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Efficient Route to Tetramethylalumoxane and Carboxylate Alumoxanes through the Alkylation of Phthalic Acid**

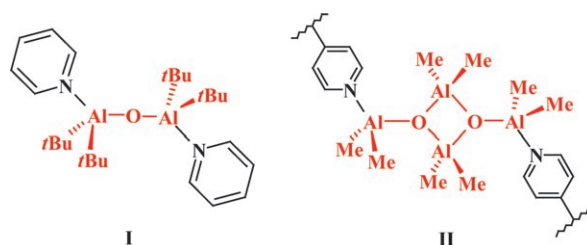
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Dedicated to Professor Herbert W. Roesky on the occasion of his 70th birthday

The chemistry of alumoxanes and organoaluminum carboxylates has been under investigation in the last few decades, and in some ways, studies on these two quite different entities have often overlapped. Alumoxanes are attracting attention as highly active catalysts or co-catalysts as a result of their importance for the polymerization of a wide range of organic monomers, and initial studies into these systems trace back to the end of the 1950s.^[1] Renewed interest in alkylalumoxanes was generated in the 1980s primarily from the work of Kaminsky and co-workers.^[2] Most commonly, alumoxanes of general formula $(R_2AlOAlR_2)_n$ or $(RAIO)_n$ are formed by the controlled hydrolysis of alkylaluminum compounds.^[3] However, a number of alternative routes have also been investigated which are essentially based on reactions of trialkylaluminum compounds with oxygen-containing inorganic or organic compounds,^[4] including preparation by the alkylation of aluminum carboxylates.^[5] Organoaluminum carboxylates and particularly carboxylate alumoxanes are very useful precursors in materials science.^[6] The synthesis of well-defined carboxylate-substituted alumoxanes has been nicely developed by Barron and co-workers, who employed the traditional synthetic route from alumoxanes and carboxylic acids as well as a “top-down” approach from boehmite and carboxylic acids.^[6c,7]

Despite long-lasting studies, there is a relative paucity of structural data for both classes of compounds. The exact composition and structure of alumoxanes featuring short-chain alkyl substituents are still not entirely clear because of the presence of multiple equilibria and rapid exchange reactions. The reported structures for simple systems are

limited only to the anionic species $[Al_7O_6Me_{16}]^{-[4a]}$ and $[(Me_2AlOAlMe_3)_2]^{2-,[4b]}$. The significant steps in determining the structure of alumoxane species have been achieved by Barron and co-workers. The authors, by employing sterically demanding *tert*-butylaluminum derivatives, structurally authenticated the first tetraalkylalumoxane $[(tBu_2AlOAltBu_2)_2]$, its Lewis acid/base adduct with pyridine $[tBu_2(py)AlOAltBu_2(py)]$ (structure I), and a series of



$[(tBuAlO)_n]$ cage clusters.^[5b,8] With regard to the study described herein, it is also pertinent to note that Pasykiewicz and co-workers extensively studied the solution structures of tetramethylalumoxane and its adducts with monodentate and bidentate Lewis bases. Based on spectroscopic data, the authors postulated the formation of various monomeric or oligomeric alumoxane species supported by benzonitrile or *N,N,N',N'*-tetramethylethylenediamine ligands.^[9] More recently, in the course of numerous investigations of the hydrolysis of alkylaluminum compounds and other reaction systems, several interesting alumoxanes (or alumoxane units involved in organometallic cluster backbones) have been isolated and structurally characterized.^[4b,e,f,h] Particularly noteworthy are the achievements of Roesky and co-workers, whereby sterically encumbering β -diketimines were used as supporting ligands for alumoxane units.^[10] The first crystallographic evidence for organoaluminum carboxylate species was given by Atwood and co-workers with the structural determination of $[MeCO_2(AlMe_3)_2]^{-}$.^[11] More recently, dialkylaluminum monocarboxylates^[12] and a series of alkylaluminum compounds that were derived from bifunctional carboxylic acids have been crystallographically characterized.^[5b,13] The latter studies by several research groups have provided a variety of novel multinuclear clusters, and subsequent discoveries indicate that the chemistry of aluminum carboxylates remains largely unexplored.

