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Synthesis of 2,6-dialkoxylphenyllanthanoid complexes and their polymerization catalysis[1]

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Abstract

The 1:1–2:1 reaction of $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C_6H_3}]\mathrm{Li}$ with anhydrous $\mathrm{SmCl_3}$ in THF gave $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C_6H_3}]_3$ Sm **1** exclusively, while the 3:1 reaction gave $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C_6H_3}]_4\mathrm{SmLi}$ **2** as major product, which crystallizes in the monoclinic space group $C2/c$(No. 15) with $a = 47.52(1)$ Å, $b = 11.680(9)$ Å, $c = 18.862(9)$ Å, $\beta = 112.19(3)°$, $V = 9694(8)$ Å^3, $Z = 8$, $R = 0.077$ and $R_w = 0.074$. In a similar manner, $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C_6H_3}]_3\mathrm{La}$ was obtained by reacting with $\mathrm{LaCl_3(THF)_2}$. The 2:1 reaction of $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C_6H_3}]\mathrm{Li}$ with $\mathrm{YbCl_3}$ gave $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C_6H_3}]_2\mathrm{YbCl}$, which produces $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C_6H_3}]_2\mathrm{Yb[CH(SiMe_3)_2]_2Li}$ **4** by reaction with $\mathrm{(SiMe_3)_2CHLi}$. Polymerizations of ϵ-caprolactone and alkyl isocyanates were examined using the resulting complexes. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tri(phenyl)samarium; Polymerization catalyst; Methyl methacrylate; ϵ-Caprolactone; Hexyl isocyanate; Butyl isocyanate; Rare earth metal compound

1. Introduction

Reported synthetic pathways to homoleptic lanthanoid aryls of $\mathrm{R_2Ln}$ and $\mathrm{R_3Ln}$ type are not of general utility for the entire lanthanoid series. Thus, the reaction of PhLi with $\mathrm{LnCl_3}$ yields $\mathrm{Ph_3Sc}$ and $\mathrm{Ph_3Y}$, whereas the anionic $\mathrm{(Ph_4Ln)Li}$ complexes were isolated in the case of La and Pr [1]. Chelating (aminotolyl)-lithium reagents allowed the synthesis of σ-aryls $(o\text{-}\mathrm{Me_2NCH_2C_6H_4})_3\mathrm{Ln}$ of Sc, Y, Pr, Yb, and Lu [2–4]. However no characterizable products have been isolated in the case of Pr, Nd, Sm and Tb [3]. Transmetalation reactions of $\mathrm{R_2Hg}$ with metallic lanthanoids have been successfully attempted for preparation of polyfluorophenyl complexes $\mathrm{R_2Ln}$ ($\mathrm{R = C_6F_5}$, $o\text{-}\mathrm{HC_6F_4}$, $p\text{-}\mathrm{HC_6F_4}$; Ln = Sm, Eu, Yb) [5–7] and (benzene)tricarbonylchromium derivatives $\mathrm{[(OC)_3CrPh]_2Ln(THF)}_n$ (Ln = Sm, Eu, Yb; $n = 1–2$) [8]. Diphenylmercury was found to be unreactive toward free Yb [6], while slow interaction was observed with the amalgamated metal [8], and violent reaction has been reported for ytterbium metal activated with $\mathrm{CH_2I_2}$ [9]. Phenylytterbium species are formed in these processes in 35–75% yields and identified in situ by reactions with $\mathrm{H_2O}$, $\mathrm{Ph_3SnCl}$, and 9-fluorenone to be $\mathrm{Ph_2Yb}$ [8,9]. More recently, synthesis of $\mathrm{Ph_3Ln}$ (Ln = Er, Tm) in the presence of catalytic amounts of $\mathrm{LnI_3}$ was reported [10]. (Naphtharene)Yb compound $\mathrm{C_{10}H_8Yb(THF)_2}$ was reported to react readily with $\mathrm{Ph_2Hg}$ to form the binuclear complex $\mathrm{(THF)Ph_2Yb(\mu\text{-}Ph)_3Yb(THF)_3}$ [11]. Among $\mathrm{(aryl)_3Ln}$ compounds, X-ray structural data are available only for $(o\text{-}\mathrm{Me_2NCH_2C_6H_4})_3\mathrm{Lu}$ [11] and the binuclear derivative $\mathrm{(THF)Ph_2Yb(\mu\text{-}Ph)_3Yb(THF)_3}$, consisted of $\mathrm{Ph_2Yb^{II}(THF)}$ and $\mathrm{Ph_3Yb^{III}(THF)_3}$ [11].

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[1] Dedicated to Professor Akira Nakamura on the occasion of his retirement.

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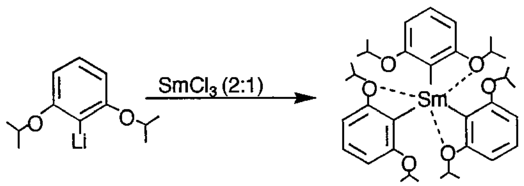

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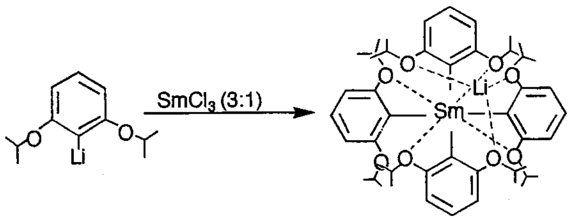
Scheme 1.



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Scheme 2.

The reactions of PhLnI (Ln = Yb, Sm, Eu) with PhFC = CF_2 [12], PhCH = CHC(O)Ph [13], and CF_2 = CF_2 [14] were reported. Fine review articles concerning cyclopentadienyl group-free organolanthanide chemistry should be consulted on the recent development in this area [15]. This paper describes the synthesis of (2,6-dialkoxyphenyl)$_3$Ln (Ln = Sm, La, Y) and (2,6-dialkoxyphenyl)$_4$LnLi by reaction of (2,6-dialkoxyphenyl)lithium with $LnCl_3$ and the polymerization of several monomers using these compounds.

2. Results and discussion

2.1. Synthesis of [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_3$Sm and [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_4$SmLi

The 2:1 or 1:1 reaction of [2,6-(^{i}PrO)$_2$C$_6$H$_3$]Li with anhydrous $SmCl_3$ in THF gave air-sensitive yellow single crystals of [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_3$Sm **1** in 70–80% yield based on [2,6-(^{i}PrO)$_2$C$_6$H$_3$]Li (Scheme 1). Sm^{3+} exhibits intermediate ionic radius (0.96 Å) among the rare earth metal. The resulting compound is insoluble in hexane but soluble in benzene, toluene and THF, revealing the monomeric nature in benzene (observed $M_w = 740$ determined by cryoscopic method in benzene, calc. 729.4). We have failed the X-ray diffraction analysis of this compound, because of the presence of high symmetric structure (X-ray analysis is unsuited for the molecules with very high symmetry). ^{1}H-NMR spectrum of this compound showed the presence of the Me signal of the isopropyl group (a,a′) at 1.47 and 0.86 ppm to indicate that these isopropyl groups are in different environments (Fig. 1). The structure shown in Fig. 1 is the most conceivable. On the other hand, protons at *meta* and *para* position showed a doublet at 5.42 ppm and a triplet at 6.58 ppm, respectively. In

