

A STUDY CONCERNING THE MECHANISM
OF THE OLEFIN METATHESIS REACTION USING THE
METATHESIS OF LABELED 2,8-DECADIENES

By

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ABSTRACT

A STUDY CONCERNING THE MECHANISM OF THE OLEFIN METATHESIS REACTION USING THE METATHESIS OF LABELED 2,8-DECADIENES

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The mechanism of the olefin metathesis reaction has been under intensive investigation in recent years. Previous experiments that have studied the metathesis of deuterium labeled diolefins have indicated that a non-pairwise carbene mechanism is operating rather than the originally proposed pairwise schemes. However, these studies did not precisely account for possible isotopic scrambling in the reactants or products that would, if occurring, lead to ambiguous results.

This study investigates the metathesis of isotopically labeled 2,8-decadienes which allows the monitoring of all of the competing metathesis processes and accounts for the scrambling of the labels in the starting material and products.

Initially the metathesis of isomerically labeled cis, cis-2,8-decadiene was investigated. This reaction, catalyzed by several transition metal based non-supported catalysts, yields cyclohexene and cis- and trans-2-butene

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irreversibly in high yield and selectivity. In the early stages of the reaction the formation of cis-2-butene is favored over trans-2-butene, and then the butenes are isomerized by a metathesis process to give a thermodynamically stable mixture eventually. At the same time, the starting material isomerizes by a similar process. The two isomerizations have been related by graphical methods, and a kinetics model accounts for this relationship.

The results of the studies of the metathesis of isomerically labeled decadienes are used to interpret the results obtained from the metathesis of mixtures of d_0 - and d_6 -2,8-decadiene. It was found that the 2-butenes can be sampled at conversions of starting material of $\leq 40\%$ which will give isotopic distributions that will distinguish between the non-pairwise and pairwise schemes. The non-pairwise mechanism has been implicated from the results obtained.

Some evidence was also found for possible initiation and termination modes of the olefin metathesis reaction. An initiating metal-methylene species was trapped with one end of 2,8-decadiene to yield propylene. The source of each fragment of propylene was determined by deuterium labeling. Ethylene was also observed and is believed to arise from a slow dimerization of the metal-methylene.

To
Bonnie

"I know a passion still more deeply charming
That fever'd youth e'er felt; and that is love,
By long experience mellow'd into friendship."

-Thomson

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I would like to take this opportunity to express my appreciation for the guidance and patience extended to me by my research preceptor, Dr. Robert H. Grubbs, and to wish him and his family well on the occasion of their move to Pasadena and Caltech.

I would also like to recognize the members of my research committee, Dr. Michael W. Rathke, Dr. Carl H. Brubaker and Dr. Richard H. Schwendeman, who have provided helpful input into this work.

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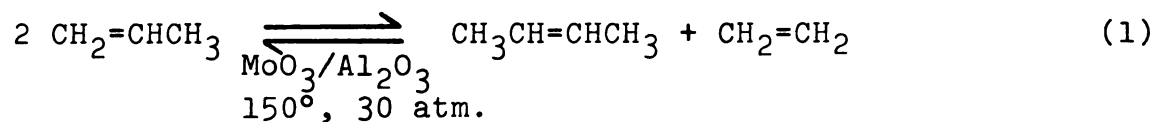
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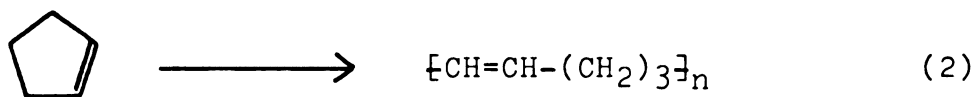
INTRODUCTION

One of the most interesting reactions in organic chemistry is the olefin metathesis reaction which involves a unique transition metal catalyzed transalkylidenation between olefins. Since its discovery a large volume of research directed towards the elucidation of the mechanism and exploitation of the versatility of the metathesis reaction has been reported and reviewed.¹ Some of the general features of the reaction will be outlined along with a review of recent published results that are pertinent to the results presented here.

In 1964, Banks and Bailey² reported that propylene disproportionates over a heterogeneous catalyst yielding 2-butene and ethylene (equation 1).



Later, Calderon³ found several homogeneous systems capable of metathesizing a wide variety of linear olefins. At about the same time, similar catalysts were found to promote the ring opening polymerization of cycloolefins such as cyclopentene (equation 2).⁴



It was soon determined that these two processes, disproportionation and ring-opening polymerization, were specific cases of a new general type of reaction. The term "olefin metathesis" was then proposed to describe this reaction.⁵

The olefin metathesis reaction is initiated by a wide variety of transition metal based catalytic systems. These catalyst recipes have been grouped into two general types based on their preparation and handling.

The first group of catalysts are the "supported catalysts". These typically involve transition metal compounds impregnated on an inert, high surface area support and have found some use in industrial processes.⁶ Some typical systems are shown in Table 1. Although most of these catalysts require high operating temperatures and pressures, the rhenium oxide based system can promote metathesis at ambient temperature and pressure.⁷

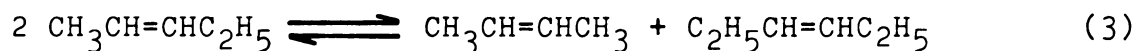
This body of work deals exclusively with the second type of catalytic systems referred to as the "non-supported catalysts". Typical examples are also given in Table 1. These systems generally contain a mixture of a transition metal complex of either tungsten, molybdenum or rhenium with a main group metal alkyl "co-catalyst" in an inert non-polar solvent. Some catalytic systems require promoters such as oxygen or ethanol.¹² The resulting catalysts are capable of

Table 1. Typical Olefin Metathesis Catalytic Systems

Supported	Reference
$\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$	7
$\text{MoCO}_6/\text{Al}_2\text{O}_3$	8
$\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$	9
WO_3/SiO_2	10
$\text{MoO}_3/\text{Al}_2\text{O}_3$	2,11
Non-Supported	Reference
$\text{WCl}_6/\text{EtAlCl}_2/\text{EtOH}$	3,12
$\text{WCl}_6/\text{nBuLi}$	13
$\text{WCl}_6/\text{SnMe}_4$	14
$\text{Mo}(\text{NO})_2\text{Cl}_2(\text{P}\phi_3)_2/\text{Me}_3\text{Al}_2\text{Cl}_3$	15
$\text{Re}(\text{CO})_5\text{Cl}/\text{EtAlCl}_2$	16
$\text{W}(\text{CO})_6/\text{CCl}_4/h\nu$	17
$\text{WOCl}_4/\text{Me}_2\text{Zn}$	18

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promoting metathesis in very low concentrations. Typical reactions are conducted with olefin/metal ratios between two hundred and five hundred. Hughes¹⁹ has found that the rates of reaction are generally first order in both catalyst and olefin under these conditions. He has also found that the energy of activation is under 10 kcal/mole. This implies that entropy differences are important contributors to product distribution since the difference in the ground state energies between most olefins is small. The metathesis of 2-pentene illustrates this point. By using several different catalysts an equilibrium is quickly reached between the products and reactants shown in equation 3



based solely on a statistical distribution of olefins.¹⁹ Thus, in the case of most olefins, conversions of starting material to products can be at the most 50%.

As seen in Table 1 there are a wide variety of catalytic systems differing in oxidation states, ligands and co-catalysts that can all promote the same reaction. It is then difficult to describe the nature of true catalytic site especially when the non-supported catalysts may be either homogeneous or heterogeneous. Most of these catalysts are quite sensitive to oxygen or moisture and usually do not tolerate the presence of functional groups other than the carbon-carbon double bond.²⁰ A discussion describing recent

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results regarding the interaction of transition metal complexes with main group compounds in metathesis systems will be presented later. At this point an outline of the important mechanistic studies published recently regarding the actual rearrangement step of the metathesis process will be presented.

The first mechanistic consideration of the olefin metathesis reaction was to determine whether the rearrangement involved a transalkylation (Figure 1) or a transalkylidenation (Figure 2). The process illustrated in Figure 1 is a redistribution of alkyl groups around an ethylene nucleus. The second possibility requires an unprecedented carbon-carbon double bond cleavage and scrambling of alkylidene units (Figure 2).

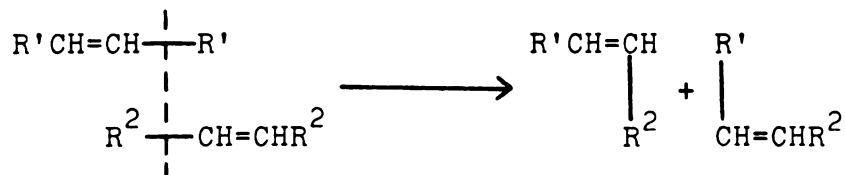


Figure 1. Transalkylation

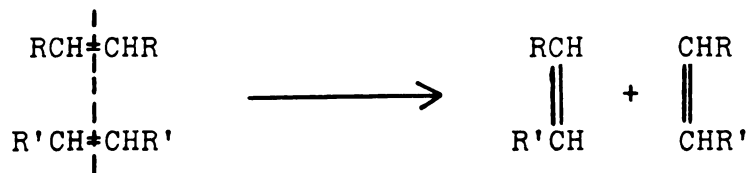
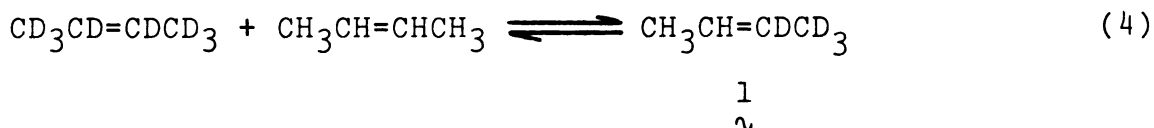


Figure 2. Transalkylidenation

Calderon²¹ devised a simple experiment from which he concluded that a transalkylidenation is operative. He studied the metathesis of a mixture of fully labeled and unlabeled 2-butene according to equation 4



and found only one new olefin 1. This product can only arise via a carbon-carbon double bond cleavage. Similar studies performed with other catalysts using C¹⁴ labeled olefins reached the same conclusion.²²

The first mechanistic schemes proposed to account for this unique process generally called for the scheme shown in Figure 3. This involves the initial formation of a bis-olefin metal complex 2 followed by a rearrangement to a new bis-olefin complex 4 through a "quasi-cyclobutane" transition state 3 where M denotes the active catalyst.²³ Most of the support for such a concerted rearrangement was based on theoretical discussions that attempted to illustrate how low lying metal d-orbitals could promote a non-allowed Woodward-Hoffman 2 + 2-cycloaddition.²⁴

Pettit²⁵ found that cyclobutanes are unreactive to metathesis conditions and are never found as products. As an alternative to the quasicyclobutane model he proposed a tetramethylene metal species 5.

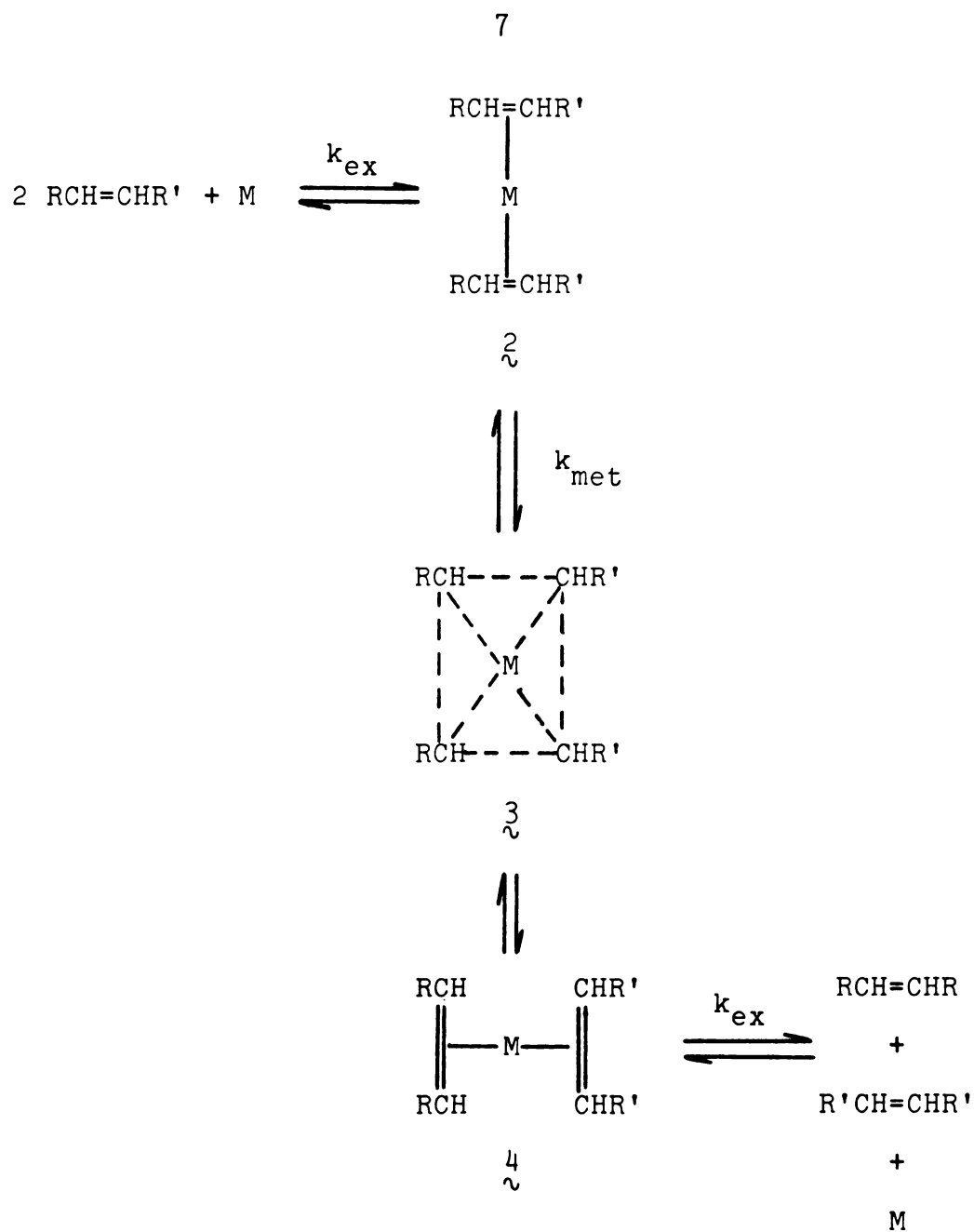
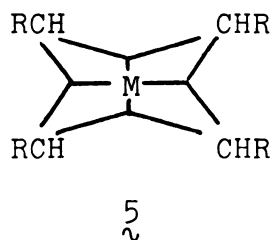


Figure 3. The pairwise quasicyclobutane scheme



Grubbs²⁶ proposed that a metallocyclopentane intermediate may be involved in a pairwise scheme as shown in Figure 4. Experimental evidence supporting such a scheme was found by preparing a tungsten metallocyclopentane and subjecting it to metathesis conditions. Through appropriate labeling studies it was discovered that the olefins produced could be best explained by a rearrangement of intermediates such as 6 and 7. There have been several precedents for such metallocyclopentanes, and they are presently being investigated extensively.²⁷ However, one of the objections to all of the pairwise schemes mentioned here was the questionable existence of bis-olefin complexes 2 and 4. Such complexes have never been isolated from metathesis reactions and are rare in transition metal chemistry.¹

During the time the pairwise schemes were being presented, experimental evidence was found that seemed to contradict these schemes. Dolgoplosk²⁸ found that induction periods are required for ring-opening polymerizations, and high molecular weight products are observed in the early stages of the reaction. These are both qualities of a chain reaction. Scott²⁹ discovered that these high molecular

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weight polyalkenamers are linear and that the low molecular weight oligomers are macrocyclic. It was also found that these macrocycles did not result from an intermolecular reaction between two smaller rings which a pairwise scheme requires.

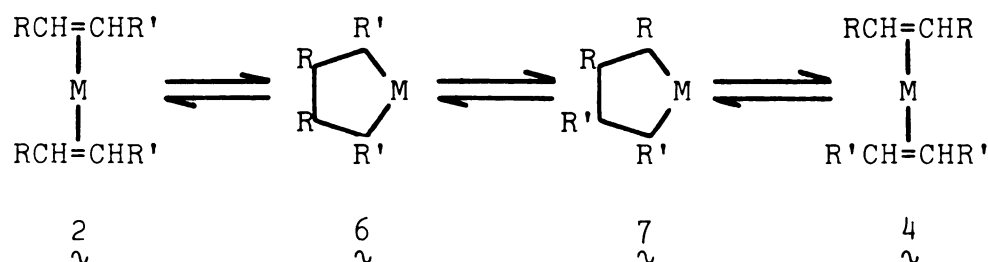


Figure 4. Metallocyclopentane mechanism for olefin metathesis

The pairwise scheme can still conceivably account for these seemingly contradictory results. The formation of linear polymers in ring-opening polymerizations can be explained by the reaction of a trace acyclic olefin impurity with a large macrocycle. Theoretically only one molecule would be capable of opening a ring with a molecular weight of several thousand. The accumulation of high molecular weight products in the early stages of the reaction can be explained by a kinetics argument. Referring back to Figure 3, one need only consider the respective rates of the olefins onto and off of the metal center (k_{ex}) and the rate of the actual metathesis rearrangement step

(k_{met}). If $k_{\text{ex}} \ll k_{\text{met}}$ the olefins would remain attached to the metal during several metatheses before dissociating from the metal. In this way high molecular weight products are accumulated very quickly. This possibility, once referred to as the "sticky-olefin" hypothesis, has been challenged by Hughes¹⁹ and recently by Katz³⁰ who maintain that the metathesis step is rate determining, i.e., $k_{\text{met}} \ll k_{\text{ex}}$.

A new type of mechanistic scheme was proposed by Chauvin³¹ the better to explain the kinetics and product distributions typical of cycloolefin polymerizations. The scheme shown in Figure 5 differs from the other schemes in that it is a non-pairwise chain reaction involving odd number carbon intermediates. The first step involves the formation of an initiating metal carbene 8 (also referred to as a metal alkylidene) that reacts with a single olefin creating a species that may resemble a metallocyclobutane 9 . This three carbon metallocycle is then cleaved along a different axis to give a new propagating metal carbene 10 and a new olefin. During the past few years much work, including the study presented here, has been directed toward the distinction between the pairwise schemes and this non-pairwise pathway.

Calderon and Kelly³² have used this scheme to account for the product distributions of the macrocyclic oligomers from ring-opening polymerizations. As mentioned earlier it was found that these products are not formed from the

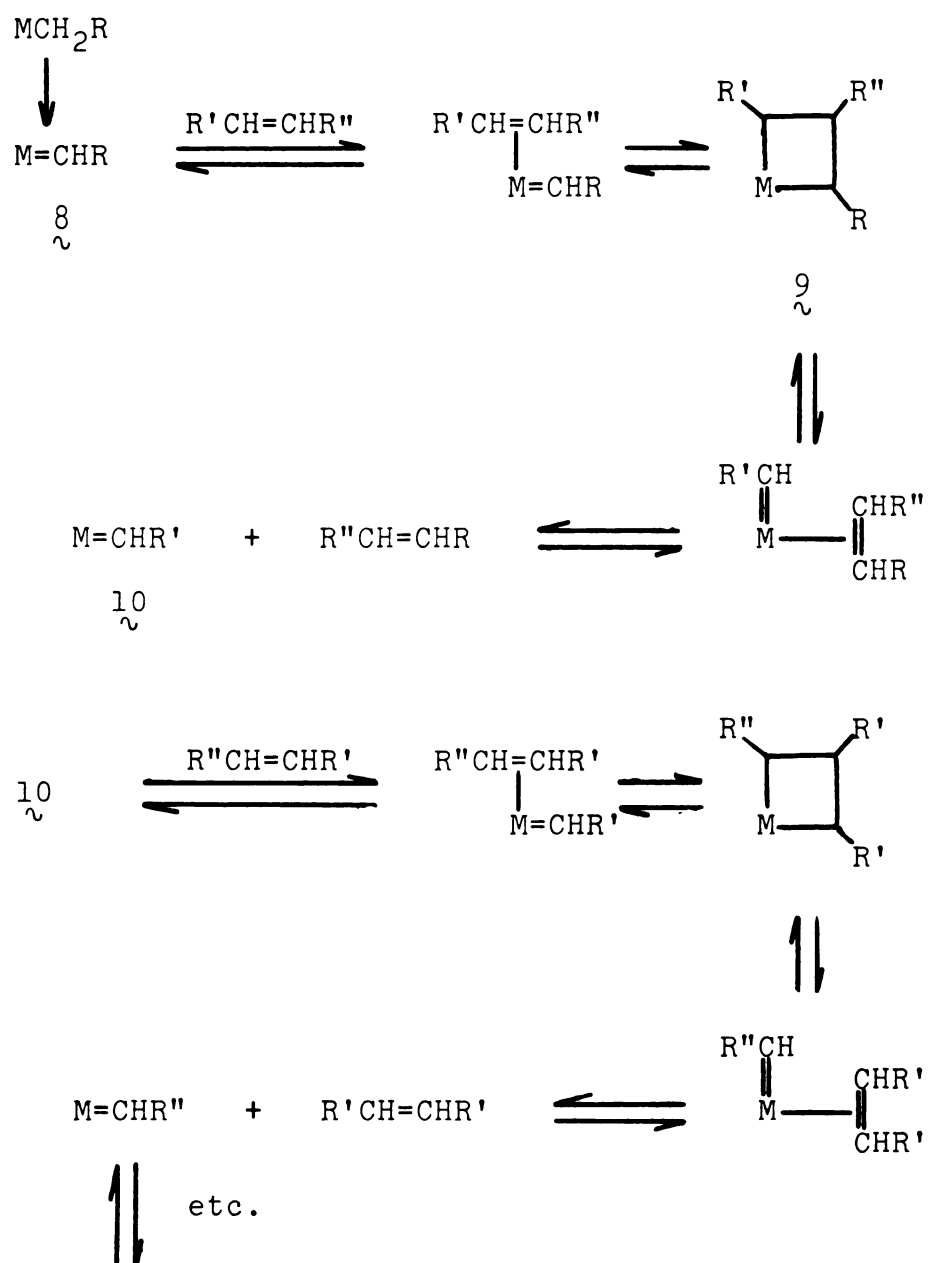
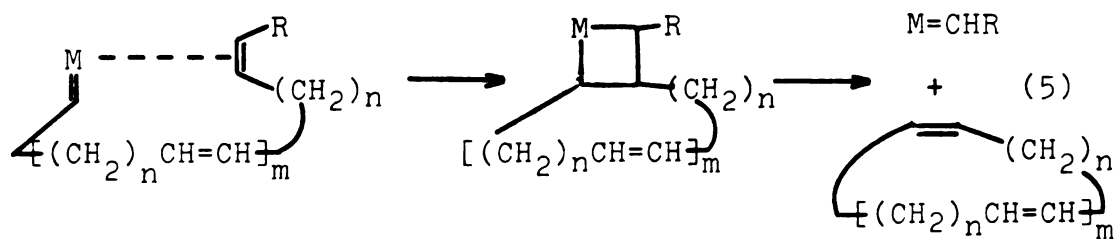


Figure 5. The non-pairwise carbene chain mechanism

intermolecular reaction from two smaller rings, and so a metal carbene "back-biting" scheme was proposed (equation 5).



Katz³⁰ conducted several experiments that produce results favoring the odd-carbon carbene scheme. He studied the cross products formed at low conversion between cyclooctene and symmetrical olefins. In a typical study (Figure 6) the concentrations of the C₁₄ cross product $\frac{1}{2}$ were significant at very low conversions. A pairwise scheme would predict that only the C₁₂, C₆ and C₁₆ products will be formed initially. Katz found that the C₁₄/C₁₆ and the C₁₄/C₁₂ ratios were approximately 2:1 which matches the random distribution of alkylidenes predicted by the Chauvin scheme. However, as Katz admits, this distinction is only valid if the metathesis step is rate determining. As in the other experiments, the other extreme, $k_{\text{ex}} \ll k_{\text{met}}$, can be used to explain the results by a pairwise scheme.

