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# Kinetics and mechanism of the addition of methoxide ion to the $\pi$-hydrocarbon ligands in $[HOs_3(\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$ and $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CH_2)]PF_6$

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## Abstract

Kinetic data are reported for the addition of $MeO^-$ to the $\eta^2$-vinyl ligand of the cluster $[HOs_3(CHCH_2)(CO)_{10}]$ (II), and compared with analogous data for the related mononuclear complex $[CpFe(CO)_2(C_2H_4)]^+$. For both substrates the simple rate law, Rate $= k_1$[complex][$MeO^-$], is obeyed, consistent with direct bimolecular addition of $MeO^-$ to the $\pi$-hydrocarbon ligand in both cases. Comparison with results of previous kinetic studies on II reveals the overall nucleophilicity order $MeO^- > P(4\text{-}MeOC_6H_4)_3 > P(4\text{-}MeC_6H_4) > PPh_3$ for attack on this cluster substrate. This is similar to the order for the monomeric complex $[CpFe(CO)_2(C_2H_4)]^+$ except for the position of $MeO^-$, which is surprisingly reactive towards the triosmium complex. This observation suggests that caution should be taken in extending to related metal clusters mechanistic conclusions drawn from mononuclear $\pi$-hydrocarbon complexes.

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## Introduction

Recent kinetic studies have provided considerable information on the mechanisms of nucleophilic attack at coordinated $\pi$-hydrocarbon complexes and on the factors controlling the reactivity of such species [1–3]. However, almost all the data to date have involved neutral nucleophiles and mononuclear organometallic substrates [1]. Apart from one recent study [4], no kinetic/mechanistic information has been reported for nucleophilic addition at $\pi$-hydrocarbons coordinated to multinuclear metal centres, and quantitative studies with anionic nucleophiles are rare [3,5].

We report here the kinetics of addition of the methoxide ion to the $\pi$-hydrocarbon ligands in $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CH_2)]PF_6$ (I) and the cluster $[HOs_3(\eta^2\text{-}CH{=}CH_2)(CO)_{10}]$ (II) (eq. 1 and 2, respectively). The results provide useful insights into the influence of charge on nucleophilicity and of the mechanistic significance of multi-metal coordination in clusters.

$$\underset{\text{(I)}}{[\mathrm{CpFe(CO)_2(C_2H_4)}]^+} + \mathrm{MeO^-} \xrightarrow{k_1} \underset{\text{(III)}}{[\mathrm{CpFe(CO)_2(C_2H_4OMe)}]} \qquad (1)$$

$$\underset{\text{(II)}}{[\mathrm{HOs_3(CO)_{10}(CHCH_2)}]} + \mathrm{MeO^-} \xrightarrow{k_1} \underset{\text{(IV)}}{[\mathrm{HOs_3(CO)_{10}(CHCH_2OMe)}]} \qquad (2)$$

## Experimental

### *Materials*

The complexes $[\mathrm{CpFe(CO)_2(\eta^2\text{-}C_2H_4)]PF_6}$ and $[\mathrm{HOs_3(\eta^2\text{-}CH{=}CH_2)(CO)_{10}}]$ were prepared and purified by published procedures [6,7]. Analytical grade methanol was dried by a standard procedure [8]. A stock solution of sodium methoxide was prepared by dissolving sodium metal in dry methanol, stored under nitrogen, and diluted to the appropriate concentration immediately prior to the kinetic runs.

### *Kinetic studies*

Reactions 1 and 2 were rapid, and could be conveniently studied using a thermostatted (±0.1° C) stopped-flow spectrometer. The processes were monitored at 390 nm, at which wavelength a large decrease in absorbance occurred during each reaction.

Both processes were studied under pseudo-first-order conditions by use of a large excess of $[\mathrm{MeO^-}]$ ($[\mathrm{Fe}] = 7 \times 10^{-4}$ mol dm$^{-3}$, $[\mathrm{MeO^-}] = 4\text{–}30 \times 10^{-3}$ mol dm$^{-3}$; $[\mathrm{Os_3}] = 3 \times 10^{-4}$ mol dm$^{-3}$, $[\mathrm{MeO^-}] = 4\text{–}40 \times 10^{-3}$ mol dm$^{-3}$). Pseudo-first-order rate constants, $k_{obs}$, were calculated from the slopes of plots of $\log(A_t - A_\infty)$ vs. time using a least-squares program. These plots were generally linear for at least two half-lives. Each run was carried out in quadruplicate, with an average reproducibility of ±7%.

