Kinetics of formation of dihydrogen complexes: protonation of *cis*-[FeH$_2${P(CH$_2$CH$_2$PPh$_2$)$_3$} with acids in tetrahydrofuran †

Manuel G. Basallote,* Joaquín Durán, M. Jesús Fernández-Trujillo, M. Angeles Máñez and Javier Rodríguez de la Torre

Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real 11510, Cádiz, Spain

Reaction of *cis*-[FeH$_2${P(CH$_2$CH$_2$PPh$_2$)$_3$}] with acids in tetrahydrofuran solution leads first to *cis*-[FeH(H$_2$){P(CH$_2$CH$_2$PPh$_2$)$_3$}]$^+$ followed by slower substitution of co-ordinated H$_2$ by N$_2$ or the anion of the acid. The kinetics of formation of the dihydrogen complex has been studied electrochemically by following the time dependence of the current intensity under conditions at which the starting dihydride is oxidised and the dihydrogen complex is not. The protonation reactions are first order with respect to the concentration of both the iron complex and the acid HX, with second-order rate constants at 25 °C ranging from 1.7×10^{-4} (HBF$_4$·Et$_2$O) to 3.4×10^{-2} dm^3 mol^{-1} s^{-1} (HBr). Reactions with DX are faster and the resulting values of the kinetic isotope effect (k.i.e.) are 0.45 (CF$_3$SO$_3$H), 0.62 (HCl) and 0.64 (HBr). The inverse k.i.e. for these reactions differs markedly from the normal k.i.e. observed in reactions of metal hydrides with bases and suggests a late transition state with a structure close to that of the dihydrogen complex. Chemical transformations along the reaction coordinate are proposed to consist of a series of hydrogen-bonded structures ranging from a weakly hydrogen-bonded metal hydride to a weakly hydrogen-bonded dihydrogen complex.

Since the initial discovery of metal complexes containing the η^2-H$_2$ ligand,[1] most work on them has concentrated on their synthesis, characterisation and reactivity[2] but the kinetic and mechanistic aspects of their reactions have been little explored. Protonation of hydride complexes with strong protic acids is today a routine procedure for the preparation of dihydrogen complexes,[3–6] but there are also some reports of protonations with weak acids such as alcohols and thiols.[7,8] Although the reaction can be formally represented by equation (1), the site
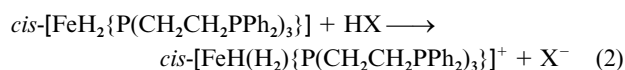
$$L_nMH + H^+ \longrightarrow L_nM(H_2)^+ \qquad (1)$$

for the initial proton attack and the nature of the protonating species are not clear. Several possibilities have been discussed,[3] including attack at the metal centre or at a ligand (H or L). Evidence suggests that proton attack on a co-ordinated hydride or the M−H bond is the initial step in the mechanism of protonation of hydride complexes with strong acids,[3,9] but protonations are usually carried out in aprotic solvents in which most acids are weak and so protonation with weak acids is more representative of the general synthetic reaction. As a continuation of our interest in the mechanistic aspects of reactions of molybdenum[10] and iron[11] complexes with polydentate phosphines, we decided to carry out a kinetic study of the protonation of the hydride complex *cis*-[FeH$_2${P(CH$_2$CH$_2$PPh$_2$)$_3$}] with several acids in tetrahydrofuran (thf) solution, because in this solvent acids as strong in water as HCl and triflic acid (CF$_3$SO$_3$H) are weak.[12,13] On the other hand, the presence of the tripodal ligand P(CH$_2$CH$_2$PPh$_2$)$_3$ avoids the possibility of *cis–trans* isomerisation and protonation leads directly to the dihydrogen complex without possible complications caused by side-reactions. The synthesis and properties of the starting complex and the reaction product, *cis*-[FeH(H$_2$){P(CH$_2$CH$_2$PPh$_2$)$_3$}]$^+$, are well illustrated in the literature.[14–16] The mechanistic aspects of the protonation reaction are discussed in
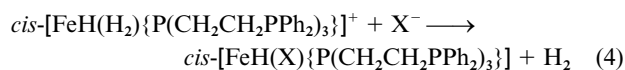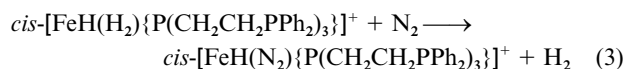
this work and compared with those reactions of acidic metal hydrides.[17] The differences in the kinetics of proton transfers from metal hydrides to bases and from acids to metal hydrides suggest different geometries of the transition state for both types of reaction.

