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Articles

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Crystal and Molecular Structure of Bis(diisopropylphenylphosphine)hexahydridoosmium, $[OsH_6(PC_{12}H_{19})_2]$: Single-Crystal Neutron Diffraction Study at 20 K

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The crystal and molecular structure of the hexahydridoosmium complex $[OsH_6(PC_{12}H_{19})_2]$, determined from a low-temperature X-ray diffraction analysis, has been refined on the basis of neutron diffraction data obtained at 20 K. The dodecahedral ML_2H_6 core has approximate *mm* symmetry with the phosphines in equivalent B (five-neighbor) sites and a P–Os–P angle of 155.2 (1)°. The Os–H distances range from 1.637 (4) to 1.668 (4) Å, with a mean value of 1.649 (5) Å. Crystal data at 20.0 (5) K: a = 17.016 (3) Å, b = 13.762 (3) Å, c = 10.857 (3) Å, β = 98.91 (2)°, V = 2512 (1) Å^3, monoclinic, $P2_1/n$, Z = 4, M_r 584.8.

Introduction

Of the polyhydrido complexes of the third transition series the osmium hexahydrides $[OsH_6(PR_3)_2]$[1,2] (PR_3 = tertiary phosphine) have received relatively little attention. In contrast an extensive organometallic chemistry has evolved around $[ReH_7(PR_3)_2]$,[3,4] and $[IrH_5(PR_3)_2]$[3,5] has been studied recently as a precursor of species active in C–H bond cleavage.

Structurally, the polyhydrides are interesting because they belong to the class of coordination compounds with high coordination numbers,[6] and within that class they are chemically unique. We have previously described the structures of $[WH_6(PC_{12}H_{19})_3]$,[7] $[ReH_7(PC_{12}H_{19})_2]$, and $[ReD_7(PC_{12}H_{19})_2]$[8] although solid-state disorder has precluded definitive analyses of the last two crystalline solids.

Recently the discovery and structural characterization of molecular hydrogen complexes[9,10] has prompted Crabtree et al.[11] to reformulate several of the established polyhydrides as hydrido(dihydrogen) species on the basis of the observed NMR relaxation parameter T_1. In this context it is interesting to note that Ginsberg[12] has previously calculated that intramolecular H···H interactions make a contribution to the stability of $[ReH_9]^{2-}$ and $[ReH_8PR_3]^-$ species, although not in the sense of strong localized H–H bonding. We here report the neutron diffraction structure of $[OsH_6(PC_{12}H_{19})_2]$ a complex that conforms to the established norms of eight-coordination and classical hydride ligation.

Neutron Data Collection and Refinement of the Structure of $[OsH_6(PC_{12}H_{19})_2]$

Hexahydridobis(diisopropylphenylphosphine)osmium was prepared from $[OsCl_2O_2(PC_{12}H_{19})_2]$ as reported previously.[2] Large crystals were grown from a supersaturated solution in hexane at 4 °C. Pure, freshly grown crystals were colorless, but they darkened on standing at room temperature.

A gray/brown transparent tabloid-shaped crystal of $[OsH_6(PC_{12}H_{19})_2]$ (approximate dimensions 1.8 × 1.7 × 0.8 mm^3 and developed faces ⟨011⟩, (001), and (00$\bar{1}$)) was glued to a hollow-point aluminum pin. The mounted crystal was sealed under helium in an aluminum container mounted in a closed-cycle refrigerator[13] and placed on a four-circle diffractometer[14] at the Brookhaven High Flux Beam Reactor. Monochromatization from the 220 planes of a Ge single crystal with a 37° takeoff angle gave a neutron wavelength of 1.15933 (8) Å calibrated by using a KBr crystal (a_0 = 6.6000 (1) Å at 298 K).[15] The sample temperature was decreased at a rate of approximately 2 deg min^{-1} from 298 to 20.0 (5) K and remained constant thereafter.[16] The intensity of the 444 reflection was monitored and the centering successively adjusted as the temperature was slowly decreased. The unit cell data listed in Table I were obtained from a least-squares fit of the $\sin^2\theta$ values for 64 centred reflections (32 Friedel pairs).