Second-order rate constants, $k_1$, together with their standard errors of estimate, were calculated from the slopes of plots of $k_{obs}$ vs. $[\mathrm{MeO^-}]$ by a least-squares analysis. The activation enthalpy for reaction **1** was calculated from a least squares fit to the Arrhenius equation of the temperature dependence data in Table 1. The error quoted is the standard deviation from the least squares analysis. The entropy

Table 1

Kinetic results for the addition of $\mathrm{MeO^-}$ to the cluster $[\mathrm{HOs_3(\eta^2\text{-}CH{=}CH_2)(CO)_{10}}]$ in MeOH at 20 °C. $[\mathrm{Os_3}] = 3.0 \times 10^{-4}$ mol dm$^{-3}$

| $10^2[\mathrm{MeO^-}]$ (mol dm$^{-3}$) | $k_{obs}$ (s$^{-1}$) | $k_1$ (mol$^{-1}$ dm$^3$ s$^{-1}$) |
|---|---|---|
| 0.40 | 0.94 | |
| 0.80 | 1.72 | |
| 1.00 | 2.03 | |
| 1.20 | 2.68 | |
| 2.00 | 3.78 | |
| 4.00 | 7.90 | 190(9) |

Table 2

Kinetic results for the addition of $MeO^-$ to $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CH_2)]PF_6$ in MeOH. $[Fe] = 7 \times 10^{-4}$ mol $dm^{-3}$)

| Temperature (° C) | $10^2[MeO^-]$ (mol $dm^{-3}$) | $k_{obs}$ ($s^{-1}$) | $k_1$ ($mol^{-1}$ $dm^3$ $s^{-1}$) |
|---|---|---|---|
| 0.3 | 1.60 | 2.30 | |
| 5.0 | 1.60 | 2.93 | |
| 10.2 | 1.60 | 4.62 | |
| 15.5 | 1.60 | 7.30 | |
| 20.0 | 0.40. | 2.85 | 712(45) |
| | 0.80 | 7.05 | |
| | 1.60 | 11.1 | |
| | 2.00 | 16.0 | |
| | 3.00 | 21.7 | |
| 25.0 | 1.60 | 16.5 | |

of activation was estimated by use of the calculated second-order rate constant, $k_1$, at 20 ° C.

## Results and discussion

Previous synthetic and spectroscopic studies [6,7] have confirmed that $MeO^-$ attacks the $\pi$-hydrocarbon ligands of complexes I and II to give the adducts III and IV, respectively, as shown in eq. 1 and 2.

Kinetic results for these two reactions in methanol at 20 ° C are summarised in Tables 1 and 2. Plots of $k_{obs}$ vs. $[MeO^-]$ are shown in Fig. 1a and 1b. Within experimental error, the rate law 3 is seen to be obeyed by both reactions; the estimated second-order rate constants at 20 ° C are 712(45) $mol^{-1}$ $dm^3$ $s^{-1}$ and 190(9) $mol^{-1}$ $dm^3$ $s^{-1}$ for reactions 1 and 2, respectively.

$$\text{Rate} = k_{obs}\,[\text{complex}]$$

$$k_{obs} = k_1\,[MeO^-] \qquad (3)$$

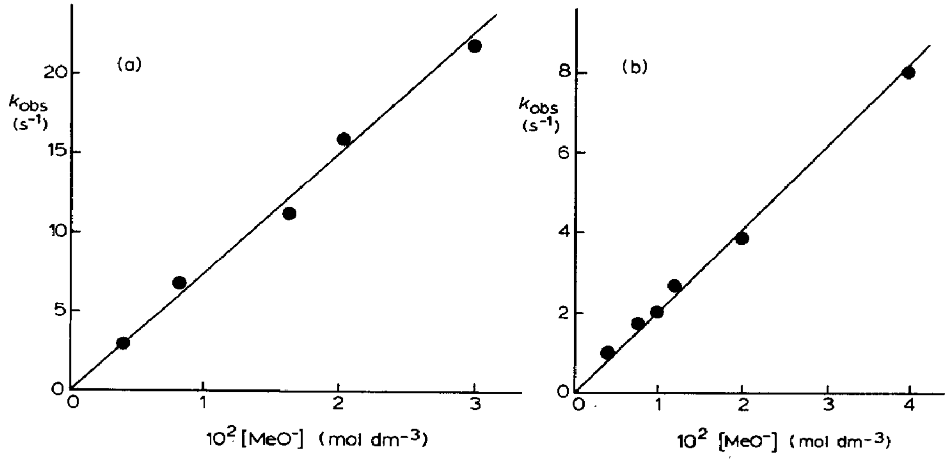

Fig. 1. (a) Plot of $k_{obs}$ vs. $[MeO^-]$ for the addition of $MeO^-$ to I in MeOH at 20 ° C. (b) Plot of $k_{obs}$ vs. $[MeO^-]$ for the addition of $MeO^-$ to II in MeOH at 20 ° C.

