 (5)	57 (3)	91 (6)	−13 (3)	34 (5)	−25 (4)
H(212)	−19538 (38)	16066 (33)	17844 (43)	79 (5)	63 (4)	113 (6)	−9 (3)	67 (5)	14 (4)
H(213)	−19563 (39)	26754 (33)	6957 (44)	70 (5)	58 (4)	113 (6)	17 (3)	39 (5)	26 (4)
H(221)	−279 (40)	25441 (31)	43327 (42)	105 (6)	54 (3)	109 (6)	−12 (3)	83 (5)	−6 (4)
H(222)	2758 (43)	36883 (28)	35688 (42)	140 (6)	24 (3)	109 (6)	12 (3)	80 (6)	4 (3)
H(223)	17440 (38)	29060 (32)	49453 (40)	69 (5)	63 (4)	79 (6)	−13 (3)	29 (4)	−18 (4)
H(311)	41577 (45)	8281 (33)	17303 (47)	131 (7)	54 (4)	120 (7)	9 (4)	85 (6)	−7 (4)
H(312)	36174 (41)	2508 (31)	27955 (48)	92 (6)	41 (3)	159 (7)	−9 (3)	72 (6)	5 (4)
H(313)	54564 (38)	6498 (32)	36740 (44)	61 (5)	48 (3)	133 (7)	20 (3)	29 (5)	17 (4)
H(321)	55092 (38)	17704 (36)	57507 (41)	59 (5)	93 (4)	81 (6)	−4 (4)	26 (4)	27 (4)
H(322)	37310 (41)	13323 (35)	50269 (43)	98 (6)	77 (4)	97 (6)	−20 (4)	58 (5)	26 (4)
H(323)	41744 (43)	27186 (35)	54286 (42)	121 (6)	72 (4)	81 (6)	0 (4)	67 (5)	1 (4)
H(141)	20296 (42)	13643 (29)	−7506 (44)	126 (6)	36 (3)	127 (6)	−20 (3)	98 (6)	−15 (4)
H(151)	33252 (46)	2818 (31)	−15221 (49)	152 (7)	34 (3)	167 (8)	−14 (4)	118 (7)	−19 (4)
H(161)	49656 (44)	11916 (33)	−20124 (43)	131 (6)	58 (4)	147 (7)	10 (4)	115 (6)	−7 (4)
H(171)	52574 (42)	31911 (32)	−17604 (46)	117 (6)	60 (4)	133 (7)	−13 (4)	102 (6)	−5 (4)
H(181)	39933 (39)	42604 (28)	−9620 (42)	107 (6)	32 (3)	121 (6)	−10 (3)	87 (5)	−1 (3)
H(241)	13150 (41)	10369 (30)	53733 (40)	127 (6)	40 (3)	84 (5)	3 (3)	79 (5)	0 (3)
H(251)	18892 (44)	−8329 (32)	62365 (42)	139 (7)	52 (3)	185 (6)	7 (4)	76 (5)	21 (4)
H(261)	18571 (40)	−22737 (29)	46513 (41)	104 (6)	31 (3)	92 (6)	8 (3)	44 (5)	18 (3)
H(271)	12462 (54)	−18031 (30)	21655 (42)	153 (5)	33 (3)	81 (6)	−4 (4)	61 (5)	−10 (4)
H(281)	7095 (44)	807 (29)	13122 (39)	151 (7)	37 (3)	60 (5)	−3 (4)	60 (5)	0 (3)
H(341)	53505 (39)	40171 (29)	51008 (41)	105 (6)	49 (3)	102 (6)	−8 (3)	81 (5)	−23 (3)
H(351)	72460 (41)	52446 (31)	54982 (44)	109 (6)	44 (3)	110 (6)	−25 (3)	67 (5)	−26 (4)
H(361)	82576 (39)	50165 (31)	40225 (43)	91 (6)	55 (3)	112 (6)	−25 (3)	65 (5)	−12 (4)
H(371)	72557 (38)	35074 (31)	21852 (41)	90 (5)	59 (3)	98 (6)	−9 (3)	74 (5)	−6 (4)
H(381)	54975 (37)	22575 (29)	18177 (39)	86 (5)	46 (3)	77 (5)	−13 (3)	57 (4)	−15 (3)

CAD-3 quarter-circle diffractometer with zirconium-filtered Mo Kα radiation ($\lambda = 0.7107$ Å). Least-squares refinement based upon the positions of 30 carefully centered reflections gave the cell parameters $a = 11.498$ (4) Å, $b = 12.441$ (4) Å, $c = 11.103$ (4) Å, $\alpha = 90.54$ (2)°, $\beta = 124.63$ (2)°, and $\gamma = 89.83$ (2)° ($V = 1306.8$ Å^3, $F(000) = 1216.8$). ω scans indicated acceptable crystal quality with a reflection full width at half-height of about 0.19° at low 2θ. Data collection was done by the $\theta/2\theta$ scan technique with a scan rate of 10°/min and a fixed scan width of 1.4°. Each reflection was scanned two to six times, depending on its intensity. Precalibrated zirconium foil attenuators

Table I (*Continued*)

