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New Insights into the Mechanism of Proton Transfer to Hydride Complexes: Kinetic and Theoretical Evidence Showing the Existence of Competitive Pathways for Protonation of the Cluster $[W_3S_4H_3(dmpe)_3]^+$ with Acids**

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Abstract: The reaction of the hydride cluster $[W_3S_4H_3(dmpe)_3]^+$ (**1**, dmpe = 1,2-bis(dimethylphosphanyl)ethane) with acids (HCl, CF_3COOH, HBF_4) in CH_2Cl_2 solution under pseudo-first-order conditions of excess acid occurs with three kinetically distinguishable steps that can be interpreted as corresponding to successive formal substitution processes of the coordinated hydrides by the anion of the acid (HCl, CF_3COOH) or the solvent (HBF_4). Whereas the rate law for the third step changes with the nature of the acid, the first two kinetic steps always show a second-order dependence on acid concentration. In contrast, a single kinetic step with a first-order dependence with respect to the acid is observed when the experiments are carried out with a deficit of acid. The decrease in the T_1 values for the hydride NMR signal of **1** in the presence of added HCl suggests the formation of an adduct with a W−H···H−Cl dihydrogen bond. Theoretical calculations for the reaction with HCl indicate that the kinetic results in CH_2Cl_2 solution can be interpreted on the basis of a mechanism with two competitive pathways. One of the pathways consists of direct proton transfer within the W−H···H−Cl adduct to form W−Cl and H_2, whereas the other requires the presence of a second HCl molecule to form a W−H···H−Cl···H−Cl adduct that transforms into W−Cl, H_2 and HCl in the rate-determining step. The activation barriers and the structures of the transition states for both pathways were also calculated, and the results indicate that both pathways can be competitive and that the transition states can be described in both cases as a dihydrogen complex hydrogen-bonded to Cl^- or HCl_2^-.

Keywords: cluster compounds • hydride ligands • kinetics • protonation • reaction mechanisms

Introduction

The understanding of the kinetics and reaction mechanisms for proton-transfer processes is a fundamental problem in chemistry, and research in the last few decades has established that most proton-transfer processes such as those represented in Equation (1) are fast and are often diffusion-controlled reactions.[1] Moreover, the availability in recent years of ultrafast instrumentation and more powerful computational tools is revealing more detailed knowledge of the intimate mechanistic details of these reactions.[2] In addition to these rapid processes, in some cases proton transfer occurs significantly slower than expected for diffusion control. Although the reactions of carbon acids are the most studied of these "slow" proton-transfer processes,[1,3] another important example of non-diffusion-controlled reactions of this type are those in which the proton to be transferred is initially coordinated to a metal centre [Eq. (2)].[4]

$$A{-}H + B^- \rightarrow A^- + H{-}B \qquad (1)$$

$$L_nM{-}H + B^- \rightarrow L_nM^- + H{-}B \qquad (2)$$

However, in addition to the processes represented by Equation (2), in which the L_nMH complex behaves as an

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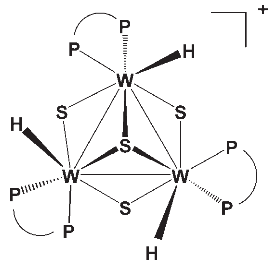
[**] dmpe = 1,2-bis(dimethylphosphanyl)ethane.

acid, many hydride complexes are basic enough to behave as a base and to accept a proton.[5] Although attack by the proton at the metal centre can not be completely ruled out in all cases, most of the information available to date indicates that attack occurs preferentially at the coordinated hydride[6] and leads to formation of a dihydrogen complex [Eq. (3)], which can be stable or release H_2 in a subsequent step.[5] The reverse of the process in Equation (3) leads from an H_2 molecule to a proton and a coordinated hydride, and so proton transfer to hydride complexes is relevant to heterolytic splitting of H_2, a topic of current interest for its relevance to biological dihydrogen activation, ionic hydrogenations and catalytic applications of dihydrogen complexes.[7] For this reason, there is also considerable interest in studying the kinetic and mechanistic aspects of these protonation reactions, and the information currently available reveals an important role of dihydrogen-bonded species (M−H···H−X) as transition states or real intermediates during proton transfer.[8–17] However, some mechanistic diversity may result as a consequence of formation of homoconjugated HB_2^- species with an active role in proton transfer,[14–16] and because ion pairing with external anions may be mechanistically relevant in the solvents most commonly used to carry out the proton transfers in Equation (3).[8,9,17]

Abstract in Spanish: *La reacción del hidruro clúster* $[W_3S_4H_3(dmpe)_3]^+$ *(**1**) con ácidos (HCl,* CF_3COOH*,* HBF_4*) en disolución de* CH_2Cl_2 *bajo condiciones de pseudo-primer orden (exceso de ácido), ocurre con tres pasos distinguibles cinéticamente y que pueden asignarse a los sucesivos procesos de sustitución formal de los tres hidruros coordinados por el anión del ácido (HCl,* CF_3COOH*) o por el disolvente (*HBF_4*). Mientras que la ley de velocidad para la tercera etapa cambia con la naturaleza del ácido, las dos primeras etapas siempre muestran una dependencia de segundo orden con respecto a la concentración de ácido. Por el contrario, cuando los experimentos se realizan usando un déficit de ácido solo se observa una etapa con una dependencia de primer orden respecto al ácido. La disminución de los valores de* T_1 *para la señal de RMN del hidruro de **1** en presencia de un exceso de HCl sugiere la formación de un aducto con un enlace de dihidrógeno W−H···H−Cl. Los cálculos teóricos realizados para la reacción con HCl indican que los resultados cinéticos en disolución de* CH_2Cl_2 *pueden interpretarse considerando un mecanismo con dos caminos de reacción competitivos. Uno de los caminos consistiría en la transferencia protónica directa en el aducto W−H···H−Cl para formar W−Cl y* H_2*, mientras que el otro camino requeriría de la presencia de una segunda molécula de HCl para formar un aducto W−H···H−Cl···H−Cl que se convertiría en W−Cl,* H_2 *y HCl en la etapa controlante de la velocidad. Se han calculado también las barreras de activación y las estructuras de los estados de transición para ambos caminos, y los resultados indican que los dos caminos pueden ser competitivos y que los estados de transición pueden describirse en ambos casos como complejos de dihidrógeno formando enlaces de hidrógeno con* Cl^- *o* HCl_2^-*.*

$$L_nM{-}H + HB \rightarrow L_nM(H_2)^+ + B^- \rightarrow L_nM^+ + H_2 + B^- \qquad (3)$$

The study of processes like that in Equation (3) can be more complicated in cluster hydrides. Hydride ligands in transition metal clusters can be located in terminal, edge-bridging, face-capping and interstitial positions. In triangular cluster chalcogenides, the edge-bridging mode is dominant,[18] although ambiguity sometimes exists regarding this μ-H coordination mode versus the μ_3-H face-capping one.[19] Terminal coordination of the hydride to the metal is restricted to the phosphano incomplete cuboidal $W_3(\mu_3\text{-}Q)(\mu\text{-}Q)_3$ (Q = S, Se) complexes. This system has been widely investigated in the last few decades, motivated by the relevance of these cubane-type structures as models for several biological and industrial catalytic processes.[20,21] The comprehensive work of Sykes et al. regarding the kinetics of substitution of the terminal ligands in the aqua complexes $[M_3Q_4(H_2O)_9]^{4+}$ and $[M_4Q_4(H_2O)_{12}]^{4+}$ has lead to a very good understanding of the mechanisms involved in these processes,[20,22] but information on the kinetics and mechanisms of other reactions are practically nonexistent for these clusters. We recently reported that the protonation of the hydride cubane-type cluster $[W_3S_4H_3(dmpe)_3]^+$ (**1**; dmpe = 1,2-bis(dimethylphosphanyl)ethane, Scheme 1) with acids in MeCN and $MeCN/H_2O$ to form the corresponding $[W_3Q_4X_3(dmpe)_3]^+$ halide complexes (**2**) [Eq. (4); X = Cl, Br; $[W_3Se_4H_3(dmpe)_3]^+$ undergoes an analogous reaction] occurs with three kinetically distinguishable steps,[23,24] kinetics significantly more complicated than those observed for the substitution of the aqua ligands in the corresponding $[M_3Q_4(H_2O)_9]^{4+}$ and $[M_4Q_4(H_2O)_{12}]^{4+}$ complexes. Despite this complexity, the properties of cluster **1** (stable in air and soluble in a wide variety of solvents) make it an excellent substrate for a more detailed study of the mechanism of protonation of hydride complexes. Because the second step in the mechanism previously proposed[24] involves attack by a solvent molecule, we considered it of interest to carry out a kinetic study of the reaction in Equation (4) using a weakly coordinating solvent such as CH_2Cl_2. Surprisingly, we found that the initial proton transfer to the coordinated hydrides shows an unprecedented second-order dependence on acid concentration. To get a better understanding of the mechanistic relevance of this finding, theoretical calculations were carried out, and the experimental and computational results presented here reveal the existence of competitive reaction pathways for protonation of the hydride ligands.