Results and Discussion

Protonation of *cis*-[FeH$_2${P(CH$_2$CH$_2$PPh$_2$)$_3$}] with acids has been reported[14–16] to lead to the corresponding *cis*-hydridodihydrogen complex, and ^{31}P NMR spectra recorded at −35 °C in thf under a nitrogen atmosphere showed that reaction (2) is complete in less than 1 h when HX is HCl, HBr or

$$\begin{aligned}&\textit{cis-}[\text{FeH}_2\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}] + \text{HX} \longrightarrow \\ &\qquad \textit{cis-}[\text{FeH}(\text{H}_2)\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^+ + \text{X}^- \quad (2)\end{aligned}$$

triflic acid. No intermediates or side-products are observed and once the conversion into the dihydrogen complex has been completed no more spectral changes are observed during 1 h at −35 °C. If the sample is then warmed to room temperature the signals of the previously formed dihydrogen complex disappear slowly, with development of new signals which indicate substitution of co-ordinated H$_2$ by N$_2$ or the anion of the acid, equations (3) and (4). These substitution reactions are well

$$\begin{aligned}&\textit{cis-}[\text{FeH}(\text{H}_2)\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^+ + \text{N}_2 \longrightarrow \\ &\qquad \textit{cis-}[\text{FeH}(\text{N}_2)\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^+ + \text{H}_2 \quad (3)\end{aligned}$$

$$\begin{aligned}&\textit{cis-}[\text{FeH}(\text{H}_2)\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^+ + \text{X}^- \longrightarrow \\ &\qquad \textit{cis-}[\text{FeH}(\text{X})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}] + \text{H}_2 \quad (4)\end{aligned}$$

illustrated in the literature[14] and were not studied in detail because they are slow compared to the protonation process and also because the coupling patterns observed in the spectra of P(CH$_2$CH$_2$PPh$_2$)$_3$ complexes reduce the signal intensities and make difficult the study of the substitution process. However, it is important to note that the time-scales for the protonation and the substitution reactions are so different that the kinetics of

protonation can be studied without interference. Unfortunately, attempts to study the kinetics of reaction (2) using stopped-flow were unsuccessful because results for the reaction with some acids are not very reproducible and for other acids the spectra show the formation of species different from those in equations (2)–(4). Although the presence of traces of O_2 in the flow circuit may explain some of the complications observed in the stopped-flow measurements, we have also obtained strong evidence on the existence of photochemical processes, which may affect either the starting complex or the reaction product in equation (2). We are unable to determine at this time the nature of these processes, but our observations indicate the need for a different experimental method for studying the kinetics of formation of this kind of dihydrogen complex. For this reason we decided to use an electrochemical procedure, which avoids complications caused by photochemical processes and subsequent reactions of the dihydrogen complex. The simpler experimental set-up also reduces the possibility of oxygen intake to the reaction cell.

Kinetics of formation of the dihydrogen complex

The fundamentals of the electrochemical procedure are based on several literature reports, which show that oxidation of dihydrogen complexes occurs at potentials higher than that of the parent hydrides. Actually, an additive ligand approach has been proposed to estimate the electrochemical potentials $E_{\frac{1}{2}}$ (vs. NHE) for six-co-ordinate iron-(III) and -(II) complexes,[18] equation (5) where ΣE_L represents the contributions of the different

$$E_{\frac{1}{2}} = 1.10 \, \Sigma E_L - 0.43 \qquad (5)$$

ligands in the complex. The values of E_L are -0.4 for H^- and ≈ 0.8 for H_2,[18,19] which lead to more positive potentials for dihydrogen complexes than for hydride compounds containing the same coligands. As a consequence, for reactions such as (6)

$$L_5MH + HX \longrightarrow L_5M(H_2)^+ + X^- \qquad (6)$$

there is a wide range of potentials at which L_5MH is oxidised but the dihydrogen complex is not and so the kinetics of reaction can be monitored by measuring the time dependence of the limiting current at one of the intermediate values of potential. The values of $E_{\frac{1}{2}}$ calculated from equation (5) for the dihydride and the hydridedihydrogen iron complexes of $P(CH_2CH_2PPh_2)_3$ are 0.01 and 1.33 V, whereas the experimental values are -0.24 and 0.94 V,[14] respectively. Although the agreement between the $E_{\frac{1}{2}}$ values is not too good in this case, there is still a range of potentials wide enough to allow kinetic measurements. Since the values of E_L for Cl^-, Br^- and $CF_3CO_2^-$ are -0.24, -0.22 and -0.15,[18a] respectively, formation of the substitution products with these anions would add some contribution to the limiting current at potentials close to $E_{\frac{1}{2}}$ for cis-$[FeH(H_2)\{P(CH_2CH_2PPh_2)_3\}]^+$ and so the reaction was monitored at a potential close to $E_{\frac{1}{2}}$ for the dihydride complexes (-0.1 V). In this way complications of the kinetic traces by substitution reactions following the initial formation of the dihydrogen complex are minimised. Moreover, the experiments were carried out at low concentrations of HX under a nitrogen atmosphere to favour the formation of the hydridedinitrogen complex, which is oxidised at potentials close to that of the corresponding hydridedihydrogen compound (the value of E_L for N_2 is[18a] 0.68, and the experimental $E_{\frac{1}{2}}$ for $[FeH(N_2)\{P(CH_2CH_2PPh_2)_3\}]^+$ is 1.11 V). These experimental cautions and the much slower rate of the substitution processes make negligible the distortion of experimental kinetic traces. Thus, Fig. 1 includes a typical curve showing the time dependence of the current intensity for the reaction of cis-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ with acids in thf. Before addition of the acid, vigorous stirring of the sample keeps the intensity constant at the nega-
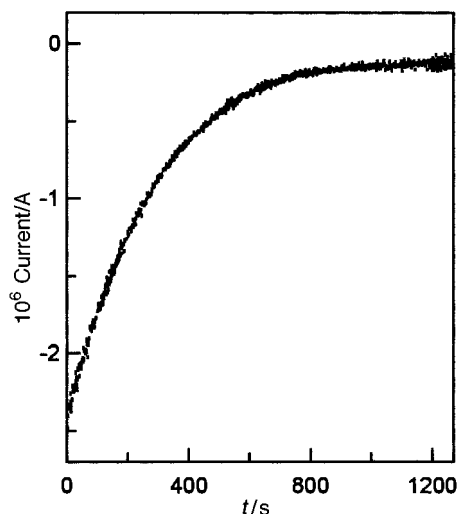

