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Olefin Metathesis Catalyzed by Zero-Valent, Anionic Group VI Metal Compounds

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Complexes of the general type R_4N^+ $[M(CO)_5X]^-$ (where R is an alkyl radical, M a group VI metal and X a halide or carboxylate group) are very active and selective catalysts for the olefin metathesis reaction. These catalysts require an alkylaluminum compound activator. Alkylaluminum dihalides are especially effective and in general an Al:M ratio of greater than 1.5:1 is necessary. Of the group VI metals it was found that the molybdenum compounds produce the most active catalysts while of all the halide and carboxylate groups tested, chloride is the most effective. Surprisingly, only certain cations, such as $(n\text{-}C_4H_9)_4N^+$, give active catalysts. The effectiveness of these catalysts for the conversion of a number of pure olefins and olefin mixtures was tested. Some information regarding the composition of the actual active catalysts has been obtained.

INTRODUCTION

Since the first homogeneous catalyst systems for olefin metathesis were introduced by Calderon, Chen and Scott (*1, 2*), quite a large number of other homogeneous catalysts for this reaction have also appeared in the literature. Many of these catalyst systems contain WCl_6 in addition to an organometallic compound of Li (*3*), Mg (*4, 5*), Al (*1, 2*) or Sn (*6*). In addition to those catalysts based on WCl_6, others are known which consist of other tungsten compounds, or any of several molybdenum complexes, all in combination with an alkylaluminum halide (*7, 8*). There also are catalysts known which are based on rhenium (*9, 10*) and some of the group VIII metal (*11*) compounds.

In general, those catalyst systems based on WCl_6 are satisfactory only for reactions in which internal olefins are employed due to competing side reactions such as polymerization of terminal olefins. Terminal olefins are however perfectly satisfactory substrates for many of the other catalysts.

A great deal of knowledge concerning the mechanism of the olefin metathesis reaction and its possible catalytic intermediates has been accumulated and published (*12*), however in almost all cases the nature of the catalytically active species is not well defined.

This work describes another very active and versatile homogeneous catalyst system based on some ionic group VI metal complexes in the zero oxidation state. These compounds are of the type A^+ $[M(CO)_5X]^-$ (where M is either Cr, Mo or W; X is a halide or carboxylate group; and A^+ is typically a quartenary ammonium ion). The halide complexes are very easily prepared and have been known for some time (*13*) although they appear to never have been investigated for catalytic activity. Other zero-valent Mo and W complexes have been used as catalysts for the olefin metathesis reaction in heterogeneous systems (*14*), however, very few examples of their use as homogeneous metathesis catalysts are known (*15, 16*). The carboxylate complexes have not been described in the literature and will form the subject of a future communication.

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TABLE 1
REACTION OF 1-PENTENE CATALYZED BY $(C_4H_9)_4N[Mo(CO)_5Cl]$

Aluminum alkyl (4:1 Al–Mo ratio)	% Isomerization	% Metathesis
$(CH_3)_3Al$	16.8	0.0
$(i\text{-}C_4H_9)_3Al$	19.4	0.0
$(i\text{-}C_4H_9)_2AlH$	15.9	0.6
$(C_2H_5)_2AlCl$	12.1	0.5
$(CH_3)_3Al_2Cl_3$	0.0	75.4
$(CH_3)_2AlCl$	0.0	3.6
CH_3AlCl_2	0.0	90.5
$C_2H_5AlCl_2$	1.2	67.1
$i\text{-}C_4H_9AlCl_2$	1.5	87.0
$(CH_3)_3Al_2Br_3$	1.3	80.2
$AlBr_3$	13.5[a]	32.5[a]

[a] Composition of the unpolymerized product.

RESULTS AND DISCUSSION

A number of variables with respect to the catalyst composition have been investigated with reference to their effect on the activity for olefin metathesis. This includes not only variation in the metal and halide or carboxylate components but also variation in the cations and also in the type and amounts of the alkylaluminum activators used. (As with most other homogeneous metathesis catalysts, the complexes discussed in this work require a cocatalyst or activator.)

