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PAPER

Alkaline earth metal complexes of a chiral polyether as initiator for the ring-opening polymerization of lactide†

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A chiral, tetradentate polyether ligand with a *trans*-1,2-cyclohexanediyl backbone, bis(methoxyethoxy)-*trans*-1,2-cyclohexane (**5**), was synthesized as both a racemate and the (*S*,*S*) enantiomer. **5** was found to form stable adducts with alkaline earth metal amides [M{N(SiMe$_3$)$_2$}$_2$(thf)$_x$] (M = Mg (x = 0), Ca (x = 2) and Sr (x = 2/3)), [Ca{N(SiHMe$_2$)$_2$}$_2$(thf)] as well as with hydrocarbyl compounds [Mg(CH$_2$SiMe$_3$)$_2$] and [Ca(η^3-C$_3$H$_5$)$_2$]. X-ray diffraction study of the bis(amide) [((*S*,*S*)-**5**)Ca{N(SiMe$_3$)$_2$}$_2$] and of the bis(allyl) [(*rac*-**5**)Ca(η^3-C$_3$H$_5$)$_2$] was performed. The complexes obtained were tested as initiators for the ring-opening polymerization of *meso*-, racemic and L-lactide.

Introduction

In 1967, Pedersen discovered that crown ethers readily coordinate a wide variety of metal cations.[1] They influence the solubility of metal complexes and crown ethers are now well established in phase-transfer catalysis.[2] Much attention has been focused on the binding properties of crown ethers to alkali metals, but to a lesser extent also to alkaline earth metals.[3,4] In their reactivity, the latter metals can sometimes be compared to rare earth metals which led to their implication as catalysts within the last decade.[5] Furthermore, alkaline earth metals are inexpensive due to their abundance and are non-toxic. Group 2 metals have been employed in ring-opening polymerization (ROP) of cyclic esters,[6] hydroamination,[7] polymerization of styrene and dienes,[8] terminal alkyne coupling,[9] hydrogenation,[10] and pyridine activation.[11] Nonetheless, little is known about crown ether coordinated alkaline earth metals as catalysts,[12] and the use of alkaline earth metal catalysts with non-cyclic polyethers as ligands is unknown.

Alkaline earth metal compounds often undergo facile ligand exchange in Schlenk-type equilibria. To avoid such redistributions we have been searching for a chiral and neutral ligand which coordinates alkaline earth metal fragments. This led us to the idea of preparing "half-crown ethers" which are flexible enough to coordinate metals of different size but are still sufficiently rigid to control the stereoselective ROP of lactide monomers. Recently, we reported the ROP of *meso*-lactide monomers with alkaline earth metal initiators that contain a cyclic polyamine (*NNNN*)-type ligand.[13] We report here a new type of chiral alkaline earth metal polyether complexes for the ROP of lactide.

Results and discussion

Synthesis of alkaline earth metal complexes

The polyether *rac*-**5** was synthesized according to modified literature procedures.[14] The first step, a *trans*-selective nucleophilic ring opening of cyclohexene oxide (**1**) with 2-methoxyethanol (**2**), led to the intermediate racemic alcohol *rac*-**3** (Scheme 1, top).

This compound was functionalized by nucleophilic substitution using MeSO$_3$CH$_2$CH$_2$OMe (**4**) which was obtained by esterification of **2** with methanesulfonyl chloride in a parallel reaction. The polyether *rac*-**5** was obtained as a colorless, viscous liquid after vacuum distillation.

To study the influence of chirality of the initiator on lactide polymerization, the dimethoxy ligand **5** was also prepared in enantiomerically pure form ((*S*,*S*)-**5**) following a synthetic route developed by Aspinall *et al.*, which involves a one step functionalization of (*S*,*S*)-*trans*-1,2-cyclohexanediol.[15]

Alkaline earth metal bis(trimethylsilyl)amides [M{N(SiMe$_3$)$_2$}$_2$(thf)$_x$] (M = Mg, x = 0; Ca,[16] x = 2; Sr,[17] x = 2/3) as well as bis(dimethylsilyl)amide [Ca{N(SiHMe$_2$)$_2$}$_2$(thf)][18] were reacted with *rac*-**5** (Scheme 1, bottom). The hydrocarbyl compounds [Mg(CH$_2$SiMe$_3$)$_2$][19] and [Ca(η^3-C$_3$H$_5$)$_2$][8c] were also reacted with *rac*-**5** to give racemic complexes. All alkaline earth metal precursors form stable, THF-free complexes with *rac*-**5** to give alkaline earth metal complexes *rac*-**6**–**11**. They were purified by crystallization at low temperature and isolated in 56 to 88% yield. The optically active calcium complex (*S*,*S*)-**8** was prepared in analogous manner using enantiopure (*S*,*S*)-**5** and isolated in 84% yield.

In this work, we have also established the composition of "[Ca{N(SiHMe$_2$)$_2$}$_2$(thf)]" that crystallizes as a dimer

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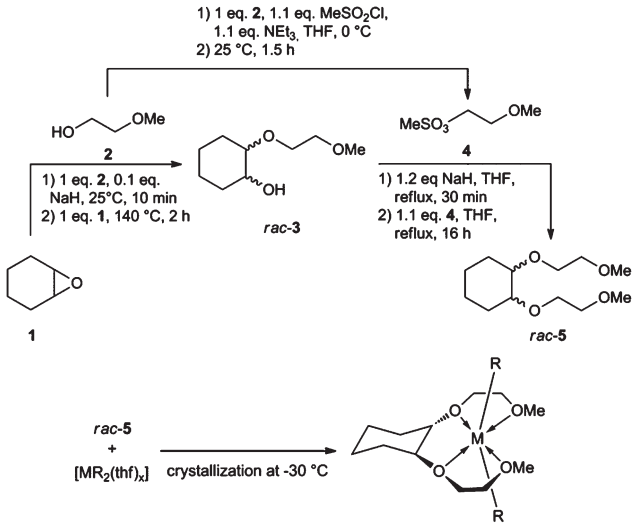


compound	M	R	x	yield
rac-**6**	Mg	$N(SiMe_3)_2$	0	72%
rac-**7**	Mg	CH_2SiMe_3	0	65%
rac-**8**	Ca	$N(SiMe_3)_2$	2	87%
(*S*,*S*)-**8***	Ca	$N(SiMe_3)_2$	2	84%
rac-**9**	Ca	$N(SiHMe_2)_2$	1	60%
rac-**10**	Ca	C_3H_5	0	56%
rac-**11**	Sr	$N(SiMe_3)_2$	2/3	88%

Scheme 1 Top: Synthesis of racemic polyether ligand *rac*-**5**. Bottom: Complexation of alkaline earth metal precursors with polyether ligand *rac*-**5**. *Synthesis performed with enantiopure ligand (*S*,*S*)-**5**.

