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Synthesis and Structural Characterization of β-Diketiminate–Lanthanide Amides and Their Catalytic Activity for the Polymerization of Methyl Methacrylate and ϵ-Caprolactone

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The synthesis and catalytic activity of lanthanide monoamido complexes supported by a β-diketiminate ligand are described. Donor solvents, such as DME, can cleave the chloro bridges of the dinuclear β-diketiminate ytterbium dichloride {[(DIPPh)$_2$nacnac]YbCl(μ-Cl)$_3$Yb[(DIPPh)$_2$nacnac](THF)} (**1**) [(DIPPh)$_2$nacnac = *N*,*N*-diisopropylphenyl-2,4-pentanediimine anion] to produce the monomeric complex [(DIPPh)$_2$nacnac]YbCl$_2$(DME) (**2**) in high isolated yield. Complex **2** is a useful precursor for the synthesis of β-diketiminate–ytterbium monoamido derivatives. Reaction of complex **2** with 1 equiv of LiNPr$^i_2$ in THF at room temperature, after crystallization in THF/toluene mixed solvent, gave the anionic β-diketiminate–ytterbium amido complex [(DIPPh)$_2$nacnac]Yb(NPr$^i_2$)(μ-Cl)$_2$Li(THF)$_2$ (**3**), while similar reaction of complex **2** with LiNPh$_2$ produced the neutral complex [(DIPPh)$_2$nacnac]Yb(NPh$_2$)Cl(THF) (**4**). Recrystallization of complex **3** from toluene solution at elevated temperature led to the neutral β-diketiminate–lanthanide amido complex [{(DIPPh)$_2$nacnac}Yb(NPr$^i_2$)(μ-Cl)]$_2$ (**5**). The reaction medium has a significant effect on the outcome of the reaction. Complex **2** reacted with 1 equiv of LiNPr$^i_2$ and LiNC$_5$H$_{10}$ in toluene to produce directly the neutral β-diketiminate–lanthanide amido complexes **5** and [{(DIPPh)$_2$nacnac}Yb(NC$_5$H$_{10}$)(THF)(μ-Cl)]$_2$ (**6**), respectively. These complexes were well characterized, and their crystal structures were determined. Complexes **4**–**6** exhibited good catalytic activity for the polymerization of methyl methacrylate and ϵ-caprolactone.

Introduction

In recent years, the application of β-diketiminates as supporting ligand systems in both main group and transition metal coordination chemistry has attracted considerable attention,[1−3] because these ligand systems and cyclopentadienyl anions are isoelectronic and both of them are monoanions in their deprotonated forms; moreover, their steric and electronic properties can be easily tuned by an appropriate choice of starting materials used in their syn-

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thesis. Especially, some of these β-diketiminate metal complexes exhibit exciting reactivity. For example, they show high activity for the polymerization of ethylene[1b] and lactide[2c,3n] and the copolymerization of carbon dioxide and epoxide.[1c,3l] Although many rare earth metal complexes supported by β-diketiminate anions have been synthesized in recent years, their catalytic activity remains relatively poorly explored.[1a,2e,4−11] Piers et al. have developed the chemistry of β-diketiminate scandium and yttrium complexes and found that related scandium alkyls showed high catalytic activity for the polymerization of ethylene in the presence of cocatalysts.[4b] β-Diketiminate− neodymium borohydride complex combining with Mg^nBu_2 can catalyze the stereospecific polymerization of isoprene.[9] We previously reported that some divalent β-diketiminate−ytterbium complexes as single-component catalysts can catalyze the polymerization of methyl methacrylate (MMA) with low activity,[7b] but the mixed-ligand trivalent β-diketiminate−ytterbium amido complexes, $[(DIPPh)_2nacnac](MeC_5H_4)YbNR_2$ (R = Ph, Pr^i) [$(DIPPh)_2$nacnac = *N*,*N*-2,6-diisopropylphenyl-2,4-pentanediimine anion], are inactive for this polymerization.[7a] Arnold et al. also reported that β-diketiminate−samarium alkyls $[(DIPPh)_2nacnac](C_5Me_5)SmR$ (R = Me, CH_2SiMe_3) and related cationic species are not active catalysts for ethylene or MMA polymerization,[10] and Hultzsch et al. reported very recently that linked bis(β-diketiminate)−rare earth metal complexes copolymerize cyclohexene oxide and CO_2 with low activity.[11] Therefore, design and synthesis of new β-diketiminate−lanthanide complexes, especially investigation of their catalytic activity, are still meaningful.[12]

We showed previously that lanthanocene amide $(MeC_5H_4)_2LnNPh_2(THF)$ is a highly active initiator for the polymerization of MMA,[13] while replacement one $MeC_5H_4^-$ group by one $[(DIPPh)_2nacnac]^-$ group caused a dramatic decrease of the catalytic activity.[7a] The reasons might be that the β-diketiminate is the more bulky and donative ligand, compared with the $MeC_5H_4^-$ group; its coordination to ytterbium atom increases the steric congestion around the central metal and decreases the electrophilicity of the metal, which makes the insertion of MMA into the Ln−N bond difficult. If the steric congestion around the metal center plays an important role in the decrease of the activity of $[(DIPPh)_2nacnac](MeC_5H_4)YbNR_2$, it is to be expected that less crowded β-diketiminate−lanthanide amides should exhibit good catalytic activity. In this paper, we synthesized new β-diketiminate−ytterbium monoamido complexes $[(DIPPh)_2nacnac]Yb(NR_2)Cl(THF)_n$ (NR_2 = NPr^i_2, NPh_2, NC_5H_{10}) and tested their catalytic activity for the polymerization of some polar monomers. Indeed, these β-diketiminate−ytterbium amido complexes can efficiently initiate the polymerization of MMA and ϵ-caprolactone. Here we report these results.

