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X-ray and Neutron Diffraction Single-Crystal Studies of Tris(phenyldiisopropylphosphine)tungsten Hexahydride $[WH_6(PPh\text{-}i\text{-}Pr_2)_3]$

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The single-crystal and molecular structure of tris(phenyldiisopropylphosphine)tungsten hexahydride has been determined by X-ray diffraction and subsequently by neutron diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$ as follows: X-ray diffraction (200 K) a = 11.490 (6) Å, b = 10.610 (3) Å, c = 16.324 (8) Å, α = 104.76 (3)°, β = 108.04 (4)°, γ = 89.92 (4)°; neutron diffraction (100 K) a = 11.427 (8) Å, b = 10.554 (6) Å, c = 16.249 (6) Å, α = 104.59 (2)°, β = 108.16 (2)°, γ = 89.88 (2)°. The molecule shows approximate C_{2v} symmetry with an asymmetric disposition of the phosphine ligands around the tungsten atom. W–P distances of 2.424 (2), 2.519 (2), and 2.524 (2) Å are observed, and W–H is observed in the range 1.718–1.745 (3) Å.

Introduction

Interest in the mononuclear polyhydrides of the general form $[MH_xL_y]$ (for example, M = W, Re, Os, Ir; L = tris(organo)phosphine) has increased in recent years.[1] The accurate location of these hydride ligands has become a reality through single-crystal neutron diffraction and to a lesser extent through low-temperature X-ray diffraction studies. There are, however, very few compounds of this type well characterized by neutron diffraction experiments.[2]

The earlier syntheses of the complexes $[WH_6(PR_3)_3]$ (R = alkyl, aryl; Ph = C_6H_5; *i*-Pr = isopropyl (C_3H_7)) were unaccompanied by structural studies. More recently[3] our extension of the synthetic route has led to the first indication of the molecular geometry for $[WH_6L_3]$ from a low-temperature X-ray diffraction study. The neutron diffraction experiment has enabled us to obtain precise confirmation of the hydrogen atom positions, which were located in the original X-ray study.

The hydrogenolysis of hexamethyltungsten[4] in the presence of tertiary phosphines affords products that depend predominantly on the ligand size. For example, L = $PPh\text{-}i\text{-}Pr_2$ and $P\text{-}i\text{-}Pr_3$ give $[WH_6L_3]$ as the major hydrocarbon soluble products, while L = $PPhMe_2$ affords principally $[WH_4(PPhMe_2)_4]$. Wilkinson and co-workers[5] have reported the preparation of $[WH_2L_5]$ from the low-pressure hydrogenolysis of $[WMe_6(PMe_3)]$ in the presence of excess trimethylphosphine.

Table I. Crystal Data and Experimental Parameters

	X-ray	neutron
mol formula	$WP_3C_{36}H_{63}$	
M_r	772.7	
a, Å	11.490 (6)	11.427 (8)
b, Å	10.610 (3)	11.554 (6)
c, Å	16.324 (8)	16.249 (6)
α, deg	104.76 (3)	104.59 (2)
β, deg	108.04 (4)	108.16 (2)
γ, deg	89.92 (4)	89.88 (2)
V, Å^3	1823	1796
space group	$P\bar{1}$	$P\bar{1}$
$F000$	795.7	4.12×10^{-12} cm
μ, cm^{-1}	33.87	3.17
D_{calcd}	1.41	1.41
Z	2	2
λ, Å√	0.710 69	1.262
monochromator	graphite	Cu (200)
$2\theta_{max}$	60	110
T, K	200	100
data collcd	9092	8028
no. of unique data used	$7583 > 1.5\sigma(I)$	$7068 > 0$
weighting scheme	$[\sigma^2(F) + 0.0003F^2]^{-1}$	$1/\sigma^2, \sigma = (4.5(F) + 10^{-6}F^5)$
scan type	ω–2θ	ω–2θ
refinement	blocked-cascade least-squares	blocked full-matrix least-squares
$R(R^1)$	0.033 (0.026)	0.049 (0.020)

Experimental Section

(a) Synthesis.[3] To a solution of hexamethyltungsten (93 mmol) in hexane (60 cm^3) was added $PPh\text{-}i\text{-}Pr_2$ (27 mmol), and the mixture was subjected to hydrogen gas at 300 atm for 5 days. The resulting dark brown solution was filtered and evaporated at reduced pressure, affording a dark oil that was dried under a good vacuum for 24 h to rēmove excess phosphine. The residue was recrystallized several times from hexane at −20 °C, yielding colorless crystals of $[WH_6(PPh\text{-}i\text{-}Pr_2)_3]$ (0.72 g; 10%). Anal. Calcd for $C_{36}H_{63}P_3W$: C, 55.95; H, 8.15. Found: C, 55.50; H, 8.30. Spectroscopic properties of this compound are described elsewhere.[3]

(b) X-ray Experiment. A small (~0.25 × 0.15 × 0.10 mm) single crystal of the title complex was mounted in a Pantak glass capillary (low-density nonhygroscopic glass) tube and sealed under nitrogen. The crystal was mounted on a Nicolet P3m automated four-circle diffractometer, and cooling was effected by a stream of cold, dry nitrogen gas. A total of 9092 intensities were collected in the range $2.9 < 2\theta < 60.0°$ by using the θ–2θ scan technique with graphite-monochromated Mo Kα X-radiation. Of the measured reflections, the 7583 used in the subsequent refinements satisfied the condition $F_{hkl}^2 > 1.5\sigma(F_{hkl}^2)$. A slight yellowing of the crystal was observed on long exposure to the X-ray beam, but the intensities of the three standard reflections showed little or no decrease during the experiment.