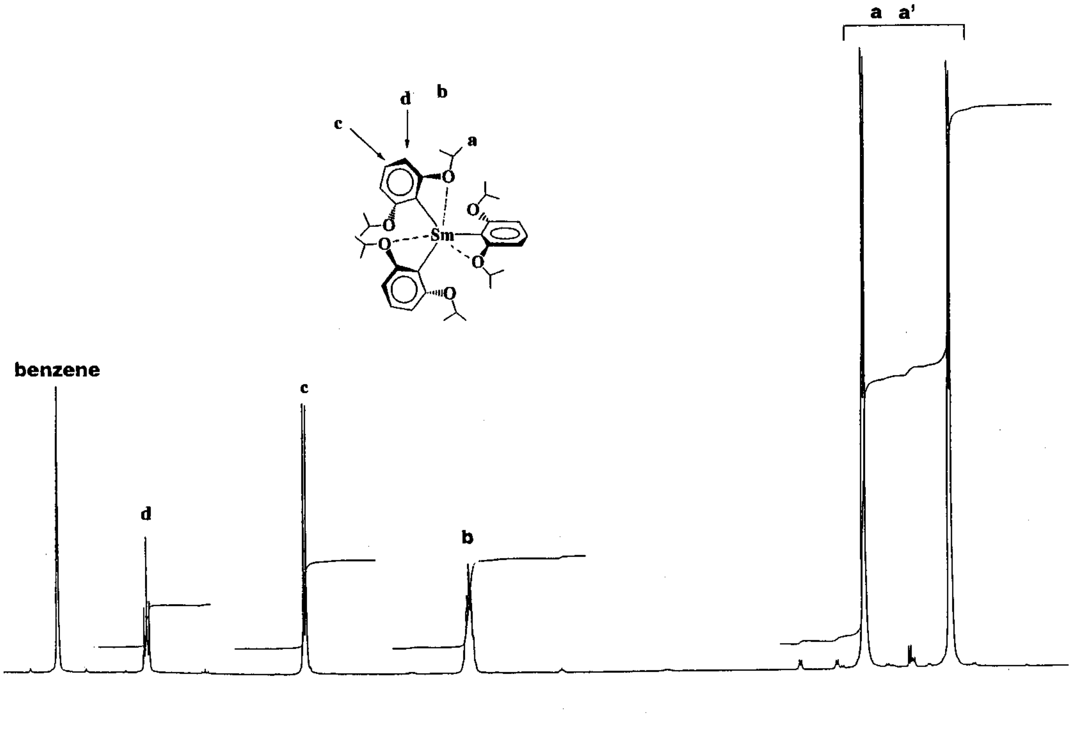


Fig. 1. ^{1}H NMR spectrum of [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_3$Sm **1** in C_6D_6.

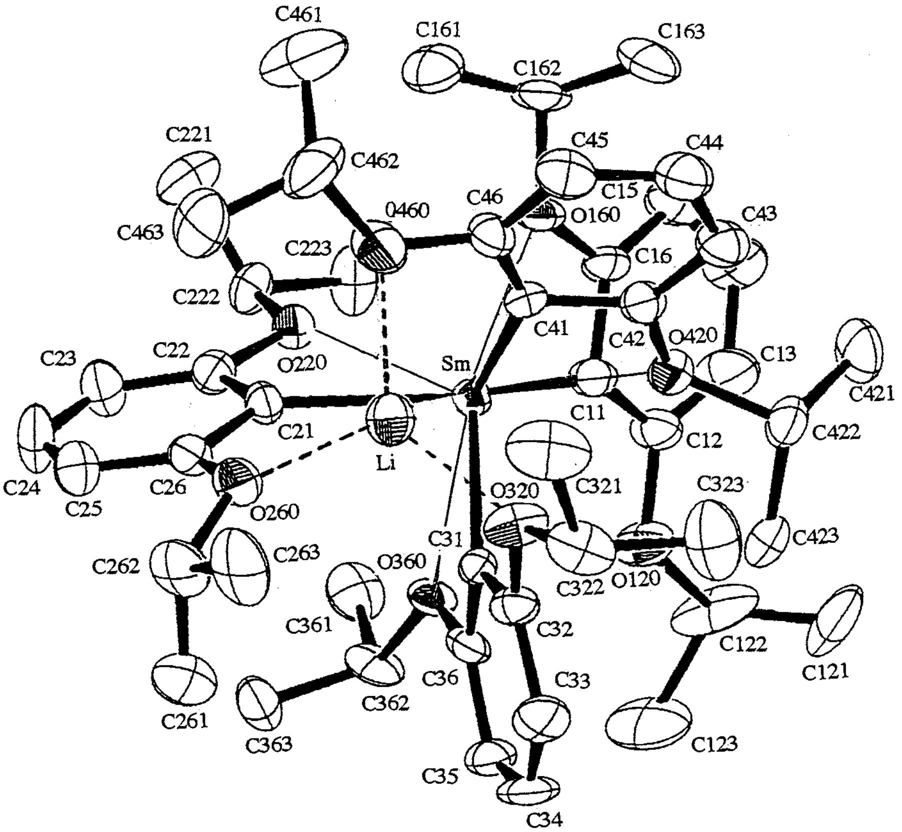


Fig. 2. ORTEP drawing of [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_4$SmLi **2**

order to estimate the strength of the co-ordination of isopropoxy group to the Sm atom, variable temperature NMR spectra were recorded. As a result, two Me groups coalesced at 90°C and a broad singlet peak was observed at 1.67 ppm, at that temperature the isopropoxy groups are magnetically equivalent with each other. When the reaction was carried out in the presence of tetramethylethylenediamine (TMEDA), [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_3$Sm was again obtained without co-ordination of TMEDA. Thus neutral triphenylsamarium was obtained as monomeric form by the assistance of alkoxy ligand. Similar assistance was already reported in the case of the phenyl group bearing the alkylamino assistant group [16,17]. The substitution of alkyl group at positions 2 and 6 by phenyl group is also effective to bring about the formation of monomeric species such as Lu(2,6-Me$_2$C$_6$H$_3$)$_4$Li(THF)$_4$ [18], although no substitution of the phenyl group very often resulted in the formation of oligomeric or polymeric species [19,20]. Exception is the formation of monomeric PhGdCl$_2$(THF)$_4$ [21]. The compound **1** is inert to hydrogen, phenylacetylene, (SiMe$_3$)$_2$NH in toluene and even to (SiMe$_3$)$_2$CHLi dissolved in toluene.

When excess of [2,6-(^{i}PrO)$_2$C$_6$H$_3$]Li was added to SmCl$_3$ (3:1–4:1), an ate complex [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_4$SmLi **2** was obtained exclusively as air-sensitive pale-yellow crystals (Scheme 2). The crystal structure was finally determined by X-ray diffraction studies and its ORTEP drawing is illustrated in Fig. 2. The Sm molecule is 9-coordinated with four bidentate isopropoxyphenyl ligands and one Li atom. Three isopropoxy groups are co-ordinated to the Li atom and this left one isopropoxy group, which is free from co-ordination.

