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Geometry change in a series of zirconium compounds during lactide ring opening polymerization

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Supporting Information Placeholder

ABSTRACT: A new series of zirconium compounds, (salfen)Zr(O^{t}Bu)$_2$ (salfen = N,N'-bis(2,4-di-*tert*-butylphenoxy)-1,1'-ferrocene-diimine), (salfen)Zr(O^{i}Pr)$_2$, and (salfen)Zr(O^{n}Pr)$_2$, was synthesized and characterized, featuring a cis-β coordination geometry for the major isomer found in solution. An isomerization between the trans and cis-β coordination geometry was observed at ca. 100 °C in solution. This isomerization was also observed in the presence of L-lactide (LA) before its ring opening polymerization could occur. The isolation of a (salfen)Zr(O^{n}Pr)$_2$ lactide intermediate supports the change to the trans coordination geometry necessary before polymerization.

INTRODUCTION

Biodegradable polymers, especially polyesters, are promising solutions to the pollution generated by conventional plastics.[1-11] While polyesters can be obtained using enzymatic methods, the ring-opening polymerization of cyclic esters catalyzed by metal complexes[11-13] or small organic molecules[13-14] is a well-known, controlled process, which allows the synthesis of polymers with specific properties. Zirconium alkoxide complexes have been used as catalysts for the ring opening polymerization of lactide for several decades.[13, 15-16] Zirconium tetra-alkoxide compounds were the first studied;[17-18] zirconium tetra-*n*-propoxide, for example, could reach 94% lactide conversion at 90 °C after 24 hours. Recently, in order to achieve controlled polymerization, the synthesis of novel zirconium compounds has been pursued. For example, ONNO-type tetradentate ligands, derived from Schiff bases (Chart 1), were successful in supporting zirconium catalysts for the ring opening polymerization of lactones.[15] Compounds featuring both a saturated backbone (Chart 1), reported by Kol et al.,[19] and unsaturated C=N backbone (Chart 1), reported by Chakraborty et al.,[20] showed a good activity toward the ring opening polymerization of cyclic esters. Zirconium precatalysts bearing other tetradentate ligands, such as the OSSO and OSNO-type, were designed and synthesized later.[21-23]

The structure of the above six-coordinated metal complexes was studied systematically, and it was shown that they can adopt three possible geometries at the metal center: cis-α, cis-β, and trans (Figure 1); among these, the cis-β geometry is non-symmetrical,[24] while the other two are symmetrical. For all the group 4 metal precatalysts, it was reported that different geometries have distinct activities during the lactone ring-opening polymerization: trans and cis-α compounds are usually active, while cis-β compounds show only a low activity.[22-29]

In 2015, B. Long and co-workers reported a titanium(IV) salfen (salfen = 1,1′- di(2,4-di-*tert*-butyl-6-salicylimine)ferrocene) complex displaying a cis-β geometry (Chart 2).[30] By comparison, the geometry of a titanium complex supported by a different ferrocene modified Schiff base, previously reported by N. Long and coworkers, was trans.[31] In B. Long's paper, the ring opening polymerization of L-LA with the reduced state catalyst was significantly slower than that with the oxidized state catalyst, which represented an opposite trend in catalytic activity as compared with most catalysts employed in redox switchable ring opening polymerization.[32-42] However, if the catalyst was oxidized in the presence of L-LA and then reduced back, the reduced species showed a dramatically increased polymerization rate. Once it was oxidized back in situ, the newly formed compound had no activity toward the ring opening polymerization of LA anymore. Although further investigations are needed to explain this phenomenon, based on the *in situ* ^{1}H NMR spectra and the cyclic voltammetry (CV) experiments, the authors proposed that the geometry of the catalyst was

changed from its original cis-β conformation to either a cis-α or trans conformation by using the redox reagents in the presence of LA. In the absence of LA, the geometry of the catalyst remained cis-β after oxidation. Thus, the authors proposed that when the oxidation and reduction reactions were carried out in the presence/absence of monomers, the polymerization activity was completely different.
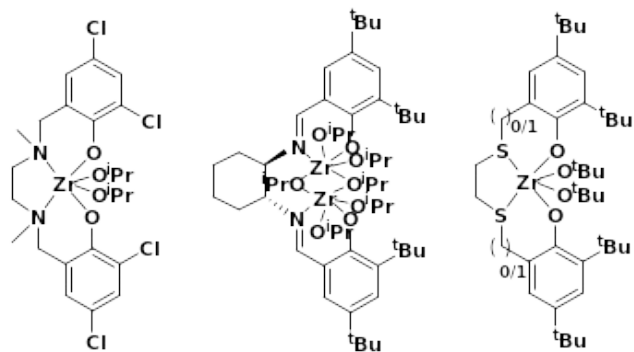
Chart 1 Zirconium complexes used as precatalysts for lactone ring opening polymerization.
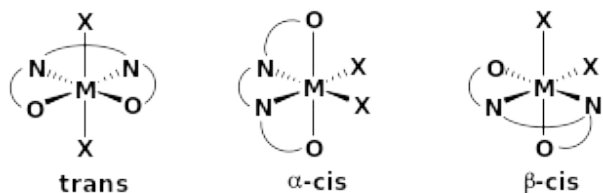

Figure 1 Different coordination geometries of group 4 metal complexes supported by tetradentate ligands.
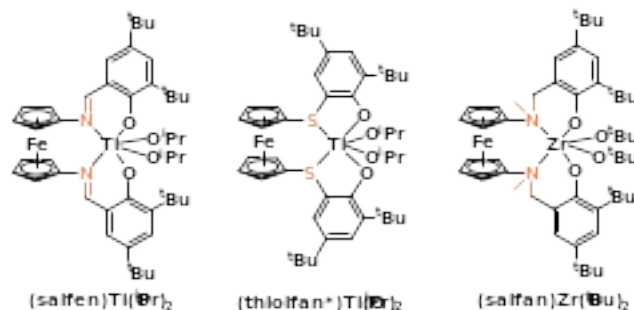

Chart 2 Previously reported ferrocene-derived Schiff base group 4 metal complexes.

