A Dibasic Carbon Centre: Kinetic and Thermodynamic Studies on the Deprotonation of *trans*-[MoCl(NCH$_2$CO$_2$Me)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$

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A kinetic and thermodynamic analysis of the reaction between *trans*-[MoCl(NCHRCO$_2$Me)(dppe)$_2$]$^+$ (R = H or Me, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and MeO$^-$ shows that when R = H both NCH_2 protons are ionisable, with the pK_as of *trans*-[MoCl(NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$ (pK_a = 11.2) and *trans*-[MoCl(NCHCO$_2$Me)(dppe)$_2$] (pK_a = 11.5) being remarkably similar.

The study of the reactions of carbon acids has been a focal point for understanding the fundamental aspects of proton transfer rates.[1] In organic compounds invariably only one proton is ionisable and doubly deprotonated species are unknown, even in the presence of an excess of base. We report here that the reaction of *trans*-[MoCl(NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$[2] with MeO$^-$ in methanol at 25.0 °C involves the sequential loss of both NCH_2 protons with the equilibrium constants for the two deprotonations differing by about a factor of two.

The reactions of base with *trans*-[MoCl(NCHMeCO$_2$Me)(dppe)$_2$]$^+$, in which only one NCH proton can be lost, act as a guide on which we can judge the studies of *trans*-[MoCl(NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$. The reaction of *trans*-[MoCl(NCHMeCO$_2$Me)(dppe)$_2$]$^+$ with either NEt$_3$[†] or NaOMe was studied by stopped-flow spectrophotometry, and shows the characteristics of a reaction going to equilibrium [eqn. (1), R = Me]. Thus, the exponential absorbance–time traces have an initial absorbance corresponding to that of the cation and a final absorbance which varies with the concentration of MeO$^-$. Analysis of these data, as shown in Fig. 1, gives $K_1^{\mathrm{Me}} = (3.4 \pm 0.2) \times 10^5$ (pK_a^{Me} = 11.2). The kinetics associated with the attainment of this equilibrium are given by the rate law shown in eqn. (2). The value of K_1^{Me} derived from this rate law, $K_1^{\mathrm{Me}} = k_1^{\mathrm{Me}}/k_{-1}^{\mathrm{Me}} = (3.3 \pm 0.4) \times 10^5$, is in excellent agreement with that derived from the absorbance changes. In addition both the forward and back rates exhibit a large primary isotope effect, $k_1^{\mathrm{H}}/k_1^{\mathrm{D}} = 7.8$ $k_{-1}^{\mathrm{H}}/k_{-1}^{\mathrm{D}} = 7.2$ (uncorrected for solvent isotope effects using MeOD).

$$\textit{trans}\text{-}[\mathrm{MoCl(NCHRCO_2Me)(dppe)_2}]^+ + \mathrm{MeO^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{trans}\text{-}[\mathrm{MoCl(NCRCO_2Me)(dppe)_2}] + \mathrm{MeOH} \tag{1}$$

$$-\frac{\mathrm{d[MoNCHMeCO_2Me]}}{\mathrm{d}t} = \{(5.0 \pm 0.2) \times 10^3\,[\mathrm{MeO^-}] + (1.5 \pm 0.2) \times 10^{-2}\,[\mathrm{MeOH}]\}\,\{[\mathrm{MoNCHMeCO_2Me}] - [\mathrm{MoNCHMeCO_2Me}]_\infty\} \tag{2}$$

Analogous studies on *trans*-[MoCl(NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$ show very similar behaviour, but with very much larger absorbance changes than those observed with *trans*-[MoCl(NCHMeCO$_2$Me)(dppe)$_2$]$^+$. Analysis of the magnitude of the absorbance changes as a function of the concentration of MeO$^-$ is shown in Fig. 1 and demonstrated that both NCH_2 protons are being removed (Scheme 1). The equilibrium constant associated with the first deprotonation , $K_1^{\mathrm{H}} = (3.7 \pm 0.2) \times 10^5$ (pK_a^{H} = 11.2) is similar to that observed with *trans*-[MoCl(NCHMeCO$_2$Me)(dppe)$_2$]$^+$. Surprisingly, the equilibrium constant for the second deprotonation, $K_2^{\mathrm{H}} = (1.6 \pm 0.8) \times 10^5$ (pK_a^{H} = 11.5) is also very little different. Despite the fact that two protons are removed in this system the kinetics of this double deprotonation are similar to those

