Applied Organometallic Chemistry (1990) 4 543–549

0268-2605/90/050543-07$05.00

The structure and dynamics of $FeH(DMPE)_2(BH_4)$, $FeH(DEPE)_2(BH_4)$ and $FeH(DPrPE)_2(BH_4)$: iron complexes containing monodentate borohydride ligands

Murray V Baker and Leslie D Field*
Department of Organic Chemistry, University of Sydney, Sydney, New South Wales 2006, Australia

Received 6 December 1989 Accepted 6 February 1990

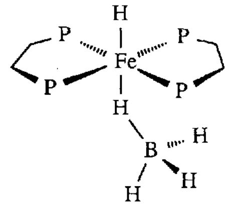
$FeH(DMPE)_2(BH_4)$ [DMPE = 1,2-bis(dimethylphosphino)ethane] is a stable, diamagnetic complex which can be synthesized readily by borohydride reduction of $FeH(DMPE)_2Cl$ or by treatment of $Fe(DMPE)_2H_2$ with borane. The complex contains an unsupported B—H—Fe hydrogen bridge. Analogous complexes with bulkier ligands, $FeH(DEPE)_2(BH_4)$, [DEPE = 1,2-bis(diethylphosphino)ethane] and $FeH(DPrPE)_2(BH_4)$ [DPrPE = 1,2-bis(di-n-propylphosphino)ethane], are less stable. In all complexes, in solution the borohydride ligand undergoes rapid internal motion, with all four boron-bound hydrogens interchanging environments. The barriers for BH_4 reorientation (measured by NMR spectroscopy) are in the sequence $FeH(DMPE)_2(BH_4) > FeH(DEPE)_2(BH_4) > FeH(DPrPE)_2(BH_4)$.

Keywords: Borohydride, iron phosphine, organoiron, NMR spectroscopy

INTRODUCTION

Complexes involving covalently bound tetrahydroborate have been reported for many transition metals.[1] While complexes where the tetrahydroborate acts as a bidentate or tridentate ligand are relatively common, those involving monodentate tetrahydroborate are extremely rare and, until recently, only one complex containing an unsupported M—H—B linkage had been characterized crystallographically.[2] With few exceptions, tetrahydroborate ligands in transition-metal complexes are fluxional in solution with the bridging and terminal boron hydrogens exchanging on an NMR timescale.

We have previously reported the preparation and X-ray crystal structure of $FeH(DMPE)_2(BH_4)$ (**1a**)[3,4] [DMPE = 1,2-bis(dimethylphosphino)ethane]. In the solid state, the BH_4 ligand is bonded via a singly bridging hydrogen to the iron atom with a bent B—H—Fe bond (B—H—Fe bond angle 161.7°) (for a review of structurally characterized complexes with bridging hydrides see Ref. 5). The Fe—H—B bond involves a three-centre interaction with orbitals from each of iron, boron and hydrogen atoms overlapping in a common region in space to form an unsupported hydrogen bridge of the 'closed'[6] type. In solution, preliminary infrared investigations indicated that the tetrahydroborate ligand was also monodentate although NMR spectroscopy demonstrated that all four hydrogen atoms in the BH_4 fragment exchanged rapidly on the NMR timescale at room temperature. At lower temperatures (<200 K) the dynamic behaviour of the complex in solution can be frozen out, clearly establishing the singly bridged structure. We report here details of NMR and infrared studies of the complex **1a**, as well as the synthesis and characterization of $FeH(DEPE)_2(BH)_4$ (**1b**) [DEPE = 1,2-bis(diethylphosphino)ethane] and $FeH(DPrPE)_2(BH_4)$, **1c**, [DPrPE = 1,2-bis(di-n-propylphosphino)ethane] which are less stable analogues of **1a**.

