Paramagnetic Hydrido-complexes of Iron(I) and Iron(III)

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The preparation and characterisation of the first paramagnetic hydrido-complexes of iron(I) and iron(III) of formula $[FeH(dppe)_2]$ and $[FeHCl(dppe)_2]X$ [dppe = $(Ph_2PCH_2)_2$; X = BF_4 or ClO_4] are described.

PARAMAGNETIC transition-metal hydrido-complexes are uncommon: few of them have been reported and most have been detected only in solution.[1,2] The paramagnetic hydrides isolated in the solid state, so far known, are $[ReHX_2(acac)(PPh_3)]$ (X = Cl or I) [3] and the very recently reported $[CoHL_4]X$ [L = $P(OEt)_2Ph$, $P(OMe)_2Ph$, or $P(OPh)_3$; X = PF_6 or BF_4].[4] Subsequent investigation of the previously reported paramagnetic $[OsHCl_2(PBu_2Ph)_3]$ [5] has led to the conclusion that the compound was incorrectly formulated.[6]

In a previous note,[7] we reported the preparation of the compound $[FeH\{(Ph_2PCH_2)_2\}_2]$, of particular interest because it provided the first example of well characterised paramagnetic hydrido-complex stable in the solid state.

Here we report the detailed preparation, the characterisation, and the properties of the above hydrido-complex of iron(I) and of new hydrido-complexes of iron(III), of formula $[FeHCl\{(Ph_2PCH_2)_2\}_2]X$ (X = BF_4 or ClO_4).

RESULTS AND DISCUSSION

The reduction of $[FeHCl(dppe)_2]$ [8] or $[FeH(dppe)_2]$-$[BPh_4]$ [9] with powdered sodium metal (molar ratio 1 : 1) in toluene or benzene under a nitrogen or argon atmosphere at room temperature gives $[FeH(dppe)_2]$ as red crystals, stable to the air for some hours, soluble in nonpolar solvents such as benzene or toluene, insoluble in pentane and in ethanol. The compound, which is rapidly destroyed on exposure to air while in solution with formation of the tertiary phosphine oxide, is paramagnetic (see Table 1) both in the solid state and in solution, and follows the Curie–Weiss law between 97 and 297 K ($\theta = 14{\cdot}5°$). It is monomeric in solution, as shown by its molecular weight in benzene.

The same compound is obtained by reaction of $[FeHCl(dppe)_2]$ with $Na[Co(N_2)(PEt_2Ph)_3]$, which leads, beside the co-ordinatively saturated iron(I) complex, to the already described [10] dinitrogen-bridged binuclear complex of cobalt(0), according to the following equation:

$$[FeHCl(dppe)_2] + Na[Co(N_2)(PEt_2Ph)_3] \longrightarrow [FeH(dppe)_2] + \tfrac{1}{2}[\{Co(PEt_2Ph)_3\}_2(N_2)] + NaCl + \tfrac{1}{2}N_2 \quad (1)$$

Mild oxidation of $[FeHCl(dppe)_2]$ with silver perchlorate or with trityl salts gives the paramagnetic hydrido-complex of iron(III), $[FeHCl(dppe)_2]X$ (X = ClO_4 or BF_4), as orange crystals, soluble in acetone, slightly soluble in ethanol, stable to air for some hours in the solid state, according to the following reactions:

TABLE 1

Magnetic susceptibilities

Compound	T/K	χcorr.	
$[FeH\{(Ph_2PCH_2)_2\}_2]$	297	1419	$\mu = 1{\cdot}80$ B.M.
	226,5	1876	$\theta = 14{\cdot}5$ K
	184	2362	
	97	4841	
$[FeHCl\{(Ph_2PCH_2)_2\}_2][BF_4]$	295	1962	$\mu = 2{\cdot}16$

$$[FeHCl(dppe)_2] + AgClO_4 \longrightarrow [FeHCl(dppe)_2][ClO_4] + Ag \quad (2)$$

$$[FeHCl(dppe)_2] + [Ph_3C][BF_4] \longrightarrow [FeHCl(dppe)_2][BF_4] + Ph_3C\cdot \quad (3)$$

When the reactions are carried out in benzene, the iron(III) complexes crystallise with two moles of solvent, which are easily lost by heating *in vacuo* at 80 °C or by crystallisation from acetone and pentane.

Although we have not isolated from the products of reaction (3) the equilibrium mixture between the trityl radical and its dimer 1-diphenylmethylene-4-tritylcyclohexa-2,5-diene, the formation of the trityl radical has been proved by the detection of $Ph_3COOCPh_3$ in the mother liquor after exposure to air.

