Heterogeneous catalysis of C–C bond formation: black art or organometallic science?

Peter M. Maitlis, Helen C. Long, Ruhksana Quyoum, Michael L. Turner and Zhi-Qiang Wang

Department of Chemistry, The University of Sheffield, Sheffield, UK S3 7HF

Methylene polymerisation, which occurs during the heterogeneously catalysed hydrogenation of CO (Fischer–Tropsch synthesis) is analysed as an example of a transition metal-promoted C–C coupling reaction. A new catalytic cycle has been proposed, the *alkenyl* mechanism, which is based on simple stoichiometric organometallic reactions. Results from experiments using isotopically $^{13}C_2$-labelled probe molecules indicate that surface vinyl/alkenyl species are directly involved in the Fischer–Tropsch polymerisation over rhodium and ruthenium surfaces. The data indicate that C–C couplings are favoured if one of the participants has a metal to sp^2 carbon bond, and that vinyl (or alkenyl) is a better combining ligand than phenyl, which in turn is better than methyl (alkyl).

C–C coupling reactions which occur during heterogeneous catalysis are well modelled by soluble organometallic metal complexes, where the C–C coupling reactions take place at one or two metal atoms. Model studies further suggest that no step of the Fischer–Tropsch process *requires* the participation of cluster arrays.

Bridges may now be built between the *reactions* which occur on metal surfaces under heterogeneous catalysis conditions, those that take place on isolated and characterised metal complexes, and those that occur under ultra-clean conditions on single planes of metal crystals.

Introduction

Heterogeneous catalysis is of almost unsurpassed industrial importance. Processes heterogeneously catalysed by transition metals have long been known, some since the early 1800s. These include the surface catalysed reaction of H_2 and O_2, the oxidation of SO_2 to SO_3, the reforming of methane, ammonia synthesis and oxidation, and ethylene hydrogenation.[1] Despite this, and the expenditure of much effort and many resources, we still know less about the *chemistry* underlying many such catalytic processes than we know about more complex biological transformations. The aim of this article is to show that the processes occurring on heterogeneous catalysts during organic transformations are rather similar to those that take place in quite simple organometallic complexes.

The direct investigation of heterogeneously catalysed reactions poses many problems, and it is only with the advent of sophisticated new instrumentation for surface studies that we have been able to begin understanding what reactions occur on a surface during catalysis. Thus to some extent heterogeneous catalysis has been a black-box technology, where the chemical engineer improves the process simply by tweaking the conditions.

In trying to understand the catalysis of organic transformations, one popular approach has involved relating metal surfaces to molecular organometallic clusters, such as the polynuclear carbonyls.[2] There are substantial structural similarities between the two, as for example in the atomic packing, and molecular clusters offer insights into the binding of some bridging ligands, as well as of certain simple transformations on surfaces, for instance H or CO migration. However, a distinguishing feature of most molecular clusters is their *kinetic inertness*, arising from the strongly bound ligands (such as carbonyl or cyclopentadienyl) which protect the metal core. By comparison, metal surfaces are *highly reactive*. One must ask whether a largely structural analogy is necessarily a good guide to reactivity.

Many reactions homogeneously catalysed by metal complexes in solution are now understood in considerable detail, and have been shown to occur at single metal centres. Evidence has also accumulated that many clusters which participate in catalytic processes first break open to create 'vacant' sites at which reaction can occur; in doing so they generate smaller, usually mononuclear, units which have much higher reactivity.[2]

Can heterogeneous catalysis occur at single sites on the metal surface?

One intriguing question that we would like to address is whether heterogeneously catalysed reactions also occur at single metal surface sites. In this sense, a metal surface can be regarded as an inhomogeneous assembly of atoms. Some, with fewer neighbour atoms, show higher reactivity (since they have more vacant coordination sites at which reaction can occur), while others, of higher coordination number, show more selectivity, since the reactive sites are more hindered. The tuning that ligands offer to homogenous reactions is mimicked on a surface by the effects of neighbouring metal atoms, supports, and promoters. The uncertainties in heterogenous catalysis come from a lack of control over the organisation and composition of the surface where reaction occurs;[3] this leads to competing processes with similar activation energies.

Most chemical transformations involved in catalysis *can* be carried out quite efficiently on only a single metal atom. These include C–H cleavage, oxidation, polymerisation, metathesis, carbonylation, hydrogenation, chiral induction, and many others.[4] Undoubtedly metal surfaces can promote some reactions so far not easily carried out under homogeneous conditions in solution; however, one must ask the question whether the main role of the surface *array* may not be simply to help assemble and support the reagents?

Ligands can of course bind adjacent metal atoms: for example, CO can bridge two or three metals (μ_2- or μ_3-CO) as well as binding terminally (M–CO). A reaction of relevance to this paper, is the formation of metal carbide complexes from metal carbonyls, but polymetallic arrays seem not *necessary* even for that type of transformation.[5]

There are also many reactions in which two metals act cooperatively;[6] but in general the metals are different and each then plays a separate role, for example, Pd and Cu in the homogeneously catalysed oxidation of ethylene to acetaldehyde (Wacker reaction),[7] or Ti and Al in the heterogeneous Ziegler–Natta olefin polymerisation.[8]

Carbon monoxide hydrogenation

These considerations have arisen through our studies of the hydrogenation of CO to linear alkenes and alkanes, the Fischer–Tropsch reaction. This is quite a complex process, but it can now be analysed into several steps, each of which can be understood in terms of simple model processes occurring on single atoms or, occasionally, on groups of two or three metal atoms.[9]†

Hydrogenation of CO is thermodynamically favourable; the first example, methanation over nickel [eqn. (1)], was reported by Sabatier and Senderens in 1902.[10]

$$CO + 3H_2 = CH_4 + H_2O;\ \Delta G_{298}\ -140\ \text{kJ mol}^{-1} \qquad (1)$$

