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Synthesis, characterization, and catalytic activity of divalent organolanthanide complexes with new tetrahydro-2*H*-pyranyl-functionlized indenyl ligands

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Abstract

Two series of new divalent organolanthanide complexes with the general formula $[\eta^5{:}\eta^1\text{-}\{1\text{-R-3-}(C_5H_9OCH_2)C_9H_5\}]_2Ln^{II}$ (R = H, Ln = Yb (**3**); R = Me_3Si, Ln = Yb (**4**); R = H, Ln = Eu (**5**); R = Me_3Si, Ln = Eu (**6**)) were prepared by reactions of 2 equiv. of 1-R-3-$(C_5H_9OCH_2)C_9H_6$ (R = H (**1**), R = Me_3Si (**2**)) with the lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-Cl})Li(THF)_3$ (Ln = Yb, Eu) via a one-electron reductive elimination process. Recrystallization of **6** from *n*-hexane afforded $[\eta^5{:}\eta^1\text{-}(C_5H_9OCH_2C_9H_5SiMe_3)]_2Eu^{II}\cdot(C_6H_{14})_{0.5}$ (**7**). All compounds were fully characterized by elemental analyses, and spectroscopic methods. The structures of complexes **4** and **7** were additionally determined by single-crystal X-ray analyses. The catalytic activity of the complexes on methyl methacrylate and ε-caprolactone polymerization was studied, and the temperatures, substituents on the indenyl ring, and solvents effects on the catalytic activity of the complexes were examined.

Keywords: Synthesis; Lanthanide complexes; Catalyst; Polymerization

1. Introduction

Organolanthanide chemistry has been a continuous interest to chemists for their potential applications as catalysts for olefins, lactones or lactides polymerization [1–3] or as catalysts in synthetic chemistry [4]. On the other hand, organolanthanide complexes have been found to exhibit a potential application in activation of small molecules such as CO_2 and CO [5], N_2 [6] and organic or inorganic compounds [7].

Recently, we found that interactions of heterocyclic functionalized indene compounds with lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-Cl})Li(THF)_3$ (Ln = Yb, Eu) produced a novel triple-deckered tetranuclear europium(II) complex with linked indenyl ligands [8], and a novel ytterbium(II) complex with indenyl ligand bonded to the metal through benzo ring with η^4 mode [9]. We have reported the synthesis and characterization of organolanthanide(II) complexes with furfuryl- or tetrahydrofurfuryl- or methoxyethyl-functionalized indenyl ligands. Studies have showed that the catalytic activity of these functionalized indenyl lanthanide(II) complexes on methyl methacrylate (MMA) or ε-caprolactone polymerization depended on

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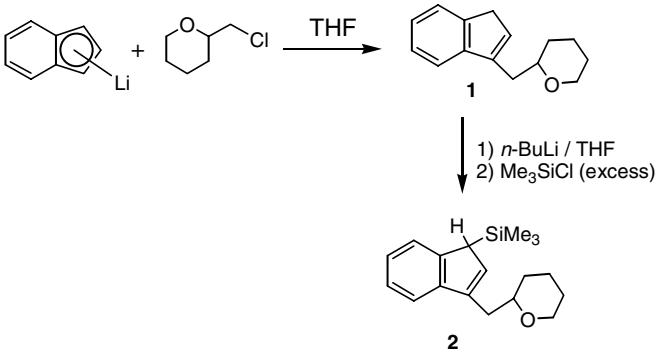
the substituents on the indenyl rings. Complexes having both oxygen containing group and silyl substituent on indenyl ligands can function as single-component ring-opening polymerization of ε-caprolactone catalysts with very high catalytic activities [3e]. Complexes with both methoxyethyl- and silyl substituents on indenyl ligands can function as single component MMA polymerization catalysts with good catalytic activity [3b]. But, complexes without the silyl substituent on the indenyl rings cannot catalyze ε-caprolactone or MMA polymerization under the given conditions. These results promoted us to extend our work to other oxygen-containing group functionalized indenyl ligands to examine the substituent effects on the catalytic activity of lanthanide(II) complexes for ε-caprolactone and MMA polymerization.

In order to study the ligands effects on the reactivity and the catalytic activity of lanthanide complexes, we will report the synthesis and characterization of two series of new divalent organolanthanide complexes having tetrahydro-2*H*-pyranyl functionalized groups on indenyl ligands with the general formula $[\eta^5{:}\eta^1\text{-}\{1\text{-R-3-}(C_5H_9OCH_2)C_9H_5\}]_2Ln^{II}$ (R = H, Me_3Si; Ln = Yb, Eu) prepared by reaction of the corresponding indene compounds with lanthanide(III) amides through a tandem silylamine elimination/homolysis of the Ln–N (Ln = Yb, Eu) bonds in this paper. Their catalytic activities on MMA and ε-caprolactone polymerization were examined, substituents on the indenyl ring, solvents, and temperature effects on catalytic activity of the complexes will be discussed.

