Highly Thermally Stable and Robust Enantiopure NNN-Scorpionate Zirconium Initiators for the Controlled Ring-Opening Polymerization of *rac*-Lactide

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ABSTRACT

A series of alkoxide and thialkoxide enantiopure zirconium derivatives [$Zr(ER)_3(\kappa^3$-*R*,*R*-fbpza)] (**1**–**6**) (E = O, R = $CHMe_2$ **1**, CHMeEt **2**, CH_2SiMe_3 **3**, 2,6-$C_6H_3Me_2$ **4**, 4-^{t}BuPh **5**; E = S, R = 4-^{t}BuPh **6**) has been prepared for their use as thermally stable and robust initiators in the ROP of *rac*-lactide, by alcoholysis or thioalcoholysis reaction of the tris(amide) precursor [$Zr(NMe_2)_3(\kappa^3$-*R*,*R*-fbpza)] [*R,R*-fbpzaH = *N*-*p*-fluorophenyl-(1*R*)-1-[(1*R*)-6,6-dimethylbicyclo[3.1.1]-2-hepten-2-yl]-2,2-bis(3,5-dimethylpyrazol-1-yl)ethylamine] with ROH and ArEH (E = O, S) in a 1:3 molar ratio. The structures of the different compounds were determined by spectroscopic methods and, in addition, the X-ray crystal structure of **6** was also established.

Interestingly, the tris(amide) precursor and complexes **2**, **5**, **6** act as single-site living initiators for the well-controlled ring-opening polymerization of *rac*-lactide both in solution and in the melt, producing polymers with medium molecular weights in good agreement with theoretical values and narrow dispersity ranges. Activity of all initiators increase notably with temperature, and more importantly, complex **2** exhibits the highest activity reported to date for a group 4-based initiators in ROP of *rac*-LA under the industrially preferred melt and solvent-free conditions. Surprisingly, complex **2** is still highly active in the melt employing unpurified monomer, showing an unprecedented tolerance to water and impurities (49% conv, 15 min, 130 ºC). Microstructural analysis of the poly(*rac*-lactide)s revealed a moderate heteroactivity in solution, with a P_s value up to 0.70.

INTRODUCTION

The production of poly(lactic) acid (PLA), an aliphatic polyester derived from the bioresourced lactic acid, has been focus of high interest due to its excellent properties and wide variety of biomedical[1] and pharmaceutical applications considering its biocompatibility with human tissue and bio-absorbable nature. In addition, PLA also founds important applications in food packaging industry[2] due to its good mechanical properties, high transparency, ease of processing and low cost. As a consequence, its production is estimated to grow over 1.2 million tonnes in 2019.[3]

In this context, the most common and useful strategy to produce PLA is by employing metal-based catalysts as initiators for the Ring-Opening Polymerization (ROP) of lactide (LA) monomers.[4] Compared with other di- and tri-valent metals, such as Zn(II), Mg(II) or Al(III), the use of Group 4 complexes in ROP of LA still remains little explored, even though in recent years numerous reports indicates a trend change.[5-8] This increasing interest is mainly due to their low toxicity, high activity and good control that metal 4-based catalysts offer during the polymerization process.[8] Thus, structurally-defined Group 4 metal alkoxide complexes supported by different ancillary ligands have been described in the literature as efficient initiators, where major advances have been reported in phenolate complexes, such as *N,O*-bidentade iminophenolate (half-salen),[9] tetradentate bis(phenolate) (ONNO)-type (salen,[10] salan,[11] salalen[12]), (OSSO)-type[13] and (ONSO)-type,[14] tetradentate amino tris(phenolate),[15] and tridentate NHC-containing bis(phenolate).[16] Most of the these polymerization studies have been undertaken in solution, but interestingly, there are comparatively few examples of using these complexes as initiators under the more industrially relevant solvent-free conditions.[17-19] Moreover, the vast majority of those complexes exhibit a great sensitivity to moisture and air, which represent a great problem to overcome for the industrial bulk production of PLA, being highly desirable the availability of initiators that tolerate air, and the significant load of moisture and impurities in the monomer.[20]

In addition to this, great efforts have been devoted to the design of initiators capable of exerting a high degree of control in the PLA microstructures.[21-23] Interestingly, despite the relevant number of group 4 initiators recently reported, the stereocontrol observed during the propagations is quite modest,[24,25] even though chiral ligands have occassionally been employed.[26,27]

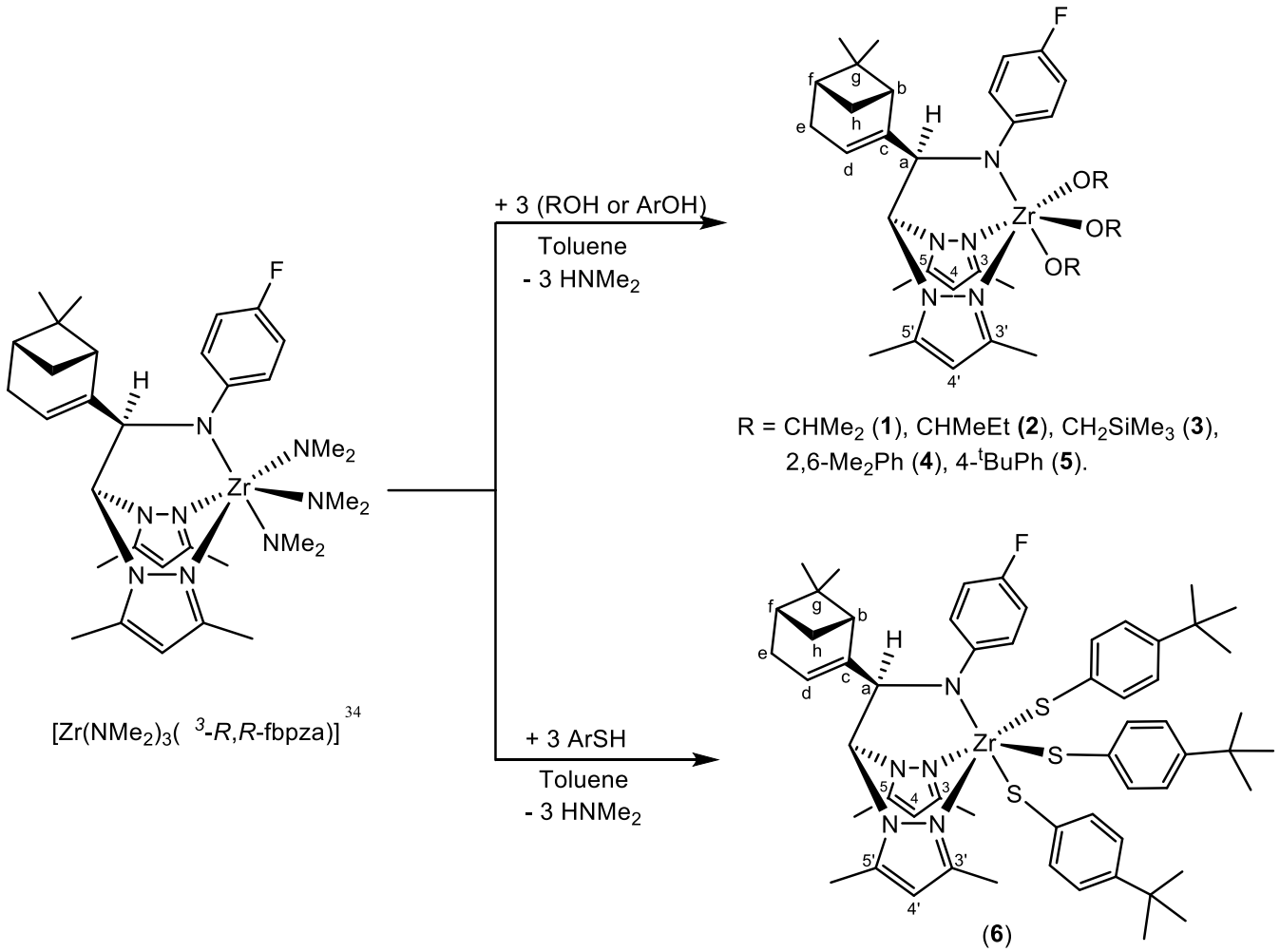
Furthermore, our research group has been interested in the last years on the search of highly active and selective initiators supported by enantiomerically pure ligands[28] for different catalytic processes.[29] Thus, we initially evaluated the influence of Group 4 complexes bearing a NNO-donor scorpionate ligand on the enantioselectivity of the asymmetric epoxidation of allylic alcohols.[30] Later, we described the significant degree of stereocontrol in the ROP of *rac*-lactide exerted by new zinc complexes assisted by this enantiopure NNO-heteroscorpionate[31] and more recently, by a NNCp hybrid scorpionate/cylopentadienyl ligand.[32,33] Now, we face the challenge to prepare group 4-based initiators supported by an alternative enantiopure NNN-scorpionate[34] and also assisted by the alkoxide and thialkoxide ligands, more efficient for the ROP of *rac*-lactide under a variety of conditions, including the more nearly industrially preferred.

