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Ring-Opening Polymerization of Lactide with Zr Complexes of {ONSO} Ligands: From Heterotactically Inclined to Isotactically Inclined Poly(lactic acid)

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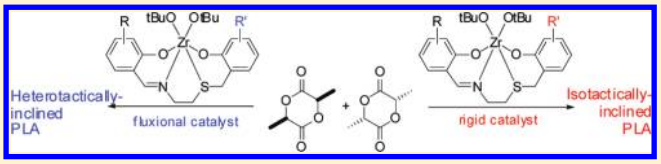
ABSTRACT: Six members of a new family of {ONSO}-type ligands—the tetradentate-diainionic imine-thiobis(phenolate) ligands—were prepared by a two-step synthesis. Their [{ONSO}Zr(O^{t}Bu)$_2$] complexes formed as single diastereomers with different degrees of fluxionality that depended on the substitution pattern of the two phenolate rings. The complexes were active in polymerization of L-lactide and *rac*-lactide. The tacticity of the poly(lactic acid) prepared from *rac*-lactide changed gradually from heterotactically inclined through atactic to isotactically inclined. The most flexible complex and the most rigid complex gave the highest degrees of heterotacticity and isotacticity, respectively.



INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable polyester derived from annually renewable resources, which finds applications as a commodity plastic and in biomedicine.[1] The physical properties and degradation tendency of PLA depend strongly on the microstructure of the polymer chains, and, in particular, on their stereochemistry.[2] The most common method of producing PLA is the ring-opening polymerization (ROP) of lactide, the cyclic dimer of lactic acid.[3] Lactide includes two stereogenic centers, which are not altered in the polymerization process by catalysts operating by the coordination−insertion mechanism. The tacticity of the obtained PLA thus depends on the constitution of the monomer and on the selectivity of the catalyst.[2a,4] Polymerization of the homochiral lactides, L-lactide and D-lactide yields the isotactic enantiomeric polymers poly(L-lactic acid), PLLA, and poly(D-lactic acid), PDLA, respectively, having a melting point of 180 °C, irrespective of the catalyst employed. For *rac*-lactide, the character of the catalyst plays a crucial role. Non selective catalysts, like the industrially employed tin octoate, give rise to atactic PLA, whereas selective catalysts may favor consecutive insertions of either the same or the opposite lactide enantiomer, with formation of isotactic or heterotactic PLA, respectively. Isoselective catalysts are relatively scarce and may operate by either the chain-end or enantiomorphic-site control mechanism. Most of the isoselective catalysts reported to date are based on aluminum complexes, which feature a low activity.[5,6] A racemic mixture of the isotactic PLLA and PDLA crystallizes as a stereocomplex whose melting point is 50 °C above that of the homochiral polymers, so an isoselective catalyst that can yield a stereocomplex PLA or its stereoblock analogues from *rac*-lactide is highly desirable.[7] Heteroselective catalysts are more abundant.[8] Suitable such catalysts should be devoid of permanent chirality that may favor a specific enantiomer. Indeed, two types of heteroselective catalysts that have emerged recently are the rigid C_s-symmetric catalysts operating by the chain-end control mechanism[9] and the fluxional-chiral catalysts that may operate by the dynamic enantiomorphic site control mechanism and are proposed to invert chirality between consecutive insertions of enantiomeric lactide monomers.[10,11] Herein, we introduce semirigid catalysts for lactide polymerization based on zirconium complexes of newly designed imine−thiobis(phenolate) ligands.[12] We demonstrate that by stepwise adjustment of the ligand character, the tacticity of the PLA produced from *rac*-lactide may be gradually shifted from heterotactically inclined to isotactically inclined.

RESULTS AND DISCUSSION

Ligand Design. Since fluxional-chiral catalysts often induce heterotacticity and rigid-chiral catalysts possibly induce isotacticity, we were intrigued by the possibility of merging these two facets in the form of semirigid complexes, i.e., complexes containing a rigid segment and a flexible segment. A possible way of achieving semirigidity is by designing a sequential tetradentate dianionic ligand that features an internal rigid anchor and an internal flexible anchor. In addition, it is preferred that the complex fluctuation would interconvert between enantiomers rather than diastereomers (so as to avoid a possible bias toward a specific lactide enantiomer by a given catalyst molecule). Therefore, upon binding to a metal, the rigid donor should be nonstereogenic and the flexible donor should be stereogenic. Suitable candidates for these distinct roles are the imine donor that typically orients its neighboring

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donors in a *meridional* arrangement,[13] and the thio donor that typically orients its neighboring donors in a *facial* arrangement,[14] respectively. The peripheral anionic arms were chosen to be of the phenolate type, because their steric and electronic

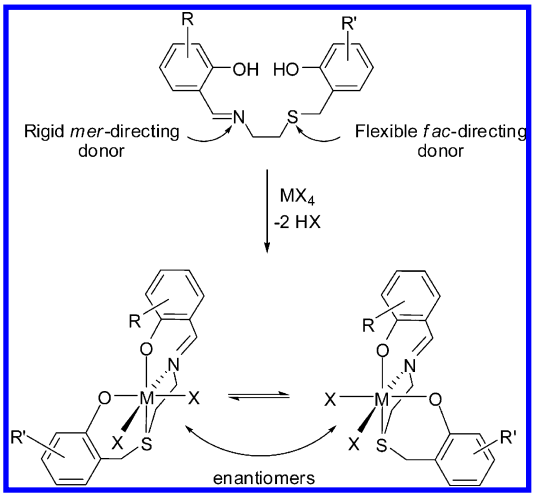


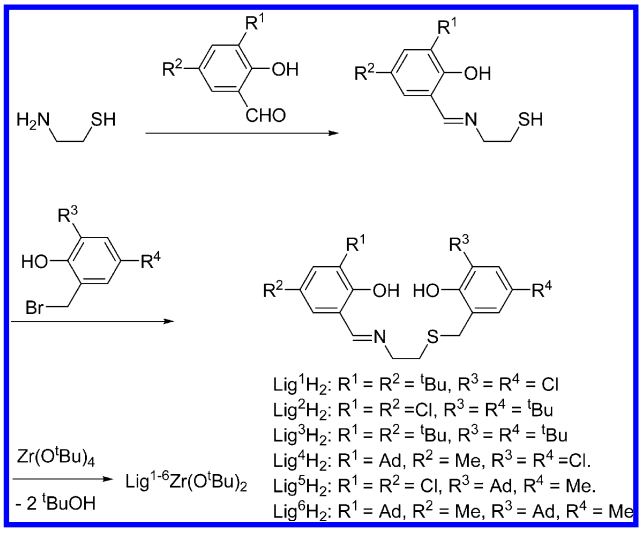
Figure 1. {ONSO} ligand design and proposed structure of semirigid octahedral complexes.

character may be accurately modified by substitutions (Figure 1).

Ligands and Complexes Synthesis and Characterization. Six imine-thiobis(phenolate) ligand precursors were targeted for this exploratory work. They include different combinations of bulky alkyl groups and electron withdrawing chloro groups in the *ortho* and *para* positions of the two phenol rings. As one of the phenol rings is bound to the flexible donor and the other is bound to the rigid donor, the placement of the substituents may play different roles on the degree of fluxionality of the corresponding complexes and on their activity in lactide polymerization. To investigate this possibility, the targeted ligands included the isomeric pairs Lig^1H_2/Lig^2H_2 and Lig^4H_2/Lig^5H_2 having inversely linked substituted phenols. The ligands were prepared in moderate yields by a two step synthesis starting from 2-aminoethanethiol: condensation of the amine functionality with the appropriate salicylaldehyde,[15] followed by nucleophilic reaction of the thiol functionality with the given bromomethyl phenol. The six $\{ONSO\}H_2$ ligand precursors were reacted with 1 equiv of $Zr(O^tBu)_4$ yielding the corresponding $[\{ONSO\}Zr(O^tBu)_2]$ complexes in high to quantitative yields, as described in Scheme 1.

