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Novel Neutral and Cationic Aluminium Alkyl Complexes Supported by Potentially Tridentate O,N,L-Type Aminophenolate Ligands and Their Use in Propylene Oxide Polymerization

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Potentially tridentate O,N,L-type aminophenol proligands of the type 2-{$CH_2N(C_4H_8L)$}-6-R-C_6H_3OH (**1a**: R = Ph, L = O; **1b**: R = Ph, L = NMe; **1c**: R = *t*Bu, L = O; **1d**: R = *t*Bu, L′ = NMe) and 6-{CH_2L}-2-CPh_3-4-Me-C_6H_2OH (**1e**: R = CPh_3, L = O; **1f**: R = CPh_3, L′ = NMe) readily react with $AlMe_3$ through an alkane elimination reaction to afford the corresponding aminophenolate aluminium dimethyl complexes η^2-*N*,*O*-[2-{$CH_2N(C_4H_8L)$}-6-R-C_6H_3O]$AlMe_2$ (**2a**: R = Ph, L = O; **2b**: R = Ph, L = NMe; **2c**: R = *t*Bu, L = O; **2d**: R = *t*Bu, L′ = NMe) and η^2-*N*,*O*-[6-{$CH_2(C_4H_8L)$}-2-CPh_3-4-Me-C_6H_2O]-$AlMe_2$ (**2e**: R = CPh_3, L = O; **2f**: R = CPh_3, L′ = NMe), respectively, as determined by X-ray crystallography in the case of compounds **2b**–**e**. These neutral Al dimethyl complexes all feature a (η^2-*O*,*N*)Al chelate, whether in solution or in the solid state, and complexes **2a**, **2b**, **2d** and **2f** may be readily ionized by $B(C_6F_5)_3$ to yield Al cations of the type (η^3-*O*,*N*,*L*)$AlMe^+$ (**3a**, **3b**$^+$, **3d**$^+$ and **3f**$^+$) as dissociated $MeB(C_6F_5)_3^-$ salts in solution. The stability of these Al cations appears to be greatly dependent on the steric crowding around the Al centre. Despite ring strain associated with the coordination of the extra L ligand, the solution behaviour of such Al cations are consistent with the effective coordination of the extra L ligand to the Al metal centre under the studied conditions. Some of these cations were found to be highly active in propylene oxide (PO) polymerization under mild conditions to yield atactic PPO with a moderate polydispersity.

Introduction

Cationic group 13 species have attracted much attention over the last 10 to 15 years, as the potent Lewis acidity of these compounds may be of interest for Lewis acid-assisted reactions, such as propylene oxide and isobutene polymerization reactions, as well as for the mediation of chemical transformations that may not be performed by their neutral analogues (alkylation of aromatics, fast *trans*-alkylating reactions).[1] Whereas low-coordinate group 13 cations, including two-and three-coordinate species of the type MR_2^+ and {LX}MR^+ (M = Al, Ga; LX$^-$ = monoanionic bidentate ligand, R = alkyl, aryl), are more reactive than their higher coordinate counterparts, such entities often exhibit a limited stability along with an increased tendency to form aggregates, which significantly hampers their scope of potential applications in catalysis.[2] As a consequence, albeit less reactive, the more stable four-coordinate group 13 alkyl cations of the type {LX}M(R)(L′)$^+$ (M = Al, Ga; R = alkyl; L′ labile), in which the metal centre adopts its preferred tetrahedral geometry, have been by far the most studied among this class of species and may be generated in a straightforward manner through ionization of neutral dialkyl precursors {LX}MR_2 by an R$^-$ abstracting reagent such as $B(C_6F_5)_3$ in the presence of an external Lewis base L′.[1b,3] Thus, over the past few years, numerous {LX}M(R)(L′)$^+$ group 13 cations, typically supported by N,N and N,O-type bidentate ligands, have been reported.[2b,2e,2g,3–5]

Following our studies on group 13 cations supported by N,O-type bidentate aminophenolate ligands,[2g,6] we have become interested in the synthesis and reactivity of cationic aluminium species supported by L_2X-tridentate aminophenolate ligands of type **A** (Scheme 1), as the derived Al cations **B** may well represent a reasonable balance between reactivity and stability.[7] Thus, the extra L donor may stabilize the formed cationic centre through coordination; yet, the latter L ligand may retain a certain lability due to ring strain resulting from an unpreferred "boat-like" conformation for the L-containing six-membered ring upon coordination to the Al centre (**B**, Scheme 1). In addition, tridentate proligands **A** were picked because: (i) they are readily accessible from a synthetic point of view, (ii) their steric properties may easily be tuned by changing the *ortho* substituent of the phenol ring and (iii) ligands bearing various extra L donors may be synthesized from readily available starting materials.

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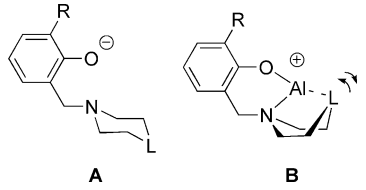


Scheme 1.

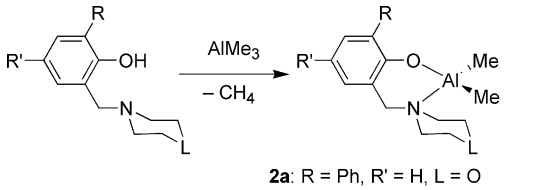
Here we report on the synthesis and structural characterization of neutral and cationic aluminium complexes of L_2X-tridentate aminophenolate ligands of type **A** as well as the reactivity of the generated cations towards polar monomers such as propylene oxide, ε-caprolactone and *rac*-lactide.

Results and Discussion

Synthesis and Structure of Aminophenolate Aluminium Dimethyl Complexes (2a–f)

Proligands **1a**–**f** were synthesized according to a literature one-pot procedure through a Mannich-type aromatic substitution reaction, involving the reaction of *ortho*-substituted phenols 2-R-C_6H_4OH (R = Ph, *t*Bu) or 2-CPh_3-4-MeC_6H_3OH with formaldehyde and the appropriate secondary amine (morpholine or *N*-methylpiperazine).[8] Compounds **1a**–**f** were all isolated in reasonable yields as colourless solids.

The reaction of proligands **1a**–**f** with one equivalent of $AlMe_3$ (CH_2Cl_2, –35 °C to r.t., 2 h) affords the quantitative formation of the corresponding aminophenolate aluminium dimethyl complexes η^2-*N*,*O*-[2-{$CH_2N(C_4H_8L)$}-6-R-C_6H_3O]$AlMe_2$ (**2a**: R = Ph, L = O; **2b**: R = Ph, L = NMe; **2c**: R = *t*Bu, L = O; **2d**: R = *t*Bu, L′ = NMe) and η^2-*N*,*O*-[6-{$CH_2(C_4H_8L)$}-2-CPh_3-4-MeC_6H_2O]$AlMe_2$ (**2e**: R = CPh_3, L = O; **2f**: R = CPh_3, L′ = NMe), respectively, which were all obtained as analytically colourless solids in good yields (Scheme 2). The solid-state molecular structures of complexes **2b**–**e** were determined by X-ray crystallographic analysis and are depicted, along with selected bonding parameters, in Figures 1 and 2 for **2b** and **2c**, respectively, whereas those for **2d** and **2e** are included in the Supporting Information (Figures S1 and S2). Crystallographic data for species **2b** and **2c** are summarized in Table 1 and those for **2d** and **2e** in the Supporting Information (Table S1). Compounds **2b** and **2c** exhibit very similar structural features, and thus, these will only be discussed in the case of **2b**.



2a: R = Ph, R' = H, L = O
2b: R = Ph, R' = H, L = NMe
2c: R = *t*Bu, R' = H, L = O
2d: R = *t*Bu, R' = H, L = NMe
2e: R = CPh_3, R' = Me, L = O
2f: R = CPh_3, R' = Me, L = NMe

Scheme 2.

