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Neutron diffraction study of the 'elongated' molecular dihydrogen complex $[(C_5Me_5)Os(H_2)H_2(PPh_3)]^+$ †

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Protonation of the osmium(IV) hydrides $(C_5Me_5)OsH_3(L)$ with HBF_4 in diethyl ether afforded the cationic dihydrogen complexes $[(C_5Me_5)Os(H_2)H_2(L)][BF_4]$, where L is PPh_3 **1** or $AsPh_3$ **2**; 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.[1-4] The H−H bond distance is a measure of the extent to which the H_2 ligand has been activated. Distances less than 0.85 Å are typical for 'normal' dihydrogen complexes while distances longer than 1.50 Å are characteristic of classical dihydrides.[5,6] A few dihydrogen complexes, however, have 'elongated' H−H bond distances of approximately 1.0 to 1.4 Å that constitute an intermediate situation.[7] Herein we report the synthesis of the first compounds of general stoichiometry $[(C_5R_5)MH_4L]^+$. Single-crystal neutron diffraction[7,8] shows that, when L = PPh_3, two of the hydrogen atoms form an 'elongated' dihydrogen ligand.

Protonation of the previously reported osmium(IV) trihydride $(C_5Me_5)OsH_3(PPh_3)$[9] with $HBF_4{\cdot}Et_2O$ in diethyl ether affords a white precipitate of stoichiometry $[(C_5Me_5)OsH_4(PPh_3)][BF_4]$ **1** in 91% yield. As we will show below, this 'tetrahydride' complex is best formulated as the dihydrogen–dihydride species $[(C_5Me_5)Os(H_2)H_2(PPh_3)][BF_4]$.‡ The analogous triphenylarsine compound $[(C_5Me_5)Os(H_2)H_2(AsPh_3)][BF_4]$ **2** can be prepared similarly.§ Interestingly, attempts to prepare the analogous ruthenium compound, $[(C_5Me_5)RuH_4(PPh_3)]^+$, have been unsuccessful, evidently because this complex is unstable toward loss of H_2.[10]

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, two classical hydride ligands, and a non-classical dihydrogen ligand.¶ The phosphine is '*trans*' to the dihydrogen ligand and the H−H distance within the latter refined to 0.8(1) Å. The metric parameters of the dihydrogen ligand deduced from X-ray data are, however, likely to have large errors,|| and in order to establish more definitively the presence of a molecular dihydrogen ligand, time-of-flight neutron diffraction data were collected from a 4 mm^3 single crystal of **1**.

The neutron diffraction data clearly reveal the presence of a dihydrogen ligand *trans* to the phosphine (Fig. 1). The H−H distance of 1.014(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 H_2 ligand. Corrections of this type lengthen the H−H bond by *ca.* 0.02 to 0.1 Å.[7a,8a]) In contrast to the X-ray results,|| the dihedral angle between the $Os{-}H_2$ and P−Os−Cn 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 $(C_5Me_5)OsH_3(PPh_3)$ by X-ray diffraction.[12] 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 [J_{HP}(ave) = 14.2 Hz] for the four osmium-bound hydrogen atoms; thus, exchange of the classical and non-classical hydrogen atom sites is fast on the NMR timescale 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 hydride resonance remains sharp down to approximately −100 °C, at which point it begins to broaden. At −140 °C (in $CDFCl_2$), the hydride 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 in **2** is 6.0 kcal mol^{-1}.

Additional insight into the solution structure can be obtained from the NMR spectra of partially deuteriated isotopologs. Approximately 2.5 of the 4 hydrogen atoms are deuteriated upon stirring a CH_2Cl_2 solution of **1** under 2 atm of D_2 for 24 h. A ^1H NMR spectrum of the partially deuteriated material at 25 °C shows a doublet [$^2J_{HP}$(ave) = 14.7 Hz] of multiplets; the multiplet splitting gives J_{HD}(ave) = 3.6 Hz. These coupling con-

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

Supplementary data available (No. SUP 57272, 3 pp.): a plot of T^{-1}/K *vs.* ln(T_1) for $[(C_5Me_5)Os(H_2)H_2(PPh_3)][BF_4]$. See instructions for Authors, 1997.

Non-SI units employed: cal ≈ 4.18 J, atm = 101 325 Pa.

‡ Complex **1** (Found: C, 49.6; H, 5.05; P, 4.27. Calc: C, 49.6; H, 5.05; P, 4.56%). IR (Nujol, cm^{-1}): 2108m (ν_{Os-H}), 2063m (ν_{Os-H}). ^1H NMR (CD_2Cl_2, 22 °C): δ 7.5 (m, *o*−CH and *m*−CH), 7.3 (m, *p*−CH), 2.06 (d, J_{PH} = 1.4 Hz, C_5Me_5), −9.61 (d, J_{PH} = 14.2 Hz, Os−H).