The trityl cation has been usually used to remove a

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hydride from hydrido-complexes of transition metals[11] or from hydrocarbon ligands in π-complexes of transition metals;[12] however, it has been shown[4] that this cation can also act as an oxidising agent toward hydrido-complexes which contain a particularly inert metal–hydrogen bond. Actually the Fe–H bond in $[FeHCl(dppe)_2]$ is not cleaved by cold hydrochloric acid and it is thermally stable (the compound decomposes at 195 °C).

The i.r. spectra (Table 2) of $[FeH(dppe)_2]$ and $[FeHCl(dppe)_2]X$ in the solid state show respectively a strong absorption band at 1790 cm^{-1} and a medium absorption band at 1865 cm^{-1}, assignable to ν(Fe–H). This latter band is weaker and shifted to 1880 cm^{-1} in the iron(III) complexes containing benzene of crystallisation. As the compounds are paramagnetic, their ^1H n.m.r. spectra show only broadened resonances due to the diphosphine ligand protons, and no signals which may be assigned to a hydrogen bound to iron.

TABLE 2

I.r. stretching frequencies

Compound	(ν_{Fe-H}/cm^{-1})
$[FeH\{(Ph_2PCH_2)_2\}_2]$	1790vs
$[FeHCl\{(Ph_2PCH_2)_2\}_2][BF_4]\cdot2C_6H_6$	1880w
$[FeHCl\{(Ph_2PCH_2)_2\}_2][BF_4]$	1865m
$[FeHCl\{(Ph_2PCH_2)_2\}_2][ClO_4]$	1865m

The presence of the hydride ligand in these complexes has been confirmed as follows. $[FeH(dppe)_2]$ Reacts with trityl salts in benzene at room temperature under nitrogen atmosphere to give the known[9] $[FeH(N_2)(dppe)_2]X$ ($X = BF_4$, ClO_4) according to reaction (4) and with the stoicheiometric amount of HCl

$$[FeH(dppe)_2] + [Ph_3C]X + N_2 = [FeH(N_2)(dppe)_2]X + Ph_3C\cdot \quad (4)$$

or $HClO_4$ in ethanol according to equations (5) and (6):

$$[FeH(dppe)_2] + HCl \longrightarrow [FeHCl(dppe)_2] + 0{\cdot}5\ H_2 \quad (5)$$

$$[FeH(dppe)_2] + HClO_4 + N_2 \longrightarrow [FeH(N_2)(dppe)_2][ClO_4] + 0{\cdot}5\ H_2 \quad (6)$$

The reaction with the acids may procede either by an electrophilic attack of the proton to the hydride ligand:

$$[FeH(dppe)_2] + H^+ \longrightarrow [Fe(dppe)_2]^+ + H_2 \quad (7)$$

or, most probably, by an oxidative addition of the proton to give an unstable iron(III) dihydrido-complex:

$$[FeH(dppe)_2] + H^+ \longrightarrow [FeH_2(dppe)_2]^+ \quad (8)$$

which decomposes to hydrogen and $[Fe(dppe)_2]^+$. This cation may undergo a further oxidation addition [equation (9)] followed by reduction by the iron(I) complex:

$$[Fe(dppe)_2]^+ + H^+ \longrightarrow [FeH(dppe)_2]^{2+} \quad (9)$$

$$[FeH(dppe)_2]^{2+} + [FeH(dppe)_2] \longrightarrow 2[FeH(dppe)_2]^+ \quad (10)$$

The second mechanism is supported by the fact that the trityl cation does not abstract the hydride ligand either from $[FeH(dppe)_2]$ or from $[FeH_2(dppe)_2]$. Moreover, this dihydrido-complex reacts with an excess of the trityl cation at room temperature (see Table 3) according to the equation:

$$[FeH_2(dppe)_2] + 4[Ph_3C]^+ \longrightarrow [Fe(dppe)]^{2+} + 2Ph_3C\cdot + [\{Ph_2(Ph_3C)PCH_2\}_2]^{2+} + H_2 \quad (11)$$

The reaction actually proceeds through the formation of an unstable intermediate product, most probably the unstable $[FeH_2(dppe)_2]^+$, according to the sequence:

$$[FeH_2(dppe)_2] + [Ph_3C]^+ \longrightarrow [FeH_2(dppe)_2]^+ + Ph_3C\cdot$$

$$[FeH_2(dppe)_2]^+ \longrightarrow [Fe(dppe)_2]^+ + H_2$$

$$[Fe(dppe)_2]^+ + 3[Ph_3C]^+ \longrightarrow [Fe(dppe)]^{2+} + [\{Ph_2(Ph_3C)PCH_2\}_2]^{2+}$$

