Synthesis and characterization of new divalent lanthanide complexes supported by amine bis(phenolate) ligands and their applications in the ring opening polymerization of cyclic esters†

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Treatment of an array of bis(phenol)s H_2L^x {L^x = [($^-OC_6H_2$(2,4-R)(6-CH_2))$_2$ NCH_2CH_2X], where X = CH_2NMe_2, NMe_2, NEt_2, OMe and R = Bu^t, Pe^t where Pe^t = C(CH_3)$_2$Et} with [Ln(N($SiMe_3$)$_2$)$_2$(THF)$_2$] (Ln = Yb, Sm) in a 1:1 molar ratio in hexanes afforded a multitude of new divalent lanthanide bis(phenolate) complexes: [L^{2c}Yb]$_2$ (X = NEt_2, R = Bu^t) **1**, [L^{2b}Yb]$_2$ (X = CH_2NMe_2, R = Bu^t) **2**, [L^{3a}Yb]$_2$ (X = NMe_2, R = Pe^t) **3**, [L^{3b}Yb]$_2$ (X = OMe, R = Pe^t) **4**, [L^{2c}Sm] (X = NEt_2, R = Bu^t) **5**, [L^{3c}Yb] (X = NEt_2, R = Pe^t) **6**, [L^{3c}Sm] (X = NEt_2, R = Pe^t) **7**. X-Ray crystallographic analyses of compounds **1** and **3** reveal dimeric, centrosymmetric structures with 5-coordinate ytterbium centers arising from bridging and terminal phenolate groups. A selection of divalent compounds (**1**, **3**, **4**, **5**, **6** and **7**) were tested as catalyst precursors in the polymerization of ε-caprolactone and/or *L*-lactide which resulted in high molecular weight polymers with PDIs of 1.11–2.81 and 1.13–1.56 for ε-caprolactone and *L*-lactide respectively. All polymerization studies were performed in either toluene or THF and at room temperature (ε-caprolactone) or 70 °C (*L*-lactide) at a variety of catalyst:monomer ratios (1:100–1:300). Kinetics analyses of the polymerization of *L*-lactide by compounds **1** and **5** indicated pseudo-first order response with respect to *L*-lactide.

Introduction

The synthetic challenges, novel chemical properties and availability of the lanthanide elements continue to drive significant research efforts towards further understanding this often misunderstood group of elements. One area to receive increasing research efforts is the synthesis and stabilization of the ephemeral (and often elusive) divalent lanthanide compounds.[1–4] More recently, groundbreaking research accomplishments have shattered the commonly held belief that only samarium, ytterbium and europium possess accessible divalent elements under standard laboratory conditions (*i.e.* solution chemistry)‡.[5–8] Key to the stabilization of these divalent lanthanide compounds[9–11] is the use of versatile, bulky, high-coordination number ligands (*e.g.* the cyclopentadienyl family) despite their hydrolytic sensitivity. In addition to the intrinsic interest posed by divalent lanthanide compounds, many researchers have capitalized on their one-electron reducing capabilities[12–16] with continued focus on small molecule activation (*e.g.* CO_2 and COS by [(C_5Me_5)$_2$Sm(THF)$_2$][17]) and polymerization reactions {[(C_5Me_5)Ln(CH($SiMe_3$)$_2$)(C_5Me_5)K(THF)$_2$]$_n$ (Ln = Eu, Yb) in the polymerization of styrene and ethylene[18]}.

Recently, interest in divalent lanthanides has progressed to include ligands with less organometallic Ln–C character[19,20] and more Ln–X (X = N, O, S *etc.*)[21,22] heteroatom bonding character (*e.g.* amides,[4,23] bis(phenolate)s,[14,24] β-diketiminates[25,26]). The motivation for this progression away from organometallic ligand systems lies primarily in the ability of these ligands to impart greater stability to the catalytic systems without loss of ligand versatility. This becomes apparent where these divalent lanthanide systems are used as catalyst precursors in polymerization reactions.[27–29] Although divalent lanthanide compounds are highly reactive and air- and moisture-sensitive, typically a pre-polymerization oxidation of the lanthanide(II) compound occurs (with concomitant reduction of an equivalent of the monomer)[27–30] to afford the catalytically active trivalent lanthanide compound which then is available for the propagating polymerization reactions. The use of multidentate O, N donor ligands (rather than Cp ligands) imparts greater stability to the catalytically active trivalent systems which have significantly reduced propensity towards hydrolysis—inevitably arising from trace moisture/air contamination typically found in monomer feedstocks.

Among the recently reported non-cyclopentadienyl lanthanide compounds ligands, those containing bis(phenolate) ligands[31–33] (Chart 1) have received interest due to their ease of preparation and chemical versatility (both electronic and steric). This versatility has led to the generation of a number of lanthanide bis(phenolate) compounds which have displayed impressive catalytic activities towards polar monomers such as lactide,[33–37] ε-caprolactone[14,15,36,38–40] and methylmethacrylate.[41] Only a handful of these examples[14,15] contained divalent lanthanide precursors, despite their conceptually similar synthesis to their trivalent counterparts (Scheme 1). In addition to their catalytic properties, these

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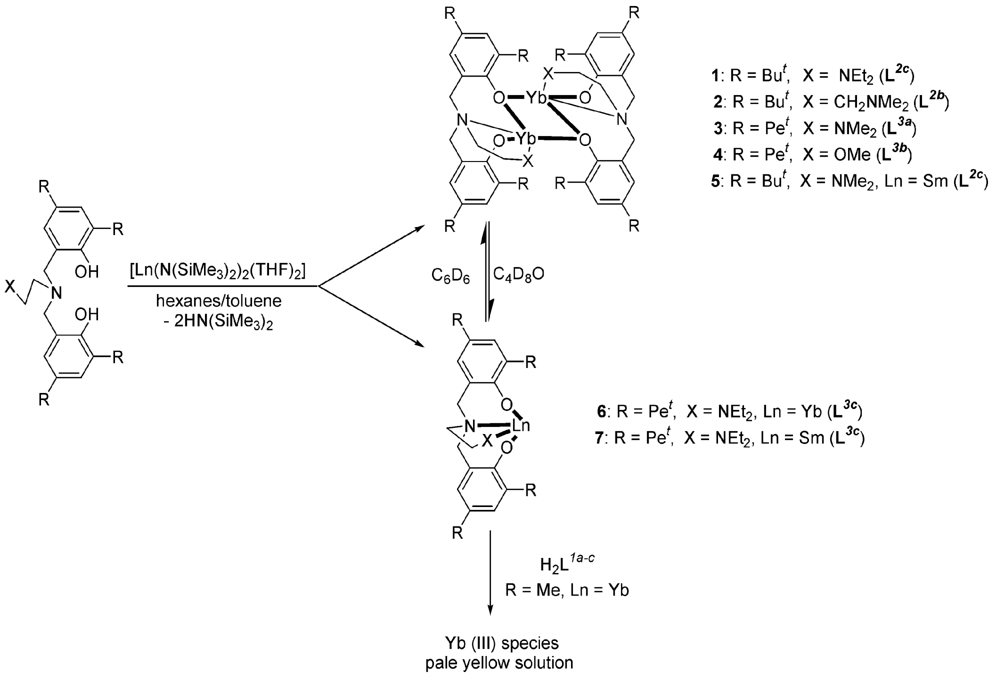
‡ Indeed Tm, Nd, Ho *etc.* divalent compounds, derived from novel solution chemistry, are all well established.[5–8]



Scheme 1 Synthesis of divalent samarium and ytterbium bis(phenolate) compounds.

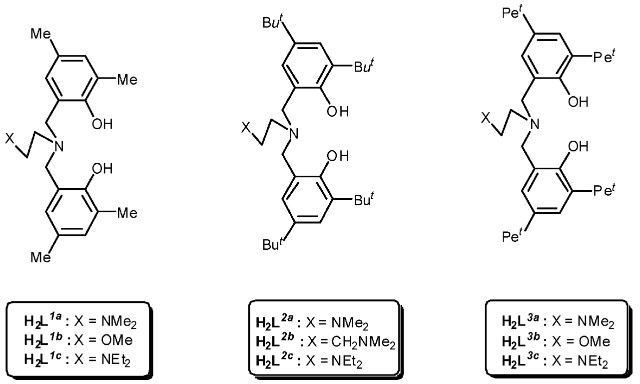


Chart 1 Matrix of bis(phenol) ligands synthesized.

divalent lanthanide bis(phenolate) compounds also demonstrate superior pathways to heteroleptic trivalent lanthanide complexes *via* oxidation reactions;[14,15] compared to the traditional salt metathesis reactions.[39,42]

Previously the authors reported the *first* solvent-free Yb(II) bis(phenolate) dimer, $\{Yb[OC_6H_2(2,4\text{-}Bu^t)(6\text{-}CH_2)]_2NCH_2CH_2NMe_2\}_2$ which displayed promising catalytic activity towards ε-caprolactone in addition to oxidative reactivity towards a variety of anhydrous alcohols to afford a multitude of ytterbium(III) bis(phenolate) alkoxide heteroleptics.[14] Subsequently, three new divalent Yb and Eu bis(phenolate) compounds, similar to that presented above, have been reported by Shen and Yao *et al.*[24] Reported herein is a sizable expansion of the authors' previous work, where syntheses involving several bis(phenolate) ligands coordinated to ytterbium and samarium, along with structural investigations (solution and solid-state), are presented. In addition, catalytic properties of these lanthanide compound towards ring opening polymerization (ROP) studies of cyclic esters (ε-caprolactone and *L*-lactide) have also been evaluated.

