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Article

Synthesis and Structure of Neutral and Cationic Aluminum Complexes Supported by Bidentate *O,P*-Phosphinophenolate Ligands and Their Reactivity with Propylene Oxide and ε-Caprolactone

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The *O,P*-type phosphinophenol ligands **1a**−**c** were found to readily react with 1 equiv of $AlMe_3$ to afford in high yields the corresponding Al chelate complexes $\{\eta^2$-O,P-(2-PPh_2-4-R′-6-R-$C_6H_2O)\}$-$AlMe_2$, **2a**−**c** (R = Me, R′ = H, **2a**; R = Ph, R′ = H, **2b**; R = ^{t}Bu, R′ = Me, **2c**). The bis-adduct Al methyl complexes $\{\eta^2$-O,P-(2-PPh_2-4-R′-6-R-$C_6H_2O)\}_2$AlMe (R = Ph, R′ = H, **3b**; R = ^{t}Bu, R′ = Me, **3c**) also formed quantitatively upon reaction of phosphinophenols **1b**,**c** with 0.5 equiv of $AlMe_3$. Both the mono- and bis-adduct Al methyl species **2a**−**c** and **3b**,**c** are stable monomeric species whether in solution or in the solid state and remain stable in coordinating solvents such as thf. In contrast, the bis-adduct Al methyl complex **3c** undergoes a ligand exchange reaction in the presence of an alcohol source (^{i}PrOH, BnOH) to generate the homoleptic tris-adduct Al complex $\{\eta^2$-O,P-(2-PPh_2-4-Me-6-^{t}Bu-$C_6H_3O)\}_3$Al (**5c**), as determined from X-ray crystallographic studies. Both the mono- and bis-adduct Al methyl species **2b**,**c** and **3b**,**c** react fast with $B(C_6F_5)_3$ via a methide abstraction reaction to afford the stable and well-defined Al cationic species $\{\eta^2$-O,P-(2-PPh_2-6-Ph-$C_6H_3O)\}$Al(Me)(THF)$^+$ (**6b**,**c**$^+$) and $\{\eta^2$-O,P-(2-PPh_2-4-R′-6-R-$C_6H_3O)\}_2Al^+$ (**7b**,**c**$^+$), respectively, which were found to be highly active in propylene oxide polymerization to afford atactic poly(propylene oxide). These cations also readily initiate the ring-opening polymerization of ε-caprolactone via successive ring-opening insertions of the monomer into the Al−O phenoxide bond of the phosphinophenolate chelating ligand to exclusively afford linear poly(ε-caprolactone) capped, at the ester end, with a (phosphino oxide)phenolate group, as deduced from NMR and MALDI-TOF data. In these cationic systems, the PO^- chelating moiety may thus act as both a supporting ligand and an initiating group for the ROP of ε-CL.

Introduction

Cationic aluminum species, which are of interest for their enhanced Lewis acidity versus that of their neutral analogues, have established themselves over the last 10 years as a novel class of highly electrophilic species, able to efficiently mediate and/or catalyze a variety of organic transformations.[1] While some of these cations, namely, low-coordinate Al alkyl cations, may be involved in stoichiometric reactions such as the alkylation of benzene and as fast transalkylating agents in the presence of a terminal olefin,[2] the vast majority of Al cations have been primarily used in polymerization catalysis and were found to be effective initiators of oxiranes and isobutene polymerization.[2,3] Although less studied thus far, the use of cationic aluminum species for the ROP of cyclic esters such as *rac*-lactide and ε-caprolactone has also been the subject of a few reports;[2c,4] some of these cations were found to exhibit high activity in ε-caprolactone polymerization.[2c,4b]

Aluminum cations are typically supported by bi-, tri-, and tetradentate chelating and anionic ligands containing, in various combination, nitrogen and oxygen hard donors and whose steric properties greatly impact the structure and stability of the derived cationic species.[1b] In contrast, thus far, whether in neutral or in cationic aluminum chemistry, anionic chelating ligands incorporating L-type soft donors such as phosphine donors have been much less explored as supporting ligands for coordination to the hard metal center Al(III); examples in this area include the use of bidentate and tridentate amidophosphine-type anionic

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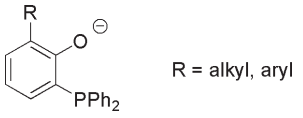
Chart 1



ligands and of bidentate monoanionic phosphinomethanide ligands.[5] This lack of interest may arise from the expected decreased stability that such complexes would exhibit compared to more classical hard-donor-stabilized Al species. Nevertheless, recent work on early transition-metal and high-oxidation-state complexes such as group 4 metal complexes strongly suggests that the use of ancillary ligands with softer L donors, such as phosphorus and sulfur, may be beneficial for olefin polymerization activity.[6]

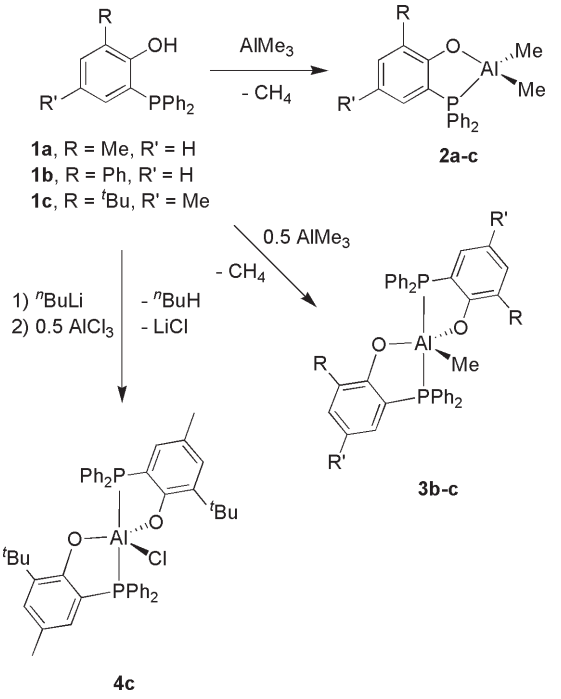
Within the above context, we have become interested into the synthesis of cationic aluminum compounds supported by bidentate ligands with softer donor atoms to evaluate their potential interest in polymerization catalysis. Bidentate phosphinophenolates of type **A** (Chart 1) appeared suitable for such studies, as they combine a hard phenoxide donor, able to anchor the ligand onto the Al(III) hard metal center, with a soft phosphine donor able to coordinate to the aluminum center, to yield the formation of a stable five-membered {PO}Al chelate. In addition, such phosphinophenols may be synthesized in a straightforward manner and their steric properties may easily be tuned via introduction of various *ortho* substituents on the phenol ring.[7] The latter feature is of importance given the general tendency of aluminum to readily form aggregates.

Here we report the synthesis and structural characterization of cationic aluminum supported by one or two bidentate phosphinophenolate ligands as well as those of the neutral aluminum alkyl precursors prepared along the way. Both neutral and cationic aluminum derivatives were tested as propylene oxide, ε-caprolactone, and *rac*-lactide polymerization initiators, and the results of these studies are also discussed herein.

Results and Discussion

Synthesis and Structure of Mono(phosphinophenolate)Al Dimethyl Complexes (2a−c). The phosphinophenolate aluminum dimethyl complexes $\{\eta^2$-O,P-(2-PPh_2-4-R′-6-R-$C_6H_2O)\}$-$AlMe_2$, **2a−c** (R = Me, R′ = H, **2a**; R = Ph, R′ = H, **2b**; R = ^{t}Bu, R′ = Me, **2c**; Scheme 1), were found to be readily accessible in high yields via an alkane elimination route involving the reaction of 1 equiv of the corresponding phosphinophenol proligand **1a−c** and $AlMe_3$. X-ray-quality crystals of **2c** were grown from a saturated 1:1 Et_2O/pentane solution, and its molecular structure was determined by X-ray crystallographic

Scheme 1



analysis, establishing its monomeric nature. The molecular structure of **2c** and selected bond distances and angles are shown in Figure 1, and crystallographic data are given in the Supporting Information (Table S2). Compound **2c** crystallizes as a monomer in which the Al center adopts a distorted tetrahedral geometry due to the rather acute η^2-Al-bonded phosphinophenolate bite angle (O−Al−P = 81.42(7)°). The latter structural feature results in the opening of the C(1)−Al−C(2) and O−Al−C bond angles (average 121.4(1)° and 112.9(1)°, respectively). The C−Al−P bond angles (110.6(1)°) are very close to the ideal tetrahedral angle (109.49°). The five-membered-ring Al metallacycle is significantly puckered, with the $AlMe_2$ moiety well above the nearly planar O−C(3)−C(4)−P chelating ligand backbone, as shown by the P−Al−O−C(3) and C(4)−P−Al−O torsion angles (40.4(1)° and 28.6(1)°, respectively). The Al−P and Al−C bond distances (2.469(1) and 1.948(1) Å, respectively) are shorter than those in the Al-phosphine adduct $(PPh_3)AlMe_3$ (2.535 and 1.981 Å, respectively), which may reflect a more electron-deficient Al center in **2c** versus $(PPh_3)AlMe_3$.[8] While the Al−P bond distance lies within the normal range for aluminum phosphine bonds (from 2.4 to 2.8 Å),[5b] the Al−O bond distance (1.791(2) Å) is a bit above that found for aluminum phenolates (1.640(5)−1.773(2) Å).[3d,9] Interestingly, this comes along with a relatively more acute Al−O−C(3) bond angle (119.2(2)°) compared to other aluminum phenoxides;[9] the latter structural feature is most likely imposed by the five-membered-ring {PO}Al chelate. On the basis of structural and theoretical studies reported on aluminum phenoxide derivatives,[9,10] the longer Al−O bond distance observed here might arise from decreased π-symmetry interactions between the oxygen phenoxide and the Al center as a result of the smaller O−Al−C bond angle.

