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Synthesis, Reactivity, and Characterization of Amine Bis(phenolate) Lanthanide Complexes and Their Application in the Polymerization of ϵ-Caprolactone

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A series of amine bis(phenolato)lanthanide methyl and amido complexes were synthesized by general salt metathesis reaction in this paper. The reaction of anhydrous lanthanide trichlorides with 1 equiv of sodium amine bis(phenolate) LNa$_2$ [L = $Me_2NCH_2CH_2N\{CH_2$-(2-O-C_6H_2-Bu$^t_2$-3,5)$\}_2$] in THF at room temperature gave the amine bis(phenolate) lanthanide chlorides LLnCl(THF) (Ln = Yb (**1**), Ln = Er (**2**)). Complexes **1** and **2** can be used as starting materials to prepare amine bis(phenolate) lanthanide derivatives. Complexes **1** and **2** reacted with lithium methyl and lithium amide, respectively, to give the corresponding lanthanide methyl and amido products LLnMe(THF) (Ln = Yb (**3**), Ln = Er (**4**)) and LLnNPh$_2$(THF) (Ln = Yb (**5**), Ln = Er (**6**)). These complexes were well characterized by elemental analyses and IR spectra. The definitive molecular structures of complexes **1**, **2**, **3**, **5**, and **6** were provided by single-crystal X-ray analyses. Reactivity studies of complexes **3**, **5**, and **6** have shown them to be efficient initiators for the ring-opening polymerization of ϵ-caprolactone.

Introduction

Over the past decade, significant efforts to explore ligands other than the traditional ancillary ligand bis(cyclopentadienyl) set in organometallic chemistry have led to the fruitful design of new nonmetallocene complexes.[1] Of these new alternatives, bridged bis(phenolate) ligands have received increasing attention as ancillary ligands, because they, as dianionic ligands, have the advantage of avoiding ligand redistribution reactions and can easily be prepared in one step from simple reagents, which thus allows for the systematic variation of the steric and electronic properties of the bisphenolic portion. Moreover, many of these kinds of complexes of transition and main group metals have been found to be active catalytic precursors for the polymerization of olefins and α-olefins in the presence of cocatalysts, and efficient initiators for the polymerization of some polar monomers.[2−4] In recent years, the application of bridged bis(phenolate) anions as ancillary ligands in group 3 and lanthanide chemistry led to a variety of heteroatom-bridged phenoxo lanthanide derivatives and to subtle reactions in this chemistry.[5] For example, biphenolate rare-earth-metal amido complexes were active catalysts for the hydroamination/cyclization of aminoalkynes and aminoalkenes;[5e] alkoxy-amino bis(phenolate) lanthanide alkyl and amido complexes can initiate the ring-opening polymerization of lactide in a controlled manner.[5f] To systematically study the effect of a bridged bis(phenolate) Ln fragment on the reactivity of a Ln−X bond (X = C, N, etc.), the synthesis of bridged bis(phenolate) lanthanide alkyl and amido complexes

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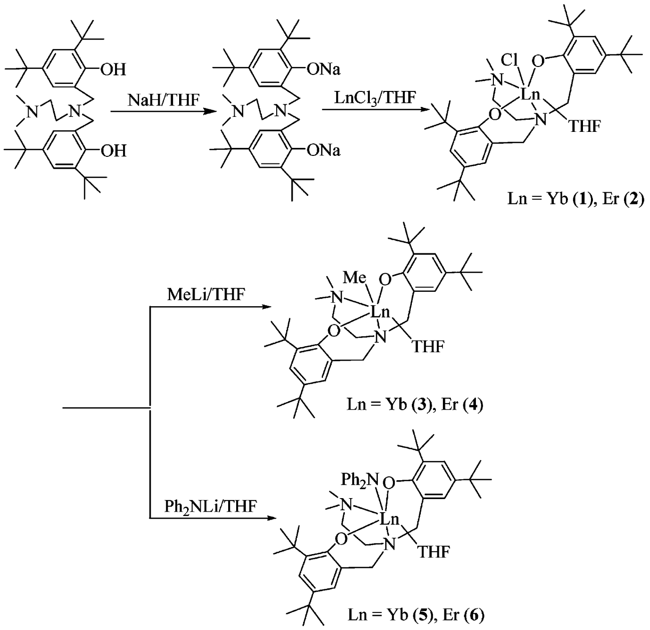
is meaningful. Generally, the metathesis reaction of bridged bis(phenolate) lanthanide halides with lithium alkyls or amides, like that of bis(cyclopentadienyl) lanthanide halides,[6] should be a convenient method for the synthesis of these complexes. Surprisingly, although a lot of amine bis(phenolate) lanthanide alkyl and amido complexes have been synthesized in the literature, the methods that are used to synthesize these lanthanide derivatives are relatively limited. Almost all of these complexes are prepared by protonolysis reactions using bulky trisalkyl- or trisamido-lanthanide complexes, such as $Ln(CH_2SiMe_3)_3(THF)_2$, $Ln[N(SiMe_3)_2]_3$, or $Ln[N(SiMe_2H)_2]_3(THF)_2$, as starting materials.[5c−g] There is only one paper in the literature that deals with the synthesis and reactivity of bridged bis(phenolate) lanthanide chlorides. Unfortunately, the yttrium and scandium chlorides supported by the tetradentate diamino-bis(phenolate) ligands $O_2{}^{tBu}NN'$ [$O_2{}^{tBu}NN' = (2\text{-}C_5H_4N)CH_2N\{CH_2\text{-}(2\text{-}OC_6H_2{}^tBu_2\text{-}3,5)_2\}$], which were synthesized by the metathesis reactions of YCl_3 or $ScCl_3$ with $Na_2O_2{}^{tBu}NN'$, were reported to be inactive for many halide substitution reactions.[5i]

Recently, we became interested in studying the synthesis and reactivity of lanthanide complexes that are supported by bulky bridged bis(phenolate) ligands.[5h,j] We found that lanthanide chlorides supported by the amine bis(phenolate) ligand $Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t{}_2\text{-}3,5)\}_2$ can be conveniently prepared in a high yield and that these lanthanide chlorides can be used as useful precursors to the synthesis of the corresponding lanthanide derivatives by simple metathesis reactions. Furthermore, the amine bis(phenolate) lanthanide methyl and amido complexes are efficient initiators for the ring-opening polymerization of ϵ-caprolactone. Here we report these results.

