Preparation and Reactions of $[MoH(\eta^3\text{-}C_4H_7)(Ph_2PCH_2CH_2PPh_2\text{-}\kappa^2P)(Ph_2PCH_2CH_2PPh_2\text{-}\kappa P)]$: the Intramolecular Interconversion between η^3-2-Methylallyl and η^4-Trimethylenemethane Ligands

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The complex $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) has been prepared. Variable-temperature ^1H, ^{13}C and ^{31}P NMR spectroscopy demonstrates that this 16-electron, η^3-2-methylallyl species (the dominant form at 25 °C) rapidly interconverts, intramolecularly, to the 18-electron, η^4-trimethylenemethane species, $[MoH_2(\eta^4\text{-}C_4H_6)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ (the dominant form at −80 °C). Protonation of $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ with HCl at 25 °C gives stoichiometric yields of $[MoH_2Cl_2(dppe\text{-}\kappa^2P)_2]$ and $Bu^tCH_2C(Me)CH_2$. Stopped-flow spectrophotometric studies of the protonation reaction indicate that the alkene formation involves rapid protonation of the molybdenum to give $[MoH_2(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]^+$, which undergoes rate-limiting intramolecular hydrogen migration to form $[MoH(\eta^2\text{-}Me_2C{=}CH_2)(dppe\text{-}\kappa^2P)_2]^+$. Subsequent formation of $Bu^tCH_2C(Me){=}CH_2$ occurs rapidly and is not amenable to kinetic analysis. However, the dimerisation is too fast to be catalysed by the excess of HCl alone, and a mechanism involving formation of $Bu^tCH_2C(Me){=}CH_2$ at the molybdenum centre is proposed.

Recently we have been interested in the mechanisms of protonation of co-ordinated unsaturated hydrocarbons and understanding how the site of proton attack can define the product released.[1-3] In a further development of these studies we here report the preparation, characterisation and protonation of $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), containing the 2-methylallyl ligand. This species rapidly interconverts into $[MoH_2(\eta^4\text{-}C_4H_6)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$, containing the trimethylenemethane ligand. This is the first demonstration of an intramolecular interconversion between the 2-methylallyl and trimethylenemethane residues, and complements the earlier studies on the intramolecular migration of hydrido ligands onto unsaturated hydrocarbons in $[MoH(\eta^2\text{-}C_2H_4)_2(dppe\text{-}\kappa^2P)_2]^+$ and $[MoH(\eta^3\text{-}C_3H_5)(dppe\text{-}\kappa^2P)]$.[4]

Experimental

All manipulations in both the preparative and analytical aspects of this work were routinely performed under an atmosphere of dinitrogen using Schlenk or syringe techniques as appropriate. The reagents $SiMe_3Cl$, MeOH, MeOD, 2-methylpropene and dppe (Aldrich) were used as received; $[MoCl_4(dppe\text{-}\kappa^2P)]$ was prepared by the literature method.[5] The solvent, tetrahydrofuran (thf), was distilled from sodium–benzophenone immediately prior to use.

Preparations.—$[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$. A suspension of $[MoCl_4(dppe\text{-}\kappa^2P)]$ (2.50 g, 4.0 mmol) and dppe (2.60 g, 6.5 mmol) in thf (*ca.* 100 cm^3) was saturated with 2-methylpropene by bubbling the gas for about 15 min. During this time sodium amalgam (5 g of 10% amalgam) was added. The atmosphere of 2-methylpropene was replenished, and two further portions of sodium amalgam (5 g of 10% amalgam) were added over the course of the next 4 h. After stirring the mixture at room temperature for *ca.* 18 h the mixture had become a homogeneous dark red-brown solution. It was filtered through Celite to remove the sodium amalgam, and the filtrate concentrated *in vacuo* to *ca.* 30 cm^3. Addition of methanol (*ca.* 200 cm^3) precipitated the product, which was filtered off, washed with methanol, then dried *in vacuo*. Recrystallisation from thf–methanol gave the pure, green microcrystalline product (Found: C, 70.5; H, 5.5. Calc. for $C_{56}H_{56}MoP_2$: C, 70.9; H, 5.9%).

trans-$[Mo(\eta^2\text{-}Me_2CCH_2)_2(dppe\text{-}\kappa^2P)_2]$. This compound was prepared as an orange solid by an identical method to that described above, except that an excess of 2-methylpropene was maintained at all times, by ensuring a slight pressure of 2-methylpropene throughout the 18 h of the reaction by several replenishments of the gas, particularly during the active reduction stage, *i.e.* in the period 1.5–6 h (Found: C, 71.5; H, 6.2. Calc. for $C_{60}H_{64}MoP_2$: C, 71.7; H, 6.4%). NMR spectra: ^1H, δ 1.29 (s, 12 H, Me), 4.6 (s, 4 H, CH_2) and 6.9–7.8 (m, 40 H, Ph), $^{31}P\text{-}\{^1H\}$, δ −58.6 (s).

