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Monomethylaluminum and dimethylaluminum pyrrolylaldiminates for the ring-opening polymerization of *rac*-lactide: effects of ligand structure and coordination geometry†

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Two series of aluminum alkyl complexes supported by pyrrolylaldiminate ligands, $LAlMe_2$ (**1a–7a**) and L_2AlMe (**1b–7b**), were successfully synthesized and characterized by NMR spectroscopy and elemental analysis. Reactions of trimethylaluminum with the corresponding pyrrolylaldiminate ligands in the molar ratios of 1 : 1 and 1 : 2 yielded dimethylaluminum pyrrolylaldiminates (**1a–7a**) and monomethylaluminum pyrrolylaldiminates (**1b–7b**), respectively, in good yields. The structure of **3b**, determined by single-crystal X-ray diffraction, displayed a distorted trigonal bipyramidal geometry with the τ value of 0.65. Upon addition of 1 equivalent of benzyl alcohol, all complexes promoted the living ring-opening polymerization of *rac*-lactide with a good control over molecular weights and polydispersities. Complexes **6a** and **7a** were found to efficiently mediate the immortal polymerization in the presence of excess equivalents of benzyl alcohol (up to 5 equivalents), as evidenced by the narrow PDI values and the good agreement between the experimental M_n values and monomer/benzyl alcohol ratios. The steric and electronic effects of the imine nitrogen substituents had a strong influence on the polymerization activities both in catalytic activity and polymer microstructure. The catalytic activity decreased as follows: 4-Me-C_6H_4 (**3**) > C_6H_5 (**1**) ≈ 4-F-C_6H_4 (**2**) ≈ 2-Me-C_6H_4 (**5**) > 4-OMe-C_6H_4 (**4**) ≫ 2-^{t}Bu-C_6H_4 (**6**) > adamantyl (**7**). In comparison, the catalytic activity of the monomethylaluminum complex is slightly higher than that of the dimethylaluminum counterpart. The polymerization of *rac*-lactide by **6b** yielded heterotactically enriched polylactide (P_r = 0.60) whereas the isotactic-enriched polymer (P_m = 0.74) was obtained from **7b**.

Introduction

The ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA) to form polylactide (PLA) is a topic of interest in both academic and industrial research due to the biomedical, pharmaceutical, and agriculture applications of polylactide.[1] The ROP of *rac*-LA occurs *via* a coordination–insertion mechanism initiated by metal alkoxides or amide complexes.[2] Among the metal-based initiators, aluminum complexes have received considerable attention because of their good control over the polymerization reaction, ability to control the polymer microstructure *via* ligand modification, high Lewis acidity and low toxicity, although their activity is low.[3]

Over the past few decades, particular attention has been given to aluminum complexes supported by tetradentate ligands, such as Salen,[4] Salan,[5] and Salalen.[6] These complexes have been reported to display excellent molecular weight and stereoselectivity control. Recently, the anilido–aldimine ligand, closely related to the Salen framework, has been used for the synthesis of dimethylaluminum complexes.[7] These complexes were found to be effective initiators for the controlled ROP of *rac*-LA. For the bidentate aluminum complexes, most studies have focused on the use of these complexes for the ROP of ε-caprolactone.[8] Only a few studies have been reported on low-coordinate aluminum complexes bearing bidentate ligands for the ROP of LA and other lactone monomers.[9] For example, aluminum complexes supported by bidentate phenoxy–thioether ligands have been recently exploited to polymerize ε-caprolactone, L-LA, and *rac*-LA in a controlled fashion and the steric and electronic characteristics of the ligands were found to have moderate influence on the polymerization

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performance of the complexes.[10] The ROP of L-LA with high conversions obtained in a short period of time was achieved by employing aminoarenethiolate aluminum complexes.[11] Recently, it has been found that dimethylaluminum complexes stabilized by salicylaldiminate ligands promoted the living and well-controlled polymerization of *rac*-LA with various polymer microstructures, depending upon the imino substituents of the ligand framework.[12]

Unlike the closely related salicylaldiminate ligands, the pyrrolylaldiminate ligands have received much less attention. The synthesis of pyrrolylaldiminate complexes of Zn, Cr, Ti, Mg, Al, Sm and Y have been reported.[13] To the best of our knowledge, there is no such report on the use of aluminum pyrrolylaldiminates for the application in the ROP of lactide and other cyclic ester monomers. Thus, herein we report the synthesis of two novel series of aluminum complexes supported by bidentate pyrrolylaldiminate ligands. The catalytic performance of these complexes for the ROP of *rac*-LA is also presented. Additionally, the effects of the structure of the ancillary ligands and the coordination geometry around the metal center on the polymerization activity are discussed.

Results and discussion

Synthesis and characterization of aluminum pyrrolylaldiminate complexes 1a–7a and 1b–7b

The pyrrolylaldiminate ligands (**HL^1**–**HL^7**) were synthesized by reacting pyrrole-2-carboxaldehyde with an equimolar amount of the corresponding primary amines in ethanol with a small amount of formic acid as a catalyst according to the literature procedure.[13c,14] As illustrated in Scheme 1, dimethylaluminum pyrrolylaldiminate complexes (**1a–7a**) were prepared in good yields (42–89%) by the stoichiometric reaction of the appropriate ligands with one equivalent of $AlMe_3$ in toluene at room temperature. Treatment of $AlMe_3$ with the appropriate ligands in the molar ratio 1 : 2 in toluene at 100 °C afforded monomethylaluminum pyrrolylaldiminates (**1b–7b**) in good yields (50–91%).

All aluminum complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The formation of aluminum complexes was demonstrated by the disappearance of the N–H signal of the free ligands and the appearance of the methyl protons bound to the aluminum in the high field region (δ −0.26 to −0.69 ppm) of the NMR spectra, which is characteristic of an Al–CH_3 group (see Fig. S1–S14 in ESI†).[15] The integration ratio of the signals ascribed to the imine and the methyl protons of the aluminum methyl for complexes **1a–7a** was 1 : 6, demonstrating the formation of the four-coordinate aluminum complexes, whereas the integration ratio of 2 : 3 was observed for five-coordinate aluminum counterparts **1b–7b**.

Single crystals of **3b** suitable for X-ray diffraction analysis were grown from a saturated hexane solution at −20 °C. The molecular structure of **3b** features a monomeric molecule with a five-coordinate aluminum center in a geometry best described as a distorted trigonal bipyramid with a τ value of 0.65.[16] An ORTEP view and selected bond lengths and angles are shown in Fig. 1 (see Tables S1 and S2 in ESI† for the crystallographic details). The pyrrolyl nitrogen atoms (N1 and N15) and the methyl carbon atom (C29) arrange at the equatorial positions and axial positions are occupied by the two imino

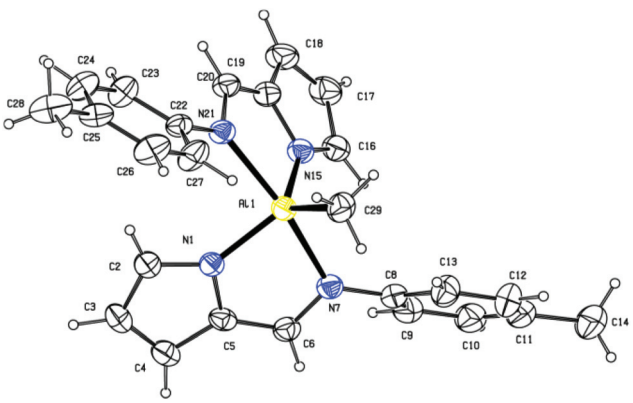
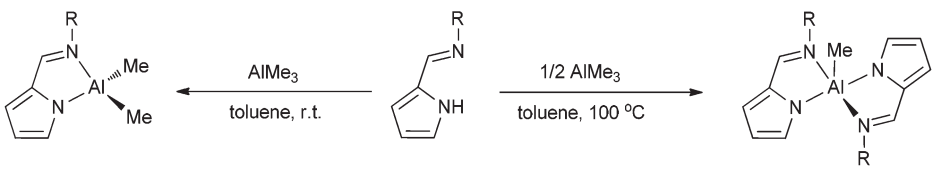


Fig. 1 Molecular structure of L^1_2AlMe (**1b**). Selected bond lengths (Å) and angles (°) are as follows: Al1–N21, 2.125(2); Al1–N7. 2162(2); Al1–N1, 1.912(2); Al1–N5, 1.908(2); Al1–C29, 1.963(3); N1–Al1–N15, 115.47(9); N1–Al1–N21, 90.74(8); N1–Al1–N7, 80.23(8); N1–Al1–C29, 125.3(1); N15–Al1–N21, 81.38(9); N15–Al1–N7, 91.13(9); N15–Al1–C29, 119.3(1); N21–Al1–N7, 164.53(9); N21–Al1–C29, 97.9(1); N7–Al1–C29, 97.5(1).



