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Protonation of the nitrile ligand *versus* protonation of rhenium at *cis*- or *trans*-[ReCl(NCC$_6$H$_4$R-4)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (R = Cl, F, Me or MeO). A mechanistic study

João J.R. Fraústo da Silva [a], M. Fátima C. Guedes da Silva [a], Richard A. Henderson [b], Armando J.L. Pombeiro [a] and Raymond L. Richards [b]

[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisbon codex (Portugal)*

[b] *AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ (UK)*

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Abstract

Stopped-flow kinetic studies have shown that in tetrahydrofuran the protonation, by HCl, of *cis*-[ReCl(NCC$_6$H$_4$R-4)(dppe)$_2$] (R = Cl, F, Me or OMe; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) or *trans*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$] to give [ReCl(H)(NCC$_6$H$_4$R-4)(dppe)$_2$]$^+$ involves a rapid β-proton addition to the nitrile ligand forming the corresponding methyleneamido-intermediate [ReCl(N=CHC$_6$H$_4$R-4)(dppe)$_2$]$^+$ which, upon rearrangement or further metal-protonation/ligand-deprotonation steps, forms the final hydride product.

1. Introduction

As part of our research on the activation of small molecules by electron-rich metal sites, we have an interest in defining the sites of protonation of their complexes, both to establish the fundamental reactivity of these systems and, in some cases, as models for the action of the metalloenzyme nitrogenase [1]. To these ends we have studied complexes containing dinitrogen [2], alkynes [3], isocyanides [4], nitriles [5], alkenes [6] and hydride [7].

Of particular relevance would be the understanding of the competition between the metal and the ligand for the proton and here we report the first kinetic analysis of the protonation of nitrile ligands and its role in the formation of hydride complexes. In addition this study provides an insight into the factors which determine the formation or cleavage of metal–hydrogen or carbon–hydrogen bonds, a matter of well-recognized significance in catalysis [8].

The mechanistic studies, by stopped-flow spectrophotometry, were performed on the protonation of *cis*-[ReCl(NCC$_6$H$_4$R-4)(dppe)$_2$] (R = Cl, F, Me or MeO; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and *trans*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$] by HCl.

Previously, it has been shown that, using HBF$_4$ under carefully controlled conditions, either methyleneamido-complexes, [ReCl(NCHC$_6$H$_4$R-4)(dppe)$_2$]$^+$ [5], or hydrido-species [ReCl(H)(NCC$_6$H$_4$R-4)(ddpe)$_2$]$^+$ [9], can be isolated. For the kinetic studies we have, in general, avoided using HBF$_4$ for three reasons. First, this acid is prone to rapidly polymerise the solvent of choice, THF (tetrahydrofuran). Secondly, and much more problematical, it is not clear what proportion of the solution is HBF$_4$ and what proportion is HF; or, indeed, which of these two acids is the "active" component; and finally there is the possibility of F$^-$ attacking the metal. In order to circumvent these problems we have studied the reactions of [ReCl(NCC$_6$H$_4$R-4)(dppe)$_2$] with anhydrous HCl in THF. This change of acid has the effect that the ultimate product for all systems is the hydrido-complex, but, as we shall see, the methyleneamido-species is a detectable intermediate in this reaction.

2. Results and discussion

When studied with a stopped-flow spectrophotometer it becomes clear that the reaction of [ReCl-

Correspondence to: Dr. R.A. Henderson or Dr. A.J.L. Pombeiro.

