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PAPER

Al and Zn complexes bearing *N*,*N*,*N*-tridentate quinolinyl anilido-imine ligands: synthesis, characterization and catalysis in L-lactide polymerization†

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Reactions of *N*,*N*,*N*-tridentate quinolinyl anilido-imine ligands with $AlMe_3$ afford mononuclear aluminum complexes $\{\kappa^3$-[{2-[ArN=C(H)]C_6H_4}N(8-C_9H_6N)]}$AlMe_2$ (Ar = 2,6-$Me_2C_6H_3$ (**1a**), 2,6-$Et_2C_6H_3$ (**1b**), 2,6-$^iPr_2C_6H_3$ (**1c**)) or dinuclear complexes $AlMe_3\{\kappa^1$-[{2-[ArN=C(H)C_6H_4]N(8-C_9H_6N)}-κ^2]$AlMe_2$ (R = 2,6-$Me_2C_6H_3$ (**2a**), 2,6-$Et_2C_6H_3$ (**2b**), 2,6-$^iPr_2C_6H_3$ (**2c**)) depending on the ratios of reactants used. Similar reactions of $ZnEt_2$ with these ligands give the monoligated ethyl zinc complexes $\{\kappa^3$-[{2-[ArN=C(H)]C_6H_4}N(8-C_9H_6N)]}ZnEt (Ar = 2,6-$Me_2C_6H_3$ (**3a**), 2,6-$Et_2C_6H_3$ (**3b**), 2,6-$^iPr_2C_6H_3$ (**3c**)) or bisligated complexes $\{\kappa^3$-[{2-[ArN=C(H)]C_6H_4}N(8-C_9H_6N)]}Zn$\{\kappa^2$-[{2-[ArN=C(H)]C_6H_4}-N(8-C_9H_6N)]} (Ar = 2,6-$Me_2C_6H_3$ (**4a**), 2,6-$Et_2C_6H_3$ (**4b**), 2,6-$^iPr_2C_6H_3$ (**4c**)). These complexes were well characterized by NMR and the structures of **1a**, **2a**, **2c**, **3b** and **4c** were confirmed by X-ray diffraction analysis. The aluminum and zinc complexes were tested to initiate lactide polymerization in which the zinc complexes show moderate to high activities in the presence of benzyl alcohol.

Introduction

The polylactides (PLAs) prepared from renewable sources have been widely used in the biomedical, pharmaceutical and agricultural fields as promising alternatives to synthetic petrochemical-based polymers.[1] PLAs are usually prepared by ring-opening polymerization of lactides with metal alkoxides as initiators. A large number of alkoxides of Sn,[2] Al,[3] Zn,[3d,4] Mg,[5,4d] Fe,[6] Ti,[7] In,[8] and some rare-earth metals[9] with or without ligands have been extensively investigated in lactide polymerization. The aluminum- and zinc-based systems seem to be the best candidates in the preparation of PLAs due to their high Lewis acidity and low toxicity. The ancillary ligands in the complexes were proven to play an important role in preventing the epimerization and transesterification which leads to uncontrolled molecular weight, broad molecular weight distributions and formation of macrocycles or oligomers. Over the past decades significant efforts have been devoted to the design and synthesis of appropriate ancillary ligands to improve the performance of the complexes in polymerization. It has been reported that some Al and Zn complexes with salen/salan and β-diketiminate ligands show high activities for the ring-opening polymerization of lactides.[10] Some anilido-imine ligands were also used to support the aluminum or zinc complexes and the complexes show high productivities for ε-caprolactone and L-lactide ring-opening polymerization in the presence of benzyl alcohol.[11] Side-arms were introduced into the anilido-imine ligands to strengthen the steric control abilities. The rare-earth metal alkyls bearing methoxyl group decorated anilido-imine tridentate ligands can initiate the polymerization of lactide in a single-site manner. The methoxyl group was believed to prevent the back-biting reaction in polymerization.[12] Recently we have introduced the rigid quinolinyl group into the anilido-imine ligand and the rare-earth metal alkyl complexes with such tridentate ligands can catalyze the ε-caprolactone polymerization.[13] The coordination of the quinolinyl group to the metal center inhibits the transesterification and the polymerization is performed in a living manner.

Herein, we wish to report the synthesis and characterization of a series of aluminum and zinc complexes supported by quinolinyl anilido-imine ligands. Their catalytic behavior as initiators for the ring-opening polymerization of L-lactide were also investigated.

Results and discussions

Synthesis and characterization of aluminum complexes

The quinolinyl anilido-imine ligands were prepared according to the literature[13] and were well characterized by NMR spectroscopy. All the ^1H NMR spectra of the ligands show a resonance at 12.2 ppm for the amine proton suggesting the existence of a hydrogen bond between NH and imine groups.[14] Addition of 1 equiv of $AlMe_3$ to the toluene solution of the ligands at 0 °C resulted in immediate color change from orange to deep red. Evaporation of the solvent and recrystallization of the residue with hexane and toluene afforded the mononuclear

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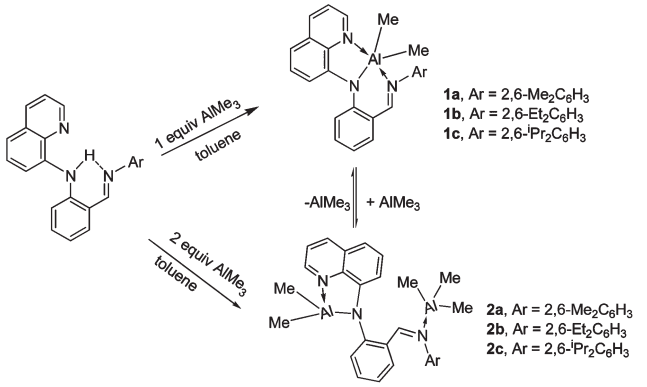


Scheme 1 Synthetic route for the mononuclear and dinuclear aluminum complexes.

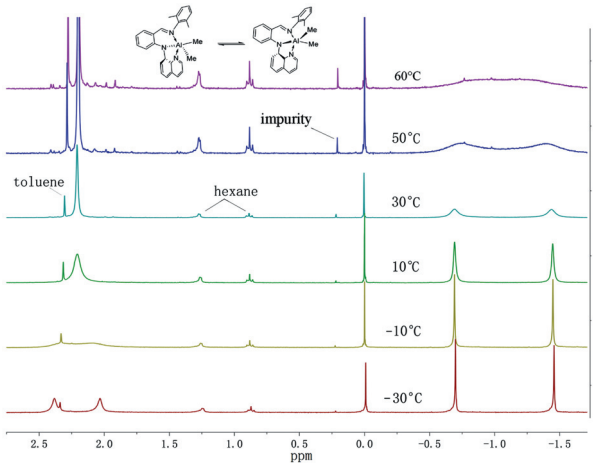


Fig. 1 Stacked plot of variable-temperature ^{1}H NMR spectra of **1a**.

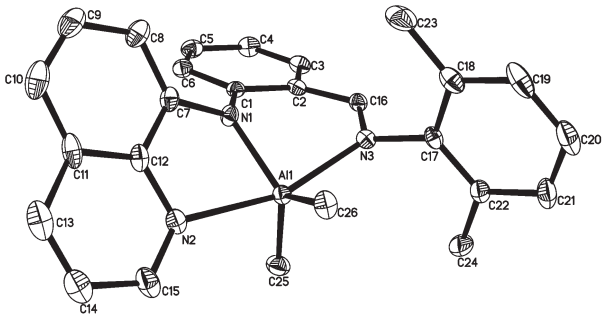


Fig. 2 Perspective view of complex **1a** with thermal ellipsoids drawn at 30% probability level. Uncoordinated solvents and hydrogens are omitted for clarity.

aluminum complexes **1a–1c** as orange powders in moderate yields as shown in Scheme 1.

The aluminum complexes **1a–1c** were characterized by elemental analysis and NMR spectroscopy. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of these complexes at room temperature exhibit similar patterns. For all complexes, the singlet for N*H* in free ligands disappeared and the singlet resonances for the *H*C═N proton at 8.14–8.16 ppm were observed, which shift to high field with respect to the free ligands. It is worth noting that the ^{1}H NMR spectra of these complexes show two sets of broad singlets in the range of −1.45 to −1.42 ppm and −0.72 to −0.69 ppm for the two methyl groups attached to the aluminum center (Me–Al). This behavior indicates that the two methyl groups are in non-equivalent environments and a fluxional exchange between two isomers may exist in solution at room temperature. The fluxional behavior of **1a** was further studied by variable-temperature ^{1}H NMR spectroscopy (Fig. 1). The VT NMR analysis showed that when the temperature was decreased to −30 °C, the singlet at 2.30 ppm for the two methyl groups of *N*-aryl moiety (Me–Ar) broadened and became resolved into two singlets, probably owing to the lack of rotation of the C–N_{imino} bond at low temperature. Upon increasing the temperature from 10 °C, the resonances of the two Me–Al methyl groups broadened and eventually fused together as one broad signal at 60 °C. This may be attributed to the fast exchange of the molecule between two isomers at high temperature (see Fig. 1). Similar phenomena was also observed in rare-earth metal alkyl complexes bearing such ligand.[13] In fact the X-ray diffraction analysis of **1a** shows that the two isomers do exist in the solid state.