Results and Discussion

Synthesis and Reactivity of Amine Bis(phenolate) Lanthanide Complexes. Following the addition of 1 equiv of LNa_2 [$L = Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t{}_2\text{-}3,5)\}_2$], which was prepared by the reaction of NaH and LH_2 in THF, to a suspension of anhydrous lanthanide trichlorides in THF, the color of the solution gradually changed to yellow (for Yb) or pink (for Er). After workup, novel amine bis(phenolate) lanthanide chlorides with general formula LLnCl(THF) (Ln = Yb (**1**), Er (**2**)) were obtained in a high isolated yield as analytically pure light yellow or pink crystals from a concentrated toluene solution, as shown in Scheme 1. Elemental analyses revealed that the complex consists of one amine bis(phenolate) ligand, one chlorine atom, and one coordinated THF molecule at the metal center. Complexes **1** and **2** were stable enough when stored in a sealed flask, but their exposure to air led to a rapid color change with obvious deliquescence.

Scheme 1



Complexes **1** and **2** are good precursors for the preparation of well-defined amine bis(phenolate) lanthanide derivatives by simple metathesis reaction. They reacted smoothly with 1 equiv of MeLi in THF after careful workup to afford the amine bis(phenolate) lanthanide methyl complexes LLnMe(THF) (Ln = Yb (**3**), Er (**4**)) in moderate isolated yields at low temperature, which were identified by elemental analyses and, in the case of complex **3**, single-crystal X-ray diffraction study. The direct reactions of complexes **1** and **2** with Ph_2NLi that was prepared in situ were similar to those of MeLi, except that the reactions were performed at room temperature. Well-defined amine bis(phenolate) lanthanide amido complexes $LLnNPh_2(THF)$ (Ln = Yb (**5**), Er (**6**)) can be conveniently prepared in THF and isolated from concentrated toluene solution in high isolated yields. Complexes **5** and **6** were confirmed by elemental analyses and structure determination (Scheme 1).

Complexes **3**−**6** are extremely sensitive to air and moisture. The crystals decompose in a few minutes when they are exposed to air, but neither the crystals nor the solution showed any sign of decomposition after several months when stored under argon. The lanthanide methyl complexes are moderately soluble in donor solvents, such as THF and DME, and slightly soluble in toluene and benzene, but insoluble in hexane. The corresponding amido complexes are freely soluble in THF and moderately soluble in toluene. These complexes did not provide any resolvable ^1H NMR spectra, due to the strong paramagnetism of the lanthanide ions.

These results are quite different from the cases of the diamio-bis(phenolate) yttrium and scandium chlorides, $[Y(O_2{}^{tBu}NN')(\mu\text{-}Cl)(py)]_2$ and $Sc(O_2{}^{tBu}NN')Cl(py)$ [$O_2{}^{tBu}NN' = (2\text{-}C_5H_4N)CH_2N\{CH_2\text{-}(2\text{-}OC_6H_2{}^tBu_2\text{-}3,5)_2\}$], in

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Table 1. Details of the Crystallographic Data and Refinements for Complexes 1, 2, 3, 5, and 6

	1·0.75toluene	**2**·0.75toluene	**3**	**5**	**6**
empirical formula	$C_{43.25}H_{68}ClN_2O_3Yb$	$C_{43.25}H_{68}ClErN_2O_3$	$C_{39}H_{65}N_2O_3Yb$	$C_{50}H_{72}N_3O_3Yb$	$C_{50}H_{72}ErN_3O_3$
fw	872.49	866.71	782.97	936.15	930.37
temp (K)	193(2)	193(2)	193(2)	193(2)	193(2)
λ (Å)	0.7107	0.7107	0.7107	0.7107	0.7107
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$	$P2_1/c$
a (Å)	37.9817(12)	38.036(3)	48.357(5)	10.7360(6)	10.7883(12)
b (Å)	14.6308(4)	14.6408(7)	11.9624(9)	22.4429(13)	22.409(2)
c (Å)	36.1234(12)	36.156(3)	36.189(4)	19.8725(12)	19.903(2)
β (deg)	118.8420(10)	118.8470(10)	130.326(1)	100.018(2)	100.151(3)
V (Å^3)	17583.8(9)	17636.2(19)	15959(3)	4715.2(5)	4736.4(9)
Z	16	16	16	4	4
density (Mg/m^3)	1.318	1.306	1.303	1.319	1.305
abs coeff (mm^{-1})	2.225	2.001	2.379	2.025	1.814
F(000)	7240	7208	6512	1948	1940
θ_{max} (deg)	27.48	27.48	27.48	27.48	27.48
no. of reflns collected	65 454	89 420	85 385	52 220	52 137
no. of unique reflns	20 024	20 113	11 895	10 780	10 818
no. of reflns obsd	17 819	17 930	18 195	10 780	10 818
no. of params refined	944	936	842	529	529
R [$I > 2\sigma(I)$]	0.0425	0.0421	0.0375	0.0411	0.0386
R_w	0.0884	0.0941	0.0808	0.0842	0.0798
GOF on F^2	1.108	1.123	1.162	1.159	1.149

