Protonation of an internal alkyne produces a terminal alkene: reactivity of [Mo(η²-MeCCMe)(Ph₂PCH₂CH₂PPh₂)₂]

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Structurally defined [Mo(η²-MeCCMe)-(Ph₂PCH₂CH₂PPh₂)₂] reacts with anhydrous HCl in thf to give predominantly *trans*-[MoCl₂(Ph₂PCH₂CH₂PPh₂)₂] with but-1-ene (69 ± 6%) and *cis*-but-2-ene (10 ± 2%); in addition, some [MoH₂Cl₂(Ph₂PCH₂CH₂PPh₂)₂] and but-2-yne (21 ± 5%) are produced; the mechanistic features by which protonation of an internal alkyne yields a terminal alkene are enumerated.

The stereoselective protonation of coordinated alkynes to give the corresponding *cis*- or *trans*-alkenes has been described, and the origins of this stereospecificity shown to be a consequence of protonation at the metal or the alkyne ligand, respectively.[1–3] Herein, we report the first example of the protonation of a coordinated internal alkyne to give a terminal alkene. The identification of the minor hydrocarbons produced, together with a kinetic analysis of the reaction, defines some of the features necessary for a metal site to accomplish this type of transformation.

The complex, [Mo(η²-MeCCMe)(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂), is isolated (2–5% yield) as dark-green (almost black) needles, from the reduction of a mixture of [MoCl₄(dppe)], dppe and but-2-yne in thf. X-Ray crystallographic analysis† confirms the formulation established on the basis of spectroscopic studies.‡ The structure in Fig. 1 shows a five-coordinate Mo atom with trigonal-bipyramidal geometry. The alkyne ligand is bound side-on, parallel to the *trans* P–Mo–P vector with the outer Me groups each bent *ca.* 47° from linearity.

Thus, it has been established unambiguously that during this preparation no gross change to the hydrocarbon occurs. However, upon protonation rapid rearrangement of this internal alkyne to form a terminal alkene occurs. Reaction of [Mo(η²-MeCCMe)(dppe)₂] with an excess of anhydrous HCl in thf gives but-1-ene (69 ± 6%), *cis*-but-2-ene ((10 ± 2%) and but-2-yne (21 ± 5%) (all detected by GLC, using a Poropak Q column operating at 130 °C), with the metal product being predominantly *trans*-[MoCl₂(dppe)₂] (isolated), together with some [MoH₂Cl₂(dppe)₂] (detected in the reaction solution by $^{31}P\{^{1}H\}$ NMR spectroscopy:[4] δ −70, −98). This product distribution does not depend on the concentration of acid, and accounts for the quantitative transformation of [Mo(η²-MeCCMe)(dppe)₂].

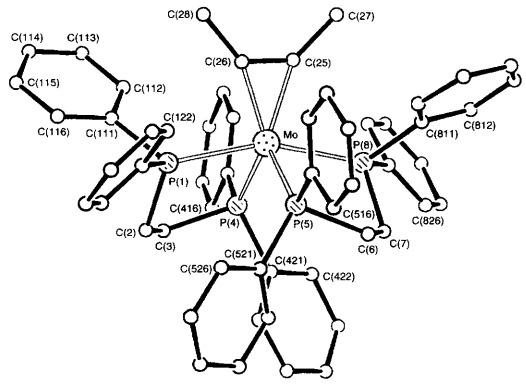


Fig. 1 View of the molecule of [Mo(η²-MeCCMe)(dppe)₂]. Selected molecular dimensions: mean axial Mo–P 2.456(10), mean equatorial Mo–P 2.421(15), Mo–C(25) 2.081(13), Mo–C(26) 2.044(13), C(25)–C(26) 1.290(14) Å; *trans* P–Mo–P 158.0(1), mean chelating P–Mo–P 78.1(5), C(27)–C(25)–C(26) 135.5(12), C(25)–C(26)–C(28) 129.6(12)°.

Stopped-flow spectrophotometry shows that the hydrocarbon mixture is produced very rapidly {within 5 s of adding the acid to [Mo(η²-MeCCMe)(dppe)₂]} and that two protons must be added to the complex before the products are formed. In the absence of acid but-2-yne is the only hydrocarbon product, and is released slowly over the course of *ca.* 5 h.

The absorbance–time trace shown in Fig. 2, illustrates the variation of the [Mo(η²-MeCCMe)(dppe)₂] concentration in the first 5 s after the addition of an excess of anhydrous HCl: an initial protonation of the complex (complete within the dead time of the apparatus) is followed by an exponential decay to give the products. The kinetics of the slower stage exhibit a first-order dependence on the concentration of [Mo(η²-MeCCMe)(dppe)₂] and a non-linear dependence on the concentration of HCl, as shown in Fig. 2.

This behaviour is consistent with the mechanism shown in Scheme 1, which uniquely rationalises two key observations concerning the products formed in this reaction: (i) but-1-ene and *cis*-but-2-ene, but no *trans*-but-2-ene, are produced in this reaction, and (ii) some but-2-yne is always released.

