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Stereoselective Ring-Opening Polymerization of *rac*-Lactides Catalyzed by Chiral and Achiral Aluminum Half-Salen Complexes†

Donald J. Darensbourg* and Osit Karroonnirun

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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A new series of aluminum half-salen complexes have been synthesized from either chiral or achiral tridentate Schiff base ligands derived from amino alcohols or amino acids. All aluminum complexes have been shown to be active catalysts for the ring-opening polymerization (ROP) of *rac*-lactide in toluene at 70 °C, producing polylactides with controlled molecular weights and narrow molecular weight distributions. Both chiral and achiral aluminum complexes showed moderate selectivity to the ROP of *rac*-lactide to produce isotactic polylactide with a P_m value up to 0.76. In addition, epimerization of *rac*-lactide to *meso*-lactide was observed during the polymerization process for some of the complexes studied.

Introduction

Polylactides are biodegradable polymers derived from renewable resources such as corn, wheat, and sugar beets.[1] These polymeric materials have received much attention over the past decade because of their attractive physical and mechanical properties, which lend them to having numerous applications in medical[2] and microelectronic areas.[3] Of importance, polylactides and various copolymers thereof are readily metabolized in the human body by normal metabolic pathways.[4] The thermal properties of polylactides are highly dependent on the microstructures of the polylactides. Therefore, researchers have focused their studies on synthesizing stereocomplex polylactides from *rac*-lactide, utilizing catalytic systems which can control the tacticity of the polymers formed. Stereocomplexed polylactides can thereby be produced from a blend of poly-L-lactide and poly-D-lactide which have melting temperatures up to 230 °C.[5]

The use of metal-based catalysts, especially those derived from a biocompatible metal, for the ring-opening polymerization (ROP) of cyclic esters has been the subject of numerous reviews.[2c,6] Relevant to this topic, we have recently reported the ROP of *rac*-lactide using zinc-based half-salen complexes derived from chiral natural amino acids as catalysts.[7] Although these complexes were chiral, our observations revealed these zinc complexes underwent ROP of *rac*-lactide via a chain-end control mechanism to provide heterotactic polylactide.[8] While chiral ligands bound to active metal centers are typically expected to play a major role in stereoselectivity via an enantiomorphic site control mechanism,[9] it is generally not true for the ROP of cyclic esters by zinc-catalyzed systems. Indeed, zinc complexes derived from chiral[7,10] or achiral ligands[11] which have been

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*To whom correspondence should be addressed. E-mail: djdarens@mail.chem.tamu.edu. Fax (979)845-0158.

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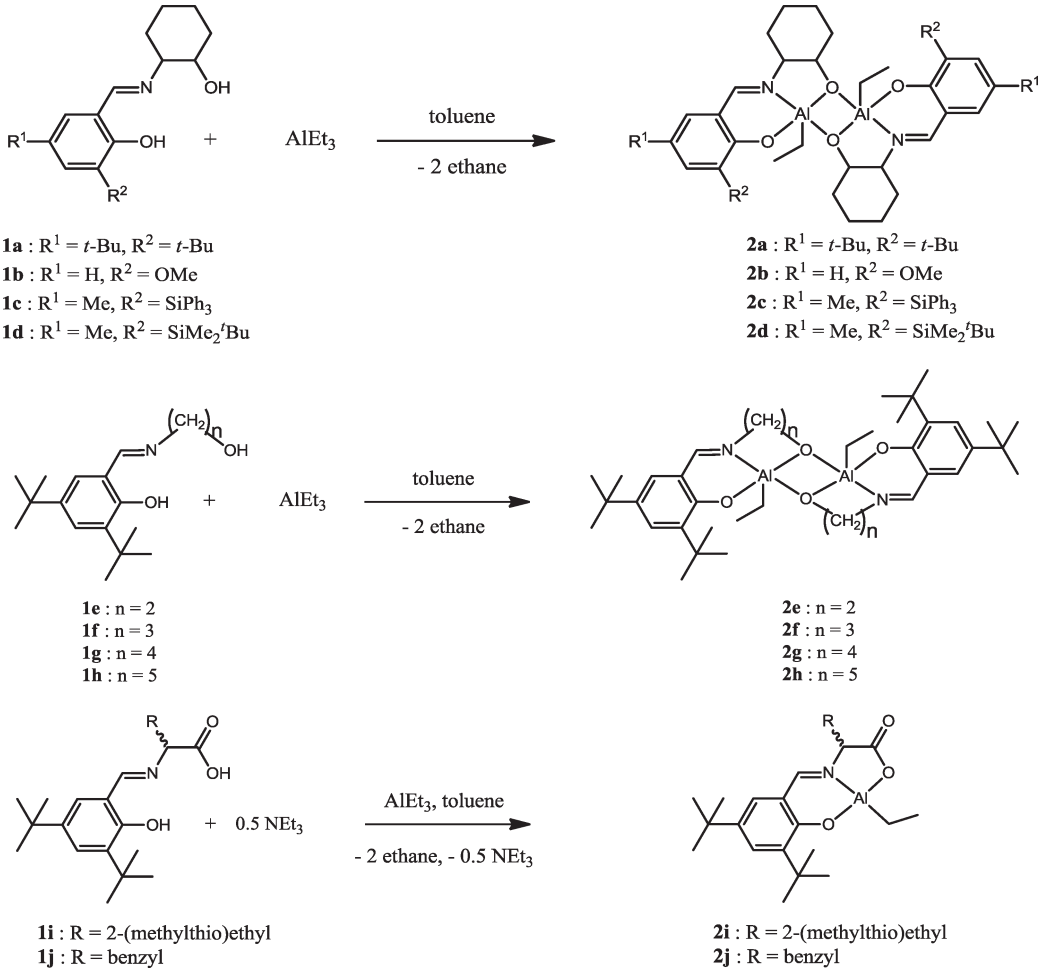
Scheme 1



reported in the literature thus far undergo a chain-end control mechanism to produce heterotactic polylactides. On the other hand, chiral[5,12] and achiral[8b,9b,13] complexes of aluminum have shown significant stereocontrol for the ROP of *rac*-lactide to afford polylactides with high degrees of isotactic enrichment. Chisholm and co-workers have shown that, in addition to chiral ligands bound to aluminum, other factors such as the chirality of the alkoxide initiator and solvents can contribute to the stereoselectivity in the ROP of lactides when utilizing aluminum salen catalysts.[12h,i]

Herein we have synthesized and characterized structurally a series of aluminum half-salen complexes containing both chiral and achiral ligands and report some of our preliminary observations on their use as catalysts for the ring-opening polymerization of lactides.

Results and Discussion

The ligands used in our studies were derived from either amino alcohols or amino acids by condensation reactions with the corresponding aldehydes to afford compounds **1a**−**j**. Reactions of these ligands with triethylaluminum in dry toluene resulted in the formation of complexes **2a**−**j**, as depicted in Scheme 1. In this manner three series of closely related aluminum half-salen complexes were synthesized whose ligand backbones were easily modified by chiral amino alcohols (**2a**−**d**), aliphatic amino alcohols (**2e**−**h**), and amino acids (**2i**,**j**). The reactivity and selectivity of aluminum complexes **2a**−**j** for catalyzing the ROP of *rac*-lactide are provided in Table 1.

