Mechanism of the Formation of Carbyne Complexes of Rhenium upon Protonation of Vinylidene Precursors

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The reactions of *trans*-[ReX(=C=CHR)(dppe)$_2$] with [NHEt$_3$][BPh$_4$] to form the carbyne complexes *trans*-[ReX(≡CCH$_2$R)(dppe)$_2$]$^+$ (X = Cl; R = Ph, C$_6$H$_4$Me-4, Bu^t, CO$_2$Me, CO$_2$Et; X = F; R = CO$_2$Et; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) have been studied by stopped-flow spectrophotometry and shown to proceed via three pathways whose relative contribution depends on the nature of R and X. The most direct pathway involves regiospecific protonation at the β-carbon of the vinylidene. However, under some conditions initial protonation at the metal to form [Re(H)X(=C=CHR)(dppe)$_2$]$^+$ is more rapid, and this hydride subsquently rearranges to form the carbyne by an intramolecular pathway or by protonation of [Re(H)X(=C=CHR)(dppe)$_2$]$^+$ at the β-carbon of the vinylidene ligand to give [Re(H)X(≡CCH$_2$R)(dppe)$_2$]$^{2+}$, which then undergoes deprotonation to form [ReX(≡CCH$_2$R)(dppe)$_2$]$^+$. For the R = C$_6$H$_5$ or C$_6$H$_4$Me-4 complexes, kinetic analysis indicates that all three pathways occur, whereas for the bulky R = Bu^t analogue, the pathways that involve direct addition to the vinylidene ligand do not operate. For [ReX(=C=CHCO$_2$R)(dppe)$_2$] (R = Et, Me) the strong electron-withdrawing effect of the ester group results in slow proton transfer from [NHEt$_3$]$^+$ to the vinylidene ligand in [Re(H)Cl(=C=CHCO$_2$R)(dppe)$_2$]$^+$. The formation of an adduct is evident from the kinetic studies with these complexes and is proposed to be the species in which [NHEt$_3$]$^+$ is hydrogen-bonded to the β-carbon of the vinylidene ligand. Rate-limiting proton transfer within this adduct completes the reaction and is associated with a large primary isotope effect. The way in which the *trans*-halide influences this reactivity has also been investigated and fluoride shown to highly promote the rate of protonation.

Introduction

Protonation of small unsaturated molecules, activated by coordination to a transition metal center, is of current interest in coordination chemistry, particularly applied to catalysis[1] or to mimic the elementary reactions of enzymes such as nitrogenases.[2] The investigation of the mechanisms of such reactions with, for example, nitriles,[3] allenes,[4] isocyanides,[5] ethylene,[6a] or alkynyl,[6b] using rapid techniques such as stopped-flow spectrophotometry, can define the sites of protonation and the factors that determine the rate of formation or cleavage of metal−hydrogen or carbon−hydrogen bonds.

A particulary simple reaction (at least stoichiometrically) is the protonation of vinylidene ligands to give the corresponding carbyne (alkylidyne) species,[7] in which an apparently regiospecific proton addition to the remote β-carbon atom of the vinylidene has occurred, at a variety of transition metal centers. We have prepared[8] a series of rhenium carbyne complexes of the type *trans*-[ReX(≡C-CH$_2$R)(dppe)$_2$]$^+$ (X = Cl, F; R = alkyl, aryl, ester), upon protonation of the corresponding vinylidene complexes *trans*-[ReX(=C=CHR)(dppe)$_2$] (eq

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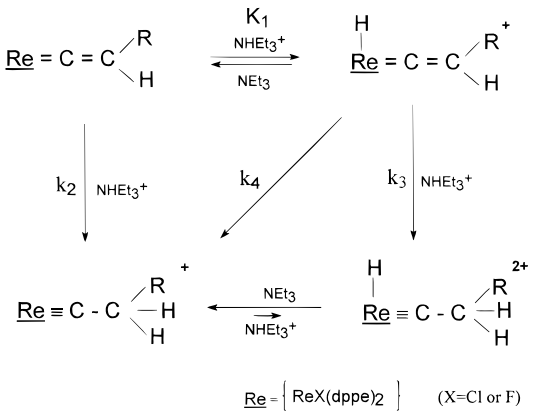
Scheme 1



1), and in a preliminary kinetic study[9] of the reaction

$$\textit{trans}\text{-}[ReX(=C=CHR)(dppe)_2] + H^+ \rightarrow \textit{trans}\text{-}[ReX(\equiv CCH_2R)(dppe)_2]^+ \quad (1)$$

of *trans*-[ReCl(=C=CHPh)(dppe)$_2$] with [NHEt$_3$][BPh$_4$], the complexity of the rate law is incompatible with regiospecific protonation but rather demonstrates that the reaction occurs by three pathways (Scheme 1; X = Cl, R = Ph): (i) direct protonation at the remote carbon; (ii) protonation of the metal followed by intramolecular migration, or (iii) protonation of the metal followed by an acid-catalyzed rearrangement pathway.

In this paper, we report further kinetic studies on complexes of this type which show that with a variety of R substituents (R = Bu^t, C$_6$H$_4$Me-4, CO$_2$Me, CO$_2$Et) on the vinylidene ligand these three pathways are observed and that the nature of R influences which pathway dominates. In addition, the effect of changing the *trans*-halide from X = Cl to X = F was also investigated. Complexes with carbene or carbyne ligands stabilized by a *trans*-fluoro ligand are rare[10] and these systems provide an opportunity to compare the effect of F$^-$ and Cl$^-$ ligands

Results and Discussion

The reaction of *trans*-[ReCl(=C=CHR)(dppe)$_2$] with anhydrous HCl in THF (THF = tetrahydrofuran) to form [ReCl(≡CCH$_2$R)(dppe)$_2$]$^+$ is complete within the dead time of the stopped-flow apparatus (2 ms). However, with the weaker acid [NHEt$_3$][BPh$_4$], the reaction is sufficiently slow to be studied by this technique.

For all vinylidene complexes studied in this work, the absorbance−time traces show a similar behavior.

When reaction 1 is studied on a stopped-flow apparatus, it occurs in two distinct stages: an initial absorbance change complete within the dead time of the apparatus followed by an exponential absorbance−time curve whose final absorbance (A_∞) is that of the carbyne product. This behavior is consistent with an initial rapid reaction, complete within the dead time of the apparatus, to form an intermediate that subsquently converts to the carbyne product.

