Investigations on the Interaction of Dichloroaluminum Carboxylates with Lewis Bases and Water: an Efficient Road toward Oxo- and Hydroxoaluminum Carboxylate Complexes

Wojciech Bury,† Elżbieta Chwojnowska,‡ Iwona Justynia,† Janusz Lewiński,*,†‡ Aneta Affek,† Ewa Zygadło-Monikowska,† Joanna Bąk,§ and Zbigniew Florjančy‡

†Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
‡Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
§Department of Chemistry, University of Warsaw, Pasteura 1, 00-093 Warsaw, Poland

ABSTRACT: A series of dichloroaluminum carboxylates [Cl₂Al(O₂CR)]₂ (were R = Ph (1a), Bu (1b), CH₃CH₂ (1c) and C₁₁H₂₃ (1d)) were prepared and extended investigations on their structure and reactivity toward various Lewis bases and H₂O performed. Compounds [Cl₂Al(O₂CR)]₂ and their adducts with Lewis bases show a large structural variety, featuring both molecular and ionic forms with different coordination numbers of the metal center and various coordination modes of the carboxylate ligand. Upon addition of a Lewis base of moderate strength the molecular form [Cl₂Al(O₂CR)]₂ equilibrate with new ionic forms. In the presence of 4-methylpyridine the six-coordinate Lewis acid–base adducts [Cl₂Al(l₂-O₂CR)(py-Me)]₂ [R = Ph (3a), Bu (3b)] with a chelating carboxylate ligand were formed. The reactions of 1a, 1b, and 1d with 0.33 equiv of H₂O in THF-toluene solution lead to oxo carboxylates [(Al₃O)(O₂CR)₆(THF)₃][AlCl₄] [where R = Ph (4aTHF), Bu (4bTHF), and C₁₁H₂₃ (4dTHF)] in high yield. The similar reaction of 1c in tetrahydrofuran (THF) afforded the chloro(hydroxo)aluminum acrylate [(Cl₃Al)(OH)-(O₂CC₂H₃)₂(THF)₄][AlCl₄] (5), while the hydrolysis of 1b in MeCN lead to the hydroxoaluminum carboxylate [Al₂(OH)(O₂CR)₂(Bu)(MeCN)]₆[AlCl₄] (5) (6). All compounds were characterized by elemental analysis, ³¹H, ²⁷Al NMR, and IR spectroscopy, and the molecular structure of 1a, 3a, 3b, 4aTHF, 4bTHF, 4bpy-Me, 5, and 6 were determined by single-crystal X-ray diffraction. The study provides a platform for testing transformations of secondary building units in Al–Metal–Organic Frameworks toward H₂O and neutral donor ligands.

INTRODUCTION

Aluminum is the third most abundant element in the shallow Earth, where it forms a rich array of solute molecules and solids, including clays and aluminum hydroxide phases. The hydrolysis of aluminum compounds is one of the key steps in sol–gel routes to commercially important ceramics based on alumina and fabrication of metalumoloxon e oligomers that are used in industry as cocatalysts for the polymerization of olefins using group 4 metalocene catalysts. In the past two decades considerable efforts were made to obtain hybrid inorganic–organic polymers containing alumina core decorated with carboxylate ligands, where the synthetic methods applied include the reactions of aluminum hydroxides (especially boehmite) with carboxylic acids, or controlled hydrolysis of dialkylaluminum carboxylates. Several reports also describe the application of carboxylic aluminoxanes as reinforcing nanofillers for polymers, catalysts supports, protecting layers, and processable precursors for ceramic materials. In this regard, carboxylate anions play an important role in self-assembly pathways of the metastable species and in the change of morphology and hydrophobicity of the oligomeric aluminum salts formed in these systems. This flexibility of the carboxylate coordination in various systems is referred to as a carboxylate shift; however, the chemistry of aluminum carboxylates is largely an unexplored area because of a relative paucity of structural data for simple aluminum-carboxylate systems. Valuable models for elucidation of the preferred coordination mode of a carboxylate ligand to aluminum center concern the [MeCO₂(AlMe₃)₂]⁻ anion with the monodentate carboxylate ligand I, a dimeric [R₂Al(l₂-O₂CR)]₂ complexes with carboxylate bridging mode II, and a number of crystallographically characterized alkylaluminum compounds derived from bifunctional carboxylic acids exhibiting a large structural variation (Scheme 1). Surprisingly, the chelating mode III was not observed, and it was argued that this coordination mode is unavailable for carboxylates on aluminum because of the ring strain associated with the AlO₂CR cycle.

