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Synthesis, structure, and catalytic activity of tetracoordinate lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Nd, Sm, Eu)

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Abstract

Interaction of anhydrous lanthanide(III) chlorides (Ln = Nd, Sm, Eu) with 3 equiv. of lithium bis(trimethylsilyl)amide $(Me_3Si)_2NLi$ in THF, followed by recrystallization from toluene, produced tetracoordinate lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Nd (**1**), Sm (**2**), Eu (**3**)). Sublimation of **1**, **2** and **3** afforded the corresponding complexes $[(Me_3Si)_2N]_3Ln$ (Ln = Nd, Sm, Eu). The structures of complexes **2** and **3** were determined by the single-crystal X-ray diffraction. These complexes can function as single-component MMA polymerization catalysts in THF, DME, toluene and *n*-hexane. It was found that the activities of the catalysts, stereo-regularity of PolyMMA, and the molecular weight of polymers were dependent on the solvents, temperatures, and the catalyst/MMA mole ratios.

Keywords: Lanthanides; Amides; Compound; Catalysis; Polymerization; Polymer

1. Introduction

Cyclopentadienyl-free transition metal complexes have attracted much attention for their applications as catalysts in the olefin polymerization reaction [1]. The bulky bis(trimethylsily)amido ligand was initially introduced to lanthanide chemistry by Bradley in 1973 [2]. The X-ray crystal structures of three-coordinate lanthanide(III) amides $[(Me_3Si)_2N]_3Ln$ (Ln = Nd [3], Eu [4], and Yb [5]) and lanthanide(II) complexes $[(Me_3Si)_2N]_2Sm(THF)_2$, $\{[(Me_3Si)_2N]Sm(\mu\text{-}I)(DME)(THF)\}_2$ $NaM[N(SiMe_3)_2]_3$ (M = Yb, Eu) have been reported [6]. Recent studies showed that these kinds of complexes are active catalysts for the Tishchenko reaction [7], ring-opening polymerization of ε-caprolactone and δ-valerolactone [8]. The ternary system $[(Me_3Si)_2N]_3Nd/(^iBu)_3Al/Et_2AlCl$ was used to polymerize butadiene to highly *cis*-1,4-polybutadiene [9]. On the other hand, organolanthanide complexes derived from these kinds of amides showed catalytic activities in olefin polymerization [10] and hydroamination/cyclization reactions [11–13].

The tetracoordinate neodymium complex $[(Me_3Si)_2N]_3Nd(\mu\text{-}Cl)Li(THF)_3\cdot OC_4H_8$ was reported as a byproduct in 1994, and the structure of the complex was described [14]. To extend the scope of chemistry of tetracoordinate lanthanide amides, we report herein the rational synthesis, structural characterization and catalytic activities of tetracoordinate lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Nd(**1**), Sm (**2**), Eu (**3**)).

2. Results and discussion

2.1. Syntheses and characterization of the complexes

The title complexes $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Nd (**1**), Sm (**2**), Eu (**3**)) were synthesized by dropwise addition of 3 equiv. of lithium bis(trimethylsi-

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lyl)amide in THF to a suspension of anhydrous lanthanide chlorides in THF, followed by removal of solvents and recrystallization from toluene. The complexes are air- and moisture-sensitive, and are soluble in DME, THF and toluene, and slightly soluble in *n*-hexane. The 'ate' complexes can be transformed into their neutral forms [(Me$_3$Si)$_2$N]$_3$Ln by sublimation. All the transformations are summarized in Scheme 1. All compounds were fully characterized by elemental and spectroscopic analyses. The structures of complex **2** and **3** were determined by single-crystal X-ray diffraction.

It was found that the compounds are isostructural. Fig. 1 shows a representative structure diagram. Structural analysis showed that each lanthanide metal is coordinated by three amide ligands and a chloride bridges the lithium and lanthanide centers.

A key feature of all structures described herein is that three amide nitrogens and a chlorine atom surround the metal atom in a distorted tetrahedral coordination sphere. The angles formed around the metal center Cl–Ln–N(1), Cl–Ln–N(2), and Cl–Ln–N(3) are about 100° ± 1° (Table 1), and the angles N(1)–Ln–N(2), N(1)–Ln–N(3), and N(2)–Ln–N(3) in the range of 114°–119° (Table 1) differ slightly from each other. These values are comparable to those found in [(Me$_3$Si)$_2$N]$_3$Nd(μ-Cl)Li(THF)$_3$·OC$_4$H$_8$ [14]. The N–Ln–N angles found in these complexes are close to the corresponding average values of 116.6° and 117.8° found in pyramidal three-coordinate complexes [(Me$_3$Si)$_2$N]$_3$Ln (Ln = Nd [3], Eu [4]).

