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Carbon–carbon bond formation at dinuclear metal centres

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The Fischer–Tropsch synthesis of hydrocarbons probably involves an array of carbon–carbon bond-formation processes occurring to unite carbene, carbyne, alkyl, olefin, and related species on a metal surface. In seeking to understand the nature of such processes, model diruthenium complexes have been prepared and the products of their thermolysis and reactions with unsaturated hydrocarbons investigated. The combination at a diruthenium centre of two carbenes, of a carbene and an alkyne, and of a carbyne and an olefin is described, and the possible implications for metal surface processes are emphasized.

1. Introduction

The transition metal catalysed Fischer–Tropsch synthesis of hydrocarbons by the hydrogenation of carbon monoxide is believed to involve an initial dissociative chemisorption of CO and H_2 on the metal surface. This provides a surface 'carbide', which is rapidly and successively hydrogenated to yield surface CH, CH_2 and CH_3 species. These then combine to produce the characteristic longer-chain hydrocarbons. It is the way (or ways) in which this combination occurs that is obscure. Strong evidence for the crucial role played by surface methylene groups has been obtained by Pettit & Brady (1980), who, in a revival of the original suggestion of Fischer & Tropsch, see the carbon chain growth occurring through alkyl–methylene combination

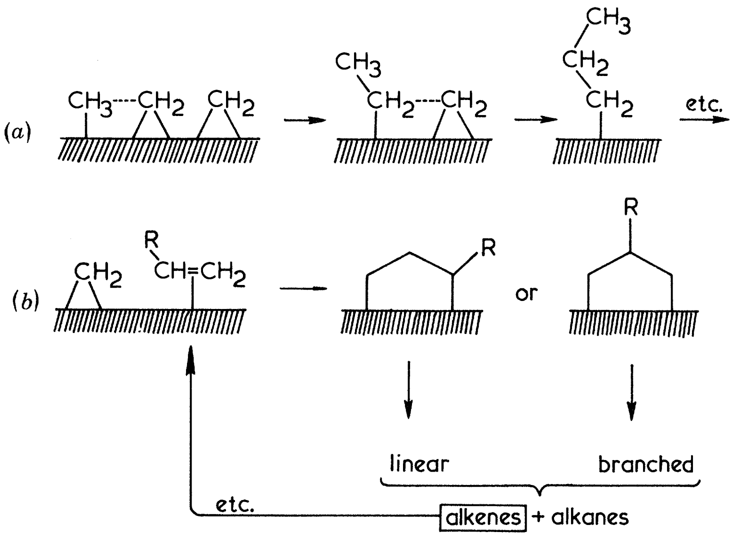
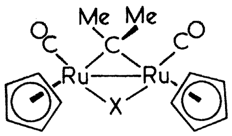


Figure 1. The Pettit (*a*) and Basset (*b*) proposals for carbon chain growth in Fischer–Tropsch synthesis.

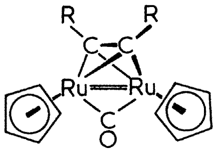
5-2

on the metal surface (figure 1*a*). More recently, Basset *et al.* (1981) have proposed that chain growth could proceed by olefin–methylene combination (figure 1*b*). In each case the chain is terminated by β-elimination or reductive elimination with surface hydrogen, or both, generating an olefin or alkane. Whereas, without refinement, the Pettit mechanism accounts only for the production of the high yield of straight-chain hydrocarbons, the Basset mechanism encompasses both straight-chain and branched-chain hydrocarbon formation. The mechanisms should not, however, be seen as mutually exclusive. It is likely that an array of carbon–carbon bond formation processes occurs on the metal surface to unite carbene, carbyne, alkyl, olefin, and related species, leading to the typical wide spectrum of hydrocarbon products of the Fischer–Tropsch synthesis.

In seeking to understand the nature of carbon–carbon bond formation processes at metal centres, model diruthenium complexes have been prepared and their reactivities studied. This paper describes some aspects of these studies.



