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Kinetics of protonation of *cis*-[$FeH_2(dppe)_2$]: formation of the dihydrogen complex *trans*-[$FeH(H_2)(dppe)_2$]$^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) †

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Reaction of *cis*-[$FeH_2(dppe)_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) with acids in tetrahydrofuran solution led to formation of *trans*-[$FeH(H_2)(dppe)_2$]$^+$, although co-ordinated H_2 was substituted for N_2 or the anion of the acid in a slower process. The kinetics of the initial protonation reaction with several acids has been studied using an electrochemical procedure. The protonations are first order with respect to both the concentrations of the iron complex and the acid, with second-order rate constants (in $dm^3\ mol^{-1}\ s^{-1}$) at 25 °C of 9.7×10^{-3} ($HBF_4{\cdot}Et_2O$), 1.39×10^{-2} (CF_3CO_2H), 2.14×10^{-2} (CF_3SO_3H), 4.8×10^{-2} (HCl) and 1.48×10^{-1} (HBr). The ordering of rate constants within this series of acids is similar to that found for the reactions with *cis*-[$FeH_2\{P(CH_2CH_2PPh_2)_3\}$]. There is a good correlation between the values of log k_{HX} for the two complexes, which suggests a common mechanism for the formation of dihydrogen complexes in these cases. Kinetic data show that reactions of the dppe complex with all acids are faster than those of the analogous $P(CH_2CH_2PPh_2)_3$ compound. The reaction of *cis*-[$FeH_2(dppe)_2$] with deuteriated acids DX is faster than with HX, and the values of the kinetic isotope effect (k.i.e.), expressed as k_{HX}/k_{DX}, are 0.21 (CF_3SO_3H), 0.36 (HCl) and 0.55 (HBr). The inverse k.i.e. suggests that protonation occurs through a late transition state, and comparison with *cis*-[$FeH_2\{P(CH_2CH_2PPh_2)_3\}$] and with theoretical values indicates that protonation of *cis*-[$FeH_2(dppe)_2$] occurs through a transition state closer to the dihydrogen complex than in the case of the related $P(CH_2CH_2PPh_2)_3$ compound.

Protonation of metal hydrides with protic acids is a quite general procedure for the preparation of dihydrogen complexes,[1] although few mechanistic details of these reactions have been reported.[2] In a previous paper we showed that the kinetics of reaction of *cis*-[$FeH_2\{P(CH_2CH_2PPh_2)_3\}$] with acids to form *cis*-[$FeH(H_2)\{P(CH_2CH_2PPh_2)_3\}$]$^+$ can be monitored using an electrochemical procedure which, at least from the theoretical point of view, is of wide applicability to study the protonation of other hydride complexes,[2] and so we decided to use the same procedure to study the kinetics of reactions of the closely related complex *cis*-[$FeH_2(dppe)_2$]. The comparison between kinetic data for the two complexes is expected to lead to a better understanding of the mechanism of formation of dihydrogen complexes, especially the role of isomerisation processes accompanying the protonation process because protonation of the $P(CH_2CH_2PPh_2)_3$ complex leads directly to the dihydrogen complex, but the reaction of the dppe analogue with strong and weak acids occurs with isomerisation to give *trans*-[$FeH(H_2)(dppe)_2$]$^+$.[3–6] Another complication comes from the fact that reaction with stoichiometric amounts of HCl in tetrahydrofuran (thf) has been shown to lead to *trans*-[$FeH(Cl)(dppe)_2$], which releases dppe and forms tetrahedral [$FeCl_2(dppe)$] upon reaction with HCl in excess.[7] Results presented in this paper show clearly that the initial product in the reaction of *cis*-[$FeH_2(dppe)_2$] with several acids is the dihydrogen complex and so the kinetic data can be directly compared with those obtained for *cis*-[$FeH_2\{P(CH_2CH_2PPh_2)_3\}$].

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 were obtained from SDS and were dried and deoxygenated immediately before use. The complexes *cis*-[$FeH_2(dppe)_2$][8] and *trans*-[$FeH(H_2)(dppe)_2$]BF_4[3] were prepared by literature procedures. Hydrogen chloride and HBr were generated from methanol and chloro- or bromo-trimethylsilane, respectively. The deuteriated acids DCl and DBr were obtained in a similar way using CD_3OD. All other reagents were obtained from Aldrich.

