Formation of Molecular Hydrogen Complexes of Iron by the Reversible Protonation of Iron Dihydrides with Alcohols

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Reversible protonation of *cis*-FeH$_2$(PP)$_2$ [PP = R$_2$PCH$_2$CH$_2$PR$_2$] complexes by ethanol produces the η^2-co-ordinated molecular hydrogen complexes *trans*-FeH(H$_2$)(PP)$_2$+ which readily undergo substitution with loss of H$_2$.

Over recent years, the protonation of various metal hydrides with strong acids has produced a number of 'nonclassical' molecular hydrogen complexes. Molecular hydrogen complexes have been observed or isolated for tungsten,[1,2] molybdenum,[1,2] iridium,[3—5] osmium,[6] ruthenium,[3,4,7,8] iron,[3,4,6] rhodium,[9] and chromium.[10] For at least two complexes, W(CO)$_3$(H$_2$)(Pr$^i_3$P)$_3$ (ref. 1) and [*trans*-FeH(H$_2$)-(DPPE)$_2$]BF$_4$ (ref. 4) [DPPE = 1,2-bis(diphenylphosphino)-ethane], X-ray diffraction studies have confirmed the η^2 mode of co-ordination of the dihydrogen ligand. In solution, n.m.r. spectroscopy has been used extensively to study molecular hydrogen complexes and it has been consistently found that the co-ordinated H$_2$ has a relatively short T_1 (longitudinal relaxation time) and that this is characteristic of the η^2 type of hydrogen co-ordination.[3,5—9]

We report here the *reversible* protonation of *cis*-FeH$_2$(PP)$_2$ (**1**) [PP = R$_2$PCH$_2$CH$_2$PR$_2$, where R = Me (PP = DMPE), Et (PP = DEPE), or Pr^n (PP = DPrPE)] by ethanol (and other simple alcohols) to yield solutions of the corresponding *trans* molecular hydrogen complexes (**2**) (Scheme 1) where the iron bears one σ-bonded H ligand and an η^2-co-ordinated H$_2$ ligand.

In ethanol solution at −6 °C, *cis*-FeH$_2$(DMPE)$_2$ (**1a**) exists in equilibrium with the corresponding protonated complex (**2a**) [for a solution 67 mM with respect to Fe, (**1a**):(**2a**) = 1:5]. The protonation is reversible and temperature dependent (Figure 1) and as shown by ^{1}H and ^{31}P n.m.r. (Table 1), the dihydrides (**1a**), (**1b**), and (**1c**) are completely protonated

in ethanol and methanol at −50 °C.† The temperature dependence of the equilibrium constant for the reaction (**1a**) $\rightleftharpoons$ (**2a**) (determined by integration of the ^{31}P n.m.r. spectra) affords $\Delta H = -36.8 \pm 2$ kJ mol^{-1} and $\Delta S = -192 \pm 7$ J K^{-1} mol^{-1}. In terms of acidity, the trihydride (**2a**) has a pK_a comparable to that of ethanol (*ca.* 15.85[11]); as shown by n.m.r. spectroscopy, (**1a**) is fully protonated by methanol at room temperature and not detectably protonated by isopropanol.‡

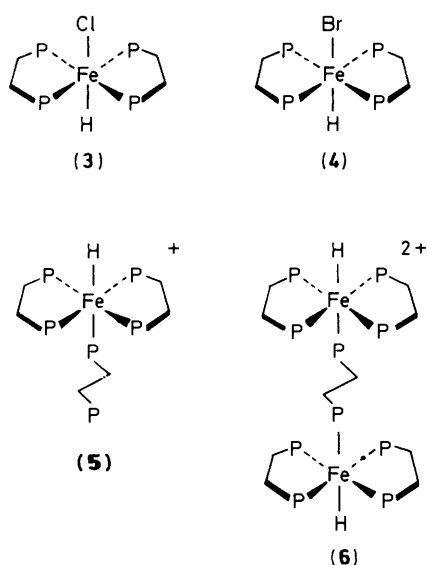a; P⎯⎯⎯P = DMPE
b; P⎯⎯⎯P = DEPE
c; P⎯⎯⎯P = DPrPE
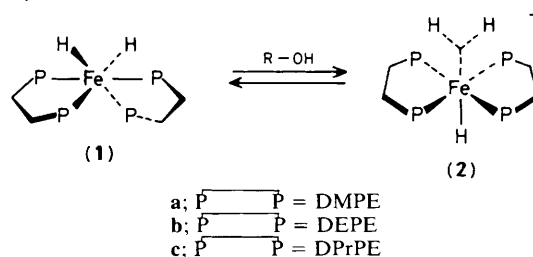
Scheme 1

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† As expected,[3,5—9] the η^2-co-ordinated H$_2$ ligand in (**2a**) has a relatively short T_1 value (20 ms at −31 °C in ethanol solution) compared to that of the terminal σ-co-ordinated H (T_1 49 ms). In the same solution, the iron-bound protons of FeH$_2$(DMPE)$_2$ (**1a**) have a T_1 value of *ca.* 370 ms.

