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Olefin Metathesis by Rhenium Carbonyl Halide–Alkylaluminum Halide Catalysts. Direct Evidence for a Coordinated Carbene Initiated Process

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Received December 23, 1975 AIC50913W

The $Re(CO)_5X/RAlCl_2$ system was found to be an effective, long-lived catalyst for the metathesis of terminal and internal olefins. Where X = Cl and R = C_2H_5, gas evolution studies and analysis of the minor components of the metathesis of 1,7-octadiene indicate that a coordinated propylidene is formed on Re by attack of ethyl on coordinated CO, followed by oxygen for hydrogen exchange. Investigation of the first-formed olefins in the metathesis of 1,7-octadiene and 4-octene indicates that propylidene is the initiating carbene in the reaction. The first-formed olefins in the metathesis of 1,7-octadiene were identified as 1-butene and 1,7-decadiene, while that of 4-octene was identified as 3-heptene. When CH_3AlCl_2 was used as the cocatalyst, the first-formed olefins were identified as propylene and 2-hexene, for the metathesis of 1,7-octadiene and 4-octene, respectively. This work provides direct evidence that the process of olefin metathesis is both initiated and propagated by coordinated carbenes.

Introduction

Whereas the large majority of homogeneous olefin metathesis catalysts are based on compounds of the group 6B metals, several rhenium complexes have been reported to be active in homogeneous systems. The $ReCl_5/(n\text{-}C_4H_9)_4Sn$ system is active at room temperature, but extended times (46 h) are required to reach equilibrium conversions.[1] Triphenylphosphine complexes of $ReCl_4$ and $ReOX_3$ (X = Cl, Br) are also active in homogeneous systems at room temperature or below.[2] Both catalysts require the synergistic use of alkylaluminum cocatalysts. The $ReCl_5/(C_2H_5)_3Al$ system is not active in metathesis by itself but becomes active in the presence of catalytic amounts of oxygen.[3] The system is relatively long-lived and is active at room temperature.

Among carbonyl derivatives of the group 7 metals, $Re_2(CO)_{10}$ has been reported to be active at high temperatures (160 °C) in the presence of alkylaluminum halides.[4]

Anionic complexes containing group 6B–7B metal–metal bonds of the type $A[(CO)_5M\text{–}M'(CO)_5]$ (where A is an alkali metal or tetraalkylammonium ion, M is Mo or W, and M′ is Mn or Re), are active with cocatalysts. The Re derivatives were found to be far more effective in promoting olefin metathesis than the corresponding Mn complexes.[5]

We have investigated the properties of group 7B pentacarbonyl halides and, particularly for Re, have found them to be not only very effective in promoting olefin metathesis reactions but also long-lived, as well. A preliminary communication on these systems has been published.[6]

Experimental Section

Starting Materials. Chlorobenzene, used as the solvent for all reactions, was purified by distillation; the first 15% of the distillate was discarded, and the remainder was collected over molecular sieves and stored under nitrogen. The olefins used in this work were purchased from either Aldrich Chemical Co. or Chemical Samples Co. and used as received.

Rhenium pentacarbonyl halides were prepared by methods analogous to those reported for $Mn(CO)_5X$[7] and were identified by comparing their infrared spectra with those reported by Abel et al.[8]

Ethylaluminum dichloride was purchased as a 25% solution in heptane from Texas Alkyls and transferred to 4-oz. bottles equipped with screw caps with self-sealing liners. These solutions were always sampled by needle and syringe, displacing the removed solution by an equal volume of dry nitrogen. Methylaluminum dichloride, a product of Texas Alkyls, was kindly supplied by Goodyear Research, Akron, Ohio, as a 20% solution in chlorobenzene, and sampled as described for the ethyl derivative.

A. General Metathesis Reactions. Conditions and Apparatus. All reactions were carried out under dry nitrogen in a dry, 100-ml, three-neck flask fitted with a nitrogen inlet, a condenser connected to an oil bubbler, and a septum. The reaction mixtures were magnetically stirred and heated by means of an oil bath. Where low-boiling components were used (such as propylene), a dry ice condenser was used.

Physical Methods and Identification of Products. For the analysis of products in the general metathesis reactions, a Hewlett-Packard 5750-B Research Gas Chromatography unit was used. This was equipped with a stainless steel column of dimensions 6 ft × $^1/_8$ in. which was packed with 10% VCW-98 on 80–100 mesh silica. Helium was employed as the carrier gas and the unit was equipped with a thermal conductivity detector.

