

Phenoxytriamine complexes of yttrium: synthesis, structure and use in the polymerization of lactide and ϵ -caprolactone†

Ian Westmoreland and John Arnold*

Received 20th January 2006, Accepted 30th May 2006

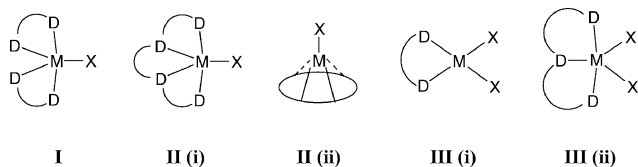
First published as an Advance Article on the web 15th June 2006

DOI: 10.1039/b600939e

Reaction of the phenoxytriamine proligands 2,4-dimethyl-6-bis(2-(diethylamino)ethyl)aminomethylphenol (HL^1) and 2,4-di-*tert*-butyl-6-bis(2-(diethylamino)ethyl)aminomethylphenol (HL^2) with $\text{Y}[\text{N}(\text{SiMe}_2\text{H})_2]_3(\text{THF})_2$ in pentane gave the monomeric complexes $\text{L}^1\text{Y}[\text{N}(\text{SiMe}_2\text{H})_2]_2$ (**1**) and $\text{L}^2\text{Y}[\text{N}(\text{SiMe}_2\text{H})_2]_2$ (**2**). X-Ray structural analysis of **2** shows a 5-coordinate yttrium center. The complexes **1** and **2** catalyze the ring opening polymerization of D-L-lactide and ϵ -caprolactone leading to narrow product polydispersities under mild conditions.

Introduction

Organolanthanide complexes supported by cyclopentadienyl (Cp) ligands have been demonstrated as effective precatalysts for a variety of homogeneous processes.^{1–5} Lanthanide elements lend themselves to complexation by hard sigma donors, since they are highly acidic and form hard M^{3+} ions. However, an ideal ligand system must also possess enough steric bulk to prevent unwanted ligation by solvent, complex dimerisation, aggregation, and ligand redistribution, without compromising the intended catalytic activity of the system. While multidentate ligands are often utilized to prevent ligand redistribution—particularly those with donors that do not engage in bridging bonding modes—the formal charge of the ancillary is also of paramount importance. Recent ligand design has sought to supplant the formerly ubiquitous Cp fragment, resulting in a deluge of new complexes.^{6–9}

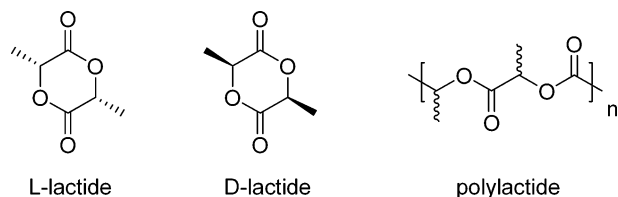


$\text{M} = \text{Sc, Y, Ln}; \text{X} = \text{C, N, O}; \text{D} = \text{N, O}$ = porphyrin dianion

One approach is to prepare monomeric complexes of the form L_2MX , (**I**) where L is bidentate, monoanionic ancillary, M is a G 3 or lanthanide element, and X is an alkoxy, alkyl, or amido coligand. Examples of such systems include benzamidinato complexes,^{10,11} and the related guanidinate-supported compounds.¹² Mixed N, O donor sets include a topographically similar chelating siloxy amido framework,¹³ and the C_2 -symmetric bis(oxazolines),¹⁴ A second class of compounds of the form LMX (**II**) exists where L is a dianionic ancillary. Many such examples have been prepared by the linking together of two monoanionic amidinate¹⁵ or amionopyridinate¹⁶ fragments in a

manner reminiscent of the G 4 *ansa*-metallocenes.^{17,18} Bridged bis(phenolate) ligands have found a variety of applications within lanthanide chemistry,^{19–26} and porphyrin rings have also been extensively employed as dianionic ligands.^{27–30}

Perhaps more desirable are comparatively understudied complexes of the form LMX_2 , (**III**) where L is also monoanionic. These complexes are advantageous to catalysis because they contain a pair of metal–organo bonds which offer themselves for catalysis; for the case of the lanthanide bis(oxazolines), generation may be effected simply by adjusting reagent stoichiometry.¹⁴ Perhaps a more obvious strategy is to increase the ligand bulk, as demonstrated for the amidinates with yttrium³¹ and scandium.³² We have also previously described a bulky guanidinate-supported lanthanum bis(alkoxide) which is a moderately successful initiator for the ring opening polymerization (ROP) of lactide.³³



Poly(lactic acid)s (PLAs) are the subject of much current interest since their biodegradable and biocompatible nature is ideal for a range of ecologically friendly applications to the medical, agricultural and packaging industries.^{34–39} The availability of monomer feedstocks from renewable resources has given PLAs an increasing prominence in the market place.⁴⁰ While a variety of lanthanide alkoxide initiators have shown a high activity for ROP reaction,^{41–44} recent developments have led to new discrete complexes based on a range of metals.^{45–47} The β -diketiminate anion⁴⁸ has been used independently by Coates *et al.*^{49,50} and Chisholm *et al.*^{51,52} to prepare efficient zinc-based initiators for PLA production, and Shen *et al.*⁵³ have recently performed the reaction with lanthanide complexes of the form **III** supported by these ligands. Chisholm *et al.* have described similar catalytic activity manifested by tris(pyrazolato) borate-supported complexes of magnesium,⁵⁴ and calcium,^{55,56} although bulkier ligands are required to elicit catalytically active complexes of yttrium.^{57,58}

Department of Chemistry, University of California, Berkeley and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720-1460

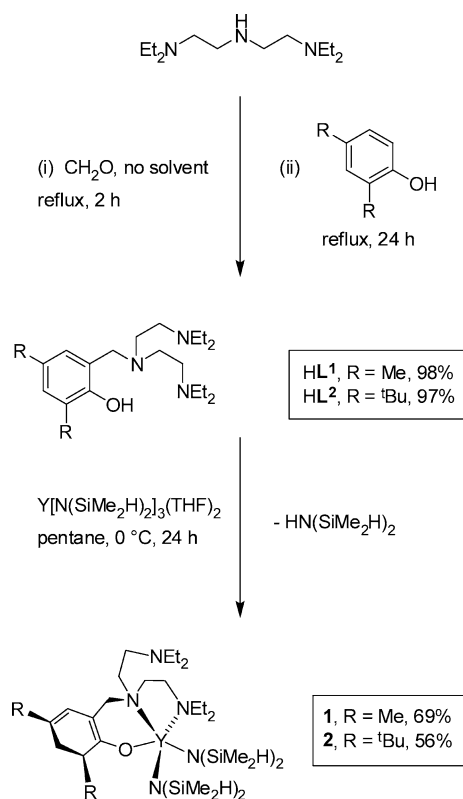
† Electronic supplementary information (ESI) available: Additional crystal and NMR data. See DOI: 10.1039/b600939e

The addition of neutral pendant arms is a convenient means of increasing denticity, and modifying metal/ligand stoichiometry, as demonstrated for the lanthanides with amidinate,⁵⁹ β -diketiminato⁶⁰ and triazacyclononane-derived moieties.⁶¹ The addition of pendant donors to bis(phenolate) ligands has produced efficient lanthanide based ROP initiators⁶² and a recent report has described a new class of mono(phenolate) ligands in which a pair of neutral pendant arms are used to support G 4 complexes.⁶³ Inoue and Matyjaszewski have used a similar phenoxytriamine ligand HL¹ to form non-colligand bearing Cu(I) complexes which exhibit moderate catalytic activity for the polymerization of acrylate, but monoanionic ancillaries with two neutral donors have yet to appear in lanthanide chemistry.⁶⁴ We envisaged that lanthanide complexes of the form LLnX₂ supported by such ligands would have excellent potential as initiators for the ROP reaction.

