

A new view of the Fischer-Tropsch polymerisation reaction

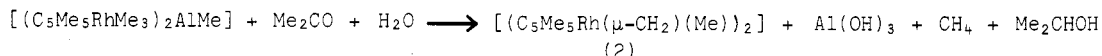
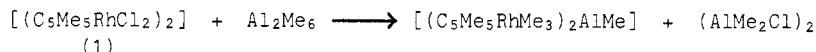
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Abstract - The decompositions of complex $[(C_5Me_5Rh(\mu-CH_2)(Me))_2]$, (2), and a variety of its isotopomers, thermally ($\geq 250^\circ C$) and by reaction with one electron oxidisers ($20-50^\circ C$), to give propene and methane, have been investigated. Decomposition of $[(C_5Me_5Rh(\mu-CH_2)(CD_3))_2]$ with $IrCl_6^{2-}$ or $FeCl_3$, gave CD_3H and $CD_2=CH-CH_2D$, mechanisms for the formation of which are discussed. A key step in the formation of propene is the coupling of μ -methylene and σ -vinyl ligands, which is shown in another model complex by the reaction of $AgBF_4$ in MeCN with $[(C_5Me_5Rh(\mu-CH_2)(vinyl))_2]$ (4), to give $[(C_5Me_5Rh(\eta^3-CH_2CHCH_2)(MeCN))BF_4]$, (6). This concept is applied as a new model for the polymerisation part of the heterogeneous Fischer-Tropsch reaction on supported metals, and involves chain growth via reaction of surface alkenyls with surface methylenes. The advantages of this new mechanism in explaining a number of features of the Fischer-Tropsch reaction are discussed.

THE SYNTHESIS AND REACTIONS OF $[(C_5Me_5Rh(\mu-CH_2)(Me))_2]$, (2)

The rhodium complex (1) $[(C_5Me_5MCl_2)_2]$ (ref. 1), readily catalyses a host of hydrogen transfer processes. One of these reactions led to the novel complex, $[(C_5Me_5Rh(\mu-CH_2)(Me))_2]$ (2), (Fig. 1), formed by the following route (ref. 2)



Investigation of the reactivity of (2) showed that the complex was rather stable but that the rhodium-bound methyls were removed by reaction with acids such as HCl. Complex (2),

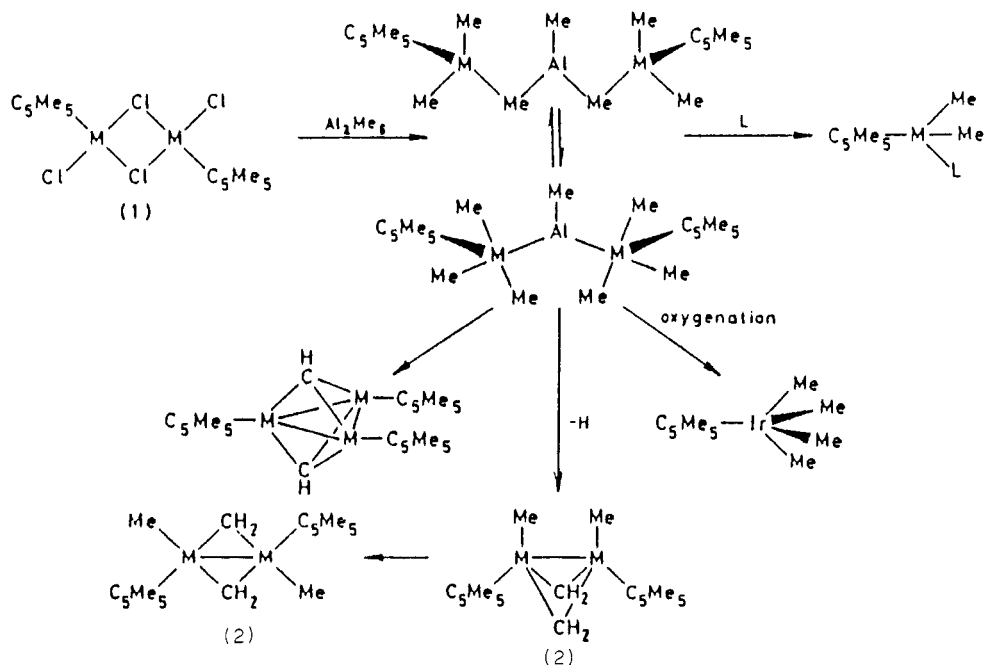


Fig. 1

with two μ -methylenes and two methyls on two adjacent metals, appeared to have useful potential as a model for the Fischer-Tropsch process.

THE FISCHER-TROPSCH REACTION AND PROPOSED MECHANISM

The Fischer-Tropsch reaction has many forms. The most common version, and the one considered here, is the formation of hydrocarbons by reaction of carbon monoxide and hydrogen (syn-gas) over a heterogeneous catalyst, typically iron (or ruthenium) supported on an oxide such as silica, often promoted with potassium and other additives.

