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Syntheses of bis- and tetra(trimethylsilyl) substituted lanthanocene methyl complexes and their catalyses for polymerizations of methyl methacrylate, ϵ -caprolactone and L-lactide

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Abstract

Bis- and tetra(trimethylsilyl) substituted lanthanocene methyl complexes, $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{SmMe}]_2$ (**2**) $\{[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmMe}\}_2$ (**4**) and $\{[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{NdMe}\}_2$ (**5**) were prepared in high yield from trimethylsilyl- or bis(trimethylsilyl)cyclopentadienyllithium and $\text{LnCl}_3(\text{THF})_2$ followed by the reaction with a stoichiometric amount of MeLi. The molecular structures of **2** and **4** as well as their precursors, $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{SmCl}]_2$ (**1**) and $[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmCl}_2\text{Li}(\text{THF})_2$ (**3**) were determined by X-ray crystallographic analyses. The complexes **2**, **4** and **5** perform the living polymerization of methyl methacrylate and the block copolymerizations of L-lactide with ϵ -caprolactone in high yields in the absence of any cocatalysts.

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Keywords: Methyl methacrylate; ϵ -Caprolactone; L-Lactide; Trimethylsilyl substituted samarocene methyl; Neodocene methyl; Living polymerizations; Samarocene methyl

1. Introduction

Rare earth metal complexes such as $(\text{C}_5\text{Me}_5)_2\text{LnMe}(\text{THF})$ ($\text{Ln} = \text{Sm}, \text{Yb}, \text{Y}, \text{Lu}$) and $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ were found to perform the living polymerizations of alkyl methacrylates [1,2], alkyl acrylates [3], lactones [4] and cyclic carbonates [5]. These initiators produce (1) high molecular weight polymers with extremely narrow polydispersities, (2) in high yield in a short polymerization time, and give rise to (3) high syndiotactic or high isotactic [6] polymers in the cases of alkyl methacrylates. However, the cost for production of these kinds of complexes is very high to have scruples about practical use in industry, i.e. 1,2,3,4-tetramethylcyclopentenone, a starting material for preparation of 1,2,3,4,5-pentamethylcyclopentadiene, costs 980 \$ per 500 g (Aldrich), while di(cyclopentadiene), a starting material for cyclopentadiene, costs only 20 \$ per 500 g. The use of

cyclopentadiene ligand itself is known to be less effective to perform the living polymerization [2]. Therefore, we examined here the preparation of bis- or tetra(trimethylsilyl) substituted samarocene methyl complexes, $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{SmMe}]_2$ (**2**) and $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmMe}\}_2$ (**4**) and tetra(trimethylsilyl) substituted neodocene methyl complexes, $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{NdMe}\}_2$ (**5**) to examine the ability for performing the living polymerizations of methyl methacrylate, ϵ -caprolactone and L-lactide.

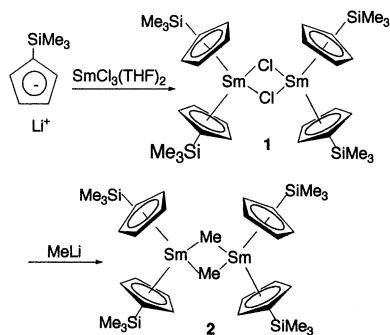
2. Results and discussion

2.1. Synthesis of $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{SmMe}]_2$

Bis(trimethylsilyl) substituted samarocene chloride **1** was prepared as yellow crystals by the reaction of $\text{Me}_3\text{SiC}_5\text{H}_4\text{Li}$ with a stoichiometric amount of anhydrous $\text{SmCl}_3(\text{THF})_2$ in 37% yield (Scheme 1). Its electron impact mass spectrum (EIMS) indicates the dimeric structure ($[\text{M}^+ - \text{Me}_3\text{SiC}_5\text{H}_4]$ peak was observed), and THF is not coordinated to the Sm metal

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Scheme 1.

as revealed by the $^1\text{H-NMR}$ spectrum. Its constitution was determined from the elemental analysis (see the Section 3). X-ray analysis of **1** shows the pseudo tetrahedral geometry around the Sm metal (Fig. 1). The Sm–Cl bond length (2.739–2.760 Å) of **1** is shorter than 2.876 Å (avg) of $[(\text{C}_5\text{Me}_5)_3\text{Sm}(\mu\text{-Cl})]_3$, [7] and 2.798 and 2.827 Å of $[\text{Li}(\text{dme})_3][(\text{C}_5\text{H}_5)_3\text{Sm}]_2(\mu\text{-Cl})$ [8], because of the sterically less crowding around the Sm

metal in the case of **1**. Cl–Sm–Cl* angle (81.70°) of **1** is a little smaller than 83.2° (avg) of $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Cl})]_3$. The Sm–Cl–Sm* angle (98.3°) is much smaller than 156.7° in $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Cl})]_3$ and 146.5° in $[(\text{C}_5\text{H}_5)_3\text{Sm}]_2(\mu\text{-Cl})[\text{Li}(\text{dme})_3]$. The Sm–Sm distance (4.10 Å) is far from the bonding distance (Table 1).

The reaction of **1** with a stoichiometric amount of MeLi in toluene at 0°C produces $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{SmMe}]_2$ (**2**) in 46% yield as yellow crystals. The constitution of the resulting complex agreed well with that of $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{SmMe}$, and the complex exists as a dimeric structure as revealed by the EIMS spectrum (parent peak, $[\text{M}^+] = 887$). X-ray analysis of **2** finally revealed its dimeric structure bridged by Me group (Fig. 2). Sm–Me bond (2.556 and 2.590 Å) is a little longer than 2.48 Å of $(\text{C}_5\text{Me}_5)_2\text{SmMe}(\text{THF})$ [9]. The Cp'(centroid)–Sm–Cp'(centroid)* angle (128.5°) is smaller than 139.4° of $(\text{C}_5\text{Me}_5)_2\text{SmMe}(\text{THF})$, 140.2° of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{DME})$ [10], $130\text{--}138^\circ$ of $[\text{CH}_3\text{C}_5\text{H}_4]_2\text{SmC}\equiv\text{C}-t\text{Bu}]_2$ [12] and 139.3° of $(\text{C}_5\text{Me}_5)_2\text{SmCl}(\text{THF})$ [13] due to the steric effect of the double bridges, Sm–Me–Sm*, existing in **2**.

