Selectivity Aspects in Cross Metathesis Reactions

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ABSTRACT

When certain catalysts that display a low apparent metathesis activity on terminal olefins are employed on mixtures of terminal and internal olefins, they lead to a selective formation of cross metathesis products. Critical experimentation using deuterated 1-pentene reveals that terminal olefins prefer to scramble "head-to-tail." A study of the macrocyclics distribution produced at various conversions during 1,5-cyclooctadiene polymerization suggests that these are being formed exclusively via an intramolecular transalkylidenation. The significance of the two sets of results is discussed in terms of two basic mechanistic schemes.

INTRODUCTION

Molecular weight regulation in ring-opening polymerization of cyclo-olefins is accomplished by the introduction of controlled amounts of

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*Contribution #535.

acyclic olefins [1-3]. The cross metathesis of the acyclic olefin with the high molecular weight chain results in a net scission of the poly-alkenamer chain:

$$(1)$$
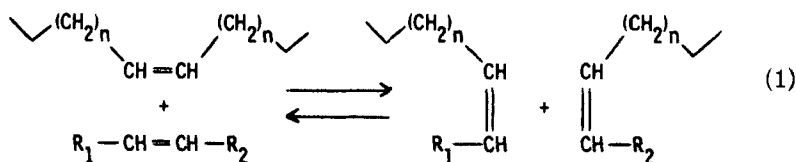
Thus the alkylidene moieties of the acyclic olefins [$R_1 CH=$] and [$R_2 CH=$] end up as chain ends. It can be easily shown that at extremely high acyclic/cyclic olefin ratios the main reaction products will be homologous series of low molecular weight polyenes.

Gunther et al. [2] compared the chain scission efficiency of terminal vs internal olefins in cyclopentene polymerization under identical reaction conditions. They concluded that 1-butene is considerably more efficient than either cis- or trans-2-butene in lowering the molecular weight of polypentenamer; suggesting a higher affinity of terminal than internal olefins to cross metathesis with vinylene double bonds. Herisson and Chauvin [4] studied the distribution of polyene reaction products produced by the cross metathesis of 2-pentene and cyclopentene by employing $WOCl_4/Sn(C_4 H_9)_4$ or $WOCl_4/(C_2 H_5)_2 AlCl$ catalytic systems. The cross metathesis of cyclopentene with 2-pentene provides three homologous series (symmetric/unsymmetric/symmetric) of polyenes:

$$(2)$$
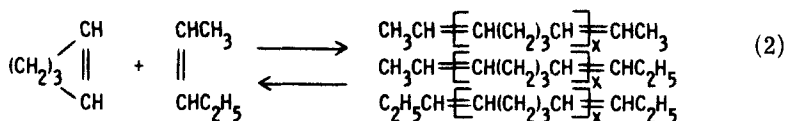
If the controlling factor of the process is primarily entropy and the reaction is carried to equilibrium, one expects a molar distribution of 1/2/1 between the respective symmetric/unsymmetric/symmetric series. Indeed, Herisson and Chauvin observed approximately a 1:2:1 distribution for the respective homologous series.

Several three-component metathesis catalysts, prepared by combining WCl_6 with an alcohol and further reacting with an organoaluminum

halide, are known to be sluggish toward the self-metathesis of terminal olefins [5]. For example, the catalyst combination $C_2H_5AlCl_2/WCl_6/C_2H_5OH$ (Al/W/O molar ratio 4/1/1), when employed at normal levels of olefin/W ratio of 5,000 to 10,000, exhibit very little metathesis of 1-pentene; about 1.0 mole % of the respective ethylene and 4-octene is produced. The lack of apparent metathesis activity of terminal olefins could not be rationalized on grounds of steric hindrance that prevents accommodation of the terminal olefin within the coordination sphere of the metal. It is a well-established fact that the steric requirements of terminal olefins are less than those of internal olefins. Further, in view of Gunther's results, one could not invoke electronic considerations to rationalize the lack of self-metathesis of terminal olefins. Gunther's results obtained with $R_2AlCl/WCl_6/ClC_2H_4OH$ catalyst point to the fact that terminal olefins are more reactive than internal olefins in cross metathesis reactions with a —CH=CH— type of unsaturation.

To resolve this apparent dilemma, an extensive study of the cross metathesis reactions of 1-pentene with 2-pentene and 1-pentene with cyclopentene was conducted. The results demonstrate that certain metathesis catalysts exhibit a considerable degree of selectivity in rendering a products mixture which is not dictated by a random scrambling of alkylidene moieties. The observed selectivity in the metathesis of terminal with internal olefins is accountable if one assumes a higher affinity of terminal olefins toward the catalyst and a specific geometry of the olefinic substrates on the catalyst site.

The formation of low molecular weight oligomers during cycloolefin polymerization has been reported [6]. Three basic features have been established:

1. The oligomers are macrocyclic.
2. The population of macrocyclics is controlled primarily by the double bond frequency along the polymeric chain.
3. The oligomeric macrocyclics and their corresponding high molecular weight polyalkenamer are interconvertible.

Hence 1,5-cyclooctadiene has been shown to yield two series of macrocyclics; one which contains "whole" multiples of the monomer $(C_8H_{12})_n$ and a second consists of the "sesqui"-oligomers $(C_8H_{12})_n-C_4H_6$, where $n \geq 2$.

By determining quantitatively the relative occurrence of "sesqui"- and "whole" oligomers at various conversions, it was possible to elucidate a pathway by which the macrocyclics are being formed.

