

A quantitative measure of the ionicity of selected iron hydride species by examination of the deuterium quadrupole coupling constant (DQCC)

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Abstract

The ionicity of the metal hydride bonds of a series of iron hydrides supported by multidentate phosphine donors has been determined by means of DQCC measurements of the isotopically labelled hydrides in concentrated solution in toluene.

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1. Introduction

The nature of the transition metal hydrogen bond is a key question in inorganic chemistry, not least because metal hydride species are key components in catalysis, and hydride migration to a small molecule bound to the metal centre is typically the penultimate step in catalytic cycles such as hydrogenation or hydrocyanation, and olefin polymerization [1]. It is common to regard hydride complexes as basic in the Brønsted/Lowry sense, based on the fact that many transition metal hydrides behave as proton acceptors, nevertheless, acidic behaviour can be observed in polar media [2]. The extent to which the metal hydrides are basic or acidic can be a useful guide to reactivity; strongly basic hydrides are more prone to undergo migration reactions to small molecules [3].

Quantitative measurement of hydride basicity is therefore of legitimate interest, and a variety of techniques have been employed to assess the basicity or a transition metal hydride. For terminal hydrides in conventional octahedral

coordination, these include (i) chemical assays by way of reaction of the transition metal hydride with a suitable Lewis acid, e.g. BF_3 , $\text{B}(\text{C}_6\text{F}_5)_3$ and Ph_3C^+ [4]; (ii) measurement of the hydrogen bonding between the hydride and added acidic substrates [5–7] and (iii) studies of migration/insertion behaviour [8]. A fourth, more direct assessment of hydride basicity or, more correctly, hydride ionicity is by reference to the deuterium quadrupole coupling constant (DQCC) of the metal hydride, whose magnitude may be easily determined by T_1 measurement of the corresponding metal deuteride, and the value so obtained is manipulated to give an estimate of hydride ionicity [9]. Measurement of DQCC for Mo, W, Zr, Mn, Re, Os and Rh metal hydrides has been made previously, where the metal centres possess standard octahedral geometries, and the hydride ligands have been *trans* to different ligands; DQCC values for bridging deuterides in rhenium carbonyl clusters has been the subject of a recent work [10], and have also been used as evidence for intermolecular hydrogen bonding to an η^2 -bound dihydrogen ligand [11]. Here, DQCC values of a series of iron hydrides, supported by chelating phosphines in octahedral array, are measured and assessed, and thus information about the Fe–D bonding mode and, by extension, the Fe–H bond becomes available for comparison.

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2. Experimental

Unless otherwise stated, all reactions and manipulations were performed under an atmosphere of inert gas by means of Schlenk or glovebox techniques. All solvents were rigorously dried over appropriate drying agents. NMR solutions were prepared from rigorously degassed *protio* and *deutero* solvents, and distilled from trap to trap immediately before use. ^1H and $^2\text{H}\{^1\text{H}\}$ NMR spectra were referenced to the residual *protio/deutero* shift of the methyl resonance in toluene- d_8/h_8 (2.09 ppm); $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced to external neat $\text{P}(\text{OMe})_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm). ^1H , $^{31}\text{P}\{^1\text{H}\}$ and $^2\text{H}\{^1\text{H}\}$ NMR spectra were acquired upon a Bruker DRX400 instrument operating at 400.132, 161.979 and 61.421 MHz, respectively. T_1 relaxation times were determined by a standard inversion-recovery sequence (π pulse; variable delay (τ); $\pi/2$ pulse) over a range of temperatures. A typical experiment involved a 0.56 mol L^{-1} solution and data collection from $16 \times 1\text{D}$ experiments, with incrementally varying delay, and application of a non-linear, three-parameter fitting routine of the xWINNMR software package. Radio frequency pulse durations (π and $\pi/2$) were recalibrated at each temperature step. The temperature was calibrated by ^1H NMR spectroscopy with respect to a neat methanol sample. All hydrides were prepared by literature procedures [12]. *cis*- $\text{Fe}(\text{dmpe})_2\text{D}_2$ (**1-d₂**) and *cis*- $\text{Fe}(\text{PP}_3)\text{D}_2$ (**2-d₂**) were prepared by recrystallization of the parent hydrides from $\text{MeOH-}d_4$. *trans*- $\text{Fe}(\text{dmpe})_2(\text{OC}=\text{OD})\text{D}$ (**3-d₂**) was prepared by following the literature for **3** [13].

