Table V. Statistically Corrected Consecutive Complexity Constants for the Process $ob_3 \rightarrow lel_3$[a]

| | $[Co(chxn)_3]^{3+}$ | | $[Co(pn)_3]^{3+}$ | |
|---|---|---|---|---|
| | $\Delta H'^\circ$, kJ | $K$(cor) | $\Delta H'^\circ$, kJ | $K$(cor) |
| $ob_3 \rightarrow ob_2lel$ | −1.07 | 1.41 | −1.35 | 1.55 |
| $ob_2lel \rightarrow lel_2ob$ | −2.79 | 2.45 | −2.58 | 2.30 |
| $lel_2ob \rightarrow lel_3$ | −4.34 | 4.05 | −2.92 | 2.56 |

[a] Based upon the data from Table II. The relation $\Delta H'^\circ = -RT \ln [K(\text{cor})]$, $T = 373$ K, has been employed.

in these systems well-defined equilibrium constants with a magnitude of 1–4 corresponding to standard free energies of 0–4 kJ/mol, i.e., quantities that are small even in comparison with van der Waals energies and yet varying in a highly systematic way. The fact that intramolecular considerations lead to such regularities means that the free energy of solvation of the isomers is almost invariant or at least varies monotonically through the series $ob_3$, $ob_2lel$, $lel_2ob$, $lel_3$. Further, it is remarkable that the two tris(diamine) systems resemble one another as far as to the deviations between the experimental results and the pair relationship model.

**Acknowledgments.** We are indebted to Ole Monsted for interesting and stimulating discussions on the statistical parts of this paper and for his permission to use his computer programs for the treatment of the data. Thanks are due to S. Kallesoe Hansen for her repetition of the equilibrium experiments.

**Registry No.** Λ-$[Co((+)chxn)_3\text{-}\delta\delta\delta]Cl_3$, 59671-81-7; Δ-$[Co((+)chxn)_3\text{-}\delta\delta\delta]Cl_3$, 59727-64-9; Λ-$[Co((+)chxn)_2((-)chxn)\text{-}\delta\delta\lambda]Cl_3$, 59727-65-0; Δ-$[Co((+)chxn)_2((-)chxn)\text{-}\delta\delta\lambda]Cl_3$, 59727-63-8; Λ-$[Co((-)chxn)_2((+)chxn)\text{-}\lambda\lambda\delta]Cl_3$, 59727-66-1; Δ-$[Co((-)chxn)_2((+)chxn)\text{-}\lambda\lambda\delta]Cl_3$, 59727-62-7; Λ-$[Co((-)chxn)_3\text{-}\lambda\lambda\lambda]Cl_3$, 34369-95-4; Δ-$[Co((-)chxn)_3\text{-}\lambda\lambda\lambda]Cl_3$, 31537-08-3; *trans*-$[Co(py)_4Cl_2]Cl$, 27883-34-7.

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# Exchange of *N,N*-Dimethylacetamide on Dioxopentakis(*N,N*-dimethylacetamide)uranium(VI) Ion. Proton Magnetic Resonance Study

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*Received March 9, 1976* AIC60185S

The species $UO_2(DMA)_5^{2+}$ is shown from $^1H$ NMR studies to be the greatly predominant dioxouranium(VI) species existing in a series of dilute *N,N*-dimethylacetamide (DMA) solutions in $CD_2Cl_2$ diluent. Complete line shape analyses of exchange-modified $^1H$ NMR DMA line shapes show the rate law for DMA exchange to be $5k_{ex}[UO_2(DMA)_5^{2+}]$ over a 24.05-fold variation of [DMA]. The mechanism of the DMA exchange is considered to be of the D type. A typical set of rate parameters are $k_{ex}(260\text{ K}) = 81 \pm 2\ s^{-1}$, $\Delta H^{\ddagger} = 10.2 \pm 0.2$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -10.4 \pm 0.7$ cal deg$^{-1}$ mol$^{-1}$ for a solution in which $[UO_2(DMA)_5^{2+}]$, [DMA], and $[CD_2Cl_2]$ are respectively 0.1518, 0.7108, and 14.15 M.

