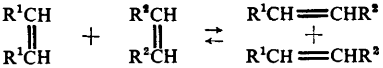
Olefin Metathesis and its Catalysis

By R. J. Haines
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CAPE TOWN,
CAPE TOWN, REPUBLIC OF SOUTH AFRICA

and G. J. Leigh
SCHOOL OF MOLECULAR SCIENCES, UNIVERSITY OF SUSSEX,
BRIGHTON, BN1 9QJ

1 Introduction

The olefin metathesis reaction (1) is one of the most remarkable catalytic reactions discovered in recent years.[1]*



$$\begin{matrix} R^1CH \\ \| \\ R^1CH \end{matrix} + \begin{matrix} R^2CH \\ \| \\ R^2CH \end{matrix} \rightleftarrows \begin{matrix} R^1CH{=}CHR^2 \\ + \\ R^1CH{=}CHR^2 \end{matrix} \qquad (1)$$

A non-catalytic counterpart of this reaction was observed in 1931 by Schneider and Frohlich,[2] who established that at 725 °C propylene could be converted into ethylene and butene. However, it was not until the discovery of heterogeneous and homogeneous catalysts, which can promote the reaction at much lower temperatures and minimize side-reactions, that the potential of the metathesis reaction could be realized. The reaction is essentially thermoneutral, involving just the making and breaking of carbon–carbon double bonds. Equilibrium can be reached from either side of reaction (1), and the distribution of products is then statistical. The thermal activation of this entropy-controlled reaction is symmetry forbidden according to the Woodward–Hoffman rules,[3] which is consistent with the high temperatures necessary for the reaction discovered by Schneider and Frohlich.

The catalysis of the reaction was first reported by Banks and Bailey,[1] their discovery stemming from a study of the catalytic activity of activated molybdenum hexacarbonyl supported on alumina. They found that over this system linear olefins of three to eight carbon atoms were readily converted into mixtures of homologues of lower and higher molecular weight, and in particular that propylene was converted into ethylene and but-2-ene according to equation (2).

*This reaction has been variously called the 'olefin disproportionation reaction'[1] and the 'olefin dismutation reaction'[4] but because it involves the interchange of alkylidene radicals (transalkylidenation) we prefer the term 'olefin metathesis' originally proposed by Calderon.[5]

[1] R. L. Banks and G. C. Bailey, *Ind. and Eng. Chem.* (*Product Res. and Development*), 1964, **3**, 170.

[2] V. Schneider and P. K. Frohlich, *Ind. and Eng. Chem.*, 1931, **23**, 1405.

[3] See, for example, R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17.

[4] C. P. C. Bradshaw, A. J. Howman, and L. Turner, *J. Catalysis*, 1967, **7**, 269.

[5] N. Calderon, H. Y. Chen. and K. W. Scott, *Tetrahedron Letters*, 1967, 3327.

$$2 \text{ propylene} \rightleftharpoons \text{ethylene} + \text{but-2-ene} \qquad (2)$$

They also observed the formation of cyclopropane and methylcyclopropane from ethylene, and this has still not been adequately explained. Temperatures of *ca.* 150 °C and pressures of *ca.* 30 atmospheres were employed.

Prior to Banks and Bailey's discovery, the polymerization of cyclic olefins by both heterogeneous (*e.g.* molybdenum oxide supported on alumina)[6] and homogeneous catalysts [*e.g.* tungsten(VI) chloride–triethylaluminium][7–9] had been reported, but it was not recognized at the time that the ring-opening implicit in the polymerization involved olefin metathesis. The proposed mechanism involved cleavage of a bond adjacent to the olefinic bond.

The first homogeneous catalysis of olefin metathesis was reported by Calderon and co-workers in 1967.[5,10] They used $[WCl_6]$–EtOH–$EtAlCl_2$ as a catalyst mixture, and were the first to recognize that olefin metathesis involves trans-alkylidenation, and that ring-opening polymerization employing molybdenum or tungsten systems as catalysts also involves this step.[11]

The object of this review is to describe the scope of the reaction, to enumerate the theories which have been advanced to explain its catalysis (with particular emphasis on the nature of the catalysts), to evaluate critically the available literature (there is undoubtedly much industrial research which has not been revealed), and to attempt to present a model consistent with all observations. We shall discuss homogeneous systems in more detail than heterogeneous systems. Several reviews and catalogues on, and related to, this topic have appeared in the literature[12–24] but none adequately covers all the aspects discussed in this review, and a number are unavailable to the average reader.

---

[6] H. S. Eleuterio, Ger. Offen., 1960, 1 072 811 (*Chem. Abs.*, 1961, **55,** 16 005 *h*).

[7] G. Natta, G. Dall'Asta, G. Mazzanti, and G. Motroni, *Makromol. Chem.*, 1963, **69,** 163.

[8] G. Natta, G. Dall'Asta, and G. Mazzanti, *Angew. Chem. Internat. Edn.*, 1964, **3,** 723.

[9] G. Natta, G. Dall'Asta, I. W. Bassi, and G. Carella, *Makromol. Chem.*, 1966, **91,** 87.

[10] N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, 1968, **90,** 4133.

[11] K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, Abstracts 155th NationalMeeting of the American Chemical Society, San Francisco, April 1968, paper L54; *Advances in Chemistry Series*, 1969, **91,** 399.

[12] G. C. Bailey, *Catalysis Rev.*, 1969, **3,** 37.

[13] F. D. Mango, *Adv. Catalysis*, 1969, **20,** 307.

[14] S. Yoshitomi, *Sekiyu Gakkai Shi*, 1970, **13,** 92 (*Chem. Abs.*, 1970, **73,** 3386y); *Sekiyu to Sekiyu Kagaku*, 1971, **15,** 89 (*Chem. Abs.*, 1971, **75,** 119 670g); *Nenryo Kyokaishi*, 1967, **46,** 514 (*Chem. Abs.*, 1968, **68,** 29 168a).

[15] J. Tsuji, *Kagaku No Ryoiki, Zokan*, 1970, **89,** 169 (*Chem. Abs.*, 1970, **73,** 35 770k).

[16] C. Inoue and K. Hirota, *Yuki Gosei Kagaku Kyokai Shi*, 1970, **28,** 744 (*Chem. Abs.*, 1970, **73,** 98 312h).

[17] M. L. Khidekel, A. D. Shebaldova, and I. V. Kalechits, *Russ. Chem. Rev.*, 1971, **40,** 669.

[18] F. D. Mango and J. H. Schachtschneider, 'Transition Metals in Homogeneous Catalysis', ed. G. N. Schrauzer, Marcel Dekker, New York, 1971, p. 223.

[19] N. Calderon, *J. Macromol. Science*, 1972, **C7,** 105.

[20] N. Calderon, *Accounts Chem. Res.*, 1972, **5,** 127.

[21] L. Marko, *J. Hung. Chem. Soc.*, 1972, **27,** 213.

[22] D. J. Cardin, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2,** 99.

[23] R. L. Banks, *Fortschr. Chem. Forsch.*, 1972, **25,** 39.

[24] W. B. Hughes, *Organometallic Chem. Synth.*, 1972, **1,** 341.

2 Scope of the Reaction

A. Acyclic Olefins.—(*i*) *Mono-olefins.* Whereas acyclic unsaturated hydrocarbons containing internal olefinic bonds are generally inert towards homopolymerization involving addition across the double bond, such as Ziegler–Natta polymerization,[25] they participate almost as readily as alkenes containing terminal olefinic bonds in the olefin metathesis reaction. This reaction thus provides a valuable route to the synthesis of new alkenes from those which may be more readily available.

Its potential for redistribution of olefinic bonds in systems containing functional groups is considerable, although thus far little exploited. Isolated examples are the metathesis of methyl oleate employing $[WCl_6]$–$[Me_4Sn]$ as catalyst to give octadec-9-ene and the dimethyl ester of octadec-9-enedioic acid,[26] and the metathesis of acrylonitrile and propylene over a heterogeneous catalyst derived from ammonium tungstate, to give ethylene and 1-cyanopropylene.[27] Some problems may arise using olefins of this type due to catalyst poisoning, for example, where halogenocarbons are used, but they should be surmountable by suitable choice of catalyst. Thus *p*-chlorovinylbenzene and pent-2-ene, and 5-bromopent-1-ene and pent-2-ene, undergo metathesis over $[WCl_6]$–$EtAlCl_2$ in benzene.[28] The metathesis of simple alkenes, particularly employing heterogeneous catalytic systems, has, in contrast, been extensively studied. For a comprehensive catalogue of these reactions the reader is referred to the review by Bailey,[12] as well as to those by Banks[23] and Hughes.[24]

The rate of reaction of olefins in the metathesis reaction is sterically controlled, as demonstrated by the decrease along the series $CH_2{=} > RCH_2CH{=} > R_2CHCH{=} > R_2C{=}$.[20] Substitution of vinylic hydrogens by chlorine has been shown to deactivate the double bond towards metathesis.[20]

The industrial potential of the olefin metathesis reaction is considerable and obvious. The first commercial plant to utilize it, using in particular the Phillips Triolefin process to convert propylene into polymerization-grade ethylene and high-purity butene, was in operation within three years of the first report of the catalysed olefin metathesis reaction.[29] Numerous industrial processes have been patented in which olefin metathesis is an integral step,[12,17] for instance, a new route to high-octane alkylate. The process involves the alkylation of ethylene and but-2-ene, obtained by disproportionation of propylene, to di-isopropyl and but-2-ene alkylate.[30] It has also been shown that the yield of ethylene from a naphtha cracker can be economically increased through the addition of a propylene metathesis stage.[31]

---

[25] There are numerous reviews on this topic: see, for example, C. E. H. Bawn and A. Ledwith, *Quart. Rev.*, 1962, **16**, 361; J. Boor, *Ind. and Eng. Chem.* (*Product Res. and Development*), 1970, **9**, 437, and references therein.

[26] P. B. van Dam, M. C. Mittelmeijer, and C. Boelhouwer, *J.C.S. Chem. Comm.*, 1972, 1221.

[27] G. Foster, Ger. Offen., 1971, 2 063 150 (*Chem. Abs.*, 1971, **75**, 63 172b).

[28] J. I. O'Hara and C. P. C. Bradshaw, B.P., 1972, 1 283 348 (*Chem. Abs.*, 1972, **77**, 113 786u).

[29] Anon., *Chemical Week*, July 23, 1966, p. 70.

[30] R. S. Logan and R. L. Banks, *Oil Gas J.*, 1968, 66, 131; see also *Hydrocarbon Process*, 1968, **47**, 135.

[31] R. E. Dixon, J. F. Hutto, R. T. Wilson, and R. L. Banks, *Chem. Age*, 1967, **2**, 49.

The metathesis reaction has provided a valuable method for characterizing polymer structures. For example, the monomer sequence distribution in a number of styrene–butadiene copolymers was determined by treating the polymer with a high proportion of but-2-ene in the presence of a suitable catalyst. This degraded the polymer to low-molecular-weight species, which were analysed by g.l.c.[32] This method has also been used to determine the extent of double-bond migration during free-radical cross-linking of butadiene.[33]

(*ii*) *Di- and tri-olefins*. Acyclic unsaturated hydrocarbons containing more than one olefinic bond also undergo the olefin metathesis reaction, although yields may be somewhat low over heterogeneous catalysts owing to coke formation on the surface. They can react either intermolecularly or intramolecularly. Intermolecular metathesis is effected on treatment of buta-1,3-diene with a tungsten oxide–silica catalyst that has previously been treated with sodium carbonate, to give ethylene and cyclohexadiene.[34] For simple metathesis, hexatriene should be obtained as product, and this must have cyclized to cyclohexadiene under the reaction conditions. Deca-1,5,9-triene is formed on metathesis of hexa-1,5-diene by $[Mo(NO)_2(PPh_3)_2Cl_2]$–$[Me_3Al_2Cl_3]$.[35] However, octa-1,7-diene reacts intramolecularly on treatment with $[Mo(NO)_2(PPh_3)_2Cl_2]$–$[Me_3Al_2Cl_3]$ to give cyclohexene as a major product.[35] Other reported reactions involving dienes include metathesis of buta-1,3-diene with propylene,[34] of buta-1,3-diene with isobutene,[34] and of penta-1,4-diene.[36]

B. Cyclic Olefins.—Metathesis is not restricted to acyclic olefins. As mentioned above, early reports showed that polyalkenamers of the general formula $[\text{—CH=CH(CH}_2)_n\text{—}]$ (n = 2, 3, 5, 6, or more) are produced by treatment of the appropriate cyclic mono-olefin with heterogeneous catalysts such as molybdenum oxide supported on alumina or homogeneous catalytic systems such as $[WCl_6]$–$AlEt_3$.[6–9] Although it was not appreciated at the time that the reaction involves olefin metathesis, it was realized that the polymerization involves ring opening and not an addition polymerization of the Ziegler–Natta type because the latter would have yielded polymers containing cyclic repeat units. Further evidence against an addition mechanism was that cyclic olefins in which the rings are not highly strained were found not to be polymerized by normal Ziegler–Natta catalysts. The polymers formed were assumed to be essentially linear, and a mechanism in which a carbon–carbon bond adjacent to the olefinic bond is cleaved was proposed.[8]

Calderon and co-workers subsequently made a detailed study of the polymerization of cyclo-octene and cyclo-octa-1,5-diene using $[WCl_6]$–$EtAlCl_2$ as

---

[32] L. Michajlov and H. J. Harwood, *Amer. Chem. Soc., Div. Polym. Chem., Preprints*, 1970, **11**, 1197.