1 X=C(H)Me
2 X=C=CH2



3 R=H
4 R=Ph

2. Combination of two carbenes

The di-μ-carbene complexes $[Ru_2(CO)_2(\mu\text{-}CMe_2)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ (**1**) and $[Ru_2(CO)_2(\mu\text{-}CMe_2)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ (**2**) are readily prepared (Knox *et al.* 1981*a*). When the former was treated with ethyne under u.v. irradiation, the expected (Knox *et al.* 1980*b*) 'insertion' of the alkyne into a μ-carbene did not occur. Instead, the complex $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2H_2)(\eta\text{-}C_5H_5)_2]$ (**3**) was formed; both μ-carbenes had been displaced and a four-electron μ-ethyne ligand bridged a ruthenium–ruthenium double bond (see later). The possibility that the carbenes had coupled to produce an olefin led us to study the thermal decompositions of **1** and **2**.

Heating **1** at 200 °C *in vacuo* resulted in the identification, by g.l.c., of the organic products: ethylene (21% of total), propylene (17%), $Me_2C{=}C(H)Me$ (46%), $CH_2{=}C(Me)Et$ (14%), and $CH_2{=}C(H)(^iPr)$ (4%). The formation of ethylene and propylene clearly results from the separate release of :CHMe and :CMe_2 from the diruthenium centre, and subsequent rearrangement. However, the remaining products each contain a five-carbon skeleton derived from the coupling of CHMe with CMe_2. The absence of cross-coupling products with four-carbon or six-carbon skeletons, such as butenes or $Me_2C{=}CMe_2$, establishes that the carbene coupling occurs at the diruthenium centre rather than in the gas phase subsequent to release. It may be noted that an X-ray diffraction study of **1** revealed a non-bonding C...C distance of 3.20 Å† separating the two μ-carbenes (Knox *et al.* 1981*a*).

Heating **2** to 200 °C resulted in the formation of a hydrocarbon product mixture very similar to that obtained from **1**. Clearly an intramolecular carbene coupling again occurs, but either in association with, or preceded by, hydrogenation of the vinylidene ligand.

The detailed mechanism of combination is not known (e.g. whether a transiently terminal carbene is involved), but an insight has recently been obtained by Shapley *et al.* (1981*b*), who observed that two methylene groups combine at a diosmium centre to provide an $Os_2(\mu\text{-H})(\mu\text{-CHCH}_2)$ system with bridging hydride and vinyl. Such a system is known to generate ethylene.

The studies described in this section suggest how olefins could be created by combination of carbenes at a dimetal centre on a metal surface. In this way the Basset mechanism of carbon chain growth could be initiated.

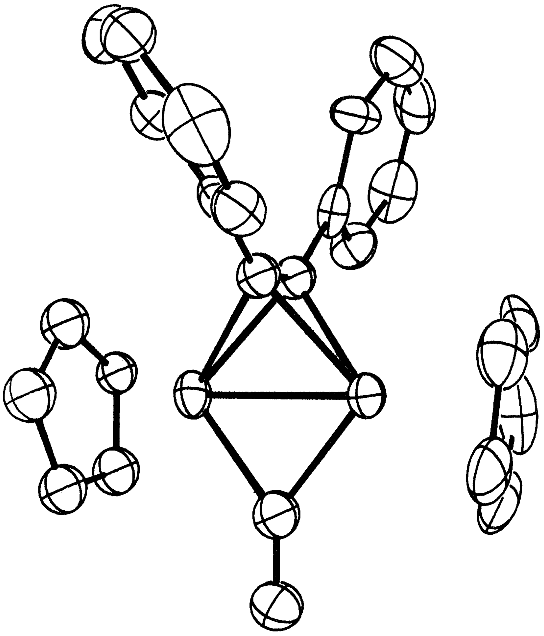


FIGURE 2. The molecular structure of $[Ru_2(\mu\text{-CO})(\mu\text{-C}_2Ph_2)(\eta\text{-C}_5H_5)_2]$ (**4**).