The coordination number of uranium(VI) in dioxouranium(VI) species ranges from 6 or 7 with monodentate oxygen donor equatorial ligands to 8 with oxygen donor bidentate ligands, and the axial uranium(VI) to oxygen bonds are usually close to collinearity as shown in a number of solid-state studies.[1-6] Similar geometries appear to exist for monomeric dioxouranium(VI) species in solution, but it is only recently that NMR solution studies have determined the stoichiometry of the complex ions[7-9] $UO_2(H_2O)_4^{2+}$, $UO_2(DMSO)_4^{2+}$, and $UO_2(DMF)_5^{2+}$, where DMSO and DMF are dimethyl sulfoxide and *N,N*-dimethylformamide, respectively. The inert nature[10,11] of the axial oxygens presents the unusual situation where, in dioxouranium(VI) species, the processes of ligand substitution are likely to be restricted to rearrangements in a single plane during the formation of the transition state. Mechanistic interpretation is simplified by the absence of overall geometric and stoichiometric change accompanying identical ligand-exchange processes, and accordingly the exchange of *N,N*-dimethylacetamide (DMA) on $UO_2(DMA)_5^{2+}$ has been selected as a simple process through which to study ligand-substitution processes on dioxouranium(VI).

## Experimental Section

Dioxopentakis(*N,N*-dimethylacetamide)uranium(VI) perchlorate was prepared under dry nitrogen by refluxing hydrated dioxouranium perchlorate (G. Frederick Smith) (2.5 g) with triethyl orthoformate[12,13] (4.0 g) at 320–330 K for 1 h. Dry *N,N*-dimethylacetamide (2.0 g) was then added at room temperature and the resultant yellow crystals

Table I. Solution Compositions and Kinetic Parameters for the Exchange of DMA on $[UO_2(DMA)_5](ClO_4)_2$

| Soln | $[UO_2(DMA)_5{}^{2+}]$,[a] M | [DMA],[b] M | $[CD_2Cl_2]$, M | CN[c] | k(260 K),[d] $s^{-1}$ | $\Delta H^‡$,[e] kcal $mol^{-1}$ | $\Delta S^‡$,[e] cal $deg^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| i | 0.1518 | 0.7108 | 14.15 | 5.1 ± 0.1 | 81 ± 2 | 10.2 ± 0.2 | −10.4 ± 0.7 |
| ii | 0.0846 | 0.3495 | 14.27 | 5.0 ± 0.1 | 81 ± 3 | 9.7 ± 0.3 | −12.3 ± 1.1 |
| iii | 0.0297 | 0.1627 | 14.48 | 5.1 ± 0.1 | 90 ± 4 | 10.8 ± 0.5 | −4.0 ± 0.9 |
| iv | 0.0136 | 0.0747 | 15.02 | 5.0 ± 0.1 | 90 ± 5 | 9.6 ± 0.4 | −6.3 ± 0.7 |
| v | 0.0049 | 0.0296 | 15.05 | 5.0 ± 0.1 | 74 ± 7 | 8.9 ± 0.2 | −15.5 ± 0.8 |

[a] Added as $[UO_2(DMA)_5](ClO_4)_2$. [b] Added as DMA. [c] CN = number of DMA molecules bound per $UO_2{}^{2+}$ ion as determined from integration of the bound and free DMA resonances within the temperature range 180–235 K. [d] Errors quoted are the typical standard deviations obtained for each solution from the best fit of the experimental and theoretical line shapes. [e] Errors quoted are the standard deviation from the linear least-squares fit.

were filtered off, washed with dry ether, and pumped down on a vacuum line for 2 days. At all times exposure of the product to light was kept to a minimum to minimize the possibility of photochemically induced redox processes.[14] Anal. Calcd for $[UO_2(DMA)_5](ClO_4)_2$: C, 26.56; H, 5.01; N, 7.74; $UO_2$, 29.85. Found: C, 26.48; H, 5.15; N, 7.86; $UO_2$, 29.61. The yield was 97%. Analyses for $UO_2{}^{2+}$ were made with an ion-exchange technique,[15] and C, H, and N analyses were carried out by the Australian Microanalytical Service, Melbourne. No explosion hazard was encountered with $[UO_2(DMA)](ClO_4)_2$ but it should be noted that *such perchlorate salts are potentially explosive.*

Solutions of $[UO_2(DMA)_5](ClO_4)_2$ and DMA in $CD_2Cl_2$ diluent (CEA, 99.4%) were prepared under dry nitrogen in 2-$cm^3$ volumetric flasks. Each solution was transferred to a 5-mm o.d. NMR tube and was degassed on a vacuum line prior to sealing under vacuum not more than 1 h before commencement of the NMR experiment. The redistilled DMA (BDH) and $CD_2Cl_2$ were thoroughly dried over Linde 4A molecular sieves prior to use.

