Synthesis, Characterization, and Structure of the Complex $[FeH(H_2BH_2)\{CH_3C(CH_2PPh_2)_3\}]$ †

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By reaction of $[Fe(H_2O)_6][BF_4]_2$ with 1,1,1-tris(diphenylphosphinomethyl)ethane, tppme, and an excess of sodium tetrahydroborate, in boiling tetrahydrofuran, the red crystalline complex $[FeH(H_2BH_2)(tppme)]$ has been synthesized. Its crystal structure has been determined from counter diffraction data [orthorhombic, space group $Pn2_1a$, $a = 20.803(7)$, $b = 16.964(5)$, $c = 10.242(3)$ Å, and $Z = 4$] and refined by full-matrix least squares to R and R' of 0.042 and 0.041 respectively for 1 191 reflections having $I \geqslant 3\sigma(I)$. The iron atom is six-co-ordinated by the three phosphorus atoms of the ligand, two hydrogen atoms of the BH_4 group, and a hydridic hydrogen atom. Variable-temperature ^1H and ^{31}P n.m.r. studies have shown that at low temperature (< 253 K) the molecule is rigid also in solution. On raising the temperature, scrambling of the three metal-bound hydrogens occurs and the ligand phosphorus atoms, co-ordinated to the metal, become magnetically equivalent.

The tetrahydroborate ion BH_4^- has been shown in various structural studies to bond to a wide variety of metal ions as a uni-, bi-, or tri-dentate ligand.[1,2] However, the use of n.m.r. spectroscopy to determine the type of $M-BH_4$ bonding in solution was generally unfruitful. Indeed the protons of the tetrahydroborate ligand have been found to be equivalent in nearly all of these compounds, due to rapid equilibration on the n.m.r. time-scale.[2] Only recently some non-fluxional tetrahydroborate complexes were reported.[3] In particular, $[RuH(H_2BH_2)(bdpp)]$ [where bdpp is the linear-chain ligand $PPh(CH_2CH_2CH_2PPh_2)_2$] shows discrete ^1H n.m.r. signals at room temperature for the metal hydride, each of the two bridging protons, and the two terminal B–H protons. On raising the temperature, complete scrambling of the BH_4^- protons occurs.

We now describe the synthesis, i.r. and n.m.r. spectroscopic and *X*-ray structural characterization of the new complex $[FeH(H_2BH_2)(tppme)]$ [where tppme is the tripodal ligand $CH_3C(CH_2PPh_2)_3$]. This complex, although isoelectronic with $[RuH(H_2BH_2)(bdpp)]$, containing the same donor-atom set, shows quite different molecular dynamics in solution. A brief communication has been published previously.[4]

Experimental

Unless otherwise stated, all reactions and manipulations were performed under a nitrogen atmosphere; solvents were purified by standard methods. Infrared spectra were measured on a Perkin-Elmer 283 instrument from 200 to 4 000 cm^{-1} using Nujol mulls. Phosphorus-31 n.m.r. spectra were recorded on a Varian CFT-20 spectrometer, equipped with a ^{31}P probe which operated at 32.2 MHz. Chemical shifts are reported in p.p.m. relative to 85% H_3PO_4, downfield values being taken as positive. Proton n.m.r. spectra were obtained on a Varian CFT-20 instrument equipped with a ^1H probe which operated at 80 MHz, and a Varian XL-200 spectrometer of the University of Siena. Selective phosphorus-decoupling experiments were carried out on a Bruker WM 250 instrument of the Eidgenössische Technische Hochschule (E.T.H.) (Zürich); $SiMe_4$ was used as internal standard.

Preparation of $[FeH(H_2BH_2)(tppme)]$.—A solution of $NaBH_4$ (8 mmol) in ethanol (25 cm^3) was added to a solution of $[Fe(H_2O)_6][BF_4]_2$ (1 mmol) and tppme (1 mmol) in tetrahydrofuran (thf) (40 cm^3). The resultant solution was heated to reflux for 5 min to give a bright red solution and a white solid. The solution was filtered and the solvent was distilled off until bright red crystals precipitated. The mother-liquor was decanted off and the crystals were washed twice by decantation with ethanol; then they were filtered off, washed with light petroleum, and dried in a stream of nitrogen, yield 65% (Found: C, 70.6; H, 6.4; Fe, 7.9. Calc. for $C_{41}H_{44}BFeP_3$: C, 70.7; H, 6.35; Fe, 8.0%).