$[C\{N(SiHMe_2)_2\}_2(thf)]_2$ from concentrated pentane solution. The crystal structure obtained by X-ray diffraction shows that two of the amide groups are bridging the metal centers (ESI, Fig. S13†). The solid-state structure of complex *rac*-**9**, obtained from the calcium amide $[Ca\{N(SiHMe_2)_2\}_2(thf)]_2$ shows a similar coordinative environment to the amide complex *rac*-**8** (ESI, Fig. S14†).

The ^{1}H NMR spectrum of **5** in C_6D_6 shows two multiplets at 3.37–3.48 and 3.61–3.74 ppm due to the OCH_2CH_2O moieties. A further multiplet at 3.20–3.29 ppm is assigned to the protons of the CHO group within the cyclic backbone. Coordination to a metal center leads to significant change in the chemical shifts as well as in multiplicity, suggesting that coordination had occurred. The more rigid orientation in the metal compound renders the protons of the OCH_2CH_2O moieties diastereotopic. The complexation of $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ by *rac*-**5** to give *rac*-**8** leads to four signals for the OCH_2CH_2O moieties of equal intensity spread out over a large chemical shift range (see experimental section and Fig. S1 and S8 in the ESI†).

The structures of (*S*,*S*)-**8** and *rac*-**10** in the solid state were established by X-ray diffraction and are shown in Fig. 1. The latter adopts crystallographic C_2 symmetry. Calcium is coordinated by four oxygen atoms of the polyether ligand and by either the two amido nitrogen atoms in (*S*,*S*)-**8** or by both η^3-coordinated allyl ligands in *rac*-**10**. The arrangement of oxygen atoms can roughly be considered as planar. The arrangement of the two remaining ligands on opposite sides of this plane (with a N1–Ca1–N2 angle of 135.84(6)° and a C2–Ca1–C2′ angle of 150.8(2)°) leads to a coordination geometry around calcium

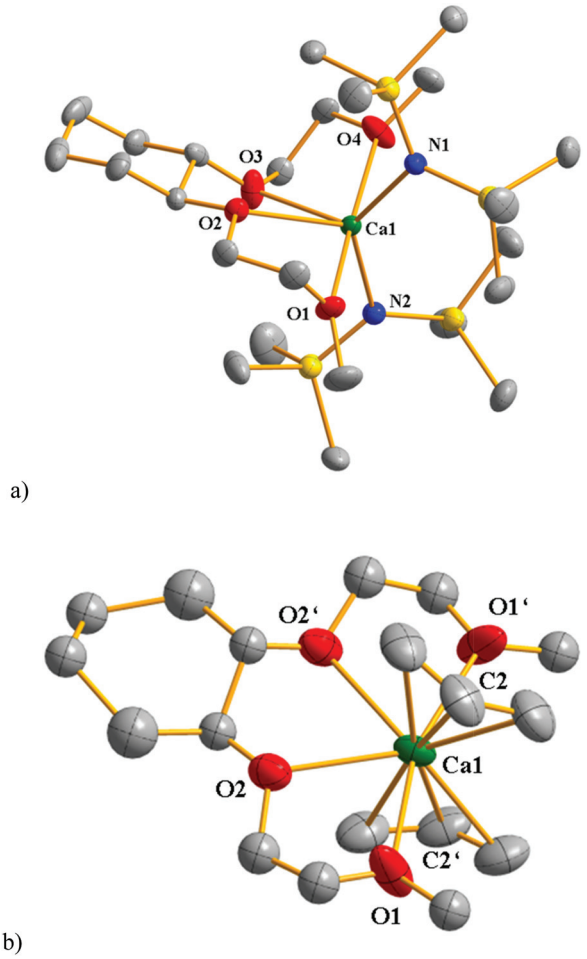
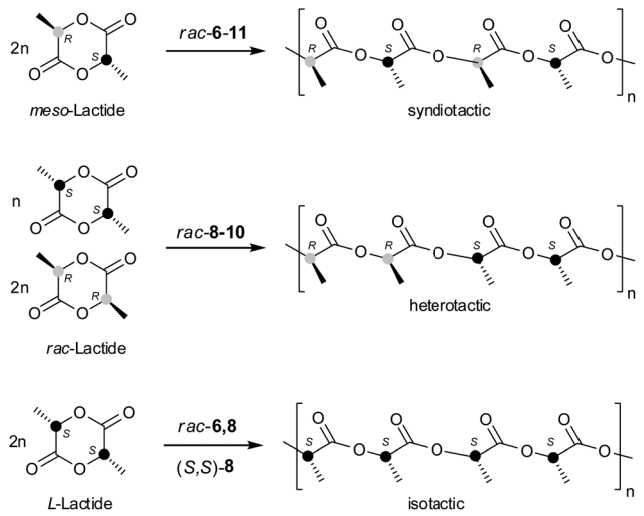


Fig. 1 Molecular structures of (*S*,*S*)-**8** (a) and *rac*-**10** (b). Hydrogen atoms were omitted for the sake of clarity. Selected bond lengths (Å) and angles (°): (a) Ca1–N1 2.393(2), Ca1–N2 2.377(2), Ca1–O1 2.4235(19), Ca1–O2 2.5358(19), Ca1–O3 2.509(2), Ca1–O4 2.4739(18); N1–Ca1–N2 135.84(6), O1–Ca1–O4 172.37(9), O2–Ca1–O3 63.57(5). (b) Ca1–C2 2.691(3), Ca1–O1 2.439(2), Ca1–O2 2.511(3); O1–Ca1–O1′ 161.89(15), O2–Ca1–O2′ 65.26(11), C2–Ca1–C2′ 150.8(2).

that can be described as pentagonal bipyramid with a vacant site in the equatorial plane. In (*S*,*S*)-**8**, the Ca1–N1 distance (2.393(2) Å) is 0.12 Å longer than the Ca–N distance to the terminal amido ligands in the four coordinated calcium compound $[Ca\{N(SiMe_3)_2\}_2]_2$ [16b] (2.27 Å). The structure of *rac*-**10** is similar to that of the triglyme adduct [(triglyme-κ^4)Ca(η^3-$C_3H_5)_2$].[8c] The coordination by the polyether hardly affects the bond distances between the allyl fragment and the metal center. The distance Ca1–C2 in *rac*-**10** (2.691(3) Å) is only 0.02 Å larger than in [(triglyme-κ^4)Ca(η^3-$C_3H_5)_2$] (2.671 Å).

