Aluminum Alkoxides as Synthons for Methylalumoxane (MAO): Product-Catalyzed Thermal Decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$

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The thermal decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$, to yield Ph_3CMe and methylalumoxane ($[MeAlO]_n$, MAO), is initially catalyzed by the addition of $AlMe_3$; however, the reaction is also catalyzed by the MAO product. The overall reaction rate takes the form: rate = $k_{TMA}[\{Me_2Al(\mu\text{-}OCPh_3)\}_2][AlMe_3] + k_{MAO}[\{Me_2Al(\mu\text{-}OCPh_3)\}_2][MAO]$, where $k_{MAO} \gg k_{TMA}$. The $\Delta H^{\ddagger}$ for the $AlMe_3$- and MAO-catalyzed reactions have been determined as 175 ± 8 and 190 ± 15 $kJ\cdot mol^{-1}$, respectively. Both reactions show a large positive value of $\Delta S^{\ddagger}$ (41 ± 8 eu and <53 eu, respectively), indicative of a dissociative reaction. The thermal decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ is also catalyzed by Lewis acids, including $AlCl_3$, $AlCl_2Me$, and $AlClMe_2$. On the basis of the relative rates of the $AlMe_3$-catalyzed thermal decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$, $[Me_2Al(9\text{-Ph-fluoroxy})]_2$ (**1**), and $[Me_2Al(9\text{-Me-fluoroxy})]_2$ (**2**) and the MAO-catalyzed C-methylation of $[Me_2Al(\mu\text{-}OR)]_2$ [R = $CMePh_2$ (**3**), CMe_2Ph (**4**), CH_2Ph, C_6H_{11}, $C_6H_4\text{-4-}^tBu$ (**5**)], it is proposed that the rate-determining step for C-methylation involves heterolytic cleavage of the O−C bond and the formation of a carbonium ion. The more stable the carbonium ion, the faster the reaction. Additionally, it is proposed that Lewis acid catalysis is due to the formation of an asymmetrically bridged hemi-alkoxide, whose formation is an equilibrium process such that the observed rate of the reaction will be dependent on the equilibrium for the reaction of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with the Lewis acid.

Introduction

In 1974, Mole and co-workers published a series of papers describing the $AlMe_3$ C-methylation of tertiary alcohols, ketones, and carboxylic acids.[2−4] Ordinarily, the reaction of $AlMe_3$ with tertiary alcohols, R_3COH, would be expected to yield the alkoxide, i.e., eq 1.[5]

$$AlMe_3 + R_3COH \rightarrow \frac{1}{2}[Me_2Al(\mu\text{-}OCR_3)]_2 + CH_4 \quad (1)$$

When $AlMe_3$ was reacted with a tertiary alcohol in toluene solution at room temperature, then heated in a sealed ampule at temperatures ranging from 80 to 300 °C for up to 36 h, the C-methylation products were isolated, eq 2.[2]

$$R_3COH \xrightarrow{AlMe_3} R_3CMe \quad (2)$$

This reaction was found to be generally applicable for tertiary alcohols as well as secondary and primary alcohols, where one of the substituents was an aryl group; however, as the number of aryl substituents was reduced, the reaction was found to require more heat and longer reaction times.

Based on the isolation of similar products from the thermolysis of a mixture of R_3COH and $AlMe_3$ as well as the previous isolation of $[Me_2Al(\mu\text{-}OCR_3)]_2$, it was proposed that the C-methylation reaction occurs via the aluminum alkoxide compound.[2] The thermolysis of the alkoxide compounds was found to be slow unless performed in the presence of an excess of $AlMe_3$. It was noted by Mole and co-workers that the role of the $AlMe_3$ in increasing the rate of the reaction, and reducing the occurrence of side products, was due to the possible formation of the hemi-alkoxide, $Me_2Al(\mu\text{-}OCR_3)(\mu\text{-}Me)AlMe_2$. Despite this, the mechanism of C-methylation was proposed to involve protonation of the alkoxide oxygen since water was observed to further catalyze the C-methylation.[2,6] Although the specific role of the addition of the Lewis acid was unclear, it was known at that time that addition of water to $AlMe_3$ yields the formation of methylalumoxane ($[MeAlO]_n$, MAO).[7]

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[1] (a) Rice University. (b) University of Houston.

[2] Harney, D. W.; Meisters, A.; Mole, T. *Aust. J. Chem.* **1974**, *27*, 1639.

[3] Meisters, A.; Mole, T. *Aust. J. Chem.* **1974**, *27*, 1655.

[4] Meisters, A.; Mole, T. *Aust. J. Chem.* **1974**, *27*, 1665.

[5] (a) Mole, T. *Aust. J. Chem.* **1966**, *19*, 373. (b) Rogers, J. H.; Apblett, A. W.; Cleaver, W. M.; Tyler, A. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 3179.

[6] The effect of water in increasing the rate of MAO formation has been confirmed, as well as the effect of solid MAO; see: Sangokoya, S. A. US Patent, 6,013,820 2000.

[7] It should be noted that at this time it was known that addition of water to $AlMe_3$ yields the formation of methylalumoxane (MAO); see for example: Manyik, R. M.; Walker, W. E.; Wilson, T. P. U.S. Patent 3,242,099, 1966.

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At the simplest mechanistic level, it is possible to envision that the formation of the C-methylated products would result from a S_N2-type methylation of the quaternary carbon, i.e., a hydroxide/methyl exchange reaction (eq 3) related to the reaction of Ph$_3$EOH (E = Sn, Pb) and [(^{t}Bu)$_2$Ga(μ-OH)]$_3$ with AlMe$_3$.[8]

$$R_3C{-}OH + Me_2Al{-}Me \rightarrow R_3C{-}Me + Me_2Al{-}OH \quad (3)$$

Since tertiary alcohols generally do not undergo hydroxide/methyl exchange reactions, this mechanism is open to question.[9] We and others have reported that the reaction of Ph$_3$COH with AlMe$_3$ at room temperature gave [Me$_2$Al(μ-OCPh$_3$)]$_2$ in quantitative yield.[2,8]

Given the unusual nature of the C-methylation reaction and the similarity to the synthesis of catalytically active MAO through the hydroxide/methyl exchange between Ph$_3$EOH (E = Sn, Pb) with AlMe$_3$,[8] we have undertaken a study of the thermal decomposition of [Me$_2$Al(μ-OCPh$_3$)]$_2$ and the role of Lewis acids in catalyzing its thermal decomposition.

Results and Discussion

Thermolysis of [Me$_2$Al(μ-OCPh$_3$)]$_2$ in toluene-d_8 for 24 h at 100 °C results in no change in the ^{1}H NMR spectrum or precipitation from solution. Subsequent addition of 1 molar equiv of AlMe$_3$ (per alkoxide dimer) shows no reaction at room temperature for 8 h. Upon heating the reaction mixture to 80 °C, conversion of [Me$_2$Al(μ-OCPh$_3$)]$_2$ to Ph$_3$CMe was complete in 16 h. A comparable result was reported by Mole and coworkers.[2]

The aliphatic region of the ^{1}H NMR spectrum of the reaction mixture shows, in addition to the methyl peak of Ph$_3$CMe (δ = 2.01 ppm) and the toluene-d_7 septet (δ = 2.09 ppm), a broad two-component feature between 0 and −0.5 ppm. The sharper resonance ($\delta = -0.4$ ppm) is due to AlMe$_3$,[10] and the broad resonance is generally indicative of methylalumoxane ([MeAlO]$_n$, MAO).[11] The identity of the products was confirmed by NMR and catalytic activity (see Experimental Section) to be Ph$_3$CMe and MAO, eq 4.[12]

$$\frac{1}{2}[Me_2Al(\mu\text{-}OCPh_3)]_2 \xrightarrow{AlMe_3\ catalyst} [MeAlO]_n + Ph_3CMe \quad (4)$$

