

Homolysis of the Ln–N bond: Synthesis, characterization and catalytic activity of organolanthanide(II) complexes with furfuryl- and tetrahydrofurfuryl-functionalized indenyl ligands

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Abstract

A series of new organolanthanide(II) complexes with furfuryl- and tetrahydrofurfuryl-functionalized indenyl ligands were synthesized via one-electron reductive elimination reaction. Treatments of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (Ln = Yb, Eu) with 2 equiv. of $\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_7$ (**1**) or $\text{C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_7$ (**2**), respectively in toluene at moderate high temperatures produced, after workup, the corresponding organolanthanide(II) complexes with formula $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_6)_2\text{Ln}^{\text{II}}$ (Ln = Yb (**5**), Ln = Eu (**6**)) and $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_6)_2\text{Ln}^{\text{II}}$ (Ln = Yb (**7**), Ln = Eu (**8**)) in reasonable to good yields. Treatments of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (Ln = Yb, Eu) with 2 equiv. of $\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_6\text{SiMe}_3$ (**3**) or $\text{C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_6\text{SiMe}_3$ (**4**), respectively, in toluene at moderate high temperatures afforded, after workup, the corresponding organolanthanide(II) complexes with formula $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Ln}^{\text{II}}$ (Ln = Yb (**9**), Ln = Eu (**10**)) and $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Ln}^{\text{II}}$ (Ln = Yb (**11**), Ln = Eu (**12**)) in good to high yields. All the compounds were fully characterized by spectroscopic methods and elemental analyses. The structure of complex **9** was additionally determined by single-crystal X-ray analyses. Studies on the catalytic activities of complexes showed that the complexes having silyl group functionalized indenyl ligands have high catalytic activities on ϵ -caprolactone polymerization. The temperatures, substituted groups on the indenyl ligands of the complexes, and solvents effects on the catalytic activities of the complexes were examined.

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1. Introduction

The chemistry of organolanthanide complexes is one of the most active fields among the transitional metal chemistry for their unique structures and reactivity [1]. It has been found that organolanthanide complexes

behaves a diverse chemistry including catalytic transformations of olefins and lactones polymerization [2], hydroamination/cyclization [3], hydrosilylation [4], hydrophosphination [3b,5], and hydroboration [6]. Organolanthanide(II) complexes are one of the family among the organolanthanide complexes, which can effect various reactions including activation of small molecules such as N_2 [7], CO [8], unsaturated hydrocarbons [9], carbonyl [10], as well as polymerization of ethylene [2], styrene [2], acrylonitrile [11], methyl methacrylate and lactones [2,12]. Among the reactivity of

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organolanthanide(II) complexes, the ring-opening polymerization of lactones provides a convenient route to biodegradable polyesters, which are of interest for a variety of practical applications [1,13].

We have reported that the interactions of functionalized indene compounds having internal donor substituted groups such as *N,N*-dimethylaminoethyl group [12b,12c], methoxyethyl groups [12d] with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$) afforded organolanthanide(II) complexes. Interactions of $\text{C}_9\text{H}_6\text{-1-R-3-CH}_2\text{SiMe}_2\text{NC}_4\text{H}_8$ ($\text{R} = \text{H}, \text{CH}_3$) with $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Eu}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ resulted in the isolation and characterization of a series of novel tetranuclear triple-decker and monomeric europium(II) complexes [12e]. The reaction pathway was proposed to involve tandem silylamine elimination/homolysis of the Ln-N ($\text{Ln} = \text{Yb}, \text{Eu}$) bond based on the experimental results. It is found that organolanthanide(II) complexes prepared by this method can function as single-component of MMA polymerization catalysts.

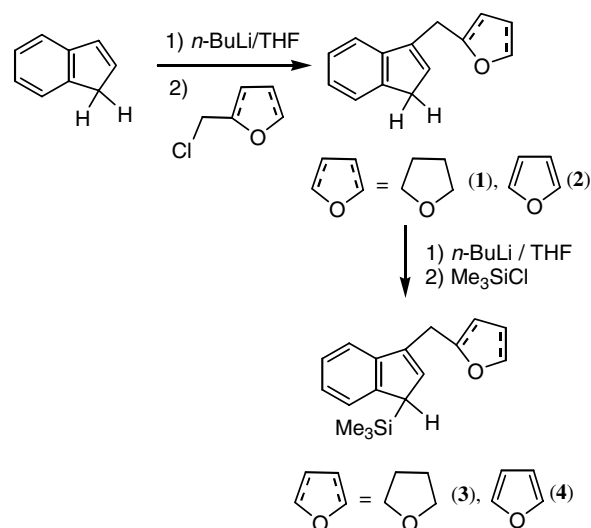
In this paper, we will report the synthesis, characterization and catalytic activities of a series of new organolanthanide(II) complexes having furfuryl- or tetrahydrofurfuryl-functionalized indenyl ligands. The studies on the catalytic activities of the complexes indicated that the complexes having both trimethylsilyl and furfuryl- or tetrahydrofurfuryl substituents on the indenyl ligands showed high catalytic activities on ring-opening polymerization of ϵ -caprolactone, while the complexes with only furfuryl- or tetrahydrofurfuryl-functionalized indenyl ligands cannot catalyze the ϵ -caprolactone polymerization. To the best of our knowledge, the complexes **10** and **12** represent the first examples of europium(II) complexes as the single-component of ring-opening polymerization of ϵ -caprolactone catalysts with high catalytic activities [2,13]. The solvents, polymerization temperatures, and solvent/monomer and monomer/catalyst ratio effects on the catalytic activities of the complexes and polymerization were examined.

2. Results and discussion

2.1. Synthesis and characterization of the ligands

The furfuryl- and the tetrahydrofurfuryl-substituted indene compounds **1** and **2** were synthesized according to the literatures with slightly modified procedures [14,15]. The substituted indene compounds were then transferred to the corresponding lithium salts, treatment of the freshly prepared indenyl lithium with excess of Me_3SiCl gave, after workup, the corresponding indene compounds **3** and **4** in good yield. The full synthetic procedures were outlined in Scheme 1.

The indene compounds were fully characterized by spectroscopic and high-resolution MS methods. ^1H



Scheme 1.

NMR analyses showed that the furfuryl or the tetrahydrofurfuryl-substituted group connects to the sp^2 carbon of the five-membered ring of the indene ring, and the Me_3Si functional group of the compounds **3** and **4** connected to the sp^3 carbon of the indene ring.