Table I. Experimental Parameters for the Neutron Diffraction Study

space group	$P2_1/n$ (nonstandard setting of No. 14)
V	2512 (1) Å^3
M_r	584.8
a	17.016 (3) Å
b	13.762 (3) Å
c	10.857 (3) Å
β	98.91 (2)°
D_c(20 K)	1.55 g cm^{-3}
D_m(298 K) [flotation]	1.48 g cm^{-3}
temp	20.0 (5) K
wavelength	1.15933 (8) Å
monochromator	Ge (220)
cryst color	gray/brown transparent tablet (298 K)
cryst dimens	1.8 × 1.7 × 0.8 mm^3
scan widths ($\Delta 2\theta$)	(a) 2.8° ($0.038 \leq (\sin\theta)/\lambda \leq 0.431$ Å^{-1}) (b) 0.6° + 3.858 tan θ ($0.431 \leq (\sin\theta)/\lambda \leq 0.684$ Å^{-1})
scan time	(a) 70 steps of 80000 monitor counts (~2 s) per step (b) ≥60 steps of 80000 monitor counts per step
abs coeff	μ_{20K} = 3.115 cm^{-1}
transmissn coeff	0.5807–0.7956
R_{ave}[a]	$0.0503 = \sum_{i=1}^{n_0}\sum_{j=1}^{m}\lvert\bar{F}_{ij}^2 - \bar{F}_i^2\rvert / \sum_{i=1}^{n_0} m\lvert\bar{F}_i^2\rvert$
no. of reflcns obsd	7161
no. of std reflcns	120
no. of reflcns obsd twice (n_0)	358
no. reflcns available for struct refinement	6683
reflcns used in least-squares refinement ($F_o > 2\sigma(F_o)$)	5246
no. of ls params	641
R	$0.0687 = \sum\lvert(F_o - F_c)\rvert/\sum\lvert F_o\rvert$
R'	$0.0433 = \sum[w^{1/2}\lvert(F_o - F_c)\rvert]/\sum[w^{1/2}\lvert F_o\rvert]$
weighting scheme	$w = [\sigma^2(F) + 0.00005F^2]^{-1}$
goodness of fit	1.383

[a] Where n_0 is the number of reflections having more than one equivalent and m is the number of equivalents for each reflection (generally m = 2).

