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Aminoarenethiolate Aluminum Complexes: Synthesis, Characterization, and Use in L-Lactide Polymerization

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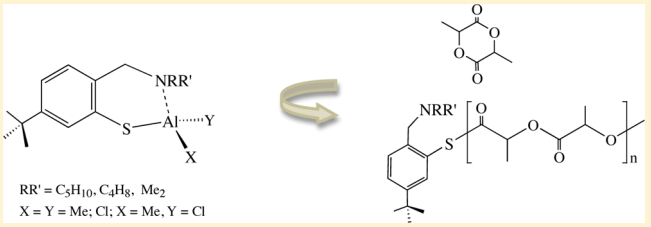
Supporting Information

ABSTRACT: Reaction of $AlMe_3$ with $S(SiMe_3)(C_6H_3\text{-}2\text{-}CH_2NRR'\text{-}5\text{-}^tBu)$ (RR′ = C_5H_{10} (**1a**), C_4H_8 (**1b**), Me_2 (**1c**)), at ambient temperature, affords the amino adducts $[AlMe_3\{S(SiMe_3)(C_6H_3\text{-}2\text{-}CH_2NRR'\text{-}5\text{-}^tBu)\}\text{-}\kappa N]$ (RR′ = C_5H_{10} (**2a**), C_4H_8 (**2b**), Me_2 (**2c**)), which undergo TMS elimination upon heating to give the monomeric aminoarenethiolate aluminum complexes $[AlMe_2\{S(C_6H_3\text{-}2\text{-}CH_2NRR'\text{-}5\text{-}^tBu)\text{-}\kappa^2S,N\}]$ (RR′ = C_5H_{10} (**3a**), C_4H_8 (**3b**), Me_2 (**3c**)). Following the same procedure, treatment of $AlCl_2Me$ and $AlCl_3$ with **1** yields analogous aminoarenethiolate aluminum complexes with different degrees of methylation, the chloro methyl and dichloro complexes $[AlClMe\{S(C_6H_3\text{-}2\text{-}CH_2NRR'\text{-}5\text{-}^tBu)\text{-}\kappa^2S,N\}]$ (RR′ = C_5H_{10} (**4a**), C_4H_8 (**4b**), Me_2 (**4c**)) and $[AlCl_2\{S(C_6H_3\text{-}2\text{-}CH_2NRR'\text{-}5\text{-}^tBu)\}\text{-}\kappa^2S,N]$ (RR′ = C_5H_{10} (**5a**), C_4H_8 (**5b**) Me_2 (**5c**)), respectively. These complexes have been characterized by multinuclear NMR spectroscopy and elemental analysis. Moreover, the molecular structures of **3a**,**b** have been determined by X-ray diffraction methods. Aluminum complexes **3** have been investigated for the ring-opening polymerization (ROP) of L-lactide, achieving high conversions in relatively short periods of time. The PLAs obtained feature an aminoarenethiolate end functionality, as inferred from MALDI-TOF mass analysis.



INTRODUCTION

Polylactic acid (PLA) is a highly versatile and biodegradable aliphatic polyester derived from 100% renewable resources, such as corn and sugar beets.[1] The combination of such characteristics and its well-suited mechanical and physical properties make PLA an environmentally friendly and sustainable alternative to traditional petrochemical-based plastics, mainly in packaging, coating, and fiber applications.[2] In addition, PLA is suitable for more sophisticated fields such as scaffolds in tissue repair and engineering, in drug-controlled delivery systems, and in microelectronics.[3]

Among the wide variety of ways exploited, the ring-opening polymerization (ROP) of lactide (LA) promoted by organometallic compounds via a coordination−insertion mechanism represents the most efficient and versatile method to prepare PLAs with controlled microstructural properties such as molecular weight, polydispersity, and stereoregularity.[2a,3b,4] Although the activity of aluminum species is significantly lower than that of other metals, typically used in these processes, they generally exert good polymerization control. Thus, a wide variety of aluminum(III) compounds, particularly those supported by Salen or Salan ancillary ligands, have been demonstrated to show excellent molecular weight and stereochemical control in the ROP of lactide.[5]

The majority of organometallic complexes tested in ROP bearing multidentate ligands contain, in various combinations, nitrogen and oxygen hard donor atoms.[6] In contrast, thus far, monoanionic chelating ligands incorporating soft donors, either anionic or neutral, coordinated to a hard metal center are scarce, even though recent reports have shown that the use of ancillary ligands with softer donors could affect the Lewis acidity of the metal center, with remarkable effects on catalytic performance.[7]

In contrast, the synthesis of well-defined aliphatic polyesters with precisely controlled end-group functionalities is a target of current interest. In this regard, aluminum thiolates have proved excellent initiators to prepare polyesters with an end thioester, a functional group that may next be utilized in further chemical reactions, making them useful candidates in a wide variety of applications.[8] For instance, dimethylaluminum thiolates $AlMe_2(SR)$ initiate polymerization of lactones in a living fashion, leading to the formation of heterobifuntional polyesters (i.e., one hydroxy functional end and one thioester, −COSR′, end group), which further reacts with poly(ethylene glycol) (PEG) derivatives, affording a PCL-PEG copolymer.[8b]

With this in mind, we decided to explore the formation of aluminum derivatives by coordinating different bidentate aminothiolate ligands to be tested as a catalyst/initiator in the polymerization of L-lactide. Herein, we report the synthesis and structural characterization of novel aluminum complexes bearing an aminoarenethiolate ligand with the aim of studying their catalytic performance in the ring-opening polymerization of L-lactide and analyze the role played by the thiolate group in