With a strong excess of hydrochloric acid and at the temperature of 80 °C $[FeH(dppe)_2]$ reacts (see Table 3) according to equation (12):

$$[FeH(dppe)_2] + 2HCl \longrightarrow [FeCl_2(dppe)] + dppe + 1{\cdot}5H_2 \quad (12)$$

$[FeH(dppe)_2]$ Is oxidised by the stoicheiometric amount of iodine to $[FeHI(dppe)_2]$, and by $AgClO_4$ to the cationic hydrido-complex of iron(II) $[FeH(dppe)_2][ClO_4]$. However, in this case some decomposition of the iron complex occurs, according to the equation:

$$[FeH(dppe)_2] + Ag^+ \longrightarrow [Ag(dppe)_2]^+ + Fe + \tfrac{1}{2}H_2 \quad (13)$$

On treating $[FeHCl(dppe)_2][BF_4]$ with a stoicheiometric amount of powdered sodium metal in benzene, the starting hydride $[FeHCl(dppe)_2]$ may be isolated in almost 100% yield.

By reaction of the hydrido-complex of iron(III) with hydrochloric acid in ethanol, hydrogen is evolved according to equation (14):

$$[FeHCl(dppe)_2][BF_4] + HCl \longrightarrow [FeCl_2(dppe)] + dppe + H^+ + [BF_4]^- + \tfrac{1}{2}H_2 \quad (14)$$

This reaction seems to procede through a nucleophilic attack of the halide on the cationic complex to give an unstable seven-co-ordinate hydrido-complex of iron(III), which decomposes to the iron(II) complex and hydrogen. This mechanism is supported by the reaction of $[FeHCl(dppe)_2][BF_4]$ with Bu_4NBr in ethanol, which occurs according to equation (15):

$$[FeHCl(dppe)_2][BF_4] + Br^- \longrightarrow [FeClBr(dppe)] + dppe + [BF_4]^- + \tfrac{1}{2}H_2 \quad (15)$$

The hydrido-complex of iron(I), $[FeH(dppe)_2]$, is isomorphous with $[CoH(dppe)_2]$,[13] and its toluene solution shows at room temperature a strong e.s.r. signal centred at $g = 2{\cdot}085$, with a poorly resolved hyperfine structure, probably due to the interaction of the unpaired electron of the iron(I) with the phosphorus atoms.

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The e.s.r. spectrum of $[FeHCl(dppe)_2][ClO_4]$ shows no signal at room temperature either in acetone solution or in the solid state; as the temperature is lowered a weak spectrum appears and at liquid nitrogen temperature strong signals are observed. This behaviour has been observed for a number of low-spin d^5 complexes of transition metals, which normally show a rapid spin-lattice relaxation.[14,15] The acetone solution of the hydrido-complex of iron(III) shows a rather large and distorted spectrum at 77 K: the g values are 2·180, 2·083, 2·003 ($\langle g \rangle$ 2·086). The powdered compound shows, at the same temperature, a well resolved spectrum: the g values are 2·185, 2·100, 1·981 ($\langle g \rangle$ 2·088). Three distinct g values are normally observed in low-spin octahedral complexes with a C_{2v} or a lower symmetry.[15]

EXPERIMENTAL

All the solvents were of reagent grade quality and were dried, distilled, and stored under argon. All reactions and subsequent handling were performed under an argon or a nitrogen atmosphere by standard vacuum-line techniques. Samples for melting point or decomposition point (d.p.) were contained in tubes sealed under vacuum or nitrogen. I.r. spectra were recorded as Nujol mulls on a Perkin-Elmer 457 spectrometer. ^1H N.m.r. spectra were recorded on a Varian H 100 and e.s.r. spectra on a Varian VH 502 spectrometer. Gas chromatographic determinations of H_2 and N_2 were carried out by a C. Erba Fractovap Mod. B as previously described,[16] and benzene determination by a Hewlett-Packard 5750 apparatus. Magnetic susceptibilities were measured under a nitrogen atmosphere by the Faraday method using an Alpha Mod. 9500 magnet, an Alpha Mod. 100-20 B power supply, and a Cahn Electrobalance as previously described.[17] Molecular-weight measurements were performed by Clark's modification of the Signer procedure.[18]