2.1. *cis*- $\text{Fe}(\text{dmpe})_2(\text{SC}(\text{=NMe})\text{D})\text{D}$ (**4-d₂**) and *trans*- $\text{Fe}(\text{dmpe})_2(\text{SC}(\text{=NMe})\text{D})\text{D}$ (**5-d₂**)

$\text{Me-N}=\text{C}=\text{S}$ (6 mg, 0.084 mmol) in THF was added to an NMR tube containing **1-d₂** (30 mg, 0.084 mmol). ^{31}P NMR spectroscopy indicated quantitative formation of two new species: (i) *cis*- $\text{Fe}(\text{dmpe})_2(\text{SC}(\text{=NMe})\text{D})\text{D}$ (**4-d₂**); and (ii) *trans*- $\text{Fe}(\text{dmpe})_2(\text{SC}(\text{=NMe})\text{D})\text{D}$ (**5-d₂**), in a ratio of 3:1. Upon standing for 3 h, **5-d₂** had formed exclusively. Recrystallization from Et_2O gave **5-d₂** as a red solid (21 mg, 58%). Compound **4-d₂**: ^1H NMR (THF- d_8): δ 8.23 (s, residue, *SCHNMe*), 2.99 (s, 3H, *SCHNMe*), 1.43, 1.36 (m, 8H, *CHH'*), 1.23, 1.12 (m, 24H, *PMeMe'*), -11.46 (m, residue, Fe-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8): δ 55.5 (ddd, $^2J_{\text{PP}} = 21$, 21, 33 Hz, 1P), 67.8 (ddd, $^2J_{\text{PP}} = 21$, 42, 151 Hz, 1P), 71.4 (ddd, $^2J_{\text{PP}} = 33$, 42, 151 Hz, 1P), 73.1 (ddd, $^2J_{\text{PP}} = 21$, 21, 42 Hz, 1P). ^2H NMR (THF- h_8): δ 8.4 (s, 1H, *N(Me)D*), -11.5 (br s, 1H, Fe-D). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- h_8): 184.1 (br s, *SCDNMe*), 48.6 (s, *SCHNMe*), 35.7, 34.0, 30.2, 28.4, 22.0, 21.1, 18.4, 17.1, 16.3 (m, $\text{CH}_2\text{CH}_2\text{PMeMe}'$). Compound **5-d₂**: ^1H NMR (THF- d_8): δ 8.44 (s, residue, *SCH*), 2.96 (s, 3H, *NMe*), 2.22, 1.59 (m, 8H, *CHH'*), 1.47, 1.26 (m, 24H, *PMeMe'*), -25.44 (q, residue, $J_{\text{PH}} = 50$ Hz, Fe-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8): δ 71.6 (m). ^2H NMR (THF- h_8): δ 8.4 (s, 1H,

N(Me)D), -25.4 (s, 1H, Fe-D). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- h_8): 174.4 (br s, *SCDNMe*), 47.2 (s, *SCDNMe*), 32.8 (m, *PCH}_2*), 25.4, 16.9 (m, *PMe*).

2.2. *trans*- $\text{Fe}(\text{dmpe})_2(\text{SC}(\text{=N}^+(\text{Me})\text{C}(\text{=S})\text{N}^-\text{Me})\text{D})\text{D}$ (**6-d₂**)