The products are water and linear hydrocarbons, though some branched hydrocarbons (mono- and some di- methyl-) are formed (ref. 3). The initial products are generally agreed to be α -olefins which are hydrogenated in a later step. The overall reaction,



with n typically 4 - 20, closely resembles a polymerisation and the product normally shows Schulz-Flory molecular weight distributions. Fischer and Tropsch suggested early that the reaction was really a methylene (CH_2) polymerisation, a view which was elegantly brought up to date and extended by Pettit in 1980 and by Biloen and Sachtler at the same time (ref. 4 & 5).

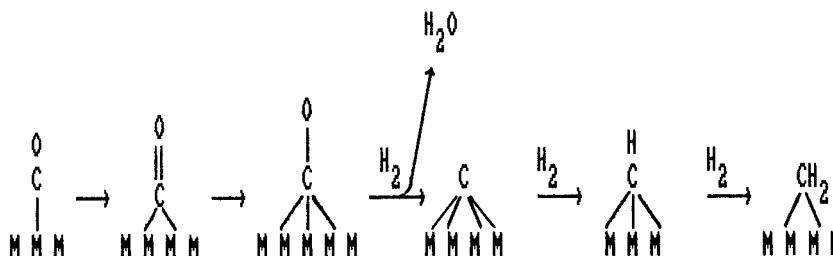
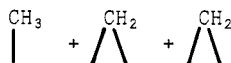


Fig. 2

The revised Fischer-Tropsch-Brady-Pettit-Biloen-Sachtler (FTBPBS) mechanism included the following key steps (Fig. 2):

1. The adsorption of carbon monoxide and its hydrogenative dissociation on a metal surface.
2. The formation on the surface of species such as carbide ($\text{C}\equiv$), carbyne ($\text{HC}\equiv$), methylene ($\text{H}_2\text{C}\equiv$), and methyl ($\text{H}_3\text{C}-$).
3. The polymerisation of surface methylenes; this was believed to be initiated by a surface hydrogen or methyl.

The picture drawn by Pettit of the polymerisation process on the metal surface,



had so many features in common with the structure of complex (2) that it was decided to examine the reactions of complex (2) in detail to see whether it could usefully model the polymerisation step of the overall Fischer-Tropsch reaction.

THERMAL AND OXIDATIVE DECOMPOSITION OF $[(\text{C}_5\text{Me}_5\text{Rh}(\mu\text{-CH}_2)(\text{Me}))_2]$, (2)

Although (2) was rather stable, when it was strongly heated ($> 250^\circ\text{C}$), it decomposed to give methane (37-65%) and propene (23-41%) as the main products. Some ethene (8-27%) was also formed, together with small amounts of ethane and traces of propane. There were some variations with temperature, more coupling products being seen at higher temperatures. No C_4 hydrocarbons were found, but under such strong heating the pentamethylcyclopentadienyl to rhodium bond was broken and $\text{C}_5\text{Me}_5\text{H}$ and $\text{C}_5\text{Me}_4\text{CH}_2$ were detected.

A variety of labelled complexes were made (Fig. 3). GC-MS studies carried out on the products of decomposition of $[(\text{C}_5\text{Me}_5\text{Rh}(\mu\text{-}^{13}\text{CH}_2)(^{13}\text{Me}))_2]$ and $[(\text{C}_5\text{Me}_5\text{Rh}(\mu\text{-CH}_2)(^{13}\text{Me}))_2]$

