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Synthesis, Characterization, and Catalytic Activity of Some Neodymium(III), Ytterbium(II), and Europium(II) Complexes with Pyrrolidinyl- and Piperidinyl-Functionalized Indenyl Ligands

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A series of organolanthanide complexes with pyrrolidinyl- and piperidinyl- functionalized indenyl ligands were synthesized by reaction of $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu, Nd) with the corresponding indene compounds. Treatment of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv. of C_9H_6-1-R-3-$CH_2SiMe_2NC_4H_8$ (R = H, CH_3) in refluxing toluene produced the corresponding organoytterbium(II) complexes with formula $[\eta^m{:}\eta^1\text{-}C_9H_5\text{-}1\text{-}R\text{-}3\text{-}CH_2SiMe_2NC_4H_8]_2Yb^{II}$ [m = 5, R = H (**2**); m = 3, R = CH_3 (**3**)] in 49 and 58 % yield, respectively. Treatment of $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu, Nd) with 2 equiv. of $C_9H_7CH_2SiMe_2NC_5H_{10}$ (**1**) in toluene at moderately high temperatures afforded, after workup, the corresponding organolanthanide complexes with formula $[\eta^5{:}\eta^1\text{-}C_9H_6CH_2SiMe_2NC_5H_{10}]_2Yb^{II}$ (**4**), $[\eta^5{:}\eta^1\text{-}C_9H_6CH_2SiMe_2NC_5H_{10}]_2Eu^{II}$ (**5**), and $[C_9H_6CH_2SiMe_2NC_5H_{10}]_3Nd^{III}\cdot THF$ (**6**) in 37, 71, and 29 % yield, respectively. All the compounds were fully characterized by spectroscopic methods and elemental analyses. The structures of complexes **2**, **3**, **5**, and **6** were additionally determined by single-crystal X-ray analyses. The catalytic properties of all the organolanthanide complexes on the ring-opening polymerization of ε-caprolactone have been studied. The effects of temperature, solvent, and coordination on the catalytic activities of the complexes were examined.

Introduction

Over the past few decades, great progress has been made in the chemistry of divalent organolanthanide complexes. Divalent organolanthanide complexes exhibited a particularly rich reaction chemistry based on their strong reductive properties.[1] A variety of complexes have been synthesized and used in organic synthesis and polymer chemistry.[2] Generally, divalent organolanthanide complexes were synthesized by metathesis reaction of alkaline metal salts of a ligand with LnI_2 or by reductive reaction of lanthanide(III) halides with metallic atoms.[3]

Lanthanide complexes have received much interest for their potential application as homogeneous catalysts or catalyst precursors for various useful transformations such as olefin polymerization,[4] hydroamination of olefins and alkynes,[5] hydrophosphination of olefins and alkynes,[6] Tishchenko reactions,[7] ring-opening polymerization of ε-caprolactone and δ-valerolactone,[8] and insertion reactions.[9] Recently, our group has reported that the tetracoordinate lanthanide amides $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ can work as efficient catalysts for the aldol-condensation reaction,[10] or initiators for the Cannizzaro-type disproportionation of aromatic aldehydes to amides and alcohols.[11]

At the same time, we have also demonstrated that the interactions of indene compounds having nitrogen-containing substituents or oxygen-containing substituents with the lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) produced organolanthanide(II) complexes.[12] The formation pathway of the organolanthanide(II) complexes is proposed to proceed through a tandem silylamine elimination[13]/homolysis of the Ln–N bonds, thus it provides a new methodology for the preparation of the lanthanide(II) complexes. Especially, the reaction of heterocyclic-functionalized indene compound $C_9H_7CH_2SiMe_2NC_4H_8$ with the europium(III) amide $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ has led to the isolation and characterization of the unexpected novel triple-decker tetranuclear europium(II) complex with the linked indenyl ligands,[12e] and a novel ytterbium(II) complex having the indenyl ligand bonded to the metal through a benzo ring with an η^4 hapticity has been isolated and characterized by treatment of the *N*-piperidinylethyl functionalized indene compound with the ytterbium(III) amide $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$,[12d] indicating the ligands' effects on the reactivity patterns and coordination modes. In order to further study the reduction potentials of the lanthanides and the ligands' effect on reactivity patterns and the bonding modes between the ligands

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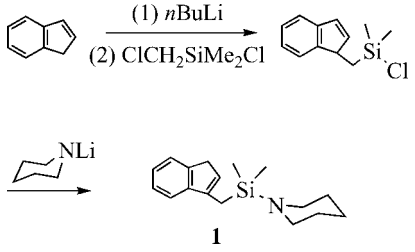
and the lanthanide metals, we have studied the reactions of C_9H_6-1-R-3-$CH_2SiMe_2NC_4H_8$ (R = H, Me), and $C_9H_7CH_2SiMe_2NC_5H_{10}$ with the lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu, Nd).

In this paper, we will report the interactions of C_9H_6-1-R-3-$CH_2SiMe_2NC_4H_8$ (R = H, Me), and $C_9H_7CH_2SiMe_2NC_5H_{10}$ with the lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu, Nd) leading to preparation and characterization of a series of new organolanthanide(II) complexes and an organoneodymium(III) complex. The catalytic activities of these complexes as single-component ε-caprolactone polymerization catalysts were also examined.

Results and Discussion

Synthesis and Characterization of $C_9H_7CH_2SiMe_2NC_5H_{10}$ (1)