The NMR spectra were recorded with a Varian Unity 400 spectrometer. The positions of the signals observed at room temperature for the complexes discussed do not differ significantly from those published previously.[3,5] The protonation reactions were monitored by recording phosphorus spectra at low temperature using the experimental procedure described for the case of *cis*-[$FeH_2\{P(CH_2CH_2PPh_2)_3\}$].[2]

Solutions of acids used in the kinetic studies were prepared and titrated with KOH immediately before kinetic runs. Kinetic experiments were carried out using an EG&G Princeton Applied Research model 263A potentiostat/galvanostat, and the experimental details have been described recently.[2] Kinetic data were obtained at 25.0 °C under a nitrogen atmosphere and in the presence of 0.05 mol dm^{-3} NBu_4BF_4. All measurements were carried out under pseudo-first-order conditions (acid excess) using a potential of 0.1 V *vs.* NHE. The curves representing the time dependence of the current intensity were fitted by a single exponential, and the first-order dependence on the concentration of iron complex was confirmed by the independence of the observed pseudo-first-order rate constant with the concentration of complex.

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† *Supplementary data available*: observed rate constants. For direct electronic access see http://www.rsc.org/suppdata/dt/1998/2205/, otherwise available from BLDSC (No. SUP 57383, 3 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

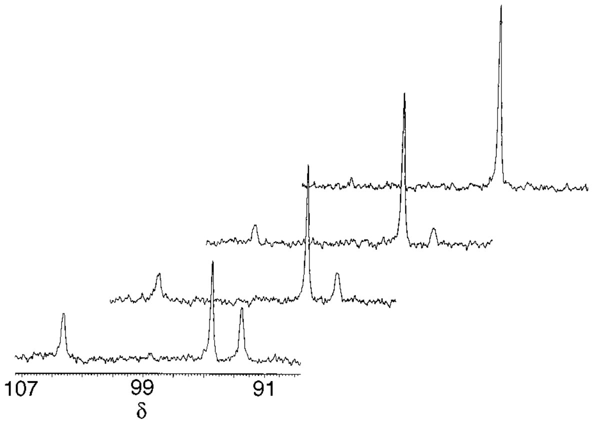
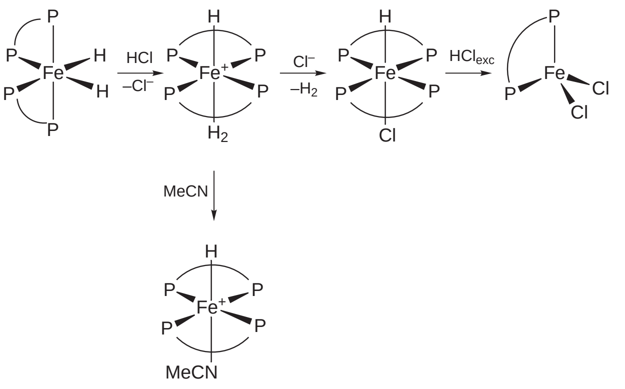


Fig. 1 The ^{31}P-{^1H} NMR spectra showing the conversion of *cis*-$[FeH_2(dppe)_2]$ into *trans*-$[FeH(H_2)(dppe)_2]^+$. The spectra were obtained at −35 °C in $[^2H_8]$thf using an excess of HCl. Time interval between spectra is 512 s