3. COMBINATION OF CARBENE WITH ALKYNE

The complex $[Ru_2(\mu\text{-CO})(\mu\text{-C}_2Ph_2)(\eta\text{-C}_5H_5)_2]$ (**4**), a diphenylacetylene analogue of **3**, has been subjected to X-ray diffraction study. Significant features, seen in figure 2, are a laterally bridging four-electron alkyne ligand and a short metal–metal separation of 2.505(1) Å, according with the ruthenium–ruthenium double bond required by 18-electron rule considerations. In contrast, in complex **1** a formally single Ru–Ru bond of 2.701(1) Å is observed.

Herrmann (1982) has established that an unsaturated dinuclear metal centre, like that in **4**, can be expected to react readily with a diazoalkane to generate a μ-carbene system. Complex **4** does indeed react readily, at room temperature, with diazomethane but there is incorporation of two methylene groups rather than the one anticipated. The product is $[Ru_2(CO)(\mu\text{-CH}_2)\{\mu\text{-C(Ph)C(Ph)CH}_2\}(\eta\text{-C}_5H_5)_2]$ (**5**), whose structure was firmly established by X-ray diffraction and is displayed in figure 3. The CO that was bridging in **4** is now terminally bound, and has been replaced by a bridging methylene group. The other methylene is linked with the alkyne in a C_3 ligand of a type previously produced in reactions of alkynes with μ-carbene complexes (Knox *et al.* 1980*b*). There are grounds for viewing this ligand in the way it is depicted in **5**, i.e. as a coordinated vinylcarbene. The presence of two bridging carbon

† 1 Å = 10^{-10} m = 10^{-1} nm.

atoms associated with the diruthenium unit, and previous experience with complexes **1** and **2** (see §2), led us to envisage that thermolysis of **5** would effect their linking, producing perhaps 2,3-diphenylbuta-1,3-diene. Heating **5** to 200 °C did provide six hydrocarbon products; these are not at present identified, but certainly none of them is that diene. A possible explanation of this apparent failure to link the bridging carbons arose in the molecular structure of **5**.

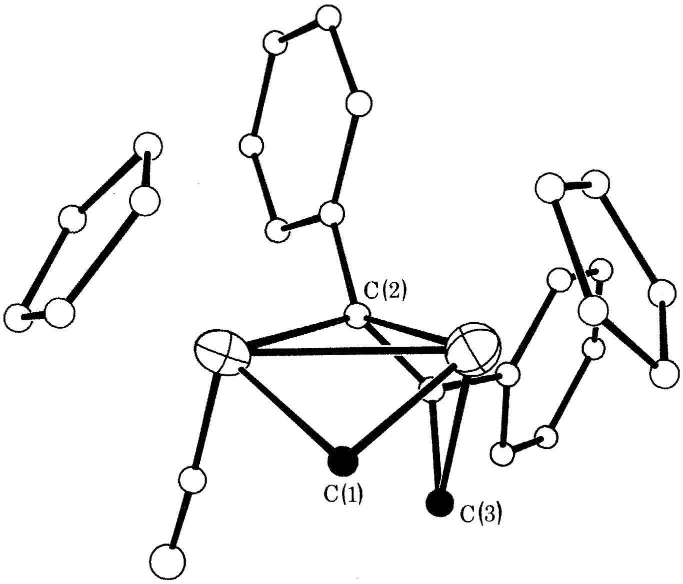
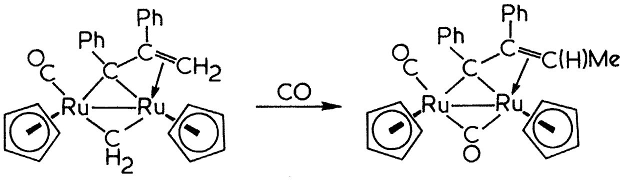


FIGURE 3. The molecular structure of $[Ru_2(CO)(\mu\text{-}CH_2)\{\mu\text{-}C(Ph)C(Ph)CH_2\}(\eta\text{-}C_5H_5)_2]$ (**5**).