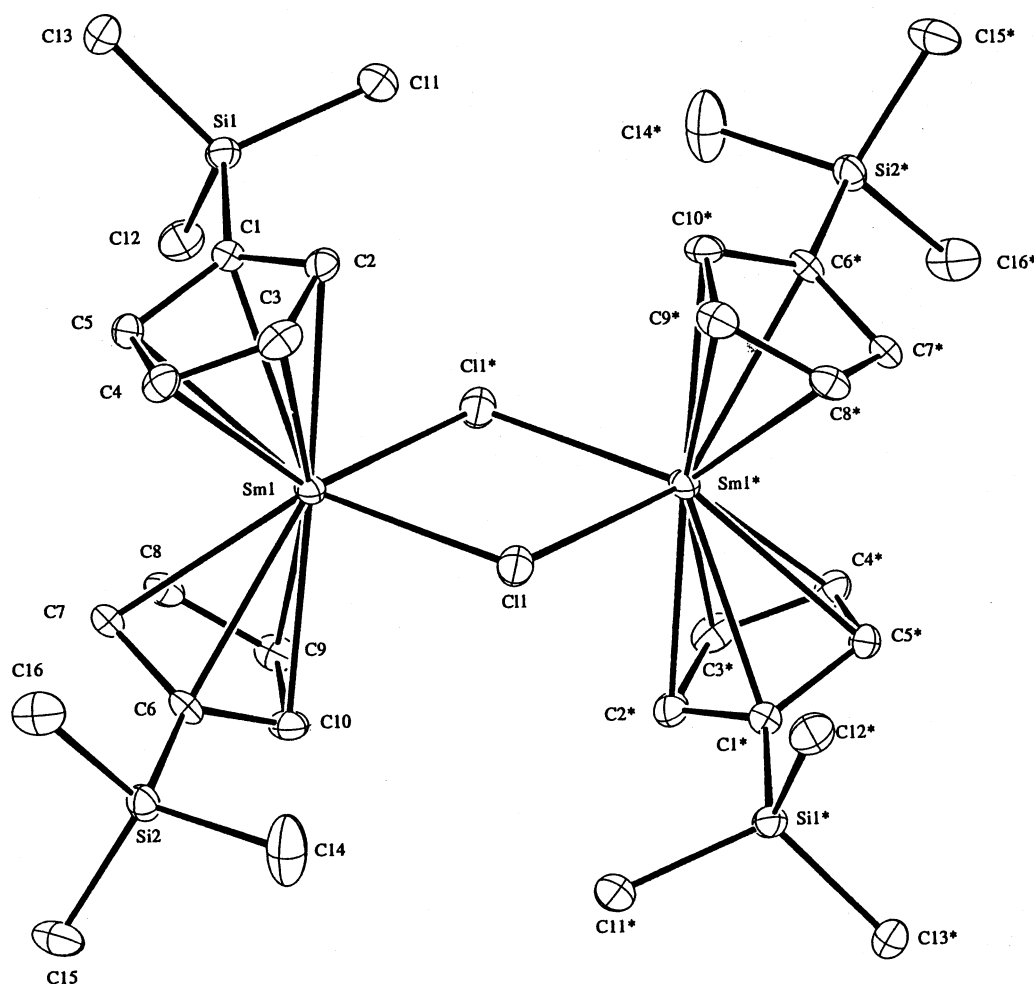
Fig. 1. Molecular structure of $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{Sm}(\mu\text{-Cl})]_2$.

Table 1
Selected bond lengths (Å) and angles (°)

Complex	1	2	3	4
<i>Bond lengths</i>				
Sm(1)–Sm(1)*	8.6066(5)	3.6651(3)		3.7153(6)
Sm–Cp'(C)avg	2.693	2.711	2.724	2.729
	2.688	2.718	2.718	2.740
Sm–Cp'(centroid 1)	2.408(2)	2.433(2)	2.442(1)	2.451(2)
Sm–Cp'(centroid 2)	2.403(2)	2.437(2)	2.435(1)	2.460(2)
Sm–C(brid) or Cl(brid)	2.7393(9)	2.556(4)	2.708(1)	2.578(5)
Sm–C(brid)* or Cl(brid)*	2.7598(9)	2.590(4)	2.711(1)	2.580(5)
<i>Bond angles</i>				
Cp'(centroid 1)–Sm–Cp'(centroid 2)	129.6	128.5	126.1	127.3
Dihedral angles (Cp'–Cp')	51.4(2)	53.2(2)	54.8(1)	54.5(2)
C(brid)–Sm–C(brid)*		89.2(1)		87.8(2)
Cl(brid)–Sm–Cl(brid)*	81.70(3)		82.82(4)	
Sm–C(brid)–Sm*		90.8(1)		92.2(2)
Sm–Cl(brid)–Sm*	98.30(3)			

2.2. Synthesis of $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmMe}\}_2$

Tetra(trimethylsilyl) substituted samarocene chloride·LiCl(THF) **3** was prepared as yellow crystals by the

reaction of 1,3-bis(trimethylsilyl)cyclopentadienyllithium with a stoichiometric amount of anhydrous $\text{SmCl}_3(\text{THF})_2$ in 68% yield. The constitution of the complex agreed well with that of $[1,3(\text{Me}_3-$