The deuteriated complex $[FeD(D_2BD_2)(tppme)]$ was prepared analogously, by using $[Fe(D_2O)_6][BF_4]_2$, $NaBD_4$, and C_2H_5OD.

Crystallography.—The crystal used for *X*-ray data collection was an irregular prism of dimensions *ca.* 0.10 × 0.30 × 0.40 mm. The unit-cell parameters were obtained from a least-squares fit of 20 reflections, carefully centered on a Philips PW 1100 automatic diffractometer.

Crystal data. $C_{41}H_{44}BFeP_3$, $M = 696.4$, orthorhombic, space group $Pn2_1a$, $a = 20.803(7)$, $b = 16.964(5)$, $c = 10.242(3)$ Å, $U = 3\,614$ Å^3, $Z = 4$, $D_c = 1.279$ g cm^{-3}, $F(000) = 1\,464$, $\lambda(Mo\text{-}K_\alpha) = 0.7107$ Å.

Data collection was carried out using the $\omega-2\theta$ scan technique and graphite monochromated Mo-K_α radiation within $2\theta \leqslant 40°$. After correction for background, the standard deviation, $\sigma(I)$, of the intensity I was calculated as described elsewhere[5] using the value of 0.03 for the instability factor k. The intensity data were corrected for Lorentz-polarization effects and for absorption [$\mu(Mo\text{-}K_\alpha) = 5.74$ cm^{-1}], the transmission factors ranging from 0.95 to 0.87. Both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms.[6] Of the total 1 954 reflections, 1 191 were considered observed [$I \geqslant 3\sigma(I)$].

Solution and refinement of the structure. The calculations were

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† Hydrido(tetrahydroborato-*HH'*)[1,1,1-tris(diphenylphosphinomethyl)ethane-*PP'P''*]iron.

Supplementary data available (No. SUP 56134, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Positional parameters (× 10^4) of complex (**2**)

Atom	*x*	*y*	*z*
Fe	−659(1)	−1 320*	626(2)
P(1)	344(2)	−1 278(3)	1 224(3)
P(2)	−544(2)	−146(2)	−160(3)
P(3)	−960(2)	−872(2)	2 579(4)
C(1)	367(6)	957(7)	2 947(11)
C(2)	56(5)	255(7)	2 252(11)
C(3)	598(6)	−271(7)	1 726(12)
C(4)	−369(5)	579(7)	1 133(11)
C(5)	−349(5)	−203(7)	3 255(11)
C(6)	601(4)	−1 899(4)	2 621(9)
C(7)	1 161(4)	−1 751(4)	3 328(9)
C(8)	1 345(4)	−2 260(4)	4 331(9)
C(9)	968(4)	−2 916(4)	4 627(9)
C(10)	407(4)	−3 063(4)	3 920(9)
C(11)	224(4)	−2 555(4)	2 917(9)
C(12)	975(4)	−1 566(5)	56(7)
C(13)	1 593(4)	−1 249(5)	126(7)
C(14)	2 068(4)	−1 503(5)	−740(7)
C(15)	1 924(4)	−2 074(5)	−1 676(7)
C(16)	1 307(4)	−2 391(5)	−1 746(7)
C(17)	832(4)	−2 137(5)	−880(7)
C(18)	103(4)	30(4)	−1 363(7)
C(19)	479(4)	711(4)	−1 377(7)
C(20)	943(4)	815(4)	−2 343(7)
C(21)	1 033(4)	237(4)	−3 296(7)
C(22)	658(4)	−444(4)	−3 282(7)
C(23)	193(4)	−548(4)	−2 316(7)
C(24)	−1 219(4)	317(5)	−1 030(8)
C(25)	−1 291(4)	1 134(5)	−997(8)
C(26)	−1 799(4)	1 490(5)	−1 664(8)
C(27)	−2 234(4)	1 029(5)	−2 365(8)
C(28)	−2 162(4)	212(5)	−2 398(8)
C(29)	−1 654(4)	−144(5)	−1 731(8)
C(30)	−1 116(4)	−1 545(4)	3 953(7)
C(31)	−857(4)	−1 431(4)	5 195(7)
C(32)	−1 008(4)	−1 952(4)	6 203(7)
C(33)	−1 417(4)	−2 588(4)	5 969(7)
C(34)	−1 676(4)	−2 702(4)	4 727(7)
C(35)	−1 526(4)	−2 181(4)	3 719(7)
C(36)	−1 702(4)	−217(5)	2 734(7)
C(37)	−1 825(4)	147(5)	3 880(7)
C(38)	−2 368(4)	626(5)	3 970(7)
C(39)	−2 789(4)	687(5)	2 914(7)
C(40)	−2 666(4)	269(5)	1 767(7)
C(41)	−2 123(4)	−210(5)	1 677(7)
B	−1 317(12)	−2 261(14)	162(25)
H(1)	−1 349(51)	−1 484(75)	54(100)
H(2)	−775(53)	−2 281(62)	510(102)
H(3)	−1 197(42)	−2 661(54)	−654(92)
H(4)	−1 704(63)	−2 341(76)	846(126)
H(5)	−465(43)	−1 582(52)	−624(95)