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

	1a	**1b**	**2a**	**2b**
Ln(1)–O(1)	2.116(3)	2.093(3)	2.116(3)	2.145(3)
Ln(1)–O(2)	2.106(3)	2.086(3)	2.112(3)	2.125(3)
Ln(1)–O(3)	2.310(3)	2.318(3)	2.331(3)	2.330(3)
Ln(1)–N(1)	2.484(3)	2.484(3)	2.520(3)	2.510(3)
Ln(1)–N(2)	2.518(3)	2.468(3)	2.492(3)	2.544(3)
Ln(1)–Cl(1)	2.5363(10)	2.5289(11)	2.5513(12)	2.5571(11)
C(1)–O(1)	1.337(4)	1.339(5)	1.337(5)	1.336(5)
C(7)–O(2)	1.327(5)	1.334(5)	1.332(5)	1.335(5)
C(1)–O(1)–Ln(1)	134.8(2)	136.7(2)	137.0(3)	134.5(2)
C(7)–O(2)–Ln(1)	140.9(2)	143.5(3)	144.2(3)	141.2(2)
O(3)–Ln(1)–N(2)	174.28(2)	167.44(12)	167.50(12)	174.72(11)
O(1)–Ln(1)–N(1)	80.18(10)	81.57(10)	80.38(11)	79.54(10)
N(1)–Ln(1)–O(2)	80.01(10)	79.26(10)	78.42(11)	79.11(10)
O(2)–Ln(1)–Cl(1)	100.42(8)	99.21(8)	100.12(8)	101.34(8)
N(1)–Ln(1)–Cl(1)	164.45(8)	166.31(8)	165.91(8)	163.65(8)
O(1)–Ln(1)–O(2)	155.58(11)	156.82(11)	154.82(11)	153.99(11)

which the substitution of the chloride with a range of lithium or magnesium alkyls or $LiN(SiMe_3)_2$ was unsuccessful.[5i] The difference between the amine bis(phenolate) ligands $[Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t{}_2\text{-}3,5)\}_2]$ and $O_2{}^{tBu}NN'$ is that the sidearm donor in the former is dimethylamido, while pyridine in the later. These results reveal that the sidearm donor has a significant effect on the reactivity of amine bis(phenolate) lanthanide complexes.

Crystal Structure Analyses. Although many amine bis(phenolate) lanthanide complexes have been synthesized, few have been structurally characterized.[5d,f,g,i] To provide complete structural information for these novel amine bis(phenolate) species, single-crystal X-ray structural investigations were carried out for complexes **1**, **2**, **3**, **5**, and **6**. Details of the intensity data collection and the crystal data are given in Table 1.

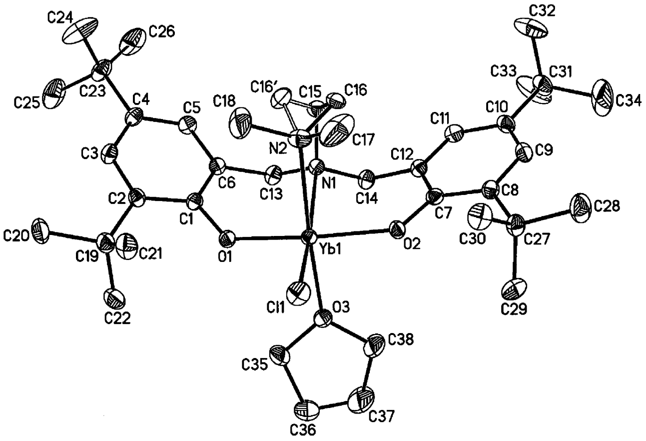

Figure 1. ORTEP diagram of complex **1** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 25% probability level. Hydrogen atoms are omitted for clarity.

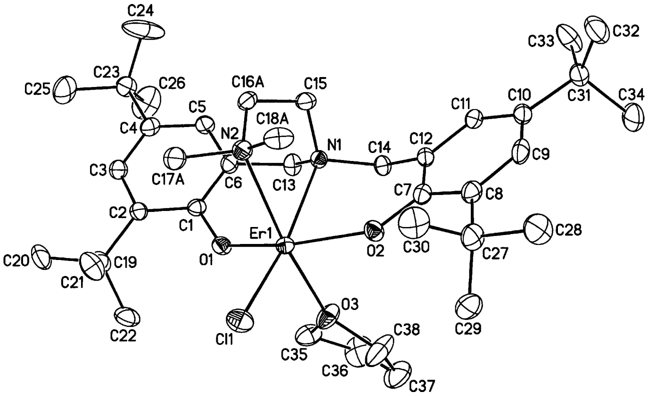

Figure 2. ORTEP diagram of complex **2** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Crystals of complexes **1** and **2** that were suitable for an X-ray structure determination were obtained from concentrated toluene solution at room temperature. Both complexes **1** and **2** crystallize with two crystallographically independent but chemically similar molecules (**1a**, **1b**; **2a**, **2b**) in the unit cell. The selected bond lengths and angles are provided in Table 2 for both molecules. ORTEP diagrams of molecules **1a** and **2a** are depicted in Figures 1 and 2, respectively. Complexes **1** and **2** are isostructural, and both have a monomeric structure. Like other amine bis(phenolate) lanthanide complexes,[5d,f] the sidearm amido group was found to bind to the metal center in the solid state. The central metal atom is coordinated 6-fold by two oxygen atoms

