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Rare Earth Complexes of Phenoxy-Thioether Ligands: Synthesis and Reactivity in the Ring Opening Polymerization of Cyclic Esters.

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Abstract

The potential of the phenoxy-thioether moieties as ancillary ligands in the coordination chemistry of group 3 metals was described. The amine elimination reactions between yttrium and scandium amido precursors {M $[N(SiHMe_2)_2]_3$ $(THF)_n$ } with the proligands {4,6-tBu_2-OC_6H_2-2-CH_2S(2-R-C_6H_4)}H [R = H (**L_1-H**), CH_3 (**L_2-H**), Br (**L_3-H**), CF_3 (**L_4-H**)] bearing different substituents at the *ortho* position of the thiophenol aryl ring, were studied. The outcome of aminolysis reactions gave different results depending on the structure of the proligand and the reaction conditions. Heteroleptic scandium and yttrium amido complexes with general formula {$(L)_2M$ $[N(SiHMe_2)_2]$ $(THF)_n$} were prevailingly obtained from phenoxy-thioether proligands **L_1-H** and **L_4-H**. On the contrary, homoleptic yttrium complexes bearing three phenoxy-thioether ligands were favored with **L_2-H** and **L_3-H**. The activities of all the synthesized complexes toward the ring-opening polymerization of ε-caprolactone and L- and *rac*-lactide were investigated, also in combination with an alcohol as external chain transfer. Polyesters with controlled molecular parameters (M_n, end groups) and low polydispersities were obtained. The monoinsertion adduct, produced by the reaction of {$(\mathbf{L_1})_2ScN(SiHMe_2)_2$} and 1 equiv of ε-caprolactone, was isolated proving that a coordination-insertion mechanism of ring-opening polymerization was operative. In the polymerization of *rac*-lactide, yttrium complexes exerted high degree of stereocontrol producing heterotactic polylactide (P_r up to 0.91).

Introduction

Aliphatic polyesters derived from renewable resources have recently attracted considerable attention as biocompatible and biodegradable alternatives to conventional oil-based polymers.[1-4] Among them, poly(ε-caprolactone) (PCL) and poly(lactide) (PLA) are thermoplastic polymers that efficiently combine the film-barrier properties of polyesters with the mechanical performance of polyolefins and thus they have been successfully employed in biomedical and pharmaceutical applications such as controlled drug delivery, medical implants and scaffolds for tissue engineering.[5-7] More recently, the ability to obtain polyesters with better defined microstructures and tunable chemical and physical properties broadened the range of their possible applications to different industrial areas such as packaging and fibers.[8]

Ring-opening polymerization (ROP) of cyclic esters by single-site metal-based catalysts is the most efficient synthetic approach to obtain polymers with controlled molecular weight, narrow molecular weight distribution and desired tacticity.[9, 10] Among the large variety of metal complexes investigated as initiators, group 3 metal complexes have been shown to be particularly interesting because of their very high activity, low toxicity and good control.[11]

Homoleptic alkoxides and aryloxides of group 3 and lanthanide metals are very active initiators for the ring-opening polymerization of lactones and lactides but they are frequently rather difficult to characterize and poorly soluble, showing, in some cases, low control of the polymerization reactions.[12-14] These polymerizations have some living character, but large molecular weight distributions of polymers are obtained as a consequence of frequent transesterification reactions. To overcome these limitations heteroleptic complexes of the type [L_nMX], where L is an ancillary ligand and X is an initiating group have been developed. Sterically demanding ligands added to metal centre generally prevent the coordination of the growing chains to the metal and, therefore, reduce inter and intramolecular transesterification reactions allowing a more efficient control on the molecular weights of the polymeric products.[15-32]

Recently, several group 3 metal complexes bearing sterically encumbered ligands have been synthesized and studied for the controlled ROP of ε-CL and lactide.[33-36] They exhibit high polymerization rates and some of them are able to exert tacticity control.[37-42]Among these, group 3 metal complexes with phenoxy-based ligands represent the most abundant examples. Due to the hard Lewis acidic nature of the group 3 metal complexes, phenoxide donors tend to be matched with relatively hard first-row nitrogen-based donors.[43-48]

In recent studies new coordination environments have been explored, and there is a growing evidence that softer second-row donors may offer beneficial stabilization of highly reactive metal centres.[49,50]

Okuda et al. reported that rare earth metal complexes bearing 1,ω-dithiaalkanediyl-bridged bis(phenolato) ligands efficiently initiate the ring-opening polymerization of lactides.[51] By variation of the ligand architecture, moderate to high heteroselectivity for the ROP of *rac*-LA have been obtained.[36,52]

We recently reported the synthesis of a new class of bidentate phenoxy-thioether ligands for the synthesis of group 4 metal[53] and aluminum complexes.[54] Aiming at extending the use of these ligands to the coordination chemistry of group 3 metals, in this paper we report the synthesis and coordination modes of scandium and yttrium amide complexes whit phenoxy-thioether ligands. The

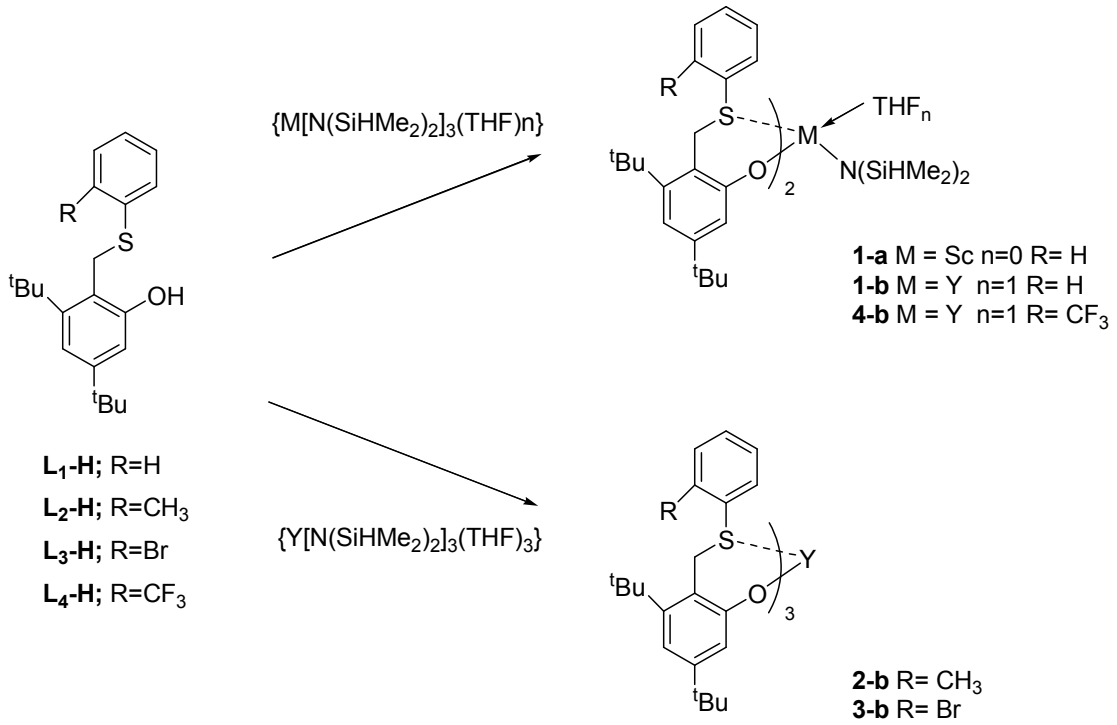
obtained complexes, characterized by NMR analysis, were tested as initiators in the ring-opening polymerization of the cyclic esters, such as □-caprolactone and lactides (L- and *rac*).

Results and Discussion

Synthesis and characterization of the metal complexes.

Since group 3 metals are highly Lewis acidic, their complexes are prone to ligation by coordinating solvents or to the formation of dimeric structures. As a consequence of this tendency to aggregate, low energy pathways for ligands redistribution around the metal centre are frequently observed.[55] Thus the design of an opportune coordinative environment by varying the steric and electronic properties of the ancillary ligands is necessary to form heteroleptic stable complexes. Significant differences are often observed in the coordination chemistry at the metal centre as consequence of minimal variations of the ligand structure.

To explore the potential of the phenoxy-thioether moieties as ancillary ligands in the coordination chemistry of group 3 metals, the amine elimination reactions between the pro-ligands **L_{1-4}-H** (see scheme 1) and the silylamido metal precursors {M $[N(SiHMe_2)_2]_3$ $(THF)_n$ } (M = Sc, n = 2; M = Y, n = 3) were studied.



Scheme 1. Structures of $\mathbf{L_{1\text{-}4}–H}$ protio ligands and synthesis of the group 3 metal complexes.