The results reported in the present paper are accountable by either mechanism proposed heretofore. Two basic schemes for the trans-

alkylidenation step have been advanced. One requires the initial for-
mation of a bisolefin-metal entity, bearing two olefinic ligands in a
cis configuration about the metal:

$$
\begin{array}{c}
\text{M} \\
\diagup \diagdown \\
\text{R--CH} \diagup \quad \diagdown \text{CH--R} \\
\text{||} \diagup \qquad \diagdown \text{||} \\
\text{R--CH} \qquad \text{CH--R}
\end{array}
\qquad (3)
$$
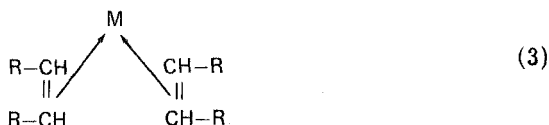
Several views regarding the nature of the electronic transformation
occurring within the coordination sphere of the metal, which provide
the actual alkylidene scrambling, have been proposed, e.g., quasi-
cyclobutane [7, 8], tetramethylene-metal complex [9], and metallocycle
[10]. Recently, a carbene-type mechanism was proposed [4, 11, 12]
that does not necessarily require the initial formation of a bisolefin-
metal complex (Eq. 3).

EXPERIMENTAL

Materials

Benzene solvent (reagent grade) was dried by passing over silica
gel and alumina prior to use. Cyclohexane (reagent grade ACS, MCB)
was distilled over CaH_2 and kept under a nitrogen atmosphere. Tung-
sten hexachloride (Shieldalloy Inc.) was used without prior purification
as were the catalytic modifiers: absolute ethanol (Gold Shield), 2,2,2-
trichloroethanol, and 2-chloroethanol (Aldrich Chemical Co.). Cyclo-
pentene (Arapahoe), 1-pentene (Phillips Pure Grade), and cis-2-pentene
(Phillips Technical Grade) were purified by distillation and dried by
passing over activated silica gel and alumina. 1-Pentene-d_{10} (Merck
Sharp & Dohme of Canada Ltd., 99% isotopic purity) was used without
prior purification. 1,5-Cyclooctadiene (Columbian Carbon) was purified
by distillation over sodium.

Analytical Procedures

Analyses by gas-liquid chromatography were performed on an F&M
810 Model Gas Chromatograph, employing either a 20-ft silicone gum
Hi Pak column (Hewlett Packard Co), programmed from 50 to 300°C at

10°C/min, or a 10-ft carborane-siloxane column (Analabs Inc.), pro-
grammed from 70 to 350°C at 10°C/min. Additional gas chroma-
tography was performed on a Varian Aerograph Model 1200 employing
a 200-ft squalene-coated capillary column at 27° C. Mass spectromet-
ric analyses were conducted on a low resolution CEC 21-103 mass
spectrometer.

Preparation of Catalyst Solutions

The 0.05 $\underline{M}$ WCl_6 solutions were prepared by dissolving 1.0 g WCl_6
in 50 ml of the appropriate solvent. The specified amounts of alcoholic
modifiers were added to the tungsten solutions and allowed to react at
room temperature for a minimum period of 30 min prior to use. (WCl_6/
ROH molar ratios of 1/1 and 1/2 were employed.) Ethylaluminum di-
chloride (EADC) and diethylaluminum chloride (DEAC) (Texas Alkyls)
were diluted in the appropriate solvent to form 0.2 $\underline{M}$ solutions.

Metathesis of 1-Pentene with cis-2-Pentene

A mixture consisting of 10 ml of each olefin (91.3 mmoles 1-pentene
and 94.1 mmoles cis-2-pentene) was prepared in a 2-oz bottle, equipped
with a self-sealing gasket and Teflon liner, in the absence of diluent.
Catalyst was introduced by syringe, 0.02 mmole of $WCl_6/2$ $ClCH_2CH_2OH$
in benzene followed by 0.04 mmole of DEAC in benzene, and the prog-
ress of the reaction was monitored by gas-liquid chromatography.

Metathesis of 1-Pentene with Cyclopentene

In a typical experiment the reactants were passed under a nitrogen
atmosphere over a silica gel/alumina column and collected in a 2-oz
bottle equipped with a self-sealing gasket and Teflon liner. The bottles
were sparged with nitrogen prior to the addition of catalyst. The tung-
sten component (presparged) followed by the aluminum cocatalyst were
injected into the solution with hypodermic syringes. The reactions were
shortstopped at the appropriate time by the addition of 0.1 ml methanol.
In the first series, experiments were conducted at 0 and 25°C using
an acyclic/cyclic olefin ratio of 2.4/1 at neat conditions (no solvent
added except catalyst carrier) and employing an olefin/W ratio of
3800/1. Catalyst: $EADC/WCl_6/Cl_3CCH_2OH$ (Al/W/O = 2/1/2). The
reactions were terminated after various times. In a second series,
experiments were conducted at 0 and 25°C employing a similar catalyst

combination as above, using an acyclic/cyclic olefin ratio of 0.77/1
in the presence of benzene diluent (50%) and an olefin/W ratio of
2100/1. In the third series, conducted at 0 and 25°C, a $EADC/WCl_6/$
$ClCH_2CH_2OH$ catalyst system was employed (Al/W/O = 2/1/2) in
the presence of benzene diluent (50%) at an acyclic/cyclic olefin ratio
of 4.7/1, and an olefin/W ratio of 3000/1. In the fourth series, the
effect of reaction time on conversions at varied temperature was
studied employing $DEAC/WCl_6/ClCH_2CH_2OH$ catalyst (Al/W/O =
2/1/2) with other variables maintained as in the third series.