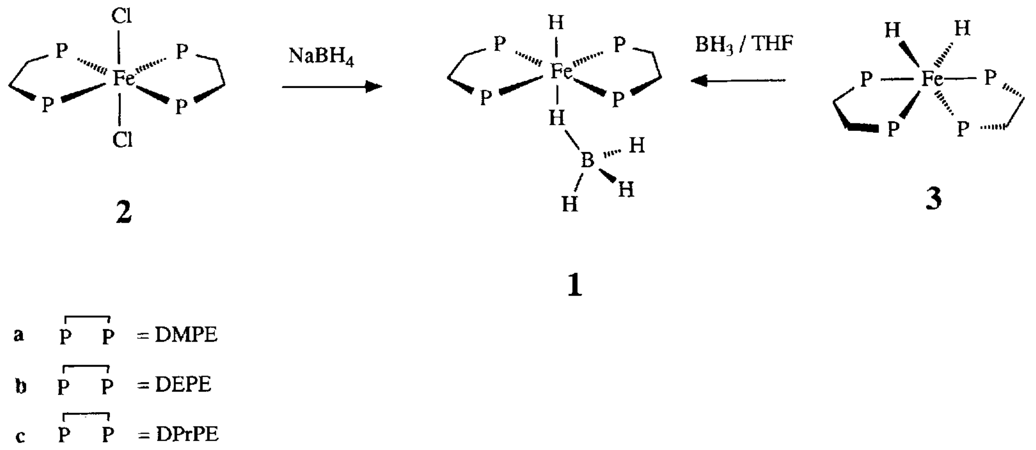


1a P P = DMPE
1b P P = DEPE
1c P P = DPrPE

Structure 1

---

* Author to whom correspondence should be addressed.



Scheme 1

RESULTS AND DISCUSSION

FeH(DMPE)$_2$(BH$_4$)

When an isopropanol solution of *trans*-FeCl$_2$(DMPE)$_2$ (**2a**) was treated with excess sodium borohydride or when FeH$_2$(DMPE)$_2$ (**3a**) was treated with borane in THF solution, the borohydride complex (**1a**) was formed cleanly and in high yield (Scheme 1). In the absence of air, **1a** was thermally stable, both in the solid state and in solution (a sample dissolved in toluene-d$_8$ in a sealed tube remained unchanged after 12 months at room temperature). In solution, **1a** decomposes slowly in light to give a complex mixture of products. The complex is diamagnetic and at 298 K the proton-coupled ^{31}P NMR spectrum of **1a** consists of a doublet at $\delta + 71.2$ ppm, with a splitting of 50.1 Hz due to coupling to the terminal Fe—H proton. No splitting due to ^{11}B–^{31}P coupling or ^{31}P coupling to the BH$_4$ protons was resolvable and the presence of only a single phosphorus resonance confirms that the complex has the *trans* stereochemistry in solution. The ^{11}B NMR spectrum of **1a** at 298 K is a single resonance at δ −38.1 ppm, which appears as a quintet (spacing 82 Hz) due to coupling to four dynamically equivalent protons. In the ^{1}H NMR spectrum at 298 K, the four protons attached to boron appear as an exchange-broadened resonance centred at δ −4.9 ppm, while the terminal Fe–H proton appears as a sharp quintet at δ −26.9 ppm (spacing 50.1 Hz).

When a dilute benzene solution of **1a** was shaken with D$_2$O, only the terminal Fe—H hydrogen exchanged rapidly with deuterium to give FeD(DMPE)$_2$(BH$_4$) (**4**). The pentadeuteride, FeD(DMPE)$_2$(BD$_4$) (**5**) was synthesized by reduction of **2a** with NaBD$_4$ and the tetradeuteride, FeH(DMPE)$_2$(BD$_4$) (**6**) was obtained by exchange of the terminal deuteride of **5** with H$_2$O in dilute benzene solution. The ^{1}H NMR spectrum of **6** exhibits a terminal Fe—H proton resonance at δ −26.793 ppm i.e. the Fe—H proton experiences an isotope-induced shift of 61.0 Hz to low-field on substitution of a *trans*-BD$_4$ ligand for the *trans*-BH$_4$ ligand in **1a**. Similarly, the ^{31}P NMR of **4**, **5** and **6** show resonances at δ 80.30 ppm, δ 80.33 ppm and δ 80.36 ppm respectively.