Our group has been interested in the redox switchable polymerization of lactide and its copolymerization with other monomers.[35-39, 41-50] We were able to show that changing the oxidation state of iron in a ferrocene-based ligand modified the reactivity of a metal complex toward a certain monomer. Various ferrocene ligands were designed in the past few years and their corresponding metal compounds showed orthogonal activity toward cyclic ester

polymerization. For example, (thiolfan*)Ti(O^{i}Pr)$_2$ (Chart 2, thiolfan* = 1,1'-di(2,4-di-*tert*-butyl-6-thiophenoxide)ferrocene) can polymerize L-lactide (LA) in the reduced state and ε-caprolactone in the oxidized state; (salfan)Zr(O^{t}Bu)$_2$ (Chart 2, salfan = 1,1'-bis(di-2,4-*tert*-butyl-6-N-methylmethylenephenoxy)ferrocene) can polymerize LA in the reduced state and cyclohexene oxide (CHO) in the oxidized state.[39] We became interested in studying a ferrocene-derived Schiff base zirconium complex in order to simplify the ligand design and to compare its activity with that reported by Long et al. for the corresponding titanium complex. Herein, we discuss our results that indicate that a geometry change is observed for the corresponding zirconium complexes at a temperature above ambient conditions. Furthermore, such a geometry change is necessary for these precatalysts to become active in lactide ring opening polymerization.

RESULTS AND DISCUSSION

Synthesis and characterization of the zirconium complexes. Three compounds, (salfen)Zr(O^{t}Bu)$_2$, (salfen)Zr(O^{i}Pr)$_2$, and (salfen)Zr(O^{n}Pr)$_2$, were synthesized from the reaction of H$_2$(salfen) with Zr(O^{t}Bu)$_4$, Zr(O^{i}Pr)$_4$·HO^{i}Pr and Zr(O^{n}Pr)$_4$·HO^{n}Pr (Scheme 1).
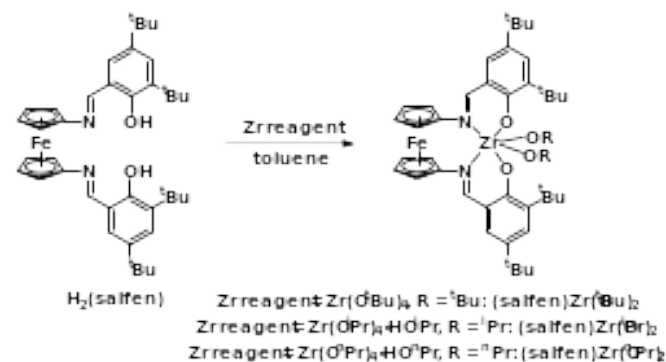
Scheme 1 Synthesis of zirconium complexes.

The ^{1}H NMR spectrum (Figure 2) of (salfen)Zr(O^{t}Bu)$_2$ indicated a non-symmetrical geometry at zirconium, and was different from the ^{1}H NMR spectrum of the symmetrical compound (salfan)Zr(O^{t}Bu)$_2$ (salfan = 1,1'-bis(di-2,4-*tert*-butyl-6-N-methylmethylenephenoxy)ferrocene), previously reported by our group.[39] This asymmetry made each proton on the aryl, imine, ferrocene, and alkoxide moieties to be magnetically nonequivalent. The solid state molecular structure (Figure 3) indicated a cis-β coordination geometry, which explained the asymmetrical peaks observed in the ^{1}H NMR spectrum.[24, 30]
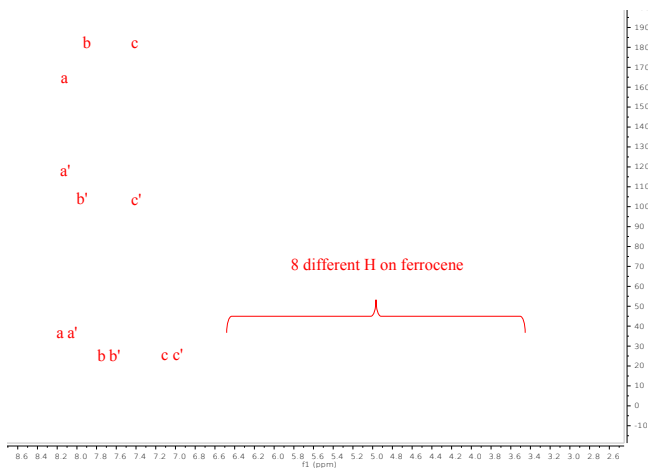
Figure 2 ^{1}H NMR spectrum (500 MHz, 25 °C, C_6D_6) of (salfen)Zr(O^{t}Bu)$_2$.
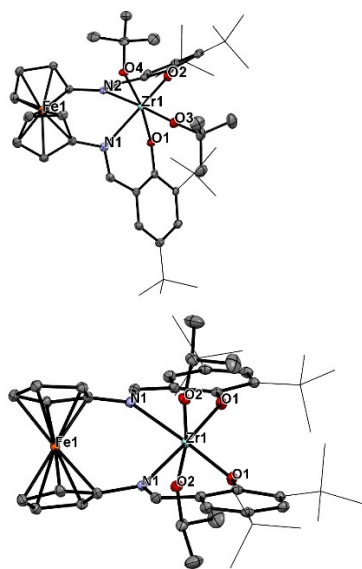

Figure 3 Thermal ellipsoid (50% probability) representation of (salfen)Zr(O^{t}Bu)$_2$ (left, cis-β) and (salfen)Zr(O^{i}Pr)$_2$ (right, trans). Hydrogen atoms were removed and aryl *t*-butyl groups are drawn as sticks for clarity.