Results and discussion

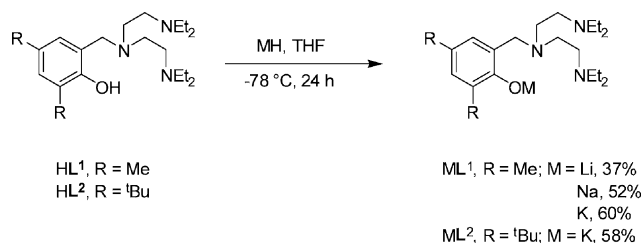
Synthesis of proligands and complexes

The potentially monoanionic proligands HL¹ (R = Me) was prepared in quantitative yield from 2,4-dimethylphenol, *N,N,N',N'*-tetraethyldiethylenetriamine and *para*-formaldehyde in methanol, *via* a two step method, modified from the literature procedure (Scheme 1).⁶⁴ We found that an increased reaction time for the first step gave an improvement in the yield of the final product. A concomitant increase in the purity of isolated material rendered chromatographic purification unnecessary. The *tert*-butyl-substituted analogue HL² was also prepared *via* this method from the appropriate phenol.



Scheme 1

Treatment of HL¹ with lithium hydride in THF at low temperature is low yielding, the salt LiL¹ being obtained in only 37% as colorless prisms after recrystallisation from pentane (Scheme 2). We were able to increase the productivity slightly by affecting deprotonation with either LiN(SiMe₃)₂ or ^{*n*}BuLi, which afford crystalline product in respectively 47% and 48% recovery. Carrying out the reaction with either sodium or potassium hydride in THF gives slightly higher yields of NaL¹ or KL¹ respectively. We were unable to access LiL² *via* any of the methods used to prepare LiL¹, and deprotonation with NaH was also failed to give NaL². However, we were ultimately able to obtain KL² in 58% yield *via* reaction of the proligand with potassium hydride.



Scheme 2

The ¹H NMR spectrum of LiL¹ recorded in *d*₈-toluene at 298 K shows a complex series of resonances in the region 2.0–3.0 ppm. A pair of singlets are observed at 2.35 and 2.40 ppm arising from the two aromatic methyl groups, while the remaining signals are attributed to the 14 terminal and bridging methylene protons—the benzyl protons nitrogen manifest as a broad singlet at $\delta = 3.77$. These broad resonances are indicative of a fluxional solution environment perhaps involving rapid exchange of the pair of pendant arms. Cooling of the sample to 273 K leads to a broadening of all the methylene resonances; further cooling giving increasingly broad signals. By 193 K the benzyl signal appears as a pair of broad singlets downfield at $\delta = 4.30$ and 4.53 ppm; presumably the slowing of exchange processes renders these protons inequivalent (see below). The remainder of the aliphatic region contains a series of broad overlapping resonances at this temperature. Warming the sample to its original temperature gives an identical spectrum. Further heating through the range 303–343 K results in similar resonance broadening to that observed at low temperatures. By 363 K the benzyl protons resonant as a sharp singlet at $\delta = 3.75$ ppm, and the remaining methylene protons manifest as a broad peak centered at $\delta = 2.55$ ppm (see ESI† for details). Similar spectra were recorded for NaL¹ and KL¹.

Our initial attempts to access complexes of the form LLnCl₂ were based on the assumption that salt metathesis of either YCl₃(THF)₃ or LnCl₃ with isolated ML¹ (M = Li, Na, K) or KL² would be reasonably straightforward. However this approach failed to yield any tractable products when performed in THF either at ambient temperature or 65 °C. When carried out in refluxing toluene over a period of several days we were similarly unable to isolate LLnCl₂. The reaction of HL with Ln[N(SiMe₃)₂]₃ (Ln = Y, La) was not a viable route to LLn[N(SiMe₂H)₂]₂ under various conditions. Treatment of either proligand with Y(CH₂SiMe₃)₃(THF)₂ also failed to yield tractable products.

We were slightly surprised by these results, however it has been shown that the introduction of sterically demanding ligands to lanthanide complexes can depend more on the precise nature

of the f element precursor than on the new ligand itself.^{65,66} This is born out by the result of the reaction of HL¹ with the less sterically congested silylamide Y[N(SiMe₂H)₂]₃(THF)₂ which provides facile access to L¹Y[N(SiMe₂H)₂]₂ (**1**) as an off-white oil in 69% yield; the complex L²Y[N(SiMe₂H)₂]₂ (**2**) is similarly obtained as a yellow microcrystalline solid from HL² in 56% yield (Scheme 1).

Molecular structure of L²Y[N(SiMe₂H)₂]₂ (**2**)

Single crystals of **2** were obtained as colorless prisms upon prolonged cooling of a pentane solution to -35 °C, and the structure determined by X-ray diffraction (Table 1). The compound crystallizes in the chiral monoclinic space group *P*2₁ and the primitive unit cell contains two independent molecules (Fig. 1). Three of the available four donor atoms in the phenoxytriamine fragment form bonds with the yttrium atom in **2** and the 5-coordinate center is completed by a pair of *N*-bound silylamido

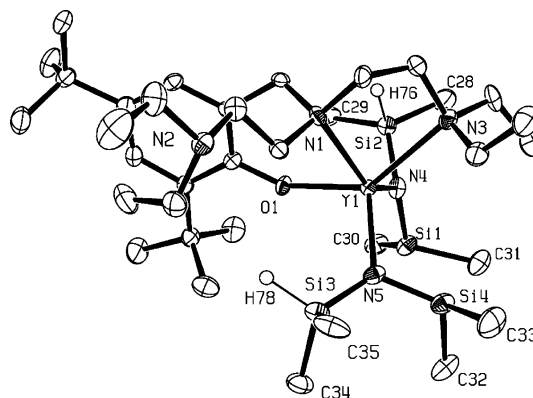


Fig. 1 Molecular structure of **2** with thermal ellipsoids drawn at the 30% probability level.

Table 1 Experimental data for the X-ray diffraction study of **2**

Empirical formula	C ₃₅ H ₇₈ N ₅ Si ₄ YO
Formula weight	786.28
Color	Colorless
Habit	Plates
Dimensions/mm	0.17 × 0.15 × 0.10
System	Monoclinic
<i>a</i> /Å	10.023(1)
<i>b</i> /Å	18.636(2)
<i>c</i> /Å	12.370(1)
β /°	101.087(1)
Volume/Å ³	2267.4(4)
Space group	<i>P</i> 2 ₁
<i>Z</i>	2
Calculate density/g cm ⁻³	1.152
<i>F</i> ₀₀₀	852.00
Exposure time/s	20
μ /mm ⁻¹	2.72
Temperature/°C	-160
$2\theta_{\max}$ /°	49.5
Total reflections	10290
Independent reflections	6857 (<i>R</i> _{int} = 0.035)
No. observations (<i>I</i> > 3.00σ(<i>I</i>))	3958
Reflection/parameter ratio	9.56
Residuals: <i>R</i> ; <i>R</i> _w ; <i>R</i> _{all}	0.066; 0.059; 0.066
Goodness of fit	1.08
Flack parameter	0.017(8)

coligands. The geometry at yttrium is best described as distorted from square-based pyramidal. Three of the basal positions are occupied by the aryl oxygen, the central nitrogen, one of the two diethylamino pendant donors which hang from the former; one of the silylamido coligands takes up the fourth basal while the second such coligand occupies the apical station. The second pendant arm does not coordinate to the metal. A similar situation has been observed in an aryl siloxide-bridged complex of yttrium where one of a pair of dimethylamido donors is bound to the lanthanide and a second such donor is not coordinated.⁶⁷

The coordinated arm bonds to the metal with a N(3)–Y(1) distance of 2.596(7) Å, which falls within the range 2.28–2.62 Å observed for N–Y bonds as does the N(1)–Y(1) contact of 2.607(5) Å between the central nitrogen and yttrium (Table 2).^{31,57,61,68–70} The latter interaction forms a N(1)–Y(1)–N(3) angle of 70.8(2)° with the pendant amido, and completes a 6-membered ring formed with the phenoxy oxygen atom, the pertinent features of which are the O(1)–Y(1) bond distance of 2.055(5) Å, and the acute N(1)–Y(1)–O(1) bond angle of 76.2(2)°. The pair of silylamido ligands form a N(4)–Y(1)–N(5) angle of 115.2(2)° at the metal, and have slightly different N–Y bond lengths of 2.221(6) and 2.307(6) Å for the basal and apical ligands respectively. There are subtle differences in the Y–Si inter-atomic distances also, the Y(1)–Si(2) and Y(1)–Si(4) measurements of *ca.* 3.15 and 3.24 Å respectively being significantly shorter than the comparable Y(1)–Si(1) and