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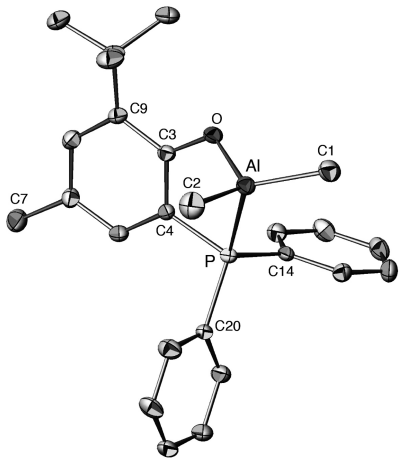


Figure 1. Molecular structure (ORTEP drawing) of the Al complex **2c**. The hydrogen atoms are omitted for clarity. Selected bond distances (Å): Al−O = 1.791(2), Al−C(1) = 1.948(3), Al−C(2) = 1.949(3), Al−P = 2.469(1). Selected bond angles (deg): O−Al−C(1) = 113.7(1), O−Al−C(2) = 112.0(1), O−Al−P = 81.42(7), Al−O−C(3) = 119.2(2).

The NMR data for compounds **2a**−**c** are overall similar to one another and are consistent with the effective chelation of one phosphinophenolate ligand to the aluminum center. For instance, the ^{1}H NMR spectra of **2a**−**c** all contain a characteristic doublet resonance (average δ 0.38, d, $^3J_{HP}$ = 4 Hz) assigned to the $AlMe_2$ moiety, which indicates the effective coordination of phosphorus to aluminum. These data also agree with an overall C_s-symmetry for **2a**−**c** on the NMR time scale in C_6D_6 or CD_2Cl_2 at room temperature, indicating a fast conformation change of the five-membered-ring Al metallacycle under these conditions. No reaction was observed between either **2b** or **2c** after 2 days at 65 °C in thf-d_8, indicating the unreactivity of the {PO}Al chelate with regard to an external Lewis base such as thf. In contrast, under these conditions, compound **2a** was found to readily and quantitatively decompose to unidentified species. Such a difference of reactivity between **2a** and **2b**,**c** presumably results from a better steric protection of the Al center in **2b**, **c** versus **2a**.

Synthesis and Structure of Bis(phosphinophenolate)Al Methyl and Chloro Complexes (3b,c and 4c) and of a Tris-(phosphinophenolate)Al Complex (5c). Trimethylaluminum reacts fast (toluene,−35 °C to room temperature, 3 h) with 2 equiv of the phosphinophenol proligand **1b**,**c** to cleanly afford the corresponding bis(phosphinophenolate)Al methyl complexes $\{\eta^2$-O,P-(2-PPh_2-4-R′-6-R-$C_6H_2O)\}_2AlMe$ (R = Ph, R′ = H, **3b**; R = ^{t}Bu, R′ = Me, **3c**; Scheme 1) in good yields as analytically pure colorless solids. The corresponding Al chloro derivative $\{\eta^2$-O,P-(2-PPh_2-4-Me-6-^{t}Bu-$C_6H_3O)\}_2AlCl$ (**4c**, Scheme 1) could also be prepared and isolated in good yield via a salt metathesis route involving the reaction of the Li salt [2-PPh_2-4-Me-6-^{t}Bu-C_6H_3O]Li, generated *in situ* by reaction of **1c** with ^{n}BuLi at −78 °C, with 0.5 equiv of $AlCl_3$. In contrast, the Me-*ortho*-substituted-phenol proligand **1a** yields an intractable mixture upon reaction with $AlMe_3$ at low temperature (−35 and −78 °C), which further highlights the importance of steric hindrance around aluminum for the synthesis of well-defined species. The salt metathesis reaction of the Li salt [2-PPh_2-6-Me-C_6H_3O]Li, generated *in situ* by reaction of **1a** with ^{n}BuLi at −78 °C, with 0.5 equiv of $AlCl_2Me$ also was unsuccessful.

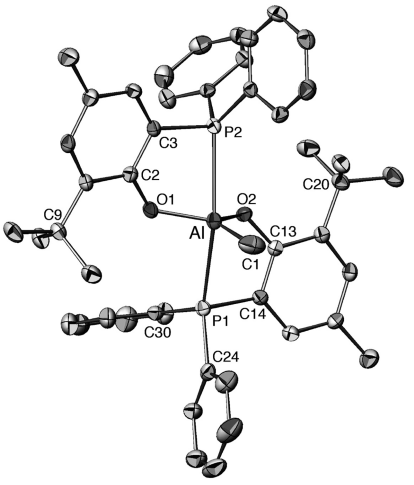


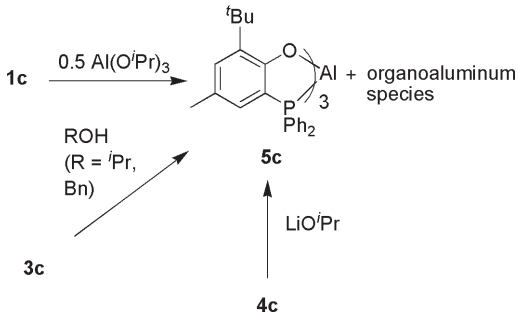
Figure 2. Molecular structure (ORTEP drawing) of the Al complex **3c**. The hydrogen atoms are omitted for clarity. Selected bond distances (Å): Al−O(1) = 1.774(2), Al−O(2) = 1.768(2), Al−P(1) = 2.705(1), Al−P(2) = 2.607(1), Al−C(1) = 1.951(3). Selected bond angles (deg): O(2)−Al−O(1) = 122.06(9), O(2)−Al−C(1) = 118.2(1), O(1)−Al−C(1) = 119.6(1), O(1)−Al−P(2) = 79.48(6), O(2)−Al−P(1) = 75.30(6), P(2)−Al−P(1) = 158.71(4), C(2)−O(1)−Al = 125.3(1), C(13)−O(2)−Al = 123.6(1).

As a comparison, the methane elimination reaction between $AlMe_3$ and 2 equiv of *N,O*-and *N,N*-based bidentate proligands (LX-H-type proligands) generally affords the monochelate $\{LX\}AlMe_2$ when performed under the above conditions; subsequent heating is usually required to promote the reaction between the formed $\{LX\}AlMe_2$ species and the second equivalent of proligand. For instance, the reaction of $AlMe_3$ with 2 equiv of aminophenol 2-CH_2NMe_2-6-^{t}Bu-C_6H_3OH at room temperature quantitatively yields the mono(aminophenolate) Al dimethyl complex $\{\eta^2$-O,N-(2-CH_2NMe_2-6-^{t}Bu-$C_6H_3O)\}$-$AlMe_2$,[3d] which may then be slowly converted to the corresponding bis(aminophenolate) Al species (toluene, 100 °C, 2 days, 20% conv by NMR).[11] In the present case, the increased reactivity of phosphinophenols **1b**,**c** toward Al alkyls has to be related to the decreased stabilizing properties of phosphines versus amines as supporting ligands for Al, which, in the former case, renders the Al center more electrophilic and thus more susceptible to increase its coordination.