Kinetic Studies.—The reaction between $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ and anhydrous HCl was studied in thf at 25.0 °C using a Hi-Tech SF51 spectrophotometer modified to handle air-sensitive compounds as described before.[6] The data were collected and analysed on a Viglen computer interfaced *via* an analogue-to-digital converter to the stopped-flow apparatus.

Stock solutions of anhydrous HCl in thf were prepared by mixing equimolar amounts of $SiMe_3Cl$ and MeOH. Dilute solutions of acid were prepared from this stock solution and used within 1 h of preparation. The kinetics of the reaction was studied in the range λ = 350–550 nm but must of the data were collected at λ = 420 nm. At all wavelengths the behaviour was identical: an initial rapid decrease in absorbance (complete within the dead-time of the stopped-flow apparatus, 2 ms), followed by a biphasic absorbance *vs.* time curve to yield the product, $[MoH_2Cl_2(dppe\text{-}\kappa^2P)_2]$ (see Fig. 3). All the kinetic studies were performed under pseudo-first-order conditions, $[HCl]/[Mo] \geqslant 20$.

Spectroscopic Studies.—Proton, ^{31}P and ^{13}C NMR spectra were recorded on a JEOL GSX270 spectrometer using $[^2H_8]$thf as solvent. All chemical shifts quoted are *versus* $SiMe_4$ (^1H and

^{13}C) or $P(OMe)_3$ (^{31}P). The UV/VIS spectra were recorded on a Perkin-Elmer Lambda 5 and IR spectra on a Perkin-Elmer 227 spectrometer. The GLC experiments were performed on a Philips PU4400 gas–liquid chromatograph and computing integrator PU4815 using a Poropak Q column operating at 130 °C. 2-Methylpropene has a retention time of *ca.* 5.3 ± 0.1 min, and eluted as a rather broad band from this column.

Results and Discussion

The reduction of a mixture of $[MoCl_4(dppe\text{-}\kappa^2P)]$ and dppe, with sodium amalgam, under an atmosphere of an excess of 2-methylpropene gives the very labile *trans*-$[Mo(\eta^2\text{-}Me_2CCH_2)_2(dppe\text{-}\kappa^2P)_2]$. The ^1H NMR spectrum of this species (measured rapidly) demonstrates the presence of the co-ordinated alkene (see Experimental section). In addition, the $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits a singlet consistent with the *trans* geometry. However, over protracted accumulation times (*ca.* 30 min) a singlet attributable to *trans*-$[Mo(N_2)_2(dppe\text{-}\kappa^2P)_2]$ is observed (δ 75.1)[7] which progressively increases in intensity until the peak due to *trans*-$[Mo(\eta^2\text{-}Me_2CCH_2)_2(dppe\text{-}\kappa^2P)_2]$ disappears. Independent GLC experiments demonstrate that 2-methylpropene is evolved during this reaction.

During the formation of *trans*-$[Mo(\eta^2\text{-}Me_2CCH_2)_2(dppe\text{-}\kappa^2P)_2]$ an intermediate green species is apparent. We have been able to isolate this material under conditions where the amount of alkene is limited and spectroscopic characterisation identifies it as $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ as shown in Scheme 1. Despite repeated attempts we have been unable to grow crystals of this complex suitable for X-ray crystallography. Hence we cannot be dogmatic about the co-ordination geometry. Certainly, a square-based configuration cannot be ruled out on the spectroscopic characterisation described below.

Characterisation of $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$.—The ^1H NMR spectrum of this complex exhibits a complicated pattern in the region δ 6.5–7.4 attributable to the phenyl groups of the dppe ligands, but more importantly also shows signals associated with the methyl group [δ 1.30 (s, 3 H)] and the methylene groups [δ 2.49 (s, 4 H)] of the 2-methylallyl ligand. In addition, the presence of a hydride residue [δ 1.1 (q, 1 H, J(PH) = 52.4 Hz], which is also observed in the IR spectrum [ν(MoH) = 1960w cm^{-1}], is confirmed from ^1H NMR studies. However, in the ^1H NMR spectrum the quartet of the hydride is partially obscured by the methyl signal of the 2-methylallyl ligand.

The presence of the 2-methylallyl ligand in this complex is confirmed by ^{13}C NMR spectroscopy. The signal associated with the methyl group is observed at δ 30.5 [q, J(CH) = 122.1 Hz] and the methylene groups at δ 32.1 [t, J(CH) = 122 Hz]. The central carbon of this residue, $MeC(CH_2)_2$, is observed at δ 144.0 which is unaffected by ^1H decoupling. These spectra are shown in Fig. 1. In addition, the ^{13}C NMR spectrum reveals two other signals, attributable to the methylene groups of the bi- and mono-dentate dppe ligands {δ 48.1 [t, J(CH) = 180 Hz] and 21.4 (t)}. These residues are also distinguished in the ^1H NMR spectrum but are characteristically broad resonances centred at δ 2.3 and 2.6. The rather unexpected result that both mono- and bi-dentate dppe ligands are present in this molecule is immediately apparent from the $^{31}P\text{-}\{^1H\}$ NMR spectrum with a signal at δ −153.5, J(PP) = 35.5 Hz, close to that of free dppe, δ −155. Other signals at δ −52.6 [d, 1 P, J(PP) = 35.4 Hz] and −54.6 (s, 2 P) are assignable to the co-ordinated end of the monodentate dppe and to the bidentate dppe respectively.