Herein, we describe the preparation and structural characterization of new enantiopure NNN-scorpionate alkoxide, aryloxide or arylthioxide zirconium complexes of the type [$ZrX_3(\kappa^3$-NNN)] for their use as thermally stable and robust initiators in the ROP of melt and unpurified *rac*-LA, closely to the highly demanding industrial conditions.

RESULTS AND DISCUSSION

Several alkoxide, aryloxide or thioaryloxide derivatives have been prepared by using the tris(amide) precursor [Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)][34] by alcoholysis or thioalcoholysis reaction with ROH (R = CHMe$_2$, CHMeEt, CH$_2$SiMe$_3$) or ArEH (E = O, Ar = 2,6-C$_6$H$_3$Me$_2$, 4-^{t}BuPh; E = S, Ar = 4-^{t}BuPh), in a 1:3 molar ratio, to yield the enantiopure derivatives [Zr(ER)$_3$(κ^3-*R*,*R*-fbpza)] (**1**–**6**) (E = O, R = CHMe$_2$ **1**, CHMeEt **2**, CH$_2$SiMe$_3$ **3**, 2,6-C$_6$H$_3$Me$_2$ **4**, 4-^{t}BuPh **5**; E = S, R = 4-^{t}BuPh **6**) as white solids in *ca*. 75% isolated yield (Scheme 1).

Scheme 1. Synthesis of the enantiopure NNN-scorpionate alkoxide, aryloxide or thioaryloxide zirconium complexes (**1**–**6**).



The ^{1}H and $^{13}C(^{1}H)$ -NMR spectra of **1–6** each exhibit one sets signals, which is consistent with the presence of one diastereoisomer. Furthemore, the addition of a chiral shift reagent did not modifiy their ^{1}H NMR spectra. The ^{1}H NMR spectra of these complexes show two singlets for each of the H^{4}, Me^{3} and Me^{5} pyrazole protons, one singlet for each of the methine groups (CH bridge of pyrazole rings and CH^{a}), the signals for the bicyclic moiety bound to the methylene bridge and also those for the aryl substituent on the nitrogen atom. In addition, three sets of signals with a 1:1:1 integral ratio, corresponding to the OR or EAr ligands were observed. This behavior indicates that the three alkoxide/thialkoxide ligands did not exchange their positions rapidly at room temperature. The ^{1}H NOESY-1D experiments enabled the unequivocal assignment of all ^{1}H resonances. The results are consistent with an octahedral structure resulting from the κ^{3}-*NNN*-coordination of the scorpionate-ligand to the metal center (Scheme 1). The geometry found in solution was also confirmed in the solid state by an X-ray structural analysis of complex **6** (Figure 1). Selected bond lengths and angles are listed in Table 1 and the crystallographic details are reported in Table S1 in the Electronic Supplementary Information (ESI†). The scorpionate ligand retains the *R*-configuration for the C^{a} (C12) atom. The structure consists of a heteroscorpionate ligand bonded to the zirconium atom in a κ^{3}-*NNN*-coordination mode through the two nitrogen atoms of pyrazole rings, with Zr-N bond lengths well-balanced [Zr(1)-N(1) = 2.333(13) Å and Zr(1)-N(3) = 2.424(15) Å], and the nitrogen atom of the amide group, with a bond length considerably shorter [Zr(1)-N(5) = 2.106(13) Å]. In addition, the zirconium center is coordinated to three thioariloxide ligands, with similar Zr(1)-S(1,2) bond lengths of 2.485(5) Å and 2.519(5) Å, respectively, but with Zr(1)-S(3) bond length slightly longer 2.574(5) Å. The zirconium center has a distorted octahedral environment with a major distortion in the S(3)–Zr(1)–N(5) angle and S(1)–Zr(1)–N(1) angle, which have values of 154.0(4)º and 161.6(4)º, respectively. The Zr(1)–N(1) and Zr(1)–N(3) bond distances [2.333(13) Å and 2.424(15) Å, respectively], which are longer than those in similar heteroscorpionate complexes,[35] indicate that the thioariloxide ligands exert a *trans* influence.[36] The X-ray diffraction results confirm the presence in the solid state of one diastereoisomer for this complex.