In dilute solution or in the solid state, there is no significant intramolecular exchange between the terminal Fe—H proton and the protons of the BH$_4$ ligand. Compound 6 shows no incorporation of deuterium at the terminal Fe—H site if it is left to stand for several days in dilute solution (2 mg ml^{-1} in benzene). However, in more concentrated solution, the terminal Fe—H and the —BH$_4$ protons equilibrate slowly, presumably by disproportionation of the complex to the dihydride **3a**, followed by an intermolecular recombination (cf. Scheme 1). When an approximately equimolar mixture of FeH(DMPE)$_2$(BH$_4$) and FeD(DMPE)$_2$(BD$_4$) was prepared in benzene-d$_6$ solution at 298 K, the compounds equilibrated over a period of several hours to give a mixture of the ten possible protio-/deuterio- complexes in a near-statistical ratio. The approach of the mixture to equilibrium was followed conveniently by ^{1}H NMR spectroscopy by observing the Fe—H region of the spectrum (δ −26 to δ −28 ppm). The terminal Fe—H protons of the complexes containing H—Fe—(BH_4), H—Fe—(BH_3D), H—Fe—(H_2BD_2), H—Fe—(HBD_3) and H—Fe—(BD_4) appear at δ −26.945, δ −26.905, δ −26.869, δ −26.829 and δ −26.793 ppm respectively, i.e. exhibiting a systematic downfield isotopic shift of approximately 15.4 Hz for each successive deuterium atom substituted into the BH_4 residue.

Dynamics of the borohydride ligand

On cooling solutions of **1a**, the proton NMR resonance at δ −4.9 ppm broadened and merged into the spectrum baseline. At temperatures below 240 K, the signal re-emerged as two resonances at δ 0.8 ppm (partly superimposed on the aliphatic ligand resonances) and at δ −22.4 ppm, with intensities in the ratio 3H:1H respectively. We have assigned the signal at δ −22.4 ppm to the bridging Fe—H—B proton, and that at δ 0.8 ppm to the terminal —BH_3 protons.[3] The intensity-weighted average of the chemical shifts for these protons is close to the chemical shift observed at room temperature for the BH_4 protons in rapid exchange. Even at 190 K, the resonances of the Fe—H—B and terminal —BH_3 protons were significantly broadened (probably as a result of H—H and B—H coupling). At 190 K, the multiplet of the terminal Fe—H proton at δ −26.9 ppm exhibits a clearly resolved doublet splitting ($^2J_{H-Fe-H} = 7.1$ Hz) due to coupling across the iron atom to the bridging Fe—H—B proton. At 298 K, the splitting is averaged to a smaller value with higher multiplicity.

As with **1a**, the exchange of the bridging and terminal deuterium atoms in the pentadeuterio-compound, **5**, can be slowed sufficiently at low temperature to reveal the resonances of the terminal and bridging deuterium atoms in the ^2H NMR spectrum. Lineshape analysis of the ^1H NMR spectra of **1a** and ^2H NMR spectra of **5** over a range of temperatures (190–360 K), details of

