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Synthesis of Lewis Acidic, Aromatic Aminotroponiminate Zinc Complexes for the Ring-Opening Polymerization of Cyclic Esters

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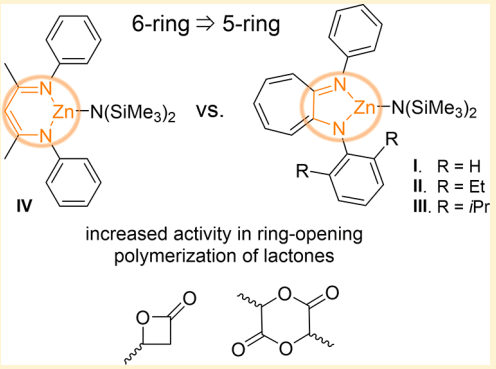
Supporting Information

ABSTRACT: Three novel aminotroponiminate (ATI) zinc complexes **I**−**III** (**I** = [(Ph$_2$)ATI]Zn−N(SiMe$_3$)$_2$, **II** = [(C$_6$H$_3$-2,6-C$_2$H$_5$/Ph)ATI]Zn−N(SiMe$_3$)$_2$, and **III** = [(C$_6$H$_3$-2,6-CH(CH$_3$)$_2$/Ph)ATI]Zn−N(SiMe$_3$)$_2$) were synthesized and tested in the ring-opening polymerization of the lactones *β-rac*-butyrolactone (BBL) and *rac*-lactide (LA). The ligands, with two of them literature unknown, were readily obtained via a three-step synthesis from tropolone. Forming a five-membered metallacycle with zinc, the complexes were further structurally examined via single-crystal X-ray analysis and compared with that of the established, 6-ringed *β*-diiminate (BDI) complex **IV** ([CH(CMeNPh)$_2$]Zn−N(SiMe$_3$)$_2$). The influence of the varying metallacycle ring size on the polymerization was evaluated. *In situ* IR measurements indicate a higher catalytic activity of the novel ATI complexes **I**−**III** for BBL compared with the BDI system **IV**. The activity and degree of control were further improved by an *in situ* generated alkoxy initiating group generated after the addition of 2-propanol. An enhanced initiator efficiency allowed the synthesis of polymers with controlled molecular weights and narrow polydispersities. Furthermore, **II** and **III** exhibited a high activity in the ring-opening polymerization of *rac*-LA. Hereby, reaction time and initiator efficiency could also be optimized at a higher temperature or by the addition of 2-propanol.



INTRODUCTION

Polyesters, particularly poly(hydroxybutyrate) (PHB) and poly(lactide) (PLA), can be produced by the ring-opening polymerization (ROP) of lactones. These aliphatic polyesters represent a valuable group of polymers with a great range of thermo-mechanical properties along with a renewable origin of quite a number of cyclic esters.[1] PHB, initially identified in *Bacillus megaterium* by M. Lemoigne, serves as a bacterial storage material.[2] In nature, the polymer is produced in its strictly isotactic form; however, controlling the microstructure via synthetic approaches has been attempted for decades. Ring-opening polymerization of *β-rac*-butyrolactone (BBL) offers the most promising way of controlling the microstructure with different metals such as aluminum,[3] zinc,[4] chromium,[5] and yttrium.[6] Thereby, *β*-diiminate (BDI) zinc complexes[4d] by Coates et al., yielding atactic PHB, and amino-alkoxy-bis(phenolate) yttrium complexes[6a] by Carpentier et al., giving a syndiotactic microstructure, were introduced as highly active catalysts. In contrast to PHB, the synthesis of PLA is industrially already more applied, making it the leading bioderived polymer. It is usually obtained from lactic acid through condensation reaction or, more promising, from lactide via ring-opening polymerization. The access via ROP enables the production of polymers with high molecular weights, narrow dispersities, and stereoselectivity.[7] Pioneering works using chiral salen aluminum complexes in the polymerization of *rac*-LA showed high isoselectivity.[8] Since then, a variety of ligands were coordinated to different central metals to realize either hetero- or isotactic-enriched PLA.[9] Figure 1 gives an overview of catalysts used in ROP of *rac*-LA starting with a *β*-diiminate zinc complex[4c] producing heterotactic-enriched PLA and ending with the most active and isoselective systems using zinc, yttrium, or indium.

Because the development of new and efficient initiators for this type of polymerization is still an ongoing challenge, the catalytic behavior of a novel type of ligands, the aminotroponimines (ATIHs), was investigated.

Aminotroponimines are a well-known class of ligands initially discovered in 1960. After the insertion of tetrafluoroethylene into cyclopentadiene, the fluorinated cycloheptadiene is subsequently converted into the corresponding ATIHs via

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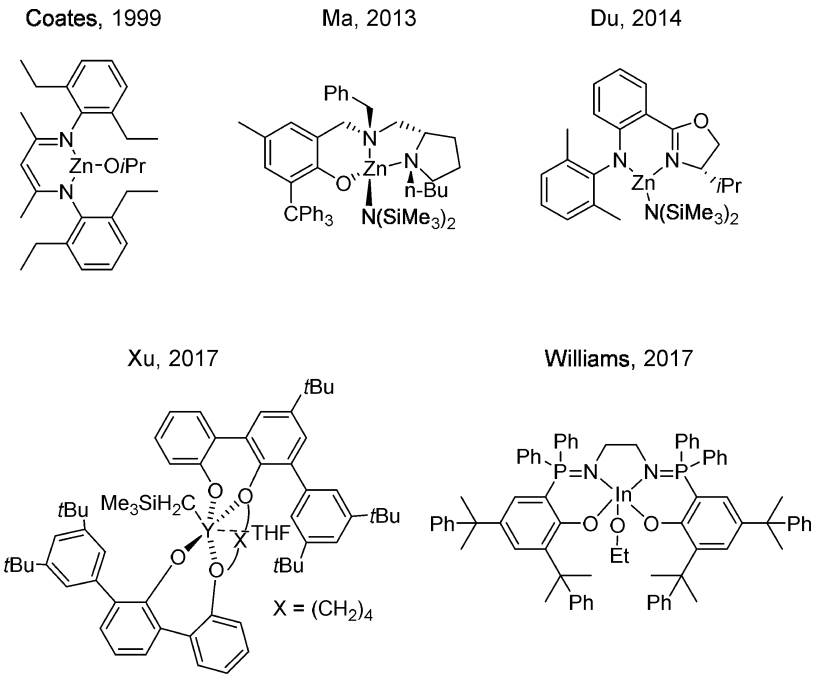

Figure 1. Active complexes for ROP of *rac*-LA with a focus on zinc as central metal.[4c,9b,c,d,g]

