Structure and Reactivity of Organoaluminum Derivatives of Amino Acids

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The reaction of AlR_3 with 1 molar equiv of anthranilic acid yields the dimeric carboxylates $[R_2Al(O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$ [(R = Me (**3a**) or Et (**3b**)] in high yields. The addition of 2 molar equiv of AlR_3 to anthranilic acid results in the formation of the tetranuclear complexes $[R_2Al]_4[\mu\text{-}O_2CC_6H_4\text{-}2\text{-}\mu\text{-}NH]_2$ [(R = Me (**4a**) or Et (**4b**)], where both protic functionalities are involved in the alkane elimination. The addition of γ-picoline to a solution of **4b** in toluene results in a disruption of the tetranuclear cluster and affords $Et_2Al(\eta\text{-}O_2CC_6H_4\text{-}2\text{-}NH)AlEt_2$(py-4-Me) (**5**). The reaction of 2 molar equiv of $AlMe_3$ with glycine yields the alkylaluminum carboxylate $Me_2Al(O_2CCH_2NH_2)AlMe_3$ (**6**), in which only the carboxylic group is deprotonated. When more equivalents of $AlMe_3$ are employed, the alkylation of the carboxylate group of glycine occurs and the aluminum alkoxide $Me_2Al[OC(CH_3)_2CH_2NH_2]AlMe_3$ (**7**) was isolated as one of the products of the complex postreaction mixture. The resulting compounds have been characterized by NMR and IR spectroscopy, and the molecular structure of compounds **4b** and **7** has been confirmed by X-ray crystallography. On the basis of the reported studies, the general pathway for an interaction of amino acids with aluminum alkyls is proposed and some new insight into the reaction mechanism of the carboxylate group alkylation is provided.

Introduction

The study of the reaction of carboxylic acids with aluminum compounds is applicable to material science,[1] bioinorganic chemistry,[2] and organic synthesis.[3] With a view to investigate what effect both the metal alkyl and the organic residue have on the formation of group 13 carboxylates, we have carried out reactions of MR_3 (M = Al, Ga, and In; R = Me, Et, or ^{t}Bu) with a variety of bifunctional carboxylic acids, LH_2 type reagents.[4−8] The organoaluminum derivatives of salicylic acid (2-hydroxybenzoic acid) or phthalic acid, the tetranuclear $[R_2Al]_4[L]_2$ type complexes, are interesting models for exploring the coordination chemistry of aluminum carboxylates. In particular, we have demonstrated that the *anti* direction is the most likely location of the aluminum center relative to the carboxylate group and proved that a bidentate carboxylate group is isomorphic with an alkoxide ligand.[4−6] On the other hand, we have demonstrated that organometallic complexes derived from anthranilic acid and related carboxylic acids provide the means to study intra- and intermolecular forces resulting from donor−acceptor and hydrogen-bonding interactions. For instance, the reaction of anthranilic acid with 1 and 2 equiv of $Al(^tBu)_3$ afforded the dimeric carboxylate $[(^tBu_2)Al(O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$ (**1**), consisting of the weak intramolecular hydrogen bonding and the dialuminumcarboxylate chelate complex $(^tBu_2)Al(O_2CC_6H_4\text{-}2\text{-}NH_2)Al(^tBu)_3$ (**2**), respectively.[7] In both cases only the CO_2H proton was involved in the alkane elimination and the carboxylate moiety acts as a monoanionic LH ligand, and for compound **1** the NH_2 group does not participate in the coordination to the metal center but is involved in an intramolecular hydrogen bond.[7]

We report here on the related reactions of lower aluminum alkyls with anthranilic acid and glycine. The obtained results provide some new insight into the reaction mechanisms of amino acids with aluminum alkyls and the reaction stages of the carboxylate group

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(1) Yamane, H.; Kimura, Y. *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRS Press: Boca Raton, FL, 1996; Vol. 1, p 202, and references therein. Landry, C. C.; Pappe, N.; Mason, M. R.; Apblett, A. W.; Tyler, A. N.; McInnes, A. N.; Barron, A. R. *J. Mater. Chem.* **1995**, *5*, 331. Kareiva, A.; Harlan, C. J.; McQueen, D. B.; Cook, R. L.; Barron, A. R. *Chem. Mater.* **1996**, *8*, 2331. Defriend, K. A.; Barron, A. R. *J. Mater. Sci.* **2003**, *38*, 927.

(2) See for example: Powell, A. K.; Heath, S. L. *Coord. Chem. Rev.* **1996**, *149*, 59, and references therein. Kiss, T.; Sóvágó, I.; Tóth, I.; Lakatos, A.; Bertani, R.; Tapparo, A.; Bombi, G.; Martin, R. B. *J. Chem. Soc., Dalton Trans.* **1997**, 1967.

(3) Gibson, V. C.; Redshaw, C.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 79.

(4) Lewiński, J.; Zachara, J.; Justyniak, I. *Organometallics* **1997**, *16*, 3859.

(5) Lewiński, J.; Zachara, J.; Justyniak, I. *Inorg. Chem.* **1998**, *37*, 2575.

(6) Lewiński, J.; Justyniak, I.; Lipkowski, J.; Zachara, J. *Inorg. Chem. Commun.* **2000**, *3*, 700.

(7) Branch, C. S.; Lewiński, J.; Justyniak, I.; Bott, S. G.; Lipkowski, J.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **2001**, 1253.

(8) For selected examples on the reactions of aluminum alkyls with monodentate carboxylic acids, see: Bethley, C. E.; Aitken, C. L.; Harlan, C. J.; Koide, Y.; Bott, S. G.; Barron, A. R. *Organometallics* **1997**, *16*, 329. Pietrzykowski, A.; Pasynkiewicz, S.; Popławska, J. *Main Group Metal. Chem.* **1996**, *18*, 651.