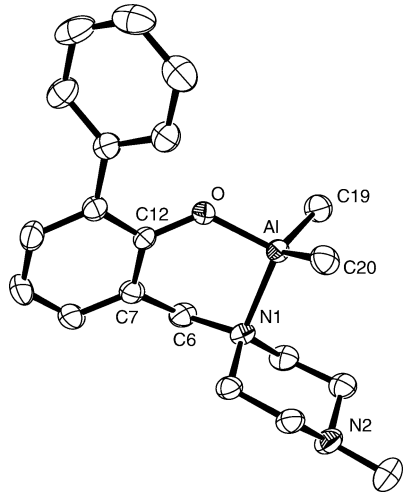


Figure 1. Molecular structure (ORTEP drawing) of complex **2b** with partial atom labelling. The H atoms are not shown for clarity. Selected bond lengths [Å]: Al–O 1.761(1), Al–N1 2.045(1), Al–C19 1.958(2), Al–C20 1.955(2); selected bond angles [°]: O–Al–N1 97.16(6), C20–Al–C19 119.35(8), C20–Al–N1 112.93(7), O–Al–C20 108.70(7); selected torsion angles [°]: C12–O–C7–C6 3.2(2), O–Al–C12–C7 33.6(2), N1–Al–C6–C7 65.65(1).

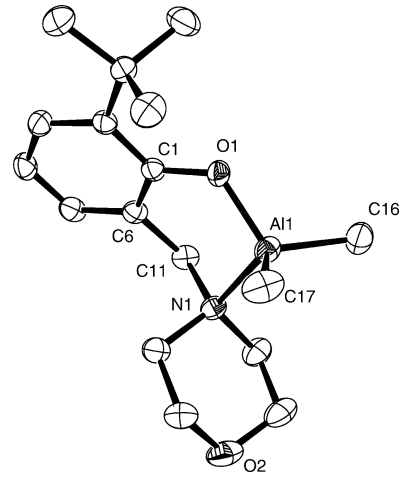


Figure 2. Molecular structure (ORTEP drawing) of complex **2c** with partial atom labelling. The H atoms are not shown for clarity. Selected bond lengths [Å]: Al1–O1 1.761(1), Al1–N1 2.050(1), Al1–C16 1.964(2), Al1–C17 1.954(2); selected bond angles [°]: O1–Al–N1 97.97(5), C17–Al–C16 116.20(8), C16–Al1–N1 107.73(6), C16–Al1–O1 111.47(6), selected torsion angles [°]: O1–C1–C6–C11 0.1(2), C11–C6–N1–Al1 65.9(1), C1–C6–C11–N1 59.2(2).

Complex **2b** crystallizes as a monomer in which the Al centre adopts a slightly distorted tetrahedral geometry and is effectively chelated in a η^2-fashion by the aminophenolate ligand. The bite angle of the η^2-(*O*,*N*)-bonded aminophenolate [O–Al–N1 97.16(6)] results in an opening of the C20–Al–C19 bond angle [119.35(8)], whereas the O–Al–C and N–Al–C bond angles remain close to the ideal tetra-

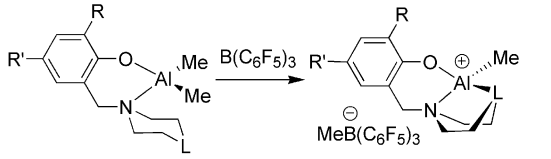
hedral angle (109.49°). The six-membered-ring Al metallacycle is significantly puckered; the Al–N(C_4H_8NMe) moiety is well above the nearly planar C12–O–C7–C6 backbone [3.2(2)°], as shown by the values of the torsion angles O–Al–C12–C7 and N1–Al–C6–C7 [33.6(2) and 65.65(1), respectively]. The Al–O and Al–N1 bond lengths [1.761(1) and 2.045(1) Å, respectively] are in the normal range for aluminium phenolates [1.640(5)–1.773(2) Å] and Al–N dative bonds [1.957(3)–2.238(4) Å], respectively.[9,10]

All X-ray-characterized complexes **2b**–**e** thus feature a η^2-coordinated aminophenolate ligand to Al with no interaction between the metal centre and the extra L-type arm (N or O). As a comparison, related potentially tridentate N,O,N-Schiff base chelating ligands were found to coordinate aluminium in a η^3-fashion, albeit the interaction between the Al metal centre and the nitrogen side arm appears to be substantially weaker than that of classical Al–N dative bonds.[7c] In the case of complexes **2b**–**e**, the absence of interaction between Al and the L-type arm may be rationalized, at least partially, by unfavourable ring strain that would otherwise result upon coordination of the L side arm to the four-coordinate Al metal centre.

The ^{1}H NMR spectroscopic data for Al dimethyl complexes **2a**–**f** are consistent with the chelation of one aminophenolate ligand to the Al centre and, in the case of complexes **2b**–**e**, with their solid-state structure being retained in solution. These data also agree with an effective C_s symmetry on the NMR timescale in C_6D_6 or CD_2Cl_2 at room temperature, which is most likely due to a fast conformation change of the six-membered-ring Al metallacycle under the studied conditions.

Synthesis of Cationic Al Alkyls Derived from Complexes 2a–f

The ionization of Al dimethyl complexes **2a**–**f** was studied with the methide abstracting reagent $B(C_6F_5)_3$. Thus, the reaction of Al complexes **2a** and **2b** with one equivalent of $B(C_6F_5)_3$ yields the quantitative formation of the corresponding four-coordinate Al cations η^3-*N*,*O*,*L*′-{2-[$CH_2N(C_4H_8L')$]-6-Ph-C_6H_3O}AlMe$^+$ (**3a**$^+$: L′ = O; **3b**$^+$: L′ = NMe; Scheme 3) as dissociated $MeB(C_6F_5)_3^-$ salt species in CD_2Cl_2 at room temperature.[11] The salts [**3a**,**b**][$MeB(C_6F_5)_3$], which are stable for days in CD_2Cl_2 solution, could not be isolated in a pure form due to their oily nature. The solution structure of Al cations **3a** and **3b**$^+$ was deduced from ^{1}H and ^{13}C NMR spectroscopic data (CD_2Cl_2, room temperature). These data are consistent with C_1-symmetric structures for both cations **3a** and **3b**$^+$, which is consistent with the effective coordination of the L side arm (N or O) to the Al centre under the studied conditions, and thus resulting, despite ring strain, in the formation of robust four-coordinate (η^3-*N*,*O*,*L*′)Al chelate cations. As an example, the ^{1}H NMR spectrum of salt species [**3b**][$MeB(C_6F_5)_3$] is shown in Figure 3. In an analogous manner, Al dimethyl complexes **2d** and **2f** are readily ionized by one equivalent of $B(C_6F_5)_3$ to afford the corresponding Al cations η^3-*N*,*O*,*N*-(2-{$CH_2N(C_4H_8NMe)$}-6-*t*BuC_6H_3O)AlMe$^+$ (**3d**$^+$) and η^3-*N*,*O*,*N*-(6-{$CH_2N(C_4H_8NMe)$}-2-CPh_3-4-Me-C_6H_3O)AlMe (**3f**$^+$), respectively, as fully dissociated $MeB(C_6F_5)_3^-$ salts, as deduced from NMR spectroscopic data (CD_2Cl_2, room temperature; Scheme 3). These data are also consistent with the effective coordination of the *N*Me side arm onto the Al cationic centre under the studied conditions. However, unlike cations **3a** and **3b**$^+$, cations **3d**$^+$ and **3f**$^+$ are unstable in CD_2Cl_2 at room temperature and slowly decompose into unidentified species over the course of several hours (**3d**$^+$ $t_{1/2}$ = 16 h; **3f**$^+$ $t_{1/2}$ = 12 h). The decreased stability observed when going from **3b**$^+$ to **3d**$^+$ and **3f**$^+$ may be related to the increased steric bulk around the Al metal centre in **3d**$^+$ and **3f**$^+$ vs. **3b**$^+$ as a result of the more encumbering phenolate *ortho* substituents (*t*Bu and CPh_3 vs. Ph). In the present case, this increased steric crowding around Al apparently significantly limits the stability of the resulting cationic Al species.



3a$^+$: R = Ph, R' = H, L = O
3b$^+$: R = Ph, R' = H, L = NMe
3d$^+$: R = *t*Bu, R' = H, L = NMe
3f$^+$: R = CPh_3, R' = Me, L = NMe

Scheme 3.

