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The kinetics and mechanisms of reactions involving the dihydrogen complex *trans*-$[FeH(H_2)(DPPE)_2]^+$ and related compounds

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Abstract

The kinetic and mechanistic aspects of reactions involving the dihydrogen complex *trans*-$[FeH(H_2)(DPPE)_2]^+$ and related Fe(II) and Ru(II) complexes are reviewed. Despite the observation that substitution of coordinated H_2 usually goes through a limiting dissociative mechanism, the reactions of the title complex involve associative activation and are proposed to occur through the initial opening of a DPPE chelate ring followed by rate-determining attack by the entering ligand. The kinetics of reactions between *cis*-$[MH_2(diphosphine)_2]$ compounds and acids to form dihydrogen complexes is also reviewed. The rate of protonation is strongly dependent on the nature of the acid and shows an inverse kinetic isotope effect; the mechanism proposed consists of attack by the acid to yield a transition state involving a dihydrogen-bonded adduct. For these complexes, the kinetics of protonation can be summarised in two parameters, *R* and *S*, that measure the intrinsic reactivity and selectivity of the complexes towards acids. The lack of reaction of [CpRuH(diphosphine)] complexes with some acids poses some questions about the validity of an aqueous pK_a scale to measure the acidity of dihydrogen complexes.

Keywords: Dihydrogen complexes; Mechanism; Substitution; Kinetic data

1. Introduction

One of the major focuses of the research work about metal hydrides in the last years has been the study of dihydrogen complexes and, as a result, our understanding about their structures, properties and reactivity has increased significantly [1,2]. Nevertheless, relatively little attention has been paid to the kinetic and mechanistic aspects of reactions in which they participate. Although there are some kinetic data about fluxional processes and substitution reactions [1], a comprehensive kinetic study is still lacking, probably because quantitative measurements are hindered by the high sensitivity of most dihydrogen complexes towards traces of O_2 or water. However, a better understanding of the mechanisms of these reactions can only be achieved through a detailed analysis of the way in which the whole set of kinetic data are affected by factors such as the nature of the reagents or the solvent. For this reason, we undertook a few years ago a kinetic study of the reactions of dihydrogen complexes that was initially focused on the reactions of one of the best characterised dihydrogen complexes, *trans*-$[FeH(H_2)(DPPE)_2]^+$. The work has been later extended to some related complexes and the results available at this time are discussed in this paper.

Among the reactions of dihydrogen complexes described in the literature, substitution of coordinated H_2 is one of the most relevant (Eq. (1)) and so, we have examined the kinetics of these reactions and compared them with analogous reactions in which other monodentate ligands are substituted (Eq. (2)). Protonation of metal hydrides is a common procedure for the synthesis of dihydrogen complexes (Eq. (3)) and we have also obtained kinetic data for these reactions. The

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material in the paper is organised in two major sections dedicated to the substitution and the protonation reactions, the presentation being essentially based on the results obtained by our group.

$$L_nM(H_2) + X \rightarrow L_nMX + H_2 \quad (1)$$

$$L_nMX + Y \rightarrow L_nMY + X \quad (2)$$

$$L_nMH + HX \rightarrow L_nM(H_2)^+ + X^- \quad (3)$$

2. The kinetics and mechanisms of substitution of coordinated dihydrogen

The experimental evidence indicates that the M–H_2 bonds are usually not very strong [1], which suggests that a dissociative mechanism is a feasible route for substitution of coordinated dihydrogen (Eq. (1)). The existence of several 16-electron complexes [3–6] that only differ from 18-electron dihydrogen complexes in the absence of coordinated H_2 supports this prediction and, actually, the operation of the equilibrium shown in Eq. (4) has been observed for some complexes [7–10]. For these cases, substitution reactions can occur easily through a limiting dissociative (D) mechanism with formation of L_nM as the reaction intermediate (Eq. (5)).

$$L_nM(H_2) \rightleftarrows L_nM + H_2 \quad (4)$$

$$L_nM(H_2) \overset{-H_2}{\rightleftarrows} L_nM \overset{+X}{\rightleftarrows} L_nMX \quad (5)$$