Polymerization of lactide monomers

Compounds *rac*-**6–11** (Scheme 1, bottom) were used in the ROP of *meso*-lactide leading to full conversion in toluene in less than 30 min at room temperature (Scheme 2). The data in Table 1 show the formation of syndiotactically enriched polylactide, albeit with low control of polymerization ($1.49 < M_w/M_n <$



Scheme 2 Polymerization of lactide monomers.

Table 1 Polymerization of *meso*-lactide using complexes *rac*-**6–11**[a]

Entry	Init.	Conv.[b] [%]	$M_{n,exp}$[c] [g mol^{-1}]	M_w/M_n[c]	P_s[d]
1	*rac*-**6**	>99	12 500	1.58	0.69
2	*rac*-**7**	>99	10 250	1.49	0.61
3	*rac*-**8**	98	18 000	1.63	0.73
4	*rac*-**9**	>99	11 500	2.29	0.72
5	*rac*-**10**	>99	7500	1.98	0.68
6	*rac*-**11**	95	16 000	1.58	0.70

[a] *Polymerization conditions*: $[mon]_0/[initiator]_0 = 100$, $[LA]_0 = 0.520$ M, 30 min, toluene, 25 °C, 2 mL. [b] Conversion of monomer $(([mon]_0 - [mon]_t)/[mon]_0)$. [c] Measured by GPC, calibrated with PS standards.[20] [d] P_s is the probability for the formation of a new *s* dyad, calculated from $^1H\{^1H\}$ NMR spectra.[21]

2.29). This can be explained by the high speed of the polymerization resulting in chain transfer reactions such as transesterification. The experimental molecular weights indicate that one chain was initiated using complexes *rac*-**6–9** and **11** ($10\,250 < M_{n,exp} < 18\,000$ g mol^{-1}) and two using *rac*-**10** ($M_{n,exp}$ of 7500 g mol^{-1}). Variation of $[LA]_0/[init]_0$ for *meso*-lactide polymerization with *rac*-**8** shows a linear dependence (ESI, Fig. S15†). For high monomer initiator ratio (400), lower $M_{n,exp}$ was observed which is most probably caused by increasing viscosity and tendency to undergo transesterification.

The polymerization of *meso*-lactide by the amido magnesium complex *rac*-**6** (25 °C, toluene, initiator–monomer ratio of 1 : 100) led to syndiotactically enriched PLA ($P_s = 0.69$) with broad polydispersity ($M_w/M_n = 1.58$, Table 1, entry 1).

The polymerization of *meso*-lactide proceeds with higher syndioselectivity (P_s from 0.61 to 0.69) when the initiating group at the magnesium center was changed from the CH_2SiMe_3 group (*rac*-**7**, entry 2) to the $N(SiMe_3)_2$ group (*rac*-**6**, entry 1).[22] At 25 °C, similar results were obtained with calcium complexes. The initiating group $N(SiMe_3)_2$ in *rac*-**8** led to the highest syndiotacticity ($P_s = 0.73$) comparable to $N(SiHMe_2)_2$ in *rac*-**9** ($P_s = 0.72$) and to C_3H_5 in *rac*-**10** ($P_s = 0.68$). For the calcium amido complexes, decreasing the temperature from 25 to 10 °C led to higher syndiotacticity (*rac*-**8**: from P_s of 0.73 to P_s of 0.81; *rac*-**9**: from P_s of 0.72 to P_s of 0.79). These syndiotacticity values are higher than those obtained previously using alkaline earth complexes containing a (*NNNN*)-type macrocycle, whilst the rate of the polymerization is similar (Fig. 2).[13]

No pronounced effect on the polydispersity or syndiotacticity of the PLA was noted when the metal was changed from magnesium (*rac*-**6**) to calcium (*rac*-**8**) and strontium (*rac*-**11**) (Table 1, entries 1, 3 and 6). When the enantiopure complex (*S*,*S*)-**8** was used to polymerize *meso*-lactide, the syndiotacticity (0.73 for *rac*-**8** and 0.74 for (*S*,*S*)-**8**) was similar to that observed for *rac*-**8**.

Apparently, a chiral backbone in the ligand does not affect the stereoselectivity during ROP of lactide monomers. The polymerization of *meso*-lactide led to similar results when using a complex with a ligand that contains a chiral backbone (*rac*-**8**) or with an achiral one such as the triglyme complex [(triglyme-κ^4)-$Ca\{N(SiMe_3)_2\}_2$], as shown by the syndiotacticity (P_s of 0.73 *vs.* 0.71).

Complexes *rac*-**6**, **8–10** and (*S*,*S*)-**8** were used in the ROP of *rac*- and L-lactide. The polymerization data are collated in Table 2. The amido and alkyl alkaline earth metal complexes led to full conversion of *rac*- or L-lactide in less than 1 h at room temperature in THF that is among the highest rate reported for alkaline earth metal complexes.[6c–f]

The molecular weight of the poly(*rac*-lactide) decreased with the steric bulk of the initiating group from $N(SiMe_3)_2$ (*rac*-**8**,

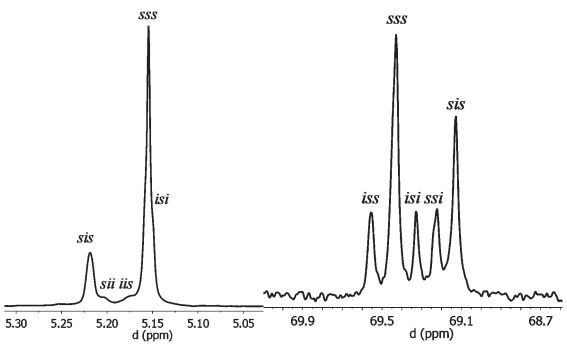


Fig. 2 NMR spectra of the methine region of poly(*meso*-lactide) obtained at 25 °C with *rac*-**8**: (a) $^1H\{^1H\}$ and (b) $^{13}C\{^1H\}$.