Results and Discussion

Synthesis and Characterization of β-Diketiminate−Lanthanide Complexes. We previously reported the synthesis and characterization of the dinuclear β-diketiminate−ytterbium dichloride {$[(DIPPh)_2nacnac]YbCl(\mu\text{-}Cl)_3Yb[(DIPPh)_2nacnac](THF)$} (**1**), which has a rare triply chloro-bridged structure.[7a] Further study revealed that the bridged structure of complex **1** can be easily broken by DME

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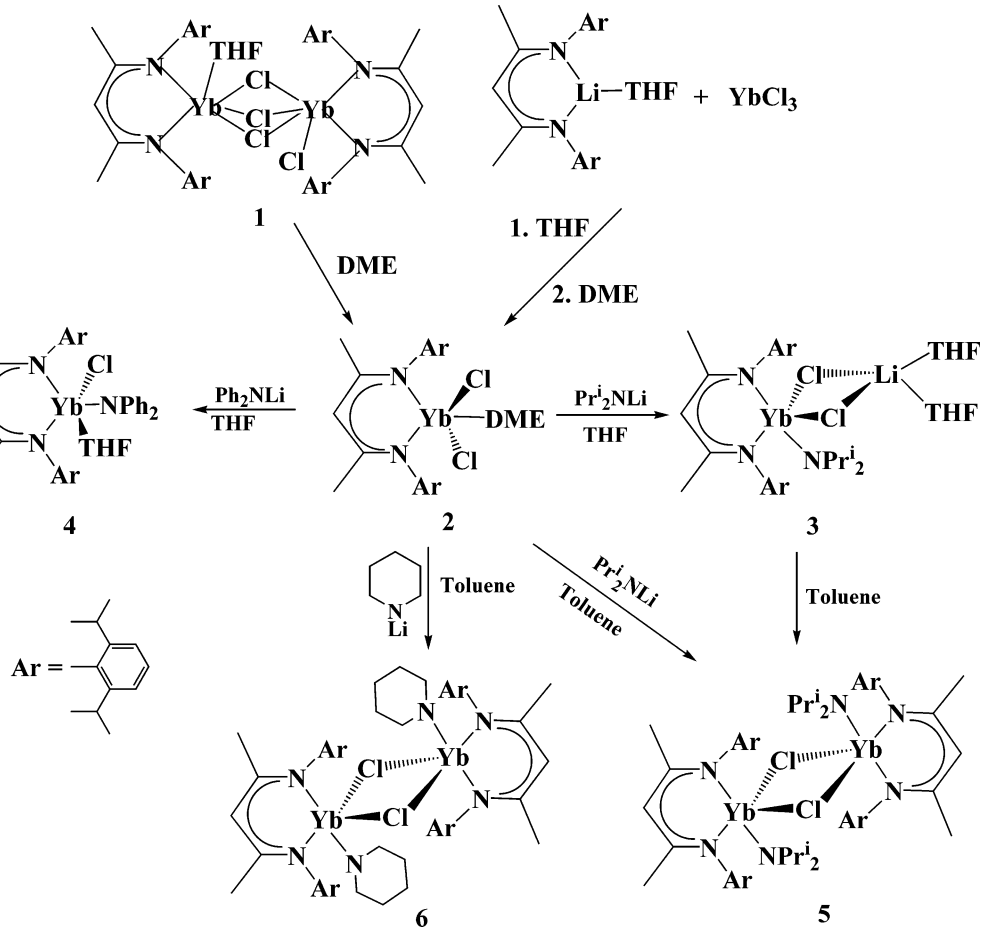
Scheme 1



to produce the monomeric ytterbium dichloride [(DIPPh)$_2$-nacnac]YbCl$_2$(DME) (**2**), which was identified by elemental analysis and an X-ray structure determination. Complex **2** can also be conveniently prepared in high yield by the reaction of [(DIPPh)$_2$nacnac]Li with YbCl$_3$ in THF, followed by the crystallization from toluene in the presence of DME.

Complex **2** is a good starting synthon for the β-diketiminate−ytterbium derivatives via metathesis reactions. Thus, complex **2** reacted with 1 equiv of LiNPr$^i_2$ in THF, and the color of the solution immediately changed from red to purplish red. After careful workup, purplish red crystals (**3**) were obtained in good isolated yield from THF/toluene mixed solvent. The composition of complex **3** was established as [(DIPPh)$_2$nacnac]Yb(NPr$^i_2$)Cl$_2$Li(THF)$_2$ by elemental analyses (C, H, N, Ln, and Li); further structural characterization reveals that complex **3** is an "ate" species as shown in Scheme 1. Complex **2** reacted with LiNPh$_2$ in a 1:1 molar ratio, after crystallization from THF/toluene mixed solvent, to give the neutral product [(DIPPh)$_2$nacnac]Yb(NPh$_2$)Cl-(THF) (**4**). These results can be attributed to the difference in bulkiness of the amido groups. Prolonged heating of a toluene solution of complex **3** led to remove the coordinated LiCl and to give the neutral β-diketiminate−ytterbium amide [{(DIPPh)$_2$nacnac}Yb(NPr$^i_2$)(μ-Cl)]$_2$ (**5**) in a 72% isolated yield. Elemental analysis revealed that complex **5** consists of one β-diketiminate ligand, one diisopropylamido group, and one chlorine atom at the metal center. When complex **2** reacted with 1 equiv of LiNPr$^i_2$ and LiNC$_5$H$_{10}$ in toluene, after careful workup, the neutral β-diketiminate−ytterbium amido complexes **5** and [{(DIPPh)$_2$nacnac}Yb(NC$_5$H$_{10}$)-(μ-Cl)]$_2$ (**6**) could be isolated directly in high yield, respectively, as shown in Scheme 1. These results show that the reaction medium has significant effect on the outcome of these reactions.

The IR spectra of complexes **2**−**6** exhibited strong absorptions near 1554 and 1532 cm^{-1}, which were consistent with partial C═N double bond character.[14] All the complexes have good thermal stability. Complex **2** is moderately sensitive to air and moisture, and the crystals can be exposed to air for a few hours without apparent decomposition. In contrast, complexes **3**−**6** are extremely sensitive to air and moisture. The crystals decompose in a few minutes and the colors of the solutions changed immediately, when they are exposed to air, but the crystals and the solution showed no sign of decomposition after several months when stored under argon. Complexes **2**−**6** are freely soluble in donor solvents such as THF and DME and moderately soluble in toluene and benzene. Complexes **3**−**6** are slightly soluble in hexane, while complex **2** is insoluble. These complexes did not provide any resolvable ^{1}H NMR spectra; the resonances are broad and shifted due to the strong paramagnetic nature of ytterbium ion.

