

Synthesis and Characterization of Lanthanide(III) Bis(guanidinate) Derivatives and the Catalytic Activity of Methyllanthanide Bis(guanidinate) Complexes for the Polymerization of ϵ -Caprolactone and Methyl Methacrylate

Yunjie Luo,^[a] Yingming Yao,^[a] Qi Shen,^{*[a]} Kaibei Yu,^[b] and Linhong Weng^[c]

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The synthesis and structure of new lanthanide complexes with the guanidinate ligand $[(\text{Me}_3\text{Si})_2\text{NC}(\text{NiPr})_2]^-$ are described. Reaction of a THF slurry of LnCl_3 with a hexane solution of $[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]\text{Li}$ (**1**) in a 1:2 molar ratio afforded the new soluble organolanthanide complexes $[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ [$\text{Ln} = \text{Yb}$ (**2**), Nd (**3**)]. Alkylation of **2** and **3** with 2 equiv. of MeLi in hexane gave $[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]\text{Ln}(\mu\text{-Me})_2\text{Li}(\text{TMEDA})$ [$\text{Ln} = \text{Yb}$ (**4**), Nd (**5**)] in good yield as crystalline solids. The molecular structures of **2** and **5** were determined by single-crystal X-ray ana-

lysis. The lanthanide ions in these complexes display a distorted pseudo-octahedral coordination geometry. Complexes **4** and **5** exhibited extremely high activity for the ring-opening polymerization of ϵ -caprolactone to give high molecular weight polymers. Complex **5** also showed good catalytic activity for the syndiotactic polymerization of methyl methacrylate.

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Introduction

Guanidinate anions, $[(\text{RN})_2\text{C}(\text{NR}_2')^-]$, are isoelectronic alternatives to cyclopentadienyl ligands and their electronic properties and steric bulk can be modified by variation of the substituents on the nitrogen atoms. As a result, guanidates have attracted increasing attention as ancillary ligands in the coordination and organometallic chemistry of main group and transition metals,^[1] and some of these complexes have been reported to exhibit interesting reactivity. For example, neutral and cationic Zr^{IV} bis(guanidinate) complexes are catalysts for the polymerization of α -olefins,^[2] and mono- and dianionic guanidinate complexes of Ta^{IV} and (hydrocarbyl) Zr^{IV} bis(guanidinate) complexes react with Me_3SiCl , ArNC ,^[3] and 2,6-dimethylphenyl isocyanide,^[4] respectively. However, the application of guanidinate ligands in organolanthanide chemistry has been quite limited; to date, only three papers concerning the synthesis and characterization of lanthanide guanidinate complexes have been published,^[5–7] with one of these discussing the catalytic activity of $\text{La}[\text{CyNC}\{\text{N}(\text{SiMe}_3)_2\}\text{NCy}](\text{OC}_6\text{H}_3\text{tBu}_2\text{-2,6})_2$

complexes for the ring-opening polymerization of D,L-lactide.^[7]

We have recently become interested in understanding the chemistry of organolanthanide complexes with nitrogen-based polydentate ligands.^[8] As an extension of our studies in this area, we have prepared the lanthanide guanidinate complexes $[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ [$\text{Ln} = \text{Yb}$ (**2**), Nd (**3**)] and $[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]\text{Ln}(\mu\text{-Me})_2\text{Li}(\text{TMEDA})$ [$\text{Ln} = \text{Yb}$ (**4**), Nd (**5**)]. Complexes **4** and **5** are highly active for the ring-opening polymerization of ϵ -caprolactone, and **5** is also able to catalyze the polymerization of methyl methacrylate.

Results and Discussion

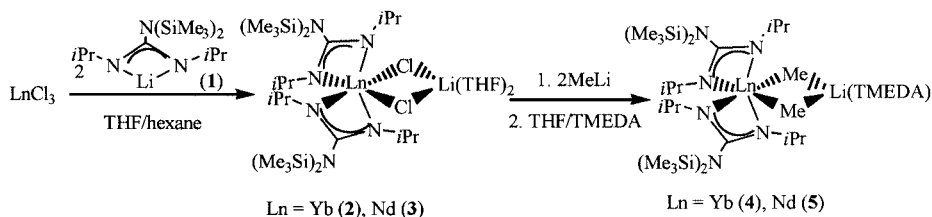
Synthesis and Characterization of the Chloro and Methyl Complexes **2**, **3** and **4**, **5**