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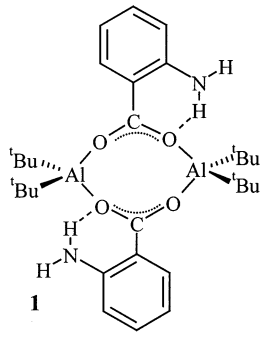

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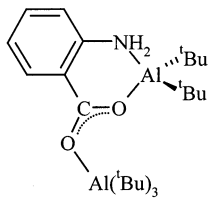


2

C-alkylation proposed by Mole.[9] Our data are also of particular interest with respect to the recent report of Gibson and co-workers where the reaction of $AlMe_3$ with anthranilic acid, followed by treatment with acetonitrile, has been recognized as a potentially valuable tool for preparing N-heterocycles.[3] An additional interesting aspect of the latter reaction is the presence of alumoxane moieties in the organometallic product backbone, which indicates that aluminum carboxylates can serve as interesting starting materials for various aluminoxanes.[10]

Results and Discussion

Synthesis and Structure of Alkylaluminum Derivatives of Anthranilic Acid. The reaction of AlR_3 (R = Me or Et) with 1 molar equiv of anthranilic acid yields the dimeric carboxylates $[R_2Al(O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$ (**3**) in high yields. Both compounds, the methyl (**3a**) and ethyl (**3b**) derivatives, are unstable at ambient temperature in a solution that follows from the ^1H NMR study. The low-temperature NMR and IR spectra are consistent with that observed for the *tert*-butyl derivative **1**,[7] which indicates that all three compounds have similar structures. Unfortunately, difficulties in isolating **3a** or **3b** preclude its structural characterization by X-ray crystallography.

The addition of 2 molar equiv of AlR_3 (R = Me or Et) to anthranilic acid results in the formation of the tetranuclear complexes $[R_2Al]_4[\mu\text{-}O_2CC_6H_4\text{-}2\text{-}\mu\text{-}NH]_2$ (**4**). Thus, in this case both protic functionalities (i.e., CO_2H and NH_2 groups) are involved in the alkane elimination, unlike the analogous reaction with $Al(^tBu)_3$.[7] Compound **4** is the only product formed even when excess AlR_3 is employed, which indicates that the carboxylate group of the aromatic acid derivative is resistant to C-alkylation (vide infra). The methyl derivative **4a** is insoluble in common noncoordinating solvents and was characterized only by IR spectroscopy. It is solubilized upon addition of γ-picoline (py-4-Me), followed by heating in dichloromethane. Filtration and cooling to room temperature afforded **4a** as bright yellow crystals. Undoubtedly, the solubilization is accompanied by a complex formation of **4a** with added py-4-Me (vide infra). The ethyl compound **4b** is isolated as a yellow aromatic hydrocarbon-soluble, oxygen- and moisture-sensitive crystalline solid. No decomposition of **4a** and **4b** was observed after refluxing in toluene for several hours. The molecular structure of **4b** has been determined by a single-crystal X-ray diffraction study, and the solution structure has been confirmed by NMR and IR spectroscopy and cryometric molecular weight measurements.

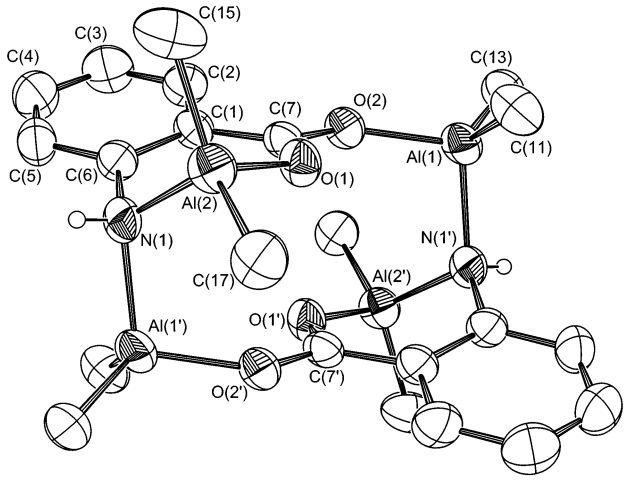


Figure 1. ORTEP view of $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}NH]_2$ (**4b**) with atom-numbering scheme. Thermal ellipsoids are shown at the 30% probability level. Methyl groups of the ethyl substituents are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 4b and 7

4b[a]		**7**	
Al(1)−O(2)	1.835(3)	Al(1)−O(1)	1.8890(14)
Al(1)−N(1′)	1.990(4)	Al(2)−O(1)	1.8332(15)
Al(1)−C(11)	1.950(2)	Al(2)−N(1)	1.998(2)
Al(1)−C(13)	1.962(3)	Al(1)−C(7)	1.976(3)
Al(2)−O(1)	1.843(3)	Al(1)−C(8)	1.986(2)
Al(2)−N(1)	1.953(4)	Al(1)−C(9)	1.970(2)
Al(2)−C(15)	1.950(2)	Al(2)−C(5)	1.945(3)
Al(2)−C(17)	1.950(2)	Al(2)−C(6)	1.950(3)
O(1)−C(7)	1.265(4)	O(1)−C(1)	1.463(2)
O(2)−C(7)	1.272(4)	N(1)−C(2)	1.474(4)
N(1)−C(6)	1.444(4)	C(1)−C(2)	1.523(4)
O(2)−Al(1)−N(1′)	101.14(13)	O(1)−Al(2)−N(1)	86.83(8)
O(1)−Al(2)−N(1)	90.36(14)	Al(1)−O(1)−Al(2)	118.90(7)
Al(2)−N(1)−Al(1′)	116.76(17)	C(5)−Al(2)−C(6)	120.69(14)
C(7)−O(1)−Al(2)	126.2(2)	C(1)−O(1)−Al(1)	126.46(12)
C(7)−O(2)−Al(1)	132.1(3)	C(1)−O(1)−Al(2)	114.15(12)
C(6)−N(1)−Al(2)	110.4(2)	C(2)−N(1)−Al(2)	105.86(15)
C(6)−N(1)−Al(1′)	114.6(3)	C(2)−C(1)−O(1)	105.15(19)
O(1)−C(7)−O(2)	120.3(4)		
O(1)−C(7)−C(1)	121.4(3)		
O(2)−C(7)−C(1)	118.4(3)		

[a] Data for one of two similar molecules in the unit cell. Atoms labeled with a prime belong to the centrosymmetric counterpart of the dimeric units, symmetry code (−*x*, −*y*, −*z*).

