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Preliminary Communication

Carbon is not the initial site of attack in the protonation of an allene ligand to give an η^2-vinyl species: kinetic studies on *trans*-[ReCl(CH$_2$CCPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]

Richard A. Henderson [a], Armando J.L. Pombeiro [b], Raymond L. Richards [a] and Yu Wang [b]

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

[b] *Centro de Quimica Estrutural, Complexo I, Institut Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex (Portugal)*

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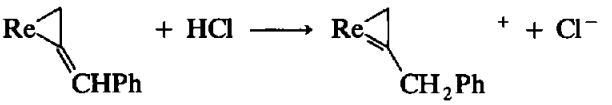
Abstract

The reaction between *trans*-[ReCl(CH$_2$CCHPh)(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and anhydrous HCl in tetrahydrofuran to give trans-[ReCl(C(CH$_2$Ph)CH$_2$)(dppe)$_2$]$^+$ is associated with a complicated rate law which is inconsistent with a simple, direct protonation at the phenyl-substituted carbon atom. A mechanism is proposed involving initial protonation of the metal, followed by intramolecular and acid-base catalysed rearrangements. This mechanism is consistent with earlier extended Hückel calculations which indicate that the HOMO of the complex is predominantly metal-based.

We are developing a detailed understanding of the mechanisms of protonation of unsaturated hydrocarbons bound to electron-rich metal sites [1–3].

This entails definition of the positions of proton attack and the factors which define the subsequent product-forming pathways which can only be accomplish by a detailed kinetic analysis of the reactions involving structurally well-defined reactants and products. In this paper we report the kinetics and mechanism of the novel, and apparently simple, protonation of the substituted allene ligand in *trans*-[ReCl(CH$_2$CCHPh)(dppe)$_2$] [4] to give an η^2-vinyl species as shown in eqn. (1).



(1)

When this reaction is carried out in THF (THF = tetrahydrofuran) at 25.0°C, using stopped-flow spectrophotometry, exponential absorbance-time traces are observed, with an initial absorbance corresponding to that of the allene complex and a final absorbance which is that of the η^2-vinyl species. This behaviour is consistent with a simple first order dependence on the concentration of complex. However, the influence of acid on the reaction rate is more complicated. With a large excess of HCl ([HCl] > 10[Re]) the dependence

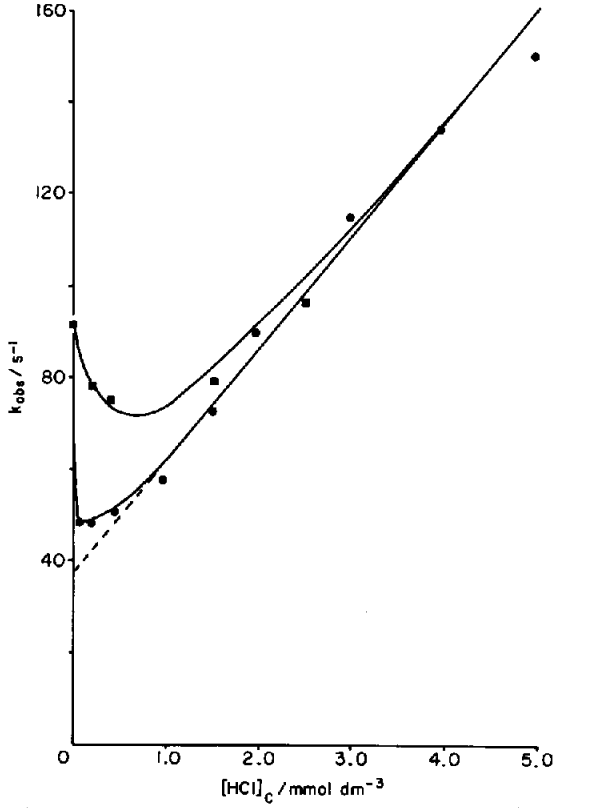


Fig. 1. Dependence of k_{obs} on the concentration of HCl for the reaction of *trans*-[ReCl(CH$_2$CCHPh)(dppe)$_2$] in THF at 25.0°C, [Re] = 0.05 mmol dm^{-3} (●) and [Re] = 0.5 mmol dm^{-3} (■). Curves drawn are those defined by eqn. (4). Studies performed at λ = 435 nm.

*Correspondence to: Dr. R.A. Henderson.