The kinetics of Eq. (4) has been studied for several compounds and the results indicate that the process is first order with respect to the metal complex. The activation parameters for H_2 dissociation are also available in some cases [7–11] and relevant data are included in Table 1. These data indicate that $\Delta H^{\neq}$ is usually small (40–75 kJ mol^{-1}), whereas most of the $\Delta S^{\neq}$ values are positive. Although negative values of $\Delta S^{\neq}$ have been measured in some cases, they are probably caused by the large errors involved in its determination. The values of $\Delta H°$ and $\Delta H^{\neq}$ for Eq. (4) are clearly related to the M–H_2 bond strength, but they also include contributions from the solvation of the different species and from any possible structural rearrangement of the coordinatively unsaturated L_nM complex. Thus, Hoff and co-workers [7] showed years ago that H_2 dissociation from $M(CO)_3(PCy_3)_2(H_2)$ involves the simultaneous formation of an agostic interaction in $M(CO)_3(PCy_3)_2$ that compensates, at least in part, the electron deficiency in the unsaturated complex. In other cases, the unsaturated intermediate can be stabilised by an increase in the π-donation from an ancillary X^- ligand [8,9] or by the approach of some coordinated phosphines to the metal centre [16]. If any of these interactions occurs simultaneously with the formation and the breaking of the M–H_2 bond, it will cause a contribution of several kJ mol^{-1} to the activation barrier that will complicate the correlation between measured enthalpies and M–H_2 bond strengths.

Although a dissociative mechanism is well substantiated for those cases in which an unsaturated compound is formed in equilibrium with the dihydrogen complex, there are many other cases in which the coordinatively unsaturated L_nM analogue of a $L_nM(H_2)$ complex is unknown or it is not observed during the course of the substitution reactions. A D mechanism with formation of a highly reactive intermediate is also possible in those cases, but alternative mechanisms may also operate. Thus, some of the $\Delta H^{\neq}$ values for dissociative loss of H_2 are close to the values found for dissociation of other monodentate ligands and substitution reactions can then occur at coordination sites different from that occupied by the H_2 ligand. This latter possibility becomes even more plausible for compounds containing polydentate phosphines with bulky substituents; the opening of a chelate ring would relieve steric constraints in these compounds and facilitate the attack by the nucleophile.

We have found strong evidence for the operation of this kind of chelate ring-opening mechanism for the substitutions of H_2 in *trans*-$[FeH(H_2)(DPPE)_2]^+$ (Eq. (6)) [12]. For this compound, the experimental rate law depends on the nature of the solvent and changes from a first order dependence on the metal complex (acetone solution) to saturation kinetics (THF solution). Although the values of the rate constants, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are not very different from those found for other $[FeH(H_2)(diphosphine)_2]^+$ complexes that undergo dissociatively activated substitutions [13–15], the activation volumes ($\Delta V^{\neq}$) for Eq. (6) are very negative and clearly indicate associative activation (see Table 1).

$$trans\text{-}[FeH(H_2)(DPPE)_2]^+ + L \rightarrow trans\text{-}[FeH(L)(DPPE)_2]^+ + H_2 \quad (6)$$

The kinetic data for these reactions have been interpreted [12] in terms of the mechanism shown in Eqs. (7)–(9) that involves the initial opening of a chelate ring followed by rate-determining attack by the entering ligand and rapid reorganisation to give the final substituted product.

$$trans\text{-}[FeH(H_2)(DPPE)_2]^+ \rightleftarrows trans\text{-}[FeH(H_2)(\eta^1\text{-}DPPE)(\eta^2\text{-}DPPE)]^+;\ k_1,\ k_{-1} \quad (7)$$

$$trans\text{-}[FeH(H_2)(\eta^1\text{-}DPPE)(\eta^2\text{-}DPPE)]^+ + L \rightarrow trans\text{-}[FeH(L)(H_2)(\eta^1\text{-}DPPE)(\eta^2\text{-}DPPE)]^+;\ k_2 \quad (8)$$

$$trans\text{-}[FeHL(H_2)(\eta^1\text{-}DPPE)(\eta^2\text{-}DPPE)]^+ \rightarrow trans\text{-}[FeH(L)(DPPE)_2]^+ + H_2;\ \text{fast} \quad (9)$$