The crystal data and experimental factors for compound **2** is shown in Table 1. The selected bond distances and angles are listed in Table 2. The C(11)–Sm–C(21) angle (141.4°) is wider than 129.7–115.5° observed for Cp(centroid)–Sm–I angle of [(C$_5$Me$_5$)$_2$Sm(μ-I)(THF)$_2$]$_2$ [22] and 104.5° observed for O(1)–Sm–Cp(centroid) in (C$_5$Me$_5$)$_2$SmMe(THF) [23] while the angles of C(21)–Sm–C(31), C(21)–Sm–C(41) and C(31)–Sm–C(41) are narrower than these angles. The observed Sm-phenyl distance is longer than 2.511 Å in (C$_5$Me$_5$)$_2$SmPh [24]. The Sm–O(160) and Sm–O(220) distances are nearly equal to the Sm–O distance (2.62–2.64 Å) of (C$_5$Me$_5$)$_2$Sm(THF)$_2$ [22] but Sm–O(360) and Sm–O(420) distances are shorter than those of (C$_5$Me$_5$)$_2$Sm(THF)$_2$. However, these values are apparently longer than Sm–O distance (2.473 Å) in

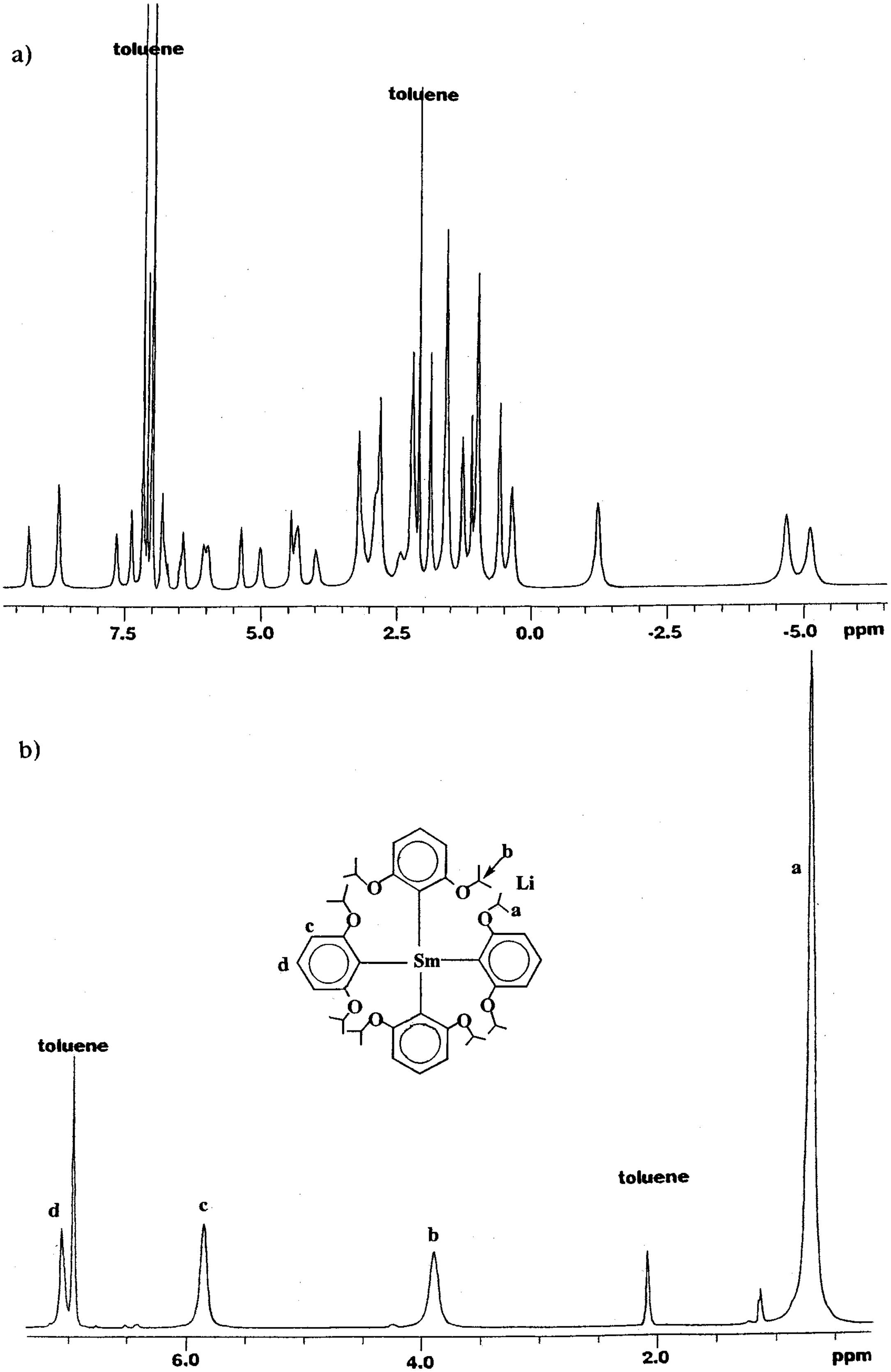


Fig. 3. ^{1}H-NMR spectrum of [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_4$SmLi **2** in C$_6$D$_5$CD$_3$, (a) −78°C and (b) 90°C.

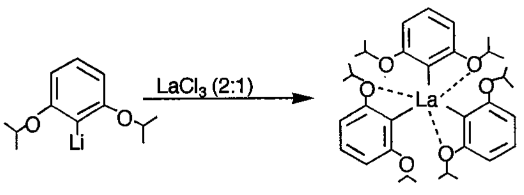
Table 1
Crystal data and experimental factoris for $[2,6\text{-}(^iPrO)_2C_6H_3]_4SmLi$ **2**

Experimental formula	$C_{48}H_{68}O_8SmLi$
Formula weight	930.4
Crystal color	Colorless
Space group	$C2/c$ (# 15)
Temperature	23°C
a (Å)	47.52(1)
b (Å)	11.680(9)
c (Å)	18.862(9)
β (°)	112.19
V (Å^3)	9694(8)
Z	8
$D_{calc.}$ (g cm^{-3})	1.450
F(000)	3880
(MoK$_\alpha$) (cm^{-1})	12.62
Crystal dimension	$03 \times 0.25 \times 0.20$ mm
2θ range (°)	$3 < 2\theta < 55$
Scan width 2θ	$1.37 + 0.35 \tan \theta$
Scan speed (° min^{-1})	10.0
Back ground(s)	5 = 0.07sured 11911
Reflection observed	6296
Radiation damage	No
Number of variables	523
GOF	4.91
R	0.077
R_w	0.074

$(C_5Me_5)_2SmMe(THF)$ [23]. Therefore, co-ordination strength of isopropoxy group in the present compound seems weaker than that in $(C_5Me_5)_2SmMe(THF)$. To evaluate this nature, variable temperature NMR spectra were recorded. At −90°C, ^1H NMR spectrum shows very complicated spectrum, while simple spectrum was observed at 100°C to indicate that all the isopropoxy groups are equivalent because of the cleavage of their co-ordination to the Sm atom (Me 1.72 ppm, CH 3.95 ppm, m-C_6H_3 5.92 ppm, p-C_6H_3 7.12 ppm) (Fig. 3).

2.2. Synthesis of $[2,6\text{-}(^iPrO)_2C_6H_3]_3La$

The La atom exhibits the largest ionic radius (1.03 Å) among the rare earth metals. Therefore, higher catalytic activity is expected to the corresponding trivalent compound. The 2:1 reaction of $[2,6\text{-}(^iPrO)_2C_6H_3]Li$ with $LaCl_3(THF)_2$ gave colorless crystals of $[2,6\text{-}(^iPrO)_2C_6H_3]_3La$ **3** in high yield (Scheme 3), whose NMR spectrum is quite the same as that of $[2,6\text{-}(^iPrO)_2C_6H_3]_3Sm$ (Me, d 0.74 ppm; Me, d 1.72 ppm, CH, sept 4.3 ppm; m-C_6H_3, d 6.35 ppm; p-C_6H_3, t 6.95 ppm). This compound shows monomeric structure as revealed by measurement of molecular weight. However, the present compound was found to be inert toward the polymerization of methyl methacrylate.