Metathesis of 1-Pentene-d_{10} with 1-Pentene

A sample vial containing 1.0 g of 1-pentene-d_{10} was cooled in
liquid nitrogen, cracked open, and 5.0 ml of freshly distilled 1-
pentene was syringed into the vial. The contents were then trans-
ferred to a flask containing 45 ml of freshly distilled cyclohexane.
The vial was rinsed a second time with 5.0 ml of 1-pentene which
was also transferred to the cyclohexane solution.

Purification of the premix solution was achieved by passing
through an alumina/silica gel column, and finally diluted to a total of
125 ml. The column-passed solution was stored in the cold under
nitrogen.

Two 15-ml samples were transferred to 2-oz vials and used for
this study. Into one of the vials catalyst solutions, 0.0075 mmoles
of $WCl_6/CH_3CH_2OH(1/1)$ in cyclohexane followed by 0.02 mmoles of
EADC in cyclohexane were added, and after 10 min it was quenched
with 0.1 ml of isopropyl alcohol. The second vial containing unre-
acted material was used as a standard solution.

The samples were analyzed for composition on a capillary gas-
liquid chromatographic column and the mass spectrometric samples
were obtained via preparative gas chromatography using a 10-ft,
0.5 in. diameter SGR column on an F&M 810 instrument.

Metathesis of 1,5-Cyclooctadiene to Form
Macrocyclics

A mixture consisting of 1,5-cyclooctadiene (11.4%), n-eicosane
(n- $C_{20}H_{42}$, 0.13%), antioxidant (2,6-di-t-butyl-p-cresol), and benzene
was column passed under nitrogen over silica gel/alumina/silica gel.
Samples were collected as 50 ml aliquots in 2-oz bottles, sealed and
capped as described earlier, and were sparged with nitrogen prior
to catalyst addition. First the tungsten component, 0.02 mmole of

WCl$_6$/CH$_3$CH$_2$OH in benzene, was introduced followed by the aluminum cocatalyst, 0.04 mmole of EADC in benzene (Al/W/O = 2/1/1). At appropriate time intervals the polymerization was shortstopped by the addition of 0.15 ml of CH$_3$OH. Each cement was then quantitatively analyzed by gas–liquid chromatography for oligomer composition.

<div align="center">RESULTS AND DISCUSSION</div>

Metathesis of 1-Pentene with cis-2-Pentene

Table 1 presents the relative distribution of the various cross metathesis products after the reaction proceeded to a point where ~25% of the original 2-pentene has been consumed (50% from theoretical equilibrium).

The self-metathesis of either olefin leads to symmetric products; ethylene and 4-octene from 1-pentene, and 2-butene and 3-hexene from 2-pentene. The products from the cross metathesis are unsymmetric. Depending on the alignment of the olefin substrates on the catalyst site, one can obtain either propylene and 3-heptene, or 1-butene and 2-hexene. The significance of the results of Table 1 is in the fact that, although 1-pentene undergoes little self-metathesis, it readily reacts with 2-pentene to produce the cross reaction unsymmetric products. Furthermore, the data suggest that the affinity of 2-pentene to cross metathesize with 1-pentene is eight times greater than its affinity to self-metathesize.

TABLE 1. Cross Metathesis of 1-Pentene and cis-2-Pentene

<div align="center">C$_3$H$_7$CH=CH$_2$ + C$_2$H$_5$CH=CHCH$_3$</div>

Relative concentrations[a]			
Symmetric		Unsymmetric	
CH$_2$=CH$_2$	1	CH$_3$CH=CH$_2$	4
C$_3$H$_7$CH=CHC$_3$H$_7$	1	C$_2$H$_5$CH=CHC$_3$H$_7$	4
CH$_3$CH=CHCH$_3$	2	C$_2$H$_5$CH=CH$_2$	12
C$_2$H$_5$CH=CHC$_2$H$_5$	2	CH$_3$CH=CHC$_3$H$_7$	12

[a]Values at 50% from theoretical equilibrium.

Metathesis of 1-Pentene with Cyclopentene

Three series of polyenes can be produced by the cross metathesis
of 1-pentene and cyclopentene:

