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Rare earth metal complexes supported by 1,ω-dithiaalkanediyl-bridged bis(phenolato) ligands: synthesis, characterization and ring-opening polymerization catalysis of L-lactide †

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Monomeric rare earth metal bis(phenolato) complexes $[(L^{s,s})Ln\{N(SiHMe_2)_2\}(THF)]$ (**1a**–**4c**) were isolated from the reaction of silylamido complexes $[Ln\{N(SiHMe_2)_2\}_3(THF)_x]$ (Ln = Sc, $x = 1$; Ln = Y, Lu, $x = 2$) and one equivalent of tetradentate 1,ω-dithiaalkanediyl-bridged bis(phenol)s etbmpH_2, ptbmpH_2, edtbpH_2 and pdtbpH_2 in moderate to high yields. In contrast to the unsymmetrical scandium complexes **1a** and **3a**, the scandium complex **2a**, the yttrium complexes **1b** and **4b** as well as the lutetium complexes **1c**–**4c** show C_s or C_2 symmetry due to the relatively fast dissociation of THF on the NMR time scale at room temperature. The monomeric structures of the complexes **2a** and **4b** were confirmed by X-ray diffraction studies. The six-coordinate central metal with the tetradentate ligand, the silylamido group, and one THF, adopts a C_1 symmetrical configuration with *trans*(O,O) or *cis*(O,O) orientation of the two oxygen donors of the ligand. Distorted octahedral and trigonal prismatic coordination geometries are found for **2a** and **4b**. Substitution reaction with 2,2,6,6-tetramethyl-3,5-heptanedione afforded the corresponding complexes **6b**, **6c**, **7c** and **8b** with dimeric structures and with trityl alcohol the alkoxide complex $[(etbmp)Y(OCPh_3)(THF)]$ (**9**). All new complexes efficiently initiated the ring-opening polymerization of L-lactide in THF. High molecular weight poly(L-lactide)s with narrow molecular weight distributions (M_w/M_n 1.15–1.41) were obtained using complexes **1a**–**4c**. Dimeric β-diketonato complexes were only active in the presence of THF or excess isopropanol.

Introduction

As sterically bulky monoanions occupying three coordination sites, cyclopentadienyl (Cp) ligands have been widely used for the stabilization of the organolanthanide derivatives.[1] More recently, polydentate non-Cp ligands such as β-diketiminato,[2] iminophenolato,[3] bis(phenolato),[4] Schiff base,[5] and other systems,[6] have been introduced as alternatives for the bis(Cp) ancillary ligand set. They differ in their electron-donating ability, structural flexibility as well as in their steric hindrance. Recently group 4 metal complexes with a 1,4-dithiabutanediyl-bridged bis(phenolato) ligand were reported to be highly active precursors for the isospecific polymerization of styrene,[7,8] suggesting that suitable, weaker sulfur-coordination at a Lewis-acidic metal center has a crucial influence on the catalytic behavior of such compounds. Similar effects by sulfur coordination in other transition metal complexes were also reported.[9] There are however still only a few reports on thioether-coordinated lanthanide complexes.[10]

High molecular weight polylactides as important biodegradable materials prepared from renewable sources for biomedical, pharmaceutical and agricultural applications can be obtained by ring-opening polymerization of lactides using anionic, cationic or coordinate type initiators.[11] Among the variety of initiators, such as tin octoate,[12] aluminium acetylacetonate and alkoxides of different metals (aluminium,[13] zinc, magnesium,[14] tin,[15] titanium[16] and rare earth metals[17]), lanthanide complexes,[18] especially lanthanide oxo isopropoxides[19] have proved to be highly efficient initiators for the living ring-opening polymerization of lactides. Compared to other metals,[20] structurally well-characterized rare earth metal complexes which initiate controlled ring-opening polymerization of lactide are rather scarce.[21] Here we report the synthesis of some structurally well-characterized monomeric rare earth metal complexes $[(L^{s,s})Ln\{N(SiHMe_2)_2\}(THF)]$ ligated by 1,ω-dithiaalkanediyl-bridged bis(phenolato) ligands[2b,5a,22] along with some substitution products as active initiators for the ring-opening polymerization of L-lactide.

Results and discussion

Synthesis of bis(phenolato) rare earth metal complexes

When an NMR-scale reaction of scandium silylamide $[Sc\{N(SiHMe_2)_2\}_3(THF)]$ with one equiv. of 1,4-dithiabutanediyl-bis(6-*tert*-butyl-4-methylphenol) (etbmpH_2) was carried out in C_6D_6, complete complexation at room temperature was reached after 4 to 5 days. From the reactions of scandium silylamide and corresponding bis(phenol)s in toluene at 50 °C on the synthetic scales, derivatives $[(L^{s,s})Sc\{N(SiHMe_2)_2\}(THF)]$ (**1a**–**3a**) could be isolated in moderate yields as analytically pure colourless crystals after careful work-up and recrystallization from *n*-pentane (Scheme 1). Spectroscopic data and elemental analyses are consistent with the structure with one bis(phenolato) ligand, one bis(dimethylsilyl)amido group and one coordinated THF molecule at the metal center. As shown by X-ray diffraction on a single crystal (Fig. 1), the complex **2a** is monomeric.

Complexation of $[Sc\{N(SiHMe_2)_2\}_3(THF)]$ with 1,5-dithiapentanediyl-bis(4,6-di-*tert*-butylphenol) (pdtbpH_2) failed to give a single product, three sets of signals for the $[(pdtbp)Sc\{N(SiHMe_2)_2\}]$ unit were observed in the NMR spectra (*e.g.*, for SiH, three multiplets at δ 5.80 (trace), 5.46 (minor), 5.34 (major)), indicating the formation of several isomers.

The lithium containing scandium silylamide $[Sc\{N(SiHMe_2)_2\}_3\{LiN(SiHMe_2)_2(THF)\}]$ (**5**) was also treated with etbmpH_2 to give a mixture of products: **1a**, the lithium 'ate' complex **5a**, and the lithium bis(phenolate) **5d** (Scheme 2), which were all characterized by spectroscopic methods with complex **5a** further characterized by X-ray diffraction (Fig. 2).

The reactions of the yttrium complex $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ with bis(phenol)s were similar except that *n*-hexane was used as solvent and that the reaction was performed at

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† Electronic supplementary information (ESI) available: Variable temperature ^1H NMR spectra for complexes **1a** and **1c** in d_8-toluene, d_8-THF as well as the $^{13}C\{^1H\}$ NMR spectra of poly(L-lactide) and homodecoupled proton, $^{13}C\{^1H\}$ NMR spectra of poly(*rac*-lactide). See http://www.rsc.org/suppdata/dt/b3/b311604b/

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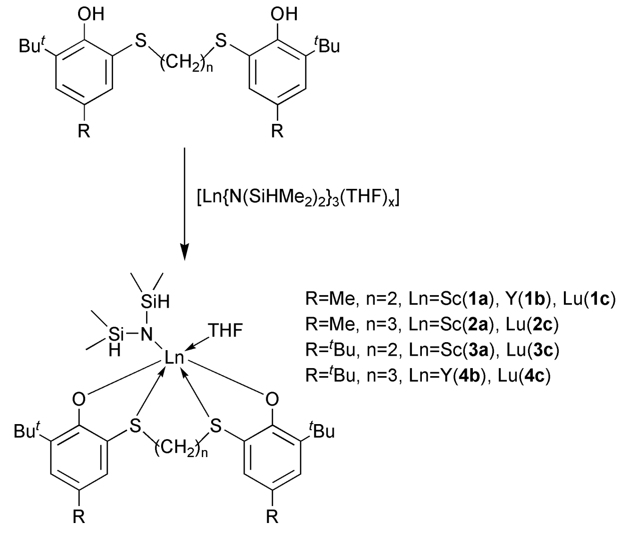


Scheme 1

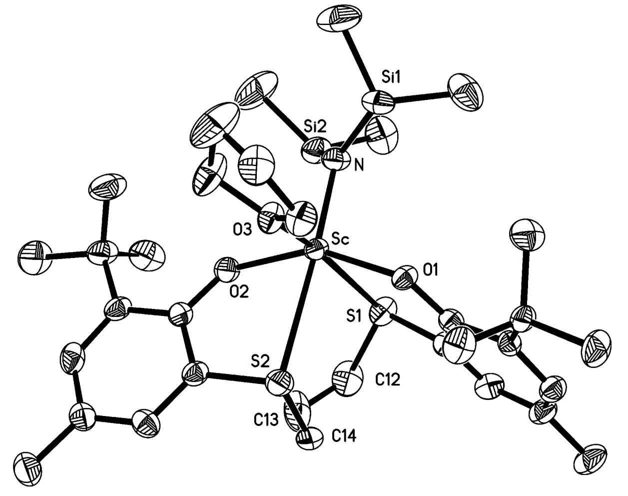


Fig. 1 ORTEP diagram of the molecular structure of [(ptbmp)Sc{N(SiHMe$_2$)$_2$}(THF)] **2a**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

room temperature. Complexes [(etbmp)Y{N(SiHMe$_2$)$_2$}(THF)] (**1b**) and [(pdtbp)Y{N(SiHMe$_2$)$_2$}(THF)] (**4b**) were obtained in 93 and 80% yields, respectively, as analytically pure colourless crystals (Scheme 1). Suitable single crystals of complex **4b** were obtained by slow evaporation of *n*-hexane solutions. An NMR-scale reaction of [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] with 1,4-dithiabutanediyl-bis(4,6-di-*tert*-butylphenol) (edtbpH$_2$), or 1,5-dithiapentanediyl-bis(6-*tert*-butyl-4-methylphenol) (ptbmpH$_2$) afforded the desired products, however the isolation of pure products was again unsuccessful due to the formation of isomers upon removing the solvents.

In contrast to the difficulties encountered during the synthesis of Sc and Y complexes, the corresponding lutetium complexes ligated by the four different bis(phenolato) ligands could be easily isolated in high yields as colourless crystals either by recrystallization (for **1c**) or by solvent evaporation (for **2c**–**4c**). This series of bis(phenolato) complexes of Sc, Y and Lu generally are extremely soluble in saturated hydrocarbons. The ligand structure strongly influences the solubility of the complexes: **1a**–**1c** with the etbmp ligand can easily be recrystallized from saturated *n*-pentane solutions in high yields upon cooling or concentration, while complexes with 1,5-dithiapentanediyl-bridged ligands can only be recovered from *n*-pentane or *n*-hexane with great difficulty. Furthermore, the new silylamido bis(phenolato) complexes were somewhat unstable in solution, especially in THF. Partial decomposition was observed when THF solutions were kept overnight. Compared to the precursor complexes [Ln{N(SiHMe$_2$)$_2$}$_3$(THF)$_x$], complexes [(L^{s,s})Ln{N(SiHMe$_2$)$_2$}(THF)] seemed to be more sensitive to any proton source. The decomposition could not be prevented even with the most careful exclusion of moisture. Despite the low stability in solution, all of the solid complexes can be stored at room temperature for prolonged periods without any decomposition.