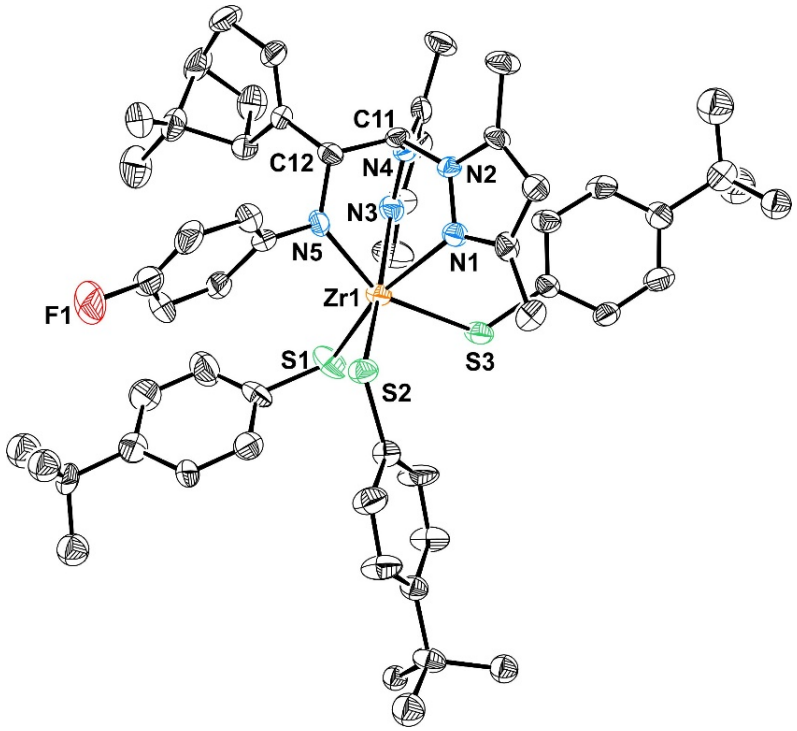


Figure 1. ORTEP view of the complex [Zr(S-4-^{t}BuPh)$_3$(κ^3-*R*,*R*-fbpza)] (**6**). Ellipsoids are at the 30% probability level and hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **6×0.25C$_4$H$_8$O**.

Bond lengths		*Angles*	
Zr(1)-N(1)	2.333(13)	N(1)-Zr(1)-S(1)	161.6(4)
Zr(1)-N(3)	2.424(15)	N(3)-Zr(1)-S(2)	169.3(4)
Zr(1)-N(5)	2.106(13)	N(5)-Zr(1)-S(1)	116.2(4)
Zr(1)-S(1)	2.519(5)	C(12)-N(5)-Zr(1)	127.2(10)
Zr(1)-S(2)	2.485(5)	N(2)-C(11)-C(12)	112.3(13)
Zr(1)-S(3)	2.574(5)	N(4)-C(11)-N(2)	111.6(13)
		N(4)-C(11)-C(12)	113.4(13)
		N(5)-C(12)-C(13)	113.0(13)
		N(5)-C(12)-C(11)	112.5(12)
		C(13)-C(12)-C(11)	108.4(13)

Polymerization Studies.

These studies have the main objective to evaluate the activity and stereoselectivity of the previously reported tris(amide) complex [$Zr(NMe_2)_3(\kappa^3$-*R*,*R*-fbpza)][34] in the ring-opening polymerization (ROP) of the polar monomer *rac*-lactide (*rac*-LA), and compare these results with trials performed with the new enantiopure complexes **2**, **5** and **6** under very demanding conditions; the results are collected in Table 2. Initial studies focused in tetrahydrofuran solution using [$Zr(NMe_2)_3(\kappa^3$-*R*,*R*-fbpza)] showed no activity after 40 h at 70 °C, and only traces of polymer were obtained (entry 1). Contrarily, when toluene was employed as solvent, 98% of the monomer was converted by the tris(amide) zirconium complex after 24 h at the same temperature (entry 6).

This reduction in activity observed in tetrahydrofuran can be attributed to the competition between the solvent and monomer moiety for the metal center. Our research group has previously observed similar competition for hybrid scorpionate/cyclopentadienyl alkyl magnesium catalysts[37] for the ROP of LA, and Zhao et al. have reported similar behavior employing group 4 metal complexes as initiators.[38] Remarkably, when temperature is reduced to 50 °C, the tris(amide) zirconium complex is still active in toluene, and the activity was only mildly decreased (entry 2). The experimental M_n values are in good agreement with the expected theoretical calculated values considering one polymer chain per zirconium center [M_n(calcd)PLA_{100} = 14 400 g·mol^{-1}] (Table 2).

The living character of the polymerization employing the tris(amide) complex at 70 °C was also investigated (entries 3–6), resulting well controlled as evidenced by the linear correlation between molecular weights and percentage conversion, in conjunction with narrow range of dispersity values (1.08–1.15) (see Figure S1 in the ESI†). Additionally, the living character was further evidenced by a double-feed experiment, which resulted in a polymer chain extension with similar material features (entry 7). Furthermore, MALDI-ToF MS analysis in Figure S2 (ESI†) of low-molecular-weight poly(*rac*-lactide) oligomers produced by the tris(amide) complex showed end-capped chains with amide groups, evidencing that the polymerization occurs by the initial addition of the amide fragment to the

monomer with cleavage of the acyl-oxygen bond,[39,40] followed by further monomer additions to the (macro)alcohols.

Moreover, the enantiopure complexes **2**, **5** and **6** were systematically evaluated in the ROP of *rac*-LA by also employing toluene as solvent. Unfortunately, these complexes resulted less active than the precursor tris(amide) in solution at low temperatures. Thus, alkoxide and aryloxide complexes **2** and **5**, respectively, drastically reduce the catalytic activity under mild conditions (50 ^{o}C), and only traces of polymer were recovered after 48 h in both cases (entries 9 and 13), whilst complex **6** exhibited a very low activity, leading to 10% conv under otherwise identical conditions (entry 16).

Interestingly, when temperature was raised to 70 ^{o}C, a slight increase of the productivity was observed for complex **5** (entry 14), whilst activity is markedly improved by complexes **2** and **6**, reaching conversions about 40% (entries 10 and 17), although both values were near the half found for the tris(amide) precursor (entry 6) in that conditions. However, complexes **2**, **5** and **6**, analogously to the tris(amide) precursor, offer a great level of control in the polymerization process, due to the close agreement between theoretical and observed molecular weights, and the fact that the PLA materials showed a quite narrow dispersity range values (1.07–1.34).

Furthermore, we investigated the feasibility of these complexes for the ROP of *rac*-LA under more extreme conditions, particularly, in solvent-free melt conditions, and a notable increase of the activity was observed in all the cases (entries 8, 11, 15, 18). Remarkably, the tris(amide) precursor almost consume 300 equiv of monomer feed in only 6 minutes (entry 8), and more surprisingly, the aliphatic alkoxide **2** led to almost quantitative consumption of monomer in just 1 minute (entry 11). This activity [TOF value 16 740 h^{-1}] is considerable higher than that found for the most active zirconium complexes reported to date under such extreme conditions of temperature, such as the zirconium amine tris(phenolate) alkoxide described by Davidson *et al*.[15] [TOF value of 2 340 h^{-1}], the zirconium imine-thiobis(phenolate) bis(alkoxide) published by Kol *et al*.[41] [TOF value of 2 494 h^{-1}] or the dithiolate zirconium bis(alkoxide) communicated also by Kol *et al*. [TOF value of 7 380 h^{-1}].[42] In addition, in this particular work, authors reported the most active group 4 metal initiator in melt conditions to date (at a

slightly higher temperature, 142 ºC), namely a dithiolate hafnium bis(alkoxide) complex with an activity value [TOF value 15 660 h^{-1}], which compares well with that obtained by **2**.