1a: R = C_6H_5
2a: R = 4-F-C_6H_4
3a: R = 4-Me-C_6H_4
4a: R = 4-OMe-C_6H_4
5a: R = 2-Me-C_6H_4
6a: R = 2-^{t}Bu-C_6H_4
7a: R = Adamantyl

HL^1: R = C_6H_5
HL^2: R = 4-F-C_6H_4
HL^3: R = 4-Me-C_6H_4
HL^4: R = 4-OMe-C_6H_4
HL^5: R = 2-Me-C_6H_4
HL^6: R = 2-^{t}Bu-C_6H_4
HL^7: R = Adamantyl

1b: R = C_6H_5
2b: R = 4-F-C_6H_4
3b: R = 4-Me-C_6H_4
4b: R = 4-OMe-C_6H_4
5b: R = 2-Me-C_6H_4
6b: R = 2-^{t}Bu-C_6H_4
7b: R = Adamantyl

Scheme 1 Synthesis of pyrrolylaldiminate aluminum complexes.

nitrogen atoms (N7 and N21). The Al–$N_{pyrrole}$ distances of 1.912(2) Å and 1.908(2) Å are longer than those in the recently reported compound AlMe{2-[(3′,5′-$Me_2C_3N_2C_6H_4N$=CH)-C_4H_3N]}$_2$ [1.899(4) Å and 1.901(4) Å],[17] while the Al–CH_3 bond [1.963(3) Å] is longer than that found in AlMe{2-[(3′,5′-$Me_2C_3N_2C_6H_4N$=CH)C_4H_3N]}$_2$ [1.949(5) Å]. The Al–N_{imino} distances in complex **3b** [2.125(2) Å and 1.162(2) Å] are longer than those reported in AlMe{2-[(3′,5′-$Me_2C_3N_2C_6H_4N$=CH)-C_4H_3N]}$_2$ [2.115(3) Å and 2.112(4) Å][17] and AlCl{2-[(2′,6′-$^iPr_2C_6H_3N$=CH)C_4H_3N]}$_2$ [1.993(1) Å and 1.962(1) Å].[13a]

Ring-opening polymerization of *rac*-lactide

Polymerizations of *rac*-LA using dimethylaluminum pyrrolylaldiminate complexes (**1a–7a**) and monomethylaluminum pyrrolylaldiminates (**1b–7b**) in the presence of 1 equivalent of benzyl alcohol to form *in situ* aluminum alkoxide species were carried out at 70 °C in toluene. The molar ratio of *rac*-LA to initiator was fixed at 100 : 1 ($[LA]_0/[Al]$ = 100; $[LA]_0$ = 0.83 M; [Al] = 8.33 mM; M_n (theory) = 14 400). All complexes were effective for the polymerization of *rac*-LA, as shown in Table 1. The molecular weights and PDIs (M_w/M_n) were determined by gel permeation chromatography (GPC) using the Mark–Houwink correction factor of 0.58.[18] All of the initiator systems exhibited molecular weights in close agreement with theoretical values and narrow molecular weight distributions in accord with controlled living polymerizations (entries 1–14). For complexes **1a–5a** and **1b–5b**, the polymerizations proceeded to conversion over 84% within 8 hours (in the range of 84–92%) while the polymerizations using complexes **6a** and **6b** reached 58% and 65% conversion, respectively, at the same period of time. Changing the substituted phenyl group with the adamantyl moiety (7) resulted in a significant decrease of the catalytic activity. The polymerization time of 108 hours was required for complexes **7a** and **7b** to achieve 91% and 95% conversion, respectively. The living characteristic of the polymerization was also demonstrated by a linear relationship between the number-averaged molecular weights (M_n) and monomer conversion with narrow molecular weight distributions, as illustrated in Fig. 2 (see also Fig. S15–S27 in ESI†).

In the case of dimethylaluminum pyrrolylaldiminate complexes (**1a–7a**), a good correlation between the experimental and theoretical M_n values demonstrated that a single polymer chain was produced per aluminum center, reflecting the single-site nature of the active species. When two equivalents of benzyl alcohol were added, the molecular weights of polymers produced by **1a–5a** were significantly lower than the theoretical values and the PDI values became broader (entries 1–5, Table 2), suggesting that benzyl alcohol acted as a chain transfer agent in these catalytic systems.[12b] However, in the case of complexes **6a** and **7a**, the immortal polymerization condition[3h,12a,19] was observed as evidenced by the narrow PDI values and the good agreement between the observed M_n values and the monomer/alcohol ratio (entries 6 and 10, Table 2). The immortal character of both complexes was further investigated using excess equivalents of benzyl alcohol

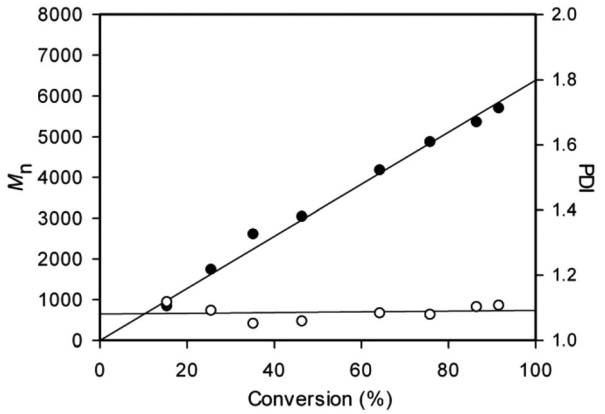


Fig. 2 Plots of PLA M_n (●) and PDI (○) as a function of monomer conversion for a *rac*-LA polymerization using **1a**/$PhCH_2OH$ ($[LA]_0/[Al]$ = 50, toluene, 70 °C).

Table 1 Polymerization of *rac*-lactide using complexes **1a–7a** and **1b–7b** in the presence of 1 equivalent of benzyl alcohol[a]

Entry	Complex	Time (h)	Conversion[b] (%)	M_n (theory)[c] (g mol^{-1})	M_n (GPC)[d] (g mol^{-1})	M_w/M_n [d]	P_r [e]	P_m [e]
1	**1a**	8	86	12 500	11 500	1.16	0.50	0.50
2	**1b**	8	91	13 200	12 400	1.28	0.47	0.53
3	**2a**	8	92	13 400	12 400	1.24	0.46	0.54
4	**2b**	8	86	12 500	11 700	1.15	0.47	0.53
5	**3a**	8	90	13 100	11 600	1.21	0.46	0.54
6	**3b**	8	92	13 400	12 100	1.16	0.48	0.52
7	**4a**	8	90	13 100	12 100	1.18	0.48	0.52
8	**4b**	8	89	12 900	11 600	1.14	0.47	0.53
9	**5a**	8	84	12 200	9800	1.19	0.44	0.56
10	**5b**	8	92	13 400	12 100	1.21	0.45	0.55
11	**6a**	8	58	8500	6000	1.06	0.58	0.42
12	**6b**	8	65	9500	7100	1.12	0.60	0.40
13	**7a**	108	91	13 200	14 000	1.06	0.37	0.63
14	**7b**	108	95	13 800	13 300	1.04	0.26	0.74

[a] $[LA]_0/[Al]$ = 100, $[Al]/[PhCH_2OH]$ = 1, $[LA]_0$ = 0.83 M, toluene, 70 °C. [b] As determined *via* integration of the methine resonances (^{1}H NMR) of LA and PLA ($CDCl_3$, 400 MHz). [c] Calculated by [($[LA]_0/[Al]$) × 144.13 × conversion] + 108.14. [d] Determined by gel permeation-chromatography (GPC) calibrated with polystyrene standards in THF and corrected by a factor of 0.58 for PLA. [e] P_m and P_r are the probability of *meso* and *racemic* linkages between monomer units, respectively.

Table 2 Polymerization of *rac*-lactide using complexes **1a–7a** in the presence of benzyl alcohol[a]

Entry	Complex	$[LA]_0 : [Al] : [PhCH_2OH]$	Time (h)	Conversion[b] (%)	M_n (theory)[c] (g mol^{-1})	M_n (GPC)[d] (g mol^{-1})	M_w/M_n [d]
1	**1a**	100 : 1 : 2	12	95	7000	3700	1.93
2	**2a**	100 : 1 : 2	12	97	7100	3900	1.94
3	**3a**	100 : 1 : 2	12	94	6900	4000	1.98
4	**4a**	100 : 1 : 2	12	98	7200	2700	1.75
5	**5a**	100 : 1 : 2	12	95	7000	5000	2.44
6	**6a**	100 : 1 : 2	24	95	7000	7700	1.10
7	**6a**	100 : 1 : 3	12	94	4600	4000	1.05
8	**6a**	100 : 1 : 4	12	94	3500	3200	1.05
9	**6a**	100 : 1 : 5	12	96	2900	2800	1.03
10	**7a**	100 : 1 : 2	108	95	7000	8100	1.10
11	**7a**	100 : 1 : 3	24	96	4700	5600	1.14
12	**7a**	100 : 1 : 4	24	96	3600	4000	1.14
13	**7a**	100 : 1 : 5	24	98	2900	3200	1.10

[a] $[LA]_0$ = 0.83 M, toluene, 70 °C. [b] As determined *via* integration of the methine resonances (^{1}H NMR) of LA and PLA ($CDCl_3$, 400 MHz). [c] Calculated by ([([LA]$_0$/[Al]) × 144.13 × conversion]/[$PhCH_2OH$]) + 108.14. [d] Determined by gel permeation-chromatography (GPC) calibrated with polystyrene standards in THF and corrected by a factor of 0.58 for PLA.