Crystals of **1a** suitable for X-ray diffraction analysis were grown from hexane. The molecular structure is depicted in Fig. 2. Crystallographic data and selected bond distances and angles are given in Tables 1 and 2. It can be seen that the Al atom is five-coordinated and the geometry around it can be best described as a distorted trigonal bipyramid. The two methyls bonded to the Al center and the N_{amido} atom are in the equatorial plane and the other two nitrogen atoms are in apical positions. The Al atom lies out of the coordinated plane (N1–C_1–C_2–C_{16}–N_3) by 0.9436(31) Å, but is essentially coplanar with the quinolinyl ring. The dihedral angle between the plane (N1–C_1–C_2–C_{16}–N_3) and quinolinyl ring is 42.65(9)°. The Al–N_{amido} bond lengths of 1.920(3) Å are slightly shorter than the Al–N_{imine} (2.203(2) Å) and Al–$N_{quinolinyl}$ (2.117(2) Å), but is longer than those of 1.870(4)–1.890(4) Å for Al–N bonds in similar anilido-imino Al complexes.[11a]

Additions of one equiv of $AlMe_3$ to **1a–1c** or treatments of two equivalent of $AlMe_3$ with the ligands, after the appropriate workup and recrystallization from hexane, afford pale yellow powders which were proven to be dinuclear complexes **2a–2c** (Scheme 1). The ^{1}H NMR spectra of **2a–2c** exhibit a singlet (−1.37 to −1.39 ppm) for the methyl protons of $AlMe_3$ coordinated to the N_{imino} atoms. It is worth noting that the spectra showed two separated singlets (−0.53 to −0.58 ppm) for the methyl protons of $AlMe_2$ chelated by the aminoquinolinyl moiety, along with two sets of signals for the *ortho* groups of the *N*-aryl moiety, suggesting that both of the two methyls are bonded to the aluminum center (Me–Al) and the two *ortho* substituents of the *N*-aryl moiety (R–Ar) are in non-equivalent environments respectively. The coordination of $AlMe_3$ to N_{imino} atoms may inhibit the rotations about the C–N_{imino} and C–N_{amido} bond. The molecular structures of **2a** and **2c** were established by X-ray diffraction studies and their molecular structures are depicted in Fig. 3 and 4 respectively. Complexes **2a** and **2c** are isostructural dinuclear complexes in which one aluminum is chelated by the N_{amido} atom and $N_{quinolinyl}$ atom while the other

Table 1 Crystal data and structure refinement for complexes **1a**, **2a**, **2c**, **3b** and **4c**

	1a	**2a**	**2c**	**3b**	**4c**
Formula	$C_{59}H_{60}Al_2N_6$	$C_{29}H_{35}Al_2N_3$	$C_{39}H_{57}Al_2N_3$	$C_{28}H_{29}N_3Zn$	$C_{115}H_{119}N_{12}Zn_2$
F_w	907.09	479.56	621.84	472.91	1799.96
Cryst syst	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	32.1381(16)	9.7793(8)	12.1624(7)	10.7628(7)	11.438(2)
b (Å)	8.4504(4)	11.1335(9)	12.6833(7)	10.9313(7)	13.475(3)
c (Å)	18.4874(9)	14.3337(11)	13.7183(8)	11.4905(8)	17.838(4)
α (°)	90	71.6540(10)	80.7440(10)	69.8200(10)	101.71(3)
β (°)	93.3180(10)	72.7750(10)	78.2440(10)	88.4390(10)	94.18(3)
γ (°)	90	79.3680(10)	73.3270(10)	66.2230(10)	108.97(3)
v (Å^3)	5012.4(4)	1407.67(19)	1972.82(19)	1151.30(13)	2517.2(9)
Z	4	2	2	2	1
μ (mm^{-1})	0.103	0.124	0.101	1.087	0.530
R_{int}	0.0204	0.0161	0.0154	0.0116	0.1271
GOOF	1.033	1.025	1.027	1.063	1.018
R_1 [a]	0.0558	0.0544	0.0545	0.0327	0.1131
wR_2 [b]	0.1464	0.1343	0.1347	0.0833	0.2288

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for **1a**, **2a**, **2c**, **3b** and **4c**

1a			
Al(1)–N(1)	1.920(3)	N(1)–Al(1)–N(3)	85.41(9)
Al(1)–N(2)	2.203(2)	N(1)–Al(1)–N(2)	78.20(10)
Al(1)–N(3)	2.117(2)	N(2)–Al(1)–N(3)	161.48(10)
Al(1)–C(25)	1.978(3)	C(25)–Al(1)–C(26)	125.57(14)
Al(1)–C(26)	1.979(3)		
2a			
Al(1)–N(1)	1.891(2)	Al(2)–C(25)	1.971(3)
Al(1)–N(2)	1.973(2)	Al(2)–C(26)	1.981(3)
Al(1)–C(23)	1.947(3)	Al(2)–C(27)	1.974(3)
Al(1)–C(24)	1.958(3)	N(1)–Al(1)–N(2)	84.73(9)
Al(2)–N(3)	2.0418(19)	C(23)–Al(1)–C(24)	119.04(13)
2c			
Al(1)–N(1)	1.892(2)	Al(2)–C(25)	1.977(3)
Al(1)–N(2)	1.980(3)	Al(2)–C(26)	1.973(3)
Al(1)–C(23)	1.953(3)	Al(2)–C(27)	1.976(3)
Al(1)–C(24)	1.954(3)	N(1)–Al(1)–N(2)	84.29(10)
Al(2)–N(3)	2.045(2)	C(23)–Al(1)–C(24)	121.82(15)
3b			
Zn(1)–N(1)	1.9927(16)	N(1)–Zn(1)–N(2)	80.52(7)
Zn(1)–N(2)	2.1018(17)	N(1)–Zn(1)–N(3)	85.75(6)
Zn(1)–N(3)	2.1335(16)	N(2)–Zn(1)–N(3)	115.50(6)
Zn(1)–(27)	1.975(2)		
4c			
Zn(1)–N(1)	1.988(6)	N(1)–Zn(1)–N(2)	78.8(3)
Zn(1)–N(2)	2.093(7)	N(1)–Zn(1)–N(3)	83.2(2)
Zn(1)–N(3)	2.131(6)	N(2)–Zn(1)–N(3)	125.3(3)
Zn(1)–N(4)	1.968(6)	N(4)–Zn(1)–N(5)	80.3(2)
Zn(1)–N(5)	2.167(6)		

is coordinated by the N_{imine} atom. The Al(1) is essentially coplanar with the quinolinyl group with the deviation of 0.0591(23) Å in **2a** and 0.0942(25) Å in **2c**. The Al–N_{amido} bond lengths of 1.891(2) Å in **2a** and 1.892(2) Å in **2c** are comparable to that of 1.920(3) Å in **1a**. The quinolinyl ring is almost vertical to the phenyl ring (C1 to C6) with a large dihedral angle of 74.0° in **2a** and 70.0° in **2c**. The ^{1}H NMR analysis reveal that **2a–2c** are not stable in the solid state and the $AlMe_3$ attached to the imino group can be released gradually forming the corresponding mononuclear complexes.

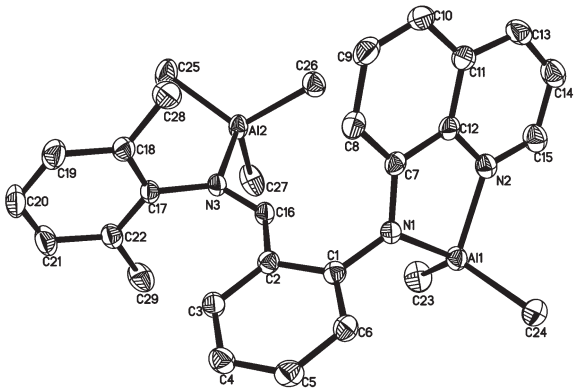


Fig. 3 Perspective view of complex **2a** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity.

