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## POSSIBLE MECHANISMS FOR ETHYLENE DIMERISATION DERIVED BY USE OF A NEW COMPUTER PROGRAM

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### Summary

A number of general reactions of organometallic systems have been classified and entered in a computer program. The use of the program is exemplified by generating possible mechanisms for the catalytic formation of butenes via ethylene dimerisation.

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The use of computers as an aid to choice of routes in the synthesis of organic compounds has been increasingly developed within the last decade [1]. In essence, the wide variety of known reactions of organic compounds are carefully classified as far as possible into what is presumed to be the basic minimum reactions or key steps. Representations of these reactions are then stored in the computer. Rules concerning the application and manipulation of these steps or building blocks are also given to the computer program. The program can then be used to suggest possible routes for the synthesis of any organic compounds. Clearly the computer may not suggest a new reaction step but lacking prejudice and by relentless systematic searching it may suggest mechanisms and synthetic routes which have escaped the attention of even the most vigilant chemist.

Transition metal compounds are increasingly finding applications as stoichiometric reagents in organic synthesis and have long been the active centers in homogeneous and heterogeneous catalysts for reactions of hydrocarbons such as polymerisation, hydroformylation, olefin oxidation, etc. We have, therefore, set out to extend the application of computer techniques in organic synthesis to incorporate transition metal systems. Here we report our initial studies which have been primarily concerned with the classification of the better known reactions between hydrocarbon moieties which may attach to

TABLE 1  
KEY REACTIONS BETWEEN ORGANIC COMPOUNDS AND TRANSITION METALS

Reaction name	Commonly used description	Computer representation	General description
<i>Oxidative addition</i>			
M + alkane(CH <sub>4</sub> )	$\rightarrow$		$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
M + olefin	$\rightarrow$		$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
M + Acetylene	$\rightarrow$		$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
M-η <sup>1</sup> -allyl → M-η <sup>3</sup> -allyl	$\rightarrow$		$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
M + butadiene	$\rightarrow$		$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
Addition of H <sub>2</sub>	$\rightarrow$		$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
Addition of CO	$\rightarrow$ M-CO or M←CO	M=C=O	$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
Alkyl migration			$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
1-2 hydrogen shift		$\rightarrow$	$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
1-3 hydrogen shift		$\rightarrow$	$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
Insertion of M into C-C bond	$M + \begin{matrix} C \\   \\ C \end{matrix} \rightarrow M \begin{matrix} C \\ / \\ C \end{matrix}$ n = 1, 2	$\rightarrow$	$M + \begin{matrix} A \\   \\ B \end{matrix} \rightarrow M \begin{matrix} A \\ / \\ B \end{matrix} [+X_2]$
<i>Reductive elimination</i>			
Dihydrogen elimination		$\rightarrow$ M +	$M \begin{matrix} A \\ / \\ B \end{matrix} \rightarrow M + \begin{matrix} A \\   \\ B \end{matrix} [-X_2]$
Olefin elimination			$M \begin{matrix} A \\ / \\ B \end{matrix} \rightarrow M + \begin{matrix} A \\   \\ B \end{matrix} [-X_2]$

TABLE 1 (continued)