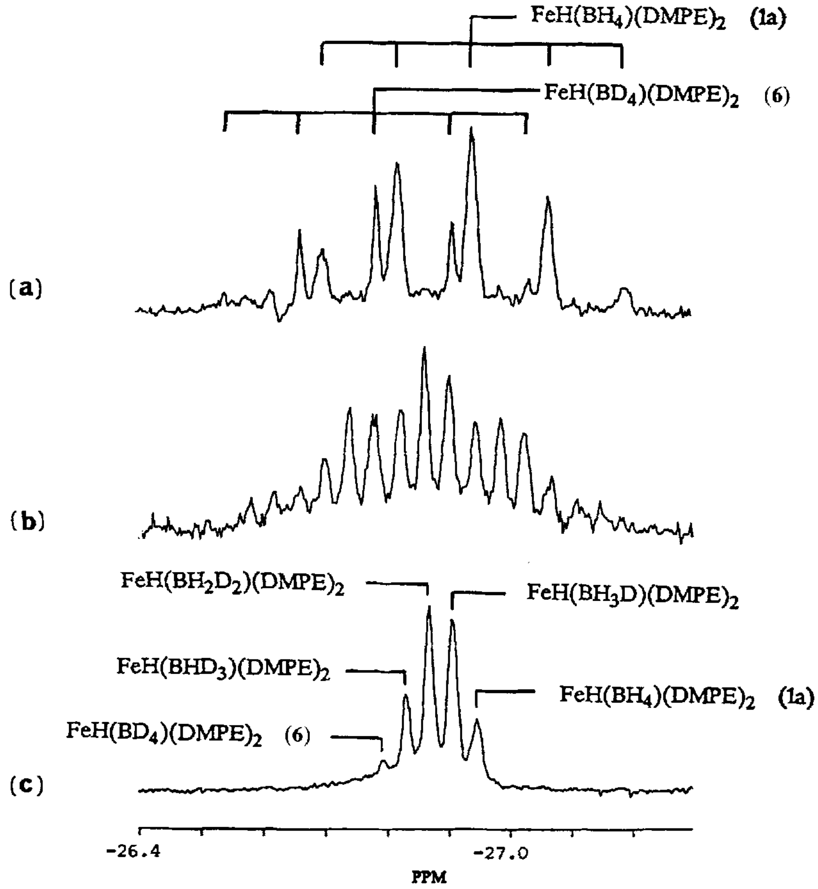


Figure 1 The high-field Fe—H region of the ^1H NMR spectrum (400 MHz, 298 K) of an equilibrating mixture consisting initially of **1a** and **5** in approximately equal amounts, (a) 5 min after mixing, (b) 1 day after mixing, and (c) as for (b) but ^{31}P-decoupled.

which will be published elsewhere, was used to estimate activation parameters for the exchange of the terminal and bridging atoms. The exchange is significantly slower in the deuterated complex **5** ($\Delta G\ddagger = 47.1 \pm 1$ kJ mol^{-1} at 250 K) compared with that in the protonated isotopomer **1a** $\Delta G\ddagger = 46.1 \pm 1$ kJ mol^{-1} at 250 K). Examples of stable, doubly hydrogen-bridged metal borohydrides are well documented and such a species would be a reasonable intermediate for the interchange of the bridging and terminal hydrogens (Scheme 2).

FeH(DEPE)$_2$(BH$_4$) and FeH(DPrPE)$_2$(BH$_4$)

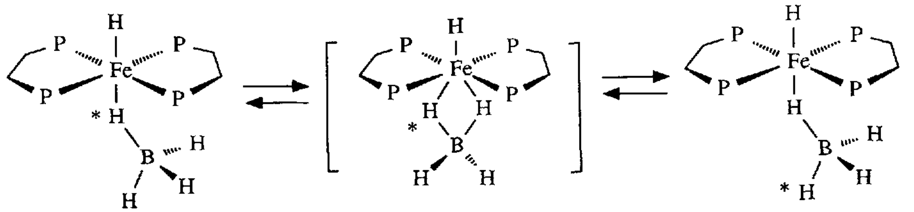
Iron–borohydride complexes with DEPE and DPrPE ligands, **1b** and **1c** respectively, are significantly less stable than the complex with DMPE ligands (**1a**). The complexes **1b** and **1c** were synthesized *in situ* by treatment of the respective dihydrides, **3b** and **3c**, with borane in THF solution but could not be obtained as pure compounds in the solid state. Removal of the solvent from solutions of **1b** or **1c** and redissolution of the residue indicated extensive decomposition of the iron–borohydride complexes with reformation of the corresponding dihydrides, **3b** and **3c**, and formation of the stable diphosphine–borane adducts, **7** and **8**. Phosphine–borane adducts can be formed easily by the reaction of free phospines with borane, and the formation of **7** and **8** probably reflects the greater tendency for the complexes **1b** and **1c** to disproportionate to borane and their respective dihydrides as well as an increased lability of the bulkier diphosphine ligands.[7]