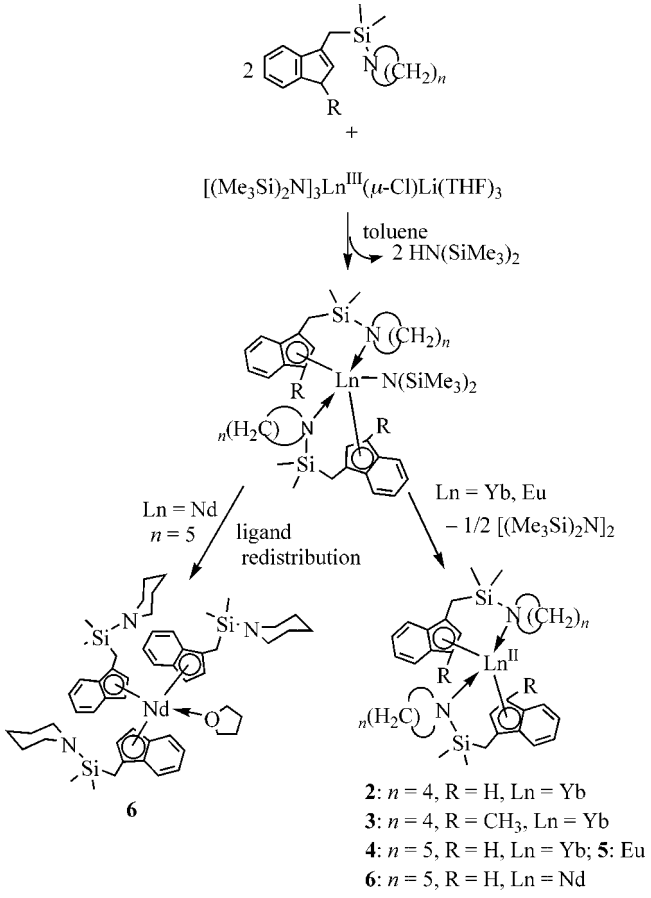
Interaction of C_9H_7Li with 1 equiv. of $ClSiMe_2CH_2Cl$, followed by treatment with 1 equiv. of lithium piperidinide $C_5H_{10}NLi$, gave piperidinyl-functionalized indene compound $C_9H_7CH_2SiMe_2NC_5H_{10}$ (**1**) in good yield (Scheme 1). The compound was fully characterized by spectroscopic methods and elemental analysis. The nucleophilic substitution reaction of C_9H_7Li with $ClSiMe_2CH_2Cl$ occurs at the C–Cl bond, not at the Si–Cl bond on the basis of the NMR analyses of the reaction products. Similar results were observed in the reaction of C_5Me_4HLi or Ph_2PLi with $ClSiMe_2CH_2Cl$, giving the corresponding product $C_5HMe_4CH_2SiMe_2Cl$[14] or $Ph_2PCH_2SiMe_2Cl$,[15] indicating the electronic and steric effects on the reactivity of the C–Cl and Si–Cl bonds.



Scheme 1.

Synthesis and Characterization of Organolanthanide Complexes with Pyrrolidinyl- and Piperidinyl-Functionalized Indenyl Ligands

Treatment of the lanthanide(III) amides $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) with 2 equiv. of C_9H_6-1-R-3-$CH_2SiMe_2NC_4H_8$ (R = H, CH_3) and $C_9H_7CH_2SiMe_2NC_5H_{10}$ in toluene produced the lanthanide(II) complexes with formula $[\eta^m\text{:}\eta^1\text{-}C_9H_5\text{-}1\text{-}R\text{-}3\text{-}CH_2SiMe_2NC_4H_8]_2Yb^{II}$ [*m* = 5, R = H (**2**); *m* = 3, R = CH_3(**3**)] and $[\eta^5\text{:}\eta^1\text{-}C_9H_6CH_2SiMe_2NC_5H_{10}]_2Ln^{II}$ [Ln = Yb(**4**); Ln = Eu(**5**)] (Scheme 2). The complexes **2**, **3**, **4**, and **5** are sensitive to air and moisture, they are soluble in polar solvents such as THF, DME, and pyridine, and slightly soluble in toluene, but insoluble in *n*-hexane. All the complexes were fully characterized by spectroscopic methods and elemental analyses. The structures of the complexes **2**, **3**, and **5** were determined by single-crystal X-ray analyses. X-ray analyses showed that the complexes **2**, **3**, and **5** were a monomeric structure, not a triple-decker sandwich tetranuclear structure analogous to the complex[12e] from the reaction of $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-}Cl)Li(THF)_3$ with $C_9H_7CH_2SiMe_2NC_4H_8$, probably due to different reduction potentials of lanthanide ions, and the ligands' steric and electronic effects.



Scheme 2.

Estimated Ln^{3+}/Ln^{2+} reduction potentials are as follows:[16] $E°(Eu^{3+}/Eu^{2+})$ = –0.35 V, $E°(Yb^{3+}/Yb^{2+})$ = –1.15 V, $E°(Nd^{3+}/Nd^{2+})$ = –2.62 V. This suggested that europium(III) and ytterbium(III) could be more easily reduced to europium(II) and ytterbium(II) than other lanthanide(III) metal ions. To probe reduction potential effects on the reactivity, the reaction of $[(Me_3Si)_2N]_3Nd^{III}(\mu\text{-}Cl)Li(THF)_3$ with $C_9H_7CH_2SiMe_2NC_5H_{10}$ (**1**) was studied.

The reaction of $[(Me_3Si)_2N]_3Nd^{III}(\mu\text{-}Cl)Li(THF)_3$ with 2 equiv. of $C_9H_7CH_2SiMe_2NC_5H_{10}$ (**1**) in refluxing toluene produced, after recrystallization from *n*-hexane, a neodymium(III) complex $[C_9H_6CH_2SiMe_2NC_5H_{10}]_3Nd^{III}\cdot THF$ (**6**) (Scheme 2). The complex is sensitive to air and moisture. It is soluble in THF, DME, toluene, and pyridine, and slightly

soluble in *n*-hexane. The complex was fully characterized by spectroscopic methods and elemental analysis. Its structure was determined by single-crystal X-ray analysis. X-ray analysis showed that complex **6** is a trivalent neodymium(III) complex composed of three indenyl ligands π-bonded with the central metal and one coordinated tetrahydrofuran. Homolysis of the Nd–N bond was not observed probably due to the reduction potential of the Nd^{3+}/Nd^{2+} and steric effects.

We have proved that the interactions of indene compounds without donor-substituted groups on the indene ring with lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) produced lanthanide(III) amides $(Ind')_2LnN(SiMe_3)_2$ (Ind′ = indenyl- or ethylene-bridged indenyl ligands), while the interactions of the heteroatom side-arm functionalized indene compounds with $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) produced lanthanide(II) complexes; the formation pathway of the lanthanide(II) complexes has been proposed via a tandem silylamine elimination/homolysis of the Ln–N bond (Ln = Yb, Eu) based on the experimental results.[12] Thus, the formation of the above europium(II) and ytterbium(II) complexes is proposed to go through a tandem silylamine elimination/homolysis of the Ln–N (Ln = Yb, Eu) bonds, but the formation of neodymium(III) complex **6** may go through a silylamine elimination, followed by a ligand redistribution reaction (Scheme 2).

