Differential electronic effects and the selective protonation of mutually *trans* ligands

Valerie Autissier,[a] Richard A. Henderson*[a] and Christopher J. Pickett[b]

[a] *Department of Chemistry, Bedson Building, University of Newcastle, Newcastle-upon-Tyne, UK NE1 7RU. E-mail: r.a.henderson@ncl.ac.uk*

[b] *Department of Biological Chemistry, John Innes Centre, Norwich Research Park, Norwich, UK NR4 7UH*

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The rate of protonation of the nitrile carbon in *trans*-[Mo(N$_2$)(NCC$_6$H$_4$R-4)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (R = MeO, Me, H, Cl, MeCO or NO$_2$) shows an unusual non-linear dependence on the identity of R, revealing how both kinetic and thermodynamic factors control the site of protonation in complexes containing a variety of protonatable ligands.

Understanding the factors which define where protons bind to metal complexes is important in gaining insight into the reactivity of certain metalloenzymes,[1] and in controlling the regio-, stereo- and product-specificities of metal-mediated reactions.[2,3] However, we are still some way from being able to predict where protons will bind to complexes containing a variety of potential sites, as is evident when we consider the reactions shown in Fig. 1.

Some years ago,[4] protonation of *trans*-[Mo(N$_2$)(NCPr^n)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] was found to occur at dinitrogen, forming the corresponding hydrazide (top line). However recently, the analogous *trans*-[Mo(N$_2$)(NCPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] was shown to protonate at the nitrile carbon[5] (bottom line). This observation is rather unexpected since earlier investigations[6,7] showed that protonation of end-on coordinated dinitrogen is rapid (probably diffusion-controlled), whereas protonation at carbon sites is usually several orders of magnitude slower, even when bound to electron-rich metal centres[2,3,8] indicating that hydrazides would always be formed in such reactions. Given that in *trans*-[Mo(N$_2$)(NCPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] both dinitrogen and nitrile are bound to the same centre it is difficult to reconcile why carbon should be the preferred protonation site. Herein, we report kinetic studies on the family of reactions represented in eqn. (1) (R = MeO, Me, H, Cl, MeCO or NO$_2$),[9] and show that R affects the protonation chemistry of the dinitrogen and nitrile ligands in quite different ways.

trans-[Mo(N$_2$)(NCC$_6$H$_4$R-4)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] + HCl ⟶
trans-[MoCl(NCH$_2$C$_6$H$_4$R-4)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$ + Cl$^-$ (1)

When the reaction between *trans*-[Mo(N$_2$)(NCPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] and an excess of anhydrous HCl is studied in thf, using stopped-flow spectrophotometry, a single exponential absorbance–time curve is observed. Under all conditions, the initial absorbance corresponds to the reactant and final absorbance† to *trans*-[MoCl(NCH$_2$Ph)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$. The kinetics of this reaction exhibit a first order dependence on the concentration of *trans*-[Mo(N$_2$)(NCPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] but the dependence on the concentration of HCl is markedly non-linear, such that at high concentrations of HCl the rate is independent of the concentration of acid (Fig. 2).

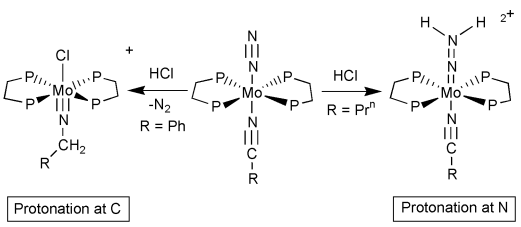

Fig. 1 Protonation of dinitrogen *vs.* nitrile in *trans*-[Mo(N$_2$)(NCR)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$].

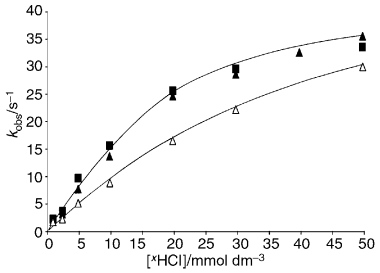

Fig. 2 Dependence on the concentration of ^{x}HCl for the reaction with *trans*-[Mo(N$_2$)(NCPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] in thf at 25.0 °C. The data points correspond to: [Mo] = 0.2 mmol dm^{-3} (■) and [Mo] = 0.4 mmol dm^{-3} (▲). Data collected in the reaction with ^{2}HCl (△) are also shown. The data were analysed by plotting $1/k_{obs}$ *vs.* 1/[HCl], from the straight line the intercept = $1/k_2$ and gradient = $1/k_1$.

