Classical *versus* Non-classical Polyhydride Complexes: Single Crystal Neutron Diffraction Study of 1,2-Bis(diphenylphosphino)ethaneheptahydridorhenium(VII) [ReH_7(dppe)] using a Position-Sensitive Detector

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The polyhydride complex [ReH_7(dppe)] [dppe = $Ph_2P(CH_2)_2PPh_2$] has C_{2v} co-ordination geometry with seven discrete 'classical' hydride ligands, as determined by neutron diffraction data collected using a position-sensitive detector.

The long accepted[1] formulation of rhenium polyhydrides such as [$ReH_7(PPh_3)_2$] and [ReH_7(dppe)] [dppe = 1,2-bis(diphenylphosphino)ethane] as complexes of Re^{VII} with seven discrete hydride ligands has recently been called into question and alternative formulations *e.g.* [$ReH_5(H_2)$(dppe)] involving Re^{V} and a molecular hydrogen ligand have been suggested[2] in solution on the basis of ^1H n.m.r. relaxation parameters (T_1) and by analogy with other recently characterised molecular hydrogen complexes.[3]

We have previously determined the structures of several third transition series polyhydrides by single crystal neutron diffraction,[4] including [$ReH_7(PPr^i{}_2Ph)_2$] in two different crystalline modifications. Both [$WH_6(PPhPr^i{}_2)_3$] and [$OsH_6(PPhPr^i{}_2)_2$] have six discrete hydride ligands and co-ordination geometries which may be described as tricapped trigonal prismatic and triangular dodecahedral, respectively. Unfortunately positional disorder of the hydride ligands in the case of the rhenium complex precluded definitive elucidation of the molecular structure.

One of the first polyhydride complexes, reported by Chatt and Coffey,[5] was [ReH_7(dppe)], for which Crabtree and co-workers have postulated a 'non-classical' complexed dihydrogen structure in solution.[2] The general stability of this compound made it a suitable subject for a detailed structural study. Large crystals of [ReH_7(dppe)]·2thf were grown by the slow cooling of a tetrahydrofuran (thf) solution to −20 °C. As the crystals deteriorate in minutes through solvent loss on exposure to a thf-free atmosphere, the data crystal was sealed into a fine-walled silica tube in the presence of thf. Intensity measurements[†] were recorded at 200 K on the new D19 normal beam diffractometer at I.L.L. Grenoble, using a Displex cryorefrigerator and a curved two-dimensional position-sensitive detector (64° × 4°). The previously-determined low-temperature *X*-ray structure was used successfully as the starting model for refinement with the neutron data, resulting in the accurate resolution of all hydrogen atom positions including the core hydride ligands (Figure 1). The molecule lies astride a two-fold rotation axis and this symmetry allows description of the geometrical arrangement of the nine ligands either as a distorted tricapped trigonal prism (as established for ReH_9^{2-})[6] with the phosphorus atoms occupying two eclipsed prism positions {as we observed in [$WH_6(PPhPr^i{}_2)_3$]},[4a] with H(1), H(2), and H(2a) capping the prism faces. Alternatively it may be viewed as a monocapped square antiprism with H(1) in the capping position and the diphosphine occupying diagonal positions on the uncapped square face. There are no intramolecular H · · · H separations less than 1.77 Å [H(1) · · · H(4)] and the closest intermolecular contact occurs for O(thf) · · · H(methylene of dppe) (2.32 Å). Thus [ReH_7(dppe)] must be described as a 'classical' heptahydrido complex in this crystalline form and the question of the discrepancy between the solid state and solution results must be addressed.

Kubas[3] has noted the small energy differences that exist between isomeric dihydride and dihydrogen forms of [$W(CO)_3(H_2)(PPr^i{}_3)_2$] such that both species may be observed in equilibrium in solution. Conroy-Lewis and Simpson[7] have observed that small changes in the co-ordination sphere of the metal, such as the angle of bite of a chelating diphosphine, can shift stability from one form to the other. It would therefore be reasonable to suggest that [ReH_7(dppe)] might adopt a different structure in solution.

We have examined the i.r. spectrum of [ReH_7(dppe)] dissolved in various solvents and in the solid state in both solvated and unsolvated forms. The absence of an obvious H–H stretching band does not preclude a dihydrogen complex as such bands are known to be weak[3] and may be obscured by other vibrations [*e.g.* ν(C–H)]. However, the ν(M–H) bands (1997sh, 1978s, 1906m cm^{-1}) observed for the solvated crystalline solid change very little in other media, suggesting a common structure, although the dihydrogen form may be present as a minor isomer in solution. We have no immediate explanation of the very short T_1 values which have been observed for [ReH_7(dppe)] but Pregosin[8] has recently drawn attention to some of the complex factors influencing T_1 values in transition metal hydride complexes.

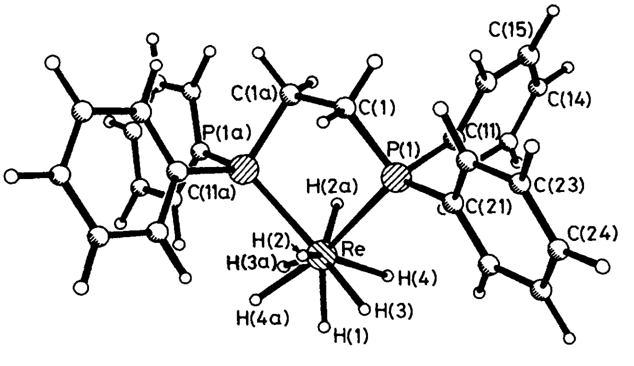

Figure 1. Molecular structure of [ReH_7(dppe)] showing atomic numbering scheme. Atom M(*na*) is related to Atom M(*n*) by a crystallographic two-fold rotation axis. Re–P(1) 2.425(3) Å, P(1)–Re–P(1a) 83.0°, P(1)–C(1) 1.838(4), C(1)–C(1a) 1.539(6), Re–H(1) 1.660(9), Re–H(2) 1.689(6), Re–H(3) 1.669(7), Re–H(4) 1.671(6) Å.

[†] *Crystal data* for [ReH_7(dppe)]·2thf: [$C_{26}H_{31}P_2Re$].$2C_4H_8O$, M = 719.89, monoclinic, space group *C2/c*, a = 17.2625(7), b = 11.4085(5), c = 17.6088(6) Å, β = 107.786(2)°, U = 3302 Å^3, Z = 4, T = 200 K, D_c = 1.45 g cm^{-3}, Ge-monochromated thermal neutrons, λ = 1.3168(1) Å, μ = 2.64 cm^{-1}. 6922 Intensity measurements yielded 2985 unique data of which 2295 have $I \geqslant 4\sigma(I)$. Current $R(R_w)$ = 0.085 (0.084), [$w^{-1} = \sigma^2(F)$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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