Consideration of the Mechanism of the Metal Catalyzed Olefin Metathesis Reaction[1,2]

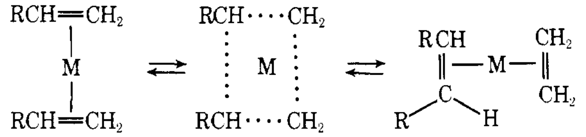
Robert H. Grubbs,* [3] D. D. Carr, C. Hoppin, and P. L. Burk

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received July 22, 1975*

Abstract: The mechanism of the olefin metathesis has been examined using mixtures of 1,7-octadiene and 1,7-octadiene-*1,1,8,8*-d_4 as the olefin and three basically different catalyst systems. Two different mechanisms were considered and the expected ratios of ethylene-d_4, -d_2, and -d_6 for each mechanism were considered. This labeled olefin system allows a distinction to be made between those mechanisms which involve a diolefin intermediate and a one carbon chain (carbenoid) intermediate. The results obtained are most consistent with the carbene mechanism.

The olefin metathesis reaction has provided one of the most challenging mechanistic problems in organometallic chemistry.[4,5] Model and theoretical studies have provided evidence for at least three distinct mechanisms. The first mechanism proposed involved a metal-cyclobutane complex either as an intermediate or as a transition state.[6] This mechanism fulfilled the requirements of the early labeling studies which indicated that the reaction involved the cleavage of the C–C double bond and not the transfer of groups attached to the double bond.[7]

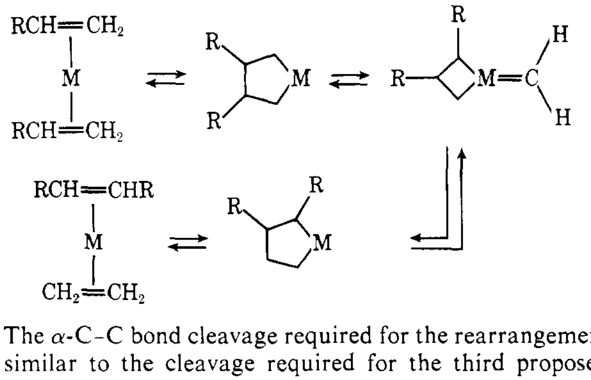
Scheme I



This mechanism was supported by numerous considerations of the orbital symmetry of this reaction and the ability of the olefin–metal orbital interactions to provide a low energy pathway for the reaction to proceed.[8] This scheme received minimal support from experimental studies.[9]

A second scheme which involved the "pairwise" exchange between two olefins in the coordination sphere of a metal required a tetramethylene metallocycle as an intermediate.[10] This reaction received support from the studies of the metal catalyzed [2 + 2] cycloaddition reaction.[11-14]

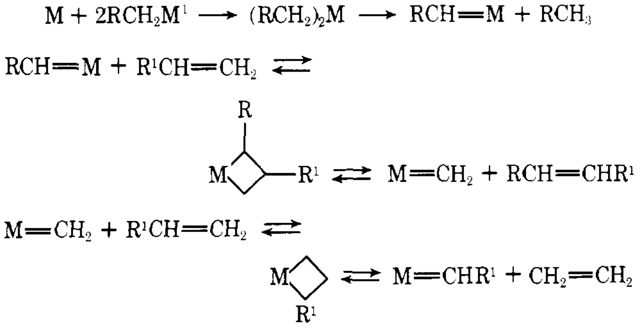
Scheme II



The α-C–C bond cleavage required for the rearrangement is similar to the cleavage required for the third proposed mechanism. This mechanism was supported by trapping studies and the reactions of tetramethylene metallocycles prepared under the reaction conditions.[15]

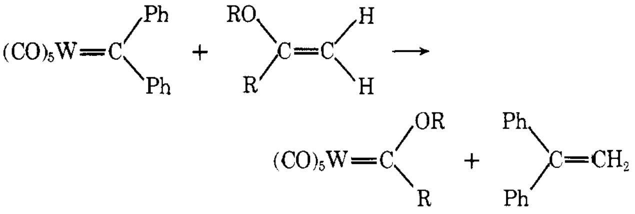
A third scheme which is distinctly different from the other two involves a chain reaction in which a carbene-metal complex is the active catalyst. This scheme is presented below.

Scheme III



etc.

Herrisson and Chauvin[16] proposed this scheme in 1970 in a paper which was apparently overlooked by most other workers in the field. They suggested that this scheme would account for the appearance of cross-products in the early stages of the reaction between cyclic and unsymmetrically substituted acyclic olefins. The possible sources of the catalytic carbenoid species have only recently become apparent. The preparation of stable alkyl carbenes from metal alkyls provided a good model for this reaction.[17,18] Good models for the reaction of carbenes with olefins to produce products resulting from an interchange of the carbene carbon with one of the carbons of the olefin were provided by the work of Casey[18] and Lappert.[19]



Since the model work supported two alternate mechanisms, studies of the metathesis of olefin systems designed to distinguish between these two mechanism were carried out. Katz[20] reexamined the reaction of unsymmetrical acyclic olefins with cyclic olefins. He found that the cross coupled products appeared before a significant buildup of the scrambled acyclic olefin.

This result supported the carbene (Scheme III) mechanism. In this study, however, it was impossible to rule out experimentally the possibility that the products were produced by the subsequent cleavage of a polymer formed from cyclooctene.

We[21] reported earlier a study of the metathesis of a 1:1 mixture of 1,7-octadiene and 1,7-octadiene-*1,1,8,8*-d_4. The metathesis of 1,7-octadiene produces high yields of cyclohexene and ethylene. The analysis of the ethylenes produced on metathesis of the deuterated mixture under nonequilibrating conditions gave results which were most consistent with the carbene scheme (Scheme III). We now report the complete analysis of the ratios of ethylenes expected for each mechanism and new experimental results which further support Scheme III.