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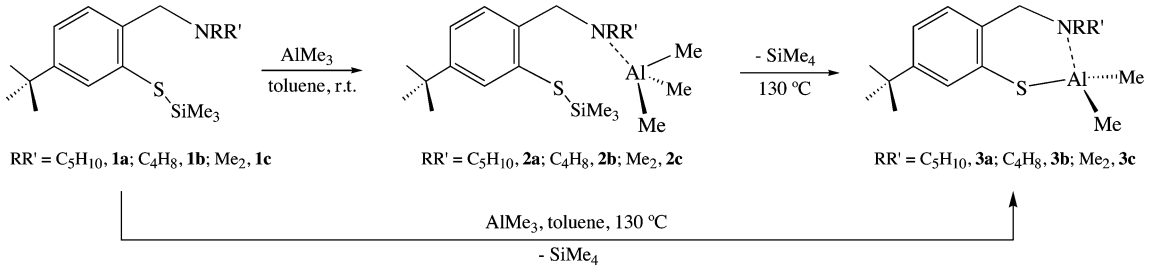
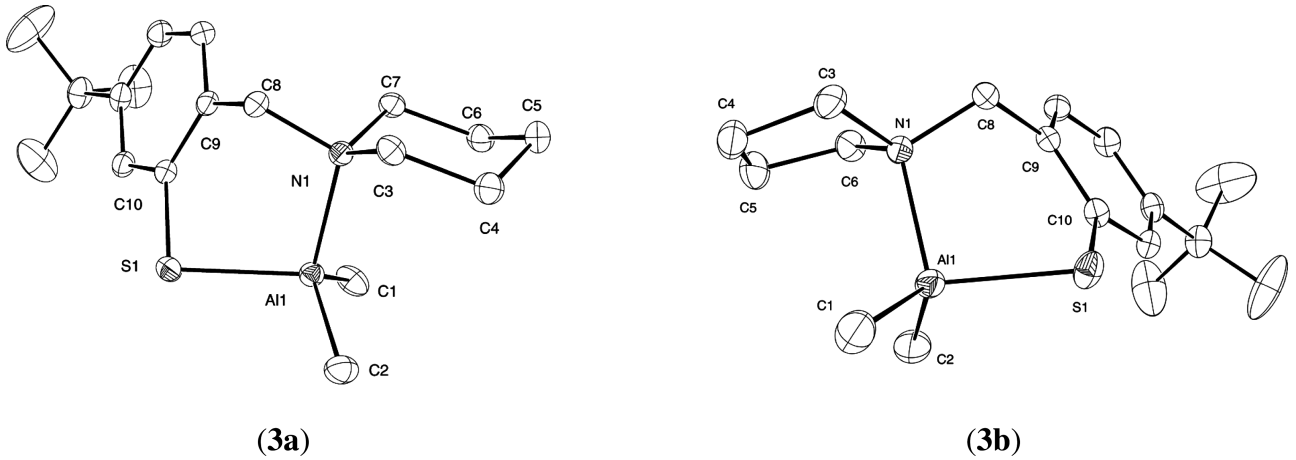
Scheme 1. Reactions of $AlMe_3$ with Trimethylsilyl-Protected Aminoarenethiolates





(3a) (3b)

Figure 1. X-ray structures of **3a,b**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

the process, either as a supporting ligand or as an initiator group.

RESULTS AND DISCUSSION

Synthesis of Aminoarenethiolate Aluminum Complexes. Following the protocol established by van Koten et al. to synthesize arenethiolate copper[9] and zinc[10] derivatives, we decided to explore the synthesis of the targeted complexes using trimethylsilyl-protected aminoarenethiolate proligands $S(SiMe_3)(C_6H_3\text{-}2\text{-}CH_2NRR'\text{-}5\text{-}^tBu)$ (RR′ = C_5H_{10} (**1a**), C_4H_8 (**1b**), Me_2 (**1c**)).[9a]

Reaction of $AlMe_3$ with an equimolar amount of the corresponding trimethylsilyl-protected aminoarenethiolate proligands **1** at room temperature affords a mixture of two new aluminum derivatives in the molar ratio 9:1 (as observed by ^1H NMR). The major component of the reaction mixture is the four-coordinated adduct $[AlMe_3\{S(SiMe_3)(C_6H_3\text{-}2\text{-}CH_2NRR'\text{-}5\text{-}^tBu)\}\text{-}\kappa N]$ (RR′ = C_5H_{10} (**2a**), C_4H_8 (**2b**), Me_2 (**2c**)), with the amine nitrogen coordinated to the aluminum atom, as inferred from the NMR study. Such behavior is in agreement with the strong tendency shown by $AlMe_3$ to form four-coordinate adducts, as reported elsewhere.[5d] The minor compound is the corresponding monomeric dimethyl aluminum complex $[AlMe_2\{S(C_6H_3\text{-}2\text{-}CH_2NRR'\text{-}5\text{-}^tBu)\}\text{-}\kappa^2S,N]$ (RR′ = C_5H_{10} (**3a**) C_4H_8 (**3b**), Me_2 (**3c**)), which bears a chelating monoanionic aminoarenethiolate ligand, stemming from the elimination of $SiMe_4$ (Scheme 1).

Compounds **2** can be isolated from the reaction mixture by fractional crystallization from *n*-hexane, in only modest to poor yields (40−45%). Unfortunately, although these compounds are obtained as NMR pure compounds, their microanalyses values are not optimal, due to their oily nature.

On heating the aforementioned mixture at 130 °C for 3 days, the amino adducts **2** evolve $SiMe_4$, affording the corresponding aminoarenethiolate dimethyl complexes **3** in a quantitative manner, as judged by NMR spectroscopy (Scheme 1). After workup, complexes **3** are isolated as white crystalline solids in high yield (78−82%). Complexes **3** are conveniently prepared when the reaction of **1** with $AlMe_3$ is carried out at 130 °C.

Although compounds **2** and **3** are very moisture sensitive in solution, they are thermally stable at room temperature and their solutions can be kept under rigorously dry conditions for a long period of time without noticeable decomposition, enabling suitable crystals for X-ray analysis to be obtained for some of them. Both types of complexes are quite soluble in most common solvents.