In the course of our investigations on the effect of both the metal-bound alkyl group and the organic residue on the structure of Group 13 carboxylates, we have revealed an alkylation of the carboxylate group of glycine with concomitant methylalumoxane $(MAO)_n$ formation in the reaction with $AlMe_3$.^[5b] However, in the analogous reaction system involving anthranilic acid, the carboxylate group of the aromatic acid appeared resistant to C-alkylation.^[5b] These findings have prompted our study on the reaction of phthalic acid with an excess of $AlMe_3$, and herein we report on the effective non-hydrolytic synthesis of tetramethylalumoxane and novel carboxylate-substituted alumoxanes. In addition, we demonstrate that alumoxanes and carboxylate alumox-

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anes can be successfully utilized as secondary building units in the construction of extended assemblies (structural motif **II**).

Addition of two equivalents of AlMe_3 to phthalic acid resulted in the quantitative formation of the tetranuclear adduct $[\{(\text{AlMe}_2)_2(\mu\text{-O}_2\text{C})_2\text{-1,2-C}_6\text{H}_4\}_2]$ (**1**).^[13b] However, an excess of AlMe_3 dramatically changes the distribution and structure of the products, as depicted in Scheme 1. The reaction of phthalic acid with three equivalents of AlMe_3 proceeded with a color change of the solution from colorless to yellow after four hours, which was accompanied by the appearance of signals attributed to carbon-bound methyl groups in the aliphatic region of the ^1H NMR spectrum of the reaction mixture. These new resonances are indicative of C-methylation of the carboxylate group. Subsequent addition of 0.5 equivalents of 1,2-bis(4-pyridyl)ethane to the reaction mixture at ambient temperature resulted in slow deposition of colorless crystals of the novel carboxylate alumoxane **2** (path a, Scheme 1). Interestingly, analysis of the reaction mixture confirmed the conversion of approximately half of an equivalent of phthalic acid into 3,3-dimethyl-2-benzofuran-1(3*H*)-one (**A**).^[14] Thus, the additional equivalent of AlMe_3 leads to C-alkylation of the carboxylate group with the concomitant formation of the cyclic ester **A** and tetramethylalumoxane, and the latter alumoxane species is subsequently trapped by unreacted **1**. The ^1H NMR spectrum of **2** supports this formulation (see Experimental Section).

Compound **2** crystallized as a monomer with C_1 symmetry (Figure 1). The structure consists of a hexanuclear cluster in which two tetramethylalumoxane moieties are entrapped by the monomeric subunit of the alkylaluminumphthalate **1**, and is completed by the 1,2-bis(4-pyridyl)ethane ligand, which links the alumoxane Al centers to afford a 22-membered macrocyclic ring system. An alternative view of the composition of **2** is as a carboxylate alumoxane consisting of two tetramethylalumoxane moieties which are mounted on the phthalic acid carboxylate group and bridged by the dicationic $\{\text{Me}_2\text{Al-NC}_3\text{H}_4(\text{CH}_2\text{CH}_2)\text{C}_3\text{H}_4\text{N-AlMe}_2\}^{2+}$ spacer. Thus, the carboxylate groups act as bridging ligands between the two dimethylaluminum units of each alumoxane moiety, and the observed coordination mode confirms a high affinity of the