In contrast, substitution of coordinated acetonitrile in *trans*-$[FeH(MeCN)(DPPE)_2]^+$ occurs with large positive $\Delta V^{\neq}$ (Table 1), consistent with a limiting D mechanism similar to that shown in Eq. (5) [13]. The different mechanisms for the substitution of H_2 and MeCN in the related *trans*-$[FeH(L)(DPPE)_2]^+$ complexes are also revealed in their reactions with the bidentate phosphine DMPE. The substituted product *trans*-$[FeH(\eta^1\text{-DMPE})(DPPE)_2]^+$ is not observed in any case, thus showing that the simple substitution reaction is not favoured thermodynamically. As dissociation of the leaving ligand is the only reaction pathway available for substitution in the acetonitrile complex, there is no reaction of *trans*-$[FeH(MeCN)(DPPE)_2]^+$ with an excess of DMPE after 24 h at room temperature. In contrast, the dihydrogen complex reacts with DMPE even at low temperature with formation of free DPPE. In this case, the reaction begins with the opening of a DPPE chelate ring and attack by DMPE leads to an intermediate with two bidentate ligands coordinated in a monodentate way; the favoured pathway from this intermediate is the closure of the DMPE ring and the release of DPPE [13].

The reasons for the operation of a chelate ring-opening mechanism for substitutions in *trans*-$[FeH(H_2)(DPPE)_2]^+$ instead of the simpler mechanism involving dissociative loss of H_2 must be related to the relative strengths of the Fe–H_2 and Fe–P(chelate) bonds and to the fluxional behaviour of the complex. The latter process exchanges the H atoms between the hydride and the dihydrogen ligands, thus stabilising the leaving ligand and hindering a simple dissociative mechanism. For the case of *trans*-$[FeH(MeCN)(DPPE)_2]^+$, there is no fluxional process involving the leaving ligand and the activation barrier for substitution of acetonitrile is lower through a D mechanism. For the analogous

Table 1
Summary of activation parameters for H_2 dissociation from dihydrogen complexes and for substitution reactions in dihydrogen complexes and related compounds

Starting complex	Reaction product	Solvent	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V^{\neq}$ (cm^3 mol^{-1})
$Cr(CO)_3(PCy_3)_2(H_2)$ [a]	$Cr(CO)_3(PCy_3)_2(H_2)$	Toluene	50	−8	
$W(CO)_3(PCy_3)_2(H_2)$ [a]	$W(CO)_3(PCy_3)_2(H_2)$	Toluene	71	43	
$Ir(H)_2(H_2)Cl(P^tBu_2Me)_2$ [b]	$Ir(H)_2Cl(P^tBu_2Me)_2$	Toluene	39	10	
$Ir(H)_2(H_2)Br(P^tBu_2Me)_2$ [b]	$Ir(H)_2Br(P^tBu_2Me)_2$	Toluene	43	10	
$Ir(H)_2(H_2)I(P^tBu_2Me)_2$ [b]	$Ir(H)_2I(P^tBu_2Me)_2$	Toluene	45	12	
$Os(H)_2(H_2)(CO)(P^tBu_2Me)_2$ [c]	$Os(H)_2(CO)(P^tBu_2Me)_2$	Toluene	50	−63	
$RuH_2(H_2)(PPh_3)_3$ [d]	$RuH_2(^t\text{BuNC})(PPh_3)_3$	CD_2Cl_2	75	12	
trans-$[FeH(H_2)(DPPE)_2]^+$ [e]	*trans*-$[FeH(MeCN)(DPPE)_2]^+$	Acetone	86	−4	−18
		THF	80	−25	−23
		Acetonitrile	78	−29	−35
trans-$[FeH(MeCN)(DPPE)_2]^+$ [f]	*trans*-$[FeH(PhCN)(DPPE)_2]^+$	Acetone	102	27	28
		THF	91	−16	20
		Methanol	106	42	34
		Benzonitrile	110	44	35
	trans-$[FeH(2\text{-}MeOC_6H_4CN)(DPPE)_2]^+$	Acetone	84	−34	25
	trans-$[FeH\{2,6\text{-}(MeO)_2C_6H_3CN\}(DPPE)_2]^+$	Acetone	81	−40	40
		THF	84	−40	28
trans-$[RuH(H_2)(DPPE)_2]^+$ [g]	*trans*-$[RuH(MeCN)(DPPE)_2]^+$	Acetone	92	88	
		THF	89	73	
		Acetonitrile	85	65	
trans-$[FeH(H_2)(DEPE)_2]^+$ [h]	*trans*-$[FeH(MeCN)(DEPE)_2]^+$	Acetone	112	48	
		THF	122	77	
trans-$[FeH(N_2)(DEPE)_2]^+$ [h]	*trans*-$[FeH(MeCN)(DEPE)_2]^+$	Acetone	107	40	
		THF	116	68	
trans-$[FeH(N_2)(DMPE)_2]^+$ [h]	*trans*-$[FeH(MeCN)(DMPE)_2]^+$	Acetone	121	73	
		THF	122	76	