Table 2 Polymerization of *rac*- and L-lactide (LA) using complexes *rac*-**6**, *rac*-**8–10** and (*S*,*S*)-**8**[a]

Entry	Init.	LA	Conv.[b] [%]	$M_{n,exp}$[c] [g mol^{-1}]	M_w/M_n[c]	P_i[d]
1	*rac*-**8**	*rac*-	>99	21 500	1.34	0.51
2	*rac*-**9**	*rac*-	>99	13 250	1.41	0.48
3	*rac*-**10**	*rac*-	>99	7500	1.29	0.53
4	*rac*-**6**	L-	>99	19 000	1.62	0.97
5	*rac*-**8**	L-	>99	10 750	1.68	0.99
6	(*S*,*S*)-**8**	L-	>99	9000	1.62	0.96

[a] *Polymerization conditions*: $[mon]_0/[initiator]_0 = 100$, $[LA]_0 = 0.520$ M, 60 min, THF, 25 °C, 2 mL. [b] Conversion of monomer $(([mon]_0 - [mon]_t)/[mon]_0)$. [c] Measured by GPC, calibrated with PS standards.[20] [d] P_i is the probability for the formation of a new *s* dyad, calculated from $^1H\{^1H\}$ NMR spectra.

$M_{n,exp}$ = 21 500 g mol^{-1}) to N(SiHMe$_2$)$_2$ (*rac*-**9**, $M_{n,exp}$ = 13 250 g mol^{-1}) and to C_3H_5 (*rac*-**10**, $M_{n,exp}$ = 7500 g mol^{-1}). All polymers obtained were atactic. Poly(*rac*-lactide) that was synthesized previously using group 2 metal complexes gave heterotactic,[23] isotactic,[24] or atactic[25] PLAs.

The polymerization of L-lactide with the magnesium compound *rac*-**6** led to polymers with higher molecular weight ($M_{n,exp}$ = 19 000 g mol^{-1}) as compared to those obtained using the calcium homologue *rac*-**8** ($M_{n,exp}$ = 10 750 g mol^{-1}). All resulting polymers are highly isotactic indicating the absence of epimerization.[23d,26]

Conclusions

The synthesis of a tetradentate chiral polyether and its complexation with alkaline earth metals magnesium, calcium, and strontium are reported. The resulting complexes are relatively inert, suggesting that the 1,2-*trans*-cyclohexandediyl backbone is capable of generating a rigid coordination sphere even for the large metal calcium. Whilst relatively high activity toward ROP of *meso*-, *rac*- and L-lactide using the described complexes was observed, they failed to show pronounced stereoselectivity during the formation of isotactic and syndiotactic PLA.

Experimental

General procedures

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glove-box techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed to a vacuum–argon cycle three times. Toluene, pentane, THF, [D$_8$]THF and C$_6$D$_6$ were distilled under argon from sodium–benzophenone ketyl prior to use. CDCl$_3$ was distilled from CaH$_2$ prior to use. NMR spectra were recorded on a Varian Mercury 200 BB (^{1}H, 200.0 MHz) or Bruker DRX 400 spectrometer (^{1}H, 400.1 MHz; ^{13}C{^{1}H}, 100.6 MHz) at 25 °C unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C{^{1}H}NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Specific rotation was measured using a JASCO P-2000 Digital Polarimeter (path length 10 cm, volume 1 mL, λ = 589.3 nm at 24 °C). Mass spectrometry data was obtained with a Finnigan MAT95 mass spectrometer. *meso*-Lactide (Uhde Inventa-Fischer), *rac*- and L-lactide were recrystallized from isopropanol at −30 °C, washed with diethyl ether, and dried under vacuum. [Mg{N(SiMe$_3$)$_2$}$_2$] was purchased from Sigma-Aldrich and used without further purification. [Mg(CH$_2$SiMe$_3$)$_2$],[19] [Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$],[16] [Ca{N(SiHMe$_2$)$_2$}$_2$(thf)],[18] [Ca(η^3-C$_3$H$_5$)$_2$][8c] and [Sr{N(SiMe$_3$)$_2$}$_2$(thf)$_{2/3}$][17] were prepared following procedures reported in the literature. (*S*,*S*)-*trans*-1,2-Cyclohexanediol was obtained from resolution of racemic *trans*-1,2-cyclohexanediol.[27] All alkaline earth complexes are air sensitive. As a result complete satisfactory elemental analyses could not be obtained, even upon glovebox handling. This is a frequent problem for alkaline earth metal compounds.[28]

Synthesis of 4. 2-Methoxyethanol (**2**) (7.61 g, 100 mmol) and methanesulfonyl chloride (12.6 g, 110 mmol) were dissolved in 200 mL THF. Triethylamine (11.1 g, 110 mmol) was slowly added *via* a syringe and the mixture was stirred for 18 h. The reaction mixture was filtered, the organic phase was washed with dilute hydrochloric acid and dried over MgSO$_4$. After removal of the solvent, a yellow oil was obtained. Vacuum distillation (75 °C, 5 × 10^{-4} mbar) gave **4** as a colorless liquid. Yield: 12.7 g (82.0 mmol, 82%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.04 (s, 3H, C*H*$_3$SO$_3$); 3.38 (s, 3H, OC*H*$_3$); 3.63–3.65 (m, 2H, OC*H*$_2$C*H*$_2$O); 4.34–4.36 (m, 2H, OC*H*$_2$C*H*$_2$O) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 37.6 (O*C*H$_3$); 59.0 (*C*H$_3$SO$_3$); 68.9 (O*C*H$_2$*C*H$_2$O); 70.2 (O*C*H$_2$*C*H$_2$O) ppm. Anal. Calcd for C$_4$H$_{10}$O$_4$S (154.18 g mol^{-1}): C 31.16, H 6.54. Found: C 31.20, H 6.71%.