The molecular structure of **4b** and atom-numbering scheme are shown in Figure 1, and selected bond lengths and angles are given in Table 1. The unit cell contains two unique molecules which reside on inversion centers and are essentially identical. The central core in **4b** consists of two dianionic anthranilate moieties joined by two bridging diethylaluminum species. Additionally, the diethylaluminum units form intramolecular bridges between the carboxylate and amide functionalities. The carboxylate group is rotated about the C−C bond relative to the aromatic ring by 17.3(2)°, and the O(1)−Al(2)−N(1) bite angle is 90.4(1)°. The carboxylate groups display a bidentate coordination

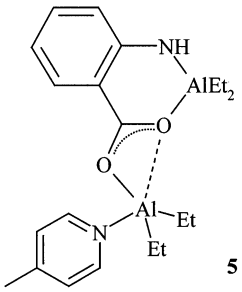
(9) Meisters, A.; Mole, T. *Aust. J. Chem.* **1974**, *27*, 1665.

(10) Very recently, the formation of alumoxane moieties in the organometallic backbone has also been observed in the reaction of hydroxy carboxylic acids with $AlMe_3$. Skrok, T.; Pietrzykowski, A.; Radzymiński, T. *XIVth FECHEM Conference on Organometallic Chemistry*, Gdańsk, 2001; Book of Abstracts, p 33.

mode in a *syn-anti* conformation with two aluminum atoms. These metal centers are slightly deviated above and below the plane of the carboxylate group [0.145(5) Å, Al(1), and 0.260(5) Å, Al(2)]. The N(1)−Al(2) bond length [1.953(4) Å] is shorter than that observed for N(1)−Al(1′) [1.990(4) Å]. As seen from Figure 1, the Al(1′)−N(1) bond lies in the plane almost perpendicular to the aromatic ring, as indicated by the Al(1′)−N(1)−C(6)−C(5) torsion angle of 89.0(4)°. The Al(2)−O(1) bond situated in the *anti* direction with respect to the carboxylate group [1.843(3) Å] is slightly longer than that in the *syn* direction [1.835(3) Å], which is opposite the expected strength order in regard to the preferred coordination mode of aluminum relative to a carboxylate group.[5] Finally, the structure of **4b** is of the same morphology as the related aluminum derivative of salicylic acid, $[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}O]_2$.[4]

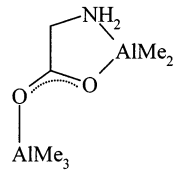
The tetranuclear structure of compound **4b** is retained in solution. The ^{1}H NMR spectrum consists of two overlapping pairs of quartets for the methylene Al-CH_2-CH_3 protons and four well-separated triplets for the methyl Al-CH_2CH_3 protons. These four pairs of ethyl resonances correspond to the equivalent in pairs of ethyl groups of the diethylaluminum units in the dimeric compound. The ^{13}C NMR data are also consistent with the tetranuclear structural motif. The ^{27}Al NMR spectrum of **4b** shows one broad resonance at 140.5 ppm, whose chemical shift is similar to that observed for other four-coordinate dialkylaluminum complexes with *O*,*N*-bidentate ligands.[11] It is worth noting that the intensity of the resonance signal is relatively low and there is a problem with the detection of resonance signals resulting from the quadruple moment of aluminum and nitrogen.[12]

Addition of γ-picoline to a solution of **4b** in toluene results in a disruption of the tetranuclear cluster to afford $Et_2Al(\eta\text{-}O_2CC_6H_4\text{-}2\text{-}NH)AlEt_2$(py-4-Me) (**5**). The resulting compound has been characterized by ^{1}H and ^{13}C NMR and IR spectroscopy and cryometric molecular weight measurements. The molecular weight measurements have revealed that **5** occurs as a monomeric species in solution. The ^{1}H NMR spectrum of compound **5** contains two types of Al-Et groups and one Me group of py-4-Me. On the basis of the integrations, only one py-4-Me is coordinated to one of the Et_2Al moieties. On the basis of these data and the structure characterization of the related gallium derivative of salicylic acid, $Me_2Ga(\eta^2\text{-}O_2CC_6H_4\text{-}2\text{-}O)GaMe_2$(py-4-Me),[13] the structure of adduct **5** may be best described as a monomeric complex in which one $AlEt_2$ moiety is chelated by the carboxylate oxygen and amide nitrogen and the second $AlEt_2$ moiety is terminally bonded to the carboxylate group. To the terminal $AlEt_2$ unit is additionally coordinated one py-4-Me molecule. Adduct **5** is relatively unstable in solution and slowly disproportionates to unidentified products. Unfortunately, difficulties in isolating **5** preclude its structural characterization by X-ray crystallography.



5

Reactions of Glycine with $AlMe_3$. The reaction of 2 molar equiv of $AlMe_3$ with glycine yields the alkylaluminum carboxylate $Me_2Al(O_2CCH_2NH_2)AlMe_3$ (**6**), in which only the carboxylic group is deprotonated. Compound **6** is stable below 0 °C in solution and has been characterized by low-temperature ^{1}H and ^{13}C NMR and IR spectroscopy. The ^{1}H NMR spectrum of **6** shows one resonance pattern with a broad single resonance of the Al-Me protons in the temperature range 0 to −70 °C. On the basis of the reported structure of the *tert*-butyl derivative **2**,[7] it is reasonable to assume an analogous structure for adduct **6**. The occurrence of one broad signal due to the Al-Me groups indicates the operation of a dynamic process. However, we cannot exclude other type species in solution.