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Scheme 3.

2.3. Synthesis of $[2,6\text{-}(^iPrO)_2C_6H_3]_2Yb[CH(SiMe_3)_2]_2Li$

Among the heavy rare earth metals, the element Yb was selected because its ionic radius is very small (0.87 Å). The 2:1 reaction of $[2,6\text{-}(^iPrO)_2C_6H_3]Li$ with $YbCl_3$ in THF gave polymeric species as orange powder, presumably $\{[2,6\text{-}(^iPrO)_2C_6H_3]_2YbCl\}_n$ (Scheme 4). The resulting compound is soluble in toluene and showed paramagnetic nature as revealed by NMR studies. When $(Me_3Si)_2CHLi$ was added to this compound, vigorous reaction takes place to give a red solution. After the recrystallization in toluene/hexane, single crystal of ate complex, $[2,6\text{-}(^iPrO)_2C_6H_3]_2Yb[CH(SiMe_3)_2]_2Li$ **4**, was obtained in high yield. Compound **4** exhibits a monomeric nature as evidenced by the molecular weight measurement. The presence of the Li atom is clarified by the titration with aq. HCl (observed 0.97 eq., calc. 1.0). ^1H NMR spectrum of **4** is shown in Fig. 4. The 2H protons which were ascribed to p, m-phenyl group were observed at 17.28, 19.98, 24.59, 46.35 and 54.19 ppm. The 6H(doublet) protons for Me groups were observed at 5.77, 16.44, 22.33, and 36.92 ppm, to indicate that rotation around the ligand is restricted in the observed temperature (25°C).

Table 2
Selected bond distances (Å) and angles (°) of compound **2**

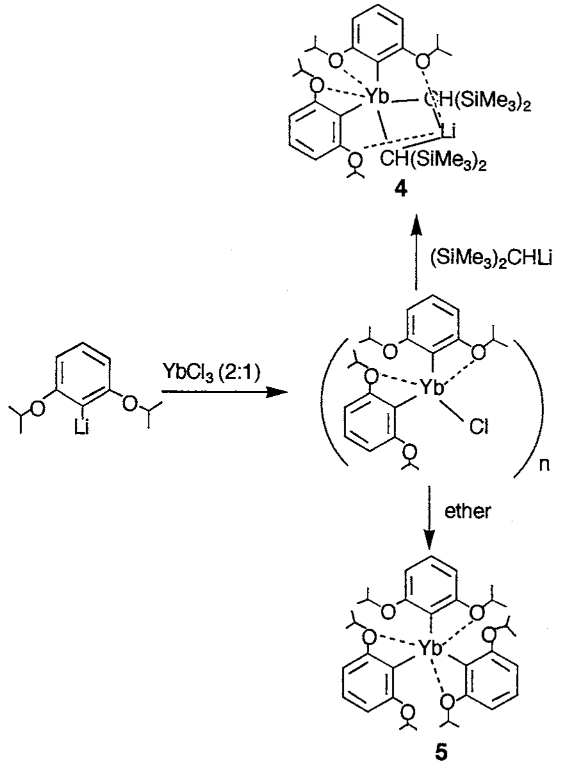
Sm–Li	3.01(4)	Sm–C(11)	2.58(2)	Sm–0(160)	2.61(1)
Li–0(260)	1.97(4)	Sm–C(21)	2.62(2)	Sm–0(220)	2.67(1)
Li–0(320)	2.22(4)	Sm–C(31)	2.60(2)	Sm–0(360)	2.57(1)
Li–0(460)	2.26(4)	Sm–C(41)	2.60(2)	Sm–0(420)	2.59(1)
C(11)–Sm–C(21)		141.4(6)	C(21)–Sm–C(31)		80.1(6)
C(11)–Sm–C(31)		124.1(6)	C(21)–Sm–C(41)		90.3(6)
C(11)–Sm–C(41)		120.5(6)	C(31)–Sm–C(41)		81.1(6)

When the compound $[2,6\text{-}(^{i}PrO)_2C_6H_3]_2YbCl$ was kept in ether at room temperature for two or three weeks, a disproportionation reaction occurred to precipitate $[2,6\text{-}(^{i}PrO)_2C_6H_3]_3Yb$ **5** in ca 45% yield. ^1H NMR spectrum of **5** shows the same pattern as that of **1** (Me −4.88, 15.38 ppm, CH 18.03 ppm, *p*- and *m*-C_6H_3 19.36, 20.92 ppm) although chemical shift values are different due to its paramagnetic nature.

2.4. Synthesis of $[2,6\text{-}(cyclo\text{-}C_6H_{11}\text{-}O)_2C_6H_3]_3Sm$

Introduction of the bulky alkoxy group may result in the enhanced stability of the compound and 1,3-bis(cyclohexyloxy)phenyl ligand was synthesized as mentioned in Section 3. After treating it with *n*-BuLi, the resulting $2,6\text{-}(cyclo\text{-}C_6H_{11}O)_2C_6H_3Li$ was reacted with anhydrous $SmCl_3$ in 2:1 ratio to give $[2,6\text{-}(cyclo\text{-}C_6H_{11}O)_2C_6H_3]_3Sm$ **6**, as yellow crystals exclusively without formation of $[2,6\text{-}(cyclo\text{-}C_6H_{11}O)_2C_6H_3]_2SmCl$ (Scheme 5). The compound **6** is monomeric as evidenced by the molecular weight measurement. ^1H NMR spectrum of **6** is shown in Fig. 5. The signal of *m*- and *p*-C_6H_3 groups were observed at 5.63 and 6.62 ppm, respectively. No co-ordination of solvent was observed, even when the compound was dissolved in THF.

Thus $[2,6\text{-}(cyclo\text{-}C_6H_{11}\text{-}O)_2C_6H_3]_2SmCl$ formed as transient intermediate was more reactive than $SmCl_3$. Thus, we have failed the synthesis of $[2,6\text{-}(cyclo\text{-}C_6H_{11}O)_2C_6H_3]_2SmCl$, despite the introduction of bulky group.



Scheme 4.

2.5. Polymerization behavior of ϵ-caprolactone and alkyl isocyanates

Among the organolanthanide compounds synthesized in this paper, we have explored the catalytic action of **1**, **2** and **5** toward the polymerization of ϵ-caprolactone, alkyl isocyanates and methyl methacrylate. The polymerizations of alkyl isocynates and ϵ-caprolactone by **1** is given in Table 3. Polymerization of *n*-hexyl isocyanate could be performed at temperatures higher than 0°C as was observed in the case of $TiCl_3(CH_2CF_3)$ which gave very narrow molecular weight distribution at room temperature ($M_w/M_n = 1.1\text{–}1.3$) [25], while most organolanthanides such as $Ln(O\text{–}^{i}Pr)_3$ show good catalytic activity only at lower temperature ($< 40°C$) to give high molecular weight ($M_n > 10^6$) poly(hexyl isocyanate) with M_w/M_n of 2.08–3.16 [26]. Hexyl isocyanate was converted to cyclic trimer when the reaction was carried out at room temperature. The polymerization of ϵ-caprolactone proceeded smoothly to give high molecular weight polymers with relatively low polydispersity. On the other hand, this complex conducted no polymerization of methyl methacrylate and styrene. The complex **2** serves as good initiator for the polymerization of ϵ-caprolactone and produced poly(ϵ-caprolactone) quantitatively within 3 h under the mild conditions (25°C) (Table 4). Polymerization of methyl methacrylate also proceeds by **2**, but the resulting yield and stereospecificity is very low. Polymerization of ϵ-caprolactone is also conducted by **5**. The polymer was obtained quantitatively at 0°C ($M_n = 5.2 \times 10^4$, $M_w/M_n = 1.43$). Polymerization of *n*-hexyl isocyanate occurs at 0°C, but the yield is rather low due to the contamination by cyclic trimers. Thus, the compounds **1**, **2** and **5** are effective for the polymerization of ϵ-caprolactone.