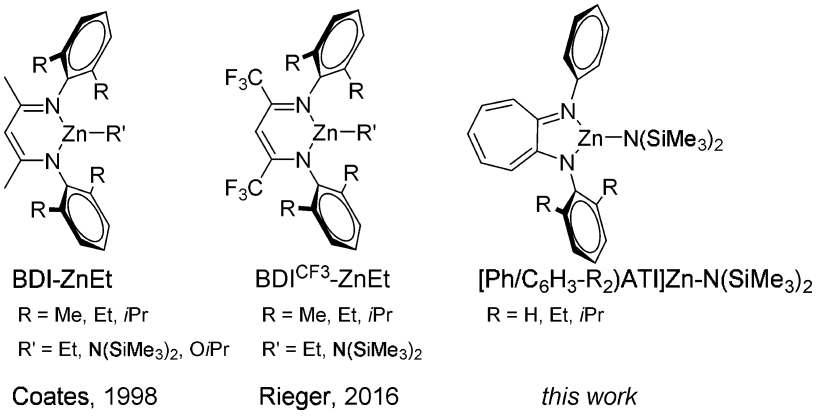

Figure 2. BDI zinc complexes established in polymerization catalysis by Coates (left); introduction of electron-withdrawing groups at the pentane backbone (center); realization of a five-membered metallacycle by synthesis of aminotroponiminate complexes (right).[14,15a]

condensation reaction with primary amines.[10] Deprotonated ATIHs act as anionic, bidentate ligands with a delocalization of the negative charge over the 7-membered ring, giving a 10π-electron backbone. A wide range of main group, transition, and f-block elements[11] have been introduced as central metal, but Roesky et al. were the first to bring aminotroponiminate (ATI) ligands into the coordination sphere of zinc.[12] A vast variety of ATI ligands with different amines were converted to zinc complexes and tested in intramolecular hydroamination reactions.[13] However, to the best of our knowledge, they have not been used in ROP.

Recently, we showed that BDI complexes bearing two electron-withdrawing trifluoromethyl groups in the pentane backbone show enhanced activity in the ring-opening polymerization of lactones when compared with BDI-ZnEt.[14] This can be attributed to an increased Lewis acidity at the metal center. Thus far, the influence of substituted anilines, the pentane backbone, and the initiating group on the catalytic activity was systematically investigated.[4c,d,15] Nevertheless, the 6-membered ring structure around the zinc center was not modified yet. It is expected that changing the ring size will have a decisive influence in terms of catalytic activity of the corresponding complexes (Figure 2).

In this work, we report on the synthesis of three novel, aromatic aminotroponiminate complexes **I**–**III**. Two of the ligands have not been previously reported. The complexes were structurally compared with the BDI model complex **IV** via single-crystal X-ray diffraction (SC-XRD), and the catalytic activity in ring-opening polymerization of BBL and *rac*-LA was examined.

RESULTS AND DISCUSSION

Synthesis. Aromatic aminotroponimine ligands were obtained via a 3-step synthesis starting from tropolone. First, trifluoromethanesulfonyl was introduced as a good leaving group for the following cross-coupling. The palladium-catalyzed Buchwald–Hartwig-like coupling converts the triflatotropone to the aminotropones **1a**–**3a**. This readily works for sterically hindered anilines substituted in the 2,6-position.[16] After activation with Meerwein's salt, the resulting

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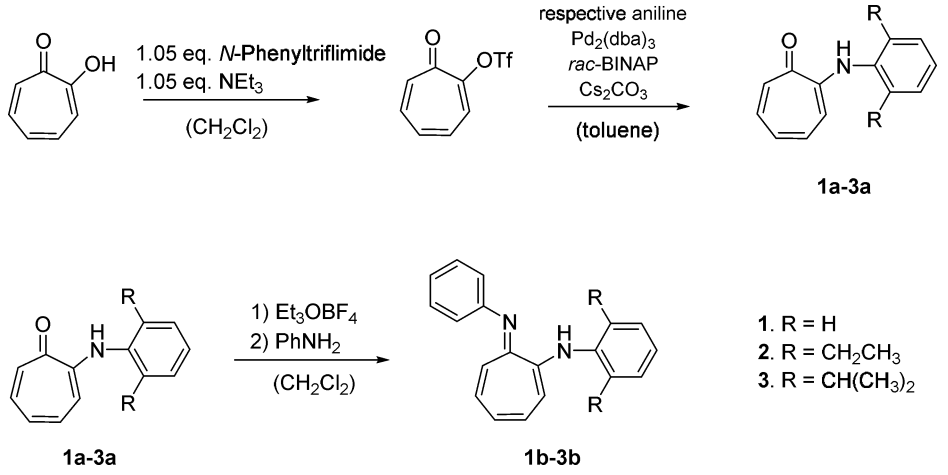
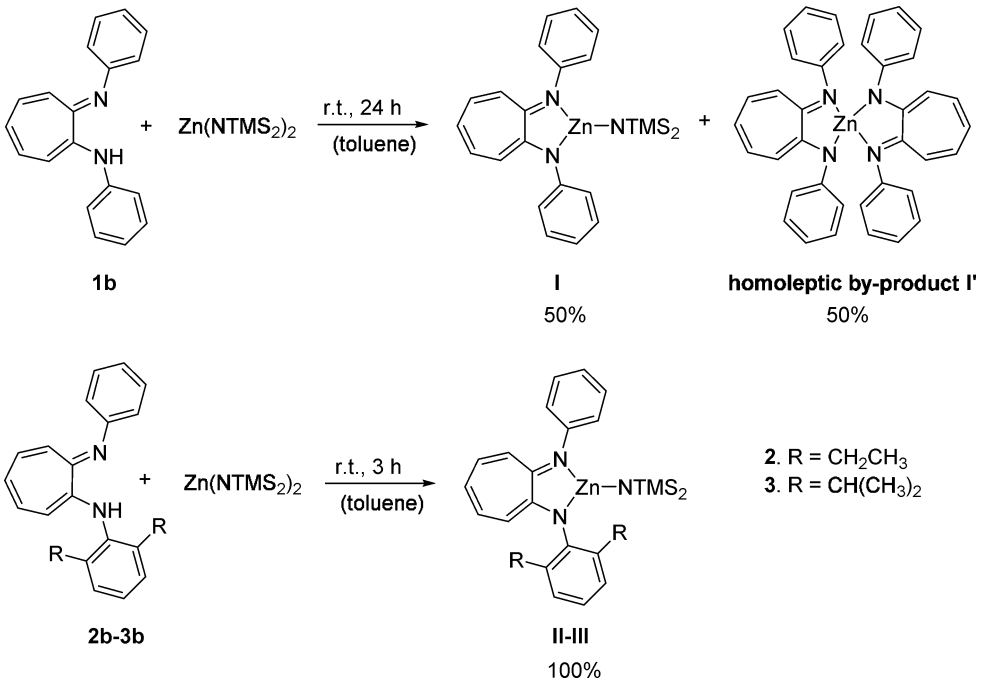
Scheme 1. Synthesis Route toward Aminotroponimine Ligands 1b−3b



Scheme 2. Complex Synthesis with Ligands 1b−3b and $Zn(NTMS_2)_2$



vinylogous ether was converted by aminolysis to the respective aminotroponimines (**1b−3b**).[13] Thus, bidentate, N-donor ligands bearing two different rests (**2**: R = CH_2CH_3; **3**: R = $CH(CH_3)_2$) at the 2,6-positions of one of the anilines were obtained (Scheme 1). In order to realize symmetrical, 2,6 disubstituted ATIHs, the aim was to introduce another triflate leaving group at the aminotropone **2a** and subsequently couple this with a 2,6 disubstituted aniline. The reduction of the carbonyl unit with lithium diisopropylamide was unsuccessful, most likely, because of the conjugated system at the amide. Therefore, only unsymmetrical ATIHs were accessible via this synthesis route.

