

## Synthesis, Structure and Catalytic Activity Comparison of Tris- and Tetracoordinated Lanthanide Amides

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Tetracoordinated lanthanide amides  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  ( $\text{Ln}=\text{La}$  (**1**),  $\text{Pr}$  (**2**)) were synthesized by the reaction of anhydrous lanthanide(III) chlorides  $\text{LnCl}_3$  ( $\text{Ln}=\text{La}$ ,  $\text{Pr}$ ) with 3 equiv. of lithium bis(trimethylsilyl)amide  $(\text{Me}_3\text{Si})_2\text{NLi}$  in THF, followed by recrystallization from toluene. Sublimation of **1** and **2** afforded the triscoordinate lanthanide amides  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}$  ( $\text{Ln}=\text{La}$ ,  $\text{Pr}$ ). The crystal structure of **2** was determined by X-ray diffraction analysis. The catalytic activity studies show that the tetracoordinate amides can be used as single-component MMA (methyl methacrylate) polymerization catalysts, while the triscoordinate amides showed poor activity on MMA polymerization under the same conditions.

**Keywords** synthesis, lanthanide, catalyst, MMA, polymerization

### Introduction

The development of lanthanide chemistry has primarily focused on complexes derived from cyclopentadienyl ligands.<sup>1</sup> Recently, considerable efforts have been devoted to the studies of lanthanide complexes supported by cyclopentadienyl-free ligation for their applications as catalyst in the olefin polymerization reaction.<sup>2</sup> Among various cyclopentadienyl alternatives, amide ligands  $[\text{NR}_2]^-$  offer a great potential in ligand design by virtue of their different electronic and steric properties with different R substituents and metal amides have attracted considerable attention over the past 30 years.<sup>3</sup> The sterically hindered ligand, bis(trimethylsilyl)amido, was initially introduced to lanthanide chemistry by Bradley and coworkers in 1973, and a series of lanthanide(III or II) complexes containing the ligand have been reported.<sup>4</sup> Studies show that these lanthanide complexes are active catalysts for the Tishchenko reaction,<sup>5</sup> ring-opening polymerization of  $\epsilon$ -caprolactone,<sup>6</sup> hydroamination/cyclization reaction<sup>7-9</sup> and olefin polymerization.<sup>10</sup> However, the study on tetracoordinated lanthanide complexes containing bis(trimethylsilyl)amido ligand was limited. Recently, we have reported the rational synthesis of tetracoordinate lanthanide amides  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  ( $\text{Ln}=\text{Nd}$ ,  $\text{Sm}$ ,  $\text{Eu}$ ) and

the catalytic activity of these complexes on MMA (methyl methacrylate) polymerization was studied. Results showed that they can function as single-component MMA polymerization catalysts.<sup>11</sup> Considering that the complexes of the light lanthanide might have a different activity because of their larger ionic radius, we synthesized  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  [ $\text{Ln}=\text{La}$  (**1**),  $\text{Pr}$  (**2**)] and investigated their catalytic activity. We report herein the synthesis, structure and catalytic activity comparison of low coordinate lanthanide amides.

### Experimental

All manipulations of the air- and moisture-sensitive materials were performed under dry argon atmosphere. Solvents were dried with appropriate drying agents ( $\text{LiAlH}_4$  or sodium benzophenone ketyl) prior to use. MMA was degassed and dried over  $\text{CaH}_2$  overnight and immediately distilled before use.  $\text{LnCl}_3$ <sup>12</sup> and  $(\text{Me}_3\text{Si})_2\text{NLi}$ <sup>4</sup> were prepared by published procedures. Gel permeation chromatography (GPC) analyses of the polymer samples were carried out at 30 °C using THF as eluent on a waters-150C instrument and calibrated by using monodispersed polystyrene standards at a flow rate of 1.0 mL/min. Number-average molecular weight and

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polydispersities of polymers were given relative to PS standards.  $^1\text{H}$  NMR was recorded on a Bruker AV-300 NMR spectrometer in  $\text{CDCl}_3$ .<sup>13</sup>

### Preparation of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ( $\text{Ln}=\text{La}, \text{Pr}$ )

To a stirred suspension of anhydrous  $\text{LnCl}_3$  (20 mmol) in THF (30 mL) in a 100 mL-Schlenk flask was added freshly prepared solid  $(\text{Me}_3\text{Si})_2\text{NLi}$  (60 mmol). The reaction mixture was stirred overnight at room temperature. The resulting clear solution was evaporated to dryness under vacuum. Following extraction with hot toluene and removal of lithium chloride by filtration via cannula technique, the solution was concentrated. Crystalline solid was obtained upon standing the solution at  $0^\circ\text{C}$  for several days.