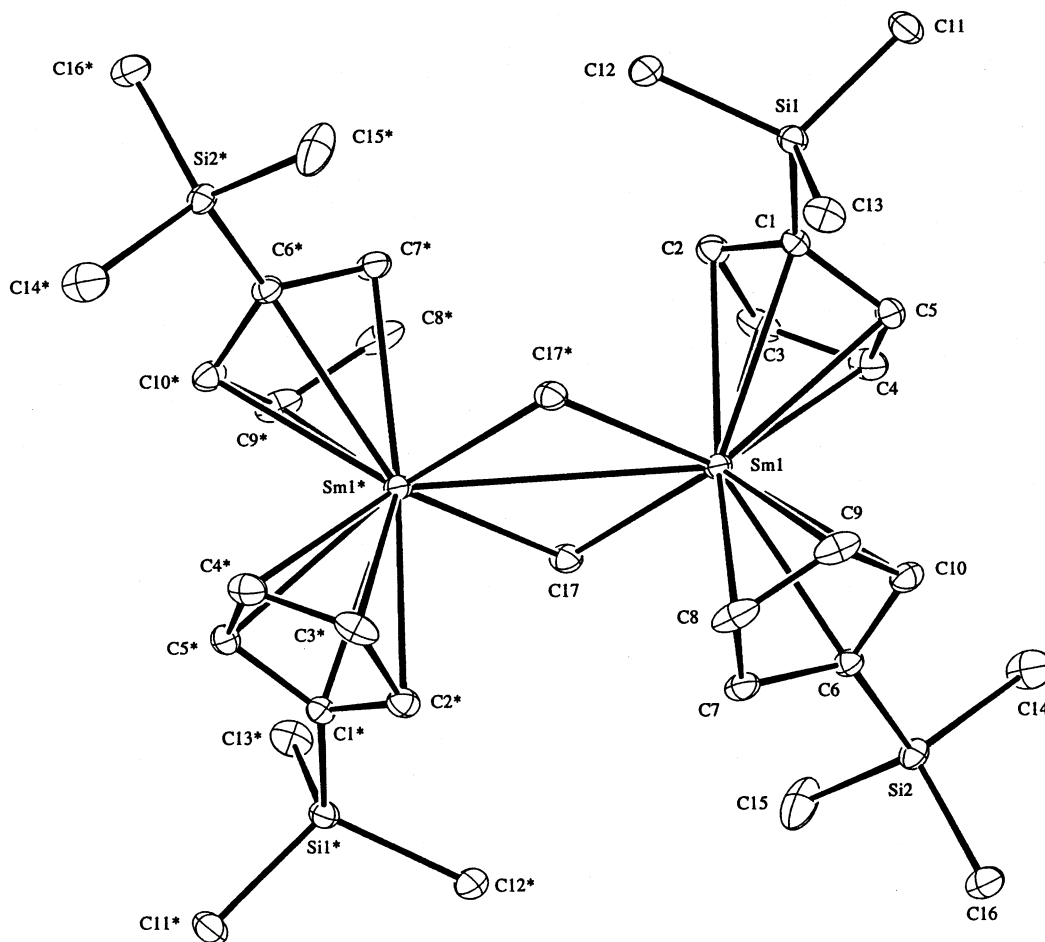
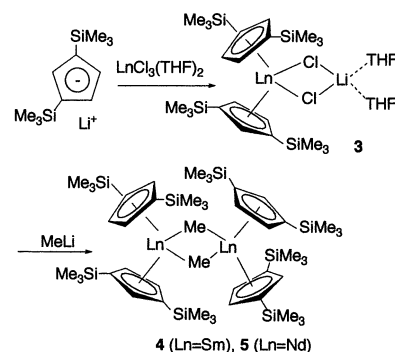


Fig. 2. Molecular structure of $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{Sm}(\mu\text{-Me})]_2$.

$(\text{SiMe}_3)_2\text{C}_5\text{H}_3\text{]}_3\text{SmCl}_2\text{Li}(\text{THF})_2$ as evidenced by elemental analysis, although the corresponding complex, $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmCl}_2$, was prepared by Xie et al. starting from $[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]\text{Sm}$ [13]. The X-ray analysis finally revealed the formation of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmCl}_2\text{Li}(\text{THF})_2$ (Fig. 3). The bond lengths of Sm–Cl is 2.708–2.711 Å and Cp'(centroid)–Sm bond distance is 2.442 and 2.435 Å. The Sm–Cp' distances (avg), 2.718–2.724 Å, are in the range of normal values [7–12]. Cp'(centroid)–Sm–Cp'(centroid)* angle (126.1°) is comparable with that (127.2°) of **1**. The Cl–Sm–Cl angle (82.82°) is also consistent with 82.43° of **1**.

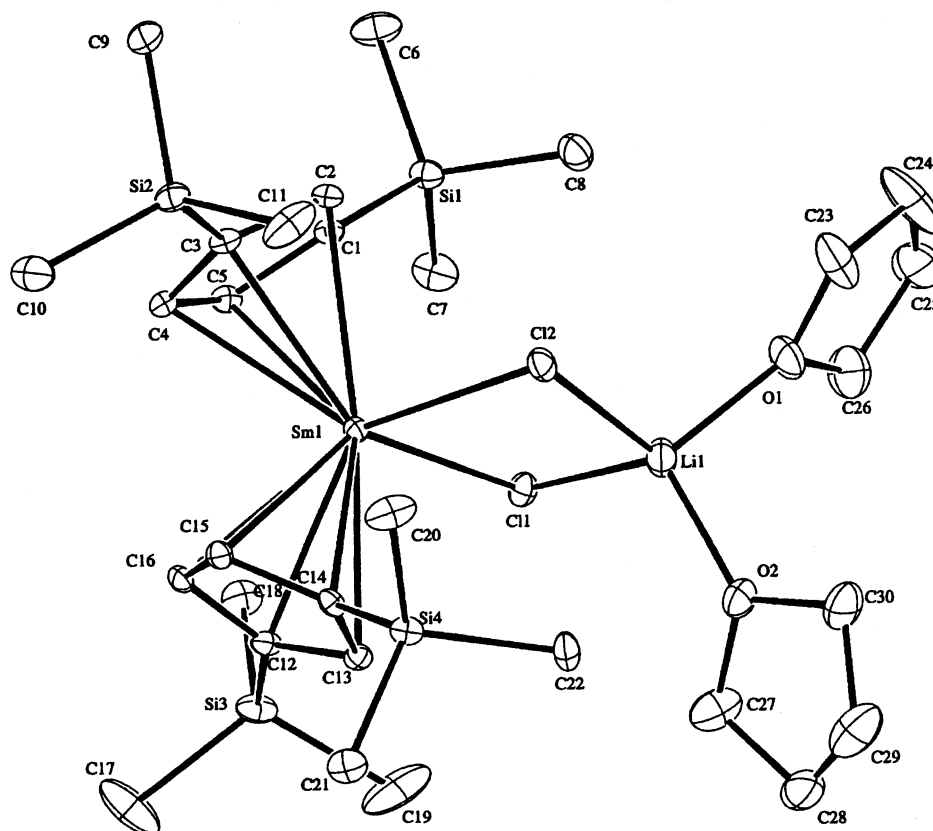
The reaction of **1** with 1.1 equivalents of MeLi in toluene for 12 h resulted in the formation of $\{[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmMe}\}_2$ (**4**) in 46% yield as yellow crystals (Scheme 2). The constitution of **4** was analyzed by elemental analysis, and the EIMS measurement reveals its dimeric structure. The molecular structure of **4** was finally determined by X-ray analysis (Fig. 4). The molecule has dimeric structure with two Me bridges. The bite angle of C(brid)–Sm–C(brid)* is higher than Cl–Sm–Cl* angle of **1**. The Sm–C(brid)–Sm* angle (92.2°) is smaller than the Sm–Cl–Sm* angle (98.3°) in **1** but larger than 90.8° of complex **3**.