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Scheme 1.

$$[W_3S_4H_3(dmpe)_3]^+ + 3\,HX \rightarrow [W_3S_4X_3(dmpe)_3]^+ + 3\,H_2 \qquad (4)$$

Results and Discussion

Reaction kinetics of $[W_3S_4H_3(dmpe)_3]^+$ with acids in CH_2Cl_2 solution: The reaction of **1** with an excess of HCl in dichloromethane solution occurs according to Equation (4) (X = Cl), and typical results of the stopped-flow experiments are illustrated in Figure 1.

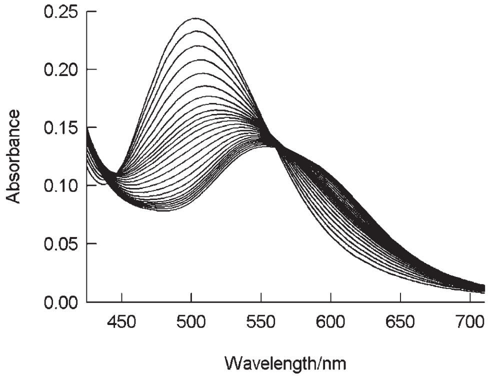

Figure 1. Typical spectral changes with time for the reaction of cluster **1** with HCl in CH_2Cl_2 solution at 25.0 °C. The data were recorded during 1000 s with a logarithmic time base, although for simplicity only every twentieth acquired spectrum is shown.

The formation of $[W_3S_4Cl_3(dmpe)_3]^+$ as the reaction product was confirmed in independent NMR and MS experiments. Analysis of the spectral changes shown in Figure 1 reveals that the process occurs with three kinetically distinguishable steps with rate constants k_{1obs}, k_{2obs} and k_{3obs}. No changes in the observed rate constants were observed when the cluster concentration was changed, which indicates that all three constants show a first-order dependence on the concentration of **1**. Although the absorbance band of **1** at 502 nm disappears in the first step, the band typical of the trichloro complex only appears in the last step, that is, two reaction intermediates $\mathbf{I_1}$ and $\mathbf{I_2}$ are previously formed. The electronic spectra calculated for these intermediates are included in Figure 2 and show that the maximum of the absorption band is displaced to longer wavelength as the reaction progresses. Although the spectra of **1** and **2** are little affected by the solvent, the spectra calculated for the intermediates in dichloromethane differ from those obtained in MeCN and $MeCN/H_2O$ solutions,[23] which suggests that the nature of the intermediates changes with solvent. Moreover, the effect of the solvent on the kinetics of Equation (4) is not limited to changes in the spectra of the reaction intermediates, but the dependence of the observed rate constants on acid concentration is also different. Previous studies in MeCN-containing solutions revealed that k_{1obs} changes linearly with concentration of HCl, whereas k_{2obs} and k_{3obs} are independent of acid concentration. In contrast, the plots in Figure 3 show that the observed rate constants for the first and second steps in dichloromethane solution have a second-order dependence on acid concentration. The fit of the experimental data by Equation (5) (X = Cl; i = 1, 2) leads to $k_1 = (2.41 \pm 0.06) \times 10^5\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$ and $k_2 = (1.03 \pm 0.03) \times 10^4\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$. The values obtained for k_{3obs} in CH_2Cl_2 solution only show random changes with acid concentration, which indicates zero order with respect to HCl; the k_3 value is $(4 \pm 1) \times 10^{-3}\,\mathrm{s}^{-1}$.

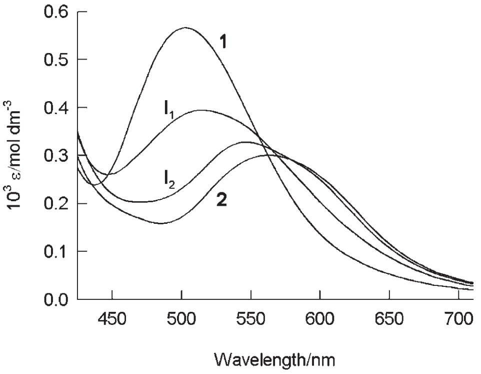

Figure 2. Electronic spectra calculated for starting complex **1**, reaction intermediates $\mathbf{I_1}$ and $\mathbf{I_2}$ and the final reaction product **2** from the spectral changes observed during the reaction of cluster **1** with HCl in CH_2Cl_2 solution.

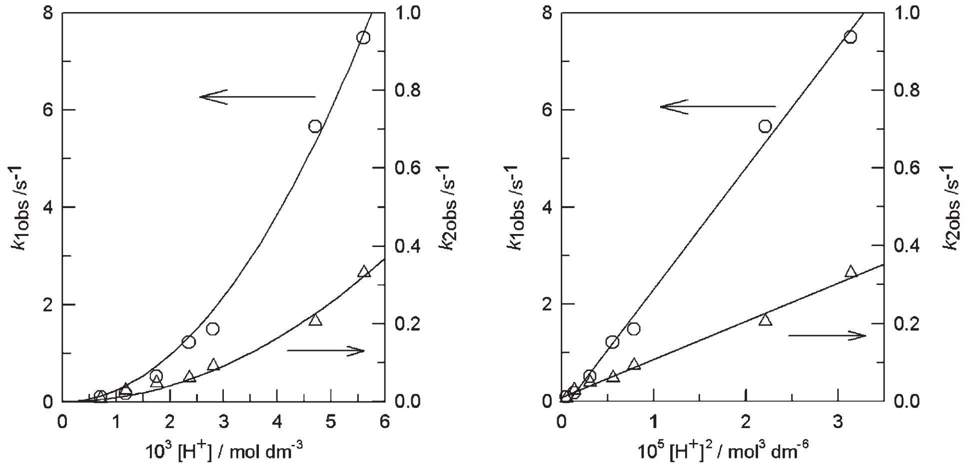

Figure 3. Plots of the observed rate constants vs $[H^+]$ (left) and $[H^+]^2$ (right) for the first (○) and second (△) steps in the reaction of **1** with HCl in CH_2Cl_2 solution at 25.0 °C. Note that the rate constants of each step are plotted with different scales (see arrows).

$$k_{i\text{obs}} = k_i[\text{HX}]^2 \qquad (5)$$

To our knowledge, these results are the first example of proton-transfer processes to a hydride complex with second-order dependence on acid concentration. To add further support to this finding, additional evidence was sought by studying the kinetics of reaction of **1** with other acids in dichloromethane solution. The results obtained with HBF_4 and CF_3COOH are quite similar to those with HCl: the reaction occurs with three kinetic steps for HBF_4 and two steps for CF_3COOH, but in both cases $k_{1\text{obs}}$ and $k_{2\text{obs}}$ show a second-order dependence on acid concentration. However, whereas the $k_{1\text{obs}}$ values can be well fitted by Equation (5), the fit of $k_{2\text{obs}}$ with these acids requires an additional acid-independent term [Eq. (6) with $i=2$, see Figure 4] which suggests that the second step actually occurs under equilibrium conditions with some contribution from the reverse reaction to the rate measured for this step. The values of $k_{3\text{obs}}$ obtained for HBF_4 change linearly with acid concentration and can be fitted by Equation (7). As occurs with HCl, the maximum of the absorption band is displaced to longer wavelength as the reaction with HBF_4 or CF_3COOH progresses, although the actual values are specific for each acid. The values of the rate constants and the absorption maxima of the reaction intermediates observed in dichloromethane solution for the three acids studied are summarised in Table 1.

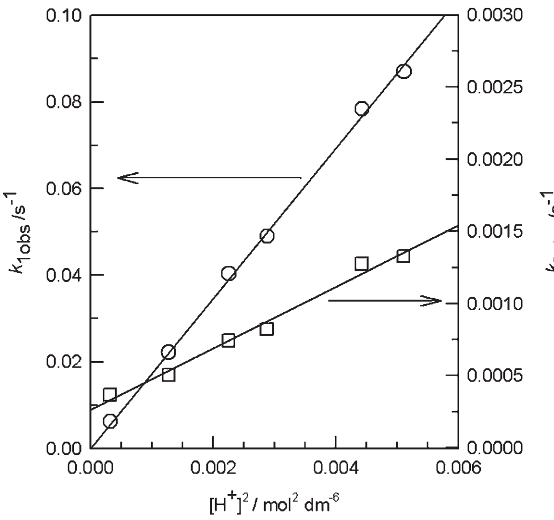

Figure 4. Plots of the observed rate constants versus $[H^+]^2$ for the first (○) and second (□) steps in the reaction of **1** with CF_3COOH in CH_2Cl_2 solution at 25.0 °C. Note that the rate constants for the two steps are plotted with different scales (see arrows).

