

## Dicationic dihydrogen complexes of iron with almost no Fe- $\eta^2$ -H<sub>2</sub> back-bonding

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Transition metal hydride complexes of the type *trans*-[(dpe)<sub>2</sub>Fe(H)(RCN)][BF<sub>4</sub>] (dpe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>; R = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>=CH, C<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>) have been prepared by substitution of the  $\eta^2$ -H<sub>2</sub> ligand in *trans*-[(dpe)<sub>2</sub>Fe(H)( $\eta^2$ -H<sub>2</sub>)][BF<sub>4</sub>] with the corresponding nitriles. Protonation of these hydride complexes using HBF<sub>4</sub>·Et<sub>2</sub>O gives the dicationic dihydrogen complexes *trans*-[(dpe)<sub>2</sub>Fe( $\eta^2$ -H<sub>2</sub>)(RCN)][BF<sub>4</sub>]<sub>2</sub>. The intact nature of the H-H bond in these derivatives has been established by the observation of substantial H-D coupling constants for the  $\eta^2$ -HD isotopomers and the short spin lattice relaxation times (*T*<sub>1</sub>) for the  $\eta^2$ -HD ligand. The H<sub>2</sub> ligand in these complexes is not substantially elongated indicating reduced or almost no Fe-H<sub>2</sub> back-bonding. The bound H<sub>2</sub> ligand is quite labile, upon its loss, one of the BF<sub>4</sub><sup>-</sup> counterions binds with the metal to afford *trans*-[(dpe)<sub>2</sub>Fe(BF<sub>4</sub>)(RCN)][BF<sub>4</sub>] derivative. Reactivity behaviour of the dihydrogen complexes toward Lewis bases such as acetonitrile, triethylamine, and piperidine has been studied. The X-ray structure of *trans*-[(dpe)<sub>2</sub>Fe(H)(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN)][BF<sub>4</sub>] has been determined.

### Introduction

Ever since the discovery of transition metal dihydrogen complexes by Kubas and co-workers<sup>1</sup> a large number of them have been synthesized and characterized<sup>2-5</sup>. It was found that the nature of the metal center and the ancillary ligands significantly influence the properties of the dihydrogen complexes<sup>2-4</sup>. Systematic investigations have been carried out on dihydrogen complexes of the type [(diphosphine)<sub>2</sub>M( $\eta^2$ -H<sub>2</sub>)(L)]<sup>n+</sup> (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  $\eta^2$ -H<sub>2</sub> moiety in order to study their influence on the properties of those complexes<sup>2-9</sup>. The bonding in dihydrogen complexes could be described as two-component type:  $\sigma$ -donation of electron density from the H<sub>2</sub> to vacant metal *d*-orbitals and back-donation of electron density from the filled metal *d*-orbitals to the  $\sigma^*$  orbitals of the H<sub>2</sub>. The back-bonding is important for the stabilization of the M-H<sub>2</sub> interaction; however, significant back-donation leads to the cleavage of the H-H bond<sup>10</sup>. Morris *et al.*<sup>11</sup> found that despite the absence of back-bonding in *trans*-[(dpe)<sub>2</sub>Fe( $\eta^2$ -H<sub>2</sub>)(CO)][OTf]<sub>2</sub> to be stable with respect to loss of H<sub>2</sub>. The stability was attributed to the strong  $\sigma$ -bond between the metal and the H<sub>2</sub>. Such instances of almost no back-bonding from the metal to the H<sub>2</sub> moiety are relatively scarce. The H<sub>2</sub> ligand under conditions of no back-donation (M→H<sub>2</sub>) usually

exhibits tremendous lability, which could be exploited in homogeneous catalysis.

We have previously reported a series of dicationic dihydrogen complexes of ruthenium *trans*-[(diphosphine)<sub>2</sub>Ru( $\eta^2$ -H<sub>2</sub>)(L)][BF<sub>4</sub>]<sub>2</sub> (diphosphine = dpe; L = nitrile<sup>12</sup>, phosphine and phosphite<sup>13</sup>, diphosphine = dpmm (Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>), L = phosphine, phosphite<sup>14</sup>). In order to study the influence of the group 8 metal on the properties of dihydrogen complexes of the type *trans*-[(dpe)<sub>2</sub>M( $\eta^2$ -H<sub>2</sub>)(RCN)]<sup>2+</sup> (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 H<sub>2</sub> or Ar. 1,2-bis(diphenylphosphino)ethane (dpe)<sup>15</sup>, (dpe)<sub>2</sub>Fe(H)<sub>2</sub>·2C<sub>7</sub>H<sub>8</sub>, (ref. 16) and *trans*-[(dpe)<sub>2</sub>Fe(H)( $\eta^2$ -H<sub>2</sub>)][BF<sub>4</sub>]<sup>6</sup> were prepared according to literature methods.