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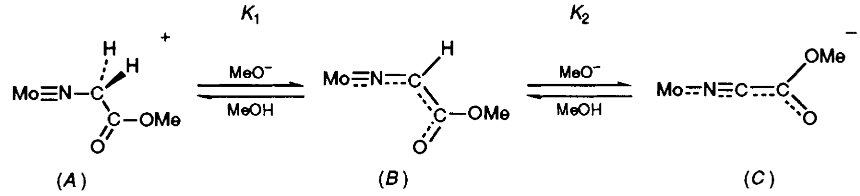
[†] The kinetics and absorbance changes in the studies with NEt$_3$ are identical to those using NaOMe provided the concentration of MeO$^-$ generated at each concentration of NEt$_3$ is calculated using pK_a^{MeOH} = 16.67[3] and p$K_a^{\mathrm{NHEt_3^+}}$ = 8.9. Both these values refer to the acid dissociation constants in methanol; the latter derived from the analysis in this paper for the studies on *trans*-[MoCl(NCHMeCO$_2$Me)(dppe)$_2$]$^+$; in water, p$K_a^{\mathrm{NHEt_3^+}}$ = 10.7.[4]



Scheme 1

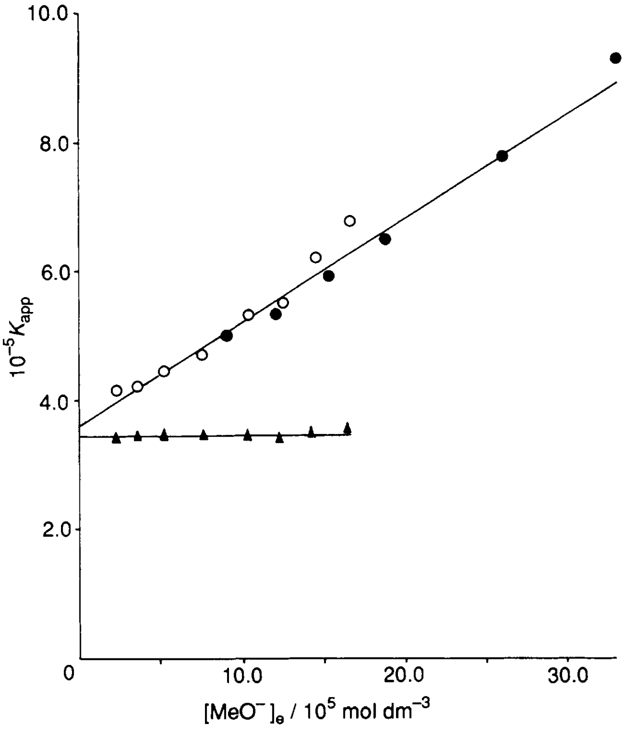


Fig. 1 Graph of K_{app} against concentration of MeO^- for the reactions of *trans*-[MoCl(NCHMeCO$_2$Me)(dppe)$_2$]$^+$ ▲, where K_{app} = [MoNCMeCO$_2$Me]$_e$[MeOH]/[MoNCHMeCO$_2$Me]$_e$[MeO$^-$]$_e$; and *trans*-[MoCl(NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$ (○, base = NEt$_3$;† ●, base = NaOMe), where K_{app} = {[MoNCHCO$_2$Me]$_e$ + [MoNCCO$_2$Me]$_e$}[MeOH]/[MoNCH$_2$CO$_2$Me]$_e$[MeO$^-$]$_e$. From the graph, $K_{app} = K_1 + K_1K_2[MeOH]_e/[MeOH]$.[8] Subscript e designates the concentration at equilibrium. All equilibrium concentrations were determined from the final absorbance of the reaction mixture at λ = 400 nm using Beer's law. The molar absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) used were: for *trans*-[MoCl(NCHMeCO$_2$Me)(dppe)$_2$]$^+$, $\varepsilon_{CHMe} = 2.4 \times 10^2$; for *trans*-[MoCl(NCMeCO$_2$Me)(dppe)$_2$], $\varepsilon_{CMe} = 2.0 \times 10^3$. These values were determined from the absorbance of *trans*-[MoCl(NCHMeCO$_2$Me)(dppe)$_2$]$^+$ and the final absorbance of the reaction mixture at high concentrations of MeO^- respectively. For the studies on *trans*-[MoCl(NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$ ε values used were: for *trans*-[MoCl(NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$, $\varepsilon_{CH2} = 3.2 \times 10^2$; for *trans*-[MoCl(NCCO$_2$Me)(dppe)$_2$]$^-$, $\varepsilon_C = 1.3 \times 10^4$.

for *trans*-[MoCl(NCHMeCO$_2$Me)(dppe)$_2$]$^+$, as described by eqn. (3) and shown in Fig. 2.‡

$$-\frac{d[MoNCH_2CO_2Me]}{dt} = \{(5.8 \pm 0.2) \times 10^3 [MeO^-] + (1.4 \pm 0.2) \times 10^{-2} [MeOH]\} \{[MoNCH_2CO_2Me] - [MoNCH_2CO_2Me]_\infty\} \quad (3)$$