Di[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydridoiron*(I), $[FeH\{(Ph_2PCH_2)_2\}_2]$.—(*a*) Di[1,2-bis(diphenylphosphino)ethane]chloro(hydrido)iron(II) (1·35 g) and powdered sodium (0·035 g) were stirred in benzene (30 ml) at room temperature until complete disappearance of the sodium (*ca.* 5 days). The solution, whose colour turned from bright to deep red, was filtered and evaporated under vacuum to *ca.* 15 ml. The solution was cooled to 0 °C, pentane was added to it, and it was then set aside; deep red crystals which formed were filtered off, washed with pentane, and dried *in vacuo* (70%). This product, which contains 1·3—2·0 mol of C_6H_6 per mol of iron, was recrystallised from toluene by addition of pentane; d.p. 188—190 °C (Found: C, 73·35; H, 5·85; Fe, 6·55; P, 14·5. Calc. for $C_{52}H_{49}FeP_4$: C, 73·15; H, 5·8; P, 14·5; Fe, 6·55); *M* (in benzene): Found 862, Calc. 853·6.

(*b*) The same product, recognised by its d.p. and i.r. spectrum, was obtained from di[1,2-bis(diphenylphosphino)ethane]dinitrogenhydridoiron(II) tetraphenylborate (1·20 g) and powdered sodium (0·023 g) in benzene.

(*c*) A solution of di[1,2-bis(diphenylphosphino)ethane]chloro(hydrido)iron(II) (0·62 g) in THF (20 ml) was slowly added to a stirred solution of sodium tris(diethylphenylphosphine)dinitrogencobaltate(I) (0·44 g) in THF (10 ml) at 0 °C. The solution was filtered, evaporated under reduced pressure to *ca.* 15 ml, diluted with 5 ml of pentane, and left at 0 °C for two days to give deep red crystals (40%) which were recognised by their d.p. and i.r. spectrum as $[FeH\{(Ph_2PCH_2)_2\}_2]$. The mother liquor when cooled to −20 °C gave deep brown crystals of $[\{Co(PEt_2Ph)_3\}_2(N_2)]$, characterised on the basis of its m.p., i.r. spectrum, and elemental analysis.

Reactions of $[FeH\{(Ph_2PCH_2)_2\}_2]$.—(a) *With* $[Ph_3C][ClO_4]$. Trityl perchlorate was added to an equimolecular amount of the hydrido-complex in benzene solution at room temperature under a nitrogen atmosphere with stirring. The colour of the solution changed from red to pale yellow to give yellow crystals of di[1,2-bis(diphenylphosphino)ethane]dinitrogenhydridoiron(II) perchlorate, which were filtered off, washed with ethanol and pentane, and dried. The product was characterised on the basis of its i.r. spectrum and analysis (Found: N, 2·8; Cl, 3·65; Fe, 5·7; P, 12·55. $C_{52}H_{49}ClFeN_2O_4P_4$ requires N, 2·85; Cl, 3·6; Fe, 5·7; P, 12·65%).

(b) *With* HCl. A 0·1 molar solution of HCl in ethanol was added to an equimolecular amount of the hydrido-complex in toluene solution at −70 °C under a nitrogen atmosphere. When the temperature was slowly raised the colour of the solution turned to bright red and a brisk evolution of gas, recognised as H_2, was observed. Addition of pentane gave red crystals of di[1,2-bis(diphenylphosphino)ethane]chlorohydridoiron(II), recognised by comparison with an authentic sample.

(c) *With* $HClO_4$. Di[1,2-bis(diphenylphosphino)ethane]dinitrogenhydridoiron(II) perchlorate was similarly obtained by treating with an ethanolic solution of $HClO_4$, under nitrogen, a toluene solution of the hydrido-complex.

With I_2. Di[1,2-bis(diphenylphosphino)ethane]hydridoiodoiron(II) was similarly obtained by treating with a toluene solution of iodine (0·5 mol) a toluene solution of the hydrido-complex (Found: Fe, 5·75; I, 13·0; P, 12·6. Calc. for $C_{52}H_{49}IFeP_4$: Fe, 5·7; I, 12·95; P, 12·65%).

With $AgClO_4$. An acetone solution of $AgClO_4$ was added with stirring to an equimolecular amount of the hydrido-complex (0·201 mmol) in toluene at room temperature under a nitrogen atmosphere.

The solution, whose colour changed from red to pale yellow, was filtered and evaporated under reduced pressure to give yellow crystals of di[1,2-bis(diphenylphosphino)ethane]dinitrogenhydridoiron(II) perchlorate, recognised by its i.r. spectrum. The black residue, after washing with acetone and acetic acid, was dissolved in nitric acid and the resulting solution was analysed [Found: Ag, 0·128 mmol (63·7%); Fe, 0·063 mmol (31·3%)].