Table 3

Rate and activation parameters for the addition of anionic and neutral nucleophiles to $[CpFe(CO)_2[\eta^2\text{-}C_2H_4)]^+$

| Nucleophile | $k_1$ (20 °C) ($mol^{-1} dm^3 s^{-1}$) | $\Delta H_1^{\neq}$ ($kJ mol^{-1}$) | $\Delta S_1^{\neq}$ ($J K^{-1} mol^{-1}$) | Ref. |
|---|---|---|---|---|
| $C_6H_{11}NH_2$ [b] | 1380 | – | – | 9 |
| $MeO^-$ [a] | 712 | 52.0(1.4) | −15(5) | This work |
| $P(4\text{-}MeOC_6H_4)_3$ [b] | 408 | – | – | 9 |
| $PPh_3$ [b] | 82 | 30 | −107 | 9 |
| Pyridine | 45 | 31 | −108 | 9 |

[a] Solvent methanol. [b] Solvent acetone.

The rate law 3 is most readily rationalised in terms of direct addition, $k_1$, of $MeO^-$ to the hydrocarbon ligand of both I and II. Such bimolecular addition is supported by the moderate enthalpy of activation $\{\Delta H_1^{\neq} = 52.0(1.4)$ kJ $mol^{-1}\}$ and the negative entropy of activation $\{\Delta S^{\neq} = -15$ (5) J $K^{-1}$ $mol^{-1}\}$ estimated for the reaction of $MeO^-$ with I. However, it is significant that this $\Delta S_1^{\neq}$ value is very much less negative than that recently found [9] for the related additions of the neutral nucleophiles pyridine and triphenylphosphine to cation I (Table 3). This difference may arise from a transition state for the methoxide reaction resembling an ion-pair ($[I]^+ \ldots {}^-OMe$), with encounter and desolvation of the anionic nucleophile providing the major contributions to the free energy of activation. Desolvation would be expected to be much less important with the neutral nucleophiles previously studied.

A similar proposal has been made by Ritchie [10] for the addition of anions to free carbonium ions. "Early" ion-pair-type transition states for anion addition to ferrocenyl-stabilized carbocations have also been proposed by Burton and Watts [5]. They postulated that for addition of anionic nucleophiles to the ferrocenylmethyl cation there is little or no change in $sp^2$ orbital hybridisation at the α-carbon reaction centre on going to the transition state.

The relative nucleophilicity of neutral nucleophiles towards cation I is seen from Table 3 to decrease in the order $C_6H_{11}NH_2 > P(4\text{-}MeOC_6H_4)_3 > PPh_3 >$ pyridine (rel. rates 17/5/1/0.5). A very similar order of neutral nucleophile reactivity is observed towards the cluster II ($C_6H_{11}NH_2 > P(4\text{-}MeOC_6H_4)_3 > PPh_3$; rel. rates 18/7.5/1) (Table 4). This suggests that similar factors control the reactivity of these two organometallic substrates towards neutral nucleophiles.

Table 4

Rate and activation parameters for the addition of anionic and neutral nucleophiles to $[HOs_3(\eta^2\text{-}CHCH_2)(CO)_{10}]$

| Nucleophile | $k_1$ (20 °C) ($mol^{-1} dm^3 s^{-1}$) | $\Delta H_1^{\neq}$ ($kJ mol^{-1}$) | $\Delta S_1^{\neq}$ ($J K^{-1} mol^{-1}$) | Ref. |
|---|---|---|---|---|
| $MeO^-$ | 190 | – | – | This work |
| $C_6H_{11}NH_2$ | 85 | – | – | 4 |
| $P(4\text{-}MeOC_6H_4)_3$ | 35 | – | – | 4 |
| $PPh_3$ | 4.6 | 27.2 | −138 | 4 |

However, significant differences are noted between the monomeric cation I and the cluster II in their behaviour towards $MeO^-$ as nucleophile. While this anionic nucleophile is somewhat less reactive than $C_6H_{11}NH_2$ towards I, it is the most reactive nucleophile towards the cluster II (Tables 3, 4). This behaviour is the reverse of what one would have expected if electrostatic factors were the dominant factor in controlling the relative nucleophilicities. The cause of the high reactivity of $MeO^-$ towards the neutral cluster II is uncertain, but could be associated with an enhanced ability to delocalise the negative charge generated in the transition state in such a multi-metal system. Of more general significance, these observations indicate that mechanistic conclusions drawn from the extensive kinetic studies [1] of mononuclear π-hydrocarbon complexes may not be assumed to hold for related metal cluster complexes. More extensive mechanistic studies are clearly required on cluster substrates in order to delineate the factors controlling their reactivity.

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