2. Results and discussion

2.1. Synthesis of the ligands

The $C_5H_9OCH_2C_9H_7$ (**1**) were prepared in 73% yield by the reaction of lithium indenide with 2-tetrahydropyranylmethyl chloride $C_5H_9OCH_2Cl$ in THF. ^1H NMR analyses showed that the 2-tetrahydro-2*H*-pyranylmethyl group connects to the sp^2 carbon at 3-position of the indenyl ring. Treatment of **1** with 1 equiv. of *n*-BuLi followed by reaction with excess Me_3SiCl produced the $C_5H_9OCH_2C_9H_6SiMe_3$ (**2**) in 96% yield. Compounds **1** and **2** were fully characterized by spectroscopic methods and elemental analyses. The full synthetic procedures were outlined in Scheme 1.

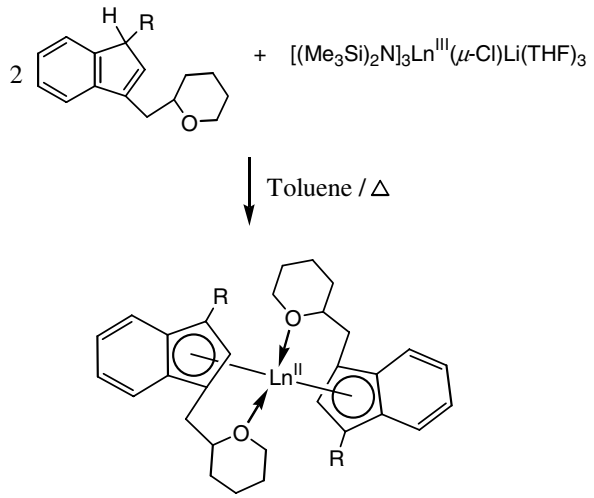


Scheme 1.

2.2. Synthesis and characterization of ytterbium(II) and europium(II) complexes

Treatments of lanthanide(III) amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) with 2 equiv. of 1-R-3-$(C_5H_9OCH_2)C_9H_6$ (R = H (**1**), R = Me_3Si (**2**)) in hot toluene gave, after workup, the lanthanide(II) complexes with general formula $[\eta^5{:}\eta^1\text{-}\{1\text{-R-3-}(C_5H_9OCH_2)C_9H_5\}]_2Ln^{II}$ (R = H, Ln = Yb (**3**); R = Me_3Si, Ln = Yb (**4**); R = H, Ln = Eu (**5**); R = Me_3Si, Ln = Eu (**6**)) in good yield (Scheme 2). Recrystallization of **6** from *n*-hexane gave $[\eta^5{:}\eta^1\text{-}(C_5H_9OCH_2C_9H_5SiMe_3)]_2Eu^{II}\cdot(C_6H_{14})_{0.5}$ (**7**). These complexes are extremely sensitive to air and moisture, but they are stable in inert atmosphere for months. They are soluble in solvents such as THF, DME, and toluene, only slightly soluble in benzene, and *n*-hexane. NMR analyses showed that complexes **3** and **4** behaved a diamagnetic property, indicating that the oxidation state of the central metal in the complexes is +2. However, the NMR spectra analyses of complexes **5**, **6** and **7** failed due to lack of locking signals for the paramagnetic property of the complexes. The elemental analyses data are in good agreement with the proposed formula. In order to get further information about the structures of the complexes, the structures of complexes **4** and **7** were determined by single-crystal X-ray diffraction study.

X-ray analyses revealed that the central lanthanide atoms in complexes **4** (Fig. 1) and **7** (Fig. 2) are coordinated by two indenyl ligands through the five-membered ring in η^5-fashion, and two oxygen atoms of the tetrahydropyranyl ring in η^1-mode. The coordination geometry of the central ytterbium or europium atoms can be described as a distorted tetrahedron. These results suggested the central



R = H, Ln = Yb (**3**), Eu (**5**); R = Me_3Si-, Ln = Yb (**4**), Eu (**6**)

Scheme 2.

