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Kinetic studies on the reactions of HCl with *trans*-[MoL(CNPh)($Ph_2PCH_2CH_2PPh_2$)$_2$] (L = N_2, H_2 or CO)

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Dedicated to Professor A.G. Sykes

Abstract

The kinetics of the reactions between anhydrous HCl and *trans*-[MoL(CNPh)($Ph_2PCH_2CH_2PPh_2$)$_2$] (L = CO, N_2 or H_2) have been studied in thf at 25.0 °C. When L = CO, the product is [MoH(CO)(CNPh)($Ph_2PCH_2CH_2PPh_2$)$_2$]$^+$, and when L = H_2 or N_2 the product is *trans*-[MoCl(CNHPh)($Ph_2PCH_2CH_2PPh_2$)$_2$]. Using stopped-flow spectrophotometry reveals that the protonation chemistry of *trans*-[MoL(CNPh)($Ph_2PCH_2CH_2PPh_2$)$_2$] is complicated. It is proposed that in all cases protonation occurs initially at the nitrogen atom of the isonitrile ligand to form *trans*-[MoL(CNHPh)($Ph_2PCH_2CH_2PPh_2$)$_2$]$^+$. Only when L = N_2 is this single protonation sufficient to labilise L to dissociation, and subsequent binding of Cl^- gives *trans*-[MoCl(CNHPh)($Ph_2PCH_2CH_2PPh_2$)$_2$]. At high concentrations of HCl a second protonation occurs which inhibits the substitution. It is proposed that this second proton binds to the dinitrogen ligand. When L = CO or H_2, a second protonation is also observed but in these cases the second protonation is proposed to occur at the carbon atom of the aminocarbyne ligand, generating *trans*-[MoL(CHNHPh)($Ph_2PCH_2CH_2PPh_2$)$_2$]$^{2+}$. Addition of the second proton labilises the *trans*-H_2 to dissociation, and subsequent rapid binding of Cl^- and dissociation of a proton yields the product *trans*-[MoCl(CNHPh)($Ph_2PCH_2CH_2PPh_2$)$_2$]. Dissociation of L = CO does not occur from *trans*-[Mo(CO)(CHNHPh)($Ph_2PCH_2CH_2PPh_2$)$_2$]$^{2+}$, but rather migration of the proton from carbon to molybdenum, and dissociation of the other proton produces [MoH(CO)(CNPh)($Ph_2PCH_2CH_2PPh_2$)$_2$]$^+$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics and mechanism; Molybdenum complexes; Isocyanide complexes; Dinitrogen complexes; Protonation reaction

1. Introduction

Understanding the factors controlling the sites and rates of protonation of electron-rich complexes is fundamental to establishing a predictable basis for the application of regio-, stereo- and product-selective reactions, and in defining the elementary reactions of selected metalloenzymes [1–3]. To this end, studies on the reactivity of complexes of the type, *trans*-[MoL_2(dppe)$_2$] ((dppe = $Ph_2PCH_2CH_2PPh_2$); L = N_2 [4], RNC [5], C_2H_4 [6,7] RCCH [8,9] or 2H [10]) have been particularly revealing. Protonation can occur at the metal or L, or even both. In addition, movement of protons between ligand and metal can occur rapidly, either by intramolecular or acid–base-catalysed routes as shown in Fig. 1. Consequently, the isolation of the product of a reaction between acid and *trans*-[MoL_2(dppe)$_2$] does not necessarily reveal the true and complete protonation chemistry of the complex. Most particularly, it does not necessarily establish the initial site of protonation. In order to define the protonation chemistry of electron-rich complexes it is necessary to obtain a detailed kinetic analysis of the reaction using rapid reaction techniques.

Further elaboration of the above studies has involved investigation of the protonation reactions of *trans*-[MoLL′(dppe)$_2$] (L = RCN or ArCN, L′ = N_2) [11]. By studying these complexes it should be possible to establish the factors which differentiate between protonation of L, L′ or Mo. Recently, Hidai and co-workers have reported [12–14] the preparation of a series of complexes, *trans*-[MoL(CNPh)(dppe)$_2$] (L = N_2, H_2 or CO) and studied the products of protonation of the complexes. A variety of products are obtained, which at face value indicate protonation can occur at isonitrile

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($L = N_2$ or H_2) or molybdenum ($L = CO$) [14]. In this paper, we report the results of studying the reactions of HCl with *trans*-[MoL(CNPh)(dppe)$_2$] using stopped-flow spectrophotometry, which reveals the following features: (i) the initial site of protonation is always the isonitrile ligand; (ii) the protonation chemistry of *trans*-[MoL(CNPh)(dppe)$_2$] is much more complex than is evident from isolation of the products of the reactions and, (iii) the ultimate product is formed by a combination of reactions including protonation, labilisation of the *trans*-ligands, proton migration to the metal ($L = CO$) and proton dissociation.

2. Experimental

All manipulations in both the synthetic and kinetic aspects of this work were performed under an atmosphere of dinitrogen or argon (for *trans*-[Mo(η^2-H_2)(CNPh)(dppe)$_2$]) using Schlenk or syringe techniques as appropriate. All solvents were dried over the appropriate agent and distilled immediately prior to use: diethylether (sodium); thf (sodium/benzophenone); dichloromethane (P_2O_5); and benzene (sodium).

The following reagents were purchased and used as received: $Ph_2PCH_2CH_2PPh_2$ (Lancaster); $MoCl_5$ (Aldrich); and PhCHNPh (Lancaster). The following compounds were prepared by the methods described in the literature: *trans*-[Mo(N_2)$_2$(dppe)$_2$] [15]; *trans*-[Mo(N_2)-(CNPh)(dppe)$_2$]; *trans*-[Mo(η^2-H_2)(CNPh)-(dppe)$_2$]; and *trans*-[Mo(CO)(CNPh)(dppe)$_2$] [13].

The product of the reaction between *trans*-[Mo(CO)-(CNPh)(dppe)$_2$] and anhydrous HCl in thf was confirmed to be [MoH(CO)(CNPh)(dppe)$_2$]$^+$ using $^{31}P\{^1H\}$ NMR spectroscopy which was identical to that in the literature (δ 70 ppm) [14]. The product of the reaction between anhydrous HCl and either *trans*-[Mo(N_2)-(CNPh)(dppe)$_2$] or *trans*-[Mo(η^2-H_2)(CNPh)(dppe)$_2$] was isolated and shown to be *trans*-[MoCl(CNHPh)-(dppe)$_2$] by elemental analysis and spectroscopic characterisation.