The molecular structures of compounds **3b** and **3c** were determined by X-ray crystallographic analysis, establishing their monomeric nature (see Figure 2 for **3c** and Supporting Information for **3b**). Selected bond distances and angles for **3c** are given in Figure 2, and crystallographic data are summarized in the Supporting Information (Table S2). Compounds **3b**,**c** exhibit very similar structural features, and thus, only those for **3c** will be discussed. As illustrated in Figure 2, the geometry of the Al center in **3c** is best described as a slightly distorted trigonal-bipyramidal structure, in which the oxygen phenoxides and the Al-*Me* group occupy the equatorial positions while the phosphines are axially coordinated and thus *trans* to one another (P(1)−Al−P(2) = 158.71(4)°). The bond angles O(1)−Al−O(2), O(1)−Al−C(1), and O(2)−Al−C(1) (122.06(9)°, 119.6(1)°, and 118.2(1)°, respectively) are similar to one another, and their sum nearly perfectly equals 360°, thus reflecting that the Al metal is centrally located in the O(1)−C(1)−O(2) bipyramidal base. The Al−O and Al−C bond

(11) Lavanant, L.; Dagorne, S. Unpublished results.

Scheme 2



distances (1.770(1) and 1.951(3) Å average, respectively) in **3c** are normal while the Al−P bond distances (2.656(1) Å average) are significantly longer than those in the monophosphinophenolate analogue **2c** (2.469(1) Å).

The NMR data for compounds **3b**,**c** are consistent with their solid-state structure being retained in solution and with effective C_2-symmetric structures in C_6D_6 or CD_2Cl_2 at room temperature. In particular, the ^{1}H NMR spectra of **3b**,**c** both contain a characteristic triplet resonance (average δ −0.37, t, $^3J_{HP}$ = 4 Hz) assigned to the Al*Me* group, indicating the effective coordination of both phosphorus atoms to aluminum under the studied conditions. On the basis of NMR data, the Al chloro analogue **4c** most probably adopts a structure similar to those of **3b**,**c**.

In attempts to prepare the bis(phosphinophenolate) aluminum alkoxide derivative $\{\eta^2$-O,P-(2-PPh$_2$-4-Me-6-^{t}Bu-C$_6$H$_2$O)$\}_2$AlO^{i}Pr, thought to be of potential interest as a ROP initiator of cyclic esters,[12] the corresponding Al tris-adduct $\{PO\}_3$Al was prepared instead. Thus, the reaction of phosphinophenol **1c** with 0.5 equiv of Al(O^{i}Pr)$_3$ (toluene, 12 h, 80 °C) afforded the Al tris-adduct $\{\eta^2$-O,P-(2-PPh$_2$-4-Me-6-^{t}Bu-C$_6$H$_2$O)$\}_3$Al (**5c**) as the major product along with other organoaluminum species (Scheme 2). Changing the reaction conditions resulted either in no reaction, when the reaction was carried out at room temperature, or in a lower yield in **5c** at shorter reaction time (toluene, 2 h, 80 °C). A ^{1}H NMR monitoring of the latter reaction in C_6D_6 at 75 °C revealed the presence of the desired Al alkoxide $\{PO\}_2$AlOR all along the reaction process, albeit consistently as a minor component: the considered $\{PO\}_2$AlOR species is unstable under the conditions required for its formation and undergoes a ligand exchange reaction to yield the Al tris-adduct **5c**, presumably the thermodynamic product. It should also be pointed out that both the reaction of bis(phosphinophenolate)Al methyl complexes **3c** with 1 equiv of ROH (R = Bn, ^{i}Pr) and that of the Al chloro derivative **4c** with 1 equiv of LiO^{i}Pr also yielded the isolation of the trisphosphinophenolate Al species **5c**, which illustrates the propensity of the bis (phosphinophenolate) aluminum complexes of the type described here to undergo ligand exchange reactions in the presence of an alcohol or an alkoxide source.

As determined by X-ray crystallography, the molecular structure of **5c** features a central hexacoordinated Al atom adopting a slightly distorted octahedral geometry, in which all three oxygens of the phosphinophenolate bidentate ligands are coordinated in a *mer*-fashion (Figure 3). Its principal structural features including the O−Al−P bite

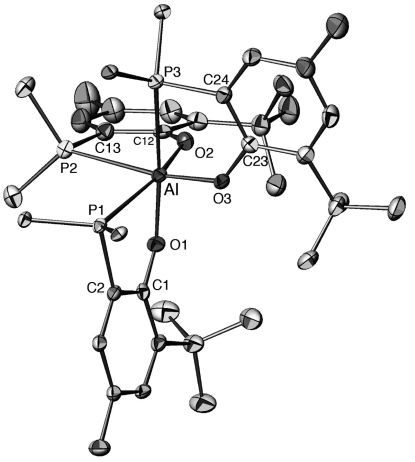


Figure 3. Molecular structure (ORTEP drawing) of the Al complex **5c**. The hydrogen atoms and the phenyl groups of the PPh$_2$ moieties are omitted for clarity. Selected bond distances (Å): Al−O(1) = 1.791(4), Al−O(2) = 1.783(4), Al−O(3) = 1.787(4), Al−P(1) = 2.647(2), Al−P(2) = 2.714 (2), Al−P(3) = 2.659(3). Selected bond angles (deg): O(2)−Al−O(1) = 122.06(9), O(2)−Al−C(1) = 118.2(1), O(1)−Al−C(1) = 119.6(1), O(1)−Al−P(2) = 79.48(6), O(2)−Al−P(1) = 75.30(6), P(2)−Al−P(1) = 158.71(4), C(2)−O(1)−Al = 125.3(1), C(13)−O(2)−Al = 123.6(1).

angles (average 78.7(1)°) and the Al−P and Al−O bond distances (2.673(4) and 1.786(5) Å, respectively) compare to those of the bis-adduct Al methyl analogue **3c**. As for its solution structure, the ^{1}H and ^{13}C NMR spectra (C_6D_6, RT) exhibit only one set of resonances for the chelating ligand, while the ^{31}P NMR spectrum consists of a sharp singlet resonance; thus, these data are consistent with compound **5c** retaining its solid-state structure in solution under the studied conditions.

Synthesis of Mono(phosphinophenolate) and Bis(phosphinophenolate) Al Methyl Cationic Complexes (6b,c$^+$, 7b,c$^+$, and 8c$^+$). While the ionization chemistry of *N,N*- and *N,O*-based Al neutral dialkyls has yielded novel families of highly Lewis acidic Al species, the synthesis and use in catalysis of cationic Al alkyls supported by "softer" chelating ligands have not been investigated.[1] Thus, the prepared mono- and bis-phosphinophenolate Al methyl complexes (**2a**−**c** and **3b**,**c**) were reacted with methide abstracting reagents such as B(C$_6$F$_5$)$_3$ and [Ph$_3$C][B(C$_6$F$_5$)$_4$] so as to generate the corresponding Al cations.

The reaction of complexes **2b**,**c** with 1 equiv of B(C$_6$F$_5$)$_3$ (CH_2Cl_2, RT, 10 min) in the presence of 1 equiv of THF quantitatively affords the corresponding Al-THF cationic adducts $\{\eta^2$-O,P-(2-PPh$_2$-4-R′-6-R-C$_6$H$_2$O)$\}$Al(Me)(THF)$^+$ (R = Ph, R′ = Ph, **6b**$^+$; R = ^{t}Bu, R′ = Me, **6c**$^+$; Scheme 3) as MeB(C$_6$F$_5$)$_3^-$ salts. The salt species [**6b**,**c**][MeB(C$_6$F$_5$)$_3$], which were isolated as analytically pure colorless solids in good yields, are air-stable in the solid state and stable in solution (CH_2Cl_2) under N_2 for days. Compounds [**6b**,**c**][MeB(C$_6$F$_5$)$_3$] are fully dissociated in CD_2Cl_2 with no cation−anion interaction at room temperature, as deduced from ^{1}H and ^{19}F NMR data.[13] Key characteristic ^{1}H NMR resonances for cations **6b**,**c**$^+$ include (i) the AlMe$^+$ resonances (δ −0.21, −0.12 for **6b**,**c**$^+$, respectively) are downfield shifted as compared to those in the neutral precursors **2b**,**c** (δ −0.73, −0.68), a result of the cationic

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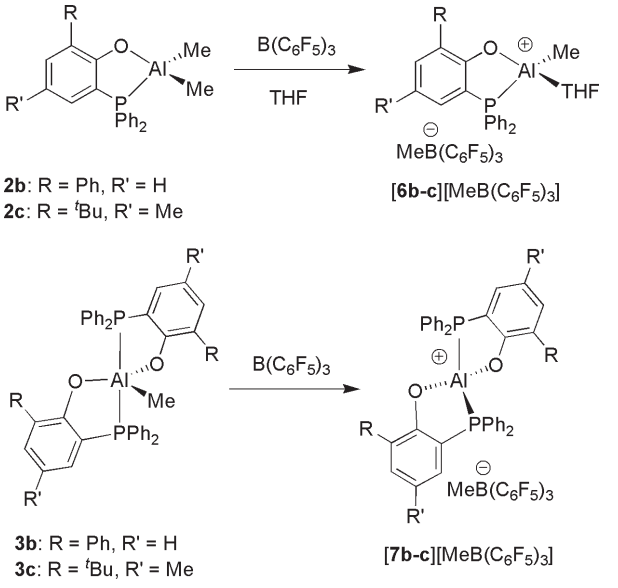
Scheme 3



charge on the Al metal center, and (ii) the THF resonances (δ (average) 4.18, 1.96) also appear at lower field than those for free THF (δ 3.67, 1.81), showing effective THF coordination to the cationic Al center.