Another characteristic structural feature of the compounds reported herein is that the chlorine bridge linking the lithium and lanthanide metals is almost linear (> 175°, Table 2), and the Li–Cl–Ln angle is larger than those (170 ± 2°) found in Ln{$\overline{\mathrm{N[Si(Me_2)_2CH_2CH_2Si}}(Me)_2$]}$_3$(μ-Cl)Li(L)$_3$ (L = THF or Et$_2$O) [15]. These deviations may be due to steric effects. The Ln–Cl and Li–Cl bond distances are almost identical to those found in Ln{$\overline{\mathrm{N[Si(Me_2)_2CH_2CH_2Si}}(Me)_2$]}$_3$(μ-Cl)Li(L)$_3$ (L = THF or Et$_2$O) [15].

The Ln–N bond distances decrease as the ionic radius decrease along the sequence of Nd > Sm > Eu. The Sm–N bond lengths of 2.304(6)–2.321(6) Å in **2** are longer than those of Sm–N bond distances of 2.262(3)–2.268(3) Å found in Sm{$\overline{\mathrm{N[Si(Me_2)_2CH_2CH_2Si}}(Me)_2$]}$_3$(μ-ClLi(THF)$_2$(Et$_2$O) [15]. The average Sm–N bond distance is 0.055 Å longer than the Sm–N bond length found in Sm{$\overline{\mathrm{N[Si(Me_2)_2CH_2CH_2Si}}(Me)_2$]}$_3$(μ-Cl)Li(THF)$_2$(Et$_2$O) [15]. It was found that the Eu–N bond distances, and average Eu–N bond lengths are longer than the corresponding values found in Ln{$\overline{\mathrm{N[Si(Me_2)_2CH_2CH_2Si}}(Me)_2$]}$_3$(μ-Cl)Li(L)$_3$ (Ln = Eu, L = THF). The above deviation of angles and bond lengths may be due to steric effects.

$$3\,(\mathrm{Me_3Si})_2\mathrm{NLi} + \mathrm{LnCl_3} \xrightarrow{\mathrm{THF}} [(\mathrm{Me_3Si})_2\mathrm{N}]_3\mathrm{Ln}(\mu\text{-Cl})\mathrm{Li(THF)_3} \; +2\,\mathrm{LiCl}$$

$$\mathrm{Ln} = \mathrm{Nd}(\mathbf{1}),\ \mathrm{Sm}(\mathbf{2}),\ \mathrm{Eu}\ (\mathbf{3})$$

$$\Big\downarrow \begin{array}{l}\text{sublimation}\\ \text{-LiCl, -THF}\end{array}$$

$$\begin{array}{c}[(\mathrm{Me_3Si})_2\mathrm{N}]_3\mathrm{Ln}\\ \mathrm{Ln} = \mathrm{Nd,\ Sm,\ Eu}\end{array}$$

Scheme 1.

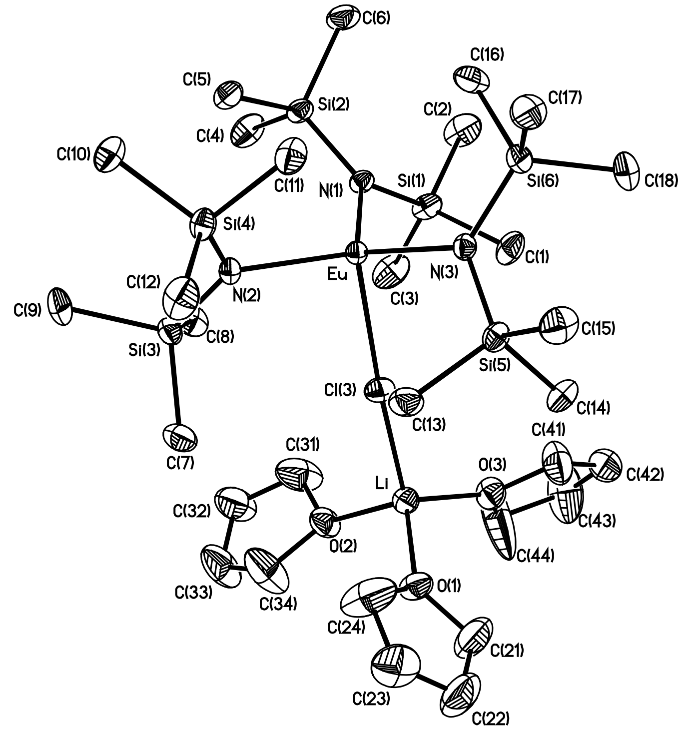

Fig. 1. Representative molecular structure of [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$.

