Carbon–Carbon Bond Formation promoted by Electrophiles and the Mechanism of the Fischer–Tropsch Reaction

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Decomposition of *trans*-$[(C_5Me_5RhMe)_2(\mu\text{-}CH_2)_2]$ takes place at 20 °C in the presence of 1-electron oxidisers to give methane, ethylene, and notably propylene, by coupling of C_1 ligands (thermally the same reactions only occur at 250 °C); the analogy to Fischer–Tropsch reactions on rhodium surfaces is noted.

The promotion of C–C coupling reactions, in addition to the formation of R–E, by the action of electrophiles (E^+) on alkyl metal complexes has been known for some time.[1] Kochi and others have pointed out that for a number of complexes of the type $[L_nMR_2]$, ($M = Fe^{II}, Ni^{II}, Co^{III}$, *etc.*) reductive elimination to give R–R proceeds most easily if a one-electron oxidation occurs first; this step can be induced by a large number of electrophiles.[2]

We now report, (i) that C–C coupling is promoted by electrophiles even in much higher oxidation state complexes, (ii) that electrophiles will also promote the coupling of three C_1 ligands on a metal complex, and (iii) on the relevance of these observations to current models for Fischer–Tropsch reactions on metal surfaces.

The Ir^V complex $C_5Me_5IrMe_4$[3] is rather stable; it decomposes on pyrolysis, yielding methane ($\geqslant 99\%$), but temperatures of >200 °C are needed to get useful rates and high degrees of decomposition. By contrast, Na_2IrCl_6 in MeCN causes a fast (stoicheiometric) reaction even at 20 °C that gives ethylene, ethane, and methane in a 6:6:88 ratio, together with some methyl chloride. Although the reaction is complex some electrophile promoted coupling has clearly occurred.

More informative are the reactions of the *trans*-dimethyldi-μ-methylenedirhodium(IV) complex (**1**).[4,5] With iodine (and bromine) a two-stage reaction occurs, yielding methyl halide and the dihalogeno-di-μ-methylene complex (**2**),[6] which reacts with more X_2 to eliminate ethylene and give (**3**) (Scheme 1).

Acids react in a similar two-step process. Methane is of course the main product but some ethylene and ethane, and, particularly notably, propylene are also obtained (Table 1). The proportion of propylene (and of ethylene and ethane) increases when other (oxidizing) electrophiles are used. The reaction with Na_2IrCl_6 in MeCN is especially noteworthy since it gives a very similar distribution of C_1, C_2, and C_3 products to those obtained by pyrolysing (**1**).[†] However, in

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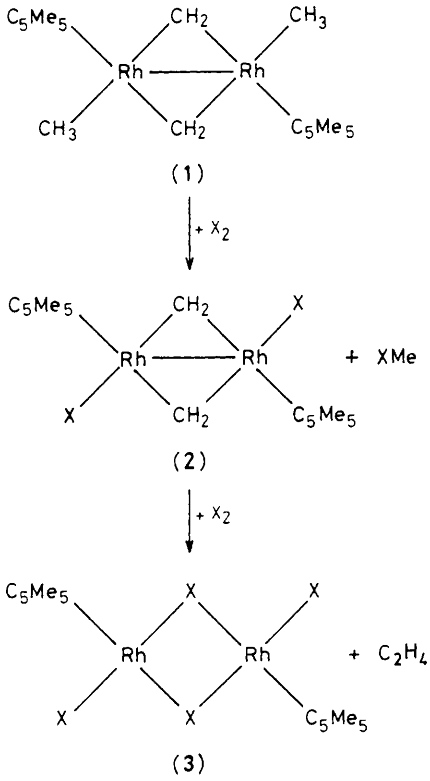
[†] Propylene only becomes a significant product in the thermal decomposition at *higher* temperatures suggesting that there is a substantial activation barrier towards the $3 \times C_1$ coupling process.



Scheme 1

Table 1. Products from the decomposition of $[(C_5Me_5RhCH_3)_2(\mu\text{-}CH_2)_2]$, (**1**).