Table 1. Rate constants and absorption maxima calculated for the species formed during the protonation of **1** with different acids in CH_2Cl_2 solution at 25.0 °C.

Acid	Rate constants			Absorption maxima [nm]			
	k_1 [$\text{M}^{-2}\,\text{s}^{-1}$]	k_2 [$\text{M}^{-2}\,\text{s}^{-1}$]	k_3[a]	**1**	$\mathbf{I}_1$	$\mathbf{I}_2$	**P**
HCl	$(2.41\pm0.06)\times10^5$	$(1.03\pm0.03)\times10^4$	$(4\pm1)\times10^3\,\text{s}^{-1}$	502	516	547	562
HBF_4	$(8.0\pm0.4)\times10^4$	$(1.11\pm0.06)\times10^4$[b]	$11.9\pm0.6\,\text{M}^{-1}\,\text{s}^{-1}$	502	509	535	541
CF_3COOH	17.3 ± 0.2	0.21 ± 0.01[c]	[d]	502	513	540	–[d]

[a] Because of the different rate laws observed for this step, the units of each rate constant are given. [b] Data fitted by Equation (6) with $k_{2b}=(2.4\pm0.6)\times10^{-2}\,\text{s}^{-1}$. [c] Data fitted by Equation (6) with $k_{2b}=(2.6\pm0.4)\times10^{-4}\,\text{s}^{-1}$. [d] Only two steps are observed for this acid. Although NMR experiments provide evidence for the formation of small amounts of the product corresponding to the third step, this occurs over very long reaction times, much longer than those used in the stopped-flow measurements.

Note that despite the complex multistep kinetics, a satisfactory analysis can be achieved in all cases, and the second-order dependence with respect to the acid is always clear for the first two steps. However, the results obtained for the third step differ for the different acids: it is absent for CF_3COOH and shows order zero for HCl and order one for HBF_4.

$$k_{i\text{obs}} = k_i[\text{HX}]^2 + k_{i\text{b}} \qquad (6)$$

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

NMR experiments and the number and nature of the reaction intermediates: Although none of the intermediates detected in the kinetic studies described above could be isolated, the changes in the position of the absorption maxima of the intermediates $\mathbf{I_1}$ and $\mathbf{I_2}$ with the nature of the acid indicates that the mechanism previously proposed for this reaction in neat MeCN and MeCN/H_2O is not valid in CH_2Cl_2 solution. Of special relevance is the position of the band for intermediate $\mathbf{I_1}$, which according to the previous proposal[23] should contain a vacant coordination site and have a spectrum independent of the nature of the acid. However, the data in Table 1 clearly indicate that this is not the case for the reaction in dichloromethane, where the changes in the band position when the acid is replaced suggest coordination of the anion of the acid. Additional evidence supporting this conclusion was obtained when the reactions with the three acids were monitored by NMR spectroscopy. When different aliquots of a solution of the acid are added to an NMR tube containing a concentrated solution of **1**, a careful selection of the amount of acid added allows the reaction to be stopped at different conversions. The proton and phosphorus spectra recorded after each addition of acid show the appearance and disappearance of signals, as well as intensity changes between successive spectra. This information can be used to determine the number of intermediates and to assign their NMR signals. For the reaction with HCl, only two intermediates were observed between **1** (with three W–H bonds) and the final product **2** (with three W–Cl bonds), and the signals in the $^{31}P\{^1H\}$ and ^1H NMR spectra of both intermediates are summarised in Table 2. Both clusters **1** and **2** have a C_3 axis and show two phosphorus signals associated with the presence of two kinds of phosphorus atoms, located below (*trans* to the capping sulfur atom) and above (*trans* to the bridging sulfur atom) the plane defined by the three metal atoms. The six phosphorus signals observed for

Table 2. $^{31}P\{^1H\}$ and ^1H NMR signals in CD_2Cl_2 solution at 25.0 °C for all the species observed during the reaction between **1** and different acids.

			HCl		HBF$_4$[a]		CF$_3$COOH	
Species	**1**	$\mathbf{I_1}$	$\mathbf{I_2}$	**P**	$\mathbf{I_1}$	$\mathbf{I_1}$	$\mathbf{I_2}$	**P**
δ_P [ppm]	13.7	13.9	10.9	6.8	12.7	11.2	11.7	11.1
	−5.6	10.8	7.3	6.2	11.1	10.6	10.3	7.7
		5.7	4.9		2.5	10.4	10.0	
		0.3	4.6		1.8	−0.8	7.7	
		−2.4	−1.2		−2.8	−0.9	−1.2	
		−8.8	−1.9		−11.9	−9.9	−2.7	
δ_H [ppm]	−1.09	−0.30	−0.04[b]	–[c]	0.04	−0.07	−0.13	–[c]
$J_{H,P}$ [Hz]	29.4, 45.4	33.0, 45.1			(33.2, 44.9)	29.8, 50.5	28.6, 49.5	
		−0.60			−0.43	−0.52		
		27.3, 46.0			28.9, 44.0	28.6, 44.8		

[a] The signals corresponding to intermediate $\mathbf{I_2}$ and final product **P** could not be assigned for the case of HBF_4 because abstraction of fluoride occurs during the long time required to acquire the NMR spectra, which leads to a complex mixture of species with an exceedingly large number of signals in the experimental spectra. [b] The coupling constants for this signal could not be precisely assigned because it overlaps with those of the Si-containing products. [c] No hydride signal was observed for this species.

both $\mathbf{I_1}$ and $\mathbf{I_2}$ indicate lowering of symmetry in the intermediates that makes the dmpe ligands coordinated to the three metal centres nonequivalent. As the proton spectra show the existence of two W–H signals for $\mathbf{I_1}$ and only one for $\mathbf{I_2}$, the most plausible interpretation is that intermediate $\mathbf{I_1}$ is actually $[W_3S_4H_2Cl(dmpe)_3]^+$ and $\mathbf{I_2}$ is $[W_3S_4HCl_2(dmpe)_3]^+$. In the third step, the reaction is completed at the third metal centre, and so there is no W–H signal in the proton spectrum. As the C_3 symmetry is recovered, only two phosphorus signals are observed for $[W_3S_4Cl_3(dmpe)_3]^+$ (**2**). Although some of the signals for the intermediates are split by P,P coupling, no attempt was made to measure the corresponding coupling constants due to their expected relatively low values ($J_{P,P}$ are less than ca. 5 Hz for similar tungsten complexes)[24,25] and the recording conditions of the spectra (dilute solutions, large number of signals), which require routine application of line-broadening procedures to increase the sensitivity to a satisfactory level. When HCl is replaced by CF_3COOH two intermediates are also observed. Although the intermediates have the same number of NMR signals for both acids (see Table 2), the chemical shifts are different in each case, which adds further support to the formulation of $\mathbf{I_1}$ and $\mathbf{I_2}$ as $[W_3S_4H_2X(dmpe)_3]^+$ and $[W_3S_4HX_2(dmpe)_3]^+$ respectively, where X^- is the anion of the acid, an interpretation that would also explain the differences in Table 1 between the UV/Vis spectra for the intermediates with different acids. The final product in the reaction with CF_3COOH, that is, $[W_3S_4(CF_3COO)_3(dmpe)_3]^+$, is only detected in the NMR experiments as a minor product after 18 h of reaction at room temperature with relatively high acid concentrations (ca. 0.1 M). This observation agrees with the kinetic results that show the existence of only two steps for this acid, the third step being undetectable under the conditions of the stopped-flow experiments.

The interpretation of the NMR monitoring of the reaction between **1** and HBF_4 in dichloromethane is not so clear as for the other acids. Formation of species $[W_3S_4H_nX_{3-n}(dmpe)_3]^+$ is not expected due to the weak coordinating ability of BF_4^-, and in fact the only intermediate ($\mathbf{I_1}$) whose signals could be unambiguously assigned does not show the P–F couplings expected for a species with coordinated BF_4^- (see Table 2). The phosphorus spectra recorded at later stages of the reaction could not be interpreted because they are complicated by the presence of a large number of signals, many of them split by P–F coupling. At the end of the reaction, formation of $[W_3S_4F_3(dmpe)_3]^+$ was observed; its signals in CD_2Cl_2 ($\delta_P = 12.4$ ppm, $^2J_{P,F} = 61.6$ Hz and $\delta_P = 9.1$ ppm, $^2J_{P\text{-}F} = 97.6$ Hz) showed only small changes with respect to those observed in MeCN solution.[23] Monitoring the reaction by ^{19}F NMR spectroscopy confirmed that no fluorine-containing coordinated species are formed during the early stages of the reaction and, in agreement with the phosphorous spectrum for $[W_3S_4F_3(dmpe)_3]^+$, the fluorine spectrum shows a doublet of doublets (centred at $\delta = -201.1$ ppm) with identical $^2J_{P,F}$ coupling constants. Although no definitive conclusions can be made, the similarities between the reaction kinetics of **1** with HBF_4 and with the other acids leads us to think that the complexities observed during the NMR monitoring of the reaction with HBF_4 are due to fluorine-abstraction processes that are slow on the stopped-flow timescale but do occur during the long times required to acquire the NMR spectra with a reasonable signal-to-noise ratio. The $\mathbf{I_1}$, $\mathbf{I_2}$ and **P** species formed in the kinetic experiments would then be $[W_3S_4H_n(dmpe)_3]^{(4-n)+}$ (with $3-n$ vacant coordination sites) or $[W_3S_4H_n(CH_2Cl_2)_{3-n}(dmpe)_3]^{(4-n)+}$ (with $3-n$ weakly coordinated solvent molecules). The results of theoretical calculations (see below) favour the latter formulation.

