Dicaticionic dihydrogen complexes of iron with almost no 
Fe-η²-H₂ back-bonding

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Introduction
Ever since the discovery of transition metal dihydrogen complexes by Kubas and co-workers1, a large number of them have been synthesized and characterized2-5. It was found that the nature of the metal center and the ancillary ligands significantly influence the properties of the dihydrogen complexes2-4. Systematic investigations have been carried out on dihydrogen complexes of the type [(diphosphine)M(η²-H₂)(L)]⁺⁺ (M = Fe, Ru, Os; n =1,2) by varying the steric and the electronic properties of the ancillary ligands and the ligand trans to the η²-H₂ moiety in order to study their influence on the properties of those complexes5-9. The bonding in dihydrogen complexes could be described as two-component type: σ-donation of electron density from the H₂ to vacant metal d-orbitals and back-donation of electron density from the filled metal d-orbitals to the σ* orbitals of the H₂. The back-bonding is important for the stabilization of the M-H₂ interaction; however, significant back-donation leads to the cleavage of the H-H bond10. Morris et al.11 found that despite the absence of back-bonding in trans-[(dppe)₂Fe(η²-H₂)(CO)][OTf]₂ to be stable with respect to loss of H₂, the stability was attributed to the strong σ-bond between the metal and the H₂. Such instances of almost no back-bonding from the metal to the H₂ moiety are relatively scarce. The H₂ ligand under conditions of no back-donation (M→H₂) usually exhibits tremendous lability, which could be exploited in homogeneous catalysis.

We have previously reported a series of dicaticionic dihydrogen complexes of ruthenium trans-[(diphosphine)₂Ru(η²-H₂)(L)][BF₄]₂ (diphosphine = dppe; L = nitrile12, phosphine and phosphite13, diphosphine = dppe (Ph₂PCH₂PPh₂), L = phosphine, phosphite14). In order to study the influence of the group 8 metal on the properties of dihydrogen complexes of the type trans-[(dppe)₂M(η²-H₂)(R-CN)][BF₄] (M = group 8 metal) we sought to prepare a series of hydride and dihydrogen complexes of iron analogous to those of ruthenium that we reported earlier and thus understand the periodicity of their properties.

Materials and Methods
All operations were performed under an atmosphere of dry and purified nitrogen using standard Schlenk and inert atmosphere techniques. Manipulations involving dihydrogen complexes were carried out either under an atmosphere of H₂ or Ar. 1,2-bis(diphenylphosphino)ethane (dppe)15, (dppe)₂Fe(H)₃:2C₂H₆, (ref. 16) and trans-[(dppe)₂Fe(H)(η²-H₂)][BF₄]₁⁰ were prepared according to literature methods. The ¹H and ³¹P NMR spectra were recorded using an AMX Bruker 400 MHz instrument. The shift of the residual protons of the deuterated solvent was used as
an internal reference. $^{31}$P NMR chemical shifts have been measured relative to 85% $\text{H}_3\text{PO}_4$ (as an external standard) in CD$_2$Cl$_2$ and $^{19}$F NMR spectra with respect to CFCl$_3$. All $^{31}$P NMR spectra were proton decoupled unless otherwise noted. The proton $T_1$ measurements were carried out at 400 MHz using the inversion recovery method. Elemental analyses were carried out using a Heraeus CHNO Rapid elemental analyzer, however, due to the high fluorine content in the samples, the data obtained was found to be unsatisfactory except for 6a. Therefore, we do not report the analytical data herein. Nevertheless, the purity of the samples was ensured using NMR spectroscopy.

Observation of H-D isotopomers trans-[(dppe)$_2$Fe(H)(CH$_3$CN)][BF$_4$] (1a)

An acetonitrile (10 mL) solution of trans-[(dppe)$_2$Fe(H)(H$_2$)][BF$_4$] (200 mg, 0.2 mmol) under an atmosphere of H$_2$ was stirred at room temperature for 12 h. The reaction mixture turned from pale yellow to dark yellow. It was then concentrated to ca. 2 mL and 20 mL of Et$_2$O was added to cause the precipitation of a dark yellow solid of 1a. The solid was separated and dried under vacuo. The product was crystallized from a CH$_2$Cl$_2$ solution containing the hydride complex and a few drops of the nitrile via diffusion of Et$_2$O at room temperature over a period of several days. Yield 72% (150 mg).

