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Synthesis and properties of bis(dialkylphosphino)ethane iron dihydrides

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Syntheses and properties of the iron bisphosphinoethane complexes $FeH_2(PP)_2$ and $FeHCl(PP)_2$ [$PP = R_2PCH_2CH_2PR_2$, where R = Me (PP = DMPE), Et (PP = DEPE), and n-Pr (PP = DprPE)] are reported. The complexes can be formed by reduction of the corresponding dichlorides $FeCl_2(PP)_2$ with lithium aluminium hydride in THF solution provided that ethanol or more acidic reagents are not employed during the reaction work-up. The dihydrides are notably basic compounds and can be protonated reversibly by alcohols.

The dihydrides exist as equilibrating mixtures of *cis* and *trans* isomers in solution. The *cis* isomers of each of the dihydrides are fluxional on the NMR timescale and NMR studies indicate that the interconversion of *cis* isomers does not necessarily proceed via the *trans* isomer.

Keywords: Metal hydride, iron phosphine, organoiron, NMR spectroscopy

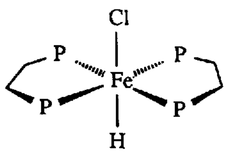
INTRODUCTION

For studies of C—H bond activation[1] and complexes of molecular hydrogen[2] we required the chlorohydrido complexes $FeHCl(PP)_2$ (**1**) and the dihydrido complexes $FeH_2(PP)_2$ [$PP = R_2PCH_2CH_2PR_2$, R = $-CH_3$ (PP = DMPE), R = $-CH_2CH_3$ (PP = DEPE), and R = $-CH_2CH_2CH_3$ (PP = DPrPE)]. Syntheses of $FeHCl(DMPE)_2$ (**1a**) and $FeHCl(DEPE)_2$ (**1b**) have been reported, and involve reduction of the corresponding dichloride complexes with lithium aluminium hydride in THF solution. $FeH_2(DMPE)_2$ (**2a**) has been prepared previously by reaction of $Fe(C_8H_8)_2$ with excess DMPE under a hydrogen atmosphere,[3] and by reduction of $FeHNp(DMPE)_2$ [Np = 2-naphthyl] with hydrogen gas.[4] Here we report improved syntheses and selected properties of the halohydrides (**1a–2c**) and dihydrides (**2a–2c**).

RESULTS AND DISCUSSION

Synthesis and properties of halohydrido complexes $FeHX(PP)_2$

The first preparations of $FeHCl(DMPE)_2$ (**1a**) and $FeHCl(DEPE)_2$ (**1b**) involved reductions of the corresponding dichlorides[5] with lithium aluminium hydride in THF solution followed by the addition of ethanol to decompose excess lithium



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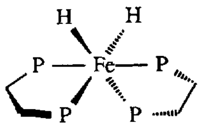

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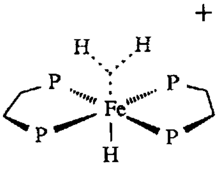

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a P P = DMPE
b P P = DEPE
c P P = DPrPE

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aluminium hydride. In our experience, impure products are invariably obtained when this procedure is followed and a detailed investigation of the course of these reactions[2b] has demonstrated that they proceed via over-reduction of the dichlorides to give the corresponding dihydrides, followed by protonation (by ethanol)[2a] to give intermediate molecular hydrogen complexes $[FeH(H_2)(DMPE)_2]^+$ (**3a**) or $[FeH(H_2)(DEPE)_2]^+$ (**3b**) in high yield. Displacement of the weakly coordinated H_2 by Cl^- affords the desired chloroiron hydrides, but these are contaminated by dichlorides (presumably due to a second protonation and substitution by Cl^-).[2b]

The required chlorohydride complexes can be obtained in a pure form by careful reduction of the corresponding dichlorides with lithium aluminium hydride. However, even with slow titration of a vigorously stirred tetrahydrofuran (THF) solution $FeCl_2(DMPE)_2$ with lithium aluminium hydride in THF, it is not possible to form $FeHCl(DMPE)_2$ in the absence of some over-reduction to $FeH_2(DMPE)_2$. In contrast, careful titration of a THF solution of $FeBr_2(DMPE)_2$ with lithium aluminium hydride in THF effects quantitative conversion of the dibromide to the bromohydride $FeHBr(DMPE)_2$ without detectable formation of $FeH_2(DMPE)_2$ or $[FeH(H_2)(DMPE)_2]^+$