In 1926 Fischer and Tropsch published their classic papers in which they disclosed that linear aliphatic hydrocarbons (alkenes and alkanes) are formed at atmospheric pressure at 200–300 °C over Co or Fe catalysts [eqns. (2) and (3)]:[11]

$$n\text{CO} + (2n + 1)\text{H}_2 = \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \qquad (2)$$

$$2n\text{CO} + (n + 1)\text{H}_2 = \text{C}_n\text{H}_{2n+2} + n\text{CO}_2 \qquad (3)$$

Since syngas ($CO + H_2$) is readily available from a variety of fossil fuels, including coal, the process became industrially important for economies which had good supplies of cheap coal but which lacked oil. Thus by 1939 Fischer–Tropsch plants in Germany were making up to 600 000 tonnes per year of liquid hydrocarbons for petrol, aviation fuel, and diesel,[12] while during the 1970s in South Africa the Sasol plant used analogous technology to make liquid fuels.[13] Quite recently Shell brought on stream in Malaysia a major plant to make waxes, which are then hydro-cracked to gasoline and diesel fuels;[14] in that case methane is the source of the syngas. The versatility of Fischer–Tropsch technology allows ready adaptation to changing economic conditions: the Sasol plant is now producing propene.[15]

The catalysts are metals of the Group 8–10 transition series, supported on oxides, and containing a wide variety of 'promoters'. Iron gives mainly linear alkenes and oxygenates, cobalt mostly linear alkanes, nickel mainly methane, while ruthenium, one of the most active catalysts, can give high molecular mass hydrocarbons.[16] A recent innovation has been the use of rhodium as a catalyst which makes oxygenates in addition to hydrocarbons.[17] Under normal conditions (low pressure and low temperature, ≤200 °C) the initial hydrocarbons tend to be alk-1-enes (which are subsequently hydrogenated into alkanes or isomerised into internal olefins) and this article will concentrate on the reactions which produce them.

In their classic papers Fischer and Tropsch discussed the reactions in terms of the initial formation of surface carbides which reacted with hydrogen to give methylenes, which in turn polymerised. Studies of organic ligands on metals in the 1970s and early 1980s began to offer structural models, and an understanding of this on a molecular level. Labelling studies on catalysts,[18] supported by surface studies,[19] and by organometallic models,[20] confirmed that the first step is to transform coordinated (chemisorbed) CO into a type of surface carbide, and that this carbide is hydrogenated *via* surface methyne (CH) to surface methylene (CH_2), methyl (Fig. 1), and finally, methane. Although a number of alternative theories have been formulated,[21] there now is general agreement that these are the initial steps in the formation of hydrocarbons.

This view is also supported by the experiments of Iglesia *et al.* which show that Fischer–Tropsch reactions are not structure sensitive, in other words, they do not depend on the position of the reacting metal atom(s) in the surface.[22]

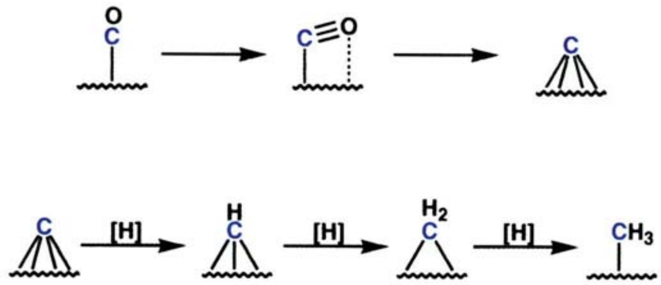

Fig. 1 Proposed route for the generation of surface CH_2 from chemisorbed CO *via* carbide and surface methyne (CH). The surface methylene can be further hydrogenated to methyl and methane.

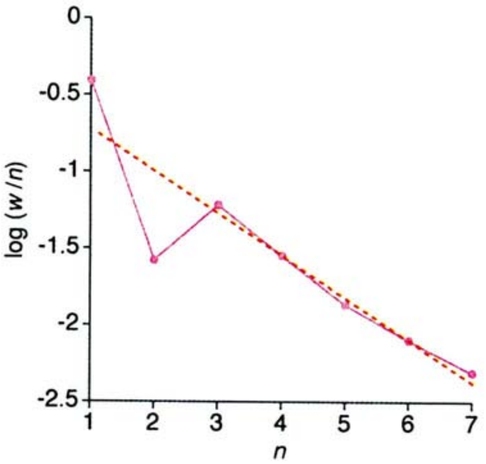

Fig. 2 An experimental molecular mass distribution for a Fischer–Tropsch reaction, plotting log (w/n) against n (w = weight fraction, n = number of carbon atoms in that fraction). The deviations from the Anderson–Schulz–Flory distribution (dotted line) at C_1 and C_2 are characteristic features of the Fischer–Tropsch synthesis. The monotonic decrease from C_3 to C_7 products is indicative of a step-growth polymerisation.

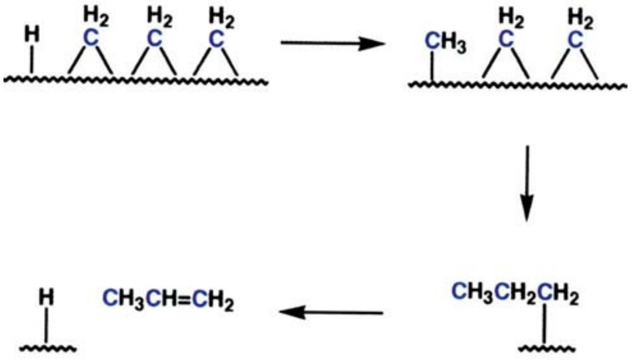

Fig. 3 Representation of the Brady–Pettit alkyl mechanism for the polymerisation of CH_2 on a metal surface, initiated by surface hydride or CH_3. Chain growth proceeds by coupling between formally sp^3 carbons, and the chain is terminated as the alk-1-ene by β-elimination of hydride.