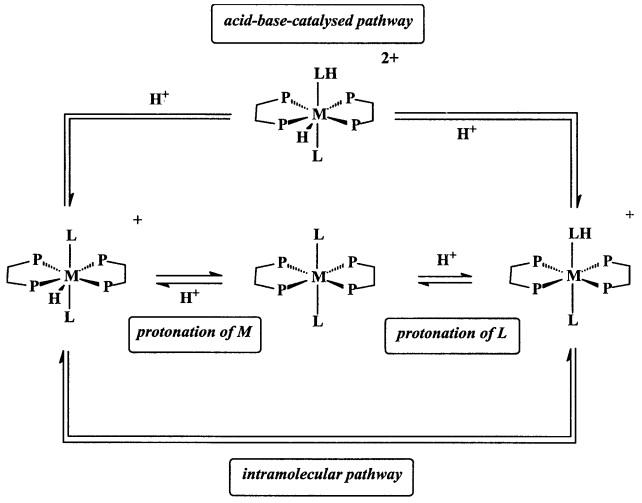

Fig. 1. Summary of the general pathways for the protonation of metal and ligand and the mechanisms by which protons can move between these two sites.

2.1. Preparation of [MoCl(CNHPh)(dppe)$_2$]

To a stirred slurry of *trans*-[Mo(N_2)(CNPh)(dppe)$_2$] (0.2 g; 0.2 mmol) in thf (approximately 20 ml) was added MeOH (0.1 ml) followed by $SiMe_3Cl$ (0.32 ml). Immediately the solution changed colour from red to orange. After stirring the solution for 1 h, all volatiles were removed in vacuo to give an orange–brown solid. The solid was dissolved in dichloromethane (approximately 20 ml) and then diethyl ether (approximately 80 ml) was added slowly. After standing overnight orange plate-like crystals had formed together with some amorphous grey–green solid. The amorphous solid was removed by decantation and the orange crystals washed onto a sinter using diethyl ether. The crystals were washed with a further portion of diethyl ether then dried in vacuo. Yield = 0.13 g, 65%. Elemental analysis. Found: C, 68.5; H, 5.2; N, 1.6. Calc. for $C_{59}H_{54}$-NP_4ClMo: C, 68.6; H, 5.2; N, 1.4%. ^1H NMR ($CDCl_3$): δ 3.0 (br, 4H, P–CH_2), 3.4 (br, 4H, P–CH_2), 5.8–6.3 (m, 5H, NC$_6H_5$), 7.0–8.0 (m, 40H, PC$_6H_5$), 11.8 (br, 1H, N–*H*). ^{31}P NMR (ppm): δ 55. IR (cm^{-1}): ν_{CN} 1500.

The same product was isolated in an analogous manner from the reaction of *trans*-[Mo(η^2-H_2)(CNPh)(dppe)$_2$] with anhydrous HCl.

2.2. Kinetic studies

All kinetic studies were performed using an Applied Photophysics SX.18MV stopped-flow spectrophotometer, modified to handle air-sensitive solutions. The temperature was maintained at 25.0 ± 0.1 °C using a Grant LT D6G thermostat recirculating tank.

Solutions were prepared under an atmosphere of dinitrogen and transferred by gas-tight, all-glass syringes to the stopped-flow spectrophotometer. Stock 100 mmol dm^{-3} solutions of anhydrous HCl were prepared by mixing equimolar amounts of MeOH (0.1 ml) and $SiMe_3Cl$ (0.32 ml) in thf (25.0 ml). Dilute solutions of anhydrous HCl were prepared from the stock solution. All solutions were used within 1 h of preparation to minimise complications due to acid-catalysed ring-opening and polymerisation of thf.

All kinetics were studied under pseudo first-order conditions with the acid in a large excess ($>$ tenfold) over the concentration of the complex. The absorbance–time curves were fitted using the Applied Photophysics computer programme and the values of the observed rate constants (k_{obs}) were obtained from

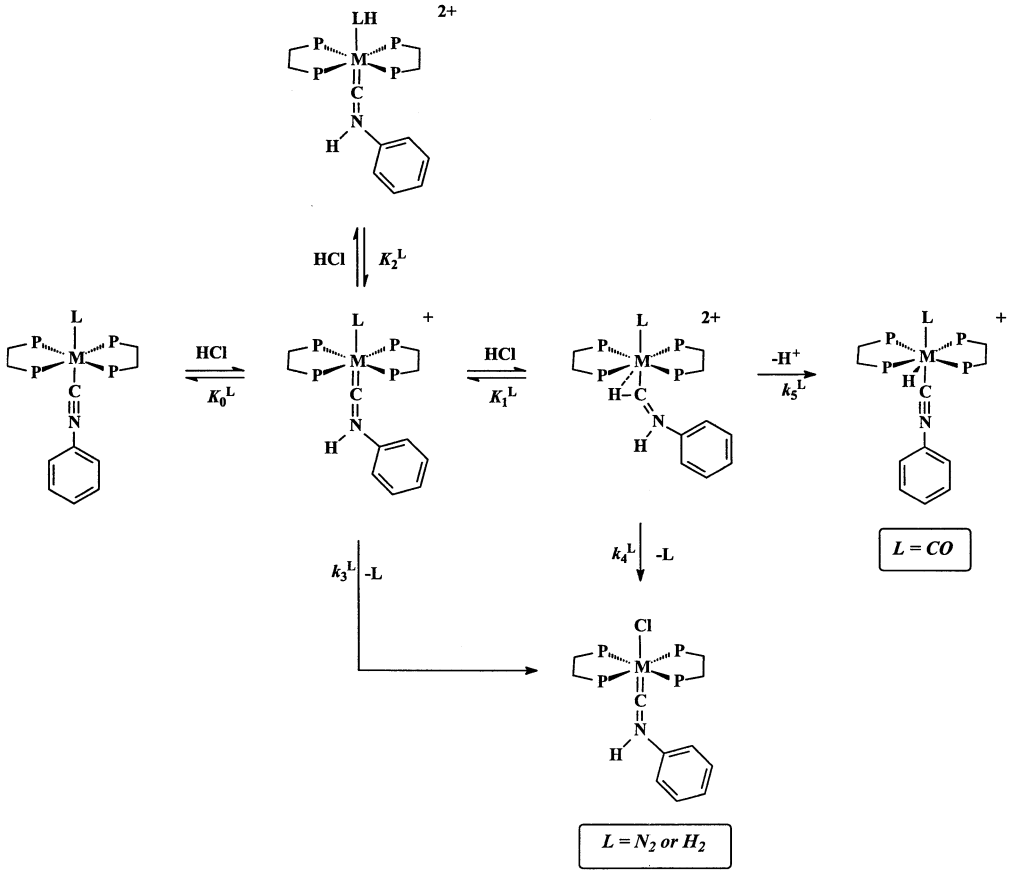

Fig. 2. Pathways observed in the reaction of *trans*-[MoL(CNPh)($Ph_2PCH_2CH_2PPh_2$)$_2$] with anhydrous HCl in thf at 25.0 °C.

the analysis. Derivation of the rate laws for the various reactions were established by the normal kinetic analysis of the data as indicated in Section 3.