$FeHCl(DMPE)_2$, $FeHCl(DEPE)_2$, and $FeHCl(DPrPE)_2$ are soluble in non-polar solvents, including THF, benzene and ether. Solubility of the chlorohydrides in light petroleum increases with increasing alkylation:

$$FeHCl(DPrPE)_2 > FeHCl(DEPE)_2 > FeHCl(DMPE)_2.$$

The halohydride complexes exist exclusively as the *trans* stereoisomers. Each complex gives rise to a single resonance in the $^{31}P\{^1H\}$ NMR spectrum (due to four equivalent phosphorus atoms) (Table 1), and a quintet to extreme high field in the ^1H NMR spectrum (due to the iron-bound hydride) as expected for *trans*-halohydride complexes. $FeHCl(DMPE)_2$ and $FeHCl(DEPE)_2$ have previously been assigned as *trans* complexes on the basis of their ^1H NMR hydride resonances.[5a]

In benzene solution, compounds **1a–1c** are converted to the corresponding halodeuterides by shaking with D_2O; this exchange probably occurs by deuteration of the chlorohydride (with D^+) to give the η^2-(H—D) complexes. In contrast, the corresponding DPPE iron halohydride complexes [$DPPE = Ph_2PCH_2CH_2PPh_2$] are resistant to H/D exchange with D_2O.

Table 1 ^{31}P and selected ^1H NMR spectral data[a] for haloiron hydride complexes (**1a–1c**).

Complex	$\delta\ ^{31}P$	$\delta\ ^1H$ Fe—H
$FeHCl(DMPE)_2$ (**1a**)	70.34	-32.28 ($J_{PH} = 49.4$)
$FeHCl(DEPE)_2$ (**1b**)	89.96	-31.94 ($J_{PH} = 48.1$)
$FeHCl(DPrPE)_2$ (**1c**)	82.20	-32.04 ($J_{PH} = 48.6$)
$FeHBr(DMPE)_2$	65.58	-31.30 ($J_{PH} = 50.4$)

[a] Benzene-d_6 solution, 300 K. Coupling constants are in Hertz and signs of coupling constants are not implied.

Synthesis and properties of dihydride complexes $FeH_2(PP)_2$

$FeH_2(DMPE)_2$ (**2a**) can be obtained most conveniently by reduction of the corresponding dichloride with excess lithium aluminium hydride, provided that ethanol, or any more acidic reagent, is not used during the work-up. Indeed, after the reaction mixture obtained by treatment of $FeCl_2(DMPE)_2$ with excess lithium aluminium hydride in THF is stripped of solvent and extracted with light petroleum, removal of solvent affords $FeH_2(DMPE)_2$ as a pale yellow solid which is sufficiently pure for most purposes. This material can be further purified by sublimation if required.

Treatment of THF solutions of either $FeCl_2(DEPE)_2$ and $FeCl_2(DPrPE)_2$ with excess lithium aluminium hydride affords a dark green mixture; this has been observed previously in the case of $FeCl_2(DEPE)_2$.[5b] Removal of the solvent leaves a green, gummy residue, from which the dihydrides $FeH_2(DEPE)_2$ or $FeH_2(DPrPE)_2$ can be extracted with light petroleum. The green gums which remain after the extraction are soluble in THF and ^{31}P NMR spectroscopy indicates that they contain the molecular hydrogen complexes $[FeH(H_2)(DEPE)_2]^+$ (**3b**) or $[FeH(H_2)(DPrPE)_2]^+$ (**3c**) as major components. Crude $FeH_2(DEPE)_2$ and $FeH_2(DPrPE)_2$ products prepared in this way are yellow to pale brown oils or waxy solids, and although these materials have the expected ^1H and ^{31}P NMR spectra, they contain some chlorinated impurities (probably residual $AlH_{4-n}Cl_n$ species). Neither **2b** or **2c** could be obtained in an analytically pure form by recrystallization or by sublimation.

