Imidazolidine Adduct of 1. The synthesis of the formaldehyde adduct was identical with previous published procedures; recrystallized from benzene-petroleum ether, mp 208–209°, λ_{max} (50% v/v dioxane-water) 260 (ϵ 28,135). *Anal.* Calcd for $C_{16}H_{16}N_3Cl$: C, 67.23; H, 5.65; N, 14.71. Found: C, 67.34; H, 5.81; N, 14.72.

All utilized kinetic procedures have already been described in ref 2.

Acknowledgment. This research was supported by Research Grant GB-7246 from the National Science Foundation.

Homogeneous Catalysts for Olefin Disproportionations from Nitrosyl Molybdenum and Tungsten Compounds

E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman

Contribution from the Research and Development Department, Phillips Petroleum Company, Bartlesville, Oklahoma. *Received June 2, 1969*

Abstract: Homogeneous catalyst systems have been discovered which have effected the disproportionation of a variety of olefins. The catalysts are obtained from the reaction of nitrosyl molybdenum and tungsten derivatives with such organoaluminum compounds as $C_2H_5AlCl_2$ and $(CH_3)_3Al_2Cl_3$. Suitable group VIB element catalyst components include the known dichlorodinitrosylmolybdenum(II) and -tungsten(II) complexes or a large number of *in situ* preparations resulting from nitric oxide treatment. Among the possible olefin reactions are the conversion of 1-pentene to ethylene and 4-octene and the ethylene cleavage of 1,5-cyclooctadiene to give 1,5,9-decatriene.

The discovery of the olefin disproportionation process over heterogeneous catalysts[1,2] has been the impetus for further exploratory investigations into this unique reaction.[3,4] In a previous communication,[5] combinations of nitrosyl molybdenum and tungsten compounds with organoaluminum halides were reported to give homogeneous catalysts which exhibited this unusual property. This article will more clearly define these soluble systems, as well as broaden the scope of their preparation and utility.

Soluble catalyst systems derived from WCl_6–$EtAlCl_2$,[6,7] WCl_6–EtOH–$EtAlCl_2$,[6,7] and WCl_6–*n*-BuLi[8] have recently been disclosed. The new catalysts described herein not only contain a number of different ligands but also specify the singular effectiveness of the nitrosyl ligand. In contrast to the above systems from WCl_6[6–8] in which only internal olefins were satisfactory substrates, these nitrosyl-containing catalysts will effect disproportionation of α-olefins as well as ethylene-cleavage reactions.

Treatment of the green nitrosyl complex, $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$,[9] with $(CH_3)_3Al_2Cl_3$ in chlorobenzene at 0–5° resulted in a brown homogeneous solution. This was then treated with 1-pentene, under conditions wherein the ethylene formed could be vented at atmospheric pressure. Hydrolysis after 50 min followed by glpc analysis employing *n*-heptane as a standard indicated the presence of 48 mol % of 4-octene[4] and 48% of unreacted 1-pentene; no additional products other than ethylene were detected. A comparable reaction mixture allowed to stand 21 hr at ambient temperature gave, upon analysis using a cyclohexane standard, 33% of 1-pentene, 0.6% of C_6 olefins, 0.6% of C_7 olefins, and 61% of 4-octene. This catalyst combination with 1-octene at 0–5° for 30 min afforded 7-tetradecene[4] in 37% yield.

In the above reactions, little isomerization of the olefins was detected. However, when $C_2H_5AlCl_2$ was used as the cocatalyst with the above molybdenum compound, isomerization occurred to give a distribution of olefinic products (Table I). A comparison of the 1-pentene reaction with the above 1-pentene–$(CH_3)_3$-

Table I. Reactions with $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$ and $C_2H_5AlCl_2$[a]