In this context, Schaper *et. al*.[43] have also described a zirconium alkoxide complex bearing a bridged diketiminate ligand displaying an exceptionally high polymerization activity, giving 86% conversion of 300 equivalents of *rac*-LA in THF at room temperature in only 1 min [TOF 15 480 h^{-1}],[43] although these authors also remark that the stability of this initiator, even under these mild polymerization conditions, is limited, and deviations in kinetic studies are attributed to catalyst decomposition. Therefore, to the best of our knowledge, complex **2** is the highest active group 4 initiator in ROP of *rac*-LA reported to date under the industrially preferred melt and solvent-free conditions.

Considering this exceptional activity and high stability found for this initiator under this severe temperature conditions, we decided to explore its tolerance to less anhydrous environments. Thus, complex **2** was employed as catalyst in the melt using commercial non-purified *rac*-LA as monomer.

At this point, it is worth mentioning that the vast majority of well-defined initiators require a highly purified *rac*-lactide to exert a good-controlled ROP process, and therefore, multiple sublimation as well as re-crystallisation cycles are necessary, in conjunction with rigorous anhydrous manipulations, to achieve catalytic activity (see *rac*-lactide purification in the Experimental Section). Remarkably, complex **2** was still active under these demanding conditions, and although activity was significantly reduced to almost 50% conv (Table 2, entry 12) [TOF 588 h^{-1}], that still is comparatively higher than the robust zirconium N-heterocyclic carbene complex described by Dagorne *et. al*.[16] [TOF 13 h^{-1}], and compares well with the chiral zirconium alkoxide initiators reported by Davidson *et. al*.[27] [TOF 570 h^{-1}]. This reduction in the activity value are attributed to the presence of impurities such as lactic acid and/or water in the commercially available monomer.[27] However, this extraordinary robustness shown by catalysts **2** is undoubtedly due to the presence of the two remaining alkoxide groups in the active species, which are responsible to decrease the oxophilic character of the zirconium active center. Under these demanding conditions, a detrimental effect in the experimental molecular weight and a relatively broader molecular weight distribution were also observed in the obtained material (Table 2, entry 12),

which can be attributed to the presence of impurities such us water content, lactic acid and others, which provokes possible side reactions.

Finally, the microstructure analysis of the PLAs, through inspection of the methine region of the homonuclear decoupled ^{1}H NMR spectrum of the polymers, revealed that complexes **5** and **6** provide moderate levels of heterotactic enrichment on the growing polymer chains at 70 ºC [P_s values of 0.67 and 0.70, respectively; Table 2, entries 14 and 17, respectively, see Figure S3 (ESI†)], whereas complexes **2** and the tris(amide) precursor afforded almost atactic materials (P_s∼0.5, Table 2, entries 2–12). Expectedly, the effect of higher temperatures clearly reduced the heterotacticity values in the polymer microstructures, resulting in atactic materials.

These findings suggest that, in this particular case, even in the presence of a chiral ancillary ligand or chiral substituent groups close to the active site of zirconium (as in complex **2**), a chain-end control mechanism predominates. Therefore, the presence of more sterically demanding environments around the zirconium centre (as in complex **5** and **6**) exert certain level of influence in the promotion of heterotactic bias in the poly(*rac*-lactide) materials.

Table 2. Polymerization of *rac*-Lactide Catalyzed by [Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)],[34] 2, 5 and 6.[a]

entry	initiator	Temp. (°C)	Time (h)	yield (g)	conv (%)[b]	TOF (h^{-1})[c]	$M_{n(theor)}$ (Da)[d]	M_n (Da)[e]	M_w/M_n[e]	P_s[f]
1	**[Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)]**[g]	70	40	traces	-	-	-	-	-	-
2	**[Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)]**	50	24	0.74	57	2	8 200	7 500	1.09	0.52
3	**[Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)]**	70	5	0.25	19	4	2 700	2 200	1.08	-
4	**[Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)]**	70	10	0.54	42	4	6 000	6 500	1.08	-
5	**[Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)]**	70	18	0.94	72	4	10 400	10 900	1.11	-
6	**[Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)]**	70	24	1.27	98	4	14 100	14 400	1.13	-
7	**[Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)]**	70	48	2.50	96	4	27 600	27 900	1.15	0.57
8	**[Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)]**[h]	130	6 min	3.81	98	2 940	42 300	40 300	1.24	0.56
9	**2**	50	48	traces	-	-	-	-	-	-
10	**2**	70	24	0.52	40	2	5 700	6 200	1.07	0.58
11	**2**[h]	130	1 min	3.62	93	16 740	40 200	39 100	1.29	0.57
12	**2**[i]	130	15 min	1.91	49	588	43 200	34 200	1.44	0.57
13	**5**	50	48	traces	-	-	-	-	-	-
14	**5**	70	48	0.16	12	-	1 700	2 200	1.08	0.67
15	**5**[h]	130	6 min	1.75	45	1 350	19 400	18 300	1.22	0.61
16	**6**	50	48	0.13	10	-	1 400	1 900	1.09	0.67
17	**6**	70	24	0.56	43	2	6 200	5 500	1.10	0.70
18	**6**[h]	130	6 min	2.72	70	2 100	30 200	28 900	1.32	0.61

[a] Polymerization conditions: 90 μmol of zirconium centers; [*rac*-LA]$_0$/[Zr]$_0$ = 100; 20 mL of toluene. [b] Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) × 100]. [c] TOF = (conversion/100) × (loading/time). [d] Theoretical M_n = [*rac*-LA]$_0$/[Zr]$_0$ × (%

conv) × (M_w of *rac*-LA). [e] Determined by size exclusion chromatography relative to polystyrene standards in tetrahydrofuran. Experimental M_n was calculated considering Mark–Houwink's corrections[44,45] for M_n [M_n(obsd) = 0.58 × M_n(GPC)]. [f] The parameter P_s (s = syndiotactic) is the probability of syndiotactic (racemic) linkages between monomer units and is determined on the basis of the relative intensity of the tetrad signals of the methine region in the homonuclear decoupled ^{1}H NMR spectra by $P_s = 2I_1/(I_1+I_2)$, with I_1 = δ 5.20–5.25 ppm (*sis*, *sii*/*iis*) and I_2 = δ 5.13–5.20 ppm (*iis*/*sii*, *iii*, *isi*).[46] [g] Employing 10 mL of THF as solvent. [h] $[Zr]_0$ = 90 μmol and $[rac\text{-LA}]_0/[Zr]_0$ = 300. [i] $[Zr]_0$ = 90 μmol and $[rac\text{-LA}]_0/[Zr]_0$ = 300, employing unpurified *rac*-lactide.