Preparation of trans-[(dppe)$_2$Fe(H)(RCN)][BF$_4$] (2a)

All of these compounds were prepared using the procedure employed for that of 1a. Yield of 2a: 59% (125 mg). Yield of 3a: 69% (148 mg). Yield of 4a: 79% (166 mg). Yield of 6a: 66% (150 mg); Anal. Calcd for C$_8$H$_5$BF$_4$NP$_2$Fe·CH$_2$Cl$_2$: C, 64.38; H, 5.22; N, 1.09.

Preparation of trans-[(dppe)$_2$Fe($\eta^2$-H$_2$)(RCN)][BF$_4$] (3a)

Red crystals of 3a were obtained via slow diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of trans-[(dppe)$_2$Fe(H)(CH$_3$CH$_2$CH$_2$CN)][BF$_4$] at room temperature over a period of several days. The unit cell parameters and intensity data were collected on a Bruker SMART APEX CCD diffractometer equipped with a fine focus Mo-Kα X-ray source. The SMART software was used for data acquisition and the SAINT software for data abstraction. Absorption corrections were made using the SADABS and the pre-scans methods. The structure was solved and refined using the SHELX programs. The Fe atom position was located from the Patterson method and the non-hydrogen atoms were located from successive difference Fourier map and were refined anisotropically except the counteranion (BF$_4$) which exhibited structural disorder. The two fluorine atoms exhibited positional disorder and were assigned partial occupancies and refined isotropically. All other hydrogen atoms were geometrically fixed and refined using a riding model.
Results and Discussion

Synthesis of new hydride complexes

The new iron hydride complexes trans-[(dppe)Fe(H)(RCN)][BF₄] (R = CH₃ 1a, CH₂CH₂ 2a, CH₃CH₂CH₂ 3a, CH₂=CH 4a, C₆H₅ 5a, p-CH₃C₆H₄CH₂ 6a) have been prepared by substitution of the H₂ ligand in the dihydrogen complex trans-[(dppe)Fe(H)(η²-H₂)][BF₄] analogous to the preparation of certain ruthenium derivatives that we reported earlier (Eq. 1)¹². The compounds 1a and 5a have been reported by other groups²¹,²². The products were obtained as dark yellow solids in yields ranging from 59 to 79%.

![Image of a chemical structure]

The ¹H NMR spectra of the hydride complexes (Table 1) show a quintet for the hydride ligand in the range δ -19.03 to -20.91 due to coupling with four cis phosphorus nuclei with a J (H, Pcis) of ca. 46.0 to 47.0 Hz. The ³¹P¹H NMR spectra (Table 1) display only a singlet in the range δ 82.7-84.6 confirming the trans disposition of the hydride and the nitrile ligands and the planarity of all the four P atoms. The ¹H NMR chemical shifts of Fe-H are upfield shifted compared to those of Ru-H in trans-[(dppe)Ru(H)(RCN)][BF₄]²¹ complexes whereas the ³¹P¹H NMR signals for the dppe phosphorus nuclei experience downfield shifts of ca. 20 ppm. The upfield shift of the M-H signal in the ¹H NMR spectra could be traced to the importance of σ-bonding between the metal and the hydride ligand as is well-documented in the literature; the basicity of the metal increases down the group (Fe, Ru, Os), iron being less basic (and hydride, a strong field ligand) forms the stronger σ-bond effecting the high field shift of the hydride ligand. On the other hand, the upfield shift of the ³¹P¹H NMR chemical shifts on going from 3d to 4d to 5d could be traced to the additional π component in the binding of the phosphine to the metal; it could be attributed to an increase in the metal-phosphorus π-back-bonding due to an increase in π-basicity of the metal down the iron triad²³. In order to obtain some insight into the cavity formed by the sterically encumbered [(dppe)Fe(H)]⁺ fragment which will help us in choosing appropriate ligands for the preparation of dihydrogen complexes with desired properties and also to compare the structural features of the iron hydride complexes with those of the ruthenium analogs, we sought to examine the crystal structure of 3a.