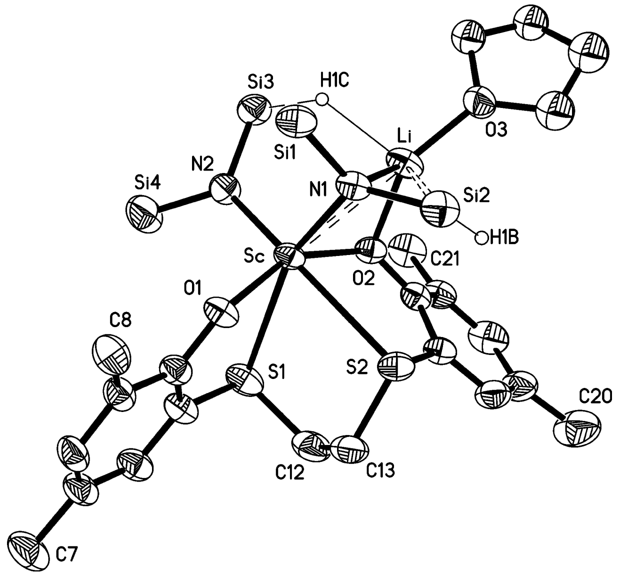
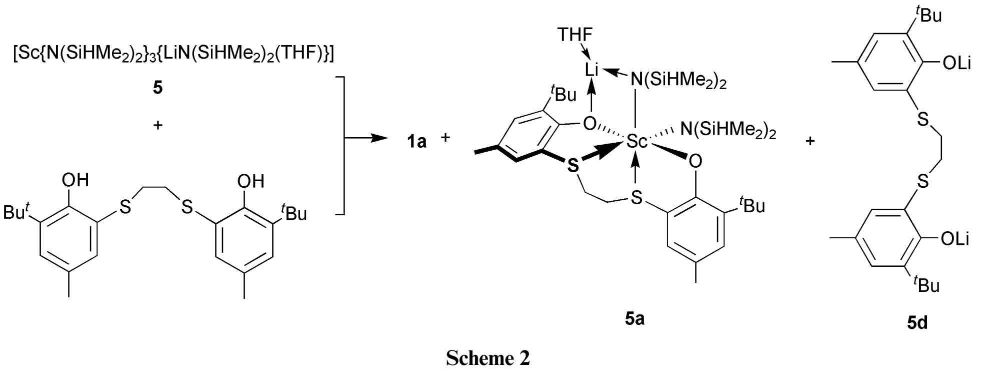
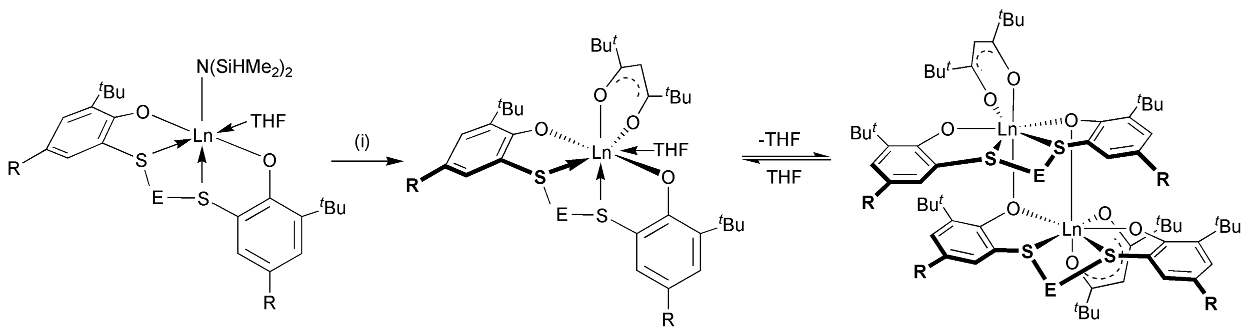


Fig. 2 ORTEP diagram of the molecular structure of [(etbmp)Sc{N(SiHMe$_2$)$_2$}{LiN(SiHMe$_2$)$_2$ (THF)}] **5a**. Thermal ellipsoids are drawn at the 30% probability level. Only the hydrogen atoms attached to Si2 and Si3 are shown. For clarity, the methyl carbon atoms of the SiHMe$_2$ fragments are omitted. For all of the *tert*-butyl groups, only the carbon atoms connected to the phenyl rings are shown.

The residual silylamido group in this family of complexes could be further substituted by a β-diketonato or an alkoxy ligand. From the reaction of **1b** with 2,2,6,6-tetramethyl-3,5-heptanedione in *n*-hexane, the dimeric β-diketonato complex **6b** could be isolated in high yield as hexane-insoluble, white precipitates (Scheme 3). The ^{1}H NMR spectrum of **6b** in C_6D_6 shows two sets of signals for the ligand as well as the



Scheme 2



(i) 2,2,6,6-tetramethyl-3,5-heptanedione

E= -CH$_2$CH$_2$CH$_2$-, R= ^{t}Bu, Ln =Y(**8a**)

E= -CH$_2$CH$_2$-, R = Me, Ln = Y(**6b**), Lu(**6c**)
E= -CH$_2$CH$_2$-, R = ^{t}Bu, Ln = Lu(**7c**)
E= -CH$_2$CH$_2$CH$_2$-, R= ^{t}Bu, Ln = Y(**8b**)

Scheme 3

β-diketonato moiety, indicating an unsymmetric ligand environment. Addition of a few drops of THF led to the rapid dissociation of the dimer, giving a simplified NMR spectrum with patterns similar to **1b**. Reaction of **4b** and the β-diketone afforded the desired monomeric complexes with one coordinated THF in solution. However, upon exposure to vacuum or a sequential recrystallization procedure from non-coordinating solvents, the weakly coordinated THF was lost easily under the formation of the dimeric structure. Due to low solubility, the dimeric complex **8b**[23] could be isolated from the reaction mixture. In addition, the purely monomeric complex **8a** could be recrystallized from *n*-hexane with a small amount of THF.

Reactions between lutetium complexes **1c** and **3c** with 2,2,6,6-tetramethyl-3,5-heptanedione proceeded in a similar way, with dimeric complexes **6c** and **7c** obtained in poor yields (Scheme 3). Large amounts of free phenol were recovered from the reaction mixture.

Reactions of **4b** with alcohols such as methanol and *tert*-butanol failed to give any tractable products. However, the reaction of **1b** with trityl alcohol afforded the desired alkoxide complex [(etbmp)Y(OCPh)$_3$)(THF)] (**9**). Although trace amount of dimer was also formed, monomeric complex **9** could be isolated in moderate yield as analytically pure crystals.

Crystal structures of 2a, 5a and 4b

Single crystals of **2a**, **5a** and **4b** suitable for X-ray diffraction were obtained by slow evaporation of the saturated *n*-pentane or *n*-hexane solutions at room temperature. Crystallographic data and results of the refinements are summarized in Table 1, selected bond lengths and angles are listed in Tables 2 and 3.

As depicted in Fig. 1, the scandium atom in **2a** is six-coordinate with the tetradentate bis(phenolato) ligand, one bis(dimethylsilyl)amido group and one coordinated THF molecule adopting a distorted octahedral geometry. The silylamido ligand is located *cis* to THF and *trans* to one of the sulfur atoms; the two oxygen donors of the ligand are arranged *trans* to each other, as indicated by the corresponding angles N–Sc–O3 100.6(2)°, N–Sc–S2 173.3(1)°, O1–Sc–O2 151.1(2)°. The molecule shows C_1 symmetry and both enantiomers are found in the centrosymmetric crystal structure. The Sc–N bond length of 2.071(5) Å is comparable to the average bond length of 2.069 Å in the four-coordinated precursor [Sc{N(SiHMe$_2$)$_2$}$_3$-(THF)],[24] and slightly longer than 2.060(2) Å in the similar bis(dimethylsilyl)amido scandium complex with the *O*-benzylated-calix[4]arene ligand.[22a] As expected, the Sc–O1 and Sc–O2 bond lengths of 2.004(4) and 2.007(4) Å in **2a** are longer than the average length of 1.91 Å in the above mentioned five-coordinated complex[22a] and of 1.87 Å in the three-coordinated complex [Sc(OC$_6$H$_2$^{t}Bu$_2$-2,6-Me-4)$_3$].[25] However, due to the constraints imposed by the ligand, the O1–Sc–O2 angle of 151.1(2)° is significantly smaller than 180°. A similar effect is also found in the aryloxide complexes of the type [Ln(OC$_6$H$_3$-Pr$^i_2$-2,6)$_3$(THF)$_2$] (155.9(3)–158.9(4)°).[26] The two Sc–S distances of 2.744(2) Å and 2.853(2) Å in **2a** are apparently longer than the sum of the covalent radii (r_c (Sc) + r_c (S) = 1.44 + 1.02 = 2.46 Å), but still much shorter than the sum of metal radius r_m(Sc) and van der Waals radius r_v(S) [r_m(Sc) + r_v(S) = 1.628 + 1.80 = 3.428 Å],[27] indicating the presence of coordinative bonds. The Sc–S1 and Sc–S2 bond lengths differ from each other by about 0.1 Å, with an elongated Sc–S2 bond *trans* to the N(SiHMe$_2$)$_2$ moiety. This can be explained by the stronger electron-donating ability of the silylamido group that weakens the opposite Sc–S2 bond. Evidence for β(Si–H) agostic interaction that is frequently observed in similar complexes[28] is not conclusive for **2a**: compared to the close Sc ··· Si contacts of 2.989(1)–3.052(1) Å in the precursor,[24] the Sc ··· Si1 distance of 3.198(2) Å in **2a** is somewhat longer, but still shorter than the corresponding distance in **5a** (3.233(2) Å). The angles at the silylamido nitrogen in **2a** deviate slightly from ideal sp^2 hybridization. On the other hand, the enlarged Si1–N–Si2 angle of 125.5(3)° compared to ideal 120° might be also caused by the short Si–N bond lengths of 1.704(5) and 1.717(5) Å which fall into the range of 1.698–1.715 Å observed in complex [Sc{N-(SiHMe$_2$)$_2$}$_3$(THF)],[24] but which are significantly shortened compared to 1.751(2) Å in [Sc{N(SiMe$_3$)$_2$}].[29] These findings are further supported by the spectroscopic data of **2a**, where the septet signal of SiH at 5.36 ppm is significantly downfield shifted compared to 5.03 ppm in [Sc{N(SiHMe$_2$)$_2$}$_3$(THF)].[24]

The molecular structure of the lithium 'ate' complex **5a** is shown in Fig. 2. The scandium atom adopts a similar coordination geometry as found for **2a**, where the second bis(dimethylsilyl)amido group replaces the coordinated THF in **2a**. The Li(THF) moiety is located between the two amide groups and is stabilized by one oxygen donor of the ligand, one nitrogen donor and THF. Close contacts between lithium and Sc as well as Si2 are detected. The coordination of N1 to Li(THF) also brings the Me–Si2–Me fragment close to lithium. However, steric repulsion forces this moiety away from the lithium atom as indicated by the enlarged Sc–N1–Si2 angle of 126.0(2)° (Table 3). Compared to **2a**, the Sc–S bond lengths in **5a** are slightly elongated with distances of 2.873(1) and 2.863(1) Å, which can be explained by the *trans* effects of two silylamido ligands in the structure. The Sc–N1 bond length of 2.183(3) Å is slightly longer than the Sc–N2 distance of 2.111(3) Å, because the coordination of N1 to lithium brings the electron density partly to lithium, weakening the bond between Sc and N1. The other structural features of **5a** are similar to **2a** without evidence for β(Si–H) agostic interactions.

