CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200601112

Well-Defined Cationic Alkyl– and Alkoxide–Aluminum Complexes and Their Reactivity with ε-Caprolactone and Lactides

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Abstract: We describe the synthesis, structure, and reactivity of low-coordinate Al–alkyl and –alkoxide cationic complexes incorporating the sterically bulky aminophenolate bidentate ligand 6-(CH_2NMe_2)-2-CPh_3-4-Me-$C_6H_2O^-$ (*N,O*). These complexes are derived from the ionization of neutral dialkyl Al complexes (*N,O*)AlR_2 (**1a**, R = Me; **1b**, R = *i*Bu), readily obtained by alkane elimination between AlR_3 and the corresponding aminophenol ligand, with the alkyl abstracting reagents B(C_6F_5)$_3$ and [Ph_3C][B(C_6F_5)$_4$]. The reactions of **1a**,**b** with B(C_6F_5)$_3$ yield complicated mixtures or decomposition products, however the ionization of the Al–diisobutyl derivative **1b** with [Ph_3C][B(C_6F_5)$_4$] affords a stable four-coordinate Al–PhBr cationic adduct [(*N,O*)Al(*i*Bu)(PhBr)]$^+$ (**3**$^+$), as deduced from elemental analysis data. Complex **3**$^+$ readily coordinates Lewis bases such as THF to form the corresponding adduct [(*N,O*)Al(*i*Bu)(thf)]$^+$ (**4**$^+$), and also rapidly chain-transfers with 1-hexene to yield the three-coordinate Al–hexyl cation [(*N,O*)Al–hexyl]$^+$ (**5**$^+$). Both cations **3**$^+$ and **5**$^+$ slowly dimerize to form unprecedented organoaluminum dications [(*N,O*)AlR^+]$_2$ (**3′**$^{++}$, R = *i*Bu; **5′**$^{++}$, R = hexyl) as deduced from X-ray crystallographic analysis. Cation **3**$^+$ reacts quickly with *i*PrOH to form a stable Lewis acid/base adduct [(*N,O*)Al(*i*Bu)(HO*i*Pr)]$^+$ (**6**$^+$), which constitutes the first X-ray characterized adduct between an Al–alkyl complex and a simple ROH. The Al–RO*H* proton in **6**$^+$ is readily abstracted by NMe_2Ph to form the neutral isopropoxide Al complex [(*N,O*)Al(*i*Bu)(O*i*Pr)] (**7**). Upon reaction with THF, cation **6**$^+$ undergoes an intramolecular proton transfer to yield the ammonium Al–THF complex [(η^1-H*N,O*)Al(*i*Bu)(O*i*Pr)(thf)] (**8b**$^+$), in which the aminophenolate is η^1-coordinated to the Al center. Cation **8b**$^+$ can then be converted to the desired Al–alkoxide derivative [(*N,O*)Al(O*i*Pr)(thf)]$^+$ (**10**$^+$), by an intramolecular protonolysis reaction, as confirmed by X-ray crystallography. The synthesized Al–alkyl cations form robust four-coordinate adducts in the presence of cyclic esters such as ε-caprolactone and (D,L)-lactide, but no insertion chemistry occurs, illustrating the poor ability of the Al–R$^+$ moiety to ring-open. In contrast, the Al–alkoxide cation **10**$^+$ polymerizes ε-caprolactone in a controlled manner with excellent activity, but is inactive in the polymerization of (D,L)-lactide and L-lactide. Control experiments with L-lactide show that cation **10**$^+$ ring-opens L-lactide to yield a robust five-coordinated Al–lactate cation [(*N,O*)Al(η^2-L-lactate-O*i*Pr)(thf)]$^+$ (**13**$^+$), derived from a monoinsertion of L-lactide into the Al–O*i*Pr bond of **10**$^+$, that does not further react. Cation **13**$^+$ may be regarded as a structurally characterized close mimic of the initial intermediate in the ring opening polymerization (ROP), of lactides by [{LX}M(OR)(L)] (where LX$^-$ = bidentate monoanionic ligand and L = labile ligand) metal complex initiators.

Keywords: aluminum · aminophenolate · cations · lactones · ring-opening polymerization

Introduction

Neutral aluminum AlX_3 species have long been known as Lewis acid reagents and, as such, have found widespread applications in organic and organometallic chemistry.[1] More recently, cationic aluminum species have received increased interest because their enhanced Lewis acidity relative to that of neutral analogues may be of potential interest in catalysis, as well as in the mediation of other reactions requir-

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ing a Lewis acid species.[2] In this regard, some of these cations have already been used as alkene oxide,[3] (D,L)-lactide,[4] ε-caprolactone,[5] and olefin[6] polymerization catalysts. Among this class of compounds, four-coordinate Al–alkyl cations of the type $[\{LX\}Al(R)(L)]^+$ ($LX^- =$ bidentate monoanionic ligand, L = labile ligand) are the most studied as they combine a low-coordination with a cationic metal center, resulting in highly Lewis acidic species.[3d,6b,c,7] Interest in these cations has been generated by their ease of synthesis through an alkyl abstraction of neutral precursors $[\{LX\}AlR_2]$ with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ in the presence of a Lewis base L.[6b] If this ionization reaction is performed in the absence of a Lewis base, a more reactive three-coordinate Al–alkyl cation $[\{LX\}AlR]^+$ may, in principle, be generated. However, the often poor stability of such highly electron deficient Al cations, combined with their high tendency to form aggregates, have thus far limited their accessibility. Examples in this area have been restricted to the synthesis of $[\{LX\}AlR]^+$ cations bearing stabilizing π-delocalized *N,N*-bidentate ligands; these species were shown to be stable provided a sterically bulky bidentate ligand as well as an inert counterion were used.[3d,8]

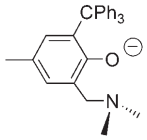
Reactivity studies performed by Jordan et al. on three-coordinate $[\{ATI\}AlR]^+$ chelate cations ($ATI^- = N,N'$-aminotroponiminate bidentate ligand) showed that generally, such species behave as potent Lewis acids because they form strong adducts with Lewis bases such as amines and acetonitrile, and they initiate the polymerization of isobutene and propylene oxide, presumably by a cationic Lewis acid-assisted mechanism. In contrast, these low-coordinate Al cations exhibit a poor insertion reactivity into the Al–C bond. In this regard, they appear to be less reactive than neutral AlR_3 species. Rather, they show a selective and exclusive preference for β-hydride transfer to unsaturated substrates such as ethylene and acetone. Notably $[\{ATI\}AlR]^+$ was found to catalytically dimerize *t*BuC≡CH by an insertion/σ-bond metathesis cycle.[3d,8]

In contrast to other classes of Al cations, well-defined Al–alkoxide cations, whether with a low- or higher-coordinated Al center, are not well known. This is rather surprizing, in view of the current interest in Al–alkoxide complexes as initiators of the controlled ring-opening polymerization (ROP) of cyclic esters, such as lactides and lactones the polymers of which may be of interest for their biodegradability and biocompatibility.[9] Examples of Al–alkoxide cations include 1) a robust four-coordinate Al–alkoxide dicationic dimer,[10a] and 2) six-coordinate iminophenolate Al–alkoxide cations. The latter were found to be active in ε-CL (CL = caprolactone) polymerization but solution structure may be complicated by ligand-exchange reactions between the Al cation and its counterion.[10b]

The lack of studies in the aforementioned area and our current interest in group 13 species prompted us toward the synthesis of *well-defined* and *low-coordinate* Al–alkoxide cations of the type $[\{LX\}AlOR]^+$ and $[\{LX\}Al(OR)(L)]^+$. Such cations may be useful in catalysis as they associate a highly Lewis acidic metal center with an Al–OR^+ moiety that may undergo insertion reactions in the Al–O bond. In particular, these derivatives may be of interest as initiators of the ring opening polymerization (ROP) of cyclic esters. In addition, such highly Lewis acidic Al–alkoxides may well exhibit interesting structural and reactivity features that may differ from those of their neutral analogues.

By analogy to the reactivity of neutral Al–alkyls, it was envisioned that $[\{LX\}AlOR]^+$ and $[\{LX\}Al(OR)(L)]^+$ cations should, in principle, be available by a simple alcoholysis reaction between ROH and the corresponding Al–alkyl cation $[\{LX\}AlR]^+$ and $[\{LX\}Al(R)(L)]^+$.

For this study, the choice of the aminophenolate (**A**) seemed appropriate because its significant steric bulk should limit the formation of aggregates, a common feature in Al^{III} chemistry, and may yield stable mononuclear Al cations. Such bidentate aminophenolate ligands are easily synthesised and are suitable for the synthesis of stable Al cations.[3f,11]



A

Our work was first directed toward the synthesis of well-defined, stable, and low-coordinate Al–alkyls incorporating the bidentate *N,O*-aminophenolate **A**. A particular emphasis was given to the synthesis of stable three-coordinate Al cations, as they remain structural curiosities and may, upon reaction with ROH, yield highly reactive $[\{LX\}AlOR]^+$ cations. The reactivity of low-coordinate Al–alkyl cations toward cyclic esters such as ε-caprolactone and lactides is also of interest and remains largely unexplored.[5]

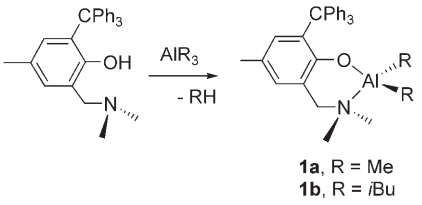
Here, we report the synthesis and structures of well-defined, low-coordinate Al–alkyl and –alkoxide cationic complexes incorporating a bulky aminophenolate ligand. The reactivity of these cations toward ε-caprolactone and lactides, as well as the characterizations of a few structurally unusual Al complexes, are also presented.

Results and Discussion

The first part of this work concerned the synthesis of low-coordinate alkyl-aluminum cations bearing **A**. The corresponding neutral Al–dialkyl derivatives were synthesized and their ionization chemistry studied with the alkyl-abstracting reagents $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$.

Synthesis of neutral aminophenolate–Al–dialkyl complexes 1a,b and their reaction with $B(C_6F_5)_3$: The neutral Al complexes $[\{6\text{-}(CH_2NMe_2)\text{-}2\text{-}CPh_3\text{-}4\text{-}Me\text{-}C_6H_2O\}AlR_2]$ (**1a**, R = Me; **1b**, R = *i*Bu; Scheme 1) were readily available through a classical alkane elimination route, by reaction between the aminophenol ligand $6\text{-}(CH_2NMe_2)\text{-}2\text{-}CPh_3\text{-}4\text{-}Me\text{-}C_6H_2OH$[11] and one equivalent of AlR_3 (R = Me or *i*Bu), and were isolated in near-quantitative yields (see Experimental Section).

The molecular structure of **1b**, as determined by X-ray crystallography, establishes its monomeric nature in the



Scheme 1.

solid state and clearly shows the significant steric hindrance around the Al center provided by the CPh_3 group (Figure 1). The NMR data for **1a,b** at room temperature are consistent with an overall C_s symmetry, which conforms with a rapid conformation change of the six-membered-ring Al–metallacycle under these conditions.

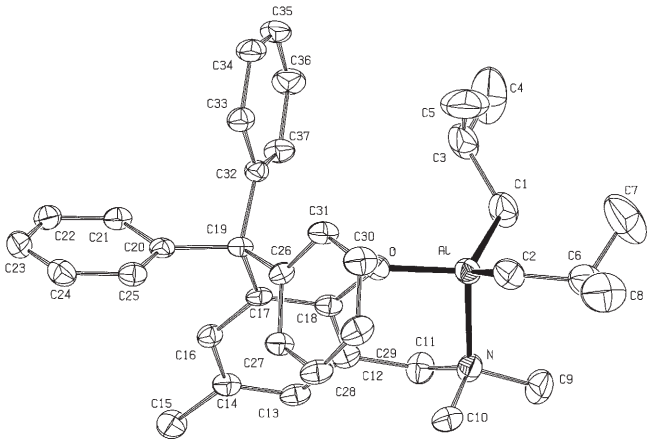
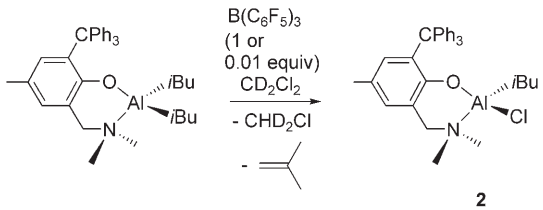


Figure 1. ORTEP view of the Al–diisobutyl complex **1b**. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Al–O = 1.764(2), Al–N = 2.023(2), Al–C1 = 1.968(3), Al–C2 = 1.974(3). Selected bond angles (°): O-Al-N = 93.98(8), O-Al-C1 = 110.50(10), O-Al-C2 = 112.36(10), C2-Al-C1 = 121.63(11).

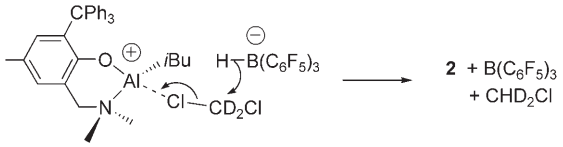
The reaction of **1a** with $B(C_6F_5)_3$ in CD_2Cl_2 yields unidentified species, whereas the reaction of Al–diisobutyl complex **1b** with one equivalent of $B(C_6F_5)_3$ (CH_2Cl_2, RT, 15 min) yields the quantitative formation of the monochloro complex [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)(Cl)] (**2**, Scheme 2), which was isolated in good yield.

On an NMR scale, this reaction (CD_2Cl_2, RT, 15 min) yields isobutene and CHD_2Cl along with **2**, as deduced from



Scheme 2.

^1H NMR data.[12] Interestingly, the ^{19}F NMR spectrum of the reaction mixture, contains signals for only $B(C_6F_5)_3$, suggesting that this borane may act as a catalyst in the reaction. Consistent with this proposal, the monochlorination of **1b** proceeded smoothly, cleanly, and in a similar manner when 0.01 equivalents of $B(C_6F_5)_3$ is used. As illustrated in Scheme 3, a possible mechanism for the formation of **2** may

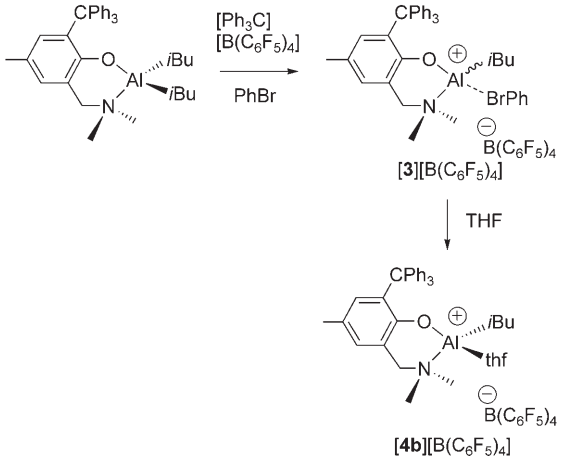


Scheme 3.

involve an initial hydride abstraction by $B(C_6F_5)_3$ at a Al–*iBu* group of **1b** to yield a transient and highly unstable Al–CD_2Cl_2 cationic adduct as a $[HB(C_6F_5)_3]^-$ salt. This putative transient species may decompose by a chlorine transfer to the Al center, concomitant with a hydride attack by the $[HB(C_6F_5)_3]^-$ borohydride at the Al–CD_2Cl_2 moiety, thus forming CHD_2Cl and regenerating $B(C_6F_5)_3$. It should be noted that a salt species associating a low-coordinate Al–alkyl cation with a $[HB(C_6F_5)_3]^-$ anion has been previously characterized.[11]

Attempts to perform these ionization reactions in a less-reactive solvent such as C_6D_5Br afforded, whether for **1a** or **1b**, an intractable mixture of products.