The reaction of *N,N'*-diisopropylcarbodiimide with 1 equiv. of $\text{LiN}(\text{SiMe}_3)_2$ in hexane gives a quantitative yield of $[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]\text{Li}$ (**1**); thus, in most cases a freshly prepared solution of the lithium guanidinate was used directly in the following metathesis reactions. Treatment of a hexane solution of **1** with a THF slurry of LnCl_3 in a 2:1 molar ratio at room temperature afforded after workup the chlorolanthanide guanidinate complexes $[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ [$\text{Ln} = \text{Yb}$ (**2**), Nd (**3**)] in 76 and 82% yield, respectively.

^[a] Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, People's Republic of China
Fax: (internat.) + 86-0512/65112371
E-mail: qshen@suda.edu.cn

^[b] Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, People's Republic of China

^[c] Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China



Scheme 1

Elemental analyses show both **2** and **3** to be lanthanide monochloride bis(guanidinate)s, complexed with $\text{LiCl} \cdot 2\text{THF}$. An X-ray determination of the structure of **2** reveals it to be an “ate” complex possessing two chloro bridges to an Li cation as shown in Scheme 1 and Figure 1.

Complexes **2** and **3** are useful precursors for further transformation. They react with 2 equiv. of MeLi in hexane to produce the μ -methyl “ate” derivatives **4** and **5** in 72 and 76% yield, respectively (Scheme 1). Use of 1 equiv. of MeLi gave the same methyl complexes, albeit in quite low yield.

All the complexes synthesized are air- and moisture-sensitive and have good solubility in toluene, diethyl ether and tetrahydrofuran (THF).

The $\text{N}=\text{C}=\text{N}$ stretch of the parent carbodiimide (2117 cm^{-1}) is absent in the IR spectra of these complexes while a $\text{C}=\text{N}$ stretch at approximately 1640 cm^{-1} is observed. These data suggest that the π -electrons within the double bonds of the $\text{N}-\text{C}-\text{N}$ linkage are delocalized in all the complexes.^[9]

Crystals of **2** suitable for X-ray diffraction were grown from THF, while **5** crystallized from a solution of a mixture of THF and TMEDA.

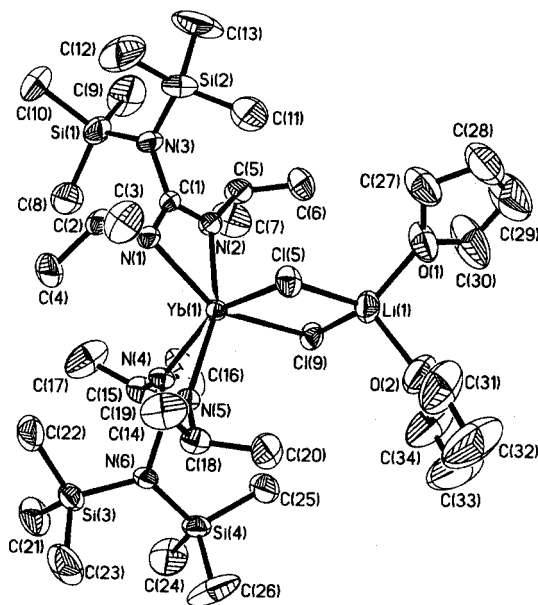


Figure 1. ORTEP diagram of $[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]_2\text{Yb}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (**2**) showing non-hydrogen atom numbering scheme