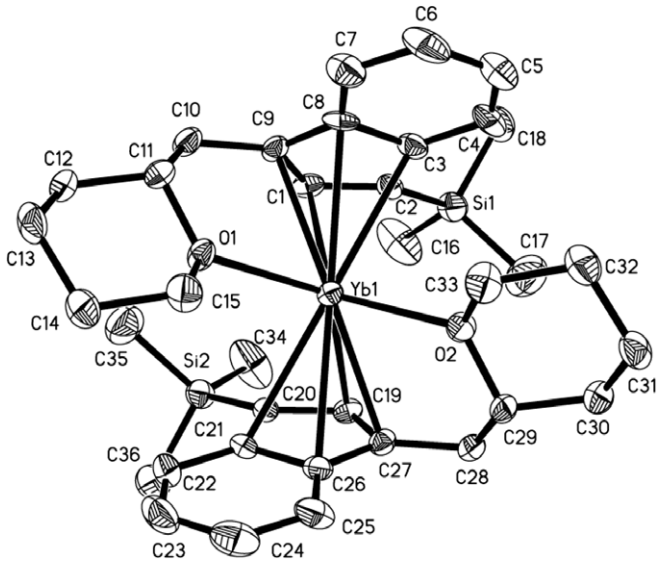


Fig. 1. Molecular structure of complex **4**, hydrogen atoms are omitted for clarity.

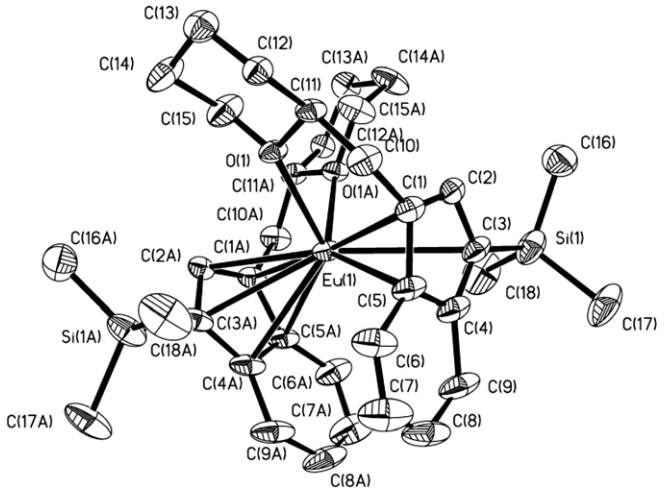


Fig. 2. Molecular structure of complex **7**, hydrogen atoms and solvated *n*-hexane molecule in the unit cell are omitted for clarity.

metals of the complexes are in the oxidation state of +2, indicating that the formation of the complexes goes through a one-electron reductive elimination reaction. This process is in accordance with our previous works [3].

The selected bond distances and angles of the complexes **4** and **7** are given in Table 1. From Table 1, we can see that

Table 1
Selected bond distances (Å) and angles (°) for **4** and **7**

Compound **4**		Compound **7**	
Yb(1)–O(1)	2.433(4)	Eu(1)–O(1)	2.582(6)
Yb(1)–O(2)	2.434(4)	Eu(1)–C(1)	2.768(8)
Yb(1)–C(1)	2.659(6)	Eu(1)–C(2)	2.869(9)
Yb(1)–C(2)	2.790(6)	Eu(1)–C(3)	2.928(11)
Yb(1)–C(3)	2.898(6)	Eu(1)–C(4)	2.887(10)
Yb(1)–C(8)	2.860(6)	Eu(1)–C(5)	2.801(9)
Yb(1)–C(9)	2.696(7)	O(1)–Eu(1)–O(1)#1	89.9(3)
Yb(1)–C(19)	2.633(6)		
Yb(1)–C(20)	2.791(6)		
Yb(1)–C(21)	2.930(6)		
Yb(1)–C(26)	2.879(7)		
Yb(1)–C(27)	2.674(7)		
O(1)–Yb(1)–O(2)	122.77(16)		

the Yb–C distances ranged from 2.659(6) Å to 2.898(6) Å for Yb to one indenyl ring; and from 2.674(7) Å to 2.930(6) Å for Yb to the another indenyl ring, with an average of 2.781(7) Å. This average distance is shorter than the corresponding value of 2.851(9) Å found in **7**, the average Yb–O distance of 2.434(4) Å is shorter than the Eu–O distance of 2.582(6) Å. These differences are mainly due to the lanthanide contraction [10].