Access to a low-coordinate aminophenolate–Al–alkyl cation (3^+) derived from 1b and its reactivity with 1-hexene and THF: The use of the trityl salt $[Ph_3C][B(C_6F_5)_4]$, the $[B(C_6F_5)_4]^-$ ion of which is less reactive than $[RB(C_6F_5)_3]^-$ or $[HB(C_6F_5)_3]^-$, allowed access to a well-defined Al cation derived from **1b**.[13] The reaction of the Al–diisobutyl complex **1b** with $[Ph_3C][B(C_6F_5)_4]$ (C_6D_5Br, RT, 10 min) affords the quantitative formation of the Al cation [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)(PhBr)]$^+$ (**3**$^+$, Scheme 4) as a



Scheme 4.

fully dissociated $[B(C_6F_5)_4]^-$ salt, along with poly(isobutene), as observed by ^1H and ^{19}F NMR spectroscopy.

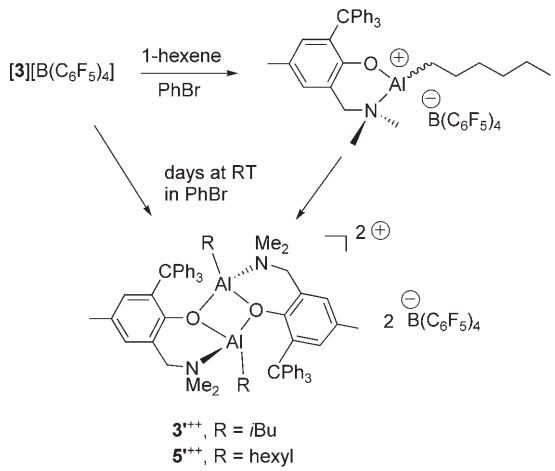
The salt species [**3**][$B(C_6F_5)_4$] is stable for days in C_6D_5Br at room temperature and could be isolated in a pure form after being generated on a preparative scale in PhBr. In contrast, cation $\mathbf{3}^+$ decomposes within seconds at room temperature in CH_2Cl_2. The NMR data for $\mathbf{3}^+$ are essentially unchanged between room temperature and −30 °C, which, under the studied conditions, is consistent with an overall C_s-symmetric structure for $\mathbf{3}^+$. For example, the ^1H NMR spectrum of [**3**][$B(C_6F_5)_4$] in C_6D_5Br exhibits two characteristic singlet resonances ($\delta = 2.09$, 3.05 ppm) which are assigned to the N*Me*$_2$ and Ph*C*H_2 moieties, respectively. In addition, the Al*C*H_2 resonance ($\delta = -0.04$ ppm) is shifted downfield relative to the corresponding resonance in **1b** ($\delta = -0.38$ ppm), a result of the cationic charge on the Al center. These NMR data, along with the elemental analysis for [**3**][$B(C_6F_5)_4$], strongly suggest that the Al cation $\mathbf{3}^+$ is a four-coordinate Al–BrC_6H_5 cationic adduct that undergoes rapid face solvent exchange under the conditions studied. Solid-state structures of four-coordinate cationic Al–ClPh adducts have been previously reported, thus supporting the above proposal.[14] Alternatively, the highly Lewis acidic cation $\mathbf{3}^+$, may well be a five-coordinate cationic species in solution to which two molecules of bromobenzene bind as labile axial ligands.

Aluminum cations such as $\mathbf{3}^+$ generally exhibit a poor stability and are usually fleetingly observed, if at all. In the case of $\mathbf{3}^+$, the significant steric crowding around the Al center provided by the CPh_3 and Al–*iBu* groups most likely accounts for the observed stability. The stability of $\mathbf{3}^+$ allowed studies of its reactivity with THF and 1-hexene.

As expected, the salt [**3**][$B(C_6F_5)_4$] readily reacts (C_6D_5Br, RT, 10 min) with a Lewis base such as THF (1 equiv) to quantitatively form the robust four-coordinate Al–THF cationic adduct [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)(thf)]$^+$ ($\mathbf{4b}^+$, Scheme 4) as a fully dissociated $[B(C_6F_5)_4]^-$ salt (as deduced from ^1H and ^{19}F NMR spectroscopy). The ^1H and ^{13}C NMR spectra for $\mathbf{4b}^+$ in C_6D_5Br at room temperature agree with an overall C_1-symmetric structure, consistent with an effective coordination of THF to the cationic Al center.

The Lewis acidic cation $\mathbf{3}^+$ also appears to react rapidly with olefins such as 1-hexene. The NMR-tube reaction of [**3**][$B(C_6F_5)_4$] with one equivalent of 1-hexene (C_6D_5Br, RT, 10 min) results in the quantitative conversion to the Al–hexyl cation [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(C_6H_{13})]$^+$ ($\mathbf{5}^+$, Scheme 5) as a fully dissociated $[B(C_6F_5)_4]^-$ salt, in addition to poly(isobutene), as observed by NMR spectroscopy.

This chain-transfer reaction most likely proceeds by a β-H transfer from $\mathbf{3}^+$ to 1-hexene to yield $\mathbf{5}^+$ and isobutene. Isobutene is then readily polymerized, presumably by a cationic mechanism, by $\mathbf{3}^+$ and/or $\mathbf{5}^+$. The rapid chain-transfer reaction observed for $\mathbf{3}^+$ confirms a reactivity trend previously observed for related *N*,*N*-based [{ATI}Al*i*Bu]$^+$ systems, which were found to chain transfer over the course of several hours upon reaction with an excess of ethylene.[3d] The present observation is also in agreement with theoretical studies that predict chain transfer becomes easier with an electron-deficient Al metal center.[15] The rapid chain transfer observed for $\mathbf{3}^+$ may reflect the high electron-deficiency of the Al center in this complex.



Scheme 5.

Dimerization of Al cations $\mathbf{3}^+$ and $\mathbf{5}^+$: Despite significant steric crowding and coulombian repulsion, the monomeric cations $\mathbf{3}^+$ and $\mathbf{5}^+$ slowly dimerize. If left for days at room temperature in a concentrated bromobenzene solution, compounds [**3**][$B(C_6F_5)_4$] and [**5**][$B(C_6F_5)_4$] slowly crystallize as highly insoluble Al dicationic dimers [({6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}AlR)]$_2^{++}$ ($\mathbf{3'}^{++}$, R = *i*Bu; $\mathbf{5'}^{++}$, R = C_6H_{13}; Scheme 5) as $[B(C_6F_5)_4]^-$ salts, which were both isolated as crystalline colorless solids.

The molecular structure of dication $\mathbf{5'}^{++}$ was determined by X-ray crystallography of salt species [$\mathbf{5'}$][{$B(C_6F_5)_4$}$_2$], which crystallizes as discrete $\mathbf{5'}^{++}$ dications and $[B(C_6F_5)_4]^-$ anions. The molecular structure of dication $\mathbf{5'}^{++}$ is illustrated in Figure 2, a summary of crystallographic data is given in Table 1, and selected bond lengths and angles are summarized in Table 2. This organoaluminum dication is a centrosymmetric dimer and can be seen as two three-coordinate Al cations [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(C_6H_{13})]$^+$, linked through two oxygen (μ_2-O) atoms (O and O'). As a result of the symmetry, the two CPh_3 groups point away from one another, which greatly minimizes the steric interactions in the complex. The Al_2O_2 four-membered ring moiety is nearly square, as shown by the bond angles of O-Al-O' and Al-O-Al′ (83.3(1) and 96.7(1)°, respectively). The nearly identical Al–O and Al′–O bond lengths (1.870(2) and 1.874(3) Å), comparable to those in [Et_2Al(μ-2,6-Me_2PhO)AlEt_2] (average 1.86(1) Å),[16] indicate that the aminophenolate oxygen (μ_2-O) centers symmetrically bridge Al and Al′. The Al centers in $\mathbf{5'}^{++}$ adopt slightly distorted tetrahedral structures with N-Al-O bite angles (96.0(1)°) similar to those of the neutral precursor **1b** (93.98(8)°). The Al–N bond lengths (1.955(3) Å) are significantly shorter

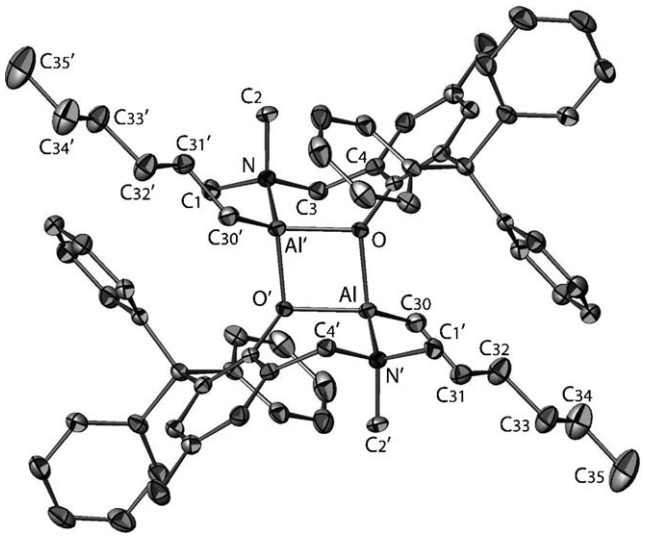


Figure 2. ORTEP view of the Al–hexyl dication $\mathbf{5'}^{++}$ with a partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity. Symmetry operators for generating equivalent positions are: $2-x, 1-y, 1-z$ (for $\mathbf{5'}^{++}$).

than those in **1b** (2.023(2) Å) and are at the bottom of the normal range for Al–N dative bonds (1.957(3)–2.238(4) Å),[17] reflecting an increased ionic character of the Al–N bonds in $\mathbf{5'}^{++}$ due to the presence of a cationic Al center. All other geometrical and bonding parameters closely relate to those of **1b**. In particular, the Al–aminophenolate chelate six-membered metallacycles are also significantly puckered in $\mathbf{5'}^{++}$, with the NMe_2 moiety lying well outside the rest of the ring. The flexibility of the aminophenolate Al chelate ring allows an adaptation to the steric and electronic requirements of $\mathbf{5'}^{++}$. This flexibility may play a crucial role in the stability and robustness of this dication.

Due to their poor solubility, the solution structures of the salt species $[\mathbf{3'}][(B(C_6F_5)_4)_2]$ and $[\mathbf{5'}][(B(C_6F_5)_4)_2]$ could be studied by ^1H and ^{19}F NMR spectroscopy only. The NMR data for $\mathbf{3'}^{++}$ and $\mathbf{5'}^{++}$ exhibit very similar features to one another (with the exception of the Al–*R* moiety) and suggest overall centrosymmetric structures for both dications at room temperature in C_6D_5Br. This indicates that $\mathbf{3'}^{++}$ and $\mathbf{5'}^{++}$ adopt similar structures and do not readily dissociate in solution. Attempt to dissociate these species at higher temperatures in bromobenzene or in THF resulted in decomposition reactions prior to the observation of any dissociation reaction. These observations suggest that the formation of $\mathbf{3'}^{++}$ or $\mathbf{5'}^{++}$ from the corresponding monomeric cation is irreversible under the conditions studied.

Synthesis of low-coordinate aminophenolate–Al–alkoxide cations: The second part of our work aimed to synthesize low-coordinate alkoxy Al cations of the type $[\{LX\}AlOR]^+$ and $[\{LX\}Al(OR)(L)]^+$ by reaction of the corresponding alkyl-Al cations with ROH. This simple route was less straightforward than initially anticipated and was found to

Table 1. Summary of crystallographic data for **1b**, $[\mathbf{5'}][(B(C_6F_5)_4)_2]$, $[\mathbf{6}][B(C_6F_5)_4]$, and $[\mathbf{9a}][MeB(C_6F_5)_3]$.

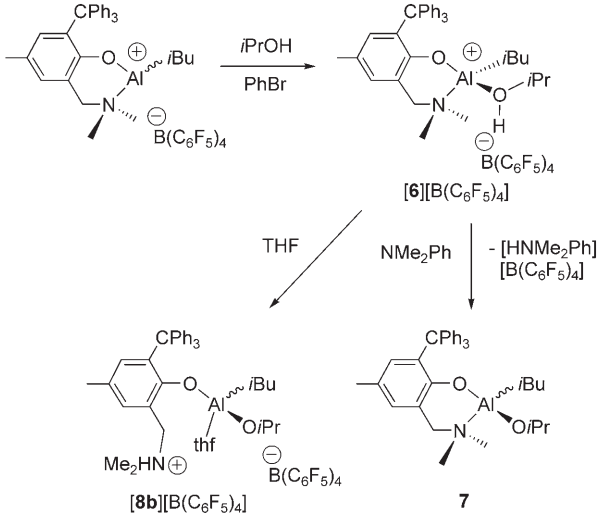
	1b	$[\mathbf{5'}][(B(C_6F_5)_4)_2]$	$[\mathbf{6}][B(C_6F_5)_4]$	$[\mathbf{9a}][MeB(C_6F_5)_4]$
formula	$C_{37}H_{46}AlNO$	$C_{142}H_{102}Al_2B_2Br_4F_{40}N_2O_2$	$C_{66}H_{50}AlBBrF_{20}NO_2$	$C_{59}H_{48}AlBF_{15}NO_3$
M_r	547.73	3023.48	1386.77	1141.77
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	38.341(2)	13.3900(10)	10.728(2)	12.331(5)
b [Å]	9.550(4)	15.008(2)	14.714(3)	12.446(6)
c [Å]	17.812(9)	17.583(3)	19.341(5)	18.612(9)
α [°]	90.00	102.58(5)	98.58(5)	105.37(2)
β [°]	102.74(5)	110.11(5)	96.13(5)	90.66(2)
γ [°]	90.00	99.57(5)	91.36	102.41(2)
V [Å^3]	6361(4)	3124.3(19)	2999.2(11)	2683(2)
Z	8	1	2	2
ρ_{calcd} [g cm^{-3}]	1.144	1.607	1.536	1.413
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.092	1.419	0.810	0.137
F[000]	2368	1520	1404	1172
data collection				
T [K]	173(2)	173(2)	173(2)	173(2)
θ range [°]	2.55–29.16	1.90–29.98	1.40–24.71	1.14–30.10
h,*k*,*l* indices	−52/51, 0/13, 0/24	−18/17, −21/20, 0/24	−12/12, −16/17, −22/22	−17/17, −17/15, −24/26
total reflns	8530	18115	8394	15676
unique reflns/$R_{[int]}$	4916/0.0000	10004/0.0000	5240/0.0431	8900/0.0428
observed data	$>2\sigma(I)$	$>2\sigma(I)$	$>2\sigma(I)$	$>2\sigma(I)$
refinement				
reflections/parameters	8530/361	18116/874	8394/774	15676/725
R_1/R_2	0.0752/0.1580	0.0718/0.1473	0.1229/0.1754	0.0883/0.1654
wR_1/wR_2	0.1392/0.1656	0.1620/0.1957	0.2517/0.2813	0.1850/0.2303
GoF indicator	0.989	0.979	0.976	0.953
min/max residual density [e Å^{-3}]	−0.278/0.345	−1.095/0.762	−0.991/1.002	−0.467/0.935

Table 2. Selected bond lengths [Å] and angles [°] for the Al cations $\mathbf{5'^{++}}$, $\mathbf{6^+}$ and $\mathbf{9a^+}$.