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3, 5, and 6

	3a	**3b**	**5**	**6**
Ln(1)−O(1)	2.119(2)	2.124(2)	2.115(2)	2.135(2)
Ln(1)−O(2)	2.131(2)	2.130(2)	2.112(2)	2.134(2)
Ln(1)−O(3)	2.325(3)	2.330(2)	2.338(2)	2.350(2)
Ln(1)−N(1)	2.518(3)	2.513(3)	2.516(3)	2.549(3)
Ln(1)−N(2)	2.536(3)	2.546(3)	2.509(3)	2.527(3)
Ln(1)−C(35)	2.440(4)	2.442(3)	3.044(4)	3.035(3)
Ln(1)−N(3)			2.256(3)	2.279(3)
C(1)−O(1)	1.333(7)	1.338(4)	1.335(4)	1.340(4)
C(7)−O(2)	1.341(4)	1.333(4)	1.342(4)	1.339(4)
C(1)−O(1)−Ln(1)	137.8(2)	136.6(2)	141.0(2)	141.3(2)
C(7)−O(2)−Ln(1)	135.5(2)	138.5(2)	141.6(2)	142.0(2)
O(3)−Ln(1)−N(2)	173.23(11)	175.90	159.73(10)	159.38(9)
O(1)−Ln(1)−N(1)	79.89(9)	81.14(9)	79.71(9)	79.03(8)
N(1)−Ln(1)−O(2)	80.41(9)	79.21(9)	79.34(9)	78.60(8)
N(1)−Ln(1)−C(35)	160.58(12)	159.04(11)		
N(1)−Ln(1)−N(3)			169.67(11)	168.17(11)
O(1)−Ln(1)−O(2)	154.35(10)	154.06(10)	154.76(9)	153.51(9)
O(2)−Ln(1)−C(35)	103.56(12)	102.56(11)		
C(35)−Ln(1)−O(1)	100.48(12)	101.86(11)		
O(2)−Ln(1)−N(3)			103.41(11)	104.69(10)
N(3)−Ln(1)−O(1)			99.71(11)	100.09(10)

and two nitrogen atoms from the amine bis(phenolate) ligand, one THF molecule, and one chlorine atom in a distorted octahedron. The overall coordination geometry is similar to that of Sc(O_2^{tBu}NN′)Cl(py),[5i] but different from those of [(O_2^{tBu}NN′)Y(μ-Cl)(py)]$_2$[5i] and [(O_2^{tPe}NN′)Gd(μ-Cl)(THF)]$_2$ [O_2^{tpe}NN′ = $Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Pe^t_2\text{-}3,5)\}_2$],[5g] in which metal centers are seven-coordinate. In complexes **1** and **2**, O(1), Cl(1), O(2), and N(1) can be considered to occupy equatorial positions within the octahedron about the lanthanide center. O(3) and N(2) occupy axial positions, and the O(3)−Ln−N(2) angle is slightly distorted away from the idealized position of 180° to 174.5(2)° for complex **1a** and 167.5(1)° for complex **2a**.

The Yb−O(Ar) bond lengths of 2.119(5) and 2.102(5) Å in complex **1** are comparable to the corresponding values in [Y(O_2^{tBu}NN′)(μ-Cl)(py)]$_2$[5i] and [(O_2^{tPe}NN′)Gd(μ-Cl)(THF)]$_2$,[5g] when differences in ionic radii are considered. The Yb−Cl bond length of 2.536(1) Å in complex **1** is in agreement with the data found in the other ytterbium chlorides, $(ArO)_2YbCl(THF)_2$ (2.4770(9) Å),[7] $Yb(ArO)Cl_2(THF)_3$ (2.555(2) Å) (ArO = OC_6H_2-2,6-Bu^t_2-4-Me),[8] $YbCl_3(THF)_3$ (2.52(7) Å),[9] and $CpYbCl_2(THF)_3$ (2.594(3) Å),[10] when the difference in coordination number is considered. The Yb(1)−N(2) bond length of 2.517(5) Å is in accordance with the corresponding values in [Y(O_2^{tBu}NN′)(μ-Cl)(py)]$_2$[5i] and [(O_2^{tPe}NN′)Gd(μ-Cl)(THF)]$_2$,[5g] and the Yb(1)−N(1) bond length of 2.482(4) Å is apparently shorter than the bond lengths that were observed in the aforementioned amine bis(phenolate) lanthanide complexes.

The Er−O(Ar) bond lengths of 2.116(3) and 2.112(3) Å in complex **2** are comparable to the corresponding bond lengths in complex **1** when the difference in ionic radii is considered. However, these Er−O(Ar) bond lengths are slightly shorter than those for the other aryloxo erbium complexes, such as K[Er($OC_6H_3Pr^i_2$-2,6)$_4$],[11] [Na(diglyme)$_2$][Er($OC_6H_3Pr^i_2$-2,6)$_4$] (diglyme = bis(2-methoxyethyl) ether),[12] and $(ArO)_2ErCl(THF)_2$,[7] when the effect of the coordination number on the effective ionic radius is considered. The Er−Cl bond length of 2.551(1) Å in complex **2** is slightly longer than that of $(ArO)_2ErCl(THF)_2$.[7] The average C−O bond length of the bis(phenolate) ligand is 1.334(5) Å, which is similar to that of complex **1** (1.332(4) Å), but apparently shorter than the single-bond length, which reflects a substantial electron delocalization of oxygen into the aromatic rings.