2.2. Synthesis and characterization of organolanthanide(II) complexes with furfuryl- and tetrahydrofurfuryl-substituted indenyl ligands

Treatment of lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Yb}, \text{Eu}$) with 2 equiv. of the corresponding tetrahydrofurfuryl-substituted indene compound **1** or the furfuryl-substituted indene compound **2** in toluene at moderate high temperatures produced, after workup, the organolanthanide(II) compounds with formula $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_7\text{OCH}_2\text{C}_9\text{H}_6)]_2\text{Ln}^{\text{II}}$ ($\text{Ln} = \text{Yb}$ (**5**), Eu (**6**)), and the organolanthanide(II) complexes with general formula $[\eta^5:\eta^1\text{-}(\text{C}_4\text{H}_3\text{OCH}_2\text{C}_9\text{H}_6)]_2\text{Ln}^{\text{II}}$ ($\text{Ln} = \text{Yb}$ (**7**), Eu (**8**)) (Scheme 2). The complexes were fully characterized by IR and elemental analyses. The complexes **5** and **7** were also characterized by ^1H NMR spectra analyses; the diamagnetic properties of complexes **5** and **7** from the ^1H NMR spectra indicated that the central ytterbium metals in complexes are in the oxidation state +2. The ^1H NMR spectra of complexes **6** and **8** were not informative due to lack of locking signal for the paramagnetic property of the complex. The complexes were extremely air and moisture sensitive solid, they are soluble in polar solvents such as THF, DME and pyridine, slightly soluble in toluene, and insoluble in *n*-hexane.

The formation of divalent complexes **5–8** is believed to go through one-electron reductive elimination process. To extend the reaction scopes, to improve the solubility of the organolanthanide(II) complexes in nonpolar solvent such as toluene, the interactions of indene

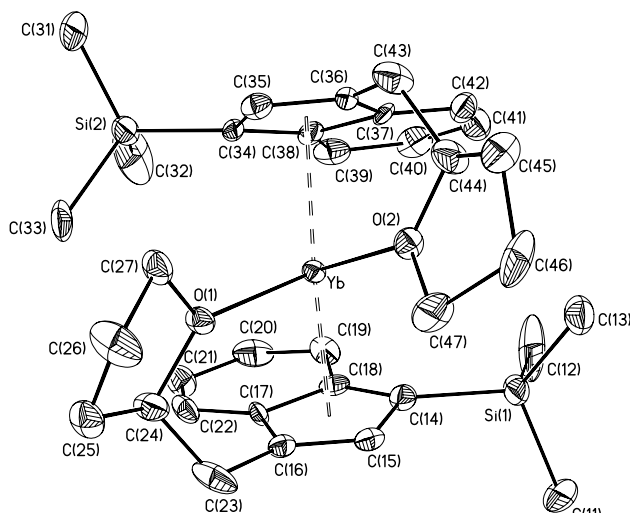
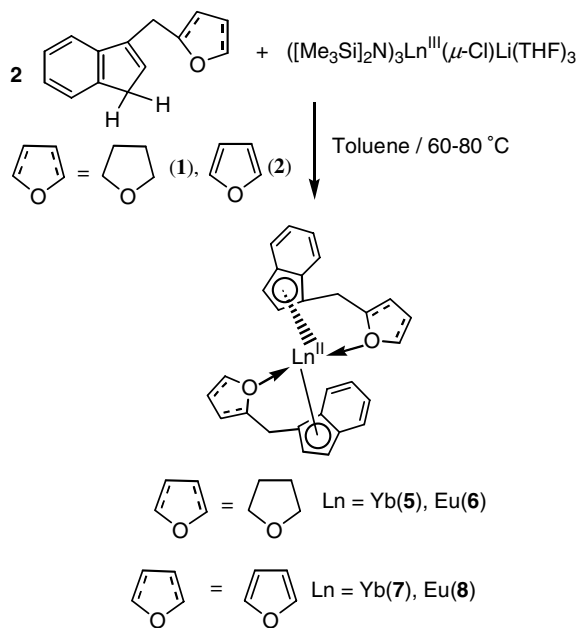


Fig. 1. Molecular structure of $[\eta^5:\eta^1-(C_4H_7OCH_2C_9H_5SiMe_3)_2]_2Yb^{II}$ (**9**). Hydrogen atoms are omitted for clarity.

compounds having both silyl-functionalized and tetrahydrofurfuryl or furfuryl-substituted groups with the lanthanide(III) amides $[(Me_3Si)_2N]_3Ln^{III}(\mu-Cl)Li(THF)_3$ ($Ln = Yb, Eu$) were studied.

Treatments of lanthanide(III) amides $[(Me_3Si)_2N]_3Ln^{III}(\mu-Cl)Li(THF)_3$ ($Ln = Yb, Eu$) with 2 equiv. of the silyl-functionalized and tetrahydrofurfuryl- or furfuryl-substituted indene compounds $C_4H_7OCH_2C_9H_6SiMe_3$ (**3**) and $C_4H_3OCH_2C_9H_6SiMe_3$ (**4**), respectively, in toluene at moderate high temperature gave the corresponding organolanthanide(II) complexes with formula $[\eta^5:\eta^1-(C_4H_7OCH_2C_9H_5SiMe_3)_2]_2Ln^{II}$ ($Ln = Yb$ (**9**), $Ln = Eu$ (**10**)) and $[\eta^5:\eta^1-(C_4H_3OCH_2C_9H_5SiMe_3)_2]_2Ln^{II}$ ($Ln = Yb$ (**11**), $Ln = Eu$ (**12**)) in good to high yields

(Scheme 3). The complexes are extremely sensitive to air and moisture, they are soluble in toluene, THF, DME and pyridine, but only slightly soluble in *n*-hexane. Complexes **9–12** were well characterized by IR and elemental analyses. Compounds **9** and **11** were also characterized by 1H NMR spectroscopic methods; the diamagnetic properties of complexes **9** and **11** from the 1H NMR spectra indicated that the central ytterbium metals in complexes are in the oxidation state +2. But, no information can be obtained from the 1H NMR spectra of complexes **10** and **12** for lacking of the locking signals for the paramagnetic properties of the complexes. Complex **9** was additionally characterized by single-crystal X-ray analysis. X-ray analysis of complex **9** confirmed that the oxidation state of the central ytterbium metal is +2, the results further confirmed that the formation of the above organolanthanide(II) complexes involves one-electron reductive elimination process.

X-ray analysis reveals that the central metal is coordinated by two indenyl ligands in η^5 -mode, and by two oxygen atoms of the tetrahydrofuran rings in η^1 -mode. So, the coordination geometry of the central ytterbium(II) metal can be described as a distorted tetrahedral (see Fig. 1).

From Table 1, we can see that the Yb–C distances range from 2.669(17) to 2.799(14) Å, with an average of 2.732(18) Å, which is comparable to the average Yb–C distance of 2.737(4), and 2.75 Å found in $[\eta^5:\eta^1-(MeOCH_2CH_2C_5H_4)_2]Yb^{II}(THF)$ [16], and $[Me_3Si(C_5H_4)_2]Yb(THF)_2$ [17], respectively. This average Yb–C distance found in **9** is shorter than the average Yb–C distance of 2.741(14) Å found in $[\eta^5:\eta^1-(MeOCH_2CH_2C_9H_5SiMe_3)_2]Yb^{II}$ [12d]. The average Yb–C distance of 2.732(18) Å found in **9** can be