$$C_3H_7CH \quad CH \atop \underset{CH_2}{\overset{\parallel}{}} + \underset{CH}{\overset{\parallel}{}} \diagdown (CH_2)_3 \underset{\longleftarrow}{\overset{\longrightarrow}{}} \begin{array}{l} CH_2 = CH(CH_2)_3CH = CH_2 \quad \text{Symmetric} \\ CH_2 = CH(CH_2)_3CH \frac{}{x} = CHC_3H_7 \quad \text{Unsymmetric} \\ C_3H_7CH = CH(CH_2)_3CH \frac{}{x} = CHC_3H_7 \quad \text{Symmetric} \end{array} \qquad (4)$$
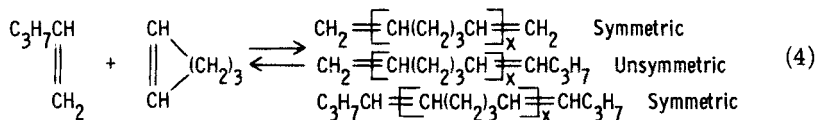
The unsymmetric series have carbon numbers C_{10}, C_{15}, C_{20}, C_{25}, etc.
while the two symmetric series have the carbon numbers C_7, C_{12}, C_{17},
C_{22}, etc. and C_{13}, C_{18}, C_{23}, C_{27}, etc., respectively. Figure 1 illustrates
a typical chromatogram of the 1-pentene + cyclopentene reaction prod-
ucts. The main peaks are attributed to the unsymmetric homologous
series $CH_2 = CH(CH_2)_3CH \frac{}{x} CHC_3H_7$. Integration of the total minor
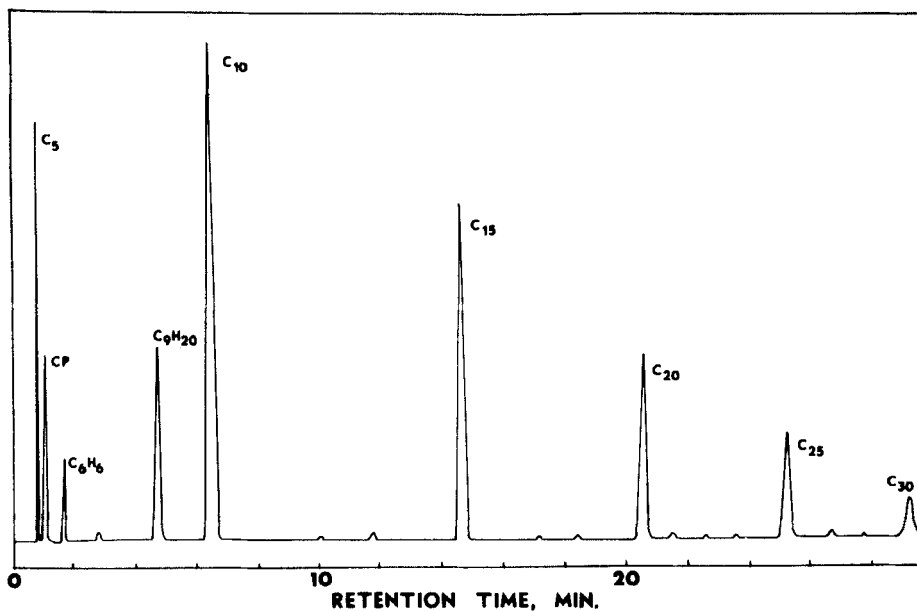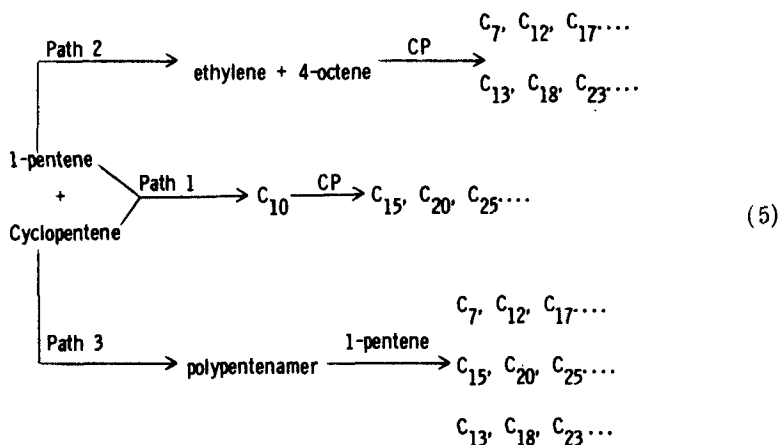

FIG. 1. Gas chromatogram of polyenes obtained in the [1-pentene
+ cyclopentene] cross metathesis.

peaks vs the major C_{10}, C_{15}, C_{20} components indicates the symmetric polyenes constitute less than 5% of the total product.

Table 2 summarizes the results obtained in the cross metathesis of 1-pentene with cyclopentene under various reaction conditions. The data were treated in a manner to account for the conversion of cyclopentene into the various C_{10}, C_{15}, C_{20}, and C_{25} unsymmetric polyenes vs its conversion to other products. In all cases the reaction was not allowed to proceed to maximum conversion in order to minimize loss of reactants to side products. The conversion vs time curves, illustrated in Figs. 2 and 3, indicate a leveling-off trend in the yield of the desired polyenes after 60 mins, except in the case where the reaction was carried out in benzene diluent using $EADC/WCl_6/CCl_3CH_2OH$ catalyst at 0°C (see Table 2, series 2). The best overall conversion and selectivity to unsymmetric polyenes was experienced in the experiment represented in Table 2, series 2 (0°).

Three reaction pathways for the formation of the polyenes are to be considered. Schematically, these are:

$$\begin{array}{l}
\text{Path 2} \longrightarrow \text{ethylene} + \text{4-octene} \xrightarrow{\ CP\ } \begin{array}{l} C_7,\ C_{12},\ C_{17}\cdots \\ C_{13},\ C_{18},\ C_{23}\cdots \end{array} \\[1em]
\begin{array}{l} \text{1-pentene} \\ + \\ \text{Cyclopentene} \end{array} \xrightarrow{\ \text{Path 1}\ } C_{10} \xrightarrow{\ CP\ } C_{15},\ C_{20},\ C_{25}\cdots \\[1em]
\text{Path 3} \longrightarrow \text{polypentenamer} \xrightarrow{\ \text{1-pentene}\ } \begin{array}{l} C_7,\ C_{12},\ C_{17}\cdots \\ C_{15},\ C_{20},\ C_{25}\cdots \\ C_{13},\ C_{18},\ C_{23}\cdots \end{array}
\end{array} \tag{5}$$

Path 1 assumes the selective cross metathesis of 1-pentene with cyclopentene followed by further incorporation of cyclopentene units. If this process is dominating unsymmetric polyenes will be formed preferentially. Path 2 assumed a selective self-metathesis of 1-pentene forming ethylene and 4-octene. Each of these symmetric olefins can incorporate cyclopentene units, thus resulting in the two symmetric polyene series. Path 3 assumes the initial self-metathesis of cyclopentene to a high molecular weight polypentenamer, followed by

TABLE 2. Conversion of Cyclopentene into Polyenes (%)