^1H NMR characterization of the complexes revealed that they had all formed as single diastereomers, and supported their mononuclear structures. As expected, the complexes were fluxional. Having a C_1-symmetry on the slow-exchange regime, and an average C_s-symmetry of the fast-exchange regime, the geometry of these complexes is consistent with the proposed *meridional* (imine)/*facial* (thio) wrapping of the {ONSO} ligand around the octahedral metal center (Figure 1). Variable temperature NMR experiments revealed that the barriers for interconversion ranged from $\Delta G^{\ddagger}$ of 13.3 to >19.0 kcal/mol. Bulkier substituents led to higher rigidity, especially if they were located in the *ortho* position of the flexible-segment phenol. For example, $Lig^3Zr(O^tBu)_2$ having two *tert*-butyl groups on both phenol arms exhibited a $\Delta G^{\ddagger}$ of 17.1 kcal/mol. Replacing the two *tert*-butyl groups on the rigid-side phenol with chloro

Scheme 1. Synthesis of the {ONSO} Ligand Precursors and their Zirconium Complexes



groups led to a mild decrease of the interconversion barrier to $\Delta G^{\ddagger}$ = 15.6 kcal/mol ($Lig^2Zr(O^tBu)_2$), while the analogous replacement on the flexible-side phenol led to a more pronounced decrease of the interconversion barrier to $\Delta G^{\ddagger}$ = 13.3 kcal/mol ($Lig^1Zr(O^tBu)_2$). The same trend was found for the complexes of the three other ligands, $Lig^{4-6}Zr(O^tBu)_2$ having interconversion barriers of $\Delta G^{\ddagger}$ = 15.5, 17.7, and >19.0 kcal/mol, respectively, with the highest barrier found for the most crowded complex, containing *ortho*-adamantyl groups on both phenolate rings (Figure 2).

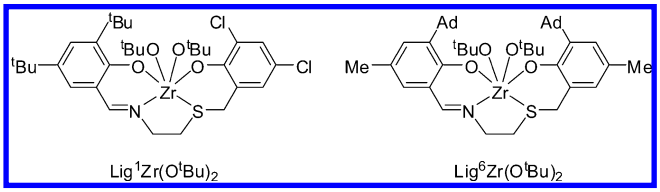


Figure 2. The most fluxional complex ($Lig^1Zr(O^tBu)_2$; $\Delta G^{\ddagger}$ = 13.3 kcal/mol) and the most rigid complex ($Lig^6Zr(O^tBu)_2$; $\Delta G^{\ddagger}$ > 19.0 kcal/mol) described in this work.

Lactide Polymerization. The performance of these $[\{ONSO\}Zr(O^tBu)_2]$ complexes in polymerization of L-lactide and *rac*-lactide was investigated. The complexes exhibited high catalytic activities in the polymerization of both monomers at 140 °C. As may be appreciated from Tables 1 and 2, high conversions of monomer to polymer were usually obtained within a few minutes, and in certain cases almost complete conversions were attained (entries 1 and 3 in Tables 1 and 2). The complex of the bulkiest {ONSO} ligand—$Lig^6Zr(O^tBu)_2$ seemed to be somewhat slower requiring longer times to reach high conversions of both L-lactide and *rac*-lactide. For L-lactide, the molecular weight distributions were relatively narrow (PDI as low as 1.10) which seems to support a living polymerization, however, in several polymerizations, the molecular weights were higher than calculated based on a single growing polymer chain for each catalyst molecule. For example, $Lig^1Zr(O^tBu)_2$ led to PLLA with M_n = 72 600 g mol^{-1} whereas the calculated molecular weight for 87% conversion of 300 equiv of L-lactide is $M_{n,calc}$ = 37 500 g mol^{-1}. This is consistent with partial activation of the catalyst. Slightly broader molecular weight

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Table 1. Polymerization of L-Lactide at 140 °C

entry	initiator[a]	L-lactide (g)	time (min)	PLA obtained (g)	convn	M_n[b] (g mol^{-1})	$M_{n,calc}$[c] (g mol^{-1})	PDI
1	Lig^{1}Zr(O-*tert*-Bu)$_2$	0.62	15	0.54	0.87	72 600	37 500	1.10
2	Lig^{2}Zr(O-*tert*-Bu)$_2$	0.58	14	0.18	0.31	22 300	13 400	1.12
3	Lig^{3}Zr(O-*tert*-Bu)$_2$	0.60	10	0.55	0.92	49 200	39 700	1.39
4	Lig^{4}Zr(O-*tert*-Bu)$_2$	0.58	13	0.41	0.71	20 300	30 600	1.16
5	Lig^{5}Zr(O-*tert*-Bu)$_2$	0.58	6	0.40	0.69	23 000	30 000	1.47
6	Lig^{6}Zr(O-*tert*-Bu)$_2$	0.49	54	0.28	0.57	29 100	24 500	1.17

[a]10 mg of catalyst were employed. [b]Correction parameter 0.58 × M_n polystyrene standards. [c]calculated from 144.13 × (LA/I) × conversion of monomer.

Table 2. Polymerization of *rac*-Lactide at 140 °C

entry	initiator[a]	*rac*-lactide (g)	time (min)	PLA obtained (g)	convn	M_n[b] (g mol^{-1})	$M_{n,calc}$[c] (g mol^{-1})	PDI	P_r/P_m[d]
1	Lig^{1}Zr(O-*tert*-Bu)$_2$	0.62	6	0.58	0.92	16 300	39 500	1.55	0.63/0.37
2	Lig^{2}Zr(O-*tert*-Bu)$_2$	0.61	5	0.46	0.75	17 700	32 500	1.38	0.58/0.42
3	Lig^{3}Zr(O-*tert*-Bu)$_2$	0.63	7	0.61	0.97	20 300	42 000	1.57	0.50/0.50
4	Lig^{4}Zr(O-*tert*-Bu)$_2$	0.58	8	0.42	0.72	9500	31 000	1.44	0.50/0.50
5	Lig^{5}Zr(O-*tert*-Bu)$_2$	0.58	6	0.41	0.70	7000	30 000	1.44	0.50/0.50
6	Lig^{6}Zr(O-*tert*-Bu)$_2$	0.52	18	0.32	0.61	20 300	26 500	1.34	0.55/0.45

[a]10 mg of catalyst were employed. [b]Correction parameter 0.58 × M_n polystyrene standards. [c]Calculated from 144.13 × (LA/I) × conversion of monomer. [d]P_r and P_m are the probability for heterotactic and isotactic enchainment calculated from homonuclear decoupled ^{1}H NMR spectrum.