[a] Ref. [7].
[b] Ref. [9].
[c] Ref. [10].
[d] Ref. [11].
[e] Ref. [12].
[f] Ref. [13].
[g] Ref. [14].
[h] Ref. [15].

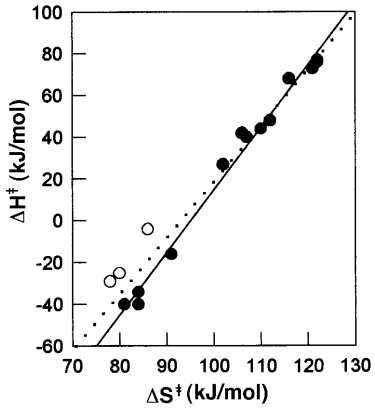


Fig. 1. Plot of $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ for the substitution reactions in *trans*-[FeH(L)(diphosphine)$_2$]$^+$ complexes. (●), reactions occurring through a D mechanism; (—) least-squares fit of these data. (○) values for *trans*-[FeH(H_2)(DPPE)$_2$]$^+$; (···) least-squares fit for the whole set of data in the plot.

ruthenium complex *trans*-[RuH(H_2)(DPPE)$_2$]$^+$, the M–H_2 bond is weaker and the larger size of the metal centre stabilises the Ru–P(chelate) bonds; as a result, substitutions occur through a D mechanism [14]. Thus, it appears that the energies of the M–H_2 and M–P(chelate) bonds in these compounds are close to each other and that the operation of different substitution mechanisms in closely related compounds results from subtle effects caused either by fluxional processes or by the nature of the metal and the ancillary ligands.

At this time, the operation of an associatively activated mechanism for substitution of coordinated dihydrogen is well founded only for the case of *trans*-[FeH(H_2)(DPPE)$_2$]$^+$, but there are previous proposals invoking the opening of a phosphine chelate ring during other reactions of complexes containing polydentate phosphines [5,17]. So, it is reasonable to question whether the operation of a mechanism different from the simple dissociative loss of the leaving ligand is limited to this single case. It would be important to determine the mechanistic details of substitutions in those complexes where some doubt could exist about the operation of a D mechanism. For these cases, the observation of a coordinatively unsaturated compound during the course of the substitution would constitute strong evidence of a D mechanism, although its existence is not enough to assign this mechanism and it must really behave as a reaction intermediate. For example, the synthesis of [FeH(DPPE)$_2$]$^+$ has been reported [6,18] but it can be only prepared under very drastic conditions and there is no evidence on its formation during substitutions in *trans*-[FeH(H_2)(DPPE)$_2$]$^+$. In contrast, the complex [RuH(DPPE)$_2$]$^+$ is detected during the substitution reactions of *trans*-[RuH(H_2)(DPPE)$_2$]$^+$ and suggests a D mechanism that is also supported by the kinetic data [14].

Although a correlation is expected between the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for a series of closely related reactions occurring through a common D mechanism, this kind of correlation must be also taken with care because of the possibility of accidental correlation. For example, Fig. 1 shows a nice correlation between the thermal activation parameters for substitutions in *trans*-[FeH(L)(diphosphine)$_2$]$^+$ complexes (L = H_2, N_2, MeCN) that go through a D mechanism (solid line); the points corresponding to *trans*-[FeH(H_2)(DPPE)$_2$]$^+$ are not very far from the regression line and they can even be reasonably well correlated (dotted line) with the other points despite the different mechanism. Only the very different values of the activation volume and the release of DPPE in the competition experiments with DMPE provide information about the operation of a chelate ring-opening mechanism. As the information about activation volumes and competition experiments is not available for most dihydrogen complexes, it is therefore possible that some other compounds do not substitute H_2 through a simple D mechanism.

