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Group 3 Metal Initiators with an [OSSO]-Type Bis(phenolate) Ligand for the Stereoselective Polymerization of Lactide Monomers

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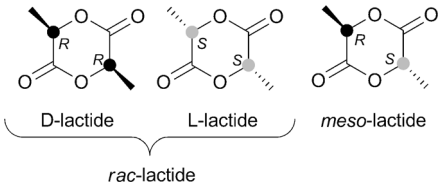
Abstract: A series of 1,ω-dithiaalkanediyl-bridged bis(phenols) of the general type [OSSO]H_2 with variable steric properties and various bridges were prepared. The stoichiometric reaction of the bis(phenols) 1,3-dithiapropanediyl-2,2′-bis(4,6-di-*tert*-butylphenol), 1,3-dithiapropanediyl-2,2′-bis[4,6-di(2-phenyl-2-propyl)phenol], *rac*-2,3-*trans*-propanediyl-1,4-dithiabutanediyl-2,2′-bis[4,6-di(2-phenyl-2-propyl)phenol], *rac*-2,3-*trans*-butanediyl-1,4-dithiabutane diyl-2,2′-bis[4,6-di(2-phenyl-2-propyl)phenol], *rac*-2,3-*trans*-hexanediyl-1,4-dithiabutanediyl-2,2′-bis[4,6-di(2-phenyl-2-propyl)phenol], 1,3-dithiapropanediyl-2,2′-bis[6-(1-methylcyclohexyl)-4-methylphenol] (C_1, R = 1-methylcyclohexyl), and 1,4-dithiabutanediyl-2,2′-bis[6-(1-methylcyclohexyl)-4-methylphenol] with rare-earth metal silylamido precursors [Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$] (Ln = Sc, x = 1 or Ln = Y, x = 2; thf = tetrahydrofuran) afforded the corresponding scandium and yttrium bis(phenolate) silylamido complexes [Ln(OSSO){N(SiHMe$_2$)$_2$}(thf)] in moderate to good yields. The monomeric nature of these complexes was shown by an X-ray diffraction study of one of the yttrium complexes. The complexes efficiently initiated the ring-opening polymerization of *rac*- and *meso*-lactide to give heterotactic-biased poly(*rac*-lactides) and highly syndiotactic poly(*meso*-lactides). Variation of the ligand backbone and the steric properties of the *ortho* substituents affected the level of tacticity in the polylactides.

Keywords: lactides · lanthanides · polymers · ring-opening polymerization · stereoselectivity

Introduction

Polylactide (PLA) is currently attracting interest as a biodegradable thermoplastic derived from "carbon-neutral" biomass feedstocks.[1] The production of isotactic poly(L-lactide) has been commercialized with an annual production capacity exceeding 10^5 metric tons. The monomer L-lactide (L-LA) is produced by thermolysis of oligo(L-lactide).[2] Because there are two stereogenic centers in one lactide molecule, three stereoisomers—(*S*,*S*)-LA, (*R*,*R*)-LA, and *meso*-LA—can be distinguished. A racemic mixture of (*S*,*S*)-LA and (*R*,*R*)-LA is called *rac*-lactide (*rac*-LA; Scheme 1).

The physical and mechanical properties of a polymeric material are dependent on many factors, such as molecular weight, molecular weight distribution, and stereochemistry. Polymers that have stereocenters in the repeating unit can exhibit two structures of maximum order: isotactic and syndiotactic. Due to their stereoregularity, isotactic (T_m > 180 °C) and syndiotactic polymers (T_m = 152 °C) are typically crystalline; an important feature for many applications. Heterotactic PLAs are amorphous and no melting temperatures have been reported to date.



Scheme 1. Lactide monomers with the stereochemistry of the stereogenic centers indicated.

Molecularly defined single-site initiators for the ring-opening polymerization (ROP) of lactide monomers are based on Lewis acidic di-,[3] tri-,[4] and tetravalent[5] metals. Polymerization of L-lactide leads to isotactic poly(L-lactide), whereas polymerization of *rac*-lactide can lead to atactic, heterotactic, stereoblock, or stereocomplex PLA. Stereocontrolled polymerization of *meso*-lactide, which is a byproduct during the production of L-lactide, can give syndiotactic and heterotactic poly(*meso*-lactides). To date, only a limited number of polymerization initiators for *meso*-lactide are known.[6] We previously reported the use of trivalent metal complexes with an [OSSO]-type bis(phenolate) ligand for the ROP of *rac*-lactide to form heterotactic poly(*rac*-lactides) and *meso*-lactide to form highly syndiotactic poly(*meso*-lactides) (Scheme 2).[4g,h,7]

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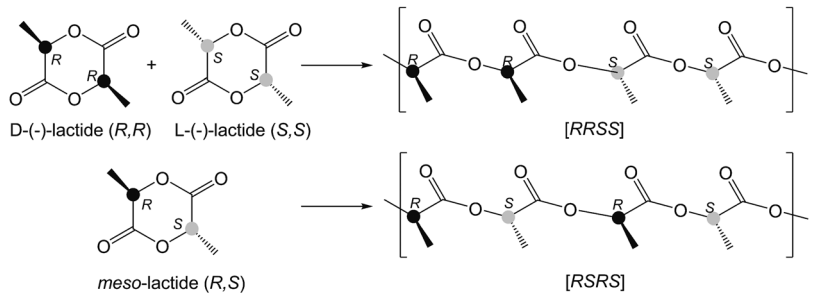


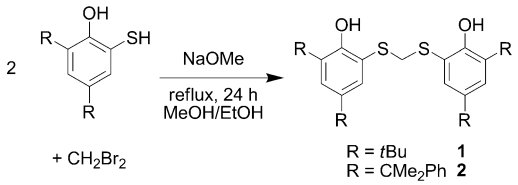
Scheme 2. Synthesis of heterotactic PLA and syndiotactic PLA from *rac*- and *meso*-lactide.

The steric bulk of the *ortho* substituent has a profound effect on both the polymerization rates and the stereocontrol. Hetero- and syndioselective stereocontrol during the ROP of *rac*- and *meso*-LA is essentially governed by steric factors: larger *ortho* substituents result in higher tacticity of the polymers due to controlled monomer coordination to the metal center. Additionally, chirality in the complex backbone appears to have a strong influence on the control of both efficiency and stereocontrol.[8] We report herein the synthesis and lactide polymerization behavior of a new series of Group 3 metal silylamide complexes containing a bis(phenolate) ligand with various chiral and achiral backbones and *ortho* substituents.

Results and Discussion

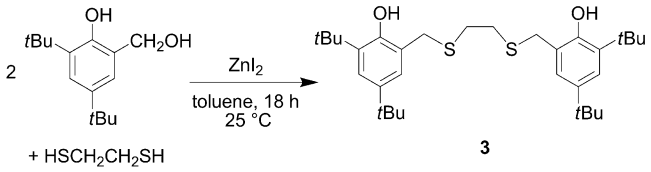
Synthesis of the Proligands

Following a variation of the procedure reported for the synthesis of proligand **1**,[9] 2-mercapto-4,6-bis(2-phenylpropan-2-yl)phenol was treated with NaOMe and CH_2Br_2 in a mixture of methanol and ethanol at reflux for 24 hours (Scheme 3). After workup, proligand **2** (chelate ring size 5-4-5) was obtained as a colorless solid in 15% yield.



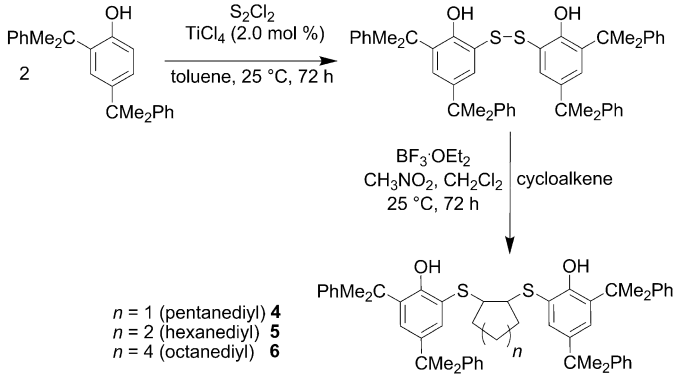
Scheme 3. Synthesis of proligands **1** and **2**.

We have previously reported that flexible 1,5-dithiapentanediyl-bridged scandium complexes form highly heterotactic,[4g] poly(*rac*-lactides), and syndiotactic[7] poly(*meso*-lactides). Another possibility to increase the flexibility of the bridge was to synthesize a ligand with a methylene linker between the sulfur atom and the aromatic group. Following a modification of the literature procedure,[10] proligand **3** (giving a 6-5-6 chelate array) has been synthesized in one pot, whereby ZnI_2 was added to (2-hydroxy-3,5-di-*tert*-butyl)benzyl alcohol in toluene, followed by the addition of 1,2-ethylenedithiol (Scheme 4). After workup, proligand **3** was obtained as a colorless solid in 63% yield.



Scheme 4. Synthesis of proligand **3**.

We have introduced various chiral backbones with different ring sizes. Proligands **4** and **6** were synthesized by following a modification of a procedure by Doye et al.[11] Cycloalkene was treated with bis(phenol) disulfide 2,2′-dithiobis[4,6-di(2-phenyl-2-propyl)phenol] in the presence of $BF_3{\cdot}OEt_2$ in a mixture of nitromethane and dichloromethane (Scheme 5).



Scheme 5. Synthesis of proligands **4**–**6**.

After workup and recrystallization, yellow (**4**) and orange (**6**) solids were obtained in 74 and 15% yields, respectively. Proligands **7**, with a 5-4-5 chelate array, and **8**, with a 5-5-5 chelate array, were prepared by following literature reports[12a,b] and isolated as brown powders in low yields (Scheme 6). Proligands **1**–**8** are air-stable crystals and were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis.

Synthesis of the Complexes

Group 3 metal initiators containing a 1,ω-dithiaalkanediyl-bridged bis(phenolate) ligand are readily synthesized in 40–70% yields by treatment of one equivalent of rare-earth

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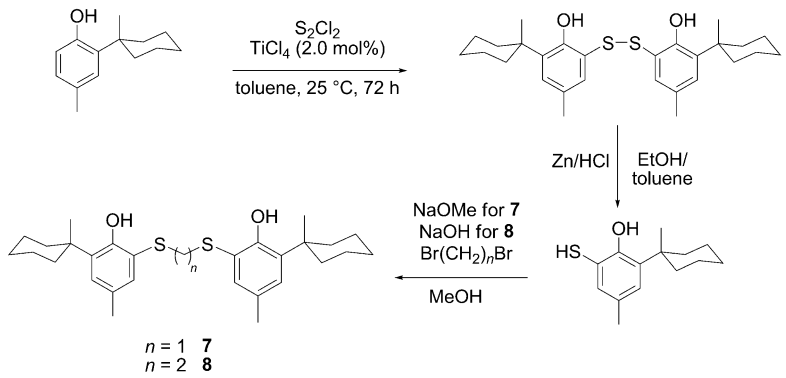
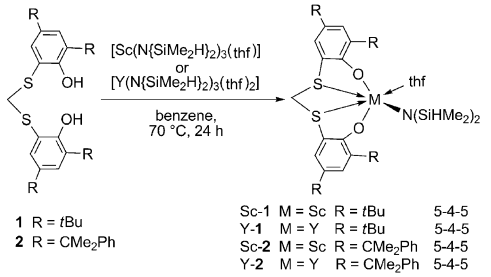
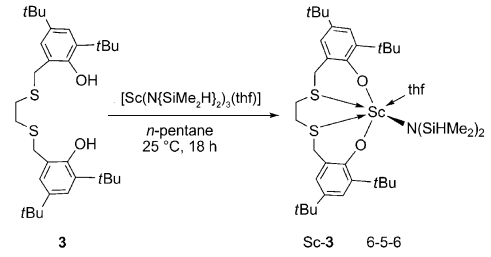


Scheme 6. Synthesis of proligands **7** and **8**.

metal tris(dimethylsilylamide) precursors with one equivalent of proligands **1**–**8** (Schemes 7 and 8).

