Synthesis and *X*-Ray Crystal Structure of Tris(phenyldi-isopropylphosphine)-tungsten Hexahydride

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Summary Hydrogenolysis of hexamethyltungsten in the presence of $PPhPr^i_2$ affords $[WH_6(PPhPr^i_2)_3]$, which is shown by ^{31}P n.m.r. spectroscopy and *X*-ray diffraction to have approximate C_{2v} symmetry in the solid and in solution.

Since the original synthesis of the complexes $[WH_6(PR_3)_3]$ ($PR_3 = PMe_2Ph$, PEt_2Ph) by Moss and Shaw,[1] their structures have remained a matter of conjecture, with perhaps the most appealing possibility being a tricapped trigonal prismatic co-ordination geometry (D_{3h}) with the capping positions occupied by the phosphine ligands.[2] We have sought to improve the synthetic routes to complexes of this type and to establish their structures.

The products of the hydrogenolysis (250 atm; 288 K) of hexamethyltungsten[3] in the presence of a tertiary phosphine are dependent on the size of the ligand. Thus while $PPhPr^i_2$ and PPr^i_3 give $[WH_6(PPhPr^i_2)_3]$ (**1**), and $[WH_6(PPr^i_3)_3]$ respectively, as the principal hydrocarbon-soluble products, PMe_2Ph affords mainly $[WH_4(PMe_2Ph)_4]$.[2] It is interesting to note that Wilkinson and co-workers[4] have recently reported that the low-pressure hydrogenolysis of $[WMe_6(PMe_3)]$ in the presence of an excess of PMe_3 produces $[WH_2(PMe_3)_5]$.

$[WH_6(PPhPr^i_2)_3]$
(**1**)

The stereochemical non-rigidity of nine-co-ordinate complexes is well known and the particular case of $[WH_6(PMe_2Ph)_3]$ was commented on by Moss and Shaw.[1] In agreement with these previous observations, the room temperature ^1H n.m.r. spectrum (100 MHz; $[^2H_8]$toluene) of (**1**) consisted of a sharp quartet, τ13·4 [J(PH) 36, J(WH) 26 Hz], in the high-field region. At 220 K the two central lines of the quartet were much broader whilst the outer lines remained sharp, consistent with a dynamic model in which the hydrogens exchange between identical sites in the co-ordination sphere, *i.e.* consistent with a tricapped trigonal prismatic structure (D_{3h}). However, at 190 K the outer lines also collapsed and the hydride signal became broad and featureless, suggesting that the hydrogens were moving between inequivalent sites in a structure of lower symmetry. In order to establish the solid state geometry we undertook a single crystal *X*-ray diffraction study of (**1**).†

Crystal data: $C_{36}H_{63}P_3W$, M 772·7, triclinic, space group $P\bar{1}$ (No. 2), $a = 11{\cdot}490(6)$, $b = 10{\cdot}610(3)$, $c = 16{\cdot}324(8)$ Å, $\alpha = 104{\cdot}76(3)$, $\beta = 108{\cdot}04(4)$, $\gamma = 89{\cdot}92(4)°$, $U = 1823{\cdot}28$ Å^3, $Z = 2$, $D_m = 1{\cdot}36$, $D_c = 1{\cdot}41$ g cm^{-3}, $F(000) = 786$, μ(Mo-K_α) = 33·87 cm^{-1}. Current $R = 0{\cdot}030$ ($R' = 0{\cdot}026$) for 7 371 absorption-corrected intensities [200 K, $2{\cdot}9° \leqslant 2\theta \leqslant 60°$, $I \geqslant 2\sigma(I)$, Syntex $P3$ diffractometer, Mo-K_α ($\lambda = 0{\cdot}710\ 69$ Å)].