	Reactant Products, wt %[b]	
	1-Pentene	1-Octene
C_4H_8	18 (16 + 0)[c]	7
C_5H_{10}	25 (23 + 0.1)	2
C_6H_{12}	28 (27 + 0.1)	3
C_7H_{14}	11 (10 + 1.5)	8
C_8H_{16}	16 (18 + 0.1)	20
C_9H_{18}	t[d]	18
$C_{10}H_{20}$		3
$C_{11}H_{22}$		4
$C_{12}H_{24}$		9
$C_{13}H_{26}$		13
$C_{14}H_{28}$		12
$C_{15}H_{30}$		0.4

[a] Both reactions were conducted utilizing 0.5 mmol of the molybdenum complex and 0.2 ml of $C_2H_5AlCl_2$ at ambient temperature for 16 hr. The 1-pentene reaction mixture contained 10 ml of the olefin and 10 ml of chlorobenzene, while the other system contained 20 ml of 1-octene and 20 ml of chlorobenzene. [b] Ethylene and propylene were present in both products but excluded from the calculations. [c] These percentages were obtained by glpc capillary column analysis of the hydrogenation product; the first number in each group refers to the linear product and the second to the branched material. [d] Traces of higher olefins were present.

---

(1) R. L. Banks and G. C. Bailey, *Ind. Eng. Chem. Prod. Res. Develop.*, 3, 170 (1964).

(2) The terms "dismutation" and "metathesis" have also been employed to describe this reaction.

(3) C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, 7, 269 (1967).

(4) D. L. Crain, *ibid.*, 13, 111 (1969).

(5) E. A. Zuech, *Chem. Commun.*, 1182 (1968).

(6) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, 3327 (1967).

(7) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, 90, 4133 (1968).

(8) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, 33, 3794 (1968).

(9) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, 3, 1609 (1964).

Al_2Cl_3 reaction of 21 hr duration conducted under similar conditions reveals the extent of olefin scrambling; approximately equivalent percentages of C_5 olefins remained, but only 16% of this product was in the C_8 olefin *vs.* 61% in the former. Hydrogenation of the 1-pentene product (percentages in parentheses) showed that only small amounts of branched olefins were being formed. As depicted, 1-octene also gave a mixture of olefins ranging from C_2 to C_{15}.

To determine the effectiveness of the catalyst from $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$ parallel preparations were made with $C_2H_5AlCl_2$, $(CH_3)_3Al_2Cl_3$, $(C_2H_5)_3Al_2Cl_3$, and $(C_2H_5)_2AlCl$. In the temperature range from 0° to 100°, the systems from $C_2H_5AlCl_2$ and $(CH_3)_3Al_2Cl_3$ were clearly superior to those from the other organoaluminum compounds. The preparations from $(CH_3)_3Al_2Cl_3$ appeared to be slightly more active than those from $C_2H_5ClAl_2$ at lower temperatures, but the latter were better at the higher temperatures. In general, both the $C_2H_5AlCl_2$ and $(CH_3)_3Al_2Cl_3$ systems exhibited olefin isomerization at the higher reaction temperatures, but none of the combinations effected isomerization to any extent at low temperatures (0–5° or lower) and at short reaction times. Studies regarding the catalyst activity as a function of the molar ratios of molybdenum to aluminum components will be forthcoming.[10]

Other nitrosyl molybdenum complexes were also examined. The dichlorodinitrosylmolybdenum(II) compound described as polymeric,[9] when treated with $(CH_3)_3Al_2Cl_3$, converted 1-pentene to 4-octene in 24 wt % yield upon reaction at 0–5° for 1 hr. However, this catalyst was insoluble in chlorobenzene and gave a considerable quantity of polymeric material as only 23% of the 1-pentene was recovered. With the exception of solubility differences, preparations from the pyridine derivative, $(C_5H_5N)_2Cl_2(NO)_2Mo$,[9] behaved similarly to those from the corresponding $(C_6H_5)_3P$ compound. Examples of this complex in conjunction with three organoaluminum compounds are illustrated in Table II. As in the $(C_6H_5)_3P$ case, the $(C_2H_5)_3Al_2Cl_3$ combination was not as active. With this pyridine system, reactions were completed with catalyst levels as low as 0.07 mmol of complex per mol of olefin. The lowered catalyst levels diminished the repeatability of the reactions which may be a reflection of the impurities concomitant in the system, olefin and solvent.