The spectroscopic behavior of compounds **2** and **3** is in agreement with C_s symmetry in solution, consistent with the proposed structures. A striking spectroscopic feature of the ^1H NMR spectra of the amino adduct **2** is the presence of two sharp singlets at high field of equal intensity, each integrating for nine protons, confirming the coordination of the $AlMe_3$ moiety (δ −0.16 (**2a**), −0.30 (**2b**), −0.30 (**2c**)) along with retention of the $SiMe_3$ group (δ 0.15 (**2a**), −0.09 (**2b**), 0.07 (**2c**)) in the molecule. According to the aforementioned symmetry, protons ascribed to the Ar−CH_2−N methylene group are equivalent, as are each pair of methylene (in **2a,b**) or methyl groups (in **2c**) of the fragment "RR" attached to nitrogen. However, unlike the case for the free ligand, each pair of protons CH_2 of the piperidinyl and pirrodinyl rings is nonequivalent, as shown by ^1H−^{13}C HMQC and ^1H-TOCSY measurements, a consequence of the coordination of the nitrogen atom to aluminum. Complexation with aluminum blocks the inversion of the tertiary nitrogen and differentiates

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the geminal protons of all piperidinyl and pirrodinyl methylene moieties.[11]

The features of the ^{1}H NMR spectra of complexes **3** are similar to those observed in the spectra of compounds **2**, except for the disappearance of the singlet ascribed to the $SiMe_3$ group and a one-third decrease of the relative intensity of the resonance attributed to magnetically equivalent methyls on aluminum, which confirms the elimination of TMS and the formation of the desired thiolate complex.

The ^{13}C NMR spectra of these complexes are consistent with those predicted, in agreement with the C_s symmetry of these species in solution. A relevant feature of these spectra is the number of resonances for the carbon atoms of the piperidinyl and pyrrodinyl rings, three (21.5, 22.6, 51.3, **2a**; 21.5, 24.7, 53.8, **3a**) and two (24.4, 52.0, **2b**; 22.0, 55.8, **3b**), respectively, which confirms the equivalence of each pair of the methylene groups of these heterocycles.

Single crystals of **3a**,**b** suitable for X-ray diffraction analysis were grown in hexane solutions at −10 °C, and the molecular structure was established by X-ray diffraction studies. Molecular structures of **3a**,**b** are illustrated in Figure 1, and selected bond lengths and angles are given in Table 1. These complexes crystallize in the monoclinic system.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3a,b

	3a	3b
Al(1)−S(1)	2.2712(11)	2.2673(10)
Al(1)−N(1)	2.059(2)	2.041(2)
Al(1)−C(1)	1.967(3)	1.965(3)
Al(1)−C(2)	1.965(3)	1.953(3)
S(1)−C(10)	1.771(3)	1.778(2)
N(1)−Al(1)−S(1)	101.38(7)	99.50(6)
C(1)−Al(1)−S(1)	109.37(11)	110.36(11)
C(1)−Al(1)−C(2)	120.07(15)	117.72(16)
C(1)−Al(1)−N(1)	108.33(12)	109.70(11)
C(10)−S(1)−Al(1)	96.74(9)	93.30(8)

X-ray diffraction analysis establishes the monomeric nature of both complexes and confirms that the aluminum atom bears a monoanionic *S*,*N*-chelating arenethiolate ligand. The resulting Al(1)−S(1)−C(10)−C(9)−C(8)−N(1) six-membered metallacycle displays a twisted-boat conformation, with the sulfur and methylenic carbon atoms occupying the upper positions. Instead, the piperidinyl and pirrodinyl rings adopt chair and half-chair conformations, respectively, with the aluminum atom located in an *axial* disposition.

The tetracoordinated aluminum atom has a distorted-tetrahedral geometry, which is apparent from the N−Al−S bite angles of 101.38(7) and 99.50(6)° in **3a**,**b**, respectively. Also, the angles C−S−Al of 96.74(9) and 93.30(8)° in **3a**,**b**, respectively, are too acute for an sp^3-hybridized sulfur atom. The bond distances of Al−C (1.967(3), 1.965(3) Å in **3a** and 1.953(3), 1.965(3) Å in **3b**), Al−S (2.2712(11) Å in **3a** and 2.2673(10) Å in **3b**) and Al−N (2.059(3) Å in **3a** and 2.041(2) Å in **3b**) are all within the expected range for tetracoordinated aluminum complexes.[12]

In an attempt to improve the synthetic strategy for the dimethyl aluminum complexes **3**, we envisioned that the use of $AlClMe_2$ would allow more convenient experimental conditions, via a classical $SiClMe_3$ elimination route. Thus, we tested the reaction of $AlClMe_2$ with an equimolar amount of the appropriate compound **1**; these reactions actually proceed at room temperature and occur much faster than previously described. However, such reactions are not specific and along with the targeted compound **3** the formation of the new chloro methyl aminoarenethiolate complex [AlClMe{S(C_6H_3-2-CH_2NRR′-5-^{t}Bu)}-κ^2*S*,*N*] (RR′ = C_5H_{10} (**4a**) C_4H_8 (**4b**), Me_2 (**4c**)) is observed, in a low molar ratio, ∼8 (**3**):2 (**4**). The formation of complexes **4** involves the competitive elimination of $SiMe_4$ (Scheme 2). A similar outcome is reached when $AlCl_2Me$ is used as the starting material; in this case the major component of the reaction mixture is the expected complex **4**, contaminated with a minimal amount (below a molar ratio of 5%) of the corresponding dichloro derivatives [$AlCl_2${S(C_6H_3-2-CH_2NRR′-5-^{t}Bu)}-κ^2*S*,*N*] (RR′ = C_5H_{10} (**5a**), C_4H_8 (**5b**), Me_2 (**5c**)). To verify the nature of the latter, complexes **5** are specifically prepared, on an NMR tube scale, by treatment of $AlCl_3$ with a stoichiometric amount of the appropriate compound **1**. Consequently, the dichloro aminoarenethiolate complexes **5** have been characterized only by NMR spectroscopy.

None of these reactions afforded the transient amino adduct analogous to those isolated in the reactions with $AlMe_3$, probably because the higher acidity of the aluminum atom in the chloro derivatives favors the next substitution process, as inferred from the increased rate and greater facility with which these reactions proceed at room temperature. Complexes **4** are obtained as analytically pure white solids by fractional crystallization from toluene, in moderate yields (60−65%).