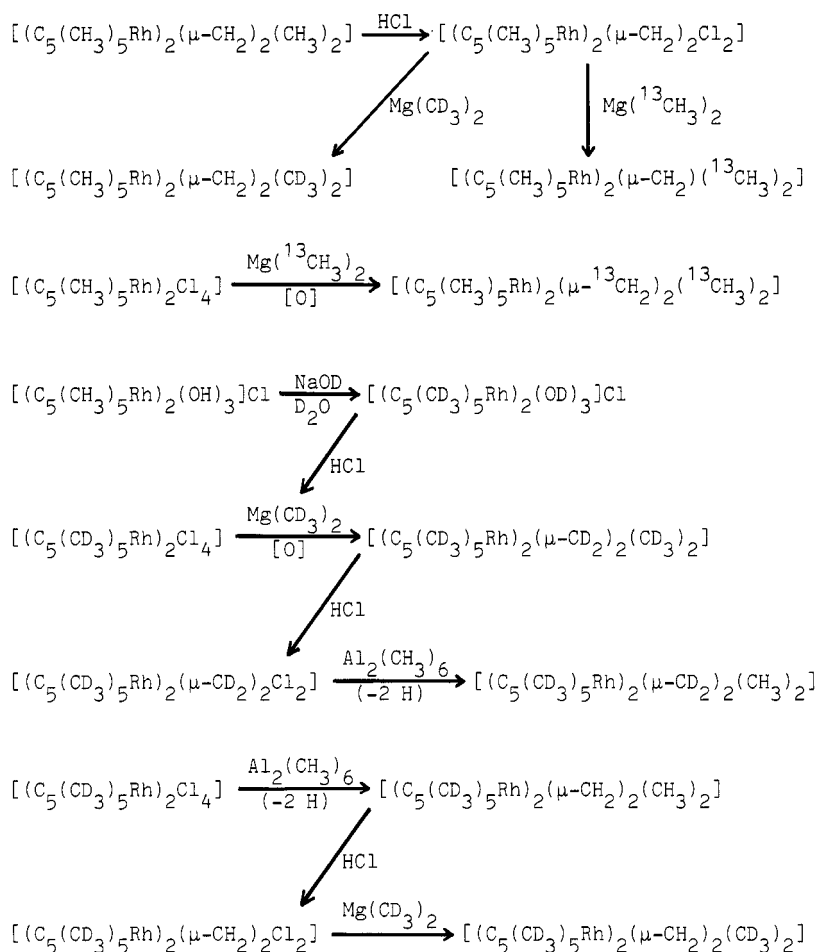


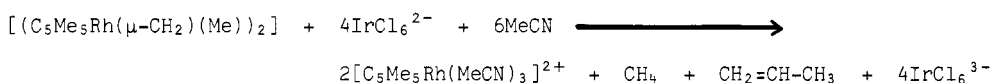
Fig. 3

showed that,

- i) the C₁, C₂, and C₃ gases all came from the C₁ ligands,
- ii) the gases were formed in unimolecular decompositions, and
- iii) the ethene from [(C₅Me₅Rh(μ-CH₂)(¹³CH₃))₂] was ¹³C¹²CH₄, formed from one methyl and one methylene, and the propene was ¹³C¹²C₂H₆, formed from one methyl and two methylenes (ref. 6).

Thus three of the C₁ ligands in (2) come together to make propene with considerable specificity. ¹³C NMR spectroscopy showed that the propene from [(C₅Me₅Rh(μ-CH₂)(¹³Me))₂] contained only labels at the terminal carbons and no label at the central carbon but, because of scrambling which occurred readily at the decomposition temperatures, it was not possible to ascertain more detail by further labelling experiments.

During the investigations of (2) it had been found that it degraded rapidly and completely at, or a little above, ambient temperature, in the presence of one-electron oxidisers and some electrophiles. The products [propene, methane (typically 55-60% and 25-27% respectively), ethene (ca. 10%), and ethane (5-7%)] and their ratios were similar to those from the thermal decomposition. A rhodium(III) complex could also be isolated. Using hexachloroiridate(IV) in acetonitrile as oxidant, some 70% of the reaction proceeded according to,



Again, GC-MS studies on the gases formed on decomposition of $[(C_5Me_5Rh(\mu-^{13}CH_2)(^{13}Me))_2]$ and $[(C_5Me_5Rh(\mu-CH_2)(^{13}Me))_2]$ showed that,

- i) the C_1 , C_2 , and C_3 gases all came from the C_1 ligands,
- ii) the gases were formed in intramolecular decompositions, and
- iii) the ethene from $[(C_5Me_5Rh(\mu-CH_2)(^{13}CH_3))_2]$ was $^{13}C^{12}CH_4$, formed from one methyl and one methylene, while the propene was $^{13}C^{12}C_2H_6$, from one methyl and two methylenes (ref. 6).

Since the conditions for these experiments were much milder (20–50 °C), further details could be elicited from the ^{13}C , 2H , and 1H NMR spectroscopic studies of the decomposition products. Thus, the propene from $[(C_5Me_5Rh(\mu-CH_2)(^{13}Me))_2]$ was largely (80–85%) $^{13}CH_2=CH-CH_3$ (and 15–20% $^{13}CH_3-CH=CH_2$), while that from $[(C_5Me_5Rh(\mu-CH_2)(CD_3))_2]$ was mainly $CD_2=CH-CH_2D$ (75%, plus 25% $CD_3-CH=CH_2$) (ref. 7). The methane was mainly CD_3H , the hydrogen of which came from a methylene group.

Very similar results were obtained when the closely related complex $[(C_5Me_5Rh-\mu-CH_2)_2(CD_3)(MeCN)]^+$, (3), and which lacked one methyl, was reacted under these conditions. The major product was again $CD_2=CHCH_2D$ (ref. 8).

The cyclic voltammograms of (2) showed, first, a reversible 1-electron oxidation, followed by a further, but this time irreversible, 1-electron oxidation. The evidence indicates that the methane is formed during the second 1-electron oxidation.

