**5526** *Inorg. Chem.* **2009**, *48*, 5526–5534
DOI: 10.1021/ic900161w

Inorganic Chemistry
Article

# Indium Complexes Supported by 1,$\omega$-Dithiaalkanediyl-Bridged Bis(phenolato) Ligands: Synthesis, Structure, and Controlled Ring-Opening Polymerization of L-Lactide

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Received January 25, 2009

Indium bis(phenolato) complexes [In(L)R(THF)$_n$] (L = 1,4-dithiabutanediylbis(4,6-di-*tert*-butylphenolato) (etbbp), R = Cl, $n$ = 0, **1**; L = 1,3-dithiapropanediylbis(6-*tert*-butyl-4-methylphenolato) (mtbmp), R = Me, $n$ = 1, **2**; L = 1,4-dithiabutanediyl-bis(6-*tert*-butyl-4-methyl-phenolato) (etbmp), R = Me, $n$ = 0, **3**; L = etbbp, R = CH$_2$SiMe$_3$, $n$ = 0, **4**; L = 1,4-dithiabutanediylbis{4,6-di(2-phenyl-2-propyl)phenolato} (etccp), R = CH$_2$SiMe$_3$, $n$ = 0, **5**) were prepared from indium trichloride or from the corresponding tris(alkyl) complexes and 1 equiv of tetradentate 1,$\omega$-dithiaalkanediyl-bridged bis(phenol) LH$_2$. The monomeric nature of the alkyl indium complexes was shown by X-ray diffraction studies of the complexes [In(mtbmp)Me(THF)] (**2**), [In(etbbp)(CH$_2$SiMe$_3$)] (**4**), and [In(etccp)(CH$_2$SiMe$_3$)] (**5**). Pseudo-octahedral configuration was found for **2**, while square pyramidal structure was observed for **4** and **5**. The isopropoxy complexes [In(L)(O$^i$Pr)] (L = etbbp, **6**; etccp, **7**) were synthesized starting with indium tris(isopropoxide). Complex **6** crystallized as homochiral dimer of pseudo-octahedral fragments with bridging $\mu_2$-alkoxide ligands, but in solution two diastereomers were observed. The isopropoxy complexes efficiently initiated the ring-opening polymerization of L-lactide in toluene to give isotactic poly(L-lactides) with narrow molecular weight distribution ($M_w/M_n$ = 1.03−1.18).

## Introduction

For the production of biodegradable and biocompatible polyester polylactide (PLA) by ring-opening polymerization (ROP) a significant number of discrete initiators based on Lewis acidic metals,[1] including metal alkoxy complexes of lithium,[2] magnesium,[3] tin,[4] zinc,[3,5,7d] lanthanides,[6] and aluminum[7] have been introduced. Our interest in indium alkoxides as initiator for ROP of PLA stems from their homologous relation to aluminum and certain analogy to group 3 metal and lanthanide alkoxides[6a,8] and from their similarity to tin-based initiators,[4] currently in commercial

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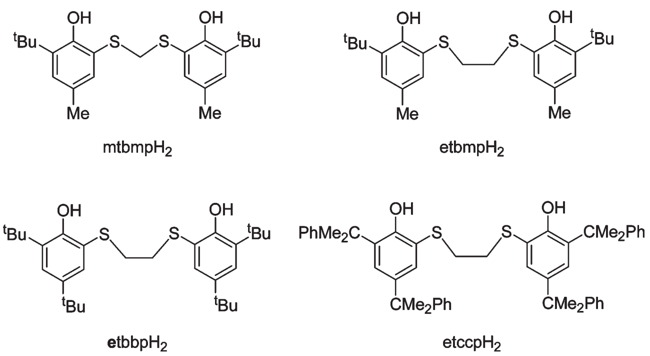
**Chart 1**

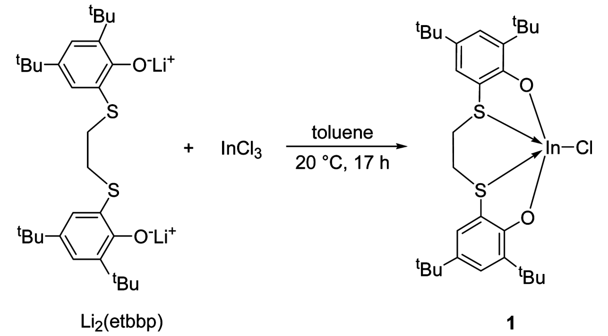


use. Important factors in the polymerization process such as activity[3b,3d,5] and stereoselectivity[3b,3j] still need to be addressed for indium-based initiators.[9] Only one report on structurally defined indium-based initiators has appeared so far in the literature: Mehrkhodavandi et al.[10a] recently introduced a highly active dimeric initiator featuring a chiral diamine mono(phenolate) ligand of (NNO)-type. Indium reagents are becoming increasingly important in organic synthesis because of their new reactivity profile, low toxicity, and water tolerance.[11] We report here structurally well-defined indium complexes with a tetradentate (OSSO)-type ligand (Chart 1)[12] and the suitability of some of them as initiators for the controlled ROP of L-lactide.

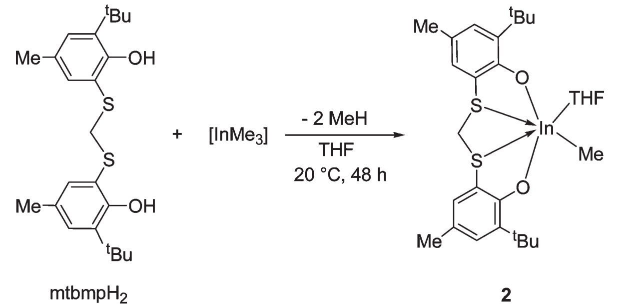
## Results and Discussion

**Chloro and Alkyl Complexes.** To test the coordination behavior of the tetradentate (OSSO)-type ligand in indium coordination chemistry, indium trichloride was first reacted with the lithium salt of 1,4-dithiabutanediylbis

**Scheme 1**



**Scheme 2**



(4,6-di-*tert*-butylphenol) (etbbpH$_2$). The chloro complex [In(etbbp)Cl] (**1**) was obtained in good yield as colorless powder (Scheme 1). Because of its low solubility in nonpolar solvents, we assume **1** to be dimeric.

When trimethylindium [InMe$_3$][13] was reacted with 1,3-dithiapropanediyl-bis(6-*tert*-butyl-4-methyl-phenol) (mtbmpH$_2$) in tetrahydrofuran (THF) at room temperature over a period of 2 days, the new methyl complex was formed under methane elimination and isolated as a white powder in 36% yield as mono(THF) adduct [In(mtbmp)Me(THF)] (**2**) (Scheme 2). NMR spectroscopic and analytical data of **2** indicate a structure with a tetradentate bis(phenolato) ligand, one methyl group, and one THF ligand coordinated to the indium center. Single crystals were grown from a THF/pentane solution. As shown in Figure 1, the indium center in **2** is six-coordinated by the tetradentate bis(phenolato) (OSSO)-type ligand, one methyl group, and one THF molecule adopting a distorted octahedral geometry (Tables 1 and 2). The methyl ligand is located *cis* to the THF ligand and *trans* to one of the sulfur atoms; both oxygen donors of the bis(phenolato) ligand are in a *trans* arrangement, as indicated by the corresponding angles C1−In−O3 102.82(6), C1−In−S1 103.33(5), and O1−In−O2 149.54(5)°.

The In−S1 and In−S2 distances are 2.8087(5) and 2.7920(5) Å. The only structurally characterized compound reported with coordinative In−S(thioether) bonds is [InMe$_3$(1,4-dithiane)] with bond lengths of 2.970(1) and 3.134(1) Å.[14] The In−O bond lengths of 2.1112(12) and 2.1498(12) Å in the bis(phenolate) ligand and of 2.2455(12) Å for the THF ligand in **2** fall into the range of terminal In−O bond lengths in octahedral complexes.