Interestingly, the outcome of aminolysis reactions gave different results depending on the structure of the proligand.

Scandium complex 1-a: synthesis and characterization.

Heteroleptic bis(phenoxythioether) scandium-amido complex **1-a** was prepared by direct aminolysis of the scandium silylamide precursor {Sc $[N(SiHMe_2)_2]_3(THF)_2$ } with two equivalents of the proligand $\mathbf{L_1\text{-}H}$ (Scheme 1) at room temperature, equally in benzene or in hexane solution. Removal of the volatiles under reduced pressure yielded a white solid that was washed with a minimum amount of cold hexane to obtain the product in high yield (>90%). It showed a very high stability in aromatic and aliphatic solvent solution at room temperature and, as a solid compound, it could be stored at room temperature for prolonged periods without any decomposition.

Complex **1-a** was characterized by multinuclear NMR spectroscopy and elemental analysis, which indicated a pentacoordinate metal centre bearing two phenolato ligands and one bis(dimethylsilyl)amido group.

At room temperature, the ^{1}H NMR spectrum of **1-a** in C_6D_6 showed a single set of signals for the two coordinated ligands, a single doublet for methyl protons and one septet for the proton of the $SiHMe_2$ amido fragment. The chemical shift for the Si-*H* (δ 4.73 ppm) proton, shifted upfield with respect to the chemical shift in the {Sc $[N(SiHMe_2)_2]_3(THF)_2$} (δ 5.11 ppm), suggested the presence of a β(Si-H) agostic interaction with the scandium centre. The coordination of the sulphur neutral donor of the chelating ligand to the metal centre was suggested by the downfield shift of the S*CH*$_2$ protons (4.23 ppm) observed in complex **1-a** compared to the corresponding signal of the free ligand (see Table 1). The S*CH*$_2$ protons appear as a single sharp resonance indicating a symmetry higher than that conceivable for a pentacoordinate complex with such a coordination environment,[40] suggesting a fast fluxional process on the NMR timescale (e.g. intramolecular rearrangements and/or monomer/dimer equilibration).

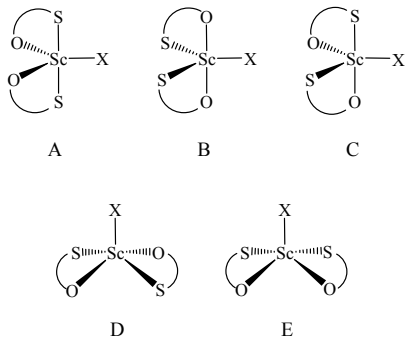
To assess the presence of symmetric dimeric structures in solution, complex **1-a** was analyzed by 2D DOSY-^{1}H NMR measurements (Diffusion Ordered SpectroscopY).[56] This NMR technique provides information of the translational diffusion coefficient of the molecular species in solution and it has been successfully used for characterizing various organometallic systems[57-59] and supramolecular structures in solution.[60, 61]

The PGSE (Pulsed field Gradient Spin-Echo) method assesses translational motion of the analyte in solution through determination of the diffusion coefficient *D*, a quantity inversely related to its effective hydrodynamic volume. The hydrodynamic radium, determined for **1-a** from the 2D DOSY experiment (r_H = 7.16 Å), was compared with the molecular radium (r'= 6.87 Å) estimated from DFT optimized structure by measuring the lengths between centers of distant hydrogen atoms on the molecular periphery. The experimental values of *D* and r_H and the calculated ones for complex **1-a** are listed in Table S1 of the Supporting Information. A good agreement was observed, supporting the hypothesis of the monomeric nature of **1-a** in solution. This result suggests that the high symmetry observed in solution at room temperature for complex **1-a** is related to intramolecular rearrangements.

Despite several attempts, we could not obtain single crystals of complex **1-a** suitable for an X-ray structure analysis. To propose reasonable structures and explain the fluxional behavior suggested for this complex by the NMR analysis, DFT calculations were performed.

For a monomeric pentacoordinate complex, such as scandium complex **1-a** binding two non-symmetrical bidentate ligands and one monodentate ligand, different isomers are possible (Scheme 2). In the optimized structure of diastereoisomer A, the Sc atom adopts a distorted trigonal-

bipyramidal coordination geometry in which the axial positions are occupied by two sulphur atoms and the equatorial positions are occupied by two oxygen atoms and the amido ligand. The Sc-O (1.94 Å, 1.95 Å) and Sc-S (2.77 Å, 2.79 Å) bond lengths can be favorably compared with the corresponding distances in related Sc complexes featuring OSSO bisphenolato ligands.[51] This indicates that the quantum chemical methods used faithfully model the overall geometry for this class of complexes. Any attempt to obtain minimum energy structures for diastereoisomers B and D led to diastereoisomer A. Attempts to obtain minimum energy structure for diastereoisomer C led to a highly distorted tetrahedral species in which one OS ligand employs only the anionic oxygen donor to bind the metal centre. The formation of this species is thermodynamically unfavored due to the high internal and free energies (these values, in gas phase and benzene, are reported in Table S2). Minimum energy structure for diastereoisomer E was successfully located by DFT calculations, the free-energy difference with respect to diasteroisomer A is 4.2 kcalmol^{-1} in favor of isomer A. The small energy difference between A and E suggests that these isomers can be simultaneously present in solution.



Scheme 2. Possible stereoisomers for Sc complex **1-a**. For the chiral structures A–C, only one of the two enantiomers is shown.

^{1}H NMR monitoring from 20 °C to -80 °C for **1-a**, in methylene dichloride-d_2 solution, was performed to get more information on this issue (see figures S1 and S2 in the Supporting Information). Decreasing the temperature of the sample below room temperature, the spectra broaden and become more complex, effectively indicating the existence of a fluxional process. Despite the complexity of some areas of the spectra, valuable information was obtained from a careful analysis of these results. At 193 K the presence of two patterns of signals with different intensities indicated the coexistence of two species at a ratio 4:1. For each species, two signals for the methyl protons of the amido group, two signals for the methyl protons of the tert-butyl groups

and an AB pattern for the protons of the bridging methylene were observed. The described patterns are consistent with the symmetries predictable for stereoisomers A and E in scheme 2, (C_2 and C_S symmetry, respectively). Taking into account the results of DFT calculations we propose the existence of an equilibrium between these isomers. The interconversion between these species should occur by the moving of the sulphur donors from axial to equatorial positions.

Yttrium complexes: synthesis and characterization.

Treatment of proligands **L_{1-4}-H** with the yttrium precursor {Y $[N(SiHMe_2)_2]_3(THF)_3$} resulted in different products depending on the structure of the proligand and on the reaction conditions. In all cases, an indication that the proligands behave as bidentate ligands, i. e. the neutral sulphur atoms are coordinated to the metal centre, comes from the downfield shift of the signals of the protons of the methylene bridge with respect to those of the corresponding free ligands; this is consistent with a decrease in electron density due to coordination at the metal centre. These values are reported in Table 1.

Table 1. Chemical shift values for the methylene group SCH_2 in the free ligands and in the synthesized yttrium complexes.

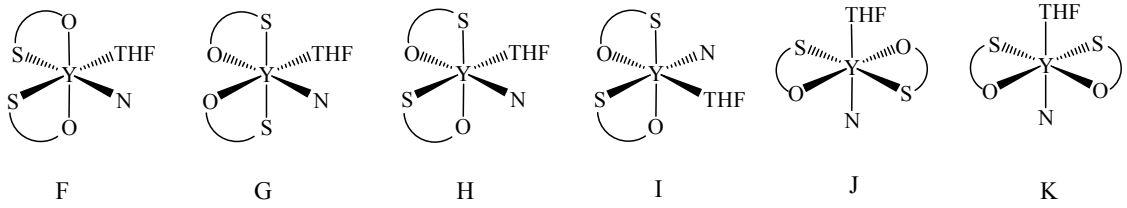
	L^n-H	$(L^n)_2YNR_2$	$(L^n)_3Y$
n = 1	3.76	4.11	-
n = 2	3.73	-	4.05
n = 3	3.77	-	4.09
n = 4	3.72	4.17; 4.36	-

Spectroscopic studies and elemental analyses for yttrium complex **1-b** were coherent with a structure within the metal centre was coordinated to two phenolato ligands, one bis(dimethylsilyl)amido group and one THF molecule. The interaction between the coordinated THF and the metal centre resulted quite strong: in fact solvent dissociation was not achieved, even after evaporation *in vacuo* for prolonged times.

