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Olefin Metathesis by Pyridinepentacarbonylmolybdenum and Related Catalysts: Reactions and Mechanism

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The catalytic system $Mo(CO)_5py/RAlCl_2/(C_4H_9)_4NCl$ ($R = C_2H_5$, CH_3) was found to promote the metathesis of terminal olefins. Gas evolution studies indicated that the formation of the initial coordinated carbene which promotes metathesis is dependent on the solvent. In chlorobenzene, the initial carbenes are ethylidene and methylene with cocatalysts $C_2H_5AlCl_2$ and CH_3AlCl_2, respectively, but in heptane solvent, coordinated propylidene and ethylidene arise from the respective cocatalysts. Studies on the first-formed olefin in solution (other than the normal metathesis products) in the metathesis of 1,7-octadiene revealed that the amount of first-formed olefin varied directly with the amount of catalyst added to the solution, but was independent of the initial amount of olefin. Interpretation of these data is in accord with current theories on the mechanism of the olefin metathesis reaction, wherein the reaction is both initiated and propagated by coordinated carbenes. In addition, processes for the formation of the initial coordinated carbene in chlorobenzene and heptane are proposed.

Introduction

Recent research has shown that the olefin metathesis reaction in homogeneous catalyst systems is both initiated and propagated by coordinated carbenes.[1-3] In some reactions promoted by the catalyst $W(CO)_5C(C_6H_5)_2$, the coordinated carbene is reactive toward metathesis and no cocatalyst is required.[4] However, homogeneous catalysts which do not initially contain a carbene group require the synergistic use of an organometallic cocatalyst to show activity. One of the purposes of the cocatalyst is to furnish an alkyl group to the transition metal from which the coordinated carbene is formed. At least two methods of formation of the initial carbene have been reported: for tungsten chloride systems, coordination of an alkyl group to tungsten followed by α-hydrogen abstraction,[5] and in the case of $Re(CO)_5Cl$, attack of alkyl on carbonyl carbon followed by hydrogen-for-oxygen exchange. These methods of carbene formation can be distinguished by gas evolution studies in the formation of the active catalyst.

A report in the patent literature claimed that the system $Mo(CO)_5py/(CH_3)_3Al_2Cl_3/R_4NCl$ constituted an effective catalyst for the metathesis of olefins.[6] This research is concerned with studies on modified forms of the catalyst system, particularly in the alkylaluminum cocatalyst, in reactions and mechanism of the metathesis reaction.[7]

Experimental Section

Starting Materials. Acyclic olefins were obtained from Aldrich, Chemical Samples, or J. T. Baker and were purged with nitrogen gas while cyclic olefins were distilled immediately before use. Chlorobenzene solvent was purified by distillation; the first 10% of the distillate was discarded and the remainder collected and stored over molecular sieves.

Ethylaluminum dichloride was purchased as the neat substance from Ethyl Corp. and made up in 2.0 M solutions in chlorobenzene and heptane under nitrogen. The solutions were contained in 4-oz. bottles with perforated screw-cap lids containing a self-sealing rubber liner. Methylaluminum dichloride (2.0 M in chlorobenzene) was kindly

donated by Goodyear Research. Methylaluminum dichloride (2.0 M solution in hexane) was purchased from Ethyl Corp.

Tetrabutylammonium chloride was purchased from Eastman, dried in vacuo, and stored in a nitrogen-atmosphere glovebox.

$Mo(CO)_5py$,[8] $Mo(CO)_4py_2$,[8] $Mo(CO)_4bpy$,[9,10] and $Mo(CO)_5$-$P(C_6H_5)_3$[11] (py = pyridine; bpy = 2,2'-bipyridyl) were prepared and purified by literature methods. Characterization of the carbonyl derivatives was accomplished by comparison of the CO stretching bands and melting points with those reported in the literature.

Physical Methods. For the analyses of products in metathesis reactions, a Hewlett-Packard 5750-B gas chromatography unit was employed. A stainless steel column of dimensions 10 ft $\times$ $^1/_8$ in. containing 5% silicone rubber UCW-982 on 80–100 Mesh silica was incorporated in the unit; helium was the carrier gas and a thermal conductivity detector was employed. The products were identified by a comparison of retention times with those of authentic samples. The areas of the peaks were determined by triangulation and these were converted to molar amounts by the use of a known amount of bromobenzene as the internal standard, correcting for detector response ratios.

