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

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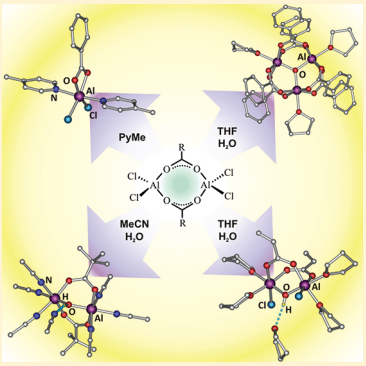
Supporting Information

ABSTRACT: A series of dichloroaluminum carboxylates $[Cl_2Al(O_2CR)]_2$ (were R = Ph (**1a**), ^{t}Bu (**1b**), $CHCH_2$ (**1c**) and $C_{11}H_{23}$ (**1d**)) were prepared and extended investigations on their structure and reactivity toward various Lewis bases and H_2O performed. Compounds $[Cl_2Al(O_2CR)]_2$ 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 $[Cl_2Al(O_2CR)]_2$ equilibrates with new ionic forms. In the presences of 4-methylpyridine the six-coordinate Lewis acid−base adducts $[Cl_2Al(\lambda_2\text{-}O_2CR)(py\text{-}Me)_2]$ [R = Ph (**3a**), ^{t}Bu (**3b**)] with a chelating carboxylate ligand were formed. The reactions of **1a**, **1b**, and **1d** with 0.33 equiv of H_2O in THF-toluene solution lead to oxo carboxylates $[(Al_3O)(O_2CR)_6(THF)_3][AlCl_4]$ [where R = Ph (**4a**$_{THF}$), ^{t}Bu (**4b**$_{THF}$), and $C_{11}H_{23}$ (**4d**$_{THF}$)] in high yield. The similar reaction of **1c** in tetrahydrofuran (THF) afforded the chloro(hydroxo)aluminum acrylate $[(ClAl)_2(OH)(O_2CC_2H_3)_2(THF)_4][AlCl_4]$ (**5**), while the hydrolysis of **1b** in MeCN lead to the hydroxoaluminum carboxylate $[Al_2(OH)(O_2C^tBu)_2(MeCN)_6][AlCl_4]_3]$ (**6**). All compounds were characterized by elemental analysis, ^{1}H, ^{27}Al NMR, and IR spectroscopy, and the molecular structure of **1a**, **3a**, **3b**, **4a**$_{THF}$, **4b**$_{THF}$, **4b**$_{py\text{-}Me}$, **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 H_2O 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[1] and fabrication of methylalumoxane oligomers[2] that are used in industry as cocatalysts for the polymerization of olefins using group 4 metallocene 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,[3] or controlled hydrolysis of dialkylaluminum carboxylates.[1] Several reports also describe the application of carboxylate alumoxanes[4] as reinforcing nanofillers for polymers,[3d,5] catalysts supports,[6] protecting layers, and processable precursors for ceramic materials.[1] 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 $[MeCO_2(AlMe_3)_2]^-$ anion with the monodentate carboxylate ligand **I**,[7] the dimeric $[R_2Al(\mu\text{-}O_2CR')]_2$ complexes with carboxylate bridging mode **II**,[4b,8] and a number of crystallographically characterized alkylaluminum compounds derived from bifunctional carboxylic acids exhibiting a large structural variation (Scheme 1).[9] 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 AlO_2C cycle.[8a]

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 Al_8,[10a] Al_{13},[10b,c] Al_{30},[10d,e] or Al_{32}.[10c] These

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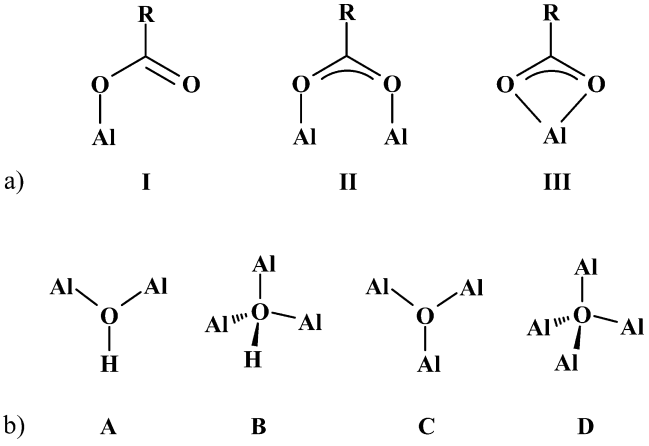
Scheme 1. Selected Coordination Modes of Both (a) the Carboxylate Ligand to Al Center and (b) the Oxo- and Hydroxoaluminum Building Units



complexes structurally represent the Baker–Figgis–Keggin isomers having the stoichiometry $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$(aq) where oxo- and hydroxoaluminum building units display usually trigonal **A** and tetrahedral **B** or **D** coordination geometries (Scheme 1).[11] The trigonal coordination mode **C** is rather unique, and to date there are only two examples of well-defined complexes with incorporated Al_3O moiety, both involving acetate ligands.[12,13] 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.[14] Other unique clusters such as the Al_{13}, Al_{14}, or Al_{15} were isolated in the presence of multifunctional carboxylate ligands.[15]

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 chloroaluminum benzoates featuring both molecular and ionic forms with different coordination numbers of the metal center and various coordination modes of the carboxylate ligand.[16] Herein we present systematic investigations on the structure of $[Cl_2Al(O_2CR)]_n$-type compounds and their transformation in the presence of various Lewis bases under anhydrous conditions, as well as in the presence of water. The study reports on the first examples of aluminum complexes with a chelating carboxylate ligand as well as a convenient method for the synthesis of oxo- and hydroxoaluminum complexes with bridging carboxylate units. An excellent platform for testing transformations of secondary building units in Al-MOFs toward H_2O and neutral donor ligands is also provided.

RESULTS AND DISCUSSION

Synthesis and Structure Characterization of Dichloraluminum Carboxylates. The reactivity of dichloroaluminum carboxylate complexes toward Lewis bases of different strength as well as water was investigated in a series of control experiments. As starting reagents we selected four dichloroaluminum carboxylates derived from benzoic, pivalic, acrylic, or laurylic acid, that is, $[(RCO_2)AlCl_2]_2$-type compounds (where R = Ph (**1a**), ^{t}Bu (**1b**), $CHCH_2$ (**1c**), and $C_{11}H_{23}$ (**1d**)). The carboxylate ligands differ in the steric and electronic character including one highly lipophilic ligand with a long aliphatic chain. These compounds were obtained in equimolar reactions of $EtAlCl_2$ with the corresponding carboxylic acid. Compounds **1a**, **1b**, and **1c** were isolated in high yield as colorless crystals, whereas **1d** formed a viscous liquid, and fully characterized spectroscopically in solution, and additionally the molecular structure of **1a** was determined by single crystal X-ray diffraction studies (because of a low quality of crystals of **1b** and **1c**, we were unable to obtain a proper data set to perform a reliable X-ray analysis).