Experimental Section

Mass spectral analyses were performed using a Hitachi-Perkin-Elmer RMU-6 mass spectrometer. Gas samples were analyzed by the use of a Varian aerograph 90-P gas chromatograph equipped with thermal conductivity detectors and a 10 ft × 0.25 in. 7% paraffin wax on alumina column. Liquid samples were analyzed using a Varian aerograph gas chromatograph equipped with a flame ionization detector and a 10 ft × ⅛ in. 5% Carbowax on Chromosorb W. Samples of liquid reaction products were purified for mass spectrometry by the use of the thermal conducicitivity gas chromatograph equipped with a 5 ft 10% Carbowax 20M on Chromasorb W.

Preparation of 1,7-Octadiene-*1,1,8,8*-d_4. To a solution of 7.5 g (0.18 mol) of lithium aluminium deuteride in 100 ml of tetrahydrofuran (THF) was added 25 ml (0.13 mol) of dimethyl suberate in 50 ml of THF. The mixture was refluxed for 3 h. After cooling to room temperature, 7.5 ml of H_2O, 7.5 ml of 15% NaOH solution, and 23 ml of water were added in order. The salts were removed by filtration, and the filtrate was concentrated to yield 25.9 g of crude 1,8-octanediol-*1,1,8,8*-d_4. Recrystallization from benzene-ligroin gave white crystals: mp 62-63 (lit. 62-63°);[22] NMR ($CDCl_3$) δ 1.33 (m, 12 H), 1.60 (s, 2 H).

The crude diol from above was mixed with 0.5 ml of pyridine and heated to 140°. Acetic anhydride (40 ml) was added dropwise. After refluxing for 2.5 h the excess acetic anhydride was removed in vacuo and the crude reaction product distilled (121° (1.5 mm)) to give 27.0 g (91% from diester) of 1,8-diacetoxyoctane-*1,1,8,8*-d_4: NMR ($CDCl_2$) δ 1.3-1.6 (m, 12 H) and 2.0 (s, 6 H). The corresponding 1,8-diformate could be prepared by standard literature procedures[23] in a similar yield.

Under a 3 l./h flow of nitrogen, 27.0 g of 1,8-diacetoxyoctane-*1,1,8,8*-d_4 was added dropwise to a tube (2.5 × 580 cm) filled with 48 cm of glass helices and heated to 580°. The product was washed with saturated sodium bicarbonate solution, extracted with pentane (3 × 20 ml), dried, and distilled to give 6.5 g (49%) of 1,7-octadiene-*1,1,8,8*-d_4: NMR ($CDCl_3$) δ 1.10-1.70 (m, 8 H), 5.30 (m, 2 H), 4.93 (m, 0.4 H).

In a similar way 1,8-diformyloctane-*1,1,8,8*-d_4 was pyrolyzed at 480° to give a 50% yield of 1,7-octadiene-*1,1,8,8*-d_4: NMR ($CDCl_3$) δ 1.10-1.70 (m, 8 H) δ 5.30 (m, 2 H), 4.93 (m, 0.8 H).

Catalyst Preparation. WCl_6-BuLi System.[24] To a centrifuge tube fitted with a rubber septum and filled with N_2 was added 2.5 ml of 0.1 M tungsten hexachloride in benzene, 2.5 ml of oxygen-free benzene, and 0.39 ml of 2.6 M butyllithium in hexane. The mixture was shaken for 10 min and centrifuged, and the supernate liquid was removed with a syringe and discarded. The solid was washed with 5 ml of benzene in the same way, and then used as a suspension in benzene.

Phenyltrichlorotungsten-Aluminum Chloride.[25] To a centrifuge tube fitted with a rubber septum and filled with nitrogen was added 0.368 g (1 mmol) of phenyltrichlorotungsten[26] and 0.134 g (1 mmol) of aluminum chloride. This mixture was shaken with 25 ml of oxygen-free chlorobenzene for 30 min and then centrifuged. The supernate liquid which contained the active catalyst was transferred to other tubes for use in metathesis.

$[(C_6H_5)_3P]_2Cl_2(NO)_2Mo + (CH_3)_3Al_2Cl_3$.[27] To a centrifuge tube fitted with a rubber septum was added 15 ml of a 0.01 M solution of the molybdenum complex and 0.25 ml of a 1 M $(CH_3)_3Al_2Cl_3$ solution in chlorobenzene. The mixture was centrifuged and the superated removed with a syringe. The solution contained the catalytically active species.

Metathesis of 1,7-Octadiene (I)–1,7-Octadiene-*1,1,8,8*-d_4 (II) Mixtures. The mixtures of I and II were prepared by mixing weighed samples of I and II. The ratio was checked by comparing the integral of the peaks in the NMR at δ 5.3 and 4.93. The ethylene samples were removed from the reaction mixture by means of a syringe and purified by GLC. The ethylene peak was collected in a large surface area collection tube cooled in liquid N_2. The samples were analyzed by mass spectrometry using an ionization voltage of 14 eV and a sufficiently high resolution to separate the residual N_2 peak from the C_2H_4 peak and the O_2 peak from the peak for C_2D_4. At least six spectra were run on each gas mixture and the relative amounts of each ethylene were determined by peak height comparisons and/or by cut and weighing the individual peaks from an expanded spectrum. The relative ratios of the peaks remained constant from the first to the last sample of a reaction mixture. Also the ratio of the ethylenes in a reaction mixture was independent of whether the first or last half of the ethylene GLC peak was collected. The 1,7-octadiene mixtures were recovered from the reaction by GLC and introduced into the mass spectrometer through the gas inlet system. A sample of the starting mixture of I and II was prepared by collection from the GLC and the sample was analyzed by mass spectrometry at the identical machine conditions as the reaction mixture.