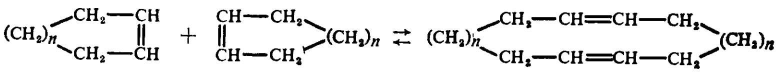
[33] W. Ast and K. Hummel, *Kautschuk Gummi Kunststoffe*, 1971, **24**, 220.

[34] L. F. Heckelsberg, R. L. Banks, and G. C. Bailey, *J. Catalysis*, 1969, **13**, 99.

[35] E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Amer. Chem. Soc.*, 1970, **92**, 528.

[36] G. Doyle, Ger. Offen., 1971, 2047 270 (*Chem. Abs.*, 1971, **75**, 5202a); *J. Catalysis*, 1973, **30**, 118.

catalyst, and they established that the polymerization mixtures contained low- as well as high-molecular-weight species.[11,37] By means of selective and fractional extraction they isolated the former, and by gas chromatography, mass spectrometry, and n.m.r. spectroscopy showed that they were macrocycles and multiplets of the parent compound or, in the case of the cyclo-octa-1,5-diene reaction, oligomers of formula $(C_8H_{12})_nC_4H_6$.[11] They also showed that further treatment of the high-molecular-weight species with $[WCl_6]$–$EtAlCl_2$ led to the formation of low-molecular-weight macrocycles. These results led to the conclusion that the ring-opening polymerization of cyclic olefins by catalysts of the type $[WCl_6]$–R_xAlCl_{3-x} is a special case of the olefin metathesis reaction essentially involving macrocyclization of the parent compound (1) by consecutive



(1)

metathesis of larger and larger ring systems as shown. Intramolecular metathesis leading to ring reduction will obviously occur concurrently, and this explains why low- as well as high-molecular-weight species are found at equilibrium. On this basis, cyclic olefins that can be considered as multiples of the same mono-olefin should afford the same equilibrium mixture, and this has been observed.[37] Strong evidence for the involvement of olefin metathesis in ring-opening polymerization has come from studies of the ozonolysis products of the random copolymer produced from cyclo-octene and $[1\text{-}^{14}C]$cyclopentene with a $[WOCl_4]$–$EtAlCl_2$–benzoyl peroxide catalyst.[38] The high-molecular-weight species formed in the product mixtures obtained by polymerization of cyclic olefins are suspected to be primarily linear and not macrocyclic,[39] but their formation is readily explained in terms of trace amounts of acyclic olefins being present in the reaction mixture and participating in the polymerization.

The polyalkenamers obtained by ring-opening polymerization of cyclic olefins range from amorphous elastomers to crystalline materials, depending on the structure of the repeat units and the configuration about the olefinic bonds.[40] The crystallizability of these polymers in general is associated with their stereoregularity. Significantly, polymerization of substituted unsaturated cyclic olefins of medium ring size by this method is a conventional route to perfectly alternating copolymers, provided that side-reactions do not occur during the polymerization process. For instance, ring-opening of 5-methylcyclo-octene by

---

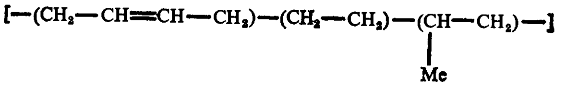
[37] N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polymer Sci.* (*Polymer Chem.*), 1967, **5A**, 2209.

[38] G. Dall'Asta and G. Motroni, *European Polymer J.*, 1971, **7**, 707.

[39] K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, *Rubber Chem. Technol.*, 1971, **44**, 1341.

[40] N. Calderon and M. C. Morris, *J. Polymer Sci.* (*Polymer Phys.*), 1967, **5A**, 1283.

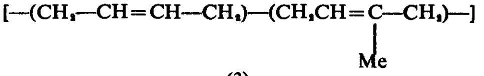
[WCl$_6$]–EtAlCl$_2$ gives a polymer with the repeat unit (2), which is equivalent to



$$[-(CH_2-CH{=}CH-CH_2)-(CH_2-CH_2)-(\underset{\displaystyle Me}{\underset{|}{CH}}-CH_2)-]$$

(2)

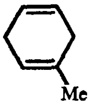
the alternating copolymer of butadiene, ethylene, and propylene.[37] Similarly, a polyalkenamer containing the repeat unit (3), and equivalent to the alternating



$$[-(CH_2-CH=CH-CH_2)-(CH_2CH=\underset{\displaystyle Me}{\underset{|}{C}}-CH_2)-]$$

(3)

copolymer of butadiene and isoprene, is obtained[20] by ring opening of (4).



(4)

It has been established that the yield of low-molecular-weight macrocycles in the ring-opening polymerization of olefins is considerably increased under certain reaction conditions, *e.g.* high dilutions.[11,41–43] For instance, metathesis of cyclo-octene in dilute benzene solution by [WCl$_6$]–EtAlCl$_2$–EtOH gives a mixture which contains the three low-molecular-weight species $(C_8H_{14})_n$ (n = 1, 2, or 3) in high yield.[41] Ring opening of cyclo-olefins by metathesis thus provides a convenient method for the synthesis of macrocycles, which are useful intermediates in the preparation of perfume bases.

Intramolecular metathesis of cyclic diolefins can lead to products not obtainable by more conventional routes. For example, catenanes have been identified in mixtures obtained by catalytic metathesis of cyclododecene by [WCl$_6$]–EtAlCl$_2$–EtOH.[44,45] It has been proposed that these are formed by a 360° twist of the cyclic olefin prior to the metathesis reaction, as shown in Scheme 1.

Although most alicyclic olefins possessing more than one double bond readily undergo ring-opening polymerization, they do so only if these bonds are not conjugated.[19] Thus the metathesis of cyclopentadiene, cyclo-octa-1,3-diene, or cyclohepta-1,3,5-triene has not been effected. It is believed that this inertness results from catalyst de-activation. For instance, addition of small amounts of cyclo-octa-1,3-diene to a tungsten–aluminium-catalysed polymerization of

---

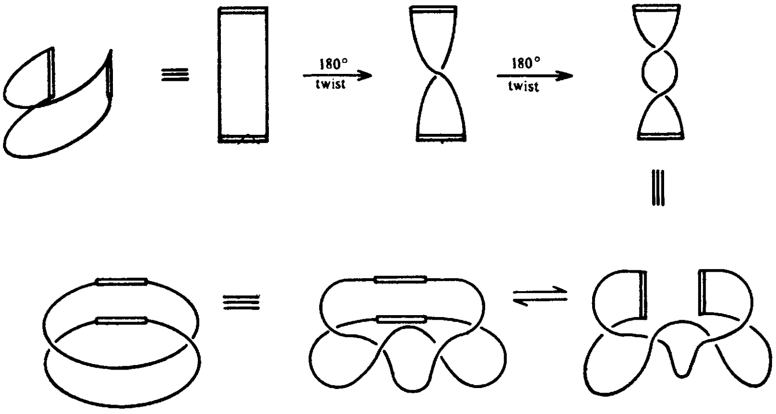
[41] N. Calderon, U.S. P., 1969, 3 439 056 (*Chem. Abs.*, 1969, **71**, 38 438c).

[42] N. Calderon, U.S. P., 1969, 3 439 057 (*Chem. Abs.*, 1969, **71**, 80 807x).

[43] E. Wasserman, D. A. Ben-Efraim, and R. Wolovsky, *J. Amer. Chem. Soc.*, 1968, **90**, 3286.

[44] R. Wolovsky, *J. Amer. Chem. Soc.*, 1970, **92**, 2132.

[45] D. A. Ben-Efraim, C. Batich, and E. Wasserman, *J. Amer. Chem. Soc.*, 1970, **92**, 2133.



Scheme 1

cyclo-octene drastically reduces the activity of the catalyst.[19] For a comprehensive review on the polymerization of cyclic olefins, see the excellent article by Calderon.[19]

C. Metathesis of Cyclic Olefins with Acyclic Olefins.—Cross-metathesis of cyclic and acyclic olefins is a convenient method for the synthesis of polyene species. For instance, it has been shown that the interaction of ethylene with cyclopentene, cyclo-octene, or cyclohexene over $[Mo(CO)_6]$–Al_2O_3 or cobalt molybdate on alumina gives hepta-1,6-diene, deca-1,9-diene, or octa-1,7-diene, respectively.[46] Similarly, treatment of cyclo-octa-1,5-diene with ethylene in the presence of $[Mo(NO)_2(PPh_3)_2Cl_2]$–$[Al_2Me_3Cl_3]$ gives deca-1,5,9-triene.[35] The acyclic triene $C_{14}H_{24}$, the tetraene $C_{19}H_{32}$, and the pentaene $C_{24}H_{40}$, as well as the diene C_9H_{16}, have been isolated from the reaction of cyclopentene with pent-2-ene.[47]

D. Alkynes.—Metathesis of alkynes has also been observed, although the reaction has received far less attention than reactions involving alkenes. Pent-2-yne has been converted into but-2-yne and hex-3-yne, employing tungsten oxide–silica as catalyst, and of the 44% of the initial pentyne undergoing reaction, 53% was converted into hexyne and butyne.[48] Terminal alkynes, *e.g.* propyne, also participate in this type of reaction, but in all cases studied the selectivity is low.[49] This is because these alkynes preferentially cyclotrimerize to yield derivatives of benzene under the conditions required for metathesis.

---

[46] G. C. Ray and D. L. Crain, Fr. P., 1968, 1 511 381 (*Chem. Abs.*, 1969, **70**, 114 580q).
[47] J.-L. Herisson and Y. Chauvin, *Makromol. Chem.*, 1970, **141**, 161.
[48] F. Pennella, R. L. Banks, and G. C. Bailey, *Chem. Comm.*, 1968, 1548.
[49] J. A. Moulijn, H. J. Reitsma, and C. Boelhouwer, *J. Catalysis*, 1972, **25**, 434.

3 Catalyst Systems and the Nature of the Catalytic Site

Both heterogeneous and homogeneous systems have been employed as catalysts in the olefin metathesis reaction.[12,23,24] The former are normally composed of a 'promoter', such as molybdenum or tungsten oxide, and a refractory 'support' having a high surface area, such as alumina or silica. However, the functions of the components cannot be rigidly defined, and the terms 'promoter' and 'support' should be used with caution. The homogeneous catalysts are generally derived from a transition-metal complex, *e.g.* [WCl_6] and an organometallic derivative or a Lewis acid such as $EtAlCl_2$ or LiBu.

A. Heterogeneous Catalysts.—Of the heterogeneous systems thus far studied, those derived from oxides or carbonyls of molybdenum, tungsten, or rhenium exhibit the highest catalytic activity.[1,50–53] The sulphides of molybdenum and tungsten and the oxides of iridium, lanthanum, niobium, osmium, ruthenium, rhodium, tantalum, tellurium, and tin have also been found to be effective promoters, but the catalytic activity of systems containing these species is considerably less.[54–56]

Various refractory materials have been employed as supports. These include magnesium silicate, magnesia–titania, alumina–titania, the oxides of metals such as zirconium and titanium, and the phosphates of aluminium and magnesium.[54] Silica and, in particular, alumina have been found to be the most effective and are the most widely used. In fact, alumina has been observed to effect the metathesis of propene in the absence of any promoter, although its activity for such is low.[57]

Generally, heterogeneous catalyst systems require activation before use. Many of the metal oxide systems need to be heated for up to five hours in a stream of an inert gas, optionally containing dioxygen, to temperatures of 600 °C. It is believed that the high temperatures effect some chemical interaction between the promoter and the support, and also desorb polar material which may poison the catalyst surface. The activity of a number of catalysts based on metal oxides can be increased by modifying their preparation. For example, the alumina used as support in some systems has been pretreated with a strong inorganic or organic acid (hydrochloric or acetic acids) prior to impregnation with the oxide.[58] Rhenium oxide has been sublimed directly on to the alumina support.[59,60] Hydrochloric acid and chlorinated hydrocarbons which yield

[50] R. L. Banks, U.S. P., 1966, 3 261 879 (*Chem. Abs.*, 1966, **65**, 12 105e).

[51] L. F. Heckelsberg, R. L. Banks, and G. C. Bailey, *Ind. and Eng. Chem.* (*Product Res. and Development*), 1968, **7**, 29.

[52] British Petroleum Co. Ltd., Dutch P., 1966, 6 511 659 (*Chem. Abs.*, 1966, **64**, 19 408c).

[53] K. V. Williams and L. Turner, B. P., 1968, 1 116 243 (*Chem. Abs.*, 1968, **69**, 29 085s).