$5'^{++}$			
Al–O	1.870(2)	O-Al-O′	83.34(10)
Al–O’	1.874(3)	O-Al′-N′	96.03(12)
Al–C(30)	1.924(3)	Al-O-Al′	96.66(10)
Al–N	1.955(3)	O-Al-C30	126.27(13)
6^+			
Al1 –O1	1.713(5)	O1-Al1-N1	97.5(3)
Al1 –O2	1.845(7)	O1-Al1-O2	100.6(3)
Al1 –C11	1.917(10)	O1-Al1-C11	125.0(4)
Al1 –N1	1.961(7)	O2-Al1-C11	114.2(4)
$9a^+$			
Al–O3	1.709(2)	C2-O1-Al	130.7(2)
Al–O1	1.749(3)	C12-O3-Al	167.0(2)
Al–O2	1.865(3)	O3-Al-O1	104.50(12)
Al–C1	1.935(4)	O3-Al-O2	99.89(11)

proceed stepwise by the formation of kinetically stable intermediates.

Reaction of cation 3^+ with ROH: The reaction of [**3**][B(C_6F_5)$_4$] with one equivalent of *i*PrOH (C_6D_5Br, RT, 10 min) yields quantitatively the corresponding cationic Al–alcohol adduct [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)-(HO*i*Pr)]$^+$ ($\mathbf{6^+}$, Scheme 6) as a dissociated [B(C_6F_5)$_4$]$^-$ salt,



Scheme 6.

as observed by ^{1}H and ^{19}F NMR spectroscopy. The salt species [**6**][B(C_6F_5)$_4$], which was isolated in good yield as a highly air-sensitive colorless solid after being generated in PhBr, decomposes within seconds in CH_2Cl_2 at room temperature to unidentified species, but is stable for days at room temperature and for several hours at 60 °C in C_6D_5Br. However, cation $\mathbf{6^+}$ decomposes to unidentified species when heated at 80 °C in C_6H_5Br, showing that this alcohol adduct does not undergo a clean alcoholysis reaction, as could be envisaged.

The observation of a kinetically stable Al–alcohol complex such as $\mathbf{6^+}$ is unusual, as such adducts, which are proposed intermediates in the alcoholysis reaction of organoaluminum complexes and ROH, are not generally observed.[18] Although a few related neutral Al complexes have been reported,[19] cation $\mathbf{6^+}$ constitutes the first example of a stable Lewis acid-base adduct between a cationic Al–alkyl complex and a simple alcohol ROH.

The molecular structure of cation $\mathbf{6^+}$ was determined by X-ray crystallography and is shown in Figure 3. A summary of crystallographic data and selected bond lengths and

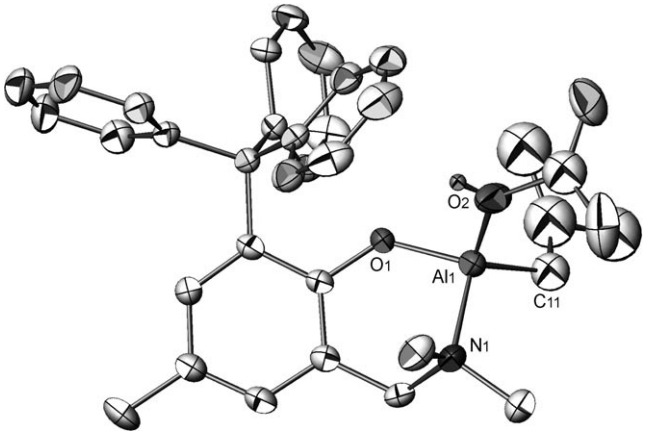


Figure 3. ORTEP view of the Al–alcohol cationic adduct $\mathbf{6^+}$ with a partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms (except for those on O2) are omitted for clarity.

angles are given in Tables 1 and 2, respectively. Cation $\mathbf{6^+}$ is a four-coordinate cationic Al Lewis acid/base adduct between [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)]$^+$ ($\mathbf{3^+}$) and *i*PrOH, with an overall structure quite similar to that of the four-coordinate Al–NMe_2Ph cation [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)(NMe_2Ph)]$^+$ previously reported.[11] The Al–O(2) bond length (1.845(7) Å) of the Al–HO*i*Pr moiety is comparable to that of the Al–THF bond length in the cationic Al complex [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(O*i*Pr)(thf)]$^+$ ($\mathbf{10^+}$, vide infra, Al–THF = 1.829(3) Å), whereas it is significantly longer than the Al–O*i*Pr bond length in $\mathbf{10^+}$ (1.657(3) Å), which is consistent with *i*PrOH coordinating as the labile ligand (L) to the Al cationic center in $\mathbf{6^+}$.

The NMR data for $\mathbf{6^+}$ agree with its solid-state structure being retained in solution, indicating remarkable robustness. In particular, these data are consistent with an overall C_1-symmetric structure for this cation in solution between room temperature and 60 °C in C_6D_5Br. In addition, the ^{1}H NMR spectrum of $\mathbf{6^+}$ contains a characteristic doublet resonance ($\delta = 2.69$ ppm, $^3J(H,H) = 7.4$ Hz), which was assigned to the Al–*H*O*i*Pr proton.

In sharp contrast to the reactivity of *i*PrOH, the reaction of the Al–alkyl cation $\mathbf{3^+}$ with either PhOH or MeOH yields a mixture of unidentified products, showing that at

least the sterics of ROH are crucial for the formation of stable cationic Al–HOR adducts such as $\mathbf{6}^+$.

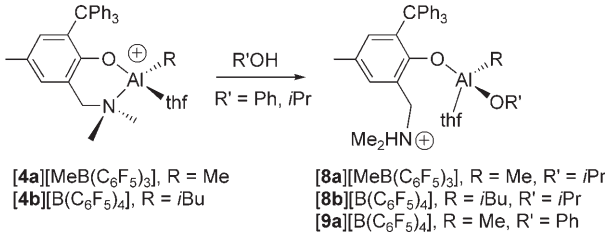
Alcoholysis reactions of Al complexes are believed to proceed by the formation of an Al–alcohol adduct such as $\mathbf{6}^+$, from which intramolecular protonolysis occurs possibly through a planar four-centered transition state.[17] In the case of $\mathbf{6}^+$, such a protonolysis may not take place for steric reasons, as it would most likely require severe distortions to provide a geometry for a concerted four-membered transition state. The exceptional stability of $\mathbf{6}^+$ may also be due to electronic factors, as an intramolecular protonolysis reaction would probably yield a less-stable three-coordinate Al species, poorly susceptible to the formation of aggregates given the overall steric bulk. Overall, a subtle balance between electronics and sterics, whether for ROH or for the Al cationic complex, most likely accounts for the observed stability of $\mathbf{6}^+$.

Reactivity of $\mathbf{6}^+$ with NMe_2Ph and THF: The decomposition of $\mathbf{6}^+$ upon heating, prior to any clean alcoholysis, as well as its unusual structure, prompted us to further study the reactivity of this robust cation. The reactivity of $\mathbf{6}^+$ with Lewis bases such as NMe_2Ph and THF was investigated.

The salt [**6**][$B(C_6F_5)_4$] readily reacts with one equivalent of NMe_2Ph (C_6D_5Br, RT, 10 min) to quantitatively form a 1:1 mixture of the neutral monoalkoxy-Al complex [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(O*i*Pr)(*i*Bu)] (**7**) and the ammonium salt [$NHMe_2Ph$][$B(C_6F_5)_4$], as observed by ^1H NMR spectroscopy (Scheme 6). This reaction, in which NMe_2Ph acts as a base, clearly indicates the acidic nature of the Al–*H*O*i*Pr proton in $\mathbf{6}^+$, which results from a strong activation of *i*PrOH by the Al center. The observed reactivity further illustrates the potent Lewis acid character of low-coordinate Al cations and represents a spectacular illustration of the general concept of Lewis acid-activated Brønsted acids.[20] To our knowledge, deprotonation reactions of a metal complex-activated alcohol by an amine have not yet been observed.

If cation $\mathbf{6}^+$ is reacted with THF, the outcome is somewhat different and an intramolecular proton transfer is observed. Thus, [**6**][$B(C_6F_5)_4$] reacts quickly with one equivalent of THF (C_6D_5Br, RT, 10 min) to form the ammonium–Al–alkyl complex [η^1-{6-(CH_2NHMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(^{i}Bu)(O*i*Pr)(thf)]$^+$ ($\mathbf{8b}^+$, Scheme 6) as a fully dissociated $B(C_6F_5)_4^-$ salt, as observed by ^1H and ^{19}F NMR spectroscopy. The NMR data for $\mathbf{8b}^+$ support an overall C_1-symmetric structure and the effective coordination of THF to the Al center. In addition, the presence of a deshielded broad resonance ($\delta = 11.40$ ppm), is assigned to the N*H*Me_2^+ proton and is consistent with the proposed structure. An intramolecular acid–base reaction results in the generation of $\mathbf{8b}^+$, promoted by the addition of THF, in which the Al–*H*O*i*Pr proton is transferred to the NMe_2 moiety of the aminophenolate to afford $\mathbf{8b}^+$. The ability of the *N*Me_2 nitrogen to be protonated indicates that the η^2-aminophenolate-Al chelate may not be kinetically stable.

In a comparable approach, the reaction of *i*PrOH with the cationic Al–THF adducts $\mathbf{4a,b}^+$, yields the immediate and quantitative formation of $\mathbf{8a,b}^+$, respectively (Scheme 7). Similarly, [**4a**][$MeB(C_6F_5)_3$][21] was found to



Scheme 7.

react with one equivalent of PhOH (CD_2Cl_2, RT, 10 min) to afford the corresponding ammonium Al–OPh species $\mathbf{9a}^+$ (Scheme 7) as a fully dissociated $[MeB(C_6F_5)_3]^-$ salt, whose molecular structure was determined by X-ray crystallography and confirmed the proposed structure for $\mathbf{9a}^+$ and other analogues.

As illustrated in Figure 4, cation $\mathbf{9a}^+$ is a tetrahedral Al–methyl complex, incorporating a η^1-bonded *N*Me_2-protonated aminophenolate ligand. An interesting structural feature

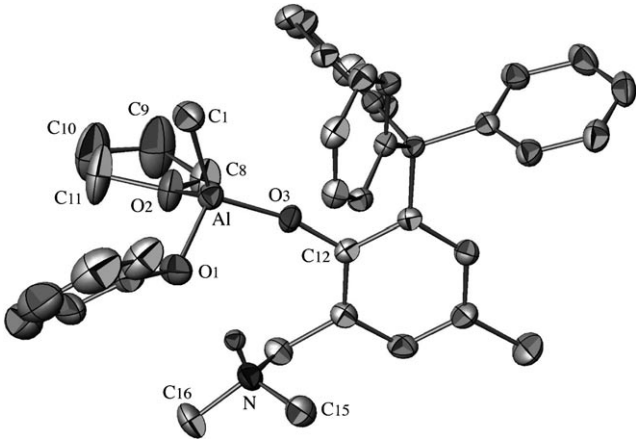
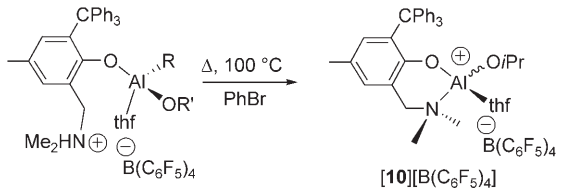


Figure 4. ORTEP view of the Al–OPh–ammonium cation $\mathbf{9a}^+$ with a partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms (except for those on N) are omitted for clarity.

of this complex is the different bonding and geometrical parameters of the two phenolate rings. The unsubstituted phenolate exhibits a Al–O length (Al–O1 = 1.749(3) Å) and an Al-O-C angle (Al-O1-C2 = 130.7(2)°) that are both within the expected range, whereas the Al–O bond length of the CPh_3 phenolate is rather short (Al–O(3) = 1.709(2) Å) and the Al-O-C angle is unusually obtuse (Al-O3-C12 = 167.0(2)°). Similar structural observations for several Al phenoxide derivatives have been previously reported by Barron et al.; thorough structural and theoretical studies by these authors concluded that π-symmetry interactions be-

tween the phenoxide-oxygen lone pairs and the Al center might account for both the short Al–O length and the obtuse Al-O-C angle in such Al–phenolate complexes.[22]

The ammonium Al–alkyl salt species [**8a**][$MeB(C_6F_5)_3$], [**8b**][$B(C_6F_5)_4$], and [**9a**][$MeB(C_6F_5)_3$] are kinetically stable at room temperature but undergo alkane elimination at higher temperature, by an intramolecular protonolysis of the Al–C bond with the N*H*Me_2^+ proton. Complex [**8b**][$B(C_6F_5)_4$] (C_6D_5Br, 80 °C, 16 h) can be cleanly and quantitatively converted to the Al–alkoxide cationic complex [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(O*i*Pr)(thf)]$^+$ (**10**$^+$, Scheme 8) as a fully dissociated $[B(C_6F_5)_4]^-$ salt, along with



Scheme 8.

formation of isobutane, as observed by ^1H and ^{19}F NMR spectroscopy. Similarly, the salts [**8a**][$MeB(C_6F_5)_3$] and [**9a**]-[$MeB(C_6F_5)_3$] afford **10**$^+$ and the corresponding cation, Al–OPh$^+$, however, the presence of minor products precluded full characterization of the obtained species.