Parenthetically, it is worth reminding ourselves at this stage that $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ is an intermediate on the pathway to *trans*-$[Mo(\eta^2\text{-}Me_2CCH_2)_2(dppe\text{-}\kappa^2P)_2]$. This is manifest, not only in the metal having a formal oxidation state (Mo^{II}) which is intermediate between that of $[MoCl_4(dppe\text{-}\kappa^2P)]$ (Mo^{IV}) and *trans*-$[Mo(\eta^2\text{-}Me_2CCH_2)_2(dppe\text{-}\kappa^2P)_2]$ (Mo^0), but also in having a 'dangling' phosphine, rendering the complex a formal 16-electron species. However, variable-temperature NMR studies reveal that the 16-electron 2-methylallyl species rapidly interconverts intramolecularly into the 18-electron trimethylenemethane species as shown in Fig. 1.

The 2-Methylallyl–Trimethylenemethane Interconversion.—Upon varying the temperature of a solution of $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ from ambient to −80 °C, distinct, *reversible* structural changes are observed as shown in Fig. 1. To the best of our knowledge this is the first time that the intramolecular interconversion between a 2-methylallyl and a trimethylenemethane, hydride species has been observed.[8]

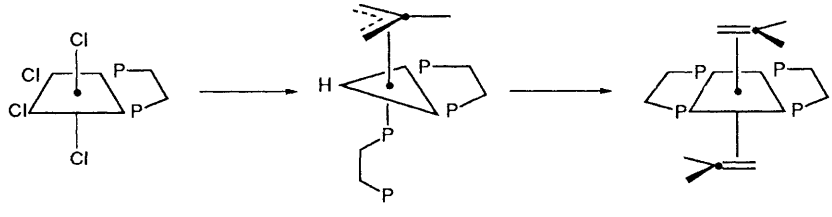
The ^1H NMR spectrum clearly demonstrates the rearrangement of the hydrocarbon fragment. At −80 °C the signal attributable to the methylene groups has now shifted to slightly lower field [δ 3.07 (s, 6 H)] and the methyl signal at δ 1.30, observed under ambient conditions, has now vanished. In addition, the signal assigned to the hydride has changed markedly {δ 1.11 [q, 2 H, J(PH) = 31.6 Hz]}. The intramolecular rearrangement is confirmed by ^{13}C NMR spectroscopy where signals due to the trimethylenemethane ligand are observed at −80 °C {δ 33.0 [t, J(CH) = 128 Hz, $C(CH_2)_3$] and 143.3 [s, $C(CH_2)_3$]}. The quality of the ^{13}C NMR spectrum is limited by the length of time that −80 °C can be maintained (*ca.* 4 h) on the spectrometer, but the spectra are sufficiently clear to demonstrate the formation of the trimethylenemethane ligand.

Reaction of $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ *with* HCl.—Treatment of a thf solution of the parent complex with anhydrous HCl gives $[MoH_2Cl_2(dppe\text{-}\kappa^2P)_2]$ quantitatively as shown in equation (1). The stoichiometry was established by

$$[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)] + 2HCl \longrightarrow [MoH_2Cl_2(dppe\text{-}\kappa^2P)_2] + (Me_2C{=}CH_2)_n \quad (1)$$

spectrophotometric titration as shown in Fig. 2. The identity of the metal-containing product was established as $[MoH_2Cl_2(dppe\text{-}\kappa^2P)_2]$ (even in the presence of an excess of HCl) from its characteristic $^{31}P\text{-}\{^1H\}$ NMR spectrum {δ −70.4 [t, J(PP) = 10.0] and −97.2 [t, J(PP) = 10.0 Hz]}, hydride signal in the ^1H NMR spectrum {δ −4.5 [qnt, J(PH) = 45 Hz]} and IR spectrum [ν(MoH) = 1880 cm^{-1}].[9] Clearly protonation of the pendant phosphorus atom in $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ during this reaction is readily reversible so that chelate formation can ensue.

The GLC experiments clearly showed that no volatile



Scheme 1 Pathway for the reduction of $[MoCl_4(dppe\text{-}\kappa^2P)]$ in the presence of dppe and $Me_2C{=}CH_2$