B. Results from the X-Ray Diffraction Analysis

Atom	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Os	1534 (1)	2757 (1)	1403 (1)	92 (1)	50 (0)	87 (1)	4 (0)	48 (0)	13 (0)
P(1)	1982 (3)	3617 (2)	−123 (3)	123 (4)	53 (2)	100 (4)	4 (2)	61 (3)	16 (2)
P(2)	511 (3)	2056 (2)	2491 (3)	106 (4)	63 (2)	125 (4)	5 (2)	68 (3)	14 (2)
P(3)	3828 (3)	2158 (2)	3118 (3)	95 (3)	59 (2)	118 (4)	9 (2)	53 (3)	26 (2)
C(11)	2934 (14)	4892 (9)	537 (14)	194 (17)	49 (8)	150 (20)	−13 (9)	108 (16)	13 (10)
C(12)	430 (13)	4047 (10)	−1866 (13)	156 (18)	92 (9)	115 (18)	26 (11)	64 (16)	47 (11)
C(13)	2889 (12)	2885 (9)	−786 (11)	139 (15)	64 (8)	71 (16)	−5 (9)	57 (13)	5 (9)
C(14)	2713 (14)	1783 (9)	−1003 (14)	160 (19)	65 (10)	159 (19)	5 (11)	95 (17)	7 (11)
C(15)	3437 (18)	1208 (11)	−1437 (16)	253 (26)	77 (10)	200 (25)	5 (13)	140 (23)	−5 (13)
C(16)	4388 (18)	1701 (12)	−1684 (16)	260 (26)	110 (12)	161 (23)	3 (15)	158 (22)	−4 (13)
C(17)	4526 (16)	2823 (12)	−1497 (17)	196 (23)	116 (13)	189 (25)	11 (14)	139 (21)	17 (14)
C(18)	3912 (13)	3389 (10)	−1102 (14)	153 (18)	88 (8)	152 (20)	−4 (10)	110 (17)	20 (10)
C(21)	−1407 (13)	1876 (11)	1202 (17)	108 (15)	107 (11)	221 (23)	12 (10)	98 (16)	45 (13)
C(22)	637 (14)	2842 (11)	3963 (16)	180 (18)	90 (9)	195 (23)	0 (11)	146 (19)	−2 (12)
C(23)	994 (10)	699 (8)	3263 (11)	98 (12)	63 (7)	93 (14)	−8 (8)	51 (11)	−3 (8)
C(24)	1286 (12)	423 (10)	4588 (13)	122 (15)	97 (10)	112 (19)	9 (10)	68 (15)	35 (11)
C(25)	1606 (13)	−624 (10)	5097 (14)	132 (16)	87 (10)	126 (18)	−12 (10)	58 (14)	18 (11)
C(26)	1626 (13)	−1405 (10)	4249 (14)	129 (17)	176 (9)	131 (19)	−7 (10)	36 (15)	24 (11)
C(27)	1319 (14)	−1182 (10)	2864 (15)	152 (18)	66 (9)	167 (23)	−18 (11)	61 (18)	13 (12)
C(28)	1006 (13)	−100 (9)	2378 (14)	145 (17)	65 (9)	130 (20)	−4 (10)	55 (16)	9 (11)
C(31)	4335 (12)	845 (10)	2764 (14)	123 (16)	60 (8)	162 (21)	11 (9)	57 (16)	2 (10)
C(32)	4324 (14)	1963 (12)	4943 (14)	154 (16)	108 (12)	115 (16)	−17 (11)	66 (14)	26 (11)
C(33)	5272 (10)	3038 (8)	3437 (11)	76 (11)	53 (7)	103 (14)	16 (7)	40 (11)	21 (8)
C(34)	5750 (10)	3869 (8)	4458 (11)	161 (11)	64 (7)	108 (14)	−3 (7)	74 (11)	−25 (8)
C(35)	6826 (13)	4559 (9)	4677 (13)	138 (19)	75 (8)	180 (17)	−5 (10)	68 (16)	2 (10)
C(36)	7369 (14)	4422 (10)	3862 (16)	119 (18)	101 (9)	142 (24)	0 (10)	76 (18)	20 (12)
C(37)	6892 (12)	3595 (11)	2838 (14)	108 (14)	96 (11)	114 (19)	7 (10)	59 (15)	30 (12)
C(38)	5842 (12)	2893 (10)	2624 (13)	109 (14)	78 (10)	104 (17)	16 (10)	61 (13)	32 (11)

[a] The thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{12}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

were automatically inserted to prevent the count rate from exceeding 2500 counts/s. Background counts were measured with stationary crystal and detector at both ends of each scan such that the total time for counting the background (t_b) was equal to one-half the time used to scan the peak (t_c). The intensities of three standard reflections were measured at 75 reflection intervals. No significant change in these intensities occurred during data collection. A total of 3995 unique reflections were measured out to $2\theta_{max}$ = 50° ($\sin\theta/\lambda$ = 0.595 Å^{-1}).

Raw intensities, I, and their standard deviations,[6] $\sigma(I)$, were calculated as

$$I = [C - (t_c/t_b)B]$$

C = total peak count; B = total background count

$$\sigma(I) = [C + (t_c/t_b)^2B + (0.02I)^2]^{1/2}$$

Values for F_o^2 were obtained by correcting I for Lorentz and polarization effects and applying an empirical absorption correction[7] (normalized absorption coefficients ranged from 0.84 to 1.22, μ = 53.6 cm^{-1}). Agreement factors for data averaging are R = 0.023 and R_w = 0.033.

Positions of the osmium and phosphorus atoms were determined from a three-dimensional Patterson synthesis. Two successive difference-Fourier syntheses revealed the locations of the 24 carbon atoms. Atomic scattering factors[8] employed include anomalous components for osmium and phosphorus. Least-squares refinement[9] was carried out using 3486 reflections with $I/\sigma(I) > 3$, minimizing the quantity $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$. Initial full-matrix least-squares refinement was done with anisotropic thermal parameters for osmium and phosphorus and isotropic for carbon to yield[10] R_F = 0.071 and R_{wF} = 0.082. The carbon atoms were then allowed to refine anisotropically. An analysis of variance at this point indicated that the weighting scheme is acceptable: no significant dependence of $|F_o - F_c|/\sigma(F_o)$ on F_o or $\sin\theta/\lambda$ was found. Hydrogen atoms were not included in the refinement of the x-ray data and thus the final model accounts for only 92% of the total electron density. Refinement converged at R_F = 0.055 and R_{wF} = 0.060; the standard deviation of an observation with unit weight is 2.21. Standard deviations in bond lengths and angles were calculated by program ORFFE,[11] making use of the variance-covariance matrix from the final cycle of refinement.

