Metal alkyl complexes as models for catalytic intermediates

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Abstract

Many catalytic reactions, whether homogeneous or heterogeneous, involving hydrocarbons and transition metals are believed to go through transition metal alkyl intermediates. Transition metal alkyl complexes, which can be isolated, fully characterized and their properties investigated, can be used as models for metal alkyl intermediates in catalytic reactions and thus give us information regarding the behaviour of the catalytic intermediates. In this paper we describe the results of some of our work on metal alkyl complexes of the types $RMn(CO)_5$ (R = alkyl group) and $CpM(CO)_2R$ (Cp = η^5-C_5H_5, M = Fe, Ru or Os) as well as the binuclear complexes $Cp(CO)_2Ru(CH_2)_2Ru(CO)_2Cp$. These results may give us a better understanding of catalytic reactions.

Keywords: Metal complexes; Alkyl complexes; Model; Complex; Intermediates

1. Introduction

Metal alkyl species are believed to be key intermediates in many catalytic reactions involving hydrocarbons and transition metals [1,2]. This applies to both homogeneous and heterogeneous catalytic reactions. Some examples are shown in Table 1.

In homogeneous catalytic reactions, it is sometimes possible to detect metal alkyl intermediates directly by spectroscopic methods. Thus Maitlis and co-workers have described the direct observation of rhodium methyl intermediates, by IR and NMR, in the Monsanto acetic acid synthesis [3].

However, in heterogeneous reactions, it is much more difficult to detect catalytic intermediates directly, because of the lack of suitable methods. One way to overcome this problem is to use transition metal complexes as models for the proposed catalytic intermediate. The model complexes should have the same important groups attached to the same metal, as in the supposed catalytic intermediate, yet they can be isolated, fully characterized both structurally and spectroscopically, and their chemistry can be investigated. Thus fundamental studies on metallocene complexes of Sc [4], Ti [5] and Zr [6] have recently led to the development of new, single site, selective catalysts for the polymerisation of alkenes [7]. In addition, it has been found in some cases, that species chemisorbed on a metal surface can show similar IR and Raman spectra to model compounds [8,9]. Thus, for example, there is a good correlation between the spectra of the model compound, $(\eta^2$-$C_2H_4)Os(CO)_4$, and ethylene chemisorbed on a metal surface [8]. This recent evidence further supports the idea that metal complexes may be good models for surface species.

In this paper, we describe results of some of our recent studies on well-characterized transi-

Table 1
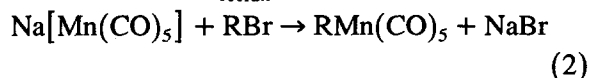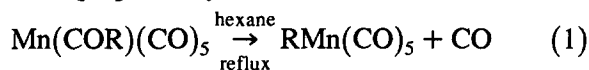Some examples of metal alkyl intermediates in catalytic reactions

Metal-alkyl species	Catalytic reaction
Ti–R	alkene polymerisation
Zr–R	alkene polymerisation
W–R	alkene metathesis
Fe–R	Fischer–Tropsch process
Ru–R	Fischer–Tropsch process
Co–R	hydroformylation and Fischer–Tropsch
Rh–R	alkane activation
Rh–R	hydroformylation and acetic acid synthesis
Pd–R	co-polymerisation of CO and C_2H_4
Pt–R	alkene hydrogenation

tion metal alkyl complexes which we believe are useful models for metal alkyl intermediates in catalytic reactions.