An ORTEP diagram of **2** is shown in Figure 1. Crystal and structural refinement data are listed in Table 1, and selected bond lengths and angles are given in Table 2. As shown in Figure 1, **2** is a dinuclear lanthanide–lithium complex with two chloro bridges. The $[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]_2\text{Yb}$ 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 Yb ion displays a distorted octahedral geometry defined by the four nitrogen atoms of the two chelating bidentate guanidinate ligands and the two chloride ligands, while the Li ion adopts a distorted tetrahedral geometry. The nearly identical C–N distances within the chelating guanidinate ligands (see Table 2) suggest that the π -electrons within the NCN fragments are delocalized. The guanidinate ligands bind to Yb through two nitrogen atoms to yield a planar four-membered ring with bite angles of $57.09(13)^\circ$ and $57.18(12)^\circ$. The Yb–N bond lengths vary from $2.295(3)$ to $2.332(3)\text{ \AA}$, similar to the values reported for $[(\text{SiMe}_3)_2\text{NC}(\text{NCy})_2]_2[\text{N}(\text{SiMe}_3)_2]\text{Yb}^{[5]}$ and $\{[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]_2\text{Y}(\mu\text{-Cl})\}_2$.^[6] The Yb–Cl bond lengths are $2.6076(14)$ and $2.6306(13)\text{ \AA}$, respectively, which are similar to those in $\text{Li}[\text{YbCl}_2(\text{C}_5\text{H}_4\text{SiCH}_3\text{Ph}_2)_2](\text{Et}_2\text{O})_2$.^[10] The $\text{C}(1)-\text{Yb}-\text{C}(14)$ angle is $131.09(12)^\circ$, similar to that found in $[(\text{SiMe}_3)_2\text{NC}(\text{NCy})_2]_2\text{YbN}(\text{SiMe}_3)_2$ (130.5°)^[5] but greater than the corresponding angle in $\{[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]_2\text{Y}(\mu\text{-Cl})\}_2$ [$123.09(15)^\circ$].^[6] The $\text{Cl}(1)-\text{Yb}-\text{Cl}(2)$ angle [$84.42(4)^\circ$] is also greater than that in $\{[(\text{SiMe}_3)_2\text{NC}(\text{NiPr})_2]_2\text{Y}(\mu\text{-Cl})\}_2$ [$76.30(4)^\circ$],^[6] and smaller than that in $\text{Li}[\text{YbCl}_2(\text{C}_5\text{H}_4\text{SiCH}_3\text{Ph}_2)_2](\text{Et}_2\text{O})_2$ [$87.14(3)^\circ$].^[10]

The orientation of the $\text{N}(\text{SiMe}_3)_2$ groups relative to the NCNYb plane is approximately perpendicular and is similar to the analogous $\text{Sm}^{[5]}$, $\text{Yb}^{[5]}$ and $\text{Y}^{[6]}$ complexes. This disposition prevents π -overlapping between these two moieties; however, it increases the steric bulk above and below the planar guanidinate ligand.

An ORTEP diagram of **5** is presented in Figure 2. Details concerning the data collection are listed in Table 1 and selected bond lengths and angles are given in Table 3.

The crystal structure of **5** is similar to that of **2**, even though **5** is only monomeric in the solid state. The geometry of the Nd ion is best described as a distorted pseudo-octahedron defined by the four nitrogen atoms of the two chelating bidentate guanidinate ligands and the two μ -methyl groups. The Li ion adopts a distorted tetrahedral geometry with two μ -Me groups and two N atoms of a TMEDA molecule coordinated to it.

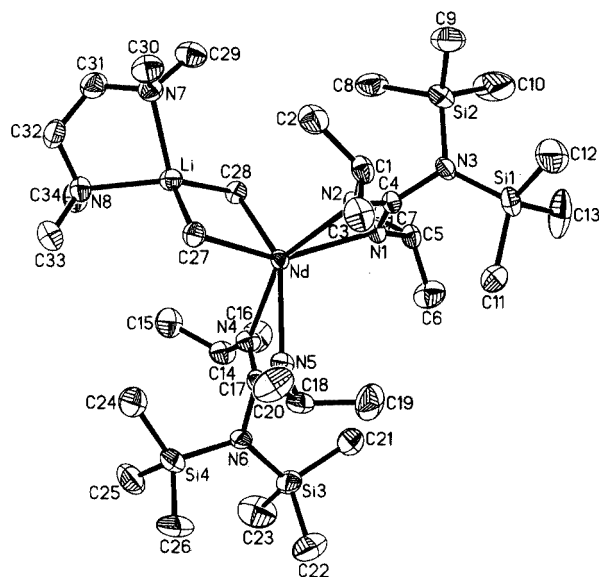
Table 1. Details of the crystallographic data and refinements for **2** and **5**