Unlike compounds **2b**,**c**, complex **2a** reacts with $B(C_6F_5)_3$ in the presence of 1 equiv or excess of THF to afford a mixture of products. The ionization of **2a** is evidenced by the formation of the $MeB(C_6F_5)_3^-$ anion, as observed in NMR spectroscopy; nevertheless, the lack of steric protection at the Al center in the resulting cationic species probably favors the formation of aggregates, which precluded, in the present case, the isolation of a well-defined salt species. In addition, two experimental observations should also be pointed out: (i) all three neutral precursors **2a**−**c** afforded decomposition products when ionized by $B(C_6F_5)_3$ in the absence of an external Lewis base, such as THF, to stabilize the formed Al cationic center and (ii) no reaction was observed between complexes **2a**−**c** and $[Ph_3C][B(C_6F_5)_4]$ under the studied conditions (CD_2Cl_2, RT, 2 h) whether or not in the presence of THF. Such a lack of reactivity of $[Ph_3C][B(C_6F_5)_4]$ versus $B(C_6F_5)_3$ toward {LX}$AlMe_2$-type species is unusual.

The bis(phosphinophenolate) aluminum methyl complexes **3b**,**c** cleanly and quantitatively react with 1 equiv of $B(C_6F_5)_3$ (CH_2Cl_2, RT, 10 min) to afford the corresponding Al cations $\{\eta^2$-O,P-(2-PPh_2-4-R′-6-R-$C_6H_2O)$\}$_2Al^+$ (R = Ph, R′ = H, **7b**$^+$; R = ^{t}Bu, R′ = Me, **7c**$^+$; Scheme 3) as $MeB(C_6F_5)_3^-$ salts in good yields. Both salt species are air-stable whether in the solid state or in CH_2Cl_2 solution. The NMR data for [**7b**,**c**][$MeB(C_6F_5)_3$] (CD_2Cl_2, room temperature) feature one set of resonances for the phosphinophenolate ligand, which is consistent with a symmetrical environment at Al in solution, and no cation−anion interactions are observed under these conditions.[13] The molecular structure of [**7c**][$MeB(C_6F_5)_3$], as determined by X-ray crystallographic analysis, unambiguously establishes cation **7c**$^+$ as a four-coordinate Al cation effectively η^2-chelated by two bidentate phosphinophenolate ligands and with no interaction with the $MeB(C_6F_5)_3^-$ anion in the solid state (Figure 4). Selected bond distances and angles for **7c**$^+$ are given in Figure 4, and crystallographic data are summarized in the Supporting Information (Table S2). The Al center in cation

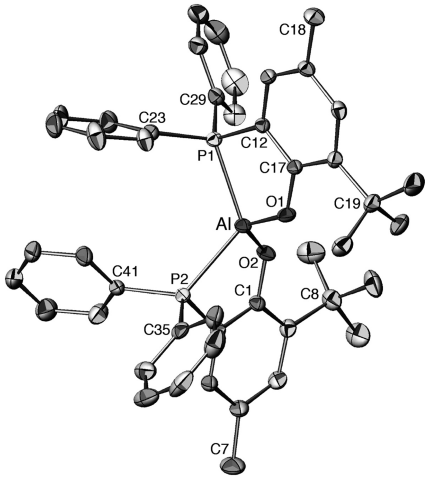


Figure 4. Molecular structure (ORTEP drawing) of the Al cation **7c**$^+$. The hydrogen atoms are omitted for clarity. Selected bond distances (Å): Al−O(1) = 1.732(1), Al−O(2) = 1.725(1), Al−P(1) = 2.367(7), Al−P(2) = 2.3890(8). Selected bond angles (deg): O(2)−Al−P(2) = 88.10(5), O(2)−Al−P(1) = 88.92(5), O(1)−Al−P(2) = 120.18(6), O(2)−Al−P(1) = 125.47(6), P(2)−Al−P(1) = 120.00(3).

7c$^+$ adopts a distorted tetrahedral structure with both P−Al−O bite angles (average 88.5(1)°) being significantly wider than those in the neutral Al precursors **2c** (81.42(7)°) and **3c** (77.4(1)° average), which arises, at least in part, from shorter Al−P and, to a lesser extent, Al−O bond distances in **7c**$^+$ (average 2.378(5) and 1.72(1) Å, respectively) versus those in **2c** (2.469(1) and 1.791(2) Å) and **3c** (average 2.656(1) and 1.770(1) Å, respectively). The latter bonding parameters reflect an increased electrophilicity of the cationic Al center in **7c**$^+$ versus neutral analogues. In solution, despite its excellent stability and the tetrahedral environment at Al, the four-coordinate Al cation **7c**$^+$ remains quite Lewis acidic, as it reacts fast with 1 equiv of NMe_2Ph (CD_2Cl_2, RT, 10 min) to yield the corresponding pentacoordinate Al-NMe_2Ph adduct **8c**$^+$, as deduced by ^{1}H and ^{31}P NMR spectroscopy.

Reactivity of Phosphinophenolate Al Complexes with Propylene Oxide (PO). While all neutral phosphinophenolate Al complexes synthesized in the present work are inactive in PO polymerization at room temperature in CH_2Cl_2, the more Lewis acidic Al cations **6b**,**c**$^+$ and **7b**,**c**$^+$ were all found to initiate the polymerization of PO. Thus, the monophosphinophenolate Al-THF adduct cations **6b**,**c**$^+$ readily polymerizes PO to afford atactic poly(propylene) oxide (PPO), as deduced from ^{13}C NMR data [RT, 15 min, CH_2Cl_2; 100 equiv of PO ($[PO]_0$ = 1 M); yield in PPO: **6b**$^+$, 52%, **6c**$^+$, 61%]. As estimated from SEC data, both systems appear to be similar to one another and feature a monomodal low-molecular-weight distribution with a moderate polydispersity (**6b**$^+$, M_n = 3120, M_w/M_n = 1.45; **6c**$^+$, M_n = 3540, M_w/M_n = 1.63). For both **6b**,**c**$^+$ cations, longer reaction time did not improve conversion to PPO, suggesting a fast deactivation/decomposition of the catalytically active species under the studied conditions. Nevertheless, in the case of **6c**$^+$, higher molecular weight PPO, along with a better conversion of PO to PPO, was achieved at lower temperature [0 °C, CH_2Cl_2, 1 h; 100 equiv of PO ($[PO]_0$ = 1 M); 79% yield in PPO; M_n = 7420, M_w/M_n = 1.68]. Analyses of the latter PPOs by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy are consistent

with the absence of aromatics and phosphorus in the synthesized materials, which suggests that, unlike that of ε-CL (*vide infra*), the polymerization process may not proceed via insertion into the Al−phenolate bond. Presumably, the present PO polymerization catalysis proceeds via a Lewis acid-assisted cationic mechanism, as observed in related *N,N*- and *N,O*-supported Al cationic systems.[3c,3d] Overall, the catalytic activity of **6b**,**c**$^+$ at room temperature compares with that of aminophenolate-supported Al methyl cations and Schiff base-$AlEt_2Cl$ initiating systems as well as with that of (Salen)Al(thf)$_2^+$ and (Salpen)Al(thf)$_2^+$ Al cations.[3d,14]

Although less reactive than cations **6b**,**c**$^+$, the bis-phosphinophenolate Al cations **7b**,**c**$^+$ also initiate the polymerization of PO under mild conditions to afford atactic PPO in high yield (RT, 12 h, CH_2Cl_2; 100 equiv of PO ([PO]$_0$ = 1 M); yield in PPO: **7b**$^+$, 87%, **7c**$^+$, 92%). The SEC data for **7b**,**c**$^+$ exhibit a monomodal molecular weight distribution along with significantly higher M_n values than those observed with the **6b**,**c**$^+$ systems (**7b**$^+$, M_n = 7789, M_w/M_n = 1.74; **7c**$^+$, M_n = 8740, M_w/M_n = 1.57). The higher M_n values and the better conversion in PPO observed for **7b**,**c**$^+$ versus **6b**,**c**$^+$ Al cations most likely reflect the better stability of the former systems under the studied catalytic conditions. Overall, the catalytic activity of **7b**,**c**$^+$ at room temperature compares with that of (Salen)Al(thf)$_2^+$ and (Salpen)Al(thf)$_2^+$ Al cations, although the molecular weight of the obtained PPO is much higher with the Salen systems.[3c]