These observations are consistent with the mechanism shown in Fig. 3. Initial protonation of the nitrile carbon (k_1) generates [Mo(N$_2$)(NCHPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$. Protonation of the nitrile diminishes the electron density at the metal, and because dinitrogen is a strong π-acceptor ligand, this has two effects on its reactivity: (i) decreasing the basicity of dinitrogen thus suppressing protonation and (ii) increasing the lability of dinitrogen. Dissociation of dinitrogen (k_2) and subsequent rapid binding of chloride facilitates further protonation of carbon to form *trans*-[MoCl(NCH$_2$Ph)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$. An analogous mechanism has been proposed for the reactions of acid with *trans*-[Mo(N$_2$)$_2$(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$][6,7] (R = Ph or Et), involving rapid protonation of one dinitrogen followed by rate-limiting dissociation of the other. The important difference in the two systems is that for *trans*-[Mo(N$_2$)(NCPh)(Ph$_2$PCH$_2$-

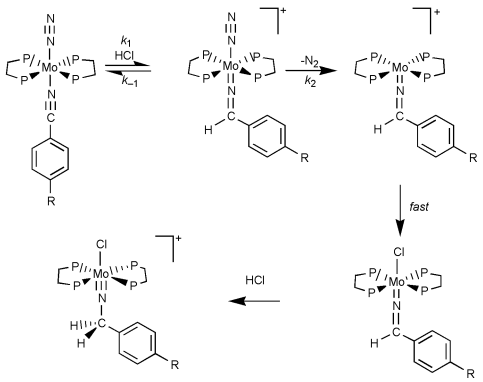

Fig. 3 Mechanism for the formation of *trans*-[MoCl(NCH$_2$C$_6$H$_4$R-4)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] in the reactions of anhydrous HCl with *trans*-[Mo(N$_2$)(NCC$_6$H$_4$R-4)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$].

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$CH_2PPh_2)_2$] the protonation at carbon is rate-limiting at low concentrations of HCl, and consequently the reaction with DCl is associated with a primary isotope effect (k_1^H/k_1^D = 1.8; Fig. 2). Only at high concentrations of acid does the unimolecular dissociation of dinitrogen become rate-limiting, and under these conditions there is no isotope effect (k_2^H/k_2^D = 1.0).

Studies on *trans*-[Mo(N_2)(NCC_6H_4R-4)($Ph_2PCH_2CH_2PPh_2)_2$] (R = MeO, Me, Cl, MeCO or NO_2) show analogous behaviour to that of *trans*-[Mo(N_2)(NCPh)($Ph_2PCH_2CH_2PPh_2)_2$] and allow investigation into how k_1 and k_2 are affected by the electronic influences of R (Fig. 4).

The effect of R on the lability of dinitrogen (k_2) is not unexpected. As R is varied and becomes more electron-releasing, the dinitrogen becomes less labile. This is in line with the labilities of dinitrogen previously observed in the reactions of *trans*-[Mo(N_2)$_2${(4-RC_6H_4)$_2PCH_2CH_2P(C_6H_4$R-4)$_2$}$_2$] (R = CF_3, Cl, H, Me or MeO).[10] The effect of R on the rate of protonation at the nitrile carbon is less straightforward. It is anticipated that k_1 would be affected by both the electron density at the carbon and the barrier to structural rearrangement (rehybridisation).[11] Certainly, there is a general increase in the rate of protonation as R becomes more electron-releasing but the trend is markedly non-linear, and with the most strongly electron-releasing substituents the rate of protonation is essentially independent of the nature of R. The reason R affects protonation of the nitrile and dinitrogen ligands so differently becomes clearer after considering the effect R has on the IR stretching frequencies, $\upsilon(N_2)$ and υ(CN) (Fig. 4, insert).[9] It is evident that R affects $\upsilon(N_2)$ and υ(CN) in a manner which parallels the rates of dinitrogen dissociation and protonation of carbon, respectively. The values of $\upsilon(N_2)$ and υ(CN) reflect the bond orders in these groups, which are affected by the backbonding from {Mo($Ph_2PCH_2CH_2PPh_2)_2$} to each of the π-acceptor ligands. The substituent R will modulate this effect, but because it is sited on the nitrile, R affects the backbonding to dinitrogen and nitrile differently.

For the *trans*-dinitrogen, as R is varied and made more electron-releasing the backbonding from Mo to dinitrogen is reinforced resulting in a decrease in $\upsilon(N_2)$ and dinitrogen lability (k_2) (and, as noted above, an increase in basicity). In contrast, the effect of an electron-releasing R will oppose the backbonding from Mo to nitrile. This counterbalance of the electron-releasing effect of R and the backbonding from Mo results in the increasing insensitivity of υ(CN) and the rate of protonation of the nitrile carbon as R becomes more electron-releasing ($k_1^{max} \approx 1 \times 10^4$ dm^3 mol^{-1} s^{-1}). Understanding the electronic origins of these effects allows us to appreciate that it is a combination of kinetic and thermodynamic factors which control product-selectivity in the reactions of acid with *trans*-[Mo(N_2)(NCR)($Ph_2PCH_2CH_2PPh_2)_2$] (Fig. 1).