The crystal structure of the yttrium complex **4b** shows a different configuration than **2a** and **5a** (Fig. 3). In **4b**, the yttrium atom is six-coordinate, adopting a distorted trigonal-prismatic geometry, where the two oxygen donors of the bis(phenolato)

Table 1 Crystallographic data for **2a**, **4b** and **5a**

	2a	**4b**	**5a**
Formula	$C_{33}H_{56}NO_3S_2ScSi_2$	$C_{39}H_{68}NO_3S_2Si_2Y$	$C_{36}H_{68}LiN_2O_3S_2ScSi_4$
M	680.05	808.15	805.30
Crystal size/mm	0.5 × 0.5 × 0.2	0.60 × 0.40 × 0.35	0.68 × 0.40 × 0.32
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/n$
a/Å	8.951(3)	14.021(3)	15.613(1)
b/Å	11.127(4)	15.195(4)	18.363(1)
c/Å	20.548(2)	22.294(3)	16.5110(9)
α/°	102.28(2)	90	90
β/°	99.60(2)	98.23(1)	90.013(5)
γ/°	95.03(3)	90	90
U/Å	1956 (1)	4701 (2)	4733.7 (5)
Z	2	4	4
D_c/g cm^{-3}	1.155	1.142	1.130
μ/mm^{-1}	0.386	1.412	0.377
F(000)	732	1728	1736
θ Range/°	2–26	3–25	3–26
Data collected (hkl)	±11, ±13, ±25	−16 to 7, 0 to 18, ±26	0 to 19, 0 to 22, ±20
No. of reflections collected	15277	11999	9589
No. of independent refl.	7643	8220	9233
R_{int}	0.0736	0.0709	0.0401
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0789, 0.1957	0.0714, 0.1065	0.0629, 0.1280
R_1, wR_2 (all data)	0.1609, 0.2360	0.2478, 0.1470	0.1424, 0.1580
Goodness of fit on F^2	0.984	0.942	1.012
$\Delta\rho_{max,min}$/e Å^{-3}	0.775, −0.494	0.256, −0.231	0.302, −0.225

Table 2 Selected bond lengths (Å) and angles (°) in **2a**, **4b**

	2a (Ln = Sc)	**4b** (Ln =Y)
Ln–N	2.071(5)	2.240(5)
Ln–O1	2.004(4)	2.151(5)
Ln–O2	2.007(4)	2.132(5)
Ln–O3	2.179(4)	2.382(5)
Ln–S1	2.744(2)	2.948(2)
Ln–S2	2.853(2)	2.973(2)
N–Si1	1.704(5)	1.682(6)
N–Si2	1.717(5)	1.688(6)
O1–Ln–S1	72.6(1)	66.1(1)
O2–Ln–S1	97.5(1)	135.2(1)
O3–Ln–S1	162.8(1)	133.8(1)
O1–Ln–S2	80.9(1)	107.1(1)
O2–Ln–S2	71.0(1)	67.7(1)
O3–Ln–S2	83.6(1)	152.7(1)
S1–Ln–S2	84.10(7)	73.4(6)
O1–Ln–O2	151.1(2)	105.1(2)
O1–Ln–O3	93.6(2)	86.5(2)
O2–Ln–O3	89.8(2)	86.2(2)
N–Ln–O1	104.0(2)	136.5(2)
N–Ln–O2	103.6(2)	118.0(2)
N–Ln–O3	100.6(2)	89.9(2)
N–Ln–S1	92.9(2)	86.3(1)
N–Ln–S2	173.3(1)	95.5(2)
Ln–N–Si1	115.5(3)	115.9(3)
Ln–N–Si2	118.8(2)	114.5(3)
Si1–N–Si2	125.5(3)	129.6(3)
Ln ··· Si1	3.198 (2)	3.338 (2)
Ln ··· Si2	3.265 (2)	3.318 (3)

Table 3 Selected bond lengths (Å) and angles (°) in **5a**

Sc–N1	2.183(3)	Sc–N2	2.111(3)
Sc–O1	1.987(3)	Sc–O2	2.078(3)
Sc–S1	2.873(1)	Sc–S2	2.863(1)
N1–Si1	1.723(4)	N2–Si3	1.705(4)
N1–Si2	1.723(3)	N2–Si4	1.688(4)
O2–Li	1.963(8)	O3–Li	1.871(8)
N1–Li	2.148(8)		
O1–Sc–S1	71.26(8)	O1–Sc–S2	86.59(9)
O2–Sc–S1	87.92(8)	O2–Sc–S2	70.24(8)
O2–Sc–N1	89.3(1)	O1–Sc–N2	105.7(1)
O1–Sc–N1	103.6(1)	O2–Sc–N2	93.1(1)
N1–Sc–S1	158.46(9)	N2–Sc–S1	94.4(1)
N1–Sc–S2	85.39(9)	N2–Sc–S2	159.4(1)
N2–Sc–N1	107.1(1)	S1–Sc–S2	73.56(4)
Sc–N1–Si1	111.2(2)	Sc–N2–Si3	120.1(2)
Sc–N1–Si2	126.0(2)	Sc–N2–Si4	120.1(2)
Si1–N1–Si2	116.7(2)	Si3–N2–Si4	119.7(2)
O1–Sc–O2	152.7(1)		
Sc ··· Si1	3.233(2)	Sc ··· Li	2.818(7)
Li ··· Si2	2.794(7)		

ligand are *cis*-oriented, as indicated by O1–Y–O2 angle of 105.1(2)°. Such a configuration is also found in an yttrium–salen complex.[5a] The Y–O(ligand) bond lengths of 2.151(5) and 2.132(5) Å are comparable to the terminal Y–O bond lengths in the octahedral complexes (2.157–2.177 Å),[5a,30] and slightly longer than those in five-coordinate complexes, such as [(η^5-C_5Me_5)Y($OC_6H_3{}^tBu_2$-2,6)$_2$] (2.096(4), 2.059(3) Å),[31] [{*O*-$SiHMe_2$-calix[4]arene}Y(THF)]$_2$ (2.061–2.069 Å)[32] and [(1,3-($SiMe_3$)$_2$-2-Ph-β-diketiminato)$_2$Y($OC_6H_3{}^tBu_2$-2,6-Me-4)] (2.075(2) Å).[21c] The Y–N bond length of 2.240(5) Å matches the values (2.229(4)–2.276(4) Å) found for the corresponding precursor.[24] Similar values are also found in [Me_2Si(2-Me-Ind)$_2$-Y{N($SiHMe_2$)$_2$}] (2.237(4) Å),[28] [{1,3-(2,6-^{i}Pr$_2$-Ph)$_2$-2-Tol-β-diketiminato}Y{N($SiHMe_2$)$_2$}$_2$(THF)] (2.250(3), 2.258(3) Å).[21c] The Y–S distances of 2.948(2) and 2.973(2) Å are longer than the bridging bond in [(Et_3CS)$_2$Y(μ-$SCEt_3$)Py_2]$_2$ (Y–S, 2.848, 2.850 Å)[33] and slightly longer than those in similar sulfur-coordinated yttrium complexes (2.9379(6)–2.9572(6) Å).[10] Furthermore, **4b** exhibits a short average N–Si bond length of 1.69 Å and a large Si1–N–Si2 angle of 129.6 (3)°. The absence of Y ··· Si and Y ··· H contacts excludes a β(Si–H) agostic interaction.

Metal complexes that have an open-chain ligand (such as the [OSSO]$^{2-}$ bisphenolato ligand) "wrapped" around the six-coordinate metal center generally can adopt three possible configurations (Scheme 4). Configuration **A** is normally found with planar salen-type ligands, but configurations **B** and **C** are also possible. By comparing the structures of **2a**, **5a** and **4b** in the solid state, we find two of the three possible configurations. The scandium complexes **2a** and **5a** have configuration **B**, whereby the yttrium complex **4b** is best described by configuration **C**. Similarly, the 1,4-dithiabutanediyl-bridged ligand "wraps" around a group 4 metal atom resulting in

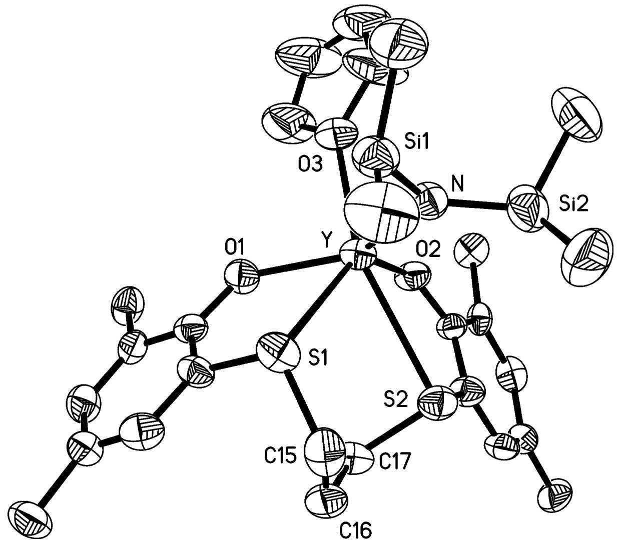
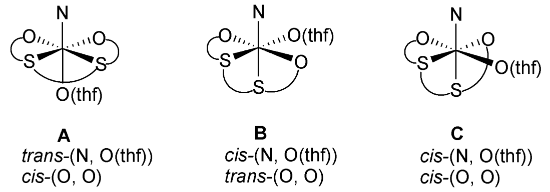


Fig. 3 ORTEP diagram of the molecular structure of [(pdtbp)Y{N(SiHMe$_2$)$_2$}(THF)] **4b**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Only one position for the disordered *tert*-butyl groups is shown, and for all of the *tert*-butyl groups only the carbon atoms connected to the phenyl rings are shown.

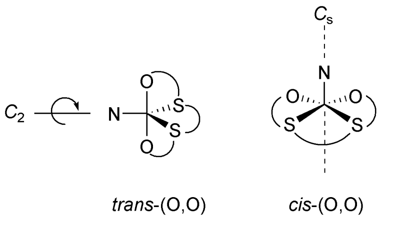


Scheme 4

configuration **B**, whereas the 1,5-dithiapentanediyl-bridged ligand adopts configuration **C**.[7]

Structures in solution

As characterized by X-ray diffraction studies, the silylamido complexes **1a**–**4c** are monomeric and show C_1 symmetrical configuration in the solid state. However, **1a**–**4c** show fluxional behavior in solution and the rigid C_1 configuration is no longer present, as indicated by the presence of less than the expected number of peaks in the ^{1}H NMR spectra. The S–Ln coordination binding in the new complexes still exists as probed by the NMR spectra that there are slight to apparent downfield-shifts of the SCH$_2$ protons in **1a**–**4c** compared to the corresponding bis(phenol)s. The mentioned fluxional phenomena are observed quite often for rare earth metal complexes[21c,34] and other transition-metal complexes.[35] Commonly the reversible THF-dissociation process is suggested to be responsible for this fluxional behavior. Here the fast dissociation of THF on the NMR time scale will lead to a pseudo-five coordinated environment around the metal center with either C_2 (trigonal bipyramidal) or C_s symmetry (square pyramidal) (Scheme 5). This renders both phenyl moieties in the same ligand chemically equivalent, and only one set of signals is observed in the NMR spectra.



