Organometallics **2001,** *20,* 5119−5124

A Lewis Base Promoted Alkyl/Alkoxide Ligand Redistribution: Reaction of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with THF

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Received May 14, 2001

The reaction of $[Me_2Al(\mu\text{-}OEPh_3)]_2$ with pyridine yields the expected acid−base complexes $AlMe_2(OEPh_3)(py)$ [E = C (**1**) and Si (**2**)]. In contrast, the reaction with THF yields $AlMe(OEPh_3)_2(THF)$ [E = C (**5**) and Si (**6**)], although the dimethyl compounds, $AlMe_2(OEPh_3)(THF)$ [E = C (**3**) and Si (**4**)], are observed in THF-d_8 solution. The reaction of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with THF was followed by ^1H NMR and found to occur by a two-step process. First, the Al_2O_2 core of $[Me_2Al(\mu\text{-}OEPh_3)]_2$ is cleaved by THF to form compound **3**. Second, two molecules of $AlMe_2(OCPh_3)(THF)$ react with each other, with prior dissociation of THF from at least one complex, resulting in the ligand redistribution and the formation of **5** and $AlMe_3(THF)$. The conversion of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ into compound **3** is exothermic, and the subsequent formation of **5** and $AlMe_3(THF)$ is endothermic. The rate equations for the formation of **3** and its conversion to **5** have been determined. The observation of both alkoxide cleavage and alkyl/alkoxide exchange requires a fine balance between a Lewis base that is of sufficient strength to cleave the dimeric alkoxide, $[R_2Al(\mu\text{-}OR')]_2$, while being sufficiently weak to allow dissociation from the monomeric complex, $AlR_2(OR')(L)$.

Introduction

In 1958 Bradley summarized the structural trends in the chemistry of main group and transition metal alkoxides as “alkoxide derivatives adopt the smallest structural unit consistent with all atoms attaining a higher coordination sphere”.[2] The archetypal example of this effect is the structural reorganization exhibited by $Al(O^iPr)_3$. When freshly prepared, $Al(O^iPr)_3$ is trimeric in which each aluminum has a coordination number of four. Under ambient conditions, the trimeric structure converts to a tetrameric structure in which three aluminums are four-coordinate and one has a six-coordinate geometry.[3] Reoligomerization reactions are a common feature of alkylaluminum alkoxides, but they do not necessarily result in higher coordination numbers. For example, in the absence of overwhelming steric bulk, dimethylaluminum alkoxides, $[Me_2Al(\mu\text{-}OR)]_n$, are trimeric when synthesized at low temperatures, but reoligomerize to dimers at elevated temperatures.[4] Increased steric bulk, of either the alkoxide or the aluminum alkyl groups, results in dimeric structures for $[R_2Al(\mu\text{-}OR')]_n$.[4] It is only with sufficiently exaggerated steric bulky ligands, such as the 2,6-di-*tert*-butyl-4-methylphenol ligand, that monomeric structures are formed.[5] Unlike the dimer/trimer equilibria, potential monomer/dimer systems have not been studied, due to the presence of additional complicating disproportionation reactions.[6] Ligand disproportionation reactions between AlR_3 and $[R'_2Al(\mu\text{-}OR'')]_2$ have also been studied in detail,[7] and the disproportionation of $[Me_2Al(\mu\text{-}OMe)]_3$ in THF or pyridine has been reported.[8] During our investigation of the thermal decomposition of $[Me_2Al(\mu\text{-}OCPh_3)]_2$,[9] we noted the formation of $AlMe(OCPh_3)_2(THF)$ when the former was exposed to traces of THF. This observation prompted an investigation of the reaction of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with Lewis bases.

Results and Discussion

Reaction of $[Me_2Al(\mu\text{-}OEPh_3)]_2$ (E = C, Si) with an excess of pyridine gives the expected monomeric Lewis acid−base complex, $AlMe_2(OEPh_3)(py)$, E = C (**1**), Si (**2**).[10] The cleavage of the alkoxides' Al_2O_2 core by the pyridine agrees with our previous studies.[11] Dissolution of $[Me_2Al(\mu\text{-}OEPh_3)]_2$ in THF-d_8 also results in the formation of the Lewis acid−base complexes, $AlMe_2(OEPh_3)(THF\text{-}d_8)$, E = C (**3**), Si (**4**). Isolation of either compound followed by redissolution in C_6D_6 gives a