3. The kinetics and mechanism of protonation of metal hydrides to form dihydrogen complexes

The reaction of metal hydrides with acids is frequently used for the preparation of dihydrogen complexes (Eq. (3)) and it is of interest to make a comparison between these reactions, in which the hydride complex behaves as a base, and those in which they behave as acids (Eq. (10)). Kinetic data are now available for both types of reaction that reveal significant differences between both processes.

$$L_nMH + B \rightarrow L_nM^- + HB^+ \quad (10)$$

Norton and co-workers [19] showed years ago that reactions in Eq. (10) exhibit a first order dependence with respect to both the metal hydride and the base. The rate constants for proton transfers *from* metal hydrides follow a Brønsted relationship and the reactions occur with a normal kinetic isotope effect (KIE, $k_H/k_D > 1$). More recently, we have obtained kinetic data for reactions of the type shown in Eq. (3), i.e. proton transfers *to* metal hydrides [14,20,21]. The reactions of several *cis*-dihydrides with acids to form [MH(H_2)(diphosphine)$_2$]$^+$ (Eqs. (11)–(13)) are also second order processes (Eq. (14)), but they occur with an inverse KIE ($k_{HX}/k_{DX} < 1$, Table 2) close to the values calculated for a mechanism in which the acid and the hydride interact through a series of dihydrogen-bonded structures (Eq. (15)). The alternative possibility of protonation at the metal centre followed by intramolecular H,H coupling would lead to a normal KIE far from those observed experimentally. The existence of several dihydrogen-bonded adducts similar to those proposed

in Eq. (15) has been reported in recent years [4,22] and they can be considered to provide further evidence favouring this mechanism; when the acidity of the donor in Eq. (15) is insufficient to cause complete proton transfer to the acceptor, the adducts are sufficiently stable and long-lived to allow isolation or characterisation.

Table 2
Summary of kinetic data for protonation of metal hydrides to form dihydrogen complexes in THF solution at 25.0°C

Starting complex	Acid	k_{HX} ($dm^3\ mol^{-1}\ s^{-1}$)	k_{HX}/k_{DX}	$(k_{HX}/k_{DX})_{theor}$ [a]
cis-[FeH_2-(PP_3)] [b]	HBF_4	1.7		
	CF_3COOH	11.2		
	CF_3SO_3H	17.6	0.45	(0.06, 0.87) [c]
	HCl	1.32×10^2	0.62	0.47
	HBr	3.4×10^2	0.64	0.39
cis-[FeH_2-(DPPE)] [d]	HBF_4	0.97×10^2		
	CF_3COOH	1.39×10^2		
	CF_3SO_3H	2.14×10^2	0.21	(0.06, 0.87) [c]
	HCl	4.8×10^2	0.36	0.47
	HBr	1.48×10^3	0.55	0.39
cis-[RuH_2 (DPPE)] [e]	HBF_4	1.12×10^3		
	CF_3COOH	9.2×10^4	0.80	0.87
	HCl	1.7×10^6	0.38	0.47
[CpRuH-(DPPE)] [f]	HBF_4	70		
[CpRuH-(DPPM)] [f]	HBF_4	1.86×10^2		
[CpRuH-(PPh_3)$_2$] [f]	HBF_4	1.69×10^2		

[a] Theoretical values calculated with Eq. (15) of Ref. [20].
[b] Ref. [20].
[c] The value of 0.06 is calculated assuming free H^+, whereas 0.87 results from considering the existence of OH groups.
[d] Ref. [21].
[e] Ref. [14].
[f] Ref. [24].