Scheme 5

At room temperature, the ^{1}H NMR spectra (in C_6D_6) show that the C_1 symmetrical conformation of the 1,4-dithiabutanediyl-bridged scandium complexes **1a** and **3a** is still maintained. Two phenyl groups of the ligand are unsymmetrical, showing four sets of doublets for the aromatic protons, two singlets for the methyl groups and two singlets for the *tert*-butyl groups. The silylamido group displays two sets of SiMe doublets, but only one SiH septet. No clear coupling pattern can be found for the ethylene bridge, since the four protons appear as two multiplets in 3 : 1 ratio (Table 4). The protons of α-CH$_2$ in THF is also split into two multiplets of equal intensity. Variable-temperature ^{1}H NMR spectra of **1a** in toluene-d_8 indicate that all of the above mentioned features at 25 °C are still present at −80 °C. Above 25 °C, the signals begin to broaden. The spectrum at 100 °C shows sharp signals typical for C_2 or C_s symmetry. Two doublets for the four aromatic protons, two singlets for the methyl and *tert*-butyl, and one doublet for the SiMe group are recorded. The unsymmetrical signals of the ethylene bridge also coalesce to give one broad signal. From the Eyring equation, the activation energy of this process for **1a** is found to be $\Delta G^{\neq} = 69.79$ kJ mol^{-1} ($\Delta\nu = 27.65$ Hz, $T_c = 57$ °C for the SiMe signals).

When the spectra of **1a** are recorded in THF-d_8, the ligand shows symmetrical features even at −80 °C. The four protons of the ethylene bridge show two AB spin patterns (δ 2.89, 2.26) at room temperature which broaden and appear as four broad signals at −100 °C (δ 3.07, 2.92, 2.21, 2.05). The silylamido unit still shows two doublets for SiMe with one SiH septet below 25 °C. The gradual coalescence of SiMe signals is observed above room temperature. It is clear that the existence of excess THF facilitates the dissociation from C_1 to symmetrical configuration.

For the 1,4-dithiabutanediyl-bridged lutetium complexes **1c** and **3c**, the dissociation of THF seems to be easier than for the corresponding scandium complexes. At room temperature in C_6D_6, the two phenyl groups of the ligand are already symmetrical, only the fluxionality of the ethylene-bridge and SiMe is frozen out on the NMR time scale, showing two broad signals for the ethylene bridge and one broad doublet for the SiMe moiety (Table 4). The activation energy for **1c** is found to be $\Delta G^{\neq} = 63.5$ kJ mol^{-1} (for the SiMe signals, $\Delta\nu = 24.8$ Hz, $T_c = 27$ °C).

Compared to the rigid structure of 1,4-dithiabutanediyl-bridged complexes (except for **1b**), 1,5-dithiapentanediyl-bridged complexes are more flexible (Table 4). For example, the yttrium complex **4b** remains fluxional with apparent C_s symmetry in solution over the entire temperature range of −80 to +100 °C. The variable-temperature measurements have not been performed for all complexes, but similar fluxional behavior can be inferred.

Ring-opening polymerization of L-lactide

As shown in Table 5 the silylamido complexes **1a**–**4c** are active initiators for the ring-opening polymerization of L-lactide under mild conditions. The resulting polymers have high molecular weights with narrow molecular weight distributions of 1.15–1.41. In most cases, the calculated molecular weight is close to the measured values of M_n, indicating controlled behaviour during the polymerization. These features are comparable to the controlled polymerizations by other transition metal alkoxides.[14b,20a,e,f,35]

As can be seen from Table 5, the complexes with a 1,4-dithiabutanediyl-bridged ligand generally are more active than the 1,5-dithiapentanediyl-bridged analogues. Furthermore, for complexes with a given ligand, the lutetium complexes are slightly more active than the yttrium complexes, but both are significantly more active than the corresponding scandium complexes (see entries 10, 4, 1 for **1c**, **1b** and **1a**). It is evident that the 1,5-dithiapentanediyl-ligand will form a more crowded

Table 4 Selected ^{1}H NMR spectroscopic data of some rare earth metal complexes[a]

	SiH[b]	SCH_2	$–CH_2–$	$SiCH_3$
1a	5.26	2.42 (m, 3H), 2.19 (m,1H)	–	0.46 (d, 6H), 0.39 (d, 6H)
1a[c]	4.81	2.91 (d, 2H), 2.25 (d, 2H)	–	0.05 (d, 6H), 0.004 (d, 6H)
1b	5.19	2.45 (br s, 4H)	–	0.41 (d,12H)
1c	5.12	2.52 (br m, 2H), 2.36 (br m, 2H)	–	0.45 (d, 6H), 0.41 (d, 6H)
3a	5.26	2.49 (m, 3H), 2.23 (m, 1H)	–	0.42 (d, 6H), 0.36 (d, 6H)
3c	5.11	2.58 (br s, 2H), 2.41 (br s, 2H)	–	0.41 (d, 6H), 0.40 (d, 6H)
5a	5.15	2.49 (d, 2H), 2.12 (d, 2H)	–	0.52 (d, 12H), 0.47 (d, 12H)
2a	5.36	2.46 (t, 4H)	1.37 (br s, 2H)	0.43 (d, 12H)
2c	5.07	2.62 (t, 4H)	1.46 (qnt, 2H)	0.43 (d, 12H)
4b	5.10	2.67 (t, 4H)	1.55 (qnt, 2H)	0.39 (d, 12H)
4c	5.07	2.68 (t, 4H)	1.54 (qnt, 2H)	0.42 (d, 12H)

[a] Measured in C_6D_6, 25 °C, ppm. [b] Septet, 2H. [c] Measured in d_8-THF, 25 °C.

Table 5 Ring-opening polymerization of L-lactide [a]

Entry	Catalyst	$[M]_0/[Ln]_0/[^iPrOH]_0$	Solvent	Time/h	Conv.[b] (%)	$10^{-4}M_c$ [c]	$10^{-4}M_n$	M_w/M_n
1	**1a**	300/1/0	THF	4	66	2.85	2.95	1.37
2	**2a**	300/1/0	THF	24	42	1.82	2.79	1.41
3	**3a**	300/1/0	THF	20	98	4.23	5.40	1.20
4	**1b**	300/1/0	THF	0.17	99	4.28	4.99	1.17
5		300/1/1	Toluene	24	34			
6		300/1/2	Toluene	24	94			
7	**4b**	300/1/0	THF	24	97	4.19	4.20	1.15
8		300/1/1	Toluene	20	100	4.33	4.39	1.15
9		300/1/2	Toluene	1	92	1.99	2.03	1.15
10	**1c**	300/1/0	THF	0.1	97	4.19	5.76	1.17
11		1500/1/0[d]	THF	1	96			
12		300/1/0	CH_2Cl_2	1	87			
13		300/1/0	Toluene	1	85			
14		300/1/1	Toluene	25	14			
15		300/1/2	Toluene	25	42			
16	**2c**	300/1/0	THF	47	49	2.10	2.42	1.31
17	**3c**	300/1/0	THF	0.5	93	4.02	2.38	1.24
18		750/1/0	THF	1	82			
19	**4c**	300/1/0	THF	48	60	2.59	3.41	1.18
20	**6b**	300/1/0	THF[e]	23	96	4.15	4.41	2.42[h]
21		300/1/0	Toluene[f,g]	23	97	4.19	3.85	2.95
22		300/1/2	Toluene[g]	20	40			
23	**8a**	300/1/1	Toluene	19	93	4.02	4.25	1.28
24	**8b**	300/1/0	THF[e]	24	93	4.02	1.23	6.99[h]
25		300/1/0	Toluene[f,g]	24	99	4.28	2.40	4.33
26		300/1/2	Toluene	20	100	2.17	2.72	1.23
27	**9**	300/1/0	THF	0.5	71			

[a] Polymerization carried out with 0.87 M solution of L-lactide at 25 °C unless otherwise indicated. [b] Determined by the integration ratio of the methine protons in monomer and polymer. [c] $M_c = ([M]_0/[Ln]_0) \times 144.13 \times$ conv.%; with the presence of ^iPrOH, $M_c = ([M]_0/[^iPrOH]_0) \times 144.13 \times$ conv.% + 60. [d] Concentration of initiator, $[Ln]_0 = 1.45 \times 10^{-3}$ mol L^{-1}; concentration of monomer, $[M]_0 = 2.17$ mol L^{-1}. [e] At 60 °C. [f] At 90 °C. [g] A drop of THF was added to the catalyst solution. [h] Bimodal.

configuration when "wrapped around" the metal center than the 1,4-dithiabutanediyl-ligand. As a result, the coordination and/or the nucleophilic attack of the monomer are hindered. Similarly, since lutetium and yttrium are larger, the ligand environment around scandium should be considerably more crowded as compared to that around lutetium and yttrium, leading to a poor catalytic performance. This is also consistent with the report that the complexes of larger rare earth metal normally show higher activities.[19a,e]

Among the investigated complexes, **1c** is most active for the ring-opening polymerization of lactide: complete conversion of 300 equivalents of monomer was reached after several minutes and the obtained polylactide has high molecular weight with a narrow molecular weight distribution of 1.17 (entry 10). Furthermore, 1500 equivalents of monomer could be efficiently polymerized using a relatively low initiator concentration (entry 11). There is some deviation of the observed molecular weights from the calculated values. Most likely it is due to the partial deactivation of the catalyst by impurities (trace amount of free lactide acid, moisture) in the monomer, since this class of compounds are highly sensitive to any proton source. Compared to the corresponding precursors $[Ln\{N(SiHMe_2)_2\}_3(THF)_x]$ (Ln = Sc, Y, Lu), **1a**–**1c** are even more active and show better control of the polymerization. Comparative runs with $[Ln\{N(SiHMe_2)_2\}_3(THF)_x]$ show that they initiate rapid polymerization, but produce polylactides with broad distributions.[21c,36]

The ring-opening polymerization of *rac*-lactide by **4b** under the similar condition afforded the heterotactic enriched polylactide (~70% *isi* + *sis* tetrads) as characterized by homodecoupled ^{1}H and $^{13}C\{^1H\}$ NMR spectra.[36] The insertion of a different (*R*,*R*) or (*S*,*S*) monomer from the last one is preferred in sequence.

Complexes **1a**–**4c** are generally more active in THF than in CH_2Cl_2 or toluene. From the ^{1}H NMR spectra of the polylactide (prepared by L-lactide/**1c** with the ratio of 20 : 1), no $N(SiHMe_2)_2$ end groups could be observed. On the other hand, polymerizations of L-lactide by **1a**–**4c** resulted in purely isotactic polylactide, the $^{13}C\{^1H\}$ NMR spectra showing only signals for isotatic sequences. High molecular weight polymers with narrow distribution were obtained in each case and the ligand environment has a crucial influence on the catalytic behavior. All these features argue against any ionic process. We therefore suggest that the polymer chain may be propagated via a coordinating insertion mode[13e,20a,e,f,i] after the initiation step.

When the reaction mixture of **4b** and excess isopropanol was used to polymerize L-lactide, both –O^{i}Pr and HOC(H)(CH$_3$)CO– end groups could clearly be identified in the ^{1}H NMR spectra of the polylactides. The polymerization with the 2 : 1 ratio of isopropanol to **4b** was faster than that with 1 : 1 ratio. By NMR spectroscopy, the reaction of **4b** with isopropanol in 1 : 1, 1 : 2, 1 : 3 ratio afforded nearly the same signal pattern,[37] except that the multiplets for methine protons of the O^{i}Pr group at 4.66 ppm (1 : 1) shifted to 4.22 ppm (1 : 2), 4.05 ppm (1 : 3) and were broadened. Obviously, an exchange process with free isopropanol was involved. So far, we were not able to isolate any pure complexes, but we suggest that the O^{i}Pr group remains bonded to the metals in the bridging mode. The μ-O^{i}Pr group is not active in the polymerization of lactide. The exchange with free isopropanol probably activates the –O^{i}Pr group. A similar effect was also found in **1a**/ ^{i}PrOH, **1c**/ ^{i}PrOH systems as well as in the β-diketonato complexes/^{i}PrOH systems (Table 5).