[54] L. F. Heckelsberg, R. L. Banks, and G. C. Bailey, *Ind. and Eng. Chem.* (*Product Res. and Development*), 1969, **8**, 259.

[55] L. Turner and K. V. Williams, B. P., 1967, 1 096 200 (*Chem. Abs.*, 1968, **68**, 77 691n).

[56] R. B. Regier, U.S. P., 1972, 3 652 703 (*Chem. Abs.*, 1972, **76**, 139 910j).

[57] G. V. Isagulyants and L. F. Rar, *Izvest. Akad. Nauk S.S.S.R.*, *Ser. khim.*, 1969, 1362.

[58] British Petroleum Co. Ltd., Dutch P., 1966, 6 610 196 (*Chem. Abs.*, 1967, **67**, 53 607t).

[59] British Petroleum Co. Ltd., Dutch P., 1966, 6 605 329 (*Chem. Abs.*, 1967, **66**, 48 081s).

[60] L. Turner and C. P. C. Bradshaw, B. P., 1968, 1 103 976 (*Chem. Abs.*, 1968, **68**, 86 834p);

hydrogen chloride at the activation temperature also increase the catalytic activity of WO_3–SiO_2 systems.[61] The activity and selectivity of oxide-based catalysts can also be increased by controlled treatment after activation, with gases such as CO and H_2,[50,51,62,63] although prolonged treatment deactivates them. Certain reducing agents have also been observed to have a beneficial effect on the activity of heterogeneous catalytic systems. For instance, the conversion of pent-2-ene by WO_3–SiO_2 is increased by the addition of tributylphosphine to the feed,[64] and the activity of supported oxides of molybdenum, tungsten, rhodium, vanadium, niobium, or tantalum is increased by treating with triethylaluminium.[65]

The catalysts derived from metal carbonyls normally require much lower activation temperatures (120—140 °C), and are deactivated by air.[66] Thus they must be activated under a high vacuum or in an inert atmosphere. Kemball and co-workers have established, by i.r. spectroscopy, that during the activation of $[Mo(CO)_6]$–Al_2O_3, 2 or 3 moles of carbon monoxide are evolved.[66] However, it has been shown subsequently that $Mo(CO)_4$ is not an active species, and probably the active sites are completely free of CO[67] and possibly oxidized.[67,68] The activity of $[Mo(CO)_6]$–Al_2O_3 is enhanced by treatment with halogeno-olefins before admission of reactants.[69]

Allyls of molybdenum, tungsten, and rhenium are apparent exceptions in not requiring activation, since, when adsorbed on alumina, they are immediately active catalysts. However, possibly they activate rapidly as metathesis commences.[70]

Heterogeneous catalysts can function over a wide range of temperatures, the optimum temperature depending both on the nature of the support and on the promoter employed. Catalysts containing molybdenum or tungsten oxide generally require temperatures that are higher by about 100 °C to effect metathesis than the corresponding catalysts derived from molybdenum or tungsten hexacarbonyl. A higher operating temperature by about 200 °C is also required for systems containing silica as support compared with those using alumina. Silica-supported catalysts have the advantage that by operating at high temperatures (*ca.* 400 °C[51]) they are considerably more resistant to poisoning by polar molecules. Catalysts derived from rhenium oxide and alumina are noted for

---

[61] F. Pennella, Belg. P., 1968, 713 187.

[62] L. F. Heckelsberg, U.S. P., 1968, 3 365 513 (*Chem. Abs.*, 1968, **68**, 61 424s).

[63] E. A. Zuech Ger. Offen., 1971, 2 017 841 (*Chem. Abs.*, 1971, **74**, 5300).

[64] L. F. Heckelsberg, Belg. P., 1968, 713 185.

[65] Shell Internationale Research Maatschaapij N.V., Dutch P., 1969, 6 814 835 (*Chem. Abs.*, 1969, **71**, 49 211z).

[66] E. S. Davie, D. A. Whan, and C. Kemball, *Chem. Comm.*, 1969, 1430; *J. Catalysis*, 1972, **24**, 272.

[67] R. F. Howe, D. E. Davidson, and D. A. Whan, *J.C.S. Faraday I*, 1972, **68**, 2266.

[68] D. A. Whan, M. Barber, and P. Swift, *J.C.S. Chem. Comm.*, 1972, 198.

[69] E. S. Davie, D. A. Whan, and C. Kemball, *Chem. Comm.*, 1971, 1202.

[70] A. Morris, H. Thomas, and C. J. Attridge, Ger. Offen., 1972, 2 213 948 (*Chem. Abs.*, 1973, **79**, 65 769h); J. P. Candlin, A. H. Mawby, and H. Thomas, Ger. Offen., 1972, 2 213 947 (*Chem. Abs.*, 1973, **79**, 97 101e); I.C.I. Ltd., Fr. P., 1972, 2 120 509 (*Chem. Abs.*, 1973, **79**, 115 104h).

their activity at relatively low temperatures, as demonstrated by a 38% conversion of a but-1-ene feed into ethylene and hexenes with a 95.5% selectivity at 25 °C, at atmospheric pressure and at a 1600 vol./vol. gas hourly space velocity.[52]

B. Homogeneous Catalysts.—The first homogeneous system reported to catalyse the olefin metathesis reaction was tungsten hexachloride–ethylaluminium dichloride–ethanol.[5] Equilibrium is attained within minutes for a W:Al ratio of 1:4 and a W:olefin ratio of 1:10 000.[10] Neither constituent of this catalytic mixture catalyses metathesis alone. Subsequent studies have revealed that a wide range of organometallic or hydridic derivatives of Main Groups I, II, III, or IV may be employed as co-catalyst in conjunction with [WCl_6]. These include LiR (R = Bu^n or Bu^s),[71] RMgX (X = Cl, R = Bu^n or n-C_5H_{11}; X = Br, R = Pr^n, Bu^n, or n-C_5H_{11}; X = I, R = Bu^n),[72–75] R_2AlCl,R_3Al (R = Et or Bu^i), $EtAlCl_2$,[76–78] SnR_4 (R = Me or Bu^n),[79] $LiAlH_4$, and $NaBH_4$.[80]

There is, however, no firm dividing line between homogeneous and heterogeneous catalysis. Thus [WCl_6]–$EtAlCl_2$ (a homogeneous catalyst) acts heterogeneously when adsorbed on alumina.[81]

It was initially believed that the function of the organometallic species was to reduce [WCl_6] to tungsten tetrachloride since the [WCl_6]–$LiBu^n$ system shows a maximum of activity for a Li:W ratio of 2:1. Complexation of the olefin would then give [WCl_4(olefin)$_2$], the actual catalyst, in which the olefins are bonded in *cis*-positions. This is supported by the fact that [WCl_6]–Et_3Al exhibits maximum activity over only a narrow range of W:Al molar ratios, the optimum being *ca.* 0.5—0.6. With an excess of Et_3Al the activity is decreased, possibly due to over-reduction, but it may be restored by treatment of the mixture with dioxygen.[77]

However, WCl_4 obtained by reduction of [WCl_6] with H_2 at high temperatures or prepared *in situ* by treatment of [WCl_6] with reducing agents such as zinc, magnesium, or sodium amalgam is not a metathesis catalyst,[20,80] although the addition of aluminium trichloride to WCl_4 so prepared gives a highly active catalyst.[82] Significantly, [WCl_6] and [WBr_6] also form active metathesis cata-

---

[71] J.-L. Wang and H. R. Menapace, *J. Org. Chem.*, 1968, **33**, 3794.

[72] M. L. Khidekel, V. I. Marin, A. D. Shebaldova, T. A. Bolshinskova, and I. V. Kalechits, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1971, 663.

[73] P. A. Raven and E. J. Wharton, *Chem. and Ind.*, 1972, 292.

[74] T. Takagi, T. Hamaguchi, K. Fukuzumi, and M. Aoyamo, *J.C.S. Chem. Comm.*, 1972, 838.

[75] V. I. Marin, A. Shebaldova, T. A. Bolshinskova, M. L. Khidekel, and I. V. Kalechits, *Kinetika i Kataliz*, 1973, **14**, 613.

[76] A. Uchida, Y. Mukai, Y. Hamano, and S. Matsudu, *Ind. and Eng. Chem.* (*Product Res. and Development*), 1971, **10**, 369.

[77] Y. Uchida, M. Hidai, and T. Tatsumi, *Bull. Chem. Soc. Japan*, 1972, **45**, 1158.

[78] N. Calderon and H. Y. Chen, B. P., 1968, 1 125 529 (*Chem. Abs.*, 1968, **69**, 105 851f).

[79] C. P. C. Bradshaw, B. P., 1970, 1 208 068 (*Chem. Abs.*, 1970, **72**, 12 047v).

[80] J. Chatt, R. J. Haines, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1972, 1202; see also S. A. Matlin and R. G. Sammes, *ibid.*, 1973, 174.

[81] C. P. C. Bradshaw and J. I. Blake, B. P., 1972, 1 266 340 (*Chem. Abs.*, 1972, **76**, 126 352d).

[82] D. M. Singleton, U.S. P., 1970, 3 530 196 (*Chem. Abs.*, 1970, **72**, 89 734z).

lysts with the non-reducing $AlCl_3$ or $AlBr_3$[20,83,84] but it is conceivable that olefins can insert into aluminium–halogen bonds similar to the well-known olefin-insertion into aluminium–hydrogen bonds,[85] forming aluminium chloroalkyls, and it is unlikely that the final systems contain W^V or W^{VI}.

The organometallic or hydridic species which interacts with the tungsten compound to form the catalyst may bond through chloride, hydride, or alkyl bridges and/or may function as a Lewis acid, giving rise to acid–base equilibria of the type:

$$[WCl_x] + [AlCl_3] \rightleftharpoons [WCl_{x-1}]^+ + [AlCl_4]^-$$

in the case of $AlCl_3$, the removal of a chloride ion from the tungsten providing an additional vacant co-ordination site for the incoming olefin.[20] The addition of $AlCl_3$ or $AlBr_3$ to $[WCl_6]$–$2LiBu^n$ increases the catalytic activity of this system considerably, and this may also be explained by the aluminium halide acting as a Lewis acid and effecting rapid isomerization of *trans*-$[WCl_4(olefin)_2]$ to *cis*-$[WCl_4(olefin)_2]$ by the mechanism outlined in Scheme 2.[86]

$$\begin{tikzcd} \textit{trans}\text{-}[WCl_4(\text{olefin})_2] \arrow[r, leftrightharpoons, "AlCl_3"] & {[WCl_3(\text{olefin})_2]^+ [AlCl_4]^-} \arrow[d, "-AlCl_3"] \\ & \textit{cis}\text{-}[WCl_4(\text{olefin})_2] \end{tikzcd}$$

Scheme 2

The ability of lithium alkyls, tin tetra-alkyls, lithium aluminium hydride, or sodium borohydride to produce active metathesis catalysts with $[WCl_6]$ would imply that although acid–base equilibria of the type described above can lead to an increase in the rate of metathesis, it is not an essential part of the catalyst constitution.

The homogeneous catalyst mixture $[WCl_6]$–$LiBu^n$ appears to yield substantially the same product from the metathesis of but-2-ene throughout the range 60—130 °C, although the rate increases with temperature. Above 130 °C, the catalyst is deactivated or destroyed.[87]

Controlled treatment of $[WCl_6]$ with protic solvents such as ethanol, phenol, water, or acetic acid prior to the addition of the organoaluminium compound increases the catalytic activity of systems $[WCl_6]$–R_xAlCl_{3-x}.[5,10,78,88] The reaction of $[WCl_6]$ with ethanol produces a stoicheiometric amount of HCl together with species such as $[WCl_5(OEt)]$.[20] It is therefore not suprising that compounds such as $[WOCl_4]$, WO_3, $[\{o\text{-}(MeO_2C)C_6H_4O\}WCl_5]$, $[W(OPh)_6]$,

---

[83] P. R. Marshall and B. J. Ridgewell, *European Polymer J.*, 1969, **5**, 29.

[84] J.-L. Herisson, Y. Chauvin, N. H. Phung, and G. Lefebvre, *Compt. rend.*, 1969, **269**, *C*, 661.

[85] See, for example, R. Köster and P. Binger, *Adv. Inorg. Radiochem.*, 1965, **7**, 263.

[86] J.-L. Wang, H. R. Menapace, and M. Brown, *J. Catalysis*, 1972, **26**, 455.

[87] J.-L. Wang and H. R. Menapace, *J. Catalysis*, 1973, **28**, 300.