Thus, AlMe$_3$ appears to catalyze the thermal decomposition of [Me$_2$Al(μ-OCPh$_3$)]$_2$. This is confirmed by the observation that the initial rate increases with increased AlMe$_3$ concentration; see below. Furthermore, the overall reaction time decreases with increased AlMe$_3$ concentration. For example, the reaction of [Me$_2$Al(μ-OCPh$_3$)]$_2$ with 1/2, 1, 2, and 3 equiv of AlMe$_3$ at 90 °C reaches final completion after 350, 302, 204, and 141 min, respectively. The catalytic nature of the AlMe$_3$ is such that the reaction proceeds, albeit slowly, with as little as 10^{-5} molar equiv of AlMe$_3$. It is thus difficult to measure the uncatalyzed reaction time; however, extrapolation of the total reaction time as a function of the AlMe$_3$/[Me$_2$Al(μ-OCPh$_3$)]$_2$ mole ratio provides an estimate that the presence of trace quantities of AlMe$_3$ is sufficient to promote C-methylation. This result also demonstrates the importance of using material that has been repeatedly recystallized for the kinetic measurements, described below, to ensure the removal of traces of AlMe$_3$. As would be expected, as the concentration of AlMe$_3$ gets very large, the total reaction time becomes infinitely small. This relationship is observed experimentally as a large excess of AlMe$_3$ in the reaction mixture allows the decomposition of [Me$_2$Al(μ-OCPh$_3$)]$_2$ even at room temperature.

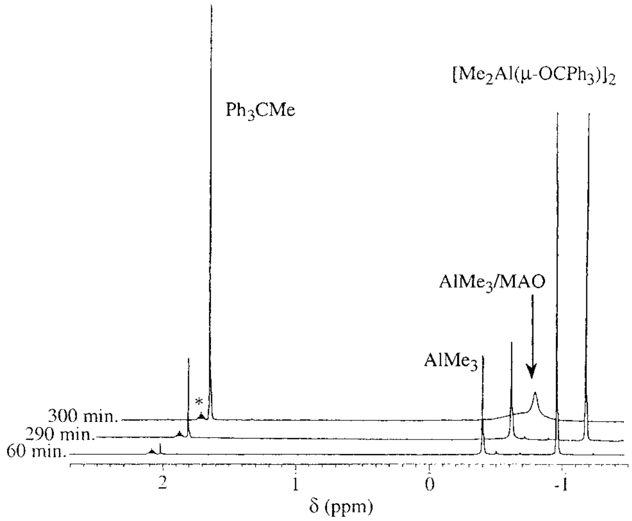

Figure 1. Representative ^{1}H NMR spectra, at 60, 290, and 300 min, for the thermolysis of [Me$_2$Al(μ-OCPh$_3$)]$_2$ with 1 equiv of AlMe$_3$ in toluene-d_8 at 90 °C.

Mole and co-workers[2] noted that the C-methylation reactions were all initially slow, but showed an increased reaction rate with reaction time. They proposed that the reaction was "autocatalytic". To better understand the formation of MAO, the product formation was followed by ^{1}H NMR as a function of reaction time.

A solution of [Me$_2$Al(μ-OCPh$_3$)]$_2$ in toluene-d_8 with 1 equiv of AlMe$_3$ was heated to 90 °C and the ^{1}H NMR spectrum collected every 10 min. Typical ^{1}H NMR spectra are shown in Figure 1. During the first 200 min the ^{1}H NMR remains almost unchanged, with only the slow growth in the CH_3 peak due to Ph$_3$CMe, and the concomitant decrease in the Al-CH_3 peak due to [Me$_2$Al(μ-OCPh$_3$)]$_2$ (δ −0.81 ppm).[13] The extent of the reaction as a function of time was measured by the relative conversion of [Me$_2$Al(μ-OCPh$_3$)]$_2$ to Ph$_3$CMe; see Figure 2. The formation of Ph$_3$CMe does not follow simple first-order kinetics over the entire reaction lifetime. Instead,

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[8] Obrey, S. J.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **2001**, 2456.

[9] Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1986; Vol. 1, Chapter 6.

[10] See: Apblett, A. W.; Barron, A. R. *Organometallics* **1990**, *9*, 2137, and references therein.

[11] See for example: Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* **1990**, *23*, 4489.

[12] It should be noted that MAO is known to be mixture of species, ordinarily obtained by adding water to AlMe$_3$, in which the Al:Me ratio is variable; however, for the present study a general formula of [MeAlO]$_n$ will be employed for convenience.

[13] During the course of the reaction small peaks are observed at −0.52, −0.72, and −1.27 ppm. These resonances are not present in the [Me$_2$Al(μ-OCPh$_3$)]$_2$ or AlMe$_3$ starting materials, and their relative concentrations remain constant until the end of the reaction when they are no longer observed. The chemical shift of these peaks is typical of an Al-CH_3 group, and they may be indicative of an intermediate species.

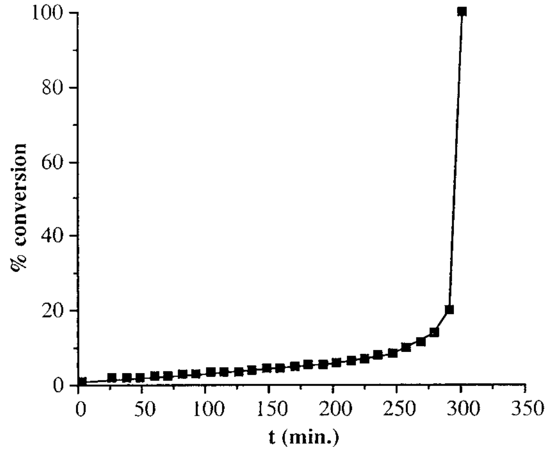

Figure 2. Plot of the % formation of Ph_3CMe as a function of time (min) for the thermolysis of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with 1 equiv of $AlMe_3$ in toluene-d_8 at 90 °C.

the rate of Ph_3CMe formation is initially slow with only 6% conversion after 200 min, at which point a rapid increase in rate is observed, such that 80% of the reaction is complete in the final 10 min. The form of Figure 2 suggests that the reaction is catalyzed not only by the $AlMe_3$ (eq 4) but also by the MAO product, i.e., eq 5.

$$\frac{1}{2}[Me_2Al(\mu\text{-}OCPh_3)]_2 \xrightarrow{\text{MAO catalyst}} [MeAlO]_n + Ph_3CMe \quad (5)$$

Product catalysis was confirmed by the addition of 10 mol % of commercial MAO solution to a solution of $[Me_2Al(\mu\text{-}OCPh_3)]_2$; see Experimental Section. With the addition of MAO complete conversion of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ to Ph_3CMe and MAO occurred in 30 min at only 80 °C. This should be compared to >200 min for the reaction with an equivalent amount of $AlMe_3$.

$AlMe_3$- versus MAO-Catalyzed Decomposition. To gain a better understanding of the overall decomposition reaction, as well as the relative effects of $AlMe_3$ and the MAO product, we have undertaken a kinetic study using ^1H NMR spectroscopy. For simplicity, the process will be considered as two separate reactions, in which $AlMe_3$ catalysis (eq 4) is operable during the initial reaction and MAO catalysis is dominant after sufficient product (i.e., MAO) has been produced. While the former reaction is relatively straightforward to study, the latter requires several assumptions; see below.

