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Molecular hydrogen complexes as intermediates in the synthesis of iron phosphine complexes; a reinvestigation of the preparation of bis(diphosphine)chlorohydridoiron complexes

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Abstract

Treatment of iron dichloride complexes $FeCl_2(PP)_2$ (PP = DMPE, DEPE, DPrPE) with lithium aluminium hydride in THF, followed by addition of ethanol, affords the molecular hydrogen complexes $[FeH(H_2)(PP)_2]^+$. The coordinated H_2 molecule is labile, and readily displaced by other ligands. The standard procedure in the literature for producing $FeHCl(DMPE)_2$ proceeds via over-reduction of the dichloride to the dihydride, followed by protonation (by ethanol) to give the intermediate $[FeH(H_2)(DMPE)_2]^+$ in high yield. In the presence of Cl^- in the polar ethanolic solution, displacement of H_2 by Cl^- affords the desired $FeHCl(DMPE)_2$, but parallel and/or subsequent reactions lead to contamination of the product with $FeCl_2(DMPE)_2$.

Introduction

During our studies of C–H bond activation [1], we required the chloroiron hydride complexes $FeHCl(PP)_2$ **2** [**2a**, PP = DMPE = 1,2-bis(dimethylphosphino)ethane; **2b**, PP = DEPE = 1,2-bis(diethylphosphino)ethane; **2c**, PP = DPrPE = 1,2-bis(di-n-propylphosphino)ethane]. Syntheses of **2a** and **2b** have been reported previously [2], and involve treatment of the corresponding dichloride complexes $FeCl_2(PP)_2$ **1** [2,3] with lithium aluminium hydride in THF, followed by addition of ethanol. Despite numerous attempts, however, we were unable to prepare pure samples of the desired complexes by the published procedure; the required chlorohydride products were invariably contaminated with significant amounts of the dichloride starting materials, and these could not be removed by recrystallisation. Using ^{31}P and ^{1}H NMR spectroscopy, we have conducted a detailed examination of

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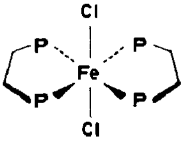
the course of the $LiAlH_4$ reduction of **1a** to give **2a**, and identified the dihydride **3a** and the molecular hydrogen complex **4a** as intermediates in the reaction.



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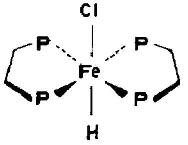

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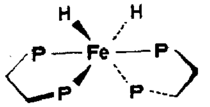

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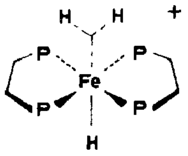

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a $\overline{P\quad P}$ = DMPE,
b $\overline{P\quad P}$ = DEPE,
c $\overline{P\quad P}$ = DPrPE,

Results and discussion

A solution of $FeCl_2(DMPE)_2$ (4.11 g, 2.9 mmol) in THF (60 ml) was titrated with a solution of lithium aluminium hydride (ca. 0.3 *M* in THF), and aliquots of the reaction mixture were examined at various times by ^{31}P and ^1H NMR spectroscopy (Fig. 1 and 2). After the addition of 1.2 equivalents of H^-, the colour of the mixture had changed from green to orange. ^1H and ^{31}P NMR spectroscopy (Fig. 1b and Fig. 2a) indicated that it contained the starting dichloride $FeCl_2(DMPE)_2$ (**1a**) ($\delta(^{31}P)$ 61.8 ppm), and three distinct hydrido complexes, the chlorohydride $FeHCl(DMPE)_2$ (**2a**) ($\delta(^{31}P)$ 72.3 ppm, $\delta(^1H) - 32.3$ ppm Fe–H), the dihydride $FeH_2(DMPE)_2$ (**3a**) [4] ($\delta(^{31}P)$ 77.9, 68.8 ppm, $\delta(^1H) - 14.3$ ppm FeH_2), and the molecular hydrogen complex $[FeH(H_2)(DMPE)_2]^+$ (**4a**) [5] ($\delta(^{31}P)$ 70.0 ppm, δ $(^1H) - 11.9$ Fe–H_2 and -17.1 ppm Fe–H), in the approximate ratio of 7/11/1/1.