CONCLUSIONS

A new family of alkoxide and thioalkoxide zirconium complexes [$Zr(ER)_3(\kappa^3$-NNN] (E = O, S) bearing an enantiopure NNN-donor scorpionate ligand has been prepared in good yields through the alcoholysis or thioalcoholysis reaction of the tris(amido) precursor [$Zr(NMe_2)_3(\kappa^3$-NNN)],[34] for their use as thermally stable and robust initiators in the ROP of *rac*-lactide. X-ray diffraction analysis of the thioaryloxide derivative **6** revealed that the chiral configuration of the scorpionate ligand is also maintained in the solid state and crystals contain only one diastereomer.

Interestingly, these complexes were shown to be active as effective single-site living initiators for the well-controlled ring-opening polymerization of *rac*-lactide in toluene at 70 °C. Increase of the temperature led to an unprecedented growth in activity with no observable catalyst degradation, and very interestingly, total consumption of 300 equiv of monomer was achieved within 1 min for the zirconium alkoxide complex **2**, which represents the highest productivity reported to date[42] for all group 4-based initiators under this nearly industrially more preferred melt conditions (TOF = 16 740 h^{-1}). Remarkably, **2** confirmed its extraordinary robustness when polymerization was conducted in the melt using unpurified monomer, reaching near 50% conv in 15 min. Finally, microstructural analysis of the materials produced in solution revealed moderate heteroselectivity levels when employed sterically hindered substituents in the initiators (P_s = 0.70), whilst the less sterically demanding catalysts afforded almost atactic materials.

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or a glovebox. Solvents were predried over sodium wire and distilled under nitrogen from sodium (toluene and *n*-hexane) or sodium-benzophenone (THF and diethyl ether). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. The starting materials *R,R*-fbpzaH[34] and [$Zr(NMe_2)_3(\kappa^3$-*R,R*-fbpza)][34] were prepared as reported previously. The different alcohols or thioalcohols were purchased from Aldrich. 2,6-Dimethylphenol was sublimed twice under reduced pressure and stored in a glovebox. 2,6-Dimethylthiophenol was degassed by several freeze thraw cycles and stored over 4 Å molecular sieves. *rac*-Lactide, when required, was sublimed twice, recrystallized from THF and finally sublimed again prior to use.

Instruments and Measurements

NMR spectra were recorded on a Varian Inova FT-500 spectrometer and were referenced to the residual deuterated solvent signal. ^{1}H NMR homodecoupled and NOESY-1D spectra were recorded on the same instrument with the following acquisition parameters: irradiation time 2 s and 256 scans, using standard VARIAN-FT software. 2D NMR spectra were acquired using the same software and processed using an IPC-Sun computer.

Microanalyses were performed with a Perkin-Elmer 2400 CHN analyzer. The specific rotation $[\alpha]_D^{22}$ was measured at a concentration of 0.1% w/v in toluene or chloroform at 22 ºC on a JASCO P2000 Polarimeter equipped with a sodium lamp operating at 589 nm with a light path length of 10 cm.

The molecular weights (M_n) and the molecular mass distributions (M_w/M_n) of polymer samples were measured by Gel Permeation Chromatography (GPC) performed on a Shimadzu LC-20AD GPC equipped with a TSK-GEL G3000Hxl column and an ELSD-LTII light-scattering detector. The GPC column was eluted with THF at 40 ºC at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580–483 000 Da.

MALDI-ToF MS data were acquired with a Bruker Autoflex II ToF/ToF spectrometer, using a nitrogen laser source (337 nm, 3 ns) in linear mode with a positive acceleration voltage of 20 kV. Samples were prepared as follows: PLA (20 mg) was dissolved in HPLC quality THF with matrix and NaI in a 100:5:5 ratio. Before evaporation, 10 μL of the mixture solution was deposited on the sample plate. External calibration was performed by using Peptide Calibration Standard II (covered mass range: 700–3 200 Da) and Protein Calibration Standard I (covered mass range: 5 000–17 500 Da). All values are the average of two independent measurements.

The microstructures of PLA samples were determined by examination of the methine region in the homodecoupled ^{1}H NMR spectrum of the polymers recorded at room temperature in $CDCl_3$ on a Varian Inova FT-500 spectrometer with concentrations in the range 1.0 to 2.0 mg/mL.

Preparation of compounds 1–6.

Synthesis of [Zr(OCHMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)] (1). In a 250 cm^3 Schlenk tube, [Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)] (1.00 g, 1.49 mmol) was dissolved in dry toluene (50 cm^3). A solution of isopropanol (0.27 g, 4.47 mmol) in toluene was added and the resulting solution was stirred overnight at room temperature. The solvent was removed under vacuum and washed with *n*-hexane to give complex **1** as a white solid. This solid was crystallized from *n*-hexane. 0.84 g (Yield 79%). $[\alpha]_D^{25}$ +18.74 (*c* 1.00, THF). Anal. Calcd for $C_{36}H_{54}FN_5O_3Zr$: C, 60.47; H, 7.61; N, 9.79. Found: C, 60.42; H, 7.74; N, 9.83. ^{1}H NMR (C_6D_6, 297 K): δ 6.72 (dd, 2 H, J_{HH} = 8.8 Hz, J_{HF} = 4.5 Hz, *o*-H), 6.53 (d, 1 H, CH), 5.56 (s, 1 H, H^4), 6.31 (t, 2 H, J_{HH} = J_{HF} = 8.8 Hz, *m*-H), 5.55 (s, 1 H, H$^{4'}$), 5.53 (bs, 1 H, CH^a), 4.78 (m, 3 H, OC*H*(CH$_3$)$_2$), 3.85 (d, 1 H, H^d), 2.31 (s, 3 H, Me^3), 2.24 (s, 3 H, Me$^{3'}$), 2.24 (m, 2 H, H^e), 2.16 (s, 3 H, Me^5), 2.16 (m, 1 H, H^b), 2.15 (s, 3 H, Me$^{5'}$), 1.95 (m, 1 H, H^{h,h}), 1.78 (m, 1 H, H^f), 1.42 (d, 6 H, OCH(*CH$_3$*)$_2$), 1.39 (d, 6 H, OCH(*CH$_3$*)$_2$), 1.34 (d, 6 H, OCH(*CH$_3$*)$_2$), 1.11 (s, 3 H, Me^g), 0.76 (d, 1 H, H^{h,h}), 0.42 (s, 3 H, Me^g). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 155.0 (d, J_{CF} = 232.7 Hz, *p*-C), 152.4 (*ipso*-C), 147.6 (C^c), 144.7–143.7 (C$^{3,3'}$), 141.1–140.3 (C$^{5,5'}$), 122.9 (C^d), 115.5 (d, J_{CF} = 22.1 Hz, *m*-C), 115.0 (d, J_{CF} = 6.8 Hz, *o*-C), 107.8–106.6 (C$^{4,4'}$), 74.2 (CH), 71.3 [OC*H*(CH$_3$)$_2$], 70.9 [OC*H*(CH$_3$)$_2$],

69.8 [OC*H*(CH_3)$_2$], 60.2 (C^a), 42.2 (C^b), 40.8 (C^f), 39.9 (C^g), 38.1 (C^e), 31.9 (C^h), 27.2–26.9 [OCH(*CH_3*)$_2$], 26.8–26.7 [OCH(*CH_3*)$_2$], 26.7–26.5 [OCH(*CH_3*)$_2$], 26.3 (Me^g), 21.2 (Me^g), 13.7–13.5 ($Me^{3,3'}$), 11.4–11.1 ($Me^{5,5'}$).

