

The salt-free diamido complexes of lanthanide supported by β -diketiminate: Synthesis, characterization, and their catalytic activity for the polymerization of acrylonitrile and ϵ -caprolactone

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Abstract

The synthesis and structure of the salt-free diamido complexes of lanthanide supported by β -diketiminate ligand (2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$) are described. The β -diketiminate lanthanide dichloride $\text{LLnCl}_2(\text{THF})_2$ ($\text{L} = N,N'$ -bis(2,6-dimethylphenyl)-2,4-pentanediiiminate) [$\text{Ln} = \text{Yb}$ (**1**), Nd (**2**)] was prepared by the metathesis reaction of LLi with anhydrous LnCl_3 in a 1:1 molar ratio in THF at room temperature. Reactions of **1** and **2** with 2 equiv. of LiNPh_2 in THF gave the salt-free complex $\text{LLn}(\text{NPh}_2)_2(\text{THF})$ [$\text{Ln} = \text{Yb}$ (**3**), Nd (**4**)] in good yield as crystalline solids. Both compounds were characterized crystallographically. The coordinated geometry around the central metal can be described as a distorted trigonal bipyramid. Complexes **3** and **4** showed good catalytic activity for the polymerization of acrylonitrile and high activity for the ring-opening polymerization of ϵ -caprolactone at room temperature.

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Keywords: Salt-free diamido complex; β -Diketimininate ligand; Polymerization; Acrylonitrile; ϵ -Caprolactone

1. Introduction

The organolanthanide amide has been found to be the important precatalysts in a variety of homogeneous catalysis, including hydroamination of alkyne and alkene and the polymerization of polar monomers [1–5]. However, almost all of the work focused on the complexes with a dianionic ancillary ligand and one amido group. There are only a few papers dealing with the synthesis of well-defined compounds of general formula $\text{LLn}[\text{NR}_2]_2$, where L is a monoanionic ancillary ligand [6,7]. The lack in synthesizing these targets may result from the tendency of these types of compounds to un-

dergo complexation by salts [8]. It's obvious that the key to solve the problem is to choose a suitable ligand.

Recently, β -diketiminate anion, as an isoelectronic alternative to cyclopentadienyl ligand, has attracted increasing attention in organometallic chemistry for their electronic and steric properties can be easily tuned through an appropriate choice of amine and β -diketone used in their synthesis. The application of β -diketiminate in organolanthanide chemistry has also led to the synthesis of a variety of corresponding compounds [9–12]. Moreover, the use of a sterically demanding β -diketiminate ligand in the preparation of dialkyl scandium compounds has made great success [13]. All these work published encouraged us to attempt to synthesize bis-amido complexes of lanthanide element by use of β -diketiminate as an ancillary ligand. Very recently, the synthesis of diprimary amido compound of scandium

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supported by β -diketiminato was reported [14]. During the sending of this manuscript we saw the publication described the synthesis and molecular structure of bis-di-trimethylsilylamido complex supported by β -diketiminato [15].

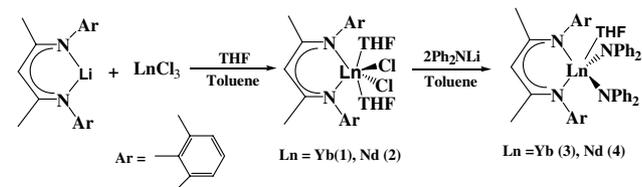
We have previously shown that the $\text{LYbCl}_2(\text{THF})_2$ can be synthesized in high yield where the β -diketiminato ligand is N,N' -bis(2,6-diisopropylphenyl)-2,4-pentanediiiminate or N,N' -bis(2,6-dimethylphenyl)-2,4-pentanediiiminate [16]. Here, we used the dichloride of lanthanide with the later one as the starting material and synthesized bisdiphenylamino complexes of Yb and Nd. The catalytic activity of the novel compounds synthesized was also tested. Both of the complexes showed good activity for the polymerization of acrylonitrile and ϵ -caprolactone. We would like to report the results.