BDI complexes bearing bis(trimethylsilyl)-amido ($NTMS_2$) initiators coordinated to the zinc center show high activities in the ring-opening polymerization of lactones.[17] Therefore, **1b−3b** were treated with $Zn(NTMS_2)_2$ to obtain ATI zinc amido complexes. Recently, Roesky et al. reported the complexation of aminotroponimines with $ZnMe_2$ and $ZnEt_2$. Depending on the substituents of the amines, either the desired complex with the general formula [(R_2)ATI]Zn-Alkyl (R = cyclohexyl, 1-ethylpropyl) or the corresponding homoleptic complex [(R_2)ATI]$_2$Zn (R = Ph, Me, *i*Pr) was obtained.[20] Complexation of the symmetric, unsubstituted ligand **1b** with $Zn(NTMS_2)_2$ at room temperature resulted in the formation of two different products (Scheme 2): The target structure **I** was only formed to an amount of 50%, whereas the homoleptic byproduct constituted the remaining 50%. Metal−organic complexes used in polymerization catalysis usually bear a nucleophilic group that serves as an initiator for the ring-opening step. Although there are some systems of homoleptic complexes which are active in polymerization, it is assumed for ATI-based complexes that an initiating group is necessary.[1d,18] Hence, **I′**, in contrast to **I**, might be inactive in ROP of lactones (tested for BBL polymerization, result shown in Table 1, entry 13). In order to overcome this high amount of homoleptic byproduct **I′**, different temperatures were applied and the influence on the complexation behavior was investigated (Table S1): Performing the complexation reaction

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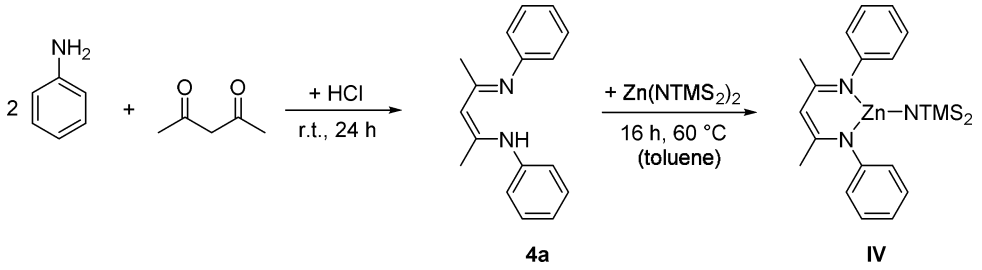
Scheme 3. Synthesis of β-Diiminate Zinc Complex IV. Reaction of BDI Ligand 4a with the Zinc Precursor



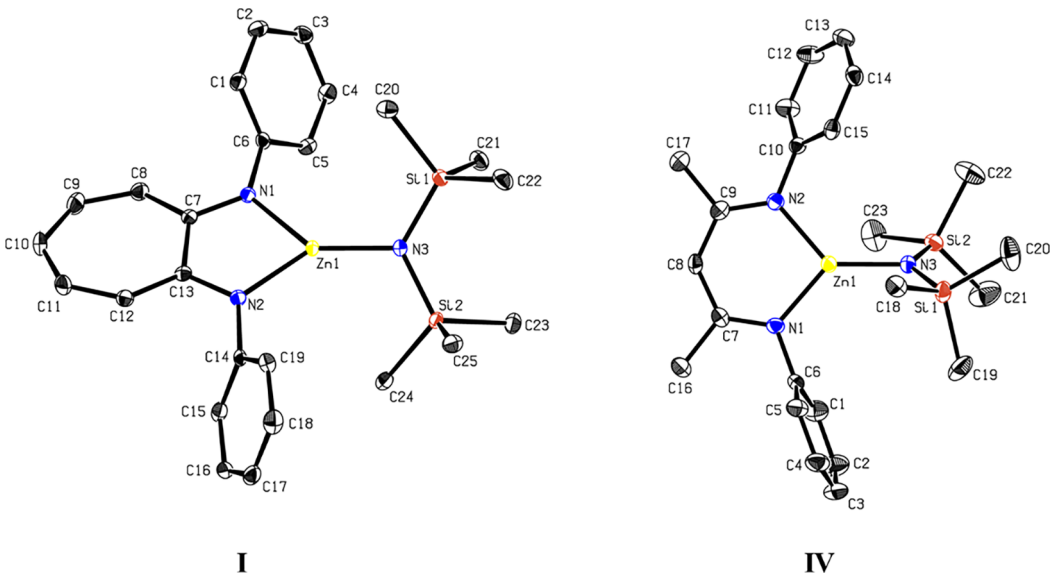


Figure 3. ORTEP style representation of **I** (left, CCDC 1837008) and **IV** (right, CCDC 1837010) with ellipsoids drawn at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **I**. Zn1−N1 1.9659(16), Zn1−N2 1.9707(17), Zn1−N3 1.8653(16), N1−Zn1−N2 82.41(7), Zn1−N1−C6 123.67, and Zn1−N2−C14 124.19; **IV**. Zn1−N1 1.9460(16), Zn1−N2 1.9530(16), Zn1−N3 1.8832(16), N1−Zn1−N2 98.59(7), Zn1−N1−C6 117.73, and Zn1−N2−C10 119.46.

at 100 °C resulted in the formation of 59% homoleptic complex **I′**. Lower temperatures, in this case 0 °C, result again in an equal 50/50 mixture of **I** and **I′**. ^{1}H NMR spectroscopy still shows the presence of unreacted ligand **1b**. Thus, a temperature of 25 °C for 24 h was chosen as the best condition for the complexation reaction of **1b**. Treatment of ligands **2b** and **3b**, bearing substituents at the 2,6-positions of the aniline, with the zinc precursor led to the exclusive formation of the desired structures [(C_6H_3-R_2/Ph)ATI]Zn−$NTMS_2$ **II**−**III**. This clearly shows that the steric demand of the ligand plays a decisive role in the complexation reaction.

The mixture of **I** and **I′** was separated based on the different crystallization behavior: Diffusion of pentane into a saturated solution of **I** and **I′** in dichloromethane at −35 °C selectively led to the crystallization of **I′**, whereas **I** remained in solution. Thus, aminotroponiminate complexes derived from aromatic anilines with the general formula [Ph_2ATI]Zn−initiator were isolated for the first time. Crystals suitable for single-crystal X-ray diffraction analysis were obtained via recrystallization of a saturated solution of **I** in pentane at −35 °C.

It is of interest to compare the molecular structure and the activity of the novel ATI complexes with the established BDI complexes. Via acid-catalyzed condensation reaction of aniline and acetylacetone, BDI ligand **4a** was obtained[19] and readily converted to the respective zinc−$NTMS_2$ complex **IV** by stirring the ligand **4a** with Zn($NTMS_2$)$_2$ in toluene at 60 °C for 16 h (Scheme 3). Recrystallization from toluene at −35 °C afforded colorless crystals that were suitable for X-ray diffraction.