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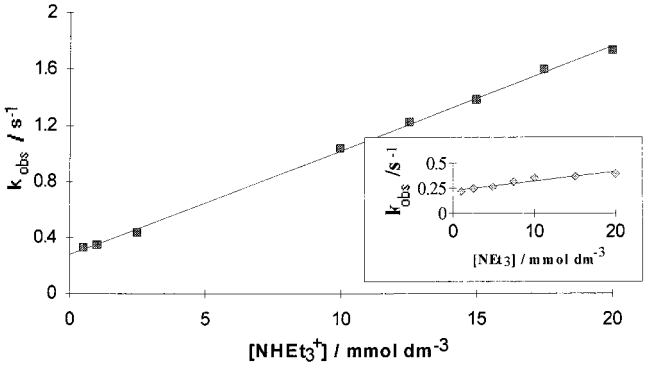

Figure 1. Kinetic data for the reaction of *trans*-[ReCl(=C=CHC$_6$H$_4$Me-4)(dppe)$_2$] (1.0×10^{-4} mol dm^{-3}) with [NHEt$_3$][BPh$_4$] in THF, at 25 ± 0.1 °C, monitored at λ = 420 nm. The line drawn is that defined by eq 2 and the values given in the text. Inset: k_{obs} vs [NEt$_3$] for a constant concentration of [NHEt$_3$][BPh$_4$] (1.0×10^{-3} mol dm^{-3}).

In a previous study[9] with *trans*-[ReCl(=C=CHPh)(dppe)$_2$], we have proposed that initial protonation occurs at rhenium to form [Re(H)Cl(=C=CHPh)(dppe)$_2$]$^+$, although spectroscopic confirmation for this proposal has not yet been obtained. The kinetics of the conversion of this intermediate to give [ReCl(≡CCH$_2$Ph)(dppe)$_2$]$^+$ can occur by an acid-independent pathway. This can be rationalized only if protonation of the complex has already occurred, albeit at the "wrong" site.

The exponential nature of the absorbance−time curves for all the complexes *trans*-[ReCl(=C=CHR)(dppe)$_2$] indicates that the kinetics exhibit a first-order dependence on the concentration of the complex. However, the dependence on the acid concentration varies with the nature of the substituent R and X as will be outlined in the following discussion.

***trans*-[ReCl(=C=CHC$_6$H$_4$Me-4)(dppe)$_2$].** The reaction of *trans*-[ReCl(=C=CHC$_6$H$_4$Me-4)(dppe)$_2$] with [NHEt$_3$][BPh$_4$] shows a dependence on the concentration of acid as described by eq 2 and shown in Figure 1 (here

$$k_{obs} = k_4 + k_3[NHEt_3] \quad (2)$$

and throughout this paper, k_{obs} is the observed pseudo-first-order rate constant measured under conditions where [NHEt$_3^+$]/[Re] ≥ 10). The rate constants k_3 and k_4 correspond to the elementary reactions shown in Scheme 1.

Analysis of the data in Figure 1 gives k_4 = 0.28 ± 0.01 s^{-1} and k_3 = 74 ± 1 dm^3 mol^{-1} s^{-1}.

The addition of the conjugate base, NEt$_3$, while keeping the concentration of [NHEt$_3^+$] constant, perturbs the kinetics (Figure 1 inset).

Consideration of the mechanism shown in Scheme 1 leads to the rate law of eq 3 (see Appendix 1 for derivation of this rate law). This mechanism describes three pathways for the formation of the carbyne, and the derivation of the rate law assumes that the rate-limiting steps for each of these pathways are k_2, k_3, and k_4 and that initial protonation of the metal by [NHEt$_3$]$^+$ (K_1) is a rapidly established equilibrium. A linear dependence on the concentration of NEt$_3$ is observed (Figure 1) and hence we can conclude that, in the denominator, K_1[Et$_3$NH$^+$]/[NEt$_3$] >> 1. Under these

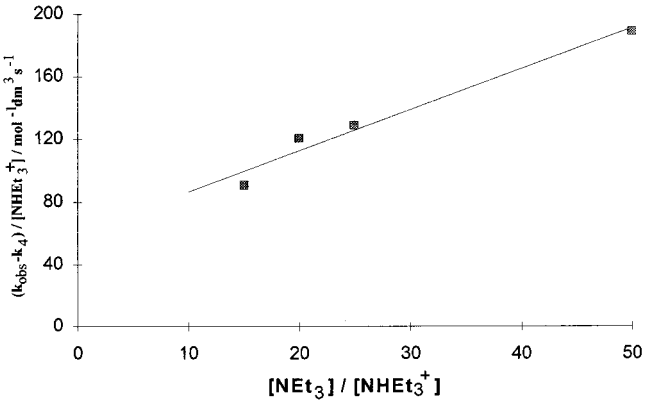

Figure 2. $(k_{obs} - k_4)/[NHEt_3^+]$ vs $[NEt_3]/[NHEt_3^+]$, for $[NHEt_3^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, for the reaction of *trans*-[ReCl(=C=CHC$_6$H$_4$Me-4)(dppe)$_2$] (1.0×10^{-4} mol dm^{-3}) with $[NHEt_3][BPh_4]$ in THF, at 25 ± 0.1 °C, monitored at $\lambda = 420$ nm. The points corresponding to $[NEt_3]/[NHEt_3^+] \leq 10$, for which k_{obs} approaches k_4, have not been considered in this analysis because of the great errors associated to them. The line drawn is that defined by eq 4 and the values given in the text.

conditions eq 3 simplifies to eq 4, from which eq 5 is

$$-\frac{d[Re]}{dt} = (k_4 K_1[NHEt_3^+]/[NEt_3] + (k_3 K_1[NHEt_3^+]/[NEt_3] + k_2)[NHEt_3^+])/(1 + K_1[NHEt_3^+]/[NEt_3])[Re] \quad (3)$$

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

$$\frac{k_{obs} - k_4}{[NHEt_3^+]} = k_3 + \frac{k_2}{K_1}\frac{[NEt_3]}{[NHEt_3^+]} \quad (5)$$

obtained upon simple rearrangement. Since $K_1[Et_3NH^+]/[NEt_3] >> 1$, the equilibrium concentration of [Re(H)Cl(=C=CHC$_6$H$_4$Me-4)(dppe)$_2$]$^+$ is much higher than that of [ReCl(=C=CHC$_6$H$_4$Me-4)(dppe)$_2$]. Addition of NEt_3 perturbs the K_1 protolytic equilibrium back towards the vinylidene complex. With appreciable amounts of [ReCl(=C=CHC$_6$H$_4$Me-4)(dppe)$_2$] present, the slow but direct protonation of the vinylidene ligand (k_2 route) makes a significant contribution to the reaction rate.