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The methyl complex [In(etbmp)(Me)] (**3**) was prepared in a similar manner from [$InMe_3$] and etbmp$H_2$ in hexane under methane elimination. According to analytical and NMR spectroscopic data, **3** does not contain a THF molecule. When [$In(CH_2SiMe_3)_3$][15] was reacted with 1,4-dithiabutanediylbis(4,6-di-*tert*-butylphenol) (etbbp$H_2$) complex [In(etbbp)($CH_2SiMe_3$)] (**4**) was obtained. Analogously, the reaction of [$In(CH_2SiMe_3)_3$] with 1,4-dithiabutanediylbis{4,6-di(2-phenyl-2-propyl) phenolato} (etccp) gave the compound [In(etccp) ($CH_2SiMe_3$)] (**5**) which were isolated as colorless crystals in high yield (Scheme 3).

Complex [In(etbmp)($CH_2SiMe_3$)] (**4**) crystallizes with the indium center in a square pyramidal coordination (Figure 2). The oxygen and sulfur atoms of the (OSSO)-type ligand occupy the basal positions, and the trimethylsilylmethyl group is situated in the axial position. No additional donor molecules such as THF coordinate to the metal center, as found for **2**. We ascribe this to the more encumbered site, generated by the 1,4-dithiabutanediyl-bridged ligand in **4** as compared to the shorter 1,3-dithiapropanediyl-bridge in **2**.[20] The In−S distances are 2.6372(6) and 2.8177(6) Å and somewhat shorter than the values found in **2**. The In−O bond lengths of 2.0993(14) and 2.0720(14) Å are also shorter than the bond lengths found in **2**.

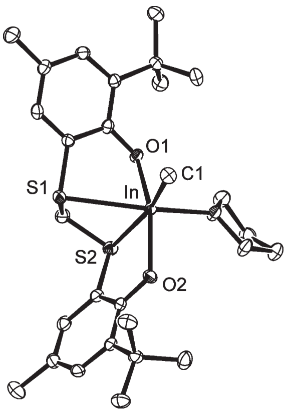


**Figure 1.** ORTEP diagram of the molecular structure of [In(mtbmp)(Me)(THF)] (**2**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, as well as the non coordinated solvent molecule THF, are omitted for clarity.

Figure 3 shows the results of a single crystal X-ray diffraction study of **5**, confirming the square pyramidal coordination geometry as in **4**. The molecule is disordered in the solid state and split positions were introduced in the refinement. The distance between the metal center and the sulfur atom S1 that is refined without split positions is 2.7966(17) Å and is similar to those in **4**. In solution, the introduction of cumyl substituents with diastereotopic methyl groups, in addition to the methylene protons of the trimethylsilylmethyl group, allow the study of configurational stability in solution (Figure 4). Variable-temperature NMR spectra of **5** in THF-$d_8$ over the temperature range −60 °C to +55 °C are displayed in Figure 5. Broad signals at 1.48 (6 H) and 1.57 (6 H) ppm are observed for the methyl groups for the *ortho*-$CMe_2Ph$ substituent groups and at 1.64 (12 H) ppm for the resonances of the cumyl-groups in *para* position at −60 °C. With increasing temperature, the *ortho*-signals shift together to one broad signal at 1.56 (12 H) ppm at 55 °C, but no complete coalescence of the signals could be observed within the measured temperature range. Measurements up to +90 °C in toluene-$d_8$ did not show any significant shift of those signals. We explain this observation by a high barrier of the square pyramidal ground state structure to any more symmetrical geometry in which the diastereotopic groups become equivalent.

**Isopropoxy Compounds.** The chloro complex **1** did not undergo clean nucleophilic substitution with alkali metal isopropoxide. Alcoholysis experiments with isopropanol

**Table 1.** Crystallographic Data for Compounds **2**, **4**, **5**, and **6**

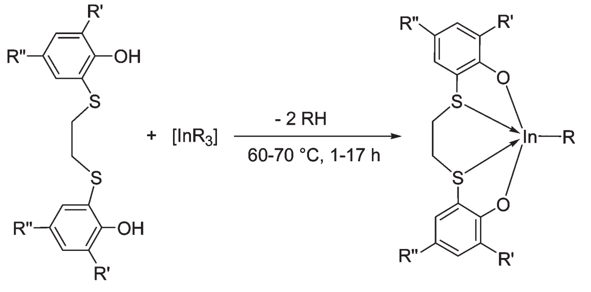
| | **2** | **4** | **5** | **6** |
|---|---|---|---|---|
| empirical formula | $C_{28}H_{41}InO_3S_2 \cdot C_4H_8O$ | $C_{34}H_{55}InO_2S_2Si$ | $C_{54}H_{63}InO_2S_2Si$ | $C_{66}H_{102}In_2O_6S_4 \cdot 4(C_7H_8)$ |
| $M_r$ (g·mol$^{-1}$) | 676.65 | 702.81 | 951.07 | 1717.89 |
| crystal size (mm) | 0.31 × 0.18 × 0.17 | 0.26 × 0.17 × 0.10 | 0.24 × 0.17 × 0.08 | 0.28 × 0.21 × 0.18 |
| crystal color and habit | colorless block | colorless plate | colorless block | colorless block |
| crystal system | triclinic | triclinic | monoclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ |
| $a$ (Å) | 9.3348(8) | 9.4901(9) | 11.5395(7) | 16.0249(17) |
| $b$ (Å) | 12.2093(11) | 13.7106(13) | 21.0783(13) | 16.5918(18) |
| $c$ (Å) | 14.7162(13) | 14.8931(14) | 20.0309(13) | 19.590(2) |
| α (deg) | 92.3820(12) | 75.9303(15) | 90 | 111.8279(15) |
| $\beta$ (deg) | 102.4243(12) | 74.9451(15) | 96.922(12) | 108.6914(16) |
| $\gamma$ (deg) | 97.0638(12) | 79.3503(15) | 90 | 90.3753(16) |
| $V$ (Å$^3$) | 1621.5(2) | 1799.8(3) | 4836.7(5) | 4533.1(8) |
| $Z$ | 2 | 2 | 4 | 2 |
| $D_{calc}$ (g·cm$^{-3}$) | 1.386 | 1.297 | 1.306 | 1.259 |
| $T$ (K) | 130(2) | 130(2) | 130(2) | 130(2) |
| $\mu$ (mm$^{-1}$) | 0.891 | 0.833 | 0.639 | 0.651 |
| $F$(000) | 708 | 740 | 1992 | 1816 |
| $\theta$ range (deg) | 2.3 − 30.9 | 2.2 − 30.4 | 2.2 − 24.9 | 2.2 − 29.8 |
| no. of refl. collected | 24651 | 27628 | 50681 | 66960 |
| no. of independent refl. | 9325 | 10390 | 8351 | 25242 |
| $R_{int}$ | 0.0359 | 0.0566 | 0.0678 | 0.0591 |
| $R1$, $wR2$ [$I > 2\sigma(I)$] | 0.0299, 0.0628 | 0.0362, 0.0619 | 0.0623, 0.1389 | 0.0533, 0.1331 |
| $R1$, $wR2$ (all data) | 0.0357, 0.0642 | 0.0533, 0.0655 | 0.0900, 0.1553 | 0.0857, 0.1462 |
| goodness of fit on $F^2$ | 0.948 | 0.768 | 1.034 | 0.952 |
| $\Delta\rho_{max, min}$/e Å$^{-3}$ | 0.926, −0.573 | 1.072, −0.651 | 1.090, −2.459 | 2.623, −0.899 |

