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Preliminary communication

GENERATION OF HYDROCARBONS FROM OLIGO-METHYLENE CHAINS LINKING TWO METAL CENTRES

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Summary

The evolution of hydrocarbons from $[(\eta\text{-}C_5H_5)(CO)_2M\{\mu\text{-}(CH_2)_n\}M(CO)_2\text{-}(\eta\text{-}C_5H_5)]$ (M = Fe, n = 3—5; M = Ru, n = 3) has been investigated and the results interpreted in terms of a transient dimetallocycle which undergoes decomposition via β-elimination and reductive elimination processes.

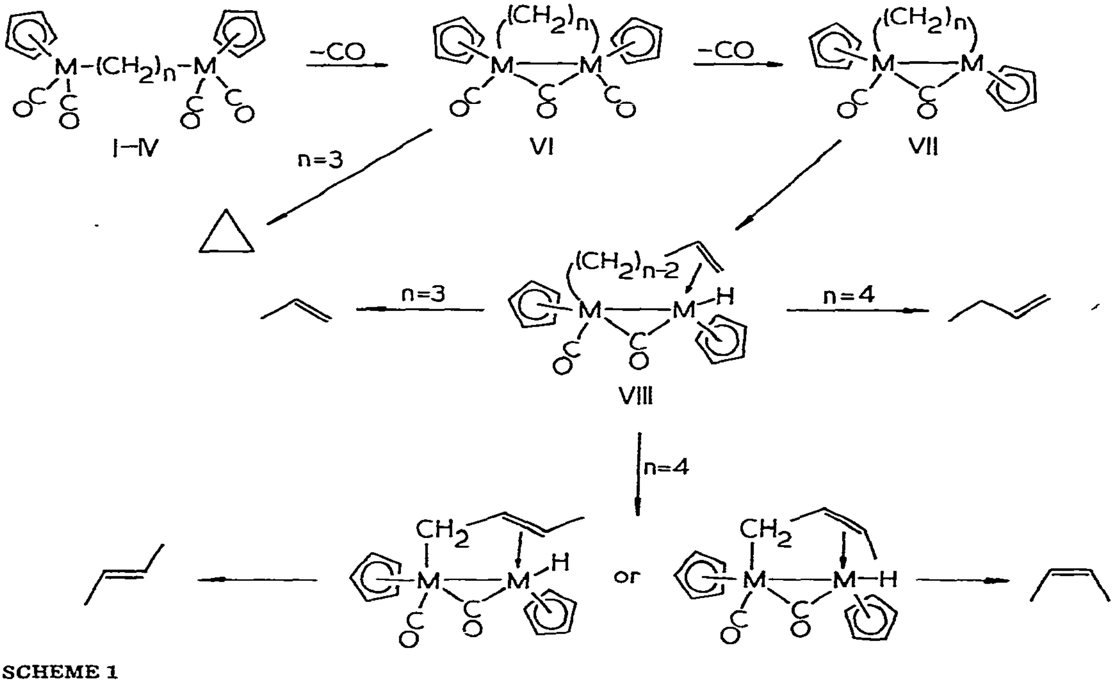
Two credible mechanisms for the Fischer—Tropsch Synthesis of hydrocarbons have been advanced recently. Both assert the importance of methylene groups on the metal surface, but while one has carbon chain growth occurring through combination of methylene with a surface alkyl [1], the other sees this arising from combination of methylene and an olefin [2]. The latter can account for the low yield of branched hydrocarbons (as can the combination of an electrophilic surface carbyne with an α-olefin [3]). The "methylene plus olefin" mechanism allows for the formation of a transient dimetallocyclopentane ring which decomposes via β-elimination and/or reductive elimination to give a new olefin or saturated hydrocarbon. Dimetallocyclopentanes have also been mentioned as possible intermediates in olefin metathesis [4,5]. However, there is as yet little information on the evolution of hydrocarbons from extended chains of methylene groups linking two metal atoms, other than the work of Pettit [6] and Bergman [7]. We are, therefore, prompted to describe the preliminary results of an investigation of hydrocarbon generation from the compounds $[(\eta\text{-}C_5H_5)(CO)_2Fe\{\mu\text{-}(CH_2)_n\}Fe(CO)_2(\eta\text{-}C_5H_5)]$ (I, n = 3; II, n = 4; III, n = 5) [8] and related species.

Decomposition of I in a sealed, evacuated glass tube at temperatures in the range 125—200°C produced cyclopropane and propene (GLC analysis) in 2.3 ± 0.3/1 ratio, with less than 1% of methane, ethane, and ethylene combined. The ratio of cyclopropane to propene was more than doubled when I was heated to decomposition in various solvents (toluene, octane, acetonitrile).