Results and discussion

Synthesis of bis(phenolate) ligands

The ligands (Chart 1) were prepared following literature procedures[31] as analytically pure white powders *via* a single-step Mannich type condensation reaction of the commercially available formaldehyde, the appropriate substituted phenols and primary amines. Optimal balance between steric and electronic properties in stabilizing these lanthanide complexes were considered in ligand selection. Using similar protocols, ligands H_2L^{3b} and H_2L^{3c}, which have not been previously reported, were also synthesized with their identities being confirmed by typical spectroscopic techniques including elemental analysis, melting point, high-resolution mass spectrometry, and IR- and NMR-spectroscopy.

Synthesis of divalent lanthanide bis(phenolate) complexes

Access to divalent ytterbium and samarium bis(phenolate) compounds was readily achieved by reaction of the appropriate $[Ln(N(SiMe_3)_2)_2(THF)_2]^4$ amide with one of the various bis(phenol) ligands displayed in Chart 1. A number of trends have been observed which indicated that steric encumbrance of the phenolate ligand along with metal selection play an important role in influencing overall stability and ultimately the solid-state and solution properties of the lanthanide bis(phenolate) compounds.

Unstable ytterbium(II) bis(phenolates) where R = Me (*i.e.* ligands L^{1a-c}). Initially the bis(phenol) ligands, H_2L^{1a-c} (Chart 1) (the methyl substituted phenols) were treated with $[Ln(N(SiMe_3)_2)_2(THF)_2]$ (1:1 molar ratio) in hexanes in an attempt to isolate the corresponding divalent ytterbium phenolate compound. However, upon reagent mixing, the initially formed brick-red solution (typical of Yb(II)[14,15]) rapidly became pale-yellow within 20 minutes and deposited a yellow precipitate indicative of likely oxidation to Yb(III) (Scheme 1). Unfortunately the highly paramagnetic nature of the trivalent ytterbium precluded any meaningful NMR spectra to be obtained. Moreover, this provides *indirect* evidence of trivalent ytterbium since an intelligible spectrum from any divalent (diamagnetic) ytterbium would be anticipated. Since these reaction systems were found to be reproducible, oxidation by adventitious air/moisture can be eliminated; a more likely explanation would attribute oxidation of sub-stoichiometric quantities of the divalent ytterbium bis(phenolate) complex with free bis(phenol) [*i.e.* H_2L^{1a-c} in a typical Ln(II) redox reaction producing H_2 as a by-product (Scheme 1)[14,43,44]]. These results infer that the less sterically demanding bis(phenol)/(phenolate) ligands possibly have greater access to the redox active lanthanide metal center, thus facilitating these oxidation reactions.§

Dimers: ytterbium(II) bis(phenolate) where R = Bu^t, Pe^t (*i.e.* ligands $L^{2b,c}$, $L^{3a,b}$).

Compounds 1–4. Substituting the methyl groups for the bulkier tertiary butyl ($L^{2b,c}$) or tertiary pentyl ($L^{3a,b}$) groups in the bis(phenol) ligands provided a convenient mechanism to accessing the analytically pure divalent ytterbium phenolate compounds **1**–**4** (Scheme 1) in good yields (65–83%). The proposed formulations (discussed below) are supported by typical analytical techniques (see Experimental) including IR- and NMR-spectroscopy, elemental analysis (which in some cases returned %C values which were low, but within the commonly held acceptable range for extremely air-sensitive divalent Ln compounds) and for compounds **1** and **3**, X-ray crystallography.

X-ray crystallographic analysis of compounds **1** $[YbL^{2c}]_2$ and **3** $[YbL^{3a}]_2$, of which the crystals were obtained from non-donor solutions, revealed dimeric structures with a centrosymmetric YbO_2Yb core and bridging and terminal phenolate oxygen donor atoms (*vide infra*). Detailed ^{1}H NMR spectroscopic studies indicated that the solid-state structure is preserved in non-donor deuterated solvents such as C_6D_6 or C_7D_8 but the bis(phenolate) ligands become symmetrical and the ytterbium complex monomeric, upon addition of donor solvents such as C_4D_8O (Scheme 1). Moreover, this dynamic solution behavior from dimer to monomer is totally reversible and has been noted by the authors previously for a related ytterbium bis(phenolate) complex $\{Yb[OC_6H_2(2,4\text{-}Bu^t)(6\text{-}CH_2)]_2NCH_2CH_2NMe_2\}_2$.[14] Subsequent research efforts by Shen and co-workers[15] reported monomeric THF analogue of this compound which support the suppositions inferred from the aforementioned solution NMR spectroscopic studies.

Though it was not possible to obtain solid state structures for **2** $[YbL^{2b}]$ and **4** $[YbL^{3b}]$, all spectroscopic and analytical data not only supported the dimeric formulation '$[YbL]_2$' but also the dynamic solution behavior in donor/non-donor solvents such that both solid-state structures are considered dimeric *i.e.* $[YbL]_2$ since each were isolated as solids from toluene/hexanes solutions.

Monomers: ytterbium and samarium bis(phenolates) where R = Bu^t, Pe^t (*i.e.* ligand, L^{3c}).

Compounds 6,7. It was postulated that further increasing the steric constraints exerted by the bis(phenolate) ligands may suppress the propensity of these lanthanide bis(phenolate) complexes to exist as aggregates (or dimers) in the presence of non-donor solvent systems (see discussion above). As such, treatment of the appropriate $[Ln(N(SiMe_3)_2)_2(THF)_2]$ with H_2L^{3c} (Chart 1), (where the side-arm substituents in $H_2L^{3a,b}$ have been modified from X = NMe_2 or OMe to the bulkier NEt_2 group) in 1:1 molar ratio in hexanes afforded compounds **6** $[YbL^{3c}]$ and **7** $[SmL^{3c}]$. Unlike compounds **1**–**4**, longer reaction times¶ (9 and 24 h for compounds **6** and **7** respectively *cf.* 4 h for **1**–**4**) were necessary to achieve quantitative protiolytic ligand exchange. Repeated attempts to obtain X-ray crystallographic quality crystals of compounds **6** and **7** were thwarted by formation of microcrystalline powders. However, the solution properties of both compounds were investigated by ^{1}H and ^{13}C NMR spectroscopic studies and revealed only one phenolate environment (as evidenced by only two unique aromatic C–H groups) which is consistent with a *monomeric* structural motif; akin to those described above and reported previously for the analogous THF adduct reported by Shen and coworkers.[15] Moreover, NMR spectra of both **6** and **7** in C_4D_8O were almost identical to those recorded in C_6D_6, further supporting the supposition of predominant monomeric divalent lanthanide bis(phenolate) compounds. Not surprisingly, monomeric compound **7** $[SmL^{3c}]$ exhibited greater air-sensitivity than its ytterbium analogue, compound **6** $[YbL^{3c}]$, and both displayed greater air-sensitivity than the aggregated compounds **1**–**4** as ascertained semi-quantitatively by relative oxidation rates of the solids in air.

Samarium bis(phenolate) where R = Bu^t, (*i.e.* ligand L^{2c}).

Compound 5. Several attempts to synthesize a number of divalent samarium bis(phenolate) compounds analogous to the ytterbium compounds described above were unsuccessful as indicated by typical auto-oxidation of the divalent samarium compound[24] upon addition of the bis(phenol) reagent. Specifically, Shen noted that SmL^{2a} could *not* be synthesized from $[Sm(N(SiMe_3)_2)_2(THF)_2]$ and H_2L^{2a}. These observations are not surprising given the relative reducing power of the Sm(II) *vs.* Yb(II)[45] {*e.g.* $(C_5Me_5)_2Ln$ (Ln = Sm, Yb) reacts with PhC≡CH to afford the *pure* Sm(III) complex $[(C_5Me_5)_2Sm]_2(PhC{=}C{=}C{=}CPh)$[46] *vs.* the *mixed* valent Yb complex $[(C_5Me_5)_2Yb(III)]_2(\mu\text{-}C{\equiv}CPh)_4Yb(II)$[47]}. In addition, the larger ionic radius of Sm(II) *vs.* Yb(II)[45] undoubtedly enhances oxidation reactions by providing greater access of the bis(phenol) ligand substrate to the metal center. Similar oxidation reactions of Sm(II) involving less bulky bis(phenolate) ligands have been observed previously.[48] Given these constraints, the successful isolation of a samarium(II) bis(phenolate) compound $[SmL^{2c}]$ **5**, is a remarkable achievement (Scheme 1, Chart 1) given the L^{2c} ligand is significantly less sterically demanding than that found in compound **7**, L^{3c} (described above). In the absence of any X-ray crystallographic analyses,‖ it is difficult to explain the

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§ Indeed a number of other systems involving less encumbered bis(phenol) ligand reproducibly yielded oxidized products.[14]

¶ Within 4 h only 60% of compound **6** formed as monitored by ^{1}H NMR spectroscopy.

