Alkylaluminum Alkoxides Derived from Donor-Functionalized Alcohols: Factors Controlling the Formation and Redistribution of Products

Janusz Lewiński,*,[†] Iwona Justyniak,[‡] Paweł Horeglad,[†] Ewa Tratkiewicz,[†] Janusz Zachara,[†] and Zbigniew Ochal[†]

Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland, and Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Kasprzaka 44/52, 01-224 Warsaw, Poland

The reaction of R^*R^*-[Me$_2$Al(μ-*elac*)]$_2$ (**1**) (where *elac* = deprotonated *rac*-ethyl lactate) with Me$_3$Al results in the quantitative formation of the Lewis acid−base adduct R^*R^*-[Me$_2$-Al(μ-*elac*·AlMe$_3$)]$_2$ (**2**). Under ambient conditions the tetranuclear dimer **2** obtained as an oily substance changes gradually to give a white crystalline solid, which was identified as the monomeric binuclear adduct Me$_2$Al(*elac*)·AlMe$_3$ (**3**). Compound **3** is also formed directly when 2 equiv of Me$_3$Al reacts at −78 °C with 1 equiv of *elac*-H in CH$_2$Cl$_2$ solution. In contrast, the reaction of conjugated hydroxycarbonyl ligand, methylsalicylate (*mesal*-H), with 2 equiv of Me$_3$Al yields exclusively Me$_2$Al(*mesal*)AlMe$_3$ (**4**), irrespectively of the conditions applied. The implications of the differences in products are discussed with respect to the reaction conditions and the ligand identity. The molecular structure of compound **4** was determined by X-ray crystallography. The structure of **4** consists of a dinuclear monomer in which an AlMe$_3$ molecule is complexed to the aryloxide oxygen of the monomeric dimethylaluminum chelate complex. The geometry and orientation of the Me$_3$Al unit and the C(12)···Al(2) distance all indicate that there is a weak noncovalent interaction between one methyl group of Me$_3$Al and the metal center of the Me$_2$Al unit. For **3** and **4** the exchange of the methyl groups between the two aluminum centers occurs, for which $\Delta G^{\ddagger}_{302K} = 69.7 \pm 1$ kJ mol^{-1} and $\Delta G^{\ddagger}_{328K} = 77.0 \pm 1$ kJ mol^{-1}, respectively, were determined, and the mechanism of exchange reactions is discussed.

Introduction

The addition of carbon nucleophiles to 2,3-epoxy alcohols is a classic organic reaction of great importance to regio- and stereoselective organic synthesis.[1] In this regard, aluminum alkyls have proven to be very important reagents; however, to date the reaction mechanism involving organoaluminum compounds as well as factors that determine the selectivity of nucleophilic ring-opening of 2,3-epoxy-1-alkanols are not well understood. As stated by Eisch, undoubtedly the alkoxyaluminum intermediate is decisive on the course of addition.[2] In this regard, we have recently initiated systematic studies on the selective alkyl addition to 2,3-epoxy alcohols choosing the group 13 metal alkyls and *rac*-glycidol (*epol*-H, **A**) as a simple model system.[3] Preliminary studies have shown that this model offers an ideal chance to investigate mechanistic aspects of the ring-opening transformations mediated by the group 13 organometallic compounds. For example, the reaction

between *epol*-H and Me$_3$Ga has succeeded in the isolation and structure characterization of the first example of group 13 metal-epoxide complex **I**, which may mimic a potential intermediate complex in the ring-opening reaction of glycidol mediated by aluminum alkyl reagents.[3] Moreover, control experiments on the reaction of *rac*-glycidol with R$_3$Al disclosed that the ring-opening reaction of 2,3-epoxy-1-alkanols is a multichannel process and more than one type of intermediate species have to be considered to explain the obtained data.

(**I**)
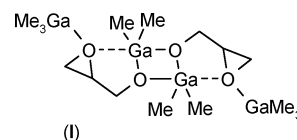
However, due to the high reactivity of *rac*-glycidol toward aluminum alkyls, we were not able to isolate any intermediates in the reaction. Therefore, we turned our attention to α-hydroxycarbonyl compounds, which have been developed with success in our earlier studies on the nature of aluminum alkoxides.[4] We anticipated that alkylaluminum alkoxides derived from *rac*-ethyl

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* Corresponding author. E-mail: lewin@ch.pw.edu.pl.
[†] Warsaw University of Technology.
[‡] Polish Academy of Sciences.
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(3) Lewiński, J.; Zachara, J.; Horeglad, P.; Glinka, D.; Lipkowski, J.; Justyniak, I. *Inorg. Chem.* **2001**, *40*, 6086.

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lactate (*elac*-H) (**B**) may mimic corresponding derivatives of 2,3-epoxy-1-alkanols. In addition to the inertness of the ester group, we chose *rac*-ethyl lactate for the structure investigation in the expectation that IR spectroscopy could be a sensitive probe for detecting equilibria between various types of the resulting hemilable complexes.
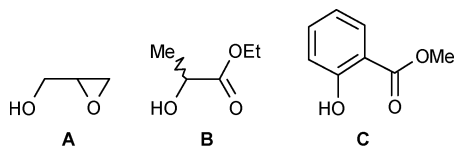
On the other hand, there are additional aspects that prompted the investigation of solution chemistry of alkylaluminum derivatives of hydroxycarbonyl compounds, including methylsalicylate (*mesal*-H) (**C**) as β-hydroxy ester with a conjugated unsaturated bond system. During the course of earlier studies on the solid state and solution structure of the group 13 metal alkyls derived from unsaturated bidentate ligands, we have found that the Me$_3$Al/acetylacetone reaction system for the 2:1 molar ratio affords the trinuclear complex of type **IX** in high yield.[5] Our interest in the employment of *mesal*-H arose from the desire to prepare the complex of type **VI** as a potential intermediate in the latter reaction. Furthermore, although alkylaluminum derivatives of nondelocalized alcohols (or phenols) with neutral Lewis base termini (i.e., H-*O,X* pro-ligands; where X = OR′, SR′, or NR′$_2$) have been under investigation for over four decades from the fundamental[6] and practical points of view,[7] the solution chemistry of the resulting complexes, especially those resulting from the reaction of 2 equiv of R$_3$Al and 1 equiv of bifunctional alcohol, still remains an undeveloped area. The schematic representation of the structurally characterized complexes derived from the reaction between aluminum alkyls and donor-functionalized alcohols at various molar ratios of reactants is demonstrated in Scheme 1. There is only one example of type **II** complex, namely, the Lewis acid–base adduct between ^{t}Bu$_3$Al and 3-(dimethylamino)-1-propanol, in which the kinetic stabilization is provided by the steric bulk of the ^{t}Bu substituents and the intramolecular hydrogen bonding to a tertiary amine.[8] Usually, the equimolar reaction results in