Neutron Diffraction. A large crystal of $H_4Os(PMe_2Ph)_3$ was grown from a seed by slowly cooling a saturated hexane solution from room temperature to −20 °C. The large size of this crystal (ca. 170 mm^3) would have given rise to a serious absorption problem, so a small fragment (4.4 × 2.6 × 1.5 mm) was broken off and used for data collection. The crystal, mounted along its $\bar{1}3\bar{1}$ axis on an aluminum pin, was placed inside a Displex closed-cycle helium refrigerator.[12] The crystal was cooled at 1 °C/min to 90 K; no phase change occurred. Neutron diffraction data were collected at the Brookhaven high flux beam reactor, on a four-circle diffractometer operated under the Reactor Experimental Control Facility.[13] The wavelength used was 1.01939 (2) Å, calibrated with Al_2O_3 powder.[14] Least-squares refinement based upon the positions of 59 carefully centered reflections with $2\theta > 23°$ gave the cell parameters at 90 K as a = 11.409 (2) Å, b = 12.388 (2) Å, c = 11.098 (2) Å, α = 90.36 (5)°, β = 125.07 (1)°, and γ = 90.06 (4)°. ω scans of several peaks indicated the crystal to be of good quality with a peak full width at half-height of 0.15° at the focusing angle (2θ = 30°). Although background levels were generally low, high backgrounds were observed in several narrow 2θ regions. The abnormal background levels were found to be due to the aluminum cryostat and it was possible to index this background scattering in terms of the known aluminum diffraction pattern.

The $\pm h$, $+k$, $\pm l$ hemisphere of data was collected using the $\theta/2\theta$ scan technique. A fixed scan width of 2.6° in 2θ was used for $2\theta < 48°$ and a variable scan width defined by $-1.88\,(1 - 5.0 \tan\theta)$ was used in the range $48° \leq 2\theta \leq 80°$. Each scan consisted of 40–65 steps, depending on its length, with each step being counted for 80 000 monitor counts (approximately 2 s). Low-angle data were then recollected in the $\pm h$, $-k$, $\pm l$ hemisphere using an ω scan (1.3° width) out to 2θ = 33° and a $\theta/2\theta$ scan (2.6° width) over $33° < 2\theta \leq 48°$. The $80\bar{4}$ and $\bar{1}6\bar{4}$ reflections were collected at 60 reflection intervals; no significant change in their intensities was found to occur over the course of data collection.

Peak profiles for all 6220 reflections recorded were integrated and corrected for background by an algorithm that divides the profile in such a way that $\sigma(I)/I$ is minimized.[15] Visual inspection of the peak profiles indicated that 678 reflections had not been integrated properly owing to abnormally high background levels arising from the alumi-