Structure of trans-[(dppe)Fe(H)(CH₂CH₂CH₂CN)][BF₄] 3a

The ORTEP diagram of the trans-[(dppe)Fe(H)(CH₂CH₂CH₂CN)]⁺ cation is shown in Fig. 1. The cation is made up of an octahedrally

<table>
<thead>
<tr>
<th>R (Compd no)</th>
<th>¹H NMR spectral data (δ) for trans-[(dppe)Fe(H)(RCN)][BF₄] complexes in CDCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃ (1a)</td>
<td>δ(Fe-H) = -20.81 (qnt, 1H) J(H,Pcis) = 1.76 (s, 3H, CH₃) δ(Fe-H) = 2.47 (m, 4H) δ(Ph) = 6.66-7.34 (m, 40H) δ(dppe) = 83.9</td>
</tr>
<tr>
<td>CH₂CH₂ (2a)</td>
<td>δ(Fe-H) = -20.88 (qnt, 1H) J(H,Pcis) = 2.42 (q, 2H, CH₂) δ(Fe-H) = 2.42 (m, 4H) δ(Ph) = 6.61-7.48 (m, 40H) δ(dppe) = 82.7</td>
</tr>
<tr>
<td>CH₃CH₂CH₂ (3a)</td>
<td>δ(Fe-H) = -20.91 (qnt, 1H) J(H,Pcis) = 2.22 (m, 4H, CH₂CH₂) δ(Fe-H) = 2.42 (m, 4H) δ(Ph) = 6.57-7.28 (m, 40H) δ(dppe) = 83.6</td>
</tr>
<tr>
<td>CH₂=CH (4a)</td>
<td>δ(Fe-H) = -19.03 (qnt, 1H) J(H,Pcis) = 5.03 (d, 2H, CH₂=CH) δ(Fe-H) = 2.35 (m, 4H) δ(Ph) = 6.56-7.61 (m, 40H) δ(dppe) = 82.7</td>
</tr>
<tr>
<td>C₆H₅ (5a)</td>
<td>δ(Fe-H) = -19.27 (qnt, 1H) J(H,Pcis) = 6.81-7.44 (m, 5H, C₆H₅) δ(Fe-H) = 2.57 (m, 4H) δ(Ph) = 6.81-7.86 (m, 40H) δ(dppe) = 84.6</td>
</tr>
<tr>
<td>p-CH₃C₆H₄CH₂ (6a)</td>
<td>δ(Fe-H) = -20.60 (qnt, 1H) J(H,Pcis) = 3.65 (m, 2H, CH₂) δ(Fe-H) = 2.41 (m, 4H) δ(Ph) = 6.42-7.55 (m, 40H) δ(dppe) = 82.8</td>
</tr>
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Fig. 1—ORTEP view of the trans-
[(dppe)2Fe(H)(CH2CH2CH2CN)]2+ 3a cation at the 50% probability level.

cordinated iron defined by the four coplanar dppe phosphorus atoms, butyronitrile moiety and the hydride. The hydride ligand was located from the difference Fourier map; in addition, 1H NMR spectroscopy also provides evidence of its presence. The iron atom is displaced out of the equatorial plane formed by the four phosphorus atoms towards the nitrile by 0.1 Å. The Fe-N distance in the iron complex is much shorter than that in the trans-
[(dppe)Ru(H)(P-Ch3-CH2-C6H4-CH2-CN)][BF4]12 (1.913(6) Å). The crystallographic data and the pertinent bond lengths and angles have been summarized in Tables 2 and 3 respectively.

Protonation reactions of the hydride complexes trans-
[(dppe)2Fe(H)(RCN)][BF4] (R = CH3 1a, CH2CH2 2a, CH2CH2CH2 3a, CH2=CH 4a, C6H5 5a, p-CH3C6H4CH2 6a)

The protonation of the hydride complexes in CD2Cl2 with 2 equiv of 54% HBF4·Et2O at room temperature afforded the corresponding dihydrogen complexes of the type trans-
[(dppe)2Fe(η2-H2)-
(RCN)][BF4][24] (R = CH3 1b, CH2CH2 2b, CH2CH2CH2 3b, CH2=CH 4b, C6H5 5b, p-CH3C6H4CH2 6b) (Scheme 1). The 1H NMR spectra (Table 4) consist of a broad singlet in the range δ = 16.40 to 17.99 for the Fe-H2; definitive assignments of the 1H NMR signals of the other moieties of the dihydrogen complexes were precluded due to the broadness of the remaining signals rendered by a Fe(III) species that was formed along with the dihydrogen complex. The 31P [1H] NMR spectra (Table 4) exhibit a singlet in the region δ 69.0–71.0 (dppe) for the dihydrogen complexes. In addition, the 31P [1H] NMR spectroscopy indicates the presence of two other species along with some unreacted starting hydride complex; these species were identified as trans-
[(dppe)2Fe(BF4)(RCN)][BF4] 7 (31P [1H]: δ 51.0 (s, 4P); 19F: δ = −144.36 (s, 4F, Fe-BF4), −160.05 (br s, free BF4−) and dppeH+ (10.4, s, 2P)10 respectively. Addition of a further two equiv of the acid results in the complete consumption of the
starting material to yield a mixture of the dihydrogen complex, dppeH⁺, and the trans-[(dppe)Fe(H₂)(RCN)][BF₄] derivative (Scheme 1). The pathway to the side components is unclear at this time, however, it is reasonable to expect the formation of the Fe(III) species from the product that undergoes cleavage of one of the chelating phosphines due to its protonation. On the other hand, the BF₄⁻-bound iron derivative could result from the dihydrogen complex that loses the H₂ ligand due to its lability (see text later). Morris and co-workers observed a similar behaviour in the case of an iron complex wherein the H₂ bound trans to CO was found to be quite labile and underwent substitution by BF₄⁻ counterion.