The ^{1}H NMR spectrum of **1-b** in C_6D_6 recorded at room temperature showed a single set of signals for the two coordinated ligands, equivalent on the NMR timescale, as well as one doublet for methyl protons and one septet for the proton of the $SiHMe_2$ amido fragment. The resonances relative to the protons of the coordinated THF molecule at 3.63 ppm and 1.28 ppm resulted shifted downfield with respect to the free THF. The presence of a weak β(Si-H) agostic interaction is

evidenced by an upfield shift of the Si-*H* proton (δ 4.73 ppm) compared to the chemical shift (δ 5.00 ppm) of the yttrium precursor.[62, 63] The peak of the SCH_2 protons was broad. Raising the temperature to 50 °C, all peaks resulted sharp, highlighting the existence of a fluxional behavior also for complex **1-b**. Decreasing the temperature of the sample below room temperature, resulted in complex spectra which could not provide further information.

For **1-b** different stereoisomers are plausible (Scheme 3). DFT calculations were performed to propose reasonable structures.



Scheme 3. Representative stereoisomers for the yttrium complex **1-b**.

In the optimized structures of the diasteroisomer F, the yttrium atom binds two bidentate OS ligands, one amido group and one coordinated THF molecule adopting a distorted octahedral geometry. The THF is located *cis* to amido ligand and *trans* to one of the sulphur atoms; the two oxygen donors of the ligand are arranged *trans* to each other (O-Y-O 151.8°). The Y–N and Y-O bond lengths are comparable to the average bond lengths in similar six-coordinated Y complexes with OSSO bisphenolato ligands.[52] The two Y–S bond lengths differ from each other by about 0.22 Å, with an elongated Y–S bond *trans* to the amido group. This can be ascribed to a stronger electron-donating ability of the amido group that weakens the opposite Y–S bond.

Minimum energy structures for the diastereoisomers G-K were successfully located by DFT calculations as well. The corresponding internal and free energies in gas phase and benzene are reported in Table S2. Diasteroisomers F and G have very similar energies and can be considered as the most stable species. Diasteroisomers H and I show slightly higher energies with respect to F. The diasteroisomers J and K are thermodynamically less favored.

It is reasonable to presume that diasteroisomers F and G are present in solution. The number of possible isomers could be even higher as the reversible THF-dissociation cannot be ruled out. This would lead to a five coordinated species that can adopt different configurations. All these species

could rapidly rearrange in solution at room temperature leading to the observation of an unique species with an average high symmetry.

This is in line with the complicated scenario showed by VT NMR analysis and with numerous literature examples describing fluxional phenomena for rare earth metal complexes,[64, 65] even more frequently observed when a coordinating solvent is included in the coordination sphere.

The reaction between yttrium amide and the proligand **L_2-H** produced a mixture of three products: the homoleptic tris-phenolate complex **2-b** (Scheme 1) and two heteroleptic amide yttrium stereoisomers bearing two phenoxy-based ligands, an amide group and a THF molecule. The composition of the mixture depends on the reaction conditions, but in all cases the homoleptic complex was achieved as the prevailing product with a yield ranging from 60%, when the reaction was performed in THF, to 67% when hexane or benzene was used as reaction solvent. The mixture composition did not change increasing the temperature until 70 °C or recording the NMR spectrum in more coordinating solvents such as THF-d_8. Several attempts to separate the components of the mixture allowed to isolate exclusively the homoleptic complex **2-b** as pure compound.

Likewise, the reaction between two equivalents of the **L_3-H** proligand and the amide yttrium precursor, performed in hexane or in THF, furnished the homoleptic tris-phenolate complex **3-b** as a single product (Scheme 1).

Reasonably, the monoamido complexes first formed, gradually react with the residual proligands furnishing the homoleptic products. This behavior could be possibly attributed to the instability of the low coordinated monoamido complexes, already observed for Schiff base group 3 metal complexes.[45]

Next, the homoleptic yttrium complexes **2-b** and **3-b** were purposely prepared by reaction of the yttrium precursor with three equivalents of the opportune proligand in benzene solution at room temperature, and characterized by NMR spectroscopy and elemental analysis.

The ^{1}H NMR spectra of the homoleptic complexes **2-b** and **3-b** suggest a high symmetry for these species. The coordinated ligands appear equivalent giving rise to a unique pattern of resonances consistent with an octahedral C_3-symmetric structure resulting from the κ^2-O,S coordination of the three ligands at the metal centre.

Different results were obtained by using proligand **L_4-H**. In this case an asymmetric heteroleptic amide yttrium complex was achieved as the prevailing product (92%). The component present in minor percentage (about 8%) was a symmetric homoleptic species. The composition of the mixture

did not change after treatment at higher temperature (50 °C). For complex **4-b** β(Si-H) agostic interaction with the yttrium centre was not observed.

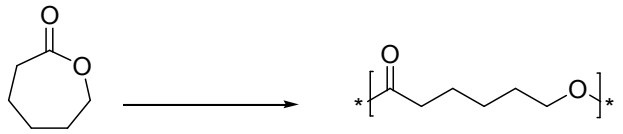
The behavior of these four phenoxy-thioether proligands in the coordination chemistry of yttrium complexes was tentatively rationalized as follows. As monoanionic bidentate ligands they tend to saturate the electronic and coordinative requests of the metal by forming homoleptic yttrium complexes. In the case of complex **1-b** the β(Si-H) agostic interaction would stabilize the heteroleptic monoamido complex hampering the chelation of a third ligand. Similarly, for complex **4-b** a Y-F interaction[66] would led to the same result, in this latter case the size of the CF_3 substituents could reasonably play a role as well.

Unfortunately, several attempts to grow single crystals suitable for X-ray analysis were unsuccessful, due to the extreme solubility of the compounds even in non-polar solvents.

Ring-opening polymerization of ε- caprolactone.

The reactivity of new bis (phenoxy-thioether) scandium and yttrium amide complexes (**1-a**, **1-b** and **4-b**) in the ring-opening polymerization of ε-CL was studied (scheme 4). Polymerization screenings were performed, under a nitrogen atmosphere, in a toluene or THF solution of ε-CL and the proper metal complex. The polymers, precipitated from the reaction solution by addition of hexane, were analyzed by NMR and gel permeation chromatography (GPC).

The main results of the polymerization studies are summarized in Table 2.



Scheme 4. Ring-opening polymerization of ε-caprolactone

The scandium complex **1-a** revealed to be an efficient initiator for the ROP of □-CL showing a strong dependence of the reactivity on the reaction conditions such as temperature and solvent. At high temperature (70°C) **1-a** allowed a quantitative conversion of 500 equivalents of monomer in about 5 mins (run 1, Table 2) whereas one hour was required when the polymerization was performed at 25 °C (run 2, Table 2).

The yttrium complex **1-b** resulted a more active initiator for the polymerization of ε-CL than the related scandium complex **1-a** (cf runs 2 and 3, Table 2). The monomer was polymerized rapidly and quantitatively at 25 °C in toluene in 30 minutes. This is consistent with literature data that report the complexes of larger/bigger rare earth metals normally show higher activities.[51, 67-69] This behavior may be due to the increase in ionic radii from Sc → Y and to the consequent less steric crowding created by the two stationary ligands around the active metal centre, which would favour advantage the coordination of the incoming ε-caprolactone monomer, a necessary step required prior to ring-opening.

Lower catalytic activities were observed when the polymerization runs were performed by using THF as the solvent (runs 4 and 5, Table 2). In this case after 1 hour a conversion of 30 % was observed and the quantitative consume of 500 equivalents of monomer was achieved only after 4h. This decrease of activity can probably be accounted for the competing role of THF versus the monomer in the coordination to the oxophilic metal centre, thus ultimately resulting in a slower propagation process. This solvent effect has been observed for several initiators although an opposite effect was reported for the dithiaalkanediyl-bridged bis(phenolate)[70] and the alkoxy-amino bridged bis(phenolate) rare-earth metal amido systems.[71]

The GPC analyses of the polymers obtained by both complexes **1-a** and **1-b** showed monomodal distributions of the molecular weights and polydispersity indexes (M_w/M_n) moderately narrow ranging from 1.31 to 2.08. The number-average molecular weights (M_{nGPC}) increased monotonously with the monomer/initiator ratio and the monomer conversion (see Figure S3 of Supporting Information) but were systematically higher than those calculated on the assumption that a single PCL chain is produced per metal centre. These are among the highest molecular weights observed for rare-earth metal ε-caprolactone polymerization.[72-75]

These observations suggest that only a fraction of the metal complexes was involved in the polymerization reaction, most likely as a result of an inefficient initiation by the poor nucleophilic amide group.[76] In fact, it is commonly observed that amido initiators such as -$N(SiMe_3)_2$, and -$N(SiHMe_2)_2$ are less efficient initiating groups for the ROP of cyclic esters at room temperature than alkoxide derivatives. Thelateer are expected to be better initiators due to reduced steric hindrance and higher nucleophilicity of alkoxide initiating groups. Alkoxide initiators can be generated *in situ* by alcoholysis of amido complexes with alcohols. At the same time, the alcohol present in excess can convert the growing chains into "dormant" hydroxyl end-capped (macro)molecules allowing the growing of new chains on the metal centres. If the exchange

equilibria between "active" growing chains (i.e. coordinated to the metal centre) and the "dormant" chains are rapid enough compared to the initiation and subsequent propagation steps, an efficient control on the molecular weights is obtained.[77]