A further key point on which there is general agreement is that the Fischer–Tropsch reaction is a *stepwise polymerisation of methylenes*.[23,24] The experimental molecular mass distribution of hydrocarbons shows good agreement with that expected on the basis of Anderson–Schulz–Flory (ASF) polymerisation kinetics (Fig. 2). The main exception is that the amount of C_2 is invariably lower than expected; see below.

A mechanism by which methylenes polymerise to give alk-1-enes was proposed by Brady and Pettit.[24] As illustrated in Fig. 3, polymerisation of surface methylenes was initiated by a surface hydride (or methyl), and proceeded by coupling between formally sp^3 carbons; chain growth was terminated by β-elimination of hydride from the growing alkyl chain on the surface. This we have termed the *alkyl mechanism*.

It is with this polymerisation that we have chiefly concerned ourselves, since it is here that one might hope to influence and

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† The models for these reactions are taken largely from organometallic chemistry, but an increasing number of pertinent observations now stem from stoichiometric reactions which can actually be studied as they occur on the faces of clean metal single crystals. These are normally carried out under ultra-high vacuum conditions (and often at low temperatures), but despite that there is a clear relationship to real catalytic systems.[9]

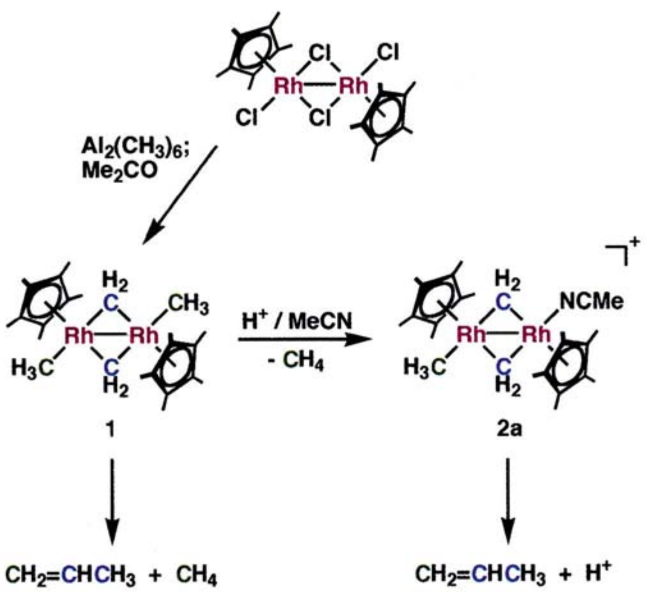

Fig. 4 Synthesis of $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)(Me)\}_2]$ **1**, containing two methyl and two μ-methylene ligands, and of the cation, $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]^+$ **2a**, which contains one methyl and two μ-methylene ligands. The decomposition, especially under the influence of one-electron oxidisers, gives largely propene and methane from **1**, and propene from **2a**.

further expand the reactions. A review of the alkyl mechanism is demanded by three considerations: (*i*) the dip found at C_2 in the Anderson–Schulz–Flory distribution, indicating a discontinuity and possibly a difference of mechanism; (*ii*) the formation of small amounts of branched chain products, which are not allowed for by the alkyl chain mechanism; and (*iii*) the β-elimination of hydride from the growing alkyl chain, on a surface already covered with hydride, to give the alk-1-enes.

Several of these points have also been addressed by other researchers in the field, and for example McCandlish[25] has proposed a vinylidene/methylene polymerisation scheme to explain the second of these problems. However, that proposal has been questioned, because models do not bear out the proposed route, which should give more branched hydrocarbons than are actually found.[26]

Homogeneous model complexes

Our work in this field grew out of the synthesis and structural characterisation of $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)(Me)\}_2]$ **1**, containing two methyl and two μ-methylene ligands, and the closely related cation, $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(MeCN)]^+$ **2a**, which contains one methyl and two μ-methylene ligands (Fig. 4).[27] The arrangement of methyl and methylene ligands closely modelled that expected on a surface where a Fischer–Tropsch reaction was proceeding, and allowed us to test the validity of the alkyl mechanism.

Complex **1** was in fact rather kinetically inert and needed heating to quite high temperatures (≥300 °C) before C–C coupling occurred. However, the cation **2a** decomposed more easily, as did **1**, in the presence of one-electron oxidisers [eqns. (4) and (5)].

$$\underset{\mathbf{1}}{[\{(C_5Me_5)Rh(\mu\text{-}CH_2)(Me)\}_2]} - 4e^- + \text{solv} \rightarrow \\ MeCH{=}CH_2 + CH_4 + 2\,[(C_5Me_5)Rh(\text{solv})_n]^{2+} \quad (4)$$

$$\underset{\mathbf{2}}{[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Me)(\text{solv})]^+} - 4e^- + \text{solv} \rightarrow \\ MeCH{=}CH_2 + H^+ + 2[(C_5Me_5)Rh(\text{solv})_n]^{2+} \quad (5)$$

The results from ^2H- and ^{13}C-labelling experiments showed that the main products (propene and methane from **1**, and propene from **2a**) were only derived from the C_1 ligands.[28] NMR analyses on the propene derived from decomposition of $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(^{13}CH_3)(MeCN)]^+$ **2b**, and of $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(CD_3)(MeCN)]^+$ **2c**, indicated that it was more than 70% $^{13}CH_2{=}CHCH_3$ and *ca.* 90% $CH_2DCH{=}CD_2$ respectively. The products expected on a simple Me + CH_2 + CH_2 coupling model would be $^{13}CH_3CH{=}CH_2$ and $CD_3CH{=}CH_2$, and since these were only detected to a small extent, we were forced to abandon that as a paradigm for the reaction. Such a clean result can only arise by a very specific multistep pathway, and we have suggested that the key feature is the intermediacy of a Rh–σ-vinyl, which couples with a μ-methylene.