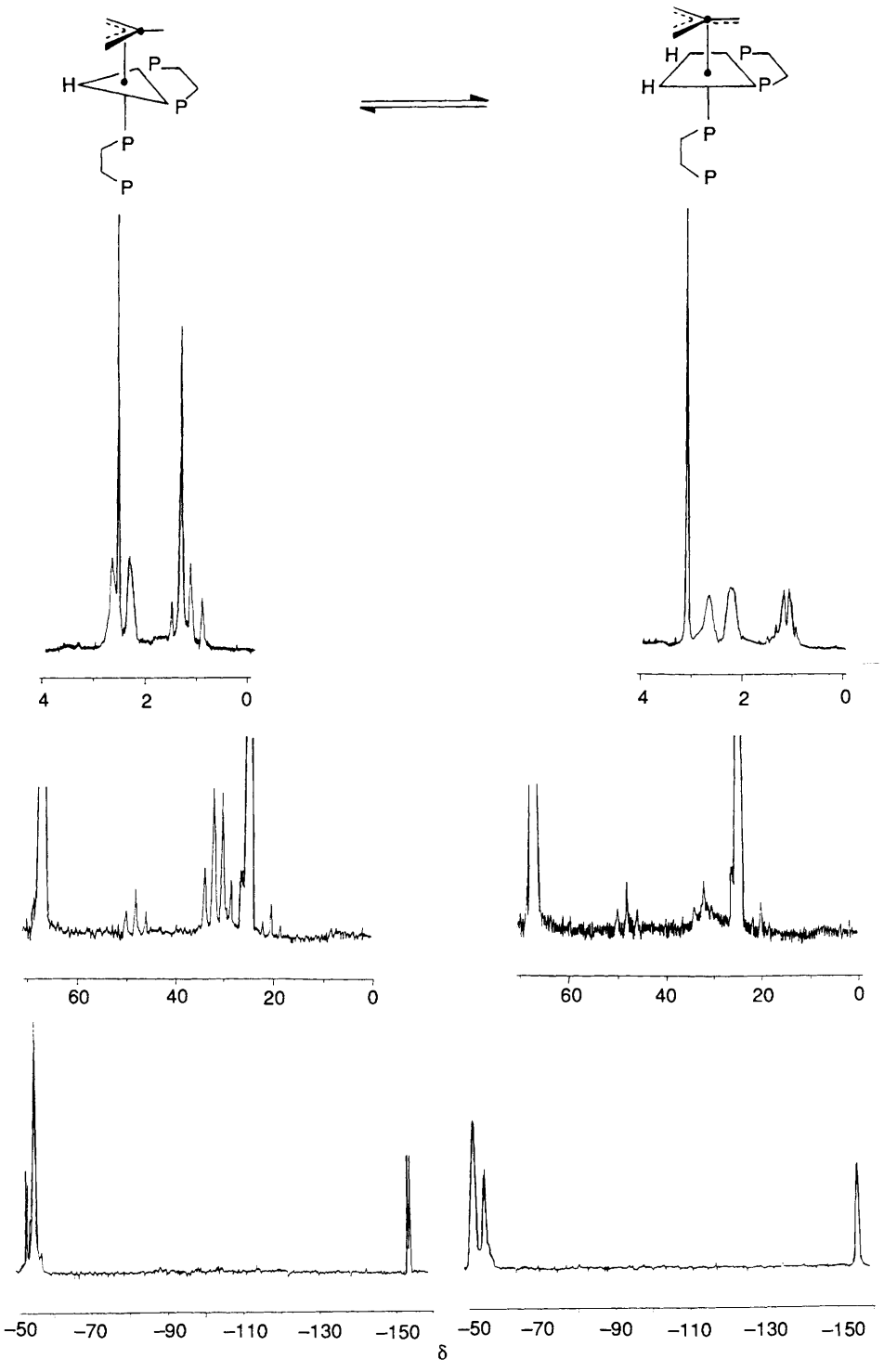


Fig. 1 Proton (top), ^{13}C (middle) and ^{31}P NMR spectra of [MoH(η^3-C_4H_7)(dppe-κ^2P)(dppe-κP)] (left, 25 °C) and [MoH_2(η^4-C_4H_6)(dppe-κ^2P)(dppe-κP)] (right, −80 °C)

hydrocarbon is produced in the reaction with HCl. This is due to the rapid dimerisation of 2-methylpropene to give 2,4,4-trimethylpentene, $Bu^tCH_2C(Me)CH_2$. Proton NMR spectroscopic studies of the reaction mixture formed with 5 mol equivalents of HCl showed {besides the peaks attributable to [MoH_2Cl_2(dppe-$\kappa^2P)_2$]} signals at δ 0.91 (s, Bu^t) and 1.93 [d, Me, J(HH) = 69 Hz] identical to those observed for an authentic sample of $Bu^tCH_2C(Me)CH_2$. These signals are also observed for a sample where the solvent has been allowed to evaporate under ambient conditions, indicating the non-volatility of this compound.

2-Methylpropene is well known to dimerise rapidly and this process can be catalysed by acid.[10] However, under the conditions of our experiments, GLC and ^1H NMR spectroscopy showed that the amount of 2-methylpropene released in the protonation reaction would not be significantly dimerised even after 2 h, with [HCl] = 100 mmol dm^{-3}. Consequently we propose that the dimerisation is catalysed by a metal-containing species (see below).