The products were identified by comparing their retention times at two temperatures with those of authentic compounds. The percent yields of products were determined by integration of the peak areas with respect to bromobenzene, which was used as the internal standard. The thermal conductivity response ratios of bromobenzene to the olefins were determined for all olefins in separate experiments. Therefore,

Table I. Experimental Details of Catalyst Systems and Olefins

Olefin	Catalyst system, reaction conditions	Major products; yield
Propylene	$Re(CO)_5Cl/C_2H_5AlCl_2$, Re:Al = 1:8, 95 °C, 1.5 h	Ethylene + 2-butene; 20%
Isobutylene	$Re(CO)_5Cl/C_2H_5AlCl_2$, Re:Al = 1:8, 94 °C, 1.5 h	No reaction
Isoprene	$Re(CO)_5Cl/C_2H_5AlCl_2$, Re:Al = 1:4, 90 °C, 20 min	No metathesis products, 82% polymerization
cis-2-Pentene	$Re(CO)_5Cl/C_2H_5AlCl_2$, Re:Al = 1:8, 96 °C, 25 min	3-Hexene + 2-butene; 82%
trans-4-Nonene	$Re(CO)_5Cl/C_2H_5AlCl_2$, Re:Al = 1:8, 90 °C, 45 min	4-Octene + 5-decene; 50%
1,7-Octadiene	$Re(CO)_5Cl/C_2H_5AlCl_2$, Re:Al = 1:8, 90 °C, 20 min	Ethylene + cyclohexene; 96%
1-Hexene	$Re(CO)_5Cl/C_2H_5AlCl_2$, Re:Al = 1:8, 90 °C, 15 min	Ethylene + 5-decene; 67%
1-Hexene	$Re(CO)_5Cl/C_2H_5AlCl_2$, Re:Al = 1:2, 90 °C, 30 min	Ethylene + 5-decene; 60%
1-Hexene	$Re(CO)_5Cl/C_2H_5AlCl_2$, Re:Al = 1:1, 90 °C, 45 min	No reaction
1-Hexene	$Re(CO)_5Br/C_2H_5AlCl_2$, Re:Al = 1:4, 99 °C, 30 min	Ethylene + 5-decene; 60%
1-Hexene	$Re(CO)_5Cl/CH_3AlCl_2$, Re:Al = 1:4, 89 °C, 15 min	Ethylene + 5-decene; 16%, mostly polymerization

it was possible to determine the amount of olefin present when a known amount of bromobenzene was used.

The percent yields are expressed as molar percents. For example, 2 mol of 1-hexene would react to give 1 mol of ethylene and 1 mol of 5-decene. This is expressed as 100% yield. The theoretical equilibrium yield of metathesis where all reactants and products remain in solution is 50%; i.e., the reactant would be 50% consumed; each product would be expressed as 50% yield.

Metathesis of 1-Hexene. The metathesis reactions were all conducted in essentially the same manner; therefore, only the reaction of one of these, namely, 1-hexene, will be described in detail. Details of the metathesis of other olefins, catalysts, and cocatalysts are shown in Table I.

Into the flask were placed 10 ml (6.73 g, 80 mmol) of 1-hexene, 0.18 g (0.5 mmol) of $Re(CO)_5Cl$, 2.00 ml (19 mmol) of bromobenzene (internal standard), and 10 ml of chlorobenzene. The system was then flushed well with nitrogen, and the contents of the flask were heated to 90 °C. After the desired temperature was reached, 2.4 ml (4 mmol) of $C_2H_5AlCl_2$ was injected through the septum. Upon addition of ethylaluminum dichloride, the solution turned from a cloudy, off-white to a light yellow homogeneous solution. A reaction of the olefin immediately ensued, as evidenced by the evolution of gas. The reaction was continued until the evolution of gas ceased (~15 min). At that point, several routes were possible. Additional olefin could be added for further metathesis, or the reaction could be deactivated by cooling to room temperature, storing in a refrigerator, and reactivated later by reheating to 90 °C and adding more olefin. Finally, the reaction could be terminated irreversibly by addition of 4 ml of methanol, and the products subjected to analysis.

Table I presents the experimental details of the metathesis of a variety of olefins. The major products were analyzed by gas chromatography on the VCW-98 column, described above.

Variation in Catalyst and Conditions. Not shown in Table I are the minor products of the reaction which arise from isomerization and subsequent metathesis. A study was carried out on 1-hexene in order to optimize the conditions and catalyst–cocatalyst ratios in olefin metathesis reactions. The experimental details are shown in Table II.

Catalyst Longevity. The metathesis of 1-hexene was carried out as described above until the evolution of ethylene ceased. Gas chromatographic analysis of the product mix indicated the yield of 5-decene was 67%. The reaction mixture was allowed to cool to room temperature under a slow stream of nitrogen gas. The mixture was allowed to stand for 48 h at room temperature; after that time 10 ml of 1-hexene was injected through the septum, and the mixture was heated to 90 °C. Rapid evolution of ethylene was observed and continued for 45 min. Gas chromatographic analysis of this product mix indicated that the yield of 5-decene, based on the amount of the second portion of 1-hexene added, was 72%. This mixture was allowed to cool to room temperature under nitrogen and placed in a refrigerator at 4 °C for 72 h. A third portion of 1-hexene was added, the mixture was heated to 90 °C, and after gas evolution ceased, gas chromatographic analysis revealed the yield of 5-decene from this portion of 1-hexane to be 31%. The mixture was then stored in a refrigerator for 6 weeks. During that time, the solution, which was clear yellow, turned black and opaque. This final mixture was inactive toward the metathesis of 1-hexene.

B. Mechanistic Studies. Conditions and Apparatus. All reactions were carried out under a dry, nitrogen atmosphere in a 25-ml, three-neck flask equipped with a nitrogen inlet, a condenser connected to an oil bubbler, and a rubber septum. Reactions were heated to the indicated temperature by means of an oil bath; all reactions were stirred magnetically.