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Table 1. Details of the Crystallographic Data and Refinements for Complexes **2**−**6**

param	**2**·C_7H_8	**3**	**4**	**5**·C_6H_6	**6**·C_7H_8
Formula	$C_{40}H_{59}Cl_2N_2O_2Yb$	$C_{43}H_{71}Cl_2LiN_3O_2Yb$	$C_{45}H_{59}ClN_3OYb$	$C_{76}H_{116}Cl_2N_6Yb_2$	$C_{75}H_{110}Cl_2N_6Yb_2$
Fw	843.83	912.94	866.44	1530.723	1512.72
T (K)	193(2)	193(2)	193(2)	193(2)	193(2)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1$	$C2/m$	$P2_1/n$
unit cell					
a (Å)	11.847(5)	13.0993(13)	11.6162(17)	17.189(2)	14.0042(11)
b (Å)	12.410(5)	16.367(2)	32.010(3)	19.4375(16)	13.3892(9)
c (Å)	14.660(6)	21.975(2)	12.5587(17)	14.0992(18)	19.5533(13)
α (deg)	100.760(2)				
β (deg)	102.184(3)	102.260(4)	114.488(6)	126.923(4)	91.474(5)
γ (deg)	102.135(4)				
V (Å^3)	1998.6(14)	4603.8(8)	4249.7(10)	3765.9(8)	3665.1(5)
Z	2	4	4	2	2
D_{calc} (g cm^{-3})	1.402	1.317	1.354	1.350	1.371
μ (mm^{-1})	2.507	2.182	2.299	2.582	2.652
F(000)	866	1892	1780	1576	1552
cryst size (mm)	0.61 × 0.52 × 0.31	0.15 × 0.36 × 0.80	0.80 × 0.30 × 0.15	0.51 × 0.35 × 0.20	0.40 × 0.60 × 0.24
$2\theta_{max}$ (deg)	55.0	55.0	55.0	55.0	55.0
reflcns collcd	19 434	51 107	41 971	20 646	39 563
ind reflcns	8850	10 310	19 009	4343	8116
obsd reflcns	8616	7870	18527	4246	8012
GOF	1.060	1.067	1.112	1.130	1.292
R	0.0273	0.0410	0.0376	0.0411	0.0424
wR_2	0.0692	0.1250	0.0738	0.1001	0.0901

Crystal Structural Analyses. To provide full structural information for these β-diketiminate−ytterbium species, single-crystal X-ray structural investigations were carried out for complexes **2**−**6**. Details of the intensity data collection and the crystal data are given in Table 1. The molecular structures of complexes **2**−**6** are shown in Figures 1−5. Their selected bond lengths and angles are listed in Tables 2 and 3, respectively.

Complex **2** has a monomeric structure in the solid state. The ytterbium atom is six-coordinate with two nitrogen atoms of the β-diketiminate ligand, two chlorine atoms, and two oxygen atoms from one DME molecule in a distorted octahedron. N(1), Cl(1), O(2), and Cl(2) can be considered to occupy equatorial positions within the octahedron about the ytterbium center, and O(1) and N(2) occupy axial positions. The coordination geometry around ytterbium atom is similar to those of monomeric β-diketiminate−lanthanide dichlorides.[7c−e]

In complex **2**, the β-diketiminate ligand is symmetrically coordinated to the ytterbium atom with Yb−N bond lengths of 2.275(2) and 2.282(2) Å, giving the average Yb−N bond length of 2.278(2) Å, which is similar to that in complex **1**.[7a] There is expected delocalization within the π-system of the β-diketiminate ligand, and the β-diketiminate ligand is coordinated to the ytterbium atom in an η^2 manner. Two Yb−Cl bond lengths are 2.5464(11) and 2.5496(10) Å, respectively, which are slightly longer than the terminal Yb−Cl bond length in complex **1**.[7a]

Complex **3** is a dinuclear ytterbium−lithium complex with two chloro bridges. The [(DIPPh)$_2$nacnac]Yb(NPr$^i_2$) moiety is bonded through two chloro bridges to a lithium cation, which in turn is bonded to two oxygen atoms of two THF molecules. The coordination geometry around the ytterbium atom in complex **3** is different from that in complex **2**. The

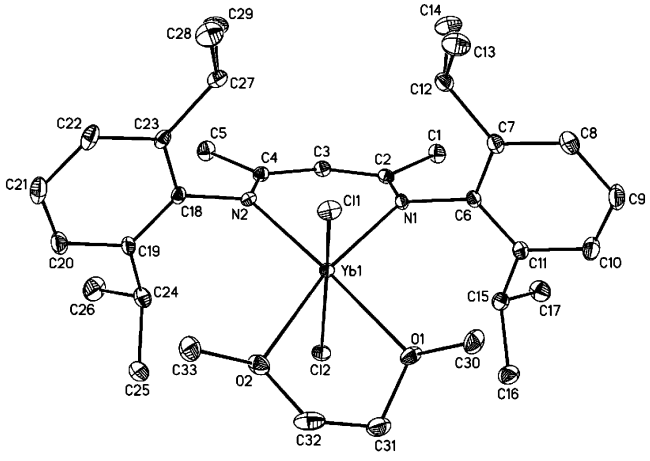

Figure 1. ORTEP diagram of complex **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

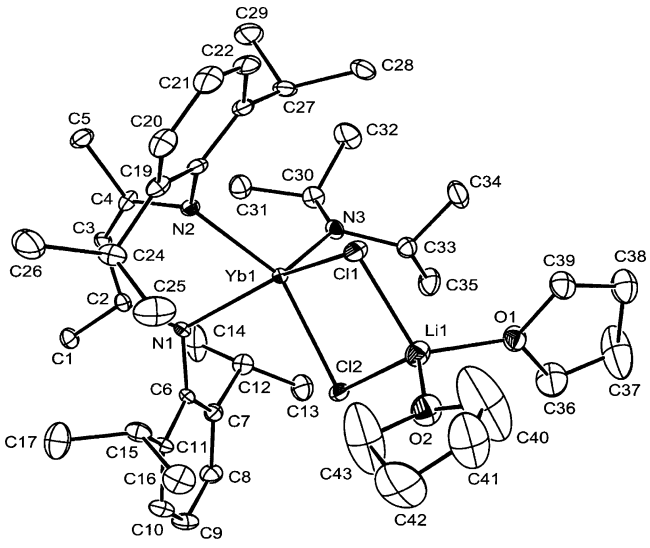

Figure 2. ORTEP diagram of complex **3** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