The <sup>1</sup>H and <sup>31</sup>P 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.  $^{31}\text{P}$  NMR chemical shifts have been measured relative to 85%  $\text{H}_3\text{PO}_4$  (as an external standard) in  $\text{CD}_2\text{Cl}_2$  and  $^{19}\text{F}$  NMR spectra with respect to  $\text{CFCl}_3$ . All  $^{31}\text{P}$  NMR spectra were proton decoupled unless otherwise noted. The proton  $T_1$  measurements were carried out at 400 MHz using the inversion recovery method<sup>17</sup>. 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.

*Preparation of trans-[(dppe)<sub>2</sub>Fe(H)(CH<sub>3</sub>CN)][BF<sub>4</sub>]  
(1a)*

An acetonitrile (10 mL) solution of *trans*-[(dppe)<sub>2</sub>Fe(H)( $\eta^2$ -H<sub>2</sub>)] [BF<sub>4</sub>] (200 mg, 0.2 mmol) under an atmosphere of H<sub>2</sub> 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<sub>2</sub>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<sub>2</sub>Cl<sub>2</sub> solution containing the hydride complex and a few drops of the nitrile via diffusion of Et<sub>2</sub>O at room temperature over a period of several days. Yield 72% (150 mg).

*Preparation of trans-[(dppe)<sub>2</sub>Fe(H)(RCN)][BF<sub>4</sub>] (R = CH<sub>3</sub>CH<sub>2</sub> 2a, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> 3a, CH<sub>2</sub>=CH 4a, C<sub>6</sub>H<sub>5</sub> 5a, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> 6a)*

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<sub>61</sub>H<sub>58</sub>BF<sub>4</sub>NP<sub>4</sub>Fe·CH<sub>2</sub>Cl<sub>2</sub>: C, 64.38; H, 5.22; N, 1.21. Found: C, 64.92; H, 5.66; N, 1.09.

*Preparation of trans-[(dppe)<sub>2</sub>Fe( $\eta^2$ -H<sub>2</sub>)(RCN)][BF<sub>4</sub>]<sub>2</sub> (R = CH<sub>3</sub> 1b, CH<sub>3</sub>CH<sub>2</sub> 2b, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> 3b, CH<sub>2</sub>=CH 4b, C<sub>6</sub>H<sub>5</sub> 5b, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> 6b)*

Similar procedures were employed for the preparation of these derivatives. A 20 mg portion of *trans*-[(dppe)<sub>2</sub>Fe(H)(RCN)][BF<sub>4</sub>] was placed in a 5 mm NMR tube capped with a septum. The tube was evacuated and filled with H<sub>2</sub> gas in three cycles after which time it was dissolved in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub> and then 4 equiv (11  $\mu\text{L}$ ) of HBF<sub>4</sub>·Et<sub>2</sub>O were added. The dihydrogen complexes formed were characterized using NMR spectroscopy.

*Observation of H-D isotopomers trans-[(dppe)<sub>2</sub>Fe( $\eta^2$ -HD)(RCN)][BF<sub>4</sub>]<sub>2</sub> (R = CH<sub>3</sub> 1c, CH<sub>3</sub>CH<sub>2</sub> 2c, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> 3c, CH<sub>2</sub>=CH 4c, C<sub>6</sub>H<sub>5</sub> 5c, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> 6c)*

The HD isotopomers were obtained as follows: A 20 mg portion of *trans*-[(dppe)<sub>2</sub>Fe(H)(RCN)][BF<sub>4</sub>] dissolved in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub> in a 5 mm NMR tube under an atmosphere of H<sub>2</sub> was allowed to freeze in a liquid N<sub>2</sub> bath. About 25  $\mu\text{L}$  of DBF<sub>4</sub> [prepared from HBF<sub>4</sub>·Et<sub>2</sub>O and D<sub>2</sub>O in the ratio 3:1 (v/v)] was added and the tube warmed up to room temperature. The tube was then transferred to the NMR probe and the probe rapidly cooled to 253 K. The HD isotopomers formed were observed by  $^1\text{H}$  NMR spectroscopy using the inversion recovery method.