2. Results and discussion

2.1. Alkyl pentacarbonyl complexes RMn(CO)₅

The first transition metal carbonyl alkyl complex to be prepared was $CH_3Mn(CO)_5$ in 1957 [10]. This compound has been used extensively as a model complex for the important carbonyl insertion reaction (which is also known as the alkyl migration reaction). It is a key step in many catalytic reactions, for example the hydroformylation of alkenes. In many catalytic reactions, the alkyl intermediate involved has more than one carbon atom and thus, we envisaged that longer chain alkyl compounds would be better models. We thus investigated the preparation, characterisation and chemistry of a series of compounds of the type $RMn(CO)_5$ (where $R = CH_3$ to n-$C_{18}H_{37}$) [11]. These compounds were prepared by two routes

$$Mn(COR)(CO)_5 \xrightarrow[\text{reflux}]{\text{hexane}} RMn(CO)_5 + CO \quad (1)$$

$$Na[Mn(CO)_5] + RBr \rightarrow RMn(CO)_5 + NaBr \quad (2)$$

These alkyl compounds are discrete molecular complexes and are isolated as pale yellow oils or low-melting crystalline solids. They were fully characterized by elemental analysis, IR, ^1H NMR, ^{13}C NMR and mass spectrometry

[11]. We then investigated the rates of the alkyl migration reaction for these compounds by monitoring the following reaction

$$RMn(CO)_5 + PPh_3$$
$$\rightarrow cis\text{-}Mn(CO)_4(PPh_3)(COR) \quad (3)$$
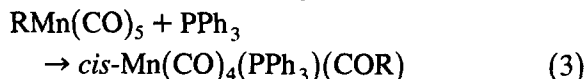
We found [11] that the rate of this reaction depends on the nature of the n-alkyl group as shown in Fig. 1. This sort of behaviour had not been observed before, although Berke and Hoffman predicted that the rate of alkyl migration should depend on the number of carbon atoms in the alkyl chain [12]. We believe that this behaviour is due to a combination of steric and electronic effects, with the electronic effects dominating at low carbon numbers. We have also seen this pattern with other metal alkyls with different ligand systems (see later) and therefore believe that this pattern is a consequence of R, rather than the metal and ligand system. Thus we expect that the same sort of dependence of the rate of alkyl migration, with R, might be seen in other systems.
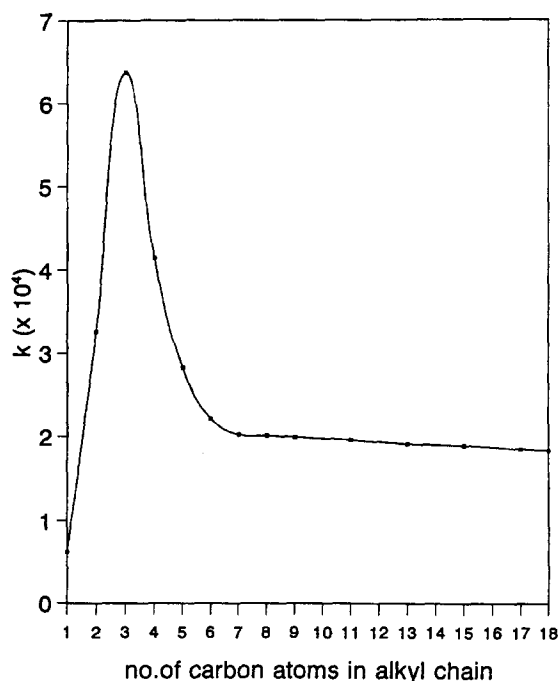
These results may help to explain why the

Fig. 1. Plot of k_{obs} versus the number of carbon atoms in the alkyl chain for the reaction of $RMn(CO)_5$ with PPh_3.

rate of hydroformylation of long chain α-olefins is slower than that for short chain α-olefins. Other reactions involving alkyl migrations (e.g. alkene polymerisations) may also show similar dependency on R.

We have also found that the reaction of $RMn(CO)_5$ with synthesis gas yields exclusively alcohols [13].

$$2RMn(CO)_5 + 2CO \xrightarrow{H_2} 2RCH_2OH$$

$$+ Mn_2(CO)_{10} \qquad (4)$$
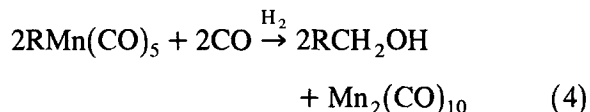
This reaction may be a direct pathway for alcohol formation, from metal alkyl species, in the hydroformylation reaction or even in the Fischer–Tropsch process.