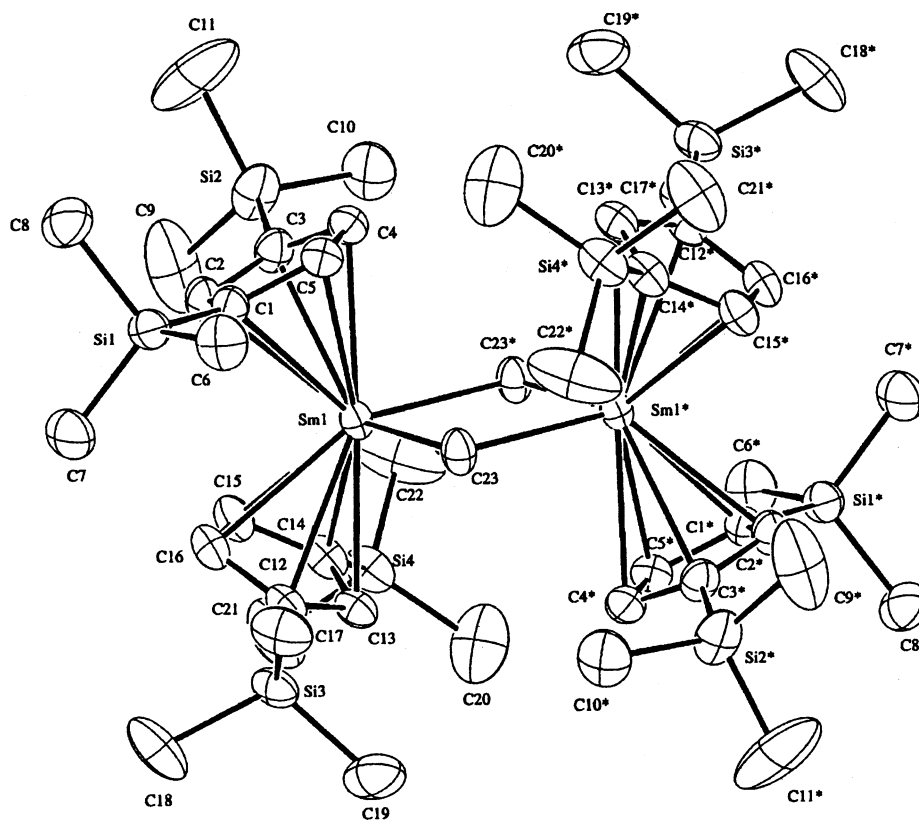
The molecular structures of the corresponding $[(1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3)\text{LnCl}]$ complexes, i.e. $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2-$



Scheme 2.

$\text{NdCl}_2\text{Li}(\text{THF})_2$ [14], $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{NdCl}\cdot\text{AsPh}_4$ [15], $[(\text{Me}_3\text{Si})\text{C}_5\text{H}_4]_2\text{YCl}_2\text{Li}(\text{THF})_2$ [16], $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{PrCl}\}_2$ [17] and $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{LuCl}\}_2$ [18], have been already reported. However, the structures of their alkyl complexes are still unknown. Therefore, we prepared $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{NdMe}\}_2$ (**5**) starting from $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{NdCl}_2$ and MeLi. We have analyzed its molecular structure by X-ray analysis, although its structural accuracy was rather poor [19]. Mass spectrum and X-ray analysis revealed its dimeric structure.

Fig. 3. Molecular structure of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Sm}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2$.

Fig. 4. Molecular structure of $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Sm}(\mu\text{-Me})\}_2$.

2.3. Polymerization of methyl methacrylate

The polymerization of MMA with complexes **2**, **4** and **5** in the absence of cocatalyst was carried out under the similar conditions employed for $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$. The polymerizations with complexes **2**, **4** and **5** proceed in high yield to result in the formation of polymers with very narrow molecular weight distribution at -40 to 78 °C whereas the molecular weight distribution increases with raising the polymerization temperature (Table 2). Syndiotacticity decreases as compared with

$[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ irrespective of the polymerization temperatures. $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ gave syndiotacticity of 92% at -78 °C, while 86–90% syndiotacticity was achieved using **2**, **4** and **5**. Although the catalytic activity of **2**, **4** and **5** were poor as compared with that of $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ especially at higher temperatures, 25 °C, the initiator efficiency (82%) was much improved as compared with that of $[\text{YMe}(\text{C}_5\text{H}_5)_2]_2$ (60%) [2].

The addition of MeMgCl (1.1 equivalents) to **1** or **3** resulted high catalytic activities, i.e. polymer yield after 12 h at -78 °C, 86 and 89%, molecular weights 65 000

Table 2
Polymerization of MMA with complexes **2**, **4** and **5**

Complex	Time (min)	Temperature(°C)	Yield (%)	M_n (10^4)	M_w/M_n	Tacticity <i>rr:mr:mm</i> (%)
2	30	25	79	5.1	1.82	73:25:2
	30	0	90	6.6	1.47	76:22:2
	60	-78	99	7.5	1.05	86:14:0
4	30	25	41	6.7	1.43	73:25:2
	30	0	88	7.7	1.27	76:23:1
	30	-40	99	7.1	1.05	80:20:0
5	60	-78	99	6.9	1.05	87:13:0
	30	25	91	4.5	1.31	72:23:5
	30	0	99	5.1	1.26	75:22:3
$[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$	60	-78	35	8.8	1.05	90:9:1
	30	25	99	5.7	1.02	80:19:1
	30	0	99	5.8	1.02	82:17:1
	60	-78	97	8.2	1.04	92:7:1

Conditions, $[\text{monomer}]/[\text{Sm or Nd}] = 500 \text{ mol mol}^{-1}$, $[\text{Sm or Nd}] = 0.02 \text{ mmol}$, solvent toluene 10 ml.