6

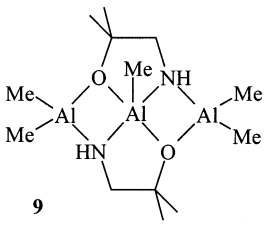
Several attempts to obtain crystals of compound **6** suitable for X-ray analysis were unsuccessful. Surprisingly, this effort yielded a small amount of the aluminum alkoxide $Me_2Al[OC(CH_3)_2CH_2NH_2]AlMe_3$ (**7**). The isolation of compound **7** as a side product, in ca. 5% yield, from the reaction mixture indicated the alkylation of the carboxylate group during the course of the reaction. Therefore we have also studied the reaction of glycine with greater than 2 equiv of $AlMe_3$. The addition of excess $AlMe_3$ to glycine results in the formation of a complex mixture of products as determined by ^{1}H and ^{13}C NMR spectroscopy. In this case, undoubtedly the alkylation reaction is favored, which was confirmed by the observation of a resonance in the ^{13}C NMR for a quaternary carbon and the loss of the carboxylate resonance. In fact, it is also likely that additional $AlMe_3$ promotes the subsequent alkane elimination in compound **4**, which afforded the glycinate analogue of the tetranuclear compound **4**, i.e., the intermediate compound $[Me_2Al]_4[\mu\text{-}O_2CCH_2\text{-}\mu\text{-}NH]_2$ (**8**), as well as the deprotonation of the amine in compound **7**, resulting in the formation of the trinuclear compound $[AlMe_2]_2[\{OC(CH_3)_2CH_2NH\}_2AlMe]$ (**9**). We have been unable to isolate compounds **8** and **9** from the postreaction mixtures, but formulation of **8** is consistent with the reaction of anthranilic acid with $AlMe_3$, and formu-

(11) Lewiński, J. Heteronuclear NMR Applications (B, Al. Ga, In, Tl), In *Encyclopedia of Spectroscopy and Spectrometry*; Lindon J. C., Tranter G. E., Holmes J. L., Eds.; Academic Press: London, 1999; Vol. 1, pp 691−703.

(12) We have observed the same effect for dialkylaluminum chelate complexes derived from *N*-phenylsalicylideneimine: Lewiński, J.; Zachara, J.; Starowieyski, K. B.; Ochal, Z.; Justyniak, I.; Kopeć, T.; Stolarzewicz, P.; Dranka, M. *Organometallics* **2003**, *18*, 3773.

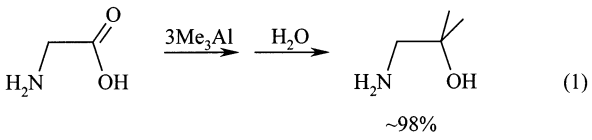
(13) Justyniak, I.; Lewiński, J.; Zachara, J. *XIIIth FECHEM Conference on Organometallic Chemistry*; Lisboa, 1999; Book of Abstracts, p 210.

lation of **9** is consistent with our previous studies that have demonstrated the ready formation of analogous trinuclear compounds in the reaction of 2 equiv of $AlMe_3$ with 2-(hydroxymethyl)aniline, i.e., $[AlMe_2]_2[(OCH_2C_6H_4\text{-}2\text{-}NH)_2AlMe]$.[14]



9

The observed complexity of the postreaction mixture may also result from the fact that the carboxylate C-alkylation appears to proceed with concomitant alumoxane (MAO) formation (vide infra). Notably, the ^1H NMR spectrum of the reaction mixture (i.e., glycine with 3 equiv of $AlMe_3$) shows, in addition to other Al-Me signals, a well-separated broad resonance at −0.30 ppm, which is often interpreted as indicative of methylalumoxane.[15] On the other hand, the recent studies show that $(MeAlO)_n$ units are often involved in the organometallic product backbone[3,10,16] and can even catalyze some transformations.[15a] Therefore, it is reasonable to assume that the reaction of glycine with more than 2 equiv of $AlMe_3$ affords some organometallic species involving alumoxane and alkoxyaluminum moieties. It is worth noting that the analysis of the outcome of the reaction of glycine with 3 equiv of $AlMe_3$ confirms complete conversion of glycine toward 1-amino-2-methyl-2-propanol after hydrolysis of the postreaction mixture (eq 1).



(1)

The molecular structure of the alkoxide adduct **7** has been determined by a single-crystal X-ray diffraction study, and the solution structure has been confirmed by ^1H and ^{13}C NMR spectroscopy (see Experimental Section). The molecular structure of compound **7** (Figure 2) is analogous to the previously reported dinuclear adducts derived from aluminum alkyls and amine alcohols.[17] The alkoxide ligand with amine termini chelates the $Me_2Al(2)$ moiety, while the $Me_3Al(1)$ unit binds to the alkoxide oxygen atom. The Al(2)−O(1) and Al(2)−N(1) bond distances are 1.8332(15) and 1.998(2) Å, respectively, and are comparable with the distances observed in analogous complexes.[17] The aluminum coordination sphere is distorted from an ideal tetrahedral geometry due to the small bite angle of the chelate ligand [O(1)−Al(2)−N(1) 86.83(8)°]. The five-membered chelate ring Al(2)−O(1)−C(1)−C(2)−N(1) is puckered, as demonstrated by the twisting on the C(1)−C(2) bond in order to minimize the ring strain.