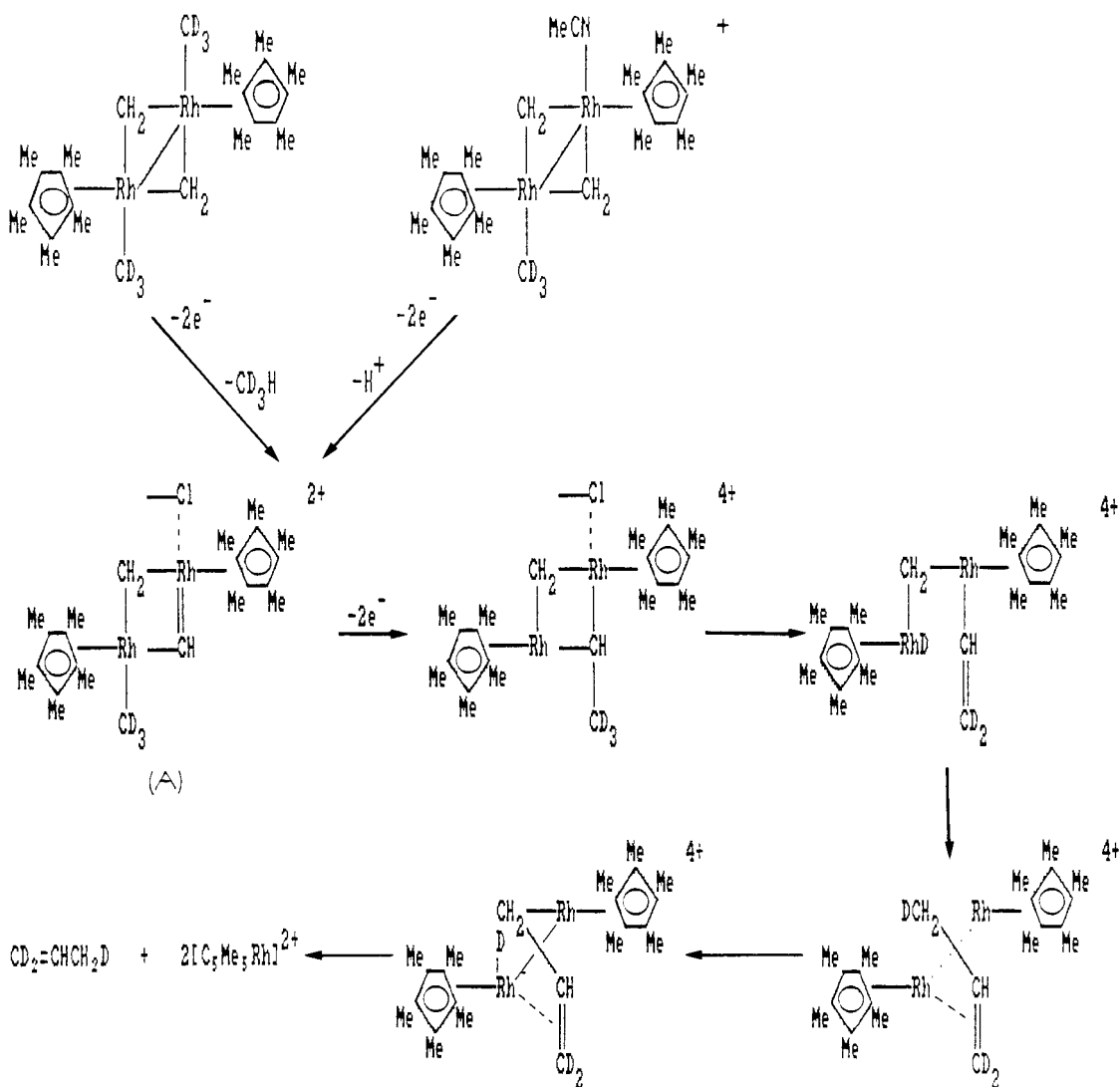


Fig. 4

The first step by which the propene is formed from (2) or (3) is the 2-electron oxidation to give methane and a dicationic species, which we represent by (A), which has two rhodiums, one bearing a methyl, joined by one μ -methylene and one μ -methyne. Attempts to prove this structure, either spectroscopically or by trapping experiments, have failed and we conclude that (A) decomposes very easily further and is very short-lived. The pattern of labelling seen in the propene from $[(C_5Me_5Rh(\mu-CH_2)(CD_3))_2]$, (2), and from $[(C_5Me_5Rh-\mu-CH_2)_2(CD_3)(MeCN)]^+$ (3), mostly $CD_2=CH-CH_2D$, means that the methyl forms not the methyl, but the vinylic carbon, in the propene. This in turn means that one H(D) from the methyl must transfer to the $\mu-CH_2$ in (A), and that the carbon which was the methyl must link to the methyne. Several minor variations on ways in which this can occur are possible; we presently favour the one shown in Fig. 4.