Table 3
Polymerization of ethylene with complexes **2** and **4**

Complex	Time (min)	Activity 10^{-4} ^a	M_n (10^4) ^b	M_w/M_n ^b	T_m (°C) ^c
2	120	No polymerization			
4	2	4.2	2.0	2.95	138
	10	2.4	2.9	2.62	141
	10 ^d	1.2	0.1	5.91	122

Conditions, solvent 20 ml of toluene, polymerization temperature 25 °C, complex 0.02 mmol, ethylene 1 atm.

^a gPE mol⁻¹ h⁻¹ atm⁻¹.

^b Determined by GPC.

^c Determined by DSC.

^d Polymerization temperature 60 °C.

and 58 000, molecular weight distribution 1.33 and 1.35, respectively. However, the catalyst systems, **1**–MeMgCl and **3**–MeMgCl, prepared in situ exhibit less catalytic activities than the complexes **2** and **4**, regarding the polymer yield, molecular weight, molecular weight distribution and syndiotacticity. Thus, rare earth metal complexes, **2**, **4** and **5**, exhibiting high catalytic activities

for polymerization of MMA could be prepared in low cost as compared with [(C₅Me₅)₂SmH]₂.

2.4. Polymerization of ethylene

Polymerization of ethylene was examined using **2** and **4** as initiators (Table 3). The activity of **2** is completely

Table 4
Polymerization of CL and L-LA

Complex	Monomer	Temperature (°C)	Yield (%)	M_n (10^4)	M_w/M_n	T_m (°C)	$-\Delta H$ J g ⁻¹	T_g (°C)
2	L-LA	25	25	3.0	1.76	158.9	59.7	57.0
	L-LA	60	77	8.8	1.86	156.9	42.3	57.0
	CL	25	99	13.1	1.56	59.5	98.5	-64.5
	CL	0	99	19.7	1.40	60.4	92.5	-64.0
4	L-LA	25	67	0.8	1.59	155.9	52.1	52.3
	L-LA	60	91	9.3	1.72	159.9	40.9	57.1
	CL	25	82	13.6	1.58	59.7	98.3	-63.5
	CL	0	85	15.7	1.43	60.2	94.0	-64.0
5	L-LA	25	78	3.1	1.77	159.8	50.5	53.67
	CL	25	86	14.5	1.65	60.5	94.2	-64.0
[(C ₅ Me ₅) ₂ SmH] ₂	L-LA	100	85	12.2	1.72	158.9	583	56.9
	CL	0	88	7.7	1.08	60.1	94.2	-64.0

Conditions: solvent 5 ml of toluene, reaction time 6 h, Sm complex 0.01 mmol, monomer/[Sm] = 500 mol mol⁻¹.

Table 5
Copolymerizations of CL with LA

Complex	Type	CL/LA		Temperature (°C)	Time (h)	Yield (%)	M_n (10^4)	M_w/M_n
		Feed	Observed					
2	Block	50/50	47/53	25–60	6–6	84	133	1.61
	Block	70/30	72/28	25–60	6–6	86	12.1	1.45
	Random	50/50	7/93	80	6	31	3.5	1.93
	Random	30/70	5/95	80	6	29	3.7	1.85
4	Block	50/50	48/52	25–60	10–6	99	16.3	1.60
	Block	70/30	72/28	25–60	11–6	98	13.5	1.44
	Random	50/50	6/94	80	12	42	3.7	1.75
	Random	30/70	5/95	80	12	39	3.9	1.77
5	Block	50/50	48/52	25–60	10–6	99	15.5	1.56
	Random	50/50	6/94	80	12	45	3.8	1.67

Conditions: solvent 5 ml of toluene, Sm complex 0.01 mmol, monomer/[Sm] = 500 mol mol⁻¹. See Section 4 for detailed method of block and random copolymerizations.

Table 6
Thermal properties of LA/CL copolymers

Complex	Type	CL/LA observed	T_m (°C)	$-\Delta H$ (J g ⁻¹)	T_g (°C)
2	Block	47/53	58.6	53.3	-63.1
			153.9	6.7	53.3
4	Random	7/93	143.2	30	46.9
	Block	48/52	56.9	38.1	-62.5
			167.0	24.7	51.9
5	Random	6/94	156.6	51.3	52.8
	Block	48/52	57.5	54.5	-63.0
			155.2	9.8	52.9
	Random	6/94	153.3	30.2	49.8

lost. The activity of **4** is consistent with that of a C₁ symmetric Sm(III) complex, Me₂Si[2,4-(Me₃-Si)₂C₅H₂][3,4-(Me₃Si)₂C₅H₂]SmCH(SiMe₃)₂ (**6**) [20], *rac*-Sm(II) complexes, Me₂Si[2-(Me₃Si)-4-(*t*BuMe₂-Si)C₅H₂]Sm(THF) and Me₂Si[2-SiMe₃-4-*t*Bu-C₅H₂]Sm(THF) [21], while (C₅Me₅)₂MCH(SiMe₃)₂ (M = La, Nd, Lu) and a *rac*-Sm(III) complex, Me₂Si[2,4-(Me₃-Si)₂C₅H₂]SmCH(SiMe₃) [22] exhibit no catalysis towards the polymerization of ethylene. In sharp contrast to Sm-alkyl complexes, rare earth metal hydrides show much higher activities [23]. The reason why the catalytic activities of complexes **2** and **4** for polymerization of ethylene was low as compared with silylene complexes may be attributed to the large empty orbital around the Sm metal of the latter, as a result of silylene bridge; i.e. Cp*–Sm–Cp* angle of **2** and **4** (128.6 and 127.2°) were much smaller than that of **6**.

2.5. Polymerization of L-lactide and ε-caprolactone

As an extension of this study, homopolymerizations of L-LA and CL as well as random and block copolymerizations of these two monomers were examined. Table 4 shows the result of homopolymerizations. Homo-polymerization of L-LA with **2** and **4** at 60 °C resulted in high yield and high molecular weights. Some epimerization (1–2%) occurs during the polymerization, because of the decrease of T_m from idealized polymers ($T_m = 178.5$ °C) [24]. Homopoly (CL) could be prepared with **2** or **4** at lower temperatures such as 0 or 25 °C to give high molecular weight polymers. Their T_m values are normal, and they are highly crystalline polymers as evidenced from the heat of fusion ($-\Delta H$).

