Synthesis, structure and oxidation of new ytterbium(II) bis(phenolate) compounds and their catalytic activity towards ε-caprolactone†

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Received 15th September 2006, Accepted 20th October 2006
First published as an Advance Article on the web 7th November 2006
DOI: 10.1039/b613409b

Two ytterbium(II) bis(phenolate) complexes, [L^RYb] where R = NMe_2 **1** and OMe **2**, have been synthesized and characterized, with **1** being structurally defined to be a dimeric species with an unsymmetrical coordination of the bis(phenolate) ligand which is preserved in solution. Both **1** and **2** have been oxidized by a variety of oxidants (AgX, ROH) to form heteroleptic ytterbium(III) bis(phenolate) complexes: [(L^{NMe_2})YbPF_6] (**3**), [(L^{NMe_2})YbOSO_2CF_3(thf)] (**4**), [(L^{NMe_2})YbOBu^t] (**5**), [(L^{NMe_2})YbOPh] (**6**), [(L^{OMe})YbOPh] (**7**). Compound **4** has been structurally characterized as having a quasi-octahedral environment around ytterbium, with significant inter species hydrogen bonding between CH_x and triflate fluorine atoms. Ligand exchange between Yb(N($SiMe_3$)$_2$)$_3$(thf)$_2$ and H_2L^R yielded [(L^{NMe_2})YbN($SiMe_3$)$_2$] (**8**) and [(L^{OMe})YbN($SiMe_3$)$_2$] (**9**), while metathesis from YbI_2(thf)$_2$ and K_2L^{OMe} reproducibly afforded the surprising oxidized product [(L^{OMe})$_2$YbK(dme)$_2$] (**10**), which was structurally characterized as having a distorted octahedral environment around the ytterbium(III) centre. Compounds **1–9** were used to polymerize ε-caprolactone at room temperature in toluene, with only compounds **1**, **2**, **8** and **9** exhibiting significant catalytic activities. The polycaprolactone formed in these reactions was generally of high molecular weight and polydispersities <1.90 in all but one case.

Introduction

Divalent lanthanide compounds have been known for many years, the most familiar example being samarium diiodide which has found countless applications in organic synthesis.[1–4] The ability of divalent samarium and ytterbium compounds to reduce a number of organic and inorganic substrates illustrates a unique versatility which can provide simple and elegant synthetic pathways to a number of heteroleptic trivalent lanthanide compounds.[5–7] These synthetic, redox pathways are superior to traditional metathesis salt elimination pathways, since product separation is usually more straightforward and salt inclusion compounds,[8] common among the lanthanides, are avoided. Furthermore, synthesis of an array of heteroleptic trivalent lanthanide compounds can be readily accessed from homoleptic divalent precursors by simple reaction with one of a number of oxidizing agents.[9–12] Simple synthetic routes to heteroleptic lanthanide(III) compounds are of interest, these species having demonstrated great utility in catalysis[13–15] and luminescence[16,17] studies.

More recently there has been interest in ring-opening polymerization reactions of cyclic esters such as lactide and ε-caprolactone by heteroleptic lanthanide compounds.[18–25] To date, many of the studies have involved the synthesis of the lanthanide compounds which have the general formula LMX, where L = a dianionic stationary ancillary ligand, M = a trivalent lanthanide metal and X = a monoanionic initiating group. Generally these catalyst precursors have been synthesized by reaction of the appropriate trivalent homoleptic lanthanide amide with an equivalent LH_2 ligand *via* a protiolytic ligand exchange (or transamination) reaction (eqn (1), R = Me, R′ = H or R, R′ = Me).[19–21,25]

$$[Ln(N(SiR_2R')_2)_3] + LH_2 \rightarrow [LLnN(SiR_2R')_2] + 2\,HN(SiR_2R')_2 \quad (1)$$

Modification of the initiating group requires the synthesis of a different homoleptic starting material. In addition to ligand exchange pathways, Shen and co-workers recently reported the successful synthesis of ytterbium(III) bis(phenolate) complexes, free from salt inclusion complications, by metathesis.[26] Their work, however, represents an exception to the general rule that metathetical synthesis of the lanthanide complexes is generally problematic.

Presented here is an alternative synthetic pathway to an LMX motif which arises from oxidation (by XY, where Y = Ag, H) of a homoleptic divalent LYb species. This study focuses on the synthesis and characterization of two new divalent ytterbium phenolate compounds and their subsequent oxidation to trivalent ytterbium heteroleptic compounds. Both divalent and trivalent ytterbium species presented herein have been examined in their reactivity towards the ring-opening polymerization of ε-caprolactone.

Results and discussion

Synthesis of divalent ytterbium compounds

The readily prepared H_2L^R ligands[27,28] (R = NMe_2, OMe) were treated with [Yb(N($SiMe_3$)$_2$)$_2$(thf)$_2$][29] in 1 : 1 molar ratio in hexanes depositing brick red crystals of **1** and a yellow powder of **2** (Scheme 1). The dimeric nature of **1** was confirmed by X-ray crystallography (see below). ^{1}H and ^{13}C NMR spectra in C_4D_8O

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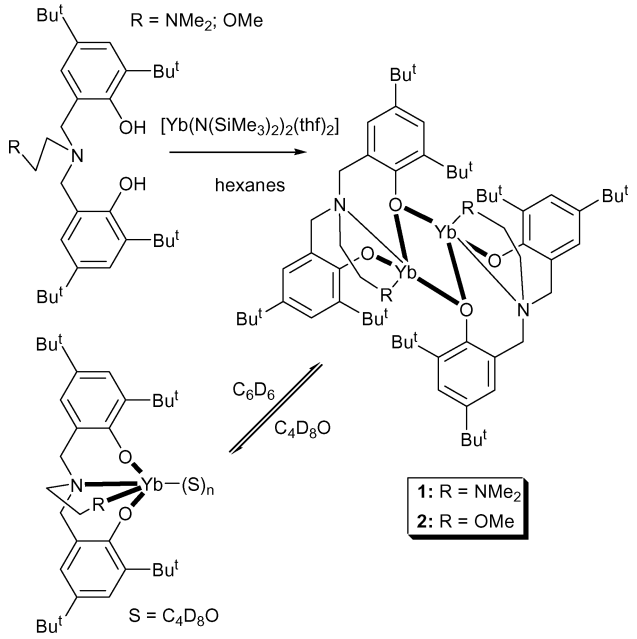
† The HTML version of this article has been enhanced with colour images.



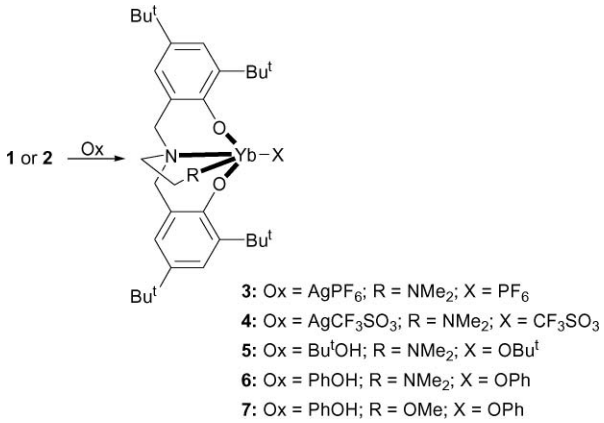
Scheme 1 Synthesis of **1** and **2**.

indicated a symmetrical arrangement of the bis(phenolate) ligands. Recording the ^{1}H NMR spectrum in C_6D_6 or C_7D_8 revealed a loss of symmetry of the bis(phenolate) ligand such that four Bu^{t} and aromatic hydrogen signals were observed, and consistent with the dimeric structure obtained in the solid state. A variable-temperature ^{1}H NMR study of **1** in C_7D_8 was unsuccessful in clearly resolving the $NCH_2CH_2NMe_2$ protons in the aliphatic region of the spectrum. This could suggest a fluxional process where the NMe_2 group reversibly coordinates to ytterbium in solution. It was not possible to obtain a NMR spectrum of **2** in C_6D_6 due to its poor solubility in non-donor solvents. Indeed, attempts to probe the dimeric nature of **2** in solution in more polar non-donor solvents such as dried CD_2Cl_2 were unsuccessful since immediate oxidation was observed and an unhelpful paramagnetic spectrum was recorded. From the similar solubility properties of **1** and **2** it may be that **2** also has a dimeric structure in the solid state and in non-donor solvents. Several attempts to grow crystals of **2** from a variety of solvent systems were unsuccessful. It is worthy of note that the aggregated dimers are readily broken up by the introduction of C_4D_8O as indicated by the ^{1}H and ^{13}C NMR spectra of **1** and **2**, where equivalent and symmetrical bis(phenolate) ligands were observed (Scheme 1). The coordinated solvent was, however, very labile since removal of the solvent in **1** followed by recording of the spectrum in C_6D_6 demonstrated the return of the dimeric species.