Table II. Bond Lengths and Angles

	X ray	Neutron		X ray	Neutron
Os-H(1)		1.663 (3)	P(2)-C(21)	1.837 (13)	1.842 (2)
Os-H(2)		1.648 (3)	P(2)-C(22)	1.834 (14)	1.836 (3)
Os-H(3)		1.644 (3)	P(2)-C(23)	1.836 (11)	1.836 (3)
Os-H(4)		1.681 (3)			
			C(23)-C(24)	1.357 (15)	1.402 (2)
Os-P(1)	2.305 (3)	2.317 (2)	C(24)-C(25)	1.389 (17)	1.403 (2)
Os-P(2)	2.291 (3)	2.307 (2)	C(25)-C(26)	1.356 (19)	1.390 (3)
Os-P(3)	2.334 (3)	2.347 (2)	C(26)-C(27)	1.399 (19)	1.400 (2)
			C(27)-C(28)	1.422 (17)	1.395 (2)
P(1)-C(11)	1.825 (12)	1.837 (3)	C(23)-C(28)	1.398 (17)	1.407 (2)
P(1)-C(12)	1.818 (12)	1.835 (3)			
P(1)-C(13)	1.819 (12)	1.850 (3)	P(3)-C(31)	1.846 (12)	1.837 (3)
			P(3)-C(32)	1.785 (13)	1.834 (3)
C(13)-C(14)	1.385 (16)	1.405 (2)	P(3)-C(33)	1.847 (11)	1.838 (3)
C(14)-C(15)	1.373 (19)	1.400 (2)			
C(15)-C(16)	1.412 (21)	1.400 (2)	C(33)-C(34)	1.390 (15)	1.403 (2)
C(16)-C(17)	1.405 (21)	1.391 (2)	C(34)-C(35)	1.410 (18)	1.400 (2)
C(17)-C(18)	1.327 (18)	1.400 (2)	C(35-C(36)	1.369 (19)	1.398 (2)
C(13)-C(18)	1.441 (16)	1.404 (2)	C(36)-C(37)	1.388 (18)	1.394 (2)
			C(37-C(38)	1.397 (16)	1.406 (2)
Average C-C	1.390 (6)	1.400 (1)	C(33)-C(38)	1.395 (15)	1.400 (2)
P(1)-Os-P(2)	165.24 (10)	166.07 (8)°	Os-P(2)-C(21)	112.6 (5)	113.08 (11)°
P(1)-Os-P(3)	97.56 (11)	97.08 (7)	Os-P(2)-C(22)	117.4 (4)	117.88 (11)
P(2)-Os-P(3)	97.21 (11)	96.85 (8)	Os-P(2)-C(23)	119.6 (4)	119.57 (11)
Os-P(1)-C(11)	116.5 (4)	116.28 (11)	Os-P(3(-C(31)	117.3 (4)	117.73 (11)
Os-P(1)-C(12)	115.5 (4)	115.34 (11)	Os-P(3)-C(32)	117.2 (5)	117.35 (11)
Os-P(1)-C(13)	118.9 (4)	119.27 (11)	Os-P(3)-C(33)	116.1 (3)	115.78 (11)
C(18)-C(13)-C(14)	116.5 (11)	118.55 (14)	C(25)-C(26)-C(27)	121.5 (12)	119.21 (15)
C(13)-C(14)-C(15)	120.9 (12)	120.59 (15)	C(26)-C(27)-C(28)	117.8 (13)	120.27 (15)
C(14)-C(15)-C(16)	122.2 (13)	120.21 (15)	C(27)-C(28)-C(23)	120.3 (12)	121.00 (15)
C(15)-C(16)-C(17)	116.2 (13)	119.55 (15)			
C(16)-C(17)-C(18)	122.1 (14)	120.34 (15)	C(38)-C(33)-C(34)	120.3 (10)	118.73 (13)
C(16)-C(17)-C(18)	122.1 (14)	120.34 (15)	C(38)-C(33)-C(34)	120.3 (10)	118.73 (13)
C(17)-C(18)-C(13)	122.0 (12)	120.71 (15)	C(33)-C(34)-C(35)	119.5 (12)	121.25 (14)
			C(34)-C(35)-C(36)	120.0 (12)	119.63 (15)
C(28)-C(23)-C(24)	118.8 (11)	118.29 (15)	C(35)-C(36)-C(37)	120.7 (12)	119.66 (14)
C(23)-C(24)-C(25)	122.2 (12)	120.49 (15)	C(36)-C(37)-C(38)	120.0 (12)	120.63 (14)
C(24)-C(25)-C(26)	119.4 (12)	120.73 (15)	C(37)-C(38)-C(33)	119.5 (11)	120.10 (14)
C(11)-P(1)-C(12)	99.7 (6)	100.12 (12)	P(1)-Os-H(1)		92.90 (14)
C(11)-P(1)-C(13)	104.0 (6)	103.36 (11)	P(1)-Os-H(2)		83.71 (14)
C(12)-P(1)-C(13)	99.2 (6)	99.47 (12)	P(1)-Os-H(3)		83.93 (15)
			P(1)-Os-H(4)		91.31 (14)
C(21)-P(2)-C(22)	102.0 (7)	101.11 (12)			
C(21)-P(2)-C(23)	99.6 (6)	99.18 (12)	P(2)-Os-H(1)		89.61 (14)
			P(2)-Os-H(3)		84.94 (15)
C(31)-P(3)-C(32)	100.2 (7)	99.66 (13)	P(2)-Os-H(4)		92.73 (14)
C(31)-P(3)-C(33)	101.9 (5)	102.53 (12)			
C(32)-P(3)-C(33)	101.3 (6)	100.99 (11)	P(3)-Os-H(1)		79.66 (14)
			P(3)-Os-H(2)		149.05 (16)
			P(3)-Os-H(3)		143.02 (15)
			P(3)-Os-H(4)		73.04 (14)
			H(1)-Os-H(2)		69.39 (20)
			H(1)-Os-H(3)		137.31 (19)
			H(1)-Os-H(4)		152.69 (18)
			H(2)-Os-H(3)		67.93 (20)
			H(2)-Os-H(4)		137.90 (19)
			H(3)-Os-H(4)		69.98 (19)

C-H Bond Lengths from Neutron Data

C(11)-H(111)	1.087 (4)	C(21)-H(211)	1.090 (5)	C(31)-H(311)	1.094 (5)
C(11)-H(112)	1.102 (4)	C(21)-H(212)	1.095 (4)	C(31)-H(312)	1.087 (4)
C(11)-H(113)	1.085 (4)	C(21)-H(213)	1.100 (5)	C(31)-H(313)	1.098 (4)
C(12)-H(121)	1.100 (4)	C(22)-H(221)	1.086 (4)	C(32)-H(321)	1.094 (5)
C(12)-H(122)	1.086 (4)	C(22)-H(222)	1.103 (4)	C(32)-H(322)	1.093 (4)
C(12)-H(123)	1.094 (4)	C(22)-H(223)	1.098 (4)	C(32)-H(323)	1.096 (5)
C(14)-H(141)	1.085 (4)	C(24)-H(241)	1.079 (4)	C(34)-H(341)	1.094 (4)
C(15)-H(151)	1.091 (4)	C(25)-H(251)	1.088 (4)	C(35)-H(351)	1.090 (4)
C(16)-H(161)	1.093 (4)	C(26)-H(261)	1.085 (4)	C(36)-H(361)	1.096 (4)
C(17)-H(171)	1.094 (4)	C(27)-H(271)	1.089 (4)	C(37)-H(371)	1.085 (4)
C(18)-H(181)	1.088 (4)	C(28)-H(281)	1.089 (4)	C(38)-H(381)	1.087 (4)

Average methyl C-H: 1.094 (2) Å
Average phenyl C-H: 1.089 (1) Å

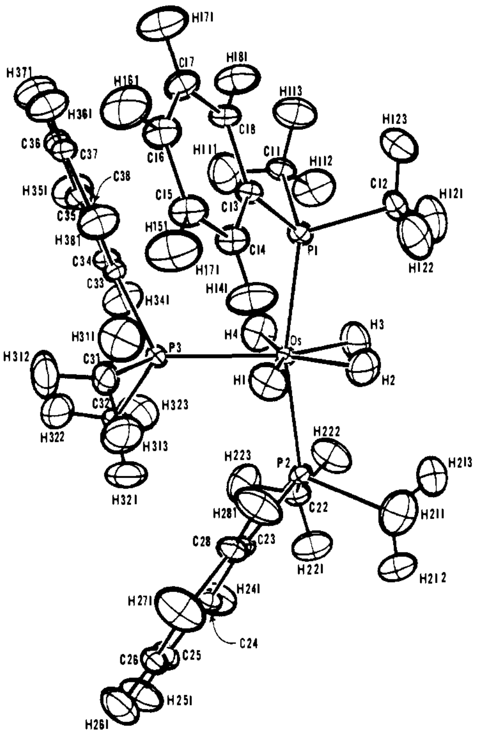


Figure 1. ORTEP drawing of $H_4Os(PMe_2Ph)_3$ indicating the numbering scheme used. The atoms in this and all following diagrams are drawn with 50% probability thermal ellipsoids determined in the neutron diffraction study.