Table 3. Polymerization of *rac*-Lactide at 70 °C in Toluene

entry	initiator[a]	*rac*-lactide (g)	PLA obtained (g)	convn	M_n[b] (g mol^{-1})	$M_{n,calc}$[c] (g mol^{-1})	PDI	P_r/P_m[d]
1	Lig^{1}Zr(O-*tert*-Bu)$_2$	0.64	0.63	0.98	8500	42 000	1.45	0.72/0.28
2	Lig^{2}Zr(O-*tert*-Bu)$_2$	0.59	0.51	0.87	14 700	37 500	1.50	0.65/0.35
3	Lig^{3}Zr(O-*tert*-Bu)$_2$	0.62	0.50	0.81	21 300	35 000	1.70	0.50/0.50
4	Lig^{4}Zr(O-*tert*-Bu)$_2$	0.57	0.40	0.70	11 200	30 000	1.42	0.50/0.50
5	Lig^{5}Zr(O-*tert*-Bu)$_2$	0.59	0.44	0.75	8700	32 500	1.56	0.38/0.62
6	Lig^{6}Zr(O-*tert*-Bu)$_2$	0.56	0.09	0.18	18 000	8000	1.17	0.33/0.67

[a]10 mg of catalyst and 5 mL of toluene were employed. Polymerization time was 20 h. [b]Correction parameter 0.58 × M_n polystyrene standards. [c]Calculated from 144.13 × (LA/I) × conversion of monomer. [d]P_r and P_m are the probability for heterotactic and isotactic enchainment calculated from homonuclear decoupled ^{1}H NMR spectrum.

distributions and lower molecular weights were found for polymerizations of *rac*-lactide with these catalysts at 140 °C, and the molecular weights of the PLA did not exceed the calculated values (Table 2). The solution polymerizations of *rac*-lactide were pursued for 20 h (Table 3). Most catalysts, except for Lig^{6}Zr(O^{t}Bu)$_2$, exhibited high conversions after that period. The molecular weights and molecular weight distributions were generally in line with the values obtained for the polymerizations run in the melt. The polymerization of *rac*-lactide versus time by Lig^{2}Zr(O^{t}Bu)$_2$ in toluene-d_8 at 90 °C was monitored by ^{1}H NMR spectroscopy. Following an induction period of a few minutes (that may be caused by catalyst activation as well as monomer dissolution), the polymerization was found to be first order with respect to lactide up to a conversion of 88% (8 h), as evident from a linear relationship of ln([lactide]$_{t=0}$/[lactide]$_t$) versus time (Figure 3).

We found that the microstructure of the PLA obtained in the polymerization of *rac*-lactide could be gradually shifted by variation of the phenolate substituents. Significantly, the character of the substituents on the flexible segment phenol played a major role, and the character of the substituents on the rigid segment phenol played a minor role, in parallel to their effects on the fluxionality of the complexes. This phenomenon, clearly observable in the homodecoupled ^{1}H NMR spectra of the PLA was more apparent for the solution polymerizations run at 70 °C. The most flexible complex—Lig^{1}Zr(O^{t}Bu)$_2$—which includes chloro substituents on the flexible segment

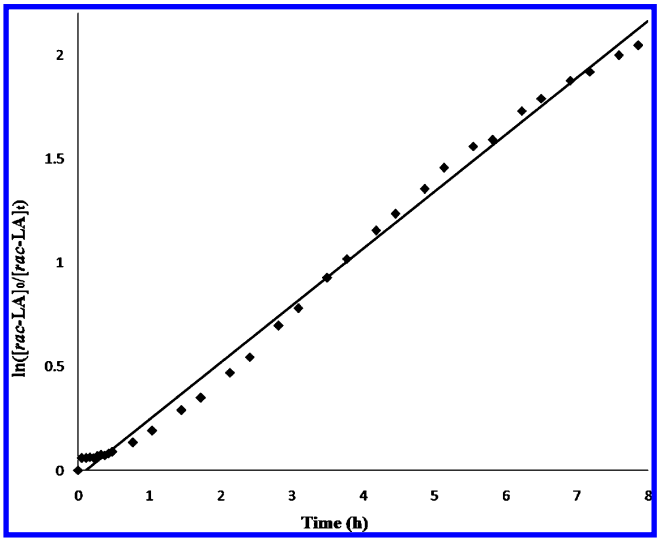

Figure 3. Semilogarithmic plot of *rac*-LA conversion versus time employing Lig^{2}Zr(O^{t}Bu)$_2$ in toluene-d_8 at 90 °C. [*rac*-LA]$_{t=0}$ = 0.34 M. [*rac*-LA]$_{t=0}$: [Zr] = 80. r^2 = 0.994.

phenol and *tert*-butyl substituents on the rigid segment phenol led to PLA having the highest degree of heterotacticity, with P_r = 0.72 at 70 °C. The degree of heterotacticity was diminished to P_r = 0.63 at 140 °C. Lig^{4}Zr(O^{t}Bu)$_2$, the analogous complex

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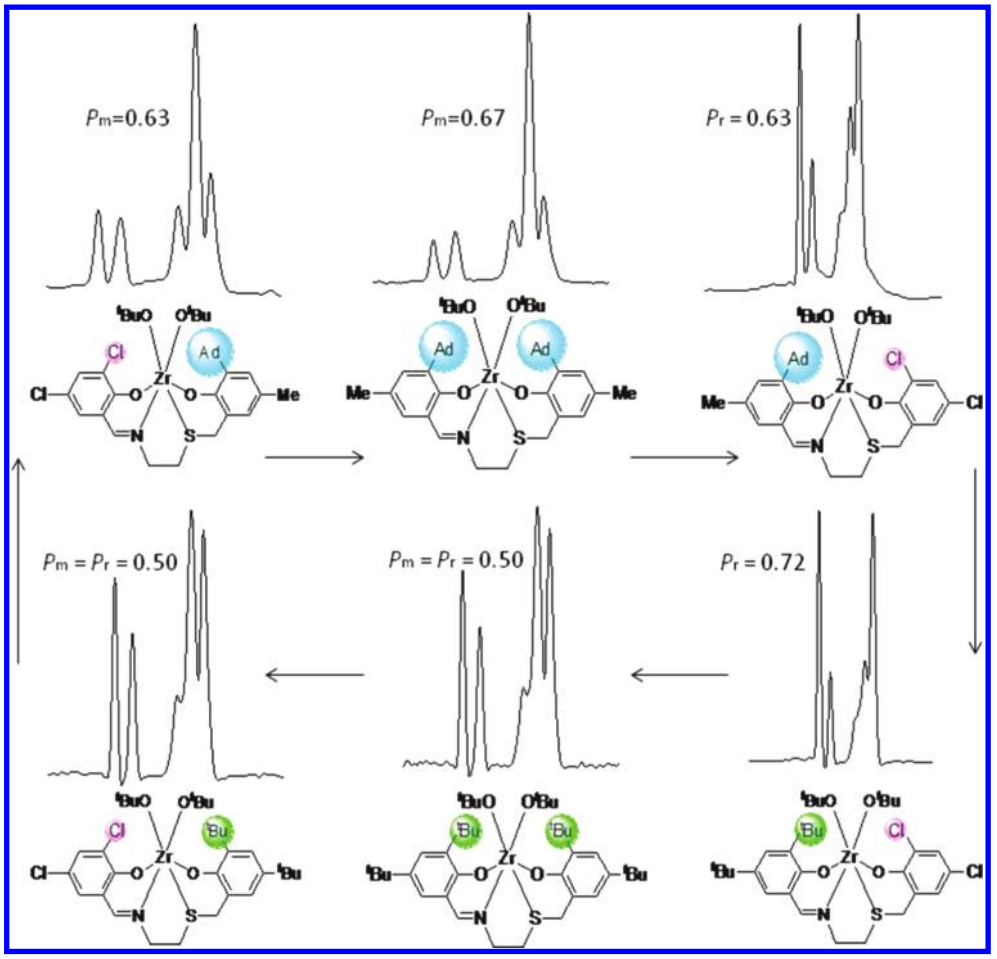

Figure 4. Homo-decoupled ^{1}H NMR of the polymer samples prepared from catalysts Lig$^{1-6}$Zr(O^{t}Bu)$_2$ at 70 °C in toluene.

