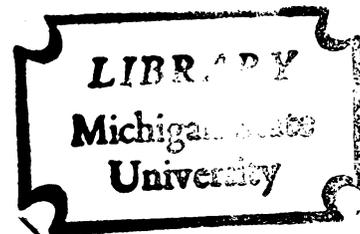




THESIS



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Part I. An Investigation of the Mechanism of the Olefin Metathesis Reaction using a Heterogeneous Catalyst; Part II. Development of a Polymer-Bound Catalyst for the Olefin Metathesis Reaction.

presented by

Sandra Jean Swetnick

has been accepted towards fulfillment  
of the requirements for

Ph.D. degree in Chemistry



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PART I

AN INVESTIGATION OF THE MECHANISM OF THE OLEFIN  
METATHESIS REACTION USING A HETEROGENEOUS CATALYST

PART II

DEVELOPMENT OF A POLYMER-BOUND CATALYST FOR THE  
OLEFIN METATHESIS REACTION

By

Sandra Jean Swetnick

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1979

ABSTRACT

PART I

AN INVESTIGATION OF THE MECHANISM OF THE OLEFIN  
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The mechanism of the olefin metathesis reaction is examined using mixtures of cis,cis-2,8-decadiene and cis,cis-2,8-decadiene-1,1,1,10,10,10-d<sub>6</sub> over two heterogeneous catalysts. The metathesis of these diene mixtures produces a ratio of labelled and unlabelled butenes which can be compared to butene ratios predicted for a number of mechanisms.

Previous studies using homogeneous catalysts have indicated that a non-pairwise exchange of alkylidene units is occurring. A metal carbene, initially formed by the interaction of the catalyst and the co-catalyst has been

proposed as the active site for this reaction. Most heterogeneous catalysts do not require such alkylating co-catalysts and therefore require an alternate source of the initial carbene for a metal-carbene chain mechanism to occur.

Evidence to be presented here supports a non-pairwise exchange mechanism for olefin metathesis. The experimental ratio of labelled butenes formed is that previously predicted for a chain mechanism. In addition, the identification of transient products has allowed the proposal of an initiation scheme which would produce the required metal-carbene active site during the "break-in" period observed with heterogeneous catalysts. The combination of these two pieces of experimental evidence strongly supports a metal-carbene chain mechanism for olefin metathesis with a heterogeneous catalyst.

The second part of this investigation has studied the feasibility of using a polymeric co-catalyst to develop a polymer-bound metathesis catalyst. This is an unusual development in that the co-catalyst would serve both to activate the transition metal and to link it to the polymer support. A polymer-bound metathesis catalyst was successfully prepared using polystyryltrimethyltin with tungstenhexachloride.

To

The MSU Tolkien Fellowship  
without whom I never would have survived

## ACKNOWLEDGMENTS

I would like to thank Dr. Robert H. Grubbs for his guidance, support and patience during the completion of this work.

I also thank my father, my mother and my sister who offered unlimited love and support when I needed it most.

I would like to mention Mrs. Bernice Wallace who simply believed I could do it.

My fellow graduate students, in particular, Bob DeVries, Mir Mohammed Mohaddes, Cindy Huang Su, and Gwen Goretsas made graduate school more enjoyable.

Finally, I cannot express the love, acceptance and deeply moving friendships I have experienced as a member of the MSU Tolkien Fellowship.

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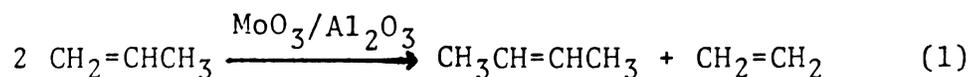
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## INTRODUCTION

Since its discovery in 1964, olefin metathesis has received an ever increasing effort directed toward understanding and controlling this reaction. A reasonable mechanism has been proposed for metathesis when conducted over non-supported catalysts. This study represents an effort to study the mechanism of metathesis when promoted by a heterogeneous catalyst. Although the reaction does not necessarily proceed by the same mechanism in both cases, similarities have already been observed. In order to demonstrate these similarities and to point out differences, the current research using homogeneous catalysts will be reviewed. This will be followed by an outline of relevant studies of the metathesis reaction promoted by heterogeneous catalysts.

The disproportionation of olefins was first recognized by Banks and Bailey.<sup>1</sup> They found that propene, exposed to a heterogeneous catalyst, exchanged olefin substituents to produce ethylene and butene (Eq. 1).



Later, a variety of homogeneous systems were reported which catalyzed the reaction at significantly lower temperatures.<sup>2</sup> Many of the homogeneous systems are very rapid, producing an



equilibrium mixture of products in a matter of seconds.

Prior to the discovery of this reaction, similar catalysts had been used to promote the polymerization of cyclic olefins. This ring-opening polymerization was later recognized as a special case of the metathesis reaction.<sup>3</sup>

The majority of metathesis-promoting catalysts contain molybdenum, tungsten or rhenium and a non-transition metal component. The homogeneous catalysts and the insoluble non-supported catalysts are generally prepared from soluble precursors. The heterogeneous catalysts are solid materials prepared by combining a soluble metal complex with a solid support.

Homogeneous catalyst systems are generally prepared by reducing transition metal complexes with non-transition metal organometallic co-catalysts. A survey of typical homogeneous systems is given in Table I. The majority of these systems show a high activity and selectivity under very mild conditions. The variety of metal complexes and co-catalysts which can be combined to produce an active metathesis catalyst has led to an intensive study of how these components interact. Some of the results of these investigations will be presented later.

Heterogeneous catalysts were the first to be recognized and developed. These are generally prepared by impregnating high-surface area supports with solutions of transition metal oxides or carbonyls. The solvent is removed under vacuum and the solid catalyst activated by heating in air



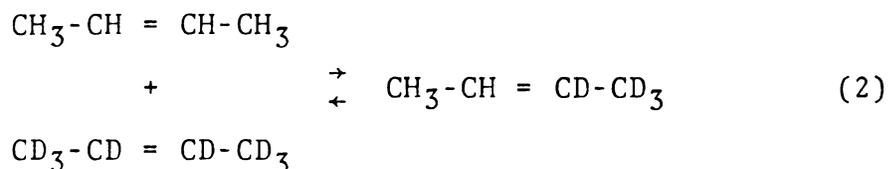
Table 1. Typical Metathesis Catalysts.

Catalyst	Temp. K	Ref.
$WCl_6-C_2H_5AlCl_2-C_2H_5OH$	Ambient	2
$WCl_6-(C_2H_5)_3Al$	243	6
$WCl_6-LiAlH_4$	Ambient	7
$MoCl_2(NO)_2[P(C_6H_5)_3]_2-$ $(CH_3)_3Al_2Cl_3$	273-278	8
$ReCl_5-(NC_4H_9)_4Sn$	Ambient	9
Supported Catalyst	Temp. K	Ref.
$MoO_3-CoO-Al_2O_3$	436	1
$MoO_3-SiO_2$	811	10
$Mo(CO)_6-Al_2O_3$	344	1
$WO_3-SiO_2$	700	11
$Re_2O_7-Al_2O_3$	298	12
$Re_2(CO)_{10}-Al_2O_3$	373	13

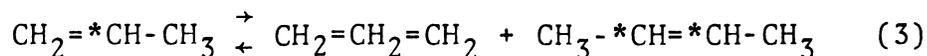


at 500-600°C. It is then cooled to the reaction temperature in a stream of inert gas.<sup>4</sup> As shown in Table 1, these catalysts are optimally active at higher temperatures than comparative homogeneous systems. Supported catalysts tend to show an induction period before reaching maximum activity. This induction period has been carefully studied and will be discussed later.

The earliest investigations determined that transalkylation, cleavage of the double bond itself, was occurring. Calderon et al.<sup>26</sup> demonstrated double bond cleavage in a study of the metathesis of a mixture of 2-butene and perdeutero-2-butene over a homogeneous catalyst. The only new product was 2-butene-1,1,1,2-d<sub>4</sub> (Eq. 2).



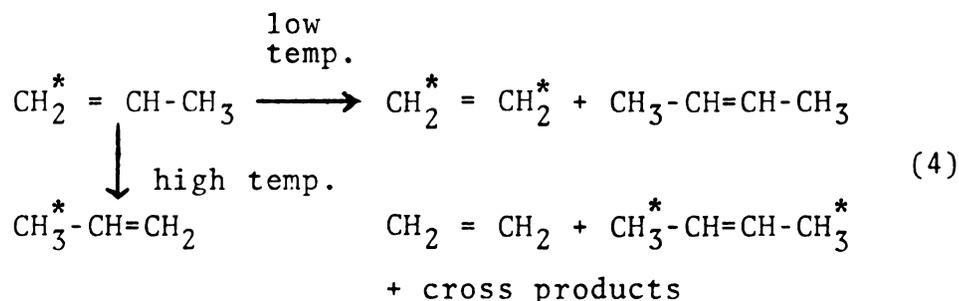
Similar results were obtained by Mol et al.<sup>14</sup> in the metathesis of propene-2-<sup>14</sup>C over a heterogeneous catalyst, Re<sub>2</sub>O<sub>7</sub>-Al<sub>2</sub>O<sub>3</sub> (Eq. 3).



The ethene showed essentially no radioactivity whereas the butene showed a radioactivity twice as high as that of the

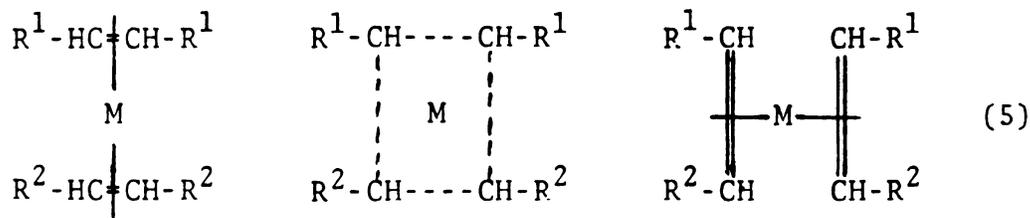


starting material. These results were verified by Clark and Cook<sup>15</sup> using MoO<sub>3</sub>-CoO-Al<sub>2</sub>O<sub>3</sub>. Experiments with 1-<sup>14</sup>C-propene and 3-<sup>14</sup>C-propene were conducted using a variety of heterogeneous catalysts in an effort to examine the possibility of an allyl intermediate. Mol et al.<sup>16</sup> used Re<sub>2</sub>O<sub>7</sub> and observed that the two methyl groups retained their identity. A similar study by Clark and Cook<sup>15</sup> catalyzed by MoO<sub>3</sub>-CoO-Al<sub>2</sub>O<sub>3</sub> was consistent with Mol's work at low temperatures. However, at higher temperatures the propene isomerized prior to disproportionation. This was confirmed in a separate study by Woody<sup>17</sup> et al. Woody noted however that isomerization of the 2-butene product was negligible (Eq. 4).

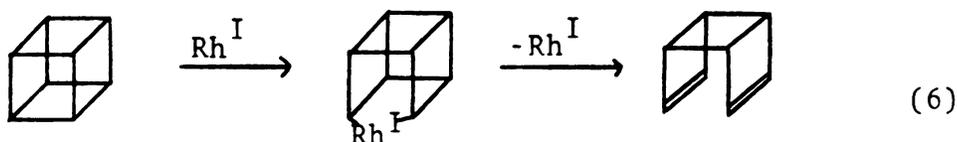


The authors concluded that an allylic intermediate was excluded at low temperatures but could not definitely be excluded at higher temperatures.

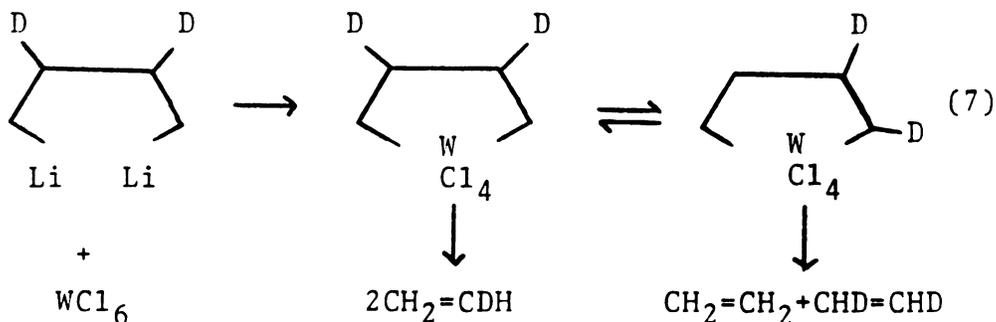
The first mechanistic schemes involved a concerted 2 + 2 addition of 2 complexed olefins to form a "quasi-cyclobutane" metal complex which could then decompose to give two new olefins<sup>18</sup> (Eq. 5)



Experimentally it was found that cyclobutanes, were unreactive under metathesis conditions and were not observed as metathesis side-products.<sup>19</sup> Also recent work demonstrated that similar processes occurred by non-concerted pathways<sup>20</sup> (Eq. 6).



The first non-concerted mechanisms involved the coordination of two olefins to the metal center and a "pairwise" exchange of alkylidene units via a five-membered metallocycle.<sup>21</sup> This proposal was based on the synthesis and decomposition of a tungsten metallocycle. Under metathesis conditions this metallocycle gave metathesis-like products (Eq. 7).



Further support for this proposal developed from the isolation and characterization of metallocycles of iridium,<sup>22</sup> platinum<sup>23</sup> and titanium.<sup>24</sup> In such a pairwise exchange the fates of the two ends of an olefin are linked and should give predictable products. The observation of unexpected products lead to the proposal of yet another mechanism.

In 1970, Herisson and Chauvin<sup>25</sup> proposed a chain reaction mechanism which provides a pathway for the scrambling of the alkylidene units in a non-pairwise fashion (Figure 1). This metal-carbene, chain reaction mechanism was proposed to explain a variety of experimental observations which seemed inconsistent with a pairwise exchange.

The ring-opening polymerization of cyclic olefins had been utilized even before the metathesis reaction was recognized by Banks and Bailey.<sup>3</sup> A careful study of the products of these reactions revealed that high molecular weight linear polymers were formed early in the reaction. Calderon<sup>26</sup> et al. reported a polymer of molecular weight 200,000-300,000 at 6% conversion of cyclooctene. Also formed in this reaction were low molecular weight macrocyclic oligomers. A pairwise scheme could account for these products only if the growing polymer preferentially remained attached to the catalytic site. This would require that the exchange of olefins onto and off of the metal center be slower than the actual metathesis. However, recent studies have demonstrated that olefin exchange is much faster than



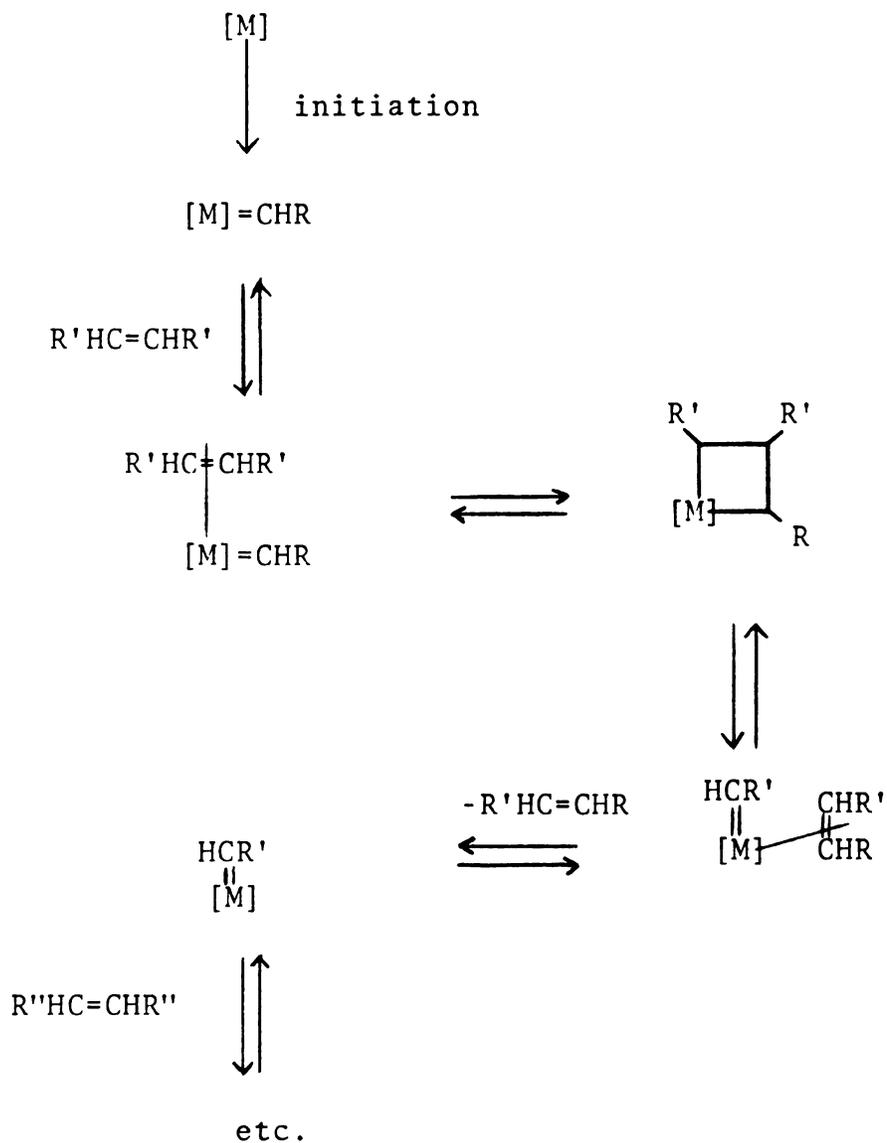
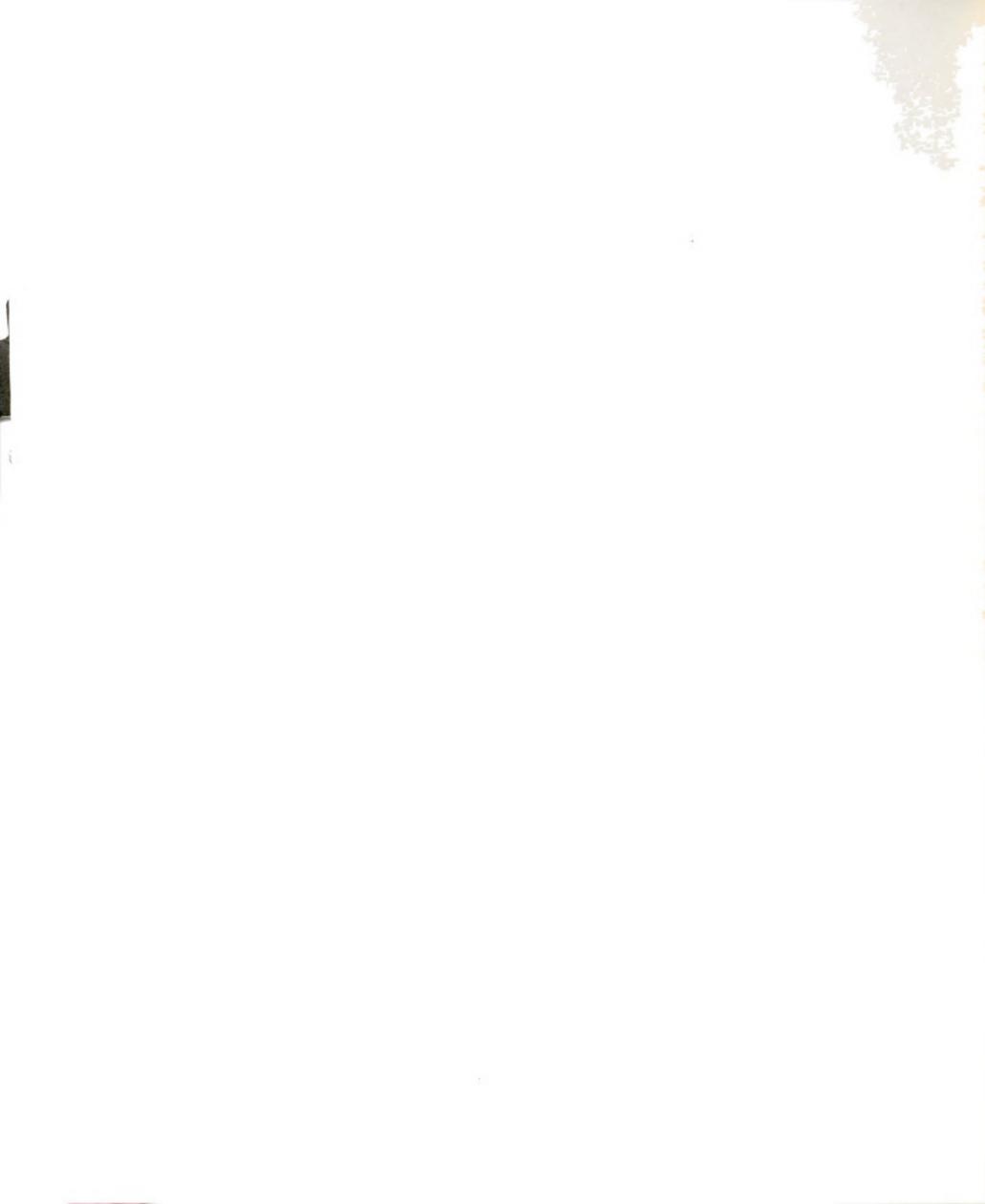


Figure 1. The carbene initiated chain mechanism for the metathesis of olefins.



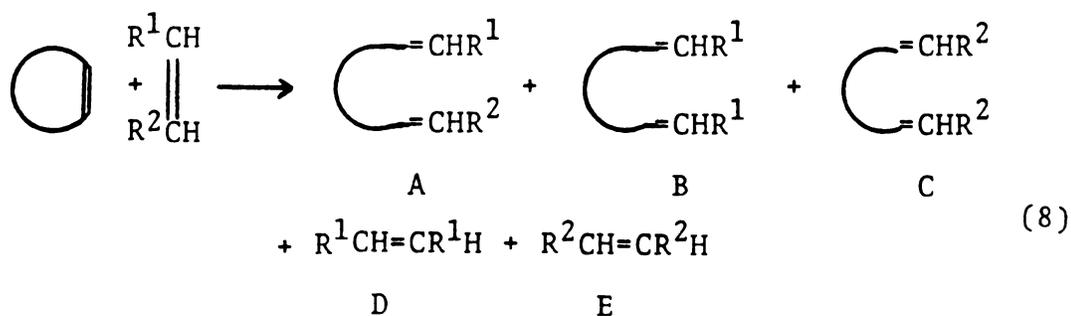
metathesis.<sup>27</sup> Dolgoplosk<sup>28</sup> suggested that a pairwise scheme ought to give low molecular weight products early in the reaction which slowly build to higher polymers. The observed products were more characteristic of a chain mechanism.

Chauvin's carbene, chain mechanism could explain these unexpected results. High molecular weight products would be expected early in a chain mechanism and, as shown in Figure 2, these polymers would be expected to be linear. The lower molecular weight cyclic oligomers would be formed by a "back-biting" process as also shown.

Scott<sup>29</sup> verified that the high molecular weight products are linear and more importantly that the macrocycles are formed by an intramolecular process. This is in agreement with the proposed "back-biting" scheme.

A pairwise mechanism would be expected to form macrocycles by the intermolecular reaction between two smaller rings. The only intramolecular pairwise reaction would be a "pinching-off" of a larger ring to form two small rings.<sup>30</sup>

Chauvin's carbene scheme was originally proposed to explain the products resulting from the metathesis of a mixture of a cyclic olefin and an unsymmetrical olefin (Eq. 8).





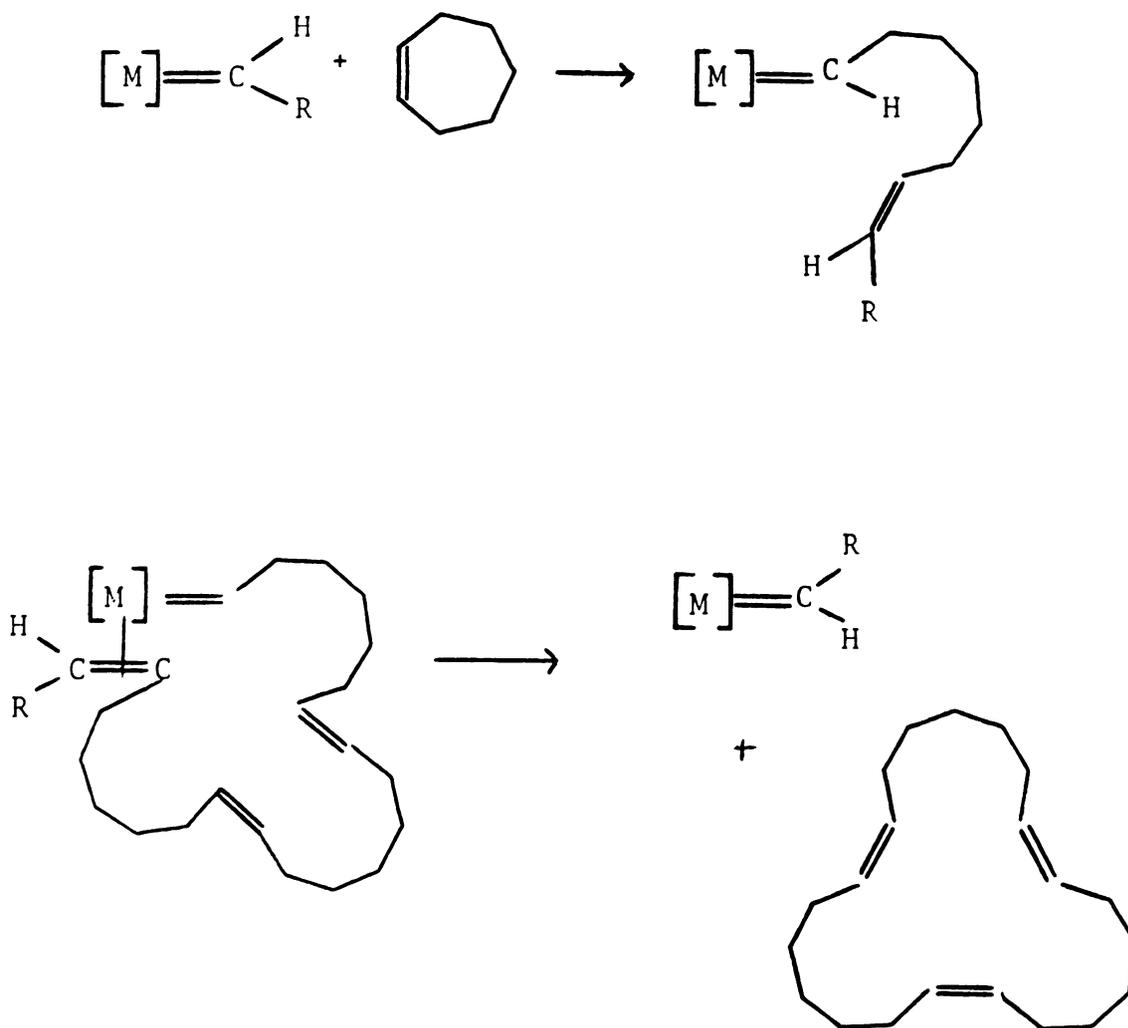


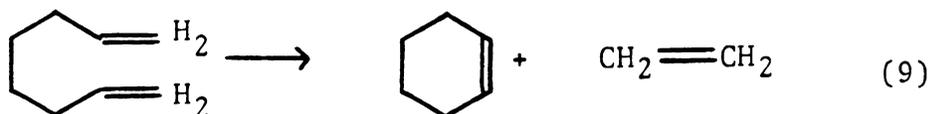
Figure 2. Carbene initiated, ring-opening polymerization.



In two independent studies, the symmetrical products B and C were observed early in the reaction.<sup>25,31</sup> Pairwise exchange of alkylidene units would yield only product A from the starting materials. B and C could only arise by a secondary metathesis between D and E and the cyclic olefin. This would again require olefin exchange onto and off the catalytic center to be slow compared to metathesis. On the other hand, Chauvin's carbene scheme would uncouple the alkylidene units of the starting olefin and allow the direct formation of B and C.

If the products are allowed to equilibrate, either mechanism would be expected to give the observed products. These investigations prompted more exact studies into the mechanism of metathesis.

Olefin reactants which would be less likely to equilibrate in secondary reactions were designed using derivatives of 1,7-octadiene. Metathesis of 1,7-octadiene produces an almost quantitative yield of cyclohexene and ethylene<sup>32</sup> (Eq. 9).

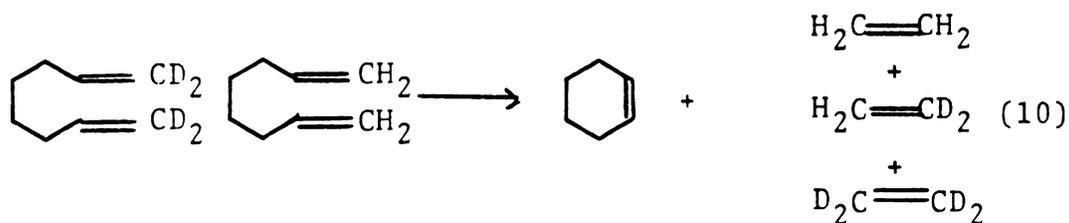


Cyclohexene is one of the few simple olefins that does not undergo metathesis. The volatile ethene can be easily removed from the reaction vessel and analyzed. The inertness of cyclohexene and the rapid removal of ethylene allows equilibration of these products to be minimized.