Scheme 1. Schematic Representation of the Structurally Characterized Alkylaluminum Derivatives of Hydroxy Compounds with Neutral Termini
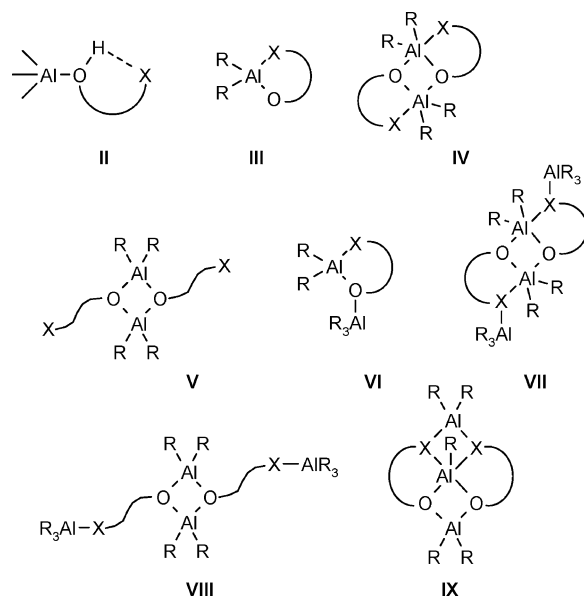
alkane elimination and the formation of aluminum alkoxide complexes of type **III**, **IV**, or **V**, and the latter type complexes have been studied most extensively.[8–13]

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Especially large effort has been devoted to the ligand-dependent equilibria between dimeric four-coordinate $[R_2Al(\mu,\eta^1\text{-}O,X)]_2$ (**V**) and five-coordinate $[R_2Al(\mu,\eta^2\text{-}O,X)]_2$ (**IV**) complexes resulting from the fluxional behavior of hemilabile *O,X*-ligands and involving dissociation and recoordination of the weakly bonding neutral donor group X.[14] Our group has delineated factors that provide a better understanding of the structural and bonding parameters for the aluminum alkyl derivatives of saturated and unsaturated donor-functionalized hydroxy compounds upon moving from monomeric chelate complexes $R_2Al(\eta^2\text{-}O,X)$ (**III**) to five-coordinate adducts **IV**.[4b,c] Furthermore, in the case of dialkylaluminum alkoxides derived from chiral donor-functionalized alcohols, we have also demonstrated that the formation of dimeric species is often a highly stereoselective reaction.[4] Type **IV** and **V** complexes have also been used as model compounds for the analysis of the borderline distances and trajectory for the approaching ligand on the metal's fifth coordinate site and to map out the minimum-energy pathways in associative reactions (e.g., the S_N2-type reaction at tetrahedral Al^{III}).[15]

In addition, fewer studies on the reactions involving the 2:1 ratio of reactants have been reported that proved the formation of type **VI**−**IX** complexes.[5,6,12f,h,k,l,16] In this case, from the earliest studies it has been noted that in solution the degree of association of resulting products was higher than that expected for the monomeric species **VI**, which indicated the presence of some amount of the dimeric form **VII**.[6a,b,16a] However, the influence of reaction conditions on redistribution of the monomeric and dimeric species has not been studied systematically nor were clear indications which factors govern the formation of monomeric versus dimeric complexes given. More recently, Barron and co-workers observed the formation of type **VI** and **VII** complexes in the reaction of $^tBu_3Al$ with dialkylaluminum derivatives of amine alcohols, $[R_2Al(\mu\text{-}O,N)]_2$ (where R = Me or ^tBu), and the authors indicated that for these sterically encumbered species the isolation of monomeric adduct $R_2Al(N,O)\cdot Al^tBu_3$ versus dimeric complex $[R_2Al(\mu\text{-}O,N)Al^tBu_3)]_2$ was determined by the steric bulk of the aluminum alkyl groups.[16b] Due to significant uncertainties concerning factors controlling the reaction course and redistribution of products in the reaction involving especially lower aluminum alkyls, we have decided on the systematic examination of the $Me_3Al/$ *rac*-ethyl lactate system, as a representative case, at various molar ratios of reactants and different experimental conditions, and the results of these studies are presented herein. Our interest in the reactions involving a racemic mixture of alcohols with neutral base termini results also from ongoing investigations on the factors controlling a highly stereoselective association of the group 13 metal alkoxides.[4a,c]

Results and Discussion

Me₃Al/*rac*-Ethyl Lactate System. We have previously shown that the reaction of Me_3Al with 1 equiv of

rac-ethyl lactate (*elac*-H) results in the quantitative formation of the racemic mixture of homochiral dimeric complex $R^*R^*\text{-}[Me_2Al(\mu\text{-}elac)]_2$ (**1**).[4a,b] To ascertain the effect of additional equivalents of Me_3Al as the Lewis acid on the structure of alkylaluminum alkoxides, we have examined the reaction of **1** with Me_3Al as well as the Me_3Al/rac-ethyl lactate reaction system for the 2:1 molar ratio at different temperatures. Interaction of **1** with 2 equiv of Me_3Al at −78 °C results in the quantitative formation of the Lewis acid−base adduct $R^*R^*\text{-}[Me_2Al(\mu\text{-}elac\cdot AlMe_3)]_2$ (**2**), according to eq 1.