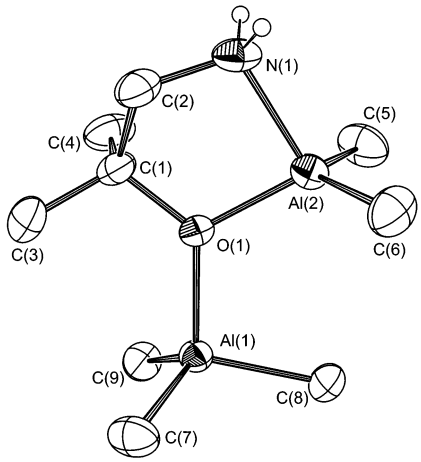


Figure 2. ORTEP view of $Me_2Al[OC(CH_3)_2CH_2NH_2]AlMe_3$ (**7**) with atom-numbering scheme. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms (excluding amine hydrogens) are omitted for clarity.

Mechanistic Considerations. On the basis of our studies we propose the following general pathway for an interaction of amino acids with aluminum alkyls and provide some new insight into the reaction mechanism of the carboxylate group alkylation (Scheme 1). Initially, depending on the reactant molar ratio, the reaction of amino acids with AlR_3 leads to compound **I** or **II**, which consist of only a deprotonated carboxylic group. The relative stability of the type **I** and **II** compounds is determined by the nature of both the amino acid and aluminum-bonded alkyl substituents. For the lower alkyls the adduct **II** can readily be transformed into tetrametallic compound **III** upon deprotonation of the amine functionality (*path 1*), or the C-monoalkylation of the carboxylate group with the formation of species **IV** can take place (*path 2*), depending on the nature of the amine carboxylate ligand. Clearly, the further reaction course is controlled by the Brönsted acidity of the amine termini and the carboxylate group propensity toward C-alkylation. Thus, the more acidic anthranilate NH_2 group undergoes alkane elimination according to *path 1*, whereas the less acidic glycinate NH_2 remains intact in similar reaction conditions and the C-alkylation is favored. According to Scheme 1, the formation of the alkoxide compound **VI**, an analogue of the isolated $Me_2Al[OC(CH_3)_2CH_2NH_2]AlMe_3$ (**7**), is initiated by the attack of the Al-Me group at the carboxylate electrophilic carbon atom of **II** to produce intermediate **IV**. In the presence of an excess of Me_3Al the subsequent C-nucleophile addition, for example proceeding throughout intermediate **V**, leads to dimetallic adduct **VI** with concomitant formation of an alumoxane moiety, MAO.[18,19] Thus, according to our mechanistic consideration, alu-

(14) Lewiński, J.; Zachara, J.; Kopeć, T. *Inorg. Chem. Commun.* **1998**, *1*, 182.

(15) See for example: (a) Obrey, S. J.; Bott, S. G.; Barron, A. R. *Organometallics* **2001**, *20*, 5162. (b) Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* **1990**, *23*, 4489.

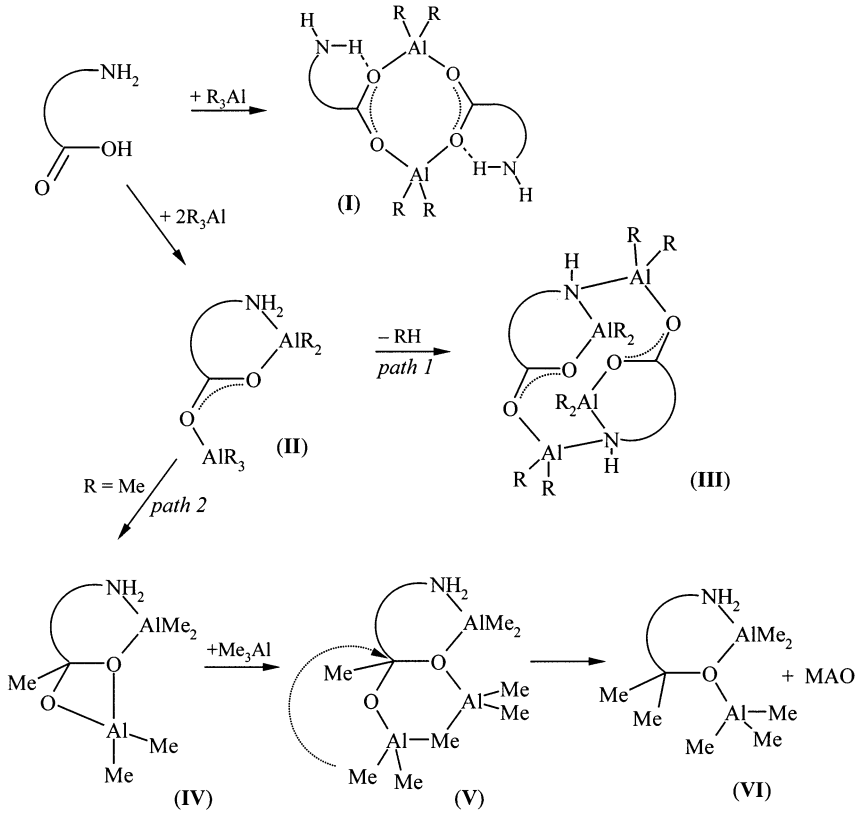
(16) Sobota, P.; Utko, J.; Ejfler, J.; Jerzykiewicz, L. B. *Organometallics* **2000**, *19*, 4929.

(17) van Vliet, M. R. 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. Atwood, D. A.; Gabbai, F. P.; Lu, J.; Remington, M. P.; Rutherford, D.; Sibi, M. P.; *Organometallics* **1996**, *15*, 2308. McMahon, C. N.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1998**, 3301.

(18) 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 $[MAO]_n$ will be employed for convenience.