Similar ^{1}H NMR spectra were obtained for (salfen)Zr(O^{i}Pr)$_2$ and (salfen)Zr(O^{n}Pr)$_2$. For both cases, however, there was always a set of small peaks that corresponded to another isomer (Figure 4), which could not be separated by purification through filtration or crystallization. The single crystals obtained from these solutions corresponded to these minor isomers, which showed a trans geometry in the solid state structure (Figure 3). Therefore, we hypothesized that the two isomers are in equilibrium with each other, with the cis-β geometry as the major isomer in solution at room temperature. This hypothesis was probed by variable temperature ^{1}H NMR spectroscopy (Figure 5) performed on (salfen)Zr(O^{n}Pr)$_2$. At 100 °C, the peaks coalesce, indicating the existence of a fast equilibrium on the NMR timescale between the two isomers. The

^{1}H NMR spectrum reverted to that of the original sample after cooling to room temperature. The trans and cis-β geometry isomer percent content for all three zirconium complexes is listed in Table 1.
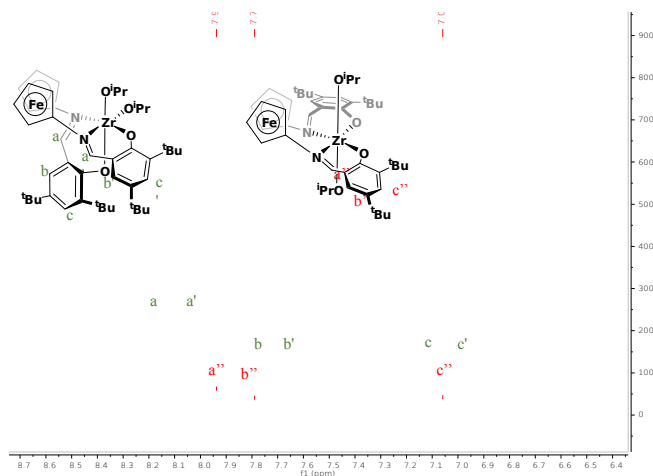
Figure 4 ^{1}H NMR spectrum (500 MHz, 25 °C, C_6D_6) of (salfen)Zr(O^{i}Pr)$_2$.
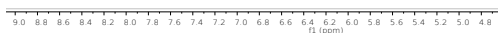
Figure 5 ^{1}H NMR spectra (500 MHz, d_8-toluene) of (salfen)Zr(O^{n}Pr)$_2$ at 25 °C (bottom), 70 °C (middle), and 100 °C (top).

Table 1 cis-β and trans geometry isomer contribution for each zirconium alkoxide in C_6D_6 solution at room temperature.

Compound	cis-β	trans
(salfen)Zr(O^{t}Bu)$_2$	95%	5%
(salfen)Zr(O^{i}Pr)$_2$	84%	16%
(salfen)Zr(O^{n}Pr)$_2$	71%	29%

DFT calculations were performed to compare the ground state energies of the zirconium complexes in both isomeric forms (Table S3, entries 1-8). For a model compound, in which the ^{t}Bu groups on the phenoxides and the alkoxides

(R = ^{t}Bu, ^{i}Pr, and ^{n}Pr) were replaced with H and methoxides, respectively, the trans isomer was found to be 1.7 kcal/mol higher in energy than the cis-β isomer, in agreement with experimental observations. Calculations on the full molecules also agree with the experimental observations (salfen)Zr(O^{t}Bu)$_2$ and (salfen)Zr(O^{i}Pr)$_2$, for which the cis-β isomer is more stable than the trans isomer by 1.1 and 0.4 kcal/mol, respectively. In the case of (salfen)Zr(O^{n}Pr)$_2$, the trans appeared slightly more favorable by 0.4 kcal/mol than the cis-β isomer. Although the calculations on the full molecules do not reproduce the expected isomer ratio for (salfen)Zr(O^{n}Pr)$_2$, the trend of an increasing amount of trans isomer present at room temperature from (salfen)Zr(O^{t}Bu)$_2$ to (salfen)Zr(O^{i}Pr)$_2$ and to (salfen)Zr(O^{n}Pr)$_2$ is reproduced well.

Polymerization of LA with the three zirconium complexes. The three compounds were then used as pre-catalysts for LA homopolymerization reactions (Table 2). Compound (salfen)Zr(O^{t}Bu)$_2$ did not work (Table 2, entry 1), but both (salfen)Zr(O^{i}Pr)$_2$ (entry 2) and (salfen)Zr(O^{n}Pr)$_2$ (entry 3) showed good activity for LA polymerization, with (salfen)Zr(O^{i}Pr)$_2$ giving a slightly better yield: at 100 °C in benzene solution, (salfen)Zr(O^{i}Pr)$_2$ reacted with 100 equiv. LA in 24 hours to give a 70% conversion, and (salfen)Zr(O^{n}Pr)$_2$ reacted with 100 equiv. LA in 24 hours to give a 60% conversion.