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10.1021/om010394i CCC: $20.00
Publication on Web 11/02/2001

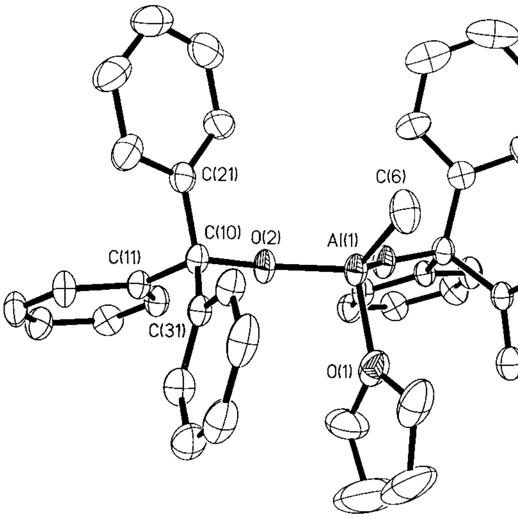

Figure 1. Molecular structure of $AlMe(OCPh_3)_2(THF)$ (**5**). Thermal ellipsoids are shown at the 20% level, and hydrogen atoms attached to carbon are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−O(2) = 1.710(4), Al(1)−O(1) = 1.853(8), Al(1)−O(2)−C(10) = 141.2(4).

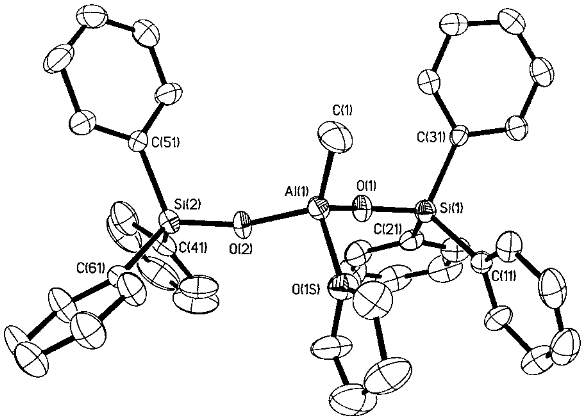

Figure 2. Molecular structure of $AlMe(OSiPh_3)_2(THF)$ (**6**). Thermal ellipsoids are shown at the 20% level, and hydrogen atoms attached to carbon are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−O(1) = 1.715(4), Al(1)−O(2) = 1.699(3), Al(1)−O(1S) = 1.869(5), Si(1)−O(1) = 1.596(4), Si(2)−O(2) = 1.596(4), Al(1)−O(1)−Si(1) = 149.8(2), Al(1)−O(2)−Si(2) = 165.5(3).

complex ^1H NMR spectrum. The use of only a trace of THF results in the isolation of the dialkoxide complex, $AlMe(OCPh_3)_2(THF)$ (**5**).[12] A similar reaction occurs for the reaction of $[Me_2Al(\mu\text{-}OSiPh_3)]_2$ to give $AlMe(OSiPh_3)_2(THF)$ (**6**).

Compounds **1**, **2**, **5**, and **6** have been characterized by NMR spectroscopy. The ^{27}Al NMR spectra are consistent with analogous $AlR_2(OR)(L)$ and $AlR(OR)_2(L)$ environments.[13] The solid state structures of compounds **5** and **6** have been confirmed by X-ray diffraction and are shown in Figures1 and 2. As we have previously observed,[11,14] the coordination geometry in compounds **5** and **6** is dominated by the sterically bulky alkoxide and siloxide ligands. The Al−O and Si−O bond distances are essentially independent of the Al−O−Si angle. This is expected when considered with regard to the structures of other $Al-OSiPh_3$ compounds; see Figure 3.[15]

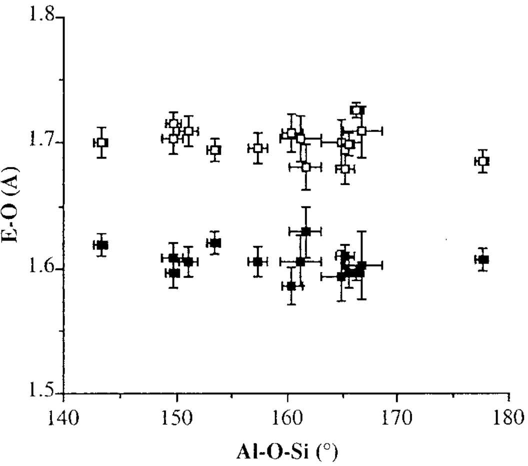

Figure 3. Plot of Al−O (□) and Si−O (■) bond distance (Å) as a function of Al−O−Si bond angle (deg) for triphenylsiloxide compounds of aluminum.