Table II. $(C_5H_5N)_2Cl_2(NO)_2Mo$ Systems with 1-Octene[a]

	Organoaluminum products, wt %[b]		
	$(CH_3)_3$-Al_2Cl_3	C_2H_5-$AlCl_2$	$(C_2H_5)_3$-Al_2Cl_3
C_7H_{14}	t[c]	2	1
C_8H_{16}	40	25	50
C_9H_{18}		3	t
$C_{12}H_{24}$		1	
$C_{13}H_{26}$	t	5	t
$C_{14}H_{28}$	60	64	49

[a] The reactions were conducted utilizing 0.1 mmol of the molybdenum complex, 10 ml of chlorobenzene, 0.1 ml of aluminum compound, and 10 ml of olefin at 50° for 25 min. [b] The gaseous products were vented at atmospheric pressure; the C_2 to C_6 olefins present were excluded from the calculations. [c] Traces were present.

In the evaluation of other molybdenum compounds, it was found that a variety of them were satisfactory catalyst precursors after treatment with gaseous nitric oxide (NO). The NO treatment was accomplished by subjecting the molybdenum derivative and solvent to an NO pressure of 1.7 atm for as little as 30 min. The excess NO was removed by evacuation prior to the introduction of the organoaluminum compound. In Table III, a number of molybdenum compounds are illustrated which were found to give excellent catalyst systems after such a treatment. The systems from the interaction of NO with $MoOCl_3$ and $MoCl_5$ were not entirely soluble in the reaction medium; however, with $MoCl_5$, *in situ* treatment with pyridine or phosphine ligands prior to the introduction of NO afforded soluble catalysts. Both of the pyridine-containing preparations of Table III had a catalytic activity upon interaction with $(CH_3)_3Al_2Cl_3$ nearly identical with that from pure $(C_5H_5N)_2Cl_2(NO)_2Mo$. In the absence of NO, some of the molybdenum compounds described in this table will afford catalyst systems which have demonstrated relatively small amounts of disproportionation under certain conditions, but a significant increase in activity is attained by the NO treatment procedure.

Table III. Catalysts Derived by Treatment with NO[a]

Mo compound	Mmol of Mo	Olefin	Time, min	RCH=CHR,[b] wt %
$[(C_6H_5)_3P]_2MoCl_4$[c]	0.2	1-C_8H_{16}	30	48
$(C_5H_5N)_2MoCl_4$[c]	0.2	1-C_8H_{16}	90	47
$(n\text{-}C_3H_7CN)_2MoCl_4$[d]	0.5	1-C_8H_{16}	60	40
$C_5H_5Mo(CO)_3I$[e]	0.2	1-C_8H_{16}	240	17
$(C_6H_5CO_2)_2MoCl_3$[f]	0.2	1-C_5H_{10}	27	60
$MoO_2(CH_3COCHCOCH_3)_2$	0.2	1-C_5H_{10}	60	18
$MoOCl_3$	0.5	1-C_5H_{10}	30	55
$MoCl_5$	0.1	1-C_5H_{10}	30	43
$MoCl_5 + C_5H_5N$[g]	0.1	1-C_8H_{16}	60	38
$MoCl_5 + (C_6H_5)_3PO$[h]	0.5	1-C_5H_{10}	60	45
$MoCl_5 + (n\text{-}C_8H_{17})_3PO$[h]	0.1	1-C_5H_{10}	30	17
$MoCl_5 + (n\text{-}C_4H_9)_3P$[h]	0.1	1-C_5H_{10}	60	58

[a] NO was pressured into a mixture of the molybdenum compound and chlorobenzene. All the reactions were conducted utilizing $(CH_3)_3Al_2Cl_3$ at ambient temperature. [b] Represents either 7-tetradecene or 4-octene as wt % of total products. [c] E. A. Allen, K. Feenan, and G. W. A. Fowles, *J. Chem. Soc.*, 1636 (1965). [d] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *ibid.*, 4531 (1964). [e] E. W. Abel, A. Singh, and G. Wilkinson, *ibid.*, 1321 (1960). [f] L. L. Melvin, U. S. Patent 3,042,694 (1962). [g] Excess pyridine was added and the resultant solid filtered. [h] A 1:3 ratio of $MoCl_5$ to ligand was utilized.