Physical Methods. In the gas evolution studies, an F & M Scientific Hewlett-Packard Model 700 gas chromatographic unit was employed. This instrument was equipped with a thermal conductivity detector and the column (6 ft × 0.25 in. o.d.) was packed with 4A molecular sieves (20–100 mesh). Helium was the carrier gas. Authentic samples of CO, C_2H_5, C_2H_4, and N_2 were cleanly separated on this column when a 1 ml sample was injected, and the instrument was programmed from 70 to 250 °C at a rate of 7.5 °C/min.

The analyses of the various components of the metathesis reactions were carried out at the Research Division, Goodyear Tire and Rubber Co., Akron, Ohio. Gas chromatography was carried out on a Hewlett-Packard Model 5710A equipped with a flame ionization detector and a capillary column of dimensions 600 ft × 0.01 in. (i.d.). The column was coated with squalane and injections were 0.2 μl which were split so that only 0.5% of the sample was separated in the column. The oven temperature was 86 °C. This system was used in the analysis of both metathesis reactions studied: 4-octene and 1,7-octadiene.

Most products in these reactions were identified by comparison of their retention times with those of authentic samples separated under

Table II. Variations on Catalyst and Conditions in the Metathesis of 1-Hexene

Catalyst system	Reaction time, Temp	Conversion, %	% yield of products		
			5-Decene	4-Nonene	4-Octene
$Re(CO)_5Cl/C_2H_5AlCl_2$ (Re:Al = 1:8)	15 min, 90 °C	95	67	2.6	2.5
$Re(CO)_5Br/C_2H_5AlCl_2$ (Re:Al = 1:8)	30 min, 90 °C	95	63	0.8	0.4
$Re(CO)_5Cl/C_2H_5AlCl_2$ (Re:Al = 1:4)	180 min, 90 °C	97	52	4.6	1.6
$Re(CO)_5Cl/CH_3AlCl_2$ (Re:Al = 1:4)	180 min, 75 °C	97	14.5	7.4	2.4
$Re(CO)_5Cl/C_2H_5AlCl_2$ (Re:Al = 1:4)	1 h, 55 °C		0		
$Re(CO)_5Cl/C_2H_5AlCl_2$ (Re:Al = 1:4)	1 h, 72 °C		3.5		

Table III. Gas Chromatographic–Mass Spectrometric Analysis of the Metathesis of 1,7-Octadiene by $Re(CO)_5Cl/C_2H_5AlCl_2$

Area %	Parent Peak, *m/e*	Formula	Compd
0.034	44	$C_3H_8^+$	Propane[a]
0.048	56	$C_4H_8^+$	1-Butene[a]
0.005	64	$C_2H_5Cl^+$	Chloroethane[a]
0.015	68	$C_5H_8^+$	1,3-Pentadiene[a]
0.067	70	$C_5H_{10}^+$	2-Pentene (cis and trans)[a,b]
0.06	70	$C_5H_{10}^+$	Ethylcyclopropane[c]
16.48	82	C_6H_{10}	Cyclohexene[a]
0.02	98	C_7H_{14}	1,2-Diethylcyclopropane[c]
38.60	100	$C_7H_{16}^+$	*n*-Heptane[a]
0.61	110	C_8H_{14}	1,7-Octadiene[a]
43.17	112	C_6H_5Cl	Chlorobenzene;[a]
0.19	124		see Table IV
0.07	138	$C_{10}H_{18}^+$	1,7-Decadiene[a,d]
0.1	250	$C_{18}H_{18}O^+$	Unknown
0.08	324	Unknown	Unknown
0.08	326	Unknown	Unknown

[a] Compound identified by GC on the 600-ft column and also by *m/e* fragments on the GC–MS tandem. [b] The cis and trans isomers of 2-pentene were separated; the area percent is the combined total. [c] Structure proposed from mass measurement. [d] Stereochemistry about the double bond not determined.

identical conditions;[9] area integration was normalized by computer.

In addition to using the 600-ft column described above, the analysis of the products from the metathesis of 1,7-octadiene was carried out on a gas chromatography–mass spectrometer unit, also at Goodyear Research. The gas chromatography instrument was an F & M Scientific Model 810 equipped with a 22 ft × 1/8 in. stainless steel column packed with 3% Dexsil-300 on 60–80 mesh Chromosorb W. The mass spectrometer employed was a Du Pont Model 21-110C high-resolution, magnetic, double-focusing instrument. Thus, for the metathesis of 1,7-octadiene, all compounds reported were identified by at least mass spectral data; most were identified by the combination of gas chromatography–mass spectral studies.

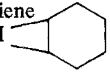
Gas Evolution Studies. These measurements were carried out by displacing mercury in a gas buret in the metathesis of *trans*-4-nonene. The reaction was carried out in a 25-ml, three-neck flask, with the center neck equipped with a condenser attached to the gas buret. The reaction mixture contained 2.00 ml (1.497 g, 12 mmol) of the olefin, 0.5423 g (1.5 mmol) of $Re(CO)_5Cl$, and 3.4 mmol of $C_2H_5AlCl_2$ dissolved in 5.2 ml of chlorobenzene solvent. After the initial reading was recorded at 23 °C, the mixture was heated to 97 °C for 35 min and cooled to 23 °C, and the final reading was taken. Samples of gas for analysis were removed from the volume immediately above the liquid.