*Reaction of trans-[(dppe)<sub>2</sub>Fe( $\eta^2$ -H<sub>2</sub>)(CH<sub>3</sub>CN)][BF<sub>4</sub>]<sub>2</sub> with Lewis bases*

The dihydrogen complex was generated as described above in a 5 mm NMR tube and the NMR spectrum was recorded. Then excess (10 equiv) base was added and the spectrum recorded again.

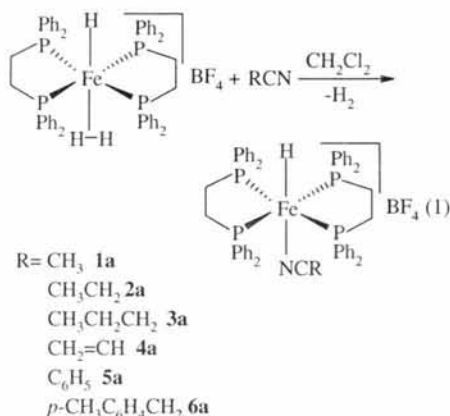
*X-ray structure determination of trans-[(dppe)<sub>2</sub>Fe(H)(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN)][BF<sub>4</sub>] 3a*

Red crystals of **3a** were obtained via slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of *trans*-[(dppe)<sub>2</sub>Fe(H)(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN)][BF<sub>4</sub>] 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-K $\alpha$  X-ray source. The SMART software was used for data acquisition and the SAINT software for data abstraction<sup>18</sup>. Absorption corrections were made using the SADABS and the pre-scans methods<sup>19</sup>. The structure was solved and refined using the SHELX programs<sup>20</sup>. 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<sub>4</sub>) which exhibited structural disorder. The two fluorine atoms exhibited positional disorder and were assigned partial occupancies and refined isotropically. The hydride ligand was located from a difference Fourier map 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*-[(dpepe)<sub>2</sub>Fe(H)(RCN)][BF<sub>4</sub>] (R = CH<sub>3</sub> **1a**, CH<sub>3</sub>CH<sub>2</sub> **2a**, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> **3a**, CH<sub>2</sub>=CH **4a**, C<sub>6</sub>H<sub>5</sub> **5a**, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> **6a**) have been prepared by substitution of the H<sub>2</sub> ligand in the dihydrogen complex *trans*-[(dpepe)<sub>2</sub>Fe(H)(η<sup>2</sup>-H<sub>2</sub>)] [BF<sub>4</sub>]<sup>6</sup> analogous to the preparation of certain ruthenium derivatives that we reported earlier (Eq. 1)<sup>12</sup>. The compounds **1a** and **5a** have been reported by other groups<sup>21,22</sup>. The products were obtained as dark yellow solids in yields ranging from 59 to 79%.



The <sup>1</sup>H 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, P<sub>cis</sub>) of *ca.* 46.0 to 47.0 Hz. The <sup>31</sup>P{<sup>1</sup>H} 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 <sup>1</sup>H NMR chemical shifts of Fe-H are upfield shifted compared to those of Ru-H in *trans*-[(dpepe)<sub>2</sub>Ru(H)(RCN)][BF<sub>4</sub>]<sup>12</sup> complexes whereas the <sup>31</sup>P{<sup>1</sup>H} NMR signals for the dpepe phosphorus nuclei experience downfield shifts of *ca.* 20 ppm. The upfield shift of the M-H signal in the <sup>1</sup>H 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<sup>6</sup>; 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 <sup>31</sup>P{<sup>1</sup>H} 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 triad<sup>23</sup>. In order to obtain some insight into the cavity formed by the sterically encumbered [(dpepe)<sub>2</sub>Fe(H)]<sup>+</sup> 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*-[(dpepe)<sub>2</sub>Fe(H)(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN)][BF<sub>4</sub>] **3a**

The ORTEP diagram of the *trans*-[(dpepe)<sub>2</sub>Fe(H)(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN)]<sup>+</sup> cation is shown in Fig. 1. The cation is made up of an octahedrally

Table 1—<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectral data (δ) for *trans*-[(dpepe)<sub>2</sub>Fe(H)(RCN)][BF<sub>4</sub>] complexes in CD<sub>2</sub>Cl<sub>2</sub>