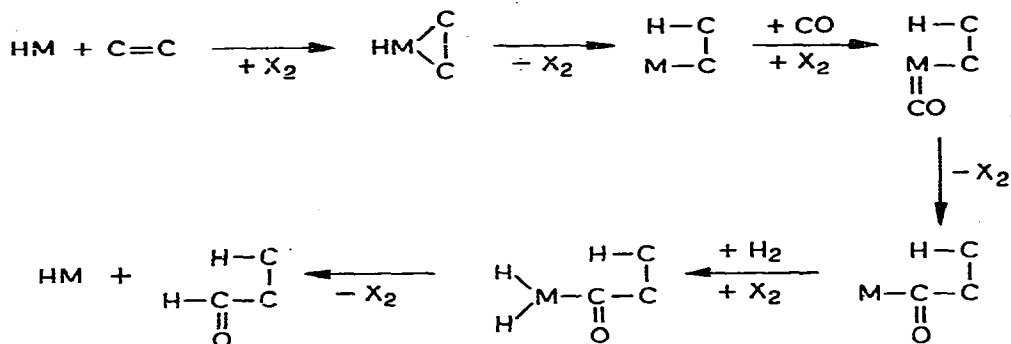
Reaction name	Commonly used description	Computer representation	General description
Acetylene elimination	$M-\overset{\text{C}}{\parallel}{\underset{\text{C}}{\parallel}} \rightarrow M + \overset{\text{C}}{\parallel}{\underset{\text{C}}{\parallel}}$	$M \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \rightarrow M + \overset{\text{C}}{\parallel}{\underset{\text{C}}{\parallel}}$	$M \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{B} \end{array} \rightarrow M + \begin{array}{c} \text{A} \\   \\ \text{B} \end{array} [-X_2]$
Formation of CH bond	$M \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \rightarrow M + \overset{\text{H}}{ }{\text{C}}$	$M \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \rightarrow M + \overset{\text{H}}{ }{\text{C}}$	$M \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{B} \end{array} \rightarrow M + \begin{array}{c} \text{A} \\   \\ \text{B} \end{array} [-X_2]$
Dimerisation of olefin	$\begin{array}{c} \text{C}=\text{C} \\   \\ \text{M} \\   \\ \text{C}=\text{C} \end{array} \rightarrow \begin{array}{c} \text{C}-\text{C} \\   \quad   \\ \text{M} \\   \quad   \\ \text{C}-\text{C} \end{array}$	$\begin{array}{c} \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{M} \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \end{array} \rightarrow \begin{array}{c} \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{M} \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \end{array}$	$M \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{B} \end{array} \rightarrow M + \begin{array}{c} \text{A} \\   \\ \text{B} \end{array} [-X_2]$
Acetylene trimerisation	$\begin{array}{c} \text{C} \equiv \text{C} \\ \diagup \quad \diagdown \\ \text{M} \\ \diagdown \quad \diagup \\ \text{C} \equiv \text{C} \\ \diagup \quad \diagdown \\ \text{C} \equiv \text{C} \end{array} \rightarrow M + \text{C}_6\text{H}_6$	$\begin{array}{c} \text{C} \equiv \text{C} \\ \diagup \quad \diagdown \\ \text{M} \\ \diagdown \quad \diagup \\ \text{C} \equiv \text{C} \\ \diagup \quad \diagdown \\ \text{C} \equiv \text{C} \end{array} \rightarrow \text{C}_6\text{H}_6$	$M \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{B} \end{array} \rightarrow M + \begin{array}{c} \text{A} \\   \\ \text{B} \end{array} [-X_2]$
Formation of CC bond	$M \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \rightarrow M + \begin{array}{c} \text{C} \\   \\ \text{C} \end{array}$	$M + \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \quad n = 1, 2$	$M \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{B} \end{array} \rightarrow M + \begin{array}{c} \text{A} \\   \\ \text{B} \end{array} [-X_2]$
Olefin insertion	$\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{M} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \end{array} \rightarrow \begin{array}{c} \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{M} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{M} \\ \diagdown \quad \diagup \\ \text{C} \end{array} \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \rightarrow \begin{array}{c} \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{M} \\ \diagdown \quad \diagup \\ \text{C} \end{array}$	$M \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{B} \end{array} \rightarrow M + \begin{array}{c} \text{A} \\   \\ \text{B} \end{array} [-X_2]$
CO elimination	$M-\text{CO} \rightarrow M + \text{CO}$	$M=\text{C}=\text{O} \rightarrow M + \text{CO}$	$M \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{B} \end{array} \rightarrow M + \begin{array}{c} \text{A} \\   \\ \text{B} \end{array} [-X_2]$
Alkyl migration	$\begin{array}{c} \text{CO} \\   \\ \text{M}-\text{R} \end{array} \rightarrow \begin{array}{c} \text{O}=\text{C}-\text{R} \\   \\ \text{M} \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{C} \\   \\ \text{M}-\text{R} \end{array} \rightarrow \begin{array}{c} \text{O}=\text{C}-\text{R} \\   \\ \text{M} \end{array}$	$M \begin{array}{c} \text{A} \\ \diagup \quad \diagdown \\ \text{B} \end{array} \rightarrow M + \begin{array}{c} \text{A} \\   \\ \text{B} \end{array} [-X_2]$

transition metals and the application of this classification to the possible mechanisms of simple hydrocarbon reactions, catalysed by transition metals.

Examination of the literature identifies a number of key reactions which are common to a very wide variety of reactions between organic compounds and transition metals. These are listed in Table 1. The second column in this Table gives the commonly used description of these reaction steps. In the third column we show how these steps have been represented in the computer. In essence, the formalism which has been adopted has been to represent all hydrocarbon-metal interactions in terms of an idealised valency bond model; this allows the computer to identify four bonds to the carbon at any time.