Gas evolution studies on the metathesis of *trans*-4-nonene were carried out three times under identical conditions; the amount of gas evolved in each case was in the 9–9.5 ml range. The average value found was 9.3 ml. Gas chromatographic analysis of the evolved gas on the molecular sieve column revealed, in addition to N_2, that the sole evolved gas which could be detected, within the limits of the instrument, was ethane. The presence of CO and ethylene could not be confirmed in this study.

A blank standard was carried out in an identical manner as that described above with the exception that $Re(CO)_5Cl$ was omitted from the reaction solution. The total amount of gas evolved (average of three runs) was 10.1 ml. Gas chromatographic analysis of the evolved gases confirmed the presence of ethane and ethylene at a ratio of about 4:1, respectively, but the presence of CO could not be confirmed within the limits of detection of the instrument.

Metathesis of 1,7-Octadiene. In this reaction, a dry ice–acetone condenser was employed. A mixture of 2.5 ml of chlorobenzene, 2.0 ml (1.464 g, 13.4 mmol) of 1,7-octadiene, and 0.8245 g (2.3 mmol) of $Re(CO)_5Cl$ was heated to 94 °C, followed by addition of 3.0 ml (5.1 mmol) of $C_2H_5AlCl_2$ solution. The heating was continued for 3 min, whereupon the reaction was terminated by immersing the reaction flask in a dry ice–acetone bath and adding 1 ml of methanol. The liquid portion of the reaction was analyzed on the 600-ft column and also by gas chromatography–mass spectrometry. In addition, the sample was subjected to preparative gas chromatography in order to concentrate a high-boiling fraction which appeared in the gas chromatogram in small amounts (i.e., the *m/e* 124 component). Table III shows the results of analysis of the product mix from the metathesis of 1,7-octadiene.

Table IV. Mass Spectrometric Data on the *m/e* 124 Peak in the Metathesis of 1,7-Octadiene by $Re(CO)_5Cl/C_2H_5AlCl_2$

Area %[a]	Parent peak, *m/e*	Formula	Compd[b]
0.13	124.0902	$C_9H_{16}O^+$	$CH_2{=}CHCOCH_2CH_2CH_2CH{=}CH_2$
0.02	124.1254	$C_9H_{16}^+$	1,7-Nonadiene
0.04	124.1255	$C_9H_{16}^+$	CH_3CH_2CH 

[a] Area percents normalized with those of Table III. [b] Structure proposed from mass measurement.

Table V. Minor Components in the Metathesis of *trans*-4-Octene by $Re(CO)_5Cl/C_2H_5AlCl_2$

Product[a]	Area %	Product[a]	Area %
2-Pentene	0.13	3-Octene	0.17
3-Hexene	0.38	4-Nonene	0.32
3-Heptene	0.43	5-Decene	0.05

[a] Compound identified by GC on the 600-ft column.

Table VI. Products of the Reaction of *trans*-4-Octene with $Re(CO)_5Cl/CH_3AlCl_2$

Product	Area %	Product	Area %
2-Pentene	3.2	4-Octene	38.7
2-Hexene	4.3	4-Nonene	16.1
3-Hexene	12.0	5-Decene	9.6
3-Heptene	16.1		

The *m/e* 124 peak appeared only in very small amounts (area % = 0.19) and was obviously composed of several different compounds. This peak was concentrated by preparative gas chromatography and subjected to high resolution GC–MS analysis. The results are presented in Table IV.

In a second reaction, a solution containing 2.7 ml of chlorobenzene, 2.0 ml (1.46 g, 13.4 mmol) of 1,7-octadiene, and 0.8266 g (2.3 mmol) of $Re(CO)_5Cl$ was heated to 70 °C followed by the addition of 3.0 ml (5.9 mmol) of CH_3AlCl_2 solution. The reaction mixture was heated to 101 °C and continued for 15 min; the reaction was then terminated by cooling to room temperature and adding 1 ml of methanol. The volatile gases from this reaction were passed through a 2% solution of bromine in carbon tetrachloride in order to trap the olefins. The CCl_4 was removed by distillation, and the brominated olefins were analyzed by gas chromatography on the VCW-98 column.

The only compounds that could be detected by this method of analysis were 1,2-dibromoethane and 1,2-dibromopropane which were present in the relative amounts 43:1, respectively.

Metathesis of *trans*-4-Octene. A solution containing 1.0 ml of chlorobenzene, 1.0 ml (0.714 g, 6.4 mmol) of *trans*-4-octene, and 0.90 g (2.5 mmol) of $Re(CO)_5Cl$ was heated to 88 °C whereupon 3.3 ml (5.6 mmol) of ethylaluminum dichloride solution was added. The temperature was raised to 94 °C and continued for 40 min. After that time the reaction was cooled to room temperature and 0.5 ml of anhydrous methanol was added. The liquid was isolated and analyzed by gas chromatography on the 600-ft column. The results of the analysis are presented in Table V; only the minor components are shown.