The molecular structure of **1a** consists of two Cl_2Al units bridged by benzoate groups (Figure 1). The Al–O bond

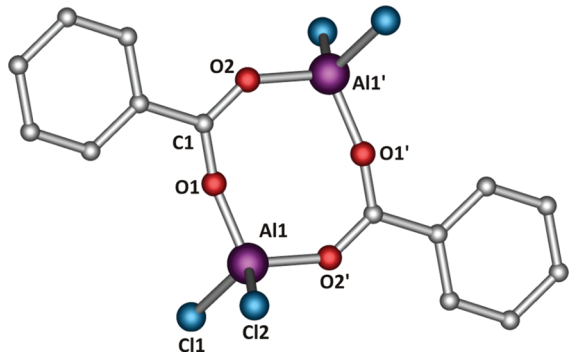


Figure 1. Molecular structure of **1a**; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1–O1, 1.755(3); Al1–Cl1, 2.095(1); Al1–Cl2, 2.099(2); Al1–O2′, 1.777(3); Cl1–Al1–Cl2, 115.6(6); O1–Al1–Cl1, 108.2(1); O1–Al1–Cl2, 108.8(1); O1–C1–O2, 121.4(4).

lengths (Al–$O_{av.}$ = 1.766 Å) are slightly shorter than those in the aluminum alkyl analogues characterized previously (cf. Al–$O_{av.}$ = 1.810 Å),[17] reflecting the different Lewis acidity of the X_2Al species involved. Interestingly, in the structure of **1a** the central eight-membered $Al_2O_4C_2$ ring is almost flat, in contrast to the chairlike conformation of $[^tBu_2Al(\mu\text{-}O_2CPh)]_2$. The IR spectrum of **1a** (in CH_2Cl_2) shows two characteristic bands at 1562 cm^{-1} [$\nu_{asymm}(CO_2)$] and 1497 cm^{-1} [$\nu_{symm}(CO_2)$] 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 ($\upsilon_{asymm}CO_2$) and 1488 ($\upsilon_{symm}CO_2$) 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 $[(RCO_2)AlCl_2]_2$ 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.[18]) This signal is, however,

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accompanied by a number of lower intensity resonances in the higher and lower field (Figure 2a and 2b). Similar spectrum of

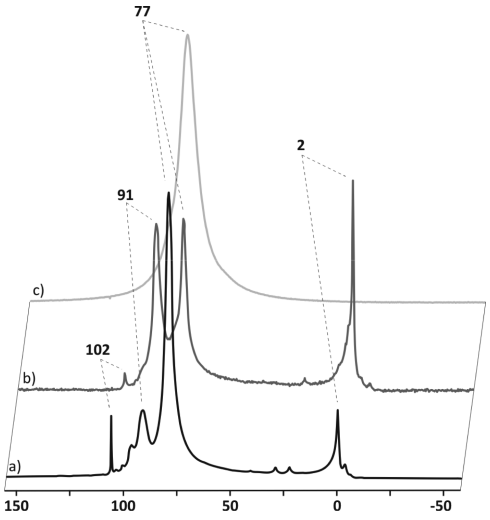

Figure 2. ^{27}Al NMR solution spectra of (a) **1a**, (b) **1b**, and (c) **1d** in $CDCl_3$ at 20 °C.

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 [$Cl_2Al(acac)$] 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-methylpyridine (*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

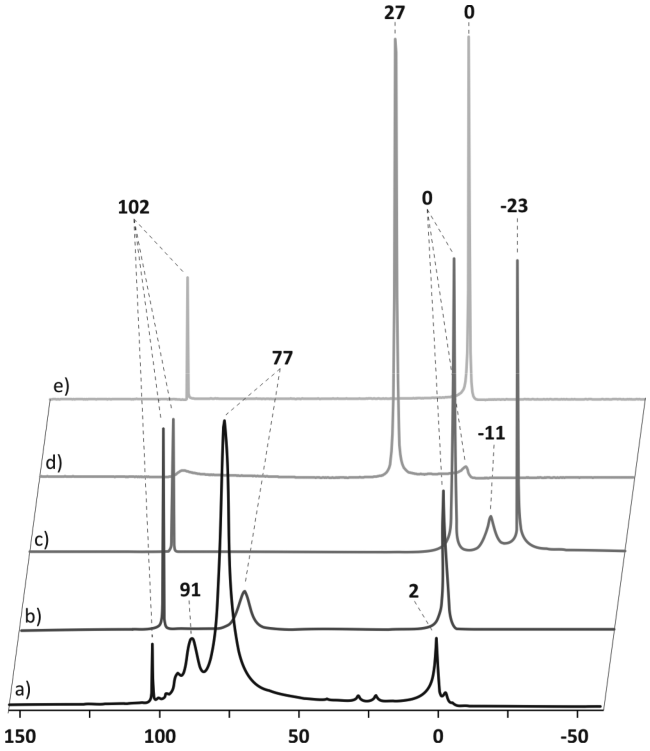

Figure 3. ^{27}Al NMR solution spectra of **1a** in various solvents: (a) $CDCl_3$, (b) THF, (c) MeCN, (d) *py*-Me; (e) **1a**:water (1:0,33) in THF at 20 °C.

with a new ionic form which we tentatively ascribed as $[(RCO_2)_2Al(THF)_x]^+[AlCl_4]^-$ ($\mathbf{2}_{THF}$) (Scheme 2) based on our earlier observations for the related dichloroaluminum acetylacetonate systems.[20]

Scheme 2

$$[(RCO_2)AlCl_2]_2 \underset{}{\overset{L}{\rightleftharpoons}} [(RCO_2)_2Al(L)_x][AlCl_4]$$

L = THF, MeCN

1a (R = Ph); **1b** (R = ^{t}Bu); **1d** (R = $C_{11}H_{23}$)

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 $[AlCl_2(DME)_2]^+[AlCl_4]^-$ ($\mathbf{2}_{DME}$) 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

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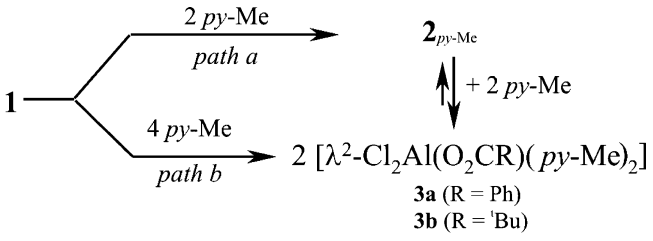
Scheme 3



appearance of two sharp signals at 102 ppm and 0 ppm (see Supporting Information, Figure S3 and S4) which likely correspond to ionic species $[(RCO_2)_2Al(py\text{-}Me)_x]^+[AlCl_4]^-$ ($\mathbf{2}_{py\text{-}Me}$). However, the use of an excess of *py*-Me in all above-mentioned systems leads to the formation of a dominating signal at 27 ppm which can be attributed to the six-coordinate complex $[Cl_2Al(O_2CR)(py\text{-}Me)_2]$ (**3**) along with significantly lower intensity resonances corresponding to ionic forms.