‖ Several attempts to obtain a solid state structure of **5** were thwarted by crystal twinning.

stability of this system; however an intimate balance between metal size and ligand bulk likely saturates the coordination environment about the metal center, protecting the metal center from further redox chemistry. The '[SmL^{2c}]' formulation proposed for compound **5**, which may be dimeric or monomeric, was supported by elemental analysis,**[49] IR spectroscopy and NMR spectroscopy (see Experimental). Compound **5** was insoluble in non-donor solvents such as C_6D_6 or C_7D_8 precluding probing the degree of possible solution and solid-state aggregation. However, given similarities between compounds **5** and **1** [LnL^{2c}], similar aggregation properties are likely wherein compound **1** was deemed as dimeric in non-donor solvents (see aforementioned discussion). For this reason, compound **5** is grouped with compounds **1–4** in Scheme 1.

X-Ray crystallography of compounds 1 and 3

The results from single crystal X-ray structure determinations of compounds **1** and **3** are consistent with the proposed formulations, [YbL]$_2$, in terms of stoichiometry and connectivity *i.e.* dimers with bridging and terminal asymmetric phenolate groups (Fig. 1 and 2 and Tables 1 and 2 respectively). Compound **1** was solved in the triclinic space group $P\bar{1}$ with one molecule of toluene, while compound **3** crystallizes in the monoclinic space group $P2_1/n$.

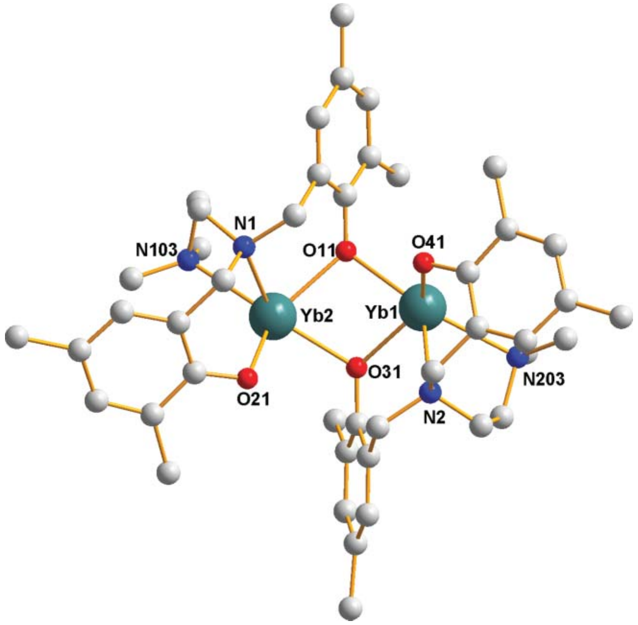

Fig. 1 Projection of one molecule of **1**, with hydrogen, *tert*-butyl methyl groups and toluene solvent molecule omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) for **1**

Bond distances (Å)			
Yb1-O41	2.229(4)	Yb2-O21	2.245(4)
Yb1-O31	2.324(4)	Yb2-O11	2.328(3)
Yb1-O11	2.357(3)	Yb2-O31	2.371(4)
Yb1-N2	2.537(4)	Yb2-N1	2.521(4)
Yb1-N203	2.593(4)	Yb2-N103	2.582(5)
Angles (°)			
O41-Yb1-O31	131.66(14)	O21-Yb2-O11	133.09(14)
O41-Yb1-O11	89.56(13)	O21-Yb2-O31	90.87(13)
O31-Yb1-O11	73.20(12)	O11-Yb2-O31	72.86(12)
O41-Yb1-N2	81.07(14)	O21-Yb2-N1	82.07(14)
O31-Yb1-N2	79.17(13)	O11-Yb2-N1	79.18(13)
O11-Yb1-N2	132.83(13)	O31-Yb2-N1	133.76(13)
O41-Yb1-N203	112.11(15)	O21-Yb2-N103	112.34(15)
O31-Yb1-N203	103.08(14)	O11-Yb2-N103	102.22(15)
O11-Yb1-N203	150.65(14)	O31-Yb2-N103	148.84(15)
N2-Yb1-N203	72.37(14)	N1-Yb1-N103	72.39(15)

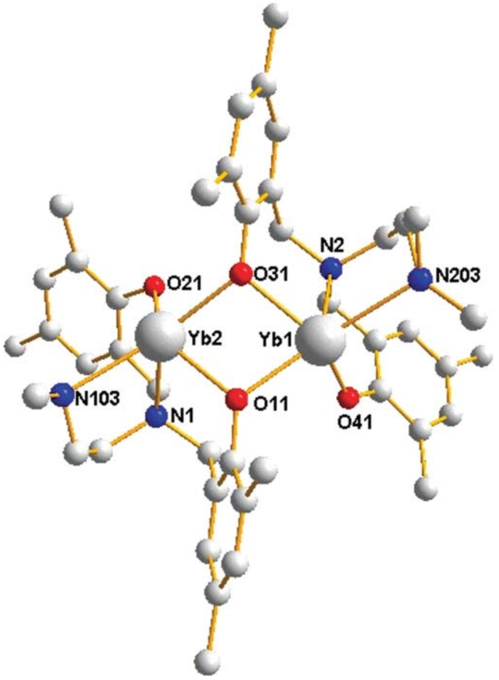

Fig. 2 Projection of one molecule of **3**, with hydrogen and *tert*-pentyl methyl and ethyl groups omitted for clarity. Only one component of the disordered atoms is shown.

Each compound can be described as having an η^4-bis(phenolate) ligand coordinated to the ytterbium(II) metal center with coordination saturation being fulfilled through additional oxygen coordination (*via* bridging) from a neighboring η^4-bis(phenolate) unit to give an overall 5-coordinate, dimeric ytterbium complex. These 5-coordinate ytterbium atoms gain additional electron density *via* agostic interactions of the *tert*-butyl and *tert*-pentyl hydrogen atoms in compounds **1** and **3** respectively. As expected, these agostic interactions†† are more significant in **3** which is probably due to the closer proximity of the *tert*-pentyl hydrogens to ytterbium in **3** *versus* those found in the *tert*-butyl groups of **1**. Ignoring these Yb···H interactions, the formal 5-coordination environment about ytterbium does not readily fit either symmetrical trigonal bipyramidal or square-based pyramid models, which is probably attributed to the overall conformational rigidity of the bis(phenolate) ligands. The YbO_2Yb cores in both compounds

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** Albeit 1.7% low in carbon. Given the *extreme* air-sensitivity of lanthanide(II) toward oxidation, repeated attempts at obtaining "satisfactory" elemental analyses were thwarted presumably by imperfect analyses techniques.[49]

†† Which were not observed in solution, as identified by ^1H NMR spectroscopy.

Table 2 Selected bond distances (Å) and angles (°) for **3**

Bond distances (Å)			
Yb1-O41	2.208(5)	Yb2-O21	2.250(3)
Yb1-O31	2.316(5)	Yb2-O11	2.298(5)
Yb1-O11	2.326(4)	Yb2-O31	2.333(4)
Yb1-N2	2.530(4)	Yb2-N103	2.532(5)
Yb1-N203	2.580(5)	Yb2-N1	2.531(6)
Angles (°)			
O41-Yb1-O31	139.35(17)	O21-Yb2-O11	130.66(12)
O41-Yb1-O11	95.26(17)	O21-Yb2-O31	89.23(14)
O31-Yb1-O11	72.52(16)	O11-Yb2-O31	72.72(16)
O41-Yb1-N2	79.74(16)	O21-Yb2-N103	110.37(17)
O31-Yb1-N2	79.76(15)	O11-Yb2-N103	104.76(17)
O11-Yb1-N2	130.20(16)	O31-Yb2-N103	153.12(16)
O41-Yb1-N203	100.88(18)	O21-Yb2-N1	78.85(14)
O31-Yb1-N203	105.73(17)	O11-Yb2-N1	79.73(18)
O11-Yb1-N203	154.74(16)	O31-Yb2-N1	130.93(16)
N2-Yb1-N203	72.33(15)	N103-Yb2-N1	72.78(16)

have symmetrical bridging modes with almost equivalent Yb–(μ-O) bond lengths which were longer (by *ca.* 0.10 Å) than terminal Yb–O bond lengths. In addition, all anionic Yb–O bond lengths are shorter than Yb–N coordinate bonds; all of which are comparable to other bridged Yb(II) bis(phenolate)s including the related $\{Yb[OC_6H_2(2,4\text{-}Bu^t)(6\text{-}CH_2)]_2NCH_2CH_2NMe_2\}_2$.[14]

Polymerization of ε-caprolactone and *L*-lactide

While there are a numerous examples of trivalent lanthanide catalyst precursors for the ring opening polymerization (ROP) of cyclic esters such as lactide[33,34,36,50,51] and lactones,[36,38–40,52,53] there are surprisingly few instances where divalent lanthanide compounds have been employed.[14,15,30,54] The divalent ytterbium and samarium bis(phenolate) compounds **1–7** (*vide supra*) represent ideal candidates for *preliminary* exploration into the propensity of these compounds to function as catalyst precursors in ROP of *L*-lactide and/or ε-caprolactone to produce polymers which have numerous applications from bio-friendly packaging materials to bio-assimilable drug-delivery agents.[55–57] Reported herein are our results from *initial* ROP studies employing a variety of divalent lanthanide bis(phenolate) compounds. A number of trends were observed, including: 1) Divalent lanthanide bis(phenolate)s effectively polymerize both ε-caprolactone and the more challenging *L*-lactide quantitatively 2) Samarium bearing catalysts are more active than comparable ytterbium analogues 3) Donor solvents such as THF suppress polymerization rates.