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	U^a
Os	2513 (1)	294 (1)	231 (1)	4 (1)
P(1)	2984 (1)	967 (1)	−1492 (2)	4 (1)
P(2)	2319 (1)	−950 (1)	1631 (2)	5 (1)
C(11)	3500 (1)	90 (1)	−2405 (1)	6 (1)
C(12)	3675 (1)	476 (1)	−3659 (1)	11 (1)
C(13)	4275 (1)	−286 (1)	−1633 (1)	9 (1)
C(21)	2203 (1)	1501 (1)	−2676 (1)	6 (1)
C(22)	1598 (1)	735 (1)	−3227 (2)	11 (1)
C(23)	1783 (1)	2353 (1)	−2156 (2)	10 (1)
C(31)	3703 (1)	1968 (1)	−1198 (1)	6 (1)
C(32)	3797 (1)	2664 (1)	−2113 (1)	8 (1)
C(33)	4323 (1)	3436 (1)	−1842 (1)	9 (1)
C(34)	4763 (1)	3532 (1)	−652 (2)	10 (1)
C(35)	4693 (1)	2834 (1)	251 (2)	9 (1)
C(36)	4166 (1)	2055 (1)	−20 (1)	7 (1)
C(41)	2197 (1)	−511 (1)	3217 (1)	7 (1)
C(42)	2341 (1)	−1282 (1)	4246 (1)	10 (1)
C(43)	1369 (1)	−57 (1)	3197 (2)	11 (1)
C(51)	3148 (1)	−1840 (1)	1953 (1)	6 (1)
C(52)	3934 (1)	−1345 (1)	2508 (2)	11 (1)
C(53)	3246 (1)	−2420 (1)	790 (2)	10 (1)
C(61)	1443 (1)	−1733 (1)	1227 (1)	6 (1)
C(62)	1412 (1)	−2682 (1)	1691 (1)	7 (1)
C(63)	721 (1)	−3241 (1)	1413 (2)	9 (1)
C(64)	49 (1)	−2854 (1)	681 (2)	9 (1)
C(65)	67 (1)	−1908 (1)	224 (2)	11 (1)
C(66)	759 (1)	−1354 (1)	488 (1)	9 (1)
H(1)	2357 (3)	−629 (3)	−757 (3)	31 (1)
H(2)	1592 (2)	322 (4)	−516 (4)	35 (1)
H(3)	2333 (3)	1463 (3)	169 (4)	32 (1)
H(4)	3377 (2)	−255 (3)	325 (4)	33 (1)
H(5)	3186 (3)	753 (3)	1362 (4)	35 (1)
H(6)	1975 (3)	778 (3)	1200 (4)	36 (1)
H(11)	3075 (2)	−521 (3)	−2574 (3)	21 (1)
H(12a)	3142 (2)	690 (3)	−4292 (4)	31 (1)
H(12b)	3970 (3)	−92 (3)	−4129 (4)	31 (1)
H(12c)	4082 (3)	1098 (3)	−3539 (4)	32 (1)
H(13a)	4174 (2)	−625 (3)	−771 (4)	31 (1)
H(13b)	4700 (2)	305 (3)	−1399 (4)	31 (1)
H(13c)	4548 (2)	−827 (3)	−2176 (4)	30 (1)
H(21)	2510 (2)	1768 (3)	−3430 (3)	19 (1)
H(22a)	1243 (2)	497 (3)	−2521 (4)	32 (1)
H(22b)	1870 (2)	89 (3)	−3575 (4)	31 (1)
H(22c)	1193 (2)	1046 (3)	−4011 (4)	31 (1)
H(23a)	1378 (2)	2696 (3)	−2904 (4)	28 (1)
H(23b)	1436 (3)	2107 (3)	−1454 (4)	31 (1)
H(23c)	2204 (2)	2901 (3)	−1732 (4)	30 (1)
H(32)	3457 (2)	2628 (3)	−3047 (3)	25 (1)
H(33)	4377 (2)	3978 (3)	−2555 (4)	27 (1)
H(34)	5155 (2)	4155 (3)	−442 (4)	26 (1)
H(35)	5036 (2)	2894 (3)	1179 (3)	27 (1)
H(36)	4095 (2)	1526 (3)	696 (3)	23 (1)
H(41)	2649 (2)	70 (3)	3405 (3)	21 (1)
H(42a)	1958 (3)	−1908 (3)	4030 (4)	28 (1)
H(42b)	2202 (3)	−983 (3)	5118 (3)	33 (1)
H(42c)	2955 (2)	−1539 (3)	4416 (4)	29 (1)
H(43a)	907 (2)	−615 (3)	3064 (4)	31 (1)
H(43b)	1346 (3)	298 (3)	4093 (4)	31 (1)
H(43c)	1230 (3)	493 (3)	2470 (4)	31 (1)
H(51)	2978 (2)	−2344 (3)	2653 (3)	18 (1)
H(52a)	3884 (2)	−910 (3)	3335 (4)	29 (1)
H(52b)	4140 (2)	−873 (3)	1823 (4)	34 (1)
H(52c)	4395 (2)	−1901 (3)	2774 (4)	31 (1)
H(53a)	2709 (2)	−2832 (3)	438 (4)	30 (1)
H(53b)	3378 (3)	−1946 (3)	45 (4)	33 (1)
H(53c)	3734 (2)	−2936 (3)	1010 (4)	31 (1)
H(62)	1919 (2)	−3000 (3)	2275 (3)	22 (1)
H(63)	721 (2)	−3974 (3)	1782 (4)	26 (1)
H(64)	−489 (2)	−3288 (3)	469 (4)	28 (1)
H(65)	−462 (2)	−1601 (3)	−333 (4)	30 (1)
H(66)	783 (2)	−621 (3)	121 (4)	26 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

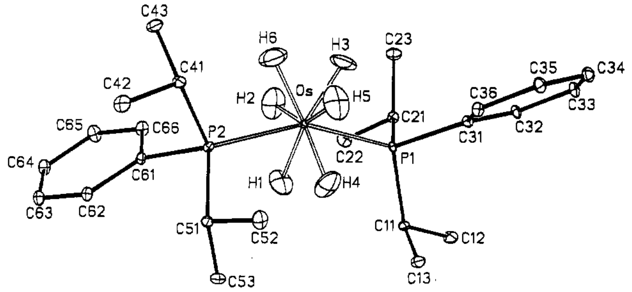

Figure 1. Molecular structure of $[OsH_6(PC_{12}H_{19})_2]$ showing atomic numbering scheme and thermal ellipsoids drawn to enclose 50% probability.[7] Hydrogen atoms were omitted from phosphine ligands for clarity.