The thermal decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ shows a first-order dependence during the early stages of the reaction. A plot of k_{obs} versus $[AlMe_3]$ also shows a first-order dependence; see Figure 3. Thus, the initial reaction takes the form of eq 6 (where k_{TMA} is the rate constant associated with eq 4). A summary of values for k_{TMA} is given in Table 1.

$$-d[\{Me_2Al(\mu\text{-}OCPh_3)\}_2]/dt = k_{TMA}[\{Me_2Al(\mu\text{-}OCPh_3)\}_2][AlMe_3] \quad (6)$$

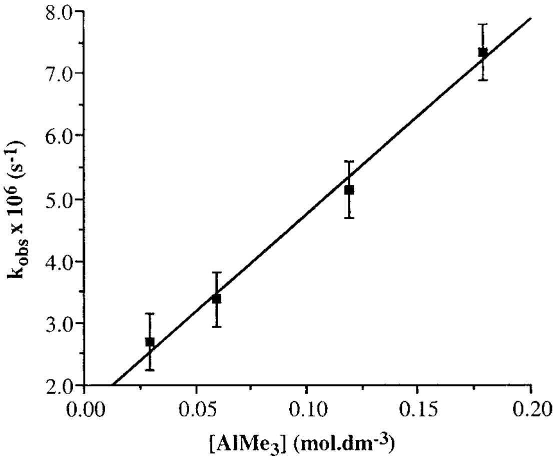

Figure 3. Plot of k_{obs} versus $[AlMe_3]$ for the decomposition at 90 °C of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ catalyzed by $AlMe_3$ ($k_{TMA} = 3.120 \times 10^{-5}$ $mol^{-1}\cdot dm^3\cdot s^{-1}$, $R = 0.993$).

Table 1. Selected Kinetic Data for the Decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ Catalyzed by $AlMe_3$ (k_{TMA}) and MAO (k_{MAO})

temperature (°C)	k_{TMA} ($mol^{-1}\cdot dm^3\cdot s^{-1}$)	k_{MAO} ($mol^{-1}\cdot dm^3\cdot s^{-1}$)
80	8.218×10^{-6}	9.991×10^{-3}
90	3.120×10^{-5}	1.402×10^{-2}
100	2.101×10^{-4}	1.860×10^{-1}

Determination of the temperature dependence for k_{TMA} allows for the determination of $\Delta H^{\ddagger}$ (175 ± 8 $kJ\cdot mol^{-1}$) and $\Delta S^{\ddagger}$ (41 ± 8 eu). The large positive value of $\Delta S^{\ddagger}$ indicates a dissociative reaction,[14] while the value for $\Delta H^{\ddagger}$ suggests of significant bond breaking in reaching the transition state.

It would be desirable to directly measure the MAO-catalyzed rate directly by the addition of MAO to $[Me_2Al(\mu\text{-}OCPh_3)]_2$; however, such a comparison is difficult for three reasons: (a) the presence of significant quantities of $AlMe_3$ (and other proprietary additives) in commercial samples,[15] (b) uncertainties as to the nature of MAO (oligomerization and structure distribution), and (c) uncertainties as to whether the MAO formed from $[Me_2Al(\mu\text{-}OCPh_3)]_2$ has the same composition as that formed from the hydrolysis of $AlMe_3$. We have, therefore, used the rate data from the final stage of the reaction.

During the final (rapid) stage of the thermal decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ the rate shows first-order dependence with respect to the concentration of remaining $[Me_2Al(\mu\text{-}OCPh_3)]_2$. A plot of k_{obs} versus the concentration of aluminum that is present as MAO (i.e., $[Al_{MAO}]$) also shows a first-order dependence. Thus, the MAO-catalyzed rate equation takes the form shown in eq 7 (where k_{MAO} is the rate constant associated with eq 5).

$$-d[\{Me_2Al(\mu\text{-}OCPh_3)\}_2]/dt = k_{MAO}[\{Me_2Al(\mu\text{-}OCPh_3)\}_2][Al_{MAO}] \quad (7)$$

The values for k_{MAO} are approximately 2 orders of magnitude larger than those for k_{TMA} under the same reaction conditions (Table 1).

Determination of the temperature dependence for k_{MAO} gives a value for $\Delta H^{\ddagger}$ of 190 ± 15 $kJ\cdot mol^{-1}$. Due

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(14) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; VCH: New York, 1997; p 14.

(15) Barron, A. R. *Organometallics* **1995**, *14*, 3581.

Table 2. Relative Catalytic Activity of Lewis Acids for the Decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$

	time for complete reaction		
Lewis acid	25 °C	50 °C	80 °C
MAO	<1 h		
$AlCl_3$	<1 h		
$AlCl_2Me$	<24 h		
$AlClMe_2$	no reaction	<24 h	
$AlMe_3$	no reaction	slow reaction	<24 h

to the uncertainties in the MAO speciation, only an estimation of $\Delta S^{\ddagger}$ can be obtained (<53 eu).[16] It is interesting that the activation parameters for the MAO-catalyzed reaction (eq 5) are essentially the same as those for the $AlMe_3$-catalyzed reaction (eq 4). The similarity between the $\Delta H^{\ddagger}$ for the MAO- and $AlMe_3$-catalyzed reactions is unexpected given an empirical observation of the relative rates. The mechanistic implication of this observation is discussed below. On the basis of the above the overall rate for the thermal decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ is given by eq 8.

$$-\mathrm{d}[\{Me_2Al(\mu\text{-}OCPh_3)\}_2]/\mathrm{d}t = (k_{TMA}[AlMe_3] + k_{MAO}[Al_{MAO}])[\{Me_2Al(\mu\text{-}OCPh_3)\}_2] \quad (8)$$

Reaction of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with Lewis Acids. To determine the generality of the Lewis acid-catalyzed decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$, the effects of the Lewis acids $AlCl_3$, $MeAlCl_2$, and Me_2AlCl were compared to that of $AlMe_3$ and MAO.

Reaction of an equimolar solution of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ and the appropriate Lewis acid resulted in the formation of MAO and Ph_3CMe; see Experimental Section. The relative rate of the reaction was found to increase with the accepted increased Lewis acidity of these compounds, i.e., $AlCl_3 > AlCl_2Me > AlClMe_2 > AlMe_3$. The reaction with $AlCl_3$ was found to be comparable to that with MAO, both reactions being complete in less than 1 h at 25 °C (Table 2). It should be noted that during reaction of $AlCl_3$ with $[Me_2Al(\mu\text{-}OCPh_3)]_2$, a bright yellow color appeared which persisted for 15 min; the presence and significance of this color change is discussed below.

The ability of any Lewis acid to catalyze the thermal decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ and the proportionality of the reaction rate to the Lewis acid strength suggest that the C-methylation reaction is not catalyzed by protonation of the alkoxide as previously suggested,[2] but by Lewis acid activation of the alkoxide.

Affect of Carbonium Ion Stability. During the investigation of the reaction of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with Lewis acids, we have noticed the presence of a transient bright yellow color. In the case of the reaction with $AlCl_3$, this color persists for 15 min during the initial reaction sequence even at elevated temperatures. In contrast, the reaction with $AlMe_3$ is colorless under the conditions required for reaction to proceed (≥80 °C). However, if the reaction mixture is cooled (25 °C) during the reaction, a bright yellow color is observed, but goes away again as the reaction is reheated to 80 °C. The source of this color may be identified by UV−visible spectroscopy (λ_{max} = 430 nm) as being due to the formation of the $[Ph_3C]^+$ carbonium.[17] In addition, quenching the yellow reaction mixture with EtOH results in the formation of Ph_3COEt.

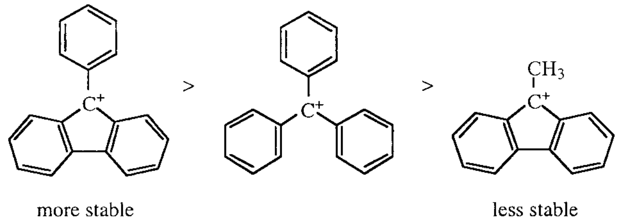

Figure 4. Relative stability of [9-phenylfluorene]$^+$, $[Ph_3C]^+$, and [9-methylfluorene]$^+$ carbonium ions.