3. Results and discussion

The work presented in this paper describes the kinetics of the reactions between anhydrous HCl and *trans*-[MoL(CNPh)(dppe)$_2$] (L = CO, H_2 or N_2) in thf [14]. The pathways, which will be outlined herein, are summarised in Fig. 2. A key feature of Fig. 2 is that all species presented, except *trans*-[Mo(LH)(CNHPh)-(dppe)$_2$]$^{2+}$, have been isolated and characterised. However, *trans*-[Mo(LH)(CNHPh)(dppe)$_2$]$^{2+}$ has only been invoked in the reaction of L = N_2. Protonation of coordinated dinitrogen is not without precedent, particularly at the {Mo(dppe)$_2$} site. A variety of complexes of the type *trans*-[Mo(NNH)(L′)(dppe)$_2$]$^{2+}$ (L′ = N_2, EtCN, halide, etc.) [16] have been isolated and characterised. The discussion hereafter will focus around Fig. 2.

One feature which is common to the reactions of HCl with all *trans*-[MoL(CNPh)(dppe)$_2$] is the absorbance–time behaviour. Consequently, it is worth outlining the general characteristics of the absorbance–time curves from the beginning. A typical curve is shown in Fig. 3. When studied at a single wavelength, it is clear that the reactions of anhydrous HCl with *trans*-[MoL(C-NPh)(dppe)$_2$] in thf is clear that the reaction occurs in three phases. The first phase is an initial absorbance decrease, which is complete within the dead-time of the stopped-flow apparatus (approximately 2 ms) and hence too rapid to be studied. A further appreciable absorbance decrease follows, which is complete over the course of a few seconds. The second and third phases are associated with the absorbance–time curve. This curve can be fitted to two exponentials of approximately equal absorbance change. Analysis of the data reveals that the second phase exhibits a complicated dependence on the concentration of HCl, the specifics of which will be discussed for each system presented below. The third phase occurs at a rate, which is independent of the concentration of acid for all the complexes studied, but the associated rate constant depends on the nature of the complex.

3.1. Protonation of *trans*-[Mo(CO)(CNPh)(dppe)$_2$]

When studied on a stopped-flow apparatus, the reaction between anhydrous HCl and *trans*-[Mo(CO)-

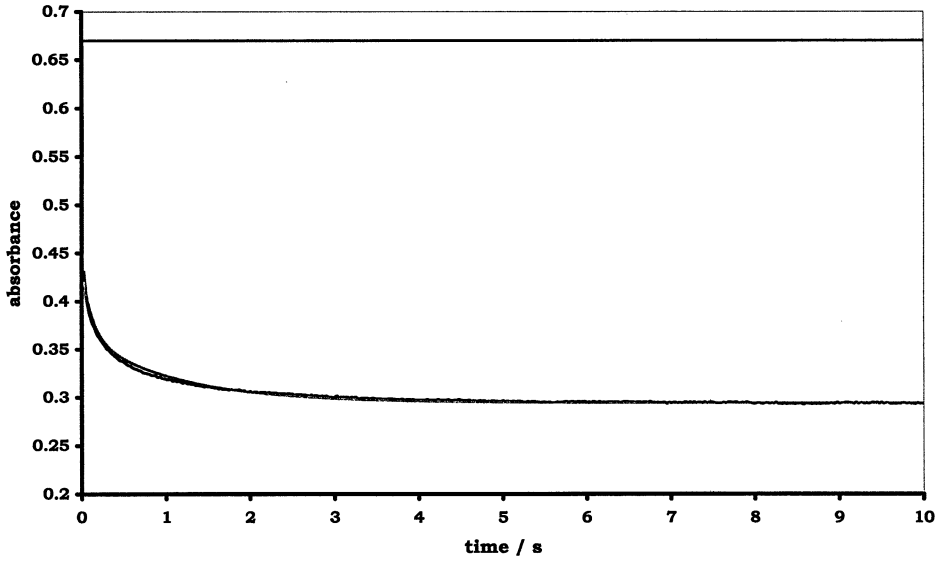

Fig. 3. Stopped-flow absorbance–time curve for the reaction of *trans*-[$Mo(N_2)(CNPh)(Ph_2PCH_2CH_2PPh_2)_2$] with anhydrous HCl in thf at 25.0 °C, typical of that observed for all *trans*-[$MoL(CNPh)(Ph_2PCH_2CH_2PPh_2)_2$]. The line at $A = 0.67$ is the absorbance of *trans*-[$Mo(N_2)(CNPh)(Ph_2PCH_2CH_2PPh_2)_2$]. The fit to the absorbance–time curve is shown superimposed on the data and is defined by the equation $A_t = 0.294 + 0.07\exp(-8.0t) + 0.07\exp(-0.9t)$.

$(CNPh)(dppe)_2$] occurs in the three phases typified by the absorbance–time curve in Fig. 3. The final absorbance corresponds to that of the product [Mo-$H(CO)(CNPh)(dppe)_2]^+$. The absorbance–time curve corresponds to the second and third phases. Each phase exhibits a different dependence on the concentration of HCl.