$$\text{(1)}$$
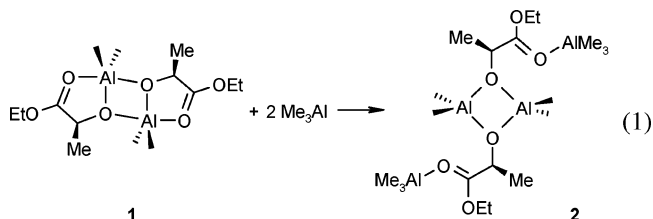
When freshly prepared, compound **2** is a viscous liquid (see Experimental Section) and was found to exist as a tetranuclear dimer on the basis of solution molecular weight studies. The IR spectrum of **2** revealed the presence of a strong band of the carbonyl group at $\nu_{C=O}$ = 1638 cm^{-1}, which is red shifted by 92 cm^{-1} with respect to the free ligand value. Such a large shift is characteristic for a carbonyl group coordinated to a highly acidic Lewis acid center and in this case indicating that $AlMe_3$ is coordinated to the terminal ester group. The ^1H and ^{13}C NMR spectra of **2** are also consistent with the complexation of the ester moiety by Me_3Al. The ^1H NMR spectrum at room temperature shows one set of signals, which indicates the presence exclusively of *R,R* and *S,S* diastereoisomers in the postreaction mixture. In addition, the occurrence of a single broad resonance due to the Al-Me groups indicates the operation of a dynamic process with very fast, on the NMR time scale, inter- or intramolecular exchange of the methyl groups between different aluminum moieties. Cooling a toluene-d_8 solution of **2** results in the decoalescence of this signal, to give two resonances with relative intensities of 2:3, which are consistent with the proposed tetranuclear dimeric structure. The room-temperature ^{13}C NMR spectrum shows two broad resonances of the Al-Me groups and one set of signals corresponding to the ligand carbon atoms. The coordination of Me_3Al to the ester group is accompanied by a significant low-field shift of the resonances associated with the carbonyl and ethylene carbon atoms as compared to their counterparts in compound **1** (ca. 5 ppm). The ^{27}Al NMR spectrum of **2** consists of one broad signal of ca. 150 ppm. This observation is in good agreement with all other data, as it represents the four-coordinate metal center in the coordinated Me_3Al and the Me_2Al moiety, respectively.[17]

In the course of investigations we observed that under ambient conditions the tetranuclear dimer **2** obtained as an oily substance changes gradually (in days) to give a white crystalline solid, which was identified as the monomeric binuclear adduct $Me_2Al(elac)\cdot AlMe_3$ (**3**). This

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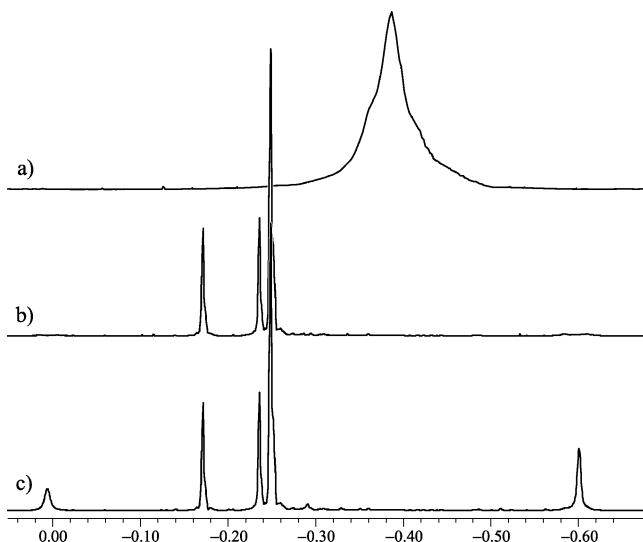
Figure 1. Variable-temperature ^{1}H NMR spectra of Me$_2$-Al(*elac*)·AlMe$_3$ in the region of the Al-Me signals at (a) 20 °C, (b) −70 °C, and (c) −70 °C with an excess of Me$_3$Al.

process could be monitored by IR spectroscopy, which revealed the appearance of a new band $\nu_{C=O}$ = 1694 cm^{-1} and a decrease in intensity of the parent carbonyl group band after 24 h. After a period of 3 days the band at 1638 cm^{-1} almost disappeared, leaving only the strong band at 1694 cm^{-1}, corresponding to adduct **3**. The NMR spectroscopic data of the solid material are also consistent with the proposed monomeric binuclear structure of **3**. The room-temperature ^{13}C NMR spectrum of **3** shows two broad resonances of the Al-Me groups and one set of signals corresponding to the ligand carbon atoms. Interestingly, while the $\nu_{C=O}$ frequencies observed for **3** and **2** differ significantly ($\Delta\nu$ = 56 cm^{-1}), the ^{13}C NMR chemical shifts of the corresponding resonances are very similar for both compounds. Furthermore, the room-temperature ^{1}H NMR spectrum of **3** in a toluene-d_8 solution shows essentially a single, broad resonance for the Al-Me groups, a quartet and a doublet for the CH and CH$_3$ protons, respectively, which are associated with the chiral center, as well as a bulky signal and a triplet for the OCH$_2$CH$_3$ protons (Figure 1a). However, this signal splits into three well-separated singlets with relative intensities of 1:1:3 at −70 °C (Figure 1b), which is fully consistent with the monomeric structure of **3**. The lower field signals of equal intensity correspond to the inequivalent methyl groups of the AlMe$_2$ unit, and the third signal is due to the AlMe$_3$ moiety. The single resonance of the AlMe$_3$ protons is evidence for apparently rapid rotation around the O−AlMe$_3$ bond even at −70 °C. The presence of three sharp singlets in the Al-Me protons region reflects the lack of symmetry present in the complex and indicates that the structure of **3** is relatively rigid on the NMR time scale at −70 °C.