Fig. 1 Typical kinetic trace for the reaction of cis-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ with acid excess in thf at 25 °C ($[HBF_4 \cdot Et_2O] = 23.19 \times 10^{-4} \text{ mol dm}^{-3}$). Ordinate values represent the intensity of current measured at a platinum-disc electrode maintained at -0.1 V (vs. NHE) with vigorous stirring

tive value corresponding to the limiting current for oxidation of the dihydride complex. Following the addition of an excess of acid, formation of the dihydrogen complex decreases the concentration of cis-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ and the intensity changes to zero. These curves can be fitted by a single exponential and the values derived for the rate constants, k_{obs}, have been deposited. The reproducibility of the data and the internal consistency of k_{obs} values reveal that this electrochemical procedure overcomes the problems quoted above for stopped-flow measurements. The dependence of k_{obs} on the concentration of acid is illustrated in Fig. 2 for the reaction with CF_3SO_3H and CF_3SO_3D. Fig. 3 shows that the linear dependence is maintained for all the other acids, equations (7) and (8). The values

$$k_{obs} = k_{HX}[HX] \qquad (7)$$

$$k_{obs} = k_{DX}[DX] \qquad (8)$$

of the second-order rate constants k_{HX} and k_{DX} in thf solution at 25.0 °C are included in Table 1 and reveal a significant effect of the nature of the acid. The kinetic isotope effect (k.i.e.), expressed as k_{HX}/k_{DX}, is also included in Table 1 and is always lower than one, showing that reaction (2) occurs with an inverse k.i.e.

Mechanism of formation of the dihydrogen complex

Protonation of cis-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ with acids [equation (2)] can be formally considered as acid–base equilibria involving proton transfer from HX to a co-ordinated hydride. Kinetic results show that formation of the dihydrogen complex occurs without accumulation of any reaction intermediate, and the values of the rate constants in Table 1 indicate that protonation is slow, as observed for other proton-transfer reactions which also require extensive electronic reorganisation, such as reactions of carbon acids,[20] proton transfers from metal hydrides,[17] and reactions of complexes containing co-ordinated dinitrogen[21] or unsaturated hydrocarbons.[22] For example, self-exchange proton transfer in acidic metal hydrides, equation (9),

$$L_nMH + L_nM^- \longrightarrow L_nM^- + L_nMH \qquad (9)$$

and their reactions (10) with a base B are also slow processes,

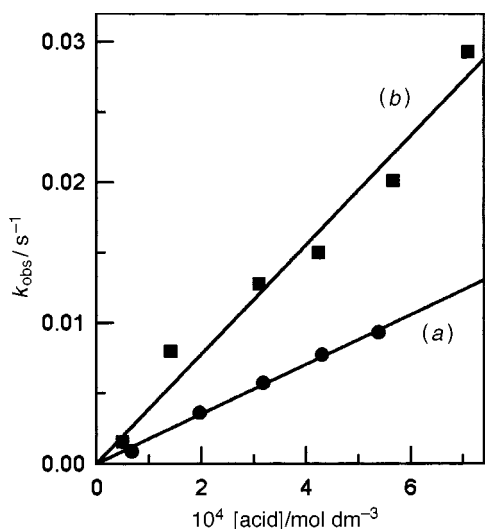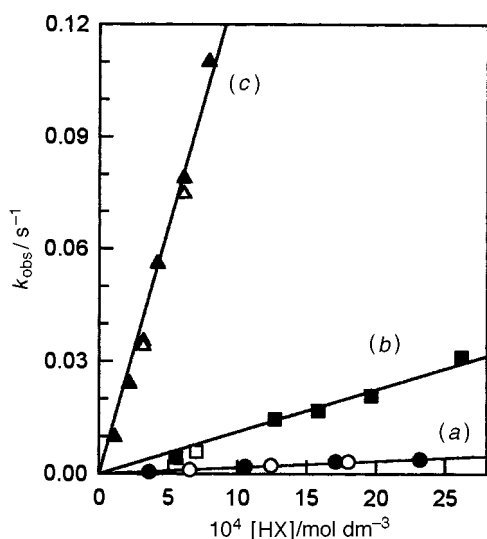$$L_nMH + B \longrightarrow L_nM^- + HB^+ \qquad (10)$$