(c) Neutron Experiment. The neutron data were collected at the Institut Laue Langevin, using the four-circle diffractometer D8 and a closed-loop helium cryorefrigerator.[6] A large (~1.86 × 1.9 × 1.4

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Table II. Fractional Atomic Coordinates for $[WH_6(PPh\text{-}i\text{-}Pr_2)_3]$ (Neutron Study)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
W	0.22878 (9)	0.4439 (1)	0.21116 (7)	C51	0.43662 (7)	0.39186 (8)	0.7795 (5)
P1	0.30165 (9)	0.67626 (9)	0.30527 (6)	H51	0.3732 (2)	0.4600 (2)	0.0499 (2)
P2	0.33822 (9)	0.30335 (9)	0.12258 (6)	C52	0.48189 (8)	0.30936 (9)	0.00376 (6)
P3	0.03037 (9)	0.3813 (1)	0.23335 (7)	H521	0.4070 (2)	0.2611 (3)	−0.0569 (2)
H1	0.2716 (2)	0.4369 (2)	0.3227 (2)	H522	0.5411 (2)	0.2357 (3)	0.0260 (2)
H2	0.1193 (2)	0.5411 (2)	0.1664 (2)	H523	0.5376 (2)	0.3728 (2)	−0.0156 (2)
H3	0.3886 (2)	0.4615 (2)	0.2587 (2)	C53	0.54629 (8)	0.47179 (9)	0.15499 (6)
H4	0.2745 (2)	0.5282 (2)	0.1463 (2)	H531	0.5173 (2)	0.5406 (2)	0.2049 (2)
H5	0.2227 (2)	0.2813 (2)	0.2156 (2)	H532	0.6014 (2)	0.5266 (3)	0.1295 (2)
H6	0.1269 (2)	0.3630 (2)	0.1074 (2)	H533	0.6071 (2)	0.4080 (2)	0.1887 (2)
C12	0.21252 (8)	0.88893 (8)	0.41316 (6)	C61	0.24624 (7)	0.17726 (8)	0.01965 (5)
C13	0.15627 (8)	0.94056 (9)	0.47788 (6)	H61	0.3146 (2)	0.1261 (2)	−0.0085 (2)
C14	0.11484 (8)	0.85933 (9)	0.52015 (6)	C62	0.16122 (8)	0.23756 (9)	−0.05107 (6)
C15	0.13100 (8)	0.72576 (9)	0.49764 (6)	H621	0.2100 (2)	0.3088 (3)	−0.0690 (2)
C16	0.18713 (7)	0.67440 (8)	0.43324 (5)	H622	0.0897 (2)	0.2865 (3)	−0.0277 (2)
C11	0.22802 (7)	0.75434 (8)	0.38916 (5)	H623	0.1160 (2)	0.1604 (3)	−0.1121 (2)
H12	0.2430 (2)	0.9552 (2)	0.3816 (2)	C63	0.17386 (8)	0.07660 (9)	0.04201 (6)
H13	0.1451 (2)	1.0452 (2)	0.4953 (2)	H631	0.2342 (2)	0.0274 (3)	0.0884 (2)
H14	0.0706 (2)	0.8999 (3)	0.5700 (2)	H632	0.1228 (2)	0.0017 (2)	−0.0192 (2)
H15	0.0982 (2)	0.6605 (3)	0.5294 (2)	H633	0.1080 (2)	0.1224 (3)	0.0727 (2)
H16	0.1984 (2)	0.5700 (2)	0.4146 (2)	C72	−0.13821 (7)	0.48673 (8)	0.32724 (5)
C21	0.29601 (7)	0.80278 (8)	0.24273 (5)	C73	−0.20968 (8)	0.58415 (9)	0.35640 (6)
H21	0.3279 (2)	0.8968 (2)	0.2940 (2)	C74	−0.20690 (8)	0.70480 (9)	0.33673 (6)
C22	0.38346 (8)	0.78142 (8)	0.18684 (6)	C75	−0.13227 (8)	0.72682 (9)	0.28777 (6)
H221	0.4800 (2)	0.7833 (3)	0.2274 (2)	C76	−0.06044 (7)	0.62955 (8)	0.25921 (5)
H222	0.3781 (2)	0.8601 (2)	0.1535 (2)	C71	−0.06151 (7)	0.50778 (8)	0.27864 (5)
H223	0.3581 (2)	0.6883 (2)	0.1354 (2)	H72	−0.1444 (2)	0.3932 (2)	0.3427 (2)
C23	0.16454 (8)	0.81194 (9)	0.18399 (6)	H73	−0.2684 (2)	0.5649 (3)	0.3935 (2)
H231	0.1005 (2)	0.8313 (2)	0.2226 (2)	H74	−0.2631 (2)	0.7800 (2)	0.3589 (2)
H232	0.1299 (2)	0.7210 (2)	0.1313 (2)	H75	−0.1294 (2)	0.8206 (2)	0.2717 (2)
H233	0.1622 (2)	0.8920 (2)	0.1522 (2)	H76	−0.0018 (2)	0.6475 (2)	0.2213 (2)
C31	0.46773 (7)	0.69908 (8)	0.37788 (5)	C81	0.03767 (8)	0.26420 (8)	0.30327 (5)
H31	0.5164 (2)	0.6584 (2)	0.3300 (2)	H81	−0.0578 (2)	0.2462 (2)	0.3012 (2)
C32	0.49176 (8)	0.61837 (9)	0.44657 (6)	C82	0.11717 (8)	0.3203 (1)	0.40150 (6)
H321	0.4611 (3)	0.5156 (2)	0.4150 (2)	H821	0.0854 (2)	0.4111 (3)	0.4336 (2)
H322	0.4443 (2)	0.6542 (3)	0.4954 (2)	H822	0.2128 (2)	0.3394 (3)	0.4061 (2)
H323	0.5899 (2)	0.6266 (3)	0.4841 (2)	H823	0.1146 (2)	0.2502 (3)	0.4403 (2)
C33	0.51736 (8)	0.84198 (8)	0.42609 (6)	C83	0.08052 (9)	0.13139 (9)	0.26474 (7)
H331	0.5138 (2)	0.9028 (2)	0.3805 (2)	H831	0.0310 (3)	0.0890 (2)	0.1934 (2)
H332	0.6138 (2)	0.8452 (2)	0.4676 (2)	H832	0.0657 (3)	0.0615 (2)	0.3008 (2)
H333	0.4665 (2)	0.8871 (2)	0.4713 (2)	H833	0.1782 (2)	0.1395 (3)	0.2725 (2)
C42	0.48770 (8)	0.22678 (9)	0.27426 (6)	C91	−0.08969 (7)	0.29392 (8)	0.12523 (5)
C43	0.57661 (9)	0.15573 (9)	0.31948 (6)	H91	−0.0370 (2)	0.2236 (2)	0.0915 (2)
C44	0.62988 (8)	0.05756 (9)	0.27196 (6)	C92	−0.13958 (8)	0.3876 (1)	0.06655 (6)
C45	0.59167 (8)	0.02882 (9)	0.17881 (6)	H921	−0.0663 (2)	0.4426 (3)	0.0576 (2)
C46	0.50227 (7)	0.09943 (8)	0.13370 (5)	H922	−0.1960 (2)	0.4573 (3)	0.0955 (2)
C41	0.44960 (7)	0.20107 (8)	0.18048 (5)	H923	−0.1985 (2)	0.3317 (3)	0.0002 (2)
H42	0.4458 (2)	0.3031 (3)	0.3117 (2)	C93	−0.19671 (8)	0.21874 (9)	0.13475 (6)
H43	0.6052 (3)	0.1777 (3)	0.3924 (2)	H931	−0.1683 (2)	0.1397 (3)	0.1660 (2)
H44	0.6999 (2)	0.0024 (2)	0.3075 (2)	H932	−0.2629 (2)	0.1748 (3)	0.0681 (2)
H45	0.6312 (2)	−0.0488 (3)	0.1408 (2)	H933	−0.2466 (2)	0.2833 (3)	0.1732 (2)
H46	0.4741 (2)	0.0736 (2)	0.0610 (2)				

