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Dinucleating Ligand Platforms Supporting Indium and Zinc Catalysts for Cyclic Ester Polymerization

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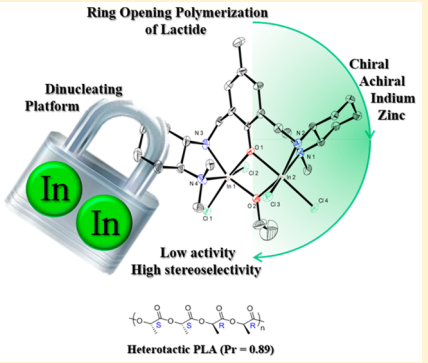
Supporting Information

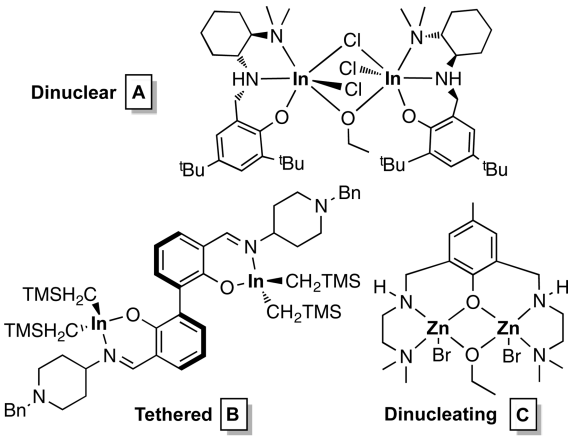
ABSTRACT: The synthesis of the first alkoxide-bridged indium complex supported by a chiral dinucleating ligand platform (**1**), along with its zinc analogue (**2**), is reported. Both complexes are synthesized in a one-pot reaction starting from a chiral dinucleating bis(diamino)phenolate ligand platform, sodium ethoxide, and respective metal salts. The dinucleating indium analogue (**7**) based on an achiral ligand backbone is also reported. Indium complexes bearing either the chiral or achiral ligand catalyze the ring-opening polymerization of racemic lactide (*rac*-LA) to afford highly heterotactic poly(lactic acid) (PLA; $P_r > 0.85$). The indium complex bearing an achiral ligand affords essentially atactic PLA from *meso*-LA. The role of the dinucleating ligand structure in catalyst synthesis and polymerization activity is discussed.



INTRODUCTION

Synthetic chemists have long taken inspiration from tandem catalysis, prevalent in nature,[1] to develop multimetallic systems in catalysis. In particular, studies have explored cooperative bimetallic mechanisms in polymerization catalysis, for example, for polyolefins[2] and CO_2-based polymers.[3] The involvement of two metals in catalysis can take different forms (Chart 1):

Chart 1. Dinuclear Indium[13,15,16] and Zinc[8,17] Complexes



dinuclear or dimeric species arise from the aggregation of two discrete metal centers through bridging ligands, tethered species involve two nonbridged metal centers on the same ligand architecture that can react independently, and dinucleating catalysts involve a multidentate ligand platform bound to two different metals, which are also bridged by a secondary ligand and can react in tandem. Bimetallic catalysts, either dimeric, tethered, or dinucleating, have also received attention as catalysts for the ring-opening polymerization of lactide (LA) to form poly(lactic acid) (PLA). Examples of dinuclear initiators for cyclic ester polymerization include species involving Y,[4] rare earths,[5] group IV,[6] Fe,[7] Co,[8] Mg,[9] Cu,[10] Zn,[11] and Al.[12]

We reported the first indium-based initiator (**A**) for the efficient and highly controlled ring-opening polymerization of LA (Chart 1).[13] Since then, several other indium-based catalysts for ring-opening polymerization have been reported.[14] Although these include both mononuclear[14b−i] and dimeric[14j−r] indium species, there is only one report of a tethered bimetallic indium catalyst for the ring-opening polymerization of cyclic esters (**B**)[15] (Chart 1). To our knowledge, no examples of a dinucleating ligand platform for indium have been reported.

We are interested in the role of the nuclearity of **A** on the polymerization mechanism. Complex **A** is a highly controlled catalyst for the living[18] and immortal[19] polymerization of cyclic esters, and we have demonstrated experimentally[16] and computationally[20] that the propagating species for catalyst **A** is dinuclear. In contrast, indium complexes with tridentate[21] or tetradentate[22] supports developed in our group that do not retain a dinuclear structure during polymerization do not show the same control of the polymer molecular weight, dispersity, or selectivity. The importance of catalyst nuclearity is greatly reduced for a tethered system; in complex **B**, the two indium centers act as two distinct initiating points for the immortal polymerization of LA, with reactivity comparable to that of the monomeric analogue.[15]

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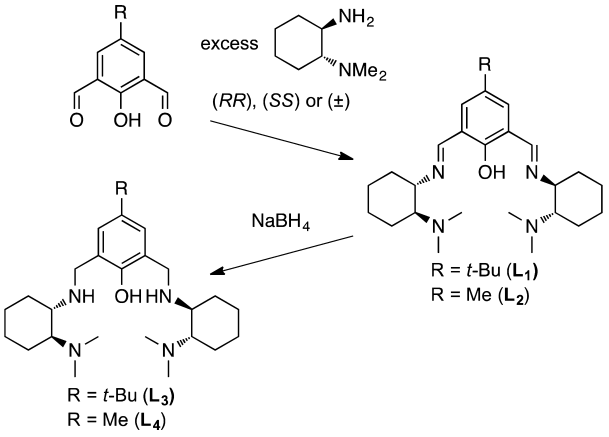
We were interested in seeing if replacing the dinuclear or tethered motif in indium complexes with a dinucleating motif, such as the bis(diamino)phenolate supports reported for zinc complexes (Chart 1, **C**),[8,17] would allow us to explore nuclearity in our systems. Initial studies for the polymerization of *rac*-LA with **C** or its analogues showed high activity but no stereocontrol.[8,17a] Magnesium and cobalt analogues were also not selective and showed lower activity than the zinc analogues.[8] Subsequently, expansion of the ligand framework to include secondary amine and imine donors showed that the secondary amine zinc bromide complex (**C**) is one of the most efficient catalysts for the polymerization of *rac*-LA, reaching >90% conversion to form atactic PLA within 1 min.[17b]

Herein, we report the synthesis of a chiral bis(diamino)-phenolate ligand platform inspired by **C** and explore the synthesis and reactivity of corresponding indium and zinc complexes through various synthetic strategies including an easy and efficient one-pot reaction. Using this process, we report the first examples of indium metals supported by a dinucleating platform. The reactivity of these complexes as catalysts for the ring-opening polymerization of LA will also be discussed.