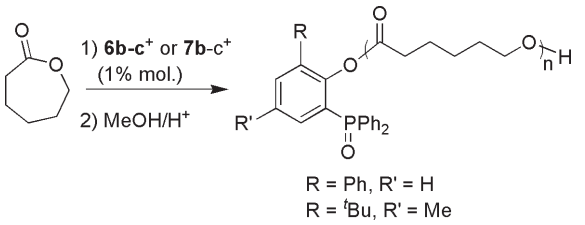
Reactivity of Phosphinophenolate Al Complexes with *rac*-Lactide (*rac*-LA) and ε-Caprolactone (ε-CL). The reactivity of cationic Al complexes toward cyclic esters such as *rac*-lactide and ε-caprolactone has thus far been the subject of very few studies despite the potential interest of such Lewis acidic and electrophilic species as initiators of the ROP of cyclic esters.[2c,4] In particular, while a couple of Al alkoxide cations of the type {LX}Al(OR)(L)$^+$ have been reported to be highly active in the ROP of ε-CL,[2c,4b] the potential in such catalysis of Al cations of the types {LX}Al(Me)(L)$^+$ and {LX}$_2$Al$^+$ remains to be explored. Thus, all phosphinophenolate Al cations were tested in the ROP of *rac*-LA and ε-CL. While none of the synthesized Al cations were found to initiate the ROP of *rac*-LA under the studied conditions (100 equiv of *rac*-LA, toluene, 75 °C, 12 h), they all, but cation **8c**$^+$, readily and quantitatively polymerize ε-CL to yield poly(ε-caprolactone) (100 equiv of ε-CL, toluene, 75 °C, 2 h), as summarized in Table 1. The SEC data for all polymers exhibit monomodal molecular weight distributions along with rather narrow polydispersities (Table 1), which agrees with a relatively well-behaved polymerization process. Nevertheless, in all cases, the M_n values are much higher than those expected for a "living"-type polymerization proceeding in ideal conditions and suggest that roughly only 30% of the initial catalyst is actually involved in the polymerization process, implying the presence of a rate-limiting initiation step prior to chain propagation. To gain more insight into the nature of the formed polymers, the identity of their end-groups was determined by NMR spectroscopy and MALDI-TOF spectrometry. Thus, the reactions of cations **6b**,**c**$^+$ and **7b**,**c**$^+$ with 5 equiv of ε-CL (toluene, 75 °C, 1 h) all yielded, after workup, the isolation

Table 1. Polymerization of ε-CL Initiated by the Al Cations 6b,c$^+$ and 7b,c$^+$[a]

catalyst	conv (%)[b]	yield (%)	M_n(obsd)[c]	PDI	M_n(theor)[d]
6b$^+$	>95	84	37 700	1.33	11 400
6c$^+$	>95	78	36 500	1.24	11 400
7b$^+$	>95	91	32 100	1.31	11 400
7c$^+$	>95	95	37 400	1.35	11 400

[a] Polymerization conditions: toluene, 75 °C, 2 h, [ε-CL]$_0$/Al = 100, [ε-CL]$_0$ = 1 M. [b] As determined by ^{1}H NMR spectroscopy. [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)].[17] [d] Calculated for one growing chain per aluminum atom.

Scheme 4



of poly(ε-caprolactone) with a (phosphine oxide)phenolate end-group (Scheme 4).[15] In particular, the ^{1}H NMR spectra of all polymers contain one set of (phosphine oxide)phenolate resonances, while the ^{31}P NMR spectra exhibit only a single sharp resonance (δ average 41.2) consistent with the presence of a phosphine oxide moiety. In addition, the MALDI-TOF spectrum recorded with the ε-PCL derived from the polymerization of 100 equiv of ε-CL by cation **7b**$^+$ is also consistent with a (phosphine oxide)phenolate end-group (presence of M-Na$^+$ and M-K$^+$ ions; see Supporting Information). Altogether, these data agree with a ε-CL polymerization proceeding via an initial insertion of ε-CL into the Al−O bond of the phosphinophenolate Al chelate, very likely to be the rate-limiting initiation step, and subsequent faster insertions allowing the polymer chain to grow. Notably, both cations **6b**,**c**$^+$ and **7b**,**c**$^+$ exhibit similar catalytic activities, and the formed polymers are also closely related, as deduced from SEC data and end-group analysis; this suggests, in the case of the bis-phosphinolate Al cations **7b**,**c**$^+$, the presence of only one growing chain per metal center during the polymerization process. In the present cationic systems, the chelating phosphinophenolate moiety thus appears to act as both the ancillary ligand and the initiating group, which is rather uncommon. On that matter, these results may be related to earlier observations on neutral bis-thiophenolate Al systems that were found to be active in the ROP of *rac*-lactide and in which the thiophenolate ancillary ligand is believed to also initiate the polymerization, as deduced from end-group analysis.[16]

As a comparison, it is noteworthy that the neutral Al complexes **2a**−**c** and **3a**,**b** were found to initiate the ROP of both *rac*-LA and ε-CL (toluene, 75 °C, 12 h) to yield the corresponding polyester materials albeit, in the case of ε-CL polymerization, with an activity lower than that of the cationic derivatives. Nevertheless, as deduced from SEC data, in all cases, the molecular weight distribution is multimodal along with a wide polydispersity (ranging from 2.5 to 4), indicating an uncontrolled polymerization process.

(14) (a) Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2013. (b) Vincens, V.; Le Borgne, A.; Spassky, N. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 623.

(15) The oxidation of the phosphine end-group presumably arises from the workup conditions (MeOH with a few drops of CH_3COOH). Likewise, phosphinophenols **1a**−**c** were found to readily and quantitatively oxidize when left a few hours in acidic MeOH medium.

(16) Huang, C.-H.; Wang, F.-C.; Ko, B.-T.; Yu, T.-L.; Lin, C.-C. *Macromolecules* **2001**, *34*, 356.

(17) Barakat, I.; Dubois, P.; Jérome, R.; Teyssié, P. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 505.

Summary and Conclusion

The present work shows that bidentate *O,P*-phosphinophenolates, which combine a hard phenoxide donor with a soft phosphine, are suitable ligands for coordination to Al(III), as they readily form stable and monomeric mono- and bis-adducts of the type $\{PO\}AlMe_2$ and $\{PO\}_2AlX$ (X = Me, Cl) provided a sufficient steric protection of the metal center is achieved. While the formed $\{PO\}AlMe_2$ and $\{PO\}_2AlMe$ complexes are stable in the presence of Lewis bases such THF, the bis-adduct Al species $\{PO\}_2AlX$ (X = Me, Cl) disproportionate in the presence of an alcohol or an alkoxide source, respectively, to yield the corresponding tris-adduct $\{PO\}_3Al$, thereby precluding access to Al alkoxide species of the type $\{PO\}_2AlOR$ under the studied conditions. Both $\{PO\}AlMe_2$ and $\{PO\}_2AlMe$ react fast with $B(C_6F_5)_3$ to yield the quantitative formation of stable and well-defined cationic Al species of the type $\{PO\}Al(Me)(THF)^+$ and $\{PO\}_2Al^+$, respectively, which are highly active in PO polymerization to yield atactic PPO via presumably a Lewis acid-assisted cationic mechanism. These cations also readily initiate the ROP of ε-CL via successive ring-opening insertions of the monomer into the $Al-O_{PhO}$ bond of the phosphinophenolate chelating ligand to exclusively afford ε-PCL capped, at the ester end, with a phosphinophenolate oxide group. Thus, in these cationic systems, the $\{PO\}^-$ chelating moiety may act as both a supporting ligand and an initiating group for the ROP of ε-CL.