R (Compd no)	δ(Fe-H)	<i>J</i> (H,P <sub>cis</sub> )	<sup>1</sup> H δ(R)	δ(CH <sub>2</sub> -CH <sub>2</sub> )	δ(Ph)	<sup>31</sup> P δ(dpepe)
CH <sub>3</sub> ( <b>1a</b> )	-20.81 (qnt, 1H)	46.0	1.76 (s, 3H, CH <sub>3</sub> )	2.47 (m, 4H) 1.96 (m, 4H)	6.56-7.34 (m, 40H)	83.9
CH <sub>3</sub> CH <sub>2</sub> ( <b>2a</b> )	-20.88 (qnt, 1H)	47.0	2.42 (q, 2H, CH <sub>2</sub> ) 0.66 (t, 3H, CH <sub>3</sub> )	2.42 (m, 4H) 1.92 (m, 4H)	6.61-7.48 (m, 40H)	82.7
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ( <b>3a</b> )	-20.91 (qnt, 1H)	46.0	2.22 (m, 4H, CH <sub>2</sub> CH <sub>2</sub> ) 0.47 (t, 3H, CH <sub>3</sub> )	2.42 (m, 4H) 1.92 (m, 4H)	6.57-7.28 (m, 40H)	83.6
CH <sub>2</sub> =CH ( <b>4a</b> )	-19.03 (qnt, 1H)	47.0	5.03 (d, 2H, CH <sub>2</sub> =CH) 5.33 (t, 1H, CH <sub>2</sub> =CH)	2.35 (m, 4H) 1.88 (m, 4H)	6.56-7.61 (m, 40H)	82.7
C <sub>6</sub> H <sub>5</sub> ( <b>5a</b> )	-19.27 (qnt, 1H)	47.0	6.81-7.44 (m, 5H, C <sub>6</sub> H <sub>5</sub> )	2.57 (m, 4H) 2.09 (m, 4H)	6.81-7.86 (m, 40H)	84.6
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ( <b>6a</b> )	-20.60 (qnt, 1H)	46.0	3.65 (m, 2H, CH <sub>2</sub> ) 2.25 (m, 3H, CH <sub>3</sub> ) 6.42-7.55 (m, 5H, C <sub>6</sub> H <sub>4</sub> )	2.41 (m, 4H) 1.93 (m, 4H)	6.42-7.55 (m, 40H)	82.8

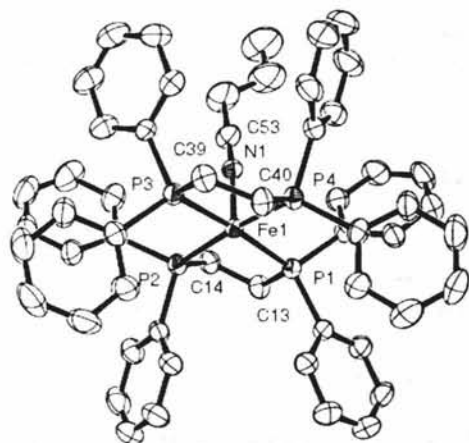


Fig. 1—ORTEP view of the *trans*-[(dppe)<sub>2</sub>Fe(H)(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN)]<sup>+</sup> **3a** cation at the 50% probability level.

coordinated 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, <sup>1</sup>H 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 dppe bite angles P(1)-Fe-P(2) and P(3)-Fe-P(4) are 83.30(4) and 83.73(4)° respectively. The Fe-P (dppe) bond lengths vary from 2.2343(11) to 2.2682(11) Å and the Fe-N(1) distance is 1.933(3) Å; the Fe-N bond length in *trans*-[(dppe)<sub>2</sub>Fe(CH<sub>3</sub>CN)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub><sup>24</sup> complex is 1.913(6) Å. The metal-N distance in the iron complex is much shorter than that in the *trans*-[(dppe)<sub>2</sub>Ru(H)(*p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>CN)][BF<sub>4</sub>] [2.134(8) Å]<sup>12</sup>. 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)<sub>2</sub>Fe(H)(RCN)][BF<sub>4</sub>] (R = CH<sub>3</sub> **1a**, CH<sub>3</sub>CH<sub>2</sub> **2a**, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> **3a**, CH<sub>2</sub>=CH **4a**, C<sub>6</sub>H<sub>5</sub> **5a**, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> **6a**)*