Table 2. Polymerization of LA or ε-caprolactone (CL) with the three zirconium alkoxides.[a]

Entry	precatalyst	Temp. (°C)	Time (h)	Conv.[b] (%)
1	(salfen)Zr(O^{t}Bu)$_2$	100	24	<3
2	(salfen)Zr(O^{i}Pr)$_2$	100	24	70
3	(salfen)Zr(O^{n}Pr)$_2$	100	24	60
4	(salfen)Zr(O^{i}Pr)$_2$	70	24	<3
5	(salfen)Zr(O^{i}Pr)$_2$	100/70	2/22	21
6	(salfen)Zr(O^{i}Pr)$_2$	100	24	<3
7	(salfen)Zr(O^{n}Pr)$_2$	100	24	<3

[a] All experiments were conducted in 0.8 mL of C$_6$D$_6$, with 0.004 mmol zirconium compound and 0.4 mmol LA, except for entries 6 and 7, when CL was used (1:100 equivalents), and hexamethylbenzene as an internal standard; [b] the conversion was calculated from the integration of ^{1}H NMR peaks against those of hexamethylbenzene. Dispersity and molar mass information can be found in Table S1.

^{1}H NMR monitoring experiments showed that (salfen)Zr(O^{i}Pr)$_2$ and (salfen)Zr(O^{n}Pr)$_2$ experienced a geometry change during polymerization after 2 hours at 100 °C (Figures S17-18). On the other hand, such a change was not observed for (salfen)Zr(O^{t}Bu)$_2$ at 100 °C after 24 hours (Figure S19). After the geometry change, (salfen)Zr(O^{i}Pr)$_2$ and (salfen)Zr(O^{n}Pr)$_2$ started catalyzing the polymerization of LA. Such activity was not observed for (salfen)Zr(O^{t}Bu)$_2$, an observation consistent with similar reports indicating no activity for cis-β geometry compounds.[24, 51-52] The same reaction (Table 2, entry 4) was tested at 70 °C, but less than 5% conversion was observed after 24 hours. A control experiment (Table 2, entry 5) was designed as follows: firstly, the sample was heated at 100 °C for 2 hours, then at 70 °C for 22 hours. This experiment showed 7% conversion after the first two hours of heating at 100 °C and then 21% overall conversion, demonstrating that the geometry change from cis-β to trans is necessary for the polymerization to occur.

(salfen)Zr(O^{i}Pr)$_2$ and (salfen)Zr(O^{n}Pr)$_2$ were also tested for CL homopolymerization (Table 2, entry 6 and 7) but neither of them showed activity. No polymerization or geometry change of the zirconium compound was observed after heating either zirconium complex at 100 °C for 24 hours in the presence of CL. Though it was proved that the zirconium compounds could isomerize to the trans geometry at 100 °C by themselves, CL did not allow the geometry change to occur.

Although (salfen)Zr(O^{i}Pr)$_2$ did not react with ε-caprolactone, we reasoned that once the geometry change can be induced, the results would be different. Therefore, an experiment was designed to have (salfen)Zr(O^{i}Pr)$_2$ and 100 equivalents of LA reacting for 24 hours at 100 °C first, giving a conversion of 74%, after which, 100 equivalents of CL was added and reacted for another 24 hours at 100 °C, giving a CL conversion of 12% and LA conversion of 90%. This result shows that during the second 24 hours, CL did get polymerized. DOSY NMR spectroscopy was used to show that the product is a copolymer (Figure S16).

In order to understand further the relationship between polymerization and geometry change, we decided to isolate the product of a 1:1 molar equivalent reaction between a zirconium alkoxide and LA (Eq 1). Compound (salfen)Zr(O^{n}Pr)$_2$ was chosen since it has the highest trans geometry isomer ratio at 298 K. The (salfen)Zr(O^{n}Pr)$_2$-LA addition compound was successfully synthesized and isolated as a precipitate from n-hexane. The corresponding NOESY (Figure S20) spectrum indicated that the structure is consistent with a ring opened lactide product.

Variable temperature ^{1}H NMR spectroscopic studies with (salfen)Zr(O^{n}Pr)$_2$-LA complex (Figures S11, S22, and S23) indicate that, at room

temperature, a mixture of the two isomers, cis-β and trans is present. At -30 $^{\circ}$C, the trans isomer predominates, indicating that it is the thermodynamically favored isomer, unlike the case of the zirconium bis-alkoxide complexes. As the temperature was increased, the trans to cis-β interconversion became faster, indicated by the broadening of the NMR peaks.