num cryostat. Of these, 315 reflections were discarded because their backgrounds made reliable integration impossible.[16] By placing constraints on sections of profile to be considered peak and background regions, it was possible to obtain reliable integrations of the remaining 363 reflections. Observed intensities were corrected for absorption by numerical integration over a 1000-point Gaussian grid[17] (μ = 2.23 cm^{-1});[18] calculated transmission coefficients range from 0.546 to 0.718. After applying the Lorentz correction, Friedel pairs and multiply measured reflections were averaged to give 4210 unique reflections; 3481 of these with $I/\sigma(I) > 3$ were used for least-squares refinement. Agreement factors for data averaging are $R = 0.030$ and $R_w = 0.015$. No systematic differences were observed between the intensities of the $\theta/2\theta$ and ω-scan data.

Neutron scattering lengths[19] used are $b_{Os} = 1.07$, $b_P = 0.51$, $b_C = 0.6626$, and $b_H = -0.3723$ ($\times 10^{-12}$ cm). Initial atomic positions of the 24 nonhydrogen atoms were taken from the x-ray structure determination and positions of the 15 phenyl group hydrogen atoms were calculated assuming a 1.08 Å C–H bond length. One difference-Fourier synthesis gave the positions of the remaining 22 hydrogen atoms. Least-squares refinement was carried out minimizing the quantity $\Sigma w(|F_o| - |F_c|)^2$ ($w = 1/\sigma^2(F_o)$) as in the x-ray refinement. Full-matrix refinement[9] with isotropic temperature factors for all atoms converged at $R_F = 0.143$ and $R_{wF} = 0.199$. All temperature factors were then allowed to refine anisotropically and an isotropic extinction parameter was included.[20] The large number of parameters (587) made the use of full-matrix least-squares refinement inconvenient and expensive, so the anisotropic refinement was carried out by blocked-matrix least squares. Prior to the final cycles of refinement, the effects of background due to aluminum were reinvestigated. One hundred reflections showed especially poor agreement between $|F_o|$ and $|F_c|$. All of these reflections fell in regions where serious background problems had previously been found. Many of these reflections had a very small $|F_c|$ and $|F_o| \gg |F_c|$, suggesting that the integrated peak was mostly, or entirely, due to aluminum, rather than the $H_4Os(PMe_2Ph)_3$ sample. The profiles of some stronger reflections showed high or asymmetric backgrounds, giving rise to $|F_o| \ll |F_c|$. The accuracy of these reflections was considered suspect and thus they were not included in the final cycles of refinement. When the refinement had converged, two additional cycles were done by full-matrix least squares, but not refining thermal parameters, to prepare a variance-covariance matrix for use in calculating errors in bond lengths and angles. On the last cycle, none of the positional parameters changed by more than 0.05 times its standard deviation. The final agreement factors $R_F = 0.044$ and $R_{wF} = 0.042$ were obtained using 3381 reflections with $I/\sigma(I) > 3$. The isotropic extinction parameter,[20] g', converged to 0.7507, and 74% of the reflections had an extinction correction that reduced the intensity by more than a factor of 0.99. The reflection most seriously affected by extinction is the 111 reflection whose extinction is 0.50.

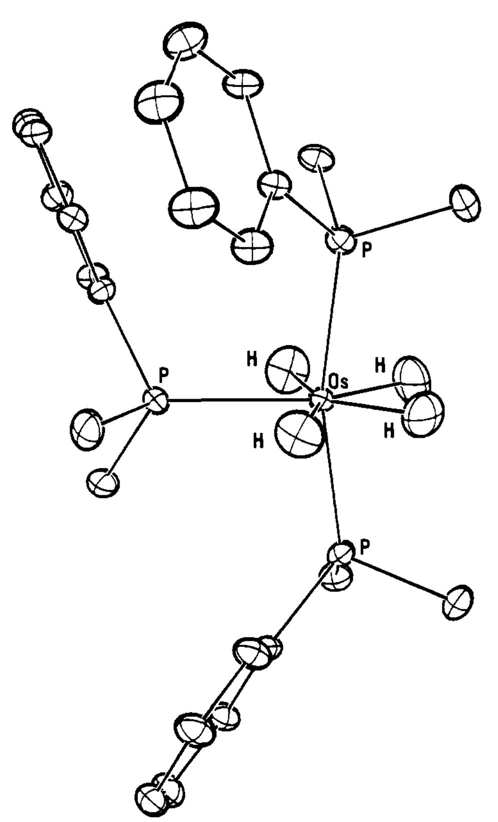


Figure 2. Same view of the molecule as that of Figure 1, with the phenyl and methyl hydrogen atoms removed for clarity. Note the distorted T shape of the OsP_3 group, with the axial phosphine ligands slightly bent away from the equatorial one. P–Os–P angles are 97.08 (7), 96.85 (8), 166.07 (8)°, and Os–P distances are 2.317 (2) (axial), 2.307 (2) (axial), 2.347 (2) Å (equatorial).