A total of 7161 neutron intensity data were collected in the θ–2θ step scan mode. The intensities of three monitor reflections ($5,\overline{10},1$, $10,\bar{4},3$, and $4\bar{8}4$), measured every 200 reflections, showed no significantly systematic variation (<6.5%) during data collection. Background intensity was based on the intensity level of the first and last 10% of each scan. The net intensities were corrected for Lorentz and absorption effects.[17]

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Table III. Bond Lengths (Å) and Angles (deg)

Os-H(1)	1.658 (4)	Os-H(2)	1.650 (4)
Os-H(3)	1.637 (4)	Os-H(4)	1.643 (4)
Os-H(5)	1.668 (4)	Os-H(6)	1.638 (5)
Os-P(1)	2.338 (2)	Os-P(2)	2.347 (2)
P(1)-C(11)	1.866 (3)	P(1)-C(21)	1.851 (2)
P(1)-C(31)	1.838 (2)	P(2)-C(41)	1.866 (2)
P(2)-C(51)	1.860 (2)	P(2)-C(61)	1.835 (2)
C(11)-C(12)	1.533 (2)	C(11)-C(13)	1.539 (2)
C(21)-C(22)	1.530 (2)	C(21)-C(23)	1.526 (2)
C(31)-C(32)	1.405 (2)	C(31)-C(36)	1.400 (2)
C(32)-C(33)	1.392 (2)	C(33)-C(34)	1.397 (2)
C(34)-C(35)	1.391 (2)	C(35)-C(36)	1.399 (2)
C(41)-C(42)	1.533 (2)	C(41)-C(43)	1.538 (2)
C(51)-C(52)	1.539 (2)	C(51)-C(53)	1.525 (2)
C(61)-C(62)	1.404 (2)	C(61)-C(66)	1.407 (2)
C(62)-C(63)	1.397 (2)	C(63)-C(64)	1.393 (2)
C(64)-C(65)	1.396 (2)	C(65)-C(66)	1.395 (2)
H(1)-Os-H(2)	69.8 (2)	H(1)-Os-H(3)	135.7 (2)
H(2)-Os-H(3)	78.4 (2)	H(1)-Os-H(4)	74.9 (2)
H(2)-Os-H(4)	144.5 (2)	H(3)-Os-H(4)	127.9 (2)
H(1)-Os-H(5)	142.1 (2)	H(2)-Os-H(5)	147.6 (2)
H(3)-Os-H(5)	76.2 (2)	H(4)-Os-H(5)	67.9 (2)
H(1)-Os-H(6)	132.6 (2)	H(2)-Os-H(6)	74.0 (2)
H(3)-Os-H(6)	60.5 (2)	H(4)-Os-H(6)	137.0 (2)
H(5)-Os-H(6)	76.2 (2)	H(1)-Os-P(1)	80.0 (2)
H(2)-Os-P(1)	90.8 (2)	H(3)-Os-P(1)	70.3 (2)
H(4)-Os-P(1)	79.5 (2)	H(5)-Os-P(1)	99.1 (2)
H(6)-Os-P(1)	130.3 (2)	H(1)-Os-P(2)	80.5 (1)
H(2)-Os-P(2)	96.7 (2)	H(3)-Os-P(2)	134.4 (2)
H(4)-Os-P(2)	80.7 (2)	H(5)-Os-P(2)	87.1 (2)
H(6)-Os-P(2)	74.5 (2)	P(1)-Os-P(2)	155.2 (1)
Os-P(1)-C(11)	114.6 (1)	Os-P(1)-C(21)	114.5 (1)
C(11)-P(1)-C(21)	103.6 (1)	Os-P(1)-C(31)	117.4 (1)
C(11)-P(1)-C(31)	102.8 (1)	C(21)-P(1)-C(31)	102.1 (1)
Os-P(2)-C(41)	114.1 (1)	Os-P(2)-C(51)	115.1 (1)
C(41)-P(2)-C(51)	103.2 (1)	Os-P(2)-C(61)	117.6 (1)
C(41)-P(2)-C(61)	102.1 (1)	C(51)-P(2)-C(61)	102.8 (1)

The absorption correction was based on a numerical integration over a Gaussian grid of 10 × 16 × 16 points along the a^*, b^*, and c^* directions, respectively. Averaging of symmetry-related data resulted in structure factors for 6683 unique reflections.

