

Preliminary communication

A comparison of the rates of alkyl migration in the complexes
[CpM(CO)₂R] (M = Fe, Ru, Os; Cp = η⁵-C₅H₅)

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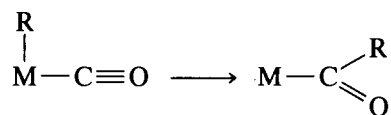
Received 2 August 1995

Abstract

The rates of alkyl migration for selected members of the series [CpM(CO)₂R] (M = Fe, Ru, Os; Cp = η⁵-C₅H₅; R = CH₃ to *n*-C₁₈H₃₇) show dependence on both the alkyl group and the metal.

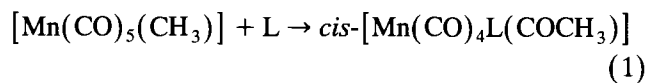
Keywords: Iron; Ruthenium; Osmium; Cyclopentadienyl; Alkyl migration; Carbonyl

Alkyl migration to CO at a metal centre is a fundamental step in many important catalytic reactions including hydroformylation of alkenes, the Monsanto acetic acid synthesis and the co-polymerisation of ethylene and CO [1].



It has also been proposed that this reaction may lead to the production of oxygenates in the Fischer–Tropsch process [2]. The closely related process of alkyl migration to a surface methylene may also be the important chain growth step in the Fischer–Tropsch process [3].

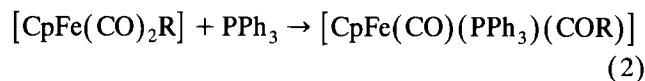
Although the alkyl migration reaction has been known for many years, there are fundamental questions still to be answered: for example, what is the role of the metal and the supporting ligands [4]? The classic example of the alkyl migration reaction (also known as CO insertion or migratory insertion) is for [Mn(CO)₅(CH₃)] [5].



This system has been studied extensively but most of the studies have involved changing the ligand (L), the solvent or the reaction conditions. Few reports have

investigated changing the alkyl ligand in [Mn(CO)₅R]. Recently an extensive series of alkyl complexes of the type [Mn(CO)₅R] has been prepared (R = CH₃ to *n*-C₁₈H₃₇) and the rates of the alkyl migration reaction, with PPh₃, have been measured and found to depend on the number of carbon atoms in the alkyl chain as shown in Fig. 1 [6].

We were now interested to see if this dependence of rate of alkyl migration on the nature of the alkyl group would be found in other metal ligand systems. We were also interested to establish how the rate of alkyl migration depended on the nature of the metal for three transition metals in one group in the periodic table. The type of alkyl compound we selected for these studies was [CpM(CO)₂R] (where M = Fe, Ru or Os). We had previously prepared some Fe and Ru compounds of this type to use as models for alkyl intermediates in the Fischer–Tropsch reaction [7]. Previously alkyl migration studies on [CpFe(CO)₂R] have been carried out, mainly for R = CH₃ [8] but some with other R groups [9]. We now investigated the reaction



for R = CH₃, C₂H₅, *n*-C₃H₇, *n*-C₄H₉, *n*-C₆H₁₃, *n*-C₈H₁₇, *n*-C₁₀H₂₁, *n*-C₁₂H₂₅ and *n*-C₁₈H₃₇. The rates were all measured under pseudo 1st order conditions in the presence of an excess of PPh₃ (10 ×) in xylene at 45°C. The results are shown in Fig. 2. The shape of this

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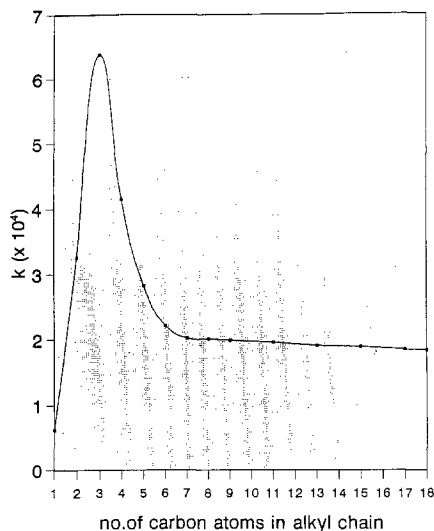


Fig. 1. Plot of the pseudo first order rate constants k versus the number of carbon atoms in the alkyl chain for the reaction of $[\text{Mn}(\text{CO})_5\text{R}]$ with PPh_3 [6].

curve (Fig. 2) is very similar to the shape of the curve we obtained previously (Fig. 1) for the rate of alkyl migration in $[\text{Mn}(\text{CO})_5\text{R}]$ complexes [6]. Thus, complexes $[\text{CpFe}(\text{CO})_2\text{R}]$ and $[\text{Mn}(\text{CO})_5\text{R}]$ show a similar dependence of the rate of alkyl migration on the number of carbon atoms in the linear alkyl group. Thus the nature of the metal and associated ligands affects the absolute value of the rates of alkyl migration but the dependence of the rate on R is a consequence of the chain length of the alkyl group. This could also pertain to migration of alkyl groups to other ligands e.g. methylene and may therefore be important for surface reactions in heterogeneous catalysis e.g. the Fischer–Tropsch reaction.