Analysis of the data requires a knowledge of the value of $k_4 = 0.28$ s^{-1} established from the studies in the absence of NEt_3 (eq 2). The graph of $(k_{obs} - k_4)/[NHEt_3^+]$ vs $[NEt_3]/[NHEt_3^+]$ gives $k_2/K_1 = 2.6 \pm 0.3$ dm^3 mol^{-1} s^{-1} and $k_3 = 60 \pm 10$ dm^3 mol^{-1} s^{-1}, which is in good agreement with the value obtained for the studies in the absence of NEt_3 (Figure 2).

The important chemical feature about this kinetic treatment is that the data demonstrate that at least three pathways will convert vinylidene species to carbyne complexes and that the values of the elementary rate and equilibrium constants are similar to those obtained for the analogous *trans*-[ReCl(=C=CHPh)(dppe)$_2$] as would be expected. This kinetic approach is employed with other vinylidene complexes described in this paper. Which of the three pathways dominates with these vinylidene complexes depends on both the electronic and steric effects of R, as well as on the electronic effect of the halide ligand (chloride or fluoride) *trans* to the metal-binding vinylidene (Table 1).

The k_2 route corresponds to the direct β-protonation of the vinylidene ligand, whereas the k_3 and k_4 ones involve a prior protonation of the metal followed by an acid-catalyzed rearrangement (k_3) or by an intramolecular 1,3-hydrogen migration (k_4) from the metal to the vinylidene β-carbon. The last route (k_4) can be considered to occur either by hopping of the hydrogen atom along from the Re to the β-carbon atom or through a more complex acid-catalyzed pathway such as that postulated in Scheme 2. This involves an initial slow insertion step (k_4) of the vinylidene ligand into the Re−H bond, a process that parallels the known[11] hydride migration to a carbene ligand in other systems. The derived vinyl ligand, in *Re*-C(H)=CHR$^+$, following a type of process reported[12] for other vinyl complexes, would then undergo proton addition at the β-carbon to form the carbene species *Re*=C(H)CH$_2$R^{2+} which, upon proton loss, would give the final carbyne product.

***trans*-[ReCl(=C=CHBu^t)(dppe)$_2$].** The reaction of *trans*-[ReCl(=C=CHBu^t)(dppe)$_2$] with $[NHEt_3][BPh_4]$ in THF occurs at a rate that shows no systematic variation with the concentration of acid or base as shown in Figure 3. This behavior is consistent with the reaction proceeding exclusively by the hydride migration pathway (k_4). The *tert*-butyl group is a good electron donor and hence would be expected to render the β-carbon atom sufficiently basic to be protonated; however, its bulky nature does not allow the close approach of the relatively large $[NHEt_3]^+$ to the β-carbon site. Consequently, a pathway involving less unfavorable steric interactions dominates, in which initial protonation of the metal (complete within the dead time of the apparatus) is followed by rate-limiting intramolecular migration ($k_4 = 0.16 \pm 0.04$ s^{-1}). We can establish a limit for K_1 for this reaction, by considering that even when $[NHEt_3^+] = 5.0 \times 10^{-3}$ mol dm^{-3} and $[NEt_3] = 10 \times 10^{-3}$ mol dm^{-3} (highest concentration of base) at least 90% of the rhenium is present as [Re(H)Cl(=C=CHBu^t)(dppe)$_2$]$^+$ and hence $K_1 \geq 18$.

We can also estimate that $k_3 \leq 1.6$ dm^3 mol^{-1} s^{-1} for the reaction of *trans*[ReCl(=C=CHBu^t)(dppe)$_2$]. This estimate is reached by considering that perhaps a small (less than 10%) contribution from the acid-dependent step may have gone undetected. This would give $k_3[NHEt_3^+] \leq 0.1k_4$, i.e., $k_3 < 1.6$ dm^3 mol^{-1} s^{-1}.

***trans*-[ReCl(=C=CHCO$_2$Me)(dppe)$_2$].** If the substituent on the vinylidene ligand is an electron-withdrawing ester group (CO$_2$Me or CO$_2$Et), then the kinetics of formation of the carbyne complex are quite different. Although a first-order dependence on the concentration of the complex is still observed, the dependence on the concentration of $[NHEt_3]^+$ is more complicated.

The reaction of *trans*-[ReCl(=C=CHCO$_2$Me)(dppe)$_2$] with $[NHEt_3][BPh_4]$ in THF exhibits a nonlinear dependence on the acid concentration as shown in Figure

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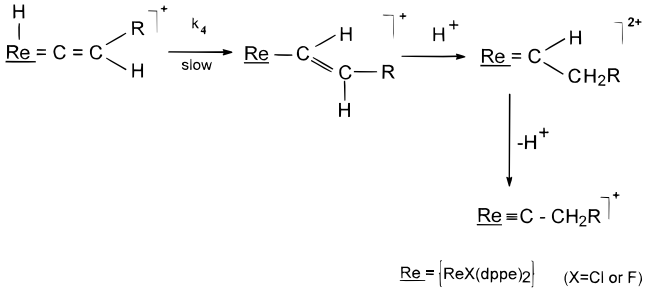
Table 1. Rate Constants for Protonation Reactions of Vinylidene Complexes

compound	mechanism type[a]	k_2/K_1 (or K_1)[b] ($dm^3\ mol^{-1}\ s^{-1}$)	k_4 (s^{-1})	k_3 ($dm^3\ mol^{-1}\ s^{-1}$)	K_5 ($dm^3\ mol^{-1}$)	k_6 (s^{-1})
trans-[ReCl(=C=CHPh)(dppe)$_2$]	1	17.6 ± 0.5	0.073 ± 0.002	9.4 ± 0.5		
trans-[ReCl(=C=CHC$_6$H$_4$Me-4)(dppe)$_2$]	1	2.6 ± 0.3	0.28 ± 0.01	74 ± 1		
trans-[ReCl(=C=CHBu^t)(dppe)$_2$]	1	($K_1 \geq 18$)[c]	0.16 ± 0.04	≤1.6[d]		
trans-[ReCl(=C=CHCO$_2$Me)(dppe)$_2$]	2	≤3.8[e] ($K_1 \geq 36$)[c]	0.084 ± 0.005		213 ± 1	0.54 ± 0.05
trans-[ReCl(=C=CHCO$_2$Et)(dppe)$_2$]	2	7.3 ± 0.5	0.023 ± 0.004		24 ± 1	0.7 ±0.3
trans-[ReF(=C=CHCO$_2$Et)(dppe)$_2$]	1	0	10 ± 6	$9.2 \times 10^3 \pm 0.8 \times 10^3$		

[a] Types 1 and 2 correspond to Schemes 1 and 2, respectively. [b] K_1 values (dimentionless) given in parentheses. [c] Assuming K_1 equilibrium lying at least 90% to the right-hand side. [d] Assuming that the k_3 pathway contributes less than 10% for k_{obs}. [e] Assuming the k_2 pathway contributes less than 10% for k_{obs}.