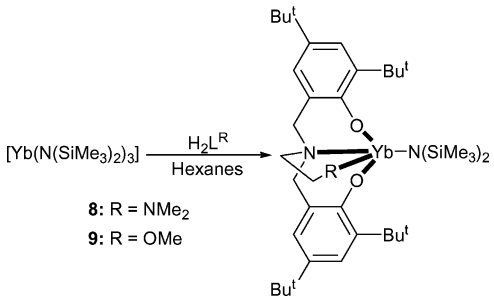
Oxidation of divalent ytterbium compounds

The successful synthesis of homoleptic (in the sense of one type of ligand) compounds **1** and **2** has now provided a pathway to a variety of different ytterbium(III) heteroleptic bis(phenolate) complexes by simple reaction with the appropriate oxidant. Several types of heteroleptic ytterbium(III) bis(phenolate) compounds were examined in search of the general LMX formulation (see Introduction), as these make ideal catalyst precursors for the ring-opening polymerization reactions of cyclic esters such as lactide and ε-caprolactone.

A number of different X groups have been attached to the metal atom by oxidation of the ytterbium(II) centre using an equivalent of the appropriate oxidizing agent (Scheme 2). As a result a series of ytterbium(III) bis(phenolate) alkoxides (X = OR; **5**, **6**, **7**) and cationic ytterbium(III) bis(phenolate) compounds (X = PF_6, O_3SCF_3; **3** and **4**) were synthesized. It was not possible to access the analogous amides *via* this route. Instead, protiolytic ligand exchange (transamidation) of $[Yb(N(SiMe_3)_2)_3]$ with an equivalent of the appropriate bis(phenol) (LH_2) was required (Scheme 3). It is not surprising that oxidation of **1** or **2** by $HN(SiMe_3)_2$ is not observed since no oxidation was seen in the initial exchange reaction between the bis(phenol), H_2L^R and $[Yb(N(SiMe_3)_2)_2(thf)_2]$ (Scheme 1) where **1** and **2** are generated in the presence of the free amide by-product, $HN(SiMe_3)_2$.



Scheme 2 Oxidation of homoleptic **1** or **2** to give LMX compounds.



Scheme 3 Synthesis of **8** and **9** *via* ligand exchange.

The cationic species $[(L^{NMe_2})Yb][PF_6]$ **3** and $[(L^{NMe_2})Yb][O_3SCF_3]$ **4** (Scheme 2) were simply generated in moderate yield by reducing the appropriate silver salt (to silver metal) in hexanes and thf respectively at room temperature. It is worthy of note that a donor solvent was required in generating **4**, as repeating the procedure in hexanes resulted in no reaction. Redox transmetalation reactions such as these often require the use of donor solvents to aid in the electron transfer process.[9] The paramagnetic nature of the ytterbium(III) compounds precluded acquisition of any usefully meaningful NMR spectroscopic data, but good quality elemental analysis data supports the formulations of **3** and **4**, along with melting point, and X-ray crystallographic characterization of **4** (see below). In the case of

4, elemental analysis calculations included coordination of thf and a dme molecule of solvation, since the same batch of crystals were used for elemental analysis and the X-ray study. The impetus behind the synthesis of compounds **3** and **4** was to investigate the effect of poorly nucleophilic initiating groups on the propensity towards ring-opening polymerization ability of cyclic esters, compared to nucleophilic alkoxide and amide groups (see below for polymerization results).

Compounds $[(L^{NMe_2})YbOBu^t]$ **5**, $[(L^{NMe_2})YbOPh]$ **6** and $[(L^{OMe})YbOPh]$ **7** were generated in a similar fashion to **4** and **5**, by reduction of the appropriate anhydrous alcohol (Scheme 2). However the oxidation reaction was very sluggish and required heating (50 °C). Indeed, the reactivity of **1** and **2** towards oxidation was both solvent and alcohol dependent, so that thf or dme were required for reduction of these sterically bulky alcohols. Surprisingly, heating **1** with Bu^tOH in hexanes for several days produced no visible signs of oxidation and only addition of thf (to break up aggregation) slowly causes oxidation to colorless **5** after 24 h of heating at 50 °C. This lack of reactivity towards the alcohols (especially in non-donor solvents), whilst not typical in these types of reactions, is probably best explained by the combination of inertness of the dimeric nature of **1** and **2** and the bulkiness of the substrate alcohol. A general reactivity profile indicated that reactivity mirrored both steric and electronic differences of the alcohols such that MeOH > PhOH > Pr^iOH > Bu^tOH. (Note that the corresponding isopropoxide and methoxide compounds are not reported here as repeated attempts to obtain analytically pure samples were unsuccessful.[30]) However, based on color change alone of each reaction (which is indicative of Yb(II) → Yb(III) oxidation), the reactivity order was readily established. Again the resulting paramagnetic, trivalent ytterbium species precluded any useful NMR spectroscopic data being obtained. However, satisfactory elemental analyses were obtained for all three compounds; note that for **5**, good analysis was found for the unsolvated form, whereas for **6** and **7** a molecule of dme was included in the analysis. Attempts to prove the presence of dme by way of obtaining a hydrolyzed NMR spectrum using CD_3CN/CF_3CO_2D to obtain a L^R : dme ratio were unsuccessful since there were many overlapping signals in the methyl and methylene region. However, the assumption of the presence of dme in **6** and **7** is reasonable for several reasons. Based on the X-ray crystal structures of **1**, **4** and **10**, which have five-, seven- and six-coordinate ytterbium respectively (see below), it is not unreasonable for **6** and **7** to have a unidentate or bidentate dme, which would give a six- or seven-coordinate ytterbium respectively (assuming L^R is four-coordinate). Further, in **6** and **7**, the OPh ligand offers less steric hindrance compared with the more bulky OBu^t ligand found in **5**. As such, coordination of thf in **5** is not feasible but dme coordination is likely in **6** and **7** on steric and other grounds.

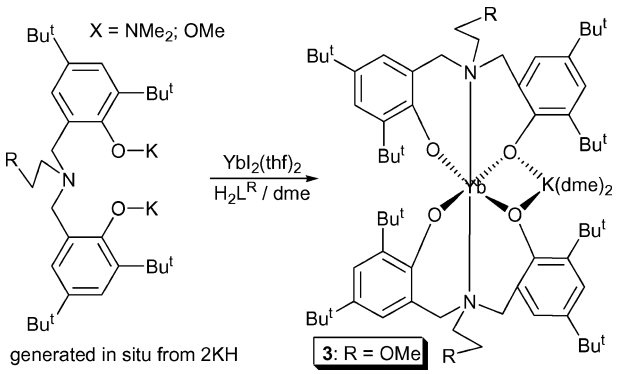
Synthesis of trivalent ytterbium compounds by ligand exchange reactions

In order to establish a greater understanding of the role of the initiating group (X) on the ring-opening polymerization of cyclic esters by ytterbium compounds, $[(L^{NMe_2})YbN(SiMe_3)_2]$ (**8**) and $[(L^{OMe})YbN(SiMe_3)_2]$ (**9**), which contained the amide initiator, were synthesized and characterized (Scheme 3). This was achieved by treatment of trivalent $[Yb(N(SiMe_3)_2)_3]$ with the appropriate H_2L^R (R = NMe_2 or OMe respectively). It is worthy of note that lanthanide ligand exchange reactions involving the sterically crowded $N(SiMe_3)_2$ ligand have been problematic, especially where the exchanging ligand is also sterically bulky.[31–33] This has led to other researchers using the less encumbered $[Ln(N(SiHMe_2)_2)_3(thf)_x]$ systems to achieve exchange with bis(phenol) compounds.