Experimental Section

General Procedures. All experiments were carried out under N_2 using standard Schlenk techniques or in a Mbraun Unilab glovebox. Toluene, pentane, diethyl ether, and tetrahydrofuran were collected after going through drying columns (SPS apparatus, MBraun) and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. CH_2Cl_2, CD_2Cl_2, and C_6D_6 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. $B(C_6F_5)_3$ was purchased from Strem and used as received. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Asahi Glass Europe, while 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 over CaH_2 prior to use. NMR spectra were recorded on Bruker AC 300 or 400 MHz NMR spectrometers, in Teflon-valved J-Young NMR tubes at ambient temperature, unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. ^{11}B, ^{19}F, and ^{31}P chemical shifts are reported versus BF_3-Et_2O in CD_2Cl_2, neat $CFCl_3$, and 85% H_3PO_4 in aqueous solution, respectively. Elemental analyses for all compounds were performed at the Services de Microanalyse of the Université Pierre et Marie Curie (Paris, France) and the Université de Strasbourg (Strasbourg, France). SEC analyses were performed at the Institut Charles Sadron (Strasbourg, France) on a system equipped with a Shimadzu RID10A refractometer detector using dry THF (on CaH_2) as an eluant. Molecular weights and polydispersity indices (PDIs) were calculated using polystyrene standards. In the case of molecular weights, these were corrected with Mark−Houwink corrections for M_n [M_n(obsd) = $0.56M_n$(SEC)].[16] MALDI-TOF mass spectroscopic analyses were performed at the Service de Spectrométrie de Masse de l'Institut de Chimie de Strasbourg and run in a positive mode, and samples were prepared by mixing a solution of the polymers in CH_2Cl_2 with a 0.5 mg/100 mL concentration; 2,5-dihydroxybenzoic acid (DHB) was used as the matrix in 5:1 volume ratio.

All the salt species were obtained as dissociated Al cations and $MeB(C_6F_5)_3^-$ salts in solution. The NMR data for the $MeB(C_6F_5)_3^-$ anion are listed below for all of the compounds.

Data for $MeB(C_6F_5)_3^-$. ^1H NMR (400 MHz, CD_2Cl_2): δ 0.48 (B*Me*). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ −11.9 (br s, *B*Me). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 9.8 (br, B*Me*), 136.7 (d, $^1J_{CF}$ = 233 Hz, *m*-C_6F_5), 137.9 (d, $^1J_{CF}$ = 238 Hz, *p*-C_6F_5), 148.6 (d, $^1J_{CF}$ = 233 Hz, *o*-C_6F_5). ^{19}F NMR (376 MHz, CD_2Cl_2): δ −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 (m, $^3J_{FF}$ = 19 Hz, 2F, *m*-C_6F_5).

Phosphinophenols 1a−c. The *O,P* pro-ligands **1a−c** were all synthesized according to known literature procedures, and the NMR data for **1b** matched those reported in the literature.[6d,7]

Data for 2-PPh_2-6-Me-C_6H_3OH (1a):. 65% isolated yield. Anal. Calcd for $C_{19}H_{17}OP$: C, 78.07; H, 5.87. Found: C, 77.93; H, 5.76. ^1H NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H, Me), 6.30 (m, 1H, PhO), 6.70 (m, 1H, PhO), 6.74 (m, 1H, PhO), 7.23 (m, 10H, PPh_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 16.2 (Me), 120.1, 120.7, 124.5, 128.6, 128.9, 132.4, 132.9, 133.5, 135.2, 157.6. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −31.1.

Data for 2-PPh_2-4-Me-6-^{t}Bu-C_6H_2OH (1c):. 55% isolated yield. Anal. Calcd for $C_{23}H_{25}OP$: C, 79.29; H, 7.23. Found: C, 78.86; H, 7.32. ^1H NMR (300 MHz, C_6D_6): δ 1.51 (s, 9H, ^{t}Bu), 1.96 (s, 3H, Me), 6.91 (m, 1H, PhO), 6.96−7.00 (m, 6H, Ph), 7.20 (m, 1H, Ph), 7.32−7.38 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 20.7 (Me), 29.7 (^{t}Bu), 35.0 (^{t}Bu), 121.0, 128.8, 129.5, 130.5, 132.7, 133.6, 135.6, 136.3, 156.8 (one resonance is presumably obscured by the solvent peak). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −32.0.

{η^2-O,P-(2-PPh_2-6-Me-C_6H_3O)}$AlMe_2$ (2a), {η^2-O,P-(2-PPh_2-6-Ph-C_6H_3O)}$AlMe_2$ (2b), and {η^2-O,P-(2-PPh_2-4-Me-6-^{t}Bu-C_6H_2O)}$AlMe_2$ (2c). The three phosphinophenolate aluminum dimethyl complexes **2a−c** were all synthesized using an identical synthetic procedure and were isolated in good yields (**2a**, 78%; **2b**, 73%; **2c**, 82%). As an example, the experimental procedure for **2c** is described here.

In a glovebox filled with N_2, a pentane solution (5 mL) of $AlMe_3$ (52.6 mg, 0.729 mmol) and a 1:1 toluene/pentane solution (5 mL) of **1c** (254.0 mg, 0.729 mmol) are prepared in two separate vials and are stored in a freezer at −35 °C for 1 h. After this time, both vials were taken out and the phosphinophenol solution was added via a pipet to the $AlMe_3$ solution under vigorous stirring, which provoked immediate methane bubbling. The resulting colorless solution was allowed to warm to room temperature and then stirred for a couple of hours, after which it was evaporated to dryness to yield a colorless solid. Pure compound **2c** was obtained as colorless crystals (242 mg, 82% yield) from a 1:1 Et_2O/pentane solution stored overnight at −35 °C.

Data for 2a:. 78% yield (260 mg) from a Et_2O solution stored overnight at −35 °C. Anal. Calcd for $C_{21}H_{22}AlOP$: C, 72.40; H, 6.37. Found: C, 72.56; H, 6.19. ^1H NMR (300 MHz, CD_2Cl_2): δ −0.73 (d, $^3J_{HP}$ = 3.5 Hz, 6H, $AlMe_2$), 2.13 (s, 3H, Me), 6.72−6.86 (m, 2H, Ph), 7.20−7.23 (m, 1H, Ph), 7.35−7.45 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ −9.2 ($AlMe_2$), 16.5 (Me), 118.6 (*o*-PhO), 119.9 (*p*-PhO), 128.5 (Ph), 129.8 (Ph), 130.4 (C_{quat}), 130.6 (C_{quat}), 131.4 (Ph), 133.2 (Ph), 133.8 (Ph), 161.5 (C_{ipso}-PhO). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −27.8.

Data for 2b:. 73% yield (425 mg) from a Et_2O solution stored overnight at −35 °C. Anal. Calcd for $C_{26}H_{24}AlOP$: C, 76.09; H, 5.89. Found: C, 76.25; H, 5.86. ^1H NMR (300 MHz, C_6D_6): δ −0.23 (d, $^3J_{HP}$ = 4.1 Hz, 6H, $AlMe_2$), 6.76 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ph), 7.04−7.27 (m, 15H, Ph), 7.85 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ −9.2 (AlMe), 117.9, 126.4, 128.1, 128.8, 129.4, 130.0, 130.9, 131.6, 132.8, 133.3, 133.5, 134.2, 139.9, 160.3 (C_{ipso}-PhO). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −29.8.

Data for 2c:. 82% yield (242 mg) from a 1:1 Et_2O/pentane solution stored overnight at −35 °C. Anal. Calcd for $C_{24}H_{28}AlOP$:

C, 73.83; H, 7.23. Found: C, 73.98; H, 7.19. ^{1}H NMR (300 MHz, C_6D_6): δ −0.18 (d, $^3J_{HP}$ = 4.0 Hz, 6H, $AlMe_2$), 1.61 (s, 9H, ^{t}Bu), 2.01 (s, 3H, Me), 6.86−6.94 (m, 7H, Ph), 7.27−7.34 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ −9.8 ($AlMe_2$), 20.9 (Me), 29.8 (^{t}Bu), 35.6 (^{t}Bu), 115.5 (C_{quat}), 116.0 (C_{quat}), 127.3 (C_{quat}), 129.2 (Ph), 130.7 (Ph), 131.0 (Ph), 132.9 (Ph), 133.5 (Ph), 139.8 (C_{quat}), 165.0 (C_{ipso}-PhO). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −26.6.

{η^2-O,P-(2-PPh_2-6-Ph-C_6H_3O)}$_2$AlMe (3b) and {η^2-O,P-(2-PPh_2-4-Me-6-^{t}Bu-C_6H_2O)}$_2$AlMe (3c). The bis-phosphinophenolate aluminum dimethyl complexes **3b** and **3c** were both synthesized using the same synthetic procedure and were isolated in 65% and 61% yield, respectively. The experimental procedure for **3c** is described below.

In a glovebox filled with N_2, a toluene solution (3 mL) of $AlMe_3$ (82.0 mg, 1.14 mmol) and a toluene solution (10 mL) of phosphinophenol **1c** (793.0 mg, 2.28 mmol) were prepared in two separate vials and stored in a freezer at −35 °C for 1 h. After this time, both vials were taken out, and the phosphinophenol solution was added via a pipet to the $AlMe_3$ solution under vigorous stirring, which provoked immediate methane bubbling. The resulting colorless solution was allowed to warm to room temperature and then stirred for a couple of hours, after which it was evaporated to dryness to yield a colorless foam. Addition of pentane and subsequent trituration provoked the precipitation of a colorless solid, which was filtered through a glass frit. Drying of the latter solid *in vacuo* afforded pure **3c** (510 mg, 61% yield).