The second phase exhibits a complicated dependence on the concentration of HCl as shown in Fig. 4. At low concentration of acid the reaction is first order in the concentration of HCl, but at high concentrations of acid the rate of the reaction is independent of the concentration of HCl. Analysis of the curve yields the rate law shown in Eq. (1), with $a = (1.3 \pm 0.2) \times 10^2$ and $b = 330 \pm 20$.

$$\frac{-\mathrm{d}[\mathrm{Mo(CO)(CNHPh)(dppe)_2^+}]}{\mathrm{d}t} = \frac{a[\mathrm{HCl}][\mathrm{Mo(CO)(CNHPh)(dppe)_2^+}]}{1 + b[\mathrm{HCl}]} \quad (1)$$

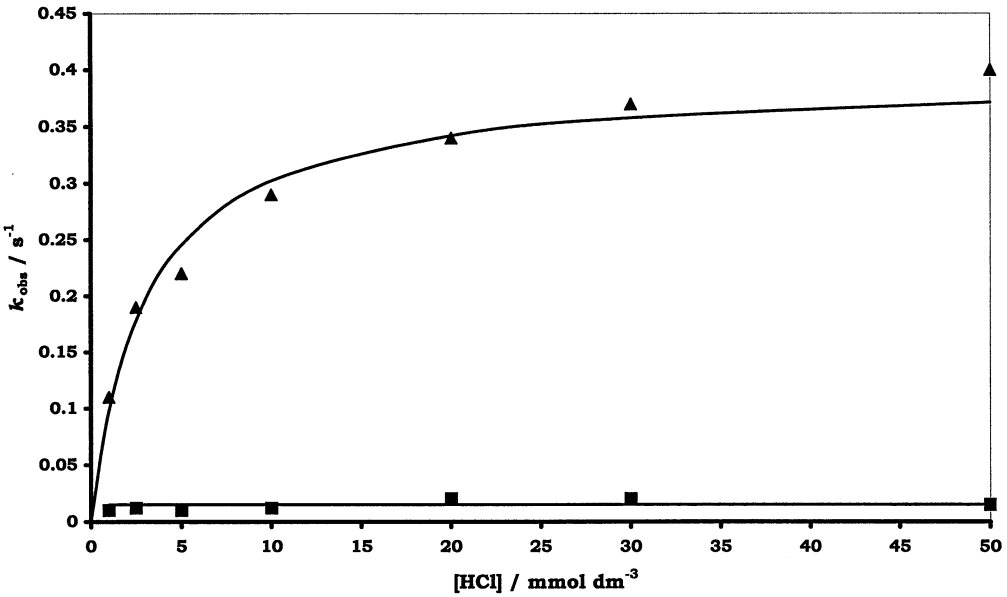

Fig. 4. Kinetic data for the acid dependence in the reaction between *trans*-[$Mo(CO)(CNPh)(Ph_2PCH_2CH_2PPh_2)_2$] and anhydrous HCl in thf at 25.0 °C. The data corresponds to the fast phase (▲) and the slow phase (■). The curve drawn is that defined by Eq. (1) with $a = (1.3 \pm 0.2) \times 10^2$ $dm^3\ mol^{-1}\ s^{-1}$ and $b = 330 \pm 20$ $dm^3\ mol^{-1}$.

Both the absorbance–time behaviour and the rate law in Eq. (1) are consistent with the second phase occurring by the pathway shown in the centre of Fig. 2. The absorbance change which occurs within the dead-time of the stopped-flow apparatus indicates rapid, initial protonation, presumably at the nitrogen atom of the isonitrile ligand to form *trans*-[Mo(CO)(CNHPh)(dppe)$_2$]$^+$. The rate law of Eq. (1) indicates that this cation is further protonated. It seems likely that the second proton binds to the carbon of the aminocarbyne ligand to generate *trans*-[Mo(CO)(CHNHPh)(dppe)$_2$]$^{2+}$. Certainly the analogous *trans*-[Mo(CO)(CHNH^{t}Bu)(dppe)$_2$]$^{2+}$, containing the electron-releasing ^{t}Bu group has been isolated [14]. Spectroscopic characterisation of *trans*-[Mo(CO)(CHNH^{t}Bu)(dppe)$_2$]$^{2+}$ indicates that an agostic hydrogen effectively bridges between the carbon and the molybdenum, as shown in Fig. 2.

The reaction of *trans*-[Mo(CO)(CHNHPh)(dppe)$_2$]$^{2+}$ is completed by the hydrogen migrating from carbon to metal to produce *trans*-[MoH(CO)(CNHPh)(dppe)$_2$]$^{2+}$. However, the combination of protonation of the metal and the CO ligand renders the aminocarbyne ligand sufficiently acidic that the amino-proton is released to produce, *trans*-[MoH(CO)(CNPh)(dppe)$_2$]$^+$.

Consideration of the mechanism described above indicates that initial protonation of the isonitrile nitrogen atom is enforced since the nitrogen atom is the most basic site. However, it is the further (presumably slower) protonation of the carbon which facilitates the formation of the hydride product. By the same token, it is the combination of the electron-withdrawing CO ligand, and the second protonation which renders the aminocarbyne ligand sufficiently acidic to release the amino-proton at the end of the reaction.

If protonation of the carbon atom in *trans*-[Mo(CO)(CNHPh)(dppe)$_2$]$^+$ is a rapidly established equilibrium, prior to the rate-limiting transfer of the proton from carbon to molybdenum, the rate law associated with the pathway described above is given by Eq. (2). Comparison of Eqs. (1) and (2) gives $K_1^{CO} = (3.3 \pm 0.2) \times 10^2$ dm^3 mol^{-1} and $k_5^{CO} = 0.39 \pm 0.03$ s^{-1}.

$$\frac{-\mathrm{d}[\mathrm{Mo(CO)(CNHPh)(dppe)_2^+}]}{\mathrm{d}t} = \frac{K_1^{CO} k_5^{CO} [\mathrm{HCl}][\mathrm{Mo(CO)(CNHPh)(dppe)_2^+}]}{1 + K_1^{CO}[\mathrm{HCl}]} \quad (2)$$

The mechanism associated with the third phase is less certain, in part because of the simplicity of the kinetics. That the rate of the reaction exhibits a first order dependence on the concentration of complex but is independent of the concentration of HCl ($k^{CO} = (1.5 \pm 0.2) \times 10^{-2}$ s^{-1}) is consistent with the isomerisation of *trans*-[Mo(CO)(CNHPh)(dppe)$_2$]$^+$ to *cis*-[Mo(CO)(CNHPh)(dppe)$_2$]$^+$ as shown in Fig. 5. Earlier, X-ray crystallography of the product isolated from the reaction between *trans*-[Mo(CO)(CNPh)(dppe)$_2$] and 1 mol. equiv. of [Me$_2$OH]BF$_4$ in thf demonstrated that the product is *cis*-[Mo(CO)(CNHPh)(dppe)$_2$]$^+$ [14]. In the presence of an excess of acid, it is anticipated that *cis*-[Mo(CO)(CNHPh)(dppe)$_2$]$^+$ will be converted to *trans*-[MoH(CO)(CNPh)(dppe)$_2$]$^+$ by a series of steps analogous to those described above for the *trans*-isomer.