In solution, the complexes **1b** and **1c** show analogous ^{31}P and ^{1}H spectra to **1a**, with the protons of the BH$_4$ group exchanging rapidly on the NMR timescale at room temperature. As with **1a**, the motion of the BH$_4$ ligand can be slowed sufficiently at low temperature to reveal the bridging Fe—H—B and terminal —BH$_3$ proton resonances in the ratio 3H:1H, consistent with singly bridged structures for **1b** and **1c**. The rate of exchange of the terminal —BH$_3$ protons with the bridging Fe—H—B proton was estimated by NMR spectroscopy using saturation transfer methods. (Statistically, there are 12 degenerate terminal ⇄ bridging exchange processes for the protons in the BH$_4$ group in **1a**; hence the rate of proton exchange is one-twelfth of the rate of magnetization transfer. For a general discussion of the saturation transfer technique, see Ref. 8.) At 197 K, irradiation of the —BH$_3$ protons in **1a**, **1b** or **1c** with a saturating radiofrequency field resulted in a decrease in the intensity of the resonance of the Fe—H—B proton by saturation transfer (Fig. 2). The rate of exchange of the —BH$_3$ protons with the bridging Fe—H—B proton was obtained from a measurement of the apparent relaxation time ($T_{1\mathrm{sat}}$) of the Fe—H—B proton while saturating the —BH$_3$ protons[8] (Table 1).

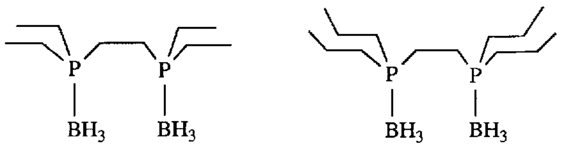
The terminal-H/bridging-H exchange in **1b** and **1c** is significantly slower than in **1a** and this can be ascribed to the increased steric crowding afforded by the bulkier alkyl substituents on the ligands in these complexes. Steric crowding by the ligands of the iron atom would hinder the capacity of the BH$_3$ group to attain a stable bonding arrangement with the iron and hydrogen in the Fe—H—B bridge. If the transition state for the bridging-H to terminal-H exchange demands a tighter association of the boron and the iron (as with the doubly bridged intermediate proposed in Scheme 2), the barrier to rotation would increase with increased crowding around the metal centre. This rationalization would also be consistent with the reduced chemical stability of the Fe—H—B linkage in **1b** and **1c** compared with **1a** and the increased tendency for them to dissociate to BH$_3$ and their respective dihydrides.

Infrared spectra

Infrared spectroscopy has been used extensively in the past for the characterization of borohydride complexes of transition metals,[1] both in solution and in the solid state. The infrared spectrum of FeH(BH$_4$)(DMPE)$_2$ (**1a**) (Table 2) shows bands



Scheme 2



Structures 7 and 8

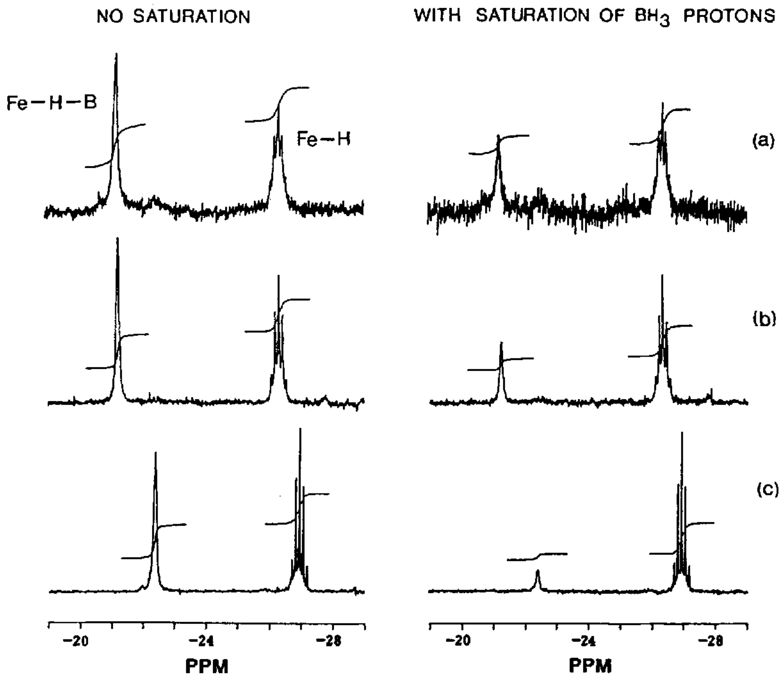


Figure 2 The extreme high-field Fe—H region of the ^{1}H NMR spectra (400 MHz, 197 K, ^{11}B-decoupled) of **1a**, **1b** and **1c**, with and without saturation of —BH_3 protons. (a) $FeH(DPrPE)_2(BH_4)$, **1c**; (b) $FeH(DEPE)_2(BH_4)$, **1b**; (c) $FeH(DMPE)_2(BH_4)$, **1a**.