If we choose not to distinguish between carbon, hydrogen, or indeed any other atoms we may represent the reactions in column three as shown in column four of Table 1. Inspection of this column shows that there are, in fact, only two steps required for classification of all these reactions, namely as addition of  $X_2$  to the metal (written as  $+X_2$ ) or removal of  $X_2$  from the metal

## SCHEME 1



( $-\text{X}_2$ ). In other words all the reactions in Table 1 may be viewed as either oxidative-addition or as reductive-elimination reactions. In Scheme 1 we have written the commonly accepted mechanism for the hydroformylation of olefins and using the above formalism we show that the reaction sequence for this synthesis may be reduced to an alternating sequence of  $+\text{X}_2$  and  $-\text{X}_2$  steps.

It follows that we can encode the computer to incorporate all the reactions listed in Table 1 in terms of just these two formal steps.

Electron number rules are widely applicable in organotransition metal chemistry and, when used judiciously, can provide a useful guide to likely products of reactions. Further it appears, at present, that the great majority of organometallic reactions proceed via intermediates the transition state for which do not exceed the appropriate electron number rules nor the normal valency rules for the metal system in question.

Therefore, given these assumptions, we may limit possible applications of Table 1 by instructing the computer to, in effect, count electrons. For example, an 18-electron intermediate would not be allowed to undergo a  $+\text{X}_2$  reaction since this would give rise to a forbidden 20-electron intermediate (or transition state).

The resulting computer program may be used in the following manner. The reactants may be put in the computer acting as the reaction vessel. The program may then be instructed to generate all possible reaction products by application of  $+\text{X}_2$  or  $-\text{X}_2$  reactions within the scope of, say, the eighteen electron rule. If Table 1 contains all the possible key steps then the computer should generate all possible products. Further, if the reaction proceeds via two electrons (non-radical) pathways, and does not involve intermediates with electron numbers greater than 18, then we should have also generated all possible mechanisms.

It remains for the computer predictions to be examined in the light of known reaction products and relevant data to identify the likely mechanism(s) of the reaction.

We have carried out the above operation for the reaction between a metal hydride MLH and two molecules of ethylene. It was specified that the MLH was a 16-electron system. L represents any leaving group such as CO,  $\text{PR}_3$ , etc.

The reactions pathways and the products for the reactions are shown in Fig. 1, 2 and 3. There have been omitted from the Scheme only those interme-