Furthermore, the intensive structural investigations concerning the structure of hydroxo- and oxoaluminum complexes resulted in the isolation of large purely inorganic model aggregates such as Al₃⁺, Al₁₀⁺, Al₁₀⁺, Al₁₀⁻, Al₁₂⁻. These complexes have been successfully applied as cocatalysts for the polymerization of olefins using Group 4 metalocene catalysts, as supports, as protecting layers, or as processable precursors for ceramic materials.
complexes structurally represent the Baker–Figgis–Keggin isomers having the stoichiometry AlO$_2$Al$_2$(OH)$_3$(H$_2$O)$_2$~$n$aq where oxo- and hydroxoaluminum building units display usually trigonal A and tetrahedral B or D coordination geometries (Scheme 1). The trigonal coordination mode C is rather unique, and to date there are only two examples of well-defined complexes with incorporated Al$_3$O moiety, both involving acetate ligands. Recently, the μ$_3$-oxo-centered trinuclear aluminum clusters have received special attention because their employment as building units for the formation of metal–organic framework (MOF) materials with giant pores. Other unique clusters such as the Al$_{15}$ or Al$_{13}$ were isolated in the presence of multifunctional carboxylate ligands.

In a search for prototypical low-nuclear oxo- and hydroxoaluminum clusters decorated with carboxylate ligands as novel suitable precursors of higher aggregates or the predesigned molecular platform for modeling the reactivity of prototypical Al-MOFs toward water and/or neutral donor molecules we considered the use of chloroaluminum carboxylates that can be obtained in the reaction of aluminum alkyl chlorides with carboxylic acids. Surprisingly, this class of aluminum-halogen complexes has not been explored so far. Only recently we communicated a complex nature of aluminum alkyl analogues characterized previously (cf. Al$_2$O$_3$~$m$ = 1.810 Å), reflecting the different Lewis acidity of the X$_2$Al species involved. Interestingly, in the structure of 1a the central eight-membered Al$_2$O$_2$C$_5$ ring is almost flat, in contrast to the chairlike conformation of [Bu$_6$Al(μ-O$_2$-CPh)]. The IR spectrum of 1a in CH$_2$Cl$_2$ shows two characteristic bands at 1562 cm$^{-1}$ [$\nu$asym(CO$_2$)] and 1497 cm$^{-1}$ [$\nu$sym(CO$_2$)] that can be attributed to the stretching vibrations of the bridging carboxylate group; however, additional vibrations in this spectral range are also present, which indicate a more complex nature of this system in solution. Similar characteristic pattern can be observed in the IR spectrum of 1b–d also (see the Experimental Section). The IR spectra of 1d nujol film (see the Supporting Information) and its solutions in benzene reveal exclusively the presence of intensive bands at 1572 (νasym(CO$_2$)) and 1488 (νsym(CO$_2$)) cm$^{-1}$ indicating the presence of bridging carboxylate units.