The NMR chemical shifts of the dihydrogen complexes follow the same trend as the precursor hydrides in comparison to their ruthenium counterparts. Once again the basicity of the metal seems to play a vital role in dictating the bonding situations of these derivatives. This property is reflected to a greater extent in the H-H distances obtained from NMR spectroscopy for the HD isotopomers (see later).

The dihydrogen complexes (1b-6b) resemble certain dihydrogen complexes trans-[(diphosphine)₂Fe(H₂)(X)] (diphosphine = dppe, depe; X = Cl, Br) with respect to the cleavage of the chelating phosphine and elimination as the protonated form as reported by Henderson. Within a short period of time, our dihydrogen complexes lose the bound H₂ ligand (free H₂ IH NMR: δ 4.60, s) to afford a pink solution that was identified as 7, this solution slowly precipitates a pink solid of the BF₄⁻ bound derivative. When the pink solid was dissolved in CH₃CN gave a compound of the formulation trans-[(dppe)₂Fe(CH₃CN)₂][BF₄] (8-H₃) that was reported earlier.

**HD isotopomers and stabilities of the dihydrogen complexes**

The HD isotopomers trans-[(dppe)₂Fe(η²-H₂)(RCN)][BF₄] (R = CH₃ 1c, CH₂CH₂ 2c, CH₃CH₂CH₂ 3c, CH₃-CH 4c, C₆H₅ 5c, p-CH₃C₆H₄CH₂ 6c) were generated by the addition of DBF₄ to the iron hydride complexes in CD₂Cl₂. The HD isotopomers formed were observed using IH NMR spectroscopy at 253 K using the inversion recovery pulse (180°-τ-90°)²⁷. The IH NMR spectra display a triplet (Fig. 2) for the η²-HD moiety. The J(H,D) obtained were in the range 32 to 33 Hz from which the H-H distances (d_HH) were calculated (Table 5)²⁶,²⁷.

The d_HH fall in the range 0.86 to 0.88 Å indicating that there is no substantial activation of the H-H bond upon binding with the iron center. The remarkably similar J(H,D) in all these derivatives suggests that the variation of η-acidities of the trans nitrile ligand has no effect on the coupling constant. A somewhat analogous observation has been made by others for the coupling of HD trans to CO; it was found that the J(H,D) (between 32 and 34 Hz) was insensitive for complexes with trans CO regardless of the other ligands involved. In the ruthenium analogs we observed J(H,D) of 27-28 Hz for the η²-HD moiety that corresponds to d_HH of 0.95-0.96 Å indicating that there is no substantial activation of the H-H bond upon binding with the iron center.
substantial elongation of the H-H bond\textsuperscript{12}. This is a result of a greater degree of back-bonding between the metal and the σ\textsuperscript{*} orbitals of the H\textsubscript{2} moiety. We determined the pK\textsubscript{a}s of the ruthenium derivatives and found that all of them to be quite low indicating that the bound dihydrogen ligand is very acidic.