Table 2. Ring-Opening Polymerization of ε-CL initiated by complexes **1-a**, 1–**b** and **4-b**

[a]Run	Cat	iPrOH (eq)	Solvent	Temp (°C)	Time (min)	[b]Conv (%)	[c]Mn_{th} (x 10^3)	[d]Mn_{GPC} (x 10^3)	[d]Mw/Mn
1	**1-a**	-	Tol	70	5	100	57.1	207.6	1.74
2	**1-a**	-	Tol	25	60	100	57.1	242.2	1.82
3	**1-b**		Tol	25	30	100	57.1	150.5	2.08
4	**1-a**	-	THF	25	60	30	17.1	50.8	1.31
5	**1-b**	-	THF	25	30	70	40.0	311.8	1.90
6	**1-a**	2	Tol	25	10	59	16.8	14.1	1.07
7	**1-b**	4	Tol	25	10	100	14.0	13.7	1.06
8	**1-b**	10	Tol	25	15	100	5.7	6.7	1.07
[e]9	**1-b**	2	Tol	25	2	87	99.3	87.4	1.08
[e]10	**4-b**	2	Tol	25	2	98	111.8	121.6	1.09

[a]All reactions were carried out with in 4 mL of solvent, $[I]_0$= 3.12 mM, and $[\varepsilon\text{-CL}]_0/[I]_0$=500. [b]Conversion of ε-CL as determined by ^{1}H NMR spectral data. [c]Experimental M_n (in gmol^{-1}) and M_w/M_n (PDI) values were determined by GPC in THF using polystyrene standards and corrected using the factor of 0.56. [d] Mn_{th} (in gmol^{-1}) =114,14 x ($[\varepsilon\text{-CL}]_0/[I+$ iPrOH $]_0$) x conversion ε-CL. [e]Toluene = 6 mL; [CL]/[Y] = 1000.

Polymerization experiments were conducted by adding different equivalents of alcohol (runs 6-8, Table 2). All the obtained PCLs showed unimodal molecular weight distributions with very narrow polydispersity indexes (M_w/M_n = 1.06 – 1.09) and M_n values inversely proportional to the quantity

of added isopropanol. As expected, all metal sites resulted active in this case as testified by the good agreement between the experimental molecular weight values and the theoretical ones.

The activities of complexes **1-b** and **4-b** in the polymerization of □-CL were compared under optimized reaction conditions (runs 9 and 10, Table 2). Complex **4-b** showed the highest activity with turnover frequencies (TOF) of 28500 h^{-1}. The introduction of an electron-withdrawing group on the phenyl ring bound sulphur atom resulted in a beneficial effect on the catalytic activity likely due to the increase of the electrophilicity of the metal. [47]

Mechanism and kinetic analyses of ring-opening polymerization of ε-caprolactone by 1-a and 1-b.

To get more information about the mechanism of polymerization of ε-CL promoted by this class of complexes the reaction between complex **1-a** and 1 equivalent of monomer was followed by NMR spectroscopy. The Sc–caprolactone adduct was formed quantitatively confirming that the reaction proceeds via the well-established coordination-insertion mechanism involving the labile silylamide ligand as the initiating group and the cleavage of acyl-oxygen bond of the monomer. This experiment also established that both phenolate ligands remain bound, as spectator ligands, to the reactive metal centre during the polymerization reaction.

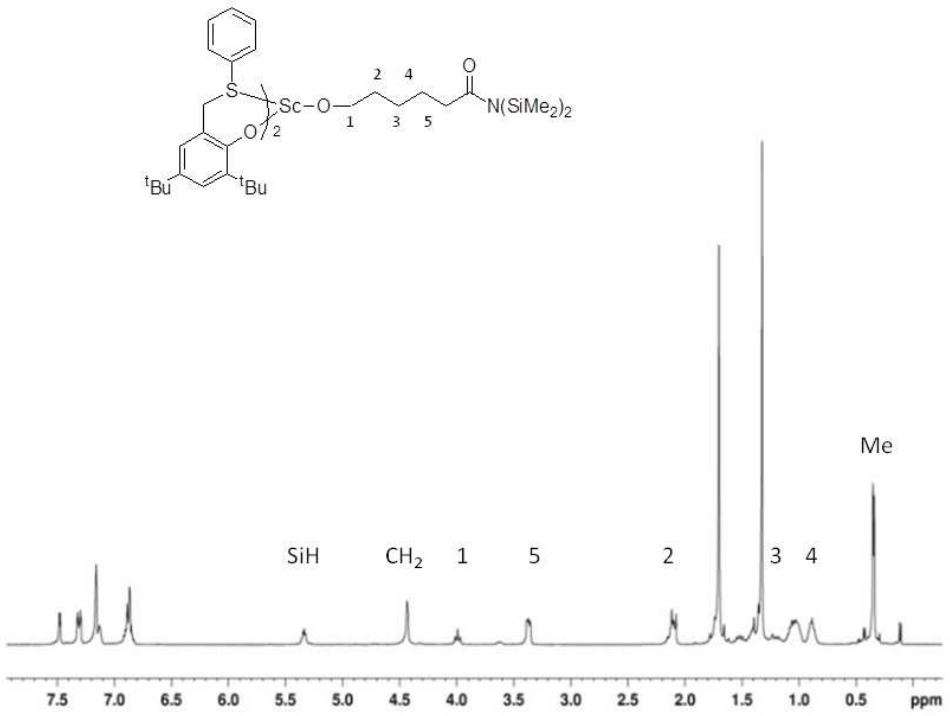


Figure 1. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of the **1a**-CL adduct formed by addition of 1 equiv. of □-CL to a solution of **1-a.**

We also determined the hydrodynamic volume of the propagating specie **1a**-CL by DOSY NMR experiments.[78] The latter indicated that the propagating species, formed by reaction of **1-a** and 1 equivalent of ε-caprolactone, has a monomeric structure in aromatic solvents, as observed for the scandium precursor **1-a**, ruling out the hypothesis of aggregation phenomena of the active species occurring during the polymerization.

^{1}H NMR analysis of a low molecular weight PCL sample obtained by carrying out a polymerization experiment in the presence of 10 equivalents of isopropanol (run 8, Table 2) disclosed the presence of isopropyl ester end groups (-COOCH$(CH_3)_2$; 1.28 ppm), generated via insertion of the monomer unit into the Y-O CH$(CH_3)_2$ bond, and hydroxyl end groups (CH_2CH_2OH; 3.62 ppm), generated by hydrolysis of the growing chain (see figure S7 of Supporting Information). These data suggest that, in the presence of isopropanol, the terminal alkoxide OiPr group is the only initiating moiety therefore a coordination-insertion mechanism should be operative also under these polymerization conditions.

Detailed kinetic studies on **1-a** and **1-b** were used to determine the reaction order in monomer. The percentage of conversion of monomer was evaluated by ^{1}H NMR spectroscopy and was monitored until at least 90% conversion to polycaprolactone was achieved.

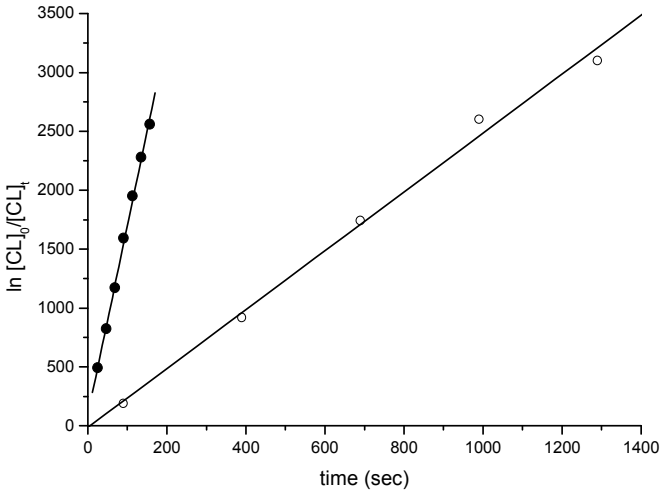


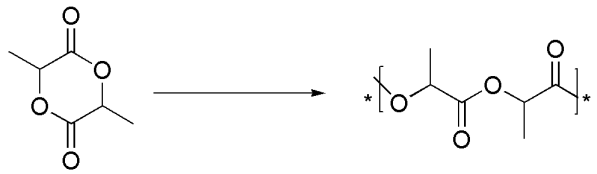
Figure 2. Pseudo-first-order kinetic plots for ROP of ε-caprolactone promoted by complexes **1-a** (○) and **1-b** (●). Pseudo-first-order rate constants are k_{app} = (2.38 ± 0.09) × 10^{-3} s^{-1} R = 0,9938 and k_{app} = (1.61 ± 0.03) ×10^{-2} s^{-1} *R*=0.99883 respectively. ([I]$_0$ = 6.0 × 10^{-3} M; [□-CL]$_0$/[I]$_0$= 100; C_7D_8 as solvent; T= 298 K).

