Protonation of the osmium(IV) hydrides (C₅Me₅)OsH₂L with HBF₄ in diethyl ether afforded the cationic dihydrogen complexes [(C₅Me₅)OsH₂L][HBF₄], where L is PPh₃ or AsPh₃. A single-crystal neutron diffraction study of 1 reveals that the H–H distance is 1.014(11) Å.

Since their discovery, molecular dihydrogen complexes have generated considerable interest because they represent a midway point along the reaction coordinate that leads to the oxidative addition of dihydrogen by transition-metal centers. The H–H bond distance is a measure of the extent to which the H bond is lengthened during oxidative addition. The H–H bond distance in complexes of general stoichiometry (C₅Me₅)Os(H₂)L₄(BF₄)₂ is about 0.8 Å longer than the normal H–H bond distance of 0.75 Å.

A few dihydrogen ligands have been 'elongated' H–H bond distances of approximately 1.0 to 1.4 Å that constitute an intermediate between the classical and non-classical hydrogen atom sites. These complexes are known as 'tetrahydrides'.

Protonation of the previously reported osmium(IV) trihydride (C₅Me₅)OsH₂(PPh₃)₂ with HBF₄·Et₂O in diethyl ether affords a white precipitate of stoichiometry (C₅Me₅)OsH₂(PPh₃)₂[BF₄]₂. This complex is isomorphous with the analogous triphenylarsine compound [(C₅Me₅)OsH₂(PAsPh₃)](BF₄)₂. In contrast, attempts to prepare a ruthenium analogue, [(C₅Me₅)RuH₂(PPh₃)](BF₄)₂, have been unsuccessful, evidently because this complex is unstable toward loss of H₂.

An X-ray crystallographic study of complex 1 conducted at 198 K strongly suggested that it adopts a four-legged piano stool geometry in which the four legs are described by the phosphine ligand, a single classical dihydrogen ligand, and a non-classical dihydrogen ligand. The phosphine is 'trans' to the dihydrogen ligand and the H–H distance is 0.02 to 0.1 Å. The metric parameters of the dihydrogen ligand deduced from X-ray data are, however, likely to have large errors.

† Dedicated to the memory of Geoffrey Wilkinson, whose work will long stand as a landmark and an inspiration.

‡ Complex 1 (Found: C, 46.09; H, 0.50; P, 4.27. Calc: C, 46.8; H, 5.05; P, 4.56%). IR (Nujol, cm⁻¹): 2108 cm⁻¹ (νOs–H); 1063 cm⁻¹ (νAs–H). NMR (CDCl₃, 22 °C): 6.75 (m, o–CH and m–CH), 7.3 (m, p–CH), 2.13 (s, C₅Me₅), −9.88 (s, Os–H).

The neutron diffraction data clearly reveal the presence of a dihydrogen ligand trans to the phosphine (Fig. 1). The H–H distance of 1.041(11) Å shows that the dihydrogen ligand is of the 'elongated' variety. The value of 1.014 Å is not corrected for librational motion of the H₂ ligand. Corrections of this type lengthen the H–H bond by ca. 0.02 to 0.1 Å. In contrast to the X-ray results, the dihedral angle between the Os–H₂ and P–Os–C₅ planes refined to a chemically reasonable value of 8.7°. The angle between the mutually 'trans' terminal hydrides [H(1)–Os–H(3)] of 132.6(5)° is considerably larger than the corresponding 119(2)° angle measured for the neutral complex (C₅Me₅)OsH₂(PPh₃)₂ by X-ray diffraction. This difference signals a change in the hybridization of the metal–ligand bonding orbitals upon protonation of the metal center.

The room-temperature ¹H NMR spectrum of complex 1 features a doublet at δ = 9.61 [JₚH(ave) = 14.2 Hz], the four osmium-bound hydrogen atoms; thus, exchange of the classical and non-classical hydrogen atom sites is fast on the NMR time-scale at 25 °C. The room-temperature ¹H NMR spectrum of 2 is similar except that the Os–H resonance appears as a singlet at δ = 9.88. For both compounds, the hydrogen resonance remains sharp down to approximately −100 °C, at which point it begins to broaden. At −140 °C (in D₂O), the hydrogen resonance of 1 remains a broad singlet, but the resonance of 2 decoalesces to two broad equal-intensity features separated by 1.0 ppm. The activation free energy for the dihydrogen-hydride exchange process is 2 ± 0.6 kcal mol⁻¹.