In summary, the set of stopped-flow and NMR experimental data for the reaction of **1** with different acids in CH_2Cl_2 solution can be rationalised according to a mechanism in which the three observed steps correspond to sequential acid-promoted substitution of the three hydride ligands at the different metal centres. Schematically, the process can be represented by Equation (8), where the dmpe ligands have been omitted for clarity and X^- represents the anion of the acid, except for HBF_4, for which these coordination sites are probably occupied by solvent molecules.

$$W_3S_4H_3^+ \xrightarrow{k_{1obs}} W_3S_4H_2X^+ \xrightarrow{k_{2obs}} W_3S_4HX_2^+ \xrightarrow{k_{3obs}} W_3S_4X_3^+ \qquad (8)$$

According to this scheme, all three steps are similar processes, and hence the same rate law is expected for each of them. However, whereas a second-order dependence on acid concentration is evident for k_{1obs} and k_{2obs}, the rate law for the third step differs from one acid to another. Although the reasons for the different behaviour observed for k_{3obs} are not clear at this moment, a plausible explanation would be a less thermodynamically favoured reaction at the third metal centre that would result in a higher contribution of the reverse process to the net reaction rate and would mask the dependence of the forward process on the acid. This contribution and the accumulation of experimental and fitting errors could be responsible for the different kinetic results obtained for the third step. For this reason, the discussion in the next sections is focussed on the second-order dependence observed for the first two steps, although some comments about the formal aspects of the kinetics of reaction must be made first.

Comprehensive work by Sykes et al.[20,22] indicates that the kinetics of substitution reactions in $[M_3Q_4(H_2O)_9]^{4+}$ clusters (M = Mo, W; Q = S, Se) occurs with statistically controlled kinetics; that is, the rates of substitution at the three metal centres are in a 3:2:1 ratio. It can be demonstrated that if the three chromophores behave independently, there is a simplification of the rate equations and the expected three-exponential kinetics reduce to a single exponential with an observed rate constant that corresponds to reaction at the third metal centre.[26] Our previous results for the acid-assisted substitution of coordinated hydrides in $[W_3Q_4H_3(dmpe)_3]^+$ complexes in MeCN and MeCN/H$_2$O solutions also favour the occurrence of statistically controlled kinetics.[23] In contrast, the results in dichloromethane solution can not be explained by invoking statistically controlled kinetics, and this indicates an important effect of the solvent that warrants future work to get a better understanding of the reasons for deviations from the statistical reaction kinetics of this kind of complexes. From the results in the present work, the k_1/k_2 ratio is 7, 23 and 82 for the reaction of **1** with HBF$_4$, HCl and CF$_3$COOH, respectively. All of these ratios are higher than the value expected from statistics (3:2 = 1.5), and the significant differences between the three acids indicate an important effect of the entering ligand on the deviation from the statistical prediction.

In an attempt to obtain new information about these deviations, the kinetics of the reaction in Equation (4) were also studied under conditions of an excess of metal complex **1**. Unfortunately, in most cases the absorbance changes are very small and occur over such a long time that a satisfactory kinetic analysis is precluded. Only for the case of HBF$_4$ with acid concentrations lower than but close to the complex concentration were good spectral changes obtained. As expected from the deficit of acid, the spectral changes are typical of a single-step process, and a satisfactory fit can be obtained with a "**1**+HBF$_4$→products" scheme with first-order dependence on the concentration of both **1** and the acid and a rate constant $k_1 = 0.040 \pm 0.007\,\text{M}^{-1}\,\text{s}^{-1}$. No significant improvement in the quality of the fit is obtained by introducing a second-order dependence with respect to the acid, which seems to indicate that the deficit of acid causes a change in the rate law from the second-order dependence observed with excess acid to a less acid dependent form when there is a deficit of acid. The change in the rate law observed for HBF$_4$ under acid deficit together with the impossibility of studying the reaction with other acids with an excess of metal hydride precludes a more detailed analysis of the deviations from statistical behaviour.

The T_1 values for the hydride signal of $[W_3S_4H_3(dmpe)_3]^+$ and the mechanism of proton transfer from acids: The unprecedented second-order dependence on acid concentration observed for proton transfer from acids HX to **1** under pseudo-first-order conditions of excess acid indicates that two molecules of acid are required to complete proton transfer to the hydride complex. As previous work[24] with the Se analogue of **1** showed that the T_1 values for the hydride signal in the presence of acid provides strong evidence for initial attack by the acid at the hydride ligands, a similar study was now also carried out for the S cluster. The results in Figure 5 show that whereas the addition of the weak hydrogen donor (CF$_3$)$_2$CHOH does not cause any significant decrease in the T_1 values for the hydride signal in the ^{1}H NMR spectrum of **1** in CD$_2$Cl$_2$ solution, the presence of an excess of HCl leads to a small but significant decrease that can be interpreted by considering the formation of a dihydrogen-bonded W−H···H−Cl adduct. If this adduct contains a single W−H···H−Cl interaction and the other two hydrides continue to relax at the same rate, $(1/T_1)_{obs}$ will be the average of the rates of relaxation of the three hydrides, and a value of 0.458 s can be deduced for the relaxation

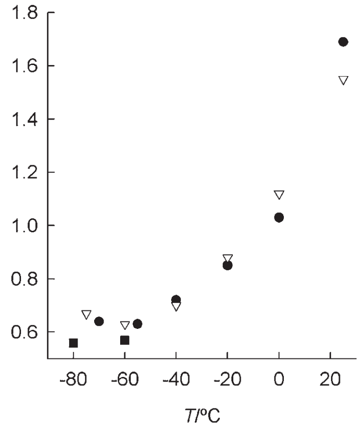

Figure 5. Temperature dependence of the T_1 value for the hydride signal of complex **1** in CD$_2$Cl$_2$ solution: complex alone (●), complex plus an excess of (CF$_3$)$_2$CHOH (▽) and complex plus an excess of HCl (■). For the case of HCl, measurements could not be made at higher temperatures because the proton-transfer process is accelerated and the hydride signal disappears.

time of the dihydrogen-bonded hydride ligand. If conversion of the complex to the adduct is considered to be complete, a H···H distance of about 2.33 Å can be estimated from the decrease in T_{1min} (from 0.63 to 0.458 s) by using Equation (9),[24,27] where r_{H-H} is the H···H distance in Å, T_{1min} is the relaxation time corresponding to the dihydrogen interaction and ϑ is the working frequency of the NMR spectrometer.

$$r_{H-H} = 5.815\sqrt[6]{\frac{T_{1min}}{\nu}} \tag{9}$$

To obtain additional information on the interaction of cluster **1** with HCl, a theoretical study has been done by using $[W_3S_4H_3(PH_3)_6]^+$ (**3**) as molecular model. The calculations show formation of an adduct with a W–H···H–Cl dihydrogen interaction and the optimised geometry shown in Figure 6. The calculated H···H distance is 1.36 Å, and this interaction stabilises the adduct by 3.07 kcal mol^{-1} with respect to its components. Thus, both the theoretical calculations and the decrease in the T_1 values support the formation of a dihydrogen-bonded W–H···H–X adduct, although the difference between the H···H distances calculated by the two procedures is large. An explanation for this difference is given below in the context of a discussion of the intimate mechanism for proton transfer.

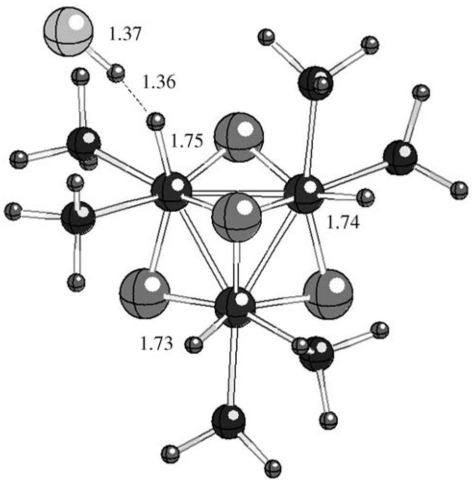

Figure 6. Optimised geometry for the W–H···H–Cl adduct resulting from the interaction of $[W_3S_4H_3(PH_3)_6]^+$ with HCl. Relevant distances are expressed in Å.