To have a better view on the structure of products formed in reactions of **1a**−**1d** with Lewis bases, we performed separate experiments in Schlenk tubes, and many efforts were made to obtain well-defined crystalline aluminum carboxylate adducts with the corresponding donor ligand.

However, only in the reaction involving *py*-Me and **1a** or **1b** did we successfully isolated from the postreaction mixture crystals of suitable quality for X-ray analysis. In both cases the reactions afforded the six-coordinate molecular Lewis acid−base adduct $[Cl_2Al(\lambda^2\text{-}O_2CR)(py\text{-}Me)_2]$ (R = Ph (**3a**), ^{t}Bu (**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 pyridine 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[22]). 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.[16]

Interestingly, analysis of the crystal structure of **3a** revealed that the monomeric units self-assemble via $C-H_{aliph}\cdots\pi$ and $C-H_{ar}\cdots Cl$ interactions to produce two-dimensional (2D) grids, which are further organized by complementary $C-H_{ar}\cdots O$ 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 $[Cl_2Al(\lambda^2\text{-}O_2C^tBu)(py\text{-}Me)_2]$ units into one-

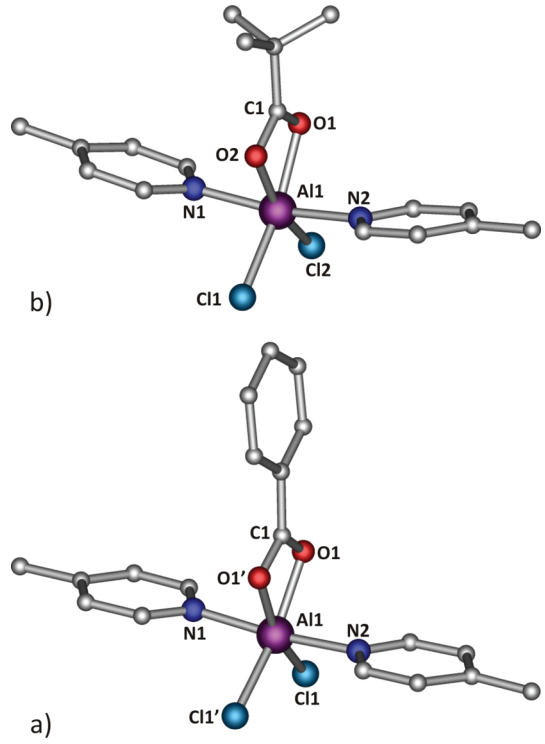


Figure 4. Molecular structures of (a) **3a** and (b) **3b**; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): (a): Al1−Cl1, 2.232(1); Al1−Cl1′, 2.232(9); Al1−O1, 1.975(2); Al1−O1′, 1.975 (2); Al1−N1, 2.057(3); Al1−N2, 2.065(3); N1−Al1−N2, 174.1(1); O1−C1−O1′, 115.8(3); O1−Al1−O2, 66.4(1); (b): Al1−Cl1, 2.249(1); Al1−Cl2, 2.214(1); Al1−O1, 1.986(2); Al1−O2, 1.977(2); Al1−N1, 2.043(3); Al1−N2, 2.046(3); N1−Al1−N2, 170.2(1); O1−C1−O2, 115.7(3); O1−Al1−O2, 65.9(1).

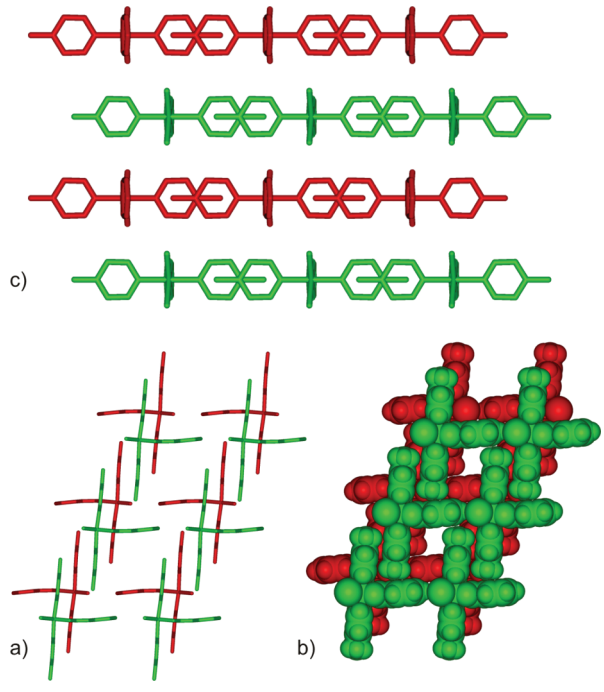


Figure 5. Crystal packing diagrams for **3a**, view along the (a) *b* axis (stick model), (b) *b* axis (space-fill model), and (c) *c* axis (stick model).

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dimensional (1D) chains stabilized by weak $\pi\cdots\pi$-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.

