

Protonolysis Reactions of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{thf})_3$ with $t\text{BuSH}$ or EtSH : Isolation, Structures and Catalytic Properties of Dinuclear Complexes $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Ln}(\mu\text{-S}t\text{Bu})]_2$ and Tetranuclear Complexes $[\text{Li}(\text{thf})_4]\{[(\text{Me}_3\text{Si})_2\text{N}]_4\text{Ln}_4(\mu_4\text{-SEt})(\mu\text{-SEt})_8\}$ ($\text{Ln} = \text{Pr}, \text{Sm}$)

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Reactions of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{thf})_3$ (**1**: $\text{Ln} = \text{Pr}$; **2**: $\text{Ln} = \text{Sm}$) with an equimolar amount of $t\text{BuSH}$ or EtSH gave rise to four amidolanthanide alkylthiolate complexes $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Ln}(\mu\text{-S}t\text{Bu})]_2$ (**3**: $\text{Ln} = \text{Pr}$; **4**: $\text{Ln} = \text{Sm}$) and $[\text{Li}(\text{thf})_4]\{[(\text{Me}_3\text{Si})_2\text{N}]_4\text{Ln}_4(\mu_4\text{-SEt})(\mu\text{-SEt})_8\}$ (**5**: $\text{Ln} = \text{Pr}$; **6**: $\text{Ln} = \text{Sm}$). Compounds **3–6** were characterized by elemental analysis, IR and ^1H NMR spectroscopy and single-crystal X-ray diffraction, and their catalytic properties were also investigated. Compounds

3 and **4** are thiolate-bridged dimers in which each Ln atom adopts a distorted tetrahedral coordination. Compounds **5** and **6** contain a Ln_4 square plane, which is capped by a $\mu_4\text{-SEt}^-$ ligand. The edges of the square are bridged by four pairs of SEt^- ligands on both sides of the Ln_4 plane. Each Ln atom has a distorted octahedral geometry.

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Introduction

In the past decades, synthesis of lanthanide chalcogenolates has attracted much attention due to their interesting structures^[1] and their potential applications in advanced materials and catalytic processes.^[2] Among these complexes, only a dozen of lanthanide alkylthiolate complexes^[3] have been structurally characterized, though some lanthanide alkylthiolate complexes (e.g. $[\text{Gd}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-S}t\text{Bu})]_2$ ^[4] and $[\text{Cp}_2\text{Lu}(\mu\text{-S}t\text{Bu})_2\text{Li}(\text{thf})_2]$ ^[5]) were reported in 1985. These alkylthiolate complexes can be mainly classified into two types: mononuclear structures {e.g. $[\text{Li}(\text{tmeda})_3]\text{Yb}(\text{S}t\text{Bu})_6$; $\text{tmeda} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ }^[3c] and dinuclear structures {e.g. $[\text{Yb}(\text{S}t\text{Bu})_2(\mu\text{-S}t\text{Bu})(\text{bipy})]_2$ }^[3a]. Most of these compounds were prepared by metathesis of lanthanide halides or (substituted) cyclopentadienyl lanthanide complexes with alkali metal thiolates,^[3b,3c,3g,4] by insertion reactions of S_8 into the Ln–carbon bond^[3h] or by protonolysis reactions of (substituted) cyclopentadienyl lanthanide complexes with alkylthiols.^[3a,3d–3f,5] It is noted that reactions of amidolanthanide complexes with alkylthiols appear to be less explored. Aspinall et al. reported the first amidolanthanide *tert*-butylthiolate complexes $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-S}t\text{Bu})]_2$ ($\text{Ln} = \text{Gd}, \text{Eu}$), which were prepared from protonolysis reactions of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}$ with an equimolar amount of $t\text{BuSH}$ in toluene/thf at -23°C . However, these compounds readily decomposed into insoluble polymeric materials at ambient temperature.^[4]