The stoichiometric reaction of $[Ln\{N(SiHMe_2)_2\}_3(thf)_x]$ (Ln = Sc, $x = 1$ or Ln = Y, $x = 2$; thf = tetrahydrofuran) with **1** or **2** in benzene for 24 hours at 70 °C led to the formation of Sc–**1**, Y–**1**, Sc–**2**, and Y–**2** (chelation ring size 5-4-5), which were isolated in moderate to good yields as colorless powders after recrystallization from *n*-pentane at −30 °C (Scheme 7). The ^{1}H and ^{13}C NMR spectra of complexes Ln–**1** and Ln–**2** display similar signals. The ^{1}H NMR spectra shows the SCH_2S protons of the bridge as a singlet at similar shifts for Sc–**1** ($\delta = 3.71$ ppm), Y–**1** ($\delta = 3.86$ ppm), and Y–**2** ($\delta = 3.64$ ppm). As a consequence of the rigid geometry around the scandium center in Sc–**2**, the SCH_2S protons appear to be diastereotopic, as indicated by two broad signals at $\delta = 3.50$ and 3.64 ppm. Two broad resonances at about $\delta = 1.0$–1.5 and 3.0–4.1 ppm indicate the presence of one THF molecule attached to the metal center. A septet at $\delta = 5.1$ ppm with $^3J(H,H) = 3.0$–3.2 Hz and $^1J(Si,H) = 170.0$–180 Hz is assigned to the SiHMe$_2$ protons and a doublet at around $\delta = 0.5$ ppm is assigned to SiHMe_2 of the amide ligand. The coupling constant ^1J(Si,H) indicates a weak β-Si–H interaction with the metal.[13] The ^{13}C NMR spectra show the SCH_2S resonances at about $\delta =$ 50.0 ppm.





Scheme 7. Synthesis of complexes Ln–**1** to Ln–**3**.

The stoichiometric reaction of $[Ln\{N(SiHMe_2)_2\}_3(thf)_x]$ (Ln = Sc, $x = 1$ or Ln = Y, $x = 2$) with proligands **7** and **8** in *n*-pentane for 48 hours at 25 °C afforded Sc–**7**, Y–**7**, Sc–**8**, and Y–**8** (Scheme 8). After recrystallization from *n*-pentane, colorless solids were isolated in good yields. Complexes Sc–**7** and Sc–**8** seem to be more fluxional in solution than Y–**7** and Y–**8**. In the scandium complexes, one broad signal at about $\delta = 1.30$ ppm for the β-protons and two signals of equal intensity are detected between $\delta = 4.00$–4.10 and 4.20–4.30 ppm for the α-protons of THF. For the *para*-methyl groups, two signals at about $\delta = 2.2$–2.3 ppm are recorded. The methyl protons of the 1-methylcyclohexyl group appear

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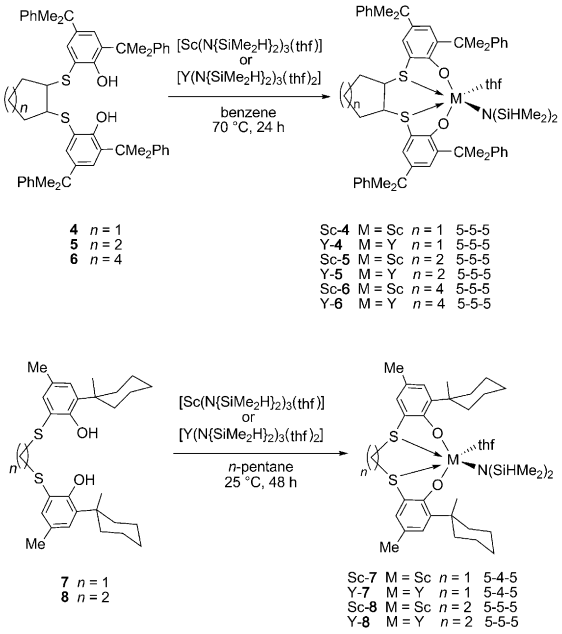


Scheme 8. Synthesis of complexes Ln–**4** to Ln–**8**.

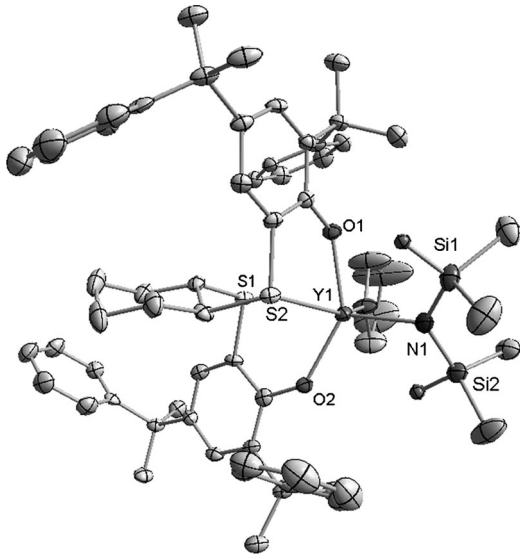


Figure 1. Molecular structure of Y–**5**. Hydrogen atoms, except for Si–H, and solvent were omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–O1 2.147(2), Y1–O2 2.147(2), Y1–O3 2.317(2), Y1–S1 2.9641(8) Y1–S2 2.8502(8), Y1–N1 2.242(3); O1-Y1-O2 143.64(8), S1-Y1-S2 74.03(2), N1-Y1-S1 173.74(7), N1-Y1-O3 103.16(9), O3-Y1-S2 153.58(6).

as two singlet signals between about $\delta = 1.75$ and 1.90 ppm. For the aromatic protons, four signals are observed for Ph-*H*3, Ph-*H*3′, Ph-*H*5, and Ph-*H*5′ between $\delta = 7.00$ and 7.40 ppm. Similar signal patterns and splitting of the signals for the α-THF protons were observed previously.[4g] The ^{1}H NMR spectra of complexes Y–**7** and Y–**8** showed diagnostic resonances. Broad NMR signals for the protons of the 1-methylcyclohexyl groups in Ln–**7** and Ln–**8** (Figures S29, S31, S33, and S35 in the Supporting Information) indicate slow rotation of the bonds at room temperature.

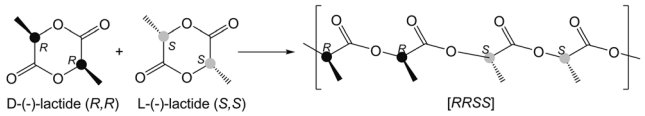
Crystal Structure of Y–5

Single crystals of Y–**5** suitable for X-ray diffraction analysis were obtained by cooling a saturated solution of Y–**5** in *n*-pentane. The molecular structure is depicted in Figure 1.

The yttrium center in Y–**5** is six coordinate with a distorted octahedral geometry; bonded to the tetradentate bis(phenolate) [OSSO]-type ligand, the bis(dimethylsilyl)amido group, and one THF ligand. Both enantiomers of the C_1-symmetric molecule are found in the centrosymmetric crystal. The two oxygen donors of the bis(phenolate) ligand are arranged *trans* to each other, as indicated by the corresponding angles N1-Y1-O3 103.16(9), N1-Y1-S1 173.74(7), and O1-Y1-O2 143.64(8)°. The Y–O(phenolate) bond length (2.147(2) Å in Y–**5**) is within the range of Y–O bond lengths reported in the literature (2.104–2.177 Å).[14–16] The Y–N bond length of 2.242(3) Å is close to the values found for the yttrium amide precursor (2.229(4)–2.276(4) Å).[13a]

Polymerization of *rac*-Lactide

The bis(phenolate) complexes Ln–**1** to Ln–**8** were tested in the polymerization of *rac*-lactide (Scheme 9). The results are summarized in Table 1.



Scheme 9. Formation of heterotactic PLA from *rac*-lactide.

Most of the polymerizations in THF proceeded rapidly with high monomer conversions in less than 3 hours. The scandium complexes Sc–**1**, Sc–**2**, and Sc–**7** (with a 5-4-5 chelate array based on a rigid [OSSO]-type ligand) polymerized *rac*-lactide with low conversions of 21–35% and gave atactic poly(*rac*-lactides) (Table 1, entries 1, 3, and 12). This finding indicates that a highly rigid system lowers the polymerization rate. We suggest that the coordination sphere around the metal center is too crowded to coordinate the *rac*-lactide monomers. In addition, bis(dimethylsilylamido) groups are less nucleophilic than alkoxides, thus leading to a slow initiation of ROP. With the homologous yttrium complexes Y–**1**, Y–**2**, and Y–**7**, conversions of 81, 93, and 97%, respectively, were achieved, giving slightly heterotactic enriched poly(-*rac*-lactides). In most cases, due to the larger metal center and the larger coordination sphere for the lactide monomer, the yttrium complexes were more active than the scandium complexes. This trend has been reported in earlier reports on rare-earth metal bis(phenolate) complexes in lactide pol-

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Table 1. ROP of *rac*-lactide initiated by complexes Ln–**1** to Ln–**8**.[a]

Entry	Init.	Conversion[b] [%]	$M_{n,exptl}$[c] [g mol^{-1}]	M_w/M_n[c]	P_r[d]
1	Sc–**1**	26	6000	1.13	0.49
2	Y–**1**	81	8250	1.05	0.59
3	Sc–**2**	35	12000	1.19	0.50
4	Y–**2**	93	18250	1.65	0.61
5	Sc–**3**	91	18500	1.53	0.72
6	Sc–**4**	80	24500	1.11	0.85
7	Y–**4**	55	12500	1.10	0.68
8	Sc–**5**	98	11250	1.09	0.74
9	Y–**5**	98	20750	1.15	0.68
10	Sc–**6**	86	18250	1.65	0.64
11	Y–**6**	98	17000	1.42	0.63
12	Sc–**7**	21	22000	1.24	0.50
13	Y–**7**	97	20000	1.45	0.57
14	Sc–**8**	94	23750	1.61	0.71
15	Y–**8**	98	12250	1.66	0.54

[a] Polymerization conditions: $[LA]_0/[Init]_0 = 100$, 3 h, THF, 1 mL, 25 °C. [b] Conversion of monomer $(([LA]_0-[LA]_t)/[LA]_0)$. [c] Measured by gel-permeation chromatography (GPC), calibrated with polystyrene (PS) standards in THF.[17] [d] P_r is the probability of obtain *isi* or *sis* tetrads.[18]

ymerization.[4h,7] However, Y–**4** (with a 5-5-5 chelate array) was less active than the scandium homologue.

By contrast, when the C_1-bridged complexes Ln–**1** and Ln–**2** based on 5-4-5 [OSSO]-type ligands were used for the polymerization of *rac*-lactide, the yttrium complexes showed higher heterotacticity than the homologous scandium complexes, indicating that less compact yttrium complexes with 5-4-5 [OSSO]-type ligand were more prone to stereocenter inversion. This is a rare example for Group 3 metal [OSSO]-type bis(phenolate) complexes, in which the larger yttrium complex is both more active and selective than the homologous scandium complexes in the ROP of lactide monomers.

Despite variation in the initial initiator/monomer ratio and polymerization time, the poly(*rac*-lactides) obtained when using complex Y–**1** as the initiator showed the same level of heterotacticity (59–62 %) and polydispersity (Table S1 in the Supporting Information).

The polymer synthesized from *rac*-lactide displayed similar properties ($M_{n,exptl} = 18500$ g mol^{-1}, $M_w/M_n = 1.53$, heterotacticity of 72 %), when complex Sc–**3** based on 6-5-6 [OSSO]-type ligand was used (Table 1, entry 5). The poly(*rac*-lactide) obtained when using a scandium complex based on the 5-5-5 [OSSO]-type ligand without a methylene linker was comparable ($M_{n,exptl} = 18000$ g mol^{-1}, $M_w/M_n = 1.66$, heterotacticity of 78 %). These results indicate that adding flexibility in the ligand has no direct effect. In contrast, the flexibility of the backbone has a direct effect, as indicated by the high heterotacticity (95 %) found with a scandium complex based on a 5-6-5 [OSSO]-type ligand.[4g]

When complexes Ln–**4** to Ln–**6** (based on 5-5-5 chelating [OSSO]-type ligands, but differing in the cycloalkane ring size) were compared, a decrease in the heterotacticity was noted with increasing ring size for the scandium complexes (heterotacticities of 85, 74, and 61 %, respectively). More rigid 1,2-cycloalkanediyl backbones led to higher heterotacticity. Complexes Ln–**4** and Ln–**5** produced polymers with low polydispersity ($M_w/M_n < 1.15$; Table 1, entries 6–9).