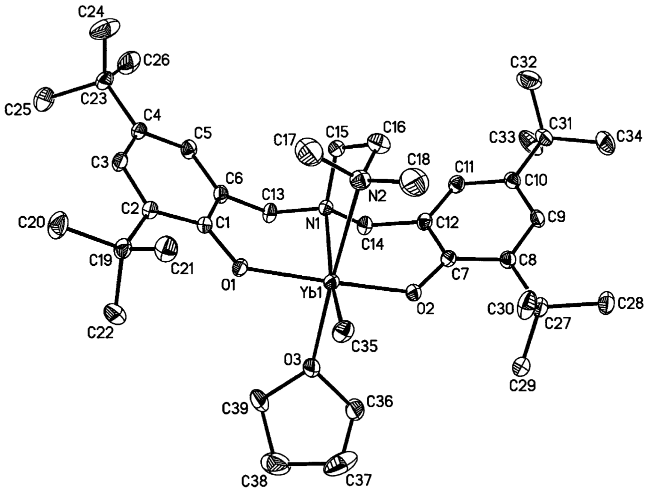

Figure 3. ORTEP diagram of complex **3** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Crystals of complex **3** that were suitable for an X-ray structure determination were obtained from a concentrated toluene solution at −15 °C. The unit cell of complex **3** contains two half-molecules of LYbMe(THF). The selected bond lengths and angles are provided in Table 3 for both molecules. No significant differences were observed between the two crystallographically independent molecules (**3a** and **3b**), and for the purposes of this discussion only those that contain Yb(1) will be considered. An ORTEP of molecule **3a** is depicted in Figure 3. Complex **3** has a monomeric structure. The overall molecular geometry of complex **3** is somewhat similar to that of complex **1**, with the main difference being that one methyl group instead of a chlorine atom coordinates with the ytterbium atom. The coordination geometry is also similar to that of the yttrium atom in [$MeOCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t_2\text{-}3,5)\}_2$]Y($CH_2SiMe_3$)(THF).[5d] The Yb−O and Yb−N bond lengths in complex **3** are rather similar to those that were observed in complex **1** and [$MeOCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t_2\text{-}3,5)\}_2$]Y($CH_2SiMe_3$)(THF).[5d] The Yb(1)−C(35) bond length of 2.440(4) Å compares well with the Ln−C bond length in the other lanthanide alkyl complexes, such as [$MeOCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t_2\text{-}3,5)\}_2$]Y($CH_2SiMe_3$)(THF) (2.431(6) Å),[5d] [MeY(THF)$_6$][BPh_4]$_2$ (2.418(3) Å),[13a] and $(C_5Me_5)_2LnCH(SiMe_3)_2$ (2.468(7) Å),[13b] but significantly longer than the value observed in $(C_5H_5)_2YbMe(THF)$ (2.362(11) Å).[13c]

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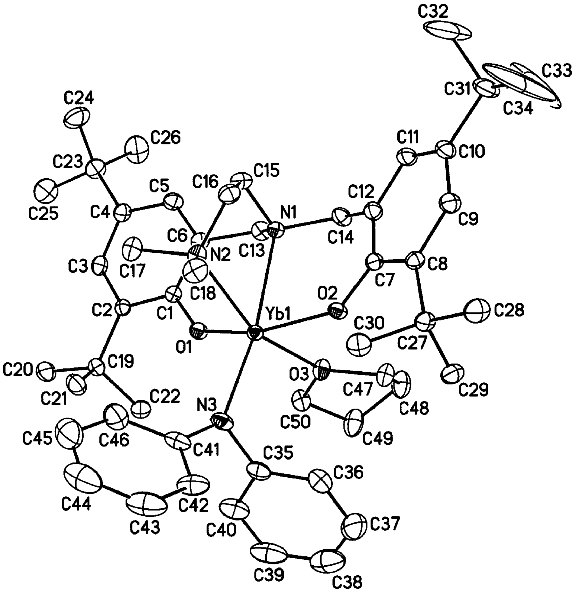

Figure 4. ORTEP diagram of complex **5** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Suitable crystals of complexes **5** and **6** for X-ray structure determination were obtained from a concentrated toluene solution at room temperature. Their molecular diagrams are depicted in Figures 4 and 5, and their selected bond lengths and angles are provided in Table 3. Complexes **5** and **6** are isostructural, and both have monomeric structures. The metal center in these two complexes is coordinated by three oxygen atoms and three nitrogen atoms to form a slightly distorted octahedron. The overall molecular geometry of complexes **5** and **6** is similar to that observed in [MeOCH$_2$CH$_2$N-{CH$_2$-(2-O-C$_6$H$_2$-Bu$^t{}_2$-3,5)}$_2$]Y[N(SiMe$_2$H)](THF)[5d] and in complexes **1**–**3**.