due to the iron-bound hydride and the tetrahydroborate ligand at 1060, 1800, 2075, and 2350 cm^{-1}. Comparison of these values with those expected[1] for complexes containing monodentate, bidentate, or tridentate tetrahydroborate ligands shows that the infrared data are incompatible with both the bidentate and tridentate BH_4 coordination. The complexes **1a**, **4**, **5** and **6** were examined by infrared spectroscopy and the assignments of absorptions (Table 2) have been made by comparison with documented vibration frequencies.[1] The similarity of the infrared spectra of **1a** recorded in benzene solution and in nujol mull confirms that there is no significant change in the bonding of the BH_4 ligand from the solid state to solution.

Table 1 Kinetics of Fe—H—B $\rightleftarrows$ —BH_3 proton exchange by ^{1}H NMR (saturation transfer at 197 K)

Complex	Ligand	T_{1sat} (ms)	$\Delta M/M^a$	k^b (s^{-1})
1a	DMPE	33 ± 3	0.84	2.1
1b	DEPE	53 ± 3	0.66	1.0
1c	DPrPE	51 ± 3	0.57	0.93

[a] Factor by which intensity of the Fe—H—B proton resonance decreases on saturation of the —BH_3 resonance. [b] Rate of terminal-H/bridging-H exchange:[8]

$$k=(\Delta M/M.[\tfrac{1}{12}.T_{1sat}]$$

The band at 1800 cm^{-1} seen in the spectra of **1a** and **6** is assigned to the terminal Fe—H stretch, while the band at 1310 cm^{-1} present in the spectrum of **5** but not in those of **1a** or **6** is assigned to the terminal Fe—D stretch. The band at 1060 cm^{-1} in the spectrum of **1a** is assigned to the

Table 2 Infrared Frequencies for Iron-borohydride and -borodeuteride Complexes.

Complex	Phase	Infrared bands (cm^{-1})	Assignments
$FeH(DMPE)_2(BH_4)$ (**1a**)	Nujol mull	2350	BH_3
		2075	Fe—H_b, B—H_b
		1800	Fe—H_t
		1060	BH_3 deformation
$FeH(DMPE)_2(BH_4)$ (**1a**)	Benzene solution	2350	BH_3
		2030	Fe—H_b, B—H_b
		1788	Fe—H_t
		1045	BH_3 deformation
$FeD(DMPE)_2(BD_4)$ (**5**)	Nujol mull	1750	BD_3
		1490	Fe—D_b, B—D_b
		1310	Fe—H_t
$FeH(DMPE)_2(BD_4)$ (**6**)	Nujol mull	1800	Fe—H_t
		1750	BD_3
		1490	Fe—D_b, B—D_b

BH_3 deformation, but no comparable BD_3 deformation was seen in the spectra of **5** or **6**. Bands at 2350 and 2075 cm^{-1} in the spectrum of **1a** were assigned to the terminal B—H, and bridging B—H and Fe—H stretches respectively, and the spectra for **5** and **6** show the expected isotope-shifted bands, at 1750 and 1490 cm^{-1} respectively.

CONCLUSIONS

$FeH(DMPE)_2(BH_4)$ is a stable, diamagnetic complex which can be synthesized readily by borohydride reduction of the $Fe(DMPE)_2Cl_2$ or by treatment of $Fe(DMPE)_2H_2$ with borane. The complex is one of the few known compounds containing an unsupported B—H—Fe hydrogen bridge. In the solid state, the B—H—Fe group is bent, consistent with a three-centre, two-electron bond. In solution, the borohydride ligand undergoes rapid internal motion, with all four boron-bound hydrogens interchanging environments. Experiments involving equilibration of $FeH(DMPE)_2(BH_4)$ and $FeD(DMPE)_2(BD_4)$ indicate that intermolecular hydride exchange proceeds slowly, probably by reversible dissociation of BH_3 or BD_3 from the complexes.