For gas analysis, the same gas chromatography system was used, except that the columns (6 ft $\times$ $^1/_4$ in.) were packed with 4A molecular sieves. The gases investigated were carbon monoxide, ethylene, ethane, methane, and nitrogen. In order to separate methane, nitrogen, and carbon monoxide from each other, it was necessary to cool the columns with dry ice. Any ethane or ethylene injected with the other gases was retained by the column at this temperature. After elution of the former gases, the temperature of the column was raised to 250 °C whereupon the ethylene and ethane were eluted and separated.

Metathesis Reactions. The experimental procedures for all metathesis reactions are analogous; therefore, only the metathesis of 1-hexane is given in detail. Differences in procedures are pointed out where appropriate.

Into a 100-mL, three-neck flask fitted with a nitrogen inlet, a condenser connected to an oil bubbler, and a septum, were placed 0.16 g (0.50 mmol) of $Mo(CO)_5py$, 0.07 g (0.25 mmol) of $(C_4-H_9)_4NCl$, and 10 mL of chlorobenzene. The system was flushed with nitrogen and heated to 70 °C. Through the septum was injected 2.0 mL (4.0 mmol) of ethylaluminum dichloride–chlorobenzene solution. Finally, 10 mL of 1-hexene was injected slowly so that it was added

Table I. A Comparison of the Activity of Mo Catalysts in the Metathesis of 1-Hexene[a]

Catalyst	% yield of 5-decene
$Mo(CO)_5py$	73.2
$Mo(CO)_5P(C_6H_5)_3$	70.1
$Mo(CO)_4(py)_2$	17.5
$Mo(CO)_4bpy$	12.7

[a] Conditions: temperature 70 °C; 30 min; Al:Mo:$(C_4H_9)NCl$ = 8:1:0.5.

Table II. A Comparison of Cocatalysts CH_3AlCl_2 and $C_2H_5AlCl_2$[a]

	% yield of product	
Olefin	CH_3AlCl_2	$C_2H_5AlCl_2$
1,7-Octadiene	98.4	95.2
1-Hexene	73.1	25.3
1-Pentene	16.6	7.5

[a] Conditions: temperature 58 °C; 15 min; Al:Mo:$(C_4H_9)_4NCl$ = 8:1:0.5.

Table III. Effect of Temperature on Yield in the Metathesis of 1-Hexene[a]

Temp, °C	% yield of 5-decene	Temp, °C	% yield of 5-decene
26	39.1	70	73.2
50	64.7	100	56.5

[a] Conditions: 30 min; Al:Mo:$(C_4H_9)_4NCl$ = 8:1:0.5.

Table IV. Effect of Variations of the Al:Mo Ratio in the Metathesis of 1-Hexene[a]

Al:Mo	% yield of 5-decene	Al:Mo	% yield of 5-decene
1:1	0.0	4:1	20.0
2:1	0.0	6:1	29.1
3:1	0.0	8:1	73.2

[a] Conditions: 70 °C, 30 min.

over a 10-min period. Gas evolution was noted upon addition of the olefin, and the reaction was allowed to proceed until gas evolution ceased (ca. 30 min). After that time, the reaction was terminated by the addition of 5 mL of methanol, followed by the addition of 1 mL (10 mmol) of bromobenzene as the internal standard. Gas chromatographic analysis indicated that the major product, 5-decene, was produced in 75% yield.

The following olefins were also subjected to metathesis conditions using the $Mo(CO)_5py$ catalyst system: 1-pentene, 1,7-octadiene, isoprene, isobutylene, 1,5-hexadiene, cyclopentene, cyclooctene, 2-pentene, 2-hexene, 2-heptene, 3-heptene, 4-nonene, acrylonitrile, and N,N-dimethylacrylamide. The only olefins that underwent the metathesis reaction were 1-hexene, 1-pentene (50.7% yield), and 1,7-octadiene (100% yield); all other olefins were either inert to metathesis or polymerized to an undetermined degree.

Other catalyst systems investigated were $Mo(CO)_4py_2$, $Mo(CO)_4bpy$, and $Mo(CO)_5P(C_6H_5)_3$ in the metathesis of some of the olefins mentioned above. Once again, only the terminal olefins underwent metathesis. Table I shows a comparison of the activities of the catalysts toward the metathesis of 1-hexene.

Also investigated with the $Mo(CO)_5py$ catalyst was the cocatalyst CH_3AlCl_2, in the metathesis of 1-pentene, 1-hexene, and 1,7-octadiene. Since the catalyst system containing CH_3AlCl_2 is much more active than that with $C_2H_5AlCl_2$, a comparison of the two systems is shown in Table II under less harsh conditions.

Other factors affecting the performance of the $Mo(CO)_5py$ catalyst were also investigated, such as temperature, the Al:Mo ratio, and the Mo:$(C_4H_9)_4NCl$ ratio. Table III shows the metathesis of 1-hexene with variations in temperature while Table IV shows the effect of the Al:Mo ratio.