RESULTS AND DISCUSSION

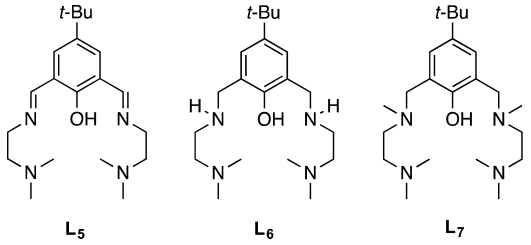
Synthesis of Proligands L_1–L_7. Chiral pentadentate aminophenolate proligands L_1 and L_2 can be synthesized through modification of reported procedures from condensation of an excess amount of freshly distilled (±)-, (*RR*)- or (*SS*)-*N*,*N*-dimethylcyclohexyldiamine[23] and 2,6-diformyl-4-*tert*-butylphenol or 2,6-diformyl-4-methylphenol (Scheme 1).[17b,24]

Scheme 1. Synthesis of Proligands L_1–L_4



The ^{1}H NMR spectra of L_1 and L_2 show broad singlets at 7.63/7.43 and 8.53/8.49 ppm corresponding to the Ar–*H* and imine N=C*H* protons, respectively, regardless of the stereochemistry (Figures S3 and S4). Excess amine is required to generate the bis(imine) species (see the Supporting Information). The reduction of L_1 and L_2 with $NaBH_4$ forms proligands L_3 and L_4 as low-melting-point solids resistant to crystallization. Purification of L_1–L_4 using various methods was attempted without success; therefore, full characterization of ligands L_1–L_4 was not undertaken. Achiral pentadentate aminophenolate proligands L_5–L_7 can be synthesized according to similar procedures, characterized, and used without further purification (Chart 2).[17]

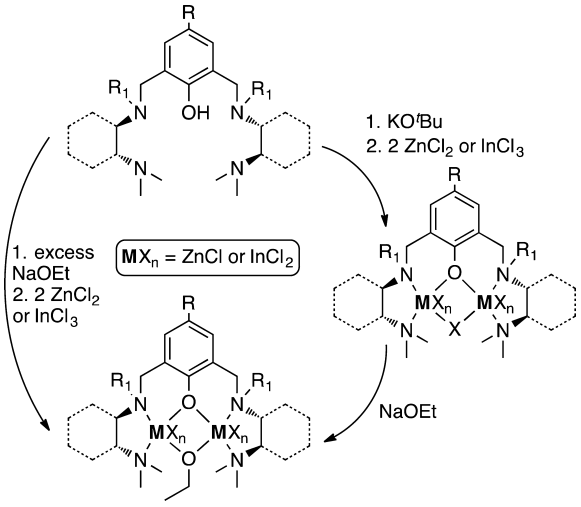
Chart 2. Achiral Pentadentate Bis(diamino)phenol Proligands with Ethylene Backbones L_5–L_7[17]



The ^{1}H NMR spectra of enantiopure analogues of L_3 and L_4 show characteristic singlets for Ar–*H* protons in addition to a set of diastereotopic protons corresponding to NH–CH_2–Ar. In contrast, the ^{1}H NMR spectra of L_3 and L_4 generated from racemic amine show several sets of peaks, suggesting the presence of several diastereomers (Figures S6 and S8). The ^{1}H NMR spectra of (*RR*/*RR*)- and (*SS*/*SS*)-L_4 are identical and different from that of the racemic species (±)-L_4, which includes the two enantiomers as well as (*SS*/*RR*)- L_4 (Figure S10). The same observations can be made for L_3 (Figure S11). Only the enantiopure (*RR*/*RR*)-L_4 is used in further reactions.

Synthesis of Indium and Zinc Alkoxide Complexes Bearing Chiral Ligand Backbones. Dinucleating proligands L_1–L_7 were screened as supports for both zinc and indium, but different strategies had to be used for different complexes. These strategies were not successful for L_5 and L_6. Syntheses of indium and zinc alkoxide complexes of L_1–L_7 were attempted through two pathways (Scheme 2): (1) deprotonation of the

Scheme 2. Pathways for the Synthesis of Zinc and Indium Alkoxide Complexes Supported by L_1–L_7



proligand, salt metathesis to yield the dinucleating halide-bridged intermediate, and further reaction with alkoxide salts to form the targeted dinucleating alkoxide initiator[17] and (2) a one-pot synthesis with the proligand, metal halide, and alkoxide salt.[13,22b,c]

Proligand L_4 is the only chiral proligand that forms isolable alkoxide complexes. The reaction of (*RR*/*RR*)-L_4 with 4 equiv of sodium ethoxide (NaOEt) in toluene at room temperature for 16 h, followed by the addition of $InCl_3$ or $ZnCl_2$, forms (*RR*/*RR*)-[(L_4)In_2Cl_4](μ-OEt) [(*RR*/*RR*)-**1**] and (*RR*/*RR*)-[(L_4)Zn_2Cl_2](μ-OEt) [(*RR*/*RR*)-**2**] (Scheme 3). Low-yielding

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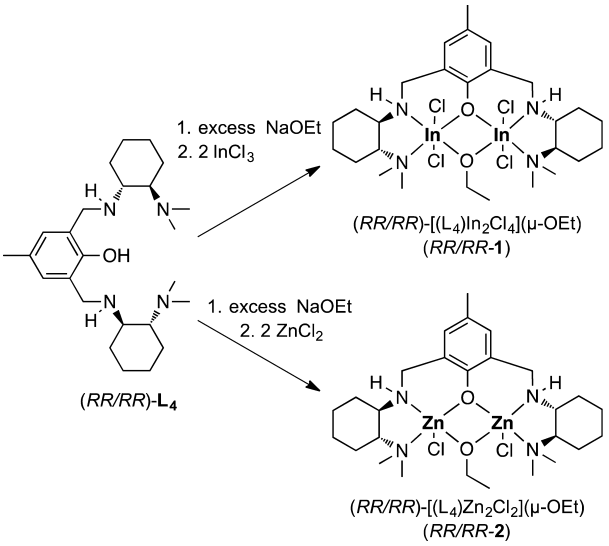
Scheme 3. One-Pot Syntheses of (*RR*/*RR*)-1 and (*RR*/*RR*)-2



recrystallization from toluene affords pure complex (*RR*/*RR*)-**1**. The NMR spectra of complexes **1** and **2** indicate a high degree of symmetry (Figures S18−S21). Complex **1** exhibits a sharp singlet for the aromatic protons at 6.82 ppm as well as the two distinct methyl groups borne by the terminal amines at 2.81 and 2.40 ppm. A set of doublets is observed for the diastereotopic methylene protons Ar−CH_2−NH. Finally, the alkoxide peaks are diagnostic of the desired product, with a triplet for CH_3−CH_2−O− at 1.49 ppm and two resonances for CH_3−CH_2−O at 4.35−4.39 and 4.44−4.48 ppm, as is often observed for these alkoxide-bridged species. The ^{1}H NMR spectrum of complex **2** is similar, with signals at slightly lower chemical shifts.

Single crystals of complex **1** can be obtained from a saturated solution of $CHCl_3$ and diethyl ether at room temperature.[25] The molecular structure of **1**, obtained by single-crystal X-ray crystallography (Figure 1), shows six-coordinate distorted octahedral indium centers bridged through the phenolic and alkoxide oxygen atoms. The chloride atoms coordinated to each indium center point in different directions to retain C_2 symmetry along the O1−Ar−Me axis. Each arm is highly twisted to accommodate the presence of the chloride atoms. The In−N distances for the central nitrogen atoms are shorter (2.226 and 2.235 Å) than the terminal ones (2.388 and 2.380 Å). Note that the complex crystallizes in a racemic centrosymmetric space group containing the two enantiomers (*SS*/*SS*)-Δ,Δ and (*RR*/*RR*)-Λ,Λ.[25]