In order to determine whether the length of the polymer chain has an influence on the cis-β to trans isomerization, we performed another set of variable temperature NMR experiments while the LA polymerization was ongoing (100 equivalents LA added but conversion stoppedonly at 40%). In this case, there was no difference between the spectra taken at temperatures ranging from 25 $^{\circ}$C to 100 $^{\circ}$C (Figure S25). The spectra are consistent with the presence of the trans isomer.
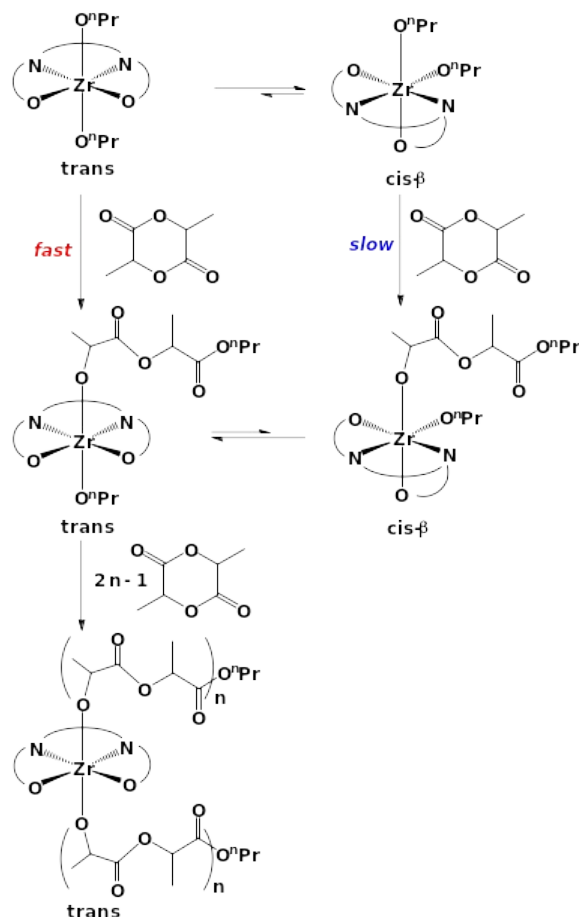
Scheme 2 Proposed reactions between (salfen)Zr(O^{n}Pr)$_2$ and LA.

A comparison of ^{1}H NMR spectra corresponding to (salfen)Zr(O^{n}Pr)$_2$, (salfen)Zr(O^{n}Pr)$_2$-LA and (salfen)Zr-polymer (Figures S26-27) showed that peaks for cis-β (salfen)Zr(O^{n}Pr)$_2$ were present alongside the mixture of trans and cis-β isomers of (salfen)Zr(O^{n}Pr)$_2$-LA. This finding indicates that it is possible that the cis-β isomer reacts with LA to form cis-β (salfen)Zr(O^{n}Pr)$_2$-LA or that cis-β (salfen)Zr(O^{n}Pr)$_2$-LA originates only from the trans to cis-β isomerization and the amount of cis-β (salfen)Zr(O^{n}Pr)$_2$ present at the end of the

reaction is unreacted starting material. These possibilities are shown in Scheme 2.

Computational studies also support the fact that the trans isomer of (salfen)Zr(O^{n}Pr)$_2$-LA is more stable than the cis-β form. The products of the ring opening polymerization of one L-lactide by cis-β and trans zirconium modeled complexes (aryl ^{t}Bu groups replaced by hydrogen atoms) were calculated with the full O^{t}Bu, O^{i}Pr, and O^{n}Pr ligands (Table S3, entries 18-23). In all cases, trans (salfen)Zr(O^{n}R)$_2$-LA is more favorable than the cis-β isomer by xx, yy, and zz kcal/mol, respectively.

CONCLUSION

We synthesized and characterized a series of zirconium alkoxide complexes bearing a ferrocene unit in the ligand backbone. All three compounds adopted a cis-β coordination geometry as the major isomer in solution in room temperature. The solid state molecular structures showed, however, that although (salfen)Zr(O^{t}Bu)$_2$ crystallized as the cis-β isomer, the trans isomer of (salfen)Zr(O^{i}Pr)$_2$ and (salfen)Zr(O^{n}Pr)$_2$ was characterized by single crystal X-ray diffraction. An equilibrium between the cis-β and trans isomers is established in solution as supported by variable temperature ^{1}H NMR spectroscopy. Compounds (salfen)Zr(O^{i}Pr)$_2$ and (salfen)Zr(O^{n}Pr)$_2$ catalyzed the ring opening polymerization of LA after a geometry change to the trans isomer occurred. The product isolated from a 1:1 LA to (salfen)Zr(O^{n}Pr)$_2$ addition, along with computational studies, also supported the conclusion that a geometry change to the trans isomer is necessary for the reaction with LA to occur.

EXPERIMENTAL SECTION

General considerations. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[53] and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. ^{1}H NMR spectra were recorded on Bruker 300 and Bruker 500 spectrometers at room temperature in C$_6$D$_6$ or CDCl$_3$. Chemical shifts are reported with respect to internal solvent: 7.16 ppm (C$_6$D$_6$) and 7.26 ppm (CDCl$_3$) for ^{1}H NMR spectra. Cyclohexene oxide and 1,2-difluorobenzene were distilled over CaH$_2$ and brought into the glovebox without exposure to air. L-Lactide and hexamethylbenzene were recrystallized from toluene at least twice before use. 2,4-Di-*tert*-butylphenol, *n*-BuLi, cobaltocene, Zr(O^{t}Bu)$_4$, Zr(O^{i}Pr)$_4$·HO^{i}Pr and Zr(O^{n}Pr)$_4$·HO^{n}Pr were purchased from VWR and used as received. ^{Ac}FcBAr^{F54} and H$_2$(salfen)[39] were synthesized following previously published procedures. Molar masses of the polymers were determined with a GPC-MALS instrument at UCLA. GPC-MALS uses a Shimadzu Prominence-i LC 2030C 3D instrument equipped with an autosampler,

two MZ Analysentechnik MZ-Gel SDplus LS 5 μm, 300 × 8 mm linear columns, and Wyatt DAWN HELEOS-II and Wyatt Optilab T-rEX apparatus. The column temperature was set at 40 °C. A flow rate of 0.70 mL/min was used, and samples were dissolved in chloroform or THF. dn/dc values were calculated for PLA and PCHO by making five solutions of increasing concentration (0.1− 1.0 mg/mL), directly injecting them into the RI detector sequentially, and using the batch dn/dc measurement methods in the Astra software. The dn/dc values for PLA and PCHO were calculated to be 0.024 and 0.086 mL/g, respectively, over three trials.