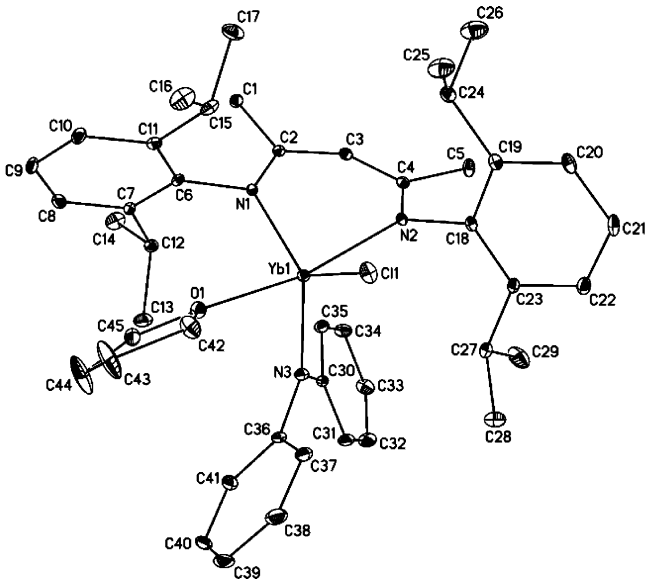

Figure 3. ORTEP diagram of complex **4a** showing the atom-numbering scheme. (Only one of the two independent molecules is shown.) Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

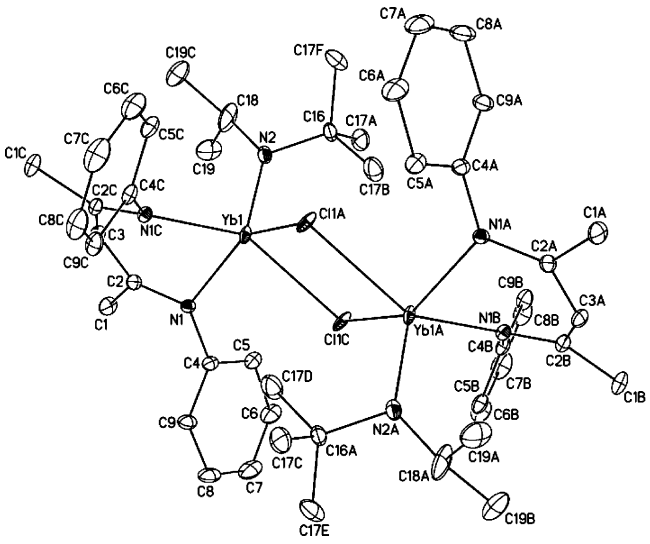

Figure 4. ORTEP diagram of complex **5** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 25% probability level. Isopropyl groups on the arene rings and hydrogen atoms are omitted for clarity. Two disordered carbon atoms (C17A,B,F) are shown in three possible orientations. The disordered chlorine atom is shown in one possible orientation.

Yb^{3+} ion displays a distorted pseudo-trigonal bipyramidal geometry defined by the two nitrogen atoms of the chelating bidentate *β*-diketiminate ligand, one nitrogen atom from diisopropylamido group, and two chlorine atoms (N(1), N(3), and Cl(1) form a plane; N(2) and Cl(2) serve as two vertexes), while the Li ion adopts a distorted pseudotetrahedral geometry formed by two chlorine atoms and two oxygen atoms of two THF molecules.

The *β*-diketiminate ligand is symmetrically coordinated with the ytterbium atom, which is similar to that found in complex **2** but different from that in [(DIPPh)$_2$nacnac]ScCl$_2$(THF).[15] The Yb(1)−N(3) bond is shorter (2.124(5) Å) than

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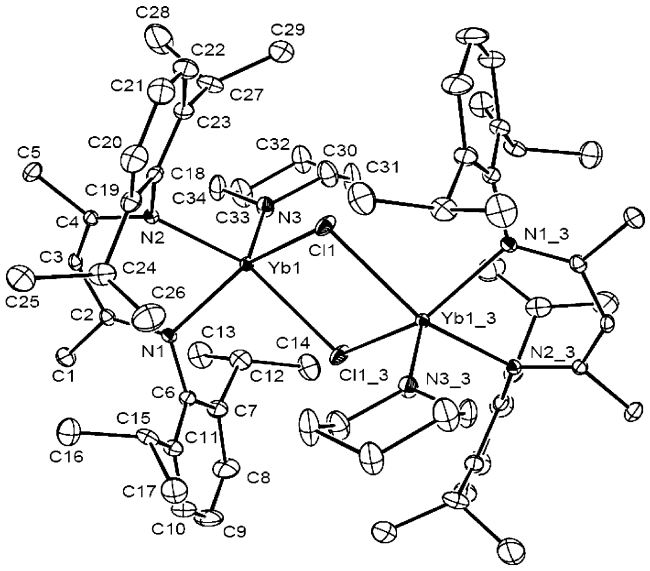

Figure 5. ORTEP diagram of complex **6** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in Complexes **2**−**4**