2. Results and discussion

2.1. Synthesis

Complex **1** can be conveniently synthesized in high yield by metathesis reaction of YbCl_3 with β -diketiminato lithium [16]. Thus, the corresponding Nd complex can also be prepared by the same method. LiLi reacted with 1 equiv. of anhydrous NdCl_3 in THF after workup to afford the desired β -diketiminato neodymium dichloride which was identified by elemental analysis as two THF-solvated complex $\text{LNdCl}_2(\text{THF})_2$ (**2**) in 71% yield as green crystals (Scheme 1). The IR spectrum of complex **2** exhibited the strong absorptions near 1550 cm^{-1} , which was consistent with partial $\text{C}=\text{N}$ double bond character.

Complexes **1** and **2** are useful precursors for further transformation. The metathesis reaction of **1** and **2** with 2 equiv. of LiNPh_2 in THF allowed for the replacement of chloride and the production of the one THF-solvated diamido complex $\text{LLn}(\text{NPh}_2)_2(\text{THF})$ [$\text{Ln} = \text{Yb}$ (**3**), Nd (**4**)] in 72% and 80% yield, respectively (Scheme 1). Recrystallization from concentrated toluene solution gave **3** as blue crystals while **4** as light purple crystals. They were characterized by elemental analyses, IR spectra and NMR spectroscopy. The infrared spectra of these complexes showed characteristic absorptions of the β -diketiminato ligand. Although ^1H NMR for both



Scheme 1.

complexes provided evidence of the presence of the substituents, the paramagnetic nature of these complexes hindered full interpretation of the spectra. Definitive formulation of the structural features of **3** and **4** was given by single-crystal X-ray crystallography. The crystal structural studies provided the coordination geometry of the central metal and the connectivity of the ligand. Complexes **3** and **4** are air- and moisture-sensitive and have good solubility in THF and DME and moderate solubility in toluene.

2.2. Molecular structures

The molecular structures of complexes **3** and **4** are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in Table 1. Complexes **3** and **4** are isostructural. Both of them have solvated monomeric structure with a five-coordinate lanthanide center ligated by two nitrogen atoms of the chelating bidentate β -diketiminato anion, two nitrogen atoms from two diphenylamino groups, and one oxygen atom of the THF molecule. The coordination geometry around the lanthanide ion for each complex can be described as a distorted trigonal bipyramid. In each complex, N(1), N(3) and N(4) form the equatorial vertices (the sum of these bond angles is 359.6° for **3** and 359.99° for **4**), another nitrogen atom [N(2)] and the oxygen atom of the THF occupy the apical positions [the angle of $\text{N}(2)\text{--Yb}(1)\text{--O}(1)$, $170.0(1)^\circ$; $\text{N}(2)\text{--Nd}(1)\text{--O}(1)$, $174.92(4)^\circ$; see Table 1]. The structures of the five-coordinate dichloride and dimethyl complexes supported by β -diketiminato are reported [13,17]. Thus, the structural features of the diamido congener can be comparable with them. The corresponding values of $175.5(3)^\circ$ in dimethyl complex and $175.31(16)^\circ$ in dichloride were found [13,17].

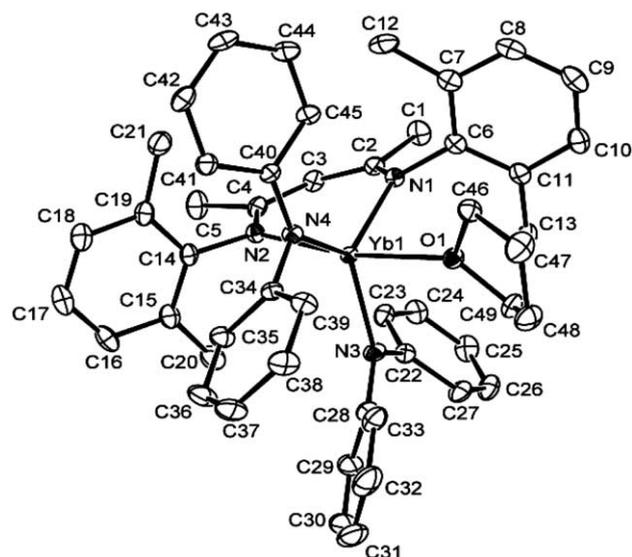


Fig. 1. The molecular structure of complex **3**.