In complexes **5** and **6**, the Ln–O and Ln–N(amido) bond lengths lie within the range of the corresponding Ln–O(phenoxy) and Ln–N(amido) bond lengths found in complexes **1**, **2**, and **3**. The Ln–N(Ph) bond lengths of 2.256(3) Å in complex **5** and 2.279(3) Å in complex **6** are comparable to the corresponding values that have been reported for (CH$_3$C$_5$H$_4$)$_2$YbNPh$_2$(THF), (C$_5$Me$_5$)$_2$-YbNPh$_2$,[14] (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$nacnac]YbNPh$_2$ ((DIPPh)$_2$-nacnac = *N,N*-diisopropylphenyl-2,4-pentanediimine anion),[15] DanipYb[N(SiMe$_3$)$_2$] and DanipYb[N(SiHMe$_2$)$_2$]$_2$ (Danip = 2,6-di(*o*-anisol)phenyl),[16] and [Na(THF)$_2$(μ-η^5:η^5-CH$_3$C$_5$H$_4$)$_2$Er(NPh$_2$)$_2$]$_n$.[17] It is worth noting that there is an agostic interaction of the α carbon atom of the diphenylamido group with the central metal atom. The Ln–C(35) bond lengths are 3.044(4) Å in complex **5** and 3.035(3) Å in complex **6**, which are comparable to those of 3.067(5) Å for η^3-diketiminate bonding in (CH$_3$C$_5$H$_4$)-[(DIPPh)$_2$nacnac]YbCl,[15] 2.986(6) and 3.180(9) Å for bridging η^2-C$_5$H$_5$ bonding in (C$_5$Me$_5$)$_2$Sm(μ-C$_5$H$_5$)Sm(C$_5$-Me$_5$)$_2$,[18] 2.814(4)–3.148(6) Å for chelating η^6-, η^1-Ph–Yb bonding in [Yb(Odpp)$_3$]$_2$ (Odpp = 2,6-diphenylphenolate),[19] and 2.986(6) and 3.053(6) Å for chelating Yb–η-Ph intramolecular interaction in (C$_5$Me$_5$)$_2$YbNPh$_2$.[14] Variations in the Ln–N–C angles are associated with the existences of agostic interactions in these complexes. The angles that are associated with the nearby carbon atoms (Ln(1)–N(3)–C(35)) are 109.3(2)° in complex **5** and 107.8(2)° in complex **6**, and the other angles (Ln-(1)–N(3)–C(41)) are 136.9(3)° and 138.5(3)°, respectively; the C(35)–N(3)–C(41) angles slightly deviated from 120° to 113.6(3)° in these two complexes. The O(3)–Ln(1)–N(2) bond angles of 159.73(10)° in complex **5** and 159.38(9)° in complex **6** are apparently more obtuse than the corresponding bond angles in complexes **1**–**3**. It is reasonable to ascribe the difference in bond parameters to the increased steric congestion in complexes **5** and **6** that results from the replacement of the chlorine atom or methyl group by a bulky diphenylamido group.

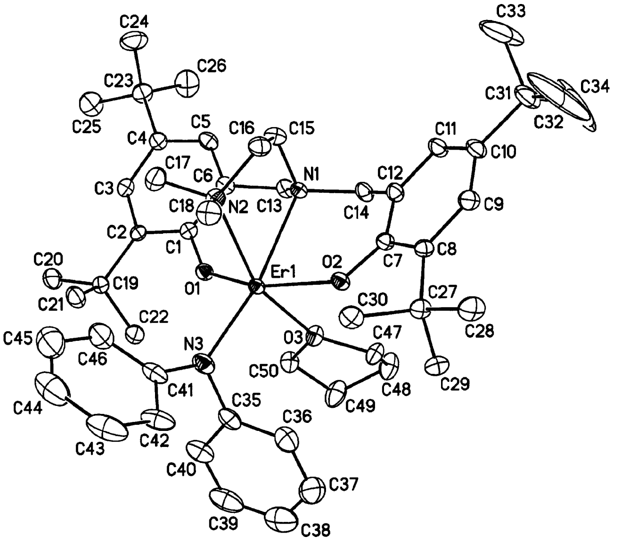

Figure 5. ORTEP diagram of complex **6** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Ring-Opening Polymerization of ε-Caprolactone. The aliphatic polyesters, such as poly(ε-caprolactone) (PCL) and poly(lactide) (PLA), and their copolymers have found wide application in the medical field as biodegradable surgical sutures or as a delivery medium for controlled release of drugs due to their biodegradable, biocompatible, and permeable properties.[20] The major method that is used to synthesize these polymers is the ring-opening polymerization of lactones/lactides and functionally related compounds (eq 1). Many kinds of organometallic and coordination complexes have been reported to be efficient initiators for the ring-opening polymerization of lactones/lactides. All the systems give the polymers with both high molecular

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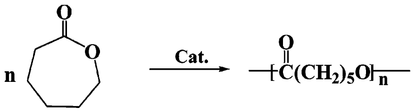
Table 4. Ring-Opening Polymerization of ϵ-Caprolactone by 3, 5, and 6[a]

entry	initiator	T/°C	[M]/[I]	t/h	M_n($\times 10^4$)	M_w/M_n[b]	yield[c]
1	**3**	−10	200	1.2	1.30	1.47	37
2	**3**	0	200	2	0.84	1.62	71
3	**3**	25	200	0.8	0.93	1.59	99
4	**3**	25	500	9	5.05	1.49	99
5	**3**	25	1000	30	2.76	1.45	33
6	**5**	25	200	30 s	1.73	1.89	92
7	**5**	54	200	30 s	1.96	1.69	92
8	**5**	25	500	30 s	3.03	1.71	95
9	**5**	25	1000	1 min	4.60	1.94	97
10	**5**	25	2000	1 min	9.64	2.58	99
11	**5**	25	2500	4 h			64
12	**5**	25	3000	6 h			0
13	**6**	25	1000	1 min	3.36	1.84	95
14	**6**	25	2000	1 min	6.28	1.93	96
15	**6**	25	3000	1 h			52

[a] General polymerization conditions: in toluene, solvent/monomer = 4 (v/v). [b] Measured by GPC calibrated with standard polystyrene samples. [c] Yield: weight of polymer obtained/weight of monomer used.

weights and high yields.[21] Among these initiators, the structurally well-defined catalyst systems are especially interesting, as they afford the possibility of understanding the catalyst structure/reactivity relationships.[21a]



(1)