Table I

Time (min)	Ethylene d_4	d_2	d_0
39	1.0	2.23 ± 0.13	1.42 ± 0.10
176	1.0	2.23 ± 0.14	1.43 ± 0.10
373	1.0	2.34 ± 0.10	1.39 ± 0.13
1280	1.0	2.31 ± 0.13	1.44 ± 0.11

Table II

m/e	114	113	112	111	110
Starting diene	1.0	0.45 ± 0.03	0.26 ± 0.03	0.19 ± 0.01	0.89 ± 0.02
Product diene	1.0	0.42 ± 0.03	0.25 ± 0.04	0.18 ± 0.03	0.90 ± 0.04

Table III

	d_4	d_3	d_2	d_1	d_0
Product ethylene	1.0	0.11 ± 0.01	0.21 ± 0.01	0.01 ± 0.01	0.05 ± 0.01
Product ethylene when C_2H_4 added	1.0	0.09 ± 0.01	0.29 ± 0.01	0.04 ± 0.01	0.93 ± 0.04

With Phenyltrichlorotungsten-Aluminium Chloride. In a 25 × 250 mm test tube fitted with a rubber septum and filled with argon was added 5 ml of the title catalyst solution and 0.4 ml of a 1.1:1 mixture of I:II. The solution was shaken at room temperature and periodically an aliquot of the gas above the solution was removed. The analysis of the ethylenes with time are given in Table I. Over the reaction period, 10% cyclohexene was produced. At the end of the reaction, the remaining 1,7-octadiene mixture was collected and analyzed by mass spectrometry. These results are in Table II.

In an identical reaction with 1,7-octadiene (I) alone the yield of ethylene was 8 ± 1.5% and the yield of cyclohexene was 10 ± 2%.

The above reaction was repeated using two tubes containing 5 ml of the same catalyst solution and 0.1 ml of 1,7-octadiene-*1,1,8,8*-d_4. To one of the tubes was added 0.5 ml of ethylene-d_0. After 75 min the ethylenes over the reaction mixture were removed and analyzed. The results are in Table III.

With $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo + (CH_3)_3Al_2Cl_3$. The reactions with this catalyst were carried out in two ways: (a) in a flow system to remove the ethylene as formed and (b) in sealed tubes as described above. The 1,7-octadiene-d_4 prepared by the pyrolysis of 1,8-diformyloctane-d_4 was used in these reactions.

(a) The flow system was constructed from 2.25 × 250 mm test tubes each containing a gas dispersion tube and an outlet tube. The tubes were connected so that a gas introduced through the gas dispersion tube of the first test tube passed out of the gas outlet of the second test tube. The outlet gas passed into a sand trap cooled with liquid N_2. The test tubes were flushed with helium, and to each was added 15 ml of the catalyst solution. Helium was introduced at a rate of 50-100 ml/min. The sample of the mixture of I and II was introduced into the second tube. The ethylene produced was collected in the sand bath, purified by GLC, and analyzed by mass spectrometry. A first sample was collected in the first 15 min and then approximately 10 ml of ethylene was introduced into the gas line between the two tubes and

Table IV

I/II	Exptl d_4:d_2:d_0	Calcd Scheme III d_4:d_2:d_0	Calcd Scheme VI d_4:d_2:d_0
1.1 ± 0.03	1:2.19 ± 0.03:1.18 ± 0.02[a] 1:2.11 ± 0.02[b] 1:2.17 ± 0.06:1.32 ± 0.03[c]	1:1.69:1.12	1:2.2 ± 0.06:1.2 ± 0.05
3.08 ± 0.05	1:6.15 ± 0.07:9.65 ± 0.12[a] 1:6.69 ± 0.1[b] 1:6.57 ± 0.21:10.92 ± 0.32[c]	1:4.0:7.25	1:6.16 ± 0.1:9.49 ± 0.12
0.49 ± 0.03	1:0.91 ± 0.02:0.29 ± 0.01[a] 1:0.96 ± 0.04[b] 1:0.97 ± 0.02:0.25 ± 0.01[c]	1:0.81:0.27	1:0.98 ± 0.02:0.24 ± 0.2
2.85 ± 0.23	1:5.95 ± 0.03:9.85 ± 0.07[a]	1:3.7:7.2	1:5.7 ± 0.3:8.1 ± 0.9
0.33 ± 0.01	1:0.66 ± 0.01:0.12 ± 0.01[c]	1:0.68:0.15	1:0.66 ± 0.02:0.11 ± 0.01

[a] Obtained in flow system. [b] Ratios with ethylene-d_0 added. [c] Sealed tube reaction.

Table V[a]

1,7-Octadiene mixture	Ratio I/II	m/e 114-d_4	m/e 112-d_2	m/e 110-d_0
Starting	2.85	1	0.4. ± 0.05	1.94 ± 0.16
Product		1	0.83 ± 0.07	2.33 ± 0.15
Starting	1.1	1	0.28	0.65
Product		1	0.53	1.00
Starting	0.33	1	0.21 ± 0.01	0.43 ± 0.01
Product		1	0.43 ± 0.02	0.41 ± 0.02

[a] The percent rearrangement was calculated by: % 1,7-octadiene-d_2 produced ≈ [(112 peak of product) − (112 peak start)]/[(114 peak product) + (112 peak product) + (110 peak product)].

a second sample was collected. The results of the ethylene analysis are in Table IV. The reaction was run for 15 min with 1,7-octadiene-d_0. Propane as an internal standard was added to the resultant ethylene sample and the solution quenched with 10% HCl and benzene was added as an internal standard. The yield of ethylene was 13 ± 3% and the yield of cyclohexene was 14 ± 2%.

