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Preliminary communication

An exceptionally stable *cis*-(hydride)(η^2-dihydrogen) complex of iron

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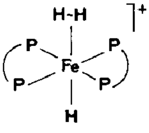
Abstract

The *cis*-(H)(H_2) complex $[(PP_3)Fe(H)(H_2)]BPh_4$ ($PP_3 = P(CH_2CH_2PPh_2)_3$) has been made by reaction of the chloride $[(PP_3)FeCl]BPh_4$ in THF with $NaBH_4$ under 1 atm of H_2. In the solid state and in solution at low temperature the complex is octahedral, and the hydride and dihydrogen ligands occupy mutually *cis* positions. At ambient temperature in solution the complex is trigonal-bipyramidal, and an "H_3" unit occupies an axial position *trans* to the bridgehead phosphorus atom of PP_3; this results in exceptional thermal and chemical stability of the complex.

The complexes $[Fe(H)(R_2PCH_2CH_2PR'_2)]^+$ (**1**) (R = R′ = Ph [1,2], Et [2,3], Me [3], Pr [3]; R = Ph, R′ = Et [4]) have proved particularly suitable systems for the formation of η^2-H_2 adducts in which dihydrogen and hydride ligands occupy mutually *trans* positions of the octahedral coordination polyhedron. Salient features of these complexes are: a fast displacement in solution of the η^2-H_2 molecule by various monofunctional ligands, a relatively low thermal stability, and a fast exchange of dihydrogen and hydride ligands at the metal center in solution at ambient temperature. This exchange is believed to occur through fluxional seven-coordinate trihydride intermediates. Since minor changes in the phosphine coligands adjacent to η^2-H_2 can change the properties of this ligand [4–7], it was reasonable to expect tying four phosphine donors to each other, as in the tripodal ligand $P(CH_2CH_2PPh_2)_3$, PP_3, might be greatly alter the properties of the dihydrogen ligand. We have found that the *cis*-(H)(η^2-H_2) complex $[(PP_3)Fe(H)(H_2)]BPh_4$ (**2**) does, in fact, display exceptional stability, both in the solid state and in solution.



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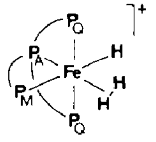

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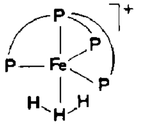

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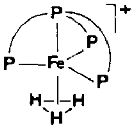

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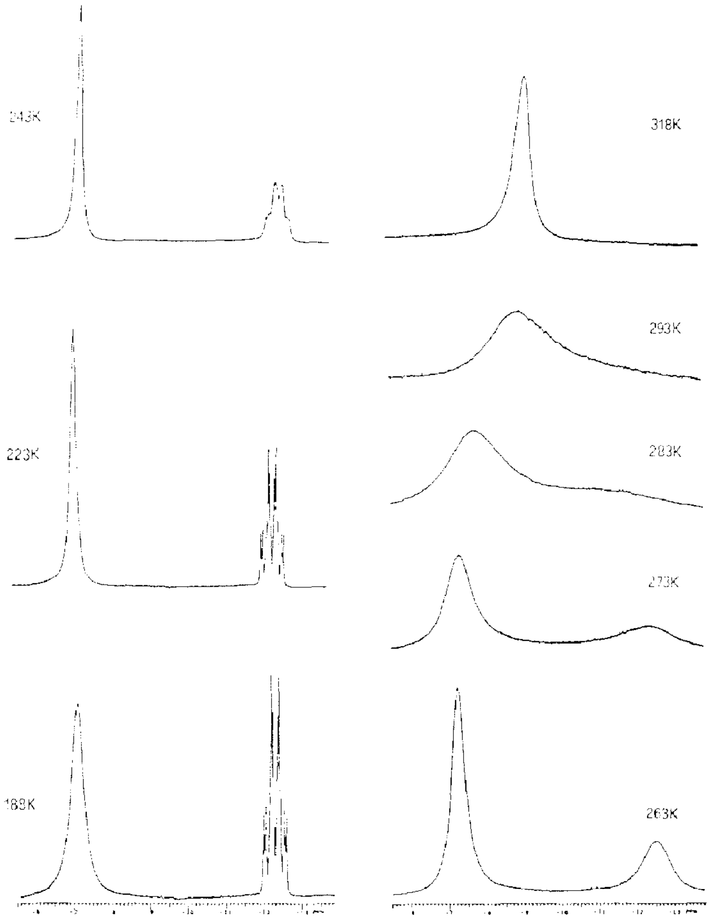

Fig. 1. Variable temperature ^{1}H NMR spectra (acetone-d_6, 300 MHz) of **2**; Me_4Si reference.