param	**2**	**3**	**4a**	**4b**
Yb(1)−Cl(1)	2.5496(10)	2.607(1)	2.5095(14)	2.5174(14)
Yb(1)−Cl(2)	2.5464(11)	2.629(1)		
Yb(1)−N(1)	2.275(2)	2.351(4)	2.293(4)	2.298(4)
Yb(1)−N(2)	2.282(2)	2.332(4)	2.320(4)	2.317(4)
Yb(1)−N(3)		2.124(5)	2.217(4)	2.207(4)
Yb(1)−O(1)	2.374(2)		2.361(4)	2.360(4)
Yb(1)−O(2)	2.436(2)			
Yb(1)−C(36)			3.103(5)	3.108(5)
Yb(1)−C(2)	3.215(3)	3.297(5)	3.327(5)	3.316(5)
Yb(1)−C(3)	3.220(3)	3.571(5)	3.648(5)	3.632(5)
Yb(1)−C(4)	3.501(3)	3.263(5)	3.312(5)	3.300(5)
N(1)−C(2)	1.331(3)	1.331(7)	1.340(6)	1.337(7)
N(2)−C(4)	1.335(3)	1.345(6)	1.341(6)	1.341(6)
C(2)−C(3)	1.412(4)	1.407(7)	1.395(7)	1.402(7)
C(3)−C(4)	1.401(4)	1.357(6)	1.412(7)	1.398(7)
Cl(1)−Yb(1)−N(1)	101.60(6)	143.4(1)	131.38(11)	130.08(11)
Cl(1)−Yb(1)−N(2)	99.48(6)	87.5(1)	87.24(10)	87.48(11)
Cl(2)−Yb(1)−N(1)	92.32(6)	86.6(1)		
Cl(2)−Yb(1)−N(2)	92.00(6)	143.4(1)		
N(1)−Yb(1)−N(2)	82.21(8)	80.8(1)	79.57(14)	79.99(15)
Cl(1)−Yb(1)−N(3)		104.7(1)	119.03913)	119.72(13)
N(1)−Yb(1)−N(3)		111.9(2)	109.53(16)	110.17(16)
N(2)−Yb(1)−N(3)		111.4(2)	102.85(16)	102.75(16)

Yb−N bonds to the *β*-diketiminate ligand (see above). The bond lengths of Yb−Cl(1) and Yb−Cl(2) are apparently longer than those in complex **2** due to the formation of the bridge bonds. The *β*-diketiminate ligand is also coordinated to the ytterbium atom in an η^2 manner.

Crystals of complex **4** suitable for an X−ray structure determination were obtained from concentrated hexane solution at room temperature. Complex **4** crystallizes with two crystallographically independent but chemically similar molecules (**4a**,**b**) in the unit cell. An ORTEP of molecule **4a** is depicted in Figure 3. Complex **4** has a solvated monomeric structure in the solid state. The ytterbium atom is five-coordinated by two nitrogen atoms from the *β*-diketiminate ligand, one nitrogen atom from diphenylamido group, one chlorine atom, and one oxygen atom from THF molecule

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) in Complexes **5** and **6**

param	**5**	**6**
Yb(1)−Cl(1)	2.655(7)	2.651(1)
Yb(1)−N(1)	2.290(3)	2.289(3)
Yb(1)−N(2)	2.290(3)	2.290(3)
Yb(1)−N(3)	2.140(6)	2.091(3)
Yb(1)−C(2)	3.074(4)	3.180(4)
Yb(1)−C(3)	3.256(6)	3.444(1)
Yb(1)−C(4)		3.183(4)
N(1)−C(2)	1.340(5)	1.339(4)
C(2)−C(3)	1.403(5)	1.403(5)
C(3)−C(4)		1.402(5)
N(2)−C(4)		1.332(4)
Cl(1)−Yb(1)−N(1)	140.62(11)	144.22(9)
Cl(1)−Yb(1)−N(2)		89.11(8)
Cl(1)−Yb(1)−N(3)	111.54(13)	109.5(1)
N(1)−Yb(1)−N(2)	85.19917)	83.4(1)
N(1)−Yb(1)−N(3)	107.66(13)	106.3(1)
N(2)−Yb(1)−N(3)	107.66(13)	102.77(15)

to form a slightly distorted trigonal bipyramidal geometry. N(1), N(3), and Cl(1) can be considered to occupy equatorial positions within the trigonal bipyramid, and N(2) and O(1) occupy axial positions. The Yb(1)−N(1) and Yb(1)−N(2) bond lengths are 2.293(4) and 2.320(4) Å, respectively, which is slightly greater than the corresponding bond lengths in [(DIPPh)$_2$nacnac](MeC$_5$H$_4$)YbNPh$_2$.[7a] As expected, the Yb(1)−N(3) bond length of 2.217(4) Å is lower than the Yb−N bond to the β-diketiminate ligand, but this bond length is apparently higher than the corresponding Yb−N bond length in complex **3**. This can be attributed to the more crowded coordination environment around ytterbium atom in complex **4**. 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(36) bond length is 3.103(5) Å in complex **4a**, which is comparable to those of 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$_5$)$_2$,[16] and 2.814(4) to 3.148(6) Å for chelating η^6-,η^1-Ph−Yb bonding in [Yb(Odpp)$_3$]$_2$ (Odpp = 2,6−diphenylphenolate).[17]

Crystals of complex **5** that were suitable for an X-ray structure determination were obtained from concentrated toluene solution at −5 °C. Complex **5** has a neutral dimeric structure, and two [(DIPPh)$_2$nacnac]Yb(NPr$^i_2$) moieties are linked through two chloro bridges. The coordination geometry around the ytterbium atom can be best described as a distorted pseudo-trigonal bipyramidal, which is similar to that in complex **3**. Two chlorine atoms and one isopropyl containing C(17A−C) of the diisopropylamido group are disordered due to strong thermal motion. The chlorine atom has been resolved into three atoms with occupancy of one-third, respectively. The two carbon atoms of the isopropyl group have been resolved into three atoms with occupancy of 0.75, 0.75, and 0.5, respectively. It is worthy to note that there is a benzene molecule in the unit cell. The benzene molecule should be a toluene molecule, but it lies on an inversion center and has an average centrosymmetric structure. Only the benzene ring can be found in the crystal structure, and it is not possible to assign the methyl group.[18] The Yb−N(1) bond length of 2.290(3) Å is about 0.05 Å lower than the average Yb−N bond to the β-diketiminate ligand in complex **3**. The amide displays shorter bond to ytterbium (2.140(6) Å) than does the β-diketiminate ligand. The Yb−C(2) distance is 3.074(4) Å, which indicates that the complex may be considered to involve π coordination of the β-diketiminate ligand to the ytterbium atom.

Crystals of complex **6** suitable for an X-ray structure determination were obtained from a concentrated toluene solution at room temperature. Complex **6** has crystallographically imposed 2-fold symmetry; the overall molecular structure of complex **6** resembles that of complex **5**. Like that in complex **5**, the β-diketiminate ligand is symmetrically coordinated to the ytterbium atom. The Yb−N(1) and Yb−N(2) bond lengths of 2.287(3) and 2.289(3) Å, respectively, are in accordance with the corresponding bond length in complex **5**, but are slightly shorter than those in complex **3**. The Yb−N(3) bond length of 2.089(4) Å is about 0.13 and 0.05 Å shorter than the corresponding bond lengths in complexes **4** and **5**, respectively, which can be attributed to piperidyl having less steric bulk than diisopropylamido and diphenylamido groups. There is only purely σ bonding between the β-diketiminate ligand and the ytterbium atom, which is different from that observed in complex **5**.