FeH$_2$(DEPE)$_2$ and FeH$_2$(DPrPE)$_2$ can also be formed by treatment of the chlorohydrides **1b** or **1c** with n-butyllithium, cyclohexylmagnesium bromide or potassium hydride. However, attempted reduction of FeCl$_2$(DEPE)$_2$ or FeCl$_2$(DPrPE)$_2$ with sodium borohydride resulted in significant decomposition of the complexes with formation of the phosphine–borane adducts $H_3B{:}P(CH_2CH_3)_2CH_2CH_2(CH_3CH_2)_2P{:}BH_3$ and $H_3B{:}P(CH_2CH_2CH_3)_2CH_2CH_2(CH_3CH_2CH_2)_2P{:}BH_3$. [Authentic samples of the phosphine–borane adducts $H_3B{:}P(Me)_2CH_2CH_2(Me)_2P{:}BH_3$ ($\delta\ ^{31}P = 7.30$, $\delta\ ^{11}B = -38.97$ ppm, J_{PB} 55 Hz in C$_6$D$_6$ solution), $H_3B{:}P(Et)_2CH_2CH_2(Et)_2P{:}BH_3$ ($\delta\ ^{31}P = 22.43$, $\delta\ ^{11}B = -41.78$ ppm, J_{PB} 56 Hz in C$_6$D$_6$ solution) and $H_3B{:}P$ (n-Pr)$_2$CH$_2$CH$_2$)-n-Pr)$_2$P:BH$_3$ ($\delta\ ^{31}P = 18.65$, $\delta\ ^{11}B = 41.18$ ppm, C$_7$D$_8$ solution) were prepared by treatment of THF solutions of the appropriate bisphosphine with excess borane followed by removal of the solvent.]

The dihydride complexes **2a–2c** are extremely soluble in most neutral organic solvents (THF, benzene, pentane) but react with hydroxylic solvents. The iron bis(dialkylphosphino)ethane dihydrides are remarkably basic and are easily protonated with strong acid. The protonation of the aryl-substituted complex FeH$_2$(DPPE)$_2$ with HBF$_4$ has been reported to form the stable, crystalline, molecular hydrogen complex [FeH(H$_2$)(DPPE)$_2$]$^+$.[6] Complexes **2a–2c** are protonated even by ethanol to give solutions of the molecular hydrogen complexes **3a–3c**.[2a] In a related reaction, we have previously reported the reaction of **2a** with BH$_3$ (a Lewis acid) to form a stable adduct with a single hydrogen atom bridging iron and boron.[7]

Cis/trans isomerism and fluxionality in FeH$_2$(PP)$_2$

FeH$_2$(DMPE)$_2$ (**2a**) has been assigned the *cis* stereochemistry on the basis of its infrared and NMR[9] spectrum, and it has been noted that the complex is fluxional on the NMR timescale.[9] In solution, the complexes **1a–1c** exist as equilibrium mixtures of *cis* and *trans* stereoisomers. [The related iron dihydrides, FeH$_2$(PPh(OEt)$_2$)$_4$, FeH$_2$(PPh(OMe)$_2$)$_4$, and FeH$_2$(DEPB)$_2$ [DEPB = 1,2-bis(diethylphosphino)benzene] have been reported to exist in solution as mixtures of *cis* and *trans* stereoisomers.[9]] The ^{31}P{^{1}H} NMR spectrum (162 MHz) of FeH$_2$(DMPE)$_2$ (**2a**) at ambient temperature is dominated by two apparent triplet resonances, due to the four phosphorus atoms of the *cis* isomer (an AA′XX′ spin system). The hydride region of the ^{1}H NMR spectrum (400 MHz) of **2a** at ambient temperature is a complex multiplet (Table 2) and the shape of the hydride multiplet does not change significantly when the temperature is lowered to −50°C. For FeH$_2$(DMPE)$_2$, the *trans* stereoisomer is a very minor component of the mixture.