$\text{Me-N}=\text{C}=\text{S}$ (6 mg, 0.084 mmol) was added to a THF solution of **5-d₂**. The mixture was allowed to stand for 1 h, at the end of which time NMR spectroscopy indicated quantitative formation of *trans*- $\text{Fe}(\text{dmpe})_2(\text{SC}(\text{=NMe})\text{DC}=\text{SNMe})\text{D}$ (**6-d₂**). ^1H NMR (THF- d_8): δ 10.84 (s, residue, *SC(=N(Me)C=SNMe)H*), 3.46 (s, 3H, *SC(=N(Me)C=SNMe)H*), 3.07 (s, 3H, *SC(=N(Me)C=SNMe)H*), 2.11, 1.78 (m, 8H, *CHH'*), 1.48, 1.39 (m, 24H, *PMeMe'*), -24.21 (q, residue, $J_{\text{PH}} = 51$ Hz, Fe-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8): δ 69.1 (m). ^2H NMR (THF- h_8): δ 10.8 (s, 1H, *N(Me)D*), -24.2 (br s, 1H, Fe-D). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): 194.6 (s, *SC(=NMe)DC=SNMe*), 173.2 (br s, (*SC(=NMe)DC=SNMe*)), 41.7 (s, *SC(=NMe)DC=SNMe*), 33.1 (s, *SC(=NMe)DC=SNMe*), 32.2 (m, *PCH}_2*), 24.4, 15.7 (m, *PMe*).

2.3. $\text{Fe}(\text{PP}_3)(\text{tolyl-}d_7)\text{D}$ (**7**)

A solution of **2-d₂** (10 mg, 28×10^{-6} mol) in toluene- d_8 (0.5 mL) was irradiated for 2 h. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicated complete consumption of the starting material and formation of isomeric $\text{Fe}(\text{PP}_3)(\text{tolyl-}d_7)\text{D}$ (**7**), presumably *meta* and *para* with respect to the aryl C-Me bonds of toluene- d_8 . ^2H NMR (toluene- d_8): δ -15.0, -15.1 (m, Fe-D). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8): δ 176.3 (dt, 1P, $J_{\text{PP}} = 19$ Hz), 63.1 (dd, 2P, $J_{\text{PP}} = 21$ Hz), 57.6 (dt, 1P).

3. Results and discussion

T_1 relaxation of ^2H nuclei depends almost exclusively on quadrupole interactions with the electric field gradient at the nucleus and is given by Eq. (1) [9,14–16]. Inasmuch as the electric field gradient is not influenced by excited electronic states [10], the DQCC value should be a fairly sensitive measure of structure and geometry of the deuteride ligand:

$$\frac{1}{T_1} = \frac{3\pi^2}{50} \left\{ \frac{(2I+3)(\text{DQCC})^2(1+\eta^2/3)}{I^2(2I-1)} \right\} \left\{ \frac{\tau_c}{(1+\tau_c^2\omega^2)} + \frac{4\tau_c}{(1+4\tau_c^2\omega^2)} \right\} \quad (1)$$

I = nuclear spin, ω = Larmor frequency, η = asymmetry parameter of electric field gradient, τ_c = molecular rotational correlation time.

Since T_1 minima ($T_{1\text{min}}$) occur when $\omega\tau_c = 0.62$ for ^1H and ^2H nuclei [9], Eq. (1) then allows for calculation of DQCC based upon: (i) the measured values of $T_{1\text{min}}$, and (ii) the frequency of the deuterium channel on the NMR

spectrometer (61.421 MHz for this work). Since the asymmetry parameter, η , is small or zero for terminal deuterides, the η^2 term is generally ignored and substitution of $I = 1$ values gives the simplified Eq. (2) and thus a measure of DQCC [15,17]

$$(\text{DQCC})^2 = \frac{1.489 \times 61.421 \text{ (MHz)}}{T_{1\text{min}} \text{ (s)}} \quad (2)$$