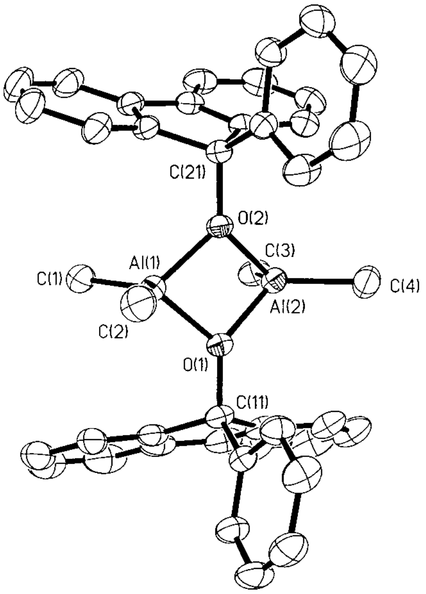

Figure 5. Molecular structure of $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (**1**). Thermal ellipsoids are shown at the 20% level, and hydrogen atoms are omitted for clarity.

The transient observation of the carbonium ion, $[Ph_3C]^+$, suggests that its formation is important in the catalyzed decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ to give MAO. If this is true, then the rate of $AlMe_3$-catalyzed decomposition of $[Me_2Al(\mu\text{-}OR)]_2$ will be dependent on the stability of the carbonium ion $[R]^+$. With this in mind, the relative decomposition rates of three structurally related compounds have been investigated on the basis of carbonium ions with differing stabilities: 9-phenylfluorene, Ph_3C, and 9-methylfluorene (Figure 4). The choice of the fluorene derivatives was dictated by the desire to provide carbonium ions that were comparatively more and less stable than $[Ph_3C]^+$.

The syntheses of $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (**1**) and $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (**2**) were accomplished by the reaction of $AlMe_3$ with 9-phenylflourenol and 9-fluorenone, respectively (see Experimental Section). Compounds **1** and **2** were characterized by ^1H, ^{13}C, and ^{27}Al NMR spectroscopy and mass spectrometry. Their dimeric nature in solution and solid state was confirmed by molecular weight measurements and X-ray crystallography. The molecular structures of $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (**1**) and $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (**2**) are shown in Figures 5 and 6; selected bond lengths and angles are given in Tables 3 and 4, respectively. The steric bulk

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(16) The extent of MAO oligomerization will have no effect on the slope of $-\ln(k_5/T)$ versus $1/T$, but will affect the intercept, i.e., the value for $\Delta S^{\ddagger}$.

(17) Katz, T. J.; Gold, E. H. *J. Am. Chem. Soc.* **1964**, *86*, 1600.

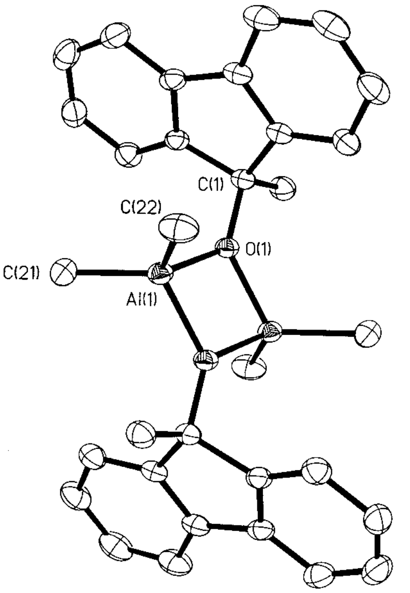

Figure 6. Molecular structure of $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (**2**). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (1)

Al(1)−O(1)	1.864(2)	Al(1)−O(2)	1.851(2)
Al(1)−C(1)	1.937(4)	Al(1)−C(2)	1.942(4)
Al(2)−O(1)	1.858(2)	Al(2)−O(2)	1.861(2)
Al(2)−C(3)	1.943(3)	Al(2)−C(4)	1.947(3)
O(1)−C(11)	1.461(3)	O(2)−C(21)	1.470(3)
O(1)−Al(1)−O(2)	79.39(9)	O(1)−Al(1)−C(1)	112.3(1)
O(1)−Al(1)−C(2)	110.7(1)	O(2)−Al(1)−C(1)	110.5(1)
O(2)−Al(1)−C(2)	112.8(2)	C(1)−Al(1)−C(2)	122.8(2)
O(1)−Al(2)−O(2)	79.29(9)	O(1)−Al(2)−C(3)	110.6(1)
O(1)−Al(2)−C(4)	113.0(1)	O(2)−Al(2)−C(3)	113.2(1)
O(2)−Al(2)−C(4)	110.7(1)	C(3)−Al(2)−C(4)	122.1(2)
Al(1)−O(1)−Al(2)	99.0(1)	Al(1)−O(1)−C(11)	130.2(2)
Al(2)−O(1)−C(11)	128.8(2)	Al(1)−O(2)−Al(2)	99.3(1)
Al(1)−O(2)−C(21)	129.2(2)	Al(2)−O(2)−C(21)	129.8(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (2)

Al(1)−O(1)	1.853(2)	Al(1)−C(21)	1.945(3)
Al(1)−C(22)	1.944(3)	O(1)−C(1)	1.454(3)
O(1)−Al(1)−O(1′)	80.17(7)	O(1)−Al(1)−C(21)	113.9(1)
O(1)−Al(1)−C(22)	112.5(1)	C(21)−Al(1)−C(22)	117.8(2)
Al(1)−O(1)−Al(1′)	99.83(7)	Al(1)−O(1)−C(1)	131.6(1)

of the 9-alkylfluoroxy ligands appears to control the orientation of the alkoxide ligand and consequently the geometry of the Al_2O_2 unit. The 9-Me-fluoroxy ligands in compound **2** are in an *anti* conformation with a centrosymmetric structure to the dimer and as expected a planar Al_2O_2 core.[18] In contrast, compound **1** crystallizes as a dimer with the 9-Ph-fluoroxy in an eclipsed conformation, resulting in a noncrystallographic mirror plane coplanar with the $AlMe_2$ moieties. The asymmetry with respect to the Al_2O_2 core causes a slight buckling of the core [the fold angle along the Al(1)···Al(2) vector is 160°]. Despite this slight distortion all the bond lengths and angles are within previously reported ranges.[19] It is worth noting that the O−C distances in compound **1** [1.461(3) and 1.470(3) Å] are slightly longer than those in compound **2** [1.454(3) Å] due to the greater steric bulk of the 9-Ph-fluoroxy ligand in the former.

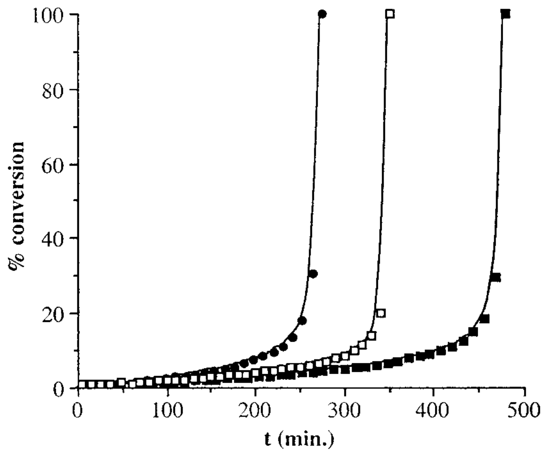

Figure 7. Plot of the reaction of $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (●), $[Me_2Al(\mu\text{-}OCPh_3)]_2$ (□), and $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (■) with 1 equiv of $AlMe_3$ at 60, 90, and 130 °C, respectively.