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on the concentration of acid is as shown in Fig. 1, and approximates to eqn. (2).

$$-\frac{d[Re]}{dt} = \{(36 \pm 2) + (2.4 \pm 0.1) \times 10^4[HCl]\}[Re] \quad (2)$$

At lower concentrations of HCl ([HCl] < 10[Re]) two surprising features are evident: (i) the absorbance-time traces remain exponential, provided [HCl] > [Re], and (ii) the data points do not lie on the line defined by eqn. (2), but above it. This second feature is more pronounced at higher concentrations of complex as shown in Fig. 1.

The data at relatively low acid concentrations can be analysed in the following manner. First, correct the concentration of HCl, allowing that the complex has rapidly (within the dead-time of the stopped-flow apparatus, 2 ms) bound one mole-equivalent of acid, *i.e.* $[HCl]_c = [HCl] - [Re]$. Secondly, correct the observed first order rate constant (k_{obs}) for the simple behaviour observed at high concentrations of acid as described by eqn. (2), *i.e.* $k^1_{obs} = k_{obs} - (36 + 2.4 \times 10^4[HCl]_c)$. After these manipulations the data define the curve shown in Fig. 2.

Analysis of these data gives the rate law shown in eqn. (3), which describes the kinetics of reaction (1) under all conditions.

$$k^1_{obs} = (58 \pm 2) / \left\{1 + (1.37 \pm 0.1)\frac{[HCl]_c}{[Re]}\right\} \quad (3)$$

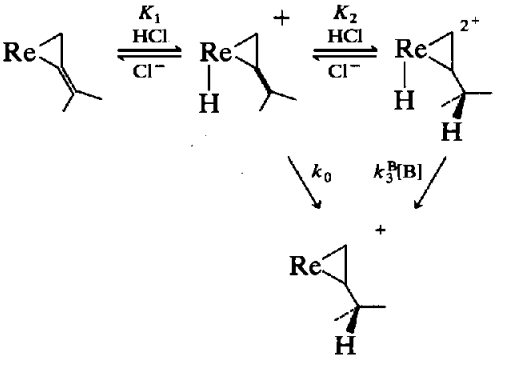
Clearly the term involving [Re] is only an apparent dependence on this species, otherwise non-exponential absorbance-time traces would be observed. Our analysis of the data presupposes that the allene complex reacts stoichiometrically with one mole-equivalent of HCl, within the dead-time of the stopped-flow apparatus. As a consequence an equimolar amount of Cl^- is present. Note that this is the only free Cl^- in the system, since HCl is a weak acid in THF [5]. Making the substitution $[Cl^-] = [Re]$ into eqn. (3), and rearranging, gives eqn. (4):

$$k_{obs} = \frac{(94 \pm 4) + \frac{[HCl]_c}{[Cl^-]}\{50.4 \pm 2) + (2.4 \pm 0.1) \times 10^4[Cl^-] + (3.4 \pm 0.2) \times 10^4[HCl]_c\}}{\left\{1 + (1.37 \pm 0.1)\frac{[HCl]_c}{[Cl^-]}\right\}} \quad (4)$$

The complexity of this rate law is inconsistent with any trivial mechanism involving direct protonation at the phenyl-substituted carbon atom, but rather dictates a mechanism in which the initial protonation occurs at the "wrong" site, and the terms in eqn. (4) reflect the rearrangement pathways to produce the η^2-vinyl complex subsequently.

We suggest that the initial protonation occurs at the metal to give a hydrido-species ($K_1 > 80$, $k_1 > 1 \times 10^6$ dm^3 mol^{-1} s^{-1}). This proposal is consistent with earlier extended Hückel calculations on a model for *trans*-[ReCl(CH$_2$CCHPh)(dppe)$_2$], which indicate that in the HOMO the highest electron density is the d_{xy}/d_{yz} orbitals on rhenium (54%) [4]. The remaining electron density resides on the phenyl-substituted carbon (36%) and the unsubstituted carbon atom (10%).