In this study, difficulties were encountered in achieving complete exchange in the attempted synthesis of the analogous lanthanum complexes of **8** and **9**, using $[La(N(SiMe_3)_2)_3]$. It may have been anticipated that the smaller ytterbium centre would have been less likely to cleanly displace two $N(SiMe_3)_2$ ligands but this was not the case. Possibly the smaller ytterbium results in such ligand crowding that in solution there maybe asymmetry in the Yb–N bond distances, such that one $N(SiMe_3)_2$ group becomes more labile and susceptible to protiolytic ligand exchange and displacement by the bis(phenol) group. As with the other ytterbium(III) compounds presented here, the principal source of characterization was by elemental analysis which gave good results for the predicted formulation.

Synthesis of a bimetallic ytterbium compound

As already mentioned in the introduction, metathetical synthesis of lanthanide compounds is often troublesome and plagued with salt inclusion or generation of lanthanide 'ate' complexes, this, however, in spite of Shen and Yao *et al.*[26] recently successfully synthesizing $L^{NMe_2}YbX$ where X = NPh_2, Me by a metathesis route *via in situ* generation of $Na_2L^{NMe_2}$ and $YbCl_3$. Similar attempts were employed in this study to synthesize compounds **1** and **2** by metathesis from ytterbium(II) iodide and the *in situ* generated dipotassium salt of the appropriate bis(phenolate). An unexpected potassium ytterbium(III) bis(phenolate) complex $[(L^{OMe})_2YbK(dme)_2]$ **10** formed, as identified by an X-ray study (see below) and elemental analysis (Scheme 4). It is believed that incomplete deprotonation of the bis(phenol) by potassium hydride caused oxidation of the ytterbium(II) centre and generation of **10**. Indeed, addition of at least a five-fold excess of potassium hydride to ensure complete deprotonation of the bis(phenol) yielded **1** and **2**. Furthermore, **10** could be reproducibly isolated by addition of H_2L^R to a reaction mixture of K_2L^R and YbI_2 in dme (R = OMe; NMe_2). Since compounds **1** and **2** have moderate and poor solubility respectively in non-donor solvents, metathesis



Scheme 4 Synthesis of the novel potassium–ytterbium(III) bimetallic compound **10**.

was abandoned since product separation from KI would be challenging. Characterization of **10** by elemental analysis gave satisfactory results by including one or two dme molecules in the calculated formulation. The X-ray crystal structure confirms two dme molecules present per molecule; desolvation upon drying the compound for elemental analysis can be accommodated by either formulation.

In a related study, Shen and co-workers[34] synthesized a similar alkali-metal ytterbium(III) bimetallic series *via* a more traditional route involving metathesis with two equivalents of $M_2L^{NMe_2}$ where M = Li, Na, K, with an equivalent of $YbCl_3$ to afford $[(L^{NMe_2})Yb_2M(thf)_x]$. Indeed **10** has been synthesized deliberately using a similar protocol to that of Shen's.

X-Ray crystallography of 1, 4 and 10

The results of the single crystal X-ray structure determination of **1** are consistent with that formulation in terms of stoichiometry and connectivity, as a dimer of $Yb_2(L^{NMe_2})_2$ stoichiometry, modelled as solvated with a molecule (disordered) of hexane; one half of the dimeric formula unit comprises the asymmetric unit of the structure. As in all of the present determinations, the ligand in **1** (Fig. 1) is a dianion, coordinating quasi 'mer' in **4** and **10** (Fig. 2 and 3, respectively). The centrosymmetric complex is unusual among lanthanide complexes of this ligand, not only in being binuclear, but also in that the YbO_2Yb core of the molecule is bridged by phenoxide oxygen atoms, the remainder of the metal atom coordination environment being made up of the other donors (N,N′,O) of the ligand, so that it is five-coordinate N_2YbO_3 (Fig. 1; Tables 1 and 2), the oxygen atoms being much more strongly bound than the nitrogen atoms. The oxygen atoms, nevertheless, comprise one face of the coordination polyhedron, the overall consequence being a residual void in an unusually sparse coordination sphere, partly compensated by an agostic approach from a *tert*-butyl hydrogen atom from the ligand in the alternate half of the dimer (Yb···C(133), H(133c) (1 − *x*, *y*, 1 − *z*) 3.271(9), 2.40 (est.) Å). The ligand disposition appears somewhat strained; the two

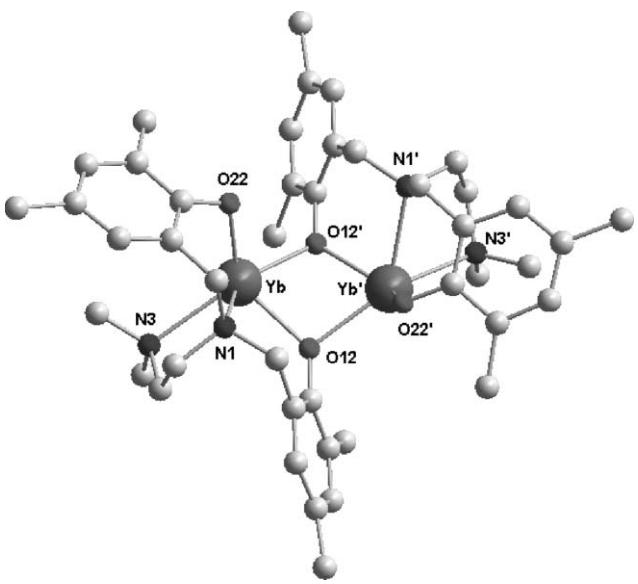


Fig. 1 Projection of a centrosymmetric dimer of **1**, normal to the YbO_2Yb 'plane'.

Table 1 The ytterbium environment, **1**

Atom	*r*	O(12)	O(22)	N(3)	O(12′)
N(1)	2.545(6)	79.6(2)	81.1(2)	72.4(2)	134.3(2)
O(12)	2.297(5)		129.9(2)	101.7(2)	71.6(2)
O(22)	2.225(6)			115.6(2)	90.9(2)
N(3)	2.569(7)				147.1(2)
O(12′)	2.349(5)				

Yb···Yb′ is 3.5651(9); O(12)···O(12′) is 2.717(7) Å; Yb–O(12)–Yb′ is 100.2(2), Yb,Yb′–O(12)–C(12) are 129.3(5), 122.7(4) and Yb–O(22)–C(22) 112.7(5)°.

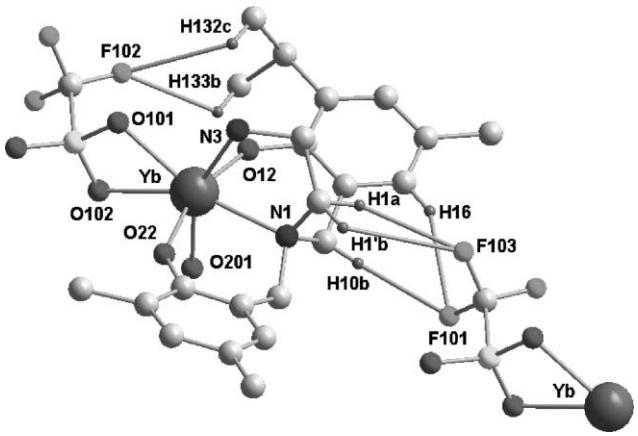


Fig. 2 Projection of a molecule of **4** showing selected hydrogen bonds. Selected carbon and hydrogen atoms have been omitted for clarity.