A detailed insight into the solution structure can be obtained from the NMR spectra of partially deuterated isopolys. Approximately 2.5 of the 4 hydrogen atoms are deuterated upon stirring a CH₂Cl₂ solution of 1 under 2 atm of D₂ for 24 h. A ¹H NMR spectrum of the partially deuterated material at 25 °C shows a doublet [JₚH(ave) = 14.7 Hz] of multiplets; the multiplet splitting gives JₚH(ave) = 3.6 Hz. These coupling constants and order to establish more definitively the presence of a molecular dihydrogen ligand, time-of-flight neutron diffraction data were collected from a 4 mm³ single crystal of 1.

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reaches a minimum of 99 ms at structure of temperature, the exchange between the Os is in the fast exchange limit, and thus the observed relaxation min) distances (Å) and angles (°) are shown for the Os-H ligands while spheres of arbitrary size are shown for all other atoms. Selected bond distances (Å) and angles (°) (all taken from the neutron study except the first two): Os-P 2.331(4), Os-C 2.251(6), H(2)-H(4) 1.014(11), Os-O(1) 1.654(9), Os-O(1) 1.631(9), Os-O(4) 1.680(9), H(2)-Os-H(4) 35.4(4), H(2)-Os-H(3) 68.0(5), H(2)-Os-H(1) 71.2(5), H(1)-Os-H(3) 122.6(5), H(3)-Os-H(4) 84.3(5), H(1)-Os-H(4) 76.2(5), H(1)-Os-P 77.3(3), H(2)-Os-P 83.0(4), H(3)-Os-P 74.9(3), H(4)-Os-P 117.9(4)

These estimated relaxation rates lead to a value of 12.96 s−1 for the Os-H ligands. If we assume that the geminal 2J(H-H) couplings are all between 0 and 1 Hz,3 then the intrinsic 2J(H-H) couplings within the bound HD ligand is between 20.6 and 21.6 Hz. [The thermodynamic site preferences (i.e., deuterium in the dihydrogen vs. hydride sites) are small as shown by the invariance of 2J(H-H) to the extent of deuteration.] These values, when substituted into Morris's empirical equation 4

\[
\Delta \omega_{nm} = -0.0167 \times 2J(H-H) + 1.42 \times 10^{-6} \text{Hz} \times \text{distances (Å) of Os-H}
\]

A value of 1.06 to 1.08 Å is calculated. This calculated distance is in good agreement with that derived from the neutron diffraction data, especially after correction for librational effects, and we conclude that the structure of 1 in solution is similar to that seen in the solid state.

We have also carried out variable-temperature 1H NMR studies of the spin-lattice relaxation time of deuteriated samples of 1. At 500 MHz in CD2Cl2, the 2J(H-H) of the Os-H resonance reaches a minimum of 99 ms at ~70 °C (Su P 57272). At this temperature, the exchange is fast in the Os-H and Os-H2 sites is the fast exchange limit, and thus the observed relaxation time is an average given by the expression 2J(H-H) + R(c, min) + R(n, min), where R(c, min) and R(n, min) are the relaxation rates (R = 1/T1) for the classical and non-classical hydrogen sites at ~70 °C. By using Halpern's method 44 to sum dipole-dipole relaxation rates calculated from the interatomic distances determined crystallographically, we can calculate that R(c, min) is approximately 4.14 s−1 and that the relaxation rates of the hydrogen atoms in the H2 ligand (excluding the dipole-dipole interaction within the H2 ligand itself) are 3.94 s−1 for hydrogen atom H(2) and 2.25 s−1 for hydrogen atom H(4). These estimated relaxation rates lead to a value of 12.96 s−1 for the relaxation rate due just to the dipole-dipole interaction within the H2 ligand [i.e., T1(n, min) = 77 ms]. If we assume that the dihydrogen ligand rotation rate is fast compared with the molecular tumbling rate, then from the expression 45

\[
\Delta \omega_{nm} = \frac{5.81}{\sqrt{T_1(n, min)/2}} \times 10^{-6} \text{Hz}.
\]

The value agrees with the distance deduced from 2J(H-H) and from the neutron diffraction data.

We are continuing our studies of this new class of dihydrogen complexes.

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**References**


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