	2	5
Empirical formula	C ₃₄ H ₈₀ Cl ₂ LiN ₆ O ₂ Si ₄ Yb	C ₃₄ H ₈₆ LiNdN ₈ Si ₄ ·0.375C ₆ H ₁₂
Formula mass	968.28	902.21
<i>T</i> [K]	293(2)	291(2)
λ [Å]	0.71073	0.71073
Crystal system	Triclinic	triclinic
Space group	P $\bar{1}$	P $\bar{1}$
Unit cell dimensions		
<i>a</i> [Å]	9.972(3)	12.981(6)
<i>b</i> [Å]	14.912(5)	14.008(5)
<i>c</i> [Å]	18.456(6)	17.476(7)
α [°]	75.717(4)	101.16(2)
β [°]	87.347(4)	93.52(4)
γ [°]	79.438(4)	108.87(3)
<i>V</i> [Å ³]	2614.8(15)	2924(2)
<i>Z</i>	2	2
Density [Mg/m ³]	1.230	1.025
μ [mm ⁻¹]	2.013	0.997
<i>F</i> (000)	1010	966
θ range [°]	1.60–25.01	1.58–25.00
No. of reflns. collected	10703	11029
No. of ind. reflections	9112 [<i>R</i> (int) = 0.0298]	10189 [<i>R</i> (int) = 0.0327]
No. of data/restraints/param.	9112/0/452	10189/7/464
Final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0352	0.0597
<i>R</i> _w	0.0816	0.1716
GOF on <i>F</i> ²	1.056	1.005

Table 2. Selected Bond lengths [Å] and angles [°] for **2**

Yb(1)–N(4)	2.295(3)	Yb(1)–N(1)	2.299(3)
Yb(1)–N(2)	2.330(4)	Yb(1)–N(5)	2.332(3)
Yb(1)–Cl(1)	2.6076(14)	Yb(1)–Cl(2)	2.6306(13)
Yb(1)–C(1)	2.742(4)	Yb(1)–C(14)	2.745(4)
Yb(1)–Li(1)	3.470(9)	Li(1)–O(1)	1.916(12)
Li(1)–O(2)	1.946(12)	Li(1)–Cl(1)	2.318(11)
Li(1)–Cl(2)	2.348(11)	N(1)–C(1)	1.310(6)
N(4)–C(14)	1.316(5)	N(2)–C(1)	1.322(6)
N(5)–C(14)	1.328(5)	N(3)–C(1)	1.448(6)
N(6)–C(14)	1.437(5)		
N(1)–Yb(1)–N(2)	57.09(13)	N(4)–Yb(1)–N(5)	57.18(12)
Cl(1)–Yb(1)–Cl(2)	84.42(4)	C(1)–Yb(1)–C(14)	131.09(12)
C(1)–Yb(1)–Li(1)	112.4(2)	C(14)–Yb(1)–Li(1)	116.5(2)
O(1)–Li(1)–O(2)	103.3(5)	Cl(1)–Li(1)–Cl(2)	97.9(3)
Li(1)–Cl(1)–Yb(1)	89.4(3)	Li(1)–Cl(2)–Yb(1)	88.2(3)
C(1)–N(3)–Si(1)	117.0(4)	C(1)–N(3)–Si(2)	118.6(4)
C(14)–N(6)–Si(4)	118.3(3)	C(14)–N(6)–Si(3)	118.4(3)
N(1)–C(1)–N(2)	114.4(4)	N(3)–C(1)–Yb(1)	173.6(3)
N(4)–C(14)–N(5)	113.7(4)	N(6)–C(14)–Yb(1)	171.4(3)

The Nd–N bond lengths within each NdN₂C moiety differ by approximately 0.05 Å. The Nd–C_{methyl} bond lengths are 2.590(8) and 2.595(8) Å, which are identical to those in [(*t*BuCp)₂Nd(μ-Me)]₂ [2.594(15) Å]^[11] and similar to those in [(SiMe₃)₂NC(NiPr)₂Y(μ-Me)₂Li(TMEDA)] [2.505(4) and 2.508(4) Å].^[6] The bite angles of the two ligands are 53.5(2) and 54.0(2)°, which are close to that found in [(SiMe₃)₂NC(NiPr)₂Y(μ-Me)₂Li(TMEDA)] [55.36(10)°].^[6] The Me–Nd–Me angle of 89.3(2)° is similar to the angle in [(*t*BuCp)₂Nd(μ-Me)]₂ [88.4(7)°].^[11]

Figure 2. ORTEP diagram of [(SiMe₃)₂NC(NiPr)₂]₂Nd(μ-Me)₂Li(TMEDA) (**5**) showing the atom-numbering scheme; hydrogen atoms have been omitted for clarity

Polymerization of ε-Caprolactone and Methyl Methacrylate by Complexes **4** and **5**

Both **4** and **5** were found to catalyze the polymerization of ε-caprolactone and methyl methacrylate in toluene solution. The preliminary results are listed in Tables 4 and 5, respectively.