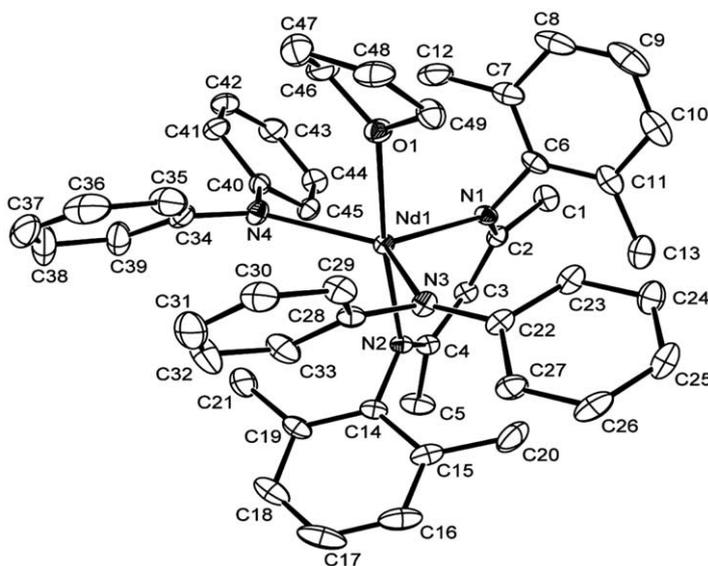


Fig. 2. The molecular structure of complex 4.

The β -diketiminato ligand is symmetrically coordinated to the center metal with the variation in Ln–N bond lengths of 0.028 Å [2.320(4) and 2.348(4) Å, respec-

Table 1
Selected bond lengths (Å) and angles (°) for 3 and 4

	3	4
<i>Bond lengths (Å)</i>		
Ln(1)–O(1)	2.396(3)	2.545(1)
Ln(1)–N(2)	2.348(4)	2.481(1)
Ln(1)–N(4)	2.212(3)	2.370(1)
N(1)–C(6)	1.455(6)	1.436(2)
N(2)–C(14)	1.457(6)	1.448(2)
N(3)–C(28)	1.409(6)	1.406(2)
N(4)–C(40)	1.388(5)	1.413(2)
C(2)–C(3)	1.395(7)	1.399(2)
C(4)–C(5)	1.519(7)	1.509(2)
Ln(1)–N(1)	2.320(4)	2.432(1)
Ln(1)–N(3)	2.238(3)	2.348(1)
N(1)–C(2)	1.347(5)	1.335(2)
N(2)–C(4)	1.325(6)	1.328(2)
N(3)–C(22)	1.415(5)	1.398(2)
N(4)–C(34)	1.430(5)	1.415(2)
C(1)–C(2)	1.520(7)	1.510(2)
C(3)–C(4)	1.409(7)	1.415(2)
<i>Bond angles (°)</i>		
O(1)–Ln(1)–N(1)	92.5(1)	101.83(4)
O(1)–Ln(1)–N(3)	88.1(1)	83.56(4)
N(1)–Ln(1)–N(2)	80.2(1)	73.68(4)
N(1)–Ln(1)–N(4)	122.3(1)	117.92(4)
N(2)–Ln(1)–N(4)	95.2(1)	99.16(4)
C(2)–N(1)–Yb(1)	125.4(3)	130.9(1)
C(3)–C(2)–N(1)	125.3(4)	124.0(1)
N(2)–C(4)–C(3)	124.0(4)	123.9(1)
O(1)–Ln(1)–N(2)	170.0(1)	174.92(4)
O(1)–Ln(1)–N(4)	82.9(1)	85.00(4)
N(1)–Ln(1)–N(3)	115.3(1)	115.14(4)
N(2)–Ln(1)–N(3)	101.2(1)	96.14(4)
N(3)–Ln(1)–N(4)	122.0(1)	126.93(4)
C(4)–N(2)–Yb(1)	127.8(3)	129.9(1)
C(4)–C(3)–C(2)	130.1(4)	128.8(1)