The effect of the Mo:$(C_4H_9)_4NCl$ molar ratio was also investigated. A series of reactions was run at 70 °C and 30 min with an Al:Mo of 8:1, varying the amount of $(C_4H_9)_4NCl$ as follows: 0, 0.035 g (0.125 mmol, Mo:R_4NCl = 4:1), 0.07 g (0.5 mmol, Mo:R_4NCl = 2:1), 0.14 g (1.0 mmol, Mo:R_4NCl = 1:1), and 0.21 g (1.5 mmol, Mo:R_4NCl

Table V. Quantities and Analyses of Gases Formed in Chlorobenzene[a]

Cocatalyst	Quantity of gas (net)[b]	Analysis of gas
CH_3AlCl_2	22.4 mL (1.0 mmol)	CH_4 (50%) + CO (50%)
$C_2H_5AlCl_2$	4.5 mL (0.2 mmol)	C_2H_6 (50%) + CO (50%)

[a] Conditions: temperature 22 °C, Al:Mo:$(C_4H_9)_4NCl$ = 8:1:0.5.
[b] Corrected to STP.

Table VI. Quantities and Analyses of Gases Formed in Heptane[a]

Cocatalyst	Quantity of gas (net)[b]	Analysis of gas
CH_3AlCl_2	24.0 mL (1.07 mmol)	C_2H_4 (100%)
$C_2H_5AlCl_2$	13.4 mL (0.60 mmol)	C_2H_4 (95%) + C_2H_6 (5%)

[a] Conditions: temperature 22 °C, Al:Mo:$(C_4H_9)_4NCl$ = 8:1:0.5.
[b] Corrected to STP.

= 0.5:1). It was found that, at a Mo:R_4NCl ratio higher than 2:1, no metathesis reaction occurred; however, at a ratio of 2:1 or less, metathesis occurred but product yields did not change significantly below this ratio.

Mechanistic Studies. In order to determine the nature of the initially formed carbene on Mo, studies were carried out on the gases evolved in the formation of the active catalyst. The amount of generated gas was determined by displacing mercury in a gas buret; the identities of the gases were determined by gas chromatography. Several blanks were run which contained the solvent chlorobenzene, tetrabutylammonium chloride, and the alkylaluminum dichloride (no molybdenum compound) in the proportions mentioned above in the metathesis of 1-hexene. The gas evolution studies were then carried out with all catalyst components (no olefin) in the proportions mentioned above; Table V shows the net quantities and identification of gases evolved in the formation of the active catalyst.

In another study gas evolution studies were carried out in a manner analogous to those described above, except in this case the solvent was heptane. The net quantities and identification of gases evolved in the formation of the active catalyst are shown in Table VI.

First-Formed Olefin Studies. A series of runs was carried out on the metathesis of 1,7-octadiene in the manner described above for the metathesis of 1-hexene in chlorobenzene solvent, except that the temperature was maintained at 55 °C under a slow but constant flow of nitrogen. The condenser was connected to a trap placed in a Dewar flask of liquid nitrogen. Reactions were allowed to proceed for 30 min. For these studies, variations in the amounts of olefin and catalyst were employed. At the end of the reaction, the material in the trap was treated with 10 mL of a 10% solution of Br_2 in CCl_4. The trap, while still at −196 °C, was evacuated at 10^{-2} Torr, then closed, removed from the liquid nitrogen, and allowed to come to room temperature. The closed system was allowed to stand 3 h in order to ensure complete bromination of any olefins contained in the trap. After that time, the contents of the trap were transferred to a 50-mL flask, the trap was washed with CCl_4 (3 × 5 mL), and the washings were added to the flask. The material in the flask was fractionally distilled using a 12-cm Vigreux column to remove most of the CCl_4 and excess Br_2. When the volume of the flask had been reduced to approximately 1 mL, 0.10 mL (1.0 mmol) of bromobenzene was added to the solution as an internal standard, and aliquots of the solution were subjected to gas chromatography, the olefins being analyzed as their brominated derivatives.

In these studies, when the quantity of the catalyst was varied, the amount of solvent was also varied so that the concentration of the catalyst always remained constant. The quantities and identities of the olefins formed in these studies other than the metathesis products (cyclohexene and ethylene) are shown in Table VII.

A series of studies was also carried out in the identification of first-formed olefins in heptane solvent in the metathesis of 1,7-octadiene. Conditions of metathesis, method of isolation, and quantitative analysis of the products were identical with those carried out in chlorobenzene solvent. The results are shown in Table VIII.