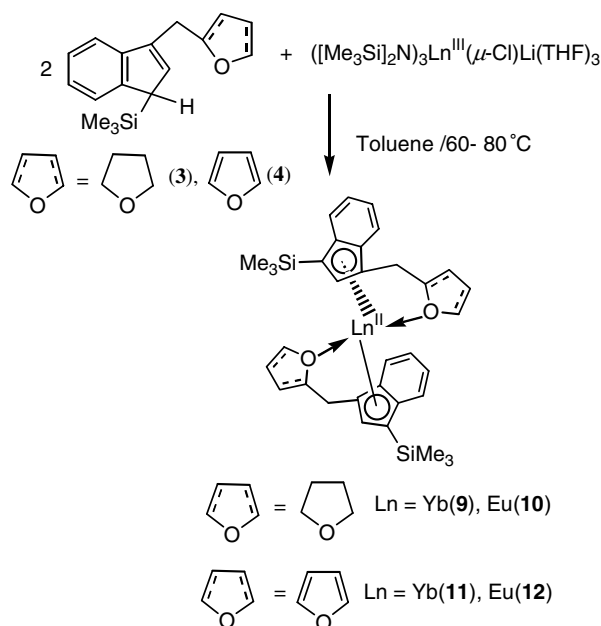


Table 1
Selected bond length (Å) and bond angle (°)

9			
Yb–O(1)	2.418(10)	Yb–C(34)	2.747(13)
Yb–O(2)	2.436(11)	Yb–C(35)	2.669(17)
Yb–O(av.)	2.427(11)	Yb–C(36)	2.698(14)
Yb–C(14)	2.709(18)	Yb–C(37)	2.799(14)
Yb–C(15)	2.701(17)	Yb–C(38)	2.767(14)
Yb–C(16)	2.718(15)	Yb–C(av.)	2.732(18)
Yb–C(17)	2.763(13)	O(1)–Yb–O(2)	83.1(4)
Yb–C(18)	2.750(15)		

compared with those of average Yb–C distances of 2.806(12), 2.778(14), 2.722(10) Å found in the corresponding indenyl ytterbium(II) complexes $[\eta^5:\eta^1\text{-Me}_2\text{-Si}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{C}_9\text{H}_5)(\text{NHBu-}t)_2\text{Yb}^{\text{II}}]$, $[\eta^5:\eta^1\text{-}(\text{Me}_2\text{N-CH}_2\text{CH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Yb}^{\text{II}}]$, and $[\eta^5:\eta^1\text{-}(\text{Me}_2\text{NCH}_2\text{-CH}_2\text{C}_9\text{H}_6)_2\text{Yb}^{\text{II}}]$ [12b]. However, this Yb–C distance of 2.732(18) Å found in **9** is shorter than the corresponding value of 2.814(7) Å found in $[\eta^5:\eta^1:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_5\text{CH}_2\text{CH}_2\text{OMe})(\text{C}_2\text{B}_{10}\text{H}_{10})\text{Yb}(\text{DME})(\text{THF})]$ [18], which has the same coordination number with complex **9**. The Yb–C distance of 2.732(18) Å found in **9** is also slightly shorter than the corresponding value of 2.750(3) Å found in $[\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{-Yb}(\text{THF})_3]$ [19], the above difference on the average Yb–C distances of different ytterbium(II) complexes may be due to steric effects and ionic radii difference [20].

The Yb–O distances are 2.418(10) and 2.436(11) Å, with an average of 2.427(11) Å. The average Yb–O distance found in **9** is shorter than the Yb–O (THF) distances of 2.494(4) Å, and the Yb–O (MeOCH₂CH₂C₅H₄) distance of 2.564(3) Å found in $[\eta^5:\eta^1\text{-}(\text{MeOCH}_2\text{CH}_2\text{-C}_5\text{H}_4)_2\text{Yb}^{\text{II}}(\text{THF})]$ [16], due to steric effects and ionic radii²⁰ difference. The average Yb–O distance 2.427(11) Å is also shorter than the average Yb–O value of 2.462(9) Å found in $[\eta^5:\eta^1\text{-}(\text{MeOCH}_2\text{CH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Yb}^{\text{II}}]$ [12d], indicating steric effects. The average Yb–O distance found in **9** is longer than the corresponding distances of 2.410 Å found in $[\text{Me}_3\text{Si}(\text{C}_5\text{H}_4)_2\text{-Yb}(\text{THF})_2]$ [17] and $(\text{C}_5\text{Me}_5)_2\text{Yb}(\text{THF})$ [21], respectively.

The O(1)–Yb–O(2) angle of 83.1(4)° is significantly smaller than the O(1)(MeOCH₂CH₂C₅H₄)–Yb–O(1)* (MeOCH₂CH₂C₅H₄) angle of 143.5(1)° found in $[\eta^5:\eta^1\text{-}(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb}^{\text{II}}(\text{THF})]$ [16]. This angle is comparable to the O–Yb–O angles of 84.5(3)° and 86.3(3)° found in $[\eta^5:\eta^1\text{-}(\text{MeOCH}_2\text{CH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Yb}^{\text{II}}]$, the O–Eu–O angle of 88.6(2)° found in $[\eta^5:\eta^1\text{-Me}_2\text{Si}(\text{MeOCH}_2\text{CH}_2\text{C}_9\text{H}_5)(\text{NHBu-}t)_2\text{Eu}^{\text{II}}]$, and O–Eu–O angles of 88.1(3)°, 83.3(3)° found in $[\eta^5:\eta^1\text{-}(\text{MeOCH}_2\text{CH}_2\text{C}_9\text{H}_5\text{SiMe}_3)_2\text{Eu}^{\text{II}}]$ [12d].

The formation of the above organolanthanide(II) complexes is believe to involve one-electron reductive elimination process. Our previous works showed that the interactions of non-heteroatom substituted indene (C₉H₈) or the bridged indene compound (CH₂)₂(C₉H₇)

with ytterbium(III) amide $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Yb}^{\text{III}}(\mu\text{-Cl})\text{-Li}(\text{THF})_3$ produced the indenyl ytterbium(III) amides (C₉H₇)₂YbN(SiMe₃)₂ or $[(\text{CH}_2)_2(\text{C}_9\text{H}_6)_2\text{YbN}(\text{SiMe}_3)_2]$ [12b], homolysis of Yb–N bond has not been observed by refluxing the ytterbium(III) amide $[(\text{CH}_2)_2(\text{C}_9\text{H}_6)_2\text{-YbN}(\text{SiMe}_3)_2]$ in toluene for 3 days [12b]. Homolysis of Ln–N (Ln = Yb, Eu) bond has not been observed either by refluxing the lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{-Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ or by sublimation of the corresponding amides [22a]. These results suggested that: (1) reductive elimination happens after the interactions of the heteroatom substituted indene compounds with lanthanide amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$; (2) heteroatom substituted groups may be responsible for the reductive process; (3) the reductive process involves indenyl lanthanide(III) amides as intermediates; (4) the reaction temperatures may not be the major factors for the homolysis of the Ln–N bonds; and (5) isolation and characterization of indenyl ytterbium(III) amides (C₉H₇)₂YbN(SiMe₃)₂ and $[(\text{CH}_2)_2(\text{C}_9\text{H}_6)_2\text{-YbN}(\text{SiMe}_3)_2]$ from the reactions of non-heteroatom substituted indene compounds with lanthanide(III) amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ strongly suggested that the reductive process is not due to the reduction of lanthanide ions by the free lithium amide LiN(SiMe₃)₂ from $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ in solution. On the basis of these evidences, formation pathway of the above organolanthanide(II) complexes is proposed to be similar with our previous works [12b–12e].