$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{La}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  (**1**) Yield 11.5 g (65%);  $^1\text{H}$  NMR ( $[\text{D}_5]\text{pyridine}$ , 300 MHz)  $\delta$ : 3.63 (t,  $J=5.94$  Hz, 12H), 1.60 (m, 12H), 0.59 (s, 54H);  $^{13}\text{C}$  NMR ( $[\text{D}_5]\text{pyridine}$ , 75 MHz)  $\delta$ : 67.63, 25.59, 5.97; IR (film)  $\nu$ : 2959, 1250, 1063, 930  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{30}\text{H}_{78}\text{ClLaLiN}_3\text{O}_3\text{Si}_6$ : C 41.00, H 8.95, N 4.78; found C 40.67, H 8.78, N 4.83.  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{La}$  was obtained by sublimation of **1** at  $100^\circ\text{C}$  *in vacuo*. Anal. calcd for  $\text{C}_{18}\text{H}_{54}\text{LaN}_3\text{Si}_6$ : C 34.87, H 8.78, N 6.77; found C 34.54, H 8.63, N 6.64.

$[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Pr}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  (**2**) Yield 13.04 g (74%); IR (film)  $\nu$ : 2957, 1249, 1051, 927  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{30}\text{H}_{78}\text{ClLiN}_3\text{O}_3\text{PrSi}_6$ : C 40.91, H 8.92, N 4.77; found C 40.58, H 8.73, N 4.65.  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Pr}$  was obtained by sublimation of **2** at  $100^\circ\text{C}$  *in vacuo*. Anal. calcd for  $\text{C}_{18}\text{H}_{54}\text{N}_3\text{PrSi}_6$ : C 34.75, H 8.75, N 6.75; found C 34.57, H 8.56, N 6.48.

### MMA polymerization procedures

MMA polymerization reactions were performed in a 50 mL-Schlenk flask and an external temperature-controlled bath on a Schlenk line. In a typical procedure, the catalyst (20–50 mg) 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 quenched with methanol after a measured interval. The polymer product was precipitated into 50 mL of methanol, filtered, washed with methanol, and dried in vacuum at  $50^\circ\text{C}$  to a constant weight.

### X-ray structure determination

A suitable crystal of  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Pr}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  with dimensions of  $0.92\text{ mm} \times 0.76\text{ mm} \times 0.48\text{ mm}$  was mounted in a sealed capillary and used for X-ray diffraction analysis. Diffraction data were performed on a Siemens SMART CCD area-detector diffraction with graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda=0.071073\text{ nm}$ ), temperature 293(2) K,  $\varphi$  and  $\omega$  scan technique. SADABS empirical absorption was applied in data reduction. Structure was solved by direct methods (SHELXS-97), completed by subsequent difference Fourier synthesis, 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  $U(\text{H})=1.5U_{\text{eq}}(\text{C})$  for hydrogen atoms on methyl groups and  $U(\text{H})=1.2U_{\text{eq}}(\text{C})$  for the remaining hydrogen atoms. All the nonhydrogen atoms were refined anisotropically. The crystal and data collection parameters for complex **2** are listed in Table 1.