For comparison of the substituents effects on the coordination mode and the bonding to the metals, some important structural parameters of the oxygen-containing substituents on the indenyl lanthanide(II) complexes are listed in Table 2. From the table, we can see that the average Yb–C distance in **4** is slightly longer than the corresponding average Yb–C distances of 2.732(15) and 2.752(12) Å found in other indenyl ytterbium(II) complexes $[\eta^5{:}\eta^1\text{-}(C_4H_7OCH_2C_9H_5SiMe_3)]_2Yb$ [3e], $[\eta^5{:}\eta^1\text{-}(CH_3OCH_2CH_2C_9H_5SiMe_3)]_2Yb$ [3b], indicating steric effects on the bonding of the ligands to the metal. However, the Yb–O distance found in **4** is comparable to those of Yb–O distances found in $[\eta^5{:}\eta^1\text{-}(C_4H_7OCH_2C_9H_5SiMe_3)]_2Yb$ [3e], $[\eta^5{:}\eta^1\text{-}(CH_3OCH_2CH_2C_9H_5SiMe_3)]_2Yb$ [3b]. The O–Yb–O angle of 122.77(16)° is significantly larger than the corresponding values found in other indenyl ytterbium(II) europium(II) complexes, suggesting that steric effects have influence on the coordination geometry of the metals. The average Eu–C (2.851(11) Å), Eu–O (2.582(6) Å) distances, and the angle of O–Eu–O (89.9(9)°) found in **7** are comparable to the corresponding Eu–C, Eu–O and the O–Eu–O values found in other substituted indenyl europium(II) complexes $[\eta^5{:}\eta^1\text{-}Me_2Si(CH_3OCH_2CH_2C_9H_5)(NH^tBu)]_2Eu$

Table 2
Comparison of selected geometric parameters in distorted tetrahedral oxygen-containing substituents on indenyl ytterbium(II) and europium(II) complexes

Complex	$(Ln–C)_{av}$ (Å)	$(Ln–O)_{av}$ (Å)	(O–Ln–O) (°)	Reference
4	2.781(6)	2.434(4)	122.77(16)	This work
7	2.851(11)	2.582(6)	89.9(3)	This work
$[\eta^5{:}\eta^1\text{-}(C_4H_7OCH_2C_9H_5SiMe_3)]_2Yb$	2.732(15)	2.427(10)	83.1(4)	[3e]
$[\eta^5{:}\eta^1\text{-}(CH_3OCH_2CH_2C_9H_5SiMe_3)]_2Yb$	2.752(12)	2.448(8)	84.5(3)	[3b]
$[\eta^5{:}\eta^1\text{-}Me_2Si(CH_3OCH_2CH_2C_9H_5)\text{-}(NH^tBu)]_2Eu$	2.858(8)	2.559(6)	88.6(2)	[3b]
$[\eta^5{:}\eta^1\text{-}(CH_3OCH_2CH_2C_9H_5SiMe_3)]_2Eu$	2.853(12)	2.585(8)	88.1(3)	[3b]

[3b], and $[\eta^5:\eta^1\text{-}(CH_3OCH_2CH_2C_9H_5SiMe_3)]_2Eu$ [3b] (Table 2), indicating that steric effects decrease as the ionic radii of the lanthanide metals increase.

2.3. Catalytic activity of the complexes

For there is a continuous interest in developing new organolanthanide(II) complexes as catalysts for olefins and lactones polymerization [1–3], we have examined the catalytic activity of the organolanthanide complexes **3**–**6** as single component catalysts on MMA and ε-caprolactone polymerization. It is found that complexes **3** and **5** cannot catalyze MMA and ε-caprolactone polymerization no matter what solvents and conditions were applied. Complexes **4** and **6** exhibited a moderate to good catalytic activity on MMA polymerization, and a high catalytic activity on ε-caprolactone polymerization, indicating substituents effects on the catalytic activity of the complexes. The results are summarized in Tables 3 and 4.

From Table 3, we can see that complex **6** exhibited a more higher activity than that of complex **4** on MMA polymerization at given conditions. Complex **6** exhibited a high

Table 3
Data for the polymerization of methyl methacrylate (MMA)

Catalyst	Solvent	Temperature (°C)	Stereoregularity			$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Conversion (%)	Activity $\times 10^{-4}$
			mm	mr	rr					
4[a]	Toluene	0	17	23	60	1.42	1.54	1.08	8.5	0.85
	THF	0	18	40	42	1.74	2.33	1.34	8.1	0.81
	THF	−30	17	37	46	2.77	4.97	1.80	19.6	1.97
6[b]	THF	30	22	38	40	1.71	2.17	1.27	63	3.78
	THF	0	9	39	52	2.41	4.22	1.70	100	5.96
	THF	−30	17	33	51	3.17	5.90	1.86	100	5.96
	THF	−60	10	29	61	1.98	3.16	1.59	54	3.24

[a] Time = 30 min, solvent/MMA (v/v) = 5:1, catalyst/MMA (mol/mol) = 1:500, activity: g · polymer/(molCatalyst · h).
[b] Time = 30 min, solvent/monomer (v/v)= 5:1, catalyst/MMA (mol/mol) = 1:300, activity: g · polymer/(molCatalyst · h).