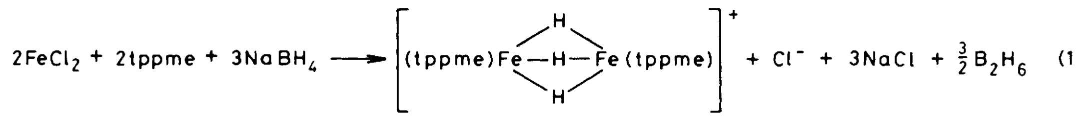
* Chosen to be in accord with the isormorphous complex [Cu(BH_4)(tppme)].

carried out using the SHELX 76 system of programs [7] on a SEL 32/77 computer. Atomic scattering factors for non-hydrogen atoms were taken from ref. 8, those for hydrogen atoms from ref. 9.

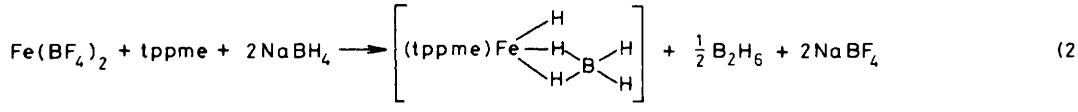
On account of the isomorphism with [Cu(BH_4)(tppme)],[10] the final parameters of the copper complex were used as starting parameters for the present iron one. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Several cycles of full-matrix least-squares refinements using anisotropic thermal parameters for the iron and phosphorus atoms and isotropic ones for the remaining non-hydrogen atoms lowered the conventional *R* factor to 0.060. Throughout the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry. The hydrogen atoms of the methyl group of the tppme ligand were located from a ΔF Fourier map, while the remaining hydrogen atoms of this ligand were introduced in calculated positions (C–H 0.95 Å). All the parameters of these hydrogen atoms were kept constant throughout the refinement. Owing to the polar nature of the space group, the absolute configuration was determined by refining the two possible configurations, which gave *R* values of 0.046 (x, y, z) and 0.047 ($\bar{x}$, $\bar{y}$, $\bar{z}$) respectively. At this point a Fourier difference map, calculated using the reflections having $\sin\theta/\lambda \leqslant 0.35$ Å^{-1}, revealed the positions of the tetrahydroborate hydrogen atoms and the hydridic hydrogen among the first six peaks, whose electron density ranged from 0.7 to 0.5 e Å^{-3}. Several full-matrix least-squares cycles, in which the tetrahydroborate hydrogen and the hydridic hydrogen atoms were refined isotropically together with all the other parameters, using the entire set of data, led to convergence at $R (= \Sigma\,||F_o| - |F_c||\,/\Sigma|F_o|)$ and $R' [= \Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]$ of 0.042 and 0.041 respectively. The largest shift/error for the hydrogen atom parameters in the final cycle was 0.2. Final positional parameters with their estimated standard deviations are given in Table 1.