In another reaction, a solution of 2.0 ml of chlorobenzene, 2.0 ml (12.8 mmol) of *trans*-4-octene, and 0.90 g (2.5 mmol) of $Re(CO)_5Cl$ was heated to 88 °C, and then 3.0 ml (5.9 mmol) of methylaluminum dichloride solution was added. The reaction was continued for 8 min, cooled to 0 °C in an ice–water bath, and terminated by addition of 1 ml of methanol. The liquid portion of this reaction was analyzed by gas chromatography on the VCW-98 column. The results of this analysis are shown in Table VI.

Results and Discussion

A. General Metathesis Reactions. The results in Table I show that the $Re(CO)_5X/RAlCl_2$ (X = Cl, Br; R = CH_3, C_2H_5) system affords an effective catalyst for the metathesis of terminal and cis and trans internal olefins. The system is generally ineffective toward the metathesis of hindered olefins such as isobutylene and isoprene. Analogous results on steric factors were reported for the WCl_6 system by Calderon.[10]

The minimum temperature for activation of the catalyst system is about 70 °C; optimum rates were obtained in the 85–95 °C range. This contrasts the behavior of the group 6B systems which are active at ambient temperatures.[11-13]

A comparison of the nature of the halides and alkyl groups with respect to rates and selectivities was also studied. In general, $Re(CO)_5Cl$ gave rates of metathesis about double those of the corresponding bromide under the same conditions. However, side reactions such as isomerization and polymerization accompanied reactions promoted by the chloride to a larger extent than when the bromide derivative was employed. In both cases, the extent of side reactions was relatively low. When CH_3AlCl_2 was used as the cocatalyst, the rates of metathesis were generally faster, and the catalyst was active at lower temperatures, but the extent of side reactions, particularly polymerization of the olefin, was high.

Table II shows the results of the metathesis of 1-hexene. The minor products 4-nonene and 4-octene arise from isomerization of 1-hexene to 2-hexene followed by metathesis with 1- or 2-hexene. The difference (% conversion – % total olefin products) may be accounted for by polymerization (small amounts of polymers were always observed to accompany these reactions).

The Al:Re molar ratio is also a major factor in the activity of the catalyst. Below 2:1, the catalyst is inactive; at exactly 2:1 the rates are generally slow but more selective. As the Al:Re ratio is increased to 8:1, the rates of metathesis increase, but the extent of side reactions also increases.

One unique feature of the $Re(CO)_5Cl/C_2H_5AlCl_2$ catalyst system is its long-lived activity, provided the reaction solution is stored under inert conditions. The system may be used continuously for 8 h, cooled to room temperature (which deactivates the catalyst), and reactivated by addition of olefin and reheating to 90 °C. This process may be repeated for about 5 days; during this time, the yield of 5-decene from the metathesis of 1-hexene drops from 67% (initial) to 31%. Among group 6B catalyst systems, $WCl_6/C_2H_5AlCl_2/C_2H_5OH$ becomes inactive in 10–25 min at 25 °C,[14] whereas the $[Mo(CO)_5Cl]^-/CH_3AlCl_2$ system may be active up to 8 h.[12] In fact, the $Re(CO)_5Cl/C_2H_5AlCl_2$ system appears to be the most long-lived homogeneous metathesis catalyst reported to date.

B. Mechanistic Studies. Of the proposals advanced to explain the mechanism of olefin metathesis, three of them invoke a concerted process whereby two olefins react simultaneously on the metal catalyst. The transition states advanced for the concerted process are "quasicyclobutane",[11] fluxional metallocycle,[15] and tetramethylene.[16] A fourth proposal involves a stepwise process in which the reaction is both initiated and propagated by a coordinated carbene.[17] Whereas it is not possible to distinguish unequivocally among the concerted processes, a stepwise from concerted process can be determined by experimentation.

Several recent reports have given attention to the differentiation between two types of processes. Katz and McGinnis[18] and Grubbs et al.[19] have demonstrated that a concerted process, in their catalytic systems, does not occur, and the mechanism must be stepwise. Casey and Burkhardt[20] presented experimental evidence in support of the mechanistic proposal of Herrison and Chauvin,[17] wherein they pointed out that coordinated diphenylcarbene underwent an exchange with several olefins. The new olefins produced could best be explained as arising from a metallocyclobutane intermediate.

The question arises, however, as to the mode of production of the initial carbene on olefin metathesis catalysts not originally containing a coordinated carbene, e.g., $WCl_6/C_2H_5AlCl_2$. Muetterties[14] has shown that in the $WCl_6/(CH_3)_2Zn$ system, coordinated methylene is produced on tungsten by abstraction of an α hydrogen from a coordinated methyl group.

In our communication[6] evidence was presented in support of a coordinated carbene mechanism. We now have direct evidence that a coordinated carbene mechanism is operative in the metathesis of olefins by our catalyst system.

Our line of reasoning is based on the fact that the *initially* formed carbene is not necessarily identical with the propagating carbenes. For example, the propagating carbenes in the metathesis of 1-butene are methylene and propylidene and the products are ethylene and 3-hexene. By selecting the R group on $RAlCl_2$ to be other than methyl or propyl, then the first-formed carbene is not one of the propagating carbenes. Suppose the initially formed carbene on the catalyst is ethylidene; then the first product from metathesis would be propylene and/or 2-pentene, depending on the mode of coordination of the olefin. Furthermore, the total amount of propylene and 2-pentene produced must equal the amount of active catalyst in the reaction. Therefore, it is possible to obtain direct evidence for a coordinated carbene mechanism by analysis of the minor products of a carefully selected olefin metathesis reaction.