The salt [**10**][$B(C_6F_5)_4$] is stable in CH_2Cl_2 at room temperature and could be isolated as a colorless powder in good yield. Its solid-state structure was determined by X-ray crystallography and consists of discrete **10**$^+$ cations and B-$(C_6F_5)_4^-$ anions that do not interact with one another. The molecular structure of **10**$^+$ is illustrated in Figure 5, crystallographic data are summarized in Table 3, and selected bond lengths and angles are given in Table 4. Cation **10**$^+$, which is a low-coordinate mononuclear Al cation bearing a terminal alkoxide group, may be seen as a three-coordinate Al–alkoxide cation complex [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(O*i*Pr)]$^+$ stabilized by THF. The Al center in **10**$^+$ adopts a slightly distorted tetrahedral geometry, similar to that of related monomeric aminophenolate-Al complexes previously characterized (e.g., **1b** and **6**$^+$), with a N-Al-O bite angle (O)-Al-N2 = 102.0(1)°) slightly larger than those of **1b** and **6**$^+$ (93.98(8) and 97.5(3)°, respectively). The Al–O2 and Al–N2 bond lengths of the Al–aminophenolate chelate (1.710(2) and 1.928(3) Å, respectively) are significantly shorter than the corresponding bond length in **1b** (1.764(2) and 2.023(2) Å, respectively), which is due to the stronger ionic character of these bonds. The Al–N bond length of **10**$^+$ (1.928(3) Å), lying below the normal range for Al–N dative bonds (1.957(3)-2.238(4) Å),[16] is dramatically shorter than **1b** (ca. 0.1 Å) and is a clear indication of the highly Lewis acidic nature of the Al center in **10**$^+$. The Al–O*i*Pr bond length (Al–O1 = 1.657(3) Å) compares to those of terminal alkoxides in the Al–alkoxide trimer [$Al(OiPr)_2(acac)]_3$ (1.662(10) Å).[23]

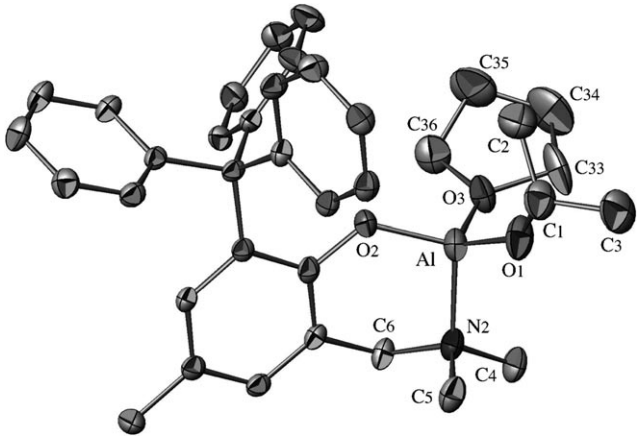


Figure 5. ORTEP view of the Al–alkoxide cation **10**$^+$ with a partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.

Reactivity of cationic aminophenolate alkyl and alkoxide cations with ε-caprolactone and lactides: The reactivity of the obtained alkyl- and alkoxide-Al cations toward ε-caprolactone and lactides was investigated, in order to probe their potential as initiators of the ROP of cyclic esters. These reactivity studies also allowed a comparison of the Al–alkyl relative to Al–alkoxide moieties as initiating groups in these cationic Al systems.

Reactivity of the Al–alkyl cations with ε-caprolactone (ε-CL) and (D,L)-lactide: The synthesized aminophenolate Al–alkyls do not initiate the ROP of either ε-CL or (D,L)-lactide under the conditions studied (45 °C in CH_2Cl_2 or 100 °C in PhBr), but do form robust Lewis acid/base adducts with these two cyclic esters. This indicates the quite polar Al–R$^+$ bond does not readily ring-open cyclic esters.

The reaction of [**3**][$B(C_6F_5)_4$] with one equivalent of ε-caprolactone (C_6D_5Br, RT, 10 min) quantitatively yields the corresponding Al(ε-CL) cationic adduct [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)(ε-CL)]$^+$ (**11b**$^+$) as a fully dissociated $[B(C_6F_5)_4]^-$ salt, as observed by ^1H NMR spectroscopy. The related Al–methyl cation **11a**$^+$ could also be generated by reaction of **1a** with $B(C_6F_5)_3$ in the presence of one equivalent of ε-CL (CD_2Cl_2, RT, 10 min). Both [**11a**][MeB-$(C_6F_5)_3$] and [**11b**][$B(C_6F_5)_4$] salts were isolated as colorless solids. Cations **11a**$^+$ and **11b**$^+$ maintain a C_1-symmetric structure in CD_2Cl_2 solution, between room temperature and 40 °C. This is in agreement with an effective coordination of ε-CL to the Al cationic center, as observed by ^1H and ^{13}C NMR spectroscopy. In the presence of excess ε-CL, these cations undergo a rapid face ε-CL exchange at room temperature on the NMR timescale, as deduced from NMR data, but do not further react upon heating.

Similarly, the Al–methyl cationic (D,L)-lactide adduct [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(Me)(D,L)-lact)]$^+$ (**12a**$^+$) (lact = lactide), is readily obtained when **1a** is reacted with $B(C_6F_5)_3$ in the presence of one equivalent of (D,L)-lactide.

Table 3. Summary of crystallographic data for [**10**][$B(C_6F_5)_4$], [**11a**][$MeB(C_6F_5)_3$], and [**13**][$B(C_6F_5)_4$].

	[**10**][$B(C_6F_5)_4$]	[**11a**][$MeB(C_6F_5)_3$]	[**13**][$B(C_6F_5)_4$]
formula	$C_{66}H_{41}AlBClF_{20}NO_3$	$C_{55}H_{44}AlBF_{15}NO_3$	$C_{68.5}H_{56}AlBF_{20}NO_7$
M_r	1349.24	1089.70	1422.93
crystal system	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a [Å]	12.5680(6)	13.3680(2)	10.324(5)
b [Å]	16.6050(12)	17.3380(3)	15.603(5)
c [Å]	16.7160(9)	22.1830(4)	41.687(5)
α [°]	101.884(4)	90.00	90.000
β [°]	109.263(5)	106.3890(8)	90.000
γ [°]	101.973(2)	90.00	90.000
V [Å^3]	3076.1(3)	4932.54(14)	6715(4)
Z	2	4	4
ρ_{calcd} [g cm^{-3}]	1.457	1.467	1.407
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.185	0.145	0.139
F[000]	1366	2232	2912
data collection			
T [K]	173(2)	173(2)	173(2)
θ range [°]	1.31–29.05	1.59–30.04	1.39–27.50
h,k,l indices	−17/15, −22/22, 0/22	−18/18, −24/21, −31/31	−8/13, −20/12, −54/43
total reflns	16321	14417	15086
unique reflns/$R_{[int]}$	7302/0.0000	7696/0.0536	8005/0.0842
observed data	$>2\sigma(I)$	$>2\sigma(I)$	$>2\sigma(I)$
refinement			Flack × 0.3(4)
reflections/parameters	16321/815	14417/674	15086/881
R_1/R_2	0.0808/0.1738	0.0935/0.2199	0.0904/0.1737
wR_1/wR_2	0.1932/0.2268	0.2141/0.2597	0.2041/0.2423
GoF indicator	1.092	1.098	1.041
min/max residual density [e Å^{-3}]	−0.903/1.226	−1.200/1.212	−0.333/0.857

Table 4. Selected bond lengths [Å] and angles [°] for the Al cations **10**$^+$, **11a**$^+$ and **13**$^+$.

10$^+$			
Al–O1	1.657(3)	O2-Al-N2	102.05(12)
Al–O2	1.710(2)	O1-Al-O3	109.48(15)
Al–O3	1.829(3)	O2-Al-O3	102.07(12)
Al–N2	1.928(3)	O1-Al-N2	107.06(15)
11a$^+$			
Al–O1	1.719(2)	O1-Al-N	99.88(13)
Al–O2a	1.828(3)	O1-Al-C1	126.10(16)
Al–C1	1.919(5)	O1-Al-O2a	105.43(13)
Al–N	1.935(3)	O2a-Al-N	115.69(15)
13$^+$			
Al–O1	1.724(4)	O1-Al-N	94.26(19)
Al–O3	1.743(4)	O1-Al-O3	137.8(2)
Al–O4	1.862(4)	O1-Al-O4	105.4(2)
Al–O2	2.018(4)	O3-Al-O4	119.9(2)
Al–N	2.047(5)	O2-Al-O3	83.14(18)
		O4-Al-O2	88.73(18)

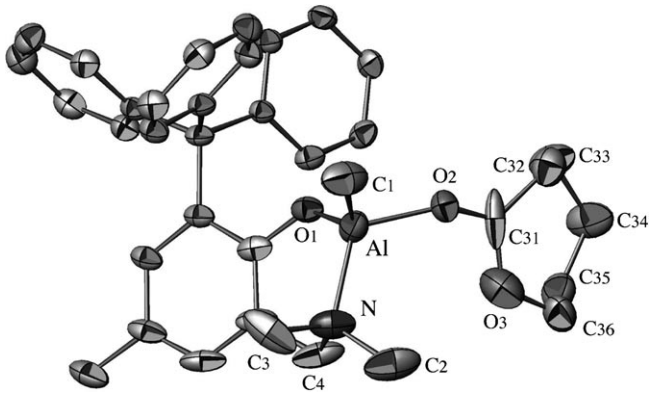


Figure 6. ORTEP view of the Al-(ε-CL) cationic adduct **11a**$^+$ with a partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.

In contrast, an intractable mixture of products is obtained from the reaction between the Al–*i*Bu$^+$ cation **3**$^+$ and one equivalent of (D,L)-lactide.

The molecular structure of the Al(ε-CL) cationic adduct **11a**$^+$ was confirmed by X-ray crystallographic analysis of [**11a**][$MeB(C_6F_5)_3$], which crystallizes as discrete **11a**$^+$ cations and [$MeB(C_6F_5)_3$]$^-$ anions. The molecular structure of cation **11a**$^+$ illustrated in Figure 6, is the first structurally characterized cationic Al(ε-CL) complex. In addition, this cation is of particular interest as it may mimic the Al(ε-CL) alkoxide cationic adduct [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(O*i*Pr)(ε-CL)]$^+$, a likely coordination adduct formed prior to the ROP of ε-CL by [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(O*i*Pr)(thf)]$^+$ (**10**$^+$, see later). It consists of a four-coordinate η^2-aminophenolate-Al cation of the type [{LX}Al(Me)(L)]$^+$, incorporating a η^1-coordinated ε-CL to the Al metal center. The overall bonding and geometrical features are similar to those of the related four-coordinate Al cations **6**$^+$ and **10**$^+$. The Al–$O_{\varepsilon\text{-CL}}$ bond length in **11a**$^+$ (1.828(3) Å) is shorter than that of the only structurally characterized Al(ε-CL) neutral analogue (1.876(3) Å), reflecting the stronger Lewis acid character of the Al center in **11a**$^+$.[24]

ROP of ε-CL by cation 10$^+$: The Al–alkoxide cation **10**$^+$ is highly active in the polymerization of ε-CL in CH_2Cl_2, as shown by the results in Table 5. With an initial Al/ε-CL ratio of 120, the polymerization proceeds rapidly, along with a great increase in the viscosity of the solution, and appears to be completed after 10 min at 40 °C and after 1 h at room temperature. The reaction was quenched after 3 min at 40 °C and 46% conversion to poly(ε-CL) was observed. The size-exclusion chromatography (SEC) data of the polyesters obtained exhibit a monomodal weight distribution, with polydispersities ranging from 1.28 to 1.53. The molecular

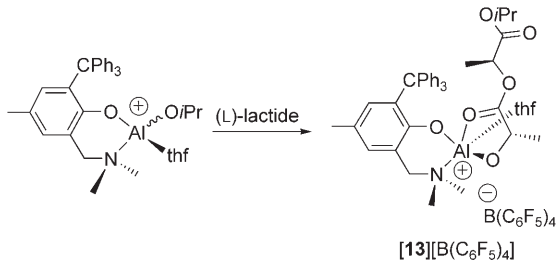
Table 5. Polymerization of ε-CL initiated by [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(O*i*Pr)(thf)][$B(C_6F_5)_4$] ([**10**][$B(C_6F_5)_4$]).[a]

Run	Time	T [°C]	Yield[b]	M_n(obsd)[c]	PDI	M_n(calcd)
1	1 h	RT	99%	14157	1.53	13698
2	15 min	45	99%	15330	1.38	13698
3	3 min	45	46%	4808	1.28	6164

[a] Polymerization conditions: CH_2Cl_2 (4 mL), ε-CL/Al = 120, [ε-CL]$_0$ = 1 M. [b] Isolated yield. [30] [c] Measured by SEC at 25 °C in THF relative to polystyrene standards with Mark–Houwink corrections for M_n [M_n(obsd) = 0.56 M_n(SEC)].

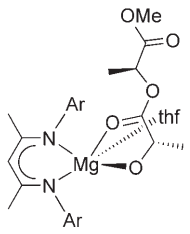
weights (M_n) are in accordance with the calculated values for one polymer chain per metal center (Table 5). In addition, the ^{1}H NMR spectrum of the poly(ε-caprolactic) oligomer, derived from the reaction of cation **10**$^+$ with 25 equivalents of ε-CL, exhibits characteristic resonances that are consistent with the presence of one O*i*Pr ester end group per CH_2OH hydroxy chain end, as deduced from comparison with reported NMR data.[25] No signals are observed in the aromatic region. These data confirm that the terminal alkoxide O*i*Pr group is the only initiating moiety involved in the polymerization process. Overall, these preliminary data agree with a fairly well controlled polymerization process. The activity of cation **10**$^+$ in the ROP of ε-CL is comparable to that of the most effective neutral Al–alkoxide complexes in this area.[26]

Reactivity of cation 10$^+$ with lactides: Cation **10**$^+$ does not polymerize either (D,L)-lactide or L-lactide (100 equiv) at up to 100 °C in PhBr. To gain insight into the origin of the dramatic reactivity difference of **10**$^+$ toward lactides relative to ε-CL, control experiments were carried out by reacting a stoichiometric amount of the Al cation **10**$^+$ with L-lactide. The salt [**10**][$B(C_6F_5)_4$] reacts quickly with one equivalent of L-lactide (CD_2Cl_2, RT, 10 min) to quantitatively yield a five-coordinate Al–lactate cation [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(η^2-L-lactate-O*i*Pr)(thf)]$^+$ (**13**$^+$, Scheme 9) as a



[**13**][$B(C_6F_5)_4$]

Scheme 9.



B

dissociated [$B(C_6F_5)_4$]$^-$ salt, as monitored by ^{1}H and ^{19}F NMR spectroscopy.

The formation of cation **13**$^+$ results from a ring-opening insertion of L-lactide into the Al–O*i*Pr$^+$ bond of **10**$^+$ and, as such, constitutes direct evidence of the high reactivity of this class of cations toward cyclic esters by insertion into an Al–terminal-alkoxide moiety. The salt [**13**][$B(C_6F_5)_4$] is stable for days in PhBr at room temperature and does not further react with excess L-lactide (100 equiv) at 100 °C in PhBr. The NMR spectra of this dissociated salt are essentially unchanged between −60 °C and room temperature in CD_2Cl_2 and are in accordance with an overall C_1-symmetric structure for **13**$^+$, as well as with an effective coordination of THF to the Al–metal center. The ^{1}H NMR spectrum of **13**$^+$ displays four characteristic doublet resonances assigned to the two O*i*Pr-methyl groups and the two O–C(H)(*Me*) lactate moieties, whereas two resonances are observed for the Hα protons of the coordinated THF. These data are not conclusive as to the chelation of the Al center by a carbonyl group of the lactate arm, whereas the IR spectrum for **13**$^+$ is more informative as it contains two strong $\nu_{C=O}$ bands of similar intensity at 1779 and 1685 cm^{-1}, corresponding to the noncoordinated carbonyl and the chelating carbonyl groups of the lactate arm, respectively. These data are consistent with **13**$^+$ being a robust five-coordinate Al–lactate cation in solution at RT.