Initial, rapid protonation of [Mo(η²-MeCCMe)(dppe)₂] most likely occurs at the metal to generate [MoH(η²-MeCC-

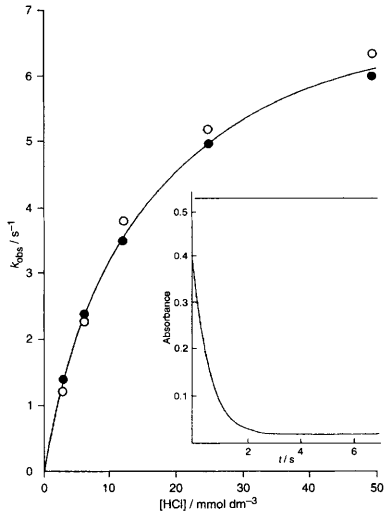


Fig. 2 Dependence of the observed rate constant, k_{obs}, on the concentration of acid for the reaction of [Mo(η²-MeCCMe)(dppe)₂] (0.05 mmol dm^{-3}) with anhydrous HCl (●) and DCl (○) in thf at 25.0 °C. Curve drawn is that defined by eqn. (1). Insert: stopped-flow absorbance–time trace for the reaction of [Mo(η²-MeCCMe)(dppe)₂] (0.05 mmol dm^{-3}) with anhydrous HCl (6.0 mmol dm^{-3}) in thf at 25.0 °C, λ = 450 nm. The curve is an excellent fit to the single exponential A_t = 0.018 + 0.40 exp (−2.1t). The absorbance of [Mo(η²-MeCCMe)(dppe)₂] is shown at A = 0.53, illustrating the absorbance jump, complete within the dead-time (2 ms) of the apparatus, upon mixing the reactants.

Me)(dppe)$_2$]$^+$ within 2 ms. Further protonation can now occur at either the metal or the alkyne, as has been observed for a variety of alkene or alkyne complexes.[1] Addition of the second proton to the metal forms [MoH$_2$(η^2-MeCCMe)(dppe)$_2$]$^{2+}$, and labilises the site to dissociation of but-2-yne with formation of [MoH$_2$Cl$_2$(dppe)$_2$]. However, this is the minor pathway, accounting for only *ca.* 20% of the product. The major pathway involves addition of the second proton to the alkyne and formation of the *trans*-vinyl species, [MoH(CMeCHMe)(dppe)$_2$]$^{2+}$, a reaction which is common for coordinated alkynes.[5]

[MoH(CMeCHMe)(dppe)$_2$]$^{2+}$ has two features which dictate its reactivity: the metal is electron deficient (formally a 14-electron species), and it is sterically congested because of the bulky phenyl substituents on the phosphine ligands. Consequently, it is difficult for nucleophiles to bind to the metal and relieve the electron deficiency. In these circumstances it is likely that the only way in which the metal can increase its formal electron count is by forming agostic hydrogen interactions with the methyl substituents on the vinyl ligand.[6] However, no such intermediate has been detected in this study and such interactions may only be transient, prior to carbon–hydrogen bond cleavage.

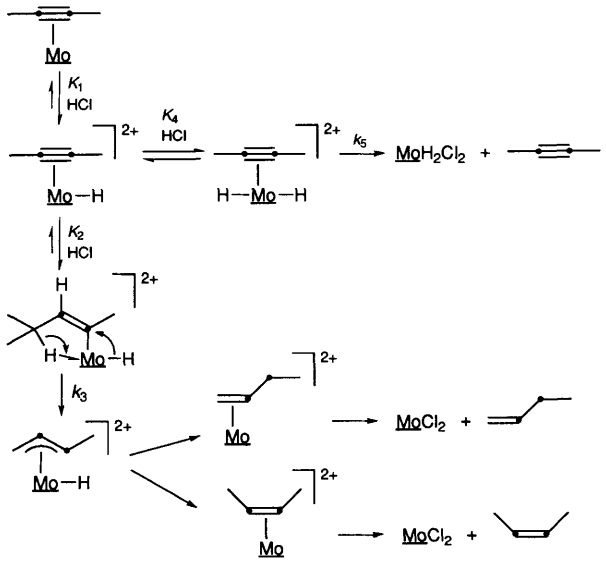
A formal 1,3-hydrogen rearrangement by intramolecular cleavage of the C–H bond and migration of the hydride ligand to the vinyl group generates the 16-electron 1-methylallyl complex. To minimise steric interactions at the metal, it is likely that the methyl substituent in the 1-methylallyl ligand is *exo*. Only two hydrocarbons can be produced from [MoH(η^3-C$_4$H$_7$)(dppe)$_2$]$^{2+}$: but-1-ene, by hydride migration to the methyl-substituted arm of the allyl group, or *cis*-but-2-ene, by migration of the hydride to the other arm. These are the only alkenes which are observed experimentally.§