A key difference between the earlier synthetic studies and the kinetic studies reported herein is that the latter are performed in the presence of a large excess of acid. It has been noted before that the presence of an excess of acid facilitates the conversion of *cis*-[Mo(CO)(CNHPh)(dppe)$_2$]$^+$ to *trans*-[MoH(CO)(CNPh)(dppe)$_2$]$^+$ [14] (Table 1).

3.2. Protonation of *trans*-[Mo(η^2-H$_2$)(CNPh)(dppe)$_2$]

The reaction of anhydrous HCl with *trans*-[Mo(η^2-H$_2$)(CNPh)(dppe)$_2$] to form *trans*-[MoCl(CNHPh)(dppe)$_2$] shows an absorbance–time curve analogous to that shown in Fig. 3. As before, the absorbance–time curve can be fitted to two exponentials, corresponding to the second and third phases. The kinetics of the second phase are shown in Fig. 6, and described by Eq. (1) with $a = (1.5 \pm 0.2) \times 10^3$ and $b = 520 \pm 50$. The third phase is independent of the concentration of acid ($k^{HH} = 0.10 \pm 0.05$ s^{-1}).

In contrast to *trans*-[Mo(CO)(CNPh)(dppe)$_2$], the reaction of *trans*-[Mo(η^2-H$_2$)(CNPh)(dppe)$_2$] with HCl result in the dissociation of dihydrogen. Thus, although the kinetics of the reaction of HCl with *trans*-[Mo(η^2-

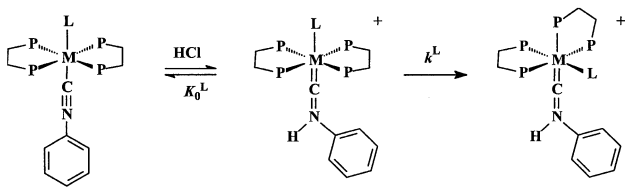

Fig. 5. Proposed general *trans*-to-*cis* isomerisation of *trans*-[MoL(CNHPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$ (L = CO, H$_2$ or N$_2$).

Table 1
Kinetic data for the reaction of *trans*-[Mo(CO)(CNPh)(dppe)$_2$] (0.2 mmol dm^{-3}) with anhydrous HCl in thf at 25.0 °C ($\lambda = 420$ nm)

[HCl] (mmol dm^{-3})	k_{obs}^{fast} (s^{-1})	k_{obs}^{slow} (s^{-1})
1.0	0.11	0.010
2.5	0.19	0.012
5.0	0.22	0.010
10.0	0.29	0.012
20.0	0.34	0.020
30.0	0.37	0.020
50.0	0.40	0.015

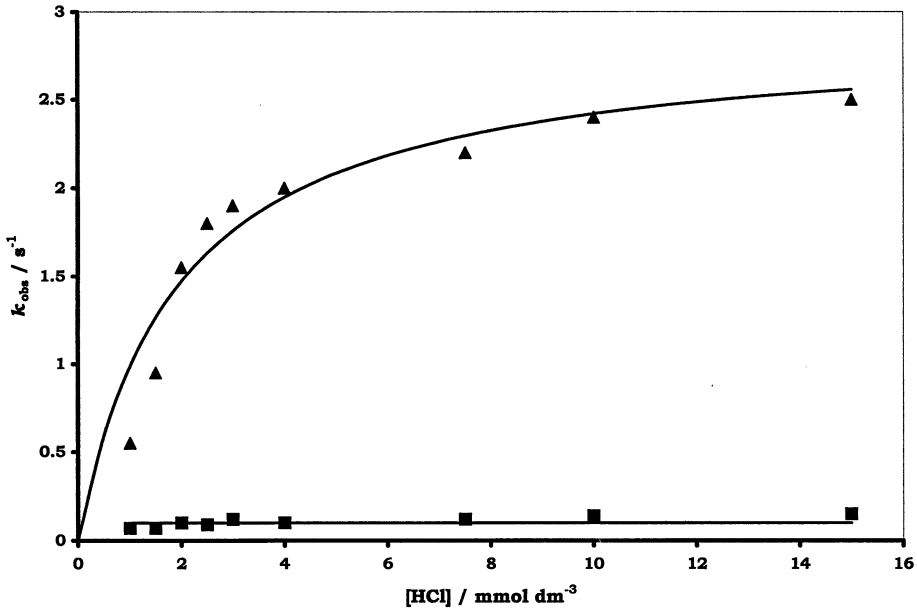

Fig. 6. Kinetic data for the acid dependence in the reaction between *trans*-[Mo(η^2-H_2)(CNPh)($Ph_2PCH_2CH_2PPh_2$)$_2$] and anhydrous HCl in thf at 25.0 °C. The data corresponds to the fast phase (▲) and the slow phase (■). The curve drawn is that defined by Eq. (1) with $a = (1.5 \pm 0.2) \times 10^3$ $dm^3\ mol^{-1}\ s^{-1}$ and $b = 520 \pm 50$ $dm^3\ mol^{-1}$.

H_2)(CNPh)(dppe)$_2$] are analogous to those of *trans*-[Mo(CO)(CNPh)(dppe)$_2$], the interpretation is quite different. The mechanism is shown in Fig. 2 in which the initial stages are analogous to those described for *trans*-[Mo(CO)(CNPh)(dppe)$_2$]: protonation of the isonitrile nitrogen atom (complete within 2 ms), and further protonation at the carbon atom produces *trans*-[Mo(η^2-H_2)(CHNHPh)(dppe)$_2$]$^{2+}$. Diprotonation of the isonitrile ligand is sufficiently electron-withdrawing that the dihydrogen ligand dissociates from the molybdenum in the rate-limiting step of the reaction. Subsequent rapid binding of chloride to the site vacated by dihydrogen completes the reaction.