[88] D. Medema, W. Brunmayer-Schilt, and R. van Helden, B. P., 1970, 1 193 943 (*Chem. Abs.*, 1970, **73**, 76 637r).

and [WO(OPh)$_4$] are active metathesis catalysts in the presence of a suitable cocatalyst.[47,84,89,90]

Group V donors reduce the activity of catalysts derived from [WCl$_6$]. Treatment of [WCl$_6$]–EtAlCl$_2$ with pyridine inhibits metathesis, as also does triphenylphosphine (but less so).[91] Pyridine reduces [WCl$_6$] to [WCl$_4$(pyridine)$_2$],[92] and the ligand may block possible co-ordination sites for the olefin. It may also be that the aluminium compound removes PPh$_3$ more readily from [WCl$_4$(PPh$_3$)$_2$] than it does pyridine from [WCl$_4$(pyridine)$_2$].[91] Direct comparison of the effects of the two ligands is not really justified, however, because although the reactions for both ligands employed a W:ligand ratio of 1:1, they used different W:Al ratios. Furthermore, for W:Al ratios greater than those employed above, [WCl$_4$(pyridine)$_2$]–EtAlCl$_2$, as well as [WCl$_3${C$_2$H$_4$(PPh$_2$)$_2$}$_2$]–EtAlCl$_2$, are effective metathesis catalysts.[93]

Systems derived from high-valent molybdenum compounds are far less effective catalysts than those obtained from the tungsten analogues. For instance, [MoCl$_5$]–Et$_3$Al,[77] [Mo(acac)$_3$]–Et$_3$Al,[77] [MoCl$_5$]–Pr^{n}MgBr,[78] and [MoCl$_5$]–LiAlH$_4$[80] show very little or no activity, although the [MoCl$_4$]–AlBr$_3$[82] system has been claimed to be effective.

Catalytic activity for a number of molybdenum systems can be induced by treatment with nitric oxide prior to addition of an organoaluminium compound. This has been established in particular for [MoCl$_4$L$_2$] (L = PPh$_3$, C$_5$H$_5$N, or Pr^{n}CN), [C$_5$H$_5$Mo(CO)$_3$I], [MoCl$_3$(PhCO$_2$)$_2$], [MoO$_2$(acac)], [MoOCl$_3$], and [MoCl$_5$] in the presence of ligands such as C$_5$H$_5$N, Ph$_3$PO, Bu$^n_3$PO, and Oct$^n_3$PO.[35] The enhancement of activity is ably demonstrated by the [MoCl$_3$(PhCO$_2$)$_2$]–[Me$_3$Al$_2$Cl$_3$] system. Treatment of the molybdenum compound with nitric oxide for 0.5 h before the addition of the aluminium sesquichloride produces a catalyst which gives a 60% yield of oct-4-ene from pent-1-ene after 17 min. Without the NO treatment this catalyst effects only a 0.8% conversion of the pent-1-ene after 1 h.[24] Interaction with nitric oxide should yield molybdenum nitrosyl species, and, consistent with this, derivatives of the type [Mo(NO)$_2$L$_2$X$_2$] (X = Cl, Br, or I *etc.*; L = PPh$_3$, AsPh$_3$, Ph$_3$PO, C$_5$H$_5$N, or EtC$_5$H$_4$N, *etc.*) are highly effective catalysts in the presence of an organoaluminium halide.[35,94] These systems have been studied in some detail, and a number of significant features have been noted.[35] For instance, a wide range of Mo:Al ratios can be employed, but 1:4—5 gives highest activity. Further, the catalyst requires a preformation period to reach maximum activity, this being 1 h in the case of [Mo(NO)$_2$(C$_5$H$_5$N)$_2$Cl$_2$]–EtAlCl$_2$. During this period the two nitrosyl stretching vibrations associated with [Mo(NO)$_2$(C$_5$H$_5$N)$_2$Cl$_2$] shift to higher frequency and eventually disappear.[24,95] This is explained as initial complexation of two

---

[89] J.-L. Wang, M. Brown, and H. R. Menapace, Ger. Offen., 1972, 2 158 990 (*Chem. Abs.*, 1972, **77**, 125 933c).

[90] H. Knoche, Ger. Offen., 1970, 2 024 835 (*Chem. Abs.*, 1971, **74**, 44 118b).

[91] M. Kothari and J. J. Tazuma, *J. Org. Chem.*, 1971, 36, 2951.

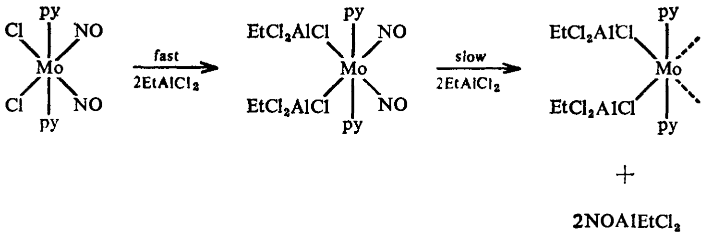
[92] R. E. McCarley and T. M. Brown, *Inorg. Chem.*, 1964, **3**, 1232.

[93] L. Bencze and L. Marko, *J. Organometallic Chem.*, 1971, **28**, 271.

[94] E. A. Zuech, Fr. P., 1969, 1 575 778 (*Chem. Abs.*, 1970, **72**, 999 882).

[95] W. B. Hughes, *J. Amer. Chem. Soc.*, 1970, **92**, 532.

equivalents of the organoaluminium reagent with the chlorides and a consequential increase in the NO stretching frequencies, followed by attack of two further equivalents of the organoaluminium compound on the oxygens of the nitrosyl groups, leading to the removal of these groups from the molybdenum,[24] as outlined in Scheme 3. In this scheme it is apparent that a function of the aluminium compound is to produce two adjacent vacant co-ordination sites.



Scheme 3

The catalytic activity of systems derived from compounds of the type [Mo$(NO)_2L_2X_2$] depends on the nature of L and of the anion X, an increase in activity being observed along the series $AsPh_3 < 4\text{-}EtC_5H_4N \simeq Ph_3PO$ and along the series I < Br < Cl.[24] It was therefore suggested that the neutral and anionic ligands are not removed from the metal in the formation of the actual catalytic intermediate. Tungsten derivatives $[W(NO)_2L_2X_2]$ also form active metathesis catalysts but their activity is not as high as that of the corresponding molybdenum systems.[35]

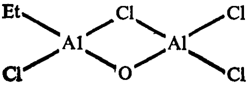
Carbon monoxide is also capable of increasing the activity of metathesis catalysts derived from Group VI metal halide complexes and organoaluminium compounds.[93] It has been found that $[WCl_4(C_5H_5N)_2]$–$EtAlCl_2$ under an atmosphere of carbon monoxide exhibits a very different catalytic activity from the same system under argon. The interaction of CO with $[WCl_4(C_5H_5N)_2]$–$EtAlCl_2$ gives tungsten carbonyl species, and this led to experiments demonstrating that $[W(CO)_3(PPh_3)_2Cl_2]$ in the presence of $EtAlCl_2$ is highly active in converting pent-2-ene into but-2-ene and hex-3-ene.[93] $[WCl_3\{C_2H_4(PPh_2)_2\}_2]$–$EtAlCl_2$ is also a metathesis catalyst, but excessive exposure to CO can destroy its activity,[93] owing to its conversion into $[W(CO)_6]$.[96]

Tungsten carbonyl derivatives $[W(CO)_5L]$ or $[W(CO)_4L_2]$ in the presence of $AlCl_3$ or $EtAlCl_2$ promote the metathesis reaction, provided that trace quantities of dioxygen are present.[97] It has been suggested that, in the presence of the tungsten complex, oxygen inserts into a carbon–aluminium bond in $[(EtAlCl_2)_2]$, and the resultant dimer then rearranges to give the species (5). This is believed to bond to the tungsten at a site originally occupied by a carbonyl group. A ten-fold excess of $EtAlCl_2$ was employed in these studies, however, and it is

---

[96] L. Bencze, *J. Organometallic Chem.*, 1972, 37, C37.

[97] L. Ramain and Y. Trambouze, *Compt. rend.*, 1971, **273**, *C*, 1409.



(5)

unlikely that all of the aluminium compound is associated with the tungsten, as must have been assumed in proposing this mechanism. The catalytic activity of $[W(PMe_2Ph)_4(N_2)_2]$–$EtAlCl_2$ is also increased in the presence of dioxygen[98] but this can be readily explained in terms of the creation of vacant or potentially vacant sites through the removal of dimethylphenylphosphine as its oxide. Dioxygen also affects the kind of product obtained from olefins and $[WCl_6]$–Et_3Al in chlorobenzene.[99]

Dioxygen does not appear to be necessary to activate metathesis catalysts derived from zero-valent halogenocarbonyl anions of molybdenum or tungsten, $[M(CO)_5X]^-$ (M = Mo or W; X = Cl or Br), and $MeAlCl_2$[36] or Grignard reagents[73] and from the related metal acyl species $[M(CO)_5(COR)]^-$ (M = Mo or W; R = Me or Ph) and alkylaluminium dichlorides or sesquichlorides.[100,101] The activity of these systems is far less than that of most of the catalytic systems described above. The order of reactivity found for the disproportionation of pent-1-ene by $MeAlCl_2$–$[M(CO)_5COR]^-$ was Mo > W and Ph > Me.[100] The dinuclear carbonyl anions $[(CO)_5M—M'(CO)_5]^{n-}$ (M = Mo or W; M′ = Mo, W, Mn, or Re; n = 1 or 2) and the metal carbene complexes $[W(CO)_5C(OMe)Et]$ and $[W(CO)_5C(NMe_2)Me]$ also form active metathesis catalysts with alkylaluminium chlorides, but only in the presence of an excess of chloride ions.[100,102] It is assumed that the function of the chloride is to produce $[M(CO)_5Cl]^-$.

Homogeneous catalysts derived from rhenium salts are very much less active than the molybdenum and tungsten species. For instance, 48 h are required for $[ReCl_5]$–$SnBu^n_4$ to convert pent-2-ene into its equilibrium mixture with but-2-ene and hex-3-ene.[103] Reactions employing $[ReCl_4(PPh_3)_2]$–$EtAlCl_2$ and $[ReOX_3(PPh_3)_2]$–$EtAlCl_2$ (X = Cl or Br) also require long reaction times.[104]

At least one transition metal from each Periodic Group has been shown to exhibit homogeneous catalytic activity in the presence of an appropriate co-catalyst. Systems reported include $[TiCl_4(C_5H_5N)_2]$–$EtAlCl_2$,[105,106] $[(C_5H_5)_2TiCl]$–$[Me_3Al_2Cl_3]$,[106] $[Zr(acac)_4]$–$[Me_3Al_2Cl_3]$,[105,106] $[NbCl_5]$–$[Me_3Al_2Cl_3]$ in the

---

[98] R. J. Haines, unpublished results.

[99] A. Uchida, K. Kobayashi, and S. Matsuda, *Ind. and Eng. Chem. (Product Res. and Development)*, 1972, **11**, 389.

[100] W. R. Kroll and G. Doyle, *Chem. Comm.*, 1971, 839.

[101] W. R. Kroll and G. Doyle, U.S. P., 1972, 3 689 433 (*Chem. Abs.*, 1972, **77**, 151 431g).

[102] W. R. Kroll and G. Doyle, *J. Catalysis*, 1972, **24**, 356.

[103] J. A. Moulijn and C. Boelhouwer, *Chem. Comm.*, 1971, 1170.

[104] E. T. Kittleman and E. A. Zuech, Fr. P., 1969, 1 561 025 (*Chem. Abs.*, 1970, **72**, 31 193f).

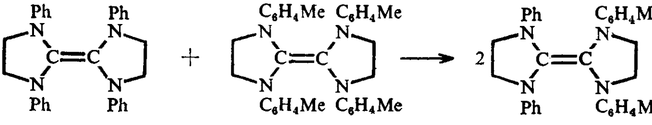
[105] D. H. Kubicek and E. A. Zuech, U.S. P., 1972, 3 670 043 (*Chem. Abs.*, 1972, **77**, 100 716w).

[106] W. B. Hughes, E A. Zuech, E. T. Kittleman, and D. H. Kubicek, 23rd I.U.P.A.C. Congress, Boston, 1971, Abstract 566.

presence of benzoic acid and nitric oxide,[107] [$\{Fe(NO)_2Cl\}_2$]–[$Me_3Al_2Cl_3$],[106,108] [$OsOCl_3(PPh_3)_2$]–[$Me_3Al_2Cl_3$],[106,108] [$CoCl_2$(4-vinylpyridine)$_2$]–[$Me_3Al_2Cl_3$],[106] [$\{Rh(NO)_2Cl\}_2$]–[$Me_3Al_2Cl_3$],[106,108] [$\{(C_3H_5)_2RhCl\}_2$]–[$Me_3Al_2Cl_3$],[106,108] [$Rh(NO)(PPh_3)_2Cl_2$]–[$Me_3Al_2Cl_3$],[106,108] [$Ir(NO)(PPh_3)_2Cl_2$]–[$Me_3Al_2Cl_3$],[106,107] $PdBr_2$–$EtAlCl_2$ in the presence of PPh_3,[109] [$Cu(PPh_3)_3Cl$]–[$Me_3Al_2Cl_3$],[106,110] [$Cu_2Cl_2(PPh_3)_2$]–$EtAlCl_2$,[111] [$Ag(PPh_3)Br$]–$EtAlCl_2$,[106,110] [$Au(PPh_3)Cl$]–[$Me_3Al_2Cl_3$],[106,110] $SmCl_3$–[$Me_3Al_2Cl_3$],[106,112] $ThCl_4$–[$Me_3Al_2Cl_3$],[106] and UCl_4–[$Me_3Al_2Cl_3$].[106] The activity of these systems is not as high as those derived from Group VI metal derivatives. For instance, the conversion of heptene was only 2.5% after 90 h at room temperature employing $SmCl_3$–[$Me_3Al_2Cl_3$] as catalyst and 0.2% after 2 h at 80 °C using [$Cu(PPh_3)_3Cl$]–[$Me_3Al_2Cl_3$] as the catalyst. The rhodium systems described above are fairly active as metathesis catalysts but, not surprisingly, they also effect rapid isomerization of the olefin.[108]

All of the systems described thus far require two components for catalytic activity. Lewandos and Pettit[113] have reported a transition-metal species which does not require the presence of a co-catalyst to promote olefin metathesis. They have shown that for a W:olefin ratio of *ca.* 1:4 and at a temperature of 98 °C, toluene tungsten tricarbonyl effects a 28% conversion of non-4-ene into oct-4-ene and dec-5-ene, in heptane as solvent, during 24 h. Metathesis was only observed when the reaction was carried out in a system where any liberated carbon monoxide could readily escape. No metathesis occurred in a closed system, or with large olefin:W ratios, or when an excess of toluene was added. On the basis of these results and electron-counting considerations,[114] they suggested that the actual catalyst is [$W(CO)_2$]. In view of the low activity of their catalyst under the experimental conditions employed, other possible mechanisms cannot be immediately discarded.