(up to 5 equivalents) (entries 7–9 and 11–13, Table 2). The increase in the ratio of benzyl alcohol led to a decrease in the molecular weight of the resulting polymer. The good degree of control over the polymerization in terms of the narrow PDI values and the good agreement between the experimental and monomer/benzyl alcohol ratios were still observed. This illustrates that the number of polymer molecules becomes larger, proportional to the number of added benzyl alcohol molecules.[19d] Taken together, these results showed that a fast reversible exchange between dormant hydroxyl-end-capped polymer chains/free alcohol and the active growing polymer chain coordinated onto the aluminum center can take place faster than the chain propagation.[19]

Kinetic studies of *rac*-LA polymerization initiated by complexes **1a–7a** and **1b–7b** in the presence benzyl alcohol were carried out in toluene at 70 °C ([LA]$_0$/[Al] = 50; [Al] = 8.33 mM; $[LA]_0$ = 0.42 M). In each case, kinetics of the first-order in monomers were observed, as evidenced from the linear relationship between ln([LA]$_0$/[LA]$_t$) and time (Fig. 3 and see Fig. S28–S33 in ESI†). In addition, the *rac*-LA polymerization displayed no induction period, indicating that the active species form instantaneously by an *in situ* alcoholysis reaction. Thus, the polymerization proceeded according to the rate law $-d[LA]/dt = k_{app}[LA]$, where $k_{app} = k_p[Al]^x$, in which k_p is the propagation rate constant. To determine the order in aluminum (x), kinetic experiments were conducted with variable concentrations of the catalyst. For example, the appropriate semi-logarithmic plots of different concentrations of dimethylaluminum complex **1a** are shown in Fig. 4. The linear relationship between ln k_{app} *versus* ln[**1a**] revealed that the order in the catalyst was *ca.* 1.0 (1.15), indicating a first-order dependence on the catalyst concentration (Fig. 5). The propagation rate constant (k_p) of 1.07 × 10^{-2} s^{-1} mol^{-1} L was obtained from the gradient of the k_{app} *versus* [**1a**] plot, as depicted in Fig. 6. Therefore, the overall rate equation is $-d[LA]/dt = k_p[LA][\mathbf{1a}]$. The same procedure was applied for the determination of the overall rate law of complexes **1b**, **4a**, and **4b** (see Fig. S34–S42 in ESI†). The order (x) in **1b** was *ca.* 1.0 (0.98) and the k_p value of 1.33 × 10^{-2} s^{-1} mol^{-1} L was obtained, exhibiting the overall

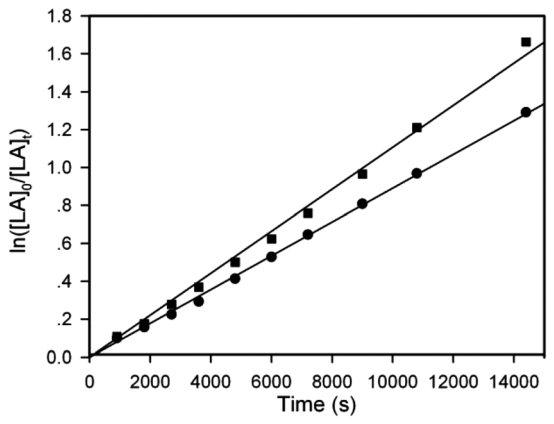


Fig. 3 Semilogarithmic plots of *rac*-lactide conversion *versus* time in toluene at 70 °C with complexes **1a** (●) and **1b** (■) ([LA]$_0$/[Al] = 50, [Al]/[$PhCH_2OH$] = 1, $[LA]_0$ = 0.42 M, [Al] = 8.33 mM).

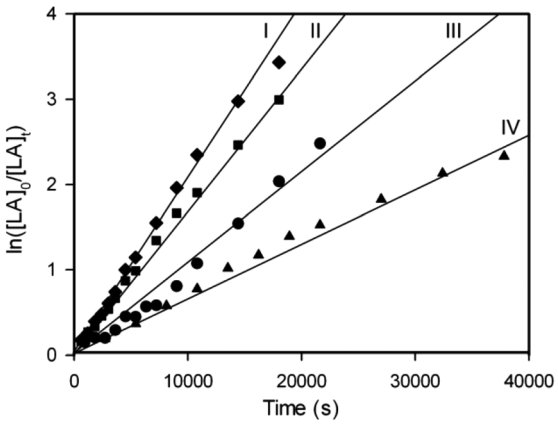


Fig. 4 Semilogarithmic plots of the *rac*-lactide conversion *versus* time in toluene at 70 °C with complex **1a**/$PhCH_2OH$ as an initiator ($[LA]_0$ = 0.42 M: I, [Al] = 16.65 mM, [LA]$_0$/[Al] = 25; II, [Al] = 12.49 mM, [LA]$_0$/[Al] = 34; III, [Al] = 8.33 mM, [LA]$_0$/[Al] = 50; IV, [Al] = 6.24 mM, [LA]$_0$/[Al] = 67).

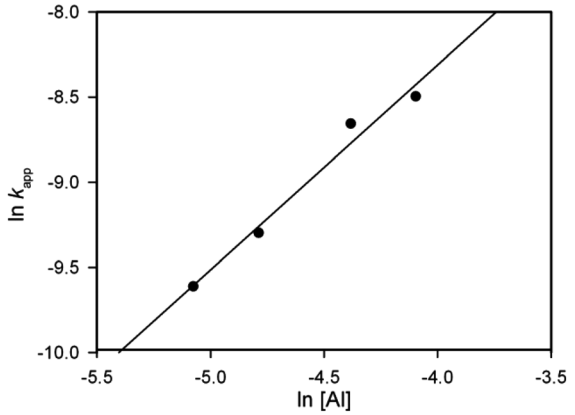


Fig. 5 Plot of ln k_{app} *versus* ln [Al] for the polymerization of *rac*-lactide with complex **1a**/$PhCH_2OH$ as an initiator (toluene, 70 °C, $[LA]_0$ = 0.42 M).

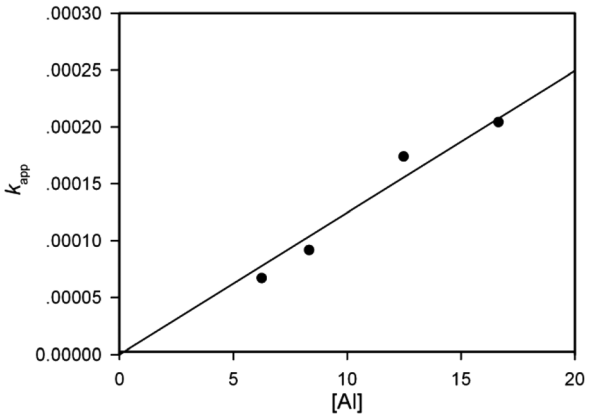


Fig. 6 Plot of k_{app} *versus* [Al] for the polymerization of *rac*-lactide with complex **1a**/$PhCH_2OH$ as an initiator (toluene, 70 °C, $[LA]_0$ = 0.42 M).

rate equation is $-d[LA]/dt = k_p[LA][\mathbf{1b}]$. In the case of complexes **4a** and **4b**, the k_p values were 1.18×10^{-2} s^{-1} mol^{-1} L and 1.32×10^{-2} s^{-1} mol^{-1} L, respectively. The order (x) values for both cases were also *ca.* 1.0 (1.20 for **4a** and 1.17 for **4b**), supporting the first-order kinetics in monomer.

The first-order rate constants (k_{app}) for the polymerization of *rac*-LA with complexes **1a–7a** and **1b–7b** were collected in Table 3. It was found that the catalytic activity of each five-coordinate aluminum complex was slightly higher than that of its four-coordinate aluminum counterpart. This can be ascribed to the more electrophilicity at the aluminum center due to the presence of two pyrrolylaldiminate ligands. The results also revealed that the imino substituents exerted great influence on the catalytic activity. The electronic factor of the *para*-substituent of the phenyl group affected the catalytic activity in the order *p*-Me (**3**) > *p*-H (**1**) ≈ *p*-F (**2**) > *p*-OMe-C_6H_4 (**4**). Complex **3b** displayed the highest catalytic activity with the k_{app} value of 144.5×10^{-6} s^{-1} (entry 6, Table 3) whereas complex **4a** exhibited the lowest catalytic activity, $k_{app} = 72.4 \times 10^{-6}$ s^{-1} (entry 7, Table 3). These results demonstrated that the presence of an electron-donating substituent increased the electron density at the metal center, leading to a decrease in activity.[5a,9h] When a fluorine atom was introduced at the *para*-position of the phenyl group (complexes **2a** and **2b**), the catalytic activities of these complexes were higher than those of complexes **4a** and **4b**, respectively, suggesting the enhancement of the catalytic activity by a decrease of electron density at the aluminum center.[20] However, in comparison with the *para*-methyl substituted complexes (**3a** and **3b**), the catalytic activities of the *para*-fluoro substituted complexes (**2a** and **2b**) slightly dropped but were comparable to those of the unsubstituted aluminum analogues (**1a** and **1b**). These complicated results were also observed for β-diketiminate aluminum complexes containing fluorine and chlorine atoms at the *para*-position of the phenyl moiety[5a] and bis(phenolato)bis(amine) aluminum complexes with a *para*-bromo phenoxy substituent.[21] In these cases, an electron-donating conjugated effect was responsible for the lower activity: *i.e.*, the lone pair in the p-orbital of the halogen atom can donate electron *via* p–π bonding to its *para*- and *ortho*-positions when it was introduced into a phenyl ring.[5a] Substitution of the methyl group at the *ortho*-position of the phenyl rings (**5a** and **5b**) resulted in a diminished activity when compared with the catalytic activities of the *para*-methyl substituted aluminum complexes (**3a** and **3b**). The steric effect was more pronounced when the bulky *tert*-butyl group was introduced at the *ortho*-position of the phenyl ring (complexes **6a** and **6b**). For example, the catalytic activity of the *ortho*-methyl phenoxy substituent complex **5a** was 144.5×10^{-6} s^{-1} (entry 6, Table 3) while the *ortho-tert*-butyl phenoxy substituent complex **6a** exhibited the lower k_{app} value of 24.7×10^{-6} s^{-1} (entry 11, Table 3). The observed lower activity was attributed to the steric protection at the aluminum center by the bulky *tert*-butyl group, which hindered the incorporation of monomer into the growing polymer chain.[22] In addition, replacing the substituted phenyl group with the sterically more congested adamantyl moiety (complexes **7a** and **7b**) led to a decrease in the catalytic activity. The lowest catalytic activity observed in this study was obtained from complex **7a** with the k_{app} value of 15.6×10^{-6} s^{-1} (entry 13, Table 3). These observations revealed that both electronic and steric effects in