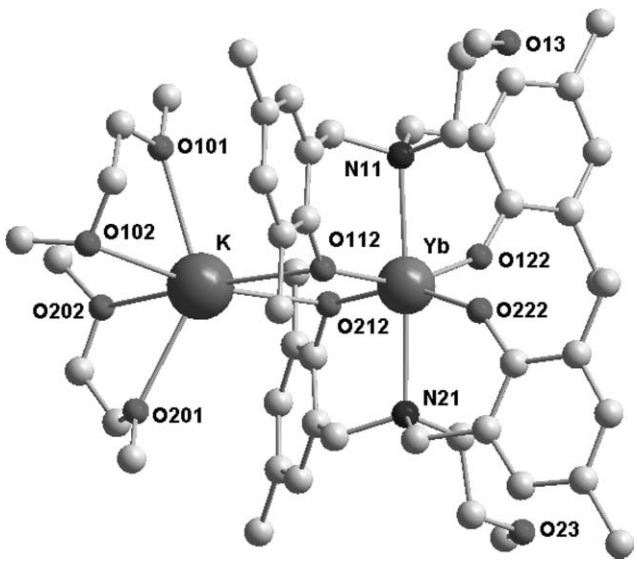


Fig. 3 Projection of a molecule of **10**, with hydrogen and *tert*-butyl methyl groups omitted for clarity.

aromatic planes lie at angles of 41.7(2), 43.1(2)° to the central Yb_2O_2 'plane' which is slightly folded ($\chi^2 = 3241$), with the YbN_2O_2 chelate ring of segment 2 severely folded across the N···O line in a 'boat' conformation, and an unusually small Yb–O–C angle at O(22).

The bulk of the bis(phenolate) ligand stabilizes the somewhat low coordination number of ytterbium(II). While there are countless examples of heteroleptic[35–39] and homoleptic[36,40–42]

Table 2 Ligand parameters, **1**, **4**, **10**

(a) The phenoxide chelate components

Compd/section	**1**/1	**1**/2	**4**/1	**4**/2	**10**/11	**10**/12	**10**/21	**10**/22
Angles (°)								
C(*n*2)–C(*n*1)–C(*n*0)	121.2(7)	119.5(7)	121.3(7)	120.7(8)	118.8(5)	119.1(4)	120.2(4)	120.2(5)
C(*n*1)–C(*n*2)–O(*n*2)	119.5(7)	119.7(7)	117.6(7)	118.0(7)	118.7(4)	119.5(5)	118.4(3)	118.8(3)
C(*n*1)–C(*n*0)–N(*n*1)	117.4(6)	112.7(6)	117.8(7)	117.5(7)	116.4(4)	118.4(4)	114.7(4)	115.8(4)
C(*n*2)–O(*n*2)–Yb	129.4(4)	112.6(4)	141.9(5)	141.0(5)	135.8(3)	144.5(4)	136.0(3)	142.5(2)
Torsion angles (°)								
O(*n*2)–Yb–N(1)–C(*n*0)	17.7(4)	0.7(4)	−32.2(6)	24.8(6)	−24.9(2)	35.7(3)	−29.3(2)	35.2(3)
Yb–N(1)–C(*n*0)–C(*n*1)	−62.8(7)	52.3(7)	66.0(8)	−61.4(9)	68.0(4)	−69.5(4)	71.0(5)	−70.9(5)
N(1)–C(*n*0)–C(*n*1)–C(*n*2)	65.2(9)	−72.5(9)	−60.4(11)	58.8(11)	−62.9(5)	58.3(5)	−63.3(7)	59.3(6)
C(*n*0)–C(*n*1)–C(*n*2)–O(*n*2)	−2.5(11)	2.8(10)	13.6(12)	−10.7(12)	1.8(6)	−9.2(5)	1.9(7)	−6.6(7)
C(*n*1)–C(*n*2)–O(*n*2)–Yb	−49.1(9)	67.3(7)	14.8(13)	−29.5(13)	45.9(6)	−15.0(6)	41.9(7)	−24.6(7)
C(*n*2)–O(*n*2)–Yb–N(1)	34.9(6)	−57.5(5)	−3.8(9)	19.3(9)	−29.0(4)	0.8(4)	−23.4(4)	8.1(5)
Ytterbium atom out-of-plane deviations, δ (Å), from the aromatic (C_6) ring planes; θ (°) is the dihedral angle between the latter								
δYb	1.22(1)[a]	2.04(1)	0.44(2)	0.86(2)	0.936(9)	0.314(10)	0.948(10)	0.565(10)
θ	50.1(3)		26.5(3)		34.9(2)		43.8(2)	

(b) Amine chelate rings of **1**, **4**

Compd/ligand	**1**	**4**[b]
Angles (°)		
Yb–N(1)–C(1)	110.5(5)	112.6(5)
N(1)–C(1)–C(2)	113.2(7)	113.6(7), 113(2)
C(1)–C(2)–N,O(3)	114.2(8)	110.6(9), 110(2)
C(2)–N(3)–Yb	103.2(5)	106.0(6), 106(2)
Torsion angles (°)		
N(3)–Yb–N(1)–C(1)	1.7(5)	−2.5(6),
Yb–N(1)–C(1)–C(2)	25.3(8)	−24.7(1), 33(2)
N(1)–C(1)–C(2)–N(3)	−57.8(10)	53(1),−58(2)
C(1)–C(2)–N(3)–Yb	54.2(7)	−52(1), 51(2)
C(2)–N(3)–Yb–N(1)	−27.8(6)	28.2(7), −24(1)

(c) dme chelate rings of **10**

Ligand *n*	1	2
O(*n*02)–K–O(*n*01)–C(*n*01)	64.1(05)	28.4(9)
K–O(*n*01)–C(*n*01)–C(*n*02)	4.7(6)	−52(2)
O(*n*01)–C(*n*01)–C(*n*02)–O(*n*02)	−52.3(10)	46(3)
C(*n*01)–C(*n*02)–O(*n*02)–K	68.9(9)	−13(2)
C(*n*02)–O(*n*02)–K–O(*n*01)	−41.3(4)	−9(1)

[a] δYb′ is −0.28(2) Å. [b] C(2) is disordered over two sites.

Table 3 [LYb(*O*-thf)X]: comparative geometries

X	*O*,*O*′-tfs[a]	Ph_2N[b]	Me (2 mols.)[b]
Distances (Å)			
Yb–N(1)	2.444(6)	2.516(3)	2.518(3), 2.513(3)
Yb–O(12)	2.093(6)	2.115(2)	2.119(2), 2.124(2)
Yb–O(22)	2.087(6)	2.112(2)	2.131(2), 2.130(2)
Yb–N(3)	2.495(9)	2.509(3)	2.536(3), 2.546(3)
Yb–O(thf)	2.366(7)	2.338(2)	2.325(3), 2.330(2)
Yb–X(X)	2.419(7) (O(101)) 2.487(7) (O(102))	2.256(3) (N)	2.440(4), 2.442(3) (C)
Angles (°)			
N(1)–Yb–O(12)	81.8(2)	79.71(9)	79.89(9), 81.14(9)
N(1)–Yb–O(22)	80.2(2)	79.34(9)	80.41(9), 79.21(9)
N(1)–Yb–N(3)	72.7(2)	70.7(1)	70.1(1), 70.2(1)
N(1)–Yb–O(thf)	83.4(3)	89.5(1)	104.3(1), 108.2(1)
N(1)–Yb–X(X)	148.0(3) (O(101)) 153.5(3) (O(102))	169.7(1) (N)	160.6(1), 159.0(1) (C)
O(12)–Yb–O(22)	160.4(2)	154.76(9)	154.4(1), 154.1(1)
O(12)–Yb–N(3)	89.0(3)	89.1(1)	96.8(1), 91.9(1)
O(12)–Yb–O(thf)	84.9(3)	82.9(1)	85.8(1), 84.1(1)
O(12)–Yb–X(X)	105.3(3) (O(101)) 101.7(3) (O(102))	99.7(1) (N)	100.5(1), 101.9(1) (C)
O(22)–Yb–N(3)	92.9(3)	89.1(1)	91.7(1), 97.2(1)
O(22)–Yb–O(thf)	85.5(3)	82.9(1)	83.4(1), 86.1(1)
O(22)–Yb–X(X)	94.1(3) (O(101)) 91.2(3) (O(102))	103.4(1) (N)	102.6(1), 102.6(1) (C)
N(3)–Yb–O(thf)	155.9(2)	159.7(1)	173.2(1), 175.9(1)
N(3)–Yb–X(X)	76.3(3) (O(101)) 133.2(2) (O(102))	99.3(1)	90.6(1), 88.9(1)
O(thf)–Yb–X(X)	127.8(3) (O(101)) 70.9(2) (O(102))	100.7(1)	95.0(2), 92.8(1)
O(101)–Yb–O(102)	56.9(3)		