Figure 3 shows the ORTEP style representations of **I** and **IV**. Both metal cores adopt a trigonal-planar geometry. Because **I** and **IV** are iminate-derived ligands without any substituents at the anilines, the 5- and 6-ringed structures can be directly compared to investigate the influence of the ring size on the molecular structure. The N1−Zn1−N2 angle was 82.41(7)° in the 5-ringed structure and 98.59(7)° in the 6-membered ring. The angle Zn1−N1−C6 also differs (123.67(5) for **I** and 117.73(4) for **IV**), indicating a larger space in **I** for a possible monomer coordination. A shortening of the Zn1−N3 bond was observed for the ATI−Zn−$NTMS_2$ **I** (1.8653(16)) with respect to the BDI−Zn−$NTMS_2$ **IV** (1.8832(16)).

Crystals suitable for SC-XRD were obtained via diffusion of pentane into a saturated solution of **II** and **III** in dichloromethane. Their molecular structures are depicted in Figure 4. The substituents in the 2,6-position of the aniline showed little influence over the molecular structure compared with **I**. Again, a trigonal-planar coordination geometry and very similar Zn1−N3 distances (**I**. 1.8653(16) Å, **II**. 1.865(4) Å, and **III**. 1.8631(17) Å) were observed. The substituted phenyl moieties were almost perpendicular to the coordination plane.

Polymerization Results. The catalytic activity of **I**−**IV** was tested in the polymerization of BBL and *rac*-LA under

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Table 1. Ring-Opening Polymerization of BBL Using Catalysts I–IV[a]

entry	cat.	T [°C]	time [h]	conv.[b] [%]	$M_{n,calc}$[c] [kg/mol]	$M_{n,exp}$[d] [kg/mol]	$Đ$[e]	P_m[f]
1	**I**	60	8	>99	52	129	1.22	55
2	**II**	60	15	>99	52	75	1.28	56
3	**III**	60	8	>99	52	122	1.16	55
4[g]	**III**	25	20	4	2	36	1.22	53
5	**III**	80	3.5	>99	52	116	1.15	54
6[h]	**III**	60	7	95	49	53	1.05	54
7[i]	**III**	60	3	98	5	7.5	1.02	53
8[j]	**III**	60	8	97	17	56	1.13	54
9[k]	**III**	60	8	96	33	65	1.51	53
10[g,l]	**III**	25	20	7	3.6	29	1.33	54
11[l]	**III**	60	14	61	31	58	1.78	55
12[h]	**I**	60	4.5	93	48	49	1.07	55
13	**I′**	60	20	2	n.d.	n.d.	n.d.	n.d.
14[m]	**I′**	60	12	1	n.d.	n.d.	n.d.	n.d.
15	**IV**	60	16	76	39	84	1.05	47

[a]All polymerizations were performed with n_{LA} = 17.4 mmol in a BBL/cat. ratio of 600 in 5.0 g of toluene in an autoclave with *in situ* IR monitoring under an argon atmosphere; polymerizations in entries 7–10 were performed in preheated glasses with magnetic stirring under anargon atmosphere, with the equivalents of BBL indicated. [b]Conversion determined by ^{1}H NMR spectroscopy. [c]$M_{n,calc}$ [kg/mol] = 0.01·conv.·86 g/mol·equiv. [d]$M_{n,exp}$ determined by GPC in THF vs polystyrene standards. [e]$Đ = M_w/M_n$. [f]Determined by ^{13}C NMR spectrum of the carbonyl C atom of PHB (Figure S5). [g]Not precipitated. [h]1.0 equiv of *i*PrOH was added. [i]10 equiv of *i*PrOH was added. [j]200 equiv of BBL was used. [k]400 equiv of BBL was used. [l]THF as solvent. [m]2.0 equiv of *i*PrOH was added.

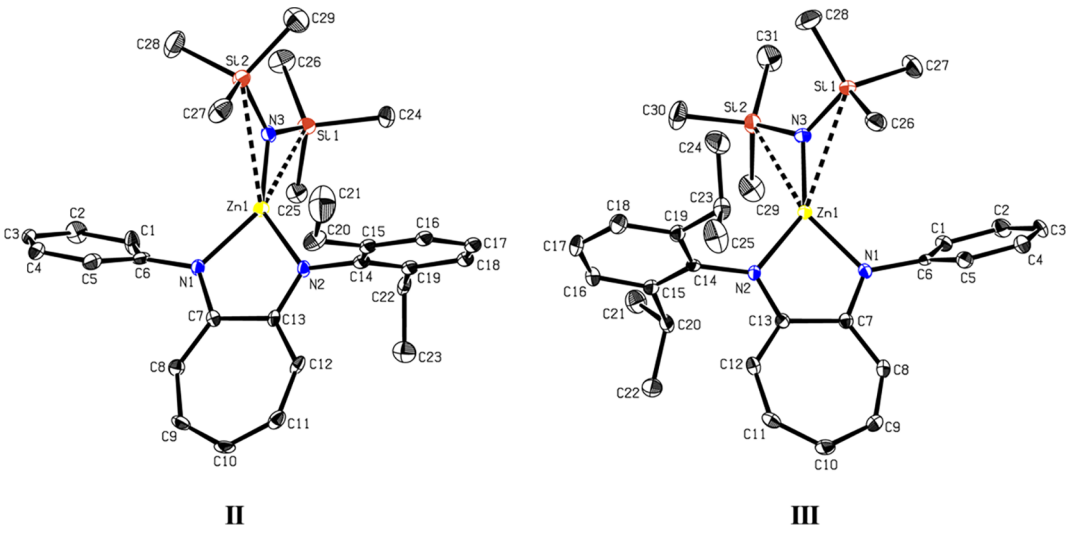

Figure 4. ORTEP style representation of **II** (left, CCDC 1837009) and **III** (right, CCDC 1837007) with ellipsoids drawn at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **II**. Zn1–N1 1.970(4), Zn1–N2 1.961(4), Zn1–N3 1.865(4), N1–Zn1–N2 82.61(16), Zn1–N1–C6 123.53, and Zn1–N2–C14 125.05; **III**. Zn1–N1 1.9547(17), Zn1–N2 1.9553(17), Zn1–N3 1.8631(17), N1–Zn1–N2 82.80(7), Zn1–N1–C6 122.75, and Zn1–N2–C14 124.48.

different conditions (Tables 1 and 2). The polymerization of BBL was conducted with a catalyst/monomer ratio of 1:600 at 60 °C in an autoclave with *in situ* IR monitoring. The three ATI-based complexes **I**–**III** were active initiators for the ring-opening of BBL, and the ligands had a different influence on the activity of the respective catalysts.