Both the ^{31}P and ^{1}H NMR spectra of FeH$_2$(DPrPE)$_2$ (**2c**) show considerably more exchange broadening than those of FeH$_2$(DMPE)$_2$. At 30°C, the hydride resonance of **2c** superficially resembles a binomial quintet, with sharp outer lines and broadened inner lines (Fig. 1) and ^{31}P spectrum shows only two broad resonances (Fig. 2). At lower temperatures the ^{31}P NMR resonances sharpen and eventually display the triplet-like multiplicity observed for FeH$_2$(DMPE)$_2$, while an additional resonance (δ 105.3 ppm), assigned to *trans*-**2c**, emerges from the baseline. The resonance assigned to *trans*-**2c** appears to a 1:2:1 triplet in the proton-coupled ^{31}P NMR spectrum and is accompanied by a quintet resonance in the ^{1}H NMR spectrum at −14.396 ppm. FeH$_2$(DEPE)$_2$ exhibits temperature-dependent ^{31}P and ^{1}H NMR spectra analogous to those of FeH$_2$(DPrPE)$_2$ (Table 2).

For **2a–2c**, the proportion of the *trans* isomer is relatively minor and the relative stability of the

Table 2 ^{31}P and selected ^{1}H NMR Spectral Data[a] for Iron Dihydride Complexes **2a–2c**

Complex	$\delta\ ^{31}P$	$\delta\ ^1H$ Fe–H
cis-FeH$_2$(DMPE)$_2$; *cis*-**2a**[b]	76.44, 66.90 (splitting 27.5)[e]	−13.95
trans-FeH$_2$(DMPE)$_2$; *trans*-**2a**[c]	77.23	−17.93 ($J_{PH} = 37.8$)
cis-FeH$_2$(DEPE)$_2$; *cis*-**2b**[d]	102.35, 89.11 (splitting 20.5)[e]	−14.65
trans-FeH$_2$(DEPE)$_2$; *trans*-**2b**[d]	111.66	−14.02 ($J_{PH} = 40.3$)
cis-FeH$_2$(DPrPE)$_2$; *cis*-**2c**[d]	97.16, 83.83 (splitting 19.6)[e]	−14.72
trans-FeH$_2$(DPrPE)$_2$; *trans*-**2c**[d]	105.30	−14.40 ($J_{PH} = 40.3$)

[a] Coupling constants are in Herz and signs of coupling constants are not implies. [b] In benzene-d$_6$ solution, at 300 K. [c] In isopropanol solution at 300 K. [d] In toluene-d$_8$ at 220 K. [e] Apparent triplets.

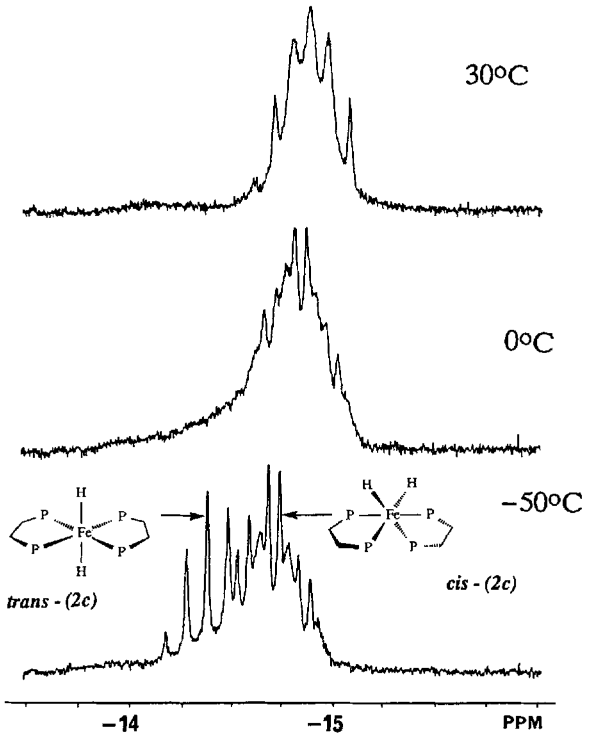

Figure 1 Temperature dependence of the hydride region of the ^{1}H NMR spectrum of $FeH_2(DPrPE)_2$ (**2c**) (400.1 MHz, toluene-d_8 solvent).