Molecular Structures of Complexes 2, 3, 5, and 6

X-ray analyses revealed that the central metal ions of the complexes **2** (Figure 1), **3** (Figure 2), and **5** (Figure 3) exist in a +2 oxidation state. The results further confirmed that the formation of these organolanthanide(II) complexes involves a one-electron reductive elimination process. The selected bond lengths and angles are listed in Table 1. It can be seen that the lanthanide contraction is clearly reflected by the average Ln–C and Ln–N distances.

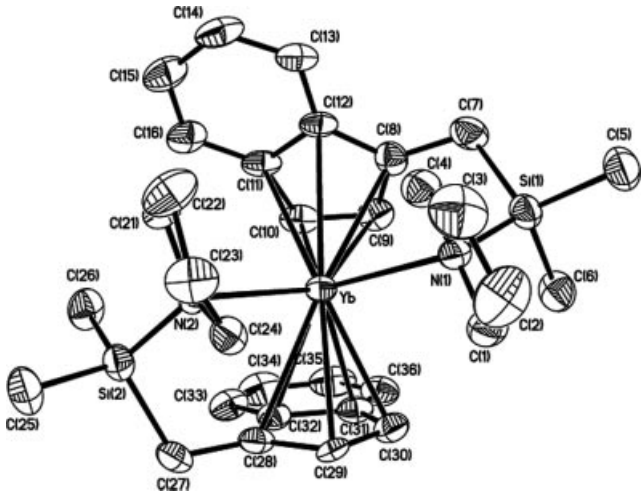


Figure 1. Molecular structure of $[\eta^5:\eta^1\text{-}(C_9H_6CH_2SiMe_2NC_4H_8)]_2Yb^{II}$ (**2**). Hydrogen atoms are omitted for clarity.

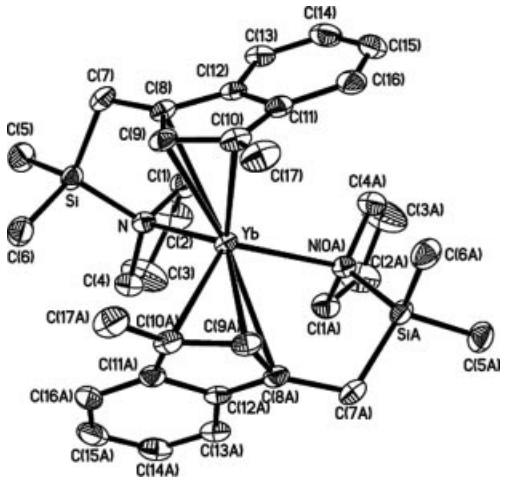


Figure 2. Molecular structure of $[\eta^3:\eta^1\text{-}C_9H_5\text{-}1\text{-}CH_3\text{-}3\text{-}CH_2SiMe_2NC_4H_8]_2Yb^{II}$ (**3**). Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and bond angles [°].

2		**3**		**5**		**6**	
Yb–N(1)	2.671(8)	Yb–N	2.634(4)	Eu(1)–N(1)	2.794(2)	Nd(1)–O(1)	2.547(4)
Yb–N(2)	2.619(7)					Nd(1)–C(1)	2.718(5)
Yb–C(8)	2.792(9)	Yb–C(8)	2.811(4)	Eu(1)–C(1)	2.802(3)	Nd(1)–C(2)	2.719(5)
Yb–C(9)	2.649(9)	Yb–C(9)	2.714(4)	Eu(1)–C(2)	2.813(3)	Nd(1)–C(3)	2.921(5)
Yb–C(10)	2.672(9)	Yb–C(10)	2.794(4)	Eu(1)–C(3)	2.941(3)	Nd(1)–C(8)	2.980(5)
Yb–C(11)	2.889(8)	Yb–C(11)	2.944(4)	Eu(1)–C(8)	2.968(3)	Nd(1)–C(9)	2.844(5)
Yb–C(12)	2.930(8)	Yb–C(12)	2.929(4)	Eu(1)–C(9)	2.900(2)	Nd(1)–C(18)	2.720(5)
Yb–C(28)	2.798(9)					Nd(1)–C(19)	2.714(5)
Yb–C(29)	2.713(8)					Nd(1)–C(20)	2.896(5)
Yb–C(30)	2.708(9)					Nd(1)–C(25)	2.966(5)
Yb–C(31)	2.840(9)					Nd(1)–C(26)	2.859(5)
Yb–C(32)	2.868(9)					Nd(1)–C(35)	2.724(5)
						Nd(1)–C(36)	2.708(5)
						Nd(1)–C(37)	2.954(5)
						Nd(1)–C(42)	3.043(5)
N(2)–Yb–N(1)	106.6(2)	N–Yb–N#1	106.50(16)	N(1)#1–Eu(1)–N(1)	109.99(8)	Nd(1)–C(43)	2.908(5)
Yb–C(av)	2.786(9)	Yb–C(av)	2.838(4)	Eu–C(av)	2.885(3)	Nd–C(av)	2.845(5)

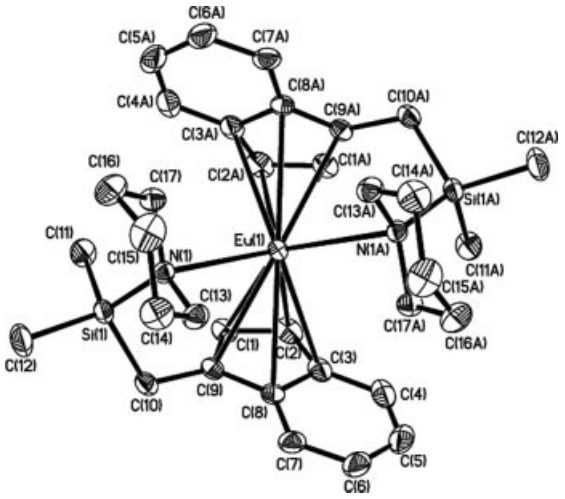


Figure 3. Molecular structure of $[\eta^5{:}\eta^1\text{-}C_9H_6CH_2SiMe_2NC_5H_{10}]_2\text{-}Eu^{II}$ (**5**). Hydrogen atoms are omitted for clarity.