Results and Discussion

Although formation of the *trans*-hydridedihydrogen complex upon reaction of *cis*-$[FeH_2(dppe)_2]$ with different acids has been previously observed,[3–5] reaction with HCl in thf has been reported to give *trans*-$[FeH(Cl)(dppe)_2]$.[7] For this reason the reaction with HCl was studied in more detail to confirm the formation of *trans*-$[FeH(H_2)(dppe)_2]^+$ and to detect possible reaction intermediates or products of side reactions. The NMR experiments in $[^2H_8]$thf show clearly that reaction of *cis*-$[FeH_2(dppe)_2]$ with HCl in excess leads initially to formation of *trans*-$[FeH(H_2)(dppe)_2]^+$. Thus, spectra in Fig. 1 show an increase with time of the amount of dihydrogen complex formed as the signals of the dihydride disappear. When the concentration of HCl is lower than that of the starting complex the spectral changes are similar, although the final spectrum shows in this case the formation of an equilibrium mixture of both *cis*-$[FeH_2(dppe)_2]$ and *trans*-$[FeH(H_2)(dppe)_2]^+$. In all experiments the protonation reaction occurs without accumulation of any NMR-detectable reaction intermediate. Once the conversion into the dihydrogen complex has been completed no more spectral changes are observed during 1 h at −35 °C. However, if the sample is then warmed to 15 °C the signal of the previously formed dihydrogen complex disappears completely. A rate constant of 1.0×10^{-3} s^{-1} can be calculated from the changes of the signal intensities with time. No other dppe complex is detected when the reaction is carried out with HCl in excess, but if there is a deficit of HCl the dihydrogen complex converts into *trans*-$[FeH(Cl)(dppe)_2]$ at a rate similar to that quoted above. No more spectral changes are observed overnight at room temperature and, for experiments with HCl in deficit, the chlorohydride and the starting *cis*-dihydride complexes coexist in solution without any evidence of reaction. If an excess of HCl is then added the solution turns colourless and the only signal in the phosphorus spectrum corresponds to free dppe, which suggests again the formation of the chlorohydride complex which reacts with HCl to form the white paramagnetic $[FeCl_2(dppe)]$ complex and dppe in a rapid process.[7] The resulting solution remains colourless for hours, although there is gradual formation of a white precipitate and the development of a slightly yellow colour, probably corresponding to slow formation of oxidation products by reaction with traces of O_2 coming into the NMR tube.

The changes observed in the NMR spectra when $[^2H_8]$thf is replaced by CD_2Cl_2, $[^2H_6]$acetone or a mixture of these solvents with thf are similar to those described above. However, in CD_3CN solution the formation of *trans*-$[FeH(H_2)(dppe)_2]^+$ is followed by its conversion into *trans*-$[FeH(CD_3CN)(dppe)_2]^+$,[4] with a rate constant also close to 1.0×10^{-3} s^{-1} at 15 °C, very similar to those obtained[9] for the limiting rate constant for substitution of co-ordinated H_2 in *trans*-$[FeH(H_2)(dppe)_2]^+$.



Scheme 1

All the NMR observations are rationalised in Scheme 1. Reaction of *cis*-$[FeH_2(dppe)_2]$ with HCl in thf leads to *trans*-$[FeH(H_2)(dppe)_2]^+$, which substitutes H_2 for Cl^- in a slower reaction to give *trans*-$[FeH(Cl)(dppe)_2]$. The chlorohydride complex is not detected in the presence of the excess of HCl because it rapidly forms the white paramagnetic tetrahedral species *trans*-$[FeCl_2(dppe)]$.[7] Substitution of co-ordinated H_2 for Cl^- has been previously observed for other dihydrogen complexes containing bidentate phosphines.[10,11] When the reaction is carried out in a better co-ordinating solvent such as acetonitrile substitution of H_2 leads directly to *trans*-$[FeH(MeCN)(dppe)_2]^+$. The possibility that this compound results from reaction of the solvent with the chlorohydride complex can be discarded because it has been shown[7] that substitution reactions of *trans*-$[FeH(Cl)(dppe)_2]$ are much slower than formation of the acetonitrile complex in the NMR experiments. On the contrary, the rate constant obtained by NMR agrees well with the values for substitution of co-ordinated H_2 in *trans*-$[FeH(H_2)(dppe)_2]^+$.[9]

Formation of *trans*-$[FeH(H_2)(dppe)_2]^+$ upon reaction of the *cis*-dihydride with other acids, such as $HBF_4 \cdot Et_2O$, CF_3SO_3H, CF_3CO_2H and HBr, was also confirmed in low-temperature NMR experiments using a mixture of thf and $[^2H_6]$acetone as solvent. However, the subsequent reactions of the dihydrogen complex were not studied in detail for these cases.

