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New insights into the mechanism of methane formation in the protonation of methyl complexes†

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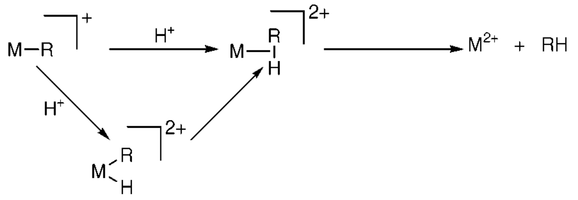
The reaction between $[\mathrm{NiMe\{(Ph_2PCH_2CH_2)_2PPh\}}]^+$ and anhydrous HCl (in MeCN) involves initial protonation of nickel to form $[\mathrm{Ni(H)Me\{(Ph_2PCH_2CH_2)_2PPh\}}]^{2+}$, but methane is not produced until after additional, direct protonation of the methyl group.

There have been many investigations into the formation of alkanes in the reaction of acid with metal–alkyl complexes,[1–3] and the consensus view is that the mechanism involves either direct protonation of the metal–carbon bond or initial protonation of the metal followed by intramolecular coupling of the hydrido and methyl ligands (Scheme 1).



Scheme 1

The kinetics of these reactions are frequently too simple to be diagnostic of one particular mechanism and consequently the detection or isolation of a hydrido species has often been invoked as evidence of the coupling pathway. Here, we describe unprecedented complex kinetics for protonation of an alkyl complex which demonstrates, for the first time, that detection of a hydrido species is an insufficient criteria to define the intimate mechanism of alkane formation. Specifically, we show that initial protonation of $[\mathrm{NiMe(triphos)}]^+$ [triphos = $(\mathrm{Ph_2PCH_2CH_2})_2\mathrm{PPh}$; eqn. (1)] occurs at nickel to form a hydrido complex, but the formation of methane has to await further direct protonation of the methyl group.

$$[\mathrm{NiMe(triphos)}]^+ + \mathrm{HCl} \rightarrow [\mathrm{NiCl(triphos)}]^+ + \mathrm{MeH} \quad (1)$$

The reaction between $[\mathrm{NiMe(triphos)}]^+$ and an excess of anhydrous HCl in MeCN occurs in two stages: a rapid, acid-dependent reaction which was studied by stopped-flow spectrophotometry, and the subsequent release of methane which was followed by GLC.

In the reaction between $[\mathrm{NiMe(triphos)}]^+$ and HCl alone, the kinetics of the first stage exhibit a first order dependence on the concentration of complex and an apparent first order dependence on the concentration of HCl as described by eqn. (2), and illustrated in Fig. 1.

$$\frac{-\mathrm{d}[\mathrm{NiMe(triphos)}^+]}{\mathrm{d}t} = (3.4 \pm 0.3)\times 10^2[\mathrm{NiMe(triphos)}^+][\mathrm{HCl}] \quad (2)$$

The simplicity of these kinetics are consistent with either of the two pathways shown in Scheme 1. However, addition of Cl^- reveals a more complicated behaviour (Fig. 1).‡ The *true* rate law is that shown in eqn. (3).

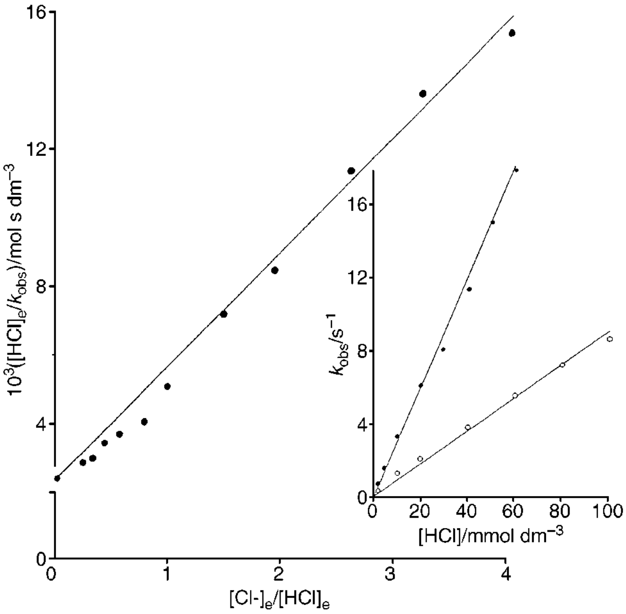
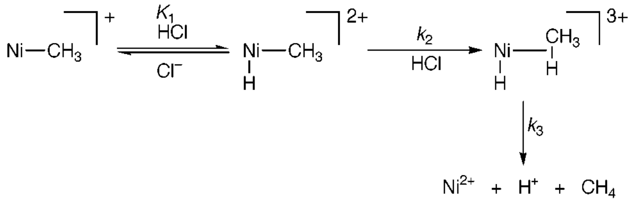