The two carbons under discussion, C(1) and C(2) of figure 3, are 3.07 Å apart, but two other carbons, C(1) and C(3), are much closer, at 2.78 Å. These are the methylene carbons introduced via diazomethane. The possibility that carbon–carbon bond formation occurred preferentially to link C(1) and C(3) of this molecule was confirmed when heating **5** in boiling xylene yielded $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(Ph)C(H)Me\}(\eta\text{-}C_5H_5)_2]$ (**6**), a compound available to us by another route. Linking of the two methylene groups, and a subsequent hydrogen shift, is associated with scavenging of CO from the presumed decomposition of **5**. Treating **5** with CO under 10 atm (*ca.* 1330 Pa) pressure at 140 °C did, as expected, afford **6**.



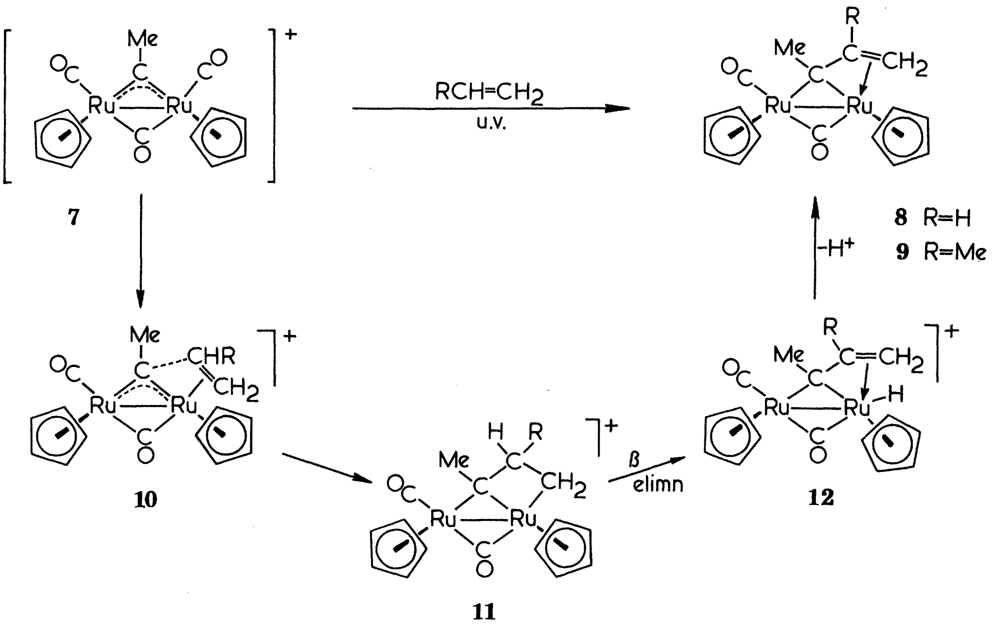
5 **6**

The sequence **4** → **5** → **6** represents a carbon chain growth with features strongly reminiscent of the Basset proposal for the mechanism of Fischer–Tropsch synthesis. The step **5** → **6** can thus be seen as a 'methylene plus olefin' combination, leading to a longer-chain olefin. Future work with derivatives of **5**, generated from reactions of **4** with other diazoalkanes, will attempt to clarify the factors controlling the carbon–carbon bond formation. The essential feature of this section is that the μ-methylene carbon in **5** becomes linked not to the other μ-carbon but to the carbon of the C_3 ligand to which it is closest.

In a recent report, Shapley *et al.* (1981*a*) has described the thermally induced linking of μ-methylene and μ-alkyne ligands separated by 2.86 Å on a triosmium cluster.

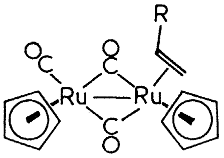
4. Combination of olefin with carbyne

We (Knox *et al.* 1980*a*) have reported the synthesis of the μ-methylcarbyne complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$ (**7**). Under u.v. irradiation in tetrahydrofuran solution the cation reacts with ethylene or propylene to give new complexes in which the olefin and μ-carbyne have become linked. These products $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Me)C(R)CH_2\}(\eta\text{-}C_5H_5)_2]$ (**8**, R = H; **9**, R = Me) are neutral, and deprotonation has evidently occurred, probably effected by the tetrahydrofuran solvent. An X-ray diffraction study (Knox *et al.* 1981*c*) on **9** confirms the conclusions, reached from n.m.r. spectra, that the new carbon–carbon bond has been formed exclusively between the μ-carbyne carbon and the carbon of propylene that bears the methyl group.