Investigation of THF-Promoted Alkyl/Alkoxide Exchange Reaction. Since dimeric dimethylaluminum alkoxides do not usually disproportionate into methylaluminum dialkoxide species in the presence of a Lewis base,[8] we deemed this reaction suitable for further investigation. In this regard, the reaction of $[Me_2Al(OCPh_3)]_2$ with 2 equiv of THF in C_6D_6 was followed by ^1H NMR over a period of one week under ambient conditions.

Upon initial analysis of the mixture, a single Al-Me resonance ($\delta = 0.81$ ppm) due to $[Me_2Al(\mu\text{-}OCPh_3)]_2$ is the only species observed. After 2 h, the integration (relative to the signal due to the residual protons in the solvent) of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ has decreased, and a resonance is observed at 0.66 ppm that may be assigned to $AlMe_2(OCPh_3)(THF)$ (**3**), i.e., eq 1.[16]

$$[Me_2Al(\mu\text{-}OCPh_3)]_2 + 2\ THF \overset{K_1}{\rightleftharpoons} \underset{\mathbf{3}}{2\ AlMe_2(OCPh_3)(THF)} \quad (1)$$

With increased reaction time the relative concentrations of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ and $AlMe_2(OCPh_3)(THF)$ continue to change; however, additional resonances due to $AlMe_3(THF)$[17] and $AlMe(OCPh_3)_2(THF)$ (**5**) are also observed. The relative ratio of $AlMe_3(THF)$ and $AlMe(OCPh_3)_2(THF)$ is approximately 1:1, suggesting that they are formed by the ligand disproportionation of $AlMe_2$-

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(12) The initial observation of this effect was due to a cross contamination of our hexane still by THF through the nitrogen lines. However, subsequent experiments have demonstrated that the synthesis of **5** and **6** may be accomplished in a rational manner by using ca. 2 equiv of THF in toluene solution.

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(16) Assignments were based upon the integration of new peaks and in comparison with the formation of $AlMe_2(OCPh_3)(THF)$ in THF-d_8.

(17) ^1H NMR: δ 3.34 (4H, m, OCH_2), 1.00 (4H, m, OCH_2CH_2), −0.41 (9H, s, Al-CH_3).

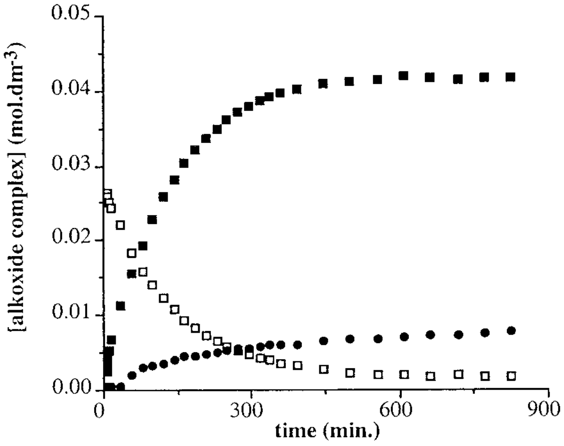

Figure 4. Plot of the formation of the relative concentration of [Me$_2$Al(μ-OCPh$_3$)]$_2$ (□), AlMe$_2$(OCPh$_3$)(THF) (■), and AlMe(OCPh$_3$)$_2$(THF) (●) as a function of reaction time for the reaction of [Me$_2$Al(μ-OCPh$_3$)]$_2$ with 2 equiv of THF at 50 °C.