(b) A 5-ml portion of the catalyst solution was placed in a 25 × 250 mm tube sealed with a rubber septum. Approximately 0.1 ml of the mixture of I and II was added and the reaction allowed to proceed for 3 min before 0.5 ml of 10% HCl was added. The ethylene was collected and analyzed by mass spectrometry. The remaining 1,7-octadienes were collected and analyzed by mass spectrometry. The results of the ethylene analysis for both methods are presented in Table IV. The analysis of representative samples of the 1,7-octadiene mixture (I/II) before and after the reactions are in Table V.

Similar reactions were carried out with 1,7-octadiene-d_0. The yield of ethylene and cyclohexene was determined by GLC. The yields were: 19% ethylene, 18% cyclohexene, and 83% recovered 1,7-octadiene; and 14% ethylene, 15% cyclohexane, and 82% recovered 1,7-octadiene.

With Tungsten Hexachloride–Butyllithium. The solid catalyst was suspended in 10 ml of benzene and 1.0 ml of a 1.1:1 mixture of I:II was added. After 28 min at room temperature the ethylene was removed and analyzed.

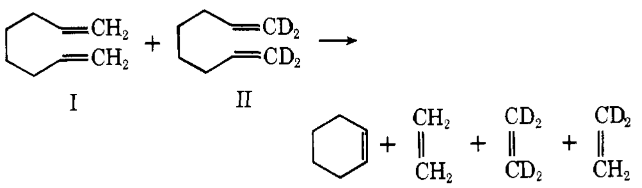
An identical reaction was carried out with 2 ml of ethylene added and analyzed before. The results are presented in Table VI. The cyclohexene from the reaction was recovered and found to contain approximately 25% cyclohexene-d_1.

Results and Discussion

The ratios of the expected deuterioethylenes produced from metathesis of mixtures of 1,7-octadiene (I) and 1,7-octadiene-*1,1,8,8*-d_4 (II) will be calculated below. A ratio of deuterated ethylenes expected from a "pairwise" exchange of carbon atoms between two olefins, Schemes I and II, are possible cases, and the ratio expected from a monocarbon, "chain transfer" reaction, such as Scheme III, will be calculated. Each calculation will assume that there is no significant scrambling of starting materials or products in the following reaction.[27] Each of these restrictions can be tested experimentally.

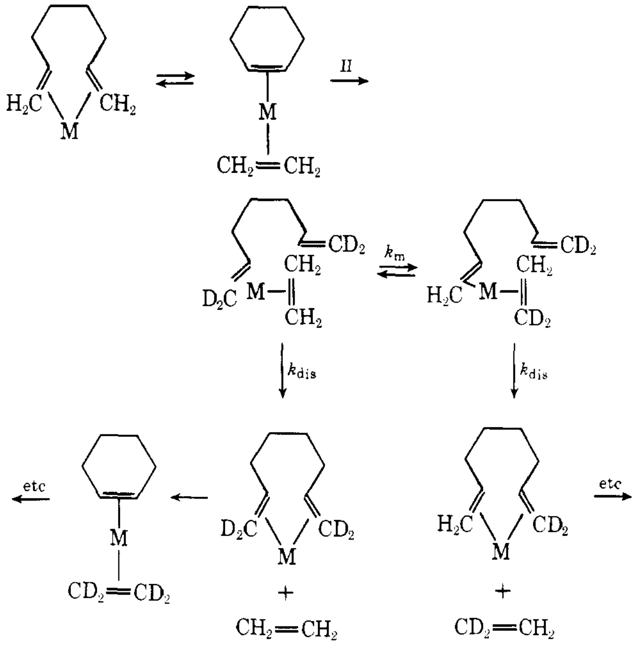
Table VI

Ethylene	d_4	d_3	d_2	d_1	d_0
—	1	0.63 ± 0.13	3.35 ± 0.2	1.02 ± 0.17	3.08 ± 0.17
Added	1	0.86 ± 0.08	4.14 ± 0.37	5.16 ± 0.5	14.81 ± 1.44
—	1	—	3.6 ± 0.2	—	3.2 ± 0.1
Added	1	—	3.7 ± 0.2	—	16.6