We have previously shown that an increase in the size of the *ortho* substituent on the aromatic rings led to an increase in heterotacticity of the poly(*rac*-lactides).[4g] However, when complexes Ln–**8** (with a 1-methylcyclohexyl group in the *ortho*-position of the 5-5-5 chelating ligand) were used to polymerize *rac*-lactide, the heterotacticity of the polymers was lower (71 % for Sc–**8** and 54 % for Y–**8**) than that obtained with rare-earth metal complexes with *tert*-butyl groups in the *ortho* positions (78 % for scandium and 68 % for yttrium).[4g] A similar trend was also observed when the heterotacticity of the polymers formed by complexes Ln–**1** (Table 1, entries 1 and 2) and Ln–**7** with a 5-4-5 chelate array (Table 1, entries 12 and 13) was compared. In comparison with the polymerization results for complexes with a cumyl group in the *ortho* position, Ln–**7** and Ln–**8** were not as active and selective.[4g]

Polymerization of *meso*-Lactide

The bis(phenolate) complexes Ln–**1** to Ln–**8** were tested in the polymerization of *meso*-lactide (Scheme 10). The results are shown in Table 2.

In contrast to the polymerization of *rac*-lactide, 1,3-dithiapropanediyl-bridged bis(phenolate)complexes Y–**1**, Y–**2**, and Y–**7** polymerized *meso*-lactide efficiently, reaching full conversion within 0.5 hours. *meso*-Lactide is polymerized faster because of its higher ring strain.[6h]

The polymerization of *meso*-lactide by the scandium complexes Sc–**2** to Sc–**8** led to high syndiotactic PLAs ($P_s > 0.84$). These syndiotacticity values are close to the highest ones reported in the literature.[6a] The syndiotacticity of the poly(*meso*-lactides) decreases with increasing the radius of the metal center because all yttrium complexes led to lower syndiotacticities ($0.70 \le P_s \le 0.83$). However, Sc–**1** (based on a rigid 5-4-5 [OSSO]-type ligand) showed a relatively low syndiotacticity ($P_s = 0.66$) even lower than the homologous yttrium complex Y–**1** ($P_s = 0.82$). Data for the polymerization of *meso*-lactide by complex Y–**1** with various initial monomer/initiator ratios are collated in Table S2 in the Supporting Information. After 3 hours, an increase from 1:100 to 1:300 resulted in increasing molecular weights ($M_{n,exptl} =$ 19500–44750 g mol^{-1}) at 25 °C and high syndiotacticity values ($P_s > 0.82$). Carpentier et al. reported similar syndiotacticity values using an yttrium alkoxyamino bis(phenolate) amide complex.[6e]

When *meso*-lactide was polymerized by the cumyl-substituted complex Sc–**2**, the poly(*meso*-lactides) obtained were

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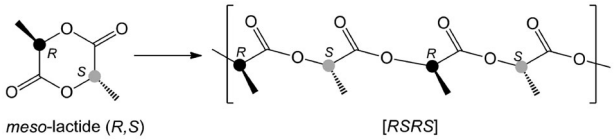

Scheme 10. Formation of syndiotactic PLA from *meso*-lactide.

Table 2. ROP of *meso*-lactide initiated by complexes Ln–**1** to Ln–**8**.[a]

Entry	Init.	Conversion[b] [%]	$M_{n,exptl}$[c] [g mol^{-1}]	M_w/M_n[c]	P_s[d]
1	Sc–**1**	96	29500	1.23	0.66
2	Y–**1**	>99	19250	1.88	0.82
3	Sc–**2**	76	21000	1.94	0.87
4	Y–**2**	>99	14250	1.99	0.83
5	Sc–**3**	>99	33250	2.08	0.87
6	Sc–**4**	93	43250	2.19	0.91
7	Y–**4**	26	18250	1.52	0.80
8	Sc–**5**	>99	32250	1.80	0.92
9	Y–**5**	79	4750	1.94	0.71
10	Sc–**6**	>99	38250	1.67	0.87
11	Y–**6**	>99	1300	7.51	0.76
12	Sc–**7**	82	33750	1.80	0.84
13	Y–**7**	>99	12250	1.19	0.74
14	Sc–**8**	95	23200	2.18	0.89
15	Y–**8**	>99	460	14.7	0.70

[a] Polymerization conditions: $[LA]_0/[Init]_0=100$, 0.5 h, toluene, 1 mL, 25 °C. [b] Conversion of monomer ($([LA]_0-[LA]_t)/[LA]_0$). [c] Measured by GPC with PS standards in THF.[17] [d] P_s is the probability of a new *s* tetrad.[18]

of higher syndiotacticity ($P_s=0.87$) than those obtained with the *tert*-butyl-substituted complex Sc–**1** ($P_s=0.66$). This indicates that there is an increase in the syndiotacticity of the poly(*meso*-lactides) with increasing the size of the *ortho* substituent.[7]

Using complex Sc–**3** (based on 6-5-6 [OSSO]-type ligand) to polymerize *meso*-lactide led to a loss over control of the polymerization relative to the analogous scandium complex based on a 5-5-5 [OSSO]-type ligand without the methylene linker ($M_w/M_n=2.08$ and 1.29 respectively). Hence, the change in the backbone resulted in increased fluxionality, which caused loss of polymerization control. The syndiotacticity of the polymer remained at a similar level.

When complexes Ln–**4** to Ln–**6** (based on 5-5-5 [OSSO]-type ligands with different cycloalkane ring sizes) are compared, all scandium complexes showed high conversion and high syndiotactic preference ($P_s>0.87$).

In contrast to the ROP of *rac*-lactide initiated by 1-methylcyclohexyl-substituted complexes Ln–**7** and Ln–**8**, stereocontrol over *meso*-lactide polymerization was comparable to the stereocontrol given by *tert*-butyl-substituted complexes.[4h] Based on a 5-4-5-chelate, syndiotacticities of $P_s=0.66$ (Sc–**1**) and 0.82 (Y–**1**) were obtained for *tert*-butyl-substituted complexes, while Sc–**7** and Y–**8** gave tacticity values of $P_s=0.84$ (Sc–**7**) and $P_s=0.74$ (Y–**7**). This might result from the different structure of the *meso*-lactide. The M_w/M_n values are high for all poly(*meso*-lactides). Only Sc–**1** and Y–**7** (based on a rigid 5-4-5 chelate) gave narrowly distributed polymers ($M_w/M_n=1.23$ (Sc–**1**), 1.19 (Y–**7**)).

Mechanistic Discussion

To understand the origin of the high syndioselectivity, one equivalent of bis(phenolate) yttrium complex Y–**5** was treated with one equivalent of (*R*)-(+)-methyl lactate or (*S*)-(−)-methyl lactate to give complexes (*R*)-Y–**5** and (*S*)-Y–**5**, respectively. The ^{1}H NMR spectra ([D$_6$]benzene) of complexes (*R*)-Y–**5** and (*S*)-Y–**5** show identical resonances diagnostic of a dimeric structure.

Furthermore, we reported that rare-earth metal bis(phenolate) complexes were able to produce highly syndiotactic PLAs with values of $P_s>0.90$, when the *ortho* substituent was cumyl.[7] Despite numerous variations in the backbone, the *ortho* position, and the leaving group, syndiotactity values above 0.94 have never been achieved. This led us to postulate intramolecular exchange of diastereomers as an explanation for this lack of syndiospecificity (Scheme 11). Transesterification due to fast polymerization rates could also explain this phenomenon.

According to chain-end control, in which the chirality of the last inserted unit influences the chirality of the next inserted monomer, metal chirality due to ligand fluxionality (Λ,*R* and Δ,*R*) may not affect syndiotacticity. Furthermore, when the rate constant for the exchange between diastereomers, k_{inv}, is lower than the rate constant for propagation, k_{prop}, the polymer should be syndiotactic. The errors in tacticity are due to exchange between diastereomers ($k_{inv} \gg k_{prop}$). Suppression of the inversion between diastereomers should lead to high syndiotactic PLAs. There is an interesting analogy: Schrock and co-workers reported recently the use of chiral-at-metal molybdenum catalysts for the ring-opening metathesis polymerization of racemic norbornene monomers that selectively gave *cis*, syndiotactic polymers.[19]

Conclusion

Structurally defined initiators based on Group 3 metal complexes with [OSSO]-type bis(phenolate) ligands and 5-4-5 and 5-5-5 chelate arrays polymerized lactide monomers efficiently. The complexes led to heterotactic-biased poly(*rac*-lactides) and highly syndiotactic poly(*meso*-lactides). The scandium complexes gave polymers with higher heterotacticity and syndiotacticity than those obtained when using the homologous yttrium compounds. The complexes based on a rigid C$_1$-bridged, 5-4-5 [OSSO]-ligand (**1**, **2**, and **7**) behaved differently. For the scandium complexes Sc–**4** to Sc–**6** (based

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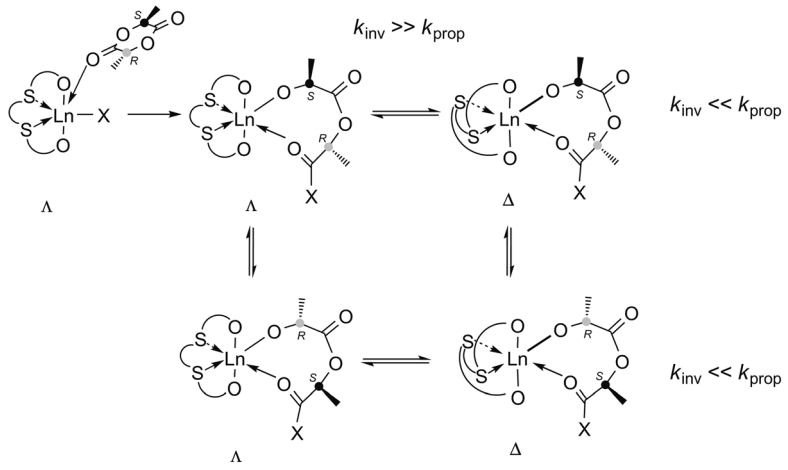

Scheme 11. Exchange of diastereomeric rare-earth metal bis(phenolato) initiators during *meso*-lactide polymerization.

on a 5-5-5 chelate array), heterotacticity decreased with increasing 1,2-cycloalkanediyl ring size. The more rigid 1,2-cycloalkanediyl backbone led to higher heterotacticity. In summary, the structure activity/stereoselectivity relationship remains challenging to elucidate.

Experimental Section

General

All operations were performed under an inert atmosphere of argon by using standard Schlenk-line or glovebox techniques. Toluene (Fisher Scientific), *n*-pentane (Fisher Scientific), and THF (Fisher Scientific) were distilled under argon from sodium/benzophenone ketyl prior to use. [D_6]Benzene (Sigma-Aldrich) and $CDCl_3$ (Sigma–Aldrich) were carefully dried and stored in a glovebox. [Ln{N($SiHMe_2$)$_2$}$_3$(thf)$_x$] (Ln = Sc, x = 1; Y, x = 2)[13c] and 2,2′-dithiobis[4,6-di-(2-phenyl-2-propyl)phenol][11] were synthesized according to literature methods.[13c] *meso*-Lactide (Uhde Inventa-Fischer) was recrystallized from isopropanol at −30 °C, washed with diethyl ether, and dried under vacuum. All other chemicals were commercially available and used after appropriate purification. Glassware and vials used for polymerization were dried in an oven at 120 °C overnight and exposed to vacuum–argon cycles three times. NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer at 25 °C (^{1}H: 400 MHz; ^{13}C: 100.1 MHz). Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally by using the residual solvent resonances and are reported relative to tetramethylsilane. Molecular weights and polydispersities were determined by size exclusion chromatography (SEC) in THF at 35 °C at a flow rate of 1 mL min^{-1} by utilizing an Agilent 1100 Series HPLC, G1310A isocratic pump, an Agilent 1100 Series refractive index detector, and 8 × 600 mm, 8 × 300 mm, 8 × 50 mm PSS SDV linear M columns. Calibration standards were commercially available narrowly distributed linear polystyrene samples that covered a broad range of molar masses ($10^3 < M_n < 2 \times 10^6$ g mol^{-1})

*Synthesis of Compounds **1**, **3**, **5**, Sc–**5**, and Y–**5***

These compounds were synthesized as previously reported.[7,9,10,20]