The effect of varying the alkylaluminum cocatalyst on the conversion of 1-pentene to ethylene and 4-octene catalyzed by $(C_4H_9)_4N[Mo(CO)_5Cl]$ is shown in Table 1. It can be readily seen that of all the compounds tested only alkylaluminum dihalides and $AlBr_3$ show substantial activity for the metathesis reaction (methylaluminum sesquichloride, which is also active, can be regarded as an equimolar mixture of the mono- and dichlorides). Trialkylaluminums and dialkylaluminum halides and hydrides show little or no activity as cocatalysts for the metathesis reaction but they do lead to substantial isomerization of 1-pentene to *cis*- and *trans*-2-pentene.

The relative ratio of the alkylaluminum activator to the transition metal catalyst is important in determining the activity of the catalyst system. The effect of varying the Al:Mo ratio on the metathesis of 1-pentene by $(C_4H_9)_4N[Mo(CO)_5Br]$ and $(C_4H_9)_4N[Mo(CO)_5Cl]$/methylaluminum dichloride (MADC) mixtures is shown in Table 2. In the case employing the $[Mo(CO)_5Br]^-$ complex, a system with fairly low activity, increasing the concentration of methylaluminum dichloride results in a steady increase in the amount of olefin metathesis but at sufficiently high Al:Mo ratios the isomerization of 1-pentene to 2-pentene also becomes quite important. With a very active system using the

TABLE 2
EFFECT OF Al–Mo RATIO ON THE METATHESIS OF PENTENE-1 CATALYZED BY $(C_4H_9)_4N[Mo(CO)_5X]$-MADC

Al–Mo ratio	X = Br		X = Cl	
	% Isomerization	% Metathesis	% Isomerization	% Metathesis
1:1	0.0	0.0	0.1	3.8
1.25:1	—	—	0.1	5.4
1.5:1	—	—	0.4	11.2
1.75:1	—	—	0.3	70.4
2:1	0.4	5.9	0.8	78.5
2.5:1	—	—	1.2	79.0
3:1	0.4	16.2	1.0	88.1
4:1	0.9	18.9	1.4	85.8
6:1	6.3	34.9	1.3	84.2
8:1	13.6	41.4	0.1	89.7

$[Mo(CO)_5Cl]^-$ complex there is little activity for the metathesis reaction at Al:Mo ratios below 1.5:1. Above ratios of 1.5:1 the activity of the system is very high and almost constant up to very high Al:Mo ratios. In this system the amount of isomerization is low over the entire range of ratios examined.

Great differences in catalytic activity are noted when one varies the metal or halide in a series of $(C_4H_9)_4N[Mo(CO)_5X]$ salts. The amount of conversion of 1-pentene to its isomerization and metathesis products catalyzed by a number of these salts in combination with methylaluminum dichloride is given in Table 3. Within a given series of anions containing the same halide but different metals, the molybdenum complexes are the most active followed by tungsten then chromium. Varying the halide in a series with the same metal shows that the chloride is by far the most active. Unfortunately we have not been able to prepare pure samples of $[M(CO)_5F]^-$ salts in order to determine their relative activity. The catalytic activity of a number of $[Mo(CO)_5(RCOO\text{–})]^-$ salts is shown in Table 4. As shown, only the trifluoroacetate complex is a useful catalyst component for the metathesis reaction.

TABLE 3

EFFECT OF METAL AND HALIDE ON THE $(n\text{-}C_4H_9)_4N[M(CO)_5X]$ CATALYZED METATHESIS OF PENTENE-1[a]

Complex anion	% Isomerization	% Metathesis
$[Cr(CO)_5Cl]^-$	0.0	14.3
$[Cr(CO)_5Br]^-$	1.1	1.8
$[Mo(CO)_5Cl]^-$	0.0	90.5
$[Mo(CO)_5Br]^-$	13.6	41.4
$[Mo(CO)_5I]^-$	0.0	0.0
$[W(CO)_5Cl]^-$	0.0	81.8
$[W(CO)_5Br]^-$	4.5	14.8

[a] Cocatalyst methylaluminum dichloride, Al:Mo ratio 8:1.

Such large differences in catalytic activity on changing the metal and halide (or carboxylate) components in these compounds are not unexpected. Much more surprising is the effect observed when seemingly minor changes are made in the structure of the cation. The results observed for a number of salts of the $[Mo(CO)_5Cl]^-$ ion are given in Table 5. It is clear that relatively few of the cations tested lead to effective catalyst components. Among them the $(C_nH_{2n+1})_4N^+$ ($n = 3\text{–}5$) and $CH_3(C_8H_{17})_3N^+$ salts are quite effective but closely related salts show greatly reduced activity.