Fig. 1 Dependence of $[\mathrm{HCl}]_e/k_{obs}$ on $[\mathrm{Cl}^-]_e/[\mathrm{HCl}]_e$ for the reaction of $[\mathrm{NiMe(triphos)}]^+$ with HCl in the presence of $[\mathrm{NEt_4}]\mathrm{Cl}$, in MeCN at 25.0 °C. Line drawn is that defined by eqn. (3). [Insert: Dependence of k_{obs} on the concentration of HCl (●) and DCl (○) in the absence of $[\mathrm{NEt_4}]\mathrm{Cl}$].

$$\frac{-\mathrm{d}[\mathrm{NiMe(triphos)}^+]}{\mathrm{d}t} = \frac{(3.0 \pm 0.4)\times 10^2[\mathrm{NiMe(triphos)}^+][\mathrm{HCl}]_e^2/[\mathrm{Cl}^-]_e}{1+(0.78 \pm 0.05)[\mathrm{HCl}]_e/[\mathrm{Cl}^-]_e} \quad (3)$$

Eqn. (3) demonstrates that two protons bind to the complex prior to methane release. Such kinetics have not been observed before but are in line with the general protonation characteristics of metal sites containing hydrocarbon residues, in which both metal and carbon can be protonated.[4,5]

The mechanism shown in Scheme 2 involves initial, rapid protonation at nickel to form the hydrido species. However, the kinetics dictate that this protonation is insufficient to produce methane. Rather formation of methane has to await additional protonation of the methyl group. Clearly, diprotonation of the



Scheme 2 Mechanism of the formation of methane in the reaction of $[\mathrm{NiMe(triphos)}]^+$ with HCl in MeCN.

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nickel is untenable since this would form a formal Ni^{VI} species.

The rate law associated with this mechanism is shown in eqn. (4) and is derived assuming that protonation at nickel is a rapidly established equilibrium, whilst protonation of the carbon is slow and irreversible.

$$\frac{-\mathrm{d}[\text{NiMe(triphos)}^+]}{\mathrm{d}t} = \frac{K_1k_2[\text{NiMe(triphos)}^+][\text{HCl}]_e^{\,2}/[\text{Cl}^-]_e}{1+K_1[\text{HCl}]_e/[\text{Cl}^-]_e} \qquad (4)$$

Comparison of eqns. (3) and (4) gives $k_2 = (3.8 \pm 0.4) \times 10^2$ dm^3 mol^{-1} s^{-1} and $K_1 = 0.78 \pm 0.05$. When [Cl$^-$] is low, eqn. (4) simplifies to eqn. (5), consistent with the experimental observations. Comparison of eqns. (2) and (5) gives $k_2 = (3.4 \pm 0.3) \times 10^2$ dm^3 mol^{-1} s^{-1}, in excellent agreement with that derived from eqn. (4).

$$\frac{-\mathrm{d}[\text{NiMe(triphos)}^+]}{\mathrm{d}t} = k_2[\text{NiMe(triphos)}^+][\text{HCl}]_e \qquad (5)$$

Consistent with the k_2 step involving rate-limiting protonation of the methyl group, studies with DCl show a primary isotope effect, $(k_2)^H/(k_2)^D = 3.5$ (Fig. 1).