*Synthesis of Compound **2***

NaOMe (5.35 g, 99 mmol, 2 equiv) was added to a mixture of 2-mercapto-4,6-bis(2-phenylpropan-2-yl)phenol (36.00 g, 99 mmol, 2 equiv) in MeOH (100 mL) and EtOH (100 mL) and then heated at reflux until all NaOMe was dissolved. The mixture was cooled to room temperature and CH_2Br_2 (3.21 mL, 46 mmol, 1 equiv) was added dropwise. The mixture was heated at reflux for 16 h and the solvents were evaporated under vacuum. Water (200 mL) was added and the mixture was extracted with Et_2O (3 × 100 mL). The organic phase was separated, dried over anhydrous $MgSO_4$, filtered, and evaporated to give a colorless foam. Recrystallization from *n*-pentane afforded colorless crystals of **2** (5.35 g, 7.26 mmol, 15 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.33–7.32 (m, 2H; Ph-*H*), 7.30–7.29 (m, 2H; Ph-*H*), 7.29–7.28 (m, 6H; Ph-*H*), 7.27–7.26 (m, 2H; Ph-*H*), 7.25–7.22 (m, 4H; Ph-*H*), 7.18–7.14 (m, 4H; Ph-*H*), 6.15 (s, 2H; PhO*H*), 3.72 (s, 2H; SCH_2S), 1.70 (s, 12H; C(CH_3)$_2$), 1.65 ppm (s, 12H; C(CH_3)$_2$); ^{13}C NMR (100.1 MHz, $CDCl_3$, 25 °C): δ = 152.9 (Ph-*C*), 150.6 (Ph-*C*), 150.2 (Ph-*C*), 142.2 (Ph-*C*), 135.1 (Ph-*C*), 132.0 (Ph-*C*), 128.2 (Ph-*C*), 128.1 (Ph-*C*), 126.8 (Ph-*C*), 125.7 (Ph-*C*), 125.6 (Ph-*C*3), 118.3 (Ph-*C*2), 42.7 (*p*-*C*(CH$_3$)$_2$), 42.6 (*o*-*C*(CH$_3$)$_2$), 42.5 (S*C*H$_2$S), 31.1 (*o*-C(*C*H$_3$)$_2$), 29.5 ppm (*p*-C(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{49}H_{52}O_2S_2$ (737.06): C 88.53, H 7.67; found: C 88.15, H 7.65.

*Synthesis of Compound **4***

Cyclopentene (1.24 mL, 14 mmol, 1 equiv) and a solution of BF_3·OEt_2 (0.25 mL) were added to a solution of 2,2′-dithiobis[4,6-di-(2-phenyl-2-propyl)phenol] (10.0 g, 14 mmol, 1 equiv) in a mixture of nitromethane (8 mL) and CH_2Cl_2 (8 mL) at −10 °C. The resulting mixture was stirred at −10 °C for 3 h and at room temperature for an additional 72 h. The resulting mixture was washed a saturated aqueous solution of $NaHCO_3$ (3 × 100 mL). After separation of the phases, the organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. Recrystallization from a mixture of acetonitrile/acetone (4:1, 200 mL) gave pure bis(phenol) *rac*-**4** as a yellow solid (8.24 g, 10.4 mmol, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.35 (d, ^3J(H,H) = 2.2 Hz, 2H; Ph-*H*), 7.30–7.27 (m, 4H; Ph-*H*), 7.27–7.25 (m, 4H; Ph-*H*), 7.25–7.20 (m, 6H; Ph-*H*), 7.19 (d, ^3J(H,H) = 2.2 Hz, 2H; Ph-*H*), 7.18–7.16 (m, 4H; Ph-*H*), 7.16–7.11 (m, 4H; Ph-*H*), 6.64 (s, 2H; PhO*H*), 2.79 (br s 2H; SC*H*), 1.77–1.75 (m, 2H; Cy-H), 1.70 (s, 12H; C(CH_3)$_2$Ph), 1.66 (s, 6H; C(CH_3)$_2$Ph), 1.65 (s, 6H; C(CH_3)$_2$Ph), 1.45–1.43 (m, 2H; Cy-*H*), 1.35–1.33 ppm, (m, 2H; Cy-*H*); ^{13}C NMR (100.1 MHz, $CDCl_3$, 25 °C): δ = 154.1 (Ph-*C*1), 151.1 (Ph-*C*), 150.8 (Ph-*C*), 142.0 (Ph-*C*4), 135.4 (Ph-*C*), 133.7 (Ph-*C*6), 128.9 (Ph-*C*), 128.3 (Ph-*C*), 128.0 (Ph-*C*), 127.0 (Ph-*C*5), 126.2 (Ph-*C*), 126.0 (Ph-*C*), 125.6 (Ph-*C*3), 119.1 (Ph-*C*2), 54.9 (S*C*H$_2$), 42.9 (*C*(CH$_3$)$_2$), 42.8 (*C*-(CH$_3$)$_2$), 31.1 (Cy-*C*), 30.2 (Cy-*C*), 29.7 (C(*C*H$_3$)$_2$), 29.6 (C(*C*H$_3$)$_2$), 27.5 (Cy-*C*), 26.2 (Cy-*C*), 25.8 (Cy-*C*), 24.9 ppm (Cy-*C*); elemental analysis calcd (%) for $C_{53}H_{58}O_2S_2$ (791.17): C 80.46, H 7.39; found: C 80.32, H 7.22.

*Synthesis of Compound **6***

Cyclooctene (7.40 mL, 56 mmol, 2 equiv) and a solution of BF_3·OEt_2 (0.25 mL) were added to a solution of 2,2′-dithiobis[4,6-di-(2-phenyl-2-propyl)phenol] (20 g, 28 mmol) in a mixture of nitromethane (15 mL) and CH_2Cl_2 (15 mL) at −10 °C. The resulting mixture was stirred at −10 °C for 3 h and at room temperature for 72 h. The mixture was washed with a saturated aqueous solution of $NaHCO_3$ (3 × 100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. Recrystallization from a mixture of acetonitrile/acetone (4:1, 200 mL) gave pure bis(phenol) *rac*-**6** as an orange solid (3.6 g, 4.3 mmol, 15 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.60 (d, ^3J(H,H) = 2.3 Hz, Ph-*H*), 7.49 (d, ^4J(H,H) = 2.8 Hz, Ph-*H*), 7.41–7.35 (m, 6H; Ph-*H*), 7.34 (d, ^4J(H,H) = 2.8 Hz, 2H; Ph-*H*5), 7.28 (d, ^4J(H,H) = 2.8 Hz, 2H; Ph-*H*3), 7.26–7.22 (m, 2H; Ph-*H*), 7.19–7.13 (m, 2H; Ph-*H*), 7.10 (s, 2H; Ph-*H*),

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2.90 (brs 2H; SC*H*), 1.84 (s, 6H; C(CH_3)$_2$Ph), 1.83 (s, 6H; C(CH_3)$_2$Ph), 1.73 (s, 12H; C(CH_3)$_2$Ph), 1.56–1.54(m, 2H; Cy-*H*), 1.44–1.42(m, 2H; Cy-*H*), 1.230–1.28 (m, 2H; Cy-*H*), 1.21–1.19 (m, 2H; Cy-*H*), 1.10–1.08 ppm (m, 2H; Cy-*H*); ^{13}C NMR (100.1 MHz, C_6D_6, 25 °C): δ = 154.1 (Ph-*C*), 151.1 (Ph-*C*), 150.8 (Ph-*C*), 142.0 (Ph-*C*), 135.4 (Ph-*C*), 133.7 (Ph-*C*), 128.9 (Ph-*C*), 128.3 (Ph-*C*), 128.0 (Ph-*C*), 127.0 (Ph-*C*), 126.2 (Ph-*C*), 126.0 (Ph-*C*), 119.1 (Ph-*C*), 54.8 (S*C*H$_2$), 42.9 (*C*(CH$_3$)$_2$), 42.8 (*C*-(CH$_3$)$_2$), 31.1 (Cy-*C*), 30.2 (Cy-*C*), 29.7 (C(*C*H$_3$)$_2$), 29.6 (C(*C*H$_3$)$_2$), 26.2 (Cy-*C*), 25.8 ppm (Cy-*C*); elemental analysis calcd (%) for $C_{56}H_{64}O_2S_2$ (832.25): C 80.72, H 7.74; found: C 79.58, H 7.71.

Synthesis of Compound ***7***

NaOMe (0.66 g, 12.2 mmol, 2 equiv) was added to a solution of 2-mercapto-4-methyl-6-(1-methylcyclohexyl)phenol (2.5 g, 12.2 mmol, 2 equiv) in MeOH (25 mL) and the mixture was heated to reflux until all NaOMe dissolved. After cooling to 0 °C, 1,1-dibromomethane (0.43 mL, 6.1 mmol, 1 equiv) was added slowly with a syringe and the mixture was heated to reflux for 1 h. After removal of the solvent under vacuum, water (100 mL) was added to dissolve NaBr. After addition of diethyl ether (100 mL), the organic phase was separated, the aqueous phase was extracted with diethyl ether (2×50 mL), and the combined organic phases were dried over Na_2SO_4. The crude product was recrystallized from *n*-pentane to afford compound **7** as a yellow powder (1.13 g, 2.33 mmol, 38 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.12 (d, ^4J(H,H) = 2.2 Hz, 2H; Ph-*H*3), 7.09 (d, ^4J(H,H) = 2.2 Hz, 2H; Ph-*H*5), 6.76 (s, 2H; Ph-O*H*), 3.90 (s, 2H; SCH_2), 2.27–2.26 (m, 2H; Ph-Cy-*H*), 2.25 (s, 6H; Ph-CH_3), 2.15–2.08 (m, 4H; Cy-*H*), 1.71–1.66 (m, 4H; Cy-*H*), 1.56–1.54 (m, 4H; Cy-*H*), 1.50–1.46 (m, 8H; Cy-*H*), 1.45–1.41 (m, 6H; Cy-*H*), 1.30 ppm (s, 6H; Cy-CH_3); ^{13}C NMR (100.1 MHz, $CDCl_3$, 25 °C): δ = 153.4 (Ph-*C*1), 135.6 (Ph-*C*6), 133.4 (Ph-*C*5), 131.4 (Ph-*C*4), 129.1 (Ph-*C*3), 118.5 (Ph-*C*2), 45.0 (S*C*H$_2$), 38.5 (Cy-*C*), 36.8 (Cy-*C*), 26.8 (Cy-*C*), 25.4 (Cy-*C*), 22.9 (Cy-*C*H$_3$), 20.8 ppm (Ph-*C*H$_3$); elemental analysis calcd (%) for $C_{29}H_{40}O_2S_2$ (484.76): C 71.85, H 8.32; found: C 71.43, H 8.84.

Synthesis of Compound ***8***

NaOH (0.85 g, 21.2 mmol, 2 equiv) was added to a solution of 2-mercapto-4-methyl-6-(1-methylcyclohexyl)phenol (5.0 g, 21.2 mmol, 2 equiv) in MeOH (50 mL) and the mixture was heated to reflux until all NaOH dissolved. After cooling to 0 °C, 1,2-dibromoethane (0.92 mL. 10.6 mmol, 1 equiv) was added slowly with a syringe and the mixture was heated at reflux for 1 h. After removal of the solvent under vacuum, water (100 mL) was added to dissolve NaBr. After addition of diethyl ether (200 mL), the organic phase was separated, the aqueous phase was extracted with diethyl ether (2×100 mL), and the combined organic phases were dried over Na_2SO_4. After filtration and removal of the solvent under vacuum, the crude product was recrystallized from *n*-pentane to afford compound **8** as a brownish powder (0.81 g, 1.63 mmol, 15 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.13–7.11 (brs, 2H; Ph-*H*3), 7.11–7.09 (brs 2H; Ph-*H*5), 7.08 (s, 2H; Ph-O*H*), 2.77 (s, 4H; SCH_2), 2.24 (s, 6H; Ph-CH_3), 2.16–2.08 (m, 4H; Cy-*H*), 1.74–1.66 (m, 4H; Cy-*H*), 1.60–1.54 (m, 4H; Cy-*H*), 1.49–1.42 (m, 8H; Cy-*H*), 1.31 ppm; (s, 6H; Cy-CH_3); ^{13}C NMR (100.1 MHz, $CDCl_3$, 25 °C): δ = 153.6 (Ph-*C*1), 135.4 (Ph-*C*6), 133.6 (Ph-*C*5), 131.0 (Ph-*C*4), 129.0 (Ph-*C*3), 118.2 (Ph-*C*2), 38.5 (Ph-*C*CH$_3$), 36.8 (Cy-*C*), 36.3 (S*C*H$_2$), 26.8 (Cy-*C*), 25.4 (Cy-*C*), 22.9 (Cy-*C*), 20.9 ppm (Ph-*C*H$_3$); elemental analysis calcd (%) for $C_{30}H_{42}O_2S_2$ (498.8): C 72.24, H 8.49; found: C 72.25, H 8.76.