As pointed out above, the second-order dependence with respect to HCl observed in CH_2Cl_2 solution indicates that protonation of the W–H bonds of cluster **1** in this solvent requires two molecules of acid. This conclusion differs from previous results for the same reaction in other solvents and for protonation of other hydride complexes, which are usually first-order with respect to the acid.[6,8–12,15,16] The simplest interpretation of the first-order dependence is a one-step mechanism that goes through a dihydrogen-bonded transition state,[8–12,15] although there are also reports suggesting the participation of two acid molecules in the protonation of metal hydrides, despite the observation of a first-order rate law.[6,14–16] In the latter case, the first-order dependence is the result of a rapid pre-equilibrium largely displaced towards formation of the dihydrogen-bonded adduct.[16] The subsequent rate-determining attack by a second molecule of acid results in formation of the dihydrogen complex and the homoconjugate species HX_2^-, a conclusion also supported by the results of theoretical calculations.[14,15] In the case of cluster **1**, the kinetic data in the present paper are consistent with this mechanism [Eqs. (10) and (11), followed in this case by rapid conversion to W–X in a later step], although the pre-equilibrium should be now displaced towards the starting species in order to explain the experimental rate law in Equation (5) as a simplification of the general expression for this mechanism [Eq. (12)]. In that case, the value derived for k_1 corresponds to the product $K_a k_{hc}$.

$$\mathrm{W{-}H + H{-}X \overset{K_a}{\rightleftharpoons} W{-}H \cdots H{-}X} \tag{10}$$

$$\mathrm{W{-}H \cdots H{-}X + H{-}X \xrightarrow{k_{hc}} W(H_2)^+ + HX_2^-} \tag{11}$$

$$k_{obs} = \frac{k_{hc}K_a[\mathrm{HX}]^2}{1 + K_a[\mathrm{HX}]} \tag{12}$$

The large difference in the H···H distances estimated from the theoretical model and the decrease in T_1 can also be easily understood on the basis of the mechanism in Equations (10) and (11) with equilibrium (10) largely displaced to the left. In our opinion, the interpretation of the kinetic results indicates that the H···H distance of ca. 2.33 Å calculated from the decrease in T_{1min} is overestimated because conversion to the adduct is only partial. In fact, if the distance in the adduct is considered to be that calculated with the theoretical model (1.36 Å), application of Equation (9) leads to a value of 15.3 s^{-1} for the excess relaxation rate of the dihydrogen-bonded hydride signal, so that $(1/T_1)_{obs}$ for the adduct is expected to be 16.4 s^{-1} by considering again that the values for the three hydride ligands are averaged. As the equilibrium in Equation (10) is established rapidly, the experimental values of $1/T_1$ ($1/T_{1obs}$) are the weighted average of the corresponding values in the free complex ($1/T_{1complex}$) and the adduct ($1/T_{1adduct}$) [Eq. (13)], and so the observed (0.596 s^{-1}) and calculated (16.4 s^{-1}) excess relaxation rates can be used to obtain the molar fraction of adduct χ_{adduct} by using Equation (14). The result of such a calculation is $\chi_{adduct} = 0.036$, which leads to a K_a value of 2.4 M^{-1} when the HCl concentration used in the T_1 experiments (0.015 M) is considered. This value of K_a is only a rough estimation but its order of magnitude clearly indicates that the equilibrium is only slightly displaced towards adduct formation under the conditions of the kinetic experiments. For the acid concentrations used, $1 \gg K_a[\mathrm{HX}]$ and a second-order dependence with respect to HX results from simplification of the rate law in Equation (12). These considerations also indicate that estimation of H···H distances from changes in T_1 values must always be made with care, because apparently unusual large distances can be the result of dihydrogen-bonded adducts with "normal" distances that exist in equilibrium with free metal hydride.

$$\frac{1}{T_{1\text{obs}}} = \frac{1}{T_{1\text{complex}}} + \chi_{\text{complex}} \frac{1}{T_{1\text{adduct}}} \chi_{\text{adduct}} \tag{13}$$

$$\frac{1}{T_{1\text{obs}}} - \frac{1}{T_{1\text{complex}}} = \left(\frac{1}{T_{1\text{adduct}}} - \frac{1}{T_{1\text{complex}}} \right) \chi_{\text{adduct}} \tag{14}$$

The small value of χ_{adduct} found for the interaction of **1** with an excess of an acid such as HCl indicates a low basicity for this hydride. For this reason, attempts were made to estimate the basicity of **1** using the Iogansen basicity factor E_j successfully employed by Shubina et al. to rationalise the basicity of other metal hydrides.[28] However, the IR spectra of solutions containing **1** and $(CF_3)_2CHOH$ do not show any ϑ_{OH}(adduct) band, which indicates that the amount of adduct formed with this fluorinated alcohol is very small and hinders the calculation of the E_j value. This finding agrees with the lack of changes in the $T_{1\text{min}}$ value for the hydride NMR signal of **1** in the presence of this alcohol (see Figure 5) and indicates that **1** is significantly less basic than the hydrides studied by Shubina et al.[28]

Theoretical studies on the existence of competitive first- and second-order pathways for the protonation of $[W_3S_4H_3(dmpe)_3]^+$ with acids: The discussion in the previous section indicates that a satisfactory explanation can be given for the kinetic and T_1 data for proton transfer from acids HX to **1** in CH_2Cl_2 solution. The process occurs with H_2 release and leads to the formal substitution of H^- by X^-, and under pseudo-first-order conditions of excess acid shows a second-order dependence on acid concentration. In contrast, the experimental data available under conditions of acid deficit indicate a first-order dependence with respect to HX, a result that agrees better with previous findings for the same reaction in other solvents and for proton transfers to other hydride complexes.[6,8–16] Thus, it appears that two competitive first- and second-order pathways exist for the protonation of the W–H bonds in cluster **1**. As the experimental data in dichloromethane solution also indicate that conversion of each W–H bond to an W–X unit occurs without accumulation of any reaction intermediate, a detailed theoretical study of the proton-transfer process is more amenable for this mechanism than for the one previously proposed to explain the data in MeCN-containing solutions.[23] The calculations were carried out on model complex **3** and HCl, a strong acid with a monoatomic anion for which theoretical studies of proton transfer to hydride complexes are lacking. For simplicity, theoretical studies were limited to proton transfer to the first W–H bond, and the calculations were carried out with special attention to the comparison of the energetic and structural changes associated with the two competitive pathways.

Our theoretical approach assumes that the attacking species in the proton transfer processes is the HX molecule, but some additional comments must be made at this point, because the precise details of the acid–base behaviour of HCl and the other acids in CH_2Cl_2 solution are unknown. However, the data available for other aprotic solvents[29] indicate that they behave as weak acids with pK_a values as low as 8.9 and 10.7 for HCl in acetonitrile and nitromethane, respectively (12.6 and 11.3 for CF_3COOH in the same solvents). In the case of HBF_4, the molecule does not exist in solution[30] but $H^+BF_4^-$ ion pairs are expected to form extensively in solvents of low dielectric constant such as dichloromethane, and indeed pK_a values close to 2 have been reported in solvents with higher dielectric constant such as *N*,*N*-dimethylformamide and acetone.[29] Thus, it can be expected from the behaviour in other solvents that dissociation of the acids [Eq. (15)] is negligible in dichloromethane, so that the solutions will essentially contain HX molecules (HCl, CF_3COOH) or ion pairs (HBF_4). Because of the low degree of dissociation, the formation of homoconjugated HX_2^- species [Eq. (16)] can be also ignored in these solutions, although they should be formed in the presence of added X^-.

$$HX \rightleftharpoons H^+ + X^- \tag{15}$$

$$HX + X^- \rightleftharpoons HX_2^- \tag{16}$$

Once the nature of the attacking species has been established, the site of attack and the details of the proton-transfer mechanism remain to be determined. Although we have previously shown that protonation of **1** with H^+ is clearly favoured at the W–H bonds with respect to attack at the bridging sulfide ligands,[23] the existence of the acids in molecular form and the requirement of two acid molecules to complete the proton transfer in CH_2Cl_2 solution led us to also calculate the energy changes associated with the interaction of HCl at different sites of the model cluster $[W_3S_4(PH_3)_6H_3]^+$ (**3**). The results are summarised in Figure 7 and indicate that formation of a **3**·HCl adduct in which the acid interacts with one of the μ_2-S^{2-} ligands leads to an stabilization of 1.98 kcal mol^{-1} in CH_2Cl_2 solution, whereas the interaction with μ_3-S^{2-} stabilizes the system only by 1.36 kcal