[a] This work (**4**). [b] Ref. 26.

(*i.e.* identical anionic ligands) ytterbium(III) aryloxide compounds, there are relatively few ytterbium(II) homoleptic derivatives.[22,42–50] Indeed, most homoleptic aryloxy divalent ytterbium compounds accommodate molecules of solvation such as thf or dme. Of these, there is only one example which is dimeric and contains only one type of ligand, namely $[(ArO)Yb(\mu\text{-}OAr)]_2$ (OAr = 2,6-di-*tert*-butyl-4-methylphenolato) reported by Lappert and co-workers.[43,49] While the structure of **1** has a similar structural motif to that of Lappert's compound, it is the first example of an ytterbium(II) bis(phenolate) compound which is solvent free. Sun and co-workers[22] reported a methylene bridged bis(phenolate) ytterbium(II) compound which was also dimeric in nature, but, because of poor solubility, they could only characterize it with donor solvents present. Furthermore, the solid-state structure, which is preserved in solution (see above for NMR discussion) is the first example showing the unsymmetrical coordination of this type of bis(phenolate) ligand L^R to a metal centre.

The results of the structure determination of **4** are consistent with that formulation $[L^{NMe_2}Yb(O,O'\text{-tfs})(O\text{-thf})]$, solvated (interestingly) with an additional lattice molecule of dme, one formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure (Fig. 2). Despite the disorder in the peripheral components of the structure, the present determination provides an opportunity for comparison with two other diversely different $[L^{NMe_2}Yb(O\text{-thf})X]$ systems previously studied,[26] wherein X = (a) CH_3, (b) Ph_2N, (c) here being an oxyanion, which, in the circumstances, is found to coordinate as an *O*,*O*′-symmetrically bidentate ligand, of small bite; if considered to occupy a single coordination site, then the complex may be considered as quasi-octahedral, as in the other two complexes, although in all cases the distortions are large (Table 3). Of the three donor types, the amide appears the most strongly bound; the present *O*,*O*′-distances, being comparable with the Yb–C distance of the methyl adduct, presumably should be considered jointly as the next strongest donor, with the central amine nitrogen donor of LN(1), *trans* to X in all cases. The methyl adduct Yb–N(1) distance is comparable with that in the amide counterpart; that in the triflate counterpart is shorter, surprisingly, by *ca.* 0.07 Å. Surprisingly large influences are seen in the *cis*-bonds as well, all those of the present adduct being more or less shorter than in the others despite the bidentate nature of the X ligand – perhaps a consequence of ionic, *cf.*, presumably, more covalent interactions. There are long fluorine–CH_x intermolecular contacts (Fig. 2), for which the shortest have F(103) ⋯ C(1) ($x - 1$, y, z) 3.52(1) Å.

A previous study[34] has described the structural characterization of $L_2YbK(thf)_3$; the determination of the structure of **10** shows it to be similar, the three unidentate thf molecules being supplanted by a pair of dme chelate groups, the symmetry of the array increasing in the process to be quasi-2 in projection down the K ⋯ Yb vector (Fig. 3; Table 4), with the potassium atom six-coordinate. One formula unit devoid of crystallographic symmetry comprises the asymmetric unit of the structure. The geometry of the potassium environment is well-removed from octahedral, two of the *trans* angles being 167.5(1), 168.1(2), with the third only 136.7(3)°. The geometries of the L_2YbK cores of the two complexes – $(dme)_2$ and $(thf)_3$ adducts – are remarkably similar (Table 4), impacting

Table 4 Comparative metal atom environments, **10**, and [$L^{NMe_2}{}_2$YbK(thf)$_3$] (values for the latter in italics)

(a) The ytterbium environment

Atom	*r*	O(112)	O(122)	N(2)	O(212)	O(222)
N(1)	2.528(4)	78.7(1)	77.6(1)	177.2(1)	99.3(1)	103.7(1)
	2.538(3)	*77.18(8)*	*77.97(9)*	*176.98(8)*	*99.53(9)*	*103.19(9)*
O(112)	2.174(4)		155.9(2)	98.9(1)	88.0(1)	94.1(1)
	2.160(2)		*154.74(8)*	*100.10(8)*	*87.01(8)*	*94.26(8)*
O(122)	2.116(3)			104.7(1)	91.5(1)	95.7(1)
	2.112(2)			*104.62(9)*	*92.69(9)*	*95.73(9)*
N(2)	2.508(4)				79.2(1)	77.7(1)
	2.499(3)				*78.90(9)*	*78.22(9)*
O(212)	2.171(2)					156.9(1)
	2.189(2)					*156.95(9)*
O(222)	2.132(3)					
	2.128(2)					

(b) The potassium environment

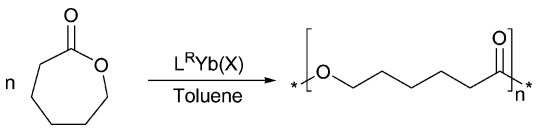
Atom	*r*	O(212)	O(101)	O(102)	O(201)	O(202)
O(112)	2.905(3)[a]	63.51(9)	96.2(1)	107.0(1)	120.6(2)	168.1(2)
O(212)	2.827(4)[a]		111.5(2)	167.5(1)	105.2(2)	104.6(2)
O(101)	2.795(6)			59.8(2)	136.7(3)	87.7(2)
O(102)	2.804(7)				86.4(2)	84.7(2)
O(201)	2.741(8)					61.1(2)
O(202)	2.813(5)					

The Yb···K distance is 4.000(1) Å; Yb–O(112, 212)–K are 102.97(9), 105.5(1)°. [a] Counterpart distances in the (thf)$_3$ complex are 2.733(2), 2.846(2) Å with an angle of 64.86(7)° between.[34]

noticeably only on the K–O(bridging) distances, the angle between also remaining essentially similar. It is noteworthy that both methoxide oxygen atoms remain pendant, unable to coordinate to the ytterbium centre presumably because of occlusion by the *tert*-butyl groups. As with **1**, the Yb–O and Yb–N bond distances of **10** are typical of six-coordinate Yb(III), with terminal Yb–O(122/212) being shorter than bridging Yb–O(112/222).