Data for 3b:. 65% yield (452 mg) in a similar manner to that used for compound **3c**. Anal. Calcd for $C_{49}H_{39}AlO_2P_2$: C, 78.60; H, 5.25. Found: C, 78.93; H, 5.02. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −0.60 (t, $^3J_{HP}$=4.1 Hz, 3H, AlMe), 6.89 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ph), 7.14−7.41 (m, 30H, Ph), 7.65 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ −9.9 (AlMe), 118.9, 126.5, 127.5, 127.8, 128.4, 128.6, 129.4, 129.5, 132.8, 133.3, 133.5, 133.7, 139.8, 155.2 (C_{ipso}-PhO). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −35.3.

Data for 3c:. 61% yield. Anal. Calcd for $C_{47}H_{51}AlO_2P_2$: C, 76.61; H, 6.98. Found: C, 76.95; H, 6.89. ^{1}H NMR (300 MHz, C_6D_6): δ −0.14 (t, $^3J_{HP}$ = 3.8 Hz, 3H, AlMe), 1.64 (s, 18H, ^{t}Bu), 2.05 (s, 6H, Me), 6.92−6.97 (m, 12H, Ph), 7.01 (d, $^4J_{HH}$ = 1.5 Hz, 2H, PhO), 7.31 (d, $^4J_{HH}$ = 1.5 Hz, 2H, PhO), 7.53−7.57 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ −8.3 (AlMe), 21.0 (Me), 30.1 (^{t}Bu), 35.5 (^{t}Bu), 119.7 (C_{quat}), 119.9 (C_{quat}), 128.9 (Ph), 129.6 (Ph), 131.6 (Ph), 131.9 (Ph), 133.0 (C_{quat}), 133.8 (Ph), 139.6 (C_{quat}), 162.8 (C_{ipso}-PhO). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −31.2.

{η^2-O,P-(2-PPh_2-4-Me-6-^{t}Bu-C_6H_2O)}$_2$AlCl (4c). In a nitrogen-filled glovebox, ^{n}BuLi (750.0 μL of a 1.6 M pentane solution, 1.20 mmol) was added dropwise via a syringe to a precooled (−35 °C) pentane solution (5 mL) of phosphinophenol **1c**. After the addition was completed, the resulting pale yellow solution was stirred for 1 h at room temperature, after which it was evaporated to dryness to afford an off-white solid residue. The latter solid was subsequently washed twice with cold pentane to yield the presumed phosphinophenolate Li salt [2-PPh_2-4-Me-6-^{t}Bu-C_6H_3O]Li (223 mg, 0.663 mmol) as a colorless solid, which was used as is. Thus, the latter Li salt was dissolved in 5 mL of toluene, and the resulting solution was added all at once (via a pipet) to a precooled (−35 °C) 1:1 THF/toluene solution (3 mL) of 0.5 equiv of $AlCl_3$ (42.0 mg, 0.330 mmol). The initially pale yellow solution became cloudy upon warming to room temperature due to the formation of LiCl. The reaction mixture was stirred at room temperature overnight, after which the volatiles were removed *in vacuo* to yield a colorless solid. Toluene was then added, and the resulting suspension was filtered through a glass frit; subsequent evaporation of the mother liquor afforded crude **4c**, which was isolated in pure form from a Et_2O solution stored at −35 °C overnight (249 mg, 69% yield). Anal. Calcd for $C_{46}H_{58}AlClO_2P_2$: C, 72.96; H, 6.39. Found: C, 72.55; H, 6.55. ^{1}H NMR (300 MHz, C_6D_6): δ 1.51 (s, 18H, ^{t}Bu), 2.03 (s, 6H, Me), 6.95−7.00 (m, 12H, Ph), 7.1 (d, $^4J_{HH}$ = 1.5 Hz, 2H, PhO), 7.28 (d, $^4J_{HH}$ = 1.5 Hz, 2H, PhO), 7.82 (br m, 8H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 20.9 (Me), 30.0 (^{t}Bu), 35.2 (^{t}Bu), 118.9 (C_{quat}), 119.4 (C_{quat}), 128.9 (Ph), 129.3 (C_{quat}), 130.1 (Ph), 130.6 (Ph), 132.1 (Ph), 134.3 (Ph), 133.8 (Ph), 139.2 (C_{quat}), 161.9 (C_{ipso}-PhO). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −36.5.

{η^2-O,P-(2-PPh_2-4-Me-6-^{t}Bu-C_6H_2O)}$_3$Al (5c). In an attempt to prepare the Al-O^{i}Pr complex {η^2-O,P-(2-PPh_2-6-^{t}Bu-C_6H_2O)}$_2$-AlO^{i}Pr by reaction between the phosphinophenol **1c** and Al(O^{i}Pr)$_3$, the tris-phosphinophenolate Al complex **5c** was instead prepared, as described below.

NMR-Scale Reaction. In a nitrogen-filled glovebox, 2 equiv of compound **1c** (30.0 mg, 0.0861 mmol) and 1 equiv of Al(O^{i}Pr)$_3$ (8.8 mg, 0.043 mmol) were charged in a J-young NMR tube and dissolved in 0.75 mL of C_6D_6 to yield a pale yellow solution. While no reaction occurred at room temperature after 18 h, as deduced from NMR monitoring, the concomitant formation of the Al-O^{i}Pr complex {η^2-O,P-(2-PPh_2-6-^{t}Bu-C_6H_2O)}$_2$AlO^{i}Pr and the tris-adduct **5c** was observed upon heating the reaction mixture at 80 °C. Compound **5c** remained the major product all along the reaction, and complete conversion (along with unidentified organoaluminum species) was observed after 18 h at 80 °C.

Preparative-Scale Reaction. Two equivalents of compound **1c** (300.0 mg, 0.861 mmol) and 1 equiv of Al(O^{i}Pr)$_3$ (87.8 mg, 0.430 mmol) were charged in a 10 mL vial sample equipped with a Teflon-capped screw-cap and dissolved in 5 mL of toluene. The resulting pale yellow solution was heated to 80 °C for 12 h, after which it was stored at −35 °C, which allowed the crystallization of compound **5c** as a colorless solid in an analytically pure form (255 mg, 83% yield). Anal. Calcd for $C_{69}H_{72}AlO_3P_3$: C, 77.51; H, 6.79. Found: C, 77.32; H, 6.85. ^{1}H NMR (300 MHz, C_6D_6): δ 1.75 (s, 27H, ^{t}Bu), 1.89 (s, 9H, Me), 6.49 (br m, 6H, Ph), 6.72−6.94 (m, 21H, Ph), 7.34 (d, $^4J_{HH}$ = 1.5 Hz, 3H, PhO), 7.51 (br m, 6H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 20.2 (Me), 29.6 (^{t}Bu), 34.9 (^{t}Bu), 118.0 (C_{quat}), 118.4 (C_{quat}), 128.9 (Ph), 129.6 (Ph), 131.6 (Ph), 131.9 (Ph), 132.9 (C_{quat}), 134.7 (Ph), 138.1 (C_{quat}), 162.7 (C_{ipso}-PhO). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ −30.4.

[{η^2-O,P-(2-PPh_2-6-Ph-C_6H_3O)}Al(Me)(THF)][$MeB(C_6F_5)_3$]- ([6b][$MeB(C_6F_5)_3$]) and [{η^2-O,P-(2-PPh_2-4-Me-6-^{t}Bu-C_6H_2O)}Al-(Me)(THF)][$MeB(C_6F_5)_3$] ([6c][$MeB(C_6F_5)_3$]). In a nitrogen-filled glovebox, an equimolar amount of the neutral dimethyl Al precursor **2b** or **2c** (**2b**, 80.2 mg; **2c**, 79.0 mg, 0.195 mmol) and $B(C_6F_5)_3$ (100.0 mg, 0.195 mmol) were charged in a small Schlenk flask and dissolved in THF (3 mL) to yield a colorless solution, which was stirred at room temperature for 1 h. The resulting colorless solution was evaporated to dryness to afford a pale yellow foam, to which cold pentane was added, causing the formation of a colorless solid. Subsequent drying *in vacuo* of the latter solid and NMR analysis identified it as the salt species [**6b**][$MeB(C_6F_5)_3$] (145 mg, 75% yield) or [**6c**][$MeB(C_6F_5)_3$] (158 mg, 82% yield) in a pure form.