Polymerization. Yasuda and co-workers first reported that lanthanocene alkyls, as single-component initiators, can initiate the living polymerization of MMA.[19] From then on, a series of lanthanocene or nonlanthanocene complexes were found to be effective initiators for MMA polymerization.[20,21] The catalytic behavior of complexes **4**−**6** for the polymerization of MMA was examined. As expected, these β-diketiminate−lanthanide monoamido complexes can be used as single-component initiators to initiate MMA polymerization in toluene. The preliminary results are summarized in Table 4. It can be seen that complexes **4**−**6** polymerize MMA with relatively good activity, and the yield can reach 75% at 0 °C in 5 h in the case of 0.5 mol % initiator concentration

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Table 4. Polymerization of MMA Initiated by Complexes **4**−**6**[a]

entry	initiator	T (°C)	yield (%)	$10^{-4}M_n$(calcd)	$10^{-4}M_n$(obsd)[b]	M_w/M_n[b]	tacticity (%)		
							mm	mr	rr
1	**4**[c]	0	24.1	0.48	2.32	2.62	17.9	36.9	45.2
2	**4**[d]	60	15.9	0.32	0.97	2.27	11.9	32.9	55.2
3	**4**	60	7.5	0.15	0.89	2.28			
4	**4**[c]	0	49.3	0.98	1.93	2.23	13.8	28.6	57.6
5	**5**[d]	60	18.1	0.36	0.69	2.09	17.7	37.1	45.2
6	**5**[d]	0	45.2	0.90	3.80	2.72	8.6	31.7	59.7
7	**5**	60	7.8	0.16	0.93	2.92			
8	**6**	0	69.2	1.28	2.88	1.87	8.9	30.2	60.9
9	**6**[c]	0	75.2	1.50	2.85	1.85	8.7	30.2	61.1
10	**6**	−78	27.9	0.56	2.52	2.58	0	19.5	80.5
11	**6**[d]	60	37.6	0.76	2.05	2.77	22.8	37.8	39.4
12	**6**	60	18.1	0.36	1.57	2.11			

[a] Polymerization conditions: in toluene, [M]/[I] = 200, solvent/monomer = 1 (v/v), t = 3 h. [b] Measured by GPC at 30 °C in THF relative to polystyrene standards with Mark−Houwink corrections.[24] [c] t = 5 h. [d] Bulk polymerization.

([M]/[I] = 200) using complex **6** as initiator. However, the activity of these complexes is apparently lower than that of lanthanocene amido complexes.[20e,f] For example, 100% of yield can be reached in 2 h even in the case of 0.2 mol % initiator concentration using $(MeC_5H_4)_2Yb(NC_5H_{10})(HNC_5H_{10})$ as initiator.[20f] The amido group has a significant effect on the activity of these β-diketiminate−lanthanide complexes. The activity order of amido group is NPh_2 < NPr^i_2 < NC_5H_{10}, which is contrary to the order of the Ln−N(amido) bond lengths in these complexes. This increasing order is in accordance with that observed in lanthanocene amide systems.[20e] Polymerization temperature affects the activity dramatically. The yields increased first with the decrease of temperature from 60 to 0 °C and then decreased with the decrease of temperature from 0 to −78 °C. The highest yields were obtained at about 0 °C. This may be because a side reaction involving a nucleophilic substitution reaction of lanthanide amido complexes to the ester group of MMA, which caused inactivation of the catalyst, occurred at high temperature,[22] and the polymerization became difficult at lower temperature. The relationship between temperature and yields for the present systems is different from that for lanthanocene amide systems. In the later case, the yields increase with decreasing of temperature.[20e] Almost all of the molecular weights of the polymers obtained are quite superior to the theoretical values, which indicated that the initiation efficiency is low. The reason may be attributed to the destruction of the extremely sensitive β-diketiminate−lanthanide amido complex by the contaminated H_2O and/or oxygen included in the system.[20b] Because the measured molecular weights are quite far from the theoretical ones, and the molecular weight distributions of these polymers obtained are relatively broad, the present polymerization systems are not well-controlled. The tacticity of the resultant PMMA was determined with reference to the reported triad.[23] The atactic PMMA is obtained using complexes **4**−**6** as initiator at or above 0 °C, while the syndiotacticity of PMMA increases with the decreasing of polymerization temperature, and the syndiotactic PMMA can be obtained at −78 °C (entry 10). The increasing of syndiotacticity with decreasing of temperature is common in organolanthanide catalyst systems.[20e]

On the basis of the wide application of poly(ϵ-caprolactone) (PCL) and its copolymers in the medical field,[25] the synthesis of these polymers by ring-opening polymerization (ROP) of lactones and functionally related compounds has attracted considerable attention. Many kinds of organolanthanide complexes have been reported to be efficient initiators for the ROP of lactones, giving polymers with both high molecular weights and high yields.[26,27] The catalytic behavior of complexes **4**−**6** for the ring-opening polymerization of ϵ-caprolactone was also examined, and the preliminary results are summarized in Table 5. It can be seen that all of these complexes are efficient initiators for this polymerization in toluene. The β-diketiminate−lanthanide amido complexes showed extremely high activity compared with the lanthanocene amido complexes. For examples, using complex **5** as initiator, nearly quantitative yield can be obtained within 1 min at 25 °C when the molar ratio of monomer to initiator is 500:1, and even when the amount of the initiator decreases to [CL]:[I] = 800:1, the polymerization still gives a 84% yield within 10 min. However, using lanthanocene amide $(MeC_5H_4)_2YbNPr^i_2(THF)$ as initiator, the yield is only 26% after 4 h in the case of 500:1 (molar ratio) of monomer to initiator.[29] Evans and co-workers also