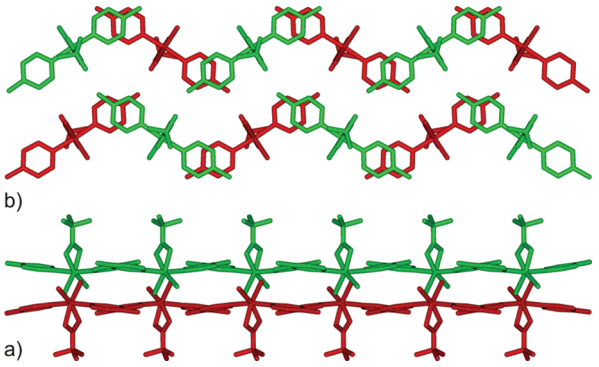
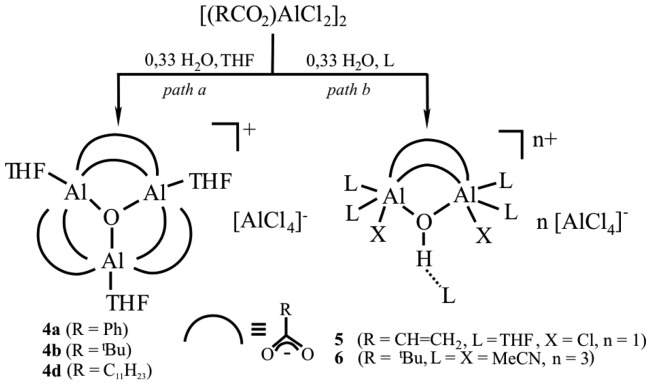


Figure 6. Crystal packing diagrams for **3b**, view along the (a) *b* axis and (b) *a* axis.

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 $[(Al_3O)(O_2CR)_6(THF)_3][AlCl_4]$ ($\mathbf{4}_{THF}$) (where R = Ph ($\mathbf{4a}_{THF}$), ^{t}Bu ($\mathbf{4b}_{THF}$), and $C_{11}H_{23}$ ($\mathbf{4d}_{THF}$)) in high yield (Scheme 4, path a). Surprisingly, when dichloroaluminum

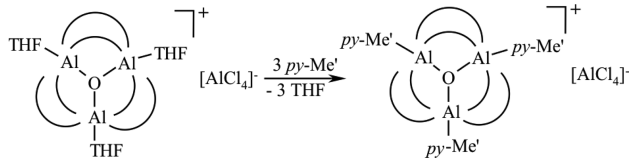
Scheme 4. Reaction Outcomes of Dichloroaluminum Carboxylates Hydrolysis Depending on the Character of the Carboxylate Ligand and/or the Donor Solvent Used



acrylate **1c** was reacted with water in THF under similar conditions, the unprecedented example of the ionic chloro(hydroxo)aluminum carboxylate $[(ClAl)_2(OH)(O_2CC_2H_3)_2(THF)_4][AlCl_4]$ (**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 aluminum hydroxide $[Al_2(OH)(O_2C^tBu)_2(MeCN)_6][AlCl_4)_3]$ (**6**) was isolated as the main product (Scheme 4, path b). The results described above show unambiguously that in the dichloroaluminum carboxylate/H_2O 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 $[(Al_3O)(O_2CR)_6(py\text{-}Me')_3][AlCl_4]$ (R = ^{t}Bu, Ph) adduct (Scheme 5). However only in one

Scheme 5



case, that is, in the reaction involving **4b** and 3-methylpyridine (*py*-Me′), were we able to isolate almost quantitatively the ionic complex $[(Al_3O)(O_2C^tBu)_6(py\text{-}Me')_3][AlCl_4]$ ($\mathbf{4b}_{py\text{-}Me'}$) 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 $\mathbf{4a}_{THF}$ and $\mathbf{4b}_{THF}$ are isostructural (the corresponding laurylate derivative $\mathbf{4d}_{THF}$ is an oily product), and the representative molecular structure of $\mathbf{4a}_{THF}$ is shown in Figure 7. The central

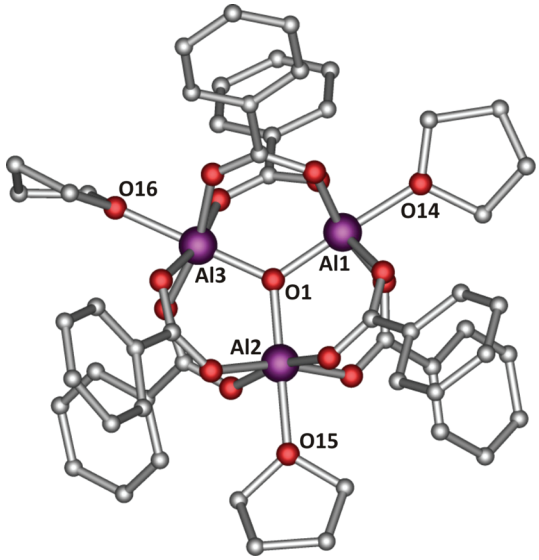


Figure 7. Molecular structure of the cationic part of $\mathbf{4a}_{THF}$; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): O1−Al1, 1.821(3); O1−Al2, 1.823(3); O1−Al3, 1.817(3); Al1−O14, 2.002(4); Al2−O15, 1.987(4); Al3−O16, 1.990(3); Al1−O1−Al2, 120.2(2); Al1−O1−Al3, 120.0(2); Al2−O1−Al3, 119.8(2).

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Al_3O 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−(μ_3-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 $\mathbf{4a}_{THF}$ and $\mathbf{4b}_{THF}$ 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 $\mathbf{4b}_{py\text{-}Me'}$ crystallizes in the monoclinic $P2_1/c$ space group and is isostructural with the previously described ionic complex $\mathbf{4b}_{THF}$ (Figure 8). Only minor differences in bond lengths

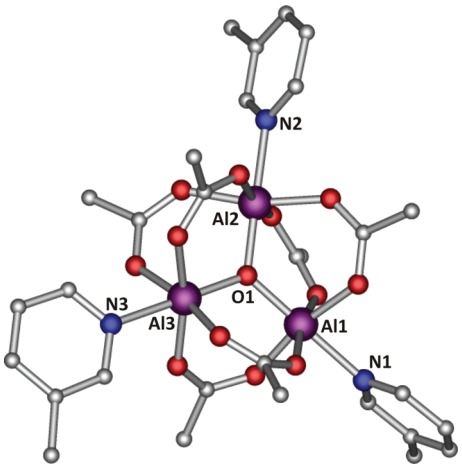

Figure 8. Molecular structure of $\mathbf{4b}_{py\text{-}Me'}$; hydrogen atoms and methyl groups of ^{t}Bu have been omitted for clarity. Selected bond lengths (Å) and angles (deg): O1−Al1, 1.819(4); O1−Al2, 1.827(4); O1−Al3, 1.820(4); Al1−N1, 2.096(5); Al2−N2, 2.102(5); Al3−N3, 2.103(5); Al1−O1−Al2, 119.7(2); Al1−O1−Al3, 120.7(2); Al2−O1−Al3, 119.6(2).

can be observed for Al−$N_{py\text{-}Me}$ and Al−O_{THF} 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 $Al_3O(O_2CR)_6$ core is very weak.