TABLE 4

REACTIVITY OF $(C_4H_9)_4N[Mo(CO)_5(O_2CR)]$ COMPLEXES FOR THE METATHESIS OF PENTENE-1[a]

Carboxylate ligand	% Isomerization	% Metathesis
Acetate	7.1	15.4
Trimethylacetate	6.9	18.9
Trifluoroacetate	0.8	77.4
Stearate	5.5	11.5
Pentafluoropropionate	10.4	23.0

[a] Cocatalyst methylaluminum dichloride, Al:Mo ratio 8:1.

In addition to studying the effects of catalyst composition on reactivity a number

TABLE 5

EFFECT OF CATION ON THE METATHESIS OF 1-PENTENE BY VARIOUS $[Mo(CO)_5Cl]^-$ SALTS[a]

Cation	% Metathesis
$(C_2H_5)_4N^+$	33.0
$(n\text{-}C_3H_7)_4N^+$	86.9
$(n\text{-}C_4H_9)_4N^+$	90.5
$(n\text{-}C_5H_{11})_4N^+$	79.1
$(n\text{-}C_7H_{15})_4N^+$	53.2
$(n\text{-}C_4H_9)_4P^+$	23.4
$(n\text{-}C_4H_9)_3NH^+$	22.4
$(CH_3)_3(C_6H_5)N^+$	10.5
$(C_{18}H_{37})_2(CH_3)_2N^+$	33.7
$(C_{18}H_{37})(CH_3)_2(C_6H_5CH_2)N^+$	22.0
$(CH_3)(n\text{-}C_3H_7)_3N^+$	14.9
$(CH_3)(n\text{-}C_4H_9)_3N^+$	17.9
$(CH_3)(n\text{-}C_6H_{13})_3N^+$	10.9
$(CH_3)(C_8H_{17})_3N^+$	88.6

[a] Cocatalyst = methylaluminum dichloride; Al: Mo ratio, 8:1.

of the reaction parameters were also investigated. Decreasing the amount of solvent used in the metathesis of 1-pentene employing a $(C_4H_9)_4N[Mo(CO)_5Cl]$–MADC catalyst has very little effect on the reaction. In a series of runs employing a constant catalyst–olefin ratio, the volume of chlorobenzene used as a solvent was decreased from 10 ml to zero while the volume of 1-pentene was held constant at 10 ml. Within experimental error, the conversion to 4-octene was the same in all cases. This is quite interesting since in the case where no solvent at all is used the reaction mixture is not completely homogeneous. The type of solvent also has little effect, provided that it is inert toward all the catalyst components. Thus, with toluene, trichloroethylene, cyclohexane, pentane, or benzene essentially the same results are obtained as with chlorobenzene although here again in many cases heterogeneous systems result.

The ratio of olefin to catalyst can be varied over a fairly large range without having much of an affect on the conversion, at least in the case of the $(C_4H_9)_4N$-$[Mo(CO)_5Cl]$–MADC catalyzed metathesis of 1-pentene. No detectable difference in yields was observed when the ratio was increased from its usual value of 180:1 to 1000:1. At a ratio of 2000:1 the percentage metathesis decreased from approximately 90 to 80%. This difference may not be real, however, since the amounts of catalyst and cocatalysts are very small in comparison to the volume of solution and even small amounts of impurities can have a very large effect under these conditions.