Due to the chirality shown by complexes **4**, their ^{1}H NMR spectra feature more complexity than those of complexes **3**. Thus, the arene−CH_2 protons display two doublets (J = 12 Hz) in the range 3−4 ppm and, additionally, all the pairs of the methylene (in **4a**,**b**) or methyl groups (in **4c**) of the fragment "RR′" attached to nitrogen are diastereotopic. Rather, the spectroscopic behavior of complexes **5** is parallel to that analyzed for complexes **3**, apart from the absence of resonances at high field attributed to the methyl groups bound to aluminum. The ^{13}C NMR spectra of these complexes are consistent with those predicted. Thus, whereas the ^{13}C NMR spectra of complexes **5a**−**c** show only three (20.9, 22.0, 54.0), two (21.7, 55.6), and one resonances (46.7), respectively, for the RR′ moiety attached to the nitrogen atom, those of compounds **4** feature five (21.0, 21.2, 22.3, 53.1, 54.4), four (21.7, 21.8, 54.4, 55.7), and two resonances (44.0, 47.0) for **4a**−**c**, respectively.

Since alkoxide ligands have been habitually used as initiator groups for lactide polymerization, we attempted to replace the methyl groups, in complexes **3**, with alkoxide ligands by treatment of these with alcohols, a procedure that has proved a convenient synthetic strategy for aluminum alkoxide derivatives.[13] Unfortunately, all these reactions caused the elimination of the thiolate ligand with the formation of intractable mixtures of various aluminum species.[13a] In view of such results, the aminoarenethiolate chelating ligand seems to be more easily released than the methyl groups. However, we decided to test directly the dimethyl derivatives **3** in the polymerization of L-lactide and to explore the role of the *S*,*N*-chelating moiety in such processes, either as a supporting ligand or as an initiating group.

L-Lactide Polymerization Initiated by Complexes 3. The dimethyl aminoarenethiolate complexes **3** are assessed in the ring-opening polymerization of L-lactide (L-LA). Polymer-

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Scheme 2. Reactions of 1 with Different Chloro Aluminum Precursors

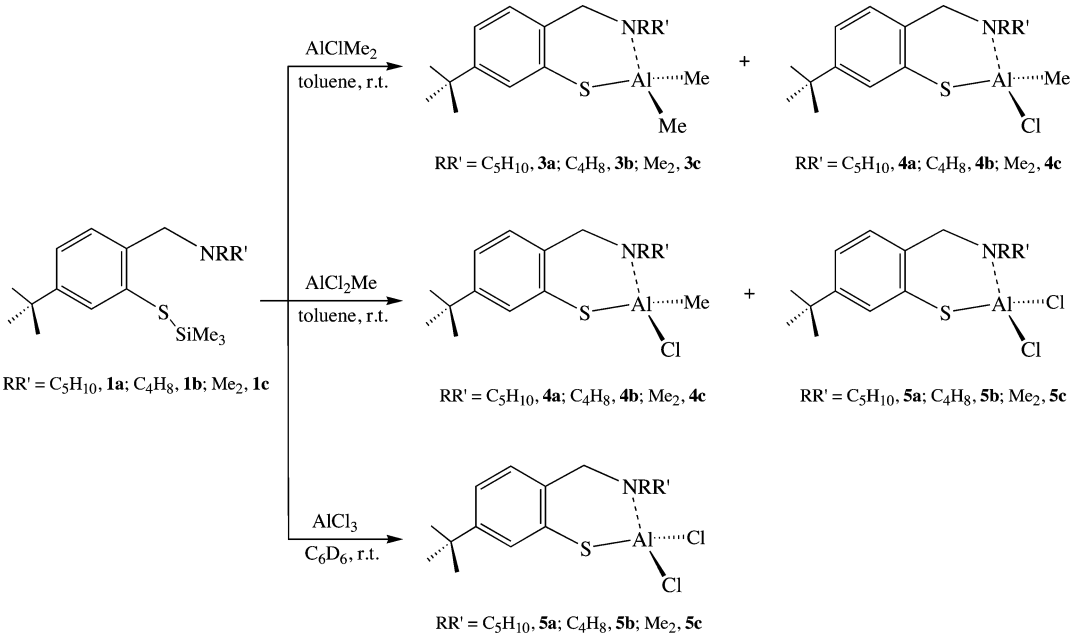

Table 2. L-Lactide Polymerization Initiated by Complexes 3

entry	initiator	[L-LA]/[Al]	time (h)	conversn (%)[b]	k_{app} (min^{-1})	M_n(calcd)[c]	M_n(obsd)[d]	M_w/M_n[d]
1	**3a**	100	4	85	8.00×10^{-3}	12240	12100	1.54
2	**3b**	100	4	80	7.64×10^{-3}	11520	13800	2.34
3	**3c**	100	4	80	7.11×10^{-3}	11520	22400	1.29

[a]Conditions: all polymerizations were carried out in toluene solution (7 mL) at 130 °C, 0.031 mmol of catalyst, 0.45 g of L-lactide. [b]Measured by ^{1}H NMR. [c]Calculated for one growing chain per aluminum atom (M_n(calcd) = (L-LA/Al) × conversion × 144). [d]Determined by gel permeation chromatography, calibrated with polystyrene standards in tetrahydrofuran and corrected by the Mark−Houuwink factor of 0.58.[14]

izations are carried out in toluene solution at 130 °C with an equivalent molar ratio of monomer to initiator of 100 ($[M]_0/[Al]_0$). All three complexes proved significantly active in comparison with previously reported aluminum thiolate compounds, achieving higher conversions in shorter periods of time.[8b] Representative results are summarized in Table 2.

The kinetics of the ring-opening polymerization of L-LA with complexes **3** by quenching samples from reactions, up to a conversion of ∼80%, have been followed by ^{1}H NMR analysis (Figure 2). Although all three values are very close, it is important to note that while the polymerization process promoted by **3a** lacks an induction period, those initiated by complexes **3b,c** possess a short induction period of ca. 15−20 min (Figure 2). In fact, after 30 min of reaction the conversion reached by **3a** is double that achieved by complexes **3b,c**.

Semilogarithmic plots of ln ($[LA]/[LA]_0$) versus polymerization time are linear, indicating that the polymerization followed pseudo-first-order kinetics in lactide concentration (Figure 3). Apparent polymerization rate constants of K_{app} = 8.00×10^{-3}, 7.64×10^{-3}, and 7.11×10^{-3} min^{-1} are found for **3a−c**, respectively.