Whereas the ionization of **2a**, **2b**, **2d** and **2f** with $B(C_6F_5)_3$ affords mononuclear tetracoordinate Al cations, a different outcome is observed in the case of **2c**. Thus, the reaction of complex **2c** with one equivalent of $B(C_6F_5)_3$ yields the quantitative formation of the dinuclear Al cation (2-{$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)AlMe·(2-{$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)AlMe$_2^+$ (**3c**$^+$, Scheme 4) as a dissociated $MeB(C_6F_5)_3^-$ salt species (CD_2Cl_2, room temperature) along with 0.5 equivalents of unreacted $B(C_6F_5)_3$, as deduced from ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data. Salt species [**3c**][$MeB(C_6F_5)_3$] is stable for days in CD_2Cl_2 at room temperature, but its isolation was precluded due to its oily nature. On the basis of NMR spectroscopic data and on the stoichiometry of its formation reaction, cation **3c**$^+$ is best formulated as a dinuclear Al cationic adduct resulting from the coordination of the oxygen ether arm in (2-{$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)AlMe$_2$ to the formally three-coordinate Al cation "(2-{$CH_2N(C_4H_8O)$}-6-*t*Bu-C_6H_3O)AlMe$^+$", as depicted in Scheme 4. In particular, the ^{1}H and ^{13}C NMR spectroscopic data (CD_2Cl_2, room temperature) for cation **3c**$^+$ feature two sets of aminophenolate resonances along with two singlet peaks (in a 2:1 ratio for the ^{1}H NMR spectrum) in the Al*Me* region, which is consistent with the proposed structure for **3c**$^+$. The overall NMR spectroscopic data for dinuclear cation **3c**$^+$ agree with an effective C_s-symmetric structure on the NMR timescale, likely to result from a fast face exchange coordination

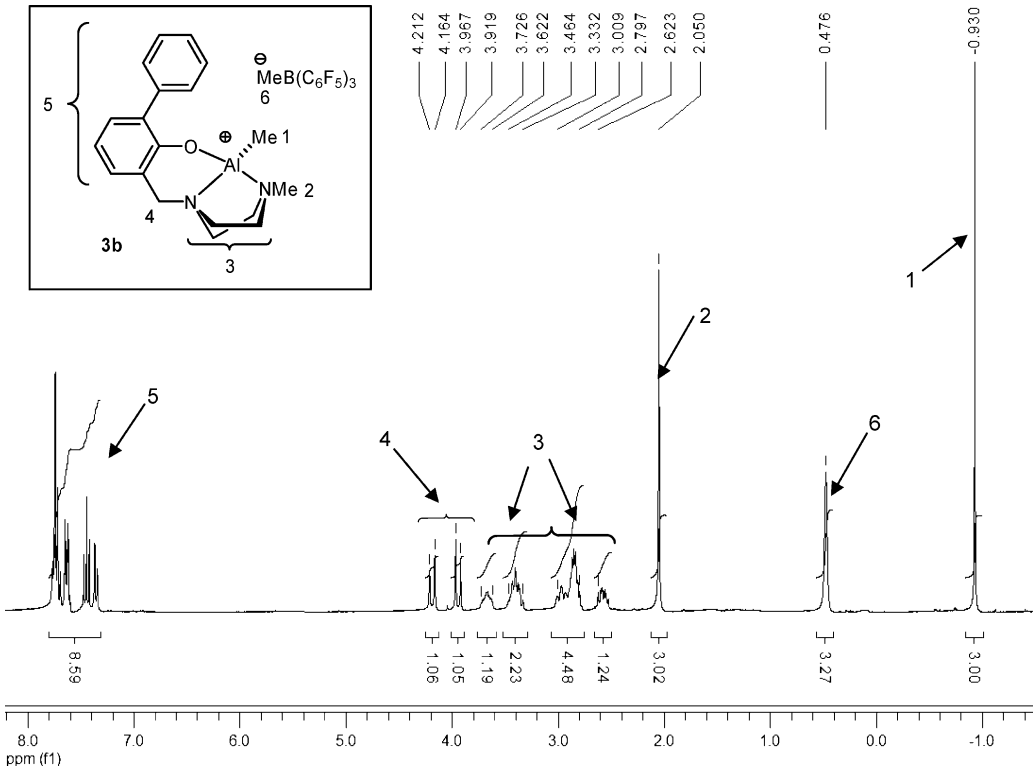
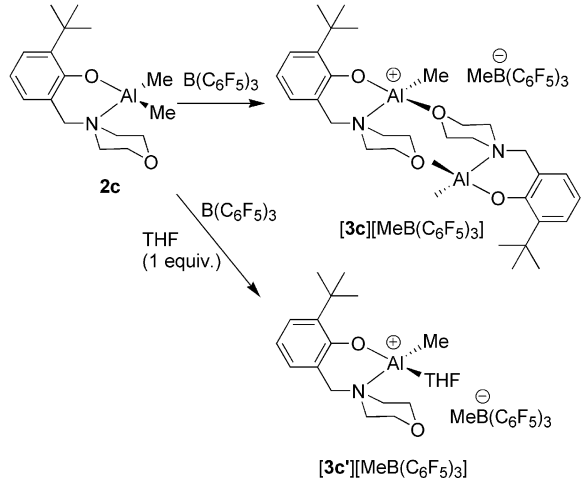


Figure 3. ^{1}H NMR spectrum of the dissociated salt species [**3b**][MeB(C_6F_5)$_3$] at room temperature in CD_2Cl_2.

of the ether oxygen in the ({$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)-$AlMe_2$ moiety to the Al cationic centre. One should also point out that the ^{13}C NMR spectroscopic data for cation **3c**$^+$ rule out its formulation as a cationic adduct in which the two moieties (2-{$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)$AlMe_2$ and (2-{$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)$AlMe^+$ would be linked by a μ-O bridging oxygen phenolate, as, on the basis of literature precedent, significant ^{13}C chemical shift differences for the ^{13}C NMR resonances of a μ-O bridging versus nonbridging phenolate are expected to be observed;[6a] such differences are not observed for cation **3c**$^+$. The adduct nature of cation **3c**$^+$ was further confirmed by its reactivity with a Lewis base such THF. Thus, the NMR-scale reaction of salt species [**3c**][MeB(C_6F_5)$_3$] with one equivalent of THF (CD_2Cl_2, room temperature) affords the quantitative formation of a 1:1 mixture of the Al·THF cationic adduct (2-{$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)$AlMe(THF)^+$ (**3c′**$^+$) and of neutral precursor **2c**, as deduced from ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data. The independent generation of cation **3c′**$^+$ confirmed its identity: thus, the ionization reaction of complex **2c** with B(C_6F_5)$_3$ in the presence of one equivalent of THF (CD_2Cl_2, room temperature) quantitatively yields the corresponding Al·THF adduct **3c′**$^+$ as a dissociated MeB(C_6F_5)$_3^-$ salt species in CD_2Cl_2 solution.

In a similar manner, the Al·THF cationic adduct (6-{$CH_2N(C_4H_8O)$}-2-CPh_3-4-MeC_6H_3O)$AlMe(THF)^+$ (**3e**$^+$) was quantitatively generated as a MeB(C_6F_5)$_3^-$ salt by reaction of complex **2e** with B(C_6F_5)$_3$ in the presence of one equivalent of THF. In contrast, the ionization of compound **2e** in the absence of an external Lewis base was found to afford an intractable mixture of products.



Scheme 4.

Reactivity of Al Alkyl Cations 3a, 3b$^+$, 3c′$^+$ and 3e$^+$ towards Propylene Oxide (PO), ε-Caprolactone (ε-CL) and *rac*-Lactide (*rac*-LA)

The Lewis acidic aminophenolate Al cations **3a**, **3b**$^+$, **3c′**$^+$ and **3e**$^+$ were all found to initiate the polymerization of PO.[12] Thus, all these cations readily polymerize PO to quantitatively afford atactic poly(propylene) oxide (PPO), as deduced from ^{1}H and ^{13}C NMR spectroscopic data [room temperature, 30 min, CH_2Cl_2; 100 equiv. of PO ([PO]$_0$ = 1 M); yield in PPO from 80 to 95% yield; see the Experimental Section]. As estimated from size-exclusion chromatography (SEC) data, all Al cationic systems exhibit

a similar catalytic activity and feature a monomodal low-molecular-weight distribution with a moderate polydispersity (**3a**$^+$: M_n = 2530, M_w/M_n = 1.4; **3b**$^+$: M_n = 3960, M_w/M_n = 1.6; **3c′**$^+$: M_n = 2760, M_w/M_n = 1.7; **3e**$^+$: M_n = 3150, M_w/M_n = 1.5). The ^{1}H NMR spectra of all PPOs only feature resonances corresponding to the polymer backbone and no end-group signal was detected. In addition, the ^{1}H NMR determined molecular weights of the PPOs agree well with those deduced from SEC data. All PPO samples were also analyzed by MALDI-TOF spectrometry for end-group analysis; these data nevertheless revealed inconclusive as to the nature of the end group in the PPO polymers and with regard to the presence of any cyclic PPOs. On the basis of literature precedent, it appears likely that PO polymerization by Al cations **3a**, **3b**$^+$, **3c′**$^+$ and **3e**$^+$ proceeds through a classical Lewis acid assisted cationic mechanism, as observed in related N,O-, P,O- and salen-supported Al cationic systems.[2g,13] Overall, the catalytic activity of **3a**, **3b**$^+$, **3c′**$^+$ and **3e**$^+$ in PO polymerization at room temperature appears to be superior to that of bidentate aminophenolate-supported Al methyl cations and compares to that of (salen)Al(thf)$_2^+$ and (salpen)Al(thf)$_2^+$ Al cations.[2g,13]