Compound **2** was obtained, as yellow crystals, by reaction of $[(PP_3)FeCl]BPh_4$ [8] (**3**) in THF with an excess of $NaBH_4$ under 1 atm of H_2. It is air stable in the solid state and does not lose H_2 when heated under vacuum (0.1 torr) to 100 °C. The IR spectrum exhibits a weak broad band at 2350 cm^{-1} and a medium band at 1935 cm^{-1}, which are assigned to ν(H–H) and ν(Fe–H), respectively [7]. The ^{1}H NMR spectrum (300 MHz) of **2** in acetone-d_6 at 233 K (Fig. 1) exhibits a broad singlet ($w_{1/2}$ 56 Hz) at −7.21 ppm, which is typical of an η^2-H_2 ligand [7]. A well resolved multiplet (tdd) at −12.47 ppm is assigned to a terminal hydride which is coupled to two equivalent ($J(HP_Q)$ 59.2 Hz) and two non-equivalent ($J(HP_A)$ 45.6 Hz; $J(HP_M)$ 15.7 Hz) phosphorus nuclei of PP_3. On decreasing the temperature, the resonance of the η^2-H_2 ligand broadens ($w_{1/2}$ 113 Hz at 188 K). A similar temperature dependence of the H_2 signal has been observed by Morris et al. for $[Fe(H)(H_2)(Ph_2PCH_2CH_2PPh_2)_2]BF_4$ [1] and ascribed to a slow rotation of the dihydrogen molecule on the square face of a square-pyramid defined by the four phosphorus donors and by the terminal hydride. A second fluxional process involving the hydride and H_2 ligands takes place above 233 K. The two resonances become broader and broader, and finally collapse into a single signal at ca. 293 K

($\Delta G^{\neq} = 12.1 \pm 0.3$ kcal mol^{-1}). When the temperature is raised, the intramolecular exchange of the hydride and dihydrogen ligands become faster, and a new resonance appears at −9.13 ppm ($w_{1/2} = 145$ Hz, 318 K). In keeping with the occurrence of two fluxional processes, the relaxation time, T_1 [9], for the terminal hydride decreases progressively when the temperature is raised (from 125 ms at 188 K to 12 ms at 273 K), whereas the T_1 value of the H_2 ligand goes through a minimum of 6 ms at 233 K (T_1 10 ms at 188 K, 10 ms at 273 K). The T_1 value of the fast exchange signal increases with temperature up to 19 ms at 313 K. The ^{1}H NMR spectrum (300 MHz, acetone-d_6, 188 K) of the isotopomer $[(PP_3)Fe(H)(HD)]BPh_4$ (**4**), (synthesized by stirring a THF solution of $[(PP_3)FeH(N_2)]BPh_4$ [8] (**5**) under 1 atm of HD for 3 h) exhibits at 1/1/1 triplet at −7.15 ppm for the η^2-HD ligand and the same tdd pattern for the terminal hydride. The J(HD) value of 28.3 Hz and the isotopic shift of 60 ppb (at 188 K $\delta(H_2)$ −7.09 ppm) are in good agreement with previously reported data on dihydrogen and deuteriumhydride complexes [2,7,10].

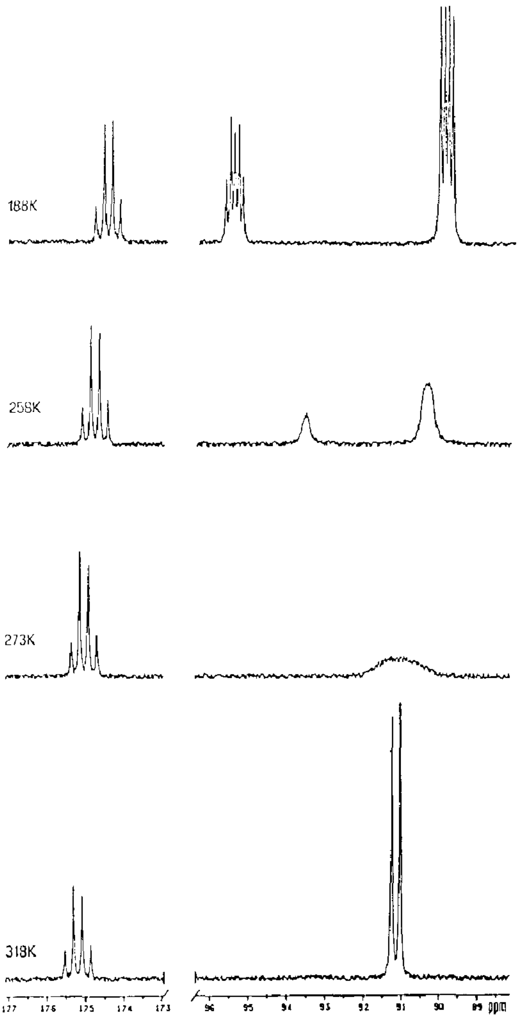

Fig. 2. Variable temperature $^{31}P\{^1H\}$NMR spectra (acetone-d_6, 121.42 MHz) of **2**; H_3PO_4 85% reference.