Each of $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (**1**), $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (**2**), and $[Me_2Al(OCPh_3)]_2$ were reacted with 1 equiv of $AlMe_3$. Initial investigations into the relative reactivities showed that the $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ reacted readily on gentle warming of the reaction mixture, while $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ required heating at 110 °C for 2 days for complete conversion. In each case the appropriate alkylation product was isolated and the resulting reaction mixture was found to contain catalytically active MAO; see Experimental Section.

To obtain an indication of the relative reactivities of these three compounds, the reactions were followed by ^1H NMR. The reactions of both $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ and $[Me_2Al(OCPh_3)]_2$ were carried out in toluene-d_8 solution at 60 and 80 °C, respectively. In contrast, to obtain a sufficiently fast reaction to be followed by NMR spectroscopy, the reaction of $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ was performed in *o*-xylene-d_{10} at 130 °C. All samples were equimolar with 1 equiv of $AlMe_3$. From the shape of the plots of % conversion versus time (Figure 7) it is clear that despite the differences in the temperature required for reaction, each compound follows a similar pathway; initial slow $AlMe_3$-catalyzed reaction, followed by rapid product (MAO)-catalyzed decomposition.

The time for the complete reaction follows the order $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (175 min @ 60 °C) > $[Me_2Al(\mu\text{-}OCPh_3)]_2$ (350 min @ 90 °C) > $Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (480 min @ 130 °C). The first-order rate constants for these reactions were determined: $Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$, $4.06 \times 10^{-5}\ mol^{-1}\cdot dm^3\cdot s^{-1}$ (@ 130 °C); $[Me_2Al(\mu\text{-}OCPh_3)]_2$, $5.45 \times 10^{-5}\ mol^{-1}\cdot dm^3\cdot s^{-1}$ (@ 80 °C); $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$, $8.69 \times 10^{-5}\ mol^{-1}\cdot dm^3\cdot s^{-1}$ (@ 60 °C). The relative rate of C-methylation for $[Me_2Al(\mu\text{-}OR)]_2$ is clearly dependent on the relative stability of the carbonium ion, $[R]^+$.

Reaction of $[Me_2Al(\mu\text{-}OR)]_2$ with MAO. As was noted earlier, Mole and co-workers investigated the reaction of a range of tertiary alcohols with a slight

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[18] In the absence of steric effects, dimeric aluminum alkoxide forms centrosymmetric dimers in which the Al_2O_2 core is planar; see: Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409.

[19] See for example: (a) Francis, J. A.; McMahon, C. N.; Bott, S. G.; Barron, A. R. *Organometallics* **1999**, *18*, 4399. (b) Francis, J. A.; Bott, S. G.; Barron, A. R. *J. Organomet. Chem.* **2000**, *597*, 29. (c) Cetinkaya, B.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F. *Polyhedron* **1990**, *9*, 239. (d) Kumar, R.; Sierra, M.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1990**, *9*, 484.

Table 5. Alkylation Products and Relative Rates for the Complete Reaction of [$Me_2Al(\mu\text{-}OR)]_2$ with MAO at 80 °C and the Comparitive Rate of the Reaction Catalyzed by $AlMe_3$

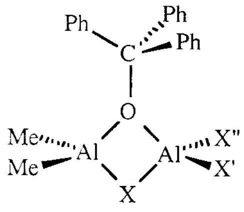
R	product	reaction time	comparison to $AlMe_3$ catalyzed
Ph_3C-	Ph_3C-Me	<30 min	6 h @ 90 °C
Ph_2MeC-	Ph_2MeCMe	<12 h	20 h @ 85 °C
$PhMe_2C-$	$PhMe_2C-Me$	<12 h	142 h @ 90 °C
$PhCH_2-$	$PhCH_2-Me$	<12 h	no reaction
9-Me-fluorone−	9,9-Me_2-fluorone	<12 h	8 h @ 130 °C
9-Ph-fluorone−	9-Me-9-Ph-fluorone	<30 min	4 h @ 60 °C
$C_6H_{11}-$	$C_6H_{11}-Me$	<3 day	no reaction
tert-butyl−	Me_3C-Me	<12 h	42 h @ 120 °C
4-*tert*-butylphenol−	no reaction	n/a	n/a

molar excess of $AlMe_3$.[2] Upon the basis of the foregoing it is reasonable to propose that these reactions occurred by the in-situ formation of the alkoxide compounds whose decomposition was catalyzed initially by the slight excess of $AlMe_3$, and subsequently by the formation of MAO as the aluminum-containing product. Even under the conditions employed, these reactions were slow and required elevated temperatures. Given the greater catalytic activity of MAO, it should be possible to decrease the reaction times of these reactions and catalyze the decomposition of previously stable alkoxides.

A series of dimethylaluminum alkoxides were synthesized by the reaction of $AlMe_3$ with the corresponding alcohol; see Experimental Section. Addition of a 10% molar equiv of commercial MAO was used as the catalyst, and the time for formation of the alkane product was monitored by ^1H NMR spectroscopy. The results of these studies are presented in Table 5. As expected, these reactions are all significantly faster than the equivalent $AlMe_3$-catalyzed reactions. However, more important is that the secondary alkoxide, [$Me_2Al(\mu\text{-}OC_6H_{11})]_2$, undergoes C-methylation. In Mole's original investigations, secondary alcohols did not undergo C-methylation.[2] Thus, MAO may be used as a catalyst for the C-methylation of secondary alcohols. We note that the 4-*tert*-butyl phenoxide does not show any reaction, even after 7 days. On the basis of our proposed reaction dependence on the stability of the carbonium ion, however, the unreactivity of phenoxide derivatives is not surprising.

Mechanism of C-Methylation. Although the C-methylation reaction was extensively studied by Mole and co-workers,[2] there were a number of questions that remained unanswered. What is the role of the Lewis acid in the facilitation of the reaction, and why are rates of the $AlMe_3$- and MAO-catalyzed reactions vastly different despite the similarity in the $\Delta H^\ddagger$ for the reactions?

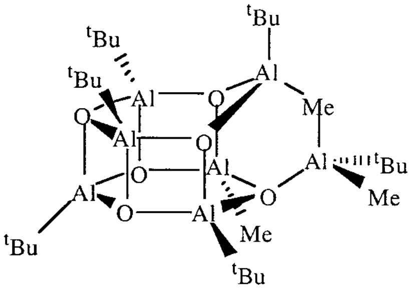
Mole and co-workers[2] postulated that the increased reaction rate in the presence of excess $AlMe_3$ was due to the formation of an asymmetrically bridged dimeric alkoxide, i.e., [$Me_2Al(\mu\text{-}OCPh_3)(\mu\text{-}Me)AlMe_2$] (**I**, $X = X' = X'' = Me$). Our observation of the reaction rate being first order with respect to both [$Me_2Al(\mu\text{-}OCPh_3)]_2$ and $AlMe_3$ agrees with this pathway. This proposal would also explain the enhancement of the rate with aluminum chlorides. Since the formation of the mixed dimer, **I**, would be an equilibrium process (eq 9). The position of the equilibrium would be dependent on the stability of the bridging group (i.e., μ-Cl versus μ-Me). Similar ligand exchange reactions are well known in the literature.[9]



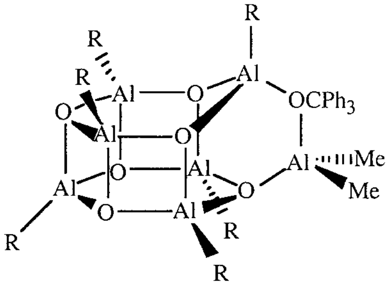
(I)

$$[Me_2Al(\mu\text{-}OCPh_3)]_2 + Al_2Me_6 \overset{K_{eq}}{\rightleftharpoons} 2[Me_2Al(\mu\text{-}OCPh_3)(\mu\text{-}Me)AlMe_2] \quad (9)$$

We have previously demonstrated that the catalytically active structures of alkylalumoxanes are caged compounds,[20] and we have proposed their activity derives from their latent Lewis acidity of the opening of the cage structure.[21] We have recently reported that $AlMe_3$ reacts with the *tert*-butylalumoxane [$(^tBu)Al(\mu_3\text{-}O)]_6$ to give cage-opened structures (e.g., **II**).[22] It is reasonable to propose that a similar structure would be formed with dimethylaluminum alkoxides, i.e., **III**.[23]



(II)



(III)

Although the formation of a complex between the Lewis acid and [$Me_2Al(\mu\text{-}OCPh_3)]_2$ is reasonable in view of the measured rate equations, it does not explain the activation parameters. The large value for $\Delta S^\ddagger$ is suggestive of a dissociative reaction, while the value for

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(20) (a) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971. (b) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, *13*, 2957.