Kinetics of formation of the dihydrogen complex

The kinetics of reaction (1) has been studied using the electrochemical procedure described previously for *cis*-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$.[2] As dihydrogen complexes are oxidised at potentials higher than the analogous hydrides, the kinetics of protonation can be measured from the time dependence of the current intensity at a potential intermediate between the half-wave potentials for both complexes. Half-wave potentials for oxidation of *cis*-$[FeH_2(dppe)_2]$ and *trans*-$[FeH(H_2)(dppe)_2]^+$ have been reported to be −0.14[6] and 1.20 V,[3] respectively, and the kinetics of reaction was studied at a potential of 0.10 V (all potentials are given *vs.* NHE). The method had proved to be more useful than conventional stopped-flow for studying protonation of the $P(CH_2CH_2PPh_2)_3$ complex,[2] and the same revealed to be also true for reactions of *cis*-$[FeH_2(dppe)_2]$ in thf. However, the kinetics of protonation could not be studied in acetonitrile solution because the reaction is too fast for the experimental procedure used. Attempts were unsuccessful even at 0 °C, showing that protonation is several orders of magnitude faster in acetonitrile than in thf.

$$\textit{cis}\text{-}[FeH_2(dppe)_2] + HX \longrightarrow \textit{trans}\text{-}[FeH(H_2)(dppe)_2]^+ + X^- \quad (1)$$

The current *vs.* time curves obtained in thf under pseudo-

Table 1 Second-order rate constants for the reaction of *cis*-[$FeH_2(dppe)_2$] and *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_4BF_4[a]

	10^{-2} k_{HX}/dm^3 mol^{-1} s^{-1}		10^{-2} k_{DX}/ dm^3 mol^{-1} s^{-1}	log k_{HX}	
HX	dppe	$P(CH_2CH_2PPh_2)_3$[b]	dppe	dppe	$P(CH_2CH_2PPh_2)_3$
$HBF_4·Et_2O$	0.97(6)	0.017(1)		1.99	0.23
CF_3CO_2H	1.39(4)	0.112(4)		2.14	1.05
CF_3SO_3H	2.14(8)	0.176(3)	10.3(5)	2.33	1.24
HCl	4.8(1)	1.32(4)	13.3(5)	2.68	2.12
HBr	14.8(5)	3.4(1)	27(2)	3.17	2.53

[a] The numbers in parentheses represent the standard deviation in the last significant digit. [b] Values from ref. 2.

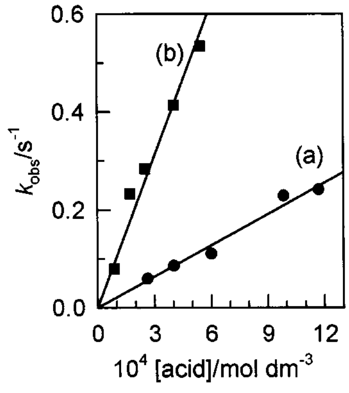


Fig. 2 Dependence of the pseudo-first-order rate constant upon acid concentration for the reaction of *cis*-[$FeH_2(dppe)_2$] with CF_3SO_3H (a) and CF_3SO_3D (b) at 25 °C in thf

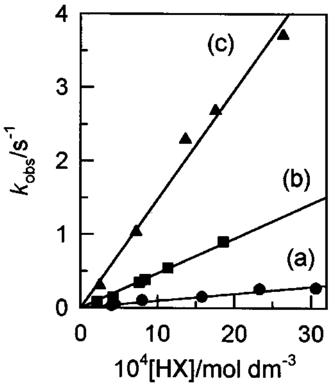


Fig. 3 Dependence of the pseudo-first-order rate constant upon acid concentration for the reaction of *cis*-[$FeH_2(dppe)_2$] with $HBF_4·Et_2O$ (a), HCl (b) and HBr (c) at 25 °C in thf

first-order conditions (acid excess) can be fitted satisfactorily by a single exponential, and the values derived for the rate constant, k_{obs}, have been deposited (SUP 57383). The dependence of k_{obs} on the concentration of acid is illustrated in Figs. 2 and 3, which show that the rate of formation of the dihydrogen complex is affected by both the nature of the acid and isotopic substitution. In all cases there is a linear dependence between k_{obs} and the acid concentration, *i.e.* equation (2) or (3), and the