DFT calculations. Calculations were performed at the density functional theory level in Turbomole.[55-56] Geometry optimizations and frequency calculations were carried out with the TPSS functional,[57-60] the def2-SVP basis set was used on all non-metal atoms[61-62] and the def2-TZVPP basis set was used for Fe and Zr.[62] Single point energies were calculated with the TPSSH functional[58-60, 63] and the def2-TZVPP basis set was used on all atoms. DFT-D3 was applied on all calculations to account for dispersion corrections.[64] For solvation effects, COSMO[65-66] was applied with the dielectric constant corresponding to benzene (ε = 2.27). All structures were confirmed by their vibrational frequencies; intermediate structures were characterized by zero imaginary frequencies. The Gibbs free energy was calculated as the sum of the *in vacuo* electronic energy, solvation free energy, zero-point energy, and the entropic and thermal corrections obtained from the frequency calculations at 298.15 K and 1 atm.

Synthesis of (salfen)Zr(O^{t}Bu)$_2$. H$_2$(salfen) (194.6 mg, 0.3 mmol) and Zr(O^{t}Bu)$_4$ (115.0 mg, 0.3 mmol) were each dissolved in 5 mL toluene. Both solutions were cooled to -78 °C for 10 min and then combined. The mixture was stirred at -78 °C for 30 min and warmed to room temperature for 2 h. The volatiles were removed under a reduced pressure and the resulting solids were dissolved into hexanes and filtered through Celite. The hexanes solution was concentrated under vacuum and put into a -30 °C freezer to give (salfen)Zr(O^{t}Bu)$_2$ as an amorphous precipitate after four days; yield: 134 mg (51%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K, δ, ppm): 8.17 (s, 1H, N=CH), 8.04 (s, 1H, N=CH), 7.76 (d, 1H, m-OC$_6$H$_2$), 7.64 (d, 1H, m-OC$_6$H$_2$), 7.11 (d, 1H, m-OC$_6$H$_2$), 6.99 (d, 1H, m-OC$_6$H$_2$), 6.27 (s, 1H, C$_5$H$_4$), 4.6-3.7 (m, 7H, C$_5$H$_4$), 1.78 (s, 9H, OC(CH$_3$)$_3$), 1.59 (s, 9H, OC(CH_3)$_3$), 1.41 (s, 9H, C(CH_3)$_3$), 1.35 (s, 9H, C(CH_3)$_3$), 1.33 (s, 9H, C(CH_3)$_3$), 1.16 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (500 MHz, C$_6$D$_6$, 298 K, δ, ppm): 174.3 (N=C), 165.3 (N=C), 162.4 (m-OC_6H$_2$), 161.7 (m-OC_6H$_2$), 139.7 (m-OC_6H$_2$), 138.6 (m-OC_6H$_2$), 138.4 (m-OC_6H$_2$), 137.5 (m-OC_6H$_2$), 130.3 (m-OC_6H$_2$), 129.6 (m-OC_6H$_2$), 129.5 (m-OC_6H$_2$), 127.3 (m-OC_6H$_2$), 123.7 (m-OC_6H$_2$), 123.2 (m-OC_6H$_2$), 111.6 (m-OC_6H$_2$), 107.6 (C_5H$_4$), 76.2 (C_5H$_4$), 75.4 (C_5H$_4$), 70.3 (C_5H$_4$), 69.2 (C_5H$_4$), 68.1 (C_5H$_4$), 67.9 (C_5H$_4$), 66.4 (C_5H$_4$), 66.3 (C_5H$_4$), 65.2 (OC(CH$_3$)$_3$), 62.6 (OC(CH$_3$)$_3$), 35.5 (C(CH$_3$)$_3$), 34.9 (C(CH$_3$)$_3$), 34.1 (C(CH$_3$)$_3$), 33.8 (C(CH$_3$)$_3$), 33.1 (C(CH$_3$)$_3$), 31.9 (C(CH$_3$)$_3$), 31.3 (C(CH$_3$)$_3$), 30.4 (C(CH$_3$)$_3$), 29.9 (C(CH$_3$)$_3$). Anal. Calcd. for (salfen)Zr(O^{t}Bu)$_2$•(C$_6$H$_{14}$)$_{0.5}$ (C$_{51}$H$_{75}$N$_2$O$_4$FeZr): C, 66.06; H, 8.15; N, 3.02; Found: C, 65.63; H, 8.52; N, 2.91.

Synthesis of (salfen)Zr(O^{i}Pr)$_2$. H$_2$(salfen) (163.0 mg, 0.25 mmol) was dissolved in toluene (5 mL) and Zr(O^{i}Pr)$_4$•HO^{i}Pr (193.9 mg, 0.5 mmol) was dissolved in toluene (10 mL), respectively. Both solutions were cooled to -78 °C for 10 min and combined. The mixture was stirred at -78 °C for 30 min and move to room temperature for 2 h. The volatiles were removed under