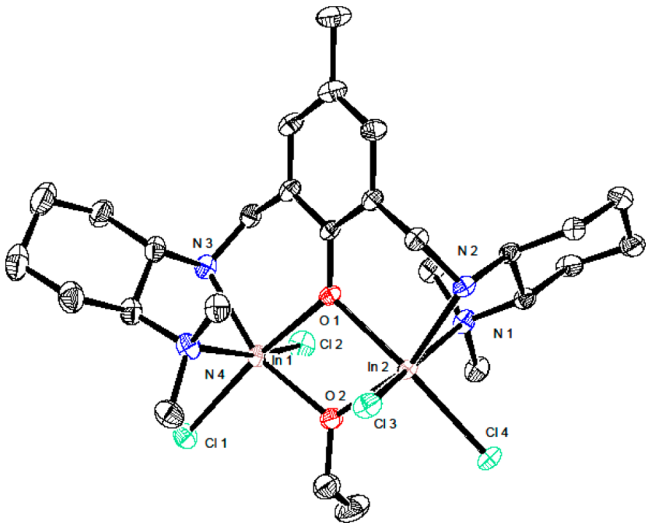
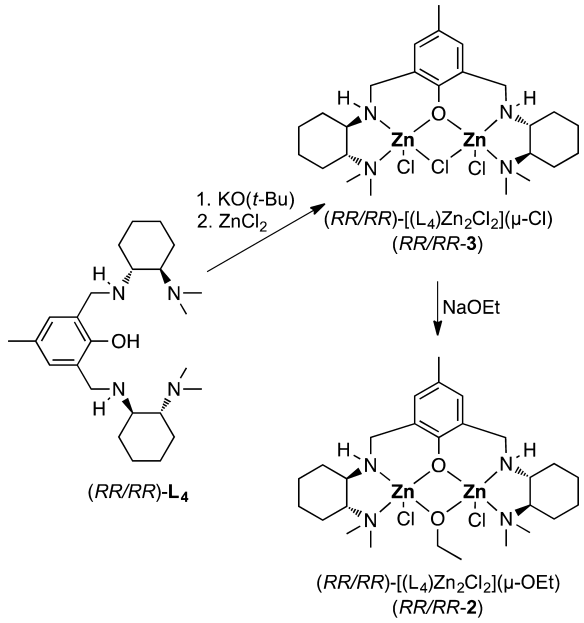


Figure 1. Solid-state structure of the complex (*SS*/*SS*)-**1** [(*SS*/*SS*)-Δ,Δ] obtained by single-crystal X-ray diffraction. Thermal ellipsoids are set at 50% probability, and hydrogen atoms and solvent are removed for clarity.

The two step methodology can only be used to generate the zinc complex **2**; the indium analogue could not be generated using this route because of the difficulty of isolating the chloride intermediates. Deprotonation of (*RR*/*RR*)-$\mathbf{L_4}$ with KO(*t*-Bu) followed by salt metathesis with $ZnCl_2$ affords (*RR*/*RR*)-[($\mathbf{L_4}$)Zn_2Cl_2](*μ*-Cl) [(*RR*/*RR*)-**3**] in 56% isolated yield (Scheme 4). Further reaction of **3** with 2 equiv of NaOEt

Scheme 4. Synthesis of (*RR*/*RR*)-2 in a Stepwise Reaction



affords **2** in 39% yield, resulting in an overall yield of 22%. Interestingly, complex **3** exhibits a triplet in addition to a doublet for the diastereotopic protons Ar−CH_2−NH at 4.11 and 3.65 ppm, which suggests the presence of different diastereomers or conformers in solution (Figures S22 and S23).[17b]

The chiral imine proligand $\mathbf{L_2}$ can be used as a dinucleating platform for zinc, but not indium, and does not support metal alkoxide formation. Deprotonation of the imine proligand (*RR*/*RR*)-$\mathbf{L_2}$ followed by salt metathesis with $ZnCl_2$ forms (*RR*/*RR*)-[($\mathbf{L_2}$)Zn_2Cl_2](*μ*-Cl) [(*RR*/*RR*)-**4**] in 56% yield (Scheme 5). The ^{1}H and ^{13}C{^{1}H} NMR spectra show only one set of signals (Figures S24 and S25). As observed for complexes **1** and **2**, complex **4** is highly symmetrical, with only one singlet at 8.29 ppm corresponding to imine N=C*H*−Ar and another at 7.14 ppm corresponding to the aromatic protons. Only two singlets for the N−CH_3 protons are observed at 2.63 and 2.43 ppm.

Single crystals of (*RR*/*RR*)-**4** can be obtained from a saturated solution of tetrahydrofuran (THF) and diethyl ether at room temperature and analyzed by single-crystal X-ray crystallography (Figure 2a). The solid-state structure shows five-coordinate zinc centers bridged by the phenolic oxygen

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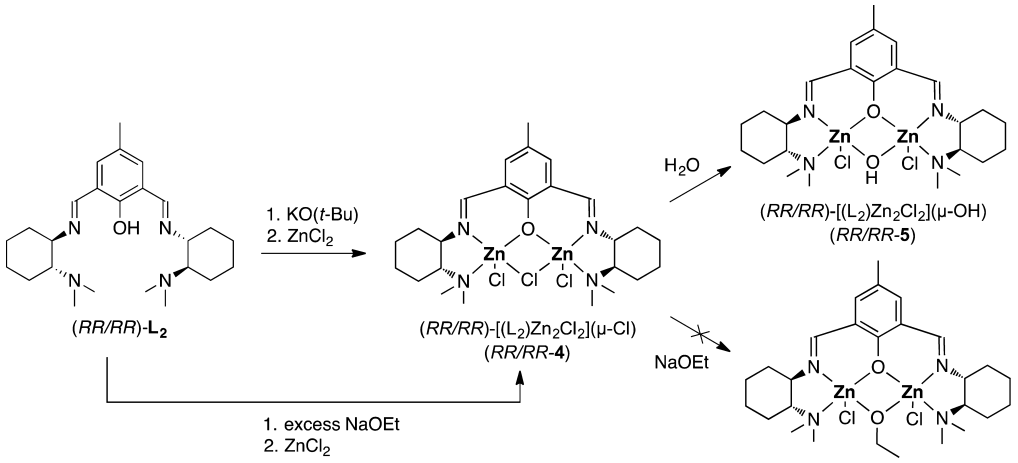
Scheme 5. Attempted Synthesis of Zinc Alkoxide Complex with the Imine Ligand (*RR*/*RR*)-L_2



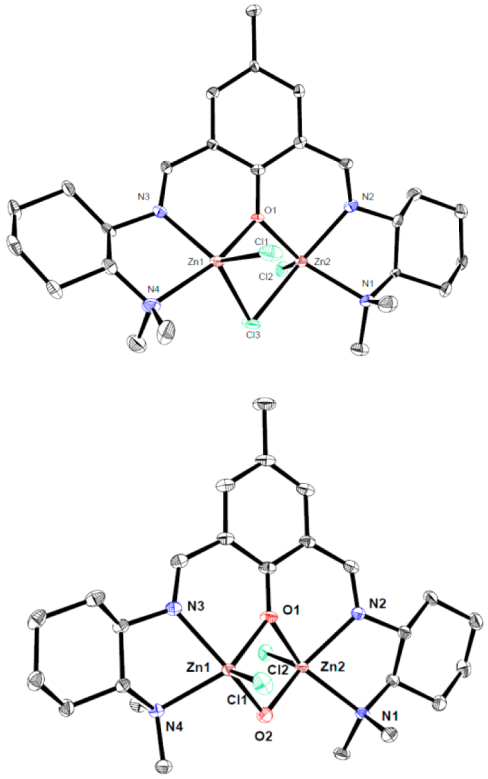


Figure 2. Solid-state structures of complexes (*RR*/*RR*)-**4** (a, top) and (*RR*/*RR*)-**5** (b, bottom) obtained by single-crystal X-ray diffraction. Thermal ellipsoids are set at 50% probability, and hydrogen atoms and solvent are removed for clarity. The unit cell for complex **4** contains two distinct diastereomers, **4a** and **4b**, differing in the positions of the chloride ligands around the zinc centers. Only **4a** is depicted here.

atom and a chloride ligand. The geometry of the zinc centers is between square pyramidal and trigonal bipyramidal. The unit cell contains two diastereomers, **4a** and **4b**, with different chiralities at the zinc centers (Figure S36), as observed for the related aminozinc complexes bearing achiral ligands.[17b] C_2 symmetry is retained through the O1−Ar−Me axis.