According to *in situ* IR spectroscopy (Figure 5), complex **I** (Table 1, entry 1) showed the highest activity of all the catalysts used with an induction period of about 30 min. The obtained polymer has a molecular weight of 129 kg/mol and a narrow polydispersity index ($Đ$) of 1.22. The more sterically demanding complexes **II** and **III** (Table 1, entries 2 and 3) also exhibited good activity along with a molecular weight of 75 kg/mol using **II** and 122 kg/mol with **III**. Different conditions such as temperature, addition of an external alcohol, concentration, and THF as solvent were tested using complex **III**. At first, polymerizations at 25 °C (Table 1, entry 4) and 80 °C (Table 1, entry 5) were performed. Activity and initiator efficiency at room temperature were low for **III**, leading to 4% conversion and a molecular weight of 36 kg/mol. Higher temperatures resulted in increased activity of **III** and the same initiator efficiency as for 60 °C. A plot of the *in situ* IR spectroscopy versus reaction time for the three temperatures is shown in Figure S1. The influence of adding an external alcohol, in this case, 1.0 equiv of 2-propanol, on complex **III** was studied via ^{1}H NMR spectroscopy. After 10 min reaction time, –O*i*Pr is bonded to the metal center, creating an alkoxy initiating group by a release of $HNTMS_2$ (see Figure S2). This *in situ* formed catalyst was subsequently tested in ROP of BBL at 60 °C (Table 1, entry 6), revealing a higher activity

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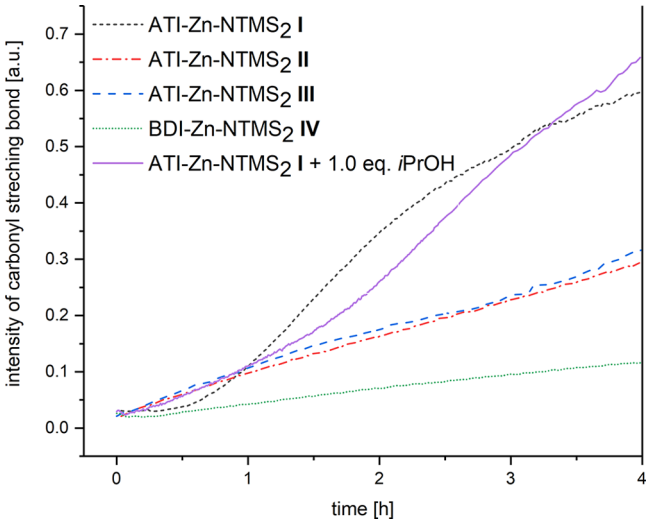

Figure 5. Polymerization of BBL with catalysts **I**–**IV** under the same conditions monitored by *in situ* IR spectroscopy ($\nu_{C=O,\ PHB}$ = 1750 cm^{-1}).

compared to **III** without the addition of *i*PrOH (Figure S3). Most importantly, the initiator efficiency of the *in situ* formed alkoxy group is higher, enabling the synthesis of controlled molecular weights and narrow polydispersities. This worked also for 10 equiv of *i*PrOH, producing PHB with 7.5 kg/mol (Table 1, entry 7). By variation of the monomer-to-catalyst ratio, polymers with different chain lengths were accessible in still good conversions (Table 1, entries 8 and 9). Polymerization experiments using THF as coordinating solvent (Table 1, entries 10 and 11) were successful, although lower conversions were observed compared to toluene as solvent. The use of THF did not influence the stereoselectivity of the reaction. In all polymerizations, atactic PHB was obtained. As mentioned, complex **I** showed an induction time of about 30 min. This can be overcome by adding 1.0 equiv of *i*PrOH prior to monomer addition (Table 1, entry 12). An immediate start of the polymerization as well as controlled molecular weights could be observed. The homoleptic complex **I′** with the general formula $[(Ph_2)ATI]_2Zn$ was also tested (Table 1, entry 13) in the polymerization. **I′** did not show significant activity, demonstrating that the catalyst requires a nucleophilic leaving group to start the ring-opening of the monomer. Complex **I′** was treated with 2.0 equiv of *i*PrOH to check if an active complex can be formed by the addition of an alcohol. No conversion to PHB could be observed after a reaction time of 12 h at 60 °C. This clearly demonstrates that no active complex could be formed by the addition of 2-propanol.

Once the behavior of the ATI complexes in the polymerization of BBL was evaluated, they were compared with the BDI complex model system, in this case, exemplary with complex **IV**: Both **I** and **IV** have the same initiating group and were synthesized from unsubstituted anilines, allowing a direct comparison of the influence of the 5- vs 6-membered ring around zinc. BDI complex **IV** showed lower activity in polymerization compared with **I**, yet the molecular weight (84 kg/mol) and *Đ* (1.05) were still in a good range. There may be various steric and electronic effects involved; thus, the reason for the higher activity is difficult to address. According to the molecular structures of **I** and **IV**, revealing a larger Zn1–N1–C6 angle for **I** compared to **IV** (**I**. 123.67(5)°, **IV**. 117.73(4)°), steric reasons seem to be more decisive rather than electronic effects.

As an example, catalyst **II** was tested in the ring-opening polymerization reaction to assess the possible living-type character (Figure 6). The conversion–time plot is shown on the left. Molecular weights, as well as the polydispersity indices as a function of the conversion, show a linear increase, indicating a living-type character of the polymerization.

Coates et al. investigated the influence of the initiating group of BDI zinc complexes in the ROP of LA. In that work, $-N(SiMe_3)_2$ substituted complexes show slightly lower activity than the –O*i*Pr substituted analogue but maintained a good control of the molecular weight with a moderate *Đ* of 2.95.[4b] Catalysts **I**–**IV** were also tested in the ROP of *rac*-LA under different conditions (Table 2).

Both **II** and **III** (Table 2, entries 2 and 3) were active initiators at room temperature, producing PLA in high conversion and very high molecular weight, whereas catalyst **I** had a very poor activity, resulting in a low conversion of 12% after 16 h. The obtained molecular weights indicate a rather low initiator efficiency of **II** and **III** at room temperature. It can also be concluded that ATI complexes with a higher steric demand of the ligand had better activity in the *rac*-LA polymerization. To get a closer insight why complex **I** showed such a low activity, the stability of **I** and **III** was investigated in different solvents (toluene-d_8 and dichloromethane-d_2, 15 min and 12 h) via ^{1}H NMR spectroscopy and ^{1}H DOSY NMR. In both solvents, **I** and **III** remained stable and showed a single diffusion coefficient for all resonances. Hence, the reason for this activity difference might be caused by the steric demand of the aniline rests. The substituted complexes **II** and **III** likely enable a better coordination of *rac*-LA, thus accelerating the

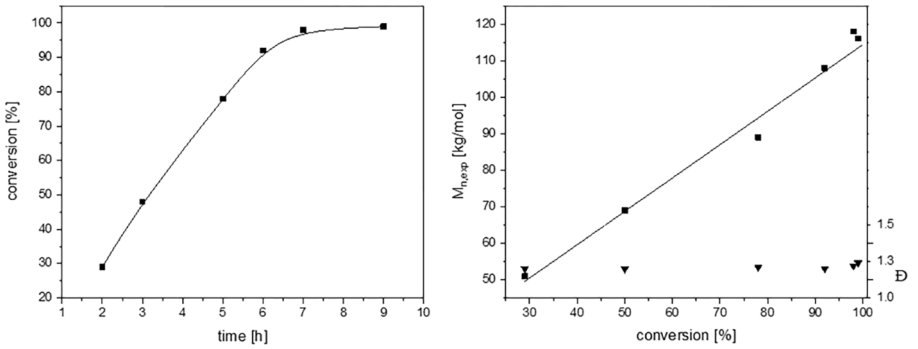

Figure 6. Polymerization of BBL with catalyst **II**. Plot of PHB conversion (%) vs time (h) (left), and PHB molecular weight ■ ($M_{n,\ exp}$ vs polystyrene standard in THF) and polydispersity index ▼ as a function of conversion (right).