Scheme 2



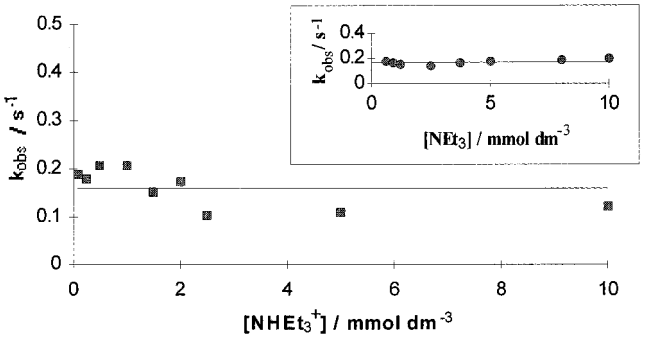


Figure 3. Dependence of k_{obs} vs acid concentration for the reaction of *trans*-[ReCl(=C=CHBu^t)(dppe)$_2$] (1.0×10^{-4} mol dm^{-3}) with [NHEt$_3$][BPh$_4$] in THF, at 25 ± 1 °C, monitored at λ = 420 nm. Inset: Dependence of k_{obs} vs base concentration at constant [NHEt$_3$][BPh$_4$] = 5.0×10^{-3} mol dm^{-3}.

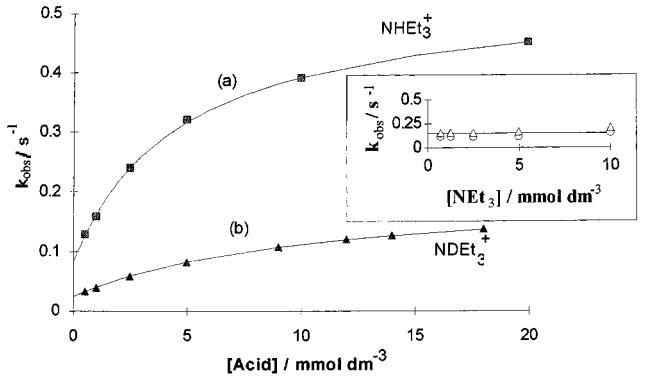


Figure 4. k_{obs} vs acid concentration for the reaction of *trans*-[ReCl(=C=CHCO$_2$Me) (dppe)$_2$] (1.0×10^{-4} mol dm^{-3}) with [NHEt$_3$][BPh$_4$] (a) or [NDEt$_3$][BPh$_4$] (b) in THF, at 25 ± 1 °C, monitored at λ = 350 nm. Inset: k_{obs} vs base (NEt$_3$) concentration, at [NHEt$_3$][BPh$_4$] = 2.5 (○) or 5.0 mmol dm^{-3} (△). The curves drawn are those defined by eq 7 and the rate and equilibrium constants given in the text.

4a. Thus, at low concentrations of acid, the rate of the reaction exhibits a first order dependence on the concentration of [NHEt$_3^+$], but at high concentrations, the rate is independent of the concentration of acid. In addition, the curve does not go through the origin but has an intercept of $k_{obs} = 0.084 \pm 0.005\ s^{-1}$. Analysis of these data gives the empirical rate law shown in eq 6. This rate law is consistent (see below) with the

$$-\frac{d[ReCl(=C=CHCO_2Me)(dppe)_2]}{dt} = \frac{0.084 + 114[NHEt_3^+]}{1 + 213[NHEt_3^+]}[ReCl(=C=CHCO_2Me)(dppe)_2] \quad (6)$$

mechanism shown in Scheme 3, which is an elaboration of the mechanism in Scheme 1. The only distinction between the two schemes is the timing of proton transfer from [NHEt$_3$]$^+$ to the vinylidene ligand. In Scheme 1, protonation of the vinylidene ligand is a single, thermodynamically favorable reaction. In Scheme 3 proton transfer involves two steps: formation of a hydrogen-bonded adduct (which accumulates to detectable concentrations) followed by rate-limiting proton transfer. This nonlinear dependence on the concentration of [NHEt$_3$]$^+$ is due to the electron-withdrawing ester substituent, which decreases electron density at the β-carbon, and thus proton transfer from [NHEt$_3$]$^+$ becomes slow. Consequently, [NHEt$_3$]$^+$ hydrogen bonds to the vinylidene carbon, but transfer of the proton from N to C occurs slowly within the hydrogen-bonded complex.

The addition of the conjugate base NEt$_3$ at a constant acid concentration did not affect the rate of the reactions (Figure 4 inset).

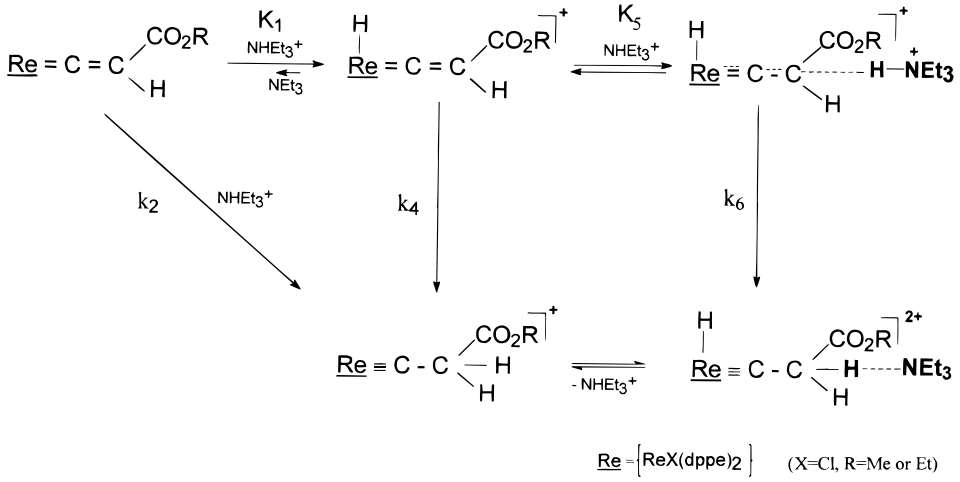
The general rate law associated with the mechanism in Scheme 3 is given by eq 7. In deriving this rate law

$$-\frac{d[ReCl(=C=CHCO_2R)(dppe)_2]}{dt} = \left(k_2[NHEt_3^+] + (k_4 + K_5k_6[NHEt_3^+])K_1\frac{[NHEt_3^+]}{[NEt_3]}\right) \Big/ \left(1 + (1 + K_5[NHEt_3^+])K_1\frac{[NHEt_3^+]}{[NEt_3]}\right)[ReCl(=C=CHCO_2R)(dppe)_2] \quad (7)$$

$$-\frac{d[ReCl(=C=CHCO_2R)(dppe)_2]}{dt} = \frac{k_4 + K_5k_6[NHEt_3^+]}{1 + k_5[NHEt_3^+]}[ReCl(=C=CHCO_2R)(dppe)_2] \quad (8)$$