From Table 1, we can see that the Yb–C bond lengths in complex **2** range from 2.649(9) to 2.930(8) Å, with an average of 2.786(9) Å, which is comparable to the average Yb–C distances of 2.806(12) and 2.778(14) Å found in the corresponding indenyl ytterbium(II) complexes $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)]_2Yb^{II}$,[12a] $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Yb^{II}$.[12a] This average Yb–C distance of 2.786(9) Å found in **2** is longer than the corresponding values of 2.722(10) Å found in $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_6)]_2Yb^{II}$,[12a] 2.723(14) Å found in $[\eta^5{:}\eta^1\text{-}(2\text{-}C_5H_4NCH_2)C_9H_6]_2Yb^{II}$,[12f] 2.737(4) Å found in $[\eta^5{:}\eta^1\text{-}(MeOCH_2CH_2C_5H_4)]_2Yb^{II}(THF)$,[17] and 2.75 Å found in $[Me_3Si(C_5H_4)]_2Yb(THF)_2$.[18] The above differences in the average Yb–C distances of different ytterbium(II) complexes may be due to steric effects and ionic radii differences.

The Yb to C(11) and C(12), which are shared by both C5 and C6 rings, distances of 2.944(4) and 2.929(4) Å in complex **3** are significantly longer than those of others [ranging from 2.714(4) to 2.811(4) Å], suggesting that the Yb atom tends to bond with indenyl ligands in an η^3-mode. The average Yb–C distance of 2.838(4) Å found in **3** is obviously longer than the corresponding value of 2.786(9) Å found in **2**. This distance is also longer than those of 2.818(3) Å in $[\eta^5\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Yb(THF)[(\mu\text{-}\eta^5){:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Na(THF)_3$,[19] 2.814(7) Å in $[\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2OMe)(C_2B_{10}H_{10})]Yb(DME)\text{-}(THF)$,[20] 2.806(12) Å in $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2\text{-}C_9H_5)(NHtBu)]_2Yb^{II}$,[12a] 2.778(14) Å found in $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Yb^{II}$,[12a] and 2.732(18) Å in $[\eta^5{:}\eta^1\text{-}(C_4H_7OCH_2C_9H_5SiMe_3)]_2Ln^{II}$,[12g] indicating steric and electronic effects.

The average Yb–N bond length of 2.645(8) Å in **2** is compared with the average Yb–N distances of 2.634(4) Å in **3**, 2.673(11) Å in $[\eta^5{:}\eta^1\text{-}Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)]_2\text{-}Yb^{II}$,[12a] and 2.650(12) Å in $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_5Si\text{-}Me_3)]_2Yb^{II}$,[12a] but longer than those of 2.561(7) Å in $[\eta^5{:}\eta^1\text{-}(2\text{-}C_5H_4NCH_2)C_9H_6]_2Yb^{II}$,[12f] and 2.588(7) Å in $[\eta^5{:}\eta^1\text{-}(Me_2NCH_2CH_2C_9H_6)]_2Yb^{II}$,[12a] respectively. The above difference in the average Yb–N distances in different ytterbium(II) complexes may be due to steric effects and

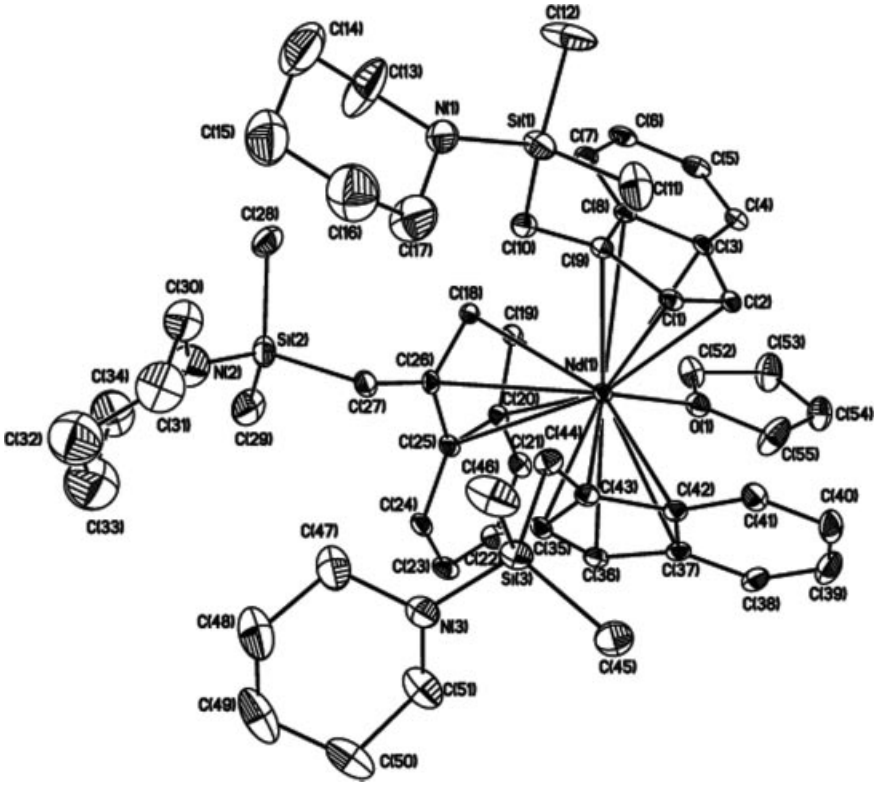


Figure 4. Molecular structure of $[C_9H_6CH_2SiMe_2NC_5H_{10}]_3Nd^{III}\cdot THF$ (**6**). Hydrogen atoms are omitted for clarity.

the hybridization state of nitrogen atoms. The N–Yb–N angle of 106.6(2)° in **2** is comparable to the corresponding angle of 106.50(16)° in **3**, but larger than the corresponding angles of 95.1(4), 92.8(5), and 103.7(2)° found in $[\eta^5{:}\eta^1$-$Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)]_2Yb^{II}$,[12a] $[\eta^5{:}\eta^1$-$(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Yb^{II}$,[12a] and $[\eta^5{:}\eta^1$-$(Me_2NCH_2CH_2C_9H_6)]_2Yb^{II}$,[12a] respectively, suggesting steric and electronic effects.

The average Eu–C bond length of 2.885(3) Å in complex **5** is comparable to the average Eu–C bond lengths of 2.883(11), 2.873(10), and 2.841(7) Å found in the corresponding indenyl europium(II) complexes $[\eta^5{:}\eta^1$-$Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)]_2Eu^{II}$,[12c] $[\eta^5{:}\eta^1$-$(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Eu^{II}$,[12c] and $[\eta^5{:}\eta^1$-$(Me_2NCH_2CH_2C_9H_6)]_2Eu^{II}$,[12c] but shorter than that of 2.911(18) Å in $[\eta^5{:}\eta^1$-C_9H_5-1-Me-3-$CH_2SiMe_2NC_4H_8]_2Eu^{II}$.[12e] The above differences in the average Eu–C bond lengths of different europium(II) complexes may be due to steric effects.