$$k_{obs} = k_{HX}[HX] \qquad (2)$$

$$k_{obs} = k_{DX}[DX] \qquad (3)$$

values obtained for the second-order rate constants k_{HX} and k_{DCl} are given in Table 1. The kinetic isotope effects (k.i.e.s), expressed as k_{HCl}/k_{DCl}, are included in Table 2 and compared with theoretical values calculated with a model that considers formation of a very late transition state and which takes into account only contributions from the differences in the zero-point energies.[2] For comparative purposes both tables include the values previously reported[2] for protonation of *cis*-[$FeH_2\{P(CH_2CH_2PPh_2)_3\}$].

Table 2 Kinetic isotope effect at 25.0 °C for the reaction of *cis*-[$FeH_2(dppe)_2$] and *cis*-[$FeH_2\{P(CH_2CH_2PPh_2)_3\}$] with acids at 25.0 °C in thf[a]

	k_{HX}/k_{DX}		
HX	dppe	$P(CH_2CH_2PPh_2)_3$[b]	Calculated[c]
CF_3SO_3H	0.21(1)	0.45(2)	0.06,[d] 0.87[e]
HCl	0.36(2)	0.62(3)	0.47
HBr	0.55(4)	0.64(4)	0.39

[a] The numbers in parentheses represent the standard deviation in the last significant digit. [b] Values from ref. 2. [c] Values calculated with equation (15) of ref. 2. [d] Value assuming free H^+. [e] Value assuming OH groups.

Mechanism of formation of *trans*-[$FeH(H_2)(dppe)_2$]$^+$ and comparison with the related $P(CH_2CH_2PPh_2)_3$ complex

The formation of dihydrogen complexes through protonation of metal hydrides is slow compared to acid–base reactions involving nitrogen and oxygen acids in water, but occurs at rates comparable to other proton transfers, such as reactions of carbon acids[12] and proton transfers from acidic metal hydrides.[13] On the other hand, protonation of other co-ordinated ligands such as dinitrogen[14] and unsaturated hydrocarbons are rapid, although they are usually followed by slower reactions of the initial protonation product.[15] Kinetic data for the formation of dihydrogen complexes have been interpreted in terms of a mechanism involving a series of hydrogen-bonded structures, and the observation of an inverse k.i.e. was considered indicative of a transition state with a structure close to that of the reaction product.[2] Actually, the theoretical values of k.i.e. in Table 2 were calculated for a very late transition state, and they are of similar magnitude to those found experimentally for protonation of both *cis*-[$FeH_2(dppe)_2$] and *cis*-[$FeH_2\{P(CH_2CH_2PPh_2)_3\}$], although the values for the latter complex are always larger and suggest a somewhat earlier transition state for its reactions. The possibility of an alternative mechanism involving initial protonation at the metal centre to form a classical trihydride followed by rate-determining intramolecular H,H coupling to give the dihydrogen complex can be ruled out because this mechanism would lead to the observation of normal isotope effects, quite the reverse of the experimental observations.[2]

Data in Table 1 show that the dppe complex reacts with all acids faster than does the analogous $P(CH_2CH_2PPh_2)_3$ compound. Moreover, the reactivity with the different acids follows the same ordering for both complexes, showing that it is not accidental. We previously[2] proposed that this ordering is the result of a slower reactivity of H^+X^- ion pairs with respect to HX molecules and according to this interpretation the reactivity of a series of acids with different metal hydrides must follow the same ordering. Actually, there is a good correlation between the data for both complexes, which is illustrated in Fig. 4 by the