mm) colorless single crystal of $[WH_6(PPh\text{-}i\text{-}Pr_2)_3]$, grown from a seeded solution in hexane, was glued to an aluminum pin and mounted on the diffractometer. From the orientation matrix calculated at room temperature, the intensity of one strong reflection (60$\bar{2}$) was monitored carefully as the temperature was reduced slowly to 100 K. The sample suffered no degradation during the test, and the original intensity was regained on warming to room temperature. During data collection the temperature was maintained at 100 ± 1 K, as measured by a chromel/Au–0.7 Fe thermocouple. At low temperature, the cell parameters and instrumental offsets were calculated by a least-squares refinement using the observed setting angles for 31 centered reflections, in the range $9.7 < 2\theta < 96.2°$. Two standard reflections, monitored every 50 reflections, showed no decrease in intensity during the period of data collection. Data reduction was by the profile analysis method of Lehmann and Larsen.[7] The observed intensities were corrected for neutron absorption effects and then sorted and merged ($R = 0.02$). R(merge) is defined as $\sum[(F_o^2 - \bar{F}_o^2)]/\sum F_o^2$ where $\bar{F}_o^2$ is the mean value of a multiply observed reflection. A total of 8028 intensities were recorded, yielding 7068 unique reflections with $I > 0$. The linear absorption coefficient of 3.17 cm^{-1} was calculated from the crystal transmission coefficient measured at room temperature (3.11 cm^{-1}). A numerical absorption correction was applied with the program ABSCO2.[8] A summary of the experimental conditions and crystal data is given in Table I.