Compound **5** crystallizes in the monoclinic $P2_1/c$ space group (Figure 9). The cationic unit consists of two six-coordinate aluminum atoms which are bridged by two acrylate ligands and a hydroxo μ_2-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 $[Al_2(OH)(O_2C_3H_3)_3(THF)_4]^+$ cation forms an intermolecular hydrogen bond with additional THF molecule, where O5−H50···O10 distance is 2.734 Å.

Compound **6** crystallizes in the monoclinic $P2_1/c$ space group with one $[Al_2(OH)(O_2C^tBu)_2(MeCN)_6]^{3+}$ cation and three $AlCl_4^-$ anions in the unit cell (Figure 10). The cation represents an idealized 2-fold symmetry and contains two six-coordinated aluminum atoms, which are connected by a bridging μ_2-OH hydroxide anion and two bridging carboxylate ligands. The octahedral coordination sphere of aluminum

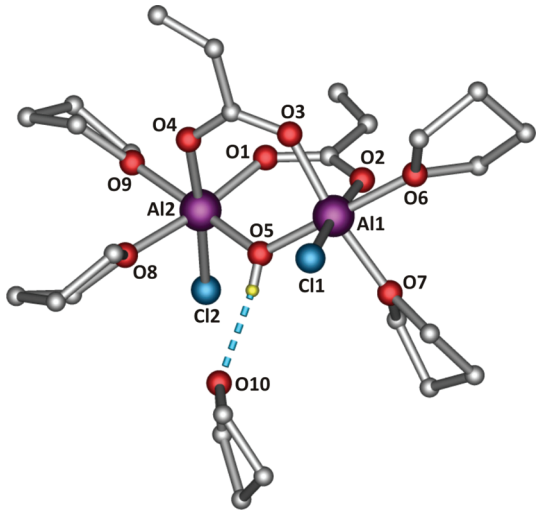

Figure 9. Molecular structure of the cationic part of **5**; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): O5−Al1, 1.825(1); O5−Al2, 1.823(1); Al1−Cl1, 2.259(5); Al2−Cl2, 2.270(5); Al1−O5−Al2, 125.8(6); O5−Al1−Cl1, 94.3(3); O5−Al1−Cl2, 93.6(3).

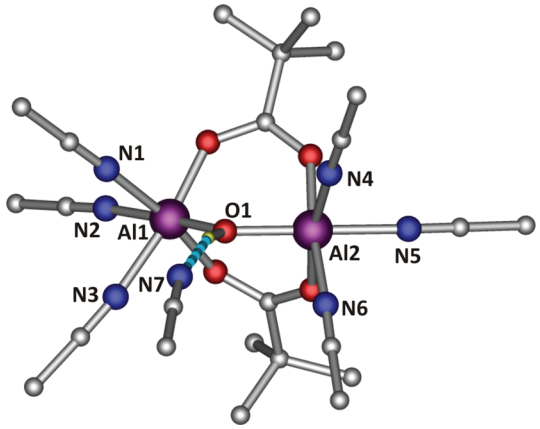

Figure 10. Molecular structure of the cationic part of compound **6**; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): O1−Al1, 1.819(2); O1−Al2, 1.821(2); Al1−O2, 1.857(2); Al1−O4, 1.860(2); Al1−N1, 2.000(3); Al2−N4, 2.003(3);Al1−O1−Al2, 121.5(1); O1−Al1−O2, 94.5(1); O1−Al1−O4, 95.1(1); O1−Al1−N2, 177.1(1); O1−Al2−N5, 178.6(1).

cations is completed by three acetonitrile molecules. This structural motif is analogous to that previously observed in the $[Al_2(\mu\text{-}CH_3CO_2)_2(\mu\text{-}OH)(CH_3CO_2C_2H_5)_6][AlCl_4]_3$ aggregate.[23] The more detailed analysis of the crystal structure indicated that, similarly as in compound **5**, the hydroxo group is involved in the formation of the intermolecular O−H···N hydrogen bond with an additional acetonitrile molecule, where the O1−H1···N7 distance is 2.758 Å.

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

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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 $[Cl_2Al(\lambda_2\text{-}O_2CR)(py\text{-}Me)_2]$ 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 Al-MOF 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 P_2O_5. $EtAlCl_2$ (1.8 M in toluene, Aldrich) was used as received. NMR spectra were recorded on a Varian Mercury-400 spectrometer; IR spectra were recorded on FTIR Perkin-Elmer System 2000.

Synthesis of $[Cl_2AlO_2CPh]_2$ (1a). A solution of benzoic acid (1.196 g, 9.8 mmol) in CH_2Cl_2 (6 mL) was cooled to −78 °C, and a solution of $MeAlCl_2$ in hexane (9.8 mL of 1 M solution in hexane, 9.8 mmol) was added dropwise. Then the reaction mixture was warmed to room temperature and stirred for 2 h. Small rhombic colorless crystals were obtained from CH_2Cl_2/hexane mixture crystallized at 0 °C overnight. The isolated yield: 1.932 g (90%). Elemental analysis (%) calcd for $C_7H_5AlCl_2O_2$: C 38.39, H 2.30, Al 12.32, Cl 32.38; found: C 38.46, H 2.37, Al 12.25, Cl 32.31. ^{1}H NMR ($CDCl_3$): δ = 7.63 [m, 2H, CH_{Ar}], 7.87 [m, 1H, CH_{Ar}], 8.27 [m, 2H, CH_{Ar}]; ^{27}Al NMR ($CDCl_3$): δ = 2.0, 77.0, 91.0, 102.0. IR (Nujol, cm^{-1}): 560; 677; 715; 1376; 1452; 1495; 1566; 1598; 1618.

Synthesis of $[Cl_2AlO_2C^tBu]_2$ (1b). 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 $EtAlCl_2$ 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. Crystals of **1b** were isolated from the concentrated postreaction mixture at 0 °C after 24 h. The isolated yield: 1.677 g (86%). Elemental analysis (%) calcd for $C_5H_9AlCl_2O_2$: C 30.18, H 4.56, Al 13.56, Cl 35.63; found: C 30.14, H 4.50, Al 13.46, Cl 35.56. ^{1}H NMR ($CDCl_3$): δ = 1.37 [s, 12H, $(C\underline{H}_3)_3CCO_2$]; ^{27}Al NMR ($CDCl_3$): δ = 2.0; 77.0; 91.0; 101.9. IR (Nujol, cm^{-1}): 542; 607; 690; 787; 1038; 1235; 1377; 1460; 1493; 1575.

