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Organometallic Models for Metal Surface Reactions: Chain Growth Involving Electrophilic Methylidynes in the Fischer–Tropsch Reaction

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Abstract A new mechanism involving metal-bound surface *electrophilic* methylidynes is proposed for chain growth in the Fischer–Tropsch reaction to give 1-alkenes.

Keywords Fischer–Tropsch · Mechanism · Surface *electrophilic* methylidynes

1 Introduction

Charged species (nucleophiles and electrophiles) play key roles in organometallic and organic reactions in solution. We here suggest [1] that they can also be significant in reactions such as carbon monoxide hydrogenation (the Fischer–Tropsch, F–T, reaction) that occur on transition metal catalysts.

The hydrogenation of CO over various metals (especially Fe, Co, Ru, or Rh supported on oxides) at mildly elevated temperatures to yield hydrocarbons is of considerable economic interest today [2] and is once again the focus of substantial research. The main products are methane and linear olefins (chiefly 1-alkenes) as well as *n*-alkanes. Although there is still no complete consensus over the mechanisms involved, there is substantial agreement that the primary ("kinetically" favoured) $C_{\geq 2}$ products are 1-alkenes, and that the various internal alkenes, and at least part of the alkanes also produced, are derived from the 1-alkenes in subsequent isomerisation and hydrogenation processes. Researches by the Sheffield group indicate there to be substantial similarities in the product distributions afforded by the various metals even though the precise conditions may be rather different [3–5].

The balance of evidence over the first steps of the F–T reaction favours adsorption of CO at specific metal sites followed by hydrogen-assisted C–O cleavage to surface carbides, $C_{(ad)}$, which are then hydrogenated sequentially [6–8],

$$CO_{(ad)} \rightarrow C_{(ad)} \rightarrow CH_{(ad)} \rightarrow CH_{2(ad)} \rightarrow CH_{3(ad)} \rightarrow CH_{4(g)}$$

Many of the surface species have been detected and characterised.

One area where there is still little agreement concerns the precise reactions that occur between the $C_{1(ad)}$ species to form the coupled products. One previously popular proposal [6] involved the coupling of methylenes, $CH_{2(ad)}$, followed by β-elimination of the 1-alkene from a surface alkyl, for example,

$$H_{(ad)} + CH_{2(ad)} + CH_{2(ad)} + CH_{2(ad)} \rightarrow CH_3CH_2CH_{2(ad)}$$
$$CH_3CH_2CH_{2(ad)} \rightarrow CH_3{-}CH{=}CH_2 + H_{(ad)}$$

However this requires two steps neither of which seems favourable: the coupling of two $CH_{2(ad)}$ species (containing sp^3 carbons) [9], and the β-elimination of H onto a metal surface already covered by hydrogen.

An alternative thesis that arose from our labelling studies [3], and which also explains experimental observations that polymerisation is initiated by a $C_{2(ad)}$ [10, 11] rather than a $C_{1(ad)}$ species, involves the coupling of surface alkenyl (vinyl) and methylene, followed by a 1,3-H-migration to regenerate a metal-alkenyl containing an sp^2

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carbon which can then react with further methylene, $CH_{2(ad)}$, to continue the cycle [3],

$$CH_2{=}CH_{(ad)} + CH_{2(ad)} \rightarrow CH_2{=}CH{-}CH_{2(ad)}$$
$$R{-}CH{=}CHCH_{2(ad)} \rightarrow RCH_2{-}CH{=}CH_{(ad)}$$

This still looks a reasonable and plausible mechanism; however, attention has been drawn to surface studies which show that $CH_{2(ad)}$ loses H very readily, even at 200 K, well below the temperature of the F–T reactions, to generate the more stable triply coordinated surface methylidyne, $CH_{(ad)}$ [12–14]. It has therefore been suggested [15, 16] that methylidyne is the chain carrier in the F–T reaction, and that chain growth occurs in two stages: a C–C coupling that is then followed by a separate hydrogen transfer step:

$$RCH_{(ad)} + CH_{(ad)} \rightarrow RCHCH_{(ad)}$$
$$RCHCH_{(ad)} + H_{(ad)} \rightarrow RCH_2CH_{(ad)}, \text{ etc.}$$