Table 3 Kinetic results of *rac*-lactide polymerization using complexes **1a–7a** and **1b–7b** in the presence of 1 equivalent of benzyl alcohol[a]

Entry	Complex	k_{app} ($\times 10^{-6}$ s^{-1})
1	**1a**	89.1
2	**1b**	110.7
3	**2a**	88.7
4	**2b**	115.6
5	**3a**	113.0
6	**3b**	144.5
7	**4a**	72.4
8	**4b**	95.5
9	**5a**	83.6
10	**5b**	107.1
11	**6a**	24.7
12	**6b**	34.4
13	**7a**	15.6
14	**7b**	19.7

[a] $[LA]_0/[Al] = 50$, $[Al]/[PhCH_2OH] = 1$, $[LA]_0 = 0.42$ M, toluene, 70 °C.

the imino substituent had a strong impact on the catalytic activity. For this study, the activity decreased in the order 4-Me-C_6H_4 (**3**) > C_6H_5 (**1**) ≈ 4-F-C_6H_4 (**2**) ≈ 2-Me-C_6H_4 (**5**) > 4-OMe-C_6H_4 (**4**) ≫ 2-^{t}Bu-C_6H_4 (**6**) > adamantyl (**7**).

The polymer microstructure of the PLA was determined by the inspection of the methine region of the homonuclear decoupled ^{1}H NMR spectra of the resultant polymers (Fig. 7 and Fig. S37–S48 in ESI†).[23] Complexes **1a–5a** and **1b–5b** polymerized *rac*-LA to atactic polylactides with the P_m = 0.50–0.56 (entries 1–10, Table 1). Heterotactic-enriched polylactides were produced by complexes **6a** (P_r = 0.58) and **6b** (P_r = 0.60) with the *ortho-tert*-butyl substituent on the phenyl ring (entries 11 and 12, Table 1). Apparently, the steric hindrance at the *ortho*-position of aniline derivatives had a certain effect on the stereoselectivity. Exchanging the substituted phenyl unit with the adamantyl group resulted in the production of isotactic-enriched polylactide. PLA with a P_m value of 0.63 was obtained from complex **7a** (entry 13, Table 1). The use of five-coordinate aluminum complex **7b** with the *N*-adamantyl substituent gave rise to isotacticity enhancement of the polymerization. The PLA produced by **7b** was isotactic with a P_m value of 0.74 (entry 14, Table 1), as evidenced by the observed strong *mmm* tetrad in Fig. 7b.

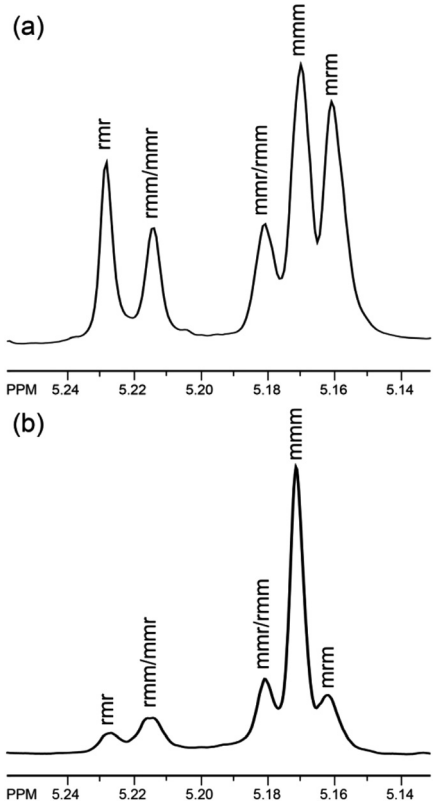


Fig. 7 Homonuclear decoupled ^{1}H NMR spectra of the methine region of PLA prepared from *rac*-lactide at 70 °C in toluene (500 MHz, $CDCl_3$) with (a) **6b**/$PhCH_2OH$ and (b) **7b**/$PhCH_2OH$.

Ring-opening polymerization of ε-caprolactone

As a result of the good performance in the polymerization of *rac*-LA, all monomethyl aluminium and dimethylaluminum pyrrolaldiminate complexes have been further applied to catalyze the ROP of ε-caprolactone (ε-CL). The polymerizations were carried out under the identical conditions for the polymerization of *rac*-LA and the results are summarized in Table 4. The molecular weights and PDIs (M_w/M_n) were determined by gel permeation chromatography (GPC) using the Mark–Houwink correction factor of 0.56.[24] It was revealed that all complexes exhibited high activity. More than 99% monomer conversion was achieved within 15 min in all cases. A good agreement between the experimental and the theoretical M_n values and a narrow molecular weight distribution were observed, indicating the single-site nature of these catalysts. The results clearly indicate that these catalysts also initiate the ROP of ε-CL in a controlled manner.

Conclusions

In conclusion, the synthesis and characterization of two series of aluminum complexes supported by pyrrolylaldiminate ligands, $LAlMe_2$ (**1a–7a**) and L_2AlMe (**1b–7b**), were reported. All complexes were found to be efficient catalysts for the polymerization of *rac*-lactide and ε-caprolactone in the presence of one equivalent of benzyl alcohol, displaying controlled and living polymerization. The imino substituent and the number of ligands coordinated onto the aluminum center had a strong effect on the catalytic activity and stereoselectivity. In particular, the steric hindrance at the *ortho*-position of the phenyl group of the imino substituent was detrimental to the catalytic activity. The five-coordinate aluminum complex exhibited a slightly higher catalytic activity than its four-coordinate counterpart. In addition, the polymer microstructure of polylactides can be varied from heterotactic-bias to isotactic-bias, depending on the use of imino substituent. Further study will be focused on the fine tuning of the imino substituent in order to enhance the catalytic activity and improve the stereoselectivity of these groups of complexes.

Experimental section

Materials and methods

All manipulations with air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using standard Schlenk and cannula techniques in oven dried glassware or in a glove box. Toluene was distilled from Na-benzophenone before use. Hexane and pentane were distilled from CaH_2 prior to use. Benzyl alcohol was refluxed over sodium and then freshly distilled onto activated 4 Å molecular sieves. All solvents were degassed prior to use unless stated otherwise. NMR solvents were dried over 4 Å molecular sieves and degassed prior to use. Aniline (99%), 4-fluoroaniline (99%), 4-methylaniline (99%), 4-methoxyaniline (99%), 2-methylaniline (99%),

Table 4 Polymerization of ε-caprolactone using complexes **1a–7a** and **1b–7b** in the presence of benzyl alcohol[a]

Entry	Complex	Time (min)	Conversion[b] (%)	M_n (theory)[c] (g mol^{-1})	M_n (GPC)[d] (g mol^{-1})	M_w/M_n [d]
1	**1a**	15	>99	11 500	10 900	1.13
2	**1b**	15	>99	11 500	11 300	1.16
3	**2a**	15	>99	11 500	11 500	1.18
4	**2b**	15	>99	11 500	10 100	1.15
5	**3a**	15	>99	11 500	10 700	1.25
6	**3b**	15	>99	11 500	10 700	1.17
7	**4a**	15	>99	11 500	11 200	1.17
8	**4b**	15	>99	11 500	10 400	1.21
9	**5a**	15	>99	11 500	11 300	1.20
10	**5b**	15	>99	11 500	10 300	1.18
11	**6a**	15	>99	11 500	10 100	1.09
12	**6b**	15	>99	11 500	11 300	1.14
13	**7a**	15	>99	11 500	11 500	1.15
14	**7b**	15	>99	11 500	11 500	1.13

[a] $[CL]_0/[Al] = 100$, $[Al]/[PhCH_2OH] = 1$, $[CL]_0 = 0.83$ M, toluene, 70 °C. [b] As determined *via* integration of the methylene resonances (^{1}H NMR) of CL and PCL ($CDCl_3$, 400 MHz). [c] Calculated by [([CL]$_0$/[Al]) × 114.13 × conversion] + 108.14. [d] Determined by gel permeation-chromatography (GPC) calibrated with polystyrene standards in THF and corrected by a factor of 0.56 for PCL.

2-*tert*-butylaniline (99%), 1-adamantylamine (97%), pyrrole-2-carboxaldehyde (98%) and trimethyl aluminum (2.0 M solution in toluene) were purchased from Aldrich and used as received. The monomer *rac*-lactide (Aldrich) was sublimed three times prior to use. All other chemicals were commercially available and used as received unless otherwise stated.