To have a better understanding of equilibria present in solutions we performed $^{27}$Al NMR spectral studies for 1a–d in a noncoordinating solvent. The $^{27}$Al NMR spectra of 1a and 1b in CDCl$_3$ display a dominating signal of the dimeric [(RCO$_2$)$_2$AlCl$_2$]$_2$ species at 77 ppm (this chemical shift is similar to that observed for the chemically closely related four-coordinate dichloroaluminum acetylacetonate complex exhibiting the $^{27}$Al resonances at 88 ppm. This signal is, however,
accompanied by a number of lower intensity resonances in the higher and lower field (Figure 2a and 2b). Similar spectrum of $1c$ was very complex and featureless. These observations indicate that the dimeric form of $1a−1c$ is unstable in solution and rearranges to a number of likely neutral and ionic aluminum species with four- and six-coordinate aluminum centers.$^{18,19}$ Surprisingly, the $^{27}$Al NMR spectra of $1d$ recorded in noncoordinating solvents like benzene or chloroform reveal only a single resonance at 77 ppm characteristic of the dimeric form (Figure 2c). The dimeric character of $1d$ was confirmed by molecular weight measurements in benzene solution; the calculated value for the dimer is 594 g/mol whereas the experimental data were around 600 g/mol. Thus, the data clearly indicate that the relative concentration of neutral and ionic species of dichloroaluminum carboxylates and their association degree in solution strongly depend on the character of the carboxylate ligand, and the more lipophilic ligand bearing a long alkyl chain stabilizes the dimeric form with bridging carboxylate ligands.

**Investigations on the Interaction of Dichloroaluminum Carboxylates with Lewis Bases.** The revealed solution behavior of dichloroaluminum carboxylates exhibits a number of common features with those observed previously for dichloroaluminum acetylacetonate [Cl$_2$Al(acac)] complex, that is, both types of compounds form labile molecular species which readily equilibrate with ionic species in solution,$^{18}$ and the latter acetylacetonate derivative was highly reactive toward Lewis bases.$^{20,21}$ Therefore, we were also curious as to how the addition of different Lewis bases might impact on the structure of chloroaluminum carboxylate species. In the next step we performed $^{27}$Al NMR studies for $1a$, $1b$, and $1d$ in the presence of THF, acetonitrile (MeCN), and 4-methylypyridine ($py$-Me). The $^{27}$Al NMR spectra of $1a$, $1b$, and $1d$ in THF solution are similar and consist of two dominating signals at 104 ppm and around 0 ppm, which are characteristic for AlCl$_4^-$ anion and a cationic aluminum carboxylate species, respectively.$^{19}$ However, the characteristic resonance of a lower intensity at 77 ppm from the dimeric form of the parent carboxylate can also be observed (Figure 3b, Supporting Information, Figures S1b and S2a). These observations indicate that upon addition of THF the molecular form of dichloroaluminum carboxylates equilibrates with a new ionic form which we tentatively ascribed as $[(RCO_2)_2Al(THF)_x][AlCl_4]^{-2(THF)}$ (Scheme 2) based on our earlier observations for the related dichloroaluminum acetylacetonate systems.$^{20}$

$$\begin{align*}
\text{Scheme 2} \\
\text{[(RCO}_2\text{Cl}_2)_2 \xrightarrow{L} [(RCO}_2\text{Cl}]_2\text{Al(L)}_3[\text{AlCl}_4]^{-2(\text{THF})]} \\
L = \text{THF, MeCN} \\
1a (R = \text{Ph});
1b (R = \text{Bu});
1d (R = C_11H_{23})
\end{align*}$$

When MeCN was used as a solvent, the corresponding spectra of $1a$, $1b$, and $1d$ revealed a complete disappearance of the resonance at 77 ppm and appearance of additional resonances at −11 and −23 ppm (Figure 3c, Supporting Information, Figures S1c and S2b) which indicates that MeCN drives the transformations of the studied systems to a larger number of ionic forms of as yet unidentified structure. Some additional light on the character of possible species formed provide the investigations involving dimethoxyethane (DME) as a bidentate Lewis base. The addition of 4 molar equiv of DME to a toluene solution of $1a$, $1b$, or $1d$ led to the precipitation of the ionic complex $[\text{AlCl}_4(DME)_2]^{-}[\text{AlCl}_4]^{-2(\text{DME})}$ in high yield (the molecular structure was confirmed by single-crystal X-ray diffraction, see Supporting Information, Figure S7 and Table S2).