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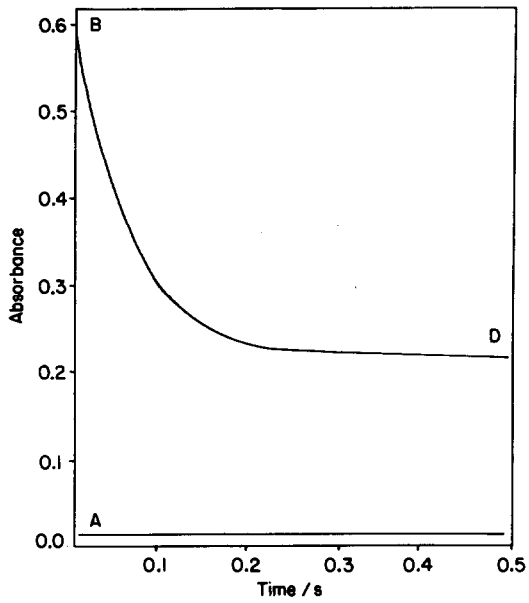


Fig. 1. Absorbance-time curve for the reaction of *trans*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$] ([Re] = 1.0×10^{-4} mol dm^{-3}) with HCl ([HCl] = 3.1 mmol dm^{-3}) in THF at 25.0°C, λ = 420 nm. Also shown is the absorbance (0.01) of the nitrile complex (A) in the absence of acid.

(NCC$_6$H$_4$R-4)(dppe)$_2$] with an excess of anhydrous HCl occurs in two distinct phases. A typical absorbance-time curve (for the reaction of HCl with *trans*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$] is shown in Fig. 1, from which it can be seen that there is an initial rapid increase in absorbance (to yield an intermediate), which is complete within the dead-time of the apparatus (2 ms), followed by the relatively slower exponential decay of this intermediate to form the hydrido-product.

The kinetics of the slower phase (the formation of the hydrido-complex) exhibit a simple first-order dependence on the concentration of the rhenium complex, as is evident from the single exponential absorbance-time curves and the constancy of the value of k_{obs} over a range of concentrations of the rhenium complex (see Table 1). Here and throughout this paper, k_{obs} is the pseudo-first-order rate constant measured in the presence of an excess of HCl ([HCl]/[Re] $\geq$ 10). The dependence of the reaction rate on the concentration of HCl is that shown by the general relationship eqn. (1), and illustrated (for *cis*-[ReCl(NCC$_6$H$_4$OMe-4)(dppe)$_2$] in Fig. 2.

$$k_{obs} = a + b[HCl] \quad (1)$$

For the *cis*-isomer, (R = F): $a = (1.55 \pm 0.10)\times10^{-2}$ s^{-1}, $b = 3.5 \pm 0.1$ dm^3 mol^{-1} s^{-1}; R = Cl: $a = (5.5 \pm 0.2)\times10^{-2}$ s^{-1}, $b = 12.8 \pm 0.5$ dm^3 mol^{-1} s^{-1}; R = Me: $a = (1.17 \pm 0.02)\times10^{-1}$ s^{-1}, $b = 10.4 \pm 0.2$ dm^3 mol^{-1} s^{-1}; R = MeO: $a = (1.0 \pm 0.2)\times10^{-2}$ s^{-1}, $b = 4.3 \pm 0.2$ dm^3 mol^{-1} s^{-1}; and for the *trans*-isomer, (R = F): $a = 11.8 \pm 1.2$ s^{-1}, $b = (3.4 \pm 0.4)\times10^3$ dm^3 mol^{-1} s^{-1}.

TABLE 1. Kinetic data for the reactions of *cis*-[ReCl(NCC$_6$H$_4$R-4)(dppe)$_2$] (R = Cl, F, Me or MeO) or *trans*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$] with HCl in THF at 25.0°C

[HCl]/ mmol dm^{-3}	k_{obs} [c] /s^{-1}				
	trans-isomer	*cis*-isomer			
	R = F [a]	R = F [a,b]	Cl [a]	Me [a]	MeO [b]
1.5	18	–	0.08	0.118	–
3.1	20	0.021	0.10	0.123	0.033
6.3	29	0.032	0.15	0.127	0.044
12.5	49	–	0.27	0.133	0.063
25.0	84	0.118	0.36	0.146	0.11
50.0	–	0.171	–	0.170	0.23

[a] Reaction monitored at 420 nm. [b] Reaction monitored at 380 nm. [c] For a given concentration of HCl the value of k_{obs} did not vary in the range [Re] = $1.0–0.25\times10^{-3}$ mol dm^{-3}.