2.3. Ring-opening polymerization of lactones

The complexes as single-component catalysts on γ -valerolactone and ϵ -caprolactone polymerization were examined. It is found that complexes **5–8** with non-silyl substituted indenyl ligands can not catalyze ring-opening polymerization of γ -valerolactone and ϵ -caprolactone in toluene, THF and DME, however, the complexes **9–12** with both silyl substituted and furfuryl- or tetrahydrofurfuryl-functionalized indenyl ligands showed very high catalytic activities (up to 5.82×10^6 g polymer/mol catalyst h) on ring-opening polymerization of ϵ -caprolactone in toluene, this founding can not be simply explained by the solubility of the complexes in solvents, the silyl group effects on the catalytic activity of complexes are to be elucidated. The results are listed in Tables 2–4. The catalytic activities of complexes **9–12** on ring-opening polymerization of ϵ -caprolactone can be compared with those of (C₁₃H₉)₂Sm(THF)₂ [13b], (OAr)₂Sm(THF)₃ and $[(\text{C}_5\text{Me}_5)\text{Sm}(\text{OAr})_2]$ [23].

To explore the solvents tolerance and solvents effects on the catalytic activities of the catalysts. Solvents such as toluene, THF, DME, and CH₂Cl₂ were used in studying of the catalytic activities of the complex **9** on

ring-opening polymerization of ϵ -caprolactone (Table 2). It was found that complex **9** behaved high catalytic activities on ring opening polymerization of ϵ -caprolactone in toluene and DME (Table 3), and showed a catalytic activity up to 5.82×10^6 g polymer/mol catalyst h in toluene at 0 °C as the solvent/monomer ratio was fixed on 5:1, and the monomer/catalyst ratio on 1000:1 (Table 4). But, it cannot catalyze ϵ -caprolactone polymerization in THF, and it shows poor catalytic activity in CH_2Cl_2 , indicating the solvents have influences on the catalytic activities of the catalysts.

For the complexes **9–12** showed high catalytic activities on the ring-opening polymerization of ϵ -caprolactone in toluene, the temperature effects on the catalytic activities of the complexes **9–12** were studied. The results are listed in Table 3. From the table, we can see that complexes **9–12** showed high catalytic activities in temperature range of 30 to -60 °C in toluene. The catalytic

activities of the complexes slightly decrease as the polymerization temperatures are below 0 °C. It was also found that the molecular weights of the polymers generally increase (M_n about 10^5) as the polymerization temperatures decrease, indicating that chain propagation process be favored at low temperature. It is also interesting to note that the molecular weight distributions of the polymers become narrow (M_w/M_n as lower as 1.34) as the polymerization temperatures decrease.

The solvent/monomer and monomer/catalyst ratio effects on the polymerization were also studied (Table 4). When the monomer/catalyst ratio were fixed on 500:1, all the complexes showed high catalytic activities, the catalytic activities of the catalysts **9–12** almost did not change when the solvent/monomer ratio were changed from 2:1 to 10:1, however, the molecular weights of the polymers showed a decrease order as the solvent/monomer ratio increase in cases the catalysts **9**, **10** and **12** were

Table 2

Solvents effects on the catalytic activity of catalyst (**9**) on ϵ -caprolactone (CL) polymerization

Solv.	Temp. (°C)	Time (min)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Conv. (%)	Activity $\times 10^{-6}$
Tolu.	60	1	3.72	6.62	1.78	53	1.82
	30	1	1.80	3.70	2.05	88	3.01
	0	1	3.22	6.41	1.99	99	3.39
	-30	1	5.04	8.24	1.63	85	2.91
	-60	1	14.31	19.73	1.38	87	2.98
	DME	30	1	1.14	1.19	1.05	46
0		1	6.57	11.79	1.79	87	2.98
-30		1	8.87	13.75	1.55	74	2.53
-60		20	9.86	14.22	1.44	10	0.02
CH_2Cl_2	0	20	5.30	7.99	1.51	23	0.04
THF	0	20	–	–	–	0	0.00

Condition: solvent/ ϵ -CL (V/V) = 5:1; Cat./ ϵ -CL (mol/mol) = 1:500; Activity: g polymer/molcatalyst h.

Table 3

Temperatures effects on catalytic activity of the catalysts on ϵ -caprolactone (CL) polymerization

Cat.	Temp. (°C)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Conv. (%)	Activity $\times 10^{-6}$
5	0	–	–	–	0	0
6	0	–	–	–	0	0
7	0	–	–	–	0	0
8	0	–	–	–	0	0
9	60	3.72	6.62	1.78	53	1.82
	30	1.80	3.70	2.05	88	3.01
	0	3.22	6.41	1.99	99	3.39
	-30	5.04	8.24	1.63	85	2.91
	-60	14.31	19.73	1.38	87	2.98
	10	30	3.87	7.85	2.03	98
0		4.72	8.77	1.86	92	3.15
-30		10.05	17.71	1.76	91	3.12
-60		11.38	18.58	1.63	22	0.38
11	30	6.96	14.44	2.08	87	2.98
	0	7.75	14.47	1.87	99	3.39
	-30	7.36	13.73	1.86	98	3.35
12	-60	8.19	11.01	1.34	95	2.29
	30	4.14	7.46	1.80	93	3.18
	0	7.52	14.13	1.88	97	3.32
	-30	11.80	16.28	1.38	56	1.92
	-60	12.80	18.17	1.42	67	1.15

Condition: solvent: toluene; time = 1 min.; solvent/ ϵ -CL (V/V) = 5:1; cat./ ϵ -CL (mol/mol) = 1:500; Activity: g polymer/molcatalyst h.

Table 4
Solvent/monomer and monomer/catalyst ratio effects on the ϵ -caprolactone polymerization

Cat.	Sol.	Sol./mon. (V/V)	Mon./cat. (mol/mol)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Conv. (%)	Activity $\times 10^{-6}$	
9	Tolu.	2:1	500:1	7.43	12.78	1.72	99	3.39	
		5:1		3.22	6.41	1.99	99	3.39	
		10:1		2.67	4.79	1.79	97	3.32	
		5:1		250:1	3.44	6.81	1.98	82	1.40
				500:1	3.22	6.41	1.99	99	3.39
				750:1	4.10	7.40	1.80	98	5.03
				1000:1	4.28	7.30	1.70	85	5.82
	DME	2:1	500:1	8.41	14.61	1.74	90	3.08	
		5:1		6.57	11.79	1.79	87	2.98	
		10:1		4.28	10.12	2.36	78	2.67	
		5:1		250:1	1.41	1.82	1.29	55	0.94
				500:1	6.57	11.79	1.79	87	2.98
				750:1	5.91	12.38	2.10	30	1.54
		10		Tolu.	2:1	500:1	5.15	9.42	1.83
5:1	4.72		8.77		1.86		92	3.15	
10:1	2.75		4.54		1.65		93	3.18	
5:1	250:1		4.83		8.47		1.75	88	1.51
	500:1		4.72	8.77	1.86	92	3.15		
	750:1		5.54	8.72	1.58	85	4.37		
11	Tolu.		2:1	500:1	4.67	9.16	1.96	91	3.12
		5:1	7.75		14.47	1.87	99	3.39	
		10:1	9.04		15.56	1.72	95	3.25	
		5:1	250:1		6.67	12.96	1.94	94	1.61
			500:1		7.75	14.47	1.87	99	3.39
			750:1		8.63	16.22	1.88	98	5.03
12	Tolu.	2:1	500:1	12.07	17.81	1.48	100	3.42	
		5:1		7.52	14.13	1.88	97	3.32	
		10:1		3.34	8.95	2.68	93	3.18	
		5:1		250:1	9.91	15.81	1.60	100	1.71
				500:1	7.52	14.13	1.88	97	3.32
				750:1	6.09	10.47	1.72	84	4.31