(see Apendix 2) it is assumed that (i) protonation of the metal is rapid and complete within the dead time of the stopped-flow apparatus, and (ii) k_4 and k_6 are rate-

Scheme 3



limiting, with K_5 being a rapidly established equilibrium. Moreover, when $K_1[NHEt_3^+]/[NEt_3] >> 1$, essentially stoichiometric concentrations of $[Re(H)X(=C=CHR)(dppe)_2]^+$ are formed within the dead time of the stopped-flow apparatus and hence the k_2 pathway does not operate. Under these conditions eq 7 simplifies to eq 8, which is of the same form as that observed experimentally (eq 6). Comparison of eqs 6 and 8 gives $k_4 = 0.084 \pm 0.005$ s^{-1} (intercept of the curve), $K_5 = 213 \pm 1$ dm^3 mol^{-1} and $k_6 = 0.54 \pm 0.05$ s^{-1}.

Parenthetically it is worth emphasizing the similarity between the mechanisms in Schemes 1 and 3. Equation 8 (Scheme 3) is similar to eq 2 (Scheme 1), except that the term k_3 has now been replaced by $K_5k_6/(1 + K_5[NHEt_3^+])$; this replacement merely reflects the slow proton transfer to the β-carbon atom in $[ReH(=C=CHCO_2R)(dppe)_2]^+$ and hence the accumulation of the hydrogen-bonded intermediate.

In this system, the limit $K_1 \geq 36$ can be estimated by considering that at least 90% of the rhenium complexes are present as $[Re(H)Cl(=C=CHCO_2Me)(dppe)_2]^+$, even at the highest base concentration ($[NEt_3] = 10$ mmol dm^{-3}), and $[NHEt_3^+] = 2.5$ mmol dm^{-3}. We can also estimate a limit for k_2/K_1 if in the studies with NEt_3 a 10% contribution from the k_2 pathway, to the total rate, has been overlooked. The general rate law (7) assumes the simplified form (9) if we employ the usual (see above)

$$k_{obs} = \frac{(k_2/K_1)[NEt_3] + k_4 + K_5k_6[NHEt_3^+]}{1 + K_5[NHEt_3^+]} \quad (9)$$

$$\frac{k_2[NEt_3]}{K_1\{1 + K_5[NHEt_3^+]\}} \leq 0.1k_{obs} \quad (10)$$

simplification $K_1[NHEt_3^+]/[NEt_3] >> 1$, and eq 10 follows if the above contribution from k_2 is included.

Since $K_5 = 213$ dm^3 mol^{-1} when $[NHEt_3^+] = 2.5$ mmol dm^{-3} and $k_{obs} = 0.25$ s^{-1} (see Figure 4), and the highest concentration of NEt_3 used is $[NEt_3] = 10.0$ mmol dm^{-3}, we calculate $k_2/K_1 \leq 3.8$ dm^3 mol^{-1} s^{-1}.

Spectroscopic evidence for the formation of the hydrogen-bonded adduct is obtained by careful inspection of the absorbance−time curves. The initial absorbance of these depends on the concentration of $[NHEt_3^+]$. At high concentration of acid, the initial absorbance is that of the hydrogen-bonded adduct $\{Re{=}C{=}CHCO_2Me\cdots H^+NEt_3\}$, from which the molar extinction coefficient $\epsilon = (7.0 \pm 0.1) \times 10^3$ dm^3 mol^{-1} cm^{-1} can be calculated. At low concentrations of acid, the absorbance is that of $[Re(H)Cl(=C=CHCO_2Me)(dppe)_2]^+$ with $\epsilon = (5.90 \pm 0.05) \times 10^3$ dm^3 mol cm^{-1}. At intermediate concentrations of $[NHEt_3]^+$, a mixture of these two species is formed. Analysis[13] of the effect of acid concentration on the initial absorbance gives $K_5 = 210 \pm 60$ dm^3 mol^{-1}, in good agreement with the value determined kinetically. The relatively large error associated with K_5 estimated spectrophotometrically is a consequence of the relatively small difference in molar extinction coefficients of $[Re(H)Cl(=C=CHCO_2Me)(dppe)_2]^+$ and its hydrogen-bonded adduct with $[HNEt_3]^+$ (see above) and of the consequent error of the estimated molar extintion coefficient of the latter complex.

Corroboration that both k_4 and k_6 steps involve rate-limiting proton transfer is the observation that both steps show a primary kinetic isotope effect. The kinetics of the reaction between *trans*-$[ReCl(=C=CHCO_2Me)(dppe)_2]$ and $[NDEt_3]^+$ show the same kinetic behavior as for the reaction with $[NHEt_3^+]$ (Figure 4b). Analysis of the data with $[NDEt_3^+]$ gives $k_4^D = 0.025 \pm 0.003$ s^{-1}, $k_6^D = 0.15 \pm 0.02$ s^{-1}, and $K_5^D = 127 \pm 8$ dm^3 mol^{-1}, with the corresponding isotope effects $k_4^H/k_4^D = 3.4$, $k_6^H/k_6^D = 3.0$, and $K_5^H/K_5^D = 1.6$. The marked primary isotope effect for k_6 confirms that slow proton transfer is occurring in this step. Significantly, the k_4 step is also associated with a primary isotope effect. This is consistent with our proposal that the k_4 step corresponds to intramolecular migration of the hydrido ligand from rhenium to the β-carbon site. The origin of this hydride ligand is the acid, and thus, in the reactions with $[NDEt_3]^+$, $[Re(D)Cl(=C=CHCO_2Me)(dppe)_2]^+$ is formed and the migration of the deuteride is slower than the analogous hydride. The smaller difference between

(13) Assuming that protonation of the metal is rapid and complete within the dead time of the stopped-flow apparatus and that K_5 is a rapidly established equilibrium, the initial absorption (A_i) is given by the following expression:

$$A_i = \frac{\{\epsilon(ReH) + \epsilon(ReH\cdot NHEt_3)K_5[NHEt_3^+]\}[Re]}{1 + K_5[NHEt_3^+]}$$

In this equation [Re] is the total concentration of rhenium, $\epsilon(ReH) = (7.0 \pm 0.1) \times 10^3$ dm^3 mol^{-1} cm^{-1} and $\epsilon(ReH\cdot NHEt_3) = (5.90 \pm 0.05) \times 10^3$ dm^3 mol^{-1} cm^{-1}. From the data with $[Re] = 1.0 \times 10^{-4}$ mol dm^{-3}, $K_5 = 210 \pm 60$ dm^3 mol^{-1}.