Proton NMR spectra were run at 90 MHz on a Bruker HX90E spectrometer in PFP mode using a deuterium lock. Depending upon the concentration of the sample, up to ten spectra were computer (Nicolet BNC 12) averaged and these spectra were then digitized onto paper tape (averaging from 300 to 1000 data points per spectrum respectively ranging from fast to slow exchange conditions) prior to line shape analysis through a CDC 6400 computer. The spectrometer temperature control was better than ±0.3 K.

## Results and Discussion

Under slow-exchange conditions the doublet arising from the *N*-methyl groups and the singlet arising from the acetyl group of coordinated dimethylacetamide appear downfield from the analogous resonances of free dimethylacetamide in the $^1H$ NMR spectrum as may be seen in Figure 1. Over the temperature range 180–235 K, in which chemical exchanged induced line shape modification was negligible, the ratios of the integrated areas of the coordinated and free doublets were consistent[16,17] with $UO_2(DMA)_5^{2+}$ being the greatly predominant species over the 24.05-fold concentration variation of the exchanging species as may be seen in Table I. The absence of any significant variation of the number of coordinated DMA molecules over this concentration range and the equivalence of these DMA molecules, as indicated by the absence of splitting of the coordinated resonances, indicates that perchlorate does not enter the first coordination sphere of uranium(VI) as is also observed in water,[7] DMSO,[8] and DMF.[9] It is concluded that the structure of $UO_2(DMA)_5^{2+}$ is a regular pentagonal bipyramid with DMA occupying all five equatorial sites. The factors which determine that water and DMSO occupy only four sites in the equatorial plane of dioxouranium(VI) species in solution while DMA and DMF occupy five are not apparent from this study, but these observations are consistent with conclusions drawn from the solid state that such occupancies permit optimum bonding distances with minimum steric hindrance.[1]

The kinetic parameters for the exchange of DMA on $UO_2(DMA)_5^{2+}$ were derived from a complete line shape analysis of the exchange-modified DMA line shapes over the temperature range 241–290 K (no line shape modification due to rotation about the C–N bond in DMA occurs within the experimental temperature range of this study[18]) using a previously described computer program.[19] Typical experimental and computed best fit line shapes are shown in Figure 1. The mean site lifetimes of coordinated and free DMA, $\tau_C$ and $\tau_F$, respectively, are related by eq 1 in which $\chi_C$ and $\chi_F$

$$\tau_C/\chi_C = \tau_F/\chi_F = 1/k_{ex}\chi_C \tag{1}$$

are mole fractions of coordinated and free DMA, respectively, and $k_{ex}$ is the first-order rate constant which may be expressed as in eq 2.

$$k_{ex} = (kT/h)\exp(-\Delta H^‡/RT)\exp(\Delta S^‡/R) = \text{rate}/5\,[UO_2(DMA)_5{}^{2+}] \tag{2}$$