Formation of the bridging alkoxide complex through further reactivity of **4** or through a one-pot reaction was not achieved (Scheme 5). The reaction of (*RR*/*RR*)-**4** with various equivalents of NaOEt leads to a mixture of compounds including unreacted **4** (Figure S2). Attempted recrystallization from a saturated solution of THF and diethyl ether leads to isolation of the hydroxyl-bridged byproduct (*RR*/*RR*)-[($\mathbf{L_2}$)-Zn_2Cl_2](μ-OH) [(*RR*/*RR*)-**5**]. Complex **5** was characterized by single-crystal X-ray diffraction (Figure 2b). The solid-state structures of **4** and **5** show similar geometry around the zinc centers (Table S2). The one-pot reaction of (*RR*/*RR*)-$\mathbf{L_2}$ and 4 equiv of NaOEt, followed by the addition of $ZnCl_2$, forms pure (*RR*/*RR*)-**4**; mixtures containing the desired alkoxide complex are not observed.

The analogous indium complexes bearing imine proligand (*RR*/*RR*)-$\mathbf{L_2}$ could not be synthesized under these conditions. The crystal structure of complex **1** shows that the ligand arms must be twisted to accommodate the chloride present on each indium center. The rigid backbone in the imine ligand (N═CH−Ar−CH═N is planar)[26] does not allow such a thermodynamically stable structure and prevents the formation of the desired complex (Figure S38).

Synthesis of Indium Alkoxide Complexes Bearing Achiral Ligand Backbones. In an attempt to draw comparisons with the previously reported zinc complexes **C**,[8,17] we attempted the synthesis of indium complexes with achiral proligands $\mathbf{L_5}$−$\mathbf{L_7}$. Only $\mathbf{L_7}$ was successful. Indium alkoxide complexes can be prepared by both stepwise and one-pot routes (Scheme 6). Deprotonation of $\mathbf{L_7}$ followed by salt metathesis with $InCl_3$ forms [($\mathbf{L_7}$)In_2Cl_4](μ-Cl) (**6**) with 33% isolated yield. Further reaction with 2 equiv of NaOEt forms [($\mathbf{L_7}$)In_2Cl_4](μ-OEt) (**7**) in 21% yield (overall yield of 7%). Alternatively, a one-pot reaction can directly access complex **7** in 34% isolated yield.

As observed with analogous zinc complexes,[17b] the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of complexes **6** and **7** show that they are highly symmetric (Figures S26−S29). Complex **6** exhibits sharp singlets for the aromatic protons at 7.05 ppm and the N−CH_3 protons of the central amines at 3.02 ppm. The diastereotopic protons of Ar−CH_2−NH appear as a set of doublets, while the N−$(CH_3)_2$ protons appear as two broad singlets at 2.60 and 2.87 ppm. Complex **7** exhibits a similar ^{1}H NMR signature, with the two broad singlets for the N−$(CH_3)_2$ protons observed at 2.86 and 3.02 ppm ($CDCl_3$, 25 °C). Variable-temperature ^{1}H NMR spectra of complex **7** (toluene-d_8, −35 to +75 °C) show that these two broad signals sharpen to two singlets at 2.29 and 2.63 ppm at −35 °C (Figure S30). Coalescence is observed at 40 °C, although peak overlap prevents calculation of the exchange rate.

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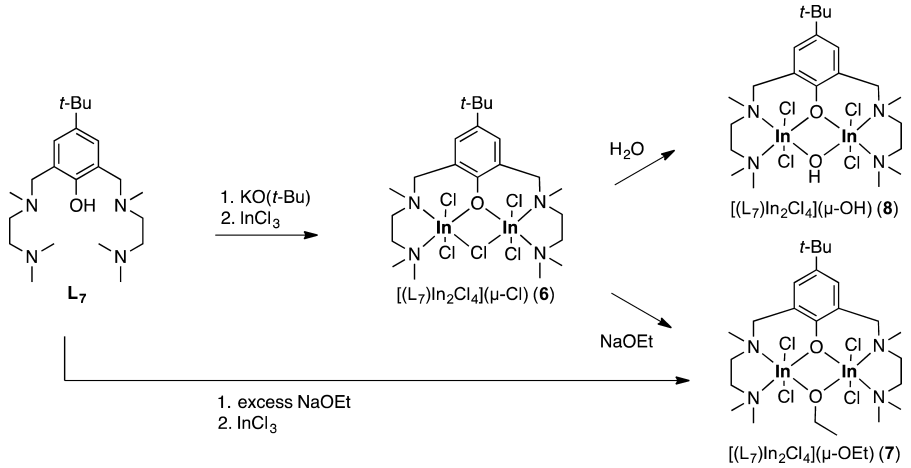
Scheme 6. Synthesis of 6−8



One sharp singlet is observed at 2.49 ppm at 65 °C. This fluxionality strongly suggests possible decoordination of the terminal amine. A more complex mechanism involving equilibrium between the two isomers, by N-inversion at the central amine, would require dissociation of both the terminal and internal amines and would lead to observation of equivalent benzylic CH_2−N protons; this is not observed.

Single crystals of complex **7** were obtained from a saturated solution in toluene and analyzed by single crystal X-ray diffraction (Figure 3a). Attempts to crystallize complex **6** from a saturated solution of acetonitrile result in isolation of the hydrolysis complex [(**L**$_7$)In$_2$Cl$_4$](μ-OH) (**8**), as determined by single-crystal X-ray diffraction (Figure 3b). The solid-state structures of complexes **7** and **8** are similar to that of **1**, with six-coordinate distorted octahedral indium centers bridged through the phenolic and alkoxy or hydroxy oxygen atoms. The solid-state structures of **7** and **8** show Λ,Λ chirality at the metal centers. Although the Δ,Δ enantiomer (Figure S39) was not observed, complexes **6**−**8** are likely obtained as a mixture of the two enantiomers. The bond lengths and angles around the indium centers for **7** and **8** are comparable (Table S4). As observed for complex **7**, the relative positions of the chloride ligands and the arms are critical to retaining C_2 symmetry along the O1−Ar−*t*-Bu axis and affording the thermodynamically stable complex.

Polymerization of LA. Complexes (*RR*/*RR*)-**1**, (*RR*/*RR*)-**2**, and **7** show higher selectivity and lower activity as catalysts for the ring-opening polymerization of *rac*-LA compared to analogous mononuclear indium[13,16,22a,c] and mononuclear and dinucleating zinc[11b,17] complexes (Table 1). Polymerization of 200 equiv of *rac*-LA catalyzed with **1** (~2 mM in CH_2Cl_2) reaches 82% conversion after 11 days; complex **7** reaches 97% conversion after 8 days. Both complexes **1** and **7** yield highly heterotactic PLA with P_r values of 0.89 and 0.87, respectively.

Polymerization of *meso*-LA by complex **7** results in essentially atactic PLA (P_r = 0.46). Complex **2** reaches 95% conversion after 5 days under identical reaction conditions, yielding PLA with a heterotactic bias (P_r = 0.64). In contrast, the zinc complex **C** polymerizes 200 equiv of *rac*-LA in less than 1 min to yield atactic PLA.[17b] Given that the chirality of the complexes has little impact on the stereoselectivity of the catalysts, we postulate a chain-end control mechanism for this system.

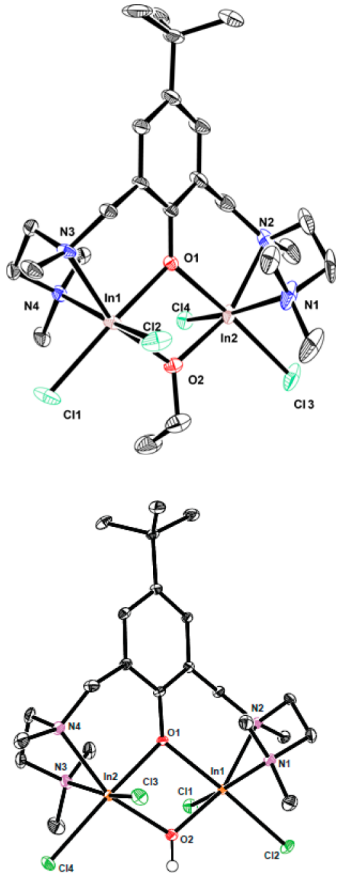


Figure 3. Solid-state structures of **7** (a, top) and **8** (b, bottom) obtained by single-crystal X-ray diffraction. Thermal ellipsoids are set at 50% probability, and hydrogen atoms and solvent are removed for clarity. The unit cell for complex **7** contains two distinct conformations differing in the position of the ethoxide groups; only one is depicted here.