Polymerization of ε-caprolactone by various LMX complexes

The ytterbium compounds synthesized here present ideal candidates for studying the ring-opening polymerization of cyclic esters such as ε-caprolactone. This is because the compounds here contain a highly electropositive metal (ytterbium) and a stationary spectator ligand (L^R), both of which can lead to rapid and efficient polymerization of these monomers (Scheme 5). Polycaprolactone is among a growing number of polyesters to receive attention because of its numerous applications ranging from packaging



Scheme 5 Polymerization of ε-caprolactone by ytterbium compounds.

to drug delivery materials.[18,51–53] Recently Shen and Yao and coworkers[26] have investigated the ring-opening polymerization of ε-caprolactone by three ytterbium(III) bis(phenolate) compounds. The current study expands on their findings by investigating the effect of the initiating group (X) on polymerization activities. Compounds **1–4**, **6**, **8** and **9** were used to polymerize ε-caprolactone at various [monomer : catalyst] ratios at room temperature in toluene for various reaction times (Table 5). Of the catalysts investigated, complexes **8** and **9** (entries 6 and 10) were the most effective with high yields of polycaprolactone forming within 10 min (room temperature at 200 : 1 [monomer : catalyst]). Compounds **1** and

Table 5 Results from the polymerization of ε-caprolactone[a]

Entry	Initiator	Time/min	$[M]_0/[I]_0$	Yield[b] (%)	M_n (10^4) calc.[c]	$10^{-4}M_n$ (obs.)[d]	PDI
1	**1**	10	200	75	1.71	3.37	1.69
2	**1**	20	300	60	2.05	3.68	1.72
3	**1**	20[e]	300	70	2.40	3.29	1.67
4	**1**	20	400	52	2.37	3.10	1.69
5	**2**	30	200	48	1.10	7.12	1.63
6	**8**	7	200	85	1.94	0.90	1.49
7	**8**	10	200	100	2.28	1.59	1.63
8	**8**	20	300	70	2.40	5.08	1.80
9	**8**	40	400	54	2.47	6.75	1.90
10	**9**	10	200	90	2.05	1.28	2.27

[a] Polymerization conditions: toluene solvent, T = RT, $V_{tol}/V_{\varepsilon\text{-CL}} = 1.86$, [b] Yield: weight of dry polymer/weight of monomer used. [c] MW of ε-CL × $[M]_0/[I]_0$ × (% yield). [d] Determined by GPC analysis in toluene with calibration to polystyrene standards. [e] $T = 70°$ C.

2 (entries 1 and 5) were also effective in these polymerization reactions but were less active than **8** or **9**. Since **1** and **2** are both ytterbium(II) species, it is presumed that an initial oxidation (and concomitant monomer reduction) precedes the ring-opening polymerization of ε-caprolactone. The exact nature of these intermediates was not determined, although reaction of **1** with L-lactide and ε-caprolactone in a 1 : 1 Yb(II) : cyclic ester yields an instant color change from deep red to pale yellow which is indicative of ytterbium oxidation,[54] so that the reduced catalytic activity of **1** and **2** *vs.* **8** and **9** may be attributable to a deactivation process as a result of the initial redox chemistry.

The cationic compounds **3** and **4**, as well as the ytterbium(III) alkoxide compounds **5–7**, exhibited no activity towards polymerization of ε-caprolactone even with heating over extended reaction times (*i.e.* 80 °C, 24 h). It is clear from these data that initiating groups (*i.e.* the X in LMX) do certainly affect polymerization activities of ε-caprolactone. Most likely the initial ring-opening is very slow for compounds which show no polymerization of ε-caprolactone. Either lack of nucleophilicity of the non-coordinating anions, [PF_6] and [O_3SCF_3], or the large steric bulk of the alkoxide groups (OR) make compounds **4–7** poor initiating groups.

Increasing the monomer to catalyst ratio from 200 : 1 to 300 : 1 and 400 : 1 for catalysts **1** and **8** produced a steady decrease in percentage yield of polymer, consistent with a slower rate of polymerization due to lower catalyst concentration.

GPC analysis of the polymer samples indicated the rapid formation of high-molecular weight polymer at room temperature. Polydispersities, obtained for all but one (entry 10: 2.27), fell within a range from 1.43–1.90, indicative of some transesterification, with longer reaction times producing broader polydispersities. The efficacy of compound **9**, which produced polymer with a significant larger polydispersity in contrast to that produced by **8**, is most probably explained by the difference in side arm (OMe *vs.* NMe_2) coordination to the metal. If the OMe group in **9** was not coordinated to the ytterbium centre as tightly as the NMe_2 group in **8**, then possibly a larger catalytic pocket exists in **9** which facilitates transesterification reactions. A somewhat unusual finding was that some calculated molecular weights M_n were lower than the observed values. This could be because of partial catalyst deactivation resulting in fewer active sites and therefore higher molecular weight polymer being formed. This was most noticeably observed for the divalent ytterbium catalysts **1** and **2**. Possibly the redox chemistry involved in the first step of polymerization leads to extensive catalyst deactivation, leaving a smaller number of activation sites available for ring-opening polymerization and hence higher M_n values in these systems.

Conclusions

A number of ytterbium bis(phenolate) compounds have been synthesized and characterized which have the general LMX formulation by oxidation of the homoleptic divalent ytterbium compounds **1** and **2**. In three cases, **1**, **4** and **10**, the X-ray characterizations performed support the proposed formulations of these compounds. Alteration of the X group was shown to have a dramatic effect on ring-opening polymerization reactions of ε-caprolactone. In cases where the X group was an alkoxide (OR) or a non-coordinating anion (PF_6 or triflate) no ring-opening polymerization was observed.

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 were dried over sodium metal and purified by vacuum transfer. The reagents [$Yb(N(SiMe_3)_2)_2(thf)_2$],[29] [$Yb(N(SiMe_3)_2)_3$],[55] and H_2L^R (R = NMe_2; OMe)[27,28] were synthesized by the reported procedures indicated. The synthesis of $YbI_2(thf)_2$ was based on the reported method[56] (for lanthanide(III) chlorides) from ytterbium metal and mercury(II) iodide in thf by redox transmetalation. The anhydrous $YbCl_3$ was purchased from Cerac and used as received and stored in the glovebox. All other reagents were purchased from Acros and used as received except for ε-caprolactone which was dried over CaH_2 for 48 h and distilled at 10^{-4} Torr. In addition, light-sensitive silver salts were stored in the dark. 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 (^1H) and C_6D_6 or C_4D_8O (^{13}C). Elemental analyses (sealed ampoules under inert atmosphere) were performed by Midwest Microlab, Indianapolis IN. Lanthanide analyses were determined by EDTA titration using xylenol orange indicator and hexamine buffer.[57]

$[L^{NMe_2}Yb]_2$ (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 $H_2L^{NMe_2}$ (0.52 g, 1.00 mmol) at room temperature for 4 h. Upon addition, an immediate color change to deep red was observed with deposition of **1**·C_6H_{14} (0.52 g, 70%) as dark red crystals. Mp 220–222 °C (Found: C, 59.6; H, 8.3; N, 3.8. $C_{74}H_{122}N_4O_4Yb_2$ requires (**1**·C_6H_{14}) C, 60.1; H, 8.3; N, 3.8%); $\tilde{\nu}_{max}/cm^{-1}$ 2855s, 1601w, 1443s, 1415s, 1358m, 1304s, 1261s, 1203m, 1165m, 1107m, 1026s, 930m, 910m, 879m, 829m, 806s, 737m, 683w, 644w, 582w, 517w, 424w (Nujol); δ_H (500.1 MHz, C_4D_8O, 298 K) 1.25 (18H, s, Bu^t), 1.46 (18H, s, Bu^t), 1.78 (6H, s, NMe_2), 1.80 (2H, s, $NCH_2CH_2NMe_2$), 2.51 (2H, s, $NCH_2CH_2NMe_2$), 2.89 (2H, d, *J* 11.7, $ArCH_2N$), 4.14 (2H, d, *J* 11.7, $ArCH_2N$), 6.83 (2H, s, Ar), 7.08 (2H, s, Ar), δ_H (500.1 MHz, C_6D_6) 1.98–1.24 (36H, overlapping signals of Bu^t and $CH_2CH_2NMe_2$), 2.47 (12H, s, NMe_2), 2.96 (2H, d, *J* 12.0, $ArCH_2N$), 3.03 (2H, d, *J* 12.0, $ArCH_2N$), 4.87 (2H, d, *J* 12.0, $ArCH_2N$), 5.75 (2H, d, *J* 12.0, $ArCH_2N$), 7.12 (1H, s, Ar), 7.21 (1H, s, Ar), 7.51 (1H, s, Ar), 7.53 (1H, s, Ar), $\delta_{C\{H\}}$ (125.8 MHz, C_4D_8O, 298 K) 30.5 (CMe_3), 32.6 (CMe_3), 34.3 (CMe_3), 35.9 (CMe_3), 45.7 (NMe_2), 47.9 ($NCH_2CH_2NMe_2$), 60.3 ($NCH_2CH_2NMe_2$), 65.4 ($ArCH_2N$), 123.7 (arom-CH), 124.9 (arom-CBu^t), 127.2 (arom-CH), 129.1 (arom-CBu^t), 135.3 (arom-CCH_2N), 166.9 (arom-CO).