When we measure the rates of the alkyl migration for

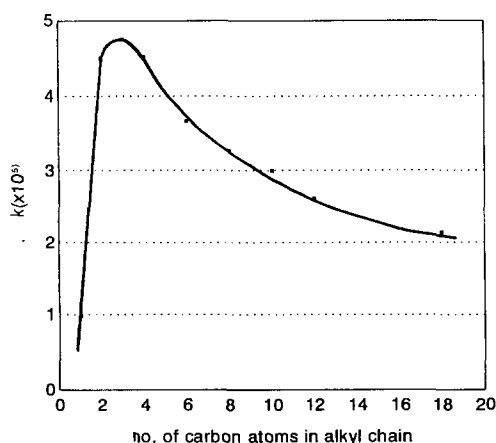


Fig. 2. Plot of the pseudo first order rate constants k versus the number of carbon atoms in the alkyl chain for the reaction of $[\text{CpFe}(\text{CO})_2\text{R}]$ with PPh_3 at 45°C in xylene.

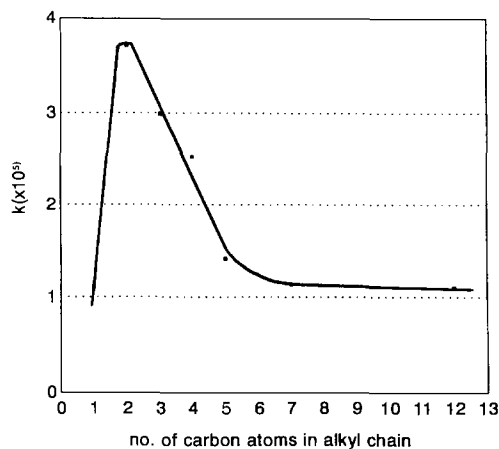
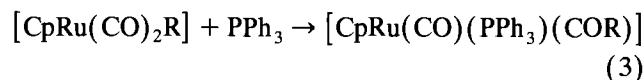


Fig. 3. Plot of the pseudo first order rate constants k versus the number of carbon atoms in the alkyl chain for the reaction of $[\text{CpRu}(\text{CO})_2\text{R}]$ with PPh_3 at 137°C in xylene.

$[\text{CpRu}(\text{CO})_2\text{R}]$, a similar trend is again seen (see Fig. 3); although the peak in this case is at C_2 . Reactions of some compounds of the type $[\text{CpRu}(\text{CO})_2\text{R}]$ with PPh_3 had been carried out before [10], however we could find no reports of any alkyl migration rate measurements for mononuclear ruthenium alkyl compounds. We have now investigated the reaction



for $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, n\text{-C}_5\text{H}_{11}, n\text{-C}_7\text{H}_{15}, n\text{-C}_{12}\text{H}_{25}$ and $n\text{-C}_{18}\text{H}_{37}$. The rates were measured in xylene at 137°C in the presence of excess PPh_3 (10 times). The rate constant for the reaction of $[\text{CpFe}(\text{CO})_2(n\text{-C}_{18}\text{H}_{37})]$ was also measured at 137°C in xylene and found to be $1.7 \times 10^{-2} \text{ s}^{-1}$, compared to $7.6 \times 10^{-6} \text{ s}^{-1}$ for $[\text{CpRu}(\text{CO})_2(n\text{-C}_{18}\text{H}_{37})]$ under similar conditions. Thus changing the metal from Fe to Ru, while keeping all the ligands the same, causes a decrease in the rate of alkyl migration of about 10^3 . This could help to explain why iron catalysts in the Fischer–Tropsch process produce more oxygenates than ruthenium catalysts [11].

We were then interested to attempt the same alkyl migration reaction for $[\text{CpOs}(\text{CO})_2\text{R}]$ compounds. The

¹ The compounds $[\text{CpOs}(\text{CO})_2\text{R}]$ were prepared by the reaction of $[\text{CpOs}(\text{CO})_2\text{Br}]$ with the appropriate alkyl lithium; satisfactory elemental analyses were obtained for both compounds. For $\text{R} = \text{CH}_3$: white crystals, 80% yield, m.p. 77°C – 80°C ; IR $\nu(\text{CO})$ (hexane) 2011 s^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 5.36 (s C_5H_5), δ 0.66 (s CH_3). For $\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$: colourless oil, 42% yield; IR $\nu(\text{CO})$ (hexane) 2008 s^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 5.23 (s C_5H_5), δ 1.82 (m OsCH_2), δ 1.53 (m OsCH_2CH_2), δ 1.23 (m CH_2CH_3), δ 0.86 (t CH_3).

reaction of $[\text{CpOs}(\text{CO})_2\text{R}]$ ($\text{R} = \text{CH}_3$ or $n\text{-C}_4\text{H}_9$)¹ with excess PPh_3 (10 times) was investigated in xylene at 137°C . For both compounds under these conditions there was no detectable reaction at all, after 4 days for $\text{R} = \text{CH}_3$ and 6 days for $\text{R} = n\text{-C}_4\text{H}_9$. Thus, the rate of alkyl migration for the osmium alkyls must be at least 10^4 times slower than for the analogous ruthenium compound. This compares with an estimated difference of 10^5 between similar Rh and Ir alkyls recently obtained by Haynes et al. [12]. Thus the rate of alkyl migration for the $[\text{CpM}(\text{CO})_2\text{R}]$ complexes follows the order $\text{Fe} > \text{Ru} \gg \text{Os}$. This may be a general trend for alkyl migration in other groups of transition metals in the periodic table.

Acknowledgements

We thank the University of Cape Town, the Foundation for Research Development, AECI Ltd and SASOL for their support. We thank Mark Dry and Eric van Steen for helpful discussions.

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