The molecular structure of **13**$^+$ was determined by X-ray crystallography, confirming the insertion of L-lactide into the Al–O*i*Pr bond of **10**$^+$. The salt species [**13**][$B(C_6F_5)_4$] crystallizes as discrete **13**$^+$ and [$B(C_6F_5)_4$]$^-$ ions, and the molecular structure of **13**$^+$ is illustrated in Figure 7. Cation **13**$^+$ is a chiral five-coordinate Al cation coordinated by an η^2-aminophenolate ligand, a η^2-lactate ligand, and one THF molecule. As illustrated in Figure 7, the Al center in **13**$^+$ adopts a slightly distorted trigonal-bipyramidal structure, with the chelating carbonyl of the lactate arm and the NMe_2 moiety occupying the axial positions (N-Al-O2 = 173.7(2)°). In accordance with its geometry, the Al atom lies approxi-

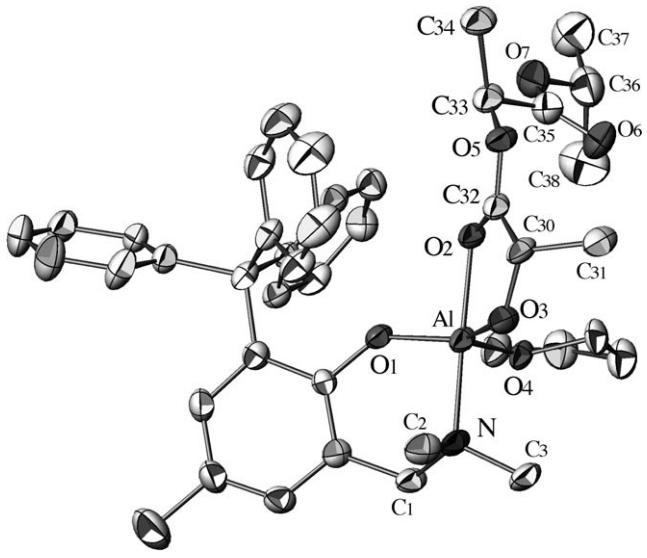


Figure 7. ORTEP view of the Al–lactate chelate cation **13**$^+$ with a partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.

mately in the plane defined by O1, O3, and O4, as deduced from the sum of the corresponding O-Al-O angles (359°). The five-membered ring η^2-lactate-Al unit is rather normal, with the Al–alkoxide bond length (Al–O3 = 1.743(4) Å) comparable to that of **10**$^+$, while the axial Al–O_{ester} bond length (Al–O2 = 2.018 Å) is significantly shorter than analogous Al–O lengths in the neutral lactate Al dimer [Me_2Al-(μ-OCH(Me)CO_2Et)]$_2$, which also incorporates a η^2-lactate arm chelating each Al center.[27] Due to its axial position, the Al–N bond length (2.047(5) Å) is significantly longer than those of other cationic Al analogues. Overall, the strong electron-deficient character of the metal center is most likely the determining factor for the exceptional stability and robustness of the lactate chelate **13**$^+$.

Although the effective chelation by the lactate arm both electronically and sterically stabilizes **13**$^+$, one would still expect the coordinated THF in **13**$^+$ to be readily replaced by an incoming L-lactide under polymerization conditions. If an incoming lactide displaces THF and coordinates to the Al center in **13**$^+$ under these conditions, it clearly does not ring-open. As a comparison, control experiments established that cation **13**$^+$ polymerizes the more reactive and less sterically demanding ε-CL (100 equiv), albeit with an activity lower than that of **10**$^+$ (75% conversion to poly(ε-CL) after 1 h at 40 °C in CD_2Cl_2), as monitored by ^{1}H NMR spectroscopy. The lower activity of **13**$^+$ relative to **10**$^+$ in ε-CL polymerization is certainly due to the lactate chelation in the former cation.

Notably, that cation **13**$^+$ is structurally very similar to the five-coordinate magnesium–lactate complex **B**, which, on the basis of theoretical calculations, has been postulated to be an initial intermediate in the highly effective ROP of (D,L)-lactide by the β-diketiminate–magnesium complex [{HC(CMeN-2,6-*i*PrC_6H_3)$_2$}Mg(OMe)(thf)].[28] The analogous overall coordination environment of the metal center in [{LX}Mg(OMe)(thf)] relative to [{LX}Al(OR)(thf)]$^+$ may rationalize the structural similarity of **B** and **13**$^+$. Thus, the structurally characterized **13**$^+$ may be seen as a close mimic of the initial intermediate in the ROP of lactides by [{LX}M(OR)(L)] metal-complex initiators.

Conclusion

Well-defined and low-coordinate Al-alkoxide cations of the type {LX}Al(OR)(L)$^+$, may be accessible by an alcoholysis reaction between the corresponding cationic Al-alkyls and an appropriate ROH. Structural and reactivity studies of the Al–O*i*Pr derivative **10**$^+$ demonstrate that such species may be highly Lewis acidic, while still retaining a quite reactive Al–OR moiety susceptible to insertion reactions, as illustrated in the case of cyclic esters. Cation **10**$^+$ is highly active in the ROP of ε-CL, whereas in lactide polymerization, **10**$^+$ is inactive and forms a robust monoinsertion product **13**$^+$, which may closely mimic the initial intermediate in the ROP of lactides by [{LX}M(OR)(L)] metal complexes. The stability of **13**$^+$, which can be ascribed to the strong Lewis acidity of the Al metal center, may rationalize the lack of activity of **10**$^+$ in lactide polymerization. In addition, the significant steric bulk around the metal center provided by the ancillary ligand and the lactate chelate may also play a determining role.

The stepwise synthetic route described here to access [{LX}Al(OR)(L)]$^+$ species provides insight into the type of reactivity that low-coordinate Al–alkyls might exhibit with protic substrates. This route allowed the characterization of key intermediates, some of which are unprecedented, at every step of the synthesis. Although the presence of protic sources are typically thought to be detrimental for the formation and/or reactivity studies of highly reactive low-coordinate Al species, due to decomposition reactions and uncontrollable chemistry, the results obtained here show that well-defined and controlled derivatization chemistry may be performed in this area. The use of various protic sources may allow access to new families of low-coordinate Al cations and extend the scope of applications of such potent Lewis acids.

Experimental Section

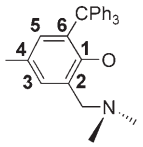
General Procedures: All experiments were carried out under N_2 byusing standard Schlenk techniques or in a Mbraun Unilab glovebox. Toluene, pentane, and diethyl ether were distilled from Na/benzophenone and stored over activated molecular sieves (4 Å) in a glovebox prior to use. CH_2Cl_2, CD_2Cl_2, C_6D_6, C_6H_5Br and C_6D_5Br, were distilled from CaH_2, degassed under a N_2 flow, and stored over activated molecular sieves (4 Å) in a glovebox prior to use. The Al–diisobutyl derivative [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)$_2$] (**1b**) was prepared by following a literature procedure.[11] $B(C_6F_5)_3$ was purchased from Strem and extracted with dry pentane prior to use. [Ph_3C][$B(C_6F_5)_4$] was purchased from Asahi Glass Europe and all deuterated solvents were obtained from Eurisotop (CEA, Saclay, France). All other chemicals were purchased from Aldrich and were used as received, except NMe_2Ph, which was stored over activated molecular sieves (4 Å) prior to use. NMR spectra were recorded by using Bruker AC 300 or 400 MHz NMR spectrometers, in Teflon-valved J-Young NMR tubes at ambient temperature, unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. ^{11}B and ^{19}F chemical shifts are reported relative to BF_3·Et_2O in CD_2Cl_2 and neat $CFCl_3$, respectively. Elemental analyses were performed by Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany). SEC analysis were performed at the Institut Charles Sadron (Strasbourg, France) by using a system equipped with a Shimadzu RID10 A refractometer detector using dry THF (on CaH_2) as an eluant. Molecular weights and polydispersity indices (PDIs) were calculated by using polystyrene standards.

The salts species were obtained as weakly interacting Al cations and [$MeB(C_6F_5)_3$]$^-$ or [$B(C_6F_5)_4$]$^-$ salts in solution. NMR data for the [$MeB(C_6F_5)_3$]$^-$ and [$B(C_6F_5)_4$]$^-$ anions are listed below for all of the compounds.

Data for [$MeB(C_6F_5)_3$]$^-$: ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 0.48$ ppm (B*Me*); ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): $\delta = -11.9$ ppm (br s, *B*Me); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): $\delta = 136.7$ (d, $^1J_{CF} = 233$ Hz, *m*-C_6F_5), 137.9 (d, $^1J_{CF} = 238$ Hz, *p*-C_6F_5), 148.6 ppm (d, $^1J_{CF} = 233$ Hz, *o*-C_6F_5); ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -133.5$ (d, $^3J_{FF} = 19$ Hz, 2F; *o*-C_6F_5), −165.7 (t, $^3J_{FF} = 20$ Hz, 1F; *p*-C_6F_5), −168.2 ppm (m, $^3J_{FF} = 19$ Hz, 2F; *m*-C_6F_5).

Data for [$B(C_6F_5)_4$]$^-$: ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): $\delta = 140.6$ (d, $^1J_{CF} = 241$ Hz, *m*-C_6F_5), 139.1 (d, $^1J_{CF} = 239$ Hz, *p*-C_6F_5), 150.3 ppm (d,

$^1J_{CF}=243$ Hz, *o*-C_6F_5); ^{19}F NMR (376 MHz, C_6D_5Br): $\delta=-165.9$ (m, $^3J_{FF}=19$ Hz, 2F; *m*-C_6F_5), −162.1 (t, $^3J_{FF}=20$ Hz, 1F; *p*-C_6F_5), −131.8 ppm (d, $^3J_{FF}=18$ Hz, 2F; *o*-C_6F_5).



The combination of ^{13}C NMR , DEPT, and HMQC NMR data allowed the assignment of most resonances for all compounds. In the case of the phenolate ring, the carbon and protons signals were assigned according to the labeling scheme shown below.

[{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}$AlMe_2$] (1a): In a glove box, a pentane suspension (5 mL) of 6-(CH_2NMe_2)-2-Ph-C_6H_3OH (1.00 g, 2.43 mmol) precooled at −40 °C was slowly added by using a pipette to a 10-mL vial containing a pentane solution (5 mL) of $AlMe_3$ (177 mg, 2.43 mmol), also precooled at −40 °C. After addition, the resulting colorless mixture was allowed to warm to RT in a loosely capped vial to allow methane to escape, and was stirred for 18 h. The obtained suspension was then filtered through glass frit to afford pure **2** as a analytically pure, colorless solid (975 mg, 92 %). ^{1}H NMR (400 MHz, C_6D_6): $\delta=-0.88$ (s, 6H; Al*Me*$_2$), 1.50 (s, 6H; N*Me*$_2$), 2.17 (s, 3H; *Me*Ph), 3.04 (s, 2H; PhCH_2), 6.43 (d, $^4J=2$ Hz, 1H; O-*Ph*), 7.01 (m, 3H; C*Ph*$_3$), 7.11 (t, $^3J=7.0$ Hz, 6H; C*Ph*$_3$), 7.40 (d, $^4J=2$ Hz, 1H; O-*Ph*), 7.52 ppm (m, 6H; Ph); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta=-11.6$ (Al*Me*$_2$), 21.0 (*Me*Ph), 43.7 (N*Me*$_2$), 62.5 (PhCH_2), 64.1 (*C*Ph$_3$), 120.7 (Ph), 124.5 (Ph), 125.5 (Ph), 127.2 (Ph), 129.2 (Ph), 131.7 (Ph), 132.5 (Ph), 137.2 (Ph), 147.1 (Ph), 156.0 ppm (O-C_{ipso}-Ph); elemental analysis calcd (%) for $C_{31}H_{34}AlNO$: C 80.31, H 7.39; found: C 79.71, H 7.54.

[{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)(Cl)] (2)

NMR-scale reaction: In a glovebox, the diisobutyl complex **1b** (33 mg, 0.060 mmol) was dissolved in CD_2Cl_2 (0.75 mL) and the solution charged in a J-Young NMR tube. The addition of $B(C_6F_5)_3$ (0.05 equiv, 1.5 mg, 0.003 mmol) provoked an immediate vigorous bubbling. The NMR sample was quickly capped and ^{1}H and ^{19}F NMR spectra were immediately recorded showing the quantitative formation of the chloro Al complex [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)(Cl)], along with isobutene and CH_2DCl. The ^{19}F NMR spectrum exhibits resonances for B-(C_6F_5)$_3$ only, which is consistent with this borane acting as a catalyst.

Preparative-scale reaction: Complex **1b** (200.0 mg, 0.365 mmol) and B-(C_6F_5)$_3$ (0.05 equiv, 9.3 mg, 0.0365 mmol) were charged in a 10-mL vial sample. Addition of 3 mL of CH_2Cl_2 resulted in a vigorous bubbling for a few seconds. The resulting pale yellow solution was left stirring at RT for 2 h, after which it was evaporated to dryness in vacuo. Trituration of the colorless foamy residue with cold pentane caused the precipitation of a colorless solid which, after filtration and further drying under vacuum, was shown to be analytically pure **2** (151 mg, 84 %). ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=-0.33$ (dd, $^2J=14.1$ Hz, $^3J=7.3$ Hz, 1H; CH_2-*i*Bu), −0.31 (dd, $^2J=14.1$ Hz, $^3J=6.8$ Hz, 1H; CH_2-*i*Bu), 0.65 (d, $^3J=6.4$ Hz, 3H; CH_3-*i*Bu), 0.74 (d, $^3J=6.2$ Hz, 3H; CH_3-*i*Bu), 1.53 (septet, $^3J_{HH}=6.7$ Hz, 1H; C*H*-*i*Bu), 2.16 (s, 3H; *Me*-Ph or N*Me*), 2.46 (s, 3H; *Me*-Ph or N*Me*), 3.39 (d, $^2J=14.1$ Hz, 1H; Ph-CH_2), 4.23 (d, $^2J_{HH}=14.1$ Hz, 1H; Ph-CH_2), 6.74 (brs, 1H; O-*Ph*), 7.01 (brs, 1H; O-*Ph*), 7.21–7.10 ppm (m, 15H; CPh_3); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta=18.1$ (br, *C*H_2-*i*Bu), 20.9 (*Me*Ph), 25.6 (*C*H-*i*Bu), 27.7 (*C*H_3-*i*Bu), 28.2 (*C*H_3-*i*Bu), 42.5 (N*Me*$_2$), 44.9 (N*Me*$_2$), 62.2 (PhCH_2), 64.0 (*C*Ph$_3$), 120.4 (Ph), 125.6 (Ph), 126.0 (Ph), 127.4 (Ph), 129.1 (Ph), 131.6 (Ph), 132.7 (Ph), 137.6 (Ph), 146.7 (Ph), 154.3 ppm (O-C_{ipso}); elemental analysis calcd (%) for $C_{33}H_{37}AlClNO$: C 75.34, H 7.09; found : C 75.78, H 7.24.

Data for isobutene: ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=1.72$ (s, 6H), 4.65 ppm (s, 2H).

Data for CHD_2Cl: ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=2.92$ ppm (quintuplet, $^2J_{HD}=2.0$ Hz, 2H).

[{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)(PhBr)][$B(C_6F_5)_4$] ([3][B-(C_6F_5)$_4$])

NMR-scale reaction: In a glovebox, equimolars amount of the diisobutyl complex **1b** (30.0 mg, 0.055 mmol) and [Ph_3C][$B(C_6F_5)_4$] (50.5 mg, 0.055 mmol) were charged in a J-Young NMR tube. The addition of C_6D_5Br (0.75 mL) yielded the formation of a bright-red solution that became bright-yellow within a few seconds. ^{1}H and ^{19}F NMR spectra were immediately recorded, showing the quantitative formation of the Al cation **3**$^+$ as a $B(C_6F_5)_4^-$ salt, along with poly(isobutene) and 1 equiv of Ph_3CH.