(19) For structural aspects of alumoxanes see for example: Pasynkiewicz, S. *Polyhedron* **1990**, *9*, 429. Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

Scheme 1



Scheme 2. Reaction Stages for the C-Alkylation of the Carboxylate Group by $AlMe_3$ Proposed by Mole[9]

$$RCO_2H \xrightarrow{Me_3Al} RCO_2AlMe_2$$

$$RCO_2AlMe_2 \xrightarrow{Me_3Al} RCOMe$$

$$RCOMe \xrightarrow{2Me_3Al} RCMe_2OAl_2Me_5$$

moxanes (or MAO) can be easily formed in the reaction of carboxylic acids with aluminum alkyls even at ambient temperature. It is worth noting that the literature precedent for the C-alkylation of the carboxylate group by $AlMe_3$ includes the conversion of aluminum carboxylates to corresponding ketones, which is followed by further methylation to a hemialkoxide (Scheme 2).[9]

Furthermore, on the basis of our studies it becomes clear that the reaction of Me_3Al with anthranilic acid followed by treatment with acetonitrile, recently described by Gibson et al.,[3] involves formation of the tetrametallic complex **4a**, its adduct with a Lewis base, **VII**, and a subsequent N-heterocycle **VIII** formation (Scheme 3). In this reaction acetonitrile addition to the methyl compound **4a** is essential for the generation of the soluble monomeric analogue of compound **5a**, i.e., $Me_2Al(\eta^2\text{-}O_2CC_6H_4\text{-}2\text{-}NH)AlMe_2(CH_3CN)$. Further, according to the authors' suggestion the final reaction product arises via insertion of acetonitrile into Al−N bonds, and in the latter reaction MAO is involved in the organometallic product backbone.

Experimental Section

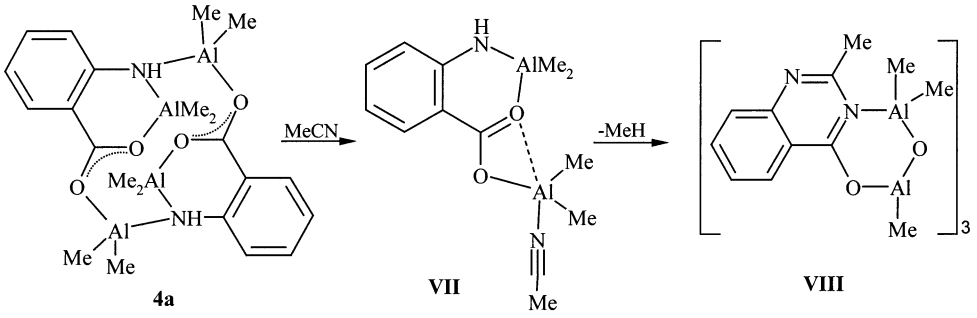
All operations were carried out under a nitrogen atmosphere using standard Schlenk and high-vacuum techniques. Solvents were purified and dried by standard techniques. The NMR spectra, in C_6D_6 unless otherwise stated, were recorded on a Varian 300VXL spectrometer, and the IR spectra (4000−400 cm^{-1}) were recorded as CH_2Cl_2 solution or Nujol mulls on a Specord-75IR spectrophotometer. Molecular weight measurements were carried out cryoscopically in benzene. Commercially available reagents were used as purchased.

$[Me_2Al(O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$ (3a). To a suspension of anthranilic acid (0.96 g, 7 mmol) in CH_2Cl_2 (15 mL) was added dropwise $AlMe_3$ (0.50 g, 7 mmol) at −78 °C. The reaction mixture was allowed to warm to 10 °C and then cooled to −30 °C for 1 day to yield yellow crystals (1.18 g, 87%). Anal. Calcd for $C_{18}H_{24}Al_2N_2O_4$: C 55.96, H 6.26, N 7.25. Found: C 55.78, H 6.34, N 7.18. IR (Nujol, cm^{-1}): 3510 (w), 3399 (w), 1616 (m), 1576 (m), 1533 (m), 1461 (s), 1413 (m), 1378 (w), 1301 (w), 1254 (m), 1164 (m), 751 (w), 524 (w). ^1H NMR (d_8-toluene, 0 °C): δ −0.25 (s, 6H, Al-CH_3), 4.92 (s, 2H, NH_2), 5.95 (d, 1H, CH), 6.37 (t, 1H, CH), 6.91 (t, 1H, CH), 7.95 (d, 1H, CH). ^{27}Al NMR: δ 149 ($w_{1/2}$ = 2190 Hz).

$[Et_2Al(O_2CC_6H_4\text{-}2\text{-}NH_2)]_2$ (3b). This compound was prepared in an analogous manner to compound **3a** using $AlEt_3$ (0.80 g, 7 mmol) and anthranilic acid (0.96 g, 7 mmol). Yield: 1.40 g, 90%. Anal. Calcd for $C_{22}H_{32}Al_2N_2O_4$: C 59.72, H 7.29, N 6.33. Found: C 59.61, H 7.37, N 6.31. IR (Nujol, cm^{-1}): 3503 (w), 3389 (w), 1620 (m), 1576 (m), 1539 (m), 1458 (s), 1439 (m), 1377 (w), 1304 (w), 1258 (m), 1161 (m), 986 (w), 753 (w), 709 (w), 530 (w). ^1H NMR (d_8-toluene, 0 °C): δ 0.39 [q, 4H, Al(CH_2CH_3)], 1.37 [t, 6H, Al(CH_2CH_3)], 4.97 (s, 2H, NH_2), 5.98 (d, 1H, CH), 6.39 (t, 1H, CH), 6.91 (t, 1H, CH), 8.05 (d, 1H, CH). ^{27}Al NMR: δ 151 ($w_{1/2}$ = 2550 Hz).