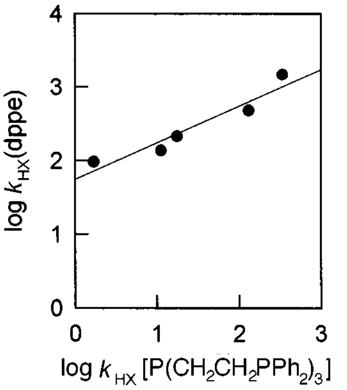


Fig. 4 Plot showing the linear dependence between the values of log k_{HX} for the complexes *cis*-[FeH$_2$(dppe)$_2$] and *cis*-[FeH$_2${P(CH$_2$CH$_2$PPh$_2$)$_3$}]

linear dependence between the values of log k_{HX}, equation (4)

$$\log k_{HX}(\text{dppe}) = A \log k_{HX}[\text{P(CH}_2\text{CH}_2\text{PPh}_2)_3] + B \quad (4)$$

with $A = 0.50$ and $B = 1.75$. This relationship is of the same mathematical form as the correlations observed for the substitution reactions of platinum complexes with nucleophiles and for the catalysed and uncatalysed hydrolysis of chloropentaammine complexes.[16] If the values of log k_{HX} for the P(CH$_2$CH$_2$PPh$_2$)$_3$ complex are taken as a reference to define the reactivity of the acids, a positive value of B and a value of A lower than 1 would be a measure of the higher intrinsic reactivity of *cis*-[FeH$_2$(dppe)$_2$] and of its lower selectivity towards acids, respectively. On the other hand, the correlation in equation (4) indicates that, despite the very different nature of the acids employed, the rate constants for protonation of both complexes can be fitted to a Brønsted-type relationship,[12,17] *i.e.* equations (5) and (6), where K_{HX} is the dissociation constant of

$$k_{HX}(\text{dppe}) = G(\text{dppe})K_{HX}^{\alpha(\text{dppe})} \quad (5)$$

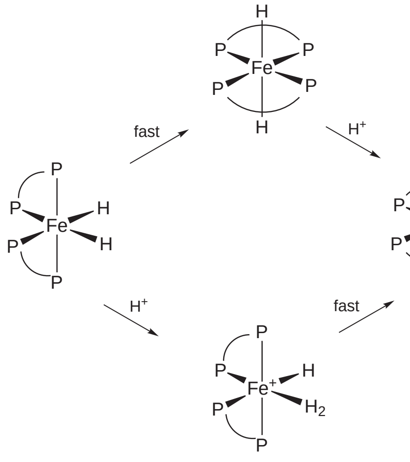
$$k_{HX}[\text{P(CH}_2\text{CH}_2\text{PPh}_2)_3] = G[\text{P(CH}_2\text{CH}_2\text{PPh}_2)_3]K_{HX}^{\alpha[\text{P(CH}_2\text{CH}_2\text{PPh}_2)_3]} \quad (6)$$

the acid HX, G is a factor which remains constant within the series of reactions and includes the acidity constants of the dihydrogen complexes, and the exponents α are usually between 0 and 1. Although the values of K_{HX} in thf are not available in most cases, they can be eliminated between equations (5) and (6) to obtain (4). It can easily be demonstrated that the value of A in equation (4) corresponds to the quotient α(dppe)/α[P(CH$_2$CH$_2$PPh$_2$)$_3$], and that B is a function of the values of α and G for both complexes. As indicated above, A represents a measure of the relative kinetic selectivity of the two complexes towards reactions with acids, although its value can be now correlated with the exponents in the Brønsted equations.

According to equations (5) and (6), the reaction rates of a substrate with a series of related acids are expected to increase with the difference in acidity between the two reagents. We previously commented on the difficulties in expanding these ideas to a solvent like thf,[2] in which few pK_a values have been determined, and with a chemistry dominated by ion-pairing and homoconjugation equilibria, which makes experimental pK_a values doubtful as a measure of the acid strength. However, the problem can be faced now from a different perspective. Thus, Morris and co-workers[1,6] have constructed a pK_a scale for dihydrogen complexes by measuring equilibrium constants for either protonation of the metal hydrides or deprotonation of their conjugated bases, *i.e.* the dihydrogen complexes. The values are referenced to an aqueous scale for ease of comparison with common acids, and the pK_a of the complex *cis*-[FeH$_2$(dppe)$_2$] in this aqueous scale is close to 12. Although the value for the P(CH$_2$CH$_2$PPh$_2$)$_3$ complex has not been reported, it must be higher than 12 because we have observed that *trans*-[FeH(H$_2$)(dppe)$_2$]$^+$ is deprotonated in thf by an excess of NEt$_3$ whereas *cis*-[FeH(H$_2$){P(CH$_2$CH$_2$PPh$_2$)$_3$}]$^+$ is not.[18] The Brønsted equation for reaction of both iron dihydrides with a common acid is of the form[12] (7) where G_{HX} includes now the