The β-diketonato complexes **6b** and **8b** were not active at room temperature in toluene, however, slow polymerization was observed when THF was used as solvent. Therefore we conclude that the dimers are not active for the polymerization. Upon addition of THF, monomers were formed, responsible for the smooth polymerization. The polymers obtained at 60 °C in THF display a bimodal distribution, indicating the existence of at least two different active species. When the polymerization was performed in toluene with a few drops of added THF to dissociate the dimer, monomodal polymer was obtained, although the distribution remained broad. When excess isopropanol was used, fast polymerization and narrow molecule weight distribution were observed for both **6b** and **8b**. Monomeric complex **8a** shows behavior similar to that of THF dissociated **8b**.

The alkoxide complex **9** is also active in the polymerization of lactide. However no OCPh$_3$ end group could be identified. The GPC measurement was not successful due to the poor solubility of the polymer in THF (possibly, polymers with rather high molecular weight were formed). Judged from the color change from pink to purple to dark blue during the polymerization at 60 °C (the color of free radical $^\bullet$CPh$_3$), some free radical processes seem to be involved in the polymerization.

Conclusion

Through the so-called extended silylamine route, several monomeric rare earth metal complexes ligated by sulfur bridged bis(phenolato) ligands were synthesized and structurally characterized. The complexes **1a**–**4c** are active initiators for the ring-opening polymerization of L-lactide in a controlled manner, producing high molecular weight poly(L-lactide)s with narrow molecular weight distributions. Work is underway to determine the polymerization mechanism using these initiators.

Experimental

General considerations

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glove box techniques. Toluene, *n*-hexane and THF were distilled under argon from sodium/benzophenone ketyl prior to use. *n*-Pentane was purified by distillation from sodium/triglyme benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Anhydrous lanthanide trichlorides (Aldrich or Strem products) were used as received. [Ln{N(SiHMe$_2$)$_2$}$_3$(THF)$_x$] (Ln = Sc, Y, Lu; x = 1, 2) were synthesized according to the literature methods.[24,38] 1,ω-Dithiaalkanediyl-bridged bis(phenol)s were synthesized according to a modification of the methods reported in the literature.[7] All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Bruker DRX 400 spectrometer at 25 °C (^{1}H, 400.1 MHz, ^{13}C, 100.6 MHz) unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Elemental analyses were performed by the Microanalytical Laboratory of this department. In some cases where the results were not satisfactory, metal analysis was performed by complexometric titration using xylenol orange as indicator.

Syntheses of complexes

[(etbmp)Sc{N(SiHMe$_2$)$_2$}(THF)] (1a). A solution of etbmpH$_2$ (0.418 g, 1 mmol) in toluene (10 mL) was added dropwise to a solution of [Sc{N(SiHMe$_2$)$_2$}$_3$(THF)] (0.513 g, 1 mmol) in toluene (15 mL) at r.t.. The colourless solution was stirred for 5 days at 50 °C and the solvent removed *in vacuo* to afford a foam-like solid, which was dried in high vacuum for several hours. The powder obtained was then dissolved with 5 mL of *n*-pentane and filtered. The clear filtrate was concentrated and the residue redissolved in minimum amount of *n*-pentane (~1.5 mL) to give colourless crystals after standing at r.t. for 2 days (500 mg, 74%) (Found: C, 58.63; H, 8.05; N, 2.13; S, 9.39. $C_{32}H_{54}NO_3S_2ScSi_2\cdot 0.2C_5H_{12}$ requires C, 58.31; H, 8.36; N, 2.06; S, 9.43%); δ_H (C$_6$D$_6$) 7.24 (d, 1H, 5-H, *J* = 2.2 Hz), 7.20 (d, 1H, 5′-H, *J* = 2.2 Hz), 7.04 (d, 1H, 3-H, *J* = 2.2 Hz), 6.88 (d, 1H, 3′-H, *J* = 2.2 Hz), 5.26 (sep, 2H, SiH, *J* = 3.0 Hz), 4.14 (m, 2H, THF), 3.96 (m, 2H, THF), 2.42 (m, 3H, SCH$_2$CH$_2$S), 2.19 (m, 1H, SCH$_2$CH$_2$S), 2.14 (s, 3H, 4-Me), 2.13 (s, 3H, 4′-Me), 1.75 (s, 9H, 6-^{t}Bu), 1.65 (s, 9H, 6′-^{t}Bu), 1.19 (br s, 4H, THF), 0.46 (d, 6H, SiMe$_2$, *J* = 3.0 Hz) and 0.39 (d, 6H, SiMe$_2$, *J* = 3.0 Hz); δ_H (d_8-Tol, 25 °C) 7.18 (s, 1H, 5-H), 7.13 (s, 1H, 5′-H), 6.99 (s, 1H, 3-H), 6.83 (s, 1H, 3′-H), 5.18 (sep, 2H, SiH, *J* = 3.0 Hz), 4.17 (m, 2H, THF), 3.99 (m, 2H, THF), 2.42 (m, 3H, SCH$_2$CH$_2$S), (1H, SCH$_2$CH$_2$S, overlapped), 2.14 (s, 3H, 4-Me), 2.11 (s, 3H, 4′-Me), 1.70 (s, 9H, 6-^{t}Bu), 1.61 (s, 9H, 6′-^{t}Bu), 1.29 (br s, 4H, THF), 0.39 (d, 6H, SiMe$_2$, *J* = 3.0 Hz) and 0.32 (d, 6H, SiMe$_2$, *J* = 3.0 Hz); δ_H (d_8-Tol, 100 °C) 7.09 (d, 2H, 5-H, *J* = 2.2 Hz), 6.88 (d, 2H, 3-H, *J* = 2.2 Hz), 5.11 (sep, 2H, SiH, *J* = 3.0 Hz), 4.09 (t, 4H, THF, *J* = 6.3 Hz), 2.40 (br s, 4H, SCH$_2$CH$_2$S), 2.09 (s, 6H, 4-Me), 1.57 (s, 18H, 6-^{t}Bu), 1.44 (m, 4H, THF) and 0.27 (d, 12H, SiMe$_2$, *J* = 3.0 Hz); δ_C (C$_6$D$_6$) 167.1 (Ar-C1), 166.6 (Ar-C1′), 138.4 (Ar-C6), 137.4 (Ar-C6′), 132.1 (Ar-C3), 132.0 (Ar-C3′), 130.3 (Ar-C5), 130.2 (Ar-C5′), 126.2 (Ar-C4), 125.5 (Ar-C4′), 118.9 (Ar-C2), 118.2 (Ar-C2′), 72.3 (THF), 37.3 (SCH$_2$CH$_2$S), 36.9 (SCH$_2$*C*H$_2$S), 35.5 [6-*C*(CH$_3$)$_3$], 35.3 [6′-*C*(CH$_3$)$_3$], 30.1 [6-C(*C*H$_3$)$_3$], 29.9 [6′-C(*C*H$_3$)$_3$], 25.1 (THF), 20.7 (4 and 4′-Me), 3.7 (SiMe$_2$) and 3.6 (SiMe$_2$).

[(ptbmp)Sc{N(SiHMe$_2$)$_2$}(THF)] (2a). Following a procedure similar to that to prepare **1a**, the reaction of [Sc{N(SiHMe$_2$)$_2$}$_3$(THF)] (0.228 g, 0.44 mmol) and ptbmpH$_2$ (0.192 g, 0.44 mmol) gave white prisms (200 mg, 67%) (Found: C, 58.30; H, 8.25; N, 2.01; S, 9.56. $C_{33}H_{56}NO_3S_2ScSi_2$ requires C, 58.28; H, 8.30; N, 2.06; S, 9.43%); δ_H (C$_6$D$_6$) 7.18 (d, 2H, 5-H, *J* = 2.0 Hz), 6.97 (d, 2H, 3-H, *J* = 2.0 Hz), 5.36 (sep, 2H, SiH, *J* = 3.0 Hz), 4.07 (t, 4H, THF, *J* = 6.4 Hz), 2.46 (t, 4H, SC*H*$_2$CH$_2$C*H*$_2$S, *J* = 5.8 Hz), 2.17 (s, 6H, 4-Me), 1.69 (s, 18H, 6-^{t}Bu), 1.37 (br s, 2H, SCH$_2$C*H*$_2$CH$_2$S), 1.22 (m, 4H, THF, *J* = 6.4 Hz) and 0.43 (d, 12H, SiMe$_2$, *J* = 3.0); δ_C (C$_6$D$_6$) 164.9 (Ar-C1), 137.7 (Ar-C6), 131.4 (Ar-C3), 129.9 (Ar-C5), 125.6 (Ar-C4), 121.6 (Ar-C2), 71.4 (THF), 35.4 [6-*C*(CH$_3$)$_3$], 35.3 (S*C*H$_2$CH$_2$*C*H$_2$S), 30.0 [6-C(*C*H$_3$)$_3$], 25.2 (THF), 23.8 (SCH$_2$*C*H$_2$CH$_2$S), 20.8 (4-Me) and 3.4 (SiMe$_2$).

[(edtbp)Sc{N(SiHMe$_2$)$_2$}(THF)] (3a). The procedure was similar to that to prepare **1a**, using edtbpH$_2$ (0.490 g, 0.95 mmol) and [Sc{N(SiHMe$_2$)$_2$}$_3$(THF)] (0.479 g, 0.95 mmol).

White crystals precipitated upon standing at r.t. (440 mg, 62%) (Found: C, 61.71; H, 9.00; N, 1.56; S, 9.03. $C_{38}H_{66}NO_3S_2ScSi_2\cdot 0.36\ C_5H_{12}$ requires C, 61.51; H, 9.12; N, 1.80; S, 8.25%); δ_H (C_6D_6) 7.59 (d, 1H, 5-H, J = 2.2 Hz), 7.55 (d, 1H, 5′-H, J = 2.1 Hz), 7.38 (d, 1H, 3-H, J = 2.2 Hz), 7.22 (d, 1H, 3′-H, J = 2.1 Hz), 5.26 (sep, 2H, SiH, J = 3.0 Hz), 4.13 (m, 2H, THF), 3.96 (m, 2H, THF), 2.49 (m, 3H, SCH_2CH_2S), 2.23 (m, 1H, SCH_2CH_2S), 1.80 (s, 9H, 6-^{t}Bu), 1.70 (s, 9H, 6′-^{t}Bu), 1.28 (s, 9H, 4-^{t}Bu), 1.25 (s, 9H, 4′-^{t}Bu), 1.15 (br s, 4H, THF), 0.42 (d, 6H, $SiMe_2$, J = 3.0 Hz) and 0.36 (d, 6H, $SiMe_2$, J = 3.0 Hz); δ_C (C_6D_6) 167.0 (Ar-C1), 166.5 (Ar-C1′), 139.8 (Ar-C6), 139.3 (Ar-C6′), 137.9 (Ar-C4), 137.0 (Ar-C4′), (Ar-C3 and C3′ overlapped by solvent signal), 126.5 (Ar-C5), 126.1 (Ar-C5′), 118.7 (Ar-C2), 118.0 (Ar-C2′), 72.3 (THF), 37.5 ($S\mathit{C}H_2CH_2S$), 37.1 ($S\mathit{C}H_2CH_2S$), 35.9 [6-$\mathit{C}(CH_3)_3$], 35.7 [6′-$\mathit{C}(CH_3)_3$], 34.4 [4 and 4′-$\mathit{C}(CH_3)_3$], 31.9 [4 and 4′-$C(\mathit{C}H_3)_3$], 30.2 [6-$C(\mathit{C}H_3)_3$], 30.0 [6′-$C(\mathit{C}H_3)_3$], 25.1 (THF), 3.7 ($SiMe_2$) and 3.6 ($SiMe_2$).