Synthesis of *rac*-3. 2-Methoxyethanol (**2**) (7.61 g, 100 mmol) was slowly added to NaH (0.24 g, 10 mmol) giving a yellow slurry solution. After addition of cyclohexene oxide (**1**) (9.81 g, 100 mmol) the mixture was heated to 140 °C for 3 h. Then the crude product was dissolved in 50 mL of CH$_2$Cl$_2$ and the organic phase was washed with brine and water. After a second extraction of the aqueous phase with CH$_2$Cl$_2$ the combined organic phases were dried over MgSO$_4$ and the solvent was removed under reduced pressure yielding a yellow oil which was purified *via* vacuum distillation (60 °C, 5 × 10^{-4} mbar) to obtain *rac*-**3** as a colorless, viscous liquid. Yield: 11.4 g (65.5 mmol, 65%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.10–1.30 (m, 4H, C$_6$H$_{10}$ C*H*$_2$); 1.59–1.74 (m, 2H, C$_6$H$_{10}$ C*H*$_2$); 1.92–2.04 (m, 2H, C$_6$H$_{10}$ C*H*$_2$); 2.97–3.06 (m, 1H, C$_6$H$_{10}$ C*H*O); 3.36 (s, 3H, OC*H*$_3$); 3.37–3.45 (m, 1H, C$_6$H$_{10}$ C*H*O); 3.48 (s, 1H, O*H*); 3.50–3.54 (m, 2H, OC*H*$_2$C*H*$_2$O); 3.54–3.59 (m, 1H, OC*H*$_2$C*H*$_2$O); 3.81–3.87 (m, 1H, OC*H*$_2$C*H*$_2$O) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 24.0 (C$_6$H$_{10}$ *C*H$_2$); 24.4 (C$_6$H$_{10}$ *C*H$_2$); 29.8 (C$_6$H$_{10}$ *C*H$_2$); 32.1 (C$_6$H$_{10}$ *C*H$_2$); 58.9 (O*C*H$_3$); 68.6 (O*C*H$_2$*C*H$_2$O); 72.2 (O*C*H$_2$*C*H$_2$O); 73.9 (C$_6$H$_{10}$ *C*HO); 84.9 (C$_6$H$_{10}$ *C*HOH) ppm. EI-MS: *m*/*z* 174 (0.2) [M]$^+$, 157 (0.7) [M − OH]$^+$, 115 (20) [C$_6$H$_{11}$O$_2$]$^+$. Anal. Calcd for C$_9$H$_{18}$O$_3$ (174.24 g mol^{-1}): C 62.04, H 10.41. Found: C 61.54, H 10.57%.

Synthesis of *rac*-5. To NaH (864 mg, 36 mmol) suspended in 50 mL of THF was added neat *rac*-**3** (5.23 g, 30 mmol) *via* a syringe and the mixture was heated to reflux for 30 min. After a short cooling period, **4** (5.09 g, 33 mmol) was added and the mixture was heated to reflux for a further 18 h. The reaction was quenched by addition of a small amount of water, the organic phase was washed with water and brine and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried with MgSO$_4$, filtered and the solvent was removed in vacuum. The crude product was obtained as yellow oil. Vacuum distillation (65 °C, 5 × 10^{-4} mbar) afforded *rac*-**5** as a colorless liquid. Yield: 5.09 g (21.9 mmol, 73%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.03–1.30 (m, 4H, C$_6$H$_{10}$ C*H*$_2$); 1.49–1.69 (m, 2H, C$_6$H$_{10}$ C*H*$_2$); 1.82–2.02 (m, 2H, C$_6$H$_{10}$ C*H*$_2$); 3.08–3.21 (m, 2H, C$_6$H$_{10}$ C*H*O); 3.32 (s, 6H, OC*H*$_3$); 3.39–3.56 (m, 4H, OC*H*$_2$C*H*$_2$O); 3.62–3.77 (m, 4H, OC*H*$_2$C*H*$_2$O) ppm. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.03–1.13 (m, 2H, C$_6$H$_{10}$ C*H*$_2$); 1.24–1.40 (m, 2H, C$_6$H$_{10}$ C*H*$_2$); 1.44–1.57

(m, 2H, C_6H_{10} CH_2); 1.84–1.98 (m, 2H, C_6H_{10} CH_2); 3.20–3.29 (m, 2H, C_6H_{10} CHO); 3.18 (s, 6H, OCH_3); 3.37–3.48 (m, 4H, OCH_2CH_2O); 3.61–3.74 (m, 4H, OCH_2CH_2O) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 23.6 (C_6H_{10} CH_2); 30.3 (C_6H_{10} CH_2); 58.8 (OCH_3); 69.3 (OCH_2CH_2O); 72.3 (OCH_2CH_2O); 82.1 (C_6H_{10} CHO) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 23.7 (C_6H_{10} CH_2); 30.1 (C_6H_{10} CH_2); 59.1 (OCH_3); 69.9 (OCH_2CH_2O); 73.2 (OCH_2CH_2O); 81.6 (C_6H_{10} CHO) ppm. EI-MS: *m/z* 233 (0.3) $[M + H]^+$. Anal. Calcd for $C_{12}H_{24}O_4$ (232.32 g mol^{-1}): C 62.04, H 10.41. Found: C 61.50, H 9.92%.

Synthesis of enantiomerically pure (*S*,*S*)-5

Tosylation of 2-methoxyethanol. 2-Methoxyethanol (7.61 g, 0.1 mol) was dissolved in 50 mL of CH_2Cl_2 and 20 mL of pyridine and cooled to 0 °C with an ice bath. 4-Methylbenzene-1-sulfonyl chloride (20.97 g, 0.11 mol) in 100 mL of CH_2Cl_2 was added to the stirred mixture *via* a dropping funnel. Stirring was maintained for 1 h at 0 °C and then overnight at ambient temperature. The organic phase was washed with diluted NaOH and dried over $MgSO_4$ before the solvent was evaporated. The remaining yellowish liquid was fractionally distilled under vacuum (110 °C, 6×10^{-3} mbar). The product was isolated as a clear, viscous liquid. Yield: 14.87 g (64.6 mmol, 65%).

^1H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H, *p*-CH_3); 3.29 (s, 3H, OCH_3); 3.55–3.575 (m, 2H, OCH_2CH_2O); 4.13–4.155 (m, 2H, OCH_2CH_2O); 7.31–7.35 (m, 2H, C_6H_4 CH); 7.77–7.81 (m, 2H, C_6H_4 CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.6 (*p*-CH_3); 59.0 (OCH_3); 69.0 (OCH_2CH_2O); 69.9 (OCH_2CH_2O); 127.9 (C_6H_4 CH); 129.8 (C_6H_4 CH); 133.0 (C_6H_4 CCH_3); 144.8 (C_6H_4 CSO_3) ppm. Anal. Calcd for $C_{10}H_{14}O_4S$ (230.28 g mol^{-1}): C 52.16, H 6.13. Found: C 52.01, H 5.85%.