Condition: solvent: toluene; time = 1 min.; temp. = 0 °C; Activity: g polymer/molcatalyst h.

used, and the molecular weights of the polymers increase as the solvent/monomer ratio increase in case the catalyst **11** was utilized. When the solvent/monomer ratio was fixed on 5:1, the catalytic activities of complexes **9–12** increase as the monomer/catalyst ratio increase from 250:1 to 750:1, and the molecular weights of the polymers increase as the monomer/catalyst ratio increase from 250:1 to 750:1 in cases the catalysts **9–11** were used, the molecular weights of polymers decrease slightly as the monomer/catalyst ratio increase from 250:1 to 750:1 in case the catalyst **12** was applied. The molecular weight distributions of the polymers are around 2.0, these values are comparable to those obtained by other lanthanide(II) complexes [13b,23]. However, the substituents effects on the catalytic activity of the organolanthanide(II) complexes remains to be elucidated.

3. Conclusion

In summary, a series of new organolanthanide(II) complexes with furfuryl- and tetrahydrofurfuryl-func-

tionalized indenyl ligands were synthesized by tandem silyl amine elimination/homolysis of the Ln–N (Ln = Yb, Eu) bonds reaction. This work demonstrated that the method for the preparation of organolanthanide(II) complexes through tandem silyl amine elimination/homolysis of the Ln–N (Ln = Yb, Eu) bonds can be extended to the oxygen containing heterocyclic-functionalized indene systems. We have developed a new series of complexes having both oxygen containing heterocyclic- and silyl-functionalized indenyl ligands as single-component ring-opening polymerization of ϵ -caprolactone catalysts with very high catalytic activities. The substituent effects cannot be simply explained by the solubility of the complexes. Complexes **10** and **12** also represent the first examples of europium(II) complexes with indenyl ligands as single-component of ring-opening polymerization of ϵ -caprolactone catalysts with high catalytic activities. The complexes with non-silyl-functionalized indenyl ligands cannot catalyze the ϵ -caprolactone polymerization. The examinations on the solvents, temperatures, solvent/monomer and monomer/catalysts ratio effects on catalytic activities of

complexes indicated that these catalysts have wide temperatures and solvents tolerance.

4. Experimental

4.1. Materials and methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out on flamed Schlenk-type glassware on a Schlenk line. All solvents were refluxed and distilled over either finely divided LiAlH₄ or sodium benzophenone ketyl under argon prior to use unless otherwise noted. CDCl₃ was dried over activated 4 Å molecular sieves. ε-caprolactone (ε-CL) were dried over finely divided CaH₂, distilled before use. [(Me₃Si)₂N]₃Ln^{III}(μ-Cl)Li(THF)₃ (Ln = Yb, Eu) [12b,22], C₄H₇OCH₂Cl [14], and C₄H₃OCH₂Cl [15] were prepared according to the reported procedures. Elemental analysis data were obtained on a Perkin–Elmer 24100 Series II elemental analyzer. IR spectra were recorded on a Perkin–Elmer 983(G) spectrometer (CsI crystal plate, Nujol and Fluoroble mulls). Melting points were determined in sealed capillaries without corrections. GC–MS analyses were carried out on an Agilent 6890/Micromass GCT–MS instrument. ¹H NMR and ¹³C NMR spectra for analyses of compounds were recorded on a Bruker DPX-300 NMR spectrometer in pyridine-*d*₅ for lanthanide complexes and in CDCl₃ for organic compounds and polymers, and chemical shifts for ¹H and ¹³C NMR spectra were referenced to internal solvent resonances. Gel permeation chromatography (GPC) analyses of polymer samples were carried at 30 °C using THF as an eluent on a Waters-150C instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 mL min⁻¹. Number-average molecular weight and polydispersities of polymers were given relative to PS standards.

4.2. Synthesis of C₄H₇OCH₂C₉H₇ (1)

To a solution of indene (5.69 mL, 48.5 mmol) in 50.0 mL of THF was slowly added a 1.77 M *n*-BuLi solution (27.4 mL, 48.5 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature and was then cooled to 0 °C. To C₄H₇OCH₂Cl (5.85 g, 48.5 mmol) in 10.0 mL of THF was slowly added the reaction mixture. The reaction mixture was stirred for 12 h at room temperature and then it was hydrolyzed with the iced water (40.0 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 20.0 mL). The organic fractions were combined and dried with anhydrous MgSO₄, filtered, and evaporated under vacuum. The pale yellow oily product (6.83 g, 71%) was obtained by flash column chromatography on silica gel. ¹H NMR (CDCl₃): δ_H 7.47–7.20 (m,

4H) (C₉H₇), 6.31 (t, *J* = 1.2 Hz, 1H) (C₉H₇), 4.26 (m, 1H) (C₄H₇O, α-H), 3.93(m, 1H) (C₄H₇O, α-H), 3.78 (m, 1H) (C₄H₇O, α-H), 3.35 (d, *J* = 2.1 Hz, 2H) (C₉H₇), 2.87 (m, 1H) (C₄H₇O, β-H), 2.72 (m, 1H) (C₄H₇O, β-H), 2.01 (m, 1H) (C₄H₇O, β-H), 1.92 (m, 2H) (C₄H₇OCH₂), 1.62 (m, 1H) (C₄H₇O, β-H); ¹³C NMR (CDCl₃): δ 145.3, 144.2, 141.2, 129.5, 125.9, 124.4, 123.6, 118.9 (C₉H₇), 77.7 (C₄H₇O), 67.9 (C₄H₇O), 37.8 (C₉H₇), 34.0 (C₄H₇O), 31.4(C₄H₇O), 25.6 (C₄H₇OCH₂); IR ν (cm⁻¹): 3064 (m), 3017 (w), 2973 (s), 2940 (m), 2874 (s), 1690 (m), 1608 (s), 1575 (m), 1463 (v), 1395 (s), 1356 (w), 1283 (w), 1209 (w), 1168 (w), 1067 (v), 1015 (m), 972 (m), 910 (m), 870 (w), 824 (w),768 (v),720 (v); EIMS *m/z* (fragment, relative intensity, %): 71 (C₄H₇O⁺, 100), 115 (C₉H₇⁺, 13), 128 (C₉H₆CH₂⁺, 32), 200 (M⁺, 24), 201([M + 1]⁺, 4); HRMS/MALDI [C₁₄H₁₆O + H]⁺, Calc. for: 201.1268. Found: 201.12739.