Results and Discussion

Of the catalysts investigated, the $Mo(CO)_5py/RAlCl_2/R_4NCl$ system seems to be the most active. It is to be noted that, in contrast to the $Re(CO)_5Cl/RAlCl_2$ metathesis catalyst, which required a minimum Al:Re ratio of 2:1 for activity, the

Table VII. Quantities and Identities of First-Formed Olefins in the Metathesis of 1,7-Octadiene (Chlorobenzene)

1,7-Octadiene, mmol	Mo(CO)$_5$py, mmol	Cocatalyst	First-formed olefin,^{a} mmol	
			Propylene	1-Butene
10	2.5	C$_2$H$_5$AlCl$_2$	0.11 ± 0.01	0.04 ± 0.01
20	2.5	C$_2$H$_5$AlCl$_2$	0.10 ± 0.01	0.03 ± 0.01
30	2.5	C$_2$H$_5$AlCl$_2$	0.10 ± 0.01	0.02 ± 0.01
40	2.5	C$_2$H$_5$AlCl$_2$	0.10 ± 0.01	Trace
10	3.75	C$_2$H$_5$AlCl$_2$	0.15 ± 0.01	0.04 ± 0.01
10	5.0	C$_2$H$_5$AlCl$_2$	0.19 ± 0.01	Trace
10	2.5	CH$_3$AlCl$_2$	0.0	0.0
10	5.0	CH$_3$AlCl$_2$	0.0	0.0

^{a} The numbers are the averages of three runs each.

Table VIII. Quantities and Identities of First-Formed Olefins in the Metathesis of 1,7-Octadiene (Heptane)

1,7-Octadiene, mmol	Mo(CO)$_5$py, mmol	Cocatalyst	First-formed olefin,^{a} mmol	
			Propylene	1-Butene
10	2.5	C$_2$H$_5$AlCl$_2$	0.0	0.46 ± 0.03
20	2.5	C$_2$H$_5$AlCl$_2$	0.0	0.50 ± 0.03
30	2.5	C$_2$H$_5$AlCl$_2$	0.0	0.46 ± 0.03
40	2.5	C$_2$H$_5$AlCl$_2$	0.0	0.46 ± 0.02
10	3.75	C$_2$H$_5$AlCl$_2$	0.0	0.75 ± 0.04
10	5.0	C$_2$H$_5$AlCl$_2$	0.0	0.97 ± 0.04
10	2.5	CH$_3$AlCl$_2$	1.22 ± 0.07	0.0
20	2.5	CH$_3$AlCl$_2$	1.27 ± 0.08	0.0
30	2.5	CH$_3$AlCl$_2$	1.20 ± 0.07	0.0
40	2.5	CH$_3$AlCl$_2$	1.22 ± 0.06	0.0
10	3.75	CH$_3$AlCl$_2$	1.81 ± 0.09	0.0
10	5.0	CH$_3$AlCl$_2$	2.40 ± 0.15	0.0

^{a} The numbers are the averages of three runs each.

Mo(CO)$_5$py system requires at least 4:1 (Al:Mo), and activity increases toward 8:1. With respect to cocatalysts, systems are far more active with CH$_3$AlCl$_2$ than C$_2$H$_5$AlCl$_2$. In addition, an activator is also necessary for the catalyst to promote olefin metathesis, in a maximum ratio Mo:R$_4$NCl of 2:1.

One of the important observations noted in the reactions is that the catalyst systems investigated promote only the metathesis of terminal olefins. Indeed, in cross-metathesis reactions attempted using 1- and 2-hexene, only the presence of 5-decene was noted in the product mix. Gas chromatographic analysis revealed that 2-hexene was inert to metathesis. These results are in contrast to the order of reactivity of various types of olefin toward metathesis reported by the research groups of Katz[12] and Casey,[13] who found that terminal olefins are slowest to metathesize with certain tungsten-based catalysts. We are not yet in a position to give a detailed explanation for these unexpected data; however, the answer may lie in the area of polarization of the metal–carbene bond and electrophilic vs. nucleophilic addition to olefins, recently investigated by Gassman and Johnson.[14]

The bulk of this research was directed toward mechanistic aspects of the olefin metathesis reaction. Taking advantage of the fact that only terminal olefins undergo metathesis by the Mo(CO)$_5$py catalyst system, it is possible to obtain direct evidence for a metal–carbene-initiated process once the nature of the *initially formed* coordinated carbene is elucidated.