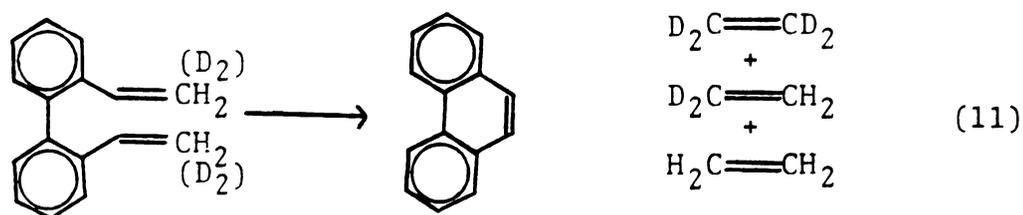
The first of these systems was designed by Grubbs<sup>33</sup>



using mixtures of 1,7-octadiene and 1,7-octadiene-1,1,8,8- $d_4$  (Eq. 10).



A similar system was developed by Katz<sup>34</sup> using mixtures of deuterated and non-deuterated 2,2'-divinylbiphenyl (Eq. 11).



Both of these diolefin mixtures produce a mixture of labelled and unlabelled ethenes. By a pairwise mechanism, formation of this ethene would be an intramolecular process and a majority of the fully deuterated and the non-deuterated products would be expected. Partially deuterated ethene would arise from the cross metathesis of products or from label scrambling in the reactants. Calculations based on a pairwise model indicate that the ratio of ethene- $d_0$ : ethene- $d_2$ :ethene- $d_4$  products would be 1:1.6:1 from the metathesis of 1:1 mixture of labelled and unlabelled starting materials.<sup>33,34</sup> This is the maximum amount of ethene- $d_2$ , the cross product, expected by any pairwise exchange of alkylidene units prior to equilibration.



A carbene chain mechanism would uncouple the alkylidene units and ethene formation would no longer be an intramolecular process. Such a process would randomly recombine the alkylidene units giving an equilibrium mixture of products. Starting with a 1:1 mixture of labelled and unlabelled diolefins this random process would produce a 1:2:1 ratio of ethene- $d_0$ :ethene- $d_2$ :ethene- $d_4$ .

Experimental results from both Katz's and Grubbs' work indicated a random mixture of labelled and unlabelled products. The authors proposed that this supported a carbene mechanism.

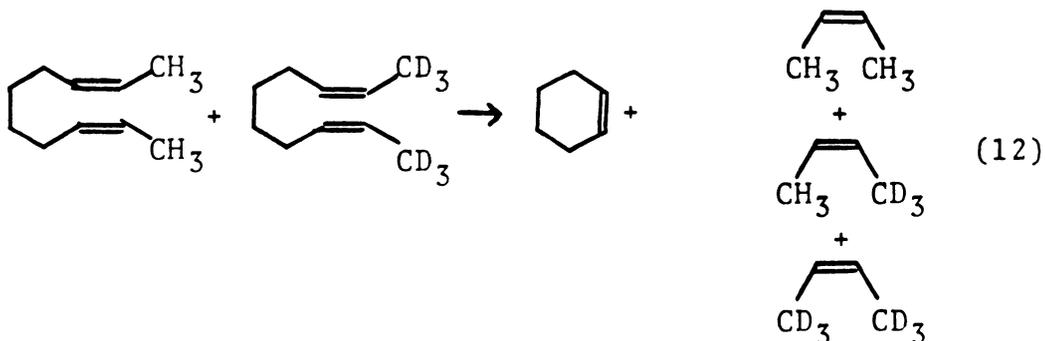
Criticism of both these experimental schemes centered on the fact that equilibration of product ethenes would produce the observed random labelling pattern regardless of which mechanism was operating. Although a variety of techniques were attempted, an irrefutable lack of scrambling was not demonstrated.

A more elaborate experiment was designed to eliminate the possibility of product equilibration. Utilizing both the selectivity of a 1,7-octadiene system and the stereoselectivity exhibited by metathesis catalysts, Hoppin<sup>35</sup> repeated these investigations with labelled and unlabelled cis,cis-2,8-decadienes. The products from this metathesis would be cyclohexene and a mixture of labelled and unlabelled cis- and trans-2-butenes.

The stereoselectivity of the metathesis reaction has been clearly demonstrated. In metathesis, cis olefins produce predominantly cis products and trans olefins form



predominantly trans products. Casey<sup>36</sup> has proposed a puckered metallocyclobutane model to explain these observations. Basset<sup>37</sup> suggested that this stereoselectivity is actually controlled by the approach of the olefin to the metal carbene. As the reaction continues an equilibrium mixture of cis and trans products are formed. Hoppin and Grubbs proposed that this stereoselectivity could be used as an internal probe to check the extent of reaction and by analogy, the extent of scrambling (Eq. 12).



A 1:1 mixture of labelled and unlabelled 2,8-decadienes was metathesized and the cis-2-butenes analyzed for isotopic distribution. Using the trans:cis 2-butene ratio as a measure of the extent of reaction, the isotopic labelling pattern was extrapolated to zero stereoisomeric scrambling. The authors suggest this extrapolated value is the isotopic ratio at zero label scrambling. As in the earlier investigations, the product ratio was that expected for a carbene mechanism.

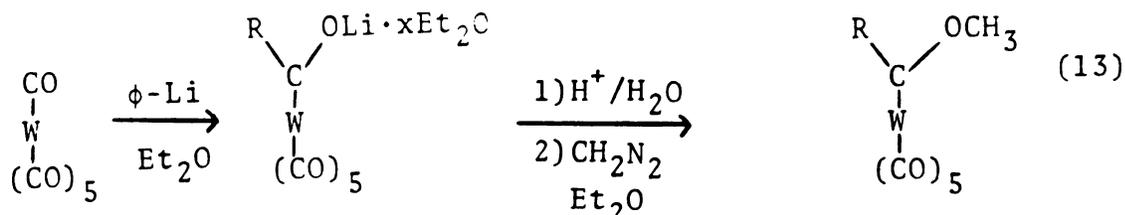
The experiments with 1,7-octadiene derivatives were all conducted over homogeneous catalysts. In an effort to distinguish between a pairwise and non-pairwise mechanism



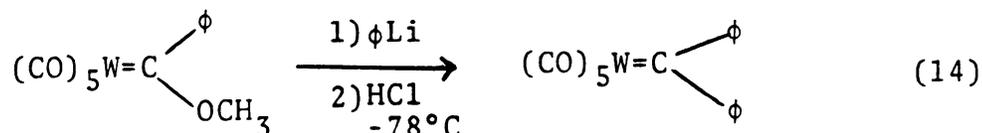
over a heterogeneous catalyst, the study using cis-, cis-2,8-decadienes has been repeated using a molybdenum on alumina catalyst. The results obtained allow insight to both the mechanism of such catalysts and the initiating scheme necessary for such a mechanism. At this point, the characteristics of carbenes and carbene initiation schemes will be discussed. Following this will be an outline of pertinent investigations over heterogeneous catalysts.

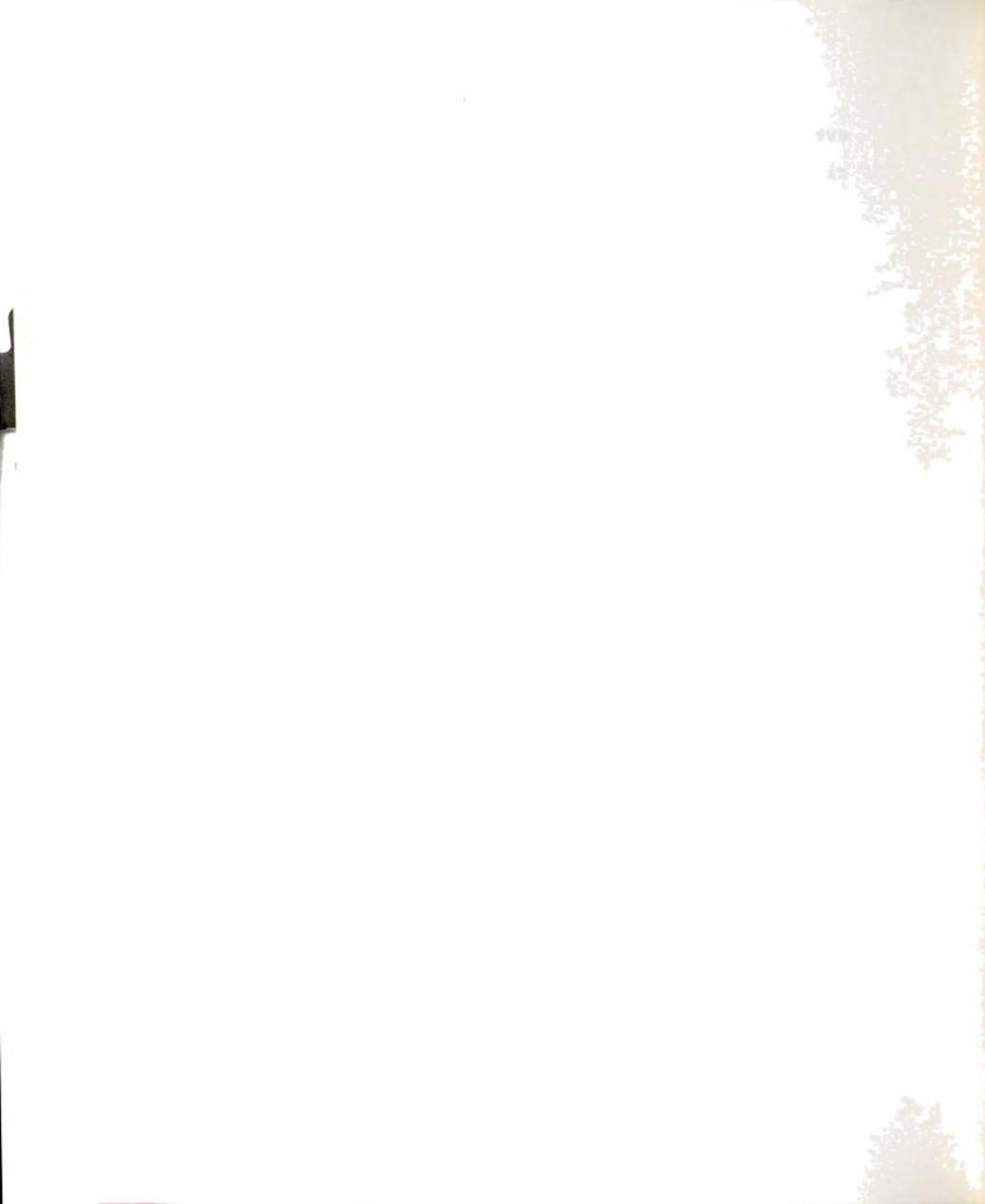
As evidence built indicating a non-pairwise mechanism, effort was directed at demonstrating a metal-carbene intermediate.

In 1964, Fischer et al.<sup>38</sup> reported a stable carbene complex prepared from tungsten hexacarbonyl and phenyllithium. In these early complexes, the carbenoid carbon was substituted with an electron-rich heteroatom (Eq. 13).

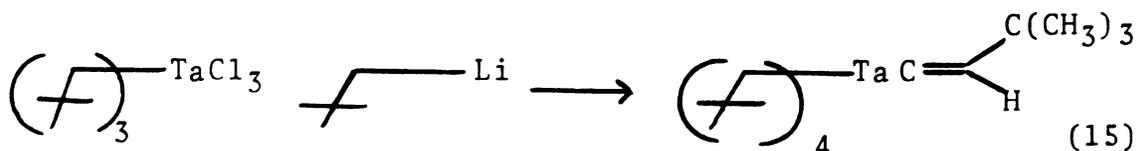


Casey<sup>39</sup> and Berkhardt prepared one of the first stable carbene complexes which was not heteroatom-stabilized (Eq. 14).

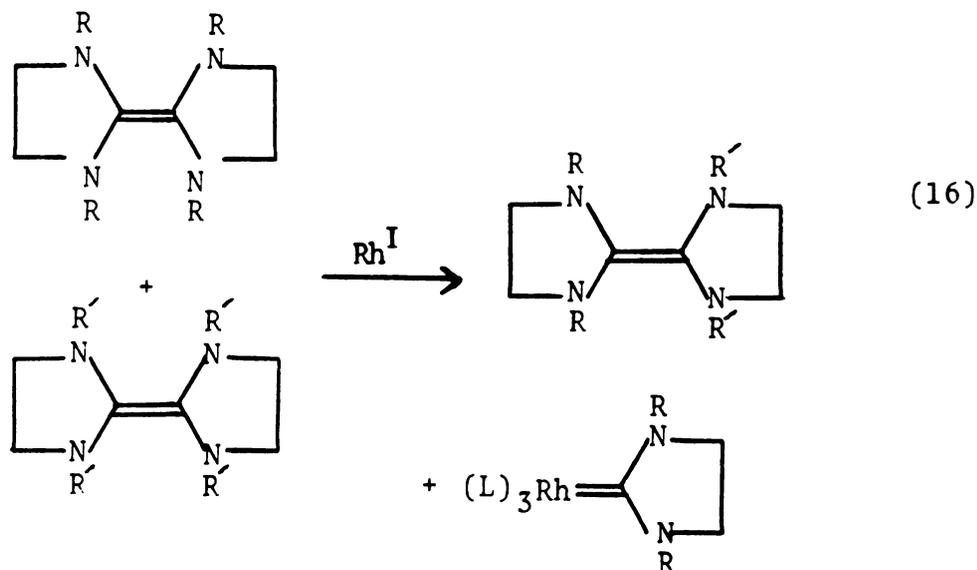




This was followed by Schrock's<sup>40</sup> isolation and characterization of a simple carbene from the reaction of a metal alkyl with a transition metal halide. Analysis by X-ray and NMR indicated the presence of a true double bond (Eq. 15).

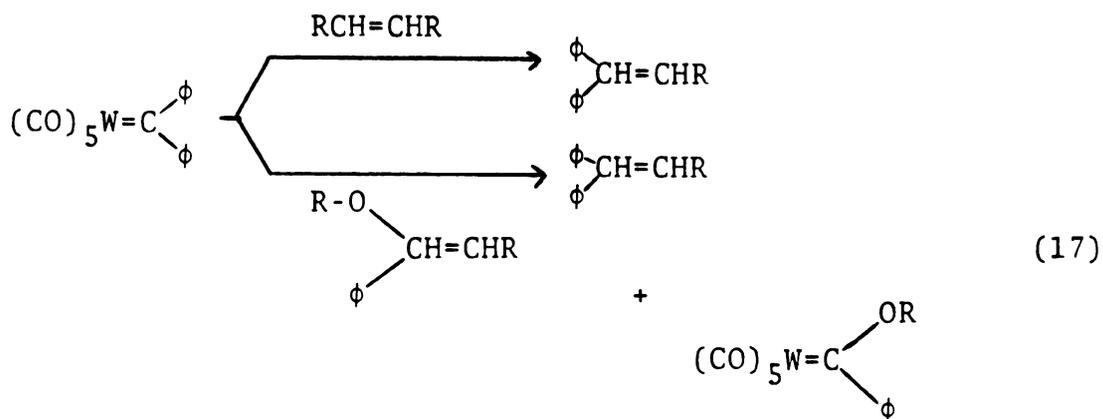


The first demonstration of a carbene initiated metathesis was reported by Cardin<sup>89</sup> using a mixture of substituted unsaturated amines with a rhodium-phosphine catalyst. A heteroatom stabilized rhodium-carbene was isolated from the reaction (Eq. 16).



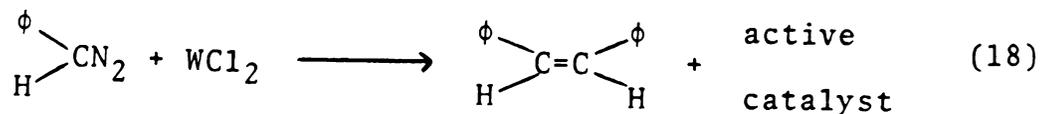
Casey<sup>41</sup> reported that the diphenylcarbene tungsten complex would undergo alkylidene exchange with simple olefins and carbene exchange with substituted olefins (Eq. 17).





This exchange is an excellent demonstration of the capability of such complexes to initiate metathesis like reactions. However, this exchange was not catalytic. In a related study, Katz<sup>42</sup> has reported the use of the diphenylcarbene tungsten complex at higher temperatures to metathesize simple olefins. However, an attempt to repeat this investigation has failed.<sup>43</sup>

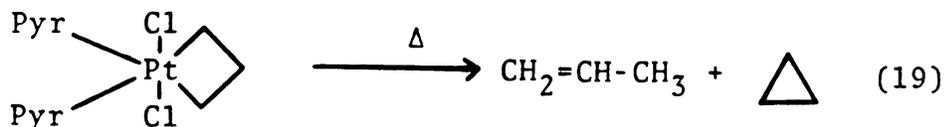
Dolgoplosk<sup>44</sup> decomposed phenyldiazomethane to nitrogen and stilbene using tungsten hexachloride. The reaction mixture was shown to be an active ring-opening polymerization catalyst (Eq. 18)



Cyclopropanes are a common side product in many of these studies. Metallocyclobutanes are known to decompose to give mixtures of olefins and cyclopropanes. Puddhatt<sup>45</sup> decomposed a platinocyclobutane and the



major products were the result of either reductive elimination to produce cyclopropanes or hydrogen transfer to yield olefins (Eq. 19).

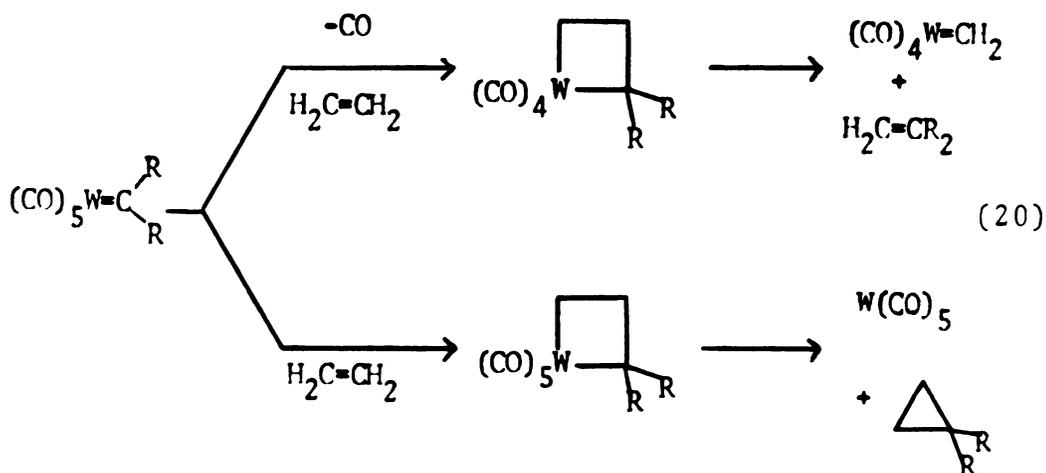


Such studies suggest metallocyclobutanes as a secondary intermediate in the metathesis of olefins.

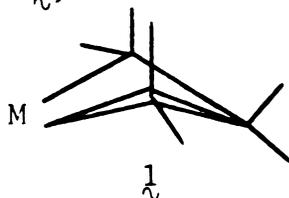
Casey<sup>36,41,46</sup> prepared a series of substituted metal carbene complexes and studied their reactions with olefins. Sterically hindered carbenes produced mostly the expected olefins, but less hindered carbenes formed a high percentage of cyclopropanes. Casey suggested that the hindered carbenes might lose a carbonyl ligand and then add the olefin to form a tetracarbonyl metallocyclobutane. This would cleave to give a new olefin and a new metal carbene. On the other hand, less hindered complexes might add an olefin without the loss of a carbonyl ligand. This would produce a pentacarbonyl tungsten metallocyclobutane which could eliminate  $\text{W}(\text{CO})_5$  producing the observed cyclopropanes (Eq. 20).

Gassman<sup>42</sup> has demonstrated that metathesis catalysts can be used to convert cyclopropanes to olefins. However, as indicated by Casey's work, different active species may be involved in this process.

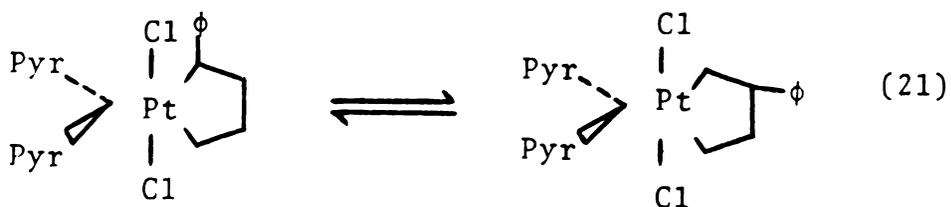




Metallocyclobutanes have been isolated from the reaction of cyclopropanes with platinum complexes. Crystal structure analysis of these compounds has indicated that the metallocycle is bent, an observation which has been used to explain the stereospecificity observed in the metathesis of olefins (structure 1).<sup>36</sup>



As mentioned earlier, these platinocyclobutanes decompose upon heating to form olefins and cyclopropanes. A unique rearrangement observed by Puddephat<sup>45</sup> may relate to the actual process occurring during a metathesis alkylidene exchange (Eq. 21).









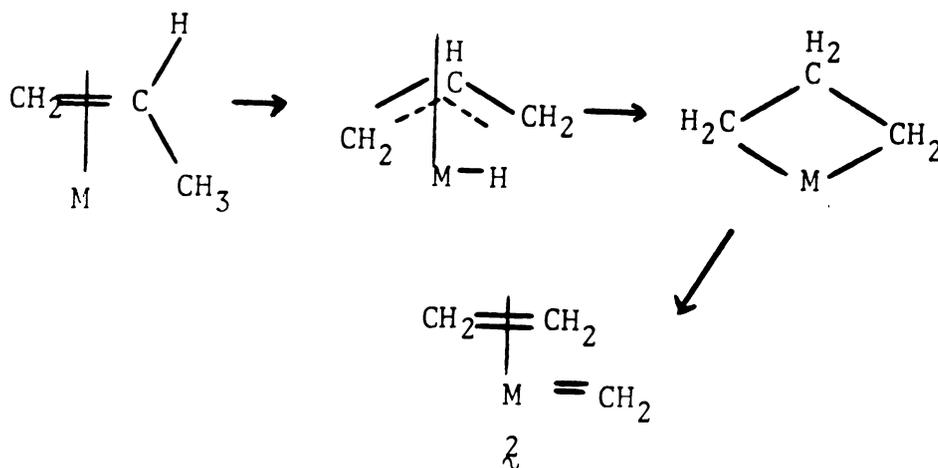


Figure 3. Carbene initiation via an allyl intermediate.

The initiation of the carbene chain carrying species has been carefully investigated. For those catalyst systems which use an organometallic co-catalyst a reasonable pathway has been proposed. The co-catalyst, appears to alkylate the transition metal forming a  $\sigma$ -bonded species which can transform to the active carbene. This pathway was suggested by Muettterties,<sup>49</sup> who observed the production of alkanes during the interaction of dimethyl zinc and tungsten hexachloride. The use of a deuterated solvent did not produce deuterated methane. In place of the simple complex shown here, Muettterties suggested that a bridged species involving both tungsten and zinc would be more likely as an intermediate for the alkylation and subsequent  $\alpha$ -H elimination shown in Figure 4.



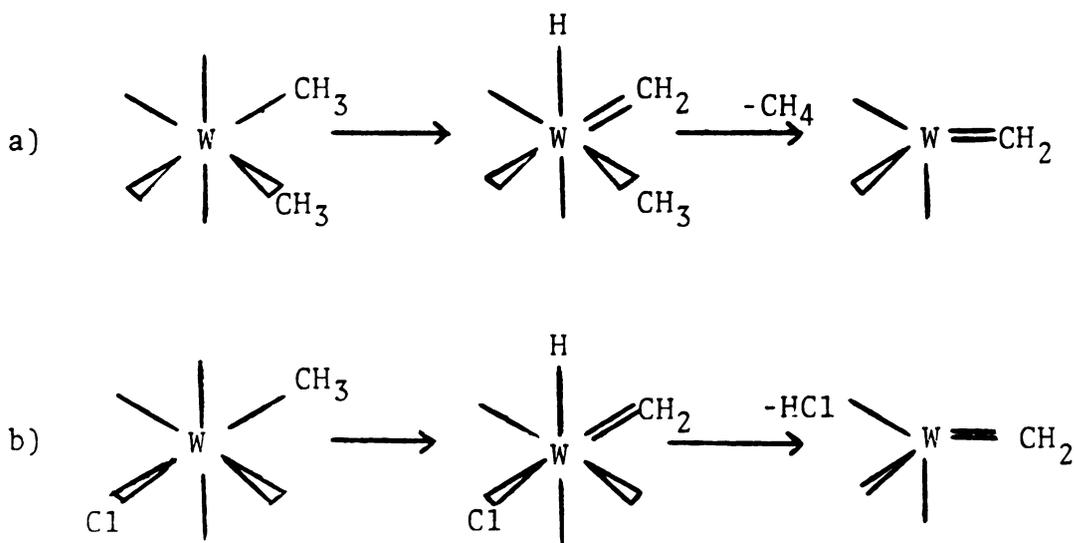
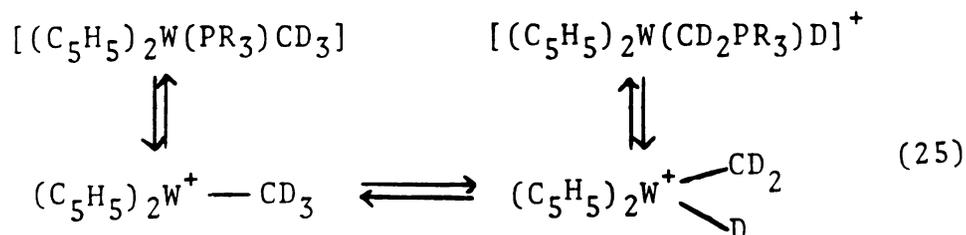


Figure 4. Initiation via alkylation and  $\alpha$ -elimination.

A reversible  $\alpha$ -hydrogen migration has also been proposed by Green<sup>50</sup> to explain the following rearrangement.



Hoppin<sup>35</sup> recently published supporting evidence indicating that the initial carbene is formed from alkyl groups originating in the co-catalyst. Metathesis of 2,8-decadiene theoretically produces only cyclohexene and 2-butene. However the metathesis of 2,8-decadiene using  $\text{WCl}_6/\text{SnMe}_4$  produced an initial burst of propene. Following



this initial propene production, only normal metathesis products were observed. Metathesis of 2,8 decadiene (1,1,1,10,10,10-d<sub>6</sub>) with this same catalyst produced propene-3,3,3-d<sub>6</sub>. Use of a deuterated co-catalyst produced propene-1,1-d<sub>2</sub>, Figure 5. Similar results were obtained with  $ML_2(NO)_2Cl_2/Me_3Cl_3Al_2$ .

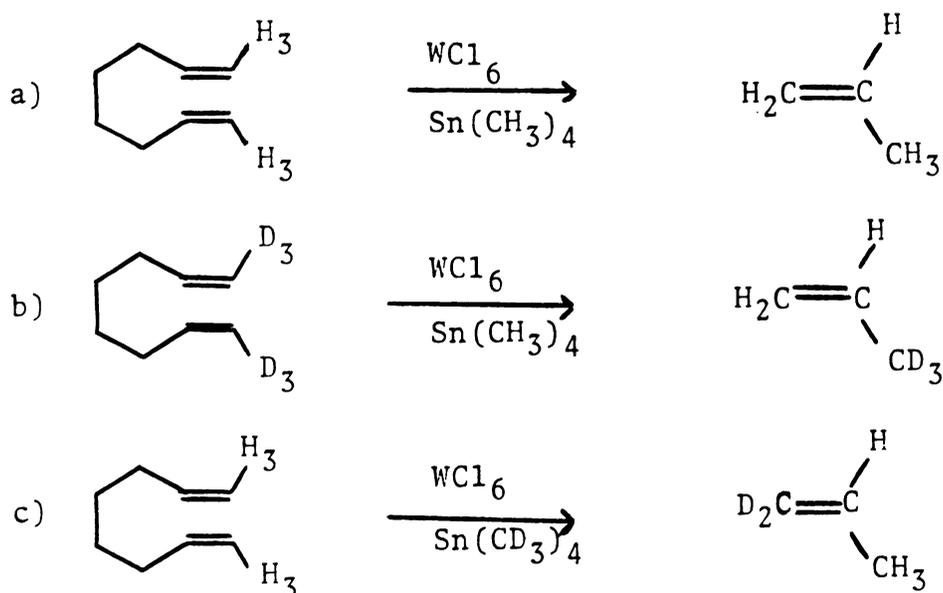
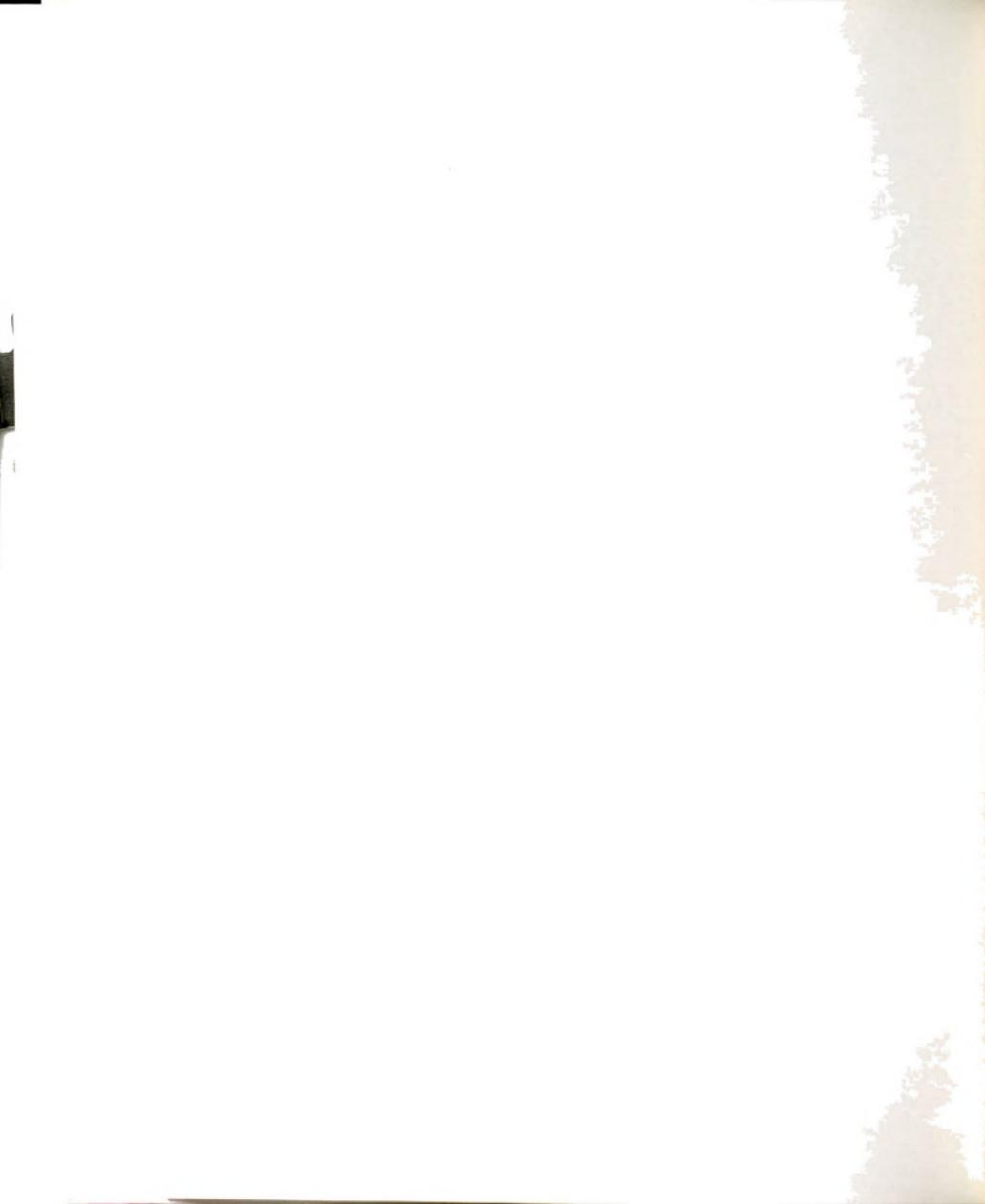


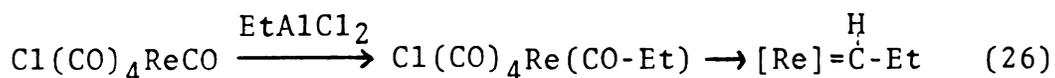
Figure 5. Labelling studies of carbene initiation.