Determination of the hydridic hydrogen. Samples of the hydrido-complex were treated, in current of argon, with an excess of the reagent in an apparatus connected to the gas chromatographic apparatus, as previously described.[16] Table 3 shows the results.

Di[1,2-*bis*(*diphenylphosphino*)*ethane*]*chlorohydridoiron*(III) *Tetrafluoroborate*, $[FeHCl\{(Ph_2PCH_2)_2\}_2][BF_4]$.—Trityl tetrafluoroborate (0·55 mmol) was added with stirring to a benzene solution of di[1,2-bis(diphenylphosphino)ethane]chlorohydridoiron(II) (0·50 mmol) at room temperature. After a few minutes the trityl salt almost completely

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dissolved and the solution, whose colour turned to orange, was quickly filtered. The solution was cooled to 5 °C and set aside to give orange crystals of the product. The compound crystallises with two molecules of benzene, recognised by gas chromatographic analysis of its thermal decomposition products; d.p. 135—137 °C (Found: C, 67·0; H, 5·2; Cl, 3·25; Fe, 5·02; P, 10·4. Calc. for $C_{64}H_{61}BClF_4FeP_4$: C, 67·9; H, 5·45; Cl, 3·15; Fe, 4·95; P, 10·95%).

TABLE 3

Gas chromatographic analyses

	Amount of compd.			H_2 evolved	
Compound	µmol	Reagent	t/°C	µmol	Ratio H_2/Fe
$[FeH\{(Ph_2PCH_2)_2\}_2]$	38·4	HCl aq.	80	59·6	1·55
	32·1	HCl–EtOH	80	47·7	1·49
	25·3	I_2–C_6H_6	80	5·1	0·20
$[FeHCl\{(Ph_2PCH_2)_2\}_2][BF_4]$	21·8		200	11·3	0·52
	27·7	Bu_4NBr	50	14·0	0·51
	25·8	HCl–EtOH	20	13·9	0·54
$[FeH_2\{(Ph_2PCH_2)_2\}_2]$	28·4	Ph_3CClO_4–C_6H_6	25	27·5	0·97

By heating the product at 80 °C *in vacuo* or by crystallising it from acetone and pentane, orange crystals containing no solvent were obtained, d.p. 160—162 (Found: C, 64·1; H, 5·05; Cl, 3·65; Fe, 5·8; P, 12·6. Calc. for $C_{52}H_{49}BClF_4FeP_4$: C, 64·0; H, 5·05; Cl, 3·65; Fe, 5·7; P, 12·7%).

Di[1,2-*bis*(*diphenylphosphino*)*ethane*]*chlorohydridoiron*(III) *Perchlorate*, $[FeHCl\{(Ph_2PCH_2)_2\}_2][ClO_4]$.—(*a*) This compound was similarly obtained from trityl perchlorate and $[FeHCl\{(Ph_2PCH_2)_2\}_2]$; it had d.p. 110—113 °C (Found: C, 64·1; H, 5·05; Cl, 7·2; Fe, 5·65; P, 12·4. Calc. for $C_{52}H_{49}Cl_2FeO_4P_4$: C, 63·2; H, 5·0; Cl, 7·15; Fe, 5·65; P, 12·55%). Molar conductance ($1·2 \times 10^{-3}$M solution in nitrobenzene at 22 °C): 22 Ω^{-1} cm^2 mol^{-1}.

(*b*) $AgClO_4$ (0·43 mmol) in acetone was slowly added to $[FeHCl\{(Ph_2PCH_2)_2\}_2]$ (0·41 mmol) in acetone at 0 °C with stirring to give an orange solution which was filtered and diluted with a little pentane; when set aside the solution gave orange crystals (Found: Cl, 7·1; Fe, 5·7; P, 12·45%).

Reactions of $[FeHCl\{(Ph_2PCH_2)_2\}_2][BF_4]$.—*With* Na. The hydrido-complex and powdered sodium in a molar ratio 1 : 1 were stirred in benzene at room temperature until complete disappearance of the sodium. By addition of pentane to the filtered solution, red crystals of $[FeHCl\{(Ph_2PCH_2)_2\}_2]$, characterised by comparison with an authentic sample, were obtained.

With $[Bu_4N]Br$. An acetone solution of tetrabutylammonium bromide was added to the hydrido-complex (molar ratio Br/Fe = 1·5) in a phial sealed under nitrogen and kept at about 50 °C for 1 h.

The evolved gas was analysed gas chromatographically (see Table 3).

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