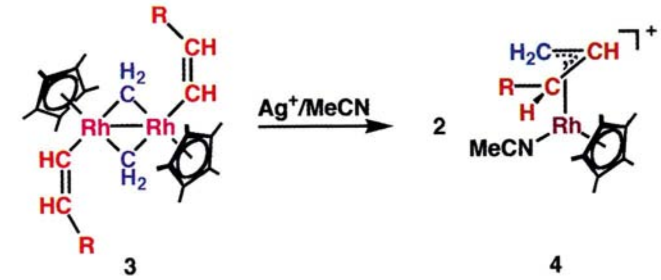

Fig. 5 The alkenyl and the μ-methylene in **3** couple under ambient conditions in the presence of Ag^+ in acetonitrile to give the allylic complex **4**. When the alkenyl is *Z*-propenyl (R = Me), the reaction gives the *anti*-1-methylallyl.

Vinylic intermediates in the Fischer–Tropsch reactions?

Further work showed that such vinylic couplings are important in other reactions of model complexes. Thus, in the dialkenyl-di-μ-methylene complexes $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)(CH{=}CHR)\}_2]$ **3**, the alkenyl and the μ-methylene couple under ambient conditions in the presence of a one-electron oxidiser (Ag^+) in acetonitrile to give the allylic complexes, $[(C_5Me_5)Rh(\eta^3\text{-}CH_2CHCHR)(MeCN)]^+$ **4**. When the alkenyl is *Z*-propenyl (R = Me), the reaction gives the *anti*-1-methylallyl (Fig. 5). The stereospecificity indicates the great ease with which coupling occurs.[29]

These results suggested the possible involvement of vinyl/alkenyl intermediates in the Fischer–Tropsch reactions themselves.[30] We have therefore investigated this by adding vinylic probes to Fischer–Tropsch reactions over rhodium catalysts.‡ Rhodium was chosen since it allowed a metal match to our model systems, and because it shows interesting Fischer–Tropsch behaviour. Since heterogeneous catalytic reactions are so difficult to investigate directly, we chose a kinetic approach, adding doubly labelled probe molecules to the Fischer–Tropsch reaction. If the probes were closely related to the intermediate species involved in the surface reactions, they should readily be incorporated.

We elected to use the doubly ^{13}C-labelled vinyls (*a*) $^{13}CH_2{=}^{13}CHBr$, (*b*) $(^{13}CH_2{=}^{13}CH)_4Si$, and (*c*) $^{13}CH_2{=}^{13}CH_2$, as probes since they would give maximum unambiguous mechanistic information.[31]§ Analysis of the mass spectra of the organic products would immediately show, (*i*) whether the $^{13}C_2$-probe had been incorporated into the products, and to what degree, (*ii*) whether C–C cleavage of the probe to C_1 was significant, and whether any hydrocarbons were formed by such

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‡ The catalyst, Rh (4%), CeO_2 (9%), on silica, was prepared by the incipient wetness technique;[31] similar procedures were used to prepare the Rh (4%), and the Ru (4%) on silica catalysts. Reactions were carried out by injecting the probe molecules into the syngas feed (at a given temperature, normally 200 °C, and one atmosphere), and analysing the products by GC and GC-MS. Ceria was added to the rhodium catalyst to increase the productivity; under these conditions there was very little difference in selectivity.

§ Deuterium is not suitable as a label since scrambling occurs on heating deuterio-organics, especially over metals under hydrogen.

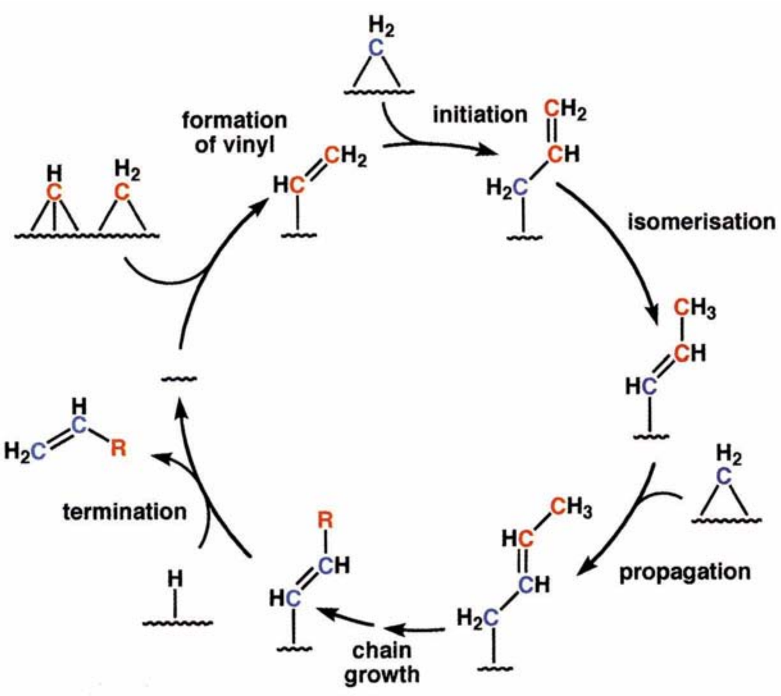

Fig. 6 The alkenyl mechanism for the Fischer–Tropsch reaction expressed as a catalytic cycle. Initiation is by the coupling of a surface methyne and methylene (top left) to give the surface vinyl. This then undergoes chain growth by reaction with surface methylene to give surface allyl. The allyl isomerises to alkenyl which in turn homologates with more methylene. Termination is by reaction of the alkenyl with surface hydride, giving the alkene directly.

paths, (*iii*) whether the C_2-probe initiated or propagated methylene oligomerisation or both, and (*iv*) what other organic reactions were occurring on the surface.

The results from these experiments were completely clear: $^{13}CH_2{=}^{13}CH{-}$ (and also $CH_2{=}CH{-}$) from the three vinyl probes were very obviously incorporated, while for example, ethyl from ethyl bromide or tetraethylsilane, was not.[31] Over rhodium the most active probe was derived from vinyl bromide, which was an extremely effective initiator. While there was substantial incorporation of $^{13}C_2$ from initiation of the polymerisation, there was no evidence either for the intermediacy of vinyl in propagation, or of significant amounts of cleavage of the vinyl initiator to C_1 fragments.¶ There was, however, evidence for probe coupling, see below.