By this method it is only possible to reach the temperature range for ^2H $T_{1\text{min}}$ in viscous media (160–250 K), and therefore spectra were acquired from concentrated solutions in toluene- h_8 or toluene- d_8 (0.5–0.6 mol L $^{-1}$) [9,16]. Depending on the viscosity of the solution, the temperature at which $T_{1\text{min}}$ is reached may vary, but the value of $T_{1\text{min}}$ by definition remains constant. Applied to the purely covalent H–D molecule, the measured DQCC value of 227 kHz represents the covalent limit, and estimates of ionicity may be made on this simple basis (Eq. (3)) [9]

$$\text{ionicity (\%)} = (1 - (\text{DQCC}/227))100\% \quad (3)$$

The smallest experimental DQCC value is that of 33.0 kHz for lithium deuteride, which corresponds to a ionicity of 85.1%. A theoretical DQCC value of 19.74 kHz has been calculated for Rb–H [18], although for the alkali metal hydrides, a correlation between the DQCC value and M–H distance is unsupportable, given that (i) M–H bond lengths vary by some 1.0 Å down Group 1, and (ii) DQCC is theoretically a function of the M–H bond distance [9]. Transition metal hydrides exhibit much higher DQCC values, and consequently return ionicities that are generally substantially less (10–20%) than these values. Because transition metal hydrides lie in a fairly uniform range with respect to M–H bond length, even across a period, or down a group, DQCC measurements should reasonably reflect the degree of polarization of the transition metal hydride bond; selected values appear in Table 1.

The iron hydrides, *cis*-Fe(dmpe) $_2$ H $_2$ (**1**) (dmpe = 1,2-dimethylphosphino)ethane), and *cis*-Fe(PP $_3$)H $_2$ (**2**) (PP $_3$ = P(CH $_2$ CH $_2$ PM e_2) $_3$) are in fact Brønsted bases. Both **1** and **2** may be protonated by weak acids such as MeOH or EtOH to give cationic iron hydrides possessing both terminal hydrides and η^2 -bound dihydrogen donors. As Lewis bases, both **1** and **2** will also undergo irreversible reaction with stoichiometric BH $_3$ ·THF to give Lewis base/BH $_3$ adducts in which the metal centre is bound to a terminal and bridging hydride to the boron centre [19,20]. In the absence of any quantitative measure of the degree of polarization of Fe–H bonds, an estimate of DQCC values for these and related hydrides is desirable. Preparation of phosphine-stabilized iron deuterides is straightforward; dissolution of **1** and **2** in MeOH- d_4 or EtOH- d_6 efficiently labels the hydride positions to give **1-d $_2$** and **2-d $_2$** , *cis*-Fe(dmpe) $_2$ D $_2$ and Fe(PP $_3$)D $_2$ respectively. The reaction is reversible and was monitored by ^1H and ^2H NMR spectroscopy and the endpoint was signalled by quantitative formation of the η^2 -dihydrogen complex (Scheme 1); removal of the solvent gave pure **1-d $_2$** and **2-d $_2$** .

The T_1 relaxation time for the equivalent ^2H nuclei of **1-d $_2$** was measured over a range of temperatures in a concentrated toluene- h_8 solution (0.56 mol L $^{-1}$). $T_{1\text{min}}$ occurred at 170 K with a value of 19.0 ms (Fig. 1).

Substitution of this value into Eqs. (2) and (3) gives DQCC = 69.4 kHz, and a basicity of 69.4%. In the case of *cis*-Fe(PP $_3$)H $_2$ (**2**), use of the quadridentate phosphine results in two chemically different hydrides, H $_a$, and H $_b$, *trans* and *cis* to the apical phosphine, respectively. The deuterium nuclei in **2-d $_2$** rapidly equilibrate at room temperature but as the temperature is lowered to 190 K, two separate environments become distinguishable (Fig. 2).

The mechanism of exchange, may involve the loss of phosphine arm to form a 5-coordinate iron centre, how-

Table 1
 $T_{1\text{min}}$, DQCC, and ionicity values for selected metal hydrides