Table 3. Selected bond lengths [Å] and angles [°] for **5**

Nd–N(5)	2.476(7)	Li–N(8)	2.191(15)
Nd–N(1)	2.477(6)	Li–C(27)	2.215(16)
Nd–N(2)	2.513(6)	Li–C(28)	2.244(15)
Nd–N(4)	2.523(6)	N1–C(4)	1.338(9)
Nd–C(27)	2.590(8)	N2–C(4)	1.315(9)
Nd–C(28)	2.595(8)	N3–C(4)	1.457(9)
Nd–C(4)	2.931(7)	N4–C(17)	1.352(10)
Nd–C(17)	2.936(8)	N5–C(17)	1.328(9)
Nd–Li	3.129(13)	N6–C(17)	1.455(10)
Li–N(7)	2.147(15)		
N(1)–Nd–N(2)	53.5(2)	C(4)–N(3)–Si(1)	118.8(5)
N(5)–Nd–N(4)	54.0(2)	C(4)–N(3)–Si(2)	117.2(5)
C(27)–Nd–C(28)	89.3(2)	C(17)–N(4)–Nd	93.6(4)
C(4)–Nd–C(17)	128.5(2)	C(17)–N(5)–Nd	96.3(5)
C(4)–Nd–Li	116.0(3)	C(17)–N(6)–Si(4)	116.6(5)
C(17)–Nd–Li	115.5(3)	C(17)–N(6)–Si(3)	118.5(5)
N(7)–Li–N(8)	85.3(5)	N(2)–C(4)–N(1)	115.6(6)
C(27)–Li–C(28)	109.6(6)	N(3)–C(4)–Nd	174.0(5)
C(4)–N(1)–Nd	95.7(4)	N(5)–C(17)–N(4)	115.7(7)
C(4)–N(2)–Nd	94.8(4)	N(6)–C(17)–Nd	174.7(5)

Table 4. Ring-opening polymerization of ϵ -caprolactone initiated by [(SiMe₃)₂NC(NiPr)₂Ln(μ-Me)₂Li(TMEDA)] [Ln = Yb (**4**), Nd (**5**)]

Entry ^[a]	Initiator	T _p [°C]	[M]/[I]	Yield ^[b] (%)	M _n (× 10 ^{−4})	M _w /M _n ^[c]
1	5	20	300	100	7.44	1.92
2	5	20	500	100	9.18	1.99
3	5	20	700	100	8.08	2.35
4	5	20	1000	100	6.35	2.21
5	5	40	1000	100	6.45	2.20
6	5 ^[d]	20	1000	100	11.03	2.54
7	5 ^[e]	20	1000	100	9.87	2.96
8	4	20	500	61.2	8.68	2.33
9	4	20	700	46.6	9.59	2.35
10	4	20	1000	27.2	9.22	2.18

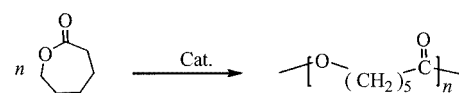
^[a] General polymerization conditions: in toluene, 15 min, solvent/monomer = 10 (v/v). ^[b] Yield: weight of polymer obtained/weight of monomer used. ^[c] Measured by GPC calibrated with standard polystyrene samples. ^[d] Polymerization time: 60 min. ^[e] Polymerization time: 14 h.

Table 5. Polymerization of methyl methacrylate by [(SiMe₃)₂NC(NiPr)₂Nd(μ-Me)₂Li(TMEDA)] (**5**)

Entry ^[a]	T _p [°C]	Yield ^[b] (%)	M _n (× 10 ^{−4})	M _w /M _n ^[c]	Stereochemistry (%)		
					rr	mr	mm
1	−78	10	15.7	2.15	58.90	19.16	21.94
2	−35	12	7.8	2.59	56.96	29.86	13.18
3	4	21	5.6	1.98	53.22	25.67	21.11
4	25	36	6.0	3.21	49.56	28.67	21.77
5	40	82	10.8	2.16	44.59	26.15	29.26

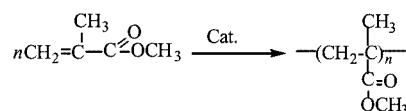
^[a] General polymerization conditions: catalyst concentration 0.5 mol % monomer, solvent toluene, solvent/monomer 2 (v/v), polymerization time 3 h. ^[b] Yield: weight of polymer obtained/weight of monomer used. ^[c] Measured by GPC calibrated with standard polystyrene samples.