The catalytic behavior of complexes **3**, **5**, and **6** for the ring-opening polymerization of ϵ-caprolactone was examined, and the preliminary results are summarized in Table 4. It can be seen that all of the complexes are efficient initiators for the polymerization of ϵ-caprolactone in toluene, and the resulting polymers have a high molecular weight and relatively narrow molecular weight distributions (M_w/M_n). The lanthanide amido complexes showed extremely high activity compared with the lanthanide methyl complex. For example, for the amido complexes **5** and **6**, nearly quantitative yield is obtained within 1 min at 25 °C when the molar ratio of monomer to initiator is 2000:1, and even when the amount of the initiator decreases to [CL]:[I] = 3000:1, as in the case of **6**, the polymerization still gives a 52% yield within 1 h. However, for the methyl complex **3**, the yield is only 33% after 30 h; even the molar ratio of monomer to initiator is 1000:1. The catalytic activity of complexes **5** and **6** is much higher than those found in the systems with amine bis(phenolato)lanthanide amides reported.[5g] For example, few complexes showed activity for this polymerization; moreover, the yield reaches 100% in 1 h only when the loading of the initiator is as high as 1:100 (molar ratio of initiator to monomer). In comparison with the analogous methyl and amido complexes supported by cyclopentadienyl ligands, the activity of the amido complexes here is also much higher than that of lanthanocene amides,[22] while almost the same reactivity was found for the methyl complex.[23] For the analogous lanthanide amido complexes, the difference in catalytic activity between erbium and ytterbium complexes was also observed. The yield reaches 52% in 1 h for complex **6** when the molar ratio of monomer to initiator is increased to 3000:1, while no polymer is obtained at the same molar ratio even when the polymerization time is prolonged to 6 h for complex **5**. The observed increasing order, Er > Yb, is in agreement with the order of ionic radii. This may be because the larger ionic radii result in the greater opening of the metal coordination sphere in the vicinity of the σ ligand, which makes the insertion of ϵ-caprolactone into Ln−N bonds easier. The molecular weight distributions of the resulting polymers range from 1.45 to 2.58, and decreasing of the polymerization temperature for the methyl complex led to almost no change of the molecular weight distribution. Normally, the broader molecular weight distribution may mainly contribute to the transesterification reaction during the polymerization process.[24] These results indicate that the transesterification reaction during the polymerization of ϵ-caprolactone in the present systems cannot be effectively suppressed.

Conclusion

In summary, we have successfully synthesized a series of new amine bis(phenolate) lanthanide methyl and amido complexes. Their structure features have been determined by X-ray diffraction study. Using amine bis(phenolate) L^{2-} [L = $Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}Bu^t{}_2\text{-}3,5)\}_2$] as an ancillary ligand, the amine bis(phenolate) lanthanide chlorides can be prepared in high yield. These lanthanide chlorides are useful precursors for the synthesis of amine bis(phenolate) lanthanide methyl and amido complexes by simple salt metathesis reaction. The catalytic behavior of these amine bis(phenolate) lanthanide methyl and amido complexes for ring-opening polymerization of ϵ-caprolactone was also studied. The lanthanide amido complexes showed extremely high activity for ϵ-caprolactone polymerization. Further studies on the synthesis of lanthanide complexes that are supported by amine bis(phenolate) ligands bearing different sidearm donors and the effect of the sidearm donor on their reaction chemistry are in process in our laboratory.

Experimental Section

General Considerations. All of the manipulations were performed in a purified argon atmosphere using standard Schlenk techniques. The solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. Ligand LH_2[25] and anhydrous $LnCl_3$[26] were prepared according to the procedures that are recommended in the literature. ϵ-Caprolactone was purchased from Acros, dried by CaH_2 for 48 h, and then distilled under reduced pressure. All of the other reagents were purchased from Aldrich and used as received without further purification. The uncorrected melting points were determined in sealed Ar-filled capillary tubes. Lanthanide analyses were carried out by complexometric titration, and chloride analysis was performed using the Volhard method. Carbon, hydrogen, and nitrogen analyses

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were preformed by direct combustion with a Carlo-Erba EA 1110 instrument. The IR spectra were recorded with a Nicolet-550 FT-IR spectrometer as KBr pellets. The molecular weight and molecular weight distributions were determined against polystyrene standards by gel permeation chromatography (GPC) at 30 °C with a Waters 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4) using THF as the eluent.

LYbCl(THF) (1). A solution of LH_2 (2.63 g, 5.01 mmol) in THF (20 mL) was added dropwise to a NaH suspension (10.02 mmol) in THF at room temperature. The stirring was continued for 14 h, and the mixture was then filtered. The resulting pale yellow solution was added to a suspension of $YbCl_3$ (1.40 g, 5.01 mmol) in THF (20 mL). After stirring the solution overnight at room temperature, the precipitation was separated from the reaction mixture by centrifugation. The solvent was removed in a vacuum, and the residue was extracted with toluene. Light yellow crystals were obtained from toluene solution at room temperature in a few days (3.21 g, 79.5%). Mp: 180−182 °C (dec). Anal. Calcd for $C_{38}H_{62}ClN_2O_3Yb$: C, 56.81; H, 7.78; N, 3.49; Cl, 4.41; Yb, 21.54. Found: C, 57.11; H, 7.32; N, 3.62; Cl, 4.52; Yb, 21.42. IR (KBr pellet, cm^{-1}): 2959 (s), 2905 (s), 2866 (s), 1767 (m), 1601 (m), 1562 (m), 1474 (s), 1416 (m), 1389 (m), 1362 (m), 1250 (m), 1165 (m), 1107 (m), 1022 (m), 880 (m), 841 (m), 806 (m), 775 (m), 733 (m), 532 (s).

LErCl(THF) (2). Complex **2** was prepared by a procedure that was analogous to the procedure for complex **1**, except anhydrous $ErCl_3$ (1.66 g, 6.07 mmol) was used instead of $YbCl_3$. Pink crystals were obtained from concentrated toluene solution at room temperature in a few days (4.0 g, 82.6%). Mp: 178−180 °C (dec). Anal. Calcd for $C_{38}H_{62}ClErN_2O_3$: C, 57.22; H, 7.83; N, 3.51; Cl, 4.44; Er, 20.97. Found: C, 57.41; H, 7.91; N, 3.43; Cl, 4.36; Er, 20.80. IR (KBr pellet, cm^{-1}): 2959 (s), 2904 (s), 2870 (s), 1624 (m), 1531 (m), 1481 (s), 1416 (m), 1389 (m), 1362 (m), 1227 (s), 1157 (s), 1045 (m), 879 (m), 841 (m), 779 (m), 637 (m), 556 (m), 505 (s).