Nitrosyl tungsten derivatives also exhibited disproportionation activity upon treatment with organoaluminum halides. In Table IV, reactions conducted with $[(C_6H_5)_3P]_2Cl_2(NO)_2W$ are illustrated in which 2-pentene should afford 2-butene and 3-hexene as the primary products. In the cases investigated, the tungsten-containing systems appeared to be less active than those from the analogous molybdenum compounds.

Utilizing the technique of direct treatment with NO, it was also possible to prepare a number of tungsten catalyst precursors *in situ*. Treatment of a suspension of WCl_6 in chlorobenzene with NO at 1.7 atm followed by the addition of pyridine gave the preparation utilized in Table V. Reactions at higher temperature indicated

---

(10) W. B. Hughes, *J. Amer. Chem. Soc.*, **92**, 532 (1970).

Table IV. $[(C_6H_5)_3P]_2Cl_2(NO)_2W$ Systems with 2-Pentene[a]

	Organoaluminum products, wt %[b] $(CH_3)_3Al_2Cl_3$	$C_2H_5AlCl_2$
C_4H_8	9	14
C_5H_{10}	75	50
C_6H_{12}	15	28
C_7H_{14}	1	3
C_8H_{16} plus	0.1	7

[a] The reactions were conducted utilizing 0.11 mmol of the tungsten compound, 10 ml of chlorobenzene, 1 mmol of the organoaluminum compound, and 10 ml of 2-pentene at ambient temperature for 2 hr. [b] Traces of ethylene and propylene were excluded from the calculations.

Table V. WCl_6–NO–C_6H_5N Catalyst with 1-Octene[a]

	Organoaluminum products, wt %[b] $(CH_3)_3Al_2Cl_3$	$C_2H_5AlCl_2$
C_7H_{14}		0.2
C_8H_{16}	71	50
C_9H_{18}		2
$C_{10}H_{20}$		2
$C_{13}H_{26}$		2
$C_{14}H_{28}$	29	42

[a] The complex was prepared by treating WCl_6 with NO followed by pyridine (1:3 ratio). The reactions were conducted utilizing 0.1 mmol of tungsten, 10 ml of chlorobenzene, 0.2 ml of organoaluminum, and 10 ml of 1-octene at 50° for 1 hr. [b] Where present, the C_2 to C_6 product was excluded from the calculations.

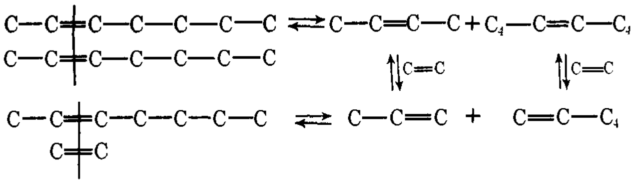
some evidence for the formation of polymeric materials. The lesser activity of this tungsten system under these reaction conditions to that from the comparable molybdenum system is readily apparent by comparison with Table II.

The formation of each carbon-number olefin, as described in Table I, for example, requires the interaction of a combination of α and internal olefins. The multiplicity of olefin reactions with these catalysts can be demonstrated with a variety of olefins. In a reaction of an internal olefin such as 2-heptene with itself the primary disproportionation products are 2-butene and 5-decene; however, when ethylene is present, propylene and 1-hexene are also produced (Table VI). These results are consistent with the double bonds undergoing an alignment on the catalyst to form a four-center intermediate, perhaps in a pseudo-cyclobutane arrangement.[3,4,6,7,10] The reaction of two molecules of 2-heptene in the designated orientation would produce 2-butene and 5-decene, but should one of the 2-heptene molecules be in the opposite orientation no new olefins

Table VI. Reaction of 2-Heptene with Ethylene[a]