(21) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465.

(22) Watanabe, M.; McMahon, C. N.; Harlan, C. J.; Barron, A. R. *Organometallics* **2001**, *20*, 460.

(23) It should be noted that while a bridging alkoxide ligand in **III** would be preferential on electronic grounds, steric factors may favor a terminal alkoxide.

$\Delta H^{\ddagger}$ is larger than we have determined for the base cleavage of the $[Me_2Al(\mu\text{-}OCPh_3)]_2$ [73(3) kJ·mol^{-1}].[24] Therefore, the rate-determining step in the reaction shown in eq 4 is not associated with cleavage of the dimer; that is, eq 9 is not the rate-determining step but a preequilibrium reaction.

The similarities of the $\Delta H^{\ddagger}$ for the $AlMe_3$- and MAO-catalyzed reactions suggest a commonalty of rate-determining steps. Given that the formation of **I** and **III** would be expected to energetically different, it is unlikely that the formation of these species is the rate-determining step. We have demonstrated that the stability of the carbonium ion is of primary importance in determining the rate of C-methylation reaction. In addition, we have observed the formation of $[CPh_3]^+$ spectroscopically. This suggests that the heterolytic cleavage of the O−C bond is important and the measured values for $\Delta H^{\ddagger}$ (175−190 kJ·mol^{-1}) would be appropriate for the cleavage of an O−C bond.[25] We propose, therefore, that the formation of the carbonium ion from the mixed dimer, **I**, is the rate-determining step (eq 10). The formation of $MeCPh_3$ will undoubtedly occur via abstraction of Me^- from the anionic alumoxane (cf., eq 10).

$$[Me_2Al(\mu\text{-}OCPh_3)(\mu\text{-}Me)AlMe_2] \xrightarrow{k_{O-C}} [Me_2Al(\mu\text{-}O)(\mu\text{-}Me)AlMe_2]^- + [CPh_3]^+ \quad (10)$$

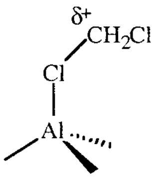
If the cleavage of an O−C bond is the rate-determining step, then the rate will follow that of a classical preequilibrium system in which the mixed intermediate, e.g., $[Me_2Al(\mu\text{-}OCPh_3)(\mu\text{-}Me)AlMe_2]$, is in equilibrium with the reactants. The rate law will have the form of second-order reaction (eq 11) with a composite rate constant dependent on the equilibrium constant for the formation of the adduct (K_{eq}, cf. eq 9) with the Lewis acid and the rate of O−C bond cleavage (k_{O-C}), eq 12.

$$-d[\{Me_2Al(\mu\text{-}OCPh_3)\}_2]/dt = k[\{Me_2Al(\mu\text{-}OCPh_3)\}_2][\text{Lewis acid}] \quad (11)$$

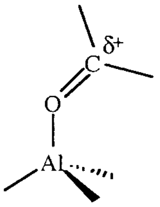
$$k = k_{O-C}K_{eq} \quad (12)$$

Thus, the activation energy will be solely dependent on the cleavage of the O−C bond, which in turn is a function of the stability of the resulting carbonium ion. However, the observed rate of the reaction will be dependent on the equilibrium for the reaction of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with the Lewis acid. On the basis of the stability of the bridging ligands, the K_{eq}, and hence the reaction rate, would be expected to follow the order $AlCl_3 > AlCl_2Me > AlClMe_2 > AlMe_3$. This is indeed observed. Furthermore, the relative rate of the MAO-catalyzed reaction suggests that the formation of a complex with $[Me_2Al(\mu\text{-}OCPh_3)]_2$ is favored in comparison with the more traditional Lewis acids.

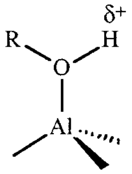
Given the formation of a Lewis acid complex with $[Me_2Al(\mu\text{-}OCPh_3)]_2$, why should this activate the O−C bond toward cleavage? We have previously discussed the generality of the effect on a coordinated ligand by a group 13 Lewis acid as being the increase of positive charge on the β-substituent, for example, the Lewis acidic group 13 halide activation of (a) alkyl halides for Friedel−Craft alkylation of aromatic hydrocarbons (**IV**),[26] (b) organic carbonyls toward alkylation and reduction (**V**),[27,28] and (c) weak protic acids (water and alcohols) toward alkane elimination (**VI**).[29] Recently, we have reported examples in which a group 13 Lewis acid will activate a second metal through a similar effect (**VII**).[30]



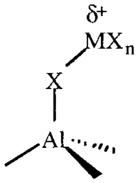
(IV)



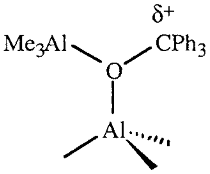
(V)



(VI)



(VII)



(VIII)

The formation of $[Me_2Al(\mu\text{-}OCPh_3)(\mu\text{-}Me)AlMe_2]$ may be considered as a Lewis acid−base complex between $AlMe_3$ and the oxygen atom of the aluminum alkoxide. In this regard, it is expected that an increased positive charge would be placed on the alkoxide's quaternary carbon (**VIII**), which in turn will promote the heterolytic cleavage of the O−C bond. A similar effect would be expected for MAO and the alkylaluminum chlorides.

Conclusions

We propose the following general pathway for the Lewis acid-catalyzed C-methylation of aluminum alkoxides resulting in the formation of methylalumoxane (MAO). The dimethylaluminum alkoxide reacts with a Lewis acid to form a mixed intermediate (**I**). This equilibrium reaction (cf. eq 9) is dependent on the identity and concentration of the Lewis acid. The Lewis acid activation of the alkoxide's quaternary carbon results in the heterolytic cleavage of the O−C bond and the formation of an ion pair.[31] Although we have no

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[24] Obrey, S. J.; Bott, S. G.; Barron, A. R. *Organometallics* **2001**, in press.

[25] Typical values for an alcohol O−C bond strength are 380 kJ·mol^{-1}: Lowery, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper Collins: New York, 1987; pp 161−162.

[26] (a) Whitmore, F. C. *J. Am. Chem. Soc.* **1932**, *54*, 3274. (b) Olah, G. A.; Kuhn, S. J.; Flood, S. H. *J. Am. Chem. Soc.* **1962**, *84*, 1688. (c) Olah, G. A.; Kobayashi, S.; Tashiro, M. *J. Am. Chem. Soc.* **1972**, *94*, 7448.

[27] See: Power, M. B.; Nash, J. R.; Healy, M. D.; Barron, A. R. *Organometallics* **1992**, *11*, 1830, and references therein.