However, photochemically induced decomposition (250 W mercury lamp, silica glass flask, toluene solution) strongly favoured generation of propene, with the propene/cyclopropane ratio reaching 50/1. Interestingly, an equally high production of propene relative to cyclopropane was achieved when $[(\eta\text{-}C_5H_5)(CO)_2Ru\{\mu\text{-}(CH_2)_3\}Ru(CO)_2(\eta\text{-}C_5H_5)]$ (IV) was decomposed at 200°C, quite opposite to the behaviour of the iron analogue I.

With compound II, containing a tetramethylene chain, decomposition at 200°C provided only acyclic but-1-ene and but-2-ene, in ca. 1/15 ratio, the latter as *cis* and *trans* isomers (1/4). In contrast, decomposition of $[(\eta\text{-}C_5H_5)(CO)_2Fe\{\mu\text{-}CH(Me)CH_2CH_2\}Fe(CO)_2(\eta\text{-}C_5H_5)]$ (V) at 150°C evolves but-1-ene and but-2-ene in 1/30 ratio, but the latter is present exclusively as the *trans* isomer, a result with mechanistic implications which are discussed below. Still different behaviour is apparent in the decomposition of pentamethylene III at 200°C, when pentane (70%), pent-1-ene (25%), and *cis*- and *trans*-pent-2-ene (4%) are formed. In each of these decompositions quantitative production of $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Fe or Ru) is observed.

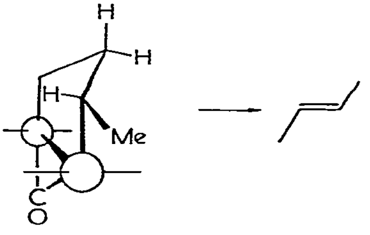
The preferential formation of pentane from III is clear evidence of a predominantly radical mechanism for the decomposition of this compound. Only traces of saturated hydrocarbons are evolved from I, II, IV and V, however, and we suggest that the pathway outlined in Scheme 1 best accounts for the products of these decompositions. This envisages the successive formation of dimetallocycles VI and VII through CO loss. The very related dimetallocycle $[Co_2\{\mu\text{-}(CH_2)_3\}(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ has actually been shown to evolve cyclopropane and propene on heating, and such a mechanism is implicated [7]. For n = 1, VI is known for ruthenium [9]. Reductive elimination from the dinuclear metal centre in VI will, for n = 3, provide a route to cyclopropane. On



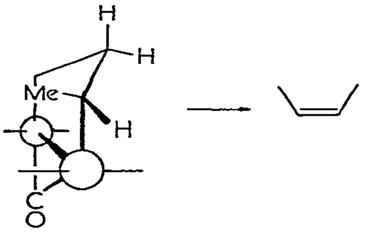
SCHEME 1

the other hand, the vacant site in VII will allow β-elimination to proceed, giving VIII, from which propene or but-1-ene may be generated by conventional reductive elimination, after hydride migration from one metal centre to the other. The formation of but-2-enes requires an isomerisation within the hydrocarbon chain of VIII (n = 4), for which there is ample precedent. The overwhelming formation of propene when I is subjected to UV radiation is readily understood in terms of Scheme 1, since such conditions favour the creation of the vacant site required for β-elimination. In addition, the high yield of propene from the decomposition of diruthenium IV may be attributed to the stronger metal—carbon bonds and increased metal—metal distances in the dimetallocyclopentane (VI) for ruthenium compared with iron, factors restricting reductive elimination of cyclopropane relative to CO loss and subsequent β-elimination.

Strong evidence for the intermediacy of a dimetallocycle in these decompositions is provided by the selective formation of *trans*-but-2-ene upon thermolysis of V. Consideration of molecular models indicates that the conformation of a dimetallocyclopentane ring allows two orientations for a methyl substituent on an α-carbon. These are illustrated as IX and X. In IX the C—Me bond is nearly parallel with the metal—metal axis, while in X it lies perpendicular to it, in a region where steric interaction with other ligands is much more severe. On this basis IX is the favoured dimetallocycle and it can be seen that β-elimination will bring the central *endo*-hydrogen of the ring to the metal



IX



X

centre and create a *trans*-carbon skeleton in an eventual olefin. A *cis*-carbon skeleton would be generated from X.

We conclude that in the system under study three- and four-carbon chains release hydrocarbons preferentially from an intermediate in which the two metal atoms they link have come together; i.e. decomposition occurs at a dinuclear metal centre. This process is less significant with five-carbon (and longer?) chains. Fracture of the carbon chains is of low importance, an observation which argues against a dimetallocyclopentane intermediate in olefin metathesis.

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