In view of recent reports on the ring-opening polymerization (ROP) of cyclic esters initiated by four-coordinate Al alkyl cations,[2g,7e,13b] Lewis acidic Al cations **3a**, **3b**$^+$, **3c′**$^+$ and **3e**$^+$ were tested for their activity in the ROP of ε-CL and *rac*-LA. Thus, whereas none of these cations were found to be active in the ROP of *rac*-LA, these Al cations were all found to polymerize ε-CL (100 equiv. of ε-CL, CH_2Cl_2, 38 °C, 12 h) to quantitatively yield poly(ε-CL) on the basis of ^{1}H and ^{13}C NMR spectroscopic data. Nevertheless, as deduced from SEC data, in all cases, the molecular weight distribution is multimodal along with a relatively large polydispersity (ranging from 1.6 to 2.0), indicating an uncontrolled polymerization process.

Conclusions

Potentially tridentate O,N,L-type aminophenolate chelating ligands of the type described here are suitable for coordination to aluminium and may allow access to stable neutral and cationic Al alkyl species. Whereas neutral Al dimethyl complexes all feature a (η^2-*O*,*N*)Al chelate, whether in solution or in the solid state, these may be readily ionized by $B(C_6F_5)_3$ to yield Al cations of the type (η^3-*O*,*N*,*L*)-AlMe$^+$, whose stability appears to be greatly dependent upon the steric crowding around the Al centre. Despite ring strain associated with the coordination of the extra L ligand, the solution behaviour of such Al cations is consistent with the effective coordination of the extra L ligand to the Al metal centre under the studied conditions. Some of these cations were found to be highly active in PO polymerization under mild conditions to yield atactic PPO with a moderate polydispersity.

Experimental Section

General Procedures: All experiments were carried out under an atmosphere of nitrogen by using standard Schlenk techniques or in an Mbraun Unilab glove box. Toluene, pentane, diethyl ether and tetrahydrofuran were collected after passing through drying columns (SPS apparatus, MBraun) and stored over activated molecular sieves (4 Å) for 24 h in a glove box prior to use. CH_2Cl_2, CD_2Cl_2 and C_6D_6 were distilled from CaH_2, degassed under an atmosphere of nitrogen flow and stored over activated molecular sieves (4 Å) in a glove box prior to use. $B(C_6F_5)_3$ was purchased from Strem Chemicals and used as received. All deuterated solvents were obtained from Eurisotop (CEA, Saclay, France). All other chemicals were purchased from Aldrich and were used as received with the exception of propylene oxide (PO) and ε-caprolactone (ε-CL), which were distilled from CaH_2 prior to use. The cyclic ester *rac*-lactide (*rac*-LA) was purchased from Aldrich and sublimed twice prior to use. NMR spectra were recorded with 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 $BF_3{\cdot}Et_2O$ in CD_2Cl_2 and neat $CFCl_3$, respectively. Elemental analyses for all compounds were performed at the Service de Microanalyse of the Université de Strasbourg (Strasbourg, France). Size-exclusion chromatography (SEC) analyses of PPO samples were carried out at the ESPCI (Paris, France) by using a Waters 150CV instrument (M590 pump, U6K injector) equipped with a R410 refractometer and a Waters capillary viscometer and five Ultrastyragel columns (Waters). The SEC columns were eluted with THF at 40 °C at 1 mL min^{-1}. All the results for PPO are given in real molecular weight averages due to a universal calibration procedure. SEC analysis of poly(ε-CL) was performed at the Institut Charles Sadron (Strasbourg, France) with a system equipped with a Shimadzu RID10A refractometer detector by using dry THF (on CaH_2) as an eluent. Molecular weights and polydispersity indices (PDIs) of poly(ε-CL) samples were calculated by using polystyrene standards. All the salts species were obtained as dissociated Al cations and $MeB(C_6F_5)_3^-$ salts in solution. The NMR spectroscopic data for the $MeB(C_6F_5)_3^-$ anion are listed below for all compounds.

$MeB(C_6F_5)_3^-$: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.48 (B*Me*) ppm. ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ = –11.9 (br. s, *B*Me) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 9.8 (br., B*Me*), 136.7 (d, $^1J_{C,F}$ = 233 Hz, *m*-C_6F_5), 137.9 (d, $^1J_{C,F}$ = 238 Hz, *p*-C_6F_5), 148.6 (d, $^1J_{C,F}$ = 233 Hz, *o*-C_6F_5) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –133.5 (d, $^3J_{F,F}$ = 19 Hz, 2 F, *o*-C_6F_5), –165.7 (t, $^3J_{F,F}$ = 20 Hz, 1 F, *p*-C_6F_5), –168.2 (m, $^3J_{F,F}$ = 19 Hz, 2 F, *m*-C_6F_5) ppm.

2-{CH_2L}-6-PhC_6H_3OH [1a, L = N(C_4H_8O); 1b, C_4H_8NMe]: A 250-mL round-bottom flask was charged with 2-PhC_6H_4OH (4.42 g, 25.9 mmol), formaldehyde (3 equiv., 77 mmol, 5.92 mL of a 37%-weight water solution), morpholine or *N*-methylpiperazine (1.2 equiv.) and ethanol (70 mL). The mixture was heated at reflux, and the reaction was monitored by TLC revealing that the reaction was complete after 12 h. The mixture was then allowed to cool to room temperature, and the volatiles were removed under vacuum. Aminophenols **1a** and **1b** were isolated as analytically pure colourless solids after purification of the crude mixture by silica gel column chromatography. Data for **1a**: Yield: 2.4 g, 35%. R_f = 0.4 (pentane/Et_2O, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.60 (br. s, 4 H, N-CH_2CH_2-O), 3.72 (br. s, 4 H, N-CH_2CH_2-O), 3.77 (s, 2 H, PhCH_2), 6.84 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, *Ph*), 7.00 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 7.24–7.36 (m, 2 H, *Ph*), 7.39–7.47 (m, 2 H, *Ph*), 7.57–7.63 (m, 2 H, *Ph*), 11.07 (br. s, 1 H, O*H*) ppm. ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$): δ = 52.8 (N-*C*H_2CH_2-O), 62.1 (Ph*C*H_2), 66.7 (N-CH_2*C*H_2-O), 119.3 (*Ph*), 121.0 (*Ph*), 126.9 (*Ph*), 128.1 (*Ph*), 128.2 (*Ph*), 129.0 (*Ph*), 129.3 (*Ph*), 130.1 (*Ph*), 138.4

(*Ph*), 154.7 (*Ph*) ppm. $C_{17}H_{19}NO_2$ (269.34): calcd. C 75.81, H 7.11, N 5.20; found C 76.06, H 6.74, N 5.22. Data for **1b**: Yield: 5.4 g, 74%. R_f = 0.12 (Et_2O/EtOH, 7:3). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.17 (s, 3 H, N*Me*), 2.44 (m, 8 H, N-CH_2CH_2-N), 3.64 (s, 2 H, PhCH_2), 6.74 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, *Ph*), 6.87 (dd, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*), 7.16–7.38 (m, 4 H, *Ph*), 7.64 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.6 Hz, 2 H, *Ph*), 10.50 (br. s, 1 H, O*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 45.9 (N*Me*), 52.5 (N-*C*H_2CH_2-N), 54.8 (N-*C*H_2CH_2-N), 61.6 (Ph*C*H_2), 119.1 (*Ph*), 121.6 (*Ph*), 126.8 (*Ph*), 128.0 (*Ph*), 128.1 (*Ph*), 128.8 (*Ph*), 129.4 (*Ph*), 130.0 (*Ph*), 138.6 (*Ph*), 154.9 (*Ph*) ppm. $C_{18}H_{22}N_2O$ (282.38): calcd. C 76.56, H 7.85, N 9.92; found C 76.45, H 7.78, N 9.82.