Structure Solution and Refinement

(a) X-ray Diffraction. Preliminary X-ray photographic work yielded a triclinic unit cell. The X-ray intensities, corrected for Lorentz and polarization effects, were used to calculate a Patterson map. Solution in $P\bar{1}$ revealed the position of the W atom, and subsequent difference Fourier syntheses allowed the location of all remaining non-hydrogen atoms. An empirical absorption correction was applied, after which the positions of the hydridic and organic hydrogen atoms were revealed by difference Fourier maps. The W atom and all P and C atoms were refined with individual anisotropic temperature parameters, while the H atoms were tied to common isotropic temperature factors according to type. The refinement was carried out by using the blocked-cascade

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Table III. Bond Lengths (Å) and Bond Angles (deg) for $[WH_6(PPh\text{-}i\text{-}Pr_2)_3]$ Omitting Those Involving Organic H (Neutron Study)

(a) Bond Lengths

W-P1	2.524 (2)	W-P2	2.424 (2)
W-P3	2.519 (2)	W-H1	1.745 (3)
W-H2	1.718 (3)	W-H3	1.737 (3)
W-H4	1.729 (3)	W-H5	1.739 (3)
W-H6	1.727 (2)	P1-C11	1.842 (2)
P1-C21	1.861 (2)	P1-C31	1.875 (2)
P2-C41	1.852 (2)	P2-C51	1.875 (2)
P2-C61	1.861 (2)	P3-C71	1.846 (2)
P3-C81	1.863 (2)	P3-C91	1.872 (2)
C11-C12	1.402 (2)	C12-C13	1.396 (2)
C13-C14	1.390 (2)	C14-C15	1.392 (2)
C15-C16	1.390 (2)	C16-C11	1.399 (2)
C21-C22	1.528 (2)	C21-C23	1.526 (2)
C31-C32	1.528 (2)	C31-C33	1.530 (2)
C41-C42	1.401 (2)	C42-C43	1.394 (2)
C43-C44	1.388 (2)	C44-C45	1.390 (2)
C45-C46	1.393 (2)	C46-C41	1.401 (2)
C51-C52	1.529 (2)	C51-C53	1.531 (2)
C61-C62	1.530 (2)	C61-C63	1.527 (2)
C71-C72	1.401 (2)	C72-C73	1.393 (2)
C73-C74	1.392 (2)	C74-C75	1.390 (2)
C75-C76	1.392 (2)	C76-C71	1.399 (2)
C81-C82	1.532 (2)	C81-C83	1.531 (2)
C91-C92	1.532 (2)	C91-C93	1.527 (2)