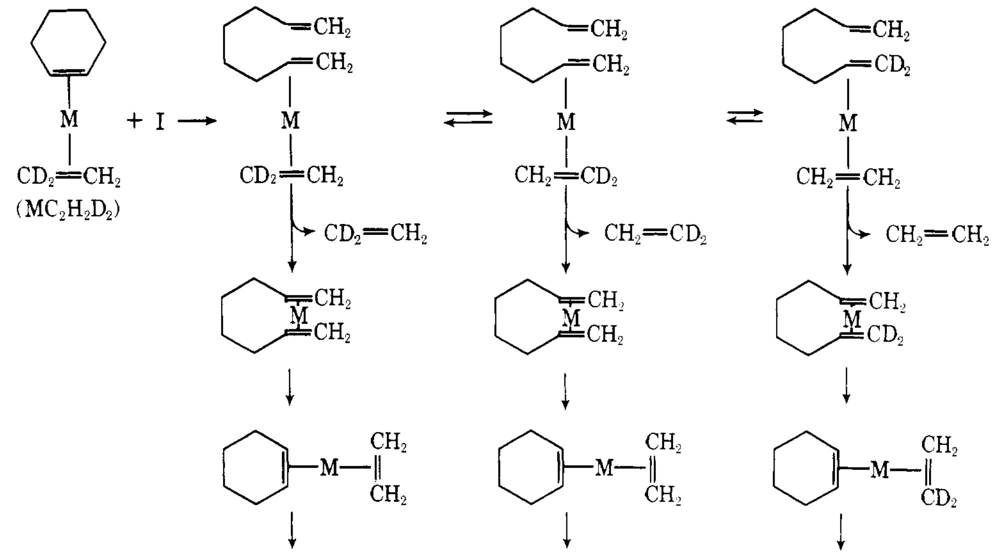


The following is a mechanistic scheme which does not distinguish between the concerted (Scheme I) or the metallocycle (Scheme II) mechanism. Only those steps which produce ethylene are considered. As indicated in this outline, the ratio of C_2D_4 to $C_2H_2D_2$ would depend on the relative values for the rates of metathesis (k_m) and the rate of displacement of ethylene (k_{dis}) from the intermediate 1,7-octadiene–ethylene–metal complex. Consequently, the two extreme cases, $k_{dis} \gg$

Scheme IV



Scheme V



k_m and $k_{dis} \ll k_m$ will be considered.[28] The ethylene ratio values for any other relative values of k_{dis} and k_m will fall between the values calculated for these extreme cases.

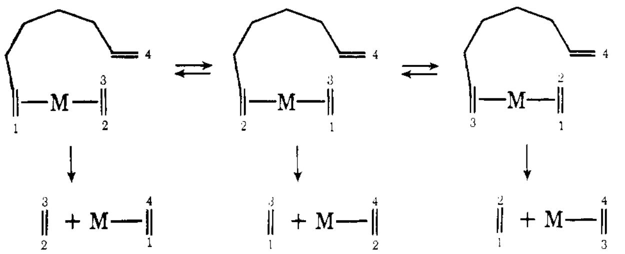
If $k_{dis} \gg k_m$; only those ethylenes resulting from intramolecular "pairwise" exchange will result. Therefore, if 1,7-octadiene (I) and 1,7-octadiene-*1,1,8,8*-d_4 (II) are present in the reaction, only ethylene-d_4 and ethylene will be produced. If the value of the ratio of I/II used in the reaction is *A* then the expected ratio of ethylene-d_4:d_2:d_0 will be *1:0:A* if the ethylene is not allowed to equilibrate in the reaction medium.

If $k_m \gg k_{dis}$, the calculation of the expected ratios is much more complex. Scheme IV gives only one of the six possible reactions which must be considered, since there will be three metal–ethylene complexes in solution (MC_2H_4, $MC_2H_2D_2$, and MC_2D_4) which can each interact with equal probability with either 1,7-octadiene (I) or 1,7-octadiene-*1,1,8,8*-d_4 (II). Each of these interactions will produce a different ratio of the three possible ethylenes and a new ratio of metal–ethylene complexes. These are the only steps which must be considered if I and II do not equilibrate.

The example presented in Scheme V allows for the total equilibration of all methylene units complexed to the metal. This allows maximum equilibration of the CD_2 and CH_2 units and should produce the highest ethylene-d_2/-d_4 ratio.

A general reaction scheme can be generated from the example shown in Scheme VI.

Scheme VI



If isotope effects are considered insignificant (see below) each of the diene–ethylene complexes will be produced in equal amounts and each reaction leading to products will proceed at the same rate.

On first glance, the equilibration of the methylene units such as in Schemes V and VI should produce a random distribution of deuterated ethylenes. However, pathways for the total equilibration of I and II into 1,7-octadiene-*1,1*-d_2 (III) and the entrance of this unit into the ethylene generating reactions are required for complete scrambling of the ethylenes. The expected values will now be calculated.

There are six possible assignments of the methylene units, 1,2,3,4. They are: (a) $CD_2 = 1 = 4 = 2 = 3$, (b) $CD_2 = 1 = 4 = 2 \neq 3$, (c) $CD_2 = 1 = 4 \neq 2 = 3$, (d) $CH_2 = 1 = 4 \neq 2 = 3$, (e) $CH_2 = 1 = 4 = 2 \neq 3$, and (f) $CH_2 = 1 = 4 = 2 = 3$. For example, (b) is equivalent to the interaction of 1,7-octadiene-d_4 (II) with a metal–ethylene-d_2 complex. Referring back to Scheme VI, it is apparent that for the (b) assignment, the ethylenes-d_4, -d_2, and -d_0 are produced in the ratio of 1:2:0 and the resulting metal–ethylene-d_4, -d_2, -d_0 complexes are produced in the ratio of 2:1:0. Similar ratios are easily obtained for the other five equally possible assignments of the methylene groups.

The relative amounts of each ethylene and metal–ethylene complex can be calculated from the following general equation.

$$\begin{aligned}\text{(olefin or metal–ethylene complex)} &= P_a(1,7\text{-}d_4)(\text{M-E-}d_4) \\ &\quad + P_b(1,7\text{-}d_4)(\text{M-E-}d_2) \\ &\quad + P_c(1,7\text{-}d_4)(\text{M-E-}d_0) + P_d(1,7\text{-}d_0)(\text{M-E-}d_4) \\ &\quad + P_e(1,7\text{-}d_0)(\text{M-E-}d_2) + P_f(1,7\text{-}d_0)(\text{M-E-}d_0)\end{aligned}$$

where $(1,7\text{-}d_4)$ = mole fraction of 1,7-octadiene-d_4 (II), $(1,7\text{-}d_0)$ = mole fraction of 1,7-octadiene-d_0 (I), $(\text{M-E-}d_4)$ = mole fraction of the metal–ethylene-d_4 complex.