L^{OMe}Yb (2). 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_2L^{OMe} (0.51 g, 1.00 mmol) in hexanes (20 mL) precipitated a fine yellow powder from a red solution. Isolation of the powder from the red solution yielded **2** (0.46 g, 67%). Mp 178–180 °C (Found: C, 57.7; H, 7.6; N, 2.0. $C_{33}H_{51}NO_3Yb$ requires C, 58.05; H, 7.5; N, 2.05%); $\tilde{\nu}_{max}/cm^{-1}$ 2853s, 1601w, 1440s, 1412m, 1362m, 1323m, 1300m, 1260s, 1200w, 1165w, 1088s, 1065s, 1030s, 930m, 879m, 802s, 737w, 687w, 609w, 517w (Nujol); δ_H (500.1 MHz, C_4D_8O, 298 K) 1.24 (18H, s, Bu^t), 1.43 (18H, s, Bu^t), 2.58 (2H, t, *J* 5.0, NCH_2CH_2O), 2.81 (3H, s, OMe), 2.97 (2H, d, *J* 12.0, $ArCH_2N$), 3.02 (2H, t, *J* 5.0, NCH_2CH_2O), 4.17 (2H, d, *J* 12.0, $ArCH_2N$), 6.83 (2H, s, Ar), 7.08 (2H, s, Ar), $\delta_{C\{H\}}$ (125.8 MHz, C_4D_8O, 298 K) 22.7 (CMe_3), 22.8 (CMe_3), 31.6 (CMe_3), 33.1 (CMe_3), 46.2 (NCH_2CH_2O), 55.4 (NCH_2CH_2O), 62.0 (O*Me*), 70.5 ($ArCH_2N$), 120.8 (arom-*C*H), 122.1 (arom-*C*Bu^t), 124.3 (arom-*C*H), 129.1 (arom-*C*Bu^t), 132.8 (arom-*C*CH_2N), 163.9 (arom-*C*O).

$[(L^{NMe_2})YbPF_6]$ (3). A deep red hexanes (6 mL) solution of **1**·C_6H_{14} (0.74 g, 0.50 mmol) was treated with a hexanes (8 mL) solution of $AgPF_6$ (0.25 g, 1.00 mmol) at room temperature for 24 h. An immediate color change to pale yellow was accompanied by formation of a black precipitate (silver metal). The black solids were separated from the yellow solution and the hexanes removed *in vacuo* to reveal a yellow solid which was recrystallized from hexanes to afford a yellow powder of **3** (0.55 g, 62%). Mp 184–186 °C (Found: C, 50.2; H, 7.0; N, 3.2. $C_{37}H_{61}F_6N_2O_2PYb$ requires C, 50.3; H, 7.0; N, 3.2%); $\tilde{\nu}_{max}/cm^{-1}$ 1414m, 1202w, 1166w, 1103s, 1024s, 926w, 876w, 842s, 805s, 723s (Nujol).

$[(L^{NMe_2})YbOSO_2CF_3(thf)]$ (4). To a brick red powder of **1**·C_6H_{14} (0.68 g, 0.46 mmol) and a white powder of $AgOSO_2CF_3$ (0.26 g, 1.00 mmol) thf (9 mL) was added at room temperature for 12 h. The resulting pale yellow solution was separated from the black precipitate and concentrated to yield a yellow solid which was recrystallized from hexanes to yield **4** (0.49 g, 58%). X-Ray quality crystals were grown from a dme/hexanes mixture at room temperature. Mp 180–182 °C (Found: C, 51.4; H, 7.5; N, 2.7. $C_{43}H_{72}F_3N_2O_8SYb$ requires (**4**·dme) C, 51.3; H, 7.2; N, 2.8%); $\tilde{\nu}_{max}/cm^{-1}$ 1165m, 1103s, 1026s, 926w, 875m, 802s, 725w, 675w, 640w (Nujol).

$[(L^{NMe_2})YbOBu^t]$ (5). A thf (10 mL) solution of *tert*-butanol (0.10 g, 1.35 mmol) was added to a thf (10 mL) solution of **1**·C_6H_{14} (0.40 g, 0.27 mmol) and heated at 50 °C for 24 h. It took several hours of heating before any discernable color change was observed. After 24 h the solvent was removed to afford a light green yellow solid of **5** (0.33 g, 80%). Mp 175–178 °C (Found: C, 59.4; H, 7.95; N, 3.3. $C_{38}H_{63}N_2O_3Yb$ requires C, 59.35; H, 8.3; N, 3.6%); $\tilde{\nu}_{max}/cm^{-1}$ 2852s, 2360w, 1766w, 1604w, 1416s, 1362m, 1304s, 1261s, 1203m, 1165m, 1095s, 1025s, 914w, 875m, 833s, 802s, 744m, 675m, 528m, 447m (Nujol).

$[(L^{NMe_2})YbOPh]$ (6). A dme (10 mL) solution of phenol (0.26 g, 2.77 mmol) was added to a stirred dme (15 mL) solution of **1**·C_6H_{14} (1.00 g, 0.67 mmol) and heated at 50 °C for 11 h to give a yellow solution after which time the dme was removed to yield a yellow solid. Light yellow crystals of **6** (0.95 g, 81%) were grown at room temperature from a hexanes solution. Mp 173 °C (Found: C, 60.2; H, 7.6; N, 2.9. $C_{40}H_{59}N_2O_3Yb$ requires (for no dme) C, 60.9; H, 7.5; N, 3.55%. $YbC_{44}H_{69}N_2O_5$ requires (for one dme) C, 60.1; H, 7.9; N, 3.2%); $\tilde{\nu}_{max}/cm^{-1}$ 2854s, 1592w, 1335w, 1203w, 1161w, 1076s, 1022s, 924w, 875w, 802s, 760m, 694w, 579w, 528w, 451w (Nujol).

$[(L^{OMe})YbOPh]$ (7). Using a similar procedure to that described for the synthesis of **6**, treatment of **2** (0.50 g, 0.73 mmol) with phenol (0.10 g, 1.10 mmol) in dme (25 mL) with heating at 50 °C for 11 h, afforded a green yellow solution. Solvent removal and recrystallization from hexanes afforded crystals of **7** (0.48 g, 85%). Mp 171–173 °C (Found: C, 59.7; H, 7.55; N, 1.6. $C_{39}H_{56}NO_4Yb$ requires (for no dme) C, 60.4; H, 7.3; N, 1.8% $YbC_{43}H_{66}NO_6$ requires (for 1 dme) C, 59.6; H, 7.7; N, 1.6%); $\tilde{\nu}_{max}/cm^{-1}$ 2858s, 1770w, 1592m, 1296s, 1265s, 1203m, 1165m, 1076s, 1022s, 910w, 833m, 802m, 759m, 694m, 602w, 579w, 528w, 455w.