2.2. MMA polymerization

The catalytic activities in MMA polymerization were examined. The polymerization reactions were carried out in a series of solvents, and after a measured interval, the polymers were quenched with acidic methanol. The microstructures of the polymers were analyzed by ^{1}H and ^{13}C NMR spectra. The polydispersities of the polymers were determined by GPC technique. We found that some of the PMMA obtained from the toluene system cannot be dissolved in THF or passed through the GPC columns. The results are summarized in Tables 2–4.

By studying the solvents effects on MMA polymerization (Table 2), it was found that these complexes showed activities in catalyzing MMA polymerization in a series of solvents such as DME, THF, toluene, and *n*-hexane. It is also interesting to note that the catalytic activities of complexes in polar solvents are higher than those in non-polar solvents at 0 °C (Table 2), These

Table 1
Selected interatomic distances (Å) and angles (°) for **2** and **3**

Compound	Ln–N(1) Ln–N(2) Ln–N(3)	Ln–Cl	Cl–Li	Li–Cl–Ln	Cl–Ln–N(1) Cl–Ln–N(2) Cl–Ln–N(3)	N(1)–Ln–N(2) N(1)–Ln–N(3) N(2)–Ln–N(3)
2	2.321(6)	2.681(2)	2.354(15)	175.3(5)	99.38(16)	119.0(2)
	2.333(6)				98.97(16)	115.1(2)
	2.304(6)				100.32(16)	117.7(2)
3	2.286(5)	2.650(2)	2.333(17)	175.9(4)	99.90(16)	114.9(2)
	2.307(6)				99.47(16)	118.0(2)
	2.306(6)				99.49(15)	118.9(2)

Table 2
Solvent effects on the MMA polymerization

Catalyst	Solvent	Conv. (%)	rr	mr	mm
1 [a]	toluene	15	33	38	29
	THF	95	60	31	9
	DME	51	63	31	6
2 [b]	toluene	29	27	37	36
	THF	97	57	34	9
	DME	79	56	32	12
3 [b]	toluene	25	26	22	52
	hexane	16	25	39	36
	THF	85	65	29	6
	DME	93	66	29	5

[a] Conditions: cat./MMA (mol/mol) = 1:700, polymerization time: 3 h, $T = 0$ °C, MMA/solvent (v/v) = 1:2.

[b] Conditions: cat./MMA (mol/mol) = 1:500, polymerization time: 3 h, $T = 0$ °C, MMA/solvent (v/v) = 1:2.

results indicate that the polar solvents may be favorable to the initiation and propagation process. The polydispersities of polymers are dependent on the solvents used in the catalytic systems. When the polymerization processes are carried out in a polar solvent such as THF or DME, high syndiotactic (~60%) PMMA were obtained. These results are comparable to those obtained from a catalytic system [Me$_2$C(2,7-^{t}Bu-Flu)(Cp)]YCH(TMS)$_2$ [16] and Me$_2$Si(Flu)(Cp)LnE(TMS)$_2$ (Ln = Dy, Er, E = CH, N) [10b].

Temperature effects on the activities of catalysts, molecular weight of polymers, and molecular weight distribution were studied. It was found that activities of catalysts are temperature dependent, and the catalyst showed the highest activities at 0 °C. The molecular weight of polymers increase as the MMA polymerization temperatures decrease, and the molecular weight distributions of polymers slightly increase (Table 3).

For the highest activity of catalysts **1** and **2** in THF at 0 °C, the effects of catalyst and MMA monomer mole ratios on MMA polymerization were studied (Table 4). The results showed that the ratios not only influence the activities of the catalyst, but also affect the molecular weight of polymers. As the ratio changed from 1:200 to 1:1000, the molecular weight of polymers increased, and the activity slightly decreased. These results suggest that the polymer chains propagation will be favorable as the concentration of the catalysts decrease. The stereoregularity and molecular weight distribution only slightly changed. It is interesting to note that the results are the same if the catalytic reactions at 0 °C proceed for 1.5 or 3.0 h when the catalyst/MMA monomer mole ratio is 1:500 for the catalyst **2**. When the ratio reaches 1:1500, the catalyst is almost inactive.