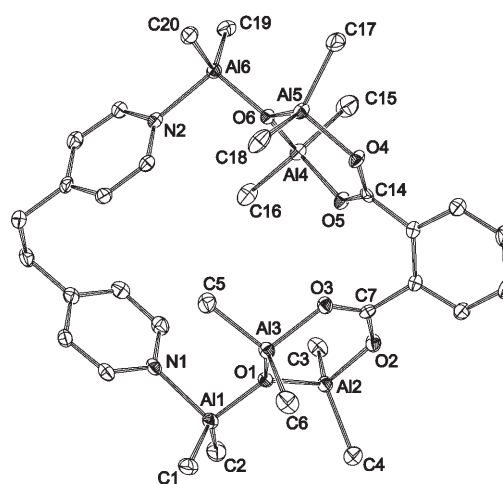
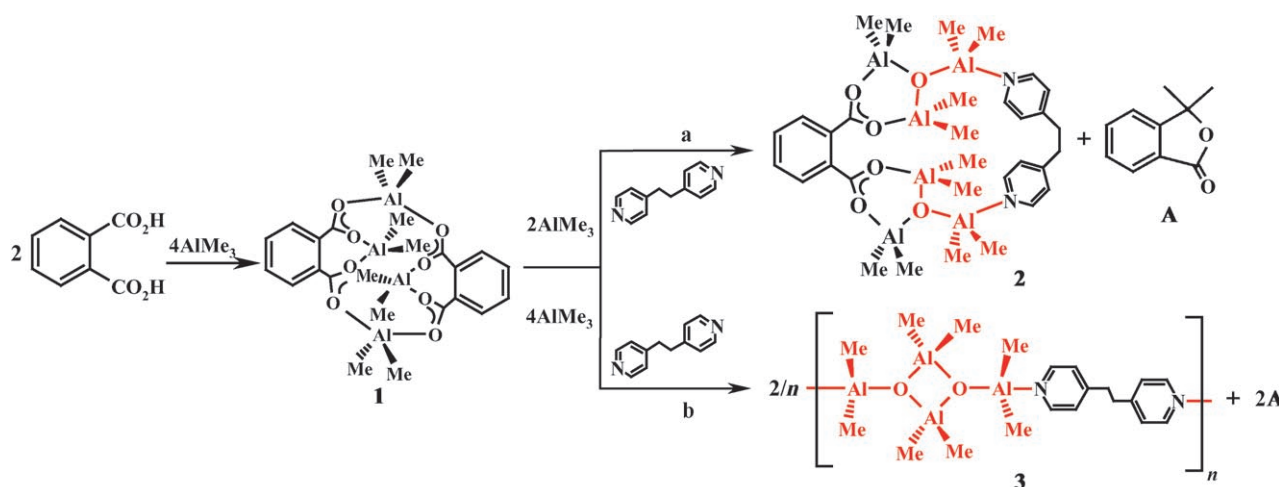


Figure 1. Molecular structure of **2** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1-O1 1.801(2), Al2-O1 1.809(2), Al3-O1 1.810(2), Al1-N1 1.988(3), Al2-O2 1.871(2), Al3-O3 1.863(2), Al4-O6 1.810(2), Al4-O5 1.864(2), Al5-O6 1.810(2), Al5-O4 1.867(2), Al6-O6 1.803(2), Al6-N2 1.984(2); Al1-O1-Al2 117.69(11), Al1-O1-Al3 119.09(10), Al2-O1-Al3 121.05(11), Al6-O6-Al4 120.63(10), Al6-O6-Al5 116.43(11), Al4-O6-Al5 120.60(11).

carboxylate group toward the $\{\text{AlOAl}\}$ unit.^[7] The geometry of the $\{\text{Al}_3(\mu_3\text{-O})\}$ moiety deviates slightly from planarity, with the oxygen atoms positioned above the plane defined by the aluminum atoms (average distance from the O atom to the Al_3 plane: 0.157 Å). The Al–O bond lengths involving the oxo oxygen atom are essentially equal (average: 1.808 Å) and are slightly shorter than the carboxylate Al–O bond lengths (average: 1.867 Å). The 1,2-bis(4-pyridyl)ethane ligand adopts a *gauche* conformation with a dihedral angle of 48.74° between the phenyl rings.

Similar treatment of phthalic acid with four equivalents of AlMe_3 in CH_2Cl_2 for 24 hours followed by addition of one equivalent of 1,2-bis(4-pyridyl)ethane afforded the crystalline Lewis acid/base tetramethylalumoxane/bipyridine adduct **3** and the cyclic ester **A** in good yield (path b,



Scheme 1. Synthesis of **2** (path a) and **3** (path b).

Scheme 1). Strikingly, when phthalic acid was treated with more than four equivalents of AlMe_3 under similar conditions, the alkylation of the second carboxylic group was not observed. Moreover, our attempts to convert **2** into **3** failed; the addition of one equivalent of AlMe_3 to **2** in CH_2Cl_2 resulted in the formation of the Lewis acid adduct $[\{1,2\text{-bis}(4\text{-pyridyl})\text{ethane}\}(\text{AlMe}_3)_2]$, which retarded further transformations.^[15] Compound **3** was characterized spectroscopically, and its molecular structure was determined by X-ray crystallography. The structural analysis of **3** revealed an unprecedented zigzag coordination polymer resulting from self-assembly of the dimeric $\{\text{Me}_2\text{Al}(\mu\text{-O})\text{AlMe}_2\}_2$ alumoxane units with the bipyridine spacer in an *anti* conformation (Figures 2 and 3). Thus, 1,2-bis(4-pyridyl)ethane is a very flexible ligand that may act as a spacer in both an intra- and intermolecular fashion. The $\{\text{Al}_3(\mu_3\text{-O})\}$ alumoxane moieties in **3**, in contrast to those in **2**, are planar. The Al–O bond lengths (average: 1.828 Å) are slightly longer than those