The observed broad resonance for the Al-Me protons at ambient temperature reflects a dynamic process involving a rapid exchange of the methyl groups between the two aluminum centers. From the coalescence temperature of this exchange, the approximate value for the free energy of activation for the exchange process was calculated, $\Delta G^{\ddagger}_{302K}$ = 69.7 ± 1 kJ mol^{-1}. Interestingly, when an excess of AlMe$_3$ was added to the parent

solution of **3**, the additional well-separated singlets with relative intensities of 1:2, corresponding to the Me$_2$Al-(μ-Me)$_2$AlMe$_2$ dimer, appeared in the spectrum (Figure 1c). The observed distinctive resonances imply that the latter species does not interact with adduct **3** at −70 °C (we note that all Al-Me resonances coalesce to a single broad signal at room temperature, showing that the aluminum-bound methyl groups are undergoing a chemical exchange process). In the room-temperature ^{1}H NMR spectrum of **3** a new set of signals appears after 1 day, which corresponds to the dimeric adduct **2**.

In fact, compound **3** is readily prepared by the direct reaction of 2 equiv of Me$_3$Al with 1 equiv of *elac*-H in CH$_2$Cl$_2$ solution and at −78 °C (eq 2) (see also Experimental Section). Under these conditions **3** is formed exclusively. However, when the analogous reaction was conducted at 0 °C, the reaction outcome consisted of a mixture of **2** and **3**, as judged by the IR and NMR spectra.
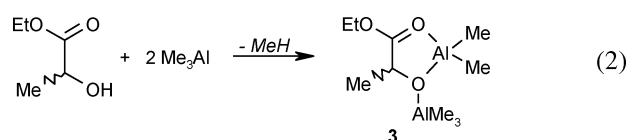
An effort was taken to confirm the structure of **3** by X-ray crystallography. However, despite many attempts, and contrary to expectations, only crystals of the racemic mixture of homochiral dimeric complex **1** were obtained in each case (the formation of the homochiral dimer was confirmed by ^{1}H NMR spectroscopy and X-ray analysis).[4a,b] Thus, this surprising result demonstrates that the presence of the Lewis acid does not affect the highly stereoselective association of the dialkylaluminum alkoxides derived from *rac*-ethyl lactate previously revealed by our group.[4a,b] Moreover, the latter result as well as other data reported herein clearly show that alkylaluminum alkoxides derived from *rac*-ethyl lactate are hemilabile compounds in solution at ambient temperature.

Me$_3$Al/Methylsalicylate System. In contrast, the reaction of a conjugated hydroxycarbonyl ligand, methyl salicylate (*mesal*-H), with 2 equiv of Me$_3$Al yields exclusively Me$_2$Al(*mesal*)AlMe$_3$ (**4**), irrespective of the conditions applied. Compound **4** is found to exist as a dinuclear monomeric species on the basis of solution molecular weight studies. Thus, the presence of a monoanionic bifunctional ligand with a delocalized bond system favors the formation of dinuclear adducts of type **IV**. The room-temperature ^{1}H NMR spectrum of **4** shows two sharp singlets of the Al-Me groups (−0.24 and −0.16 ppm) and one set of signals corresponding to the ligand protons (Figure 2). The higher field signal corresponds to methyl groups of the AlMe$_2$ unit, and the second signal is due to the AlMe$_3$ moiety. The ^{13}C NMR spectroscopic behavior of **4** is consistent with the ^{1}H NMR data. The ^{27}Al NMR spectrum of **4** consists of one broad resonance of ca. 145 ppm.

The presence of two sharp signals in the Al-Me protons region in the ^{1}H NMR spectrum of **4** indicated that the methyl groups did not undergo a rapid intramolecular exchange on the NMR time scale at ambient temperature. Thus, this observation could suggest that at room temperature the exchange of the
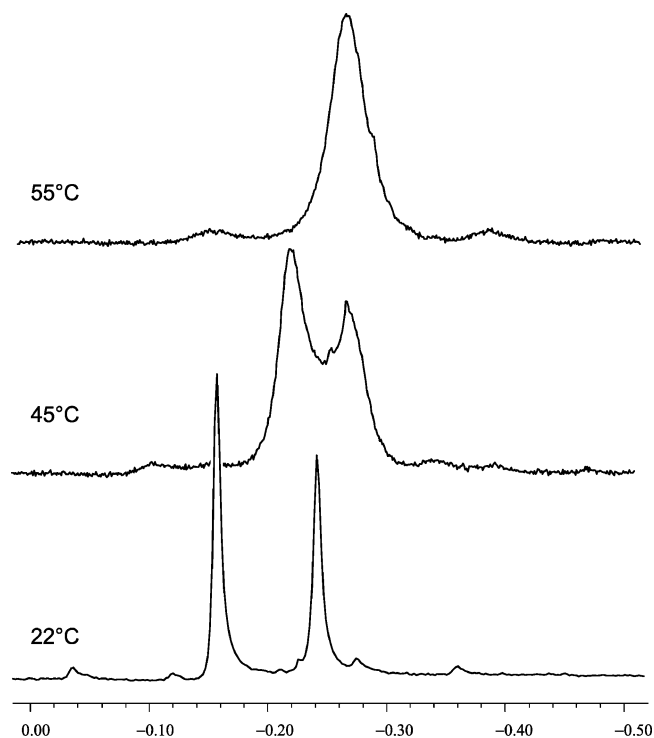
Figure 2. Variable-temperature ^{1}H NMR spectra of Me$_2$-Al(*mesal*)·AlMe$_3$ in the region of the Al-Me signals.