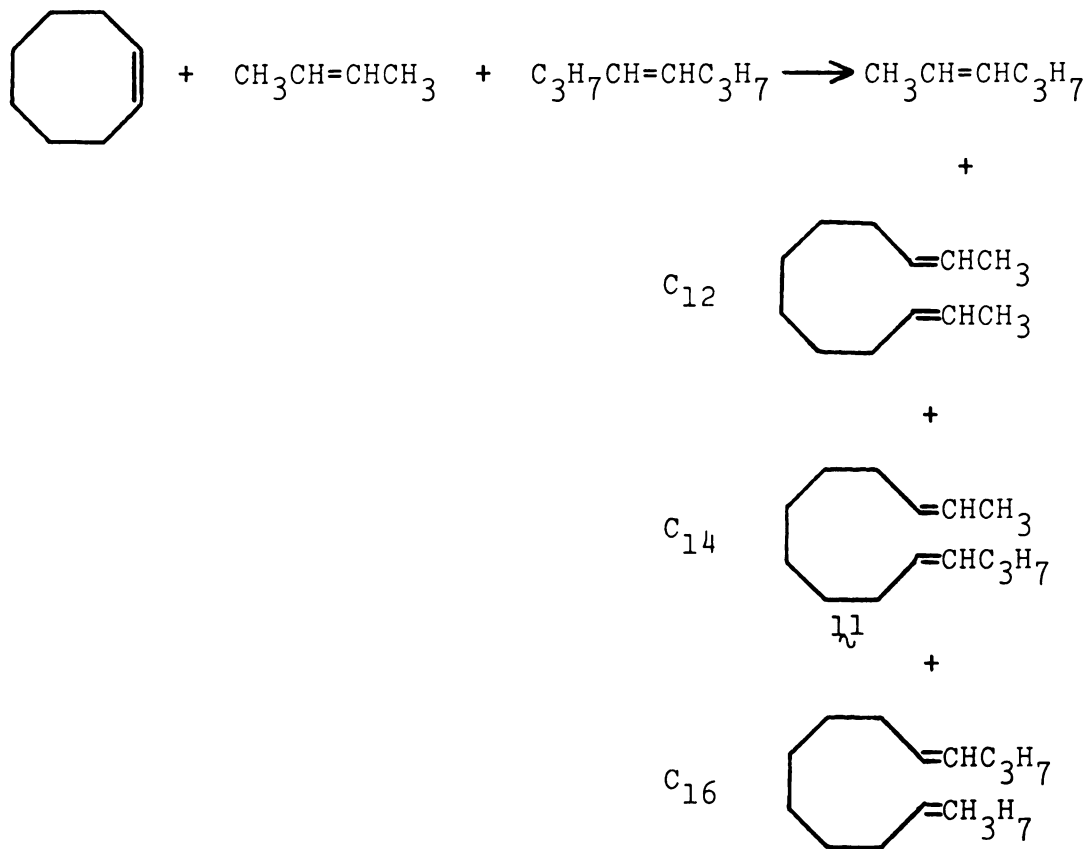
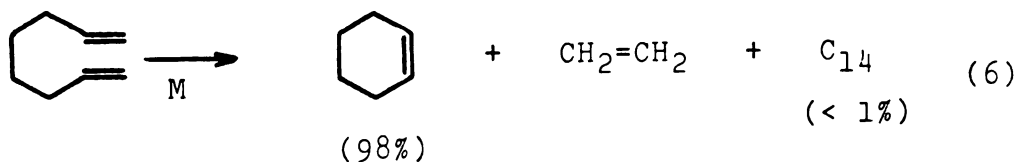
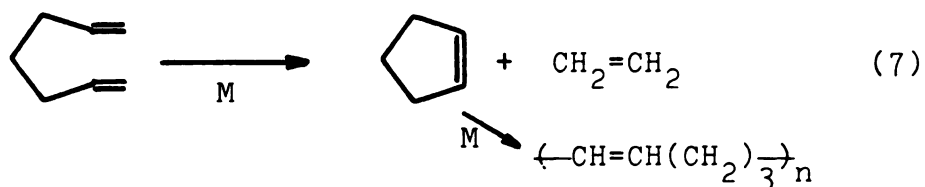


Figure 6. Cross product metathesis studies

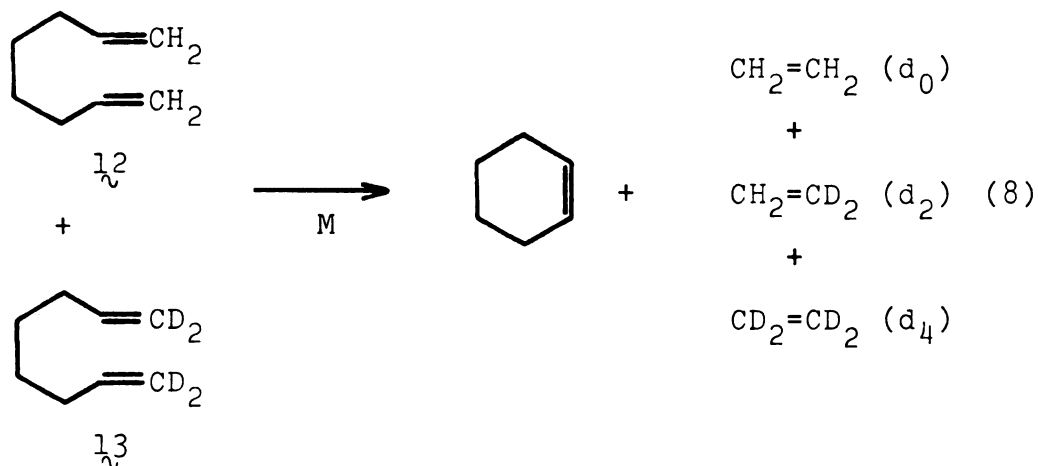
Work in this laboratory has exploited the unique metathesis of 1,7-octadiene to distinguish between the two schemes. As shown in equation 6,



1,7-octadiene undergoes an intramolecular cyclization to form cyclohexene and ethylene in high yield and selectivity. Cyclohexene is one of the few simple olefins that remarkably does not undergo further metathesis.³³ With any other α,ω diolefin the resulting cyclic olefin formed polymerizes to form polyalkenamers as shown for 1,6-heptadiene in equation 7.



Grubbs³⁴ has reported the metathesis of mixtures of terminally labeled and unlabeled 1,7-octadienes with three different catalysts giving cyclohexene and labeled ethylenes as shown in equation 8.



It is possible to predict the distribution of the labeled ethylenes according to either scheme and compare the calculated values with those obtained experimentally. All of the pairwise schemes, regardless of the particular key intermediate, can be considered together. If a pairwise scheme were operating, then the two extreme cases mentioned earlier must be considered. Referring once more to Figure 3, if the metathesis step is rate determining, $k_{\text{met}} \ll k_{\text{ex}}$, then it is easy to see that d_2 -ethylene cannot be formed in the initial stages of the reaction. Assuming a 1:1 mixture of 1,2:1,3, then the $\text{d}_0:\text{d}_2:\text{d}_4$ ethylene ratios would be 1:0:1. The second extreme for the pairwise scheme, $k_{\text{ex}} \ll k_{\text{met}}$, involves a much more difficult calculation. Using an iterative scheme described elsewhere, a 1:1.6:1 ratio for the $\text{d}_0:\text{d}_2:\text{d}_4$ ethylene is predicted. These numbers arise from the intramolecular nature of the reaction. The carbene scheme predicts a random distribution of the

methylene units, or a 1:2:1 distribution. The key distinction then is between the "sticky-olefin" pairwise scheme, where $k_{\text{ex}} \ll k_{\text{met}}$, and the random distribution for the carbene scheme. Any intermediate pairwise scheme where k_{ex} is comparable to k_{met} will fall between the two extremes. The predicted values for the ethylene distributions for the reaction where $1_2:1_3$ is 1:1 are summarized in Table 2.

Table 2. Predicted Ethylene Distributions for the Metathesis of a 1:1 Mixture of 1_2 and 1_3

Scheme	Calculated		
	d_0	d_2	d_4
Pairwise			
$k_{\text{met}} \ll k_{\text{ex}}$	1	0	1
$k_{\text{ex}} \ll k_{\text{met}}$	1	1.6	1
Carbene	1	2	1

By using different ratios of $1_2:1_3$ and different catalysts, Grubbs found that the ethylene distributions at low conversions most closely match the predicted carbene ratios. Katz³⁵ conducted a very similar study to this and came to a similar conclusion. The mechanism was postulated to follow the scheme shown in Figure 7. The results account for the propagation steps of the chain mechanism proposed by Chauvin. In this case the chain carrying species is the metal-methylene moiety. The initiation and termination

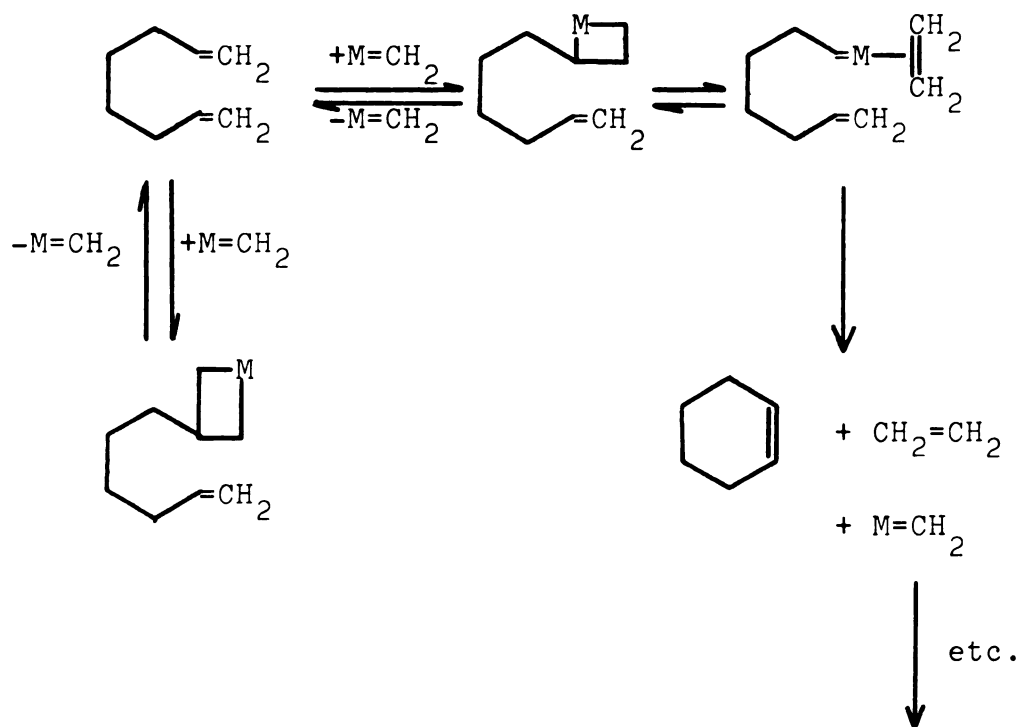


Figure 7. Proposed mechanism of 1,7-octadiene metathesis

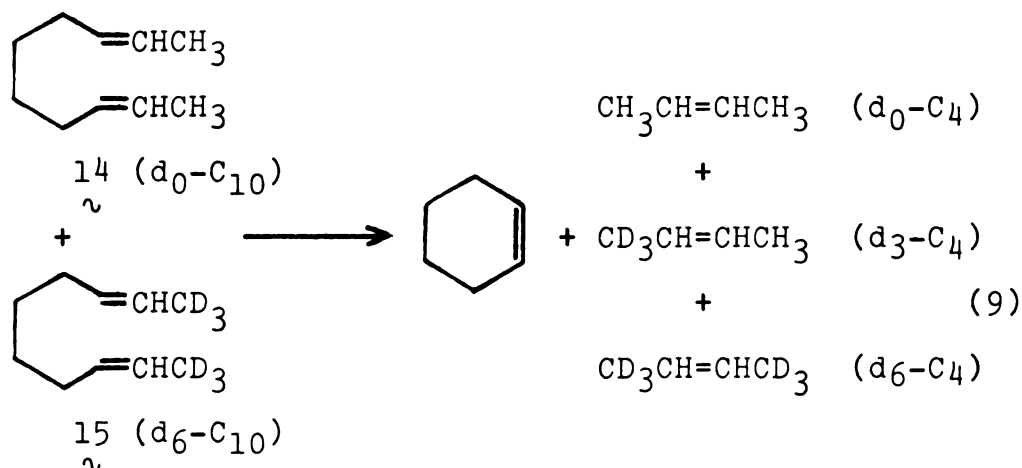
steps will be considered later.

There are some important restrictions that must be placed on the study of the 1,7-diene systems. It is obvious that if there is an intermolecular scheme that scrambles the labels in the starting material upon immediate contact with the metal then isotopic distribution in the ethylenes would be the same for either mechanism. During Grubbs' study of the low conversion metathesis of $12:13$ mixtures, the starting material was isolated and found to have undergone minimal scrambling. At higher conversions significant scrambling occurred via a degenerate metathesis, but was not studied precisely.

Another possible complication is that the labeled and unlabeled ethylenes produced, may scramble via metathesis or other pathways at the metal center before dissociating from the catalyst, again giving ambiguous results. To check for this possibility d_0 ethylene was passed through the reaction vessel, and the new ethylene mixture was isolated. If there were a secondary scrambling scheme, the external ethylene would change the equilibrium between the deuterated ethylenes. This was not found since the $d_2:d_4$ ratio remained the same. However, this is an external probe, and it is not certain whether the ethylene can be properly mixed with the catalyst to achieve realistic results.

A new set of experiments was proposed to more precisely account for the isotopic scrambling in the starting material and products. It was decided to turn to

the study of the metathesis of mixtures of unlabeled $\underset{\sim}{14}$ and labeled $\underset{\sim}{15}$ 2,8-decadienes according to equation 9.



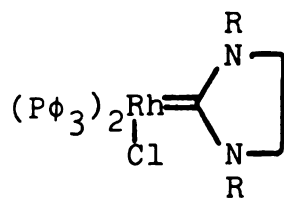
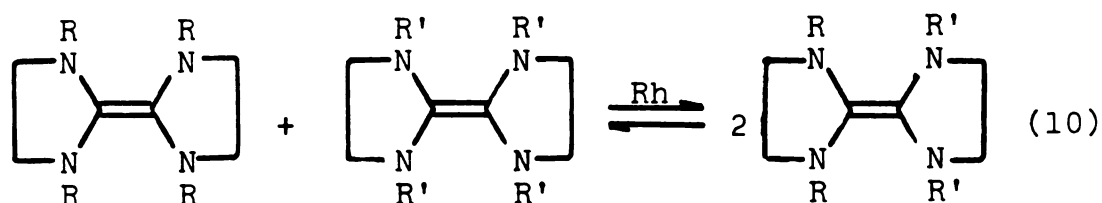
In a study analogous to the studies of the 1,7-octadiene system the 2-butenes were isolated during the reaction and analyzed for isotopic distribution. At the same time the starting material was also isolated and examined for scrambling. By understanding the isotopic scrambling processes competing with productive metathesis, $\text{d}_0:\text{d}_3:\text{d}_6$ -2-butene ratios were obtained which satisfy the restrictions placed on such studies mentioned earlier. In order to follow this scrambling process the metathesis of isomerically pure *cis,cis*-2,8-decadiene was initially studied in some detail. The isomeric scrambling, or isomerization, is then compared to the isotopic scrambling.

Results were also obtained from the 2,8-decadiene metatheses that pertain to the initiation and termination steps of the olefin metathesis reaction. At this point a

discussion is presented on published results dealing with these processes and the involvement of metal carbenes in the reaction. This discussion will be followed by a review of some of the important stereochemical studies of metathesis reported in the literature.

As stated earlier, the results from the 1,7-octadiene studies indicated that the propagating steps in the olefin metathesis reaction seem to involve a metal carbene odd-carbon interchange. The involvement of carbenes in the metathesis reaction has been implied by other recent studies.

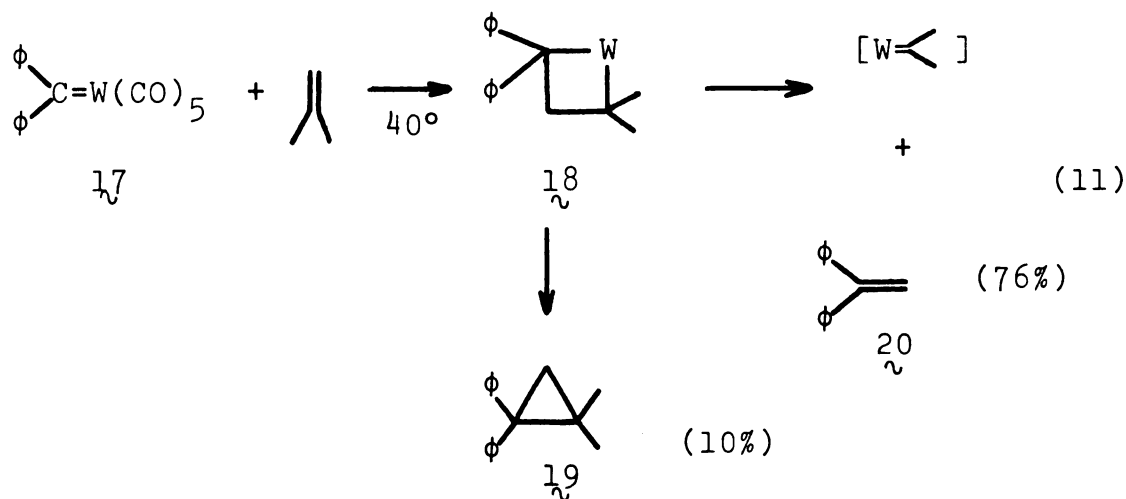
Cardin³⁶ isolated a heteroatom stabilized rhodium carbene 16 during the metathesis of the amines shown in equation 10.



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O'Neill³⁷ and Dolgoplosk²⁸ independently found that diazo compounds decompose under metathesis conditions to nitrogen and an olefin. Dolgoplosk also generated an active catalyst from WCl_6 and phenyldiazomethane and proposed that the active catalyst is a metal carbene species.

Casey has synthesized some non-heteroatom stabilized tungsten carbenes and has studied their reactions with olefins. The diphenyl tungsten carbene **17**³⁸ reacts with isobutylene to give a new olefin **20** and a cyclopropane **19** (equation 11).

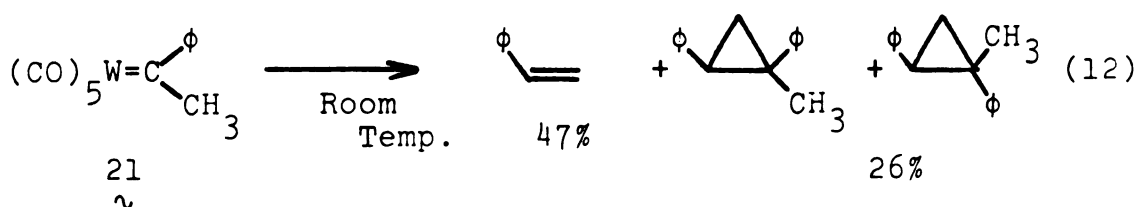


An intermediate metallocyclobutane **18** was proposed as a common intermediate for both products with the formation of **20** via a Chauvin type of pathway. No other olefins were produced in this stoichiometric reaction implying that the most substituted carbene is favored due to an electrophilic

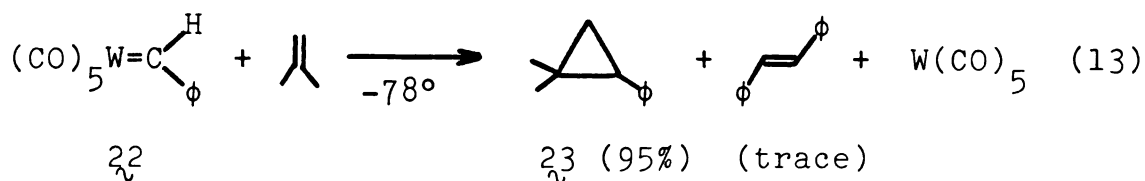
character of the carbene carbon.

Although this reaction is irreversible Katz³⁹ has reported that $\underset{\sim}{17}$ is a clean catalyst for the metathesis of many different olefins. However, others have been unable to repeat this work.⁴⁰

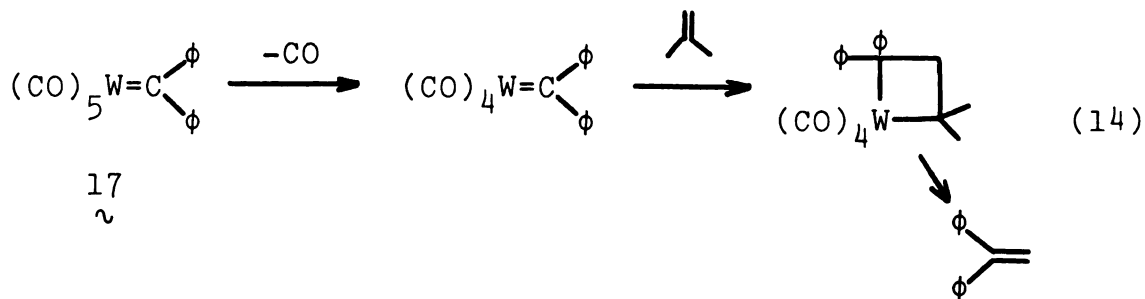
More recently Casey⁴¹ has studied the reactions of some unsymmetrical metal carbenes. Preparation of a methylphenyl carbene $\underset{\sim}{21}$ was conducted at low temperature, but when warmed to room temperature decomposed to styrene and some cyclopropanes (equation 12).



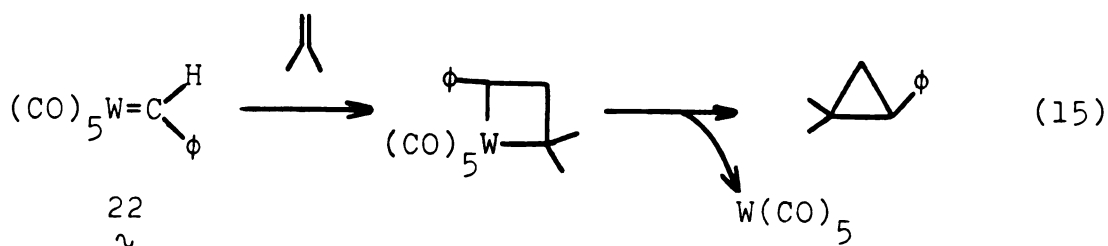
Although it was first believed that the cyclopropanes resulted from an intermediate metallocycle from the reaction of the carbene with styrene, it was found that external olefins are not incorporated in the products. Thus $\underset{\sim}{21}$ decomposes faster than reaction with olefins. Casey postulated a different scheme that did not involve metallocyclobutane intermediates. Casey⁴² also reported that the reaction of $\underset{\sim}{22}$ with isobutylene (and other olefins) forms almost exclusively the cyclopropane $\underset{\sim}{23}$ and a trace of stilbene according to equation 13.



The difference in reactivity and product distributions between the reactions of $\text{17}_{\sim}$ and $\text{22}_{\sim}$ with isobutylene has been noted by Casey.⁴² He has interpreted these results as evidence that $\text{17}_{\sim}$ must lose a CO ligand before olefin coordination can occur because of steric effects. This process affords a carbene olefin complex that can reversibly form a six coordinate metallocyclobutane which yields metathesis products (equation 14).

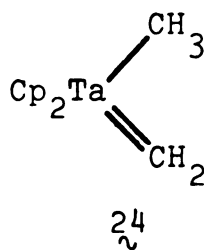


The less sterically hindered $\text{22}_{\sim}$ adds an olefin without loss of CO to form a seven coordinate metallocycle which then eliminates W(CO)_5 directly to give a cyclopropane (equation 15).