which includes chloro substituents on the flexible segment phenol and an *o*-adamantyl substituent on the rigid segment phenol led to PLA with a slightly lower heterotacticity of P_r = 0.65 at 70 °C and P_r = 0.58 at 140 °C. Lig^{2}Zr(O^{t}Bu)$_2$ and Lig^{3}Zr(O^{t}Bu)$_2$, the two complexes featuring *tert*-butyl groups on the flexible segment phenol, yielded atactic PLA at both 70 °C and at 140 °C. Most unusually, Lig^{5}Zr(O^{t}Bu)$_2$ and Lig^{6}Zr(O^{t}Bu)$_2$, the two complexes featuring the bulky 1-adamantyl *ortho*-substituent on the flexible segment phenol led to clear isoselective polymerization at 70 °C, which was more apparent for the more rigid of the two—Lig^{6}Zr(O^{t}Bu)$_2$ that yielded PLA with P_m = 0.67. The isoselectivity was reduced for the two complexes at 140 °C. The transition between tacticity types can be clearly appreciated in the homodecoupled ^{1}H NMR spectra of the corresponding polymers in Figure 4. Notably, reverse tacticity induction could be attained by merely inverting the substitution patterns on the two different phenol arms, as apparent for the isomer pair Lig^{4}Zr(O^{t}Bu)$_2$ (P_r = 0.63) and Lig^{5}Zr(O^{t}Bu)$_2$ (P_m = 0.63). To our knowledge, the only precedence for reversal of tacticity of PLA in *rac*-lactide polymerization upon a change of the substitution pattern of a given ligand bound to a given metal involved Salan and related ligands bound to aluminum.[16] While the tacticities reported herein are not exceptionally high, the ability to manipulate them by ligand modifications, and the relatively high catalytic activities indicate that such design motifs may be important for future stereoselective catalysts.

CONCLUSIONS

In summary, zirconium complexes of tetradentate ligands that combine a rigid segment and a flexible segment were described. These tailor-made complexes exhibited broad ranges of steric congestion on each of the different phenol arms that was manifested in their degree of fluxionality. Notably, the substitution pattern on the phenolate rings was shown to play equivalent roles in the degree of fluxionality of the complexes and in their tendencies to insert the same or the opposite lactide enantiomer, i.e., their tendency to form isotactic or heterotactic PLA from *rac*-lactide. It still needs to be established whether the reversal of stereoselectivity is a direct consequence of the change of ligand substitution pattern, or results from the change of complex fluxionality. Current efforts in our groups include the development of rigid analogues of the above systems aiming at catalysts of higher isoselectivity based on the findings introduced herein.

EXPERIMENTAL SECTION

General Information. All reactions with air- and/or water sensitive compounds were carried out under dry nitrogen atmosphere in a glovebox. Ether was purified by distillation under dry argon atmosphere from purple Na/benzophenone solution. Pentane was washed with HNO_3/H_2SO_4 prior to distillation from Na/benzophenone/tetraglyme. Toluene was refluxed over Na and distilled. 3,5-Dichloro-2-hydroxybenzaldehyde, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 2-aminoethanethiol, triethylamine, and Zr(*tert*-butoxide)$_4$ were purchased from Aldrich and used as received. D-Lactide and L-lactide were obtained by Purac and used as received, *rac*-lactide was prepared

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by mixing equal molar amounts of L-lactide and D-lactide and crystallizing from toluene. 3-Adamantyl-2-hydroxy-5-methylbenzaldehyde,[17] 2-(bromomethyl)-4,6-dichlorophenol,[18] 2-(bromomethyl)-4,6-di-*tert*-butylphenol,[18] and 2-(bromomethyl)-4-methyl-6-adamanthylphenol[19] were synthesized according to published procedures.

All NMR data were recorded on a Bruker Avance-400 spectrometer. C_6D_6 (impurities in benzene-d_6 at δ 7.15, and ^{13}C chemical shift of benzene at δ 128.70 were used as reference) and C_7D_8 (impurities in toluene-d_8 at δ 2.09, 6.98, 7.00, 7.09) were used as NMR solvents for the metal complexes. $CDCl_3$ was used as NMR solvent for the PLA samples (chemical shift of TMS at δ 0.00 as reference). Elemental analyses were performed in the microanalytical laboratory at the Hebrew University of Jerusalem. PLA molecular weights were determined by gel permeation chromatography (GPC) using TSKgel GMHHR-M and TSKgel G 3000 HHR columns set on a Jasco instrument equipped with a refractive index detector. Molecular weight determination was carried out relative to polystyrene standards using THF (high-performance liquid chromatography grade, distilled and filtered under vacuum prior to use) as the eluting solvent.

Synthesis of 2-(Mercaptoethylimino)methyl-4,6-ditert-butylphenol. 2-Aminoethanethiol (0.88 g, 11.4 mmol) was added to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.68 g, 11.4 mmol) in benzene and refluxed for 2 h. The solvent was evaporated yielding a yellow solid (3.14 g, 93%). MS(APPI): calcd for $C_{17}H_{27}NOS$, 293.5; found, 294.1.

Synthesis of Lig^{1}H$_2$. A solution of 2-(bromomethyl)-4,6-dichlorophenol (1.40 g, 5.5 mmol) in THF (20 mL) was added dropwise to a solution of 2-(mercaptoethylimino)methyl-4,6-di-*tert*-butylphenol (1.61 g, 5.5 mmol) and triethylamine (0.75 mL) in THF (20 mL) and stirred for 2 h. The solid that had formed was filtered out, the solvent was removed under vacuum. The crude product was purified by flash chromatography over Silica gel 60 with a mixture of petroleum ether/dichloromethane in increasing polarity as eluent. The pure product was obtained as a yellow solid in a final yield of 40%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H, NCH), 7.39 (d, 1H, J = 2.4 Hz, ArH), 7.23 (d, 1H, J = 2.4 Hz, ArH), 7.15 (d, 1H, J = 2.4 Hz, ArH), 7.09 (d, 1H, J = 2.4 Hz, ArH), 3.76 (s, 2H, $ArCH_2S$), 3.74 (t, 2H, J = 6.7 Hz, CH_2), 2.80 (t, 2H, J = 6.7 Hz, CH_2), 1.44 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100.66 MHz, $CDCl_3$), δ 167.3 (CN), 158.1 (C), 148.6 (C), 140.2 (C), 136.8 (C), 129.1 (CH), 127.7 (CH), 127.3 (C), 127.2 (CH), 126.1 (CH), 125.3 (C), 121.1(C), 117.7 (C), 59.2 (CH_2), 35.1 (C), 34.2 (C), 32.6 (CH_2), 31.5 (CH_3), 31.3 (CH_2), 29.5 (CH_3). MS(APPI): calcd for $C_{32}H_{49}NO_2S$, 511.8; found, 534.3 (MNa^+). Anal. Calcd for $C_{24}H_{31}Cl_2NO_2S$: C, 61.53; H, 6.67; N, 2.99. Found: C, 61.95; H, 6.65; N, 2.82.

Synthesis of 2-(Mercaptoethylimino)methyl-4-methyl-6-adamantylphenol. 2-Aminoethanethiol (0.30 g, 3.88 mmol) was added to a solution of 3-adamantyl-2-hydroxy-5-methylbenzaldehyde (1.05 g, 3.88 mmol) in benzene and refluxed for 2 h. The solvent was removed under reduced pressure yielding a yellow solid (0.91 g, 71%). MS(APPI): calcd for $C_{20}H_{27}NOS$, 329.5; found, 330.1.