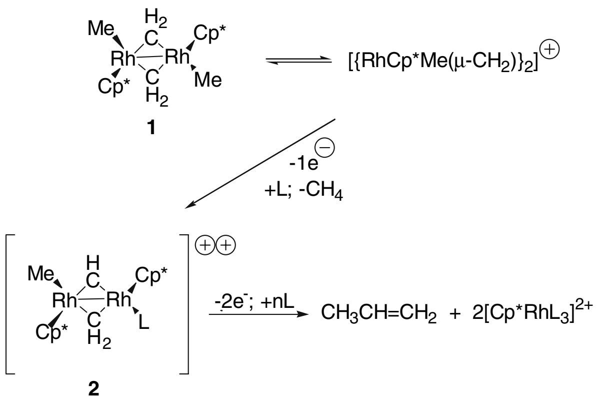
2 Electrophilic Methylidyne Hypothesis

Reactions such as the hydrogenation of CO in which surface metal atoms react with organic entities involve surface organometallic species, the properties of which must be parallel to those of organometallic complexes in homogeneous media. Studies of reaction mechanisms of organotransition metal complexes in solution are therefore instructive in providing models for reactions on surfaces. One key type of reaction is reductive elimination in which two organic ligands (R^1 and R^2) on a metal centre couple to give R^1–R^2 together with a species that has the metal in a lower oxidation state,

$$M(R^1)(R^2)L_n \rightarrow ML_n + R^1 - R^2$$

Reductive eliminations often show significant rate accelerations when the formal positive charge on the initial complex is increased. Thus for example the rate of methyl + methyl coupling to ethane from $Rh(Cp^*)Me_2(PPh_3)$ was accelerated by $>3 \times 10^9$ when the complex was oxidized with ferricinium, $FeCp_2^+$ [17]; similar effects were reported for the elimination of ethane from $AuMe_2^-$ [18]. Hahn has collected together other instances where a formal electron loss results in much faster coupling reactions [19]. It has also been noted that methyl migration, involving the formation of a C–C bond, is much easier in the neutral $IrMe(CO)_3I_2$ than in the anionic $IrMe(CO)_2I_3^-$ [20].

We have modelled C–C–C coupling processes with the dinuclear $[\{RhCp^*Me\}_2(\mu\text{-}CH_2)_2]$ (**1**, $Cp^* = \eta^5{-}C_5Me_5$). This is a thermally very stable (to 300 °C) red crystalline solid; however on oxidation (for example by $IrCl_6^{2-}$ or Ag^+ in MeCN = L) three C_1 ligands in one molecule combine to give propene, already at room temperature. Detailed ^{13}C and D-labelling and electrochemical studies have suggested a reaction path as shown in Scheme 1 [21–23].



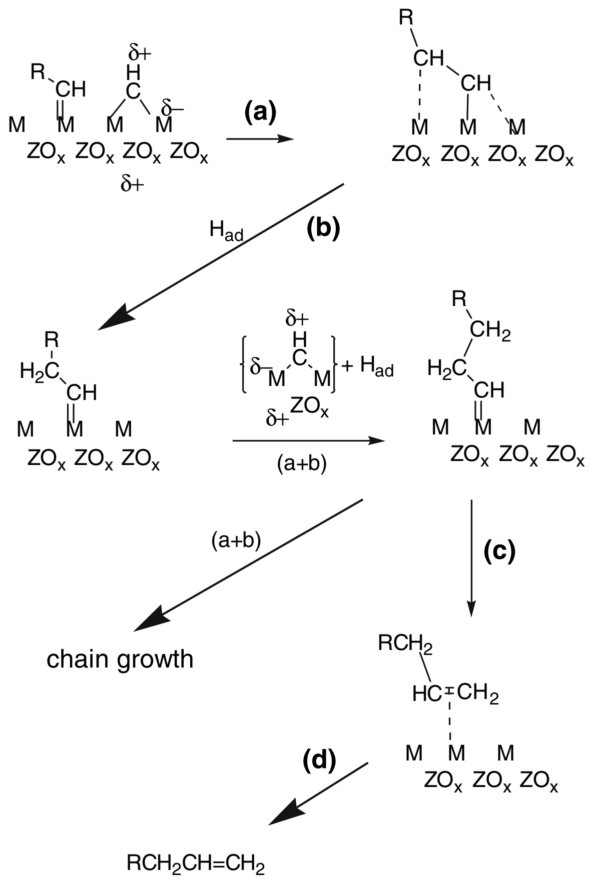
Scheme 1 Proposed steps in the formation of propene from the oxidative coupling of three C_1 ligands on the dirhodium complex **1**, $[\{RhCp^*Me\}_2(\mu\text{-}CH_2)_2]$ ($Cp^* = \eta^5{-}C_5Me_5$)