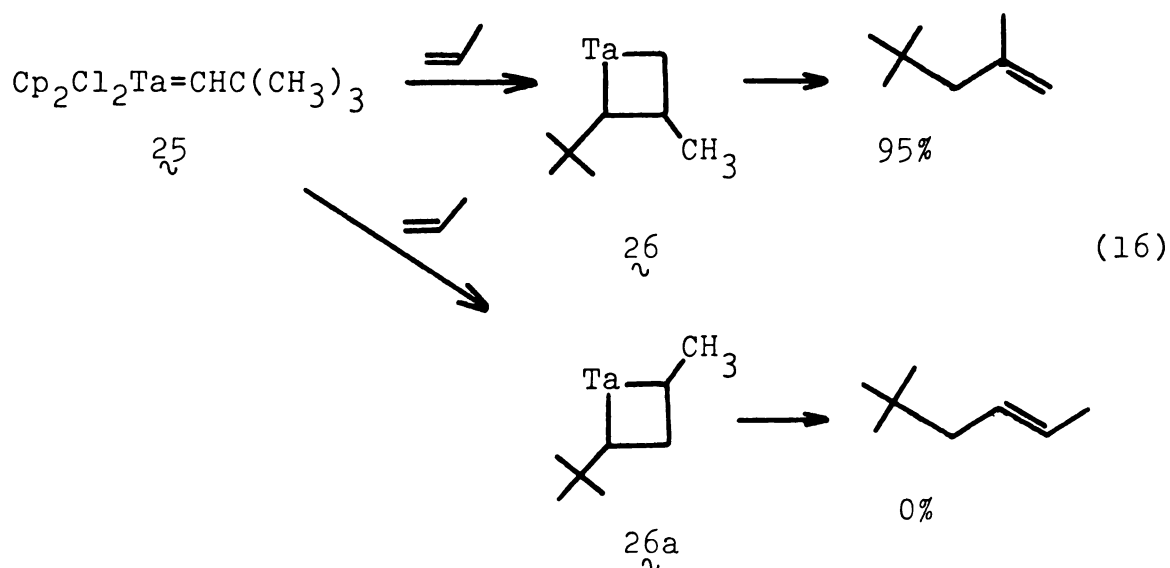


Gassman⁴³ has illustrated that cyclopropanes can be converted completely to olefins by a metathesis catalyst. He has also trapped a carbenoid species in very low yields with several Michael acceptors. In contrast to Casey's studies, these results imply a nucleophilic character of the metal carbene carbon.

Schrock⁴⁴ has isolated many tantalum and niobium alkylidenes. X-ray and NMR analysis of $\text{Cp}_2\text{Ta}(\text{CH}_3)=\text{CH}_2$ ⁴⁵ indicated that there is a high barrier of rotation in the metal-carbon bond implying the presence of a true double bond.



The chemistry of these metal carbenes most closely resembles that of phosphorus ylides.⁴⁶ Propylene was found to react in high yield with a neopentylidene 25 to give a new olefin in high yield (equation 16).



However, this reaction is irreversible, and there are no known tantalum or niobium based metathesis catalysts. Schrock also says that the preference of 26 over 26a could be explained by either electronic or steric arguments.

All of these model metal carbene studies have shown that carbenes may initiate metathesis and have been reacted with olefins to give products from a pathway believed to involve metallocyclobutanes.

Much work has also been conducted in the study of stable metallocyclobutanes. Green⁴⁸ has studied the formation of tungsten and molybdenum cyclobutanes formed by reduction of a tungsten π -allyl complex (Figure 8). Treatment of these metallocycles with acid yields the propylene hydride complex shown. From these results Green has postulated a scheme whereby an initiating carbene species is formed from an olefin and the active catalyst (Figure 9).

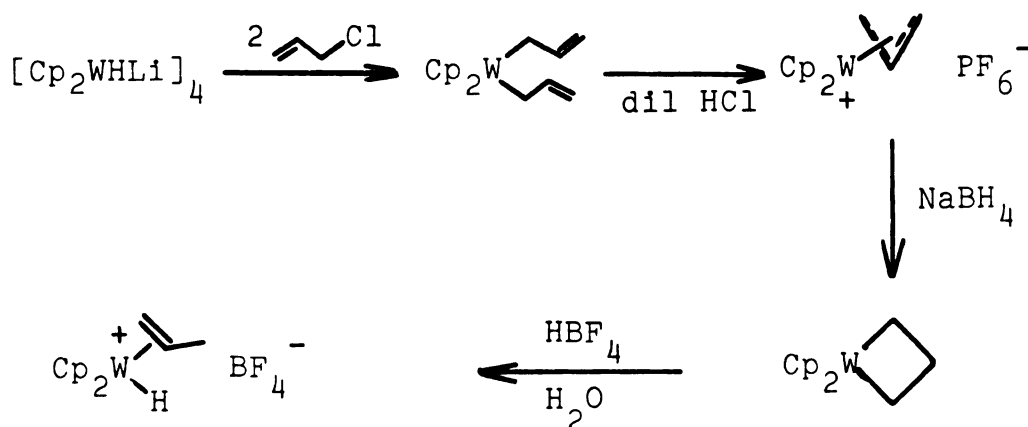


Figure 8. Formation of a tungsten metallocyclobutane

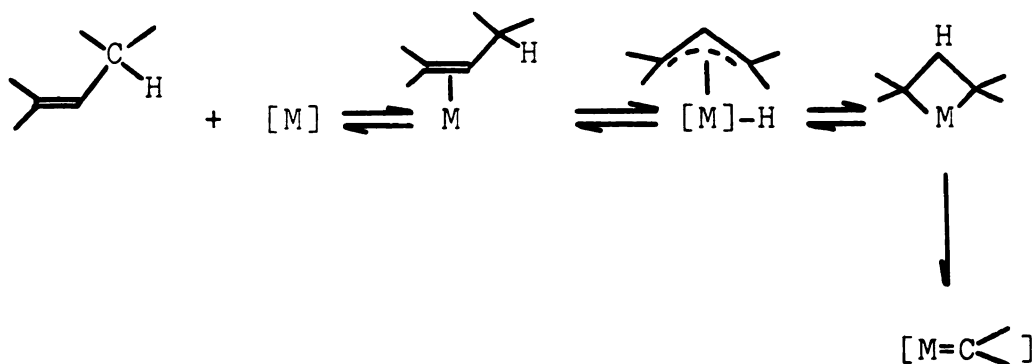
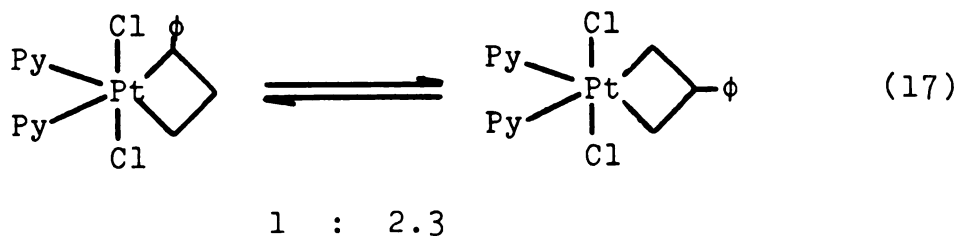


Figure 9. Proposed formation of a metal carbene from an olefin and an active metathesis catalyst

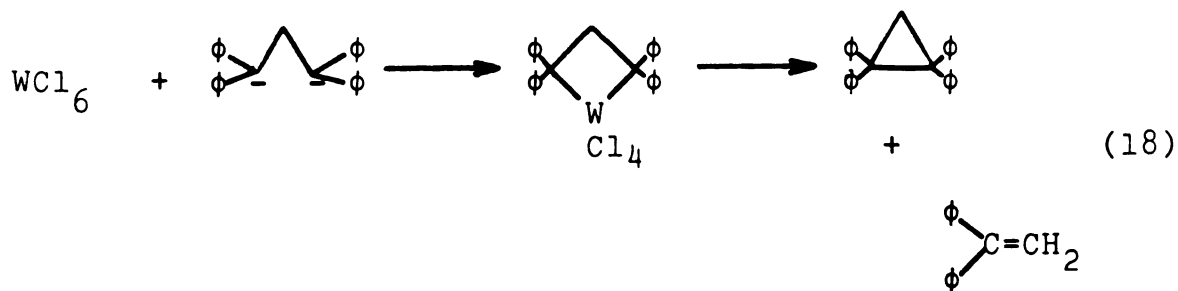
Puddephatt⁴⁹ has reported the isomerization of a platinum metallocycle which forms an equilibrium mixture in the relative amounts shown in equation 17.



He also reports that the data is most consistent with a concerted process without formation of an intermediate carbene complex. Thermolysis of these metallocyclobutanes yields quantities of propenylbenzenes and phenylcyclopropane. Styrene or ethylene was not observed from a metathesis process.

The platinum metallocyclobutanes have been characterized by x-ray crystallography. These results indicate that the ring is puckered significantly and that there is a tetrahedral distortion around the platinum center.⁵⁰

Another group⁵¹ has studied the in situ formation of tungsten metallocycles from the reaction of tungsten halides with the dianion shown in equation 18.



The metallocycles decompose to give mostly cyclopropanes and quantities of 1,1-diphenylethylene, the expected metathesis product.

Although most of the metallocyclobutanes described above yield cyclopropanes in varying yields, cyclopropanes are never found in significant quantities in metathesis systems. According to Gassman's work, if cyclopropanes are formed, they are converted to olefins by some other process.⁴³

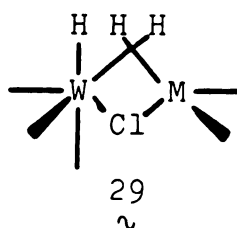
Mango⁵² has recently published a paper in which he used a classical thermodynamics argument to question the complete validity of the Chauvin scheme. He assumes that the proposed pathway is an equilibrium catalytic reaction. In other words, the distribution of products should be based only on the difference in the respective free energies of the products and reactants. If olefin A metathesizes to a new olefin B, then cyclopropanes should also originate from a common intermediate in the Chauvin scheme. Mango argued that since the differences in free energies between cyclopropanes and olefins are not great a significant amount of these cyclopropanes should be found in the reaction mixture. He concluded that whereas metal carbenes do react with olefins to give cyclopropanes and some metathesis products, these model studies only resemble the actual chemistry of olefin metathesis.

Judging from the results of Casey it can be argued that under metathesis conditions only six coordinate metallocyclobutanes are present. These decompose to give olefins exclusively. The formation of cyclopropanes would arise from some other intermediate such as a seven coordinate metallocycle which may not be available during metathesis. This would invalidate Mango's first assumption that cyclopropanes and olefins arise from a common intermediate.

There has been some evidence presented that implies that preformed metal carbenoids may arise from a catalyst mixture and act as the metathesis initiating species. It should be noted that most of the non-supported systems require an alkylating co-catalyst (Table 1). It is generally believed that the alkyl group from the main group metal co-catalyst is transferred to the transition metal, and a carbene is eventually formed.

Muetterties⁵³ examined several tungsten hexachloride based catalysts. In particular he found that when WCl_6 is treated with dimethylzinc, methane is evolved. When a deuterated solvent is used no deuterium incorporation in the methane is observed. Muetterties proposed that dimethylzinc methylates the tungsten in two steps yielding the dimethyl tungsten species 27 . This species undergoes a rapid α -elimination followed by a reductive elimination of methane to yield a methylene tungsten carbenoid 28 as shown in Figure 10. Ichikawa⁵⁴ also reported similar results from other WCl_6 based systems and found that the main group metal must be capable of donating a carbanion to tungsten.

Muetterties⁵³ doubts that a simple methylene species such as 28 is a likely metathesis precursor because of its expected high reactivity and instability under metathesis conditions. He proposed that some bridged bis-metal species such as 29 may be a more accurate description of the initiating species.



He noted that all metathesis catalysts involve halides and most often contain chloride ligands. This bridged model would better facilitate the required α -hydride elimination, Muetterties claims.

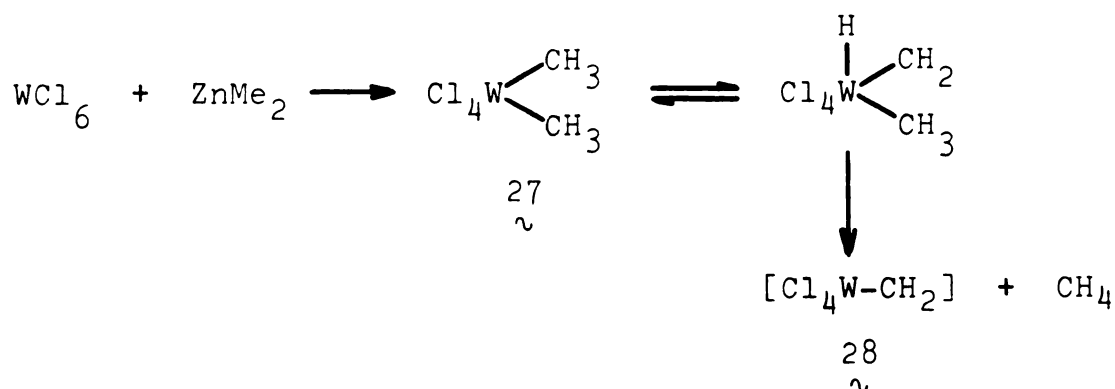
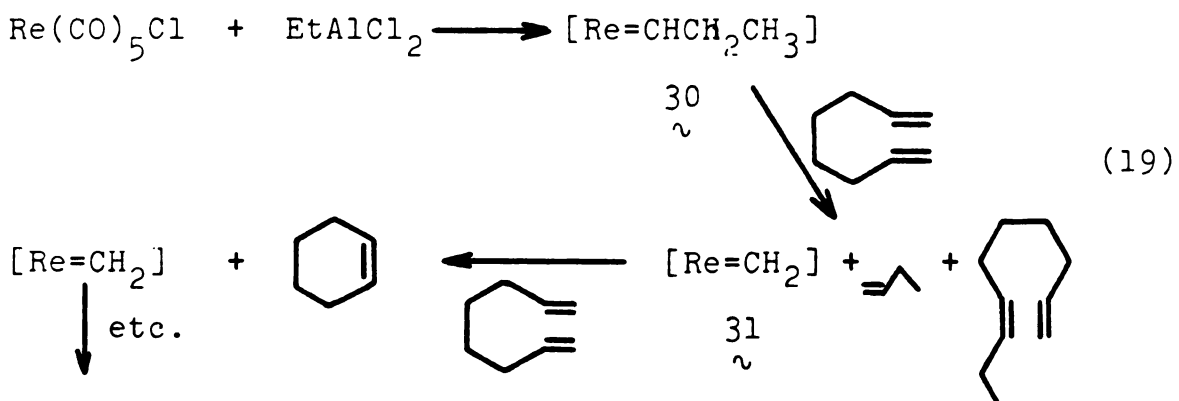


Figure 10. Formation of initiating metal carbene

Tebbe⁵⁵ has also noted types of compounds similar to 29 with organo-aluminum and tantalum hydride interactions. Benzce⁵⁶ studied the infrared spectra of several non-supported catalysts in solution and found evidence for Lewis-salt adduct formation between the transition metal complex and the co-catalyst.

Farona⁵⁷ reported the isolation of products which may have resulted from the reaction of an initiating metal carbene with an olefin. He studied the metathesis of 1,7-octadiene catalyzed by $\text{Re}(\text{CO})_5\text{Cl}/\text{EtAlCl}_2$. The product mixture was found to contain, besides cyclohexene, catalytic amounts of 1-butene and 1,7-decadiene. Farona proposed that these products originate from the reaction of a three carbon rhenium carbene $\overset{\sim}{\text{C}}_3$ with one end of 1,7-octadiene (equation 19).



These products are formed initially along with the propagating carbene $\overset{\sim}{31}$ which continues on to produce cyclohexene after the first catalytic turnover. The formation of $\overset{\sim}{30}$ was proposed to originate from the scheme shown in Figure 11. Compound $\overset{\sim}{32}$ was found in small amounts in the product mixture.

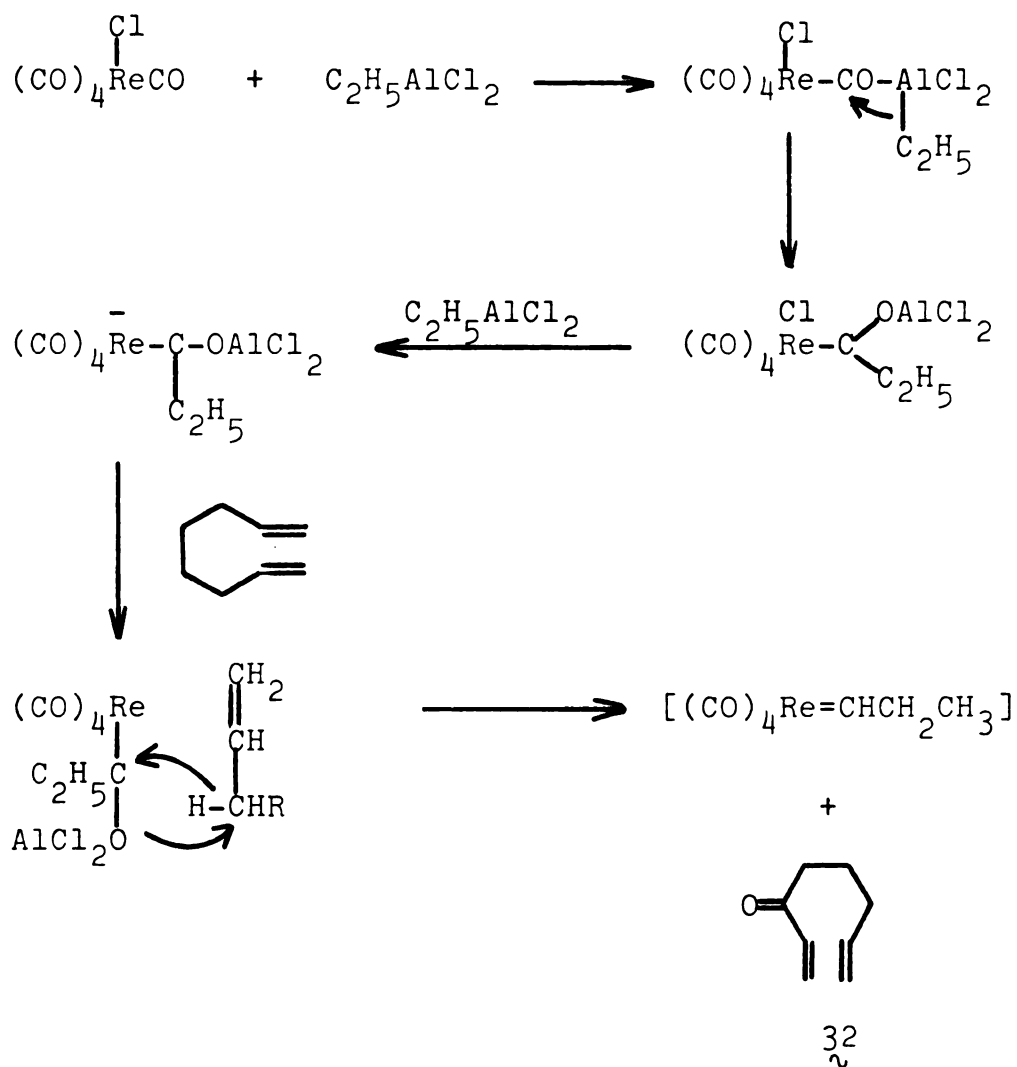
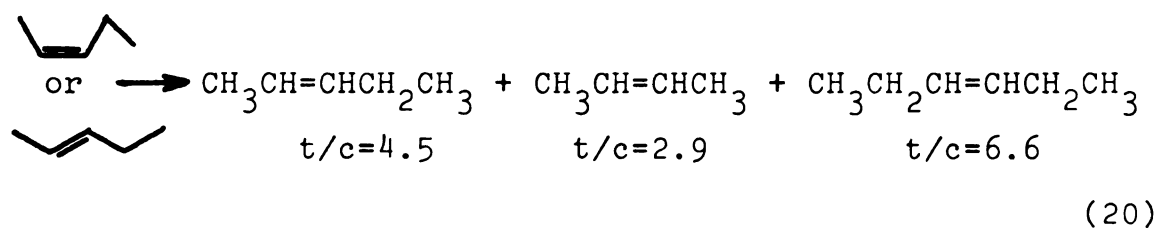


Figure 11. Proposed formation of an initiating metal carbene from a non-supported catalyst system and 1,7-octadiene

The stereochemistry of the olefin metathesis reaction has been studied and some stereospecificity has been observed. For example, the ring-opening polymerization of cyclopentene yields a linear polypentenamer with >95% cis double bond content.⁵⁸ The metathesis of acyclic olefins, however, generally shows moderate specificity only in the early stages of the reaction. Initially, cis olefins give cis products and trans olefins give trans products. As the reaction proceeds, the products and starting material isomerize, eventually yielding a thermodynamic mixture of isomers no matter which isomer is originally present. For example, Hughes⁵⁹ found that metathesis of either pure cis-2-pentene or pure trans-2-pentene eventually gives the same equilibrium mixture of 2-pentenenes, 2-butenes and 3-hexenes (equation 20).



However, in the early part of the metathesis of cis-2-pentene the trans/cis-2-butene ratio is less than one.

In most stereochemical studies of the olefin metathesis reaction, the change in the trans/cis ratios (t/c) is plotted against time or percent conversion of starting material. The latter plots are generally non-linear overall, but are roughly linear until about 40 percent

conversion of starting material.^{13,60} This section of the curve is usually extrapolated to 0% conversion, and a t/c ratio is obtained that reflects the stereospecificity during the first catalytic turnovers. These values change significantly with changes in the catalytic systems. In general, molybdenum catalysts are more specific than tungsten based catalysts.⁶¹ The specificity is also dependent on traces of oxygen,^{60a} the co-catalyst⁶² and the concentration of the catalyst.^{60a} These factors have made any systematic comparison of catalyst specificity difficult. However, some general trends have been noticed, and consistent results may be obtained from any particular catalyst.

Several groups⁶³ found that the olefin reactivity decreases in the following order: ethylene>terminal monosubstituted>internal disubstituted>trisubstituted>>tetrasubstituted. This order simply reflects the ease with which an olefin can complex with the active catalyst. Among terminal monosubstituted olefins, the alkyl group length does not affect the rate of metathesis.^{60b} For example, 1-pentene will metathesize at about the same rate as 1-hexene.

The metathesis of internal olefins has been studied extensively. It was found that cis isomers react faster than trans isomers.^{13,21,60a,62} Very pure trans olefins will metathesize only after an induction period of varying length. This induction period is lost when traces of

terminal or cis olefins are present.⁶⁴ Apparently trans olefins are not capable of participating in the initiating steps of metathesis.

There is good evidence that the isomerization of internal olefins as shown in equation 20 involves a metathesis reaction.^{19,21,60a,62} The isomerization process is referred to as a "degenerate" metathesis because no new olefins are formed. The normal "productive" metathesis produces olefins with a different number of carbons. Terminal olefins undergo degenerate metathesis much faster than productive metathesis. This fact was found only by labeling studies because this degenerate process will not exhibit isomerization.⁶⁵ Simple disubstituted olefins undergo degenerate and productive metathesis at about the same rate.⁶⁶ This characteristic should then be expected for the metathesis of 2,8-decadienes.

The difference between the degenerate and productive metathesis processes has been explained using a metal carbene scheme and is illustrated in Figure 12. When R' is hydrogen (terminal olefins) the degenerate metathesis is favored, or $k_d \gg k_p$, and when R' is a linear alkyl then $k_d \approx k_p$. The large difference in rates exhibited by terminal olefins has been attributed to either the preferred transfer of the alkyl group to the least hindered end of the olefin or to the formation of a more substituted carbene.⁶⁵ The isomerization of internal olefins can be seen to arise from the degenerate pathway. Any stereochemical study, such as

the 2,8-decadiene experiments presented here, must account for these competing processes.