Gas evolution studies in the formation of the active catalyst can distinguish between the two methods reported for the formation of the initial coordinated carbene species. If the process occurs according to that suggested by Muetterties,[5] then in the case of C$_2$H$_5$AlCl$_2$ as the cocatalyst, ethane must be evolved. Furthermore, two coordinatively unsaturated sites must be present for the coordination of the alkyl groups and, later, the olefin. The first open site can occur by abstraction of pyridine; the second must come from dissociation of CO. Therefore, in order for the initial carbene to be formed in this manner, 1 mol of ethane and 1 mol of CO must be evolved per mole of active catalyst formed. In the case of CH$_3$AlCl$_2$ as the cocatalyst, a 50:50 mixture of CH$_4$ and CO must be
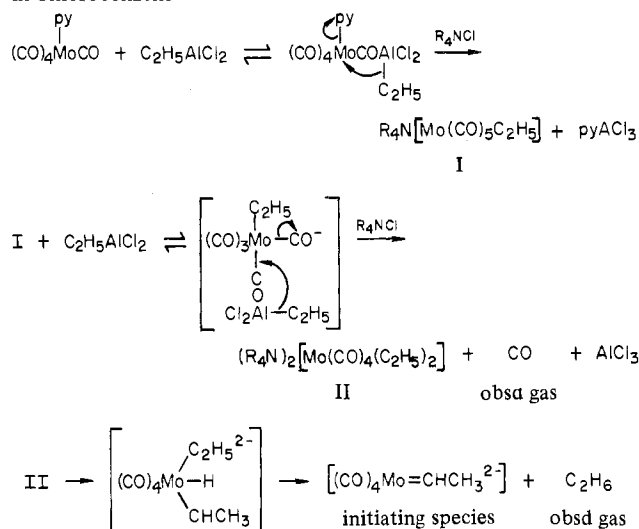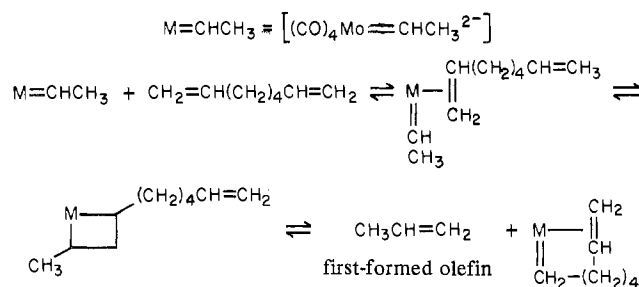
evolved in the formation of the active catalyst.

If the formation of the initial carbene proceeds according to the method proposed by Greenlee and Farona for Re(C-O)$_5$Cl, then with either C$_2$H$_5$AlCl$_2$ or CH$_3$AlCl$_2$ as the cocatalyst, gas evolution should not occur.

Examination of the data in Table V reveals that in chlorobenzene, and CH$_3$AlCl$_2$ as the cocatalyst, a 50:50 mixture of CH$_4$ and CO was detected. In the case of C$_2$H$_5$AlCl$_2$ as the cocatalyst, ethane and CO were evolved in equal amounts. Also in keeping with the observation that catalytic activity is greater with CH$_3$– than with C$_2$H$_5$AlCl$_2$ as the cocatalyst is the fact that considerably more gas is evolved with the former than the latter. Apparently, active catalyst forms to a greater extent with CH$_3$AlCl$_2$, accounting for the greater yields of metathesis products.

Gas evolution studies in chlorobenzene indicate that the initially formed carbene with C$_2$H$_5$AlCl$_2$ is ethylidene and that with CH$_3$AlCl$_2$ is methylene. Therefore, in the metathesis of 1,7-octadiene, where the products of metathesis are cyclohexene and ethylene, the first-formed olefin with Mo=CHCH$_3$ is propylene and that with M=CH$_2$ is ethylene. Furthermore, the amount of propylene formed should vary directly with the initial amount of Mo(CO)$_5$py catalyst used in the reaction but be independent of varying amounts of 1,7-octadiene. Where M=CH$_2$ is the initiating species, the first-formed olefin (ethylene) is the same as the product and indistinguishable from it in relative amounts. However, in order that the first-formed olefin truly come from an initiating carbene, there should be an absence of propylene where CH$_3$AlCl$_2$ is used as the cocatalyst.

Data in Table VII clearly show the effect mentioned above. The amount of propylene found in the product mix varied directly with the initial amount of Mo catalyst but was independent of the initial amount of starting olefin. With CH$_3$AlCl$_2$ as the cocatalyst, the generation of propylene was not observed within the limits of detection of the GC instrument.

Small amounts of 1-butene detected apparently come from the mode of formation as found in heptane solvent (see below).