Data for [6b][$MeB(C_6F_5)_3$]. Anal. Calcd for $C_{48}H_{32}AlBF_{15}O_2P$: C, 57.97; H, 3.24. Found: C, 58.23; H, 3.56. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −0.21 (d, $^3J_{HP}$ = 5.0 Hz, 3H, AlMe), 1.99 (br, 4H, THF), 4.21 (br, 4H, THF), 6.75 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ph), 7.32−7.58 (m, 15H, Ph), 7.84 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ −6.2 (AlMe), 24.3 (THF), 70.5 (THF), 117.9, 126.1, 126.9, 127.4, 128.6, 129.0, 129.4, 129.9, 132.9, 133.6, 134.0, 134.7, 139.5, 156.2 (C_{ipso}-PhO). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −38.1.

Data for [6c][$MeB(C_6F_5)_3$]. Anal. Calcd for $C_{47}H_{38}AlBF_{15}O_2P$: C, 57.10; H, 3.87. Found: C, 57.63; H, 4.12. ^{1}H NMR (300 MHz, CD_2Cl_2): δ −0.12 (d, $^3J_{HP}$ = 5.4 Hz, 3H, AlMe), 1.47 (s, 9H, ^{t}Bu), 1.94 (4H, THF), 2.24 (s, 3H, Me), 4.16 (4H, THF), 6.91 (m, 1H, Ph), 7.34 (br s, 1H, Ph), 7.33−7.56 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ −7.1 (AlMe), 22.0 (Me), 27.3 (THF), 30.1 (^{t}Bu), 36.2 (^{t}Bu), 72.4 (THF), 116.5 (C_{quat}), 116.9 (C_{quat}), 128.3 (C_{quat}), 129.9 (Ph), 131.7 (Ph), 132.0 (Ph), 132.9 (Ph), 133.8 (Ph), 142.3 (C_{quat}), 162.4 (C_{ipso}-PhO). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ −34.8.

[{η^2-O,P-(2-PPh$_2$-6-Ph-C$_6$H$_3$O)}$_2$Al][MeB(C$_6$F$_5$)$_3$] ([7b][MeB(C$_6$F$_5$)$_3$]) and [{η^2-O,P-(2-PPh$_2$-4-Me-6-^{t}Bu-C$_6$H$_2$O)}$_2$Al][MeB(C$_6$F$_5$)$_3$] ([7c][MeB(C$_6$F$_5$)$_3$]). In a nitrogen-filled glovebox, an equimolar amount of the neutral bis-phosphinophenolate methyl Al precursor **3b** or **3c** (**3b**, 146.0 mg; **3c**, 143.7 mg, 0.195 mmol) and B(C$_6$F$_5$)$_3$ (100.0 mg, 0.195 mmol) were charged in a small Schlenk flask and dissolved in CH_2Cl_2 (3 mL) to yield a colorless solution, which was stirred at room temperature for 1 h. The resulting colorless solution was evaporated to dryness to afford a pale yellow foam, to which cold pentane was added, causing the formation of a colorless solid. Subsequent drying *in vacuo* of the latter solid and NMR analysis identified it as the salt species [**7b**][MeB(C$_6$F$_5$)$_3$] (175 mg, 71% yield) or [**7c**][MeB(C$_6$F$_5$)$_3$] (146 mg, 60% yield) in a pure form.

Data for [7b][MeB(C$_6$F$_5$)$_3$]. Anal. Calcd for $C_{67}H_{39}AlBF_{15}O_2P_2$: C, 63.83; H, 3.12. Found: C, 64.25; H, 3.33. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.96 (t, $^3J_{HH}$ = 7.9 Hz, 2H, Ph), 7.35−7.69 (m, 30H, Ph), 8.12 (d, $^3J_{HH}$ = 7.8 Hz, 4H, Ph). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 117.0, 124.3, 125.7, 127.8, 128.2, 129.0, 129.5, 130.7, 133.9, 134.8, 135.0, 136.7, 139.5, 154.7 (C$_{ipso}$-PhO). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ −38.1.

NMR data for [7c][MeB(C$_6$F$_5$)$_3$]. Anal. Calcd for $C_{65}H_{51}AlBF_{15}O_2P_2$: C, 62.51; H, 4.12. Found: C, 62.73; H, 4.22. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.45 (s, 18H, ^{t}Bu), 2.28 (s, 6H, Me), 7.03 (m, 2H, Ph), 7.42−7.48 (m, 18H, Ph), 7.62 (m, 4H, Ph). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 20.2 (Me), 28.8 (^{t}Bu), 34.9 (^{t}Bu), 111.7 (C$_{quat}$), 120.7 (C$_{quat}$), 129.7 (Ph), 130.0 (Ph), 130.1 (Ph), 131.5 (C$_{quat}$), 132.9 (Ph), 135.0 (Ph), 139.9 (C$_{quat}$), 160.4 (C$_{ipso}$-PhO). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ −36.3.

Generation of [{η^2-O,P-(2-PPh$_2$-4-Me-6-^{t}Bu-C$_6$H$_2$O)}$_2$Al(NMe$_2$Ph)][MeB(C$_6$F$_5$)$_3$] ([8c][MeB(C$_6$F$_5$)$_3$]). In a nitrogen-filled glovebox, a J-young NMR tube was charged with the salt species [**7c**][MeB(C$_6$F$_5$)$_3$] (40 mg, 0.032 mmol) and dissolved in 0.75 mL of CD_2Cl_2. *N,N*-Dimethylaniline (4.1 μL, 0.032 mmol) was then syringed in the NMR tube. The tube was tightly capped and vigorously shaken, and a ^{1}H NMR spectrum was immediately recorded showing the quantitative formation of the Al-NMe$_2$Ph cationic adduct {η^2-O,P-(2-PPh$_2$-4-Me-6-^{t}Bu-C$_6$H$_3$-O)}Al(NMe$_2$Ph)$^+$ (**8c**$^+$).

NMR data for 8c$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.33 (s, 18H, ^{t}Bu), 2.28 (s, 6H, Me), 2.90 (s, 6H, NMe), 6.92−6.99 (m, 6H, Ph), 7.11−7.18 (m, 10H, Ph), 7.27 (br, 6H, Ph), 7.38 (s, 2H, Ph), 7.45−7.51 (m, 5H, Ph). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 20.2 (Me), 29.6 (^{t}Bu), 34.7 (^{t}Bu), 49.6 (br, NMe), 113.7 (C$_{quat}$), 114.3 (C$_{quat}$), 120.0 (Ph), 128.0 (Ph), 129.1 (Ph), 129.7 (C$_{quat}$), 129.9 (Ph), 130.1 (Ph), 131.1 (Ph), 132.9 (Ph), 133.8 (Ph), 138.2 (C$_{quat}$), 145.1 (C$_{ipso}$-PhN), 160.3 (C$_{ipso}$-PhO). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ −37.3.

Typical Procedure for ε-Caprolactone Polymerization. In a nitrogen-filled glovebox, the Al initiator (0.0150 mmol) was charged in a 5 mL sample vial (equipped with a magnet stirring bar) and dissolved in 1.50 mL of toluene. One hundred equivalents of ε-caprolactone (172.6 mg, 1.50 mmol) was then added; the sample was tightly closed with a Teflon-tight screw-cap, and the mixture was heated to the appropriate temperature for the desired time. After this time, an aliquot was then taken and an ^{1}H NMR spectrum was then recorded to determine the monomer conversion. The overall reaction mixture was quenched with MeOH and a few drops of acetic acid, provoking the precipitation of poly(ε-caprolactone) as a colorless solid. This solid was washed several times and dried *in vacuo* until constant weight, after which it was subjected to NMR and SEC analysis as well as, in one case, to MALDI-TOF mass spectrometry.

Typical Procedure for Propylene Oxide Polymerization. In a nitrogen-filled glovebox, the Al initiator (0.0150 mmol) was charged in a 5 mL sample vial (equipped with a magnet stirring bar) and dissolved in 1.50 mL of toluene. One hundred equivalents of propylene oxide (88 mg, 1.50 mmol) was then added; the sample was tightly closed with a 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 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 colorless oil that revealed to be atactic poly(propylene oxide) (PPO), as deduced from ^{1}H and ^{13}C{^{1}H} NMR analysis. All PPO samples were analyzed by SEC.

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Supporting Information Available: Crystallographic data for compounds **2c**, **3b**, **3c**, **5c**, and **7c** and an ORTEP drawing of the Al complex **3b** as well as the MALDI-TOF spectrum of the ε-PCL obtained by ROP of ε-CL initiated by cation **7b**$^+$. This material is available free of charge via the Internet at http://pubs.acs.org.