Synthesis of $[Cl_2AlO_2CC_2H_3]_2$ (1c). A similar procedure as for **1b** using acrylic acid (1.960 g, 9.8 mmol) and $EtAlCl_2$ 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 **1c** as a polycrystalline product. The isolated yield: 1.408 g (85%). Elemental analysis (%) calcd for $C_3H_3AlCl_2O_2$: C 21.33, H 1.79, Al 15.97, Cl 41.97; found: C 21.26, H 1.84, Al 15.90, Cl 41.92.

Synthesis of $[Cl_2AlO_2CC_{11}H_{23}]_2$ (1d). A similar procedure as for **1b** using lauric acid (1.960 g, 9.8 mmol) and $EtAlCl_2$ in toluene (5.4 mL, 1.8 M). The product **1d** was isolated as an orange-colored viscous liquid. Elemental analysis (%) calcd for $C_{12}H_{23}AlCl_2O_2$: C 48.50, H 7.80, Al 9.08, Cl 23.86; found: C 48.42, H 7.86, Al 9.14, Cl 23.91. ^{27}Al NMR ($CDCl_3$): δ = 77.0. IR (cm^{-1}): 516; 549; 693; 718; 1066; 1118; 1326; 1461; 1565; 2850; 2920; 2950, IR (benzene, cm^{-1}): 464; 524; 564; 692; 1028; 1080; 1120; 1376; 1392; 1488; 1572.

Reaction of 1a, 1b, 1d with DME (2_{DME}). To a solution of **1a** (0.438 g, 1.0 mmol), **1b** (0.398 g, 1.0 mmol), or **1d** (0.594 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added DME (0.360 g, 4.0 mmol). Large block-shaped colorless crystals were obtained quantitatively from CH_2Cl_2 at 0 °C after 2 h. Elemental analysis (%) calcd for $C_8H_{20}Al_2Cl_6O_4$: C 21.50, H 4.51, Al 12.07, Cl 47.60; found: C 21.44, H 4.45, Al 12.11, Cl 47.54. ^{27}Al NMR (DME): δ = 24.0, 102,1. IR (Nujol, cm^{-1}): 487; 855; 1006; 1063; 1187; 1248; 1287; 1376; 1454.

Synthesis of $[Cl_2Al(\lambda^2\text{-}O_2CPh)(py\text{-}Me)_2]$ (3a). To a solution of **1a** (0.438 g, 1.0 mmol) in CH_2Cl_2 (5 mL) was added *py*-Me (0.372 g, 4.0 mmol). Large block-shaped colorless crystals were obtained from CH_2Cl_2/toluene mixture crystallized at 0 °C. The isolated yield: 0.778 g (96%). **3a** is soluble in THF, CH_2Cl_2, and poorly soluble in aromatic solvents. Elemental analysis (%) calcd for $C_{19}H_{19}AlCl_2N_2O_2$: C 56.31, H 4.73, Al 6.66, Cl 17.50, N 6.91; found: C 56.35, H 4.78, Al 6.60, Cl 17.55, N 6.98. ^{1}H NMR ($CDCl_3$): δ = 2.40 [sb, 6H, CH_3], 7.25 [mb, 6H, CH_{Ar}], 7.48 [mb, 1H, CH_{Ar}], 7.81 [mb, 1H, CH_{Ar}], 7.90 [mb, 1H, CH_{Ar}], 8.70 [mb, 2H, CH_{Ar}], 9.09 [mb, 2H, CH_{Ar}]; ^{27}Al NMR ($CDCl_3$): δ = 0.2, 26.9, 102.0. IR (cm^{-1}): 519; 558; 687; 699; 731; 813; 894; 1036; 1060; 1071; 1078; 1104; 1171; 1209; 1234; 1262; 1306; 1339; 1378; 1451; 1506; 1563; 1575; 1592; 1602; 1627.

Synthesis of $[Cl_2Al(\lambda^2\text{-}O_2C^tBu)(py\text{-}Me)_2]$ (3b). A similar procedure as for **3a** using **1b** (0.398 g, 1.0 mmol) and *py*-Me (0.372 g, 4.0 mmol) as reagents. The isolated yield: 0.709 g (92%). Elemental analysis (%) calcd for $C_{17}H_{23}AlCl_2N_2O_2$: C 53.00, H 6.02, Al 7.00, Cl 18.40, N 7.27; found: C 52.92, H 6.05, Al 6.93, Cl 18.35, N 7.21. ^{1}H NMR ($CDCl_3$): δ = 1.01 [s, 9H, $(C\underline{H}_3)_3CCO_2$], 2.68 [s, 6H, CH_3], 7.78 [d, 4H, CH_{Ar}], 8.64 [d, 4H, CH_{Ar}]; ^{27}Al NMR ($CDCl_3$): δ = 0.2, 27.0, 102.0. IR (Nujol, cm^{-1}): 509; 561; 625; 725; 818; 1036; 1067; 1213; 1233; 1377; 1455; 1502; 1518; 1562; 1626.

Synthesis of $[Al_3O(O_2CPh)_6(THF)_3][AlCl_4]$ ($4a_{THF}$). To a toluene solution of **1a** (1.314 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 (%) calcd for $C_{54}H_{54}Al_4Cl_4O_{16}$: C 53.66, H 4.50, Al 8.93, Cl 11.73; found: C 53.60, H 4.45, Al 8.89, Cl 11.70. ^{1}H NMR ($CDCl_3$): δ = 2.12 [4H, s, $(C\underline{H}_2CH_2)_2O$], 4.49 [4H, s, $(CH_2C\underline{H}_2)_2O$], 7.42 [2H, m, CH_{Ar}], 7.52 [1H, s, CH_{Ar}], 8.01 [2H, s, CH_{Ar}], ^{27}Al NMR ($CDCl_3$): δ = 2.4, 102.3. IR (cm^{-1}): 464; 554; 656; 698; 746; 868; 1010; 1090; 1263; 1443; 1520; 1556; 1581; 1610; 2904; 2965; 3059; 2500−3500(w).