As noted in Table 1, complex **2a** did not polymerize *rac*-lactide in $CDCl_3$ after 66 h at 60 °C (entry 2); however, in toluene a 57% conversion to polylactide was observed over the same time period at 70 °C (entry 4). For complexes in the series **2a**−**d** and the substituents (R^2) on the phenoxide of the half-salen ligand increase in size (R^2 = $SiPh_3$) or are more

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Table 1. Reactivity and Selectivity of Aluminum Complexes 2a−j for the ROP of *rac*-Lactide[a]

entry	M	time (h)	conversn (%)[b]	*meso*[c]	M_n theor[d]	M_n 0.58$M_{n,GPC}$[e]	PDI	P_m[f]
1	**2a**[g]	20	0	no				
2	**2a**[h]	66	0	yes				
3	**2a**	15	0	yes				
4	**2a**	66	57	yes	4107	7938	1.05	70
5	**2b**	15	0	yes				
6	**2b**	69	43	yes	3243	3844	1.08	< 50
7	**2c**	15	0	yes				
8	**2c**	168	45	yes	3207	4962	1.09	< 50
9	**2d**	15	0	yes				
10	**2e**	15	64	yes	4614	6987	1.04	62
11	**2f**	15	0	yes				
12	**2g**	15	34	no	2446	2456	1.07	76
13	**2h**	15	50	no				73
14	**2i**	15	36	no	2594	3916	1.07	74
15	**2j**	15	42	no	3026	4043	1.03	72

[a] Unless otherwise specified, the polymerization reactions were performed in sealed reaction tubes under the following conditions: [*rac*-LA]/[Al] = 50, in toluene at 70 °C. [b] Obtained from ^{1}H NMR spectroscopy. [c] *meso*-Lactide was obtained from epimerization of L- or D-lactide during the polymerization process. [d] Theoretical M_n = (M/I) × (% conversion) × (mol wt of lactide). [e] M_n values were corrected by the equation M_n = 0.58 $M_{n,GPC}$.[14] [f] P_m values were calculated from the ratio of the (area of iii)/(total area in methine proton region). [g] $CDCl_3$ was used as the solvent at ambient temperature. [h] $CDCl_3$ was used as the solvent at 60 °C.

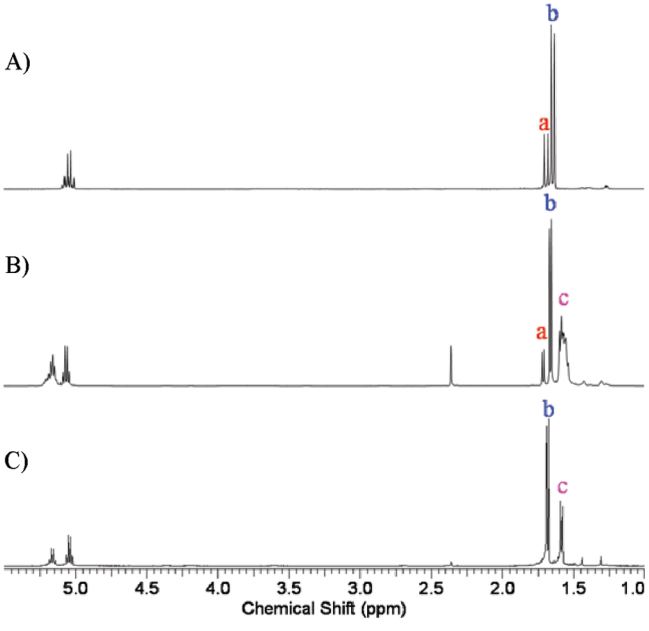

Figure 1. ^{1}H NMR spectrum ($CDCl_3$, room temperature) of the reaction mixtures during the ROP of L-lactide in the presence of complex **2a** (A), **2e** (B), **2g** (C) (entries 3, 10, and 12 in Table 1, respectively). The polymerization reactions were performed in toluene at 70 °C for 15 h. Methyl protons of *meso*-lactide, L-lactide, and polylactide were observed at 1.70 (a), 1.66 (b), and 1.57 (c), respectively.

electron donating (R^2 = OMe), the rate of lactide polymerization decreases (entries 6 and 8). Similar observations have been previously reported by Normura and co-workers and Gibson and co-workers.[13a,c] Complex **2a** afforded a moderately isotactic polymer with a P_m value of 0.70, while complexes **2b**,**c** yielded polylactides with P_m values less than 0.50. The

Table 2. ROP of *rac*- and L-Lactide Using Aluminum Complexes 2e−g,i,j[a]

entry	M	lactide	conversn (%)[b]	*meso*[c]	M_n theor[d]	M_n 0.58$M_{n,GPC}$[e]	PDI	P_m[f]
1	**2e**	*rac*	64	yes	4614	6987	1.04	62
2	**2e**	L	77	yes	4107	7938	1.05	52
3	**2f**	*rac*	0	yes				
4	**2f**[g]	L	36	yes	2600	3726	1.07	< 50
5	**2g**	*rac*	34	no	2446	2456	1.07	76
6	**2g**	L	44	no	3164	N/A[h]	N/A[h]	100
7	**2i**	*rac*	34	no	2594	3916	1.07	74
8	**2i**	L	54	no	3891	N/A[h]	N/A[h]	100
9	**2j**	*rac*	42	no	3026	4043	1.03	72
10	**2j**	L	45	no	3243	N/A[h]	N/A[h]	100

[a] Unless otherwise specified, the polymerization reactions were performed in sealed reaction tubes under the following conditions: [LA]/[Al] = 50, in toluene at 70 °C for 15 h. [b] Obtained from ^{1}H NMR spectroscopy. [c] *meso*-Lactide was obtained from epimerization of L- or D-lactide during the polymerization process. [d] Theoretical M_n = (M/I) × (% conversion) × (mol wt of lactide). [e] M_n values were corrected by the equation M_n = 0.58$M_{n,GPC}$.[14] [f] P_m values were calculated from the ratio of the (area of iii)/(total area in methine proton region). [g] The reaction time was 76 h. [h] The molecular weight was not measured because of the polymer's insolubility in THF, due to its high crystallinity.

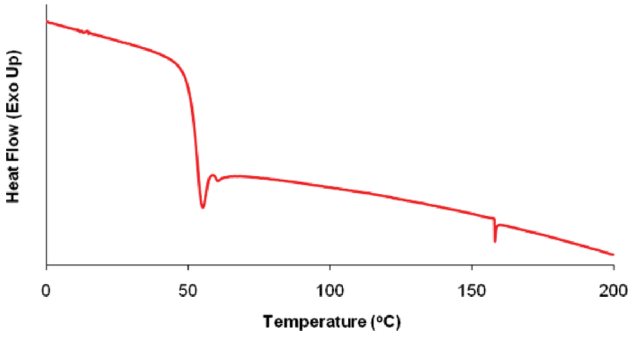

Figure 2. DSC curves (second heating run) of polylactide from *rac*-lactide catalyzed by complex **2i**.

complexes with achiral aliphatic backbone with the exception of **2f**, i.e., complexes **2e**,**g**,**h**, were found to catalyze the ROP of *rac*-lactide at rates faster than that of complex **2a** to give isotactic polylactides with P_m values of 0.62, 0.76, and 0.73, respectively. Similarly, the complexes derived from *rac*-amino acids, **2i**,**j**, were also found to be active for the ring-opening polymerization of *rac*-lactide, providing substantially isotactic polymers with P_m values of 0.74 and 0.72, respectively.

A noteworthy point of importance is that for several of these aluminum-catalyzed systems, namely **2a**−**f**, a ^{1}H NMR signal at 1.70 ppm appears during the polymerization process, while polymerization reactions catalyzed by complexes **2g**−**j** did not exhibit such a ^{1}H NMR signal (see resonance labeled **a** in Figure 1). This ^{1}H NMR peak is assigned to intermediate formation of *meso*-lactide from epimerization of L- and D-lactide during the ROP process. In order to further confirm this occurrence, select aluminum complexes **2e**−**g**,**i**,**j** were used to catalyze the ROP of L-lactide. In these instances, if there is no epimerization occurring during the

(14) The M_n values for polylactide were corrected from the M_n values determined by GPC vs polystyrene standards, according to the equation M_n = 0.58$M_{n,GPC}$, as previously reported in the literature: (a) Barakat, I.; Dubois, P.; Jérôme, R.; Teyssié, P. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 505–514. (b) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Rapid Commun.* **1997**, *18*, 325–333.