Synthesis of Lig^{2}H$_2$. A solution of 2-(bromomethyl)-4,6-dichlorophenol (0.60 g, 2.3 mmol) in THF (20 mL) was added dropwise to a solution of 2-(mercaptoethylimino)methyl-4-methyl-6-adamantylphenol (0.76 g, 2.3 mmol) and triethylamine (0.32 mL) in THF (20 mL) and stirred for 2 h. The reaction mixture was worked up as described above for Lig^{1}H$_2$ giving Lig^{2}H$_2$ in a final yield of 50%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H, NCH), 7.25 (d, 1H, J = 2.3 Hz, ArH), 7.16 (d, 1H, J = 2.4 Hz, ArH), 7.08 (d, 1H, J = 1.9 Hz, ArH), 6.90 (d, 1H, J = 3.3 Hz, ArH), 3.75 (s, 2H, $ArCH_2S$), 3.75 (t, 2H, J = 8.3 Hz, CH_2), 2.80 (t, 2H, J = 6.7 Hz, CH_2), 2.28 (s, 3H, $ArCH_3$), 2.16 (bs, 6H, adamantyl), 2.07 (bs, 3H, adamantyl), 1.78 (m, 6H, adamantyl). ^{13}C NMR (100.66 MHz, $CDCl_3$): δ 167.7 (CN), 159.1 (C), 149.3 (C), 138.2 (C), 131.5 (CH), 130.3 (CH), 129.8 (CH), 128.5 (CH), 127.8 (C), 127.5 (C), 126.0 (C), 121.8 (C), 118.9 (C), 59.9 (CH_2), 41.0 (CH_2), 37.9 (CH_2), 37.7 (C), 33.1 (CH_2), 32.0 (CH_2), 29.8 (CH), 21.4 (CH_3). MS(ESI): calcd for $C_{27}H_{31}Cl_2NO_2S$, 504.5; found, 504.2. Anal. Calcd for $C_{27}H_{31}Cl_2NO_2S$: C, 64.28; H, 6.19; N, 2.78. Found: C, 63.14; H, 5.89; N, 2.51.

Synthesis of 2-(Mercaptoethylimino)methyl-4,6-dichlorophenol. 2-Aminoethanethiol (0.99 g, 12.9 mmol) was added to a solution of 3,5-dichloro-2-hydroxybenzaldehyde (2.46 g, 12.9 mmol) in ethanol and stirred for 2 h at room temperature. The solvent was removed under reduced pressure yielding a yellow solid (2.88 g, 89%). MS(APPI): calcd for $C_9H_9Cl_2NOS$, 250.1; found, 250.0.

Synthesis of Lig^{3}H$_2$. A solution of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (1.52 g, 5.1 mmol) in THF (20 mL) was added dropwise to a solution of 2-(mercaptoethylimino)methyl-4,6-dichlorophenol (1.27 g, 5.1 mmol) and triethylamine (0.70 mL) in THF (20 mL) and stirred for 2 h. The reaction mixture was worked up as described above for Lig^{1}H$_2$ giving Lig^{3}H$_2$ in a final yield of 53%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H, NCH), 7.41 (d, 1H, J = 2.5 Hz, ArH), 7.28 (d, 1H, J = 2.4 Hz, ArH), 7.13 (d, 1H, J = 2.5 Hz, ArH), 6.92 (d, 1H, J = 2.7 Hz, ArH), 3.83 (s, 2H, $ArCH_2S$), 3.68 (t, 2H, J = 6.4 Hz, CH_2), 2.74 (t, 2H, J = 6.6 Hz, CH_2), 1.42 (s, 9H, $C(CH_3)_3$), 1.28 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100.66 MHz, $CDCl_3$), δ 164.5 (CN), 156.6 (C), 151.9 (C), 142.5 (C), 137.3 (C), 132.4 (CH), 129.1 (CH), 125.3 (CH), 123.9 (CH), 122.9 (C), 122.7 (C), 121.4 (C), 119.3 (C), 58.1 (CH_2), 34.9 (C), 34.4 (CH_2), 34.2 (C), 31.6 (CH_3), 31.3 (CH_2), 29.8 (CH_3). MS(APPI): calcd for $C_{24}H_{31}Cl_2NO_2S$, 468.5; found, 506.2 (MK^+). Anal. Calcd for $C_{24}H_{31}Cl_2NO_2S$: C, 61.53; H, 6.67; N, 2.99. Found: C, 60.94; H, 6.58; N, 2.69.

Synthesis of Lig^{4}H$_2$. A solution of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (1.46 g, 4.9 mmol) in THF (20 mL) was added dropwise to a solution of 2-(mercaptoethylimino)methyl-4,6-di-*tert*-butylphenol (1.43 g, 4.9 mmol) and triethylamine (0.68 mL) in THF (20 mL) and stirred for 2 h. The reaction mixture was worked up as described above for Lig^{1}H$_2$ giving Lig^{4}H$_2$ in a final yield of 30%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H, NCH), 7.38 (d, 1H, J = 2.0 Hz, ArH), 7.27 (d, 1H, J = 2.1 Hz, ArH), 7.06 (d, 1H, J = 1.9 Hz, ArH), 6.95 (d, 1H, J = 2.0 Hz, ArH), 3.85 (s, 2H, $ArCH_2S$), 3.67 (t, 2H, J = 6.7 Hz, CH_2), 2.72 (t, 2H, J = 6.6 Hz, CH_2), 1.43 (s, 9H, $C(CH_3)_3$), 1.42 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$), 1.27 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100.66 MHz, $CDCl_3$), δ 167.2 (CN), 158.0 (C), 152.0 (C), 142.3 (C), 140.2 (C), 137.2 (C), 136.8 (C), 127.2 (CH), 125.9 (CH), 125.3 (CH), 123.8 (CH), 121.6 (C), 117.7 (C), 59.2 (CH_2), 35.0 (CH_2), 34.5 (CH_2), 34.2 (C), 34.1 (C), 31.6 (CH_3), 31.5 (CH_3), 31.3 (C), 29.8 (CH_3), 29.4 (CH_3), 29.3 (C). MS(APPI): calcd for $C_{32}H_{49}NO_2S$, 511.8; found, 534.3 (MNa^+). Anal. Calcd for $C_{32}H_{49}NO_2S$: C, 75.10; H, 9.65; N, 2.74. Found: C, 75.26; H, 9.36; N, 2.44.

Synthesis of Lig^{5}H$_2$. A solution of 2-(bromomethyl)-4-methyl-6-adamanthylphenol (1.00 g, 3.0 mmol) in THF (20 mL) was added dropwise to a solution of 2-(mercaptoethylimino)methyl-4,6-dichlorophenol (0.75 g, 3.0 mmol) and triethylamine (0.42 mL) in THF (20 mL) and stirred for 2 h. The reaction mixture was worked up as described above for Lig^{1}H$_2$ giving Lig^{5}H$_2$ in a final yield of 31%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H, NCH), 7.41 (d, 1H, J = 2.4 Hz, ArH), 7.14 (d, 1H, J = 2.4 Hz, ArH), 6.99 (d, 1H, J = 1.6 Hz, ArH), 6.73 (s, 1H, ArH), 3.78 (s, 2H, $ArCH_2S$), 3.66 (t, 2H, J = 6.3 Hz, CH_2), 2.74 (t, 2H, J = 6.5 Hz, CH_2), 2.24 (s, 3H, $ArCH_3$), 2.12 (bs, 6H, adamantyl), 2.07 (bs, 3H, adamantyl), 1.77 (bs, 6H, adamantyl). ^{13}C NMR (100.66 MHz, $CDCl_3$): δ 165.3 (CN), 157.3 (C), 152.9 (C), 138.9 (C), 133.1 (CH), 129.9 (C), 129.8 (CH), 129.4 (CH), 128.4 (CH), 123.7 (C), 123.4 (C), 122.8 (C), 120.1 (C), 58.7 (CH_2), 41.4 (CH_2), 37.8 (CH_2), 37.6 (C), 34.8 (CH_2), 32.1 (CH_2), 29.8 (CH), 21.5 (CH_3). MS(APPI): calcd for $C_{27}H_{31}Cl_2NO_2S$, 504.5; found, 526.1 (MNa^+). Anal. Calcd for $C_{27}H_{31}Cl_2NO_2S$: C, 64.28; H, 6.19; N, 2.78. Found: C, 63.83; H, 6.11; N, 2.74