In this mechanism from (A) to propene, the linking of the three C_1 fragments occurs via primary migration of the CD_3 onto the $\mu-CH$; the resultant $\mu-CH-CD_3$ β -eliminates one D onto the rhodium, leaving a $\mu-(\sigma, \pi)$ vinyl ($CH=CD_2$). This then couples with the $\mu-CH_2$ to give the allylic fragment, $CD_2=CH-CH_2-Rh$, which reductively eliminates with the $Rh-D$ to give the observed $CD_2=CHCH_2D$. The scheme can also be used to explain the formation of ethene, $CD_2=CH_2$, by protonation or hydrogen transfer to the vinyl.

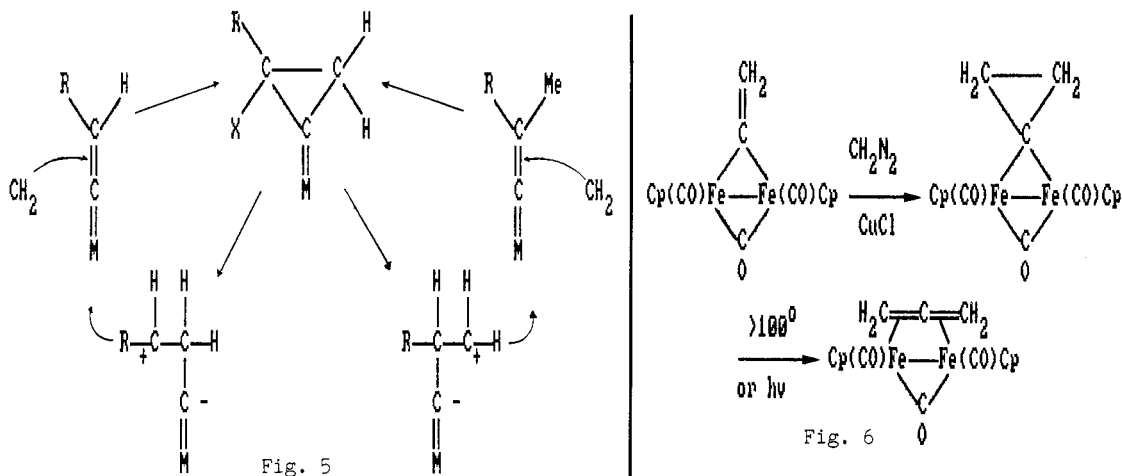
Although the most detailed information has come from the lower temperature oxidative decomposition, rather than the thermal reactions which might be expected to mimic the FT reactions more closely, the similarity between the data, where comparisons can be drawn, suggests the two decomposition processes are likely to be very similar.

FURTHER CONSIDERATIONS OF FISCHER-TROPSCH (FT) MECHANISMS

Although the data available are in general agreement with the FTBPBS mechanism, they indicate that something more than just a straight methylene polymerisation induced by a hydride or a methyl is occurring. Because of scrambling under FT conditions, only rather simple labelling studies can be carried out on FT reactions; this means that only very indirect experiments can throw new light on what is happening. One example of the sort of indirect information which may be useful, is the implication from our data on complex (2) that electrophiles or oxidisers promote C-C coupling reactions very markedly. The parallel in the FT reaction may be the effect of different supports. Since the dissociation and the hydrogenation of CO on surfaces can be very fast, the coupling could be rate-determining, and hence any factor which accelerated it should accelerate the overall process.

A number of authors have also pointed out shortcomings in the FTBPBS view. McCandlish noted that it could not account for the formation of branched chains among the linear hydrocarbon products (ref. 9a). A further problem, also noted by a number of authors, which does not fit easily into the FTBPBS mechanism, is that the amount of C_2 hydrocarbons formed is too low, by comparison with what would be expected on the basis of a Schulz-Flory distribution. This suggests that the step forming C_2 products is significantly different from the other (later) polymerisation steps.

To account for these discrepancies, McCandlish put forward an intriguing theory in which the polymerisation of methylene groups in the surface occurred by addition to surface vinylidenes, via intermediate cyclopropylidenes, which then ring-opened (Fig. 5). Hoel and his colleagues tested this idea by making some di-iron cyclopropylidenes, but found that they gave allenes and did not react in the required manner (Fig. 6, ref. 10).