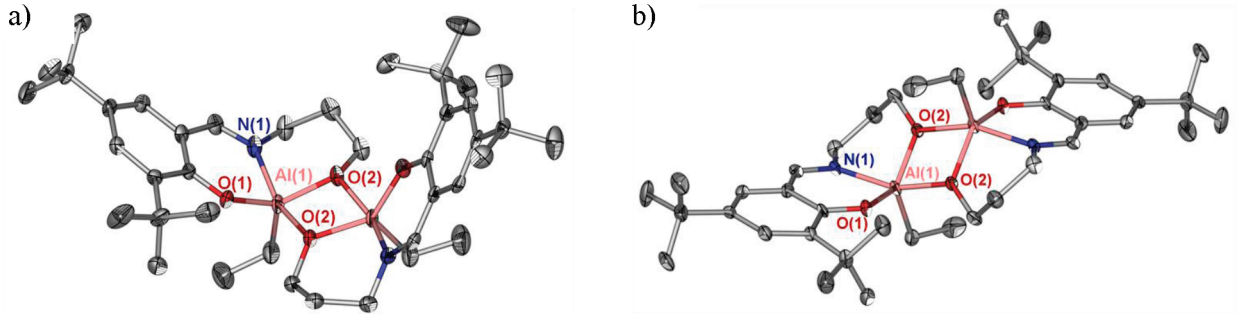

Figure 3. X-ray crystal structures of (a) **2f** (cis), (b) **2f** (trans). Thermal ellipsoids represent the 50% probability surfaces. Hydrogen atoms are omitted for the sake of clarity.

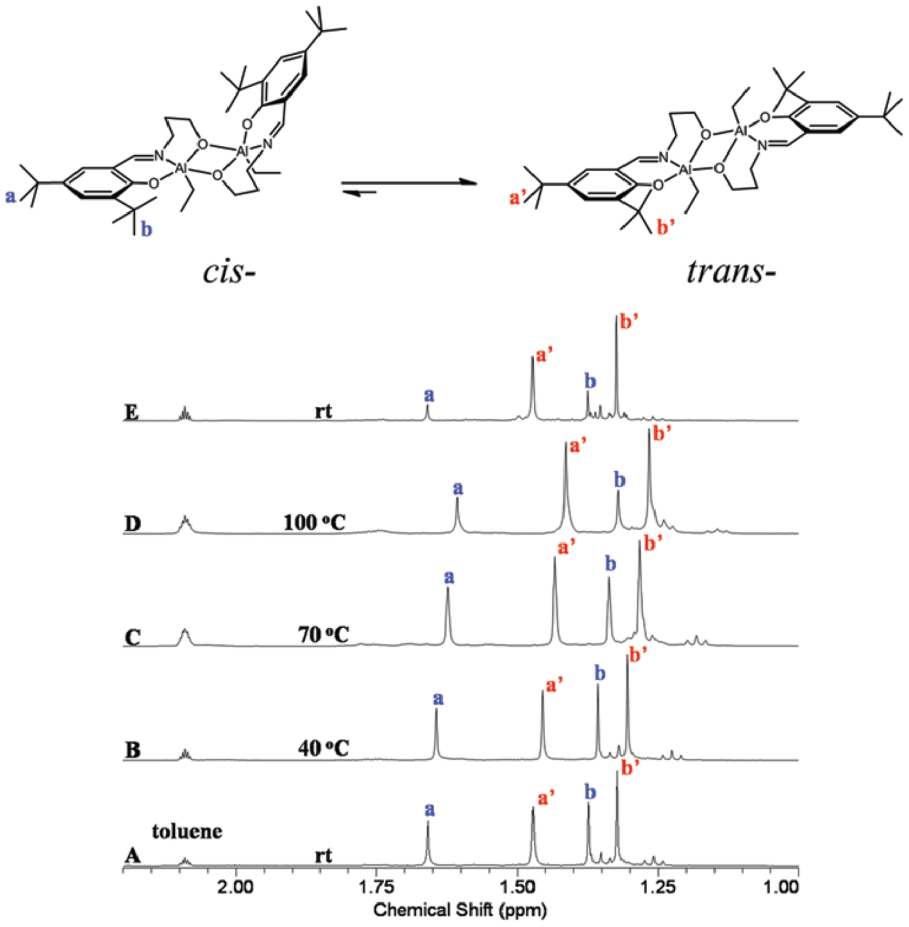

Figure 4. Variable-temperature ^{1}H NMR spectrum (500 MHz) of complex **2f** in deuterated toluene taken sequentially at different temperatures: (A) room temperature; (B) 40 °C; (C) 70 °C; (D) 100 °C; (E) sample cooled from 100 °C to room temperature, spectrum taken 2 days later.

polymerization process, only isotactic polylactide will be formed. As anticipated, complexes **2e**,**f** polymerized L-lactide to afford atactic polylactide with P_m values of 0.52 and < 0.50, respectively, while complexes **2g**,**i**,**j** provided isotactic polylactide with a P_m value of 1, indicative of an absence of epimerization in these instances (Table 2).

The observed molecular weights of all the polymer produced via catalysis with the aluminum complexes employed in this study, i.e., complexes **2a**−**j**, were found to closely parallel the theoretical values. In addition, the polymers thus afforded had polydispersity indices ranging from 1.03 to 1.08. The ring-opening polymerization was shown to be first order in [monomer] and [catalyst]. Hence, these catalytic systems have the characteristic of well-controlled polymerization processes. The thermal properties of a purified polylactide sample produced from the ROP of *rac*-lactide by complex **2i** (P_m = 74%) were determined by differential scanning calorimetry (DSC). The T_m and T_g values of the polymer were found to be 158 and 52 °C, respectively (Figure 2). The observed T_m value is consistent with a moderately isotactic polylactide.

In an effort to understand the catalytic differences noted for the ROP of lactides by the closely related aluminum complexes **2e**−**h**, we report here the structural characterization of one of these derivatives. Specifically, complex **2f** was synthesized and isolated according to Scheme 1, except