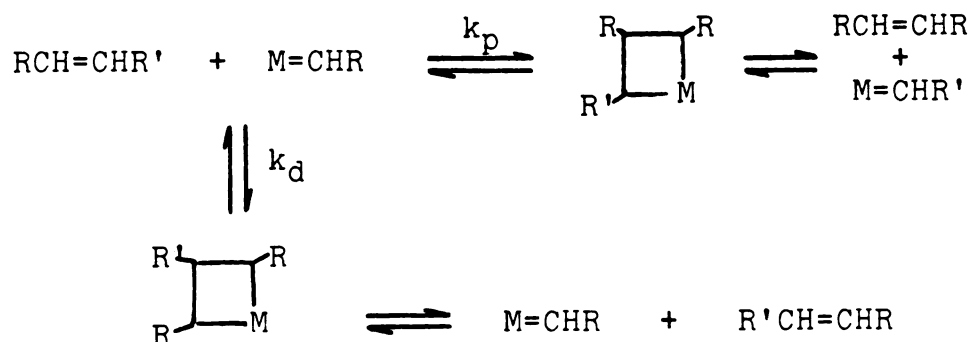


Figure 12. Degenerate and productive metathesis processes

Two different arguments have been presented to describe the origin of the specificity in the metathesis of internal olefins. Casey⁴² has discussed the selectivity in terms of the steric interactions in an intermediate puckered metallocyclobutane. By using the model shown in Figure 13, where L represents a relatively large substituent and S a smaller substituent, Casey proposed that the 1,3-diaxial interaction must be minimized.

This model successfully predicts that cis olefins will give cis products. The formation of a trans olefin must arise from a metallocycle that has a larger 1,3-diaxial interaction indicated by the asterisk in Figure 13. The same model will predict that trans olefins will preferentially metathesize to new trans olefins. This cyclobutane model has also been used by Casey^{41,42} to predict the

stereospecificity found in cyclopropane formation. Katz⁶⁷ has used a similar model to explain the specificity exhibited in ring-opening polymerizations.

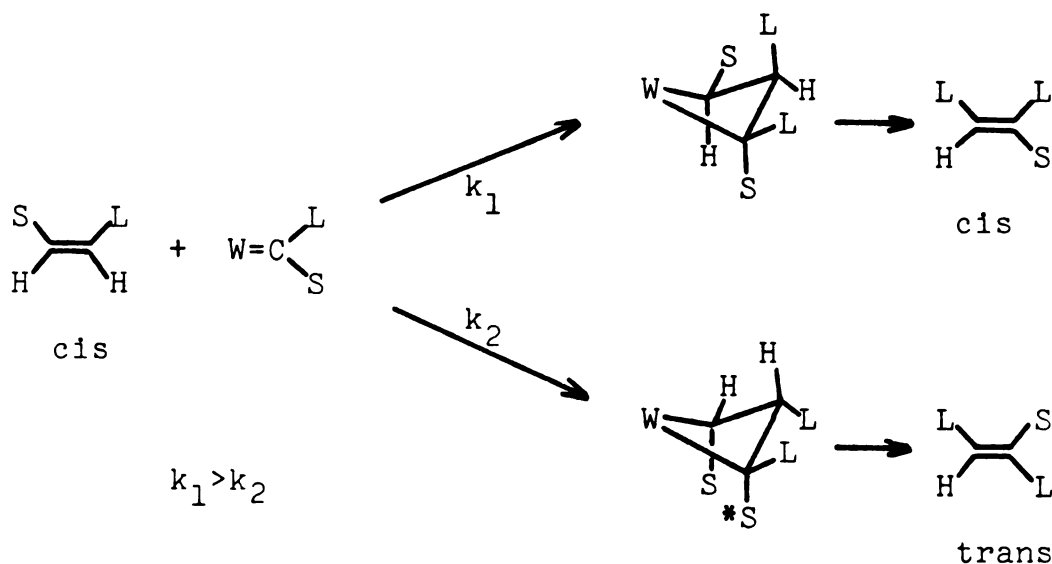


Figure 13. Metallocyclobutane model for explaining stereospecificity

Basset⁶⁵ has chosen a different model that considers only the approach of the olefin to the metal carbene as the important contributor to stereospecificity. This model focuses on the interaction of the empty metal p_z orbital with a π -bond of the approaching olefin. An intermediate metallocyclobutane may still be involved, but is not important for steric considerations. Basset's model, shown in Figure 14, illustrates the case where a cis olefin approaches a metal carbene containing two ligands (X) that are involved in determining the orientation of the approach of the olefin. Basset assumes that the metal carbene is in a fixed configuration where the alkyl group is opposite to

one of the ligands. The olefin will then approach in a way that minimizes the steric interaction between the olefin alkyl groups and the metal ligands. This model also successfully predicts that cis products will be formed from cis olefins. The same holds true for consideration of trans olefin metathesis. Basset observed that when X is changed from chlorine to the larger bromine atom the specificity increases.

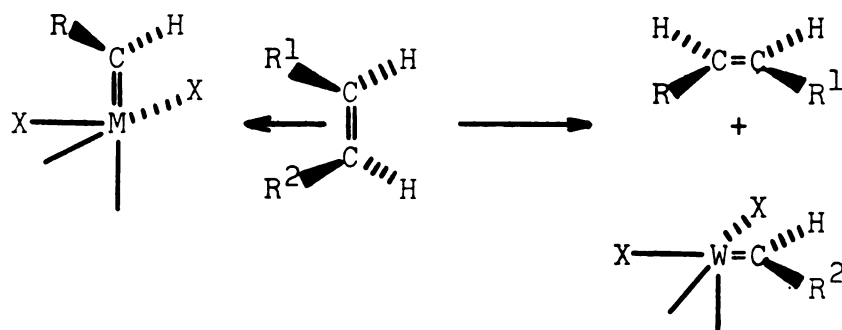


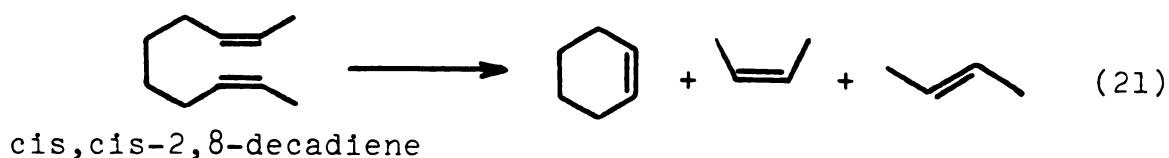
Figure 14. Predicted orientation of the approach of a cis olefin to a metal carbene

Basset⁶⁵ has used this model in a study of the metathesis of cis- and trans-2-pentene at low conversion. As seen in equation 20, 2-pentene, as well as other methyl olefins, yield 2-butene as one product. This means that these stereochemical studies can be compared with the 2,8-decadiene studies presented here. Basset found that cis-2-pentene metathesizes to give a trans/cis-2-butene (t/c-C₄) ratio of 0.78 at 0% conversion. The same specificity was noted for the other product, 3-hexene. This slight preference for the cis products indicates that the model shown in

Figure 14 exhibits only subtle steric constraints. The specificity increases when heterogeneous catalysts are used ($t/c-C_4=.4$), and this is attributed to surface phenomena. The metathesis of trans-2-pentene yields an initial $t/c-C_4$ ratio of 2.0. All of these ratios were found using similar tungsten based catalysts and are averages of several runs.

As the metathesis of internal olefins such as cis-2-pentene proceeds the products and starting material isomerize by the competing degenerate process shown in Figure 12. Eventually the thermodynamically stable mixture is obtained (equation 20). Basset observed that the trans/cis-2-pentene ratio changes linearly with the $t/c-C_4$ ratio (or the t/c -3-hexene ratio) as the reaction proceeds. By using a kinetics argument based on the carbene scheme, this linear relationship was derived semi-empirically. This derivation involved the consideration of thirty-two possible interactions of the two possible metal carbenes, $M=CHCH_3$ and $M=CHCH_2CH_3$, with each isomer of the three olefins present in the reaction mixture. Basset derived rate equations for the formation of each isomer and made estimates of the relative rate constants for each interaction from experimental data. He then used these rate constants to calculate the relative amounts of t/c -2-pentene and t/c -2-butene at a particular stage in the reaction. As expected, the calculated relationship was valid only at low conversions of starting material (~10%), when the competing processes are not as important.

The studies of the metathesis of *cis,cis*-2,8-decadiene presented here will be compared to the results Basset obtained. The metathesis of *cis,cis*-2,8-decadiene is expected to give cyclohexene, *trans*-2-butene and *cis*-2-butene (equation 21).



At the same time the starting material should also isomerize and must be accounted for. Similar stereochemical plots will be reported, and a kinetics model derived in a way analogous to Basset's will be presented. This reaction, however, will cut the possible competing metathesis processes from thirty-two to only twelve because it involves an irreversible reaction to cyclohexene. This means that the 2,8-decadienes will eventually be completely consumed, and only the 2-butenes will metathesize in a degenerate isomerization process.

The results of the studies on isomeric scrambling will be used to interpret the experiments dealing with the deuterium labeled 2,8-decadienes described earlier (Figure 9). The isotopic scrambling in the starting material and products must be accounted for according to the restrictions mentioned earlier concerning such labeling studies. The scrambling of the isotopic labels should be

an entirely analogous reaction as the scrambling of the isomeric labels (isomerization) because they are both degenerate processes. These results will give an indication of how accurate the sampling of the labeled 2-butenes is in distinguishing between the pairwise and non-pairwise schemes. The labeled starting materials were also exploited for experiments concerning the initiation and termination of the olefin metathesis reaction.

RESULTS AND DISCUSSION

Synthesis of Olefins

The study of the metathesis of 2,8-decadienes required the synthesis of isomerically and isotopically pure compounds. The synthetic scheme adopted for terminally labeled d_6 -cis,cis-2,8-decadiene is outlined in Figure 15. The first step involved the dilithiation of commercially available 1,7-octadiyne and subsequent treatment with fully labeled methyl iodide. The labeled diyne was isolated and characterized and then hydrogenated stereospecifically with Lindlar's catalyst (5% Pd on BaSO₄) in pyridine. The material isolated was found to have a high cis content ($97 \pm 2\%$) and complete ($\geq 99\%$) deuterium incorporation.

The corresponding d_0 -cis,cis-2,8-decadiene was prepared in the same way except that unlabeled methyl iodide was used. The d_0 -trans,trans-2,8-decadiene isomer is commercially available and found to have $>99\%$ trans content. Reduction of 2-decyne with Lindlar's catalyst afforded cis-2-decene in high yield and specificity.

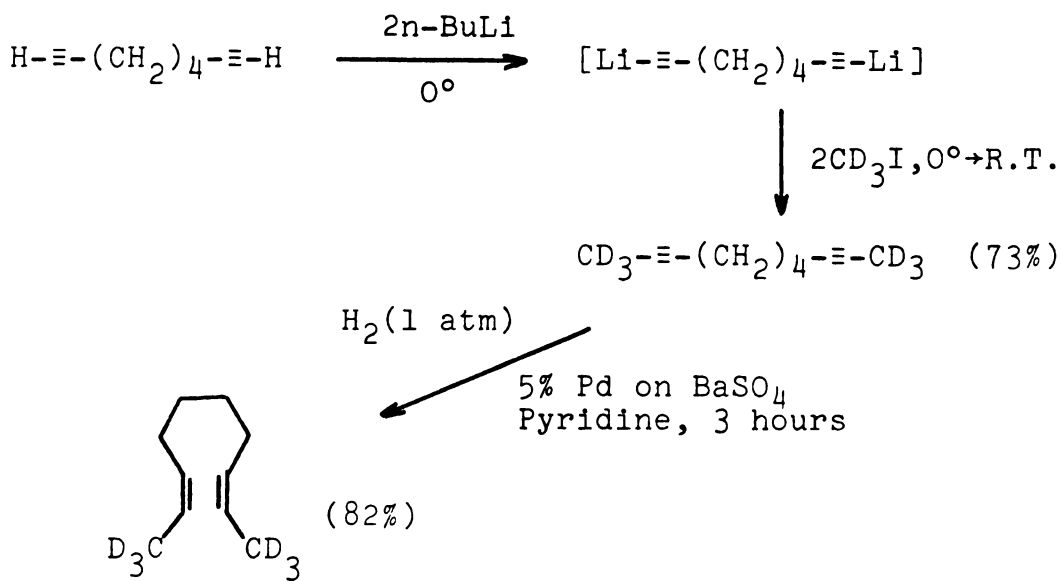


Figure 15. Synthesis of d_6 -cis,cis-2,8-decadiene

Catalysts and Metathesis Reactions

The non-supported catalytic systems used in these studies are typical of those described in the literature. The $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{P}\phi_3)_2/\text{Me}_3\text{Al}_2\text{Cl}_3$ system, referred to as catalyst A, was used extensively because of its high selectivity for metathesis and relatively long lifetime.¹⁵ The mixture produced when $\text{Al}/\text{Mo} = 7$ and the concentration of molybdenum is $.01\text{M}$, is homogeneous in chlorobenzene, and is light brown. The solution is allowed to "incubate", or stir without any substrate, for thirty minutes at room temperature before adding the olefin. The catalyst solution must be kept under argon at all times since brief exposure to oxygen will destroy the activity. The catalyst solution may be frozen with dry ice and be stored for several days with only slight loss of activity

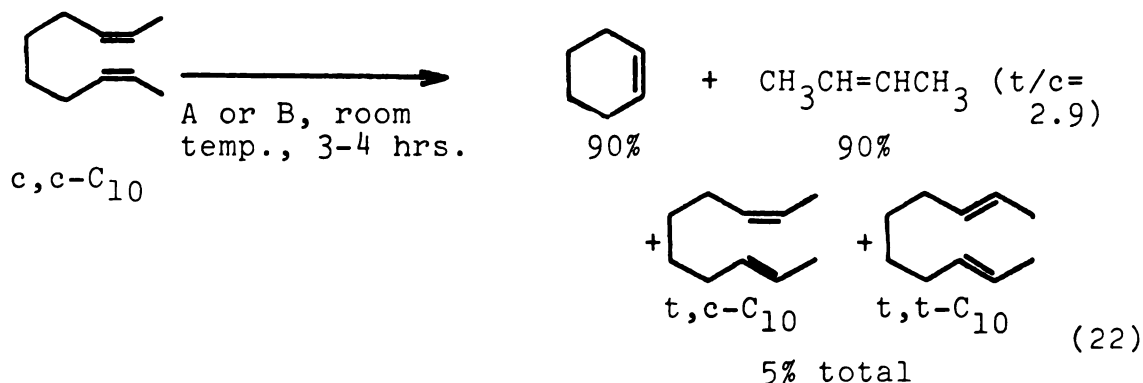
upon thawing. While incubating, methane and traces of ethylene and HCl are observed in the gas above the solution. The olefin : metal ratio is typically 150-200 : 1, but may be higher if desired.

The other system studied extensively was the mixture of $WCl_6/SnMe_4$,¹⁴ referred to as catalyst B. In this case a Sn/W ratio of 2 is used, and the solution in chlorobenzene is mostly homogeneous exhibiting a dark reddish-brown color. Most WCl_6 based systems are believed to be partially heterogeneous in nature.¹⁸ Incubation of this catalyst lead to a decrease in activity, and so the olefin was added prior to the addition of the co-catalyst, $SnMe_4$. Methane is detected over the catalyst solution, and in the absence of an olefin, ethylene is found in trace amounts. Olefin to tungsten ratios of 100-150 were used.

All of the metathesis reactions were conducted in sealed tubes under argon. The reactions were continuously monitored by withdrawing small liquid and gas samples and analyzing via glc. Deuterium content of olefins was indicated by mass spectral analysis.

Metathesis of cis,cis-2,8-decadiene

The metathesis of cis,cis-2,8-decadiene yields cyclohexene and a thermodynamic mixture of cis- and trans-2-butene in high yield and selectivity (equation 22).



After only a few hours at room temperature conversions as high as 95% could be obtained with either the molybdenum (A) or tungsten (B) based catalysts mentioned before. The yield of cyclohexene is usually about 90% while the remainder of the *cis,cis*-diene is isomerized to the two other possible 2,8-diene isomers. Only a trace of a C_{16} olefin arising from an intermolecular reaction between two dienes was observed, and no other C_{10} isomers were found in the product mixture.

As with the metathesis of other isomerically pure olefins, the metathesis of this *cis,cis*-diene shows moderate stereospecificity at low conversions giving predominantly *cis*-2-butene. As the reaction proceeds, *trans*-2-butene production increases until the thermodynamic equilibrium is reached, or the *t/c*-2-butene ratio (*t/c*- C_4) is about 2.9. During these reactions small gas samples were withdrawn at several time intervals and analyzed for the gaseous *t/c*- C_4 ratio.⁶⁸ Other gaseous products observed, such as propylene, will be considered later. The

$t/c-C_4$ ratios obtained were plotted against time, and as in other stereochemical studies, the curve is linear. The curve for the *cis,cis*-diene metathesis using catalyst A is shown in Figure 16. Extrapolation of this curve to $t = 0$ gives the $t/c-C_4$ ratio at 0% conversion. In this case, a value of about $.25 \pm .03$ is obtained which is reproducible. Other olefins were metathesized and extrapolated $t/c-C_4$ values found. These values are given in Table 3 along with examples of the work of Basset.

Table 3. Extrapolated $t/c-C_4$ Values at 0% Conversion

Olefin	Catalyst	$t/c-C_4$ (0%)
<i>cis,cis</i> -2,8-decadiene	A	$.25 \pm .03$
<i>cis,cis</i> -2,8-decadiene	B	$.61 \pm .04$
<i>cis</i> -2-decene	A	$.21 \pm .03$
<i>cis</i> -2-decene	B	$.62 \pm .04$
<i>cis</i> -2-pentene	B	$.73 \pm .05^{65}$
<i>trans,trans</i> -2,8-decadiene	A	$2.0 \pm .2$
<i>trans,trans</i> -2,8-decadiene	B	$1.9 \pm .2$
<i>trans</i> -2-decene	A	$2.1 \pm .2^{69}$
<i>trans</i> -2-pentene	B	2.0^{65}

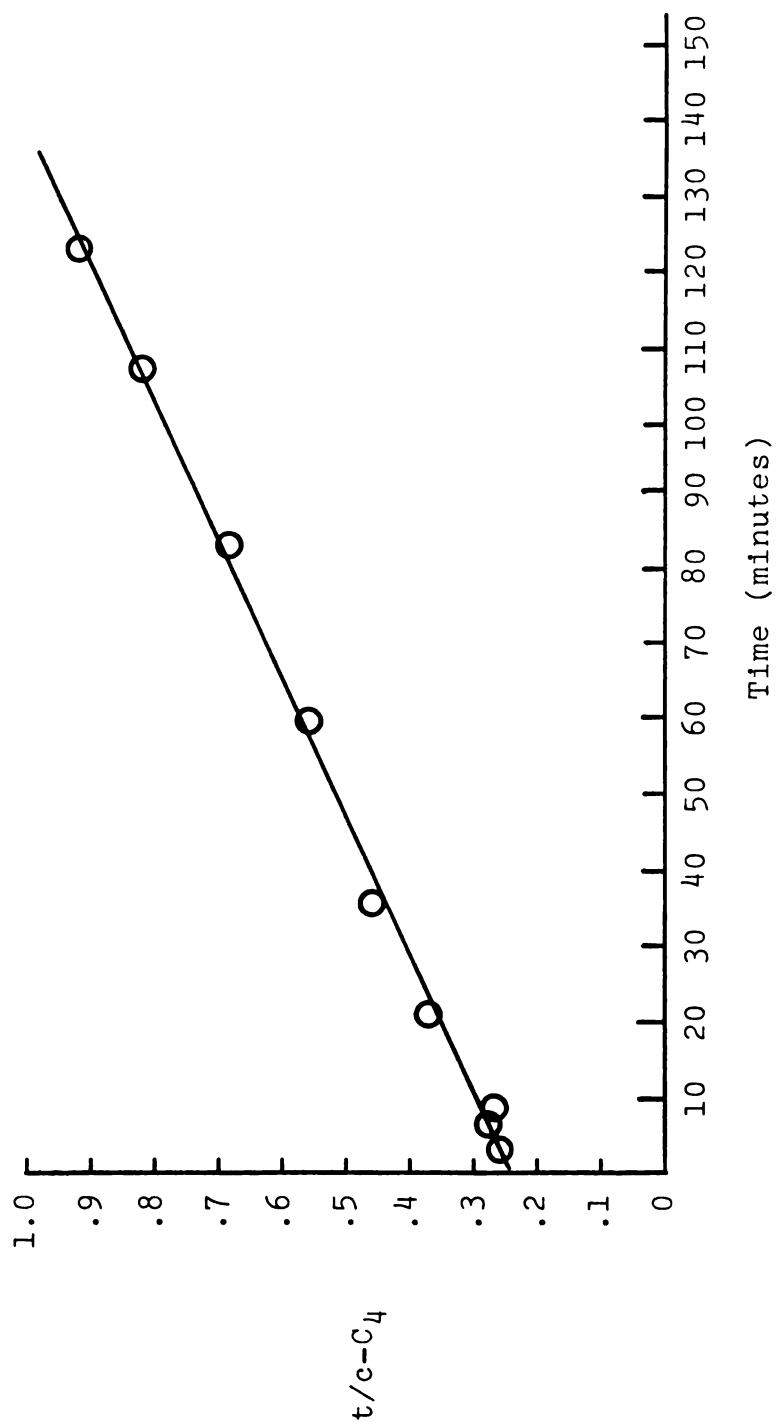


Figure 16. Change in the t/c-2-butene ratio during the metathesis of cis,cis-2,8-decadiene

It is difficult to compare the results given here with the work of others due to the complex dependency of the specificity of metathesis reactions on the conditions employed. Nonetheless, it was surprising to discover the relatively high degree of specificity exhibited during the metathesis of *cis,cis*-2,8-decadiene with catalyst A. Initially it was assumed that this phenomenon was due to the intramolecular nature of the reaction. However, the intermolecular metathesis of the corresponding mono-olefin, *cis*-2-decene, with the same catalyst exhibited about the same specificity at 0% conversion which implies that the double bonds in the diene are acting independently.

Differences in catalyst specificity can also be noted in Table 3. Molybdenum catalysts are generally known to be more specific than tungsten based catalysts,⁶¹ but differences in co-catalysts may also be involved. Basset also used a molybdenum catalyst similar to the one studied here and found a moderate increase in stereospecificity,⁶⁵ but this was not as dramatic a difference as shown here between catalysts A and B. The specificity observed with catalyst B is comparable to the results found by Basset using the same catalyst for the metathesis of *cis*-2-pentene. He also studied many other tungsten based systems, and all exhibited about the same specificity. These results seem to indicate that *cis*-2-pentene, *cis*-2-decene and *cis,cis*-2,8-decadiene exhibit roughly the same specificity in the

early part of the reaction. This further implies that the length of an alkyl group on one side of a methyl olefin does not markedly affect the stereospecificity.

The metathesis of trans,trans-2,8-decadiene was also studied. These reactions generally displayed induction periods varying from a few minutes to about thirty minutes. Conversion to cyclohexene and 2-butene then proceeds at approximately half the rate as the cis,cis-isomer. Addition of a trace of 1-hexene eliminated the induction period, but did not increase the rate of conversion. These results confirm other studies that concluded that trans olefins react slower than cis olefins and that trans olefins do not participate in the initiating steps of metathesis.^{60a} A preference for trans-2-butene was found at low conversions, and after about 30% conversion the thermodynamic mixture of 2-butene isomers was observed.