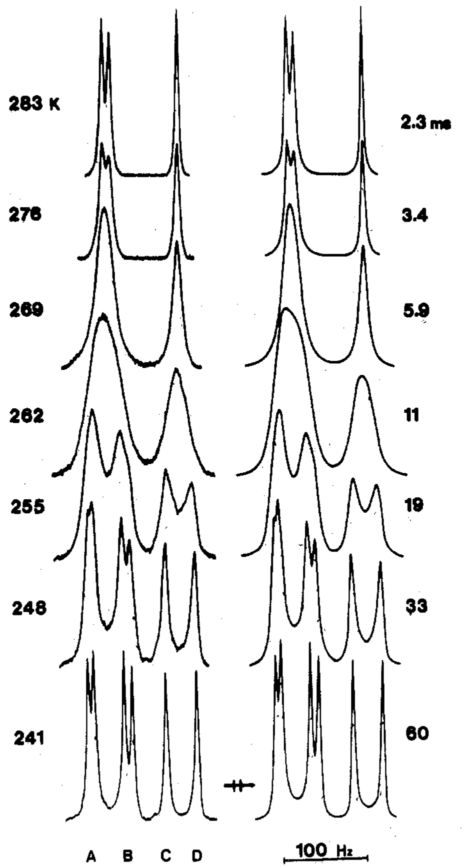

Figure 1. Experimental (left-hand side) and best fit computed $^1H$ NMR line shapes of a $UO_2(DMA)_5^{2+}$ (0.1518 M)–DMA (0.7108 M)–$CD_2Cl_2$ (14.15 M) solution. The experimental temperatures (K) and the best fit $\tau_C$ values appear on the left- and right-hand sides of the figure, respectively. The *N*-methyl doublet signals of coordinated and free DMA are labeled A (0.0 and 6.7) and B (41.8 and 51.6), respectively, and the coordinated and free acetyl signals are labeled C (91.1) and D (127.3), respectively. The numbers in parentheses are the chemical shifts (Hz) at 241 K relative to the low-field component of doublet A.

The observed $\tau_C$ values for the five solutions listed in Table I are plotted in Figure 2, from which it is apparent there is

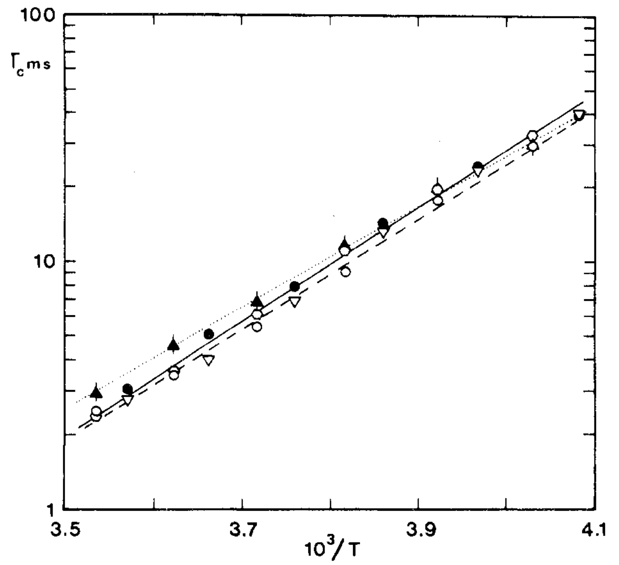

**Figure 2.** Semilogarithmic plots of $\tau_C$ data for the $UO_2(DMA)_5^{2+}$ system. The individual data for solutions i–v in sequence are respectively represented by hexagons, closed circles, triangles, circles, and closed triangles. The linear least-squares lines for solutions i, iv, and v are respectively represented by solid, dashed, and dotted lines. The analogous lines for solutions ii and iii are omitted for clarity.

no marked systematic trend in $\tau_C$ with solution composition. Activation parameters were calculated using $\tau_C$ values derived from experimental line shapes in the 248–283 K temperature range. The $k_{ex}$ values quoted for 260 K (the temperature in the midst of the line shape coalescence region which is considered to yield the most accurate data) in Table I are derived from a least-squares fit of $\tau_C$ to eq 2.

It is apparent from Figure 2 and the $k_{ex}$ (260 K) values in Table I that the rate of DMA exchange is almost independent of [DMA] and therefore the most likely exchange mechanism is either dissociative (D) or dissociative interchange ($I_d$)[20,21] as shown by eq 3 and 4, respectively, in which the asterisks

$$\begin{aligned}&UO_2(DMA)_5^{2+} + DMA^* \xrightarrow[\text{slow}]{k} UO_2(DMA)_4^{2+} + DMA + DMA^* \\ &UO_2(DMA)_4^{2+} + DMA + DMA^* \xrightarrow[\text{fast}]{} UO_2(DMA)_4DMA^{*2+} + DMA\end{aligned} \tag{3}$$

$$\begin{aligned}&UO_2(DMA)_5^{2+} + DMA^* \underset{\text{fast}}{\overset{K_{assn}}{\rightleftharpoons}} UO_2(DMA)_5^{2+}\cdots DMA^* \\ &UO_2(DMA)_5^{2+}\cdots DMA^* \underset{\text{slow}}{\overset{k'}{\rightleftharpoons}} UO_2(DMA)_4DMA^{*2+}\cdots DMA\end{aligned} \tag{4}$$