Fig. 2 Dependence of the pseudo-first-order rate constant on the acid concentration for the reaction of cis-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ with CF_3SO_3H (*a*) and CF_3SO_3D (*b*) at 25 °C in thf and 0.05 mol dm^{-3} NBu$_4$BF$_4$

Fig. 3 Dependence of the pseudo-first-order rate constant on the acid concentration for the reaction of cis-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ with HBF$_4$·Et$_2$O (*a*), CF$_3$CO$_2$H (*b*) and HCl (*c*). All data were obtained in thf at 25.0 °C in the presence of NBu$_4$BF$_4$ at a concentration of 0.05 (filled symbols) or 0.10 mol dm^{-3} (hollow symbols)

with rate constants that correlate well with the thermodynamic driving force for the reaction and yield excellent Bronsted plots.[17] The kinetic isotope effect observed for these reactions in which the metal hydride acts as the proton donor is normal and close to 3.7, in agreement with values calculated from a weak interaction model.[23] On the contrary, reactions in which the metal hydride acts as the proton acceptor [equation (2)] occur with an inverse k.i.e., and the rate of reaction does not always appear to increase with the strength of the acid.

The effect of the acid. Although the values of k_{HX} in Table 1 span over two orders of magnitude, it is not possible to establish a detailed correlation with pK_a values because of the lack of extensive acidity data in thf. The rate of protonation seems to increase with the acidity of HX when X$^-$ is CF$_3$CO$_2^-$, Cl$^-$ or Br$^-$, but the k_{HX} increase is very small for what one would expect from the acidity of these compounds in water. Moreover, the smaller values of k_{HX} are obtained for the stronger acids HBF$_4$·Et$_2$O and CF$_3$SO$_3$H.

Literature values of pK_a in thf show that the acids used in this work are very weak in this solvent. Thus, a pK_a of 7.83 has

Table 1 Second-order rate constants and kinetic isotope effects for the reaction of cis-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ with acids in thf at 25.0 °C in the presence of 0.05 mol dm^{-3}NBu$_4$BF$_4$[a]

HX	$10^{-2}k_{HX}/dm^3$ mol^{-1} s^{-1}	$10^{-2}k_{DX}/dm^3$ mol^{-1} s^{-1}	k_{HX}/k_{DX} exptl.	calc.[b]
HBF$_4$·Et$_2$O	0.017(1)			
CF$_3$CO$_2$H	0.112(4)			
CF$_3$SO$_3$H	0.176(3)	0.39(2)	0.45(2)	0.06,[c] 0.87[d]
HCl	1.32(4)	2.14(9)	0.62(3)	0.47
HBr	3.4(1)	5.3(3)	0.64(4)	0.39

[a] The numbers in parentheses represent the standard deviation in the last significant digit. [b] Values calculated with equation (15). [c] Calculated assuming free H$^+$. [d] Calculated for OH groups.

been reported[13] for triflic acid, and most of the other acids are expected to be even weaker. However, it must be remembered that the pK_a value refers to the concentration of H$^+$ in solution, and it does not distinguish between the fractions of acid which exist as HX molecules and as ion pairs. For a solvent of low relative permittivity as thf, the behaviour of acids must be represented as in equation (11),[13] where K_d represents the ten-

$$HX \overset{K_d}{\rightleftharpoons} H^+ + X^- \overset{K_{ip}}{\rightleftharpoons} (H^+, X^-)_{ip} \qquad (11)$$
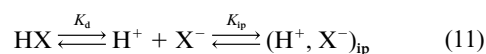
dency of HX to dissociate and K_{ip} is a measure of the stability of the ion pair. Homoconjugation equilibria may also lead to the formation of HX$_2^-$ species, but it is reasonable to think that these species are not formed to a great extent under the low concentrations of acid used in this work. So, the experimental values of K_a correspond to equation (12) which is related to K_d

$$K_a = \frac{[H^+][X^-]}{[HX] + [(H^+, X^-)_{ip}]} \qquad (12)$$

and K_{ip} by expression (13). The value of K_a reduces to K_d or to

$$K_a = K_d/(1 + K_d K_{ip}) \qquad (13)$$

$1/K_{ip}$ for acids with low or high tendency to dissociation, respectively. As the values of K_{ip} in thf are of the order of 10^6 dm^3 mol^{-1} and higher,[13] the concentration of H$^+$ is very low even in solutions of highly dissociated acids, and there is thus the possibility that the low values of k_{HX} for reaction (2) are the result of slow formation of the dihydrogen complex through attack on cis-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ by H$^+$ at low concentration. However, this possibility can be ruled out because in that case the reaction should be retarded by addition of X$^-$, and deposited results and Fig. 3 show that the value of k_{HX} for HBF$_4$·Et$_2$O remains unchanged within error when the concentration of NBu$_4$BF$_4$ increases from 0.05 to 0.10 mol dm^{-3}. Lower concentrations of electrolyte could not be used because they lead to poorly defined kinetic traces. As this acid is so strong that it does not exist in molecular form,[24] it can be concluded that the dihydrogen complex is formed through reaction of cis-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$ with the ion pair. For the other acids, HX molecules provide an additional reaction pathway and the experimental values of k_{HX} may include contributions from attacks on the dihydride by the molecules and the ion pairs. As all experiments were carried out in the presence of NBu$_4$BF$_4$ excess, dissociated H$^+$ will be ion-paired preferentially to BF$_4^-$ and the larger values of k_{HX} for the other acids indicate a significant contribution of the HX attack to the rate of reaction. Deposited data and Fig. 3 show that the effect of the concentration of NBu$_4$BF$_4$ on the value of k_{HX} is also negligible for the other acids, which suggests that reaction with these acids occurs essentially through attack by HX molecules. Thus, the apparently anomalous sequence of k_{HX} values with