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

Y(1)–O(1)	2.055(5)	O(1)–Y(1)–N(1)	76.2(2)	O(1)–Y(1)–N(3)	141.1(2)
Y(1)–N(1)	2.607(5)	O(1)–Y(1)–N(4)	93.6(2)	O(1)–Y(1)–N(5)	101.4(2)
Y(1)–N(3)	2.596(7)	N(1)–Y(1)–N(3)	70.8(2)	N(1)–Y(1)–N(4)	141.5(2)
Y(1)–N(4)	2.221(6)	N(1)–Y(1)–N(5)	103.2(2)	N(3)–Y(1)–N(4)	99.5(2)
Y(1)–N(5)	2.307(6)	N(3)–Y(1)–N(5)	105.6(2)	N(4)–Y(1)–N(5)	115.2(2)
Si(1)–N(4)	1.705(6)	N(4)–Si(1)–C(30)	115.1(3)	N(4)–Si(1)–C(31)	113.1(4)
Si(2)–N(4)	1.691(7)	C(30)–Si(1)–C(31)	107.4(4)	N(4)–Si(2)–C(28)	114.2(3)
Si(3)–N(5)	1.692(6)	N(4)–Si(2)–C(29)	117.3(4)	C(28)–Si(2)–C(29)	109.0(4)
Si(4)–N(5)	1.707(6)	N(5)–Si(3)–C(34)	114.0(4)	N(5)–Si(3)–C(35)	112.0(4)
Y(1)–Si(1)	3.478(8)	C(34)–Si(3)–C(35)	109.1(4)	N(5)–Si(4)–C(32)	116.4(4)
Y(1)–Si(2)	3.159(2)	N(5)–Si(4)–C(33)	115.7(4)	C(32)–Si(4)–C(33)	106.5(4)
Y(1)–Si(3)	3.541(7)	N(4)–Si(1)–H(78)	106.9	C(30)–Si(1)–H(78)	106.9
Y(1)–Si(4)	3.245(3)	C(31)–Si(1)–H(78)	107.0	N(4)–Si(2)–H(77)	105.0
Y(1)–H(75)	3.425(2)	C(28)–Si(2)–H(77)	105.1	C(29)–Si(2)–H(77)	105.1
Y(1)–H(76)	2.852(5)	N(5)–Si(3)–H(76)	107.2	C(34)–Si(3)–H(76)	107.2
Y(1)–H(77)	3.547(4)	C(35)–Si(3)–H(76)	106.9	N(5)–Si(4)–H(75)	105.8
Y(1)–H(78)	2.827(5)	C(32)–Si(4)–H(75)	105.5	C(33)–Si(4)–H(75)	105.9

Y(1)–Si(3) distances of 3.47 and 3.54 Å. The silyl hydrogen atoms H(76) and H(78) were located from the difference map, and sit at Y–H distances of 2.852(5) and 2.827(5) Å respectively. Although this is probably too far from the metal center to suggest there is additional stabilization of yttrium by the type of β (SiH) agostic interactions observed by Anwander *et al.*, the distances between the lanthanide and the other pair of silyl protons H(75) and H(77) are significantly greater at 3.425(2) and 3.547(4) Å respectively.⁶⁶

NMR Characterization of $L^2Y[N(SiMe_2H)_2]_2$ (**2**)

Variable temperature 1H NMR spectra of **2** recorded in d_8 -toluene are shown in Fig. 2. At 293 K a broad resonance with some fine structure is observed at 5.08 ppm, arising from the four silyl protons. A second broad signal at 4.29 ppm is attributed to the benzyl CH_2 , while the remaining methylene signals give a complex

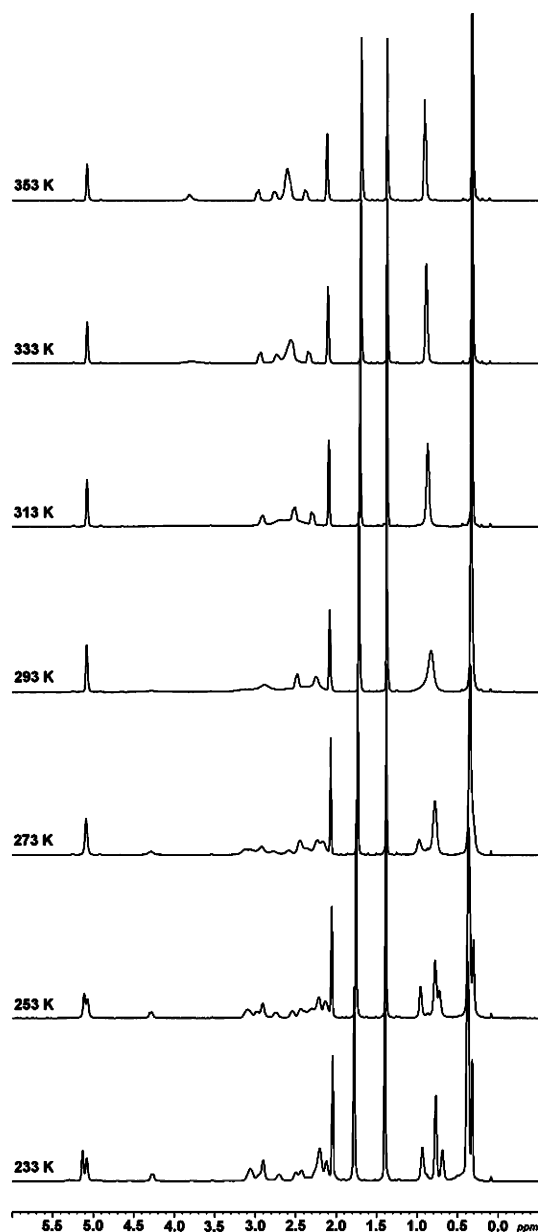


Fig. 2 Variable temperature 1H NMR spectra of **2**.

series of resonances between 3.30 and 2.10 ppm. Two sets of methyl resonances arise from the terminal groups on the donor arms silyl-bound groups on the coligands, and manifest themselves as broad singlets at 0.83 and 0.33 ppm respectively. The remainder of the spectrum is completed by *tert*-butyl signals at 1.72 and 1.38 ppm and the solvent. These features are consistent with the system being in rapid exchange on the NMR timescale.

Cooling to 273 K leads to a sharpening in the silyl proton signal, and a splitting of the methylene resonances into nine broad, overlapping peaks. The terminal methyl groups appear as two unequal resonances at 0.98 and 0.78 which integrate in the ratio 1 : 3. Further cooling to 253 K evokes additional splitting in the larger such resonance, and by 233 K, a set of peaks of relative integral 1 : 2 : 1 is observed in this region. The silyl-proton signal dissolves to a pair of resonances of equal intensity but differing shape over this temperature range, and this splitting pattern is replicated in the benzyl signal. At 253 K the silylmethyl groups give a pair of overlapping signals, which, on further cooling separate to a pair of signals of relative intensity 1 : 3. The methylene region undergoes a general broadening on initial cooling, followed by sharpening; we also know from 1H – 1H correlation spectra recorded over the same temperature range that resonances in this region undergo considerable chemical shift changes on cooling making direct inferences difficult (see ESI†). Further cooling leads to a broadening of all signals, and coalescence of all non-methylene resonances is observed at 203 K. Reheating the sample to 298 K gives a spectrum identical to that originally recorded. Increasing the temperature to 313 K sharpens the spectrum, apart from in the methylene region where there is some broadening. At 353 K the methylene region is resolved into four separate signals of relative integral 1 : 1 : 3 : 1. The system is presumably in the fast exchange regime under these conditions.

