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The Detection and Reactivity of $[MoH_4(\eta^2\text{-}H_2)(Ph_2PCH_2CH_2PPh_2)_2]^{2+}$

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The reaction between $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ and HCl in tetrahydrofuran involves the detected, transient intermediate, $[MoH_4(\eta^2\text{-}H_2)(Ph_2PCH_2CH_2PPh_2)_2]^{2+}$, a species which must contain at least one co-ordinated dihydrogen molecule if the maximum oxidation state of the molybdenum is not to be exceeded; the reactivity of polyhydridic sites towards protons, particularly with respect to the dinitrogen-binding site in the enzyme nitrogenase, is discussed in the light of this study.

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In the three years since the first report[1] of a compound containing a co-ordinated dihydrogen molecule (η^2-H_2) this area of chemistry has advanced rapidly.[2] However there is one intriguing class of polyhydrido-complex which has so far eluded detection, that is, compounds of the general formula, $[MH_xL_y]^{n+}$, where the value of $(x + n)$ exceeds the maximum oxidation state of the metal.[3] Herein we report the first detection of such a species, namely $[MoH_6(dppe)_2]^{2+}$ (dppe = $Ph_2PCH_2CH_2PPh_2$). Consequently we are able to discuss, in more detail than has hitherto been possible, the factors influencing the reactivity of polyhydrido-complexes towards protons: a process of direct relevance to the dinitrogen-binding mode of the nitrogen fixing enzyme nitrogenase.

Upon mixing tetrahydrofuran (thf) solutions of $[MoH_4(dppe)_2]$ and anhydrous HCl ([HCl]/[Mo] $\geq$ 15, $[MoH_4(dppe)_2]$ 0.5—2.5 $\times$ 10^{-4} mol dm^{-3}; ionic strength 0.1 mol dm^{-3}, $[Bu_4N][BF_4]$), there is rapid evolution of dihydrogen (identified by mass spectrometry) and formation of $[MoH_2Cl_2(dppe)_2]$, as described by equation (1). Monitoring this reaction by stopped-flow spectrophotometry (λ = 400 nm) reveals that the formation of the product occurs in two observable stages as shown in Figure 1: an initial absorbance jump, which is complete within the dead-time of the apparatus (3.3 ms), followed by a relatively slow exponential decay. As Figure 1 illustrates, both the magnitude of the initial absorbance jump, and the rate constant ($k_{obs.}$) associated with the slow phase are dependent upon the concentration of HCl. Analysis of the influence of HCl concentration on the initial absorbance jump reveals the dependence described by equation (2)† and shown in Figure 2a, where K_1 = 67.2 $\pm$ 3 and K_2 = 31.6 $\pm$ 3 dm^3 mol^{-1}. For the slow phase, the dependence of $k_{obs.}$ on the concentration of HCl is that shown in Figure 2b and described by equation (3), where K_2 = 32.6 $\pm$ 5 dm^3 mol^{-1} and k_3 = 1.3 $\pm$ 0.2 s^{-1}. The values of K_1, K_2, and k_3 are unchanged whether the reaction is studied in thf saturated with argon or dihydrogen.

$$[MoH_4(dppe)_2] + 2HCl \rightarrow [MoH_2Cl_2(dppe)_2] + 2H_2 \quad (1)$$

$$K_{app.} = K_1 + K_1K_2[HCl] \quad (2)$$

$$k_{obs.} = \frac{k_3K_2[HCl]}{1 + K_2[HCl]} \quad (3)$$

The behaviour described by equations (2) and (3), and, incidentally, the excellent agreement between the two independently determined values of K_2, indicate the mechanism shown in Scheme 1, in which diprotonation of $[MoH_4(dppe)_2]$ occurs prior to the rate-limiting loss of dihydrogen (k_3), and at high concentrations of HCl the species $[MoH_6(dppe)_2]^{2+}$ can be detected. It is important to emphasise that this species is not invoked solely to explain an experimental rate law, but is a complex capable of being observed, albeit with a lifetime of 0.75 s.