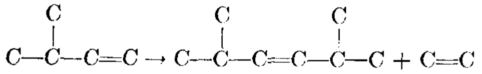
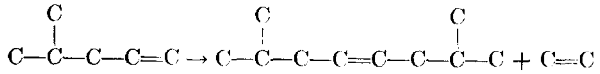
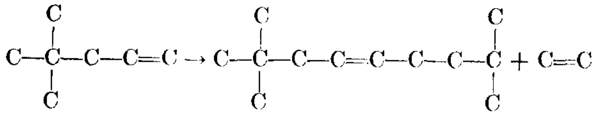
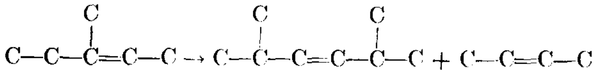
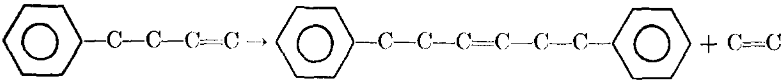
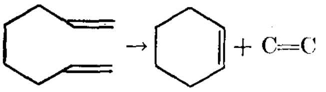
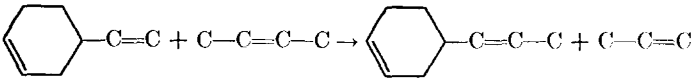
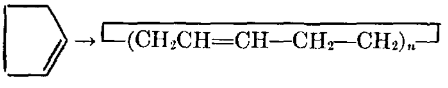
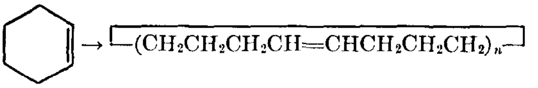
The rate of reaction can be somewhat accelerated by heating to moderate temperatures. Although no quantitative measurements were made, it appears that the rate increases steadily at least up to 60°C. At high temperatures, i.e., above 90°C, the amount of metathesis starts to fall to zero, probably due to the decomposition of the catalyst at higher temperatures.

In addition to 1-pentene, the olefin metathesis reaction has been carried out with many other olefins of several different types. The catalyst employed in most cases was $(n\text{-}C_4H_9)_4N[Mo(CO)_5Cl]$ with methylaluminum dichloride in a 4:1 or 8:1 Al–Mo ratio. The results of such metathesis reactions will not be described in detail; however, some general comments concerning the results of these experiments will be made. Many of these reactions are shown in Table 6.

Terminal normal olefins in general appear to be very reactive. Although some decrease in rate can be detected with the higher olefins, even 1-eicosene reacts rapidly to give good yields of 19-octatricontene. Internal normal olefins also appear to be very reactive, thus 2-pentene gives 2-butene and 3-hexene in a statistical distribution in a short time. Alkyl or aryl substitution on an olefin has a detrimental effect on the yields for the olefin metathesis reactions depending on the position and type of substituent. Thus vinyl cyclohexane gives no conversion and 3-methyl-1-butene gives only 35% yields of 2,5-dimethyl-3-hexene. Allylbenzene is unreactive but 4-phenyl-1-butene gives good yields of 1,6-diphenyl-3-hexene. Unconjugated diolefins can undergo either intra- or intermolecular metathesis. For example, 1,4-pentadiene gives fairly good yields of 1,4,7-octatriene while 1,7-octadiene gives quantitative yields of cyclohexene. A mixture of 1,5,9-decatriene, 1,5,9,13-tetradecatetraene and higher linear products is obtained from 1,5-hexadiene. In all cases where a single olefin was used as a starting material, the selectivity to the predicted symmetrical products was excellent.

Reactions between two different olefins to give cross products can easily be carried out, but in general complex mixtures are obtained. If, for example, 1-pentene and 2-pentene are reacted, all eight of the predicted products are observed which result from both "cross" metathesis and also the "homo" metathesis of each of the two starting olefins. If one employs two symmetrical olefins, or a relatively unreactive olefin and a symmetrical olefin, then "clean" reactions are possible. This is illustrated by the reaction of 4-octene and

