

Alkylaluminum Derivatives of Diphenic Acid: Novel Aluminum Carboxylates

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The reaction of trialkylaluminum compounds with diphenic acid in a 2:1 molar ratio results in the formation of novel dialkylaluminum dicarboxylates [Et₂Al₂(OCC₁₂H₈COO)]₃ (**1**) and [Bu₂Al₂(OCC₁₂H₈COO)]₂ (**2**). Molecular structures of the compounds have been determined by X-ray crystallography. Compound **1** is a hexamer with a skeleton framework consisting of four fused heterocyclic rings, one 27-membered and three Al₂O₄C₂ 8-membered. Compound **2** is a centrosymmetric tetramer with a skeleton framework consisting of three fused heterocyclic rings, one 18-membered and two Al₂O₄C₂ 8-membered. The structures of the compounds reveal R₂Al₂O₄C₂ subunits, each linked through diphenyl C₁₂H₈ bridges. Each of the aluminum atoms is bonded to two alkyl groups and two oxygen atoms originating from two different dicarboxylate moieties.

Organoaluminum derivatives of carboxylic acids are interesting models for exploring the coordination chemistry of aluminum because of the variety of potential binding modes of the carboxylate ligands to the metal centers. Dialkylaluminum carboxylates [R₂Al(μ-O₂CR')]₂ (**I**; Scheme 1) have been reported as the major product from the reaction of trialkylaluminum with carboxylic acids. It has been shown that dialkylaluminum carboxylates are dimers that consist of 8-membered rings with bridging carboxylate anions.¹

Aluminum carboxylates have been attracting attention because of their usefulness as precursors in materials science.² Carboxylate alumoxanes, prepared by Barron from the reaction of boehmite [Al(O)(OH)]_n with carboxylic acids, have the following applications: as inorganic components and functionalized cross-linking agents in polymers, as binders in green body processes, as precursors of nanosized alumina and ceramic materials, and as supports for olefin polymerization catalysts.³ Carboxylic acids functionalized by NH₂ (anthranilic acid and glycine) and OH groups [salicylic acid and Schiff base 3,5-Bu₂-2-(OH)C₆H₂CHNC₆H₄-2-(CO₂H)] react with trialkylaluminum compounds, yielding di- and tetranuclear complexes depending on the reaction conditions.⁴ On the other hand, the reaction of anthranilic acid followed by treatment with acetonitrile affords a hexanuclear aluminum-containing ring system.⁵ Amino acids and related ligand complexes with Me₃Al have been studied extensively by Redshaw and co-workers. Hexa- and dodecanuclear organoaluminum ring structures were isolated and structurally characterized.⁶

In comparison with aluminum monocarboxylates, literature data concerning aluminum dicarboxylates are modest. The first aluminum dicarboxylate was derived from Me₃Al and phthalic acid as the dimeric tetranuclear compound **II** (Scheme 1).⁷

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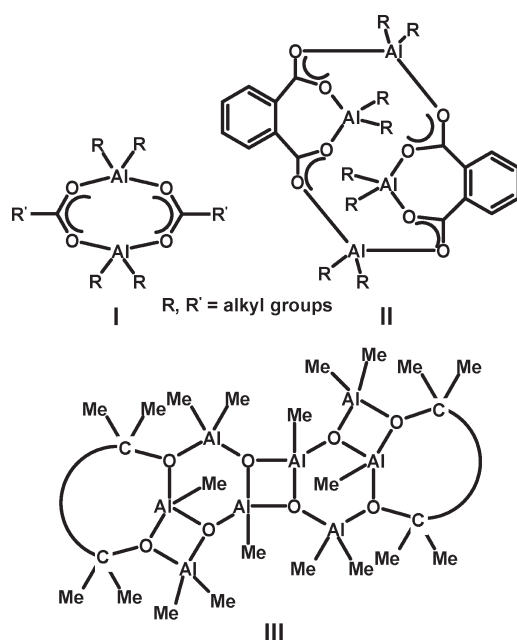
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Scheme 1



It has been reported recently that the compound was the starting material for the nonhydrolytic synthesis of tetramethylalumoxane and carboxylate-substituted alumoxanes.⁸ Succinic, itaconic, and homophthalic acids reacted with 4 equiv of Me_3Al to yield the product III (Scheme 1) with a $Me_{12}Al_8O_8$ core, which could be regarded as a model of methyl aluminum oxide.⁹ In the reaction, C-double methylation of the carboxylate groups occurs, which results in a transformation of the carboxylate groups into alkoxy groups. The above literature data show that the structures of aluminum dicarboxylates strongly depend on the kind of dicarboxylic acid.

