The Coupling of Vinyl and μ-Methylene Ligands: A New View of the Mechanism of the Fischer–Tropsch Polymerisation Reaction

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The ready decomposition of the divinyl-di-μ-methylene-dirhodium complex, $[\{C_5Me_5Rh(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$, to give C_3 (propene or η^3-allylic ligands) by linking of the vinyl and methylene ligands, prompts the proposal of a new mechanism for the polymerisation step in the Fischer–Tropsch reaction in which the polymer chain carriers are surface alkenyls rather than alkyls.

We report that the divinyl-di-μ-methylene complex (**1**) undergoes extremely facile coupling of the vinyl and the methylene. Complex (**1**) was synthesised (85%) by reaction of the dichloro-complex (**2**)[1] with vinylmagnesium bromide (Scheme 1), and was identified as the *trans*-isomer spectroscopically [^{1}H n.m.r. spectrum, δ 1.63 (s, C_5Me_5), 4.59 (dm), 5.21 (dm), and 5.97 [ddt; vinyl; *J*(H–H) 8.5; 16.5 Hz; *N*(Rh–H) 1.6 Hz], and 8.09 [t; μ-CH_2, *J*(Rh–H) 1 Hz]; i.r. spectrum, ν(C=C) 1559 cm^{-1} (s)], and by a single crystal *X*-ray determination.† This showed the expected centrosymmetric geometry (Figure 1) with the rhodiums directly linked [2.588(2) Å], each bearing an η^5-bonded C_5Me_5 and a σ-vinyl [Rh–C 2.001(10) Å], and bridged by two μ-methylenes [Rh–C 1.982(9), 2.011(6) Å].

Complex (**1**) underwent reaction with HCl gas in chloroform to give, initially, the η^3-allylic complex (**3**), and then propene and the dichloride complex (**4**).‡

$$\underset{(\mathbf{1})}{[\{C_5Me_5Rh(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]} + 2HCl \longrightarrow \underset{(\mathbf{3})}{2[C_5Me_5Rh(\eta^3\text{-}C_3H_5)Cl]}$$

$$(\mathbf{3}) + HCl \longrightarrow \underset{(\mathbf{4})}{1/2[\{C_5Me_5RhCl_2\}_2]} + CH_2{=}CHCH_3$$

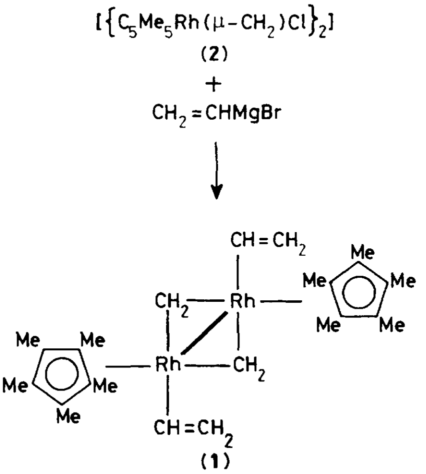
A parallel reaction occurred easily and cleanly when (**1**) was reacted with $AgBF_4$ in MeCN–tetrahydrofuran(thf) to give the η^3-allylic cation (**5**) in 85% isolated yield.

$$\underset{(\mathbf{1})}{[\{C_5Me_5Rh(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]} + 2AgBF_4 + MeCN/thf \longrightarrow \underset{(\mathbf{5})}{2[C_5Me_5Rh(\eta^3\text{-}C_3H_5)(MeCN)]BF_4}$$

Complex (**1**) also decomposed on heating (330 °C) to give propene (88%) and methane (8%) with traces of C_2 and C_4 hydrocarbons, and it reacted with a large excess of moist ferric chloride in heptane (20 °C) to give largely C_3 compounds [propene (21%) and allyl chloride (68%), together with small amounts of C_1, C_2, and C_4 hydrocarbons].

These reactions all show that the combination of a μ-CH_2 and a σ-$CH{=}CH_2$ occurs readily. As we have indicated elsewhere, such a reaction can also explain the formation of propene from the dimethyl-μ-dimethylene complex, $[\{C_5Me_5Rh(\mu\text{-}CH_2)Me\}_2]$.[2,3]

There is general agreement that the Fischer–Tropsch reaction, in which hydrocarbons are formed from hydrogen and carbon monoxide mixtures over heterogeneous metal catalysts, proceeds *via* dissociation of CO to carbide on the surface.[4] This carbide is then hydrogenated stepwise to μ-methyne, μ-methylene, and methyl (Scheme 2, reaction i; evidence for the three last species has been reported[5]). There is also general agreement with the thesis originally advanced by Fischer and Tropsch[6] and later developed by Brady and Pettit, and by Biloen and Sachtler (FTBPBS), that the reaction proceeds by a surface polymerisation of μ-methylenes.[7]



Scheme 1

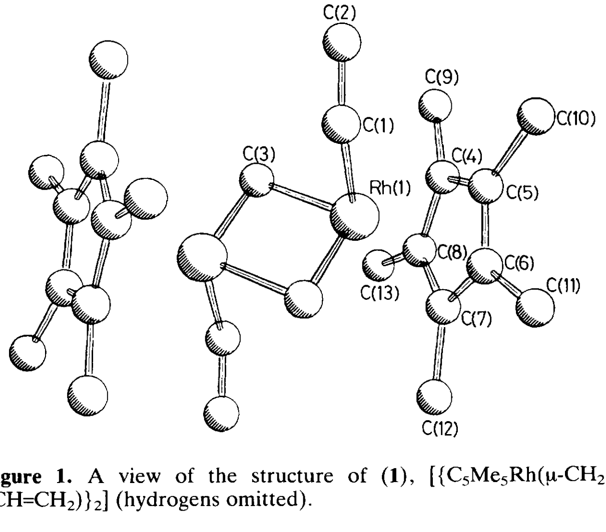


Figure 1. A view of the structure of (**1**), $[\{C_5Me_5Rh(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$ (hydrogens omitted).