It is reasonable to make a comparison of catalytic activity on MMA polymerization between the tetracoordinate lanthanide amides [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$ (Ln = Nd, Sm, Eu) and the triscoordinate lanthanide amides [(Me$_3$Si)$_2$N]$_3$Ln (Ln = Nd, Sm, Eu). It is found that the tetracoordinate lanthanide amides showed the highest activities at 0 °C in solvents such as THF, DME, and toluene, but the corresponding triscoordinate lanthanide amides[(Me$_3$Si)$_2$N]$_3$Ln showed a poor activity with less than 1% conversion at the same conditions. The results suggested that the active species of the catalysts [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$ (Ln = Nd, Sm, Eu) may not be the triscoordinate lanthanide amides [(Me$_3$Si)$_2$N]$_3$Ln (Ln = Nd, Sm, Eu) formed through the Ln(μ-Cl)Li linkage broken.

The proposed polymerization mechanism involves 1,4 addition of the Ln–N(SiMe$_3$)$_2$ functionality to MMA to generate an enolate [17,18], which then undergoes rapid, subsequent conjugate addition sequences.

In summary, three tetracoordinate lanthanide amides [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$ (Ln = Nd, Sm, Eu) were rationally synthesized and fully characterized. These complexes can function as single-component MMA polymerization catalysts. The results showed that the solvents, temperatures, and the catalyst/monomer mole ratios have influences on the activities of catalysts, molecular weight of polymers, and stereoregularity of polymers. The triscooordinate lanthanide amides [(Me$_3$Si)$_2$N]$_3$Ln showed a poorer activity in comparison with the corresponding tetracoordinate lanthanide amides [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$ at the same conditions.

Table 3
Temperatures effects on MMA polymerization [a,b]

Cat.	Solvent	T (°C)	rr	mr	mm	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	Conv. (%)
1 [a]	THF	30	56	36	8	70.8	46.7	1.52	44
		0	60	31	9	111.6	62.8	1.76	95
		−30	61	29	10				31
	DME	30	55	37	8	27.3	22.2	1.23	16
		0	63	31	6	53.6	31.1	1.62	51
		−30							< 1
	toluene	30	29	34	37				4
		0	33	38	29				15
		−30	37	33	30				3
2 [b]	THF	30	59	34	7	56.3	37.3	1.51	49
		0	57	34	9	118.3	61.98	1.91	97
		−30	61	30	9	598.6	272.8	2.19	7
	DME	30	56	37	7	18.5	13.1	1.41	30
		0	56	32	12	58.7	37.5	1.56	79
		−30	68	27	5	334.8	135.1	2.48	12
	toluene	30	27	36	37	23.6	16.6	1.42	10
		0	27	37	36	36.97	22.87	1.62	29
		−30	26	26	48				3
3 [b]	THF	30	56	35	9	73.64	48.55	1.52	85
		0	65	29	6	143.3	99.9	1.43	85
		−30	68	24	8	754.4	391.3	1.93	10
	DME	30	58	35	7	36.4	20.56	1.77	59
		0	66	29	5	50.9	26.4	1.93	93
		−30	64	26	10	291.6	204.9	1.42	9
	toluene	30	24	27	49	31.34	22.7	1.38	12
		0	26	22	52				25
		−30	31	34	35				7
	hexane	30	23	39	38	46.0	28.8	1.59	31
		0	25	39	36	55.2	22.8	2.42	16
		−30	32	39	29	42.66	28.45	1.5	2

[a] Cat./MMA (mol/mol) = 1:700, other conditions are the same as those of in this Table.

[b] The conditions are the same as those of in Table 2.