^{1}H (399.87 MHz) and ^{13}C (100.55 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova 400 MHz spectrometer at 300 K. Homonuclear decoupled ^{1}H NMR experiments were performed on Bruker Avance 500 MHz spectrometer. NMR spectra were referenced internally to the residual protio impurity peaks in the $CDCl_3$ solvent (δ ^{1}H: 7.26, ^{13}C: 77.0). The following abbreviations have been used for multiplicities: s (singlet); d (doublet); t (triplet); q (quartet); sept (septet); dd (doublet of doublets); dt (doublet of triplets); td (triplet of doublets); m (unresolved multiplet); br (board). Elemental analysis data (C, H, N) were obtained from a LECO Elemental Analyser CS-932H. Gel permeation chromatography (GPC) measurements were conducted on a Polymer Laboratories PL-GPC-220 instrument equipped with PLgel 5 μm MIXED-D 300 × 7.5 mm columns and tetrahydrofuran (THF) was used as the eluent (flow rate: 1 mL min^{-1} at 40 °C). The number averaged molecular weights (M_n) and polydispersity index (M_w/M_n) were calibrated against polystyrene (PS) standards. To account for the difference in the hydrodynamic volume of polystyrene and polymer, M_n values of PLAs and PCLs were corrected with a Mark–Houwink factor of 0.58[18] and 0.56,[24] respectively.

Synthesis of ligands

Synthesis of phenyl(1*H*-pyrrol-2-ylmethylene)amine, (HL^1). The reaction was performed according to the procedure previously reported in the literature.[13c,14] To a stirred solution of pyrrole-2-carboxaldehyde (1.00 g, 10.52 mmol) in methanol (15 mL) was slowly added aniline (0.98 g, 10.52 mmol). The reaction mixture was stirred and a catalytic amount of formic acid was added. The reaction mixture was stirred at room temperature, during which a white precipitate formed. The mixture was stirred for 5 hours and the white solid was filtered and dried *in vacuo*. Yield: 0.52 g, 29%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (1H, s, NC*H*), 7.42–7.38 (2H, m, *o*-C$_6$*H*$_5$), 7.25–7.20 (3H, m, *m*/*p*-C$_6$*H*$_5$), 6.83–6.81 (1H, m, pyrrole-*H*), 6.71 (1H, dd, $^4J_{HH}$ = 1.4, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.27 (1H, dd, $^3J_{HH}$ = 2.6, $^3J_{HH}$ = 3.6, pyrrole-*H*).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 151.8 (*i*-*C*$_6$H$_5$), 150.2 (N*C*H), 130.65 (pyrrole-*C*), 129.2 (*o*-*C*$_6$H$_5$), 125.4 (pyrrole-*C*H), 123.5 (*p*-*C*$_6$H$_5$), 120.9 (*m*-*C*$_6$H$_5$), 116.9 (pyrrole-*C*H), 110.3 (pyrrole-*C*H).

Anal. calcd for $C_{11}H_{10}N_2$ (170.21): C, 77.62; H, 5.92; N, 16.46%. Found C, 77.73; H, 5.89; N, 16.63%.

Synthesis of (4-fluorophenyl)(1*H*-pyrrol-2-ylmethylene)amine (HL^2). The synthesis of **HL^2** was performed according to the same procedure as for **HL^1**. Yield: 1.40 g, 70%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.42 (1H, br s, pyrrole-N*H*), 8.26 (1H, s, NC*H*), 7.20–7.16 (2H, m, C$_6$*H*$_4$), 7.10–7.05 (2H, m, C$_6$*H*$_4$), 6.81–6.80 (1H, m, pyrrole-*H*), 6.71 (1H, dd, $^4J_{HH}$ = 1.4, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.29 (1H, dd, $^3J_{HH}$ = 2.6, $^3J_{HH}$ = 3.6, pyrrole-*H*).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162.0 (Ar*C*F), 159.6 (Ar*C*F), 150.0 (N*C*H), 147.7 (Ar*C*N), 130.4 (pyrrolyl-*C*), 123.7 (pyrrole-*C*H), 122.2 (Ar*C*F), 122.2 (*C*$_6$H$_4$), 117.2 (pyrrole-*C*H), 116.0 (Ar*C*F), 115.8 (*C*$_6$H$_4$), 110.4 (pyrrole-*C*H).

Anal. calcd for $C_{11}H_9FN_2$ (188.20): C, 70.20; H, 4.82; N, 14.88%. Found C, 69.99; H, 4.70; N, 14.68%.

Synthesis of (4-methylphenyl)(1*H*-pyrrol-2-ylmethylene)-amine (HL^3). The synthesis of **HL^3** was performed according to the same procedure as for **HL^1**. Yield: 1.03 g, 53%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (1H, br s, pyrrole-N*H*), 8.29 (1H, s, NC*H*), 7.21–7.19 (2H, m, C$_6$*H*$_4$), 7.15–7.12 (2H, m, C$_6$*H*$_4$), 6.82–6.80 (1H, m, pyrrole-*H*), 6.68 (1H, dd, $^4J_{HH}$ = 1.4, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.28 (1H, dd, $^3J_{HH}$ = 2.6, $^3J_{HH}$ = 3.5, pyrrole-*H*), 2.39 (3H, s, *p*-C*H*$_3$C$_6$H$_4$).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 149.5 (N*C*H), 149.2 (*i*-*C*$_6$H$_4$), 135.2 (*p*-*C*$_6$H$_4$), 130.8 (pyrrole-*C*), 129.8 (*C*$_6$H$_4$), 123.4 (pyrrole-

*C*H), 120.8 (C_6H_4), 116.6 (pyrrole-*C*H), 110.2 (pyrrole-*C*H), 20.9 (p-$CH_3C_6H_4$).

Anal. calcd for $C_{12}H_{12}N_2$ (184.24): C, 78.23; H, 6.57; N, 15.21%. Found C, 78.30; H, 6.53; N, 15.47%.

Synthesis of (4-methoxyphenyl)(1*H*-pyrrol-2-ylmethylene)-amine (HL[4]). The synthesis of **HL[4]** was performed according to the same procedure as for **HL[1]**. Yield: 0.80 g, 40%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (1H, s, NC*H*), 7.21–7.178 (2H, m, C_6H_4), 6.94–6.91 (2H, m, C_6H_4), 6.85–6.83 (1H, m, pyrrole-H), 6.65 (1H, dd, $^4J_{HH}$ = 1.4, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.27 (1H, dd, $^3J_{HH}$ = 2.6, $^3J_{HH}$ = 3.6, pyrrole-*H*), 3.83 (3H, s, p-O$CH_3C_6H_4$).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 151.0 (p-O$CH_3C_6H_4$), 148.4 (N*C*H), 144.7 (i-C_6H_4), 130.9 (pyrrole-*C*), 123.0 (pyrrole-*C*H), 121.940 (C_6H_4), 116.2 (pyrrole-*C*H), 114.4 (C_6H_4), 110.2 (pyrrole-*C*H), 55.49 (p-O$CH_3C_6H_4$).

Anal. calcd for $C_{12}H_{12}N_2O$ (200.24): C, 71.98; H, 6.04; N, 13.99%. Found C, 71.13; H, 5.89; N, 13.33%.

Synthesis of (2-methylphenyl)(1*H*-pyrrol-2-ylmethylene)-amine (HL[5]). The synthesis of **HL[5]** was performed according to the same procedure as for **HL[1]**. Yield: 1.13 g, 59%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.74 (1H, br s, pyrrole-N*H*), 8.23 (1H, s, NC*H*), 7.34–7.28 (2H, m, C_6H_4), 7.23–7.18 (1H, m, C_6H_4), 7.06–7.03 (1H, m, C_6H_4), 6.72 (1H, dd, $^4J_{HH}$ = 1.4, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.54–6.56 (1H, m, pyrrole-*H*), 6.26 (1H, dd, $^3J_{HH}$ = 2.6, $^3J_{HH}$ = 3.6, pyrrole-*H*), 2.42 (3H, s, o-$CH_3C_6H_4$).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 151.0 (i-C_6H_4), 150.2 (N*C*H), 131.7 (o-C_6H_4), 130.6 (pyrrole-*C*), 130.4 (C_6H_4), 126.9 (C_6H_4), 125.3 (C_6H_4), 123.7 (C_6H_4), 118.4 (pyrrole-*C*H), 116.7 (pyrrole-*C*H), 110.1 (pyrrole-*C*H), 17.9 (o-$CH_3C_6H_4$).

Anal. calcd for $C_{12}H_{12}N_2$ (184.24): C, 78.23; H, 6.57; N, 15.21%. Found C, 78.43; H, 6.44; N, 15.56%.