Rhodium(I) complexes in the absence of any co-catalyst effect the metathesis of electron-rich olefins.[115] Thus [$Rh(PPh_3)_2LCl$] (L = CO or PPh_3) catalyses the reaction of olefin (6) with olefin (7) to give (8), the yield of (8) approaching



(6) (7) (8)

---

[107] W. B. Hughes and E. A. Zuech, U.S. P., 1971, 3 562 178 (*Chem. Abs.*, 1971, **75**, 10 868b); U.S. P., 1972, 3 691 253 (*Chem. Abs.*, 1973, **78**, 3657r).

[108] W. B. Hughes and E. A. Zuech, U.S. P., 1971, 3 558 517 (*Chem. Abs.*, 1970, **72**, 99 985w).

[109] P. H. Phung and G. Lefebvre, Fr. P., 1970, 1 594 582 (*Chem. Abs.*, 1971, **74**, 87 316g).

[110] D. H. Kubicek and E. A. Zuech, U.S. P., 1971, 3 558 520 (*Chem. Abs.*, 1971, **74**, 99 441g).

[111] D. H. Kubicek and E. A. Zuech, U.S. P., 1972, 3 703 561 (*Chem. Abs.*, 1973, **78**, 71 378a).

[112] E. T. Kittleman and E. A. Zuech, U.S. P., 1971, 3 554 924 (*Chem. Abs.*, 1971, **74**, 99 440 f); U.S. P., 1973, 3 708 551 (*Chem. Abs.*, 1973, **78**, 71 382x).

[113] G. S. Lewandos and R. Pettit, *J. Amer. Chem. Soc.*, 1971, **93**, 7087.

[114] G. S. Lewandos and R. Pettit, *Tetrahedron Letters*, 1971, 789.

[115] D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1972, 927.

the statistical value after 2 h in xylene at 140 °C. A mechanism involving a four-membered metallocycle as transition state has been proposed, but whether this can be applied generally to reactions involving normal olefins remains an open question.

One other system, *viz.* $[WOCl_4]$, has been reported to catalyse olefin metathesis in the absence of a co-catalyst, but its activity is exceptionally low.[84]

The determination of the nature of the catalytic site for olefin metathesis is difficult. In most cases the catalyst is generated by interaction of a transition-metal compound with an organometallic species, and a wide range of products are possible. The catalyst may only be present in solution in low concentration. However, molybdenum and tungsten species form the most effective catalysts, a co-catalyst capable of bonding to the molybdenum or tungsten through halogen, alkyl, or hydride bridges being required. Thus, for $[WCl_6]$–$EtAlCl_2$–EtOH, the catalyst is claimed to be a complex of the transition metal with an aluminium compound, with two tungsten–carbon bonds,[116] and transition metal–aluminium complexes are formed by Ziegler–Natta catalysts. It is possible that more than one oxidation state is capable of promoting metathesis, but +II is most likely for Mo and W. In any case it is possible to over-reduce the catalyst, so that oxidation states greater than zero seem likely.

C. Catalytic Selectivity.—The catalysts employed in olefin metathesis can also promote other types of reaction, including olefin isomerization, olefin oligomerization/polymerization, and, in the case of homogeneous systems, alkylation of aromatic solvents.

Double-bond migration is readily effected by supported metal oxide metathesis catalysts. This explains why Banks and Bailey observed the formation of a large number of unsaturated hydrocarbons in their original studies on but-1-ene, pent-1-ene, and hex-1-ene.[1] It can be minimized by poisoning of the isomerization sites on the heterogeneous system with alkali-metal, alkaline-earth, or thallium(I) ions.[4,117,118] These presumably reduce surface acidity and inhibit isomerization occurring by a cationic mechanism.[117] The effectiveness increases along the series Na < K < Rb ~ Tl^I < Cs, which is the order of the ionic radii.[117] In some chemical processes, for instance the formation of detergent-range olefins from propylene, double-bond isomerization activity is essential. Magnesium oxide is a very selective catalyst for double-bond migration and has been employed in conjunction with metathesis catalysts for obtaining mixtures containing a wide range of olefins.[119]

Isomerization has also been observed for most homogeneous catalytic systems. For instance, the metathesis of oct-1-ene by $[Mo(NO)_2(PPh_3)_2Cl_2]$–$EtAlCl_2$ at ambient temperature affords, after 16 h, a mixture of all olefins from ethylene to pentadecene, and not just ethylene and tetradecene as expected.[35] Olefin isomeri-

---

[116] H. Hoecker and F. R. Jones, *Makromol. Chem.*, 1972, **161**, 251.

[117] T. P. Kobylinski and H. E. Swift, *J. Catalysis*, 1972, **26**, 416.

[118] Shell Internationale Research Maatschaapij N.V., Dutch P., 1967, 6 607 427 (*Chem. Abs.*, 1968, **69**, 43 389a).

[119] R. L. Banks and J. R. Kenton, Belg. P., 1968, 713 190.

zation is generally considerably slower than olefin metathesis, and can be minimized in metathesis reactions by performing the latter at low temperatures and for short periods. Thus little isomerization of pent-1-ene or oct-1-ene by $[Mo(NO)_2(PPh_3)_2Cl_2]$–$EtAlCl_2$ is observed after 1 hour at 0—5 °C.[35] Terminal olefins are isomerized more readily by metathesis catalysts than internal olefins. For example, whereas only but-2-ene, pent-2-ene, hex-3-ene, and ethylene are found in the reaction mixture obtained by metathesis of pent-2-ene by $[ReCl_5]$–$AlEt_3$–O_2, all olefins from ethylene to octene are formed in the corresponding metathesis of pent-1-ene.[77] The extent of isomerization also depends on the non-transition-metal component of the catalyst. The catalytic system $[Mo(NO)_2(PPh_3)_2Cl_2]$–$EtAlCl_2$ promotes isomerization more readily than $[Mo(NO)_2(PPh_3)_2Cl_2]$–$[Me_3Al_2Cl_3]$, suggesting that for these systems isomerization is effected by a cationic mechanism, as found for heterogeneous catalysts.[35]

Oligomerization and/or polymerization of olefins has been reported for a number of homogeneous metathesis catalysts. Although definite attempts have not been made to identify the oligomers in the various reactions nor to establish the nature of the oligomerizations, it has been ascertained that the so-called oligomers formed on metathesis of pent-1-ene by $[WCl_6]$–Et_3Al or $[MoCl_5]$–Et_3Al in chlorobenzene are not alkylated products of the solvent.[77] Further, the small amounts of branched olefins formed in the disproportionation of pent-1-ene by $[Mo(NO)_2(PPh_3)_2Cl_2]$–$[Me_3Al_2Cl_3]$ can only be explained by some dimerization process.[35] Terminal olefins are oligomerized far more readily than internal olefins, as demonstrated by some reactions involving $[WOCl_4]$–$EtAlCl_2$ as catalyst.[84] Whereas oligomers in yields of 50 and 30%, respectively, were produced on metathesis of propylene and pent-1-ene employing this catalytic system, only disproportionation products were observed in the corresponding reactions involving pent-2-ene and hept-3-ene. These results are not particularly surprising when one considers that the metathesis catalysts are Ziegler–Natta in type. The oligomerization behaviour of $[WCl_6]$–Et_3Al, $[MoCl_5]$–Et_3Al, or $[ReCl_5]$–Et_3Al is destroyed by addition of an excess of Et_3Al or PPh_3.[77] In fact, it has been found that the oligomerization behaviour of $[WCl_6]$–Et_3Al towards oct-1-ene in benzene increases rapidly as the W:Al ratio is varied from 0.25 to 1.0 whereas the disproportionation activity decreases.[99] These results suggest that the oligomerization is effected by a species of higher oxidation state than is active in the metathesis; a carbonium-ion process participating in oligomerization was eliminated because alkylbenzenes were not detected in the reaction of $[WCl_6]$–Et_3Al with oct-1-ene in benzene.[99]

Heterogeneous catalytic systems for metathesis also readily promote the oligomerization of olefins, as demonstrated by the reaction of CoO–MoO_3–Al_2O_3 with but-1-ene.[4] Over 80% of the octenes formed in this metathesis reaction are branched, and this can only be attributed to dimerization of the butenes present in solution. A cationic polymerization mechanism[120] has been proposed to account for this dimerization, and, consistent with this proposal, it is found that

---

[120] C. E. H. Bawn, *Proc. Chem. Soc.*, 1962, 165.

the oligomerization process can be eliminated by poisoning of the acid sites with sodium carbonate.[4] Addition of fluoride ions to oxide catalysts of molybdenum or rhenium also inhibits oligomerization.[121]

A side-reaction often encountered when aromatic solvents are employed in metathesis reactions utilizing homogeneous catalysts is the Friedel–Crafts alkylation of the solvent by the olefin. The mixture [WCl_6]–$EtAlCl_2$ is a particularly effective alkylation catalyst under certain conditions. Thus, addition of pent-2-ene to a premixed solution of [WCl_6] and $EtAlCl_2$ in toluene results in the almost exclusive alkylation of the solvent, and di- as well as mono-pentyltoluenes are formed.[91] On the other hand, however, if the [WCl_6]–$EtAlCl_2$ catalyst is prepared in the presence of the pent-2-ene, rapid metathesis occurs.[91] The tungsten species [WCl_6] promotes the Friedel–Crafts alkylation of benzene with propylene in the absence of any $EtAlCl_2$, although at temperatures up to 150 °C (much higher than those for [WCl_6]–$EtAlCl_2$). It has been suggested that the actual catalyst in the [WCl_6]–$EtAlCl_2$ system is a derivative containing the highly active Friedel–Crafts catalyst $AlCl_3$, formed by the reaction of [WCl_6] with $EtAlCl_2$, co-ordinated to a reduced tungsten species.[91,122] On this basis, it would be expected that [WCl_6]–Et_3Al would be a less effective alkylation catalyst than [WCl_6]–$EtAlCl_2$ under comparable conditions, and this is found to be the case for both terminal and internal olefins.[76,99,123] In fact, in the complete absence of water or dioxygen, [WCl_6]–Et_3Al does not effect the alkylation of benzene with oct-1-ene.[99] The inability of [WCl_6]–$LiAlH_4$ to promote alkylation of aromatic solvents is further indirect evidence for the suggested intermediate.[80] Addition of pyridine and triphenylphosphine to [WCl_6]–$EtAlCl_2$ has been shown to inhibit the alkylation without completely curtailing the metathesis reaction.[91] Like [WCl_6], [$MoCl_5$] and [$ReCl_5$] also promote the alkylation of aromatic solvents by olefins,[122,124] but in the presence of $SnBu^n_4$ the [$ReCl_5$] loses its alkylating ability while remaining an effective metathesis catalyst.[103]

4 The Mechanism of the Olefin Metathesis Reaction

No single mechanism has been suggested to explain all olefin metathesis reactions and, indeed, it may proceed by more than one mechanism. Nor is it necessary that the reaction route should be the same for both homogeneous and heterogeneous reactions. It is apparent that even different homogeneous catalysts use different mechanisms. A satisfactory mechanism should be extendable to heterogeneous alkyne metathesis, which occurs in conditions very similar to those which promote olefin metathesis.[48,49]

We first consider the general experimental evidence upon which the mechanisms must be based.

A. Factors to be Considered in Proposing a Mechanism.—(*i*) *The Olefins*. The

---

[121] R. Arganbright, U.S. P., 1972, 3 697 613.

[122] J. R. Graham and L. H. Slaugh, *Tetrahedron Letters*, 1971, 787.

[123] A. Uchida, Y. Hamano, Y. Mukai, and S. Matsuda, *Ind. and Eng. Chem. (Product Res. and Development)*, 1971, **10**, 372.