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Table 5. Polymerization of ϵ-Caprolactone Initiated by Complexes **4**−**6**[a]

entry	initiator	[M]/[I]	$V_{solvent}/V_{monomer}$	t (min)	yield (%)	$10^{-4}M_n$(calcd)	$10^{-4}M_n$(obsd)[b]	PDI
1	**4**	200	4	1 min	100	2.28	0.946	1.46
2	**4**	500	4	1 min	100	5.70	0.874	1.71
3	**4**	500	9	10 min	70.1	3.99	1.01	1.62
4	**5**	200	4	1 min	100	2.28	0.823	1.61
5	**5**	200	4	48 h	100	2.28	1.20	1.95
6	**5**	500	4	1 min	100	5.70	0.823	1.64
7	**5**	800	4	10 min	84.1	7.66	0.935	1.61
8	**5**	500	9	10 min	65.8	3.75	0.846	1.69
9	**6**	200	4	1 min	100	2.28	0.403	1.68
10	**6**	500	4	1 min	100	5.70	0.515	1.43
11	**6**	500	9	10 min	75.6	4.31	0.605	1.50
12	**2**	200	4	16 h	16.1	0.464	0.599	1.14

[a] Polymerization conditions: in toluene, $T = 25$ °C. [b] Measured by GPC at 30 °C in THF relative to polystyrene standards with Mark−Houwink corrections for M_n [M_n(obsd) = $0.56M_n$(GPC)].[28]

found that the activity of the divalent samarium amide $[(Me_3Si)_2N]_2Sm(THF)_2$ for ϵ-caprolactone polymerization is much higher than that of $(C_5Me_5)_2Sm(THF)_x$.[26a] Considered the stronger electron-donating ability of the β-diketiminate ligand in comparison with cyclopentadienyl group, it can be concluded that increasing of electron density of the ligand around metal center might be beneficial to the increase of activity of Ln−N(amido) bond for ϵ-caprolactone polymerization. The polymerization rate decreases with decreasing monomer concentration. For example, the polymerization gives a 100% yield in 1 min when the volume ratio of solvent to monomer is 4, while a 65.8% yield is obtained when the volume ratio increases to 9 under the same polymerization conditions (entries 3, 8). The effect of the amido groups in these complexes on the polymerization was not observed. All of these ytterbium amido complexes show a similar catalytic behavior under present polymerization conditions. Because complex **2** can only initiate ϵ-caprolactone polymerization in very low activity (entry 12), the polymerization initiated by the Ln−N bonds from the β-diketiminate group can be ignored, and the polymerization was initiated by the Ln−N(amido) bond. However, the molecular weights of the polymers obtained are time inferior to expected theoretical ones, and no linear relationship between monomer-to-initiator ratio and molecular weight can be observed. Meanwhile, the molecular weight distributions of the resultant polymers are relatively broad (range from 1.43 to 1.71). The low molecular weights and broad PDIs in these systems might be attributed mainly to a back-biting reaction, caused by the catalyst, leading to intramolecular transesterification. Further experiment reveals that the molecular weight increases and molecular weight distribution broadens as the polymerization time prolonged to 48 h, which can be attributed to the intermolecular transesterification.[30] These results indicate that the transesterification reaction during the polymerization process in the present systems cannot be effectively suppressed.

Conclusion

In summary, we have successfully synthesized a series of new β-diketiminate ytterbium monoamido complexes [(DIPPh)$_2$nacnac]Yb(NPh$_2$)Cl(THF) and [{(DIPPh)$_2$nacnac}-Yb(NR$_2$)Cl]$_2$ (NR$_2$ = NPr$^i_2$, NC$_5$H$_{10}$) via metathesis reaction using the β-diketiminate−ytterbium dichloride [(DIPPh)$_2$-nacnac]YbCl$_2$(DME) as a synthon. Their structure features have been determined by X-ray diffraction study. These new β-diketiminate−ytterbium monoamido complexes exhibit good activity for MMA polymerization. These results indicate that decreasing the steric bulkiness around the central metal should increase the reactivity of the complexes. However, the activity of these β-diketiminate−ytterbium monoamido complexes is still apparently lower than that of lanthanocene amido complexes. Furthermore, these β-diketiminate−ytterbium amido complexes showed high catalytic activity for the ring-opening polymerization of ϵ-caprolactone, but the polymerization is not well-controlled. Although a lot of lanthanide complexes bearing other ligand environments exhibit high catalytic activity and controlled polymerization behavior for the polymerization of MMA and ϵ-caprolactone, design and synthesis of new β-diketiminate−lanthanide complexes to exhibit these features is still a challenge. Studies are still in process in our laboratory.

Experimental Section

All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. {[(DIPPh)$_2$nacnac]YbCl(μ-Cl)$_3$Yb[(DIPPh)$_2$nacnac]-(THF)} (**1**) was prepared according to the literature method.[7a] ϵ-Caprolactone and methyl methacrylate were purchased from Acros, dried by CaH_2 for 48 h, and then distilled under reduced pressure. The uncorrected melting points were determined in sealed Ar-filled capillary tubes. Ytterbium analysis was carried out by complexometric titration. The content of lithium was determined on a Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed 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. 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 an eluent.

[(DIPPh)$_2$nacnac]YbCl$_2$(DME) (2). Method a. A 2 mL volume of DME was added to a toluene solution of complex **1** (0.86 g,

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0.62 mmol, 80 mL) by syringe, and the color of the solution changed immediately from purplish red to red. Then the solution was concentrated to about 5 mL and cooled at −5 °C. The red crystals of complex **2** were collected in two crops by filtration (0.76 g, 83%). Mp: 155−157 °C (dec). Anal. Calcd for $C_{33}H_{51}Cl_2N_2O_2Yb$: C, 52.73; H, 6.84; N, 3.73; Yb, 23.02. Found: C, 53.12; H, 6.51; N, 3.48; Yb, 22.89. IR (KBr, cm^{-1}): 2963 (s), 2932 (s), 2866 (m), 1624 (vs), 1555 (vs), 1481 (m), 1462 (s), 1437 (s), 1385 (m), 1360 (s), 1322 (s), 1292 (s), 1254 (m), 1177 (m), 1088 (m), 1026 (m), 937 (w), 798 (m).