Continued addition of $LiAlH_4$ to the sample led to a decrease in the amount of $FeCl_2(DMPE)_2$ present, and an increase in the quantities of $FeH_2(DMPE)_2$ and $FeHCl(DMPE)_2$, with no significant change in the amount of $[FeH(H_2)(DMPE)_2]^+$ (**4a**). The formation of **4a** during the early stages of the lithium aluminium hydride reduction has not been investigated in detail. It is possible that **4a** arises by reaction of H_2 (generated by the reaction of $LiAlH_4$ with adventitious moisture) with iron complexes, for example $[FeH(DMPE)_2]^+$. It has been observed [6] that $[FeH(DPPE)_2]^+$ reacts with H_2 to form $[FeH(H_2)(DPPE)_2]^+$, and a reaction involving adventitious moisture would be consistent with the observation that the molecular hydrogen complex was formed during the early stages of the $LiAlH_4$ reduction.

After a total of 2.7 equivalents of H^- had been added to the reaction mixture, all of the $FeCl_2(DMPE)_2$ and $FeHCl(DMPE)_2$ had been converted to $FeH_2(DMPE)_2$ [7*], and the sample contained only $FeH_2(DMPE)_2$ and $[FeH(H_2)DMPE)_2]^+$, in a ratio of approximately 19/1 (Fig. 1c and Fig. 2b). No other products were detected by NMR spectroscopy, and at this stage the mixture was very pale yellow, consistent with that in the reported synthetic procedure [2a]. Addition of more lithium aluminium hydride to the reaction mixture did not bring about further change.

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* Reference number with asterisk indicates a note in the list of references.

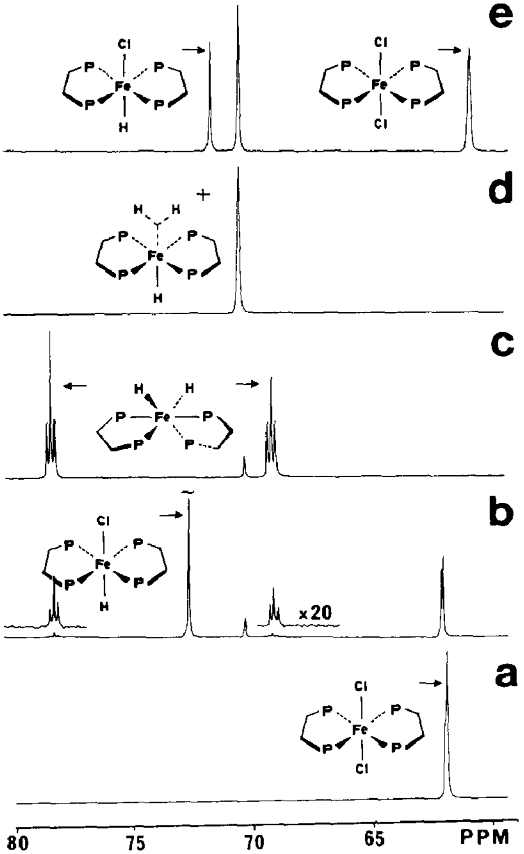


Fig. 1. $^{31}P\{^1H\}$ NMR spectra (162 MHz, −50 °C) of: (a) A solution of $FeCl_2(DMPE)_2$ (**1a**) (2.9 mmol) in THF (60 mls); (b) and (c) the same solution after addition of lithium aluminium hydride (0.3 *M* in THF) 1.3 and 1.95 mmol respectively; (d) an aliquot (0.4 mls) of reaction (d) after addition of ethanol (0.2 ml) at −50 °C; (e) reaction (d) after warming to room temperature for 30 minutes.