Table 4
Data for the polymerization of ε-caprolactone (ε-CL)

Catalyst	Solvent	Monomer/catalyst (mol/mol)	Temperature (°C)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	Conversion (%)	Activity $\times 10^{-6}$
4	THF	500:1	30	3.46	6.13	1.77	62	4.23
	THF	500:1	0	1.45	1.53	1.06	74	5.04
	THF	500:1	−30	4.16	7.12	1.71	100	7.15
	THF	300:1	30	3.91	6.96	1.78	100	4.08
	THF	300:1	0	4.66	7.74	1.66	98	4.01
	THF	300:1	−30	3.58	6.33	1.77	90	3.73
	THF	300:1	−60	4.17	7.36	1.76	100	4.11
	Toluene	500:1	30	3.51	5.97	1.70	81	5.51
	Toluene	500:1	0	3.05	5.36	1.76	100	7.90
	Toluene	500:1	−30	2.21	3.70	1.67	100	7.90
	Toluene	500:1	−60	2.37	4.09	1.72	15	0.98
	Toluene	300:1	30	2.97	5.46	1.84	100	4.11
	Toluene	300:1	0	1.67	2.21	1.32	100	4.11
	Toluene	300:1	−30	6.05	8.52	1.41	99	4.07
	Toluene	300:1	−60	6.13	8.44	1.38	95	3.92
6	THF	500:1	30	1.40	1.46	1.04	100	7.15
	THF	500:1	0	1.37	1.42	1.03	25	1.79
	THF	500:1	−30	–	–	–	–	–
	THF	500:1	−60	1.77	2.45	1.39	2	0.14
	THF	300:1	30	1.44	1.55	1.07	81	3.33
	THF	300:1	0	1.41	1.48	1.05	70	2.88
	THF	300:1	−30	2.33	3.98	1.71	100	4.11
	THF	300:1	−60	3.69	6.13	1.66	73	3.00
	Toluene	500:1	0	1.64	2.24	1.37	68	4.86
	Toluene	500:1	−30	1.39	1.42	1.02	94	6.72
	Toluene	500:1	−60	2.25	3.93	1.74	100	7.15
	Toluene	300:1	30	1.62	2.23	1.32	92	3.78
	Toluene	300:1	0	1.98	3.16	1.59	100	4.11
	Toluene	300:1	−30	1.40	1.45	1.03	100	4.11
	Toluene	300:1	−60	11.74	12.29	1.05	100	4.11

Conditions: Time = 0.5 min, solvent/ε-CL (v/v) = 5:1, activity: g · Polymer/(molCatalyst · h).

catalytic activity at the temperature range 0 to −30 °C producing the polymers with dominant syndiotacticity with narrow molecular weight distributions ($M_w/M_n = 1.27$–1.86). The content of syndiotacticity of the polymers generally increases as the polymerization temperatures decrease. The co-existence of different tacticity polymers may be due to the *rac*/*meso* interconversion. This interconversion is commonly promoted by the donor solvents such as THF, DME and lithium salt, such conversion has also been observed in the ether-bridged lanthanidocene chlorides [11]. The polymerization mechanism may follow the supposition that initiation with a divalent lanthanidocence complex occurs through reductive dimerization of MMA to form a bis-initiator, comprising two lanthanide(III) enolated joined through their double-bond termini [12]. The fact that the M_w/M_n values are far from unity may be explained by the effect of partial chain termination caused by deactivation of the catalysts with trace amounts of impurities present in the system for the lanthanide(II) complexes and the intermediates formed during the polymerization process are very sensitive to these impurities.

From Table 4, we can see that complexes **4** and **6** generally exhibited a high catalytic activity for ε-caprolactone polymerization (generally $> 10^6$ g · Polymer/(molCatalyst · h)) either in toluene or in THF within a temperature range 30 to −60 °C. Polymers with narrow molecular weight distributions can be obtained when the polymerization reactions were carried out at relatively high temperature in THF, for example, the M_w/M_n values are only 1.03–1.04 when the monomer to catalyst ratio was 500:1 at the temperature range 30–0 °C when catalyst **6** was applied, and the corresponding M_w/M_n values are only 1.05–1.07 when the monomer to catalyst ratio was 300:1 within a temperature range 30–0 °C in the same catalytic system. The narrow molecular weight distributions can also be observed when the polymerization reactions were carried out at relatively low temperature in toluene, for example, the M_w/M_n values are 1.03–1.05 when the monomer to catalyst ratio was 300:1 at the temperature range −30 to −60 °C in case catalyst **6** was used. Change of the catalysts loading generally has only a little influence on the catalytic activity of the catalysts. The high molecular weight polymers (11.74×10^4) can be obtained when the polymerization reactions were carried out in toluene at low temperature.