Synthesis of (2-*tert*-butylphenyl)(1*H*-pyrrol-2-ylmethylene)-amine (HL[6]). The synthesis of **HL[6]** was performed according to the same procedure as for **HL[1]**. Yield: 1.57 g, 66%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (1H, br s, pyrrole-N*H*), 8.12 (1H, s, NC*H*), 7.40 (1H, dd, $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 7.8, C_6H_4), 7.24 (1H, td, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 7.5, C_6H_4), 7.16 (1H, td, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 7.5, C_6H_4), 6.96–6.94 (1H, m, pyrrole-*H*), 6.84 (1H, dd, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 7.5, C_6H_4), 6.68 (1H, dd, $^4J_{HH}$ = 1.3, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.33 (1H, dd, $^3J_{HH}$ = 2.7, $^3J_{HH}$ = 3.6, pyrrole-*H*), 1.47 (9H, s, o-C$(CH_3)_3C_6H_4$).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 151.64 (i-C_6H_4), 148.0 (N*C*H), 142.8 (o-C_6H_4), 131.4 (pyrrole-*C*), 127.1 (C_6H_4), 126.0 (C_6H_4), 125.1 (C_6H_4), 122.6 (C_6H_4), 119.7 (pyrrole-*C*H), 115.4 (pyrrole-*C*H), 110.4 (pyrrole-*C*H), 35.6 (o-*C*$(CH_3)_3C_6H_4$), 30.8 (o-C$(CH_3)_3C_6H_4$).

Anal. calcd for $C_{15}H_{18}N_2$ (226.32): C, 79.61; H, 8.02; N, 12.38%. Found C, 79.90; H, 8.04; N, 12.31%.

Synthesis of (1-adamantyl)(1*H*-pyrrol-2-ylmethylene)amine (HL[7]). The synthesis of **HL[7]** was performed according to the same procedure as for **HL[1]**. Yield: 1.11 g, 46%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (1H, br s, pyrrole-N*H*), 7.78 (1H, s, NC*H*), 6.95–7.01 (1H, m, pyrrole-*H*), 6.59 (1H, d, $^4J_{HH}$ = 1.6, pyrrole-*H*), 6.25 (1H, dd, $^3J_{HH}$ = 2.8, $^3J_{HH}$ = 3.2, pyrrole-*H*), 2.16 (3H, br s, C*H*), 1.82 (6H, d, $^3J_{HH}$ = 2.4, NCH_2), 1.57–1.69 (6H, m, CH_2).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.9 (N*C*H), 146.1 (pyrrole-*C*), 124.6 (pyrrole-*C*H), 117.2 (pyrrole-*C*H), 110.4 (pyrrole-*C*H), 57.1 (N*C*$(CH_2)_3$), 42.9 (C(*C*$H_2)_3$), 36.4 (CH(*C*$H_2)_3$), 29.5 (*C*H$(CH_2)_3$).

Anal. calcd for $C_{15}H_{20}N_2$ (228.33): C, 78.90; H, 8.83; N, 12.27%. Found C, 79.09; H, 8.79; N, 12.46%.

Synthesis of complexes

Synthesis of L[1]AlMe$_2$ (1a). To a stirred solution of **HL[1]** (0.80 g, 4.70 mmol) in toluene (20 mL) was slowly added $AlMe_3$ (2.35 mL of a 2.0 M solution in toluene, 4.70 mmol). The reaction mixture was stirred at 100 °C for 24 hours, after which the volatiles were removed *in vacuo* to yield an orange oil. The product was obtained as a yellow crystal by sublimation under reduced pressure at room temperature. Yield: 0.45 g, 42%.

^{1}H NMR (400 MHz, CDCl3): δ 8.36 (1H, d, $^4J_{HH}$ = 1.1, NC*H*), 7.45–7.40 (2H, m, Ar*H*), 7.35–7.31 (3H, m, Ar*H* and pyrrole-*H*), 7.30–7.25 (1H, m, Ar*H*), 7.05 (1H, dd, $^4J_{HH}$ = 1.0, $^3J_{HH}$ = 3.7, pyrrole-H), 6.48 (1H, dd, $^4J_{HH}$ = 1.80, $^3J_{HH}$ = 3.7, pyrrole-*H*), −0.62 (6H, s, Al$(CH_3)_2$).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 153.8 (N*C*H), 144.1 (Ar*C*), 137.2 (pyrrole-*C*H), 136.4 (pyrrole-*C*), 129.9 (Ar*C*H), 126.6 (Ar*C*H), 121.4 (Ar*C*H), 120.4 (pyrrole-*C*H), 116.0 (pyrrole-*C*H).

Anal. calcd for $C_{13}H_{15}N_2Al$ (226.25): C, 69.01; H, 6.68; N, 12.38%. Found: C, 68.95; H, 7.09; N, 12.19%.

Synthesis of L[2]AlMe$_2$ (2a). To a stirred suspension of **HL[2]** (1.60 g, 8.50 mmol) in toluene (20 mL) was slowly added $AlMe_3$ (4.25 mL of a 2.0 M solution in toluene, 8.50 mmol). The reaction mixture was stirred at room temperature for 24 hours, after which the volatiles were removed *in vacuo* to leave an orange oil. After recrystallization in hexane at −20 °C, pale yellow crystals formed. Yield: 1.31 g, 63%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (1H, d, $^4J_{HH}$ = 1.0, NC*H*), 7.34–7.32 (1H, m, pyrrole-*H*), 7.29–7.25 (2H, m, Ar*H*), 7.13–7.07 (2H, m, Ar*H*), 7.03 (1H, dd, $^4J_{HH}$ = 0.9, $^3J_{HH}$ = 3.7, pyrrole-*H*), 6.46 (1H, dd, $^4J_{HH}$ = 1.1, $^3J_{HH}$ = 3.7, pyrrole-*H*), −0.63 (6H, s, Al$(CH_3)_2$).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 162.4 (Ar*C*F), 159.9 (Ar*C*F), 153.9 (N*C*H), 140.4 (Ar*C*N), 137.3 (pyrrolyl-*C*H), 136.2 (pyrrole-*C*), 121.8 (Ar*C*H), 121.8 (pyrrole-*C*H), 121.5 (Ar*C*H), 116.8 (Ar*C*H), 116.6 (Ar*C*H), 116.1 (pyrrole-*C*H).

Anal. calcd for $C_{14}H_{14}N_2FAl$ (244.24): C, 63.93; H, 5.78; N, 11.47%. Found: C, 64.02; H, 5.41; N, 11.70%.

Synthesis of L[3]AlMe$_2$ (3a). To a stirred suspension of **HL[3]** (1.00 g, 5.43 mmol) in toluene (20 mL) was slowly added $AlMe_3$ (2.71 mL of a 2.0 M solution in toluene, 5.43 mmol). The reaction mixture was stirred at room temperature for 45 min, after which the volatiles were removed *in vacuo* to leave a yellow oil. Yield: 1.16 g, 89%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (1H, d, $^4J_{HH}$ = 1.1, NC*H*), 7.32–7.30 (1H, m, pyrrole-*H*), 7.21 (4H, s, Ar*H*), 7.00 (1H, dd, $^4J_{HH}$ = 0.9, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.45 (1H, dd, $^4J_{HH}$ = 1.8, $^3J_{HH}$ = 3.7, pyrrole-*H*), 2.36 (3H, s, ArCH_3), −0.63 (s, 6H, Al$(CH_3)_2$).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 153.3 (N*C*H), 141.6 (Ar*C*N), 136.7 (pyrrolyl-*C*H), 136.7 (pyrrole-*C*H), 136.6 (pyrrole-*C*),

136.3 (Ar*C*), 130.4 (Ar*C*H), 120.8 (pyrrole-*C*H), 120.1 (Ar*C*H), 115.7 (pyrrole-*C*H), 21.0 (Ar*C*H$_3$), −0.49 (Al(*C*H$_3$)$_2$).

Anal. calcd for $C_{14}H_{17}N_2Al$ (240.28): C, 69.98; H, 7.13; N, 11.66%. Found: C, 69.86; H, 7.70; N, 11.49%.

Synthesis of L^{4}AlMe$_2$ (4a). To a stirred suspension of **HL^4** (0.90 g, 4.49 mmol) in toluene (20 mL) was slowly added AlMe$_3$ (2.25 mL of a 2.0 M solution in toluene, 4.49 mmol). The reaction mixture was stirred at room temperature for 24 hours, after which the volatiles were removed *in vacuo* to leave a brown oil. After recrystallization in hexane at −20 °C, yellow crystals formed. Yield: 0.71 g, 62%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.27 (1H, d, $^4J_{HH}$ = 1.0, NC*H*), 7.28–7.23 (1H, m, pyrrole-*H*), 6.98 (1H, dd, $^4J_{HH}$ = 0.9, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.96–6.91 (2H, m, Ar*H*), 6.44 (1H, dd, $^4J_{HH}$ = 1.8, $^3J_{HH}$ = 3.6, pyrrole-*H*), 3.82 (3H, s, ArOC*H*$_3$), −0.63 (6H, s, Al(C*H*$_3$)$_2$).

^{13}C NMR (100.6 MHz, CDCl$_3$): δ 158.4 (Ar*C*OCH$_3$), 152.9 (N*C*H), 137.4 (Ar*C*N), 136.3 (pyrrolyl-*C*H), 136.2 (pyrrole-*C*), 121.4 (Ar*C*H), 120.4 (pyrrole-*C*H), 115.5 (pyrrole-*C*H), 115.0 (Ar*C*H), 55.54 (ArO*C*H$_3$), −10.2 (Al(*C*H$_3$)$_2$).

Anal. calcd for $C_{14}H_{17}N_2OAl$ (256.28): C, 65.61; H, 6.69; N, 10.93%. Found: C, 65.57 H, 6.28; N, 11.06%.