Figure 3. ORTEP diagram of Me$_2$Al(*mesal*)AlMe$_3$ (**4**) showing 30% probability thermal ellipsoids. The dashed lines represent a weak intramolecular Me···Al noncovalent interaction.

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compound 4

Al(1)−O(1)	1.969(2)	Al(2)−O(1)	1.862(2)
Al(1)−C(11)	1.960(3)	Al(2)−O(2)	1.854(2)
Al(1)−C(12)	1.958(3)	Al(2)−C(9)	1.930(3)
Al(1)−C(13)	1.953(3)	Al(2)−C(10)	1.933(3)
O(1)−C(1)	1.366(3)	O(2)−C(7)	1.241(3)
O(3)−C(7)	1.298(3)	O(3)−C(8)	1.445(3)
C(1)−C(6)	1.400(3)	C(6)−C(7)	1.443(3)
Al(1)···Al(2)	3.165(2)	Al(2)···C(12)	3.084(4)
Al(1)−O(1)−Al(2)	111.36(8)	O(1)−Al(2)−C(9)	110.74(11)
O(1)−Al(1)−C(11)	106.12(12)	O(1)−Al(2)−C(10)	116.06(11)
O(1)−Al(1)−C(12)	102.01(11)	O(2)−Al(2)−C(9)	105.27(12)
O(1)−Al(1)−C(13)	104.91(11)	O(2)−Al(2)−C(10)	100.89(11)
O(1)−C(1)−C(6)	122.6(2)	C(9)−Al(2)−C(10)	124.14(15)
C(1)−C(6)−C(7)	121.9(2)	C(6)−C(7)−O(2)	124.4(2)
Al(2)−O(1)−C(1)−C(6)	−13.1(3)	Al(2)−O(2)−C(7)−C(6)	−7.5(3)

aluminum-bound methyl groups does not occur for the complexes involving the chelate ligand with a conjugated bond system or is significantly slower than similar processes for the related complexes based on non-delocalized ligands, cf., Me$_2$Al(*elac*)·AlMe$_3$ adduct. To clarify this problem, we have warmed the NMR sample and found that the two Al-Me signals coalesce to one singlet at −0.26 ppm. These ^{1}H NMR spectral changes support the occurrence of the exchange process. The free energy of activation for this process has been determined from the ^{1}H NMR coalescence point, $\Delta G^{\ddagger}_{328K} =$ 77.0 ± 1 kJ mol^{-1}. Thus, for **4** a significant reduction in the rate of the exchange reaction and an increase in the activation barrier are observed when compared to the related data for **3**.[18] It should be also mentioned at this point that Kroll et al. studied exchange reactions between dimethylaluminum acetylacetonate and the four-coordinate methylaluminum complex Me$_3$Al(L) or Me$_2$Al (DBM) (were BBM = 1,3-diphenyl-1,3-propanedionate); however, no evidence was found by the authors for the intermolecular exchange process of the methyl groups on the NMR time scale at ambient temperature.[19]

The monomeric bimetallic structure of Me$_2$Al(*mesal*)-AlMe$_3$ (**4**) was determined by X-ray crystallography, and this study appeared very helpful for the consideration on the mechanism of the alkyl group exchange reaction. The molecular structure of **4** is shown in Figure 3, and selected bond lengths and angles are given in Table 1. The structure of **4** consists of a binuclear monomer in which an AlMe$_3$ unit is complexed to the aryloxide
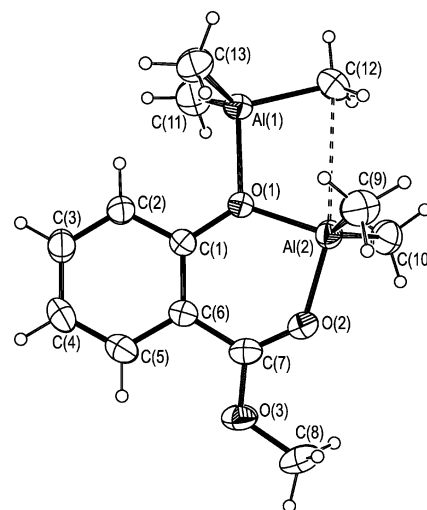
oxygen of the monomeric dialkylaluminum chelate complex Me$_2$Al(*mesal*); one should note that the latter mononuclear complex was previously characterized by our group.[11a] In principle, the structure features of **4** are consistent with previous reports of the type **VI** aluminum complexes.[16] The aluminum centers are four-coordinated with a distorted tetrahedral structure. The bifunctional ligand and both aluminum atoms lie within one plane. Interestingly, the distances of Al(2) to O(1) and O(2) are quite similar (1.862(2) and 1.854(2) Å, respectively), despite the distinct identity of both oxygen centers, while the Al(1)−O(1) bond is significantly longer, 1.969(2) Å. All of the bond lengths and angles associated with the chelate ligand are within the ranges expected.[12a] Interestingly, a consideration of the orientation of the Me$_3$Al unit shows that one Me group is directed to the Al(2) atom along the minimum energy pathway recently revealed by us for a ligand exchange reaction at a tetrahedral Al center.[15] The resulting C(12)···Al(2) distance of 3.084(4) Å is considerably shorter than the sum of the van der Waals radii for C (1.7 Å) and Al (2.0 Å).[20] In addition, the Me$_3$Al moiety is slightly inclined toward the Al(2) atom; thus the C(12)−Al(1)−O(1) bond angle [102.01(11)°] is the smallest of the three C−Al(1)−O(1) angles formed by the

(18) It should be noted that we cannot exclude that the dissociation of the AlMe$_3$ unit occurs to some degree for **4** at 50°, and this may affect an averaging process of the signals. This seems less likely for **3** at the studied temperature range.

(19) Kroll, W. R.; Kuntz, I.; Birnbaum, E. *J. Organomet. Chem.* **1971**, *26*, 313.