In binding a proton to the complex, albeit at the "wrong" site, the stoichiometric requirement of reaction (1) has been met. Consequently the observed



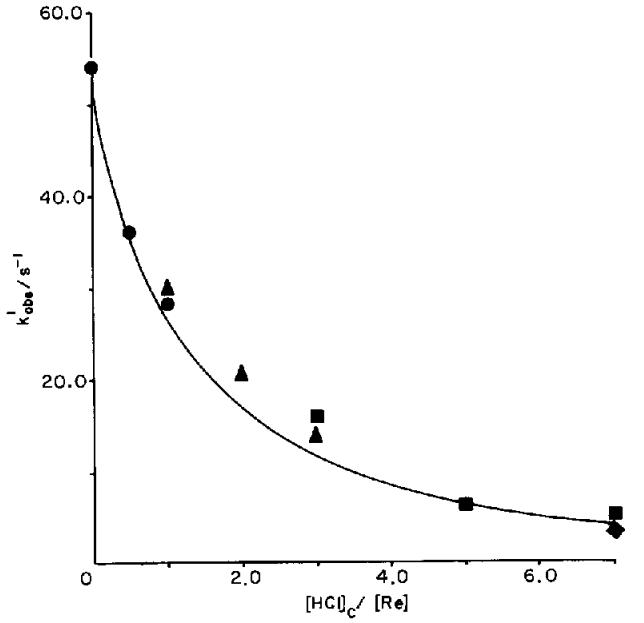


Fig. 2. Dependence of k^1_{obs} on $[HCl]_c/[Re]$ for the reaction of *trans*-[ReCl(CH$_2$CCHPh)(dppe)$_2$] with HCl in THF at 25.0°C (λ = 435 nm). The data points correspond to: [Re] = 0.5 mmol dm^{-3} (●), [Re] = 0.25 mmol dm^{-3} (▲), [Re] = 0.125 mmol dm^{-3} (■), [Re] = 0.063 mmol dm^{-3} (◆). The curve drawn is that defined by eqn. (3).

absorbance-time curves, which are associated with the subsequent rearrangements, will always be exponential. That is, any further dependence on the concentration of HCl is entirely catalytic.

The hydrido-species goes on to produce the η^2-vinyl complex by two pathways. The first route involves the intramolecular migration of the hydride from the metal to the hydrocarbon fragment $\{k_0 = (94 \pm 4)s^{-1}\}$, and reflects the term in eqn. (4) which is independent of acid. Consideration of the X-ray crystal structure of *trans*-[ReCl(CH$_2$CCHPh)(dppe)$_2$] [6] indicates that a putative Re–H bond ($r_{ReH} \sim 1.5$Å) could be as close at 1.5–1.8 Å to the phenyl-substituted carbon atom. Certainly sufficiently close to permit a reasonably facile migration.

In addition to this intramolecular route, an acid-base catalysed pathway is observed, reflecting all the acid-dependent terms in eqn. (4). This pathway involves the rapid protonation of the remote carbon ($K_2 = 1.37 \pm 0.1$), followed by rate-limiting general base catalysed removal of the hydrido-group. All bases in the system are capable of removing this proton: THF$\{k_3^{THF} = (2.7 \pm 0.3)$ dm^3 mol^{-1} s$^{-1}\}$, Cl$^-$ $\{k_3^{Cl} = 1.7 \pm 0.2 \times 10^4$ dm^3 mol^{-1} s$^{-1}\}$ and even the weak acid HCl $\{k_3^{HCl} = (2.4 \pm 0.2) \times 10^4$ dm^3 mol^{-1} s$^{-1}\}$.

Since our kinetic analysis dictates that the hydrido-species is formed stoichiometrically, and assuming that both K_1 and K_2 are rapidly established equilibria, the rate law for the mechanism shown in the Scheme is as shown in eqn. (5), fully consistent with that determined experimentally.

$$\frac{-d[ReH]}{dt} = \frac{\left(k_0 + K_2\frac{[HCl]_e}{[Cl^-]}\{k_3^{THF}[THF] + k_3^{Cl}[Cl^-] + k_3^{HCl}[HCl]_e\}\right)[ReH]}{\left(1 + K_2\frac{[HCl]_e}{[Cl^-]}\right)} \quad (5)$$

This kinetic study demonstrates that two sites on *trans*-[ReCl(CH$_2$CCHPh)(dppe)$_2$] (presumably those of highest electron density as defined by extended Hückel calculations) [4] are protonated on the pathways that result ultimately in the formation of *trans*-[ReCl{C(CH$_2$Ph)CH$_2$}(dppe)$_2$]$^+$. In addition the most readily protonated site (the metal) is that associated with the greatest electron density. The consequence of an initial, facile protonation at the "wrong" site is that the system has to undergo a variety of intramolecular and acid-base catalysed rearrangements to form the thermodynamically-favoured product. We have observed this feature in other protonation reactions of complexes containing unsaturated hydrocarbons [1–3], but it is only through detailed kinetic studies that such features become evident.

Acknowledgements

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