Synthesis of L^{5}AlMe$_2$ (5a). To a stirred solution of **HL^5** (0.83 g, 4.50 mmol) in toluene (20 mL) was slowly added AlMe$_3$ (2.25 mL of a 2.0 M solution in toluene, 4.50 mmol). The reaction mixture was stirred at room temperature for 24 hours. The mixture was then concentrated *in vacuo*. Pale yellow crystals were then formed at room temperature. Yield: 0.895 g, 83%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (1H, d, $^4J_{HH}$ = 1.0, NC*H*), 7.34–7.32 (1H, m, pyrrole-*H*), 7.29–7.17 (3H, m, Ar*H*), 7.06–7.03 (1H, m, Ar*H*), 7.00 (1H, dd, $^4J_{HH}$ = 0.9, $^3J_{HH}$ = 3.7, pyrrole-*H*), 6.46 (1H, dd, $^4J_{HH}$ = 1.8, $^3J_{HH}$ = 3.6, pyrrole-*H*), 2.29 (3H, s, ArC*H*$_3$), −0.69 (6H, s, Al(C*H*$_3$)$_2$).

^{13}C NMR (100.6 MHz, CDCl$_3$): δ 159.5 (N*C*H), 144.4 (Ar*C*N), 136.7 (pyrrolyl-*C*H), 135.8 (Ar*C*), 131.4 (Ar*C*H), 131.1 (pyrrole-*C*), 126.9 (Ar*C*H), 126.9 (Ar*C*H), 124.0 (Ar*C*H), 120.7 (pyrrole-*C*H), 115.5 (pyrrole-*C*H), 18.3 (Ar*C*H$_3$), −10.4 (Al(*C*H$_3$)$_2$).

Anal. calcd for $C_{14}H_{17}N_2Al$ (240.28): C, 69.98; H, 7.13; N, 11.66%. Found: C, 70.00; H, 7.32; N, 11.68%.

Synthesis of L^{6}AlMe$_2$ (6a). To a stirred suspension of **HL^6** (0.77 g, 3.40 mmol) in toluene (20 mL) was slowly added AlMe$_3$ (1.70 mL of a 2.0 M solution in toluene, 3.40 mmol). The reaction mixture was stirred at room temperature for 24 hours, after which the volatiles were removed *in vacuo* to leave a white solid as the product. Yield: 0.873 g, 81%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.91 (1H, d, $^4J_{HH}$ = 1.0, NC*H*), 7.54 (1H, dd, $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 8.0, Ar*H*), 7.34–7.33 (1H, m, pyrrole-*H*), 7.26 (1H, dt, $^4J_{HH}$ = 1.0, $^3J_{HH}$ = 7.3, Ar*H*), 7.20 (1H, dt, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 7.3, Ar*H*), 6.98 (1H, dd, $^4J_{HH}$ = 0.9, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.95 (1H, dd, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 7.7, Ar*H*), 6.46 (1H, dd, $^4J_{HH}$ = 1.8, $^3J_{HH}$ = 3.6, pyrrole-*H*), 1.38 (9H, s, ArC(C*H*$_3$)$_3$), −0.64 (6H, s, Al(C*H*$_3$)$_2$).

^{13}C NMR (100.6 MHz, CDCl$_3$): δ 160.8 (N*C*H), 144.3 (Ar*C*N), 143.8 (Ar*C*), 136.8 (pyrrolyl-*C*H), 135.3 (pyrrole-*C*), 128.8 (Ar*C*H), 127.3 (Ar*C*H), 127.0 (Ar*C*H), 126.7 (Ar*C*H), 120.5 (pyrrole-*C*H), 115.4 (pyrrole-*C*H), 36.0 (Ar*C*(CH$_3$)$_3$), 33.0 (ArC(*C*H$_3$)$_3$), −9.3 (Al(*C*H$_3$)$_2$).

Anal. calcd for $C_{17}H_{23}N_2Al$ (282.36): C, 72.31; H, 8.21; N, 9.92%. Found: C, 72.10; H, 8.62; N, 9.80%.

Synthesis of L^{7}AlMe$_2$ (7a). To a stirred suspension of **HL^7** (1.00 g, 4.38 mmol) in toluene (20 mL) was slowly added AlMe$_3$ (2.20 mL of a 2.0 M solution in toluene, 4.40 mmol). The reaction mixture was stirred at room temperature for 4 hours, after which the volatiles were removed *in vacuo* to leave a white solid. Recrystallization from hexane at −20 °C afforded colorless crystals. Yield: 0.762 g, 61%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.17 (1H, s, NC*H*), 7.19 (1H, dd, $^3J_{HH}$ = 1.0, $^3J_{HH}$ = 1.0, pyrrole-*H*), 6.84 (1H, dd, $^3J_{HH}$ = 2.5, $^4J_{HH}$ = 1.0, pyrrole-*H*), 6.40 (1H, dd, $^3J_{HH}$ = 2.5, $^4J_{HH}$ = 1.0, pyrrole-*H*), 2.22 (3H, br s, C*H*), 1.96 (6H, d, $^3J_{HH}$ = 2.4, NC*H*$_2$), 1.71–1.74 (6H, m, C*H*$_2$), −0.64 (6H, s, Al(C*H*$_3$)$_2$).

^{13}C NMR (100.6 MHz, CDCl$_3$): δ 155.2 (N*C*H), 135.4 (pyrrole-*C*), 134.0 (pyrrole-*C*H), 117.8 (pyrrole-*C*H), 114.1 (pyrrole-*C*H), 56.9 (N*C*(CH$_2$)$_3$), 42.6 (C(*C*H$_2$)$_3$), 36.0 (CH(*C*H$_2$)$_3$), 29.5 (*C*H(CH$_2$)$_3$).

Anal. calcd for $C_{17}H_{25}N_2Al$ (284.38): C, 71.80; H, 8.86; N, 9.85%. Found: C, 71.99; H, 8.22; N, 9.65%.

Synthesis of L$^1_2$AlMe (1b). To a stirred solution of **HL^1** (1.00 g, 5.88 mmol) in toluene (20 mL) was slowly added AlMe$_3$ (1.47 mL of a 2.0 M solution in toluene, 2.97 mmol). The reaction mixture was stirred at 100 °C for 3 days. The volatiles were removed *in vacuo* to leave an orange oil which was then recrystallized for hexane at −20 °C to afford the product as a yellow solid. Yield: 0.54 g, 50%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.51 (2H, d, $^4J_{HH}$ = 0.9, NC*H*), 7.57–7.52 (4H, m, Ar*H*), 7.45–7.38 (4H, m, Ar*H*), 7.29–7.24 (2H, m, Ar*H*), 6.90–6.87 (4H, m, pyrrole-*H*), 6.25 (2H, dd, $^4J_{HH}$ = 2.1, $^3J_{HH}$ = 3.5, pyrrole-*H*), −0.46 (3H, s, AlC*H*$_3$).

^{13}C NMR (100.6 MHz, CDCl$_3$): δ 152.5 (N*C*H), 146.2 (Ar*C*), 136.9 (pyrrole-*C*H), 136.6 (pyrrole-*C*), 129.5 (Ar*C*H), 126.2 (Ar*C*H), 121.4 (Ar*C*H), 119.6 (pyrrole-*C*H), 114.3 (pyrrole-*C*H).

Anal. Calcd for $C_{23}H_{21}N_4Al$ (380.42): C, 72.62; H, 5.56; N, 14.73%. Found: C, 72.75; H, 5.65; N, 14.77%.

Synthesis of L$^2_2$AlMe (2b). To a stirred suspension of **HL^2** (1.00 g, 5.31 mmol) in toluene (20 mL) was slowly added AlMe$_3$ (1.33 mL of a 2.0 M solution in toluene, 2.66 mmol). The reaction mixture was stirred at 100 °C for 24 hours. The volatiles were removed *in vacuo* to leave a yellow solid which was then washed with hexane and dried *in vacuo*. Yield: 0.82 g, 74%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.38 (2H, d, $^4J_{HH}$ = 0.8, NC*H*), 7.46–7.40 (4H, m, Ar*H*), 7.07–7.01 (4H, m, Ar*H*), 6.82 (2H, dd, $^4J_{HH}$ = 1.0, $^3J_{HH}$ = 3.5, pyrrole-*H*), 6.78–6.76 (2H, m, pyrrole-*H*), 6.19 (2H, dd, $^4J_{HH}$ = 2.0, $^3J_{HH}$ = 3.5, pyrrole-*H*), −0.58 (3H, s, AlCH$_3$).

^{13}C NMR (100.6 MHz, CDCl$_3$): δ 162.3 (Ar*C*F), 159.8 (Ar*C*F), 152.5 (N*C*H), 152.5 (N*C*H), 142.4 (Ar*C*N), 142.4 (Ar*C*N), 136.8 (pyrrolyl-*C*H), 136.5 (pyrrole-*C*), 122.8 (Ar*C*H), 122.8 (Ar*C*H), 119.8 (pyrrole-*C*H), 116.5 (Ar*C*H), 116.2 (Ar*C*H), 114.5 (pyrrole-*C*H).

Anal. calcd for $C_{23}H_{19}N_4F_2Al$ (416.40): C, 66.34; H, 4.60; N, 13.45%. Found: C, 66.31; H, 4.83; N, 13.44%.