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) of [In(mtbmp)Me(THF)] (**2**) (R1 = C1, R2 = O3), [In(etbbp)($CH_2SiMe_3$)] (**4**) (R1 = C31), [In(etccp)($CH_2SiMe_3$)] (**5**) (R1 = C51a), and [{In(etbbp)($O^iPr$)}$_2$] (**6**) (R1 = O3, R2 = O4)[a]

| | **2** | **4** | **5** | **6** |
|---|---|---|---|---|
| In−O1 | 2.1498(12) | 2.0993(14) | 2.062(3) | 2.097(2) |
| In−O2 | 2.1112(12) | 2.0720(14) | 2.070(4) | 2.103(2) |
| In−S1 | 2.8087(5) | 2.6372(6) | 2.7966(17) | 2.6734(10) |
| In−S2 | 2.7920(5) | 2.8177(6) | 2.749(2) | 2.6828(10) |
| In−R1 | 2.1421(19) | 2.127(2) | 2.144(13) | 2.125(2) |
| In−R2 | 2.2455(12) | | | 2.110(2) |
| O1−In−O2 | 149.54(5) | 92.00(6) | 90.90(14) | 157.56(10) |
| O1−In−R1 | 101.98(6) | 110.92(7) | 113.9(4) | 89.36(9) |
| O2−In−R1 | 108.19(6) | 123.64(8) | 104.8(4) | 111.53(10) |
| O1−In−S2 | 75.91(3) | 149.65(4) | 109.55(11) | 95.50(7) |
| O2−In−S2 | 73.68(4) | 75.38(4) | 77.48(11) | 76.42(7) |
| R1−In−S2 | 168.71(5) | 98.91(6) | 136.4(4) | 91.80(7) |
| O1−In−S1 | 71.15(3) | 76.23(4) | 75.33(10) | 76.55(7) |
| O2−In−S1 | 97.38(4) | 97.58(4) | 140.03(10) | 81.80(7) |
| R1−In−S1 | 103.33(5) | 136.90(6) | 115.1(4) | 164.97(7) |
| S1−In−S2 | 65.421(14) | 78.215(19) | 72.51(6) | 84.48(3) |

[a] For **5**, the values relate to the sulfur atom S2a.

**Scheme 3**



R = Me, R' = $^tBu$, R'' = Me, **3**;
R = $CH_2SiMe_3$, R' = R'' = $^tBu$, **4**;
R = $CH_2SiMe_3$, R' = R'' = $CMe_2Ph$, **5**

using [In(L)($CH_2SiMe_3$)] (**4**, **5**) resulted in the release of the bis(phenol) ligand. Thus, the isopropoxy complexes **6** and **7** were synthesized via the tris(isopropoxide) indium complex,[16,17] prepared by salt metathesis of indium trihalide with sodium isopropoxide, followed by protonolysis with etbbp$H_2$ and etccp$H_2$.

The $^1$H NMR spectrum in THF-$d_8$ of **6** displays two full sets of signals with a 1:1 ratio which does not vary in intensity between +65 and −60 °C. The observation of two septets at $\delta$ 4.59 and 4.77 ppm for the isopropoxy methine protons in **6** over the whole temperature range from −60 °C to +65 °C suggests the presence of two dimers of this bis(phenolate) isopropoxide complex. One signal set represents the *meso* ($\Lambda$,$\Delta$); the second set, the racemic mixture of $\Lambda$,$\Lambda$ and $\Delta$,$\Delta$ isomers. We assume that the formation of dimer is irreversible and that the monomer is not in a fast equilibrium in solution with the dimers (Scheme 4). There was no change upon addition of pyridine to the toluene solution of **6**, indicating that the dimer is stable toward Lewis bases at ambient temperature.

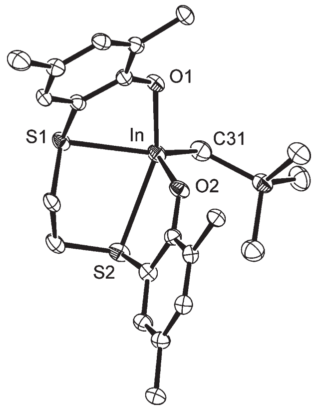


**Figure 2.** ORTEP diagram of the molecular structure of [In(etbmp)($CH_2SiMe_3$)] (**4**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. For *tert*-butyl groups, only carbon atoms connected to the phenyl rings are shown.

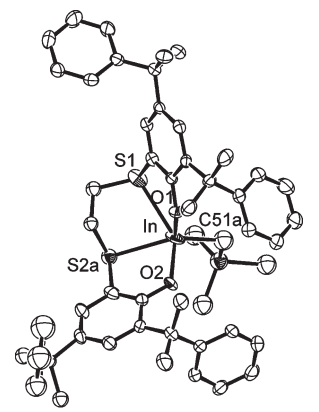


**Figure 3.** ORTEP diagram of the molecular structure of [In(etccp)($CH_2SiMe_3$)] (**5**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 6 shows the homochiral indium alkoxide complex **6** which crystallizes as a dimer with two bridging $\mu_2$-oxygen atoms of the isopropoxide ligands. Both indium centers are found in a distorted octahedral geometry, as reflected in the values for the angles O1−In1−O2 157.56(10)° and O5−In2−O6 153.99(10)° (*cis*-α configuration). The In−S bond lengths of 2.6734(10) and 2.6828(10) Å, as well as 2.6591(9) and 2.6936(10) Å, are shorter than those in the previously mentioned complexes **2**, **4**, and **5**. The In−O($O^iPr$) distances are 2.110(2), 2.125(2) Å, 2.100(2), and 2.123(2) Å. With an average value of 2.11 Å, the coordinative bonds are about 0.2 Å shorter than those in the oxygen centered cluster [$In_5(\mu_5\text{-}O)(\mu_3\text{-}O^iPr)_4(\mu_2\text{-}O^iPr)_4(O^iPr)_5$] reported by Bradley et al.[17] Noteworthy is the large angle of 57.48(2)° between the planes spanned by S1−In1−S2 and S3−In2−S4.[18]

The $^1$H NMR spectrum of complex **7** displays only one set of signals in THF-$d_8$, excluding the presence of diastereomers. Two doublets at 1.01 and 1.17 ($^3J_{HH}$ = 6.0 Hz) ppm of equal intensity as well as one septet at 3.55

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(17) (a) Bradley, D. C.; Chudzynska, H.; Frigo, D. M.; Hammond, M. E.; Hursthouse, M. B.; Mazid, M. A. *Polyhedron* **1990**, *9*, 125. (b) Neumüller, B.; Heravi, M. M.; Chamazi, N. N. *Z. Anorg. Allg. Chem.* **2006**, *632*, 2043.

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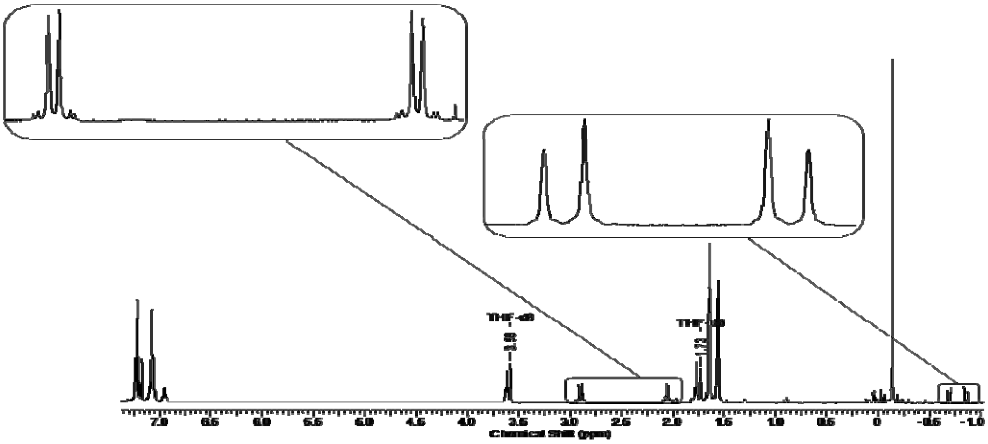


**Figure 4.** $^1$H NMR spectrum of **5** in THF-$d_8$ at 25 °C. The right inset shows the AA′BB′ signal due to the methylene protons of the $CH_2SiMe_3$ group; the left inset depicts that of the $CH_2CH_2$ backbone of the ligand.