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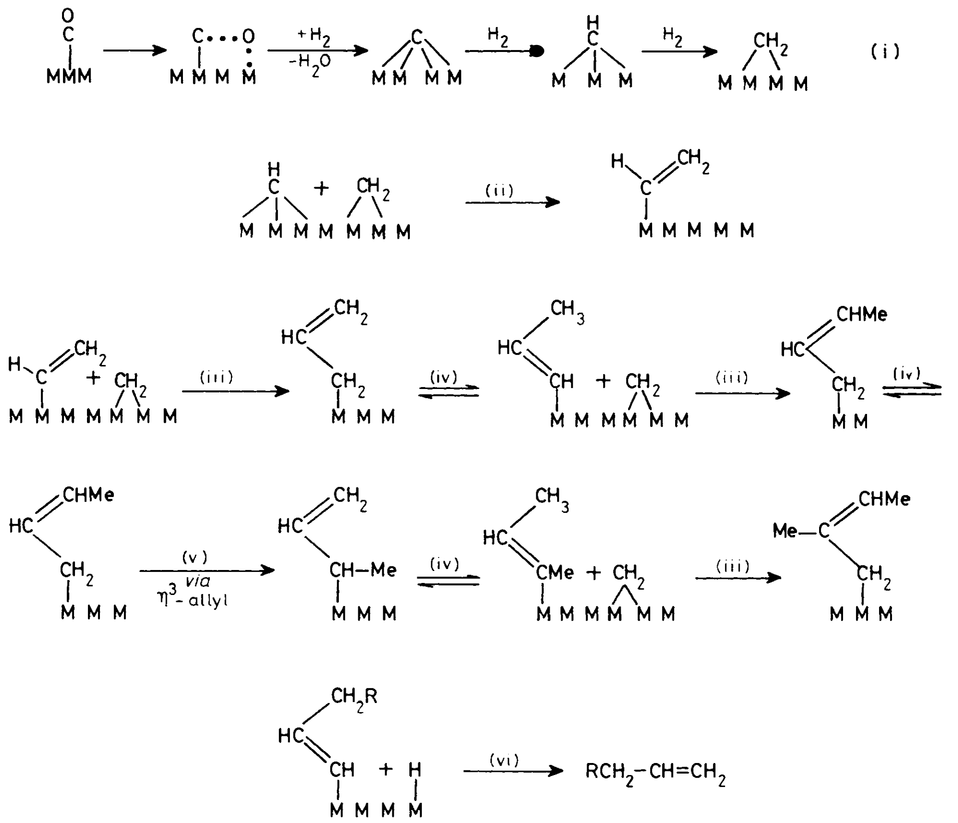
† *Crystal data*: $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CH_2)(CH{=}CH_2)\}_2]$; monoclinic; *a* = 8.261(5), *b* = 15.055(14), *c* = 10.257(9) Å, β = 108.72(6)°, *U* = 1208.1(17) Å^3; D_c = 1.535 g cm^{-3}, *Z* = 2; space group $P2_1/n$ (a non-standard setting of $P2_1/c$, C_{2h}^5, No. 14), (Mo-K_α). For the 1801 reflections collected with a Nicolet R3 diffractometer with $|F|/\sigma(|F|) > 3.0$ the final *R* = 0.0447. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Recent work has shown this to be a complex reaction with different products formed under different conditions. Details will be published shortly.



Scheme 2. Postulated mechanism for a modified Fischer–Tropsch polymerisation.

Agreement is however lacking as to, (i) why the initial products are alkenes, rather than alkanes, (ii) why, although the product distributions generally follow the expected Schulz–Flory pattern for polymerisations, this is not true of the C_2 fraction, which is generally low, and (iii) why, although the major products are linear, small amounts of branched hydrocarbons are also formed (for example, refs. 8, 9).

We therefore propose a modification of the FTBPBS hypothesis, in which the initiating species is a σ-vinyl and polymerisation proceeds by reaction of methylenes but with σ-alkenyls rather than alkyls as chain carriers. This requires formation of surface σ-vinyls (for example by combination of a μ-methyne with a μ-methylene, step ii; see ref. 10 for a model), their reaction with μ-methylenes on the surface to give, initially σ-allyls (step iii, modelled in this work; see also ref. 11), their isomerisation to σ-alkenyls (step iv; modelled in ref. 12), which again react with methylenes to repeat the cycle. Some branching is accommodated by σ-allyl interconversion *via* η^3-allyls (step v); this will be minor since alkenyls will prefer to react at the less substituted end. The C_2 hydrocarbons will arise from the vinyls; since the formation of vinyls (step ii) will be different in nature from the further polymerisations (step iii), the amounts of C_2 produced would not be expected to be related to the amounts of $C_{>3}$.

This mechanism also explains easily the formation of α-alkenes as the primary products since these would arise very simply from σ-alkenyl species, either by reaction with surface hydrides (step vi) or with Brønsted acid sites, *e.g.* on a silica support.

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