2.2. CpM(CO)₂R complexes (M = Fe, Ru or Os): models for Fischer–Tropsch intermediates

We have investigated the structure, properties and chemistry of complexes of the type $CpM(CO)_2R$. These complexes may be useful models for surface alkyls in the Fischer–Tropsch process and other important catalytic reactions. We suggest that improved knowledge of the chemistry of the $Fe–CH_2$ bond in $CpFe(CO)_2R$ may give us useful information as to how the $Fe–CH_2$ bond of surface alkyl species in the Fischer–Tropsch process may behave.

We are comparing

R
|
Fe
///////

surface alkyl species

R
|
Fe
/ | \
Cp CO CO
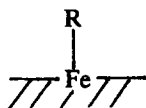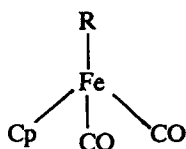
metal alkyl complex

2.2.1. Structures of metal alkyl complexes

Although structures of many metal complexes have been determined in the past, most of these are on short chain alkyl complexes, with C_1 to C_4 alkyl groups. Since, in the Fischer–Tropsch process, long chain alkyl intermediates are to be expected, we sought to obtain suitable crystals of long chain alkyl metal complexes for X-ray crystal structure studies. We have determined the crystal structure of several long chain alkyl complexes including $Cp^*Fe(CO)_2(n-C_5H_{11})$ (where $Cp^* = C_5(CH_3)_5$) [14] and $Co(DMG)_2(py)(n-C_{14}H_{29})$ [15] (see Figs. 2 and 3). Both these metals are Fischer–Tropsch active metals. The $Fe–CH_2$ and $Co–CH_2$ bond lengths in these compounds are 2.069(10) Å and 1.97(1) Å, respectively, consistent with $Fe–CH_2$ and $Co–CH_2$ single bonds. Also, in both compounds, the hydrocarbon chain is extended. Thus, for surface alkyl species in the Fischer–Tropsch process, we would expect an $Fe–CH_2$ bond length of about 2.07 Å with the hydrocarbon chain extending out from the surface (see Fig. 4).

We also envisage that the Fischer–Tropsch catalyst surface would have some close analogies to monolayer films of n-alkanethiols [16] or ultrathin films of n-alkanes [17] on metal surfaces.

We would expect the $Fe–CH_2$ bond for the surface alkyl species in the Fischer–Tropsch process to be subject to some of the same rules of chemical bonding, as found for the complex $CpFe(CO)_2R$. We have performed molecular orbital calculations on $CpFe(CO)_2(CH_2CH_3)$ to try and discover likely reaction pathways for such complexes [14], and then to extend this to surface alkyl species. It is interesting to note that our results so far [14] suggest that β-elimination from $CpFe(CO)_2(CH_2CH_3)$ is not a favourable process. This agrees with our experimental findings on $CpFe(CO)_2R$ which do not easily decompose to give α-olefins. Thus, for surface alkyl species in the Fischer–Tropsch process, β-elimination may not be the mode of chain termination to yield α-olefins.
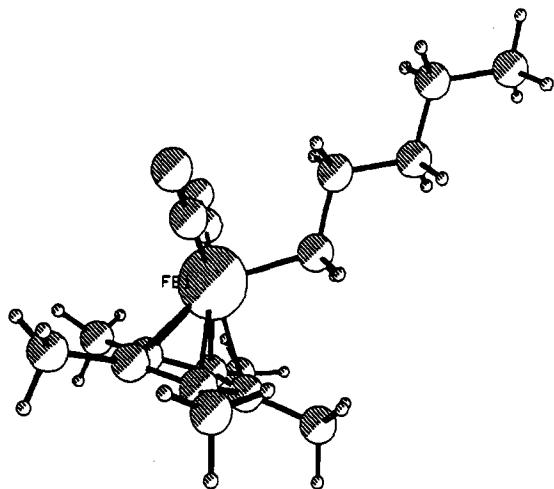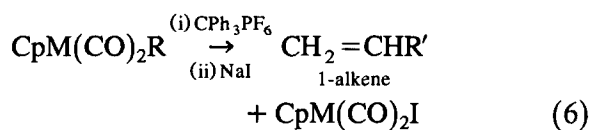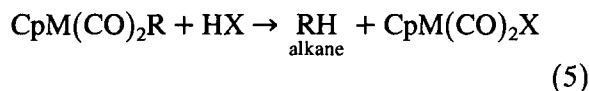
Fig. 2. A view of the molecular structure of $(\eta^5$-$C_5Me_5)Fe(CO)_2(n$-$C_5H_{11})$ showing the extended alkyl chain.