We have also revealed that in the presence of $py$-Me as a significantly stronger Lewis base, the character of chloroaluminum carboxylate species formed highly depends on the reagents molar ratio (Scheme 3). The addition of 1 equiv of $py$-Me to the solutions of $1a$, $1b$, and $1d$ results in a disappearance of the $^{27}$Al resonances because of the parent dimeric forms and the
The carboxylate ligand (structurally characterized analogous gallium of monomeric aluminum carboxylates with a chelating organization of \([\text{Cl}_2\text{Al}(\lambda^2\text{O}_2\text{CR})(\text{py-Me})_2]\) (3a) or \([\text{Cl}_2\text{Al}(\lambda^2\text{O}_2\text{CR})(\text{py-Me})_2]\) (3b) in high yield. The molecular structures of 3a and 3b consist of discrete mononuclear units with the aluminum centers in a distorted octahedral configuration (Figure 4). In both cases, the carboxylate group acts as a symmetrical chelating ligand (O−Al−O = 66.4(1)° or 65.9(1)° and O−C−O = 115.8(3)° or 115.7(3)°, for 3a or 3b, respectively). The pyridyl ligands are mutually trans (N−Al−N = 174.1(1)° or 170.2(1)°, with coplanar aromatic rings, and the Cl1−Al−Cl1′ angle of 101.4(5)° or Cl1−Al−Cl2 angle of 100.1(5)° for 3a or 3b, respectively. Both the Al−O = 1.975(1) Å or Al1−O1 = 1.986(2) Å and Al1−O2 = 1.977(2) Å, (for 3a or 3b) and the Al−Cl (2.232(1) Å) or Al1−Cl1 = 2.249(1) Å and Al1−Cl1′ = 2.214(1) Å (for 3a or 3b, respectively) distances are slightly longer than those observed for the four-coordinate dimer 1a, and the axial Al1−N1 distances are 2.057(3) or 2.043(3) and Al1−N2 distances are 2.065(3) Å or 2.046(3) for 3a or 3b, respectively. Compounds 3a and 3b represent unique examples of monomeric aluminum carboxylates with a chelating carboxylate ligand (structurally characterized analogous gallium carboxylate was also reported very recently\(^2\)). It is worthy to note that our previous theoretical calculations on the relative stability of various structures of the type 3 adducts confirmed that the formation of the six-coordinate chelate structure is thermodynamically preferred which is in agreement with the experimental data.\(^3\)

Interestingly, analysis of the crystal structure of 3a revealed that the monomeric units self-assemble via C−H···π and C−H···Cl interactions to produce two-dimensional (2D) grids, which are further organized by complementary C−H···O interactions into a three-dimensional (3D) network with open channels directed along the b axis (Figure 5). In contrast, the analysis of the crystal structure of 3b revealed the self-organization of \([\text{Cl}_2\text{Al}(\lambda^2\text{O}_2\text{CtBu})(\text{py-Me})_2]\) units into one-
dimensional (1D) chains stabilized by weak π···π-stacking interactions between aromatic rings of 4-methylpyridine (Figure 6) which results in a close packing of molecules without empty spaces in the crystal lattice.

Investigations on the Interaction of Dichloroaluminum Carboxylates with Water. Upon the addition of water to dichloroaluminum carboxylates we expected a more complicated situation to that observed in the reactions with a Lewis base, as water molecules can act as both a neutral donor ligand and a proton donor. However, in contrast to expectation, these reactions appeared as a convenient method for the synthesis of oxo- and hydroxoaluminum carboxylates.