Results and Discussion

Final fractional atomic coordinates and thermal parameters are given in Table I. Observed and calculated structure factors are available.[21] Selected interatomic distances and angles are given in Table II. Root mean square vibrational amplitudes determined from the neutron diffraction experiment varied from 0.09 to 0.29 Å. The atoms showing the most anisotropy in the thermal parameters are the methyl group hydrogen atoms. The largest ratio of maximum to minimum root mean square vibrational amplitudes is 2.1 for H(322); that for nonhydrogen atoms is 1.8 for C(32). Because thermal motion is small and fairly isotropic at 90 K, thermal corrections[22] for bond lengths and angles were found to amount to only one or two standard deviations and have not been applied to the molecular parameters reported here. No corrections for thermal motion were calculated for the x-ray data.

Higher precision was obtained with the neutron data than with the x-ray data, especially for light atoms, so the following discussion will use the neutron results rather than those derived from the x-ray study. A reasonable mount of contraction was observed upon cooling the crystal to 90 K for data collection, as the unit cell volume changed by 1.8%. The expected apparent bond lengthening was observed at the lower temperature, but no phase change or change in molecular geometry occurred.

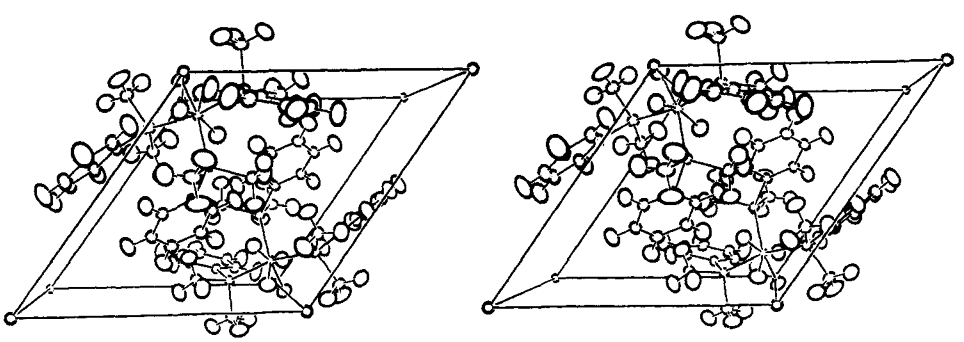


Figure 3. A stereoscopic plot of the unit cell of $H_4Os(PMe_2Ph)_3$, viewed along the *b* axis.

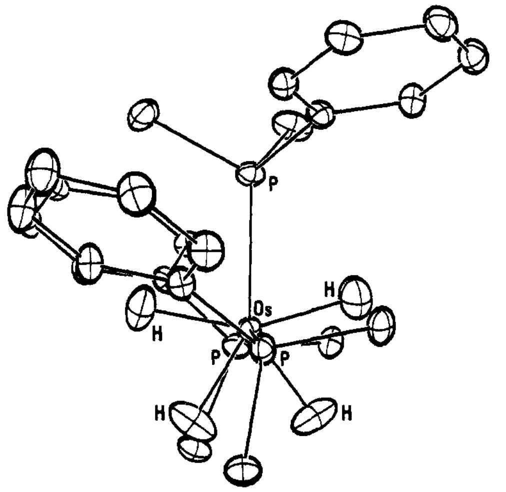


Figure 4. A drawing of $H_4Os(PMe_2Ph)_3$ projected almost along the P(1)-P(2) axis, showing the near mirror-image relationship between the two axial phosphine ligands.

Table III. Nonbonding H···H Contact Distances (Å)

Intramolecular Contacts (<2.4 Å)	
H(2)···H(3)	1.840 (6)
H(1)···H(2)	1.883 (5)
H(3)···H(4)	1.909 (5)
H(1)···H(141)	2.098 (5)
H(1)···H(281)	2.267 (5)
Intermolecular Contacts (<2.4 Å)	
H(2)···H(271)	2.055 (5)
H(3)···H(121)	2.194 (5)
H(122)···H(271)	2.374 (6)
H(122)···H(261)	2.376 (5)
H(281)···H(281)	2.391 (7)
Average methyl H···H contact:	1.784 (2)
Average phenyl H···H contact (ortho):	2.481 (5)

Table IV. The Equatorial Plane

	Displacements[a] (Å)
Os	0.001 (2)
P(3)	0.009 (5)
H(1)	−0.017 (8)
H(2)	0.018 (8)
H(3)	−0.008 (9)
H(4)	−0.003 (8)

[a] Deviations of atoms from the pentagonal plane through Os, P(3), and the hydride ligands. Standard deviations are given in parentheses. The equation of the plane is $-8.4862x - 5.0519y + 9.5787z + 1.3436 = 0$. All six atoms were given equal weight in the calculation.

An overall view of $H_4Os(PMe_2Ph)_3$ with the atomic numbering scheme is shown in Figures 1 and 2, and a stereoscopic packing diagram is presented in Figure 3. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell, and thus no symmetry is imposed on the molecule by the space group. Two of the dimethylphenylphosphine ligands are related by a noncrystallographic mirror plane defined by the osmium, four hydride atoms, and the third phosphorus (Figure 4). No unusually short nonbonding intermolecular interactions are present (Table III).

The arrangement of phosphine ligands found in the x-ray study rules out two of the four possible geometries (I-IV), and argues strongly against a third. The observed trans P-Os-P angle (165.2°) and average cis P-Os-P angle (97.4°) are not possible in a capped trigonal prismatic geometry (III) or the "piano stool" configuration (IV). The two remaining configurations are both consistent with a T-shaped OsP_3 skeleton, but II would predict it to be slightly nonplanar while I would demand strict planarity for it. Since planarity of the OsP_3 fragment was in fact observed, the evidence in favor of I was compelling. Still, it was not possible to tell with the x-ray data if the equatorial H_4OsP group is planar or buckled. Neutron diffraction provided the final answer by showing the four hydride ligands to be essentially coplanar with the osmium and equatorial phosphorus atoms, the average deviation from the plane being only about 0.01 Å (Table IV). Coplanarity is also indicated by the fact that the angles in this plane around osmium add to 360.00°.