Hydride/deuteride	$T_{1\text{min}}$ (ms)	T (K)	DQCC (kHz)	Ionicity (%)	Reference
Li–D			33.0	85	[27]
ZrCp $_2$ D $_2$			46.7	79	[28]
MoCp $_2$ D $_2$			52.0	77	[29]
Rh(PP r_3) $_2$ Cl $_2$ D			136.0	40	[9]
W(PMe $_3$) $_2$ (CO) $_2$ (NO)D	22.7	178	55.0	76	[9]
W(PPh $_3$) $_2$ (CO) $_2$ (NO)D	22.7	178	55.0	76	[9]
Mn(PEt $_3$) $_2$ (CO) $_3$ D	15.4	183	66.7	71	[9]
<i>cis</i> -Re(PMe $_3$) $_4$ (CO)D	12.4	163	74.4	67	[9]
Re(PMe $_3$) $_2$ (NO)(CO)D $_2$	14.0, 16.1	173	70.0, 65.3	69, 71	[9]
Ru(PP $_3$) $_2$ D $_2$	17.0, 15.8		73.3, 76.1	68, 66	[17]
PP $_3$ ' = P(CH $_2$ CH $_2$ PPh $_2$) $_3$					
Os(PP $_3$) $_2$ D $_2$	14.4		79.7	65	[17]
Rh(triphos)H $_3$	16.5		83.2	63	[30]
triphos = MeC(CH $_2$ PPh $_2$) $_3$					
<i>trans</i> -Mo(dmpe) $_2$ (NO)D	53		36.0	84	[24]
<i>mer</i> -Mo(PMe $_3$) $_3$ (CO)(NO)D	48		38.0	83	[24]
[Ru(binap)(η^6 -C $_6$ H $_6$)D] $^+$	16		89.0	60	[31]
<i>trans</i> -Mo(depe) $_2$ (=NBt $_3$)D			43.0	81	[32]

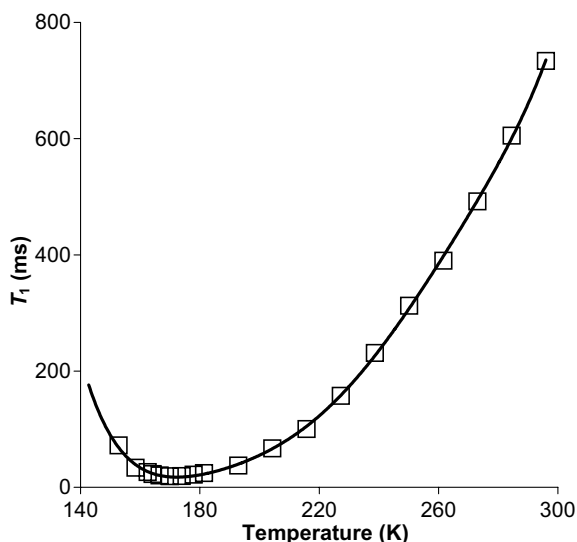
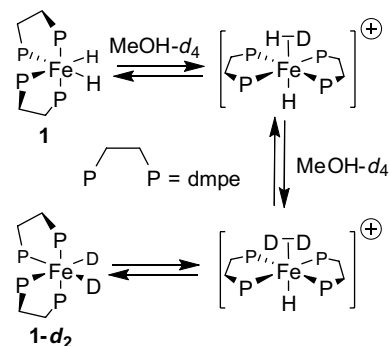


Fig. 1. The dependence of ^2H T_1 (ms) with temperature (K) for *cis*- $\text{Fe}(\text{dmpe})_2\text{D}_2$ (**1-d₂**) in toluene-*h*₈ (0.56 M solution) at 61.421 MHz.

ever, this has not been established unequivocally [21]. T_1 measurements in the ^2H NMR spectrum at temperatures close to coalescence were not attempted as the observed resonances were too broad. The minimum T_1 relaxation

times for each deuteride occurred between 175 and 180 K. At these temperatures, however, the deuterides were presumed to be exchanging sufficiently rapidly to average the measured $T_{1\text{min}}$ (Fig. 3). The average $T_{1\text{min}}$ was estimated to be 20.6 ms, which corresponds to a DQCC value of 66.6 kHz and a ionicity of 70.7%. The electronic similarity between **1** and **2**, *viz.* each metal centre binds to a chelating array of four alkylphosphine donors and two hydride ligands, is sufficient to account for the very similar ionicities observed.