Results and Discussion

As previously reported,[11] iron(II) salts such as $FeCl_2$, $FeBr_2$, and $[Fe(H_2O)_6][ClO_4]_2$ react, in the presence of tppme, with sodium tetrahydroborate to yield the dimeric blue hydride [(tppme)Fe(μ-H)$_3$Fe(tppme)]$^+$ (**1**) [equation (1)]. We have now found that an analogous reaction, using the tetrafluoroborate salt $[Fe(H_2O)_6][BF_4]_2$, produces only the red complex [FeH(BH_4)(tppme)] (**2**) [equation (2)]. Reaction (2) is favoured by an excess of $NaBH_4$ and high temperature, but the use of the tetrafluoroborate salt seems to be the decisive factor.



(**1**)



(**2**)

Table 2. Selected bond distances (Å) and angles (°)

Fe–P(1)	2.175(3)	Fe–B	2.16(2)	P(1)–C(6)	1.856(9)	P(3)–C(30)	1.841(8)
Fe–P(2)	2.162(4)	B–H(1)	1.32(12)	P(1)–C(12)	1.842(9)	P(3)–C(36)	1.857(9)
Fe–P(3)	2.230(4)	B–H(2)	1.18(10)	P(2)–C(4)	1.843(12)	C(1)–C(2)	1.53(2)
Fe–H(1)	1.58(11)	B–H(3)	1.10(9)	P(2)–C(18)	1.849(9)	C(2)–C(3)	1.54(1)
Fe–H(2)	1.65(10)	B–H(4)	1.08(13)	P(2)–C(24)	1.840(9)	C(2)–C(4)	1.55(1)
Fe–H(5)	1.41(9)	P(1)–C(3)	1.860(12)	P(3)–C(5)	1.840(11)	C(2)–C(5)	1.54(1)
P(1)–Fe–P(2)	88.2(2)	H(2)–Fe–H(5)	71(5)	Fe–P(1)–C(6)	118.4(3)	Fe–P(3)–C(36)	119.8(3)
P(1)–Fe–P(3)	90.3(1)	B–Fe–P(1)	134.0(7)	Fe–P(1)–C(12)	119.5(3)	C(5)–P(3)–C(30)	102.5(4)
P(2)–Fe–P(3)	92.9(1)	B–Fe–P(2)	132.1(6)	C(3)–P(1)–C(6)	103.1(5)	C(5)–P(3)–C(36)	101.8(5)
P(1)–Fe–H(1)	170(4)	B–Fe–P(3)	105.7(7)	C(3)–P(1)–C(12)	102.7(4)	C(30)–P(3)–C(36)	97.4(4)
P(1)–Fe–H(2)	101(4)	Fe–H(1)–B	96(7)	C(6)–P(1)–C(12)	98.3(4)	C(1)–C(2)–C(3)	107.8(9)
P(1)–Fe–H(5)	90(4)	Fe–H(2)–B	98(7)	Fe–P(2)–C(4)	111.6(4)	C(1)–C(2)–C(4)	108.0(9)
P(2)–Fe–H(1)	97(4)	H(1)–B–H(2)	96(7)	Fe–P(2)–C(18)	118.5(3)	C(1)–C(2)–C(5)	108.3(10)
P(2)–Fe–H(2)	154(4)	H(1)–B–H(3)	124(7)	Fe–P(2)–C(24)	119.3(3)	C(3)–C(2)–C(4)	111.4(10)
P(2)–Fe–H(5)	85(4)	H(1)–B–H(4)	98(8)	C(4)–P(2)–C(18)	103.1(5)	C(3)–C(2)–C(5)	110.0(9)
P(3)–Fe–H(1)	98(4)	H(2)–B–H(3)	90(7)	C(4)–P(2)–C(24)	102.4(4)	C(4)–C(2)–C(5)	111.2(9)
P(3)–Fe–H(2)	111(4)	H(2)–B–H(4)	121(9)	C(18)–P(2)–C(24)	99.5(4)	P(1)–C(3)–C(2)	115.0(8)
P(3)–Fe–H(5)	178(4)	H(3)–B–H(4)	126(9)	Fe–P(3)–C(5)	110.7(4)	P(2)–C(4)–C(2)	114.0(8)
H(1)–Fe–H(2)	71(5)	Fe–P(1)–C(3)	112.4(4)	Fe–P(3)–C(30)	121.6(3)	P(3)–C(5)–C(2)	116.0(8)
H(1)–Fe–H(5)	82(5)						