Both complexes showed high activity for the ring-opening polymerization of ϵ -caprolactone (Scheme 2). The identity of the central metal atom has a large effect on the catalytic activity. For example, using **5** as a catalyst gives yields as high as 100% in 15 min over [M]/[I] mol ratios of 500:1 to 1000:1 at 20 °C, while under the same conditions **4** gave yields of only 61.2–27.2%. The order of reactivity Nd > Yb is in agreement with that found for metallocene-based organolanthanide catalysts.^[12] The polymerization systems give high molecular weight polymers (M_n > 10⁴). The molecular mass distributions are broader than those obtained with the homoleptic (phosphoraniminato)lanthanide complexes,^[13] especially when long reaction times are used (Entries 4, 6 and 7); this may be due to a transesterification reaction.



Scheme 2

Complex **5** also exhibits good catalytic activity for the polymerization of methyl methacrylate (Scheme 3). Triad microstructural analysis of the polymers was carried out using ¹H NMR spectra in CDCl₃. The catalytic activity increased with increasing polymerization temperature. For example, only a 10% yield was obtained at −78 °C, while at 40 °C, a yield of 82% could be realized. Moreover, the present polymerization system gives the syndio-rich polymers, and the syndiotacticity decreases with increasing polymerization temperature.



Scheme 3

Conclusions

In summary, we have successfully synthesized a series of new soluble lanthanide bis(guanidinate) complexes free of cyclopentadienyl ligands, and characterized some of their structural features by X-ray crystallography. Moreover, we have found that the “ate” methylanthanide bis(guanidinate) complexes show highly catalytic activity for the ring-opening polymerization of ϵ -caprolactone, and good catalytic activity for the polymerization of methyl methacrylate to give syndiotactic polymers. A systematic study of the catalytic activity of methylanthanide guanidinate complexes in the polymerization of other monomers is ongoing in our laboratory.

Experimental Section

General Procedures: All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl prior to use. Deuterated benzene was dried with sodium and vacuum-transferred. Anhydrous LnCl_3 [14] and $\text{LiN}(\text{SiMe}_3)_2$ [15] were prepared according to literature procedures. N,N' -Diisopropylcarbodiimide was purchased from Aldrich and purified by distillation. ϵ -Caprolactone was purchased from Acros, dried by stirring with CaH_2 for 48 h, then distilled under reduced pressure. Methyl methacrylate was dried by stirring with CaH_2 for 48 h, 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. The content of lithium was determined with 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 Magna-IR 550 spectrometer. ^1H and ^{13}C NMR spectra were obtained 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 and HR-4) using THF as the eluent.

Synthesis of $[(\text{SiMe}_3)_2\text{NC}(\text{N}i\text{Pr})_2]\text{Li}$ (1): $\text{LiN}(\text{SiMe}_3)_2$ (1.67 g, 10.00 mmol) in hexane (30 mL) was added dropwise to a hexane solution (50 mL) of N,N' -diisopropylcarbodiimide (1.6 mL, 10.00 mmol) at room temperature. The resulting reaction mixture was stirred for 30 min and gave a clear pale-yellow solution. After removal of the reaction solvent, crude **1** was isolated as a white powder (2.88 g, 9.81 mmol, 98.3%). $\text{C}_{13}\text{H}_{32}\text{LiN}_3\text{Si}_2$ (293.60): calcd. C 53.19, H 11.01, N 14.32; found C 52.79, H 11.24, N 13.82. ^1H NMR ($[\text{D}_6]\text{benzene}$): δ = 3.78 (m, 2 H, CHMe_2), 1.17 [d, 12 H, $\text{CH}(\text{CH}_3)_2$], 0.35 [s, 18 H, $\text{Si}(\text{CH}_3)_3$] ppm. ^{13}C NMR ($[\text{D}_6]\text{benzene}$): δ = 164.36 (CN_3), 46.17 (CHMe_2), 28.19 [$(\text{CH}_3)_2\text{CH}$], 3.03 [$\text{CN}[\text{Si}(\text{CH}_3)_3)_2$] ppm. IR (KBr pellets): $\tilde{\nu}$ = 3449 (s), 2963 (m), 1636 (s), 1450 (m), 1389 (m), 1327 (m), 1258 (m), 1173 (m), 1049 (m), 957 (m), 841 (s), 686 (m) cm^{-1} .