Scheme I. Formation of Initial Coordinated Carbene in Chlorobenzene

$$(CO)_4MoCO + C_2H_5AlCl_2 \rightleftharpoons (CO)_4MoCOAlCl_2 \xrightarrow{R_4NCl}$$

$$R_4N[Mo(CO)_5C_2H_5] + pyAlCl_3$$
$$I$$

$$I + C_2H_5AlCl_2 \rightleftharpoons \left[(CO)_3Mo \begin{matrix} C_2H_5 \\ C \\ | \\ C \\ O \end{matrix} CO^- \\ Cl_2Al-C_2H_5 \right] \xrightarrow{R_4NCl}$$

$$(R_4N)_2[Mo(CO)_4(C_2H_5)_2] + CO + AlCl_3$$
$$II \qquad\qquad obsd\ gas$$

$$II \rightarrow \left[(CO)_4Mo\begin{matrix}C_2H_5\\-H\\CHCH_3\end{matrix}\right]^{2-} \rightarrow [(CO)_4Mo=CHCH_3]^{2-} + C_2H_6$$
$$initiating\ species \qquad obsd\ gas$$

Scheme II. Production of First-Formed Olefin

$$M=CHCH_3 \equiv [(CO)_4Mo=CHCH_3]^{2-}$$

$$M=CHCH_3 + CH_2=CH(CH_2)_4CH=CH_2 \rightleftharpoons M-\begin{matrix}CH(CH_2)_4CH=CH_3\\||\\CH_2\\CH\\CH_3\end{matrix} \rightleftharpoons$$

$$\begin{matrix}M\\CH_3\end{matrix}\diagdown\diagup(CH_2)_4CH=CH_2 \rightleftharpoons CH_3CH=CH_2 + M-\begin{matrix}CH_2\\||\\CH\\|\\CH_2-(CH_2)_4\end{matrix}$$
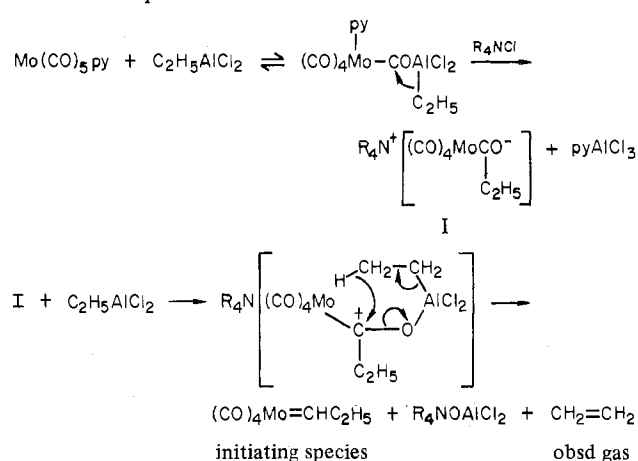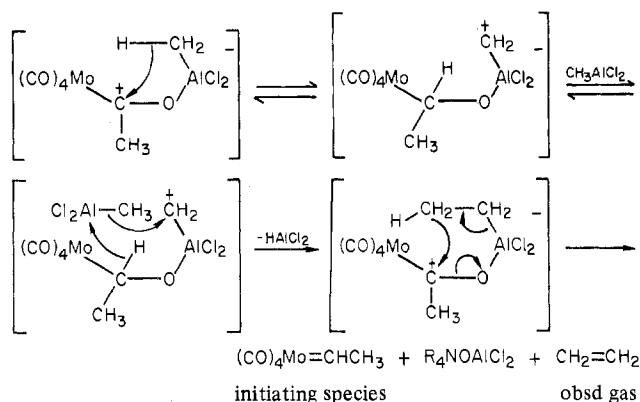$$first\text{-}formed\ olefin$$

This mode of formation is the minor pathway and occurs with irregularity from run to run.

The reactions accounting for the formation of the initiating species along with the generation of alkane and CO gas observed are shown in Scheme I. Scheme II shows the reactions leading to production of the first-formed olefin in the metathesis of 1,7-octadiene.

The process shown in Scheme I for the formation of the initiating carbene and subsequent generation of alkane and CO gas is in keeping with recently advanced concepts for production of the active catalyst. For example, coordination of Al on carbonyl oxygen is consistent with the mechanism invoked for the Re(CO)$_5$Cl catalyst system[3] and also shown to occur with some rhenium carbonyl species.[15] The actual loss of aluminum compound is speculative at best, but the proposed mechanism accounts for the role of (C$_4$H$_9$)$_4$NCl in the formation of the active catalyst. Another possibility for the removal of aluminum compound from the active catalyst could also be with the assistance of another molecule of alkylaluminum dichloride, forming some ionic species. Nonetheless, the proposed mechanism explains the observations that ethane (or methane) and CO must be evolved in equal amounts in the formation of the active catalyst; more importantly, the mechanism predicts that coordinated ethylidene (or methylene) is the initiating carbene.