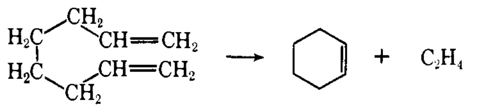
Products, wt %	Time, hr 1[c]	1[d]	3[d]	18[b,d]
C_3H_6		6	6	8
C_4H_8	12	3	5	8
C_6H_{12}		19	19	17
C_7H_{14}	61	66	55	47
$C_{10}H_{20}$	27	7	15	20

[a] The reactions were conducted utilizing 0.1 mmol of $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$, 10 ml of chlorobenzene, 0.1 ml of $(CH_3)_3Al_2Cl_3$, and 10 ml of 2-heptene at ambient temperature. [b] Traces of C_5H_{10}, internal C_6H_{12}, and C_9H_{18} were also detected. [c] No ethylene present. [d] Ethylene, 1.35 atm.

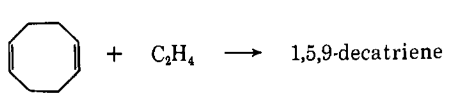


would be formed. Cleavage of 2-heptene with ethylene would give propylene and 1-hexene, but these products can also arise from the ethylene cleavage of 2-butene and 5-decene, respectively. In view of the facts that all olefins are eligible for reaction and that the reactions are reversible over these catalysts,[10] the products are readily interconvertible as depicted.

The reactions of α,ω-dienes and cyclic olefins with ethylene further illustrate the versatility of these catalysts. 1,7-Octatriene apparently underwent intramolecular disproportionation to give primarily cyclohexene. On the other hand, 1,5-hexadiene gave 1,5,9-decatriene by simple intermolecular reaction, with no cyclobutene being detected. 1,5,9-Decatriene can also be prepared by the ethylene cleavage of 1,5-cyclooctadiene.



The cleavage of cyclic olefins such as cyclooctene and cyclododecene in a similar manner produced 1,9-decadiene and 1,13-tetradecadiene, respectively.



Experimental Section

All reactions (involving moisture and/or air-sensitive compounds) were conducted under nitrogen in previously dried equipment. Analyses by gas–liquid partition chromatography (glpc) were performed on a F & M Model 720 and on a capillary Perkin-Elmer Model 226 chromatograph. Unless otherwise stated, the reactions were conducted in 7-oz clear-glass beverage-type bottles equipped with neoprene seals and perforated crown caps for syringe utilization. For the most part, Phillips Research or Pure Grade olefins were used. Cyclooctene, cyclododecene, and 1,7-octadiene were purchased from Columbian Carbon Co. 1,5-Hexadiene was obtained from Aldrich Chemical. The olefins were purified by passage over activated silica gel and magnesium oxide and/or distillation from calcium hydride. Solvents such as chlorobenzene were purged with nitrogen and stored over indicating molecular sieves. The aluminum alkyls were purchased from Texas Alkyls, Inc. Nitric oxide was obtained from the Matheson Co., Inc. The hexacarbonyls and halides of molybdenum and tungsten were purchased from Climax Molybdenum Co. The following descriptions are illustrative of the methods employed in conducting the various reactions collected in the Tables I–VI.

Reaction of 1-Pentene with $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$ and $(CH_3)_3Al_2Cl_3$. $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$ (0.5 mmol) and 10 ml of chlorobenzene, maintained in an ice bath, were treated with 0.2 ml of $(CH_3)_3Al_2Cl_3$ to give a clear brown solution. Utilizing an arrangement whereby the pressure was kept at atmospheric, 10 ml (6.4 g) of 1-pentene was introduced. After 50 min, the evolution of ethylene had essentially stopped and the mixture was hydrolyzed. Employing an *n*-heptane standard, glpc analysis indicated the presence of 3.1 g (48%) of unreacted 1-pentene and 2.5 g (48 mol %) of 4-octene. Except for ethylene, no other olefins were detected. From an analogous reaction mixture the 4-octene was found to contain 84% of the *trans* and 16% of the *cis* isomers.