[(etbmp)Y{N(SiHMe$_2$)$_2$}(THF)] (1b). etbmpH$_2$ (0.836 g, 2 mmol) was slowly added to the solution of [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (1.26 g, 2 mmol) in hexane (30 mL) at r.t. The colourless reaction mixture was stirred for 3 days. After filtration to remove trace amount of solid, the clear solution was concentrated *in vacuo* to afford a foam-like solid, which was further dried for hours. The powder obtained was recrystallized from *n*-pentane (5 mL) at −30 °C to afford colourless crystals (1.33 g, 93%) (Found: C, 54.03; H, 7.84; N, 1.88; S, 8.98. $C_{32}H_{54}NO_3S_2Si_2Y$ requires C, 54.14; H, 7.67; N, 1.97; S, 9.03%); δ_H (C_6D_6) 7.21 (d, 2H, 5-H, J = 2.4 Hz), 6.97 (d, 2H, 3-H, J = 2.4 Hz), 5.19 (sep, 2H, SiH, J = 3.0 Hz), 3.85 (m, 4H, THF), 2.45 (br s, 4H, SCH_2CH_2S), 2.15 (s, 6H, 4-Me), 1.69 (s, 18H, 6-^{t}Bu), 1.18 (br s, 4H, THF) and 0.41 (d, 12H, $SiMe_2$, J = 3.0 Hz); δ_C (C_6D_6) 165.9 (Ar-C1), 138.3 (Ar-C6), 132.3 (Ar-C4), 130.1 (Ar-C3), 125.2 (Ar-C5), 118.3 (Ar-C2), 70.9 (THF), 37.0 (SCH_2CH_2S), 35.5 [6-$\mathit{C}(CH_3)_3$], 29.8 [6-$C(\mathit{C}H_3)_3$], 25.1 (THF), 20.7 (4-Me) and 3.7 ($SiMe_2$).

[(pdtbp)Y{N(SiHMe$_2$)$_2$}(THF)] (4b). The procedure was similar to that of **1b**, using [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (1.26 g, 2 mmol) and pdtbpH$_2$ (1.032 g, 2 mmol). The powder obtained was recrystallized from *n*-hexane (~5 mL) at −30 °C to give colorless crystals (1.28 g, two crops, 80%) (Found: C, 57.91; H, 8.51; N, 1.79; S, 8.04. $C_{39}H_{68}NO_3S_2Si_2Y$ requires C, 57.96; H, 8.48; N, 1.73; S, 7.93%); δ_H (C_6D_6) 7.48 (d, 2H, 5-H, J = 2.5 Hz), 7.31 (d, 2H, 3-H, J = 2.5 Hz), 5.10 (sep, 2H, SiH, J = 2.95 Hz), 4.19 (t, 4H, THF, J = 6.6 Hz), 2.67 (t, 4H, $S\mathit{CH_2}CH_2\mathit{CH_2}S$, J = 6.1 Hz), 1.64 (s, 18H, 6-^{t}Bu), 1.55 (qnt, 2H, $SCH_2\mathit{CH_2}CH_2S$, J = 6.1 Hz), 1.40 (m, 4H, THF), 1.30 (s, 18H, 4-^{t}Bu) and 0.39 (d, 12H, $SiMe_2$, J = 2.95 Hz); δ_C (C_6D_6) 165.1 (Ar-C1), 138.6 (Ar-C6), 137.5 (Ar-C4), 127.4 (Ar-C3), 125.1 (Ar-C5), 120.3 (Ar-C2), 71.3 (THF), 35.8 [4-$\mathit{C}(CH_3)_3$], 34.3 [6-$\mathit{C}(CH_3)_3$], 34.1 ($S\mathit{C}H_2CH_2\mathit{C}H_2S$), 31.9 [4-$C(\mathit{C}H_3)_3$], 29.9 [6-$C(\mathit{C}H_3)_3$], 25.3 (THF), 23.6 ($SCH_2\mathit{C}H_2CH_2S$) and 3.2 ($SiMe_2$).

[(etbmp)Lu{N(SiHMe$_2$)$_2$}(THF)] (1c). etbmpH$_2$ (0.418 g, 1 mmol) was added slowly to a solution of [Lu{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (0.715 g, 1 mmol) in *n*-hexane (20 mL) at r.t.. A colourless solution was obtained which was stirred for 4 days at the same temperature. Some white precipitates formed. All violates were removed under vacuum to afford a foam-like solid. After dissolving in 10 mL of *n*-pentane and filtration, the clear solution was concentrated to *ca.* 4 mL, kept at −30 °C to give colourless crystals (0.6 g, 72%) (Found: C, 49.41; H, 7.41; N, 1.59; S, 7.87. $C_{32}H_{54}LuNO_3S_2Si_2\cdot 0.5C_5H_{12}$ requires C, 49.80; H, 7.27; N, 1.68; S, 7.71%); δ_H (C_6D_6) 7.22 (d, 2H, 5-H, J = 2.1 Hz), 6.97 (d, 2H, 3-H, J = 2.1 Hz), 5.12 (sep, 2H, SiH, J = 3.0 Hz), 3.92 (s, br, 4H, THF), 2.52 (m, 2H, SCH_2CH_2S), 2.36 (m, 2H, SCH_2CH_2S), 2.15 (s, 6H, 4-Me), 1.69 (s, 18H, 6-^{t}Bu), 1.15 (br s, 4H, THF), 0.45 (d, 6H, $SiMe_2$, J = 3.0 Hz) and 0.41 (d, 6H, $SiMe_2$, J = 3.0 Hz); δ_C (C_6D_6) 168.0 (Ar-C1), 139.0 (Ar-C6), 132.4 (Ar-C3), 130.3 (Ar-C5), 125.2 (Ar-C4), 117.7 (Ar-C2), 71.7 (THF), 37.0 (SCH_2CH_2S), 35.4 [6-$\mathit{C}(CH_3)_3$], 30.0 [6-$C(\mathit{C}H_3)_3$], 25.1 (THF), 20.7 (4-Me) and 3.8 ($SiMe_2$).

[(ptbmp)Lu{N(SiHMe$_2$)$_2$}(THF)] (2c). The procedure was similar to that to prepare **1c**, using ptbmpH$_2$ (0.216 g, 0.5 mmol) and [Lu{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (0.357 g, 0.5 mmol). After filtration, the solution was concentrated *in vacuo* to dryness to afford a white powder in quantitative yield (Found: C, 47.77; H, 7.60; N, 1.96; S, 7.85; Lu, 21.60. $C_{33}H_{56}LuNO_3S_2Si_2$ requires C, 48.93; H, 6.97; N, 1.73; S, 7.82; Lu, 21.29%); δ_H (C_6D_6) 7.16 (d, 2H, 5-H, J = 1.5 Hz), 6.97 (d, 2H, 3-H, J = 1.5 Hz), 5.07 (sep, 2H, SiH, J = 3.0 Hz), 4.12 (br s, 4H, THF), 2.62 (t, 4H, $S\mathit{CH_2}CH_2\mathit{CH_2}S$, J = 6.1 Hz), 2.18 (s, 6H, 4-Me), 1.62 (s, 18H, 6-^{t}Bu), 1.46 (qnt, 2H, $SCH_2\mathit{CH_2}CH_2S$, J = 6.1 Hz), 1.34 (m, 4H, THF) and 0.43 (d, 12H, $SiMe_2$, J = 3.0 Hz); δ_C (C_6D_6) 165.8 (Ar-C1), 138.7 (Ar-C6), 131.3 (Ar-C3), 129.3 (Ar-C5), 125.0 (Ar-C4), 120.1 (Ar-C2), 71.9 (THF), 35.4 ($S\mathit{C}H_2CH_2\mathit{C}H_2S$), 34.3 [6-$\mathit{C}(CH_3)_3$], 29.9 [6-$C(\mathit{C}H_3)_3$], 25.2 (THF), 23.7 ($SCH_2\mathit{C}H_2CH_2S$), 20.7 (4-Me) and 3.3 ($SiMe_2$).

[(edtbp)Lu{N(SiHMe$_2$)$_2$}(THF)] (3c). The procedure was similar to that to prepare **2c**, using edtbpH$_2$ (0.251 g, 0.5 mmol) and [Lu{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (0.357 g, 0.5 mmol). A white powder was obtained in quantitative yield (Found: C, 51.07; H, 7.75; N, 1.93; S, 7.65. $C_{38}H_{66}LuNO_3S_2Si_2$ requires C, 51.85; H, 7.56; N, 1.59; S, 7.29%); δ_H (C_6D_6) 7.57 (d, 2H, 5-H, J = 2.5 Hz), 7.30 (d, 2H, 3-H, J = 2.5 Hz), 5.11 (sep, 2H, SiH, J = 3.0 Hz), 3.90 (br s, 4H, THF), 2.58 (br s, 2H, SCH_2CH_2S), 2.41 (br s, 2H, SCH_2CH_2S), 1.74 (s, 18H, 6-^{t}Bu), 1.27 (s, 18H, 4-^{t}Bu), 1.12 (br s, 4H, THF), 0.41 (d, 6H, $SiMe_2$, J = 3.0 Hz) and 0.40 (d, 6H, $SiMe_2$, J = 3.0 Hz); δ_C (C_6D_6) 167.9 (Ar-C1), 138.9 (Ar-C6), 138.6 (Ar-C4), 128.6 (Ar-C3), 126.4 (Ar-C5), 117.6 (Ar-C2), 71.7 (THF), 37.1 (SCH_2CH_2S), 35.8 [6-$\mathit{C}(CH_3)_3$], 34.3 [4-$\mathit{C}(CH_3)_3$], 31.9 [4-$C(\mathit{C}H_3)_3$], 30.0 [6-$C(\mathit{C}H_3)_3$], 25.1 (THF) and 3.7 ($SiMe_2$).

[(pdtbp)Lu{N(SiHMe$_2$)$_2$}(THF)] (4c). The procedure was similar to that to prepare **2c**, using pdtbpH$_2$ (0.258 g, 0.5 mmol) and [Lu{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (0.357 g, 0.5 mmol). A white powder was obtained in quantitative yield (Found: C, 50.98; H, 8.29; N, 1.69; S, 7.28, Lu, 19.49. $C_{39}H_{68}LuNO_3S_2Si_2$ requires C, 52.38; H, 7.66; N, 1.57; S, 7.17; Lu, 19.57%); δ_H (C_6D_6) 7.49 (d, 2H, 5-H, J = 2.5 Hz), 7.29 (d, 2H, 3-H, J = 2.5 Hz), 5.07 (sep, 2H, SiH, J = 3.0 Hz), 4.13 (br s, 4H, THF), 2.68 (t, 4H, $S\mathit{CH_2}CH_2\mathit{CH_2}S$, J = 6.1 Hz), 1.65 (s, 18H, 6-^{t}Bu), 1.54 (qnt, 2H, $SCH_2\mathit{CH_2}CH_2S$, J = 6.1 Hz), 1.34 (m, 4H, THF), 1.28 (s, 18H, 4-^{t}Bu) and 0.42 (d, 12H, $SiMe_2$, J = 3.0 Hz); δ_C (C_6D_6) 165.6 (Ar-C1), 138.7 (Ar-C6), 138.2 (Ar-C4), 127.4 (Ar-C3), 125.2 (Ar-C5), 119.9 (Ar-C2), 71.9 (THF), 35.7 [4-$\mathit{C}(CH_3)_3$], 34.4 [6-$\mathit{C}(CH_3)_3$], 34.3 ($S\mathit{C}H_2CH_2\mathit{C}H_2S$), 31.9 [4-$C(\mathit{C}H_3)_3$], 29.3 [6-$C(\mathit{C}H_3)_3$], 25.2 (THF), 23.2 ($SCH_2\mathit{C}H_2CH_2S$) and 3.3 ($SiMe_2$).