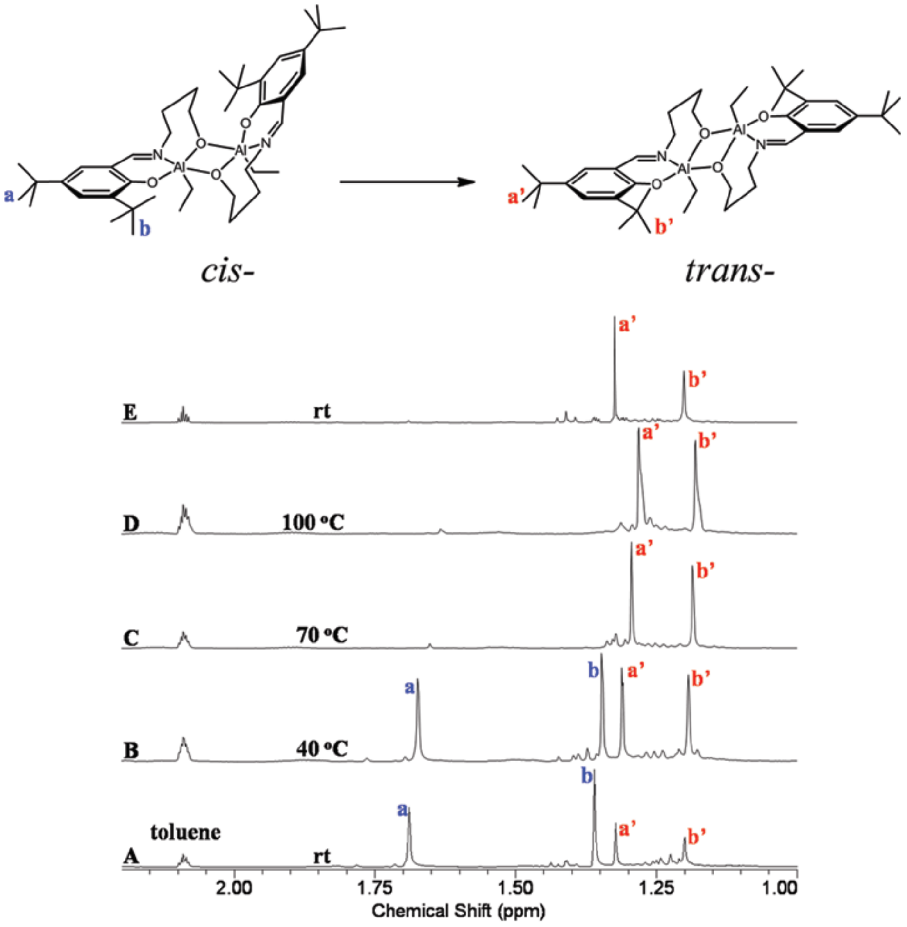

Figure 5. Variable-temperature ^{1}H NMR spectra (500 MHz) of complex **2g** in deuterated toluene taken sequentially at different temperatures: (A) room temperature; (B) 40 °C; (C) 70 °C; (D) 100 °C; (E) sample cooled from 100 °C to room temperature, spectrum taken 2 days later.

pentane was used as solvent, which allowed the complex to precipitate out of solution during its preparation. Single crystals suitable for X-ray structural analysis were obtained upon recrystallization from dichloromethane at −10 °C. In this manner both platelike crystals and blocklike crystals were obtained. X-ray crystallography revealed the blocklike crystals to be dimeric, with bridging oxygen atoms. The two five-coordinate aluminum centers possess a distorted-bipyramidal geometry with the ethyl group of each metal cis to one another, as shown in Figure 3a. Similarly, the solid-state structure of the platelike crystals was shown to be dimeric, except that the ethyl groups on the aluminum centers were trans to one another (Figure 3b).

Since this difference in dimeric aluminum structures may be related to the disparity in catalytic reactivity for the ROP of lactides noted above, and the ROP processes are carried out in solution at 70 °C, it is important to examine the structures of these aluminum complexes in solution. We therefore performed variable-temperature ^{1}H NMR spectroscopic studies of complex **2f** in deuterated toluene. As observed in Figure 4, the ^{1}H NMR spectrum of complex **2f** at ambient temperature reveals two sets of methyl group protons from the *tert*-butyl substituents of the phenoxide ligands (resonances **a** and **a′** and **b** and **b′**). As the temperature was increased, the intensity of the proton signals **a′** and **b′** increased with a concomitant decrease in the ^{1}H NMR signals at **a** and **b**. Both set of resonances were noted at 100 °C, with those of **a′** and **b′** being more intense. Once the distribution of the isomeric complex mixture was reached at 100 °C, this complex mixture remained the same after the solution stood at ambient temperature for 2 days (spectrum **E** in Figure 4). As indicated in Figure 4, we propose the isomeric mixture of aluminum complexes favors the trans arrangement of ethyl groups. That is, due to the decrease in steric repulsion of the bulky phenyl ring, the trans isomer is thermodynamically more stable.

As indicated by the variable-temperature ^{1}H NMR study, complex **2f** exists as both the cis and trans isomers in toluene solution at the ROP temperature of 70 °C. We propose that one of these isomeric forms of the aluminum complex **2f** is responsible for *meso*-lactide formation: i.e., the cis form (vide infra). In much the same way, the ^{1}H NMR spectrum of complex **2e** exhibited two sets of *tert*-butyl group methyl protons at ambient temperature. However, in this case, upon increasing the temperature to 100 °C with periodic monitoring of the spectra, no spectral changes were observed. This result strongly suggests that the structural rearrangements seen in these aluminum dimers are related to the length of the carbon chain backbone in the amino−alkoxide bridging ligand, with the five-membered ring (**2e**) being, as expected, more stable than the six-membered ring (**2f**). In support of this contention, upon examination of the variable-temperature ^{1}H NMR spectra of complex **2g**, which contains a longer four-carbon-chain backbone leading to a seven-membered amino−alkoxide bridging ligand, a facile isomeric exchange reaction was observed (Figure 5). That is, at ambient

temperature the ^{1}H NMR spectrum revealed the presence of both isomers in solution, with the cis isomer in larger quantity. As the temperature was increased, the distribution of isomers converted to all trans by 70 °C, with no further change occurring with either an increase in temperature to 100 °C or a decrease down to ambient temperature.[15] As evident from Table 1, when complexes **2g**,**h** (four- or five-membered carbon chain backbone) were employed as catalysts for the ROP of *rac*-lactide, no *meso*-lactide formation was observed. These observations confirm our suggestion that the cis isomer is responsible for the epimerization of lactide prior to the ring-opening polymerization process.

Conclusions

Herein we have reported the synthesis of a series of tridentate NOO Schiff base ligands along with their aluminum complexes. These metal complexes were dimeric and exhibited two isomeric structures, one with the initiators on the two aluminum centers cis to one another and the other with the trans arrangement. The latter form was shown to be thermodynamically more stable by variable-temperature ^{1}H NMR studies. All complexes were shown to polymerize *rac*-lactide in toluene at 70 °C. The molecular weights of the afforded polylactides correlated well with monomer/initiator and conversion level and displayed narrow distributions with PDI values ranging from 1.03 to 1.08. It was established that complexes which existed in both cis and trans forms under the conditions of the ring-opening polymerization reaction led to partial epimerization of D- and L-lactide to *meso*-lactide prior to polymerization. On the other hand, complexes which exist in the trans isomeric form led to polymerization of *rac*-lactide with no epimerization and concomitantly a polylactide with a high degree of isotacticity (P_m = 76%). We are in the process of performing more detailed studies of the mechanistic aspects of the ROP of lactides, employing a complete series of structurally well-characterized aluminum dimeric complexes.

Experimental Section

Methods and Materials. All manipulations were carried out using a double-manifold Schlenk vacuum line under an argon atmosphere or an argon-filled glovebox unless otherwise stated. Toluene was freshly distilled from sodium/benzophenone before use. Methanol and dichloromethane were purified by an MBraun Manual Solvent Purification System packed with Alcoa F200 activated alumina desiccant. Pentane was freshly distilled from CaH_2. Deuterated chloroform and deuterated benzene from Cambridge Isotope Laboratories Inc. were stored in the glovebox and used as received. L- and D-lactide and *rac*-lactide were gifts from PURAC America Inc. These lactides were recrystallized from toluene, dried under vacuum at 40 °C overnight, and stored in the glovebox. 4-Amino-1-butanol and triethylaluminium were purchased from TCI America and Sigma-Aldrich, respectively, and used without further purification. Ethanolamine, 3-amino-1-propanol, 5-amino-1-pentanol, *trans*-2-aminocyclohexanol hydrochloride, 2-hydroxy-3-methoxybenzaldehyde, *rac*-methionine, *rac*-phenylalanine, and *tert*-butyldimethylchlorosilane were purchased from Alfa Aesar and used as received. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde and 3-(*tert*-butyldimethylsilyl)-2-hydroxy-5-methylbenzaldehyde were prepared according to the published procedure.[16] All other compounds and reagents were obtained from Sigma-Aldrich and were used without further purification. Analytical elemental analysis was provided by Canadian Microanalytical Services Ltd.