Synthesis of $[(\text{SiMe}_3)_2\text{NC}(\text{N}i\text{Pr})_2]\text{Yb}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (2): A hexane solution (50 mL) of in situ generated $[(\text{SiMe}_3)_2\text{NC}(\text{N}i\text{Pr})_2]\text{Li}$ (**1**) (3.90 g, 13.30 mmol) was added to a slurry of YbCl_3 (1.85 g, 6.62 mmol) in THF (30 mL). The reaction mixture was stirred for 24 h at room temperature and the solvents were stripped off in vacuo. The residual yellow powder was extracted with diethyl ether and LiCl was centrifuged off. The yellow supernatant was then concentrated and cooled to -15 °C overnight to give bright-yellow crystals. Yield: 4.87 g (5.03 mmol, 76%). M.p. 165–168 °C. $\text{C}_{34}\text{H}_{80}\text{Cl}_2\text{LiN}_6\text{O}_2\text{Si}_4\text{Yb}$ (968.28): calcd. C 42.17, H 8.34, Li 0.72, N 8.68, Yb 17.87; found C 41.63, H 8.26, Li 0.81, N 8.41, Yb 18.52. ^1H NMR ($[\text{D}_6]\text{benzene}$): δ = 4.15, 3.84 (m, 4 H, CHMe_2), 3.64 (m, 8 H, $\text{THF-}\alpha\text{-CH}_2$), 1.47 (m, 8 H, $\text{THF-}\beta\text{-CH}_2$), 1.33, 1.09 [d, 24 H, $\text{CH}(\text{CH}_3)_2$], 0.23 [s, 36 H, $\text{Si}(\text{CH}_3)_3$] ppm. IR (KBr pellets): $\tilde{\nu}$ = 3283 (m), 3182 (m), 2966 (m), 1635 (s), 1466 (m), 1388 (m), 1321 (m), 1253 (s), 1172 (m), 1057 (s), 952 (m), 841 (s), 756 (m), 686 (m) cm^{-1} .

Synthesis of $[(\text{SiMe}_3)_2\text{NC}(\text{N}i\text{Pr})_2]\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$ (3): As for the synthesis of **2**, using **1** (11.38 mmol), NdCl_3 (1.40 g, 5.59 mmol), and THF (60 mL). Recrystallization from toluene yielded blue purple needles of **3** (4.31 g, 4.58 mmol, 82%). M.p. 176–178 °C. $\text{C}_{34}\text{H}_{80}\text{Cl}_2\text{LiN}_6\text{NdO}_2\text{Si}_4$ (939.48): calcd. C 43.46, H 8.60, Li 0.74, N 8.95, Nd 15.35; found C 42.76, H 8.78, Li 0.71, N

8.34, Nd 15.72. ^1H NMR ($[\text{D}_6]\text{benzene}$): δ = 4.15, 3.85 (m, 4 H, CHMe_2), 3.61 (m, 8 H, $\text{THF-}\alpha\text{-CH}_2$), 1.45 (m, 8 H, $\text{THF-}\beta\text{-CH}_2$), 1.33, 1.09 [d, 24 H, $\text{CH}(\text{CH}_3)_2$], 0.23 [s, 36 H, $\text{Si}(\text{CH}_3)_3$] ppm. IR (KBr pellets): $\tilde{\nu}$ = 3296 (m), 2971 (m), 1636 (s), 1466 (m), 1373 (m), 1327 (m), 1258 (s), 1172 (m), 1057 (s), 941 (s), 833 (s), 756 (m), 686 (m) cm^{-1} .