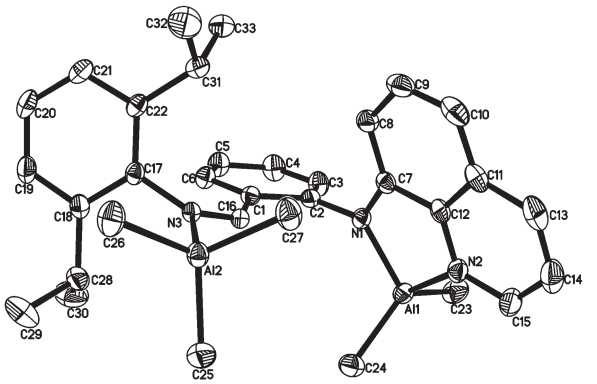
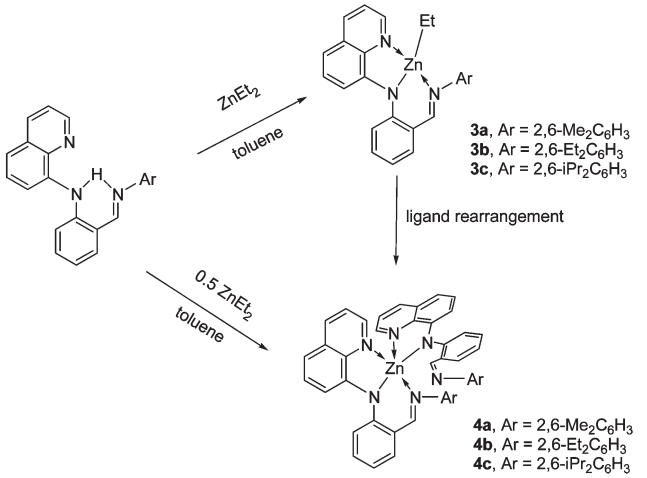


Fig. 4 Perspective view of complex **2c** with thermal ellipsoids drawn at 30% probability level. Uncoordinated solvent and hydrogens are omitted for clarity.

Synthesis and characterization of zinc complexes

The *N*,*N*,*N*-tridentate zinc complexes were also prepared in a similar procedure to that for the aluminum complexes as shown



Scheme 2 Synthetic route for the zinc complexes.

in Scheme 2. Reactions of the ligands with one equivalent of $ZnEt_2$ give the complexes **3a–3c** in high yields. The identities of these complexes were determined by ^1H NMR, $^{13}C\{^1H\}$ NMR analysis and were corroborated by elemental analyses. X-ray quality crystals of **3b** were obtained *via* recrystallization in hexane and its structure was elucidated (Fig. 5). The zinc atom in **3b** is in a distorted tetrahedral geometry ligated by the *N*,*N*,*N*-tridentate ligand and an ethyl group. The zinc atom is essentially coplanar with the aminoquinolinyl plane with a maximum deviation of 0.1069(36) Å, and the Zn–N bond distances (1.9927(16)–2.1335(16) Å) are comparable to those in β-diketiminate zinc alkyl complexes.[15] The other bond distances and angles for this complexes are unexceptional and fall in the range of values reported for related zinc complexes.

Monitoring by ^1H NMR spectroscopy showed that monoligated complexes **3a** and **3b** are stable in hexane or toluene solutions. Whereas **3c** is unstable and disproportionates in solution into bisligated complex **4c** over a period of several days at room temperature. Similar ligand rearrangement was also observed in the zinc complexes supported by β-diketiminato,[16] fluorous imino-alkoxide,[17] tris(pyrazolyl)borate ligands,[18] and NCN pincer ligands.[19] Alternatively the bisligated complexes **4a–4c** can be synthesized in high yields by deprotonation of the ligands with 0.5 equivalent of $ZnEt_2$ in toluene. It is worth noting that the ^1H NMR spectra of these complexes show broad signals for *ortho* groups of *N*-aryl moieties at room temperature suggesting that some kind of fluxional exchange may exist in solution. However, the variable-temperature ^1H NMR study of **4c** shows no obvious changes with the variation of the temperature. The molecular structure of **4c** was established by an X-ray diffraction study (Fig. 6). In **4c**, the five-coordinated zinc atom is in a trigonal bipyramidal geometry with one *N*-aryl moiety coordinating to the zinc atom and the other *N*-aryl moiety dangling away. No detectable difference between the two *N*-aryl moieties was observed in the VT NMR, suggesting that in solution the bisligated zinc complexes may exist in a four-coordinated form with both of the two *N*-aryl moieties dangling away from the metal center.

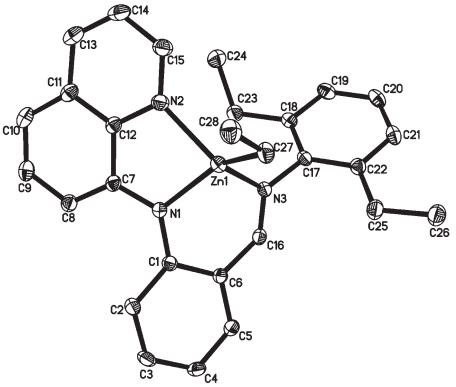


Fig. 5 Perspective view of complex **3b** with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity.

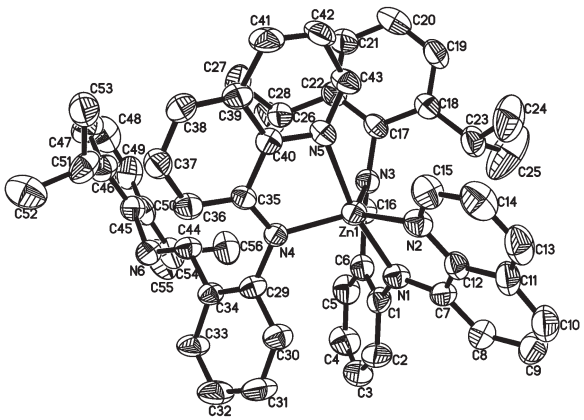


Fig. 6 Perspective view of complex **4c** with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity.

Polymerization of L-lactide

The aluminum and zinc complexes were investigated as initiators for the ring-opening polymerization of L-lactide. The polymerizations were carried out in toluene at 70 °C and the representative polymerization results are summarized in Table 3. When used as single component, all the aluminum complexes are almost inert for lactide polymerization and no polymer was obtained even at high temperature. While when activated with benzyl alcohol, the activities were improved and about 75–95% conversions were achieved in 24 h. It is worth noting that in both catalytic systems (**1a–1c**)–BnOH and (**2a–2c**)–BnOH, the activities and M_w of the resulted polymer show no dependence on the bulkiness of *ortho*-groups of *N*-aryl moieties. The monoligated zinc complexes show varied activities in the absence of benzyl alcohol and the conversions of 9.1–63.26% were achieved within 30 min, affording high molecular weight polymer with broad PDI (entries 7–9). The low activities and uncontrollable behavior may due to the poor nucleophilicity of the alkyl groups and inefficient initiation.[20] Whereas the bisligated complexes **4a–4c** are more active than the corresponding monoligated complexes under the same conditions. This may be attributed to the different initial

Table 3 Polymerization of L-lactide initiated with zinc complexes[a]

Entry	Cat	[M]/[I]/[BnOH]	Time (min)	Yield[b] (%)	M_c [c] ($\times 10^4$)	M_n [d] ($\times 10^4$)	PDI[d]
1	**1a**	100/1/2	1440	77.79	0.56	0.87	1.13
2	**1b**	100/1/2	1440	75.73	0.55	0.80	1.14
3	**1c**	100/1/2	1440	76.08	0.55	0.76	1.12
4	**2a**	100/1/5	1440	90.60	0.26	0.27	1.13
5	**2b**	100/1/5	1440	94.68	0.27	0.39	1.21
6	**2c**	100/1/5	1440	94.62	0.27	0.38	1.23
7	**3a**	100/1/0	30	63.26	0.91	10.94	1.09
8	**3b**	100/1/0	30	27.50	0.40	8.03	1.29
9	**3c**	100/1/0	30	9.10	0.13	2.36	1.26
10	**4a**	100/1/0	30	85.90	1.24	3.67	1.87
11	**4b**	100/1/0	30	49.50	0.71	10.8	1.23
12	**4c**	100/1/0	30	54.80	0.79	10.8	1.21
13	**3a**	100/1/1	30	95.18	1.37	1.39	1.16
14	**3b**	100/1/1	30	94.00	1.35	1.35	1.13
15	**3c**	100/1/1	30	92.12	1.33	1.36	1.09
16	**4a**	100/1/1	30	99.38	1.43	1.29	1.34
17	**4b**	100/1/1	30	98.32	1.42	1.50	1.17
18	**4c**	100/1/1	30	90.03	1.30	1.51	1.10
19	**3a**	300/1/1	120	100	4.33	4.15	1.22
20	**3a**	500/1/1	120	100	7.21	6.58	1.27
21	**3a**	700/1/1	120	100	10.09	9.65	1.30
22	**3a**	900/1/1	120	94.40	12.25	11.35	1.35
23	**3a**	100/1/2	30	94.37	0.68	0.87	1.29
24	**3a**	100/1/3	30	96.20	0.46	0.60	1.29
25	**3a**	500/1/5	30	93.03	1.34	1.67	1.15
26	**3a**	500/1/10	30	97.83	0.71	0.87	1.09