Important information on the exchange mechanism of the hydride and dihydrogen ligands at iron is provided by variable-temperature $^{31}P\{^{1}H\}$ NMR spectroscopy (121.42 MHz, acetone-d_6, H_3PO_4 85% reference) (Fig. 2). In the temperature range 188–273 K, the spectrum consists of a first-order AMQ_2 splitting pattern typical of octahedral PP_3 metal complexes I [11] (at 188 K; $\delta(P_A)$ 174.49, $\delta(P_M)$ 95.44, $\delta(P_Q)$ 89.93 ppm, $J(P_AP_M) \cong J(P_AP_Q) = 26.0$ Hz, $J(P_MP_Q) = 14.0$ Hz). When the temperature is raised a dynamic process takes place and at ca. 273 K this makes equivalent the three terminal phosphorus atoms of PP_3, as is the case when the $(PP_3)M$ fragment adopts a C_{3v} symmetry [11] (trigonal-bipyramidal geometry) (AM_3 spin system: $\delta(P_A)$ 175.20, $\delta(P_M)$ 91.13, $J(P_AP_M)$ 27.1 Hz).

The ^{31}P NMR data clearly indicate that above 273 K the three hydrogen atoms occupy an axial position on a trigonal bipyramid, *trans* to the bridgehead phosphorus of PP_3. This rules out any seven-coordinate trihydride intermediate in the exchange mechanism, but does not discriminate between the two possible structures through which hydride and dihydrogen ligands are believed to exchange, i.e. the open II or close III H_3 units [12,13]. Whatever the structure, the H_3 moiety is strongly bound to the metal center, and the three hydrogen atoms are strongly bound to each other, since **2** is fairly stable in refluxing THF and does not undergo H/D exchange when treated in THF for 3 h with D_2 or D_2O. Similarly, the perdeuterated complex $[(PP_3)Fe(D)(D_2)]BPh_4$ (**8**) obtained by use of $NaBD_4$ and D_2, does not form any isotopomeric derivative when stirred for 3 h in THF under 1 atm of H_2. Replacement of H_2 with N_2 or MeCN is a feasible reaction pathway but quite long times are required for appreciable formation of the corresponding N_2 (**5**) or MeCN, $[(PP_3)Fe(H)(MeCN)]BPh_4$ (**9**) [8], derivatives (75% conversion to **5** in 3 days, THF, 1 atm of N_2; 40% conversion to **9** in 2 h, neat MeCN). In contrast, the regeneration of **2** from **5** and **9** is a very fast reaction, complete within ca. 30 min.

References

1 R.H. Morris, J.F. Sawyer, M. Shiralian, J.D. Zubkowsky, J. Am. Chem. Soc., 107 (1985) 5581.
2 M.T. Bautista, K.A. Earl, R.H. Morris, A. Sella, J. Am. Chem. Soc., 1079 (1987) 3780.
3 M.V. Baker, L.D. Field, D.J. Young, J. Chem. Soc., Chem. Commun., (1988) 546.
4 M.T. Bautista, K.A. Earl, R.H. Morris, Inorg. Chem., 27 (1988) 1124.
5 C. Bianchini, C. Mealli, M. Peruzzini, F. Zanobini, J. Am. Chem. Soc. 107 (1987) 5548.
6 M. Antberg, K.-M. Frosin, L. Dahlenburg, J. Organomet. Chem., 338 (1988) 319.
7 G.J. Kubas, Acc. Chem. Res., 21 (1988) 120, and ref. therein.
8 P. Stoppioni, F. Mani, L. Sacconi, Inorg. Chim. Acta, 11 (1974) 227.
9 R.H. Crabtree, M. Lavin, L. Bonneviot, J. Am. Chem. Soc., 108 (1986) 4032.
10 F.M. Conroy-Lewis, S.J. Simpson, J. Chem. Soc., Chem. Commun., (1986) 506; M.S. Chinn, D.M. Heinekey, J. Am. Chem. Soc., 109 (1987) 5865.
11 C. Bianchini, M. Peruzzini, F. Zanobini, J. Organomet. Chem., 326 (1987) C79.
12 J.K. Burdett, M.R. Pourian, Organometallics, 6 (1987) 1684; J.K. Burdett, J.R. Phillips, M.R. Pourian, M. Poliakoff, J.J. Turner, R. Upmacis, Inorg. Chem., 26 (1987) 3054.
13 D.M. Heinekey, N.G. Payne, G.K. Schulte, J. Am. Chem. Soc., 110 (1988) 2303.