TABLE 6
SOME TYPICAL OLEFIN METATHESIS REACTIONS CATALYZED BY $(n\text{-}C_4H_9)_4N[Mo(CO)_5Cl]$-MADC

Reaction	% Conversion
a. C—C—C—C=C → C—C—C—C=C—C—C—C + C=C	90
b. $C_{18}H_{37}CH{=}CH_2 \rightarrow C_{18}H_{37}CH{=}CHC_{18}H_{37} + C{=}C$	75
c.  $C{-}\overset{C}{\overset{\mid}{C}}{-}C{=}C \rightarrow C{-}\overset{C}{\overset{\mid}{C}}{-}C{=}C{-}\overset{C}{\overset{\mid}{C}}{-}C + C{=}C$	35
d.  $C{-}\overset{C}{\overset{\mid}{C}}{-}C{-}C{=}C \rightarrow C{-}\overset{C}{\overset{\mid}{C}}{-}C{-}C{=}C{-}C{-}\overset{C}{\overset{\mid}{C}}{-}C + C{=}C$	72
e.  $C{-}\underset{C}{\overset{C}{C}}{-}C{-}C{=}C \rightarrow C{-}\underset{C}{\overset{C}{C}}{-}C{-}C{=}C{-}C{-}C{-}\underset{C}{\overset{C}{C}} + C{=}C$	75
f.  $C{-}C{-}\overset{C}{\overset{\mid}{C}}{=}C{-}C \rightarrow C{-}\overset{C}{\overset{\mid}{C}}{-}C{=}C{-}\overset{C}{\overset{\mid}{C}}{-}C + C{-}C{=}C{-}C$	49
g. 	60
h. C—C—C—C—C=C—C → C—C—C—C—C=C—C—C—C—C + C—C=C—C	50
i. 	100
j. C=C—C—C=C → C=C—C—C=C—C—C=C + C=C	70
k. C—C—C—C=C—C—C—C + C—C=C—C → 2C—C—C—C=C—C	50
l. 	30
m. 	90
n. 	80

2-butene to give 2-hexene in excellent yields and by the reaction of 2-butene and vinylcyclohexene to give propylene and propenylcyclohexene. The use of two different reactive olefins, although usually giving a mixture of products, is sometimes useful in preparing certain unsymmetrical products. For instance 1-pentene/1-hexene mixtures give predominately 4-nonene while 1-pentene/4-methyl-2-pentene mixtures give mainly 2-hexene and 2-methyl-3-heptene although in both cases some homometathesis products are also produced.

The reaction of a mixture of *cis*-2-pentene and 4-methyl-1-pentene has been investigated in some detail and is perhaps somewhat typical of the behavior of mixtures of two fairly reactive olefins. The reaction was conducted in a manner that allowed the ethylene and most of the propylene to escape but all other products were confined. It is evident from the data shown in Fig. 1 that the reaction is very rapid, the product composition being nearly constant after 10 min. Perhaps the most interesting point to note in this reaction is

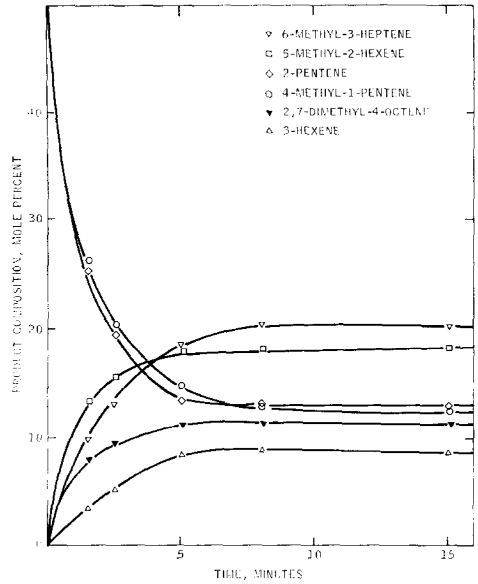
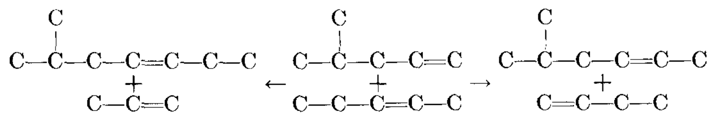


FIG. 1. Product composition vs time for the metathesis of a mixture of 4-methyl-1-pentene and 2-pentene.

the variation with time of the products of the cross-metathesis reaction.



$$C{-}\overset{C}{\overset{|}{C}}{-}C{-}C{=}C{-}C{-}C + C{-}C{=}C \leftarrow C{-}\overset{C}{\overset{|}{C}}{-}C{-}C{=}C + C{-}C{-}C{=}C{-}C \rightarrow C{-}\overset{C}{\overset{|}{C}}{-}C{-}C{=}C{-}C + C{=}C{-}C{-}C$$

Although thermodynamic data are lacking one would expect a somewhat greater conversion to 6-methyl-3-heptene than 5-methyl-2-hexene since in the former case a volatile product (propylene) is also being formed. This is, of course, exactly what is observed at long reaction times, however during the early stages of reaction the conversion to 5-methyl-2-hexene is considerably higher than to 6-methyl-3-heptene. The reaction therefore appears to be kinetically controlled at its early stages. The *cis-trans* ratio for some of the reaction products (given in Table 7) shows a preference for the formation of the *cis* isomer for only the products derived from *cis*-2-pentene at the early stages and is further evidence of the stereoregularity of the reaction.