$[Me_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}NH]_2$ (4a). To a suspension of anthranilic acid (0.96 g, 7 mmol) in CH_2Cl_2 (15 mL) was added dropwise $AlMe_3$ (1.00 g, 14 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature. After stirring for an additional 1 h at ambient temperature, the resulting mixture was filtered. Yield: 1.55 g, 89%. Anal. Calcd for $C_{22}H_{34}Al_4N_2O_4$: C 53.01, H 6.88, N 5.62. Found: C 52.79, H 6.97, N 5.64. IR (Nujol, cm^{-1}): 3233 (w), 1614 (s), 1601 (m),

Scheme 3



1559 (m), 1461 (s), 1426 (m), 1377 (w), 1334 (w), 1307 (w), 1259 (w), 1200 (m), 1164 (w), 1101 (w), 942 (w), 825 (w), 804 (w), 575 (w).

$[Et_2Al]_4[(\mu\text{-}O_2C)C_6H_4\text{-}2\text{-}\mu\text{-}NH]_2$ (4b). To a suspension of anthranilic acid (0.96 g, 7 mmol) in CH_2Cl_2 (15 mL) was added dropwise $AlEt_3$ (1.6 g, 14 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature. After stirring for an additional 1 h, the solution was concentrated and then cooled to −15 °C for 1 day to yield yellow crystals (1.94 g, 91%). Anal. Calcd for $C_{30}H_{50}Al_4N_2O_4$: C 59.01, H 8.25, N 4.59. Found: C 58.88, H 8.31, N 4.58. IR (CH_2Cl_2, cm^{-1}): 3376 (w), 1619 (s), 1568 (s), 1524 (s), 1464 (s), 1416 (m), 1352 (m), 1304 (w), 1232 (w), 1212 (w), 1160 (m), 1068 (w), 1044 (m), 988 (m), 952 (w), 812 (m), 532 (w), 492 (w). ^{1}H NMR (25 °C): δ −0.18 [m, 8H, Al(CH_2CH$_3$)], 0.44 [q, 8H, Al(CH_2CH$_3$)], 0.88 [t, 6H, Al(CH$_2$$CH_3$)], 1.12 [t, 6H, Al(CH$_2$$CH_3$)], 1.25 [t, 6H, Al(CH$_2$$CH_3$)], 1.44 [t, 6H, Al(CH$_2$$CH_3$)], 2.91 (s, 2H, NH); 6.04 (d, 2H, CH), 6.62 (t, 2H, CH), 6.86 (t, 2H, CH), 7.98 (d, 2H, CH). ^{13}C NMR: δ −2.43, −1.16, −0.68, −0.35, 7.96, 8.09, 8.72, 9.09, 121.04, 124.10, 125.05, 133.412, 136.17, 147.98, 176.22. ^{27}Al NMR δ 140.5 (broad). Cryoscopic molecular weight, benzene solution, formula weight calcd for $C_{30}H_{50}Al_4N_2O_4$: 610.65, found 610.

$Et_2Al(\eta\text{-}O_2CC_6H_4\text{-}2\text{-}NH)AlEt_2$(py-4-Me) (5). To a solution of **4b** (0.98 g, 1.6 mmol) in toluene (5 cm^3) was added γ-picoline (0.30 g, 3.2 mmol) at room temperature. After stirring for 5 min, solvent and excess γ-picoline were removed in vacuo to leave quantitatively a yellow solid, which was then washed with hexane. Anal. Calcd for $C_{21}H_{32}Al_2N_2O_2$: C 63.30, H 8.09, N 7.03. Found: C 63.24, H 8.18, N 7.08. IR (CH_2Cl_2, cm^{-1}): 3376 (w), 1616 (s), 1568 (s), 1524 (s), 1464 (s), 1416 (m), 1352 (m), 1304 (w), 1232 (w), 1212 (m), 1188 (w), 1160 (m), 1068 (w), 1044 (m), 988 (m), 952 (w), 920 (w), 852 (w), 812 (m), 648 (s), 492 (w). ^{1}H NMR (25 °C): δ 0.27 [q, 4H, Al(CH_2CH$_3$)], 0.43 [q, 4H, Al(CH_2CH$_3$)], 1.35 [t, 6H, Al(CH$_2$$CH_3$)], 1.39 [t, 6H, Al(CH$_2$$CH_3$)], 2.32 (s, 3H, CH_3), 3.97 (s, 1H, NH), 6.19 (d, H, CH), 6.32 (t, H, CH), 6.35 (d, 2H, $CH_{py-4-Me}$), 6.94 (t, H, CH), 8.01 (d, 2H, $CH_{py-4-Me}$), 8.03 (d, 1H, CH). ^{13}C NMR: δ −1.39, −0.77, 8.58, 9.65, 21.4, 107.42, 112.71, 121.15, 126.33, 132.72, 135.75, 146.71, 153.54, 160.78, 175.80. ^{27}Al NMR δ = 141 (broad). Cryoscopic molecular weight, benzene solution, formula weight calcd for $C_{21}H_{32}Al_2N_2O_2$: 398.45, found 401.

$Me_2Al(O_2CCH_2NH_2)AlMe_3$ (6). To a suspension of glycine (0.60 g, 8 mmol) in toluene (15 mL) was added dropwise $AlMe_3$ (1.15 g, 16 mmol) at −78 °C. The reaction mixture was allowed to warm to 0 °C and then to stir for 3 h. Addition of hexane at −20 °C followed by filtration afforded a white solid precipitate. Yield: 1.35 g, 83%. Anal. Calcd for $C_7H_{19}Al_2NO_2$: C 41.38, H 9.42, N 6.89. Found: C 41.12, H 9.48, N 6.94. IR (CH_2Cl_2, cm^{-1}): 3944 (w), 3300 (w), 1632 (s), 1548 (s), 1442 (s), 1352 (w), 1262 (s), 896 (m), 604 (w), 596 (w), 564 (w), 488 (w). ^{1}H NMR (d_8-toluene, 0 °C): δ −0.51 (s, 15H, Al−CH_3), 3.64 (s, 2H, CH_2), 3.02 (br, 2H, NH_2). ^{13}C NMR (d_8-toluene, 0 °C): δ −8.67 (broad), 53.42, 186.5. ^{27}Al NMR (d_8-toluene, 0 °C): δ 148 (broad).

