

The Formation of Metal Hydrido Complexes *via* Protonation of Coordinated Ethylene: Relative Rates of Protonation of Coordinated Ethylene and Metal

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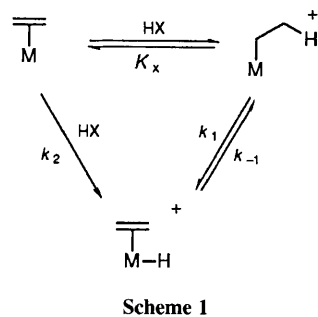
The formation of $[\text{MH}(\text{C}_2\text{H}_4)_2(\text{dppe})_2]^+$ from the reaction of *trans*- $[\text{M}(\text{C}_2\text{H}_4)_2(\text{dppe})_2]$ with HX (M = Mo or W, dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, X = Cl or Br) has been studied in tetrahydrofuran at 25 °C by stopped-flow spectrophotometry, and shown to occur by two pathways: the slow direct protonation of the metal, and the rapid protonation of the ethylene ligand followed by relatively slow intramolecular β -hydrogen migration from the derived ethyl ligand to the metal.

Our understanding of the protonation of alkene complexes is now well advanced: the sites at which the proton ultimately resides,¹ the stereochemistry of the addition in polyene complexes,² and the intimate details of the interconversion mechanisms between the alkene, hydride species and the corresponding alkyl complex.³ However, although deuteration studies can indicate those atoms (both carbon and metal) at which exchange has taken place, there has been no kinetic study which defines the relative rates of protonation at the various sites. We report herein a study on the protonation of

trans- $[\text{W}(\text{C}_2\text{H}_4)_2(\text{dppe})_2]$ (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) in tetrahydrofuran (thf) [eqn. (1)], which for the first time defines the relative rates of protonation of the metal and the hydrocarbon moiety, and shows that the final residence of the proton is not the most rapidly protonated site.



The product of reaction (1)⁴ has a static, pentagonal bipyramidal structure at 25 °C as shown by its ¹H NMR spectrum [δ 0.19, triplet of triplets; $J(\text{P}^1\text{-H}) = 61.3$ Hz,



$J(\text{P}2\text{-H}) = 11.1 \text{ Hz}$, (W-H)] and ^{31}P NMR spectrum [$\delta -88.6$ to -90.4 and $\delta -127.6$ to -129.4 , symmetrical multiplets, AA'XX' pattern (PPh₂)].[†] Since this system is free of the complications associated with the product ethylene, hydride species interconverting to the corresponding ethyl species (*i.e.* k_{-1} in Scheme 1 is negligibly small), it is a good choice for studying the rates of protonation at the metal and coordinated ethylene.

When *trans*-[W(C₂H₄)₂(dppe)₂] and anhydrous HCl, under an atmosphere of argon, are mixed in thf on a stopped-flow apparatus at 25 °C, the reaction is observed to proceed in two distinct phases: an initial absorbance jump complete within the dead-time of the stopped-flow apparatus (2.0 ms), followed by a single exponential absorbance decay to give the hydrido product. Both the magnitude of the initial absorbance jump and the rate associated with the exponential absorbance decay depend on the concentration of acid. Analysis of the extent of the initial absorbance jump as a function of the concentration of HCl is shown in Fig. 1 (insert), from which it is clear that the rapid reaction occurring within the dead-time of the stopped-flow apparatus corresponds to a single protonation of the tungsten complex ($K_{\text{Cl}} = 4.1 \pm 0.3 \text{ dm}^3 \text{ mol}^{-1}$). The kinetics for the subsequent decay of this equilibrium mixture to give [WH(C₂H₄)₂(dppe)₂]⁺ exhibit a simple first-order dependence on the concentration of tungsten complex and a dependence on the concentration of acid as shown by Fig. 1 (main) and eqn. (2).

$$k_{\text{obs}} = (0.15 \pm 0.02) + (2.0 \pm 0.1) \times 10^2 [\text{HCl}] \quad (2)$$

These data are consistent with the mechanism shown in Scheme 1. The most rapidly ($k > 1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) protonated residue on *trans*-[W(C₂H₄)₂(dppe)₂] is the ethylene ligand, to produce the corresponding ethyl complex. However, although this protonation is rapid, even at the highest concentrations of acid used, stoichiometric concentrations of the ethyl complex are not produced ($K_{\text{Cl}} = 4.1 \pm 0.3 \text{ dm}^3 \text{ mol}^{-1}$). Consequently the subsequent exponential absorbance decay corresponds to the reactions of an equilibrium mixture of the ethyl complex and parent ethylene complex. Formation of the hydrido product from this equilibrium mixture can occur by the relatively slow, but irreversible, protonation of *trans*-[W(C₂H₄)₂(dppe)₂] at the metal [$k_2 = (2.0 \pm 0.1) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{\text{H}}/k_{\text{D}} = 2.43$], or by β -hydrogen atom migration from the ethyl complex ($k_1 = 0.15 \pm 0.02 \text{ s}^{-1}$). An analogous behaviour is seen in the reaction with HBr, the major differences being: (i) a larger concentration of HCl is required to produce the same magnitude of absorbance jump as that observed with HBr [$K_{\text{Br}} = (2.6 \pm 0.2) \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$], and (ii) the rate constant for direct protonation of the tungsten by HBr [$k_2 = (4.7 \pm 0.4) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_{\text{H}}/k_{\text{D}} = 1.10$] is faster than with HCl. Both of these observations are consistent with the non-leveling of HCl and HBr in thf, and the greater strength of the latter acid in