3. Experimental section

3.1. General

All manipulations were carried out by using a standard Schlenk technique under an argon atmosphere. Toluene and THF were dried over calcium hydride, then over sodium benzophenone ketyl and distilled before use. NMR spectra were recorded on a JEOL JNM-LA400 and Bruker AM-X400wb instruments. Chemical shifts were calibrated using benzene (7.2 ppm), chloroform (7.26 ppm) and toluene (2.09 ppm).

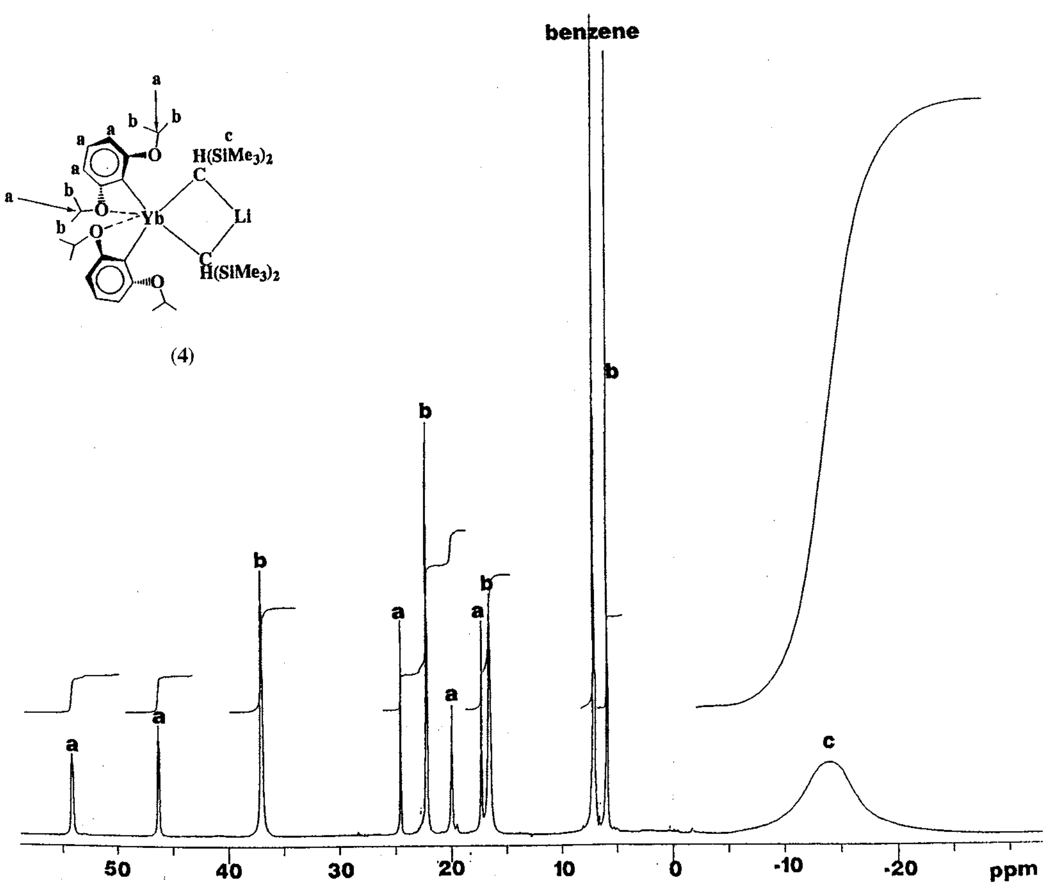
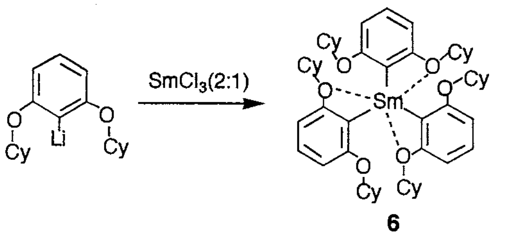


Fig. 4. ^{1}H NMR spectrum of [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_2$Yb[CH(SiMe$_3$)$_2$]$_2$Li **4** in C$_6$D$_6$.

The X-ray diffraction data were collected on a Rigaku AFCSR diffractometer using a suitable crystal sealed in a thin-walled glass capillary tube under argon. Number-average molecular weights and molecular weight distributions of the resulting polymers were determined by gel-permeation chromatography on a Tosoh SC- 8010 high speed liquid chromatograph equipped with a differential refractometer using columns TSK gel G1000, G2000, G3000 and G4000 in CHCl$_3$ at 40°C. The molecular weights of polymers were determined with calibration curves obtained using standard polystyrene.



Scheme 5.

3.2. Synthesis of SmCl$_3$ and LaCl$_3$(THF)$_2$

A mixture of Sm$_2$O$_3$ (10 g, 28.7 mmol), NH$_4$Cl (10 g, 186 mmol) and 150 ml of 12N aq. HCl were placed in a 500 ml round flask, fitted with a reflux condenser. The suspension was refluxed for 5 h and the color of the solution turned from yellow to gray. Removal of the solvent by flash distillation resulted in a white solid. Sublimation (360°C, 30 h) of the solid to remove the excess NH$_4$Cl gave anhydrous SmCl$_3$ (13.86 g, 27 mmol) in 94% yield as residue.

Suspension of 1.0 g (7.20 mmol) of powdered La metal and 3.0 g (12.7 mmol) of C$_2$Cl$_6$ in 40 ml of THF were treated in an ultrasonic bath at room temperature until all the metal powder disappeared, after ca. 5 h. Hexane (20 ml) was added to the resulting white suspension and the liquid was decanted from the white precipitate, which was then washed with hexane several times. Drying the white solid in vacuo for 1 h resulted in LaCl$_3$(THF)$_2$ (2.24 g, 5.76 mmol) in 80% yield.