2-{CH_2L}-6-*t*BuC_6H_3OH [1c, L = N(C_4H_8O); 1d, N(C_4H_8NMe)]: A 100-mL round-bottom flask was charged with 2-*t*BuC_6H_4OH (2 mL, 13.3 mmol), formaldehyde (3 equiv., 40 mmol, 3 mL of a 37% weight water solution), morpholine or *N*-methylpiperazine (1.2 equiv., 16 mmol, 1.8 mL) and ethanol (40 mL). The mixture was heated at reflux, and the reaction was monitored by TLC revealing that the reaction was complete after 10 h. The mixture was then allowed to cool to room temperature, and the volatiles were removed under vacuum. Aminophenols **1c** and **1d** were isolated as analytically pure colourless solids after purification of the crude mixture by silica gel column chromatography. Data for **1c**: Yield: 1.64 g, 50%. R_f = 0.32 (pentane/Et_2O, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.65 (s, 9 H, *t*Bu), 1.92 (br. s, 4 H, NCH_2), 3.15 (s, 2 H, PhCH_2), 3.37 (br. s, 4 H, OCH_2), 6.71 (dd, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*), 6.83 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, *Ph*), 7.31 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*), 11.31 (br. s, 1 H, O*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 29.5 (C*Me*$_3$), 34.7 (*C*Me$_3$), 45.4 (N*Me*), 52.4 (N-*C*H_2CH_2-O), 54.6 (N-CH_2*C*H_2-O), 61.9 (Ph*C*H_2), 118.6 (*Ph*), 121.0 (*Ph*), 126.3 (*Ph*), 136.4 (*Ph*), 156.9 (*Ph*) ppm. $C_{15}H_{23}NO_2$ (249.35): calcd. C 72.25, H 9.30, N 5.62; found C 72.39, H 9.20, N 5.56. Data for **1d**: Yield: 2.3 g, 66%. R_f = 0.27 (Et_2O/EtOH, 4:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.67 (s, 9 H, *t*Bu), 1.94 (s, 3 H, N*Me*), 2.06–2.16 (br., 8 H, N-CH_2CH_2-N), 3.22 (s, 2 H, PhCH_2), 6.76 (dd, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*), 6.86 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, *Ph*), 7.31 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*), 11.31 (br., 1 H, O*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 29.5 (C*Me*$_3$), 34.7 (*C*Me$_3$), 45.4 (N*Me*), 52.0 (N-*C*H_2CH_2-N), 54.6 (N-*C*H_2CH_2-N), 61.5 (Ph*C*H_2), 118.4 (*Ph*), 121.4 (*Ph*), 126.1 (*Ph*), 127.4 (*Ph*), 136.4 (*Ph*), 157.2 (*Ph*) ppm. $C_{16}H_{26}N_2O$ (262.39): calcd. C 73.24, H 9.99, N 10.68; found C 73.18, H 10.03, N 10.60.

6-{CH_2L}-2-CPh_3-4-MeC_6H_2OH [1e, L = N(C_4H_8O); 1f, N(C_4H_8NMe)]: A 100-mL round-bottom flask was charged with disubstituted phenol 2-CPh_3-4-MeC_6H_3OH[14] (1.00 g, 2.85 mmol), formaldehyde (10 equiv., 28.5 mmol, 1.00 mL of a 37% weight water solution), morpholine (1.2 equiv., 3.42 mmol, 0.30 mL) and ethanol (40 mL). The mixture was heated at reflux, and the reaction was monitored by TLC revealing that the reaction was complete after 40 h. Upon cooling to room temperature, the aminophenol precipitated out of the solution as a colourless solid. The mixture was then filtered, and the colourless solid was washed with cold ethanol and pentane and dried under vacuum. Data for **1e**: Yield: 800 mg, 63% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.17 (s, 3 H, PhCH_3), 2.19–2.25 (m, 4 H, N-CH_2CH_2-O), 3.33–3.49 (m, 4 H, N-CH_2CH_2-O), 3.57 (s, 2 H, PhCH_2), 6.76 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 6.90 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 7.11–7.23 (m, 15 H, C*Ph*$_3$), 10.36 (br. s, 1 H, O*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 20.91 (Ph-*C*H_3), 52.3 (N-*C*H_2CH_2-O), 61.5 (N-CH_2*C*H_2-O), 63.2 (Ph*C*H_2), 66.3 (*C*Ph$_3$), 121.4 (*Ph*), 125.4 (*Ph*), 126.5 (*Ph*), 126.9 (*Ph*), 128.8 (*Ph*), 130.8 (*Ph*), 131.01 (*Ph*), 134.4 (*Ph*), 146.01 (*Ph*), 153.5 (*Ph*) ppm. $C_{31}H_{31}NO_2$ (449.58): calcd. C 82.82, H 6.95, N 3.12; found C 82.01, H 7.00, N 2.92. Data for **1f**: Yield: 900 mg, 70%. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.16 (s, 3 H, NCH_3), 2.18 (s, 3 H, PhCH_3), 2.31–2.52 (m, 8 H, N-CH_2CH_2-N), 3.70 (s, 2 H, PhCH_2), 6.75 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 6.90 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 7.16 (m, 15 H, C*Ph*$_3$), 10.18 (br. s, 1 H, O*H*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 20.9 (Ph-*C*H_3), 45.8 (N*C*H_3), 52.0 (N-*C*H_2CH_2-N), 54.4 (N-*C*H_2CH_2-N), 61.1 (Ph*C*H_2), 63.2 (*C*Ph$_3$), 121.9 (*Ph*), 125.4 (*Ph*), 126.4 (*Ph*), 126.9 (*Ph*), 128.6 (*Ph*), 130.7 (*Ph*), 131.1 (*Ph*), 134.2 (*Ph*), 146.1 (*Ph*), 153.7 (*Ph*) ppm. $C_{32}H_{34}N_2O$ (462.63): calcd. C 83.08, H 7.41, N 6.06; found C 83.40, H 7.56, N 5.59.

η^2-*N*,*O*-[2-{CH_2N(C_4H_8L′)}-6-PhC_6H_3O]AlMe_2 (2a, L′ = O; 2b, L′ = NMe): In a glove box, a dichloromethane solution (5 mL) of aminophenol **1a** or **1b** (4.40 mmol) precooled to –35 °C was slowly added by a pipette to a 20-mL vial containing a dichloromethane solution (5 mL) of $AlMe_3$ (317 mg, 4.40 mmol) also precooled to –40 °C. With a loosely capped vial to allow methane to escape, the reaction mixture was warmed to room temperature and stirred for 2 h. The obtained white suspension was then evaporated to yield a colourless solid as a crude product. Recrystallization of this solid from pentane/Et_2O (10:1) at –40 °C afforded in both cases pure aluminium dimethyl complexes **2a** and **2b** as colourless solids. Data for **2a**: Yield: 87%. ^1H NMR (300 MHz, C_6D_6): δ = –0.55 (s, 6 H, AlMe_2), 1.61–1.70 (m, 2 H, N-CH_2CH_2-O), 2.40–2.45 (m, 2 H, N-CH_2CH_2-O), 3.11–3.18 (m, 4 H, PhCH_2 and N-CH_2CH_2-O), 3.25–3.34 (m, 2 H, N-CH_2CH_2-O), 6.63 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 6.78 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, *Ph*), 7.15 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, *Ph*), 7.33 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, *Ph*), 7.46 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 7.89 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 H, *Ph*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = –9.1 (AlMe_2), 52.9 (N-*C*H_2CH_2-O), 60.8 (N-CH_2*C*H_2-O), 62.6 (Ph*C*H_2), 117.3 (*Ph*), 120.5 (*Ph*), 126.5 (*Ph*), 127.9 (*Ph*), 129.0 (*Ph*), 129.5 (*Ph*), 131.3 (*Ph*), 131.9 (*Ph*), 139.5 (*Ph*), 157.3 (*Ph*) ppm. $C_{19}H_{24}AlNO_2$ (325.38): calcd. C 70.13, H 7.43, N 4.30; found C 69.9, H 7.53, N 4.39. Data for **2b**: Yield: 75%. ^1H NMR (300 MHz, C_6D_6): δ = –0.48 (s, 6 H, Al*Me*$_2$), 1.83 (s, 3 H, N*Me*), 1.95–1.98 (m, 6 H, N-CH_2CH_2-N), 2.65–2.70 (m, 2 H, N-CH_2CH_2-N), 3.26 (s, 2 H, PhCH_2), 6.68 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 6.79 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, *Ph*), 7.14 (t, $^3J_{H,H}$ = 8.6 Hz, 1 H, *Ph*), 7.32 (t, $^3J_{H,H}$ = 8.5 Hz, 2 H, *Ph*), 7.47 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 7.93 (dd, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.8 Hz, 2 H, *Ph*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = –9.1 (Al*Me*$_2$), 45.2 (N*Me*), 50.1 (N-*C*H_2CH_2-N), 52.4 (N-*C*H_2CH_2-N), 59.4 (Ph*C*H_2), 117.2 (*Ph*), 120.9 (*Ph*), 126.4 (*Ph*), 129 (*Ph*), 129.6 (*Ph*), 130.2 (*Ph*), 131.4 (*Ph*), 131.8 (*Ph*), 139.7 (*Ph*), 157.5 (*Ph*) ppm. $C_{20}H_{27}AlN_2O$ (338.42): calcd. C 70.98, H 8.04, N 8.28; found C 70.74, H 8.05, N 8.29.