The average Eu–N bond length of 2.794(2) Å in **5** is longer than those of 2.753(16), 2.748(9), 2.744(8), and 2.711(6) Å found in $[\eta^5{:}\eta^1$-C_9H_5-1-Me-3-$CH_2SiMe_2NC_4H_8]_2Eu^{II}$,[12e] $[\eta^5{:}\eta^1$-$Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)]_2Eu^{II}$,[12c] $[\eta^5{:}\eta^1$-$(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Eu^{II}$,[12c] and $[\eta^5{:}\eta^1$-$(Me_2NCH_2CH_2C_9H_6)]_2Eu^{II}$,[12c] respectively, suggesting steric effects. The N–Eu–N angle of 109.99(8)° in **2** is close to the corresponding angle of 110.19(15)° in $[\eta^5{:}\eta^1$-C_9H_5-1-Me-3-$CH_2SiMe_2NC_4H_8]_2Eu^{II}$,[12e] but larger than those of 96.1(3), 92.9(3), and 104.7(2)° found in $[\eta^5{:}\eta^1$-$Me_2Si(Me_2NCH_2CH_2C_9H_5)(NHtBu)]_2Eu^{II}$,[12c] $[\eta^5{:}\eta^1$-$(Me_2NCH_2CH_2C_9H_5SiMe_3)]_2Eu^{II}$,[12c] and $[\eta^5{:}\eta^1$-$(Me_2NCH_2CH_2C_9H_6)]_2Eu^{II}$,[12c] respectively, indicating steric and electronic effects.

X-ray analysis reveals that the central metal ion of complex **6** (Figure 4) exists in a +3 oxidation state, and the central metal in complex **6** is coordinated by three indenyl ligands tending to η^3 bonding modes based on the determined Nd–C distances, and by an oxygen atom of the tetrahydrofuran in η^1-mode.

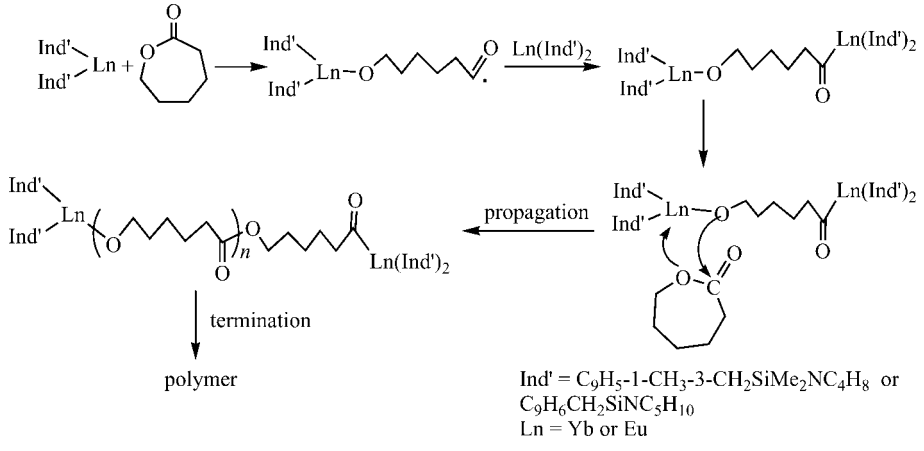
The average value of the Nd–C distances of 2.845(5) Å found in **6** is longer than the average Nd–C distances of 2.83(3) Å found in $(C_9H_7)_3Nd{\cdot}THF$,[21] 2.836(9) Å found in $[Na(C_4H_8O)_6][Nd(\eta^5$-$C_9H_7)_3(\mu$-C1)$Nd(\eta^5$-$C_9H_7)_3]$,[22] but shorter than the average Nd–C distance of 2.91(5) Å found in $(C_5Me_5)_3Nd$,[23] indicating steric effects on the coordination and bonding.

Ring-Opening Polymerization of ε-Caprolactone

The complexes as single-component catalysts in ε-caprolactone polymerization were examined. It was found that all of the complexes exhibited good catalytic activities for ring-opening polymerization of ε-caprolactone in toluene, THF, and DME (Table 2). From Table 2, we can see that the complexes with piperidinyl-functionalized indenyl ligands exhibited higher catalytic activities in temperature ranges of 60 to –30 °C than those of the complexes with pyrrolidinyl-functionalized indenyl ligands, indicating the ligands' effects on catalytic activities of the complexes. From Table 2, we can also see that the catalyst **3** showed a higher catalytic activity than that of the catalyst **2** especially at relatively high temperatures, probably due to different bonding modes between the ligands and the central metals.

Examination of the solvents effects on the catalytic activities of the catalysts **2**–**6** indicated that the catalytic activities of the catalysts have good activity in toluene, THF, or DME. Simultaneously, we found that the molecular weights of the polymers obtained in toluene were higher than those obtained in THF and DME, indicating the solvents' effects on the chain propagation process. It was also found that the molecular weight distributions of the polymers obtained in toluene were slightly broader than those obtained in THF and DME.

The results of the temperature effects on the catalytic activities of the complexes **2**–**6** are listed in Table 2. In the table, we can see that the complexes **4**–**6** showed high catalytic activities in temperature ranges of 60 to –30 °C, but the complexes **2**, and **3** showed the highest catalytic activities at 0 °C. It was also found that the molecular weights of the polymers generally increase as the polymerization temperatures decrease, indicating that a chain propagation process is favored at relatively low temperatures.



Scheme 3.

Table 2. Data for the polymerization of ε-caprolactone (ε-CL).[a]