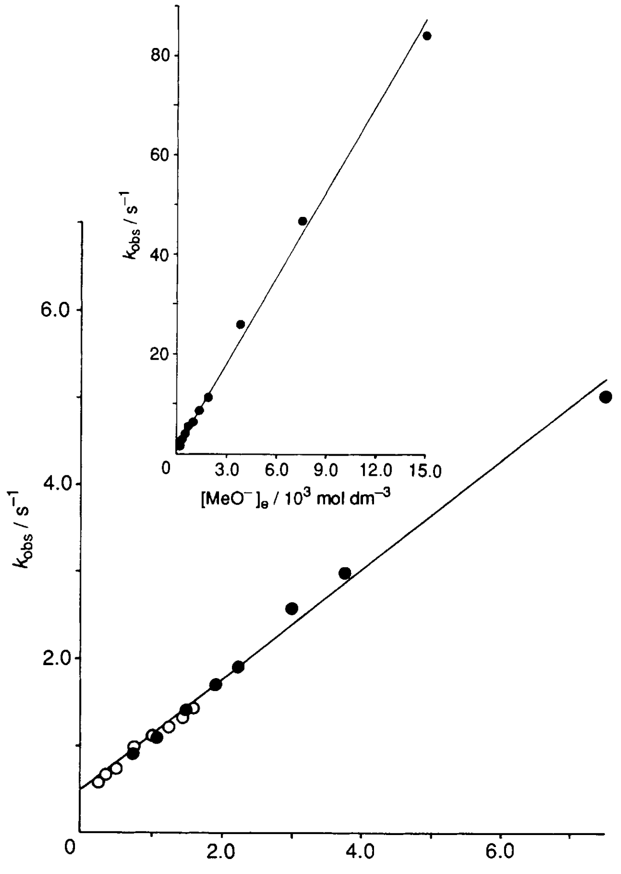


Fig. 2 Graph of k_{obs} (the pseudo first-order rate constant) against the concentration of MeO^- in methanol at 25.0 °C for the equilibrium reaction of *trans*-[MoCl(NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$ with base (○, base = NEt$_3$;† ●, base = NaOMe). From the graph, $k_{obs} = k_1 [MeO^-] + k_{-1}[MeOH]$,[9] where [MeOH] = 31.3 mol dm^{-3}.

The equilibrium constant derived from this kinetic analysis is in excellent agreement with the value of K_1^H derived from the absorbance measurements, $K_1^H = (4.1 \pm 0.4) \times 10^5$ though this may be accidental. Both the forward and back reactions are associated with large primary isotope effects, $k_1^H/k_1^D = 8.8$ $k_{-1}^H/k_{-1}^D = 10.1$ (uncorrected for solvent isotope effects or secondary isotope effects).[5]

During the course of all these ligand-based deprotonation reactions the coordination sphere of the molybdenum remains intact as shown by, (*i*) the complete reversibility of the system over the course of at least 1 h and (*ii*) the insensitivity of the kinetics and absorbance changes to the presence of a large excess of chloride ion ([Mo] = 0.05 mmol dm^{-3}, [Cl$^-$] = 0–40 mmol dm^{-3}).

The acidity of the C–H protons in species (*A*) and (*B*) will be influenced by: (*i*) the formal oxidation state of the molybdenum, (*ii*) the π-donation and π-accepting capabilities of the metal, (*iii*) the presence of the ester function, (*iv*) the charge on the complex and (*v*) the hybridisation of the carbon atom to

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‡ The apparent simplicity of the kinetics observed in this system is misleading. Although all absorbance–time traces are excellent exponentials which can be curve-fitted to at least 95% conversion using a single rate constant, they can also be fitted to two exponentials with rate constants differing by the small amount expected from the values of K_1^H and K_2^H.

which the proton is bound. Although simple organic compounds containing the C*H*–C=O group are known to be good acids,[6] due to the delocalisation of the charge onto the electronegative oxygen, it is the additional presence of the molybdenum which permits the double deprotonation observed in the system described in this paper. Both the ester function and the Mo=N fragment can readily enter into conjugation with the deprotonated carbon centre and hence, act as efficient electron-sinks to dissipate the electron-density away from the site of deprotonation. Indeed this effect is so powerful in this system that the expected statistical factor of $K_1 = 4K_2$ (at least)[7] is overcome and $K_1^H = 2.3\,K_2^H$, even with both protons removed from the same atom. We should point out that the state of hybridisation of the deprotonation site is different in species (*A*, sp^3 carbon) and (*B*, sp^2 carbon), and the inherent acidity of protons at these sites may, in part, be responsible for the similarity of the equilibrium constants.

The poor solubility of *trans*-[MoCl(NCHRCO$_2$Me)(dppe)$_2$]$^+$ (R = H or Me) in methanol precludes studies on these equilibrium reactions by NMR spectroscopy.

Finally, the reaction of *trans*-[MoCl(NCH$_2$CO$_2$Me)(dppe)$_2$]$^+$ with an excess of NEt$_3$ in tetrahydrofuran (THF) only produces *trans*-[MoCl(NCHCO$_2$Me)(dppe)$_2$]. This is because, at least in part, of the poor solvation of anions by aprotic solvents, and probably the weaker basicity of NEt$_3$ in THF than MeO$^-$ in methanol.

Received, 23rd September 1992; Com. 2/05098F

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