[a] *Polymerization conditions*: 30 μmol of initiator; T = 70 °C; 15 mL toluene. [b] Determined by ^{1}H NMR. [c] Calculated from ($[LA]_0/[I]_0$) × conversion × 144 or ($[LA]_0/[BnOH]_0$) × conversion × 144. [d] Determined by GPC against polystyrene standards in THF, multiplied by 0.58.[22]

groups used in the two kinds complexes. The Zn–N bonds in the bisligated complexes are believed to be more active than Zn–C bonds in the monoligated complexes. Additionally, the activities of the catalytic systems are strongly affected by the *ortho* substituents (entries 7–12). In both cases, there is a sharp decrease in activity as the *ortho* substituent goes from 2,6-methyl to isopropyl, probably owing to the growing bulkiness at the metal centers which inhibits the insertion of the monomer to the Zn–C and Zn–N bonds. Upon activation with benzyl alcohol (BnOH), the productivities of the zinc complexes are all dramatically improved and up to 99.38% conversion can be achieved within 30 min (entries 13–18). The M_n values of the polymers obtained from these binary systems are very close to the M_c values calculated according to the monomer/initiator (M/I) molar ratio. At the same time, the PDIs are all quite narrow ranging from 1.09 to 1.17, which is indicative of single-site catalyst or initiator systems. The performances of the binary catalytic system were further investigated by using **3a**–BnOH. Polymerizations with different monomer/initiator (M/I) molar ratios were carried out to test the control abilities of the catalytic system (entries 13, 19–22). It was found that the M_n of the resulted polymer increases with the increase of the M/I molar ratio and the PDI gets slightly broader. The relatively broad PDIs may be attributed to intermolecular transesterification and intramolecular transesterification (cyclization). Similar intermolecular and intramolecular transesterifications have also been observed in magnesium phenoxides[5b] and silylamido lanthanide[21] initiating systems. Studies on the relationship of molecular weight *vs.* conversion were also conducted with a **3a**–BnOH binary system (as shown in Fig. 7). It shows that the molecular weight of the resultant polymer increases linearly with the increase of the monomer

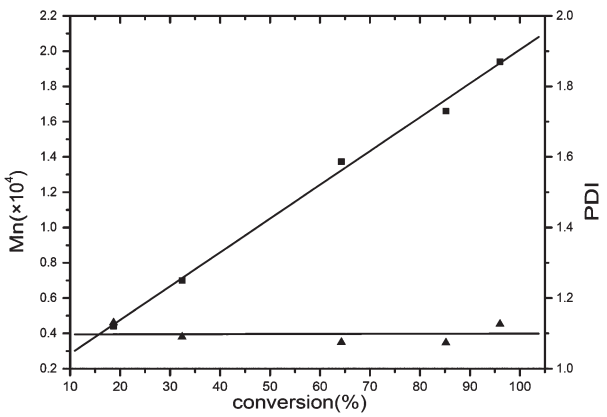


Fig. 7 Plot of molecular weight M_n *vs.* monomer conversion for **3a**–BnOH initiated polymerization of L-lactide. *Reaction conditions*: 30 μmol of initiator, M/I/B = 100 : 1 : 1, 10 mL toluene, 70 °C.

conversion and the PDIs of these polymer are kept in a narrow range (1.05–1.14) suggesting the living feature of the binary system. It was found that the molecular weight (M_n) of the resultant polymer decreases gradually with the increase of the BnOH/M molar ratios (entries 20, 25–26). The corresponding PDIs are kept narrow and the measured M_n values fit well with the calculated values according to the M/BnOH molar ratio, indicating somewhat "immortal" behavior of the binary system.

In order to further understand the polymerization reaction of L-lactide initiated by these binary systems, the reaction of complexes with BnOH was monitored *in situ* by ^{1}H NMR at room temperature. The ^{1}H NMR results reveal that when BnOH was

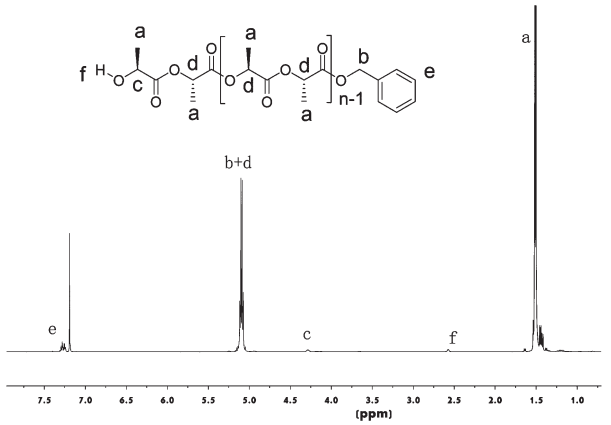
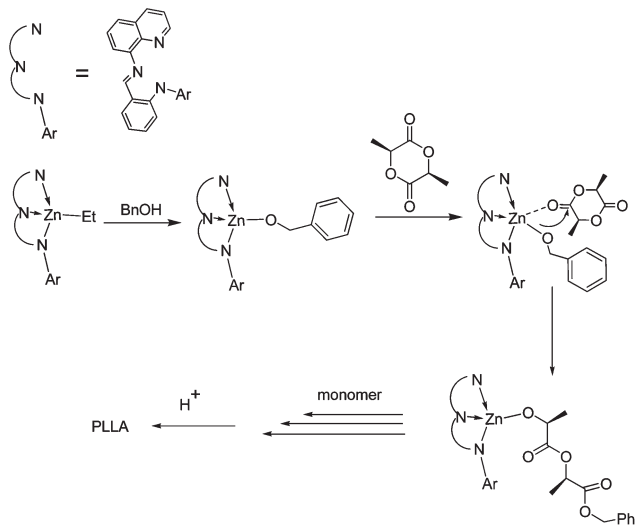


Fig. 8 ^{1}H NMR spectrum of a polymer sample obtained from the **3a**–BnOH system with M/I/B = 25 : 1 : 1 (in $CDCl_3$).



Scheme 3 Proposed mechanism for the ROP of L-lactide initiated by **3a–3c**–BnOH.

added, the aluminum complexes (**1a–1c** and **2a–2c**) decompose to corresponding free ligands along with the formation of the benzyloxy aluminum complexes. This result is well consistent with the independence of the catalytic behaviour on the ancillary ligands. When the zinc complexes were reacted with benzyl alcohol, the ^{1}H NMR spectrum shows the disappearance of the resonances for protons of $ZnCH_2CH_3$ in the high-field region and the appearance of a broad $PhCH_2OZn$ signal in the region of 4.0–4.5 ppm, demonstrating the formation of a benzyloxy zinc complex. The initiation mechanism was elucidated by end-group analysis of the oligomer of L-lactide, which was synthesized by the polymerization of the lactide at low monomer-to-initiator ratio (M/I/B = 25 : 1 : 1) (Fig. 8). End-group analysis shows that the polymer chains are capped with a benzyl ester group, indicating that the alkyl zinc complex has been converted to benzyloxy zinc species at the beginning of the polymerization and the real initiator is the benzyloxy zinc species as shown in Scheme 3.

Conclusions

A series of mononuclear/binuclear aluminum complexes bearing *N*,*N*,*N*-tridentate quinolinyl anilido-imine ligands have been synthesized and structurally characterized. Mononuclear aluminum complexes exhibit a trigonal bipyramidal coordination around the metal center, while in binuclear complexes all the aluminum atoms are in a tetrahedral geometry. Analogous monoligated/bisligated zinc complexes were also prepared. The zinc atoms in monoligated complexes are in a tetrahedral geometry, while in bisligated complexes they have trigonal bipyramidal geometries. The Zn complexes are efficient initiators for L-lactide ring-opening polymerization in the presence of benzyl alcohol, and the polymerization can be performed in an immortal manner.