The alkenyl mechanism for the Fischer–Tropsch polymerisation on rhodium

In order to understand the $^{13}C_2$-incorporation data further, we have developed a new *alkenyl mechanism* for Fischer–Tropsch polymerisation of surface methylenes. The adsorption, activation, and cleavage of CO to a surface carbide species, and the hydrogenation of the carbide to surface methyne and methylene, are generally agreed to proceed as shown in Fig. 1. However, we need to diverge from previous hypotheses involving alkyl chain propagation, since we now have to accommodate the new data showing the incorporation of C_2 (vinyl). It is particularly significant that vinyl, especially derived from vinyl bromide, is an excellent initiator. By contrast, there was no evidence for incorporation of ethyl from ethyl bromide. We therefore propose that the participation of vinyl is an integral part of the surface polymerisation mechanism. This is shown in the form of a catalytic cycle in Fig. 6, where the first step (top left) is the formation of a surface vinyl. Each succeeding step is the (irreversible) linear homologation of a surface alkenyl species with surface methylene, followed by an isomerisation of the resulting allylic species to another alkenyl. Growth is terminated by reaction with surface hydrogen, giving the alk-1-ene directly, or by coupling. For simplicity the diagram is restricted to the linear propagation; however, since allylic intermediates such as η^1-$CH_2CH{=}CHR$ can also isomerise to η^1-$CHRCH{=}CH_2$, reaction with surface CH_2 is then possible at the tertiary alkenyl C of η^1-$CR{=}CHCH_3$. This will be inhibited on steric grounds, which explains both the formation of branched chain isomers and their low abundance. It may also be noted that as industrial Fischer–Tropsch reactions are carried out under more severe conditions (*e.g.* pressure), further reactions occur, for example the reabsorption of product alkenes into the cycles.[22] We have not observed the reabsorption of higher alkenes but our mechanism can easily be extended to accommodate them.

A simple mathematical treatment of the steady-state kinetics for the system, based upon the propagation and termination steps of the catalytic cycle shown in Fig. 6, accounts well for the observed effect of $^{13}C_2$ vinyl initiation.‖ The quality of agreement between the theoretical and the experimental for rhodium can be seen from the graphs in Fig. 7(*a*), where the degree of initiation of various coverages of labelled surface vinyl is related to the amounts of ^{13}C label found in the product alk-1-enes.

¶ Oxygenates (methanol, acetaldehyde, and ethanol) are also formed, but they contain no significant amounts of ^{13}C, and must arise by other routes. The point that oxygenates and hydrocarbons arise by different paths has also been made by other authors, see refs. 17 and 21.

‖ If the rate constants (k_p) for each step of the linear propagation of each surface alkenyl species ($-CH{=}CHR = A_n$) with methylene ($>CH_2 = M$) are similar, then the rate of appearance of a species A_n will be given by the rate of reaction to form it, $k_p[A_{n-1}][M]$. Under steady-state conditions, the rate of formation must equal the rate of disappearance by, (*a*) propagation, $k_p[A_n][M]$, plus (*b*) chain termination by hydrogen transfer, $k_t[A_n][H]$, and (*c*) coupling with an A_2 species, $k_c[A_n][A_2]$. Hence,

$$d[A_n]/dt = k_p[A_{n-1}][M] - k_p[A_n][M] - k_t[A_n][H] - k_c[A_n][A_2] = 0$$

from which $[A_n]/[A_{n-1}]$, is given by:

$$[A_n]/[A_{n-1}] = k_p[M]/\{k_p[M] + k_t[H] + k_c[A_2]\} = \alpha'$$

where α' is the chain growth probability during probe addition, which can be measured directly from an ASF plot.