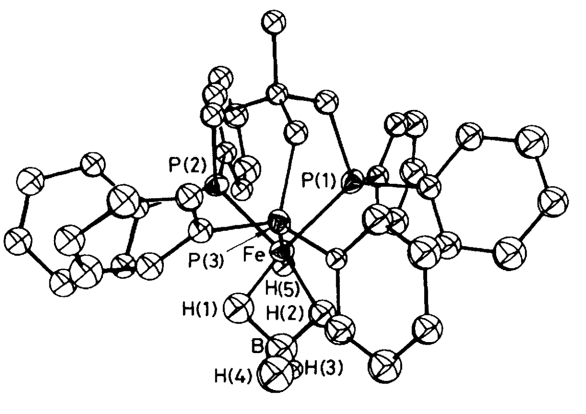


Figure 1. Perspective view of the complex [FeH(H_2BH_2)(tppme)]. ORTEP drawing with 30% probability ellipsoids

Indeed, experiments under different conditions (temperature, solvent, molar ratio of the reagents) have shown that complex (**2**) can be obtained only when iron(II) tetrafluoroborate is used as starting material, whereas compound (**1**) can not be obtained from this salt.

Complex (**2**), which is diamagnetic and very air sensitive, is moderately soluble in methylene chloride and slightly soluble in tetrahydrofuran, benzene, and toluene. It does not react with carbon monoxide at room temperature and atmospheric pressure.

Description of the Structure.—The molecular structure of complex (**2**) consists of discrete [FeH(H_2BH_2)(tppme)] molecules, shown in perspective in Figure 1. Selected bond distances and angles are given in Table 2.

The metal atom is co-ordinated by the three phosphorus atoms of the tppme ligand, by two bridging hydrogen atoms of the BH_4^- group, and by an hydridic hydrogen atom in a distorted octahedral environment. The bridging hydrogen atoms and the hydride atom are each *trans* to the three phosphorus atoms of tppme, the corresponding axial angles being significantly different; while the angle involving the hydridic hydrogen, 178(4)°, is very close to 180°, the other two angles involving the bridging tetrahydroborate hydrogens, owing to the BH_4^- bite angle, differ significantly from the ideal value [170(4) and 154(4)°]. Moreover, the reduced steric requirements of the hydride with respect to the other ligands is evidenced by the displacement of the metal atom (0.25 Å) from the equatorial plane, the four basal ligands being bent towards the hydride atom.

The BH_4^- ligand is definitely bidentate, as demonstrated by the Fe–B distance of 2.16(2) Å. This value is fully comparable with those reported for 3*d* metal complexes where the tetrahydroborate anion acts as a bidentate ligand; M–B separations ranging from 2.14(1) to 2.21(3) Å have been reported for cobalt,[12,13] nickel,[14] and copper[15] complexes. In this context the value of the Cu–B distance [2.44(2) Å] in the isomorphous copper derivative [Cu(BH_4)(tppme)],[10] where the BH_4^- acts as a unidentate ligand, is of interest.

The Fe–H_b (b = bridging) bond distances are 1.58(11) and 1.65(10) Å, while the Fe–H_t (t = terminal) bond distance, [1.41(9) Å] is shorter than the usual values (1.49—1.57 Å) reported for such distances.[1] Although this difference may not be significant considering the large values of the standard deviations, the stronger attachment of the terminal hydrogen ligand is supported by the lengthening of the *trans* Fe–P bond distance with respect to the other ones which are *cis* to the hydridic hydrogen ligand [2.230(4) *vs.* 2.175(3) and 2.162(4) Å].

As regards the BH_4^- group, the B–H_b distances [1.32(12) and 1.18(10) Å] are, as expected, longer than the terminal ones [1.10(9) and 1.08(13) Å].

Considering the isomorphous five-co-ordinated cobalt[12] and four-co-ordinated copper[10] derivatives, containing a bidentate and a unidentate BH_4^- respectively, noteworthy are the average values of the P–M–P angles, which take account of the steric hindrance of the ancillary ligand [P–M–P(av.) 90.5 (present compound), 91.5 (five-co-ordinated cobalt complex), 94.0° (four-co-ordinated copper complex)].