‡ Chinn and Heinekey[8] have noted that the pK_a of CpRu(H$_2$)(DMPE) in acetonitrile solution is *ca.* 17.6.

Table 1. $^1H^a$ and $^{31}P^b$ n.m.r. data for the molecular hydrogen complexes (2a—c).

Complex		$^1H/\delta$ Fe–H	$^1H/\delta$ Fe–(H$_2$)	$^{31}P/\delta$
[FeH(H$_2$)(DMPE)$_2$]$^+$	(2a)	−17.071	−11.823	68.86
		(quintet, J_{PH} 50.3)		
[FeH(H$_2$)(DEPE)$_2$]$^+$	(2b)	−14.461	−10.464	95.18
		(quintet, J_{PH} 47.3)		
[FeH(H$_2$)(DPrPE)$_2$]$^+$	(2c)	−14.620	−10.657	89.90
		(quintet, J_{PH} 48.5)		

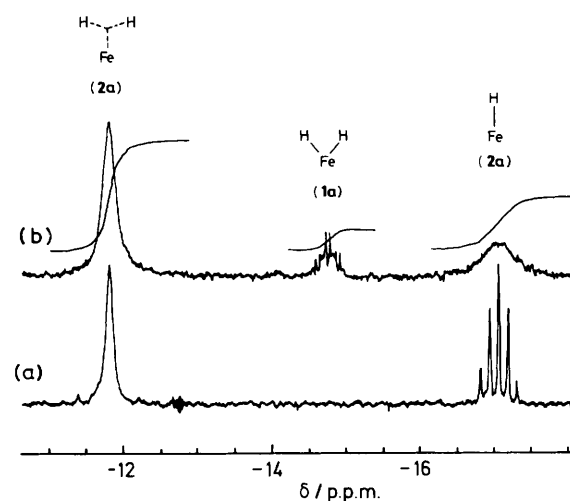^{a} ^1H spectra recorded at 400 MHz in anhydrous ethanol solution at −50 °C. Chemical shifts (δ) referenced to the methyl resonance of the ethanol solvent (taken as δ 1.200). Coupling constants in Hz, and signs are not implied. ^{b} ^{31}P spectra recorded at 162 MHz in anhydrous ethanol solution at −50 °C. Chemical shifts (δ in p.p.m.) referenced to external, neat, trimethyl phosphite (taken as 140.85 p.p.m.).

(3) **(4)**

(5)

(6)

Figure 1. The hydride region of the ^1H n.m.r. spectrum (400.1 MHz) of (2a) (67 mM) in ethanol solution at (a) −50 °C and (b) −6 °C.

On warming (2a), (2b),[6] or (2c) (in ethanol) above −50 °C, the three iron-bound hydrogens exchange *intramolecularly* in a fashion analogous to that reported for [FeH(H$_2$)(DPPE)$_2$]$^+$.[4] As the temperature is raised above −50 °C, the Fe–H and Fe(H$_2$) resonances in the hydride region of the ^1H n.m.r. spectrum broaden, and eventually coalesce near room temperature. At 25 °C, the ^1H-coupled ^{31}P n.m.r. spectrum of (2a) shows a broadened quartet, with a splitting of ca. 19 Hz owing to coupling of the three dynamically equivalent Fe–H and Fe(H$_2$) protons. If the value of J_{PH} for the Fe–H proton at room temperature is assumed to be 50.3 Hz (as observed at −50 °C), then the averaged value of ca. 19 Hz indicated J_{PH} ~3.4 Hz for the *cis*-P–Fe(H$_2$) coupling between phosphorus and the H$_2$ protons.§ Intermolecular exchange of the iron-bound protons of (2a) with either the acidic protons of alcoholic solvents or with the hydridic protons of (1a) is slow on the n.m.r. timescale at room temperature. However, in deuterated (or partially deuterated) alcohol solution, all three iron-bound protons of (2a) can be exchanged for deuterium.¶

Addition of excess LiCl or LiBr to an ethanolic solution of (2a) at room temperature resulted in the quantitative formation of the corresponding halo-hydrides FeHCl(DMPE)$_2$ (3) or FeHBr(DMPE)$_2$ (4), respectively.‖ Obviously, the ease with which H$_2$ can be displaced has synthetic potential. Addition of DMPE (0.5 equiv.) to an equilibrium mixture of (1a) and (2a) in ethanol (at room temperature) afforded initially a species [(DMPE)$_2$HFe–PMe$_2$CH$_2$CH$_2$PMe$_2$]$^+$ (5) (detectable by n.m.r. spectroscopy††). Eventually (5) was completely converted into the DMPE-bridged dimer [(DMPE)$_2$HFe–DMPE–FeH(DMPE)$_2$]$^{2+}$ (6) which could be isolated as its tetrafluoroborate salt by the addition of NaBF$_4$.††