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Table 2. Ring-Opening Polymerization of *rac*-LA Using Catalysts I–IV[a]

entry	cat.	T [°C]	time [h]	conv.[b] [%]	$M_{n,calc}$[c] [kg/mol]	$M_{n,exp}$[d] [kg/mol]	$Đ$[e]	P_r[f]
1[g]	I	25	16	12	3.5	7.5	1.28	n.d.
2	II	25	16	91	26	168	1.63	50
3	III	25	16	97	28	125	1.89	54
4	II	40	8	97	28	41	1.69	60
5[h]	II	25	1.5	90	26	26	1.23	50
6[h]	II	40	1.5	97	28	30	1.74	60
7[i]	II	40	16	99	56	68	2.05	55
8[j]	II	40	16	94	84	111	1.83	57
9[k]	II	25	16	62	18	109	2.43	47
10[k]	II	40	8	86	25	70	1.81	53
11	IV	25	16	94	27	101	1.43	62

[a]All polymerizations were performed, except otherwise indicated, with n_{LA} = 0.8 mmol in a *rac*-LA/cat. ratio of 200 in 2.65 mL of dichloromethane under an argon atmosphere. [b]Conversion determined by ^{1}H NMR spectroscopy. [c]$M_{n,calc}$ [kg/mol] = 0.01·conv.·144 g/mol·equiv. [d]$M_{n,exp}$ determined by GPC in THF vs polystyrene standards; $M_{n,exp}$ values are corrected with a 0.58 factor for PLA. [e]$Đ = M_w/M_n$. [f]Determined by homo-decoupled ^{1}H NMR spectroscopy considering the methine region of PLA (Figure S6). [g]Not precipitated. [h]1.0 equiv of *i*PrOH was added. [i]400 equiv of *rac*-LA was used. [j]600 equiv of *rac*-LA was used. [k]THF as solvent.

monomer ring-opening step. Due to a low initiator efficiency, polymerizations using **II** both at higher temperature and with the addition of an external alcohol were performed. Molecular weights are determined by GPC in THF and corrected with a factor of 0.58.[1d,18] Increasing the temperature from 25 to 40 °C (Table 2, entry 4) already enhanced the initiator efficiency by a factor of 4 to a molecular weight of 41 kg/mol. The addition of 2-propanol decisively influenced the reaction time and the obtained molecular weights: Polymerizing *rac*-LA at room temperature in the presence of 1.0 equiv of *i*PrOH (Table 2, entry 5) led to full conversion within 1.5 h, compared to 16 h when no external alcohol was used. The obtained molecular weights are in good range with the theoretical values. Performing the polymerization at 40 °C in the presence of 2-propanol (Table 2, entry 6) led to the same reaction time of 1.5 h and a comparable control over the molecular weight. Additionally, polymerization experiments with different monomer-to-initiator ratios (Table 2, entries 7 and 8) and with tetrahydrofuran as coordinating solvent (Table 2, entries 9 and 10) were conducted. Because both the substituents at the ligand and the nature of the solvent influence stereoselectivity, the polymer microstructure was examined via homo-decoupled ^{1}H NMR spectroscopy. It has been reported that increased heterotacticity can be observed for complexes bearing bulkier ligands.[1d,18] This trend was also observed for the ATI complexes **II**–**III**, although P_r is generally lower when compared to BDI complexes. Complex **II** exhibited higher heterotacticity when a higher temperature (40 °C) was applied. The use of THF had no decisive influence on the tacticity of the PLA. BDI model catalyst **IV** also allowed the polymerization of *rac*-LA in 16 h with a 94% yield (M_n = 101 kg/mol, $Đ$ = 1.43). The living-type character was assessed for *rac*-LA polymerization with **III** (Figure S7).

CONCLUSION

Three novel zinc complexes **I**–**III** were synthesized from aminotroponimine ligands, two of which were literature unknown. The ligands were obtained via a three-step synthesis starting from tropolone. The molecular structures were compared with the established β-diiminate model system **IV** via SC-XRD. Catalysts **I**–**IV** were tested in the ring-opening polymerization of the cyclic esters, *rac*-BBL and *rac*-LA. *In situ* IR spectroscopy revealed a higher activity for the ATI complexes **I**–**III** in the production of PHB than the BDI model system **IV**. This clearly demonstrates that the ring size of the metal core decisively influences the catalytic behavior of the complexes. The bulkier complexes **II**–**III** were also highly active initiators in the ring-opening polymerization of *rac*-LA. For both monomers, an optimization of the reaction conditions regarding reaction time, concentration, influence of the solvent, and the addition of an external alcohol was carried out. The addition of 2-propanol generated a zinc-alkoxy initiator group showing higher activity and initiator efficiency in the ring-opening polymerization. This allowed the synthesis of polymers with controlled molecular weights and narrow polydispersities. Further modifications of the ligands' structure may improve the activity and the stereospecificity of the polymerization.

EXPERIMENTAL SECTION

General. All reactions containing air- and/or moisture-sensitive compounds were performed under an argon atmosphere using standard Schlenk or glovebox techniques. All chemicals, unless otherwise stated, were purchased from Aldrich and used as received. Dry toluene, dichloromethane, and pentane were obtained from an MBraun MB-SPS-800 solvent purification system. 2-Propanol was dried over molecular sieves.

β-Butyrolactone was treated with BaO to remove crotonic acid contaminants. After checking the purity via ^{1}H NMR spectroscopy, BBL was dried over calcium hydride and distilled prior to polymerization. NMR spectra were recorded on Bruker AVIII-300 and AVIII-500 Cryo spectrometers. ^{1}H NMR spectroscopic shifts are reported in ppm relative to tetramethylsilane and calibrated to the residual proton signal of the deuterated solvent. The deuterated solvents were obtained from Aldrich and dried over 3 Å molecular sieves. The following abbreviations are used to describe the peak patterns when appropriate: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), m (multiplet), and br (broad). *In situ* IR measurements were performed under an argon atmosphere using an ATR-IR MettlerToledo system with mechanical stirring. Gel permeation chromatography analysis was performed with a Varian PL-GPC 50 using THF (HPLC grade) with 0.22 g L^{-1} 2.6 di-*tert*-butyl-4-methylphenol and a flow rate of 1 mL/min at 40 °C. Polystyrene standards were used for calibration. Molecular weights of PLA were corrected with a Mark–Houwink factor of 0.58.[20] Elemental analysis was performed at the microanalytic laboratory of the Department of Inorganic Chemistry at the Technical University of Munich. Mass spectra were recorded with an Agilent Technologies Mass Hunter Spectrometer (EI, 70 eV). Single-crystal X-ray

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crystallography was performed at the SCXRD laboratory of the Catalysis Research Center.

Ligands. *2-Triflatotropone.* This compound was synthesized according to a modified literature procedure.[21] 2-Hydroxycyclohepta-2,4,6-trienone (tropolone) (2.50 g, 20.5 mmol, 1.00 equiv), triethylamine (2.17 g, 21.5 mmol, 1.05 equiv), and *N*-phenyltriflimide (7.68 g, 21.5 mmol, 1.05 equiv) were dissolved in dry dichloromethane and stirred for 48 h at r.t. After extraction with water (20 mL) and dichloromethane (2 × 20 mL), the main product was concentrated *in vacuo* and purified via silica gel column chromatography (hexane/ethyl acetate = 2:1, TLC R_f = 0.3) yielding a brownish oil (86%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 9.07 (br s, OH), 7.42−7.22 (m, 4H, H_{Ar}), 7.07 (t, J = 10.2 Hz, 1H, H_{Ar}). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 178.5 (s), 156.4 (s), 141.2 (s), 137.6 (s), 136.4 (s), 130.7 (s), 128.6 (s), 121.4 ($^1J_{CF}$ = 323 Hz).