Synthesis of Lig^{6}H$_2$. A solution of 2-(bromomethyl)-4-methyl-6-adamanthylphenol (0.93 g, 2.8 mmol) in THF (20 mL) was added dropwise to a solution of 2-(mercaptoethylimino)methyl-4-methyl-6-adamantylphenol (0.91 g, 2.8 mmol) and triethylamine (0.38 mL) in THF (20 mL) and stirred for 2 h. The reaction mixture was worked up as described above for Lig^{1}H$_2$ giving Lig^{6}H$_2$ in a final yield of 20%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H, NCH), 7.08 (d, 1H, J = 2.0 Hz, ArH), 6.98 (d, 1H, J = 1.9 Hz, ArH), 6.88 (d, 1H, J = 1.8 Hz, ArH), 6.76 (d, J = 1.7, 1H, ArH), 3.77 (s, 2H, $ArCH_2S$), 3.64 (t, 2H, J = 6.4 Hz, CH_2), 2.72 (t, 2H, J = 6.6 Hz, CH_2), 2.28 (s, 3H, $ArCH_3$), 2.24 (s, 3H, $ArCH_3$), 2.17 (m, 6H, adamantyl), 2.13 (m, 6H,

adamantyl), 2.07 (bs, 6H, adamantyl) 1.77 (bs, 12H, adamantyl). ^{13}C NMR (100.66 MHz, $CDCl_3$): δ 167.8 (CN), 159.1 (C), 153.1 (C), 138.8 (C), 138.2 (C), 131.5 (CH), 130.2 (CH), 129.7 (C), 129.6 (CH), 128.2 (CH), 127.5 (C), 122.9 (C), 118.9 (C), 59.9 (CH_2), 41.3 (CH_2), 41.0 (CH_2), 37.9 (CH_2), 37.8 (CH_2), 37.7 (C), 37.6 (C), 34.9 (CH_2), 32.1 (CH_2), 29.8 (CH), 29.8 (CH), 21.5 (CH_3), 21.4 (CH_3). MS(APPI): calcd for $C_{38}H_{49}NO_2S$, 583.9; found, 606.3 (MNa^+). Anal. Calcd for $C_{38}H_{49}NO_2S$: C, 78.17; H, 8.46; N, 2.40. Found: C, 77.89; H, 8.16; N, 2.12.

Synthesis of Lig^{1}Zr(O-tert-Bu)$_2$. Lig^{1}H$_2$ (47 mg, 0.10 mmol) was dissolved in ca. 2 mL of ether and was added dropwise to a solution of $Zr(O^tBu)_4$ (38 mg, 0.10 mmol) at room temperature. The solution was stirred for 2 h after which the solvent was removed under vacuum and the resulting yellow solid was washed with pentane (49 mg, 70%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.71 (d, 1H, J = 1.8 Hz, ArH), 7.29 (d, 1H, J = 1.8 Hz, ArH), 7.24 (s, 1H, NCH), 6.94 (d, 1H, J = 2.0 Hz, ArH), 6.63 (d, J = 2.4, 1H, ArH), 3.50 (bs, 2H, CH_2), 2.85 (bs, 2H, CH_2), 1.91 (m, 2H, CH_2), 1.75 (s, 9H, $C(CH_3)_3$), 1.29 (s, 27H, $C(CH_3)_3$). ^{13}C NMR (100.66 MHz, C_6D_6): δ 167.8 (CN), 160.7 (C), 158.4 (C), 139.1 (C), 138.6 (C), 129.7 (CH), 129.6 (CH), 128.5 (CH), 128.1 (CH), 124.9 (C), 123.4 (C), 122.1 (C), 119.8 (C), 59.2 (CH_2), 35.5 (CH_2), 34.5 (CH_2), 33.9 (C), 32.5 (CH_3), 31.3 (CH_3), 31.1 (C), 29.7 (CH_3). Anal. Calcd for $C_{32}H_{47}Cl_2NO_4SZr$: C, 54.60; H, 6.73; N, 1.99. Found: C, 53.82; H, 6.43; N, 1.75.

Synthesis of Lig^{2}Zr(O-tert-Bu)$_2$. Lig^{2}H$_2$ (34 mg, 0.07 mmol) was dissolved in ca. 2 mL of ether and was added dropwise to a solution of $Zr(O^tBu)_4$ (26 mg, 0.07 mmol) at room temperature. The solution was stirred for 2 h after which the solvent was removed under vacuum, yielding a yellow solid quantitatively (55 mg). ^{1}H NMR (400 MHz, C_6D_6): δ 7.34 (s, 1H, ArH), 7.30 (s, 1H, ArH), 7.28 (s, 1H, NCH), 6.65 (s, 1H, ArH), 6.63 (s, 1H, ArH), 3.68 (d, 1H, J = 11.7, CH), 3.08 (d, 1H, J = 12.6, CH), 3.02 (m, 1H, CH), 2.69 (m, 1H, CH), 2.47 (s, 3H, $ArCH_3$) 2.22 (m, 6H, adamantyl) 2.01 (m, 6H, adamantyl), 1.92 (m, 1H, CH), 1.86 (m, 3H, adamantyl), 1.67 (m, 1H, CH), 1.38 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100.66 MHz, C_6D_6): δ 167.7 (CN), 139.9 (C), 139.4 (C), 134.5 (CH), 132.5 (CH), 130.4 (CH), 126.6 (C), 125.8 (C), 124.0 (C), 123.5 (C), 120.3 (C), 59.7 (CH_2), 41.2 (CH_2), 38.0 (CH_2), 37.4 (C), 35.2 (CH_2), 33.4 (CH_3), 31.6 (CH_2), 30.1 (CH), 21.2 (CH_3). Anal. Calcd for $C_{35}H_{47}Cl_2NO_4SZr$: C, 56.81; H, 6.40; N, 1.89. Found: C, 56.98; H, 6.41; N, 1.85.

Synthesis of Lig^{3}Zr(O-tert-Bu)$_2$. Lig^{3}H$_2$ (46 mg, 0.09 mmol) was dissolved in ca. 2 mL of ether and was added dropwise to a solution of $Zr(O^tBu)_4$ (37 mg, 0.09 mmol) at room temperature. The solution was stirred for 2 h after which the solvent was removed under vacuum, resulting in a yellow solid (62 mg, 90%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.57 (d, 1H, J = 2.5 Hz, ArH), 7.40 (d, 1H, J = 2.7 Hz, ArH), 6.95 (d, 1H, J = 2.4 Hz, ArH), 6.69 (s, 1H, NCH), 6.52 (d, J = 2.7, 1H, ArH), 4.31 (d, 1H, J = 12.2, CH), 3.67 (m, 1H, CH), 3.56 (d, 1H, J = 12.5, CH), 2.11 (m, 3H, CH, CH_2), 1.63 (s, 9H, $C(CH_3)_3$), 1.58 (s, 9H, $C(CH_3)_3$), 1.38 (s, 9H, $C(CH_3)_3$), 1.23 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100.66 MHz, C_6D_6): δ 165.9 (CN), 159.8 (C), 159.5 (C), 139.4 (C), 137.0 (C), 133.9 (CH), 130.3 (CH), 126.5 (C), 126.3 (CH), 124.1 (CH), 123.1 (C), 121.4 (C), 119.6 (C), 76.9 (C), 60.0 (CH_2), 35.9 (CH_2), 35.3 (CH_2), 34.0 (C), 32.5 (CH_3), 31.7 (CH_3), 30.5 (C), 29.7 (CH_3). Anal. Calcd for $C_{32}H_{47}Cl_2NO_4SZr$: C, 54.60; H, 6.73; N, 1.99. Found: C, 54.90; H, 6.68; N, 1.70.