(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. For aluminum we assume a value of 2.0 Å, in accordance with the CSD standard.

methyl groups. In this way, the geometry and orientation of the Me$_3$Al unit and the C(12)···Al(2) distance all indicate that there is a weak noncovalent interaction between the methyl group and the metal center. This weak attractive interaction slightly eclipses also the methyl groups bonded to the Al(2) atom, and the C—Al(2)—O(1) angles (mean value of 113.4°) are much more obtuse than the C—Al(2)—O(2) angles (mean value of 103.1°). This is consistent with expectation: as the methyl group approaches the Al atom, the two alkyl substituents bend away (the closer the approach of the methyl group, the larger the deformation of the C$_2$AlO$_2$ core). It should also be noted that the C(12)···Al(2) distance is significantly shorter than those found in type **VI** complexes[6c,12k−l,16b,21] and other related adducts,[22] in which the corresponding distances vary in the narrow range around 3.50 Å. Thus, it is reasonable to regard the observed long-range interaction in **4** as the incipient intramolecular alkyl-exchange reaction between the Me$_3$Al and Me$_2$Al units. In this frozen stage of the reaction, the stage of alkyl transfer is not quite advanced. To our knowledge, there has been no prior confirmation that the observed close proximity of the methyl group and the Al center in the solid state structures actually arises through attractive forces.

Mechanistic Considerations. It seems likely that the above-mentioned intramolecular Me···Al noncovalent interaction directly mediates the alkyl group exchange between aluminum centers for type **VI** complexes, and the process in some part resembles an S$_N$2-type reaction with the expected central barrier (on the reaction profile) relatively high due to the large change in bonding having taken place in the transition state.[23] Thus, the reactants first associate to form a noncovalent complex **X** with virtually no change in the geometry of the dialkylaluminum chelate moiety. The complex then undergoes conversion to the product **XI** via the trigonal-bipyramidal transition state T1 followed by the heterolytic cleavage of the Al—O dative bond, leading to the intermediate hemialkoxide I2,[24] and further rearrangements proceed with little activation barrier (Scheme 2). Thus, the proposed mechanism of the exchange process involves both the breaking and re-forming of the Al—O(carbonyl) dative bond.

The trigonal-bipyramidal transition state T1 is analogous to the hypervalent five-coordinate complexes of

**Scheme 2. Proposed Mechanism for the Alkyl Group Exchange between Aluminum Centers for Type VI Complexes**
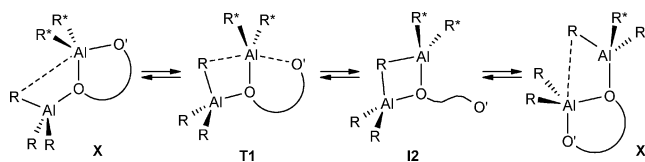
type R$_2$Al(O,O')(L), and the stability of the latter complexes has been more comprehensively discussed by our group recently.[25] In the latter studies, we have demonstrated that the formation of the three-center four-electron bond requires significant changes in conjugative interactions within the unsaturated O,O'-ligand. It is therefore quite reasonable that the alkyl exchange reaction for adduct **4** is significantly retarded by the resonance-assisted changes. This problem does not arise in the case of adduct **3**, which involves the non-delocalized O,O'-ligand, and the exchange reaction in **3** is indeed faster than the analogous process in **4**, as indicated by the experimental data (vide supra). It should also be noted that the mechanism of exchange reactions of the alkyl groups for complexes of type **VI** and **VII** has been earlier discussed by Benn et al.;[16a] however the present results discussed above provide more in-depth understanding of these processes.

Conclusions

The results presented above allow a better understanding of the reaction course and redistribution of products in the reaction involving hydroxy organic compounds bearing Lewis base termini and two or more equivalents of R$_3$Al. Apparently, different types of species may be obtained depending on the reaction condition. For example, the monomeric complex of type **VI** may be exclusively obtained in the direct reaction of the appropriate alcohol and AlMe$_3$ in the correct stoichiometry at low temperature (Scheme 3, *path 1*). A similar reaction carried out at room temperature likely affords a mixture of **VI** and **VII**. The initial exclusive formation of the tetranuclear adduct **VII** may be expected upon addition of AlMe$_3$ to dimeric complex **IV** (Scheme 3, *path 3*).

Scheme 3 Product Redistribution under Different Conditions in the Reaction Involving Donor-Functionalized Alcohols and Two or More Equivalents of R$_3$Al
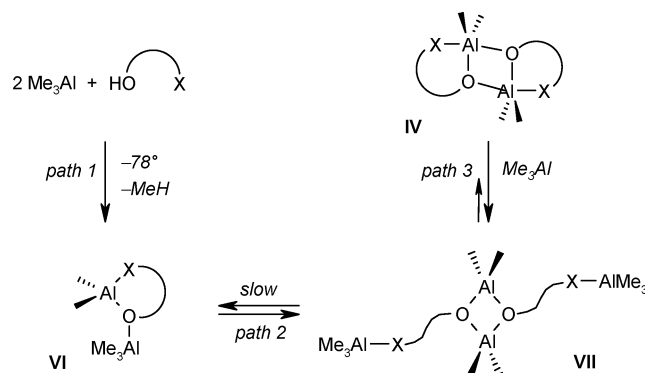
(21) Amirkhalili, S.; Hotchcok, P. B.; Smith, J. D.; Stamper, J. G. *J. Chem. Soc., Dalton Trans.* **1980**, 249. van Vliet, M. R. P.; Buysingh, P.; van Koten, G.; Rotteveel, M. A.; Schrap, M.; Vrieze, K.; Kojic-Prodic, B.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1986**, *5*, 1389. Lewiński, J.; Justyniak, I.; Zachara, J.; Tratkiewicz, E. *Organometallics* **2003**, *22*, 4151. Huang, Y. L.; Huang, B. H.; Ko, B. T.; Lin, C. C. *J. Chem. Soc., Dalton Trans.* **2001**, 1359. Huang, B. H.; Yu, T. L.; Huang, Y. L.; Ko, B. T.; Lin, C. C. *Inorg. Chem.* **2002**, *41*, 2987.