(OCPh$_3$)(THF), eq 2. The mole fractions of each species as a function of reaction time is shown in Figure 4. Both reactions reach equilibria over a wide temperature range; for example, at 50 °C equilibrium is reached after 13 h.

$$2\ \mathrm{AlMe_2(OCPh_3)(THF)} \overset{K_2}{\rightleftharpoons} \underset{\mathbf{5}}{\mathrm{AlMe(OCPh_3)_2(THF)}} + \mathrm{AlMe_3(THF)} \quad (2)$$

The equilibrium constant for the formation of AlMe$_2$(OCPh$_3$)(THF) (eq 1) as defined by eq 3 may be determined as 30.2 mol^{-1} dm^3 at 40 °C.

$$K_1 = \frac{[\mathrm{AlMe_2(OCPh_3)(THF)}]^2}{[\{\mathrm{Me_2Al(OCPh_3)}\}_2][\mathrm{THF}]^2} \quad (3)$$

Similarly, the equilibrium constant associated with the ligand exchange reaction (eq 2) may be defined by eq 4 and is 6.85 × 10^{-2} at 40 °C.

$$K_2 = \frac{[\mathrm{AlMe(OCPh_3)_2(THF)}][\mathrm{AlMe_3(THF)}]}{[\mathrm{AlMe_2(OCPh_3)(THF)}]^2} \quad (4)$$

The temperature dependence of K_1 and K_2 was measured, from which ΔH and ΔS have been determined. A summary of the thermodynamic data for eqs 1 and 2 is given in Table 1. Interestingly, the conversion of [Me$_2$Al(μ-OCPh$_3$)]$_2$ into AlMe$_2$(OCPh$_3$)(THF) is exothermic, while the subsequent formation of AlMe(OCPh$_3$)$_2$(THF) and AlMe$_3$(THF) is endothermic. Thus, the former reaction is enthalpically driven, while the latter is entropically driven.

Table 1. Summary of Thermodynamic and Kinetic Data

Reaction	ΔH (kJ.mol^{-1})	ΔS (J.K^{-1}mol^{-1})	ΔH‡ (kJ.mol^{-1})	ΔS‡ (J.K^{-1}mol^{-1})
[Me$_2$Al(μ-OCPh$_3$)]$_2$ + 2 THF $\rightleftharpoons$ 2 AlMe$_2$(OCPh$_3$)(THF)	-24(3)	-50(8)	73(3)	112(8)
2 AlMe$_2$(OCPh$_3$)(THF) $\rightleftharpoons$ AlMe(OCPh$_3$)$_2$(THF) + AlMe$_3$(THF)	43(1)^a [43(2)]^b [49(1)]^c	116(1)^a [104(5)]^b [83(3)]^c	67(4)	< 75 (est.)

^{a} Values assuming no dissociation of AlMe(OCPh$_3$)$_2$(THF). ^{b} Values assuming complete dissociation of AlMe(OCPh$_3$)$_2$(THF) to AlMe(OCPh$_3$)$_2$ and THF. ^{c} Values assuming complete dissociation of AlMe(OCPh$_3$)$_2$(THF) and taking into account potential equilibrium with excess THF.

We note that the value for ΔS determined for the reaction shown in eq 2 [116(1) J·K^{-1} mol^{-1}] is larger than would be expected for a reaction in which there is no change in molecularity, i.e., no change in the number of species. Based upon previous studies,[18] a value of between 30 and 70 J·K^{-1} mol^{-1} would be expected for such a process with aluminum. In fact, the ΔS calculated for the reaction in eq 2 appears to be similar to values obtained for the dissociation of dimeric aluminum alkyls (123−142 J·K^{-1} mol^{-1}).[19] Thus, the entropy of reaction appears to suggest a dissociative process. It is well known, however, that Lewis acid−base complexes of aluminum dissociate in solution.[18] Furthermore, the extent of dissociation is increased the greater steric bulk of the ligands. Thus, AlMe(OCPh$_3$)$_2$(THF) would be expected to be significantly dissociated in solution (i.e., eq 5), in which case K_2 could be represented by eq 6.

$$\mathrm{AlMe(OCPh_3)_2(THF)} \overset{K_3}{\rightleftharpoons} \mathrm{AlMe(OCPh_3)_2} + \mathrm{THF} \quad (5)$$

$$K_2 = \frac{[\mathrm{AlMe(OCPh_3)_2}][\mathrm{THF}][\mathrm{AlMe_3(THF)}]}{K_3[\mathrm{AlMe_2(OCPh_3)(THF)}]^2} \quad (6)$$

Like other similar reactions, the reaction shown in eq 5 would be rapid on the NMR time scale, and the traditional method of determining K_3 is complicated due to the multiple reactions.[18] Values for this modified K_2 can be estimated if complete dissociation occurs. On the basis of these assumptions the ΔH values do not vary significantly (see Table 1), and the ΔS [83(3) J·K^{-1} mol^{-1}] is closer to that expected for similar reactions; see above. We propose, therefore, that the dissociation of THF from AlMe(OCPh$_3$)$_2$(THF) is part of the driving force for the formation of AlMe(OCPh$_3$)$_2$(THF) and AlMe$_3$(THF).