(b) Bond Angles

P1-W-P2	125.54 (6)	P1-W-P3	107.88 (6)
P1-W-H1	74.10 (8)	P1-W-H2	74.01 (7)
P1-W-H3	69.34 (7)	P1-W-H4	72.11 (7)
P1-W-H5	143.55 (9)	P1-W-H6	138.96 (9)
P2-W-P3	126.49 (5)	P2-W-H1	114.07 (9)
P2-W-H2	122.05 (9)	P2-W-H3	65.18 (7)
P2-W-H4	70.13 (8)	P2-W-H5	66.25 (9)
P2-W-H6	69.97 (8)	P3-W-H1	75.15 (8)
P3-W-H2	72.44 (9)	P3-W-H3	143.9 (1)
P3-W-H4	137.60 (9)	P3-W-H5	69.21 (9)
P3-W-H6	72.06 (8)	H1-W-H2	123.9 (2)
H1-W-H3	69.5 (1)	H1-W-H4	139.0 (1)
H1-W-H5	70.1 (1)	H1-W-H6	139.4 (2)
H2-W-H3	134.9 (2)	H2-W-H4	66.9 (1)
H2-W-H5	133.1 (1)	H2-W-H6	66.87 (9)
H3-W-H4	77.3 (1)	H3-W-H5	91.7 (1)
H3-W-H6	134.6 (2)	H4-W-H5	135.6 (2)
H4-W-H6	81.4 (1)	H5-W-H6	76.4 (1)
W-P1-C11	119.51 (7)	W-P1-C21	116.23 (6)
W-P1-C31	114.38 (6)	C11-P1-C21	102.13 (7)
C11-P1-C31	100.21 (6)	C21-P1-C31	101.65 (7)
W-P2-C41	116.41 (6)	W-P2-C51	114.95 (6)
W-P2-C61	118.32 (6)	C41-P2-C51	101.97 (7)
C41-P2-C61	100.77 (6)	C51-P2-C61	101.88 (7)
W-P3-C71	121.04 (6)	W-P3-C81	117.11 (6)
W-P3-C91	112.40 (7)	C71-P3-C81	101.72 (7)
C71-P3-C91	99.72 (6)	C81-P3-C91	101.90 (7)
P1-C11-C12	124.38 (9)	P1-C11-C16	117.81 (7)
C12-C11-C16	117.80 (9)	C11-C12-C13	120.8 (1)
C12-C13-C14	120.54 (9)	C13-C14-C15	119.16 (9)
C14-C15-C16	120.3 (1)	C15-C16-C11	121.38 (9)
P1-C21-C22	112.90 (7)	P1-C21-C23	111.53 (7)
C22-C21-C23	110.46 (7)	P1-C31-C32	111.59 (7)
P1-C31-C33	114.79 (7)	C32-C31-C33	109.36 (7)
P2-C41-C42	120.38 (7)	P2-C41-C46	122.06 (7)
C42-C41-C46	117.52 (8)	C41-C42-C43	121.26 (9)
C42-C43-C44	120.28 (9)	C43-C44-C45	119.36 (9)
C44-C45-C46	120.27 (9)	C45-C46-C41	121.29 (8)
P2-C51-C52	117.09 (7)	P2-C51-C53	110.34 (7)
C52-C51-C53	109.91 (8)	P2-C61-C62	112.68 (7)
P2-C61-C63	111.53 (7)	C62-C61-C63	111.11 (7)
P3-C71-C72	123.79 (8)	P3-C71-C76	118.43 (8)
C72-C71-C76	117.68 (8)	C71-C72-C73	121.26 (9)
C72-C73-C74	120.2 (1)	C73-C74-C75	119.30 (9)
C74-C75-C76	120.36 (9)	C75-C76-C71	121.2 (1)
P3-C81-C82	113.09 (7)	P3-C81-C83	112.89 (8)
C82-C81-C83	109.85 (8)	P3-C91-C92	111.27 (7)
P3-C91-C93	115.33 (8)	C92-C91-C93	110.04 (7)

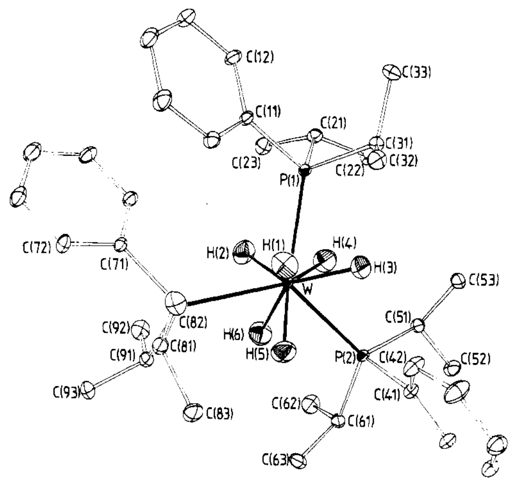

Figure 1. Molecular structure of $[WH_6(PPh\text{-}i\text{-}Pr_2)_3]$ showing atomic numbering scheme; hydrogen atoms omitted from phosphine ligands.

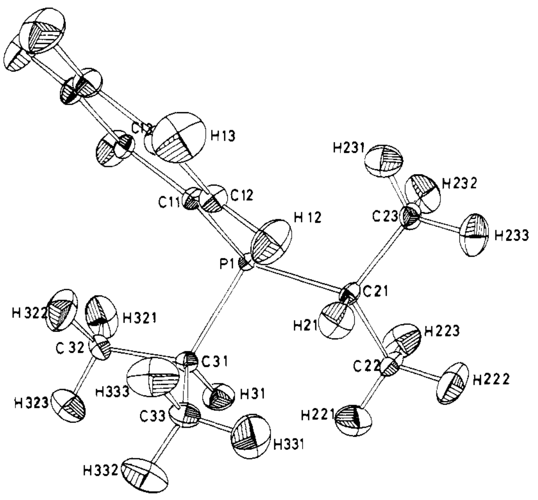

Figure 2. Atomic numbering scheme (H atoms) shown for one phosphine ligand.

Table IV. Comparison of Selected Bond Distances (Å) and Interbond Angles (deg) As Determined by X-ray and Neutron Diffraction in the "WH_6P_3" Core

	X-ray	neutron		X-ray	neutron
		Bond Lengths			
W-H1	1.69 (5)	1.745 (3)	W-H6	1.65 (4)	1.727 (2)
W-H2	1.66 (5)	1.718 (3)	W-P1	2.528 (2)	2.524 (2)
W-H3	1.72 (5)	1.737 (3)	W-P2	2.427 (2)	2.424 (2)
W-H4	1.73 (6)	1.729 (3)	W-P3	2.524 (2)	2.519 (2)
W-H5	1.66 (5)	1.739 (3)			
		Bond Angles			
H1-W-H2	123 (3)	123.88 (12)	P1-W-P2	125.41 (4)	125.54 (6)
H1-W-P2	113 (2)	114.07 (9)	P1-W-P3	107.94 (3)	107.88 (6)
H2-W-P2	123 (2)	122.05 (9)	P2-W-P3	126.56 (2)	126.49 (5)
		Nonbonded H···H Contacts (No Esd's)			
H5-H6	1.99	2.142	H1-H5	1.98	1.996
H3-H4	2.12	2.165	H1-H3	1.91	1.981
H5-H3	2.47	2.494	H2-H6	1.83	1.898
H4-H6	2.26	2.254	H2-H4	1.92	1.899
H1-H2	2.95	3.051			