[124] J. Tsuji, T. Nogi, and M. Morikawa, *Bull. Chem. Soc. Japan*, 1966, **39**, 714.

metathesis of [2-^{14}C]propene over a heterogeneous catalyst of rhenium oxide on alumina yields an ethylene sample free of ^{14}C.[125]

$$2C_3H_6 \rightleftharpoons C_2H_4 + CH_3CH{=}CHCH_3 \text{ (\textit{cis}- and \textit{trans}-isomers)}$$

This excludes a linear mechanism, *e.g.* reaction (3).

$$2C{=}\overset{*}{C}{-}C \rightarrow [C{-}\overset{*}{C}{-}C{-}C{-}\overset{*}{C}{-}C] \rightarrow C{=}\overset{*}{C} + C{-}C{=}\overset{*}{C}{-}C \qquad (3)$$

On this same catalyst, methyl groups retain their integrity throughout the reaction,[126,127] as shown by experiments with [1-^{14}C]propene and [2-^{14}C]propene. This precludes hydrogen transfer from olefin to metal and back again, and hence π-allylic intermediates. Similar studies over a cobalt molybdate–alumina catalyst yielded essentially the same results, but above 60 °C isomerization of the propene occurs,[127] and then an allylic intermediate cannot be excluded. An investigation of the homogeneous metathesis of deuteriated butenes also showed that hydrogen transfer to the metal does not occur, because no H–D exchange was observed.[5,10] This is also consistent with the results from the heterogeneous metathesis of ethylene and 2,3-dimethylbut-2-ene,[128] which show that if hydrogen does migrate to the metal it must always return to the carbon atom from which it came. This is unlikely. The observations cited are generally consistent with a transition state in which the four carbon atoms involved in the bond switching are equivalent. To account for this, Bradshaw *et al.*[4] proposed a 'quasi-cyclobutane' picture of the transition state, which has since been adopted by others.[129–131] An alternative model, which uses the same equivalence concept, pictures the four carbon atoms in the transition state as bound to a single metal ion essentially as methylene fragments.[113,114]

Kinetic studies of the classical type have done little to clarify the mechanism, because they are very difficult, and the results from different systems often conflict. Various attempts have been made to rationalize the rates of metathesis of propylene over a CoO–MoO$_3$–Al$_2$O$_3$ catalyst in the temperature range 120—200 °C. The rates are consistent with a two-site mechanism, with an activation energy of about 8 kcal mol^{-1}.[132] The rates of olefin metathesis over the homogeneous catalysts derived from molybdenum(II) dinitrosyls and alkylaluminium halides have been measured.[95] At low olefin:catalyst ratios the order of reaction with respect to olefin was found to be greater than unity, but it fell towards unity as the olefin concentration was increased. The order of reaction with respect to

---

[125] J. C. Mol, J. A. Moulijn, and C. Boelhouwer, *Chem. Comm.*, 1968, 633; *J. Catalysis*, 1968, **11**, 87.

[126] F. L. Woody, M. J. Lewis, and G. B. Wills, *J. Catalysis*, 1969, **14**, 389.

[127] A. Clark and C. Cook, *J. Catalysis*, 1969, **15**, 420.

[128] D. L. Crain, *J. Catalysis*, 1969, **13**, 110.

[129] E. A. Zuech, *Chem. Comm.*, 1968, 1182.

[130] C. T. Adams and S. G. Brandenberger, *J. Catalysis*, 1969, **13**, 360.

[131] R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss Faraday Soc.*, 1969, No. 47, p. 71.

[132] M. J. Lewis and G. B. Wills, *J. Catalysis*, 1969, **15**, 140; R. C. Luckner, G. E. McConocie, and G. B. Wills, *ibid.*, 1973, **28**, 63; A. J. Moffat and A. Clark, *ibid.*, 1970, **17**, 264.

catalyst could not be determined. The results are consistent with rapid complexing and decomplexing of the olefin, the metathesis step being rate-determining. The activation energy for the process was found to be *ca.* 7 kcal mol^{-1}, which is low, as expected for a reaction that is basically athermal and entropy-controlled.[95]

The stereochemistry of metathesis over the same homogeneous metal nitrosyl–aluminium alkyl catalysts has also been studied.[133] At equilibrium of the metathesis of pent-2-ene to but-2-ene and hex-3-ene the *cis* and *trans* pairs of each olefin are in thermodynamic equilibrium, but in the early stages of the reaction the isomer ratios depend upon the starting pent-2-ene. Thus, *cis*-pent-2-ene yields, preferentially, *cis*-but-2-ene and *cis*-hex-3-ene, and *trans*-pent-2-ene yields, preferentially, the corresponding *trans*-isomers. The rates of isomerization and metathesis appear to be related, and the observations are explicable in terms of two olefin molecules bound *cis* to molybdenum, with their axes parallel, and undergoing metathesis *via* the 'cyclobutane' transition state.[133]

The isomer ratios from pent-2-ene in contact with [WCl_6]–$EtAlCl_2$ and ethanol (1:4:1) in a homogeneous system are in sharp contrast.[10] Substantial amounts of *cis*- and *trans*-hex-3-ene are formed at the outset (*i.e.* after about 20 seconds at room temperature) regardless of which isomer of pent-2-ene is used, but *cis*-isomers are present in slightly more than equilibrium proportions initially. The residual pent-2-ene was also observed to approach slowly its equilibrium isomer content. These results are consistent with a random transalkylidenation coupled with a minimum of steric control.[10,71]

It has also been inferred that the overall mechanism of the reaction over homogeneous tungsten catalysts is different from that over molybdenum nitrosyl derivatives. Thus, investigation of cyclo-octene polymerizations shows that high-molecular-weight polymers are formed during the early stages of the reaction, and this is unexpected if olefin exchange is more rapid than metathesis[20] because otherwise the high-molecular-weight polymers would form more slowly.

The explanation for these divergences may lie in the different structures of the catalysts. The generalizations above, complex as they are, may nevertheless be an oversimplification. Many of the reactions are accompanied by isomerization, even though this is generally a slower reaction. More interesting, ethylene over a heterogeneous molybdenum–alumina catalyst at 210 °C in a static reactor, rather than in the more usual flow systems, gives propene, butene, small amounts of hexenes and heptenes, and, as the major product, pentenes.[134] The initial reaction would seem to be a reaction of ethylene to form propene, possibly *via* formation of methylene (carbene) and thence trimethylene (cyclopropane). However, a concerted reaction, such as depicted below, cannot be excluded. Reactions

$$3C_2 \rightleftharpoons 2C_3$$

producing compounds with an odd number of carbon atoms have also been

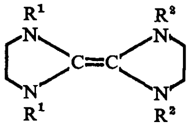
---

[133] W. B. Hughes, *Chem. Comm.*, 1969, 431.
[134] P. P. O'Neill and J. J. Rooney, *J. Amer. Chem. Soc.*, 1972, **94**, 4383.

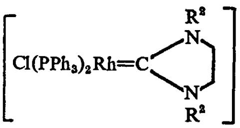
observed in homogeneous systems,[135] but these could arise by isomerization followed by metathesis.

Molybdenum hexacarbonyl–alumina catalysts also catalyse the conversion of ethylene into cyclopropane and methylcyclopropane, although the reaction temperature (140 °C) is much lower.[1] Cyclopropane itself rearranges to propene under very mild conditions, so that a common route for all these reactions seems possible. Further, olefins are converted quantitatively into the corresponding cyclopropanes by the action of carbene (derived from CH_2N_2) under the action of palladous salts.[136] All this lends credence to the idea that carbenes and olefins may exist together on an appropriate metathesis catalyst.

The metathesis reaction, whether homogeneous or heterogeneous, is rapid, isothermal, and entropy-controlled. The activation energy is less than 10 kcal mol^{-1}. This makes the formation of free carbenes unlikely, but, at least where electron-rich olefins are involved, carbene-containing products have actually been isolated. Thus in the homogeneous metathesis of (9), catalysed by $[RhCl(PPh_3)_3]$, (10) has been identified as an intermediate.[22,115] It is not clear whether intermediates of this kind form in the general case, since the olefins involved are atypical.



(9)



(10)

(*ii*) *The Catalysts.* There would seem to be no easy classification of the catalysts for either homogeneous or heterogeneous metathesis. The heterogeneous catalysts are generally compounds of molybdenum or tungsten, often supported on alumina,[54] and they are not well-defined compounds.

The homogeneous catalysts* are generally derived from high-oxidation-state halides and a reducing agent, generally a metal alkyl, such as ethylaluminium dichloride.[5,20,123] Although the proportion of the second metal to the primary metal can affect activity, and even the kind of products, neither the alkyl nor the second metal is necessary in every case; tungsten and $[(\pi\text{-}CH_3C_6H_5)W(CO)_3]$ gives rise to a catalyst by loss of carbon monoxide and toluene.[113] In the system $[WCl_3(Ph_2PCH_2CH_2PPh_2)_2]\text{–}EtAlCl_2$, carbon monoxide actually stimulates the catalyst.[93] The alkyl-metal compound apparently reduces the tungsten halide. It has not yet been unequivocally demonstrated which oxidation state(s) of tungsten are responsible for the catalysis. It is believed that the catalytic species derived from $[(PPh_3)_2Mo(NO)_2Cl_2]$ and organoaluminium halide contains molyb-

* Note added in proof: it has been suggested that the $[WCl_6]$–metal alkyl system may give rise to catalyst systems that are wholly heterogeneous; unequivocal proof would seem difficult (E. L. Muetterties and M. A. Busch, *J.C.S. Chem. Comm.*, 1974, 754).

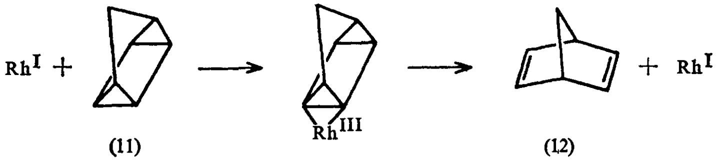
[135] K. Hummel and W. Ast, *Naturwiss.*, 1970, **57**, 245.

[136] R. Paulisson, A. J. Hubert, and P. Teyssié, *Tetrahedron Letters*, 1972, 1465.

denum(o).[35,95] In one case[66] '$Mo(CO)_4$' has been suggested as the active entity, although potentially oxidizing halogenated olefins stimulate reactivity.[69] Later, the complete loss of CO from $[Mo(CO)_6]$ was postulated in catalyst formation.[67] In another homogeneous system, a tungsten dicarbonyl fragment has been inferred as the catalyst.[113] This suggests a d^6 configuration for the transition metal, although substitution reactions at octahedral low-spin d^6-metal ions are usually slow. It is unlikely, however, that catalytic systems produced by reducing, say, $[WCl_6]$, contain W^0, and oxidation to above W^0 is required for the preparation of some of the others. Thus $[W(CO)_5(PPh_3)]$–$EtAlCl_2$[97] requires dioxygen for catalytic activity, $[WCl_6]$–$EtAlCl_2$–EtOH presumably contains tungsten in an oxidation state of at least +III,[10] and there is also the range of various tungsten halide–aluminium halide mixtures, and the majority of the heterogeneous catalysts derived from metal oxides on supports such as alumina. The catalyst for the dismutation of electron-rich olefins contains rhodium(I) or rhodium(III).[115]

In summary, although active catalytic species may be derived from Mo^0 or W^0 (d^6) in some systems, the majority probably have fewer d-electrons and higher oxidation states.

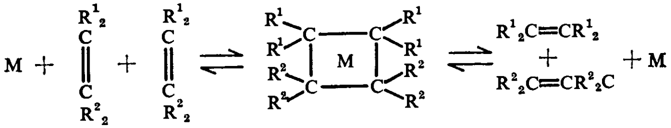
(*iii*) *The Transition State.* The synchronous making and breaking of double bonds as apparently required by the experimental evidence is thermally forbidden according to the Woodward–Hoffmann rules.[3] The transition-metal catalyst makes the reaction possible, and in the absence of such a catalyst the reaction occurs only at *ca.* 725 °C.[2] It is therefore of great theoretical interest to identify the transition state. Before considering the three current models it is worthwhile making two reservations. The first is that no mechanism yet proposed offers any role to the metal alkyl (or comparable reagent) other than that of a reducing agent or of a modifier of the base behaviour of the transition metal. Two of the models, which may apply only to specific systems, do not require a second metal compound at all. In the general case, a polynuclear metal catalysis has not been considered although the formation of compounds with halogen or hydrogen bridges between, say, tungsten and aluminium is very probable. The second reservation is that apparently synchronous transitions may be step-wise. Thus, the thermally forbidden conversion of quadricyclene (11) into norbornadiene (12) is catalysed by $[Rh_2(CO)_4Cl_2]$. The conversion involves oxidative addition of Rh^I to the quadricyclene, which is rate-determining, and the thermally forbidden



(11)
(12)

reaction is thus made possible.[137,138] The olefin metathesis reaction could be facilitated similarly.