Synthesis of [Zr(OCHMeEt)$_3$(*κ*^{3}-*R*,*R*-fbpza)] (2). The synthetic procedure was the same as for complex **1**, using [Zr(NMe_2)$_3$(*κ*^{3}-*R*,*R*-fbpza)] (1.00 g, 1.49 mmol) and 2-butanol (0.33 g, 4.47 mmol), to give **2** as a white solid. 0.79 g (Yield 70%). [*α*]$_D^{25}$ +16.52 (*c* 1.00, THF). Anal. Calcd for $C_{39}H_{60}FN_5O_3Zr$: C, 61.87; H, 7.99; N, 9.25. Found: C, 61.91; H, 8.03; N, 9.30. ^{1}H NMR (C_6D_6, 297 K): δ 6.73 (dd, 2 H, J_{HH} = 8.8 Hz, J_{HF} = 4.4 Hz, *o*-H), 6.52 (d, 1 H, CH), 6.30 (t, 2 H, J_{HH} = J_{HF} = 8.3 Hz, *m*-H), 5.56 (s, 2 H, $H^{4,4'}$), 5.52 (bs, 1 H, CH^a), 4.18 [m, 3 H, (CH_3CH_2)*CH*Me], 3.87 (d, 1 H, H^d), 2.36 (s, 3 H, Me^3), 2.28 (s, 3 H, $Me^{3'}$), 2.19 (s, 3 H, Me^5), 2.18 (s, 3 H, $Me^{5'}$), 2.11 (m, 2 H, H^e), 2.11 (m, 1 H, H^b), 1.97 (m, 1 H, $H^{h,h}$), 1.81 (m, 1 H, H^f), 1.51 [m, 3 H, (CH_3CH_2)CH*Me*], 1.39 [d, 3 H, (CH_3CH_2)CH*Me*], 1.35 [d, 3 H, (CH_3CH_2)CH*Me*], 1.13 (s, 3 H, Me^g), 1.02 [m, 6 H, (CH_3CH_2)CHMe], 0.90 [m, 9 H, (*CH_3*CH_2)CHMe], 0.79 (d, 1 H, $H^{h,h}$), 0.44 (s, 3 H, Me^g). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 156.4 (d, J_{CF} = 234.9 Hz, *p*-C), 150.9 (*ipso*-C), 147.6 (C^c), 144.6–143.6 ($C^{3,3'}$), 140.9–140.2 ($C^{5,5'}$), 122.6 (C^d), 115.5 (d, J_{CF} = 22.1 Hz, *m*-C), 115.0 (d, J_{CF} = 6.9 Hz, *o*-C), 107.7–106.5 ($C^{4,4'}$), 77.4, 76.7, 75.9 [(CH_3CH_2)*CH*Me], 74.1 (CH), 60.2 (C^a), 42.1 (C^b), 40.8 (C^f), 38.0 (C^g), 34.0 (C^e), 31.4 (C^h), 24.5, 23.9, 23.2, [(*CH_3*CH_2)CHMe], 21.3 (Me^g), 21.1 (Me^g), 13.7–13.6 ($Me^{5,5'}$), 11.5–11.2 ($Me^{3,3'}$), 10.9, 10.6, 10.5 [(CH_3*CH_2*)CHMe].

Synthesis of [Zr(OCH$_2$SiMe$_3$)$_3$(*κ*^{3}-*R*,*R*-fbpza)] (3). The synthetic procedure was the same as for complex **1**, using [Zr(NMe_2)$_3$(*κ*^{3}-*R*,*R*-fbpza)] (1.00 g, 1.49 mmol) and (trimethylsilyl)methanol (0.46 g, 4.47 mmol), to give **3** as a white solid. 0.97 g (Yield 77%). [*α*]$_D^{25}$ +15.33 (*c* 1.00, THF). Anal. Calcd for $C_{39}H_{66}FN_5O_3Si_3Zr$: C, 55.27; H, 7.85; N, 8.26. Found: C, 55.18; H, 7.92; N, 8.30. ^{1}H NMR (C_6D_6, 297 K): δ 6.73 (dd, 2 H, J_{HH} = 9.3 Hz, J_{HF} = 4.4 Hz, *o*-H), 6.53 (d, 1 H, CH), 6.30 (t, 2 H, J_{HH} = J_{HF} = 8.8 Hz, *m*-H), 5.55 (bs, 1 H, CH^a), 5.56 (s, 2 H, $H^{4,4'}$), 4.42 (s, 2 H, C*H_2*SiMe_3), 4.32 (s, 2 H, C*H_2*Si*Me_3*), 4.14 (s, 2 H, C*H_2*SiMe_3), 3.87 (d, 1 H, H^d), 2.36 (s, 3 H, Me^3), 2.28 (s, 3 H, $Me^{3'}$), 2.25 (m, 2 H, H^e), 2.19 (s, 3 H, Me^5), 2.18 (s, 3 H, $Me^{5'}$), 2.15 (m, 1 H, H^b), 1.96 (m, 1 H, $H^{h,h}$), 1.82 (m, 1 H,

H^f), 0.81 (d, 1 H, $H^{h,h}$), 1.13 (s, 3 H, Me^g), 0.44 (s, 3 H, Me^g), 0.35 (s, 9 H, $CH_2Si\mathit{Me}_3$), 0.26 (s, 18 H, $CH_2Si\mathit{Me}_3$). ^{13}C-{^1H} NMR (C_6D_6, 297 K): δ 156.3 (d, J_{CF} = 235.1 Hz, *p*-C), 147.5 (*ipso*-C), 147.5 (C^c), 144.6–143.6 ($C^{3,3'}$), 140.9–140.2 ($C^{5,5'}$), 129.2, 128.4, 128.0 ($C\mathit{H}_2SiMe_3$), 122.1 (C^d), 115.5 (d, J_{CF} = 22.2 Hz, *m*-C), 115.0 (d, J_{CF} = 7.2 Hz, *o*-C), 107.5–106.3 ($C^{4,4'}$), 74.1 (CH), 60.1 (C^a), 42.1 (C^b), 40.7 (C^f), 38.1 (C^g), 31.8 (C^e), 31.4 (C^h), 26.3 (Me^g), 21.1 (Me^g), 13.7–13.6 ($Me^{5,5'}$), 11.5–11.2 ($Me^{3,3'}$), –2.81, –2.70, –2.52 ($CH_2Si\mathit{Me}_3$).