**Table 1** Crystal and data collection parameters for complex **2**

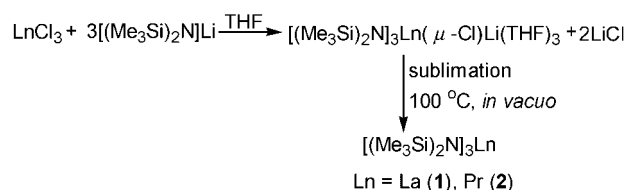
Empirical formula	$\text{C}_{30}\text{H}_{78}\text{ClLiN}_3\text{O}_3\text{PrSi}_6$
Formula weight	880.79
$T/\text{K}$	293(2)
$\lambda/\text{nm}$ Mo $\text{K}\alpha$	0.071073
Crystal system	monoclinic
Space group	$I2/a$
$a/\text{nm}$	2.54035(11)
$b/\text{nm}$	1.64729(7)
$c/\text{nm}$	2.75065(19)
$\beta/^\circ$	90.9670(10)
$V/\text{nm}^3$	11.509(11)
$D_{\text{calcd}}/(\text{g}\cdot\text{cm}^{-3})$	1.017
$Z$	8
$F(000)$	3728
$2\theta$ range	1.60–25.05
$\mu/\text{mm}^{-1}$	1.042
Reflections collected	17252
Unique reflections	9979
Parameters	406
$R [I > 2\sigma(I)]$	0.0714
$wR_2$	0.1607
Goodness-of fit	1.170

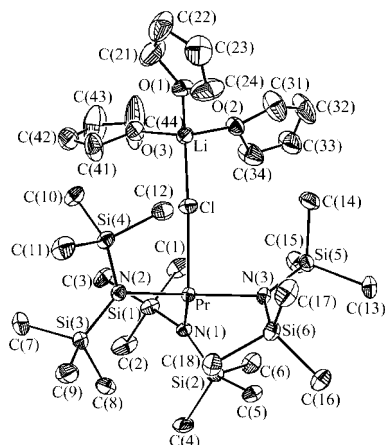
## Results and discussion

### Synthesis and characterization of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ [ $\text{Ln}=\text{La}$ (**1**), $\text{Pr}$ (**2**)]

The metathesis reaction of anhydrous  $\text{LnCl}_3$  with 3 equiv. of  $\text{LiN}(\text{SiMe}_3)_2$  in THF gives, followed by recrystallization from hot toluene, the title complexes  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  ( $\text{Ln}=\text{La}$  (**1**),  $\text{Pr}$  (**2**)) in good yield. The neutral homoleptic lanthanide derivatives  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}$  ( $\text{Ln}=\text{La}, \text{Pr}$ ) can be obtained by sublimation from the “ate-complexes” (Scheme 1). All the complexes were fully characterized by elemental

### Scheme 1





**Figure 1** Molecular structure of  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Pr}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  (**2**).

and spectroscopic analyses. The structure of complex **2** was elucidated by single-crystal X-ray diffraction analysis.

The crystal structure of complex **2** is shown in Figure 1. The selected bond lengths and bond angles are listed in Table 2. Figure 1 shows that the praseodymium is surrounded by three nitrogen atoms of bis(trimethyl)silyl groups and a chlorine atom, which bridges the lithium and praseodymium. The coordination number of Pr is 4. The bond angles of Cl-Pr-N(1), Cl-Pr-N(2), and Cl-Pr-N(3) are  $99.46(18)^\circ$ ,  $98.52(17)^\circ$ , and  $98.45(18)^\circ$ , respectively. The bond angles of N(1)-Pr-N(2), N(1)-Pr-N(3), and N(2)-Pr-N(3) are  $118.3(3)^\circ$ ,  $115.8(2)^\circ$ , and  $119.0(2)^\circ$ , respectively. These values slightly differ from those found in  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  ( $\text{Ln}=\text{Sm}$ ,  $\text{Eu}$ )<sup>11</sup> and  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{NdOC}_4\text{H}_8$ .<sup>14</sup> The values of N-Pr-N found in  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Pr}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  are close to the corresponding values found in three-coordinate pyramidal complexes  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}$  ( $\text{Ln}=\text{Nd}$ ,<sup>15</sup>  $\text{Eu}$ ,<sup>16</sup>  $\text{Yb}$ <sup>4b</sup>).

**Table 2** Selected bond lengths ( $\times 10^{-1}$  nm) and bond angles ( $^\circ$ ) of complex **2**

Pr—N(1)	2.335(6)	Cl-Pr-N(1)	99.46(18)
Pr—N(2)	2.361(6)	Cl-Pr-N(2)	98.52(17)
Pr—N(3)	2.360(6)	Cl-Pr-N(3)	98.45(18)
Pr—Cl	2.724(2)	Li-Cl-Pr	175.7(5)
Cl—Li	2.341(18)		

The bond angle of Li-Cl-Pr is  $175.7(5)^\circ$ , indicating that the chloride-bridge is almost linear. The bond angle of Li-Cl-Pr is larger than that  $[(170 \pm 2)^\circ]$  found in