These results are consistent with Meutterties' scheme in which the initial carbene formed from the co-catalyst interacts with the diolefin to produce propene in the first turnover. After this first turnover only the usual metathesis products were observed.

An alternate route was proposed by Farona<sup>10</sup> to explain



small amounts of unusual products observed early in the metathesis of 1,7-octadiene over  $\text{Re}(\text{CO})_5\text{Cl}/\text{EtAlCl}_2$ . Forona suggested alkylation of one of the carbonyl ligands as the source of the initial rhenium propylidene (Eq. 26).



The majority of investigations presented thus far have used non-supported catalysts. The initiation schemes have involved organometallic alkylating agents mixed with soluble precursors. The present investigation was designed to examine the mechanism of olefin metathesis promoted by supported catalysts. The mechanisms outlined for homogeneously catalyzed metathesis do not necessarily apply to supported catalysts. This study was undertaken to see if parallels exist between these two general classes of catalysts. Investigations into the nature of these heterogeneous catalysts will now be reviewed to set the proper framework for the new evidence to be presented in this Thesis.

As each study is reviewed those results which were formally unexplained will be reexamined in the light of new findings to be presented later in this Thesis.

As mentioned earlier, heterogeneous catalysts were the first to be developed and investigated. Mol<sup>14,16</sup> and Cook<sup>15</sup> conducted experiments with <sup>14</sup>C labelled propene over rhenium oxide-alumina and molybdenum oxide-alumina







However, results to be presented in this paper suggest the formation of an initial carbene via an initiation scheme similar to that proposed by Green would better explain the deuterium observed in the ethene, (Eq. 27).

The majority of heterogeneous catalysts have been prepared by impregnating high surface area supports with solutions of the oxides or carbonyls of molybdenum, tungsten or rhenium. These catalysts generally require activation at high temperatures. A notable exception to this are the catalysts prepared from the allyls of dinuclear and mononuclear complexes. These catalysts do not require activation at high temperatures but are immediately active for metathesis.<sup>52</sup>

A recent study<sup>90</sup> has demonstrated that the interaction of  $\text{Mo}(\pi\text{-C}_3\text{H}_5)_4$  with  $\text{SiO}_2$  at  $20^\circ$  in pentane, followed by the removal of pentane at  $20^\circ$  produces a catalyst with a high initial rate of disproportionation. Either reduction in  $\text{H}_2$  or oxidation in  $\text{O}_2$  of this catalyst at high temperatures greatly decreased its initial activity. This investigation strongly supports metal-allyl complexes as possible precursors for the active site in some heterogeneous catalysts.

The vast majority of heterogeneous catalysts require heating at high temperatures and are activated by controlled  $\text{H}_2$  treatment.

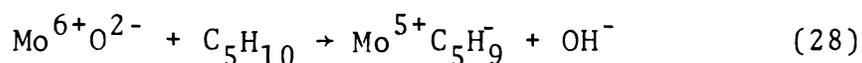
A major barrier to understanding the role of the

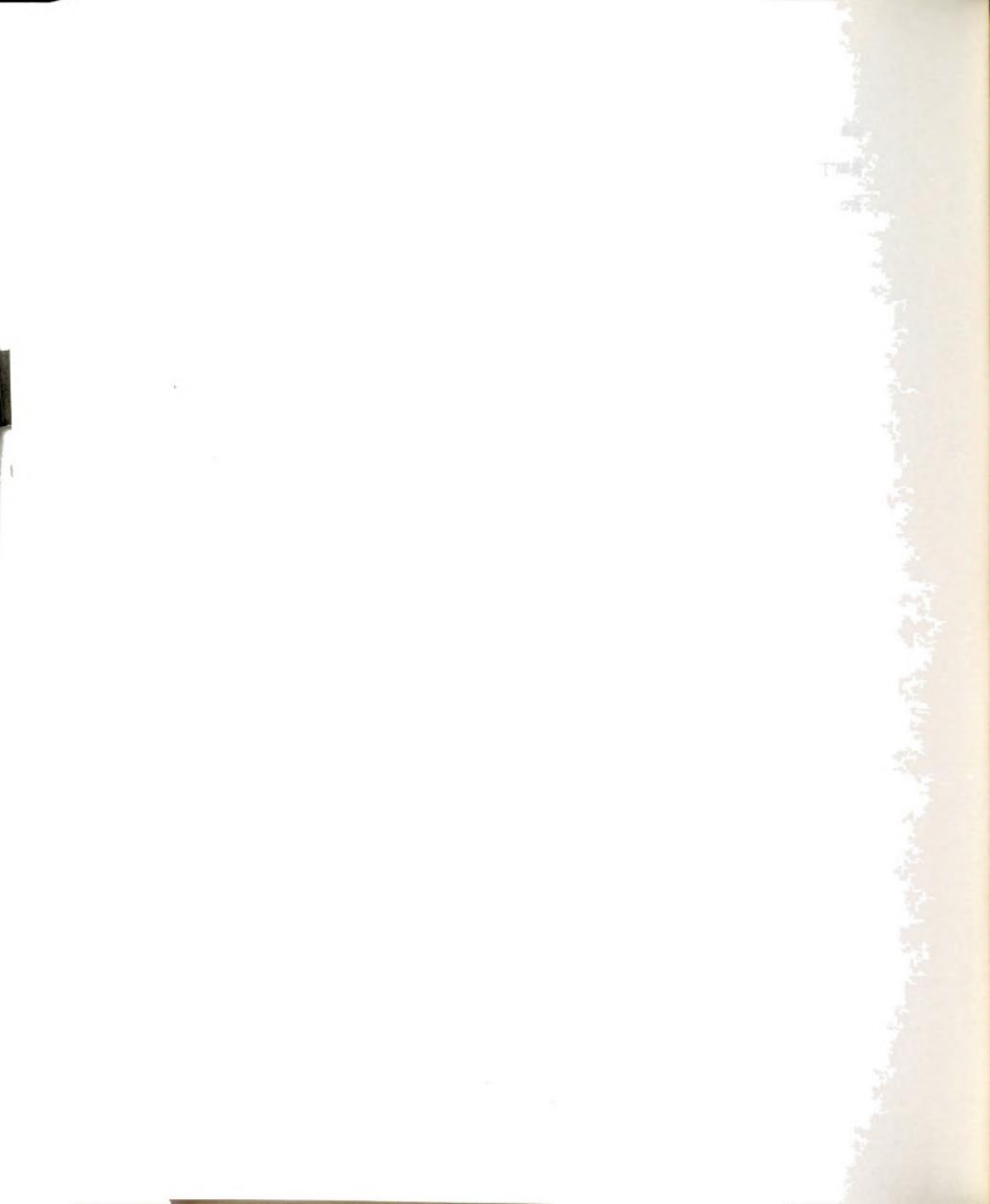


catalyst in heterogeneous metathesis has been that these supported complexes are not well defined compounds. Many sophisticated analysis techniques have been applied in an effort to identify the active site on these catalysts. This investigation has been complicated by observations such as those of Burwell and Brenner<sup>62</sup> who observed that three different forms of active catalyst can be prepared by combining  $\text{Mo}(\text{CO})_6$  and  $\text{Al}_2\text{O}_3$  under different conditions. Each of the three forms evolve different gases during preparation and exhibit different catalytic activities.

Davie et al.<sup>63</sup> reported the infrared spectra of a molybdenum hexacarbonyl alumina catalyst before and after activation at  $100^\circ$  in vacuum. Their results indicated the loss of at least one carbonyl group. Before this activation procedure the supported catalyst was not active for the metathesis of propene.

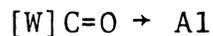
The nature of the active site in a  $\text{MoO}_3\text{-Al}_2\text{O}_3$  catalyst was investigated by Basset.<sup>60</sup> His results indicate a loss of surface  $-\text{OH}$  groups leading to an active site consisting of "an  $\text{Mo}^{6+}$  ion situated in an octahedral cavity of symmetry  $\text{C}_{4v}$ ." An ESR study of the interaction of cis 2-pentene with this catalyst indicated either the formation of a charge transfer complex or in the author's opinion a more likely "reduction of  $\text{Mo}^{6+}\text{O}^{2-}$  by the reactant with the formation of an allyl complex" (Eq. 28).











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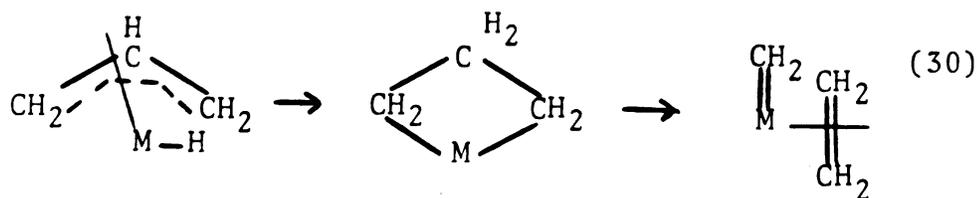
The heat activation procedure just discussed does not produce a catalyst with maximum activity, rather the activity of the catalyst gradually increases after the introduction of the olefin reactants. This has been clearly demonstrated for  $WO_3-SiO_2$ .<sup>53</sup> This catalyst significantly increased in activity during the first few hours of contact with the propylene. Concurrently, the catalyst changed in color from pale yellow to deep blue-violet. Such a color change indicates a reduction of  $WO_3$  and suggests that the propene itself is reducing the catalyst. ESR studies of  $MoO_3/Al_2O_3$  have also indicated a reduction of the  $MoO_3$  during the formation of the active species.<sup>54</sup> An increase in the initial activity of several supported catalysts could be induced by pretreatment of the catalyst with a reducing gas such as  $H_2$  or  $CO$ .

From temperature-dependent studies, deVries<sup>55</sup> concluded that active sites for metathesis are formed during this "break-in" period. It has been observed that the activity of a catalyst (one fully activated by propene) could be greatly reduced by a 3 hr purge with helium.<sup>56</sup> Retreatment with propylene induced another break-in period. Pennella<sup>57</sup> demonstrated that the activity of a tungsten silica catalyst could be greatly enhanced by adding small amounts of polyenes such as 1,5-cyclooctadiene to



the olefin starting materials. Pennella<sup>58</sup> suggested that normal break-in may involve the formation of metal ligands from the reactant olefins.

In a quantitative analysis of transient products formed during this break-in period, Luckner<sup>59</sup> demonstrated a large initial production of ethene and some butadiene along with a small amount of 2-butene during propene metathesis. A fully activated catalyst gave approximately equal amounts of ethene and 2-butene and no butadiene. With a  $\text{WO}_3\text{-SiO}_2$  catalyst he demonstrated that simple reduction with  $\text{H}_2$  did not eliminate the break-in period. Luckner suggested that some additional phenomenon is a part of this break-in process. This initial excess of ethene may be explained using the  $\pi$ -allyl-metallocyclobutane initiation scheme suggested by Green (Eq. 30)



Unusual product ratios have been observed with other catalysts during the initial contact with olefins. Basset<sup>60</sup> observed an unusually high level of butene early in the metathesis of 2-pentene over  $\text{MoO}_3\text{-Al}_2\text{O}_3$  and  $\text{MoO}_3\text{-Co-Al}_2\text{O}_3$  catalysts. Davie *et al.*<sup>61</sup> also noted a higher amount of ethene in comparison with butenes when propene was metathesized over  $\text{Mo}(\text{CO})_6\text{-Al}_2\text{O}_3$ .



The break-in period appears to involve some process which reduces the catalyst and generates active sites for metathesis. Reduction alone does not produce a fully active catalyst. These observations lend support to the  $\pi$ -allyl mechanism which will be presented in a later section.

Kinetic studies on heterogeneous catalysts have given results with poor reproducibility. Several studies by Moffat et al.<sup>64</sup> have demonstrated the non-uniformity of the surface of these catalysts. As a result the number of active sites may vary with changes in temperature. This may invalidate calculated activation energies and heats of adsorption since these are usually derived from temperature-dependent studies. This aspect of heterogeneous catalysts must be considered when evaluating such reported data.

The activation energy for metathesis has been reported as 7.7 KCal/mole for Co/MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub><sup>65</sup> and 21.6-18.6 KCal/mole for a tungsten supported system.<sup>66</sup> The activation energy during the break-in of a tungsten-silica catalyst has been reported to be 47 KCal/mole.<sup>59</sup>

Attempts to relate experimental kinetic data to model mechanisms has proved difficult. In 1967, Begley and Wilson<sup>67</sup> reported pseudo-first-order kinetics for the metathesis of propene over WO<sub>3</sub>-SiO<sub>2</sub>. From this they proposed a Langmuir-Rideal model in which a single site



chemisorbed molecule interacts with a gas-phase molecule. This model was criticized on the basis of mass transfer effects.<sup>53b</sup>

The proposal of Bradshaw's quasicyclobutane mechanism lead to a number of studies which attempted to support a dual-site mechanism. Theoretical studies centered around a Langmiur-Hinshelwood model, in which two propene molecules, adsorbed on adjacent active sites, interact.

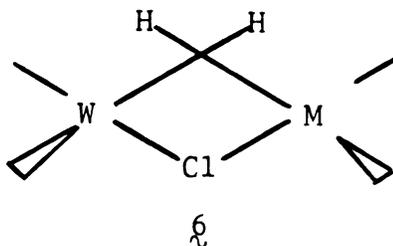
Giordano<sup>70</sup> proposed a similar four-center mechanism based on the interaction of two adjacently adsorbed molecules.

The experimental evidence supporting a carbene chain mechanism for homogeneously catalysed metathesis prompted a reevaluation of reported kinetic data for heterogeneously catalysed metathesis. Mol<sup>69</sup> established a correlation of rate data for propene metathesis with a model in which two propene molecules are successively adsorbed on the same active site. He then undertook the reevaluation of the published data which had been correlated to a dual site model. In several cases he demonstrated that a model which involves only one metal site could reconcile the data equally well. Such a single site mechanism might be expected for a carbene chain reaction.

More complex metal species have been postulated in which two transition metal atoms form an active site.<sup>52</sup> Also proposed are bridged bis-metal species involving a transition metal and a non-transition metal from either



the co-catalyst or the heterogeneous support material. Muetterties has proposed a bridged bis-metal species for a homogeneous catalyst structure  $\delta$ .<sup>49b</sup>



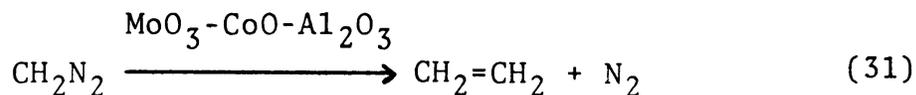
Support for such a bridged complex is varied. Halogenated olefins have been shown to increase the activity of some supported catalysts.<sup>71</sup> The halogens may facilitate formation of such bridged species. Triethyl aluminum has been used to increase the activity of a Co-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. Tributyl phosphine increased the activity of a tungsten oxide/silica catalyst.<sup>73</sup> Tetrabutyl tin has been used to promote the activity of a Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>74</sup> Formation of the proposed bridged species would explain the activating effect of these additives. In addition, Giordano<sup>70</sup> has provided evidence for dimeric Mo(V) species in MoO<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. He suggested that such configurations of bis-molybdenyl type are the active sites for this reaction.

With the proposal of a carbene mechanism for the homogeneous systems, interest began to turn toward investigating a similar mechanism in heterogeneous catalysis.

O'Neil and Rooney reported that a MoO<sub>3</sub>-CoO-Al<sub>2</sub>O<sub>3</sub>



catalyst decomposed diazomethane into nitrogen and ethene under the same conditions as for propene metathesis (Eq. 31).<sup>75</sup>

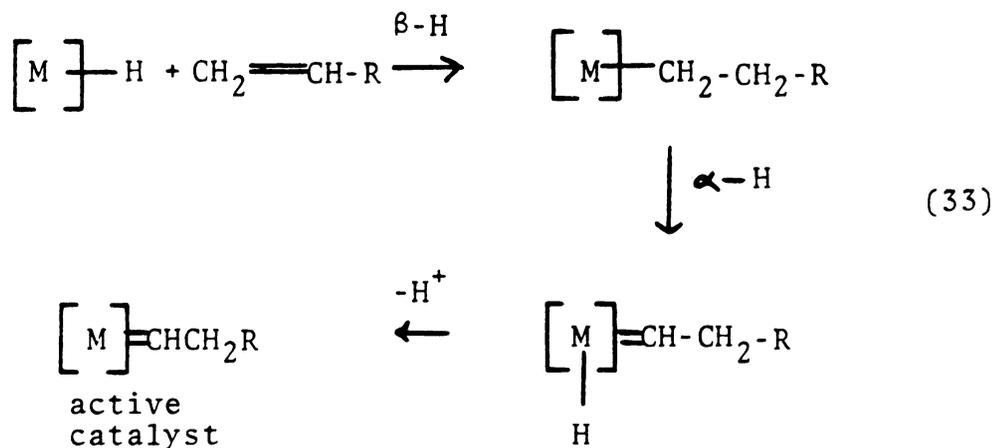


Similar studies using phenyldiazomethane were used as support for a carbene mechanism promoted by homogeneous catalysts.<sup>28</sup> This reaction has been questioned as support for such a mechanism because many catalysts will promote this conversion.<sup>76</sup>

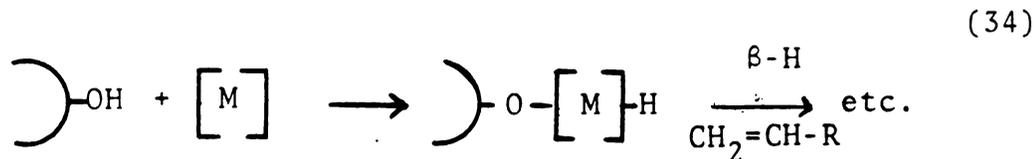
In 1969, Banks<sup>77</sup> patented a process which uses a tungsten oxide-silica catalyst to convert ethylene into propene. The assumed mechanism involved dimerization to yield butene followed by metathesis with another ethene to produce propene. More recently, O'Neil<sup>78</sup> has published a direct conversion of ethene to propene over a  $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$  catalyst. Labelling studies have indicated that this is a direct conversion and does not proceed via prior dimerization to butene. O'Neil proposed several possible mechanisms which involve splitting an ethylene into methylenes and addition of a methylene to another ethylene or, as an alternative, the recombination of three methylenes. A noteworthy development from O'Neil's work is the observation that ethene is slow to convert to propene over a fresh catalyst. However, if ethene is added to an identical system where propene has been reacting, the conversion of







This method has been suggested for the initiation of supported metathesis catalysts with the metal hydride originating from a support surface hydroxyl (Eq. 34).<sup>78</sup>



This proposal is favored by the experimental evidence of increased activity in the presence of H<sub>2</sub> or HCl.

This dissertation will present evidence favoring an allylic initiation scheme such as that proposed by Green<sup>31</sup> and later suggested by the work of O'Neil.<sup>78</sup> This allylic intermediate is further supported by Olsthoorn's<sup>81</sup> observation that "propene, butene and higher alkenes reduce a Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> metathesis catalyst at ambient temperature



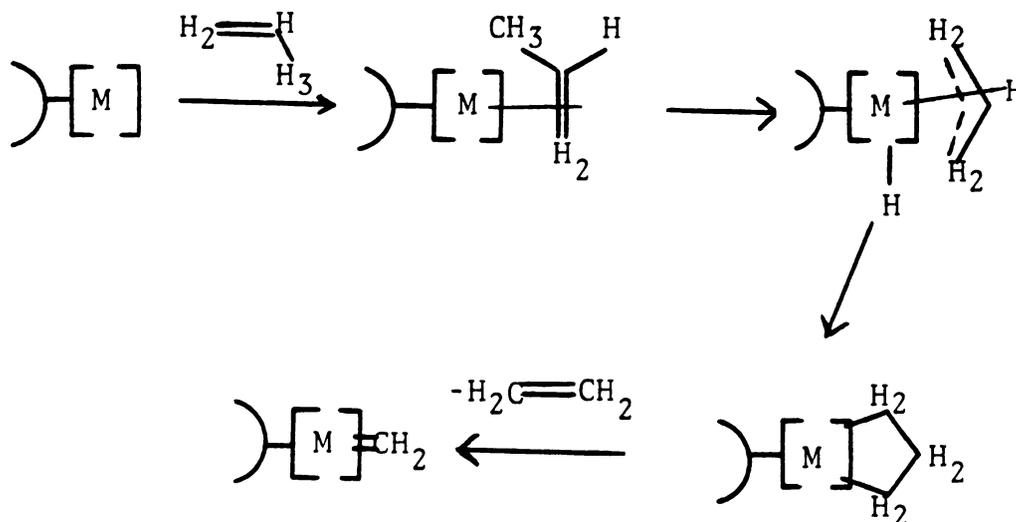


Figure 6. Carbene initiation via a  $\pi$ -allyl intermediate.

and sub-atmospheric pressures, while ethene shows hardly any reduction capacity under these conditions. The metathesis activity is generated by this reduction".

The early studies with  $^{14}\text{C}$  labelled propene excluded an allylic intermediate for the overall metathesis reaction at low temperature. However, these results do not exclude an allylic initiation scheme which would effect only the first catalytic turnover.

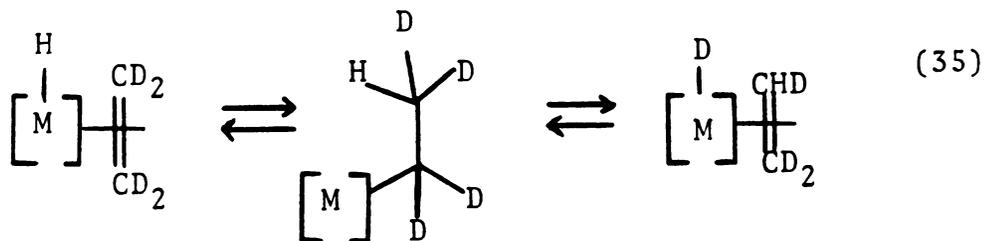
This initiation scheme is strongly supported by the immediate activity reported for  $\pi$ -allyl metal complexes supported on alumina.<sup>52</sup> It is not clear whether or not a break-in effect is observed with these catalysts.

The present investigation has repeated the work of



Hoppin with labelled 2,8-decadienes using supported catalysts. It was assumed that results similar to the homogeneous metathesis of 2,8-decadiene would be produced. That proved to be a false assumption but has resulted in an intriguing mechanistic problem. A notable difference between the two catalytic systems was the observation of an isotope effect when catalyzing the reaction with supported metal complexes.

Katz<sup>34</sup> and Grubbs considered the possible results of an isotope effect and judged such effects to be negligible with homogeneous catalysts. Grubbs noted that the catalyst formed from tungsten hexachloride and butyl lithium, which has been reported to be heterogeneous in nature, exhibited what might have been an isotope effect. However, he explained this apparent result by a mono-hydride scrambling scheme, supported by the observation of cyclohexene-1- $d_1$  and ethene- $d_1$  and - $d_3$  (Eq. 35).



In order to exclude the possibility of an isotope effect, Grubbs made use of the calculated ratio expected



in a carbene mechanism namely  $1:2A:A^2$  where A is the ratio of starting 1,7-octadiene- $d_0:d_4$ . His treatment is based on the observation that the values for the  $d_4:d_2:d_0$  ratio are exactly reversed when a  $d_0:d_4$  ratio of  $1/A$  is used in place of a  $d_0:d_4$  ratio of A. An example is shown in Table 2.

Table 2. Predicted Values for A and  $1/A$  Ratios of  $d_0:d_4$  1,7-octadienes.

$A = d_0/d_4$	$1 : 2A : A^2$
3	$1 : 6 : 9$
$1/3$	$1 : 2/3 : 1/9$
	$(9 : 6 : 1)$

An isotope effect would shift the product ratios away from this inverse symmetry. No such shift was observed experimentally from which Grubbs concluded the lack of such an isotope effect with homogeneous catalysts.

Katz<sup>34</sup> calculated the dependence of the ratio of the rates of formation of ethylene- $d_0$ ,  $-d_2$  and  $-d_4$  on an isotope effect R. He proposed that the product of the ratios  $d[C_2D_2H_2]/d[C_2H_4]$  and  $d[C_2D_2H_2]/d[C_2D_4]$  should be independent of the actual isotope effect.

As shown in Table 3 this product should be significantly different for pairwise and for carbene mechanisms.



Table 3. Product of the Ratios of Butenes Proposed for Pairwise and Non-pairwise Mechanisms.

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	$d[\text{C}_2\text{H}_2\text{D}_2]/d[\text{C}_2\text{H}_4] \times d[\text{C}_2\text{H}_2\text{D}_2]/d[\text{C}_2\text{H}_4]$
Pairwise	2.56
Carbene	4

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Katz calculated this product for a pairwise exchange and found it to be "very insensitive to R. It decreased slowly from 2.56 to 2.53 when R increased from 1 to 2.5." Assuming the validity of the mechanism used by Katz this should be a reasonable test to distinguish between the two mechanisms even in the presence of an isotope effect.

No other isotope effects have been reported for metathesis catalysts. This review will now cover isotope effects which have been reported in the catalysis of other reactions over heterogeneous systems.

Cvetanovic and Duncan<sup>84</sup> studied a silver ion-olefin complex for possible isotope effects. They found that an inverse isotope effect contributed to the stability of the various olefin complexes. Olefins which had deuterium atoms directly attached to the unsaturated carbons were stabilized the most and the effect of increased deuteration was additive. In this case, deuteration lead to an



increase in complex stability.

Adams and Jennings<sup>85</sup> proposed an allylic intermediate for the oxidation of propylene over  $\text{Bi}_2\text{O}_3/\text{MoO}_3$ . Based on the observed isotope effect of  $K_{\text{H}}/K_{\text{D}} = 1.8$ , they postulated methyl hydrogen abstraction as the rate determining step. Cant and Hall<sup>86</sup> proposed a similar mechanism for propylene oxidation over Au which demonstrated an isotope effect of 2.5.

For metathesis, an overall mechanism which involves an allylic intermediate appears unlikely. However, as demonstrated throughout this introduction, and as will be shown in the next section, an allylic intermediate is a likely candidate for the initiation of metathesis over a heterogeneous catalyst.



## RESULTS AND DISCUSSION

The original goal of this investigation was to study the ratio of labelled butenes produced in the metathesis of a mixture of labelled and unlabelled dienes over a heterogeneous catalyst and from this ratio, to deduce the mechanism of olefin metathesis.

In the course of this study a variety of unexpected observations were made which lead to an intriguing mechanistic problem. These observations will be discussed one at a time and then placed into an overall scheme which gives insight into the chemical processes occurring in heterogeneously catalyzed metathesis.

The preparation of pure cis,cis-2,8-decadiene-1,1,1,10,10,10- $d_6$  and cis,cis-2,8-decadiene was a prerequisite for conducting these experiments. Using the method devised by Hoppin,<sup>35</sup> these compounds were prepared as outlined in Figure 7. Commercially available 1,7-octadiyne was treated with n-butyl lithium yielding the dianion. Addition of methyl iodide- $d_3$  led to the formation of 2,8-decadiyne-1,1,1,10,10,10- $d_6$  which was isolated and then stereospecifically hydrogenated.