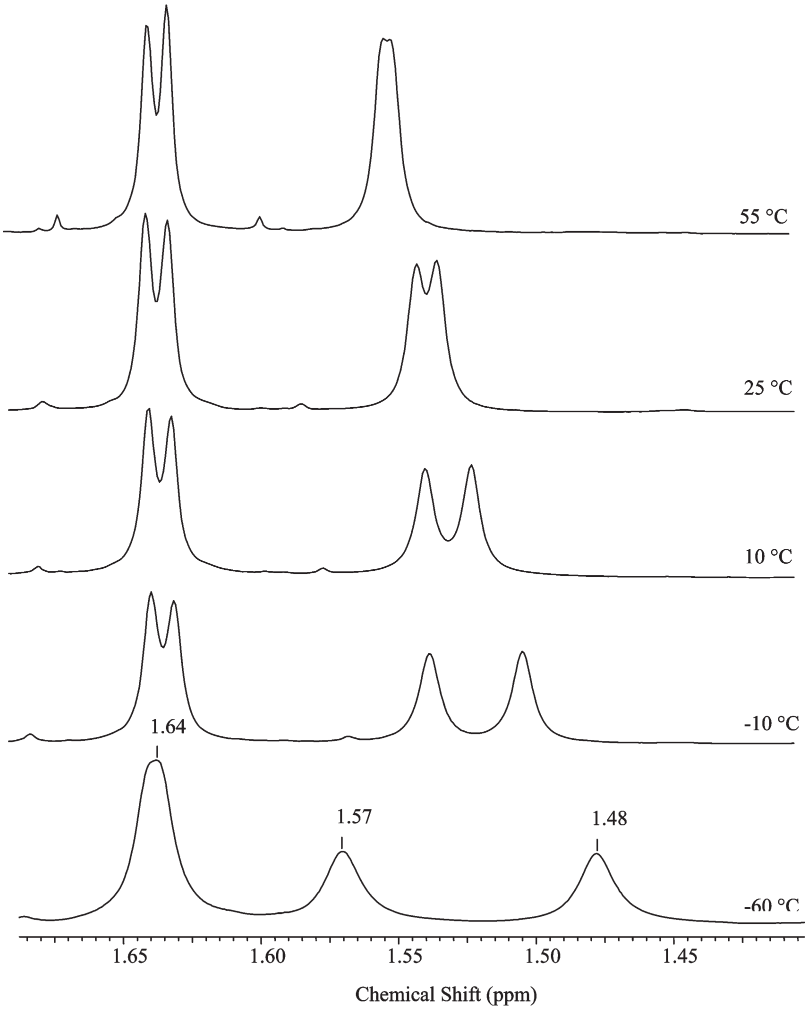


**Figure 5.** Variable temperature $^1$H NMR spectra of complex **5** in THF-$d_8$. The resonances for the $CMe_2Ph$ substituents are shown.

($^3J_{HH}$ = 6.0 Hz) ppm show the coordinated isopropoxy ligand. The characteristic AA′BB′ pattern of the $SCH_2CH_2S$ bridge is found at 2.07 and 2.85 ppm. We assume that compound **7** is monomeric in solution because of the steric hindrance caused by the etccp ligand or exists as only one diastereomer.

**ROP of L-lactide.** The isopropoxy complexes **6** and **7** were tested as initiators for the ROP of L-lactide under different conditions. Both complexes are active in the ROP of L-lactide. In reactions monitored to 90% conversion by $^1$H NMR spectroscopy (toluene-$d_8$, 20−70 °C), 100 equiv of L-lactide were converted to PLA by **7** at 50 °C in 200 min. The polymerization proceeded in a controlled fashion ($M_w/M_n$ = 1.03−1.07) over the conversion range (Table 3, Figure 7). However, inspection of the molecular weights $M_n$ as compared with calculated values show rather non-systematic deviations and no linear relationship between $M_n$ and conversion could be found.

Polymerizations carried out in the temperature range of 20 to 100 °C led to activation parameters from the Eyring plot ($\Delta H^\ddagger$ = 79(0) kJ mol$^{-1}$, $\Delta S^\ddagger$ = −41(6) J K$^{-1}$ mol$^{-1}$ for **6** and $\Delta H^\ddagger$ = 62(3) kJ mol$^{-1}$, $\Delta S^\ddagger$ = −89(1) J K$^{-1}$ mol$^{-1}$ for **7**). These values are comparable with values reported for the indium phenolate initiator reported by Mehrkhodavandi et al.[10a] ($\Delta H^\ddagger$ = 49(2) kJ mol$^{-1}$, $\Delta S^\ddagger$ = −140(12) J K$^{-1}$ mol$^{-1}$), and indicate an ordered transition state in a coordination insertion mechanism.[19] On the basis of these results, we conclude that **7** is more active than **6**. This might be the result of the different position of the monomer–dimer equilibrium for **6** or a initiation from the dinuclear species.[10a] In comparison to previously reported aluminum initiators with an (OSSO)-type ligand,[20] which gave polymers of molecular weights of up to 520,000 g mol$^{-1}$ within 2 h at 24 °C, indium initiator **7** produced polylactide with molecular weights of up to 30,000 g mol$^{-1}$. The isolated isotactic polymers are more uniform with a value for $M_w/M_n$ as low as 1.03. The polymerization experiments with *rac*-lactide resulted in atactic polylactide.

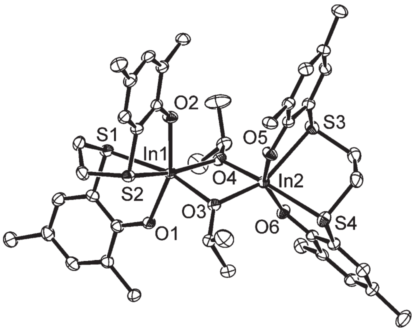


**Figure 6.** ORTEP diagram of the molecular structure of homochiral (Δ,Δ) dimer of [{In(etbbp)(O$^i$Pr)}$_2$] (**6**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, as well as the non coordinated solvent toluene molecules, are omitted for clarity. For *tert*-butyl groups, only carbon atoms connected to the phenyl rings are shown.