least-squares technique of the program SHELXTL.[9] The weighting scheme employed was $[w = (\sigma^2(F_o) + 0.0003(F_o^2))]^{-1}$. The final R factors were R (R^1) = 0.033 (0.027) $R = \sum|F_o - F_c|^2/\sum F_o^2$ and $R^1 = \sum w|F_o - F_c|^2/\sum wF_o^2$, and the maximum and minimum peaks in

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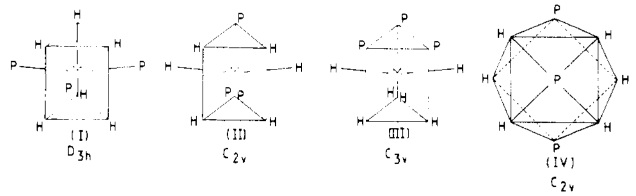
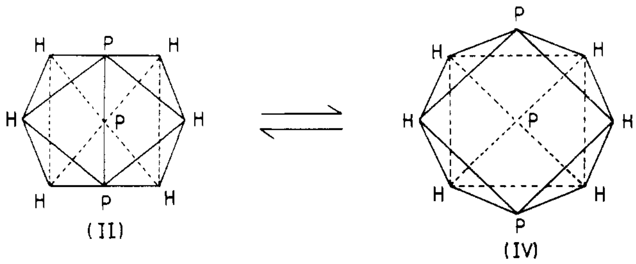
(9) Sheldrick, G. M. "SHELXTL, Program for Crystal Structure Determination"; University of Göttingen: Göttingen, 1980.

Scheme I



Scheme II



the residual density map at convergence were 1.8 and −1.2 e Å^{-3}, respectively.

(b) Neutron Diffraction. The atomic parameters obtained from the low-temperature X-ray study,[3] including the refined hydrogen atom positions, were used as the starting model for the refinement of the neutron data. Blocked full-matrix least-squares refinement, minimizing the quantity $\sum(w([F_o] - k[F_c])^2$ with $w^{-1/2} = (4.5\sigma(F_o) + 10^{-6}(F_o^5))$ converged at R (R^1) = 0.049 (0.020) after inclusion of a correction for isotropic extinction. With the weighting scheme given above, $\sum w(\Delta F^2)$ was almost constant for ranges of $[F_o]$ and $(\sin\theta)/\lambda$. All atoms were refined with anisotropic thermal parameters. The maximum and mean shift to error ratio observed in the final cycle were 0.22 and 0.1, respectively. All positional parameters, selected bond lengths, and interbond angles are given in Tables II and III. Tables of thermal parameters, extended hydrogen parameters, all X-ray experimental results, and structure factor listings are deposited as supplementary material. The neutron scattering lengths used were taken from Bacon,[10] and all calculations were carried out at the Institut Laue Langevin using the XRAY 76[11] system of programs on a DEC 10 computer.

Results and Discussion

The overall molecular configuration (Figure 1) had been determined from the low-temperature X-ray data,[3] but predictably the positions of the hydride ligands were not well-defined. The following discussion relies entirely on the results of the neutron diffraction study, from which all hydrogen atom positions were determined accurately. Some comparative bond lengths and angles concerning the inner coordination sphere of the tungsten atom are given in Table IV; the W–H separations are noticeably shorter when determined from the X-ray data. This trend is well recognized[12] from the more commonly measured C–H bonds, which appear to be shorter from the X-ray experiment than those that are calculated from neutron diffraction data on the same compound.