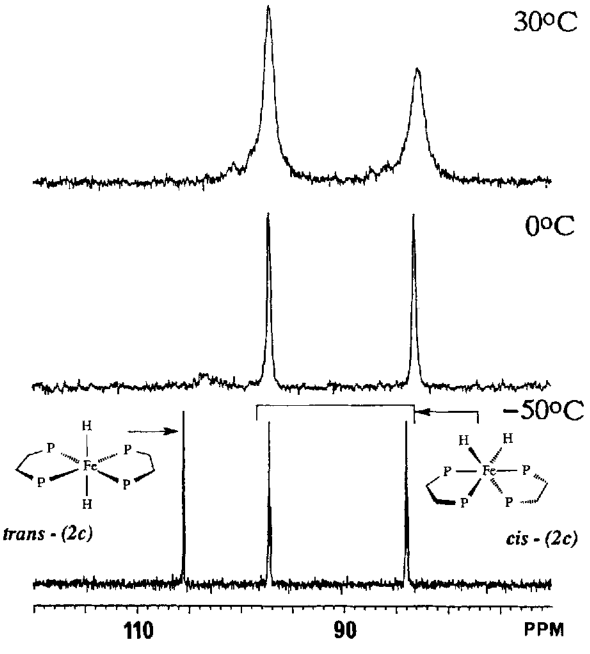

Figure 2 Temperature dependence of the ^{31}P NMR spectrum of $FeH_2(DPrPE)_2$ (**2c**) (162.0 MHz, toluene-d_8 solvent).

trans isomer apparently increases with the length of the alkyl chains substituted on phosphorus. This would be consistent with increased destabilization of the *cis* stereoisomers with increasing steric demand of the phosphine substituents. For 20 mM solutions of $FeH_2(DEPE)_2$ in THF, pentane, or toluene at −50°C, the *trans* isomer accounts for about 3% of the total dihydride, while for similar solutions of $FeH_2(DPrPE)_2$, the *trans* isomer accounts for 10–25% of the total dihydride (at −50°C). For $FeH_2(DPrPE)_2$, the *cis*:*trans* ratio displays a marked solvent dependence, with the proportion of the *trans* isomer ranging from 10% in pentane to 15% in THF and 25% in toluene (form 20 mM solutions at −50°C). The presence of the *trans* isomer of $FeH_2(DMPE)_2$ (*ca* 5%) was only detected in isopropanol solution.

The temperature dependence of the ^{31}P NMR spectra of both $FeH_2(DEPE)_2$ and $FeH_2(DPrPE)_2$ suggests that there is exchange between the *cis* and *trans* isomers on the NMR timescale. At 0°C, for **2a**–**2c**, selective saturation of the ^{31}P resonance due to the *trans* isomer caused a reduction in the intensity of both of the resonances of the *cis* isomer, by saturation transfer. Selective saturation of either of the ^{31}P resonances of the *cis* isomer at 0°C results in the removal of the other resonance of the *cis* isomer, as well as the resonance due to the *trans* isomer. Although these results clearly demonstrate exchange between the *cis* and *trans* isomers of **2a**–**2c** on the NMR timescale, lineshape analysis of the exchange-broadened ^{31}P NMR spectra as well as quantitative saturation transfer experiments indicate that the observed exchange between the degenerate *cis* isomers is too rapid to proceed entirely via the *trans* isomers and therefore there must be an additional pathway (or additional pathways) for direct *cis* $\rightleftarrows$ *cis* isomerization.[9]

CONCLUSIONS

The complexes $FeH_2(PP)_2$ and $FeHCl(PP)_2$ can be formed by reduction of the corresponding dichlorides $FeCl_2(PP)_2$ with lithium aluminium hydride in THF solution, provided that ethanol or more acidic reagents are not employed during the rection work-up. The dihydrides are notably basic compounds and can be protonated reversibly by alcohols.

The dihydrides exist as equilibrating mixtures of *cis* and *trans* isomers in solution. The *cis* isomers of each of the dihydrides are fluxional on the NMR timescale and NMR studies indicate that the interconversion of *cis* isomers does not necessarily proceed via the *trans* isomer.

EXPERIMENTAL

^{31}P NMR spectra were recorded at 162 MHz, from benzene-d$_6$ solutions, at ambient temperature. ^{31}P chemical shifts (δ) are in ppm, and were measured using external, neat, trimethyl phosphite (taken as δ 140.85) as a reference. ^{1}H NMR spectra were recorded at 400 MHz, ^{1}H chemical shifts (δ) are in ppm, and were referenced using residual solvent signals. Coupling constants are in Hz and signs of coupling constants are not implied.