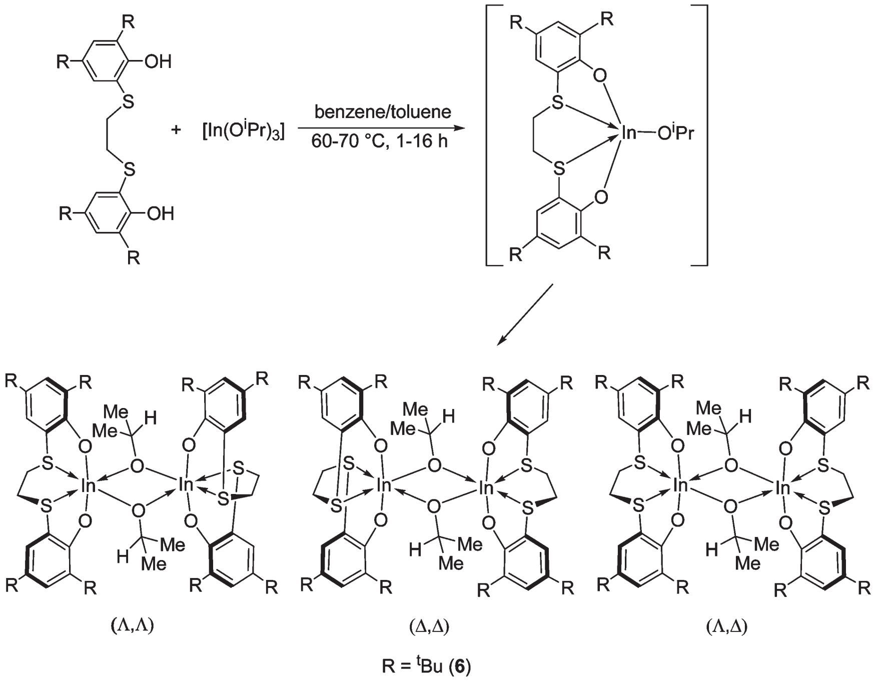
## Conclusions

Bis(phenolate) indium complexes featuring (OSSO)-type ligand can be coordinated to trivalent indium centers. Notably, square pyramidal geometry with *cis*-O donors was found for [In(etbbp)(CH$_2$SiMe$_3$)] (**4**) and [In(etccp)(CH$_2$SiMe$_3$)] (**5**) according to crystal structure analysis, while [In(mtbmp)Me(THF)] (**2**) with a 1,3-dithiapropanediyl-phenolato ligand shows local $C_2$-symmetry with *trans*-O donors (*cis*-α configuration).[21] Notably the isopropoxy complex [In(etbbp)(O$^i$Pr)] (**6**) contains this type of coordination. In the aluminum complex [Al(etbmp)(Et)], homologous to the alkyl complexes **4** and **5**, only one of the two sulfur donors is coordinated, evidently because of the significantly smaller metal center (ionic radius for Al$^{3+}$ 0.535 Å versus for In$^{3+}$ 0.800 Å, CN = 6).[20] Both In–S interatomic distances are comparable with related yttrium complexes [Y(etccp){N(SiHMe$_2$)$_2$}] which contain a larger central atom (0.900 Å for Y$^{3+}$).[22,23] Both indium isopropoxy complexes containing a (OSSO)-type ligand **6** and **7** polymerized L-lactide in toluene in a controlled ring-opening reaction to give isotactic polymers with narrow $M_w/M_n$ values. Compared to the recently introduced chiral indium initiator with a monoanionic (NNO)-type ligand by Mehrkhodavandi et al.[10a] complexes **6** and **7** require longer reaction time at elevated temperature but give narrow polydispersities. When compared with related aluminum[23] and rare-earth[20] initiators containing an (OSSO)-type ligand, the activity of the indium complexes **6** and **7** appears to be lower.

## Experimental Part

**General Considerations.** All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Toluene, hexane, and THF were distilled under argon from sodium/benzophenone ketyl prior to

**Scheme 4**



R = $^t$Bu (**6**)

use. Pentane was purified by distillation from sodium/triglyme benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Anhydrous indium trichloride (ABCR) was used as received. Benzene-$d_6$, chloroform-$d_1$, THF-$d_8$, and other reagents were carefully dried and stored in a glovebox. The used bis(phenols) 1,3-dithiapropanediyl-bis(6-*tert*-butyl-4-methyl-phenol) (mtbmp$H_2$),[24] 1,4-dithiabutanediyl-bis(6-*tert*-butyl-4-methyl-phenolato), (etbmp$H_2$),[11b] 1,4-dithiabutanediyl-bis(4,6-di-*tert*-butylphenol), (etbbp$H_2$),[11g,20,25] and 1,4-dithiabutanediylbis(4,6-dicumyl-phenol) (etccp$H_2$)[11a,11b] were synthesized according to reported methods, as were trimethylindium[13] and tris(trimethylsilylmethyl)indium.[15] L-lactide (Aldrich) was recrystallized from dry toluene and sublimed twice under vacuum at 50 °C. All other chemicals were commercially available and used after appropriate purification. Glassware and vials used in the polymerization were dried in an oven at 140 °C overnight and exposed to vacuum-argon cycle three times.

**Table 3.** ROP of L-Lactide by Indium Complexes **4**, **6**, and **7**

| entry | init. | $T$ (°C) | $(LA)_0/(In)_0$ | $t$ (h) | conv.[d] (%) | $M_{n,exp}$ ($\times 10^3$)[e] | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 1 | 4 | 100 | 100[a] | 4 | 27 | 7.54 | 1.12 |
| 2 | 7 | 50 | 100[b] | 4 | 35 | 28.88 | 1.08 |
| 3 | 7 | 100 | 100[b] | 4 | 99 | 12.41 | 1.06 |
| 4 | 7 | 50 | 100[b] | 2 | 96 | 6.03 | 1.07 |
| 5 | 7 | 100 | 100[b] | 2 | 99 | 12.30 | 1.07 |
| 6 | 7 | 50 | 100[c] | 2 | 66 | 8.87 | 1.06 |
| 7 | 6 | 50 | 100[c] | 4 | 65 | 11.54 | 1.03 |
| 8 | 6 | 50 | 100[c] | 6 | 75 | 14.56 | 1.06 |
| 9 | 6 | 50 | 100[c] | 8 | 61 | 11.43 | 1.09 |
| 10 | 6 | 100 | 100[c] | 2 | 60 | 14.44 | 1.15 |
| 11 | 6 | 100 | 100[c] | 4 | 67 | 12.24 | 1.10 |
| 12 | 6 | 100 | 100[c] | 6 | 86 | 15.83 | 1.18 |
| 13 | 6 | 50 | 25[c] | 4 | 30 | 2.44 | 1.12 |
| 14 | 6 | 50 | 50[c] | 4 | 22 | 5.57 | 1.09 |
| 15 | 6 | 50 | 75[c] | 4 | 66 | 8.70 | 1.05 |
| 16 | 6 | 50 | 150[c] | 4 | 95 | 14.91 | 1.08 |
| 17 | 6 | 50 | 200[c] | 4 | 99 | 15.89 | 1.10 |

[a] $(In)_0$ = 1.9 mmol/L. [b] $(In)_0$ = 1.97 mmol/L. [c] $(In)_0$ = 3.40 mmol/L. [d] Monomer conversion determined by $^1H$ NMR spectroscopy. [e] Determined by GPC using polystyrene standard and corrected using the Mark−Houwink factor of 0.58.

NMR spectra were recorded on Bruker DRX 400, Varian 200 and 500 spectrometers at 25 °C ($^1H$: 200, 400, 500 MHz; $^{13}C$: 50, 100, 125 MHz) unless otherwise stated. Chemical shifts for $^1H$ and $^{13}C$ NMR spectra were referenced internally using residual solvent resonances and reported relative to tetramethylsilane. NMR assignments were confirmed by APT, $^1H-^1H$ (COSY), $^1H-^{13}C$ (HMQC) experiments where necessary. Elemental analyses were performed by the microanalytical laboratory of this department. Spectroscopic analysis of polymers was performed in $CDCl_3$. Molecular weights and polydispersities of polymer samples were determined by size exclusion chromatography (GPC) in THF at 35 °C, at a flow rate of 1 mL/min 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 cover a broad range of molar masses ($10^3 < M_n < 2 \times 10^6$ g $mol^{-1}$).