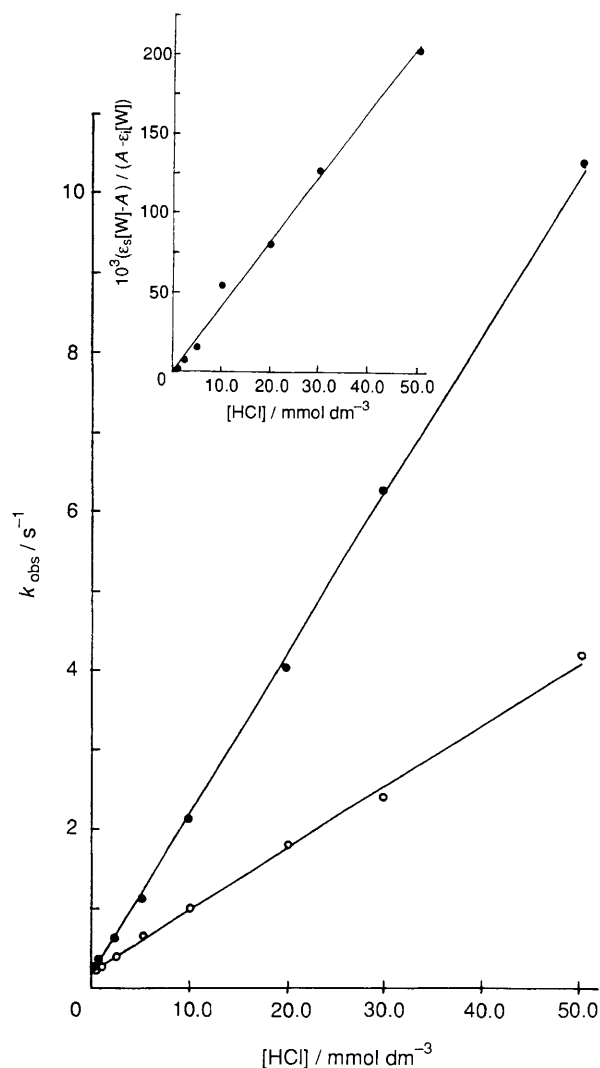


Fig. 1 Dependence of k_{obs} on the concentration of acid for the reaction of *trans*-[W(C₂H₄)₂(dppe)₂] with HCl (●) or ²HCl (○) in thf at 25 °C. Graph of $(\epsilon_s[\text{W}] - A)/(A - \epsilon_i[\text{W}])$ against the concentration of HCl, at 25 °C in thf, where A = measured initial absorbance (after 2.0 ms) determined at the particular acid concentration, $[\text{W}]$ = concentration of [W(C₂H₄)₂(dppe)₂] ($1 \times 10^{-4} \text{ mol dm}^{-3}$), ϵ_s = absorption coefficient of [W(C₂H₄)₂(dppe)₂] ($5.50 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and ϵ_i = absorption coefficient of ethyl complex ($2.00 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at $\lambda = 400 \text{ nm}$. The value of ϵ_i was determined from the maximum absorbance jump measured in the studies with HBr.

thf.⁵ This variation of the acid strengths also explains, at least in part, the variation in the deuterium isotope effect on the reaction rate. It is to be expected that the rate of β -hydrogen atom migration (k_1) is independent of the nature of the acid, but the rapidity of the reaction with HBr precludes an accurate determination of k_1 with this acid.

Consistent with the proposed rapid protonation and deprotonation of the coordinated ethylene residues in *trans*-[W(C₂H₄)₂(dppe)₂] is the observation (by ²H NMR spectroscopy) that deuterium is incorporated into the ethylene ligands during the reaction of the tungsten complex with ²HBr.

The mechanistic behaviour shown in Scheme 1 is not restricted to the tungsten system, but is also observed in the reactions of the analogous *trans*-[Mo(C₂H₄)₂(dppe)₂] with HCl. Although the molybdenum system is complicated by two features: namely, the reversibility of the β -hydrogen atom migration step^{4,6} and the slow evolution of hydrocarbons, the initial stages in the reaction between *trans*-[Mo(C₂H₄)₂(dppe)₂] and HCl exhibit the characteristic

[†] Chemical shifts quoted relative to SiMe₄ (¹H NMR) and trimethyl phosphite (³¹P NMR). Spectra were recorded in [²H₈]thf (¹H) or thf (³¹P).

absorbance-time behaviour on the stopped-flow apparatus described for the tungsten analogue. The corresponding values of the elementary rate constants and equilibrium constant for the molybdenum system are: $K_{C1} = 18.0 \pm 0.1 \text{ dm}^3 \text{ mol}^{-1}$, $(k_1 + k_{-1}) = 0.22 \pm 0.01 \text{ s}^{-1}$ and $k_2 = (4.60 \pm 0.1) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_H/k_D = 1.64$.

In conclusion, we have shown that at the electron-rich 'M(dppe)₂' site, coordinated ethylene is the most rapidly protonated residue, but that the derived ethyl complex can only relatively slowly convert to the hydrido product by an intramolecular reaction. Furthermore, proton loss from the ethyl species to give the parent ethylene complex is rapid. Hence direct, and irreversible, protonation of the metal is also observed in this system, despite the fact that protonation of the metal is *at least* 100 times slower than protonation of ethylene. The direct protonation of the metal is associated with a significant primary isotope effect as expected for a rate-limiting protonation reaction. However, it seems that the isotope effect associated with the β -hydrogen atom transfer is much smaller and could not be detected in these systems. It

remains to be seen if the reactivity pattern described in this paper for *trans*-[M(C₂H₄)₂(dppe)₂] has more general applicability to the protonation of other alkene complexes.

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