$FeBr_2(DMPE)_2$,[10] $FeCl_2(DMPE)_2$,[11] $FeCl_2(DEPE)_2$,[11] $FeCl_2(DPrPE)_2$,[10] and anhydrous $FeCl_2$[12] were synthesized by literature methods.

$FeHCl(DEPE)_2$ (1b)

A solution of $FeCl_2(DEPE)_2$ was prepared *in situ* by stirring a mixture of anhydrous $FeCl_2$ (1.33 g, 10.5 mmol) and DEPE (4.325 g, 21.0 mmol) in THF (180 ml) for several hours. This solution was titrated with a solution of lithium aluminium hydride (*ca* 0.3 M in THF) until no $FeCl_2(DEPE)_2$ remained. The solvent was removed under reduced pressure, the residue was extracted exhaustively with hot light petroleum, and the combined extracts were filtered while hot. Concentration of the filtrate afforded pure $FeHCl(DEPE)_2$ (**1b**) as dark red needles (3.07 g, 58%), m.p. 154.5–157.5°C (dec.) [lit.[5a] 154.5–155.5°C (dec)].

Analysis: Calcd for $FeClP_4C_{20}H_{49}$: C, 47.59; H, 9.78; P, 24.54. Found: C, 48.0; H, 10.1; P, 24.4%.

^{1}H {^{31}P} NMR (benzene-d$_6$ 25°C) δ 0.850 (12H, dd, J 7.6 and 7.6, $4\times CH_3$), 1.136 (4H, dq, J 14.7 and 7.6, $4\times CH_3\text{-}C\underline{H}_AH_B\text{-}$), 1.139 (12H, dd, J 7.6 and 7.6, $4\times CH_3$), 1.397, 1.778 (8H, $2\times AA'XX'$, $J_{AA},=+6.5$, $J_{xx'}=+6.6$, $J_{AX}=J_{A'X'}=+8.5$, $J_{AX'}=J_{A'X}=-13.3$, $2\times$ P-CH_2CH_2-P), 1.707 (4H, dq, J 14.7 and 7.6, $4\times CH_3\text{-}C\underline{H}_AH_B\text{-}$), 1.753 (4H, dq, J 14.7 and 7.6 $4\times CH_3\text{-}CH_A\underline{H}_B\text{-}$), −31.938 (1H, s, Fe-H) ppm.

$FeHCl(DPrPE)_2$ (1c)

$FeHCl(DPrPE)_2$ was prepared by treatment of a mixture of iron(II) chloride (1.02 g, 8.05 mmol) and DPrPE (4.14 g, 15.8 mmol) in THF (100 ml) with a solution of lithium aluminium hydride, according to the procedure used for $FeHCl(DEPE)_2$. Pure $FeHCl(DPrPE)_2$ (**1c**) was obtained from light petroleum as red cubes (1.00 g, 27%), m.p. 143–144°C (dec.).

Analysis Calcd for $FeClP_4C_{28}H_{65}$: C, 54.51; H, 10.62; P, 20.08. Found: C, 54.8; H, 10.6; P, 19.9%.

$FeHBr(DMPE)_2$

$FeHBr(DMPE)_2$ was prepared by reduction of a solution of $FeBr_2(DMPE)_2$ (0.44 g, 0.85 mmol) in THF (60 ml) with lithium aluminium hydride according to the procedure used for $FeHCl(DMPE)_2$. Pure $FeHBr(DMPE)_2$ was obtained from light petroleum as orange plates (0.16 g, 37%), which decomposed without melting at temperatures above 220°C.

Analysis: Calcd for $FeBrP_4C_{12}H_{33}$: C, 32.98: H, 7.61; P, 28.35. Found: C, 33.1; H, 7.8; P, 28.3%.