$\text{Ln}\{\text{N}[\text{Si}(\text{Me})_2\text{CH}_2\text{CH}_2\text{Si}(\text{Me})_2]\}_3(\mu\text{-Cl})\text{Li}(\text{L})_3$  ( $\text{L}=\text{THF}$  or  $\text{Et}_2\text{O}$ )<sup>17</sup> but close to that found in  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  ( $\text{Ln}=\text{Sm}$ ,  $\text{Eu}$ ).<sup>11</sup> The average bond length of Pr—N is 0.2352 nm, which is longer than the corresponding Ln—N in  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  ( $\text{Ln}=\text{Sm}$ ,  $\text{Eu}$ ).<sup>11</sup> These may be due to the difference of the ionic radius.

## MMA polymerization

The catalytic activities of the title complexes as single component MMA polymerization catalysts were investigated. The polymerization reactions were carried out in a series of solvents and the polymerization reactions were quenched with acidic methanol after a measured interval. The microstructures of the polymers were analyzed by  $^1\text{H}$  NMR spectra. The polydispersities of the polymers were determined by GPC technique. It was found that some of PMMA (polymethylmethacrylate) could not be dissolved in THF or passed through GPC column. The results are summarized in Tables 3, 4.

The solvent effects on MMA polymerization reaction were studied. The results are summarized in Table 3. It is found that complexes **1** and **2** can act as single component catalysts in THF, DME and toluene. The activities of these catalysts are solvent dependent. It was found that complexes **1** and **2** showed higher activities in polar solvent such as THF and DME, but behave poor activities in solvent toluene due to the poor solubility of the catalysts in the solvent. The results indicate that the polar solvents may be favorable to the initiation and propagation process. The polydispersities of polymers are also dependent on the solvents used. When the polymerization reactions were carried out in THF or DME, high syndiotactic (*ca.* 60%) PMMA were obtained. These results are similar to those observed from a catalytic system  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  ( $\text{Ln}=\text{Nd}$ ,  $\text{Sm}$ ,  $\text{Eu}$ ),<sup>11</sup>  $[\text{Me}_2\text{C}(2,7\text{-}t\text{-Bu-Flu})(\text{Cp})]\text{YCH}(\text{TMS})_2$ <sup>18</sup> and  $\text{Me}_2\text{Si}(\text{Flu})(\text{Cp})\text{LnE}(\text{TMS})_2$  ( $\text{Ln}=\text{Dy}$ ,  $\text{Er}$ ,  $\text{E}=\text{CH}$ ,  $\text{N}$ ).<sup>10b</sup>

Temperature effects on MMA polymerization reaction were further investigated. Results show that the activities of catalysts, molecular weight of the polymers, and molecular weight distribution were temperature-dependent. The catalysts **1** and **2** showed the highest activities at  $-30^\circ\text{C}$ , while  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$  ( $\text{Ln}=\text{Nd}$ ,  $\text{Sm}$ ,  $\text{Eu}$ ) showed the highest activities at  $0^\circ\text{C}$ .<sup>11</sup> It is found that the molecular weight and the molecular weight distributions of polymers slightly increase as the MMA polymerization temperature decreases (Table 3).

For optimized reaction conditions (solvent: THF; temperature:  $-30^\circ\text{C}$ ), the effects of catalysts and MMA monomer molar ratios on MMA polymerization were studied (Table 4). As the ratios changed from 1 : 200 to 1 : 700, the activities of the catalysts slightly decreased probably due to the existence of a very small amount of impurities. The stereoregularity and molecular distribution slightly changed as the ratios changed. However, the catalyst **1** is almost inactive when the ratio reaches 1 : 1000.