LYbMe(THF) (3). A Schlenk flask was charged with complex **1** (4.02 g, 5.00 mmol) and THF (20 mL). The solution was cooled to −15 °C, and MeLi (4.8 mL, 5.00 mmol) was added by syringe. The reaction mixture was kept at −15 °C for 1 h and was slowly warmed to room temperature and stirred overnight. After removing the volatiles in a vacuum, the yellow residue was extracted with toluene, and LiCl was removed by centrifugation. Complex **3** was obtained as yellow crystals by cooling the solution to −5 °C (1.94 g, 49.6%). Mp: 168−170 °C (dec). Anal. Calcd for $C_{39}H_{65}N_2O_3Yb$: C, 59.82; H, 8.37; N, 3.58; Yb, 22.10. Found: C, 60.15; H, 7.93; N, 3.57; Yb, 22.01. IR (KBr pellet, cm^{-1}): 2959 (s), 2905 (s), 2870 (s), 1632 (m), 1539 (m), 1544 (m), 1466 (s), 1416 (m), 1362 (m), 1228 (s), 1196 (s), 1045 (m), 987 (m), 926 (m), 799 (m), 725 (m), 637 (s), 556 (m), 505 (s).

LErMe(THF) (4). Complex **4** was prepared by a procedure that was analogous to the procedure for complex **3**, except complex **2** (4.26 g, 5.34 mmol) was used instead of complex **1**. Pink microcrystals were obtained from concentrated toluene solution at −5 °C in a few days (1.60 g, 38.6%). Mp: 172−174 °C (dec). Anal. Calcd for $C_{39}H_{65}ErN_2O_3$: C, 60.27; H, 8.43; N, 3.60; Er, 21.52. Found: C, 60.18; H, 8.17; N, 3.22; Cl, 4.41; Er, 21.54. IR (KBr pellet, cm^{-1}): 2956 (s), 2906 (s), 2867 (s), 1627 (m), 1602 (m), 1548 (m), 1470 (s), 1415 (m), 1363 (m), 1229 (s), 1194 (s), 1049 (m), 985 (m), 881 (m), 837 (m), 634 (s), 506 (s).

$LYbNPh_2$(THF) (5). A Schlenk flask was charged with Ph_2NH (1.28 g, 7.56 mmol), THF (25 mL), and a stirring bar. The solution was cooled to 0 °C, and *n*-BuLi in hexane (6.30 mL, 7.56 mmol) was added by syringe. The solution was then slowly warmed to room temperature and stirred for 1 h. This solution was added to complex **1** in 20 mL of THF, and the solution was stirred overnight at room temperature. The solvent was removed in a vacuum, the residue was extracted with toluene, and LiCl was removed by centrifugation. Yellow crystals were obtained from concentrated toluene solution at room temperature after 2 days (5.66 g, 80.0%). Mp: 164−166 °C (dec). Anal. Calcd for $C_{50}H_{72}N_3O_3Yb$: C, 64.15; H, 7.75; N, 4.49; Yb, 18.48. Found: C, 64.28; H, 7.46; N, 4.19; Yb, 18.26. IR (KBr pellet, cm^{-1}): 2959 (s), 2901 (s), 2866 (s), 1597 (s), 1526 (m), 1474 (s), 1416 (m), 1389 (m), 1362 (m), 1308 (s), 1238 (m), 1169 (m), 1026 (m), 879 (m), 837 (m), 748 (s), 690 (m).

$LErNPh_2$(THF) (6). Complex **6** was prepared by a procedure that was analogous to the procedure for complex **5**, except complex **1** (5.24 g, 6.57 mmol) was used instead of complex **2**. Light pink crystals were obtained from concentrated toluene solution at room temperature in a few days (4.65 g, 76.1%). Mp: 167−169 °C (dec). Anal. Calcd for $C_{50}H_{72}ErN_3O_3$: C, 64.55; H, 7.80; N, 4.52; Er, 17.98. Found: C, 64.26; H, 8.04; N, 4.34; Er, 18.05. IR (KBr pellet, cm^{-1}): 2955 (s), 2905 (s), 2866 (s), 1597 (s), 1478 (s), 1416 (m), 1362 (m), 1304 (s), 1238 (m), 1203 (m), 1165 (m), 1026 (m), 879 (m), 837 (m), 748 (s), 691 (m).

A Typical Polymerization Procedure. The polymerizations were carried out under dry argon atmosphere. The general procedure was as follows: a 20 mL Schlenk flask that was equipped with a magnetic stirring bar was charged with an appropriate amount of the lanthanide complex and toluene, depending upon the monomer-to-initiator ratio. To this solution was added 0.6 mL of ϵ-caprolactone by a syringe. The contents of the flask were then stirred vigorously at a fixed temperature, during which time the mixture became very viscous, which thus disrupted the stirring. The reaction mixture was quenched by the addition of methanol solution that contained 5% HCl and was then poured into ethanol to precipitate the polymer, which was dried in a vacuum and weighed.

X-ray Crystallography. Suitable single crystals of complexes **1**−**3**, **5**, and **6** were sealed in a thin-walled glass capillary to determine the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz−polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically (C−H bond lengths fixed at 0.95 Å), were assigned appropriate isotropic thermal parameters, and were allowed to ride on their parent carbon atoms. All of the H atoms were held stationary and were included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using the SHELXL-97 program.

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Supporting Information Available: Tables of X-ray diffraction data for **1**, **2**, **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org

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