Reactions of complex **7** at higher temperatures, 40 °C (CH_2Cl_2), 100 °C (toluene), and 140 °C (neat in melt), lead to higher activity but inferior selectivity and dispersity as expected (Table 1, entries 7−9). Interestingly, complex **7** is much less active in THF, reaching only 49% conversion after 7 days. This suggests that THF competes with the coordination of LA at the indium center prior to ring-opening polymerization, emphasiz-

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Table 1. Polymerization of LA by the Initiators 1, 2, and 7[a]

	catalyst	solid	T (°C)	time	[LA]/[cat]	conv[b] (%)	M_{ntheo} (Da)[c]	M_{nGPC} (Da)[d]	$Đ$[c]	P_r[e]
1	**C**[17b]	CH_2Cl_2	RT	1 min	200	92	26570	23800	1.06	*f*
2	**1**	CH_2Cl_2	RT	11 days	200	82	23640	17380	1.02	0.89
3	**1**	CH_2Cl_2	40	7 days	1000[g]	<10				
4	**2**	CH_2Cl_2	RT	5 days	200	95	27430	24290	1.04	0.64
5	**7**	CH_2Cl_2	RT	8 days	200	97	28000	17080	1.06	0.87
6	**7**	THF	RT	7 days	200	49				0.88
7	**7**	CH_2Cl_2	40	5 days	200	95	27430	15800	1.03	0.87
8	**7**	C_7H_8	100	1 days	200	94	27130	10740	1.64	0.62
9	**7**		140	3 h	200	98	28310	26080	1.80	0.60
10	**7**	CH_2Cl_2	40	7 days	1000[g]	30				
11	**7**	CH_2Cl_2	RT	8 days	200	98	28890	20670	1.17	0.46

[a]Polymerization of *rac*-LA (entries 1−10) and *meso*-LA (entry 11). [$\mathbf{L}_n\mathrm{M}_2(\mu\text{-OEt})$] = 5 mM (entry 1), [$\mathbf{L}_n\mathrm{M}_2(\mu\text{-OEt})$] = 2 mM (entries 2−11). [b]Monomer conversion determined by ^{1}H NMR spectroscopy. [c]Calculated from $[LA]_0/[initiator] \times$ LA conversion $\times M_{LA}$ (144.13) + M_{EtOH} (46.07). [d]Determined by GPC measurements in THF. [e]Calculated from the $^1H\{^1H\}$ NMR spectra and Bernoullian statistics.[27] [f]Atactic PLA. [g]Immortal polymerization of 1000 equiv of *rac*-LA with 5 equiv of benzyl alcohol as the chain-transfer agent, $[LA]_0$:[BnOH]:[$\mathbf{L}_n\mathrm{M}_2(\mu\text{-OEt})$] = 1000:5:1.

ing the delicate steric effects at the sterically congested indium centers in these complexes. In contrast to our previously published indium catalysts, the activity of complexes **1** and **7** is decreased with the addition of alcohol (Table 1, entries 3 and 10).[19] Steric bulk and less flexibility of complex **1** is likely decreasing the chain-transfer reaction rate.

Polymerization of 20 equiv of *rac*-LA with complex **7** can be carried out at room temperature to generate low-molecular-weight polymer for end-group analysis with matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) mass spectroscopy (Figure S34). The resulting polymers exhibit one distribution of peaks, separated by m/z = 144 Da, corresponding to $[H(C_6H_8O_4)_n(OC_2H_5)Na]^+$. No peaks at m/z = 72 Da, indicative of transesterification, are observed. The same results are observed in toluene at 100 °C (Figure S35). Thus, it appears that deterioration in the stereoselectivity and dispersity observed at higher temperatures does not arise from transesterification.

CONCLUSIONS

Complexes **1** and **7** were designed to prevent dissociation of the two indium centers during polymerization, therefore forcing the ring-opening polymerization to proceed via a tandem mechanism, as we reported for the dinuclear indium system **A**.[16] However, the new dinucleating indium systems are fundamentally different because they exhibit rigid octahedral structure at the indium centers, resulting in heavily congested active sites. In contrast, most of the indium catalysts in the literature have a square-pyramidal or square-planar structure around the indium centers and therefore exhibit a free coordination site available for LA coordination.[13,14,14l,q,r,15] In catalysts with high steric encumbrance, the ancillary ligand could dissociate during polymerization and liberate a site for monomer coordination.[14j,22a,b] Complex **A** is an unusual exception to this case because the asymmetrical dimer conformation allows greater steric flexibility at the indium active site.[20]

The decreased activity of the indium **1** and zinc **2** complexes, as well as the indium complex **7** may be attributed to the higher energy barrier to LA coordination. The decrease of activity in THF or in the presence of alcohols, which can directly compete with LA for a coordination site, is strong evidence to support this hypothesis. The possible ease of ligand decoordination for complex **C** compared to complex **2**, as described previously for related mononuclear zinc complexes, supports the relative differences in the reactivity of the zinc species.[28] This flexibility can also be invoked in comparing the greater reactivity of complex **7** compared to complex **1**. Designing new dinuclear indium catalysts will require a delicate steric balance to allow the isolation of thermodynamically stable complexes but also to create a favorable environment for LA polymerization. For a more active dinucleating indium catalyst, it is important to take into account the final geometry of the indium center.

EXPERIMENTAL SECTION

General Procedures. All air- and/or water-sensitive reactions were carried out under N_2 in an MBraun glovebox. Bruker Avance 600, 400, and 300 MHz spectrometers were used to record the ^{1}H, $^{13}C\{^1H\}$, and $^1H\{^1H\}$ NMR spectra, respectively. ^{1}H NMR chemical shifts are given in ppm versus residual protons in deuterated solvents as follows: δ 7.27 for $CDCl_3$. $^{13}C\{^1H\}$ NMR chemical shifts are given in ppm versus residual ^{13}C in solvents as follows: δ 77.00 for $CDCl_3$. Diffraction measurements for X-ray crystallography were made on Bruker X8 APEX II and Bruker APEX DUO diffractometers with graphite-monochromated Mo Kα radiation. The structures were solved by direct methods and refined by full-matrix least squares using the *SHELXTL* crystallographic software of Bruker AXS. Unless specified, all non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions but were not refined. Elemental analysis of CHN was performed using a Carlo Erba EA1108 elemental analyzer. The elemental composition of an unknown sample was determined by using a calibration factor. The calibration factor was determined by analyzing a suitable certified organic standard (OAS) of known elemental composition. Molecular weights were determined by gel permeation chromatography (GPC)−laser light scattering (LLS) using an Agilent liquid chromatograph equipped with an Agilent 1200 series pump and autosampler, three Phenogel 5 μm narrow-bore columns (4.6 × 300 mm with 500, 10^3, and 10^4 Å pore sizes), a Wyatt Optilab differential refractometer, a Wyatt tristar miniDAWN (LLS detector), and a Wyatt ViscoStar viscometer. The column temperature was set at 40 °C. A flow rate of 0.5 mL/min was used, samples were dissolved in THF (ca. 2 mg/mL), and a dn/dc value of 0.042 mL/g was used. Narrow-molecular-weight polystyrene standards were used for system calibration purposes.