Preparative-scale reaction: In a glovebox, equimolar amounts of complex **1b** (150.0 mg, 0.274 mmol) and [Ph_3C][$B(C_6F_5)_4$] (252.4 mg, 0.274 mmol) were charged in a small Schlenk tube. Bromobenzene (2 mL) was then added, yielding a bright-red solution that became bright-yellow within 10–15 s. This solution was evaporated to afford a sticky orange oil that was washed several times with cold pentane (−25 °C) to yield a yellow powder. The mixture was filtered through glass frit and the solid residue washed twice with toluene to afford, after drying in vacuo, pure [**3**][B-(C_6F_5)$_4$] ([**3**][$B(C_6F_5)_4$], 283 mg, 78 % yield). ^{1}H NMR (400 MHz, C_6D_5Br): $\delta=-0.04$ (d, $^3J=7.3$ Hz, 2H; CH_2-*i*Bu), 0.58 (d, $^3J=6.5$ Hz, 6H; CH_3-*i*Bu), 1.20 (septet, $^3J=6.5$ Hz, 1H; C*H*-*i*Bu), 2.02 (s, 3H; *Me*-Ph), 2.09 (s, 3H; N*Me*$_2$), 3.05 (s, 2H; Ph-CH_2), 6.42 (d, $^4J=1.7$ Hz, 1H; O-*Ph*), 6.92–7.20 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*); ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): $\delta=16.8$ (*C*H_2-*i*Bu), 20.6 (*Me*Ph), 24.3 (*C*H-*i*Bu), 27.0 (*C*H_3-*i*Bu), 43.8 (N*Me*$_2$), 62.7 (PhCH_2), 62.9 (*C*Ph$_3$), 118.4 (*C2*, PhO), 126.3 (*p-Ph*, CPh_3), 127.5 (*m-Ph*, CPh_3), 129.3 (*C3*, PhO), 130.1 (*C4*, *Ph*O), 130.7 (*o-Ph*, C*Ph*$_3$), 133.7 (*C5*, *Ph*O), 137.2 (*C6*, *Ph*O), 145.4 (C_{ipso}, C*Ph*$_3$), 150.9 ppm (*C1-Ph*O); elemental analysis calcd (%) for $C_{63}H_{42}AlBF_{20}NOBr$: C 57.04, H 3.19; found: C 57.52, H 3.26.

[({6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al*i*Bu)$_2$][($B(C_6F_5)_4$)$_2$] ([3′][($B(C_6F_5)_4$)$_2$]): In a glovebox, the salt species [**3**][$B(C_6F_5)_4$] (100.0 mg, 0.076 mmol) was charged in a crystallization tube and C_6H_5Br (1 mL) was added to yield an orange solution. The tube was taken out of the glovebox, flame-sealed under reduced pressure, and left on a lab. bench at RT for 30 days. During this time, a significant amount of a crystalline material formed. The mixture was then filtered under vacuum through a glass frit and the solid residue washed several time with cold bromobenzene and pentane. The obtained yellow solid was finally dried in vacuo to afford dication **3′**$^{++}$ as a $B(C_6F_5)_4^-$ salt (41 mg, 46 %). The very low solubility of [**3′**][($B(C_6F_5)_4$)$_2$] in bromobenzene as well as in common solvents precluded the obtainment of ^{13}C NMR data for this complex. ^{1}H NMR (300 MHz, C_6D_5Br): $\delta=-1.55$ (dd, $^2J=13.8$ Hz, $^3J=7.0$ Hz, 2H; C*H*H′-*i*Bu), −1.06 (dd, $^2J=13.9$ Hz, $^3J=6.8$ Hz, 1H; CH*H*′-*i*Bu), 0.92 (d, $^3J=6.1$ Hz, 3H; CH_3-*i*Bu), 0.98 (d, $^3J=6.2$ Hz, 3H; CH_3-*i*Bu), 1.72 (septet, $^3J=6.1$ Hz, 1H; C*H*-*i*Bu), 1.91 (s, 3H; *Me*-Ph or N*Me*), 2.20 (s, 3H; *Me*-Ph or N*Me*), 2.39 (s, 3H; *Me*-Ph or N*Me*), 3.42 (d, $^2J=14.0$ Hz, 1H; Ph-C*H*H′), 4.18 (d, $^2J=13.6$ Hz, 1H; Ph-CH*H*′), 6.51 (br.s, 1H; O-*Ph*), 6.93–7.32 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*); elemental analysis calcd (%) for $C_{114}H_{74}Al_2B_2F_{40}N_2O_2$: C 58.53, H 3.19; found: C 58.61, H 3.27.

[{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(Me)(thf)][$MeB(C_6F_5)_3$] ([4a]-[$MeB(C_6F_5)_3$]): In a glovebox, equimolar amounts of the Al–dimethyl complex **1a** (23.2 mg, 0.05 mmol) and THF (4 μL, 0.05 mmol) were dissolved in CD_2Cl_2 (0.75 mL). The resulting colorless solution was transferred into a J-Young NMR tube and a stoichiometric amount of $B(C_6F_5)_3$ was added by a spatula. The NMR tube was vigorously shaken and a ^{1}H NMR spectrum was immediately recorded, showing the quantitative formation of the corresponding Al−THF cationic adduct **4a**$^+$ as a [MeB-(C_6F_5)$_3$]$^-$ salt. The reaction mixture was then charged into a small Schlenk flask and the volatiles removed under reduced pressure to yield a colorless foam, which was used as is (47.6 mg, 91 % yield). ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta=-0.92$ (Al*Me*), 0.48 (*Me*B), 1.94 (br, 4H; THF), 2.20 (s, 3H; *Me*Ph), 2.41 (brs, 6H; N*Me*$_2$), 3.72 (br, 2H; PhCH_2), 3.81 (br, 4H; THF), 6.87 (d, $^4J=2.0$ Hz, 1H; O-*Ph*), 7.23–6.88 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): $\delta=-17.8$ (Al*Me*), 20.5 (Ph*Me*), 25.5 (THF), 44.0 (brs, N*Me*$_2$), 62.9 (PhCH_2), 63.1 (*C*Ph$_3$), 71.3 (THF), 119.0 (*C*$_2$-PhO), 125.5 (*p-Ph*, CPh_3), 126.9 (*m-Ph*, CPh_3), 128.8 (*C3*-PhO), 129.4 (*C4*-PhO), 130.5 (*o-Ph*, CPh_3), 133.2 (*C5*-PhO), 136.8 (*C6*-PhO), 145.5 (C_{ipso}, CPh_3), 151.6 ppm (*C1*-PhO). This compound could not be isolated due to its oily nature and mass spectrometric analysis was unsuccessful due to the high air and moisture sensitivity of such compounds.

[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(*i*Bu)(thf)][B(C$_6$F$_5$)$_4$] ([4b][B(C$_6$F$_5$)$_4$]): In a glovebox, equimolar amounts of complex **1b** (30.0 mg, 0.055 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (50.5 mg, 0.055 mmol) were charged in a J-Young NMR tube and C$_6$D$_5$Br (0.75 mL) was added to yield the quantitative formation of the salt compound [**3**][B(C$_6$F$_5$)$_4$]. THF (0.055 mol) was then added through a microsyringe to the yellow solution of [**3**][B(C$_6$F$_5$)$_4$]. The NMR tube was vigorously shaken and a ^{1}H NMR spectrum was immediately recorded showing the quantitative formation of the corresponding Al–THF adduct **4b$^+$** as a [B(C$_6$F$_5$)$_4$]$^-$ salt. ^{1}H NMR (400 MHz, C$_6$D$_5$Br): $\delta = -0.24$ (dd, $^2J = 13.8$ Hz, $^3J = 6.9$ Hz, 1H; AlC*H*H′), −0.14 (dd, $^2J = 13.5$ Hz, $^3J = 6.5$ Hz, 1H; AlC*H*H′), 0.65 (d, $^3J = 6.5$ Hz, 3H; C*H*$_3$-*i*Bu), 0.71 (d, $^3J = 6.5$ Hz, 3H; C*H*$_3$-*i*Bu), 1.35 (septet, $^3J = 6.7$ Hz, 1H; C*H*-*i*Bu), 1.57 (br, 4H; THF), 2.01 (s, 3H; *Me*-Ph or N*Me*), 2.11 (s, 3H; *Me*-Ph or N*Me*), 2.16 (s, 3H; *Me*-Ph or N*Me*), 3.15 (d, $^2J = 14.0$ Hz, 1H; Ph-C*H*H′), 3.41 (d, $^2J = 14.1$ Hz, 1H; Ph-CH*H*′), 3.61 (br, 2H; THF), 3.73 (br, 2H; THF), 6.58 (d, $^4J = 1.5$ Hz, 1H; O-*Ph*), 7.03–7.16 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*); ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_5$Br): $\delta = 15.2$ (br, *C*H$_2$-*i*Bu), 21.0 (*Me*Ph), 25.0 (*C*H-*i*Bu), 26.0 (THF), 27.7 (*C*H$_3$-*i*Bu), 27.8 (*C*H$_3$-*t*Bu), 43.9 (N*Me*$_2$), 44.1 (N*Me*$_2$), 62.4 (Ph*C*H$_2$), 64.4 (*C*Ph$_3$), 69.5 (THF), 119.2 (*C2*, PhO), 125.5 (*p-Ph*, CPh$_3$), 126.9 (*C3*, PhO), 128.0 (*m-Ph*, CPh$_3$), 130.6 (*C4*, *Ph*O), 131.4 (*o-Ph*, C*Ph*$_3$), 133.3 (*C5*, *Ph*O), 137.8 (*C6*, *Ph*O), 145.1 (*C$_{ipso}$*, C*Ph*$_3$), 152.2 ppm (*C1-Ph*O). This compound could not be isolated due to its oily nature and mass spectrometric analysis was unsuccessful due to the high air and moisture sensitivity of such compounds.

[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(C$_6$H$_{13}$)][B(C$_6$F$_5$)$_4$] ([5][B(C$_6$F$_5$)$_4$]) and [({6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}AlC$_6$H$_{13}$)$_2$][(B(C$_6$F$_5$)$_4$)$_2$] ([5′][(B(C$_6$F$_5$)$_4$)$_2$]): In a glovebox, the salt species [**3**][B(C$_6$F$_5$)$_4$] (100 mg, 0.076 mmol) was charged in a J-Young NMR tube, dissolved in C$_6$D$_5$Br (0.75 mL), and 1-hexene (9.5 μL, 0.076 mmol) was added through a microsyringe. The NMR tube was vigorously shaken and a ^{1}H NMR spectrum was immediately recorded, showing the conversion of **3$^+$** into the Al–hexyl cation **5$^+$** along with the formation of poly(isobutene). After NMR analysis, the orange solution of [**5**][B(C$_6$F$_5$)$_4$] was concentrated under vacuum to approximately 0.4 mL and transferred into a crystallization tube, which was flame-sealed under reduced pressure and left on a lab bench at RT for 18 days. Over this period of time, a significant amount of a crystalline material formed. The mixture was then filtered under vacuum through a glass frit and the solid residue washed several times with cold bromobenzene and pentane. The obtained yellow solid was finally dried in vacuo to afford dication **5′$^{++}$** as a B(C$_6$F$_5$)$_4^-$ salt in a pure form (74.6 mg, 41%). The very low solubility of [**5′**][(B(C$_6$F$_5$)$_4$)$_2$] in bromobenzene as well as in common solvents precluded the obtainment of ^{13}C NMR data for this complex.

Data for **5$^+$**: ^{1}H NMR (300 MHz, C$_6$D$_5$Br): $\delta = -0.24$ (t, $^3J = 7.9$ Hz, 2H; Al-C*H*$_2$), 0.75 (m, 2H; C*H*$_2$-hexyl), 1.02–1.10 (m, 6H; C*H*$_2$-hexyl), 1.19 (t, $^3J = 7.3$ Hz, 3H; CH$_3$-hexyl), 2.03 (s, 3H; *Me*-Ph), 2.08 (s, 6H; N*Me*$_2$), 3.11 (s, 2H; Ph-C*H*$_2$), 6.48 (d, $^4J = 1.3$ Hz, 1H; O-*Ph*), 7.08–7.22 (m, 15H; C*Ph*$_3$), 7.25 ppm (d, $^4J = 1.2$ Hz, 1H; O-*Ph*); ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_5$Br): $\delta = 5.5$ (Al-*C*H$_2$), 14.5 (*C*H$_3$-hexyl), 21.0 (*Me*Ph), 22.9 (*C*H$_2$-hexyl), 23.5 (*C*H$_2$-hexyl), 31.6 (*C*H$_2$-hexyl), 34.9 (*C*H$_2$-hexyl), 44.1 (N*Me*$_2$), 63.2 (*C*Ph$_3$), 63.4 (Ph*C*H$_2$), 118.9 (*C2*, PhO), 126.6 (*p-Ph*, CPh$_3$), 127.9 (*m-Ph*, CPh$_3$), 129.5 (*C3*, PhO), 130.4 (*C4*, *Ph*O), 131.1 (*o-Ph*, C*Ph*$_3$), 134.1 (*C5*, *Ph*O), 137.5 (*C6*, *Ph*O), 145.9 (*C$_{ipso}$*, C*Ph*$_3$), 152.3 ppm (*C1-Ph*O).

Data for **5′$^{++}$**: ^{1}H NMR (300 MHz, C$_6$D$_5$Br): $\delta = -1.76$ (dd, $^2J = 13.5$ Hz, $^3J = 7.5$ Hz, 1H; Al-C*H*H′), −1.27 (dd, $^2J = 13.2$ Hz, $^3J = 7.1$ Hz, 1H; Al-CH*H*′), 0.57 (m, 2H; C*H*$_2$-hexyl), 0.82–1.14 (m, 6H; C*H*$_2$-hexyl), 1.33 (t, $^3J = 7.3$ Hz, 2H; CH$_3$-hexyl), 1.93 (s, 3H; *Me*-Ph or N*Me*), 2.05 (s, 3H; *Me*-Ph or N*Me*), 2.29 (s, 3H; *Me*-Ph or N*Me*), 3.43 (d, $^2J = 13.7$ Hz, 1H; Ph-C*H*H′), 4.26 (d, $^2J = 13.6$ Hz, 1H; Ph-CH*H*′), 6.42 (brs, 1H; O-*Ph*), 6.81–7.08 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*); elemental analysis calcd (%) for C$_{118}$H$_{82}$Al$_2$B$_2$F$_{40}$N$_2$O$_2$: C 59.16, H 3.45; found: C 59.77, H 3.63.