Catalyst	Solvent	*T*p /°C	Time /min	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Conv. %	Activity ($\times 10^{-6}$)
2	THF	30	8	1.58	2.36	1.49	58	0.30
		0	1	3.77	6.48	1.58	69	2.35
		–15	10	8.67	13.70	1.72	52	0.26
		–30	20	–	–	–	0	0
	toluene	30	20	5.67	9.93	1.75	57	0.10
		0	1	1.11	3.13	2.82	67	2.78
		–15	1	6.24	16.9	2.71	47	1.96
		–30	1	8.31	15.8	1.90	63	2.59
	DME	30	20	0.99	1.45	1.46	42	1.43
		0	12	2.17	3.31	1.53	51	1.76
		–15	20	1.18	1.81	1.53	9	0.065
		–30	20	–	–	–	0	0
3	THF	60	30	1.94	3.23	1.66	48	0.055
		30	5	1.41	2.44	1.73	71	0.43
		0	1	2.39	4.58	1.92	65	1.93
		–30	30	3.98	6.97	1.75	37	0.036
	toluene	60	30	2.38	4.86	2.04	51	0.051
		30	5	2.64	4.67	1.77	78	0.47
		0	1	3.18	4.41	1.39	57	1.71
		–30	30	4.84	8.66	1.79	46	0.046
	DME	60	30	1.63	2.11	1.30	40	0.039
		30	5	3.27	5.94	1.82	67	0.40
		0	1	3.93	6.90	1.76	52	1.55
		–30	30	–	–	–	0	0
4	THF	60	2	1.47	1.59	1.09	89	1.55
		30	2	1.58	1.69	1.07	92	1.57
		0	2	2.19	3.79	1.73	83	1.41
		–30	10	3.01	5.71	1.90	68	0.239
		–60	60	5.94	10.32	1.74	52	0.0291
	toluene	60	2	5.34	14.70	2.75	94	1.60
		30	2	6.24	18.38	2.95	79	1.36
		0	10	9.86	18.21	1.87	57	0.191
		–30	10	9.40	21.82	2.32	45	0.153
		–60	60	13.50	37.23	2.76	19	0.0109
	DME	60	2	2.87	6.48	2.12	96	1.61
		30	2	1.49	1.59	1.06	86	1.45
		0	2	2.75	4.91	1.78	80	1.36
		–30	10	4.53	7.48	1.65	82	0.276
		–60	60	6.86	10.07	1.47	57	0.0327
5	THF	60	1	3.15	6.68	2.12	100	3.43
		30	1	3.26	5.73	1.76	97	3.39
		0	1	5.13	9.42	1.83	100	3.42
		–30	1	7.37	10.59	1.44	86	2.91
		–60	10	7.74	14.93	1.93	73	0.247
	toluene	60	1	10.27	26.66	2.60	92	3.12
		30	1	10.05	22.76	2.26	97	3.33
		0	1	12.91	27.03	2.09	98	3.39
		–30	1	27.11	72.11	2.66	95	3.24
		–60	10	50.66	90.27	1.78	78	0.265
	DME	60	1	1.60	2.74	1.71	96	3.29
		30	1	1.50	1.93	1.29	91	3.11
		0	1	2.22	2.61	1.17	89	3.05
		–30	1	4.85	7.37	1.52	90	3.04
		–60	10	5.32	6.32	1.18	58	0.196
6	THF	60	1	2.08	3.81	1.84	94	3.23
		30	1	2.74	5.03	1.84	88	3.07
		0	1	2.85	5.11	1.79	85	2.90
		–30	1	4.88	8.76	1.79	76	2.68
		–60	10	77.15	10.37	1.34	37	0.129
	toluene	60	1	–	–	–	93	3.20
		30	1	2.61	6.88	2.63	82	2.83
		0	1	4.85	18.83	3.88	87	2.86
		–30	1	7.68	15.21	1.98	79	2.73
		–60	10	10.29	23.55	2.29	28	0.0963
	DME	60	1	1.68	2.28	1.36	89	2.99
		30	1	1.50	2.08	1.38	86	2.97
		0	1	1.92	2.56	1.34	80	2.67
		–30	10	5.19	9.47	1.82	71	0.248
		–60	30	–	–	–	19	0.0221

[a] Condition: solvent/ε-CL (v/v) = 3:1; Cat./ε-CL (mol/mol) = 1:500; Activity: g polymer·mol^{-1}(cat)·h^{-1}; *T*p: polymerization temperature.

The proposed mechanism of the ε-CL polymerization catalyzed by the lanthanide(II) complexes is that the lanthanide(II) complexes are oxidized by the lactone at the first stage, which forms an alkoxyl lanthanide(III) species.[24] Then, the chain propagation process was performed through a coordination-insertion process (Scheme 3).[25] However, the possible mechanism of the polymerization catalyzed by the neodymium(III) complex is through a coordination–insertion process.[25]

Conclusions

In summary, a series of organolanthanide(II) complexes and an organolanthanide(III) complex with pyrrolidinyl- and piperidinyl-functionalized indenyl ligands were synthesized by the reactions of C_9H_6-1-R-3-$CH_2SiMe_2NC_4H_8$ (R = H, Me) or $C_9H_7CH_2SiMe_2NC_5H_{10}$ with the lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu, Nd). This work demonstrated that the reduction potentials of Ln^{3+}/Ln^{2+} and the ligands have an influence on the reactivity patterns. The formation pathway of the lanthanide(II) complexes and the neodymium(III) complex was proposed on the basis of our previous experimental results. Structural analyses of the complexes indicated that substituents on the ligands have an influence on the bonding modes between the ligands and the central metals. The results of the catalytic activities of the newly prepared complexes indicated that the temperatures, solvents, ligands, and the bonding modes between the ligands and the central metals have an influence on the catalytic activities of the catalysts, the molecular weights, and the molecular weight distributions of the polymers.

Experimental Section

General Remarks: All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and an oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled from either finely divided $LiAlH_4$ or sodium benzophenone ketyl under argon prior to use unless otherwise noted. $CDCl_3$ was dried with activated 4-Å molecular sieves. ε-Caprolactone (ε-CL) was dried with finely divided CaH_2 and distilled before use. $ClCH_2SiMe_2Cl$ was bought from Aldrich Chemicals and distilled before use. C_9H_6-1-R-3-$CH_2SiMe_2NC_4H_8$ (R = H, CH_3)[12e] and $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb,[12a] Eu,[26] Nd[26]) were prepared according to literature methods. Elemental analyses data were obtained with a Perkin–Elmer 2400 Series II elemental analyzer. IR spectra were recorded with a Perkin–Elmer 983(G) spectrometer (CsI crystal plate, Nujol mulls). ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded with a Bruker AV-300 NMR spectrometer in C_5D_5N ([D_5]pyridine) for lanthanide complexes and in $CDCl_3$ for organic compounds. Gel permeation chromatography (GPC) analyses of polymer samples were carried out at 30 °C using THF as an eluent with a Waters-2414 instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 mL min^{-1}.