Several features of the protonation steps deserve further elucidation. Initial protonation of $[MoH_4(dppe)_2]$ (formally a Mo^{IV}, d^2 system) generates $[MoH_5(dppe)_2]^+$ (formally a Mo^{VI}, d^0 system). Although protonation of molybdenum has already been observed in *trans*-$[MoL_2(dppe)_2]$ (L = N_2,[5] CO,[6] or MeNC[7]), $[MoH_4(dppe)_2]$ is a unique member of this family of complexes, being able to bind two protons. That $[MoH_5(dppe)_2]^+$ must protonate further in order to labilise

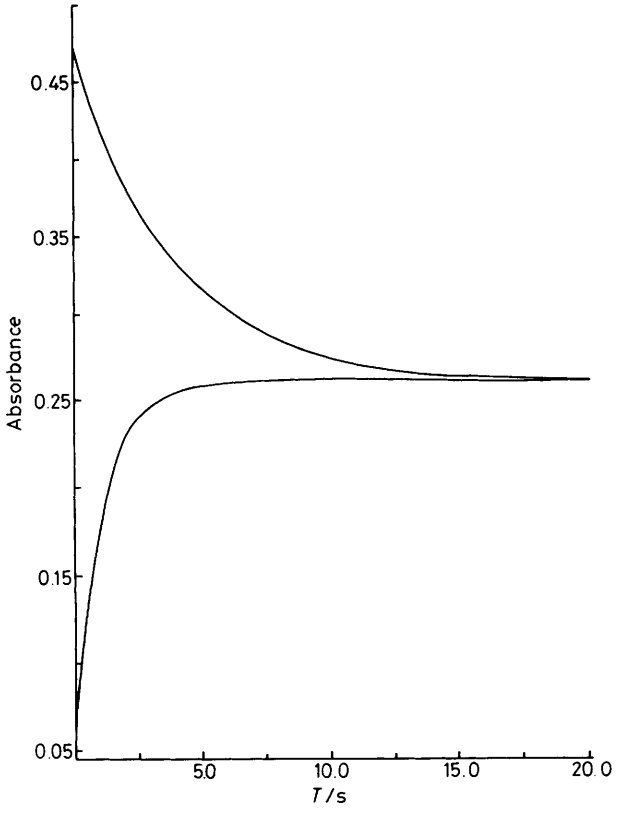

Figure 1. Superposition of two stopped-flow traces for the reaction of $[MoH_4(dppe)_2]$ with HCl in thf at 25.0 °C, λ 400 nm, ionic strength 0.1 mol dm^{-3}, ($[NBu_4][BF_4]$); $[MoH_4(dppe)_2]$ 2.31 $\times$ 10^{-4} mol dm^{-3}; [HCl] 7.5 (top curve); [HCl] 100.0 mmol dm^{-3} (bottom curve). The absorbance of $[MoH_4(dppe)_2]$ at this concentration is 0.75.

† K_{app} is the apparent equilibrium constant derived from the magnitude of the initial absorbance jump measured at λ 400 nm, at each concentration of HCl. $K_{app} = x/\{[MoH_4(dppe)_2] - x\}[HCl]$, where x is the concentration of the intermediate formed at each concentration of HCl calculated using ε_{MoH_4} 3.25 $\times$ 10^3 and ε_{MoH_6} 2.25 $\times$ 10^2 dm^3 mol^{-1} cm^{-1} (obtained from the stopped-flow traces at high concentrations of HCl). Calculated ε_{MoH_5} 3.17 $\times$ 10^2 dm^3 mol^{-1} cm^{-1}. For a derivation of equation (2) see ref. 4.