3. Experimental

All syntheses and manipulations of air- and moisture-sensitive materials were carried out on flamed Schlenk-type glassware on a Schlenk line. All solvents were refluxed and distilled over either finely divided $LiAlH_4$ or sodium benzophenone ketyl under argon prior to use unless otherwise noted. $CDCl_3$ was dried over activated Davison 4 Å molecular sieves. Methyl methacrylate (MMA) was degassed and dried over CaH_2 overnight. $LnCl_3$ was prepared by a published procedure [19], $(Me_3Si)_2NLi$ was prepared according to the reported procedures [2]. Elemental analyses data were obtained on a Perkin Elmer 2400 Series II Elemental Analyzer. IR

Table 4
Effect of catalyst/MMA monomer mole ratio on the MMA polymerization

Cat.	Ratio	rr	mr	mm	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	Conv. (%)
1 [a]	1:1500							< 1
	1:1000	64	29	7	206.0	120.4	1.71	31
	1:700	65	31	4	142.1	55.8	2.55	63
	1:500	61	32	7	77.4	41.9	1.85	94
	1:200	56	34	10				96
2 [b]	1:1500							< 1
	1:1000	60	33	7	173.35	89.45	1.94	87
	1:800	64	30	6	118.94	68.91	1.73	91
	1:500	57	34	9	118.3	61.98	1.91	97
	1:200	56	33	11	54.47	24.43	2.23	99

[a] Conditions: solvent: THF, temperature: 0 °C, polymerization time: 1 h, MMA/solvent = 1:3 (v/v), ratio = catalyst/MMA monomer mole ratio.

[b] Polymerization time: 1.5 h. other conditions are the same as those in (a) .

spectra were recorded on a Perkin–Elmer 983(G) spectrometer (CsI crystal plate, Nujol and Fluoroble mulls). Gel permeation chromatography (GPC) analyses of polymer samples were carried at 30 °C using THF as eluent on a Waters-150C instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 ml min^{-1}. Number-average molecular weight and polydispersities of polymers were given relative to PS standards. ^{1}H and ^{13}C NMR spectra for analyses of PMMA microstructures were recorded on a Bruker AV-300 NMR spectrometer in $CDCl_3$ and analyzed according to the literature [20]. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to internal solvent resonances.

3.1. Preparation of $[(Me_3Si)_2N]_3Nd(\mu\text{-}Cl)Li(THF)_3$ (**1**)

To a suspension consisting of 5.01 g of anhydrous $NdCl_3$ (20.0 mmol) in 30 ml of THF in a 100 ml Schlenk flask was added freshly prepared solid $(Me_3Si)_2NLi$ (10.00 g, 60.0 mmol). After stirring overnight, the resulting clear, pale yellow solution was reduced to dryness under vacuum. Following extraction from hot toluene and removal of lithium chloride by filtration via Cannula, the solution was concentrated. Pale blue crystalline solid was obtained upon standing the solution at room temperature for several days. Yield: 12.49 g, 71%. ^{1}H NMR ([D$_5$]pyridine): $\delta = 3.71$ (br, 12H), 1.67 (br, 12H) (OC_4H_8), 0.98 (br, 54H) ($Si(CH_3)_3$). M.p. 90–92 °C (dec.). *Anal.* Calc. for $C_{30}H_{78}ClLiN_3NdO_3Si_6$: C, 40.76; H, 8.89; N, 4.75. Found: C, 40.59; H, 8.71; N, 4.87%. IR (cm^{-1}): 2921 s, 2859 s, 1203 s, 1132 s, 965 m, 594 m. Sublimation of **1** under 10^{-4} torr at 100 °C afforded $[(Me_3Si)_2N]_3Nd$ as a blue solid upon elemental and spectroscopic analyses. *Anal.* Calc. for $C_{18}H_{54}N_3NdSi_6$: C, 34.57; H, 8.70; N, 6.72. Found: C, 34.23; H, 8.36; N, 6.85%.

3.2. Preparation of $[(Me_3Si)_2N]_3Sm(\mu\text{-}Cl)Li(THF)_3$ (**2**)

This compound was prepared as pale yellow crystals in 87% yield from the reaction of 3.85 g of anhydrous $SmCl_3$ (15.0 mmol) with $(Me_3Si)_2NLi$ (7.53 g, 45.0 mmol) followed by procedures similar to those used in preparation of **1**. M.p. 94–96 °C (dec.). ^{1}H NMR ([D$_5$]pyridine): $\delta = 3.72$ (m, 12H), 1.72 (m, 12H) (OC_4H_8), 0.71 (s, 54H) ($Si(CH_3)_3$). *Anal.* Calc. for $C_{30}H_{78}ClLiN_3O_3Si_6Sm$: C, 40.48; H, 8.83; N, 4.72. Found: C, 40.23; H, 8.71; N, 4.85%. IR (cm^{-1}): 2922 s, 2860 s, 1204 s, 1131 s, 964 m, 593 m. Sublimation of **2** under 10^{-4} torr at 100 °C afforded $[(Me_3Si)_2N]_3Sm$ as a pale yellow solid upon elemental and spectroscopic analyses. *Anal.* Calc. for $C_{18}H_{54}N_3Si_6Sm$: C, 34.23; H, 8.62; N, 6.65. Found: C, 33.97; H, 8.36; N, 6.85%.