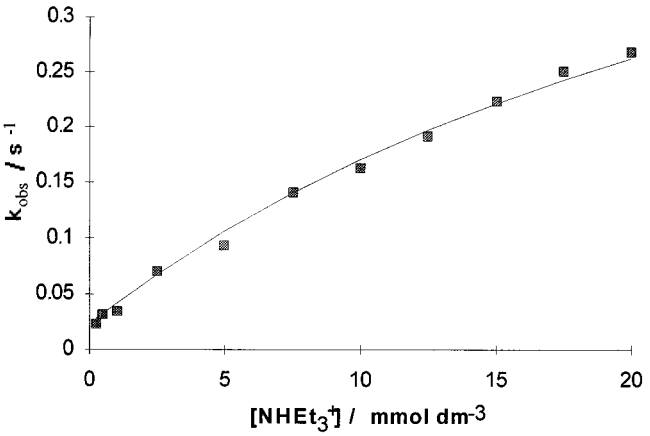


Figure 5. k_{obs} vs acid concentration for the reaction of *trans*-[ReCl (=C=CHCO$_2$Et)(dppe)$_2$] (1.0×10^{-4} mol dm^{-3}) with [$NHEt_3$][BPh_4].

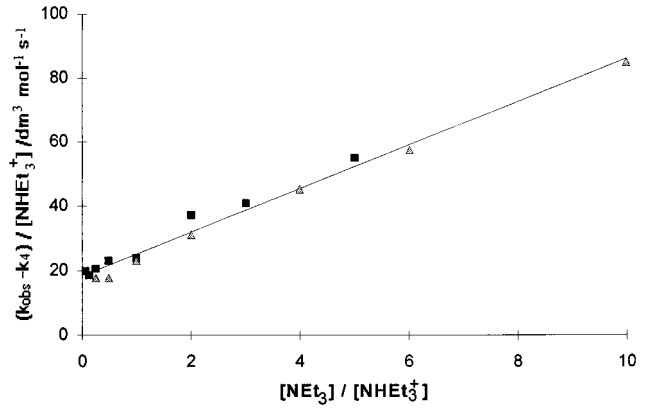


Figure 6. (k_{obs}-k_4)/[$NHEt_3^+$] vs [$NHEt_3^+$] at [$NHEt_3^+$] = 2.5 (Δ) and 5 mM (■) for the reaction of *trans*-[ReCl(=C=CHCO$_2$Et)(dppe)$_2$] (1.0×10^{-4} mol dm^{-3}) with [$NHEt_3$][BPh_4] (—, linear regression).

the K_5^H and K_5^D values is in agreement with the expected[14] isotope effects on equilibrium constants.

***trans*-[ReCl(=C=CHCO$_2$Et)(dppe)$_2$].** The reaction of *trans*-[ReCl(=C=CHCO$_2$Et)(dppe)$_2$] with [$NHEt_3$][BPh_4] shows a behavior similar to that exhibited by the methyl ester. However, the nonlinear dependence of the reaction rate on the concentration of [$NHEt_3$]$^+$ (Figure 5) is less marked with the ethyl ester. Analysis of the data in the manner described above gives k_4 = 0.023 ± 0.004 s^{-1}, k_6 = 0.7 ± 0.3 s^{-1}, and K_5 = 24 ± 1 dm^3 mol^{-1}.

It appears that the bulky ethyl substituent hinders the approach of the [$NHEt_3$]$^+$ ion to the β-carbon site more than the methyl group.

In contrast to the reaction of *trans*-[ReCl(=C=CHCO$_2$Me)(dppe)$_2$] with [Et_3NH][BPh_4] (Figure 4 inset), addition of NEt_3 in the reaction between *trans*[ReCl(=C=CHCO$_2$Et)(dppe)$_2$l and [$NHEt_3$]$^+$ perturbs the kinetics as shown in Figure 6. Addition of NEt_3 disturbs the protolytic equilibrium K_1, resulting in accumulation of the parent vinylidene complex, thus promoting the k_2 route relatively to the K_1 pathway. This can be rationalized since at low concentrations of [$NHEt_3$]$^+$, where the concentration of the hydrogen-bonded adduct does not accumulate, K_5 [$NHEt_3^+$] << 1, eq 9 simplifies to eq 11.

$$\frac{k_{obs} - k_4}{[NHEt_3^+]} = K_5 k_6 + \frac{k_2\ [NEt_3]}{K_1[NHEt_3^+]} \qquad (11)$$

Using k_4 = 0.023 s^{-1}, graphical analysis of the data (Figure 6) gives k_2/K_1 = 7.3 ± 0.5 dm^3 mol^{-1} s^{-1} and K_5k_6 = 17.4 ± 0.8 dm^3 mol^{-1} s^{-1}. The latter value is in excellent agreement with the product of the K_5 and k_6 values estimated from the data in Figure 5 (K_5 k_6 = 17 ± 2 dm^3 mol^{-1} s^{-1}).

***trans*-[ReF(=C=CHCO$_2$Et)(dppe)$_2$].** The reaction of *trans*-[ReF(=C=CHCO$_2$Et)(dppe)$_2$] with [$NHEt_3$][BPh_4] exhibits a first-order dependence on the concentration of both acid and complex (Figure 7). NEt_3 has no effect on the rate of the reaction (Figure 7 inset). This behavior is consistent with the mechanism in Scheme 1, involving initial protonation at rhenium. Direct protonation of the vinylidene (k_2 route) is not detected. Carbyne formation occurs by proton migration to the vinylidene β-carbon (k_4 route) or further proton attack at this atom (k_3 route).

Analysis of the data as outlined for the other systems in this paper, according to Scheme 1 (eq 2), gives k_3 = (9.2 ± 0.8) × 10^3 dm^3 mol^{-1} s^{-1} and k_4 = 10 ± 6 s^{-1}, respectively.