η^2-*N*,*O*-[2-{CH_2N(C_4H_8L′)}-6-*t*BuC_6H_3O]AlMe_2 (2c, L′ = O; 2d, L′ = NMe): Aminophenolate aluminium dimethyl complexes **2c** and **2d** were synthesized by using the same procedure as that used for **2a** and **2b**. Pure **2c** and **2d** were obtained as analytically pure colourless crystalline solids after recrystallization of the crude mixture from pentane/Et_2O (9:1) at –40 °C. Data for **2c**: Yield 70%. ^1H NMR (300 MHz, C_6D_6): δ = –0.48 (s, 6 H, AlMe_2), 1.63 (br. s, 11 H, *t*Bu and N-CH_2CH_2-O), 2.4–2.44 (m, 2 H, N-CH_2CH_2-O), 3.01–3.16 (br. s, 4 H, N-CH_2CH_2-O and PhCH_2), 3.25–3.34 (m, 2 H, N-CH_2CH_2-O), 6.61 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H, *Ph*), 6.76 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, *Ph*), 7.40 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H, *Ph*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = –9.0 (Al*Me*$_2$), 29.6 (C*Me*$_3$), 34.8 (*C*Me$_3$), 52.9 (N-*C*H_2CH_2-O), 54.6 (N-*C*H_2CH_2-O), 62.6 (Ph*C*H_2), 116.8 (*Ph*), 117.6 (*Ph*), 120.2 (*Ph*), 138.2 (*Ph*), 138.9 (*Ph*), 158.9 (*Ph*) ppm. $C_{17}H_{28}AlNO_2$ (305.39): calcd. C 66.86, H 9.24; found C 66.71, H 9.03. Data for

2d: Yield: 81%. ^{1}H NMR (300 MHz, C_6D_6): δ = –0.41 (s, 6 H, AlMe_2), 1.65 (s, 9 H, *t*Bu), 1.81 (s, 3 H, NMe), 1.95 (br. s, 6 H, N-CH_2CH_2-N), 2.64 (m, 2 H, N-CH_2CH_2-N), 3.24 (s, 2 H, PhCH_2), 6.65 (dd, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*), 6.80 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, *Ph*), 7.41 (dd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H, *Ph*) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = –8.9 (AlMe_2), 29.6 (CMe_3), 34.8 (*C*Me$_3$), 45.2 (NMe), 50.1 (N-*C*H_2CH_2-N), 54.6 (N-*C*H_2*C*H_2-N), 59.6 (Ph*C*H_2), 116.7 (*Ph*), 117.6 (*Ph*), 120.6 (*Ph*), 138.2 (*Ph*), 138.8 (*Ph*), 159.2 (*Ph*) ppm. $C_{18}H_{31}AlN_2O$ (318.43): calcd. C 67.89, H 9.81; found C 67.98, H 9.77.

η^2-*N*,*O*-[6-{$CH_2N(C_4H_8L')$}-2-CPh_3-4-MeC_6H_3O]$AlMe_2$ (2e, L′ = O; 2f, L′ = NMe): Aminophenolate aluminium dimethyl complexes **2e** and **2f** were synthesized by using the same procedure as that for **2a** and **2b**. Pure **2e** and **2f** were obtained as analytically pure colourless crystalline solids after recrystallization of the crude mixture from pentane/CH_2Cl_2 (9:1) at –35 °C. Data for **2e**: Yield: 90%. ^{1}H NMR (300 MHz, C_6D_6): δ = –0.85 (s, 6 H, AlMe_2), 1.63–1.72 (m, 2 H, N-CH_2CH_2-O), 2.15 (s, 3 H, PhCH_3), 2.37–2.41 (m, 2 H, N-CH_2CH_2-O), 3.10–3.20 (m, 4 H, N-CH_2CH_2-O), 3.21 (s, 2 H, PhCH_2), 6.45 (br. s, 1 H, *Ph*), 6.98–7.15 (m, 15 H, C*Ph*$_3$), 7.39 (br. s, 1 H, *Ph*) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = –9.3 (AlMe_2), 20.7 (Ph-*C*H$_3$), 51.4 (N-*C*H_2CH$_2$-O), 59.5 (N-*C*H_2CH$_2$-O), 61.6 (Ph*C*H_2), 63.7 (*C*Ph$_3$), 119.2 (*Ph*), 124.4 (*Ph*), 125.2 (*Ph*), 129.3 (*Ph*), 131.4 (*Ph*), 132.5 (*Ph*), 136.6 (*Ph*), 146.7 (*Ph*), 146.0 (*Ph*), 156.0 (*Ph*) ppm. $C_{33}H_{36}AlNO_2$ (505.63): calcd. C 78.39, H 7.18, N 2.77; found C 82.06, H 7.58, N 2.63. Data for **2f**: Yield: 88%. ^{1}H NMR (300 MHz, C_6D_6): δ = –0.80 (s, 6 H, AlMe_2), 1.82 (s, 3 H, NMe), 1.89–2.00 (m, 6 H, N-CH$_2$CH_2-N), 2.15 (s, 3 H, PhCH_3), 2.57–2.63 (m, 2 H, N-CH$_2$CH_2-N), 3.31 (s, 2 H, PhCH_2), 6.49 (br. s, 1 H, *Ph*), 7.11–7.16 (m, 9 H, C*Ph*$_3$), 7.40 (br. s, 1 H, *Ph*), 7.49–7.52 (m, 6 H, *Ph*) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = –9.3 (AlMe_2), 20.70 (Ph-*C*H$_3$), 45.20 (NMe), 49.1 (N-*C*H_2CH$_2$-O), 51.0 (N-*C*H_2CH$_2$-O), 62.5 (Ph*C*H_2), 63.7 (*C*Ph$_3$), 119.6 (*Ph*), 124.3 (*Ph*), 125.1 (*Ph*), 127.0 (*Ph*), 129.0 (*Ph*), 129.2 (*Ph*), 131.8 (*Ph*), 136.6 (*Ph*), 146.7 (*Ph*), 156.0 (*Ph*) ppm. $C_{34}H_{39}AlN_2O$ (518.67): calcd. C 78.73, H 7.58, N 5.40; found C 77.88, H 7.47, N 5.30.