Synthesis of $[Al_3O(O_2C^tBu)_6(THF)_3][AlCl_4]$ ($4b_{THF}$). To a toluene solution of **1b** (1.194 g, 3.0 mmol), water (0.018 g, 1.0 mmol) in THF (2 mL) was added, and colorless crystals suitable for X-ray analysis were isolated from the postreaction mixture after storage at 4 °C. The isolated yield: 0.751 g (69%). Elemental analysis (%) calcd for $C_{42}H_{78}Al_4Cl_4O_{16}$: C 46.33, H 7.22, Al 9.91, Cl 13.02; found: C 46.27, H 7.18, Al 9.85, Cl 13.06. ^{1}H NMR ($CDCl_3$): δ = 1.11 [9H, s, $(C\underline{H}_3)_3C$], 1.96 [4H, s, $(C\underline{H}_2CH_2)_2O$], 4.12 [4H, s, $(CH_2C\underline{H}_2)_2O$]; ^{27}Al NMR ($CDCl_3$): δ = 0.2, 104.1; ^{13}C NMR 25.0, 27.3, 39.8, 70.3, 185.8. IR (cm^{-1}): 432; 489; 515; 541; 631; 711; 801; 891; 917; 1042; 1241; 1369; 1392; 1450; 1495; 1639; 2872; 2933; 2969.

Synthesis of $[Al_3O(O_2C^tBu)_6(py\text{-}Me')_3][AlCl_4]$ ($4b_{py\text{-}Me'}$). Procedure A: to a toluene solution of $4b_{THF}$ (0.544 g, 0.5 mmol) 3-picoline (0.140 g, 1.5 mmol) was added, and colorless crystals were isolated from a concentrated postreaction mixture. The isolated yield: 0.358 g (62%). Procedure B: to a toluene solution of **1b** (1.194, 3.0 mmol) water (0.018 g, 1.0 mmol) in 3-picoline (2 mL) was added, and colorless crystals of $4b_{py\text{-}Me'}$ suitable for X-ray analysis were isolated from the postreaction mixture stored at 4 °C. The isolated yield: 0.855 g (74%). Elemental analysis (%) calcd for $C_{48}H_{75}Al_4Cl_4N_3O_{13}$: C 50.05, H 6.56, Al 9.37, Cl 12.31, N 3.65; found: C 50.01, H 6.52, Al 9.32, Cl 12.27, N 3.61. ^{1}H NMR ($CDCl_3$): δ = 1.05 [9H, s, $(C\underline{H}_3)_3C$], 2.42 [3H, s, $C\underline{H}_3C_5H_4N$], 7.10−8.90 [4H, m, CH_{Ar}]; ^{27}Al NMR ($CDCl_3$): δ = 2.1, 102.1; ^{13}C NMR ($CDCl_3$): δ 18.6, 27.2, 39.6, 123.0−149.6, 186.1. IR (cm^{-1}): 422; 477; 480; 512; 612; 695; 714; 795; 823; 1045; 1071; 1122; 1209; 1238; 1366; 1389; 1443; 1491; 1629; 2872; 2927; 2965; 3094.

Synthesis of $[Al_2(OH)Cl_2(O_2CCHCH_3)_2(THF)_4][AlCl_4]$ (5). To a toluene solution (10 mL) of **1c** (1.014 g, 3.0 mmol), water (0.018 g,

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1.0 mmol) in tetrahydrofuran (2 mL) was added slowly under vigorous stirring. Colorless crystals of **5** suitable for X-ray analysis were isolated from the concentrated postreaction mixture after storage at 4 °C. Yield: 0.415 g (56%). Elemental analysis (%) calcd for $C_{22}H_{39}Al_3Cl_6O_9$: C 35.65, H 5.30, Al 10.92, Cl 28.70; found: C 35.61, H 5.22, Al 10.86, Cl 28.62. ^{1}H NMR ($CDCl_3$): δ = 1.99 [4H, s, ($C\underline{H}_2CH_2)_2O$], 4.13 [4H, s, ($CH_2C\underline{H}_2)_2O$], 5.87 [1H, dd, $C\underline{H}_aH_bCHCOO$], 6.06 [1H, dd, $CH_aH_bC\underline{H}COO$], 6.29 [1H, dd, $CH_a\underline{H}_bCHCOO$]; ^{27}Al NMR ($CDCl_3$): δ = 1.2, 102.1. IR (cm^{-1}): 489; 541; 624; 663; 692; 721; 798; 839; 878; 923; 984; 1023; 1080; 1263; 1379; 1462; 1594; 1613; 1655; 1668; 2885; 2914; 2963; 2650−3500(w).

Synthesis of $[Al_2(OH)(O_2C^tBu)_2(MeCN)_6][AlCl_4]_3$ (6). To a toluene solution (10 mL) of **1b** (1.194 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 °C. Yield: 0.605 g (59%). Elemental analysis (%) calcd for $C_{22}H_{37}Al_5Cl_{12}N_6O_5$: C 25.76, 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. ^{1}H NMR ($CDCl_3$): δ = 1.12 [9H, s, ($C\underline{H}_3)_3CCO_2$], 2.09 [3H, s, $C\underline{H}_3CN$]; ^{27}Al NMR ($CDCl_3$): δ = 0.5, 87,1, 102.2. IR (cm^{-1}): 798; 952; 1026; 1096; 1234; 1263; 1379; 1456; 1495; 1591; 2307; 2338; 2854 2927; 2959; 2500−3500(w).

Crystallographic Data. The data were collected at 100(2) K on a Nonius Kappa CCD diffractometer[24] using graphite monochromated MoKα radiation (λ = 0.71073 Å). The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with DENZO and SCALEPACK (HKL2000 package).[25] The structure was solved by direct methods using the SHELXS97[26] program and was refined by full matrix least−squares on F^2 using the program SHELXL97.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically 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. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 737314 (**1a**), CCDC 843886 ($\mathbf{2}_{DME}$), CCDC 737315 (**3a**), CCDC 843888 (**3b**), CCDC 843889 ($\mathbf{4a}_{THF}$), CCDC 843890 ($\mathbf{4b}_{py\text{-}Me}$), CCDC 843887 ($\mathbf{4b}_{THF}$), CCDC 843891 (**5**), CCDC 843892 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

1a: $C_{14}H_{10}Al_2Cl_4O_4$: M = 437.98, triclinic, space group $P\bar{1}$ (no. 2), a = 7.1889(3) Å, b = 8.6829(3) Å c = 8.9185(4) Å, α = 113.518(2)°, β = 112.421(2)°, γ = 93.641(2)°, U = 456.33(3) Å^3, Z = 1, F(000) = 220, D_c = 1.594 g m^3, T = 100(2) K, θ_{max} = 24.10°, μ(Mo−Kα) = 0.760 mm^{-1}, 1442 unique reflections. Refinement converged at $R1$ = 0.0826, $wR2$ = 0.1779 for all data and 263 parameters ($R1$ = 0.0691, $wR2$ = 0.1576 for 1314 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal to 0.998. The residual electron density = +0.60/−0.50 e Å^{-3}.