The $P_a \ldots P_f$ are probability factors for the production of the ethylene (or metal–ethylene complex) in question by the interaction of the two following components. These *P* factors are easily determined by referring back to Scheme VI and the possible asssignments of atoms 1–4. The subscript on the *P* factor refers to the assignments of the atoms in Scheme VI.

The *P* factors for the production of ethylene-d_4 then become the following: $P_a = 1$, since all methylene units are CD_2, $P_b = \frac{1}{3}$ since only one of the three equally probable paths leads to C_2D_4, $P_c = 0$ since none of the reactions leads to C_2D_4, $P_d = \frac{1}{3}$ since one of the three reactions produce C_2D_4, $P_e = P_f = 0$ since there are not two CD_2 units present in the coordination sphere. The equation for calculating the relative amount of C_2D_4 then becomes:

$$\begin{aligned}C_2D_4 &= 1(1,7\text{-}d_4)(\text{M-E-}d_4) \\ &\quad + \tfrac{1}{3}(1,7\text{-}d_4)(\text{M-E-}d_2) + \tfrac{1}{3}(1,7\text{-}d_0)(\text{M-E-}d_4)\end{aligned}$$

Similar considerations give the *P* values for the other two ethylenes:

$$\begin{aligned}C_2H_2D_2 &= 0 + \tfrac{2}{3}(1,7\text{-}d_4)(\text{M-E-}d_2) + \tfrac{2}{3}(1,7\text{-}d_0)(\text{M-E-}d_4) \\ &\quad + \tfrac{2}{3}(1,7\text{-}d_0)(\text{M-E-}d_4) + \tfrac{2}{3}(1,7\text{-}d_0)(\text{M-E-}d_2) + 0\end{aligned}$$

$$\begin{aligned}C_2H_4 &= 0 + 0 + \tfrac{1}{3}(1,7\text{-}d_4)(\text{M-E-}d_0) + 0 \\ &\quad + \tfrac{1}{3}(1,7\text{-}d_0)(\text{M-E-}d_2) + 1(1,7\text{-}d_0)(\text{M-E-}d_0)\end{aligned}$$

Equations for the amount of each new metal-ethylene (M-E)′ can be generated in an analogous manner.

$$(\text{M-E-}d_4)' = 1(1,7\text{-}d_4)(\text{M-E-}d_4) + \tfrac{2}{3}(1,7\text{-}d_4)(\text{M-E-}d_2) + \tfrac{1}{3}(1,7\text{-}d_4)(\text{M-E-}d_0) + 0 + 0 + 0$$

$$(\text{M-E-}d_2)' = 0 + \tfrac{1}{3}(1,7\text{-}d_4)(\text{M-E-}d_2) + \tfrac{2}{3}(1,7\text{-}d_4)(\text{M-E-}d_0) + \tfrac{2}{3}(1,7\text{-}d_0)(\text{M-E-}d_4) + \tfrac{1}{3}(1,7\text{-}d_4)(\text{M-E-}d_2) + 0$$

$$(\text{M-E-}d_0)' = 0 + 0 + 0 + \tfrac{1}{3}(1,7\text{-}d_0)(\text{M-E-}d_4) + \tfrac{2}{3}(1,7\text{-}d_0)(\text{M-E-}d_2) + 1(1,7\text{-}d_0)(\text{M-E-}d_0)$$

Any starting ratio of M-E complexes can be assumed and the calculation continued until the ratio of (M-E)′ values converge.[29] With a ratio of 1,7-octadiene-d_0/-d_4 = 1 the calculation is straight forward. The mole fraction of M-E-d_4:-d_2:-d_0 at convergence, in this case, is the sum of the P factors in each equation, 1:1:1.

The calculated ratios of the ethylenes are: $C_2D_4 = \frac{5}{3}$, $C_2H_2D_2 = \frac{8}{3}$, $C_2H_4 = \frac{5}{3}$, or ethylene-d_4:-d_2:-d_0 = 1:1.6:1.

Similar calculations can be carried out for other starting ratios of I/II (see Table I): Other equilibration schemes, such as allowing only atoms 1 and 2[30] or all atoms, 1,2,3,4,[31] in Scheme VI to equilibrate, produce ethylene-d_2/-d_4 ratios of less than 1.6 at a ratio of I/II = 1. These calculations require only a change in the P factors in the above equations. Isotope effects on the ratios will be considered later.

The steps which determine the ratio of ethylenes produced by Scheme III (carbene scheme) when a mixture of I and II is considered, are:

$$\text{M=CH}_2 + \text{I} \rightarrow \text{CH}_2\text{=CH}_2 + \text{M=CH}_2 + \text{C}_6\text{H}_{10}$$

$$\text{M=CD}_2 + \text{I} \rightarrow \text{CH}_2\text{=CD}_2 + \text{M=CH}_2 + \text{C}_6\text{H}_{10}$$

$$\text{M=CH}_2 + \text{II} \rightarrow \text{CH}_2\text{=CD}_2 + \text{M=CD}_2 + \text{C}_6\text{H}_{10}$$

$$\text{M=CD}_2 + \text{II} \rightarrow \text{CD}_2\text{=CD}_2 + \text{M=CD}_2 + \text{C}_6\text{H}_{10}$$

The relative amounts of each of the ethylenes at a time in the reaction when steady state has been reached are:

$$(\text{CD}_2\text{=CD}_2) = k[\text{II}][\text{M=CD}_2]$$

$$(\text{CH}_2\text{=CD}_2) = k[\text{II}][\text{M=CH}_2] + k[\text{I}][\text{M=CD}_2]$$

$$(\text{CH}_2\text{=CH}_2) = k[\text{I}][\text{M=CH}_2]$$

Then the ratio of ethylene-d_4:-d_2:-d_0 is 1:([M=CH$_2$]/[M=CD$_2$] + [I]/[II]):([I][M=CH$_2$]/[II][M=CD$_2$]) without isotope effects, [M=CH$_2$]/[M=CD$_2$] = [I]/[II] = A and d_4:d_2:d_0 = 1:2A:A^2 where A is the ratio of starting 1,7-octadiene-d_0:-d_4. At A = 1 the predicted ratio is d_4:d_2:d_0 = 1:2:1.