The exchange processes apparent from the NMR spectra can almost certainly be attributed to exchange process involving the two pendant donor arms. The pendant arm methyl signals at 233 K can be explained as follows: as the rate of exchange is slowed, the pair of methyl groups on the coordinated arm (inequivalent by since there is no mirror plane in the complex) are exchanging at a rate slower than the NMR timescale. This is in the slow exchange regime at 233 K, hence the appearance of two singlets; comparable exchange between methyl groups on the non-coordinated donor is presumably significantly faster, and a single resonance of appropriate intensity results.

The situation is similar for the Si–H signals. We can see from the essentially distorted square-based pyramidal crystal structure of **2** (Fig. 1) that the two silylamido ligands are inequivalent in the solid state. The apical ligand forms reasonably similar angles *via* yttrium with each of the atoms at basal positions, three of these angles fall within the range 101–106° and the fourth between the two silylamido ligands is not much larger at 115°. The basal coligand however exhibits a much wider range of angles: 93–141°, the largest forming at yttrium with the phenoxy oxygen. It is our belief that the latter infers a significant *trans* effect on the basal amido. The result is evident in the 1H NMR spectrum at 233 K where we attribute the sharper downfield signal at *ca.* 5.1 ppm to the in the silyl protons on the basal ligand, and the broader upfield resonance to its apical counterpart, our reasoning being that exchange is fast about the weaker Y–N bond. The same effect is also responsible for the silyl methyl signals, where faster exchange in one ligand

gives a single resonance and slower exchange (at 233 K) gives a pair one resonances; the coincidence of the former with one half of the latter results in the resonances of relative intensity 1 : 3 observed. There was no evidence in the ^1H NMR spectra to suggest $\beta(\text{SiH})$ agostic interactions exist in solution. The $^{89}\text{Y}\{^1\text{H}\}$ NMR spectrum of **2** recorded in C_6D_6 showed a single resonance at $\delta = 384.93$ ppm, but we did not observe any yttrium–hydrogen coupling from proton detected experiments.⁷¹ We thus conclude that the ligand arrangements observed in the crystal structure are enforced by steric considerations.

Ring opening polymerization activity

Lactide. The compounds **1** and **2** are active catalysts for the ROP of lactide, leading to PLA in high yield and with narrow polydispersity (PDI) within a few minutes of initiation (Table 3). We found the activity of **1** and **2** to be very similar (compare entries 1, 7, 16 with 2, 8, 17), and both give improved conversion and substantially narrower polydispersities than those obtained with the parent yttrium tris(amide) (entries 4, 10 and 19). Moderate control of the polymer molecular weight was observed with changes in $[\text{M}] : [\text{C}]$ ratio ($\text{M} = \text{monomer}$, $\text{C} = \text{catalyst}$), the largest molecular weight being obtained at a ratio of 1000 : 1, $M_n = 150\,200$; entry 17). There was no correlation between molecular weight and polydispersity, with the latter values ranging from 1.17 to 1.48 for experiments conducted over 30 min. Taken together, these observations are inconsistent with living polymerization of lactide.⁴⁶ Analysis of low molecular weight polylactide samples by ^1H NMR spectroscopy supports the incorporation of monomer into the Y–N bond of the initiator in a coordinative insertion manner, to give the ring-opened complex

$\text{LY}[\text{OCH}(\text{Me})\text{C}(\text{O})]_n\text{N}(\text{SiMe}_2\text{H})_2$ as evidenced by the appearance of a new $\text{C}(\text{O})\text{N}(\text{SiMe}_2\text{H})_2$ resonance.

The increasing PDI and concomitant drop-off in molecular weight observed over extended reaction times (entries 12–14) indicates that **2** is also an initiator for the transesterification process when monomer consumption is almost complete. Determination of the molecular weight of PLA samples by gel permeation chromatography (GPC) gave consistently close agreement with predicted values; an error of 5–10% is reasonable for measurements calibrated with polystyrene standards. The choice of solvent for polymerization systems can often have a significant effect of molecular weight as a consequence of these processes, although in our system toluene gave broadly similar results to those obtained with dichloromethane (compare entries 2, 8, 17 with 3, 9, 18).

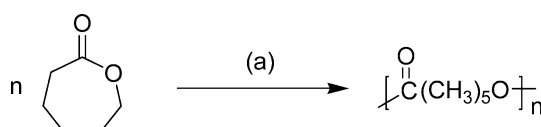
Polymer produced from D,L-lactide and analyzed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy showed no evidence of stereoselectivity in the polymerization; in essence the insertion of an (*R,R*) monomer infers no preference on the chain for a either a second such monomer, to give isotactic product, or an (*S,S*) unit forming heterotactic PLA. Similarly atactic polymer was obtained from L-lactide, this observation being consistent with epimerization during the polymerization process.

The spectroscopic studies also showed a significant amount of transesterification in products obtained from reactions run over longer than 1 h; we estimate the contribution of transesterification to the chain structure to be *ca.* 30% in these polymers based on the relative integrals of methine tetrads evident in their NMR spectra.^{72–75} Further evidence for transesterification competing with the ROP process is provided by the bimodal nature of some of the GPC traces observed for these samples.⁷⁶

Table 3 Polymerization of D,L-lactide with **1,2** and yttrium tris(amide)^a

Entry	Catalyst	Solvent	$[\text{M}]/[\text{C}]^b$	t/min	Yield ^c	$M_n (\times 10^4)$	PDI ^d
1	1	DCM	50	30	91	0.98	1.21
2	2	DCM	50	30	88	1.07	1.19
3	2	Toluene	50	30	87	1.20	1.22
4	$\text{Y}[\text{N}(\text{SiMe}_2\text{H})_2]_3(\text{THF})_2$	DCM	50	30	91	0.89	2.58
5	2	DCM	100	30	86	2.80	1.28
6	2	DCM	250	30	93	4.01	1.48
7	1	DCM	500	30	98	6.41	1.43
8	2	DCM	500	30	96	6.89	1.38
9	2	Toluene	500	30	98	7.20	1.42
10	$\text{Y}[\text{N}(\text{SiMe}_2\text{H})_2]_3(\text{THF})_2$	DCM	500	30	68	5.26	2.65
11	2	DCM	500	60	97	7.43	1.52
12	2	DCM	500	120	95	7.29	1.76
13	2	DCM	500	480	96	7.59	2.84
14	2	DCM	500	1440	97	6.21	3.20
15	2	DCM	750	30	95	11.21	1.21
16	1	DCM	1000	30	95	14.84	1.28
17	2	DCM	1000	30	97	15.02	1.17
18	2	Toluene	1000	30	95	12.95	1.18
19	$\text{Y}[\text{N}(\text{SiMe}_2\text{H})_2]_3(\text{THF})_2$	DCM	1000	30	54	12.72	3.21

^a General polymerization conditions: solvent = 10 ml; experiments conducted at 25 °C. ^b Monomer to catalyst ratio. ^c Yield: mass of polymer obtained/mass of monomer used. ^d Polydispersity index; determined by gel permeation chromatography, calibrated with polystyrene standards.

Table 4 Polymerization of ϵ -caprolactone with **2**^a

Entry	[M]/[C] ^b	t/min	Conversion ^c	M_n ($\times 10^4$)	PDI ^d
1	500	10	96	4.60	1.16
2	500	30	99	4.35	1.19
3	750	30	99	5.27	1.29
4	1000	30	98	7.54	1.24
5	1500	30	94	8.18	1.24
6	2000	30	75	7.91	1.31
7	500	60	99	6.45	1.29
8	500	120	93	8.62	1.45
9	500	240	97	9.48	1.55

^a General polymerization conditions: precatalyst = **2**; solvent = toluene, 10 ml; experiments conducted at 25 °C. ^b Monomer to catalyst ratio. ^c Conversion: determined by ¹H NMR spectroscopy. ^d Polydispersity index; determined by gel permeation chromatography, calibrated with polystyrene standards.