Preparation of $C_9H_7CH_2SiMe_2NC_5H_{10}$ (1): To a solution of indene (10.0 mL, 85.2 mmol) in THF (80.0 mL) was slowly added a 1.57-M *n*BuLi solution (54.0 mL, 85.2 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature, and was then cooled to 0 °C. To the reaction mixture was added fresh $ClSiMe_2CH_2Cl$ (11.3 mL, 85.2 mmol) in one portion. The reaction mixture was stirred for 12 h at room temperature. The solvents were pumped off under reduced pressure. The residue was extract with diethyl ether (2 × 20.0 mL), the extractions were combined, and solvent was pumped off under vacuum. Distillation of the resulting liquid gives the product $C_9H_7CH_2SiMe_2Cl$ as a colorless oil (14.9 g, 79% yield). B.p. 88–90 °C/0.02 Torr. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.52 (m, 2 H), 7.27 (m, 2 H), 7.01 (d, J = 4.52 Hz, 1 H), 6.68 (dd, J = 4.52, 6.99 Hz, 1 H), 3.78 (d, J = 6.99 Hz, 1 H), 2.80 (s, 2 H), 0.06 (s, 6 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 144.2, 144.1, 134.4, 129.8, 125.2, 123.9, 122.6, 121.2, 43.7, 24.9, –5.8 ppm. $C_{12}H_{15}ClSi$ (222.79): calcd. C 64.69, H 6.79; found C 64.51, H 7.02. To a freshly prepared THF (50 mL) solution of lithium piperidinide $C_5H_{10}NLi$ (3.37 g, 36.6 mmol) was added slowly the above prepared indene compound $C_9H_7CH_2SiMe_2Cl$ (8.14 g, 36.6 mmol) at 0 °C. The reaction mixture was then stirred for 12 h at 50 °C. The solvent was pumped off under reduced pressure. The residue was extracted with diethyl ether (2 × 20.0 mL), the extractions were combined, and the solvents were pumped off under vacuum. Distillation of the residue gave **1** as a colorless oil (8.03 g, 81% yield). B.p. 118–121 °C/0.02 Torr. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.49–7.20 (m, 4 H), 6.09 (s, 1 H), 3.39 (d, J = 7.53, 2 H), 2.87 (m, 4 H), 2.09 (s, 2 H), 1.58 (m, 4 H), 1.42 (m, 4 H), 0.09 (s, 6 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 146.4, 144.4, 141.6, 126.1, 125.8, 124.3, 123.5, 119.4, 47.3, 46.6, 37.8, 27.9, 27.0, 25.6, 17.4, –2.1 ppm. IR (Nujol mulls): $\tilde{\nu}$ = 2953 (s), 2923 (s), 2853 (s), 1601 (w), 1573 (w), 1460 (m), 1376 (m), 1252 (m), 1170 (w), 1060 (m), 962 (m), 838 (m), 765 (s), 718 (m), 413 (w) cm^{-1}. $C_{17}H_{25}NSi$ (271.47): calcd. C 75.21, H 9.28, N 5.16; found C 75.06, H 9.24, N 4.80.

Preparation of $[\eta^5{:}\eta^1\text{-}(C_9H_6CH_2SiMe_2NC_4H_8)]_2Yb^{II}$ (2): To a toluene (10.0 mL) solution of $C_9H_7CH_2SiMe_2NC_4H_8$ (0.617 g, 2.40 mmol) was added a toluene (50.0 mL) solution of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(THF)_3$ (1.096 g, 1.20 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was then refluxed for 12 h, the solution gradually changed from yellow to green to red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (10.0 mL). The resulting solid was extracted with toluene (2 × 15.0 mL). The extractions were combined and concentrated to about 15.0 mL. The red crystals were obtained by cooling the concentrated solution at 0 °C for several days (0.403 g, 49% yield). M.p. 169–170 °C. ^1H NMR (300 MHz, C_5D_5N, 25 °C): δ = 7.55 (m, 4 H), 7.18 (m, 4 H), 6.96 (m, 2 H), 6.03 (m, 2 H) (C_9H_6), 2.11 (s, 4 H) (CH_2), 2.85 (m, 8 H), 1.52 (m, 8 H) (C_4H_8N), 0.10 (s, 12 H) [$Si(CH_3)_2$] ppm. IR (Nujol mulls): $\tilde{\nu}$ = 2925 (s), 2855 (s), 2333 (w), 1714 (m), 1604 (m), 1546 (m), 1461 (m), 1377 (s), 1249 (m), 1194 (w), 1006 (m), 829 (m), 755 (m), 721 (m), 467 (w) cm^{-1}. $C_{32}H_{44}N_2Si_2Yb$ (685.02): calcd. C 56.03, H 6.47, N 4.08; found C 55.79, H 6.45, N 3.92.

Preparation of $[\eta^3{:}\eta^1\text{-}C_9H_5\text{-}1\text{-}CH_3\text{-}3\text{-}CH_2SiMe_2NC_4H_8]_2Yb^{II}$(3): This compound was prepared as red crystals in 58% yield from the reaction of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(THF)_3$ (1.096 g, 1.20 mmol) with C_9H_6-1-CH_3-3-$CH_2SiMe_2NC_4H_8$ (0.650 g, 2.40 mmol) by using procedures similar to those used for the preparation of **2**. M.p. 178–181 °C. ^1H NMR (300 MHz, C_5D_5N, 25 °C): δ = 7.36 (m, 8 H), 5.93 (s, 2 H) (C_9H_6), 2.82 (m, 8 H) (C_4H_8N), 2.03 (s, 4 H) (CH_2), 1.49 (m, 8 H) (C_4H_8N), 1.18 (m, 6 H) (CH_3), 0.06 (s, 12 H) [$Si(CH_3)_2$] ppm. IR (Nujol mulls): $\tilde{\nu}$ = 2961 (s), 2869 (m), 1603 (m), 1559 (m), 1540 (s), 1457 (m), 1354 (w), 1256 (m), 1153 (w),

1019 (m), 877 (m), 751 (m), 668 (m), 419 (w) cm^{-1}. $C_{34}H_{48}N_2Si_2Yb$ (713.97): calcd. C 57.20, H 6.78, N 3.92; found C 57.42, H 6.67, N 4.44.