Synthesis of (*S*,*S*)-5 from (*S*,*S*)-*trans*-1,2-cyclohexanediol. To a suspension of NaH (455 mg, 18.9 mmol) in 50 mL of THF stirring at 0 °C, (*S*,*S*)-*trans*-1,2-cyclohexanediol (1.0 g, 8.61 mmol) was added *via* a syringe in 40 mL of THF. After the gas evolution stopped, 15-crown-5 (3.8 g, 17.22 mmol) was added followed by the addition of neat $TsO(CH_2)_2OCH_3$ (4.36 g, 18.94 mmol). The mixture was stirred at 0 °C for an hour before it was refluxed for an additional 20 h. The reaction was quenched with brine and extracted with three portions of Et_2O (200 mL). The combined organic phases were dried over $MgSO_4$, filtered and the volatile material was removed under vacuum leaving a yellowish liquid, which was distilled under vacuum (65 °C, 5×10^{-4} mbar) to obtain a colorless liquid. Yield: 985 mg (4.2 mmol, 49%).

$[\alpha]_D^{24}$ = 28.075° in THF (c = 0.022 g mL^{-1}). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03–1.30 (m, 4H, C_6H_{10} CH_2); 1.49–1.69 (m, 2H, C_6H_{10} CH_2); 1.82–2.02 (m, 2H, C_6H_{10} CH_2); 3.08–3.21 (m, 2H, C_6H_{10} CHO); 3.32 (s, 6H, OCH_3); 3.39–3.56 (m, 4H, OCH_2CH_2O); 3.62–3.77 (m, 4H, OCH_2CH_2O) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 23.6 (C_6H_{10} CH_2); 30.3 (C_6H_{10} CH_2); 58.8 (OCH_3); 69.3 (OCH_2CH_2O); 72.3 (OCH_2CH_2O); 82.1 (C_6H_{10} CHO) ppm. EI-MS: *m/z* 233 (0.3) $[M + H]^+$. Anal. Calcd for $C_{12}H_{24}O_4$ (232.32 g mol^{-1}): C 62.04, H 10.41. Found: C 61.72, H 10.68%.

Synthesis of [(*rac*-5)Mg{N(SiMe$_3$)$_2$}$_2$] (*rac*-6). $[Mg\{(NSiMe_3)_2\}_2]$ (345.1 mg, 1.0 mmol) was dissolved in 8 mL of pentane and a solution of *rac*-**5** (232.3 mg, 1.0 mmol) in pentane (2 mL) was added. After one minute of stirring a colorless precipitate formed and the mixture was kept at −30 °C overnight to complete the precipitation. The mother liquor was removed and the remaining solid was dried in a vacuum to yield *rac*-**6** as a colorless powder. Yield: 413 mg (0.72 mmol, 72%).

^1H NMR (400 MHz, C_6D_6): δ = 0.44 (s, 36 H, $Si(CH_3)_3$); 0.85–0.95 (m, 2H, C_6H_{10} CH_2); 1.00–1.10 (m, 2H, C_6H_{10} CH_2); 1.35–1.45 (m, 2H, C_6H_{10} CH_2); 2.07–2.16 (m, 2H, $C_6H_{10}CH_2$); 3.07–3.15 (m, 2H, $C_6H_{10}CHO$); 3.11 (s, 6H, OCH_3); 3.32–3.48 (m, 8H, OCH_2CH_2O) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 7.0 ($Si(CH_3)_3$); 24.5 (C_6H_{10} CH_2); 30.5 (C_6H_{10} CH_2); 59.8 (OCH_3); 65.1 (OCH_2CH_2O); 71.9 (OCH_2CH_2O); 81.5 (CHO) ppm. Anal. Calcd for $C_{24}H_{60}N_2O_4Si_4Mg$ (577.39 g mol^{-1}): C 49.92, H 10.47, N 4.85. Found: C 48.41, H 11.57, N 5.69%.

Synthesis of [(*rac*-5)Mg(CH$_2$SiMe$_3$)$_2$] (*rac*-7). $[Mg(CH_2SiMe_3)_2]$ (128.3 mg, 0.65 mmol) was placed in a J. Young NMR tube and *rac*-**5** (150.0 mg, 0.65 mmol) was added dissolved in 0.5 mL of C_6D_6. The volatiles were removed in vacuum and the remaining solid was dissolved in pentane (1 mL) and kept at −30 °C to afford *rac*-**7** as colorless crystals. The mother liquor was removed and the residue was dried under vacuum. Yield: 181 mg (0.42 mmol, 65%).

^1H NMR (400 MHz, $CDCl_3$): δ = −1.40 (s, 4 H, $CH_2Si(CH_3)_3$); 0.43 (s, 18 H, $CH_2Si(CH_3)_3$); 0.76–1.00 (m, 4H, $C_6H_{10}CH_2$); 1.35–1.48 (m, 2H, $C_6H_{10}CH_2$); 1.82–1.95 (m, 2H, $C_6H_{10}CH_2$); 3.18–3.25 (m, 2H, OCH_2CH_2O); 3.21 (s, 6H, OCH_3); 3.32–3.43 (m, 4H, OCH_2CH_2O); 3.32–3.43 (m, 2H, C_6H_{10} CHO); 3.58–3.68 (m, 2H, OCH_2CH_2O) ppm. ^1H NMR (400 MHz, C_6D_6): δ = −1.42 (s, 4 H, $CH_2Si(CH_3)_3$); 0.42 (s, 18 H, $CH_2Si(CH_3)_3$); 0.61–0.77 (m, 2H, $C_6H_{10}CH_2$); 0.80–0.97 (m, 2H, $C_6H_{10}CH_2$); 1.16–1.30 (m, 2H, $C_6H_{10}CH_2$); 1.68–1.82 (m, 2H, $C_6H_{10}CH_2$); 3.05 (s, 6H, OCH_3); 3.06–3.11 (m, 2H, OCH_2CH_2O); 3.13–3.18 (m, 2H, OCH_2CH_2O); 3.19–3.26 (m, 2H, OCH_2CH_2O); 3.26–3.33 (m, 2H, $C_6H_{10}CHO$); 3.46–3.54 (m, 2H, OCH_2CH_2O) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = −6.0 ($CH_2Si(CH_3)_3$); 5.53 ($CH_2Si(CH_3)_3$); 23.9 ($C_6H_{10}CH_2$); 29.2 ($C_6H_{10}CH_2$); 59.2 (OCH_3); 65.6 (OCH_2CH_2O); 71.0 (OCH_2CH_2O); 82.0 (CHO) ppm. Anal. Calcd for $C_{20}H_{46}O_4Si_2Mg$ (431.05 g mol^{-1}): C 55.73, H 10.76. Found: C 53.08, H 9.53%.