*Synthesis of Sc–**1***

[Sc{N(SiMe$_2$H)$_2$}$_3$(thf)] (0.20 g, 0.4 mmol, 1 equiv) and proligand **1** (0.19 g, 0.4 mmol, 1 equiv) were dissolved in benzene (2.5 mL) and the solution stirred for 24 h at 70 °C. After removing the solvent in vacuo, the colorless solid formed was recrystallized from *n*-pentane at −30 °C to give Sc–**1** as a colorless powder (0.12 g, 0.16 mmol, 42 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.71 (d, ^4J(H,H) = 2.6 Hz, 2H; Ph-*H*), 7.51 (d, ^4J(H,H) = 2.6 Hz, 2H; Ph-*H*), 5.40 (sept, ^3J(H,H) = 3.1 Hz, 2H; Si-*H*), 4.10 (s, 4H; α-THF), 3.71 (s, 2H; SCH_2S), 1.83 (s, 18H; C(CH_3)$_3$), 1.37 (s, 18H; C(CH_3)$_3$), 1.26–1.22 (m, 4H; β-THF), 0.49 ppm (d, ^3J(H,H) = 3.1 Hz, 12H; Si-CH_3); ^{13}C NMR (100.1 MHz, C_6D_6, 25 °C): δ = 157.9 (Ph-*C*1), 139.2 (Ph-*C*6), 137.4 (Ph-*C*4), 129.0 (Ph-*C*3), 127.0 (Ph-*C*5), 123.8 (Ph-*C*2), 71.9 (α-THF), 50.8 (S*C*H$_2$S), 34.2 (*C*(CH$_3$)$_3$), 31.7 (6-C(*C*H$_3$)$_3$), 30.0 (4-C(*C*H$_3$)$_3$), 24.9 (β-THF), 3.3 ppm (Si(*C*H$_3$)$_3$); elemental analysis calcd (%) for $C_{37}H_{64}NO_3S_2ScSi_2$ (736.2): C 60.37, H 8.76, N 1.90; found: C 57.13, H 8.39, N 1.78.

*Synthesis of Y–**1***

[Y{N(SiMe$_2$H)$_2$}$_3$(thf)$_2$] (0.20 g, 0.4 mmol, 1 equiv) and proligand **1** (0.20 g, 0.4 mmol, 1 equiv) were dissolved in benzene (2.5 mL) and the solution was stirred for 24 h at 70 °C. After removing the solvent under vacuum, the colorless precipitate formed was recrystallized from *n*-pentane at −30 °C to give Y–**1** as a colorless powder (0.18 g, 0.22 mmol, 54 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.61 (d, ^4J(H,H) = 2.7 Hz, 2H; Ph-*H*), 7.39 (d, ^4J(H,H) = 2.7 Hz, 2H; Ph-*H*), 5.18 (sept, ^3J(H,H) = 3.5 Hz, 2H; Si-*H*), 3.86 (s, 2H; SCH_2S), 3.81 (s, 4H; α-THF), 1.75 (s, 18H; C(CH_3)$_3$), 1.29 (s, 18H; C(CH_3)$_3$), 1.22–1.18 (m, 4H; β-THF), 0.38 ppm (d, ^3J(H,H) = 3.0 Hz, 12H; Si(CH_3)$_2$); ^{13}C NMR (100.1 MHz, C_6D_6, 25 °C): δ = 165.6 (Ph-*C*1), 138.7 (Ph-*C*6), 138.1 (Ph-*C*4), 129.8 (Ph-*C*3), 127.2 (Ph-*C*5), 123.2 (Ph-*C*2), 69.9 (α-THF), 49.7 (S*C*H$_2$S), 36.0 (6-*C*(CH$_3$)$_3$), 34.2 (4-*C*(CH$_3$)$_3$), 31.9 (6-C(*C*H$_3$)$_3$), 30.0 (4-C(*C*H$_3$)$_3$), 24.1 (β-THF), 1.4 ppm (Si(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{37}H_{64}NO_3S_2YSi_2$ (780.1): C 56.97, H 8.27, N 1.80; found: C 55.54, H 8.19, N 1.22.

*Synthesis of Sc–**2***

A solution of proligand **2** (0.1 g, 0.14 mmol, 1 equiv) in benzene (1 mL) was added slowly to a solution of [Sc{N(SiMe$_2$H)$_2$}$_3$(thf)] (0.07 g, 0.14 mmol, 1 equiv) in benzene (1 mL) at 25 °C. The resulting orange solution was stirred at 70 °C for 24 h. Removal of the solvent under vacuum afforded a colorless powder that was dissolved in *n*-pentane (2 mL), filtered, and stored at −30 °C for 2 weeks. After recrystallization, complex Sc–**2** was isolated as a colorless powder (0.085 g, 0.09 mmol, 64 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.46 (brs 2H; Ph-*H*5), 7.32 (d, ^3J-(H,H) = 2.6 Hz, 2H; Ph-*H*3), 7.29 (d, ^3J(H,H) = 7.7 Hz, 4H; Ph-*H*), 7.21–7.16 (m, 4H; Ph-*H*), 7.15 (s, 2H; Ph-*H*), 7.13–7.00 (m, 6H; Ph-*H*), 6.94–6.92(m, 2H; Ph-*H*), 5.11 (sept, ^3J(H,H) = 3.0 Hz, 2H; Si*H*), 3.67 (brs, 1H; SCH_2S), 3.50 (brs, 1H; SCH_2S), 2.94 (brs, 4H; α-THF), 2.10–1.40 (brs, 24H; C(CH_3)$_2$), 0.91 (br, 4H; β-THF), 0.39 (d, ^3J(H,H) = 3.0 Hz, 6H; SiCH_3), 0.34 ppm (d, ^3J(H,H) = 3.0 Hz, 6H; SiCH_3); ^{13}C NMR (C_6D_6, 25 °C, 100.1 MHz): δ = 151.8 (Ph-*C*1), 138.8 (Ph-*C*6), 131.0 (Ph-*C*4), 130.2 (Ph-*C*), 128.4 (Ph-*C*), 128.2 (Ph-*C*3), 127.9 (Ph-*C*), 127.1 (Ph-*C*), 125.9 (Ph-*C*5), 125.7 (Ph-*C*2), 71.2 (α-THF), 52.4 (S*C*H$_2$S), 43.3 (*C*-(CH$_3$)$_2$), 42.7 (*C*(CH$_3$)$_2$), 31.5 (C(*C*H$_3$)$_2$), 31.2 (C(*C*H$_3$)$_2$), 25.0 (β-THF), 3.7 (Si(*C*H$_3$)$_2$), 3.0 ppm (Si(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{57}H_{72}NO_3S_2ScSi_2$ (984.4): C 69.54, H 7.37, N 1.42; found: C 66.22, H 7.20, N 1.65.

*Synthesis of Y–**2***

A solution of proligand **2** (0.1 mg, 0.14 mmol, 1 equiv) in benzene (1 mL) was added slowly to a solution of [Y{N(SiMe$_2$H)$_2$}$_3$(thf)$_2$] (0.086 g, 0.14 mmol, 1 equiv) in benzene (1 mL) at 25 °C. The orange solution was stirred at 70 °C for 24 h. The solvent was removed under vacuum to afford a colorless powder that was dissolved in *n*-pentane (2 mL), filtered, and stored at −30 °C for 2 weeks. After recrystallization, complex Y–**2** was afforded as a colorless powder (0.08 g, 0.08 mmol, 57 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.50 (d, ^4J(H,H) = 2.6 Hz, 2H; Ph-*H*5), 7.35 (d, ^4J(H,H) = 2.6 Hz, 2H; Ph-*H*3), 7.34–7.326 (m, 8H; Ph-*H*), 7.20–7.16 (m, 4H; Ph-*H*), 7.09–7.05 (m, 6H; Ph-*H*), 6.89–6.85 (m, 6H; Ph-*H*), 4.99–4.97 (m, 2H; Si*H*), 3.64 (s, 2H; SCH_2S), 3.16–3.12 (brs 4H; α-THF), 1.80 (s, 12H; C(CH_3)$_2$), 1.64 (s, 12H; C(CH_3)$_2$), 1.09–1.05 (brs 4H; β-THF), 0.40–0.38 (brs, 6H; SiCH_3), 0.37–0.35 ppm (brs, 6H; SiCH_3); ^{13}C NMR (100.1 MHz, C_6D_6, 25 °C): δ = 165.1 (Ph-*C*1), 152.1 (Ph-*C*), 151.5 (Ph-*C*), 138.1 (Ph-*C*6), 137.3 (Ph-*C*4), 131.5 (Ph-*C*3), 129.8 (Ph-*C*), 128.4 (Ph-*C*), 127.9 (Ph-*C*), 127.1 (Ph-*C*5), 126.6 (Ph-*C*), 125.9 (Ph-*C*), 124.8 (Ph-*C*), 121.1 (Ph-*C*2), 70.1 (α-THF), 51.7 (S*C*H$_2$S), 43.2 (*C*(CH$_3$)$_2$), 42.7 (*C*(CH$_3$)$_2$), 31.3 (C(*C*H$_3$)$_2$), 30.2 (C(*C*H$_3$)$_2$), 25.2 (β-THF), 3.7 (Si(*C*H$_3$)$_2$), 3.2 ppm (Si(*C*H$_3$)$_2$); elemental analysis calcd (%) for

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$C_{57}H_{72}NO_3S_2YSi_2$ (1028.39): C 66.57, H 7.06, N 1.36; found: C 65.93, H 6.77, N 1.34.

*Synthesis of Sc–**3***

Proligand **3** (0.97 g, 0.19 mmol, 1 equiv) in *n*-pentane (2 mL) was added to a solution of $[Sc\{N(SiMe_2H)_2\}_3(thf)]$ (0.1 g, 0.19 mmol, 1 equiv) in *n*-pentane (2 mL). The reaction was stirred at room temperature for 18 h. The solvent was removed in vacuo to give a white powder that was dissolved in *n*-pentane (1 mL), filtered, and stored at −30 °C for 24 h. After recrystallization, complex Sc–**3** was isolated as a colorless powder (0.11 g, 0.14 mmol, 63 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.51 (d, ^4J(H,H) = 2.6 Hz, 2H; Ph-*H*5), 6.89 (d, ^4J(H,H) = 2.6 Hz, 2H; Ph-*H*3), 5.17 (sept, ^3J(H,H) = 3.4 Hz, 2H; Si-*H*), 3.63–3.57 (br s, 8H; SCH_2S and α-THF), 1.89 (br s, 4H; Ph(CH_2)S), 1.67 (s, 18H; C(CH_3)$_3$), 1.34 (s, 18H; C-(CH_3)$_3$), 1.32–1.30 (m, 4H; β-THF), 0.47 ppm (d, ^3J(H,H) = 3.4 Hz, 12H; Si-CH_3); ^{13}C NMR (100.1 MHz, C_6D_6, 25 °C): δ = 160.3 (Ph-*C*1), 139.0 (Ph-*C*6), 137.3 (Ph-*C*4), 125.1 (Ph-*C*5), 124.8 (Ph-*C*3), 120.8 (Ph-*C*2), 68.2 (S*C*H$_2$S), 68.1 (α-THF), 35.6 (S-*C*H$_2$Ph), 32.2 (6-*C*(CH$_3$)$_3$), 32.0 (4-C-(*C*H$_3$)$_3$), 31.9 (6-C(*C*H$_3$)$_3$), 30.5 (4-C(*C*H$_3$)$_3$), 25.8 (THF), 2.8 ppm (Si-(*C*H$_3$)$_3$); elemental analysis data could not be obtained.