tively] for 3 and 0.049 Å [2.432(1) and 2.481(1) Å, respectively] for 4. The average Yb–N (β -diketiminato ligand) distance is 2.334 Å, which is also comparable to that in the analogous complex (ArO) [(DIPPh)₂nacnac]YbCl(THF) (2.339 Å) [(DIPPh)₂nacnac = *N,N'*-bis(2,6-diisopropylphenyl)-2,4-pentanedimine] [18]. The average Nd–N (β -diketiminato ligand) distance of 2.456 Å compares well with the distance in complex 3 when the difference in ionic radii between Yb³⁺ and Nd³⁺ is considered [19]. The bond distances of N(1)–C(2), C(2)–C(3), C(3)–C(4) and C(4)–N(2) in both complexes lie intermediate between the corresponding single- and double-bond distances (see Table 1), which suggest significant delocalization with the π -system of β -diketiminato backbone (NC₃N). The quite long distances between metal center and the carbon atoms of the backbone of the β -diketiminato ligand in these two complexes reveal that the β -diketiminato ligand only acts as an *N,N'*-bonded chelate; additionally, the five atoms of the ligand are virtually coplanar with the highest deviation from the plane defined by these atoms being 0.0689 Å for C(4) in 3 and 0.0504 Å for C(3) in 4, respectively. The central atom sits 0.6421 Å out of this plane for Yb and 0.7621 Å for Nd, which are comparable to 0.815 Å for dimethyl complex [13] and 0.694 Å for dichloride [17].

Ln–N(NPh₂) bond distances are 2.238(3) and 2.212(3) Å for Yb, 2.348(1) and 2.370(1) Å for Nd, respectively, which are comparable to those in lanthanocene amide complexes: (C₅Me₅)₂YbNPh₂, 2.216(5) Å [20]; [Li(DME)₃][(C₅H₅)₂Nd(NPh₂)₂], 2.421(7), 2.434(7) Å [21]. The Yb–N(NPh₂) bond distances also compare well with the distance found in another β -diketiminato lanthanide amide (CH₃C₅H₄)[(DIPPh)₂nacnac]YbNPh₂ [2.259(6) or 2.214(6) Å] [22]. The N(1)–Yb–N(2) angle is 80.2(1)°, more acute than the corresponding parameter in complexes [(DIPPh)₂nacnac]ScCl₂(THF)

[86.77(17)°] [17] and [(DIPPh)₂nacnac]Sc(Me)₂(THF) [85.2(3)°] [13]. It is reasonable to ascribe the difference in bond angle of complex **3** to the increased steric congestion of the diphenyl amino anion.

2.3. Polymerization of acrylonitrile

Several organolanthanide complexes were reported to be able to catalyze the polymerization of acrylonitrile including [(*tert*-BuCp)₂NdCH₃]₂ [23], (ArO)₂Sm [24] [(η⁵:η¹-C₅Me₄SiMe₂NCMe₃)Y(CH₂SiMe₃)(THF)] [25], La(C₅Me₅)[(CH(SiMe₃)₂)]₂(THF) [26], Ln(SAr)₃(py)₃ (La = Sm, Yb) [27] and Ln(OAr)₃ (Ln = La, Y) [28]. However, few report concerning with the reactivity of organolanthanide amide for the acrylonitrile polymerization was reported. In order to understand further the chemistry of lanthanide complex containing Ln–N bond, the catalytic activity of Yb and Nd compounds for the acrylonitrile polymerization was examined. The preliminary results are listed in Table 2. It can be seen that both of Yb and Nd complexes exhibit good catalytic activity. For example, the conversion reaches to 69% when the loading of catalyst is 1:400 (molar ratio of Ln to monomer) at 0 °C in DME for **3** (entry 5) and 51% conversion can still be obtained when the loading decreases to 1:1000 (entry 3). The catalytic activity is comparable to those of Ln(SAr)₃(py)₃ (La = Sm, Yb) [27] and Ln(OAr)₃ (Ln = La, Y) [28] and higher than those of [(*tert*-BuCp)₂NdCH₃]₂ [23] and [(η⁵:η¹-C₅Me₄SiMe₂NCMe₃)Y(CH₂SiMe₃)(THF)] [25]. The influence of catalyst concentration on the polymerization has been investigated in DME or THF at 25 °C as shown in Table 2. The data indicate that conversion depends appreciably on catalyst concentration.

The solvent has great effect on the polymer yields. The solvents with ‘high’ dielectric constant, such as DME and THF, give higher conversions for both complexes. However, the slight difference in activity existed in these two complexes. For complex **3**, the active order for solvent was DME > THF > toluene, while THF > DME > toluene for complex **4** was observed.

The polymerizations were carried out at 0 and 25 °C, respectively to see the effect of temperature. As shown in Table 2, the polymerization rate increases with the increasing temperature, while the molecular weights of the resulting polymer were almost unaffected within the polymerization temperature range. The microstructures of the resulting polymers were determined by ¹³C NMR to be atactic.