The rate law associated with this mechanism is shown in eqn. (1).

$$\frac{-\mathrm{d}[\mathrm{MoH}(\eta^2\text{-MeCCMe})(\mathrm{dppe})_2^+]}{\mathrm{d}t} = \frac{(k_3K_2 + k_5K_4)[\mathrm{HCl}][\mathrm{MoH}(\eta^2\text{-MeCCMe})(\mathrm{dppe})_2^+]}{1 + (K_2 + K_4)[\mathrm{HCl}]} \quad (1)$$

From consideration of the hydrocarbon product distribution and the observed kinetics the following values can be calculated: $k_3K_2 = (3.5 \pm 0.3) \times 10^2$ dm^3 mol^{-1} s^{-1}; $k_5K_4 = 92.8 \pm 3$ dm^3 mol^{-1} s^{-1} and $(K_2 + K_4) = 44.2 \pm 3$ dm^3 mol^{-1}.

The conversion of a coordinated alkyne to an alkene by a sequence of electron- and proton-transfer reactions is a relatively common reaction.[1–3,5] In addition, relatively slow rearrangement of coordinated alkynes to give allene complexes {*e.g.* [Re(CH$_2$CCHPh)Cl(dppe)$_2$]} have been reported.[7] However, it is only in this study that some of the features necessary for a site to mediate the protonation of an internal alkyne to give a terminal alkene have been highlighted. These features are: (i) it is sterically congested to inhibit attack of nucleophiles at the metal whilst permitting access to protons; (ii) diprotonation can occur (probably monoprotonation of both the metal and the alkyne); and, (iii) after diprotonation, the complex is capable of inducing carbon–hydrogen bond cleavage. Finally, the role of the proton in this transformation should not be underestimated. Not only does the small size of the proton mean that it can penetrate the steric barrier imposed by the bulky ligands, but also it is the proton which converts the coordinated alkyne into a vinyl ligand and is the source of the hydride ligand in [MoH(CMeCHMe)(dppe)$_2$]$^{2+}$. Effectively the proton 'primes' the site for the rapid rearrangement to form the terminal alkene.



Scheme 1 Mo = Mo(dppe)$_2$

Footnotes

† *Crystal data* for [Mo(η^2-MeCCMe)(dppe)$_2$]: C$_{56}$H$_{54}$MoP$_4$, M = 946.8, triclinic, space group $F1$ (equiv. to no. 2; preferred to $P1$ because no primitive cell has near-orthogonal dimensions), a = 13.021(1), b = 23.458(3), c = 31.261(3) Å, α = 90.291(9), β = 94.038(7), γ = 98.015(8)°, U = 9430(2) Å^3, Z = 8, D_c = 1.334 g cm^{-3}, $F(000)$ = 3936, μ(Mo-Kα) = 4.5 cm^{-1}, λ(Mo-Kα) = 0.71069 Å. 2820 Unique reflections (θ_{max} = 18.5°), 1787 'observed' with $I > 2\sigma(I)$. Structure solved by heavy-atom method (in SHELX[8]); refinement by full-matrix least-squares methods (on F^2, in SHELXL-93[9]) to R = 0.094 and wR_2 = 0.111 for all data weighted $w = \{\sigma(F^2)^2 + 37.8P\}^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/190.

‡ *Selected data*: Elemental analysis (%): C: 71.0 (71.0); H, 5.9 (5.7). Calculated values in parentheses. ^{1}H NMR (Me$_4$Si): δ 1.27 (3, s, CH$_3$CC), 2.32 (3 s, CH$_3$CC), 2.5–3.0 (8, br, PCH$_2$CH$_2$P), 6.1–7.9 (40, m, C$_6$H$_5$). ^{31}P NMR [(MeO)$_3$P]: δ −42.1 (s), −48.3 (s). ^{13}C NMR (Me$_4$Si): δ 21.0 (*C*H$_3$CC*C*H$_3$ {+}), 30.0 (PCH$_2$CH$_2$P {−}), 127–135 (C$_6$H$_5$ {+}), 144 (br, CH$_3$CCCH$_3$ {0}). Symbols in braces show orientation of resonance in ^{13}C DEPT experiments.

§ An alternative mechanism for the internal alkyne to terminal alkene reaction involves initial formation of [Mo(η^2-MeCHCHMe)(dppe)$_2$]$^{2+}$, then isomerisation (*via* a methylallyl intermediate). The distinction between this mechanism and the one shown in Scheme 1 is only the timing of the carbon–hydrogen cleavage. It is not possible to distinguish between these two descriptions, but the mechanism shown in Scheme 1 is preferred since a concerted 1,3-hydrogen atom transfer step maintains a 16-electron count for the metal, whilst the stepwise pathway involves the 14-electron species, [Mo(η^2-MeCHCHMe)(dppe)$_2$]$^{2+}$.

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Received, 13th June 1996; Com. 6/04158B