Several daughter hydrides are available with respect to **1-d₂** and **2-d₂** by insertion of a small molecule in the Fe–H bond or by C–H activation. The formato derivative, *trans*- $\text{Fe}(\text{dmpe})_2(\text{OC}=\text{OD})\text{D}$ (**3-d₂**), may be accessed from **1-d₂**, simply by placing a toluene solution of the latter under an atmosphere of CO_2 [13]. Likewise, when stoichiometric $\text{MeN}=\text{C}=\text{S}$ was added to **1-d₂**, a mixture of *cis*-(**4-d₂**) and *trans*- $\text{Fe}(\text{dmpe})_2(\text{SC}(=\text{NMe})\text{D})\text{D}$ (**5-d₂**) was obtained. A double insertion product, *trans*- $\text{Fe}(\text{dmpe})_2(\text{SC}(=\text{N}^+(\text{Me})\text{C}(=\text{S})\text{N}^-\text{Me})\text{D})\text{D}$ (**6-d₂**), was obtained by adding a second equiv $\text{MeN}=\text{C}=\text{S}$ to **5-d₂**. Finally, a C– ^2H activation product, *cis*- $\text{Fe}(\text{PP}_3)(\text{tolyl-}d_7)\text{D}$ (**7**), was

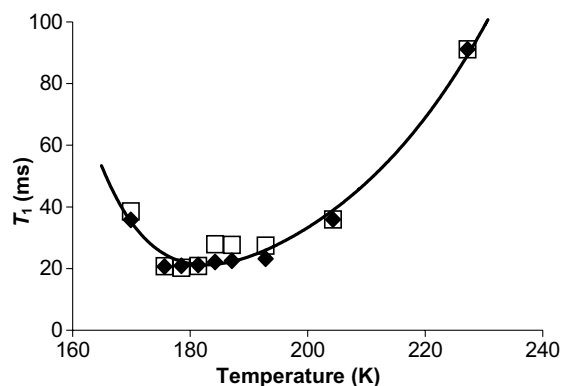


Fig. 3. The dependence of ^2H T_1 (ms) with temperature (K) for *cis*- $\text{Fe}(\text{PP}_3)\text{D}_2$ (**2-d₂**) in toluene-*h*₈ (0.56 M solution). D_a (\square) represents the deuteron *trans* to the apical phosphorus donor, and D_b (\blacklozenge), *cis* to that site.

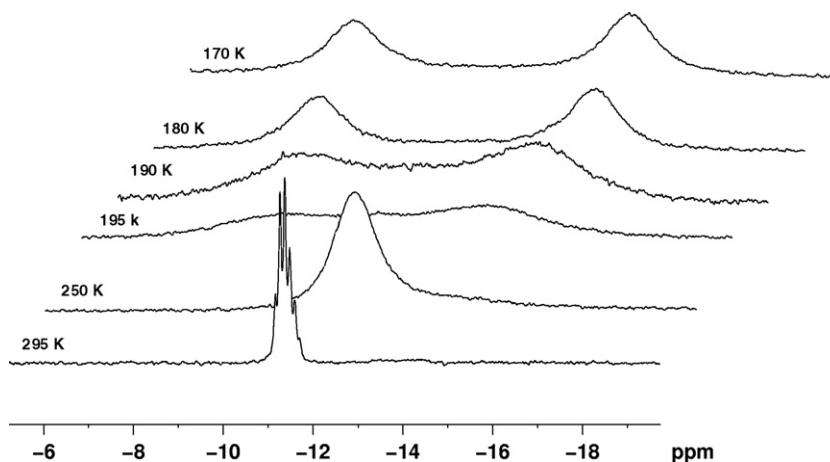


Fig. 2. Variable temperature ^2H NMR spectrum of *cis*- $\text{Fe}(\text{PP}_3)\text{D}_2$ (**2-d₂**) in toluene-*h*₈ at 61.421 MHz.

formed by irradiation of *cis*-Fe(PP₃)H₂ (**2**) in toluene-*d*₈. While isomeric *meta*-tolyl-7 and *para*-tolyl-7 were formed, the deuteride resonances were coincident and treated as identical in the DQCC experiment. The $T_{1\text{min}}$ values of **3–7** were all recorded (Fig. 4), and the DQCC values and ionicities are collected in Table 2.