ϵ -Caprolactone. The catalytic activity of **2** for the ROP of ϵ -caprolactone was also examined (Table 4). The complex is an efficient initiator for this monomer, providing essentially quantitative conversion to product of narrow PDI. Similar to the lactide, the product molecular weight increases with the [M]/[C] ratio, the highest value of M_n = 81 800 being obtained for 1 500 monomer equivalents, entry 5 and that there was no correlation between chain length and polydispersity, although the latter was similarly narrow over a 30 min at ambient temperature. Longer reaction times broadened the range of chain lengths indicating that **2** is a catalyst for the transesterification process with this monomer also (entries 7 to 9), while shorter reaction times gave results comparable results were those obtained over 30 min (entry 1). However, spectroscopic studies indicated that transesterification of products is a much more significant issue with this monomer than in the PLA produced with **2**, and this is supported by the molecular weights observed in the products, which are all substantially lower than the predicted values.

Conclusions

Yttrium complexes supported by monoanionic ligands containing two pendant donors, a relatively unexplored class of lanthanide complex, have been prepared in high yield from phenoxytriimine proligands and yttrium tris-amide.^{60,67} This route to compounds **1** and **2** circumvents the salt and solvent inclusion issues prevalent in lanthanide complexes prepared *via* salt metathesis reactions.^{31,77–81} The choice of substituents on the amide is essential for the preparation of monomeric species as evidenced by our inability to prepare analogous complexes; X-ray diffraction and solution studies of have shown that these issues are primarily due to steric factors. Complexes **1** and **2** catalyze the ring opening polymerization of D,L-lactide and ϵ -caprolactone leading to narrow product polydispersities under mild conditions. The active species is also a catalyst for the transesterification reaction, particularly for the ϵ -caprolactone monomer, where this process reduces control over the molecular weight distribution.

Experimental

General comments

Where necessary, procedures were carried out under an inert atmosphere of argon by using a dual manifold vacuum/argon line and standard Schlenk techniques, or in an MBraun dry box (<1 ppm O₂/H₂O).⁸² All glassware, cannulae and Celite were stored in an oven at >373 K. Pentane, toluene, methylene chloride, diethyl ether and THF were purified by passage through a column of activated alumina and degassed with argon prior to use.^{83,84} Deuterated solvents were vacuum transferred from sodium/benzophenone (benzene, toluene and THF) or calcium hydride (dichloromethane, pyridine and acetonitrile). Where necessary G one metal hydride dispersions in mineral oil were placed in a Schlenk vessel under an inert atmosphere and washed three times with diethyl ether to remove the oil. The solid was subsequently dried thoroughly and stored in the dry box. Pyridine, chlorotrimethylsilane and ϵ -caprolactone were distilled from CaH₂. D,L-Lactide and L-lactide were recrystallized from THF prior to use. The compounds Y[N(SiMe₃)₂]₃,⁸⁵ Y[N(SiMe₂H)₂]₃(THF)₂,⁶⁵ Y(CH₂SiMe₃)₃(THF)₂,⁸⁶ and La[N(SiMe₃)₂]₃⁸⁷ were prepared according to literature procedures. NMR spectra were recorded at ambient temperature on Bruker AV-300, AVQ-400, AVB-400 and DrX-500 spectrometers. ¹H and ¹³C chemical shifts are given relative to C₆D₅H (7.16 ppm) or CHCl₃ (7.25 ppm) and coupling constants (*J*) are given in Hz. Proton and carbon NMR assignments were routinely confirmed by ¹H–¹H (COSY) or ¹H–¹³C (HMQC and HMBC) experiments. ⁸⁹Y chemical shifts were referenced externally to a 3.0 M solution of YCl₃ in D₂O.⁷¹ Gel permeation chromatography (GPC) was performed on an Agilent 1100 Series high pressure liquid chromatograph (HPLC) equipped with a PLgel 10 μ m miniMIX-B Guard (50 \times 4.6 mm, part no. 1510–1100) and PLgel 10 μ m miniMIX-B column (250 \times 4.6 mm, part no. 1510–5100). Samples were eluted with DMF at a rate of 0.333 ml min^{–1} at 30 °C. An Agilent 1100 series refractive index detector (RID) operating at positive polarity at 0.1 V calibrated with respect to polystyrene standards with a molecular weight range of 580–1 030 000 g mol^{–1} was used to analyze the samples. Infra-red samples were prepared as Nujol mulls and taken between KBr plates. Elemental analyses and mass spectral data were determined at the College of Chemistry, University of California, Berkeley. The X-ray structural determination was performed at CHEXRAY, University of California, Berkeley.

Preparations

HL¹ was prepared according to a modified literature procedure.⁶⁴ *N,N,N',N'*-tetraethyldiethylenetriamine (20.00 ml, 77.72 mmol) was added *via* syringe to a Schlenk vessel charged with *para*-formaldehyde (2.33 g, 77.72 mmol). The white suspension thus obtained was stirred at 80 °C for 2 h. After this time a solution of 2,4-dimethylphenol (9.36 ml, 78.00 mmol) in methanol (50 ml) was added. The resulting colorless solution was heated to reflux for a further 24 h during which time it became pale yellow. The solution was allowed to cool to ambient temperature and filtered through Celite. Concentration *in vacuo* gave the title compound as a viscous yellow oil; no further purification was necessary (26.88 g, 98%).

HL² was similarly prepared from 2,4-di-*tert*-butylphenol (11.08 g, 53.70 mmol) and obtained as a viscous orange oil (22.16 g, 97%). (Found: C, 74.6; H, 12.0; N, 10.0. Calc. for C₂₇H₅₁N₃O: C, 74.8; H, 11.85; N, 9.8%); $\nu_{\max}/\text{cm}^{-1}$ 2927s, 2809s, 1765s, 1677s, 1605s, 1479m, 1444m, 1387s, 1360s, 1299s, 1237s, 1202s, 1163m, 1086m, 878m, 799m (Nujol); δ_{H} (400 MHz, 298 K, C₆D₆) 10.80 (1 H, bs, OH), 7.49 (1 H, d, $^4J_{\text{HH}} = 2$, Ar-H), 6.99 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 3.54 (2H, bs, Ar-CH₂), 2.52 (4H, m, CH₂), 2.43 (4H, m, CH₂), 2.34 (8H, m, CH₂) 1.72 (9H, s, *t*Bu), 1.38 (9H, s, *t*Bu) and 0.91 (12H, t, $^3J_{\text{HH}} = 8$, CH₃); δ_{C} (100.6 MHz, 298 K, C₆D₆) 154.7, 140.0, 135.6, 124.0, 122.7, 122.6 (Ar), 58.1 (Ar-CH₂), 51.9, 50.6, 47.2 (CH₂), 35.1, 34.0 (*t*Bu-C_q), 31.7, 29.8 (*t*Bu-Me), 11.6 (CH₃); m/z 432 (M⁺, 100%), 403 (35, M - C₂H₅).

LiL¹ Method A. A suspension of LiH (90 mg, 11.46 mmol) in THF (10 ml) was stirred and cooled to -78 °C. To this was added a solution of HL¹ (1.60 g, 4.58 mmol) in THF (10 ml). The resulting off-white suspension was stirred at this temperature for 10 min. The cold bath was then removed and the mixture allowed to warm to ambient temperature. Stirring was continued for 24 h. After this time the solution was filtered through Celite and concentrated to afford an off-white solid. Recrystallisation of the crude material from pentane at -35 °C gave the product as colorless prisms (600 mg, 37%).

Method B. A solution of HL¹ (2.13 g, 6.10 mmol) in pentane (15 ml) was added at ambient temperature to a stirred solution of LiN(SiMe₃)₂ (1.53 g, 9.15 mmol) in pentane (10 ml). The resulting turbid solution was stirred for 15 h. The mixture was filtered and concentrated under reduced pressure. The crude material was re-dissolved in pentane and cooled to -35 °C to afford the product as colorless prisms (1.03 g, 47%).