Synthesis of Lig^{4}Zr(O-tert-Bu)$_2$. Lig^{4}H$_2$ (42 mg, 0.08 mmol) was dissolved in ca. 2 mL of ether and was added dropwise to a solution of $Zr(O^tBu)_4$ (32 mg, 0.08 mmol) at room temperature. The solution was stirred for 2 h after which the solvent was removed under vacuum and the resulting yellow solid was washed with pentane affording the product quantitatively (63 mg). ^{1}H NMR (400 MHz, C_6D_6): δ 7.69 (d, 1H, J = 2.5 Hz, ArH), 7.54 (d, 1H, J = 2.2 Hz, ArH), 7.23 (s, 1H, NCH), 6.93 (d, 1H, J = 2.4 Hz, ArH), 6.89 (d, J = 2.4, 1H, ArH), 4.25 (d, 1H, J = 12.7, CH), 3.58 (d, 1H, J = 13.3, CH), 3.47 (m, 1H, CH), 2.50 (m, 1H, CH), 2.25 (m, 2H, CH_2), 1.78 (s, 9H, $C(CH_3)_3$), 1.61 (s, 9H, $C(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$), 1.35 (s, 18H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100.66 MHz, C_6D_6): δ 167.8 (CN), 160.9 (C), 139.2 (C), 138.9 (C), 138.6 (C), 138.1 (C), 130.3 (CH), 126.4 (CH), 124.7 (CH), 123.1 (CH), 121.1 (C), 76.9 (C), 75.8 (C), 60.1 (CH_2), 36.7 (CH_2), 36.3 (CH_2), 35.9 (C), 34.7 (C), 33.6 (CH_3), 32.4 (CH_3), 32.0 (CH_3), 31.9 (C), 31.6 (C), 30.6 (CH_3). Anal. Calcd for $C_{40}H_{65}NO_4SZr$: C, 64.29; H, 8.77; N, 1.87. Found: C, 63.36; H, 8.59; N, 1.54.

Synthesis of Lig^{5}Zr(O-tert-Bu)$_2$. Lig^{5}H$_2$ (49 mg, 0.10 mmol) was dissolved in ca. 2 mL of ether and was added dropwise to a solution of $Zr(O^tBu)_4$ (38 mg, 0.10 mmol) at room temperature. The solution was stirred for 2 h after which the solvent was removed under vacuum, giving a yellow solid quantitatively (76 mg). ^{1}H NMR (400 MHz, C_6D_6): δ 7.33 (d, 1H, J = 2.5 Hz, ArH), 7.07 (d, 1H, J = 2.4 Hz, ArH), 6.86 (s, 1H, NCH), 6.61 (d, 1H, J = 2.6 Hz, ArH), 6.50 (d, 1H, J = 1.8, ArH), 3.89 (d, 1H, J = 13.9, CH), 3.36 (d, 1H, J = 13.9, CH), 3.08 (m, 1H, CH), 2.40 (m, 1H, CH), 2.24 (s, 3H, $ArCH_3$), 2.14 (m, 6H, adamantyl), 1.86 (m, 6H, adamantyl), 1.70 (m, 3H, adamantyl), 1.54 (s, 9H, $C(CH_3)_3$), 1.45 (m, 1H, CH), 1.22 (m, 1H, CH), 1.14 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100.66 MHz, C_6D_6): δ 164.0 (CN), 160.9 (C), 139.0 (C), 134.5 (CH), 131.7 (CH), 129.4 (CH), 126.9 (C), 125.4 (C), 123.9 (C), 121.4 (C), 120.9 (C), 77.2 (C), 76.2 (C), 61.3 (CH_2), 41.2 (CH_2), 37.7 (CH_2), 37.5 (C), 36.5 (CH_2), 33.3 (CH_3), 33.2 (CH_3), 31.8 (CH_2), 30.1 (CH) 21.4 (CH_3). Anal. Calcd for $C_{35}H_{47}Cl_2NO_4SZr{\cdot}Et_2O$: C, 57.54; H, 7.06; N, 1.72. Found: C, 57.60; H, 6.61; N, 1.64.

Synthesis of Lig^{6}Zr(O-tert-Bu)$_2$. Lig^{6}H$_2$ (34 mg, 0.06 mmol) was dissolved in ca. 2 mL of ether and was added dropwise to a solution of $Zr(O^tBu)_4$ (22 mg, 0.06 mmol) at room temperature. The solution was stirred for 2 h after which the solvent was removed under vacuum, giving a yellow solid quantitatively (55 mg). ^{1}H NMR (400 MHz, C_6D_6): δ 7.33 (s, 1H, NCH), 7.26 (d, 1H, J = 2.2 Hz, ArH), 7.15 (s, 1H, ArH), 6.58 (d, 2H, J = 1.8 Hz, ArH), 4.05 (d, 1H, J = 13.7, CH), 3.48 (d, 1H, J = 13.7, CH), 3.11 (m, 1H, CH), 2.57 (m, 2H, CH), 2.48 (bs, 6H, adamantyl), 2.40 (m, 1H, CH), 2.31 (s, 3H, $ArCH_3$), 2.26 (m, 6H, adamantyl), 2.15 (s, 3H, $ArCH_3$), 2.10 (m, 3H, adamantyl), 1.85 (m, 12H, adamantyl), 1.64 (m, 3H, adamantyl), 1.55 (s, 9H, $C(CH_3)_3$), 1.16 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (100.66 MHz, C_6D_6): δ 166.5 (CN), 161.7 (C), 161.1 (C), 139.8 (C), 139.1 (C), 134.2 (CH), 132.7 (CH), 129.4 (CH), 128.9 (CH), 126.3 (C), 124.6 (C), 123.7 (C), 120.9 (C), 76.0 (C), 75.5 (C), 61.5 (CH_2), 41.8 (CH_2), 41.6 (CH_2), 38.2 (C), 38.0 (CH_2), 37.9 (CH_2), 37.7 (C), 36.6 (CH_2), 33.7 (CH_3), 33.3 (CH_3), 32.0 (CH_2), 30.1 (CH), 30.0 (CH), 21.4 (CH_3), 21.1 (CH_3). Anal. Calcd for $C_{46}H_{65}NO_4SZr$: C, 67.43; H, 8.00; N, 1.71. Found: C, 67.48; H, 7.52; N, 1.25.

General Polymerization Procedure. Bulk polymerizations of L-lactide and *rac*-lactide were carried out by heating the monomer and the catalyst in a closed glass vessel to 140 °C for a period of time by which the melt had become viscous. Here, 10 mg of catalyst and a 300:1 lactide to catalyst molar ratio were employed for all polymerizations. The polymerization runs were terminated by the addition of 1 mL of methanol. The reaction mixture was dissolved in dichloromethane, followed by removal of the volatiles under reduced pressure. The resulting polymer was purified by stirring with excess of methanol overnight to remove any unreacted monomer, filtered, and dried under vacuum for 2 h. ^{1}H NMR analysis of the PLA samples obtained by polymerization of L-lactide (400 MHz, $CDCl_3$) indicated that no epimerization occurred during the polymerization, and that the polymer was isotactic, as was evident from a quartet (5.16 ppm) and a doublet (1.58 ppm) in a ratio of 1:3.