In the formation of the first metallocyclobutane intermediate (Scheme II), propylene must be generated in amounts equal to the amount of active catalyst. The proposed mechanism, consistent with current theories on the mechanism of olefin metathesis, clearly explains the generation of propylene in catalytic amounts.

An additional problem arises in that, for the Re(CO)$_5$Cl system, the coordinated alkylaluminum dichloride transfers the alkyl group to a carbonyl carbon atom while for Mo-

Scheme III. Formation of Initial Coordinated Carbene in Heptane

$$Mo(CO)_5py + C_2H_5AlCl_2 \rightleftharpoons (CO)_4Mo-COAlCl_2 \xrightarrow{R_4NCl}$$
$$\overset{py}{|} \qquad\qquad \overset{|}{C_2H_5}$$

$$R_4N^+\left[(CO)_4MoCO^-\\ \overset{|}{C_2H_5}\right] + pyAlCl_3$$
$$I$$

$$I + C_2H_5AlCl_2 \rightarrow R_4N\left[(CO)_4Mo\begin{matrix}CH_2-CH_2\\H\diagup\quad\diagdown\\+\quad AlCl_2\\C-O\\|\\C_2H_5\end{matrix}\right] \rightarrow$$

$$(CO)_4Mo=CHC_2H_5 + R_4NOAlCl_2 + CH_2=CH_2$$
$$initiating\ species \qquad\qquad obsd\ gas$$

Scheme IV. Formation of Initiating Carbene in Heptane

$$\left[(CO)_4Mo\begin{matrix}H-CH_2\\+\quad AlCl_2\\C-O\\|\\CH_3\end{matrix}\right]^- \rightleftharpoons \left[(CO)_4Mo\begin{matrix}\overset{+}{C}H_2\\H\\C-O\quad AlCl_2\\|\\CH_3\end{matrix}\right]^- \xrightarrow[]{CH_3AlCl_2}$$

$$\left[(CO)_4Mo\begin{matrix}Cl_2Al-CH_3\ \overset{+}{C}H_2\\\diagdown H\\C-O\quad AlCl_2\\|\\CH_3\end{matrix}\right] \xrightarrow{-HAlCl_2} \left[(CO)_4Mo\begin{matrix}CH_2-CH_2\\H\diagup\quad\diagdown\\+\quad AlCl_2\\C-O\\|\\CH_3\end{matrix}\right] \rightarrow$$

$$(CO)_4Mo=CHCH_3 + R_4NOAlCl_2 + CH_2=CH_2$$
$$initiating\ species \qquad\qquad obsd\ gas$$

(CO)$_5$py the alkyl group is transferred to the metal. Apparently, these differences are related to the solvent medium. In heptane solvent, Table VI shows that the identities of the gases in the formation of the initial coordinated carbene are different from those formed in chlorobenzene. The evolution of ethylene for both cocatalysts and the fact that propylene and 1-butene are the first-formed olefins for cocatalysts CH$_3$AlCl$_2$ and C$_2$H$_5$AlCl$_2$, respectively, indicate that a process analogous to, but not identical with, that of Re(CO)$_5$Cl occurs in the formation of the initial coordinated carbene.

In the case of C$_2$H$_5$AlCl$_2$ as the cocatalyst, evolution of C$_2$H$_4$ can be rationalized by the reactions shown in Scheme III.

The first step of metathesis of 1,7-octadiene with (CO)$_4$-Mo=CHC$_2$H$_5$ would lead to the formation of 1-butene as the first-formed olefin. By analogous reasoning to that advanced for the initiating reactions in chlorobenzene solvent, the amount of 1-butene formed should vary directly with the amount of active catalyst formed but be independent of the amount of 1,7-octadiene introduced to the reaction. Table VIII shows this rationale to be accurate.

Where CH$_3$AlCl$_2$ is the cocatalyst, the evolution of C$_2$H$_4$ in the formation of the initial carbene can be rationalized as follows. The first few steps are analogous to the case of C$_2$H$_5$AlCl$_2$, leading to the reactions shown in Scheme IV.

The first metathesis product of 1,7-octadiene with (CO)$_4$Mo=CHCH$_3$ would be propylene, and again, the amount of propylene formed should vary directly only with the amount of active catalyst introduced to the reaction. Examination of the data in Table VIII reveals that the results are in accord with this rationale.