Aromatic 2-Aminotropones (1a−3a). In a preheated Schlenk flask, 2-triflatotropone (1.20 g, 4.72 mmol, 1.00 equiv), cesium carbonate (2.15 g, 6.61 g, 1.40 equiv), *rac*-2,2′-bis-(diphenylphosphino)-1,1′-binaphthalene (29.4 mg, 47.2 μmol, 0.01 equiv), tris(dibenzylideneacetone)dipalladium (21.6 mg, 23.6 μmol, 0.005 equiv), and the respective aniline (6.14 mmol, 1.30 equiv) were dissolved in toluene and heated to 90 °C for 24 h.[16] The crude product was filtered, concentrated *in vacuo*, and purified via silica gel chromatography (hexane/ethyl acetate = 20:1, TLC R_f = 0.2).

2-(Phenylamino)tropone ***1a.*** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 8.84 (br s, 1H, NH), 7.53−7.19 (m, 9H, H_{Ar}), 6.88 (dd, J = 7.1 Hz, J = 8.9 Hz, 1H, H_{Ar}).

2-(2,6-Diethylphenylamino)tropone ***2a.*** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 8.47 (br s, 1H, NH), 7.36−7.23 (m, 5H, H_{Ar}), 7.07 (t, J = 10.3 Hz, 1H, H_{Ar}), 6.73 (t, J = 8.9 Hz, 1H, H_{Ar}), 6.26 (d, J = 10.3 Hz, 1H, H_{Ar}), 2.55−2.42 (m, 4H, $-CH_2-$), 1.14 (t, J = 7.6 Hz, 6H, $-CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 176.5, 155.6, 142.1, 137.5, 136.7, 133.9, 129.8, 128.4, 127.0, 123.6, 110.2, 24.7, 14.9. Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found C, 80.67; H, 7.64; N, 5.46. MS (EI, 70 eV): 253.2 m/z [M^+].

2-(2,6-Diisopropylphenylamino)tropone ***3a.*** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 8.42 (br s, 1H, NH), 7.41−7.26 (m, 5H, H_{Ar}), 7.07 (t, J = 10.3 Hz, 1H, H_{Ar}) 6.73 (t, J = 9.8 Hz, 1H, H_{Ar}), 6.27 (d, J = 10.3 Hz, 1H, H_{Ar}) 2.94−2.85 (m, 2H, −CH−), 1.13 (dd, J = 20.3 Hz, J = 6.9 Hz, 6H, $-CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 176.4, 156.5, 146.9, 137.7, 136.4, 132.4, 130.0, 128.9, 124.4, 123.8, 110.7, 28.6, 24.6, 23.5. Anal. Calcd for $C_{19}H_{16}N_2$: C, 81.10; H, 8.24; N, 4.98. Found C, 81.10; H, 8.47; N, 4.74. MS (EI, 70 eV): 281.2 m/z [M^+].

***N,N′*-Disubstituted Aminotroponimines (1b−3b).** Triethyloxonium tetrafluoroborate (0.47 g, 2.48 mmol, 1.05 equiv) was dissolved in a preheated flask in dry dichloromethane and added to a solution of the respective 2-aminotropone **2a−c** (2.36 mmol, 1.00 equiv) and dichloromethane. After stirring for 3 h at r.t., aniline (1.10 g, 11.4 mmol, 5.00 equiv) was added and the resulting solution was stirred for 48 h. The crude product was extracted with a NaOH solution (1M, 10 mL) and dichloromethane (2 × 10 mL). A dark brownish oil was obtained after silica gel column chromatography (hexane/ethyl acetate = 30:1, TLC R_f = 0.6).

N-Phenyl-2-(phenylamino)troponimine ***1b.*** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 9.18 (br s, 1H, NH), 7.40 (t, J = 7.9 Hz, 4H), 7.16−7.12 (m, 6H), 6.84 (d, J = 10.4 Hz, 2H, H_{Ar}), 6.73 (t, J = 10.3 Hz, 2H, H_{Ar}), 6.34 (t, J = 9.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 152.0, 145.3, 133.6, 129.6, 124.1, 122.7, 122.2, 115.0. Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found C, 83.95; H, 6.00; N, 10.23. MS (EI, 70 eV): 273.2 m/z [M + H].

N-Phenyl-2-(2,6-diethylphenylamino)troponimine ***2b.*** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 9.10 (br s, 1H, NH), 7.41 (t, J = 7.8 Hz, 2H), 7.18−7.13 (m, 6H), 6.88 (d, J = 10.9 Hz, 1H), 6.73 (dd, J = 10.6 Hz, J = 9.5 Hz, 1H), 6.66 (dd, J = 10.6 Hz, J = 9.5 Hz, 1H), 6.28 (t, J = 9.5 Hz, 1H), 6.14 (d, J = 10.6 Hz, 1H), 2.53−2.39 (m, 4H), 7.54 (t, J = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 152.8, 151.0, 144.9, 141.9, 137.6, 133.6, 133.5, 129.6, 126.5, 125.1, 124.0, 122.9, 121.3, 115.4, 113.1, 24.8, 14.6. Anal. Calcd for $C_{23}H_{24}N_2$: C, 84.11; H, 7.37; N, 8.53. Found C, 83.83; H, 7.60; N, 8.24. MS (EI, 70 eV): 329.2 m/z [M + H].

N-Phenyl-2-(2,6-diisophenylamino)troponimine ***3b.*** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 9.16 (br s, 1H, NH), 7.46 (t, J = 7.9 Hz, 2H), 7.28−7.17 (m, 6H), 6.93 (d, J = 11.0 Hz, 1H), 6.77 (dd, J = 10.7 Hz, J = 9.6 Hz, 1H), 6.69 (dd, J = 10.7 Hz, J = 9.6 Hz, 1H) 6.31 (t, J = 9.6 Hz, 1H), 6.19 (d, J = 10.7 Hz, 1H), 2.97−2.89 (m, 2H), 1.20 (dd, J = 11.1 Hz, 6.9 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 151.3, 145.4, 142.6, 140.0, 133.5, 133.5, 129.6, 125.7, 123.9, 123.8, 122.8, 121.3, 115.1, 113.9, 28.5, 24.2, 23.5. Anal. Calcd for $C_{25}H_{28}N_2$: C, 84.23; H, 7.92; N, 7.86. Found C, 84.24; H, 8.29; N, 7.57. MS (EI, 70 eV): 357.3 m/z [M + H].

*N-(Phenylimino)pent-2-en-2-yl)aniline (****4a****).* The ligand was synthesized by a modified literature procedure.[19] A solution of 2,4-pentadione (5.00 g, 49.9 mmol, 1.00 equiv) and aniline (9.18 g, 100 mmol, 2.00 equiv) was treated with concentrated hydrochloric acid (4.90 g, 49.9 mmol) at 0 °C. After stirring the mixture for 24 h, the precipitate was filtered, washed with hexane, and dissolved in a solution of CH_2Cl_2 (4 mL), H_2O, and triethylamine (10.0 mL). The crude product was recrystallized from ethanol. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 12.7 (s, 1H, NH), 7.29 (m, 4H, H_{Ar}), 7.06 (t, J = 7.4 Hz, 2H, H_{Ar}), 6.97 (d, J = 8.5 Hz, 4H, H_{Ar}), 4.89 (s, 1H, CH), 2.01 (s, 6H, CH_3).