ε-Caprolactone polymerization. Compounds **1**, **4**, **5** and **7** polymerized ε-caprolactone quantitatively at room temperature in toluene under 45 minutes, in a variety of initiator to monomer ratios (1:100–1:300) (Table 3). In many cases, the observed molecular weights (M_n), determined by GPC, were greater than predicted by theory; likely caused by catalyst deactivation *via* the initial redox chemistry between the divalent lanthanide precursor and the monomer substrate.[14] This should lead to lower concentrations of active catalyst and consequently formation of higher molecular weight polymers. In a some cases (entries 1 and 5; Table 3) the polydispersity indices (PDIs) are quite low (1.22 and 1.11), suggesting that these catalysts **1** and **5** (which only differ in Ln metal) do not significantly promote side reactions (such as chain transfer or transesterification reactions[58]).

Table 3 Results from the polymerization of ε-caprolactone[a]

Entry	Initiator	Time/min	$[M]_0/[I]_0$	% Conv.[b]	10^{-4} M_n(obs.)[c]	PDI[c]
1	**1**	10	200	99.6	1.59	1.22
2	**4**	15	300	99.8	3.82	1.99
3	**5**	3	100	99.6	3.72	2.81
4	**5**[d]	15	100	99.7	4.67	2.62
5	**5**	7	277	99.1	3.26	1.11
6	**7**	8	100	98.9	1.92	2.14
7	**7**	13	200	98.4	1.96	1.85
8	**7**[d]	45	100	97.6	1.86	1.42

[a] Polymerization conditions: Toluene as solvent (unless otherwise stated), T = RT, V_{tol}/V_{CL} = 1.86. [b] Determined by ^1H NMR analysis. [c] Determined by GPC analysis in toluene with calibration to polystyrene standards. [d] Solvent = THF.

In general, samarium-based catalysts polymerized ε-caprolactone more rapidly than their ytterbium counterparts which is in accordance with the findings of other researchers[51–53,59,60] where larger lanthanide metal containing catalysts (*e.g.* Nd *vs.* Yb) are more active ROP catalysts than those containing smaller lanthanide ions.

Replacing toluene for donor solvents such as THF in the ROP reactions invariably suppressed polymerization rates which again is consistent with previous studies[50,52] that have attributed this to probable competition between the THF molecules and monomer substrates for coordination to the metal center (the necessary first step in the polymerization reaction). This, in turn, slows down the polymerization process.

While the molecular structure of the catalyst (*i.e.* monomer *vs.* dimer) in solution will undoubtedly have a profound effect on ROP rates, it is difficult to understand the subtleties of these effects in the present study, since the influence of the monomer substrate (*i.e.* the cyclic ester) on catalyst aggregation disruption is unknown. However, the dimeric compound **1** has a significantly lower catalytic activity compared with the analogous monomeric Yb complex $\{(THF)_2Yb[OC_6H_2(2,4\text{-}Bu^t)(6\text{-}CH_2)]_2NCH_2CH_2NMe_2\}$[15] but has comparable activity to other dimeric systems, such as $[L^*Yb(THF)_2]_2$ {L* = 2,2′-methylenebis(6-butyl-4-methylphenoxo)}.[54]

***L*-Lactide polymerization.** Although a number of ROP studies of ε-caprolactone investigating lanthanide (II) bis(phenolate) systems have been reported[14,15,54] the present study is the *first* to report in any detail on the ROP of *L*-lactide utilizing divalent lanthanide bis(phenolate) complexes. Compounds **1**, **5** and **7** were evaluated as catalysts in the ROP of *L*-lactide (Table 4) and the

Table 4 Results from the polymerization of *L*-lactide[a]

Entry	Initiator	Time/min	$[M]_0/[I]_0$	% Conv.[b]	10^{-4} M_n(obs.)[c]	PDI[c]
1	**1**[e]	24 h	100	6.34	—	—
2	**5**[e]	24 h	100	9.65	—	—
3	**1**	60	100	86.6	1.61	1.13
4	**5**	30	100	95.8	2.61	1.56
5	**5**[d]	50	100	93.6	1.96	1.25
6	**7**	45	100	94.7	3.1	1.3

[a] Polymerization conditions: toluene as solvent (except stated otherwise), T = 70 °C. [b] Determined by ^1H NMR analysis. [c] Detemined by GPC analysis in toluene with calibration to polystyrene standards. [d] Solvent = THF. [e] T = 25 °C.

reactions required heating (70 °C) to achieve respectable polymer conversions (> 85%). In general, GPC data revealed narrower PDIs than those obtained in ROP of ε-caprolactone (1.13–1.56), which reflects superior single-site control by the catalysts and may be a function of the slower polymerization rates observed in ROP lactide reactions. These differences in substrate reactivity have been previously observed[61] although no explanation was provided. Again samarium containing catalysts exhibited faster polymerization rates than the analogous ytterbium compounds (entries 3 and 4) and the polymerization reactions were faster in toluene than those performed in THF.

Finally, *pseudo*-first order kinetics in lactide were observed from $\ln\{[LA_0]/[LA]_t\}$ *vs.* time plots from systems employing catalysts **1** and **5** at initiators:monomer ratios of 1:50 and 1:100 respectively (k_{obs}(I) = 0.0416 min^{-1} and k_{obs}(II) = 0.0321 min^{-1}) (Fig. 3). These data suggest a mechanism which requires one molecule of lactide per active site of catalyst (*i.e.* one molecule LA per monomeric lanthanide catalyst or two molecules per dimeric lanthanide catalyst).

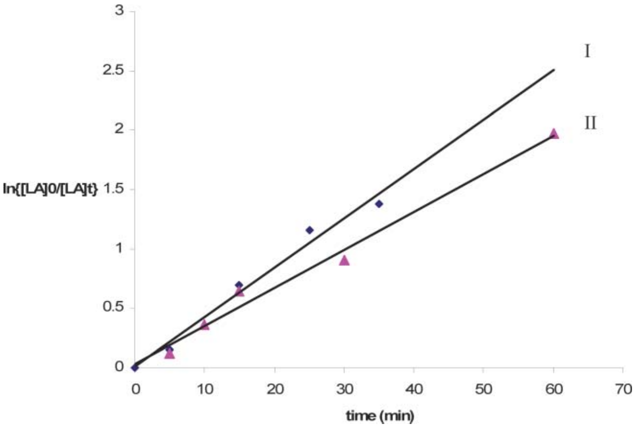

Fig. 3 *Pseudo*-first order kinetics plot of *L*-lactide polymerization catalyzed by compounds **1** and **5** in toluene at 70 °C. (I) [**1**]:[LA] = 1:50, (II) [**5**]:[LA] = 1:100.

Conclusions

A number of novel divalent ytterbium and samarium bis(phenolate) complexes have been synthesized by straightforward amine elimination reactions. The less sterically demanding bis(phenolate) ligands were found to produce trivalent lanthanide complexes. However, more bulky ligand systems produced isolable divalent lanthanide species which exist as either dimers (Ln = Yb) or monomers in solution (Ln = Yb, Sm); as determined by the intimate relationship between metal-ion size and steric demands of the ligands. X-Ray crystallographic characterization of compounds **1** and **3** revealed dimeric ytterbium(II) compounds with symmetrically-bridging bis(phenolate) ligands; supporting the proposed formulations ascertained by solution NMR spectroscopic studies. A selection of these divalent lanthanide compounds has been evaluated as catalysts in the ROP of ε-caprolactone and *L*-lactide cyclic esters. In most cases quantitative polymer conversion was established, making these catalysts the *first* group of divalent lanthanide bis(phenolate) complexes to display such activity towards *L*-lactide, the more difficult of the cyclic esters to polymerize. Finally, kinetic studies revealed that these reactions propagate with *pseudo*-first order kinetics with respect to *L*-lactide.