In general, protonation of the isonitrile ligand labilises *trans* π-acceptor ligands. Simplistically, formation of *trans*-[Mo(η^2-H_2)(CHNHPh)(dppe)$_2$]$^{2+}$ results in electron density being pulled towards the –CHNHPh ligand. This has three effects on the bonding of the *trans*-dihydrogen ligand: (i) increases σ-donation from dihydrogen to Mo; (ii) decreases π-backbonding from Mo to dihydrogen, and (iii) increases H–H bonding [17]. It is anticipated that whilst (i) would inhibit dihydrogen dissociation, both (ii) and (iii) would facilitate dissociation; (ii) by weakening the bonding between Mo and dihydrogen and (iii) by making the H–H distance closer to that of free dihydrogen (i.e. more product-like). That diprotonation labilises dihydrogen to dissociation indicates that the dihydrogen ligand is more sensitive to changes in (ii) and (iii) than it is to changes in (i). Similar effects to the bonding of other π-acceptor ligands (such as CO and dinitrogen) are expected. However, the CO ligand is less sensitive to the degree of π-backbonding and so dissociation does not ensue. We will see in the next section that dinitrogen is more sensitive to π-backbonding than the dihydrogen ligand, since dissociation of dinitrogen occurs from *trans*-[Mo(N_2)(CNHPh)(dppe)$_2$]$^+$.

The mechanism outlined above for *trans*-[Mo(η^2-H_2)(CNPh)(dppe)$_2$] is consistent with the kinetics observed in Fig. 6. If protonation of the isonitrile nitrogen atom is complete within the dead-time of the stopped-flow apparatus, and protonation of the carbon is a rapidly established equilibrium (K_1^{HH}) prior to rate-limiting dissociation of dihydrogen (k_4^{HH}) the rate law shown in Eq. (3) can be derived, with $K_1^{HH} = 520 \pm 50$ $dm^3\ mol^{-1}$ and $k_4^{HH} = 2.9 \pm 0.3\ s^{-1}$.

$$\frac{-\,d[Mo(\eta^2\text{-}H_2)(CNHPh)(dppe)_2^+]}{dt} = \frac{K_1^{HH}k_4^{HH}[HCl][Mo(\eta^2\text{-}H_2)(CNHPh)(dppe)_2^+]}{1 + K_1^{HH}[HCl]} \quad (3)$$

As with the studies on *trans*-[Mo(CO)(CNPh)-(dppe)$_2$], it is not entirely clear to what the third phase corresponds. Again, we observe that the reaction is independent of the concentration of acid ($k^{HH} = 0.10 \pm 0.05\ s^{-1}$). It seems likely that, as with the CO system, the slow phase corresponds to rate-limiting isomerisation to the *cis*-isomer. Such isomerisation could be a general phenomenon for *trans*-[MoL(CNPh)(dppe)$_2$], facilitated by protonation of the isonitrile ligand (Fig. 4). Formation of the electron-withdrawing aminocarbyne ligand *trans* to a π-acceptor ligand results in a species where two *trans* ligands are sharing the same

Table 2
Kinetic data for the reaction of *trans*-[Mo(η^2-H_2)(CNPh)(dppe)$_2$] (0.2 mmol dm^{-3}) with anhydrous HCl in thf at 25.0 °C ($\lambda = 420$ nm)

[HCl] (mmol dm^{-3})	k_{obs}^{fast} (s^{-1})	k_{obs}^{slow} (s^{-1})
1.0	0.55	0.07
1.5	0.95	0.07
2.0	1.55	0.10
2.5	1.8	0.09
3.0	1.9	0.12
4.0	2.0	0.10
7.5	2.2	0.12
10.0	2.4	0.14
15.0	2.5	0.15

d-orbitals for bonding, and thus competing for the π-electron density. By isomerising to the *cis* configuration the complex relieves the conflict of two *trans* π-acceptor ligands. It is proposed that in the presence of an excess of acid, the *cis*-isomer subsequently forms *trans*-[MoCl(CNHPh)(dppe)$_2$] by a mechanism analogous to that of the *trans*-isomer shown in Fig. 2 (Table 2).

3.3. Protonation of trans-[Mo(N$_2$)(CNPh)(dppe)$_2$]

The reaction of HCl with *trans*-[Mo(N$_2$)(CNPh)(dppe)$_2$] gives *trans*-[MoCl(CNHPh)(dppe)$_2$], the same product as with *trans*-[Mo(η^2-H_2)(CNPh)(dppe)$_2$]. Although the absorbance–time behaviour is analogous to that shown in Fig. 3, the kinetics of the reaction between HCl and *trans*-[Mo(N$_2$)(CNPh)(dppe)$_2$] are different to that observed with the other systems presented in this paper. As before, the absorbance–time curve can be fitted to two exponentials, corresponding to the second and third phases. The third phase is independent of the concentration of acid, ($k^{NN} = 0.5 \pm 0.1$ s^{-1}). As before, we attribute this phase to the isomerisation of *trans*-[Mo(N$_2$)(CNHPh)(dppe)$_2$]$^+$ to *cis*-[Mo(N$_2$)(CNHPh)(dppe)$_2$]$^+$ and then the relatively rapid substitution of the *cis* isomer.

The second phase is markedly different to that observed with L = CO or H_2 complexes. As shown in Fig. 7, increasing the concentration of HCl leads to a *decrease* in the rate of the reaction. Analysis of the data results in the rate law shown in Eq. (4). It seems likely that the identical absorbance–time behaviour, but different kinetics, observed with *trans*-[Mo(N$_2$)(CNPh)(dppe)$_2$] is because this complex contains a ligand (dinitrogen) which is uniquely capable of being protonated.

$$\frac{-\mathrm{d}[\mathrm{Mo(N_2)(CNHPh)(dppe)_2}]}{\mathrm{d}t} = \frac{10.0 \pm 1.0[\mathrm{Mo(N_2)(CNHPh)(dppe)_2}]}{1 + 52 \pm 5[\mathrm{HCl}]} \quad (4)$$

The pathway consistent with the kinetics is shown in Fig. 2. As with all the complexes discussed herein, initial rapid protonation of the isonitrile nitrogen atom produces *trans*-[Mo(N$_2$)(CNHPh)(dppe)$_2$]$^+$, within the dead-time of the stopped-flow apparatus in the first phase of the reaction. Protonation of the isonitrile withdraws electron-density from the metal site thus labilising the *trans*-dinitrogen towards dissociation. However, as the concentration of HCl is increased the kinetics indicates that a further protonation must occur