a reduced pressure for 5 h. The solids were dissolved again in toluene, stir for 2 h and the volatiles were removed under a reduced pressure again for 5 h, and repeat this "dissolve-stir-pump" procedure for one more time. The solids were dissolved into hexanes and filtered through Celite. The hexanes solution was concentrated under reduced pressure and put into freezer to give (salfen)Zr(O^{i}Pr)$_2$ as a crystalline precipitate after four days. Yield: 102 mg (47%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K, δ, ppm): 8.17 (s, 1H, N=CH), 8.03 (s, 1H, N=CH), 7.76 (d, 1H, m-OC$_6$H$_2$), 7.66 (d, 1H, m-OC$_6$H$_2$), 7.11 (d, 1H, m-OC$_6$H$_2$), 6.99 (d, 1H, m-OC$_6$H$_2$), 5.83 (s, 1H, C$_5$H$_4$), 4.60 (m, 1H, OCH(CH$_3$)$_2$), 4.30 (m, 1H, OCH(CH$_3$)$_3$), 4.4-3.8 (m, 7H, C$_5$H$_4$), 1.78 (s, 6H, OCH(CH_3)$_2$), 1.47 (s, 6H, OCH(CH_3)$_2$), 1.34 (s, 18H, C(CH_3)$_3$), 1.32 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (500 MHz, C$_6$D$_6$, 298 K, δ, ppm): 173.3 (N=C), 164.8 (N=C), 162.5 (m-OC_6H$_2$), 161.7 (m-OC_6H$_2$), 139.6 (m-OC_6H$_2$), 138.7 (m-OC_6H$_2$), 138.6 (m-OC_6H$_2$), 137.6 (m-OC_6H$_2$), 130.0 (m-OC_6H$_2$), 129.6 (m-OC_6H$_2$), 129.3 (m-OC_6H$_2$), 123.5 (m-OC_6H$_2$), 123.1 (m-OC_6H$_2$), 111.4, 107.7 (C_5H$_4$), 71.7 (C_5H$_4$), 70.6 (C_5H$_4$), 70.0 (C_5H$_4$), 69.7 (C_5H$_4$), 68.5 (C_5H$_4$), 67.9 (C_5H$_4$), 67.3 (C_5H$_4$), 66.5, (C_5H$_4$), 64.7, 62.3 (OCH(CH$_3$)$_2$), 35.5 (C(CH$_3$)$_3$), 35.1 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 33.8 (C(CH$_3$)$_3$), 31.3 (C(CH$_3$)$_3$), 30.1 (C(CH$_3$)$_3$), 29.9 (C(CH$_3$)$_3$), 27.3 (C(CH$_3$)$_3$), 26.4 (OCH(CH_3)$_2$), 26.3 (OCH(CH_3)$_2$). Anal. Calcd. for C$_{46}$H$_{64}$N$_2$O$_4$FeZr: C, 64.54; H, 7.53; N, 3.27. Found: C, 64.42; H, 7.36; N, 3.17.

Synthesis of (salfen)Zr(O^{n}Pr)$_2$. H$_2$(salfen) (163.0 mg, 0.25 mmol) was dissolved in toluene (5 mL) and Zr(O^{n}Pr)$_4$•HO^{n}Pr (193.9 mg, 0.5 mmol) was dissolved in toluene (10 mL), respectively. Both solutions were cooled to -78 °C for 10 min and combined. The mixture was stirred at -78 °C for 30 min and move to room temperature for 2 h. The volatiles were removed under a reduced pressure for 5 h. The solids were dissolved again in toluene, stirred for 2 h and the volatiles were removed under a reduced pressure again for 5 h; this "dissolve-stir-pump" procedure was repeated for one more time. Finally, the solids were dissolved into hexanes and filtered through Celite. The hexane solution was concentrated under reduced pressure and put into freezer to give (salfen)Zr(O^{n}Pr)$_2$ as a crystalline precipitate after four days. Yield: 113 mg (53%). ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K, δ, ppm): 8.17 (s, 1H, N=CH), 8.03 (s, 1H, N=CH), 7.76 (d, 1H, m-OC$_6$H$_2$), 7.65 (d, 1H, m-OC$_6$H$_2$), 7.10 (d, 1H, m-OC$_6$H$_2$), 6.98 (d, 1H, m-OC$_6$H$_2$), 5.76 (s, 1H, C$_5$H$_4$), 4.38 (m, 2H, OCH_2CH$_2$CH$_3$), 4.28 (m, 2H, OCH_2CH$_2$CH$_3$), 4.5-3.8 (m, 7H, C$_5$H$_4$), 1.88 (m, 4H, OCH$_2$CH_2CH$_3$), 1.78 (m, 6H, OCH$_2$CH$_2$CH_3), 1.47 (s, 18H, C(CH_3)$_3$), 1.33 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (500 MHz, C$_6$D$_6$, 298 K, δ, ppm): 174.2 (N=C), 169.7 (N=C), 163.4 (m-OC_6H$_2$), 162.5 (m-OC_6H$_2$), 140.6 (m-OC_6H$_2$), 138.7 (m-OC_6H$_2$), 138.6 (m-OC_6H$_2$), 137.6 (m-OC_6H$_2$), 129.9 (m-OC_6H$_2$), 129.6 (m-OC_6H$_2$), 129.4 (m-OC_6H$_2$), 124.1 (m-OC_6H$_2$), 123.9 (m-OC_6H$_2$), 112.0 (C_5H$_4$), 108.7 (C_5H$_4$), 73.3 (C_5H$_4$), 72.8 (C_5H$_4$), 72.1 (C_5H$_4$), 71.0 (C_5H$_4$), 68.5 (C_5H$_4$), 67.9 (C_5H$_4$), 67.3 (C_5H$_4$), 65.8 (C_5H$_4$), 65.6 (OCH$_2$CH$_2$CH$_3$), 63.3 (OCH$_2$CH$_2$CH$_3$), 36.8 (OCH$_2$$CH_2CH_3$), 36.4 (OCH$_2$$CH_2CH_3$), 34.6 (OCH$_2$$CH_2CH_3$), 33.8 (OCH$_2CH_2$$CH_3$), 31.3 (C(CH$_3$)$_3$), 30.1 (C(CH$_3$)$_3$), 29.9 (C(CH$_3$)$_3$), 28.9 (C(CH$_3$)$_3$), 28.5 (C(CH$_3$)$_3$), 28.1 (C(CH$_3$)$_3$). Anal. Calcd. for C$_{46}H_{64}N_2O_4$FeZr: C, 64.54; H, 7.54; N, 3.27. Found: C, 63.97; H, 7.48; N, 3.18.