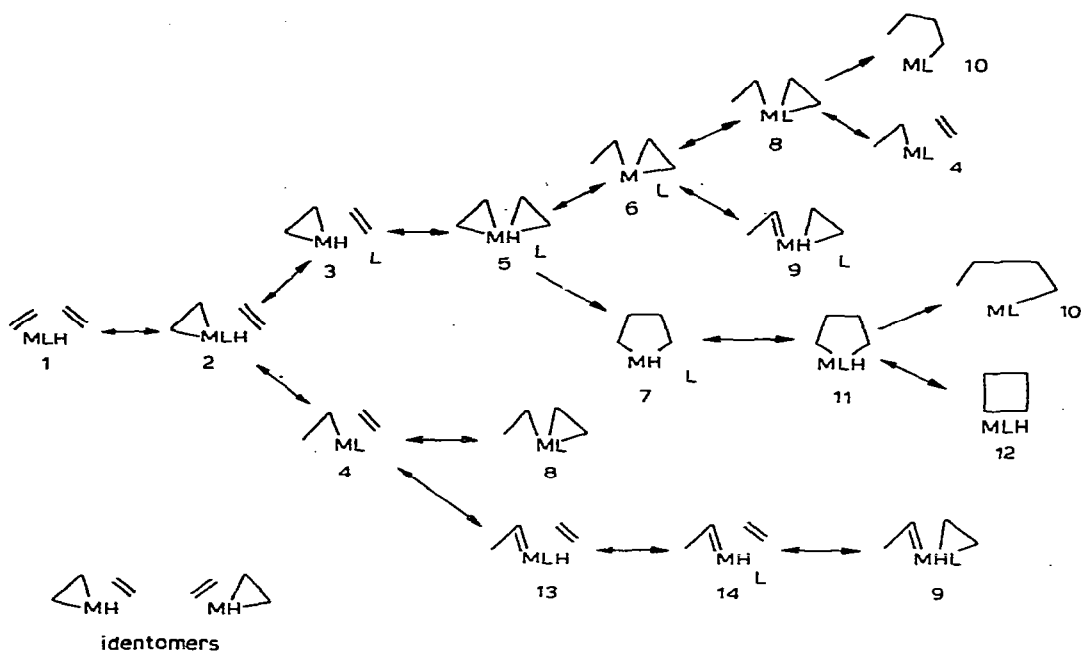


Fig. 1. (1) The compound MLH is shown together with two available ethylene molecules with which it will react. (2) Addition of one molecule of ethylene has occurred ( $+X_2$ ). (3) Elimination of the two electron ligand L. (4) Insertion of the coordinate ethylene into the M-H bond ( $-X_2$ ), etc.  $\leftrightarrow$  represents a reversible reaction.

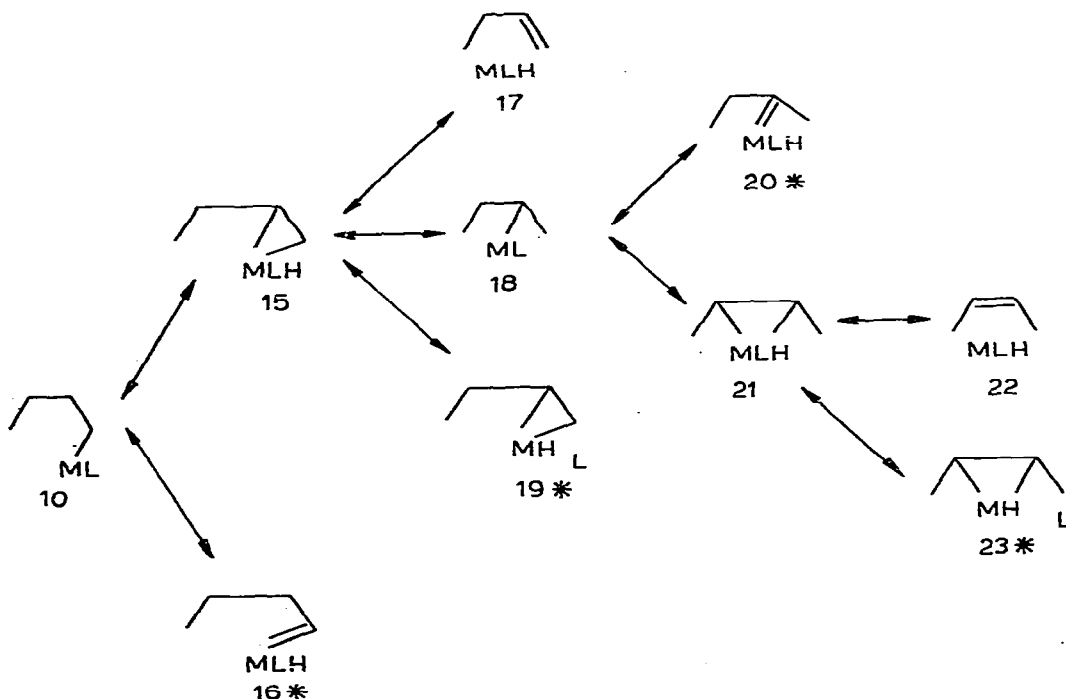


Fig. 2. Continuation of the computer derived pathway starting from compound 10 of Fig. 1. 17 and 22 show formation of free butenes. \* indicates that the computer did not find that 16 or 20 would lead to subsequent formation of free hydrocarbon products. The program does not distinguish between *cis* and *trans* stereochemistry for the 2-butene product either which may arise in formation of 21 from 18.