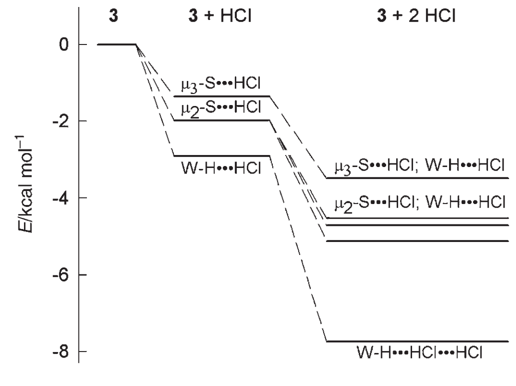

Figure 7. Relative energies for the interaction of one and two HCl molecules at different sites of model cluster **3**.

mol^{-1}. These two values are smaller than that corresponding to the interaction at the W–H bond (2.90 kcal mol^{-1} in CH_2Cl_2 solution), so that attack at the hydride position is favoured and leads to the formation of a dihydrogen-bonded W–H···H–Cl adduct with the optimised geometry shown in Figure 6. The calculations also reveal that conversion of this adduct to the final product is highly favoured thermodynamically, as indicated graphically in Figure 8 and numerically in Table 3, where the stabilization energies obtained in the gas phase and MeCN are also included for comparison with the values calculated for CH_2Cl_2 solution. The structure of the transition state for this conversion is shown in Figure 9, and the values calculated for the activation barrier are 15.14 in the gas phase, 13.38 in CH_2Cl_2 and 13.09 in MeCN (all values in kcal mol^{-1}). The structure of the transition state shows that the low activation barrier is probably a consequence of the simultaneous stabilisation caused by strengthening of the H–H and (less important) Cl–W interactions, and the destabilisation caused by weakening of the W–H and H–Cl bonds. Interestingly, the H–H distance in the transition state is very short (0.81 Å), and the two W···H distances are 1.98 and 2.18 Å, so that the transition state can be described as a dihydrogen complex slightly distorted because of ion pairing with Cl^-. The finding of the dihydrogen complex at a maximum along the reaction coordinate justifies the lack of success in detecting this species during NMR monitoring of the reaction of **1** with acids.

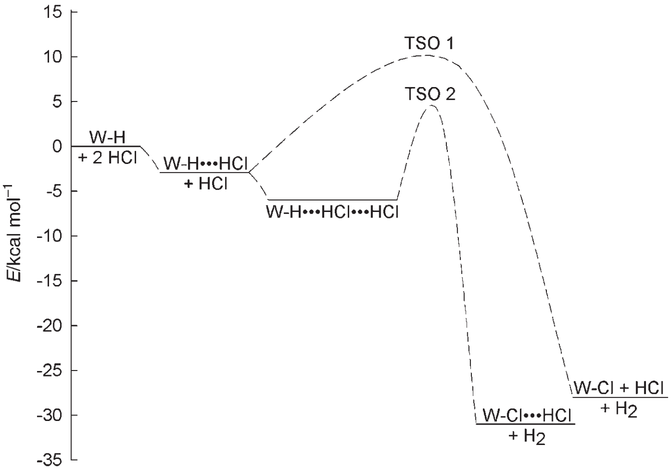

Figure 8. Energy profile showing the competitive first- and second- order pathways for the reaction between **1** and HCl. Note that, for consistency, two HCl molecules have been written for both pathways, although only one of them was used in the calculations corresponding to the upper pathway. The actual values of the energies are those obtained for CH_2Cl_2 solution, but quite similar results are obtained for other solvents (see text and Table 3).

Table 3. Relative energies to the corresponding reactants (**3** and HCl in the first pathway; **3** and 2 HCl in the second pathway).

Species[a]	Energy [kcal mol^{-1}]		
	gas phase	CH_2Cl_2 solution	MeCN solution
W–H···H–Cl	−3.07	−2.90	−2.79
TSO1[b]	12.07	10.48	10.30
W–C+H_2	−28.23	−27.36	−27.18
W–H···H–Cl···H–Cl	−9.21	−7.74	−7.45
TSO2[b]	5.42	4.49	4.44
W–C···H–Cl+H_2	−32.05	-30.61	−30.33

[a] Although the calculations considered the attack of the first HCl molecule on the $[W_3S_4H_3(PH_3)_6]^+$ cluster, for simplicity only the reacting W–H bond is written. [b] TSO1 and TSO2 refer to the transition states for the pathways showing first- and second-order dependence with respect to the acid, respectively.

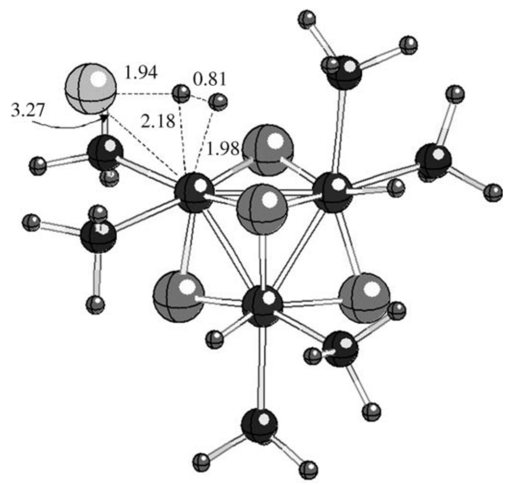

Figure 9. Optimised geometry for the transition structure TSO1 calculated for the conversion to the final products of the W–H···H–Cl adduct resulting from the interaction of $[W_3S_4H_3(PH_3)_6]^+$ with HCl. Relevant distances are expressed in Å.

The results of the theoretical calculations change significantly with the introduction of a second HCl molecule. A possible explanation for the second-order dependence with respect to the acid that was not considered in the previous section is that attack of one of the HX molecules occurs at one of the bridging sulfide ligands and facilitates attack of the second molecule at the hydride site. Actually, there are reports showing that acid-catalysed substitutions in analogous Fe clusters are caused by labilisation of the leaving ligand induced by protonation of the bridging sulfide ligands.[31] The results in Figure 7 indicate that the interaction of HCl with a W–H bond in the μ_3-S^{2-}···H–Cl adduct leads to a stabilisation of only 2.13 kcal mol^{-1} in dichloromethane. For the interaction of one HCl molecule with a W–H bond in the μ_2-S^{2-}···H–Cl adduct, three different possibilities lead to stabilisation energies between 2.55 and 3.14 kcal mol^{-1}, in the most favourable case of which the second HCl molecule attacks the hydride ligand coordinated to the W atom not bridged by the μ_2-S^{2-} ligand that interacts with the first HCl molecule. These values are close to or lower than the energy associated with formation of the W–H···H–Cl adduct, that is, the presence of an HCl molecule interacting with any of the bridging sulfide ligands does not facilitate interaction of a second HCl molecule with a W–H bond. The situation is quite different for the formation of a W–H···H–Cl···H–Cl adduct, in which the stabilisation caused by the second molecule of acid (4.84 kcal mol^{-1} in CH_2Cl_2) is significantly higher than that achieved with the first HCl molecule. Thus, the theoretical calculations support the conclusion that the interaction of both HCl molecules with a single W−H site is the most favoured possibility. The optimised geometry of the W−H···H−Cl···H−Cl adduct (Figure 10) shows that the second molecule of acid forms a hydrogen bond with the first that leads to stabilisation with respect to the adduct with a single HCl molecule (see Figure 8 and Table 3). The H−H distance in this adduct (1.15 Å) is significantly shorter than the corresponding one in the W−H···H−Cl adduct (1.36 Å), and thus addition of the second molecule strengthens the H−H interaction and prepares the system for H_2 release. Conversion of this adduct to the final product (the chloro complex hydrogen-bonded to an HCl molecule) is also highly favoured (see Figure 8 and Table 3), and it occurs through a transition state with the optimised geometry shown in Figure 11. The H−H distance in the transition state is only 0.78 Å, whereas the W−H distances are 2.10 and 2.25 Å, so that it can be described as a dihydrogen complex ion-paired with a HCl_2^- anion, which again agrees with our inability to observe signals for this kind of species in the NMR experiments. The activation barrier for this pathway is slightly lower than that for the other, in agreement with the shorter H−H distance. As a consequence, the pathway with a second-order dependence with respect to the acid is favoured, provided there is enough HCl. However, the differences between the activation barriers for the two pathways are not large, and the first-order pathway operates when there is a deficit of acid.