3. Conclusion

Two series of new divalent organolanthanide complexes having tetrahydro-2*H*-pyranyl functionalized indenyl ligands with the general formula $[\eta^5{:}\eta^1\text{-}\{1\text{-R-}3\text{-}(C_5H_9OCH_2)C_9H_5\}]_2Ln^{II}$ (R = H, Me_3Si; Ln = Yb, Eu) were prepared by reactions of the corresponding indene compounds with the lanthanide(III) amides through a tandem silylamine elimination/homolysis of the Ln–N (Ln = Yb, Eu) bonds. Examination on the catalytic activity of the complexes indicated that complexes having both oxygen-containing six-membered ring and silyl groups functionalized indenyl ligands can function as single-component ring-opening polymerization of ε-caprolactone, and polymerization of MMA catalysts. However, lanthanide(II) complexes without the silyl-substituted group on indenyl rings cannot catalyze MMA or ε-caprolactone polymerization. These results cannot be simply explained by the solubility of the complexes, for the corresponding indenyl lanthanide(II) complexes can be well dissolved in THF. The narrow molecular weight distribution polyesters can be obtained under certain conditions.

4. Experimental

4.1. Materials and methods

All the syntheses and manipulations of air- and moisture-sensitive materials were carried out on the flamed Schlenk-type glassware on a Schlenk line. All solvents were refluxed and distilled over finely divided $LiAlH_4$ or sodium benzophenone ketyl under argon prior to use unless otherwise noted. $CDCl_3$ was dried over activated 4 Å molecular sieves. MMA and ε-caprolactone (ε-CL) were dried over finely divided CaH_2, distilled before use. $[(Me_3Si)_2N]_3\text{-}Ln^{III}(\mu\text{-Cl})Li(THF)_3$ (Ln = Yb, Eu) were prepared according to reported procedures [2g,3a]. Elemental analyses data were obtained on a Vario EL III elemental analyzer. IR spectra were recorded on a R 2200 spectrometer (CsI crystal plate, Nujol and Fluoroble mulls). Melting points were determined in sealed capillaries without corrections. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-300 NMR spectrometer in C_6D_6 (benzene-d_6) for the lanthanide complexes and in $CDCl_3$ for the polymers and the indene compounds. The chemical shifts for ^1H and ^{13}C NMR spectra were recorded to the internal solvent resonances. Gel permeation chromatography (GPC) analyses of polymer samples were carried at 30 °C using THF as an eluent on a Waters-2414 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. The polymers were analyzed according to the literature [13].

4.2. Preparation of $C_5H_9OCH_2C_9H_7$ (*1*)

To a solution of indene (9.3 mL, 80.0 mmol) in 50.0 mL of THF was slowly added a 1.55 M *n*-BuLi solution (51.6 mL, 80.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight and was then cooled to 0 °C. To the reaction mixture was slowly added $C_5H_9OCH_2Cl$ (10.0 g, 102 mmol), the reaction mixture was stirred at room temperature overnight and then hydrolyzed. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2×15.0 mL). The organic fractions were combined and dried over anhydrous $MgSO_4$, filtered, and evaporated under vacuum. The pale yellow oil (12.5 g, 73%) was obtained after distillation

under reduced pressure. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.52 (m, 2H), 7.39 (m, 1H), 7.30 (m, 1H), 6.32 (s, 1H), 4.05 (m, 1H), 4.00 (m, 1H), 3.68 (m, 1H), 3.48 (s, 2H), 2.85 (m, 1H), 2.70 (m, 1H), 1.82 (m, 2H), 1.56 (m, 2H), 1.38 (m, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) 145.6, 144.5, 141.0, 130.1, 126.1, 124.6, 123.8, 119.2, 77.6, 68.7, 38.0, 35.3, 32.1, 26.2, 23.6; IR (Nujol mulls, cm^{-1}): ν 3064 (m), 3017 (m), 2924 (s), 2853 (s), 2874 (s), 1609 (w), 1460 (vs), 1396 (m), 1377 (m), 1261 (m), 1197 (m), 1088 (vs), 1044 (s), 982 (w), 963 (w), 769 (vs), 719 (s). EIMS *m*/*z* (fragment, relative intensity %): 85 ($C_5H_9O^+$, 100%), 115 ($C_9H_7^+$, 2.0%), 128 ($C_9H_6CH_2^+$, 5.98%), 214 ($[M]^+$, 5.28) 215 ($[M+H]^+$, 0.31%); HRMS (EI) $[C_{15}H_{18}O+H]^+$: Calc. 215.1436. Found: 215.1391.