Mechanism of the Reaction between [MoH(η^3-C_4H_7)(dppe-κ^2P)(dppe-κP)] *and* HCl.—When mixed in a stopped-flow

apparatus the reaction of the parent complex with HCl is observed to occur in three distinct stages as shown by the typical absorbance *vs.* time curve in Fig. 3. Thus, initially there is a rapid absorbance decrease, complete within the dead-time of the apparatus (2 ms), to generate a detected intermediate which then proceeds to form $[MoH_2Cl_2(dppe\text{-}\kappa^2P)_2]$ in the two succeeding exponential decays.

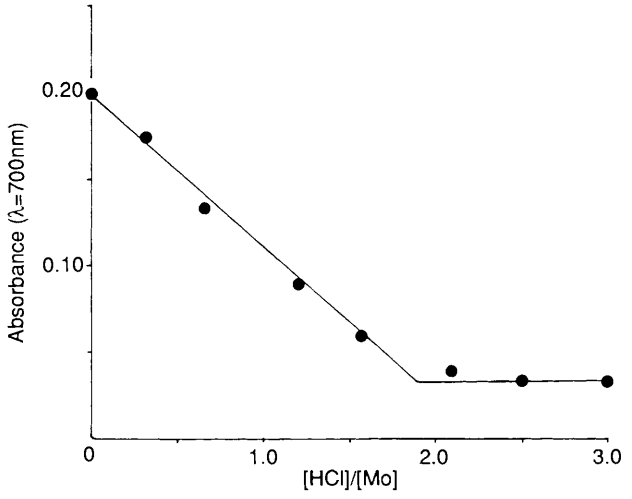


Fig. 2 Spectrophotometric titration for the reaction of anhydrous HCl with $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ in thf at 25.0 °C. Analysis performed at λ = 700 nm, [Mo] = 1.0 mmol dm^{-3}

The stoichiometry of the initial rapid stage was established by measuring the magnitude of the absorbance change at sub-stoichiometric concentrations of HCl. As shown in Fig. 3 this initial stage corresponds to the consumption of 1 mol equivalent of HCl. The visible absorption spectrum of the intermediate thus generated is also shown in Fig. 3.

The subsequent decay of the detected intermediate cannot be fitted to a single exponential, but rather the data require two exponentials to be fitted adequately. At a constant concentration of HCl, the derived values of k_{obs} (pseudo-first-order rate constants) are independent of the complex concentration {[Mo] = (5.0–0.3) × 10^{-4} mol dm^{-3}} confirming the first-order dependence on the concentration of molybdenum complex for the two steps.

The two exponentials exhibit distinctly different dependences on the concentration of HCl. The faster of the two phases shows a complicated dependence as shown in Fig. 4. Thus at low concentrations of HCl the reaction rate exhibits a first-order dependence on the acid concentration, but at high concentrations it becomes independent of the acid concentration. These data can be analysed by the normal double-reciprocal plot,[11] and hence the rate equation (2) describing the acid

$$k_{obs} = (a + b[HCl])/(1 + c[HCl]) \quad (2)$$

dependence shown can be derived, where $a = 0.7 \pm 0.1$ s^{-1}, $b = (1.5 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1} and $c = 52.2 \pm 2$ dm^3 mol^{-1}. In the presence of DCl an identical rate equation is observed with $a = 0.55 \pm 0.1$ s^{-1}, $b = (1.1 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1} and $c = 54.9 \pm 2$ dm^3 mol^{-1}. The slower phase occurs