During the past decade, we have intensively investigated reactions of group 13 metal alkyls with diols. We have synthesized a variety of structures depending on the steric hindrances of the diolate units, the electron-withdrawing effects of the ligands, and the bulkiness of the alkyl groups bonded to the metal atoms.¹⁰ We expect that systematic studies on the reactions of dicarboxylic acids with group 13 metal alkyls could also provide new products and extend the knowledge of this important group of complexes. Here, we report the results of our initial screening of novel alkylalane dicarboxylates. We describe the synthesis and structural characterization of $[Et_4Al_2(OOCC_{12}H_8COO)]_3$ and $[tBu_4Al_2(OOCC_{12}H_8COO)]_2$ adducts derived from biphenyl-2,2'-dicarboxylic acid (diphenic acid) and R_3Al ($R = Et, tBu$). In contrast to previously reported reactions of dicarboxylic acids with COOH groups positioned close to each other, we used an acid with remote carboxylic groups.

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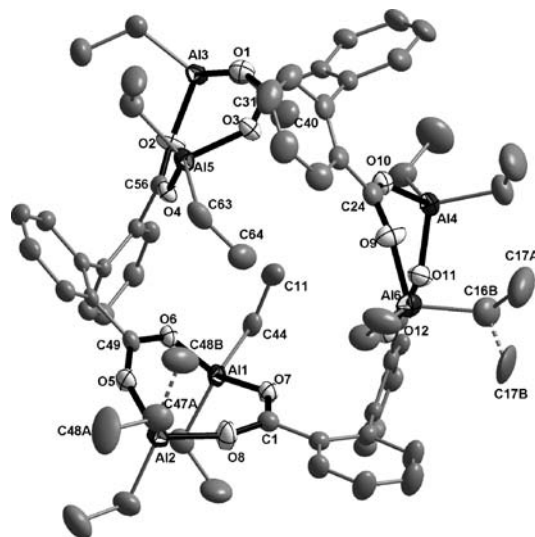
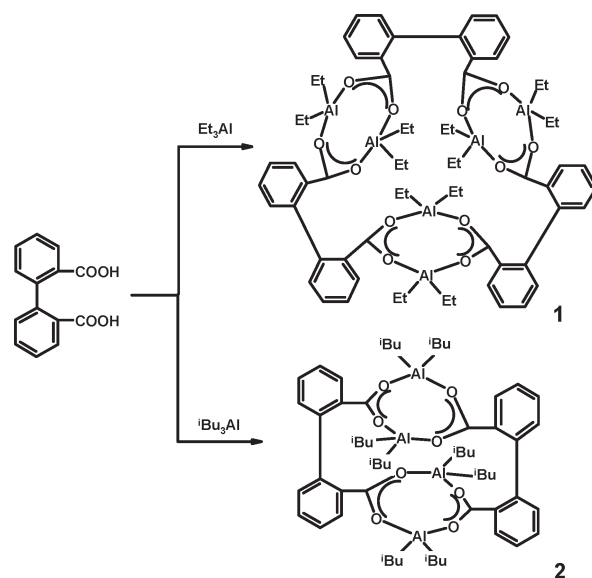


Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. For selected bond lengths and bond angles, see Figure S1 in the Supporting Information.

Scheme 2



Diphenic acid reacted with R_3Al ($R = Et, tBu$) in a 1:2 molar ratio to produce the dialkylaluminum dicarboxylates $[Et_4Al_2(OOCC_{12}H_8COO)]_3$ (**1**) and $[tBu_4Al_2(OOCC_{12}H_8COO)]_2$ (**2**) (Scheme 2). Compounds **1** and **2** were isolated in 55 and 40% yield, respectively.

The molecular structures of the compounds were determined on the basis of an X-ray diffraction study and are shown in Figures 1 and 2. Data collection and structure analysis are listed in Table S1 in the Supporting Information. The molecule of **1** consists of three biphenyl-2,2'-dicarboxylate units bonded to six four-coordinated aluminum atoms. The carboxylate groups act as bidentate bridging ligands between dicarboxylate units. Each of the aluminum atoms is bonded to two ethyl groups and two oxygen atoms originating from two different dicarboxylate moieties. This contrasts with structure II (Scheme 1) of methylaluminum phthalate, in which two aluminum atoms bridge between the carboxylate groups within the phthalate ligands with the formation of two

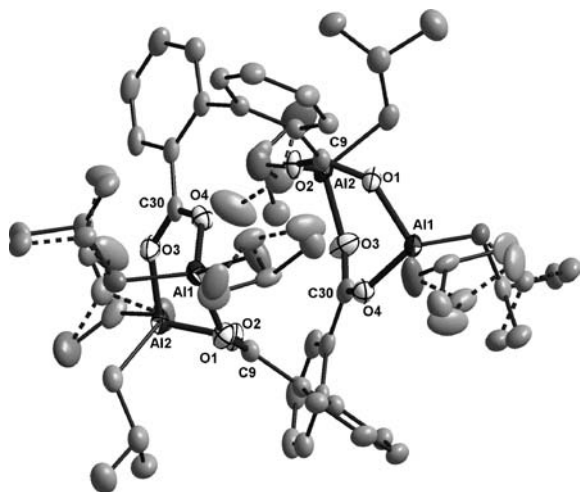


Figure 2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. For selected bond lengths and bond angles, see Figure S2 in the Supporting Information.