$$k_{HX} = G_{HX}(1/K_a)^{1-\alpha} \quad (7)$$

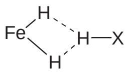
acidity constant of HX and K_a is the dissociation constant of the corresponding dihydrogen complex. If the value of α is between 0 and 1 it is expected from equation (7) that the value of log k_{HX} increases linearly with the pK_a of the dihydrogen complex and so reactions of *cis*-[FeH$_2${P(CH$_2$CH$_2$PPh$_2$)$_3$}] should be faster than those of *cis*-[FeH$_2$(dppe)$_2$]. The experimental data in Table 1 are contrary to this prediction and indicate that the value of 1 − α must be negative and α must be greater than 1. This is rather unusual, but there are some literature precedents that indicate that restriction to α values between 0 and 1 is valid only for nitrogen and oxygen acids.[19]



Scheme 2

Since kinetic data for the formation of dihydrogen complexes are very limited, it would be too speculative at this time to decide the reasons that make negative the values of 1 − α or that lead to a transition state closer to the reaction product in the reactions of *cis*-[FeH$_2$(dppe)$_2$]. In any case the observation of inverse isotope effects for the formation of *trans*-[FeH(H$_2$)(dppe)$_2$]$^+$, *cis*-[FeH(H$_2$){P(CH$_2$CH$_2$PPh$_2$)$_3$}]$^+$ and [WH(H$_2$)(η^5-C$_5$H$_5$)$_2$]$^+$ [20] and the agreement with calculated values seem to be indicative of a quite general phenomenon and contrast sharply with the kinetics of reactions in which the metal hydrides behave as acids. These last reactions occur through a symmetrical transition state and show a positive k.i.e.[13]

An interesting result of this work is that dihydrogen complexes with P(CH$_2$CH$_2$PPh$_2$)$_3$ and dppe are formed at comparable rates despite the fact that the formation of *trans*-[FeH(H$_2$)(dppe)$_2$]$^+$ requires an isomerisation process that is not possible for the analogous P(CH$_2$CH$_2$PPh$_2$)$_3$ compound. Scheme 2 shows two possible pathways for this reaction, which only differ in the order of occurrence of the protonation and isomerisation steps. Although a value of 150 s^{-1} at 22 °C has been reported for hydride exchange in *cis*-[FeH$_2$(dppe)$_2$], and the exchange process probably involves formation of the *trans* isomer either as intermediate or as transition state,[21] the NMR spectra of this compound show clearly that the major species (probably the only one) is the *cis* isomer and so formation of *trans*-[FeH(H$_2$)(dppe)$_2$]$^+$ by acid attack on the *trans*-dihydride should occur at a rate much slower than for the analogous P(CH$_2$CH$_2$PPh$_2$)$_3$ complex. Thus, the kinetic results are more consistent with rate-determining acid attack on *cis*-[FeH$_2$(dppe)$_2$] followed by rapid isomerisation to the more stable *trans*-hydridedihydrogen complex (lower pathway in Scheme 2). According to microscopic reversibility, deprotonation of *trans*-$[FeH(H_2)(dppe)_2]^+$ should occur through initial isomerisation to the *cis*-hydridedihydrogen complex. We have not obtained any evidence of reaction intermediates in a kinetic study of the deprotonation of *trans*-$[FeH(H_2)(dppe)_2]^+$.[18] Morris and co-workers[6] were also unable to detect any intermediate in a low-temperature NMR study of deprotonation of *trans*-$[FeH(H_2)(dppe)_2]^+$, but initial formation of the *trans*-dihydride was observed for the analogous complexes containing Ru and Os. Extrapolation of these results to the iron complex led them to propose that *trans*-$[FeH(H_2)(dppe)_2]^+$ is first deprotonated and then isomerises to the more stable *cis*-dihydride. However, it must be pointed out that their observations are not inconsistent with our proposal that reaction goes through the lower pathway in Scheme 2, because *cis*-$[FeH(H_2)(dppe)_2]^+$ would be also an undetectable intermediate formed under steady-state conditions. Actually, there is evidence that the relative stability of the *cis* and *trans* isomers of $[MH(H_2)(diphosphine)_2]^+$ complexes depends largely on the steric requirements of the metal centre and the chelating phosphine.[22] Another interesting observation is the existence of hydrogen bonds between the NH group and two *cis* hydrides in the $[ReH_5(PPh_3)_3]$ adducts with indole and imidazole.[23] Although the distance to one hydride is significantly shorter than to the other, this kind of tricentric interaction must be stronger than a single dihydrogen bond and may be responsible for the preferential formation of *trans*-$[FeH(H_2)(dppe)_2]^+$ through direct acid attack on *cis*-$[FeH_2(dppe)_2]$. It can be argued that the formation of this kind of dihydrogen bond is simply the result of crystal-packing effects. However, dihydrogen bonds in $[ReH_5(PPh_3)_3]$ adducts are relatively strong (close to 20 kJ mol^{-1}),[23] and IR spectra show the existence of interactions of similar magnitude in films obtained by evaporation of CH_2Cl_2 solutions.[24] Moreover, the interaction seems to be general for a variety of proton donors and metal polyhydrides, with ΔH° values that increase with the acidity of the proton donor.[24] By extrapolation of these results, it is expected that dihydrogen bonds between *cis*-$[FeH_2(dppe)_2]$ and the strong acids used in the protonation reactions are significantly stronger than 20 kJ mol^{-1}, and they finally lead to formation of the dihydrogen complex, which is the thermodynamically favoured reaction product.