Method C. A solution of HL¹ (2.53 g, 7.25 mmol) in THF (15 ml) was stirred and cooled to 0 °C. To this was added *t*BuLi (4.5 ml, 1.6 M in hexanes, 7.25 mmol) *via* syringe. The resulting pale yellow solution was stirred for 15 h and then filtered through a cannula. Concentration of the filtrate *in vacuo* gave a yellow solid. The crude material was re-dissolved in pentane and cooled to -35 °C to afford the product as colorless prisms (1.23 g, 48%). (Found: C, 70.9; H, 10.9; N, 11.6. Calc. for C₂₁H₃₈N₃OLi: C, 70.95; H, 10.8; N, 11.8%); $\nu_{\max}/\text{cm}^{-1}$ 3442s, 3261s, 1608s, 1342m, 1319m, 1091s, 1065s, 860m, 796m, 756m (Nujol); δ_{H} (400 MHz, 298 K, C₆D₆) 7.16 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 6.87 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 3.82 (2H, bs, Ar-CH₂), 2.76 (2H, m, CH₂), 2.48 (4H, m, CH₂) 2.45 (3H, s, CH₃), 2.39 (3H, s, CH₃), 2.36-2.18 (10H, m, CH₂) and 0.90 (12H, $^3J_{\text{HH}} = 8$, CH₃); δ_{C} (100.6 MHz, 298 K, C₆D₆) 173.0, 131.3, 130.2, 125.9, 123.8, 119.1 (Ar), 60.9 (CH₂) 51.0 (Ar-CH₂), 50.2, 46.0 (CH₂), 20.6, 18.4.0 (Ar-CH₃), 10.7 (CH₃); m/z 355 (M⁺, 100%), 326 (25, M - C₂H₅).

NaL¹. A suspension of NaH (260 mg, 10.82 mmol) in THF (10 ml) was stirred and cooled to -78 °C. To this was added a solution of HL¹ (1.51 g, 4.33 mmol) in THF (10 ml). The resulting pale yellow suspension was stirred for 10 min. The cold bath was then removed and the mixture allowed to warm to ambient temperature. Stirring was continued for 24 h. The solution was filtered through Celite and concentrated to afford a yellow solid. Recrystallisation from pentane at -35 °C gave the product as colorless prisms (835 mg, 52%). (Found: C, 67.8; H, 10.4; N, 11.3. Calc. for C₂₁H₃₈N₃ONa: C, 67.9; H, 10.3; N, 11.3%); $\nu_{\max}/\text{cm}^{-1}$

3441s, 3258s, 1606s, 1328m, 1178m, 1101s, 1085s, 1012s, 858m, 796m (Nujol); δ_{H} (400 MHz, 298 K, C₆D₆) 7.20 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 6.95 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 4.55 (2H, bs, Ar-CH₂), 2.44 (3H, s, Ar-CH₃), 2.33 (3H, s, Ar-CH₃), 2.19 (16H, bs, CH₂) and 0.85 (12H, t, $^3J_{\text{HH}} = 9$, CH₃); δ_{C} (100.6 MHz, 298 K, C₆D₆) 166.9, 131.7, 131.0, 125.3, 122.3, 115.9, (Ar), 70.4 (Ar-CH₂), 60.8, 50.6, 45.5 (CH₂), 20.7, 19.0 (Ar-CH₃), 9.6 (CH₃); m/z 371 (M⁺, 85%), 356 (25, M - CH₃).

KL¹. A stirred suspension of KH (487 mg, 12.18 mmol) in THF (10 ml) was cooled to -78 °C. To this was added a solution of HL² (1.70 g, 4.87 mmol) in THF (10 ml). The resulting yellow suspension was stirred for 10 min. The cold bath was then removed and the mixture allowed to warm to ambient temperature. Stirring was continued for 24 h. The solution was filtered through Celite and concentrated to afford a yellow solid. Recrystallisation from pentane at -35 °C gave the product as colorless prisms (1.13 g, 60%). (Found: C, 65.2; H, 9.9; N, 10.9. Calc. for C₂₁H₃₈N₃OK: C, 65.1; H, 9.9; N, 10.8%); $\nu_{\max}/\text{cm}^{-1}$ 3438s, 3253s, 1604s, 1338m, 1095s, 1020s, 862m, 796m (Nujol); δ_{H} (400 MHz, 298 K, C₆D₆) 7.20 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 7.00 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 3.67 (2H, bs, Ar-CH₂), 2.46 (3H, s, Ar-CH₃), 2.33 (3H, s, Ar-CH₃), 2.25 (16H, bs, CH₂) and 0.83 (12H, t, $^3J_{\text{HH}} = 9$, CH₃); δ_{C} (100.6 MHz, 298 K, C₆D₆) 167.7, 132.3, 130.9, 125.2, 122.0, 114.9 (Ar), 59.7 (Ar-CH₂), 52.3, 50.9, 45.7 (CH₂), 20.8, 19.7 (Ar-CH₃), 10.3 (CH₃); m/z 387 (M⁺, 80%), 358 (25, M - C₂H₅).

KL². A suspension of KH (600 mg, 14.78 mmol) in THF (20 ml) was stirred and cooled to -78 °C. To this was added a solution of HL² (2.56 g, 5.91 mmol) in THF (20 ml). The resulting pale yellow suspension was stirred at this temperature for 10 min. The cold bath was then removed and the mixture allowed to warm to ambient temperature. Stirring was continued for 24 h. After this time the solution was filtered through Celite and concentrated to afford a pale yellow solid. Recrystallisation from pentane at -35 °C gave the product as colorless prisms (1.61 g, 58%). (Found: C, 68.6; H, 10.7; N, 8.9. Calc. for C₂₇H₅₀N₃OK: C, 68.7; H, 10.7; N, 8.9%); $\nu_{\max}/\text{cm}^{-1}$ 3440s, 3265s, 1600s, 1461m, 1317m, 1087s, 879m, 798m, 731m (Nujol); δ_{H} (400 MHz, 298 K, C₆D₆) 7.58 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 7.26 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 2.61 (2H, s, Ar-CH₂), 2.43 (16H, bs, CH₂), 1.77 (9H, s, *t*Bu), 1.60 (9H, s, *t*Bu) and 0.93 (12H, t, $^3J_{\text{HH}} = 9$, CH₃); δ_{C} (100.6 MHz, 298 K, C₆D₆) 167.3, 135.4, 128.8, 128.7, 123.3, 122.7 (Ar), 61.0 (Ar-CH₂), 51.1, 47.0, 45.2 (CH₂), 35.1, 33.7 (*t*Bu-C_q), 32.3, 30.2 (*t*Bu-Me), 9.5 (CH₃); m/z 471 (M⁺, 100%), 456 (25, M - CH₃).

L¹Y[N(SiMe₂H)₂]₂ (1). A solution of HL¹ (210 mg, 0.60 mmol) in pentane (15 ml) was added dropwise to a stirred solution of Y[N(SiMe₂H)₂]₃(THF)₂ (378 mg, 0.60 mmol) in pentane (10 ml) at 0 °C. The resulting pale yellow solution was stirred at this temperature for 20 min. The cold bath was then removed and the solution allowed to warm to ambient temperature. Stirring was continued for a further 48 h. All volatiles were then removed under reduced pressure. The crude material was washed with pentane (3 × 15 ml) and dried *in vacuo* to afford the pure product as an off-white oil (290 mg, 69%). (Found: C, 49.5; H, 9.5; N, 10.0. Calc. for C₂₉H₆₆N₅OSi₄Y: C, 49.6; H, 9.5; N, 10.0%); $\nu_{\max}/\text{cm}^{-1}$ 2962s, 2808s, 2058s, 1585s, 1479m, 1396m, 1311m, 1260m, 1082s, 1021s, 880m, 701m (Nujol); δ_{H} (400 MHz, 298 K, C₆D₆) 7.03 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 6.72 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 5.16 (4H, sept,

$^3J_{\text{HH}} = 4$, SiMe₂H), 3.60 (2H, bs, CH₂), 2.87 (4H, m, CH₂), 2.57 (3H, s, Ar-CH₃), 2.51 (4H, m, CH₂), 2.31 (3H, m, CH₃), 2.29–2.11 (8H, m, CH₂), 0.92 (12H, t, $^3J_{\text{HH}} = 8$, CH₃), 0.43 (24H, d, $^3J_{\text{HH}} = 6$, SiMe₂H); δ_{C} (100.6 MHz, 298 K, C₆D₆) 160.1, 160.0, 132.1, 126.3, 123.5, 121.0 (Ar), 58.2 (Ar-CH₂), 49.1, 47.3, 46.7 (CH₂), 20.5, 16.9 (Ar-CH₃), 2.9 (CH₃), 1.5 (SiMe₂H); m/z 701 (M⁺, 100%), 686 (35, M – CH₃), 642 (90, M – SiMe₂H).