Series (°C)	Unreacted cyclopentene	Cyclopentene in unsymmetric polyenes: C_{10}, C_{15}, C_{20}, C_{25}	Cyclopentene in other products	Total % selectivity
1[a] (0°)	67	26.6	6.4	80.6
1 (25°)	72	21.2	6.8	75.7
2[b] (0°)	21	67.5	11.5	85.4
2 (25°)	67	18.0	15.0	54.5
3[c] (0°)	70	11.1	18.9	36.6
3 (25°)	58	22.9	19.1	54.7
4[d] (0°)	64	12.3	23.7	34.1
4 (25°)	54	27.7	18.3	60.5

[a]Series 1: neat; 1-pentene/cyclopentene = 2.4/1; EADC/WCl$_6$/CCl$_3$CH$_2$OH; reaction 30 min.
[b]Series 2: 50% benzene; 1-pentene/cyclopentene = 0.77/1; EADC/WCl$_6$/CCl$_3$CH$_2$OH; reaction 30 min.
[c]Series 3: 50% benzene; 1-pentene/cyclopentene = 4.7/1; EADC/WCl$_6$/ClCH$_2$CH$_2$OH; reaction 60 min.
[d]Series 4: 50% benzene; 1-pentene/cyclopentene = 4.7/1; DEAC/WCl$_6$/ClCH$_2$CH$_2$CH; reaction 60 min.
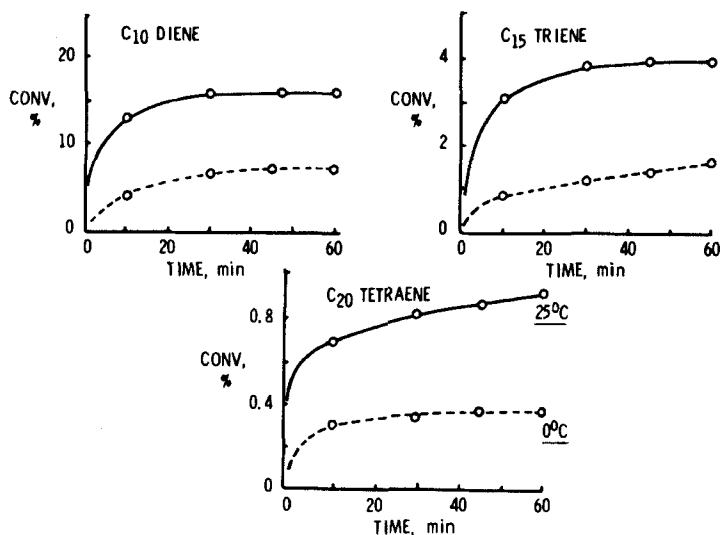
FIG. 2. Molar conversion of polyenes vs time in the [1-pentene + cyclopentene] metathesis. Data related to Table 2, series 4.
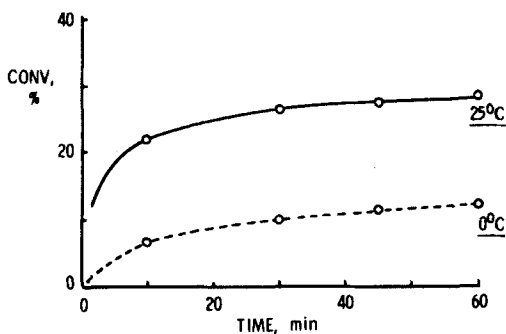
FIG. 3. Conversion of cyclopentene to unsymmetric polyenes: C_{10}, C_{15}, C_{20}, and C_{25} vs time. Data related to Table 2, series 4.

random cross metathesis scissions with 1-pentene. In the latter case one should observe a 1/2/1 molar distribution of the symmetric/unsymmetric/symmetric polyenes. The preferential formation of the unsymmetric polyene series indicates that, under the prevailing conditions employed herein, Path 1 is dominating.

The observations described heretofore are summarized as follows:

A catalyst that displays a high metathesis activity for internal ole-fins and an apparent poor activity for terminal olefins, when em-ployed on a mixture of internal plus terminal olefinic reactants, leads to a selective formation of the cross metathesis products.

A possible hypothesis for this behavior may be that terminal ole-fins, in fact, are more prone to metathesis than internal olefins, and the reason why the products of their reaction are not being observed is that they prefer to metathesize "head-to-tail," yielding back the starting material:

$$
\begin{array}{c}
C_3H_7CH=CH_2 \\
+ \\
CH_2=CHC_3H_7
\end{array}
\rightleftharpoons
\begin{array}{c}
C_3H_7CH \\
\| \\
CH_2
\end{array}
+
\begin{array}{c}
CH_2 \\
\| \\
CHC_3H_7
\end{array}
\qquad (6)
$$
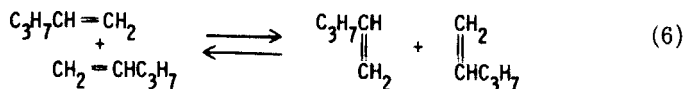
When terminal and internal olefins are mixed, the terminal olefins "flood" the catalyst sites, inhibiting the self-metathesis of the internal olefins. Hence terminal olefins keep "spinning their wheels" until an internal olefin manages to enter the complex, which after metathesis will yield an unsymmetric cross product. This hypothesis was con-firmed experimentally.

Metathesis of 1-Pentene-d_{10} and 1-Pentene

A 90/10 mixture of 1-pentene (m/e = 70) and 1-pentene-d_{10} (m/e = 80) was exposed to the EADC/WCl$_6$/C$_2$H$_5$OH catalyst and analyzed by gas chromatography/mass spectrometry. The results of this experi-ment are presented in Table 3.