Conditions[a]	μmol of products[b]				% Decomp.[c]
	CH_4	C_2H_4	C_2H_6	C_3H_6	
HBF_4–C_6H_6	26.4	3.4	0.9	0.5	49
$AgBF_4$–C_6H_6	11.6	6.4	3.4	0.7	45
$AgBF_4$–MeCN	12.7	2.0	12.6	1.3	61
$(NH_4)_4Ce(SO_4)_4.2H_2O$–MeCN	12.8	6.4	0.6	3.2	41
$Na_2IrCl_6.2H_2O$–MeCN[d]	20.6	3.0	0.5	4.6	57
Pyrolysis at 350 °C[e]	19.6	4.8	0.2	5.2	61

[a] Samples of (**1**) (10 mg) were treated with 5—6 equiv. of the named reagent in *ca.* 1 cm^3 solvent in 3 cm^3 sealed flasks at 20 °C. Reaction was instantaneous in most cases (as shown by colour changes or deposition of metal) and was completed by briefly heating to 50 °C. *cis*-(**1**) behaved similarly. [b] Analysed by g.c. on Poropak Q at 100 °C. The identities of the gases were checked by mass spectrometry which also showed no significant incorporation of deuterium from either (**1**) labelled on the C_5Me_5 ring or from CD_3CN solvent. [c] Calculation based upon the theoretical maximum amount of decomposition from 18.7 μmol of (**1**) being 4 × 18.7 (*i.e.* 74.8) μmol equiv. of C_1. [d] Small amounts of methyl chloride and propane were also detected. [e] A sample of 25 μg of complex was pyrolysed in the inlet of a Carlo Erba gas chromatograph at 350 °C and the gases were analysed. The numbers of μmol of products given have been scaled up to allow direct comparison. A small amount of propane was also detected.

contrast with the pyrolysis, which needs 350 °C, the reactions with $IrCl_6^{2-}$, and those with Ag^+ or Ce^{4+}, proceeded rapidly even under ambient conditions. Mass spectrometric analyses of the gases indicated no significant transfer of deuterium to the C_1, C_2, or C_3 products when complex (**1**) labelled only on the C_5Me_5 ring decomposed under these conditions.

Several decomposition and coupling reactions are occurring simultaneously, the significant one of which is the formation of propylene. One possible mode by which this occurs is a linking of one CH_3 and the two CH_2 ligands in an 'oxidized' form of the complex to give a C_3 ligand which β-eliminates propylene.[4]‡§

We have already noted[4] the appropriateness of complex (**1**) (and its *cis*-isomer) as models for the methylene polymerization stage in one mechanism for the Fischer–Tropsch reaction on metal surfaces.[7] One intriguing feature of the heterogeneous Fischer–Tropsch reactions is the large but poorly understood influence of promoters. The results presented here suggest that in the heterogeneous Fischer–Tropsch reaction the surface on which the metal is supported may play a hitherto unsuspected role as an electron acceptor in the polymerization stage. This is in addition to the roles already noted where the surface can act as Lewis acid and oxygen acceptor in the CO activation and reduction steps.[8] Particular point is given to this observation since a number of workers have noted that certain specific rhodium plus surface oxide combinations lead to enhanced rates of methanation of CO–H_2 mixtures and, more interestingly, to the enhanced formation of higher hydrocarbons and oxygenates when compared to rhodium metal alone.[9] It has been suggested that these effects are due to 'strong metal–support interactions'[10] in which the (oxide) support actually acts as an oxidant of the metal. Although the heterogeneous metal catalyst system is very much more complex and has many more steps than the rather simple model offered by complex (**1**), the similarity of behaviour is encouraging.

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‡ Free ethylene does not appear to be intermediate; a reaction carried out in the presence of a four-fold excess of ethylene only showed a very small increase in propylene formed.

§ One major organometallic product from such reactions of (**1**) in MeCN is $[C_5Me_5Rh(MeCN)_3]^{2+}$ suggesting that a *part* of the total reaction may be given by $[(C_5Me_5RhCH_3)_2(\mu\text{-}CH_2)_2] + 6MeCN - 4e^- \longrightarrow 2[C_5Me_5Rh(MeCN)_3]^{2+} + CH_3CH{=}CH_2 + CH_4$.