Experimental

General

Since all lanthanide complexes described herein are air- and moisture-sensitive all manipulations were performed under nitrogen atmospheres using typical Schlenk line and glove-box techniques. Solvents were dried and purified by distillation under nitrogen from sodium or potassium metal mixed with benzophenone while deuterated solvents (C_4D_8O, C_6D_6 and C_7D_8) were dried over sodium metal and purified by vacuum transfer. The lanthanide precursors $[Ln(N(SiMe_3)_2)_2(THF)_2]$ (Ln = Sm, Yb) were synthesized by the reported procedure.[4] The starting materials used for the synthesis of the ligands H_2L^R $\{L^R = [^-OC_6H_2(2,4\text{-}R)(6\text{-}CH_2)]_2NCH_2CH_2X\}$ (R = Me, Bu^t, Pe^t)[31,32] were purchased from Acros and used without further purification. Melting points were obtained from sealed capillaries on a Mel-Temp apparatus and are uncorrected. IR spectra (4000–450 cm^{-1}) were recorded as KBr Nujol mulls on an ATI Mattson Genesis Series FTIR Spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer and referenced to C_6D_5H or C_4D_7HO or $CHCl_3$ (^1H) and C_6D_6 or C_4D_8O or $CDCl_3$ (^{13}C). Elemental analyses (sealed ampoules under inert atmosphere) were performed by Midwest Microlab, Indianapolis, IN.

Synthesis of H_2L^{3b}. A mixture of 2,4-di-*tert*-pentylphenol (10.00 g, 42.7 mmol), 2-methoxyethylenediamine (2.00 mL, 21.3 mmol) and 37% aqueous formaldehyde (4.40 mL, 58.7 mmol) in methanol (10 mL) was refluxed for 20 h. The mixture was then cooled in the freezer for 4 h and the supernatant solution was decanted. The residue was triturated with ice cold methanol, filtered, washed thoroughly with cold methanol and dried *in vacuo* to give the bis-adduct H_2L^{3b} (7.24 g, 60%) as a white powder. Mp 140–143 °C. (Found: C, 78.4; H, 10.9; N, 2.6. $C_{37}H_{61}NO_3$ requires C, 78.3; H, 10.9; N, 2.6%); $\tilde{\nu}_{max}/cm^{-1}$ 3370 s, 2623 m, 2036w, 1600w, 1299 s, 1261 m, 1211w, 1095 s, 1060 m, 1018 s, 872 m, 802 m, 725 m, 601w (Nujol); MS: *m*/*z* 568.5 $[M + H]^+$. δ_H (500.1 MHz, $CDCl_3$, 298 K) 0.63 (6H, t, *J* 7.5 Hz, CCH_2CH_3), 0.65 (6H, t, *J* 7.6 Hz, CCH_2CH_3), 1.25 (12H, s, $C(CH_3)_2$), 1.33 (12H, s, $C(CH_3)_2$), 1.57 (4H, q, *J* 7.5 Hz, CCH_2CH_3), 1.92 (4H, q, *J* 7.6 Hz, CCH_2CH_3), 2.72 (2H, t, *J* 5.2 Hz, NCH_2CH_2O), 3.45 (3H, s, OCH_3), 3.51 (2H, t, *J* 5.2 Hz, NCH_2CH_2O), 3.78 (4H, s, $ArCH_2N$), 6.83 (2H, s, Ar), 7.13 (2H, s, Ar), 8.54 (2H, s, O*H*), δ_C (125.8 MHz, $CDCl_3$, 298K) 9.6 (CCH_2CH_3), 10.0 (CCH_2CH_3), 28.2 ($C(CH_3)_2Et$), 29.0 ($C(CH_3)_2Et$), 33.2 ($C(CH_3)_2Et$), 37.5 (CCH_2CH_3), 37.6 (CCH_2CH_3), 38.9 ($C(CH_3)_2Et$), 51.7 (NCH_2CH_2O), 58.5 (NCH_2CH_2O), 59.2 (OCH_3), 71.8 ($ArCH_2N$), 121.8 (arom-*C*H), 125.9 (arom-CPe^t), 126.0 (arom-*C*H), 134.6 (arom-CPe^t), 139.3 (arom-CCH_2N), 153.1 (arom-*C*O).

Synthesis of H_2L^{3c}. Following a similar procedure for the synthesis H_2L^{3b}, a mixture of 2,4-di-*tert*-pentylphenol (10.00 g, 42.7 mmol), *N*,*N*-diethylethylenediamine (3.00 mL, 21.3 mmol) and 37% aqueous formaldehyde (4.40 mL, 58.7 mmol) in methanol (10 mL) yielded a white powder of H_2L^{3c} (7.58 g, 58%). Mp

101–102 °C. (Found: C, 79.1; H, 11.1; N, 4.8. $C_{40}H_{68}N_2O_2$ requires C, 78.9; H, 11.3; N, 4.6%); $\tilde{\nu}_{max}$/cm^{-1} 3345 s, 2730w, 2356 m, 1600 m, 1261 m, 1095 s, 1049 m, 1022 s, 872w, 802 s, 725 m, 609 w (Nujol); MS: *m/z* 609.5 [M + H]$^+$. δ_H (500.1 MHz, C_4D_8O, 298 K) 0.65 (6H, t, *J* 7.0 Hz, CCH$_2$C*H*$_3$), 0.70 (6H, t, *J* 8.1 Hz, CCH$_2$C*H*$_3$), 1.51 (6H, t, *J* 7.0 Hz, N(CH$_2$C*H*$_3$)$_2$), 1.29 (12H, s, C(C*H*$_3$)$_2$), 1.41 (12H, s, C(C*H*$_3$)$_2$), 1.63 (4H, q, *J* 7.0 Hz CC*H*$_2$CH$_3$), 1.95 (4H, q, *J* 8.1 Hz, CC*H*$_2$CH$_3$), 2.68-2.63 (8H, overlapping signals of NC*H*$_2$C*H*$_2$N and N(C*H*$_2$CH$_3$)$_2$), 3.75 (4H, s, ArC*H*$_2$N), 6.88 (2H, s, Ar), 7.12 (2H, s, Ar), 9.7 (2H, s, O*H*), $\delta_{C\{H\}}$ (125.8 MHz, C_4D_8O, 298K) 9.6 (CCH$_2$*C*H$_3$), 10.0 (CCH$_2$*C*H$_3$), 28.14 (C(*C*H$_3$)$_2$Et), 29.0 (C(*C*H$_3$)$_2$Et), 33.2 (*C*(CH$_3$)$_2$Et), 34.0 (*C*(CH$_3$)$_2$Et), 37.6 (C*C*H$_2$CH$_3$), 38.9 (C*C*H$_2$CH$_3$), 45.7 (NCH$_2$*C*H$_3$), 48.1 (N*C*H$_2$CH$_3$), 49.2 (N*C*H$_2$*C*H$_2$N), 50.4 (N*C*H$_2$*C*H$_2$N), 57.1 (Ar*C*H$_2$N), 121.6 (arom-*C*H), 125.9 (arom-*C*Pe^t), 127.2 (arom-*C*H), 124.4 (arom-*C*Pe^t), 138.6 (arom-*C*CH$_2$N), 155.5 (arom-*C*O).

Synthesis of [YbL^{2c}]$_2$ (1). A deep orange hexanes solution (10 mL) of [Yb(N(SiMe$_3$)$_2$)$_2$(THF)$_2$] (0.64 g, 1.00 mmol) was treated with a colorless hexanes solution (9 mL) of H$_2$L^{2c} (0.55 g, 1.00 mmol) which resulted instantly in a coffee brown solution. Stirring was continued for 4 h at room temperature and compound **1**·C$_7$H$_8$ (0.96 g, 75%) was obtained as cubic dark brown crystals from a hexanes/toluene mixture, which was isolated and dried *in vacuo.* Mp 220–222 °C. (Found: C, 60.2; H, 7.9; N, 4.0. $C_{72}H_{116}N_4O_4Yb_2$ requires C, 59.7; H, 8.1; N, 3.9%); $\tilde{\nu}_{max}$/cm^{-1} 1738 w, 1655 m, 1260 s, 1623 m, 1260 s, 1091 s, 1022 s, 866 w, 800 s, 697 w, 570 w, 546 m (Nujol); δ_H (500.1 MHz, C_4D_8O, 298K) 0.66 (6H, t, *J* 7 Hz, N(CH$_2$C*H*$_3$)$_2$), 1.24 (18H, s, Bu^t), 1.47 (18H, s, Bu^t), 2.05 (2H, t, *J* 6.9 Hz, NC*H*$_2$C*H*$_2$N), 2.24 (4H, q, *J* 7 Hz, N(C*H*$_2$CH$_3$)$_2$), 2.25 (2H, t, *J* 6.9 Hz, NC*H*$_2$CH$_2$N), 2.89 (2H, d, *J* 12.3 Hz, ArC*H*$_2$N), 4.55 (2H, d, *J* 12.3 Hz, ArC*H*$_2$N), 6.87 (2H, s, Ar), 7.09 (2H, s, Ar), δ_H (500.1 MHz, C_6D_6) 0.67 (6H, t, *J* 7.0 Hz, N(CH$_2$C*H*$_3$)$_2$), 1.34 (6H, t, *J* 6.7 Hz, N(CH$_2$C*H*$_3$)$_2$), 1.36–1.80 (80H, overlapping signals of Bu^t and NC*H*$_2$C*H*$_2$N), 1.95 (4H, q, *J* 7.0 Hz, N(C*H*$_2$CH$_3$)$_2$), 2.97 (4H, q, *J* 6.7 Hz, N(C*H*$_2$CH$_3$)$_2$), 3.25 (2H, d, *J* 12.2 Hz, ArC*H*$_2$N), 3.47 (2H, d, *J* 12.2 Hz, ArC*H*$_2$N), 4.88 (2H, d, *J* 12.2 Hz, ArC*H*$_2$N), 5.68 (2H, d, *J* 12.2 Hz, ArC*H*$_2$N), 7.03 (2H, s, Ar), 7.14 (2H, s, Ar), 7.35 (2H, s, Ar), 7.54 (2H, s, Ar), $\delta_{C\{H\}}$ (125.8 MHz, C_4D_8O, 298 K) 5.3 (N(CH$_2$*C*H$_3$)$_2$), 27.7 (C*Me*$_3$), 29.8 (C*Me*$_3$), 33.2 (*C*Me$_3$), 37.7 (*C*Me$_3$), 41.0 ((N(*C*H$_2$CH$_3$)$_2$), 44.7 (N*C*H$_2$*C*H$_2$N), 49.2 (N*C*H$_2$*C*H$_2$N), 62.3 (Ar*C*H$_2$), 120.9 (arom-*C*H), 122.1 (arom-*C*Bu^t), 124.4 (arom-*C*H), 129.0 (arom-*C*CH$_2$N), 132.6 (arom-*C*Bu^t), 164.2 (arom-*C*O).