However, if we assume synchronous bond-making and bond-breaking, a possible transition state is (13), the 'quasi-cyclobutane' transition state.[4]



(13)

It should be emphasized that the fact that synchronous transformations of this kind are forbidden by the Woodward–Hoffmann rules simply means that they have excessively high activation energies for normal thermal activation. How a transition-metal ion might facilitate such forbidden reactions is discussed in the next section.

The cyclobutane transition state cannot represent the whole picture, because under heterogeneous conditions even-chain olefins can undergo reactions that produce odd-chain products.[134] These products could arise by isomerization, *e.g.* by but-1-ene isomerizing to but-2-ene, which then undergoes metathesis with more but-1-ene to produce propene. However, the conversion of ethylene into propene must involve the complete fission of an ethylene molecule. Diazomethane decomposes, apparently at the sites on a heterogeneous catalyst that also catalyse the metathesis reaction, to yield dinitrogen and ethylene, and the latter presumably arises by dimerization of carbene.[139] Thus, carbene is implicated to some degree in metathesis reactions involving ethylene, and carbene complexes can generate metathesis catalysts.[100]

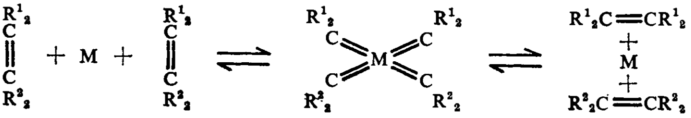
The heat of formation of two molecules of ethylene is very similar to that of cyclobutane. One would therefore expect at least some cyclobutane to be produced from ethylene and a heterogeneous metathesis catalyst, but the conversion over a heterogeneous oxide-based catalyst is less than 0.1%. Conversely, the yield of ethylene from cyclobutane over the same catalyst is only 3%. These results suggest that cyclobutane is not involved in the transition state,[114] though one can make the reservation that 'quasi-cyclobutane' is in a condition far removed from that of cyclobutane.[131]

For these reasons, an alternative mechanism involving the breaking of both σ- and π-components of the carbon–carbon double bond of the olefin has been proposed.[113,114] The transition state (14) is best described as four methylene fragments bonded to a single transition-metal ion, the carbon atoms remaining sp^3 hybridized.

Evidence from homogeneous systems supports this interpretation,[113] for example $[(\pi\text{-CH}_3\text{C}_6\text{H}_5)\text{W(CO)}_3]$ is a metathesis catalyst for non-4-ene in heptane

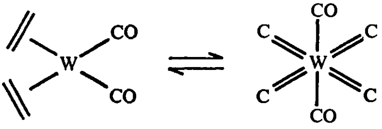
---

[137] H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, 1967, **89**, 2486.
[138] L. Cassar and J. Halpern, *Chem. Comm.*, 1970, 1082.
[139] P. P. O'Neill and J. J. Rooney, *J.C.S. Chem. Comm.*, 1972, 104.



(14)

at 98 °C when the system is open, but not when carbon monoxide is kept in the system. In these latter circumstances isomerization occurs. A large excess of olefin also suppresses metathesis relative to isomerization. An excess of toluene inhibits both reactions of the olefin. These data are consistent with a species [(olefin)$_2$W(CO)$_2$] being involved. The conversion of (15) into (16) involves a change in the number of electrons in the valence shell of tungsten from 14 to 18, and (16) thus obeys the inert-gas rule.



(15) (16)

For a corresponding alkyne metathesis, the analogue of (15) should only possess 10 electrons, which seems rather unlikely, but compounds are known in which $\equiv$CR groups are bonded to transition-metal ions, *e.g.* [M(CR)X(CO)$_4$] (M = Cr, Mo, or W; R = Me or Ph; X = Cl, Br, or I).[140]

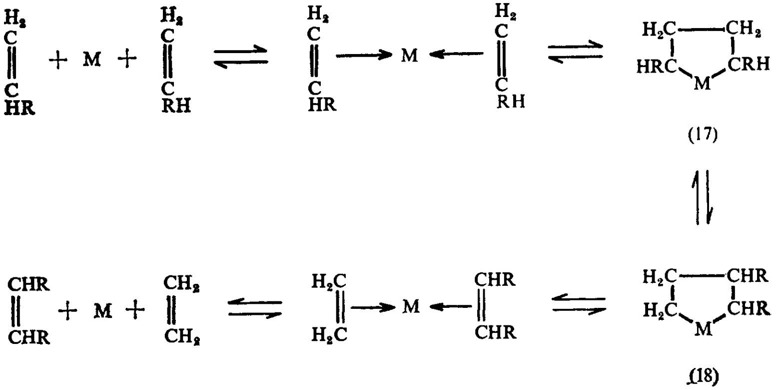
Although the evidence for the tetramethyl intermediate in these particular circumstances is convincing, the system may not be typical. Reaction temperatures are high ($\sim$100 °C), whereas homogeneous metathesis catalysis usually occurs at *ca.* 25 °C, and the reaction is inhibited by an excess of olefin. Generally, very high olefin:transition metal ratios are used (*ca.* 500:1), but in the tetramethylene system the proportions used are comparable.

A third mechanism has been suggested, stimulated by the observations that [WCl$_6$]–alkyl-lithium is most active for metathesis with a tungsten:lithium ratio of 1:2 and that rhodium-catalysed carbocyclic ring rearrangements proceed *via* metal–carbon σ-bonded intermediates.[141] A conceivable pathway is that shown in Scheme 4. To establish the feasibility of this scheme, the reaction of [WCl$_6$] with 1,4-dilithiobutane in benzene was investigated, and it was found to yield ethylene quantitatively, presumably from the breakdown of an intermediate (19) [*cf.* (17) and (18) in Scheme 4]. Experiments with deuteriated dilithiobutane, 1,4-dilithio-2,3-dideuteriobutane, produced ethylenes in the proportions

---

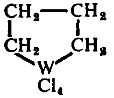
[140] E. O. Fischer, G. Kreis, C. G. Kreiter, J. Muller, G. Huttner, and H. Lorenz, *Angew. Chem. Internat. Edn.*, 1973, **12**, 564.

[141] R. H. Grubbs and T. K. Brunck, *J. Amer. Chem. Soc.*, 1972, **94**, 2538.



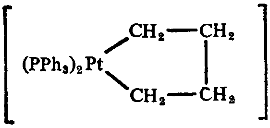
Scheme 4

$C_2H_2D_2 : C_2H_3D : C_2H_4$ = 6:88:6. Hence rearrangements or methathesis definitely occur, and subsequent experiments proved that there is stereoselectivity.



(19)

This work is only in its preliminary stages, and leaves several questions unanswered. There appears to be no reason why the transformation (17) → (18) occurs, or why it should be rapid. A subsequent paper, which describes the synthesis and structure of the complex (20), proposes two possible mechanisms,



(20)

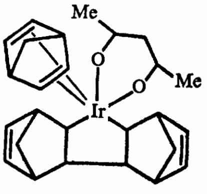
but without any supporting evidence.[142] The metallocycles of type (17) are not normally formed by ethylene,* but tetrafluoroethylene readily does so, and norbornadiene and [Ir(CO)Cl(PPh$_3$)$_2$] yield a stable complex containing a

---

* Note added in proof: there is persuasive evidence that ethylene can form such a metallocycle in a titanium complex (J. X. McDermott and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, 96, 947).

[142] C. G. Biefeld, H. A. Eick, and R. H. Grubbs, *Inorg. Chem.*, 1973, **12**, 2166.

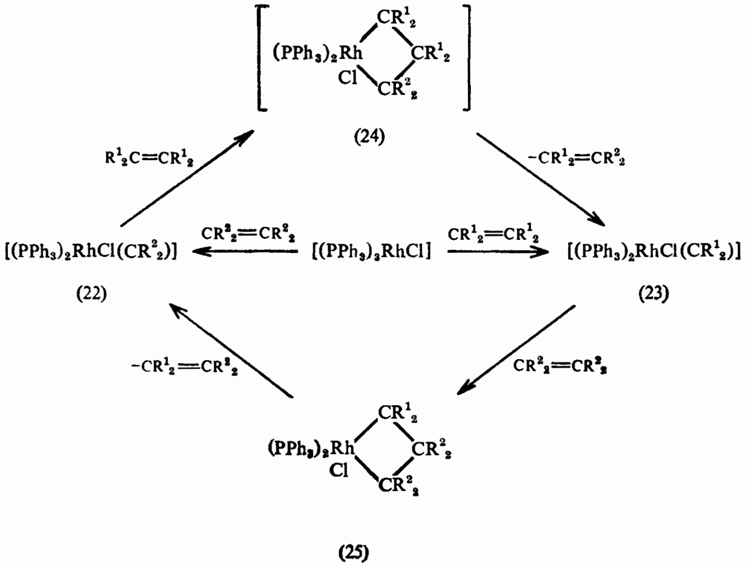
metallocycle, which, with acetylacetone, yields the compound (21).[143] Thus the identity of the five-membered metallocycle with the metathesis transition-state



(21)

is open to doubt. Thirdly, it is not yet proven that metal–hydrogen bond formation is not involved in the transformation (17) → (18), whereas experiments in other systems have excluded this route. Fourthly, the deuteriated ethylenes are not formed in the equilibrium proportions typical of the metathesis reaction. In addition, the conversion of ethylene into propylene and cyclopropane is not immediately explicable on this model. Finally, it does not explain why butadiene should be a poison for metathesis, nor how alkyne metathesis might occur. However, the transition state does overcome the activation-energy objections to synchronous mechanisms, as do the two other mechanisms so far discussed.

The most recently proposed mechanism[115] has already been mentioned, and is shown in Scheme 5. The carbene complexes (22) and (23) have been isolated,



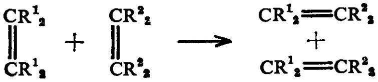
Scheme 5

---

[143] A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1973, **95**, 597.

and the metathesis has been found to take place in boiling xylene, but only when $:CR_2^1$ and $:CR_2^2$ are derived from electron-rich olefins. Although the evidence for the mechanism proposed in this particular case is compelling, it is unclear how far it can be extended to olefin metathesis reactions in general.

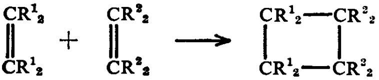
B. Theories of Catalysis.—These will be discussed in order, from the simplest to the most complete. The basic problem can be grasped by considering the rearrangement of molecular orbitals involved in the overall transition (Scheme 6).



$$CR^1_2{=}CR^1_2 + CR^2_2{=}CR^2_2 \longrightarrow CR^1_2{=}CR^2_2 + CR^1_2{=}CR^2_2$$

Scheme 6

If a cyclobutane intermediate is involved, then the transformation can be represented as the sum of two individual steps, *viz.* Scheme 7 and its converse. Considering only the *p*-orbitals involved in double-bond formation in the two ethylenes, then the two diagrams for correlation of orbitals and states shown in Figure 1 may be drawn. From either of these it is evident that the transformation



Scheme 7

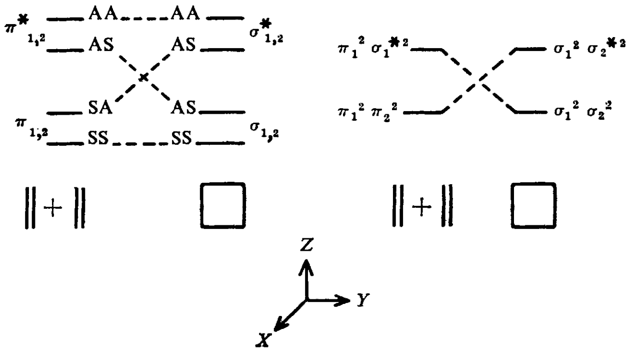
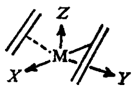


Figure 1

of the ground state of two ethylene molecules into a ground-state cyclobutane in the absence of catalyst involves the transfer of electrons from one orbital to another, a process which requires a high activation energy so that, in Woodward and Hoffmann's terms, the thermally activated process is symmetry-forbidden. The catalysis has been rationalized as follows.[144] The two olefin molecules form a complex with a transition metal, with symmetry properties as indicated in (26). The simple correlation diagrams of Figure 1 must then be redrawn to include transformations of the metal orbitals, and particularly the *d*-orbitals. The orbital-correlation diagram is now as shown in Figure 2. A ground-state reaction path from cyclobutane to the bis-(olefin) complex is now available, provided that the transition-metal ion has between 2 and 8 *d*-electrons, and this is consistent with experiment. In theory, too, a path exists for a non-transition-metal catalyst with only 2 available electrons, in an orbital that is not a *d*-orbital but of the appropriate symmetry, and such catalysts, *e.g.* potassium in graphite, are known.[145]



(26)

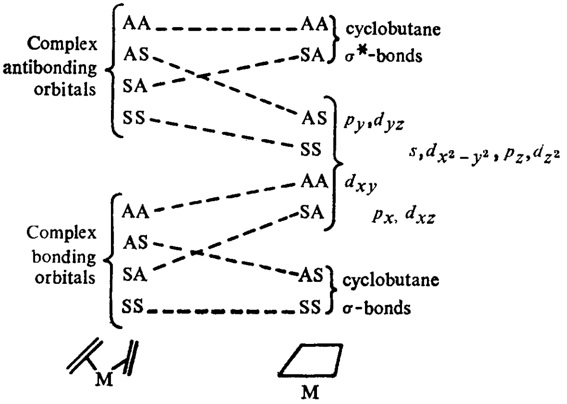


Figure 2

The tetramethylene model has received a similar treatment.[114] In this case, the metal–tetramethylene complex has a set of molecular orbitals built up from sp^3 carbon hybrid orbitals and the appropriate metal orbitals. The orbital-correlation

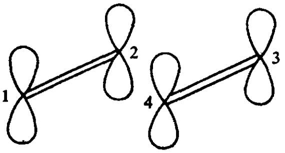
---

[144] The most recent discussion is by: F. D. Mango and J. H. Schachtschneider in 'Transition Metals in Homogeneous Catalysis', ed. G. N. Schrauzer, Marcel Dekker, New York, 1971, p. 223. See also F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, 1967, **89**, 2484.