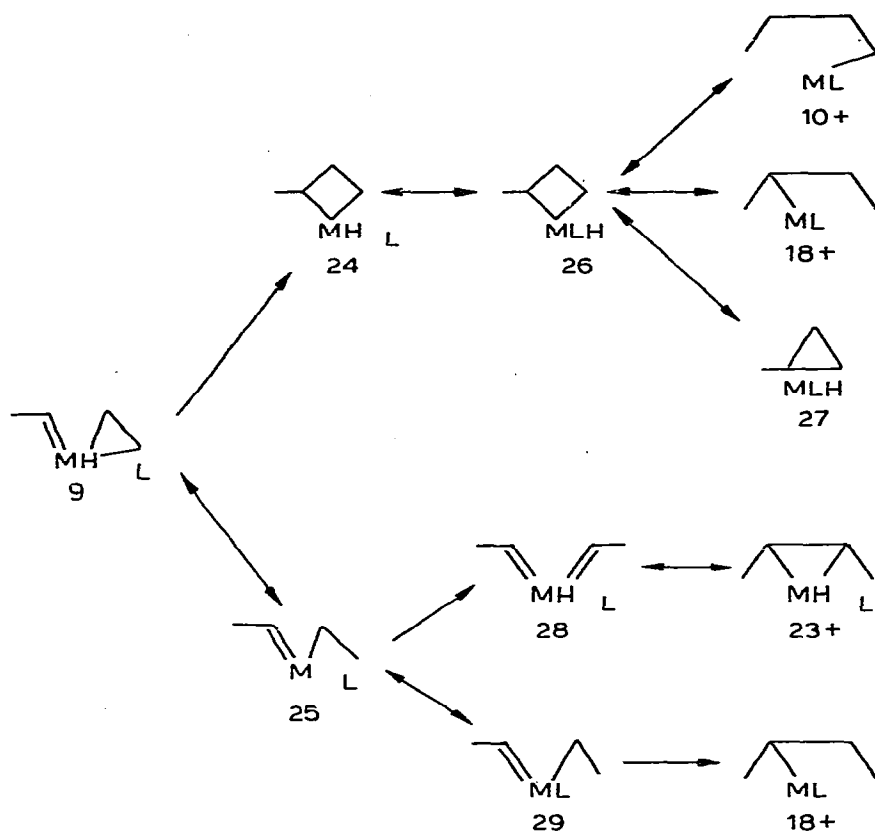


Fig. 3. Continuation of computer derived pathway starting from compound 9 of Fig. 1. + indicates that this compound is also found by an alternative route and is an intermediate leading to products.

diates which are duplicated as a result of the program being unable, at present, to distinguish between differing graphical representations of the same molecule (called isomers). For example two isomers are shown at the bottom of Fig. 1.

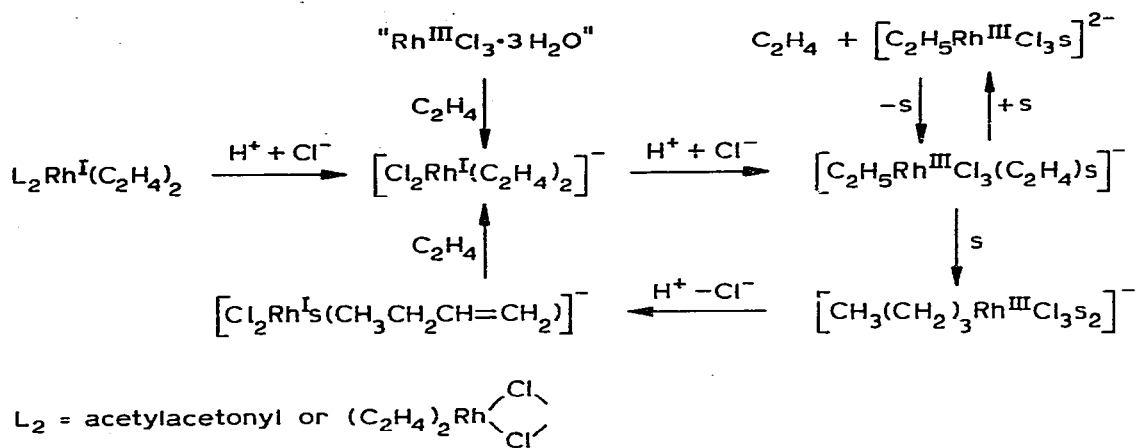
We may now examine the mechanism in the light of known data, background literature and, indeed, our prejudices. Examination of Fig. 1–3 identifies synthetic routes to butenes, methylcyclopropane and cyclobutane.

If we identify the general scheme with the particular case of the reaction between ethylene and  $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$ , we find that the only products observed are 1-butene and 2-butene [2].

In a series of elegant and classical studies of this reaction Cramer proposed the mechanism shown in Scheme 2 for formation of 1-butene [2]. Since only butenes are observed (>99%) we consider only the routes which lead to these products. The pathway to butene products are shown in Scheme 3.