The metathesis of cis,cis-2,8-decadiene by using the molybdenum based catalyst was studied in more detail. Liquid aliquots were withdrawn in addition to the gas samples as the reaction progressed. The liquid samples were analyzed for cyclohexene and for isomerization and conversion of the starting material. The changes in the trans/cis ratios for the 2-butenes (t/c-C₄) and the 2,8-decadienes (t/c-C₁₀) were plotted against percent conversion of starting material and are shown in Figure 17. The t/c-C₁₀ ratio was calculated by considering the

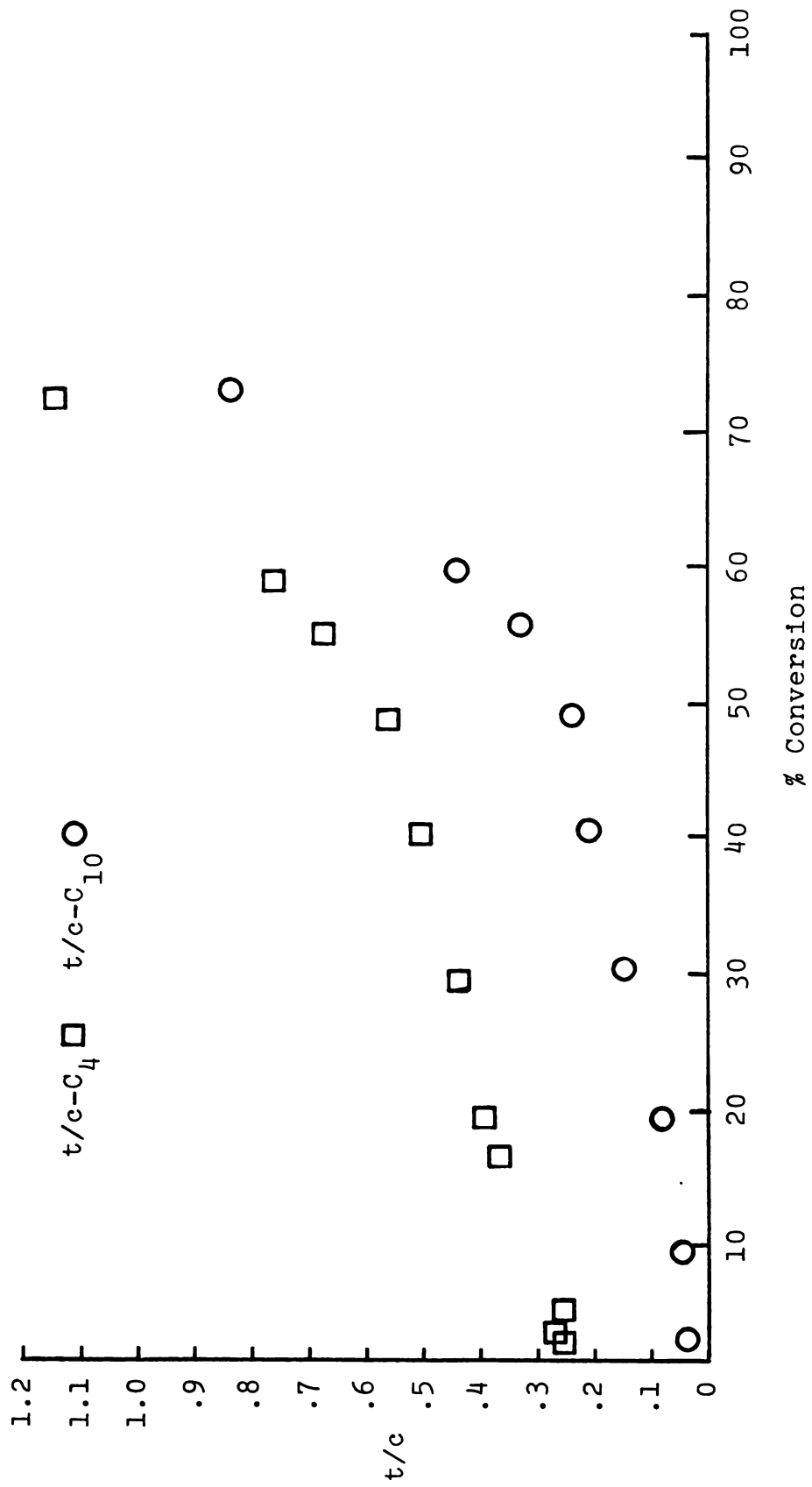


Figure 17. Isomerization of 2-butenes and starting material relative to the amount of conversion of starting material

contribution of the three possible 2,8-decadiene stereoisomers to the total trans and the total cis content of the C_{10} mixture.

It should be noted that these isomerization plots are linear until about 50% conversion. The two processes can be related by plotting $t/c-C_4$ against $t/c-C_{10}$ values observed at the same time. This plot is shown in Figure 18. The linearity of this plot implies that the two isomerization processes result from similar reaction pathways.

It has been well established that the isomerizations of olefins observed during metathesis reactions are degenerate metathesis reactions. These were described earlier in Figure 12. The intramolecular metathesis of cis,cis-2,8-decadiene, then, involves several competing metatheses. These reactions are the productive metatheses of the 2,8-decadienes which yield cyclohexene and 2-butenes irreversibly, and the reversible degenerate metatheses which isomerize the double bonds in the diene and 2-butene. Figure 19 illustrates these competing processes.

The measured $t/c-C_4$ values can now be seen to arise from a combination of three processes. Initially, only cis,cis-decadiene is present which metathesizes to give a 4 : 1 preference of cis-2-butene over trans-2-butene (Table 3). As the starting material isomerizes to give an increasing amount of trans double bonds, the ensuing productive metathesis will afford an increasing amount of

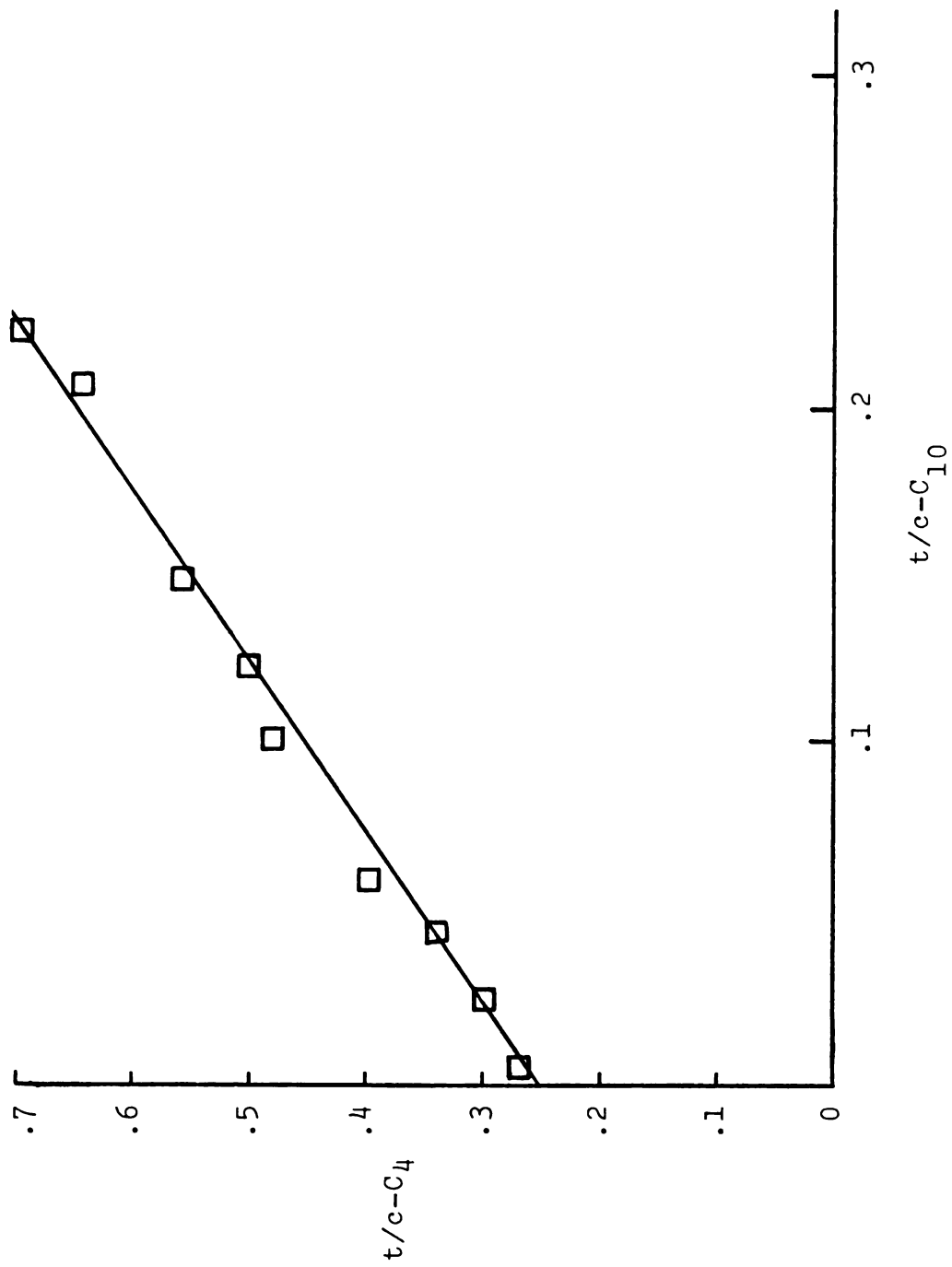
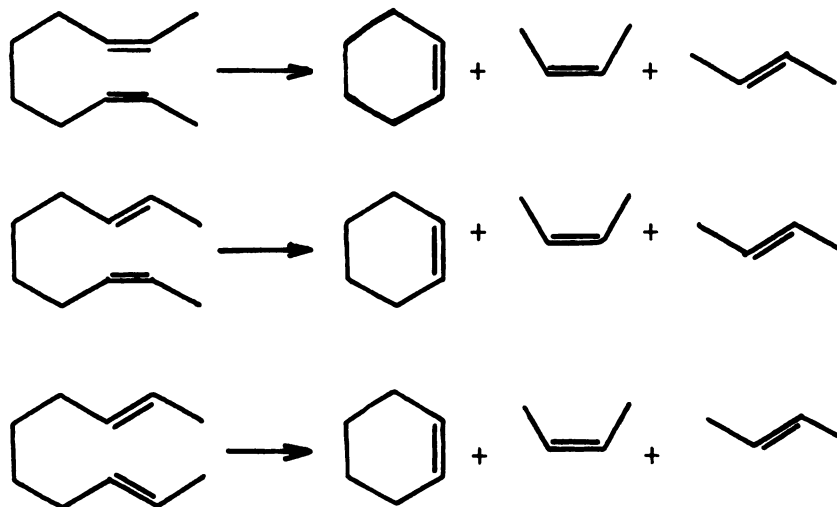


Figure 18. The relationship between $t/c-C_4$ and $t/c-C_{10}$

Productive metathesis processes:



Degenerate metathesis processes:

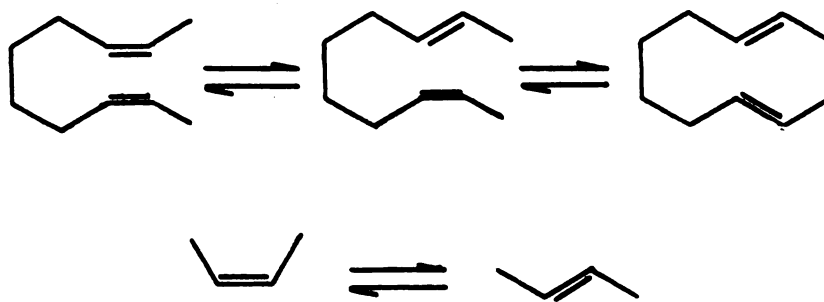


Figure 19. Competing metathesis processes during the metathesis of cis,cis-2,8-decadiene

of trans-2-butene. Also, once the concentration of the 2-butenes begins to increase they will undergo a reversible degenerate metathesis eventually yielding the thermodynamic mixture. The plots in Figure 17 and Figure 18 reflect $t/c-C_4$ values that are a composite of these three processes. The latter plot will later be accounted for with a kinetics model which considers all of these processes.

The final plot, shown in Figure 20, for the metathesis of cis,cis-2,8-decadiene indicates the relative amounts of olefins in the reaction mixture at a particular point in reaction time. It can be seen, for example, that the production of cis-2-butene begins to level off late in the reaction reflecting the dominance of the degenerate isomerization to the trans isomer. The amount of trans- C_{10} begins to level off only after most of the cis isomer is converted which reflects the slower rate of trans olefin metathesis mentioned previously.

The metathesis of cis-2-decene with catalyst A exhibits somewhat similar behavior. Figure 21 shows the comparison of the $t/c-C_4$ values obtained from the mono-olefin and the diolefin metathesis reactions versus percent conversion. The curve for the metathesis of cis-2-decene is linear only until about 20% conversion, and this linearity matches the plot obtained from the diene metathesis during the same amount of conversion. The

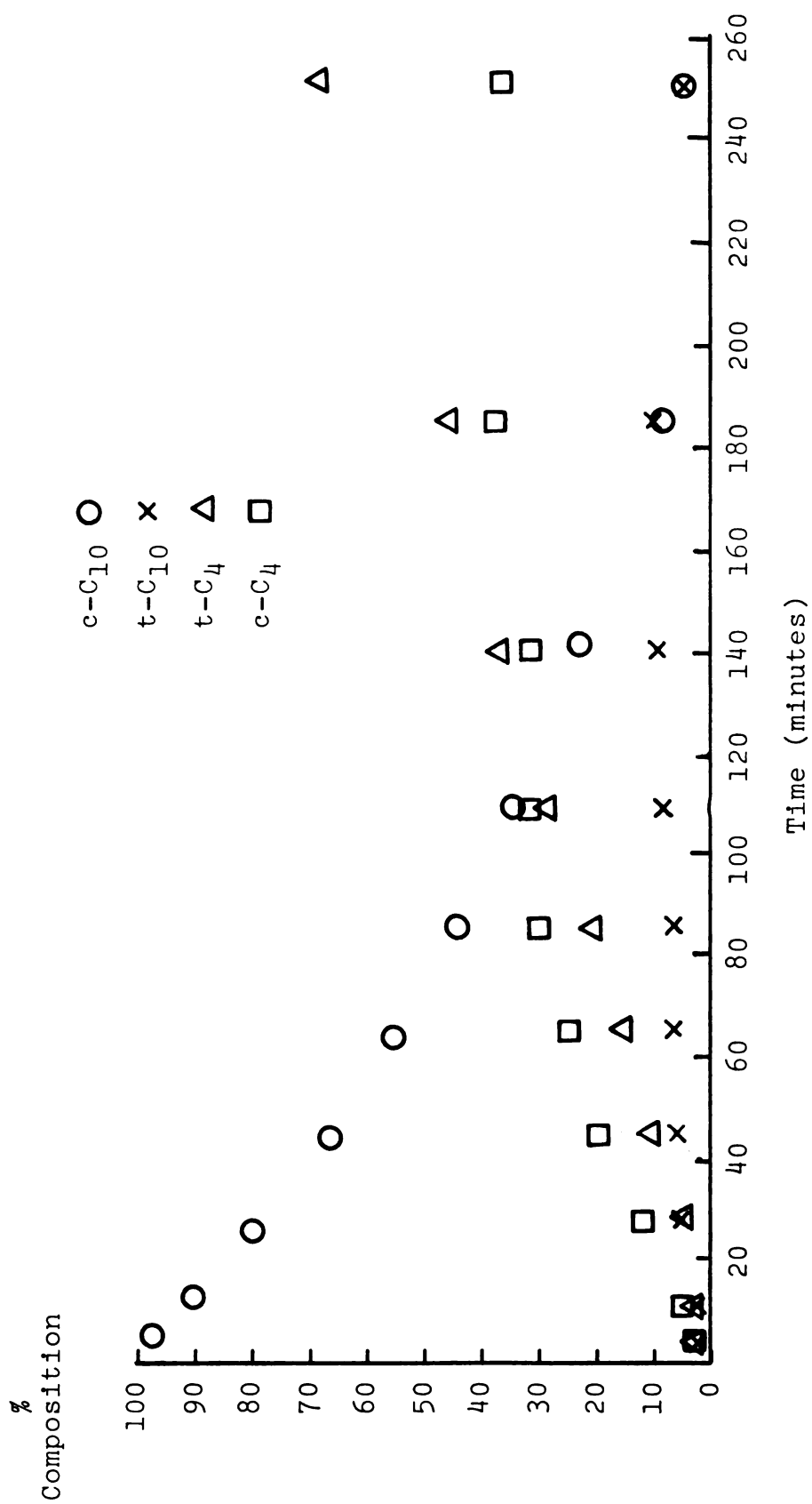


Figure 20. Relative concentrations of acyclic olefins during the metathesis of cis,cis-2,8-decadiene with catalyst A

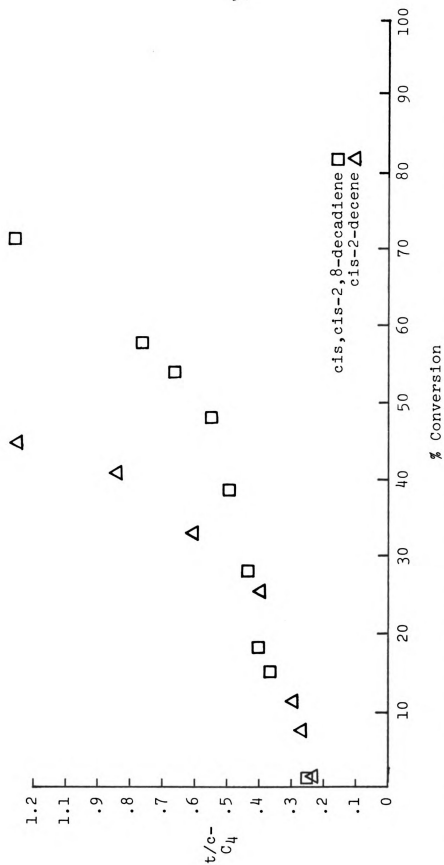


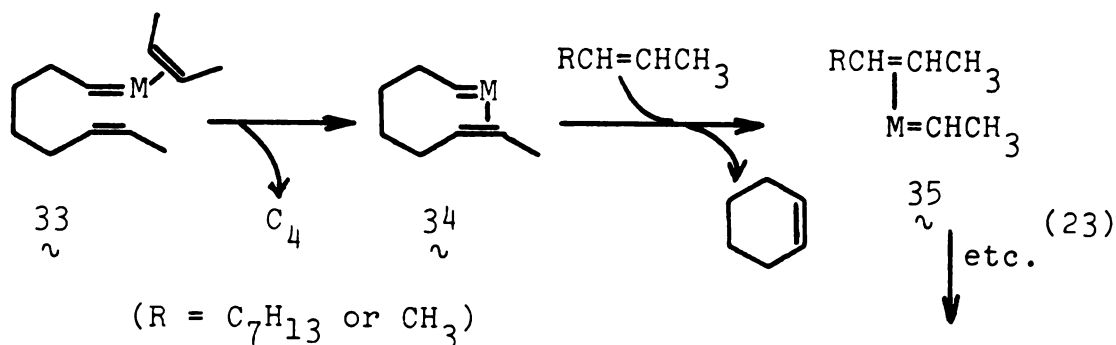
Figure 21. Comparison of t/c-C₄ ratios from the metathesis of cis-2-decene and cis,cis-2,8-decadiene

difference between the curves at higher conversions results from the inter- or intramolecular nature of the reaction. As with other simple mono-olefins, *cis*-2-decene will metathesize to two new products, 2-butene and 7-hexadecene, which can then undergo further metathesis back to the starting material. All of the competing metathesis reactions are reversible during mono-olefin metathesis unlike those during diene metathesis (Figure 19). In effect, that means that there are more ways for the olefins to metathesize and thus more ways to isomerize. It should be remembered that *cis*-2-decene is never completely consumed, and the maximum conversion is dictated by the thermodynamic equilibrium between *trans*- and *cis*-2-decene.

By using these stereochemical results it should be possible to devise a kinetics model in a way analogous to that described by Basset⁶⁵ which will supply an explanation for the origin of the relationships shown in Figure 18 and Figure 20. The model is based on a non-pairwise metal carbene scheme, the evidence for which will be presented in the next section describing the isotopic labeling studies. Only the propagating steps of the olefin metathesis reaction will be considered at this point.

The first assumption to be made is that there is an equal concentration of the two possible metal carbenes formed during the reaction. This is because there seem to be only small differences in steric effects exhibited by

most methyl olefins. The C_8 -carbene $\underset{\sim}{33}$ irreversibly cyclizes to form cyclohexene, cis- and trans-2-butene (C_4) and the C_2 -carbene $\underset{\sim}{35}$ according to equation 23.



The irreversibility of equation 23 arises from the observation that cyclohexene does not metathesize. It was also observed that no C_{16} olefin was formed from an intermolecular reaction between $\underset{\sim}{33}$ and a molecule of decadiene. This process is illustrated in Figure 22, where R is equal to the remainder of the decadiene (or C_8), and implies that $k \gg k'$. It is then also reasonable to assume that this relationship is valid when $R = CH_3$. Another assumption made is that once $\underset{\sim}{33}$ forms it will preferentially exchange olefins to complex with the readily available intramolecular carbon-carbon double bond to form $\underset{\sim}{34}$ rather than exchange with an olefin from the bulk solution. This means that $k \gg k'$.

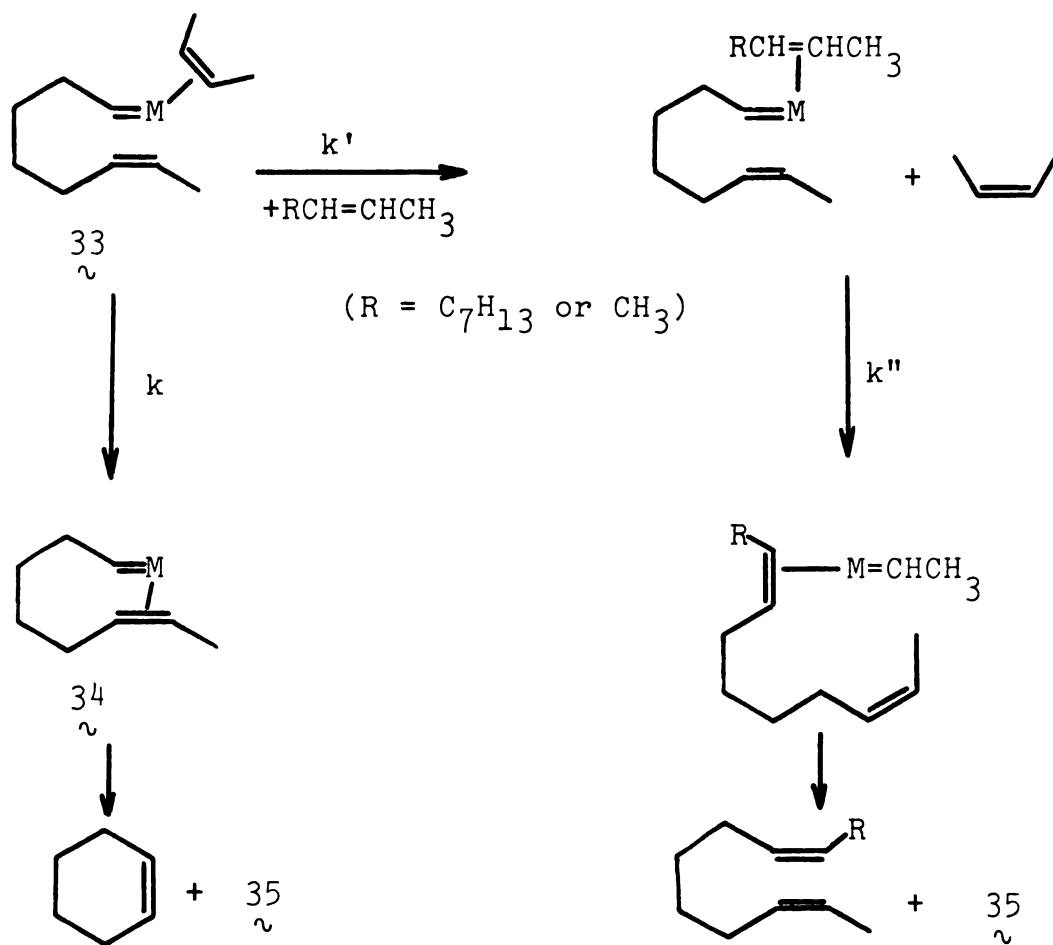


Figure 22. Possible reactions of the C_8 metal carbene **33** $\sim$

With the assumption that $k \gg k'$, one need only consider twelve possible reactions of $\underset{\sim}{35}$. Initially, only four primary reactions are possible during the early stages of the reaction, and these are shown in Figure 23.