Higher homologues of $FeH(DMPE)_2(BH_4)$ (with bulkier DEPE and DPrPE ligands) are less stable than $FeH(DMPE)_2(BH_4)$ and the rate of intramolecular bridging to terminal hydride exchange is significantly slower.

EXPERIMENTAL

Synthesis of compounds

All reactions and manipulations were performed under nitrogen or argon, in a dry box or in Schlenk apparatus. Tetrahydrofuran (THF), benzene and light petroleum (b.p. 60–70°C) were distilled from benzophenone ketyl under nitrogen prior to use. Deuterated solvents were obtained from Merck and Aldrich, and were degassed by three freeze–pump–thaw cycles. $Fe(DMPE)_2Cl_2$,[9] $Fe(DEPE)_2Cl_2$,[9] $Fe(DPrPE)_2Cl_2$[7] and BH_3/THF[10] were prepared according to literature procedures. ^1H (400.1 MHz), ^2H (62.0 MHz), ^{11}B (128.0 MHz) and ^{31}P (162.0 MHz) NMR spectra were recorded on a Brüker WM-400 spectrometer, in the solvents indicated. ^1H and ^2H NMR spectra were referenced to residual solvent resonances; ^{31}P and ^{11}B NMR spectra were referenced to external, neat trimethyl phosphate (taken as 2.90 ppm) and neat boron trifluoride etherate (taken as 0.00 ppm) respectively.

***trans*-$FeH(DMPE)_2(BH_4)$ (1a)**

Sodium borohydride (0.23 g, 6.1 mmol) was added to a stirred solution of the dichloride, **2a** (0.66 g, 1.55 mmol) in a mixture of tetrahydrofuran (7 ml) and isopropanol (30 ml). The colour of the mixture became dark brown, brick red and finally orange over a period of approximately 2.5 h. The solvent was removed under reduced pressure and the residue was extracted exhaustively with hot light petroleum. The combined extracts were filtered hot, and the precipitate which formed upon concentration was collected and washed with pentane. $\mathrm{FeH(DMPE)_2(BH_4)}$ (**1a**) was obtained as an orange crystalline solid (0.44 g, 77%), m.p. 161–162°C.

Analysis: Calcd for $\mathrm{FeP_4C_{12}H_{37}B}$: C, 38.75; H, 10.03. Found: C, 38.8; H, 10.1%.

^{1}H NMR (benzene-d_6, 298 K): δ −26.88 (1H, quintet, $^2J_{\mathrm{PH}} = 50.1$, $\mathrm{Fe{-}\underline{H}}$), −4.9 (4H, broad, $\mathrm{B\underline{H}_4}$), 1.04 (12H, m, $4\times\mathrm{C\underline{H}_3}$), 1.46 (12H, m, $4\times\mathrm{C\underline{H}_3}$), 1.35–1.77 (8H, m, $4\times\mathrm{C\underline{H}_2}$). ^{31}P {^{1}H} NMR (benzene-d_6, 298 K): δ 71.2. ^{11}B NMR (benzene-d_6, 298 K): δ −38.1 ($\mathrm{BH_4}$, $^1J_{\mathrm{BH}} = 82$ Hz).

$\mathrm{Fe(DEPE)_2H_2}$ and $\mathrm{Fe(DPrPE)_2H_2}$

A solution of $\mathrm{NaBH_4}$ (70 mg, 1.85 mmol) in isopropanol (10 ml) was added dropwise to a solution of $\mathrm{Fe(DEPE)_2Cl_2}$ (**2b**) (208 mg, 0.386 mmol) in isopropanol (30 ml), and the mixture stirred at room temperature for 72 h. The solvent was removed under reduced pressure, and the residue was extracted with pentane (3 × 10 ml). After filtration and removal of the pentane under reduced pressure, $\mathrm{FeH_2(DEPE)_2}$ was obtained as a waxy yellow solid, which was used without further purification. $\mathrm{FeH_2(DPrPE)_2}$ was prepared in a similar manner, from $\mathrm{Fe(DPrPE)_2Cl_2}$ (**2c**).

trans-$\mathrm{FeH(DPrPE)_2(BH_4)}$ (1c)