We note that the key intermediates for producing butenes arise from either of the butyl isomers 10 or 18. The key steps to these intermediates are those which give rise to carbon-carbon bond formation. These are:  $5 \rightarrow 7$ ,  $8 \rightarrow 10$ ,  $9 \rightarrow 24$ ,  $25 \rightarrow 28$ ,  $29 \rightarrow 18$ . It is assumed that these steps are irreversible. The routes incorporating these steps are labelled E, D, C, A, B respectively.

SCHEME 2



s = solvent

The mechanism C involves a 1-2 hydrogen shift and an metallacyclobutane intermediate and is similar to that recently proposed as one possibility in Ziegler-Natta polymerisation [3].

Mechanism D is in essence the scheme put forward by Cramer for dimerisation of ethylene to butene and involves the insertion of ethylene into the rhodium-ethyl bond.

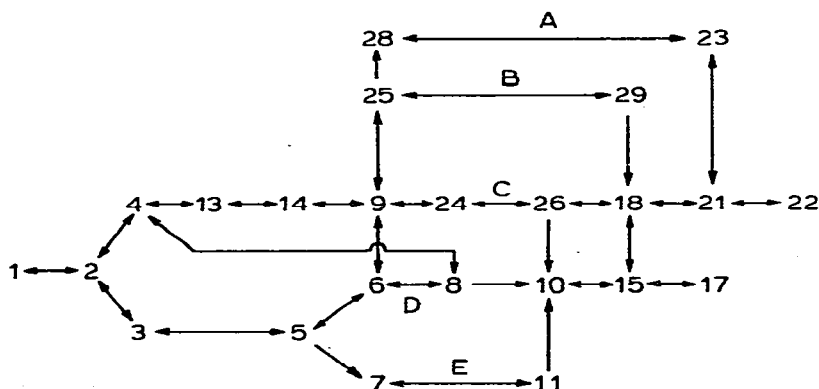
Mechanism E proceeds via a metallacyclopentane intermediate.

Routes A and B are considered to be unlikely only on the grounds of lack of any precedence in the literature.

We may consider routes C, D or E in the light of the data reported by Cramer.

A particular cogent observation is the  $^1\text{H}$  NMR spectrum of the reaction mixture which shows the presence of a ethylrhodium moiety. However this does not prove that the ethylrhodium moiety is an intermediate in the catalytic cycle, it may be present as a result of a redundant equilibrium, and we note

SCHEME 3



that ethyl derivative 6 is common to routes C or D and is also available as a redundant equilibrium for route E at an early stage in this route. Therefore, in our opinion, there is no conclusive data to distinguish between the routes C, D or E.

One other apparent fact seems relevant in consideration concerning the mechanisms C, D or E. Namely the reaction is carried out in the presence of excess of ethylene. Therefore we may enquire why there should not be any trimerisation or oligomerisation products formed if the mechanisms C or D are correct.

In other words why should the insertion of ethylene into the rhodium—ethyl bond be markedly preferred to the insertion of ethylene into the rhodium—butyl bond in species 10 or why should not the butyl derivative 10 re-enter into a hydrido-carbene equilibrium as is shown for the ethylrhodium compound 13. On the other hand, in order to form trimers by the mechanism E we must invoke a step whereby there is a ring opening between coordinated ethylene and intermediate 7. This should be a significantly different step from the formation of the metallacyclopentane 7 from 5.

Therefore, in the absence of other data to distinguish between routes C, D or E we prefer the metallacyclopentane mechanism E on the ground that it provides the most direct explanation why trimers are not, within experimental error, detected in the reaction products.

In conclusion, we have reported a preliminary attempt to classify and incorporate the synthetic role of transition metals into a program for the synthesis of organic compounds. We have illustrated the operation of the program for a very simple example. There remain many outstanding problems and improvement which can be envisaged. For example, no attempt has been made to distinguish between individual metals or metal—ligand systems. Also no account is taken of stereochemistry. The methods of eliminating highly unreasonable solutions and generation of isomers is also desirable. We are presently investigating these matters.

The computer program used for this work is described fully in ref. 1 and the program is sufficiently flexible to incorporate the instructions arising from the new reactions described in this work. The electron number constraint is applied in the following manner: at the beginning of the job the user indicates the number of electrons for the starting compound. The program will then choose only those reactions which lead to a compound with the appropriate electron number. In the given example the user instructs the program that the compound MLH is a 16 electron system; the program will try only reactions which result in addition of two electrons etc.

The program is available on computers at Oxford and at Marseille and copies together with user instructions may be obtained from R. Barone.

### Acknowledgements

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