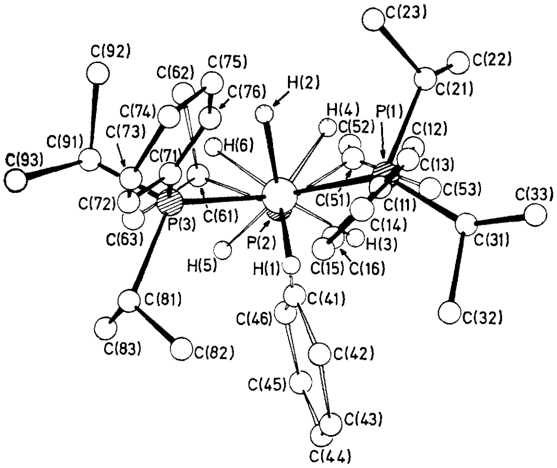

Figure. Molecular structure of $[WH_6(PPhPr^i_2)_3]$ omitting hydrogen atoms attached to the phosphine ligands. Selected distances and angles in the co-ordination sphere: W–P(1) 2·528(1); W–P(2) 2·427(1); W–P(3) 2·524(1), W–H(1) 1·69(4); W–H(2) 1·66(4); W–H(3) 1·72(4); W–H(4) 1·74(5); W–H(5) 1·66(4); W–H(6) 1·66(3) Å; P(1)–W–P(2) 125·4(1); P(2)–W–P(3) 126·6(1); P(1)–W–P(3) 107·9(1); mean P(2)–W–H(3—6) 68(2); mean P(2)–W–H(1,2) 118(2)°.

The molecule (Figure) has approximate C_{2v} symmetry, best illustrated by considering the positions of the phosphorus atoms in the co-ordination sphere. Thus P(1) and P(3) are surprisingly close together [∠P(1)–W–P(3) 107·9(1)°] and both are significantly further from the metal than is P(2). Furthermore the hydride ligands appear to be arranged in two groups [H(1) and H(2)] and [H(3)—H(6)] although their positions are subject to some uncertainty. We propose that the geometry of the co-ordination sphere be regarded as derived from a tricapped trigonal prism with one phosphorus atom [P(2)] in a capping position whilst the other two [P(1) and P(3)] occupy eclipsed positions on opposite axial prism faces.

To confirm that this structure was not peculiar to the solid state, a ^{31}P n.m.r. spectrum (^1H decoupled, toluene–Et_2O) of (**1**) was measured at low temperatures. The high-temperature singlet with ^{183}W satellites [δ 55·5 p.p.m.; J(PW) 62·5 Hz] broadened and separated on cooling so that at the low temperature limit of the instrument (180 K) there were two signals [δ 69·3 and 47·8 p.p.m., $w(\frac{1}{2}h)$ 150 Hz] of intensities 1 : 2 respectively. Unfortunately, at this temperature it is not possible to resolve J(PP). Two dynamic processes are proposed to account for the n.m.r. results: (i) a low energy 'breathing' motion which averages the chemical shifts of the different phosphorus and hydrogen nuclei but does not alter the topological relationship

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

of individual hydrogen and phosphorus atoms and (ii) a higher energy polytopal rearrangement which permutes the hydrogens with respect to the phosphorus atoms.

The results reported here suggest that the preferred site for a phosphine ligand in a nine co-ordinate polyhydride complex may well be one of the six prismatic vertices, each of which has five nearest neighbours in the co-ordination sphere, as opposed to the three capping vertices which have four nearest neighbours. This is consistent with the structure of $[MoH_4(PMePh_2)_4]$[2] in which the phosphine ligands were found to occupy the B sites[5] of a triangular dodecahedron which also have five nearest neighbours. Consequently the reported structure of $[ReH_7(PMe_2Ph)_2]$[6] might be best viewed as derived from a tricapped trigonal prism with the phosphine ligands occupying non-eclipsed vertices of opposite prism faces. This would account for the large P–Re–P angle [146·8(1)°] which has previously been attributed to steric distortion caused by the phosphine ligands, even though PMe_2Ph is a small ligand (cone angle 122°)[7].

We thank the Institut Laue-Langevin for support (D. G.).

(*Received, 25th February* 1980; *Com.* 206.)

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