are typographical distinctions only. The dissociation of a DMA molecule from $UO_2(DMA)_5^{2+}$ is the rate-determining step in both mechanisms, but while the D mechanism is characterized by an intermediate $UO_2(DMA)_4^{2+}$ of sufficiently long lifetime to react with a different DMA molecule to complete the exchange process, the $I_d$ mechanism proceeds through the associated species $UO_2(DMA)_5^{2+}\cdots DMA$ in which a DMA molecule resides in the second coordination sphere. Thus while for the D mechanism $k_{ex} = k$ and is independent of [DMA], the variation of $k_{ex}$ with [DMA] for the $I_d$ mechanism is given by eq 5. When $K_{assn}[DMA] \ll 1$, $k_{ex}$ should exhibit a

$$k_{ex} = k'K_{assn}[DMA]/(1 + K_{assn}[DMA]) \tag{5}$$

first-order dependence upon [DMA], but when $K_{assn}[DMA] \gg 1$, $k_{ex} = k'$ and is independent of [DMA]. Within the variation of $k_{ex}$(260 K) exhibited over the experimental concentration range it is evident that the variation of $k_{ex}$ will not be detected if $K_{assn} \geq 120\ M^{-1}$. This value appears improbably high when compared to $K_{assn} = 0.35$ calculated from the Fuoss[22] equation for an interaction distance of 7 Å. While this calculated $K_{assn}$ value is of the same order of magnitude commonly assumed in the interpretation of uncharged ligand substitution on divalent metal ions,[23–27] it is pertinent, in the absence of an experimental determination of $K_{assn}$, to examine the possible composition of the second coordination sphere from other considerations. A statistical distribution of solvent in the second coordination sphere requires that the $[CD_2Cl_2]$:[DMA] ratio should vary from 19.9 to 508.4 over the solution compositions shown in Table I. The self-association of DMA in benzene is very small,[28] and in carbon tetrachloride a dimerization constant of 0.37 $M^{-1}$ applies,[29] from which it appears that specific interactions between coordinated and free DMA are unlikely to be important in determining the occupancy of the second coordination sphere. In addition it has been shown that no preferential solvation of $Ni(DMF)_6^{2+}$ by DMF in $CD_3NO_2$ diluent occurs,[30] a system which in overall charge and solvent type bears a resemblance to that under study here. These considerations indicate that an occupancy of the second coordination sphere by DMA consistent with $K_{assn} \geq 120\ M^{-1}$ is improbable and that instead [DMA] in the second coordination sphere is likely to show a variation akin to the total free [DMA] experimental variation. The D mechanism therefore appears to be operative in the exchange of DMA on $UO_2(DMA)_5^{2+}$. In view of the fourfold occupancy of the dioxouranium(VI) equatorial plane by water[7] and DMSO[8] in ground-state species the postulated existence of a reactive intermediate, $UO_2(DMA)_4^{2+}$, as required by the D mechanism appears plausible. The negative $\Delta S^\ddagger$ values observed for DMA exchange may be rationalized in terms of either of two models which seek to explain the observed correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ whereby negative $\Delta S^\ddagger$ values correspond to low $\Delta H^\ddagger$ values and vice versa for dissociative solvent and ligand exchange on metal ions. The first model[25,31] considers that major contributions to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ may arise from solvent rearrangement processes outside the first coordination sphere and in the case of negative $\Delta S^\ddagger$ values postulates that the major contribution to $\Delta S^\ddagger$ arises from a net decrease in the entropy of solvent outside the first coordination sphere occurring synchronously with the formation of the dissociative transition state. The second model[32,33] attributes the major contributions to both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ to interactions occurring within the first coordination sphere as a consequence of a given ligand's characteristics as a leaving group and as a labilizing nonleaving group. Thus ligands which are weakly bonded are expected to be labile leaving groups but poor labilizing groups and vice versa. The data in Table I, which represent the only detailed study of ligand exchange on dioxouranium(VI) species, are consistent with either of the two models and discrimination between them in their applicability to dioxouranium(VI) systems must await the study of many more such systems. The exchange of methanol on neptunium(V) ($k_{ex}$(273 K) = 9 × $10^4\ s^{-1}$, $\Delta H^\ddagger = 7.5$ kcal $mol^{-1}$, $\Delta S^\ddagger = -8$ cal $deg^{-1}\ mol^{-1}$) appears to be the only other detailed study of ligand exchange on an actinide ion.[34]

**Acknowledgment.** We thank the Australian Research Grants Committe for supporting this project.

**Registry No.** $[UO_2(DMA)_5](ClO_4)_2$, 59350-30-0; DMA, 127-19-5; dioxouranium perchlorate, 13093-00-0.

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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 $A[(CO)_5M–M'(CO)_5]$ (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,