*Synthesis of Sc–**4***

A solution of proligand **4** (0.15 g, 0.19 mmol, 1 equiv) in benzene (1 mL) was added dropwise to a solution $[Sc\{N(SiMe_2H)_2\}_3(thf)]$ (0.10 g, 0.19 mmol, 1 equiv) in benzene (1 mL) at 25 °C. The orange solution was stirred at 70 °C for 24 h. The solvent was removed under vacuum to afford an orange oil, which was dissolved in a mixture of *n*-pentane/THF (1:1, 3 mL, filtered, and stored at −30 °C for 3 d. After recrystallization, complex Sc–**4** was afforded as a colorless powder (0.13 g, 0.13 mmol, 67 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.68 (d, ^4J(H,H) = 5.4 Hz, 2H; Ph-*H*5), 7.55 (d, ^3J(H,H) = 7.5 Hz, 2H; Ph-*H*3), 7.34–7.28 (br s, 10H; Ph-*H*), 7.24–7.22 (m, 6H; Ph-*H*), 7.12–7.10 (m, 4H; Ph-*H*), 5.20–5.16 (m, 2H; Si*H*), 3.27–3.21 (m, 4H; α-THF), 2.70–2.68 (m, 2H; SC*H*), 2.19 (s, 3H; C*H*$_3$), 2.10 (s, 3H; C(C*H*$_3$)$_2$), 1.96 (s, 3H; C(C*H*$_3$)$_2$), 1.78–1.76 (m, 2H; Cy-*H*), 1.73 (s, 3H; C(C*H*$_3$)$_2$), 1.70 (s, 3H; C(C*H*$_3$)$_2$), 1.60–1.58 (m, 2H; Cy-*H*), 1.48–1.46 (br s, 2H; Cy-*H*), 1.13–1.109 (m, 4H; β-THF), 0.45 (d, ^3J(H,H) = 3.1 Hz, 6H; SiC*H*$_3$), 0.42 ppm (d, ^3J(H,H) = 3.1 Hz, 6H; SiC*H*$_3$); ^{13}C NMR (100.1 MHz, C_6D_6, 25 °C): δ = 166.5 (Ph-*C*1′), 165.9 (Ph-*C*1), 151.5 (Ph-*C*), 151.3 (Ph-*C*), 151.1 (PH-*C*), 151.0 (Ph-*C*), 137.3 (Ph-*C*6′), 137.0 (Ph-*C*6), 135.2 (Ph-*C*), 133.3 (Ph-*C*4′), 133.1 (Ph-*C*4), 128.2 (Ph-*C*3′), 128.0 (Ph-*C*3), 127.3 (Ph-*C*), 126.4 (Ph-*C*), 126.3 (Ph-*C*), 125.6 (Ph-*C*), 125.2 (Ph-*C*), 125.1 (Ph-*C*), 124.5 (Ph-*C*), 124.4 (Ph-*C*), 115.7 (Ph-*C*2), 70.8 (α-THF), 53.0 (S*C*H), 50.4 (S*C*H), 43.2 (*C*(CH$_3$)$_2$), 42.6 (*C*(CH$_3$)$_2$), 42.4 (*C*(CH$_3$)$_2$), 41.9 (*C*(CH$_3$)$_2$), 33.1 (Cy-*C*), 30.7 (C-(*C*H$_3$)$_2$), 30.4 (C(*C*H$_3$)$_2$), 30.3 (C(*C*H$_3$)$_2$), 29.2 (Cy-*C*), 28.8 (Cy-*C*), 28.2 (C(*C*H$_3$)$_2$), 27.0 (C(*C*H$_3$)$_2$), 24.3 (β-THF), 22.0 (Cy-*C*), 3.7 ppm (Si-(*C*H$_3$)$_2$); elemental analysis: calcd (%) for $C_{61}H_{78}NO_3S_2ScSi_2$ (1038.53): C 70.55, H 7.48, N 1.36; found: C 68.90, H 7.49, N 0.98.

*Synthesis of Y–**4***

A solution of proligand **4** (0.12 g, 0.16 mmol, 1 equiv) in benzene (1 mL) was added dropwise to a solution of $[Y\{N(SiMe_2H)_2\}_3(thf)_2]$ (0.10 g, 0.16 mmol) in benzene (1 mL) at 25 °C. The orange solution was stirred at 70 °C for 24 h. The solvent was removed under vacuum to afford an orange oil, which was dissolved in a mixture of *n*-pentane/THF (1:1, 3 mL), filtered, and stored at −30 °C for 3 d. Complex Y–**4** was isolated as a colorless powder (0.13 g, 0.12 mmol, 61 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.59 (d, ^3J(H,H) = 2.5 Hz, 2H; Ph-*H*5), 7.34 (d, ^3J-(H,H) = 7.2 Hz, 4H; Ph-*H*3), 7.25 (dt, ^3J(H,H) = 3.1 Hz, ^4J(H,H) = 1.8 Hz, 2H; Ph-*H*), 7.21 (d, ^4J(H,H) = 2.5 Hz, 2H; Ph-*H*), 7.17 (d, ^3J(H,H) = 5.2 Hz, 2H; Ph-*H*), 7.15–7.11 (m, 6H; Ph-*H*), 7.06–7.02 (m, 4H; Ph-*H*), 4.97 (sept, ^3J(H,H) = 3.0 Hz, 2H; Si*H*), 3.42–3.38 (m, 4H; α-THF), 2.63–2.61 (m, 2H; SC*H*), 1.92 (s, 6H; C(C*H*$_3$)$_2$), 1.78 (s, 6H; C(C*H*$_3$)$_2$), 1.68–1.64 (m, 4H; Cy-*H*), 1.63 (s, 6H; C(C*H*$_3$)$_2$), 1.62–1.60 (m, 2H; Cy-*H*), 1.60 (s, 6H; C(C*H*$_3$)$_2$), 1.31–1.27 (m, 4H; β-THF), 0.36 (d, ^3J(H,H) = 3.0 Hz, 6H; SiC*H*$_3$), 0.33 ppm (d, ^3J(H,H) = 3.0 Hz, 6H; SiC*H*$_3$); ^{13}C NMR (100.1 MHz, C_6D_6, 25 °C): δ = 167.1 (Ph-*C*1), 137.3 (Ph-*C*6′), 137.2 (Ph-*C*6), 134.2 (PH-*C*), 128.4 (Ph-*C*4), 128.2 (Ph-*C*3′), 127.9 (Ph-*C*3), 127.1 (Ph-*C*), 126.4 (Ph-*C*), 125.8 (Ph-*C*), 124.9 (Ph-*C*), 116.4 (Ph-*C*2), 68.8 (α-THF), 51.9 (S*C*H), 43.1 (*C*(CH$_3$)$_2$), 42.6 (*C*(CH$_3$)$_2$), 31.2 (Cy-*C*), 31.1 (C(*C*H$_3$)$_2$), 31.0 (Cy-*C*), 28.4 (C(*C*H$_3$)$_2$), 25.6 (β-THF), 23.2 (Cy-*C*), 3.9 (Si(*C*H$_3$)$_2$), 3.8 ppm (Si(*C*H$_3$)$_2$); elemental analysis: calcd (%) for $C_{61}H_{78}NO_3S_2YSi_2$ (1082.48): C 67.68, H 7.26, N 1.29; found: C 67.08, H 6.78, N 1.10.

*Synthesis of Sc–**6***

A solution of proligand **6** (0.16 g, 0.19 mmol, 1 equiv) in benzene (1 mL) was added dropwise to a solution of $[Sc\{N(SiMe_2H)_2\}_3(thf)]$ (0.10 g, 0.19 mmol, 1 equiv) in benzene (1 mL) at 25 °C. The orange solution was stirred at 70 °C for 24 h. The solvent was removed under vacuum to afford an orange oil, which was dissolved in a mixture of *n*-pentane/THF (1:1, 3 mL), filtered, and stored at −30 °C for 3 d. After recrystallization, complex Sc–**6** was isolated as an orange powder (0.15 g, 0.14 mmol, 71 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.61–7.59 (m, 2H; Ph-*H*5), 7.45–7.43 (m, 2H; Ph-*H*3), 7.31–7.25 (m, 8H; Ph-*H*), 7.20–7.16 (m, 6H; Ph-*H*), 7.14–7.12 (m, 2H; Ph-*H*), 7.10–6.90 (m, 6H; Ph-*H*), 5.11–5.19 (m, 2H; Si*H*), 3.12–3.18 (m, 4H; α-THF), 2.83 (s, 1H; SC*H*), 2.73 (s, 1H; SC*H*), 2.36 (s, 1H; Cy-*H*), 2.21 (s, 1H; Cy-*H*), 2.09–2.03 (m, 6H; Cy-*H*), 1.82 (s, 3H; C(C*H*$_3$)$_2$), 1.72 (s, 3H; C(C*H*$_3$)$_2$), 1.67 (s, 6H; C(C*H*$_3$)$_2$), 1.63 (s, 6H; C(C*H*$_3$)$_2$), 1.59 (s, 6H; C(C*H*$_3$)$_2$), 1.38–1.34 (m, 4H; Cy-*H*), 1.03–0.98 (m, 4H; β-THF), 0.35–0.31 ppm (m, 12H; SiC*H*$_3$); ^{13}C NMR (100.1 MHz, C_6D_6, 25 °C): δ = 167.4 (Ph-*C*1′), 166.5 (Ph-*C*1), 151.9 (Ph-*C*), 137.3 (Ph-*C*4′), 137.3 (Ph-*C*6′), 137.1 (Ph-*C*6), 135.9 (Ph-*C*4), 133.3 (Ph-*C*3′), 132.6 (Ph-*C*3), 128.8 (Ph-*C*), 127.9 (Ph-*C*), 127.1 (Ph-*C*), 126.8 (Ph-*C*), 126.1 (Ph-*C*), 125.8 (Ph-*C*), 125.0 (Ph-*C*), 117.2 (Ph-*C*2′), 116.3 (Ph-*C*2), 71.4 (α-THF), 56.3 (S*C*H), 53.9 (S*C*H), 43.2 (*C*(CH$_3$)$_2$), 42.6 (*C*-(CH$_3$)$_2$), 35.3 (*C*(CH$_3$)$_2$), 34.5 (*C*(CH$_3$)$_2$), 34.3 (C(*C*H$_3$)$_2$), 34.1 (C(*C*H$_3$)$_2$), 31.3 (C(*C*H$_3$)$_2$), 31.1 (C(*C*H$_3$)$_2$), 28.5 (Cy-*C*), 27.7 (Cy-*C*), 27.4 (Cy-*C*), 27.2 (Cy-*C*), 26.9 (Cy-*C*), 26.1 (Cy-*C*), 25.7 (Cy-*C*), 25.0 (β-THF), 3.9 ppm (Si(*C*H$_3$)$_2$; elemental analysis calcd (%) for $C_{64}H_{84}NO_3S_2ScSi_2$ (1080.61): C 71.13, H 7.84, N 1.30; found: C 69.35, H 7.91, N 1.21.

*Synthesis of Y–**6***

A solution of proligand **6** (0.27 g, 0.32 mmol, 1 equiv) in benzene (1 mL) was added dropwise to a solution of $[Y\{N(SiMe_2H)_2\}_3(thf)_2]$ (0.20 g, 0.32 mmol, 1 equiv) in benzene (1 mL) at 25 °C. The solution was stirred for 3 d at room temperature. The solvent was removed under vacuum to afford an orange powder that was dissolved in a mixture of *n*-pentane/THF (1:1, 5 mL), filtered, and stored at −30 °C for 5 d. After recrystallization, complex Y–**6** was isolated as an orange powder (0.27 g, 0.24, 75 %). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.57 (d, ^4J(H,H) = 2.5 Hz, 2H; Ph-*H*5), 7.34–7.30 (m, 6H; Ph-*H*), 7.29–7.27 (m, 2H; Ph-*H*3), 7.21–7.17 (m, 4H; Ph-*H*), 7.12–7.09 (m, 4H; Ph-*H*), 7.08–7.04 (m, 4H; Ph-*H*), 6.95 (t, ^3J(H,H) = 7.3 Hz, 2H; Ph-*H*), 5.01–4.99 (m, 2H; Si*H*), 3.28–3.24 (m, 4H; α-THF), 2.66 (s, 2H; SC*H*), 1.82 (br, 6H; C(C*H*$_3$)$_2$), 1.76–1.74 (m, 2H; Cy-*H*), 1.68 (s, 6H; C(C*H*$_3$)$_2$), 1.67 (s, 6H; C(C*H*$_3$)$_2$), 1.44–1.40 (m, 4H; Cy-*H*), 1.22–1.18 (m, 4H; β-THF), 1.01–0.97 (m, 6H; Cy-*H*), 0.35 (d, ^3J(H,H) = 3.0 Hz, 6H; SiC*H*$_3$), 0.33 ppm (d, ^3J(H,H) = 3.0 Hz, 6H; SiC*H*$_3$), ^{13}C NMR (100.1 MHz, C_6D_6, 25 °C): δ = 165.0 (Ph-*C*1), 152.0 (Ph-*C*), 151.8 (PH-*C*), 136.9 (Ph-*C*), 136.8 (Ph-*C*), 132.8 (Ph-*C*), 128.2 (Ph-*C*), 127.9 (Ph-*C*), 127.2 (Ph-*C*), 126.6 (Ph-*C*), 125.3 (Ph-*C*), 124.9 (Ph-*C*), 69.6 (α-THF), 58.8 (S*C*H), 43.2 (*C*(CH$_3$)$_2$), 42.6 (*C*(CH$_3$)$_2$), 31.3 (*C*(CH$_3$)$_2$), 31.2 (C(*C*H$_3$)$_2$), 30.6 (Cy-*C*), 30.1 (Cy-*C*), 27.5 (Cy-*C*), 25.9 (Cy-*C*), 25.3 (β-THF), 3.7 ppm (Si(*C*H$_3$)$_2$); elemental analysis calcd (%) for $C_{64}H_{84}NO_3S_2YSi_2$ (1124.56): C 68.35, H 7.53, N 1.25; found: C 68.34, H 7.43, N 0.99.