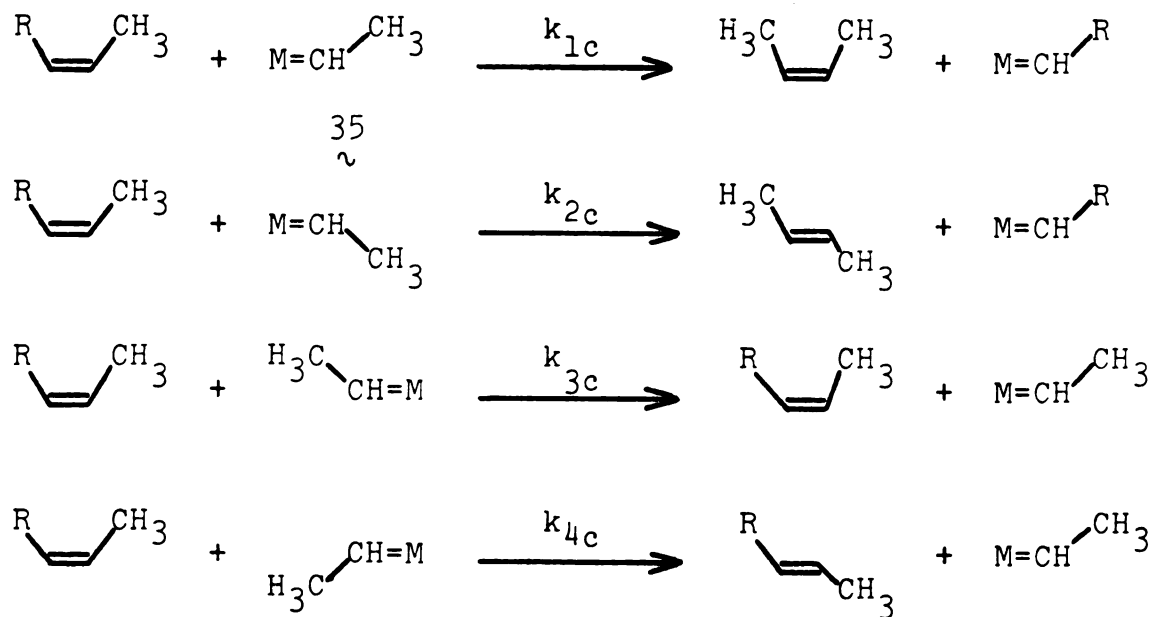


Figure 23. The four primary reactions of $\underset{\sim}{35}$ with cis,cis-2,8-decadiene

Since the double bonds in the starting material react independently, the rest of the decadiene is represented as R. The four possibilities shown arise from the different ways the olefin can coordinate with the carbene. This scheme does not reflect on the actual mode of interaction discussed in the introduction, such as the intermediacy of a puckered cyclobutane, but is simply a kinetics model. The first two reactions are the productive metathesis

reactions which yield the 2-butenes and carbene λ_3 which then cyclizes exclusively to cyclohexene and is not considered further. The latter two reactions are degenerate reactions which can reform the cis-C₁₀ isomer (k_{3c}) or isomerize to the trans isomer (k_{4c}). As the new olefins are produced eight secondary reactions must be considered and are shown in Figure 24.

Rate equations can then be written for the formation of trans-2-butene (t-C₄), cis-2-butene (c-C₄) and "trans"-decadiene (t-C₁₀). The C₂ metal carbene is simply written as [carbene] for simplification. The rate of production of cis-2-butene is derived from Figure 23 and Figure 24 and is shown in equation 24.

$$\frac{\delta c-C_4}{\delta t} = [\text{carbene}](k_{1c}[c-C_{10}] + k_{1t}[t-C_{10}] - k_{6c}[c-C_4] + k_{5t}[t-C_4]) \quad (24)$$

Similar equations are derived for t-C₄ (equation 25) and t-C₁₀ (equation 26).

$$\frac{\delta t-C_4}{\delta t} = [\text{carbene}](k_{2c}[c-C_{10}] + k_{2t}[t-C_{10}] + k_{6c}[c-C_4] - k_{5t}[c-C_4]) \quad (25)$$

$$\frac{\delta t-C_{10}}{\delta t} = [\text{carbene}](k_{4c}[c-C_{10}] - (k_{1t} + k_{2t} + k_{3t})[t-C_{10}]) \quad (26)$$

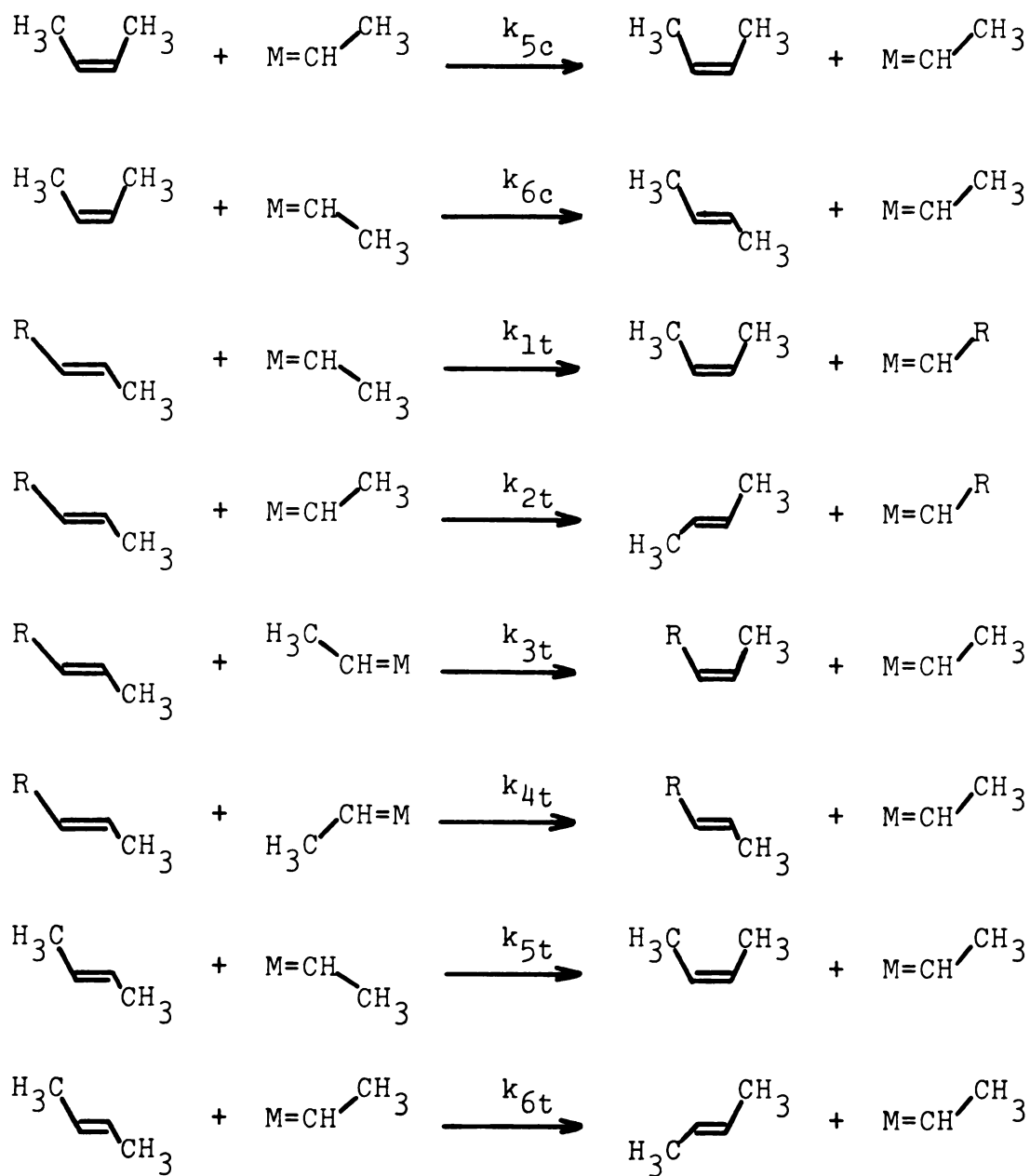


Figure 24. The eight secondary reactions of 35 with trans-C₁₀ and trans-2-butene ~

Equation 24 can be rewritten as

$$\frac{\delta c-C_4}{\delta t} = [\text{carbene}][c-C_{10}](k_{1c} + k_{1t} \frac{[t-C_{10}]}{[c-C_{10}]} - k_{6c} \frac{[c-C_4]}{[c-C_{10}]} + k_{5t} \frac{[t-C_4]}{[c-C_{10}]}).$$

Inserting $\alpha = [c-C_4]/[c-C_{10}]$ gives equation 27.

$$\frac{\delta c-C_4}{\delta t} = [\text{carbene}][c-C_{10}](k_{1c} + \alpha(k_{1t} \frac{[t-C_{10}][t-C_4]}{[t-C_4][c-C_4]} - k_{6c} + k_{5t} \frac{[t-C_4]}{[c-C_4]}) \quad (27)$$

In a similar way equation 25 can be rewritten as equation 28.

$$\frac{\delta t-C_4}{\delta t} = [\text{carbene}][c-C_{10}](k_{2c} + \alpha(k_{2t} \frac{[t-C_{10}][t-C_4]}{[t-C_4][c-C_4]} + k_{6c} - k_{5t} \frac{[t-C_4]}{[c-C_4]}) \quad (28)$$

Dividing equation 28 by equation 27 gives an equation representing the relative amounts of trans- and cis-2-butene (equation 29).

$$\frac{t-C_4}{c-C_4} = \frac{k_{2c} + \alpha(k_{2t} \frac{[t-C_{10}][t-C_4]}{[t-C_4][c-C_4]} + k_{6c} - k_{5t} \frac{[t-C_4]}{[c-C_4]})}{k_{1c} + \alpha(k_{1t} \frac{[t-C_{10}][t-C_4]}{[t-C_4][c-C_4]} - k_{6c} + k_{5t} \frac{[t-C_4]}{[c-C_4]})} \quad (29)$$

In a somewhat analogous way equation 30

$$\begin{aligned} \frac{t-C_{10}}{c-C_{10}} &= \frac{\alpha k_{4c} - \alpha^2(k_{1t} + k_{2t} + k_{3t}) \frac{[t-C_4][t-C_{10}]}{[c-C_4][t-C_4]}}{k_{1c} + \alpha(k_{1t} \frac{[t-C_{10}][t-C_4]}{[t-C_4][c-C_4]} - k_{6c} + k_{5t} \frac{[t-C_4]}{[c-C_4]})} \\ &= \frac{t-C_{10}\alpha}{c-C_4} \end{aligned} \quad (30)$$

is derived for the relative amounts of trans- and cis-decadiene.

The relative values of the rate constants can be approximated from the experimental data presented earlier. The extrapolated $t/c-C_4$ value at 0% conversion found for the metathesis of cis,cis-2,8-decadiene should correspond to the relative rates of k_{2c} and k_{1c} . This means that $k_{2c}/k_{1c} = .25$, and similarly from the studies of the metathesis of the trans,trans-diene, $k_{2t}/k_{1t} = 2.0$ (Table 3). Since the rate of metathesis of the trans,trans-diene is about half that of the cis,cis-diene, equation 31 follows.

$$k_{1t} + k_{2t} + k_{3t} + k_{4t} = .5(k_{1c} + k_{2c} + k_{3c} + k_{4c}) \quad (31)$$

There is no way to find the values for k_{3c} or k_{4t} from these experiments. However, the size of the alkyl group does not seem to have an effect on the reactivity, and so k_{3c} can be approximated as being equal to k_{1c} and k_{4t} set roughly equal to k_{2t} . At low conversions it was found that the rates of production of trans-2-butene and trans-C₁₀ were about the same.⁷⁰ This observation implies that k_{4c} is approximately equal to k_{2c} .

There have been only a few studies conducted concerning the metathesis of trans olefins, but the approximations that $k_{4t}/k_{3t} = 2.0$ and $k_{4t} = k_{2t}$ are not unreasonable. Finally, because 2-butene has an inherent C₂ axis, it may coordinate with a metal carbene in two degenerate ways to give the same product. This degeneracy means that the number of possible alignments of χ^5 with 2-butene to give a particular product must be doubled compared with the alignment of χ^5 with an unsymmetrical olefin, or one end of 2,8-decadiene, leading to the same product. By using this information the relationships shown in equation 32 are implied.

$$k_{5c} = 2k_{1c}, k_{6c} = 2k_{2c}, k_{5t} = 2k_{1t} \text{ and } k_{6t} = 2k_{2t} \quad (32)$$

The relative rate constants were calculated by using the approximations made above, equation 31 and equation 32, and by arbitrarily assigning $k_{1c} = 1.0$. The results are shown in Table 4.

Table 4. Approximated Relative Rate Constants

$$\begin{array}{ll}
 k_{1c} = k_{3c} = 1.0 & k_{1t} = k_{3t} = .21 \\
 k_{2c} = k_{4c} = .25 & k_{2t} = k_{4t} = k_{5t} = .42 \\
 k_{5c} = 2.0 & k_{6t} = .84 \\
 k_{6c} = .50 &
 \end{array}$$

At low conversions the concentrations of $t-C_{10}$ and $t-C_4$ are about the same, and the $t/c-C_4$ ratio is taken to be .25. These values along with the values in Table 4 are put into equation 29 and equation 30 to yield equation 33 and equation 34 respectively.

$$\frac{t-C_4}{c-C_4} = \frac{.25 + .5\alpha}{1 - .34\alpha} \quad (33)$$

$$\frac{t-C_{10}}{c-C_{10}} = \frac{.25\alpha - .21\alpha^2}{1 - .34\alpha} \quad (34)$$

Recall that $\alpha = c-C_4/c-C_{10}$ which is one way of measuring the amount of productive metathesis. These equations predict that the maximum amount of *cis*-2-butene present will occur when $\alpha = 1/.34 = 3.0$. This value is in rough agreement with the curve in Figure 20. It is also predicted that the amount of *trans*- C_{10} will be maximized when $\alpha = 1/.21 = 4.76$. The experimental agreement with this value is not as good, probably due to the high conversion needed to observe this occurrence. Most of the reactions conducted gave inconsistent results after long

reaction times due to the loss of catalytic activity. The equations also predict that the amount of trans-2-butene will never level off, a result of the irreversibility of the diene metathesis.

To calculate a curve for $t/c-C_4$ versus $t/c-C_{10}$, various values of α are fed into equation 33 and equation 34, and the resulting ratios are given in Table 5. This curve is plotted and shown in Figure 25. Figure 25 also contains the experimental plot shown earlier in Figure 18 for conversions of less than 50%. The calculated curve illustrates a linear relationship as predicted by this model. The slopes of the two curves are in good agreement, especially when one considers the number of assumptions made for this calculation. As a check, the points found experimentally in Figure 25 are related to the amount of conversion, and the corresponding α value is found. these α values are in general agreement with the calculated curve. More accurate curves could perhaps be found by varying the relative rate of trans and cis olefin metathesis, since only a rough approximation was employed in this model.

Table 5. Calculated t/c-C₄ and t/c-C₁₀ Values

α	t/c-C ₄	t/c-C ₁₀
0	.25	0
.05	.27	.012
.10	.31	.024
.15	.34	.034
.20	.38	.045
.30	.44	.062
.40	.52	.077

In summary, a kinetics model was devised, based on a non-pairwise carbene scheme, which successfully accounted for the experimental results obtained from the intra-molecular metathesis of cis,cis-2,8-decadiene. The number of competing metathesis reactions to be considered was reduced to twelve from the thirty-two needed in mono-olefin studies. The next section describes studies involving the metathesis of isotopically labeled decadienes and uses the results of the "isomerically labeled" decadiene metathesis reactions presented here.

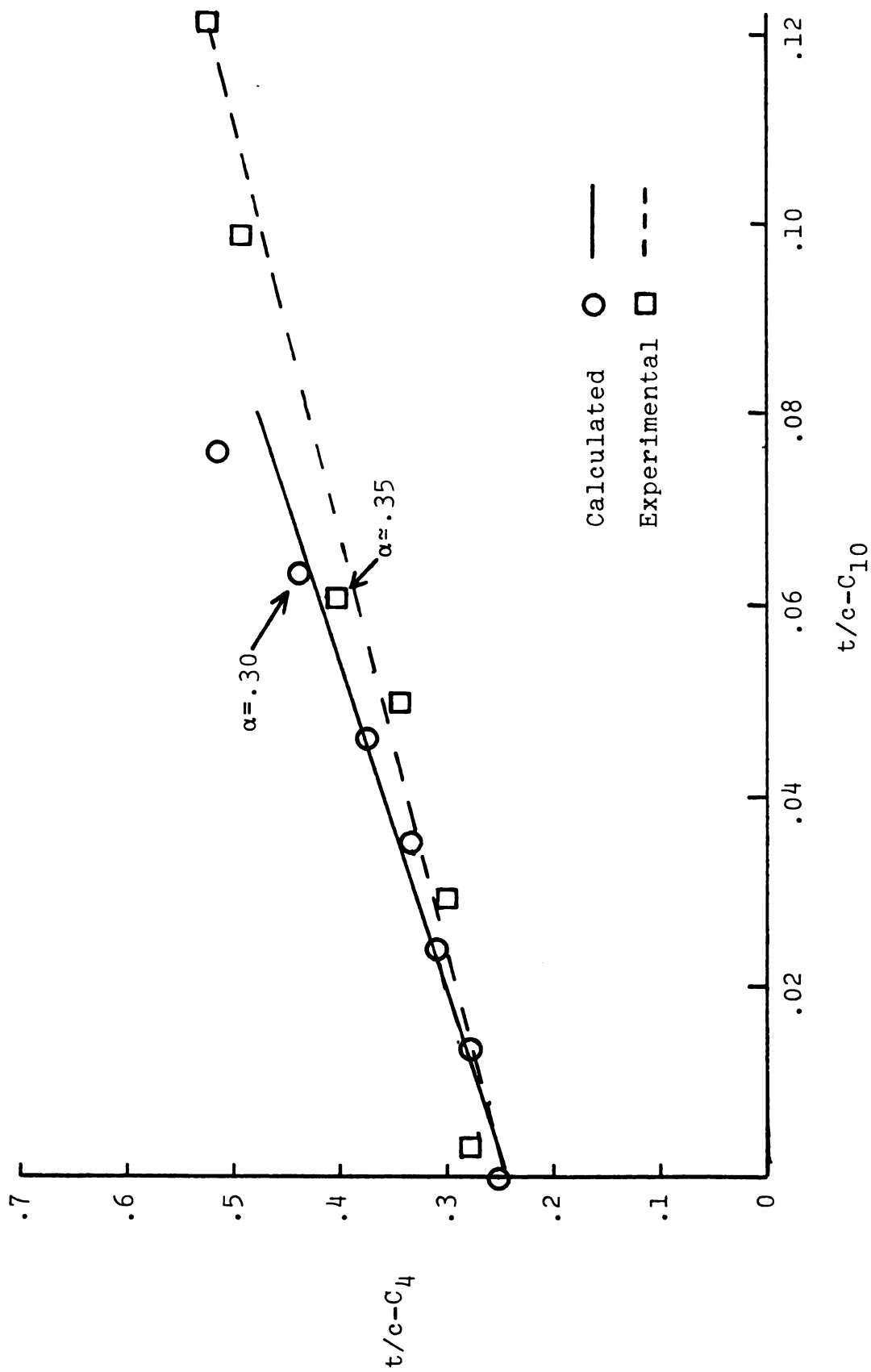


Figure 25. Comparison of the calculated and the experimental relationships between $t/c-C_4$ and $t/c-C_{10}$

Deuterium Labeling Studies

Mixtures of d_6 - and d_0 -cis,cis-2,8-decadiene were metathesized using catalyst A. At several stages of the reaction, gas and liquid samples were withdrawn and analyzed via glc. The cis-2-butene was isolated at several t/c- C_4 ratios by preparative glc and submitted for mass spectral analysis. The starting material was analyzed for isomerization, and a portion was isolated and also submitted for mass spectral analysis. In this manner, d_3/d_6 ratios were found for the cis-2-butenes and the 2,8-decadienes. Table 6 lists the values obtained for the experiment where d_0/d_6 -cis,cis-2,8-decadiene = $1.21 \pm .02$.

Table 6. Experimental Data from the Metathesis of a
1 : 1.21 d_6 : d_0 Mixture of cis,cis-2,8-
decadiene

t/c- C_4	d_3/d_6 - C_4	d_3/d_6 - C_{10}	% Conversion
.28 $\pm$.04	2.35 $\pm$.1	0.0 $\pm$.02	5 $\pm$ 2
.38 $\pm$.04	2.4 $\pm$.1	.12 $\pm$.02	15 $\pm$ 3
.54 $\pm$.05	2.4 $\pm$.1	.32 $\pm$.03	45 $\pm$ 3
.74 $\pm$.05	2.4 $\pm$.1	.60 $\pm$.05	60 $\pm$ 5
1.2 $\pm$.10	2.4 $\pm$.1	---	83 $\pm$ 4

Since the t/c- C_4 ratios change in a linear relationship in the early part of the reaction with respect to conversion (Figure 17) these t/c values can be used as an

internal measure of the extent of metathesis, differing from the 1,7-octadiene labeling studies reported earlier in which all probes were external to the system. In those studies it was not certain whether the ethylenes isolated were obtained before any of the possible equilibrations of the isotopic labels could take place. Isolation after such an equilibration would give ambiguous results. By plotting the d_3/d_6 -2-butene ratios against the $t/c-C_4$ ratios it should be possible to extrapolate the d_3/d_6 values to 0% conversion, or $t/c-C_4 = .25$. This extrapolated value should reflect a number obtained during pre-equilibrium conditions. The graph shown in Figure 26 yields a value for d_3/d_6-C_4 of $2.4 \pm .1$. The calculated ratio for a carbene scheme is $2.42 : 1$, and the expected value for a pairwise scheme was calculated to be $1.90 : 1$ at 0% conversion, or when there has been no scrambling of labels.

A more precise study was conducted in order to follow the scrambling of the isotopic labels in the starting material. This process, which is illustrated in equation 35, is very similar to the isomeric scrambling (isomerization) discussed in the previous section and shown in equation 36.