Gas Evolution Studies. These studies were carried out in order to obtain information on the nature of the initially formed coordinated carbene. If a coordinated carbene is formed in the manner presented by Muetterties[14] for WCl_6, then an ethyl group from $C_2H_5AlCl_2$ would replace Cl on the $Re(CO)_5Cl$ followed by α-hydrogen abstraction by another ethyl group. Required, therefore, would be the evolution of one molecule of ethane per molecule of catalyst: in this case, 1.5 mmol. Furthermore, in order to coordinate a molecule of olefin to react with the carbene, another coordination site would have to be created, and this would most likely come about by displacing a coordinated CO on Re; thus, 1.5 mmol of CO would also be evolved.

The experiment to study the evolved gases was carried out several times on the metathesis of *trans*-4-nonene, since in this case, both the reactant and products (4-octene and 5-decene) show only low vapor pressure at 23 °C and would not interfere significantly with the measurement of the volume of evolved gases.

In fact, only 9.3 ml of gas was evolved in this experiment, far less than expected (about 75 ml). Of the evolved gas, only the presence of ethane was detected (no CO). However, the blank run on the same system without $Re(CO)_5Cl$ evolved 10.1 ml of gas, which was identified as a mixture of mostly ethane (80%) and ethylene (20%).

It is clear, then, that a coordinated carbene cannot be formed in this system analogous to that of WCl_6.[14] Apparently, the small amount of ethane arises from reaction of $C_2H_5AlCl_2$ with residual moisture, and no gas is evolved in the formation of a coordinated carbene.

Nature of the Coordinated Carbene. If a coordinated carbene mechanism is operative in the metathesis reactions promoted by the Re–Al catalyst system, the initial carbene must be formed without evolution of gas. This requirement can be met if the initial carbene is formed by attack of an ethyl group on coordinated CO, followed by exchange of oxygen for hydrogen to create a coordinated propylidene molecule; the second site for olefin coordination would come about by transfer of Cl from Re to Al. There is considerable evidence that this process, indeed, occurs.

First of all, the presence of an oxygen-containing molecule (octa-1,7-dien-3-one) was detected in the metathesis of 1,7-octadiene (Table IV). The presence of this molecule can account for the transfer of both oxygen (from $ReCOC_2H_5$)

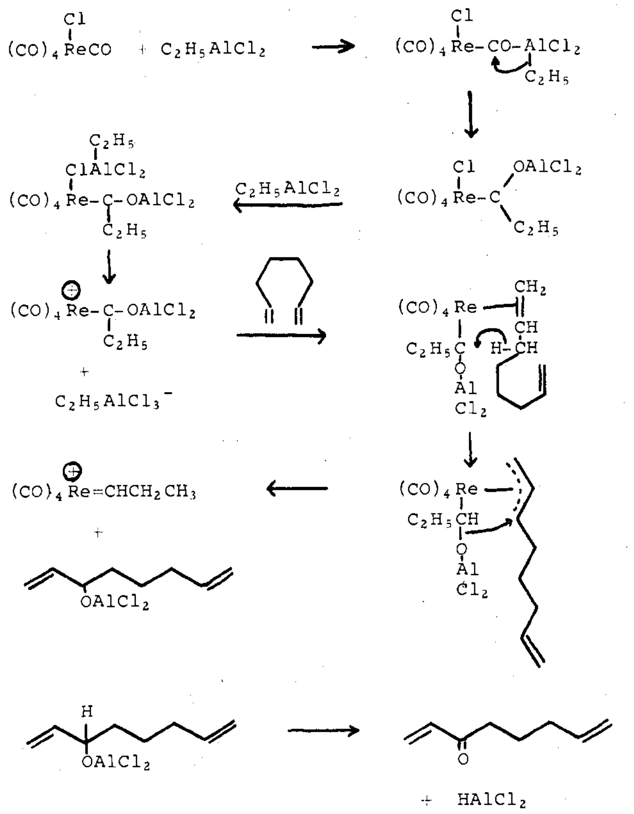


Figure 1. Possible mode of formation of coordinated propylidene.