Synthesis of (salfen)Zr(O^{n}Pr)$_2$-LA. (salfen)Zr(O^{n}Pr)$_2$ (207.6 mg, 0.24 mmol) and LA (35.7 mg, 0.24 mmol) were added to benzene (4.5 mL). The mixture was sealed in a Schlenk tube, brought out of the glovebox, heated and stirred at 100 °C overnight. The Schlenk tube was brought into the glovebox the next day. The volatiles were removed under a reduced

pressure and the solids were dissolved in hexanes and filtered through Celite. The hexanes solution was concentrated under reduced pressure and put into a freezer to give the compound as a needle-shape crystalline precipitate after 7 days. Yield: 85 mg (35%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K, δ, ppm): 8.11 (s, 2H, N=CH), 7.71 (s, 2H, m-OC$_6$H$_2$), 7.02 (s, 2H, m-OC$_6$H$_2$), 5.33 (br, 2H, C$_5$H$_4$), 4.66 (br, 2H, C$_5$H$_4$), 4.16 (br, 2H, C$_5$H$_4$), 4.07 (br, 2H, C$_5$H$_4$), 4.88 (s, 2H, OCH(CH$_3$)COO), 3.81 (br, 2H, OCH_2CH$_2$CH$_3$), 3.79 (br, 2H, OCH_2CH$_2$CH$_3$), 1.84 (br, 3H, OCH(CH_3)COO), 1.59 (br, 3H, OCH(CH_3)COO), 1.41 (br, 2H, OCH$_2$CH_2CH$_3$), 1.23 (br, 2H, OCH$_2$CH_2CH$_3$), 1.30 (br, 36H, C(CH_3)$_3$), 0.89 (br, 6H, OCH$_2$CH$_2$CH_3). ^{13}C NMR (500 MHz, C$_6$D$_6$, 298 K, δ, ppm): 176.1 (COO), 171.3 (N=C), 162.8 (m-OC_6H$_2$), 139.8 (m-OC_6H$_2$), 139.5 (m-OC_6H$_2$), 130.9 (m-OC_6H$_2$), 128.0 (m-OC_6H$_2$), 124.2 (m-OC_6H$_2$), 108.4 (C_5H$_4$), 75.0 (OCHCOO), 69.8 (C_5H$_4$), 69.3 (C_5H$_4$), 68.9 (C_5H$_4$), 68.7 (C_5H$_4$), 67.7 (C_5H$_4$), 66.5 (C_5H$_4$), 65.9 (C_5H$_4$), 64.8 (C_5H$_4$), 34.7 (C(CH$_3$)$_3$), 32.2 (C(CH_3)$_3$), 31.0 (OCH$_2$CH_2CH$_3$), 22.9 (OCH$_2$CH$_2$CH_3). Anal. Calcd. for (salfen)Zr(O^{n}Pr)$_2$-LA•(C$_6$H$_{14}$)$_{0.5}$ (C$_{55}$H$_{79}$N$_2$O$_8$FeZr): C, 63.32; H, 7.63; N, 2.69. Found: C, 63.27; H, 7.46; N, 2.65.

Polymerization of LA by (salfen)Zr(O^{i}Pr)$_2$. To a C$_6$D$_6$ (0.7 mL) solution of (salfen)Zr(O^{i}Pr)$_2$ (3.4 mg, 4.0 μmol) in a J. Young NMR tube were added a solution of hexamethylbenzene (8.1 mg, 5.0 μmol) in C$_6$D$_6$ (0.1 mL) and LA powder (57.6 mg, 0.4 mmol). The reaction mixture was heated to 100 °C for 24 hours and monitored by ^{1}H NMR spectroscopy. At the end, the reaction mixture was dissolved in CH$_2$Cl$_2$ and poured into cold methanol; a white solid precipitated briefly and was filtered.

Copolymerization of LA and CL by (salfen)Zr(O^{i}Pr)$_2$. To a C$_6$D$_6$ (0.7 mL) solution of (salfen)Zr(O^{i}Pr)$_2$ (3.4 mg, 4.0 μmol) in a J. Young NMR tube were added a solution of hexamethylbenzene (8.1 mg, 5.0 μmol) in C$_6$D$_6$ (0.1 mL) and LA powder (57.6 mg, 0.4 mmol). The reaction mixture was heated to 100 °C for 24 hours and monitored by ^{1}H NMR spectroscopy. CL (45.6 mg, 4.0 μmol) was added after, and heated for another 24 hours, monitoring by ^{1}H NMR spectroscopy. At the end, the reaction mixture was dissolved in CH$_2$Cl$_2$ and poured into cold methanol; a white solid precipitated briefly and was filtered.

ASSOCIATED CONTENT

Supporting Information. NMR spectra, GPC traces, X-ray, and DFT calculation data. This material is available free of charge via the Internet at http://pubs.acs.org. Cifs were deposited with CCDC, numbers 1864411-1864413.

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Notes
The authors declare no competing financial interest.

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