Experiment section

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk or dry box techniques. Toluene and hexane were dried over sodium–benzophenone and distilled under nitrogen prior to use. Elemental analyses were performed on a Varian EL microanalyzer. NMR spectra were recorded on a Varian Mercury-300 NMR spectrometer at room temperature in $CDCl_3$. The molecular weight and molecular weight distribution of the polymers were measured on a TOSOH HLC 8220 GPC at 40 °C using THF as eluent against polystyrene standards. *N*-(2-((2,6-diisopropylphenylimino)methyl)phenyl)quinolin-8-amine,[13] $C_6H_4F(CH{=}NC_6H_3Me_2\text{-}2,6)$[11] and $C_6H_4F(CH{=}NC_6H_3Et_2\text{-}2,6)$[11] were synthesized according to literature procedures. 2,6-Dimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline, $AlMe_3$ and $ZnEt_2$ were purchased from Aldrich.

N-(2-((2,6-Dimethylphenylimino)methyl)phenyl)quinolin-8-amine

An ^{n}BuLi solution of hexane (15 mL, 25.0 mmol) was added to a THF (40 mL) solution of 8-aminoquinoline (2.0 g, 22 mmol) at −50 °C, and the mixture was allowed to warm to room temperature overnight. The resulting solution of LiNHAr was cannula-transferred into a solution of $o\text{-}C_6H_4F(CH{=}NC_6H_3Me_2\text{-}2,6)$ (4.0 g, 20.0 mmol) in 45 mL of THF at room temperature. After stirring for 4 h at 60 °C, the reaction mixture was quenched with 10 mL of H_2O, extracted with *n*-hexane, and evaporated to dryness *in vacuo* and the aimed product was obtained by chromography in 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.32 (s, 6H, CH_3), 6.88–6.98 (m, 2H), 7.36–7.52 (m, 5H), 7.09–7.12 (m, 2H), 7.89 (d, 2H, $m\text{-}C_6H_3$), 8.11 (dd, J_{H-H} = 8.3, 1.7 Hz, 1H, 3-quinolinyl), 8.41 (s, 1H, $HC{=}N$), 8.78 (dd, J_{H-H} = 4.1, 1.7 Hz, 1H, 1-quinolinyl), 12.12 (s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 18.50 (s, CH_3), 113.13 (s, Ar), 114.80 (s, 1C, Ar), 118.47 (s, Ar), 119.26 (s, Ar), 121.01 (s, Ar), 121.45 (s, Ar), 123.77 (s, Ar), 126.56 (s, Ar), 128.03 (s, Ar), 128.06 (s, Ar), 129.03 (s, Ar), 131.57 (s, Ar), 134.69 (s, Ar), 135.76 (s, Ar), 138.92 (s, Ar), 140.67 (s, Ar), 144.12 (s, Ar), 148.22 (s, Ar), 150.73 (s, 1-quinolinyl), 164.89 (s, $CH{=}N$) ppm.

***N*-(2-((2,6-Diethylphenylimino)methyl)phenyl)quinolin-8-amine**

An ^{n}BuLi solution of hexane (15 mL, 25.0 mmol) was added to a THF (40 mL) solution of 8-aminoquinoline (2.0 g, 22.0 mmol) at −50 °C, and the mixture was allowed to warm to room temperature overnight. The resulting solution of LiNHAr was cannula-transferred into a solution of *o*-$C_6H_4F(CH{=}NC_6H_3Et_2$-2,6) (4.0 g, 20.0 mmol) in 45 mL of THF at room temperature. After stirring for 4 h at 60 °C, the reaction mixture was quenched with 10 mL of H_2O, extracted with *n*-hexane, and evaporated to dryness *in vacuo* and the target product was obtained by chromatography in 62% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.17 (t, $J_{H–H}$ = 9.0 Hz, 6H, CH_2CH_3), 2.67 (q, $J_{H–H}$ = 9.0 Hz, 4H, CH_2CH_3), 6.93–7.12 (m, 4H), 7.35–7.51 (m, 5H), 7.88 (d, 2H *m*-C_6H_3), 8.10 (dd, $J_{H–H}$ = 8.3, 1.7 Hz, 1H, 3-quinolinyl), 8.41 (s, 1H, *H*C═N), 8.72 (dd, $J_{H–H}$ = 4.1, 1.7 Hz, 1H, 1-quinolinyl), 12.07 (s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 14.61 (s, CH_2CH_3), 24.81 (s, CH_2CH_3), 113.42 (s, Ar), 114.78 (s, Ar), 118.52 (s, Ar), 119.41 (s, Ar), 120.98 (s, Ar), 121.50 (s, Ar), 124.09 (s, Ar), 126.21 (s, Ar), 126.60 (s, Ar), 128.99 (s, Ar), 131.70 (s, Ar), 133.93 (s, Ar), 134.84 (s, Ar), 135.77 (s, 9-quinolinyl), 139.94 (s, Ar), 140.79 (s, Ar), 148.35 (s, 8-quinolinyl), 150.28 (s, 1-quinolinyl), 164.75 (s, *C*H═N) ppm.

Synthesis of complex 1a. $AlMe_3$ solution in toluene (2.7 mL, 0.5 M in toluene, 1.35 mmol) was added dropwise to a solution of *N*-(2-((2,6-dimethylphenylimino)methyl)phenyl)quinolin-8-amine (0.47 g, 1.35 mmol) in 20 mL of toluene at 0 °C with stirring. The mixture was allowed to warm to room temperature gradually and stirred overnight. The solvents were removed under reduced pressure, and 5 mL hexane was added. The volume of the solvent was reduced to precipitate the product as a yellow powder. Recrystallization from hexane–toluene gave **1a** as yellow microcrystalline solid. Yield: 0.25 g (46%). Anal. Calcd for $C_{26}H_{26}AlN_3$ (%): C, 76.64; H, 6.43; N, 10.31. Found: C, 76.58; H, 6.48; N, 10.23. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ −1.45 (s, 3H, Al–CH_3), −0.70 (s, 3H, Al–CH_3), 2.30 (s, 6H, Ar–CH_3), 6.77 (t, $J_{H–H}$ = 6.0 Hz, 1H, *p*-C_6H_3), 7.06 (m, 3H, Ar–H), 7.21–7.26 (m, 1H, Ar–H), 7.33–7.37 (m, 2H, Ar–H), 7.71 (d, $J_{H–H}$ = 9 Hz, 2H, Ar–H), 8.14 (s, 1H, C*H*═N), 8.24 (dd, $J_{H–H}$ = 8.3, 1.5 Hz, 1H, 3-quinolinyl), 8.53 (dd, $J_{H–H}$ = 4.5, 1.5 Hz, 1H, 1-quinolinyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ −7.25 (s, Al–CH_3), −4.04 (s, Al–CH_3), 19.18 (s, Ar–CH_3), 117.14 (s, 7-quinolinyl), 117.26 (s, Ar), 117.70 (s, Ar), 118.04 (s, Ar), 121.21 (s, 3-quinolinyl), 122.11 (s, 5-quinolinyl), 125.73 (s, Ar), 128.30 (s, Ar), 128.57 (s, Ar), 129.19 (s, Ar), 130.95 (s, Ar), 133.61 (s, Ar), 134.97 (s, Ar), 137.51 (s, Ar), 141.61 (s, 4-quinolinyl), 144.66 (s, Ar), 146.62 (s, Ar), 150.36 (s, 8-quinolinyl), 153.36 (s, 1-quinolinyl), 168.48 (s, N═*C*H) ppm.