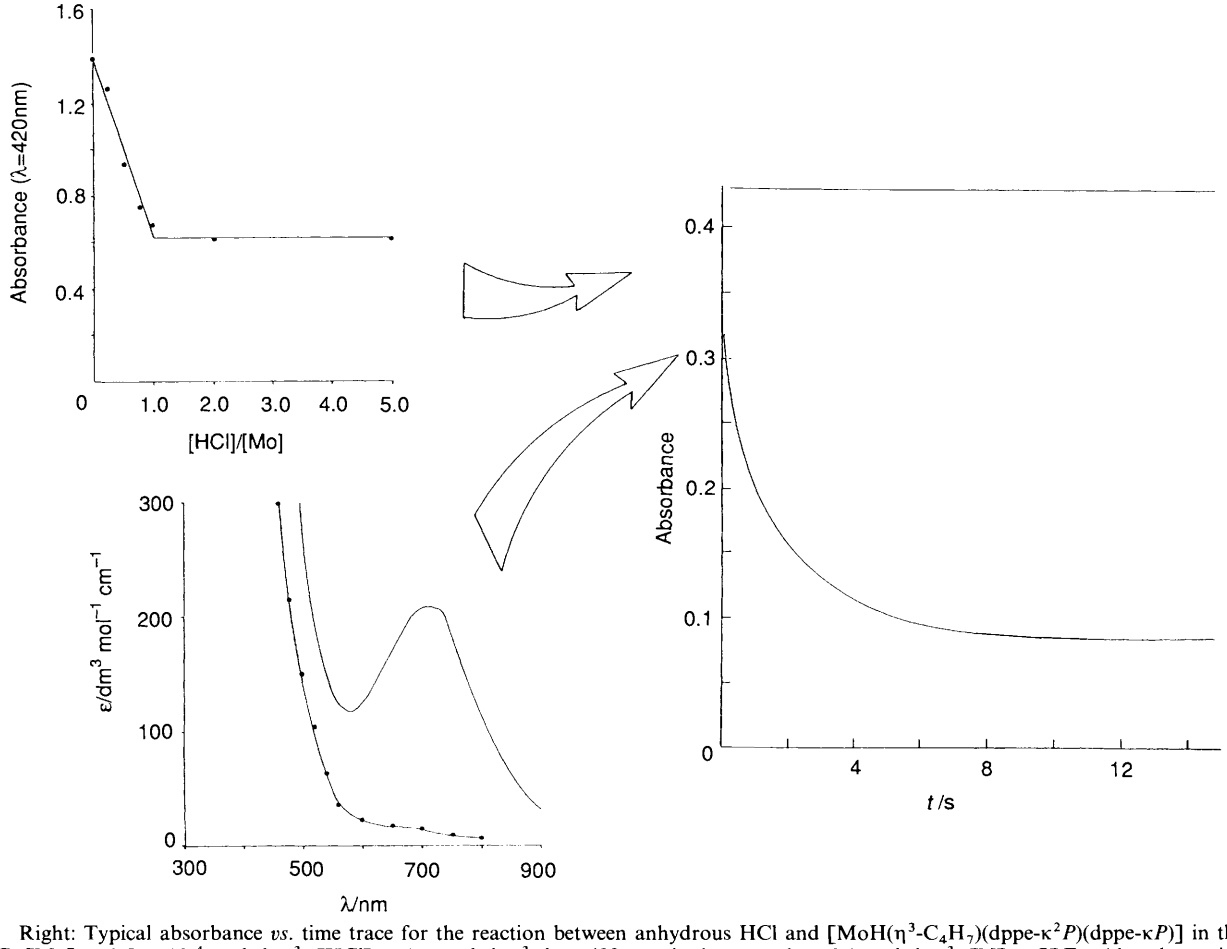


Fig. 3 Right: Typical absorbance *vs.* time trace for the reaction between anhydrous HCl and $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ in thf at 25.0 °C, [Mo] = 0.5 × 10^{-4} mol dm^{-3}, [HCl] = 1 mmol dm^{-3}, λ = 420 nm, ionic strength = 0.1 mol dm^{-3}, $[NBu^n_4]BF_4$. Also shown is the absorbance of the parent complex in the absence of acid, $A = 0.43$. Left: top shows a spectrophotometric titration to determine the stoichiometry of the initial rapid absorbance change. Bottom shows the visible absorption spectra of $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ (——) and of the detected intermediate, which is a mixture of $[MoH_2(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]^+$ and $[MoH_2(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(Hdppe\text{-}\kappa P)]^{2+}$ (●)

at a rate which is independent of acid with the corresponding rate equation (3), $d = 0.30 \pm 0.03\ s^{-1}$ and is unchanged in the presence of DCl.

$$k^{1}_{obs} = d \qquad (3)$$

The simplest mechanism with which this behaviour is consistent is shown in Scheme 2. Addition of acid to [MoH(η^3-C_4H_7)(dppe-κ^2P)(dppe-κP)] results in rapid protonation of two sites: the metal to give [MoH_2(η^3-C_4H_7)(dppe-κ^2P)(dppe-κP)]$^+$ and the pendant phosphorus, [MoH_2(η^3-C_4H_7)(dppe-κ^2P)(Hdppe-κP)]$^{2+}$. It is the protonation at the metal which gives rise to the large absorbance change (*i.e.* the initial rapid phase complete within the dead-time of the stopped-flow apparatus, Fig. 3), and the change in reactivity of the complex which ensues. Protonation of the pendant phosphorus atom which is remote from the metal-based, chromophore site is unlikely to give rise to these manifestations. Another distinction between the two sites of protonation is that protonation of the metal is essentially irreversible (*i.e.* proton dissociation from molybdenum is slow), whereas protonation of the pendant phosphorus is a readily reversible equilibrium. Consequently, at any concentration of HCl there is an equilibrium mixture consisting of [MoH_2(η^3-C_4H_7)(dppe-κ^2P)(dppe-κP)]$^+$ and [MoH_2(η^3-C_4H_7)(dppe-κ^2P)(Hdppe-κP)]$^{2+}$, the latter species predominating at high acid concentrations.