Synthesis of [(*rac*-5)Ca{N(SiMe$_3$)$_2$}$_2$] (*rac*-8) and [((*S*,*S*)-5)Ca{N(SiMe$_3$)$_2$}$_2$] ((*S*,*S*)-8). $[Ca\{(NSiMe_3)_2\}_2(thf)_2]$ (252.5 mg, 0.5 mmol) was dissolved in 2 mL of pentane and *rac*-**5** or (*S*,*S*)-**5** (116.2 mg, 0.5 mmol) was added in 1 mL of pentane. After one minute of stirring a colorless precipitate formed and the mixture was kept at −30 °C overnight to complete the precipitation. The mother liquor was removed and the precipitate was dried in vacuum to afford the complex (*rac*-**8** or (*S*,*S*)-**8**) as a colorless powder. Yield: *rac*-**8**: 257 mg (0.43 mmol, 87%); (*S*,*S*)-**8**: 246 mg (0.41 mmol, 84%).

(*S*,*S*)-**8**: $[\alpha]_D^{24}$ = 14.503° in THF (c = 0.0096 g mL^{-1}). ^1H NMR (400 MHz, C_6D_6): δ = 0.41 (s, 36 H, $Si(CH_3)_3$); 0.60–0.75 (m, 4H, $C_6H_{10}CH_2$); 1.24–1.31 (m, 2H, $C_6H_{10}CH_2$); 1.48–1.56 (m, 2H, $C_6H_{10}CH_2$); 2.71–2.78 (m, 2H, OCH_2CH_2O);

2.84–2.90 (m, 2H, OCH_2CH_2O); 3.23–3.28 (m, 2H, C_6H_{10}-C*H*O); 3.33 (s, 6H, OCH_3); 3.59–3.65 (m, 2H, OCH_2CH_2O); 3.87–3.94 (m, 2H, OCH_2CH_2O) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 7.2 (Si(*C*H_3)$_3$); 23.5 (C_6H_{10}*C*H_2); 27.7 (C_6H_{10}*C*H_2); 61.2 (O*C*H_3); 63.5 (OCH_2CH_2O); 68.6 (OCH_2-CH_2O); 78.7 (*C*HO) ppm. Elemental analysis was carried out for *rac*-**8**: Anal. Calcd for $C_{24}H_{60}N_2O_4Si_4Ca$ (593.16 g mol^{-1}): C 48.60, H 10.20, N 4.72. Found: C 48.25, H 9.85, N 4.78%.

Synthesis of [(*rac*-5)Ca{N(SiHMe$_2$)$_2$}$_2$] (*rac*-9). [Ca{(NSiHMe$_2$)$_2$}$_2$(thf)] (188 mg, 0.5 mmol) was dissolved in 2 mL of pentane and *rac*-**5** (116.2 mg, 0.5 mmol) was added in 1 mL of pentane under stirring. After adding a few drops of THF the mixture was kept at −30 °C overnight which led to the formation of block shaped colorless crystals. The mother liquor was removed and the precipitate was dried in vacuum to afford *rac*-**9** as a colorless powder. Yield: 161 mg (0.30 mmol, 60%).

^{1}H NMR (400 MHz, C_6D_6): δ = 0.46 (d, 12 H, SiH-(CH_3)$_2$, $^3J_{HH}$ = 3.0 Hz); 0.48 (d, 12 H, SiH(CH_3)$_2$, $^3J_{HH}$ = 3.0 Hz); 0.64–0.73 (m, 4H, C_6H_{10}CH_2); 1.21–1.29 (m, 2H, C_6H_{10}CH_2); 1.51–1.60 (m, 2H, C_6H_{10}CH_2); 2.75 (m, 2H, OCH_2CH_2O); 3.06 (m, 2H, OCH_2CH_2O); 3.29–3.36 (m, 2H, C_6H_{10}C*H*O); 3.29–3.36 (m, 2H, OCH_2CH_2O); 3.48 (s, 6H, OCH_3); 3.75 (m, 2H, OCH_2CH_2O); 5.06 (sept, 4H, Si*H*(CH$_3$)$_2$, $^3J_{HH}$ = 3.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 5.43 (Si(*C*H$_3$)$_3$); 5.46 (Si(*C*H$_3$)$_3$); 23.8 (C_6H_{10}*C*H$_2$); 28.2 (C_6H_{10}*C*H$_2$); 61.0 (O*C*H$_3$); 65.1 (OCH_2CH_2O); 69.8 (OCH_2CH_2O); 80.6 (*C*HO) ppm. EI-MS: *m*/*z* 537 (0.01) [M]$^+$, 404 (13) [M − N(SiHMe$_2$)$_2$]$^+$. Anal. Calcd for $C_{20}H_{52}N_2O_4Si_4Ca$ (537.06 g mol^{-1}): C 44.73, H 9.76, N 5.22. Found: C 42.44, H 12.34, N 4.83%.

Synthesis of [(*rac*-5)Ca(η^3-C$_3$H$_5$)$_2$] (*rac*-10). [Ca(η^3-C$_3$H$_5$)$_2$] (50 mg, 0.414 mmol) was dissolved in 1.5 mL of THF and *rac*-**5** (95 mg, 0.414 mmol) in 0.5 mL THF was added under stirring. The mixture was filtered and stored at −30 °C which led to the formation of a colorless precipitate after 12 h. The mother liquor was removed; the precipitate was washed with pentane and dried in a vacuum to afford *rac*-**10** as a colorless solid. Yield: 83 mg (0.23 mmol, 56%).