An intriguing feature of this study is that protonation of *trans*[ReF(=C=CHCO$_2$Et)(dppe)$_2$] is faster than that of the chloro analogue. A similar effect of the *trans*-halide group on the proton-affinity of ligands has been observed[15] in the deprotonation of *trans*-[M(NH)X(dppe)$_2$] (M = Mo or W; X = F, Cl, Br, I) and *trans*-[M(NNH$_2$)X(dppe)$_2$]$^+$. In all cases, the behavior can be rationalized if the fluoro ligand is a better overall electron releaser to the metal than the chloro ligand, thus facilitating protonation of the vinylidene group and retarding deprotonation of imide or hydrazide ligands. The stronger electron donation of fluoride compared to chloride opposes the electron-withdrawing effect of the ester group, and consequently the hydrogen-bonded adduct does not accumulate in detectable concentrations.

Conclusions

Although analysis of the product of protonation of the vinylidene ligand apparently indicates direct regiospecific protonation of the β-carbon, it is only by detailed mechanistic studies, such as those described herein, that a variety of pathways leading to the carbyne product is revealed. In particular, for electron-rich complexes initial protonation can occur at either the metal or the vinylidene ligand. In the systems discussed in this paper, the kinetically controlled product is the hydrido species [ReX(H)(=C=CHR)(dppe)$_2$]$^+$; however, subsequent rearrangement pathways ultimately result in the thermodynamic carbyne product [ReX(≡CCH$_2$R)(dppe)$_2$]$^+$ in which the proton binds the carbon ligand.

It is important to emphasize that only three pathways are necessary to describe the mechanisms by which all the vinylidene complexes discussed herein are converted to carbyne. Direct, regiospecific protonation of the β-carbon (k_2 route), regiospecific protonation at the metal (K_1 route) followed by intramolecular transfer of

(14) Bell, R. P. *The Proton in Chemistry*; 2nd ed.;Chapman and Hall: London, 1973; Chapters 11 and 12 and references therein.

(15) Lane, J. D.; Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1986**, 2155.

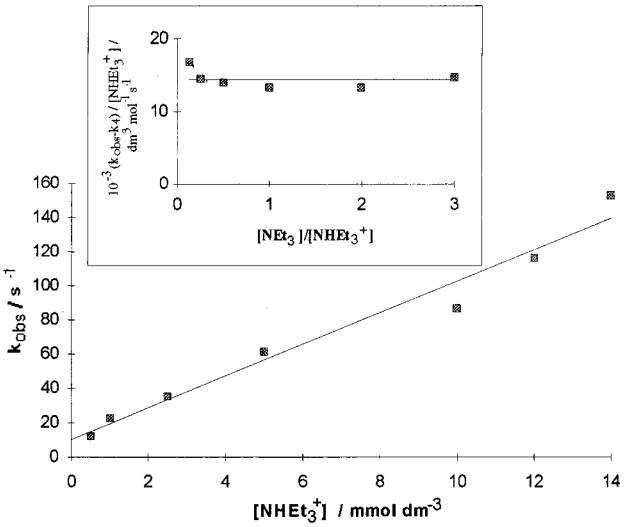


Figure 7. k_{obs} vs acid concentration for the protonation of *trans*-[ReF (=C=CHCO$_2$Et)(dppe)$_2$] (1.0×10^{-4} mol dm^{-3}) by [NHEt$_3$][BPh$_4$] in THF, at 25 ± 1 °C, monitored at λ = 420 nm. Inset: ($k_{obs} - k_4$)/[NHEt$_3^+$] vs [NEt$_3$]/[NHEt$_3^+$] at [NHEt$_3^+$] = 2.5×10^{-3} mol dm^{-3}.

the hydrogen to the β-carbon (k_4 route), or further protonation of the hydride species at the β-carbon (k_3 route).

With *trans*-[ReCl(=C=CHR)(dppe)$_2$] (R = C$_6$H$_5$, C$_6$H$_4$-Me-4), all three pathways are observed, while with the R = Bu^t complex, the bulky nature of this substituent enforces the exclusive use of the intramolecular pathway. The effect of the more electron-withdrawing ester substituents in *trans*-[ReCl(=C=CHCO$_2$R)(dppe)$_2$] (R = Me, Et) decreases the electron density at the β-carbon. This results in proton transfer to the β-carbon site becoming rate-limiting and detection of the precursor hydrogen-bonded adduct.

Finally, the mechanisms of protonation of the vinylidene ligand can be modulated by changing the *trans* halide. Thus, although *trans*-[ReCl(=C=CHCO$_2$Et)-(dppe)$_2$] reacts by all three pathways, the analogous *trans*-[ReF(=C=CHCO$_2$Et)(dppe)$_2$] reacts via the hydrido species only. In addition, the fluoro ligand apparently renders the β-carbon sufficiently basic that the hydrogen-bonded adduct is too short-lived to be detected.

In general, for an unsaturated hydrocarbon residue bound to an electron-rich site such as {M(dppe)$_2$} (M = Mo, W, Re), it appears that there is a fine balance as to which site (metal or carbon) the proton attacks most rapidly, and *a priori* it is as yet not possible to predict which of these two is protonated more rapidly. For instance, with the allene complex *trans*-[ReCl(η^2-CH$_2$-C=CHPh)(dppe)$_2$], initial protonation is at the metal (as observed in the vinylidene complexes), and only subsequently is the thermodynamic η^2-vinyl product *trans*-[ReCl{C(CH$_2$)CH$_2$Ph}(dppe)$_2$]$^+$ formed[4]. In contrast, for *trans*-[ReCl(NCR)(dppe)$_2$] (R = aryl), initial protonation is at the nitrile ligand to form a methyleneamido ligand in [ReCl(NCHR)(dppe)$_2$]$^+$. Moreover, with *trans*-[ML$_2$-(diphos)$_2$] (M = Mo, W; L = CNR (R = Me, Bu^t),[5] CH$_2$ = CH$_2$;[6a] diphos = dppe; L = N$_2$;[16] diphos = dppe, Et$_2$PCH$_2$CH$_2$PEt$_2$), initial protonation is at the ligand, although protonation to the metal can compete to form the hydrido product (as in the dinitrogen complexes). Such a metal/ligand competition for the proton has also recently been recognized[6b] for the alkynyl complex [MoH$_3$(C≡CBu^t)(dppe)$_2$].

(16) Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2259.

Experimental Section

All manipulations in the synthetic and kinetic studies were routinely performed under an atmosphere of dinitrogen using standard Schlenk or syringe techniques as appropriate. The solvent, THF, was freshly distilled immediatly prior to use.