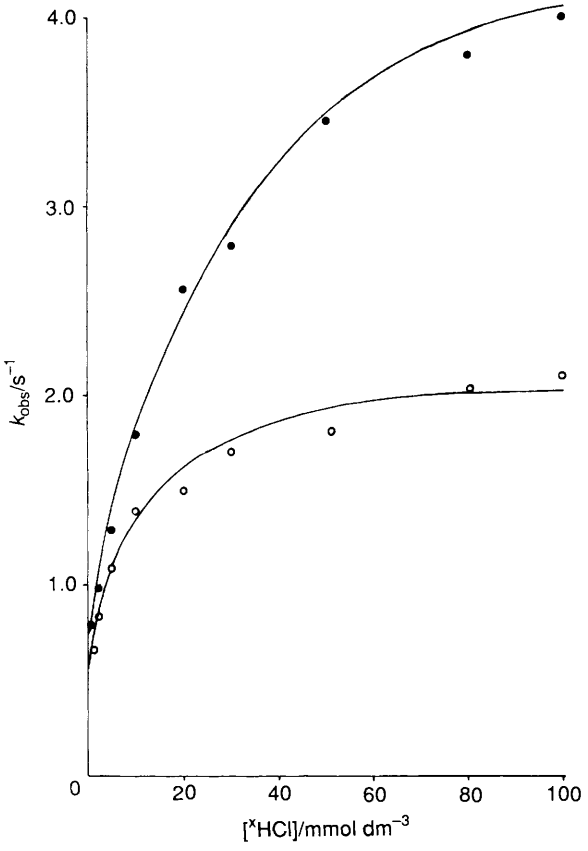


Fig. 4 Dependence of the pseudo-first-order rate constant (k_{obs}) on the concentration of anhydrous HCl for the reaction of acid with [MoH(η^3-C_4H_7)(dppe-κ^2P)(dppe-κP)] ([Mo] = 1.0×10^{-4} mol dm^{-3}) in thf at 25.0 °C, ionic strength = 0.1 mmol dm^{-3}, [NBu^n_4]BF_4, λ = 420 nm. Data points correspond to the faster of the two phases (see text) with HCl (●) or DCl (○). Curves drawn are those defined by equation (2) and the parameters listed in the text

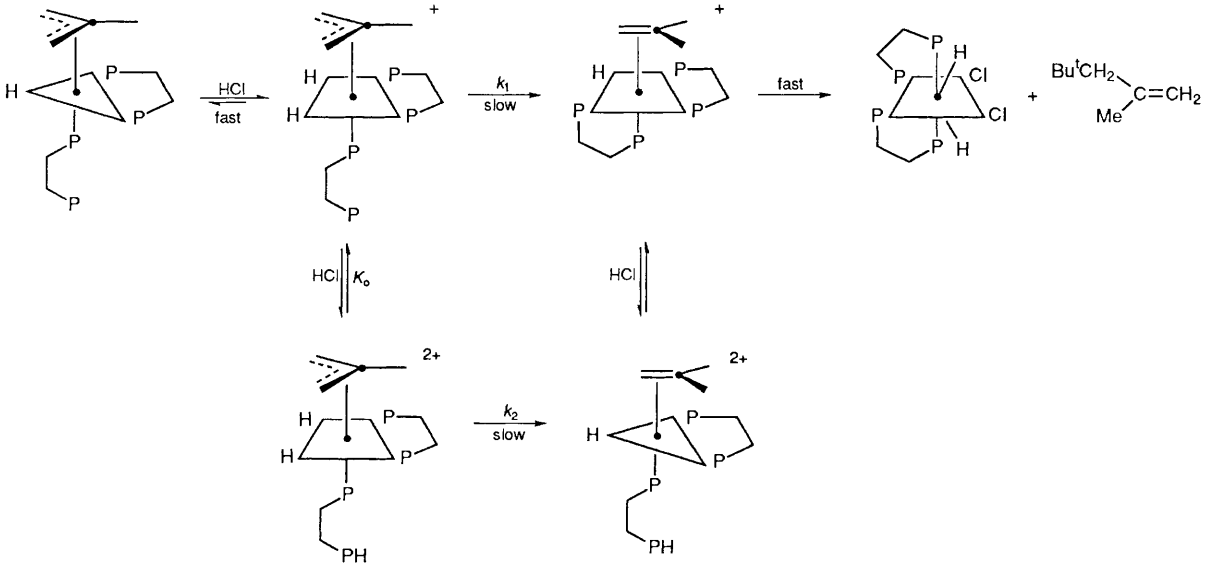
Subsequent rate-limiting hydride migration onto the 2-methylallyl ligand in these two equilibrium species gives [MoH(η^2-Me_2CCH_2)(dppe-κ^2P)$_2$]$^+$ and [MoH(η^2-Me_2CCH_2)(dppe-κ^2P)(Hdppe-κP)]$^{2+}$ respectively. Presumably the initial protonation at the metal renders these migration reactions more facile than in the parent complex. We also assume that chelate formation assists the migration, since nucleophilic attack has been shown to aid migrations in other reactions.[12] Rapid proton loss from the pendant phosphorus in [MoH(η^2-Me_2CCH_2)(dppe-κ^2P)(Hdppe-κP)]$^{2+}$ and subsequent ring closure gives [MoH(η^2-Me_2CCH_2)(dppe-κ^2P)$_2$]$^+$.