For all the systems studied there is no evidence of the reaction going to an equilibrium mixture rather than producing the hydrido-complex stoichiometrically. Thus the final absorbance observed in the stopped-flow experiments does not vary (for a given nitrile complex) with the concentration of acid over the range [HCl] = 1.5–50.0 mmol dm^{-3}. In addition, ^{31}P NMR spectroscopy experiments on the reaction between *cis*-[ReCl(NCC$_6$H$_4$R-4)(dppe)$_2$] (R = F or MeO) and HCl

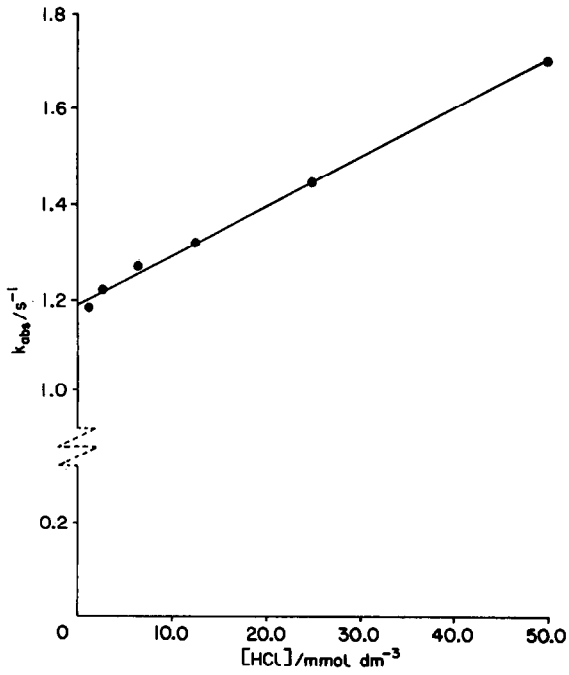
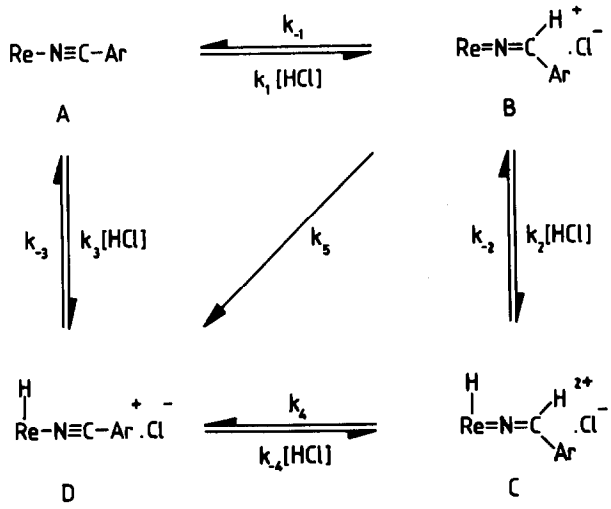


Fig. 2. Dependence of k_{obs} on the concentration of HCl for the reaction between *cis*-[ReCl(NCC$_6$H$_4$OMe-4)(dppe)$_2$] and HCl in THF at 25.0°C, λ = 380 nm, [Re] = 1.0×10^{-4} mol dm^{-3}.



Scheme 1. Pathways for the conversion of $[ReCl(NCHC_6H_4R\text{-}4)(dppe)_2]^+$ (B) to $[ReCl(H)(NCC_6H_4R\text{-}4)(dppe)_2]^+$ (D) (R = Cl, F, Me or MeO) in THF at 25.0°C. Chloride and phosphine ligands omitted for clarity.

in THF shows that only $[ReCl(H)(NCC_6H_4R\text{-}4)(dppe)_2]^+$ is produced even when stoichiometric concentrations of acid and nitrile complex are mixed; in fact, only the singlet resonances of the hydride complexes were detected [at δ − 130.12 (R = F) or − 130.52 (R = MeO) upfield from $P(OMe)_3$], rather than the complex ABCD-type patterns expected [9] for the methyleneamido-compounds.

The kinetic data for all the reactions are summarised in Table 1.