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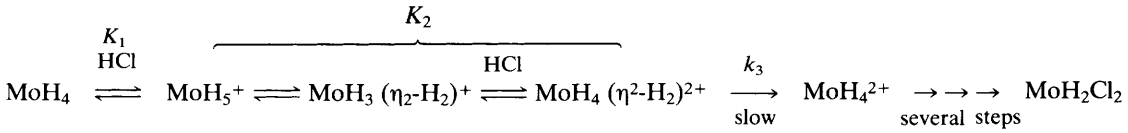


Scheme 1. Mechanism of the reaction between $[MoH_4(dppe)_2]$ and HCl in thf (phosphine ligands omitted for clarity).

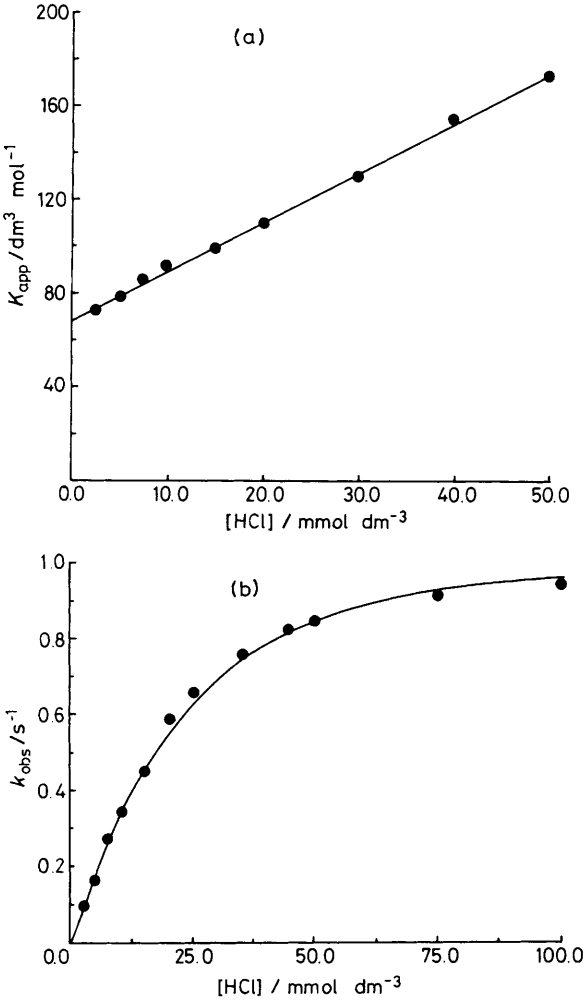
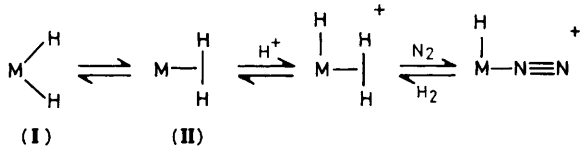


Figure 2. Graphs of (a) K_{app} and (b) k_{obs} *vs.* [HCl] for the reaction of $[MoH_4(dppe)_2]$ with HCl in thf at 25.0 °C, ionic strength 0.1 mol dm^{-3} ($[NBu_4][BF_4]$). In both graphs the data points represent the average of at least three independent determinations in the concentration range, $0.5 \times 10^{-4} < [MoH_4(dppe)_2] < 2.5 \times 10^{-4}$ mol dm^{-3}. Curves drawn are those defined by (a) equation (2) and (b) equation (3).

the site towards dihydrogen loss dictates that, in some way, the metal is capable of attaining a lower formal oxidation state, and this is only possible if $[MoH_5(dppe)_2]^+$ is in rapid equilibrium with $[MoH_3(\eta^2\text{-}H_2)(dppe)_2]^+$ (formally a Mo^{IV}, d^2 system), which upon protonation generates $[MoH_4(\eta^2\text{-}H_2)(dppe)_2]^{2+}$ (formally a Mo^{VI}, d^0 system).