[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(*i*Bu)(*i*PrOH)][B(C$_6$F$_5$)$_4$] ([6][B(C$_6$F$_5$)$_4$]): In a glovebox, equimolar amounts of the Al complex **1b** (100.0 mg, 0.184 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (168.4 mg, 0.184 mmol) were charged in a small Schlenk flask and C$_6$H$_5$Br (2 mL) was added to yield a bright yellow solution within a few seconds. An amount of *i*PrOH (14 μL, 0.184 mmol) was then added through a microsyringe, and the reaction mixture was stirred at RT for 1 h, and then evaporated under reduced pressure to yield a sticky orange oil. Trituration of this residue with cold pentane provoked the precipitation of a colorless solid. Subsequent filtration through a glass frit and drying in vacuo of the obtained solid afforded the salt species [**6**][B(C$_6$F$_5$)$_4$] as an analytically pure colorless solid (192.3 mg, 85%). ^{1}H NMR (400 MHz, C$_6$D$_5$Br): $\delta = -0.30$ (dd, $^2J = 14.8$ Hz, $^3J = 6.4$ Hz, 1H; AlC*H*H′), −0.14 (dd, $^2J = 15.2$ Hz, $^3J = 8.0$ Hz, 1H; AlC*H*H′), 0.55 (d, $^3J = 6.3$ Hz, 6H; C*H*$_3$-*i*Bu), 0.84 (t, $^3J = 5.6$ Hz, 6H; C*H*$_3$-*i*PrOH), 1.43 (septet, $^3J = 6.7$ Hz, 1H; C*H*-*i*Bu),), 1.56 (s, 3H; N*Me*), 1.93 (s, 3H; *Me*-Ph), 1.97 (s, 3H; N*Me*), 2.69 (d, $^3J = 7.4$ Hz, 1H; *i*Pr-O*H*), 2.81 (d, $^2J = 14.2$ Hz, 1H; Ph-C*H*H′), 3.67 (d, $^2J = 14.2$ Hz, 1H; Ph-CH*H*′), 3.73 (m, $^3J = 6.8$ Hz, 1H; C*H*-*i*PrO*H*), 6.50 (brs, 1H; O-*Ph*), 6.92–7.04 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*); ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_5$Br): $\delta = 15.3$ (br, Al-*C*H$_2$), 20.6 (*Me*Ph), 22.5 (*C*H$_3$-*i*PrOH), 22.6 (*C*H$_3$-*i*PrOH), 24.9 (*C*H-*i*Bu), 27.0 (*C*H$_3$-*i*Bu), 27.3 (*C*H$_3$-*i*Bu), 42.5 (N*Me*$_2$), 45.7 (N*Me*$_2$), 62.2 (Ph*C*H$_2$), 62.9 (*C*Ph$_3$), 79.3 (*C*H-*i*PrOH), 119.1 (*C2*, PhO), 126.1 (*p-Ph*, CPh$_3$), 126.7 (*C3*, PhO), 127.4 (*m-Ph*, CPh$_3$), 130.0 (*C4*, *Ph*O), 131.1 (*o-Ph*, C*Ph*$_3$), 133.7 (*C5*, *Ph*O), 136.4 (*C6*, *Ph*O), 146.3 (*C$_{ipso}$*, C*Ph*$_3$), 151.7 ppm (*C1-Ph*O); elemental analysis calcd (%) for C$_{60}$H$_{45}$AlBF$_{20}$NO$_2$: C 58.60, H 3.69; found: C 58.15, H 3.42.

[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(*i*Bu)(O*i*Pr)] (7): In a glovebox, the salt complex [**8**][B(C$_6$F$_5$)$_4$] (56.6 mg, 0.046 mmol) was charged in a J-Young NMR tube, dissolved in C$_6$D$_5$Br (0.75 mL), and NMe$_2$Ph (5.8 μL, 0.046 mmol) was added through a microsyringe. The NMR tube was capped and vigorously shaken and the cloudy C$_6$D$_5$Br solution was immediately analyzed by ^{1}H NMR. This NMR analysis revealed that the quantitative conversion of [**8**][B(C$_6$F$_5$)$_4$] into the neutral Al–O*i*Pr complex **7** had occurred along with the generation of 1 equiv. of [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$].

Data for **7**: ^{1}H NMR (400 MHz, C$_6$D$_5$Br): $\delta = -0.42$ (dd, $^2J = 14.5$ Hz, $^3J = 6.4$ Hz, 1H; AlC*H*H′), −0.33 (dd, $^2J = 14.1$ Hz, $^3J = 6.5$ Hz, 1H; AlC*H*H′), 0.66 (d, $^3J = 6.3$ Hz, 3H; C*H*$_3$-*i*Bu), 0.86 (d, $^3J = 6.4$ Hz, 3H; C*H*$_3$-*i*Bu), 0.97 (m, 6H; C*H*$_3$-OiPr), 1.46 (septet, $^3J = 6.9$ Hz, 1H; C*H*-*i*Bu), 1.86 (s, 3H; N*Me*), 2.06 (s, 3H; *Me*-Ph), 2.15 (s, 3H; N*Me*), 2.83 (d, $^2J = 13.9$ Hz, 1H; Ph-C*H*H′), 3.78 (d, $^2J = 13.8$ Hz, 1H; Ph-CH*H*′), 3.76 (s, $^3J = 6.6$ Hz, 1H; C*H*-OiPr), 6.51 (brs, 1H; O-*Ph*), 6.97–7.22 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*).

[η^1-{6-(CH$_2$NHMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(R)(O*i*Pr)(thf)][A] ([8a][MeB(C$_6$F$_5$)$_3$], R = Me; [8b][B(C$_6$F$_5$)$_4$], R = *i*Bu): In a glovebox, *i*PrOH (13.2 μL, 0.173 mmol) was added through a microsyringe to a CH_2Cl_2 solution (2 mL) of the desired salt compound [**4a**][MeB(C$_6$F$_5$)$_3$] or [**4b**][B(C$_6$F$_5$)$_4$] (0.173 mmol). The resulting colorless solution was stirred at RT for 30 min, after which it was evaporated to yield a colorless foam. Trituration of this residue with cold pentane, followed by filtration of the reaction mixture through a glass frit, afforded pure [**8a**][MeB(C$_6$F$_5$)$_3$] (149.5 mg, 78%) or [**8b**][B(C$_6$F$_5$)$_4$] (160 mg, 71%) as colorless solids.

Data for **8a$^+$**: ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = -1.56$ (s, 3H; Al*Me*), 1.11 (d, $^3J = 6.1$ Hz, 3H; C*H*$_3$-*i*Pr), 1.15 (d, $^3J = 6.1$ Hz, 3H; C*H*$_3$-*i*Pr), 1.91 (br, 4H; THF), 2.17 (s, 3H; *Me*-Ph), 2.63 (s, 3H; N*Me*$_2$), 2.78 (s, 3H; N*Me*$_2$), 3.21 (d, $^2J = 13.2$ Hz, 1H; Ph-C*H*H′), 3.42 (br, 2H; THF), 3.62 (br, 2H; THF), 3.94 (s, $^3J = 6.0$ Hz, 1H; C*H*-*i*Pr), 4.03 (d, $^2J = 13.0$ Hz, 1H; Ph-CH*H*′), 6.96 (s, 1H; *Ph*-O), 7.15–7.47 (m, 16H; C*Ph*$_3$ and O-*Ph*), 11.80 ppm (br, 1H; N*H*Me$_2$); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): $\delta = -17.2$ (Al*Me*), 19.9 (*Me*Ph), 24.9 (br, THF), 26.5 (*C*H$_3$-*i*Pr), 26.6 (*C*H$_3$-*i*Pr), 42.9 (N*Me*$_2$), 44.2 (N*Me*$_2$), 59.1 (Ph*C*H$_2$), 62.8 (*C*Ph$_3$), 63.5 (*C*H-*i*Pr), 73.1 (br, THF), 117.7 (*C2*, PhO), 125.7 (*p-Ph*, CPh$_3$), 127.2 (*m-Ph*, CPh$_3$), 127.6 (*C$_{ipso}$*, C*Ph*$_3$), 127.8 (*C4*, *Ph*O), 128.0 (*C3*, *Ph*O), 130.3 (*o-Ph*, C*Ph*$_3$), 132.7 (*C5*, *Ph*O), 137.7 (*C6*, *Ph*O), 153.2 ppm (*C1-Ph*O); elemental analysis calcd (%) for [**8a**][MeB(C$_6$F$_5$)$_3$], C$_{56}$H$_{50}$AlBF$_{15}$NO$_3$: C 60.72, H 4.55; found: C 61.13, H 3.81.

Data for **8b$^+$**: ^{1}H NMR (400 MHz, C$_6$D$_5$Br): $\delta = -0.93$ (brd, $^3J = 6.5$ Hz, 2H; AlC*H*$_2$), 0.65 (d, $^3J = 6.3$ Hz, 3H; C*H*$_3$-*i*Bu), 0.71 (d, $^3J = 6.3$ Hz, 3H; C*H*$_3$-*i*Bu), 0.82 (d, $^3J = 6.2$ Hz, 3H; C*H*$_3$-*i*Pr), 0.86 (d, $^3J = 6.1$ Hz, 3H; C*H*$_3$-*i*Pr), 1.41 (septet, $^3J = 6.5$ Hz, 1H; C*H*-*i*Bu),), 1.54 (br, 4H; THF), 2.02 (s, 3H; *Me*-Ph), 2.08 (s, 3H; N*Me*), 2.26 (s, 3H; N*Me*), 3.12 (br, 4H; THF), 3.32 (br, 4H; THF), 3.65 (br, 2H; PhC*H*$_2$), 3.74 (s, $^3J = 6.4$ Hz, 1H; C*H*-*i*Pr), 6.62 (d, $^4J = 1.5$ Hz, 1H; O-*Ph*), 7.02–7.15 (m, 16H; C*Ph*$_3$

and O-*Ph*), 11.40 ppm (br, 1H; N*H*Me$_2$); ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): δ = 16.4 (br, Al-*C*H$_2$), 20.8 (*Me*Ph), 25.0 (*C*H$_3$-*i*Pr), 25.1 (*C*H$_3$-*i*Pr), 25.9 (br, THF), 27.3 (*C*H-*i*Bu), 28.1 (*C*H$_3$-*i*Bu), 28.5 (*C*H$_3$-*i*Bu), 40.4 (N*Me*$_2$), 43.2 (N*Me*$_2$), 59.5 (Ph*C*H$_2$), 62.8 (*C*Ph$_3$), 63.8 (*C*H-*i*Pr), 68.3 (br, THF), 118.1 (*C2*, PhO), 126.5 (*p-Ph*, CPh$_3$), 127.3 (*C3*, PhO), 127.9 (*m-Ph*, CPh$_3$), 128.2 (*C4*, *Ph*O), 128.7 (*o-Ph*, C*Ph*$_3$), 133.4 (*C5*, *Ph*O), 138.5 (*C6*, *Ph*O), 146.3 (*C*$_{ipso}$, C*Ph*$_3$), 153.9 ppm(*C1-Ph*O); elemental analysis calcd for [**8b**][B(C$_6$F$_5$)$_4$], $C_{64}H_{53}AlBF_{20}NO_3$: C 59.04, H 4.10; found: C 59.27; H 3.98.

[η^1-{6-(CH$_2$NHMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(Me)(OPh)(thf)][MeB(C$_6$F$_5$)$_3$] ([9a][MeB(C$_6$F$_5$)$_3$]): In a glovebox, PhOH (16.3 mg, 0.173 mmol) was added to a CH_2Cl_2 solution (2 mL) of the Al–THF adduct [**4a**][MeB(C$_6$F$_5$)$_3$] (0.173 mmol). The resulting colorless solution was stirred at RT for 30 min, after which it was evaporated to yield a colorless foam. Trituration of this residue with cold pentane, followed by filtration of the obtained solid through glass frit, afforded [**9a**][MeB(C$_6$F$_5$)$_3$], which was used as is (177.8 mg, 91% yield). ^{1}H NMR (300 MHz, C_6D_5Br): δ = −1.28 (s, 3H; Al*Me*), 1.61 (br, 4H; THF), 2.17 (s, 3H; *Me*-Ph), 2.22 (s, 3H; N*Me*), 2.31 (s, 3H; N*Me*), 3.18 (br, 4H; THF), 3.39 (br, 4H; THF), 3.51 (br, 2H; PhC*H*$_2$), 6.76–7.02 (m, 4H), 7.23–7.39 (m, 18H), 9.42 ppm (br, 1H; N*H*Me$_2$); ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): δ = −15.3 (br, Al-*C*H$_2$), 20.7 (*Me*Ph), 25.4 (br, THF), 41.1 (N*Me*$_2$), 42.9 (N*Me*$_2$), 60.1 (Ph*C*H$_2$), 63.5 (*C*Ph$_3$), 67.6 (br, THF), 118.1, 119.6, 126.1, 127.9, 128.5, 128.9, 129.7, 130.2, 133.6, 138.5, 146.3, 147.8, 151.4, 153.9.

[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(O*i*Pr)(thf)][B(C$_6$F$_5$)$_4$] ([10][B(C$_6$F$_5$)$_4$])

NMR-scale reaction: Equimolar amounts of the Al complex **1b** (30.0 mg, 0.055 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (50.5 mg, 0.055 mmol) were charged in a J-Young NMR tube and C_6H_5Br (0.75 mL) was added to yield a bright-yellow solution within a few seconds. Some *i*PrOH (14 μL, 0.184 mmol) and THF (14.9 μL, 0.184 mmol) were then added through a microsyringe. The NMR tube was immersed in an oil bath and heated at 90 °C for 24 h. The sample was then analyzed by ^{1}H NMR spectroscopy showing the quantitative formation of the Al–O*i*Pr cation **10**$^+$ as a $B(C_6F_5)_4^-$ salt ([**12**][B(C$_6$F$_5$)$_4$]), along with isobutane.

Preparative-scale reaction: In a glovebox, equimolar amounts of the Al complex **1b** (100.0 mg, 0.184 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (168.4 mg, 0.184 mmol) were charged in a small Schlenk flask and C_6H_5Br (2 mL) was added to yield a bright-yellow solution within a few seconds. Some *i*PrOH (14 μL, 0.184 mmol) and THF (14.9 μL, 0.184 mmol) were then added through a microsyringe. The reaction mixture was immersed in an oil bath and heated at 90 °C for 24 h, after which it was allowed to cool to RT and evaporated under reduced pressure to yield a sticky orange oil. Trituration of this residue with cold pentane provoked the precipitation of a colorless solid. Subsequent filtration through a glass frit and drying in vacuo of the obtained solid afforded the salt species [**10**][B(C$_6$F$_5$)$_4$] as an analytically pure colorless solid (190 mg, 83%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 0.81 (d, ^3J = 6.1 Hz, 3H; C*H*$_3$-*i*Pr), 0.85 (d, ^3J = 6.1 Hz, 3H; C*H*$_3$-*i*Pr), 2.01 (br, 4H; THF), 2.20 (s, 3H; *Me*-Ph), 2.59 (s, 3H; N*Me*), 2.62 (s, 3H; N*Me*), 3.61 (br, 4H; THF), 3.67 (d, ^2J = 14.6 Hz, 1H; Ph-C*H*H′), 3.73 (m, ^3J = 6.8 Hz, 1H; C*H*-*i*PrO*H*), 3.82 (septet, ^3J = 6.1 Hz, 1H; C*H*-*i*Pr), 3.88 (d, ^2J = 14.7 Hz, 1H; Ph-C*H*H′), 6.87 (brs, ^4J = 1.5 Hz, 1H; O-*Ph*), 7.09–7.27 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*); ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): δ = 20.7 (*Me*Ph), 24.8 (*C*H$_3$-*i*Pr), 25.1 (*C*H$_3$-*i*Pr), 25.2 (br, THF), 42.8 (N*Me*$_2$), 44.3 (N*Me*$_2$), 62.7 (Ph*C*H$_2$), 62.9 (*C*Ph$_3$), 64.8 (*C*H-*i*Pr), 119.4 (*C2*, PhO), 126.0 (*C3*, PhO), 127.4 (*p-Ph*, CPh$_3$), 128.3 (*m-Ph*, CPh$_3$), 130.0 (*C4*, *Ph*O), 130.9 (*o-Ph*, C*Ph*$_3$), 133.5 (*C5*, *Ph*O), 136.8 (*C6*, *Ph*O), 146.0 (*C*$_{ipso}$, C*Ph*$_3$), 152.3 ppm (*C1-Ph*O); elemental analysis calcd (%) for $C_{60}H_{43}AlBF_{20}NO_3$: C 57.94, H 3.48; found: C 58.35, H 3.36.