L²Y[N(SiMe₂H)₂]₂ (2). A solution of HL² (1.08 g, 2.49 mmol) in pentane (20 ml) was added dropwise to a stirred solution of Y[N(SiMe₂H)₂]₃(THF)₂ (1.57 g, 2.49 mmol) in pentane (20 ml) at 0 °C. The resulting pale yellow solution was stirred at this temperature for 20 min. The cold bath was then removed and the solution allowed to warm to ambient temperature. Stirring was continued for a further 48 h. Removal of all volatiles *in vacuo* followed by washing with pentane (3 × 15 ml) gave a pale yellow solid. This material was re-dissolved in pentane and cooled to –35 °C to afford the product as pale yellow prisms (1.10 g, 56%). (Found: C, 53.5; H, 9.9; N, 8.8. Calc. for C₃₅H₇₈N₃OSi₄Y: C, 53.5; H, 10.0; N, 8.9%; $\nu_{\text{max}}/\text{cm}^{-1}$ 2127s, 2063s, 1602s, 1365m, 1309m, 1241m, 1093s, 1018s, 894m, 837m, 796m, 763m (Nujol); δ_{H} (400 MHz, 298 K, C₆D₆) 7.60 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 7.50 (1H, d, $^4J_{\text{HH}} = 2$, Ar-H), 5.19 (4H, sept, $^3J_{\text{HH}} = 4$, SiMe₂H), 2.94 (2H, bs, CH₂), 2.50 (8H, m CH₂), 2.28 (8H, bs, CH₂), 1.83 (9H, s, tBu), 1.45 (9H, s, tBu), 0.88 (12H, bs, CH₃) and 0.43 (24 H, d, $^3J_{\text{HH}} = 4$, SiMe₂H); δ_{C} (100.6 MHz, 298 K, C₆D₆) 160.6, 160.5, 136.6, 124.7, 123.9 (Ar), 59.7 (Ar-CH₂), 53.6, 47.6, 45.7 (CH₂), 35.2, 33.8 (tBu-C_q), 31.8, 30.4 (tBu-Me), 3.38 (CH₃), 0.17 (SiMe₂H); δ_{Y} (24.5 MHz, 298 K, C₆D₆) 384.9 ppm; m/z 785 (M⁺, 85%), 699 (90, M – (SiMe₂H, C₂H₅)), 653 (400, M – N(SiMe₂H)₂).

General procedure for the polymerization of lactide

A Schlenk vessel was charged with the precatalyst (either **1**, **2** or Y[N(SiMe₂H)₂]₃(THF)₂) (10 mg, *ca.* 12 μmol) and 50–1000 equivalents of lactide. To this was added either dichloromethane or toluene (10 ml), and the resulting solution was stirred for a pre-determined period. In most cases stirring became difficult due to the viscosity of the mixture. After the prescribed time, polymerization was quenched by addition of 10 ml of a 1 M solution of HCl in methanol. The resulting mixture was poured into cold hexane to precipitate the polymer which was collected by filtration and dried to constant mass. ¹H and ¹³C{¹H} NMR spectra of polylactide were recorded in CDCl₃.

General procedure for the polymerization of ε-caprolactone

Toluene (10 ml) was added to a Schlenk vessel charged with **2** (20 mg, 25 μmol). To the resulting solution was added 500–2000 equivalents of ε-caprolactone and the resulting mixture was stirred for a pre-determined period. In most cases stirring became difficult due to an increase in mixture viscosity. After the prescribed time polymerization was quenched by the addition of 5 drops of a 1 M solution of HCl in methanol. All volatiles were then removed *in vacuo* and monomer conversion measured by ¹H NMR spectroscopy in CDCl₃.

Crystallography

Single crystals of **2** suitable for X-ray diffraction were obtained as colorless prisms from a concentrated solution in pentane at –35 °C. A crystal of appropriate size was mounted on a Kapton loop using Paratone N hydrocarbon oil prior to transfer to a Bruker-AXS SMART three circle CCD area detector diffractometer system equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å).⁸⁸ The crystal was centered in the beam and cooled by a cold nitrogen gas stream that had been temperature calibrated. Preliminary orientation matrices and cell constants were determined by collection of 60 10 s frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected using narrow (0.3° in ω) frame exposures and the raw data integrated with SAINT to a maximum 2θ value of 49.5°.⁸⁹ Data were analyzed for agreement using XPREP.⁹⁰ An empirical absorption correction based on symmetry-equivalent and repeated reflections was applied using SADABS.⁹¹ The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The structures were solved by direct methods and refined with tEXsan.⁹² All non-hydrogen atoms were refined anisotropically. The hydrogen atoms H75 through H78 were located in the difference map and placed at calculated positions. All other hydrogen atoms were assigned calculated positions and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$ for methyl groups.

CCDC reference number 295587.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600939e

Acknowledgements

We thank Craig L. Reeder for assistance with the GPC analysis and the National Science Foundation and Department of Energy for support of our research.

References

- 1 S. Kobayashi, *Lanthanides: Chemistry and Use in Organic Synthesis*, Springer, Berlin, 1999.
- 2 Y. W. Li, P. F. Fu and T. J. Marks, *Organometallics*, 1994, **13**, 439.
- 3 M. R. Gagne, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 275.
- 4 G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8103.
- 5 L. S. Mao, Q. Shen, M. Q. Zue and J. Sun, *Organometallics*, 1997, **16**, 3711.
- 6 V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.
- 7 W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233**, 131.
- 8 P. J. Bailey and S. Pace, *Coord. Chem. Rev.*, 2001, **214**, 91.
- 9 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
- 10 R. Duchateau, C. T. Vanwee, A. Meetsma and J. H. Teuben, *J. Am. Chem. Soc.*, 1993, **115**, 4931.
- 11 J. R. Hagadorn and J. Arnold, *Organometallics*, 1996, **15**, 984.
- 12 Z. P. Lu, G. P. A. Yap and D. S. Richeson, *Organometallics*, 2001, **20**, 706.
- 13 R. Duchateau, T. Tuinstra, E. A. C. Brussee, A. Meetsma, P. T. van Duijn and J. H. Teuben, *Organometallics*, 1997, **16**, 3511.
- 14 H. W. Gortlitz, M. Spiegler and R. Anwander, *J. Chem. Soc., Dalton Trans.*, 1999, 4287.
- 15 S. Bambirra, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 2001, **20**, 782.
- 16 H. Noss, M. Oberthur, C. Fischer, W. P. Kretschmer and R. Kempe, *Eur. J. Inorg. Chem.*, 1999, 2283.