The protonation of the hydride complexes in CD<sub>2</sub>Cl<sub>2</sub> with 2 equiv of 54% HBF<sub>4</sub>·Et<sub>2</sub>O at room temperature afforded the corresponding dihydrogen complexes of the type *trans*-[(dppe)<sub>2</sub>Fe(η<sup>2</sup>-H<sub>2</sub>)(RCN)][BF<sub>4</sub>]<sub>2</sub> (R = CH<sub>3</sub> **1b**, CH<sub>3</sub>CH<sub>2</sub> **2b**, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> **3b**, CH<sub>2</sub>=CH **4b**, C<sub>6</sub>H<sub>5</sub> **5b**, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> **6b**) (Scheme 1). The <sup>1</sup>H NMR spectra (Table 4) consist of a broad singlet in the range δ -16.40 to -17.99 for the Fe-H<sub>2</sub>; definitive assignments of the <sup>1</sup>H NMR signals of the other moieties of the dihydrogen complexes were precluded due to the broadness of the remaining

Table 2—Crystallographic data for *trans*-[(dppe)<sub>2</sub>Fe(H)(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN)][BF<sub>4</sub>] **3a**

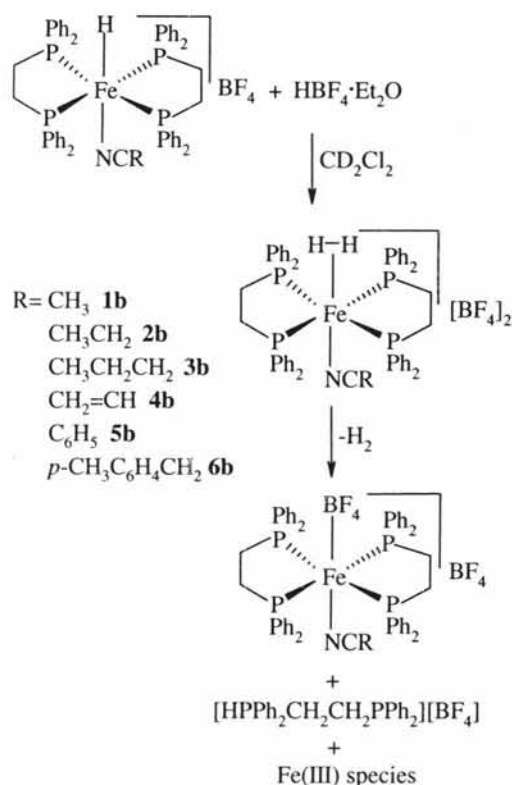
Formula	C <sub>56</sub> H <sub>56</sub> BF <sub>4</sub> NP <sub>4</sub> Fe
fw	1009.56
cryst syst	monoclinic
space group	P2 <sub>1</sub> /n
<i>a</i> , Å	13.485(2)
<i>b</i> , Å	16.926(3)
<i>c</i> , Å	21.717(3)
α, deg	90.00
β, deg	90.734(3)
γ, deg	90.00
<i>V</i> , Å <sup>3</sup>	4956.4(13)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.28
<i>T</i> , K	293(2)
<i>F</i> (000)	2104
λ, Å	0.710 73
μ, mm <sup>-1</sup>	0.488
<i>R</i> <sup>a</sup>	0.0580
<i>R</i> <sub>w</sub> <sup>a</sup>	0.1214

<sup>a</sup>*R* = Σ(|F<sub>o</sub>|-|F<sub>c</sub>|)/Σ(|F<sub>o</sub>|); *R*<sub>w</sub> = [Σ(|F<sub>o</sub>|-|F<sub>c</sub>|)<sup>2</sup>/Σw|F<sub>o</sub>|]<sup>1/2</sup> [based on reflections with *I* > 2σ(*I*)].

Table 3—Selected bond lengths (Å) and angles (deg) for *trans*-[(dppe)<sub>2</sub>Fe(H)(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CN)][BF<sub>4</sub>] **3a**