I.r. Spectra.—The i.r. spectrum of complex (**2**) (Nujol mull) shows a strong doublet at 2 380—2 320 cm^{-1} due to B–H_t stretching, a broad strong band at 1 440 cm^{-1} due to bridge deformation, and a strong absorption at 1 182 cm^{-1} due to B–H_t deformation.[2] Moreover, there is a broad medium band at 1 910 cm^{-1} which can be assigned either to B–H_b stretching or to the iron–hydride stretching. We prefer the first assignment because of the shape of the band; those for metal–hydride stretching vibrations are generally sharp. The spectrum of the deuteriated derivative of (**2**) shows two medium absorptions at

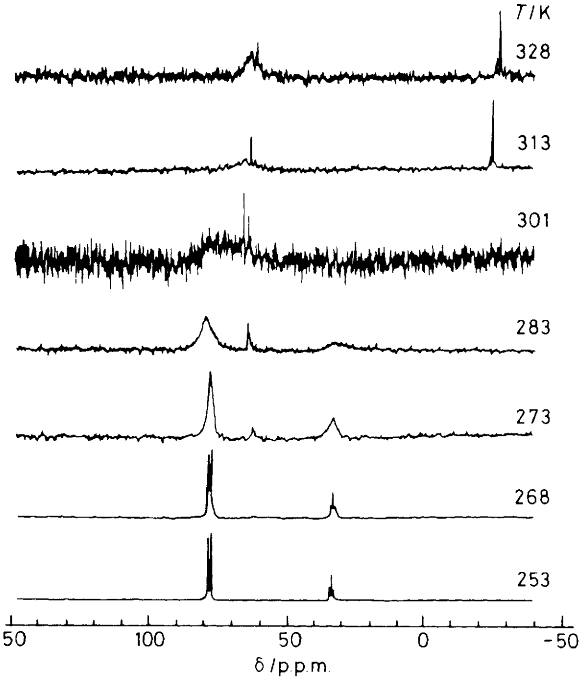


Figure 2. The 32.2-MHz $^{31}P-\{^1H\}$ n.m.r. spectra of complex (**2**) in $[^2H_8]$tetrahydrofuran over the temperature range 253—328 K

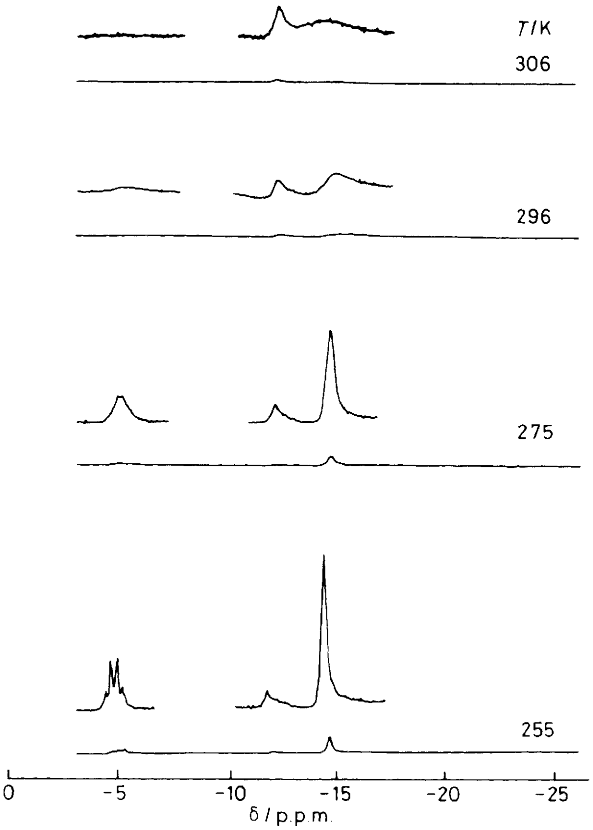


Figure 3. The 200-MHz ^1H n.m.r. spectra (hydridic hydrogen region) of complex (**2**) in CD_2Cl_2 over the temperature range 255—306 K

1 792 and 1 710 cm^{-1} due to ν(B–D$_t$) and a medium absorption at 1 060 cm^{-1} which can be assigned to bridge deformation. The other absorptions due to the BH_4^- and BD_4^- anions and to the Fe–H and Fe–D groups are either very weak or not distinguishable from those of the ligand.