The GPC data for the polymers obtained exhibit monomodal molecular weight distributions along with high number-average molecular weights (Table 2). However, these efficient catalysts afford poor control over ROP parameters, as inferred from the

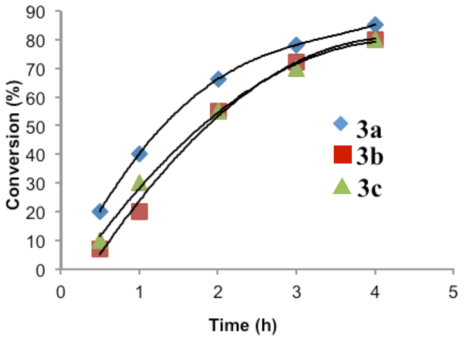

Figure 2. Kinetics of L-lactide conversion with complexes **3**.

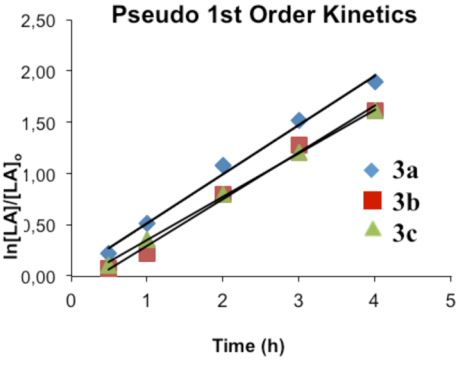

Figure 3. First-order kinetics plots for the polymerization of L-lactide promoted by complexes **3**.

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fairly broad molecular weight distribution (M_w/M_n = 2.34) shown by the polymers obtained with **3b** and the significant deviation between observed and calculated (on the basis of monomer conversion) molecular weight for those obtained with **3c**, which can be accounted for by a partial deactivation of the aluminum complex during the polymerization process. In addition, a further corroboration of this is the lack of linear dependence between the number-average molecular weight and the monomer to initiator ratio.

To establish the role played by the aminoarenethiolate ligand in these ROP polymerization experiments, we performed an end-group analysis by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry. Although, unfortunately, NMR spectroscopy did not identify this group, MALDI-TOF mass spectrometry confirmed the formation of polymers capped with an aminoarenethiolate group at one end. Thus, the aminoarenethiolate chelating moiety acts as an initiating group in these ROP processes of L-lactide.

CONCLUSIONS

Herein, we have described suitable and straightforward synthetic routes to prepare aluminum aminoarenethiolate derivatives with different degrees of methylation. The present work shows that bidentate aminothiolate ligands, which combine a soft thiolate donor with a hard amino donor, are suitable ligands in the coordination chemistry of aluminum(III), a hard Lewis acid.

The catalytic performances of dimethyl complexes **3** in L-lactide ring-opening polymerization have been explored. All three complexes have been shown as efficient catalysts, achieving high conversions in relatively short periods of time. Polymerization kinetic studies revealed a first-order dependence on monomer concentration. Although these catalysts afford poor control over ROP parameters, the thioester end group shown in the polyesters obtained may provide a suitable method for further functional procedures of such polymers.

EXPERIMENTAL SECTION

All manipulations were performed under argon using Schlenk and high-vacuum-line techniques or in a Model HE-63 glovebox. Solvents were dried and purified with an MBRAUN solvent purification system. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. $AlMe_3$ (2.0 M solution in toluene), $AlClMe_2$ (1.0 M solution in hexane), $AlCl_2Me$ (1.0 M solution in hexane), and $AlCl_3$ were purchased from commercial sources (Aldrich) and used as received. L-Lactide (Aldrich) was recrystallized from toluene, washed with diethyl ether, and sublimed at 110 °C prior to use. C, H, and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. The elemental analyses for complexes **2** deviated from acceptable limits, since hexane could not be completely removed due to the oily nature of these complexes, which explains the high carbon values. NMR spectra were recorded on a Bruker AV400 instrument (^{1}H NMR at 400 MHz, ^{13}C NMR at 100.6 MHz MHz) at 25 °C. ^{1}H and ^{13}C NMR chemical shifts (δ) were determined using residual signals of the deuterated solvents and were calibrated versus TMS. The assignment of resonances was carried out by using 1D (^{1}H, ^{13}C{^{1}H}) and 2D (HMQC, HMBC) NMR experiments.

Gel permeation chromatography (GPC) analysis was performed at 25 °C on a Varian HPLC system, using THF as the mobile phase. Gel permeation chromatography (GPC) analyses of polymer samples were carried out in THF at 25 °C (Waters GPCV-2000). The calibration curves were made using different polystyrene standards. MALDI-TOF MAS analyses were performed using an Agilent MALDI-TOF LC/MS instrument; the ionization source was a Masstech AP/MALDI. The mass spectra were recorded in positive mode. 1,8,9-Anthracenetriol was used as the matrix, and trifluoroacetic acid was added as a cationization agent.

Synthesis of [AlMe$_3${S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NC$_5$H$_{10}$-5-^{t}Bu)}-κN] (2a). A solution of 0.30 g (0.88 mmol) of S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NC$_5$H$_{10}$-5-^{t}Bu) in toluene (10 mL) was added dropwise to a toluene solution (10 mL) of $AlMe_3$ (0.48 mL, 0.96 mmol) at room temperature. The reaction mixture was stirred for 2 h. After the removal of solvent under vacuum, the resulting residue was extracted into hexane (10 mL) and isolated by fractional crystallization from *n*-hexane to give **2a** as a white oil (0.15 g, 0.35 mmol, 40%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −0.16 (s, 9H, Al*Me*$_3$), 0.15 (s, 9H, Si*Me*$_3$), 0.37, 1.05, 2.01, 2.24, 3.35 (m, 1H, 3H, 3 × 2H, NC$_5$*H*$_{10}$), 1.20 (s, 9H, C*Me*$_3$), 4.50 (s, 2H, NC*H*$_2$), 6.95 (d, 1H, ^3J = 8 Hz, C$_6$*H*$_3$), 7.07 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6$*H*$_3$), 7.62 (d, 1H, ^4J = 2 Hz, C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ −5.6 (Al*Me*$_3$), 0.67 (Si*Me*$_3$), 21.5, 22.6, 51.3 (NC$_5$H$_{10}$), 30.2 (C*Me*$_3$), 34.4 (*C*Me$_3$), 53.8 (NCH$_2$), 124.5, 134.3, 136.2 (C$_6$H$_3$), 130.4, 142.4, 152.8 (C$_6$H$_3$-*ipso*). Anal. Calcd for C$_{22}$H$_{42}$AlNSSi: C, 64.79; H, 10.40; N, 3.43. Found: C, 66.45; H, 11.73; N, 3.29.