The reactions of 1a, 1b, and 1d with 0.33 equiv of water carried out in THF-toluene mixture lead to oxoaluminum carboxylates [(Al3O)(O2CR)6(THF)3][AlCl4](THF) (where R = Ph (4aTHF), tBu (4bTHF), and C11H23 (4dTHF)) in high yield (Scheme 4, path a). Surprisingly, when dichloroaluminum acrylate 1c was reacted with water in THF under similar conditions, the unprecedented example of the ionic chloro-(hydroxo)aluminum carboxylate [(ClAl)2(OH)−(O2CC2H3)2][AlCl4] (5) was isolated as a main product (Scheme 3, path b). In another control experiment we have investigated the influence of the solvent used on the hydrolysis reactions outcome. When the hydrolysis of 1b was carried out in MeCN as a solvent the ionic aluminium hydroxide [Al(OH)2(O2CtBu)2(MeCN)6][AlCl4] (6) was isolated as the main product (Scheme 4, path b). The results described above show unambiguously that in the dichloroaluminum carboxylate/H2O system complex transformations take place which lead to the formation of various hydroxo- and oxoaluminum clusters with bridging carboxylate ligands depending on the character of carboxylate ligands and/or the solvent used. These observations also indicate that the reaction of dichloroaluminum carboxylates with water is a stepwise process in which dinuclear hydroxoaluminum complexes can be treated as intermediate species in transformations leading to oxoaluminum clusters.

It is interesting to note that the central oxoaluminium core in 4 is retained upon addition of a pyridine-type ligand, as a strong Lewis base, to a solution of 4 in THF and leads to the formation of the corresponding [(Al3O)(O2CR)(py-Me′)]−[AlCl4]− (R = tBu, Ph) adduct (Scheme 5). However only in one case, that is, in the reaction involving 4b and 3-methylpyridine (py-Me′), were we able to isolate almost quantitatively the ionic complex [(Al3O)(O2CtBu)(py-Me′)][AlCl4] (4bpy-Me′) as large block-shaped crystals suitable for X-ray crystallography. It is worthy to note that the same product was also obtained by a direct reaction of 1b with water-py-Me’ mixture in toluene (see Experimental Section).

The identity of the oxo- and hydroxoaluminum carboxylates has been confirmed by X-ray crystallography. Compounds 4aTHF and 4bTHF are isostructural (the corresponding laurylate derivative 4dTHF is an oily product), and the representative molecular structure of 4aTHF is shown in Figure 7. The central acrylate 1c was reacted with water in THF under similar conditions, the unprecedented example of the ionic chloro-(hydroxo)aluminum carboxylate [(ClAl)2(OH)−(O2CC2H3)2][AlCl4] (5) was isolated as a main product (Scheme 3, path b). In another control experiment we have investigated the influence of the solvent used on the hydrolysis reactions outcome. When the hydrolysis of 1b was carried out in MeCN as a solvent the ionic aluminium hydroxide [Al(OH)2(O2CtBu)2(MeCN)6][AlCl4] (6) was isolated as the main product (Scheme 4, path b). The results described above show unambiguously that in the dichloroaluminum carboxylate/H2O system complex transformations take place which lead to the formation of various hydroxo- and oxoaluminum clusters with bridging carboxylate ligands depending on the character of carboxylate ligands and/or the solvent used. These observations also indicate that the reaction of dichloroaluminum carboxylates with water is a stepwise process in which dinuclear hydroxoaluminum complexes can be treated as intermediate species in transformations leading to oxoaluminum clusters.

It is interesting to note that the central oxoaluminium core in 4 is retained upon addition of a pyridine-type ligand, as a strong Lewis base, to a solution of 4 in THF and leads to the formation of the corresponding [(Al3O)(O2CR)(py-Me′)]−[AlCl4]− (R = tBu, Ph) adduct (Scheme 5). However only in one case, that is, in the reaction involving 4b and 3-methylpyridine (py-Me′), were we able to isolate almost quantitatively the ionic complex [(Al3O)(O2CtBu)(py-Me′)][AlCl4] (4bpy-Me′) as large block-shaped crystals suitable for X-ray crystallography. It is worthy to note that the same product was also obtained by a direct reaction of 1b with water-py-Me’ mixture in toluene (see Experimental Section).