Synthesis of [Zr(O-2,6-Me_2Ph)$_3$(κ^3-*R*,*R*-fbpza)] (4). The synthetic procedure was the same as for complex **1**, using [Zr(NMe_2)$_3$(κ^3-*R*,*R*-fbpza)] (1.00 g, 1.49 mmol) and 2,6-dimethylphenol (0.54 g, 4.47 mmol), to give **4** as a white solid. 1.01 g (Yield 75%). $[\alpha]_D^{25}$ +12.45 (*c* 1.00, THF). Anal. Calcd for $C_{51}H_{60}FN_5O_3Zr$: C, 67.96; H, 6.71; N, 7.77. Found: C, 67.91; H, 6.73; N, 7.79. ^1H NMR (C_6D_6, 297 K): δ 6.87 (t, 2 H, J_{HH} = 7.3 Hz, J_{HF} = 4.4 Hz, *o*-H), 6.82 (s, 6 H, 2,6-$Me_2{}^m\mathit{Ph}$), 6.69 (s, 6 H, 2,6-$Me_2{}^p\mathit{Ph}$), 6.56 (t, 2 H, J_{HH} = J_{HF} = 8.8 Hz, *m*-H), 6.07 (d, 1 H, CH), 5.37 (bs, 1 H, CH^a), 5.23 (s, 1 H, $H^{4'}$), 5.22 (s, 1 H, H^4), 4.55 (d, 1 H, H^d), 2.74 (s, 18 H, 2,6-Me_2Ph), 2.21 (m, 2 H, H^e), 2.20 (m, 1 H, H^b), 2.08 (m, 1 H, $H^{h,h}$), 2.07 (s, 3 H, Me^3), 1.98 (m, 1 H, H^f), 1.89 (s, 3 H, $Me^{3'}$), 1.70 (s, 3 H, Me^5), 1.58 (s, 3 H, $Me^{5'}$), 1.05 (s, 3 H, Me^g), 0.68 (d, 1 H, $H^{h,h}$), 0.31 (s, 3 H, Me^g). ^{13}C-{^1H} NMR (C_6D_6, 297 K): δ 161.5, 160.9, 159.3, 153.5, 152.7, 151.5 (2,6-$Me_2{}^o\mathit{Ph}$), 155.9 (d, J_{CF} = 225.6 Hz, *p*-C), 152.7–151.5 ($C^{3,3'}$), 149.1 (C^c), 149.1 (*ipso*-C), 149.1, 140.0, 138.3 (2,6-$Me_2{}^{ipso}\mathit{Ph}$), 140.0–138.3 ($C^{5,5'}$), 125.9, 125.6, 122.7, 119.9, 119.5, 118.4 (2,6-$Me_2{}^m\mathit{Ph}$), 122.7 (C^d), 115.6 (d, J_{CF} = 22.2 Hz, *m*-C), 115.1 (d, J_{CF} = 7.5 Hz, *o*-C), 114.0, 113.8, 113.9 (2,6-$Me_2{}^p\mathit{Ph}$), 107.6–107.2 ($C^{4,4'}$), 71.6 (CH), 68.0 (C^a), 41.3 (C^b), 40.9 (C^f), 38.2 (C^g), 32.3 (C^e), 31.9 (C^h), 26.1 (Me^g), 20.9 (Me^g), 19.3, 18.4, 15.7 (2,6-Me_2Ph), 13.7–13.6 ($Me^{5,5'}$), 11.1–10.6 ($Me^{3,3'}$).

Synthesis of [Zr(O-4-^{t}BuPh)$_3$(κ^3-*R*,*R*-fbpza)] (5). The synthetic procedure was the same as for complex **1**, using [Zr(NMe_2)$_3$(κ^3-*R*,*R*-fbpza)] (1.00 g, 1.49 mmol) and 4-*tert*-butylphenol (0.67 g, 4.47 mmol), to give **5** as a white solid. 1.07 g (Yield 73%). $[\alpha]_D^{25}$ +11.63 (*c* 1.00, THF). Anal. Calcd for $C_{57}H_{72}FN_5O_3Zr$: C, 69.47; H, 7.36; N, 7.11. Found: C, 69.45; H, 7.39; N, 7.15. ^1H NMR (C_6D_6, 297 K): δ 7.43 (d, 2 H, J_{HH} = 8.7 Hz ^{t}Bu$^m\mathit{Ph}$), 7.39 (d, 2 H, J_{HH} = 8.7 Hz ^{t}Bu$^m\mathit{Ph}$), 7.25 (t, 2 H, J_{HH} =

7.3 Hz, J_{HF} = 4.7 Hz, *o*-H), 7.14 (d, 2 H, J_{HH} = 8.7 Hz ^{t}Bu^{m}*Ph*), 6.85 (d, 2 H, J_{HH} = 8.7 Hz ^{t}Bu^{o}*Ph*), 7.11 (d, 2 H, J_{HH} = 8.7 Hz ^{t}Bu^{o}*Ph*), 6.75 (t, 2 H, J_{HH} = J_{HF} = 9.0 Hz, *m*-H), 6.49 (d, 2 H, J_{HH} = 8.7 Hz ^{t}Bu^{o}*Ph*), 6.03 (d, 1 H, CH), 5.32 (bs, 1 H, CH^{a}), 5.26 (s, 2 H, H^{4}), 5.23 (s, 2 H, H$^{4'}$), 4.81 (d, 1 H, H^{d}), 2.40 (m, 2 H, H^{e}), 2.21 (s, 3 H, Me^{3}), 2.15 (m, 1 H, H^{b}), 2.14 (s, 3 H, Me$^{3'}$), 2.07 (m, 1 H, H^{h,h}),1.89 (m, 1 H, H^{f}), 1.68 (s, 3 H, Me^{5}), 1.63 (s, 3 H, Me$^{5'}$), 1.32, 1.23, 1.21 (s, 27 H, ^{t}*Bu*Ph), 1.25 (s, 3 H, Me^{g}), 0.45 (d, 1 H, H^{h,h}), 0.29 (s, 3 H, Me^{g}). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 161.9, 161.5, 160.8 (CH^{p}*Ph*^{t}Bu), 156.6 (d, J_{CF} = 239.1 Hz, *p*-C), 153.1, 152.0, 151.1 (CH^{ipso}*Ph*^{t}Bu), 147.6 (*ipso*-C), 147.4 (C^{c}), 141.6–141.6 (C$^{3,3'}$), 140.1–139.5 (C$^{5,5'}$), 126.4, 125.9, 125.8 (CH^{m}*Ph*^{t}Bu), 121.5 (C^{d}), 115.5 (d, J_{CF} = 21.6 Hz, *m*-C), 115.0 (d, J_{CF} = 7.2 Hz, *o*-C), 119.6, 119.2, 118.3 (CH^{o}*Ph*^{t}Bu), 106.9–107.4 (C$^{4,4'}$), 74.1, 71.3, 68.1 (*CH*Ph^{t}Bu), 71.3 (CH), 60.1 (C^{a}), 41.3 (C^{b}), 40.9 (C^{f}), 38.3 (C^{g}), 34.3 (C^{h}), 34.1 (C^{e}), 34.1, 33.9 (CHPh^{t}*Bu*), 26.2 (Me^{g}), 20.8 (Me^{g}), 13.3–13.6 (Me$^{5,5'}$), 10.3–10.7 (Me$^{3,3'}$).