Kouba and Wreford[23] have extended Muetterties and Guggenberger's[24] geometric description of seven-coordinate complexes in terms of angles between normals to the faces of the polyhedra. In $H_4Os(PMe_2Ph)_3$ the angles δ_1', δ_2', and δ_3' (as defined in ref 23) are 50.2, 51.8, and −75.3°, very close to those calculated for ideal D_{5h} geometry (54.4, 54.4, and −72.8°). In contrast, these angles would all be 24.4° for ideal C_{3v} (face-capped octahedral) geometry.

The basic pentagonal bipyramidal structure is somewhat distorted, with the axial phosphorus atoms bent away from the equatorial phosphines toward the hydride ligands. This effect is quite common in transition metal hydrides and is usually attributed to steric factors. Because of the small size of a hydrogen atom, it seems reasonable that steric interactions would cause other larger ligands to distort toward it. Elian and Hoffmann,[25] on the other hand, have presented theoretical evidence that this type of distortion may be caused by electronic effects in some organometallic complexes.

The five-membered equatorial ring around the osmium atom is also somewhat distorted (Figure 5). The discrepancy of 6.6 (2)° between the P(3)-Os-H(1) and P(3)-Os-H(4) angles is due to a short (2.10 Å) nonbonding interaction between H(1) and H(141) on a phenyl ring. H(4) is not subject to any such short nonbonding interactions with the dimethylphenylphosphine ligands (see Table III). It is interesting that while this distortion is rather substantial, with H(1) apparently moved by about 0.25 Å, there is no significant out-of-plane distortion.

Both the average axial Os-P [2.312 (2) Å] and equatorial Os-P [2.347 (2) Å] bond lengths are shorter than predicted on the basis of Pauling's covalent radii[26] (2.43 Å), or from Os-P distances found in $OsCl_4(PMe_2Ph)_2$[27] [2.448 (3) Å]. The powerful electron-donating ability of hydride relative to chloride increases electron density on the metal giving rise to an increase in metal to phosphorus π-back-bonding and consequently shorter metal-phosphorus bonds. Electronic arguments for the trans influence of hydride will explain why the equatorial Os-P(3) bond is about 0.035 Å longer than the other osmium-phosphorus bonds. Strong σ-donation by hydride ligands "trans" to P(3) will weaken the osmium-phosphorus σ bond without having much effect on any π-bond character that may be present. The same argument will explain why the Os-H(1) and Os-H(4) ("trans" to hydride) bond lengths are slightly longer than the Os-H(2) and Os-H(3) bonds ("trans" to phosphorus). Similar results have been reported for the osmium(II) hydride $HOs(Br)(CO)(PPh_3)_2$.[28] The Os-P bond trans to hydride is 2.56 Å while Os-P bond trans to phosphorus is only 2.34 Å.

The average metal-hydrogen bond length in $H_4Os(PMe_2Ph)_3$ [1.659 (3) Å] is very close to the average terminal Re-H distances in $K_2[ReH_9]$[1.68 (1) Å][29] and $H_8Re_2(PEt_2Ph)_4$ [1.669 (7) Å][30] but shorter than Ta-H in $H_3Ta(C_5H_5)_2$ [1.774 (3) Å].[31] Shorter M-H distances are found in first-row transition metal hydrides: 1.60 Å in both $HMn(CO)_5$[32] and $[HZnN(CH_3)CH_2CH_2N(CH_3)_2]_2$.[33] To date, there are no reports of accurate terminal M-H bond lengths determined by single-crystal neutron diffraction studies of second-row organometallic hydrides. However, from the known covalent radii of metals it can be estimated that M-H bond lengths are about the same for second- and third-row transition metal hydrides.

The covalent radius of osmium calculated from the Os-H bond lengths is 1.29 Å while 1.22 Å is obtained from the Os-P bond lengths. The former number should be a more reliable estimate of the covalent radius because the Os-H bond is necessarily free of π effects. This value agrees reasonably well with the 1.33 Å covalent radius[26] predicted from the Os(IV)-X bond lengths in OsX_2 (X = S, Se, Te). From the accurate M-H distances given in the previous paragraph, one can derive the values 1.40, 1.30, and 1.29 Å as good estimates of the covalent radii of Ta, Re, and Os, respectively. It is interesting to note that this trend nicely reflects the expected decrease in radius as one moves from left to right along a row of the periodic table.

The x-ray structures of two seven-coordinate rhenium hydride complexes have been reported:[34] $ReH_3(DPPE)_2$ and $ReH_3(DPPE)(PPh_3)_2$ (DPPE is bisdiphenylphosphinoethane, also known as "diphos"). These hydrides also appear to have pentagonal bipyramidal geometry. The trans P-Re-P angle in $ReH_3(DPPE)_2$ is 167.4 (5)°, very similar to the 166.1 (1)° angle in the osmium complex. All four rhenium-phosphorus bonds have essentially the same length.

$IrH_5(PEt_2Ph)_2$ also seems to be a pentagonal bipyramidal complex. Shaw[35] and co-workers predicted a trans arrangement of the two phosphine ligands on the basis of the very small dipole moment of IrH_5L_2 complexes. Preliminary results from an x-ray investigation of this compound[36] indicate that the phosphorus atoms are indeed trans.