Measurements. ^{1}H NMR spectra were recorded on Unity+ 300 or 500 MHz and VXR 300 or 500 MHz superconducting NMR spectrometers. Molecular weight determinations were carried out with a Viscotek Modular GPC apparatus equipped with ViscoGEL I-series columns (H + L) and Model 270 dual detector comprised of refractive index and light scattering detectors. DSC measurements were performed with a Polymer DSC instrument by Mettler Toledo. The samples were scanned from −100 to 200 °C under a nitrogen atmosphere. The glass transition temperature (T_g), the crystallization temperature (T_c), and the melting temperature (T_m) of polylatides were determined from the second heating at a heating rate of 5 °C/min. X-ray crystallography was done on a Bruker GADDS X-ray diffractometer under a nitrogen cold stream maintained at 110 K. Crystal data and details of the data collection for complexes **2f** (***cis***) and **2f** (***trans***) are provided in the Supporting Information (Table S1).

General Procedure for Synthesis of Tridentate Schiff Base Ligands 1a−d. *trans*-2-Aminocyclohexanol hydrochloride (1.1 equiv) and triethylamine (1.09 equiv) were added to the corresponding benzaldehyde (1.0 equiv) in MeOH (30 mL). The solution mixture was heated to reflux overnight, and the solvent was removed under reduced pressure to give a yellow solid. The resulting yellow solid was washed with water (3 × 20 mL) to remove excess *trans*-2-aminocyclohexanol hydrochloride and triethylamine. The organic layer was separated, dried over $NaSO_4$, and concentrated to dryness under reduced pressure to afford the crude products; these were crystallized in pentane to give a yellow powder in 81−95% yield.

(*E*)-2,4-Di-*tert*-butyl-6-(((*trans*-2-hydroxycyclohexyl)imino)-methyl)phenol (1a; L^1-H). Following the general procedure for synthesis of the tridentate Schiff base ligands **1a−d**, *trans*-2-aminocyclohexanol (0.711 g, 4.69 mmol, 1.1 equiv) and triethylamine (0.470 g, 4.65 mmol, 1.09 equiv) were added to 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.00 g, 4.26 mmol, 1.0 equiv) in MeOH (30 mL). The solution mixture was heated to reflux overnight, and the solvent was removed under reduced pressure to give a yellow solid. The resulting yellow solid was washed with water (3 × 20 mL) to remove excess *trans*-2-aminocyclohexanol hydrochloride and triethylamine. The organic layer was separated, dried over $NaSO_4$, and concentrated to dryness under reduced pressure to afford product **1a**, which was crystallized in pentane to give a yellow powder in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H, C(CH_3)$_3$), 1.45 (s, 9H, C(CH_3)$_3$), 1.35−2.4 (bm, 8H, CH(CH_2)$_4$CH), 2.99 (m, 1H, NCHCH$_2$), 3.69 (m, 1H, OCHCH$_2$), 7.12 (d, J = 2.38 Hz, 1H, C$_6H_2$), 7.40 (d, J = 2.38 Hz, 1H, C$_6H_2$), 8.45 (s, 1H, CH=N), 13.60 (s, 1H, OH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 24.28 (NCHCH$_2$-*C*H$_2$CH$_2$), 24.43 (OCHCH$_2$*C*H$_2$CH$_2$), 29.42 (C(^{p}*C*H$_3$)$_3$), 31.47 (C(^{o}*C*H$_3$)$_3$), 32.51 (NCH*C*H$_2$CH$_2$), 32.83 (OCH*C*H$_2$CH$_2$), 34.12 (^{p}*C*CH$_3$), 35.01(^{o}*C*CH$_3$), 73.68 (N*C*HCH$_2$), 75.55 (O*C*H-CH$_2$), 117.73, 126.04, 127.06, 136.66, 140.22, 157.97 (Ar), 166.59 (*C*=N). Anal. Calcd for $C_{21}H_{33}NO_2$: C, 76.09; H, 10.03; N, 4.23. Found: C, 75.93; H, 10.13; N, 4.16. HRMS (ESI): m/z 332.2581 [M + H$^+$], calcd for $C_{21}H_{33}NO_2$ 331.25.

(*E*)-2-(((*trans*-2-Hydroxycyclohexyl)imino)methyl)-6-methoxy-phenol (1b; L^2-H). Following the general procedure for synthesis of the tridentate Schiff base ligands **1a−d**, *trans*-2-aminocyclohexanol (1.09 g, 7.22 mmol, 1.1 equiv) and triethylamine

(15) Complex **2g** was recrystallized by heating the complex in a sealed test tube at 50 °C in dichloromethane until all of the complex was dissolved. The crystal tube was kept at −10 °C and provided crystals of the trans form exclusively, as evidenced by X-ray crystallographic studies.

(16) (a) Darensbourg, D. J.; Choi, W.; Karroonnirun, O.; Bhuvanesh, N. *Macromolecules* **2008**, *41*, 3493–3502. (b) Darensbourg, D. J.; Choi, W.; Richers, C. P. *Macromolecules* **2007**, *40*, 3521–3523. (c) Hansen, T. V.; Skattebøl, L. *Tetrahedron Lett.* **2005**, *46*, 3829–3830. (d) Thadani, A. N.; Huang, Y.; Rawal, V. H. *Org. Lett.* **2007**, *9*, 3873–3876.

(0.724 g, 7.16 mmol, 1.09 equiv) were added to 2-hydroxy-3-methoxybenzaldehyde (1.00 g, 6.57 mmol, 1.0 equiv) in MeOH (30 mL). Compound **1b** was obtained as a yellow powder in 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38, 1.62, 1.81, 2.08 (bm, 8H, CH(CH_2)$_4$CH), 3.03 (m, 1H, NC*H*CH_2), 3.66 (m, 1H, OC*H*CH_2), 3.90 (s, 3H, OCH_3) 6.78, 6.81, 6.84, 6.88, 6.91, 6.94 (m, 3H, C_6H_3), 8.42 (s, 1H, C*H*=N), 13.84 (s, 1H, O*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ 24.12 (NCHCH$_2$*C*H$_2$CH$_2$), 24.28 (OCHCH$_2$*C*H$_2$CH$_2$), 32.58 (NCH*C*H$_2$CH$_2$), 32.62 (OCH*C*H$_2$-CH$_2$), 73.59 (N*C*HCH$_2$), 74.76 (O*C*HCH$_2$), 114.08, 117.97, 118.42, 123.00, 148.50, 151.94 (Ar), 165.41 (*C*=N). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.63; H, 7.73; N, 5.60. HRMS (ESI): m/z 250.1515 [M + H$^+$], calcd for $C_{14}H_{19}NO_3$ 249.14.