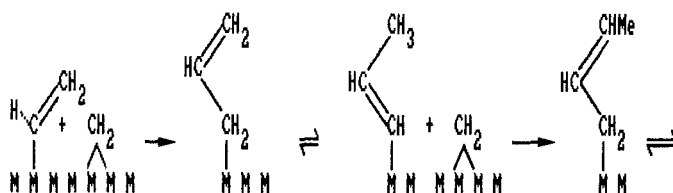
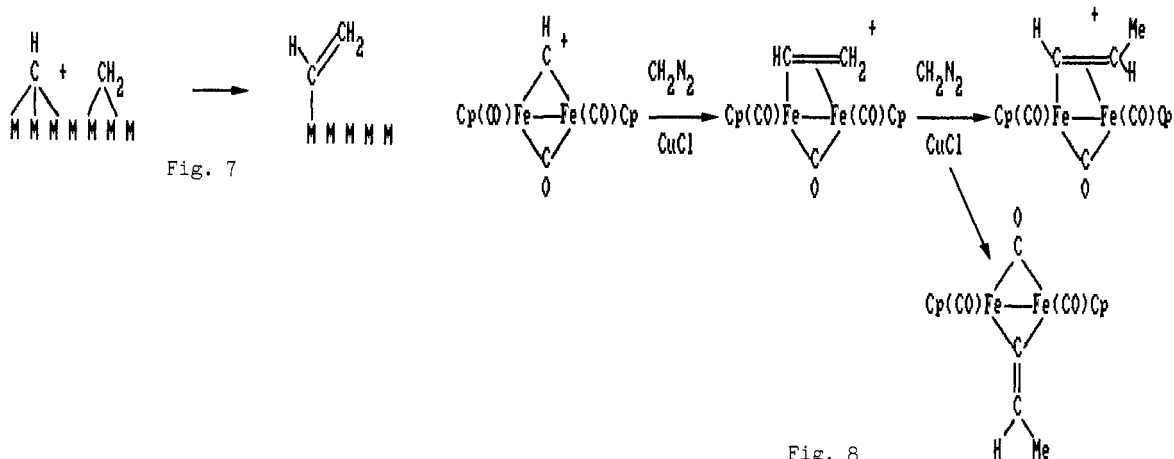


The anomalies mentioned above require further modification of the FTBPBS mechanism.

To explain the polymerisation leading to the Fischer-Tropsch α -olefin synthesis we also suggest the insertion of methylenes ($\equiv\text{CH}_2$) into metal-surface bound organic groups; however we propose them to "insert" into surface σ -vinyl (or σ -alkenyl) species. A better term would be the migration of these unsaturates onto the surface methylenes.

The initial surface σ - or σ,π -vinyl C_2 species can be formed by combination of a surface methyne and a surface methylene (Fig. 7). This reaction is quite different from the subsequent polymerisations and may well be much slower, thus accounting for the anomalously low amount of C_2 products formed.

The mechanism depicted in Fig. 4 offers precedents for such a process from organometallic models. Other useful models include the reaction of $[\text{Cp}(\text{CO})_2\text{W}=\text{CR}]$ with $[(\text{CpRu})_2(\mu\text{-CH}_2)(\mu\text{-CO})(\text{CO})(\text{MeCN})]$ to give the σ,π -alkenyl complex $[\text{RCH}=\text{CHWCp}(\text{CO})_2(\text{CpRu}(\text{CO}))_2]$ (ref. 11). Analogously, the μ -methyne-di-iron cation, $[(\text{CpFeCO})_2(\mu\text{-CO})(\mu\text{-CH})]^+$ reacted with diazomethane to give the cationic di-iron σ,π -vinyl complex $[(\text{CpFeCO})_2(\mu\text{-CO})(\sigma,\pi\text{-CH}=\text{CH}_2)]^+$. This in turn reacted with excess diazomethane to give a variety of products including $[(\text{CpFeCO})_2(\mu\text{-CO})(\sigma,\pi\text{-CH}=\text{CHMe})]^+$ (Fig. 8, ref. 12). These models indicate the feasibility of the first part of our proposed scheme.



We suggest that after the FT reaction has been initiated by a methylene and a methyne coming together to form a vinyl, this in turn reacts further with a surface methylene. The first product there must be a surface σ -allyl, which then rearranges by a 1,3-hydrogen migration into another surface alkenyl (Fig. 9).

There are various ways in which the 1,3-hydrogen shift can occur; it may occur spontaneously on the metal surface since metal hydrides, which would be intermediate, are so easily formed. It could also occur with the help of a neighbouring Brønsted acid site (HO- on silica for example). A precedent is available for this from the work of Deeming et al who showed that HCl catalyzed the isomerisation of the σ -2-methylallyl-iridium into the σ -2-methylpropenyl- complex, $[\text{CH}_2=\text{CMe}-\text{CH}_2-\text{IrX}_2\text{L}_2(\text{CO})]$ to $[\text{Me}_2\text{C}=\text{CH}-\text{IrX}_2\text{L}_2(\text{CO})]$ (L = PMe_2Ph , X = Cl or Br) (ref. 13). They also suggested that σ -alkenyl complexes might well be thermodynamically more stable than σ -allyls.

The intermediacy of allylic species also allows an explanation of the formation of branched hydrocarbon products. Since ready interconversion is possible via η^3 -allylic species, an allyl can react either at the unsubstituted or the substituted end (Fig. 10). However, because of steric hindrance, chain extension at the unsubstituted end will be easier, hence most of the product will be linear.