Synthesis of complex 1b. Complex **1b** was synthesized in the same manner as **1a** with *N*-(2-((2,6-diethylphenylimino)methyl)phenyl)quinolin-8-amine (0.44 g, 1.17 mmol), and $AlMe_3$ (2.3 mL, 0.5 M in toluene, 1.17 mmol) as starting materials or reagents. Recrystallization from hexane–toluene gave **1b** as a yellow microcrystalline solid. Yield: 0.26 g (52%). Anal. Calcd for $C_{28}H_{30}AlN_3$ (%): C, 77.21; H, 6.94; N, 9.65. Found: C, 77.15; H, 6.87; N, 9.71. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ −1.45 (s, 3H, Al–CH_3), −0.70 (s, 3H, Al–CH_3), 1.14 (t, $J_{H–H}$ = 6.0 Hz, 6H, Ar–CH_2CH_3), 2.60 (q, 4H, $J_{H–H}$ = 6.0 Hz, Ar–CH_2CH_3), 6.77 (t, $J_{H–H}$ = 6.0 Hz, 1H, Ar–H), 7.10–7.55 (m, 8H, Ar–H), 7.69–7.72 (m, 2H, Ar–H), 8.16 (s, 1H, C*H*═N), 8.23 (dd, $J_{H–H}$ = 8.3, 1.5 Hz, 1H, 3-quinolinyl), 8.53 (dd, $J_{H–H}$ = 4.5, 1.5 Hz, 1H, 1-quinolinyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ −7.87 (s, Al–CH_3), −3.82 (s, Al–CH_3), 15.36 (s, Ar–CH_2CH_3), 24.88 (s, Al–CH_2CH_3), 117.18 (s, 7-quinolinyl), 117.24 (s, Ar), 117.74 (s, Ar), 118.02 (s, Ar), 121.05 (s, 3-quinolinyl), 122.08 (s, 5-quinolinyl), 126.16 (s, Ar), 126.32 (s, Ar), 128.58 (s, Ar), 129.17 (s, Ar), 133.58 (s, Ar), 134.90 (s, Ar), 136.80 (s, Ar), 137.49 (s, Ar), 141.60 (s, 4-quinolinyl), 144.67 (s, Ar), 146.64 (s, Ar), 149.26 (s, Ar), 153.38 (s, 1-quinolinyl), 168.52 (s, N═*C*H) ppm.

Synthesis of complex 1c. Complex **1c** was synthesized in the same manner as **1a** with *N*-(2-((2,6-diisopropylphenylimino)methyl)phenyl)quinolin-8-amine (0.46 g, 1.14 mmol), and $AlMe_3$ (2.3 mL, 0.5 M in toluene, 1.15 mmol) as starting materials or reagents. Pure **1c** was obtained by recrystallization in hexane–toluene as a yellow microcrystalline solid. Yield: 0.32 g (61%). Single crystals for X-ray diffraction analysis were obtained from hexane at −30 °C. Anal. Calcd for $C_{30}H_{34}AlN_3$ (%): C, 77.72; H, 7.39; N, 9.06. Found: C, 77.52; H, 7.47; N, 9.19. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ −1.42 (s, 3H, Al–CH_3), −0.72 (s, 3H, Al–CH_3), 1.13 (d, $J_{H–H}$ = 6.0 Hz, 12H, Ar–CH(CH_3)$_2$), 3.19 (b, 2H, Ar–C*H*(CH_3)$_2$), 6.77 (t, $J_{H–H}$ = 6.0 Hz, 1H, *p*-C_6H_3), 7.14–7.55 (m, 8H, Ar–H), 7.67–7.70 (m, 2H, Ar–H), 8.15 (s, 1H, C*H*═N), 8.24 (dd, $J_{H–H}$ = 8.3, 1.5 Hz, 1H, 3-quinolinyl), 8.54 (dd, $J_{H–H}$ = 4.6, 1.5 Hz, 1H, 1-quinolinyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ −8.93 (s, Al–CH_3), −3.65 (s, Al–CH_3), 23.97 (s, Ar–CH(CH_3)$_2$), 24.85 (s, Ar–CH(CH_3)$_2$), 28.30 (s, Ar–*C*H(CH_3)$_2$), 15.36 (s, Ar–CH_2CH_3), 24.88 (s, Al–CH_2CH_3), 117.17 (s, 7-quinolinyl), 117.28 (s, Ar), 117.85 (s, Ar), 118.00 (s, Ar), 121.01 (s, 3-quinolinyl), 122.09 (s, 5-quinolinyl), 123.60 (s, Ar), 126.48 (s, Ar), 128.63 (s, Ar), 129.23 (s, Ar), 133.59 (s, Ar), 134.94 (s, Ar), 137.55 (s, Ar), 141.58 (s, 4-quinolinyl), 144.76 (s, Ar), 146.70 (s, Ar), 147.96 (s, Ar), 153.49 (s, 1-quinolinyl), 168.27 (s, N═*C*H) ppm.

Synthesis of complex 2a. Complex **2a** was synthesized in the same manner as **1a** with *N*-(2-((2,6-dimethylphenylimino)-methyl)phenyl)quinolin-8-amine (0.42 g, 1.21 mmol) and $AlMe_3$ (4.8 mL, 0.5 M in toluene, 2.42 mmol) as starting materials or reagents. Recrystallization from hexane gave **2a** as a yellow microcrystalline solid. Yield: 0.32 g (55%). Single crystals for X-ray diffraction analysis were obtained from hexane at −30 °C. Anal. Calcd for $C_{29}H_{35}Al_2N_3$ (%): C, 72.63; H, 7.36; N, 8.76. Found: C, 72.55; H, 7.28; N, 8.65. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ −1.38 (s, 9H, Al(CH_3)$_3$), −0.58 (s, 3H, AlCH_3), −0.54 (s, 3H, AlCH_3), 2.05 (s, 3H, Ar–CH_3), 2.15 (s, 3H, Ar–CH_3), 6.22 (d, $J_{H–H}$ = 6.0 Hz, 1H, Ar–H), 6.85–6.88 (m, 1H, Ar–H), 6.97 (m, 1H, 6-quinolinyl), 7.06–7.14 (m, 4H, Ar–H), 7.27 (d, $J_{H–H}$ = 6.0 Hz, 1H, 7-quinolinyl), 7.35 (t, $J_{H–H}$ = 6.0 Hz, 1H, 2-quinolinyl), 7.59 (m, 1H, Ar–H), 7.68–7.72 (m, 1H, Ar–H), 8.47 (d, $J_{H–H}$ = 9.0 Hz, 1H, 3-quinolinyl), 8.62 (d, $J_{H–H}$ = 6.0 Hz, 1H, 1-quinolinyl), 8.94 (s, 1H, C*H*═N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ −9.55 (s, Al(CH_3)$_3$), −8.59 (s, AlCH_3), −8.26 (s, AlCH_3), 18.44 (s, Ar–CH_3), 18.47 (s, Ar–CH_3), 108.36 (s, Ar), 112.13 (s, Ar), 122.21 (s, Ar),

125.70 (s, Ar), 126.76 (s, Ar), 128.25 (s, Ar), 128.28 (s, Ar), 128.62 (s, Ar), 128.91 (s, Ar), 129.12 (s, Ar), 129.52 (s, Ar), 129.60 (s, Ar), 129.87 (s, Ar), 130.12 (s, Ar), 131.16 (s, Ar), 136.72 (s, Ar), 141.35 (s, Ar), 143.75 (s, Ar), 151.65 (s, 8-quinolinyl), 152.06 (s, 1-quinolinyl), 167.75 (s, N=*C*H) ppm.

Synthesis of complex 2b. Complex **2b** was synthesized in the same manner as **2a** with *N*-(2-((2,6-diethylphenylimino)methyl)-phenyl)quinolin-8-amine (0.45 g, 1.20 mmol), and $AlMe_3$ (4.8 mL, 0.5 M in toluene, 2.40 mmol) as starting materials or reagents. Pure **2b** was obtained by recrystallization in hexane as a yellow microcrystalline solid. Yield: 0.36 g (60%). Single crystals for X-ray diffraction analysis were obtained from hexane at −30 °C. Anal. Calcd for $C_{31}H_{39}Al_2N_3$ (%): C, 73.35; H, 7.74; N, 8.28. Found: C, 73.51; H, 7.64; N, 8.19. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ −1.39 (s, 9H, Al(CH_3)$_3$), −0.58 (s, 3H, AlCH_3), −0.53 (s, 3H, AlCH_3), 1.08–1.15 (m, 6H, Ar–CH_2CH_3), 2.25–2.35 (m, 2H, Ar–CH_2CH_3), 2.55–2.63 (m, 2H, Ar–CH_2CH_3), 6.20 (dd, J_{H-H} = 6.0 Hz, 1H, Ar–H), 6.81–6.84 (m, 1H, Ar–H), 6.94 (m, 1H, Ar–H), 7.07–7.09 (m, 1H, Ar–H), 7.19–7.31 (d, J_{H-H} = 6.0 Hz, 4H, Ar–H), 7.36 (t, J_{H-H} = 9.0 Hz, 1H, Ar–H), 7.55–7.60 (m, 1H, Ar–H), 7.68–7.72 (m, 1H, Ar–H), 8.48 (dd J_{H-H} = 8.3, 1.5 Hz, 1H, 3-quinolinyl), 8.62 (dd, J_{H-H} = 4.5, 1.5 Hz, 1H, 1-quinolinyl), 8.97 (s, 1H, C*H*=N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ −9.67 (s, Al(*C*H_3)$_3$), −8.54 (s, Al*C*H_3), −8.36 (s, Al*C*H_3), 13.89 (s, Ar–CH_2*C*H_3), 14.16 (s, Ar–CH_2*C*H_3), 23.75(s, Ar–*C*H_2CH_3), 24.08 (s, Ar–*C*H_2CH_3), 108.28 (s, 7-quinolinyl), 112.12 (s, Ar), 122.04 (s, Ar), 122.21 (s, Ar), 125.39 (s, Ar), 126.08 (s, Ar), 126.50 (s, Ar), 126.67 (s, Ar), 127.10 (s, Ar), 128.58 (s, Ar), 129.87 (s, Ar), 130.14 (s, Ar), 130.34 (s, Ar), 131.05 (s, Ar), 133.54 (s, Ar), 134.71 (s, Ar), 136.71 (s, Ar), 141.35 (s, Ar), 143.75 (s, Ar), 151.73 (s, 8-quinolinyl), 152.18 (s, 1-quinolinyl), 168.27 (s, N=*C*H) ppm.