acid strength in Table 1 seems to be the result of contributions from parallel attacks by HX and $(H^+,X^-)_{ip}$ to the rate of reaction, with attack by ion pairs being slower because of the reduced probability of effective collisions between *cis*-[FeH$_2${P(CH$_2$CH$_2$PPh$_2$)$_3$}] and ion pairs.

The kinetic isotope effect and the nature of the transition state. The other significant feature of kinetic data in Table 1 is the inverse k.i.e. observed for these reactions. There are not many kinetic data in the literature for reactions of the type shown in equation (2), but Henderson and Oglieve[25] reported an inverse equilibrium isotope effect of 0.39 for the reaction of [WH$_2$(η^5-C$_5$H$_5$)$_2$] with HCl to form [WH(H$_2$)(η^5-C$_5$H$_5$)$_2$]$^+$. Unfortunately, rate constants could not be measured in that case because the reaction is too fast and the kinetics is also complicated by the subsequent conversion of the dihydrogen complex into its trihydride tautomer. Rapid formation of dihydrogen compounds as intermediates has also been observed in the formation of related polyhydride metal complexes but the kinetic details of these reactions remain unknown.[26,27] There are also several reports of inverse k.i.e. for other reactions of metal hydrides, as hydrogenation of organic substrates, reductive eliminations, and insertions into M−H bonds.[28] The inverse isotope effects for these reactions are usually interpreted either as an inverse k.i.e. on an elementary single-step reaction with a late transition state or as the result of an inverse thermodynamic isotope effect on a preequilibrium.[28]

Although theoretical calculations are often limited by the simplifications carried out, comparison of observed isotope effects with those predicted by theory are very useful to obtain mechanistic information. If it is assumed that the isotope effect results exclusively from the differences in the zero-point energies, it can be calculated[28] with equation (14), where h and k_B

$$\frac{k_{HX}}{k_{DX}} =$$
$$\exp\left\{\frac{-hc}{2k_BT}\left[\sum_i(v_{i(H)}^\ddagger - (v_{i(D)}^\ddagger)) - \sum_i(v_{i(H)} - v_{i(D)})\right]\right\} \quad (14)$$

are the Planck and Boltzmann constants, c is the speed of light, $v_{i(H)}$ and $v_{i(D)}$ are the stretching frequencies in the fundamental state for molecules containing both isotopes, and $v_{i(H)}^\ddagger$ and $v_{i(D)}^\ddagger$ are the stretching frequencies in the transition state. For reactions as those represented by equation (2), in which there is a proton transfer between two heavy fragments, further reasonable simplifications are that only vibrational modes corresponding to the stretching of bonds involving the isotopically labelled atom have to be considered and that stretching frequencies for the deuteriated and undeuteriated species differ by a factor of $2^{\frac{1}{2}}$. Under these conditions and taking numerical values, equation (14) reduces to (15), where

$$k_{HX}/k_{DX} = \exp\left[7.06 \times 10^{-4}\left(\sum_i v_{i(H)} - \sum_i v_{i(H)}^\ddagger\right)\right] \quad (15)$$

the frequencies must be expressed in cm^{-1} and summations must be taken, both for the fundamental and the transition states, over the bonds involving the proton that is being transferred. This equation predicts an inverse k.i.e. for transition states with the proton bound more strongly than in the fundamental state. Protonation of metal hydrides with HX [equation (2)] involves the breaking of the H−X bond and formation of H−H and Fe−(H$_2$) bonds. If the reaction is assumed to occur through a single-step mechanism involving a very late transition state (almost complete formation of bonds), the theoretical value can be calculated from the stretching frequencies of these three bonds. Although vibrations of co-ordinated H$_2$ are not observed usually in the IR spectra, H−H stretching is estimated to appear in the range 3100–2400 cm^{-1} for complexes with d_{H-H}
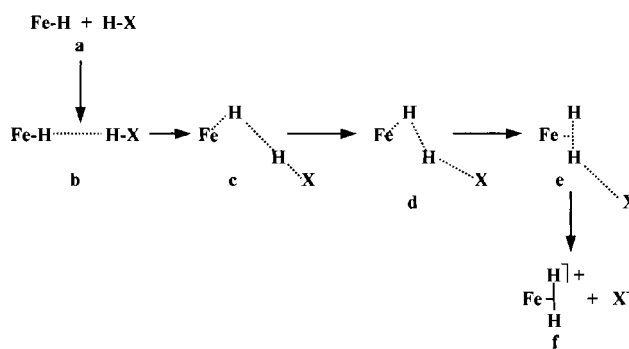
Scheme 1