Another question that arises from results in this work is the reason why the mechanisms of protonation with HCl of the complexes *cis*-$[FeH_2(dppe)_2]$ and *trans*-$[FeH(Cl)(dppe)_2]$ are so different. The differences appear mainly because HCl attack occurs at different sites in the two complexes. Reaction of the *cis*-dihydride occurs at a co-ordinated hydride and leads to the dihydrogen complex. On the contrary, protonation of the chlorohydride complex occurs[7] through the initial opening of a chelate ring with formation of an intermediate containing one protonated monodentate dppe. The basicity of co-ordinated hydrides can be estimated from the pK_a of their conjugated acids, *i.e.* the dihydrogen complexes. Morris and co-workers[6] determined a pK_a of 12 for *trans*-$[FeH(H_2)(dppe)_2]^+$ and from the values found for related complexes they conclude that the acidity of *trans*-$[FeCl(H_2)(dppe)_2]^+$ is so high that the complex cannot be obtained.[25] In that case the basicity of the conjugated base *trans*-$[FeH(Cl)(dppe)_2]$ would be so low that acid attack must occur at a different site. Attack at a phosphorus of monodentate dppe seems to be the most effective and leads to complete dissociation of dppe and formation of tetrahedral *trans*-$[FeCl_2(dppe)]$.[7] Some other examples have been reported of protonation of metal hydrides both at the metal centre[26] and at an ancillary ligand.[27]

Conclusion

Some aspects of the kinetics and mechanism of formation of dihydrogen complexes can be now rationalised on the basis of the similarity of kinetic results for protonation of *cis*-$[FeH_2(dppe)_2]$ and *cis*-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$. Thus, reactions of both complexes are second order, with rate constants that change with the nature of both the acid and the metal hydride. Despite the complex composition of acid solutions in thf there is a correlation between the values of log k_{HX} for protonation of both iron dihydrides, which suggests the existence of Brønsted-type relationships with α values greater than 1. On the other hand, formation of dihydrogen complexes occurs in all cases examined to date with an inverse k.i.e. consistent with proton attack at co-ordinated hydrides. This results in formation of dihydrogen-bonded adducts that finally convert into the dihydrogen constants. At least for the reactions of *cis*-$[FeH_2(dppe)_2]$ and *cis*-$[FeH_2\{P(CH_2CH_2PPh_2)_3\}]$, the k.i.e. values suggest a late transition state with a structure similar to that of the reaction product. More work is in progress to determine if the conclusions that emerge from the study of these complexes also apply to reactions of other metal hydrides.

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