The relationship between octahedral and pentagonal bipyramidal geometries is easily seen if one considers the octahedron as a square bipyramid. Thus the structure of *mer*-$H_3Ir(PPh_3)_3$[37] is somewhat similar to that of $H_4Os(PMe_2Ph)_3$. The trans and cis P-M-P angles are 153.0 and 102.2° in the iridium complex compared to 156.17 and 97.41° in the osmium structure. While one is tempted to attribute the larger P-M-P angle in the iridium complex to triphenylphosphine being larger than dimethylphenylphosphine, it may also be attributed to the six-coordinate complex having fewer nonbonding interactions between the hydride atoms and the phosphine ligands. The average P-Ir-P angle in *fac*-$H_3Ir(PMe_2Ph)_3$ is 101.1°.[36] The iridium-phosphorus distance for the phosphorus trans to hydride in *mer*-$H_3Ir(PPh_3)_3$ is 0.06 Å longer than that for the other two Ir-P bond lengths (2.286 vs. 2.347 Å). Lengthening of the metal-phosphorus bond is less in $H_4Os(PMe_2Ph)_3$ where the equatorial phosphorus is not strictly trans to hydride atoms (the "trans" P-Os-H angles are about 146°).

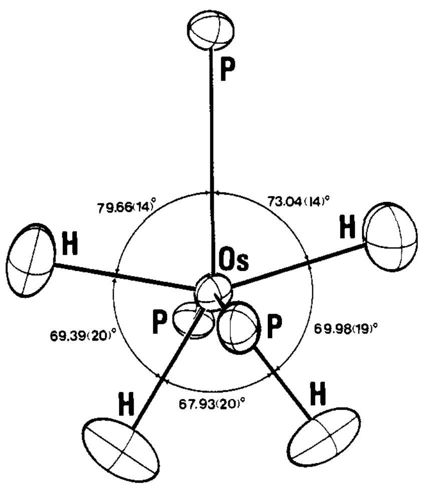


Figure 5. A plot of the H_4OsP_3 core of the molecule. H(1), the hydrogen on the extreme left, is bent away from the equatorial phosphorus atom because of interactions with the hydrogen atoms on the phosphine ligands (see Table V). Note again the slight bending of the main P-Os-P axis, which is approximately normal to the plane of the figure. Os-H bond lengths are (from left to right) 1.663 (3), 1.648 (3), 1.644 (3), 1.681 (3) Å; H···H nonbonding contact distances are 1.883 (5), 1.840 (6), 1.909 (5) Å.

The average P-C(methyl) and average P-C(phenyl) bond lengths [1.837 (2) and 1.841 (2) Å, respectively] are the same within experimental error, in agreement with P-C bond lengths found in other molecules. The average methyl and phenyl C-H bond lengths are also nearly the same: 1.094 (2) and 1.089 (2) Å. The Os-P-C angles vary from 115.34 to 119.57° and the C-P-C angles from 99.18 to 102.95°. The variation in bond angles is probably a consequence of slight bond bending to optimize nonbonding interactions. The planarity of the phenyl rings is shown in the results of best plane calculations in Table V. It is possible to estimate the standard deviations in the positions of the phenyl carbons from the deviations of these atoms from the plane.[38] This calculation gives the estimated standard deviation of about 0.0013 Å while the esd's from the least-squares refinement average about 0.0018 Å (the corresponding numbers from the x-ray refinement are 0.008 and 0.016 Å, respectively). Although esd's are often underestimated when calculated from least-squares results,[39] and especially when the complete variance-covariance matrix has not been included as is the case here, the present esd's seem to be quite reasonable.

The phosphorus atoms do not lie quite in the planes defined by their phenyl rings: the average deviation of phosphorus from the plane is 0.057 Å. This type of distortion has been noted before[40] and is probably due to steric interactions.

There is a small amount of distortion in the phenyl rings. The C-C-C angles at the carbons bonded to phosphorus [C(13), C(23), and C(33)] and at carbons across the ring [C(16), C(26), and C(36)] are less than 120° while the angles at the other carbons are greater than 120°. The observation of the

Table V. The Phenyl Rings[a]

Ring 1					
$3.0203x - 1.4972y + 7.0097z + 0.10721 = 0$					
C(13)	0.011	(+0.020)	P(1)	0.058	(0.107)
C(14)	−0.009	(−0.006)	H(141)	−0.010	
C(15)	−0.003	−0.010)	H(151)	0.002	
C(16)	0.011	(0.012)	H(161)	0.018	
C(17)	−0.006	(0.002)	H(171)	−0.017	
C(18)	−0.006	(−0.018)	H(181)	0.001	
Ring 2					
$10.239x + 2.1606y - 2.0617z - 0.45761 = 0$					
C(23)	−0.003	(0.003)	P(2)	−0.037	(−0.052)
C(24)	−0.001	(−0.004)	H(241)	0.005	
C(25)	0.004	(−0.000)	H(251)	0.011	
C(26)	−0.003	(0.005)	H(261)	−0.006	
C(27)	−0.000	(−0.005)	H(261)	−0.018	
C(28)	0.004	(0.002)	H(281)	0.016	
Ring 3					
$4.1619x - 7.4814y + 4.1581z - 1.3538 = 0$					
C(33)	0.001	(−0.001)	P(3)	−0.075	(−0.066)
C(34)	−0.003	(−0.006)	H(341)	−0.011	
C(35)	0.002	(0.008)	H(351)	0.024	
C(36)	0.002	(−0.004)	H(361)	0.003	
C(37)	−0.005	(−0.003)	H(371)	−0.008	
C(38)	0.003	(0.005)	H)381)	0.001	

[a] Deviations of atoms from least-squares phenyl planes. Planes calculated using carbon positions only. Numbers in parentheses are from the x-ray structure.

same distortion in all three rings suggests that this is a result of electronic effects rather than packing forces. Although this distortion gives the rings the same shape as *p*-benzoquinone,[41] we are reluctant to interpret these results as giving evidence for π-bonding to phosphorus. The phenyl C–C bond lengths are essentially all the same, 1.400 Å.

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Supplementary Material Available. Listings of the observed and calculated structure factor amplitudes for both the x-ray and neutron analyses (8 pages). Ordering information is given on any current masthead page.

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