3.3. Preparation of $[(Me_3Si)_2N]_3Eu(\mu\text{-}Cl)Li(THF)_3$ (**3**)

This compound was prepared as yellow crystals in 83% yield from the reaction of $EuCl_3$ (3.88 g, 15.0 mmol) with $(Me_3Si)_2NLi$ (7.53 g, 45.0 mmol) followed by procedures similar to those used in preparation of **1**. M.p. 89–91 °C (dec.).^{1}H NMR ([D$_5$]pyridine: $\delta = 4.36$ (m, 12H), 2.39 (m, 12H) (OC_4H_8), −0.08 (s, br, 54H) ($Si(CH_3)_3$). *Anal.* Calc. for $C_{30}H_{78}ClEuLiN_3O_3Si_6$: C, 40.40; H, 8.82; N, 4.71. Found: C, 40.63; H, 8.71; N, 4.56%. IR (cm^{-1}); 2926 s, 2855 s, 1185 s, 1042 m, 968 s, 595 m. Sublimation of **3** under 10^{-4} torr at 100 °C afforded $[(Me_3Si)_2N]_3Eu$ as a yellow solid upon elemental and spectroscopic analyses. *Anal.* Calc. for $C_{18}H_{54}EuN_3Si_6$: C, 34.15; H, 8.60; N, 6.64. Found: C, 34.33; H, 8.32; N, 6.44%.

3.4. MMA polymerization procedures

MMA polymerization reactions were performed in a 50 ml Schlenk flask and an external temperature-controlled bath on a Schlenk line or in a glovebox. In a typical procedure, the catalyst (0.020–0.045 g) was loaded into the Schlenk flask and solvent was added. After the external bath temperature was stabilized, MMA was added through a gas-tight syringe. The polymerization was terminated by addition of acidic methanol after a measured interval. The polymer product was precipitated into 50 ml MeOH, filtered, washed with MeOH, and dried in a vacuum oven at 50 °C overnight to a constant weight.

3.5. Collection of X-ray diffraction data, and solution and refinement of the structures

A suitable crystal of the title complexes was mounted in a sealed capillary and used for X-ray diffraction study. Diffraction data were performed on a Siemens SMART CCD area-detector diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), temperature 293(2) K, φ and ω scan technique. SADABS empirical absorption was applied in data reduction [21]. All structures were solved by direct methods (SHELXS-97) [21], completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on F^2 (SHELXS-97). The hydrogen atoms were assigned to calculated positions, riding on adjacent carbon atoms with $U(H) = 1.5U_{eq}(C)$ for hydrogen atoms on methyl groups and $U(H) = 1.2_{eq}U(C)$ for the remaining hydrogen atoms. All the nonhydrogen atoms were refined anisotropically. The crystal and data collection parameters for **2** and **3** are summarized in Table 5.

Table 5
Crystal and data collection parameters for **2** and **3**

	2	**3**
Empirical formula	$C_{30}H_{78}ClLiN_3O_3Si_6Sm$	$C_{30}H_{78}ClEuLiN_3O_3Si_6$
Formula weight	890.23	891.84
T (K)	293(2)	293(2)
λ, (Å) Mo Kα	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	*I*2/*a*	*I*2/*a*
a (Å)	25.3550(2)	25.2619(3)
b (Å)	16.5322(2)	16.4126(2)
c (Å)	27.5696(2)	27.4521(3)
β (°)	90.823(1)	90.959(1)
V (Å^3)	11555.3(2)	11380.4(2)
D_{calcd} (g cm^{-3})	1.023	1.041
Z	8	8
F(000)	3752	3760
2θ Range	4.30–49.94	4.32–50.14
μ (mm^{-1})	1.211	1.300
Reflections collected	17666	18783
Unique reflections	9946 ($R_{int} = 0.035$)	9841 ($R_{int} = 0.031$)
Parameters	406	406
R ($I > 2\sigma(I)$)	0.062	0.059
wR_2	0.147	0.133
Goodness-of-fit	1.139	1.157

4. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with Cambridge Crystallographic Data Centre CCDC Nos. 187383 and 187382 for compounds **2** and **3**, respectively. Copies of this informatiom may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (internat.) +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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