The metathesis of *trans*-3-heptene shows the stereoregularity of the metathesis reaction more clearly (see Table 8). At short reaction times before the 3-heptene has isomerized substantially, the 4-octene formed by metathesis is predominately the *trans* isomer. As the reaction proceeds the *cis–trans* ratio of both the 3-heptene and 4-octene approach the thermodynamic values. These systems therefore are very similar in behavior to that reported by Hughes (*17*) for the $Mo(NO)_2(P\phi_3)_2Cl_2$ catalyst systems.

The mechanism of the olefin metathesis reaction has been the subject of a number of papers (*12*), however, in spite of the large volume of work a great deal of speculation remains. Despite the controversy involving some of the mechanistic

TABLE 7

METATHESIS OF AN EQUIMOLAR MIXTURE OF 4-METHYL-1-PENTENE AND *cis*-2-PENTENE

Reaction time (min)	*cis/trans* ratio				
	2-Butene	2-Pentene	5-Methyl-2-hexene	6-Methyl-3-heptene	2-7-Dimethyl-4-octene
1.5	1.10	7.0	0.63	0.40	0.30
2.5	0.83	1.6	0.50	0.33	0.39
5	0.48	0.36	0.38	0.29	0.27
8	0.42	0.30	0.33	0.21	0.25
10	0.40	0.28	0.32	0.20	0.22
120	0.40	0.22	0.30	0.20	0.20

TABLE 8
METATHESIS OF *trans*-3-HEPTENE

Reaction time (min)	*trans/cis* ratio	
	3-Heptene	4-Octene
0	98	—
2	50	18
5	28	15
8	19	10
11	11	9.4
15	8.3	7.9
25	6.4	5.0
120	4.6	3.7

details the overall reaction scheme seems to be fairly well established. The first step involves the stepwise formation of a diolefin complex from the coordinately unsaturated transition metal "catalyst." An electron rearrangement takes place resulting in a new diolefin complex containing the product olefins coordinated to the metal. These new olefins are then displaced in a stepwise manner, giving the product olefins and the original diolefin complex:

$$ML_x + 2R_a\overset{|}{C}{=}\overset{|}{C}R_b \rightleftharpoons (R_a\overset{|}{C}{=}\overset{|}{C}R_b)_2ML_x, \tag{1}$$

$$(R_a\overset{|}{C}{=}\overset{|}{C}R_b)ML_x \rightleftharpoons (R_a\overset{|}{C}{=}\overset{|}{C}R_a)(R_b\overset{|}{C}{=}\overset{|}{C}{-}R_b)ML_x, \tag{2}$$

$$(R_a\overset{|}{C}{=}\overset{|}{C}R_a)(R_b\overset{|}{C}{=}\overset{|}{C}R_b)ML_x + 2R_a\overset{|}{C}{=}\overset{|}{C}R_b \rightleftharpoons (R_a\overset{|}{C}{=}\overset{|}{C}R_b)_2ML_x + R_a\overset{|}{C}{=}\overset{|}{C}R_a + R_b\overset{|}{C}{=}\overset{|}{C}R_b. \tag{3}$$

The main subject of controversy is how the second step proceeds, especially the nature of the activated complex or intermediates.

Another area where much uncertainty remains is the nature of the active transition metal catalyst. In no case thus far reported has the composition of the actual catalyst been definitely established. Most of the known homogeneous metathesis catalysts appear to have little in common making it likely that determining the catalyst structure will necessarily have to be done on an individual basis.

Although an in-depth study to determine the composition of the active catalyst derived from mixtures of $(CH_3AlCl_2)_2$ and $(C_4H_9)_4N[Mo(CO)_5Cl]_2$ and related systems, was not made, certain observations do provide some clues as to what the active catalyst is like and how it is formed.