2.2.2. Reactions of CpM(CO)₂R (M = Fe or Ru)

We have found that the compounds $CpM(CO)_2R$ (where R is a long chain alkyl ligand) undergo the following reactions [18,19] (some reactions of these types have been shown previously).

Thus

$$CpM(CO)_2R + HX \rightarrow \underset{\text{alkane}}{RH} + CpM(CO)_2X$$

$$(5)$$

$$CpM(CO)_2R \xrightarrow[\text{(ii) NaI}]{\text{(i) CPh}_3PF_6} \underset{\text{1-alkene}}{CH_2{=}CHR'}$$

$$+ CpM(CO)_2I \qquad (6)$$

In addition, we have found that the model complex $Mn(CO)_5R$ reacts with synthesis gas to give high yields of the n-alcohol as the only observable organic product [13].

$$Mn(CO)_5R \xrightarrow{CO/H_2} \underset{\text{n-alcohol}}{RCH_2OH} + Mn_2(CO)_{10} \quad (7)$$
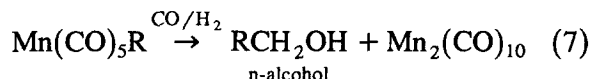
Thus model compounds give primary Fischer–Tropsch products in high yields.

2.2.3. Rates of alkyl migration from CpM(CO)₂R

We have measured the rates of the following reactions

$$CpM(CO)_2R + PPh_3$$

$$\rightarrow CpM(CO)(PPh_3)(COR) \qquad (8)$$
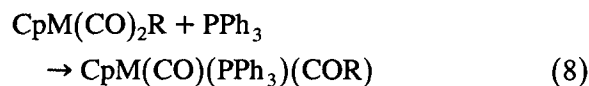
varying both R (from C_1 to C_{18}) and the metal (from Fe to Ru to Os) [18]. We observe some interesting trends

1. The same sort of dependency of the rate of alkyl migration with change in alkyl group (as was observed previously for $RMn(CO)_5$) was seen. If CO insertion occurs prior to oxygenate formation, then this may explain why more C_2 and C_3 oxygenates are formed in the Fischer–Tropsch process.

2. The rate of alkyl migration decreased in the order $Fe > Ru \gg Os$.

This may explain why more oxygenates are formed for CO hydrogenation catalyzed by Fe than Ru. We may also predict that Os would not be expected to be a particularly good catalyst for processes involving alkyl migration.

2.2.4. Poisoning of the active sites

We find that the model compound $CpFe(CO)_2R$ reacts with sulphur on heating to yield a stable product of the type