Synthesis of [YbL^{2b}]$_2$ (2). To a hexanes solution (6 mL) of [Yb(N(SiMe$_3$)$_2$)$_2$(THF)$_2$] (0.32 g, 0.50 mmol) was added a colorless hexanes solution (5 mL) of H$_2$L^{2b} (0.27 g, 0.50 mmol) which led to an instant red solution. The reaction mixture was stirred for 4 h at room temperature to afford 2 (0.23 g, 65%) as an orange precipitate which was separated from the supernatant and dried *in vacuo.* Mp 241–243 °C. (Found: C, 60.1; H, 9.1; N, 4.1. $C_{70}H_{112}N_4O_4Yb_2$ requires C, 59.2; H, 7.9; N, 3.9%); $\tilde{\nu}_{max}$/cm^{-1} 2370w, 2342w, 1603 s, 1314w, 1261 s, 1093 s, 1024 s, 871 m, 801 s, 680w, 580 m (Nujol); δ_H (500.1 MHz, C_4D_8O, 298 K) 1.28 (18H, s, Bu^t), 1.41 (18H, s, Bu^t), 1.50 (2H, m, NCH$_2$C*H*$_2$CH$_2$N), 1.79 (2H, t, *J* 7.1 Hz, NC*H*$_2$CH$_2$C*H*$_2$N), 1.84 (6H, s, N*Me*$_2$), 2.32 (2H, t, *J* 7.1 Hz, NC*H*$_2$CH$_2$C*H*$_2$N), 2.75 (2H, d, *J* 13.0 Hz, ArC*H*$_2$N), 3.93 (2H, d, *J* 13.0 Hz, ArC*H*$_2$N), 6.19 (2H, s, Ar), 7.08 (2H, s, Ar), $\delta_{C\{H\}}$ (125.8 MHz, C_4D_8O, 298K) 20.1 (NCH$_2$*C*H$_2$CH$_2$N), 29.1 (C*Me*$_3$), 31.2 (C*Me*$_3$), 32.9 (*C*Me$_3$), 34.6 (*C*Me$_3$), 44.6 (N*Me*$_2$), 46.2 (NCH$_2$CH$_2$*C*H$_2$N), 58.7 (NCH$_2$CH$_2$*C*H$_2$N), 59.8 (Ar*C*H$_2$N), 121.9 (arom-*C*H), 125.6 (arom-*C*Bu^t), 127.5 (arom-*C*H), 129.9 (arom-*C*Bu^t), 133.9 (arom-*C*CH$_2$N), 165.5 (arom-*C*O).

Synthesis of [YbL^{3a}]$_2$ (3). Using a similar procedure for the synthesis of **1**, a hexanes solution (10 mL) of [Yb(N(SiMe$_3$)$_2$)$_2$(THF)$_2$] (0.64 g, 1.00 mmol) and a colorless hexanes solution (5 mL) of H$_2$L^{3a} (0.58 g, 1.00 mmol) yielded a greenish-brown solution from which **3** (0.59 g, 78%) precipitated as dark green needle-like crystals. These were isolated from the solution and dried *in vacuo.* Mp 224–226 °C. (Found: C, 60.7; H, 8.3; N, 3.7. $C_{76}H_{124}N_4O_4Yb_2$ requires C, 61.3; H, 8.5; N, 3.9%); $\tilde{\nu}_{max}$/cm^{-1} 1739 w, 1600 w, 1299 w, 1261 s, 1214 w, 1161 w, 1095 s, 1022 s, 933 w, 872 m, 802 s, 725 m, 602 m (Nujol); δ_H (500.1 MHz, C_4D_8O, 298 K) 0.61–0.64 (12H, m, overlapping signals of *o*-C(CH$_3$)$_2$CH$_2$C*H*$_3$ and *p*-C(CH$_3$)$_2$CH$_2$C*H*$_3$), 1.20 (12H, s, C(C*H*$_3$)$_2$CH$_2$CH$_3$), 1.41 (12H, s, C(C*H*$_3$)$_2$CH$_2$CH$_3$), 1.55 (6H, s, N*Me*$_2$), 1.72 (4H, q, *J* 2 Hz, C(CH$_3$)$_2$C*H*$_2$CH$_3$), 1.81 (4H, q, *J* 2 Hz, C(CH$_3$)$_2$C*H*$_2$CH$_3$), 2.34 (2H, t, *J* 5.5 Hz, NC*H*$_2$C*H*$_2$N), 2.87 (2H, t, *J* 5.5 Hz, NC*H*$_2$C*H*$_2$N), 2.89 (2H, d, *J* 12.1 Hz, ArC*H*$_2$N), 4.14 (2H, d, *J* 12.1 Hz, ArC*H*$_2$N), 6.74 (2H, s, Ar), 6.99 (2H, s, Ar), $\delta_{C\{H\}}$ (125.8 MHz, C_4D_8O, 298K) 6.9 (C(CH$_3$)$_2$CH$_2$*C*H$_3$), 7.5 (C(CH$_3$)$_2$CH$_2$*C*H$_3$), 25.4 (C(*C*H$_3$)$_2$CH$_2$CH$_3$), 25.9 (C(*C*H$_3$)$_2$CH$_2$CH$_3$), 26.9 (*C*(CH$_3$)$_2$CH$_2$CH$_3$), 30.5 (*C*(CH$_3$)$_2$CH$_2$CH$_3$), 34.8 (C(CH$_3$)$_2$-*C*H$_2$CH$_3$), 36.5 (C(CH$_3$)$_2$*C*H$_2$CH$_3$), 42.9 (N*Me*$_2$), 44.9 (N*C*H$_2$CH$_2$N), 57.6 (N*C*H$_2$CH$_2$N), 62.7 (Ar*C*H$_2$N), 123.3 (arom-*C*H), 125.3 (arom-*C*Pe^t), 126.2 (arom-*C*H), 126.6 (arom-*C*Pe^t), 130.8 (arom-*C*CH$_2$N), 164.2 (arom-*C*O).