§ Similarly values for J_{PH} of ca. 1.8 and ca. 0 Hz can be estimated for the corresponding *cis*-P–Fe(H$_2$) coupling in [FeH(H$_2$)(DEPE)$_2$]$^+$ and [FeH(H$_2$)(DPrPE)$_2$]$^+$, respectively. Coupling between phosphorus and co-ordinated H$_2$ has been noted in other metal complexes.[5—9]

¶ In CD$_3$OD containing a trace of CD$_3$OH, the hydride resonance of [FeD(HD)(DMPE)$_2$]$^+$ is observable by ^1H n.m.r. spectroscopy (at −50 °C) and shows a one-bond proton–deuterium coupling constant $^1J_{HD}$ 31.0 Hz for co-ordinated HD.

‖ In ethanol solution, (2a) reacts cleanly with azide, pyridine, and other nucleophiles with displacement of H$_2$.

†† *Spectral data* for (5): ^{31}P-{^1H} n.m.r. (ethanol) δ 67.69 (4P, d, $^2J_{PP}$ 32.1 Hz), 14.06 (1P, doublet of quintets, $^3J_{PP}$ 19.1 Hz), −46.87 p.p.m. (1P, d); ^1H n.m.r. (ethanol) Fe–H: δ −17.66 (doublet of quintets, $^2J_{PH(cis)}$ 55.1, $^2J_{PH(trans)}$ 17.7 Hz).

For (6) (BF$_4$ salt): ^{31}P-{^1H} n.m.r. (CD$_3$OD) δ 67.44 (8P, d, $^2J_{PP}$ 31.1 Hz), 14.35 p.p.m. (2P, quintet); ^1H n.m.r. (CD$_3$OD) Fe–H: δ −17.52 (doublet of quintets, $^2J_{PH(cis)}$ 55.8, $^2J_{PH(trans)}$ 18.6 Hz). Acceptable elemental analyses (C, H, and P) were obtained; m.p. (decomp.) 303 °C.

In nitromethane solution, (**1a**) is protonated to (**2a**) which slowly decomposes with the loss of H_2 to form a number of products. The dihydride (**1a**) reacts slowly in ethanol or acetone solution over a period of several days at room temperature and decomposes completely to (**6**) (with evolution of H_2 and formation of insoluble byproducts). Although protonation of (**1a**) by acetone has not been observed directly (undoubtedly owing to the lower acidity of acetone), a small equilibrium concentration of (**2a**) would suffice to permit attack by the solvent and liberation of free DMPE with subsequent formation of (**6**).

The protonation of iron dihydrides under experimentally mild reaction conditions makes the molecular hydrogen complexes of iron a readily accessible class of organometallic compounds. The facile substitution of the co-ordinated hydrogen in these complexes means that these compounds will be versatile synthetic intermediates in the synthesis of metal hydrides.

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References

1 G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451.
2 G. J. Kubas, R. R. Ryan, and D. A. Wrobleski, *J. Am. Chem. Soc.*, 1986, **108**, 1339.
3 R. H. Crabtree and D. G. Hamilton, *J. Am. Chem. Soc.*, 1986, **108**, 3124.
4 R. H. Morris, J. F. Sawyer, M. Shiralian, and J. D. Zubrowski, *J. Am. Chem. Soc.*, 1985, **107**, 5581.
5 R. H. Crabtree, M. Lavin, and L. Bonneviot, *J. Am. Chem. Soc.*, 1986, **108**, 4032, and references therein.
6 M. Bautista, K. A. Earl, R. H. Morris, and A. Sella, *J. Am. Chem. Soc.*, 1987, **109**, 3780.
7 F. M. Conroy-Lewis and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, 1987, 1675.
8 M. S. Chinn and M. Heinekey, *J. Am. Chem. Soc.*, 1987, **109**, 5865.
9 C. Bianchini, C. Mealli, M. Peruzzini, and F. Zanobini, *J. Am. Chem. Soc.*, 1987, **109**, 5548.
10 R. K. Upmacis, G. E. Gadd, M. Poliakoff, M. B. Simpson, J. J. Turner, R. Whyman, and A. F. Simpson, *J. Chem. Soc., Chem. Commun.*, 1985, 27; S. P. Church, F.-W. Grevels, H. Hermann, and K. Schaffner, *ibid.*, 1985, 30; R. L. Sweany, *J. Am. Chem. Soc.*, 1985, **107**, 2374.
11 W. Reeve, C. M. Erikson, and P. F. Aluotto, *Can. J. Chem.*, 1979, **57**, 2747.