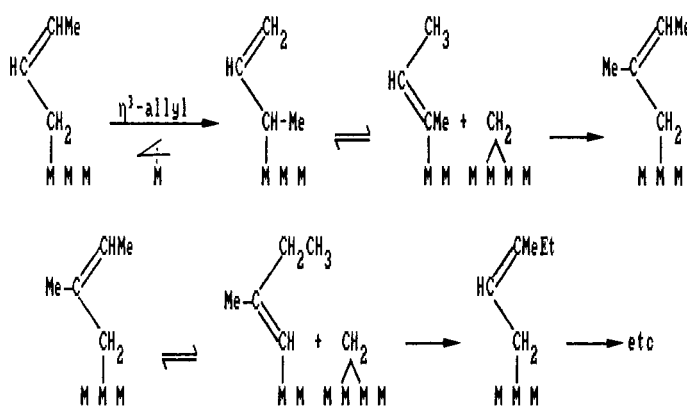
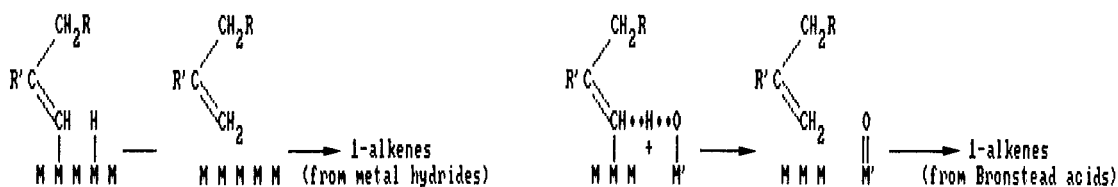


Fig. 10

The polymerisation reaction can be terminated by reaction with a metal hydride or with a Brønsted acid, Fig. 11, which breaks the metal-alkenyl bond to leave either a 1- or a 2-alkene, depending on where the proton has attacked.

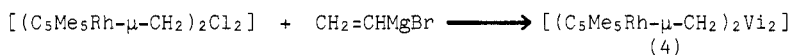
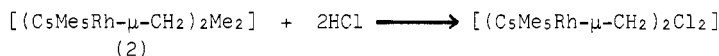


(R' = H for linear alkenes)

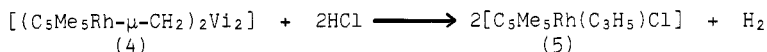
Fig. 11

ADDITIONAL EVIDENCE: SYNTHESIS AND REACTIONS OF SOME RHODIUM-VINYL COMPLEXES

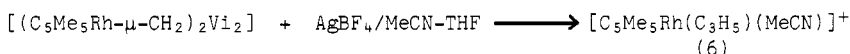
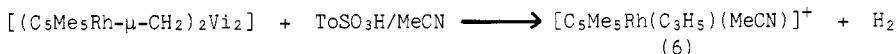
A key feature of the mechanisms being put forward for both the decomposition of (2) and for Fischer-Tropsch reaction is the reactivity of σ -vinyl species. We have therefore synthesised two such complexes and examined their reactions (ref. 14). The trans di-vinyl complex (4) has been made from (2) by the route,



The structure of (4) was shown by spectroscopy and confirmed by an X-ray determination (ref. 15). The complex (4) reacted readily with HCl in $CDCl_3$ at 0° , when it was converted into the η^3 -allyl complex, (5) and hydrogen, according to



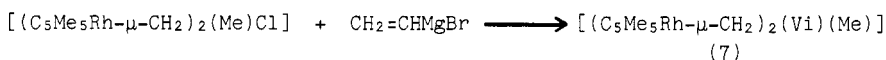
Similar reactions, giving the ionic complex (6), occurred when (4) was reacted with *p*-toluenesulphonic acid in acetonitrile and dichloromethane in the presence of KPF_6 , and when (4) was reacted with $AgBF_4$ in acetonitrile,



If reactions such as that leading to (5) are carried out at higher temperature or are left standing for longer periods of time then the yields decrease and some allyl chloride is formed. The last was the main product (together with propene, some methane and C_4 and C_5 hydrocarbons) when (5) was oxidised with a large excess of $FeCl_3$ in heptane.

Thermal decomposition of (5) 330° gave propene as the main gaseous product together with methane (8%) and traces of other hydrocarbons.

Thus we can conclude that the coupling of the μ -methylene and the σ -vinyl is indeed a very facile process, which goes easily and in very high yield, both thermally and under oxidising or even electrophilic attack conditions. The initial product is an allyl, which can ligand to the rhodium, and then reacts further to allyl chloride or, thermally, to propene. This last reaction must involve transfer of a hydrogen; this presumably occurs from a ring methyl or a Rh-methyl.



The methyl-vinyl complex (7) has also been made and decomposed. Thermally (330°) propene (73%) was again the major product, with methane (10%), ethylene (8%), and traces of ethane and C₄ and C₅ hydrocarbons. Decomposition with FeCl₃ in heptane gave propene (44%) and allyl chloride (25%), together with ethylene (22%) and ethyl chloride (4%).

Thus we may conclude that the scheme we propose, both for the oxidative decomposition of (2) and for the intimate mechanism of the Fischer-Tropsch polymerisation reaction, in which σ -alkenyls are intermediates, is well-supported.