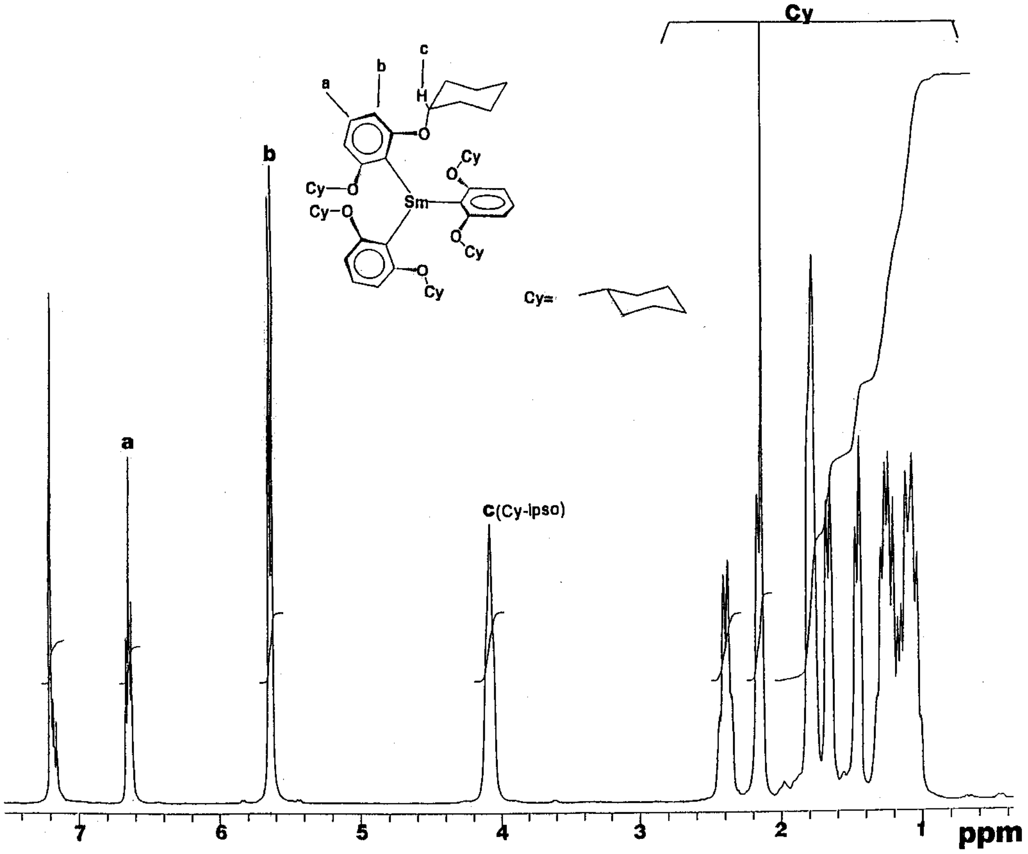


Fig. 5. ^{1}H NMR spectrum of [2,6-(cyclo-$C_6H_{11}O)_2C_6H_3]_3$Sm **5** in C_6D_6.

3.3. Synthesis of [2,6-(^{i}PrO)$_2$C$_6$H$_3$]$_3$Sm *1*

Resorcinol (5.1 g, 46.3 mmol), ^{i}Pr–Br (17 ml, 181 mmol), K_2CO_3 (25 g, 181 mmol) and 100 ml of DMF were placed in a 500 ml round bottomed flask fitted with a reflux condensor. The suspension was refluxed for at least 4h. After completion of the reaction, water (100 ml) and hexane (100 ml) were added to the reaction mixture and the organic layer was extracted using two portions of hexane (40 ml each). The combined organic solution was washed three times with 50 ml of NaOH aq. solution (1N) to remove unreacted resorcinol. Removal of the solvent by flash distillation yielded 7.3 g (37.6 mmol, 81%) of 1,3-(^{i}PrO)$_2C_6H_4$ as a pale-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.32 (d, 12H, $J = 6.2$ Hz), 4.52 (sept, 2H, $J = 6.2$ Hz), 6.45 (m,

Table 3
Polymerizations of isocyanates and ϵ-caprolactone with [2,6-(^{i}PrO)$_2C_6H_5]_3$Sm **1**

Monomer	Catalyst concentration (mol %)	Polymerization time (h)	Temperature (°C)	Yield (%)	M_n ($\times 10^4$)	M_w/ M_n
n-HexNCO	0.5[a]	24	0	0	—	—
	0.5[a]	24	25	19	74.6	2.50
	1.0[a]	24	25	32	59.0	2.28
	0.5[b]	24	0	0	—	—
	0.5[b]	24	25	0	—	—
	0.5[c]	24	25	2	9.18	8.14
n-BuNCO	0.75[d]	24	25	15	41.0	3.47
	0.75[d]	48	25	15	37.8	2.69
Caprolactone	0.5	18	−78	0		
	0.5	6	25	100	7.87	1.56

[a] Toluene 0.5 ml, initiator 0.04 mmol.
[b] THF 0.5 ml, initiator 0.04 mmol.
[c] No solvent.
[d] Toluene 0.6 ml, initiator 0.065 mmol.

Table 4
Polymerizations of caprolactone and methyl methacrylate with $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_5]_4\mathrm{SmLi}$ **2**[a]

Monomer	Catalyst concentration (mol%)	Polymerization time (h)	Temperature (°C)	Yield (%)	M_n ($\times 10^4$)	M_w/M_n
Caprolactone	0.25	3	25	84	2.9	1.53
	0.1	3	25	100	8.9	2.07
Methyl	0.4	19	0	3	1.44	3.06
Methacrylate	0.8	19	25	8	0.78	3.67
	0.8	19	50	9	0.77	4.89

[a] Toluene 10 ml, initiator 0.04 mmol.

3H), 7.14 (t, 1H). A hexane solution of *n*-BuLi (1.65 M, 8.5 ml, 14 mmol) was syringed into a solution of $1,3\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_4$ (2.7 g, 14 mmol) in THF (30 ml) at 0°C. After stirring the mixture for 3 h, it was allowed to warm to room temperature to generate $2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3\mathrm{Li}$. To a stirred suspension of SmCl_3 (4.9 g, 15.6 mmol) in THF (70 ml), $2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3\mathrm{Li}$ (30.5 ml) was added. Stirring was continued further for 30 h. The solvent was evaporated in vacuo and the residual pale orange solid was dissolved in toluene (100 ml). After the removal of LiCl by decantation, the solution was evaporated to dryness. Recrystallization of the residual powder from THF/hexane (1:1) yielded the desired $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3]_3\mathrm{Sm}$ (4.8 g, 6.6 mmol, 65%) as yellow crystals. ^{1}H NMR (CDCl_3, 400 MHz): δ 0.86 (d, 18H, $J = 6.2$ Hz), 1.47 (d, 18H, $J = 6.2$ Hz), 4.27 (sept 6H, $J = 6.2$ Hz), 5.42 (d, 6H, $J = 8.0$ Hz), 6.57 (t, 6H, $J = 8.0$ Hz).

3.4. Synthesis of$[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3]_4\mathrm{SmLi}$ **2**

At room temperature, a solution of $2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3\mathrm{Li}$ (24.7 mmol) dissolved in THF (50 ml) was added to a stirred suspension of SmCl_3 (2.07 g, 8.06 mmol) in THF (60 ml). Stirring was continued for 10 h and the solution was evaporated to dryness. The residual pale orange solid was dissolved in hexane (100 ml) and, after the removal of LiCl by decantation, THF (15 ml) was added to the hexane solution to induce the colorless crystals of $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3]_4\mathrm{SmLi}$ (2.9 g, 2.74 mmol, 45%) at −25°C. ^{1}H NMR ($\mathrm{C}_6\mathrm{D}_5\mathrm{CD}_3$, 400 MHz, 100°C): δ 0.71 (bs, 48H), 3.90 (bs, 8H), 5.86 (bs, 8H), 7.06 (bs, 4H).