Further evidence that nickel is the most rapidly protonated site comes from ^{1}H NMR spectroscopy. Our mechanism indicates that the addition of 1 mol equivalent of HCl to a MeCN solution of [NiMe(triphos)]$^+$ will produce an approximately equimolar mixture of the parent complex and [Ni(H)Me(triphos)]$^{2+}$. The ^{1}H NMR spectrum of such a mixture (Fig. 2)§ shows a multiplet at δ 9.9 (J_{HP} 50 Hz, J_{HP} 430 Hz). We tentatively attribute this low field signal to the hydride ligand in the five-coordinate, formally Ni^{IV} species, [Ni(H)Me(triphos)]$^{2+}$. This multiplet is not present in the ^{1}H NMR spectra of either [NiMe(triphos)]$^+$ or [NiCl(triphos)]$^+$.

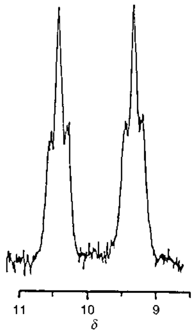

Fig. 2 The multiplet observed in the ^{1}H NMR spectrum on addition of 1 mol equivalent of HCl to [NiMe(triphos)]$^+$.

Mass spectrometry of the gas formed from the reaction of [NiMe(triphos)]$^+$ and an excess of DCl showed essentially exclusive formation of CH$_3$D, with little or no other isotopomers. This is also consistent with our mechanism since, once formed, the methane ligand does not undergo proton exchange before it dissociates.

Why does the complex bind two protons when only one is needed for the stoichiometric reaction? Clearly it does not need to. Diprotonation occurs because the nickel is protonated *faster* than the methyl group, and consequently the reaction is *enforced* to operate through the hydrido species. However, intramolecular coupling of the hydride and methyl ligands is *slow* and so methane formation can only occur *after* additional, protonation of the methyl group.

The release of methane (measured by GLC) occurs at a rate which shows a first order dependence on the concentration of complex, but is independent of the concentration of HCl [$k_3 = (4.5 \pm 0.5) \times 10^{-2}$ s^{-1}]. This indicates that, at high concentrations of acid, the putative σ-methane complex is long-lived¶ having a half-life of *ca*. 15 s. Relatively long-lived alkane complexes have been detected previously[6,7] but this kinetic approach has not been adopted before, and potentially is a general method of understanding the factors stabilising such σ-alkane complexes.

The mechanism of methane formation described herein is unexpected, but sufficiently simple that it seems likely that it is not unique to [NiMe(triphos)]$^+$. It is a salutary thought that this pathway has remained unidentified in analogous systems until now because: (i) the detection of hydrido complexes were consistent with the intramolecular coupling pathway (Scheme 1) and (ii) the kinetics of these reactions were not (or could not) be studied in the detailed manner described herein. Just because a hydrido complex is detected in solutions containing acid and a metal alkyl complex does not mean that the hydride is kinetically competent to produce alkane.

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Notes and references

‡ Anhydrous HCl was prepared *in situ* by mixing equimolar amounts of SiMe$_3$Cl and MeOH in MeCN. The reactions were deliberately performed in MeCN (dried over CaH$_2$ and distilled immediately prior to use) since solution equilibria (such as pK_a and homoconjugation constants) are known in this solvent.[8] The concentrations of [HCl$^-$]$_e$ and [Cl$^-$]$_e$ are those calculated having allowed for the homoconjugation equilibrium, HCl + Cl$^-$ $\rightleftharpoons$ HCl$_2^-$, $K_H = 158.5$ dm^3 mol^{-1}.

§ In these experiments the resonances attributable to the Me groups in [NiMe(triphos)]$^+$ (δ 0.9, unresolved multiplet) and the putative [Ni(H)Me(triphos)]$^{2+}$ are obscured by the peak due to SiMe$_3$ (from the mixture of SiMe$_3$Cl and CD$_3$OH used to generate anhydrous HCl). Further evidence that the multiplet at δ 9.9 is attributable to the hydride comes from analogous experiments with DCl where this resonance is missing.

¶ We believe that this is a true measure of the stability of the putative σ-methane complex, rather than an artefact associated with measuring the kinetics of methane transfer from solvent to gas phase, since the rate of the reaction is independent of the concentration of complex used and the speed with which the reaction mixture is agitated.

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