Cis,cis-2,8-decadiene- $d_0$  was prepared in the same manner using unlabelled methyl iodide and also by hydrogenating commercially available 2,8-decadiyne. Trans,trans-2,8-decadiene- $d_0$  was commercially available and trans,trans-



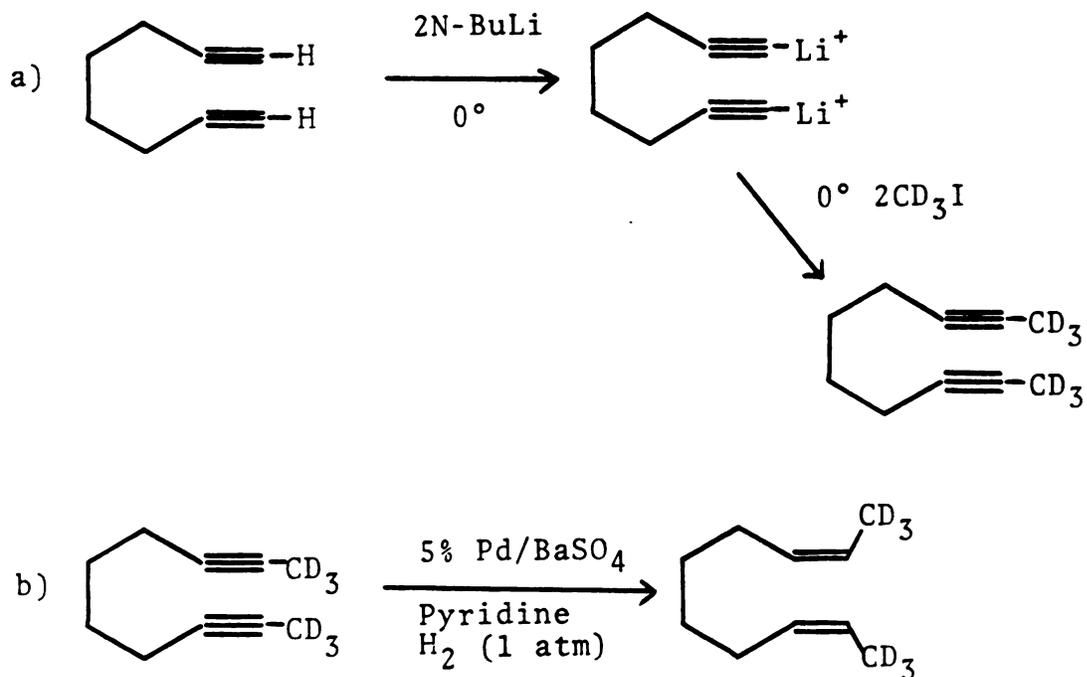


Figure 7. Preparation of *cis,cis*-2,8-decadiene- $d_6$ .

2,8-decadiene- $d_6$  was supplied by C. Hoppin.

Preliminary investigations were conducted using a commercial Molybdena-alumina catalyst which contained approximately 13%  $\text{MoO}_3$  on gamma alumina.<sup>88</sup> This was activated by heating in air at  $560^\circ$  for twelve hours followed by a 2 hour purge with argon at  $560^\circ$ . Approximately 0.5 g of catalyst was transferred under argon to a side-arm flask which was then sealed with a rubber septum. Without adding solvent, 0.2 ml of a 1.1:1 mixture of 2,8-decadiene- $d_0$  and 2,8-decadiene- $d_6$  was added. The white solid catalyst



turned black upon addition of the olefin. The reaction was followed by analyzing small ( 0.2 ml) gas samples by using gas chromatography. Larger gas samples ( 5 ml) were separated on a gas chromatograph and the butenes collected by passing the effluent gas through a gas collection tube cooled in liquid nitrogen. The collection tube was sealed off and the gas sample analyzed by mass spectroscopy. Some results of this initial study are presented in Table 4.

In these preliminary studies, the reaction began slowly and the catalyst underwent a rapid deactivation. As a result, all of the gas samples were very small. In spite of this, the resultant product ratios are reasonably consistent.

As has been noted in the Introduction, a specific ratio of  $d_6:d_3:d_0$  butenes should be produced depending on the mechanism. For a 1.1:1  $d_0:d_6$  mixture of 2,8-decadienes, a carbene chain mechanism was expected to produce a 1:2.2:1.2 ratio of  $d_6:d_3:d_0$  butenes.<sup>83</sup> For a pairwise exchange of alkylidene units a ratio of 1:1.73:1.18 was expected.

As shown in Table 4, the observed product ratios did not correspond to either of these possibilities. An excess of both  $d_0$  and  $d_3$  butenes was produced in all four runs. This excess of products containing a ( $:CH-CH_3$ ) unit suggested that whatever mechanism was operating was influenced by an isotope effect.



Table 4. Mass Spectral Analysis of Butenes Produced in the Metathesis of Labelled 2,8-decadienes, Over 13% MoO<sub>3</sub> on gamma alumina, in the Absence of a Solvent.

$A = \frac{d_0}{d_6}^a$	Temp.	Time <sup>b</sup>	$D_6 : D_3^c : D_0^d$	$\frac{\text{trans}}{\text{cis}}$
trans-trans				
1.1	85-135°	<1/2 hr	1 : 2.44 : 1.57	2.8
		>1/2 hr	1 : 2.46 : 1.67	1.9
1.1	70°	22 min	1 : 2.63 : 1.69	3.5
		136 hr	1 : 2.66 : 1.74	1.4
				$\frac{\text{cis}}{\text{trans}}$
1.1	57°	<1/2 hr	1 : 2.5 : 1.58	3.5
1.1	68°	3 hr 20 min	1 : 2.47 : 1.58	1.5
D <sub>6</sub> only	34-80°	50 min	D <sub>6</sub> only	
D <sub>0</sub> only	48°	20 min	D <sub>0</sub> only	

a)  $\pm 0.05$ .

b) Several samples collected and analyzed together.

c)  $\pm 0.05$ .

d)  $\pm 0.1$ .

e) D<sub>3</sub> and D<sub>0</sub> values corrected for ionization peaks.

111

111

As mentioned earlier, Katz developed a simple method for calculating relationships between product ratios which would theoretically cancel the effect of an isotope effect. In his work, an experimental value of 3.8 was observed for the product  $(D_2/D_0) \times (D_2/D_4)$ . As shown in Table 5, the calculated products from these preliminary experiments were somewhat higher and well above the maximum value (2.56) expected for a pairwise alkylidene exchange. This would suggest that a non-pairwise exchange of alkylidene units may occur over this heterogeneous catalyst.

The butene ratios were obtained by comparing the peak heights of butene- $d_6$  (m/e 62), butene- $d_3$  (m/e 59) and butene- $d_0$  (m/e 56) in the mass spectra. Both the butene- $d_3$  and butene- $d_0$  peaks were corrected for overlapping ionization peaks. No such correction was necessary for the butene- $d_6$  peak. The butene- $d_3$  had only a small correction, therefore the most accurate measurement of product ratios can be obtained by comparing the experimental butene- $d_3$ /butene- $d_6$  ratio to that expected theoretically. Each run in Table 4 indicated an excess of non-deuterated products.

As mentioned earlier, a number of proposed heterogeneous initiation schemes involve an attack on the olefin by surface metal-hydrides. An attack of this kind might cause an excess of non-deuterated butenes. In order to rule out this possibility,  $d_6$ - and  $d_0$ -2,8 decadiene were treated with the metathesis catalyst in separate experiments.



Table 5. Comparison of Product Ratios Using Katz's Method.

D	D <sub>6</sub>	D <sub>3</sub>	D <sub>0</sub>	$\frac{D_2}{D_0} \times \frac{D_2}{D_4}$
	1	2.44	1.57	3.79
	1	2.46	1.67	3.62
	1	2.63	1.69	4.09
	1	2.66	1.74	4.06
	1	2.5	1.58	3.95
	1	2.47	1.58	3.86

Mass spectral analysis of the cis- and trans-butenes produced by these separate runs indicated no contamination due to hydrogen sources of any kind. Cis, cis-2,8-decadiene-d<sub>6</sub> produced only 2-butene-d<sub>6</sub> (ml. wt. 62). Peaks at 59 and 56 corresponding to 2-butene-d<sub>3</sub> and d<sub>0</sub> were similar to literature values for ionization peaks. Exact values are presented in the experimental section. Similarly cis, cis-2,8-decadiene-d<sub>0</sub> produced no peaks at 62 or 59. The expected small ionization peaks were observed at m/e<sup>-</sup> 55 through m/e<sup>-</sup> 50.

These results suggested that the excess 2-butene-d<sub>0</sub> and -d<sub>3</sub> might be due to an isotope effect. This was further supported by the fact that either the d<sub>0</sub>-diene or a mixture of the d<sub>0</sub>- and d<sub>6</sub>-diene produced collectable amounts of



2-butene faster than the  $d_6$ -diene alone. As a check of this apparent rate difference, simultaneous experiments were conducted using equal amounts of catalyst, propane standard and either the  $d_0$ - or  $d_6$ -diene in separate flasks. The two flasks were stirred side by side in an oil bath at  $30^\circ$  and 0.5 ml gas samples removed and analyzed by gas chromatography. Figure 8 shows the production of cis and trans butenes and propene relative to a propane standard at various time intervals. The butenes and propene were produced more rapidly from cis, cis-2,8-decadiene- $d_0$ . A repeat of this experiment is shown in Figure 9 and again the  $d_0$ -diene produced butenes more rapidly.

Considering the sluggish reaction observed in the metathesis of ethene<sup>81,78</sup> compared to the relative ease with propene or higher alkenes, the above results might suggest  $\pi$ -allyl formation as a rate-determining step (Eq. 36).

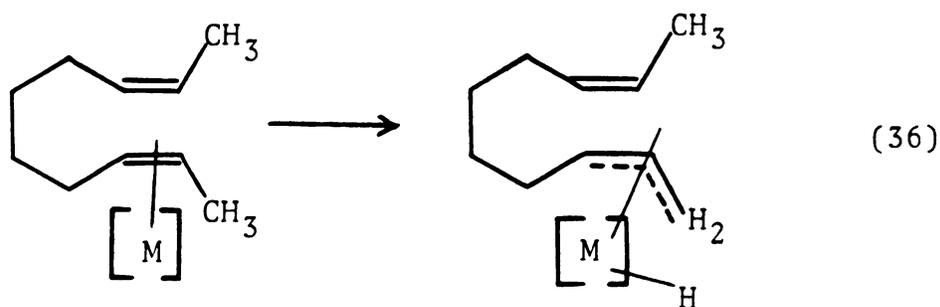


Table 4 also indicates the ratio of trans:cis products



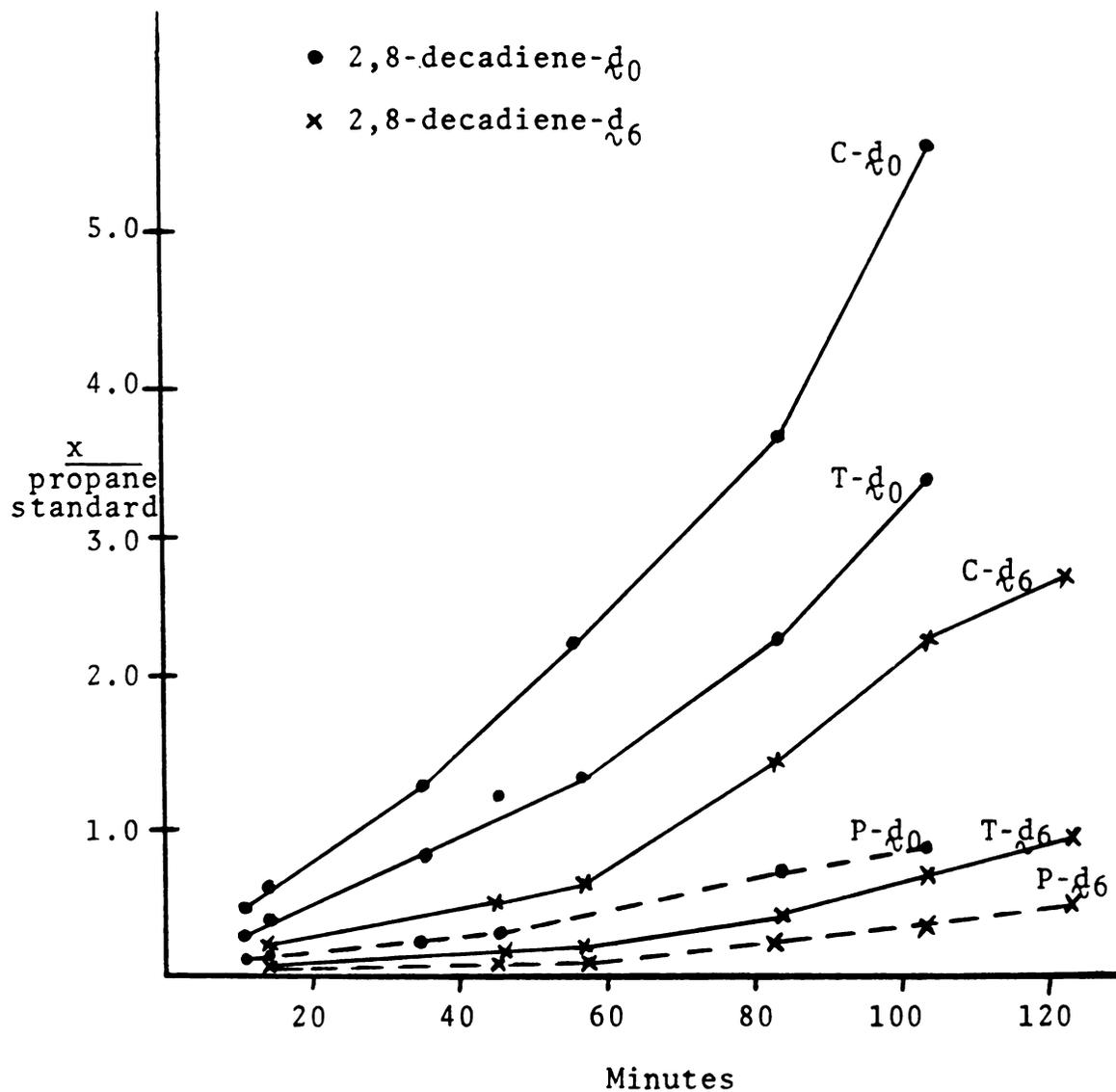


Figure 8. Comparison of the rates of formation of butenes and propenes (Run 1).



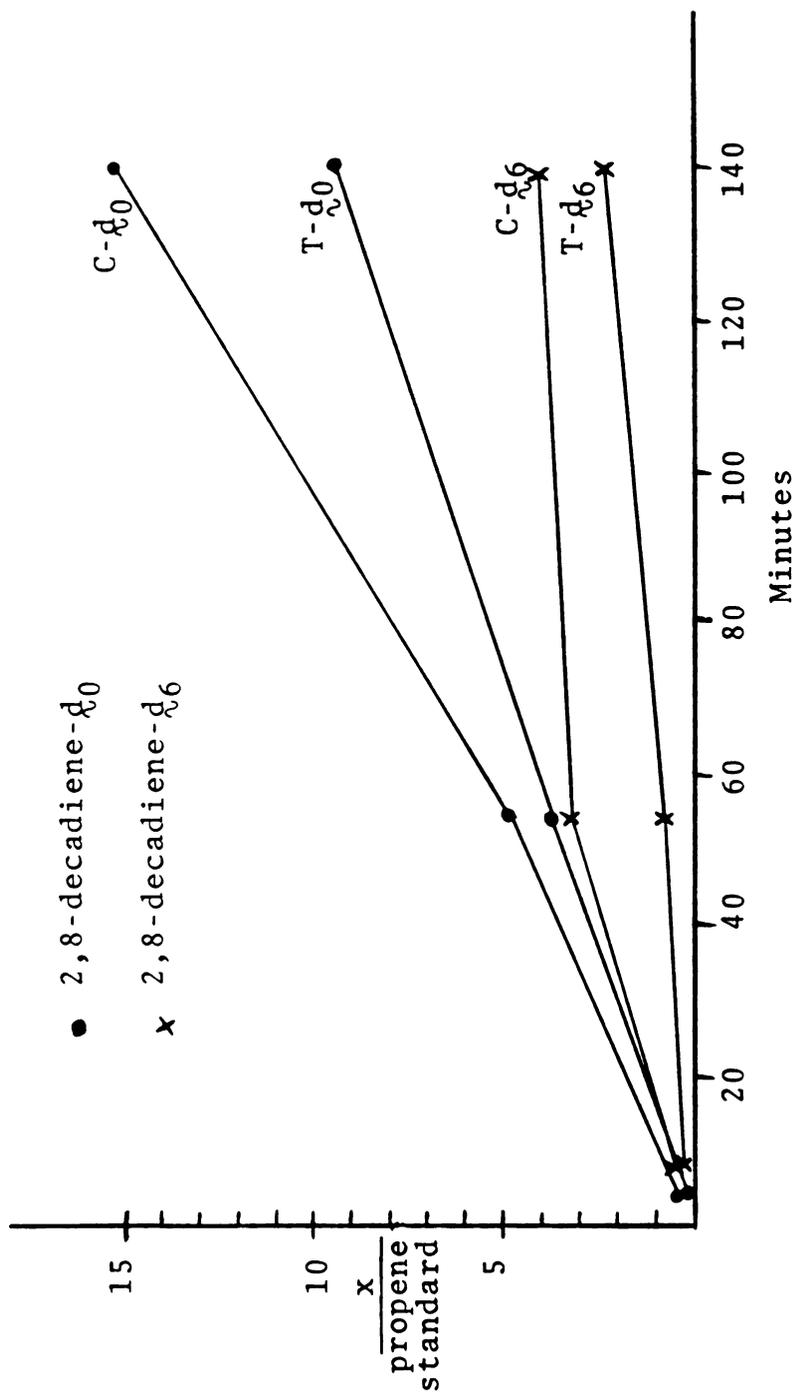


Figure 9. Comparison of the rates of formation of butenes (Run 2).



in the samples collected. This gives some indication of the extent of equilibration at the time of sampling. As noted earlier, one of the major criticisms of the early studies with labelled 1,7-octadienes was that the product ethenes could equilibrate following productive metathesis. The relatively high stereospecificity observed in the early samples suggests that the scrambling of deuterium labels by secondary metathesis reactions should be minimal.

Besides butenes, small amounts of both ethene and propene were produced in these experiments. Table 6 lists typical ratios of these products at various times. The

Table 6. Ratios of Ethene, Propene and Butene Produced During the Metathesis of *trans*, *trans*-2,8-decadiene in the Absence of a Solvent.

Time	Et	Pr	t-Butene	c-Butene
2 min 45 sec	2	--	61	--
25 min	0.5	1	104	23
31 min	----	1	110	39
62 min	----	1	166	72

source of these unexpected products will be discussed presently.

These preliminary studies were hampered by the low



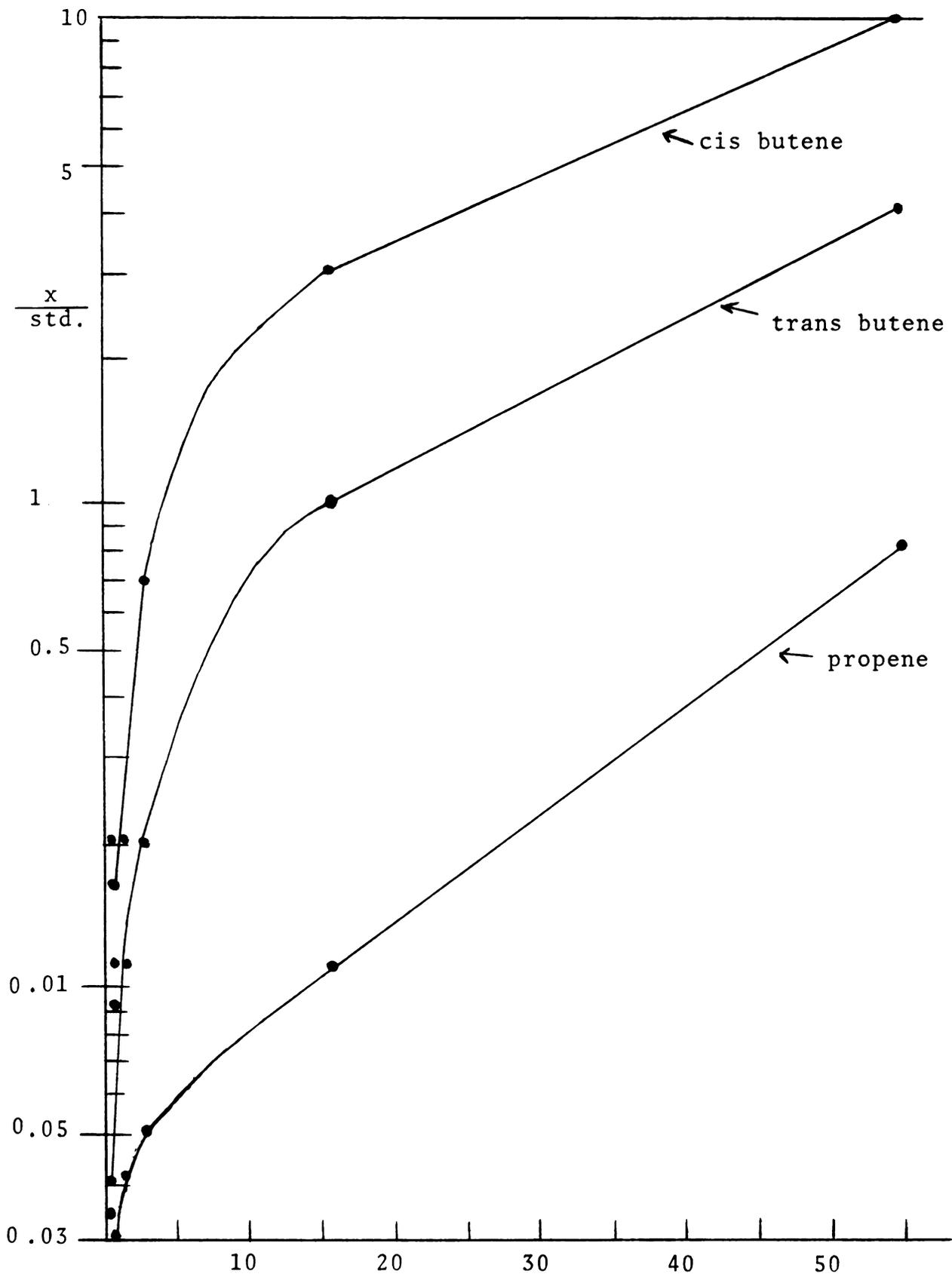
activity of the  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst. A far more satisfactory catalyst proved to be a cobalt-molybdenum-alumina extruded catalyst. Basset<sup>60</sup> studied the behavior of both  $\text{MoO}_3/\text{Al}_2\text{O}_3$  and  $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$  and noted no significant difference in the metathesis of pentene. However, the  $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$  was found to be more active for the metathesis of 2,8-decadienes. A chemical analysis of this commercial catalyst indicated 12.5%  $\text{MoO}_3$  and 3.5%  $\text{CoO}$ , supported on an alumina base. As in the initial tests, this catalyst was heated to  $560^\circ$  in air followed by an argon purge at  $560^\circ$  and then cooled to the reaction temperature under argon.

Investigations into the source of the ethene and propene have allowed some insight to the role of the catalyst and the formation of the active catalyst species. As with the preliminary studies, the  $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$  catalyst produced a tiny initial burst of ethene followed by a steady production of propene and cis- and trans-2-butene.

Figure 10 indicates the production of propene, trans-2-butene and cis-2-butene, relative to a 1/2 ml propane standard at room temperature, early in the metathesis of cis, cis-2,8-decadiene- $d_0$  over  $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$ . Ethene was occasionally observed during the first few seconds of olefin contact with the catalyst. After this initial burst, ethene was only detected if the reaction was heated to above  $90^\circ$ . Propene was also formed seconds after the addition



Figure 10. Production of propene and butenes relative to a propane standard.



Minutes  
Figure 10

100  
90  
80  
70  
60  
50  
40  
30  
20  
10  
0

100  
90  
80  
70  
60  
50  
40  
30  
20  
10  
0

of the olefin. As shown in Figures 8 and 11 the level of propene decreased significantly after about 1 hour of olefin exposure relative to the amount of butene produced. Neither of these products would be expected from the simple metathesis of 2,8-decadiene. Figure 11 shows the change in product ratios with time. The cis:trans butene ratio decreases as equilibration occurs and the relative level of propene, which is high during the first few minutes of olefin-catalyst contact, decreases steadily as the catalyst is "broken-in". As mentioned previously, heterogeneous catalysts exhibit a "break-in" period during which the activity of the catalyst gradually increases. In a careful study of this break-in period over freshly activated  $WO_3$  on silica gel, Luckner<sup>59</sup> observed a large initial production of ethene in the metathesis of propene. 2-Butene production was negligible during this break-in period. The fully activated catalyst produced nearly equal amounts of ethene and butene.

A similar break-in phenomena appears to be occurring in this study. Combining the observed isotope effect with the production of ethene and propene suggests the following initiation scheme (Figure 12).

The isotope effect observed in the formation of the labelled butenes may be due to the C-H bond cleavage inherent in the formation of the  $\pi$ -allyl species. A detailed study of this isotope effect will be presented later.



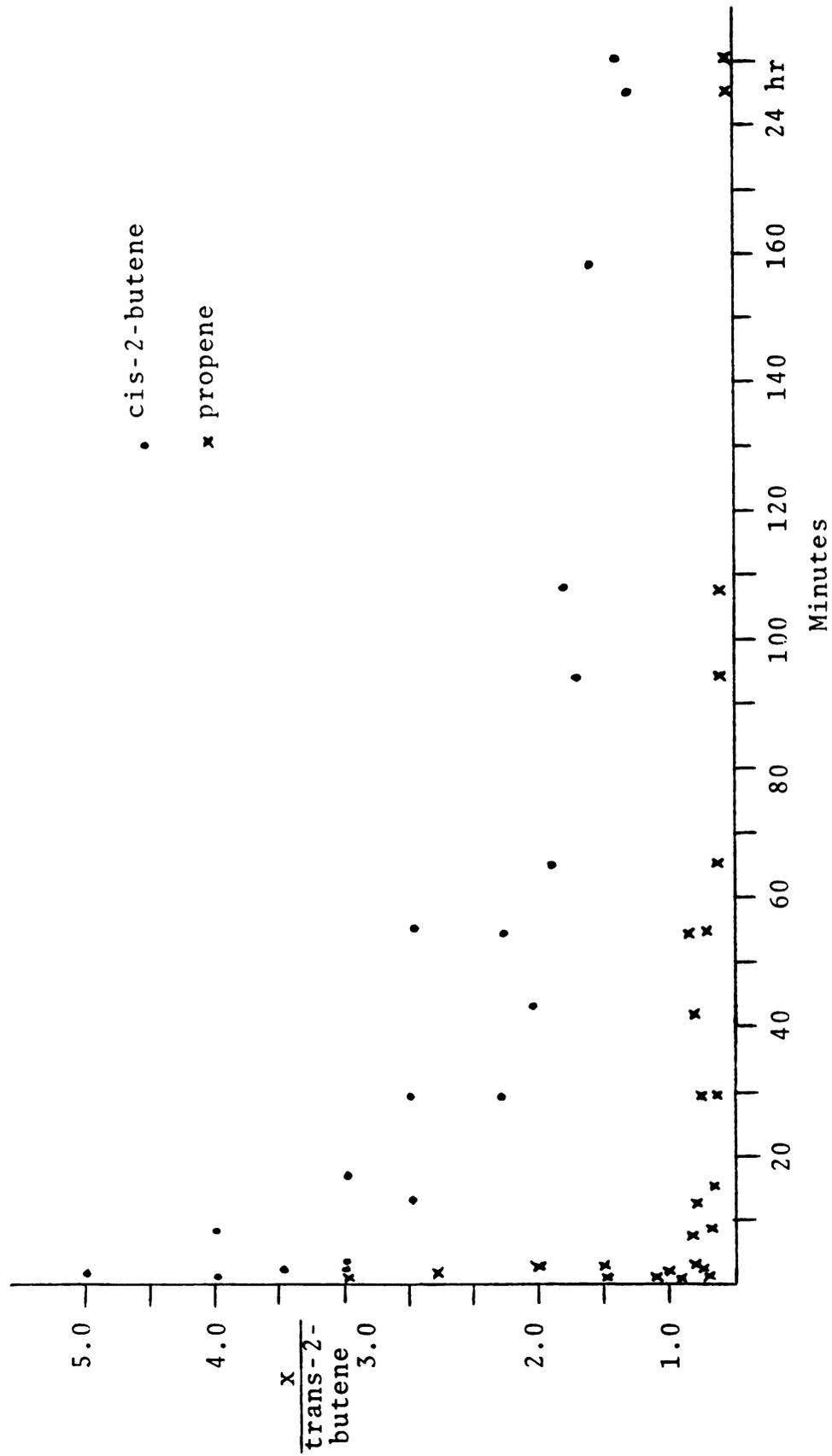


Figure 11. Production of cis-2-butene and propene relative to trans-2-butene.