(22) Atwood, J. L.; Zaworotko, M. J. *Chem. Commun.* **1983**, 302. Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1709. Zhao, Q.; Sun, H.; Chen, W.; Duan, C.; Liu, Y.; Pan, Y.; You, X. *Organometallics* **1998**, *17*, 156. Carraz, C. A.; Stephan, D. W. *Organometallics* **2000**, *19,* 3791. Robinson, G. H.; Moise, F.; Pennington, W. T.; Sangokoya, S. A. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 387.

(23) Due to the more complex character of the studied reaction, one may expect that the reaction has a potential energy surface with more wells, which are potential energy minima on the reaction path connecting reactants and products, than a classical S$_N$2 reaction.

(24) For selected examples concerning the possible formation of hemialkoxide see: Harney, D. W.; Meisters, A.; Mole, T. *Aust. J. Chem.* **1974**, *27*, 1639. Obrey, S. J.; Bott, S. G.; Barron, A. R. *Organometallics* **2001**, *20*, 5162, role of an intermediate hemialkoxide in aluminum alkoxide chemistry.

(25) Lewiński, J.; Goś, P.; Kopeć, T.; Lipkowski, J.; Luboradzki, R. *Inorg. Chem. Commun.* **1999**, *2*, 374.

In time, adduct **VII** has a tendency to dissociate to the monomeric chelate complex **VI** with AlMe$_3$ coordinated to the alkoxide oxygen atom (Scheme 3, *path 2*). It is also apparent from the present and others studies[16b] that the identity of alkyl substituents at aluminum as well as the character of the bifunctional monoanionic ligand will all control the relative stability of **IV**, **VI**, and **VII** type complexes and multiple equilibria between these species. In the similar reaction system involving unsaturated hydroxycarbonyl compounds, the product of type **VII** is formed exclusively. Furthermore, the revealed close proximity of the methyl group and the Al center in the solid state structure of **4** may be considered as the incipient intramolecular alkyl-exchange reaction between the Me$_3$Al and Me$_2$Al units in type **VI** complexes. In this regard, we propose that the mechanism of exchange reactions of the alkyl groups for this group of complexes is likely to resemble an S$_N$2-type reaction. Finally, the reported results presumably offer an interesting entry into the regioselective and stereoselective alkyl additions to 2,3-epoxy alcohols mediated by alkylaluminum reagents, which are now being explored extensively in our group.

Experimental Section

General Procedures. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. NMR spectra were recorded on a Varian Mercury 400 spectrometer. IR spectra were recorded on a Specord M80 spectrophotometer. Compounds [Me$_2$Al(*elac*)]$_2$ (**1**) and Me$_2$Al(*mesal*) were synthesized according to the literature.[4b,11a]

[Me$_2$Al(*elac*·AlMe$_3$)]$_2$ (2). To a vigorously mixing solution of [Me$_2$Al(*elac*)]$_2$ (1.74 g, 5.0 mmol) in 20 cm^3 methylene chloride was added dropwise AlMe$_3$ (0.72 g, 10.0 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature. Then the solvent was removed in vacuo, giving the product as an oily liquid, almost quantitatively. ^{1}H NMR (C$_6$D$_6$, 20 °C, δ, ppm): −0.34 (s, 12H, Al-*CH$_3$*), 0.61 (t, 6H, CH$_2$*CH$_3$*), 1.23 (d, 6H, CH*CH$_3$*), 3.44 (qd, 4H, *CH$_2$*CH$_3$), 4.41 (q, 1H, *CH*CH$_3$). ^{1}H NMR (C$_7$D$_8$, −70 °C, δ, ppm): −0.31 (s, 18H, Al-*CH$_3$*), −0.26 (s, 6H, Al-*CH$_3$*), −20 (s, 6H, Al-*CH$_3$*), 0.52 (t, 6H, CH$_2$*CH$_3$*), 1.05 (d, 6H, CH*CH$_3$*), 2.95 (qd, 4H, *CH$_2$*CH$_3$), 4.23 (q, 2H, *CH*CH$_3$). ^{13}C NMR (C$_6$D$_6$, 20 °C, δ, ppm): −8.70 (AlCH$_3$), −6.81 (AlCH$_3$), 13.04 (CH$_3$), 20.30 (CH$_3$), 69.21 (OCH$_2$), 70.56 (OCH), 188.10 (C=O). ^{27}Al NMR (C$_6$D$_6$, 20 °C, δ, ppm): 176. IR (CH$_2$Cl$_2$, cm^{-1}): 1636 (s), 1476 (m), 1460 (w), 1432 (w), 1388 (w), 1356 (w), 1312 (w), 1292 (w), 1196 (m), 1124 (m), 1092 (w), 1064 (w), 966 (w), 940 (w), 888 (w), 848 (w), 676 (m), 640 (w).