Synthesis of [YbL^{3b}]$_2$ (4). Using a similar procedure to that described for the synthesis of **1**, a reaction between [Yb(N(SiMe$_3$)$_2$)$_2$(THF)$_2$] (0.64 g, 1.00 mmol) and H$_2$L^{3b} (0.57 g, 1.00 mmol) in hexanes (25 mL) yielded a yellow microcrystalline powder of **4** (0.61 g, 83%). Mp 222–223 °C. (Found: C, 60.1; H, 8.1; N, 1.9. $C_{74}H_{118}N_2O_6Yb_2$ requires C, 60.2; H, 8.3; N, 1.9%); $\tilde{\nu}_{max}$/cm^{-1} 3370 s, 2623 m, 2036w, 1600w, 1299 s, 1261 m, 1211w, 1095 s, 1060 m, 1018 s, 872 m, 802 m, 725 m, 601 w (Nujol); δ_H (500.1 MHz, C_4D_8O, 298 K) 0.62–0.65 (12H, m, overlapping signals of *o*-C(CH$_3$)$_2$CH$_2$C*H*$_3$ and *p*-C(CH$_3$)$_2$CH$_2$C*H*$_3$), 1.22 (12H, s, C(C*H*$_3$)$_2$CH$_2$CH$_3$), 1.36 (12H, s, C(C*H*$_3$)$_2$CH$_2$CH$_3$), 1.56 (4H, q, *J* 5.1 Hz, C(CH$_3$)$_2$C*H*$_2$CH$_3$), 1.78 (4H, q, *J* 5.5 Hz, C(CH$_3$)$_2$C*H*$_2$CH$_3$), 2.59 (2H, t, *J* 4.1 Hz, NC*H*$_2$CH$_2$O), 2.81 (3H, s, OMe), 2.93 (2H, d, *J* 11.1 Hz, ArC*H*$_2$N), 2.98 (2H, t, *J* 4.1 Hz, NCH$_2$C*H*$_2$O), 6.7 (2H, s, Ar), 7.13 (2H, s, Ar), $\delta_{C\{H\}}$ (125.8 MHz, C_4D_8O, 298K) 7.2 (C(CH$_3$)$_2$CH$_2$*C*H$_3$), 7.7 (C(CH$_3$)$_2$CH$_2$*C*H$_3$), 25.6 (C(*C*H$_3$)$_2$CH$_2$CH$_3$), 25.8 (C(*C*H$_3$)$_2$CH$_2$CH$_3$), 27.1 (*C*(CH$_3$)$_2$-CH$_2$CH$_3$), 27.2 (*C*(CH$_3$)$_2$CH$_2$CH$_3$), 30.6 (C(CH$_3$)$_2$*C*H$_2$CH$_3$), 34.9 (C(CH$_3$)$_2$*C*H$_2$CH$_3$), 35.7 (N*C*H$_2$CH$_2$O), 38.8 (NCH$_2$*C*H$_2$O), 55.6 (O*C*H$_3$), 62.3 (Ar*C*H$_2$N), 122.0 (arom-*C*Pe^t), 123.3 (arom-*C*H), 125.4 (arom-*C*H), 126.9 (arom-*C*Pe^t), 131.2 (arom-*C*CH$_2$N), 164.1 (arom-*C*O).

Synthesis of [SmL^{2c}] (5). Using a similar procedure to that described for the synthesis of the divalent ytterbium complexes, a purple hexanes solution (10 mL) of [Sm(N(SiMe$_3$)$_2$)$_2$(THF)$_2$]

(0.62 g, 1.00 mmol) was stirred with a colorless hexanes solution (5 mL) of $\mathrm{H_2L}^{2c}$ (0.55 g, 1.00 mmol) to afford coffee-brown crystals of **5** (0.58 g, 83%), which were isolated from the supernatant and dried *in vacuo.* Mp 192 °C. (Found: C, 60.0; H, 8.3; N, 4.0. $\mathrm{C_{36}H_{58}N_2O_2Sm}$ requires C, 61.7; H, 8.3; N, 4.0%); $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ 1775w, 1607 m, 1442 m, 1350w, 1367w, 1323w, 1268 s, 1163w, 1098 s, 1027 s, 931w, 876 s, 803 s, 740 s, 645w (Nujol); δ_H (500.1 MHz, $\mathrm{C_4D_8O}$, 298K) 0.19 (18H, s, Bu^t), 0.33 (18H, s, Bu^t), 0.87 (6H, t, *J* 10 Hz, $\mathrm{N(CH_2C}\mathit{H}_3\mathrm{)_2}$), 1.21 (2H, d, *J* 11.5 Hz, $\mathrm{ArC}\mathit{H}_2$), 1.37 (4H, q, *J* 10.2 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_3)_2}$), 3.53 (4H, m, $\mathrm{NC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{N}$), 4.23 (2H, d, *J* 11.5 Hz, $\mathrm{ArC}\mathit{H}_2$), 6.3 (2H, s, Ar), 7.2 (2H, s, Ar), $\delta_{C\{H\}}$ (125.8 MHz, $\mathrm{C_4D_8O}$, 298K) 11.6 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_3)_2}$), 30.4 ($\mathrm{C}\mathit{Me}_3$), 30.9 ($\mathrm{C}\mathit{Me}_3$), 32.4 ($\mathit{C}\mathrm{Me_3}$), 32.9 ($\mathit{C}\mathrm{Me_3}$), 35.8 ($\mathrm{N}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2N}$), 36.1 ($\mathrm{N}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2N}$), 40.5 (($\mathrm{N(}\mathit{C}\mathrm{H_2CH_3)_2}$), 56.3 ($\mathrm{Ar}\mathit{C}\mathrm{H_2N}$), 121.5 (arom-*C*H), 122.2 (arom-*C*Bu^t), 122.4 (arom-*C*H), 123.6 (arom-$\mathit{C}\mathrm{CH_2N}$), 125.0 (arom-*C*Bu^t), 134.2 (arom-*C*O).

Synthesis of [YbL^{3c}] (6). Using a similar procedure to that described for the synthesis of **1**, a hexanes solution (10 mL) of $\mathrm{[Yb(N(SiMe_3)_2)_2(THF)_2]}$ (0.64 g, 1.00 mmol) and a colorless hexanes solution (5 mL) of $\mathrm{H_2L}^{3c}$ (0.61 g, 1.00 mmol) was stirred for 9 h and all volatiles removed to yield a brown microcrystalline powder of **6** (0.62 g, 80%). Mp 180–181 °C. (Found: C, 61.4; H, 8.6; N, 3.5. $\mathrm{C_{40}H_{66}N_2O_2Yb}$ requires C, 61.6; H, 8.5; N, 3.6%); $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ 1741w, 1612w, 1301 m, 1261 s, 1220w, 1165w, 1100 s, 1024 s, 933w, 875 m, 812 s, 725 m, 603 m (Nujol); δ_H (500.1 MHz, $\mathrm{C_4D_8O}$, 298 K) 0.62–0.66 (12H, m, overlapping signals of *o*-$\mathrm{C(CH_3)_2CH_2C}\mathit{H}_3$ and *p*-$\mathrm{C(CH_3)_2CH_2C}\mathit{H}_3$), 1.10 (4H, q, *J* 7.1 Hz, $\mathrm{C(CH_3)_2C}\mathit{H}_2\mathrm{CH_3}$), 1.21 (12H, s, $\mathrm{C(C}\mathit{H}_3\mathrm{)_2CH_2CH_3}$), 1.23 (6H, t, *J* 6.2 Hz, $\mathrm{N(CH_2C}\mathit{H}_3\mathrm{)_2}$), 1.34 (12H, s, $\mathrm{C(C}\mathit{H}_3\mathrm{)_2CH_2CH_3}$), 1.72 (4H, q, *J* 7.1 Hz, $\mathrm{C(CH_3)_2C}\mathit{H}_2\mathrm{CH_3}$), 1.91 (4H, q, *J* 6.2 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_3)_2}$), 2.26 (2H, t, *J* 7.0 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{N}$), 2.88 (2H, t, *J* 7.0 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{N}$), 3.08 (2H, d, *J* 12.3 Hz, $\mathrm{ArC}\mathit{H}_2\mathrm{N}$), 4.21 (2H, d, *J* 12.3 Hz, $\mathrm{ArC}\mathit{H}_2\mathrm{N}$), 6.66 (2H, s, Ar), 7.07 (2H, s, Ar), $\delta_{C\{H\}}$ (125.8 MHz, $\mathrm{C_4D_8O}$, 298K) 5.1 ($\mathrm{C(CH_3)_2CH_2}\mathit{C}\mathrm{H_3}$), 6.8 ($\mathrm{C(CH_3)_2CH_2}\mathit{C}\mathrm{H_3}$), 7.0 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2CH_2CH_3}$), 7.3 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2CH_2CH_3}$), 7.4 ($\mathit{C}\mathrm{(CH_3)_2}$-$\mathrm{CH_2CH_3}$), 7.5 ($\mathit{C}\mathrm{(CH_3)_2CH_2CH_3}$), 7.7 ($\mathrm{C(CH_3)_2}\mathit{C}\mathrm{H_2CH_3}$), 8.0 ($\mathrm{C(CH_3)_2}\mathit{C}\mathrm{H_2CH_3}$), 25.7 ($\mathrm{N(CH_2}\mathit{C}\mathrm{H_3)_2}$), 43.4 ($\mathrm{N(}\mathit{C}\mathrm{H_2CH_3)_2}$), 48.1 ($\mathrm{N}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2N}$), 49.4 ($\mathrm{N}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2N}$), 62.5 ($\mathrm{Ar}\mathit{C}\mathrm{H_2N}$), 119.9 (arom-*C*H), 123.4 (arom-*C*Pe^t), 125.3 (arom-*C*H), 130.8 (arom-*C*Pe^t), 151.4 (arom-$\mathit{C}\mathrm{CH_2N}$), 164.3 (arom-*C*O).