Table 5 shows the results of random (50/50 and 30/70) and block (50/50 and 70/30) copolymerizations of L-LA with CL catalyzed by **2**, **4** and **5**. Random copolymerization of L-LA with CL resulted in the preferential incorporation of L-LA unit in >93 mol.% even when the feeded ratio is 50:50. However, this ratio can be changed by proceeding the block copolymerization, i.e. CL was first polymerized at 25 °C for 6 h and then L-LA

was copolymerized at 60 °C for 6 h. Reversed addition, L-LA and then CL, did not proceed the copolymerization but gave only homopoly (L-LA) in high yield. The copolymerization with complex **5** gave nearly the same results with complex **4**. In sharp contrast to these results, Sb₂O₅, Sn(octyl)₂ [25] or Al(*i*Pr)₃ [26] initiated copolymerizations gave desired ratio between L-LA and CL, although the molecular weights are lower than those obtained by **2**, **4** and **5**.

Thermal properties of the poly(L-LA-ran-CL) were shown in Table 6. The block copolymers exhibit two T_m and T_g values reflecting the block structure, while random copolymer shows only one value.

3. Conclusion

Trimethylsilyl substituted lanthanocene methyl complexes, [(Me₃SiC₅H₄)₂SmMe]₂ (**2**), {[(Me₃Si)₂C₅H₃]₂SmMe}₂ (**4**) and {[(Me₃Si)₂C₅H₃]₂NdMe}₂ (**5**), were first prepared in high yield from trimethylsilyl- or bis(trimethylsilyl)cyclopentadienyllithium and LnCl₃-(THF)₂ (Ln = Sm, Nd) followed by the reaction with a stoichiometric amount of MeLi. The molecular structures of **2** and **4** as well as their precursors, [(Me₃-SiC₅H₄)₂SmCl]₂ (**1**) and [1,3-(Me₃Si)₂C₅H₃]₂SmCl₂Li(THF)₂ (**3**), were determined with X-ray crystallographic analyses. The resulting complexes **2** and **4** could be prepared in low cost and they perform the living polymerization of MMA and the block copolymerizations of L-LA with CL in high yields in the absence of cocatalysts.

4. Experimental

4.1. General considerations

All operations were performed under argon by using standard Schlenk techniques. ¹H-NMR spectra were recorded on a JEOL JNM-LA-400 spectrometer (400

MHz), and chemical shifts were calibrated with chloroform ($\delta = 7.26$ ppm) in CDCl_3 or benzene ($\delta = 7.20$ ppm) in C_6D_6 . Gel permeation chromatographic (GPC) analyses of MMA were run on a Tosoh model SC-8010 instrument (RI 8020 detector) with the TSK gel columns G1000, G2500, G4000, and G7000 in chloroform at 37 °C. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the polymers were determined with a calibration curve plotted with standard polystyrene, the M_w of which was estimated with light scattering method. GPC analyses of polyethylene were run on a Waters 150 C instrument using Shodex AT806MS column in 1,2,4-trichlorobenzene at 140 °C. The melting point (T_m) and heat of fusion ($-\Delta H_m$) and glass transition temperature (T_g) of the polymers were measured with a Seiko SSC5-100 DSC-22C differential scanning calorimeter with the heating rate of 5 °C min^{-1} . T_m and $-\Delta H_m$ were determined in the first heating, whereas T_g was determined in the second heating. The T_g values were defined as the midpoints of step changes in heat capacities. The T_m values were defined from the onset temperature of endothermic curves.

4.2. Materials

Tetrahydrofuran (THF), hexane, and toluene were dried over Na–K alloy and distilled before use. MMA was dried over CaH_2 , then over a dried molecular sieve 4A, and distilled before use. L-LA was dried over CaH_2 in THF for 1 week and the mixture was evaporated, and then sublimed twice. Starting $\text{SmCl}_3(\text{THF})_2$ and $\text{NdCl}_3(\text{THF})_2$ were gifted from Rhodia, France.

4.3. Synthesis of $[(\text{SiMe}_3\text{C}_5\text{H}_4)_2\text{SmCl}]_2$

To Na metal (33.9 g, 1.47 mol) dispersed in THF (450 ml) held at 0 °C was dropwise added freshly cracked cyclopentadiene (133 ml, 1.62 mol) over a period of 3 h. The mixture was stirred at room temperature until Na chips were completely consumed to give a clear colorless solution. To the solution was added trimethylchlorosilane (205 ml, 1.62 mol) at 0 °C and the mixture was stirred for 12 h at ambient temperature. The white suspension was poured into an aqueous solution (400 ml) saturated with NaHCO_3 . After organic layer was separated, the aqueous layer was extracted with three portions of hexane (100 ml \times 3) and the combined organic layer was dried over Na_2SO_4 . The solution was evaporated to dryness and the residue was distilled under reduced pressure (47 °C, 27 mm^{-1} Hg) to give $\text{Me}_3\text{SiC}_5\text{H}_5$ (94 g, 0.68 mol) in 97% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 6.50–6.60 (m, 4H, Cp–H), 3.30 (bs, 1H, Cp–H), -0.04 (s, 9H, Me_3Si).

$n\text{-BuLi}$ (1.6 M solution in hexane, 24.2 ml, 38.5 mmol) was added into a THF solution (45 ml) of

$\text{Me}_3\text{SiC}_5\text{H}_5$ (4.8 g, 35.0 mmol) at 0 °C. After stirring the mixture for 12 h, the resulting lithium salt was transferred to the suspension of $\text{SmCl}_3(\text{THF})_2$ (7.1 g, 17.9 mmol) in THF (45 ml). After refluxing overnight, the solution was evaporated to dryness and hexane (100 ml) was added. Centrifugation of the resulting suspension gave a yellow supernatant liquid. The solution was concentrated and cooled to -20 °C to give $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{SmCl}]_2$ as yellow crystals (4.23 g, 4.6 mmol) in 37% yield. $^1\text{H-NMR}$ (400 MHz, C_6D_6) δ 18.15 (s, 2H, Cp–H), 11.68 (s, 2H, Cp–H), -2.27 (s, 9H, Me_3Si). Anal. Calc. for $\text{C}_{16}\text{H}_{26}\text{ClSi}_2\text{Sm}$: C, 41.74; H, 5.69; Cl, 7.70. Found: C, 42.02; H, 5.76; Cl, 7.71%. EIMS for ^{154}Sm m/z (relative ratio): 790 [$\text{M}^+ - \text{Me}_3\text{SiC}_5\text{H}_4$, 24]; 652 [$\text{M}^+ - \text{Me}_3\text{SiC}_5\text{H}_4$]₂; 428 ($(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{Sm}$, 100); 291 ($\text{Me}_3\text{SiC}_5\text{H}_4$)Sm, 71).