^{1}H NMR (400 MHz, [D$_8$]THF): δ = 1.15–1.35 (m, 4H, C_6H_{10} CH_2); 1.56–1.66 (m, 2H, C_6H_{10} CH_2); 1.87–1.98 (m, 2H, C_6H_{10}CH_2); 2.30 (d, 8H, C_3H_5CH(CH_2)$_2$, $^3J_{HH}$ = 12.0 Hz); 3.19–3.27 (m, 2H, C_6H_{10}C*H*O); 3.32 (s, 6H, OCH_3); 3.40–3.52 (m, 4H, OCH_2CH_2O); 3.63–3.68 (m, 4H, OCH_2CH_2O); 6.25 (quint, 2H, C_3H_5 C*H*(CH$_2$)$_2$, $^3J_{HH}$ = 12.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_8$]THF): δ = 24.0 (C_6H_{10} *C*H$_2$); 30.0 (C_6H_{10} *C*H$_2$); 57.4 (C_3H_5 CH(*C*H$_2$)$_2$); 59.3 (O*C*H$_3$); 69.1 (OCH$_2$-CH$_2$OCH$_3$); 73.1 (OCH$_2$*C*H$_2$OCH$_3$); 81.6 (C_6H_{10} *C*HO); 147.7 (C_3H_5 *C*H(CH$_2$)$_2$) ppm. EI-MS: *m*/*z* 313 (0.01) [M − C_3H_5]$^+$, 157 (20) [$C_9H_{17}O_2$]$^+$. Anal. Calcd for $C_{18}H_{34}O_4Ca$ (354.54 g mol^{-1}): C 60.98, H 9.67. Found: C 60.73, H 7.67%.

Synthesis of [(*rac*-5)Sr{N(SiMe$_3$)$_2$}$_2$] (*rac*-11). To a solution of [Sr{(NSiMe$_3$)$_2$}$_2$(thf)$_{2/3}$] (276.3 mg, 0.5 mmol) in 4 mL of pentane was added *rac*-**5** (116.2 mg, 0.5 mmol) in 1 mL of pentane. After one minute of stirring a colorless precipitate formed and the mixture was kept at −30 °C overnight to complete the precipitation. The mother liquor was removed and the precipitate was dried in a vacuum to afford *rac*-**11** a colorless powder. Yield: 280 mg (0.44 mmol, 88%).

^{1}H NMR (400 MHz, C_6D_6): δ = 0.41 (s, 36 H, Si(CH_3)$_3$); 0.57–0.72 (m, 4H, C_6H_{10} CH_2); 1.25–1.32 (m, 2H, C_6H_{10}CH_2); 1.47–1.53 (m, 2H, C_6H_{10}CH_2); 2.73–2.79 (m, 2H, OCH_2CH_2O); 2.91–2.98 (m, 2H, OCH_2CH_2O); 3.14–3.19 (m, 2H, C_6H_{10}C*H*O); 3.32 (s, 6H, OCH_3); 3.37–3.43 (m, 2H, OCH_2CH_2O); 3.64–3.70 (m, 2H, OCH_2CH_2O) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 6.7 (Si(*C*H$_3$)$_3$); 23.5 (C_6H_{10}*C*H$_2$); 27.7 (C_6H_{10}*C*H$_2$); 60.8 (O*C*H$_3$); 63.2 (OCH_2CH_2O); 69.3 (OCH_2CH_2O); 78.4 (*C*HO) ppm. EI-MS: *m*/*z* 567 (0.4) [M − SiMe$_3$]$^+$, 335 (10) [Sr(N(SiMe$_3$)$_2$)(NSiMe$_3$)]$^+$. Anal. Calcd for $C_{24}H_{60}N_2O_4Si_4Sr$ (640.71 g mol^{-1}): C 44.99, H 9.44, N 4.37. Found: C 44.15, H 10.69, N 4.47%.

Crystallography. Low temperature single crystal X-ray diffraction experiments were performed with Mo-K$_\alpha$ radiation (λ = 0.71073 Å) INCOATEC microsource using ω scans and multilayer optics monochromator. Analysis of diffraction data collected with the Bruker Apex II CCD was performed by using SAINT+ within the SMART software package.[29a] Empirical absorption corrections were applied to all data using MULABS.[29b] The structures were solved by direct methods using SIR-92[29c] and refined against F^2 using all the reflections with the SHELXL-97[29d] software within the graphical interface WIN-GX.[29e] Crystals of (*S*,*S*)-**8** were twinned by lattice merohedry emulating the space group $P4_32_12$ (no 96); the twinning matrix 0 1 0 1 0 0 0 0 −1 was used and the refinement resulted in a twin fraction of 0.49. Crystal data for (*S*,*S*)-**8**: $C_{24}H_{60}$-$CaN_2O_4Si_4$, M_r = 593.18, a = 11.5590(13) Å, b = 11.5507(13) Å, c = 26.697(3) Å, U = 3564.4(7) Å^3, $P2_12_12_1$, Z = 4, 50 821 refln. measured, 9351 unique (R_{int} = 0.0669), R_1 ($I > 2\sigma(I)$) = 0.0340, wR_2 (all data) = 0.0648, GoF = 0.917, CCDC 884448; for *rac*-**10**: $C_{18}H_{34}CaO_4$, M_r = 354.53, a = 11.0925(10) Å, b = 13.1506(12) Å, c = 13.4576(12) Å, U = 1963.1(3) Å^3, $C222_1$, Z = 4, 13 645 refln. measured, 2501 unique (R_{int} = 0.1070), R_1 ($I > 2\sigma(I)$) = 0.0625, wR_2 (all data) = 0.1731, GoF = 1.135, CCDC 884449; for [Ca{N(SiHMe$_2$)$_2$}$_2$(thf)]: $C_{24}H_{72}Ca_2N_4O_2Si_8$, M_r = 753.74, a = 18.1714(18) Å, b = 23.153(2) Å, c = 21.826(2) Å, β = 97.8750(15)°, U = 9095.8(16) Å^3, $P2_1/n$, Z = 8, 123 697 refln. measured, 22 744 unique (R_{int} = 0.0811), R_1 ($I > 2\sigma(I)$) = 0.0366, wR_2 (all data) = 0.0733, GoF = 0.0850, CCDC 884449; for *rac*-**9**: $C_{20}H_{52}CaN_2O_4Si_4$, M_r = 537.08, a = 9.321(2) Å, b = 16.216(4) Å, c = 21.088(5) Å, U = 3187.4(13) Å^3, $P2_12_12_1$, Z = 4, 40 012 refln. measured, 7992 unique (R_{int} = 0.1201), R_1 ($I > 2\sigma(I)$) = 0.0907, wR_2 (all data) = 0.2200, GoF = 1.097, CCDC 884450.

Polymerization procedure. A solution of a specified amount of the initiator in 0.5 mL of toluene was added to a solution of 150 mg (1.04 mmol) of *meso*-lactide dissolved in 1.5 mL of toluene. After the desired time the polymerization mixture was quenched with moist hexanes and was added slowly to cool hexanes with stirring. The polymer was filtered over a Büchner funnel, washed with diethyl ether, and dried *in vacuo*.

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