3.5. Synthesis of $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3]_3\mathrm{YD}$ **3**

At room temperature, some $2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3\mathrm{Li}$ (24.7 mmol) was added to a stirred suspension of LaCl_3 (2.2 g, 5.7 mmol) in THF (30 ml). Stirring was continued for 10 h.

The solvent was then evaporated in vacuo and the residual pale orange solid was dissolved in toluene (100 ml). After the removal of LiCl by decantation, the solution was evaporated to dryness to give orange powder. Recrystallization of the residual powder from ether at room temperature yielded the desired $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3]_3\mathrm{La}$ (1.7 g, 2.4 mmol, 65% yield) as white crystals. ^{1}H NMR ($\mathrm{C}_6\mathrm{D}_6$, 400 MHz, 25°C): δ 0.76(α, 18H), 1.67(α, 18H), 4.41(sep. 6H), 6.37(bs, 6H), 6.98(A, 3H). Molecular weight was determined cryoscopically in benzene; calc. 717.9, observed 723, for monomeric species.

3.6. Synthesis of $[2,6\text{-}(^i\mathrm{PrO})\,_2\mathrm{C}_6\mathrm{H}_3]_2\mathrm{Yb}[\mathrm{CH}(\mathrm{SiMe}_3)_2]_2\mathrm{Li}$ **4**

A solution of $2,6\text{-}(^i\mathrm{Pr0})_2\mathrm{C}_6\mathrm{H}_3\mathrm{Li}$ (12.9 mmol) dissolved in THF (40 ml) was added at room temperature, to a stirred suspension of YbCl_3 (1.9 g, 6.8 mmol) in THF (40 ml). After stirring overnight, the solution was evaporated in vacuo and the residue was dissolved in

Table 5
Polymerization of caprolactone and hexyl isocyanate with $[2,6\text{-}(^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_5]_2\mathrm{Yb}[\mathrm{CH}(\mathrm{SiMe}_3)_2]_2\mathrm{Li}$ **4**[a]

Monomer	Catalyst concentration (mol%)	Polymerization time (h)	Temperature (°C)	Yield (%)	M_n ($\times 10^4$)	M_w/M_n
Caprolactone	0.3	−78	17	23	40	4.93
	0.3	0	4	100	4.8	1.53
	0.3	25	4	100	4.2	1.57
n-HexNCO	0.5	−78	13	0		
	0.5	0	13	18	5.5	13.8

[a] Toluene 5 ml, imitator 0.04 mmol.

Table 6
Final atomic co-ordinates and equivalent isotropic temperature factors for non-hydrogen atoms in $[2,6\text{-}({}^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3]_4\mathrm{SmLi}$ **2**

Atom	x	y	z	B_{eq} (Å^2)
Sm	0.11138(2)	0.27104(8)	0.64969(5)	2.69(2)
O(120)	0.0472(3)	0.086(1)	0.4777(9)	4.8(4)
O(160)	0.0768(3)	0.447(1)	0.5891(8)	3.8(3)
O(220)	0.0811(3)	0.301(1)	0.7425(7)	3.3(3)
O(260)	0.1848(3)	0.212(1)	0.8546(7)	4.4(3)
O(320)	0.2024(3)	0.214(1)	0.6897(9)	4.7(4)
O(360)	0.1087(3)	0.052(1)	0.6595(8)	3.7(3)
O(420)	0.1277(3)	0.335(1)	0.5396(7)	3.7(3)
O(460)	0.1852(4)	0.478(1)	0.7806(9)	5.9(4)
C(11)	0.0611(4)	0.267(2)	0.532(1)	3.6(4)
C(12)	0.0405(5)	0.204(2)	0.472(1)	3.9(5)
C(13)	0.0162(6)	0.253(2)	0.412(1)	6.2(7)
C(14)	0.0117(6)	0.367(2)	0.411(1)	6.4(7)
C(15)	0.0313(6)	0.439(2)	0.468(1)	5.2(6)
C(16)	0.0555(5)	0.385(2)	0.527(1)	3.7(5)
C(21)	0.1326(4)	0.257(2)	0.7994(9)	3.1(4)
C(22)	0.1054(4)	0.261(2)	0.810(1)	3.5(4)
C(23)	0.1009(6)	0.227(2)	0.875(1)	5.1(5)
C(24)	0.1263(6)	0.188(3)	0.935(1)	6.0(7)
C(25)	0.1540(6)	0.182(2)	0.930(1)	5.1(6)
C(26)	0.1572(5)	0.213(2)	0.863(1)	3.8(5)
C(31)	0.1558(5)	0.128(2)	0.672(1)	3.0(4)
C(32)	0.1847(4)	0.115(2)	0.670(1)	3.6(4)
C(33)	0.1947(5)	0.007(2)	0.655(1)	5.1(6)
C(34)	0.1752(6)	−0.087(2)	0.0642(1)	5.3(6)
C(35)	0.1469(5)	−0.078(2)	0.644(1)	4.1(5)
C(36)	0.1384(5)	0.036(2)	0.658(1)	3.3(4)
C(41)	0.1538(5)	0.416(2)	0.658(1)	3.3(4)
C(42)	0.1476(5)	0.422(2)	0.579(1)	3.4(4)
C(43)	0.1593(5)	0.503(2)	0.544(1)	4.5(6)
C(44)	0.1788(6)	0.584(2)	0.589(2)	5.5(7)
C(45)	0.1875(5)	0.580(2)	0.668(1)	4.9(6)
C(46)	0.1752(5)	0.497(2)	0.702(1)	3.9(5)
C(121)	0.0392(8)	0.020(3)	0.349(2)	9.2(10)
C(122)	0.0309(6)	0.010(2)	0.415(2)	7.6(8)
C(123)	0.0372(8)	−0.109(2)	0.453(2)	9.2(10)
C(161)	0.0923(6)	0.600(2)	0.678(2)	6.1(7)
C(162)	0.0750(6)	0.571(2)	0.595(1)	4.8(6)
C(163)	0.0880(7)	0.632(2)	0.542(2)	6.6(8)
C(221)	0.0497(6)	0.418(2)	0.792(2)	6.1(7)
C(222)	0.0513(5)	0.313(2)	0.746(1)	4.0(5)
C(223)	0.0280(4)	0.313(2)	0.66411)	5.1(6)
C(261)	0.1986(7)	0.009(2)	0.885(2)	7.4(9)
C(262)	0.2081(6)	0.132(2)	0.904(1)	5.7(7)
C(263)	0.2372(6)	0.163(3)	0.891(2)	8.3(8)
C(321)	0.2463(6)	0.330(2)	0.710(2)	7.8(9)
C(322)	0.2289(5)	0.221(2)	0.669(2)	5.7(6)
C(323)	0.2186(7)	0.234(3)	0.580(2)	8.4(9)
C(361)	0.0616(6)	0.009(2)	0.669(1)	5.6(6)
C(362)	0.0922(5)	−0.039(2)	0.679(1)	4.3(5)
C(363)	0.1085(7)	−0.080(2)	0.760(1)	6.3(7)
C(424)	0.1012(6)	0.358(3)	0.402(1)	6.4(7)
C(425)	0.1270(5)	0.296(2)	0.465(1)	4.2(6)
C(426)	0.1225(6)	0.165(2)	0.465(1)	5.7(7)
C(461)	0.1761(8)	0.659(3)	0.831(2)	10(1)
C(462)	0.1966(8)	0.564(3)	0.836(2)	7.5(9)
C(463)	0.2088(8)	0.504(3)	0.914(2)	9.5(10)
Li	0.1770(8)	0.289(3)	0.756(2)	4.6(8)