4.4. Synthesis of $[(\text{SiMe}_3\text{C}_5\text{H}_4)_2\text{SmMe}]_2$

A solution of $[(\text{Me}_3\text{SiC}_5\text{H}_4\text{SmCl})_2]$ (2.1 g, 2.28 mmol) in toluene (45 ml) was placed in a round bottomed flask and MeLi (1.04 M solution in ether, 5.5 ml, 5.7 mmol) was dropwise added at 0 °C. The mixture was warmed to r.t. with stirring for 12 h. The solution was evaporated to dryness and the residue was extracted with 45 ml of hexane. The hexane solution was concentrated and cooled to -20 °C to give $[(\text{SiMe}_3\text{C}_5\text{H}_4)_2\text{SmMe}]_2$ as yellow crystals (0.27 g, 0.31 mmol) in 46% yield. $^1\text{H-NMR}$ (400 MHz, C_6D_6) δ 15.62 (s, 4H, Cp–H), 10.48 (s, 4H, Cp–H), 4.01 (m, 3H, CH_3), -1.34 (s, 18H, Me_3Si). Anal. Calc. for $\text{C}_{17}\text{H}_{29}\text{Si}_2\text{Sm}$: C, 46.41; H, 6.64. Found: C, 46.49; H, 6.94%. EIMS for ^{154}Sm , m/z (relative ratio): 887 ($[\text{M}]^+$, 49); 428 ($(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{Sm}$, 90); 291 ($(\text{Me}_3\text{SiC}_5\text{H}_4)\text{Sm}$, 100).

4.5. Synthesis of $[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmCl}_2\text{Li}(\text{THF})_2$

To a THF solution (150 ml) of $\text{Me}_3\text{SiC}_5\text{H}_5$ (30 g, 0.22 mol) held at 0 °C was added dropwise $n\text{-BuLi}$ (1.56 M of hexane solution, 0.20 mol) over a period of 30 min. The mixture was stirred for 6 h at 0 °C. Trimethylchlorosilane (27.5 ml, 0.22 mol) was added to the solution at 0 °C and the mixture was stirred for 3 h at r.t. The white suspension was poured into an aqueous solution (100 ml) saturated with NaHCO_3 . After separation of the organic layer, the aqueous layer was extracted with three portions of hexane (100 ml \times 3), and combined organic layer was dried over Na_2SO_4 . The solution was evaporated to dryness and the residue was distilled under reduced pressure (57 °C, 5 mm^{-1} Hg) to give $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_4$ (36 g, 0.17 mol) in 96% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 6.47–6.68 (m, 3H, Cp–H), 0.16 (s, 1H, Cp–H), -0.07 (s, 18H, Me_3Si).

$n\text{-BuLi}$ (1.59 M solution in hexane, 19.4 ml, 30.8 mmol) solution was added to the solution of $(\text{Me}_3\text{-}$

$(\text{Si})_2\text{C}_5\text{H}_5$ (5.9 g, 28.0 mmol) in THF (45 ml) at 0 °C. After stirring the mixture for 12 h, the resulting lithium salt was transferred into the suspension of $\text{SmCl}_3(\text{THF})_2$ (5.6 g, 14 mmol) in 20 ml of THF. After refluxing the solution overnight, the solution was evaporated to dryness and the residue was extracted with 120 ml of hexane. The hexane solution was centrifuged, concentrated and cooled to –20 °C to give $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmCl}_2\text{Li}(\text{THF})_2$ (6.9 g, 8.7 mmol) as yellow crystals in 68% yield. $^1\text{H-NMR}$ (400 MHz, C_6D_6) δ 16.27 (s, H, Cp–H), 12.19 (s, 2H, Cp–H), 4.26 (m, 4H, THF- α), 1.79 (m, 4H, THF- β), –0.87 (s, 18H, Me_3Si). Anal. Calc. for $\text{C}_{30}\text{H}_{58}\text{Si}_4\text{O}_2\text{LiCl}_2\text{Sm}$: C, 45.53; H, 739. Found: C, 45.63; H, 7.40%.

4.6. Synthesis of $\{[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmMe}\}_2$

A solution of $[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmCl}_2\text{Li}(\text{THF})_2$ (2.3 g, 2.9 mmol) in toluene (45 ml) was placed in a 200 ml of round-bottomed flask and MeLi (1.04 M solution in ether, 3.94 ml, 4.1 mmol) was dropwise added to the solution at 0 °C. The mixture was warmed to r.t. with vigorous stirring for 12 h. After the solution was evaporated to dryness, the residue was extracted with hexane (45 ml). The hexane solution was centrifuged, concentrated and cooled to –20 °C to give $\{[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmMe}\}_2$ as yellow crystals (0.68 mmol) in 46% yield. $^1\text{H-NMR}$ (400 MHz, C_6D_6) δ 16.21 (s, 2H, Cp–H), 12.19 (s, 4H, Cp–H), 4.50 (m, 3H, CH_3). Anal. Calc. for $\text{C}_{23}\text{H}_{45}\text{Si}_4\text{Sm}$: C, 47.28; H, 7.76. Found: C, 47.17; H, 7.71%. EIMS for ^{154}Sm , m/z (relative ratio): 1175 ($[\text{M}]^+$, 5); 573 ($(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$) $_2\text{Sm}$, 90); 363 ($(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$) Sm , 100).

4.7. Synthesis of $\{[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{NdMe}\}_2$

This complex was prepared from $\text{NdCl}_3(\text{THF})_2$ in 35% yield in essentially the same method for preparation of $\{[1,3-(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{SmMe}\}_2$. Anal. Calc. for $\text{C}_{23}\text{H}_{45}\text{Si}_4\text{Nd}$: C, 47.78; H, 7.85. Found: C, 47.77; H, 7.71%. EIMS for ^{144}Nd , m/z (relative ratio): 1155 ($[\text{M}]^+$, 5), 563 ($(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$) $_2\text{Nd}$, 78), 353 ($(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$) Nd , 100).

4.8. Polymerization of methyl methacrylate

MMA (1 ml, 10 mmol) was added at –78 °C to an initiator (0.02 mmol) dissolved in 10 ml of toluene, and the solution was stirred at a fixed temperature for a given period. The polymerization mixture was quenched with acidic methanol, and poured into excess methanol. Then the precipitated polymer sample was dried in vacuo.