Alkylaluminum halides are widely used reagents in homogeneous catalysis and are used as alkylating agents, reducing agents or as Lewis acids. It seems clear that the function of the $(CH_3AlCl_2)_2$ in the presently discussed catalyst mixtures is as a Lewis acid which reacts with the $[Mo(CO)_5Cl]^-$ ion removing the chlorine. This is born out by the fact that catalyst mixtures containing trialkylaluminum and dialkylaluminum halides, which are better alkylating and reducing agents but poorer Lewis acids than the alkylaluminum dihalides, do not work, whereas $AlBr_3$ which is a very strong Lewis acid but possesses no alkylating or reducing power, does. It has even been possible, by adjusting the concentrations of catalyst components and solvent polarity, to isolate crystalline $(n\text{-}C_4H_9)_4N[CH_3AlCl_3]$ from these systems although under normal circumstances such compounds would remain in solution. The first step, then is the formation of $Mo(CO)_5$ by the reaction:

$$1/2[CH_3AlCl_3]_2 + (n\text{-}C_4H_9)_4N[Mo(CO)_5Cl] = (n\text{-}C_4H_9)_4N[CH_3AlCl_3] + Mo(CO)_5.$$

The $Mo(CO)_5$ apparently undergoes a type of disproportionation reaction forming $Mo(CO)_6$ and another molybdenum carbonyl species containing four or less carbonyl groups. The presence of $Mo(CO)_6$ can be detected by ir and actually isolated under some circumstances. If care is taken to optimize the yields of $Mo(CO)_6$ isolated, very nearly one-half the molybdenum used is recovered as $Mo(CO)_6$. The solution remaining after removal of the $Mo(CO)_6$ retains its catalytic activity. The unknown molybdenum carbonyl species therefore appears to be the active catalyst or a precursor to it. This material has not been isolated, however, its infrared spectrum has been recorded in the carbonyl stretching region (see Fig. 2). As shown, there are bands (or shoulders) at about 2100, 2030, 2000 and 1960 cm^{-1}. The band at 2000 cm^{-1} corresponds to Mo(CO)$_6$. The nature and number of the remaining bands suggest either a *trans* tricarbonyl or a *cis* tetracarbonyl complex or perhaps even a more complex structure with higher coordination number. Since the infrared spectrum was recorded under actual reaction conditions in the presence of an olefin (5-decene) presumably two olefin molecules are also coordinated to the molybdenum.

This description of the formation of the catalytically active species explains a number of the experimental facts, however certain other observations have not been resolved. The specificity of alkylaluminum dihalides over trialkylaluminums or dialkylaluminum halides has already been mentioned. The higher activity of the [Mo(CO)$_5$Cl]$^-$ as compared to the analogous Cr or W compounds or Br or I compounds can also be understood on the basis of an optimization of the halide as a leaving group, the metal–halide bond strength, and the stability of the resulting carbonyl complexes.

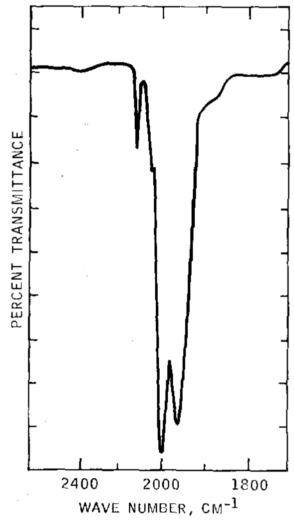


FIG. 2. Infrared spectrum of carbonyl stretching region of a mixture containing 0.103 g (n-C_4H_9)$_4$N-[Mo(CO)$_5$Cl], 0.045 g (CH_3AlCl_2)$_2$, 1.30 g 5-decene and 4.1 g chlorobenzene taken immediately after mixing.

It is well known that Mo(CO)$_5$ can be formed by irradiating solutions of Mo(CO)$_6$ and it should also be possible to form it by the reaction of Ag$^+$ with [Mo(CO)$_5$Cl]$^-$. When such reactions are carried out in the presence of an olefin, no metathesis is observed in either case. Since it seems fairly certain that Mo(CO)$_5$ is an intermediate in the catalyst formation it is not completely obvious why metathesis did not occur. If the formation of the active catalyst from Mo(CO)$_5$ is bimolecular, then one might expect the concentration of active catalyst to be very low since only low concentrations of Mo(CO)$_5$ are formed by irradiation. This problem does not occur in the reaction of Ag$^+$ with [Mo(CO)$_5$Cl]$^-$ suggesting that some species present in the (CH_3AlCl_2)$_2$–(n-C_4H_9)$_4$N-[Mo(CO)$_5$Cl] mixture, perhaps the excess (CH_3AlCl_2)$_2$, is necessary for the formation or the stabilization of the active catalyst or its precursor.