$[(L^{NMe_2})YbN(SiMe_3)_2]$ (8). To a stirred solution of $[Yb(N(SiMe_3)_2)_3]$ (0.65 g, 1.00 mmol) in hexanes (11 mL), $H_2L^{NMe_2}$ (0.52 g, 1.00 mmol) in hexanes (8 mL) was added at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for a further 48 h. The solvent was removed *in vacuo* to yield **8** as a yellow powder which was washed with cold hexanes (2 mL) to remove liberated amine (0.68 g, 79%). Mp 160–162 °C (Found: C, 57.0; H, 8.6; N, 4.6; Yb, 20.6. $C_{40}H_{72}N_3O_2Si_2Yb$ requires C, 56.1; H, 8.5; N, 4.9; Yb, 20.2%; $\tilde{\nu}_{max}/cm^{-1}$ 1257s, 1203m, 1169m, 1099m, 1022s, 984m, 926m, 876m, 930m, 837s, 741m, 675w, 526w (Nujol).

$[(L^{OMe})YbN(SiMe_3)_2]$ (9). Complex **9** was prepared by a procedure analogous to the procedure for **8**, except that H_2L^{OMe} (0.52 g, 1.00 mmol) was used in place of $H_2L^{NMe_2}$. Yellow needle-like crystals of **9** were obtained from a concentrated hexanes solution at room temperature (0.64 g, 76%). Mp 162–164 °C (Found: C, 55.3; H, 8.1; N, 3.5; Yb, 20.8. $C_{39}H_{69}N_2O_3Si_2Yb$ requires C, 55.55; H, 8.25; N, 3.3; Yb, 20.5%; $\tilde{\nu}_{max}/cm^{-1}$ 1260s, 1209m, 1140w, 1100m, 1024s, 984m, 876m, 930w, 839s, 741m, 675w (Nujol).

$[(L^{OMe})_2YbK(dme)_2]$ (10). A thf solution (10 mL) of $YbI_2(thf)_2$ (0.29 g, 0.51 mmol) was treated with a thf (8 mL) solution of K_2L^{OMe} (0.29 g, 0.50 mmol) [generated *in situ*. from KH (1.0 mmol) and K_2L^{OMe} (0.50 mmol)]. Initially a dark red solution and a white precipitate of KI formed and subsequently lightened to yellow after stirring for 2 h at room temperature. The solvent was removed to yield a pale yellow solid which was extracted with hexanes from precipitated KI. Removal of hexane and recrystallization from dme afforded yellow crystals of **10** (0.43 g, 60%). Mp 225 °C (Found: C, 63.4; H, 8.2; N, 2.05%. $C_{70}H_{112}KN_2O_8Yb$ requires (for one dme) C, 63.6; H, 8.5; N, 2.1%. $C_{74}H_{122}KN_2O_{10}Yb$ (for two dme's) C, 62.95; H, 8.7; N, 2.0%; $\tilde{\nu}_{max}/cm^{-1}$ 2850s, 2727w, 1605w, 1416m, 1300m, 1281m, 1261m, 1234m, 1203w, 1115w, 1084m, 1018w, 933w, 879w, 833m, 802m, 740w, 528w, 444w (Nujol).

A typical polymerization procedure with ε-caprolactone

A toluene (1.000 mL) solution of the appropriate catalyst (see Table 5) (0.0631 mmol for 1 : 100; 0.0315 mmol for 1 : 200; 0.0158 mmol for 1 : 300; 0.0079 mmol for 1 : 400), was added to ε-CL (0.700 mL; 6.317 mmol) and toluene (0.300 mL) at room temperature in a glovebox. After an appropriate time (Table 5) the vigorously stirred reaction mixture started to gel, at which time an aliquot (*ca.* 0.2 mL) was taken from the reaction mixture, removed

from the glovebox and quenched with 5% M HCl-MeOH solution. The precipitated polymer was filtered off from the solution and was thoroughly washed with MeOH and dried to yield a white powder which weighed to give a yield and was analyzed by ^{1}H NMR spectroscopy ($CDCl_3$) (Table 5). The polymer was also analyzed by GPC to determine molecular weight distribution data.

X-Ray crystallography-structure determinations

Single crystals suitable for X-ray crystallography of **1**·C_6H_{14}, **4**·dme and **10** were grown (see above). Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo-Kα radiation; λ = 0.7107_3 Å) yielding $N_{t(otal)}$ reflections, these merging to N unique after 'empirical/multiscan' absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered 'observed' and used in the full matrix/large block least squares refinements on F^2, refining anisotropic displacement parameter for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being included, constrained at estimates. Conventional residuals R, R_w are cited at convergence (weights: $(\sigma^2(F^2) + n_wF^2)^{-1}$. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system.[58] Pertinent results are presented below and in the Tables and Figures; where metal atom environments are shown in matrix format, r is the metal–ligand atom distance (Å), other entries being the angles (°) subtended by the relevant atoms at the head of the row and column. Individual variations in procedure are cited under 'variata'.

CCDC reference numbers 272546, 272547 and 621007.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613409b

Crystal/refinement data

1·C_6H_{14}. $C_{74}H_{122}N_4O_4Yb_2$, M = 1478.1. Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 14.049(5), b = 9.693(5), c = 26.772(8) Å, β = 91.352(5)°, V = 3645 Å^3. D_c (Z = 2 dimers) = 1.34_7 g cm^{-3}. μ_{Mo} = 2.6 mm^{-1}; specimen: 0.09 × 0.09 × 0.06 mm; 'T'$_{min/max}$ = 0.85. $2\theta_{max}$ = 58°; N_t = 34030, N = 9089 (R_{int} = 0.063), N_o = 6814; R = 0.063, R_w = 0.13 (n_w = 7.2). T *ca.* 153 K.

Variata: The solvent residue was modelled as disordered about a crystallographic inversion centre, fragment site occupancies being set at 0.5 after trial refinement.

4·dme. $C_{43}H_{72}F_3N_2O_8SYb$, M = 1007.2. Orthorhombic, space group $P2_12_12_1$ (D^4_2, no. 19), a = 11.110(1), b = 14.063(2), c = 31.033(4) Å, V = 4849 Å^3. D_c (Z = 4) = 1.38_0 g cm^{-3}. μ_{Mo} = 2.03 mm^{-1}; specimen: 0.45 × 0.18 × 0.16 mm; 'T'$_{min/max}$ = 0.74. $2\theta_{max}$ = 65°; N_t = 27152, N = 15915 (R_{int} = 0.031), N_o = 14028; R = 0.058, R_w = 0.093. T *ca.* 170 K.

Variata: Refinement on $|F|$ (n_w = 0.001); Friedel data were retained distinct, x_{abs} refining to −0.01(1). The solvent molecule was modelled as disordered over two sets of sites, as also was the R/NMe_2CH_2 component of the pendant chelate, and *tert*-butyl group 15, and the coordinated thf molecule, site occupancies of all being set at 0.5 except the *tert*-butyl components which refined to 0.71(1) and complement, in concert with the NMe_2CH_2 ring component.

10. $C_{74}H_{122}KN_2O_{10}Yb$, M = 1412.1. Triclinic, space group $P\bar{1}$ (C^1_i, no. 2), a = 14.057(1), b = 14.137(1), c = 23.703(2) Å, α = 99.451(1), β = 95.457(2), γ = 119.492(1)°, V = 3958 Å^3. D_c (Z = 2) = 1.18_4 g cm^{-3}. μ_{Mo} = 1.29 mm^{-1}; specimen: 0.35 × 0.35 × 0.25 mm; 'T'$_{min/max}$ = 0.77. $2\theta_{max}$ = 58°; N_t = 36801, N = 19227 (R_{int} = 0.026), N_o = 16330; R = 0.043, R_w = 0.084 (n_w = 14), T *ca.* 298 K.

Variata: Data were measured on a capillary mounted specimen at room-temperature; attempted measurement at low temperature was accompanied by specimen destruction. *tert*-Butyl group 225 was modelled as disordered over two sites, occupancies set at 0.5.

Acknowledgements

The authors are grateful to Professor Malcolm H Chisholm and Dr. Keith Quisenberry at The Ohio State University for supplying GPC data. Financial support from ND EPScOR program and REU NSF CHE 0243832 (for CRN) is gratefully acknowledged.

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