Addition of ethanol to an aliquot of the yellow reaction mixture at −78 °C was accompanied by some effervescence, and the colour changed to pale yellow-green. NMR spectroscopy indicated that the $FeH_2(DPME)_2$ had been converted quantitatively into $[FeH(H_2)(DMPE)_2]^+$, and the latter was observed to be stable for at least 20 h at −78 °C in the solution. In an independent experiment, treatment of an authentic sample of $FeH_2(DMPE)_2$ with ethanol afforded $[FeH(H_2)(DMPE)_2]^+$ [5].

Addition of ethanol to an aliquot of the yellow reaction mixture at room temperature initially resulted in formation of $[FeH(H_2)(DMPE)_2]^+$, but at this temperature the product was unstable, and after 30 min the colour of the aliquot changed to orange, and NMR spectroscopy indicated the formation of both $FeHCl(DMPE)_2$ and $FeCl_2(DMPE)_2$ (Fig. 1e and Fig. 2d) [8*]. After 1 h at room temperature, the aliquot was stripped of solvent, and the residue extracted with benzene. The resulting solution contained $FeHCl(DMPE)_2$ and $FeCl_2(DMPE)_2$ in a ratio of ca. 2/1 (by ^{31}P NMR).

A reaction sequence which accounts for the formation of the products observed in the lithium aluminium hydride reduction of $FeCl_2(DMPE)_2$ is depicted Scheme 1. The mechanisms by which $FeHCl(DMPE)_2$ and $FeCl_2(DMPE)_2$ are regenerated

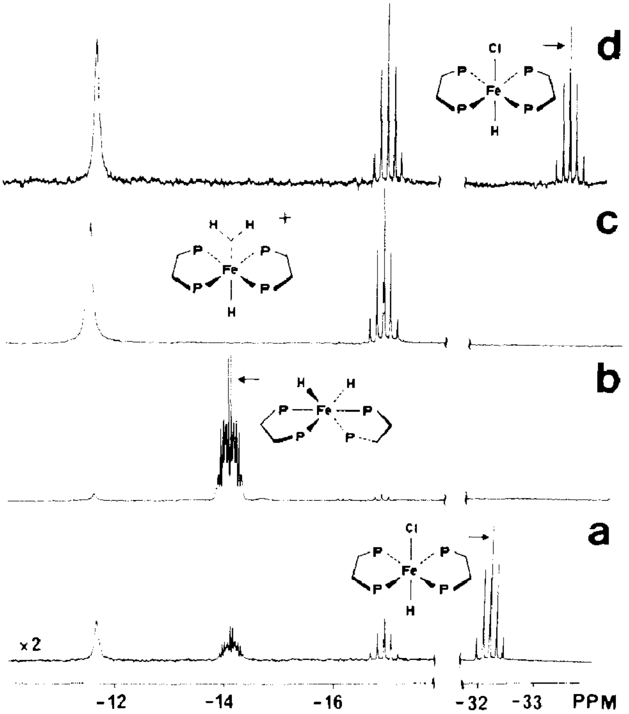
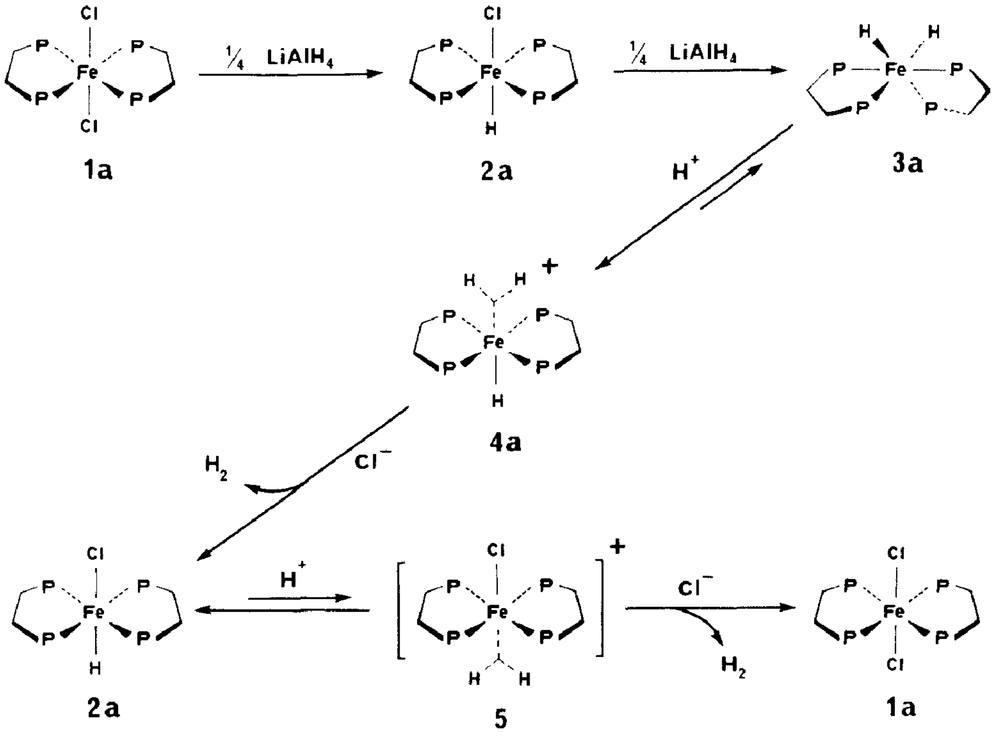