**(Chloro){1,4-dithiabutanediylbis(4,6-di-*tert*-butylphenolato)}indium (1).** To a cold suspension (−20 °C) of $InCl_3$ (50 mg, 0.2 mmol) in 5 mL of toluene was added a cold suspension of $Li_2$(etbbp) (117 mg, 0.2 mmol) in 5 mL of toluene. The mixture was allowed to warm to room temperature overnight. After the removal of all volatiles, the residue was washed with pentane (3 × 5 mL) to give a white powder; yield: 83 mg (64%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.26 (s, 2 × 9 H, $C(CH_3)_3$), 1.27 (s, 2 × 9 H, $C(CH_3)_3$), 2.46 (AA′BB′, 1 × 2 H, $^2J_{HH}$ = 10.0 Hz, $SCH_2$), 3.22 (AA′BB′, 1 × 2 H, $^2J_{HH}$ = 9.8 Hz, $CH_2S$), 7.16 (d, 1 × 2 H, $^3J_{HH}$ = 2.5 Hz, Ph-*H*), 7.18 (d, 1 × 2 H, $^3J_{HH}$ = 2.5 Hz, Ph-*H*). $^{13}C\{^1H\}$ NMR (128 MHz, $CDCl_3$): $\delta$

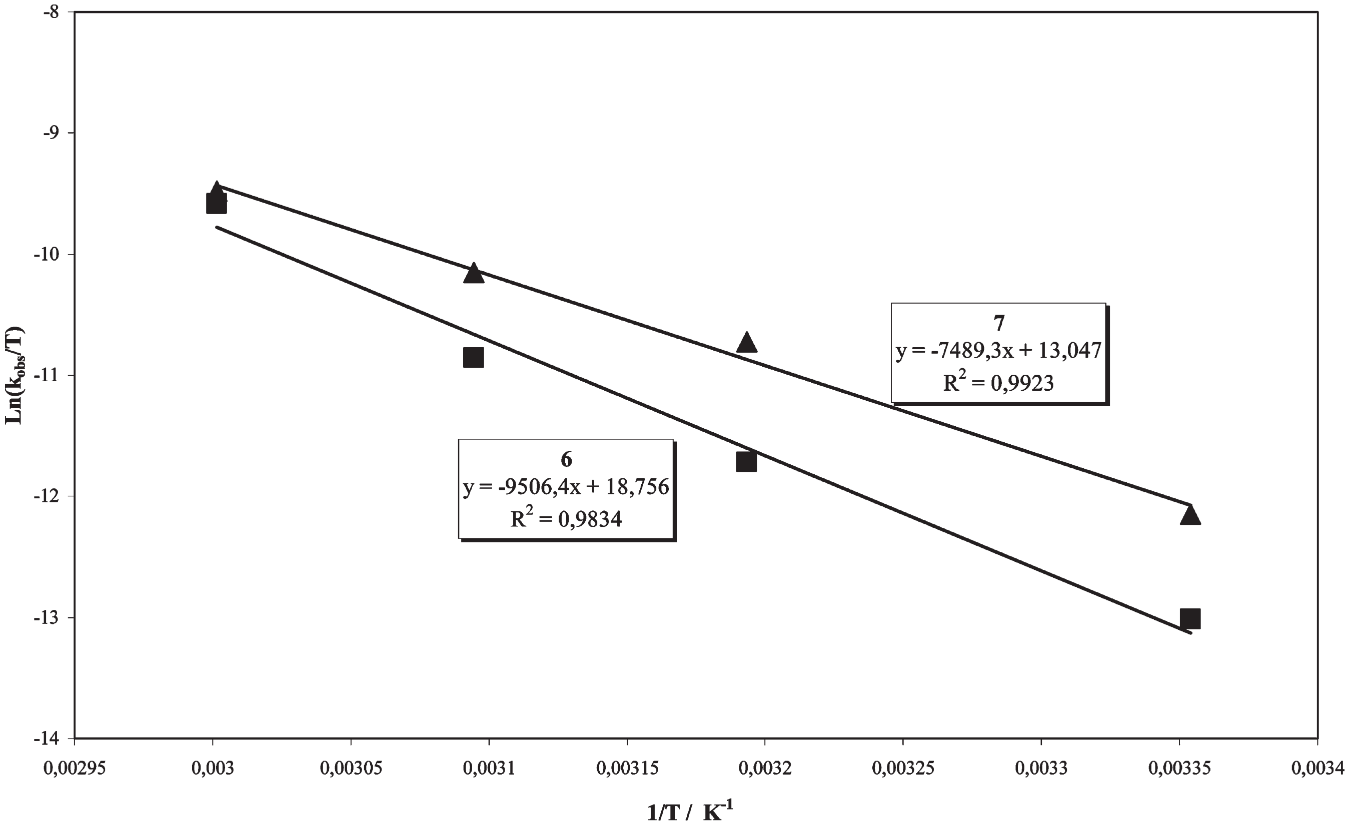


**Figure 7.** Eyring plot for the polymerization of L-lactide using **6** and **7**.

30.5 (4-C(*C*H$_3$)$_3$), 31.1 (6-C(*C*H$_3$)$_3$), 31.7 (4-*C*(CH$_3$)$_3$), 34.0 (6-*C*(CH$_3$)$_3$), 34.7 (S*C*H$_2$*C*H$_2$S), 115.5 (Ph-*C*2), 125.1 (Ph-*C*5), 129.7 (Ph-*C*3), 137.7 (Ph-*C*4), 138.1 (Ph-*C*6), 163.9 (Ph-*C*1). Anal. Calcd for $C_{30}H_{44}ClInO_2S_2$: C, 55.34; H, 6.81. Found: C, 54.77; H, 6.61.

**{1,3-Dithiapropanediylbis(6-*tert*-butyl-4-methylphenolato)}(methyl)indium (2).** To a suspension of 1,3-dithiapropandiyl-bis(6-*tert*-butyl-4-methylphenol) (253 mg, 6.25 mmol) in 5 mL of THF was slowly added a solution of trimethylindium (100 mg, 6.25 mmol) in 5 mL of THF. After 10 min the suspension became clear with concomitant methane evolution. The clear solution was stirred for 48 h at ambient temperature, all volatiles were removed *in vacuo,* and the residue was washed twice with pentane to give a white powder; yield 140 mg (36%). Crystals were grown from a THF/pentane solution at −30 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.09 (s, 1 × 3 H, InC*H*$_3$), 0.89 (s, 1 × 9 H, 6-C(C*H*$_3$)$_3$), 1.42 (s, 1 × 9 H, 6′-C(C*H*$_3$)$_3$), 2.12 (s, 1 × 3 H, 4-C*H*$_3$), 2.36 (s, 1 × 3 H, 4′-C*H*$_3$), 3.28 (AA′BB′, $^2J_{HH}$ = 13.2, 1 × 2 H, SC*H*$_2$), 4.47 (AA′BB′, $^2J_{HH}$ = 13.2, 1 × 2 H, C*H*$_2$S), 6.93 (d, $^3J_{HH}$ = 4.0 Hz, 2 × 1 H, Ph-3, Ph-3′), 7.19 (d, $^3J_{HH}$ = 4.0 Hz, 1 × 1 H, Ph-5), 7.24 (d, $^3J_{HH}$ = 4.0 Hz, 1 × 1 H, Ph-5′); $^{13}$C{$^1$H} (128 MHz, $CDCl_3$): $\delta$ 20.4 (In*C*H$_3$), 25.6 (4′-*C*H$_3$), 29.1 (4-*C*H$_3$), 29.4 (6′-*C*(CH$_3$)$_3$), 32.0 (6′-C(*C*H$_3$)$_3$), 34.8 (6-C(*C*H$_3$)$_3$), 35.6 (6-*C*(CH$_3$)$_3$), 44.7 (S*C*H$_2$*C*H$_2$S), 120.0 (Ph-*C*2′), 123.9 (Ph-*C*2), 126.8 (Ph-*C*4), 130.2 (Ph-*C*5′), 130.4 (Ph-*C*5), 130.5 (Ph-*C*3′), 131.0 (Ph-*C*3), 132.0 (Ph-*C*′), 132.7 (Ph-*C*), 140.7 (Ph-*C*6′), 140.8 (Ph-*C*6), 161.8 (Ph-*C*1′), 167.5 (Ph-*C*1). Anal. Calcd for $C_{28}H_{41}InO_3S_2$: C, 55.63; H, 6.84. Found: C, 55.53; H, 6.68.