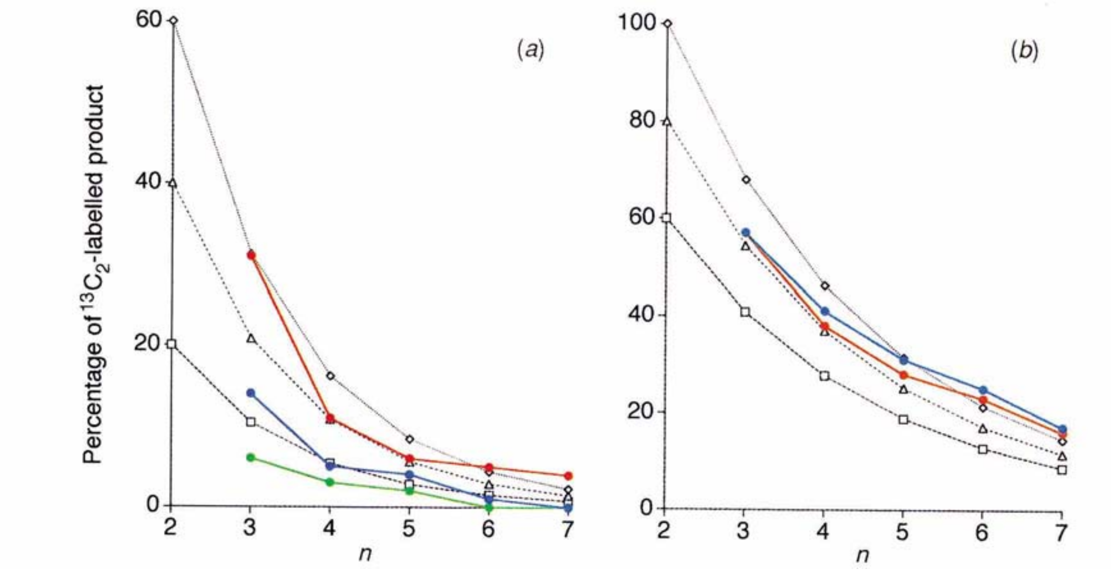

Fig. 7 (*a*) Comparison between calculated $^{13}C_2$ incorporation assuming different initial surface concentrations of $^{13}C_2H_3$ (dotted lines, ······◊······ 60%; ······△······ 40%; ······□······ 20%) and experimental $^{13}C_2$ incorporation derived from vinyl probes (bold lines, ——●——, red $^{13}C_2H_3Br$; blue $(^{13}C_2H_3)_4Si$; green $^{13}C_2H_4$) over a $Rh/CeO_2/SiO_2$ catalyst. Plot of percentage of products that are $^{13}C_2$ labelled (*y*-axis) against carbon number (*x*-axis). (*b*) Comparison between calculated $^{13}C_2$ incorporation assuming different initial surface concentration of $^{13}C_2H_3$ (dotted lines, ······◊······ 100%; ······△······ 80%; ······□······ 60%) and experimental $^{13}C_2$ incorporation derived from vinyl probes (bold lines, ——●——, blue $^{13}C_2H_4$; red $^{13}C_2H_3Br$) over a Ru/SiO_2 catalyst. Plot of percentage of products that are $^{13}C_2$ labelled (*y*-axis) against carbon number (*x*-axis).

For $^{13}C_2H_3Br$ there is some 30% incorporation of $^{13}C_2$ into the C_3 and *ca.* 11% incorporation of $^{13}C_2$ into the C_4 hydrocarbons (neglecting vinyl–vinyl coupling). These values are consistent with a level of initiation of around 60% by added $^{13}C_2H_3$. Thus vinyl bromide is an extremely effective promoter of Fischer–Tropsch polymerisation.

Similar procedures were applied to the data using $Si(^{13}C_2H_3)_4$ or $^{13}C_2H_4$ as probes; however, here the degree of incorporation of $^{13}C_2$ is significantly less. This suggests that on rhodium these molecules are less effective precursors of surface vinyls, with initiation of around 30% by added $^{13}C_2H_3$ from tetravinylsilane and 10% from ethylene. The data also show that the vinyl probes initiate, but do not significantly participate in, the chain propagation.

We suggest that in the absence of a vinylic probe, the initial formation of a surface vinyl ($-CH{=}CH_2$) occurs by the reaction of a surface methyne ($\equiv CH$) and a surface methylene ($>CH_2$). Although this reaction does not yet seem to have been demonstrated on a surface, it has been modelled in organometallic complexes; for example, the interaction of a tungsten carbyne with a diruthenium μ-methylene gives an alkenyl complex [eqn. (6)].[32]

$$\begin{aligned}&[\{(C_5H_5)Ru\}_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(MeCN)] + \\ &[\{(C_5H_5)W\}(CO)_2(\equiv CR)] \rightarrow \\ &\quad [(RCH{=}CH)\{(C_5H_5)W\}(CO)_2\{(C_5H_5)Ru(CO)\}_2] \qquad (6)\end{aligned}$$

Fischer–Tropsch reactions on ruthenium

We have now extended our studies to ruthenium, a more conventional Fischer–Tropsch catalyst. The results [Fig. 7(*b*)] are strikingly similar to those obtained for rhodium.[33] We find that ruthenium is *ca.* 2–3 times more active for Fischer–Tropsch reactions under comparable conditions, and high levels of incorporation of $^{13}C_2$, consistent with our vinyl initiation model, are again seen when $^{13}C_2H_3Br$ is used as probe. In contrast to rhodium, $^{13}C_2H_4$ is as effective a probe molecule as $^{13}C_2H_3Br$ and high levels of $^{13}C_2$ incorporation are again seen for ruthenium. Although there is some incorporation of $^{13}C_1$, C–C cleavage of the probe is quite small if the reaction temperature is kept low (⩽ 180 °C). Once again, there is no evidence for vinyl probe incorporation other than from initiation (and vinyl–vinyl coupling).

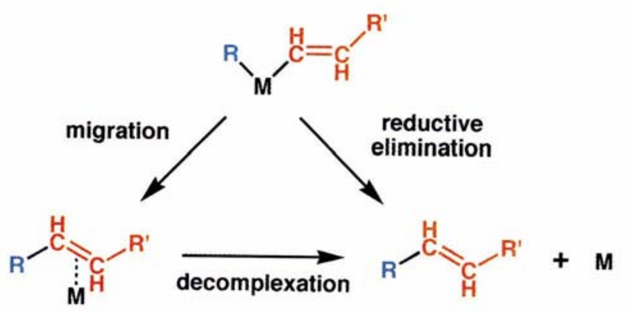

Fig. 8 Diagram illustrating two routes by which C–C coupling (C sp^2 + C sp^3) can occur on a metal atom: the *migration process* (followed by decomplexation) with a low activation energy, and the direct, higher energy *reductive elimination*

Considerable research by Knox and coworkers has shown that diruthenium model complexes can participate in C–C coupling reactions rather similar to those that we have observed in our dirhodium complexes.[34] The chief difference is that the organic ligands are not expelled (reductively eliminated) from ruthenium as easily as from rhodium; thus the transformations occur within the complexes. This may be due to the much higher formal oxidation state of the rhodium (+4) than the ruthenium (+2) in the models, which makes reductive elimination and extrusion of the organic product easier.[31]

Why vinyl?