Atomic parameters obtained from the low-temperature X-ray diffraction study[18] and hydride positions determined by difference synthesis calculated from 500 neutron data collected at the ILL, Grenoble, France,[19] were used initially for least-squares refinement against the present neutron data. All 71 atoms were refined anisotropically (641 parameters) by blocked-cascade least squares[20] with 5246 data with $F_o > 2\sigma(F_o)$. The function minimized was $\sum(w(|F_o| - k|F_c|)^2)$ with weights $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ and $g = 0.00005$ where $\sigma(F_o)$ is the standard deviation in F_o based on counting statistics. Refinement converged at R (R') = 0.0687 (0.0433) after inclusion of a correction for isotropic extinction.[21] With the weighing scheme given above $\sum w(\Delta F^2)$ was almost constant for ranges of $|F_o|$ and sin θ. The slope of the normal probability plot[22] was 1.150. The mean shift to error ratio in the last 10 cycles was 0.02 with a maximum of 0.30 for the overall scale factor in cycle 6. a final difference Fourier synthesis was essentially featureless.

Positional parameters for all atoms are given in Table II, and selected bond lengths and interbond angles are given in Table III. The neutron scattering lengths used were taken from Bacon,[23] and all refinements were performed by using the SHELXTL suite of programs[20] on a Data General S230 Eclipse computer.

Results and Discussion

The overall molecular shape of $[OsH_6(PC_{12}H_{19})_2]$ (Figure 1) had been established from the low-temperature X-ray data.[18] However, these data only gave tentative indications of the positions for three of the six hydride ligands. With a preliminary and incomplete neutron data set collected at the ILL, Grenoble, France, it was possible to confirm these three hydride positions and locate the remaining three hydride ligands by difference synthesis.[19] This model has now been refined based on the present extensive low-temperature neutron data. The molecular numbering scheme is given in Figure 1 with hydrogen atoms of the two phosphine ligands omitted for clarity.

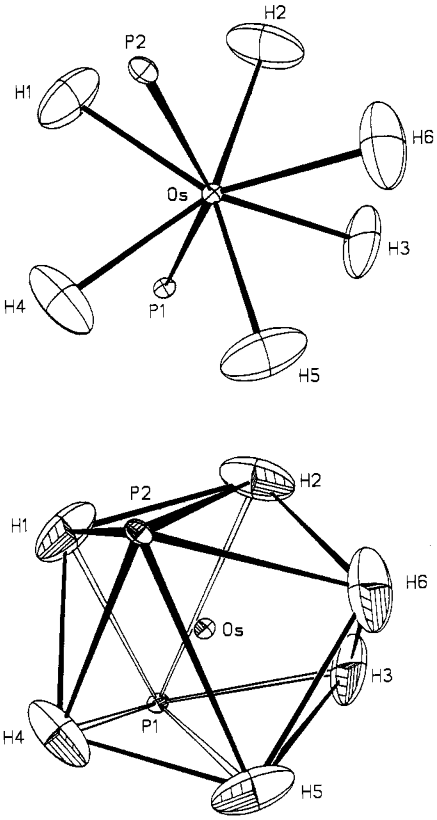

Figure 2. Perspective views of the OsH_6P_2 core, with thermal ellipsoids as in Figure 1.

The geometry of the MH_6L_2 inner coordination sphere of $[OsH_6(C_{12}H_{19}P)_2]$ (Figure 2) is that of an irregular dodecahedron. This dodecahedral coordination geometry may be discussed in terms of two intersecting orthogonal BAAB trapezoidal planes.[24] One plane contains P(1), H(3), H(6), and P(2) in which the two phosphine ligands occupy similar five-neighbor (B) sites, with a P-M-P angle of 155.2 (1)°, and the hydride ligands are in the four-neighbor A sites. The second BAAB trapezoidal plane contains H(2) and H(5) in B sites and H(1) and H(4) in A sites. The BAAB mean planes formed by atoms P(1), H(3), H(6), and P(2) (plane 1) and H(2), H(1), H(4), and H(5) (plane 2) have an interplanar angle of 87.5°. Within each BAAB trapezoidal plane there is a twist of 7.2° for the AOsA triangular plane relative to the BOsB triangular plane such that maximum displacements from plane 1 are 0.09 Å for H(3) and −0.09 Å for H(6) and, for plane 2, −0.06 Å for H(1) and 0.07 Å for H(4). The osmium atom is nearly coplanar with each BAAB trapezoid (deviations are −0.013 Å from plane 1 and 0.030 Å from plane 2).

The two Os-P bonds are chemically equivalent. Their lengths (2.338 (2) and 2.347 (2) Å) are not significantly different and lie toward the top of the range of Os-P distances determined, by neutron diffraction, in $[OsH_4(PMe_2Ph)_3]$.[24,25] Phosphine ligands tend to prefer to coordinate via the more spacious B sites in such

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dodecahedral eight-coordinate polyhydride complexes,[6,24] as witnessed in $[ReH_5(PMePh_2)_3]$,[27] and in $[MoH_4(PMePh_2)_4]$[26,28] which contains a symmetrical arrangement of A site hydrides and B site phosphine ligands.