Materials. Toluene, diethyl ether, hexane, and tetrahydrofuran (THF) were degassed and dried using alumina columns in a solvent purification system. THF was further dried over sodium/benzophenone and vacuum-transferred to a Straus flask, where it was degassed prior to use. In addition, CH_3CN, $CHCl_3$, and CH_2Cl_2 were dried over

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CaH_2 and vacuum-transferred to a Straus flask, where they were degassed prior to use. Deuterated chloroform ($CDCl_3$) and toluene (toluene-d_8) were dried over CaH_2 and vacuum-transferred to a Straus flask and then degassed through a series of freeze−pump−thaw cycles. Trifluoroacetic acid was purchased from Alfa Aesar, dried over activated 4 Å molecular sieves, and stored under N_2 prior to use. $InCl_3$ was obtained from Strem Chemicals and $ZnCl_2$ from Alfa Aesar, and both were used without further purification. *N*,*N*,*N*′-Trimethylethylenediamine, *N*,*N*-dimethylethylenediamine, potassium *tert*-butoxide, (±)-*trans*-diaminocyclohexane, *p*-cresol, and 4-*tert*-butylphenol were obtained from Alfa Aesar and used without further purification. Sodium ethoxide (NaOEt) was obtained from Alfa Aesar, dissolved in dry ethanol, stirred for 16 h, precipitated from solution with hexanes, filtered, washed with hexanes, and dried at 50 °C under vacuum. Lactide (LA) samples were obtained from Purac Biomaterials, recrystallized several times from hot, dry toluene, and dried under vacuum prior to use. Synthesis of (*R*,*R*)-, (*S*,*S*)-, and (±)-*N*,*N*-dimethyl-*trans*-1,2-diaminocyclohexane was performed according to literature procedures[23] from (±)-*trans*-diaminocyclohexane and distilled at 70 °C under reduced pressure prior to use.

*Synthesis of (±)-**L**$_1$.* Freshly distilled (±)-*N*,*N*-dimethyl-*trans*-1,2-diaminocyclohexane (1.38 g, 9.70 mmol) was added to a solution of 4-*tert*-butyl-2,6-diformylphenol (0.500 g, 2.42 mmol) in methanol (20 mL). The solution was stirred at room temperature for 19 h. Methanol was removed in vacuo at room temperature. Failure to use the excess of amine results in the formation of a monoimine analogue as a byproduct (see the Supporting Information). Excess (±)-*N*,*N*-dimethyl-*trans*-1,2-diaminocyclohexane was distilled from the residual mixture at 70 °C under dynamic vacuum. The product was obtained as a dark-orange oil (0.979 g, 89%) and used without further purification. Attempts at further purification were unsuccessful. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.53 (2H, br s, N=C*H*), 7.63 (2H, br s, Ar−*H*), 3.28 (2H, m, C*H*−N), 2.66 (2H, m, C*H*−N), 2.30 (12H, s, N−(CH_3)$_2$), 1.33 (9H, s, Ar−(CH_3)$_3$).

*Synthesis of (±)-**L**$_2$.* (±)-**L**$_2$ was prepared and purified in a manner analogous to that of *rac*-**L**$_1$ from 4-methyl-2,6-diformylphenol (0.500 g, 3.05 mmol) Yield: 1.07 g, 85%. The compound was used without further purification. Attempts at further purification were unsuccessful. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.49 (2H, br s, N=C*H*), 7.43 (2H, br s, Ar−*H*), 3.25 (2H, m, C*H*−N), 2.63 (2H, m, C*H*−N), 2.27 (12H, s, N(CH_3)$_2$), 2.22 (3H, s, Ar−CH_3). EI-LRMS. Calcd: 412.32 ([M]$^+$). Found: 412 ([M]$^+$).

*Synthesis of (±)-**L**$_3$.* $NaBH_4$ (0.326 g, 8.61 mmol) was added in small portions to a solution of **L**$_1$ (0.979 g, 2.15 mmol) in methanol (50 mL). The solution was stirred at room temperature for 16 h. Methanol was removed in vacuo at room temperature. The resulting yellow residue was redissolved in CH_2Cl_2 (10 mL) and distilled water (10 mL). Organics were extracted with more CH_2Cl_2 (2 × 10 mL), combined, dried over $MgSO_4$, and filtered. The resulting mixture was concentrated to 10 mL and filtered through a small plug of alumina. The filtrate was pumped to dryness, yielding a clear yellow oil (0.819 g, 83%). The compound was used without further purification. Attempts at further purification were unsuccessful. The product was confirmed by ^{1}H NMR spectroscopy to be a mixture of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.02 (s, 2H, Ar−*H*), 7.00 (s, 2H, Ar−*H*), 4.00−3.90 (4H, overlapping doublets, NH−CH_2−Ar), 3.80−3.70 (4H, overlapping doublets, NH−CH_2−Ar), 2.16 (12H, s, N−(CH_3)$_2$), 2.15 (12H, s, N−(CH_3)$_2$), 1.28 (18H, s, Ar−(CH_3)$_3$). EI-LRMS. Calcd: 458.40 ([M]$^+$). Found: 458 ([M]$^+$).

*Synthesis of (±)-**L**$_4$.* *rac*-**L**$_4$ was prepared and purified in a manner analogous to that of *rac*-**L**$_3$ from *rac*-**L**$_2$ (1.07 g, 2.59 mmol). Yield: 0.864 g, 80%. The compound was used without further purification. Attempts at further purification were unsuccessful. The product was confirmed by ^{1}H NMR spectroscopy to be a mixture of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.85 (s, 2H, Ar−*H*), 6.83 (s, 2H, Ar−*H*), 4.03−3.90 (4H, overlapping doublets, N−CH_2−Ar), 3.80−3.70 (4H, overlapping doublets, N−CH_2−Ar), 2.24 (3H, s, Ar−CH_3), 2.23 (3H, s, Ar−CH_3), 2.17 (12H, s, N−(CH_3)$_2$), 2.16 (12H, s, N−(CH_3)$_2$). EI-LRMS. Calcd: 416.35 ([M]$^+$). Found: 416 ([M]$^+$).

*Synthesis of (RR/RR)-**L**$_4$.* (*RR*/*RR*)-**L**$_4$ was prepared and purified in a manner analogous to that of *rac*-**L**$_4$ and (*RR*/*RR*)-**L**$_2$. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.82 (s, 2H, Ar−*H*), 3.91 (2H, d, J_{HH} = 14 Hz, N−CH_2−Ar), 3.71 (2H, d, J_{HH} = 14 Hz, N−CH_2−Ar), 2.35−2.25 (2H, m, C*H*−N), 2.22 (3H, s, Ar−CH_3), 2.16 (12H, s, N−(CH_3)$_2$).

*Synthesis of **L**$_5$−**L**$_7$.* The synthesis of these ligands was adapted from the literature[17b,24] (see the Supporting Information).