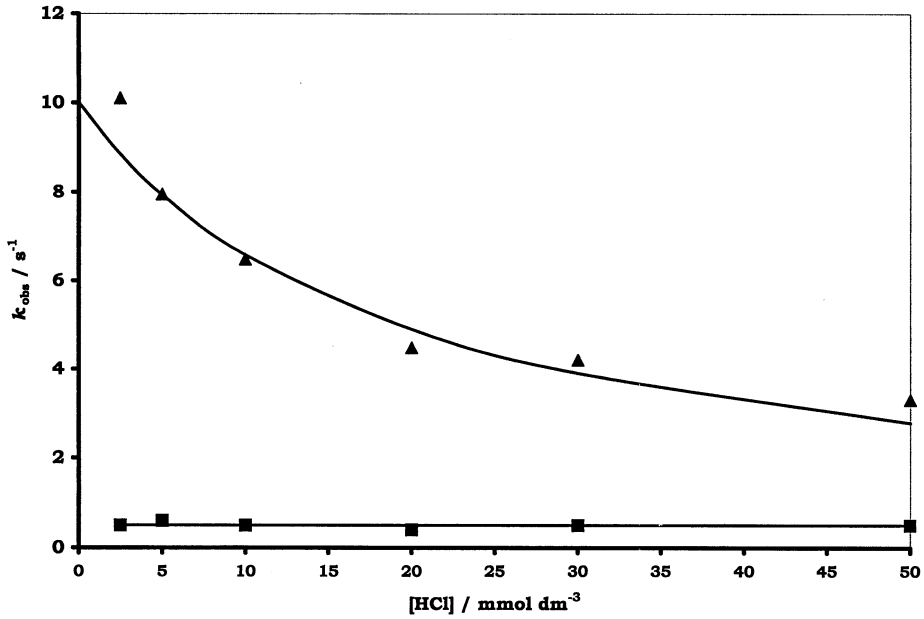

Fig. 7. Kinetic data for the acid dependence in the reaction between *trans*-[Mo(N$_2$)(CNPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] and anhydrous HCl in thf at 25.0 °C. The data corresponds to the fast phase (▲) and the slow phase (■). The curve drawn is that defined by Eq. (4).

Table 3
Kinetic data for the reaction of *trans*-[$Mo(N_2)(CNPh)(dppe)_2$] (0.2 mmol dm^{-3}) with anhydrous HCl in thf at 25.0 °C ($\lambda = 420$ nm)

[HCl] (mmol dm^{-3})	k_{obs}^{fast} (s^{-1})	k_{obs}^{slow} (s^{-1})
2.5	10.1	0.5
5.0	8.0	0.6
10.0	6.5	0.5
20.0	4.5	0.4
30.0	4.2	0.5
50.0	3.3	0.5

which suppresses this lability. Clearly, protonation at Mo or the aminocarbyne ligand would further labilise dinitrogen, since protonation at these sites would withdraw electron density and diminish the π-backbonding to dintrogen. It seems likely that the coordinated dinitrogen is protonated to generate *trans*-[Mo(NNH)-$(CNHPh)(dppe)_2]^{2+}$. Simplistically, protonation of the dinitrogen ligand increases the Mo-to-nitrogen π-backbonding, effectively annulling the electronic effect of the aminocarbyne ligand and making the diazenide a less labile ligand than dinitrogen.

Comparison with the other systems discussed in this paper indicates that the protonation of the carbon of the aminocarbyne ligand could be in competition with the protonation of dinitrogen. It is anticipated that protonation of the dinitrogen would be rapid, possibly diffusion-controlled [1,2,4]. However, earlier studies have shown that protonation at carbon sites can be appreciably slower than at the stereochemical lone pair of nitrogen atoms [1,2].

If it is assumed that the initial protonation of the isonitrile ligand is rapid and complete within the first phase, and the protonation of the dinitrogen ligand is a rapidly established equilibrium compared to the rate limiting dissociation of dinitrogen from *trans*-$[Mo(N_2)(CNHPh)(dppe)_2]^+$ the resulting rate law is that shown in Eq. (5), with $k_3^{NN} = 10.0 \pm 1.0$ and $K_2^{NN} = 52 \pm 5$ $dm^3\,mol^{-1}$. It is worth noting that the value of K_2^{NN} is an order of magnitude smaller than the values of K_1^{HH} or K_1^{CO} consistent with K_2^{NN} corresponding to protonation at a different site (Table 3).

$$\frac{-\,d[Mo(N_2)(CNHPh)(dppe)_2^+]}{dt} = \frac{k_3^{NN}[Mo(N_2)(CNHPh)(dppe)_2^+]}{1 + K_2^{NN}[HCl]} \quad (5)$$

3.4. Protonation of molecules bound to {Mo(dppe)$_2$} site

It is important to put the results presented in this paper into context. In particular, to compare the protonation chemistry proposed herein within that of other complexes containing the robust $\{Mo(dppe)_2\}$ site.

Previously, an extensive series of studies on the reactions of acid with *trans*-$[ML_2(dppe)_2]$ ($L = C_2H_4$, MeCCH, N_2, RNC or 2H) [1–10] have defined the rates and initial sites of protonation of these complexes, together with the subsequent steps which result in the movement of the proton between ligand and metal. The pathways are summarised in Fig. 1. Some general features concerning the rates of protonation have emerged. Thus, the rates of protonation vary with the site being protonated and in general protonation at the metal or a carbon site is slower than protonation of stereochemical lone pairs of electrons on nitrogen, oxygen and halogen atoms. The barrier to protonation of carbon sites is usually attributed to rehybridisation whilst the barrier to protonation of metal sites is primarily the necessary reorganisation of the ligands. In contrast, protonation of lone pairs of electrons in thermodynamically-favourable reactions are usually diffusion-controlled.

Currently, it is not possible to predict whether initial protonation occurs at metal or ligand, or how transfer of the proton occurs between the initial and final sites. Both intramolecular and acid–base-catalysed mechanisms for proton transfer have been identified. Some specific features concerning these rearrangement reactions are evident for complexes of the type *trans*-$[ML_2(dppe)_2]$. Only when L = MeCCH [8,9] is protonation directly at the ligand and no subsequent movement to another site (the metal) occurs. In all other cases the kinetics indicate a more complex pathway. When $L = C_2H_4$, or N_2 the initial site can be either the metal or the ligand depending on the nature of the co-ligands and the concentration of acid. Thus, at low concentrations of acid protonation of *trans*-$[Mo(\eta^2\text{-}C_2H_4)_2(dppe)_2]$ [6,7] occurs preferentially at the coordinated ethylene, to form *trans*-$[MoEt(\eta^2\text{-}C_2H_4)(dppe)_2]^+$, and subsequent intramolecular β-hydrogen transfer to the metal produces $[MoH(\eta^2\text{-}C_2H_4)_2(dppe)_2]^+$. Only at high concentrations of acid does the rate of the direct protonation of the metal become significant.