Preparation of $[\eta^5:\eta^1\text{-}C_9H_6CH_2SiMe_2NC_5H_{10}]_2Yb^{II}$ (4): This compound was prepared as a red powder in 37% yield from the reaction of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-Cl})Li(THF)_3$ (1.278 g, 1.40 mmol) with $C_9H_7CH_2SiMe_2NC_5H_{10}$ (**1**) (0.759 g, 2.80 mmol) in refluxing toluene by using procedures similar to those used for the preparation of **2**. M.p. 153–155 °C. ^1H NMR (300 MHz, C_5D_5N, 25 °C): δ = 7.38 (m, 8 H), 6.08 (d, 4 H) (C_9H_6), 2.69 (m, 8 H) ($C_5H_{10}N$), 2.03 (s, 4 H) (CH_2), 1.38 (m, 8 H) ($C_5H_{10}N$), 1.24 (m, 4 H) ($C_5H_{10}N$), 0.03 (m, 12 H) [$Si(CH_3)_2$] ppm. $C_{34}H_{48}N_2Si_2Yb$ (713.97): calcd. C 57.20, H 6.78, N; 3.92; found C 57.13, H 6.54, N 4.55.

Preparation of $[\eta^5:\eta^1\text{-}C_9H_6CH_2SiMe_2NC_5H_{10}]_2Eu^{II}$ (5): This compound was prepared as yellow crystals in 71% yield from the reaction of $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-Cl})Li(THF)_3$ (1.247 g, 1.40 mmol) with $C_9H_7CH_2SiMe_2NC_5H_{10}$ (**1**) (0.759 g, 2.80 mmol) in toluene at 60 °C by using procedures similar to those used for the preparation of **2**. NMR (C_5D_5N) spectra of the compound were not informative due to lack of locking signals for the paramagnetic property of the europium(II) complex. M.p. 132–133 °C. IR (Nujol mulls): $\tilde{\nu}$ = 3064 (w), 2931 (s), 2852 (m), 1540 (m), 1507 (m), 1490 (m), 1459 (m), 1448 (m), 1249 (s), 1059 (m), 962 (m), 833 (s), 766 (s), 719 (m), 668 (m) cm^{-1}. $C_{34}H_{48}EuN_2Si_2$ (692.89): calcd. 58.94, H 6.98, N 4.04; found C 58.77, H 7.32, N 3.83.

Preparation of $[C_9H_6CH_2SiMe_2NC_5H_{10}]_3Nd^{III}\cdot THF$ (6): To a toluene (10.0 mL) solution of $C_9H_7CH_2SiMe_2NC_5H_{10}$ (**1**) (0.759 g, 2.80 mmol) was added a toluene (50.0 mL) solution of $[(Me_3Si)_2N]_3Nd^{III}(\mu\text{-Cl})Li(THF)_3$ (1.238 g, 1.40 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was then refluxed for 12 h. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (2 × 15.0 mL). The extractions were combined and concentrated to about 20.0 mL. The green crystals were obtained by cooling the concentrated solution at 0 °C for several days [0.417 g, 29% yield based on $[(Me_3Si)_2N]_3Nd^{III}(\mu\text{-Cl})Li(THF)_3$]. NMR ($C_5D_5N$) spectra of the compound were not informative due to lack of locking signals for the paramagnetic property of the neodymium(III) complex. M.p. 146–148 °C. IR (Nujol mulls): $\tilde{\nu}$ = 2933 (m), 1601 (m), 1520 (m), 1445 (m), 1398 (m), 1292 (m), 1251 (s), 1203 (w), 1030 (m), 962 (m), 870 (s), 853 (s), 766 (s), 720 (m), 668 (w) cm^{-1}. $C_{51}H_{72}N_3NdSi_3$ (955.63): calcd. C 64.10, H 7.59, N 4.40; found C 64.25, H 7.16, N 5.07.

X-ray Crystallography: Suitable crystals of complexes **2**, **3**, **5**, and **6** were each mounted in a sealed capillary. Diffraction was performed with a Siemens SMART CCD-area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å); temperature 293(2) K; ϕ and ω scan technique; SADABS effects and empirical absorption were applied in the data corrections. All structures were solved by direct methods (SHELXTL-97),[27] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on F^2 (SHELXTL-97).[27] See Table 3 for crystallographic data.

CCDC-627924 (for **2**), -627925 (for **3**), -627923 (for **5**), and -627922 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ε-Caprolactone Polymerization: ε-CL polymerization reactions were performed in a 50-mL Schlenk flask, placed in an external temperature-controlled bath, on a Schlenk line or in a glovebox. In a typical procedure, the catalyst (20–50 mg) was loaded into the Schlenk flask and the solvent was added. The ε-CL was added through a gastight syringe after the external bath temperature was stabilized. The polymer product was precipitated into hydrochloric acid (0.1 M, 50.0 mL), washed with hydrochloric acid (0.1 M), and then dried to a constant weight in a vacuum oven at 50 °C. The molecular weights of the polymers were analyzed by GPC techniques.

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Table 3. X-ray experimental data of complexes **2**, **3**, **5** and **6**.

	2	**3**	**5**	**6**
Empirical formula	$C_{32}H_{44}N_2Si_2Yb$	$C_{34}H_{48}N_2Si_2Yb$	$C_{34}H_{48}EuN_2Si_2$	$C_{55}H_{80}N_3NdOSi_3$
Formula weight	685.91	713.96	692.88	1027.73
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*2(1)/*n*	*C*2/*c*	*Cc*	*P*21/*c*
a [Å]	13.7350(10)	15.7405(14)	16.518(3)	22.192(2)
b [Å]	11.9791(2)	10.2816(9)	9.6420(16)	11.5905(12)
c [Å]	19.1269(2)	19.7404(17)	20.069(3)	21.538(2)
β [°]	101.96	91.6130(10)	92.922(3)	90
V [$Å^3$]	3078.75(6)	3193.5(5)	3192.2(9)	5540.0(10)
T [K]	293(2)	293(2)	293(2)	293(2)
$D_{calcd.}$ [$g\,cm^{-3}$]	1.480	1.485	1.433	1.232
Z	4	4	4	4
F(000)	1392	1456	1412	2164
Number of reflections collected	9220	4734	7905	27380
Number of unique reflections	5296 (R_{int} = 0.0406)	2790 (R_{int} = 0.0198)	2821 (R_{int} = 0.0284)	9764 (R_{int} = 0.0474)
Number of parameters	334	177	179	622
λ [Å] (Mo-K_α)	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	3.138	3.029	2.065	1.040
θ range [deg]	2.02 to 25.01	2.37 to 25.09	2.03 to 25.02	1.89 to 25.01
Goodness of fit	1.093	1.148	1.083	1.050
R [$I > 2\sigma(I)$]	0.0566	0.0292	0.0218	0.0378
wR_2	0.1268	0.0662	0.0621	0.0890
Largest diff. peak and hole [e·$Å^{-3}$]	2.124 and –1.534	0.520 and –1.337	0.590 and –0.909	0.710 and –0.356

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