Mechanism of Alkylidyne Complex Formation by Protonation of the Vinylidene Complex *trans*-[ReCl(C=CHPh)($Ph_2PCH_2CH_2PPh_2$)$_2$]

M. Fernanda N. N. Carvalho,[a] Richard A. Henderson,[b] Armando J. L. Pombeiro,[a] and Raymond L. Richards[b]

[a] *Centro de Quimica Estrutural, Complexo 1, Instituto Superior Tecnico, Av. Rovisco Pais, 1096 Lisbon Codex, Portugal*

[b] *AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, U.K.*

Stopped-flow kinetic studies have demonstrated that in tetrahydrofuran the protonation of *trans*-[ReCl(CCHPh)($Ph_2PCH_2CH_2PPh_2$)$_2$] to form *trans*-[ReCl(CCH_2Ph)($Ph_2PCH_2CH_2PPh_2$)$_2$]$^+$ can occur by three pathways.

The protonation of vinylidene ligands bound to electron-rich metal centres invariably gives the corresponding alkylidyne species, in which apparently regiospecific attack of the acid has occurred at the remote carbon atom.[1—5] We describe herein the first kinetic analysis of such a transformation in the stoicheiometrically simple reaction shown in equation (1), (dppe = $Ph_2PCH_2CH_2PPh_2$); a study which demonstrates that the vinylidene-to-alkylidyne conversion can occur by three pathways on the kinetically robust {ReCl(dppe)$_2$} core.

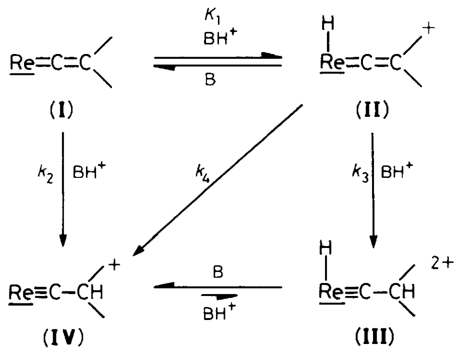
$$\textit{trans}\text{-[ReCl(CCHPh)(dppe)}_2] + \text{NHEt}_3^+ \rightarrow \textit{trans}\text{-[ReCl(CCH}_2\text{Ph)(dppe)}_2]^+ + \text{NEt}_3 \quad (1)$$

In the presence of an excess of [$NHEt_3$]BPh_4, reaction (1) is complete within a few seconds, and the kinetics exhibit a first-order dependence on the concentration of the complex and a dependence on the acid concentration as described by equation (2) and shown in Figure 1 (insert), where $k_4 = (7.3 \pm 0.3) \times 10^{-2}\ \text{s}^{-1}$ and $k_3 = 9.4 \pm 0.5\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. The most interesting (and surprising) feature of equation (2) is the

$$k_{\text{obs}} = k_4 + k_3\,[\text{NHEt}_3^+] \quad (2)$$

term independent of acid. This rate law is consistent with the mechanism shown in Scheme 1. Direct protonation of the vinylidene ligand in (**I**) (k_2) is slow and thus rapid protonation can occur most probably at the metal to yield the species (**II**), and it is the formation of the alkylidyne complex (**IV**) from this species that is being monitored in these experiments. The conversion of (**II**) to (**IV**) can occur *via* either the intramolecular pathway (k_4) or the hydride-alkylidyne species (**III**) (k_3). The proposed initial protonation to form (**II**) is consistent with the isotope effects observed with $NDEt_3^+$, k_4^H/k_4^D = 1.16 and k_3^H/k_3^D = 1.35, and the careful analysis of the stopped-flow absorbance–time traces which reveals a small, but distinct, difference between the observed initial absor-

$$-\mathrm{d}[\mathrm{Re}]/\mathrm{d}t = [\mathrm{Re}]\,\frac{\{k_4K_1[\mathrm{NHEt_3}^+]/[\mathrm{NEt_3}] + (k_3K_1[\mathrm{NHEt_3}^+]/[\mathrm{NEt_3}] + k_2)[\mathrm{NHEt_3}^+]\}}{(1 + K_1[\mathrm{NHEt_3}^+]/[\mathrm{NEt_3}])} \qquad (3)$$



Scheme 1. Re represents $\mathrm{ReCl(dppe)_2}$ and B represents $\mathrm{NEt_3}$.

bance and that expected for (**I**). Although this kinetic analysis cannot define the position of the initial protonation, we feel that the most likely formulation of (**II**) is a hydrido-vinylidene species. However in the absence of direct evidence for a Re–H bond we cannot entirely rule out the possibility that protonation has occurred at the chloro-group, particularly since extended Hückel calculations on *trans*-$\mathrm{[ReCl(CNR)(dppe)_2]}$ (R = Me or Bu^t) indicate that the chloro-group in this compound is reasonably basic.[6] Attempts to measure the ^{1}H NMR spectrum of (**II**) at low temperatures were thwarted by poor solubility.