4.3. Preparation of $C_5H_9OCH_2C_9H_6SiMe_3$ (2)

To a solution of $C_5H_9OCH_2C_9H_7$ (**1**) (4.41 g, 20.6 mmol) in 40.0 mL of THF was slowly added a 1.50 M *n*-BuLi solution (13.7 mL, 20.6 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight, and was then cooled to 0 °C. To the mixture was added freshly distilled Me_3SiCl (5.2 mL, 40.12 mmol) in one portion. The reaction temperature was gradually raised to room temperature and stirred at the temperature overnight. The solvents and excess Me_3SiCl 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 (5.66 g, 96%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.45 (m, 2H), 7.28 (m, 1H), 7.20 (m, 1H), 6.41 (s, 1H), 4.03 (m, 1H), 3.62 (m, 1H), 3.46 (m, 1H), 3.43 (s, 1H), 2.88 (m, 1H), 2.72 (m, 1H), 1.81 (m, 2H), 1.60 (m, 2H), 1.37 (m, 2H), −0.04 (s, 9H). IR (Fluoroble mulls, cm^{-1}): ν 3065 (w), 2925 (s), 2853 (s), 2733 (w), 1600 (w), 1458 (s), 1377 (m), 1248 (vs), 1089 (s), 1030 (s), 878 (m), 839 (vs), 763 (s), 734 (w), 614 (w). EIMS *m*/*z* (fragment, relative intensity %): 73 ($SiMe_3^+$, 100%), 85 ($C_5H_9O^+$, 3.07%), 128 ($C_9H_7CH_2^+$, 6.91%), 286 (M^+, 0.32%). HRMS (EI) $[C_{18}H_{26}OSi]^+$. Anal. Calc. 286.1753. Found: 286.1744.

4.4. Preparation of $[\eta^5{:}\eta^1\text{-}(C_5H_9OCH_2C_9H_6)]_2Yb^{II}$ (3)

To a toluene (30.0 mL) solution of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(THF)_3$ (1.02 g, 1.12 mmol) at room temperature was slowly added a toluene (10.0 mL) solution of $C_5H_9OCH_2C_9H_7$ (**1**) (0.48 g, 2.23 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was then refluxed for 24 h. and the color of the solution changed from yellow 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 × 10.0 mL). The toluene solution was combined and concentrated to 10.0 mL to give a purple-red crystalline solid upon standing the solution at −15 °C for several days (0.51 g, 76%). M.p. 252–254 °C. ^{1}H NMR (benzene-d_6): δ (ppm) 7.30–6.93 (m, 10H), 6.04 (s, 2H), 3.85–3.75 (m, 2H), 3.44 (m, 2H), 3.11 (m, 2H), 2.97 (s, 2H), 2.56 (m, 2H), 1.5–1.05 (m, 12H). IR (Nujol mulls, cm^{-1}): ν 3064 (m), 2933 (vs), 2845 (s), 2360 (m), 2342 (m), 1714 (w), 1603 (w), 1558 (w), 1461 (s), 1377 (m), 1261 (m), 1198 (w), 1136 (vs), 1043 (s), 899 (w), 769 (s), 720 (m), 669 (m). Anal. Calc. for $C_{30}H_{34}O_2Yb$: C, 60.09; H, 5.71. Found: C, 60.34; H, 5.63%.

4.5. Preparation of $[\eta^5{:}\eta^1\text{-}(C_5H_9OCH_2C_9H_5SiMe_3)]_2Yb^{II}$ (4)

To a toluene (30.0 mL) solution of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(THF)_3$ (1.07 g, 3.74 mmol) at room temperature was slowly added a toluene (10.0 mL) solution of $C_5H_9OCH_2C_9H_6SiMe_3$ (**2**) (1.71 g, 1.87 mmol). After the reaction was stirred at room temperature for 6 h, the mixture was then heated to 80 °C and the color of the solution changed from yellow to red. The mixture was then stirred at this temperature for 24 h. 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 × 10.0 mL). The toluene solution was combined and concentrated to 5.0 mL. Red crystals were obtained by cooling the concentrated solution at 0 °C for several days (0.93 g, 67%). M.p. 172–174 °C. ^{1}H NMR (benzene-d_6): δ (ppm) 7.70–6.74 (m, 10H), 4.22 (m, 2H), 3.82 (m, 2H), 3.64 (m, 2H), 3.03 (m, 2H), 2.70 (m, 2H), 2.22 (s, 2H), 2.02 (m, 2H), 1.68–1.00 (m, 8H), −0.08 (s, 18H). IR (Nujol molls, cm^{-1}): ν 3065 (w), 2936 (s), 2844 (s), 2359 (m), 2336 (m), 1452 (m), 1377 (w), 1248 (vs), 1196 (w), 1174 (w), 1088 (vs), 1042 (s), 993 (m), 878 (s), 839 (vs), 765 (vs), 736 (m), 697 (w), 614 (w). Anal. Calc. for $C_{36}H_{50}O_2Si_2Yb$: C, 58.09; H, 6.80. Found: C, 58.12; H, 6.77%.