[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(Me)(ε-CL)][MeB(C$_6$F$_5$)$_3$] ([11a][MeB(C$_6$F$_5$)$_3$]) and [{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(*i*Bu)(ε-CL)][B(C$_6$F$_5$)$_4$] ([11b][MeB(C$_6$F$_5$)$_3$]): In a glovebox, equimolar amounts of the Al–dialkyl complex **1a** or **1b** (0.05 mmol) and ε-caprolactone (0.05 mmol) were dissolved in CD_2Cl_2 (0.75 mL). The resulting colorless solution was transferred into a J-Young NMR tube and a stoichiometric amount of B(C$_6$F$_5$)$_3$ or [Ph$_3$C][B(C$_6$F$_5$)$_4$] was added by using a spatula. The NMR tube was vigorously shaken and a ^{1}H NMR spectrum was immediately recorded, showing the quantitative formation of the corresponding Al(ε-CL) cationic adduct **11a,b**$^+$ as a [MeB(C$_6$F$_5$)$_3$]$^-$ or a [B(C$_6$F$_5$)$_4$]$^-$ salt. The reaction mixture was then charged into a small Schlenk flask and the volatiles removed under reduced pressure to yield a colorless foam. Trituration of this residue with cold pentane provoked the precipitation of a colorless solid. Subsequent filtration through a glass frit and drying in vacuo of the obtained solid afforded the salt species [**11a,b**][MeB(C$_6$F$_5$)$_3$] as analytically pure colorless solids in 76 and 82% yield, respectively.

Data for ***11a***$^+$: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = −1.09 (s, 3H; AlMe), 1.81 (m, 6H; C*H*$_2$-CL), 2.11 (s, 3H; *Me*-Ph or N*Me*), 2.18 (s, 3H; *Me*-Ph or N*Me*), 2.58 (s, 3H; *Me*-Ph or N*Me*), 2.78 (m, 2H; O=C-C*H*$_2$-CL), 3.51 (d, ^2J = 14.1 Hz, 1H; Ph-C*H*H′), 4.06 (d, ^2J = 14.0 Hz, 1H; Ph-C*H*H′), 4.44 (m, 2H; O-C*H*$_2$-caprolactone), 6.86 (d, ^4J = 1.5 Hz, 1H; O-*Ph*), 7.03 (d, ^4J = 1.5 Hz, 1H; O-*Ph*), 7.12–7.23 ppm (m, 15H; C*Ph*$_3$); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = −18.0 (Al*Me*), 20.1 (*Me*Ph), 21.4 (*C*H$_2$-CL), 26.6 (*C*H$_2$-CL), 27.5 (*C*H$_2$-CL), 34.2 (O=C-*C*H$_2$-CL), 43.2 (N*Me*$_2$), 44.4 (N*Me*$_2$), 62.0 (Ph*C*H$_2$), 62.8 (*C*Ph$_3$), 77.9 (O-*C*H$_2$-caprolactone), 119.6 (*C2*, PhO), 125.4 (*p-Ph*, CPh$_3$), 126.8 (*m-Ph*, CPh$_3$), 127.8 (*C3*, PhO), 129.3 (*C4*, *Ph*O), 130.5 (*o-Ph*, C*Ph*$_3$), 132.8 (*C5*, *Ph*O), 136.2 (*C6*, *Ph*O), 145.8 (*C*$_{ipso}$, C*Ph*$_3$), 152.4 (*C1-Ph*O), 192.0 ppm (*C*=O); elemental analysis calcd (%) for [**11a**][MeB(C$_6$F$_5$)$_3$], $C_{55}H_{44}AlBF_{15}NO_3$: C 60.62, H 4.07; found: C 60.53, H 3.76.

Data for ***11b***$^+$: ^{1}H NMR (400 MHz, C_6D_5Br): δ = −0.30 (dd, ^2J = 13.9 Hz, ^3J = 6.7 Hz, 1H; AlC*H*H′), −0.22 (dd, ^2J = 13.9 Hz, ^3J = 6.8 Hz, 1H; AlC*H*H′), 0.62 (d, ^3J = 6.5 Hz, 3H; C*H*$_3$-*i*Bu), 0.66 (d, ^3J = 6.5 Hz, 3H; C*H*$_3$-*i*Bu), 1.32 (septet, ^3J = 6.7 Hz, 1H; C*H*-*i*Bu), 1.37 (m, 6H; C*H*$_2$-CL), 2.01 (s, 3H; *Me*-Ph or N*Me*), 2.06 (s, 3H; *Me*-Ph or N*Me*), 2.12 (s, 3H; *Me*-Ph or N*Me*), 2.30 (m, 2H; O=C-C*H*$_2$-CL), 3.33 (AB system, ^2J = 14.2 Hz, 1H; Ph-C*H*H′), 3.40 (AB system, ^2J = 14.2 Hz, 1H; Ph-C*H*H′), 4.01 (m, 2H; O-C*H*$_2$-CL), 6.58 (d, ^4J = 1.5 Hz, 1H; O-*Ph*), 7.03–7.16 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*); ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): δ = 15.2 (br, *C*H$_2$-*i*Bu), 21.0 (*Me*Ph), 21.7 (*C*H$_2$-CL), 25.0 (*C*H-*i*Bu), 27.0 (*C*H$_2$-CL), 27.7 (*C*H$_3$-*i*Bu), 27.8 (*C*H$_3$-*i*Bu), 27.9 (*C*H$_2$-CL), 34.6 (O=C-*C*H$_2$-CL), 43.9 (N*Me*$_2$), 44.1 (N*Me*$_2$), 62.4 (Ph*C*H$_2$), 64.4 (*C*Ph$_3$), 78.1 (O-*C*H$_2$-CL), 119.6 (*C2*, PhO), 126.0 (*p-Ph*, CPh$_3$), 126.6 (*C3*, PhO), 128.7 (*m-Ph*, CPh$_3$), 129.9 (*C4*, *Ph*O), 131.0 (*o-Ph*, C*Ph*$_3$), 133.8 (*C5*, *Ph*O), 137.5 (*C6*, *Ph*O), 146.4 (*C*$_{ipso}$, C*Ph*$_3$), 153.0 (*C1-Ph*O), 192.1 ppm (*C*=O); elemental analysis calcd (%) for [**11b**][MeB(C$_6$F$_5$)$_3$], $C_{63}H_{47}AlBF_{20}NO_3$: C 58.94, H 3.69; found: C 58.35, H 3.51.

[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(Me){(D,L)-lactide}][MeB(C$_6$F$_5$)$_3$] ([12][MeB(C$_6$F$_5$)$_3$]): The salt [**12**][MeB(C$_6$F$_5$)$_3$] was generated and isolated by using an identical procedure (and on 0.05 mmol scale) to that for the Al(ε-CL) adduct [**11a**][MeB(C$_6$F$_5$)$_3$] described above, except that the (DL)-lactide was used instead of ε-CL. [**12**][MeB(C$_6$F$_5$)$_3$] was isolated as a colorless solid (35.6 mg, 62%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = −1.05 (s, 3H; AlMe), 1.61 (d, ^3J = 6.7 Hz, 6H; *Me*-lactide), 2.18 (s, 3H; *Me*-Ph), 2.40 (s, 6H; N*Me*$_2$), 3.81 (s, 2H; Ph*C*H$_2$), 5.20 (q, ^3J = 6.8 Hz, 2H; C*H*-lactide), 6.88 (d, ^4J = 1.5 Hz, 1H; O-*Ph*), 7.02 (d, ^4J = 1.5 Hz, 1H; O-*Ph*), 7.10–7.23 ppm (m, 15H; C*Ph*$_3$); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = −18.3 (Al*Me*), 14.8 (*Me*-lactide), 20.1 (*Me*Ph), 43.5 (N*Me*$_2$), 62.2 (Ph*C*H$_2$), 62.8 (*C*Ph$_3$), 75.3 (*C*H-lactide), 119.2 (*C2*, PhO), 125.6 (*p-Ph*, CPh$_3$), 126.8 (*m-Ph*, CPh$_3$), 128.5 (*C3*, PhO), 129.4 (*C4*, *Ph*O), 130.5 (*o-Ph*, C*Ph*$_3$), 133.1 (*C5*, *Ph*O), 136.4 (*C6*, *Ph*O), 145.7 (*C*$_{ipso}$, C*Ph*$_3$), 151.8 (*C1-Ph*O), 183.4 ppm (*C*=O); elemental analysis calcd (%) for $C_{55}H_{42}AlBF_{15}NO_5$: C 59.00, H 3.78; found: C 58.43, H, 3.81.

[{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(η^2-{O-CHMe-C(=O)-O-CHMe-C(=O)-O*i*Pr})(thf)][B(C$_6$F$_5$)$_4$] ([13][B(C$_6$F$_5$)$_4$]): In a glovebox, equimolar amounts of the Al–O*i*Pr salt complex [**10**][B(C$_6$F$_5$)$_4$] (229.0 mg, 0.184 mmol) and L-lactide (26.5 mg, 0.184 mmol) were charged in a small Schlenk flask and C_6H_5Br (2 mL) was added to yield a colorless solution. The reaction mixture was stirred for 15 min at RT, after which it was evaporated under reduced pressure to yield a colorless solid. ^{1}H NMR analysis of this crude solid revealed the quantitative formation of the cationic lactate–Al complex **13**$^+$ as a $[B(C_6F_5)_4]^-$ salt. Trituration of this residue with cold pentane provoked the precipitation of a colorless solid. Subsequent filtration through a glass frit and drying in vacuo of the ob-

tained solid afforded the pure salt species [**13**][$B(C_6F_5)_4$] (155 mg, 61 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 1.11$ (d, $^3J = 6.3$ Hz, 3H; CH_3-*i*Pr), 1.21 (d, $^3J = 6.2$ Hz, 3H; CH_3-*i*Pr), 1.26 (d, $^3J = 6.2$ Hz, 3H; CH_3-lact), 1.42 (d, $^3J = 6.2$ Hz, 3H; CH_3-lact), 1.55 (br, 2H; THF), 1.68 (br, 2H; THF), 1.97 (s, 3H; N*Me*), 2.08 (s, 3H; N*Me*), 2.09 (s, 3H; Ph*Me*), 2.92 (d, $^2J =$ 14.2 Hz, 1H; Ph-C*H*H′), 3.45 (br, 2H; THF), 3.52 (d, $^2J = 14.2$ Hz, 1H; Ph-C*H*H′), 3.61 (br, 2H; THF), 4.18 (q, $^3J = 7.1$ Hz, 1H; C*H*-O-lact), 4.56 (q, $^3J = 7.2$ Hz, 1H; C*H*-O-lact), 4.90 (septet, $^3J = 6.2$ Hz, 1H; C*H*-*i*Pr), 6.87 (d, $^4J = 1.5$ Hz, 1H; O-*Ph*), 7.02–7.12 ppm (m, 16H; C*Ph*$_3$ and O-*Ph*); ^{13}C{^{1}H} NMR (100 MHz, C_6D_5Br): $\delta = 15.9$ (*Me*-lact), 20.4 (*Me*-lact), 20.8 (*Me*Ph), 21.3 (*C*H$_3$-*i*Pr), 21.4 (*C*H$_3$-*i*Pr), 25.5 (br, THF), 44.0 (N*Me*$_2$), 46.1 (N*Me*$_2$), 62.4 (Ph*C*H$_2$), 63.1 (*C*Ph$_3$), 68.3 (*C*H-O-lact), 71.0 (*C*H-*i*Pr), 74.4 (*C*H-O-lact), 74.8 (br, THF), 120.6 (*C2*, PhO), 125.4 (*C3*, PhO), 127.5 (*p-Ph*, CPh$_3$), 129.0 (*m-Ph*, CPh$_3$), 129.8 (*C4*, *Ph*O), 131.0 (*o-Ph*, C*Ph*$_3$), 132.4 (*C5*, *Ph*O), 135.3 (*C6*, *Ph*O), 146.2 (*C*$_{ipso}$, C*Ph*$_3$), 152.4 (*C1-Ph*O), 167.2 (*C*=O), 190.9 ppm (*C*=O); IR (CH_2Cl_2): $\tilde{\nu} = 1779$ (C=O$_{ester}$), 1685 cm^{-1} (C=O$_{chelate}$); elemental analysis calcd (%) for $C_{66}H_{51}AlBF_{20}NO_7$: C 57.12, H 3.70; found: C 56.81, H 3.47.

Polymerization of ε-CL by [10][B(C$_6$F$_5$)$_4$]: In a glove box, the salt species [**10**][$B(C_6F_5)_4$] (41.5 mg, 0.033 mmol) was dissolved in CH_2Cl_2 (4 mL) in a small Schlenk flask. The mixture was taken out of the glovebox and left at RT or immersed in an oil bath at 45 °C. The monomer ε-caprolactone (456.6 mg, 4.0 mmol, 120 equiv) was then added through a syringe to the vigorously stirring solution. The mixture was left at the desired temperature for the appropriate time, after which it was quenched with methanol and a few drops of acetic acid. The resulting colorless suspension was filtered through glass frit and dried in vacuo for several hours to afford poly(ε-CL), which was analyzed by SEC.

X-ray structure determinations: Single crystals of **1b**, [**5′**][$(B(C_6F_5)_4)_2$], [**6**][$B(C_6F_5)_4$], [**9a**][$MeB(C_6F_5)_3$], [**10**][$B(C_6F_5)_4$], [**11a**][$MeB(C_6F_5)_3$] and [**13**][$B(C_6F_5)_4$] were mounted on a Nonius Kappa-CCD area detector diffractometer ($Mo_{K\alpha}$ $\lambda = 0.71073$ Å). The complete conditions of data collection (Denzo software) and structure refinements are given. in Tables 1 and 3. The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in φ angle), each at 20 s exposure. The structures were solved by using direct methods (SHELXS97) and refined against F^2 byusing the SHELXL97 software.[29] The absorption was not corrected. All non-hydrogen atoms were refined anisotropically, excepted in specific cases (see cif files). Hydrogen atoms were generated according to stereochemistry and refined by using a riding model in SHELXL97.

CCDC 607899–607905 contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data request/cif.

Acknowledgements

We thank the French Ministry of Research for financial support through an ACI grant for young researchers (JC4045). We also gratefully thank Dr. A. De Cian (Strasbourg, France) for his help in the X-ray diffraction studies, and Dr. D. Bourissou (Toulouse, France) for helpful discussions.

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Received: July 31, 2006
Published online: January 2, 2007