$\mathbf{2}_{DME}$: $C_8H_{20}Al_2Cl_6O_4$: M = 446.90, orthorhombic, space group $Pbcm$ (no. 57), a = 6.7311(2) Å, b = 14.7242(4) Å c = 19.1681(6) Å, U = 1899.75(10) Å^3, Z = 4, F(000) = 912, D_c = 1.563 g m^3, T = 100(2) K, θ_{max} = 27.46°, μ(Mo−Kα) = 1.002 mm^{-1}, 2239 unique reflections. Refinement converged at $R1$ = 0.0374, $wR2$ = 0.0812 for all data and 98 parameters ($R1$ = 0.0329, $wR2$ = 0.0787 for 2048 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.124. The residual electron density = +0.86/−0.35 e Å^{-3}.

3a: $C_{19}H_{19}AlCl_2N_2O_2$: M = 405.24, monoclinic, space group $P21/m$ (no. 11), a = 10.5831(6) Å, b = 10.9003(8) Å, c = 11.1279(9) Å, β = 115.451(4)°, U = 1159.12(16) Å^3, Z = 2, F(000) = 420, D_c = 1.161 g m^3, T = 100(2) K, θ_{max} = 24.11°, μ(Mo−Kα) = 0.331 mm^{-1}, 1941 unique reflections. Refinement converged at $R1$ = 0.0470, $wR2$ = 0.0886 for all data and 133 parameters ($R1$ = 0.0404, $wR2$ = 0.0861 for 1707 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.093. The residual electron density = +0.27 /− 0.22 e Å^{-3}.

3b: $C_{17}H_{23}AlCl_2N_2O_2$: M = 385.25, monoclinic, space group $C2/c$ (no. 15), a = 10.3121(10) Å, b = 27.225(3) Å c = 14.6991(15) Å, β = 92.602(6)°, U = 4122.4(7) Å^3, Z = 8, F(000) = 1616, D_c = 1.241 g m^3, T = 100(2) K, θ_{max} = 21.94°, μ(Mo−Kα) = 0.369 mm^{-1}, 2478 unique reflections.. Refinement converged at $R1$ = 0.0597, $wR2$ = 0.1074 for all data and 247 parameters ($R1$ = 0.0451, $wR2$ = 0.1023 for 2060 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.058. The residual electron density = +0.84/−0.66 e Å^{-3}.

$\mathbf{4a}_{THF}$: $C_{56}H_{58}Al_4Cl_8O_{16}$: M = 1378.54, triclinic, space group $P\bar{1}$ (no. 2), a = 14.3681(3) Å, b = 14.7009(3) Å, c = 20.8981(4) Å, α = 99.2950(10)°, β = 102.4920(10)°, γ = 116.0590(10)°, U = 3702.24(14) Å^3, Z = 2, F(000) = 1420, D_c = 1.237 g m^3, T = 100(2) K, θ_{max} = 23.26°, μ(Mo−Kα) = 0.407 mm^{-1}, 10502 unique reflections. Refinement converged at $R1$ = 0.0949, $wR2$ = 0.2061 for all data and 778 parameters ($R1$ = 0.0847, $wR2$ = 0.1748 for 8861 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.028. The residual electron density = +0.92/−0.88 e Å^{-3}.

$\mathbf{4b}_{py\text{-}Me}$: $C_{48}H_{75}Al_4Cl_4N_3O_{13}$: M = 1151.83, monoclinic, space group $P21/c$ (no. 14), a = 11.3611(4) Å, b = 23.7589(9) Å, c = 24.7769(10) Å, β = 107.126(2)°, U = 6391.4(4) Å^3, Z = 4, F(000) = 2432, D_c = 1.197 g m^3, T = 100(2) K, θ_{max} = 21.97°, μ(Mo−Kα) = 0.295 mm^{-1}, 7660 unique reflections. Refinement converged at $R1$ = 0.0855, $wR2$ = 0.1872 for all data and 720 parameters ($R1$ = 0.0688, $wR2$ = 0.1661 for 6200 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.045. The residual electron density = +0.92/−0.88 e Å^{-3}.

$\mathbf{4b}_{THF}$: $C_{46}H_{82}Al_4Cl_4O_{17}$: M = 1156.84, This compound crystallizes as twins, triclinic, space group $P\bar{1}$ (no. 2), a = 13.0010(9) Å, b = 12.9510(9) Å, c = 18.4270(13) Å, α = 83.870(4)°, β = 78.589(4)°, γ = 83.782(4)°, U = 3011.8(4) Å^3, Z = 2, F(000) = 1228, D_c = 1.276 g m^3, T = 100(2) K, θ_{max} = 23.26°, μ(Mo−Kα) = 0.316 mm^{-1}, 5028 unique reflections. The goodness-of-fit on F^2 was equal to 1.066.

5: $C_{26}H_{47}Al_3Cl_6O_{10}$: M = 813.28, monoclinic, space group $P21/c$ (no. 14), a = 15.4156(11) Å, b = 14.1660(10) Å, c = 22.3022(14) Å, β = 128.659(4)°, U = 3803.1(5) Å^3, Z = 4, F(000) = 1696, D_c = 1.420 g m^3, T = 99(2) K, θ_{max} = 30.00°, μ(Mo−Kα) = 0.569 mm^{-1}, 11092 unique reflections. Refinement converged at $R1$ = 0.0382, $wR2$ = 0.0786 for all data and 410 parameters ($R1$ = 0.0303, $wR2$ = 0.0861 for 9549 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.048. The residual electron density = +1.00/−0.51 e Å^{-3}.

6: $C_{24}H_{40}Al_5Cl_{12}N_7O_5$: M = 1066.93, monoclinic, space group $P21/c$ (no. 14), a = 13.2971(4) Å, b = 19.4679(6) Å, c = 20.4001(6) Å, β = 103.408(2)°, U = 5137.0(3) Å^3, Z = 4, F(000) = 2168, D_c = 1.380 g m^3, T = 100(2) K, θ_{max} = 24.41°, μ(Mo−Kα) = 0.769 mm^{-1}, 8302 unique reflections. Refinement converged at $R1$ = 0.0658, $wR2$ = 0.1053 for all data and 530 parameters ($R1$ = 0.0500, $wR2$ = 0.0993 for 6847 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal to 1.065. The residual electron density = +0.62/−0.49 e Å^{-3}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional ^{27}Al NMR data, X-ray crystallographic files in CIF format, molecular figures and bond length/bond angle tables for compounds **1a**, $\mathbf{2}_{DME}$, **3a**, **3b**, $\mathbf{4a}_{THF}$, $\mathbf{4b}_{THF}$, $\mathbf{4b}_{py\text{-}Me'}$, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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