**{1,4-Dithiabutanediylbis(6-*tert*-butyl-4-methylphenolato)}(methyl)indium (3).** To a suspension of 1,4-dithiabutanediylbis(6-*tert*-butyl-4-methylphenol) (131 mg, 3.1 mmol) in 5 mL of *n*-hexane was slowly added a solution of trimethylindium (50 mg, 3.1 mmol) in 5 mL of hexane and stirred for 24 h at ambient temperature. All volatiles were removed *in vacuo* to give a white powder; yield 125 mg (84%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.46 (s, 1 × 3 H, InC*H*$_3$), 1.36 (s, 2 × 9 H, 6-C(C*H*$_3$)$_3$), 2.19 (s, 2 × 3 H, 4-C*H*$_3$), 3.04 (m, 1 × 2 H, SC*H*$_2$), 3.13 (m, 1 × 2 H, C*H*$_2$S), 7.03 (d, $^3J_{HH}$ = 2.3 Hz, 1 × 2 H, Ph-3, Ph-3′), 7.11 (dd, $^2J_{HH}$ = 0.8 Hz, $^3J_{HH}$ = 1.5 Hz, 1 × 2 H, Ph-5, Ph-5′). $^{13}$C{$^1$H} (128 MHz, toluene-$d_8$): $\delta$ 20.7 (In*C*H$_3$), 29.8 (4-*C*H$_3$), 35.9 (6-*C*(CH$_3$)$_3$), 38.6 (S*C*H$_2$S*C*H$_2$), 114.0 (Ph-*C*2), 124.1 (Ph-*C*3), 130.9 (Ph-*C*5), 131.8 (Ph-*C*4), 140.4 (Ph-*C*6), 162.9 (Ph-*C*1). Anal. Calcd for $C_{25}H_{35}InO_2S_2$: C, 54.94; H, 6.46. Found: C, 55.05; H, 6.23.

**{1,4-Dithiabutanediylbis(4,6-di-*tert*-butylphenolato)}-(trimethylsilylmethyl)indium(4).** To a solution of 1,4-dithiabutanediylbis(4,6-di-*tert*-butylphenol) (267 mg, 0.5 mmol) in 15 mL of toluene was added dropwise [In($CH_2Si(CH_3)_3)_3$] (200 mg, 0.5 mmol) and stirred for 17 h at 60 °C. All volatiles were removed in vacuo, and the residue washed twice with pentane to give a white powder; yield 210 mg (60%); mp 139 °C. Crystals were grown from a saturated toluene solution at −30 °C. $^1$H NMR: (400 MHz, $C_6D_6$): $\delta$ 0.20 (s, 1 × 11 H, C*H*$_2$Si*Me*$_3$), 1.31 (s, 2 × 9 H, 4-C(C*H*$_3$)$_3$), 1.69 (s, 2 × 9 H, 6-C(C*H*$_3$)$_3$), 2.12 (m, 1 × 2 H, SC*H*$_2$), 2.36 (m, 1 × 2 H, C*H*$_2$S), 7.31 (s, 2 × 1 H, Ph-3), 7.53 (s, 2 × 1 H, Ph-5). $^{13}$C{$^1$H} NMR (128 MHz, $C_6D_6$): $\delta$ 1.7 (Si(*C*H$_3$)$_3$), 29.8 (4-C(*C*H$_3$)$_3$), 31.7 (6-C(*C*H$_3$)$_3$), 34.2 (4-*C*(CH$_3$)$_3$), 36.2 (6-*C*(CH$_3$)$_3$), 38.6 (S*C*H$_2$*C*H$_2$S), 113.7 (Ph-*C*2), 127.1 (Ph-*C*5), 127.9 (Ph-*C*3), 137.8 (Ph-*C*4), 140.0 (Ph-*C*6), 162.7 (Ph-*C*1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.05 (s, 1 × 2 H, SiC*H*$_2$), 0.11 (s, 3 × 3 H, Si(C*H*$_3$)$_3$), 1.30 (s, 2 × 9 H, 4-C(C*H*$_3$)$_3$), 1.41 (s, 2 × 9 H, 6-C(C*H*$_3$)$_3$), 7.20 (s, 2 × 1 H, Ph-5), 7.26 (s, 2 × 1 H, Ph-3). $^1$H NMR (400 MHz, toluene-$d_8$): $\delta$ 0.00 (s, 1 × 11 H, C*H*$_2$Si(CH$_3$)$_3$), 1.11 (s, 2 × 9 H, 4- C(C*H*$_3$)$_3$), 1.46 (s, 2 × 9 H, 6-C(C*H*$_3$)$_3$), 2.03 (m, 1 × 2 H, SC*H*$_2$), 2.25 (m, 1 × 2 H, C*H*$_2$S), 7.11 (s, 2 × 1 H, Ph-3), 7.31 (s, 2 × 1 H, Ph-5). Anal. Calcd for $C_{34}H_{55}InO_2S_2Si$: C, 58.10; H, 7.89. Found: C, 58.16; H, 7.73.

**[1,4-Dithiabutanediylbis{4,6-di(2-phenyl-2-propyl)phenolato](trimethylsilylmethyl)indium (5).** To a solution of [In($CH_2SiMe_3)_3$] (200 mg, 0.531 mmol) in 8 mL of benzene was added a solution of 1,4-dithiabutanediylbis{4,6-di(2-phenyl-2-propyl)phenol} (399 mg, 0.531 mmol) in 8 mL of benzene. The bright yellow solution was heated for 1 h at 70 °C. After removal of all volatiles, the colorless precipitate was washed a few times with pentane and dried under reduced pressure; yield: 298 mg (59%); mp 189−191 °C. Crystals were grown from a saturated THF/pentane solution over a period of one week. $^1$H NMR (400 MHz, THF-$d_8$,): $\delta$ −0.79 (d, $^2J_{HH}$ = 12.1 Hz, 1 × 1 H, C*H*$_2$Si), −0.69 (d, $^2J_{HH}$ = 12.1 Hz, 1 × 1 H, C*H*$_2$Si), −0.14 (s, 1 × 9 H, SiC*H*$_3$), 1.57 (s, 2 × 6 H, 6-cumyl-C*H*$_3$), 1.64 (s, 2 × 6 H, 4-cumyl-C*H*$_3$), 2.07 (AA′BB′, $^2J_{HH}$ = 10.8 Hz, 1 × 2 H, SC*H*$_2$), 2.85 (AA′BB′, $^2J_{HH}$ = 10.8 Hz, 1 × 2 H, SC*H*$_2$), 6.95 (m, 4 H, Ph-*H*), 7.04−7.10 (m, 10 H, Ph-*H*), 7.15−7.24 (m, 10 H, Ph-*H*). $^{13}$C{$^1$H} NMR (128 MHz, THF-$d_8$): $\delta$ −2.3 (*C*H$_2$Si), 0.0 (Si*C*H$_3$), 27.5, 27.8, 29.1, 29.2 ((*C*H$_3$)$_2$C), 33.2 (S*C*H$_2$), 110.3 (Ph-*C*), 122.8 (Ph-*C*2), 123.8 (Ph-*C*), 124.2 (Ph-*C*), 125.2 (Ph-*C*), 125.8 (Ph-*C*), 126.2 (Ph-*C*), 127.2 (Ph-*C*), 128.7 (Ph-*C*5), 134.2 (Ph-*C*4), 136.1 (Ph-*C*6), 150.2 (Ph-*C*), 150.6 (Ph-*C*), 161.1 (Ph-*C*1). Anal. Calcd for $C_{54}H_{63}InO_2S_2Si$: C, 68.19; H, 6.68. Found: C, 67.37; H, 7.00.