(*E*)-2-(((*trans*-2-Hydroxycyclohexyl)imino)methyl)-4-methyl-6-(triphenylsilyl)phenol (1c; L^3-H). Following the general procedure for the synthesis of tridentate Schiff base ligands **1a**−**d**, *trans*-2-aminocyclohexanol (0.338 g, 2.23 mmol, 1.1 equiv) and triethylamine (0.223 g, 2.21 mmol, 1.09 equiv) were added to 2-hydroxy-5-methyl-3-(triphenylsilyl)benzaldehyde[16d] (0.800 g, 2.02 mmol, 1.0 equiv) in MeOH (30 mL). Compound **1c** was obtained as a yellow powder in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31, 1.56, 1.75, 2.03 (bm, 8H, CH(CH_2)$_4$CH), 2.19 (s, 3H, CCH_3), 2.97 (m, 1H, NC*H*CH_2), 3.59 (m, 1H, OC*H*CH_2), 3.90 (s, 3H, OCH_3) 7.07−7.64 (m, 18H, Ar), 8.41 (s, 1H, C*H*=N), 13.20 (s, 1H, O*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ 20.43 (C*C*H$_3$), 24.25 (NCHCH$_2$*C*H$_2$CH$_2$), 24.40 (OCHCH$_2$-*C*H$_2$CH$_2$), 32.59 (NCH*C*H$_2$CH$_2$), 32.76 (OCH*C*H$_2$CH$_2$), 73.42 (N*C*HCH$_2$), 75.71 (O*C*HCH$_2$), 117.73, 121.32, 127.40, 127.67, 129.24, 129.76, 134.23, 134.68, 135.16, 135.42, 136.35, 142.04, 163.98 (Ar), 165.54 (*C*=N). Anal. Calcd for $C_{32}H_{33}NO_2$-Si: C, 78.17; H, 6.76; N, 2.85. Found: C, 76.99; H, 6.67; N, 2.16. HRMS (ESI): m/z 492.2625 [M + H$^+$], calcd for $C_{32}H_{33}NO_2Si$ 491.23.

(*E*)-2-(*tert*-Butyldimethylsilyl)-6-(((*trans*-2-hydroxycyclohexyl)-imino)methyl)-4-methylphenol (1d; L^4-H). Following the general procedure for synthesis of tridentate Schiff base ligands **1a**−**d**, *trans*-2-aminocyclohexanol (0.166 g, 1.09 mmol, 1.1 equiv) and triethylamine (0.110 g, 1.08 mmol, 1.09 equiv) were added to 2-hydroxy-5-methyl-3-(triphenylsilyl)benzaldehyde[16d] (0.250 g, 0.99 mmol, 1.0 equiv) in MeOH (30 mL). Compound **1d** was obtained as a yellow powder in 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.32 (s, 6H, Si(CH_3)$_2$), 0.92 (s, 9H, C(CH_3)$_3$), 1.37, 1.63, 1.80, 2.08 (bm, 8H, CH(CH_2)$_4$CH), 2.97 (m, 1H, NC*H*-CH_2), 3.69 (m, 1H, OC*H*CH_2), 7.05 (d, J = 1.78 Hz, 1H, C_6H_2), 7.20 (d, J = 2.09 Hz, 1H, C_6H_2), 8.37 (s, 1H, C*H*=N), 12.98 (s, 1H, O*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ −4.71 (Si(*C*H$_3$)$_2$), 17.61 (Si*C*(CH$_3$)$_3$), 20.43 (C*C*H$_3$), 24.28 (NCHCH$_2$*C*H$_2$CH$_2$), 24.45 (OCHCH$_2$*C*H$_2$CH$_2$), 27.11 (SiC(*C*H$_3$)$_3$), 32.53 (NCH-*C*H$_2$CH$_2$), 32.83 (OCH*C*H$_2$CH$_2$), 73.62 (N*C*HCH$_2$), 75.74 (O*C*HCH$_2$), 117.42, 124.72, 126.81, 133.06, 140.20, 163.73 (Ar), 165.90 (*C*=N). Anal. Calcd for $C_{20}H_{33}NO_2Si$: C, 69.11; H, 9.57; N, 4.03. Found: C, 69.34; H, 9.81; N, 4.01. HRMS (ESI): m/z 348.2482 [M + H$^+$], calcd for $C_{20}H_{33}NO_2Si$, 347.23.

General Procedure for Synthesis of Tridentate Schiff Base Ligands 1e−h. The corresponding benzaldehyde (1.0 equiv) was added to the corresponding amino alcohol (1.0 equiv) in MeOH (30 mL). The solution mixture was heated to reflux overnight and dried over Na_2SO_4 followed by filtration. The volatile component was removed in vacuo to give tridentate Schiff base ligands in quantitative yield.

(*E*)-2,4-Di-*tert*-butyl-6-(((2-hydroxyethyl)imino)methyl)phenol (1e; L^5-H). Following the general procedure for synthesis of tridentate Schiff base ligands **1e**−**h**, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.00 g, 4.26 mmol, 1.0 equiv) was added to ethanolamine (0.260 g, 4.26 mmol, 1.0 equiv) in MeOH (30 mL). The solution mixture was heated to reflux overnight and dried over Na_2SO_4, followed by filtration. The volatile component was removed in vacuo to give the tridentate Schiff base ligand **1e** in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 9H, C(CH_3)$_3$), 1.37 (s, 9H, C(CH_3)$_3$), 3.68 (m, 2H, OCH_2CH$_2$), 3.86 (m, 2H, NCH_2CH$_2$), 7.03 (d, J = 2.68 Hz, 1H, C_6H_2), 7.32 (d, J = 2.68 Hz, 1H, C_6H_2), 8.35 (s, 1H, C*H*=N), 13.49 (s, 1H, O*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ 29.40 (C(^{p}*C*H$_3$)$_3$), 31.48 (C(^{o}*C*H$_3$)$_3$), 34.35 (^{p}*C*CH$_3$), 35.01 (^{o}*C*CH$_3$), 61.82 (OCH_2CH$_2$), 62.33 (NCH_2CH$_2$), 117.73, 126.05, 127.14, 136.71, 140.21, 157.95 (Ar), 168.14 (*C*=N). Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.94; H, 10.16; N, 4.70. HRMS (ESI): m/z 278.2213 [M + H$^+$], calcd for $C_{17}H_{27}NO_2$, 277.20.

(*E*)-2,4-Di-*tert*-butyl-6-(((3-hydroxypropyl)imino)methyl)-phenol (1f; L^6-H). Following the general procedure for synthesis of tridentate Schiff base ligands **1e**−**h**, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.800 g, 3.41 mmol, 1.0 equiv) was added to 3-amino-1-propanol (0.256 g, 3.41 mmol, 1.0 equiv) in MeOH (30 mL). The solution mixture was heated to reflux overnight and dried over Na_2SO_4, followed by filtration. The volatile component was removed in vacuo to give the tridentate Schiff base ligand **1f** in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H, C(CH_3)$_3$), 1.45 (s, 9H, C(CH_3)$_3$), 1.97 (m, 2H, CH$_2$CH_2CH$_2$), 3.71 (t, J = 6.84 Hz, 2H, OCH_2CH$_2$), 3.76 (t, J = 6.25 Hz, 2H, NCHCH$_2$), 7.09 (d, J = 2.38 Hz, 1H, C_6H_2), 7.38 (d, J = 2.38 Hz, 1H, C_6H_2), 8.39 (s, 1H, C*H*=N), 13.85 (s, 1H, O*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ 29.40 (C(^{p}*C*H$_3$)$_3$), 31.48 (C(^{o}*C*H$_3$)$_3$), 33.50 (CH$_2$*C*H$_2$CH$_2$) 34.11 (^{p}*C*-CH$_3$), 35.00 (^{o}*C*CH$_3$), 55.84 (OCH_2CH$_2$), 60.31 (NCH_2CH$_2$), 117.77, 125.78, 126.83, 136.65, 139.97, 158.08 (Ar), 166.35 (*C*=N). Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.05; H, 10.20; N, 4.84. HRMS (ESI): m/z 292.2394 [M + H$^+$], calcd for $C_{18}H_{29}NO_2$, 291.22.