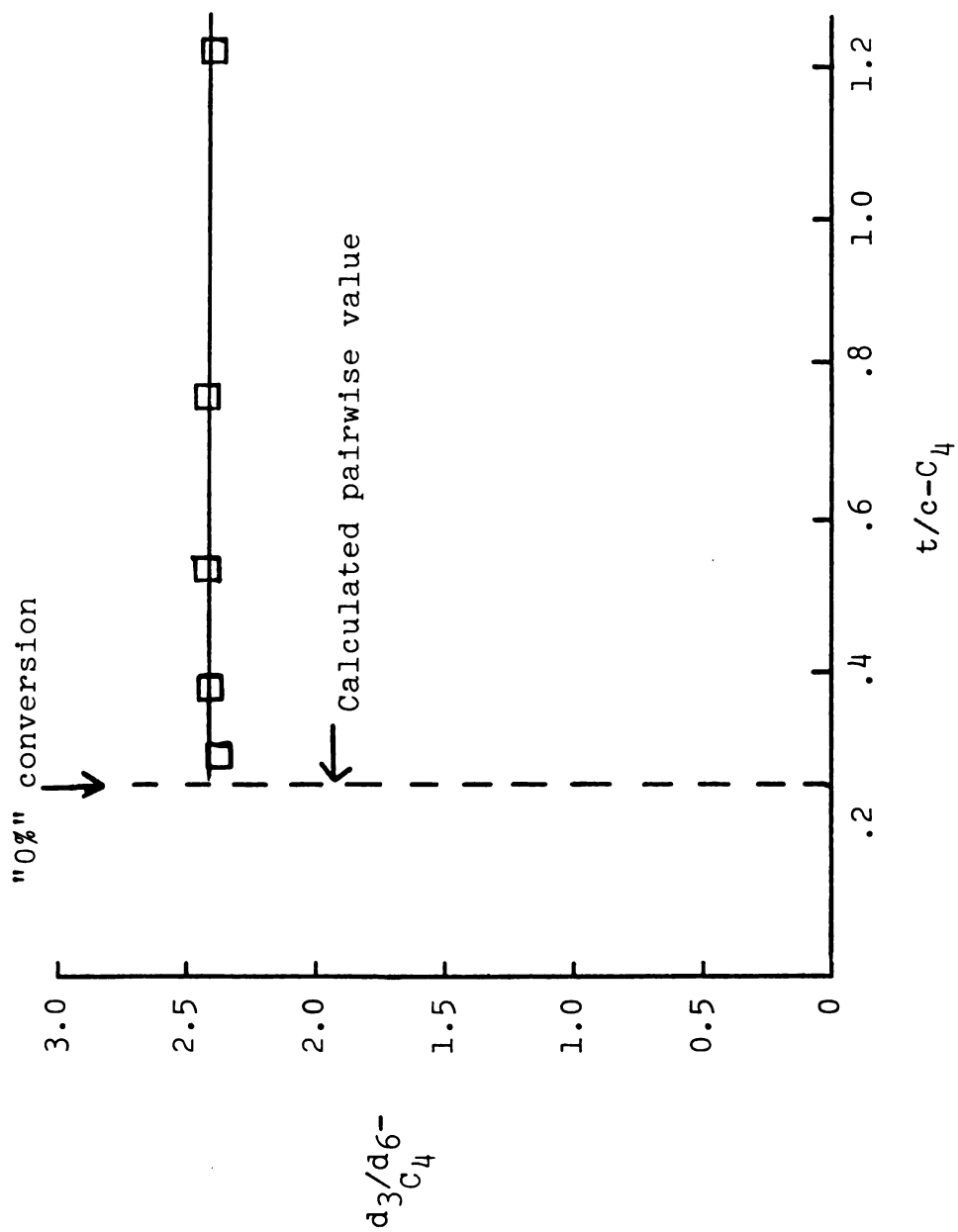
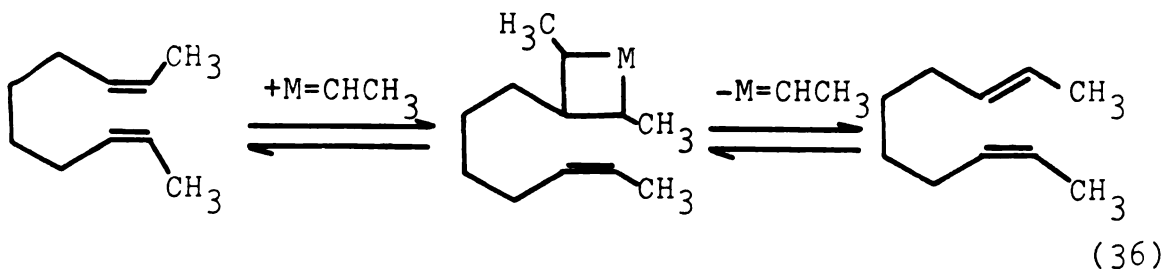
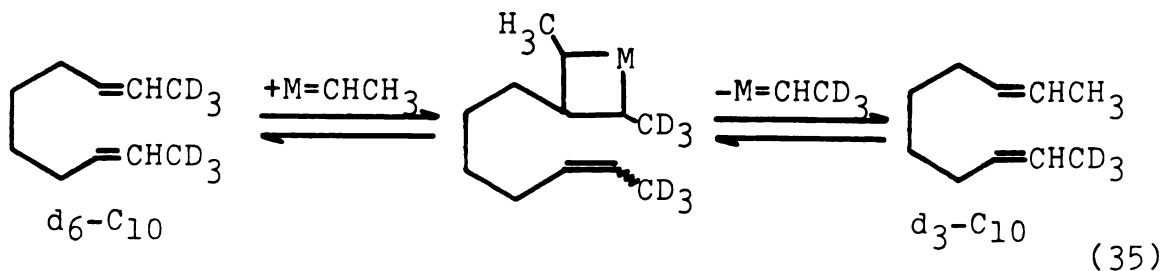


Figure 26. Observed d_3/d_6-C_4 values during the metathesis of a mixture of d_0 - and d_6 -2,8-decadiene at particular $t/c-C_4$ ratios



Both processes are degenerate metathesis reactions. The increasing $d_3/d_6\text{-C}_{10}$ ratios shown in Table 6 result from this scrambling process (equation 35). No other scrambled products were detected which could have arisen from some secondary isomerization process such as a metal-hydride reaction. Theoretically, if the labels in the starting material were completely scrambled, then a $d_0 : d_3 : d_6\text{-C}_{10}$ ratio of $(1.21)^2 : 2(1.21) : 1$ would be expected from this experiment. As seen in Table 6 the fully scrambled $d_3/d_6\text{-C}_{10}$ ratio of $2.42 : 1$ is never approached even at higher conversions. The curve of $d_3/d_6\text{-C}_{10}$ versus conversion is similar to the $t/c\text{-C}_{10}$ versus conversion (Figure 17) in that it is linear to about 50% conversion, and then the rate of scrambling increases. At 45% conversion the

isotopic scrambling is $(.32/2.42)(100)$ or 13% complete. This slow rise in isotopic scrambling during the early stages of the reaction is entirely analogous to the behavior exhibited by the isomeric scrambling and is due to the intramolecular nature of the reaction.

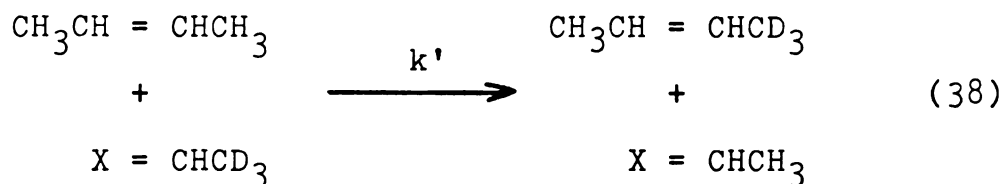
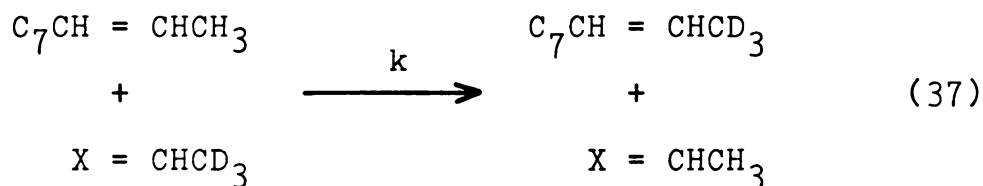
It should be recalled from the restrictions presented in the introduction that if the labels in the starting material are scrambled sufficiently the pairwise scheme and the carbene scheme will predict a random distribution of labels in the products. Calculations were undertaken for the pairwise scheme at several d_3/d_6-C_{10} ratios from zero to .5 and were accomplished by using an iterative scheme similar to ones described in previous reports.³⁴ In this instance, however, the probability of a metal-butene species interacting with the newly formed d_3 -decadiene is added on in three more terms of each calculation. These calculations are shown in more detail in the Appendix. As the amount of d_3-C_{10} increases, the amount of d_3 -2-butene increases. When the labels have completely scrambled in the starting material, or $d_3/d_6-C_{10} = 2.42$, then d_3/d_6-C_4 will also be 2.42. The calculated values are shown in Table 7. These ratios were derived by only considering the butenes arising from the starting material and should be valid at very low conversions.

Table 7. Calculated d_3/d_6-C_4 Values by a Pairwise Scheme

d_3/d_6-C_{10}	Calculated d_3/d_6-C_4
0	1.900
.116	1.926
.196	1.933
.301	1.988
.519	2.014

To adjust these calculated values to be more realistic the interaction between two butene molecules must also be considered. This means that the total d_3/d_6-C_4 ratio according to the pairwise scheme will be made up of two processes. The first process is the result of productive metathesis of the scrambled starting material, shown in Table 7, and the second process is the degenerate scrambling between the butenes. When the concentration of these butenes increases the latter process will begin to contribute more heavily to the total d_3/d_6-C_4 ratio which, of course, implies that the values in Table 7 are too low. Required now is an approximation of the extent of the independent scrambling of the isotopic labels in the 2-butenes at each new value of d_3/d_6-C_{10} .

The experimental evidence given earlier, and in other reports, indicates that size of the alkyl groups in simple disubstituted olefins does not markedly affect the rate of metathesis. This means that the isotopic scrambling in the starting material (equation 37) can be related to the scrambling in the butenes (equation 38) in a way similar to that presented in the previous section.



The examples shown in these equations illustrate possible interactions required for scrambling. In these cases the X can be a metal for the carbene scheme or an alkylidene for any pairwise scheme. Because of the C_2 axis inherent in the symmetrical 2-butenes it is reasonable to assume that $k' = 2k$ (cf. equation 32). This means that when the labels in the starting material have scrambled to an extent determined by k in equation 37, then the 2-butenes will have undergone twice as much scrambling. For example, when $d_3/d_6\text{-C}_{10}$ is .12 (Table 6), then the starting material has undergone $(.12/2.42)(100) = 5\%$ scrambling. The butenes

produced will have undergone approximately 10% scrambling independently. The adjusted d_3/d_6-C_4 calculated values are shown in Table 8. These were calculated by taking the d_3/d_6-C_4 values derived from the starting material (Table 7) and allowing the butenes to partially scramble to the random distribution according to the approximated extent of scrambling. For example, when d_3/d_6-C_{10} is .12, 10% of the corresponding d_3/d_6-C_4 ratio from Table 7 (.193) is allowed to scramble completely and then is added back into the remaining 90% of the d_3/d_6-C_4 ratio ($1.926 - .193 = 1.733$) that arises directly from the starting material by the productive metathesis.

Table 8. Adjusted d_3/d_6-C_4 Values Calculated by a Pairwise Scheme

d_3/d_6-C_{10}	d_3/d_6-C_4	% Isotopic Scrambling		Adjusted d_3/d_6-C_4
		C_{10}	C_4	
0	1.900	0	0	1.900
.116	1.926	5	10	1.970
.196	1.933	8	16	1.997
.301	1.988	12	24	2.070
.519	2.014	21.5	43	2.145

The adjusted calculated d_3/d_{6-C_4} values from Table 8 are plotted against the $d_3/d_{6-C_{10}}$ ratios, and the curve is shown in Figure 27 along with the experimental values from Table 6. It was shown earlier that the rate of isomeric scrambling begins to increase after about 50% conversion. It should then be expected that the isotopic scrambling will behave similarly meaning that this calculated pairwise curve will not be as accurate after about 40-50% conversion of starting material, or when $d_3/d_{6-C_{10}}$ is about .35-.4. After this point the approach to the random distribution of isotopic labels will change. The calculated carbene curve is, of course, a horizontal line at $d_3/d_6 = 2.42$.

Figure 27 has important implications. The difference between the two calculated curves clearly indicates that if the butenes are sampled at conversions $\leq 40\%$ of starting material, the values obtained for the isotopic distribution will, within experimental error, unambiguously distinguish between the two possible schemes. There are two data points well within this limit, and both indicate that a carbene scheme is operative. Another experiment was undertaken with the initial $d_0 : d_{6-C_{10}}$ ratio of 2.68 : 1, and a large sample of 2-butenes was isolated after about 5-6% conversion. In this case, because of the larger 2-butene sample isolated, a $d_0 : d_3 : d_{6-C_4}$ ratio was obtained. This ratio is given in the experimental section

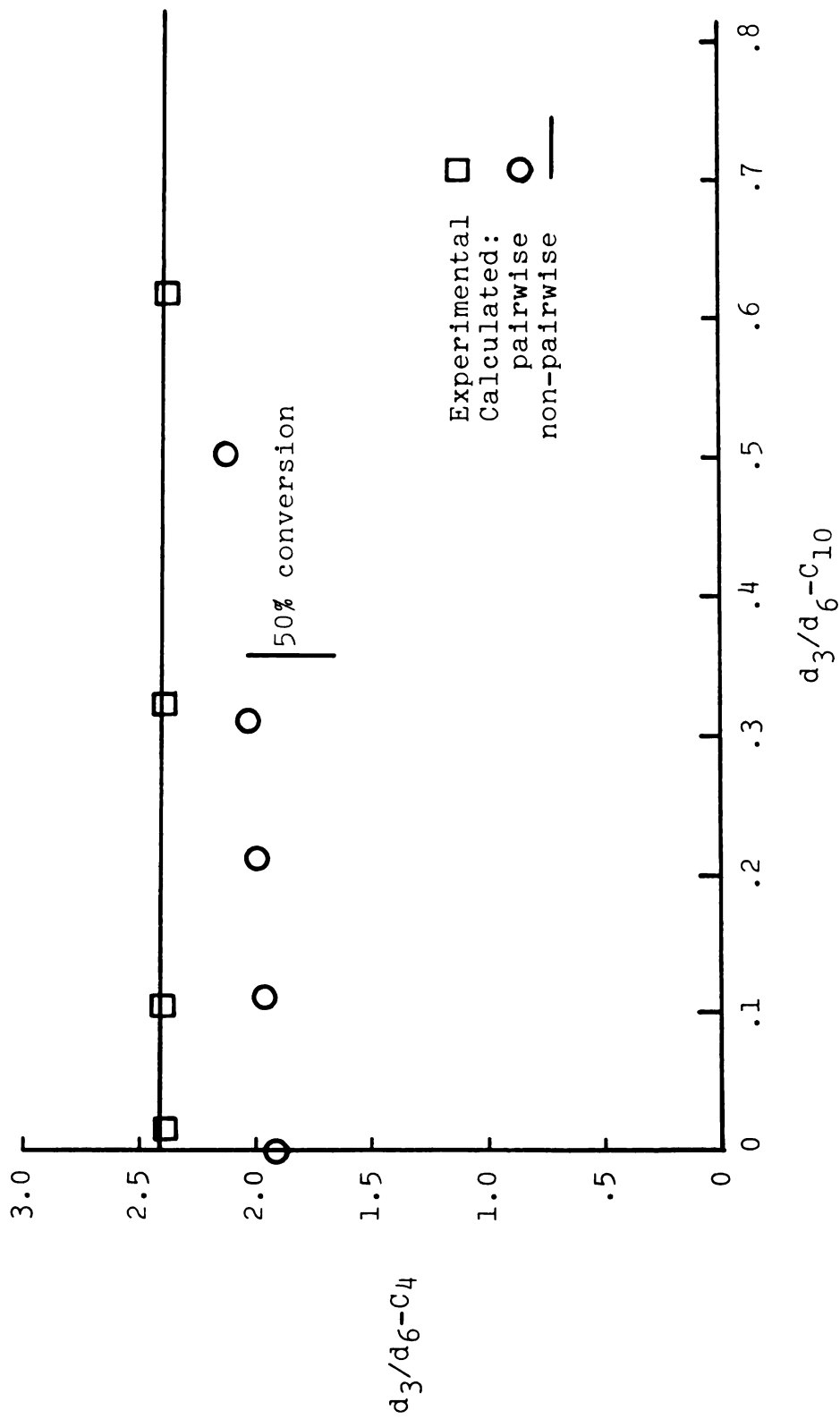


Figure 27. Observed d_3/d_{6-C_4} values compared to the calculated values for the non-pairwise(carbene) and pairwise schemes

along with the calculated ratios for both schemes. The carbene scheme is again implicated. The previous experiment (Table 6) was continuously monitored and allowed only small samples to be taken, and because of the errant background in the mass spectrometer only the $d_3/d_6\text{-C}_4$ ratio was found.

These isotopic labeling studies have taken advantage of the isomerization studies presented earlier to allow a calculation of a pairwise curve that accounts for the scrambling of the isotopic labels in the products and starting material. These processes must be considered in any such labeling study according to the restrictions discussed in the introduction. The experimental evidence given here has indicated that a non-pairwise metal carbene mechanism is a more accurate description of the olefin metathesis process rather than any pairwise scheme. Although other studies have reached the same conclusion, the studies presented here most accurately account for all of the competing metathesis processes. Values for the isotopic distribution in the products were obtained that were known to have arisen during pre-equilibrium conditions. These experiments satisfy the restrictions placed on such labeling studies.

Initiation and Termination of Olefin Metathesis⁷¹

As mentioned earlier, small amounts of methane and ethylene are produced when $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{P}\phi_3)_2$ is treated with $\text{Me}_3\text{Al}_2\text{Cl}_3$ or when WCl_6 is mixed with $\text{Sn}(\text{CH}_3)_4$. When a methyl olefin, in particular 2,8-decadiene, is added to either catalyst solution propylene is initially produced followed by the usual metathesis products such as 2-butene. The propylene could arise from an isomerization of the methyl olefin to a terminal olefin which would then react with a two-carbon metal carbene. However, this possibility seems unlikely since no other C_{10} isomers were found and since these catalysts are not known to promote such isomerizations. A more probable source of the propylene is from the reaction of a preformed methylene metal species 36 with one end of 2,8-decadiene. This process is shown in Figure 28.

The propylene observed can be seen to be produced directly by path a in Figure 28 along with the two-carbon propagating metal carbene 35 . Path b is also possible and forms 35 and a new diene 37 . This new diene 37 should cyclize rapidly through path c by interacting with 35 . This secondary process will also produce propylene. At this stage the concentration of 35 should be much higher than the concentration of 36 , and so ethylene is not expected. In fact, the ethylene observed is produced only from the catalyst solution because the addition of the

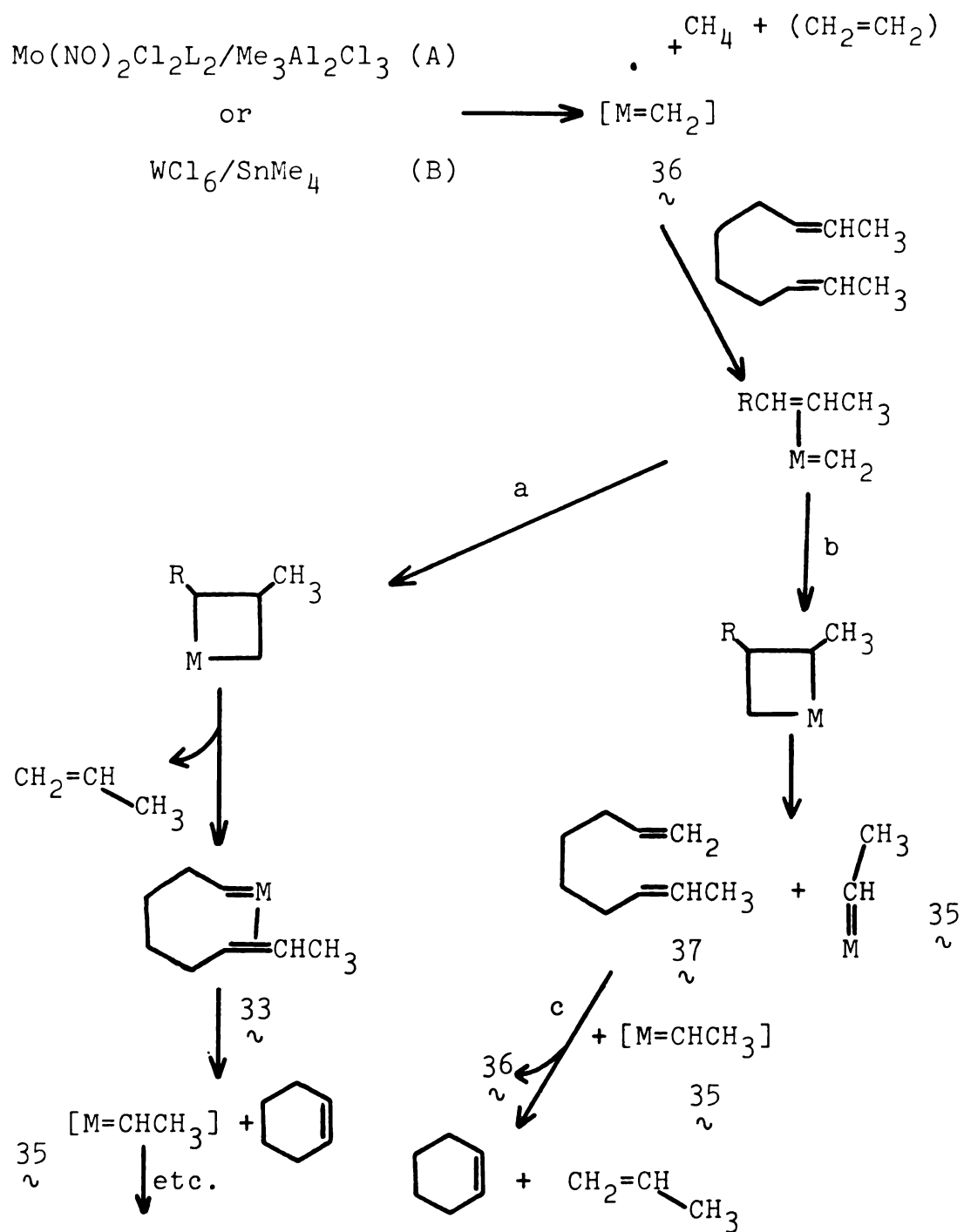


Figure 28. Origin of propylene from the interaction of $36 \sim$ with 2,8-decadiene

olefin does not increase its concentration. Terminal olefins are known to be more reactive than internal olefins. This observation implies that the terminal end of $\mathbf{37}$ should react exclusively with $\mathbf{35}$. Compound $\mathbf{37}$ was never observed in any of these studies.

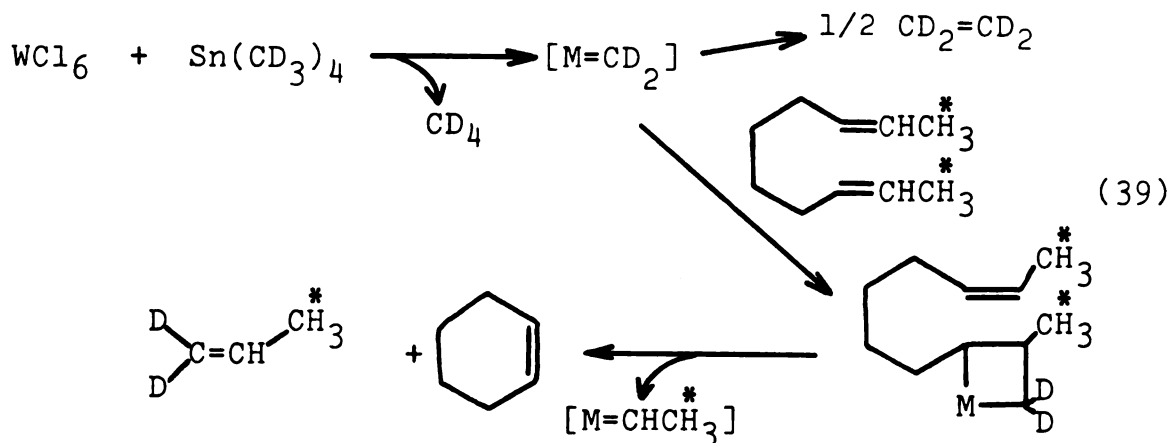
The yield of propylene produced from the reaction of 2,8-decadiene and catalyst A was found to be about 90% based on Mo using n-propane as an internal gas standard. Using catalyst B the yield is only 8-10% based on tungsten when this catalyst is allowed to incubate. The yield of propylene can be increased, as shown later, but these facts seem to indicate that the observed propylene is formed in catalytic amounts.

Propylene was not observed when 2,8-decadiene was treated with $\text{WCl}_6/\text{Sn}\phi_4$, $\phi\text{WCl}_3/\text{AlCl}_3$ or $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{P}\phi_3)_2/\text{EtAlCl}_2$. Some propylene was observed when $\text{WCl}_6/\text{SnBu}_4$ was used, but this was suppressed by addition of n-propyl acetate. This particular catalyst system is known to promote some isomerization of starting material via some pathway other than metathesis.