4.6. Preparation of $[\eta^5{:}\eta^1\text{-}(C_5H_9OCH_2C_9H_6)]_2Eu^{II}$ (5)

This compound was prepared as an orange crystalline solid in 65% yield from the reaction of $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-}Cl)Li(THF)_3$ (1.30 g, 1.46 mmol) with $C_5H_9OCH_2C_9H_7$ (**1**) (0.63 g, 2.92 mmol) by employing the procedures similar to those used for the preparation of **3**. M.p. 240–242 °C. IR (Nujol molls, cm^{-1}): ν 3064 (w), 2933 (vs), 2842 (vs), 2360 (s), 2332 (s), 1609 (w), 1461 (s), 1439 (s), 1396 (s), 1262 (vs), 1197 (m), 1173 (w), 1087 (v), 1044 (s), 980 (w), 907 (w) 769 (v), 719 (s). Anal. Calc. for $C_{30}H_{34}O_2Eu$: C, 62.28; H, 5.92. Found: C, 62.04; H, 6.01%.

4.7. Preparation of $[\eta^5{:}\eta^1\text{-}(C_5H_9OCH_2C_9H_5SiMe_3)]_2Eu^{II}$ (6)

This complex was prepared as a yellow crystalline solid in 41% yield from the reaction of $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-}Cl)Li(THF)_3$ (1.10 g, 1.24 mmol) with $C_5H_9OCH_2C_9H_6SiMe_3$ (**2**) (0.71 g, 2.47 mmol) by applying the procedures similar to those used for the preparation of **4**. M.p. 150–152 °C. IR (Nujol molls, cm^{-1}): ν 3065 (w), 2935 (s), 2843 (w), 2360 (v), 2342 (s), 1716 (w), 1601 (w), 1452 (m), 1248 (s), 1088 (s), 1043 (m), 993 (w), 878 (m), 839 (v), 764 (s), 736 (w), 691 (w), 688 (m), 649 (w), 614 (w). Anal.

Calc. for $C_{36}H_{50}O_2Si_2Eu$: C, 59.81; H, 6.97. Found: C, 59.79; H, 7.07%.

4.8. Preparation of $[\eta^5:\eta^1\text{-}(C_5H_9OCH_2C_9H_5SiMe_3)]_2\text{-}Eu^{II}\cdot(C_6H_{14})_{0.5}$ (7)

Recrystallization of **6** from hexane solution gave the europium(II) complex formulated as $[\eta^5:\eta^1\text{-}(C_5H_9OCH_2C_9H_5SiMe_3)]_2Eu^{II}\cdot(C_6H_{14})_{0.5}$ (**7**).

4.9. X-ray crystallography

Suitable crystals of the complexes **4** and **7** were mounted in a sealed capillary. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), temperature 294(2) K, ψ and ω scan technique; SADABS effects and empirical absorption were applied in the data corrections. All structures were solved by direct methods (SHELXS-97), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on F^2 (SHELXS-97). See Table 5 for crystallographic data.

4.10. MMA and ε-CL polymerizations

MMA polymerizations 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. MMA was added through a gastight syringe after the external bath temperature had been stabilized. The polymer product was precipitated into methanol (50.0 mL), washed with methanol, and then dried to a constant weight in a vacuum oven at 50 °C. The stereochemistry of the polymers and their molecular weights were analyzed by ^{1}H NMR spectroscopy and GPC techniques, respectively.

ε-CL polymerizations 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. 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 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.

Table 5
Crystal and data collection parameters for **4** and **7**

Compound	**4**	**7**
Empirical formula	$C_{36}H_{50}O_2Si_2Yb$	$C_{39}H_{57}EuO_2Si_2$
Formula weight	743.98	765.99
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1$	$I(-4)2d$
a (Å)	9.5201(13)	21.2573(10)
b (Å)	21.240(3)	21.2573(10)
c (Å)	9.5386(13)	20.8881(19)
β (°)	114.209(2)	90
V (Å^3)	1759.2(4)	9438.8(11)
T (K)	294(2)	294(2)
D_{calc} (g cm^{-3})	1.405	1.078
Z	2	8
F(000)	760	3184
Number of reflections collected	9971	26392
Number of unique reflections (R_{int})	6926 (0.036)	4839 (0.073)
Number of parameters	375	198
λ (Å) Mo Kα	0.71073	0.71073
μ (mm^{-1})	2.755	1.404
θ Range(°)	1.92–26.38	1.37–26.42
Goodness-of-fit	0.926	1.068
R [$I > 2\ \sigma(I)$]	0.039	0.049
wR_2	0.066	0.125
Absolute structure parameter	−0.015(12)	−0.02(3)
Largest difference in peak and hole (e Å^{-3})	0.805 and −1.007	0.697 and −0.374

5. Supplementary material

CCDC 625772 and 625771 contains the supplementary crystallographic data for **4** and **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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