*Synthesis of Sc–**7***

Proligand **7** (0.10 g, 0.21 mmol, 1 equiv) in benzene (1 mL) was added slowly to a solution of $[Sc\{N(SiMe_2H)_2\}_3(thf)]$ (0.11 g, 0.39 mmol) in benzene (3 mL). The yellow solution was stirred at 80 °C for 5 d. The solvent was removed under vacuum to give a yellow powder that was dissolved in *n*-pentane (3 mL), filtered, and stored at −30 °C for 3 d. After drying, complex Sc–**7** was isolated as a yellow powder (90 mg, 0.12 mmol, 57 %). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 7.30–7.20 (m, 2H; Ph-*H*5), 7.06–6.90 (m, 2H; Ph-*H*3), 5.10 (sept, ^3J(H,H) = 3.0 Hz, 2H; Si*H*), 4.14–3.90

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(m, 4H; α-THF), 3.94 (m, 2H; SCH_2), 2.53–2.30 (m, 4H; Cy-*H*), 2.16 (s, 3H; Ph-CH_3), 1.50 (s, 6H; Cy-CH_3), 1.71–1.43 (m, 16H; Cy-*H*), 1.31–1.23 (m, 4H; β-THF), 0.39 ppm (d, ^3J(H,H) = 3.0 Hz, 12H; SiCH_3); ^{13}C NMR (100.1 MHz, 25 °C, C_6D_6): δ = 164.4 (Ph-*C*1), 132.6 (Ph-*C*6), 132.1 (Ph-*C*2), 128.6 (Ph-*C*5), 127.4 (Ph-*C*4), 125.8 (Ph-*C*3), 72.1 (α-THF), 51.5 (Cy-*C*(CH_3)), 38.9 (Cy-*C*), 37.4 (S*C*H), 27.4 (Cy-CH_3), 25.2 (β-THF), 23.5 (Cy-*C*), 20.8 (Ph-CH_3), 3.02 ppm (Si(*C*H_3)); elemental analysis could not be obtained.

*Synthesis of Y–**7***

Proligand **7** (0.10 mg. 0.21 mmol, 1 equiv) was added slowly to a solution of [Y{N(SiMe_2H)$_2$}$_3$(thf)$_2$] (0.13 g, 0.39 mmol, 1 equiv) in benzene (3 mL). The yellow solution was stirred at 80 °C for 5 d. The solvent was removed in vacuo to give a yellow powder that was dissolved in *n*-pentane (3 mL), filtered, and stored at −30 °C for 3 d. After drying, complex Y–**7** was isolated as a yellow powder (98 mg, 0.13 mmol, 62 %). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 7.26 (d, ^4J(H,H) = 2.4 Hz, 2H; Ph-*H*5), 7.04 (d, ^4J-(H,H) = 2.4 Hz, 2H; Ph-*H*3), 4.97 (sept, ^3J(H,H) = 3.0 Hz, 2H; Si*H*), 3.85–3.81 (m, 4H; α-THF), 3.77 (s, 2H; SCH_2), 2.17 (s, 6H; Ph-CH_3), 2.10–1.90 (m, 4H; Cy-*H*), 1.68 (s, 6H; Cy-CH_3), 1.60–1.43 (m, 16H; Cy-*H*), 1.30–1.26 (m, 4H; β-THF), 0.39 ppm (d, ^3J(H,H) = 3.0 Hz, 12H; SiCH_3); ^{13}C NMR (100.1 MHz, 25 °C, C_6D_6): δ = 165.8 (Ph-*C*1), 133.1 (Ph-*C*6), 132.1 (Ph-*C*2), 128.2 (Ph-*C*5), 127.9 (Ph-*C*4), 125.0 (Ph-*C*3), 71.1 (α-THF), 51.7 (Cy-*C*(CH_3)), 39.0 (Cy-*C*), 37.2 (S*C*H), 27.4 (Cy-CH_3), 25.3 (β-THF), 23.5 (Cy-*C*), 20.8 (Ph-CH_3), 3.20 ppm (Si(*C*H_3)); elemental analysis could not be obtained.

*Synthesis of Sc–**8***

Proligand **8** (0.19 g, 0.38 mmol, 1 equiv) was added slowly to a solution of [Sc{N(SiMe_2H)$_2$}$_3$(thf)] (0.10 g, 0.39 mmol) in *n*-pentane (4 mL). The yellow solution was stirred at 25 °C for 48 h. The solvent was removed in vacuo to give a yellow powder that was dissolved in *n*-pentane (3 mL), filtered, and stored at −30 °C for 3 d. After drying, complex Sc–**8** was isolated as a yellow powder (209 mg, 0.28 mmol, 72 %). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 7.24 (s, 1H; Ph-*H*5′), 7.22 (s, 1H; Ph-*H*5), 7.04 (s, 1H; Ph-*H*3′), 6.88 (s, 1H; Ph-*H*3), 5.24 (sept, 1H; ^3J(H,H) = 3.1 Hz, Si*H*), 4.20–4.10 (m, 2H; α-THF), 4.04–3.93 (m, 2H; α-THF), 2.50–2.35 (m, 4H; S*CH*), 2.17 (s, 3H; Ph-CH_3), 2.16 (s, 3H; Ph-CH_3), 2.08–1.93 (m, 4H; Cy-*H*), 1.77 (s, 3H; Cy-CH_3), 1.73–1.67 (m, 6H; Cy-*H*), 1.65 (s, 3H; Cy-CH_3), 1.63–1.48 (m, 10H; Cy-*H*), 1.25–1.21 (m, 4H; β-THF), 0.46 (d, ^3J-(H,H) = 3.1 Hz, 6H; SiCH_3), 0.39 ppm (d, ^3J(H,H) = 3.1 Hz, 6H; SiCH_3); ^{13}C NMR (100.1 MHz, 25 °C, C_6D_6): δ = 167.3 (Ph-*C*1′), 166.8 (Ph-*C*1), 137.3 (Ph-*C*6′), 136.3 (Ph-*C*6), 132.0 (Ph-*C*2′), 131.8 (Ph-*C*2), 131.6 (Ph-*C*5′), 131.5 (Ph-*C*5), 126.2 (Ph-*C*4′), 125.4 (Ph-*C*4), 119.2 (Ph-*C*3′), 118.6 (Ph-*C*3), 72.3 (α-THF), 39.0 (Cy-*C*(CH_3)), 38.8 (Cy-*C*), 37.8 (Cy-*C*), 37.5 (Cy-*C*), 37.3 (S*C*H), 37.0 (Cy-*C*), 27.5 (Cy-*C*), 26.5 (Cy-CH_3), 25.2 (β-THF), 23.6 (Cy-*C*), 20.9 (Ph-CH_3), 3.8 (Si(CH_3)), 3.6 ppm (Si(CH_3)); elemental analysis calcd (%) for $C_{38}H_{62}NO_3S_2ScSi_2$ (746.16): C 61.17, H 8.38, N 1.88; found: C 56.02, H 7.53, N 1.19.

*Synthesis of Y–**8***

Proligand **8** (0.16 g, 0.32 mmol, 1 equiv) was added slowly to a solution of [Y{N(SiMe_2H)$_2$(thf)$_2$] (0.20 g, 0.32 mmol) in *n*-pentane (4 mL). The yellow solution was stirred at room temperature for 48 h. The solvent was removed in vacuo to give a yellow powder that was dissolved in *n*-pentane (3 mL), filtered, and stored at −30 °C for 3 d. After drying, complex Y–**8** was isolated as a yellow powder (0.19 g, 0.24 mmol, 76 %). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 7.23 (d, ^4J(H,H) = 2.2 Hz, 2H; Ph-*H*5), 6.98 (d, ^4J(H,H) = 2.2 Hz, 2H; Ph-*H*5), 5.20–5.16 (m, 2H; Si*H*), 3.97–3.83 (m, 4H; β-THF), 2.56–2.47 (m, 4H; SCH_2), 2.18 (s, 6H; Ph-CH_3), 1.97–1.88 (m, 4H; Cy-*H*), 1.74–1.70 (m, 4H; Cy-*H*), 1.69 (s, 6H; Cy-CH_3), 1.68–1.53 (m, 12H; Cy-*H*), 1.24–1.20 (m, 4H; α-THF), 0.43 ppm (d, ^3J(H,H) = 3.0 Hz, 12H; SiCH_3), ^{13}C NMR (100.1 MHz, 25 °C, C_6D_6): δ = 167.3 (Ph-*C*1), 137.3 (Ph-*C*4), 132.2 (Ph-*C*2), 131.5 (Ph-*C*5), 125.3 (Ph-*C*4), 118.8 (Ph-*C*3), 71.0 (α-THF), 39.0 (Cy-*C*), 37.0 (Cy-*C*), 27.5 (Cy-*C*), 26.2 (Cy-*C*(CH_3)), 25.1 (Cy-CH_3), 23.6 (Cy-CH_3), 20.9 (β-THF), 3.7 ppm (Si(CH_3)); elemental analysis could not be obtained.

*Synthesis of (S)-Y–**5***

L-Methyl lactate (0.003 g, 0.029 mmol, 1 equiv) was added to a solution of complex Y–**5** (0.030 g, 0.029 mmol, 1 equiv) in C_6D_6 (0.5 mL). The solution was reacted at room temperature for 18 h.

*Synthesis of (R)-Y–**5***

D-Methyl lactate (0.003 g, 0.029 mmol, 1 equiv) was added to a solution of complex Y–**5** (0.030 g, 0.029 mmol, 1 equiv) in C_6D_6 (0.5 mL). The solution was reacted at room temperature for 18 h.

*Crystal Structure Determination of Complexes Y–**5***

Low-temperature single-crystal X-ray diffraction experiments were performed with a $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) INCOATEC microsource by using ω scans and a multilayer optics monochromator. Single crystals were mounted on a glass fiber in viscous hydrocarbon oil. Crystals were quench-cooled to 100(2) K. Analysis of diffraction data collected with a Bruker Apex II CCD diffractometer was performed by using SAINT+ within the SMART software package.[21a] Empirical absorption corrections were applied to all data by using MULABS.[21b] The structures were solved by direct methods using IR-92[21c] and refined against F^2 using all reflections with the SHELXL-97[21d] software within the graphical interface WIN-GX.[21e] Graphics were generated by the program Diamond.[21f] All non-hydrogen atoms in the structures were refined anisotropically; all hydrogen atoms were generated in ideal positions and treated as riding by using the riding model; only the atoms H1 and H2 (that are attached to the silicon atoms) were refined in their position. Data are given in Table 3.

CCDC-841975 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Polymerization of Lactide Monomers

A solution of catalyst Y–**1** (10 mg) in toluene or THF (0.5 mL) was added to a solution of the desired amount of *meso*- or *rac*-lactide (details

Table 3. Crystallographic data for complex Y–**5**.

	Y–**5**
formula	$C_{129}H_{172}N_2O_6S_4Si_4Y_2$
M_r	2265.11
cell setting	monoclinic
space group	$P2_1/n$
a [Å]	14.9108(11)
b [Å]	20.1511(16)
c [Å]	20.9690(16)
α [°]	90.00(0)
β [°]	98.940(2)
γ [°]	90.00(0)
V [Å^3]	6224.0(8)
Z	2
ρ_{calcd} [mg m^{-3}]	1.209
radiation type	MoKα
μ [mm^{-1}]	1.086
crystal form	plate
color	colorless
data collection method	ω scan
absorption correction	multiscan
T_{min}	0.6706
T_{max}	0.9477
no. reflns measured	73781
independent reflns	12766
obsd reflns	8458
R_{int}	0.1163
no. parameters	688
R_1 ($I > \sigma(I)$)	0.0521
wR_2	0.1125

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are given in Tables 1 and 2), which was dissolved in toluene or THF (1.5 mL). After the desired time, the polymerization mixture was quenched with drops of moist hexane and was added slowly to cooled, rapidly stirred hexane. The polymer was filtered over a Büchner funnel, washed with diethyl ether, and dried in vacuo. The polymer was dissolved in a minimum quantity of CH_2Cl_2 and run through a flash silica gel column (in a Pasteur pipette) to afford a colorless solution, which was added slowly to cooled, rapidly stirred hexane. Finally, the colorless polymer was filtered and dried in vacuo.