between 0.8 and 1.0 Å.[2a] As the distance between hydrogen atoms of H$_2$ in the related complex *trans*-[FeH(H$_2$)(dppe)$_2$]$^+$ is 0.82 Å,[29] a reasonable value for $\tilde{v}_{H-H}$ is 3000 cm^{-1}. The stretching of the M−H$_2$ bonds appears in the range[2a] 850–950 cm^{-1} and so an approximate value of 900 cm^{-1} can be used for the iron complexes. Finally, the values of $\tilde{v}_{H-Cl}$, $\tilde{v}_{H-Br}$ and $\tilde{v}_{H-O}$ can be taken as 2836, 2559 and 3700 cm^{-1}, respectively.[30] Substitution of these frequencies in equation (15) leads to the calculated values of k_{HX}/k_{DX} in Table 1. The values obtained for HCl and HBr are slightly lower than those found experimentally, and the experimental value for triflic acid lies between those calculated assuming free H$^+$ and undissociated acid. Thus, despite the simplifications carried out, the theory predicts an inverse kinetic isotope effect of similar magnitude to those found experimentally for the protonation of *cis*-[FeH$_2${P-(CH$_2$CH$_2$PPh$_2$)$_3$}] and so formation of the dihydrogen complex can be represented by the mechanism outlined in Scheme 1. Electrostatic interaction between the partially negative metal-bound hydride and the partially positive proton of the acid leads initially to an adduct **b**. As the H−H interaction increases there is a weakening of the Fe−H and H−X bonds (**c**) that becomes more and more important (**d** and **e**) and finally leads to the reaction products **f**. Structures **b** to **e** represent different extents of interaction ranging from a weakly hydrogen-bonded metal hydride **b** to a weakly hydrogen-bonded dihydrogen complex **e**. The values of the kinetic isotope effect for the different acids would indicate transition states with structures close to that represented by **e** because isotope effects for very early transition states such as **b** or **c** are expected to be substantially higher. The alternative interpretation of the inverse k.i.e. as the result of an inverse isotope effect in an equilibrium previous to the rate-determining step is difficult to differentiate from the previous one and so the possibility of rapid formation of an intermediate with a structure close to that of the reaction product followed by rate-determining reorganisation of the intermediate cannot be ruled out. One possibility is that protonation occurs at the metal to form a classical trihydride in a fast preequilibrium followed by rate-determining intramolecular H, H coupling to give the dihydrogen complex (Scheme 2). As the preequilibrium involves the breaking of the H−X bond and formation of one Fe−H bond with a stretching frequency close to 1800 cm^{-1}, the values of the thermodynamic isotope effect calculated for this equilibrium are in all cases normal and very different from the experimental results. So if the inverse experimental k.i.e. is the result of an inverse thermodynamic isotope effect on a preequilibrium, the structure of the intermediate must be close to that of **d** or **e** and Scheme 1 would be then also a good representation of the structural changes along the reaction coordinate.

In the last few years there have been several reports of hydrogen-bonded species that may serve as models for the intermediate structures proposed for the formation of dihydrogen complexes. Most examples contain intramolecular hydrogen bonds between a co-ordinated hydride and acidic N−H or O−H groups of a coligand.[31] Although it can be argued that the interaction can be facilitated in these cases by the structure of
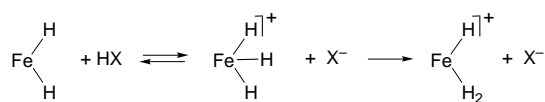
Scheme 2

the hydrogen-bond donor, which places the acidic proton at a position suitable for interaction with the basic co-ordinated hydride, there are also reports of intermolecular hydrogen bonds involving metal hydrides[32,33] or dihydrogen complexes[6,34] and a molecule or ion in the second co-ordination sphere. As an example, interaction of $[Os(H_2)Br(dppe)_2]^+$ with BF_4^- and PF_6^- places a fluorine of the anion close to the acidic H_2 ligand,[6] a situation very similar to that of structure **e** in Scheme 1. On the other hand, the classical hydride $[ReH_5(PPh_3)_3]$ forms adducts with indole and imidazole which contain $ReH \cdots H-N$ hydrogen bonds[33] similar to that shown in structure **c** of Scheme 1. These hydrogen bonds are unconventional because the acceptor does not contain a lone pair, and Crabtree and co-workers[34] proposed for them the term dihydrogen bonds. In all cases of crystallographically characterised dihydrogen bonds, the acidity of the donor is not enough to cause complete proton transfer to the acceptor, but it is reasonable to think that these adducts will be transformed into the corresponding dihydrogen complexes when the process is thermodynamically favoured.