Synthesis of [SmL^{3c}] (7). Using a similar procedure to that described for the synthesis of **1**, a purple hexanes solution (10 mL) of $\mathrm{[Sm(N(SiMe_3)_2)_2(THF)_2]}$ (0.62 g, 1.00 mmol) and a colorless hexanes solution (5 mL) of $\mathrm{H_2L}^{3c}$ (0.61 g, 1.00 mmol) were combined and this mixture stirred for 24 h to yield deep purple crystals of **7** (0.61 g, 80%) that were isolated from solution and dried *in vacuo.* Mp 224–225 °C. (Found: C, 63.7; H, 9.0; N, 3.8. $\mathrm{C_{40}H_{66}N_2O_2Sm}$ requires C, 63.4; H, 8.8; N, 3.7%); $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ 1604 m, 1413 w, 1380 m, 1362w, 1324 w, 1262 s, 1203 m, 1165 w, 1094 m, 1023 m, 933 w, 915 w, 880 s, 813 s, 7420 s, 653 w, 521 s (Nujol); δ_H (500.1 MHz, $\mathrm{C_4D_8O}$, 298 K) –6.21 (6H, t, *J* 5.3 Hz $\mathrm{C(CH_3)_2CH_2C}\mathit{H}_3$), –0.83 (6H, t, *J* 5.1 Hz, $\mathrm{C(CH_3)_2CH_2C}\mathit{H}_3$), –0.03 (12H, s, $\mathrm{C(C}\mathit{H}_3\mathrm{)_2CH_2CH_3}$), 0.16 (12H, s, $\mathrm{C(C}\mathit{H}_3\mathrm{)_2CH_2CH_3}$), 0.21 (6H, t, *J* 7.1 Hz, $\mathrm{N(CH_2C}\mathit{H}_3\mathrm{)_2}$), 0.48 (8H, m, overlapping signals of *o*-$\mathrm{C(CH_3)_2C}\mathit{H}_2\mathrm{CH_3}$ and *p*-$\mathrm{C(CH_3)_2C}\mathit{H}_2\mathrm{CH_3}$), 0.51 (4H, q, *J* 7.1 Hz, $\mathrm{N(C}\mathit{H}_2\mathrm{CH_3)_2}$), 1.26 (4H, m, $\mathrm{NC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{N}$), 1.62 (2H, d, *J* 11.1 Hz, $\mathrm{ArC}\mathit{H}_2\mathrm{N}$), 1.72 (2H, d, *J* 11.1 Hz, $\mathrm{ArC}\mathit{H}_2\mathrm{N}$), 5.22 (2H, s, Ar), 5.46 (2H, s, Ar), $\delta_{C\{H\}}$ (125.8 MHz, $\mathrm{C_4D_8O}$, 298K) 2.2 ($\mathrm{C(CH_3)_2CH_2}\mathit{C}\mathrm{H_3}$), 5.9 ($\mathrm{C(CH_3)_2CH_2}\mathit{C}\mathrm{H_3}$), 22.5 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2CH_2CH_3}$), 26.6 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_2CH_2CH_3}$), 26.9 ($\mathit{C}\mathrm{(CH_3)_2}$-$\mathrm{CH_2CH_3}$), 27.2 ($\mathit{C}\mathrm{(CH_3)_2CH_2CH_3}$), 29.8 ($\mathrm{C(CH_3)_2}\mathit{C}\mathrm{H_2CH_3}$), 32.8 ($\mathrm{C(CH_3)_2}\mathit{C}\mathrm{H_2CH_3}$), 34.6 ($\mathrm{N(}\mathit{C}\mathrm{H_2Me)_2}$), 35.7, ($\mathrm{N(}\mathit{C}\mathrm{H_2Me)_2}$), 37.1 ($\mathrm{N}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2N}$), 37.7 ($\mathrm{N}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2N}$), 44.7 ($\mathrm{Ar}\mathit{C}\mathrm{H_2}$), 103.6 (arom-*C*H), 120.6 (arom-*C*Pe^t), 122.9 (arom-*C*H), 127.7 (arom-*C*Pe^t), 133.7 (arom-$\mathit{C}\mathrm{CH_2N}$), 167.5 (arom-*C*O).

Crystal data†

Data collection was by means of a Bruker Apex I (for **1**) or Oxford Diffraction Gemini (**3**) diffractometer. Following multi-scan absorption corrections the structures were solved by direct methods and refined by full-matrix refinement on F^2 using the SHELXL 97 program.[62] Hydrogen atoms were placed in calculated positions and refined as part of riding models.

1. $\mathrm{C_{72}H_{116}N_4O_4Yb_2}$, $\mathrm{C_7H_8}$, M = 1539.9, triclinic, a = 9.8103(10) Å, b = 14.4406(10) Å, c = 28.081(3) Å, α = 85.744(2), β = 86.711(2), γ = 79.599(2), V = 3898.0(6) Å^3, T = 173(2) K, space group $P\bar{1}$, specimen: 0.45 × 0.36 × 0.25 mm^3, μ = 2.432 mm^{-1}, D_c (Z = 2) = 1.312 Mg m^{-3}, λ(Mo Kα) = 0.71073 Å, $T_{min/max}$ = 0.77, $2\theta_{max}$ = 56.5°. A total of 44182 reflections was collected, of which 17646 were unique (R_{int} = 0.023); R_1 = 0.046 ($I > 2\sigma(I)$), wR_2 = 0.125 (all data), S = 1.09; $|\rho_{max}|$ = 2.84 e Å^{-3}. The methyl groups of two *tert*-butyl methyl groups and the toluene molecule are each disordered over two sites with site occupancy factors for one *tert*-butyl methyl group (14n) and for that of the toluene set as being identical (0.62(2) and 1–0.62(2)) after trial refinement showed them to be not significantly different. The site occupancy factors for the two components of the other disordered *tert*-butyl methyl group (44n) refined to 0.76(1) and 1–0.76(1). Atoms of the minor components of *tert*-butyl methyl (44n) and also those of the solvent toluene were refined with isotropic displacement parameters. The C–C bond lengths of disordered atoms were restrained to ideal values and the carbon atom of one methyl group (C146) was refined with isotropic displacement parameters. Since the remaining atoms showed no unacceptable anisotropy, no further disordering was attempted. The atoms of both components of the solvent toluene were refined as rigid groups.

3. $\mathrm{C_{76}H_{124}N_4O_4Yb_2}$, M = 1503.87, monoclinic, a = 15.7477(3) Å, b = 32.4941(5) Å, c = 16.6133(3) Å, β = 117.374(2), V = 7549.2(3) Å^3, T = 100(2) K, space group $P2_1/n$, specimen: 0.10 × 0.04 × 0.02 mm^3, μ = 4.81 mm^{-1}, D_c (Z = 2) = 1.323 Mg m^{-3}, λ(Cu Kα) = 1.54184 Å, $T_{min/max}$ = 0.42, $2\theta_{max}$ = 135.2°. A total of 92938 reflections was collected, of which 13445 were unique (R_{int} = 0.115); $\mathrm{R_1}$ = 0.060 ($I > 2\sigma(I)$), $\mathrm{wR_2}$ = 0.188 (all data), S = 0.88; $|\rho_{max}|$ = 1.29 e Å^{-3}. The carbon atoms of one phenol group (no. 2), including the *tert*-pentyl methyl groups, another *tert*-pentyl methyl group (44n) and one coordinated $\mathrm{NMe_2}$ group, are each disordered over two sites, with site occupancy factors set at 0.5 after trial refinement. Disordered carbon atoms and those of the *tert*-pentyl methyl group (14n) and *tert*-butyl groups were refined with isotropic displacement parameters and their geometries were restrained to ideal values. The pendant atoms of ring 3 exhibited somewhat elongated ellipsoids but a satisfactory disordered model could not be obtained. These atoms were subsequently refined with isotropic displacement parameters with geometries restrained to ideal values. As a result of this disorder and subsequent restraints, geometries, in particular those of the ligands, must be considered less reliable.

Typical polymerization procedures

ε-Caprolactone polymerization. A toluene (1.000 mL) solution containing the appropriate catalyst (Table 3), was added to ε-CL (0.700 mL; 6.317 mmol) and toluene (0.300 mL) at room temperature in a glove-box. After an appropriate time (Table 3), the vigorously stirred reaction mixture began to gel at which time an aliquot which was analyzed by ^{1}H NMR spectroscopy ($CDCl_3$) to establish polymer conversion. At the conclusion of the polymerization the reaction mixture was quenched with 5% wt. HCl-MeOH solution (*ca.* 1 ml) before being analyzed by GPC to determine molecular weight distribution data.

***L*-Lactide polymerization.** To a pre-heated (70 °C) toluene solution of lactide (0.500 g; 3.469 mmol *L*-lactide, 5.000 mL toluene) another toluene solution containing the appropriate catalyst concentration (Table 4) was added and the mixture was stirred vigorously. After an appropriate time (Table 4), an aliquot was analyzed by ^{1}H NMR spectroscopy ($CDCl_3$) to establish polymer conversion. At the conclusion of the polymerization reaction a 5% wt. HCl-MeOH solution (*ca.* 1 mL) quenched the reaction mixture and precipitated the polymer. The polymer was filtered off and dried prior to GPC analyses.

Kinetics procedure. Lactide (0.200 g; 1.388 mmol) was dissolved in toluene (10 mL) and heated to 70 °C. To this an appropriate amount of the catalyst was added (0.0201 g; 0.0278 mmol of **1**; Fig. 3) and aliquots of the polymerization reaction were quenched immediately with hexanes at the appropriate intervals. The volatiles were subsequently evaporated and the amount of formed polymer was analyzed by ^{1}H NMR spectroscopy.

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