A solution of $\mathrm{FeH_2(DPrPE)_2}$ (29 mg, 50 μmol) in pentane (2 ml) was treated with borane (0.30 M in THF, 0.20 ml, 60 μmol), with stirring. The mixutre became yellow instantly, and the ^{31}P NMR spectrum of an aliquot indicated quantitative formation of $\mathrm{FeH(BH_4)(DPrPE)_2}$. The solvent was rapidly removed under reduced pressure, and the residue dissolved in toluene-d_8 for NMR studies. ^{1}H NMR (toluene-d_8, 298 K): δ −26.47 (1H, quintet, $^2J_{\mathrm{PH}} = 48.2$, $\mathrm{Fe{-}\underline{H}}$), −4.2 (4H, broad, $\mathrm{B\underline{H}_4}$), 0.91 (12H, m, $4\times\mathrm{C\underline{H}_3}$), 1.03 (12H, m, $4\times\mathrm{C\underline{H}_3}$), 1.10–1.37, 1.40–1.95, 2.45 (40H, m, $20\times\mathrm{C\underline{H}_2}$). ^{31}P {^{1}H} NMR (toluene-d_8, 298 K): δ 84.8. ^{11}B NMR (toluene-d_8 298 K): δ −36.6 (broad, $\mathrm{BH_4}$, $^1J_{\mathrm{BH}}$ unresolved).

trans-$\mathrm{FeH(DEPE)_2(BH_4)}$ (1b)

$\mathrm{FeH(BH_4)(DEPE)_2}$ was prepared from $\mathrm{FeH_2(DEPE)_2}$ by the same procedure as was used for *trans*-$\mathrm{FeH(DPrPE)_2(BH_4)}$ (**1c**). ^{1}H NMR (toluene-d_8, 298 K): δ −26.51 (1H, quintet, $^2J_{\mathrm{PH}} = 47.6$, $\mathrm{Fe{-}\underline{H}}$, −4.0 (4H, broad, $\mathrm{B\underline{H}_4}$), 0.86 (12H, m, $4\times\mathrm{C\underline{H}_3}$), 1.07 (12H, m, $4\times\mathrm{C\underline{H}_3}$), 1.07, 1.34, 1.68–1.8, 2.44 (24H, m, $12\times\mathrm{C\underline{H}_2}$). ^{31}P NMR (toluene-$d_8$, 298 K): δ 89.9. ^{11}B NMR (toluene-d_8, 298 K): δ −36.7 ($\mathrm{BH_4}$, $^1J_{\mathrm{BH}} = 77$ Hz).

Acknowledgments We gratefully acknowledge financial support from the Australian Research Council.

REFERENCES

1. For a review of Transition metal, lanthanide, and actinide tetrahydroborate complexes, see Marks, T J and Kolb, J R *Chem. Rev.*, 1977, 77: 263
2. Kutal, C, Grutsch, P, Atwood, J L and Rogers, R D *Inorg. Chem.*, 1978, 17: 3558; Takusagawa, F, Fumagalli, A, Koetzle, T F, Shore, S G, Schmitkons, T, Fratini, A V, Morse, K W, Wei, C-Y and Bau, R *J. Am. Chem. Soc.*, 1981, 103: 5165
3. Baker, M V and Field, L D *J. Chem. Soc., Comm.*, 1984, 996
4. Bau, R, Yuan, H S H, Baker, M V and Field , L D *Inorg. Chim. Acta*, 1986, 114: L27
5. Teller, R G and Bau, R *Structure and Bonding*, 1981, 44: 1
6. La Placa, S J, Hamilton, W C and Ibers, J A *Inorg. Chem.*, 1963, 3: 1491
7. Baker, M V, Field, L D and Hambley, T W *Inorg. Chem.*, 1988, 27: 2872
8. Martin, M L, Martin, G J and Delpuech, J-J *Practical NMR Spectroscopy*, Heyden, London, 1980, pp. 315–8 and references therein
9. Chatt, J and Hayter, R G *J. Chem. Soc.*, 1961, 5507
10. Brown, H C *Organic Synthesis via Boranes*, Wiley, New York, 1975, pp. 18–20