[28] See for example: (a) Power, M. B.; Bott, S. G.; Atwood, J. L.; Barron, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 3446. (b) Power, M. B.; Apblett, A. W.; Bott, S. G.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 2529. (c) Power, M. B.; Bott, S. G.; Clark, D. L.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 3086.

[29] McMahon, C. N.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 3129.

[30] (a) Borovik, A. S.; Bott, S. G.; Barron, A. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 4117. (b) Borovik, A. S.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **2001**, in press.

[31] We note that the formation of an anionic alumoxane of the formula $[Me_2Al(\mu\text{-}O)AlMe_3]^-$ has been previously reported and structurally characterized; see: Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 302.

direct evidence, it is expected that this is the rate-determining step. The ion pair will react further to alkylate the carbonium ion and form a neutral alumoxane.[32] The relative catalytic activity of a Lewis acid is dependent on its ability to form a mixed intermediate (**I**).

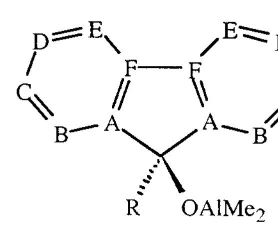
The most common method for formation of MAO is the reaction of $AlMe_3$ with water. Unfortunately, this is not an easily controlled reaction.[33] Gaining insight into the mechanism of formation for MAO is an important step in the development of synthetic strategies to yield MAO with high and (perhaps what is more important) consistent catalytic activity. The synthesis of MAO from readily prepared dimethylaluminum alkoxides with much lower sensitivity to air and moisture offers an interesting entry into the controlled synthesis of MAO. Furthermore, while we have demonstrated that the MAO prepared herein has a catalytic activity comparable to that of commercial samples, our future studies will concentrate on the reproducible nature of the reaction as well as the relative reactivities of various MAO samples. Furthermore, we note that the MAO prepared by the methods described herein is soluble in aliphatic hydrocarbon solvents. This is in contrast to MAO prepared from the hydrolysis of $AlMe_3$ that is soluble in aromatic solvents. Finally, we note that MAO appears to be suitable as an active agent for the C-methylation of alcohols that do not undergo reaction with $AlMe_3$.

Experimental Section

The syntheses of $[Me_2Al(\mu\text{-}OR)]_2$ were performed according to the literature methods.[2,5b,7,23] Ethylene (Matheson polymer grade) was used as received. MAO (30 wt % in toluene) and $AlMe_3$ were generously provided by Albemarle Corporation. Unless otherwise noted all procedures were performed under purified nitrogen or argon. All solvents were distilled and degassed before use. Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. IR spectra (4000−400 cm^{-1}) were obtained using a Nicolet 760 FT-IR infrared spectrometer. IR samples were prepared as Nujol mulls between KBr plates. NMR spectra were obtained on Bruker AM-250 and Avance 200 and 400 spectrometers using (unless otherwise stated) benzene-d_6 solutions. Chemical shifts are reported relative to internal solvent resonances (^1H and ^{13}C) and external $[Al(H_2O)_6]^{3+}$ (^{27}Al).

Thermal Decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$. $[Me_2Al(\mu\text{-}OCPh_3)]_2$ (500 mg, 0.79 mmol) was dissolved in toluene (100 mL) containing $AlMe_3$ (57 mg, 0.79 mmol). The reaction was heated for 16 h at 80 °C. The reaction mixture was divided into two parts. The first part was hydrolyzed (5 mL) followed by extraction with Et_2O (3 × 50 mL). The organic layer was washed with $NaHCO_3$ and brine and dried over $MgSO_3$. Removal of the volatiles under vacuum gave a white solid that was determined to be Ph_3CMe by ^1H and ^{13}C NMR spectroscopy.[34] To the second fraction was added Cp_2ZrCl_2 (231 μg, 0.79 μmol). Ethylene was bubbled through the reaction mixture, yielding a white solid, confirmed to be polyethylene by ^{13}C NMR spectroscopy[35] and TG/DTA.[36]

$[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (1). To a solution of $AlMe_3$ (0.500 g, 6.95 mmol) in toluene (50 mL) was added dropwise a solution of 9-phenylfluorenol (1.790 g, 6.94 mmol) in toluene (50 mL) over a period of an hour. The reaction mixture was stirred for 6 h, whereupon the solvent was removed under vacuum. The resulting white powder was redissolved in CH_2Cl_2 (50 mL) and filtered. The solution was concentrated and cooled to −33 °C. The resulting clear colorless crystals were collected by filtration. Yield: 89%. Mp: 170 °C (dec). ^1H NMR: δ 7.55 [4H, d, J(H−H) = 14.3 Hz, o-CH], 7.32 [4H, d, J(H−H) = 14.3 Hz, m-CH], 6.9−7.12 (14H, m, CH), −0.85 (12H, s, AlCH_3). ^{13}C NMR: δ 148.7 (**IX**, A), 142.8 (OCC, Ph), 141.0 (**IX**, F), 130.4 (**IX**, B), 128.8 (o-Ph), 128.0 (p-Ph), 127.3 (m-Ph), 126.9 (**IX**, C), 123.2 (**IX**, D), 121.1 (**IX**, E), 88.1 (OC), −5.76 (Al-CH_3). ^{27}Al NMR: δ 140 ($W_{1/2}$ = 7650 Hz).



(**IX**)

$[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (2). To a solution of $AlMe_3$ (1.00 g, 13.89 mmol) in toluene (50 mL) was added dropwise a solution of 9-fluorenone (2.25 g, 12.5 mmol) in toluene (50 mL) over a period of an hour. The reaction mixture was stirred for 6 h, whereupon the solvent was removed under vacuum. The resulting white powder was redissolved in CH_2Cl_2 (50 mL) and filtered. The solution was concentrated and cooled to −33 °C. The resulting colorless crystals were collected by filtration. Yield: 94%. Mp: 240−248 °C. ^1H NMR ($CDCl_2$): δ 7.59 [4H, s, J(H−H) = 7.0 Hz, CH], 7.46 [4H, d, J(H−H) = 7.0 Hz, CH], 7.36 [4 H, td, J(H−H) = 7.4 Hz, J(H−H) = 1.2 Hz, CH], 7.29 [4H, td, J(H−H) = 7.4 Hz, J(H−H) = 1.2 Hz, CH], 1.85 (6H, s, CH_3), −1.28 (12H, s, Al−CH_3). ^{13}C NMR: δ 147.5 (**IX**, A), 138.9 (**IX**, F), 129.6 (**IX**, B), 128.2 (**IX**, C), 124.7 (**IX**, D), 120.2 (**IX**, E), 82.4 (OC), 26.9 (CH_3), −7.61 (Al-CH_3). ^{27}Al NMR: 147 ($W_{1/2}$ = 7350 Hz).

Thermal Decomposition of $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$. $[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (**1**) (500 mg, 0.79 mmol) was dissolved in toluene (100 mL) containing $AlMe_3$ (57 mg, 0.79 mmol). The reaction was heated for 24 h at 60 °C. The reaction mixture was divided into two parts. The first part was hydrolyzed (5 mL) followed by extraction with Et_2O (3 × 50 mL). The organic layer was washed with $NaHCO_3$ and brine and dried over $MgSO_3$. Removal of the volatiles under vacuum gave a white solid, which was determined to be 9-methyl-9-phenylfluorene by ^1H and ^{13}C NMR spectroscopy.[37] To the second fraction was added Cp_2ZrCl_2 (231 μg, 0.79 μmol). Ethylene was bubbled through the reaction mixture, yielding a white solid confirmed to be polyethylene.[33,34]

Thermal Decomposition of $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$. $[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (**2**) (400 mg, 0.79 mmol) was dissolved in o-xylene (100 mL) containing $AlMe_3$ (57 mg, 0.79 mmol). The reaction was heated for 24 h at 130 °C. The reaction mixture was divided into two parts. The first part was hydrolyzed (5 mL) followed by extraction with Et_2O (3 × 50 mL). The organic layer was washed with $NaHCO_3$ and brine and dried over $MgSO_3$. Removal of the volatiles under vacuum

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(32) The disproportionation of $[Me_2Al]_2O$ to MAO and $AlMe_3$ has been previously discussed, see: Pasynkiewicz, S. *Polyhedron* **1990**, *9*, 429.