The behaviour described above is consistent with the mechanism shown in Scheme 1.

Within the dead-time of the stopped-flow apparatus, rapid protonation of $[ReCl(NCC_6H_4R\text{-}4)(dppe)_2]$ (A) occurs to produce the detected intermediate, $[ReCl(NCHC_6H_4R\text{-}4)(dppe)_2]^+$ (B). The identification of the intermediate as a methyleneamido-complex is consistent with the isolation of such species using HBF_4 [5]. We can put a limit to the rate constant for protonation of the nitrile ligand, $k_1 \geq 3 \times 10^5$ dm^3 mol^{-1} s^{-1}. As a consequence of this initial, rapid protonation of the nitrile ligand, the exponential absorbance-time curves that we observe correspond to the formation of the hydride, $[ReCl(H)(NCC_6H_4R\text{-}4)(dppe)_2]^+$, (D), from the methyleneamido-species $[ReCl(NCHC_6H_4R\text{-}4)(dppe)_2]^+$ (B). That is, the reaction we are monitoring is the formal transfer of a hydrogen atom from carbon to the metal. The rate law for this process [shown in eqn. (1)] indicates there are two pathways by which this rearrangement can occur: one acid-independent route and the other acid-dependent.

Conceptually, the simplest explanation for the acid-independent term in eqn. (1) would be a direct, intramolecular migration of hydrogen from carbon to rhenium. Such a pathway would be energetically feasible if the methyleneamido-ligand can adopt the bent configuration shown in Fig. 3, thus bringing the hydrogen sufficiently close to the metal to be transferred.

However, there is a less obvious explanation for the acid-independent term in eqn. (1), and that is a deprotonation/protonation pathway as shown in the Scheme. Thus the methyleneamido-complex (B) can lose a proton to regenerate $[ReCl(NCC_6H_4R\text{-}4)(dppe)_2]$ (A) which is relatively slowly protonated, but now at the rhenium atom, to give the product (D). As we will see later, both this deprotonation/protonation route and the intramolecular migration route would give rise to a term in the rate law which is independent of the concentration of acid. Based purely on this kinetic analysis we cannot discriminate between these two possible mechanisms, or indeed determine if both pathways are operating concurrently. However, other considerations (*vide infra*) lead us to favour the deprotonation/protonation mechanism as, at the least, the dominant pathway.

The acid-dependent term in eqn. (1) is consistent with a similar mechanism to that described above: a protonation/deprotonation mechanism. Formation of the hydride (D) from (B) involves protonation of the rhenium atom of the methyleneamido-complex (B) to generate the species (C). The ultimate fate of the doubly protonated intermediate (C) depends on the relative values of k_{-2} and k_4. If $k_{-2} \gg k_4$ then species (C) will return, unproductively, to (B), but if $k_4 \gg k_{-2}$ then species (D) will be produced, as indeed is observed.

It is interesting to note that for these protonation/deprotonation pathways shown in the Scheme the methyleneamido-species (B) has two very different roles depending on which mechanism is adopted. For the pathway associated with the acid-dependent term in eqn. (1), species (B) is an essential intermediate, whereas for the pathway associated with the acid-independent term species (B) is a "dead-end" species.

One further important general point to be made is that in solvents of low dielectric constant, such as THF, charged species form "tight" ion-pairs. Consequently the base, Cl^-, necessary to accomplish the deprotonation steps in these pathways is always present in the solvation sphere of the complex cation and is well situated to perform the deprotonation.

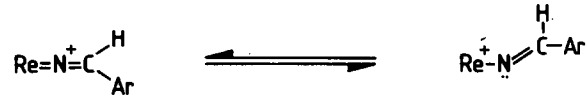


Fig. 3. Linear and bent forms of the methyleneamido-ligand.