[145] F. B. Carleton, personal communication.

diagram provides a ground-state pathway, and the metal apparently contributes 6 electrons to the bonding scheme. It will be recalled that the experimental data from which the tetramethylene model was developed were derived from a system containing tungsten(o) (d^6).[114]

The function of the metal in a quasi-cyclobutane intermediate has been described[144] as follows. The metal injects an initially non-bonding pair of *d*-electrons into a carbon–carbon antibonding orbital combination, such that bonding between C-1 and C-2 (and C-3 and C-4) is weakened [see (27)], but, as a consequence of the nodal pattern of this combination, bonding between C-2 and C-3 (and C-4 and C-1) is strengthened. At the same time, the metal withdraws an electron pair from an orbital bonding between C-1 and C-2 (and C-3 and C-4). Considerations of this kind suggest that a d^2 ion should be a better catalyst than ions with more *d*-electrons.



(27)

The metallocycle model has also been discussed in these terms.[144] Three paths for the rearrangement have been suggested, the asterisks being used in Figure 3 to denote the identities of the individual carbon atoms.

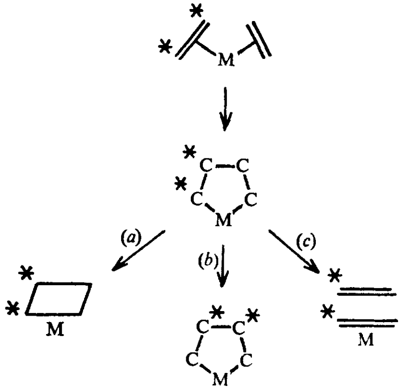
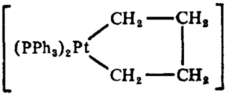


Figure 3

Pathway (*a*) involves reversible insertion of the metal into a cyclobutane ring, maintaining the cyclobutane–metal bond at all times, since cyclobutane is never evolved. This is not considered likely.* Pathway (*b*) is similarly not likely because it implies metal–carbon interactions across the ring, and these cannot be strong if the ring is planar. However, in (28) the ring is far from planar.[142] Pathway (*c*) apparently suffers from further symmetry restrictions, which a d^2 metal could not overcome because it would become d^0 in the metallocycle. Since a tetramethylene intermediate is considered improbable on activation-energy grounds, then all these theoretical discussions suggest the quasi-cyclobutane model as the only reasonable one.[144]



(28)

This kind of approach has been criticized on the grounds that orbital-correlation diagrams are not adequate, and that state-correlation diagrams should be used.[146] It is claimed that the 'allowed–forbidden' problem is quite distinct from another, which is that the activation energy is normally too high in reactions such as the metathesis reaction, for steric reasons. The lowering of the activation energy by transition-metal catalysis for certain 'forbidden' reactions may be as great as 15 kcal mol^{-1} for some d^{10} and d^8 systems (*e.g.* Ag$^{\text{I}}$ and Rh$^{\text{I}}$). A proper consideration of the state-correlation diagram for the olefin metathesis reaction shows that all the states of the bis(olefin) complex and of the cyclobutane–metal intermediate are completely symmetrical with respect to reflection in the appropriate planes, but that the ground states of the two species do not correlate. This is, however, only true if the metal ion formally has an even number of electrons, and this may not occur if odd-electron ligands such as NO are also present. The role of the metal ion is to provide excited states on the ion which are of lower energy than those excited states of the organic molecules which would have to be occupied if the non-catalysed transformation were to occur.[146]

However, in the example selected, all the states of the organic moiety–metal ion complex are of the same symmetry because of the presence of the metal ion, so that one might equally argue that catalysis occurs because forbidden transitions become allowed. In any case, it is not clear what 'forbidden' means, unless it is that the activation energy is very high.

The most sophisticated analysis of the cyclobutane system develops the arguments concerning state-correlation diagrams one stage further.[147] The additional consideration introduced is that the relative energies of the metal ion *d*-orbitals

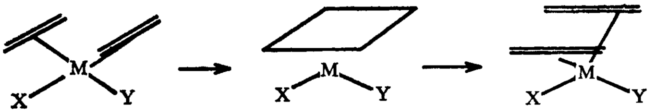
---

* Note added in proof: an analogous step for alkyne metathesis has been suggested on the basis of reaction products obtained from [Fe(CO)$_5$] and diynes (H. B. Chin and R. Bau, *J. Amer. Chem. Soc.*, 1973, **95**, 5068).

[146] W. T. A. M. van der Lugt, *Tetrahedron Letters*, 1970, 2281.

[147] G. L. Caldow and R. A. Macgregor, *J. Chem. Soc.* (*A*), 1971, 1654.

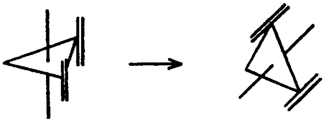
will change during the course of the reaction. Consider, for example, the usual bis-olefin to cyclobutane conversion (Scheme 8), with the transition metal



Scheme 8

initially square-planar. It is evident that the act of removing electrons from the olefinic bonds and placing electrons between the initially unbound carbon atoms means for the metal an isomerization from square-planar to tetrahedral. When this is included in the correlation argument, it becomes apparent[147] that a square-planar–tetrahedral isomerization is unlikely to be involved in the metathesis catalysis.

For an axial–equatorial trigonal-bipyramidal exchange (Scheme 9), however, catalysis does seem more likely, with low-spin d^6 metal ions, and possibly with d^1 and d^2.



Scheme 9

It must be emphasized that none of these theoretical discussions is valid if the mechanisms postulated are eventually found to be inapplicable. The recent demonstration[148] that ethylene and butadiene (a poison for metathesis catalysts) can form considerable quantities of vinylcyclobutane under the influence of a catalyst such as tetrabenzyltitanium, which in the transition state may not possess any *d*-electrons at all, suggests that there may be catalysts without transition-metal ions. It is not clear whether this system also promotes metathesis (the products of such metatheses are the same as the starting materials), but possibly unsymmetrical olefins may break orbital degeneracies and promote new reaction paths. The scope for future research seems very large.

C. A Proposed Mechanism.—It is not proven whether there is a mechanism common to all the metathesis reactions discussed. In fact, they fall into two natural divisions, those which operate at room temperature and below (most of the homogeneous systems) and those which operate at about 100 °C and above

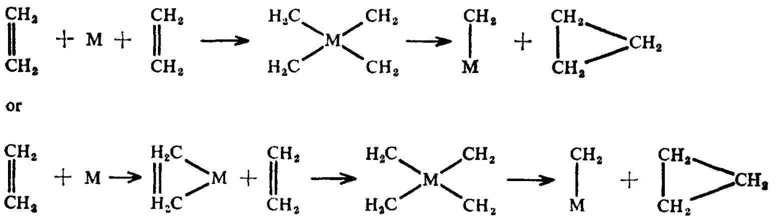
---

[148] L. G. Cannell, *J. Amer. Chem. Soc.*, 1972, **94**, 6867.

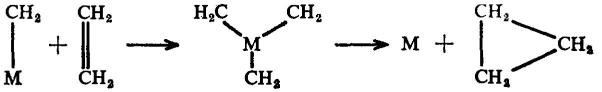
(most of the heterogeneous systems, the tetramethylene system, and the 'electron-rich-olefin' system).

All the reactions in the second group are those in which there is evidence for participation of CR_2 fragments (whether termed 'carbene' or 'methylene'). The fact that heterogeneous metathesis of propylene and the decomposition of diazomethane to yield ethylene and dinitrogen are very fast over the same catalyst may not be relevant. However, although there is good evidence that the catalysts can split the carbon–carbon double bond, the CR_2 fragments retain their integrity, and there is no evidence for hydrogen transfer to metal.

The production of cyclopropane from ethylene could occur as shown in Scheme 10. However, only one carbene (methylene) fragment is necessary, so that a process involving three carbon atoms (Scheme 11) is also feasible. Various versions of this can be sketched. Under the reaction conditions, cyclopropane will almost certainly rearrange to give propylene, and a further possibility is the insertion of a carbene fragment into cyclopropane to give methylcyclopropane, and thence various butenes. Such reactions are, however, generally of minor significance, but the intermediate (29) is adequate to explain the whole metathesis reaction, any stereoselectivity being ascribed to the steric characteristics of the catalysts, as shown in Scheme 12.

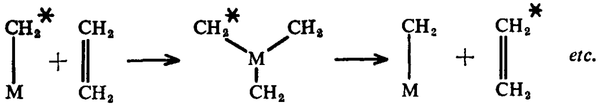


Scheme 10



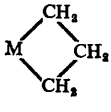
(29)

Scheme 11



Scheme 12

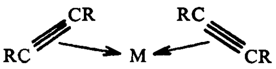
A variation of this has already been proposed,[115,138] in which a metallocycle (30) is envisaged as the transition state. It is not possible to make a definitive judgement. (30) recalls the four-carbon metallocycles (17) and (18), but in that system metathesis has not been detected with certainty, although hydrogen scrambling has been demonstrated.[124] However, neither (29) nor (30) presents any conceptual difficulty for the metathetical reactions. We prefer not to commit ourselves, and shall refer to (29) or (30) as the trimethylene model.



(30)

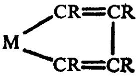
Whether this can be extended to homogeneous systems is open to question. Generally the activation energies for homogeneous systems are low, and it seems doubtful whether the activation energies for metathesis *via* metallocycle (30) with normal olefins or *via* a tetramethylene complex are small enough. It may be, however, that one function of the $EtAlCl_2$ is to generate a carbene during breakdown of an aluminium–tungsten alkyl or of a tungsten alkyl, and aluminium alkyls are known to react with some transition-metal complexes to form carbene complexes.[149] Additionally, whereas oxidative addition to Rh^{I} (to give Rh^{III}) is eminently reasonable for the route *via* (30), the corresponding transformation in the tungsten-catalysed homogeneous reaction (possible $W^{II} \rightarrow W^{IV}$) seems less likely.

We have assumed that alkyne metathesis follows a path analogous to that of olefin metathesis. If this is so, the cyclobutane model seems most appropriate. The formation of complexed cyclobutadienes from acetylenes is relatively common,[150] and these, upon thermal decomposition, would undoubtedly give the impression of alkyne metathesis. The analogue of the tetramethylene model (tetramethyne) does not seem feasible. If the effective atomic number rule is to be obeyed, then the critical transformation must be that between (31) and (32), so that M must be effectively free of any other ligands if it is to be a Group VI metal, and this is improbable. A similar objection holds to the trimethyne variant, and although metallocycles such as (33; R = H) are known,[151] their chemistry is virtually unexplored.



(31)

(32)



(33)

---

[149] W. Petz, *J. Organometallic Chem.*, 1973, **55**, C42.

[150] See, for example, P. M. Maitlis, *Adv. Organometallic Chem.*, 1966, **4**, 95.

[151] See, for example, R. P. Dodge and V. Schomaker, *J. Organometallic Chem.*, 1965, **3**, 274.

Internal acetylenes C_2R_2 react with $MoCl_5$ or WBr_5 to yield complexes $[MX_4(C_2R_2)]$ (X = Cl, M = Mo; X = Br, M = W; R = alkyl or aryl), which react with organic nitriles to yield the well-characterized $[MX_4(\text{nitrile})_2]$. The acetylene complexes are believed to contain metallocycles (33), but their thermal decomposition does not lead to metathesis products.[152]

5 Conclusions

Our understanding of the olefin metathesis reaction is in its infancy. There is obviously a close relationship between catalysts which promote this reaction and those which aid transalkylation of aromatics[122,153] and Ziegler–Natta polymerization.[154] An understanding of how these catalysts function and why minor constitutional changes endow them with such different capabilities will go far towards an important goal of organometallic chemistry, namely the design of specific catalysts for specific reactions.

[152] A. Greco, F. Pirinoli, and G. Dall'Asta, *J. Organometallic Chem.*, 1973, **60**, 115.

[153] L. Hocks. A. J. Hubert, and P. Teyssié, *Tetrahedron Letters*, 1972, 3687.

[154] G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1967, **6**, 790; see also ref. 25.