Synthesis of [AlMe$_3${S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NC$_4$H$_8$-5-^{t}Bu)}-κN] (2b). A procedure similar to that described above for **2a** was adopted using S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NC$_4$H$_8$-5-^{t}Bu) (0.32 g, 0.99 mmol) and $AlMe_3$ (0.50 mL, 1.09 mmol) to give the adduct **2b** as a pale yellow oil (0.17 g, 0.44 mmol, 45%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −0.30 (s, 9H, Al*Me*$_3$), −0.09 (s, 9H, Si*Me*$_3$), 0.98, 1.31, 2.83, 3.14 (m, 4 × 2H, NC$_4$*H*$_8$), 1.09 (s, 9H, C*Me*$_3$), 4.35 (s, 2H, NC*H*$_2$), 6.90 (d, 1H, ^3J = 8 Hz, C$_6$*H*$_3$), 7.03 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6$*H*$_3$), 7.64 (d, 1H, ^4J = 2 Hz, C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ −8.2 (Al*Me*$_3$), 0.61 (Si*Me*$_3$), 24.4, 52.0 (NC$_4$H$_8$), 31.0 (C*Me*$_3$), 34.3 (*C*Me$_3$), 61.9 (NCH$_2$), 124.4, 133.5, and 135.0 (C$_6$H$_3$), 132.2, 142.1, and 152.2 (C$_6$H$_3$-*ipso*). Anal. Calcd for C$_{21}$H$_{40}$AlNSSi: C, 64.05; H, 10.26; N, 3.55. Found: C, 66.11; H, 10.97; N, 3.22.

Synthesis of [AlMe$_3${S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NMe$_2$-5-^{t}Bu)}-κN] (2c). A procedure similar to that described above for **2a** was adopted using S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NMe$_2$-5-^{t}Bu) (0.32 g, 1.08 mmol) and $AlMe_3$ (0.60 mL, 1.19 mmol) to give the adduct **2c** as a white oil (0.15 g, 0.43 mmol, 40%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −0.30 (s, 9 H, Al*Me*$_3$), 0.07 (s, 9 H, Si*Me*$_3$), 1.16 (s, 9 H, C*Me*$_3$), 2.08 (s, 6 H, N*Me*$_2$), 4.27 (s, 2 H, NC*H*$_2$), 6.81 (d, 1 H, ^3J = 8 Hz, C$_6$*H*$_3$), 7.05 (dd, 1 H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6$*H*$_3$), 7.65 (d, 1 H, ^4J = 2 Hz, C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ −10.2 (Al*Me*$_3$), 0.65 (Si*Me*$_3$), 31.2 (C*Me*$_3$), 34.4 (*C*Me$_3$), 42.2 (N*Me*$_2$), 57.1 (NCH$_2$), 124.0, 133.4, 135.0 (C$_6$H$_3$), 131.2, 141.8, 152.8 (C$_6$H$_3$-*ipso*). Anal. Calcd for C$_{19}$H$_{38}$AlNSSi: C, 62.05; H, 10.43; N, 3.80. Found: C, 63.33; H, 10.98; N, 3.10.

Synthesis of [AlMe$_2${S(C$_6$H$_3$-2-CH$_2$NC$_5$H$_{10}$-5-^{t}Bu)}-$\kappa^2 S,N$] (3a). A solution of S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NC$_5$H$_{10}$-5-^{t}Bu) (0.96 g, 2.86 mmol) in toluene (30 mL) was added dropwise to a solution of $AlMe_3$ (1.60 mL, 3.14 mmol) in toluene (30 mL) at room temperature. The reaction mixture was heated to 130 °C and stirred for 4 days. After the mixture was cooled to room temperature, the solvent was removed under vacuum to yield a white residue that was extracted into a mixture of hexane and toluene (15 and 5 mL, respectively). The resulting solution was concentrated under vacuum to ca. 10 mL and cooled to −20 °C to give **3a** as a white solid (0.72 g, 2.28 mmol, 80%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −0.40 (s, 6H, Al*Me*$_2$), 0.81, 0.90, 1.06, 1.81, 2.59 (m, 2 × 1H, 4H, 2 × 2H, NC$_5$*H*$_{10}$), 1.18 (s, 9H, C*Me*$_3$), 3.43 (s, 2H, NC*H*$_2$), 6.79 (d, 1H, ^3J = 8 Hz, C$_6$*H*$_3$), 7.07 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6$*H*$_3$), 7.97 (d, 1H, ^4J = 2 Hz, C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ −7.2 (Al*Me*$_2$), 21.5, 24.7, 53.8 (NC$_5$H$_{10}$), 32.3 (C*Me*$_3$), 34.7 (*C*Me$_3$), 61.5 (NCH$_2$), 121.4, 130.1, 132.4 (C$_6$H$_3$), 130.4, 142.4, 152.8 (C$_6$H$_3$-*ipso*). Anal. Calcd for C$_{18}$H$_{30}$AlNS: C, 67.67; H, 9.39; N, 4.38. Found: C, 67.45; H, 9.89; N, 4.29.