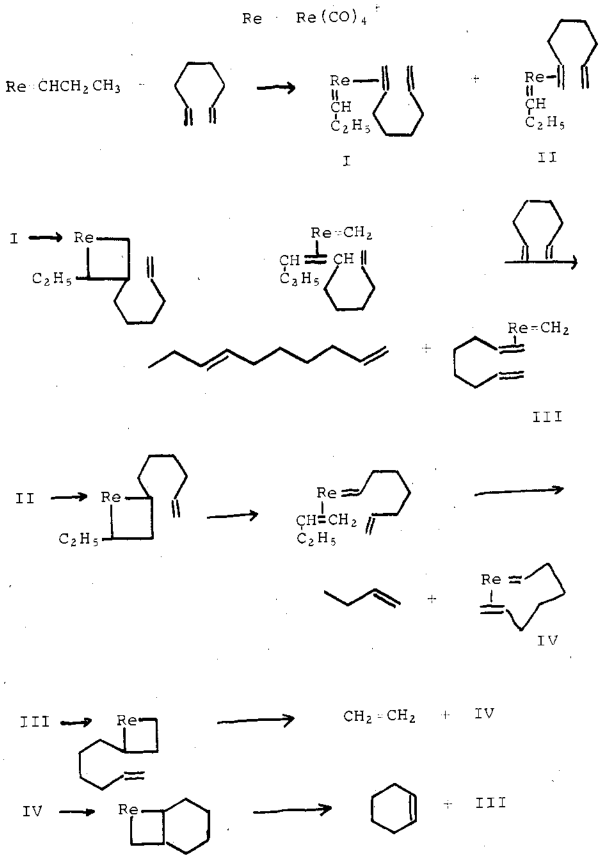


Figure 2. Possible mechanism for the metathesis of 1,7-octadiene.

and hydrogen (from 1,7-octadiene).

Very convincing of the production of coordinated propylidene as the first-formed carbene is the presence of the cyclopropane derivatives found in the analysis of the 1,7-octadiene metathesis. Tables III and IV indicate that three molecules in particular, i.e., those of *m/e* 70, 98, and 124.1255, come about by insertion of propylidene into the double bonds of ethylene (one of the major products), 1-butene, and cyclohexene (the other major product), respectively. This same type of coordinated carbene insertion reaction with olefins was observed by Casey and Burkhardt.[20]

On the basis of the above evidence, it is possible to speculate on a feasible mode of production of the first-formed carbene. This is shown in Figure 1.

The proposed mechanism for the formation of the initial carbene accounts for a number of observations. For example, in studies on the activity of the catalyst with respect to the Al:Re molar ratios, we have determined that a minimum 2:1 Al:Re is required for metathesis activity; below that ratio, little or no activity is observed. The mechanism also accounts for the observation that no gas is evolved in the formation of the active catalyst. The initial coordination of $C_2H_5AlCl_2$ on carbonyl oxygen, rather than abstraction of Cl^-, is based on the work of Chatt et al., who found that, for some rhenium carbonyl chloride complexes, aluminum alkyls and aluminum chloride preferentially coordinate to oxygen rather than chloride.[21]

Furthermore, the presence of the oxygen-containing hydrocarbon is explained. Whereas it might be expected that the molecule $ROAlCl_2$ would react with methanol to produce the alcohol of formula $C_8H_{14}O$, this molecule was not observed. Therefore, we speculate that $ROAlCl_2$ decomposes to the carbonyl ($C_8H_{12}O$, which is observed) and $HAlCl_2$, which is the reverse of the reaction of addition of dialkylaluminum hydride to a ketone reported by Schneider.[22] Also in support of this proposal for the formation of the active catalyst is the relative amount of $C_8H_{12}O$, which is approximately equal in area percent to the combined amounts of 1-butene and 1,7-decadiene. This result is required by the proposed mechanism; furthermore, the concentration of $C_8H_{12}O$ and the combined concentrations of 1-butene and 1,7-octadiene should be approximately equal to the concentration of the active catalyst, which is the case (see below).

Mechanism of the Metathesis Reaction. If the first-formed carbene on Re is propylidene as proposed above, then in the metathesis of 1,7-octadiene the first-formed olefins would be 1-butene and/or 1,7-decadiene, depending on the mode of coordination of the olefin. Furthermore, the first-formed olefins would be produced in catalytic amounts, approximately equal to the amount of Re. Thereafter, the propagating carbenes alternate between methylene and the carbene formed from the C_7 fragment. The major products are ethylene and cyclohexene. This mechanism, based on that originally proposed by Herrison and Chauvin,[17] is shown in Figure 2.

The key to the mechanism is the production of 1-butene and/or 1,7-decadiene, since the presence of these molecules would be required if the initiating carbene is propylidene. Indeed, both molecules were detected in the GC–MS analysis. It is difficult to ascertain quantitatively the amounts of the two olefins because of the complexity of the reaction, but it is possible to get a reasonable estimate of their relative quantities. By the use of internal standards and measurement of the amount of unreacted 1,7-octadiene (the reaction was terminated before complete reaction to minimize the extent of side reactions), we observed that the amounts of 1-butene and 1,7-decadiene were approximately equal, and their combined amount was approximately 1.5 mmol. This amount compares favorably with the initial amount of Re catalyst, viz., 2.3 mmol. Allowing for the possibility of escape of some 1-butene because of its high vapor pressure and also the presence of a trace amount of ethylcyclopropane, the combined amount of the first-formed olefins is very close to that of the Re catalyst. It should be noted that, whereas ethylcyclopropane could arise from insertion of propylidene into ethylene, it also could come about by insertion of methylene into 1-butene.