[η^3-*N*,*O*,*L*′-(2-{$CH_2N(C_4H_8L')$}-6-PhC_6H_3O)AlMe][MeB$(C_6F_5)_3$] (3a$^+$, L′ = O; 3b$^+$, L′ = NMe): In a glove box, neutral complex **2a** or **2b** (0.3 mmol) was charged into a small Schlenk flask and dissolved in dichloromethane (2 mL). At room temperature and under vigorous stirring, an equimolar quantity of $B(C_6F_5)_3$ (0.3 mmol) was added. The resulting colourless solution was stirred for 30 min at room temperature and then evaporated to dryness to yield a colourless oil. Trituration with cold pentane provoked the precipitation of a white solid. The solvent was filtered off, and the white solid residue was dried under vacuum to afford the corresponding salt species [**3a**][MeB$(C_6F_5)_3$] and [**3b**][MeB$(C_6F_5)_3$] in excellent yields. Data for **3a$^+$**: Yield: 97%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = –1.28 (s, 3 H, AlMe), 2.97–3.05 (m, 1 H, N-CH_2CH_2-O), 3.40–3.62 (m, 3 H, N-CH_2CH_2-O), 3.84–4.02 (m, 2 H, N-CH_2CH_2-O), 4.05–4.27 (m, 4 H, PhCH_2 and N-CH_2CH_2-O), 7.24–7.27 (m, 2 H, *Ph*), 7.35–7.37 (m, 2 H, *Ph*), 7.40–7.45 (m, 1 H, *Ph*), 7.52–7.55 (m, 3 H, *Ph*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = –13.4 (Al*C*H$_3$), 49.8 (N-*C*H_2CH$_2$-O), 57.2 (N-CH$_2$*C*H$_2$-O), 66.9 (Ph*C*H$_2$), 120.4 (*Ph*), 126.6 (*Ph*), 129.0 (*Ph*), 129.7 (*Ph*), 130.0 (*Ph*), 131.3 (*Ph*), 134.4 (*Ph*), 134.8 (*Ph*), 136.4 (*Ph*), 146.4 (*Ph*) ppm. Data for **3b$^+$**: Yield: 95%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = –0.93 (s, 3 H, AlMe), 2.05 (s, 3 H, NMe), 2.52–2.62 (m, 1 H, N-CH_2CH_2-N), 2.79–3.00 (m, 4 H, N-CH_2CH_2-N), 3.33–3.46 (m, 2 H, N-CH_2CH_2-N), 3.62–3.73 (m, 1 H, N-CH_2CH_2-N), 3.93 (d, $^1J_{H,H}$ = 14.4 Hz, 1 H, PhCH_2), 4.18 (d, $^1J_{H,H}$ = 14.4 Hz, 1 H, PhCH_2), 7.35 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H, *Ph*), 7.44 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, *Ph*), 7.60–7.65 (m, 2 H, *Ph*), 7.69–7.77 (m, 4 H, *Ph*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = –11.0 (AlMe), 43.4 (NMe), 49.8 (N-*C*H_2*C*H_2-N), 51.6 (N-*C*H_2*C*H_2-N), 58.5 (Ph*C*H_2), 121.7 (*Ph*), 127.1 (*Ph*), 129.6 (*Ph*), 129.7 (*Ph*), 130.1 (*Ph*), 131.5 (*Ph*), 133.3 (*Ph*), 135.0 (*Ph*), 136.9 (*Ph*), 147.4 (*Ph*) ppm.

[(2-{$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)AlMe·(2-{$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)$AlMe_2$][MeB$(C_6F_5)_3$] ([3c][MeB$(C_6F_5)_3$]): In a glove box, neutral complex **2c** (0.66 mmol) was added into a small Schlenk flask and dissolved in dichloromethane (2 mL). At room temperature and under vigorous stirring, an equimolar quantity of $B(C_6F_5)_3$ (0.66 mmol) was then added. The resulting colourless solution was stirred for 30 min at room temperature and then evaporated to dryness to quantitatively yield the salt species [**3c**][MeB$(C_6F_5)_3$] as a colourless oil, as deduced from ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = –0.68 (s, 6 H, AlMe_2), –0.22 (s, 3 H, AlMe), 1.35 (s, 9 H, *t*Bu), 1.38 (br. s, 9 H, *t*Bu), 2.72–2.81 (m, 4 H, N-CH_2CH_2-O), 3.11–3.41 (m, 4 H, N-CH_2CH_2-O), 3.63–3.69 (m, 2 H, N-CH_2CH_2-O), 3.93–3.99 (m, 2 H, N-CH_2CH_2-O), 4.05–4.13 (m, 2 H, N-CH_2CH_2-O), 4.22–4.33 (m, 2 H, N-CH_2CH_2-O), 4.46 (s, 2 H, PhCH_2), 4.52 (s, 2 H, PhCH_2), 6.78 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, *Ph*), 6.87 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, *Ph*), 7.06 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*), 7.13 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*), 7.42 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*), 7.51 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = –11.7 (AlMe), –9.8 (AlMe), 28.9 (CMe_3), 29.3 (CMe_3), 34.7 (*C*Me$_3$), 35.2 (*C*Me$_3$), 51.2 (N-*C*H_2*C*H_2-O), 52.3 (N-*C*H_2*C*H_2-O), 56.3 (N-*C*H_2CH_2-O), 58.7 (N-*C*H_2*C*H_2-O), 61.2 (Ph*C*H_2), 62.5 (Ph*C*H_2), 118.2 (*Ph*), 119.1 (*Ph*), 120.5 (*Ph*), 120.9 (*Ph*), 128.5 (*Ph*), 128.7 (*Ph*), 129.5 (*Ph*), 130.2 (*Ph*), 139.4 (*Ph*), 140.2 (*Ph*), 154.5 (*Ph*), 156.2 (*Ph*) ppm.

[η^2-*N*,*O*-(2-{$CH_2N(C_4H_8O)$}-6-*t*BuC_6H_3O)AlMe(THF)][MeB$(C_6F_5)_3$] ([3c′][MeB$(C_6F_5)_3$]): In a glove box, neutral complex **2c** (0.66 mmol) was added into a small Schlenk flask and dissolved in dichloromethane (2 mL). To this solution was added THF (1 equiv., 53 μL, 0.66 mmol) by syringe. At room temperature and under vigorous stirring, an equimolar quantity of $B(C_6F_5)_3$ (0.66 mmol) was then added. The resulting colourless solution was stirred for 30 min at room temperature and then evaporated to dryness to yield a colourless oil (quantitative by ^{1}H NMR). Numerous attempts to isolate the salt species [**3c′**][MeB$(C_6F_5)_3$] were unsuccessful and its identity was determined by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = –0.19 (s, 3 H, AlMe), 1.42 (br. s, 9 H, *t*Bu), 2.30 (m, 4 H, H(β)-THF), 2.80–2.88 (m, 2 H, N-CH_2CH_2-O), 3.22–3.30 (m, 2 H, N-CH_2CH_2-O), 3.72–3.80 (m, 2 H, N-CH_2CH_2-O), 4.05–4.13 (m, 2 H, N-CH_2CH_2-O), 4.16 (s, 2 H, PhCH_2), 4.46 [m, 4 H, H(*α*)-THF], 6.91 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, *Ph*), 7.06 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*), 7.42 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, *Ph*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = –14.2 (AlMe), 25.4 [C(β)-THF], 29.3 (CMe_3), 34.7 (*C*Me$_3$), 51.2 (N-*C*H_2*C*H_2-O), 58.7 (N-*C*H_2*C*H_2-O), 61.2 (Ph*C*H_2), 75.9 [C(*α*)-THF], 118.2 (*Ph*), 120.5 (*Ph*), 128.5 (*Ph*), 129.5 (*Ph*), 139.6 (*Ph*), 155.0 (*Ph*) ppm.

[η^3-*N*,*O*,*N*-(2-{$CH_2N(C_4H_8NMe)$}-6-*t*BuC_6H_3O)AlMe][MeB$(C_6F_5)_3$] ([3d][MeB$(C_6F_5)_3$]): Cationic aluminium methyl complex [**3d**][MeB$(C_6F_5)_3$] was synthesized by using the same procedure as that used for [**3a**,**b**][MeB$(C_6F_5)_3$]. Pure [**3d**][MeB$(C_6F_5)_3$] was obtained as a white solid in 90% yield but could not be obtained as an analytically pure compound, which is presumably due to its poor stability ($t_{1/2}$ ≈ 16 h in CD_2Cl_2 at room temperature). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = –0.17 (s, 3 H, AlMe), 1.41 (s, 9 H, *t*Bu), 2.86 (s, 3 H, NMe), 2.99–3.13 (m, 4 H, N-CH_2CH_2-N), 3.42–3.60

(m, 4 H, N-CH_2CH_2-N), 3.99 (d, $^1J_{H,H}$ = 16.3 Hz, 1 H, PhCH_2), 4.53 (d, $^1J_{H,H}$ = 16.3 Hz, 1 H, PhCH_2), 6.86–6.95 (m, 2 H, *Ph*), 7.33–7.38 (m, 1 H, *Ph*) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2): δ = –10.7 (Al*Me*), 29.1 (C*Me*$_3$), 34.5 (*C*Me$_3$), 43.6 (N*Me*), 50.4 (N-*C*H_2*C*H_2-N), 55.2 (N-*C*H_2*C*H_2-N), 58.7 (Ph*C*H_2), 119.2 (*Ph*), 120.0 (*Ph*), 128.0 (*Ph*), 129.1 (*Ph*), 139.3 (*Ph*), 154.2 (*Ph*) ppm.