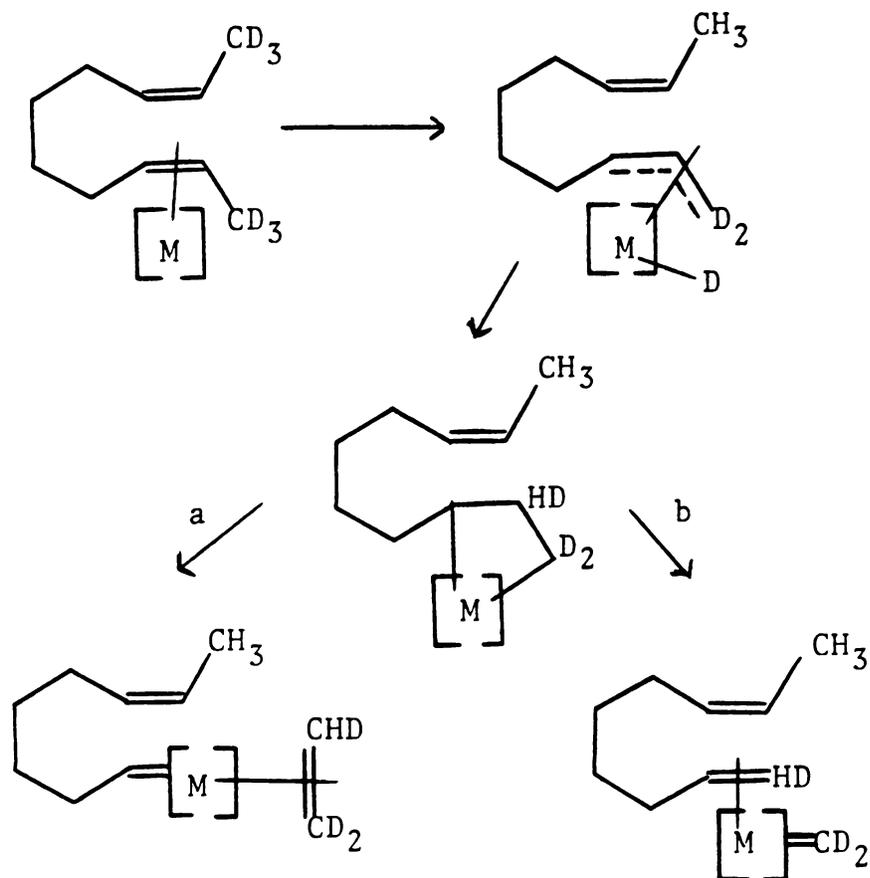


Figure 12. Initiation of the active catalyst for heterogeneously catalyzed olefin metathesis.

The ethene observed early in the reaction could be produced by the breakdown of the metallocyclobutane formed from this  $\pi$ -allyl, as shown in path a of Figure 12. The propene would then be formed by the cross-metathesis of ethene and 2,8-decadiene. Alternately, the metallocyclobutane could rearrange as in path b of Figure 12 to produce a metal-methylene complex and 1,7-nonadiene. This metal-methylene complex could undergo metathesis with 2,8-decadiene to yield propene. The ethene could be formed by



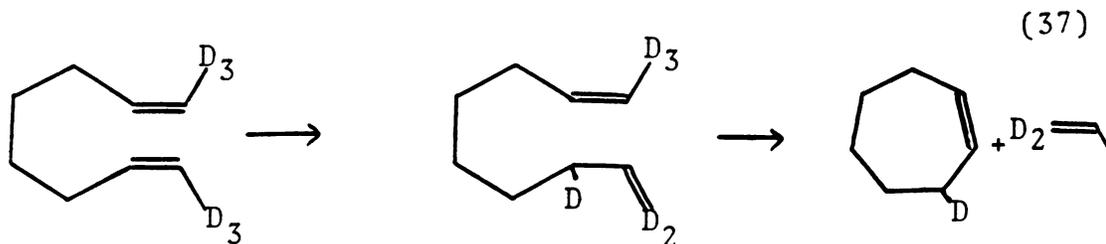
the dimerization of two metal-methylene species. Experimental conditions more than likely dictate the preferred pathway for the decomposition of the proposed metallocyclobutane. Either of these two pathways would yield nearly identical products and it would be difficult to distinguish between them.

The formation of a  $\pi$ -allyl, rearrangement to a metallocyclobutane and decomposition to a metal-carbene-olefin complex could explain the break-in effect observed with a number of heterogeneous catalysts. This initial  $\pi$ -allyl formation could also explain why little or no "break-in" effect is observed with tetrakis- $\pi$ -allylmolybdenum supported on alumina. Moreover this scheme provides the initiation step necessary for a metal-carbene-catalyzed mechanism.

The ethene and propene could also have been secondary products formed in a competing isomerization and metathesis sequence. Bradshaw<sup>93</sup> demonstrated that a  $\text{CoO}/\text{MoO}_3/\text{Al}_2\text{O}_3$  catalyst could selectively produce either ethene and 3-hexene or propene and n-pentenes from the metathesis and controlled isomerization of n-butenes. However, these investigations were conducted at temperatures of 120° and higher. Basset<sup>60</sup> has noted that isomerization is significant only at temperatures above 120° with these catalysts. In addition, isomerization could not explain the initial burst of ethene noted by Luckner<sup>59</sup> in the metathesis of propene.

100  
100  
100

If such a competing isomerization were occurring, the 2,8-decadiene would first isomerize to 1,8-decadiene and then undergo metathesis to produce propene and cycloheptene (Eq. 37).



In order to look for these products, 3 ml of cis, cis-2,8-decadiene- $d_{10}$  was treated with 3.4 g of  $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$  in the absence of a solvent. The liquid phase was analyzed by gas chromatography at 5 minutes and 30 minutes. Cyclohexene was clearly evident but no cycloheptene was observed. The absence of this product is most significant early in the reaction when the ethene and propene levels are highest relative to the butene products. Cycloheptene is known to undergo ring-opening polymerization, however some free monomer might be expected.

The ethene occurred in such small amounts that repeated efforts to trap it in a gas collection tube for mass spectral analysis failed. The propene was successfully isolated and analyzed by mass spectroscopy.

Table 7 lists the approximate percentages of propene- $d_{10}$



Table 7. Approximate Percentages of Labelled Propenes Formed in the Metathesis of a 1:1 Mixture of 2,8-decadiene- $d_0$  and  $-d_6$ .

M.W.	M.W.	Formula	Percent
	47	$C_3HD_5$	3%
	46	$C_3H_2D_4$	14%
	45	$C_3H_3D_3$	26%
	44	$C_3H_4D_2$	5%
	43	$C_3H_5D$	19%
	42	$C_3H_6$	33%



through propene- $d_5$  obtained in the metathesis of a 1.05:1 mixture of  $d_0$ -: $d_6$ -diene at room temperature. From the range of propenes produced, it appears that the major source of these products is the cross metathesis of a methylene species with the 2,8-decadiene mixture. The methylene species might be either the ethene or the metal-methylene complex formed in the decomposition of the proposed metallo-cyclobutane.

The largest fraction is that at molecular weight 42 which corresponds to propene- $d_0$ . The next largest fraction is that containing three deuterium atoms. These two products comprise approximately half the total propene. As shown in Figure 13, the expected route for the formation of these propenes would be cross-metathesis between a non-deuterated ethene and either a  $-d_0$  or  $-d_3$  2-alkene.

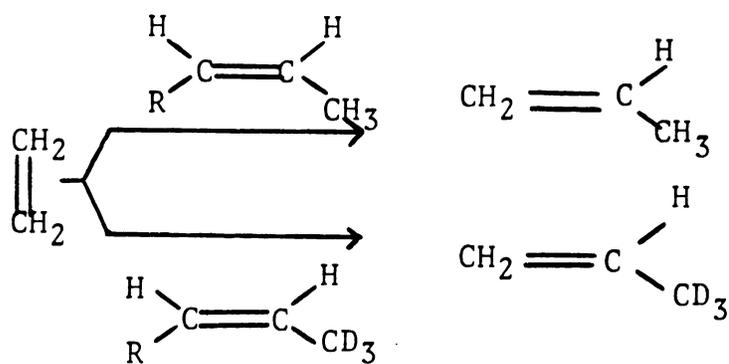


Figure 13. Formation of propene- $d_0$  and propene- $d_3$ .

The preferential formation of products resulting from

1000  
2000  
3000  
4000  
5000

ethene- $d_0$  cross-metathesis would be expected if the initiation scheme shown in Figure 12 were more rapid for non-deuterated 2,8-decadiene. The remainder of the sample was composed of propene with 1,2,4, or 5 deuterium atoms incorporated. These would be expected to form as shown in Figure 14.

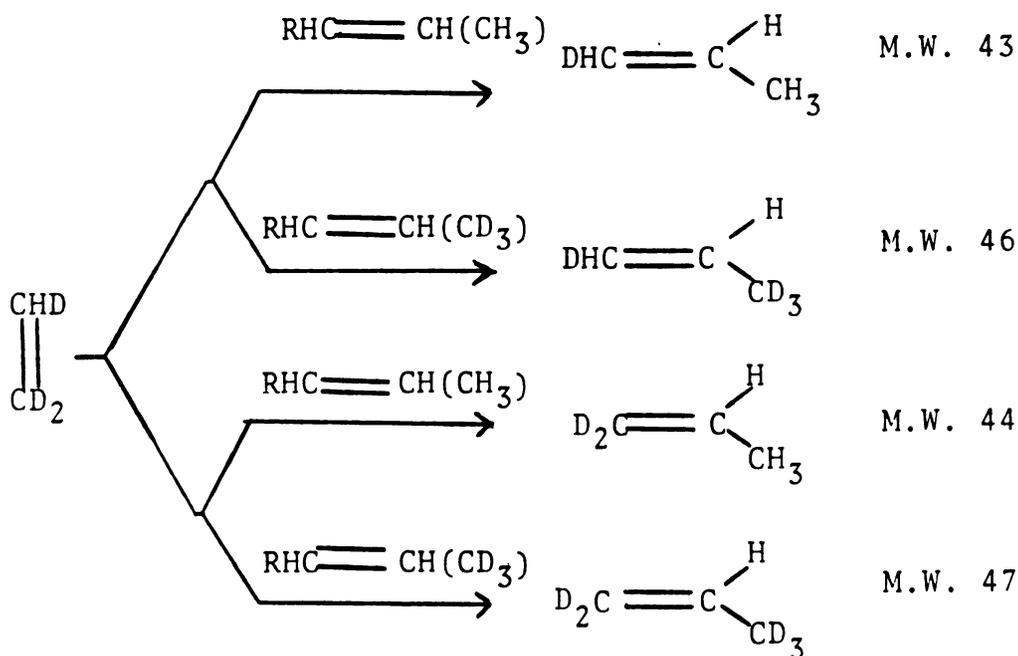


Figure 14. Formation of propene  $-d_1$ ,  $-d_2$ ,  $-d_4$  and  $-d_5$ .

Table 8 presents the percentages of labelled propenes collected in six separate experiments. The product percentages were calculated by a stepwise procedure in which the peaks due to the heavier components were successively subtracted out.<sup>106</sup> With six overlapping spectra, the

1000

1000

1000

Table 8. Approximate Percentages of Labelled Propenes.

Temp.	Time	D <sub>0</sub> :D <sub>6</sub>	C <sub>3</sub> HD <sub>5</sub>	C <sub>3</sub> H <sub>2</sub> D <sub>4</sub>	C <sub>3</sub> H <sub>3</sub> D <sub>3</sub>	C <sub>3</sub> H <sub>4</sub> D <sub>2</sub>	C <sub>3</sub> H <sub>5</sub> D	C <sub>3</sub> H <sub>6</sub>
Ambient	48 hr	1.05:1	3%	14%	26%	5%	19%	33%
75°	2 hr	1.05:1	11%	4%	24%	6%	---	55%
49°	10 min	2.25:1	---	---	8%	20%	---	71%
47°	30 hr	2.25:1	2%	3%	13%	13%	3%	65%
51°	48 hr	2.25:1	3%	3%	15%	11%	3%	65%
80°	21 hr	1:2.4	17%	9%	---	38%	---	36%



product ratios are only approximate, however experiments using the same  $D_0:D_6$  2,8-decadiene mixtures gave similar product ratios. Therefore, these product ratios should be valid for qualitative comparisons between runs. The most notable feature is the excess of products containing non-deuterated methylene units.

As in earlier studies, the extent of reaction became a key factor in the analysis of other data. Basset<sup>60</sup> had noted earlier that at the conditions used in this study, the catalyst was deactivated within a few hours. Since the goal of this study was to study the butenes formed early in the reaction, it was important to know the conversion level at short reaction times.

Figure 15 graphs the production of cyclohexene from 2,8-decadiene as a function of time. An exponential increase in cyclohexene formation is clearly demonstrated for the first hour of reaction. This increase is characteristic of an induction period which in turn suggests a chain reaction. It is during this first hour of reaction that ethene is observed and that propene is formed in the highest levels. Following this induction period, the formation of cyclohexene is linear with time and levels off. This is presumably due to catalyst deactivation. The highest conversion observed in any of these experiments was approximately 20% and many runs were well below that point. In similar studies over a



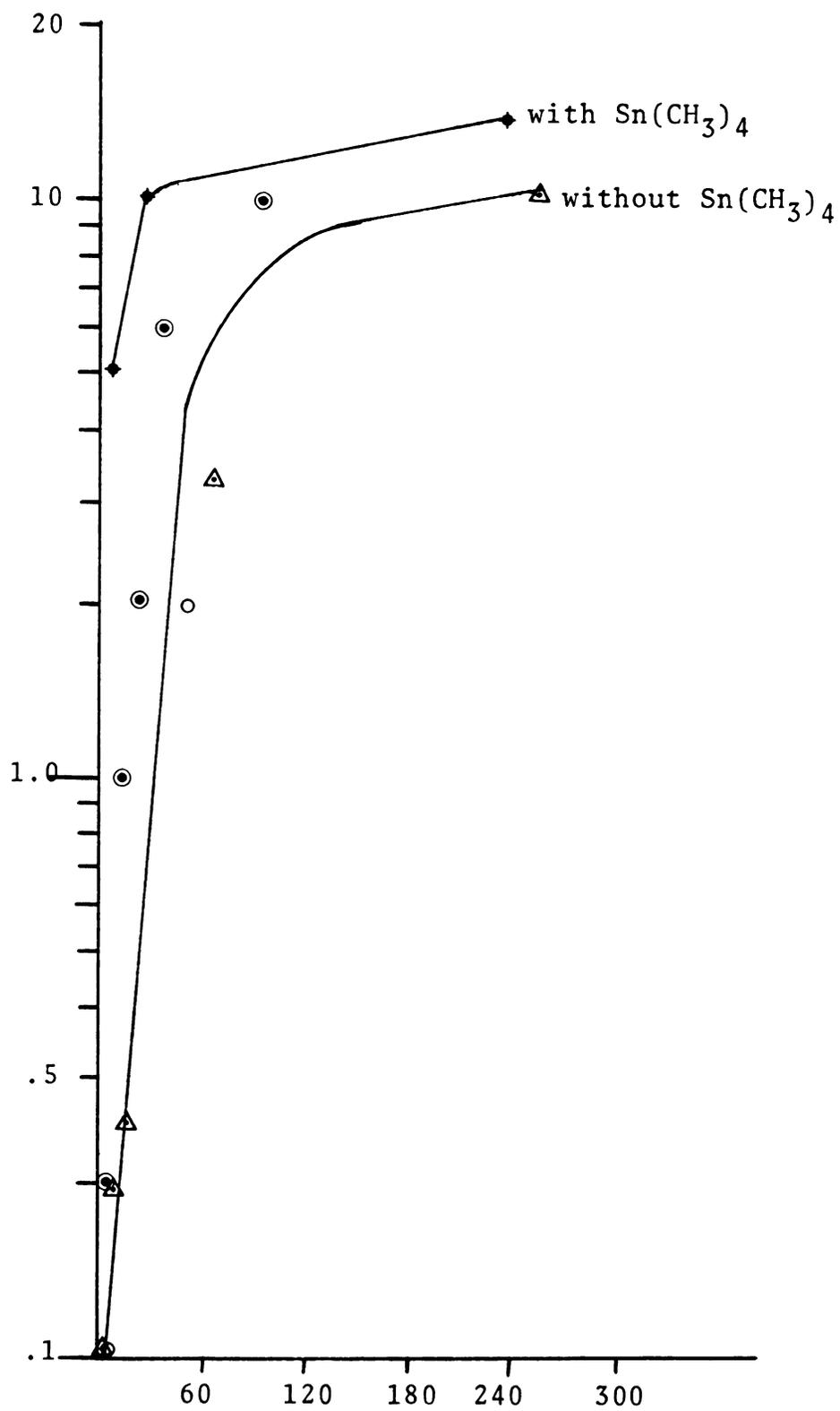


Figure 15. Conversion of 2,8-decadiene to cyclohexene.



molybdena-alumina catalyst, workers at the British Petroleum Co., Ltd.<sup>96</sup> noted conversions of less than 2% for propene metathesis at 25°C. This indicated that the turnover number was probably low and that a large fraction of the butene formed would be influenced by the processes occurring during this induction period.

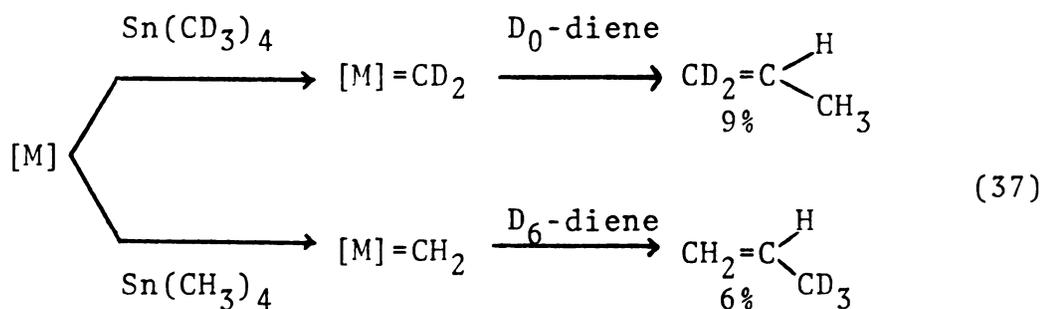
In an effort to further identify the source of the induction period and the resulting unexpected products, another study which was originally used with a homogeneous catalyst was attempted. As mentioned in the Introduction, Muetterties<sup>49</sup> has suggested alkylation followed by  $\alpha$ -elimination as the source of the chain-carrying metal-carbene species. Hoppin<sup>35</sup> supported this theory with a series of metathesis experiments using deuterium labelled olefins and co-catalysts. Heterogeneous catalysts have similarly been activated by the use of various co-catalysts.<sup>72,74</sup> An investigation of the effect of co-catalyst activation has given insight into the initiation process.

Figure 15 also demonstrates the level of cyclohexene formation when the  $\text{MoO}_3\text{-CoO-Al}_2\text{O}_3$  catalyst was treated with a tetramethyltin co-catalyst in chlorobenzene followed by the addition of the diene. The catalyst was initially more active for the production of cyclohexene. A decreased induction period was observed during which additional active sites may have been formed by normal metal-olefin break-in processes.

1910  
1911  
1912

Some active sites for olefin metathesis appear to have been generated by the interaction of the solid catalyst with the organometallic agent. In analogy with homogeneous catalysts, this could suggest that the induction period was specifically due to the formation of a metal-carbene species, and that prior formation via an alkylating agent shortened the induction period.

Analysis of the gaseous products formed during metathesis in the presence of alkyl-tin compounds gave additional support for this theory. As shown in Table 9, the propene formed in the presence of tin co-catalysts contains a higher proportion of deuterium. In each run, some of the propylene contained methylene units which could only originate in the co-catalyst (Eq. 37).



The majority of the propene appears to be due to normal break-in processes. The original goal of this investigation was to study the isotopic ratio of butenes produced prior to product equilibration. Typical product ratios will now be considered in light of the various



Table 9. Mass Spectral Analysis of Propene Formed During the Metathesis of *cis,cis*-2,8-decadiene Over  $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$  Treated with a Tetramethyltin Co-catalyst.

Co-Catalyst:	$\text{Sn}(\text{CD}_3)_4$	$\text{Sn}(\text{CD}_3)_4$	$\text{Sn}(\text{CD}_3)_4$	$\text{Sn}(\text{CH}_3)_4$
Olefin:	$\text{D}_6$ Only	$\text{D}_0$ Only	$\text{D}_6 : \text{D}_0$ 2.4 : 1	$\text{D}_6$ Only
$\text{C}_3\text{HD}_5$	78%	—	56%	71%
$\text{C}_3\text{H}_2\text{D}_4$	22%	—	21%	23%
$\text{C}_3\text{H}_3\text{D}_3$	—	—	3%	6%
$\text{C}_3\text{H}_4\text{D}_2$	—	9%	19%	—
$\text{C}_3\text{H}_5\text{D}$	—	—	—	—
$\text{C}_3\text{H}_6$	—	91%	—	—
Temp.	47°C	34°C	61°	90°
Time	62 min	30 min	29 min	3.5 hr.



reactions which appear to precede the actual catalytic metathesis of olefins.

Table 10 presents typical data obtained from an approximate 1:1 mixture of  $-d_0$  and  $-d_6$ -2,8-decadiene metathesized in chlorobenzene over a  $MoO_3/CoO/Al_2O_3$  catalyst. Chlorobenzene has been used frequently as a solvent for the homogeneous metathesis of olefins. Therefore, it was considered a reasonable choice for this investigation. The observed ratio of butene- $d_3$  and butene- $d_0$  is higher than that expected for either a carbene or a pairwise mechanism. However, even at short reaction times, the experimental butene ratio is consistent with the 1:2RA:R<sup>2</sup>A<sup>2</sup> ratio of products expected for a carbene mechanism involving an isotope effect (R). This excess of non-deuterated species decreases at longer reaction times suggesting that the preference for deuterium-free olefins occurs early in the reaction. An initially high isotope selectivity which decreases as the reaction proceeds would be expected for the initiation processes previously proposed.

The ratio of cis to trans butene is relatively high for these early samples suggesting that equilibration due to secondary metathesis processes should be minimal. With a minimum of label scrambling, these early product ratios support a non-pairwise alkylidene exchange mechanism such as Chauvin's chain-mechanism.





1910

Table 11 presents the ratios of labelled butenes produced in the metathesis of a 2.23:1 mixture of cis, cis-2,8-decadien- $d_0$  and  $-d_6$ . As in earlier experiments, an isotope effect was observed but it was somewhat smaller than that exhibited by a 1:1 mixture. In an excess of  $d_0$ -diene, the formation of active sites could proceed relatively unhindered by whatever processes slow the formation of active sites with deuterated olefins. Since the isotope effect appears to be associated with the formation of these active sites, the extent of effect would be decreased by any process which speeds up the formation of these active species. This theory is further supported by the fact that large butene samples were obtained earlier in the reaction using similar amounts of the catalyst and the diene as in previous experiments. Both runs C and D are good examples of this with three samples available within approximately one-half hour. This more rapid formation of active sites with non-deuterated olefins is also supported by Figures 8 and 9 which were discussed earlier.

The high stereoselectivity observed for early samples suggests a lack of label scrambling and the  $-d_6:-d_3:-d_0$  butene ratios are similar to that expected for a carbene-initiated, chain mechanism. As the reaction proceeds, the initially high level of  $-d_3$  and  $-d_0$  butenes decreases to nearly the level expected. These observations suggest



Table 11. Analysis of cis-butene Produced in the Metathesis of a 2.23:1 Mixture of cis, cis-2,8-decadiene-d<sub>0</sub> and -d<sub>6</sub>.

$$A = \frac{2.23}{1} \quad a \quad \frac{D_0}{D_6} \quad 1 : 2A : A^2 = 1 : 4.46 : 4.97 \quad \text{carbene} \\ 1 : 2.92 : 3.61 \quad \text{pairwise}$$

Time	$\frac{\text{cis}}{\text{trans}}$	D <sub>6</sub>	D <sub>3</sub>	D <sub>0</sub>	Isotope (R)	1:2RA:R <sup>2</sup> A <sup>2</sup>
C						
44°C						
7 min	---	1	4.60±.10	5.76±.15	1.05	1:4.68:5.48
10 min	3.1	1	4.94±.11	5.72±.16		
22 min	2.5	1	4.69±.07	6.53±.15		
8 hr	---	1	4.63±.06	5.15±.12		
24 hr	---	1	4.34±.08	5.03±.15		
D						
39°C						
14 min	3.5	1	4.95±.15	5.95±.23	1.11	1:4.95:6.12
22 min	3.0	1	5.00±.10	6.10±.20		
34 min	2.5	1	4.69±.07	5.77±.15		
1 hr 24 min	---	1	4.42±.08	5.26±.15		
E						
32°						
13 min	2.6	1	4.88±.12	5.95±.23	1.10	1:4.90:6.01
48 hr	---	1	4.52±.13	5.26±.16		

a) ±.03 analyzed by mass spectrometry.



that the isotope effect is due to some early process and that the catalytic step involves a non-pairwise exchange.

Tables 12 and 13 present data obtained from the metathesis of two mixtures of diolefins with an excess of cis, cis-2,8-decadiene- $d_6$ . In each case the data fits the pattern expected for a non-pairwise mechanism. Runs F and H exhibit the highest isotope effects. All these runs with excess diene- $d_6$  showed a low level of activity. Only a few samples could be obtained from each experiment. This low level of activity supports the theory that the initiation of active species is slower for deuterated olefins and with fewer active sites, the overall reaction is slower. Basset<sup>60</sup> has noted that at the conditions used in this study, the catalyst is deactivated within a few hours. The low overall level of activity may be due to the competition of slow formation of active sites and the deactivation of these sites. The high isotope effect is presumably due to rapid formation of active sites by the small amount of diene- $d_0$  which is available.

As a test for contamination of the decadiene- $d_6$  either before or during the actual metathesis, cis, cis-2,8-decadiene- $d_6$  was exposed to the same Mo/CoO/Al<sub>2</sub>O<sub>3</sub> catalyst and the resulting butenes analyzed. A large amount of diene- $d_6$  and catalyst were used so that products could be observed early in the reaction. As shown in Table 14, only butene- $d_6$  was produced. A second experiment

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Table 13. Analysis of cis-butenes Produced in the Metathesis of a 1:2.4 Mixture of cis,cis-2,8-decadiene-d<sub>0</sub> and d<sub>6</sub>.

$$A = \frac{1}{2.40} \frac{D_0}{D_6} \quad 1 : 2A : A^2 = 1 : .83 : .17 \quad \text{carbene}$$

$$1 : .72 : .21 \quad \text{pairwise}$$

Time	$\frac{\text{cis}}{\text{trans}}$	D <sub>6</sub>	D <sub>3</sub>	D <sub>0</sub>	Isotope (R)	1:2RA:R <sup>2</sup> A <sup>2</sup>
H 16 min	1.5	1	1.16±.08	.37±.08	1.40	1:1.16:.33
80° 30 min	1.1	1	.85±.04	.25±.08		
I 1 hr 3 min	1.6	1	.79±.07	.18±.05		
55°						

a) ±.11 Analyzed by mass spectrometry.



Table 14. Analysis of butene-d<sub>6</sub> Obtained from the  
Metathesis of cis,cis-2,8-decadiene-d<sub>6</sub> Over  
MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub>.

49°C		M/e <sup>a</sup>							
Time	62	61	60	59	58	57	56	55	
15 min	1.00	.18	.18	.03	.03	.05	.03	.03	
35 min	1.00	.18	.20	.03	.05	.07	.05	.03	
57 min	1.00	.18	.20	.03	.04	.05	.03	.01	
(trans 27 hr	1.00	.18	.20	.04	.05	.10	.07	.07	
(cis 27 hr	1.00	.18	.20	.03	.03	.05	.04	.02	
125°C		M/e <sup>a</sup>							
28 min	1.00	.18	.20	.09	.10	.09	.08	.05	

a) Peak heights are not corrected.



conducted at a much higher temperature again indicated no significant contamination from solvent, catalyst or diene.

As mentioned earlier, the activating properties of a tin co-catalyst were investigated. Table 15 demonstrates a near total loss of isotope effect with the use of a tin activating agent. In this run an excess of  $d_6$ -diene was used

Table 15. Butenes Formed Using a Catalyst Treated with  $\text{Sn}(\text{CD}_3)_4$ .

A = .41		1	:	2A	:	$A^2 = 1$	:	.82	:	.17
		$D_6$	:	$D_3$	:	$D_0$				
61°	6 min	1	:	.78	:	.18				
	16 min	1	:	.76	:	.17				
	29 min	1	:	.8	:	.24				

and would be expected to demonstrate a large isotope effect. This was not observed. The tin apparently formed an activated species which was capable of catalyzing olefin metathesis and as in the homogeneous case, did not involve an isotope effect.