Synthesis of $[(\text{SiMe}_3)_2\text{NC}(\text{N}i\text{Pr})_2]\text{Yb}(\mu\text{-Me})_2\text{Li}(\text{TMEDA})$ (4): A Schlenk bottle was charged with **2** (8.23 g, 8.5 mmol) and hexane (100 mL). The solution was cooled to -78 °C, and MeLi (11.4 mL, 16.99 mmol) was added by syringe. The reaction mixture was kept at -78 °C for 1 h, then slowly warmed to room temperature and stirred overnight. After removal of volatiles under vacuum, the yellow residue was extracted with toluene, and LiCl was removed by centrifugation. The supernatant was removed in vacuo, and THF (20 mL) containing TMEDA (1 mL) was added. Cooling to -15 °C overnight gave **3** as bright yellow cubic crystals. Yield 6.1 g (6.12 mmol, 72%). M.p. 100–102 °C. $\text{C}_{34.25}\text{H}_{90.50}\text{LiN}_8\text{Si}_4\text{Yb}$ (931.01): calcd. C 44.18, H 9.82, Li 0.75, N 12.04, Yb 18.59; found C 43.81, H 9.54, Li 0.71, N 11.98, Yb 18.32. ^1H NMR ($[\text{D}_6]\text{benzene}$): δ = 2.15 (m, 4 H, CHMe_2), 1.25 [m, 24 H, $\text{CH}(\text{CH}_3)_2$], 0.33 [s, 36 H, $\text{Si}(\text{CH}_3)_3$], -6.11 (s, 12 H, TMEDA-CH_3), -7.74 (br, 4 H, TMEDA-CH_2), -9.81 (s, 4.5 H, C_6H_{12}), -15.45 (br, 6 H, $\mu\text{-CH}_3$) ppm. IR (KBr pellets): $\tilde{\nu}$ = 3449 (m), 2963 (s), 1636 (s), 1466 (m), 1381 (m), 1327 (m), 1258 (s), 1180 (m), 1049 (m), 957 (s), 918 (m), 841 (s), 756 (m), 686 (m) cm^{-1} .

Synthesis of $[(\text{SiMe}_3)_2\text{NC}(\text{N}i\text{Pr})_2]\text{Nd}(\mu\text{-Me})_2\text{Li}(\text{TMEDA})$ (5): As for the synthesis of **4**, using **3** (5.60 mmol), MeLi (7.6 mL, 11.32 mmol), and hexane (60 mL). Recrystallization from THF containing TMEDA gave blue-purple cubic crystals. Yield 3.84 g (4.26 mmol, 76%). M.p. 118–120 °C. $\text{C}_{34.25}\text{H}_{90.50}\text{LiN}_8\text{NdSi}_4$ (902.21): calcd. C 48.26, H 10.13, N 12.42, Nd 15.99, Li 0.77; found C 47.86, H 9.90, N 11.83, Nd 15.86, Li 0.75. ^1H NMR ($[\text{D}_6]\text{benzene}$, ppm): δ = 3.51 (m, 4 H, CHMe_2), 2.83 [m, 24 H, $\text{CH}(\text{CH}_3)_2$], 2.16 [s, 36 H, $\text{Si}(\text{CH}_3)_3$], 1.24 (s, 12 H, TMEDA-CH_3), 0.51 (br, 4 H, TMEDA-CH_2), 0.19 (s, 4.5 H, C_6H_{12}), -2.21 (br, 6 H, $\mu\text{-CH}_3$) ppm. IR (KBr pellets): $\tilde{\nu}$ = 3442 (m), 2963 (s), 1636 (s), 1466 (m), 1373 (m), 1327 (m), 1258 (s), 1180 (m), 1049 (s), 957 (s), 918 (m), 841 (s), 756 (m), 686 (m) cm^{-1} .

A Typical Procedure for Polymerization Reactions: The procedures for the polymerization of ϵ -caprolactone and methyl methacrylate are similar (Table 5), and a typical polymerization procedure is given below (Entry 1, Table 5). A 50-mL Schlenk flask, equipped with a magnetic stirring bar, was charged with a 2.7 mm solution of initiator in toluene. To this solution was added 1 mL of ϵ -caprolactone using a syringe. The contents of the flask were then stirred vigorously at 20 °C for 15 min, 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 Structural Determination of **2 and **5**:** Single crystals were sealed in a thin-walled glass capillary filled with argon for X-ray structural analysis. Diffraction data for **2** were collected with a Bruker SMART CCD area detector using ω scans. Data for **5** were collected with a Siemens P4 four-circle diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures of both **2** and **5** were solved and refined using SHELXS-97 and SHELXL-97 programs, respectively. CCDC-192647 (**2**) and

-192648 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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