Experimental

All preparations and sample manipulations were carried out under an atmosphere of argon or N_2 using Schlenk and syringe techniques. Tetrahydrofuran and other solvents used in preparative work were obtained from SDS and dried and deoxygenated immediately before use. The complexes *cis*-[FeH$_2$-{P(CH$_2$CH$_2$PPh$_2$)$_3$}] and *cis*-[FeH(H$_2$){P(CH$_2$CH$_2$PPh$_2$)$_3$}]$^+$ were prepared by literature procedures,[14,15] although FeCl$_2$ was replaced in some cases by $[Fe(MeCN)_6][BF_4]_2$ as the starting iron material.[35] Hydrogen chloride and HBr were generated from methanol and chlorotrimethylsilane or bromotrimethylsilane, respectively; DCl and DBr were obtained in a similar way using CD$_3$OD. All other acids and reagents were obtained from Aldrich. The acid concentration was determined by diluting with water (50 cm^3) an aliquot (1–3 cm^3) of the thf solution and titrating with KOH using phenolphthalein indicator. The results obtained were reproducible only for freshly prepared solutions (*ca* 30 min) and so solutions for kinetic studies were prepared and titrated immediately before kinetic runs.

The NMR spectra were obtained with a Varian Unity 400 spectrometer. The positions of the signals observed at room temperature for the iron dihydride and hydridedihydrogen complexes do not differ significantly from those published previously.[14,15] Since the protonation reactions are too fast to be monitored at room temperature, NMR experiments were carried out at low temperature by adding one or two drops of acid solution to a solution of the starting complex. The addition was made with the sample placed in the magnet and previously cooled at $-90\,°C$. In this way no reaction occurs during preparation of the sample and the experiment can be started by warming the sample to the desired temperature ($-35\,°C$) before starting the acquisition of the spectra.

Kinetic experiments were carried out with an EG&G Princeton Applied Research Model 263A potentiostat/galvanostat equipped with a thermostatted cell, a platinum-disc working electrode, a platinum-wire secondary electrode and a Ag–AgNO$_3$ (acetonitrile) reference electrode. All measurements were made under a nitrogen atmosphere in the presence of 0.05 mol dm^{-3} NBu$_4$BF$_4$. Potentials were measured with respect to the ferrocenium–ferrocene couple but are reported referenced to NHE using the conversion[2a] $E_{\frac{1}{2}}$ (NHE) = $E_{\frac{1}{2}}$ (ferrocenium–ferrocene) + 0.55. The working potential for kinetic runs was -0.1 V and it was selected from cyclic voltammograms of the

iron dihydride complex before and immediately after addition of acids. For kinetic experiments, 5–8 cm^3 a vigorously stirred thf solution of the iron dihydride complex (2×10^{-5} mol dm^{-3}) and the added electrolyte were purged with N_2 and allowed to equilibrate at the selected potential. Once the reading of current intensity was stable, HX solution (0.1–0.5 cm^3) was added rapidly with a Hamilton gas-tight syringe and the resulting current intensity *vs.* time curves were recorded with the standard software of the potentiostat. The files were then exported and reformatted to be analysed in an Acorn 5000 computer using the software of an Applied Photophysics SX17MV stopped-flow instrument. All measurements were carried out under pseudo-first-order conditions using an excess of HX and the curves could be fitted well by a single exponential. The first-order dependence on the concentration of iron complex was confirmed by the absence of significant changes of the rate constant with the concentration of complex at fixed [HX].