This investigation was undertaken in an effort to understand better the mechanism of heterogeneously catalyzed olefin metathesis. The data presented strongly supports a specific initiation scheme and a carbene

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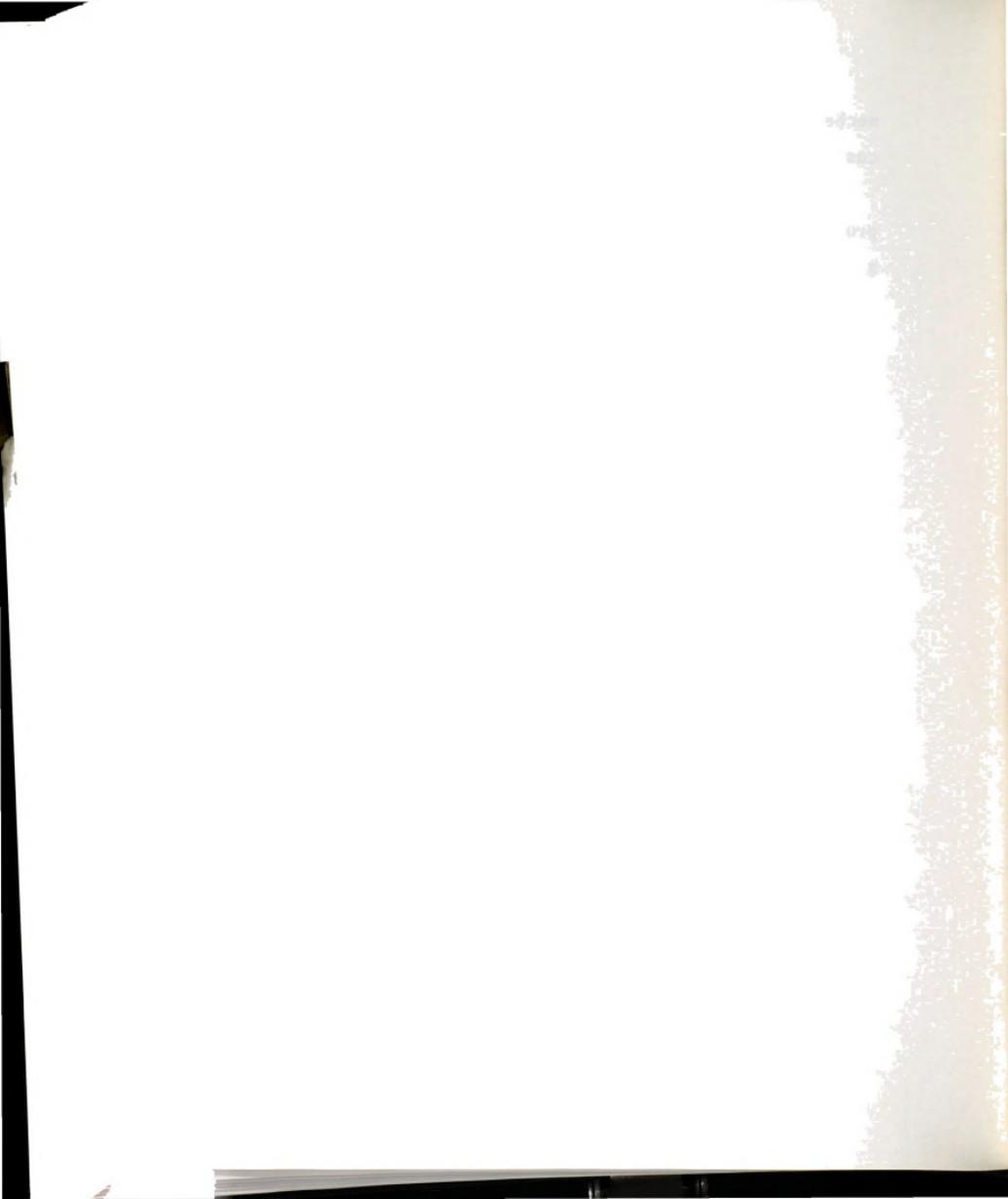
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mechanism. The steps in these processes will now be discussed and a kinetic model for the reaction formulated.

No one piece of information separately defines the processes which appear to be occurring. The key is that several processes occur simultaneously with growing and diminishing influence over the observed products. The initial formation of ethene and propene combined with the near exponential increase in cyclohexene suggests an initiation process which controls product formation during the early moments of olefin and catalyst exposure. This initiation scheme is shown in Figure 12.

Following this initiation process, the catalytic production of butene commences. Studies of the mechanism of olefin metathesis have examined the initial ratio of labelled products. However, in this study the initial ratio is affected by the apparent isotope effect. As noted in Tables 11, 12, 13 and 14, a high cis to trans butene ratio suggests a minimum of label scrambling. Therefore, the initial product ratio should allow a distinction to be made between the pairwise and the non-pairwise exchange mechanisms even though this product ratio is affected by the isotope effect.

Figure 16 presents the propagation steps in the overall metathesis reaction. At steady state, A is defined as the ratio of decadiene- $d_0$  and  $d_6$  and the ratio of  $[M_0]$  and  $[M_3]$  (Eq. 42).



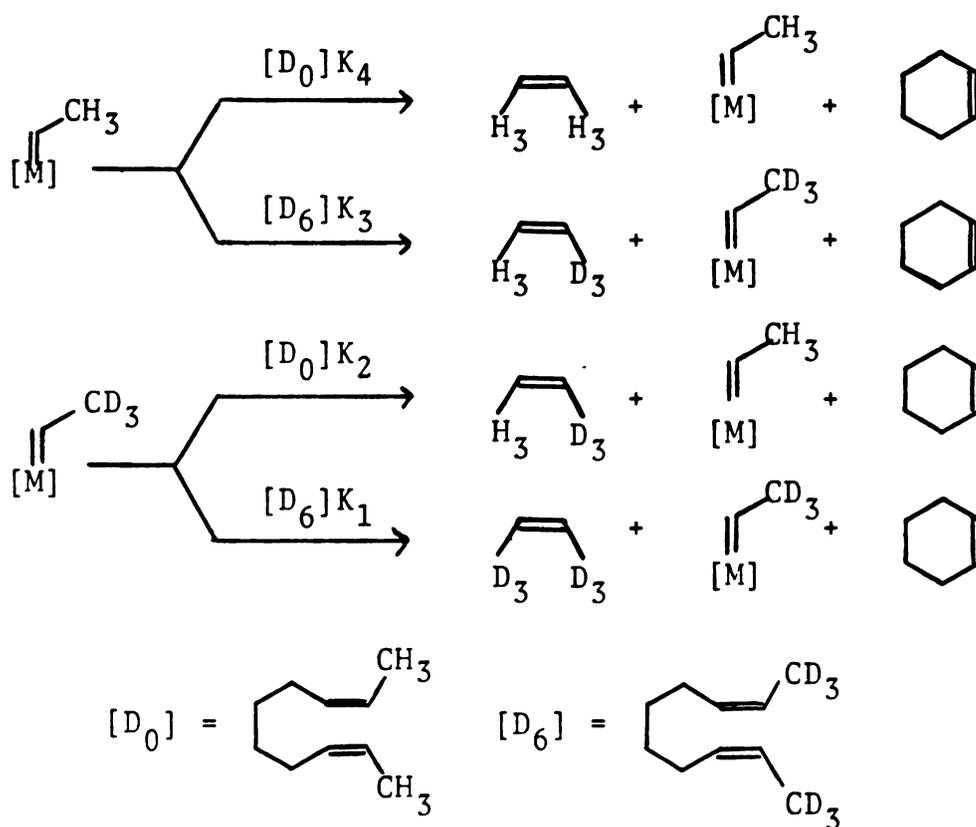


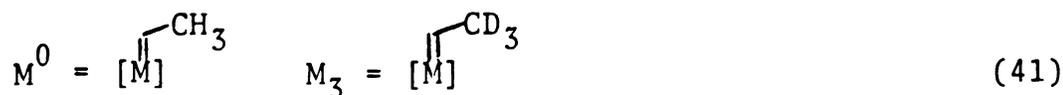
Figure 16. Propagation steps in olefin metathesis.

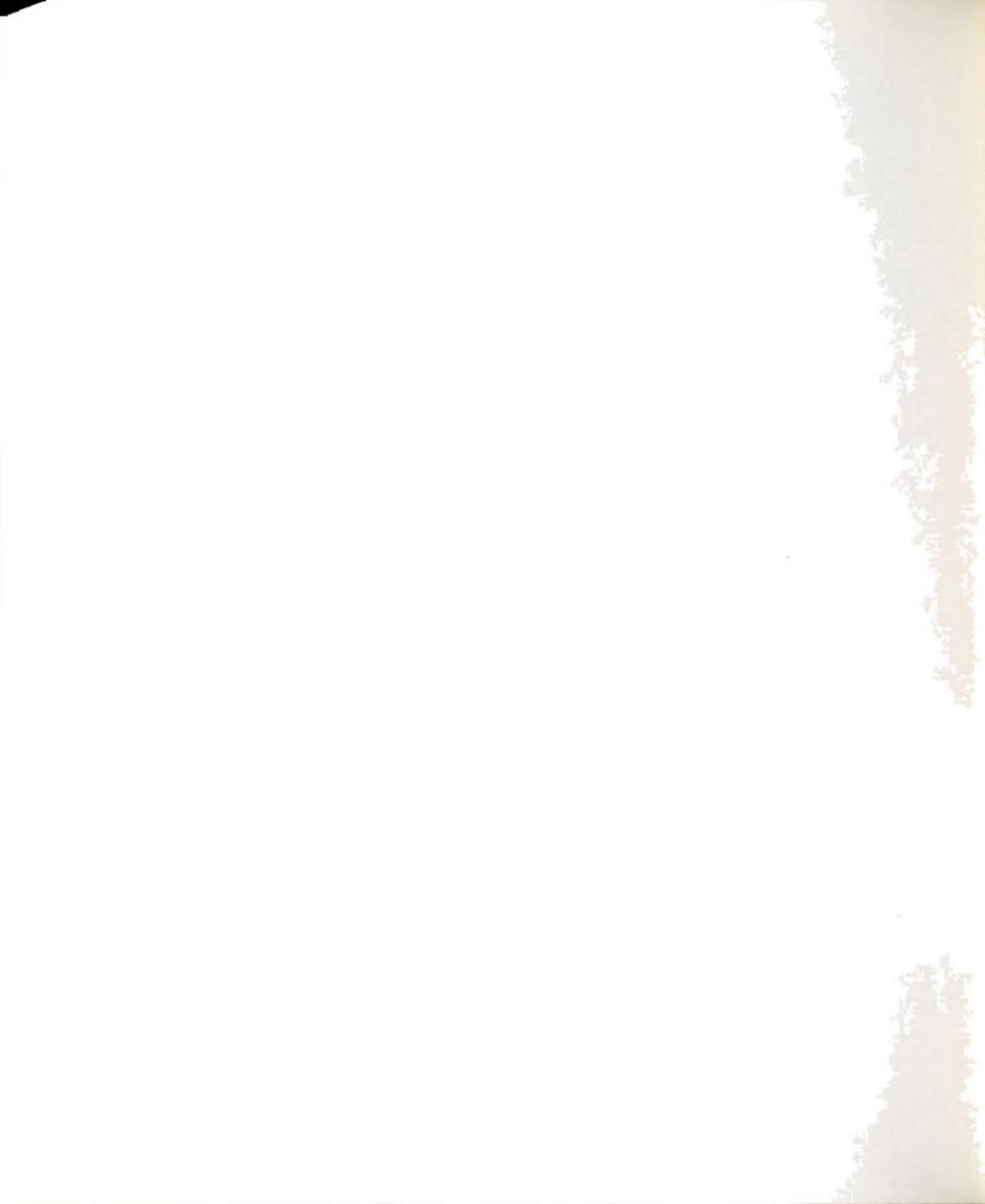
The equation for the production of each butene is:

$$d[\text{butene-d}_0]/dt = K_4[D_0][M_0] \quad (38)$$

$$d[\text{butene-d}_3]/dt = K_3[D_6][M_0] + K_2[D_0][M_3] \quad (39)$$

$$d[\text{butene-d}_6]/dt = K_1[D_6][M_3] \quad (40)$$





$$A = \frac{[D_0]}{[D_6]} = \frac{[M_0]}{[M_3]} \quad (42)$$

The isotope effect controlling the initiation step causes an apparent increase in A due to the preferential formation of  $[M_0]$  (Eq. 43) and the initially faster reaction of decadiene- $d_0$  (Eq. 44).

$$[M_0] = AR [M_3] \quad (43)$$

$$RK_1 = K_2 = RK_3 = K_4 \quad (44)$$

Substituting terms from Equations (43) and (44) into Equations (38), (39) and (40) yields:

$$\begin{aligned} d[\text{butene-}d_0]/dt &= RK_1A[D_6]RA[M_3] \\ &= (K_1[D_6][M_3])R^2A^2 \end{aligned} \quad (45)$$

$$\begin{aligned} d(\text{butene-}d_3)dt/ &= K_1[D_6]RA[M_3] + RK_1A[D_6][M_3] \\ &= K_1[D_6][M_3]) 2RA \end{aligned} \quad (46)$$

$$d(\text{butene-}d_6)/dt = K_1[D_6][M_3] \quad (47)$$

It follows from Equations (45), (46) and (47) that the distribution of butene- $d_6$ :- $d_3$ :- $d_0$  predicted by this mechanism is  $1:2RA:R^2A^2$ . As shown in Tables 11, 12 and 13, this ratio of products is formed giving support to the carbene-



chain mechanism described previously.

An alternate mechanism involving the pairwise exchange of alkylidene units has been suggested by a variety of authors. A number of papers<sup>34,35,97</sup> have presented elaborate methods for calculating the product ratios expected from this mechanism. Katz<sup>34</sup> devised a kinetic model which allowed for deviations in product ratios due to an isotope effect. A pairwise mechanism might not be expected to require an initiation step such as that observed here. Katz assumed that an isotope effect would be exclusively due to rate differences during the catalytic steps. Based on this assumption, he predicted that the product

$$\frac{d[\text{Et-d}_0]}{d[\text{Et-d}_0]} \times \frac{d[\text{Et-d}_2]}{d[\text{Et-d}_4]}$$

should be independent of the actual isotope effect. For a 1:1  $d_0$ - to  $d_{6-2,8}$ -decadiene mixture the product ratios have been predicted and used to distinguish between possible mechanisms in homogeneous metathesis. The predicted rates are shown in Table 16.



Table 16. Predicted Butene Ratios for Carbene and Pairwise Mechanisms.

	$D_6$	:	$D_3$	:	$D_0$	$(D_3)^2/D_0D_6$
Carbene	1	:	2	:	1	4
Pairwise	1	:	1.6	:	1	2.56

Table 17 lists the calculated value of  $D_3^2/D_0D_6$  for the experiments presented in Tables 11, 12, 13 and 14. In his own work with a homogeneous catalyst, Katz observed an experimental value of 3.8. This compares favorably with the value obtained early in each experiment.

The similarity between the  $D_3^2/D_0D_6$  values obtained for a homogeneous catalyst and for the heterogeneous catalyst used in this study strongly indicates a similar reaction mechanism. As noted earlier, the initiation processes for these two classes of catalyst are quite different. However, a similar non-pairwise exchange of alkylidene units appears to control the propagation step. The activation of the heterogeneous catalysts by metal-alkyl co-catalysts indicates that the active species can be similar in both homogeneous and heterogeneous catalysts. The data presented here support a non-pairwise chain mechanism and indicate a possible pathway for the formation of a metal carbene species which may be the chain carrying active site.



Table 17. Calculated Values for  $D_0/D_3 \times D_3/D_6$ .

Run	$D_6$	$D_3$	$D_0$	$(D_3)^2/D_0D_6$
A	1	2.45	1.58	3.79
B	1	2.81	2.12	3.72
C	1	4.60	5.76	3.67
D	1	4.95	5.95	4.11
E	1	4.88	5.95	4.00
F	1	1.48	.58	3.77
G	- - -	equilibrated	- - -	
H	1	1.16	.37	3.63
I	- - -	equilibrated	- - -	
Average				3.81



## EXPERIMENTAL

The gas samples were separated and collected using a Varian model 90-P gas chromatograph with a 6' x 1/4" Durapak column at 70°C. The propene and butene samples were separately collected in a gas collection tube cooled to -196°C and then analyzed on a Hitachi RMU-6E mass spectrometer. Analytical glc was conducted on a Varian series 1400 flame ionization detector chromatograph using a 20' x 1/8" Durapak column at 60° for gas samples and a 32' x 1/8" 5% Carbowax 20M on Chromosorb W at 125°C for liquid samples. NMR analysis was conducted on a Varian T-60 spectrometer.

The solid catalyst pellets were obtained from the Nalco Chemical Company, Chicago, IL. The cobalt-molybdenum-alumina catalyst contained 12.5% MoO<sub>3</sub>, 3.5% CoO on an alumina base. The molybdenum-alumina catalyst contained 13% MoO<sub>3</sub> on gamma alumina. The catalyst samples were suspended in a silica tube and heated at 560° in air for 12 hours using a Lindberg Hevi-Duty type 59344/54031-A tube furnace. The catalyst samples were then exposed to a stream of dry argon at 560° for two hours and then transferred in argon to the reaction flask and cooled to the reaction temperature.

The metathesis reactions were carried out in oven-dried side arm flasks sealed with a rubber septum. Oven



dried syringes were used to transfer solvents and reactants. Gas samples were collected through the rubber septum with a 10 ml gas syringe. The chlorobenzene was distilled from  $P_2O_5$  under argon into a side-arm flask and stored over 4A molecular sieves.

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

Approximately 80 ml of heptane was distilled from potassium directly into a 500 ml 3 neck flask fitted with a condenser and an argon bubbler. The flask was cooled to 0° and 86 ml of 1.6 M (.1375 moles) n-BuLi added to the flask. The solution was magnetically stirred. 7.3 g (.068 moles) of commercially available 1,7-octadiyne was slowly added via syringe. A white precipitate formed and the solution was refluxed for 1 hr. The reaction was then cooled to room temperature and vacuumed until dry. The 3-neck flask was fitted with an addition funnel over a condenser. Approximately 100 ml of THF distilled from Na/benzophenone was added to the flask. 100 ml of THF was added to the addition funnel and 20 g (.138 moles) methyl iodide- $d_3$  (Aldrich) added to the addition funnel. The methyl iodide- $d_3$ /THF solution was slowly dripped in at 0° and the mixture refluxed overnight. The clear gold solution was poured over ice and then extracted three times with pentane. The extractions were



combined and washed with 5% HCl, satd. NaCl, 5% NaOH, satd. NaCl, and H<sub>2</sub>O and then dried by dripping through K<sub>2</sub>CO<sub>3</sub>. The pentane was distilled off and the 2,8 decadiyne 1,1,1,10,10,10-d<sub>6</sub> distilled (30-45°C, 1.2 mm) to yield 6.8 g (71%), glc pure (16', 5% DC-550, 170°C); NMR (CDCl<sub>3</sub>) δ1.5 (m, 4, -CH<sub>2</sub>-), δ2.1 (m, 4, -CH<sub>2</sub>-C≡C-).

Preparation of 1,1,1,10,10,10-d<sub>6</sub>, cis,cis-2,8-decadiene

Approximately 150 ml pyridine (NaOH) was distilled under argon directly into an oven dried, 3 neck, 500 ml flask. The distilled diyne, 6.8 g (.048 moles), was added under argon and then .13 g 5% Pd on BaSO<sub>4</sub> (Ventron) added and stirred 12 hours with gentle warming while bubbling H<sub>2</sub> through the solution. The reaction was followed by glc (5% DC-550, 170°C). When the hydrogenation was complete, the mixture was filtered through a fine glass frit. The majority of pyridine was distilled off. The distillation residue was diluted with ether and washed with 10% HCl until glc analysis indicated the absence of pyridine. The ether extracts were then washed with satd. NaCl and dried over MgSO<sub>4</sub>. The ether was removed and the diene vacuum-distilled (b.p. 30-40° .3 mm Hg), yield 5.2 g (75%). Glc analysis indicated 1% trans isomer and no other impurity.

NMR (CDCl<sub>3</sub>) δ1.6 (m, 4, -CH<sub>2</sub>-), δ2.2 (m, 4, -CH<sub>2</sub>-C=), δ5.5 (m, 4, =CH); mass spectrum m/e 144 (parent), only negligible peaks at 143→130.

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Preparation of cis,cis-2,8-decadiene

Using the above procedure 14.73 g (.138 moles) 1,7 octadiyne was treated with 150 ml 1.85 M n-BuLi (.277 moles) followed by 41 g (.28 moles) methyl iodide. The 2,8 decadiyne was isolated, (b.p. 37-45°C 65 mm Hg) to yield 13.9 g (75%). The diyne was hydrogenated using .34 g Pd/BaSO<sub>4</sub> in pyridine and isolated (b.p. 25-40°C 25 mm Hg) yield 10.8 g (76%). GC analysis (DC 550-170°C) indicated 2% trans isomer and no other impurities. NMR (CDCl<sub>3</sub>) δ1.6 (m, 4, -CH<sub>2</sub>-), δ1.8 (d, 6, CH<sub>3</sub>), δ2.2 (m, 4, -CH<sub>2</sub>-C=), δ5.5 (m, 4, =CH); mass spectrum m/e 138 (parent).

Metathesis of trans, trans-2,8-decadiene with Mo/Al<sub>2</sub>O<sub>3</sub> -Method A

The heat activated catalyst (.65 g) was transferred to an oven-dried side arm 10 ml flask with a rubber septum on the side arm. The flask was flushed with argon and then sealed with a flo-control ground glass stopper. A mixture of commercially available trans, trans-2,8-decadiene and 1,1,1,10,10,10-d<sub>6</sub>-trans, trans-2,8-decadiene<sup>99</sup> was prepared by mixing .122 g (.847 mmoles) d<sub>6</sub>-diene and .127 g (.92 mmoles) d<sub>0</sub>-diene to yield a 1.08:1 d<sub>0</sub>:d<sub>6</sub> mixture under argon. The catalyst was stirred at 70° and the olefin mixture added to the flask through the rubber septum. Upon addition of the olefin, the tan/white catalyst pellets turned blue/black. The reaction



progress was followed by analyzing small ( $\sim 2$  ml) gas samples on an FID gas chromatograph. Gas samples ( $\sim 5$  ml) were separated on a thermal conductivity gas chromatograph and the effluent gas collected in a gas collection tube cooled in liquid nitrogen. Both cis and trans butenes were collected. The catalyst was quickly deactivated and sampling often created a vacuum. Butene samples were analyzed by mass spectrometry. Liquid analysis was not possible because the olefin was taken up into the solid catalyst by capillary action. Mass spectral analysis of a typical butene sample gave the following uncorrected peak heights:

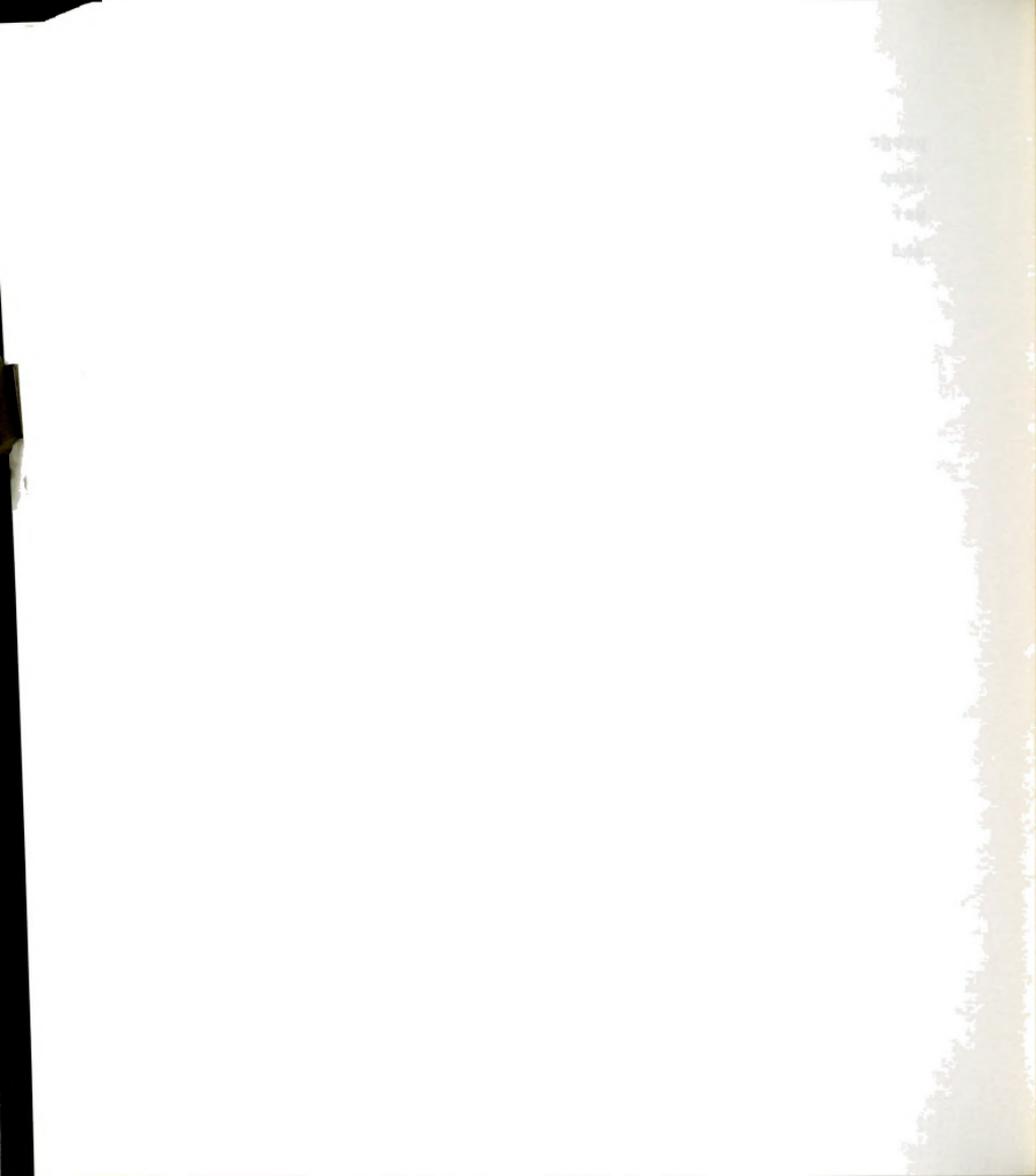
M/e	62	61	60	59	58	57	56	55	54
Intensity	.37	.03	.10	1.00	.28	.17	.71	.34	.10

The peaks at 56 and 59 were adjusted to allow for overlapping ionization peaks and the  $-d_6:-d_3:-d_0$ -butene ratios calculated from these adjusted values. The results are presented in Table 4.

### Metathesis of cis, cis-2,8-decadiene with Mo/Al<sub>2</sub>O<sub>3</sub>

#### Method A

A mixture of .289 g (2.0 mmoles)  $d_6$ -2,8-decadiene and .302 g (2.19 mmoles)  $d_0$ -2,8-decadiene was syringed into a side arm flask containing .5 g of activated catalyst



stirring at 57°C. The reaction was followed and the butene samples collected as in Method A. Mass spectral analysis of a typical sample gave the following uncorrected peak heights.

M/e	62	61	60	59	58	57	56	55	54
Intensity	.37	.05	.13	1.0	.35	.19	.73	.43	.13

The peaks at 56 and 59 were adjusted to allow for overlapping ionization peaks and the  $\text{-d}_6\text{: -d}_3\text{: -d}_0\text{-butene}$  ratios calculated from these adjusted values. The results are presented in Table 4.

#### Metathesis of cis, cis-2,8-decadiene-D<sub>6</sub> with Mo/Al<sub>2</sub>O<sub>3</sub>

##### Method A

Using Method A, outlined above, .2 ml of cis, cis-2,8-decadiene-D<sub>6</sub> was added to a side-arm flask containing approximately .3 g of the heat activated catalyst. Initially the reaction temperature was 34°C, however, after 40 min at this temperature no butenes were visible on the thermal conductivity gas chromatograph. The reaction was heated to 80°C and the resultant butenes collected, as in Method A, after 10 minutes. A mass spectral analysis indicated only D<sub>6</sub> butene products.



M/e	62	61	60	59	58	57	56	55	54
Intensity	1.00	.16	.14	.12	.08	.13	.12	.11	.07

Metathesis of cis, cis-2,8-decadiene-D<sub>0</sub> with Mo/Al<sub>2</sub>O<sub>3</sub>

Using Method A, outlined above, .2 ml of cis, cis-2,8-decadiene-D<sub>0</sub> was added to a side-arm flask containing approximately .4 g of the heat activated catalyst. After stirring at 48° for 20 minutes, a gas sample was taken and analyzed on a thermal conductivity gas chromatograph. The butenes were collected and mass spectral analysis indicated only butene-d<sub>0</sub>.

M/e	62→58	57	56	55	54	53	52
Intensity	0	.06	1.00	.45	.09	.16	.06

Comparison of Rates of Metathesis Between cis, cis-2,8-decadiene and cis, cis-2,8-decadiene-1,1,1,10,10,10-d<sub>6</sub> Over MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>

Using Method A outlined above, two nearly identical flasks were prepared. Into flask A was placed .356 g of heat activated catalyst and into flask B was placed .346 g of the same sample of heat activated catalyst. Both flasks were placed in an oil bath at 30°C and allowed to cool under argon. A propane standard (.1 ml) was added to each flask.

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Into flask A was added .216 g (1.56 mmoles) of cis, cis-2,8-decadiene and .23 minutes later, .224 g (1.55 mmoles) of cis, cis-2,8-decadiene-1,1,1,10,10,10-d<sub>6</sub> was added to flask B. Gas samples (.5 ml) were collected at various time intervals and analyzed on a FID gas chromatograph. The results are presented in Figure 8.

This procedure was repeated using .435 g of catalyst with .225 g (1.63 mmoles) of cis, cis-2,8-decadiene and .436 g of catalyst with .231 g (1.60 mmoles) of cis, cis-2,8-decadiene-1,1,1,10,10,10-d<sub>6</sub>. The results are presented in Figure 9.

### Metathesis of cis, cis-2,8-decadiene Using MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub>

#### Method B

As in Method A, .259 g of heat activated catalyst was transferred to a dry flask under argon, sealed and cooled to 35° in an oil bath. A .2 ml propane standard was syringed into the flask followed by a .2 ml sample of cis, cis-2,8-decadiene. Gas samples were taken at 30 second intervals for the first few minutes and then at longer intervals for one hour. The results are presented in Figure 10.

This procedure was repeated three additional times and the production of cis-butene and propene relative to the production of trans-butene calculated from the results. The data is presented in Figure 11.



Metathesis of cis, cis-2,8-decadiene Using MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub>:  
Analysis of the Liquid Phase

Using Method B, 3.4 g of heat activated MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> was exposed under argon to 3 ml of cis, cis-2,8-decadiene in a sealed tube at 45°C. The liquid was sampled at 5 minutes and 30 minutes and analyzed on a thermal conductivity gas chromatograph using a 16' 5% DC-550 column at 160°C. The sensitivity was adjusted to produce a large cyclohexene peak but no cycloheptene was observed at all. There were also no peaks above the 2,8-decadiene peak where a dimer of cycloheptene might be expected.