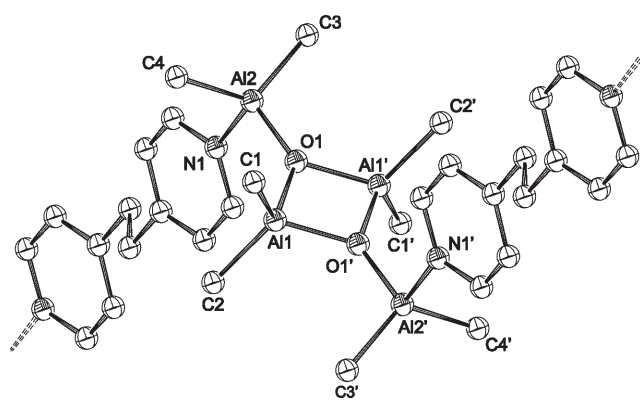


Figure 2. Molecular structure of **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. The atoms which are labeled with a prime (') are at symmetry-equivalent positions ($-x, -y, -z + 1$). Selected bond lengths [Å] and angles [°]: Al1–O1 1.831(5), Al1–O1' 1.828(5), Al1–C1 1.966(7), Al1–C2 1.985(7), Al2–O1 1.761(5), Al2–C3 1.954(8), Al2–C4 1.946(7), Al2–N1 2.001(6); O1–Al1–O1' 85.6(2), Al1–O1–Al1' 94.4(2), C1–Al1–C2 113.3(3), O1–Al1–N1 101.7(2), C4–Al2–C3 119.2(3), Al2–O1–Al1' 132.4(3), Al2–O1–Al1 133.1(3).

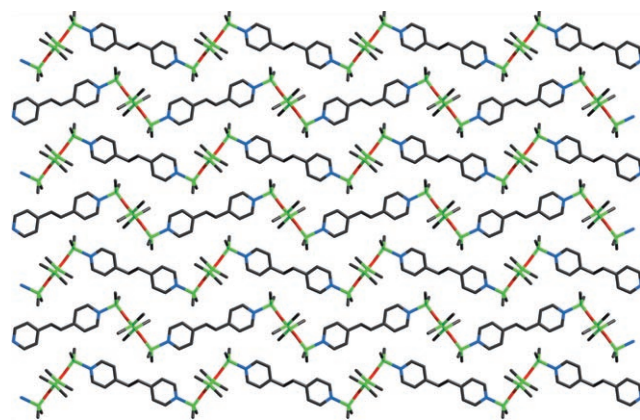


Figure 3. Crystal structure of **3** viewed along the *a* axis. The solvent molecules and hydrogen atoms are omitted for clarity.

observed in **2**, and the Al–N bond lengths are comparable to those in **2**. Compound **3** represents the first example of a structurally characterized tetramethylalumoxane species.

In conclusion, we have provided an efficient route to tetramethylalumoxane moieties and carboxylate-substituted alumoxanes by the reaction of phthalic acid with AlMe_3 . This simple method for accessing these important classes of compounds opens new opportunities to probe their reaction chemistry. In addition, we have demonstrated that alumoxanes can act as secondary building units in the construction of extended macrocyclic assemblies or functional coordination networks, which would be of interest in catalysis and materials science.

Experimental Section

2: AlMe_3 (0.216 g, 3.00 mmol) was added to a solution of phthalic acid (0.166 g, 1.00 mmol) in CH_2Cl_2 (7 mL) at -78°C . The reaction mixture was allowed to warm to room temperature with stirring. After 24 h, a solution of 1,2-bis(4-pyridyl)ethane (0.092 g, 0.50 mmol) in toluene (4 mL) was added. The solution was concentrated, and small block-shaped crystals were obtained upon overnight storage at 0°C . Compound **2** is insoluble in aromatic solvents and THF, and is sparingly soluble in CH_2Cl_2 . Yield: 0.275 g (76%); $^1\text{H NMR}$ (400 MHz, CD_2Cl_2): $\delta = -0.99$ (s, 24H, AlCH_3), -0.57 (s, 12H, AlCH_3), 3.17 (s, 4H, CH_2), 7.21 (d, $J = 5.9$ Hz, 4H, Ar), 7.65 (q, $J = 2.9$ Hz, 2H, Ar), 7.81 (q, $J = 2.9$ Hz, 2H, Ar), 8.47 ppm (d, $J = 6.6$ Hz, 4H, Ar); $^{27}\text{Al NMR}$: no signals could be observed; IR (nujol): $\tilde{\nu} = 1625(\text{m})$, 1602(m), 1575(s), 1507(m), 1495(m), 1457(s), 1378(s), 1194(m), 1068(m), 1043(m), 826(m), 727(s), 696(s), 655(m). Elemental analysis (%) calcd for $\text{C}_{32}\text{H}_{52}\text{Al}_6\text{N}_2\text{O}_6$: C 53.18, H 7.25, N 3.88; found: C 53.23, H 7.31, N 3.84 (sample was dried in vacuo for 10 h).