For comparison of the catalytic activity between the tetracoordinate and triscoordinate lanthanide amides, the catalytic activity of those neutral triscoordinate lanthanide amides  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}$  ( $\text{Ln}=\text{La}$ ,  $\text{Pr}$ ) was also studied. It is found that the tetracoordinated lanthanide amides showed good activities, but the corresponding

**Table 3** Solvent and temperature effects on the MMA polymerization<sup>a</sup>

Catalyst	Solvent	T/°C	rr <sup>b</sup>	mr <sup>b</sup>	mm <sup>b</sup>	M <sub>w</sub> × 10 <sup>-3</sup>	M <sub>n</sub> × 10 <sup>-3</sup>	M <sub>w</sub> /M <sub>n</sub>	Conversion/%
<b>1 (La)</b>	THF	25	52	39	9	31.4	20.0	1.57	72
		0	55	35	10	73.8	34.5	2.14	70
		-25	59	33	8	114.9	46.6	2.47	93
	DME	30	57	37	6	12.1	9.5	1.27	2
		0	65	30	5	33.8	14.5	2.33	35
		-30	63	30	7	94.8	41.4	2.29	40
	toluene	30	23	25	52	35.0	17.6	1.98	<1
		0	28	28	44	57.7	23.9	2.41	3
		-30	32	33	35	87.9	49.3	1.78	16
<b>2 (Pr)</b>	THF	30	56	37	7	37.8	125.9	1.46	27.4
		0	61	33	6	212.3	114.2	1.86	97
		-30	65	30	5	303.3	137.0	2.21	100
	DME	30	54	36	10	24.0	18.8	1.28	14.3
		0	62	32	6	54.7	35.9	1.52	34.3
		-30	66	27	7				45.4
	toluene	30	24	38	38				6
		0	30	36	34				16.4
		-30	39	29	32				11

<sup>a</sup> Conditions: cat. : MMA (mol : mol = 1 : 700; MMA : solvent (V : V) = 1 : 2; polymerization time: 40 min for **1** and 3 h for **2**. <sup>b</sup> rr: content of syndiotactic PMMA; mr: content of atactic PMMA; mm: content of isotactic PMMA.

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

Catalyst	Ratio	rr <sup>c</sup>	mr <sup>c</sup>	mm <sup>c</sup>	M <sub>w</sub> × 10 <sup>-3</sup>	M <sub>n</sub> × 10 <sup>-3</sup>	M <sub>w</sub> /M <sub>n</sub>	Conversion/%
<b>1 (La)<sup>a</sup></b>	1000							trace
	700	59	33	8	114.9	46.6	2.47	93
	500	65	30	5	121.6	52.9	2.30	98
	200	64	30	6	100.5	45.3	2.21	100
<b>2 (Pr)<sup>b</sup></b>	2000							trace
	1500	60	34	6	170.0	95.7	1.78	15
	1000	63	31	6	116.3	69.8	1.67	51
	700	63	32	5	107.8	62.1	1.74	75
	500	59	35	6	77.8	45.6	1.71	96
	200	63	32	5	30.5	22.8	1.34	100

<sup>a</sup> Conditions: solvent: THF, temperature: -30 °C, polymerization: 40 min, MMA : solvent = 1 : 2 (V : V), ratio = catalyst : MMA monomer molar ratio. <sup>b</sup> Temperature: 0 °C, polymerization time: 1 h, MMA : solvent = 1 : 3 (V : V), other conditions are the same as those in *a*. <sup>c</sup> rr: content of syndiotactic PMMA; mr: content of atactic PMMA; mm: content of isotactic PMMA.

triscoordinate lanthanide amides were almost inactive under the same conditions. From the results it is suggested that the active species of the catalyst [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>3</sub>Ln(μ-Cl)Li(THF)<sub>3</sub> (Ln = La, Pr) may not be the triscoordinate lanthanide amides [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>3</sub>Ln (Ln = La, Pr) through the Ln(μ-Cl)Li linkage broken.

In conclusion, the synthesis and catalytic activities of two tetracoordinate light lanthanide amides [(Me<sub>3</sub>-Si)<sub>2</sub>N]<sub>3</sub>Ln(μ-Cl)Li(THF)<sub>3</sub> (Ln = La, Pr) were reported. These complexes can function as single-component MMA polymerization catalysts. The results showed that the catalytic activities are solvent-, temperature-, and

the catalyst/monomer molar ratio-dependent. The corresponding sublimates of triscoordinate lanthanide amides showed a poor activity in comparison with the tetracoordinate lanthanide amides under the same polymerization conditions.

### Supplementary material

Crystallographic data (including structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-221101. Cop-

ies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK;

Fax: +44-1223-336-033;

E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or

www: <http://www.ccdc.cam.ac.uk>).

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