TABLE 3. Gas Chromatography/Mass Spectroscopy of 1-Pentene and 1-Pentene-d_{10} Metathesis[a]

m/e	T_0 (min)	T_{10} (min)	Equilibrium (calc)
80	0.1074	0.0395	0.0115
78	–	0.0686	0.0959
72	–	0.0771	0.0959
70	0.8926	0.8148	0.7967

[a]Traces of C_8H_{16}, $C_8H_8D_8$, and C_8D_{16} only.

Assuming that 1-pentene and 1-pentene-d_{10} experience a "head-to-tail" scrambling exclusively, forming $C_3D_7 CD=CH_2$ (m/e = 78) and $C_3H_7 CH=CD_2$ (m/e = 72), it is possible to calculate the theoretical equilibrium concentrations of the four respective 1-pentenes. The data in Table 3 indicate that after a 10-min reaction time the original mixture underwent about 70% of the theoretical scrambling with only trace amounts of the various possible 4-octenes (C_8H_{16}, $C_8H_8D_8$, and C_8D_{16}). (Monitoring of ethylene in this experiment was not attempted due to the interference posed by N_2, m/e = 28.)

Macrocyclics Formation from 1,5-Cyclooctadiene

As stated earlier, the population of macrocyclics in a given cyclo-olefin polymerization system depends on the frequency of occurrence of double bonds along the polymeric chain.

The relative concentration of macrocyclics obtained during the polymerization of 1,5-cyclooctadiene is presented in Table 4. The "whole" oligomers are multiples of the starting monomer—C_{16}, C_{24}, C_{32}, . . ., etc; the "sesqui"-oligomers are members of the C_{12}, C_{20}, C_{28}, . . ., etc. homologous series. The results of Table 4 indicate that the C_{12}/C_{16}, C_{20}/C_{16}, C_{24}/C_{16}, C_{28}/C_{16}, and C_{32}/C_{16} ratios are essentially constant throughout the polymerization. (The only variant is the C_{12}/C_{16} value at 98.5% conversion, which can be rationalized by taking into account changes in the thermodynamic equilibrium value of the C_{12} component, 1,5,9-cyclododecatriene, due to cis/trans isomerization of its double bonds.) These results are quite significant. The
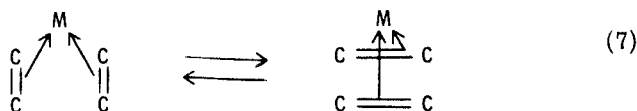
TABLE 4. Mole Ratio of Cyclic Oligomers and Sesquioligomers to Cyclohexadecadiene (C_{16}/C_{16} = 1.0)

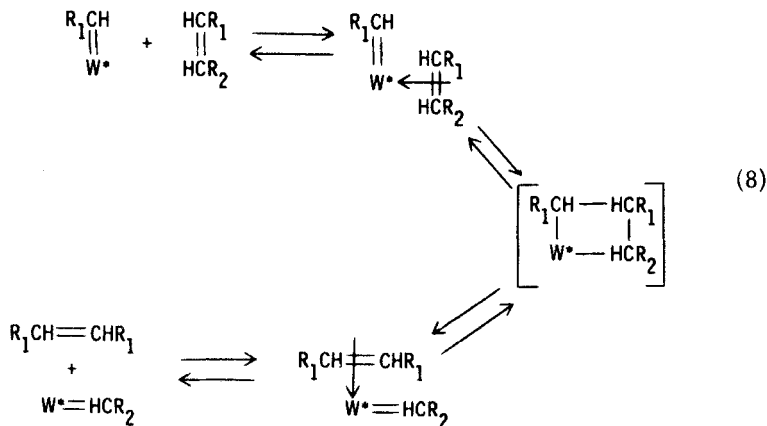| Conversion (%)	C_{12}/C_{16}	C_{20}/C_{16}	C_{24}/C_{16}	C_{28}/C_{16}	C_{32}/C_{16}
1.3	.47	.65	–	–	–
3.2	.51	.63	.32	.18	–
7.9	.55	.63	.27	.24	–
9.5	.48	.62	.28	.25	.10
19.5	.52	.59	.31	.27	.10
36.3	.52	.56	.32	.18	.13
51.1	.51	.58	.33	.26	.13
61.2	.53	.54	.30	.19	.10
98.5	.93	.65	.27	.23	.14

constant ratios of "sesqui"- vs "whole" oligomers throughout the polym-
erization strongly suggest that these are being formed exclusively via
an intramolecular metathesis occurring within a high molecular weight
macromolecule, and not via a condensation of two smaller rings. This
finding is highly compatible with the recently proposed views regard-
ing the mechanism of olefin metathesis involving carbene-metal inter-
mediates [4, 11, 12], but it does not exclude the "traditional" mech-
anisms that require the initial formation of bisolefin-metal complex.