A key question is why vinylic intermediates are now assuming so much importance. There is considerable evidence that the *cis* coupling of two sp^3 carbons on a metal is disfavoured because there is a substantial kinetic barrier to the reorientation of the two highly directional sp^3 orbitals to form the C–C bond.[35] When metal-bonded alkenyls (sp^2 carbons) are involved in coupling, the reaction is facilitated, and several workers have noted that the coupling of a metal-bonded alkenyl sp^2 carbon to a metal-bonded alkyl sp^3 carbon is preferred to the coupling between two metal-bonded alkyl sp^3 carbons.[36] It has been proposed that this is because the former can occur as a *migration* process (followed by decomplexation) with a lower activation energy, than the latter, which is a direct reductive elimination. The two paths are illustrated schematically in Fig. 8. Calhorda

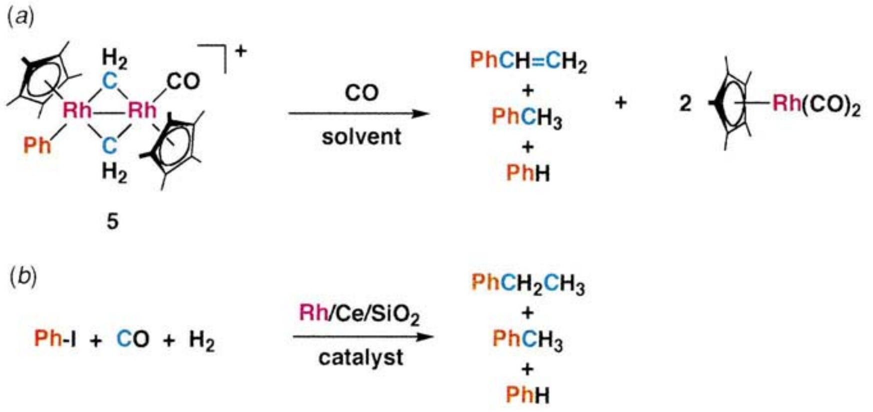

Fig. 9 (*a*) Decomposition of the rhodium complex $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Ph)(CO)]^+$ **5** (under CO) in solution to give PhCH=CH$_2$, PhMe, and C_6H_6, and $[(C_5Me_5)Rh(CO)_2]$. (*b*) Phenyl (generated from iodobenzene) reacts with surface methylene (from CO + H_2) over rhodium metal to give PhEt, PhMe, and C_6H_6.

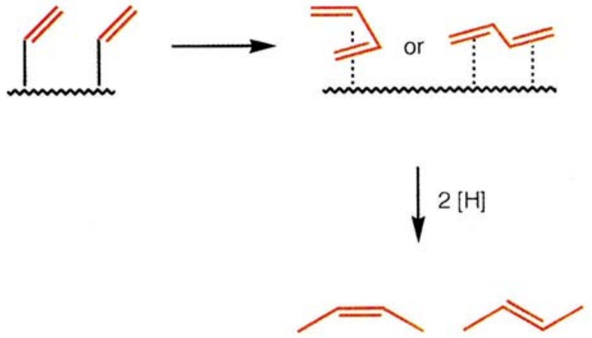

Fig. 10 Vinyl derived from vinyl bromide undergoes facile coupling under Fischer–Tropsch conditions. The products are *cis*- and *trans*-but-2-ene which are formed *via* a coordinated butadiene intermediate.

et al. have provided theoretical explanations for such concepts in coupling reactions on palladium and nickel complexes in solution.[37]

Thus we propose that in the Fischer–Tropsch reactions alkenyl intermediates will be more reactive than alkyls since they have a lower energy path to reaction with μ-methylenes ($>CH_2$). In addition to vinyl, other systems with reactive sp^2 carbons may also be expected to participate in such reactions. We have tested this approach, once again by looking at both a model complex and a heterogeneous catalyst, this time for phenyl initiation.[38] Decomposition of the rhodium complex $[\{(C_5Me_5)Rh(\mu\text{-}CH_2)\}_2(Ph)(CO)]^+$ **5** (homogeneously, under CO) in solution gave PhCH=CH$_2$, PhMe, and C_6H_6, while phenyl (from PhI) reacted with surface methylene (from CO + H_2) heterogeneously over rhodium metal to give PhEt, PhMe, and C_6H_6, (Fig. 9). The results show an interesting parallel, but while phenyl, derived from halobenzene, does initiate, the methylene oligomerisations do not extend far. We have suggested that this is due to the inaccessibility of suitable low-energy sp^2 intermediates, which may make the alternative, but higher energy, alkyl model the most reasonable propagation mechanism.

Vinyl coupling reactions on catalysts, models and surfaces

Analysis of the mass-spectrometric data of the products from Fischer–Tropsch experiments with labelled probes showed high levels of $^{13}C_4$ incorporation into hydrocarbons when $^{13}C_2H_3Br$ (over both Rh and Ru) or when $^{13}C_2H_4$ (mainly over Ru) were used. Major products were *cis*- and *trans*-[$^{13}C_4$]but-2-ene, which must arise by a coupling of two $^{13}C_2H_3$ probes to give surface [$^{13}C_4$]butadiene, which is then 1,4-hydrogenated before release (Fig. 10).[31,34] In confirmation of the last step, we have shown that addition of butadiene to a syngas stream over a ruthenium catalyst gave a very large enhancement of the but-2-enes.

Table 1 Decomposition of the iridium complex $[(C_5Me_5)Ir(CO)(R)(R')]$ **6**, under CO for various R and R′

R	R′	Decomposition conditions	Product	Yield (%)
CH$_2$=CH	CH=CH$_2$	60 °C (2 h)	CH$_2$=CHCH=CH$_2$	95
CH$_2$=CH	Me	200 °C (2 h)	CH$_2$=CHMe	56
			MeH	11
			CH$_2$=CHH	11
Ph	Me	360 °C (4 h)	PhMe	15
			MeH	21
			PhH	20
Me	Me	400 °C (6 h)	MeMe	3
			MeH	42