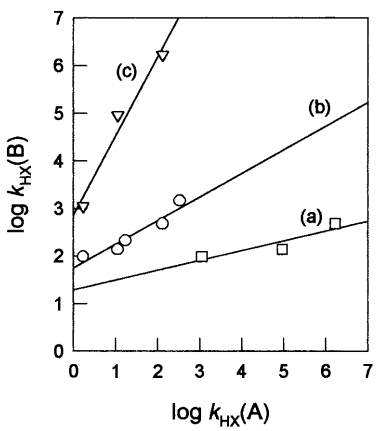


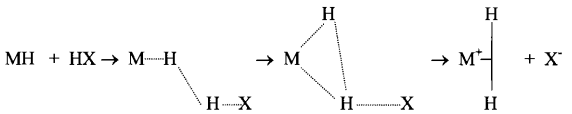
Fig. 2. Correlation between the log k_{HX} values for protonation of two hydride complexes **A** and **B** with several acids. (a) Complex **A** is *cis*-[RuH_2(DPPE)$_2$] and **B** is *cis*-[FeH_2(DPPE)$_2$]. (b) Complex **A** is *cis*-[FeH_2(PP_3)] and **B** is *cis*-[FeH_2(DPPE)$_2$]. (c) Complex **A** is *cis*-[FeH_2(PP_3)] and **B** is *cis*-[RuH_2(DPPE)$_2$].

$$cis\text{-}[FeH_2(DPPE)_2] + HX \rightarrow trans\text{-}[FeH(H_2)(DPPE)_2]^+ + X^- \quad (11)$$

$$cis\text{-}[RuH_2(DPPE)_2] + HX \rightarrow trans\text{-}[RuH(H_2)(DPPE)_2]^+ + X^- \quad (12)$$

$$cis\text{-}[FeH_2(PP_3)] + HX \rightarrow cis\text{-}[FeH(H_2)(PP_3)]^+ + X^- \quad (13)$$

$$\text{Rate} = k_{HX}[\text{hydride}][HX] \quad (14)$$



(15)

The values of the rate constant k_{HX} in THF solution for the reactions of a *cis*-[MH_2(phosphine)$_4$] complex with different acids do not increase with the strength of the acid but follow the order $HBF_4 < CF_3COOH < CF_3SO_3H < HCl < HBr$ (Table 2). The fact that the slowest reactions are observed for the strongest acids can be interpreted in terms of competitive attack by HX molecules and (H^+, X^-) ion pairs, with a lower reactivity for the ion pairs [20]. Although the lack of reliable acidity data in THF precludes a detailed analysis of the problem, the existence of a linear correlation between the sets of log k_{HX} data for any couple of complexes (Fig. 2) indicates that a Brønsted-type relationship also operates for the reactions in Eqs. (11)–(13) [14,21]. If the PP_3 complex is chosen as reference, the correlation is expressed by Eq. (16) and the slope and zero intercept of the fits lead to two parameters, R and S, that measure the intrinsic reactivity (R) and selectivity (S) of the dihydride towards acids [14].

$$\log k_{HX} = R + S \log k_{HX(Fe\text{–}PP_3)} \quad (16)$$

The values of R for the three complexes in Eqs. (11)–(13), range from 0 (*cis*-[FeH_2(PP_3)], reference compound) to 2.87 (*cis*-[RuH_2(DPPE)$_2$]), whereas S ranges from 0.50 (*cis*-[FeH_2(DPPE)$_2$]) to 1.66 (*cis*-[RuH_2(DPPE)$_2$]). Although only a very limited set of values is available, the intrinsic reactivity of the complexes can be rationalised by considering the basicity of the species attacked by the acid as well as the possibility of isomerisation of the *cis*-dihydride to a more reactive *trans* species [14]. The basicity of the metal hydrides can be measured by the pK_a of their corresponding dihydrogen complexes, and the scale proposed by Morris and co-workers [1,23] is of great utility for this purpose. However, some correction is necessary in those cases where the hydride that is attacked by acids is not the most stable isomer; in that case, the reported pK_a

values must be corrected using the equilibrium constant for *cis–trans* isomerisation. Thus, for a stable *cis*-dihydride that isomerises to a more reactive *trans* isomer before being attacked by acids to give a *trans*-hydride-dihydrogen complex, the experimental pK_a and its value in the absence of isomerisation (pK'_a) are related by Eq. (17), where K_i is the equilibrium constant for isomerisation. Once the basicity of the reactive hydride and possible isomerisation pre-equilibria are considered, the intrinsic reactivity of the complexes can be correlated with the thermodynamic driving force for the reaction and the rate increases with the difference in acidity between both acid–base conjugated pairs [14].