The conversion of [Me$_2$Al(μ-OCPh$_3$)]$_2$ into AlMe$_2$(OCPh$_3$)(THF) shows a first-order dependence on the concentration of [Me$_2$Al(μ-OCPh$_3$)]$_2$. A plot of k_{obs} versus [THF] also shows a first-order dependence. Thus, the rate of the initial reaction takes the form of eq 7.

$$-\mathrm{d}[\{\mathrm{Me_2Al}(\mu\text{-}\mathrm{OCPh_3})\}_2]/\mathrm{d}t = k_1[\{\mathrm{Me_2Al}(\mu\text{-}\mathrm{OCPh_3})\}_2][\mathrm{THF}] \quad (7)$$

Measurement of the temperature dependence for k_1 allows for the determination of $\Delta H^‡$ and $\Delta S^‡$; see Table 1. The positive value of $\Delta S^‡$ indicates a dissociative reaction.[20]

At high temperatures, K_1 is reached rapidly enough that it is possible to determine the rate for the conversion of AlMe$_2$(OCPh$_3$)(THF) to AlMe(OCPh$_3$)$_2$(THF) and

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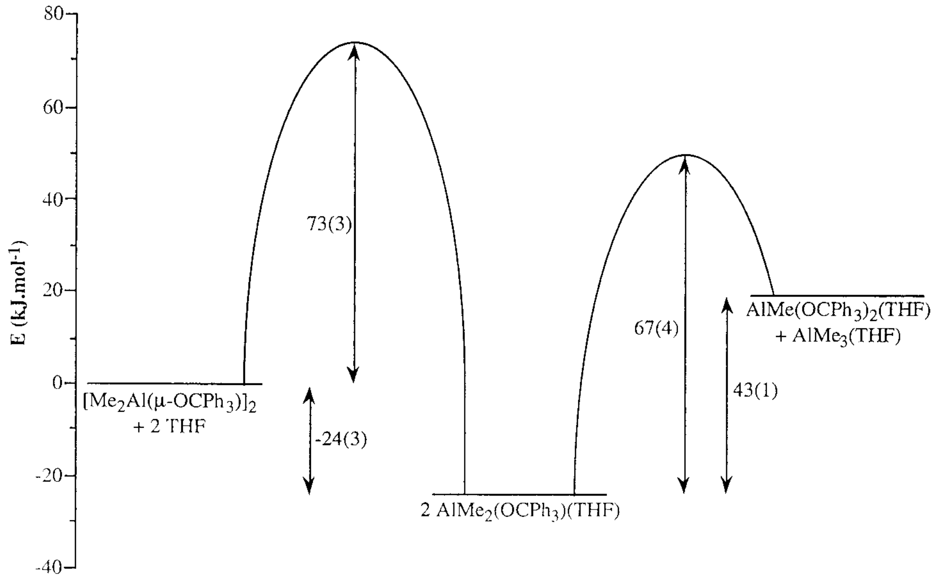

Figure 5. Reaction coordinate diagram for the reaction of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with THF.

$AlMe_3(THF)$. As may be expected of a ligand exchange reaction, the disappearance of the ^1H NMR signal due to the Al-CH_3 groups of the monomeric dimethylaluminum alkoxide species occurs in a second-order fashion, i.e., eq 8. Second-order observed rate constants, k_{obs}, were calculated from the corresponding plot of $1/[AlMe_2]$ versus time.

$$-d[AlMe_2]/dt = k_{obs}[AlMe_2]^2 \quad (8)$$

A plot of k_{obs} versus [THF] shows an inverse dependence. As is typical for Lewis acid−base complexes of group 13 metals, $AlMe_2(OCPh_3)(THF)$ undoubtedly exists in rapid equilibrium in solution (eq 9).

$$AlMe_2(OCPh_3)(THF) \xrightleftharpoons{K_{THF}} AlMe_2(OCPh_3) + THF \quad (9)$$

The inverse dependence on the THF concentration suggests that prior dissociation of THF is required for the rate-controlling reaction of an "$AlMe_2(OCPh_3)$" moiety with a second $AlMe_2(OCPh_3)(THF)$ molecule (eq 10).[21] The $AlMe(OCPh_3)_2$ is in equilibrium with its THF complex, eq 5.