toluene (100 ml). After the removal of LiC1 by decantation, toluene was evaporated in vacuo to give orange residue, which was then washed with hexane (30 ml × 3) to remove $[2,6\text{-}({}^i\mathrm{PrO})_2\mathrm{C}_6\mathrm{H}_3]_4\mathrm{YbLi}$. Drying of orange solid in vacuo for 1 h afforded orange powder of $[2,6({}^i\mathrm{Pr0})_2\mathrm{C}_6\mathrm{H}_3]_2\mathrm{YbCl}$. To a solution of $[2,6\text{-}({}^i\mathrm{Pr0})_2\mathrm{C}_6\mathrm{H}_3]_2\mathrm{YbC1}$ (3.0 mmol) in toluene (100 ml) was added ether solution of $(\mathrm{Me}_3\mathrm{Si})_2\mathrm{CHLi}$ (0.97 M, 6.2 ml, 6.0 mmol) at 0°C. After stirring the mixture for 10 h, LiC1 was removed by decantation. Solvent was evaporated and the residue was washed with hexane (100 ml). Recrystallization from toluene/hexane afforded dark red crystals of $[2,6\text{-}({}^i\mathrm{Pr0})_2\mathrm{C}_6\mathrm{H}_3]_2\mathrm{Yb}[\mathrm{CH}(\mathrm{SiMe}_3)_2]_2\mathrm{Li}$ (1.4 g, 1.6 mmol, yield 23%). ^{1}H NMR (400 MHz,$\mathrm{C}_6\mathrm{D}_6$, 25°C) δ-14.06 (bs, 36H), 5.77 (d, 6H), 16.44 (d, 6H), 17.28 (bs, 2H), 19.98 (bs, 2H), 22.33 (d, 6H), 24.59 (bs, 2H), 36.92 (d, 6H), 46.35 (bs, 4H), 54.19(bs, 2H). Molecular weight was determined cryoscopically in benzene; cakcd. 884.3, observed 890 for monomeric species (Table 5).

3.7. Synthesis of $[2,6\text{-}(\mathit{cyclo}\text{-}\mathrm{C}_6\mathrm{H}_{11}\text{–}0)_2\mathrm{C}_6\mathrm{H}_3]\mathrm{Sm}$ 6

A solution of azodicarboxylic acid diisopropyl ester (100 g, 495 mmol) in toluene (150 ml) was syringed to a mixed solution of resorcinol (20 g, 182 ml), cyclohexanol (57.6 g, 545 mmol) and triphenylphosphine (140.3 g, 535 mmol) in THF (200 ml) held at 0°C. After stirring for 24 h at room temperature, the reaction mixture was treated with 30% $\mathrm{H}_2\mathrm{O}_2$ (40 ml) to oxydize the unreacted PPh_3 to $\mathrm{PPh}_3\mathrm{O}$. Addition of hexane (300 ml) induced the precipitation of $\mathrm{PPh}_3\mathrm{O}$, which was then removed by filtration. The aqueous layer of the filtrate was separated from the organic layer, which was then extracted twice with 40 ml portions of hexane. The combined hexane solution was washed three times with 50 ml of NaOH aqueous solutions (1N) to remove unreacted resorcinol and mono-substituted compound. Removal of solvent by flash distillation yielded 1,3-(cyclo-$\mathrm{C}_6\mathrm{H}_{11}$–O)$\mathrm{C}_6\mathrm{H}_4$ as a pale yellow oil. Purification by column chromatography [Wako-gel C-200 as silica-gel and hexane/EtOAc (2:1) as eluent], followed by Kugelrour distillation afforded pure 1,3-(cyclo-$\mathrm{C}_6\mathrm{H}_{11}$–O)-$\mathrm{C}_6\mathrm{H}_4$ (bp. 170–200°C, 29 g, 106 mmol, 58% yield). ^{1}H NMR (CDCl_3, 400 MHz, 25°C): δ −1.00 to 2.00 (m, 20H), 4.13 (t, 2H, $J = 3.8$ Hz, 9.1 Hz), 6.39 (m, 3H), 7.05 m, 1H). Hexane solution of n-BuLi (1.63M, 5.3 ml, 8.6 mmol) was syringed to a solution of 1,3-(cyclo-$\mathrm{C}_6\mathrm{H}_{11}$–O)$\mathrm{C}_6\mathrm{H}_4$ (2.4 g, 8.6 mmol) in THF (20 ml) at 0°C. The color of the solution turned dark red. After stirring for 3 h at 0°C, the mixture was allowed to warm to room temperature to generate 2,6-(cyclo-$\mathrm{C}_6\mathrm{H}_{11}$–O)$\mathrm{C}_6\mathrm{H}_3$Li (90% yield). To a stirred suspension of SmCl_3 (1.9 g, 7.4 mmol) in THF (35 ml), 2,6-(cyclo-$\mathrm{C}_6\mathrm{H}_{11}$–O)$\mathrm{C}_6\mathrm{H}_3$Li (13.5 mmol) and TMEDA (4.1 ml, 27.2 mmol) was added. Stirring was continued for 2 h.

The solution was evaporated to dryness and hexane (120 ml) was added to the residual orange powder. After stirring for 3 h, the hexane soluble part was concentrated to give the desired [2,6-(cyclo-$C_6H_{11}-O)_2$-$C_6H_3]_3$Sm (0.7 g). The hexane insoluble part was dissolved in toluene (50 ml) and after the removal of LiCl, the solution was concentrated to give 2.1 g of [2,6-(cyclo-$C_6H_{11}-O)_2C_6H_3]_3$Sm. Combined yield, 64%. ^{1}H NMR (C_6D_6, 400 MHz, 25°C): δ 1.0–2.5 (m, 60H), 4.10 (bs, 6H), 5.64 (d, 6H), 6.64 (t, 6H). Molecular weight is determined cryoscopically in benzene, calc. 933.4. Observed 945.

3.8. Typical procedure for the polymerization of polar monomers (MMA, ϵ-caprolactone, alkyl isocyanate)

Monomer (MMA and ϵ-caprolactone, typically 100–200 eqivalents to initiator) was injected via a syringe into a solution of an initiator (typically 0.04 mmol) in toluene (10 ml) with vigorous stirring at the fixed temperature. When alkyl isocyanares were polymerized, 0.5 ml (or none) of toluene was used. After stirring for a fixed time, the reaction mixture was quenched by the addition of excess MeOH. The preciptated polymer was collected and dried under vacuum.

*3.9. X-ray structural determination of [2,6-(^{i}PrO)$_2$-C_6H_3]$_4$SmLi **2***

The integrated intensity data were measured on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo–K_α ($\lambda = 0.7106$A) radiation. As complex **2** is very air-sensitive, the crystals were sealed in a thin-walled glass capillary tube under argon atmosphere. The X-ray data were collected at room temperature using ω-2θ scan technique to a maximum 2θ value of 55.0°. The data were corrected for conventional absorption, Lorentz and polarization effects.

The crystal structure was solved by the heavy-atom method. The Sm atom was found in the Patterson map. Successive Fourier syntheses clearly revealed the remaining non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method, while the hydrogen atoms were fixed at their standard geometries and were not refined. All the calculations were performed using the teXsan crystallographic software package [27]. The final atomic co-ordinates and equivalent isotropic temperature factors for non-hydrogen atoms for complex **2** are listed in Table 6.

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