2.4. Ring-opening polymerization of ε-caprolactone

Complexes **3** and **4** also showed high activity for the ring-opening polymerization of ε-caprolactone under the mild conditions as shown in Table 3 (Scheme 2). The monomer conversion reached to 100% for both catalytic systems under the conditions of [M]/[I] = 1000 (mole ratio) at 0 °C in 15 min (entries 5 and 9). Even the catalytic loading decreases to [M]/[I] = 1500, the polymerization still gives the conversion as high as 86% for **3** (entry 4) and 96% for **4** (entry 8). Although there is no report on the catalytic activity of diphenyl amido complexes of lanthanide for the ring-opening polymerization of ε-caprolactone in the literature, the activity can be compared with the other amide complexes published. It was obvious that the activity of title complexes is slightly lower than that of bis(guandinato)lanthanide diisopropylamido complexes [29] while

Table 2
Polymerization of acrylonitrile with LLn(NPh₂)₂(THF) [Ln = Yb (**3**), Nd (**4**)]

Entry ^a	Initiator	T _p (°C)	Solvent	[M]/[I]	Yield ^b (%)	M _n (× 10 ⁻⁴)	Tacticity (%)		
							rr	mr	mm
1	3	25	DME	400	64	2.83			
2	3	25	DME	700	55	5.58			
3	3	25	DME	1000	51	6.11			
4	3	0	DME	400	48	3.59			
5	3 ^c	0	DME	400	69	3.79	22.2	46.6	31.2
6	3 ^d	25	DME	400	51	3.91			
7	3	25	THF	400	46	2.64			
8	3 ^c	25	THF	400	61	3.14			
9	3	25	PhMe	400	17	2.02	26.8	45.2	27.9
10	4	25	THF	400	61	1.91	26.9	41.0	32.1
11	4	25	THF	700	50	2.71	28.1	43.2	28.7
12	4	25	PhMe	400	36	1.10	25.2	42.5	32.2

^a General polymerization conditions: polymerization time 1 h, [M] = 7.5 mol/L.

^b Yield: weight of polymer obtained/weight of monomer used.

^c Polymerization time: 3 h.

^d Polymerization time: 0.5 h.

^e Polymerization time: 2 h.

Table 3
Ring-opening polymerization of ϵ -caprolactone initiated by $\text{LLn}(\text{NPh}_2)_2(\text{THF})$ [$\text{Ln} = \text{Yb}$ (**3**), Nd (**4**)]

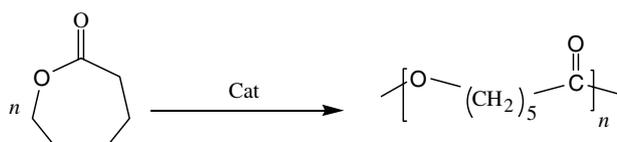
Entry ^a	Initiator	T_p (°C)	[M] (mol/L)	[M]/[I]	Yield ^b (%)	M_n ($\times 10^{-4}$)	M_w/M_n ^c
1	3	25	0.038	500	95	12.17	1.71
2	3	25	0.075	500	100	10.66	1.85
3	3	25	1.5	1000	100	11.42	1.78
4	3	25	1.5	1500	86	10.08	1.65
5	3	0	1.5	1000	100	9.61	1.35
6	4	25	1.5	1000	100	15.38	1.90
7	4 ^d	25	1.5	1000	100	11.85	1.71
8	4	25	1.5	1500	96	9.86	1.79
9	4	0	1.5	1000	100	15.97	1.50

^a General polymerization conditions: in toluene, polymerization time 15 min.

^b Yield: weight of polymer obtained/weight of monomer used.

^c Measured by GPC calibrated with standard polystyrene samples.

^d Polymerization time: 3 min.



Scheme 2.

much higher than that of the diisopropylamido complexes supported by methylcyclopentadienyl ligand [30]. The active order of $\text{Nd} > \text{Yb}$ was observed, which is in agreement with that found for metallocene-based organolanthanide catalysts [30] and guanidate ones [29]. The polymerization systems give high molecular weight polymers ($M_n > 10^4$) with a relatively narrow molecular-weight distribution ($M_w/M_n = 1.35\text{--}1.90$).