The solution-state DQCC measurements and basicity estimates made above represent the first such calculations for iron complexes, and with the manganese derivatives, e.g. Mn(PMe₃)₂(NO)₂D [9], the only examples of such measurements made for first-row transition metal hydrides. The ionicities of the iron deuteride in each case were in the range of 69–73%, and point to an average Fe–H ionicity of near 71%. These figures are directly applicable to the iron hydride parents **1**, **2**, etc., all of which share the same ionicities in that the degree of polarization towards the hydrogen nucleus must necessarily be the same as in their deuterated isotopomers. Previous estimates of Fe–H ionicity are unavailable in the literature, and estimates of ionicities based upon the difference in electronegativities are substantially lower than the values measured here, whatever electronegativity scale is chosen [22]. The classic iron

carbonyl hydride, Fe(CO)₄H₂, is a reasonably strong Brønsted acid (p*K*_a = 4.4) [2]. Nevertheless, by substituting the iron centre with electron-donating phosphorus donors the hydride ligands in Fe(dmpe)₂H₂ (**1-d**₂) and Fe(PP₃)H₂ (**2-d**₂) are rendered much more basic as evidenced by their facile reaction with weakly acidic alcohol to give η²-bound dihydrogen complexes, and also by the reduction of carbon dioxide in the case of **1** [12,23]. Even given that the present estimates of ionicity for **1** and **2** derive from an *ad hoc* scale that fixes the ionicity of the H–D molecule at 0% (Eq. (3)), designation of the hydrides as ionic is reasonable on the basis above. On the other hand, the average ionicity value of 71% observed for the FeD(H) series compares well with estimates of basicity for the W, Re and Rh etc. hydrides that were evaluated by earlier DQCC experiments (Table 1) [9]. Compound **2-d**₂, bound to the quadridentate donor P(CH₂CH₂PMe₂)₃, returned an ionicity of 71%. This is to be compared to ionicities of 68% and 65% calculated for its isostructural Group 8 congeners Ru(PP'₃)D₂ and Os(PP'₃)D₂ respectively, where the phosphine is the phenyl-substituted P(CH₂CH₂PPh₂)₃ [17]. If the difference in basicity arising from phenyl vs. methyl phosphine substitution may be disregarded, the more ionic nature of the hydride ligands in **2-d**₂ may be reasonably ascribed to reduced polarization of electron density in M–H operating in the harder, less polarizable first-row metal. The difference in basicity between the quadridentate phosphines employed works to the same end, however, on these data it is unclear how much electron density is shunted to the iron centre and in turn to the hydride ligands by virtue of electron-releasing substituents (i.e. the methyl groups) on the phosphorus donors. The most reactive transition metal hydrides identified so far, e.g. *trans*-Mo(dmpe)₂(NO)H with a ionicity of 84%, are those where the hydride is activated by a nitrosyl or carbyne ligand disposed *trans* to the hydride [24]. These species exhibit a pronounced reactivity and are able to undergo insertion reactions with a large array of small, unsaturated organic molecules, including alkynes, alkenes, aldehydes, ketones and even imines (Scheme 2) [25].

The most reactive of the iron hydrides studied in the course of this work are not under any significant *trans* influence and they only react with activated heteroallenes such as CO₂ and Me–N=C=S, cf. **3-d**₂, *trans*-Fe(dmpe)₂(OC=OD)D, and **4-d**₂, *cis*-Fe(dmpe)₂(SC(=NMe)D)D [13]. While the distribution of ionicity values was fairly nar-