The identity of the oxo- and hydroxoaluminum carboxylates has been confirmed by X-ray crystallography. Compounds 4aTHF and 4bTHF are isostructural (the corresponding laurylate derivative 4dTHF is an oily product), and the representative molecular structure of 4aTHF is shown in Figure 7. The central

![Figure 6](image-url)

**Figure 6.** Crystal packing diagrams for 3b, view along the (a) b axis and (b) a axis.

![Scheme 4](image-url)

**Scheme 4.** Reaction Outcomes of Dichloroaluminum Carboxylates Hydrolysis Depending on the Character of the Carboxylate Ligand and/or the Donor Solvent Used

![Scheme 5](image-url)

**Scheme 5**

![Figure 7](image-url)

**Figure 7.** Molecular structure of the cationic part of 4aTHF; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): O1−Al1, 1.821(3); Al1−Al2, 1.823(3); O1−Al3, 1.817(3); Al1−O14, 2.002(4); Al2−O15, 1.987(4); Al3−O16, 1.990(3); Al1−O1−Al2, 120.2(2); Al1−O1−Al3, 120.0(2); Al2−O1−Al3, 119.8(2).
Al1O core of the cationic unit in both compounds consists of a planar triangular arrangement of aluminum atoms where the Al−O−Al angles are close to 120°. Each aluminum center possesses a slightly distorted octahedral coordination sphere. The mean Al−(μ1-O) distance is 1.853 Å, and the Al−O (carboxylate) bond length (av. 1.892 Å) is smaller than that of Al−O (THF) (1.948(3) Å). The coordination sphere of the aluminum center in the anion has a slightly distorted tetrahedral environment. Analysis of the crystal structures of 4aTHF and 4bTHF revealed that molecules are organized through noncovalent interactions into microporous structures with slit-like pores along crystallographic b and a axes respectively; however, larger apertures are present in the former compound (Supporting Information, Figure S5). Compound 4bPTfMe′ crystallizes in the monoclinic P21/c space group and is isostructural with the previously described ionic complex 4bTHF (Figure 8). Only minor differences in bond lengths can be observed for Al−NpyMe and Al−OTHF distances whose mean values are 2.100 Å and 1.991 Å, respectively. The angles around the central oxygen atom remain unchanged; therefore, the effect of a Lewis base strength on the geometry of the Al1O3(O2CR)6 core is very weak.

Compound 5 crystallizes in the monoclinic P21/c space group (Figure 9). The cationic unit consists of two six-coordinate aluminum atoms which are bridged by two acrylate ligands and a hydroxo μ2-OH group. Each of the aluminum atoms is bonded to chloride ligands with a mean Al−Cl distance of 2.264 Å and additionally coordinated by two THF molecules. It is worthy to note that the O5 oxygen atom from [Al3(OH)(O2C3H3)3(thf)4]− cation forms an intermolecular hydrogen bond with additional THF molecule, where O5−Al1−Cl1, 94.3(3); O5−Al1−Cl2, 93.6(3).

CONCLUSIONS

In conclusion, the study has revealed a complex nature of chloroaluminum carboxylate complexes featuring both molecular and ionic forms with different coordination numbers of the metal center and various coordination modes of the carboxylate ligand. The data clearly indicate that the relative concentration of neutral and ionic species of dichloroaluminum carboxylates and their association degree in solution strongly depend on the...
character of the carboxylate ligand, and a more lipophilic ligand bearing a long alkyl chain stabilizes the dimeric form with bridging carboxylate ligands. Upon addition of Lewis bases of moderate strength the molecular form of dichloroaluminum carboxylates equilibrates with new ionic forms. Particularly intriguing was the use of 4-methylpyridine as a strong base which allowed for the isolation and structure characterization of the six-coordinate molecular Lewis acid–base adducts [Cl2Al(4-2-O2CR)(py-Me)2] with a chelating carboxylate ligand. Furthermore, the investigations on the interaction of dichloroaluminum carboxylates with water show that these reactions proceed via complex pathways affording various oxo- and hydroxoaluminum complexes with bridging carboxylate ligands. Finally, the data promise greater tuning of transformation involving aluminum carboxylates toward desired molecular units and may be vital for a better understanding of how water and donor solvents can affect the prototypical ALMOF structure.

**EXPERIMENTAL SECTION**

All materials were purified, stored, and used under a dry nitrogen atmosphere. Toluene and tetrahydrofuran were distilled from sodium–potassium alloy and benzophenone. Acetonitrile was distilled from P2O5. EtAlCl2 (1.8 M in toluene, Aldrich) was used as received.