[(etbmp)Sc{N(SiHMe$_2$)$_2$}{LiN(SiHMe$_2$)$_2$ (THF)}] (5a). A solution of [Sc{N(SiHMe$_2$)$_2$}$_3${LiN(SiHMe$_2$)$_2$(THF)}] (**5**) (0.327 g, 0.5 mmol) in *n*-hexane (15 mL) was treated with etbmpH$_2$ (0.209 g, 0.5 mmol) at r.t.. The obtained suspension was stirred for 5–6 days at 50 °C. After filtration, the clear solution was concentrated to dryness to afford white powder, which was characterized by ^{1}H NMR to be a mixture of complexes **1a**, **5a** and a small amount of the lithium salt **5d**. Isolation of pure **5a** by recrystallization from *n*-hexane failed due to the contamination of complex **1a**. Complex **5a** was characterized by X-ray diffraction and ^{1}H NMR. δ_H (C_6D_6) 7.16 (d, 2H, 5-H, J = 1.8 Hz), 6.94 (d, 2H, 3-H, J = 1.8 Hz), 5.15 (sep, 4H, SiH, J = 3.0 Hz), 3.23 (t, 4H, THF, J = 6.2 Hz), 2.49 (d, 2H, SCH_2CH_2S, J = 10.3 Hz), 2.12 (d, 2H, SCH_2CH_2S, J = 10.3 Hz), 2.11 (s, 6H, 4-Me), 1.69 (s, 18H, 6-^{t}Bu), 1.13 (m, 4H, THF, *J* = 6.2 Hz), 0.52 (d, 12H, SiMe$_2$, *J* = 3.0 Hz) and 0.47 (d, 12H, SiMe$_2$, *J* = 3.0 Hz). Pure **5d** was crystallized from the mother liquor. δ_H (C_6D_6) 7.18 (d, 2H, 5-H, *J* = 2.1 Hz), 7.07 (d, 2H, 3-H, *J* = 2.1 Hz), 2.73 (d, 2H, SCH$_2$CH$_2$S, *J* = 10.1 Hz), 2.30 (d, 2H, SCH$_2$CH$_2$S, *J* = 10.1 Hz), 2.18 (s, 6H, 4-Me) and 1.45 (s, 18H, 6-^{t}Bu).

[(etbmp)Y(2,2,6,6-tetramethyl-3,5-heptanedionate)]$_2$ (6b). A solution of 2,2,6,6-tetramethyl-3,5-heptanedione (0.104 g, 0.564 mmol) in *n*-hexane (5 mL) was added dropwise to a suspension of **1b** (0.400 g, 0.564 mmol) in *n*-hexane (15 mL) at r.t. A clear solution was obtained, which turned into a white suspension after several minutes. The reaction mixture was stirred for 2 days at the same temperature. After filtration, the white residue was washed with *n*-hexane (5 mL × 2), and dried under vacuum to give a white powder (0.300 g, 77%) (Found: C, 60.99; H, 7.50; S, 9.43. $C_{70}H_{102}O_8S_4Y_2$ requires C, 61.03; H, 7.46; S, 9.31%); δ_H (C_6D_6, *ca.* 50 µL of THF) 7.18 (d, 2H, 5-H, *J* = 2.2 Hz), 7.07 (d, 2H, 3-H, *J* = 2.2 Hz), 5.98 (s, 1H, β-diketonato), 2.60 (s, 4H, SCH$_2$CH$_2$S), 2.20 (s, 6H, 4-Me), 1.61 (s, 18H, 6-^{t}Bu) and 1.17 (s, 18H, ^{t}Bu, β-diketonato); δ_H (d_8-THF) 6.89 (s, 2H, 5-H), 6.86 (s, 2H, 3-H), 5.77 (s, 1H, β-diketonato), 2.53 (s, 4H, SCH$_2$CH$_2$S), 2.10 (s, 6H, 4-Me), 1.38 (s, 18H, 6-^{t}Bu) and 1.11 (s, 18H, ^{t}Bu, β-diketonato); δ_C (C_6D_6, *ca.* 50 µL of THF) 201.7 (C=O), 167.0 (Ar-C1), 138.2 (Ar-C6), 132.2 (Ar-C3), 129.5 (Ar-C5), 124.2 (Ar-C4), 118.9 (Ar-C2), 92.5 (OC–*C*–CO), 41.0 [*C*(CH$_3$)$_3$], 36.6 (SCH$_2$CH$_2$S), 35.4 [*C*(CH$_3$)$_3$], 29.8 [6-C(*C*H$_3$)$_3$], 28.4 [C(*C*H$_3$)$_3$, β-diketonato] and 20.8 (4-CH$_3$); δ_C (d_8-THF) 200.3 (C=O), 168.2 (Ar-C1), 137.8 (Ar-C6), 132.5 (Ar-C3), 129.2 (Ar-C5), 123.2 (Ar-C4), 119.4 (Ar-C2), 92.3 (OC-*C*-CO), 41.5 [C(CH$_3$)$_3$], 37.0 (SCH$_2$CH$_2$S), 35.6 [*C*(CH$_3$)$_3$], 30.2 [6-C(*C*H$_3$)$_3$], 28.9 [C(*C*H$_3$)$_3$, β-diketonato] and 20.8 (4-CH$_3$).

[(pdtbp)Y(2,2,6,6-tetramethyl-3,5-heptanedionate)(THF)] (8a) and [(pdtbp)Y(2,2,6,6-tetramethyl-3,5-heptanedionate)]$_2$ (8b). A solution of yttrium silylamido complex **4b** (0.400 g, 0.495 mmol) in *n*-hexane (15 mL) was treated with a solution of 2,2,6,6-tetramethyl-3,5-heptanedione (0.091 g, 0.495 mmol) in *n*-hexane (5 mL). The colourless solution was stirred at r.t. for 2 d. After filtration, the clear solution was concentrated to dryness, and exposed to high vacuum for several hours. Toluene (5 mL) was added to dissolve the solid, and the solvent evaporated to dryness; the same procedure was repeated three times. Then *n*-hexane was added, after filtration, the isolated white solid was further washed with small amount of *n*-hexane twice, and dried *in vacuo* to be characterized as complex **8b** (Found: C, 63.98; H, 8.27; S, 8.38. $C_{84}H_{130}O_8S_4Y_2$ requires C, 64.17; H, 8.33; S, 8.16%); δ_H (C_6D_6) 7.41 (d, 2H, 5-H, *J* = 2.2 Hz), 7.19 (d, 2H, 5′-H, *J* = 2.2 Hz), 7.05 (d, 2H, 3-H, *J* = 2.2 Hz), 6.99 (d, 2H, 3′-H, *J* = 2.2 Hz), 5.95 (s, 2H, β-diketonato), 3.22 (m, 2H, S*CH$_2$*CH$_2$*CH$_2$*S), 3.11 (m, 2H, S*CH$_2$*CH$_2$*CH$_2$*S), 2.74 (m, 2H, S*CH$_2$*CH$_2$*CH$_2$*S), 2.60 (m, 2H, S*CH$_2$*CH$_2$*CH$_2$*S), 1.86 (m, 2H, SCH$_2$*CH$_2$*CH$_2$S), 1.75 (m, 2H, SCH$_2$*CH$_2$*CH$_2$S), 1.56 (s, 18H, ^{t}Bu), 1.42 (s, 18H, ^{t}Bu), 1.38 (s, 18H, ^{t}Bu), 1.35 (s, 18H, ^{t}Bu), 1.34 (s, 18H, ^{t}Bu) and 0.80 (s, 18H, ^{t}Bu); δ_H (C_6D_6, *ca.* 50 µL of THF) 7.58 (d, 2H, 5-H, *J* = 2.3 Hz), 7.50 (d, 2H, 3-H, *J* = 2.3 Hz), 5.89 (s, 1H, β-diketonato), 2.93 (t, 4H, S*CH$_2$*CH$_2$*CH$_2$*S, *J* = 6.2 Hz), 1.68 (qnt, 2H, SCH$_2$*CH$_2$*CH$_2$S, *J* = 6.2 Hz), 1.62 (s, 18H, 6-^{t}Bu), 1.36 (s, 18H, 4-^{t}Bu) and 1.10 (s, 18H, ^{t}Bu, β-diketonato); δ_H (d_8-THF) 7.21 (d, 2H, 5-H, *J* = 2.5 Hz), 7.07 (d, 2H, 3-H, *J* = 2.5 Hz), 5.85 (s, 1H, β-diketonato), 3.03 (t, 4H, SCH$_2$CH$_2$*CH$_2$*S, *J* = 5.8 Hz), 2.18 (qnt, 2H, SCH$_2$*CH$_2$*CH$_2$S, *J* = 5.8 Hz), 1.30 (s, 18H, 6-^{t}Bu), 1.23 (s, 18H, 4-^{t}Bu) and 1.07 (s, 18H, ^{t}Bu, β-diketonato); δ_C (C_6D_6) 201.3 (C=O), 199.6 (C=O), 191.4 (Ar, C–O), 165.0 (Ar, C–O), 154.6, 141.1, 137.3, 137.1, 137.0, (Ar, C–H overlapped by solvent signals), 125.7 (Ar, C–H), 125.3 (Ar, C–H), 123.6, 121.2 (Ar, C–H), 94.2 (OC–*C*–CO), 41.4 [*C*(CH$_3$)$_3$], 40.6 (S*C*H$_2$CH$_2$CH$_2$S), 40.5 [*C*(CH$_3$)$_3$], 36.5 (SCH$_2$CH$_2$*C*H$_2$S), 36.3 [*C*(CH$_3$)$_3$], 35.8 [*C*(CH$_3$)$_3$], 34.4 [*C*(CH$_3$)$_3$], 34.2 [*C*(CH$_3$)$_3$], 34.1 [C(*C*H$_3$)$_3$], 32.0 [C(*C*H$_3$)$_3$], 31.8 [C(*C*H$_3$)$_3$], 30.7 [C(*C*H$_3$)$_3$], 29.4 [C(*C*H$_3$)$_3$], 28.2 [C(*C*H$_3$)$_3$] and 26.5 (SCH$_2$*C*H$_2$CH$_2$S); δ_C (C_6D_6, *ca.* 50 µL of THF) 201.2 (C=O), 164.3 (Ar-C1), 137.6 (Ar-C6), 137.5 (Ar-C4), 129.2 (Ar-C5), 125.4 (Ar-C3), 121.0 (Ar-C2), 92.5 (OC–*C*–CO), 40.9 [*C*(CH$_3$)$_3$], 36.0 (S*C*H$_2$CH$_2$*C*H$_2$S), 35.8 [*C*(CH$_3$)$_3$], 34.3 [*C*(CH$_3$)$_3$], 32.1 [4-C(*C*H$_3$)$_3$], 30.0 [6-C(*C*H$_3$)$_3$], 28.4 [C(*C*H$_3$)$_3$, β-diketonato] and 24.9 (SCH$_2$*C*H$_2$CH$_2$S). The mother liquor was concentrated and treated with a small amount of THF (0.5 mL). Upon cooling to −30 °C, monomeric complex **8a** was isolated (Found C, 63.10; H, 8.64; S, 7.26. $C_{46}H_{73}O_5S_2Y$ requires C, 64.31; H, 8.56; S, 7.46%); δ_H (C_6D_6) 7.58 (d, 2H, 5-H, *J* = 2.5 Hz), 7.50 (d, 2H, 3-H, *J* = 2.5 Hz), 5.89 (s, 1H, β-diketonato), 4.02 (t, 4H, THF, *J* = 6.5 Hz), 2.93 (t, 4H, S*CH$_2$*CH$_2$*CH$_2$*S, *J* = 6.0 Hz), 1.63 (s, 18H, ^{t}Bu), (CH$_2$ overlapped by 1.63 signal), 1.37 (s, 18H, ^{t}Bu), 1.29 (m, 4H, THF) and 1.10 (s, 18H, ^{t}Bu, β-diketonato).