$Me_2Al[OC(CH_3)_2CH_2NH_2]AlMe_3$ (7). This compound was prepared in a manner similar to that for compound **6**; however, the reaction mixture of glycine with 2 equiv of $AlMe_3$ was allowed to warm to room temperature and then recrystallized in CH_2Cl_2 (−20 °C), yielding colorless crystals (in ca. 15% yield). Anal. Calcd for $C_9H_{25}Al_2NO$: C 49.75, H 11.60, N 6.45. Found: C 49.55, H 11.69, N 6.38. ^{1}H NMR (25 °C): δ −0.56 (s, 6H, Al−CH_3), −0.20 (s, 9H, Al−CH_3), 1.44 (s, 6H, CH_3). 2.68 (br, 2H, CH_2), 3.07 (br, 2H, NH_2). ^{13}C NMR: δ −10.66, −8.91, 26.76, 46.34, 73.92.

Table 2. Summary of Crystal Data and Structure Determination for 4b and 7

molecular formula	$C_{30}H_{50}Al_4N_2O_4$	$C_9H_{25}Al_2NO$
fw	610.65	217.26
temperature, K	293(2)	293(2)
cryst size, mm	0.40 × 0.22 × 0.14	0.42 × 0.30 × 0.24
wavelength (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	10.6073(12)	6.9415(6)
b, Å	10.6835(11)	13.7945(12)
c, Å	17.244(2)	15.0859(13)
α, deg	97.884(9)	90
β, deg	95.339(9)	91.281(7)
γ, deg	107.868(8)	90
V, Å^3	1823.2(4)	1444.2(2)
Z	2	4
density calc, g·cm^{-3}	1.112	0.999
linear abs coeff, mm^{-1}	0.160	0.174
F(000)	656	480
θ range, deg	2.0−25.0	3.2−29.0
no. of reflns collected	6785	28 401
no. of ind reflns	6410 (R_{int} = 0.019)	3698 (R_{int} = 0.066)
no. of data/restr/params	6410/172/486	3698/0/150
goodness-of-fit on F^2	0.952	1.103
final R1, wR2 values [$I > 2\sigma(I)$][a]	0.0565, 0.1076	0.0548, 0.1339
wR2 (all data)[a]	0.1608	0.1555
residual extreme, e·Å^{-3}	+0.20/−0.18	+0.25/−0.25

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Alkylation of Glycine with $AlMe_3$. To a suspension of glycine (0.60 g, 8 mmol) in toluene (15 mL) was added dropwise $AlMe_3$ (1.73 g, 24 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and then to stir for 3 h. The solution was later treated with KF and water to form a white precipitate. Vigorous stirring of the resulting suspension was continued at ambient temperature, and after 0.5 h the organic products formed were extracted with ethyl ether. Etherate was later removed, dried with anhydrous $MgSO_4$, and analyzed by HPLC and ^{1}H NMR.

X-ray Structure Determination. Single crystals of **4b** and **7**, suitable for X-ray diffraction studies, were placed in thin walled capillary tubes (Lindemann glass 0.5 mm) in an inert atmosphere. The selected crystallographic data, the parameters of data collections, and refinement procedures are presented in Table 2. Data for compound **4b** were collected on a four-circle P3 (Siemens AG) diffractometer. The crystal class and the orientation matrix were obtained from the least-squares refinement of 26 well-centered reflections randomly selected in the 2θ range 12.9−28.3°. The intensities were

collected in the $\omega-2\theta$ mode. A meaningful crystal decay of 26% was noticed. After correction for the Lorentz−polarization effect and crystal decomposition, the equivalent reflections were averaged. The structure was solved by direct methods using the SHELXS-86 program.[20a] The distribution of the peaks showed that compound **4b** crystallizes with two crystallographically independent half-molecules in the asymmetric unit, resulting in Z of 2. Full-matrix least-squares refinement method against F^2 values was carried out by using the SHELXL-97 program.[20b] All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms except N-H atoms (refined isotropically) were refined with fixed geometry, riding on carbon atoms, with a fixed isotropic displacement parameter equal to 1.2 or 1.5 (methyl group) times the value of the equivalent isotropic displacement parameter of the parent carbon. Difference Fourier maps indicated disorder of ethyl groups in both independent molecules. Final results with $R = 0.0565$ were obtained with a restraint model in which atoms of the ethyl groups were disordered over two sets of positions with adjusted occupancy factors (the final SOF values being in the range 0.65(4)−0.81(2) for major conformers) and restraining chemically equivalent Al−C and C−C distances to be equal. Refinement of positional and thermal parameters led to convergence. The final weighting scheme for **4b** was $w^{-1} = \sigma^2(F_o^2) + (0.0586P)^2$, where $P = (F_o^2 + 2F_c^2)/3$.

Diffraction measurements of compound **7** were made on a KM4 goniometer (Kuma/Oxford Instruments) equipped with a CCD detector. Intensities of 28 968 reflections were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods and refined by using the full-matrix least-squares method on F^2.[20] All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The amine hydrogens were located from the difference Fourier map and isotropically refined. The hydrogen atoms of the methyl groups, bonded to the aluminum atom Al(2), were refined as a disordered group with two positions rotated by 60° about the Al−C vector. The remaining H atoms were introduced at geometrically idealized coordinates. Final weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (0.0768P)^2$, where $P = (F_o^2 + 2F_c^2)/3$. The largest positive and negative peaks on the difference Fourier map have no significant chemical meaning, and the maximum shift/error ratios in the final cycle of refinement were less than 0.001.

(20) (a) Sheldrick, G. M. *SHELXS-86. 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.

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Supporting Information Available: Full details of the X-ray structural analysis of **4b** and **7** including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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