Confirmation of the mechanism shown in Scheme 1 comes from further kinetic studies of reaction (1). In the presence of an excess of both $\mathrm{NHEt_3}^+$ and $\mathrm{NEt_3}$, reaction (1) still goes to completion but the base perturbs the reaction kinetics as shown in Figure 1. This behaviour is entirely consistent with Scheme 1; in the presence of an excess of $\mathrm{NEt_3}$, (**II**) and (**I**) are able to interconvert rapidly. The rate law for the complete reaction manifold of Scheme 1 is given by equation (3), which assumes rate-limiting protonation of the carbon atoms and rapid protonation/deprotonation of the metal {[Re] = [(**I**)] + [(**II**)]}.

When $K_1[\mathrm{NHEt_3}^+]/[\mathrm{NEt_3}] >> 1$, equation (3) reduces to the limiting-form shown in equation (4), where k^1_{obs} is the pseudo first-order rate constant measured in the presence of an excess of $\mathrm{NEt_3}$. Using the value of k_4 already determined above, the graph shown in Figure 1 was obtained, allowing the determination of $k_2/K_1 = 17.6 \pm 0.5$ dm^3 mol^{-1} s^{-1} and $k_3 = 10.5 \pm 0.5$ dm^3 mol^{-1} s^{-1} in excellent agreement with the value of k_3 determined above. Furthermore we can estimate that $K_1 > 4$ from these kinetic studies, and hence that $k_2 > 70.4$ dm^3 mol^{-1} s^{-1}.

$$k^1_{\mathrm{obs}} = k_4 + (k_3 + k_2[\mathrm{NEt_3}]/K_1[\mathrm{NHEt_3}^+])[\mathrm{NHEt_3}^+] \quad (4)$$

This study demonstrates that reaction (1) occurs by the three pathways shown in Scheme 1. It is important to emphasise that the formation of (**II**) is forced on the system because of the faster rate of protonation at the electron-rich metal-centre than at the vinylidene ligand in (**I**); and this protonation at the metal deactivates the vinylidene ligand towards protic attack (as is clear from the values of k_2 and k_3). Nevertheless formation of the alkylidyne product (**IV**) from (**II**) can occur *via* pathways k_3 and k_4. The pathway k_4 appears to be intramolecular but the intimate details of this reaction have yet to be defined.

Clearly, in this system the strong thermodynamic driving-force towards the formation of the alkylidyne product is usurped initially by the kinetics which defines a site of initial protonation which is not the vinylidene ligand.

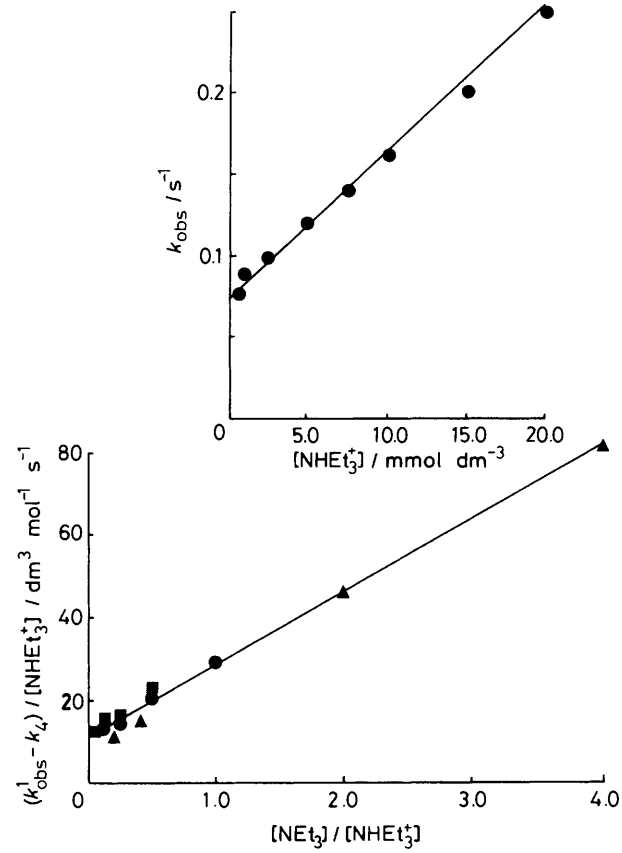


Figure 1. Kinetic data for the reaction between *trans*-$\mathrm{[ReCl(CCHPh)(dppe)_2]}$ and $\mathrm{[NHEt_3]BPh_4}$ in tetrahydrofuran (ionic strength = 50 mmol dm^{-3} $\mathrm{[NBu_4]BF_4}$; λ = 420 nm, temperature = 25.0 °C). In all experiments [Re] = 0.5—0.7 × 10^{-4} mol dm^{-3}. Insert: dependence of k_{obs} on the concentration of $\mathrm{NHEt_3}^+$ with no added $\mathrm{NEt_3}$, line drawn is that defined by equation (2). Main figure: dependence of k^1_{obs} on the concentrations of $\mathrm{NHEt_3}^+$ and $\mathrm{NEt_3}$ when both are present in an excess; $[\mathrm{NEt_3}]$ = 0.5—10.0 mmol dm^{-3}, $[\mathrm{NHEt_3}^+]$ = 2.5 mmol dm^{-3} (▲), $[\mathrm{NHEt_3}^+]$ = 10.0 mmol dm^{-3} (■) and $[\mathrm{NHEt_3}^+]$ = 20.0 mmol dm^{-3} (●). Line drawn is that defined by equation (4).

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