Synthesis of [Zr(S-4-^{t}BuPh)$_3$(*κ*^{3}-*R*,*R*-fbpza)] (6). The synthetic procedure was the same as for complex **1**, using [Zr(NMe$_2$)$_3$(*κ*^{3}-*R*,*R*-fbpza)] (1.00 g, 1.49 mmol) and 4-*tert*-butylthiophenol (0.74 g, 4.47 mmol), to give **6** as a white solid. 1.12 g (Yield 73%). $[\alpha]_D^{25}$ +14.95 (*c* 1.00, THF). Anal. Calcd for $C_{57}H_{72}FN_5S_3Zr$: C, 66.23; H, 7.02; N, 6.78. Found: C, 66.26; H, 7.05; N, 6.81. ^{1}H NMR (C_6D_6, 297 K): δ 8.19 (d, 2 H, J_{HH} = 8.1 Hz ^{t}Bu^{m}*Ph*), 7.72 (d, 2 H, J_{HH} = 8.1 Hz ^{t}Bu^{m}*Ph*), 7.28 (d, 2 H, J_{HH} = 8.1 Hz ^{t}Bu^{m}*Ph*), 7.21 (t, 2 H, J_{HH} = 7.3 Hz, J_{HF} = 4.6 Hz, *o*-H), 7.11 (d, 2 H, J_{HH} = 8.1 Hz ^{t}Bu^{o}*Ph*), 6.70 (d, 2 H, J_{HH} = 8.1 Hz ^{t}Bu^{o}*Ph*), 6.62 (t, 2 H, J_{HH} = J_{HF} = 8.8 Hz, *m*-H), 6.46 (d, 2 H, J_{HH} = 8.1 Hz ^{t}Bu^{o}*Ph*), 6.16 (d, 1 H, CH), 5.42 (bs, 1 H, CH^{a}), 5.30 (s, 2 H, H^{4}), 5.20 (s, 2 H, H$^{4'}$), 4.41 (d, 1 H, H^{d}), 2.74 (s, 3 H, Me^{3}), 2.73 (s, 3 H, Me$^{3'}$), 2.38 (m, 2 H, H^{e}), 2.09 (m, 1 H, H^{b}), 2.07 (m, 1 H, H^{h,h}), 1.98 (m, 1 H, H^{f}), 1.75 (s, 3 H, Me^{5}), 1.70 (s, 3 H, Me$^{5'}$), 1.29 (s, 3 H, Me^{g}), 1.25, 1.24, 1.12 (s, 27 H, ^{t}*Bu*Ph), 0.45 (bs, 1 H, H^{h,h}), 0.37 (s, 3 H, Me^{g}). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K): δ 159.9, 159.5, 156.8 (CH^{p}*Ph*^{t}Bu), 158.9 (d, J_{CF} = 239.1 Hz, *p*-C), 153.9, 151.2, 150.6 (CH^{ipso}*Ph*^{t}Bu), 149.6 (*ipso*-C), 145.4 (C^{c}), 140.2–140.3 (C$^{5,5'}$), 139.6–139.5 (C$^{3,3'}$), 124.8, 123.4, 122.8 (CH^{m}*Ph*^{t}Bu), 123.6 (C^{d}), 119.0, 118.3, 115.3 (CH^{o}*Ph*^{t}Bu), 113.3 (d, J_{CF} = 21.6 Hz, *m*-C), 113.0 (d, J_{CF} = 7.2 Hz, *o*-C), 103.2–103.6 (C$^{4,4'}$), 73.0,

72.1, 69.6 (*CH*Ph^{t}Bu), 70.1 (CH), 58.6 (C^{a}), 40.8 (C^{f}), 40.3 (C^{b}), 36.2 (C^{g}), 33.3, 33.1, (CHPh^{t}*Bu*), 33.2 (C^{e}), 30.3 (C^{h}), 25.8 (Me^{g}), 19.8 (Me^{g}), 13.9–13.7 (Me$^{5,5'}$), 10.9–10.8 (Me$^{3,3'}$).

General Polymerization Procedures.

Polymerizations of *rac*-lactide (LA) were performed on a Schlenk line in a flame-dried round-bottomed flask equipped with a magnetic stirrer. The Schlenk tubes were charged in the glovebox with the required amount of LA and initiator, separately, and then attached to the vacuum line. The initiator and LA were dissolved in the appropriate amount of solvent, when required, and temperature equilibration was ensured in both Schlenk flasks by stirring the solutions for 15 min in a bath. The appropriate amount of initiator was added by syringe and polymerization times were measured from that point. Polymerizations were stopped by injecting a solution of hydrochloric acid in methanol. Polymers were precipitated in methanol, filtered off, redissolved and reprecipitated in methanol, and dried in vacuo to constant weight.

X-ray Crystal Structure Determination: Single crystals of **6** were mounted on a glass fiber and transferred to a Bruker X8 APEX II diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. Data were integrated using the SAINT[47] program and were corrected for absorption effects with the semi-empirical from equivalents method using SADABS.[48] Details of crystal data, data collection, and refinement can be found in Table S1 in the ESI†. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using the software package WINGX.[49] The structure shows high disorder for ^{t}Bu groups and has been necessary to introduce restraints in the refinement. All non-hydrogen atoms were refined with anisotropic displacement coefficients except those of the disorder groups. All hydrogen atoms were added to their geometrically ideal positions.

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†Electronic supplementary information (ESI) available

Details of ring opening polymerization of *rac*-lactide and crystal data and structure refinement for **6**. CCDC-1012783.

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GRAPHICAL TABLE OF CONTENTS ENTRY

Highly Thermally Stable and Robust Enantiopure NNN-Scorpionate Zirconium Initiators for the Controlled Ring-Opening Polymerization of *rac*-Lactide

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Alcoholysis or thioalcoholysis reaction of the tris(amide) [Zr(NMe$_2$)$_3$(κ^3-*R*,*R*-fbpza)] in a 1:3 molar ratio yields the enantiopure derivatives [Zr(ER)$_3$(κ^3-*R*,*R*-fbpza)] (E = O, S) for their use as single-component living initiators in the ROP of *rac*-lactide to produce moderate levels of heteroselectivity (P_s = 0.70) in solution. More importantly, the trisalkoxide R = OCHMeEt showed the highest activity value observed for group 4-based catalysts in the melt and, surprisingly, transformed under nearly preferred industrial conditions 49% of 300 equiv of unpurified *rac*-LA in 15 min.