7-membered rings, and the two remaining aluminum atoms join the two dicarboxylate ligands.

The molecule of **1** is a highly unsymmetrical adduct with a skeleton framework consisting of four fused heterocyclic rings, one 27-membered and three $\text{Al}_2\text{O}_4\text{C}_2$ 8-membered. In contrast to the flat and chairlike conformations of $\text{Al}_2\text{O}_4\text{C}_2$ rings of dialkylaluminum monocarboxylates **I** (Scheme 1),^{1b} the $\text{Al}_2\text{O}_4\text{C}_2$ rings in compound **1** adopt a boatlike conformation. Four methyl fragments [$\text{C}(11)\text{H}_3$, $\text{C}(40)\text{H}_3$, $\text{C}(64)\text{H}_3$, and $\text{C}(48\text{B})\text{H}_3$] of ethyl groups are directed toward the center of the molecule (Figure 3S in the Supporting Information). Generally, the carboxylate's C–O bond lengths, situated in the region of 1.259–1.272 Å, are similar and show that there is complete delocalization within the O–C–O fragments. The C–O bond lengths of **1** are similar to those of dimethylaluminum phthalate **II** and the di-*tert*-butylaluminum benzoato complex.^{7,1b} The O(4)–C(56)–O(2) fragment is the only exception. The bond O(4)–C(56) [1.249(4) Å] is shorter than the remaining O–C bonds of **1**. Moreover, the difference between the O(4)–C(56) and O(2)–C(56) bond lengths (0.022 Å) indicates, in contrast to the remaining carboxylate fragments of **1**, that the group O(4)–C(56)–O(2) is unsymmetrically bonded to aluminum atoms.

On the basis of X-ray diffraction studies, we found that the molecule of **2** is a centrosymmetric tetramer with a skeleton framework consisting of three fused heterocyclic rings, one 18-membered and two $\text{Al}_2\text{O}_4\text{C}_2$ 8-membered, as indicated in Figure 2. The mode of bonding of the four aluminum atoms to the carboxylate fragments of two diphenate units is the

same as that in compound **1**. The carboxylate's O–C bond lengths [O(1)–C(9) 1.270(2) Å, C(9)–O(2) 1.267(2) Å, O(3)–C(30) 1.276(2) Å, and C(30)–O(4) 1.268(2) Å] in **2** are similar, indicative of symmetrically bound acid groups. Six of the eight isobutyl groups bonded to the aluminum atoms are disordered. The central part of the molecule is empty (Figure 4S in the Supporting Information) because all alkyl groups are directed outward, probably as a consequence of steric repulsion between the phenyl and aluminum isobutyl groups.

In conclusion, we have reported the structural characterization of two unusual dialkylaluminum dicarboxylates, $[\text{R}_4\text{Al}_2(\text{OOC}\text{C}_{12}\text{H}_8\text{COO})]_n$ [$\text{R} = \text{Et}$, $n = 3$ (**1**); $\text{R} = \textit{t}\text{Bu}$, $n = 2$ (**2**)], in reactions of diphenic acid with trialkylaluminum compounds. The structure of compound **1** reveals three subunits $\text{R}_4\text{Al}_2\text{O}_4\text{C}_2$ (**I**), each linked through diphenyl C_{12}H_8 bridges. The molecule of **2** consists of two subunits **I**, each bridged by two diphenyl groups. This contrasts with structure **II** of alkylaluminum phthalates, until now the only completely characterized alkylaluminum dicarboxylate. The difference between the structures of alkylaluminum diphenates and phthalates is a result of the bigger distance between COOH groups in diphenic acid in comparison with phthalic acid. Remote from each other, carboxylate groups of diphenic acid react independently to form $\text{Al}_2\text{O}_4\text{C}_2$ 8-membered rings similar to the monocarboxylic acids. These rings form part of the macrocyclic rings, 27-membered in **1** and 18-membered in **2**. In contrast to the favorable chairlike conformation of aluminum monocarboxylates described by Barron et al.,^{1b} the $\text{Al}_2\text{O}_4\text{C}_2$ rings of compounds **1** and **2** adopt a boatlike conformation. Probably this conformation, less advantageous for $\text{Al}_2\text{O}_4\text{C}_2$ rings, results from the fact that the rings are fragments of 27- and 18-membered macrocycles. Moreover, the structures of dialkylaluminum diphenates depend on the kinds of alkyl groups bonded to the aluminum atoms. It seems that steric repulsion between phenyl and aluminum alkyl groups plays an important role in the formation of macrocyclic aluminum carboxylates.

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Supporting Information Available: Details of syntheses, crystal data, and data collection parameters in PDF and CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.