Assuming that the protonation and deprotonation of the pendant phosphorus is a rapidly established equilibrium and that the migration steps k_1 and k_2 are rate limiting, the acid dependence of the kinetics for the conversion of [MoH_2(η^3-C_4H_7)(dppe-κ^2P)(dppe-κP)]$^+$into[MoH(η^2-Me_2CCH_2)(dppe-κ^2P)$_2$]$^+$ is given by equation (4). This is of the same form

$$k_{obs} = \frac{k_1 + k_2K_0[HCl]}{1 + K_0[HCl]} \qquad (4)$$

as that observed experimentally and comparison of equations (2) and (4) gives the values $k_1^H = 0.7 \pm 0.1\ s^{-1}$, $k_2^H = 2.9 \pm 0.2\ s^{-1}$, $K_0^H = 52.2 \pm 2\ dm^3\ mol^{-1}$; and from the DCl studies, $k_1^H/k_1^D = 1.27 \pm 0.05$, $k_2^H/k_2^D = 1.50 \pm 0.05$, and $K_0^H/K_0^D = 0.95 \pm 0.07$.

This mechanism, and in particular the rate-limiting migration step, is able to rationalise the following experimental



Scheme 2

observations. (1) Rate constants associated with apparently acid-independent steps (k_1 and k_2) exhibit primary isotope effects, since these elementary reactions are due to migration of hydrido groups, which are themselves derived from the acid. (2) Similar isotope effects are observed for k_1 and k_2, consistent with these steps being analogous reactions. (3) Only a small isotope effect is associated with the equilibrium constant, K_0.[13] (4) The stoichiometry of the initial rapid phase consumes 1 mol equivalent of HCl to form the intermediate $[MoH_2(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]^+$, and (5) the expected protonation chemistry of a pendant phosphorus atom.

The details of the subsequent formation of $Bu^tCH_2C(Me)=CH_2$ from $[MoH(\eta^2\text{-}Me_2CCH_2)(dppe\text{-}\kappa^2P)_2]^+$ are not entirely clear. Although a third phase is observed when monitoring the reaction (Fig. 3), the kinetics of this final phase is too simple to define unambiguously the formation of the alkene [equation (3)].

An important, and revealing, result in understanding the release of alkene from $[MoH(\eta^2\text{-}Me_2CCH_2)(dppe\text{-}\kappa^2P)_2]^+$ is that this system does not polymerise $Me_2C=CH_2$, only dimerises it. This was established by studying the protonation reactions of $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ in the presence of 1 mol equivalent of $Me_2C=CH_2$ in a closed vessel. Quantitative analysis of the gaseous product by GLC showed that 1 mol equivalent of $Me_2C=CH_2$ remained. This result indicates that the formation of $Bu^tCH_2C(Me)=CH_2$ results from a rapid bimolecular reaction between two $[MoH(\eta^2\text{-}Me_2CCH_2)(dppe\text{-}\kappa^2P)_2]^+$, possibly to transfer an alkene as shown in equation (5). Subsequent intramolecular coupling of the two

$$2[MoH(\eta^2\text{-}Me_2CCH_2)(dppe\text{-}\kappa^2P)_2]^+ \xrightarrow{HCl} [MoH(\eta^2\text{-}Me_2CCH_2)_2(dppe\text{-}\kappa^2P)_2]^+ + [MoH_2Cl_2(dppe\text{-}\kappa^2P)_2] \quad (5)$$

co-ordinated alkenes, and dissociation of $Bu^tCH_2C(Me)=CH_2$ from the resulting complex, would complete the reaction, equation (6). We believe that the $Bu^tCH_2C(Me)=CH_2$ is formed,

$$[MoH(\eta^2\text{-}Me_2CCH_2)_2(dppe\text{-}\kappa^2P)_2]^+ \longrightarrow [MoH\{\eta^2\text{-}Bu^tCH_2C(Me)CH_2\}(dppe\text{-}\kappa^2P)_2]^+ \quad (6)$$

and does not undergo further polymerisation, because the bulky *tert*-butyl substituent renders this alkene extremely labile, and hence is rapidly lost from the metal site before further polymerisation can ensue.

Until we can isolate species such as $[MoH(\eta^2\text{-}Me_2CCH_2)_2(dppe\text{-}\kappa^2P)_2]^+$, which are capable of undergoing intramolecular coupling reactions in the presence of acid, the final stages of this reaction will have to remain speculative. Certainly, the observed kinetics for this last phase is consistent with either of the elementary steps we have proposed, that is the rate-limiting coupling reaction or rate-limiting dissociation of $Bu^tCH_2C(Me)=CH_2$.

Previously we have summarised our findings on the sites of protonation (metal *versus* ligand) of a variety of metal complexes.[14] The work presented in this paper shows that the factors discriminating between the two sites are very subtle. In a system closely analogous to that described in this paper, protonation of $[MoH(\eta^3\text{-}C_3H_5)(dppe\text{-}\kappa^2P)_2]$ occurs at both the metal and the hydrocarbon residue in parallel reactions.[3] However, kinetic studies on $[MoH(\eta^3\text{-}C_4H_7)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]$ indicate a pathway involving protonation of the metal exclusively. Both the methyl substituent of the allyl residue, and the 'incomplete' phosphine environment in the latter complex, are, apparently, sufficient to promote protonation of the metal or disfavour protonation of the hydrocarbon ligand.

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