Reaction of 1-Pentene with $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$ and $C_2H_5AlCl_2$ (Table I). A mixture of 0.5 mmol of the molybdenum compound and 10 ml of chlorobenzene, cooled in an ice bath, was treated with 0.2 ml of $C_2H_5AlCl_2$ and 10 ml (6.4 g) of 1-pentene.

The mixture was stirred at room temperature and atmospheric pressure for 16 hr before hydrolysis. Using a cyclohexane standard for glpc, the following were obtained: C_4H_8, 1.06 g; C_5H_{10}, 1.46 g; C_6H_{12}, 1.61 g; C_7H_{14}, 0.62 g; and C_8H_{16}, 0.93 g. Only traces of higher olefins appeared, while no attempt was made to analyze for ethylene or propylene. On a weight percentage basis, the C_4 to C_8 olefins were present in 18, 25, 28, 11, and 16%, respectively. A portion of this sample was hydrogenated and analyzed by capillary glpc; the values for the linear and branched materials in each carbon number are shown in parentheses in Table I.

Nitric Oxide Reaction with $MoCl_5$–(n-Bu)$_3$P (Table III). A mixture of 1.37 g (0.005 mol) of $MoCl_5$ and 50 ml of chlorobenzene was treated with 3.0 g (0.015 mol) of (n-Bu)$_3$P and subjected to NO at 1.7 atm for 4 hr. After venting, the excess NO was removed by evacuation; 1 ml of this solution and 9 ml of chlorobenzene were then treated with 0.2 ml of $(CH_3)_2Al_2Cl_3$ followed by 10 ml of 1-pentene. The ethylene was vented at atmospheric pressure. After 1 hr, the mixture was hydrolyzed; glpc analysis showed the presence of 41 wt % of unreacted C_5H_{10}, 0.3% of C_6H_{12}, 0.7% of C_7H_{14}, and 58% of C_8H_{16} which was principally 4-octene.

Nitric Oxide with WCl_6–C_5H_5N (Table V). A mixture of 0.4 g (0.001 mol) of WCl_6 in 20 ml of chlorobenzene was treated with NO at 1.7 atm for 1 hr. After venting, the reaction vessel was evacuated, adjusted to atmospheric pressure with nitrogen, and then treated with 0.24 g (0.003 mol) of dry pyridine. The catalyst mixture was subsequently prepared from 2 ml of the above solution (0.1 mmol), 8 ml of chlorobenzene, and 0.2 ml of $C_2H_5AlCl_2$. After adjusting the temperature to 50 ± 3°, 10 ml of 1-octene was added. The mixture was hydrolyzed after 1 hr and found to contain 0.2 wt % of C_7H_{14}, 50 wt % of recovered octenes, 2 wt % each of C_9H_{18}, $C_{10}H_{20}$, and $C_{13}H_{14}$ olefins, and 42 wt % of $C_{14}H_{28}$ which was mainly 7-tetradecene.[4] Traces of olefins in the range from ethylene to hexene were present but excluded from the calculations.

Reaction of 2-Heptene with Ethylene (Table VI). The catalyst solution was prepared from 0.08 g (0.1 mmol) of $[(C_6H_5)_3P)]_2Cl_2(NO)_2Mo$, 10 ml of chlorobenzene, and 0.1 ml of $(CH_3)_3Al_2Cl_3$ in an ice bath. Ethylene was then introduced at 1.35 atm and maintained at that pressure throughout the reaction. Ten milliliters of 2-heptene was added and the homogeneous mixture allowed to warm. Samples were withdrawn after 1, 3, and 18 hr, respectively, and hydrolyzed. The resultant glpc analyses are illustrated in Table VI, along with the analysis of a comparable run of 2-heptene alone. The relative amounts of *cis* and *trans* isomers in the internal olefins proved to be informative. The 2-butene in the 1-hr sample contained 37% of the *cis* and 63% of the *trans* isomer; this changed to 29% and 71%, respectively, in the 18-hr sample. The 2-heptene was 29% *cis* and 71% *trans* after 1 hr and 20% and 80% after 18 hr. The 5-decene was initially 23% *cis* and 77% *trans* and changed to 17% and 83% in the 18-hr sample. The starting 2-heptene contained 34% of the *cis* and 66% of the *trans* isomers. Therefore, the reaction appears to exhibit an initial selectivity of *cis* going to *cis* with an eventual conversion to the thermodynamic values as the reaction proceeds.[11]