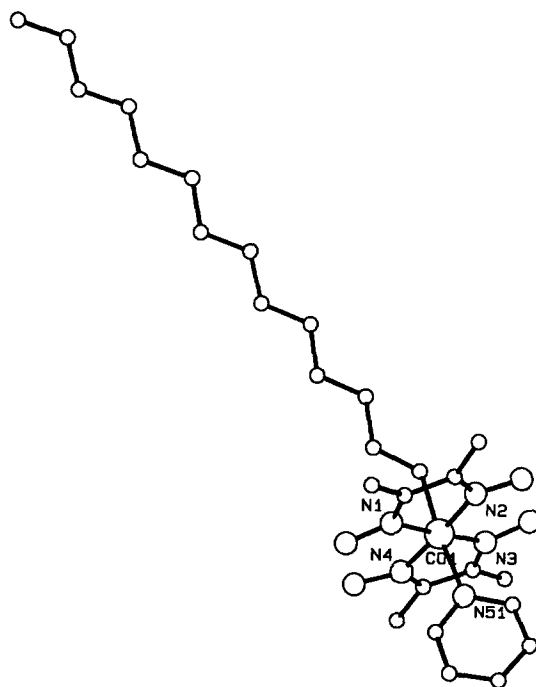Fig. 3. A view of the molecular structure of $Co(DMG)_2(py)(n$-$C_{14}H_{29})$ showing the extended alkyl chain (DMG = the monoanion of dimethylglyoxime).
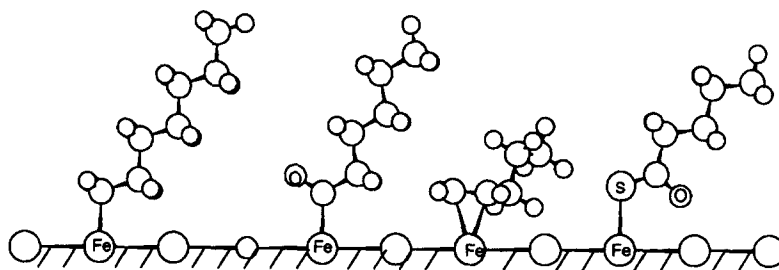
Fig. 4. A representation of what a Fischer–Tropsch catalyst surface may look like, showing from left to right, Fe–R, Fe–COR, Fe–(alkene) and Fe–SCOR species.

CpFe(CO)$_2$(SCOR) [14]. This could be a model for the poisoning of the active Fe sites by S. Thus sulphur may be inserted between the iron and the alkyl group of the growing alkyl chain, and irreversibly tying up that active site.

2.3. Structure of the chemistry of Cp(CO)$_2$RuCH$_2$CH$_2$Ru(CO)$_2$Cp

The dinuclear compound Cp(CO)$_2$RuCH$_2$CH$_2$Ru(CO)$_2$Cp has been prepared, its structure determined and its chemistry explored. This compound was used as a model for C$_2$H$_4$ on a catalyst surface [19].

1

A
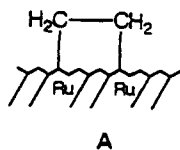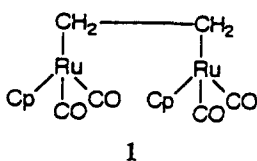
We were particularly interested to know if a species such as A could grow along the catalyst surface. We investigated model compound 1. We find that the chemistry of 1 is unusual, presumably because of the proximity of the two

metals. Thus 1 does not undergo alkyl migration reactions, neither could it be converted to the ethyl compound CpRu(CO)$_2$(CH$_2$CH$_3$) with acid. It does however readily liberate ethylene in its reactions. Thus on a Fischer–Tropsch catalyst surface, chain growth along the surface, as suggested by Craxford and Rideal [20] may not be likely and the fate of surface species A may just be to produce ethylene. In support of this, Brady and Pettit [21] found that diazomethane, on its own on a catalyst surface did not give chain growth, but chain growth was seen when hydrogen was present.

3. Conclusions

Metal alkyl complexes may be better models for catalytic alkyl species than has previously been thought. From studies on metal alkyl complexes, we can obtain new information that can give us guidance about the behaviour of catalytic intermediates. Thus, metal alkyl complexes can provide a link between homogeneous and heterogeneous catalysis since studies on metal alkyl complexes are relevant to both types of catalysis. Absolute values of rates in catalytic systems will be different to those in the complexes but it should be possible to identify trends. We can thus better understand the mechanisms of catalytic reactions and we hope that this will help in the design of more efficient and selective catalysts in the future.

Acknowledgements

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