MECHANISTIC IMPLICATIONS

Two basic views regarding the mechanism of olefin metathesis have
been advanced. The quasicyclobutane proposal, first suggested by
Bradshaw [7] and later subscribed to by Calderon and co-workers [8,
13], as well as Pettit's [9] tetramethylene-metal complex and Grubbs
[10] five-membered ring metallocycle, are all transition states that
attempt to describe the rearrangement:

$$
\begin{array}{ccc}
\underset{\substack{\| \\ C}}{C} \overset{M}{\diagup\diagdown} \underset{\substack{\| \\ C}}{C} & \rightleftharpoons & \underset{C === C}{C \overset{M}{===} C}
\end{array}
\tag{7}
$$

They all assume a priori the existence of a bisolefin-metal complex.
Lately, Herisson and Chauvin [4], Dolgoplosk and co-workers [12], and
Casey [11] have advanced the carbene-to-metallocycle scheme which
does not necessarily require the initial formation of a bisolefin-metal
complex. The mechanism is illustrated by:

$$
\tag{8}
$$

$$
\begin{array}{c}
\underset{\substack{\| \\ W\bullet}}{R_1CH} + \underset{\substack{\| \\ HCR_2}}{HCR_1} \;\rightleftharpoons\; \underset{\substack{\| \\ W\bullet\leftarrow\|\;1 \\ HCR_2}}{R_1CH}\;HCR_1 \\[2em]
\left[\begin{array}{cc} R_1CH - HCR_1 \\ | \quad\quad | \\ W\bullet - HCR_2 \end{array}\right] \\[2em]
\begin{array}{c} R_1CH = CHR_1 \\ + \\ W\bullet = HCR_2 \end{array} \;\rightleftharpoons\; \begin{array}{c} R_1CH \!\!\mp\!\! CHR_1 \\ \downarrow \\ W\bullet = HCR_2 \end{array}
\end{array}
$$

An incoming olefin undergoes π-coordination with the active metal
site (W*) which possesses a bound carbene moiety. A carbene inter-
change between the metal and the olefin is accomplished by rearrange-
ment of the complex, forming a four-membered ring metallocycle
along the reaction coordinate. Finally, the newly formed olefin mole-
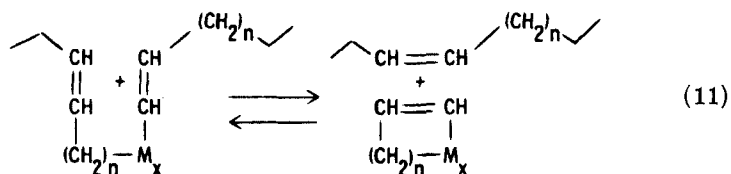cule dissociates away from the active site.

When applied to cycloolefins, the carbene-to-metallocycle mech-
anism does not postulate a polymerization via a macrocyclization
pathway as is the case for the concerted mechanism (Eq. 7), rather it
is consistent with a ring-opening polymerization by chain-end growth:
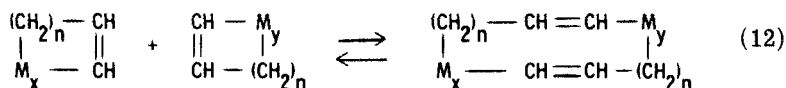
$$\text{(scheme)} \tag{9}$$

$$\text{(scheme, etc...)}$$
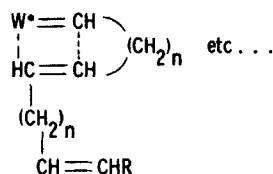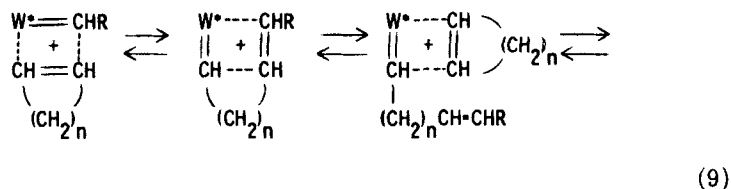
The formation of macrocyclic oligomers is accomplished by the
intramolecular "back-biting" transalkylidenation of the growing car-
bene-W chain end with any internal double bond on the same chain:
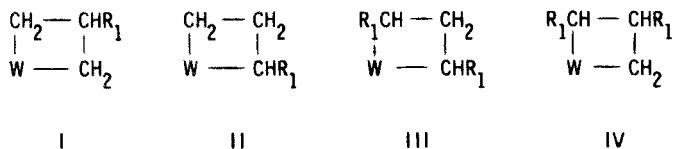
$$\text{(scheme)} \tag{10}$$
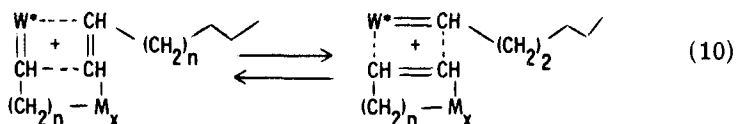
whereas in the concerted mechanism macrocyclic oligomers can be
formed either by a "pinching-off" or "condensation" processes as illus-
trated in Eqs. (11) and (12), respectively:

$$\text{(scheme)} \tag{11}$$

$$
\begin{array}{c}
\overset{(CH_2)_n}{\underset{M_x}{|}}\overset{\displaystyle CH}{\underset{\displaystyle CH}{\parallel}} \;+\; \overset{\displaystyle CH}{\underset{\displaystyle CH}{\parallel}}\overset{M_y}{\underset{(CH_2)_n}{|}} \;\rightleftharpoons\; \overset{(CH_2)_n}{\underset{M_x}{|}}\overset{\displaystyle CH=CH}{\underset{\displaystyle CH=CH}{}}\overset{M_y}{\underset{(CH_2)_n}{|}}
\end{array}
\qquad (12)
$$

The results of Table 4 are inconsistent with Eq. (12). If a given oligomer is being formed primarily by a bimolecular condensation of two smaller rings, one expects to find little or no "sesqui"-oligomers at the early stages of polymerization of 1,5-cyclooctadiene. The constant ratios of oligomers found throughout the polymerization suggest that they are being formed either via Eq. (10) or Eq. (11), depending on what mechanism one elects to apply. Both schemes require the formation of a high molecular weight polymer at the outset. Dolgoplosk [12] argued that the formation of high molecular weight polymer at the early stages of reaction serves as an indication that cycloolefin polymerization proceeds via chain-end growth. In a previous publication [13] it has been shown that a rapid increase in molecular weight is also accountable by a macrocyclization scheme, where growth may occur at any double bond along the chain.