We have recently shown that such couplings are easily modelled on mononuclear complexes,[39]** and that a poly-metal framework is not generally necessary. The ease of reductive elimination of R–R′ from the iridium(III) η^5-pentamethylcyclopentadienyl complexes $[(\eta^5\text{-}C_5Me_5)Ir(R)(R')(CO)]$ **6**, depends on R and R′ in a particularly informative way (Table 1). We have used carbon monoxide (1 atm) as promoter for these reactions to mimic more closely the heterogeneous catalysis conditions. Alkyl migration on to CO is not favoured for iridium,[40] thus coupling is favoured over carbonylation. For the reactions depicted in Table 1 the order of decreasing ease of coupling is: R, R′ = vinyl + vinyl > vinyl + methyl > phenyl + methyl >> methyl + methyl. The first reaction, of $[(\eta^5\text{-}C_5Me_5)Ir(CH{=}CH_2)_2(CO)]$ to give butadiene, occurs easily and quantitatively at ambient temperature, while in the last, $[(\eta^5\text{-}C_5Me_5)Ir(Me)_2(CO)]$, very little coupling occurs; only 3% ethane is formed even at 360 °C, and the main product is methane. Couplings to phenyl are intermediate.[41] Even though the data are only qualitative as yet, it is clear that sp^2 + sp^2 is strongly favoured, in particular for vinyl, with sp^2 + sp^3 being the next easiest (with vinyl coupling more easily than phenyl), and sp^3 + sp^3 being the most difficult. This is in good agreement with the results obtained over heterogeneous catalysts, where vinyl is a good initiator, alkyl is very poor and phenyl is intermediate.

** Two σ-vinyls on rhodium couple very easily to C$_4$ in the reaction

$$[(C_5Me_5)RhBr_2(Me_2SO)] + 2\ CH_2{=}CHMgBr \rightarrow [(C_5Me_5)RhBr(\eta^3\text{-}CH_2CHCHMe)]$$

However, this is complicated by a further reaction of the ligated butadiene to give the methylallyl complex.[39]

The advent of new surface techniques has very recently allowed vinyls to be made and studied on Ag(111), Pt(111) and Cu(100) surfaces by White, Bent and their coworkers.[42] The stoichiometric coupling of surface vinyls on Ag(111) to give butadiene, as well as their reactions with methyl and ethyl to give propylene and but-1-ene, have also been reported. Although these reactions are carried out under ultra-high vacuum conditions, and at very low temperatures on scrupulously cleaned single crystal surfaces, there is a clear analogy to the reactions we have described both on heterogeneous catalysts and in model complexes.

Conclusion

We have shown that, for a number of organic transformations, it is now possible to build bridges between the reactions which occur on metal surfaces under heterogeneous catalysis conditions, those that occur under ultra-clean conditions on single planes of metal crystals, and those that take place on isolated and characterised *low* nuclearity metal complexes.

Studies of the reductive elimination reactions in metal complexes show that the coupling of sp^2 carbons, either with another sp^2 or with an sp^3 carbon, are favoured over those involving only sp^3 carbons; there is also evidence that vinyl sp^2 carbons couple more easily than phenyl sp^2.†† The high reactivity found for metal vinyls in C–C coupling reactions allows an understanding of the importance of vinyl and alkenyl species in Fischer–Tropsch reactions; this has been demonstrated over rhodium and ruthenium heterogeneous catalysts. Related reactions occur (under ultra-clean conditions) on defined metal surfaces.

However, while the importance of metal vinyls/alkenyls has been established, since mechanisms can rarely be unambiguously proved, possible alternative explanations can still be entertained. Thus for example, while our results clearly favour the intermediacy of vinylic/alkenyl (M–CH=CHR) species in the hydrogenation of carbon monoxide, we cannot completely exclude the possibility that vinylidene/alkylidene (M=C=CHR) intermediates play a role;[43,44] the difference is only one hydrogen, and hydrogens on metal surfaces are extremely labile. Further, although our data indicate the alkenyl mechanism to be preferred since the activation needed is less, it is certainly possible that there are systems where an alkyl mechanism occurs, as for example in the formation of higher alkylbenzenes from phenyl initiation.[38]

From the model studies, there seems no obvious requirement for the majority of reactions to take place at metal cluster arrays, even in the complex transformation that occur in the Fischer–Tropsch synthesis of alk-1-enes from syngas. Recent results even suggest that ligands that do bridge several metal atoms, such as ethylidyne (MeC≡), represent relatively stable surface species rather than actual reaction intermediates.[45] The question posed at the beginning of this article is now in sharper focus: is it possible that reactions largely take place at single sites, even on metal surfaces?

The intention behind this review is to paint a broad brush picture of what we believe to be happening on a metal surface during certain catalytic reactions; we hope that this will open new avenues for synthetic and mechanistic studies. Carbon–carbon coupling reactions occur widely and most of the Group 8–10 metals and many others (such as Cu, and Ag) are active promoters. However, the activity of different metals varies substantially towards different organic substrates and further work will illuminate the specific factors that are important. Luckily the various lines now being followed look likely to reinforce each other.

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Peter Maitlis' research interests are in the interactions of metals with organic molecules, in particular catalytic reactions and their mechanisms. After obtaining his BSc (Birmingham) and PhD (Queen Mary College London) degrees, he went to North America where, following postdoctoral work at Cornell and Harvard, he joined the Faculty at McMaster University in Hamilton, Canada. He returned to Britain in 1972 to take up the Chair of Inorganic Chemistry at the University of Sheffield. He has been honoured by the awards of the Tilden Lectureship and the Sir Edward Frankland Prize Lectureship by the Royal Society of Chemistry and is the Ludwig Mond lecturer for 1996.

Helen Long graduated with First Class Honours from Sheffield University in 1992 and is currently completing her PhD thesis on the work described in the feature article.

Ruhksana Quyoum obtained her BSc (First Class Honours) and PhD degrees from the University of Salford. After a year as a postdoctoral researcher at Queen's University in Canada she returned to Britain in 1994 to join Professor Maitlis' research group.

Michael Turner obtained his BSc (First Class Honours) and PhD degrees from Bristol University. He then went to the Pennsylvania State University as a postdoctoral researcher before coming to Sheffield in 1991 where he helped pioneer much of the work described here. In 1993 he was awarded a Royal Society University Research Fellowship and is now working on the synthesis of New Materials at Sheffield University.

Zhi-Qiang Wang obtained his PhD from Dalian Institute of Chemical Physics in China in 1990. He came to Sheffield in 1992 and has been carrying out synthetic and mechanistic organometallic chemistry related to the project.

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