4.3. Synthesis of C₄H₃OCH₂C₉H₇ (2)

To a solution of indene (5.89 mL, 50.2 mmol) in 50.0 mL of THF was slowly added a 1.81 M *n*-BuLi solution (27.7 mL, 50.2 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature and was then cooled to 0 °C. To C₄H₃OCH₂Cl (5.85 g, 50.2 mmol) in 10.0 mL of THF was slowly added the reaction mixture. The reaction mixture was stirred for 12 h at room temperature and then it was hydrolyzed with the iced water (50.0 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 25.0 mL). The organic fractions were combined and dried with anhydrous MgSO₄, filtered, and evaporated under vacuum. The pale yellow oily product (6.91 g, 70%) was obtained by flash column chromatography on silica gel. ¹H NMR (CDCl₃): δ_H 7.46 (d, *J* = 7.2 Hz, 1H) (C₄H₃O, α-H), 7.37–7.20 (m, 4H) (C₉H₇), 6.32 (m, 2H) (C₄H₃O, β-H), 6.10 (t, *J* = 2.4 Hz, 1H) (C₉H₇), 3.94 (s, 2H) (C₄H₃OCH₂), 3.38 (d, *J* = 2.4 Hz, 2H) (C₉H₇); ¹³C NMR (CDCl₃):δ 153.1, 144.7, 144.3, 141.2, 140.5, 130.2, 126.0, 124.6, 123.7, 119.2, 110.3, 106.2 (C₉H₇ + C₄H₃), 37.7 (C₉H₇, saturated carbon), 27.2 (C₄H₃OCH₂); IR (cm⁻¹):ν 3065 (s), 3019 (m), 2892 (s), 1594 (s), 1505 (v), 1461 (v), 1392 (s), 1356 (w), 1319(m), 1268 (w), 1208 (w), 1143 (s), 1075 (s), 1008 (v), 971 (s), 934 (s), 766 (v), 727 (v); EIMS *m/z* (fragment, relative intensity, %): 81 (C₄H₃OCH₂⁺, 100), 115 (C₉H₇⁺, 16), 128 (C₉H₇CH₂⁺, 8), 196 (M⁺, 39), 197 ([M + 1]⁺, 6); HRMS/ MALDI [C₁₄H₁₂O + H]⁺, Calc. for: 197.0956. Found: 197.09609.

4.4. Synthesis of C₄H₇OCH₂C₉H₆SiMe₃ (3)

To a solution of C₄H₇OCH₂C₉H₇ (4.53 22.6 mmol) in 40.0 of THF was slowly added a 1.77 *n*-BuLi solution (12.8 , 22.6 mmol) at 0 °C. The reaction mixture was

stirred for 12 h at room temperature and was then cooled to 0 °C. To the mixture was added freshly distilled Me₃SiCl (5.78 mL, 45.2 mmol) in one portion. The reaction temperature was gradually raised to room temperature and stirred for 6 h at the room temperature. The solvents and excess Me₃SiCl were evaporated under vacuum. 40.0 mL of *n*-hexane was added, and the precipitate was filtered off. The solvent was pumped off, affording the product as a yellow oil (5.85 g, 95%). ¹H NMR (CDCl₃): δ_H 7.48–7.17 (m, 4H) (C₉H₇), 6.41 (m, 1H) (C₉H₇), 4.25 (m, 1H) (C₄H₇O, α-H), 3.95 (m, 1H) (C₄H₇O, α-H), 3.78 (m, 1H) (C₄H₇O, α-H), 3.73 (m, 1H) (C₉H₇), 2.97 (m, 1H) (C₄H₇O, β-H), 2.76 (m, 1H) (C₄H₇O, β-H), 1.92 (m, 2H) (C₄H₇OCH₂), 1.61 (m, 2H) (C₄H₇O, β-H), –0.08 (s, 9H) (Si(CH₃)₃); IR (cm^{–1}): ν 3075 (s), 3010 (m), 2960 (s), 2897 (m), 2867 (s), 1705 (w), 1598 (m), 1449 (s), 1403 (w), 1359 (m), 1254 (v), 1182 (m), 1067 (s), 1027 (s), 990 (m), 932 (s), 878 (m), 834 (v), 771 (v), 695 (s), 619 (s); EIMS *m/z* (fragment, relative intensity, %): 73 (SiMe₃⁺, 100), 128 (C₉H₇CH₂⁺, 26), 272 (M⁺, 5); HRMS/MALDI [C₁₇H₂₄O_{Si} + Na]⁺, Calc. for: 295.1503. Found: 295.14886.

4.5. Synthesis of C₄H₃OCH₂C₉H₆SiMe₃ (4)

To a solution of C₄H₃OCH₂C₉H₇ (4.71 g, 24.0 mmol) in 50.0 mL of THF was slowly added a 1.81 M *n*-BuLi solution (13.3 mL, 24.0 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature and was then cooled to 0 °C. To the mixture was added freshly distilled Me₃SiCl (6.13 mL, 48.0 mmol) in one portion. The reaction temperature was gradually raised to room temperature and stirred for 6 h at the room temperature. The solvents and excess Me₃SiCl were evaporated under vacuum. 40.0 mL of *n*-hexane was added, and the precipitate was filtered off. The solvent was pumped off affording the product as a yellow oil (6.20 g, 96%). ¹H NMR (CDCl₃): δ_H 7.31 (d, *J* = 7.2 Hz, 1H) (C₄H₃O, α-H), 7.29–7.04 (m, 4H) (C₉H₆), 6.29 (s, 1H) (C₉H₆), 6.17 (d, *J* = 2.0 Hz, 1H) (C₄H₃O, β-H), 5.91 (d, *J* = 3.0 Hz, 1H) (C₄H₃O, β-H), 3.87 (s, 2H) (C₄H₃OCH₂), 3.32 (s, 1H) (C₉H₆), –0.17 (s, 9H) (Si(CH₃)₃); IR (cm^{–1}): ν 3070 (s), 3018 (m), 2957 (s), 2893 (s), 1599 (v), 1507 (v), 1452 (v), 1357 (w), 1316 (w), 1253 (v), 1156 (w), 1107 (m), 1030 (s), 1009 (s), 932 (v), 879 (m), 841 (m), 765 (s), 728 (s); EIMS *m/z* (fragment, relative intensity, %): 71 (C₄H₇O⁺, 33.3%), 73 (SiMe₃⁺, 100%), 115 (C₉H₇⁺, 7.2%), 81 (C₄H₃OCH₂⁺, 11.1%), 128 (C₉H₇CH₂⁺, 19.5%), 268 (M⁺, 7.8%); HRMS/MALDI [C₁₇H₂₀O_{Si} + H]⁺, Calc. for: 269.1362. Found: 269.13562.

