An N.M.R. Study of FeH(dmpe)$_2$(BH$_4$) [dmpe = 1,2-Bis(dimethylphosphino)ethane] –an Iron Complex containing a Monodentate Borohydride Ligand

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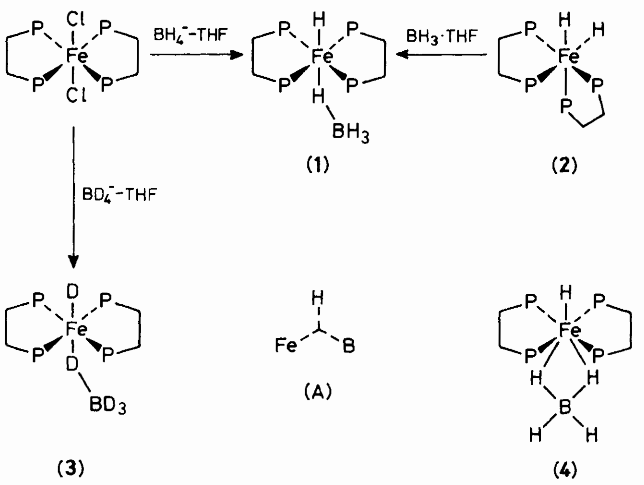
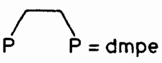
The single-hydrogen bridge attachment of BH$_4$ to iron in the complex FeH(dmpe)$_2$(BH$_4$) [dmpe = 1,2-bis(dimethylphosphino)ethane] is the first reported occurrence of that type of co-ordination of borohydride to iron; a detailed n.m.r. study has demonstrated the facile exchange of the bridging and terminal hydrogen atoms attached to the boron atom.

Compounds containing unsupported metal–hydrogen–boron bonds are very rare[1] and only in the case of Cu(PPh$_2$-Me)$_3$(BH$_4$) has the bridging hydrogen atom been structurally characterised by *X*-ray and neutron diffraction methods.[2] We report here the synthesis and properties of FeH(dmpe)$_2$(BH$_4$) (**1**) [dmpe = 1,2-bis(dimethylphosphino)ethane]. Complex (**1**) is a stable, diamagnetic iron complex, incorporating a monodentate borohydride ligand.†

Treatment of Fe(dmpe)$_2$Cl$_2$ with an excess of NaBH$_4$ (4 equiv.) in tetrahydrofuran (THF) afforded a yellow–orange solution. Removal of the solvent and recrystallisation of the residue from light petroleum gave (**1**) as a yellow solid (74%).‡ Complex (**1**) was also prepared directly by the reaction of borane in THF with the dihydride,[3] (**2**). The pentadeuterio analogue, (**3**) was synthesised from Fe(dmpe)$_2$Cl$_2$ using NaBD$_4$.



(1) (2) (3) (A) (4)



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† The structure drawn for (**1**) is not intended to imply the nature of bonding in the complex. The existence of a bridging hydrogen indicates a common overlap of an orbital from iron and an orbital from boron with the 1s orbital of the hydrogen atom *i.e.* a three-centre interaction. This means that there is a direct interaction between iron and boron and the bonding of the borohydride is probably best represented as an unsymmetrical three-centre, two-electron bond, (A).

‡ I.r. (benzene) ν 2340 (terminal B–H stretch), 2030 (bridging Fe–H and bridging B–H stretch), 1788 (terminal Fe–H stretch), and 1045 cm^{-1} (BH$_3$ deformation).