$$AlMe_2(OCPh_3) + AlMe_2(OCPh_3)(THF) \rightleftharpoons AlMe(OCPh_3)_2 + AlMe_3(THF) \quad (10)$$

Assuming that (1) the ligand redistribution occurs by the reactions given above, (2) the ligand exchange is the rate-determining step, and (3) the concentration of reactants, as determined from the ^1H NMR spectra, $[AlMe_2]$, can be expressed as eq 11, then the rate of ligand exchange can be expressed by eq 12.

$$[AlMe_2] = [AlMe_2(OCPh_3)(THF)] + [AlMe_2(OCPh_3)] \quad (11)$$

$$\text{rate} = \frac{k_2 K_{THF}[AlMe_2]^2}{[THF] + K_{THF}} \quad (12)$$

For this rate law, the dependence on THF varies from 0 to −1, depending on the relative magnitude of the two terms in the denominator. Unfortunately, we were unable to find conditions under which a zero-order rate dependence is observed, since conditions of low THF concentration do not initiate the first reaction, eq 1. Thus, k_2 cannot be determined. Since K_{THF} is a constant, $\Delta H^\ddagger$ may be determined from k_{obs} for a given concentration of THF and an upper value for $\Delta S^\ddagger$ may be estimated; see Table 1.

The reaction coordinate diagram for the reaction of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with THF is given in Figure 5.

Conclusions

The Lewis base (L) cleavage of an alkoxide dimer, $[R_2Al(\mu\text{-}OR')]_2$ (eq 1), is enthalpically driven. In contrast, the ligand redistribution reaction (eq 2) is endothermic and entropically driven. Based on the inverse dependence on the concentration of the Lewis base, it appears that a prior dissociation of the Lewis base is required (eq 9) in order for the ligand redistribution reaction to continue. If the Lewis base is a sufficiently strong donor ligand, dissociation will be negligible, and ligand redistribution will not occur. In order for ligand redistribution to be facile, the Lewis base must be a poor donor ligand (resulting in a weak Al−L bond). If the Lewis base is too weak, the cleavage of the alkoxide dimer will not proceed.

The observation of both alkoxide cleavage and alkyl/alkoxide exchange requires a fine balance between a Lewis base that is of sufficient strength to cleave the dimeric alkoxide, $[R_2Al(\mu\text{-}OR')]_2$, while being sufficiently weak to allow dissociation from the monomeric complex, $AlR_2(OR')(L)$. Such a balance in reactivity may be thought of as fitting a Goldilocks model: "not too hot, not too cold, just right". While it is clearly fortuitous[12] that THF has a near optimum Lewis basicity to allow for both cleavage and ligand redistribution reactions to occur with $[Me_2Al(\mu\text{-}OCPh_3)]_2$ and $[Me_2Al(\mu\text{-}OSiPh_3)]_2$, we are continuing to study these reactions to develop a

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[21] Presumably, two "$AlMe_2(OCPh_3)$" groups are not involved; otherwise the re-formation of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ would be favored.

predictive model of the factors controlling group 13 alkoxide oligomerization and ligand distribution.

Experimental Section

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam 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 unless otherwise stated. NMR spectra were obtained on Bruker Avance 200 and 400 MHz spectrometers using (unless otherwise stated) C_6D_6 solutions. Chemical shifts are reported relative to internal solvent resonances (^1H and ^{13}C) and external $[Al(H_2O)_6]^{3+}$(^{27}Al). $[Me_2Al(\mu\text{-}OCPh_3)]_2$ and $[Me_2Al(\mu\text{-}OSiPh_3)]_2$ were prepared according to previously described procedures.[10] Microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. All other chemicals were obtained from Aldrich and used without further purification (unless otherwise noted).

$AlMe_2(OCPh_3)(py)$ (1). $[Me_2Al(\mu\text{-}OCPh_3)]_2$ (0.100 g, 0.158 mmol) was dissolved in toluene (10 mL), and a solution of pyridine (25 mg, 0.158 mmol) in toluene (5 mL) was added slowly at room temperature. The reaction mixture was stirred for 6 h, after which the solvent was removed under vacuum, yielding a white powder. Yield: 95%. ^1H NMR: δ 8.38 [2H, d, $J(H-H) = 6.2$ Hz, *o*-C*H*, py], 7.61 [6H, d, $J(H-H) = 7.1$ Hz *o*-C*H*], 7.11 (3H, m, *p*-C*H*), 7.04 (6H, m, *m*-C*H*), 6.91 (1H, m, *p*-C*H*, py), 6.56 (2H, m, *m*-C*H*, py), −0.51 (6H, s, Al-CH_3). ^{27}Al NMR: δ 130 ($W_{1/2} = 7250$ Hz).