Fig. 2. High field region of the ^{1}H NMR spectra (400 MHz, −50 °C) of: (a) A solution of FeCl$_2$(DMPE)$_2$ (**2a**) (2.9 mmol) in THF (60 ml) after addition of 1.3 mmol of lithium aluminium hydride (0.3 *M* in THF); (b) the same solution after addition of 1.95 mmol of lithium aluminium hydride (0.3 mmol in THF); (c) an aliquot (0.4 ml) of reaction (b) after addition of ethanol (0.2 ml) at −50 °C (d) reaction (c) after warming to room temperature for 30 minutes.



Scheme 1

after the addition of ethanol have not been investigated in detail, and the possible involvement of aluminium species or solvent in the reactions has not been assessed. However, the observation that the η^2-coordinated H_2 ligand is readily displaced by CO, CH_3CN, N_2, N_3 and tertiary phosphines [5,6] suggests that molecular hydrogen is an excellent leaving group, and $FeHCl(DMPE)_2$ probably arises through displacement of H_2 in $[FeH(H_2)(DMPE)_2]^+$ by Cl^-. A similar process can account for the formation of $FeCl_2(DMPE)_2$ in the reaction mixture, but the presumed intermediate in this case, $[FeCl(H_2)(DMPE)_2]^+$ (**5**) has not been observed directly by NMR spectroscopy.

Reductions of solutions of $FeCl_2(DEPE)_2$ and $FeCl_2(DPrPE)_2$ with lithium aluminium hydride followed courses analogous to that observed for $FeCl_2(DMPE)_2$. In all attempted reductions with lithium aluminium hydride where ethanol was added, the isolated chlorohydride product was always contaminated with troublesome amounts of the dichloride **1a**. We note that in the cases of **2b** and **2c**, the dichloride impurities cannot be readily detected by NMR spectroscopy at room temperature owing to their involvment in equilibria with paramagnetic species [3].

Experimental

^{31}P NMR spectra were recorded at 162.0 MHz and were referenced to external neat trimethyl phosphite taken as 140.85 ppm; ^1H NMR spectra were recorded at 400.1 MHz and were referenced to solvent resonances. All manipulations were performed in Schlenk apparatus under argon or in an argon-filled dry box. All solvents were distilled and degassed by freeze-pump-thaw cycles prior to use.