Synthesis of complex 2c. Complex **2c** was synthesized in the same manner as **1a** with *N*-(2-((2,6-diisopropylphenylimino)-methyl)phenyl)quinolin-8-amine (0.49 g, 1.20 mmol), and $AlMe_3$ (4.8 mL, 0.5 M in toluene, 2.40 mmol) as starting materials or reagents. Recrystallization from hexane gave pure **2c** as a yellow microcrystalline solid. Yield: 0.41 g (64%). Single crystals for X-ray diffraction analysis were obtained from hexane at −30 °C. Anal. Calcd for $C_{33}H_{43}Al_2N_3$ (%): C, 73.99; H, 8.09; N, 7.84. Found: C, 74.15; H, 8.00; N, 7.95. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ −1.38 (s, 9H, Al(CH_3)$_3$), −0.57 (s, 3H, AlCH_3), −0.53 (s, 3H, AlCH_3), 0.86–1.26 (m, 12H, Ar–CH(CH_3)$_2$), 2.76 (m, 1H, Ar–C*H*(CH$_3$)$_2$), 2.99 (m, 1H, Ar–C*H*(CH$_3$)$_2$), 6.00 (d, J_{H-H} = 6.0 Hz, 1H, Ar–H), 6.76–6.78 (m, 1H, Ar–H), 6.91–6.96 (m, 1H, Ar–H), 7.16–7.37 (m, 6H, Ar–H), 7.52–7.60 (m, 1H, Ar–H), 7.68–7.72 (m, 1H, Ar–H), 8.48 (d, J_{H-H} = 6.0 Hz, 1H, 3-quinolinyl), 8.62 (d, J_{H-H} = 6.0 Hz, 1H, 1-quinolinyl), 9.00 (s, 1H, C*H*=N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ −9.77 (s, Al(*C*H$_3$)$_3$), −8.39 (s, Al–*C*H$_3$), 23.75 (s, Ar–CH(*C*H$_3$)$_2$), 24.25 (s, Ar–CH(*C*H$_3$)$_2$), 24.33 (s, Ar–CH(*C*H$_3$)$_2$), 24.41 (s, Ar–CH(*C*H$_3$)$_2$), 27.96 (s, Ar–*C*H(CH$_3$)$_2$), 28.62 (s, Ar–*C*H(CH$_3$)$_2$), 107.98 (s, Ar), 112.14 (s, Ar), 122.01 (s, Ar), 122.22 (s, Ar), 123.54 (s, Ar), 124.67 (s, Ar), 124.92 (s, Ar), 125.05 (s, Ar), 127.61 (s, Ar), 128.43 (s, Ar), 129.89 (s, Ar), 130.27 (s, Ar), 130.95 (s, Ar), 131.28 (s, Ar), 136.84 (s, Ar), 138.17 (s, Ar), 139.72 (s, Ar), 141.35 (s, Ar), 143.75 (s, Ar), 151.97 (s, 8-quinolinyl), 152.42 (s, 1-quinolinyl), 168.55 (s, N=*C*H) ppm.

Synthesis of complex 3a. $ZnEt_2$ solution in toluene (1.6 mL, 0.5 M in toluene, 0.83 mmol) was added dropwise to a toluene (20 mL) solution of *N*-(2-((2,6-dimethylphenylimino)methyl)-phenyl)quinolin-8-amine (0.25 g, 0.80 mmol) at 0 °C. The mixture was allowed to warm to room temperature gradually and stirred overnight. Evaporating the solvents to dryness afforded the product as a red powder. Recrystallization in hexane gave **3a** as microcrystalline solid. Yield: 0.26 g (75%). Anal. Calcd for $C_{26}H_{25}N_3Zn$ (%): C, 70.19; H, 5.66; N, 9.45. Found: C, 70.23; H, 5.64; N, 9.51. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.07 (q, J_{H-H} = 6.0 Hz, 2H, Zn–CH_2CH$_3$), 1.01 (t, J_{H-H} = 6.0 Hz, 3H, Zn–CH$_2$CH_3), 1.98 (s, 6H, CH_3), 6.91–7.50 (m, 9H, Ar–H), 7.58 (d, J_{H-H} = 9.0 Hz, 1H, Ar–H), 7.87 (d, J_{H-H} = 9.0 Hz, 1H, Ar–H), 8.05 (s, 1H, C*H*=N), 8.18 (d, J_{H-H} = 8.1 Hz, 1H, 3-quinolinyl), 8.45 (dd, J_{H-H} = 4.4, 1.3 Hz, 1H, 1-quinolinyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ −0.61 (s, Zn–*C*H$_2$CH$_3$), 12.96 (s, Zn–CH$_2$*C*H$_3$), 18.40 (s, Ar–*C*H$_3$), 105.40 (s, Ar), 110.95 (s, 7-quinolinyl), 119.27 (s, Ar), 121.31 (s, 5-quinolinyl), 124.53 (s, Ar), 125.41 (s, Ar), 126.02 (s, Ar), 127.78 (s, Ar), 128.52 (s, Ar), 129.49 (s, Ar), 129.73 (s, Ar), 130.24 (s, Ar), 130.82 (s, Ar), 132.59 (s, Ar), 136.04 (s, Ar), 138.69 (s, 4-quinolinyl), 145.07 (s, 8-quinolinyl), 149.56 (s, 1-quinolinyl), 168.92 (s, N=*C*H) ppm.

Synthesis of complex 3b. Following the same procedure described for the formation of **3a**, treatment of *N*-(2-((2,6-diethylphenylimino)methyl)phenyl)quinolin-8-amine (0.45 g, 1.20 mmol) in 20 mL toluene solution with $ZnEt_2$ (2.4 mL, 0.5 M in toluene, 1.20 mmol) yielded complex **3b** as a red-orange microcrystalline solid after recrystallization with hexane. Yield: 0.46 g (80%). Anal. Calcd for $C_{28}H_{29}N_3Zn$ (%): C, 71.11; H, 6.18; N, 8.88. Found: C, 71.19; H, 6.22; N, 8.81. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.07 (q, J_{H-H} = 6.0 Hz, 2H, Zn–CH_2CH$_3$), 0.94 (t, J_{H-H} = 4.0 Hz, 6H, CH$_2$CH_3), 1.00 (t, J_{H-H} = 6.0 Hz, 3H, Zn–CH$_2$CH_3), 2.35 (q, J_{H-H} = 4.0 Hz, 4H, CH_2CH$_3$), 6.91–7.50 (m, 9H, Ar–H), 7.58 (d, J_{H-H} = 9.0 Hz, 1H, Ar–H), 7.87 (d, J_{H-H} = 9.0 Hz, 1H, Ar–H), 8.05 (s, 1H, C*H*=N), 8.18 (dd, J_{H-H} = 8.3, 1.6 Hz, 1H, J_{H-H} = 4.4, 1.3 Hz, 3-quinolinyl), 8.45 (dd, J_{H-H} = 4.5, 1.5 Hz, 1H, 1-quinolinyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ −0.66 (s, Zn–*C*H$_2$CH$_3$), 12.93 (s, Zn–CH$_2$*C*H$_3$), 15.10 (s, Ar–CH$_2$CH$_3$), 24.17 (s, Ar–*C*H$_2$CH$_3$), 105.55 (s, 6-quinolinyl), 110.95 (s, Ar), 119.31 (s, Ar), 121.15 (s, Ar), 124.59 (s, 5-quinolinyl), 125.44 (s, Ar), 125.75 (s, Ar), 126.37 (s, Ar), 129.68 (s, Ar), 129.68 (s, Ar), 130.73 (s, Ar), 132.53 (s, Ar), 135.40 (s, Ar), 135.98 (s, Ar), 138.61 (s, 4-quinolinyl), 145.10 (s, Ar), 148.58 (s, Ar), 148.78 (s, 8-quinolinyl), 154.57 (s, 1-quinolinyl), 168.91 (s, N=*C*H) ppm.