Solution polymerization runs of *rac*-lactide in 5 mL of toluene were carried out at 70 °C employing 10 mg of catalyst and a 300:1 lactide to catalyst molar ratio. After 20 h the reaction was terminated by the addition of 1 mL of methanol and the volatiles were removed under vacuum. The resulting polymer was purified by stirring with excess of methanol overnight to remove any unreacted monomer, filtered, and dried under vacuum for 2 h. The homonuclear-decoupled ^{1}H NMR spectrum of the PLA samples (400 MHz, $CDCl_3$) of the methine region was consistent with the formation of chains that are predominantly heterotactic, isotactic or atactic estimated from the relative intensities of the *rmr* (δ 5.23 ppm) and the *mrm* (δ 5.16 ppm) tetrads for heterotactic sequences and the *mmm* (δ 5.17 ppm) tetrad for isotactic sequences vs other tetrads (*rmr* δ 5.23 ppm, *mrm* δ 5.16

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ppm, *rmm*/*mmr* δ 5.22 and 5.18 ppm, *mmm* δ 5.17 ppm).[20−22] Molecular weight determination and PDI analysis were done by GPC measurements.

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REFERENCES

(1) (a) Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841. (b) Auras, R.; Harte, B.; Selke, S. *Macromol. Biosci.* **2004**, 4835. (c) Albertsson, A. C.; Varma, I. K. *Biomacromolecules* **2003**, *4*, 1466.

(2) (a) Stanford, M. J.; Dove, A. P. *Chem. Soc. Rev.* **2010**, *39*, 486. (b) Becker, J. M.; Pounder, R. J.; Dove, A. P. *Macromol. Rapid Commun.* **2010**, *31*, 1923.

(3) (a) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147. (b) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11.

(4) (a) Thomas, C. M. *Chem. Soc. Rev.* **2010**, *39*, 165. (b) Dijkstra, P. J.; Du, H.; Feijen, J. *Polym. Chem.* **2011**, *2*, 520.

(5) (a) Spassky, N.; Wisniewski, M.; Pluta, C.; Le Borgne, A. *Macromol. Chem. Phys.* **1996**, *197*, 2627. (b) Ovitt, T. M.; Coates, G. W. *J. Polym. Sci., A: Polym. Chem.* **2000**, *38*, 4686. (c) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316. (d) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4510. (e) Majerska, K.; Duda, A. *J. Am. Chem. Soc.* **2004**, *126*, 1026. (f) Chisholm, M. H.; Patmore, N. J.; Zhou, Z. *Chem. Commun.* **2005**, 127. (g) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; Pugh, R. I.; White, A. J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15343. (h) Nomura, N.; Ishii, R.; Yamamoto, Y.; Kondo, T. *Chem.—Eur. J.* **2007**, *13*, 4433. (i) Pang, X.; Du, H.; Chen, X.; Wang, X.; Jing, X. *Chem.—Eur. J.* **2008**, *14*, 3126. (j) Bouyahyi, M.; Grunova, E.; Marquet, N.; Kirillov, E.; Thomas, C. M.; Roisnel, T.; Carpentier, J. −F. *Organometallics* **2008**, *27*, 5815. (k) Darensbourg, D. J.; Karroonnirun, O. *Organometallics* **2010**, *29*, 5627.

(6) For nonaluminum based catalytic systems showing isoselectivity bias, see: (a) Douglas, A. F.; Patrick, B. O.; Mehrkhodavandi, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 2290. (b) Buffet, J. C.; Okuda, J.; Arnold, P. L. *Inorg. Chem.* **2010**, *49*, 419. (c) Arnold, P. A.; Buffet, J.; Blaudeck, R. P.; Sujecki, S.; Blake, A. J.; Wilson, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 6033. (d) Jensen, T. R.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *Chem. Commun.* **2004**, 2504. (e) Whitelaw, E. L.; Davidson, M. G.; Jones, M. D. *Chem. Commun.* **2011**, 10004. (f) Dove, A. P.; Li, H.; Pratt, R. C.; Lohmeijer, B. G. G.; Culkin, D. A.; Waymouth, R. M.; Hedrick, J. L. *Chem. Commun.* **2006**, 2881. (g) Zhang, L.; Nederberg, F.; Messman, J. M.; Pratt, R. C.; Hedrick, J. L.; Wade, C. G. *J. Am. Chem. Soc.* **2007**, *129*, 12610.

(7) (a) Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S. *Macromolecules* **1987**, *20*, 906. (b) Fukushina, K.; Kimura, Y. *Polym. Int.* **2006**, *55*, 626.

(8) (a) Cheng, M.; Attygalle, A. B.; Lobkowsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583. (b) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Chem. Commun.* **2003**, 48. (c) Pietrangelo, A.; Knight, S. C.; Gupta, A. K.; Yao, L. J.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2010**, *132*, 11649.

(9) (a) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J. −F. *Chem.—Eur. J.* **2006**, *12*, 169. (b) Bouyahyi, M.; Ajellal, N.; Kirillov, E.; Thomas, C. M.; Carpentier, J. −F. *Chem.—Eur. J.* **2011**, *17*, 1872. (c) Liu, X.; Shang, X.; Tang, T.; Hu, N.; Pei, F.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 2747. (d) Clark, L.; Cushion, M. G.; Dyer, H. E.; Schwarz, A. D.; Duchateau, R.; Mountford, P. *Chem. Commun.* **2010**, 273.

(10) (a) Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7818. (b) Ma, H.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2008**, *47*, 3328. (c) Chmura, A. J.; Chuck, C. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Bull, S. D.; Mahon, M. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 2280. (d) Chmura, A. J.; Davidson, M. G.; Frankis, C. J.; Jones, M. D.; Lunn, M. D. *Chem. Commun.* **2008**, 1293.

(11) (a) Zelikoff, A. L.; Kopilov, J.; Goldberg, I.; Coates, G. W.; Kol, M. *Chem. Commun.* **2009**, 6804. (b) Sergeeva, E.; Kopilov, J.; Goldberg, I.; Kol, M. *Inorg. Chem.* **2010**, *49*, 3977.

(12) For a report on different{OSNO} ligands, see: Meppelder, G-J. M.; Fan, H.-T.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2009**, *48*, 7378.

(13) (a) Yeori, A.; Gendler, S.; Groysman, S.; Goldberg, I.; Kol, M. *Inorg. Chem. Commun.* **2004**, *7*, 280. (b) Press, K.; Cohen, A.; Goldberg, I.; Venditto, V.; Mazzeo, M.; Kol, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 3591.

(14) Cohen, A.; Yeori, A.; Goldberg, I.; Kol, M. *Inorg. Chem.* **2007**, *46*, 8114.

(15) The intermediate thio-imine monophenolate derivatives formed as a mixtures, presumably with the phenol-substituted 5-membered heterocycle thiazolidine, and were reacted without purification.

(16) For Al-Salan and related systems which revert tacticity preference upon changing of ligand substituents, see: (a) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2689. (b) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; Pugh, R. I.; White, A. J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15343. (c) Du, H.; Velders, A. H.; Dijkstra, P. J.; Sun, J.; Zhong, Z.; Chen, X.; Feijen, J. *Chem.—Eur. J.* **2009**, *15*, 9836. (d) Tang, Z.; Gibson, V. C. *Eur. Polym. J.* **2007**, *43*, 150.

(17) Bryliakov, K. P.; Talsi, E. *Eur. J. Org. Chem.* **2008**, 3369.

(18) Gendler, S.; Zelikoff, A. L.; Kopilov, J.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2008**, *130*, 2144.

(19) Cohen, A.; Kopilov, J.; Goldberg, I.; Kol, M. *Organometallics* **2009**, *28*, 1391.

(20) Thakur, K. A. M.; Kean, R. T.; Hall, E. S.; Doscotch, M. A.; Munson, E. S. *Anal. Chem.* **1997**, *69*, 4303.

(21) Thakur, K. A. M.; Kean, R. T.; Hall, E. S.; Kolstad, J. J.; Lindgren, T. A.; Doscotch, M. A.; Siepmann, I.; Munson, E. S. *Macromolecules* **1997**, *30*, 2422.

(22) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229.