Synthesis of L$^3_2$AlMe (3b). To a stirred suspension of **HL$_3$** (0.70 g, 3.80 mmol) in toluene (20 mL) was slowly added AlMe$_3$

(1.20 mL of a 2.0 M solution in toluene, 1.90 mmol). The reaction mixture was stirred at 100 °C for 24 hours. The volatiles were removed *in vacuo* to leave a yellow solid which was then washed with hexane and dried *in vacuo*. Yield: 0.56 g, 72%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (2H, d, $^4J_{HH}$ = 0.80 NCH), 7.47–7.42 (4H, m, Ar*H*), 7.24–7.19 (4H, m, Ar*H*), 8.88–6.85 (4H, m, pyrrole-*H*), 6.25–6.22 (2H, m, pyrrole-*H*), 2.38 (3H, s, ArCH_3), −0.49 (3H, s, AlCH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 151.9 (N*C*H), 143.7 (Ar*C*N), 136.6 (pyrrolyl-*C*H), 136.1 (pyrrole-*C*), 130.1 (Ar*C*H), 121.3 (Ar*C*H), 119.0 (pyrrole-*C*H), 114.0 (Ar*C*H), 21.0 (Ar*C*H_3).

Anal. calcd for $C_{25}H_{25}N_4Al$ (408.47): C, 73.51; H, 6.17; N, 13.72%. Found: C, 73.58; H, 6.81; N, 13.66%.

Synthesis of L_2^4AlMe (4b). To a stirred suspension of **HL^4** (0.86 g, 4.29 mmol) in toluene (20 mL) was slowly added $AlMe_3$ (1.07 mL of a 2.0 M solution in toluene, 2.14 mmol). The reaction mixture was stirred at 100 °C for 2 days. The volatiles were removed *in vacuo* to leave a yellow solid which was then washed with hexane and dried *in vacuo*. Yield: 0.75 g, 79%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (2H, d, $^4J_{HH}$ = 0.6, NC*H*), 7.51–7.46 (4H, m, Ar*H*), 6.96–6.91 (4H, m, Ar*H*), 6.86–6.81 (4H, m, pyrrole-*H*), 6.24–6.21 (2H, m, pyrrole-*H*), 3.82 (6H, s, ArOCH_3), −0.49 (3H, s, AlCH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.1 (Ar*C*OCH$_3$), 151.2 (N*C*H), 139.4 (Ar*C*N), 136.6 (pyrrolyl-*C*), 136.2 (pyrrole-*C*H), 122.5 (Ar*C*H), 118.6 (pyrrole-*C*H), 114.6 (Ar*C*H), 113.9 (pyrrole-*C*H), 55.46 (ArO*C*H$_3$).

Anal. calcd for $C_{25}H_{25}N_4O_2Al$ (440.47): C, 68.17; H, 5.72; N, 12.72%. Found: C, 68.10; H, 5.93; N, 12.70%.

Synthesis of L_2^5AlMe (5b). To a stirred solution of **HL$_5$** (0.83 g, 4.52 mmol) in toluene (20 mL) was slowly added $AlMe_3$ (1.13 mL of a 2.0 M solution in toluene, 2.26 mmol). The reaction mixture was stirred at 100 °C for 24 hours. The volatiles were removed *in vacuo* to leave a brown oil which was then recrystallized for hexane at −20 °C to afford the product as a white solid. Yield: 0.96 g, 72%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (2H, d, $^4J_{HH}$ = 1.0, NC*H*), 7.44–7.39 (2H, m, Ar*H*), 7.34–7.30 (2H, m, Ar*H*), 7.24–7.14 (4H, m, Ar*H*), 6.80–6.78 (2H, m, pyrrole-*H*), 6.65–6.62 (2H, m, pyrrole-*H*), 6.21–6.19 (2H, m, pyrrole-*H*), 2.33 (3H, s, ArCH_3), −0.35 (3H, s, AlCH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.3 (N*C*H), 147.8 (Ar*C*N), 136.2 (pyrrolyl-*C*H), 135.5 (pyrrole-*C*), 132.1 (Ar*C*H), 129.9 (Ar*C*CH$_3$), 126.8 (Ar*C*H), 125.9 (Ar*C*H), 124.4 (Ar*C*H), 118.9 (pyrrole-*C*H), 114.1 (Ar*C*H), 19.0 (Ar*C*H$_3$).

Anal. calcd for $C_{25}H_{25}N_4Al$ (408.47): C, 73.51; H, 6.17; N, 13.72%. Found: C, 73.64; H, 6.82; N, 13.70%.

Synthesis of L_2^6AlMe (6b). To a stirred suspension of **HL^6** (0.70 g, 3.09 mmol) in toluene (20 mL) was slowly added $AlMe_3$ (0.77 mL of a 2.0 M solution in toluene, 1.55 mmol). The reaction mixture was stirred at 100 °C for 2 days. The volatiles were removed *in vacuo* to leave a yellow solid which was then washed with hexane and dried *in vacuo*. Yield: 0.69 g, 91%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (2H, d, $^4J_{HH}$ = 1.1, NC*H*), 7.49 (2H, dd, $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 8.1, 2H, pyrrole-*H*), 7.30–7.24 (2H, m, Ar*H*), 7.23–7.16 (2H, m, Ar*H*), 7.04–6.91 (1H, br s, Ar*H*), 6.73 (2H, dd, $^4J_{HH}$ = 1.0, $^3J_{HH}$ = 3.6, pyrrole-*H*), 6.00 (2H, dd, $^4J_{HH}$ = 1.9, $^3J_{HH}$ = 3.6, pyrrole-*H*), 5.79–5.68 (2H, m, Ar*H*), 1.22 (18H, s, Ar(CH_3)$_3$), −0.64 (3H, s, AlCH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 160.8 (N*C*H), 147.5 (Ar*C*N), 143.8 (Ar*C*), 138.5 (pyrrolyl-*C*H), 134.2 (pyrrole-*C*), 128.6 (Ar*C*H), 127.7 (Ar*C*H), 126.6 (Ar*C*H), 126.6 (Ar*C*H), 119.3 (pyrrole-*C*H), 114.4 (pyrrole-*C*H), 36.1 (Ar*C*(CH$_3$)$_3$), 32.4 (ArC-(*C*H$_3$)$_3$).

Anal. calcd for $C_{31}H_{37}N_4Al$ (492.63): C, 75.58; H, 7.57; N, 11.37%. Found: C, 75.62; H, 7.62; N, 11.42%.

Synthesis of L_2^7AlMe (7b). To a stirred suspension of **HL^7** (0.80 g, 3.55 mmol) in toluene (20 mL) was slowly added $AlMe_3$ (0.89 mL of a 2.0 M solution in toluene, 1.78 mmol). The reaction mixture was stirred at 100 °C overnight during which time a white solid precipitated. Solid was isolated by filtration and dried *in vacuo.* Yield: 0.64 g, 57%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (2H, s, NC*H*), 7.07 (1H, dd, $^3J_{HH}$ = 2.0, $^3J_{HH}$ = 2.0, pyrrole-*H*), 6.65 (2H, dd, $^3J_{HH}$ = 3.5, $^4J_{HH}$ = 2.0, pyrrole-*H*), 6.25 (2H, dd, $^3J_{HH}$ = 3.5, $^4J_{HH}$ = 2.0, pyrrole-*H*), 2.20 (12H, m, NCH_2), 2.11 (6H, s, C*H*), 1.72–1.77 (12H, m, CH_2), −0.26 (3H, s, AlCH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.2 (N*C*H), 135.4 (pyrrole-*C*), 134.0 (pyrrole-*C*H), 117.8 (pyrrole-*C*H), 114.1 (pyrrole-*C*H), 56.9 (N*C*(CH$_2$)$_3$), 42.6 (C(*C*H$_2$)$_3$), 36.0 (CH(*C*H$_2$)$_3$), 29.52- (*C*H(CH$_2$)$_3$).

Anal. calcd for $C_{31}H_{41}N_4Al$ (496.67): C, 74.97; H, 8.32; N, 11.28%. Found C, 74.78; H, 8.43; N, 11.47%.

General polymerization procedure

In a nitrogen-filled glove box, *rac*-lactide (720 mg, 5.0 mmol) or ε-caprolactone (570 mg, 5.0 mmol) and benzyl alcohol (5.17 μL, 0.05 mmol) were placed in a polymerization ampoule. To this ampoule was added a solution of initiator (0.05 mmol) in toluene (6.00 mL) ([monomer] : [Al] = 100 : 1). The reaction was stirred for the desired reaction time at 70 °C. At the desired reaction time, the reaction was quenched with methanol (2–3 drops). The polymer was precipitated from excess methanol, collected by filtration and dried *in vacuo* to a constant mass. Conversions were determined by integration of the monomer *versus* polymer methane resonances in the ^{1}H NMR spectrum of crude product (in $CDCl_3$).

General procedure for kinetic studies

The polymerizations were carried out at 70 °C in a glove box. The molar ratio of monomer to initiator was fixed at 50 : 1. At appropriate time intervals, 0.5 μL aliquots were removed and quenched with methanol. The solvent was removed *in vacuo* and the percent conversion determined by ^{1}H NMR in $CDCl_3$.

Crystal structure determination

X-ray diffraction data of **3b** were measured on a Bruker–Nonius kappaCCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) at 298 (2) K. The structure was solved by direct methods with SIR97,[25] and refined with full-matrix least-squares calculations on F^2 using SHELXL-97.[26] Crystallographic data have been deposited at the Cambridge

Crystallographic Data Centre under the reference numbers CCDC 958599.

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