The chloro−vinylidene complexes were prepared by treatment of a THF or toluene solution of *trans*-[ReCl(N$_2$)(dppe)$_2$] with the appropriate l-alkyne[l7] in refluxing conditions or under tungsten filament light or sunlight.[8a] The fluoro−vinylidine complex *trans*-[ReF(=C=CHCO$_2$Et)(dppe)$_2$] was obtained by treatment of a CH$_2$Cl$_2$ solution of the carbyne complex *trans*-[ReF(≡CCH$_2$CO$_2$Et)(dppe)$_2$][BF$_4$] with [NBu$_4$]0H.[8a,18] The purity of these complexes was established by elemental analyses and IR, ^{31}P{^{1}H}, and ^{1}H and/or ^{13}C NMR spectroscopies.

Standard solutions of [NHEt$_3$][BPh$_4$], the complexes, and NEt$_3$ were prepared in THF under an atmosphere of dinitrogen. The acid or (base + acid) working solutions were prepared, in volumetric flasks, by the appropriate dilution of the corresponding standard solutions. All the solutions were transferred to the stopped-flow apparatus using gas-tight, all-glass syringes. All kinetic studies were complete within 1 h of preparing the stock acid and base solutions in order to minimize any complications associated with the acid-catalyzed ring opening of THF.

The kinetics were studied on a Canterbury SF-40 stopped-flow spectrophotometer with a spectrophotometer unit SU-40, from Hi-Tech Scientifics, at 25 °C, monitoring the absorbance changes associated with the rhenium complexes at the wavelengths shown in the figures.

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.

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Appendix 1. Derivation of the Rate Law for the Mechanism of Scheme 1

Assuming that K_1 is a rapidly established equilibrium and that the rate-limiting steps are k_2, k_3, and k_4, the rate law is given by expression A.1.

$$-\frac{d[Re]}{dt} = k_2[NHEt_3^+][Re]_e + k_3[NHEt_3^+][ReH]_e + k_4[ReH]_e \quad (A.1)$$

where [*Re*]$_e$ and [*Re*H]$_e$ stand for the equilibrium concentrations of trans-[ReX(=C=CHR)(dppe)$_2$] and [Re(H)X(=C=CHR)(dppe)$_2$]$^+$, respectively, and [Re] is

(17) Pombeiro, A. J. L.; Almeida, S. S. P. R.; Silva, M. F. C. G.; Jeffrey, J. C.; Richards, RL. *J. Chem. Soc., Dalton Trans.* **1989**, 2381.
(18) Almeida, S. S. P. R.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1993**, *450*, C7.

the total concentration of rhenium in solution, i.e.

$$[\mathrm{Re}] = [Re]_e + [ReH]_e \quad (A.2)$$

K_1 is given by

$$K_1 = \frac{[ReH]_e[NEt_3]}{[Re]_e[NHEt_3^+]} \quad (A.3)$$

From eqs A.2 and A.3, expressions relating $[Re]_e$ and $[ReH]_e$ in terms of [Re] (eqs A.4 and A.5) are derived which, upon substitution into eq A.1, lead to eq A.6 which is eq 3 of the text.

$$[Re]_e = \frac{[\mathrm{Re}]}{1 + K_1\dfrac{[NHEt_3^+]}{[NEt_3]}} \quad (A.4)$$

$$[ReH]_e = \frac{K_1\dfrac{[NHEt_3^+]}{[NEt_3]}[\mathrm{Re}]}{1 + K_1\dfrac{[NHEt_3^+]}{[NEt_3]}} \quad (A.5)$$

$$-\frac{d[\mathrm{Re}]}{dt} = \frac{k_4K_1\dfrac{[NHEt_3^+]}{[NEt_3]} + \left(k_3K_1\dfrac{[NHEt_3^+]}{[NEt_3]} + k_2\right)[NHEt_3^+]}{1 + K_1\dfrac{[NHEt_3^+]}{[NEt_3]}}[\mathrm{Re}] \quad (A.6)$$

Appendix 2. Derivation of the Rate Law for the Mechanism of Scheme 3

Assuming that K_1 and K_5 are rapidly established equilibria, and that steps k_4 and k_6 are rate-limiting, the rate law is given by expression A.7.

$$-\frac{d[\mathrm{Re}]}{dt} = k_2[NHEt_3^+][Re]_e + k_4[ReH]_e + k_6[ReH\cdot NHEt_3]_e \quad (A.7)$$

where $[Re]_e$, $[ReH]_e$, and $[ReH\cdot NHEt_3^+]_e$ are the equilibrium concentrations of *trans*-[ReX(=C=CHR)(dppe)$_2$], [Re(H)X(=C=CHR)(dppe)$_2$]$^+$, and [Re(H)(=C=CHR)(dppe)$_2$]$^+\cdots$HNEt$_3^+$, respectively, and [Re] is the total concentration of rhenium in solution i.e.

$$[\mathrm{Re}] = [Re]_e + [ReH]_e + [ReH\cdot NHEt_3^+]_e \quad (A.8)$$

K_1 and K_5 are given by eqs A.3 and A.9, respectively.

$$K_5 = \frac{[ReH\cdot NHEt_3^+]}{[ReH]_e[NHEt_3^+]} \quad (A.9)$$

From eqs A.8, A.3, and A.9, expressions relating $[Re]_e$, $[ReH]_e$ and $[ReH\cdot NHEt_3]_e$ in terms of [Re] (eqs A.10−A.12) are derived which, upon substitution into eq A.7, lead to eq A.13 which corresponds to eq 7 of the text.

$$[Re]_e = \frac{[\mathrm{Re}]}{1 + K_1\dfrac{[NHEt_3^+]}{[NEt_3]}(1 + K_5[NHEt_3^+]} \quad (A.10)$$

$$[ReH]_e = \frac{K_1[NHEt_3^+]}{[NEt_3]}[Re]_e \quad (A.11)$$

$$[ReH\cdot NHEt_3^+]_e = \frac{K_1K_6[NHEt_3^+]^2}{[NEt_3]}[Re]_e \quad (A.12)$$

$$-\frac{d[\mathrm{Re}]}{dt} = \frac{k_2[NHEt_3^+] + \{k_4 + K_5k_6[NHEt_3^+]\}K_1\dfrac{[NHEt_3^+]}{[NEt_3]}}{1 + K_1\dfrac{[NHEt_3^+]}{[NEt_3]}\{1 + K_5[NHEt_3^+]\}}[\mathrm{Re}] \quad (A.13)$$

Supporting Information Available: Tables of stopped-flow kinetic data (6 pages). Ordering information is given on any current masthed page.

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