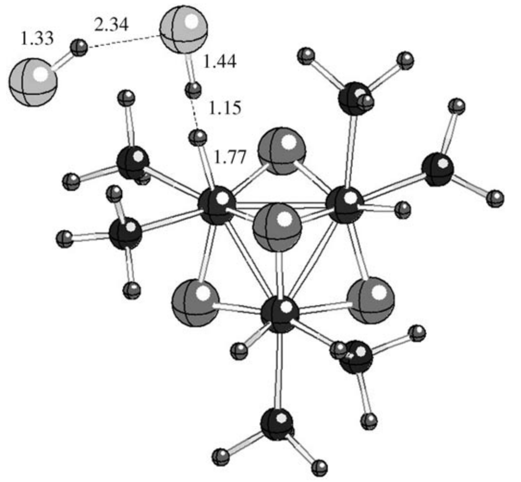

Figure 10. Optimised geometry for the W−H···H−Cl···H−Cl adduct resulting from the interaction of $[W_3S_4H_3(PH_3)_6]^+$ with two molecules of HCl. Relevant distances are expressed in Å.

At this point, some changes must be made to the mechanistic proposal in Equations (10) and (11) to conciliate the results of the theoretical calculations. As the dihydrogen complex is not an intermediate and the rate-determining step is not attack by the second molecule of acid but the release of the H_2 molecule from the W−H···H−Cl···H−Cl adduct, the mechanism is better represented by Equations (17)–(19), although Equation (20) must be added to account for the first-order pathway. The corresponding rate law is given by Equation (21), which reduces to Equation (22) when the equilibria in Equations (17) and (18) are considered to be displaced to the left. In that case, the experimental rate constant corresponds to $K_{a1}K_{a2}k_3$ when the reaction shows a second-order dependence with respect to the acid, and to $K_{a1}k_4$ when it goes through the first-order pathway.

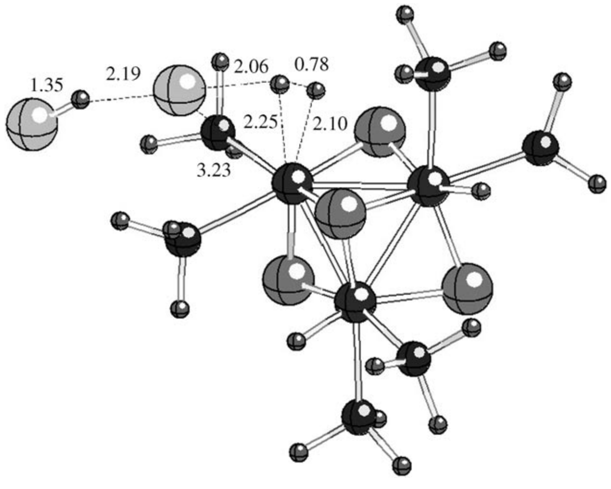

Figure 11. Optimised geometry for the transition structure TSO2 calculated for the conversion to the final products of the W−H···H−Cl···H−Cl adduct resulting from the interaction of $[W_3S_4H_3(PH_3)_6]^+$ with two molecules of HCl. Relevant distances are expressed in Å.

$$\mathrm{W{-}H} + \mathrm{H{-}X} \xrightleftharpoons{K_{a1}} \mathrm{W{-}H} \cdots \mathrm{H{-}X} \tag{17}$$

$$\mathrm{W{-}H} \cdots \mathrm{H{-}X} + \mathrm{H{-}X} \xrightleftharpoons{K_{a2}} \mathrm{W{-}H} \cdots \mathrm{H{-}X} \cdots \mathrm{H{-}X} \tag{18}$$

$$\mathrm{W{-}H} \cdots \mathrm{H{-}X} \cdots \mathrm{H{-}X} \xrightarrow{k_3} \mathrm{W{-}X} \cdots \mathrm{HX} + \mathrm{H_2} \tag{19}$$

$$\mathrm{W{-}H} \cdots \mathrm{H{-}X} \xrightarrow{k_4} \mathrm{W{-}X} + \mathrm{H_2} \tag{20}$$

$$k_{\mathrm{obs}} = \frac{k_4K_{a1}[\mathrm{HX}] + k_3K_{a1}K_{a2}[\mathrm{HX}]^2}{1 + K_{a1}[\mathrm{HX}] + K_{a1}K_{a2}[\mathrm{HX}]^2} \tag{21}$$

$$k_{\mathrm{obs}} = k_4K_{a1}[\mathrm{HX}] + k_3K_{a1}K_{a2}[\mathrm{HX}]^2 \tag{22}$$

An additional possibility that can be considered to explain the second-order dependence with respect to the acid is the formation of $(HX)_2$ dimers in CH_2Cl_2 solution [Eq. (23)] that could act as the attacking species towards the hydride ligands in cluster **1**. In the absence of information about these dimerisation processes, the problem was faced by theoretical calculations, again with HCl as the acid. The calculations indicate that formation of $(HCl)_2$ leads to a stabilisation of 2.20 kcal mol^{-1} in dichloromethane solution (1.48 kcal mol^{-1} in the gas phase), a value quite close to that corresponding to formation of the W−H···H−Cl adduct

(2.90 kcal mol^{-1} in CH_2Cl_2) but significantly smaller than that corresponding to formation of W−H···H−Cl···H−Cl (7.74 kcal mol^{-1} in CH_2Cl_2). From these values, it appears reasonable to consider that dimerisation of the acid probably occurs in the experiments with excess acid, although their interaction with the metal hydride would lead to the rapid formation of the more stable W−H···H−Cl···H−Cl adduct, which would be converted to the final products in the rate-determining step depicted in Equation (19). At low concentrations of the acid and in the presence of an excess of the hydride, formation of $(HCl)_2$ is not expected to be favoured versus W−H···H−Cl, so that the reaction will then go through the first-order pathway.

$$2\,HX \rightleftharpoons (HX)_2 \tag{23}$$

Participation of two molecules of acid in proton-transfer processes to hydride complexes has been proposed previously[6,14–16] for several systems, although in all these cases the processes lead to the formation of dihydrogen complexes. In their study on proton transfers to [Cp*Fe(dppe)H] (Cp* = η^5-C_5Me_5),[15] Lledós, Poli, Shubina et al. found that the second HX molecule increases the strength of the primary dihydrogen-bonding interaction in a way similar to that found in the present work. However, in that case an additional important role of the second HX molecule consists of stabilising the final product through formation of a homoconjugated HX_2^- anion hydrogen-bonded to the dihydrogen complex. In contrast, such a situation is unstable for proton transfers to cluster **1**, and the calculations show that the system evolves to the X^--substituted product and H_2. The role of the second HX molecule in this case is thus limited to formation of a hydrogen bond with the first molecule, which leads to an adduct with a stronger H−H interaction that facilitates the release of H_2 in the subsequent rate-determining step.

As pointed out above, the energy profiles in Figure 8 indicate that the activation barriers for the two pathways are not very different, and so they may become competitive in experimental systems. For this reason, changes in the preferred pathway may occur when the reaction conditions are varied, for example, by changing the relative concentrations of the reagents or the nature of the acid and/or the solvent. The results in the present paper indicate that the second-order pathway is preferred in dichloromethane solution for several acids of different characteristics provided the acid is in excess, but a deficit of acid changes the preferred pathway to the first-order one. On the other hand, kinetic studies on the reaction of **1** with an excess of acid in neat MeCN and MeCN/H_2O solutions showed that the process occurs with a first-order dependence on acid concentration.[23] As the calculations show that the stability of the adducts is little affected when the solvent changes from CH_2Cl_2 to MeCN (Table 3), the change in the preferred pathway should then be a consequence of a change in the relative values of k_3 and k_4 with the nature of the solvent. However, a large solvent dependence does not appear reasonable for these rate constants because they correspond to processes that occur within the adducts. As the data in Table 3 indicate that changing the solvent from CH_2Cl_2 to MeCN only causes minimal differences in the activation energies and in the energies corresponding to adduct formation, some additional contribution must be invoked to explain the change in the rate law. One possible contribution comes from the fact that the formation of dihydrogen-bonded adducts [Eq. (17) and (18)] requires reorganisation of the solvent molecules interacting directly with the reagents to allow close W−H···HX contact, that is, some contribution must be associated with changes in the specific interactions with the solvent that were not considered in the PCM model. To estimate the energy changes associated with this reorganisation, some theoretical calculations were performed with inclusion of a solvent molecule in the model. These calculations indicate that the process represented in [Eq. (24)] is favoured in CH_2Cl_2 by 1.22 kcal mol^{-1} but is disfavoured both in MeCN and H_2O by 6.35 and 11.55 kcal mol^{-1}, respectively. In the same way, the processes in Equations (25) and (26) are favoured in dichloromethane (by 3.15 and 3.48 kcal mol^{-1}, respectively) but disfavoured in MeCN (4.49 and 7.18 kcal mol^{-1}) and H_2O (9.86 and 9.75 kcal mol^{-1}). From these values, it can be concluded that in CH_2Cl_2 solution the contribution of the specific interactions with the solvent favours the breaking of solvent–HCl aggregates and the formation of W−H···HCl and W−H···HCl···H−Cl adducts. As the stabilisation is higher for the case of W−H···HCl···HCl, this would represent an additional contribution favouring the second-order pathway in this solvent. In contrast, the release of the solvent molecule adds an unfavourable contribution to adduct formation both in MeCN and water, so that the first-order pathway would be preferred in MeCN/H_2O solution to minimise the energy cost associated with solvent reorganisation.