Me$_2$Al(*elac*)·AlMe$_3$ (3). To a vigorously mixing solution of *rac*-ethyl lactate (1.06 g, 9.0 mmol) in methylene chloride (15 cm^3) was added dropwise Me$_3$Al (1.30 g, 18.0 mmol) at −78 °C. Then the reaction mixture was allowed to warm to 0 °C and the solvent was removed in vacuo, giving the product as a colorless solid. Yield: ca. 98%. Anal. Calcd for C$_{10}$H$_{24}$Al$_2$O$_3$: C 48.81, H 9.75. Found: C 48.67, H 9.84. ^{1}H NMR (C$_7$D$_8$, 20 °C, δ, ppm): −0.39 (s, 15H, Al-*CH$_3$*), 0.64 (t, 3H, CH$_2$*CH$_3$*), 1.24 (d, 3H, CH*CH$_3$*), 3.50 (qd, 2H, *CH$_2$*CH$_3$), 4.40 (q, 1H, *CH*CH$_3$). ^{1}H NMR (C$_7$D$_8$, −70 °C, δ, ppm): −0.25 (s, 9H, Al-*CH$_3$*), −0.23 (s, 3H, Al-*CH$_3$*), −0.17 (s, 3H, Al-*CH$_3$*), 0.45 (t, 3H, CH$_2$*CH$_3$*), 1.05 (d, 3H, CH*CH$_3$*), 2.88 (qd, 2H, *CH$_2$*CH$_3$), 4.21 (q, 1H, *CH*CH$_3$). ^{13}C NMR (C$_6$D$_6$, 20 °C, δ, ppm): −8.83 (AlCH$_3$), −6.84 (AlCH$_3$), 13.16 (CH$_3$), 20.36 (CH$_3$), 69.46 (OCH$_2$), 70.63 (OCH), 188.14 (C=O). ^{27}Al NMR (C$_6$D$_6$, 20 °C, δ, ppm): 150. IR (CH$_2$Cl$_2$, cm^{-1}): 1694 (s), 1476 (m), 1460 (w), 1388 (w), 1354 (w), 1312 (w), 1198 (m), 1122 (m), 1064 (w), 996 (w), 946 (w), 886 (w), 848 (w), 674 (m). Molecular weight (cryoscopically in benzene): found 248, calcd 246.2.

Table 2. Crystal Data, Data Collection, Structure Solution, and Refinement Parameters for Compound 4

formula	C$_{13}$H$_{22}$Al$_2$O$_3$
M	280.27
temperature, K	293(2)
cryst size, mm	0.32 × 0.18 × 0.16
cryst syst	monoclinic
space group, no.	C2/*c*, 15
a, Å	16.795(4)
b, Å	14.989(4)
c, Å	13.306(4)
β, deg	101.88(2)
U, Å^3	3277.8(15)
Z	8
D_{calc}, g cm^{-3}	1.136
$F(000)$	1200
radiation used	Mo Kα ($\lambda = 0.71073$ Å)
μ, mm^{-1}	0.175
θ range, deg	2.2−25.0
no. of reflns collected	2917
no. of unique data, R_{int}	2818, 0.0135
no. of obsd data [$I > 2\sigma(I)$]	1974
no. of data/param/restraints	2818/188/0
R1, wR2 (all data)^a	0.0677, 0.1110
R1, wR2 (obsd data)^a	0.0419, 0.1002
GooF (all data)	1.011
weights a, b^b	0.0591, 0.554
largest resids, e·Å^{-3}	+0.177, −0.162

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. ^{b} $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

Me$_2$Al(*mesal*)·AlMe$_3$ (4). To a vigorously mixing toluene solution (15 cm^3) of Me$_2$Al(*mesal*) (2.43 g, 11.7 mmol) was added dropwise Me$_3$Al (0.84 g, 11.7 mmol) at −78 °C. The reaction was allowed to warm to room temperature and stirred for 1 h. Then the solvent was removed in vacuo, giving the product as a colorless solid, which was later crystallized from a toluene/hexane (1:7) mixture at −4 °C. Yield: ca. 90%. Anal. Calcd for C$_{13}$H$_{22}$Al$_2$O$_3$: C 55.74, H 7.85. Found: C 55.67, H 7.92. ^{1}H NMR (C$_6$D$_6$, 20 °C, δ, ppm): −0.24 (s, 6H, Al-*CH$_3$*), −0.16 (s, 9H, Al-*CH$_3$*), 2.86 (s, 3H, O*CH$_3$*), 6.45 (t, 1H, H$_{arom}$), 6.95 (t, 1H, H$_{arom}$), 7.18 (d, 1H, H$_{arom}$), 7.42 (d, 1H, H$_{arom}$). ^{13}C NMR (C$_6$D$_6$, 20 °C, δ, ppm): −9.02 (AlCH$_3$), −9.14 (AlCH$_3$), 55.27 (OCH$_3$), 114−138 (aryl, C−H), 167 (aryl, C−O), 175 (C=O). ^{27}Al NMR (C$_6$D$_6$, 20 °C, δ, ppm): 145. Molecular weight (cryoscopically in benzene): found 280, calcd 280.3.

X-ray Structure Determination. Single crystals of **4**, suitable for X-ray diffraction studies, were grown from a toluene/hexane solution. A well-shaped crystal was placed in a thin-walled capillary tube (Lindemann glass) in an inert atmosphere. The tube was plugged with grease, then flame-sealed and mounted on a goniometer head of a four-circle P3 (Siemens AG) diffractometer. Selected crystallographic data, the parameters of data collections, and refinement procedures are presented in Table 2. The intensities were collected in the $\omega - 2\theta$ mode and corrected for Lorentz−polarization effects. The structure was solved by direct methods using the SHELXS-97 program[26a] and refined by the full-matrix least-squares method against F^2 values (SHELXL-97[26b]). Neutral-atom complex scattering factors were employed.[26c] All non-hydrogen atoms were refined with anisotropic displacement parameters. The C(12) bridging methyl group was refined as a rigid group without any directional constraint. The remaining hydrogen atoms were introduced at geometrically idealized coordinates,

(26) (a) Sheldrick, G. M. *SHELXS-97. Acta Crystallogr., Sect A* **1990**, *46*, 467. (b) Sheldrick, G. M. *SHELXL-97*: Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997. (c) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publisher: Dordrecht, 1992; Vol. C.
(27) (a) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2002. (b) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

and their isotropic thermal parameters were refined. Moreover, the hydrogen atoms of the C(9) methyl group, bonded to the aluminum atom Al(2), were modeled as a disordered group with two positions rotated by 60° about the Al−C vector. The final Fourier-difference maps have no significant chemical meaning. Computations for the crystal structure discussions were carried out with the PLATON program.[27] ORTEP drawings were made using ORTEP3 for Windows.[28]

(28) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Supporting Information Available: Crystal data for **4** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049664Y