**{1,4-Dithiabutanediylbis(4,6-di-*tert*-butylphenolato)}(isopropoxy)indium (6).** A solution of "[In(O$^i$Pr)$_3$]" (300 mg, 1.0 mmol) in 3 mL of toluene was added dropwise to a suspension of 1,4-dithiabutanediylbis(4,6-di-*tert*-butylphenol) (516 mg, 1.0 mmol) in 15 mL of toluene at −78 °C, and the reaction mixture was stirred for 1.5 h at this temperature and for 16 h at 60 °C. After the removal of the volatiles the yellow residue was dissolved in pentane and dried under reduced pressure to give a colorless powder; yield 550 mg (82%). Crystals were grown from saturated toluene solutions at −30 °C over a period of 4 months. $^1$H NMR (400 MHz, THF-$d_8$): $\delta$ 1.06 (d, 2 × 3 H, $^3J_{HH}$ = 6.0 Hz, CH(C*H*$_3$)$_2$), 1.22, 1.25, 1.26, 1.50 (s, 4 × 9 H, C(C*H*)$_3$), 1.38 (d, 2 × 3 H, $^3J_{HH}$ = 6.3 Hz, CH(C*H*′$_3$)$_2$), 2.15 (AA′BB′, 1 × 2 H, $^2J_{HH}$ = 11.3 Hz, SC*H*$_2$), 2.22 (AA′BB′, 1 × 2 H, $^2J_{HH}$ = 11.0 Hz, SC*H*′$_2$), 2.97 (AA′BB′, 1 × 2 H, $^2J_{HH}$ = 11.3 Hz, C*H*$_2$S), 3.09 (AA′BB′, 1 × 2 H, $^2J_{HH}$ = 11.3 Hz, C*H*′$_2$S), 4.59 (septet, 1 × 1 H, *OCH*), 4.77 (septet, 1 × 1 H, *OCH*′), 7.24 (d, 2 × 1 H, $^3J_{HH}$ = 2.5 Hz, Ph-5′), 7.26 (d, 2 × 1 H, $^3J_{HH}$ = 2.5 Hz, Ph-3′), 7.28 (d, 2 × 1 H, $^3J_{HH}$ = 2.8 Hz, Ph-5), 7.36 (d, 2 × 1 H, $^3J_{HH}$ = 2.8 Hz, Ph-3). $^{13}$C{$^1$H} NMR (100 MHz, THF-$d_8$): $\delta$ 28.1 (CH(*C*H$_3$)$_2$), 28.3 (CH(*C*H$_3$)$_2$), 29.0 (CH(*C*H$_3$′)$_2$), 29.6 (CH(*C*H$_3$′)$_2$), 30.6 (*C*′(CH$_3$)$_2$), 30.9 (C(*C*H$_3$)$_2$), 31.3 (C′(*C*H$_3$)$_2$), 32.8 (*C*(CH$_3$)$_2$), 35.5 (S*C*H$_2$), 35.6 (S*C*H$_2$′), 37.0 (S*C*H$_2$), 37.2 (S*C*H$_2$′), 69.2 (O*C*H), 69.5 (O*C*H′), 127.3 (Ph-*C*3), 127.4 (Ph-*C*3′), 128.3 (Ph-*C*5), 128.5 (Ph-*C*5′), 128.9 (Ph-*C*2), 129.0 (Ph-*C*2′), 138.5 (Ph-*C*4), 139.0 (Ph-*C*4′), 139.7 (Ph-*C*6), 140.3 (Ph-*C*6′), 163.6 (Ph-*C*1), 163.8 (Ph-*C*1′). Anal. Calcd for $C_{33}H_{51}InO_3S_2$: C, 58.74; H, 7.62. Found: C, 57.84; H, 7.43.

**[1,4-Dithiabutanediylbis{4,6-di(2-phenyl-2-propyl)phenolato}](isopropoxy)indium (7).** A solution of "[In(O$^i$Pr)$_3$]" (300 mg, 1.027 mol) in 10 mL of benzene was treated with a solution of 1,4-dithiabutanediylbis{4,6-di(2-phenyl-2-propyl) phenol} (711 mg, 1.027 mol) in 10 mL of benzene. The red solution was stirred at 70 °C for 1 h, and all volatiles were removed under reduced pressure. The residue was washed

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several times with pentane to give a yellow powder (859 mg, 0.931 mmol, 91%); mp 212−214 °C. $^1$H NMR (400 MHz, $C_6H_6$): $\delta$ 1.01 (d, $^3J_{HH}$ = 6.0 Hz, 1 × 3 H, CH(C$H_3$)$_2$), 1.17 (d, $^3J_{HH}$ = 6.0 Hz, 1 × 3 H, CH(C$H_3$)$_2$), 1.49 (s, 1 × 6 H, 6-cumyl-C$H_3$), 1.58 (s, 2 × 6 H, 4-cumyl-C$H_3$), 1.75 (s, 1 × 6 H, 4-cumyl-C$H_3$), 1.80 (AA′BB′, $^2J_{HH}$ = 11.3 Hz, 1 × 2 H, SC$H_2$), 2.21 (AA′BB′, $^2J_{HH}$ = 11.3 Hz, 1 × 2 H, C$H_2$S), 3.55 (septet, $^3J_{HH}$ = 6.0 Hz, 1 × 1 H, OC$H$), 6.93−7.03 (m, 12 H, Ph-$H$), 7.25−7.38 (m, 12 H, Ph-$H$). $^{13}$C{$^1$H} NMR (128 MHz, toluene-$d_8$,): $\delta$ 25.4, 31.1, 31.2, 33.2 (($C$H$_3$)$_2$Ph), 27.9, 29.3 (CH($C$H$_3$)$_2$), 35.4 (S$C$H$_2$), 124.9 (Ph-$C$2), 125.1 (Ph-C), 125.4 (Ph-C), 125.8 (Ph-C), 126.2 (Ph-C), 127.0 (Ph-C), 127.7 (Ph-$C$5), 127.8 (Ph-C), 128.0 (Ph-C), 128.2 (Ph-C), 128.6 (Ph-C), 128.8 (Ph-$C$5), 129.1 (Ph-$C$3), 129.5 (Ph-$C$4), 130.8 (Ph-$C$6), 151.4 (Ph-C), 151.9 (Ph-C), 162.3 (Ph-$C$1). Anal. Calcd for $C_{53}H_{59}InO_3S_2$: C, 68.97; H, 6.44. Found: C, 68.71; H, 6.29.

**Typical Polymerization Procedure.** In a glovebox, 0.5 mL of a stock solution of the initiator in toluene was injected sequentially to an array of Schlenk tubes loaded with L-lactide in 5.0 mL amount of dry solvent. After specified time intervals, each solution was added via pipet to a cold methane solution. All the volatiles were removed, and the residue was subjected to monomer conversion determination which was monitored by integration of monomer versus polymer methine or methyl resonances in the $^1$H NMR spectra ($CDCl_3$, 200 MHz). The precipitates collected from the bulk mixture were dried in air, dissolved in dichloromethane, and sequentially precipitated into methanol. The obtained polymer was further dried in a vacuum oven at 60 °C for 16 h and analyzed by GPC.

**Single Crystal X-ray Diffraction Studies.** X-ray diffraction measurements were performed on a Bruker AXS diffractometer with Mo K$\alpha$ radiation using $\omega$-scans. Crystal parameters and results of the structure refinements are given in Table 1. Absorption corrections were carried out with the multiscan method using Mulabs as implemented in the program system PLATON.[26] All structures were solved by direct methods (SIR-92)[27] and refined (SHELXS-97)[28] against all $F^2$ data. For the graphical representation, the Oak Ridge Thermal Ellipsoid Plot (ORTEP) program was used as implied in the program system WinGX.[29] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 709983 (**2**), 709984 (**4**), 709985 (**5**), and 709986 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+44)1223−336−033. e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**Acknowledgment.** We gratefully acknowledge the financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

**Supporting Information Available:** Crystallographic data for **2**, **4**, **5**, and **6** in a cif file; also, additional details are given in Table S1 and Figures S1−S13. This material is available free of charge via the Internet at http://pubs.acs.org

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