The rate law for the mechanism in the Scheme is that shown in eqn. (2).

$$\frac{-d[(B)]}{dt} = \left\{ \frac{k_1k_{-3} + k_3k_{-1}}{k_1 + k_3} + k_5 + \frac{(k_2k_4 + k_{-2}k_{-4})[HCl]}{k_{-2} + k_4} \right\}[(B)] \quad (2)$$

This is an entirely general rate law which treats both species (A) and (C) as steady state intermediates on the pathways to form (D), and allows for any reversibility in any of the protonation/deprotonation steps, including those involving the hydride product (D). If the formation of the hydrido-complex (D) is irreversible, as is the case in our systems, then the simplified rate law shown in eqn. (3) is readily derived, again by assuming species (A) and (C) as steady state intermediates, and that $k_{-4}[HCl]$ and k_{-3} are negligibly small.

$$\frac{-d[(B)]}{dt} = \left\{ \frac{k_3k_{-1}}{k_1 + k_3} + k_5 + \frac{k_2k_4[HCl]}{k_{-2} + k_4} \right\}[(B)] \quad (3)$$

Notice that in eqns. (2) and (3), as we pointed out before, the acid-independent term contains contributions from both the deprotonation/protonation and the migration pathways.

A further mechanistic tool which is available to us in these systems is the influence of the *para*-substituent of the nitrile ligand on the rate of the reaction.

At first sight it is a little surprising that the rates associated with either the acid-dependent or acid-independent pathways for the *cis*-isomers show little correlation with the Hammett σ_p or σ_p^+ constant [10], as illustrated in Fig. 4.

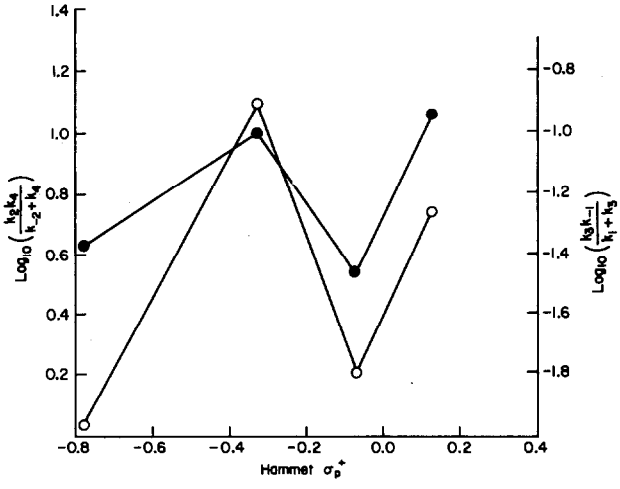


Fig. 4. Hammet plot for the acid-dependent (●) and acid-independent (○) terms of eqn. 3. Lines drawn are just to guide the eye and have no quantitative meaning.

TABLE 2. Summary of elementary rate constants for the reactions of *cis*-[ReCl(NCC$_6$H$_4$R-4)(dppe)$_2$] (R = Cl, F, Me or MeO) or *trans*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$] with HCl in THF at 25.0°C

Isomer	R	$\frac{k_3k_{-1}}{k_1+k_3}$ (s^{-1})	$\frac{k_2k_4}{k_{-2}+k_4}$ ($dm^3\ mol^{-1}\ s^{-1}$)	k_3 [a] ($dm^3\ mol^{-1}\ s^{-1}$)
cis	F	1.55×10^{-2}	3.5	$\geq 2.0\times10^2$
	Cl	5.5×10^{-2}	12.8	$\geq 7.2\times10^2$
	Me	11.7×10^{-2}	10.4	$\geq 1.3\times10^3$
	MeO	1.0×10^{-2}	4.3	$\geq 1.3\times10^2$
trans	F	1180×10^{-2}	3.4×10^3	$\geq 3.1\times10^5$

[a] Lower limit for the value of k_3 was established using the limiting values $k_1 \geq 3\times10^5$ $dm^3\ mol^{-1}\ s^{-1}$ [since the k_1 step is complete within the dead-time of the stopped-flow apparatus (2 ms) even at the lowest concentration of HCl used ([HCl] = 1.5 mmol dm^{-3})] and $K_1 = k_1/k_{-1} > 1.3\times10^4$ $dm^3\ mol^{-1}$ [since greater than 95% of (A) is converted to (B) within the dead-time of the stopped-flow apparatus even at the lowest concentration of HCl used].