The key step in the sequence involves the formation of a highly reactive cationic μ-methylidyne (μ-CH) intermediate, formulated as **2**. Related facile reactions forming C–C bonds have been shown to occur for cationic μ-methylidyne-di-ruthenium and -di-iron complexes [24–28], as for example the reaction with the C_1 source, diazomethane,

$$[\{FeCp(CO)\}_2(\mu\text{-}CO)(\mu\text{-}CH)]^+ + CH_2N_2$$
$$\rightarrow [\{FeCp(CO)\}_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)]^+$$

There is evidence of charge transport effects also in reactions on metal surfaces. For example Vannice and Garten found that some metals were much more efficient Fischer–Tropsch catalysts when supported on reduced titania [29–31]. Thus, while nickel on alumina is a methanation-only catalyst, on titania it was found to give alkanes and less methane. Watson and Somorjai showed that less methane and more $C_{\geq 2}$ hydrocarbons were formed on oxidised rhodium catalysts than on the clean metal surface [32, 33].

Based upon the reactions of organometallic complexes as models we therefore propose a path as outlined in Scheme 2 for C–C coupling in the formation of 1-alkenes in the heterogeneously catalysed hydrogenation of CO. In the sketch the surface is represented by a series of metal and metal oxide sites ($M^{\delta-}ZO_x^{\delta+}$). A methylidyne attached to the metal M acts as an electrophile to initiate the reaction with a carbene (step a; R = H). The $H_{(ad)}$ (spillover hydrogen) enters the cycle in a second step (b), and chain growth then continues by repetition of steps a + b (R = alkyl). At an appropriate point the alkylidene chain undergoes a 1,2-H shift (step c) to generate a coordinated 1-alkene which desorbs from the surface (step d). (It is also possible that, on a surface well covered with $H_{(ad)}$ two H's can add to the alkylidene chain yielding the *n*-alkane directly).



Scheme 2 Proposed path for C–C coupling involving electrophilic methylidynes giving 1-alkenes in the Fischer–Tropsch reaction on a metal surface

The steps sketched in Scheme 2 appear to account well for both the results of catalytic labelling experiments and also the conclusions from surface studies.

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Appendix

A referee has asked us to propose some experiments to support these ideas. Since the initial CO cleavage and the subsequent C–H formation steps in the Fischer–Tropsch process are probably fast on the catalytically active metal surfaces, the C–C coupling is likely to be the slowest (i.e. rate-determining) step of the overall process. One approach would thus be to increase the rate by increasing the electrophilicity of the methylidyne. This could be achievable either electrochemically or by adding a very strong Lewis acid. Komaya, Boffa, Bell and their coworkers have shown that the rate of methane formation in CO hydrogenation over Rh decorated by various metal oxides is dependent on the Lewis acidity of the oxide [34–36]. Given the very sensitive analytical techniques now available it should be relatively straightforward to extend this experiment to ascertain how the degree of chain lengthening (i.e. the rate of formation of products $C_{>1}$) is affected by different Lewis acids on a number of metals with Fischer–Tropsch activity, and comparing them to the rates of methane production.

It is also interesting that addition of potassium to a Rh(111) surface stabilised $CH_{2(ad)}$ caused it to dimerise to ethylene [37].

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