Consequently, the metathesis of mixtures of 1,7-octadiene (I) and 1,7-octadiene-*1,1,8,8*-d_4 (II) under conditions which do not allow for the scrambling of the labels in starting materials or products should allow a clear decision to be made between the "pairwise" exchange and the monocarbon "carbene" mechanism.

The easiest method for considering the isotope effect does not require an assignment and calculation involving isotope effects. This treatment is based on the observation that the values for the d_4:d_2:d_0 ratios are reversed when the inverse of the diene ratio is used. For example, in Scheme VI for a ratio of 1,7-octadiene/1,7-octadiene-d_4 of 3, the predicted ratios are 1:6:9 for d_4:d_2:d_0. For a ratio of 1,7-octadiene-d_0/-d_4 of ⅓ the values are 9:6:1 for d_4:d_2:d_0. This relationship holds for all values of A and 1/A and for all mechanisms. Any isotope effects will skew this symmetry. Consequently, if the results of the reaction of a mixture of 1,7-octadiene-d_0/-d_4 of ratio A and 1/A are compared, and the coefficients for the d_0 ethylene at A is divided by the coefficient for the d_4 ethylene at 1/A, the ratio should be 1 if there are no isotope effects or sampling errors. This is not only the easiest but also should be the most exact method of considering the isotope effects, since, in Scheme V, isotope effects would effect both the relative concentrations of the 1,7-octadiene-ethylene-metal complexes as well as the rate at which ethylene is displaced by the pendent double bond from each of these complexes. This combination of isotope effects is almost impossible to consider in an exact manner.

Consequently, the metathesis of mixtures of I and II were carried out with the three-catalyst system. Two of these systems appear to be homogeneous while the third is heterogeneous.[32] One of the two homogeneous catalysts requires an alkyl activating agent whereas the second can produce no metal alkyl bonds during activation. These three basically different catalyst systems combined with the ability to distinguish mechanisms using the mixtures of I and II should allow a choice to be made between the possible mechanisms in each case and to determine if there appears to be one general metathesis mechanism.

The first homogeneous system studied was prepared by mixing equal molar quantities of phenyltrichlorotungsten and aluminium chloride. Although this catalyst system produces ethylene at a slow rate, the active solutions are clear and appear to be homogeneous.[37] The metathesis of a 1.1:1 mixture of 1,7-octadiene-d_0:-d_4 was carried out with this catalyst system. The ratio of ethylene-d_4:-d_2:-d_0 produced was 1:2.23 ± 0.14:1.42 ± 0.1 (Table I). The values for the ratio of ethylene-d_4:-d_0 predicted by the calculations for a "pairwise" exchange for a 1.1:1 mixture I:II are 1:1.65:1.12. The "carbene" mechanism predicts a ratio of 1:2.2:1.32. It is obvious that the experimental ratio is within experimental error of the value calculated for the "carbene" mechanism. The yields of ethylene and cyclohexene produced in this reaction were the same. This suggests that the ethylene and cyclohexene are arising from the same reaction. The two restrictions placed on the calculations were tested experimentally by demonstrating that the mass spectra of the starting and recovered mixture of I and II were identical (Table II). The second restriction was shown to be valid by finding that the metathesis of 1,7-octadiene-*1,1,8,8*-d_4 in the presence of ethylene-d_0 produced no ethylene-d_2. If the random mixture of ethylenes found had resulted from the subsequent metathesis of an initially formed nonequilibrium mixture of ethylenes, this reaction would have produced significant amounts of ethylene-d_2. This catalyst, therefore, appears to proceed through a "carbenoid" intermediate.

The second apparently homogeneous system studied was the catalyst prepared from the mixture of $[(C_5H_5)_3P)_2]Cl_2(NO)_2Mo$ and methyl aluminium sesquichloride. This rapid, clean catalyst system was used to metathesize a number of different mixtures of I and II. Reactions using this catalyst system were carried out in both a flow system, to remove the gases produced rapidly, and in sealed tubes. The results from both types of reactors were identical. In the flow reactor the helium gas, used to carry the ethylenes from solution as they were formed, was purified by passing it first through a catalyst solution containing no olefins. The results of the analysis of the ethylenes produced in this reaction as well as the values calculated for each starting 1,7-octadiene mixture for each of the two mechanisms are given in Table IV. It is apparent that (1) ratios of I:II that are different than 1:1 produce larger differences in the ratios predicted by the two mechanisms and (2) in all cases the results are within experimental error of those values predicted by the carbene scheme and well away from those values predicted by the "pairwise" mechanisms. These reactions were allowed to proceed to 13-20% completion so that careful comparisons could be made between the yield of cyclohexene and ethylene. In all cases where the yields could be determined, the yields of ethylene and cyclohexene were the same within 2-3%. This indicated that the ethylene and cyclohexene were both arising in the same reaction.