Analysis of the Extent of Reaction-Production of Cyclohexene Over MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> - Method C

In an oven dried flask, .37 g (.046 g, .32 mmoles MoO<sub>3</sub>) of MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> was stirred with 1 ml chlorobenzene at 47°C. To this flask was added ~ .3 ml (.28 g, 1.9 mmoles) of a 2.25:1 mixture of cis, cis-2,8-decadiene and cis, cis-2,8-decadiene-1,1,1,10,10,10-d<sub>6</sub>. This would be a 5.9:1 catalyst:olefin ratio if all the MoO<sub>3</sub> formed active sites. At various time intervals, small liquid samples were syringed out of the flask and analyzed on a FID gas chromatograph (30', 6% Carbowax on Chromosorb G). The production of cyclohexene relative to 2,8-decadiene was determined. This experiment was repeated twice and the results are reported

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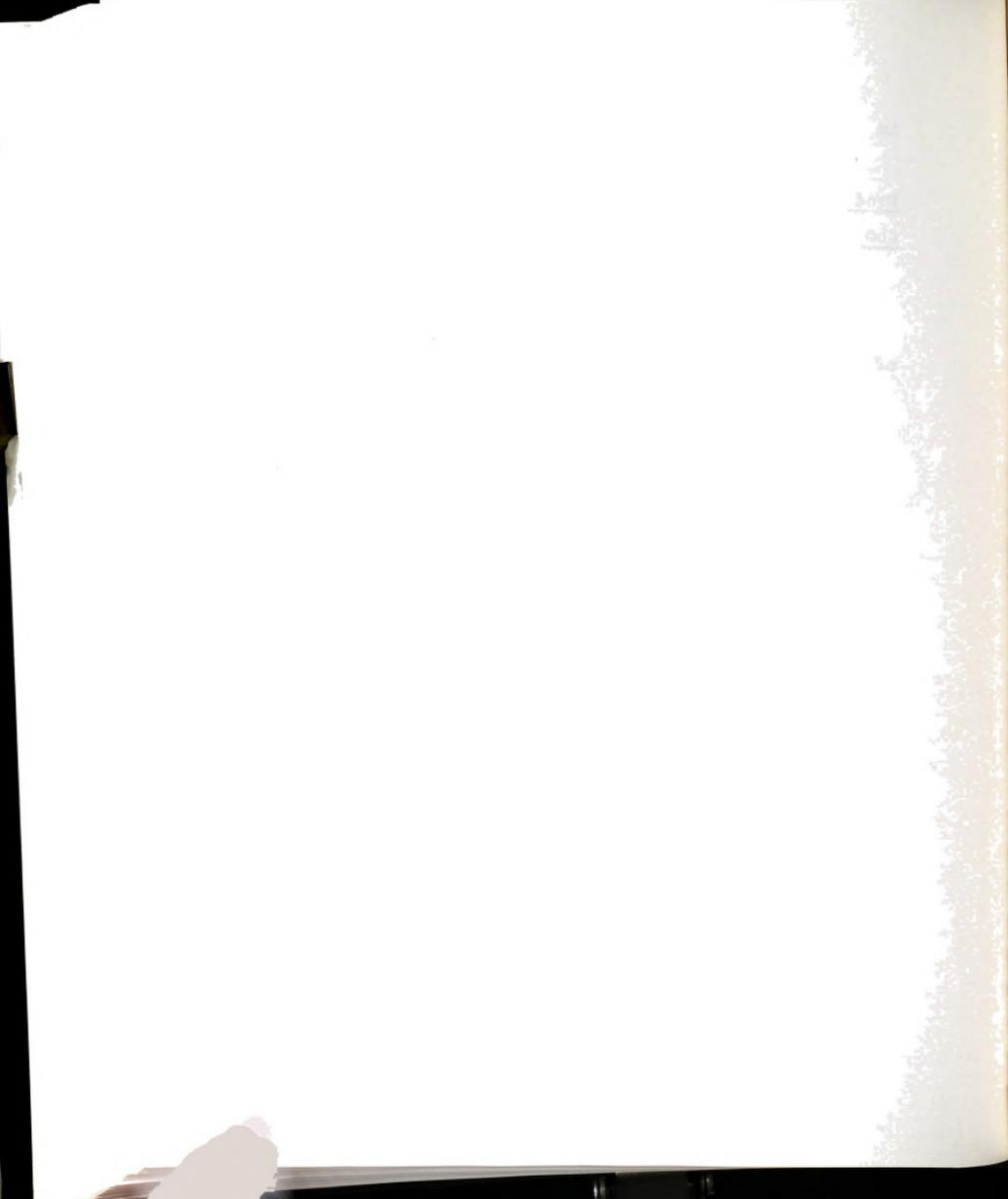
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in Figure 15.

Production of Cyclohexene, Butene and Propene Over MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> Treated with Sn(CD<sub>3</sub>)<sub>4</sub> - Method D

In an oven dried flask .34 g (.042 g, .29 mmoles MoO<sub>3</sub>) of MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> was stirred with .2 ml (.16 mmoles) of .81 M Sn(CD<sub>3</sub>)<sub>4</sub> in chlorobenzene at 61°C. Analysis of the gas phase indicated a large production of methane and some ethene and propene. To this mixture was added ~.3 ml (.297 g, .21 mmoles) of a 2.41:1 mixture of cis, cis-2,8-decadiene and cis, cis-2,8-decadiene-1,1,1,10,10,10-d<sub>6</sub>. The liquid phase was sampled with a syringe and analyzed on an FID gas chromatograph (30', 6% Carbowax on Chromosorb G). The production of cyclohexene relative to 2,8-decadiene was determined and is presented in Figure 15. The gas phase was sampled and the butene collected as in Method A. The ratios of labelled butenes formed in this reaction is presented in Table 15. The uncorrected peak heights are as follows.

	M/e	62	61	60	59	58	57	56	55
6 min intensity		1.00	.16	.21	.78	.24	.18	.21	.18
16 min		1.00	.15	.19	.77	.30	.21	.21	.18
29 min		1.00	.2	.26	.79	.32	.28	.32	.2



The propene formed in this reaction was also collected and analyzed by mass spectrometry. The results are presented in Table 9 and the uncorrected peak heights are as follows:

M/e	47	46	45	44	43	42	41	40
Intensity	.50	.41	1.00	.91	.66	.66	1.0	.45

Analysis of Propene Produced in the Metathesis of cis, cis-2,8-decadiene over MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> Treated with Tetramethyltin - Method D

In an oven dried flask, .89 g (.11 g, .77 mmoles MoO<sub>3</sub>) of heat activated MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> was mixed with .5 ml (.5 mmole) of 1M S(CH<sub>3</sub>)<sub>4</sub> in chlorobenzene at 35°C. Analysis of the gas phase products indicated approximately 1 methane: .5 ethene:.25 1-butene. After 20 minutes, .2 ml (.27 g 1.8 mmoles) of cis, cis-2,8-decadiene-d<sub>6</sub> was added and the gas phase products collected as in Method A. The earliest butene sample was contaminated with butene-d<sub>3</sub> and -d<sub>0</sub>, presumably from the 1-butene. All later samples indicated only butene-d<sub>6</sub>. Upon addition of the diene, propene was rapidly formed along with the 2-butene products. A sample collected after 3.5 hours gave the following mass spectrum:

M/e	47	46	45	44	43	42	41
Intensity	.51	.37	1.00	.51	.36	.42	.43

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In an oven dried flask, .65 g (.06 g, .42 mmole  $\text{MoO}_3$ ) was treated with .2 ml (.16 mmole) .81 M  $\text{Sn}(\text{CD}_3)_4$  in chlorobenzene. A large production of methane only was observed. Analysis of collected butenes indicated only butene- $\text{d}_6$ . Analysis of collected propene gave the following uncorrected mass spectrum.

M/e	47	46	45	44	43	42	41	40
Intensity	.38	.33	1.00	.80	---	.33	---	.33

In an oven dried flask .283 g (.035 g, .24 mmoles  $\text{MoO}_3$ ) of heat activated  $\text{MoO}_3/\text{CoO}/\text{Al}_2\text{O}_3$  was stirred with .05 ml (.04 mmole) of .81 M  $\text{Sn}(\text{CD}_3)_4$  in chlorobenzene. A large production of methane and ethene was observed. After five minutes, .2 ml (.29 g, 2.1 mmoles) of cis, cis-2,8-decadiene was added. Analysis of the earliest butene sample indicated contamination with butene- $\text{d}_3$  and butene- $\text{d}_6$ . Later samples indicated only butene- $\text{d}_0$ . The propene collected after 30 minutes gave the following uncorrected mass spectrum:

M/e	47	46	45	44	43	42	41	40
Intensity	---	---	---	.07	.09	.66	.9	.22

All of the above mass spectra were analyzed and the results are presented in Table 9.

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Metathesis of a 1.05:1 Mixture of cis, cis-2,8-decadiene and cis, cis-2,8-decadiene-d<sub>6</sub> - Method C

In an oven dried flask .59 g (.073, .51 mmole MoO<sub>3</sub>) of heat activated MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> was stirred with 2 ml of chlorobenzene at 36°C. A .1 ml (.098 g, .69 mmole) sample of a 1.05:1 mixture of cis, cis-2,8-decadiene and cis, cis-2,8-decadiene-d<sub>6</sub> was added and the gas phase products collected at various time intervals. The butenes collected at 30 min and at 28 hr gave the following uncorrected mass spectra.

Run A	M/e	62	61	60	59	58	57	56	55
30 min	intensity	.37	.08	.13	1.00	.31	.18	.72	.37
28 hr		.38	.07	.13	1.00	.37	.19	.76	.41

A repeat of this experiment gave the following uncorrected mass spectra:

Run B	M/e	62	61	60	59	58	57	56	55
10 min		.32	.04	.12	1.00	.27	.29	.77	.25
2 hr 35 min		.39	.07	.14	1.00	.38	.20	.71	.40

Adjusted butene ratios are presented in Table 10. An analysis of the propene produced in these two experiments is shown in Table 8.

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12/20/20

Metathesis of a 2.23:1 Mixture of cis, cis-2,8-decadiene and cis, cis-2,8-decadiene-d<sub>6</sub> Over MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> - Method C

In an oven dried flask .45 g (.05 g, .39 mmole MoO<sub>3</sub>) of heat activated MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> was stirred with 2 ml of chlorobenzene at 44°C. A (.28 g, 1.9 mmole) sample of a 2.23:1 mixture of cis, cis-2,8-decadiene and cis, cis-2,8-decadiene was added and the gas phase products collected at various time intervals. The butenes collected at 7 minutes and at 24 hours gave the following uncorrected mass spectra.

Run C M/e	62	61	60	59	58	57	56	55
7 min intensity	.16	---	---	.74	.19	.06	1.00	.58
24 hr	.18	.03	.08	.80	.31	.19	1.00	.51

A repeat of this experiment gave the following uncorrected mass spectra:

Run D M/e	62	61	60	59	58	57	56	55
14 min intensity	.15	.01	.03	.75	.32	.35	1.00	.47
1 hr 24 min	.16	.03	.07	.76	.28	.19	1.00	.51

A third run using this mixture gave the following uncorrected mass spectra:

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Run E	M/e	62	61	60	59	58	57	56	55
13 min	intensity	.15	.01	.03	.81	.40	.27	1.00	.43
48 hours		.17	.03	.06	.85	.29	.18	1.00	.54

Adjusted butene ratios are presented in Table 11. An analysis of the propene produced in these three experiments is shown in Table 8.

Metathesis of a 1:3.3 Mixture of cis,cis-2,8-decadiene and cis, cis-2,8-decadiene-d<sub>6</sub> Over MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> - Method C

In an oven dried flask, .32 g (.04 g, .28 mmoles) of heat activated MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> was stirred with 2 ml of chlorobenzene at 42°C. A .2 ml (.198 g, 1.4 mmoles) sample of a 1:3.29±.03 mixture of cis, cis-2,8-decadiene and cis, cis-2,8-decadiene-d<sub>6</sub> was added and the gas phase products collected at various time intervals. The butenes collected at 28 min and at 24 hours gave the following uncorrected mass spectra.

Run F	M/e	62	61	60	59	58	57	56	55
28 min	Intensity	.64	.13	.20	1.00	.34	.25	.43	.22
24 hr		1.00	.20	.31	.76	.35	.22	.26	.20

The intensities were adjusted for overlapping ionization peaks and the butene ratios calculated from these adjusted values. The ratios are presented in Table 12.

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Metathesis of a 1:2.4 Mixture of cis, cis-2,8-decadiene and cis, cis-2,8-decadiene-d<sub>6</sub> Over MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> - Method C

In an oven dried flask, 1.1 g (.137 g, .95 mmole MoO<sub>3</sub>) of heat activated MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> was stirred with 5 ml chlorobenzene at 55°C. A .4 ml (.394 g, 2.7 mmole) sample of a 1:2.4 mixture of cis, cis-2,8-decadiene and cis, cis-2,8-decadiene-d<sub>6</sub> was added and the gas phase products collected at various time intervals. The butenes collected at 16 minutes gave the following uncorrected mass spectra.

Run H	M/e	62	61	60	59	58	57	56
16 min	Intensity	.84	.17	.22	1.00	.33	.14	.38

The butene intensities were adjusted for overlapping ionization peaks and the butene ratios calculated from these adjusted values. The results are presented in Table 14. The propene collected in this experiment was analyzed and the results are presented in Table 8.

Metathesis of cis, cis-2,8-decadiene-d<sub>6</sub> Over MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> Method C

In an oven dried flask, 1.26 g (.157 g, 1.09 mmoles) of heat activated MoO<sub>3</sub>/CoO/Al<sub>2</sub>O<sub>3</sub> was stirred with 5 ml of chlorobenzene and .6 ml (.58 g, 4.0 mmoles) of cis, cis-2,8-decadiene-d<sub>6</sub> at 34°C. The gas phase products were collected

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at various time intervals. The uncorrected mass spectra of the butenes is presented in Table 14.



PART II

DEVELOPMENT OF A POLYMER-BOUND CATALYST FOR THE  
OLEFIN METATHESIS REACTION



## INTRODUCTION

Merrifield's<sup>100</sup> development of the solid phase sequential method for a peptide synthesis has led to the development of polymer-bound reagents and catalysts.<sup>101</sup> In particular, functionalized polystyrene has been used as a support for hydrogenation, hydrosilyation, hydroformylation and cyclooligomerization. In general, the transition metal catalyst has been bound to the polymer supported by means of a metal ligand, such as a phosphine or cyclopentadiene group. The polystyrene can be functionalized by chloromethylation, treatment with a variety of Lewis acids or lithiation with a mixture of BuLi and TMEDA. The active polystyrene can then be treated with solutions of the desired linking agent and finally with a transition metal complex. The metal complex is generally attached by exchange of a normal metal ligand for a polymer bound ligand. This investigation has studied the feasibility of using a polymeric co-catalyst to develop a polymer bound metathesis catalyst. This is an unusual development in that the co-catalyst would serve both to activate the transition metal and to link it to the polymer support.

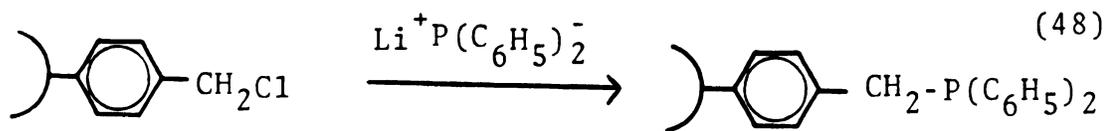
Polymer-supported catalysts lie somewhere between homogeneous and heterogeneous catalysts. As described in an earlier section of this dissertation, heterogeneous catalysts are generally less active, and require more extreme

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reaction conditions than their homogeneous counterparts. Supporting a homogeneous catalyst allows the retention of this higher activity but allows a rapid and easy separation of the catalyst once the reaction is complete. The difficulty in removing and reusing homogeneous catalysts has proved to be a major drawback for the industrial use of these catalysts.

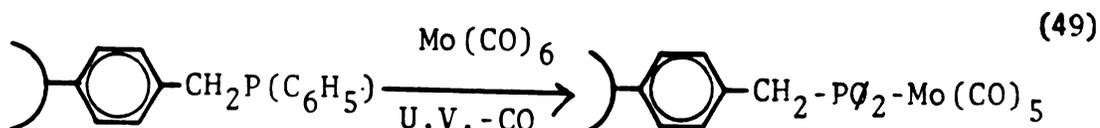
Polymer bound reagents are often less reactive than their soluble counterparts owing to the necessity for the reactants to diffuse into the polymer structure to reach an active catalytic site. This has resulted in a greater selectivity<sup>102</sup> for some sterically hindered reactants.

The first polymer-bound metathesis catalyst was reported in 1975 by Basset.<sup>103</sup> Polystyrene was chloromethylated and then treated with lithium diphenylphosphine in THF to give the phosphinated polystyrene.



The phosphinated polystyrene was then photolyzed in the presence of  $\text{Mo}(\text{CO})_6$  to produce a molybdenum carbonyl catalyst attached to a polymer support by a phosphine link.

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Analysis indicated 0.5 mequiv. Mo/g resin, and 0.4 mequiv. phosphine/g resin. The polymeric molybdenum complex was then treated with  $\text{C}_2\text{H}_2\text{AlCl}_2/\text{O}_2$  and used to metathesize cis-2-pentene. The catalyst was weakly active giving a 3.4% conversion after 20 minutes. No mention of recycling was made.

Subsequent to the present work, a similar catalyst was prepared using  $\text{W}(\text{CO})_6$  and compared to a catalyst in which the tungsten was directly bound to the chloromethylated polystyrene.<sup>104</sup> The preparation of these two compounds is outlined in Figure 17.

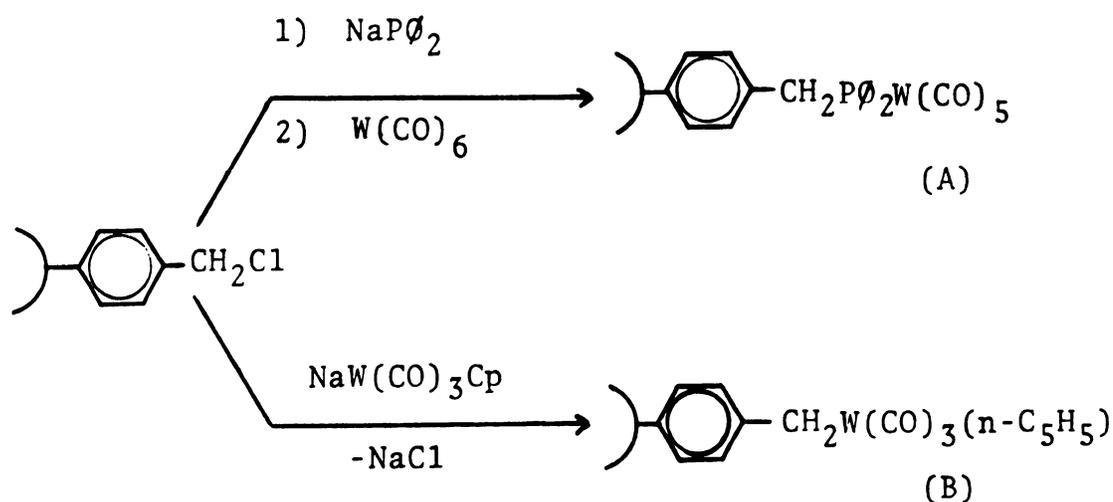


Figure 17. Preparation of polymer supported tungsten carbonyl metathesis catalysts.



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$\text{BuAlCl}_2/\text{O}_2$  was used as a co-catalyst with each of the above polymer-supported species. Compound B formed an active catalyst which did not dissociate from the polymer support, and which demonstrated a constant activity after 8 cycles of washing, vacuum drying, and reuse. It appears that fresh co-catalyst was required during each reuse.

The organo-aluminum co-catalyst cleaved the tungsten carbonyl complex from Compound A. Due to this cleavage, washing and reuse resulted in a dramatic loss of activity.

The tungsten hexachloride-tetramethyltin system was chosen for study because this was known to be a very active homogeneous catalyst. Moreover several compounds containing tin-transition metal bonds have been reported.<sup>105</sup> In particular, a polymer-supported alkyltin compound<sup>106</sup> has been used as a reagent in the preparation of bis(di-N-butylchlorotin) tetracarbonylosmium. The pertinent steps are outlined in Figure 18.

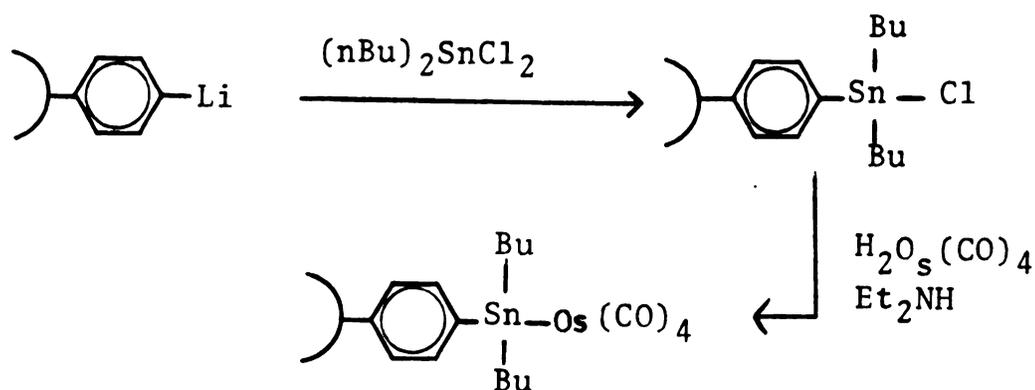


Figure 18. Preparation of a polymer supported tin-osmium complex.



The infrared spectrum of the supported complex was similar to that of  $\text{cis-}\phi_3\text{SnO}_s(\text{CO})_4\text{H}$ . After further reactions, the polymer-Sn bond was cleaved by treatment with anhydrous HCl at  $-15^\circ$  for 30 min. The strong acid needed to cleave this polymer-Sn bond suggests that such polymer-bound tin-transition metal complexes would be stable to cleavage under normal metathesis conditions.

A co-worker in this laboratory studied a polymer-supported  $(\text{Mo}(\text{O}_3\text{P})_2(\text{NO})_2\text{Cl}_2)$  complex linked through a polymeric phosphine.<sup>107</sup> Activation with  $(\text{CH}_3)_3\text{AlCl}_3$  gave an active metathesis catalyst with an activity similar to the homogeneous system. However, after filtration and washing the catalyst proved inactive unless additional co-catalyst was added. These results are similar to those obtained using the polymeric- $\text{W}(\text{CO})_3\text{Cp}$  complex. The necessity of adding fresh co-catalyst for each reuse would make these catalysts less convenient.

The present study was undertaken in an effort to develop a polymer-bound catalyst which would not require the addition of co-catalyst with each reuse.

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## RESULTS AND DISCUSSION

The polymeric Sn compound was prepared by treating lithiated polystyrene with trimethyltin chloride in THF. A large batch could be prepared and stored in a dry box until needed. The polymer supported metathesis catalyst was prepared by treating the polymeric tin compound with  $WCl_6$  in purified trichloroethylene. The reactions are outlined in Figure 19.

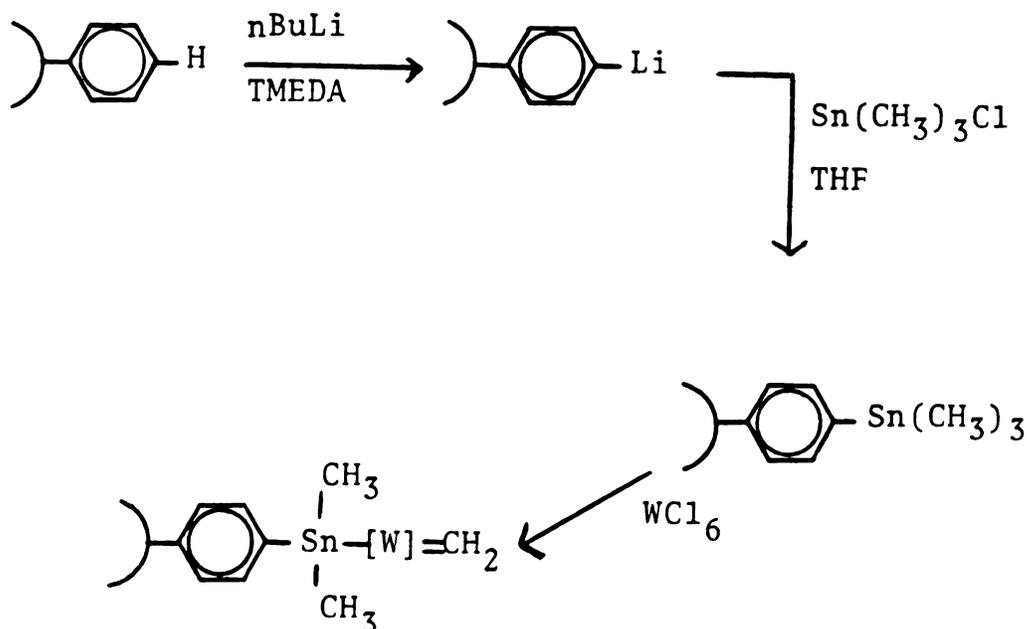


Figure 19. Preparation of the polymer-supported catalyst.

The active beads were washed with trichloroethylene and transferred to a glass column under argon. They were supported in the column on a pad of glass wool. A dilute



solution of 1,7 octadiene in trichloroethylene was slowly dripped through the beads in a continuous flow. The liquid was then collected in a side arm flask connected to the reaction column. A heating tape was wrapped around the reaction column to control the temperature. The entire system was sealed so gaseous products could be sampled. The reaction was followed by analyzing the conversion of 1,7 octadiene to cyclohexene in a gas chromatograph. Table 18 lists conversion data for a typical run. The activity of this catalyst was very low and much further development would be needed before it could be used for catalytic purposes. But the reasonably long lifetime (3.6 days) demonstrated by the run in Table 18 is comparable to homogeneous systems. The catalyst did not appear to wash off the beads as the collected liquid was generally clear. The main difficulty appears to be the extremely clean conditions required for working with this catalyst. Once formed, the blue-black polymer supported catalyst was extremely air sensitive turning pale blue at the slightest exposure to air. This pale blue complex was inactive for metathesis.

Highest catalytic activity was attained by purifying the argon with a BASF catalyst and double distilling both solvent and olefin reactants. The extreme air sensitivity of the active species was a major drawback to this catalyst and more than likely a direct cause for its low activity.