3. Conclusion

In summary, two new soluble lanthanide amides supported by β -diketiminato ligand were successfully synthesized in good yield by the metathesis reaction of β -diketiminato lanthanide dichloride with LiNPh_2 in a 1:2 molar ratio, and their crystal structures were determined. The diamido complexes supported by β -diketiminato were found to be the novel catalysts for the polymerization of acrylonitrile with good activity to give atactic polyacrylonitriles and for the ring-opening polymerization of ϵ -caprolactone with high catalytic activity. A systematic study of the catalytic activity of β -diketiminato lanthanide amides in the homogeneous catalysis is ongoing in our laboratory.

4. Experimental

All manipulations were performed under pure Ar with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were dried and freed

of oxygen by refluxing over Na or sodium benzophenone ketyl and distilled under argon prior to use. Anhydrous LnCl_3 [31] and LLi [32] were prepared according to the literature methods. LiNPh_2 was obtained by the reaction of HNPh_2 with $n\text{-BuLi}$ in a solution of toluene and hexane. Acrylonitrile and ϵ -caprolactone were dried by stirring with CaH_2 for 48 h, and then distilled under reduced pressure. Melting points were determined in argon-filled capillary tubes and are uncorrected. Lanthanide metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument; quoted data are the average of at least two independent determinations. The IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained in C_6D_6 solution for lanthanide complexes and in $\text{DMSO-}d_6$ for polymers using a Unity Inova-400 spectrometer. 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, HR-4) using THF as the eluent. The triad tacticities (mm, mr, and rr) of the PAN were determined from the ratio of intensities for three methyne-carbon peaks (26.8 ppm for mm, 27.4 ppm for mr and 27.9 ppm for rr) in the ^{13}C NMR spectrum [33]. The intrinsic viscosity of polymer was determined by Ubbelodhe-type viscometer in DMF at 25 °C and the viscosity-average molecular weights (M_η) were calculated by the following equation [34]:

$$[\eta] = 2.43 \times 10^{-2} M_\eta^{0.75}.$$

4.1. Synthesis of $\text{LNdCl}_2(\text{THF})_2$ (**2**)

A solution of LLi (30 mL, 3.72 mmol) in toluene-hexane was slowly added to a suspension of NdCl_3 (0.93 g, 3.72 mmol) in 40 mL THF at room temperature. The color of the solution gradually changed to green.

The reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuum and toluene was added to extract the product. The dissolved portion was removed by centrifugation. The green crystals were obtained from the concentrated toluene solution at room temperature (1.76 g, 71%). Mp: 175–177 °C (dec). Anal. Calc. for $C_{25}H_{33}N_2Cl_2O_2Nd$: C, 49.30; H, 5.46; N, 4.60; Nd 23.70. Found: C, 49.02; H, 5.57; N, 4.35; Nd, 23.82. IR (KBr pellet, cm^{-1}): 3137 (s), 2967 (s), 2847 (s), 2658 (w), 1597 (s), 1555 (vs), 1443 (s), 1381 (m), 1300 (s), 1200 (m), 1096 (s), 1042 (m), 968 (w), 763 (m).

4.2. Synthesis of $LYb(NPh_2)_2(THF)$ (**3**)

To a slurry of anhydrous $YbCl_3$ (1.43 g, 5.12 mmol) in about 40 mL THF was slowly added the solution of LLi (20 mL, 5.12 mmol) in toluene–hexane at room temperature. After $YbCl_3$ disappeared completely, the solution of $LiNPh_2$ (20 mL, 10.24 mmol) in THF–hexane was added slowly. After being stirred at r.t. for 48 h, the solvents were stripped off in vacuum and toluene was added to extract the product. The blue supernatant was then concentrated and cooled to -10 °C to give blue crystals (3.28 g, 72%). Mp: 135–138 °C (dec). Anal. Calc. for $C_{49}H_{53}N_4OYb$: C, 66.35; H, 6.02; N, 6.32; Yb, 19.51. Found: C, 65.93; H, 6.08; N, 6.42; Yb, 19.50. 1H NMR (C_6D_6 , ppm): 0.3–1.93 (m, 10H), 2.10–2.33 (m, 12H), 4.87–5.02 (br, 4H), 5.36 (br, 1H), 6.89–8.40 (br, 26H). IR (KBr pellet, cm^{-1}): 3044 (m), 2920 (m), 2859 (w), 1624 (m), 1593 (s), 1555 (s), 1493 (s), 1466 (m), 1420 (w), 1312 (m), 1219 (s), 1157 (s), 1092 (w), 1026 (w), 876 (w), 748 (m).