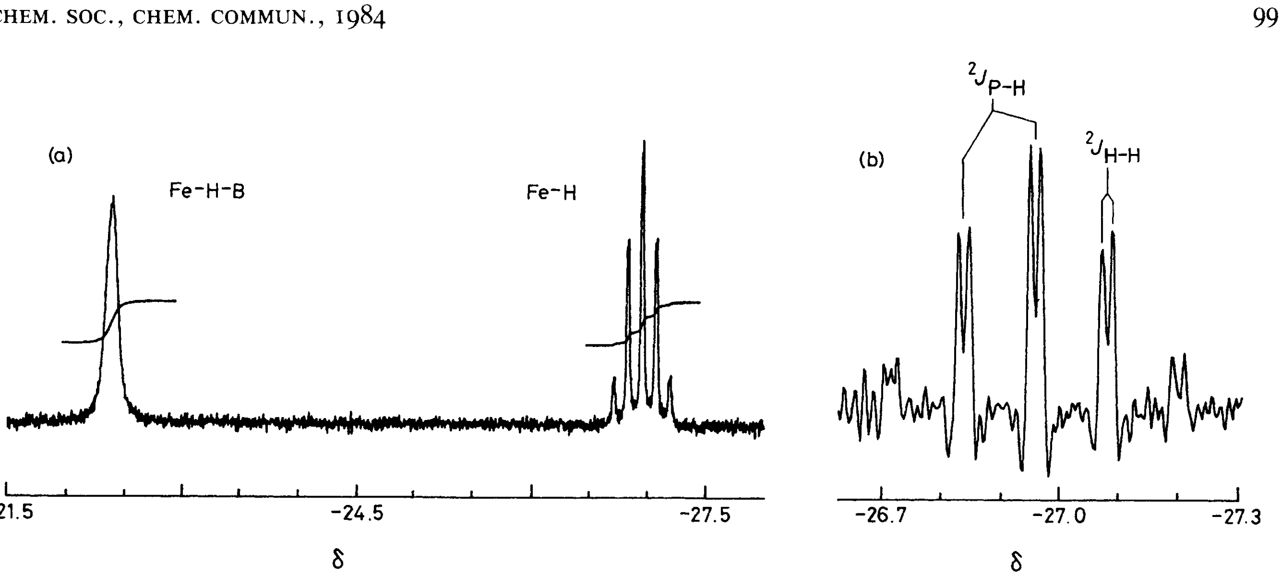

Figure 1. (a) Extreme highfield region of the ^{1}H n.m.r. spectrum of (**1**) (400 MHz, $[^2H_8]$toluene, 190 K). (b) Resolution enhancement of the Fe–H resonance to emphasise the geminal H–Fe–H– coupling ($^2J_{H-H}$ 7.1 Hz).

At 298 K, the ^{31}P n.m.r. spectrum of (**1**) consists of a single resonance at δ +71.2 p.p.m.§ with a coupling of 50.1 Hz to the free Fe–H proton. At 298 K, the ^{11}B n.m.r. spectrum of (**1**) consists of a single resonance at δ – 38.1 p.p.m.§ which is a quintet (spacing 82 Hz) due to coupling to four dynamically equivalent protons.

The ^{1}H n.m.r. spectrum of (**1**) (400 MHz, 298 K in $[^2H_8]$toluene) contains the expected resonances for co-ordinated dmpe [δ 1.46 (12H, 4 × CH$_3$), 1.04 (12H, 4 × CH$_3$), 1.37 (4H, ½ × 4–CH$_2$–), 1.76 (4H, ½ × 4–CH$_2$–)] as well as a broad signal [δ –4.9 (4H, BH$_4$)] and a broadened quintet [δ –26.9 (1H, J_{PH} 50.1 Hz, Fe–H)]. When the sample was cooled, the signal at δ –4.9 broadened and merged into the spectrum baseline. The signal re-emerged on further cooling as two resonances at δ 0.8 (partly superimposed on the aliphatic signals) and δ –22.4, with intensities in the ratio 3H : 1H, respectively. We have assigned the signal at δ –22.4 to the bridging Fe–H–B proton and that at δ 0.8 to the terminal BH$_3$ protons. Both resonances are significantly broadened even at 190 K due to H–H and B–H coupling. At low temperature, the Fe–H resonance at δ –26.9 exhibits a clearly resolved doublet splitting ($^2J_{H\text{-}Fe\text{-}H\text{-}}$ 7.1 Hz) due to coupling with the bridging Fe–H–B proton (Figure 1). At higher temperatures the splitting is averaged to a lesser value with higher multiplicity.

Treatment of (**1**) (in $[^2H_6]$benzene solution) with D$_2$O rapidly exchanged the free Fe–H hydrogen for deuterium. Neither the bridging Fe–H–B hydrogen nor the terminal BH$_3$ hydrogens were exchanged (even after several hours at 298 K). This proves the structural stability of (**1**) and shows that there is no facile intramolecular or intermolecular migration of BH$_3$ or BH$_4^-$. The temperature dependence of the ^{1}H n.m.r. spectra of (**1**) thus results from the facile exchange of the bridging Fe–H–B proton with the terminal BH$_3$ protons within a 'BH$_4$ ligand'; the rapid reorganisation of the bonding of the –H–BH$_3$ group in its co-ordination site probably proceeds *via* the doubly bridged species, (**4**).[4]

At 190 K saturation of the terminal BH$_3$ protons at δ 0.8 reduced the intensity of the resonance due to the bridging proton by a factor of 0.66 by saturation transfer.[5] The apparent spin-lattice relaxation time of the bridging proton (measured by the inversion recovery method) in the presence of a saturating R.F. field at δ 0.8 was 40 ms and this indicates a barrier ($\Delta G^\ddagger_{190}$) of 9.9 kcal mol^{-1} (1 kcal = 4.184 kJ) to the exchange of the bridging and terminal protons on boron.

Although (**1**) is an isolable, stable species, we have n.m.r. evidence which suggests that compounds analogous to (**1**) are generally formed in the reduction of metal halide complexes with BH$_4^-$. The reduction of Fe(dppe)$_2$Cl$_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] with BH$_4^-$ affords a borohydride-containing species which decomposes readily on standing in THF solution to Fe(dppe)$_2$H$_2$. Aluminium–hydrogen–metal species, analogous to (**1**) have been recently reported[6] as products in AlH$_4^-$ reductions of metal halide complexes.

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3 D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1972, **94**, 4545. FeH$_2$(dmpe)$_2$ can also be prepared by treatment of FeCl$_2$(dmpe)$_2$ with LiAlH$_4$ in THF.

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5 For a general description of the saturation transfer method see: M. L. Martin, J.-J. Delpuech, and G. J. Martin, 'Practical NMR Spectroscopy,' Heyden, London, Philadelphia, Rheine, 1980, p. 315.

6 G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1983, **105**, 6752.

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§ ^{31}P N.m.r. chemical shifts were measured relative to external trimethylphosphate taken to be 2.50 p.p.m. ^{11}B N.m.r. chemical shifts were measured relative to external boron trifluoride–diethyl ether taken to be 0.00 p.p.m. Positive values are to low field and shifts are not corrected for magnetic susceptibility.