References

1 G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451.
2 (*a*) P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1992, **121**, 155; (*b*) D. M. Heinekey and W. J. Oldham, jun., *Chem. Rev.*, 1993, **93**, 913.
3 M. T. Bautista, E. P. Cappellani, S. D. Drouin, R. H. Morris, C. T. Schweitzer, A. Sella and J. Zubkowski, *J. Am. Chem. Soc.*, 1991, **113**, 4876.
4 R. H. Morris, J. F. Sawyer, M. Shiralian and J. D. Zubkowski, *J. Am. Chem. Soc.*, 1985, **107**, 5581.
5 M. T. Bautista, K. A. Earl, P. A. Maltby and R. H. Morris, *J. Am. Chem. Soc.*, 1988, **110**, 4056; C. Bianchini, K. Linn, D. Masi, M. Peruzzini, A. Polo, A. Vacca and F. Zanobini, *Inorg. Chem.*, 1993, **32**, 2366; C. Bianchini, A. Marchi, L. Marvelli, M. Peruzzini, A. Romerosa, R. Rossi and A. Vacca, *Organometallics*, 1995, **14**, 3203; M. Schlaf, A. J. Lough, P. A. Maltby and R. H. Morris, *Organometallics*, 1996, **15**, 2270.
6 P. A. Maltby, M. Schlaf, M. Steinbeck, A. J. Lough, R. H. Morris, W. T. Klooster, T. F. Koetzle and R. C. Srivastava, *J. Am. Chem. Soc.*, 1996, **118**, 5396.
7 M. V. Baker, L. D. Field and D. J. Young, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 546.
8 N. Bampos and L. D. Field, *Inorg. Chem.*, 1990, **29**, 587; L. D. Field, T. W. Hambley and B. C. K. Yau, *Inorg. Chem.*, 1994, **33**, 2009.
9 G. Parkin and J. E. Bercaw, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 255.
10 M. A. Máñez, M. C. Puerta, P. Valerga and M. G. Basallote, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 1291; M. A. Máñez, M. J. Fernández-Trujillo and M. G. Basallote, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1717.
11 M. A. Máñez, M. J. Fernández-Trujillo and M. G. Basallote, *Polyhedron*, 1995, **14**, 1865; 1996, **15**, 2305.
12 R. A. Henderson, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 509.
13 J. Barbosa, D. Barrón, E. Bosch and M. Rosés, *Anal. Chim. Acta*, 1992, **264**, 229.
14 C. Bianchini, F. Laschi, M. Peruzzini, F. M. Ottaviani, A. Vacca and P. Zanello, *Inorg. Chem.*, 1990, **29**, 3394.
15 C. Bianchini, M. Peruzzini and F. Zanobini, *J. Organomet. Chem.*, 1988, **354**, C19.
16 J. Eckert, A. Albinati, R. P. White, C. Bianchini and M. Peruzzini, *Inorg. Chem.*, 1992, **31**, 4241.
17 R. F. Jordan and J. R. Norton, *J. Am. Chem. Soc.*, 1982, **104**, 1255; E. J. Moore, J. M. Sullivan and J. R. Norton, *J. Am. Chem. Soc.*, 1986, **108**, 2257; R. T. Edidin, J. M. Sullivan and J. R. Norton, *J. Am. Chem. Soc.*, 1987, **109**, 3945; S. S. Kristjánsdóttir and J. R. Norton, in *Transition Metal Hydrides*, ed. A. Dedieu, VCH, New York, 1992, pp. 309–359.
18 A. B. P. Lever, *Inorg. Chem.*, (*a*) 1990, **29**, 1271; (*b*) 1991, **30**, 1980.
19 R. H. Morris, *Inorg. Chem.*, 1992, **31**, 1471.
20 R. P. Bell, *The Proton in Chemistry*, Cornell University Press, Ithaca, NY, 1973.

21 R. A. Henderson, *J. Chem. Soc.*, *Dalton Trans.*, 1984, 2259 and refs. therein.
22 R. A. Henderson and K. E. Oglieve, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 584; K. E. Oglieve and R. A. Henderson, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 3295; R. A. Henderson, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 946; R. A. Henderson and K. E. Oglieve, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3397.
23 C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1988, **110**, 2418.
24 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988, p. 116.
25 R. A. Henderson and K. E. Oglieve, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 3431.
26 K. E. Oglieve and R. A. Henderson, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 441.
27 (*a*) R. A. Henderson, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 1670; (*b*) H. Rothfuss, D. G. Gusev and K. G. Caulton, *Inorg. Chem.*, 1995, **34**, 2894.
28 R. M. Bullock, in *Transition Metal Hydrides*, ed. A. Dedieu, VCH, New York, 1992, pp. 263–307 and refs. therein.
29 J. S. Ricci, T. F. Koetzle, M. T. Bautista, T. M. Hofstede, R. H. Morris and J. F. Sawyer, *J. Am. Chem. Soc.*, 1989, **111**, 8823.
30 E. A. V. Ebsworth, D. W. H. Rankin and S. Cradock, *Structural Methods in Inorganic Chemistry*, Blackwell, Oxford, 1987, p. 210.
31 A. J. Lough, S. Park, R. Ramachandran and R. H. Morris, *J. Am. Chem. Soc.*, 1994, **116**, 8356; J. C. Lee, jun., A. L. Rheingold, B. Muller, P. S. Pregosin and R. H. Crabtree, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1021; R. Ramachandran and R. H. Morris, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2201; J. C. Lee, jun., E. Peris, A. L. Rheingold and R. H. Crabtree, *J. Am. Chem. Soc.*, 1994, **116**, 11 014; E. Peris, J. C. Lee, jun., J. R. Rambo, O. Eisenstein and R. H. Crabtree, *J. Am. Chem. Soc.*, 1995, **117**, 3485; W. Xu, A. J. Lough and R. H. Morris, *Inorg. Chem.*, 1996, **35**, 1549; S. Park, A. J. Lough and R. H. Morris, *Inorg. Chem.*, 1996, **35**, 3001.
32 E. Peris, J. Wessel, B. P. Patel and R. H. Crabtree, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2175.
33 J. Wessel, J. C. Lee, E. Peris, G. P. A. Yap, J. B. Fortin, J. S. Ricci, G. Sini, A. Albinati, T. F. Koetzle, O. Eisenstein, A. L. Rheingold and R. H. Crabtree, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2507; B. P. Patel, W. Yao, G. P. A. Yap, A. L. Rheingold and R. H. Crabtree, *Chem. Commun*, 1996, 991.
34 T. B. Richardson, S. de Gala and R. H. Crabtree, *J. Am. Chem. Soc.*, 1995, **117**, 12 875.
35 B. J. Hathaway, D. G. Holah and A. E. Underhill, *J. Chem. Soc.*, 1962, 2444.