Fe(1)-N(1)	1.933(3)
Fe(1)-P(1)	2.2682(11)
Fe(1)-P(2)	2.2681(11)
Fe(1)-P(3)	2.2510(11)
Fe(1)-P(4)	2.2343(11)
N(1)-C(53)	1.134(4)
N(1)-Fe(1)-P(1)	92.70(9)
N(1)-Fe(1)-P(2)	87.37(9)
N(1)-Fe(1)-P(3)	93.17(9)
N(1)-Fe(1)-P(4)	97.85(9)
P(1)-Fe(1)-P(2)	83.30(4)
P(3)-Fe(1)-P(4)	83.73(4)
P(3)-Fe(1)-P(2)	96.56(4)
P(3)-Fe(1)-P(1)	174.11(4)
P(4)-Fe(1)-P(1)	95.88(4)
P(4)-Fe(1)-P(2)	174.75(4)

signals rendered by a Fe(III) species that was formed along with the dihydrogen complex. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra (Table 4) exhibit a singlet in the region δ 69.0-71.0 (dppe) for the dihydrogen complexes. In addition, the <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy indicates the presence of two other species along with some unreacted starting hydride complex; these species were identified as *trans*-[(dppe)<sub>2</sub>Fe(BF<sub>4</sub>)(RCN)][BF<sub>4</sub>] **7** (<sup>31</sup>P{<sup>1</sup>H}: δ 51.0 (s, 4P); <sup>19</sup>F: δ -144.36 {s, 4F, Fe-BF<sub>4</sub>}, -160.05 (br s, free BF<sub>4</sub><sup>-</sup>) and dppeH<sup>+</sup> (10.4, s, 2P)<sup>10</sup> respectively. Addition of a further two equiv of the acid results in the complete consumption of the



Scheme 1

starting material to yield a mixture of the dihydrogen complex,  $\text{dppeH}^+$ , and the  $\text{trans}[(\text{dppe})_2\text{Fe}(\text{BF}_4)(\text{RCN})][\text{BF}_4]$  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  $\text{BF}_4$ -bound iron derivative could result from the dihydrogen complex that loses the  $\text{H}_2$  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  $\text{H}_2$  bound *trans* to CO was found to be quite labile and underwent substitution by  $\text{BF}_4^-$  counterion<sup>11</sup>.

The NMR chemical shifts of the dihydrogen complexes follow the same trend as the precursor hydrides in comparison to their ruthenium counterparts<sup>12</sup>. Once again the basicity of the metal seems to play a vital role in dictating the bonding situations of these derivatives<sup>23</sup>. 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  $\text{trans}[(\text{diphosphine})_2\text{Fe}(\text{H}_2)(\text{X})]$  (diphosphine = dppe, depe;

Table 4— $^1\text{H}$  (only Fe- $\text{H}_2$  moiety) and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectral data ( $\delta$ ) for  $\text{trans}[(\text{dppe})_2\text{Fe}(\eta^2\text{-H}_2)(\text{RCN})][\text{BF}_4]_2$  complexes in  $\text{CD}_2\text{Cl}_2$

R (Compd no)	$^1\text{H}$ $\delta(\text{Fe-H}_2)^a$	$^{31}\text{P}$ $\delta(\text{dppe})$
$\text{CH}_3$ ( <b>1b</b> )	-17.09	71.8
$\text{CH}_3\text{CH}_2$ ( <b>2b</b> )	-17.45	60.5
$\text{CH}_3\text{CH}_2\text{CH}_2$ ( <b>3b</b> )	-17.42	69.5
$\text{CH}_2=\text{CH}$ ( <b>4b</b> )	-16.57	69.9
$\text{C}_6\text{H}_5$ ( <b>5b</b> )	-16.73	68.6
$p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2$ ( <b>6b</b> )	-17.48	68.7

<sup>a</sup>Broad singlet in all the cases

X = Cl, Br) with respect to the cleavage of the chelating phosphine and elimination as the protonated form as reported by Henderson<sup>25</sup>. Within a short period of time, our dihydrogen complexes lose the bound  $\text{H}_2$  ligand (free  $\text{H}_2$   $^1\text{H}$  NMR:  $\delta$  4.60, s) to afford a pink solution that was identified as **7**, this solution slowly precipitates a pink solid of the  $\text{BF}_4$  bound derivative. When the pink solid was dissolved in  $\text{CH}_3\text{CN}$  gave a compound of the formulation  $\text{trans}[(\text{dppe})_2\text{Fe}(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$  (**8-H<sub>3</sub>**) that was reported earlier<sup>24</sup>.