N.M.R. Spectra.—The n.m.r. spectra of complex (**2**) appear complicated by resonances due to impurities, either present in the starting complex or arising from its decomposition particularly at higher temperatures. The poor solubility of the complex obviously enhances this problem.

The low-temperature (<253 K) $^{31}P-\{^1H\}$ and ^1H n.m.r. spectra demonstrate a rigid stereochemistry as usually expected for six-co-ordinated molecules. The $^{31}P-\{^1H\}$ spectrum in $[^2H_8]$tetrahydrofuran, at 253 K (Figure 2), essentially consists of an A_2B pattern (the spectrum is practically first order) with a doublet at 79 p.p.m. and a triplet at 35.5 p.p.m. [intensity ratio 2:1, ^2J(P–P) = 28 Hz]. As far as we know, this is the first time that the three phosphorus atoms of the tppme ligand, all co-ordinated to a metal centre, have appeared non-equivalent on the n.m.r. time-scale, even if at low temperature. For instance, the six phosphorus atoms in the dimeric hydride [(tppme)-Fe(μ-H)$_3$Fe(tppme)]$^+$ are magnetically equivalent also at 183 K.[16]

The low-temperature ^1H n.m.r. spectrum in CD_2Cl_2, in the hydridic hydrogen range (upfield of $SiMe_4$), shows a pseudo-quartet at −5.1 p.p.m. (1 H) and a singlet at −14.7 p.p.m. (2 H) (Figure 3). Also present is a weak broad absorption at −12 p.p.m. Since the relative intensity of this signal changes with the sample, this absorption must be attributed to an impurity present in the starting complex. The multiplet at δ −5.1 p.p.m. is an example of an A_2BX pattern and can be simulated using the parameters ^2J(A–X) = 54.34, ^2J(B–X) = 51.26, and ^2J(A–B) = 28.0 Hz. Selective decoupling of the magnetically different phosphorus nuclei at 223 K (Figure 4) shows that the hydridic hydrogen atom is coupled to the phosphorus atoms of the ligand. All the other absorptions are unaffected by phosphorus decoupling. Downfield of $SiMe_4$ the spectrum shows multiplet patterns typical of the tppme ligand, centred at δ 7.30 and 6.90, 2.20 (6 H), and 1.30 (3 H) p.p.m., assigned to the C_6H_5 (first two), CH_2, and $-CH_3$ protons respectively. No other absorptions unambiguously attributable to complex (**2**) were detected.* The absorption at δ −14.7 p.p.m. is assigned to the two bridging protons, whereas the multiplet at δ −5.1 p.p.m. is assigned to the unique hydridic hydrogen. The values of these chemical shifts do not agree well with the more frequently reported values for M–H–B (δ = −3.9 to −9.1 p.p.m.)[3] and for M–H (δ = −10 to −120 p.p.m.).[17] However the intensities of the two signals preclude a reversal of their assignments. The resonance due to the two terminal BH_4 protons, expected in the range δ = 3.9—7.8,[3,18] is probably broad and obscured by the ligand signals. The magnitudes of the ^2J(P–H) values (54.3 and 51.3 Hz) are intermediate between the ranges of ^2J(P–H) values reported for a *cis* (6—32 Hz) and a *trans* geometry (73 Hz).[3,]†

On raising the temperature the ^{31}P and ^1H n.m.r. spectra (for the latter, the region upfield of $SiMe_4$) change. The $^{31}P-\{^1H\}$ n.m.r. spectra are shown in Figure 2. As the temperature is

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* It is possible that some broad absorption due to complex (**2**) is present in this range. With our spectrometer, which operates at 80 MHz, owing to the presence of the ligand resonances and signals of impurities, it is very difficult to identify such absorption. On the other hand, a few spectra collected on higher field spectrometers in other laboratories were not totally consistent. Indeed, because of the high reactivity of (**2**), a spectrum can be considered well determined in this range only after experiments on different, freshly prepared, samples. Proton n.m.r. spectra with ^{11}B decoupling might be useful in clarifying this problem.

† These results are not in accord with the molecular structure of complex (**2**), the hydridic hydrogen being *trans* with respect to one phosphorus atom and *cis* with respect to the other two.