§ Complex **2** (Found: C, 46.7; H, 4.82; As, 10.2. Calc: C, 46.6; H, 4.74; As, 10.4%). IR (Nujol, cm^{-1}): 2088w (ν_{Os-H}), 2029w (ν_{Os-H}). ^1H NMR (CD_2Cl_2 22 °C): δ 7.5 (m, *o*−CH and *m*−CH), 7.4 (m, *p*−CH), 2.13 (s, C_5Me_5), −9.88 (s, Os−H).

¶ Crystal data for complex **1** (M = 678.53). X-Ray (198 K): monoclinic, space group $P2_1/c$, a = 10.5516(4), b = 27.681(1), c = 9.4129(4) Å, β = 99.062(1)°, U = 2715.0(2), Z = 4, μ = 4.8 mm^{-1}, R_{wF^2} = 0.0863 for 336 parameters and all 6468 data. The non-hydrogen atoms were refined anisotropically. A difference map revealed four possible hydrogen atom positions. The locations of these hydrogen atoms were refined without constraints except that a common isotropic displacement parameter was assigned. The positions of the atoms converged slowly, especially that for hydrogen atom H(4). Neutron (20 K): monoclinic, space group $P2_1/c$, a = 10.4294(16), b = 27.562(4), c = 9.3218(13) Å, β = 99.690(10)°, U = 2641(1), Z = 4, R_F = 0.093, R_{wF} = 0.058 for 324 parameters and 3648 data with $I > 3\sigma(I)$. All atoms were refined isotropically except the four osmium-bound hydrogen atoms, which were refined anisotropically. CCDC reference number 186/672.

|| For example, the dihedral angle described by the $Os{-}H_2$ plane and the P−Os−Cn plane (Cn = centroid of the C_5Me_5 ring) obtained from the X-ray data set was unexpected: it was not close to either 0 or 90°, but inbetween (60.6°). Dihydrogen ligands with unusual dihedral angles are known, however.[8c]

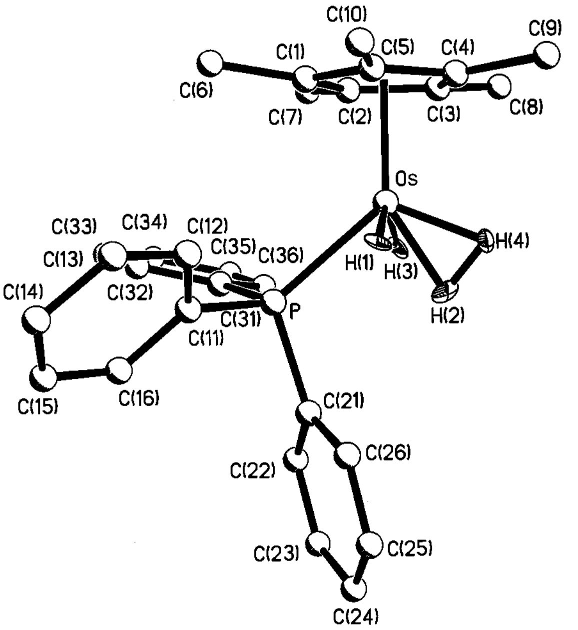

Fig. 1 An ORTEP[11] view of the molecular structure of the $[(C_5Me_5)Os(H_2)H_2(PPh_3)]^+$cation as determined by neutron diffraction; the 20% probability density surfaces are shown for the Os–H ligands while spheres of arbitrary size are shown for all other atoms. Selected bond distances (Å) and angles (°) (all taken from the neutron study except the first two): Os–P 2.334(1), Os–C_{ave} 2.251(6), H(2)–H(4) 1.014(11), Os–H(1) 1.654(9), Os–H(2) 1.659(9), Os–H(3) 1.631(9), Os–H(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) 132.6(5), H(3)–Os–H(4) 84.1(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)

stants are averages owing to the exchange process. If we assume that the geminal $^2J_{HD}$ couplings are all between 0 and 1 Hz,[5] then the intrinsic $^1J_{HD}$ coupling 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 $^2J_{HP}$(ave) to the extent of deuteriation.] These values, when substituted into Morris's empirical equation $d_{HH} = -0.0167\ J_{HD} + 1.42$,[4] yield H–H distances of 1.06 to 1.08 Å. The 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 undeuteriated samples of **1**. At 500 MHz in CD_2Cl_2, the T_1 of the Os–H resonance reaches a minimum of 99 ms at −70 °C (SUP 57272). At this temperature, the exchange between the Os–H and Os–H_2 sites is in the fast exchange limit, and thus the observed relaxation time is an average given by the expression $2R(\text{ave, min}) = R(\text{c, min}) + R(\text{n, min})$, where R(c, min) and R(n, min) are the relaxation rates ($R = 1/T_1$) for the classical and non-classical hydrogen sites at −70 °C.[13] By using Halpern's method[14] 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 H_2 ligand (excluding the dipole–dipole interaction within the H_2 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 H_2 ligand [*i.e.*, $T_1(\text{n, min}) = 77$ ms]. If we assume that the dihydrogen ligand rotation rate is fast compared with the molecular tumbling rate, then from the expression $d_{HH} = 5.81 \sqrt[6]{T_1(\text{n, min})/4\nu}$, where T_1 is in seconds and ν is the spectrometer frequency in MHz, we obtain $d_{HH} = 1.07$ Å.**[,4,15] The value agrees with the distance deduced from $^1J_{HD}$ and from the neutron diffraction data.