4.9. Copolymerization of ϵ -caprolactone with L-lactide

CL (5.0 mmol) and L-LA (5.0 mmol) were added at –78 °C to a solution of an initiator (0.01 mmol) dissolved in 10 ml of toluene to perform the random copolymerization. The solution was stirred at 80 °C for 6 h. The polymerization mixture was quenched with acidic methanol, and poured into excess methanol. Then the precipitated polymer sample was dried in vacuo.

Block copolymerization was carried out as follows. CL (5.0 mmol) was added to a toluene solution (10 ml) of an initiator (0.01 mmol) and the mixture was stirred at 25 °C for 5 h and then L-LA (5.0 mmol) was added at 25 °C. The mixture was stirred at 60 °C for 6 h, and the resulting mixture was quenched with acidic methanol. The polymer sample was poured into excess methanol, and the precipitated polymer sample was dried in vacuo.

4.10. X-ray structure determination

Single crystals of **1**, **2** and **3** sealed in a glass capillary under argon were mounted on a Rigaku RAXIS RAPID Imaging Plate. Crystal data and data collection parameters of these complexes are summarized in Table 7. Indexing was performed three oscillations which were exposed for 3.0 min. The camera radius was 127.40 mm. Readout was performed in the 0.10 mm pixel mode. A numerical absorption collection using the program NUMABS [27] was applied. The data were corrected for Lorentz and polarization effects. The structures of **1** and **2** were solved by direct methods (SHELXS-97) [28], and expanded using Fourier techniques (DIRDIF-94) [29]. The structure of **3** was solved by direct methods (SHELXS-86) [30], and expanded using Fourier techniques (DIRDIF-94) [29]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms for each complex were placed as follows; for **1** and **3** all hydrogen atoms were placed in calculated positions ($d(\text{C-H}) = 0.95 \text{ \AA}$) and kept fixed. For **2** hydrogen atoms on the bridging methyl carbon were found from a difference Fourier syntheses and were refined isotropically, and all the other hydrogen atoms were placed in calculated positions ($d(\text{C-H}) = 0.95 \text{ \AA}$) and constrained to ride on their respective carbon atoms. All calculations were performed using the TEXSAN crystallographic software package.

4.11. X-ray structure determination of **4**

A single crystal of **4** suitable for X-ray diffraction sealed in a glass capillary under an argon atmosphere was mounted on a Rigaku AFC7R four-cycle diffractometer. Crystal data and data collection parameters of these complexes are summarized in Table 7. The unit cell parameters and orientation matrix at 25 °C were determined by a least-squares fit to 2θ values of 25

Table 7
Crystal data and data collection parameters

Complex	1	2	3	4
Empirical formula	C ₃₂ H ₅₂ Cl ₂ Si ₄ Sm ₂	C ₃₄ H ₅₈ Si ₄ Sm ₂	C ₃₀ H ₅₈ Cl ₂ LiO ₂ Si ₄ Sm	C ₄₆ H ₉₀ Si ₈ Sm ₂
Formula weight	920.81	879.97	791.38	1168.70
Temperature (°C)	–150	–93	–123	25
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>Pbca</i> (#61)	<i>P</i> ₂ / <i>c</i> (#14)
<i>a</i> (Å)	8.6066(5)	8.6950(8)	12.8485(3)	20.092(4)
<i>b</i> (Å)	9.8265(9)	9.7829(3)	20.0511(5)	14.489(6)
<i>c</i> (Å)	12.598(1)	12.4680(5)	31.4357(7)	11.073(2)
α (°)	70.125(3)	70.916(2)		
β (°)	76.225(7)	77.398(4)		103.66(2)
γ (°)	88.680(5)	87.204(4)		
<i>V</i> (Å ³)	971.2(2)	977.8(1)	8098.6(3)	3132(1)
<i>Z</i>	1	1	8	2
Crystal dimensions	0.80 × 0.30 × 0.30	0.60 × 0.50 × 0.40	0.60 × 0.50 × 0.10	0.50 × 0.40 × 0.20
μ (Mo–K α) (cm ^{–1})	32.81	31.23	17.26	20.39
Diffractometer	Rigaku RAXIS-RAPID	Rigaku RAXIS-RAPID	Rigaku RAXIS-RAPID	Rigaku AFC7R
Radiation, λ (Å)	Mo–K α , 0.71069	Mo–K α , 0.71069	Mo–K α , 0.71069	Mo–K α , 0.71069
$2\theta_{\max}$ (°)	55.0	55.0	55.0	55.1
Number of reflections (total)	8526	9035	64381	8542
Number of reflections ($2\theta < 55^\circ$)	4329	4441	9273	7187
Variables	181	181	361	253
<i>R</i> ^a	0.090	0.057	0.070	0.095
<i>R</i> _w ^b	0.170	0.132	0.154	0.160
GOF	1.24	1.18	1.33	1.12

$$^a R = \Sigma(F_o^2 - F_c^2) / \Sigma F_o^2.$$

$$^b R_w = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2].$$

strong higher reflections. Three standard reflections were chosen and monitored every 150 reflections. Measured non-equivalent 7187 reflections were used for the structure determination. Over the courses of data collection, the standards decreased by 5.2%. Empirical absorption correction was carried out based on an azimuthal scan. The structure of **4** was solved by direct methods (SHELXS-86) [30], and expanded using Fourier techniques (DIRDIF-94) [29]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the bridging methyl carbon were found from a difference Fourier syntheses and were refined isotropically, and all the other hydrogen atoms were placed in calculated positions ($d(\text{C–H}) = 0.95 \text{ \AA}$) and constrained to ride on their respective carbon atoms. All calculations were performed using the TEXSAN crystallographic software package.

5. Supplementary material

Crystallographic data for the structural analysis of **1**, **2**, **3** and **4** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 186736 for [(Me₃SiC₅H₄)₂SmCl]₂ (**1**), No 186735 for [(Me₃–SiC₅H₄)₂SmMe]₂ (**2**), No. 186733 for [(Me₃–Si)₂C₅H₃]₂SmCl₂Li(THF)₂ (**3**), and No. 186734 for {[(Me₃Si)₂C₅H₃]₂SmMe}₂ (**4**), respectively. Copies of

these informations may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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