4.6. Synthesis of [η⁵:η¹-(C₄H₇OCH₂C₉H₆)]₂Yb^{II} (5)

To a toluene (50.0 mL) solution of [(Me₃Si)₂N]₃-Yb^{III}(μ-Cl)Li(THF)₃ (1.223 g, 1.34 mmol) at room tem-

perature was added to C₄H₇OCH₂C₉H₇ (1) (0.537 g, 2.68 mmol). After the reaction mixture was stirred at room temperature for 6 h, the mixture was then stirred at 80 °C for 24 h, the color of the solution was gradually changed from yellow to green to purple-red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (15.0 mL). The resulting solid was extracted with toluene (40.0 mL). The toluene solution was combined and concentrated to 10.0 mL. The purple-red solid complex was obtained by cooling the concentrated solution at 0 °C (0.326 g, 43%). ¹H NMR (C₅D₅N): δ_H 7.53–7.17 (m, 10H) (C₉H₆), 6.27 (d, *J* = 1.5 Hz, 2H) (C₉H₆), 4.18 (m, 2H) (C₄H₇O, α-H), 3.83 (m, 2H) (C₄H₇O, α-H), 3.65 (m, 2H) (C₄H₇O, α-H), 2.86 (m, 2H) (C₄H₇O, α-H), 2.70 (m, 2H) (C₄H₇O, β-H), 1.77 (m, 2H) (C₄H₇O, β-H), 1.67 (m, 4H) (C₄H₇OCH₂), 1.47 (m, 2H) (C₄H₇O, β-H); IR (cm^{–1}): ν 3050 (m), 3003 (w), 2972 (m), 2938 (s), 2870 (s), 1685 (w), 1596 (s), 1507 (w), 1465 (v), 1381 (v), 1307 (w), 1264 (s), 1149 (s), 1075 (s), 1015 (s), 987 (w), 927 (m), 890 (m), 817 (m), 780 (s), 723 (v); m.p.: 219–221 °C; Anal. Calc. for C₂₈H₃₀O₂Yb: C, 58.84; H, 5.29, Found: C, 58.46; H, 5.43%.

4.7. Synthesis of [η⁵:η¹-(C₄H₇OCH₂C₉H₆)]₂Eu^{II} (6)

To a toluene (50.0 mL) solution of [(Me₃Si)₂N]₃-Eu^{III}(μ-Cl)Li(THF)₃ (1.122 g, 1.26 mmol) at room temperature was added to C₄H₇OCH₂C₉H₇ (1) (0.504 g, 2.52 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was stirred at 60 °C for 24 h and the color of the solution changed to red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (20.0 mL). The resulting solid was extracted with toluene (40.0 mL). The toluene solution was combined and concentrated to 10.0 mL. The red solid complex was obtained by cooling the concentrated solution at 0 °C (0.225 g, 33%). IR (cm^{–1}): ν 3064 (m), 3012 (w), 2970 (m), 2936 (s), 2868 (s), 1686 (m), 1607 (s), 1505 (w), 1462 (v), 1373 (v), 1303 (m), 1261 (m), 1164 (m), 1067 (v), 1005 (m), 976 (m), 939 (w), 870 (m), 807 (w), 755 (s), 717 (s); m.p.: 329–331 °C (dec.); Anal. Calc. for C₂₈H₃₀O₂Eu: C, 61.09; H, 5.49. Found: C, 60.95; H, 5.67%.

4.8. Synthesis of [η⁵:η¹-(C₄H₃OCH₂C₉H₆)]₂Yb^{II} (7)

To a toluene (50.0 mL) solution of [(Me₃Si)₂N]₃-Yb^{III}(μ-Cl)Li(THF)₃ (1.378 g, 1.51 mmol) at room temperature was added to C₄H₃OCH₂C₉H₇ (2) (0.592 g, 3.02 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was stirred at 80 °C for 24 h. the color of the solution was gradually changed from yellow to green and finally to purple-red. The solvent was evaporated under reduced pressure. The

residue was washed with *n*-hexane (15.0 mL). The resulting solid was extracted with toluene (30.0 mL). The toluene solution was combined and concentrated to 10.0 mL. The purple-red solid complex was obtained by cooling the concentrated solution at 0 °C (0.574 g, 76%). ¹H NMR (C₅D₅N): δ_H 7.53–7.17 (m, 12H) (C₉H₆ + C₄H₃O, α-H), 6.34 (d, *J* = 7.9 Hz, 2H) (C₉H₆), 6.23–6.19 (m, 4H) (C₄H₃O, β-H), 3.91 (s, 4H) (C₄H₃OCH₂); IR (cm⁻¹): ν 3066 (m), 3009 (w), 2856 (s), 1592 (m), 1506 (v), 1461 (v), 1375 (v), 1348 (w), 1311 (w), 1261 (m), 1149 (s), 1077 (m), 1015 (s), 968 (w), 935 (m), 768 (s), 721(v); m.p.: 108–109°; *Anal.* Calc. for C₂₈H₂₂O₂Yb · 1/4 C₇H₈: C, 60.88; H, 4.12. Found: C, 60.94; H, 4.22%.

4.9. Synthesis of [η⁵:η¹-(C₄H₃OCH₂C₉H₆)]₂Eu^{II} (8)

To a toluene (50.0 mL) solution of [(Me₃Si)₂N]₃-Eu^{III}(μ-Cl)Li(THF)₃ (1.028 g, 1.15 mmol) at room temperature was added to C₄H₃OCH₂C₉H₇ (2) (0.452 g, 2.30 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was stirred at 60 °C for 24 h, and the color of the solution was changed to purple-red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (15.0 mL). The resulting solid was extracted with toluene (40.0 mL). The toluene solution was combined and concentrated to 10.0 mL. The purple solid complex was obtained by cooling the concentrated solution at 0 °C (0.132 g, 21%). IR (cm⁻¹): ν 3062 (m), 3007 (w), 2860 (s), 1598 (s), 1501 (m), 1452 (v), 1384 (v), 1355 (w), 1301 (m), 1273 (w), 1157 (s), 1078 (s), 1010 (w), 974 (w), 937 (m), 768 (s), 725 (v); m.p.: 166–169°; *Anal.* Calc. for C₂₈H₂₂O₂Eu · 1/2 C₇H₈: C, 64.29; H, 4.45. Found: C, 64.52; H, 5.05%.

4.10. Synthesis of [η⁵:η¹-(C₄H₇OCH₂C₉H₅SiMe₃)]₂Yb^{II} (9)

To a toluene (30.0 mL) solution of [(Me₃Si)₂N]₃-Yb^{III}(μ-Cl)Li(THF)₃ (1.141 g, 1.25 mmol) at room temperature was added to C₄H₇OCH₂C₉H₆SiMe₃ (3) (0.681 g, 2.50 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was then stirred at 80 °C for 24 h, the color of the solution was finally changed to red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (4.0 mL). The resulting solid was extracted with toluene (15.0 mL). The toluene solution was combined and concentrated to 4.0 mL. The red crystals were obtained by cooling the concentrated solution at 0 °C (0.779 g, 87%). ¹H NMR (C₅D₅N): δ_H 7.58–7.16 (m, 8H) (C₉H₆), 6.48 (s, 2H) (C₉H₆), 4.22 (m, 2H) (C₄H₇O, α-H), 3.84 (m, 2 H) (C₄H₇O, α-H), 3.64 (m, 2H) (C₄H₇O, α-H), 2.17 (s, 2H) (C₄H₇O, β-H), 1.81 (m, 2H) (C₄H₇O, β-H), 1.75 (m, 2H) (C₄H₇O, β-H), 1.68

(m, 4H) (C₄H₇OCH₂), 1.49 (m, 2H) (C₄H₇O, β-H), -0.08 (s, 18H) (Si(CH₃)₃); IR (cm⁻¹): ν 3068 (m), 3006 (w), 2960 (s), 2923 (m), 2853 (s), 1723 (w), 1598 (m), 1547 (m), 1461 (v), 1375 (s), 1246 (s), 1177 (w), 1063 (m), 1029 (w), 991 (w), 933 (m), 880 (m), 837 (v), 758 (v), 718 (m), 613 (m); m.p.: 97–99 °C; *Anal.* Calc. for C₃₄H₄₆O₂Si₂Yb · 1/2C₇H₈: C, 59.11; H, 6.61. Found: C, 59.03; H, 6.71%.