In contrast, protonation of dinitrogen ligands is invariably faster than protonation of the metal, but even here complications can arise. In the reaction of HCl with *trans*-$[Mo(N_2)_2(depe)_2]$ ($depe = Et_2PCH_2CH_2PEt_2$) the first product isolated is $[MoH(N_2)_2(depe)_2]^+$ apparently indicating preferential protonation at the metal [18]. However, it seems more likely that protonation at dinitrogen is more rapid than protonation of molybdenum. The reason the hydride is the first species *isolated* is because formation of *trans*-$[Mo(NNH)(N_2)(depe)_2]^+$ is readily reversible whereas the protonation of the metal is not. Thus, *isolation* of $[MoH(N_2)_2(depe)_2]^+$ is a consequence of thermodynamics rather than kinetics. At higher concentrations of acid, $[MoH(N_2)_2(depe)_2]^+$ reacts to ultimately form *trans*-$[Mo(NNH_2)Cl(depe)_2]^+$ by a pathway involving $[MoH(NNH)(N_2)(depe)_2]^{2+}$.

With *trans*-[Mo(CNR)$_2$(dppe)$_2$] initial protonation occurs at the isonitrile to produce *trans*-[Mo(CNHR)(CNR)(dppe)$_2$]$^+$. However, the proton ultimately moves to the metal by a mixture of intramolecular rearrangement pathway and an acid-catalysed route, presumably involving [MoH(CNHR)(CNR)(dppe)$_2$]$^{2+}$ [5].

Studies on the protonation of [MoH$_4$(dppe)$_2$] show that diprotonation occurs to produce a species [10] which must contain at least one dihydrogen ligand, such as [MoH$_4$(η^2-H$_2$)(dppe)$_2$]$^{2+}$. The mechanism of formation of this species could either involve direct protonation of a hydride ligand (as observed in [WH$_4$(PMePh$_2$)$_4$] [19]) or initial protonation of the metal followed by intramolecular coupling of the hydride ligands [17].

More recently, complexes of the type *trans*-[MoLL′(dppe)$_2$] have been reported and allow the study of the preferential protonation site between two basic ligands, giving further insight into the factors controlling protonation at different sites bound to the same metal. Recent studies on *trans*-[Mo(N$_2$)(NCC$_6$H$_4$R-4)(dppe)$_2$] [11] showed that although protonation at the carbon of the nitrile ligand was the initial site of protonation, the rate of protonation reached a maximum with $k = 1 \times 10^4$ dm^3 mol^{-1} s^{-1}, irrespective of the electron-releasing capability of R. The electron releasing capability of R acts in opposition to the π-backbonding from Mo to nitrile leading to a compensatory effect. However, the electron-releasing effect of R reinforces the π-backbonding from Mo to dinitrogen. Thus, with very electron-releasing nitriles protonation at the dinitrogen is observed. The important point is that the product of the reaction is controlled by a combination of kinetic and thermodynamic factors.

In this paper, we have explored the protonation of *trans*-[MoL(CNPh)(dppe)$_2$] (L = N$_2$, CO or H$_2$). Several general features have emerged from this work. (i) The initial site of protonation is always the isonitrile ligand. (ii) When L = CO, formation of [MoH(CO)(CNPh)(dppe)$_2$]$^+$ occurs via the diprotonated species *trans*-[Mo(CO)(CHNHPh)(dppe)$_2$]$^{2+}$ and the analogous *trans*-[Mo(η^2-H$_2$)(CHNHPh)(dppe)$_2$]$^{2+}$ is necessary to labilise the dihydrogen ligand to dissociate. (iii) Protonation of *trans*-[Mo(N$_2$)(CNPh)(dppe)$_2$] shows that protonation of the isonitrile ligand occurs preferentially, and only at higher concentrations of acid does protonation of dinitrogen become detectable. (iv) Surprisingly, although diprotonation of *trans*-[Mo(η^2-H$_2$)(CNPh)(dppe)$_2$] is necessary to labilise dihydrogen, only monoprotonation of *trans*-[Mo(N$_2$)(CNPh)(dppe)$_2$] is necessary to labilise dinitrogen. This last point deserves further comment.

The results presented in this paper indicate that dinitrogen is more labile to dissociation at the *trans*-{Mo(CNHPh)(dppe)$_2$}$^+$ site than is dihydrogen. From the data presented in Fig. 6 we can calculate an upper limit for $k_3^{HH} \leq 0.1$ s^{-1}, and the data in Fig. 7 shows that $k_3^{NN} = 10.0$ s^{-1}. Thus, dinitrogen is at least 100 times more labile than dihydrogen in these complexes. At first sight this appears to be surprising (and counter-intuitive) however, comparison with other systems indicates that it may be not so unusual. Studies on the labilities of L = N$_2$ and L = H$_2$ in [WL(CO)$_3$-{P(C$_6$H$_{11}$)$_3$}$_2$] show $k^{NN}/k^{HH} = 0.16$ [20]. In only one other study has the effect of protonation on the relative labilities of dinitrogen and dihydrogen ligands been quantified. In the reaction of acid with [MoH$_4$(dppe)$_2$] [10] although diprotonation is necessary to labilise the system towards dihydrogen dissociation, a limit for the rate of dissociation of dihydrogen from [MoH$_5$(dppe)$_2$]$^+$ can be estimated, $k^{HH} < 1 \times 10^{-2}$ s^{-1}. The rate of dissociation of dinitrogen from the analogous [MoH(N$_2$)$_2$(dppe)$_2$]$^+$ has been measured [4] $k^{NN} = 2 \times 10^{-2}$ s^{-1}, giving $k^{NN}/k^{HH} > 2$. It appears that protonation of a metal site labilises dinitrogen ligands more than dihydrogen. The origin of this effect is still obscure but it seems likely that it is a consequence of the subtle effects protonation has on the σ- and π-bonding between ligand and metal.

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