(*E*)-2,4-Di-*tert*-butyl-6-(((4-hydroxybutyl)imino)methyl)phenol (1g; L^7-H). Following the general procedure for synthesis of tridentate Schiff base ligands **1e**−**h**, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.00 g, 4.26 mmol, 1.0 equiv) was added to 4-amino-1-butanol (0.380 g, 4.26 mmol, 1.0 equiv) in MeOH (30 mL). The solution mixture was heated to reflux overnight and dried over Na_2SO_4, followed by filtration. The volatile component was removed in vacuo to give the tridentate Schiff base ligand **1g** in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H, C(CH_3)$_3$), 1.45 (s, 9H, C(CH_3)$_3$), 1.70 (m, 2H, CH$_2$CH_2CH$_2$), 1.79 (m, 2H, CH$_2$CH_2CH$_2$), 3.62 (t, J = 6.55 Hz, 2H, OCH_2CH$_2$), 3.70 (t, J = 6.24 Hz, 2H, NCHCH$_2$), 7.08 (d, J = 2.38 Hz, 1H, C_6H_2), 7.37 (d, J = 2.38 Hz, 1H, C_6H_2), 8.36 (s, 1H, C*H*=N), 13.90 (s, 1H, O*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ 27.19 (CH$_2$*C*H$_2$CH$_2$), 29.39 (C(^{p}*C*H$_3$)$_3$), 30.29 (CH$_2$*C*H$_2$CH$_2$), 31.48 (C(^{o}*C*H$_3$)$_3$), 34.08 (^{p}*C*CH$_3$), 34.98 (^{o}*C*CH$_3$), 59.17 (OCH_2CH$_2$), 62.56 (NCH_2CH$_2$), 117.77, 125.70, 126.72, 136.62, 139.88, 158.13 (Ar), 166.83 (*C*=N). Anal. Calcd for $C_{19}H_{31}NO_2$: C, 74.71; H, 10.23; N, 4.59. Found: C, 74.73; H, 10.32; N, 4.58. HRMS (ESI): m/z 306.2501 [M + H$^+$], calcd for $C_{19}H_{31}NO_2$, 305.24.

(*E*)-2,4-Di-*tert*-butyl-6-(((5-hydroxypentyl)imino)methyl)phenol (1h; L^8-H). Following the general procedure for synthesis of tridentate Schiff base ligands **1e**−**h**, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.00 g, 4.26 mmol, 1.0 equiv) was added to 5-amino-1-pentanol (0.440 g, 4.26 mmol, 1.0 equiv) in MeOH (30 mL). The solution mixture was heated to reflux overnight and dried over Na_2SO_4, followed by filtration. The volatile component was removed in vacuo to give the tridentate Schiff base ligand **1h** in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H, C(CH_3)$_3$), 1.45 (s, 9H, C(CH_3)$_3$), 1.48 (m, 2H, CH$_2$CH_2CH$_2$), 1.63 (m, 2H, CH$_2$CH_2CH$_2$), 1.74 (m, 2H, CH$_2$CH_2CH$_2$), 3.59 (t, J = 6.84 Hz, 2H, OCH_2CH$_2$), 3.67 (t, J = 6.54 Hz, 2H, NCHCH$_2$), 7.07 (d, J = 2.38 Hz, 1H, C_6H_2), 7.37 (d, J = 2.38 Hz, 1H, C_6H_2), 8.34 (s, 1H, C*H*=N), 13.95 (s, 1H, O*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ 23.39 (CH$_2$*C*H$_2$CH$_2$), 29.40 (C(^{p}*C*H$_3$)$_3$), 30.66 (CH$_2$*C*H$_2$CH$_2$), 31.49 (C(^{o}*C*H$_3$)$_3$), 33.44 (CH$_2$*C*H$_2$CH$_2$), 34.10 (^{p}*C*CH$_3$), 35.00 (^{o}*C*-CH$_3$), 59.43 (OCH_2CH$_2$), 62.80 (NCH_2CH$_2$), 117.80, 125.67, 126.70, 136.63, 139.86, 158.17 (Ar), 158.17 (*C*=N). Anal. Calcd

for $C_{20}H_{33}NO_2$: C, 75.19; H, 10.41; N, 4.38. Found: C, 75.10; H, 10.41; N, 4.38. HRMS (ESI): m/z 320.2708 [M + H$^+$], calcd for $C_{20}H_{33}NO_2$, 319.25.

General Procedure for Synthesis of Tridentate Schiff Base Ligands 1i,j. The corresponding amino acid (2 equiv) and triethylamine (2 equiv) were added to 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde[16a−c] (1.0 equiv) in MeOH (30 mL). The solution mixture was heated to reflux for overnight, and the solvent was removed under reduced pressure to obtain a yellow solid. The resulting yellow solid was washed with water (3 × 20 mL) to remove excess amino acid and triethylamine. The organic layer was separated, dried over $NaSO_4$, and concentrated to dryness under reduced pressure to afford the crude products with 0.5 equiv of triethylamine, which were crystallized in pentane to give a yellow powder in 81−85% yield.

(*E*)-2-((3,5-Di-*tert*-butyl-2-hydroxybenzylidene)amino)-4-(methylthio)butanoic acid (1i; L^9-H). Following the general procedure for synthesis of tridentate Schiff base ligands **1i,j**, *rac*-methionine (1.273 g, 8.535 mmol, 2 equiv) and triethylamine (0.863 g, 8.535 mmol, 2 equiv) were added to 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.00 g, 4.26 mmol) in MeOH (30 mL). Compound **1i** was obtained as a yellow powder in 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (t, J = 7.44 Hz, 4.5H, CH_2CH_3), 1.30 (s, 9H, C(CH_3)$_3$), 1.43 (s, 9H, C(CH_3)$_3$), 2.08 (s, 3H, SCH_3), 2.24 (m, 2H, $CHCH_2CH_2$), 2.52 (m, 2H, CH_2CH_2S), 3.05 (q, J = 7.73 Hz, 3H, CH_2CH_3) 4.08 (m, 1H, $NCHCH_2$) 7.10 (d, J = 2.67 Hz, 1H, C_6H_2), 7.37 (d, J = 2.38 Hz, 1H, C_6H_2), 8.48 (s, 1H, CH=N). ^{13}C NMR (300 MHz, $CDCl_3$): δ 8.41 (CH_2CH_3), 15.19 (SCH_3), 29.25 (CH_2CH_2S), 29.42 (C($^pCH_3$)$_3$), 31.30 ($CHCH_2CH_2$), 31.49 (C($^oCH_3$)$_3$), 34.10 ($^pCCH_3$), 35.01 ($^oCCH_3$), 44.99 (CH_2CH_3), 71.76 ($NCHCH_2$), 117.90, 126.24, 127.02, 136.52, 139.84, 158.22 (Ar), 167.41 (C=N), 175.78 (C=O). Anal. Calcd for $C_{46}H_{77}N_3O_6S_2$: C, 66.39; H, 9.33; N, 5.05; S, 7.71. Found: C, 66.14; H, 9.28; N, 5.07; S, 8.00. HRMS (ESI): m/z 366.2241 [M + H$^+$], calcd for $C_{46}H_{77}N_3O_6S_2$, 365.20.