4.11. Synthesis of [η⁵:η¹-(C₄H₇OCH₂C₉H₅SiMe₃)]₂Eu^{II} (10)

To a toluene (30.0 mL) solution of [(Me₃Si)₂N]₃Eu^{III}(μ-Cl)Li(THF)₃ (1.257 g, 1.41 mmol) at room temperature was added to C₄H₇OCH₂C₉H₆SiMe₃ (3) (0.768 g, 2.82 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was stirred at 60 °C for another 24 h, and the color of the reaction mixture was changed to red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (5.0 mL). The resulting solid was extracted with toluene (15.0 mL). The toluene solution was combined and concentrated to about 5.0 mL. The purple solid complex was obtained by cooling the concentrated solution at 0 °C (0.702 g, 72%). IR (cm⁻¹): ν 3061 (m), 3000 (w), 2959 (s), 2923 (m), 2856 (s), 1704 (w), 1594 (m), 1547 (m), 1461 (v), 1380 (v), 1253 (v), 1181 (w), 1067 (m), 1032 (m), 964 (m), 930 (w), 886 (m), 843 (v), 761 (s), 720 (m), 618 (m); m.p.: 150–152°; *Anal.* Calc. for C₃₄H₄₆O₂Si₂Eu: C, 58.77; H, 6.67. Found: C, 58.54; H, 6.52%.

4.12. Synthesis of [η⁵:η¹-(C₄H₃OCH₂C₉H₅SiMe₃)]₂Yb^{II} (11)

To a toluene (30.0 mL) solution of [(Me₃Si)₂N]₃-Yb^{III}(μ-Cl)Li(THF)₃ (1.203 g, 1.32 mmol) at room temperature was added to C₄H₃OCH₂C₉H₆SiMe₃ (4) (0.707 g, 2.64 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was stirred at 80 °C for 24 h and the color of the solution changed to purple-red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (5.0 mL). The resulting solid was extracted with toluene (15.0 mL). The toluene solution was combined and concentrated to about 5.0 mL. The purple-red solid complex was obtained by cooling the concentrated solution at 0 °C (0.621 g, 67%). ¹H NMR (C₅D₅N): δ_H 7.54–7.17 (m, 10H) (C₉H₆ + C₄H₃O, α-H), 6.48 (d, *J* = 0.6 Hz, 2H) (C₉H₆), 6.35 (m, 2H) (C₄H₃O, β-H), 6.18 (d, *J* = 0.6 Hz, 2H) (C₄H₃O, β-H), 3.98 (s, 4H) (C₄H₃OCH₂), -0.09 (s, 18H) (Si(CH₃)₃); IR (cm⁻¹): ν 3074 (s), 3017 (w), 2956 (s), 2891 (s), 1604 (s), 1503 (m), 1461 (v), 1383 (v), 1299 (w), 1253 (m), 1160 (w), 1101 (w), 1029 (w), 1007 (m), 930 (w), 878 (m), 837 (s), 771 (m), 722 (s); m.p.: 133–134°C; *Anal.* Calc. for

C₃₄H₃₈O₂Si₂Yb: C, 57.69; H, 5.41. Found: C, 57.30; H, 5.29%.

4.13. Synthesis of [η^5 : η^1 -(C₄H₃OCH₂C₉H₅SiMe₃)]₂Eu^{II} (**12**)

To a toluene (30.0 mL) solution of [(Me₃Si)₂N]₃Eu^{III}(μ-Cl)Li(THF)₃ (1.187 g, 1.33 mmol) at room temperature was added to C₄H₃OCH₂C₉H₅SiMe₃ (**4**) (0.714 g, 2.66 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was stirred at 60 °C for 24 h and the color of the solution changed to orange-red. The solvent was evaporated under reduced pressure. The residue was washed with *n*-hexane (5.0 mL). The resulting solid was extracted with toluene (15.0 mL). The toluene solution was combined and concentrated to about 4.0 mL. The orange-red solid complex was obtained by cooling the concentrated solution at 0 °C (0.589 g, 64%). IR (cm⁻¹): ν 3071 (s), 3011 (w), 2958 (s), 2900 (s), 1590 (s), 1506 (m), 1457 (v), 1382 (v), 1300 (w), 1258 (m), 1176 (m), 1109 (w), 1032 (w), 1010 (m), 928 (w), 884 (m), 845 (s), 772 (m), 720 (s); m.p.: 158–160 °C; Anal. Calc. for C₃₄H₃₈O₂Si₂Eu: C, 59.46; H, 5.58. Found: C, 59.74; H, 5.53%.

4.14. X-ray crystallography

Suitable crystal of complex **9** was mounted in a sealed capillary. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å);

Table 5
Crystal and data collection parameters for **9**

9	
Empirical formula	C ₃₄ H ₄₆ O ₂ Si ₂ Yb
Formula weight	8007.3(9)
Crystal system	Orthorhombic
Space group	<i>Iba</i> 2
<i>a</i> (Å)	19.0767(13)
<i>b</i> (Å)	20.0196(13)
<i>c</i> (Å)	20.9667(14)
<i>V</i> (Å ³)	2655.16(11)
<i>T</i> (K)	293(2)
<i>D</i> _{calc} (g cm ⁻³)	1.188
<i>Z</i>	8
<i>F</i> (000)	2912
Number of reflections collected	9526
Number of unique reflections	4774 (<i>R</i> _{int} = 0.044)
Number of parameters	353
λ , (Å) Mo K α	0.71073
μ (mm ⁻¹)	2.418
θ Range (°)	2.49 to 25.05
Goodness-of-fit	1.193
<i>R</i> (<i>I</i> > 2 σ (<i>I</i>))	0.057
<i>wR</i> ₂	0.118
Absolute structure parameter	-0.01(3)
Largest difference in peak and hole (e Å ⁻³)	0.773 and -0.535

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 (SHELXS-97) [24], completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on *F*² (SHELXS-97) [24]. See Table 5 for crystallographic data.

CCDC reference number 267369 for **9** was deposited.

4.15. ϵ -caprolactone polymerization

ϵ -CL polymerization reactions were performed in a 50.0 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. After the external bath temperature had stabilized, ϵ -CL was added through a gastight syringe. The polymer product was precipitated into hydrochloric acid (0.1 M, 50.0 mL), washed with 0.1 M hydrochloric acid, 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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