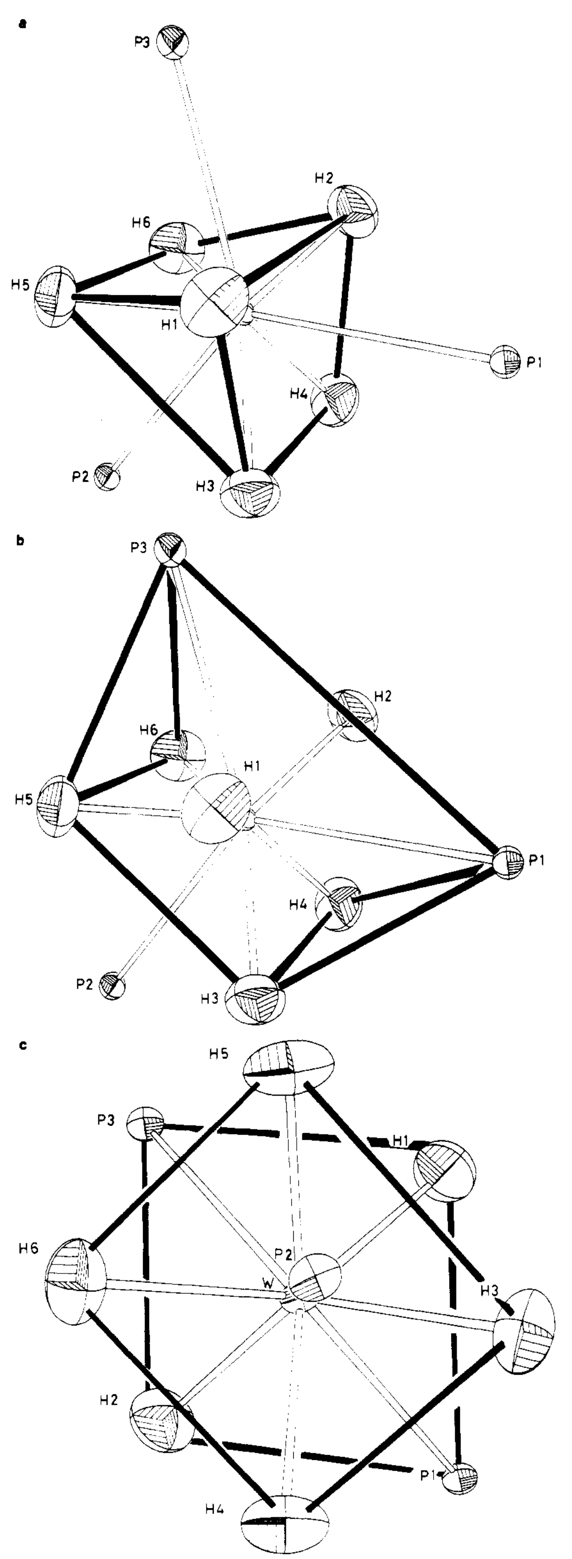


Figure 3. Coordination sphere of the molecule $[WH_6(PPh\text{-}i\text{-}Pr_2)_3]$: (a) D_{3h} (I); (b) C_{2v} (II); (c) C_{2v} (IV). Roman numerals refer to the idealized geometries of Scheme I.

The inequivalence of the W–P bond lengths is quite pronounced and lowers the molecular symmetry from a potential D_{3h} (I) to C_{2v} (II) (Scheme I). Such significant differences in the W–P separations (W–P(2) = 2.424 (2) Å; cf., W–P(1),P(3) mean 2.522 (2) Å) are unlikely to be due to packing forces alone, although steric effects are almost certainly the reason the molecule does not adopt C_{3v} (III) symmetry. The W–P(2) separation lies at the short end of the range of recently reported values 2.481–2.579 Å,[13] which encompasses the other two distances, W–P(1) and W–P(3). Calculations on the model complex $[ReH_8(PH_3)]^-$[14] and on $[ReH_9]^{2-}$[14,15] showed that back-donation from Re to P was insignificant compared with the σ interaction (P(p) → Re(5d)). This suggests that

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(11) "The X-RAY System", Technical report TR 72-192; Computer Science Center: University of Maryland, 1972.

(12) Coppens, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 32–40.

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(15) Abrahams, S. C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *3*, 558–567.

Table V. Selected Least-Squares Planes in the Form $px + qy + rz = s$, Where x, y, and z are Fractional Crystal Coordinates (Neutron Study)

plane		Δ^a				p	q	r	s
1	P1,P2,P3,W	0.010	0.013	0.010	−0.033	3.062	−5.888	12.612	0.781
2	H3,H4,H5,H6	−0.008	0.009	0.008	−0.009	−7.755	4.592	10.449	1.813
3	H1,H2,H3,H4	−0.016	0.017	0.022	−0.023	1.045	8.964	4.507	5.558
4	H1,H2,H5,H6	0.030	−0.032	−0.044	0.045	10.869	2.776	−8.336	1.444
5	H3,H5,P1,P3	−0.006	0.006	0.003	−0.003	−0.332	−3.462	15.546	2.300
6	H4,H6,P1,P3	−0.013	0.013	0.007	−0.007	6.601	−7.474	5.982	−1.244
7	H1,H2,W,P2	0.0004	0.0005	−0.0012	0.0003	7.583	7.444	−2.466	4.519
8	P3,H5,H6	0	0	0		4.459	8.204	2.219	3.779
9	P1,H4,H3	0	0	0		9.808	5.430	−6.733	4.573
10	P1,P3,H1,H2	0.33	0.33	−0.32	−0.34	−7.708	4.483	10.651	3.642

plane	angle, deg	planes	angle, deg	planes	angle, deg
1–2	87.8	2–5	64.3	1–8	86.6
1–3	89.8	2–6	62.4	1–9	94.1
1–4	91.2	2–7	89.6	8–9	43.7
2–3	51.1	5–6	53.3	7–8	21.4
2–4	51.0	5–7	90.6	7–9	22.2
		5–1	23.5	7–1	90.1
3–4	77.9	6–7	90.8		
		6–1	29.8	10–2	0.9

[a] Deviation from the mean plane (Å) of the atoms comprising the plane.

better σ overlap with the appropriate tungsten orbitals, rather than any increased π character in the W–P(2) bond, makes it shorter than the other W–P bonds.