As can be seen in Table IV, the addition of ethylene-d_0 to the reaction mixture gave ethylene-d_2/-d_4 ratios that were the same as those without added ethylene. If the statistical ratio of ethylenes were produced by further metathesis of a nonequilibrium ratio in the reaction solution, the ethylene-d_2/-d_4 ratio should have been changed significantly by the addition of ethylene-d_0. Consequently, one of the required restrictions is met. Table V shows that there was approximately 12% 1,7-octadiene-*1,1*-d_2 produced during the reaction. This is equivalent to an average of 6% 1,7-octadiene-*1,1*-d_2 being present in solution during the reaction. A calculation of the ratio of ethylenes predicted by a "pairwise" mechanism for a mixture which contains a 1:0.2:1 ratio (equivalent to 20% rearrangement) of 1,7-octadiene-d_0:-d_2:-d_4 leads to a ratio of ethylene-d_4:-d_2:-d_0 = 1:1.64:1 (compared to 1:1.6:1). Consequently, the amount of scrambling observed is insignificant when compared to the differences distinguishing between the different mechanisms. Consequently both of the required restrictions are met.

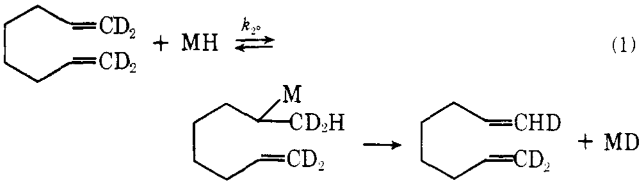
The results in Table IV provide the data for an estimate of the magnitude of the possible isotope effects. As indicated earlier, the values for the ratio of ethylene-d_4:-d_2:-d_0 determined at a ratio of I/II = *A* are equal to the values of ethylene-d_0:-d_2:-d_4 determined at 1/*A* if the isotope effects are minimal. The value determined for ratios of I/II = 3.08 and 0.33 provides the data required for this analysis. Since the ratios of I/II are not exactly the inverse of each other and the ethylene ratios contain sampling errors as well as any isotope effect, this comparison sets an upper limit on the magnitude of the isotope effects. The ethylene-d_4:-d_2:-d_0 values at a ratio of I/II of 0.33 are 9.1:6.0:1. Dividing the d_4 value by the d_0 value obtained at 3.08 gives 0.94; the divisiion of the two d_2 values yields 0.97. If there are no isotope effects and sampling errors each comparison should have yielded a value of 1.0. It is obvious that the sampling errors and isotope effects are negligible when compared to the magnitude of the differences predicted by the two mechanisms.

Consequently, the data obtained with this catalyst are most consistent with the "carbene" mechanism.

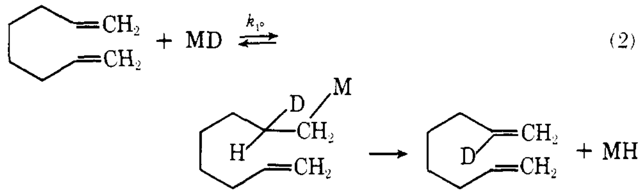
The heterogeneous catalyst prepared from WCl_6/2BuLi produced results which are clouded by interfering side reactions. As can be seen in Table VI, significant amounts of ethylene-d_1 and ethylene-d_3 were formed along with the expected ethylene-d_4, -d_2, and -d_0. The ethylenes containing odd numbers of deuterium atoms probably arise from a competing metal hydride (deuteride) exchange reaction. The ratio of ethylene-d_4:-d_2:-d_0 produced in this reaction (1:3.6:3.2) was not that expected for either mechanism based on the starting I/II ratio (1:2.2:1.32 or 1:1.65:1.12). However, the values obtained can be calculated by the equation d_4:d_2:d_0 = 1:2a:a^2 (the same form as the ratio for the carbene reaction). In all cases examined $a >$ the initial I/II ratio.[33] Consequently, the hydride exchange reaction appears to increase the I/II ratio. A reasonable mechanism for this scrambling is eq 1 and 2.

If $k_{1^\circ} > k_{2^\circ}$,[34] the deuterium would be lost from the terminal positions and consequently the ratio of terminal CH_2 groups to terminal CD_2 groups would increase as the reaction progressed and give the observed results. The finding of significant amounts of cyclohexene-d_1, in the products of this reaction, supports this mechanism.

This heterogeneous catalyst system produces a random distribution of ethylene-d_4:-d_2:-d_0. Therefore it appears as though this heterogeneous system proceeds by the "carbene" mechanism.



(1)



(2)

The results obtained using three basically different catalysts systems and different ratios of 1,7-octadiene (I) and 1,7-octadiene-*1,1,8,8*-d_4 provide strong evidence that the olefin metathesis reaction proceeds through a one carbon, chain reaction mechanism. The most reasonable intermediate is a metal-carbene complex. Whether the true catalyst is a free metal-carbene or a complex "carbenoid" precursor[1,20,35] must await further results.

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References and Notes

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(28) See ref 1 and 27 for discussion of both possibilities.
(29) For example, if the initial estimate of the metal-ethylene-d_4:-d_2:-d_0 ratio was 1:0:1, 20 cycles were required to reach convergence.
(30) If the ethylene and octadiene units are not allowed to rotate in the intermediate complexes, only atoms 1 and 2 in Scheme VI equilibrate, the predicted ratio of ethylene-d_4:-d_2:-d_0 is 1:1:1 at I/II = 1.
(31) If both double bonds are allowed to equilibrate with both methylene units of the ethylene, atoms 1, 2, 3, and 4 in Scheme VI equilibrate, a ratio of ethylene-d_4:-d_2:-d_0 of 1:1.33:1 at I/II = 1 is predicted.
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(33) The value of *a* determined experimentally is *a* = ½ the coefficient for ethylene-d_2.
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