Apparently, the role of the solvent is the stabilization of the charged species in solution. The greater dielectric constant

for chlorobenzene apparently aids in the promotion of a pathway generating the greater number of charged species in solution, whereas in heptane solvent, the initiating species is neutral, and fewer ionic intermediates are involved.

This research provides direct evidence that the olefin metathesis reaction is initiated by coordinated carbene species. In addition, the evidence indicates that in chlorobenzene solvent, the initial coordinated carbene formed on $Mo(CO)_5py$ occurs in a manner analogous to that of the tungsten-based catalysts. Where heptane functions as the solvent, a modified approach to that of $Re(CO)_5Cl$ occurs in the formation of the initial coordinated carbene.

Registry No. 1-Hexene, 592-41-6; 1,7-octadiene, 3710-30-3; 1-pentene, 109-67-1; $Mo(CO)_5py$, 14324-76-6; $Mo(CO)_5P(C_6H_5)_3$, 14971-42-7; $Mo(CO)_4(py)_2$, 33570-29-5; $Mo(CO)_4bpy$, 15668-64-1; CH_3AlCl_2, 917-65-7; $C_2H_5AlCl_2$, 563-43-9; $(C_4H_9)_4NCl$, 1112-67-0.

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X-Ray Photoelectron Spectroscopic Study of Iron(II) Spin Equilibrium Complexes and Their Cobalt(II) and Nickel(II) Analogues

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The 2p x-ray photoelectron spectra (XPS) of a series of iron(II) spin equilibrium complexes exhibit broad satellite structure. It is generally assumed that transition metal satellites are the result of either multiplet splitting or shake-up. From a comparison of the XPS spectra of the iron(II) complexes with the analogous cobalt(II) and nickel(II) systems and from temperature-dependence studies on the iron(II) spin equilibrium complexes we have been able to conclude that the satellites in these cases are associated with a decomposition product which appears upon irradiation in the spectrometer. Decomposition of the iron(II) complexes follows a pattern based on the spin state of the metal center. For the two complexes which are mostly high spin at 40 °C, decomposition appears to be complete before statistically significant spectra can be collected. The low-spin complex and the spin equilibrium complex which is mostly low spin at 40 °C did not exhibit any signs of the broad satellite associated with decomposition. At elevated temperatures (150 °C) where the latter complex approaches a 50/50 mixture of high spin and low spin decomposition is again complete before a minimal spectrum can be completed. Preliminary evidence for a correlation between the crystal field stabilization energy or the spin multiplicity of the metal center and the decomposition process is discussed.

Introduction

In recent years x-ray photoelectron spectroscopy (XPS) has been extensively applied to the study of the electronic structure of transition metal complexes. In these studies three types of spectral features have been considered. The first, and most widely studied, involves the chemical shift of the core binding energy. In addition, smaller satellite peaks at higher binding energy often accompany the main ionization peak. Two mechanisms are invoked in order to explain these additional peaks. These are known as multiplet splitting and shake-up.

Analysis of the chemical shift, multiplet splitting, and shake-up transitions in insulating solids containing transition metals has been attempted. The insulating property of these materials tends to make the chemical shifts, referenced against a given standard, somewhat unreliable.[2] Multiplet splitting of the metal ion 3s lines for paramagnetic first-row transition metal complexes is generally considered to be related to the magnetic moment localized at the metal center, i.e., to the number of unpaired electrons on the metal.[3] The effect of multiplet splitting on the metal 2p lines generally results in line broadening of the main peak accompanied by weak features in the background.[4-6] Shake-up peaks in octahedral

transition metal complexes have generally been assigned to ligand-to-metal charge-transfer transitions.[7,8] The creation of a core hole can lead to a number of final states. In one, the electrons attain a configuration characteristic of the core-hole ground state. This configuration generally produces the main ionization peak. Alternatively, an electron may be promoted, subject to the monopole selection rules, to a higher electronic level producing shake-up satellites.[8]

It was believed that some metal 2p satellite peaks in photoelectron spectra of first-row transition metal complexes were associated with paramagnetism.[4] Presently, these satellites are viewed as arising from a shake-up process in which initially unoccupied molecular orbitals with the appropriate symmetry and energy provide a large enough transition probability for the lines to be observed.[8] This provides an explanation for the observations of satellite peaks in the 2p x-ray photoelectron spectra of such diamagnetic compounds as ScF_3, TiO_2, and TiF_4.[9] In this view a change in metal ion electronic configuration from paramagnetic to diamagnetic (e.g., iron(II), d^6; nickel(II), d^8) must result in a significant raising in energy of the unoccupied states if the shake-up satellites observed in the paramagnetic complexes are to be