*Synthesis of (RR/RR)-[(**L**$_4$)In$_2$Cl$_4$](μ-OEt) (**1**).* Sodium ethoxide (NaOEt; 0.209 g, 3.07 mmol) was transferred to a solution of the proligand (*RR*/*RR*)-**L**$_4$ (0.320 g, 0.769 mmol) in toluene (10 mL). The solution was stirred at room temperature for 8 h, after which indium trichloride was added (0.340 g, 1.54 mmol). The solution was stirred at room temperature for 16 h. Then the solution was filtered through glass fiber to obtain a clear pale-yellow solution. The mixture was concentrated to 5 mL and placed in a freezer at −35 °C for 16 h, causing crystals to form. The supernatant solution was decanted, and the crystals were washed with cold toluene (2 × 5 mL), stirred for 30 min with hexanes, and then dried. A second crop can be obtained from the supernatant in a similar manner. The product was isolated as a white powder (0.134 g, 21%). Crystals suitable for X-ray analysis were grown from a saturated solution in $CHCl_3$ and diethyl ether at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.82 (2H, s, Ar−*H*), 5.54 (2H, dd, J_{HH} = 14 Hz, Ar−CH_2−N), 4.51−4.41 (1H, m, O−CH_2−CH_3), 4.40−4.30 (1H, m, O−CH_2−CH_3), 3.87 (2H, dd, J_{HH} = 14 Hz, Ar−CH_2−N), 3.27 (2H, t, J_{HH} = 11 Hz, N−C*H*), 2.81 (6H, s, N−(CH_3)$_2$), 2.61 (2H, d), 2.45 (2H, d, C*H*−N), 2.40 (6H, s, N−(CH_3)$_2$), 2.33 (2H, d), 2.23 (3H, s, Ar−CH_3), 1.92−1.80 (6H, m), 1.48 (3H, t, J_{HH} = 7 Hz, O−CH_2−CH_3), 1.44−1.00 (8H, m). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 160.26, 134.56, 127.86, 122.41, 64.02, 61.74, 54.05, 50.34, 44.09, 38.36, 31.05, 24.78, 24.31, 20.73, 20.01, 19.30. Anal. Calcd for $C_{27}H_{48}Cl_4In_2N_4O_2$: C, 38.97; H, 5.81; N, 6.73. Found: C, 38.62; H, 5.51; N, 6.19.

*Synthesis of (RR/RR)-[(**L**$_4$)Zn$_2$Cl$_2$](μ-OEt) (**2**).* NaOEt (0.133 g, 1.97 mmol) was transferred to a solution of the proligand (*RR*/*RR*)-**L**$_4$ (0.205 g, 0.492 mmol) in toluene (10 mL). The solution was stirred at room temperature for 8 h, after which zinc dichloride was added (0.134 g, 0.983 mmol). The solution was stirred at room temperature for 16 h. Then the solvent was removed in vacuo at room temperature. The residual solid was redissolved in 5 mL of CH_2Cl_2 and filtered through Celite. The resulting mixture was further concentrated to 2 mL, and ether was added, causing a solid to precipitate. The precipitate was allowed to settle, and the solution was decanted; the wet precipitate was washed with hexanes three times and dried to afford complex **2** as an off-white powder (0.183 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.74 (2H, s, Ar−*H*), 4.44 (2H, dd, J_{HH} = 13 and 3 Hz, Ar−CH_2−N), 4.23−4.15 (1H, m, O−CH_2−CH_3), 4.06−3.99 (1H, m, O−CH_2−CH_3), 3.68 (2H, dd, J_{HH} = 13 and 4 Hz, Ar−CH_2−N), 2.67 (6H, s, N−(CH_3)$_2$), 2.55 (2H, dt, J_{HH} = 11 and 3 Hz, C*H*−N), 2.29 (2H, d), 2.24 (2H, m, C*H*−N), 2.19 (9H, singlets overlapping, N−(CH_3)$_2$ and Ar−CH_3), 1.93 (2H, d), 1.81 (2H, d), 1.72 (2H, d), 1.35 (3H, t, J_{HH} = 7 Hz, O−CH_2−CH_3), 1.28−0.92 (10H, m). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 160.43, 131.68, 123.86, 121.52, 69.90, 60.74, 51.81, 47.65, 44.77, 37.98, 30.61, 24.61, 24.32, 21.25, 20.10. Anal. Calcd for $C_{27}H_{48}Cl_2Zn_2N_4O_2$: C, 48.96; H, 7.30; N, 8.46. Found: C, 48.99; H, 7.29; N, 8.07.

*Synthesis of (RR/RR)-[(**L**$_4$)Zn$_2$Cl$_2$](μ-Cl) (**3**).* Potassium *tert*-butoxide (0.077 g, 0.68 mmol) was transferred to a solution of the proligand (*RR*/*RR*)-**L**$_4$ (0.295 g, 0.709 mmol) in toluene (10 mL). The solution was stirred at room temperature for 16 h. Then the toluene was removed in vacuo at room temperature, yielding a yellow solid residue. The potassium salt was redissolved in toluene (5 mL), and zinc dichloride (0.193 g, 1.42 mmol) was transferred to this solution using toluene (5 mL). The solution was stirred at room temperature for 16 h. Then the toluene was removed in vacuo at room temperature. The residual solid was redissolved in CH_2Cl_2 (5 mL) and filtered through Celite. The resulting mixture was concentrated to 2 mL, and diethyl ether was added, causing a precipitate to form. The precipitate was allowed to settle, and the solution was decanted; the wet precipitate was washed with hexanes three times and dried to afford complex **2** as an off-white powder (0.258 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$, 25

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°C): δ 6.79 (2H, s, Ar−H), 4.11 (2H, app t, J_{HH} = 12 Hz, Ar−CH_2−N), 3.65 (2H, d, J_{HH} = 11 Hz, Ar−CH_2−N), 2.64 (2H, m), 2.62 (6H, s, N−$(CH_3)_2$), 2.49 (6H, s, N−$(CH_3)_2$), 2.41−2.51 (4H, m), 2.17 (3H, s, Ar−CH_3), 1.98 (2H, d), 1.90−1.82 (4H, m), 1.49 (2H, t), 1.32−1.10 (8H, m). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 25 °C): δ 158.97, 130.17, 125.28, 124.50, 85.66, 57.38, 51.98, 43.39, 36.68, 31.66, 24.67, 24.23, 21.06, 19.72. Anal. Calcd for $C_{25}H_{43}Cl_3Zn_2N_4O$: C, 46.00; H, 6.64; N, 8.58. Found: C, 45.66; H, 6.51; N, 8.43.

Alternative Synthesis of ***2***. NaOEt (0.021 g, 0.31 mmol) was transferred to a solution of complex **3** (0.100 g, 0.153 mmol) in toluene (10 mL). The solution was stirred at room temperature for 16 h. Then the toluene was removed in vacuo at room temperature, yielding a yellow solid residue. The residual solid was redissolved in CH_2Cl_2 (5 mL) and filtered through Celite. Solvent was removed in vacuo, and the resulting solid was washed with hexanes three times to afford complex **2** as an off-white powder (0.040 g, 40%).

*Synthesis of (RR/RR)-[(**L**$_2$)Zn$_2$Cl$_2$](μ-Cl) (**4**).* Potassium *tert*-butoxide (0.177 g, 1.58 mmol) was transferred to a solution of the proligand (*RR*/*RR*)-**L**$_2$ (0.733 g, 1.61 mmol) in toluene (5 mL). The solution was stirred at room temperature for 16 h. Then the toluene was removed in vacuo at room temperature, yielding an orange solid residue. The solid was redissolved in hexane and filtered through Celite. Hexane was removed in vacuo to afford an orange powder (0.653 g, 90%). The potassium salt (0.316 g, 0.701 mmol) was redissolved in toluene (5 mL), and zinc dichloride (0.191 g, 1.40 mmol) was transferred to this solution using toluene (5 mL). The solution was stirred at room temperature for 16 h. Then the toluene was removed in vacuo at room temperature. The residual solid was redissolved in CH_2Cl_2 (5 mL) and filtered through Celite. Solvent was removed in vacuo, and the residual solid was washed with hexanes three times and dried to afford complex **4** as an orange powder (0.290 g, 64%; i.e., total yield = 58%). Crystals suitable for X-ray analysis were grown from a saturated solution in THF and ether at room temperature. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.29 (2H, s, Ar−C*H*═N), 7.14 (2H, s, Ar−*H*), 3.41 (2H, t, J_{HH} = 9 Hz, C*H*−N), 2.92 (2H, t, J_{HH} = 9 Hz, C*H*−N), 2.63 (6H, s, N−$(CH_3)_2$), 2.48−2.46 (2H, m), 2.43 (6H, s, N−$(CH_3)_2$), 2.24 (3H, s, Ar−*H*), 2.05 (2H, d), 1.96−1.90 (4H, m), 1.30−1.40 (8H, m). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 25 °C): δ 166.31, 165.03, 140.57, 124.47, 121.55, 65.85, 60.03, 42.98, 35.95, 29.37, 24.32, 23.88, 20.98, 19.32. Anal. Calcd for $C_{25}H_{39}Cl_3Zn_2N_4O$: C, 46.29; H, 6.06; N, 8.64. Found: C, 46.02; H, 6.04; N, 8.33.