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[1] a) P. J. Dijkstra, H. Du, J. Feijen, *Polym. Chem.* **2011**, *2*, 520–527; b) C. M. Thomas, *Chem. Soc. Rev.* **2010**, *39*, 165–173; c) M. J. Stanford, A. P. Dove, *Chem. Soc. Rev.* **2010**, *39*, 486–494; d) R. H. Platel, L. M. Hodgson, C. K. Williams, *Polym. Rev.* **2008**, *48*, 11–63; e) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147–6176; f) B. J. O'Keefe, M. A. Hillmyer, W. B. Tolman, *J. Chem. Soc. Dalton Trans.* **2001**, 2215–2224.

[2] a) R. E. Drumright, P. R. Gruber, D. E. Henton, *Adv. Mater.* **2000**, *12*, 1841–1846; b) S. Inkinen, M. Hakkarainen, A.-C. Albertsson, *Biomacromolecules* **2011**, *12*, 523–532.

[3] a) M. H. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* **2005**, *44*, 8004–8010; b) M. H. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* **2004**, *43*, 6717–6725; c) M. G. Davidson, C. T. O'Hara, M. D. Jones, C. G. Keir, M. F. Mahon, G. Kociok-Köhn, *Inorg. Chem.* **2007**, *46*, 7686–7688; d) M. S. Hill, P. B. Hitchcock, *Chem. Commun.* **2003**, 1758–1759; e) V. Poirier, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Dalton Trans.* **2009**, 9820–9827; f) Y. Sarazin, V. Poirier, T. Roisnel, J.-F. Carpentier, *Eur. J. Inorg. Chem.* **2010**, 3423–3428; g) J.-C. Buffet, J. P. Davin, T. P. Spaniol, J. Okuda, *New J. Chem.* **2011**, *35*, 2253–2257.

[4] a) N. Nomura, R. Ishii, Y. Yamamoto, T. Kondo, *Chem. Eur. J.* **2007**, *13*, 4433–4451; b) N. Nomura, R. Ishii, M. Akakura, K. Aoi, *J. Am. Chem. Soc.* **2002**, *124*, 5938–5939; c) P. Hormnirun, E. L. Marshall, V. C. Gibson, R. I. Pugh, A. J. P. White, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15343–15348; d) P. L. Arnold, J.-C. Buffet, R. P. Blaudeck, S. Sujecki, A. Blake, C. Wilson, *Angew. Chem.* **2008**, *120*, 6122–6125; *Angew. Chem. Int. Ed.* **2008**, *47*, 6033–6036; e) P. L. Arnold, J.-C. Buffet, R. Blaudeck, S. Sujecki, C. Wilson, *Chem. Eur. J.* **2009**, *15*, 8241–8250; f) J.-C. Buffet, J. Okuda, P. L. Arnold, *Inorg. Chem.* **2010**, *49*, 419–426; g) H. Ma, T. P. Spaniol, J. Okuda, *Angew. Chem.* **2006**, *118*, 7982–7985; *Angew. Chem. Int. Ed.* **2006**, *45*, 7818–7821; h) H. Ma, T. P. Spaniol, J. Okuda, *Inorg. Chem.* **2008**, *47*, 3328–3339; i) L. M. Hodgson, R. H. Platel, A. J. P. White, C. K. Williams, *Macromolecules* **2008**, *41*, 8603–8607; j) R. H. Platel, A. J. P. White, C. K. Williams, *Chem. Commun.* **2009**, 4115–4117; k) A. D. Schwarz, Z. Y. Chu, P. Mountford, *Organometallics* **2010**, *29*, 1246–1260; l) J.-C. Buffet, J. Okuda, *Dalton Trans.* **2011**, *40*, 7748–7754.

[5] a) J.-C. Buffet, J. Okuda, *Chem. Commun.* **2011**, *47*, 4796–4768; b) A. J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jones, M. D. Lunn, *Chem. Commun.* **2008**, 1293–1295; c) A. J. Chmura, D. M. Cousins, M. G. Davidson, C. J. Frankis, M. D. Jones, M. D. Lunn, M. F. Mahon, *Dalton Trans.* **2008**, 1437–1443; d) C. K. A. Gregson, I. J. Blackmore, V. C. Gibson, N. J. Long, E. L. Marshall, A. J. P. White, *Dalton Trans.* **2006**, 3134–3140; e) S. Gendler, S. Segal, I. Goldberg, Z. Goldschmidt, M. Kol, *Inorg. Chem.* **2006**, *45*, 4783–4790; f) C. Romain, L. Brelot, S. Bellemin-Laponnaz, S. Dagorne, *Organometallics* **2010**, *29*, 1191–1198; g) A. D. Schwarz, A. L. Thompson, P. Mountford, *Inorg. Chem.* **2009**, *48*, 10442–10454.

[6] a) J.-C. Buffet, J. Okuda, *Polym. Chem.* **2011**, *2*, 2758–2763; b) H. Du, A. H. Velders, P. J. Dijkstra, Z. Zhong, X. Chen, J. Feijen, *Macromolecules* **2009**, *42*, 1058–1066; c) M. H. Chisholm, J. C. Gallucci, K. T. Quisenberry, Z. Zhou, *Inorg. Chem.* **2008**, *47*, 2613–2624; d) A. P. Dove, H. Li, R. C. Pratt, B. G. G. Lohmeijer, D. A. Culkin, R. M. Waymouth, J. L. Hedrick, *Chem. Commun.* **2006**, 2881–2883; e) A. Amgoune, C. M. Thomas, T. Roisnel J.-F. Carpentier, *Chem. Eur. J.* **2006**, *12*, 169–179; f) T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 1316–1326; g) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238; h) M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold, K. Phomphrai, *J. Am. Chem. Soc.* **2000**, *122*, 11845–11854; i) T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*, 4072–4073; j) A. Pietrangelo, S. C. Knight, A. K. Gupta, L. J. Yao, M. A. Hillmyer, W. B. Tolman, *J. Am. Chem. Soc.* **2010**, *132*, 11649–11657, k) J.-C. Buffet, A. N. Martin, M. Kol, J. Okuda, *Polym. Chem.* **2011**, *2*, 2378–2384.

[7] J.-C. Buffet, A. Kapelski, J. Okuda, *Macromolecules* **2010**, *43*, 10201–10203.

[8] a) N. Nakata, T. Toda, A. Ishii, *Polym. Chem.* **2011**, *2*, 1597–1610; b) E. Sergeeva, J. Kopilov, I. Goldberg, M. Kol, *Inorg. Chem.* **2010**, *49*, 3977–3979.

[9] B. Lian, K. Beckerle, T. P. Spaniol, J. Okuda, unpublished results.

[10] a) G. Piersanti, M. A. Varrese, V. Fusi, L. Giorgi, G. Zappia, *Tetrahedron Lett.* **2010**, *51*, 3436–3438; b) A. Cohen, A. Yeori, I. Goldberg, M. Kol, *Inorg. Chem.* **2007**, *46*, 8114–8116.

[11] K. Marcsekova, C. Loos, F. Rominger, S. Doye, *Synlett* **2007**, *16*, 2564–2568.

[12] a) K. Gademann, D. E. Chavez, E. N. Jacobsen, *Angew. Chem.* **2002**, *114*, 3185–3187; *Angew. Chem. Int. Ed.* **2002**, *41*, 3059–3061; b) S. D. Pastor, D. Z. Denney, *J. Heterocycl. Chem.* **1988**, *25*, 681–683.

[13] a) R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweck, M. Spiegler, *J. Chem. Soc. Dalton Trans.* **1998**, 847–858; b) J. Eppinger, M. Spiegler, W. Hieringer, W. A. Herrmann, R. Anwander, *J. Am. Chem. Soc.* **2000**, *122*, 3080–3096; c) R. Anwander, J. Eppinger, I. Nagl. W. Scherer, M. Tafipolsky, P. Stirsch, *Inorg. Chem.* **2000**, *39*, 4713–4720.

[14] a) O. Runte, T. Priermeier, R. Anwander, *Chem. Commun.* **1996**, 1385–1386; b) A. Lara-Sanchez, A. Rodriguez, D. L. Hughes, M. Schormann, M. Bochmann, *J. Organomet. Chem.* **2002**, *663*, 63–69; c) D. J. H. Emslie, W. E. Piers, M. Parvez, R. McDonal, *Organometallics* **2002**, *21*, 4226–4240; d) C. L. Boyd, T. Toupance, B. R. Tyrrell, B. D. Ward, C. R. Wilson, A. R. Cowley, P. Mountford, *Organometallics* **2005**, *24*, 309–330; e) S. C. Marinescu, T. Agapie, M. Day, J. E. Bercaw, *Organometallics* **2007**, *26*, 1178–1190.

[15] K. B. Aubrecht, K. Chang, M. A. Hillmyer, W. B. Tolman, *J. Polym. Sci. Part A* **2001**, *39*, 284–293.

[16] I. Westmoreland, J. Arnold, *Dalton Trans.* **2006**, 4155–4163.

[17] M. Save, M. Schappacher, A. Soum, *Macromol. Chem. Phys.* **2002**, *203*, 889–897.

[18] The probability of tetrad sequences in PLA are based on Bernoullian statistics: $[sss]=P_s^2+P_sP_i/2$, $[sis]=(P_i^2+P_iP_s)/2$, $[ssi]=[iss]=(P_sP_i)/2$, and $[isi]=P_i^2/2$.

[19] M. M. Flook, V. W. L. Ng, R. R. Schrock, *J. Am. Chem. Soc.* **2011**, *133*, 1784–1786.

[20] a) C. Capacchione, A. Proto, H. Ebeling, R. Mülhaupt, K. Möller, T. P. Spaniol, J. Okuda, *J. Am. Chem. Soc.* **2003**, *125*, 4964–4965; b) C. Capacchione, R. Manivannan, M. Barone, K. Beckerle, R. Centore, L. Oliva, A. Proto, A, Tuzi, T. P. Spaniol, J. Okuda, *Organometallics* **2005**, *24*, 2971–2982.

[21] a) Bruker, SAINT-Plus, Bruker AXS Inc., Madison, Wisconsin, USA, **1999**; b) A. L. Spek, *Appl. Crystallogr., Sect. A* **1990**, *46*, C34; c) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350; d) G. M. Sheldrick, *Acta. Crystallogr., Sect. A.* **2008**, *64*, 112–122; e) L. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 836–837; f) K. Brandenburg, Diamond, Crystal Impact GbR, Bonn (Germany), **2004**.

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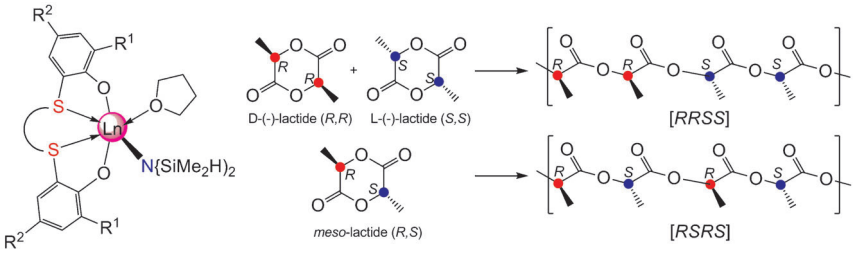
FULL PAPERS

Ring-Opening Polymerization

*Andreas Kapelski, Jean-Charles Buffet, Thomas P. Spaniol, Jun Okuda**

Group 3 Metal Initiators with an [OSSO]-Type Bis(phenolate) Ligand for the Stereoselective Polymerization of Lactide Monomers



Backbone requirements: A series of rare-earth metal bis(dimethylsilylamido) complexes with [OSSO]-type bis(phenolate) ligands [Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_x$] (Ln = Sc, x = 1; Y, x = 2; thf = tetrahydrofuran; see picture) were synthesized and used in the ring-opening polymerization of *rac*- and *meso*-lactides.

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