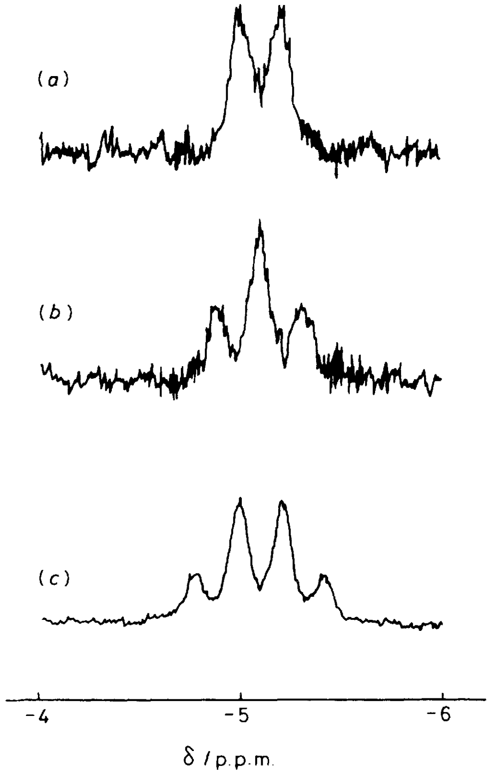

Figure 4. The Fe–H region of the 250-MHz proton n.m.r. spectra of complex (**2**) in CD_2Cl_2, at 223 K, without ^{31}P decoupling (*c*) and with selective decoupling on the two equivalent phosphorus atoms (*a*) and the unique phosphorus atom (*b*)

increased above 253 K the resonances at 79 and 35.5 p.p.m. broaden and collapse. Above 313 K these two signals disappear and a broad resonance at δ 62.5 p.p.m appears. This trend indicates that at high temperature the three phosphorus atoms are magnetically equivalent. Moreover at 268 K a new species of unknown composition is formed with an absorption at *ca.* δ 63 p.p.m. On raising the temperature this signal becomes and remains sharp. At 301 K, a singlet at δ −25 p.p.m., due to free tppme, appears, and upon addition of ligand to the solution this absorption is enhanced.* Also on raising the temperature this resonance remains sharp. At temperatures lower than room temperature the equilibrium appears completely reversible, whereas at higher temperatures the spectral behaviour is not completely reversed. Indeed the absorptions due to the uncoordinated ligand and to the unknown species remain upon lowering the temperature. These findings indicate that above 300 K also a new, probably intermolecular, process occurs which yields a new species. This process, when higher temperatures are reached, became irreversible.

Concerning the ^1H n.m.r. spectra (Figure 3), on raising the temperature above 255 K, the resonances at δ −5.1 and −14.7 p.p.m. broaden and the multiplet collapses. At 306 K only a very broad signal at δ −14.7 p.p.m. is still detectable. On raising the temperature the broad resonance at δ −12 p.p.m. remains practically unchanged both in intensity and in shape. Its intensity seems to increase only at higher temperatures. This spectral behaviour is also reversed on lowering the temperature.

All these results can be explained by taking into account a rapid, predominantly intramolecular exchange of bridging and Fe–H hydrogens. Because of rapid scrambling of the three metal-bound hydrogens, the three phosphorus atoms become magnetically equivalent. A dynamic interchange of the four BH_4 hydrogens with hydridic hydrogen was previously observed in the complex $[ZrH(BH_4)(C_5H_5)_2]$.[19] At high temperature the two terminal BH_4 hydrogens of complex (**2**) may also be involved in the dynamic process.

Conclusions

The complex $[FeH(H_2BH_2)(tppme)]$ displays a distorted octahedral geometry, the distortion being mainly due to the short bite of the bidentate BH_4^- ligand. The ^1H and ^{31}P n.m.r. spectra show a rigid stereochemistry in solution, at temperatures ⩽253 K. At higher temperatures, in solution, a fast interchange between the Fe–H and bridging hydrogens occurs, so that the phosphorus atoms become magnetically equivalent.

It is noteworthy that the isoelectronic complex $[RuH(H_2BH_2)(bdpp)]$,[3] having the same donor-atom set, shows a different dynamic behaviour, where the single metal-bound hydrogen is not involved. The different anchoring mode of the two triphosphines, *i.e.* the tripod-like tppme and the linear bdpp, probably strongly affects the molecular dynamics.

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* The addition of an excess of ligand seems to stabilize complex (**2**) in solution.