(33) For a recent review see: Barron, A. R. In *Metallocene-Based Polyolefins*; Scheirs, J., Kaminsky, W., Eds.; Wiley: Chichester, 2000; Chapter 2.

(34) ^1H NMR (C_6D_6): δ 7.00−7.14 (15H, m, C_6H_5), 2.03 (3H, s, C-CH_3). ^{13}C NMR (C_6D_6): δ 144.7 (MeCC), 131.1 (o-CH), 128.8 (m-CH), 128.47 (p-CH), 89.90 (CPh$_3$), 26.9 (CH$_3$).

(35) Vander Hart, D. L.; Pérez, E. *Macromolecules* **1986**, *19*, 1902.

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gave a white solid, which was determined to be 9,9-dimethylfluorene[38] from its melting point and ^{1}H NMR spectroscopy.[39] To the second fraction was added Cp_2ZrCl_2 (231 μg, 0.79 μmol). Ethylene was bubbled through the reaction mixture, yielding a white solid confirmed to be polyethylene.[33,34]

$[Me_2Al(\mu\text{-}OCMePh_2)]_2$ (3). To a solution of $AlMe_3$ (1.00 g, 13.89 mmol) in toluene (50 mL) was added dropwise a solution of Ph_2MeCOH (2.480 g, 12.51 mmol) in toluene (50 mL) over a period of an hour. The reaction mixture was stirred for 16 h, whereupon the solvent was removed under vacuum. Yield: 63%. Mp: 133−135 °C. ^{1}H NMR: δ 7.15−7.25 (20H, m, C_6H_5), 2.16 (6H, s, CH_3), −0.60 (12H, s, Al-CH_3). ^{13}C NMR: δ 145.9 (OC*C*, Ph), 128.8 (*o*-*C*H), 128.5 (*p*-*C*H), 127.2 (*m*-*C*H), 31.7 (*C*H$_3$), −5.26 (Al-*C*H$_3$). ^{27}Al NMR: δ 145 ($W_{1/2}$ = 8230 Hz).

$[Me_2Al(\mu\text{-}OCMe_2Ph)]_2$ (4). To a solution of $AlMe_3$ (1.00 g, 13.89 mmol) in toluene (50 mL) was added dropwise a solution of Ph_2MeCOH (1.680 g, 12.3 mmol) in toluene (50 mL) over a period of an hour. The reaction mixture was stirred for 6 h, whereupon the solvent was removed under vacuum. Yield: 68%. Mp: 100−104 °C. ^{1}H NMR: δ 7.33−7.38 (4H, m, C_6H_5), 7.09−7.15 (4H, m, C_6H_5), 7.01−7.07 (2H, m, C_6H_5), 1.53 (12H, s, CH_3), −0.56 (12H, s, Al-CH_3). ^{13}C NMR: δ 145.4 (OC*C*), 128.9 (*o*-*C*H), 128.5 (*p*-*C*H), 126.6 (*m*-*C*H), 31.3 (*C*H$_3$), −5.57 (Al-*C*H$_3$). ^{27}Al NMR: δ 137 ($W_{1/2}$ = 8230 Hz).

$[Me_2Al(\mu\text{-}OC_6H_4\text{-}4\text{-}{}^tBu)]_2$ (5). To a solution of $AlMe_3$ (1.00 g, 13.89 mmol) in toluene (50 mL) was added dropwise a solution of 4-^{t}BuPhOH (1.878 g, 12.5 mmol) in toluene (50 mL) over a period of an hour. The reaction mixture was stirred for 6 h, whereupon the solvent was removed under vacuum. Yield: 88%. ^{1}H NMR: δ 7.08 [4H, d, J(H−H) = 7.0 Hz, *o*-C*H*], 7.01 [4H, d, J(H−H) = 7.0 Hz, *m*-C*H*], 1.15 [18H, s, C(CH_3)$_3$], −0.20 (12H, s, Al-CH_3). ^{13}C NMR: δ 149.9 (O*C*), 128.7 (*o*-*C*H), 127.8 (*p*-*C*H), 118.7 (*m*-*C*H), 34.6 (*C*H$_3$), 31.8 [*C*(CH$_3$)$_3$], −10.3 (Al-*C*H$_3$).

Polymerization Test. To a sample of MAO solution formed from the Lewis acid-catalyzed decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ was added Cp_2ZrCl_2 (ca. 0.1 mol %) and the resulting mixture stirred for 30 min. Ethylene was then bubbled through the reaction mixture for 10 min, at room temperature. Quenching with methanol and filtration resulted in the isolation of polyethylene as characterized by ^{13}C CPMAS NMR and TGA analysis.[34,35]

Kinetic Measurements. Series samples were prepared in 5 mm NMR tubes from standard solutions (0.75 mL) of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ (0.0596 M) and $AlMe_3$ [0.0299 M (1/2 equiv), 0.0596M (1 equiv), 0.119 M (2 equiv), 0.178 M (3 equiv)] in toluene-d_8. All samples were heated to the appropriate temperature within the NMR spectrometer, and a series of ^{1}H NMR spectra were collected at equal time increments. The temperature of the NMR spectrometer probe was calibrated using the chemical shifts of ethylene glycol.[40] The relative integration of the triphenylethane protons was used to determine the rate of the reactions at three different temperatures until the reaction had reached completion. All calculations were performed using standard methods.[14]

Table 6. Summary of X-ray Diffraction Data

	$[Me_2Al(9\text{-}Ph\text{-}fluoroxy)]_2$ (**1**)	$[Me_2Al(9\text{-}Me\text{-}fluoroxy)]_2$ (**2**)
emp form	$C_{42}H_{38}Al_2O_2$	$C_{32}H_{34}Al_2O_2$
M_w	628.29	504.55
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	*Pbca*
a, Å	15.407(3)	7.962(2)
b, Å	10.704(2)	14.984(3)
c, Å	22.137(4)	24.378(5)
β, deg	105.14(3)	
V, Å^3	3524(1)	2907(1)
Z	4	4
D_{calc}, g·m^{-3}	1.185	1.153
μ_{calc}, mm^{-1}	0.117	0.126
no. of reflns collected	12 297	10 317
no. of ind reflns	5082	2097
no. of reflns obsd	3040	1635
weighting scheme SHELXTL params	0.0927, 0	0.10, 0
R	0.0503	0.0535
R_w	0.1336	0.1424
largest diff peak, e Å^{-3}	0.28	0.27

X-ray Crystallography. Crystals of all compounds were sealed in glass capillaries under argon. Data for compounds **1** and **2** were collected on a Bruker CCD SMART system, equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarization effects. The structures were solved using the direct methods program XS[41] and difference Fourier maps and refined by using full matrix least-squares method.[42] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms involved in hydrogen bonding were found, but not refined. Remaining hydrogen atoms were placed in calculated positions [U_{iso} = 0.08; d(C−H) = 0.96 Å] for refinement. Refinement of positional and anisotropic thermal parameters led to convergence (see Table 6).

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Supporting Information Available: Full listings of bond length and angles, anisotropic thermal parameters, and hydrogen atom parameters; elemental analysis, MS, IR spectra, and selected ^{1}H NMR and Eyring plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) Mp: 95−96 °C. ^{1}H NMR ($CDCl_3$): δ 7.67−7.05 (8H, m, fluorene), 1.45 (6H, s, CH_3).

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