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

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** The fast spinning correction is not necessary if the H_2 ligand rotates by 180° reorientation processes. In the present molecule, the $M \longrightarrow H_2$ back bonding would be weakened upon rotation of the dihydrogen ligand in **1** by 90°. This destabilizing effect, however, may be compensated by H · · · H interactions with the two classical hydride ligands.[8c] If so, then the rotation may involve 90° reorientations so that the fast rotation correction is applicable. Effects due to large torsional motion may also be important.[16]

References

1 D. M. Heinekey and W. J. Oldham, jun., *Chem. Rev.*, 1993, **93**, 913.
2 P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1992, **121**, 155.
3 G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120.
4 R. H. Morris, *Can. J. Chem.*, 1996, **74**, 1907.
5 D. G. Gusev, R. L. Kuhlman, K. B. Renkema, O. Eisenstein and K. G. Caulton, *Inorg. Chem.*, 1996, **35**, 6775. Distances cited are uncorrected for librational motion of the H_2 ligand.
6 F. Maseras, A. Lledós, M. Costas and J. M. Poblet, *Organometallics*, 1996, **15**, 2947.
7 For dihydrogen compounds with H–H distances between 1.0 and 1.4 Å as determined by neutron diffraction see: (*a*) W. T. Klooster, T. F. Koetzle, G. Jia, T. P. Fong, R. H. Morris and A. Albinati, *J. Am. Chem. Soc.*, 1994, **116**, 7677; (*b*) A. Albinati, V. I. Bakhmutov, K. G. Caulton, E. Clot, J. Eckert, O. Eisenstein, D. G. Gusev, V. V. Grushin, B. E. Hauger, W. T. Klooster, T. F. Koetzle, R. K. McMullan, T. J. O'Loughlin, M. Pélissier, J. S. Ricci, M. P. Sigalas and A. B. Vymenits, *J. Am. Chem. Soc.*, 1993, **115**, 7300; (*c*) P. A. Maltby, M. Schlaf, M. Steinbeck, A. J. Lough, R. J. Morris, W. T. Klooster, T. F. Koetzle and R. C. Srivastava, *J. Am. Chem. Soc.*, 1996, **118**, 5396; (*d*) T. Hasegawa, Z. Li, S. Parkin, H. Hope, R. K. McMullan, T. F. Koetzle and H. Taube, *J. Am. Chem. Soc.*, 1994, **116**, 4352; (*e*) L. Brammer, J. A. K. Howard, O. Johnson, T. F. Koetzle, J. L. Spencer and A. M. Stringer, *J. Chem. Soc., Chem. Commun.*, 1991, 241.
8 For other dihydrogen complexes studied by neutron diffraction see: (*a*) G. J. Kubas, C. J. Burns, J. Eckert, S. W. Johnson, A. C. Larson, P. J. Vergamini, C. J. Unkefer, G. R. K. Khalsa, S. A. Jackson and O. Eisenstein, *J. Am. Chem. Soc.*, 1993, **115**, 569; (*b*) J. S. Ricci, T. F. Koetzle, M. T. Bautista, T. M. Hofstede, R. H. Morris and J. F. Sawyer, *J. Am. Chem. Soc.*, 1989, **111**, 8823; (*c*) L. S. Van Der Sluys, J. Eckert, O. Eisenstein, J. H. Hall, J. C. Huffman, S. A. Jackson, T. F. Koetzle, G. J. Kubas, P. J. Vergamini and K. G. Caulton, *J. Am. Chem. Soc.*, 1990, **112**, 4831; (*d*) J. Eckert, C. M. Jensen, T. F. Koetzle, T. L. Husebo, J. Nicol and P. Wu, *J. Am. Chem. Soc.*, 1995, **117**, 7271.
9 C. L. Gross, S. R. Wilson and G. S. Girolami, *J. Am. Chem. Soc.*, 1994, **116**, 10 294.
10 T. Arliguie, B. Chaudret, F. A. Jalon, A. Otero, J. A. Lopez and F. J. Lahoz, *Organometallics*, 1991, **10**, 1888.
11 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
12 C. L. Gross and G. S. Girolami, unpublished work.
13 D. G. Hamilton and R. H. Crabtree, *J. Am. Chem. Soc.*, 1988, **110**, 4126.
14 P. J. Desrosiers, L. Cai, Z. Lin, R. Richards and J. Halpern, *J. Am. Chem. Soc.*, 1991, **113**, 4173.
15 M. T. Bautista, K. A. Earl, P. A. Maltby, R. H. Morris, C. T. Schweitzer and A. Sella, *J. Am. Chem. Soc.*, 1988, **110**, 7031.
16 See, for example, R. H. Morris and R. J. Wittebort, *Magn. Reson. Chem.*, 1997, **35**, 243.

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