[(etbmp)Lu(2,2,6,6-tetramethyl-3,5-heptanedionate)]$_2$ (6c). A solution of 2,2,6,6-tetramethyl-3,5-heptanedione (0.089 g, 0.48 mmol) in *n*-hexane (5 mL) was added slowly to a suspension of **1c** (0.400 g, 0.48 mmol) in *n*-hexane (15 mL) at r.t. The colourless solution was stirred overnight, some white precipitates gradually formed. After filtration, the white residue was washed with *n*-hexane twice, dried under vacuum to afford a white powder (80 mg, 21%) (Found: C, 54.01; H, 6.58; S, 8.22. $C_{70}H_{102}O_8S_4Lu_2$ requires C, 54.26; H, 6.63; S, 8.28%); δ_H (C_6D_6, *ca.* 50 µL of THF) 7.17 (d, 2H, 5-H, *J* = 2.2 Hz), 7.07 (d, 2H, 3-H, *J* = 2.2 Hz), 5.95 (s, 1H, β-diketonato), 2.62 (br s, 4H, SCH$_2$CH$_2$S), 2.20 (s, 6H, 4-Me), 1.60 (s, 18H, 6-^{t}Bu) and 1.15 (s, 18H, ^{t}Bu, β-diketonato); δ_H (d_8-THF) 6.87 (s, 2H, 5-H), 6.82 (s, 2H, 3-H), 5.77 (s, 1H, β-diketonato), 2.64 (br s, 4H, SCH$_2$CH$_2$S), 2.07 (s, 6H, 4-Me), 1.29 (s, 18H, 6-^{t}Bu) and 1.03 (s, 18H, ^{t}Bu, β-diketonato); δ_C (C_6D_6, *ca.* 50 µL of THF) 202.0 (C=O), 167.6 (Ar-C1), 138.8 (Ar-C6), 132.3 (Ar-C3), 129.4 (Ar-C5), 124.2 (Ar-C4), 118.5 (Ar-C2), 92.7 (OC–*C*–CO), 41.1 [*C*(CH$_3$)$_3$], 36.7 (SCH$_2$CH$_2$S), 35.4 [*C*(CH$_3$)$_3$], 29.8 [C(*C*H$_3$)$_3$], 28.4 [C(*C*H$_3$)$_3$, β-diketonato] and 20.8 (4-CH$_3$); δ_C (d_8-THF) 202.0 (C=O), 168.1 (Ar-C1), 138.8 (Ar-C6), 132.6 (Ar-C3), 129.3 (Ar-C5), 124.1 (Ar-C4), 118.9 (Ar-C2), 93.0 (OC–*C*–CO), 41.5 [*C*(CH$_3$)$_3$], 37.1 (SCH$_2$CH$_2$S), 35.6 [6-*C*(CH$_3$)$_3$], 30.0 [6-C(*C*H$_3$)$_3$], 28.7 [C(*C*H$_3$)$_3$, β-diketonato] and 20.8 (4-CH$_3$).

[(edtbp)Lu(2,2,6,6-tetramethyl-3,5-heptanedionate)]$_2$ (7c). To a solution of complex **3c** (0.357 g, 0.5 mmol) in *n*-hexane (10 mL) was added dropwise a solution of 2,2,6,6-tetramethyl-3,5-heptanedione (0.092 g, 0.5 mmol) in *n*-hexane (3 mL) at room temperature. A colourless solution was obtained, which was stirred for 2 d. After filtration to remove trace amount of solid, the solution was concentrated to dryness and further dried for several hours. The oily solid was dissolved in a small amount of toluene and evaporated to dryness; the same procedure was repeated twice. *n*-Hexane was added and after filtration, the solid residue was washed with *n*-hexane twice and dried under vacuum to afford a white powder (90 mg, 21%) (Found: C, 57.01; H, 7.36; S, 7.63. $C_{82}H_{126}O_8S_4Lu_2$ requires C, 57.32; H, 7.39; S, 7.47%); δ_H (C_6D_6) 7.41 (d, 4H, 5-H, *J* = 2.3 Hz), 7.32 (br s, 2H, 3-H), 6.95 (br s, 2 H, 3′-H), 5.53 (br s, 2H, β-diketonato), 3.05 (br m, 2H, SCH$_2$CH$_2$S), 2.72 (br m, 4H, SCH$_2$CH$_2$S), 2.54 (br m, 2H, SCH$_2$CH$_2$S), 2.10 (s, 18H, ^{t}Bu), 1.29 (s, 18H, ^{t}Bu), 1.25 (s, 18H, ^{t}Bu), 1.22 (s, 36H, ^{t}Bu) and 0.81 (s, 18H, ^{t}Bu, β-diketonato); δ_H (C_6D_6, *ca.* 50 µL of THF) 7.49 (d, 2H, 5-H, *J* = 2.5 Hz), 7.38 (d, 2H, 3-H, *J* = 2.5 Hz), 5.95 (s, 1H, β-diketonato), 2.65 (s, br, 4H, SCH$_2$CH$_2$S), 1.64 (s, 18H, 6-^{t}Bu), 1.32 (s, 18H, 4-^{t}Bu) and 1.14 (s, 18H, ^{t}Bu, β-diketonato); δ_C (C_6D_6, *ca.* 50 µL of THF) 202.0 (C=O), 167.4 (Ar-C1), 138.3 (Ar-C6), 137.9 (Ar-C3), 128.6 (Ar-C5), 125.4 (Ar-C4), 118.5 (Ar-C2), 92.7 (OC–*C*–CO), 41.0 [*C*(CH$_3$)$_3$], 36.9 (SCH$_2$CH$_2$S), 35.8 [*C*(CH$_3$)$_3$], 34.3 [*C*(CH$_3$)$_3$], 32.0 [4-C(*C*H$_3$)$_3$], 29.9 [6-C(*C*H$_3$)$_3$] and 28.4 [β-diketonato, C(*C*H$_3$)$_3$].

[(etbmp)Y(OCPh$_3$)(THF)] (9). To a solution of **1b** (200 mg, 0.28 mmol) in toluene (10 mL) was added solid trityl alcohol (73 mg, 0.28 mmol). The colourless solution was stirred at r.t. for two days. After filtration, the clear solution was concentrated to dryness to afford a white powder, which was recrystallized with toluene/hexane at 0 °C to give colourless crystals (150 mg, 61%) (Found: C, 67.90; H, 7.50; S, 8.07. $C_{47}H_{55}O_4S_2Y\cdot 0.5C_6H_{14}$ requires C, 68.24; H, 7.10; S, 7.28%); δ_H (C_6D_6) 7.64 (d, 6H, OCPh$_3$, J = 7.0 Hz), 7.22 (d, 2H, 5-H, J = 2.0 Hz), (6H, OCPh$_3$, overlapped by solvent signal), 7.054 (t, 3H, OCPh$_3$, J = 7.4 Hz), 6.94 (d, 2H, 3-H, J = 2.0 Hz), 3.60 (t, 4H, THF, J = 6.6 Hz), 2.48 (br s, 4H, SCH$_2$CH$_2$S), 2.17 (s, 6H, Me), 1.64 (s, 18H, ^{t}Bu) and 1.03 (m, 4H, THF, J = 6.6 Hz); δ_C (C_6D_6) 167.38, 167.35, 151.9, 138.5, 132.4, 130.2, 128.6, 127.6, 126.2, 124.9, 117.9, 70.6 (THF), 36.7 (SCH$_2$CH$_2$S), 35.4 [C(CH$_3$)$_3$], 31.9 [4-C(CH$_3$)$_3$], 29.7 [6-C(CH$_3$)$_3$], 25.1 (THF) and 20.8 (4-Me).

Typical polymerization procedure

L-Lactide (Aldrich) was sublimated at 50 °C under vacuum and then recrystallized with dry toluene prior to use. Spectroscopic analysis of polymers was performed in CDCl$_3$. Molecular weights and polydispersities were determined by size-exclusion chromatography (SEC) in THF at a flow rate of 2 mL min^{-1} utilizing a Waters pump type 510 HPLC, a Waters-410-RI detector (refractive index) and 4–5 mm PSS columns (filled with SDV gel) with pore sizes of 10^3, 10^4, 10^5 and 10^6 Å. Calibration standards were commercially available narrowly distributed linear polystyrene samples which cover a broad range of molar masses ($10^4 < M < 2 \times 10^6$ g mol^{-1}).

Room-temperature polymerization: in glove-box, L-lactide (0.125 g, 0.87 mmol, 300 equivalents per metal) was added to a small glass bottle and dissolved with THF (0.5 mL), then the freshly prepared catalyst solution in THF (0.5 mL, 0.0029 mmol metal) was combined and the mixture stirred. Monomer conversion was monitored by integration of monomer *vs.* polymer methine resonances in ^{1}H NMR (CDCl$_3$) by withdrawing some aliquots quenched with *n*-hexane and removal of the volatiles. The bulk polymer solution was quenched by adding excess amount of *n*-hexane with drops water after indicated time, the collected precipitates were further dissolved with chloroform and precipitated into methanol. The obtained polymer was dried under vacuum at 60 °C for 12 h for SEC analysis. In cases where isopropanol was used, the catalyst solution in toluene was first treated with isopropanol in toluene, before adding L-lactide. Otherwise the procedures were the same. Polymerization runs above room temperature were conducted in Schlenk flasks.

X-Ray diffraction measurements

X-Ray diffraction measurements were performed at room temperature on an Enraf Nonius diffractometer with Mo-Kα radiation using ω-scans. Crystal parameters and results of the structure refinements are given in Table 1. Data reduction and absorption corrections (semi-empirical using ψ-scans) were performed using the WinGX system of programs.[39] All structures were solved by direct methods (SHELXS-86)[40] and refined (SHELXS-97)[41] against all F^2 data. In **4b** and **5a**, the *tert*-butyl groups are disordered and were refined with split positions. Split positions were also introduced for the carbon atoms of a THF ligand in **5a** to account for disorder. Hydrogen atoms were included into calculated positions, but torsional refinement was carried out for the hydrogen atoms of the methyl groups. For all three compounds, the hydrogen atoms attached to the Si atoms as well as to the phenyl rings were refined in their positions with isotropic displacement parameters. The hydrogen atoms of the CH$_2$CH$_2$CH$_2$ unit in **4b** as well as of the CH$_2$CH$_2$ unit in **5a** were also refined. Molecular structures were generated using ORTEP.[42]

CCDC reference numbers 220241, 220242 and 220243 for **2a**, **4b** and **5a**.

See http://www.rsc.org/suppdata/dt/b3/b311604b/ for crystallographic data in CIF or other electronic format.

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