Subsequent loss of dihydrogen and binding of chloride results in the formation of $[MoH_2Cl_2(dppe)_2]$. Chloride is just one example of a range of small molecules which can be introduced into the 'Mo(dppe)$_2$' core by protonation of $[MoH_4(dppe)_2]$. In the presence of $HBF_4 \cdot OEt_2$, $[MoH_4(dppe)_2]$ will rapidly bind (and for some molecules activate), NO, MeCN, MeNC, CO, PhC≡CH, N_3^-, CO_2, SO_2, and, in low yield, N_2.[9] Preliminary kinetic studies have demonstrated that, here too, rapid formation of $[MoH_4(\eta^2\text{-}H_2)(dppe)_2]^+$ can be detected prior to rate-limiting dihydrogen loss ($k_{obs.}$ 1.3 ± 0.1 s^{-1}). Solution equilibria between a dihydrido-form and a co-ordinated dihydrogen form [(I) and (II), Scheme 2, respectively] have been detected before,[2] but it is only now that we can show that protonation of the metal in a high formal oxidation state can, in effect, trap the latter configuration. In more general terms, whether a polyhydridic site is capable of being protonated or not can depend both on its inherent basicity and also on its ability to convert from the dihydrido- to the $(\eta^2\text{-}H_2)$ form, a process intimately related to the thermodynamic stability of the metal in the formal oxidation states corresponding to the two forms.



Scheme 2

The effect of protonating a co-ordinatively-saturated polyhydridic site, which is only sufficiently basic when present in the $(\eta^2\text{–}H_2)$ form, is to labilise the site towards dihydrogen loss, thus generating a co-ordinatively-unsaturated species capable of binding other molecules. This type of activation may be important in understanding the binding of dinitrogen by the enzyme nitrogenase isolated from *Klebsiella pneumoniae*. The most comprehensive model for the mechanism of this enzyme indicates that upon binding, dinitrogen displaces dihydrogen at a metal hydride site.[9] Although it has already been proposed that the ease with which dinitrogen displaces dihydrogen in nitrogenase is suggestive of $(\eta^2\text{–}H_2)$ bonding in the enzyme,[10,11] any model for these N_2–H_2 interactions must go further. In particular the model must be able to rationalise the observations that: (i) three electrons (and inferred protons) are consumed by the enzyme before dinitrogen binds, but dinitrogen displaces only one molecule of dihydrogen, (ii) nitrogenase catalyses the formation of HD from D_2, (iii) when fixing dinitrogen in the presence of T_2, less than 2.4% of the total tritium is incorporated into the solvent (H_2O), and (iv) when fixing dinitrogen in the presence of HD, no detectable concentration of D_2 is produced.[9]

Previously these observations have been interpreted in terms of a model where a dihydridic site is attacked by a proton which itself does not bind to the metal, but, in effect, abstracts H^- from it.[9] This sort of reactivity has not, as yet, been established for any simple hydrido-complexes. However, this study suggests an alternative model as outlined in Scheme 2, in which protonation at the metal can occur only in the enforced, labile $(\eta^2\text{–}H_2)$ form. Furthermore, if the $MH(\eta^2\text{–}H_2)^+$ state is insufficiently long-lived to undergo intramolecular hydrogen exchange then observations (i), (iii), and (iv) outlined above are readily explained.

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Of course, this is not an exhaustive model for all the N_2–H_2 reactions of nitrogenase and in particular it is unable to explain the enzyme catalysed formation of HD from D_2 (ii); indeed it is difficult to rationalise observations (ii) and (iii) in any model based entirely on (η^2–H_2) ligands. In common with all previous proposals, this model does not address the crux of the biological problem. That is not *whether* dinitrogen can displace dihydrogen at a metal site (that was demonstrated several years ago,[12] and even explicitly proposed for the enzyme as early as 1968[13]), but *why* the enzyme adopts such a pathway, sacrificing two electrons *en route*, when it is well established that dinitrogen can displace water,[14] chloride,[15] or even ammonia?[16]

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