However, one feature that is evident from these points is that the rates of both the acid-dependent and acid-independent pathways respond in a similar fashion to the electron-withdrawing or electron-releasing effects of the *para*-substituents. This is consistent with the proposal that both pathways operate by similar mechanisms (the protonation/deprotonation routes shown in Scheme 1), and tends to argue against a dominant contribution from the migration mechanism. Moreover, no evident correlation of those rates with the oxidation potential (as measured by cyclic voltammetry) was detected for these complexes.

It seems likely that the lack of a good correlation of the rates of the reactions with σ_p or σ_p^+ is due to the complexity of the terms given in the rate law of eqn. (3). Electron-releasing *para*-substituents would favour the protonation steps, k_1, k_2 and k_3, whilst electron-withdrawing *para*-substituents would favour the deprotonation steps k_{-1}, k_{-2} and k_4.

Comparison of the terms in eqns. (1) and (3), and neglecting the migration pathway (k_5), allows the determination of the quotients of elementary rate constants shown in Table 2.

3. Conclusions

A fundamental conclusion from this mechanistic study is that the nitrile ligand is the most rapidly protonated site in [ReCl(NCR)(dppe)$_2$] to give [ReCl(NCHR)(dppe)$_2$]$^+$. Subsequently this methyleneamido-complex changes to the thermodynamically-controlled product, [ReCl(H)(NCR)(dppe)$_2$]$^+$. In other words, for this system, protonation of the carbon atom

in the activated nitrile ligand has a lower activation barrier than protonation of the metal.

Similar effects have been observed in the protonation of other electron-rich complexes. In particular we have shown that for *trans*-[$ML_2(dppe)_2$] (M = Mo or W, L = N_2 [2] or C_2H_4 [6]), and for the closely related [$WH_4(PMePh_2)_4$ [7] direct protonation of the ligands N_2, C_2H_4 or hydride is faster than protonation of the metal centre. However, this is by no means a general rule and in systems such as the vinylidene complex *trans*-[ReCl(CCHPh)(dppe)$_2$] [11] and the allene compound *trans*-[ReCl(CH_2CCHPh)(dppe)$_2$] [12] protonation at the metal precedes protonation of the ligand. Clearly there is a fine balance between charge-controlled and orbital-controlled protonation reactions.

4. Experimental details

All manipulations in the synthetic and kinetic studies were routinely performed under dinitrogen using standard Schlenk or syringe techniques as appropriate. The solvent, THF, was freshly distilled immediately prior to use. The nitrile complexes were prepared [9,13] by treatment of a toluene solution of *trans*-[ReCl(N_2)(dppe)$_2$] with the appropriate nitrile in sunlight for *ca.* 4 h (for the *cis*-isomers) or for longer periods (for the *trans*-isomers). Standard solutions of anhydrous HCl were prepared in THF under dinitrogen by mixing an equimolar amount of MeOH and $SiMe_3Cl$. All solutions were transferred to the stopped-flow apparatus using gas-tight, all-glass syringes. Diluted solutions of anhydrous HCl were prepared *in situ* in the syringe by dilution with degassed THF. All kinetic studies were completed within 1 h of preparing the stock acid solution in order to minimise any complications associated with the acid-catalysed ring opening of THF.

The kinetics were studied at 25°C on a Canterbury SF-40 stopped-flow spectrophotometer with a spectrophotometer unit SU-40, from HI-TECH Scientific, monitoring the absorbance changes associated with the rhenium complex at the wavelengths shown in Table 1.

The absorbance-time traces were single exponentials in all cases and the rate constants, together with the initial and final absorbances, were computed by use of the Rapid Kinetics Software Suite (version 1.0) program on a City Desk 386-SX computer interfaced to the stopped-flow spectrophotometer. Curves were exponential for at least three half-lives. A typical absorbance-time curve, for *trans*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$], is shown in Fig. 1.

Acknowledgments

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