**Synthesis of [Cl2AlO2CC11H23]2 (1d).** A solution of benzoic acid (1.314 g, 3.0 mmol), water (0.018 g, 1.0 mmol) in THF (0.544 g, 0.5 mmol) 3-picoline (0.372 g, 3.0 mmol) in toluene was added dropwise to a solution of EtAlCl2 in toluene (0.5 mL, 1.8 M) at −78 °C under nitrogen atmosphere. The reaction mixture was allowed to warm up to room temperature and stirred for 24 h. The isolated yield: 1.677 g (86%). Elemental analysis (%) calculated for C13H17Cl2O2Al: C 35.63, H 5.63; found: C 35.14, H 5.45. 27Al NMR (CDCl3): δ = 1.11 [9H, s, (CH3)2O2CH].

**Synthesis of [Cl2AlO2C2H3]2 (1c).** A similar procedure as for 1a, a toluene solution of pivalic acid (1.000 g, 9.8 mmol) was added dropwise to a solution of EtAlCl2 in toluene (5.4 mL, 1.8 M) at −78 °C under nitrogen atmosphere. The reaction mixture was allowed to warm up to room temperature and stirred for 2 h. Small rhombic colorless crystals of 1c were isolated as an orange-colored viscous liquid. The isolated yield: 1.194 g (3.0 mmol), water (0.018 g, 1.0 mmol) in THF (2 mL) was added, and the reaction mixture was stirred for 12 h. Colorless crystals suitable for X-ray analysis were isolated from the postreaction mixture after storage at −5 °C. The isolated yield: 0.919 g (76%). Elemental analysis (%) calculated for C6H11O2Al2Cl4: C 53.66, H 4.50, Al 8.93, N 11.73; found: C 53.60, H 4.45, Al 8.89, N 11.70. 27Al NMR (CDCl3): δ = 0.2, 77.0, 91.0, 102.0. IR (Nujol, cm−1): 542; 607; 760; 777; 1315; 1452; 1495; 1566; 1598; 1618.

**Synthesis of [Cl2AlO2CC11H23]2 (1d).** A slightly modified procedure as for 1a; a toluene solution of pivalic acid (1.000 g, 9.8 mmol) was added dropwise to a solution of EtAlCl2 in toluene (5.4 mL, 1.8 M) at −78 °C under nitrogen atmosphere. The reaction mixture was allowed to warm up to room temperature and stirred for 2 h. Small rhombic colorless crystals of 1d were isolated as an orange-colored viscous liquid. The isolated yield: 1.677 g (86%). Elemental analysis (%) calculated for C13H17Cl2O2Al: C 35.63, H 5.63; found: C 35.14, H 5.45. 27Al NMR (CDCl3): δ = 1.11 [9H, s, (CH3)2O2CH].

**Synthesis of [Al3O(O2CtBu)6(THF)3][AlCl4] (4b).** A similar procedure as for 1a using 1.194 g, 3.0 mmol) in THF (2 mL) was added, and the reaction mixture was stirred for 12 h. Colorless crystals suitable for X-ray analysis were isolated from the postreaction mixture after storage at −5 °C. The isolated yield: 0.919 g (76%). Elemental analysis (%) calculated for C6H11O2Al2Cl4: C 53.66, H 4.50, Al 8.93, N 11.73; found: C 53.60, H 4.45, Al 8.89, N 11.70. 27Al NMR (CDCl3): δ = 0.2, 77.0, 91.0, 102.0. IR (Nujol, cm−1): 542; 607; 760; 777; 1315; 1452; 1495; 1566; 1598; 1618.

**Synthesis of [Cl2AlO2CC11H23]2 (1d).** A similar procedure as for 1b using acrylic acid (1.960 g, 9.8 mmol) and EtAlCl2 in toluene (5.4 mL, 1.8 M). All volatile compounds were removed under vacuum, and a white powder was obtained. Recrystallization from concentrated toluene solution afforded 1e as a polycrystalline product. The isolated yield: 1.408 g (85%). Elemental analysis (%) calculated for C13H17Cl2O2Al: C 35.63, H 5.63; 27Al NMR (CDCl3): δ = 1.11 [9H, s, (CH3)2O2CH].