The Os–H distances (Table III) range from 1.637 (4) to 1.668 (4) Å and have a mean value of 1.649 (5) Å.[29] Interestingly the shortest Os–H distances of 1.637 (4) Å (to H(3)) and 1.638 (5) Å (to H(6)) involve adjacent A site hydride ligands. H(3) and H(6) subtend an angle of 60.5 (2)° at osmium (the smallest H–Os–H angle in this compound) and have an H···H intramolecular contact of 1.650 (6) Å. These two Os–H bonds, while not significantly shorter than Os–H(4) (1.643 (4) Å) or Os–H(2) (1.650 (4) Å), are significantly shorter than Os–H(1) and Os–H(5) (1.658 (4) and 1.668 (4) Å, respectively), as well as the four Os–H bonds (1.644 (3)–1.681 (3) Å) determined in $[OsH_4(PMe_2Ph)_3]$.[25] The close H(3)···H(6) nonbonded interaction of 1.650 Å is one of the shortest so far determined in these third-row transition-metal polyhydride complexes. The next shortest H···H intracore separation in the title compound is 1.848 (6) Å between H(4) and H(5) while H(2) and H(3) have the longest (2.078 (7) Å) nonbonded distance among the adjacent core hydride ligands. Short though the H(3)–H(6) separation is, it is nonetheless much longer than the observed[9] H–H separation (0.84 Å) in the neutron diffraction structure of $[W(CO)_3(H_2)(PC_9H_{21})_2]$, and there are therefore no grounds for reformulating the title compound as $[OsH_4(H_2)(PC_{12}H_{19})_2]$.

The two diisopropylphosphine ligands in the five-neighbor B sites point directly toward the osmium atom with Os–P–X angles of 178.2° at P(1) and 177.6° at P(2) (X is the center of the triangle defined by the three carbon atoms bonded to phosphorus). The phosphine ligands are perfectly ordered and were refined without geometrical constraints. The accuracy of the analysis allows observation of a significant shortening of P–C(Ph) bonds (average 1.837 (2) Å) relative to P–C(*i*-Pr) bonds (average 1.861 (4) Å) in the phosphines. The Os–P–C(Ph) angles (average 117.5 (1)°) are significantly larger than the Os–P–C(i-Pr) angles (average 114.6 (2)°), both being larger than the C–P–C angles (mean 102.8 (1)°), as is commonly observed.[8] The average C–C bond lengths (*i*-Pr) in the phosphines [$(C{-}C)_{i\text{-Pr}}$ mean 1.533 (1) Å] are remarkably close to the expected values (1.524 (15) Å). The overall mean C–H bond distance is 1.092 Å; the same value as the mean $(C{-}H)_{i\text{-Pr}}$ methyl bond lengths (1.092 (1) Å). The tertiary $(C{-}H)_{i\text{-Pr}}$ distances have a mean value of 1.103 (2) Å while the mean $(C{-}H)_{Ph}$ bond distance is 1.087 (1) Å.

The shortest intramolecular H···H contacts (other than H(3)···H(6)) are between the phosphine methyl hydrogens (≥1.743 Å) while intermolecular contacts between peripheral hydrogens in symmetry-related or translationally related molecules are ≥2.181 Å.

Conclusion

A single-crystal neutron diffraction study of $[OsH_6(PC_{12}H_{19})_2]$ at 20 K has established the eight-coordinate core geometry about the osmium atom to be that of an irregular dodecahedron. The Os–H distances range from 1.637 (4) to 1.668 (4) Å, with a very short H···H interaction (1.650 (6) Å) between the two most closely bound hydride ligands (Os–H = 1.637 (4) and 1.638 (5) Å). The two essentially equivalent phosphine ligands (Os–P = 2.338 (2) and 2.347 (2) Å) subtend an angle of 155.2 (1)° at osmium.

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Registry No. $[OsH_6(C_{12}H_{19}P)_2]$, 91030-50-1.

Supplementary Material Available: Tables listing all anisotropic displacement parameters (Table IV), all hydrogen atom coordinates (Table V), complete bond lengths and angles (Table VI), least-squares planes, and nonbonded distances (15 pages); a table of calculated and observed structure factors (31 pages).

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