The reaction kinetics featured a pseudo-first-order dependence in ε-CL concentration, as reported in Figure 3: the semilogarithmic plots of ln([ε-CL]$_0$/[ε–CL]$_t$) *vs.* time were linear with a slope of k_{app} = (2.38 ± 0.09) × 10^{-3} s^{-1} and (1.61 ± 0.03)×10^{-2} s-^{1} for **1-a** and **1-b** respectively.

A kinetic study on complex **1-a** in THF as solvent was also performed. The reduced productivity showed by **1-a** in the presence of a more coordinating was expressed by the lower k_{app} value (8.52 ± 0.32) ×10^{-3} min^{-1} (see figure S4 of Supporting Information).

Ring-opening polymerization of L- and *rac*–lactide

Complexes **1-a, 1-b** and **4-b** were also tested as initiators for the ROP of L- and *rac*-lactide (scheme 5) under a variety of experimental conditions. Polymers were characterized by NMR and GPC.[79]



Scheme 5. Ring-opening polymerization of L- and *rac*-lactide

Table 3. Ring-Opening Polymerization of L- and *rac*-LA by **1-a** ,**1-b** and **4-b**.

[a]Run	cat	Mon	Solvent	Time (h)	Temp (°C)	Yield (%)	[b]Mn_{GPC} ($\times 10^3$)	[c]Mn_{th} ($\times 10^3$)	[b]PDI	[d]P_r (%)
11	**1-a**	L-LA	Tol	24	25	30	8.2	8.6	1.40	-
12	**1-a**	L-LA	Tol	1	70	43	13.2	9.3	1.56	-
13	**1-b**	L-LA	Tol	24	25	83	3.0	2.4	1.42	-
14	**1-b**	*rac*-LA	THF	2	25	70	17.1	20.2	1.78	0.78
[e]15	**1-b**	*rac*-LA	THF	1	25	98	3.1	2.8	1.06	0.78
16	**4-b**	*rac*-LA	THF	2	25	91	28.4	26.2	1.06	0.91

[a]All reactions were carried with $[\mathbf{I}]_0$ = 5 mM and $[LA]_0$ = 1 M in 2 mL of solvent. [b]Experimental M_n (corrected using factor 0.58) and PDI values were determined by GPC analysis in THF using polystyrene standards. [c]Calculated M_n of PLA (in $gmol^{-1}$) =144,14 x ([LA]/[I+ iPrOH]) x conversion LA. [d]P_r is the probability of racemic linkages as determined by ^{1}H NMR homodecoupling experiments. [e] $[iPrOH]_0/[\mathbf{1b}]_0$ =10.

Representative data are listed in Table 3 and show that the polymerization results were dependent on the ligand structure and the nature of the metal.

The scandium complex **1-a** resulted poorly active in the ROP of L-lactide, promoting the conversion of about 50 equiv of monomer within 24 hour at 25 °C. As expected, at higher temperatures, the polymerization proceeded at a larger rate (cf. runs 11 and 12, Table 3). Compared with the scandium complex **1-a**, the yttrium complex **1-b** displayed higher activities (cf. runs 11 and 13, Table 3) in toluene solution.

All polymerizations proceeded in a controlled fashion, leading to polymers with monomodal and quite narrow molecular weight distributions (Mw/Mn = 1.4−2.1) . At variance with the polymerization of □-CL, the experimentally determined values for the number-averaged molecular weight well fit with those calculated on the basis of initial monomer-to-initiator ratio and conversion, even in the absence of alcohol. The more efficient control of LA polymerization

Is reasonably due to the lower propagation rate.

Kinetics studies showed that polymerizations of L-LA by **1-a** and **1-b** follow a first order dependency on the concentration of monomer with k_{app} = (1.05 ± 0.06) $\times 10^{-2}$ min^{-1} and k_{app} = (5.92 ± 0.04) $\times$ 10^{-2} min^{-1} respectively (see Figures S5 and S6 of the Supporting Information).

A higher activity was observed when the polymerization experiment was performed in THF (run 14, Table 3). The usual trend observed in the ROP of lactide is that reaction times are shorter in apolar, non-coordinating solvents, such as toluene, than in THF. The opposite trend showed by complex **1-b** is observed much more seldom.[72]

In the presence of 10 equiv of isopropanol the activity of the catalytic system increased further (cf runs 14 and 15, Table 3). ^{1}H NMR spectroscopic analysis of a low-molecular-weight sample of PLLA, obtained by using 20 equiv of L-LA and **4-b**/iPrOH = 1:5, show PLA chains with exclusively iPrOC(O) and HOCH-(CH_3)CO end-groups, thus supporting the transfer process of an effective "immortal" polymerization (see Figure S8 of Supporting Information). The ESI-MS analysis of the obtained low molecular weight sample confirmed that only linear oligomers of the type H-[$OCH(CH_3)C(=O)]_{2n}$-$OCH(CH_3)_2$ were formed. Less intense peaks consistent with linear oligomer chains with carboxylic acid end group, presumably arising from the hydrolysis of H-[$OCH(CH_3)C(=O)]_{2n}$- OH were also observed. No cyclic oligomers were detectable (see figure S9 of Supporting Information).

Comparing the activity showed by the yttrium complexes **1-b** and **4-b** (cf runs 14 and 16) emerges that complex **4-b** showed the highest activity (cf runs 14 and 16) in agreement with the behavior observed in the polymerization of □-CL.

The microstructure analysis of the obtained polymers revealed that the ligand sphere exerts a significant influence on the tacticity of the polymer chains. Both complexes showed substantial heterotactic selectivity with a maximum P_r of 0.91 observed for the yttrium complex **4-b** (Figure 3). This more efficient control should be due to the steric demand of the *ortho*-substituent in the thioether unit.

The stereochemistry of *rac*-lactide enchainment was evaluated by comparing the integrals in the homonuclear decoupled ^{1}H NMR spectrum, at the tetrad level, with calculated values by using Bernoullian statistic (see Table 4). The good agreement observed confirms that the stereocontrol is due to a chain end control mechanism, whereby the stereochemistry of the last inserted LA in the growing chain induces the selection of the incoming enantiomeric monomer.

The thermal analysis (DSC) of this sample revealed a Tg of 49.9 °C (see Figure S10 of Supporting Information)

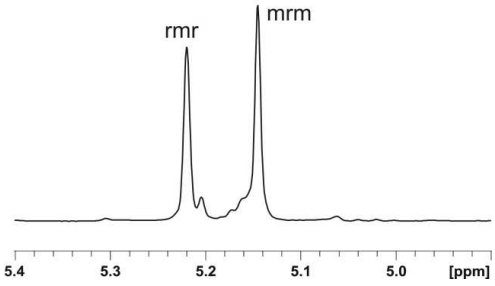


Figure 3. Methine region of the homonuclear decoupled ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of the PLA sample obtained by complex **4-b** in THF at 25 °C (run 16 in Table 3).

Table 4. Tetrad probabilities based on Bernoullian Statistic (Th) for a P_r of 0.91 and experimental values (Exp) as obtained by NMR analysis.

Tetrad	**Formula**	**Exp**	**Th**
[*mmm*]	$P_m^2+P_rP_m/2$	0.05	0.05
[*mmr*]	$P_rP_m/2$	0.04	0.04
[*rmm*]	$P_rP_m/2$	0.04	0.04
[*rmr*]	$P_r^2/2$	0.42	0.41
[*mrm*]	$(P_r^2+P_rP_m)/2$	0.45	0.46

Reactivity of homoleptic yttrium complexes 2-b and 3-b

Homoleptic complexes **2-b** and **3-b** were tested as catalysts for the ring-opening polymerization of ε-caprolactone and *rac*-lactide. Different reaction conditions were explored, some representative results are reported in Table 5.

Both complexes resulted active in the ROP of the mentioned cyclic esters.

In the polymerization of ε-caprolactone, the performance of complex **3-b** was strongly dependent on the reaction conditions, such as the temperature. At high temperature (70 °C), a conversion of 450 equivalents of monomer in one hour (run 17, Table 5) was observed. At room temperature a modest activity was detected, significantly lower than that showed by complex **2-b** under the same reaction conditions (cf runs 18 and 19, Table 5).