To accommodate the observations related to the selectivity in cross metathesis reactions of terminal with internal olefins by the carbene-to-metallocycle reaction scheme, one must invoke preference to certain transition states over others. For example, to account for 1-pentene's tendency to generate itself upon metathesis, either I ≫ II or III ≫ IV:

$$
\begin{array}{cccc}
\overset{CH_2}{\underset{W}{|}}\overset{\displaystyle CHR_1}{\underset{\displaystyle CH_2}{|}} & \overset{CH_2}{\underset{W}{|}}\overset{\displaystyle CH_2}{\underset{\displaystyle CHR_1}{|}} & \overset{R_1CH}{\underset{W}{|}}\overset{\displaystyle CH_2}{\underset{\displaystyle CHR_1}{|}} & \overset{R_1CH}{\underset{W}{|}}\overset{\displaystyle CHR_1}{\underset{\displaystyle CH_2}{|}} \\[2ex]
\mathrm{I} & \mathrm{II} & \mathrm{III} & \mathrm{IV}
\end{array}
$$

If steric hindrance around the metal is the controlling factor, the most favored metallocycle transition state will be I, and III the least favored. Thus, in analogy with the "head-to-tail" configuration proposed earlier for 1-pentene metathesis by the concerted mechanism, one may suggest that metallocycle I is preferred over II for the carbene mechanism. This type of speculation can be further extended to account for the selectivity in cross products observed in the 1-pentene/2-pentene and 1-pentene/cyclopentene metathesis.

The carbene in a metal-carbene complex is viewed as a singlet carbene; that is, having a pair of electrons occupying one orbital of an

sp^2 set. The bonding nature in a carbene-metal complex is somewhat analogous to CO or olefin bonded to a metal. Two bonding elements are involved: 1) a forward donation of an electron pair from the occupied sp^2 of the $C_{carbene}$ to the metal, and 2) a back donation element from the metal into an empty p_z orbital of the $C_{carbene}$. As illustrated in Fig. 4, the metal, $C_{carbene}$, and the two substituents (R_1 and H) all lie on the same plane. On the other hand, the complexed olefin molecule (its cis configuration is arbitrary) is on a plane that bisects the carbene-metal plane on an adjacent coordination site of the metal. (The olefinic carbons are situated above and below the carbene-metal complexation plane.) In order to achieve a transformation to a four-membered ring metallocycle, the $C_{carbene}$ expands from an sp^2 to an sp^3 hybridization. In the process the carbene-to-metal bond transforms into a conventional σ-C—M bond, and the carbon assumes a tetrahedral configuration. Simultaneously, the π-bonded olefin undergoes a process analogous to Ziegler's cis-ligand insertion, resulting in one of the C=C carbons σ-bonded to the metal and the other to the original $C_{carbene}$. The intimate electronic transformations described above are accompanied by a set of steric manipulations (Fig. 4). The sp^2 to sp^3 expansion involves trigonal to tetrahedral change of configuration,
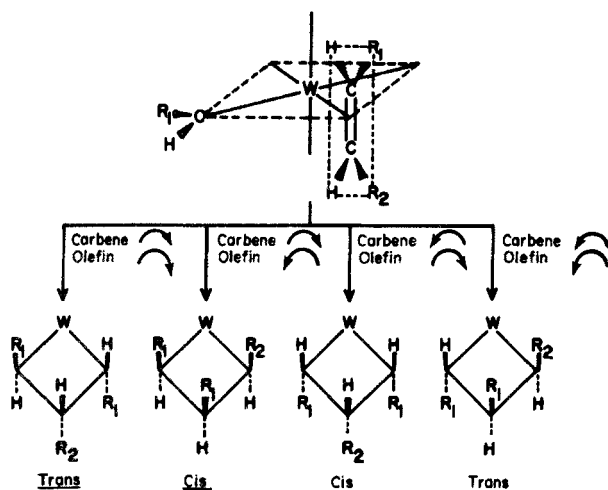

FIG. 4. Carbene-to-metallocycle mechanism; formation of various metathesis products by proper rotations of carbene and olefin substrates.

which requires either clockwise ($\frown$) or counterclockwise rotation ($\frown$) of the C$_{carbene}$ in relation to the C-W axis. Furthermore, to form the metallocycle, the complexed olefin must "slide" and rotate (clockwise or counterclockwise) to align the olefinic carbons with their respective bonding counteratoms.

To account for the ease of formation of all possible cis and trans $R_1CH=CHR_1$, $R_1CH=CHR_2$, and $R_2CH=CHR_2$ olefins from either cis or trans starting olefins, one ought to assume low stearic barriers for clockwise and counterclockwise rotations of the carbene and olefin substrates. For the specific configuration illustrated in Fig. 4, applying various clockwise and counterclockwise rotations of the respective substrates, metallocycle transition states leading to trans-$R_1CH=CHR_2$, cis-$R_1CH=CHR_1$, cis-$R_1CH=CHR_2$, and trans-$R_1CH=CHR_1$ are obtainable.

CONCLUSION

Selectivity aspects of cross metathesis reactions between terminal and internal olefins, as well as the reaction pathway for the formation of macrocyclics in cycloolefin metathesis, are compatible with concerted and nonconcerted mechanistic schemes. The nonconcerted carbene-to-metallocycle mechanism, recently proposed for olefin metathesis, involves a basic concept which is common to most transition metal catalyzed reactions; namely, the cis ligand insertion concept.

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