P(1) and P(3) are remarkably close to one another with P···P 4.08 Å; the other intramolecular P···P contacts are >4.4 Å. These unequal distances are mirrored in the P–W–P bond angles with P(1)–W–P(3) = 108° and P(2)–W–P(1) (or P(3)) = 126°. Closer ligand contacts, caused by the more acute angles subtended at the W atom by pairs of atoms at prism vertices, discourage the shortening of W–P(1) and W–P(2).

Ginsberg has shown[14] that in both $[ReH_9]^{2-}$ and $[ReH_8(PH_3)]^-$ the H···H "bonding" interactions were significant. Several H···H distances are quite short (Table IV), and it is possible that they contribute also to the overall stability of the molecule. However, such interactions do not indicate which particular geometry is most likely to be adopted.

Two idealized geometries are available to nine-coordinate complexes, the tricapped trigonal prism (II) and the monocapped square antiprism (IV), these being readily interconverted by a simple deformation mechanism[16] (Scheme II). In contrast to six-coordinate species, where the dominant configuration is the octahedron, seven- and higher coordinate complexes do not exhibit predominant polyhedral shapes.[17] The energy barriers are low for the relatively small nuclear displacement needed to interconvert the idealized geometries. Further, the size of such displacements required in these polytopal rearrangements falls with increasing coordination number. Recent calculations[18] for "WH_6P_3" for P = PH_3 show that there is very little energy difference, not only between the two C_{2v} geometries II and IV but also between I and II or I and IV.

In comparison of the observed structure of [$WH_6(PPh\text{-}i\text{-}Pr_2)_3$] with the idealized structures[17] the following points are important: (i) As noted above, the disposition of phosphine ligands suggests approximate C_{2v} symmetry rather than D_{3h} (Figure 3a), and the hydride positions also support this conclusion. (ii) P(2) lies on the approximate twofold axis and makes angles of 114.1 (1) and 122.1 (1)° at tungsten with H(1) and H(2), respectively (∠H(1)–W–H(2) = 123.9 (2)°), suggesting that P(2), H(1), and H(2) be regarded as capping the distorted trigonal prism formed by P(1), P(3), H(3), H(4), H(5), and H(6) (Figure 3b). (iii) The alternative monocapped square antiprismatic structure (Figure 3c) with P(2) occupying the unique capping position would require approximately equal angles H(1)–W–H(2) and P(1)–W–P(3) across the square face, clearly far from the observed case.

The criteria used by Muetterties and Guggenberger[16b] to distinguish between idealized geometries C_{4v} and D_{3h} for ML_9 complexes based on the dihedral angles between polyhedral faces are not easily applied to I since the phosphines necessarily distort the basic polyhedron (Table V) as the W–P bond is substantially longer than the W–H bond.

The phosphine ligands are perfectly ordered, and their geometry is unremarkable. The accuracy of the data allows the observation of a significant difference in P–C (*i*-Pr) and P–C (Ph). The latter are shorter for all three phosphines (mean P–C (*i*-Pr) = 1.868 Å, P–C(Ph) = 1.847 Å). The W–P–C angles are all larger (mean 116.7°) than the C–P–C (mean 101.3°), a commonly observed phenomenon,[19] and again a slight variation is noted for P(2).

The mean C–H(Ph) and C–H (*i*-Pr) bond lengths determined from the neutron diffraction experiment are 1.086 (3), 1.089 (3) (C–H(methyl) in *i*-Pr), and 1.098 (3) Å (C–H in *i*-Pr). Those calculated from the X-ray data, even though they are less accurate and not significantly different from each other, are 0.94 (5), 0.97 (5), and 0.98 (5) Å, respectively. This again demonstrates the fact that the X-ray diffraction experiment detects the centroid of the charge cloud and does not locate the atomic centers (c.f. the W–H bond lengths, Table IV).

Conclusion

The results of the X-ray study suggested that the preferred structure was a tricapped trigonal prism in which the phosphine ligands occupy a pair of eclipsed prism corners and one of the equatorial sites (II of Scheme I), and this has been confirmed by the neutron experiment.

Acknowledgment. We thank the I.L.L. for support (D.G.), the DENI for a studentship (D.G.T.), and J. R. Allibon for technical assistance with the neutron experiment.

Registry No. $WH_6(PPh\text{-}i\text{-}Pr_2)_3$, 75516-74-4.

Supplementary Material Available: Listings of all anisotropic thermal parameters and extended bond lengths and bond angles involving all hydrogen atoms (neutron), atomic coordinates, thermal parameters, and all bond lengths and angles (X-ray) (Tables VI–X) and observed and calculated structure factors (neutron and X-ray) (91 pages). Ordering information is given on any current masthead page.

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