The significant back-bonding between the ruthenium center and the bound H\textsubscript{2} ligand in the dihydrogen complexes trans-\{[dppe\textsubscript{2}Ru(H\textsubscript{2})\textsubscript{2}(CH\textsubscript{3}CN)]\}BF\textsubscript{4}\textsubscript{2} is reflected in their stabilities with respect to loss of the H\textsubscript{2} ligand. The ruthenium derivatives were found to be stable for periods of ca. 2 days. Morris \textit{et al.} found that despite the absence of back-bonding in trans-\{[dppe\textsubscript{2}Fe(H\textsubscript{2})\textsubscript{2}(CO)]OT\textsubscript{f}\textsubscript{2} (ref. 10) to be stable with respect to elimination of H\textsubscript{2}. The stability was attributed to the formal charge on the iron and the strong π-acceptor trans to the H\textsubscript{2} ligand resulting in a stronger σ interaction. However, in our dihydrogen complexes, a weaker π-acceptor nitrile relative to CO results in a reduced σ interaction coupled with poor back-bonding (due to the smaller basicity of iron compared to ruthenium) leads to reduced stability. We found that the iron dihydrogen complexes undergo decomposition (loss of H\textsubscript{2}) accompanied by the generation of 7 and certain Fe(III) species that we have not be been able to identify.

\textbf{1'H spin lattice relaxation time measurements}

The dihydrogen complexes were found to be unstable with respect to loss of H\textsubscript{2}, therefore, we were unable to carry out the \(T_1\) measurements at various temperatures. We however, determined the \(T_1\) values for the HD isotomers (1c-6c) using the inversion recovery method (180°-r-90° pulse sequence)\textsuperscript{17} at 253 K. The small \(T_1\) values (Table 5) for the HD complexes indicate the intact nature of the H-H bond in these derivatives.

\textbf{Reactivity studies}

The protonation of 1a in CD\textsubscript{3}CN with 4 equiv of HBF\textsubscript{4}-Et\textsubscript{2}O at room temperature affords the dihydrogen complex trans-\{[dppe\textsubscript{2}Fe(H\textsubscript{2})\textsubscript{2}(RCN)]\}BF\textsubscript{4}\textsubscript{2} as evidenced by \(^1\text{H}\) NMR spectroscopy. The dihydrogen complex shortly after its generation converts to trans-\{[dppe\textsubscript{2}Fe(CD\textsubscript{3}CN\textsubscript{2})\}BF\textsubscript{4}\textsubscript{2} (8-D\textsubscript{3}) as indicated by \(^1\text{H}\) and \(^{31}\text{P}\) NMR spectroscopy. The \(^{31}\text{P}\{'^1\text{H}\}\) NMR spectrum of 8-D\textsubscript{3} displays a singlet at δ 55.0. When the protonation was carried out in CDCl\textsubscript{3} in the presence of 10 equiv of CH\textsubscript{3}CN, the trans-\{[dppe\textsubscript{2}Fe(CH\textsubscript{3}CN\textsubscript{2})\}BF\textsubscript{4}\textsubscript{2} (8-H\textsubscript{3}) was obtained through the intermediacy of 1b. We have been unable to determine the pK\textsubscript{a}s of the dihydrogen complexes (1b-6b) due to the labile nature of the H\textsubscript{2} ligand. However, when 1b was reacted with Lewis bases such as triethylamine, pyridine, and piperidine, the H\textsubscript{2} ligand undergoes deprotonation to give the precursor hydride complex and the protonated base (Scheme 2). We found that the analogous ruthenium complex trans-\{[dppe\textsubscript{2}Ru(H\textsubscript{2})\textsubscript{2}(CH\textsubscript{3}CN)]\}BF\textsubscript{4}\textsubscript{2} also undergoes deprotonation when reacted with excess acetonitrile\textsuperscript{29}. More work is needed in order to understand the differing reactivity behaviour of the iron derivatives with respect to lability versus deprotonation of the H\textsubscript{2} ligand.

\textbf{Conclusion}

New iron hydride complexes of the type trans-\{[dppe\textsubscript{2}FeH(RCN)]\}BF\textsubscript{4} (RCN = nitrile) have been prepared and characterized. The protonation reactions of the hydride derivatives afforded the corresponding dihydrogen complexes. The H\textsubscript{2} ligand in the dihydrogen complexes do not seem to be substantially
elongated as a result of reduced/almost no back-donation of electron density from the metal to the σ* orbitals of H₂. The H₂ ligand in these complexes was found to be quite labile, upon its loss affords a BF₄⁻ bound derivative trans-[(dppe)₂Fe(BF₄)(RCN)][BF₄]. From this study it can be concluded that the nature of the metal can have a profound effect on the properties of the dihydrogen complexes.

**Supporting information available**

Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for 3a in CIF format are available from the corresponding author upon request.

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**References**

27. d[RH] (Å) = -0.167[H(D)](Hz) + 1.42.