It is not at all apparent why only a few of the many different cations used lead to catalyst systems of high activity. Solubility does not appear to be an important factor since a number of cations forming soluble salts show low activity and some compounds are highly active even when they are insoluble. It appears that it is the size and shape of the cation that is important, however, any explanation of why this is so would be highly speculative.

As with many other olefin metathesis catalyst systems the (CH_3AlCl_2)$_2$–(n-C_4H_9)$_4$N[Mo(CO)$_5$Cl] mixtures rapidly loose activity on standing. Once the catalyst components are mixed in the presence of an olefin a noticeable reduction in activity is evident after less than 2 hr, and after 8 hr the catalyst is completely inactive. If mixed in the absence of an olefin, deactivation is much more rapid. The loss of activity is probably due to decomposition of the active catalyst species. Infrared spectra of catalyst solutions after 4 hr show only extremely weak bands which we have attributed to the active catalyst in contrast to the fairly strong bands observed in freshly prepared solutions. It is also of interest to note that solutions containing only a 1:1 ratio of Al:Mo show none of the bands attributed to the active catalyst. These appear as fairly strong bands when higher Al:Mo ratios are used.

EXPERIMENTAL SECTION

All reactions were carried out in a dry box under a nitrogen atmosphere. The infrared spectra were recorded on a Beckman Model 20 spectrometer. Analyses by gas chromatography were performed on a Perkin-Elmer Model 226 or Model 900 chromatograph employing a 300 ft squalane capillary column.

Reagents

All olefins were purchased from commercial sources including Phillips Petroleum, Aldrich Chemical and Chemical Samples. The aluminum alkyls were obtained from Ethyl Corp. including a generous sample of methylaluminum dichloride. The metal carbonyls were purchased from Pressure Chemicals. Most other reagents including the tetraalkylammonium halides were purchased from Eastman Kodak, however, the methyl(trioctyl)ammonium chloride was generously supplied by General Mills. All solvents and liquid olefins were dried by standard methods and stored in a dry box under nitrogen.

Metal Pentacarbonylhalide Salts

These salts were in general prepared by the method of Able, Butler and Reid (*18*) by reacting the appropriate quaternary ammonium halide with the metal hexacarbonyl in diglyme at 130°C.

Preparation of Metal Pentacarbonylcarboxylate Salts

To a solution of 0.01 mole of the appropriate salt of the metal pentacarbonylhalide ion in 40 ml THF, is added an exactly equivalent amount of very finely ground thallium(I) or silver(I) carboxylate. This mixture is slowly brought to reflux with stirring and held at reflux for 15–20 min. The hot solution is filtered through a fine fitted glass funnel. On cooling of the filtrate, the orange yellow solid usually begins to partially crystallize, however, more complete recovery can be accomplished by the addition of pentane. The solid compound is collected on a funnel and dried. The yields are quantitative.

Olefin Metathesis Reactions

For a typical metathesis run with 1-pentene, a 50 ml flask fitted with a stopcock, sidearm, and a rubber septum closure for sample withdrawal, would be charged with 0.5 mmole Group VI metal catalyst, 10 ml solvent (chlorobenzene was used almost exclusively), 10 ml 1-pentene, and finally an appropriate quantity of the alkylaluminum compound as a 1 *M* solution in chlorobenzene. The molar ratio of 1-pentene to catalyst under these conditions is approximately 180:1. The reaction is allowed to proceed with stirring for an appropriate period of time, usually 2 hr, to insure complete reaction, and the ethylene formed is collected over H_2O in a large gas buret. The nonvolatile products are then distilled under vacuum on a rotary evaporator and analyzed by gas chromatography. In runs where olefins other than pentene were used, the 10 ml quantity was still used. In cases where two different olefins were reacted, 5 ml of each were used. For internal olefins not forming volatile products the reactions can simply be carried out in plain 2 oz glass bottles.

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