The likely pathway for the formation of **8** and **9** is one in which an initial photochemically induced dissociation of CO from **7** allows the terminal coordination of an olefin. A subsequent intramolecular electrophilic attack of the μ-carbyne carbon upon the olefin would then generate a metallocycle, which through a β-elimination and loss of a proton evolves the observed products. This sequence is shown as **7** → **10** → **11** → **12** → **8**/**9**. Strong evidence for its authenticity comes from the treatment of the ethylene complex $[Ru_2(CO)(C_2H_4)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (**13**) (Knox *et al.* 1981*b*) with methyl lithium, tetrafluoroboric acid and sodium borohydride successively, to afford **8**. The first two of these reagents are well known (Knox *et al.* 1981*a*) to convert μ-CO to μ-CMe^+ at a diruthenium centre, and there can therefore be little doubt of the intermediacy of **10** in this synthesis. The function of $NaBH_4$ would be to aid deprotonation of **12**.

An important feature of the work described in this section is that carbon–carbon bond formation occurs only between the μ-carbyne and the C(Me) carbon of propylene. It is not at present clear why this should be so. Simplistically, it could be argued that an electrophilic attack on a coordinated olefin should occur at the most electron-rich carbon, i.e. that bearing the methyl group, but this does not take into account the stability of the metallacarbonium ion formed, which is difficult to assess. Moreover, steric factors have been previously observed to be important in determining the geometry of such organodirutheniumdicyclopentadienyl complexes, and the methyl group of **9** is seen by X-ray diffraction to occupy a site of low crowding.



13 R=H

14 R=Me

An X-ray diffraction study on **14** provides no basis for the specificity; the coordination of the propylene is unremarkable and the bound carbons are nearly equidistant from the bridging sites of the diruthenium centre (figure 4).

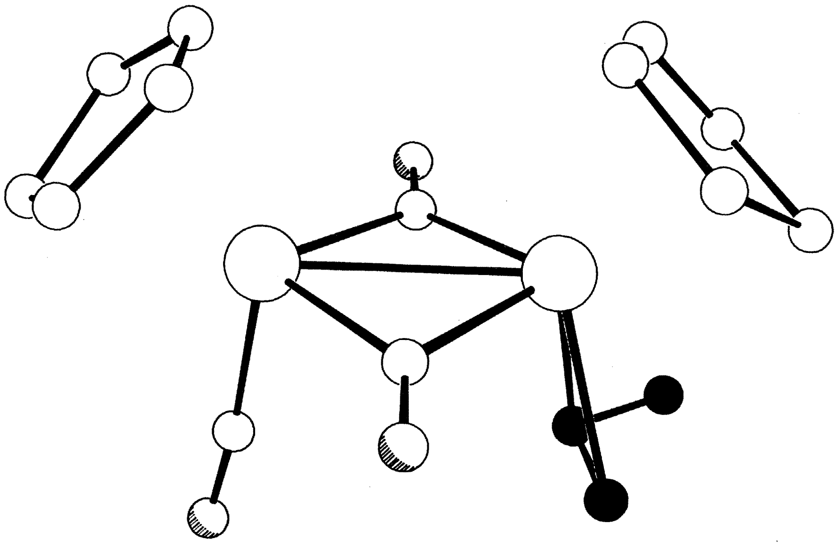


FIGURE 4. The molecular structure of $[Ru_2(CO)(C_2H_3Me)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (**14**).

The combination of μ-carbyne and propylene in the way observed leads to a branched carbon skeleton. There is significance here for the Fischer–Tropsch synthesis in that such a linking of carbyne and α-olefin on a metal surface could, after β-elimination or reductive elimination, or both, provide a route to the branched hydrocarbons which are formed in low yield.

5. Conclusions

There are indications that carbon–carbon bond formation processes may occur readily at dinuclear metal centres to link together a wide variety of simple hydrocarbon species, but much study remains before an understanding of the factors controlling these processes can be achieved.

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