1,7-Octadiene with $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$–$(CH_3)_3Al_2Cl_3$. A mixture of 0.1 g of $[(C_6H_5)_3P]_2Cl_2(NO_2)Mo$, 4 ml of chlorobenzene, and 1 ml of a 1 *M* solution of $(CH_3)_3Al_2Cl_3$ in chlorobenzene cooled in an ice bath was treated with 5 ml of 1,7-octadiene. After standing nearly 19 hr at ambient temperature, the reaction mixture was hydrolyzed. Analysis of the organic phase by glpc showed the presence of 91 wt % of cyclohexene, 6% of 1,7-octadiene, and 3% of material believed to be 1,7,13-tetradecatriene. Ethylene was present but not included in the analysis.

1,5-Hexadiene with $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$–$(CH_3)_3Al_2Cl_3$. The catalyst was prepared as described in the previous reaction and treated with 5 ml of 1,5-hexadiene while cooling in an ice bath. After 2 hr, hydrolysis and glpc analysis showed the presence of 66% unreacted 1,5-hexadiene, 24 wt % of 1,5,9-decatriene,[12] and 7% and 3%, respectively, of materials consistent with the structures 1,5,9,13-tetradecatetraene and 1,5,9,13,17-octadecapentaene. No cyclobutene could be detected and ethylene was excluded from the calculations.

Cleavage of 1,5-Cyclooctadiene with Ethylene. A catalyst was prepared from 0.1 g of $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$, 25 ml of chlorobenzene, and 0.2 ml of $(CH_3)_3Al_2Cl_3$ while cooling in an ice bath. 1,5-Cyclooctadiene (22 g) was added, followed immediately by ethylene at 20 atm. After 2 hr in the ice bath, the reaction mixture was hydrolyzed. Work-up showed the presence of 0.7 g of high molecular weight materials and 4.9 g of 1,5,9-decatriene.[12] This compound boils at 69° (29 mm) and appears to contain a *cis*-internal double bond by infrared analysis.

Cleavage of Cyclooctene with Ethylene. A mixture of 0.1 g of $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$, 25 ml of chlorobenzene, and 1 ml of a 1 *M* solution of $(CH_3)_3Al_2Cl_3$ in chlorobenzene was cooled in an ice bath. After 1 hr, the above solution was treated with ethylene at 1.35 atm, charged with 25 ml of cyclooctene, and finally pressured with ethylene to 20 atm. After 4 hr the reaction mixture was hydrolyzed. Analysis by glpc of the organic liquid indicated the presence of 83% of unreacted cyclooctene and 17 wt % of 1,9-decadiene.[12] Small quantities of high molecular weight material were also present.

Cleavage of Cyclododecene with Ethylene. A catalyst was prepared from 0.1 g of $[(C_6H_5)_3P]_2Cl_2(NO)_2Mo$, 9 ml of chlorobenzene, and 1 ml of a 1 *M* solution of $(CH_3)_3Al_2Cl_3$ in chlorobenzene. Pure cyclododecene (3 ml) was then added and the resultant mixture treated with ethylene at 27 atm. After 16 hr at ambient temperature, hydrolysis followed by glpc analysis of the organic layer showed the presence of 87% of unreacted cyclododecene and 13% of 1,13-tetradecadiene.[12] Small quantities of polymeric material were also evident.

Acknowledgments. We are indebted to Drs. D. L. Crain and R. F. Kleinschmidt for helpful discussions.

---

(11) W. B. Hughes, *Chem. Commun.*, 431 (1969).

(12) G. C. Ray and D. L. Crain, Belgian Patent 694,420.