Complexes. The ligands **1b−3b** (0.610 mmol, 1.00 equiv) were dissolved in a Schlenk flask in 10 mL of toluene. $Zn(NTMS_2)_2$ (0.670 mmol, 1.10 equiv) was added to the solution and stirred for 3 h (ligand **3a** for 24 h in the case of 0 °C/25 °C and 72 h at 100 °C) at room temperature; then the solvent was removed *in vacuo*. Complexes **II** and **III** were obtained by recrystallization in CH_2Cl_2/pentane at −35 °C. Complexation of **1b** yielded 50% homoleptic and 50% heteroleptic complex. Recrystallization of a saturated solution in CH_2Cl_2/pentane resulted in the exclusive crystallization of the homoleptic complex, whereas the heteroleptic one remains in solution and can be successfully separated.

I. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ [ppm] = 7.46 (t, J = 9.6 Hz, 4H, H_{Ar}), 7.22 (t, J = 7.3 Hz, 2H, H_{Ar}), 7.14 (dd, J = 7.4 Hz, J = 1.1 Hz, 4H, H_{Ar}), 7.07 (m, 3H, H_{Ar}), 6.72 (m, 2H, H_{Ar}), −0.18 (s, 18H, $Si-CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 160.3, 159.7, 149.4, 148.1, 135.2, 134.8, 129.9, 129.8, 124.8, 124.5, 124.1, 122.3, 117.6, 116.2. Anal. Calcd for $C_{25}H_{33}N_3Si_2Zn$: C, 60.40; H, 6.69; N, 8.45. Found C, 60.09; H, 6.79; N, 8.59.

II. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.46 (t, J = 7.9 Hz, 2H, H_{Ar}), 7.25−7.00 (m, 9H, H_{Ar}), 6.57 (t, J = 9.2 Hz, 1H, H_{Ar}), 6.53 (d, J = 11.2 Hz, 1H, H_{Ar}), 2.55−2.37 (m, 4H, $-CH_2-$), 1.15 (t, J = 7.6 Hz, 6H, $-CH_3$), −0.25 (s, 18H, $Si-CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 159.5, 159.0, 147.8, 143.7, 137.2, 135.1, 135.0, 129.7, 126.2, 125.2, 125.0, 124.7, 121.8, 117.2, 116.7, 23.9, 14.0, 4.65. Anal. Calcd for $C_{29}H_{41}N_3Si_2Zn$: C, 62.96; H, 7.47; N, 7.60. Found C, 62.63; H, 7.43; N, 7.30.

III. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.46 (t, J = 7.9 Hz, 2H, H_{Ar}), 7.26−6.97 (m, 7H, H_{Ar}), 7.07 (t, J = 10.7 Hz, 1H, H_{Ar}), 6.99 (t, J = 10.5 Hz, 1H, H_{Ar}), 6.55 (t, J = 9.4 Hz, 2H, H_{Ar}), 2.87 (m, 2H, CH), 1.22 (d, J = 6.8 Hz, 6H, CH_3), 1.04 (d, J = 6.8 Hz, 6H, CH_3), −0.23 (s, 18H, $Si-CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 160.7, 159.0, 147.6, 142.6, 142.3, 135.2, 134.8, 129.8, 125.9, 125.1, 124.8, 124.4, 122.0, 118.5, 116.9, 28.4, 25.4, 24.3, 4.78. Anal. Calcd for $C_{31}H_{45}N_3Si_2Zn$: C, 64.06; H, 7.80; N, 7.23. Found C, 63.96; H, 7.79; N, 6.96.

Ligand **4a** (0.68 mmol, 1.0 equiv) was dissolved in 5.0 mL of toluene. $Zn(NTMS_2)_2$ (0.82 mmol, 1.2 equiv) was added to the solution and stirred for 20 h at 80 °C; then the solvent was removed *in vacuo*. Complex **IV** was obtained via recrystallization in toluene at −35 °C. **IV**. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.33 (m, 4H, H_{Ar}), 7.15 (t, J = 7.4 Hz, 2H, H_{Ar}), 6.98 (d, J = 8.2 Hz, 4H, H_{Ar}), 4.91 (s, 1H, CH), 1.95 (s, 6H, CH_3), −0.33 (s, 18H, $Si-CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 167.8, 148.7, 128.9,

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125.2, 124.7, 96.2, 23.9, 4.53. Anal. Calcd for $C_{23}H_{35}N_3Si_2Zn$: C, 58.15; H, 7.43; N, 8.84. Found C, 58.18; H, 7.28; N, 8.69.

General Polymerization Procedure for BBL. The polymerizations performed in the *in situ* IR autoclave were performed in the following way: The corresponding catalyst **I**–**IV** (1.00 equiv) was dissolved in dry toluene (5.0 mL) and placed in a syringe. BBL was stored in a second syringe. The two filled syringes were transported to an *in situ* IR autoclave with mechanical stirring. The autoclave was pretempered to a certain temperature under an argon atmosphere, and the solution of the catalyst in toluene and BBL were transferred into the reactor. After full conversion, an aliquot was taken to determine the conversion via ^{1}H NMR spectroscopy. The amount of toluene was reduced under vacuum prior to precipitation of the polymer in 100 mL of pentane/diethyl ether (1:1). The polymerizations without IR monitoring were carried out in glass vials with magnetic stirring under an argon atmosphere under the same conditions as in the autoclave. In the case of using 2-propanol as external alcohol, the catalyst was dissolved in toluene and treated with the respective amount of *i*PrOH. This solution was stirred for 10 min prior to monomer addition. Conversion was determined via ^{1}H NMR spectroscopy, and the polymers were precipitated in 100 mL of pentane/diethyl ether (1:1).

General Polymerization Procedure for *rac*-Lactide. *rac*-LA was dissolved in dry dichloromethane (2.65 mL), and the respective catalyst (4.00 μmol, 1.00 equiv) was added. After stirring for a certain time, an aliquot was taken to determine the conversion via ^{1}H NMR spectroscopy. In the case of using 2-propanol as external alcohol, the catalyst was dissolved in dichloromethane and treated with the respective amount of *i*PrOH. This solution was stirred for 10 min prior to monomer addition. The polymeric solution was precipitated in 60 mL of pentane/diethyl ether (1:1); then the resulting polymer was dried *in vacuo* to constant weight.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01060.

In situ IR spectroscopy plots, NMR data for microstructure determination of PHB and PLA, ^{1}H DOSY NMRs, GPC data, and SC-XRD data (PDF)

Accession Codes

CCDC 1837007−1837010 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

M.R. substantially contributed to this work during her time as a co-worker of the Wacker-Lehrstuhl für Makromolekulare Chemie. D.H.B. did a 6-month part of his Ph.D. at the Wacker-Lehrstuhl für Makromolekulare Chemie.

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Notes

The authors declare no competing financial interest.

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