$FeH_2(DMPE)_2$ (2a)

A solution of $FeCl_2(DMPE)_2$ (1.228 g, 2.88 mmol) in THF (60 ml) was titrated with a solution of lithium aluminium hydride (0.3 M in THF) until no $FeCl_2(DMPE)_2$ or $FeHCl(DMPE)_2$ remained (as determined by ^{1}H and ^{31}P NMR spectroscopy). The mixture was stripped of solvent under vacuum, and the residue extracted exhaustively with hot light petroleum. The combined light petroleum extracts were filtered and stripped of solvent. Sublimation of the residue (50°C/10^{-5} mm) onto a cold finger (−78°C) afforded $FeH_2(DMPE)_2$ (**2a**) as a pale yellow powder (0.466 g, 45%) m.p. 80–81°C (dec.).

The residue which had been previously extracted with light petroleum was suspended in THF (5 ml) and diluted with pentane (5 ml). The mixture was filtered and stripped of solvent, and the resultant solid sublimed to afford additional $FeH_2(DMPE)_2$ (0.194 g, 19%).

$FeH_2(DEPE)_2$ (2b) and $FeH_2(DPrPE)_2$ (2c)

Potassium hydride (45 mg, 1.12 mmol) was added to a solution of $FeHCl(DEPE)_2$ (**1b**) (101 mg, 0.200 mmol) in 2:1 THF/DMF (15 ml), and the mixture stirred for 18 h. The pale yellow mixture was filtered and stripped of solvent under vacuum, and the resulting cream-coloured residue was extracted with pentane (3 × 2 ml). The combined extracts were filtered and evaporated under reduced pressure, to afford $FeH_2(DEPE)_2$ (**1b**) (95 mg, 100%) as a pale oil which partially solidified on standing. The product was shown to be essentially pure by ^1H and ^{31}P NMR, and was used without further purification.

In an analogous experiment, treatment of $FeHCl(DPrPE)_2$ (60 mg, 0.097 mmol) with potassium hydride (55 mg, 1.37 mmol) in 2:1 THF/DMF (10 ml) afforded $FeH_2(DPrPE)_2$ (**1c**) as a pale yellow oil (56 mg, 100%), which partially crystallized on standing.

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REFERENCES

1. See for example: (*a*) Baker, M V and Field, L D *Organometallics*, 1986, 5: 821; (*b*) Baker, M V and Field, L D *J. Am. Chem. Soc.*, 1986, 108: 7433; (*c*) Baker, M V and Field, L D *J. Am. Chem. Soc.*, 1986, 108: 7436; (*d*) Baker, M V and Field, L D *J. Am. Chem. Soc.*, 1987, 109: 2825

2. See for example: (*a*) Baker, M V, Field, L D and Young, D J *J. Chem. Soc., Chem. Commun.*, 1988, 546; (*b*) Baker, M V and Field, L D *J. Organomet. Chem.*, 1988, 354: 351; Boyd, S E, Field, L D, Hambley, T W and Young, D J *Inorg. Chem.*, 1990, 29: 1496.

3. Gerlach, D H, Peet, W G and Muetterties, E L *J. Am. Chem. Soc.*, 1972, 94: 4545

4. Tolman, C A, Ittel, S D, English, A D and Jesson, J P *J. Am. Chem. Soc.*, 1978, 100: 4080

5. (*a*) Chatt, J and Hayter, R G *J. Chem. Soc.*, 1961, 5507; (*b*) Mays, M J and Prayter, B E *Inorg. Synth.*, 1974, XV: 21

6. Morris, R H, Sawyer, J F, Shiralian, M and Zubkowski, J D *J. Am. Chem. Soc.*, 1985, 107: 5581

7. (*a*) Baker, M V and Field, L D *J. Chem. Soc., Chem. Comm.*, 1984, 996; (*b*) Bau, R, Yuan, H S H, Baker, M V and Field, L D *Inorg. Chim. Acta*, 1986, 114: L27

8. Aresta, M, Giannoccaro, P, Rossi, M and Sacco, A *Inorg. Chim. Acta*, 1970, 5: 115

9. Meakin, P, Muetterties, E L and Jesson, J P *J. Am. Chem. Soc.*, 1973, 95: 75

10. Baker, M V, Field, L D and Hambley, T W *Inorg. Chem.*, 1988, 27: 2872

11. Chatt, J and Hayter, R G *J. Chem. Soc.*, 1961, 5507

12. Winter, G *Inorg. Synth.*, 1973, XIV: 102