Table 5. Ring Opening Polymerization of □-CL by **2-b** and **3-b**

[a]Run	Cat	iPrOH	Temp (°C)	Time (min)	[b]Yield (%)	[c]Mn_{GPC} (x 10^3)	[d]Mn_{th} (x 10^3)	[c]Mw/Mn
17	**3-b**	-	70	60	87	193.7	49.8	1.51
18	**3-b**	-	25	180	57	166.6	32.6	1.98
19	**2-b**	-	25	60	70	277.3	39.9	1.44
20	**3-b**	2	70	60	100	70.2	28.3	2.02
21	**3-b**	5	70	60	100	20.6	11.3	1.73
22	**3-b**	10	70	60	100	14.8	5.6	1.75

[a]All reactions were carried out with in 4 mL of solvent, $[I]_0$=12.5 μmol, and $[\varepsilon\text{-CL}]_0/[I]_0$=500. [b]Conversion of ε-CL as determined by ^{1}H NMR spectral data. [c]Experimental M_n (in gmol^{-1}) and M_w/M_n (PDI) values were determined by GPC in THF using polystyrene standards and corrected using the factor of 0.56. [d] Mn_{th} (in gmol^{-1}) =114,14 x $([\varepsilon\text{-CL}]_0/[I + iPrOH]_0)$ x conversion ε-CL.

The polymers obtained by homoleptic complexes (runs 17-19, Table 5) showed molecular weights higher than those predicted theoretically with monomodal distributions (PDI= 1.44-2.02).This is coherent with a slow initiation step as a consequence of the fact that for homoleptic complexes the first insertion of ε-CL should occur on the phenoxy-yttrium bond of one of the coordinated ligands.

Additional polymerization experiments were performed in the presence of different equivalents of isopropanol. Under the explored conditions, the molecular weights of the obtained polymers (entries 20-22) were still higher than those theoretically expected, but a progressive decrease of molecular masses with the increase in the amount of alcohol was observed.

The complexes were also tested in the polymerization of *rac*-lactide. No activity was observed when the polymerization reactions were performed at room temperature. Differently, at 70 °C, in toluene, both complexes result active allowing a quantitative conversion of 100 equivalents of monomer in three hours. The obtained polymers have monomodal molecular weight distributions with polydispersivity indexes of 1.49 and 1.37 for **2-b** and **3-b** respectively. As already observed for the polymerization of ε-caprolactone, the polymers have molecular masses higher than those predicted theoretically as a consequence of a pour efficiency of the initiation reactions. NMR analysis of the produced PLAs revealed a predominantly heterotactic microstructure with Pr of 0.72 and 0.73 for **2-b** and **3-b** respectively.

Conclusions

A series of yttrium and scandium complexes supported by monoanionic phenoxy-thioether ligands have been prepared by a classical amine elimination reaction of silylamido metal precursors. With the aim to investigate the influence of this new ligand framework in the coordination chemistry of group 3 metals a series of proligands with different substituents on the *ortho* position of the thiophenol ring have been synthesized and tested.

The synthesis and stability of monoamido yttrium complexes supported by two phenoxy-thioether ligands are largely influenced by the ligand structure. Heteroleptic monoamido yttrium complexes have been obtained when additional charge transfers from the ligands toward the metal centre are possible, e.g. β(Si-H) agostic interactions; otherwise homoleptic complexes bearing three phenoxy thioether ligands are obtained.

The heteroleptic scandium and yttrium complexes are efficient initiators in □-caprolactone, L-lactide and rac-lactide polymerization. The reactivity resulted strongly dependent on the polymerization reactions (temperature and solvent), the nature of the metal and the structure of the phenoxy based ligands anchored to the reactive centre.

The presence of an excess alcohol as an initiator/chain transfer agent accelerated the reactions and a effective "immortal" polymerizations were achieved.

Furthermore, the polymerization of *rac*-lactide initiated by bis (phenoxy-thioether) yttrium amide complexes gave heterotactic enriched polymers. The heterotactic stereocontrol operates by means of a chain-end control mechanism and appears to be enhanced by the presence of the trifluoromethyl *ortho* substituent on the aromatic ring bound to sulphur atom.

Experimental section

General Considerations: Materials and Methods

All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen atmosphere using a Braun Labmaster drybox or standard Schlenk line techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed to vacuum-nitrogen cycle three times.

Hexane and THF (Carlo Erba) were purified by distillation from sodium benzophenone ketyl. Toluene (Carlo Erba) was purified by distillation from sodium. Anhydrous dimethylformamide, anhydrous yttrium trichloride and scandium trichloride (Aldrich) were used as received. All deuterated solvents were dried using molecular sieves. Lactide (Aldrich) was purified by crystallization from dry toluene and then stored over P_2O_5. ε-caprolactone (Aldrich) was dried with CaH_2 for 24 hours at room temperature and then distilled under reduced pressure. All other chemicals were commercially available and used as received unless otherwise stated.

Instruments and Measurements.

The NMR spectra were recorded on Bruker Avance 400 spectrometer (^{1}H, 400. MHz; ^{13}C, 100.62 MHz; ^{31}P 161.97 MHz) at 25 °C, unless otherwise stated. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and degassed and dried over activated 3 Å molecular sieves prior to use. Chemical shifts (δ) are listed as parts per million and coupling constants (*J*) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6 and δ 7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C_6D_6 and δ 77.23 for $CDCl_3$. ^{19}F NMR spectra are referenced to external $CFCl_3$.
Variable-temperature ^{1}H NMR experiments were performed with a Bruker Avance 400 (operating at 400.13 MHz) in CD_2Cl_2 using NMR tubes equipped with J Young valves. The molecular weights (M_n and M_w) and the molecular mass distribution (M_w/M_n) of polymer samples were measured by GPC at 30 °C, using THF as solvent, flow rate of eluent 1 mL/min, and narrow polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000-1,000,000 Å).

Every value was the average of two independent measurements. It was corrected using the factor of 0.58 for polylactide and 0.56 for polycaprolactone according to the literature. [80-82]

Elemental analyses were performed in the microanalytical laboratory of the institute.

Synthesis of the proligands and complexes

The phenoxy-thioether proligands **L_{1-4}-H** were synthesized according to previously published procedures. [53,54]

Complex 1-a. Into a stirred solution containing {Sc $[N(SiHMe_2)_2]_3(THF)_2$} (0.436 g, 0.7 mmol) in benzene (4 mL), a solution of the ligand precursor (0.489 g, 1.5 mmol) in benzene (6 mL) was added dropwise. The solution was stirred for 2 hour at room temperature. The solvent was removed under vacuum forming a white solid that was pure according ^{1}H NMR and elemental analysis. (0.328 g, 50 % yield).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.44 (d, J = 4 Hz, 2H, o-*H* -Ar), 7.30 (d, J = 8 Hz, 4H, *H*-Ar),. 6.85 (m, 6H, m-H-Ar, p-*H*-Ar), 6.68 (s, 2H, *H*-Ar), 5.42 (m, 2H, Si-*H*), 4.23 (s, 4H, CH_2), 1.64 (s, 18H, CCH_3), 1.25 (s, 18H, CCH_3), 0.26 (d, 12H, Si-CH_3).

^{13}C {^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 160. 2 q (*C*–O), 139.4 q (*C*–S), 136.44 q, 133.1 q, 126.1 (*C*H), 123.9 (*C*H), 122.2 q, 35.46 (*C*CH_3), 34.2 (*C*CH_3), 31.8 (C*C*H_3), 30.6 (C*C*H_3), 2.6 (*C*H_3Si).

Elemental analysis calcd (%) for $C_{46}H_{68}NO_2S_2ScSi_2$: C, 66.38; H, 8.24; N, 1.68; S, 7.71 found: C ,66.13; N, 1.78; H, 8.03; S, 7.22.

Complex 1-b

Into a stirred solution containing {Y$[N(SiHMe_2)_2]_3(THF)_3$} (0.496 g, 0.7 mmol) in hexane (4 mL), was added dropwise a solution of the ligand precursor (0.489 g, 1.4 mmol) in hexane (6 mL). The solution was stirred for 20 hour at room temperature. The solvent was removed under vacuum

forming a white solid that was pure according ^{1}H NMR and elemental analysis. (0.614 g, 88 % yield).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.49 (d, J = 3 Hz, 2H, *H*-Ar). 7.02 (m, 4H, *H*-Ar), 6.8 (d, J = 3 Hz, 2H, *H*-Ar),), 6.81 (m, 6H, *H*-Ar), 4.72 (m, 2H, Si-*H*), 4.11 (s, 4H, CH_2), 3.63 (s, 4H, O-CH_2 of THF), 1.68 (s, 18H, CCH_3), 1.30 (s, 18H, CCH_3), 0.31 (d, J = 4 Hz; 12H, Si-CH_3).