SUMMARY

We propose that the carrier of the Fischer-Tropsch polymerisation is a σ -alkenyl rather than the alkyl of the FTBPS picture, this offers a ready explanation for i) the formation of α -olefins as primary products, and ii) a small proportion of branched chain products.

Our suggestion that the initiating species is a σ -vinyl, produced by reaction of a surface methyne and a surface methylene, also accounts for the difference in the amounts of C₁, C₂, and C₃ hydrocarbons. The first will arise from reactions with hydrogen at one carbon. Since the formation by chain growth of the hydrocarbons is known to be fast (ref. 9b), it is probable that the formation of the C₂ surface species is in fact the rate-limiting step. Thus, if the formation of the σ -vinyl is slow and if it reacts fast with more methylenes to C₃ and higher, the amounts of ethene and ethane formed by reaction with hydrogen would be low.

A similar picture, in which the methyl (CD₃) links to the μ -methyne, β -eliminates D to Rh, and then links the σ -CH=CD₂ to the μ -CH₂ in the intermediate, followed by the transfer of RhD to the CH₂-Rh end of a σ, π -allyl, also allows the formation of CD₂=CH-CH₂D from [(C₅Me₅Rh(μ -CH₂)(CD₃))₂] to be explained, as shown in the Fig. 4. The great ease of combination of a σ -vinyl and a μ -methylene to give an allyl, has also been shown in the reactions of complex (4).

While model systems based on rhodium do not necessarily provide the closest analogy to present-day industrial Fischer-Tropsch catalysts, rhodium based catalysts are known and show some very useful features (ref. 16).

REFERENCES

1. P. M. Maitlis, *Acc. Chem. Res.*, **11**, 301 (1978); *Chem. Soc. Rev.*, **10**, 1 (1981).
2. K. Isobe, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 809 (1981); A. Vázquez de Miguel, K. Isobe, B. F. Taylor and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 758 (1982); K. Isobe, A. Vázquez de Miguel, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1441 (1983); A. Vázquez de Miguel, M. Gómez, K. Isobe, B. F. Taylor, B. E. Mann and P. M. Maitlis, *Organometallic*, **2**, 1724 (1983).
3. R. B. Anderson, *The Fischer-Tropsch Synthesis*, Academic Press, London (1984); M. Roeper in W. Keim (Ed) *Catalysis in C₁ Chemistry*, D. Reidel Publishing, Dordrecht, Holland, 1983; R. A. Sheldon, *Chemicals from Synthesis Gas*, D. Reidel Publishing, Dordrecht, Holland, 1983; A. T. Bell, *Catal. Rev.-Sci. Eng.*, **23**, 203 (1981); R. W. Joyner, *Vacuum*, (1988) to appear.
4. F. Fischer and H. Tropsch, *Brennstoff-chemie*, **4**, 276 (1923).
5. R. C. Brady and R. Pettit, *J. Am. Chem. Soc.*, **102**, 6182 (1980); **103**, 1297 (1981); P. Biloen, *J. Roy. Neth. Chem. Soc.*, **99**, 33 (1980); P. Biloen and W. M. H. Sachtler, *Adv. Catal.*, **30**, 165 (1981).
6. I. M. Saez, N. J. Meanwell, A. Nutton, K. Isobe, A. Vázquez de Miguel, D. W. Bruce, S. Okeya, D. G. Andrews, P. R. Ashton, I. R. Johnstone and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1565 (1986).
7. I. M. Saez, N. J. Meanwell, B. F. Taylor, B. E. Mann and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 361 (1987).
8. I. M. Saez, D. G. Andrews and P. M. Maitlis, *Polyhedron*, **7**, 827 (1988).
9. (a) L. E. McCandlish, *J. Catal.*, **83**, 362 (1983); (b) C. A. Mims and L. E. McCandlish, *J. Phys. Chem.*, **91**, 929 (1987).
10. E. L. Hoel, G. B. Ansell and S. Leta, *Organometallics*, **3**, 1633 (1984); **5**, 585 (1986); E. L. Hoel, *Organometallics*, **5**, 587 (1986).
11. D. L. Davies, M. J. Parrott, P. Sherwood and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1201 (1987).
12. C. P. Casey, E. A. Austin and A. L. Rheingold, *Organometallics*, **6**, 2157 (1987).
13. A. J. Deeming, B. L. Shaw and R. E. Stainbank, *J. Chem. Soc. (A)*, 374 (1971).
14. J. M. Martínez de Ilarduya and P. M. Maitlis, unpublished.
15. H. Adams, N. A. Bailey, J. M. Martínez de Ilarduya and P. M. Maitlis, unpublished.
16. P. R. Watson and G. A. Somorjai, *J. Catal.*, **72**, 347 (1981); **74**, 282 (1982); see also I. M. Saez and P. M. Maitlis, *J. Organomet. Chem.*, **334**, C12 (1987) and references therein.