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

The H-D isotopomers  $\text{trans}[(\text{dppe})_2\text{Fe}(\eta^2\text{-HD})(\text{RCN})][\text{BF}_4]_2$  (R =  $\text{CH}_3$  **1c**,  $\text{CH}_3\text{CH}_2$  **2c**,  $\text{CH}_3\text{CH}_2\text{CH}_2$  **3c**,  $\text{CH}_2=\text{CH}$  **4c**,  $\text{C}_6\text{H}_5$  **5c**,  $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2$  **6c**) were generated by the addition of  $\text{DBF}_4$  to the iron hydride complexes in  $\text{CD}_2\text{Cl}_2$ . The HD isotopomers formed were observed using  $^1\text{H}$  NMR spectroscopy at 253 K using the inversion recovery pulse ( $180^\circ\text{-}\tau\text{-}90^\circ$ )<sup>17</sup>. The  $^1\text{H}$  NMR spectra display a triplet (Fig. 2) for the  $\eta^2\text{-HD}$  moiety. The  $J(\text{H,D})$  obtained were in the range 32 to 33 Hz from which the H-H distances ( $d_{\text{HH}}$ ) were calculated (Table 5)<sup>26,27</sup>.

The  $d_{\text{HH}}$  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  $J(\text{H,D})$  in all these derivatives suggests that the variation of  $\pi$ -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  $J(\text{H,D})$  (between 32 and 34 Hz) was insensitive for complexes with *trans* CO regardless of the other ligands involved<sup>28</sup>. In the ruthenium analogs we observed  $J(\text{H,D})$  of 27-28 Hz for the  $\eta^2\text{-HD}$  moiety that corresponds to  $d_{\text{HH}}$  of 0.95-0.96 Å indicating

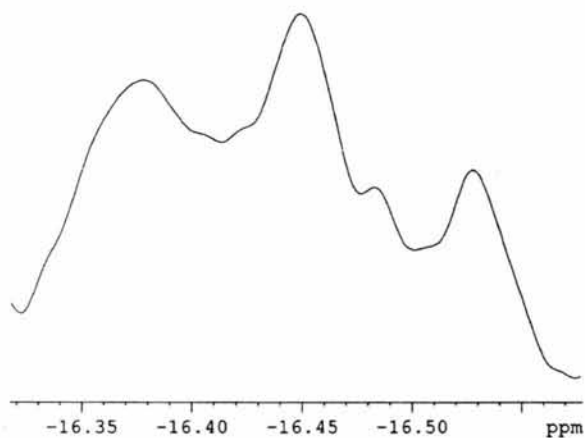


Fig. 2— $^1\text{H}$  NMR spectrum (hydride region) of *trans*-[(dppe) $_2\text{Fe}(\eta^2\text{-HD})(\text{CH}_2=\text{CHCN})][\text{BF}_4]_2$  (400 MHz, 253 K) in  $\text{CD}_2\text{Cl}_2$ . Resonance due to the  $\eta^2\text{-H}_2$  ligand has been nullified.

Table 5— $T_1$  (400 MHz, 253 K) data and the H-H distances [from  $J(\text{H,D})$ ] for *trans*-[(dppe) $_2\text{Fe}(\eta^2\text{-HD})(\text{RCN})][\text{BF}_4]_2$  complexes

R (Compd no)	$T_1$ (ms)	$J(\text{H,D})$ (Hz)	$d_{\text{H-H}}$ (Å)
$\text{CH}_3$ ( <b>1c</b> )	11.8	32	0.88
$\text{CH}_3\text{CH}_2$ ( <b>2c</b> )	12.1	33	0.86
$\text{CH}_3\text{CH}_2\text{CH}_2$ ( <b>3c</b> )	12.2	33	0.86
$\text{CH}_2=\text{CH}$ ( <b>4c</b> )	13.7	33	0.86
$\text{C}_6\text{H}_5$ ( <b>5c</b> )	12.4	33	0.86
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2$ ( <b>6c</b> )	12.1	32	0.88

substantial elongation of the H-H bond<sup>12</sup>. This is a result of a greater degree of back-bonding between the metal and the  $\sigma^*$  orbitals of the  $\text{H}_2$  moiety. We determined the  $\text{p}K_{\text{a}}$ 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  $\text{H}_2$  ligand in the dihydrogen complexes *trans*-[(dppe) $_2\text{Ru}(\eta^2\text{-H}_2)(\text{RCN})][\text{BF}_4]_2$  is reflected in their stabilities with respect to loss of the  $\text{H}_2$  ligand. The ruthenium derivatives were found to be stable for periods of *ca.* 2 days. Morris *et al.* found that despite the absence of back-bonding in *trans*-[(dppe) $_2\text{Fe}(\eta^2\text{-H}_2)(\text{CO})][\text{OTf}]_2$  (ref. 10) to be stable with respect to elimination of  $\text{H}_2$ . The stability was attributed to the formal charge on the iron and the strong  $\pi$ -acceptor trans to the  $\text{H}_2$  ligand resulting in a stronger  $\sigma$  interaction. However, in our dihydrogen complexes, a weaker  $\pi$ -acceptor nitrile relative to CO results in a reduced  $\sigma$  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  $\text{H}_2$ ) accompanied by the generation of **7** and certain Fe(III) species that we have not been able to identify.