Synthesis of complex 3c. Following the same procedure described for the formation of **3a**, treatment of *N*-(2-((2,6-diiso-propylphenylimino)methyl)phenyl)quinolin-8-amine (0.49 g, 1.20 mmol) in 20 mL toluene solution with $ZnEt_2$ (2.4 mL, 0.5 M in toluene, 1.21 mmol) and subsequent recrystallization with hexane gave **3c** as a red powder. Yield: 0.49 g (82%). Anal. Calcd for $C_{30}H_{33}N_3Zn$ (%): C, 71.92; H, 6.64; N, 8.39. Found:

C, 71.89; H, 6.59; N, 8.43. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.11 (q, J_{H-H} = 6.0 Hz, 2H, Zn–CH_2CH$_3$), 0.91 (d, 12H, Ar–CH(CH_3)$_2$), 1.04 (t, J_{H-H} = 6.0 Hz, 3H, Zn–CH$_2$CH_3), 2.83 (m, 2H, Ar–CH(CH$_3$)$_2$), 6.90–7.00 (m, 3H, Ar–H), 7.10–7.20 (m, 3H, Ar–H), 7.32–7.40 (m, 2H, Ar–H), 7.45–7.52 (m, 2H, Ar–H), 7.90 (d, J_{H-H} = 9.0 Hz, 1H, Ar–H), 8.06 (s, 1H, CH═N), 8.18 (d, J_{H-H} = 7.4 Hz, 1H, 3-quinolinyl), 8.41 (d, J_{H-H} = 3.5 Hz, 1H, 1-quinolinyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ −1.40 (s, ZnCH$_2$CH$_3$), 13.06 (s, ZnCH$_2$$CH_3$), 24.21 (s, Ar–CH(C$H_3$)$_2$), 27.96 (s, Ar–C$H$(CH$_3$)$_2$), 105.50 (s, 7-quinolinyl), 110.74 (s, Ar), 119.56 (s, Ar), 121.08 (s, 3-quinolinyl), 122.78 (s, 5-quinolinyl), 123.66 (s, Ar), 125.04 (s, Ar), 125.73 (s, Ar), 126.05 (s, Ar), 129.75 (s, Ar), 130.78 (s, Ar), 132.47 (s, Ar), 135.82 (s, Ar), 138.65 (s, Ar), 140.34 (s, 4-quinolinyl), 145.24 (s, Ar), 147.05 (s, Ar), 148.95 (s, 8-quinolinyl), 154.52 (s, 1-quinolinyl), 168.36 (s, N═CH) ppm.

Synthesis of complex 4a. $ZnEt_2$ solution in toluene (1.60 mL, 0.5 M in toluene, 0.80 mmol) was added dropwise to a toluene (20 mL) solution of *N*-(2-((2,6-dimethylphenylimino)methyl)-phenyl)quinolin-8-amine (0.50 g, 1.60 mmol) at 0 °C. The mixture was allowed to warm to room temperature gradually and stirred overnight. Evaporating the solvents to dryness and recrystallizing the residue with hexane afforded the product as a red powder. Yield: 0.51 g (80%). Anal. Calcd for $C_{48}H_{40}N_6Zn$ (%): C, 75.24; H, 5.26; N, 10.97. Found: C, 75.39; H, 5.28; N, 10.85. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.64 (s, 12H, Ar–CH_3), 6.72–7.06 (m, 18H, Ar–H), 7.21–7.27 (m, 2H, Ar–H), 7.41–7.42 (m, 2H, Ar–H), 7.54 (b, 2H, Ar–H), 7.94–7.96 (m, 4H, 2 CH═N + 2 Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 18.13 (s, Ar–CH$_3$), 107.23 (s, Ar), 109.28 (s, C_6H_3), 119.72 (s, C_6H_3), 120.63 (s, Ar), 123.82 (s, Ar), 124.19 (b, C_6H_3), 127.74 (s, Ar), 128.52 (s, Ar), 129.91 (s, C_6H_3), 132.51 (s, Ar), 138.36 (s, Ar), 139.45 (s, Ar), 143.62 (s, Ar), 150.70 (s, Ar), 154.47 (s, Ar), 166.43 (s, N═CH) ppm.

Synthesis of complex 4b. Following the same procedure described for the formation of **4a**, treatment of *N*-(2-((2,6-diethylphenylimino)methyl)phenyl)quinolin-8-amine (0.46 g, 1.20 mmol) in 20 mL toluene solution with $ZnEt_2$ (1.2 mL, 0.5 M in toluene, 0.60 mmol) and subsequent recrystallization with hexane gave **4b** as a red powder. Yield: 0.39 g (81%). Anal. Calcd for $C_{52}H_{48}N_6Zn$ (%): C, 75.95; H, 5.88; N, 10.22. Found: C, 75.83; H, 5.81; N, 10.18. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.68 (b, 12H, Ar–CH$_2$CH_3), 2.03(b, 8H, Ar–CH_2CH$_3$), 6.70–6.90 (m, 15H, Ar–H), 7.03 (m, 2H, Ar–H), 7.19–7.33 (m, 5H, Ar–H), 7.56 (b, 2H, Ar–H), 7.93–7.96 (4H, CH═N + Ar–H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 14.13 (s, Ar–CH$_2$$CH_3$), 24.34 (s, Ar–$CH_2CH_3$), 107.19 (s, Ar), 109.17 (s, C_6H_3), 119.83 (s, C_6H_3), 120.65 (s, Ar), 123.82 (s, Ar), 124.17 (s, C_6H_3), 125.65 (s, Ar), 129.96 (s, Ar), 130.44 (s, C_6H_3), 131.06 (s, Ar), 132.54 (s, Ar), 134.40 (s, Ar), 138.26 (s, Ar), 143.72 (s, Ar), 150.02 (s, Ar), 154.45 (s, Ar), 166.16 (s, N═CH) ppm.

Synthesis of complex 4c. Following the same procedure described for the formation of **4a**, treatment of *N*-(2-((2,6-diisopropylphenylimino)methyl)phenyl)quinolin-8-amine (0.49 g, 1.20 mmol) in 20 mL toluene solution with $ZnEt_2$ (1.2 mL, 0.5 M in toluene, 0.60 mmol) and subsequent recrystallization with hexane gave **4c** as a red powder. Yield: 0.37 g (70%). Anal. Calcd for $C_{56}H_{56}N_6Zn$ (%): C, 76.56; H, 6.43; N, 9.57. Found: C, 76.49; H, 6.53; N, 9.61. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.68 (b, 24H, Ar–CH(CH_3)$_2$), 2.71 (b, 4H, Ar–CH(CH$_3$)$_2$), 6.72–7.07 (m, 17H, Ar–H), 7.18–7.25 (m, 5H, Ar–H), 7.53 (b, 2H, Ar–H), 7.96–7.97 (m, 4H, CH═N + Ar–H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 23.04 (s, Ar–CH(CH_3)$_2$), 27.79 (s, Ar–CH(CH$_3$)$_2$), 106.82 (s, Ar), 108.95 (s, C_6H_3), 120.69 (s, Ar), 122.76 (s, Ar), 124.50 (s, C_6H_3), 130.09 (s, Ar), 130.67 (s, Ar), 132.50 (s, Ar), 138.28 (s, Ar), 138.76 (s, C_6H_3), 139.50 (s, Ar), 143.74 (s, Ar), 148.87 (b, Ar), 154.14 (s, Ar), 165.38 (b, N═CH) ppm.

Lactide polymerization

In a typical polymerization experiment, an aluminum or zinc complex (30 μmol), the required amount of L-lactide and benzyl alcohol in toluene (15 mL) were loaded in a flame-dried vessel containing a magnetic bar. The vessel was placed in an oil bath thermostated at 70 °C. After a certain reaction time, the polymer was isolated by precipitation with cold methanol. The precipitate was collected and dried under vacuum at 40 °C for 24 h. For some polymerization reactions, samples were taken for determining the monomer conversion by ^{1}H NMR during the reaction.

Crystal structure determination

The crystals were mounted on a glass fiber using an oil drop. Data obtained with the ω–2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods, and refined with full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL crystallographic software packages.

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Notes and references

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