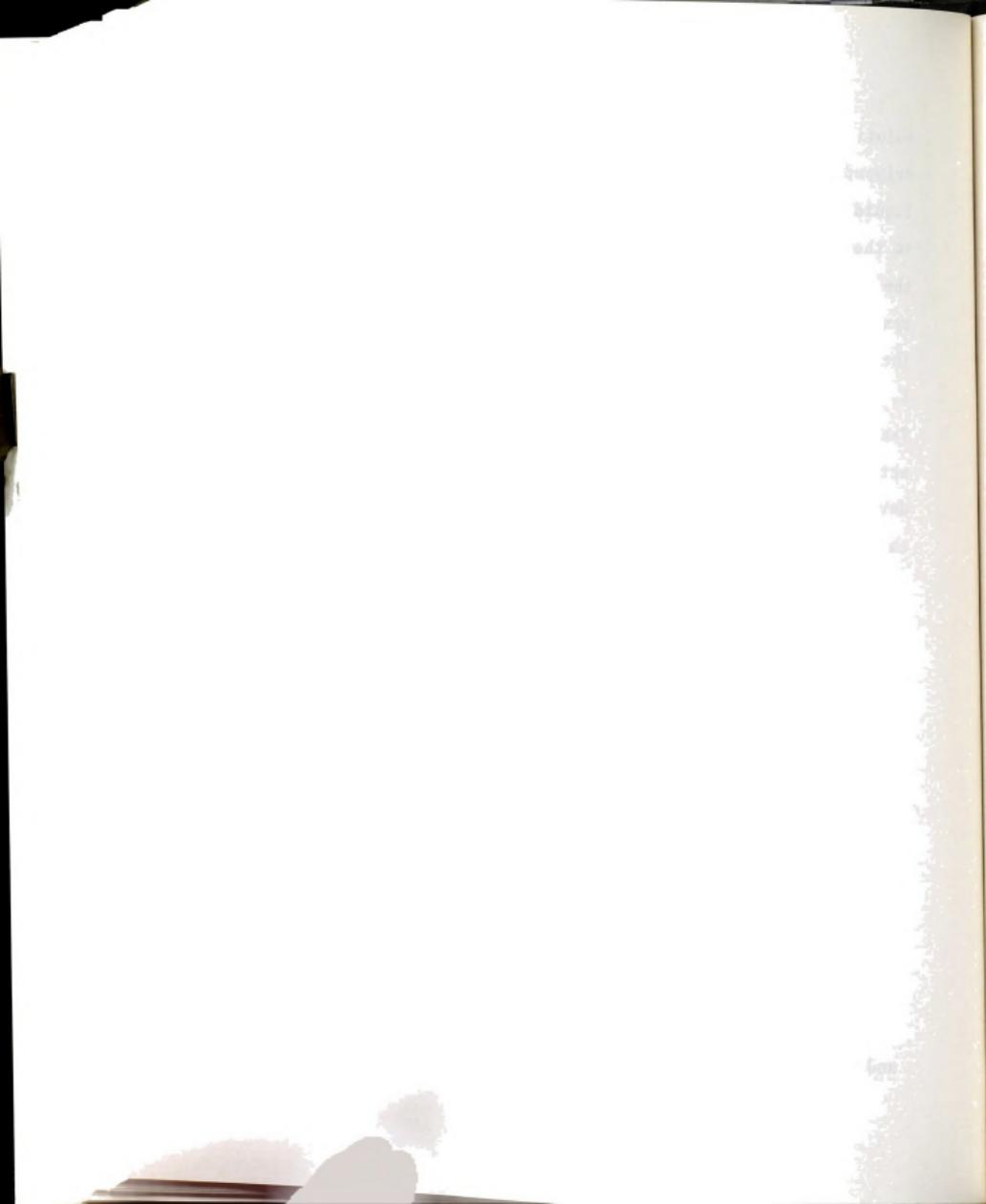
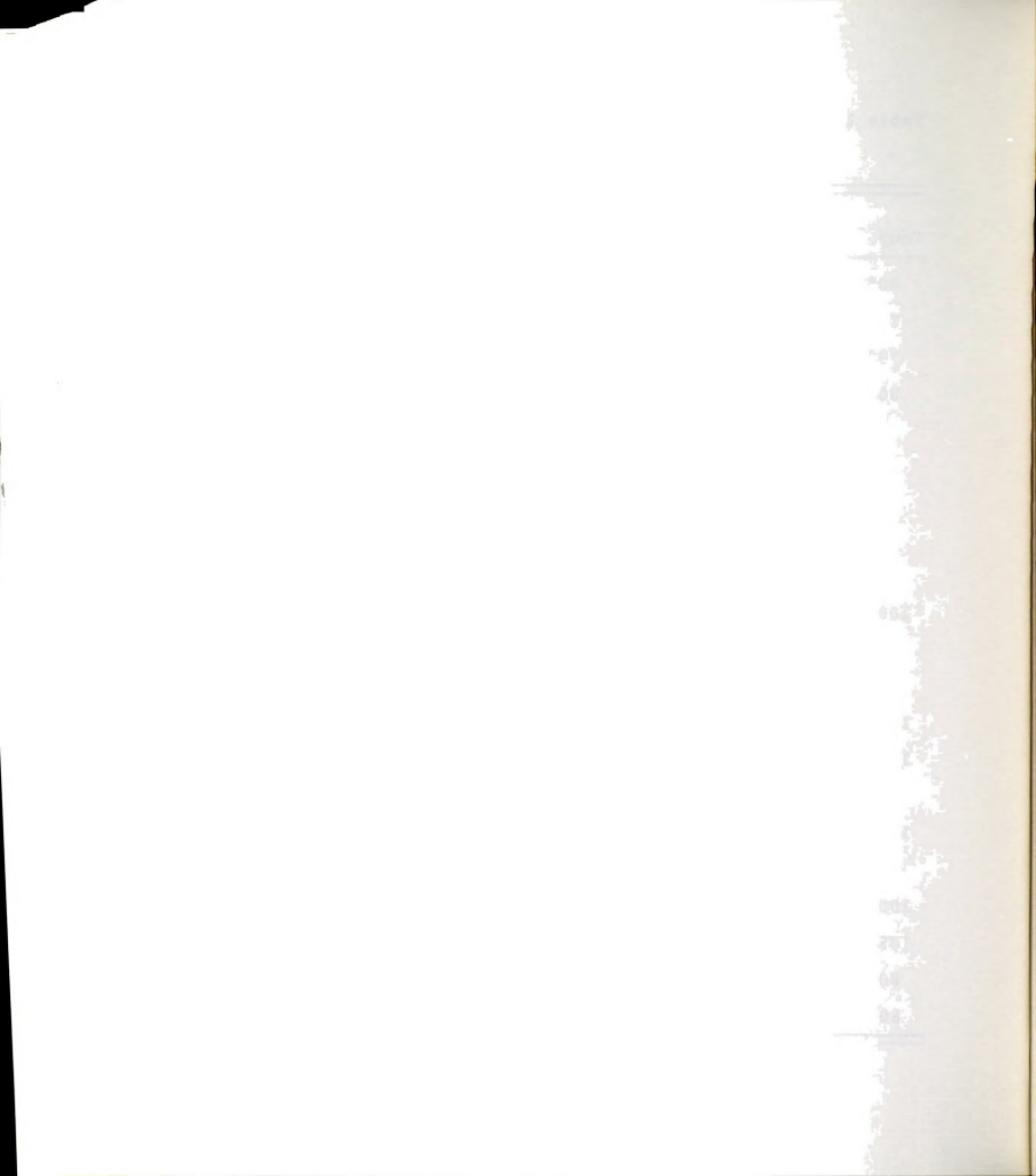
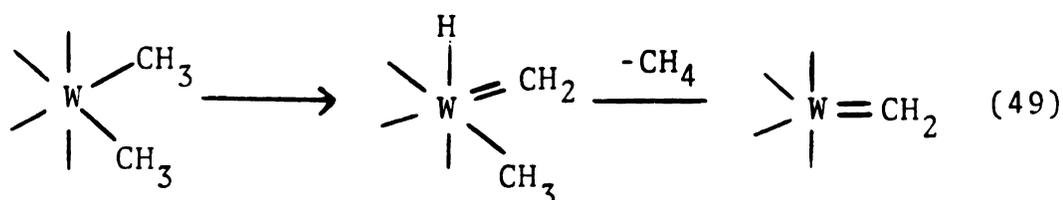


Table 18. Conversion of 1,7 Octadiene to Cyclohexene Over a Polymer Supported Catalyst.

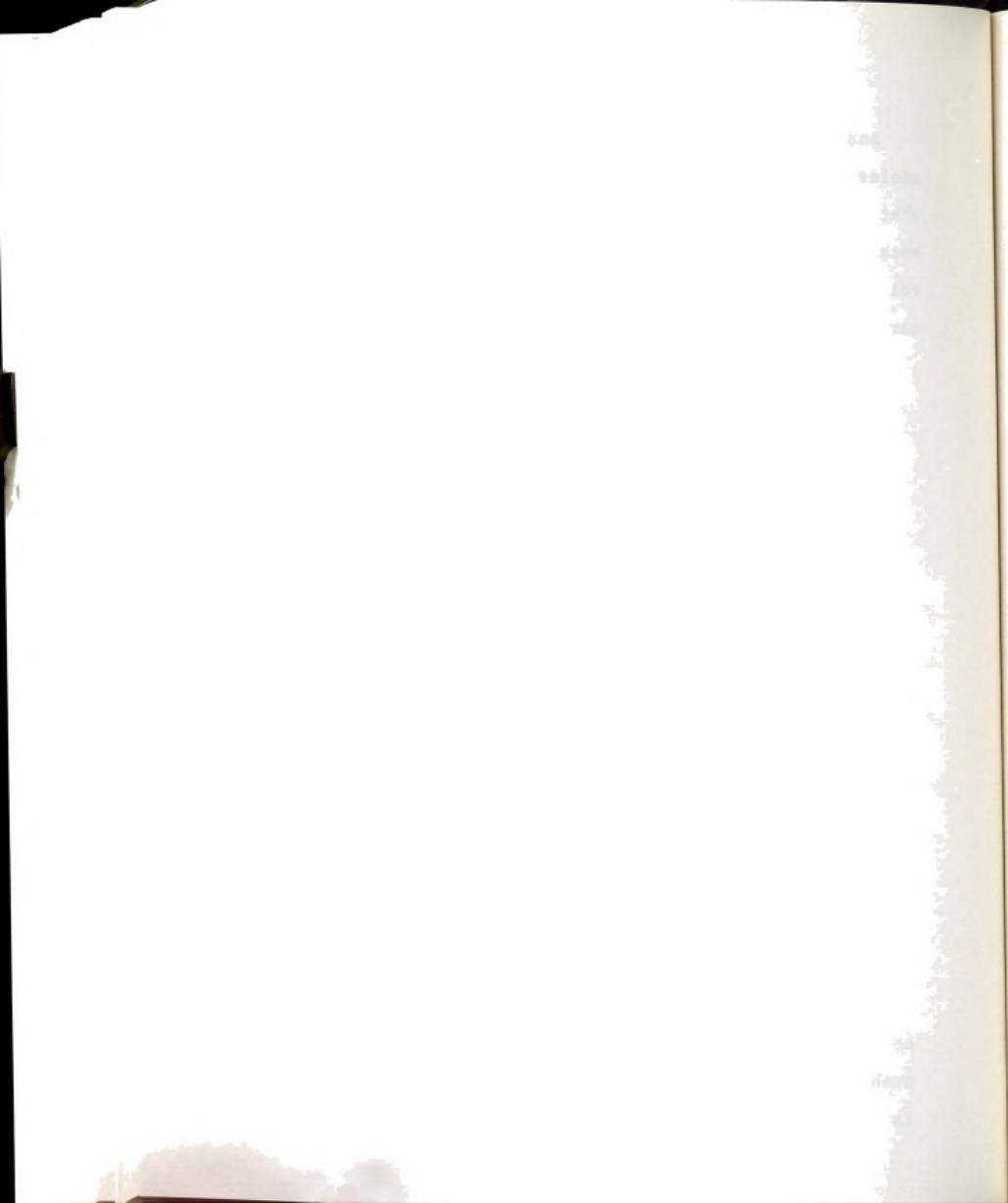
Temp.	Time	Total ml	%
80°	1 min	1	30
79°	9 hr, 10	31	55
79°	9 hr, 30	38	30
80°	10 hr, 40	58	20
"	11 hr, 30	88	10
"	11 hr, 40	95	7
"	12 hr, 40	105	15
89°	13 hr, 50	115	2
90°	15 hr, 5	117	2
100°	15 hr, 30	137	20
"	40 hr, 15	202	5
"	40 hr, 40	210	5
102°	41 hr, 15	211	55
104°	42 hr, 50	213	50
109°	44 hr, 40	225	20
101°	45 hr, 0	226	20
"	45 hr, 15	227	25
100°	62 hr, 20	241	70
105°	64 hr, 30	243	65
80°	83 hr, 0	244	40
80°	88 hr, 50	250	5



Analysis of the polymeric tin reagent indicated .476 mmoles Sn/g polymer. An experiment was undertaken to see what percent of the available tin actually formed active metathesis sites. Meutterties has proposed an alkylation followed by an elimination as the major source of active carbene species.



By this scheme the number of active sites should equal the methane produced during the interaction of the polymeric co-catalyst and tungsten catalyst. To examine the number of active sites 1.24 g (.59 mmoles) polymeric Sn was stirred in the presence of .07 g  $\text{WCl}_6$  (.17 mmoles) in trichloroethylene at  $81^\circ\text{C}$ . A propane standard was injected and the methane produced measured relative to this standard. The mixture was allowed to stir 2 hours after which  $\text{WCl}_6$  was still in excess as noted by the dark solution. Approximately .1 mmole of methane was produced. Assuming a ratio of 2 Sn:1 W this would mean that  $.1/.59 = .169 \div 2 = 8.4\%$  percent of the tin available was actually activated. A major limitation may have been a limited number of sites where two polymer-attached tin atoms were in close enough proximity to achieve the alkylation and



subsequent elimination. Following this gas study the beads were carefully washed and then 2.0 ml 1,7 octadiene added. At 80°C a 33% conversion was attained after 1 hr, 44% after 2 hours and 53% after 3 hours. Table 19 presents the pertinent data. As indicated in Table 19 this catalyst was much more active than the earliest polymer-supported metathesis system developed by Basset. It is hoped that further work may develop systems which are highly active and less sensitive to impurities.

Table 19. Calculation of the Turnover Number for the Polymeric Catalyst.

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$$.476 \text{ mmoles} \times .084 (\% \text{ active}) = .039 \text{ mmoles.}$$

$$.039 \text{ mmoles active catalyst} : 18.1 \text{ mmoles olefin}$$

$$1 \text{ hr} \quad 33\% \quad 5.9 \text{ mmoles} = 153 \text{ turnover/hr}$$

$$2 \text{ hr} \quad 44\%$$

$$3 \text{ hr} \quad 53\% \quad 9.59 \text{ mmoles} = 245 \text{ turnover/3 hr}$$

$$\text{Sn} : \text{Mo} : \text{olefin}$$

$$(\text{Assume}) \quad ? : 1 : 464.1$$


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## EXPERIMENTAL

The trichloroethene solvent was double distilled from  $P_2O_5$  leaving the last 100 ml of solvent behind. Argon was then bubbled through the trichloroethene for 2 hours to remove trace oxygen. The 1,7 octadiene was double distilled from Na and degassed with argon. The argon was purified by passing through a BASF column heated to  $100^\circ C$  and then through molecular sieves. A significant increase in activity was observed for those experiments using these purified reagents. All glassware was oven-dried and cooled in a stream of purified argon. A Varian series 1400 gas chromatograph equipped with a flame ionization detector was used to analyze the gas samples using a Durapak column at  $60^\circ C$ . Liquid samples were analyzed on a Varian Model 90-P gas chromatograph with a 25' 5% Carbowax 20M/Chromosorb W column at  $135-150^\circ C$ .

### Preparation of polystyrene trimethyltin

20% divinylbenzene/styrene copolymer beads were cleaned by washing in cyclohexane under argon. In a 250 ml side arm round bottom flask the beads were stirred with 30 ml cyclohexane (K/benzophenone), 16 ml TMEDA (Na) and 60 ml NBuLi. The mixture was stirred at  $60^\circ C$  for 12 hours followed by five washings with cyclohexane and three washings



in tetrahydrofuran (Na/benzophenone). Following this, 60 ml of THF was added and trimethyltinchloride slowly added, under argon. The bright red lithiated beads slowly turned pink and then off white as the tin compound was added. A total of 3.27 g of trimethyltinchloride was used. The beads were allowed to stir 3 days to insure complete reaction. The beads were then washed with THF and vacuumed dry overnight. Analysis (Galbraith Laboratories) 6.65% Sn (.56 mmole/gram beads). The beads were stored in a dry box and placed in the reaction tube under argon for each separate catalyst preparation.

#### Preparation of a Metathesis Catalyst From Polystyrene Trimethyltin and Tungsten Hexachloride

Inside the dry box, 1.5 g of the polystyrene trimethyltin beads prepared above were placed in a Schlenk tube with .04 g (.1 mmole)  $WCl_6$ . The tube was sealed under argon and removed from the dry box. 20 ml  $Cl_2C=CCl$  was added and the mixture stirred with warming. After two hours, the beads were carefully washed and transferred under argon to the reaction column.

#### Set Up and Analysis of a Constant Flow System

The reaction column consisted of a side arm round bottom flask topped by a 10 inch tube which was indented slightly at about the middle to support the glass wool

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96 10  
100 10

pad and catalyst beads. This was topped by an "airless-ware" addition funnel which allowed the slow addition of the dilute olefin. This was topped by a flo-control stopper and an argon bubbler. The column was set up with argon flowing through while the beads were prepared. The beads were transferred to the column under argon and the reaction begun by dripping in the dilute olefin. The liquid phase was sampled from the round bottom flask through the side arm which was stoppered with a rubber septum. The results of a column using 250 ml  $\text{Cl}_2\text{C}=\text{CCl}$ /5 ml 1,7 octadiene are shown in Table 18. A heating table wrapped around the reaction column allowed the temperature to be controlled.

Analysis of Gaseous Products in the Formation of the Polymer Supported Catalyst and Analysis of Conversion in the Metathesis of 1,7 Octadiene

In the dry box 1.24 g polystyrene trimethyltin beads (.476 mmoles/g) was placed in a Schlenk tube with .07 g  $\text{WCl}_6$ . The tube was sealed and removed from the dry box. 10 ml  $\text{Cl}_2=\text{C}$  was added and the mixture stirred for 2 hours. A propane std was added (2 ml, .089 mmole) and the methane was compared to this standard on an FID gas chromatograph. Peak heights were corrected for the influence of molecular weight. The results are shown in Table 19.

Following the above analysis, 2 ml of 1,7 octadiene was added and the reaction of the liquid phase analyzed



on a gas chromatograph. The results are presented in Table 19.



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## REFERENCES

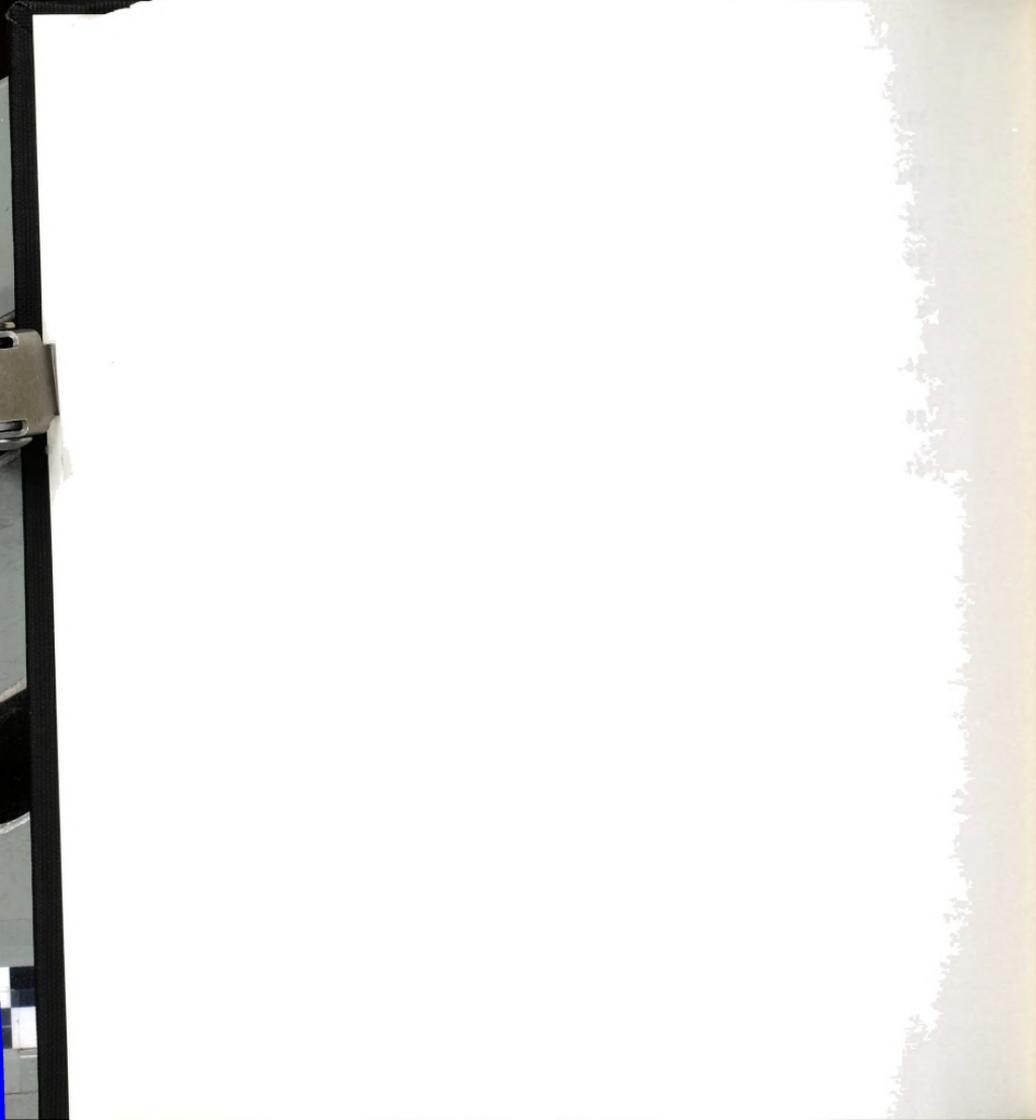
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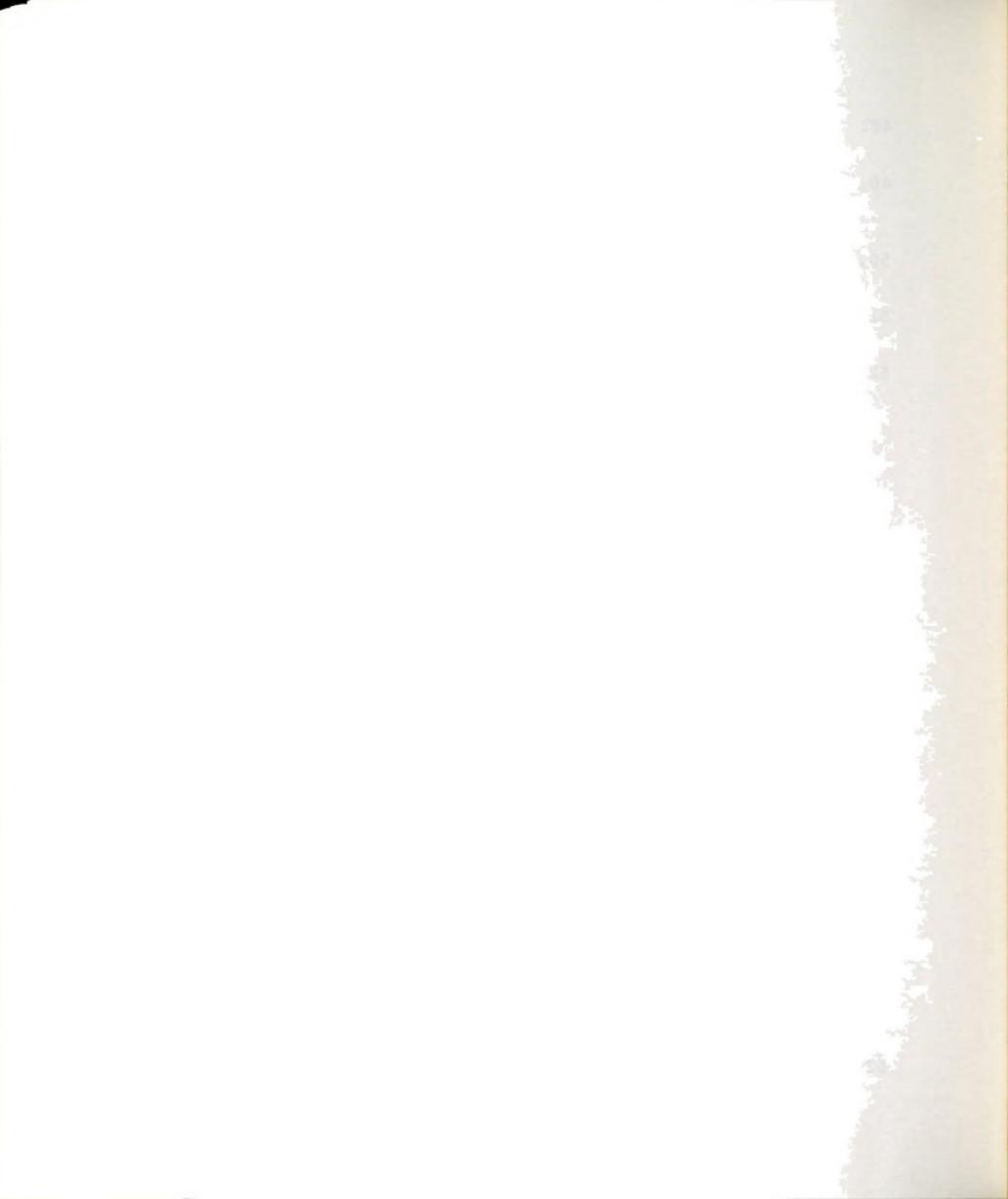
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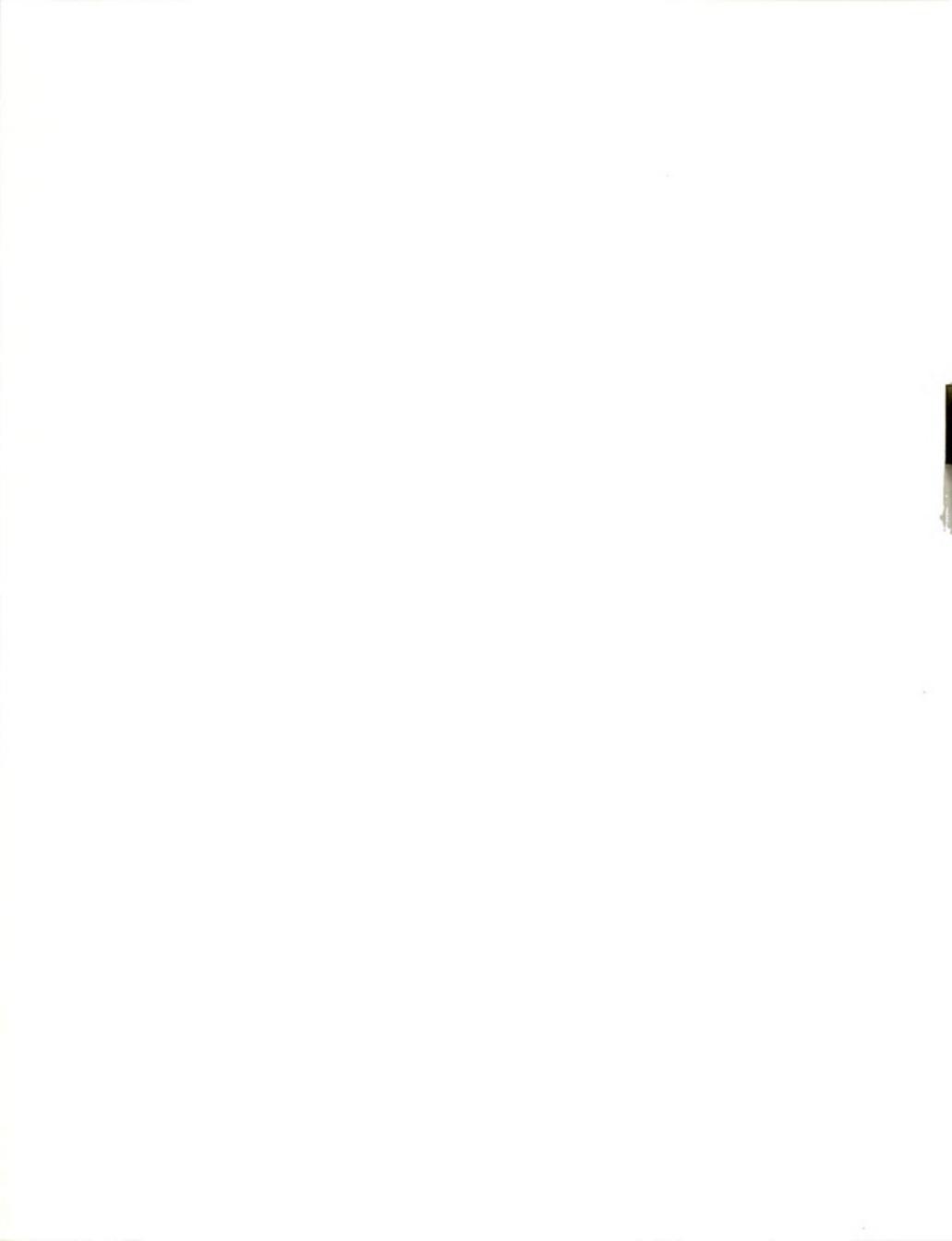


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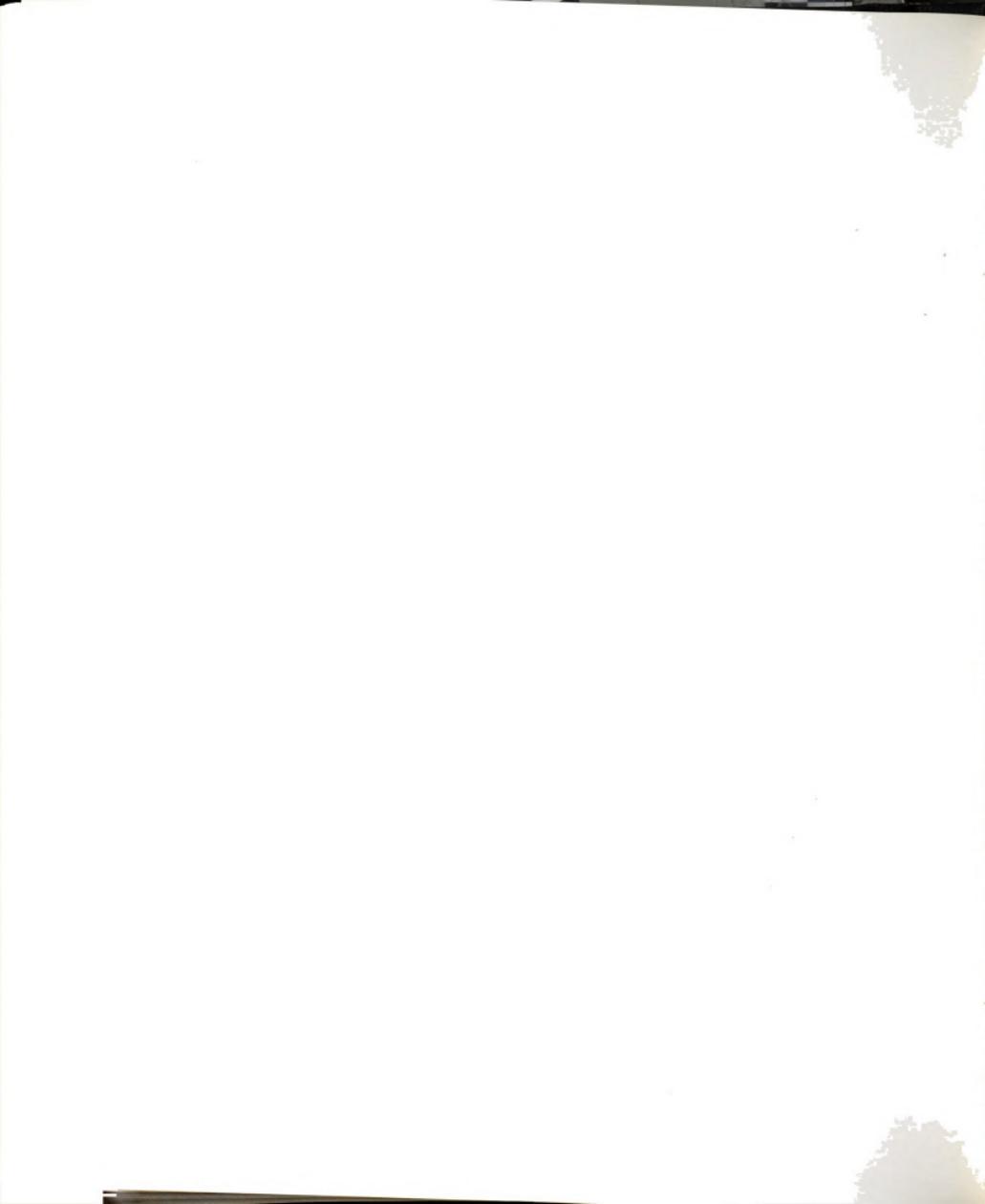


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