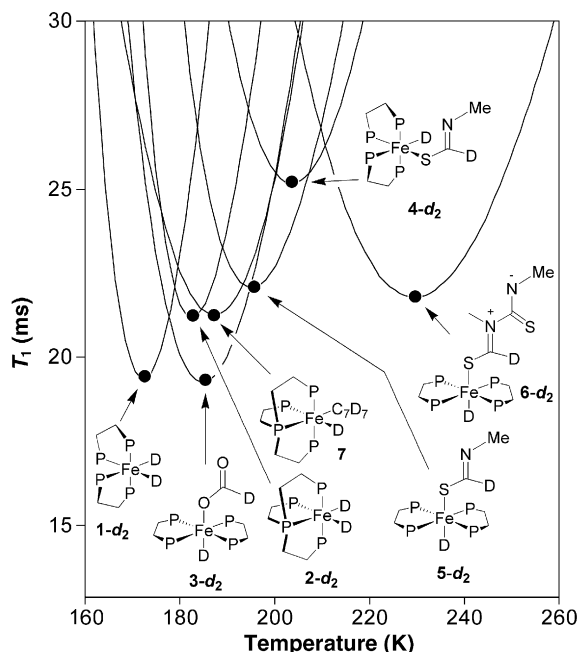
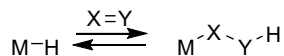


Fig. 4. The dependence of ²H T_1 (ms) with temperature (K) for iron deuteride series **1–7**, showing $T_{1\text{min}}$ (●).

Table 2

$T_{1\text{min}}$, DQCC, and ionicity values for selected transition metal hydrides

Hydride/deuteride	$T_{1\text{min}}$ (ms)	T (K)	DQCC (kHz)	Ionicity (%)
<i>cis</i> -Fe(dmpe) ₂ D ₂ (1-d ₂)	19.0	170	69.4	69
<i>cis</i> -Fe(PP ₃) ₂ D ₂ (2-d ₂)	20.6	179	66.6	71
<i>trans</i> -Fe(dmpe) ₂ (OC=OD)D (3-d ₂)	18.8	183	69.7	69
<i>cis</i> -Fe(dmpe) ₂ (SC(=NMe)D)D (4-d ₂)	25.0	201	60.5	73
<i>trans</i> -Fe(dmpe) ₂ (SC(=NMe)D)D (5-d ₂)	22.1	230	64.3	72
<i>trans</i> -Fe(dmpe) ₂ (SC(=N ⁺ (Me)C(=S)N ⁻ Me)D)D (6-d ₂)	21.8	230	64.8	72
Fe(PP ₃)(C ₇ D ₇)D (7)	20.8	187	66.3	71



Scheme 2.

row, the trends in $T_{1\text{min}}$ and DQCC values are informative. The most ionic iron hydride examined was *cis*-Fe(dmpe)₂(SC(=NMe)D)D (**4-d₂**), although insertion into its Fe–D/H bond has not yet been observed [26]. On the other hand, *trans*-Fe(dmpe)₂(SC(=NMe)D)D (**5-d₂**), less ionic than its isomer **4-d₂**, *cis*-Fe(dmpe)₂(SC(=NMe)D)D, was sufficiently nucleophilic to undergo reaction with a second equiv of Me–N=C=S to give **6-d₂**, *trans*-Fe(dmpe)₂(SC(=N⁺(Me)C(=S)N[–]Me)D)D. The less ionic complexes, *cis*-Fe(dmpe)₂D₂ (**1-d₂**), *cis*-Fe(PP₃)D₂ (**2-d₂**) and *trans*-Fe(dmpe)₂(OC=OD)D (**3-d₂**) are the only species within the series to undergo clean insertion reactions; the tolyl-derivative, **7**, gave several such insertion products. Presumably, for **7**, the aryl residue may compete in a migratory insertion reaction. For the iron centres studied in this treatment, the important observation is that both the quadridentate phosphine and 2 equiv. of the bidentate phosphine returned similar hydride ionicities when bound to a Fe(II) centre.

4. Conclusion

²H $T_{1\text{min}}$ values of iron phosphines bearing terminal deuterides have been measured and used to provide estimates of their DQCC. In turn, the DQCC values so obtained have been used to provide estimates of the deuteride/hydride ionicity of each iron complex. The experiments performed here gave an average value of 71% ionicity for phosphine supported iron hydride complexes, pointing to a substantial degree of polarization in the iron hydrogen bond.

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