(*E*)-2-((3,5-Di-*tert*-butyl-2-hydroxybenzylidene)amino)-3-phenylpropanoic acid (1j; L^{10}-H). Following the general procedure for synthesis of tridentate Schiff base ligands **1i,j**, *rac*-phenylalanine (1.409 g, 8.532 mmol, 2 equiv) and triethylamine (0.863 g, 8.532 mmol, 2 equiv) were added to 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.00 g, 4.26 mmol) in MeOH (30 mL). Compound **1j** was obtained as a yellow powder in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 (t, J = 7.23 Hz, 4.5H, CH_2CH_3), 1.25 (s, 9H, C(CH_3)$_3$), 1.43 (s, 9H, C(CH_3)$_3$), 3.00 (q, J = 7.37 Hz, 3H, CH_2CH_3) 3.14 (m, 1H, $CHCH_2$Ph), 3.37 (m, 1H, $CHCH_2$Ph), 4.10 (m, 1H, $NCHCH_2$), 6.93 (d, J = 2.46 Hz, 1H, C_6H_2), 7.10−7.21 (m, 5H, C_6H_5), 7.33 (d, J = 2.46 Hz, 1H, C_6H_2), 8.06 (s, 1H, CH=N). ^{13}C NMR (300 MHz, $CDCl_3$): δ 8.37 (CH_2CH_3), 29.42 (C($^pCH_3$)$_3$), 31.46 (C($^oCH_3$)$_3$), 34.05 ($^pCCH_3$), 35.00 ($^oCCH_3$), 40.24 ($CHCH_2$Ph), 45.10 (CH_2CH_3), 74.61 ($NCHCH_2$), 117.87, 126.17, 126.82, 128.23, 129.66, 136.39, 138.33, 139.61, 158.20 (Ar), 166.95 (C=N), 175.23 (C=O). Anal. Calcd for $C_{54}H_{77}N_3O_6$: C, 75.05; H, 8.98; N, 4.68. Found: C, 75.28; H, 9.14; N, 4.90. HRMS (ESI): m/z 382.2631 [M + H$^+$], calcd for $C_{54}H_{77}N_3O_6$, 381.23.

Preparation of Aluminum Complexes 2a−j. A solution of triethylaluminum in toluene (0.10 M, 0.25 mL, 1 equiv) was added to a solution of the corresponding ligands **1a−j** in 0.75 mL of toluene in a sealed tube, and the reaction mixture was stirred for 3 h at room temperature.

Polymerization Procedure. In a typical experiment carried out in the argon-filled glovebox, a Teflon-screw-capped heavy-walled pressure vessel containing the corresponding aluminum complex **2a−j** and 50 equiv of *rac*-lactide (per aluminum center) in 1.00 mL of toluene was stirred at 70 °C for the designated time period. Upon removal of a small sample of the crude product via syringe, it was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$. The product was isolated and purified by precipitation from dichloromethane by the addition of 5% hydrochloric acid in methanol. The solid polymer was collected and dried under vacuum to constant weight.

General Procedure for Synthesis of Tridentate Schiff Base Aluminum Complexes (2e−g; L$^{5-7}$AlEthyl). A solution of triethylaluminum (1.0 equiv) in pentane was cannulated to a solution of tridentate Schiff base ligand (1 equiv) in pentane. The reaction mixture was stirred until a yellow precipitate was formed, and this mixture was stirred at room temperature for an additional 3 h. The resulting yellow precipitate was washed with cold pentane (3 × 1 mL). The volatile component was removed under reduced pressure to give light yellow solids of complexes **2e−g**.

Synthesis of [L^{5}AlEthyl] (2e). A solution of triethylaluminum (0.463 g, 4.06 mmol, 1.0 equiv) in pentane (2 mL) was cannulated to a suspended solution of the tridentate Schiff base ligand **1e** (1.12 g, 4.06 mmol, 1 equiv) in pentane (2 mL). Complex **2e** was obtained in 62% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.37 (bm, 2H, CH_2CH_3), 0.79, 0.90 (2 sets of t, 3H, CH_2CH_3), 1.29, 1.31 (2 set of s, 9H, C(CH_3)$_3$), 1.45, 1.48 (2 set of s, 9H, C(CH_3)$_3$), 3.52, 3.83 (m, 2H, OCH_2CH_2), 4.10, 4.34 (m, 2H, $NCHCH_2$), 7.01, 7.04 (2 set of d, J = 2.67 and 2.67 Hz, 1H, C_6H_2), 7.45, 7.48 (d, J = 2.67 and 2.38 Hz, 1H, C_6H_2), 8.27, 8.22 (2 set of s, 1H, CH=N). ^{13}C NMR (300 MHz, $CDCl_3$): δ 10.10, 14.07, 22.35, 29.25, 31.43, 33.98, 35.39, 55.40, 55.80,59.31, 60.23, 118.66, 119.19, 126.91, 127.07, 129.74, 137.67, 137.93, 139.90, 139.97, 161.66, 161.93, 166.25, 166.55. Anal. Calcd for $C_{19}H_{30}AlNO_2$: C, 68.85; H, 9.12; N, 4.23. Found: C, 68.63; H, 9.40; N, 4.20.

Synthesis of [L^{6}AlEthyl] (2f). A solution of triethylaluminum (0.156 g, 1.37 mmol, 1.0 equiv) in pentane (2 mL) was cannulated to a suspended solution of the tridentate Schiff base ligand **1f** (0.400 g, 1.37 mmol, 1 equiv) in pentane (2 mL). Complex **2f** was obtained in 20% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.32, −0.14 (2 sets of m, 2H, CH_2CH_3), 0.83, 0.92 (2 set of t, 3H, CH_2CH_3), 1.28, 1.38 (2 set of s, 9H, C(CH_3)$_3$), 1.31, 1.48 (2 set of s, 9H, C(CH_3)$_3$), 1.83, 1.93, 2.21, 3.50, 3.86, 4.11, 4.39 (m, 6H, $CH_2CH_2CH_2$), 6.95, 7.00 (2 set of d, J = 2.38 and 2.67 Hz, 1H, C_6H_2), 7.40, 7.47 (d, J = 2.68 and 2.68 Hz, 1H, C_6H_2), 8.04, 8.09 (2 set of s, 1H, CH=N). ^{13}C NMR (300 MHz, $CDCl_3$): δ 10.22, 10.34, 29.44, 30.36, 31.40, 31.82, 33.89, 35.02, 35.16, 57.45, 60.77, 61.30, 63.52, 118.22, 118.66, 127.37, 127.64, 129.57, 129.69, 137.54, 137.80, 139.24, 139.51, 161.57, 161.68, 167.61, 167.92. Anal. Calcd for $C_{20}H_{32}AlNO_2$: C, 69.54; H, 9.34; N, 4.05. Found: C, 68.81; H, 9.54; N, 4.01.

Synthesis of [L^{7}AlEthyl] (2g). A solution of triethylaluminum (0.196 g, 1.71 mmol, 1.0 equiv) in pentane (2 mL) was canulated to a suspended solution of the tridentate Schiff base ligand **1g** (0.525 g, 1.71 mmol, 1 equiv) in pentane (2 mL). Complex **2g** was obtained in 21% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.34, −0.15 (m, 2H, CH_2CH_3), 0.82, 0.88 (2 sets of m, 3H, CH_2CH_3), 1.31 (s, 9H, C(CH_3)$_3$), 1.50 (s, 9H, C(CH_3)$_3$), 1.72 (m, 2H, $CH_2CH_2CH_2$), 2.17 (m, 2H, $CH_2CH_2CH_2$), 3.44 (m, 2H, OCH_2CH_2), 4.05 (m, 2H, $NCHCH_2$), 6.99 (d, J = 2.68 Hz, 1H, C_6H_2), 7.45 (d, J = 2.68 Hz, 1H, C_6H_2), 8.16 (s, 1H, CH=N), 13.90 (s, 1H, OH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 10.08, 10.52, 14.07, 22.34, 27.73, 28.68, 29.50, 31.38, 33.85, 33.94, 34.73, 35.44, 58.06, 58.35, 61.56, 62.18. Anal. Calcd for $C_{21}H_{34}AlNO_2$: C, 70.16; H, 9.53; N, 3.90. Found: C, 69.12; H, 9.91; N, 3.57.

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Supporting Information Available: A table and CIF files giving crystallographic data for complexes **2f** (cis) and **2f** (trans). This material is available free of charge via the Internet at http://pubs.acs.org.