- 17 F. Wild, L. Zsolnai, G. Huttner and H. H. Brintzinger, *J. Organomet. Chem.*, 1982, **232**, 233.
- 18 J. A. Smith, J. Vonseyl, G. Huttner and H. H. Brintzinger, *J. Organomet. Chem.*, 1979, **173**, 175.
- 19 P. L. Arnold, L. S. Natrajan, J. J. Hall, S. J. Bird and C. Wilson, *J. Organomet. Chem.*, 2002, **647**, 205.
- 20 H. Y. Ma, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2003, 4770.
- 21 Y. M. Yao, M. T. Ma, X. P. Xu, Y. Zhang, Q. Shen and W. T. Wong, *Organometallics*, 2005, **24**, 4014.
- 22 X. P. Xu, M. T. Ma, Y. M. Yao, Y. Zhang and Q. Shen, *Eur. J. Inorg. Chem.*, 2005, 676.
- 23 P. N. O'Shaughnessy, P. D. Knight, C. Morton, K. M. Gillespie and P. Scott, *Chem. Commun.*, 2003, 1770.
- 24 D. V. Gribkov, K. C. Hultsch and F. Hampell, *Chem.–Eur. J.*, 2003, **9**, 4796.
- 25 C. X. Cai, A. Amgoune, C. W. Lehmann and J. F. Carpentier, *Chem. Commun.*, 2004, 330.
- 26 C. X. Cai, L. Toupet, C. W. Lehmann and J. F. Carpentier, *J. Organomet. Chem.*, 2003, **683**, 131.
- 27 C. J. Schaverien, *Adv. Organomet. Chem.*, 1994, **36**, 283.
- 28 H. Brand and J. Arnold, *Coord. Chem. Rev.*, 1995, **140**, 137.
- 29 J. Arnold, C. G. Hoffman, D. Y. Dawson and F. J. Hollander, *Organometallics*, 1993, **12**, 3645.
- 30 C. J. Schaverien and A. G. Orpen, *Inorg. Chem.*, 1991, **30**, 4968.
- 31 S. Bambirra, M. J. R. Brandsma, E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 2000, **19**, 3197.
- 32 J. A. R. Schmidt and J. Arnold, *Chem. Commun.*, 1999, 2149.
- 33 G. R. Giesbrecht, G. D. Whitener and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 2001, 923.
- 34 E. Chiellini and R. Solaro, *Adv. Mater.*, 1996, **8**, 305.
- 35 R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841.
- 36 Y. Ikada and H. Tsuji, *Macromol. Rapid Commun.*, 2000, **21**, 117.
- 37 R. G. Sinclair, *J. Macromol. Sci., Pure Appl. Chem.*, 1996, **A33**, 585.
- 38 M. Vert, *Angew. Makromol. Chem.*, 1989, **166**, 155.
- 39 M. Vert, G. Schwarch and J. Coudane, *J. Macromol. Sci., Pure Appl. Chem.*, 1995, **A32**, 787.
- 40 S. K. Ritter, *Chem. Eng. News*, 2002, **80**, 26.
- 41 V. Simic, N. Spassky and L. G. HubertPfalzgraf, *Macromolecules*, 1997, **30**, 7338.
- 42 W. M. Stevels, M. J. K. Ankone, P. L. Dijkstra and J. Feijen, *Macromol. Chem. Phys.*, 1995, **196**, 1153.
- 43 B. M. Chamberlain, Y. P. Sun, J. R. Hagadorn, E. W. Hemmesch, V. G. Young, R. Pink, M. A. Hillmyer and W. B. Tolman, *Macromolecules*, 1999, **32**, 2400.
- 44 B. M. Chamberlain, B. A. Jazdzewski, M. Pink, M. A. Hillmyer and W. B. Tolman, *Macromolecules*, 2000, **33**, 3970.
- 45 B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.*, 2001, 2215.
- 46 O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147.
- 47 A. Lofgren, A. C. Albertsson, P. Dubois and R. Jerome, *J. Macromol. Sci., Rev. Chem. Phys.*, 1995, **C35**, 379.
- 48 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.
- 49 B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Oviatt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229.
- 50 M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 11583.
- 51 M. H. Chisholm, J. C. Huffman and K. Phomphrai, *J. Chem. Soc., Dalton Trans.*, 2001, 222.
- 52 M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2005, **44**, 8004.
- 53 M. Q. Xue, Y. M. Yao, Q. Shen and Y. Zhang, *J. Organomet. Chem.*, 2005, **690**, 4685.
- 54 M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold and K. Phomphrai, *J. Am. Chem. Soc.*, 2000, **122**, 11845.
- 55 M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2004, **43**, 6717.
- 56 M. H. Chisholm, J. Gallucci and K. Phomphrai, *Chem. Commun.*, 2003, 48.
- 57 D. P. Long, A. Chandrasekaran, R. O. Day, P. A. Bianconi and A. L. Rheingold, *Inorg. Chem.*, 2000, **39**, 4476.
- 58 D. P. Long and P. A. Bianconi, *J. Am. Chem. Soc.*, 1996, **118**, 12453.
- 59 K. Kincaid, C. P. Gerlach, G. R. Giesbrecht, J. R. Hagadorn, G. D. Whitener, A. Shafir and J. Arnold, *Organometallics*, 1999, **18**, 5360.
- 60 A. M. Neculai, D. Neculai, H. W. Roesky and J. Magull, *Polyhedron*, 2004, **23**, 183.
- 61 S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2001, 637.
- 62 F. M. Kerton, A. C. Whitwood and C. E. Willans, *Dalton Trans.*, 2004, 2237.
- 63 S. Groysman, E. Sergeeva, I. Goldberg and M. Kol, *Inorg. Chem.*, 2005, **44**, 8188.
- 64 Y. Inoue and K. Matyjaszewski, *Macromolecules*, 2003, **36**, 7432.
- 65 W. A. Herrmann, R. Anwender, F. C. Munck, W. Scherer, V. Dufaud, N. W. Huber and G. R. J. Artus, *Z. Naturforsch., B: Chem. Sci.*, 1994, **49**, 1789.
- 66 W. A. Herrmann, J. Eppinger, M. Spiegler, O. Runte and R. Anwender, *Organometallics*, 1997, **16**, 1813.
- 67 P. C. Shao, D. J. Berg and G. W. Bushnell, *Inorg. Chem.*, 1994, **33**, 6334.
- 68 P. L. Arnold, S. A. Mungur, A. J. Blake and C. Wilson, *Angew. Chem., Int. Ed.*, 2003, **42**, 5981.
- 69 M. E. G. Skinner and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 2002, 1694.
- 70 J. Wang, X. D. Zhang, D. M. Fan and X. Ling, *Chin. J. Inorg. Chem.*, 2001, **17**, 755.
- 71 D. R. Cary, G. E. Ball and J. Arnold, *J. Am. Chem. Soc.*, 1995, **117**, 3492.
- 72 J. E. Kasperczyk, *Macromolecules*, 1995, **28**, 3937.
- 73 M. Bero, J. Kasperczyk and Z. J. Jedliński, *Makromol. Chem.*, 1990, **191**, 2287.
- 74 K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, M. A. Doscotch, J. I. Siepmann and E. J. Munson, *Macromolecules*, 1997, **30**, 2422.
- 75 K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad and E. J. Munson, *Macromolecules*, 1998, **31**, 1487.
- 76 J. Baran, A. Duda, A. Kowalski, R. Szymanski and S. Penczek, *Macromol. Rapid Commun.*, 1997, **18**, 325.
- 77 Y. L. Zhou, G. P. A. Yap and D. S. Richeson, *Organometallics*, 1998, **17**, 4387.
- 78 H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, C. Janiak, C. Kolax, J. Loebel, S. Nickel and E. Palamidis, *Polyhedron*, 1988, **7**, 2307.
- 79 T. D. Tilley and R. A. Andersen, *Inorg. Chem.*, 1981, **20**, 3267.
- 80 P. L. Watson, *J. Chem. Soc., Chem. Commun.*, 1980, 652.
- 81 P. L. Watson, J. F. Whitney and R. L. Harlow, *Inorg. Chem.*, 1981, **20**, 3271.
- 82 E. F. Shriver and M. A. Bredson, *The Manipulation of Air-Sensitive Compounds*, Wiley, New York, 1986.
- 83 P. J. Alaimo, D. W. Peters, J. Arnold and R. G. Bergman, *J. Chem. Educ.*, 2001, **78**, 64.
- 84 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
- 85 D. C. Bradley, J. S. Ghotra and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021.
- 86 K. C. Hultsch, P. Voth, K. Beckerle, T. P. Spaniol and J. Okuda, *Organometallics*, 2000, **19**, 228.
- 87 W. J. Evans, R. E. Golden and J. W. Ziller, *Inorg. Chem.*, 1991, **30**, 4963.
- 88 *SMART: Area-Detector Software Package*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001–03.
- 89 *SAINTE: SAX Area-Detector Integration Program, V6.40*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003.
- 90 *XPREP: V6.12, Part of the SHELXTL Crystal Structure Determination Package*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001.
- 91 *SADABS: Bruker-Nonius Area Detector Scaling and Absorption, V2.05*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003.
- 92 *teXsan: Crystal Structure Analysis Software Package*, Molecular Structure Corporation, The Woodlands, TX, 1992–1995.