Synthesis of [AlMe$_2${S(C$_6$H$_3$-2-CH$_2$NC$_4$H$_8$-5-^{t}Bu)}-$\kappa^2 S,N$] (3b). A procedure similar to that described above for **3a** was used with S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NC$_4$H$_8$-5-^{t}Bu) (0.94 g, 2.92 mmol) and $AlMe_3$ (1.60 mL, 3.21 mmol) to afford **3b** as an orange solid (0.70 g, 2.27 mmol, 78%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −0.45 (s, 6H, Al*Me*$_2$), 1.10, 1.84, 2.56 (m, 4H, 2 × 2H, NC$_4$*H*$_8$), 1.18 (s, 9H, C*Me*$_3$), 3.33 (s,

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2H, NCH_2), 6.70 (d, 1H, ^3J = 8 Hz, C$_6H_3$), 7.05 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6H_3$), 7.97 (d, 1H, ^4J = 2 Hz, C$_6H_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ −8.5 (AlMe_2), 22.0, 55.8 (NC$_4$H$_8$), 31.3 (CMe_3), 34.5 (CMe_3), 61.9 (NCH$_2$), 120.9, 130.1, 132.2 (C$_6$H$_3$), 131.7, 141.9, 152.7 (C$_6$H$_3$-*ipso*). Anal. Calcd for $C_{17}H_{28}$AlNS: C, 66.84; H, 9.17; N, 4.59. Found: C, 66.57; H, 9.04; N, 4.46.

Synthesis of [AlMe$_2${S(C$_6$H$_3$-2-CH$_2$NMe$_2$-5-^{t}Bu)}-κ^2*S*,*N*] (3c). A procedure similar to that described above for **3a** was applied using S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NMe$_2$-5-^{t}Bu) (0.90 g, 3.04 mmol) and AlMe$_3$ (1.67 mL, 3.34 mmol) to give **3c** as a white solid (0.70 g, 2.29 mmol, 82%) after 7 days of reaction. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −0.52 (s, 6H, AlMe_2), 1.17 (s, 9H, CMe_3), 1.61 (s, 6H, NMe_2) 3.14 (s, 2H, NCH_2), 6.67 (d, 1H, ^3J = 8 Hz, C$_6H_3$), 7.12 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6H_3$), 7.96 (d, 1H, ^4J = 2 Hz, C$_6H_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ −8.7 (AlMe_2), 31.2 (CMe_3), 34.5 (CMe_3), 46.1 (NMe_2), 66.1 (NCH$_2$), 121.0, 130.6, 132.4 (C$_6$H$_3$), 131.2, 141.8, 152.8 (C$_6$H$_3$-*ipso*). Anal. Calcd for $C_{15}H_{26}$AlNS: C, 64.48; H, 9.38; N, 5.01. Found: C, 64.12; H, 9.45; N, 4.95.

Synthesis of [AlClMe{S(C$_6$H$_3$-2-CH$_2$NC$_5$H$_{10}$-5-^{t}Bu)}-κ^2*S*,*N*] (4a). A solution of S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NC$_5$H$_{10}$-5-^{t}Bu) (0.20 g, 0.59 mmol) in toluene (10 mL) was added dropwise to a solution of AlCl$_2$Me (0.65 mL, 0.65 mmol). The reaction mixture was stirred for 2 h at room temperature, at which point the volatiles were pumped off and the resulting solid was washed with hexane (3 × 5 mL) and recrystallized from toluene to give **4a** (0.12 g, 0.35 mmol, 60%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −0.26 (s, 3H, AlMe), 0.87, 0.98, 1.39, 1.83, 2.10, 2.48, 3.02 (m, 2H, 3H, 5 × 1H, NC$_5H_{10}$), 1.14 (s, 9H, CMe_3), 3.28, 3.69 (d, 2 × 1H, ^2J = 12 Hz, NCH_2), 6.71 (d, 1H, ^3J = 8 Hz, C$_6H_3$), 7.01 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6H_3$), 7.85 (d, 1H, ^4J = 2 Hz, C$_6H_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ 21.0, 21.2, 22.3, 53.1, 54.4 (NC$_5$H$_{10}$), 31.0 (CMe_3), 34.5 (CMe_3), 61.4 (NCH$_2$), 121.5, 130.8, 131.8 (C$_6$H$_3$), 129.3, 139.6, 153.3 (C$_6$H$_3$-*ipso*). Anal. Calcd for $C_{17}H_{27}$AlClNS: C, 60.06; H, 7.94; N, 4.11. Found: C, 60.75; H, 8.02; N, 4.29.

Synthesis of [AlClMe{S(C$_6$H$_3$-2-CH$_2$NC$_4$H$_8$-5-^{t}Bu)}-κ^2*S*,*N*] (4b). A procedure similar to that described above for **4a** was adopted using S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NC$_4$H$_8$-5-^{t}Bu) (0.23 g, 0.71 mmol) and AlCl$_2$Me (0.80 mL, 0.78 mmol) to obtain complex **4b** (0.15 g, 0.46 mmol, 61%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −0.34 (s, 3H, AlMe), 1.06, 1.35, 1.81, 2.03, 2.41, 3.11 (m, 3H, 5 × 1H, NC$_4H_8$), 1.07 (s, 9H, CMe_3), 3.11, 3.56 (d, 2 × 1H, ^2J = 12 Hz, NCH_2), 6.63 (d, 1H, ^3J = 8 Hz, C$_6H_3$), 7.01 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6H_3$), 7.86 (d, 1H, ^4J = 2 Hz, C$_6H_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ 21.7, 21.8, 54.4, 55.7 (NC$_4$H$_8$), 31.1 (CMe_3), 34.5 (CMe_3), 61.4 (NCH$_2$), 121.6, 130.7, 132.1 (C$_6$H$_3$), 129.3, 139.0, 153.2 (C$_6$H$_3$-*ipso*). Anal. Calcd for $C_{16}H_{25}$AlClNS: C, 58.96; H, 7.67; N, 4.29. Found: C, 59.19; H, 7.84; N, 4.16.