^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 152.2 q (*C*–O), 142.4 q (*C*–S), 137.3 q, 134.5 q, 131.7 (*C*H), 129.0 (*C*H), 127.3, 125.8, 123.8, 122.3 q, 37.7 (*C*H_2), 35.3 (*C*CH_3), 34.2 (*C*CH_3), 33.0 (C*C*H3), 31.0 (C*C*H_3), 0.5 (*C*H_3Si).

Elemental analysis calcd (%) for $C_{50}H_{76}NO_3S_2Si_2Y$: C, 63.32; H, 8.08; N 1.48; S, 6.76; found: C, 63.21 H, 8.43; N 1.36; S, 6.12.

Products obtained by reaction of {Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_3$} and L$_2$-H

Into a stirred solution containing {Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_3$} (91.97 mg, $1.46\cdot10^{-4}$ mol) in benzene (4 mL), was added dropwise a solution of the **L$_2$-H** ligand precursor (0.100 g, $2.92\cdot10^{-4}$ mol) in benzene (6 mL). The solution was stirred for 2 hour at room temperature. The solvent was removed under vacuum forming a white solid that was analyzed by ^{1}H NMR spectroscopy. (0.114g, 80 % yield).

The ^{1}H NMR spectrum revealed a complex mixture of three different products: two stereoisomers monoamide yttrium complexes and the homoleptic yttrium complex (**2-b**) with three coordinated ligands as major component.

^{1}H NMR (400.13 MHz, C_6D_6, 298 K). First isomer: δ 7.52 (d, 2H, *H*-Ar), 7.17 (d, 2H, J = 7.5 Hz, *H*-Ar), 6.92-6.74 (m, 4H, *H*-Ar), 6.68-6.72 (m, 6H, *H*-Ar), 5.20 (m, 2H, Si-*H*), 4.26 (s, 4H, CH_2), 2.43 (s, 6H, CH_3), 1.80 (s, 18H, CCH_3), 1.28 (s, 18H, CCH_3), 0.38 (d, 6H, J = 2.5 Hz, Si-CH_3).

Second isomer: δ 7.49 (d, 2H, *H*-Ar), 6.92-6.74 (m, 6H, *H*-Ar), 6.68-6.72 (m, 4H, *H*-Ar), 4.94 (m, 2H, Si-*H*), 4.18 (s, 4H, CH_2), 2.18 (s, 6H, CH_3), 1.69 (s, 18H, CCH_3), 1.27 (s, 18H, CCH_3), 0.11 (d, 6H, J = 2.5 Hz, Si-CH_3). For the homoleptic species see below.

Because of the complexity of the obtained mixture the elemental analysis data was not performed.

Complex 2-b

Homoleptic complex **2-b** was purposely prepared by reaction of the metal precursor with three equivalents of the **L_2-H** proligand. Into a stirred solution containing $\{Y[N(SiHMe_2)_2]_3(THF)_3\}$ (91.97 mg, $1.46 \cdot 10^{-4}$ mol) in benzene (4 mL), was added a solution of the ligand precursor (0.152 g, $4.38 \cdot 10^{-4}$ mol) in benzene (6 mL). The solution was stirred for 2 hour at room temperature. The solvent was removed under vacuum forming a white solid that was analyzed by ^{1}H NMR spectroscopy and elemental analysis. (0.147g, 91 % yield).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.53 (d, ^{4}J = 2.5 Hz, 3H, Ar-H), 7.12 (d, 3H, J = 7.5 Hz, Ar-H), 6.84 (d, 3H, ^{4}J = 2.5 Hz, Ar-H), 6.65 (m, 6H, Ar-H), 6.62 (m, 3H, Ar-H), 4.05 (s, 6H, CH_2), 1.75(s, 27 H, CCH_3), 1.74 (s, 9 H, CH_3), 1.35(s, 27 H, CCH_3).

^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 156.4 (q, C-O), 141.5 (q, C-S), 135.3 (q), 131.7 (*C*H-Ar), 131.2 (*C*H), 130.1 (*C*H), 129.5 q, 127.4 (*C*H), 122.9 (*C*H), 125.7 q, 124.6 (*C*H), 118.5 q, 37.2 (CH_2), 35.2 (CCH_3), 34.3 (CCH_3), 33.2 (CH_3), 32.4 (CCH_3), 31.6 (CCH_3).

Elemental analysis calcd (%) for $C_{66}H_{87}O_3S_3Y$: C, 71.19; H, 7.88; S, 8.64; found: C 71.26; H, 7.79; S, 8.35.

Complex 3-b

In a round-bottom flasks, equipped with a magnetic stirrer, a solution of the proligand **L_3-H** (0.80 g, 2.73 mmol) in 10 mL of hexane was prepared under nitrogen atmosphere. A solution of yttrium amide $\{Y[N(SiHMe_2)_2]_3(THF)_3\}$ (0.41g, 0.91 mmol) in 20 mL of hexane was added dropwise at room temperature. The mixture was stirred for 3 hours, then the solvent was removed in vacuum and the residue was crystallized from hexane affording 0.31g of a white powder (yield 67%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 7.49 (d, ^{4}J = 2.5 Hz, 3H, *H*-Ar), 7.25 (d, 3H, *H*-Ar), 7.16 (d, 3H, *H*-Ar), 6.88 (d, 3H, *H*-Ar), 6.57 (t, 3H, *H*-Ar), 6.48 (t, 3H, H-Ar), 4.09 (s, 6H, CH_2), 1.73 (s, 27 H, CCH_3)., 1.30 (s, 27 H, CCH_3),

$^{13}C\{^{1}H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 156.9 (q, C-O), 140.5 (q, C-S), 139.4 (q, C-Br), 133.7 (*C*H), 131.2 (*C*H), 130.5 (*C*H), 129.5 q, 128.4 (*C*H), 125.9 (*C*H), 125.6 (*C*H), 125.1 q, 119.8 q, 38.5 (CH_2), 35.8 (CCH_3), 34.6 (CCH_3), 32.2 (CCH_3), 30.7 (CCH_3).

Elemental analysis calcd (%) for $C_{63}H_{78}Br_3O_3S_3Y$: C, 57.85; H, 6.01; S, 7.35; found: C ,57.13; H, 5.63; S, 7.32

Complex 4-b

Into a stirred solution containing $\{Y[N(SiHMe_2)_2]_3(THF)_3\}$ (79.4 mg, $1.26\cdot10^{-4}$ mol) in benzene (4 mL), was added dropwise a solution of the ligand precursor (0.100 g, $2.52\cdot10^{-4}$ mol) in benzene (6 mL). The solution was stirred for 2 hour at room temperature. The solvent was removed under vacuum forming a white solid that was pure according ^{1}H NMR and elemental analysis. (0.113g, 93 % yield).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ7.46 (d. 1H, *H*-Ar); 7.44 (d, 1H, *H*Ar),. 7.38 (m, 2H, *H*-Ar), 7.31 (m, 2H, *H*-Ar), 7.02 (d, 1H, *H*-Ar), 6.84 (d, 1H, *H*Ar), 6.68 (m, 3H, *H*-Ar), 6.60 (m, 1H, *H*-Ar), 5.09 (m, 1H, Si-*H*), 5.12 (m, 1H, Si-*H*), 5.09 (m, 1H, Si-*H*), 4.17 (s, 2H, CH_2), 3.88 (m, 4H, THF), 1.75 (s, 9H, CCH_3), 1.60 (s, 9H, CCH_3), 1.34 (m, 4H, THF), 1.31 (s, 9H, CCH_3), 1.30 (s, 9H, CCH_3), 0.24 (d, 6H, Si-CH_3), 0.23 (d, 6H, Si-CH_3).

^{19}F NMR (376 MHz, C_6D_6, 298 K): δ -60.81 (s. 3F, CF_3); -61.16 (s. 3F, CF_3).

$^{13}C\{^{1}H\}$ NMR (100.62 MHz, C_6D_6, 298 K): δ 160.4 (q, C-O), 160.1 (q, C-O), 138.8 (q, C-S), 138.7 (q, C-S), 139.9 q, 139.6 q, 134.1 q, 134.0 q 133.3 (*C*H), 133.1 (*C*H), 126.9 (*C*H), 126.8 (*C*H), 126.5 (q, 2 C), 125.8 (*C*H), 125.6 (*C*H), 124.4 (*C*H), 124.1 (*C*H), 123.2 q, 122.8 q, ,39.8 (2, C, CF_3), 35.6 (CH_2), 35.5 (CH_2), 34.2 (CCH_3), 31.9 (CCH_3), 32.24 (CCH_3), 30.8(CCH_3), 30.6 (CCH_3), 25.2 (CCH_3), 0.6 (CH_3Si), 0.5 (CH_3Si).