3: The reaction was carried out according to the same procedure as described for **2** by using AlMe_3 (0.288 g, 4.00 mmol) and phthalic acid (0.166 g, 1.00 mmol) in CH_2Cl_2 (7 mL). After 24 h, a solution of 1,2-bis(4-pyridyl)ethane (0.184 g, 1.00 mmol) in CH_2Cl_2 (4 mL) was added, and the solution was stirred for an additional 30 minutes. The volatiles were then removed under reduced pressure, and the amorphous residue was dissolved in hot THF (7 mL). After the solution had stood overnight at 0°C , colorless square-shaped crystals were formed. Yield: 0.387 g (87%); $^1\text{H NMR}$ (400 MHz, $[\text{D}_6]\text{THF}$): $\delta = -1.03$ (s, 12H, AlCH_3), -0.81 (s, 12H, AlCH_3), 2.98 (s, 4H, CH_2), 7.19 (d, $J = 5.1$ Hz, 4H, Ar), 8.44 ppm (d, $J = 5.9$ Hz, 4H, Ar); $^{27}\text{Al NMR}$: no signal could be observed; IR (nujol): $\tilde{\nu} = 1622(\text{m})$, 1606(m), 1559(m), 1461(s), 1377(s), 1193(m), 1068(m), 1036(m), 836(mbr), 790(mbr), 720(mbr). Elemental analysis (%) calcd for $\text{C}_{20}\text{H}_{36}\text{Al}_4\text{N}_2\text{O}_2$: C 54.05, H 8.16, N 6.30; found: C 54.01, H 8.21, N 6.28 (sample was dried in vacuo for 10 h).

Crystal data for **2**-toluene, $\text{C}_{30}\text{H}_{60}\text{Al}_6\text{N}_2\text{O}_6$: $M_r = 814.77$, crystal dimensions $0.50 \times 0.30 \times 0.20$ mm³, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.6314(3)$, $b = 22.0489(6)$, $c = 20.1576(3)$ Å, $\beta = 123.911(2)^\circ$, $V = 4659.15(19)$ Å³, $Z = 4$, $F(000) = 1736$, $\rho_{\text{calcd}} = 1.162$ g cm⁻³, $\theta_{\text{max}} = 21^\circ$, $R_1 = 0.0427$, $wR_2 = 0.0896$ for 4191 reflections with $I_o > 2\sigma(I_o)$. The structure was solved by direct methods by using the program SHELXS-97^[16] and was refined by full-matrix least squares on F^2 with the program SHELXL-97.^[17] H atoms were included in idealized positions and refined isotropically. Crystal data for **3**-2 THF, $\text{C}_{28}\text{H}_{52}\text{Al}_4\text{N}_2\text{O}_4$: $M_r = 588.76$, crystal dimensions $0.40 \times 0.30 \times 0.25$ mm³, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.0731(18)$, $b = 11.6608(13)$, $c = 16.172(3)$ Å, $\beta = 96.752(6)^\circ$, $V = 1702.1(5)$ Å³, $Z = 2$, $F(000) = 636$, $\rho_{\text{calcd}} = 1.149$ g cm⁻³, $\theta_{\text{max}} = 22.71^\circ$. Several attempts to isolate suitable single crystals resulted only in twinned crystals. The structure was solved by direct methods by using the program SHELXS-97^[16] and was refined by full-matrix least squares on F^2 , including intensities of superimposed reflections of the

twin, with the program SHELXL-97.^[17] The refined fractional contribution of the minor twin component was 0.365(2). H atoms were included in idealized positions and refined isotropically. Final *R* indices: $R_1=0.0912$, $wR_2=0.2350$ for 1569 reflections with $I_o > 2\sigma(I_o)$. CCDC-292582 (**2**) and CCDC-292583 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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