Synthesis of [AlClMe{S(C$_6$H$_3$-2-CH$_2$NMe$_2$-5-^{t}Bu)}-κ^2*S*,*N*] (4c). A procedure similar to that described above for **4a** was adopted using S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NMe$_2$-5-^{t}Bu) (0.27 g, 0.91 mmol) and AlCl$_2$Me (1 mL, 1.00 mmol) to obtain complex **4c** (0.17 g, 0.59 mmol, 65%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ −0.40 (s, 3H, AlMe), 1.13 (s, 9H, CMe_3), 1.53, 1.90 (s, 2 × 3H, NMe_2), 2.93, 3.39 (d, 2 × 1H, ^2J = 12 Hz, NCH_2), 6.58 (d, 1H, ^3J = 8 Hz, C$_6H_3$), 7.02 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6H_3$), 7.84 (d, 1H, ^4J = 2 Hz, C$_6H_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ 31.2 (CMe_3), 34.5 (CMe_3), 44.0, 47.0 (NMe_2), 65.7 (NCH$_2$), 121.8, 130.7, 132.2 (C$_6$H$_3$), 130.1, 138.8, 153.4 (C$_6$H$_3$-*ipso*). Anal. Calcd for $C_{14}H_{23}$AlClNS: C, 56.07; H, 7.69; N, 4.66. Found: C, 56.63; H, 7.95; N, 4.20.

Synthesis of [AlCl$_2${S(C$_6$H$_3$-2-CH$_2$NC$_5$H$_{10}$-5-^{t}Bu)}-κ^2*S*,*N*] (5a). A 0.5 mL portion of C$_6$D$_6$ was added to a mixture of **1a** (0.030 g, 0.089 mmol) and AlCl$_3$ (0.014 g, 0.107 mmol), and the resulting solution was injected into a Teflon-valved NMR tube. The reaction was monitored by NMR spectroscopy at 25 °C, and **5a** evolved as the unique product, after 2 h of reaction time. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 0.77, 0.86, 1.01, 1.30, 2.01, 2.95 (m, 2 × 1H, 4 × 2H, NC$_5H_{10}$), 1.20 (s, 9H, CMe_3), 3.50 (s, 2H, NCH_2), 6.67 (d, 1H, ^3J = 8 Hz, C$_6H_3$), 7.03 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6H_3$), 7.77 (d, 1H, ^4J = 2 Hz, C$_6H_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ 20.9, 22.0, 54.0 (NC$_5$H$_{10}$), 31.0 (CMe_3), 34.6 (CMe_3), 61.2 (NCH$_2$), 122.4, 131.2, 131.7 (C$_6$H$_3$), 128.4, 137.4, 153.8 (C$_6$H$_3$-*ipso*).

Synthesis of [AlCl$_2${S(C$_6$H$_3$-2-CH$_2$NC$_4$H$_8$-5-^{t}Bu)}-κ^2*S*,*N*] (5b). A procedure similar to that described above for **5a** was adopted using **1b** (0.030 g, 0.093 mmol) and AlCl$_3$ (0.014 g, 0.112 mmol) to give **5b**. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 1.06, 1.34, 1.99, 2.96 (m, 4 × 2H, NC$_4H_8$), 1.08 (s, 9H, CMe_3), 3.35 (s, 2H, NCH_2), 6.59 (d, 1H, ^3J = 8 Hz, C$_6H_3$), 7.03 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6H_3$), 7.78 (d, 1H, ^4J = 2 Hz, C$_6H_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ 21.7, 55.6 (NC$_4$H$_8$), 31.1 (CMe_3), 34.5 (CMe_3), 61.3 (NCH$_2$), 122.3, 130.6, 131.9 (C$_6$H$_3$), 129.8, 136.7, 153.7 (C$_6$H$_3$-*ipso*).

Synthesis of [[AlCl$_2${S(SiMe$_3$)(C$_6$H$_3$-2-CH$_2$NMe$_2$-5-^{t}Bu)}-κ^2*S*,*N*] (5c). A procedure similar to that described above for **5a** was adopted using **1c** (0.030 g, 0.101 mmol) and AlCl$_3$ (0.016 g, 0.121 mmol) to give **5c**. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 1.11 (s, 9H, CMe_3), 1.79 (s, 6H, NMe_2), 3.13 (s, 2H, NCH_2), 6.53 (d, 1H, ^3J = 8 Hz, C$_6H_3$), 7.01 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz, C$_6H_3$), 7.74 (d, 1H, ^4J = 2 Hz, C$_6H_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ 31.0 (CMe_3), 34.5 (CMe_3), 46.7 (NMe_2), 65.7 (NCH$_2$), 122.5, 130.9, 132.1 (C$_6$H$_3$), 129.2, 136.5, 153.9 (C$_6$H$_3$-*ipso*).

Typical L-Lactide Polymerization Procedure. A 0.45 g portion (3.12 mmol) of L-lactide was added to a Teflon-valved Schlenk tube loaded with the aluminum complex (0.031 mmol) dissolved in toluene (7 mL) and equipped with a magnetic stirrer. The resulting mixture was immersed in an oil bath preset at 130 °C, and the polymerization time was measured from this point. At certain time intervals, an aliquot of the reaction mixture was taken out using a syringe to determine monomer conversion by ^{1}H NMR. Finally, when a conversion of over 80% was reached, the polymerization was quenched by the addition of 5 mL of acidified MeOH (HCl, 10 wt %). Then, the polymer was precipitated into 150 mL of methanol and washed thoroughly. The polymer was dissolved in acetone, precipitated in methanol at 0 °C, collected by filtration, and dried to constant weight in a vacuum oven at 50 °C.

Single-Crystal X-ray Structure Determination of Compounds 3a,b. Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in the Supporting Information. Suitable single crystals of **3a**,**b** for the X-ray diffraction study were selected. Data collection was performed at 200(2) K, with the crystals covered with perfluorinated ether oil. The crystals were mounted on a Bruker-Nonius Kappa CCD single-crystal diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Multiscan[16] absorption correction procedures were applied to the data. The structures were solved, using the WINGX package,[17] by direct methods (SHELXS-97) and refined using full-matrix least squares against F^2 (SHELXL-97).[18] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. C17 in **3a** and some carbon atoms in **3b** (C16, C17, and C15) show some positional disorder that was left untreated. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001. The final residual electron density maps showed no remarkable features.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-923240 (**3a**) and CCDC-923241 (**3b**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A table and CIF files giving crystallographic data, including fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates, for complexes **3a**,**b** and figures giving ^{1}H NMR spectra and MALDI-TOF mass spectra of PLA obtained by **3a**. This

material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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