$AlMe_2(OSiPh_3)(py)$ (2). $[Me_2Al(\mu\text{-}OSiPh_3)]_2$ (100 mg, 0.150 mmol) was dissolved in toluene (10 mL), whereupon a solution of pyridine (24 mg, 0.303 mmol) in toluene (5 mL) was added slowly at room temperature. The reaction mixture was stirred for 6 h, after which the solvent was removed under vacuum, yielding a white powder. Yield: 95%. ^1H NMR: δ 8.57 [2H, d, $J(H-H) = 5.7$ Hz, *o*-C*H*, py], 7.69 [6H, d, $J(H-H) = 7.1$ Hz, *o*-C*H*], 7.11 (6H, m, *m*-C*H*), 7.04 (3H, m, *p*-C*H*), 6.56 (2H, m, *m*-C*H*, py), 6.31 (1H, m, *p*-C*H*, py), −0.51 (6H, s, Al-CH_3). ^{27}Al NMR: δ 130 ($W_{1/2} = 6700$ Hz).

$AlMe_2(OCPh_3)(THF)$ (3). $[Me_2Al(\mu\text{-}OCPh_3)]_2$ (10 mg, 0.016 mmol) was dissolved in THF-d_8 (0.75 mL) and allowed to stand for 1 h at room temperature. NMR analysis showed the formation of a single product. ^1H NMR (THF-d_8): δ 7.38 [6H, d, $J(H-H) = 7.9$ Hz, *o*-C*H*], 7.18 (6H, m, *m*-C*H*), 7.08 (3H, m, *p*-C*H*), −1.09 (6H, s, Al-CH_3).

$AlMe_2(OSiPh_3)(THF)$ (4). $[Me_2Al(\mu\text{-}OSiPh_3)]_2$ (10 mg, 0.015 mmol) was dissolved in THF-d_8 (0.75 mL) and allowed to stand for 1 h at room temperature. NMR analysis showed the formation of a single product. ^1H NMR (THF-d_8): δ 7.55 (6H, m, *o*-C*H*), 7.06−7.22 (9H, m, *p*-, *m*-C*H*), −0.94 (6H, s, Al-CH_3).

$AlMe(OCPh_3)_2(THF)$ (5). A solution of THF (114 mg, 1.58 mmol) in toluene (1.0 mL) was added to a solution of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ (0.500 g, 0.791 mmol) in toluene (10 mL) and allowed to stand at room temperature for 2 weeks, after which clear, colorless crystals precipitated out of solution. Yield: 55%. Mp: 199−201 °C. ^1H NMR: δ 7.61 [12H, d, $J(H-H) = 8.0$ Hz *o*-C*H*], 7.14 (12H, m, *m*-C*H*), 7.06 (6H, m, *p*-C*H*), 3.23 (4H, m, OCH_2, THF), 0.78 (4H, m, OCH$_2$CH_2, THF), −0.99 (3H, s, Al-CH_3). ^{27}Al NMR: δ 80 ($W_{1/2} = 7090$ Hz).

$AlMe(OSiPh_3)_2(THF)$ (6). A solution of THF (108 mg, 1.506 mmol) in toluene (1.0 mL) was added to a solution of $[Me_2Al(\mu\text{-}OSiPh_3)]_2$ (0.500 g, 0.753 mmol) in toluene (10 mL) and allowed stand at room temperature for 3 weeks, after which clear, colorless crystals precipitated out of solution. Yield: 95%. ^1H NMR: δ 7.45−7.70 (12H, m, *o*-C*H*), 7.05−7.20 (18H, m, *m* and *p*-C*H*), 3.12 (4H, m, O−CH_2), 0.72 (4H, m, OCH$_2$CH_2), −1.07 (3H, s, Al-CH_3). ^{27}Al NMR: δ 85 ($W_{1/2} = 6440$ Hz).