$$pK_a = pK'_a + \log K_i \quad (17)$$

In an attempt to measure the *R*, *S* values for complexes of a different nature, we have also studied the kinetics of protonation of CpRuH(L) complexes (L = DPPM, DPPE, $2PPh_3$) [24]. The reaction of these compounds with HBF_4 in THF leads initially to the corresponding dihydrogen complexes (Eq. (18)), but the process continues in some cases to yield the classical dihydrides or a mixture of both tautomeric forms [25]. As previously reported for the reaction of $CpWH_2$ with HCl [26], the protonation of CpRuH(L) is much faster than tautomerisation and the kinetics of the two processes are clearly separated. The rate law for the reactions in Eq. (18) is also given by Eq. (14), with the values of the rate constant included in Table 2.

$$CpRuH(L) + HBF_4 \rightarrow CpRu(H_2)(L)^+ \quad (18)$$

Surprisingly, the CpRuH(L) complexes do not react with HCl or HBr, despite the fact that the measured pK_a values of their dihydrogen complexes are close to 7 and protonation with weaker acids has been reported in the literature [27]. A difference in the protonation behaviour of $Cp^*RuH_3(PCy_3)$ with HBF_4 and weaker proton donors has also been observed recently [28] and there is some evidence that it is caused by a change in the protonation mechanism. The impossibility of measuring k_{HX} for the reaction of CpRuH(L) with some acids precludes the determination of the *R* and *S* values, but the lack of reaction clearly indicates the limited utility of an aqueous pK_a scale to measure the acidity of dihydrogen complexes. In solvents of low dielectric constants, such as those commonly used for these complexes, extensive ion-pairing and homoconjugation (Eqs. (19) and (20)) lead to a species distribution in HX solutions (X = Cl, Br, etc.) very different from that in water, where solvated protons play a dominant role in the acidic behaviour. For this reason, we have proposed [24] using a non-aqueous pK_a scale, in which only the dihydrogen complexes and those species that have been directly used in the equilibrium measurements leading to the determination of their pK_a values should be included.

$$HX \rightleftarrows H^+ + X^- \rightleftarrows (H^+, X^-)_{ip} \quad (19)$$

$$HX + X^- \rightleftarrows HX_2^- \quad (20)$$

The values of $\log k_{HX}$ for reaction of the CpRuHL complexes with HBF_4 are not correlated with the pK_a values of the corresponding dihydrogen complexes. This lack of correlation can be caused by a very different selectivity of these complexes towards acids or by a change in the protonation mechanism [24]. Protonation at the metal centre or at an ancillary ligand are reasonable alternatives, but a more versatile behaviour of dihydrogen-bonded adducts can not be discarded [28].

4. Conclusion

Although comprehensive kinetic data have been obtained only for a limited number of reactions involving a few dihydrogen complexes, the results available indicate that the kinetic properties of these compounds are not necessarily simple and easy to anticipate. These first results pose some interesting questions about the chemical behaviour of these complexes:

1. Substitution reactions appear to be dominated by a D mechanism, but there is the possibility of other reaction pathways and it is necessary to determine clearly the requirements for the reactions to go through alternative mechanisms. The relevance of the chelate ring-opening mechanism, or any other alternative mechanism, to the catalytic properties of the dihydrogen complexes also needs to be explored.
2. The possibility of extending to other complexes the correlation found between the rates of formation of the $[FeH(H_2)(diphosphine)_2]^+$ compounds must also be checked because it would provide a direct route for understanding the factors that lead to the different kinetic behaviour of metal hydrides towards acids.
3. The reactivity of the CpRuH(phosphine)$_2$ complexes with acids clearly indicates the limitations of an aqueous pK_a scale for dihydrogen complexes and opens the possibility of alternative mechanisms for the protonation reactions. Any progress in the knowledge of the thermodynamic and kinetic aspects of the protonation and tautomerisation processes would be also of great help for a better understanding of the chemical properties and relative stability of dihydrogen complexes versus classical dihydrides.

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