**Synthesis of [Cl2AlO2CC11H23]2 (1d).** A similar procedure as for 1b using lauric acid (1.960 g, 9.8 mmol) and EtAlCl2 in toluene (5.4 mL, 1.8 M). The product 1d was isolated as an orange-colored viscous liquid. Elemental analysis (%) calculated for C13H17Cl2O2Al: C 48.50, H 7.30, Al 9.08, C 23.86; found: C 48.42, H 7.68, Al 9.14, C 23.91. 27Al NMR (CDCl3): δ = 1.11 [9H, s, (CH3)2O2CH].
1.0 mmol) in tetrahydrofuran (2 mL) was added slowly under vigorous stirring. Colorless crystals of $S$ suitable for X-ray analysis were isolated from the concentrated postreaction mixture after storage at 4\(^\circ\)C. Yield: 0.413 g (56%). Elemental analysis (calc) for \(\text{C}_{2}\text{H}_{2}\text{AlCl}_{3}\text{O}_{5}\): C 35.65, H 5.30, Al 10.92, Cl 28.70; found: C 35.61, H 5.22, Al 10.66, Cl 28.62. \n
**Synthesis of \(\text{Al}_{2}\text{(OH)O}_{2}\text{C}_{2}\text{Bu}_{3}\text{(MeCN)}_{2}\text{AlCl}_{4}\text{(6)}\).** To a toluene solution (10 mL) of \(1\text{b} (1.194\text{ g, 3.0 mmol})\), water (0.018 g, 1.0 mmol) in acetonitrile (2 mL) was added slowly, and this reaction mixture was stirred for 2 h. Colorless crystals of 6 suitable for X-ray analysis were isolated from the concentrated postreaction mixture after storage at 0\(^\circ\)C. Yield: 0.605 g (59%). Elemental analysis (calc) for \(\text{C}_{2}\text{H}_{2}\text{AlCl}_{3}\text{O}_{5}\): C 25.78, H 3.64, Al 13.15, Cl 41.47, N 8.19; found: C 25.70, H 3.60, Al 13.11, Cl 41.42, N 8.13. \n
**Crystallographic Data.** The data were collected at 100(2) K on a Nonius Kappa CCD diffractometer using graphite monochromated MoKα radiation. \(\lambda = 0.71073\text{ Å}\). The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with DENOVO and SCALEPACK (HKL2000 package). The structure was solved by direct methods using the SHELXS97 program and was refined by full matrix least-squares on \(F^{2}\) using the program SHELXL97. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometricalally idealized coordinates with a fixed isotropic displacement parameter equal to 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon. Additional 3\text{a}NMR data, X-ray crystallographic files in CIF format, molecular figures and bond length/bond angle tables for compounds \(1\text{a}, 2\text{a}\text{MEI}, 3\text{b}, 4\text{a}\text{THF}, 4\text{b}\text{THF}, 4\text{b}\text{Me}_{2}O\), 5, and 6. This material is available free of charge via the Internet at http://pubs.acs.org. **Article**

**ASSOCIATED CONTENT**

**Supporting Information**

Additional \(3\text{a}NMR\) data, X-ray crystallographic files in CIF format, molecular figures and bond length/bond angle tables for compounds \(1\text{a}, 2\text{a}\text{MEI}, 3\text{b}, 4\text{a}\text{THF}, 4\text{b}\text{THF}, 4\text{b}\text{Me}_{2}O\), 5, and 6. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Author**

E-mail: evala@ch.pw.edu.pl (Z.F.), lewin@ch.pw.edu.pl (J.L.).


**ACKNOWLEDGMENTS**

This work was supported by the Ministry of Science and Higher Education (N N204 128037) and European Union in the framework through the Warsaw University of Technology.
Development Programme of ESF (WB) and Warsaw University of Technology.

REFERENCES