$$\text{W−H} + \text{(solvent)-HCl} \rightarrow \text{W−H} \cdots \text{HCl} + \text{solvent} \tag{24}$$

$$\begin{aligned}&\text{W−H} \cdots \text{HCl} + \text{(solvent)-HCl} \rightarrow \\ &\text{W−H} \cdots \text{HCl} \cdots \text{HCl} + \text{solvent}\end{aligned} \tag{25}$$

$$\begin{aligned}&\text{W−H} + \text{(solvent)-HCl} \cdots \text{HCl} \rightarrow \\ &\text{W−H} \cdots \text{HCl} \cdots \text{HCl} + \text{solvent}\end{aligned} \tag{26}$$

Nevertheless, although the kinetic data in MeCN-containing solutions can be explained in terms of the competitive pathways in Figure 8, it is important to note that proton transfer in these solvents does not lead directly to the final product but to a reaction intermediate that does not contain coordinated X^-. The intermediate formed in the proton-transfer step was originally proposed to be a coordinatively unsaturated species that results from rapid release of H_2 from a dihydrogen complex,[23] but the theoretical results in the present work indicate that formation of a dihydrogen complex is not favoured. In fact, if the geometry and energy of the dihydrogen complex are optimised, the products $[W_3S_4H_2(H_2)(PH_3)_6]^{2+} + Cl^-$ are 27.18 kcal mol^{-1} higher in energy than the reagents in MeCN solution (only 11.01 kcal mol^{-1} if two HCl molecules and HCl_2^- are considered), whereas the coordinatively unsaturated species ($[W_3S_4H_2(PH_3)_6]^{2+} + Cl^- + H_2$) is destabilised by 35.24 kcal mol^{-1} in acetonitrile (19.06 kcal mol^{-1} for two HCl molecules and HCl_2^-). Any of these energies appears too high and makes unreasonable the assumption that intermediate $\mathbf{I_1}$ in MeCN (or MeCN/H_2O) solution corresponds to any of these two species. In contrast, the possibility of MeCN coordination in the intermediate formed in the proton transfer step can not be ruled out, because formation of $[W_3S_4H_2(MeCN)(PH_3)_6]^{2+}$ from the species with a vacant coordination site leads to a stabilisation of 40.04 kcal mol^{-1}, and its formation would be also favoured by the high concentration of solvent molecules surrounding the metal complex. Thus, the stabilisation associated with acetonitrile coordination provides an alternative explanation for the change in the rate law and the mechanism with respect to those observed in dichloromethane solution. Following the initial formation of a WH···H–X adduct [Eq. (17)], interaction with the solvent can lead to MeCN coordination with release of H_2 and X^- in a process [Eq. (27)] that would show a first-order dependence with respect to HX ($k_{obs} = K_{a1}k_s[HCl]$). For a solvent-assisted pathway of this kind to be competitive with those in Figure 8, the stabilisation caused by coordination of the solvent molecule must be high. When the calculations are performed for water instead of MeCN, formation of $[W_3S_4H_2(H_2O)(PH_3)_6]^{2+}$ is found to be favoured by only 29.29 kcal mol^{-1}, which indicates that water is less effective than MeCN. As expected from the lower coordination ability of dichloromethane, formation of $[W_3S_4H_2(CH_2Cl_2)(PH_3)_6]^{2+}$ results in a stabilisation of only 6.28 kcal mol^{-1}, a value too low to make the solvent-assisted pathway competitive and, as a consequence, the reaction would be forced to go through the pathways in Figure 8.

$$\mathrm{W{-}H\cdots H{-}X + MeCN \xrightarrow{k_s} W{-}NCMe + H_2 + X^-} \tag{27}$$

Conclusion

The picture that is emerging from experimental and theoretical studies of proton transfer to hydride complexes reveals that these processes may occur through complex mechanisms with alternative pathways, so that changes in the reaction conditions may lead to mechanistic changes. These changes must not be considered too surprising, because of the large differences in the properties of the hydride complexes, the acids and the solvents. The results in the present paper for the reaction of hydride complex **1** with acids in CH_2Cl_2 solution, when taken together with those previously reported for the same reaction in other solvents,[23] constitute an excellent example of the kinetic and mechanistic complexity of these processes. Thus, this system has allowed the experimental confirmation for the first time of the existence of a pathway with second-order kinetics with respect to the acid, and theoretical calculations confirmed the previous proposal[15] that the role of both HX molecules is to form a network of hydrogen bonds that decreases the activation barrier for the formation of H_2. This pathway is in competition with an alternative pathway that requires the participation of a single HX molecule and is favoured when there is a deficit of acid. For solvents with higher coordination ability, the theoretical calculations also indicate the possibility of a solvent-assisted first-order pathway in which the role of the solvent would be to favour proton transfer by stabilising the reaction product resulting from H_2 release. Finally, it has been recently shown[17] that the "inert" salts frequently used to control the ionic strength in kinetic experiments can also play an important role in proton-transfer processes involving metal hydrides. Work is in progress to determine the possible effects of added salts on the kinetics of proton transfer to hydride cluster **1** and to check how ion-pair formation affects the mechanism of proton transfer.

Experimental Section

$[W_3S_4H_3(dmpe)_3]PF_6$ was prepared by the literature procedure[32] and its purity checked by NMR and MS using a Varian 300 MHz NMR spectrometer and an Electrospray Micromass Quattro LC mass spectrometer, respectively. The chemical shifts in the NMR spectra are reported with respect to the following external references: TMS (^1H), H_3PO_4 (^{31}P) and $CFCl_3$ (^{19}F). The HCl solutions used in the kinetic studies were prepared from $ClSiMe_3$ and CH_3OH. The solvents for kinetics studies were obtained from Aldrich or SDS as anhydrous grades and taken from recently opened bottles. All other reagents used in the synthetic and kinetic studies were obtained from commercial sources and used without further purification. The measurement of the T_1 values for the hydride NMR signal of complex **1** at different temperatures was carried out with a Varian Unity 400 spectrometer using the standard inversion–recovery method. In the presence of added HCl, the measurements had to be limited to the lowest temperatures because the rate of reaction at higher temperatures is large enough to cause complete disappearance of the hydride signal.

The kinetic experiments were carried out with an Applied Photophysics SX17MV stopped-flow spectrometer provided with a PDA.1 photodiode array (PDA) detector. All experiments were carried out at 25.0°C by mixing dichloromethane solutions of $[W_3S_4H_3(dmpe)_3]PF_6$ and the acid. The solutions of the complex were prepared at concentrations of $(0.8–9.0)\times10^{-4}$ mol dm^{-3}, and preliminary experiments at two or three different concentrations were carried out in all cases to confirm the first-order dependence of the observed rate constants on complex concentration. The acid solutions were used within 2–3 h after preparation, and their concentrations were determined by titration with KOH (phenolphthalein indicator) of solutions resulting from adding an aliquot (3 mL) to 50 mL of water and stirring vigorously for 20 min. The reaction kinetics were monitored by recording the spectral changes with the PDA detector using a logarithmic time base and analysing the data with the SPECFIT program[33] and the appropriate kinetic model. Most experiments were carried out under pseudo-first-order conditions of excess acid and the analysis required the use of a multistep kinetic model. However, some experiments were also carried out with a deficit of the acid and the kinetic files could be satisfactorily fitted in these cases by a single exponential.

The theoretical study used $[W_3S_4H_3(PH_3)_6]^+$ (**3**) as molecular model for $[W_3S_4H_3(dmpe)_3]^+$. This made attainable calculation times possible without changing the $W_3S_4H_3$ cluster core where protonation takes place. The calculations were conducted with the Becke hybrid density functional (B3LYP)[34,35] method as implemented in the Gaussian98 program suite.[36] The double-ζ pseudo-orbital basis set LanL2DZ, in which W, S and P atoms are represented by the relativistic core LanL2 potential of

Los Alamos,[37] was used. All stationary points found, i.e, minima and transition structures, were characterised by the number of negative eigenvalues of the Hessian matrix (0 for a minimum, 1 for a saddle point corresponding to a transition structure). This index is also the number of imaginary wavenumbers (or frequencies) obtained in a normal-mode analysis of the corresponding molecular structure. For a transition structure, the unique imaginary frequency is associated with the transition vector. Once this vector was characterised, it was possible to trace the intrinsic reaction coordinate[38] path connecting each transition structure with the two associated minima by using the second-order González–Schlegel integration method.[39,40]

Solvent effects were taken into account by means of polarised continuum model calculations[41,42] using standard options. The energies of solvation were computed in dichloromethane ($\varepsilon=8.93$), acetonitrile ($\varepsilon=36.64$) and water ($\varepsilon=78.39$) at the geometries optimised in the gas phase.

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