Preparation of $FeHCl(DMPE)_2$. A solution of $FeCl_2(DMPE)_2$ (4.11 g, 9.62 mmol) was titrated with a solution of lithium aluminium hydride (ca. 0.3 *M* in THF) until all the starting material was just consumed (as monitored by ^{31}P NMR). At this stage, the mixture contained $FeHCl(DMPE)_2$ (**2a**) (ca. 70%), $FeH_2(DMPE)_2$ (**3a**) (ca. 25%), and $[FeH(H_2)(DMPE)_2]^+$ (**4a**) (ca. 5%). The solvent was removed, and the residue extracted exhaustively with hot light petroleum. The extracts were concentrated to give $FeHCl(DMPE)_2$ as dark orange plates (2.00 g, 53%) m.p. 180–181°C (dec.) (lit. [2a] 180°C). $^{31}P\{^1H\}$ NMR (C_6D_6, 25°C) 70.34 ppm. ^1H NMR (C_6D_6, 25°C) (1H, quintet, J(PH) 49.4 Hz, Fe–H); 1.093 (12H, m, $4 \times CH_3$); 1.494 (12H, m, $4 \times CH_3$); 1.412, 1.809 (8H, m, $2 \times PCH_2CH_2P$). Anal. Found: C, 36.5; H, 8.4; P, 31.9. $FeClP_4C_{12}H_{33}$ calcd.: C, 36.71; H, 8.47; P, 31.56%. Material obtained in this way contains no $FeCl_2(DMPE)_2$ but subsequent crops of crystals obtained by further concentration of the mother liquors are contaminated with $Fe(DMPE)_2Cl_2$, as shown by ^{31}P NMR spectroscopy.

Conclusion

The accepted literature procedure for producing $FeHCl(DMPE)_2$ proceeds via over-reduction of the dichloride to the dihyride, followed by protonation (by ethanol) to give the intermediate $[FeH(H_2)(DMPE)_2]^+$ in high yield. In the presence of Cl^- in the polar ethanolic solution, displacement of H_2 by Cl^- affords the desired $FeHCl(DMPE)_2$, but parallel and/or subsequent reactions lead to contamination of the product with $FeCl_2(DMPE)_2$. $FeHCl(DMPE)_2$ can be obtained in a pure form by careful reduction of the dichlorides with lithium aluminium hydride if ethanol is not used during the work-up. In the absence of ethanol (i.e. a protic solvent with a high dielectric constant) the formation of molecular hydrogen complexes is suppressed.

It is clear that the accepted procedures [2] for the preparation of FeHCl(DMPE)$_2$ and FeHCl(DEPE)$_2$ are incorrect. The chlorohydrides synthesised by these methods in the past were undoubtedly impure, and the accuracy of all past reports which rely on the purity of FeHCl(DMPE)$_2$, FeHCl(DEPE)$_2$, or products of the reactions of these complexes, must be treated with caution.

Acknowledgement

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7 From the quantity of $LiAlH_4$ required for complete conversion of **1a** to **3a**, it is apparent that the stoichiometry of the reaction is

$$2FeCl_2(DMPE)_2 + LiAlH_4 \rightarrow 2FeH_2(DMPE)_2 + LiAlCl_4$$

The first 1.2 equivalents of $LiAlH_4$ added to the reaction mixture effected proportionally less conversion of Fe–Cl to Fe–H than the remaining 1.5 equivalents, presumably due to traces of adventitious moisture initially present in the reaction mixture.

8 The NMR signals due to FeHCl(DMPE)$_2$ and $FeCl_2$(DMPE)$_2$ in THF solutions containing ethanol (Fig. 1e and 2d) occur at significantly different chemical shifts to those in neat THF solutions. This is possibly a consequence of solvent effects; it has been reported [9] that $FeCl_2$(DMPE)$_2$ dissolves in methanol to give a solution containing [FeCl(MeOH)(DMPE)$_2$]Cl^-.

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