#### $^1\text{H}$ spin lattice relaxation time measurements

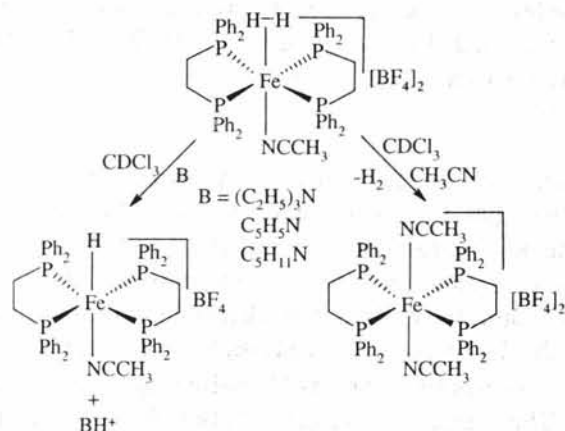
The dihydrogen complexes were found to be unstable with respect to loss of  $\text{H}_2$ , therefore, we were unable to carry out the  $T_1$  measurements at various temperatures. We however, determined the  $T_1$  values for the HD isotomers (**1c-6c**) using the inversion recovery method ( $180^\circ\text{-}\tau\text{-}90^\circ$  pulse sequence)<sup>17</sup> 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.

#### Reactivity studies

The protonation of **1a** in  $\text{CD}_3\text{CN}$  with 4 equiv of  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  at room temperature affords the dihydrogen complex *trans*-[(dppe) $_2\text{Fe}(\eta^2\text{-H}_2)(\text{RCN})][\text{BF}_4]_2$  ( $\text{R} = \text{CH}_3/\text{CD}_3$ ) as evidenced by  $^1\text{H}$  NMR spectroscopy. The dihydrogen complex shortly after its generation converts to *trans*-[(dppe) $_2\text{Fe}(\text{CD}_3\text{CN})_2][\text{BF}_4]_2$  (**8-D<sub>3</sub>**) as indicated by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **8-D<sub>3</sub>** displays a singlet at  $\delta$  55.0. When the protonation was carried out in  $\text{CDCl}_3$  in the presence of 10 equiv of  $\text{CH}_3\text{CN}$ , the *trans*-[(dppe) $_2\text{Fe}(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$  (**8-H<sub>3</sub>**) was obtained through the intermediacy of **1b**. We have been unable to determine the  $\text{p}K_{\text{a}}$ s of the dihydrogen complexes (**1b-6b**) due to the labile nature of the  $\text{H}_2$  ligand. However, when **1b** was reacted with Lewis bases such as triethylamine, pyridine, and piperidine, the  $\text{H}_2$  ligand undergoes deprotonation to give the precursor hydride complex and the protonated base (Scheme 2). We found that the analogous ruthenium complex *trans*-[(dppe) $_2\text{Ru}(\eta^2\text{-H}_2)(\text{CH}_3\text{CN})][\text{BF}_4]_2$  also undergoes deprotonation when reacted with excess acetonitrile<sup>29</sup>. More work is needed in order to understand the differing reactivity behaviour of the iron derivatives with respect to lability versus deprotonation of the  $\text{H}_2$  ligand.

#### Conclusion

New iron hydride complexes of the type *trans*-[(dppe) $_2\text{Fe}(\text{H})(\text{RCN})][\text{BF}_4]$  ( $\text{RCN} = \text{nitrile}$ ) have been prepared and characterized. The protonation reactions of the hydride derivatives afforded the corresponding dihydrogen complexes. The  $\text{H}_2$  ligand in the dihydrogen complexes do not seem to be substantially



Scheme 2

elongated as a result of reduced/almost no back-donation of electron density from the metal to the  $\sigma^*$  orbitals of  $H_2$ . The  $H_2$  ligand in these complexes was found to be quite labile, upon its loss affords a  $BF_4$  bound derivative *trans*-[(dppf) $_2$ Fe( $BF_4$ )(RCN)][ $BF_4$ ]. 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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