Deuterium labeling studies were undertaken to determine the source of each fragment of the propylene. Because d_6 -2,8-decadiene was readily available it was treated with either catalyst A or catalyst B, and the propylene was isolated and analyzed via mass spectroscopy. Both propylene samples exhibited very similar fragmentation

patterns with an M^+ peak of $m/e=45$. These spectra closely resemble a known spectrum of 3,3,3- d_3 -1-propene.⁷²

Another study was then aimed at the labeling of the co-catalyst. Several unsuccessful attempts were made to prepare fully deuterated methyl aluminum sesquichloride. Fully labeled tetramethyl tin was then prepared by reaction of d_3 -methyl magnesium iodide with tin (IV) chloride. When unlabeled 2,8-decadiene was treated with the $WCl_6/Sn(CD_3)_4$ system the isolated propylene exhibited a fragmentation pattern in the mass spectrum that is similar to the known 1,1- d_2 -propene pattern ($m/e=44$, M^+). Finally, d_5 -propene was isolated ($m/e=47$, M^+) when d_6 -2,8-decadiene was treated with the same catalyst. These results confirm the scheme in Figure 28, and equation 39



follows the isotopic labels during the reaction of deuterated catalyst B with labeled diene (indicated by asterisks).

The methane and ethylene produced from the mixture of WCl_6 and $\text{Sn}(\text{CD}_3)_4$ were isolated, and both were found to be fully deuterated. The origins of these species are shown in equation 39. Methane production probably originates from a reductive elimination of a dimethyl metal species as shown in Figure 9. The fact that it is fully deuterated indicates that a free radical decomposition, which has been observed with other metal-methyl species,⁷³ is not likely in these systems. The ethylene appears to arise from a slow dimerization between two metal methylene species. Similar dimerizations have been noticed by Schrock⁴⁶ and Casey⁴² (cf. equation 13). It should be recalled that ethylene production is absent when the olefin is added prior to the co-catalyst. This means that the metathesis reaction is much faster than carbene dimerization. The dimerization process is one mode of termination for the metathesis catalysts while most of the active species are probably destroyed by oxygen or other impurities in the system.

The activity of such methylene-metal precursor catalytic systems may be optimized using these results. The final yields of the catalytically produced products (methane, ethylene and propylene) from the metathesis of 2,8-decadiene are shown in Table 9 for the two catalysts and different conditions.

Table 9. Reaction of 2,8-decadiene Using Catalysts A and B with Olefin/Metal = 150-170

Catalyst	Conditions	Yields Based on Metal ($\pm 5\%$)		
		CH_4	$\text{CH}_2=\text{CH}_2$	$\text{CH}_2=\text{CHCH}_3$
A	Incubation 1 hr., Reaction at room temperature	95%	4%	85-90%
B	Incubation 20 min., Reaction at room temperature	70%	2%	8-10%
B	No incubation, Reaction at room temperature	75%	0%	45%
B	No incubation, Reaction at 50°C	75%	0%	65%

The activity of these catalysts can be enhanced by optimizing the yield of methane and propylene and minimizing the production of ethylene. This may be done with other, cheaper, 2-olefins and should allow rapid optimization of the reaction conditions. This method may also be used in a more detailed study of the differences between methylene-metal species formed from different catalytic systems. It was found, for example, that the rate of formation of propylene is faster with catalyst A than with catalyst B. Also, the rate of propylene formation with either catalyst is slower than metathesis indicating some differences in reactivity between 35 and 36.

In conclusion, these studies have shown that a preformed transition metal methylene species is most likely responsible for the initiation of olefin metathesis with some catalysts. The chemistry of this species appears to be different from the propagating species and undergoes a slow dimerization. This initiating species may be a bridged bis-metal species such as $\underline{29}$, and this is presently being investigated by others.

EXPERIMENTAL

General

All metathesis reactions were conducted in oven-dried glass tubes sealed with rubber caps and were alternately evacuated and flushed with argon several times on a vacuum line. The solutions of reagents and solvents were stored under argon and were transferred with oven-dried, argon-flushed syringes.

Analytical glc was conducted with a Varian Series 1400 FID chromatograph with either a 20' x 1/8" Durapak column (A) at 60° or a 32' x 1/8" 5% Carbowax 20M/Chromosorb W (B) at 100-150°C. Preparative glc was conducted with a 10' x 1/4" 7% paraffin wax/Chromosorb W column at 80° for gas samples and a 16' x 1/4" 5% DC-550/Chromosorb G column at 120° for liquid samples, both using a Varian 90-P chromatograph. NMR analyses were obtained using a Varian T-60 spectrometer and δ values were recorded relative to TMS. Infrared spectra were obtained with a Perkin-Elmer 237B and calibrated with a polystyrene standard. Mass spectra were conducted with a Hitachi RMU-6E spectrometer.

The methyl aluminum sesquichloride ($\text{Me}_3\text{Al}_2\text{Cl}_3$) was purchased from Ethyl Corporation and used as a 1M solution in chlorobenzene. The light-green $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{P}\phi_3)_2$ was

prepared according to the procedure of Cotton⁷⁴ and was stored in a desiccator. Tetramethyl tin and d_{12} -tetramethyl tin were prepared according to the procedure of Edgell and Ward.⁷⁵ The tungsten hexachloride was purchased from Ventron and used as a .05M solution in chlorobenzene under argon.

Chlorobenzene was distilled from CaH_2 or P_2O_5 under argon into a flask with a side arm with a two-way stopcock and stored over 4A sieves. A five percent forecut was discarded during the distillation. Commercially available t,t-2,8-decadiene (Chemical Samples) was stored over sieves and found to be >99% isomerically pure by glc analysis with column B. All olefins were activated prior to reaction by passing through basic Woelm alumina under an atmosphere of argon.

Preparation of 1,1,1,10,10,10- d_6 -2,8-decadiyne

In a flame-dried, argon flushed 250 ml three neck flask fitted with a gas inlet and a stir bar were placed 3.7 g (35 mmol) 1,7-octadiyne and 50 ml distilled hexane (CaH_2). The solution was cooled in an ice bath, and 35 ml of a 2.0M n-BuLi/hexane solution was added dropwise over 30 minutes with stirring. A white precipitate formed, and after complete addition the slurry was stirred for a few minutes at room temperature. The volatiles were removed in vacuo, and the remaining white solid dissolved in 100 ml oxygen-free THF (benzophenone/Na). The flask was fitted

with a Friedrichs condenser and an addition funnel, and a solution of 10.0 g (69 mmol) CD_3I (Aldrich) in 25 ml oxygen-free THF was added over 15 minutes at room temperature and then stirred overnight. The contents were poured into ice-water, and the aqueous layer extracted with three 50 ml portions of n-pentane. The combined extracts were washed with 50 ml dilute aqueous HCl (5%), 50 ml water and 50 ml saturated sodium bicarbonate and were dried over MgSO_4 . After filtering, the pentane was distilled off and the remaining light yellow liquid distilled (b.p. 85-87°/10 mm) to give 3.7 g (75%) glc pure product: IR (neat) $2140\text{ cm}^{-1}(\text{C}\equiv\text{C})$, no $3300\text{ cm}^{-1}(\text{C}\equiv\text{C}-\text{H})$; $^1\text{H NMR}(\text{CDCl}_3)$ δ 1.5(m,4,- CH_2 -), δ 2.1(m,4, $\text{C}\equiv\text{C}-\text{CH}_2$ -), no peak at δ 1.8 for terminal methyl resonances.

Preparation of 1,1,1,10,10,10- d_6 -cis,cis-2,8-decadiene

In a dry 250 ml flask with gas inlet and exit were placed 50 ml freshly distilled pyridine (BaO), 50 mg 5% Pd on BaSO_4 (Ventron) and 3.0 g (21.3 mmol) of d_6 -2,8-decadiyne. Dry hydrogen was then slowly passed through the stirring mixture with a sintered glass frit for several hours at room temperature. The progress of the reaction was easily monitored by periodic glc analysis of the reaction mixture with the 5% DC-550 column described before. Upon complete conversion of the diyne, the reaction mixture was passed through a short pad of Celite and the filtrate concentrated to about 30 ml by carefully distilling off the

pyridine using a short Vigreux column. The concentrate was taken up in 100 ml ether and washed with 50 ml 10% aq. HCl and two 50 ml portions of brine. The ether solution was dried over MgSO_4 , and after filtering the ether was removed by distillation. The remaining clear liquid was distilled (80-83°/40 mm) to give 2.52 g (82%) product. Analytical glc analysis using column B at 105° showed that the total trans content was about $2 \pm .5\%$ or 98% total cis content. $^1\text{H NMR}(\text{CDCl}_3)$ δ 1.6(m,4,- CH_2 -), δ 2.2(m,4,= $\text{CH}-\text{CH}_2$), δ 5.5(m,4,= CH); IR (neat) $1450\text{ cm}^{-1}(\text{C}=\text{C})$, no $\text{C}\equiv\text{C}$ stretch; mass spectrum (70ev) m/e (source) 144 (m^+), 126 (m^+-CD_3), 108 (m^+-2CD_3) (no significant peaks m/e 126→144).

Preparation of cis,cis-2,8-decadiene

In the same way described above 5.0 g (37.3 mmol) 2,8-decadiyne (Chemical Samples), 100 mg 5% Pd on BaSO_4 and 150 ml freshly distilled pyridine were stirred under a flow of dry hydrogen at room temperature. The product was obtained in the same way as above (b.p. 78-82°/37 mm) 3.65 g (71%) clear product. GLC analysis (column B) indicated $98 \pm 1\%$ cis content. $^1\text{H NMR}(\text{CDCl}_3)$ δ 1.6(m,4,- CH_2 -), δ 1.8(d,6, CH_3), δ 2.2(m,4,= $\text{CH}-\text{CH}_2$ -), δ 5.5(m,4,= CH); IR (neat) $1450\text{ cm}^{-1}(\text{C}=\text{C})$, $725\text{ cm}^{-1}(\text{cis C}=\text{C})$, no $\text{C}\equiv\text{C}$, 965 (vw)(trans C=C); mass spectrum (70ev) m/e 138 (m^+), m/e 123 (m^+-CH_3).

Metathesis of cis,cis-2,8-decadiene with Catalyst A

The procedure for the metathesis of cis,cis-2,8-decadiene is typical of the procedures used for metathesis reactions.

In an oven-dried 20 mm x 120 mm glass tube with a magnetic stir bar was placed 10 mg (.013 mmol) $\text{Mo}(\text{NO})_2\text{Cl}_2(\text{P}\phi_3)_2$. The tube was then fitted with a rubber serum cap and alternately evacuated and flushed with argon on a vacuum line several times. To this was added 3 ml dry chlorobenzene and .1 ml of the 1M $\text{Me}_3\text{Al}_2\text{Cl}_3$ solution via syringe. The resulting clear brown solution was stirred for thirty minutes at room temperature. Meanwhile, .20 g (1.45 mmol) cis,cis-2,8-decadiene and 50 μl (.26 mmol) n-decane (internal liquid standard) were passed under argon through 2-3 g basic alumina (Woelm) with the aid of 2 ml chlorobenzene into a small vial. This solution was then added to the incubated catalyst solution via syringe. A gas solution of n-propane in argon, 5 ml (.026 mmol) was added with a gas syringe. Gas (~.2 ml) and liquid (~.3 ml) samples were withdrawn at several intervals. The gas samples were analyzed immediately on column A using appropriate calibrations from standard samples. Liquid aliquots were quenched with a few drops of water, passed through Florosil into screw cap vials and stored at 0° until glc analysis with column B.

Reproducible results could also be obtained by running several small reactions simultaneously, quenching each at a specified time with water and analyzing the gas and liquid from the sealed reaction vessel.

Metathesis of cis,cis-2,8-decadiene with Catalyst B

In a 20 mm x 120 mm oven-dried, argon flushed tube fitted with a rubber cap was placed .5 ml of the .05M WCl_6 solution, .20 g (1.45 mmol) activated cis,cis-2,8-decadiene, 50 μl n-decane and 70 μl of a .75M SnMe_4 in chlorobenzene solution in that order. Analytical glc analysis was conducted in a similar way as above, except that liquid samples were quenched with a few drops of a dilute aq. NH_4OH solution.

Metathesis of a 1.21 $\pm$.02:1 Mixture of d_0 : d_6 -cis,cis-2,8-decadiene

This reaction was conducted by the method described above for catalyst A. To the incubated catalyst was added .153 g of a 1.21 $\pm$.02:1 mixture of d_0 and d_6 decadiene (determined by weight and mass spectral analysis). At four time intervals, 10 ml gas samples were withdrawn and replaced with an equal volume of argon. The gas was injected into the preparative gas column mentioned above and the cis-2-butenes isolated with a glass trap cooled in liquid N_2 at the exit port. The trapped butenes were then submitted for mass spectral analysis. The $\text{d}_3/\text{d}_6\text{-C}_4$ ratios listed in Table 6 were found by comparing the peak heights

at $m/e = 59$ (d_3-C_4) and $m/e = 62$ (d_6-C_4). Liquid aliquots were withdrawn and the 2,8-decadiene isolated by preparative glc with the DC-550 column mentioned above. These samples were analyzed via mass spectroscopy, and the peak heights at $m/e = 138$ (d_0-C_{10}), $m/e = 141$ (d_3-C_{10}) and $m/e = 144$ (d_6-C_{10}) were compared. No other peaks in this region were noted. The d_3/d_6-C_{10} ratios were found and are recorded in Table 6. The $t/c-C_4$ ratio was determined at each gas and liquid sampling and are also listed in Table 6.

Metathesis of a $2.68 \pm .05:1$ mixture of $d_0:d_6$ -cis,cis-2,8-decadiene

In the same way as described above, .120 g of a $2.68 \pm .05:1$ mixture of $d_0:d_6$ -cis,cis-2,8-decadiene was added to catalyst A. After ten minutes two 20 ml gas samples were withdrawn from the tube and the reaction immediately quenched with .5 ml H_2O . The 2-butenes were isolated in the same way and the collection tube submitted for analysis. A $d_0:d_3:d_6$ ratio of $1 : .72 \pm .06 : .18 \pm .03$ was found. The calculated carbene ratio is $1 : .75 \pm .04 : .14 \pm .02$, and the ratio for the pairwise scheme is $1 : .64 \pm .02 : .17 \pm .02$. The $t/c-C_4$ ratio was $.31 \pm .04$ which corresponds to about 6-8% conversion of starting material. Using n-decane as an internal liquid standard, the yield of cyclohexene was found to be $5 \pm 2\%$ based on decadiene.

Isolation of 3,3,3-d₃-1-propene

To a solution of catalyst A was added .15 g d₆-2,8-decadiene and the solution stirred overnight. The propylene was isolated with the preparative glc gas column in a trap cooled in liquid and submitted for mass spectral analysis. Mass spectrum (70ev) m/e (relative intensity); Found: 46 (87), 45 m⁺(1000), 44 (913), 43 (696), 42 (391), 41 (696); Literature⁷²: 46 (29), 45 m⁺(1000), 44 (956), 43 (635), 42 (260), 41 (496). Found (15ev): 46 (94), 45 m⁺(1000), 44 (170), 43 (94), 42 (75), 41 (38).

A similar reaction was conducted with a solution of catalyst B: mass spectrum (15ev) 46 (107), 45 m⁺(1000), 44 (285), 43 (107), 42 (71), 41 (36).

Isolation of 1,1,3,3,3-d₅-1-propene

To a solution of .013 mmol WCl₆ in chlorobenzene was added .15 g d₆-2,8-decadiene and .26 ml of a 1M Sn(CD₃)₄ in chlorobenzene in that order. After stirring overnight, the propylene was isolated as above. Mass spectrum (13ev) m/e (rel. intensity), 47 m⁺(639), 46 (203), 45 (1000), 44 (453), 43 (814), 42 (546).

Isolation of 1,1-d₂-1-propene

Using the same deuterated catalyst as above, .15 g d₀-2,8-decadiene was metathesized and the propylene isolated. Mass spectrum (50ev) m/e (rel. intensity);

Found: 44 m^+ (750), 43 (1000), 42 (429), 41 (786), 40 (214);
 Literature⁷² (70ev): 44 (797), 43 (1000), 42 (370), 41
 (366), 40 (506).

Isolation of d_4 -methane and d_4 -ethylene from a Solution of WCl_6 and $Sn(CD_3)_4$

A solution of .013 mmol WCl_6 and .026 mmol $SnMe_4$ in chlorobenzene was stirred for two hours at room temperature. Using the gas preparative glc column methane was isolated in a trap containing activated charcoal at liquid N_2 temperature. The ethylene was trapped in a long, spiral glass tube at the same temperature. Methane mass spectrum (18ev)⁷⁶: m/e (rel. intensity) 20 m^+ (1000), 18 (620), 16 (80); Literature⁷² (50ev): 20 (1000), 18 (830), 16 (125); Ethylene mass spectrum (15ev): 32 (not oxygen)(1000), 30 (trace), 28 (120); Literature⁷² (70ev): 32 (1000), 30 (618), 28 (640).

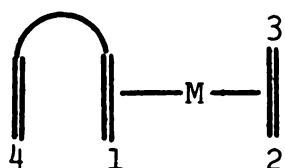
APPENDIX

APPENDIX

PROCEDURE FOR THE CALCULATION OF THE POSSIBLE d_3/d_6 -2-BUTENE RATIOS ARISING FROM A PAIRWISE MECHANISM

The procedure outlined here for the calculation of the predicted isotopic distribution between the 2-butenes (d_0 -C₄=B₀, d_3 -C₄=B₃, d_6 -C₄=B₆) arising from the metathesis of a mixture of d_0 - (D₀) and d_6 - (D₆) 2,8-decadiene is analogous to those reported by Grubbs³⁴ and Katz.³⁵ In this instance, however, the interaction of the three possible metal-butene complexes (M-B₀, M-B₃, M-B₆) with the scrambled starting material (D₃) is also considered.

The model shown below illustrates schematically the possible butenes and metal-butene complexes resulting from a pairwise metathesis between any of the three butenes and any of the three decadienes. As explained earlier this calculation considers the case where $k_{\text{met}} \gg k_{\text{ex}}$ in Figure 3 because this yields the greatest amount of scrambling.



<u>Possible B's</u>	<u>Resulting M-B's</u>
2-3	1-4
1-3	2-4
1-2	3-4

All of the possible combinations, where these four numbers can represent labeled (CHCD_3) or unlabeled (CHCH_3) ethylidene units, are considered. For example, the metathesis between fully labeled decadiene (D_6) and unlabeled 2-butene (B_0) is represented when $1=4=-\text{CHCD}_3$ and $2=3=-\text{CHCH}_3$. It can be seen from the model shown above, for instance, that the probability of forming B_0 from this interaction (2-3) is $1/3$ and the probability of forming B_3 (1-3 and 1-2) is $2/3$. There is no chance of forming B_6 in this case. The probabilities for the formation of any of the three butenes or the three metal-butene complexes may be found for all of the nine possible interactions in just this way. These probability factors (P_n) for each species are given below in a probability matrix generated from the nine interactions.

P_n values								
<u>n</u>	<u>D</u>	<u>M-B</u>	<u>B₆</u>	<u>B₃</u>	<u>B₀</u>	<u>M-B₆</u>	<u>M-B₃</u>	<u>M-B₀</u>
1	D_6	M-B_6	1	0	0	1	0	0
2	D_6	M-B_3	$1/3$	$2/3$	0	$2/3$	$1/3$	0
3	D_6	M-B_0	0	$2/3$	$1/3$	$1/3$	$2/3$	0
4	D_0	M-B_6	$1/3$	$2/3$	0	0	$2/3$	$1/3$
5	D_0	M-B_3	0	$2/3$	$1/3$	0	$1/3$	$2/3$
6	D_0	M-B_0	0	0	1	0	0	1
7	D_3	M-B_6	$2/3$	$1/3$	0	$1/3$	$2/3$	0
8	D_3	M-B_3	$1/6$	$2/3$	$1/6$	$1/6$	$2/3$	$1/6$
9	D_3	M-B_0	0	$1/3$	$2/3$	0	$2/3$	$1/3$

Using these P_n values the production of the metal-butene complexes or the 2-butenes can be found by the general equation A1.

$$\begin{aligned}
 \frac{d[B]}{dt} &= P_1[D_6][M-B_6] + P_2[D_6][M-B_3] + P_3[D_6][M-B_0] \\
 \frac{d[M-B]}{dt} &+ P_4[D_0][M-B_6] + P_5[D_0][M-B_3] + P_6[D_0][M-B_0] \\
 &+ P_7[D_3][M-B_6] + P_8[D_3][M-B_3] + P_9[D_3][M-B_0]
 \end{aligned}
 \tag{A1}$$

The first step in the calculation for a particular $D_0 : D_3 : D_6$ ratio is to find the relative M-B values using equation A1. This is accomplished by using an iterative scheme whereby any $M-B_0 : M-B_3 : M-B_6$ is initially assumed, and these values are placed in the three equations for the formation of the three metal-butenes. Solving these equations yields new relative values for the complexes which are then fed back into the three equations. This procedure is repeated until a converging ratio is found. The resulting relative M-B values are then put into the three equations describing the formation of B_0 , B_3 and B_6 . This affords the relative ratios for the labeled butenes predicted by the pairwise scheme.

The following table gives the assumed $D_0 : D_3 : D_6$ ratio and the calculated values for the relative amounts of metal-butene complexes and the butenes. The B_3/B_6 , or

d_3/d_6 -C₄, values are also shown in Table 7.

<u>Case</u>	<u>D₀ : D₃ : D₆</u>	<u>M-B₀</u>	<u>M-B₃</u>	<u>M-B₆</u>	<u>B₃/B₆</u>	<u>B₀/B₆</u>
1	1.21 : 0 : 1.0	1.33	1.15	1.00	1.896	1.408
2	1.15 : .11: .95	1.32	1.23	1.00	1.926	1.389
3	1.11 : .18: .92	1.31	1.29	1.00	1.933	1.371
4	1.06 : .27: .88	1.31	1.36	1.00	1.988	1.365
5	.98 : .42: .81	1.29	1.50	1.00	2.014	1.338

The B_3/B_6 ratios calculated above do not account for any independent isotopic scrambling of the butenes via a degenerate metathesis process. To adjust these values a portion of the relative amounts of each butene $x[B]$, where x is a fraction between zero and one, is allowed to scramble independently to the statistical distribution $[B]'$. These scrambled portions are then added back into the remainder of the labeled butenes arising only from the scrambled starting material. Thus, the adjusted relative butene values $[B]_{adj}$ for each of the three butenes are given in equations A2, A3 and A4.

$$[B_6]_{adj} = [B_6] - x[B_6] + [B_6]' \quad (A2)$$

$$[B_3]_{adj} = [B_3] - x[B_3] + [B_3]' \quad (A3)$$

$$[B_0]_{adj} = [B_0] - x[B_0] + [B_0]' \quad (A4)$$

The factor x is determined by the approximated extent of independent scrambling in the 2-butenes. This

approximation originates from the assumption that $k' = 2k$ in equations 37 and 38.

The total hydrogen content $[B_H]$ and the total deuterium content $[B_D]$ in the portion of the butenes allowed to scramble will not change. These values are found by equations A5 and A6.

$$[B_H] = x[B_0] + x/2[B_3] \quad (A5)$$

$$[B_D] = x[B_6] + x/2[B_3] \quad (A6)$$

If $[B_H]/[B_D] = A$, the statistical distribution between the scrambled portion of 2-butenes will be $A^2 : 2A : 1$ for $[B_0]' : [B_3]' : [B_6]'$.

The total amount of scrambled material must be equal to the total butene portion prior to independent scrambling as shown in equation A7.

$$[B_0]' + [B_3]' + [B_6]' = x([B_0] + [B_3] + [B_6]) \quad (A7)$$

Using equations A5, A6 and A7 a correction factor C can easily be found,

$$C = \frac{([B_0] + [B_3] + [B_6])x}{A^2 + 2A + 1}$$

which will allow calculation of the $[B]'$ values as follows;

$$[B_0]' = A^2C ; [B_3]' = 2AC ; [B_6]' = C .$$

These $[B]'$ values are substituted into equations A2, A3 and A4 to yield equations A8, A9 and A10.

$$[B_6]_{adj} = [B_6] - x[B_6] + C \quad (A8)$$

$$[B_3]_{adj} = [B_3] - x[B_3] + 2AC \quad (A9)$$

$$[B_0]_{adj} = [B_0] - x[B_0] + A^2C \quad (A10)$$

Various values of x are approximated and the adjusted $[B_3]/[B_6]$ values are calculated. These values ($d_3/d_6 - C_4$) are given in Table 8.

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