4.3. Synthesis of $LNd(NPh_2)_2(THF)$ (**4**)

The synthesis of complex **4** was carried out by the procedure for the synthesis of complex **3**, but $NdCl_3$ (1.40 g, 5.59 mmol) was used instead of $YbCl_3$. Recrystallization from toluene yielded light purple crystals of **4** (3.84 g, 80%). Mp: 122–124 °C (dec). Anal. Calc. for $C_{49}H_{53}N_4ONd$: C, 68.58; H, 6.22; N, 6.54; Nd, 16.81. Found: C, 68.11; H, 6.16; N, 6.62; Nd, 16.70. 1H NMR (C_6D_6 , ppm): 0.3–1.50 (br, 10H), 2.19 (br, 12H), 3.63 (br, 4H), 5.04 (br, 1H), 6.91–8.01 (br, 26H). IR (KBr pellet, cm^{-1}): 3044 (m), 2924 (m), 1624 (m), 1593 (s), 1551 (s), 1501 (s), 1424 (m), 1308 (m), 1242 (s), 1215 (s), 1157 (s), 1088 (w), 1026 (w), 876 (w), 748 (m) cm^{-1} .

4.4. Polymerization of acrylonitrile

A typical example of polymerization is given below. An intense orange-red solution formed as soon as acrylonitrile (0.74 mL, 0.59 g, 11.1 mmol) was added to a blue solution of $LYb(NPh_2)_2(THF)$ (24.7 mg,

0.0278 mmol) in DME (0.74 mL) at 25 °C, followed by the precipitation of yellow, atactic poly(acrylonitrile). The polymerization was terminated after 1 h by adding ethanol containing 5% HCl solution. The resulting polymer was collected by centrifugation, washed with water and ethanol, and then dried to constant weight in vacuum.

4.5. Polymerization of ϵ -caprolactone

To a toluene solution (3.8 mL) of ϵ -caprolactone (0.80 mL, 7.22 mmol) was added at once a toluene solution (1 mL) of complex **3** or **4** (7.22×10^{-3} mmol) with vigorous magnetic stirring at the desired temperature. After the polymerization was carried out for a fixed time, the reaction mixture was quenched by ethanol containing 2% HCl solution and was then poured into ethanol to precipitate the polymer, which was dried under vacuum and weighted.

4.6. X-ray structural determination of **3** and **4**

Suitable single crystals of complexes **3** and **4** were each sealed in a thin-walled glass capillary, and intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation. Details of the intensity data collection and crystal data are given in Table 4. The crystal structures of these two complexes were solved by direct

Table 4
Details of the crystallographic data collection and refinement for **3** and **4**

	3	4
Empirical formula	$C_{49}H_{53}N_4OYb$	$C_{49}H_{53}N_4ONd$
Formula weight	887.02	858.22
Temperature (K)	193.1	193.1
Wavelength (Å)	0.71070	0.71070
Crystal dimensions (mm)	$0.60 \times 0.20 \times 0.20$	$0.60 \times 0.55 \times 0.40$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (#14)	$Pbca$ (#61)
a (Å)	11.4664(10)	17.8023(9)
b (Å)	30.515(3)	15.4081(9)
c (Å)	12.2354(12)	30.469(2)
α (°)	90	90
β (°)	102.784(4)	90
γ (°)	90	90
V (Å ³)	4175.0(7)	8357.7(8)
Z	4	8
D_{calc} (g cm^{-3})	1.411	1.364
$F(000)$	1812.00	3544.00
μ (mm ⁻¹)	2.281	1.283
θ Range (°)	3.1–27.5	3.0–27.5
Reflections collected	42 105	83 834
Independent reflections (R_{int})	9506 (0.053)	9491 (0.039)
Variables	550	549
R	0.042 [$I > 2.00\sigma(I)$]	0.047 [$I > 3.00\sigma(I)$]
R_w	0.091 [$I > 2.00\sigma(I)$]	0.165 [$I > 3.00\sigma(I)$]
Goodness-of-fit on F^2	1.002	1.001

methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 271345 for complex **3** and 271346 for complex **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or on the web <http://www.ccdc.cam.ac.uk>.

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