[η^2-*N*,*O*-(6-{$CH_2N(C_4H_8O)$}-2-CPh_3-4-MeC_6H_3O)AlMe(THF)]-[MeB(C_6F_5)$_3$] ([3e][MeB(C_6F_5)$_3$]): Cationic aluminium methyl complex [**3e**][MeB(C_6F_5)$_3$] was synthesized by using the same procedure as that used for [**3c**][MeB(C_6F_5)$_3$]. NMR-Pure [**3e**][MeB(C_6F_5)$_3$] was obtained as a colourless sticky oil. ^1H NMR (300 MHz, CD_2Cl_2): δ = –0.77 (s, 3 H, Al*Me*), 2.07 (m, 4 H, H(β)-THF), 2.20 (s, 3 H, PhCH_3), 2.62–2.80 (m, 2 H, N-CH_2CH_2-O), 2.91–3.07 (m, 2 H, N-CH_2CH_2-O), 3.12–3.21 (m, 2 H, N-CH_2CH_2-O), 3.66–3.71 (m, 2 H, N-CH_2CH_2-O), 3.98–4.08 [m, 6 H, m, 4 H, H(α)-THF and PhCH_2], 6.94–7.29 (m, 17 H, *Ph* and C*Ph*$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = –14.9 (Al*Me*), 20.5 (Ph-*C*H_3), 25.2 [C(β)-THF], 51.2 (N-*C*H_2CH_2-O), 57.3 (N-*C*H_2CH_2-O), 60.7 (Ph*C*H_2), 63.0 (*C*Ph$_3$), 75.0 [C(α)-THF], 117.9 (*Ph*), 125.8 (*Ph*), 127.2 (*Ph*), 129.3 (*Ph*), 129.9 (*Ph*), 130.8 (*Ph*), 133.8 (*Ph*), 137.2 (*Ph*), 145.7 (*Ph*), 152.2 (*Ph*) ppm.

[η^3-*N*,*O*,*N*-(6-{$CH_2N(C_4H_8NMe)$}-2-CPh_3-4-MeC_6H_3O)AlMe]-[MeB(C_6F_5)$_3$] ([3f][MeB(C_6F_5)$_3$]): Cationic aluminium methyl complex [**3e**][MeB(C_6F_5)$_3$] was synthesized by using the same procedure as that used for [**3a**,**b**][MeB(C_6F_5)$_3$]. NMR-pure [**3f**][MeB(C_6F_5)$_3$] was obtained as a white solid in 96% yield. Its limited stability ($t_{1/2}$ = 12 h in CD_2Cl_2 at room temperature) precluded the obtainment of acceptable elemental analysis data. ^1H NMR (300 MHz, CD_2Cl_2): δ = –0.44 (s, 3 H, Al*Me*), 2.21 (s, 3 H, N*Me*), 2.38 (br. s, 2 H, N-CH_2CH_2-N), 2.45 (s, 3 H, PhCH_3), 2.51–2.60 (m, 1 H, N-CH_2CH_2-N), 2.77–2.92 (m, 2 H, N-CH_2CH_2-N), 2.98–3.07 (m, 1 H, N-CH_2CH_2-N), 3.41 (br. s, 2 H, N-CH_2CH_2-N), 3.83 (d, $^1J_{H,H}$ = 14.7 Hz, 1 H, PhCH_2), 4.44 (d, $^1J_{H,H}$ = 14.7 Hz, 1 H, PhCH_2), 6.86 (br. s, 1 H, *Ph*), 7.03 (br. s, 1 H, *Ph*), 7.09–7.32 (m, 15 H, C*Ph*$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = –15.9 (Al*Me*), 20.9 (Ph-*C*H_3), 42.5 (N*Me*), 47.4 (N-*C*H_2CH_2-O), 51.9 (N-*C*H_2CH_2-O), 55.9 (Ph*C*H_2), 63.9 (*C*Ph$_3$), 118.6 (*Ph*), 126.2 (*Ph*), 127.5 (*Ph*), 128.6 (*Ph*), 129.4 (*Ph*), 131.6 (*Ph*), 133.3 (*Ph*), 139.3 (*Ph*), 146.5 (*Ph*), 152.1 (*Ph*) ppm.

Typical Procedure for Propylene Oxide Polymerization: In a nitrogen-filled glove box, the Al initiator (0.0150 mmol) was charged into a 5-mL vial sample (equipped with a magnet stirring bar) and dissolved in toluene (1.50 mL). Propylene oxide (100 equiv., 88 mg, 1.50 mmol) was then added; the sample was tightly closed with Teflon-tight screw cap, and the mixture was vigorously stirred for the desired time, after which it was quenched with MeOH and a few drops of an aqueous HCl solution (0.1 M), and the solvents were evaporated to dryness to yield a pale-yellow oily residue. CH_2Cl_2 (2 mL) was added, and the resulting cloudy suspension was filtered to remove Al hydroxide residues. The filtrate was evaporated to yield a colourless oil that was revealed to be atactic poly(propylene oxide) (PPO), as deduced from ^1H and $\{^1H\}^{13}C$ NMR analysis. Yields in PPO: 85, 91, 88, 80 and 95% for cation **3a**$^+$, **3b**$^+$, **3c**$^+$, **3c′**$^+$ and **3e**$^+$, respectively. All PPO samples were dried in vacuo till constant weight and subsequently analyzed by SEC.

Crystal Structure Determinations: Single crystals of complexes **2a**, **2c**, **2d** and **2e** were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo-K_α λ = 0.71073 Å). The complete conditions of data collection (Denzo software[15]) and structure refinements are summarized in Table 1. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved by direct methods (SHELXS97) and refined against F^2 using the SHELXL97 and Crystalbuilder softwares.[16,17] The absorption was

Table 1. Crystal data and refined details for **2b** and **2c**.

Compound	**2b**	**2c**
Formula	$C_{17}H_{28}AlNO_2$	$C_{20}H_{27}AlN_2O$
Formula weight	305.38	338.42
Crystal system	monoclinic	orthorhombic
Crystal size	0.35 × 0.30 × 0.25	0.2 × 0.15 × 0.1
Crystal colour	colourless	colourless
Space group	$P2_1/c$	$P2_12_12_1$
a [Å]	11.2538(3)	9.9150(10)
b [Å]	11.8699(3)	12.2510(10)
c [Å]	15.8332(4)	15.9530(10)
α [°]	90	90
β [°]	123.530(2)	90
γ [°]	90	90
V [Å^3]	1763.07(8)	1937.8(3)
Z	4	4
D [g cm^{-3}]	1.150	1.160
μ (Mo-K_α) [mm^{-1}]	0.119	0.113
F(000)	664	728
Temperature [K]	173(2)	293(2)
θ_{min}–θ_{max} [°]	2.17–30.00	2.10–30.03
Dataset [*h*, *k*, *l*]	–15/13, –14/15, –10/22	–13/13, –15/17, –22/21
Tot., uniq. data, *R*(int)	12153, 4791, 0.0392	20290, 5661, 0.0573
Observed data [$I > 2\sigma(I)$]	3328	4294
No. reflections	4791	5661
No. parameters	190	217
R_2, R_1, wR_2, wR_1	0.0726, 0.0429, 0.1210, 0.1086	0.0857, 0.0553, 0.1023, 0.0950
Goof	1.047	1.059
Max. and av. shift/error	0.001, 0.001	0.003, 0.000
Flack *x*	–	0.00(14)
Min, max. resd. dens. [e Å^{-3}]	–0.288, 0.215	–0.312, 0.297

not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined by using a riding model in SHELXL97. CCDC-741189 (for **2a**), -741190 (for **2c**), -741191 (for **2d**) and -741192 (for **2e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ORTEP drawings for the molecular structures of Al dimethyl complexes **2d** and **2e** and a summary of their crystallographic data.

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