As noted above, the π-backbonding from the {Mo($Ph_2PCH_2CH_2PPh_2)_2$} site affects both the lability and the basicity of dinitrogen.[12] In *trans*-[Mo(N_2)(NCC_6H_4R-4)($Ph_2PCH_2CH_2PPh_2)_2$], the aryl group is poorly electron-releasing and consequently the *trans*-dinitrogen is only weakly basic. Indeed, we can estimate an upper limit for the proton-affinity of the dinitrogen in these systems [eqn. (2)]. Even at the highest concentration of HCl (50 mmol dm^{-3}), there is no spectroscopic or kinetic evidence for dinitrogen being protonated, and hence $K_3^{Ph} \leqslant 4 \times 10^{-5}$. Since $K_3^{Ph} = k_3^{Ph}/k_{-3}^{Ph}$ and assuming the thermodynamically favourable k_{-3}^{Ph} step is diffusion controlled, we can estimate $k_3^{Ph} \leqslant 4 \times 10^5$ dm^3 mol^{-1} s^{-1}. Hence in these systems, the rates of protonation of dinitrogen and the nitrile carbon are not necessarily appreciably different. Since the exclusive product is always *trans*-[MoCl(NCC_6H_4R-4)($Ph_2PCH_2CH_2PPh_2)_2$] thermodynamic factors must be controlling the outcome of the reaction.

$$Mo{-}N{\equiv}N + HCl \underset{}{\overset{K_3}{\rightleftharpoons}} Mo{=}N{=}\overset{+}{N}\overset{H}{\diagdown} + Cl^- \qquad (2)$$

As indicated above, a natural consequence of the mutually *trans* dinitrogen and nitrile both being π-acceptor ligands is that protonation at one suppresses protonation at the other. However, the unfavourable value of K_3^{Ph} means that the parent dinitrogen complex is the major component of the protolytic equilibrium mixture and is able to react by the irreversible, protonation of the nitrile carbon, resulting in the ultimate formation of *trans*-[MoCl($NCH_2C_6H_4$R-4)($Ph_2PCH_2CH_2PPh_2)_2$]$^+$.

Consider now the situation where the nitrile is *very* electron-releasing, as is the case in *trans*-[Mo(N_2)(NCPr^n)($Ph_2PCH_2CH_2PPh_2)_2$]. The Pr^{n}CN ligand is sufficiently electron-releasing[4] that dinitrogen binds two protons even with [HCl] = 10 mmol dm^{-3}, giving $K_3^{Pr} \geqslant 0.36$ and hence $k_3^{Pr} \geqslant 3.6 \times 10^9$ dm^3 mol^{-1} s^{-1} (*i.e.* close to the diffusion-controlled limit). However, the data in Fig. 4 indicate that protonation of carbon will not exceed $k_1 \approx 1 \times 10^4$ dm^3 mol^{-1} s^{-1}. Consequently both the kinetics and thermodynamics favour protonation at dinitrogen, and *trans*-[Mo(NNH_2)(NCPr^n)($Ph_2PCH_2CH_2PPh_2)_2$]$^{2+}$ is formed (Fig. 1).

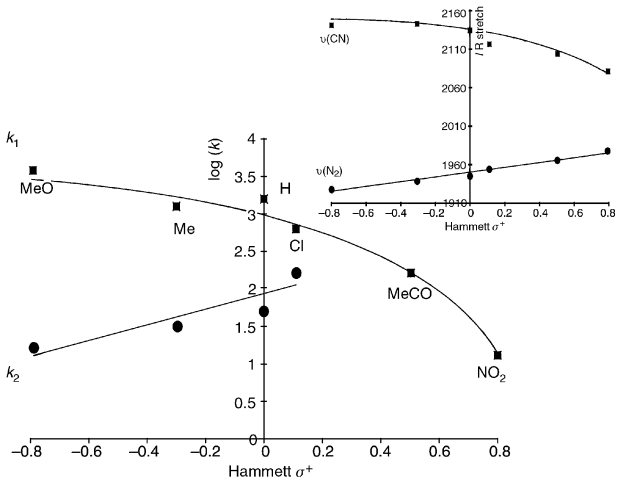

Fig. 4 Correlation of log(k) with Hammett σ^+ for the protonation of the nitrile carbon, k_1 (■) and dissociation of dinitrogen, k_2 (●) in the reactions of HCl with *trans*-[Mo(N_2)(NCC_6H_4R-4)($Ph_2PCH_2CH_2PPh_2)_2$] (R = NO_2, MeCO, Cl, H, Me or MeO) in thf at 25.0 °C. Insert: correlation of Hammett σ^+ with υ(CN) (■) and $\upsilon(N_2)$ (●).

Notes and references

† The identity of the product was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy and comparison of the spectra with those reported in the literature.[5]

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