Method b. A solution of [(DIPPh)$_2$nacnac]Li (12 mL, 3.86 mmol) in toluene/*n*-hexane (4:1) was slowly added to a suspension of $YbCl_3$ (1.08 g, 3.86 mmol) in 30 mL of THF at room temperature. The color of the solution gradually changed to red. The reaction mixture was stirred overnight at room temperature. Solvent was completely removed under vacuum, and the red residue was extracted with toluene. The dissolved portion was removed by centrifugation. The filtrate was concentrated to 15 mL, and 1 mL of DME was added. The solution was cooled at −5 °C, and red block crystals were collected in two crops by filtration in 2 days (2.04 g, 70%).

[(DIPPh)$_2$nacnac]Yb(NPr$^i_2$)(μ-Cl)$_2$Li(THF)$_2$ (3). To a THF solution (40 mL) of complex **2** (2.29 g, 3.05 mmol) was slowly added a toluene solution of $LiNPr^i_2$ (10 mL, 3.05 mmol) prepared in situ by the reaction of $HNPr^i_2$ with LiBu-*n* (1.65 M in *n*-hexane) at 0 °C. The solution was stirred at 0 °C for 1 h and then for another 24 h at room temperature. The color of the solution gradually changed from red to brown. The solution was concentrated to about 5 mL under reduced pressure, and then 20 mL of toluene was added. The brown crystals were obtained from a concentrated toluene−THF solution at −30 °C in 2 weeks (1.35 g, 49%). Mp: 109−111 °C. Anal. Calcd for $C_{43}H_{71}Cl_2LiN_3O_2Yb$: C, 56.57; H, 7.84; N, 4.60; Yb, 18.95. Found: C, 56.41; H, 7.62; N, 4.57; Yb, 18.65. IR (KBr, cm^{-1}): 2963 (s), 2928 (m), 2866 (w), 1659 (m), 1624 (s), 1551 (s), 1462 (s), 1389 (m), 1323 (w), 1262 (w), 1172 (w), 1103 (w), 1034 (w), 937 (w).

[(DIPPh)$_2$nacnac]Yb(NPh$_2$)Cl(THF) (4). The synthesis of complex **4** was carried out by the similar method for that of complex **3**, but $LiNPh_2$ (6.19 mmol) was used instead of $LiNPr^i_2$. Complex **4** was obtained as red crystals at room temperature in 2 days (3.60 g, 67%). Mp: 149−151 °C. Anal. Calcd for $C_{45}H_{59}ClN_3OYb$: C, 62.38; H, 6.86; N, 4.85; Yb, 19.97. Found: C, 62.73; H, 6.75; N, 4.81; Yb, 19.62. IR (KBr, cm^{-1}): 2963 (s), 2928 (m), 2866 (m), 1620 (s), 1593 (s), 1551 (s), 1493 (s), 1462 (m), 1385 (m), 1316 (m), 1277 (m), 1173 (w), 1099 (w), 1026 (w), 934 (w).

[{(DIPPh)$_2$nacnac}Yb(NPr$^i_2$)(μ−Cl)]$_2$ (5). Method a. A 1.20 g (1.31 mmol) amount of complex **3** was dissolved in toluene (80 mL). The solution was stirred at 80 °C in an oil bath for about 12 h, and then the precipitation was removed from the solution by centrifugation. Complex **5** was obtained as dark-red crystals from a concentrated toluene solution at −5 °C in 2 days (0.69 g, 72%). Mp: 189−191 °C. Anal. Calcd for $C_{76}H_{116}Cl_2N_6Yb_2$: C, 57.88; H, 7.63; N, 5.79; Yb, 23.82. Found: C, 58.01; H, 7.50; N, 5.39; Yb, 23.42. IR (KBr, cm^{-1}): 2963 (s), 2928 (m), 2866 (m), 1659 (m), 1624 (m), 1589 (w), 1551 (m), 1462 (m), 1439 (m), 1173 (m), 1103 (w), 1042 (w), 934 (w), 783 (m), 756 (m).

Method b. To a toluene solution (80 mL) of complex **2** (3.24 g, 4.31 mmol) was slowly added a toluene/*n*-hexane (4:1) solution of $LiNPr^i_2$ (12 mL, 4.31 mmol) prepared in situ at 0 °C. The solution was stirred at 0 °C for 1 h and then for another 24 h at room temperature. The color of the solution gradually changed from red to dark-blue. The precipitation was removed by centrifugation, and then the solution was concentrated to about 10 mL under reduced pressure. Complex **5** was obtained as dark-red crystals at −5 °C in a few days (1.96 g, 63%).

[{(DIPPh)$_2$nacnac}Yb(NC$_5$H$_{10}$)(μ-Cl)]$_2$ (6). The synthesis of complex **6** was carried out in the same way as that described for complex **5** (method b), but $LiNC_5H_{10}$ (3.60 mmol) was used instead of $LiNPr^i_2$. A 1.65 g amount of complex **6** was isolated from a concentrated toluene solution as brown crystals (65%). Mp: 218−220 °C. Anal. Calcd for $C_{75}H_{110}Cl_2N_6Yb_2$: C, 57.49; H, 7.24; N, 5.92; Yb, 24.36. Found: C, 57.16; H, 7.21; N, 5.72; Yb, 24.19. IR (KBr, cm^{-1}): 2963 (s), 2928 (s), 2866 (s), 1659 (m), 1624 (m), 1551 (s), 1524 (s), 1462 (s), 1366 (s), 1319 (w), 1254 (m), 1173 (m), 1103 (m), 1022 (m), 924 (m), 750 (m).

Typical Procedure for Polymerization Reactions. The procedures for the polymerizations of methyl methacrylate and ϵ-caprolactone are similar, and a typical polymerization procedure is given below. A 25 mL Schlenk flask, 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 1 mL of methyl methacrylate using a syringe. The contents of the flask were then stirred vigorously at 0 °C water bath for the desired time, during which time the mixture became very viscous, thus disrupting the stirring. The reaction mixture was quenched by the addition of 1 M HCl solution and was then poured into ethanol to precipitate the polymer, which was dried under vacuum and weighed.

X-ray Crystallography. Suitable single crystals of complexes **2**−**6** were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.710 70 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 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), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using the SHELEXL-97 (for complexes **2**, **4**−**6**) and CRYSTALS (for complex **3**) programs.

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

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