*Synthesis of [(**L**$_7$)In$_2$Cl$_4$](μ-Cl) (**6**).* Potassium *tert*-butoxide (0.157 g, 1.40 mmol) was transferred to a solution of the proligand **L**$_7$ (0.530 g, 1.40 mmol) in toluene (15 mL). The solution was stirred at room temperature for 16 h, after which it was pumped to dryness, yielding a yellow solid residue. Hexane was added, causing precipitation of a pale-yellow solid. The residual solid was washed three times with hexanes. The resulting solid was dried under vacuum, yielding potassium salt as a pale-yellow powder (0.425 g, 73%). The potassium salt (0.425 g, 1.02 mmol) was dissolved in THF (5 mL), and indium trichloride (0.452 g, 2.04 mmol) was transferred to this solution using THF (10 mL). The solution was stirred at room temperature for 21 h, after which it was filtered through glass fiber filter paper and concentrated in vacuo until crystals began to form (2 mL). The solution was left in the freezer (−35 °C) for several minutes, causing more crystals to form. The solution was then filtered on a glass frit and washed with cold THF, allowing isolation of a white crystalline solid (0.261 g, 33%). The crystals were stirred in ether for 30 min and dried under vacuum. ^1H NMR revealed the crystals to be pure complex **6**, whereas the filtrate residue yielded a mixture of complex **6** and unidentified byproducts. Crystals suitable for X-ray analysis were grown from a saturated solution in acetonitrile at room temperature; however, single-crystal X-ray crystallography of these crystals revealed them to be the related hydroxide-bridged complex **8**. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.05 (2H, s, Ar−*H*), 5.36 (2H, d, J_{HH} = 12 Hz, Ar−CH_2−N), 3.47 (2H, t, J_{HH} = 12 Hz, N−CH_2−CH_2N), 3.27 (2H, d, J_{HH} = 12 Hz, Ar−CH_2−N), 3.10 (2H, t, J_{HH} = 12 Hz, N−CH_2−CH_2N), 3.02 (6H, s, N−(CH_3)), 2.87 (6H, br s, N−$(CH_3)_2$), 2.60 (6H, br s, N−$(CH_3)_2$), 2.46 (2H, d, J_{HH} = 18 Hz, N−CH_2−CH_2N), 2.08 (2H, d, J_{HH} = 18 Hz, N−CH_2−CH_2N), 1.29 (9H, s, C−$(CH_3)_3$). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 25 °C): δ 158.99, 142.02, 131.66, 122.01, 63.48, 55.53, 50.82, 48.14, 47.79, 45.64, 33.86, 31.40. Anal. Calcd for $C_{22}H_{41}Cl_5In_2N_4O$: C, 33.68; H, 5.27; N, 7.14. Found: C, 33.31; H, 5.33; N, 7.04.

*Synthesis of [(**L**$_7$)In$_2$Cl$_4$](μ-OEt) (**7**).* NaOEt (0.019 g, 0.28 mmol) was transferred to a solution of complex **6** (0.112 g, 0.143 mmol) in toluene (15 mL). The solution was stirred at room temperature for 23 h, then the toluene was removed in vacuo, and the crude residue was redissolved in THF and filtered through glass fiber filter paper. The solution was concentrated in vacuo to 2 mL volume, and then ether was added, causing precipitation of an off-white solid. The solution was filtered on a glass frit and washed with ether. This yielded the purified complex as a pale-off-white solid (0.033 g, 29%). Single crystals of complex **7** were obtained from a saturated solution of the purified complex in toluene and analyzed by single-crystal X-ray crystallography. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.03 (2H, s, Ar−*H*), 5.36 (2H, d, J_{HH} = 18 Hz, Ar−CH_2−N), 4.44−4.39 (1H, m, O−CH_2−CH_3), 4.34−4.29 (1H, m, O−CH_2−CH_3), 3.51 (2H, t, J_{HH} = 12 Hz, N−CH_2−CH_2N), 3.25 (2H, d, J_{HH} = 18 Hz, Ar−CH_2−N), 3.04 (2H, t, J_{HH} = 12 Hz, N−CH_2−CH_2N), 3.02 (6H, s, N−(CH_3)), 2.86 (6H, br s, N−$(CH_3)_2$), 2.57 (6H, br s, N−$(CH_3)_2$), 2.43 (2H, d, J_{HH} = 12 Hz, N−CH_2−CH_2N), 2.04 (2H, d, J_{HH} = 12 Hz, N−CH_2−CH_2N), 1.46 (3H, t, O−CH_2−CH_3), 1.28 (9H, s, Ar−$(CH_3)_3$). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 25 °C): δ 158.93, 141.96, 131.61, 122.03, 63.46, 61.53, 55.41, 50.82, 47.96, 47.92, 45.60, 33.82, 31.38, 19.14. Anal. Calcd for $C_{24}H_{46}Cl_4In_2N_4O_2$: C, 36.30; H, 5.84; N, 7.06. Found: C, 36.61; H, 5.86; N, 7.01.

Alternative Synthesis of ***7***. NaOEt (0.626 g, 9.20 mmol) was transferred to a solution of the proligand **L**$_7$ (0.871 g, 2.30 mmol) in hexane (15 mL). The solution was stirred at room temperature for 5 h, then indium trichloride was added (1.018 g, 4.603 mmol), and the mixture was stirred for 16 h at room temperature, causing a yellow solid to precipitate. The solid was allowed to settle, and hexane was decanted. The residual wet solid was dried, dissolved in CH_2Cl_2 (15 mL), and filtered through Celite. The mixture was concentrated to 5 mL, causing an off-white solid to precipitate. CH_2Cl_2 was decanted, and the resulting solid was dried to afford pure complex **7** (0.620 g, 34%). Residual solutions were combined and concentrated, further causing more precipitate to form. ^1H NMR revealed the resulting solid to be a mixture of complexes **6** and **7** in addition to unknown byproducts.

Representative Polymerization of rac-LA. *rac*-LA or *meso*-LA (200 equiv) in CH_2Cl_2 or THF was added to a solution of the complex (5 mg) in CH_2Cl_2 or THF to obtain a 2 mM concentration of the catalyst. The mixture was allowed to stir at room temperature in a vial or at higher temperature in a vacuum-sealed bomb. For immortal polymerization, BnOH (5 equiv) was added to the *rac*-LA solution prior to the addition to the complex. The solvent was then removed in vacuo, and a small portion of the crude polymer was tested for conversion and tacticity via ^1H and $^1H\{^1H\}$ NMR spectroscopy (25 °C, $CDCl_3$). The remaining crude polymer was redissolved in a minimum of dichloromethane (1−2 mL). Methanol (2−5 mL) was then added to this solution, causing precipitation of the polymer only for the polymer samples obtained in CH_2Cl_2. For those obtained in THF, the crude polymers were soluble in this CH_2Cl_2/MeOH mixture and could not be purified. The solution was allowed to settle, and the supernatant solution was removed. This process was repeated two more times, and the resulting polymer was dried under vacuum. The polymer was tested for the presence of any remaining catalyst or monomer using ^1H NMR spectroscopy before being tested for molecular weight and PDI using GPC in THF.

■ ASSOCIATED CONTENT

Supporting Information

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Full experimental details as well as full characterization data in solution and the solid state (PDF)
X-ray crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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