Elemental analysis calcd (%) for $C_{52}H_{74}F_6NO_3S_2Si_2Y$: C, 57.60; H, 6.88; N, 1.29; S, 5.91; found C, 57.26; H, 6.15; N, 1.34;S, 5.71.

ε-Caprolactone Polymerizations. In a typical polymerization, a magnetically stirred reactor vessel (10 cm^3) was charged sequentially with a solution of precatalyst (12.5 μmol in 4 mL of

dry toluene) and monomer (6.25 mmol). Subsequently, 0.025 mL of a solution 0.1 M of isopropanol in toluene (2.5 μmol) was added. The mixture was thermostatized at the required temperature and, after the required polymerization time, poured into hexane. The precipitated polymer was recovered by filtration and dried at 40 °C in a vacuum oven. The polymer was characterized by NMR spectroscopy and GPC analysis. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.34 (m, 2H, -CH2-), 1.62 (m, 4H, -CH2-), 2.29 (t, 2H, -CH_2C(O)O-), 4.04 (t, 2H, -CH_2OC(O)-), 3.62 (t, 2H, -CH_2OH), 3.65 (s, 3H, -C(O)-OCH_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 24.7, 25.7, 28.5, 34.3, 64.3 (-OCO(CH_2)$_5$-), 51.7 (-C(O)OCH_3), 62.7 (-CH_2OH), 173.7 (-COO-).

Lactide Polymerizations. In a typical polymerization, a magnetically stirred reactor vessel (20 cm^3) was charged sequentially with the monomer (*rac*- or L-lactide, 0.288 g, 2.0 mmol), the precatalyst (10 μmol), and 2 mL of dry toluene. Subsequently, 0.20 mL of a solution 0.1 M of methanol in toluene (20 μmol) was added. The mixture was thermostatized at the required temperature. After the required polymerization time, an aliquot of the crude material was sampled by pipette and quenched in wet $CDCl_3$ to evaluate the yields. Conversions were determined by integration of the monomer vs polymer methine resonances in the ^{1}H NMR spectrum of crude product (in $CDCl_3$). The precipitated polymer was recovered by filtration and dried at 40 °C in a vacuum oven. The polymer was purified by redissolving in CH_2Cl_2 and precipitating from rapidly stirring methanol. The polymer was characterized by NMR spectroscopy and GPC analysis. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.56 (m, 6H, -$CHCH_3$-), 3.79 (s, 3H, -C(O)OCH_3), 5.18 (m, 2H, -$CHCH_3$-). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 16.8 (-C(O)$OCHCH_3$-), 69.2 (-C(O)- $OCHCH_3$-), 169.5, 169.8 (-COO-).

Lactide Polymerizations by homoleptic tris(phenoxy thioether) yttrium complexes 2-b and 3-b

A typical procedure for lactide polymerization catalyzed by complexes **2-b** and **3-b** is herein described. In a Braun Labmaster glovebox, a 10-mL vial was charged with a solution of metal initiator (10 mmol) in anhydrous toluene (0.5 mL) and the resulting solution was rapidly added to a solution 1 mM of *rac*-LA (0.214 g, 1.00 mmol, 100 equiv in toluene (1.5 mL). The mixture was immediately stirred with a magnetic stir bar at 70 °C for three hours. An aliquot of the crude material was sampled by pipette and quenched in wet $CDCl_3$. The monomer conversion was determination by ^{1}HNMR analysis.

Kinetic Experiments . In a typical experiment carried out in a Braun Labmaster glovebox, initiator solution, from a stock solution in toluene-d_8, was injected into a in Teflon-valved J. Young NMR tube loaded with the monomer dissolved in suitable amount of toluene-d_8 as dry solvent. The sample was thermo stated at the required temperature. The polymerization reaction was monitored via ^{1}H NMR analysis

The characteristic chemical shift for each monomer in deuterated toluene is 3.90 (q, CH; lactide), and 3.99 (m, CH_2; ε-caprolactone). The characteristic chemical shift for each polymer in deuterated toluene is 5.07 (q, CH; polylactide), and 3.47 (t, CH_2; poly-ε-caprolactone)

DOSY-NMR experiments details.

The measurement of diffusion has been carried out by observing the attenuation of the NMR signals during a pulsed field gradient experiment using the double stimulated echo pulse sequence.[83, 84] In particular, 2D DOSY PGSE NMR spectra were performed **1-a** and **1-a-CL** adduct (C_6D_6, 0.012 M) on a Bruker Avance 400 spectrometer at 300 K without spinning. Tetrakismethylsilylsilane (TMSS; r_H (hydrodynamic radius) ≈ r_{vdW} (van der Waals radius) = 4.28 Å) was adds as internal standard. The most intense signals were investigated. The dependence of the resonance intensity (I) on the gradient strength (g) is described by the following equation:

$$I=I_0\exp\{-D\gamma^2g^2\delta^2(\Delta-\delta/3)\}$$

where I is the observed intensity (attenuated signal intensity), I_0 is the reference intensity (unattenuated signal intensity), D is the diffusion coefficient, γ is the nucleus gyromagnetic ratio, g is the gradient strength, δ is the gradient duration, and Δ is the diffusion delay. The parameters δ and Δ were kept constant during the experiments, whereas g varied from 2 to 95% in 16 steps. The values of Δ were 1800 and 2000 μs for **1-a** and **1-a** -(CL) respectively.

A nonlinear regression on I and g^2 data was performed to obtain the coefficients D for both the samples and the corresponding internal standard signals (D^{sample} and D^{TMSS}, respectively). The

following expression (on the basis of the Stokes–Einstein equation) was applied and numerically resolved to get the hydrodynamic radius of each sample

$$D^{\text{sample}} / D^{\text{TMSS}} = c^{\text{TMSS}} r_{\text{H}}^{\text{TMSS}} / c^{\text{sample}} r_{\text{H}}^{\text{sample}}$$

The coefficients c^{sample} and c^{TMSS} can be estimated from the semiempirical equation.[85]

$$c^{\text{x}} = 6 / (1+0.695 r^{\text{solv}} / r_{\text{H}}^{\text{x}})^{2.234}$$

where x is the sample or TMSS, and $r^{\text{solv}} \approx$ van der Waals radius of the solvent (2.7 Å for C_6D_6).

The diffusion coefficients (D) can be related to the hydrodynamic radius (r) of the species in solution by the Stokes-Einstein equation where T is the temperature, η is the viscosity of the solvent, r is the hydrodynamic radius of the molecule or assembly, and K is the Boltzmann constant

Stokes-Einstein equation D= KT/ 6πηr

Hydrodynamic volumes were calculated from the respective radii: $V_{\text{H}} = 4/3\pi(r_{\text{H}})^3$.

Computational Details

All calculations were performed using the Gaussian 03 program package.[86] The complexes were energy minimized without symmetry constraints at the BP86 level, that is, by employing the exchange and correlation functionals of Becke[87] and Perdew,[88,89] respectively. The standard 6-31G(d) basis set was used for all the main group atoms. Sc and Y were described by Lanl2DZ together with the Lanl2DZ effective core potential (ECP). Stationary point geometries were characterized as local minima on the potential energy surfaces. The absence of imaginary frequencies verified that structures were true minima at their respective levels of theory. The relative energies were corrected for vibrational zero-point energies (ZPE, not scaled). The Gibbs free energy change (ΔG) are thermodynamically corrected to 298 K.

To save computational resources, we have simplified the structures of **1-a** and **1-b** replacing the t-butyl groups with hydrogen atoms and the $N(SiHMe_2)_2$ group with the $N(SiH_3)_2$ group.

Solvent effects have been estimated in single-point calculations on the gas phase optimized structures, based on the polarizable continuous solvation model IEFPCM as implemented in

Gaussian 03.[90] Benzene was chosen as model solvent. The gas-phase free energies were corrected by the solvation term.

Cartesian coordinates of all DFT optimized structures are available on request.

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Notes and references

Electronic Supplementary Information (ESI) available: [additional figures and tables]

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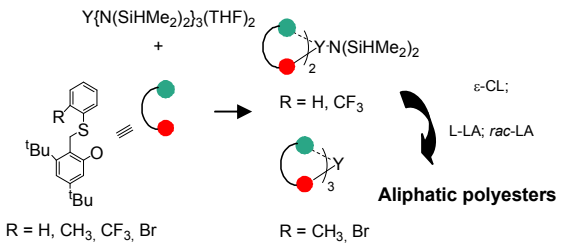

Homoleptic and heteroleptic complexes of scandium and yttrium bearing phenoxy-thioether ligands have been found active catalysts for the ring-opening polymerization of ε-caprolactone and lactides.