Kinetic Measurements. A series of samples were prepared in 5 mm NMR tubes from standard solutions of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ (0.02766 M) and THF (0.2766 M) in toluene-d_8 (0.75 mL). All samples were heated to the appropriate temperature within the NMR spectrometer, and a series of ^1H NMR spectra were collected at equal increments. The temperature of the NMR spectrometer probe was calibrated using the chemical shifts of ethylene glycol.[22] The relative integration of the aluminum methyl protons was used to determine the rate of the reactions at seven different temperatures (313−373 K) until equilibrium had been reached. The first-order observed rate constants were determined from a plot of $-\ln[\{Me_2Al(\mu\text{-}OCPh_3)\}_2]$ versus time. The second-order observed rate constant was determined from a plot of 1/[$AlMe_2$] versus time using preequilibrium kinetics.

Table 2. Summary of X-ray Diffraction Data

	$AlMe(OCPh_3)_2(THF)$ (**5**)	$AlMe(OSiPh_3)_2(THF)$ (**6**)
emp form	$C_{43}H_{41}AlO_3$	$C_{41}H_{41}AlO_3Si_2$
cryst size, mm	0.5 × 0.4 × 0.2	0.6 × 0.6 × 0.1
cryst syst	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1/c$
a, Å	8.759(2)	16.425(3)
b, Å	24.128(5)	8.740(2)
c, Å	9.213(2)	27.048(4)
β, deg	114.33(3)	105.06(3)
V, Å^3	774.1(6)	3749(1)
Z	2	4
D_{calc}, g·cm^{-3}	1.184	1.178
μ_{calc}, mm^{-1}	0.095	0.15
2θ range, deg	5 to 47	2.5 to 46.7
no. of reflns colld	6921	9558
no. of ind reflns	2646	4458
no of reflns obsd	1300	1564
weighting scheme SHELXTL params	0.10, 0.0	0.10, 0.0
R	0.114	0.0485
R_w	0.270	0.113
largest diff peak, e Å^{-3}	0.40	0.15

The rate dependence on the concentration of THF for k_1 was determined using a series of four samples of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with 1, 2, 5, and 10 equiv of THF prepared from two stock solutions. The first solution was prepared by dissolving $[Me_2Al(\mu\text{-}OCPh_3)]_2$ (90 mg) in toluene-d_8 (2.91 g). Samples of this solution (0.500 g) were accurately weighted into a series of 5 mm NMR tubes. A second solution was prepared by dissolving THF (114 mg) in toluene-d_8 (1.896 g). This solution was accurately weighed into the four NMR tubes (250, 125, 50, and 25 mg) followed by addition of toluene-d_8. All samples were heated to 353 K within the NMR spectrometer, and a series of ^1H NMR spectra were collected at equal increments.

The rate dependence on the concentration of THF for k_2 was determined using a series of four samples of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ with 5, 10, 20, and 50 equiv of THF, prepared by accurately weighting 20 mg of $[Me_2Al(\mu\text{-}OCPh_3)]_2$ into 5 mm NMR tubes followed by addition of toluene-d_8 (0.500 g). A solution of THF (455 mg) was diluted with toluene-d_8 (545 mg). This solution was prepared and accurately weighed into the NMR tubes (25, 50, 125, and 250 mg) followed by addition of toluene-d_8. All samples were heated to 353 K within the NMR spectrometer, and a series of ^1H NMR spectra were collected at equal time increments.

X-ray Crystallographic Studies. Crystals of **5** and **6** were sealed in glass capillary tubes under argon. Crystal and data collection details are given in Table 2. Standard procedures in our laboratory have been described previously.[23] Data were collected on a Bruker CCD Smart system, equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. The structures

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were solved using direct methods program XS[24] and difference Fourier maps and refined using full matrix least-squares methods.[25] The THF ligand in compound **5** resides on a crystallographic mirror plane and is, therefore, constrained to be planar. Attempts to resolve a disorderd model were unsuccessful. All atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were placed in calculated positions [$U_{iso} = 0.08$; $d(C-H) = 0.96$ Å] for refinement of positional and anisotropic parameters, leading to convergence.

Acknowledgment. Financial support for this work was provided by the Welch Foundation. The Bruker Avance 200 NMR spectrometer was purchased with funds from ONR Grant N00014-96-1-1146. $AlMe_3$ was generously provided by Albemarle Corp. The authors acknowledge the questions of one of the referees for clarifying our thoughts on the thermodynamic aspects of this paper.

Supporting Information Available: Full listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters; ^{13}C NMR, MS, IR, and analytical data; selected equilibrium and kinetic plots. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010394I

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