The presence of molecules in Tables III and IV not yet accounted for can, in general, be explained. Propane either can arise through a contaminant in the alkylaluminum dichloride (i.e., $CH_3CH_2CH_2AlCl_2$) which would evolve propane upon workup with methanol or can come about by abstraction of two hydrogen atoms on the coordinated propylidene yielding an $ReCH_2CH_2CH_3$ species; addition of methanol would yield propane. Ethyl chloride would come about by hydrochlorination of dissolved ethylene; HCl is produced in the termination of the reaction with methanol, which reacts with $C_2H_5AlCl_2$. Trace amounts of 1,3-pentadiene cannot be accounted for at present. Cyclohexene is a primary product, while chlorobenzene and heptane are solvents.

The presence of 2-pentene, common to the metathesis reactions of both 1,7-octadiene and 4-octene, could arise from diethylation of coordinated CO, followed by oxygen transfer to form a diethyl carbene. Dissociation of this molecule accompanied by hydride shift results in the production of 2-pentene.

The metathesis of 4-octene was also investigated because, for this olefin, the reactants and products are the same. Therefore, it was expected that complications interfering with the identification of first-formed olefins would be minimized. Table V reports the results of this metathesis reaction.

If the initiating carbene for the reaction is coordinated propylidene, then the first-formed olefin in the metathesis of 4-octene would be 3-heptene. Thereafter, the propagating carbenes are C_4 molecules. The results in Table V show that the reaction is far more complicated than anticipated, and the side products can all be accounted for as arising from isomerization of 4-octene to 3-octene, followed by metathesis with starting olefin or other olefins produced after isomerization–metathesis reactions. Therefore, 3-heptene can arise from metathesis of 3-octene with 4-octene, producing also 4-nonene.

Unfortunately most (>90%) of the olefins are polymerized in this reaction because of the high concentration of catalyst with respect to that of 4-octene. Nonetheless, assuming that the olefins are polymerized to an equal extent, it can be shown that not all of the 3-heptene can arise from isomerization–metathesis reactions. In fact, although the calculations are based on assumptions which cannot be totally justified, the amount of 3-heptene produced as the first-formed olefin is very close to that of the Re catalyst. Because of the assumptions involved in the determination of the concentration of 3-heptene, these results must be regarded as speculative, at best.

However, in order to provide information that, indeed, 1-butene and 1,7-decadiene are the first-formed olefins from metathesis of 1,7-octadiene and 1-heptene is that from metathesis of 4-octene, we investigated the metathesis of the same olefins using CH_3AlCl_2 as the cocatalyst. If the reaction proceeds in a manner as proposed in Figure 1, then the first-formed olefins in the metathesis of 1,7-octadiene and 4-octene are predictable. This is so since the initiating carbene in this system would be ethylidene rather than propylidene. Therefore, the expected first-formed olefin in the metathesis of 1,7-octadiene is propylene (and/or 1,7-nonadiene) and that for the metathesis of 4-octene is 2-hexene. Investigation of the minor components of the metathesis of 1,7-octadiene by gas chromatography revealed the presence of propylene (detected as 1,2-dibromopropane). Undetected, however, by our gas chromatography measurements was 1-butene; indeed, its presence in the product mix would be unexpected, according to the proposed mechanism.

The metathesis of 4-octene by $Re(CO)_5Cl/CH_3AlCl_2$ is accompanied by a fairly high degree of isomerization and polymerization. However, positively identified by qualitative gas chromatographic measurements in the product mix were small amounts of 2-hexene. This olefin was not a member of the product mix (as analyzed on the 600-ft column) where $C_2H_5AlCl_2$ was used as the cocatalyst. The presence of 3-heptene was also detected, but as pointed out previously, it is also a product of isomerization–metathesis and not necessarily a first-formed olefin.

It is clear, therefore, that the best explanation for the results presented is the formation of a carbene on coordinated CO which functions as the initiating carbene, followed by metathesis of the olefin in a manner similar to that proposed by Herrison and Chauvin.[17] Whereas other workers have shown that a stepwise process is operative in olefin metathesis, this work provides the first direct evidence for the existence of initiating and propagating carbenes.

It should be pointed out that for metal carbonyl catalysts, this process may be general. First of all, Doyle has reported that for the $[Mo(CO)_5Cl]^-/CH_3AlCl_2$ system, a minimum ratio of Al:Mo = 2:1 was required to observe appreciable activity in metathesis reactions.[12] Furthermore, in gas analysis studies reported by Basset et al.[23,24] on the metathesis catalyst system composed of $P(C_6H_5)_3W(CO)_5/C_2H_5AlCl_2/O_2$, it was found that catalytic activity decreased as evolution of CO increased. In fact, when 1.4 mol of CO was evolved/mol of tungsten, the catalyst was inactive toward olefin metathesis.

Acknowledgment. We are grateful to Goodyear Tire and Rubber Co., Research Division, Akron, Ohio, for the use of their gas chromatography–mass spectrometer apparatus.

Registry No. Propylene, 115-07-1; *cis*-2-pentene, 627-20-3; *trans*-4-nonene, 10405-85-3; 1,7-octadiene, 3710-30-3; 1-hexene, 592-41-6; *trans*-4-octene, 14850-23-8; isobutylene, 115-11-7; isoprene, 78-79-5; $Re(CO)_5Cl$, 14099-01-5; $C_2H_5AlCl_2$, 563-43-9; $Re(CO)_5Br$, 14220-21-4; CH_3AlCl_2, 917-65-7.

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