We are interested in the preparation of amidolanthanide benzenethiolate complexes from protonolysis reactions of bis(trimethylsilyl)amidolanthanide(III) chloride complexes, $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{thf})_3$, with benzenethiol.^[6] For example, reactions of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Nd}(\mu\text{-Cl})\text{Li}(\text{thf})_3$ with an equimolar amount of benzenethiol gave rise to cationic tetranuclear complex $[\text{Li}\{[(\text{Me}_3\text{Si})_2\text{N}]_4(\mu_4\text{-Cl})\text{Nd}_4(\mu\text{-SPh})_8\}]$. The facile formation of this complex and other previously reported related complexes could be attributed to the incorporation of lithium and chloride ions into their frameworks.^[6a] In addition, these complexes exhibited good catalytic activity in the ring-opening polymerization (ROP) of ϵ -caprolactone. Therefore, if the benzenethiol that was used in the above reactions were to be replaced with different alkylthiols, would reactions between $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{thf})_3$ and the alkylthiols afford amidolanthanide thiolate complexes with different structural frameworks? Moreover, would the resulting complexes show better catalytic activity in the ROP of ϵ -caprolactone? With these questions in mind, we carried out reactions of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{thf})_3$ (**1**: $\text{Ln} = \text{Pr}$; **2**: $\text{Ln} = \text{Sm}$)^[7] with two common alkylthiols, $t\text{BuSH}$ and EtSH , and two neutral binuclear complexes $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Ln}(\mu\text{-S}t\text{Bu})]_2$ (**3**: $\text{Ln} = \text{Pr}$; **4**: $\text{Ln} = \text{Sm}$) and two cationic tetranuclear complexes $[\text{Li}(\text{thf})_4]\{[(\text{Me}_3\text{Si})_2\text{N}]_4\text{Ln}_4(\mu_4\text{-SEt})(\mu\text{-SEt})_8\}$ (**5**: $\text{Ln} = \text{Pr}$; **6**: $\text{Ln} =$

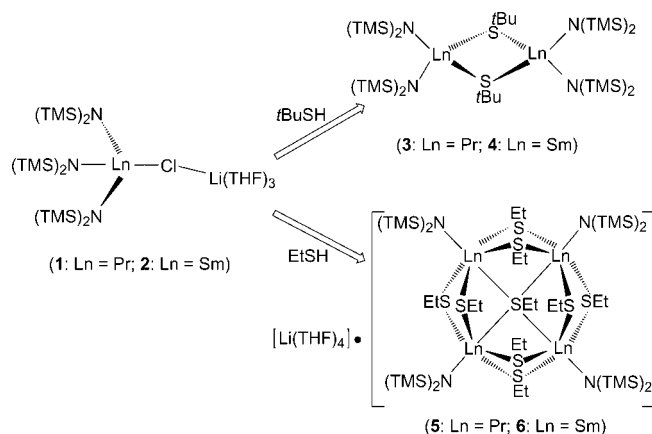
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Sm) were isolated therefrom. Compounds **3–6** did exhibit better catalytic activity in the ROP of ϵ -caprolactone than their benzenethiolate analogues. Herein, we report the synthesis, crystal structures and catalytic properties of **3–6**.

Results and Discussion

Treatment of a thf solution of **1** with an equimolar amount of *t*BuSH in thf at ambient temperature led to a yellow solution. After removal of all the volatile species in vacuo, the residue was extracted with toluene and *n*-hexane, and the insoluble LiCl precipitate was filtered off. The filtrate was allowed to stand at 2 °C for three days, which resulted in the formation of yellow crystals of **3·2(thf)_{0.5}** in 43% yield. Analogous reactions of **2** with an equimolar amount of *t*BuSH in thf gave rise to **4** in 40% yield (Scheme 1). Reactions of a thf solution of **1** or **2** in thf with an equimolar amount of EtSH at room temperature followed by a standard workup afforded **5·0.5C₇H₈** in 21% yield or **6·C₆H₆** in 17% yield, respectively (Scheme 1). The preparation of **5** and **6** was reproducible, though their yields were relatively low, which may be due to the formation of a large amount of insoluble material during the preparation. The yield of the two corresponding reactions decreased when **1** or **2** was treated with 2–3 equiv. of EtSH. Even at –20 °C, the formation of **5** or **6** was not observed, but a large amount of insoluble material was always isolated.



Scheme 1.

The protonolysis reactions of **1** and **2** with PhSH, *t*BuSH or EtSH deserve comments. Treatment of **1** or **2** with an equimolar amount of PhSH gave rise to a polymeric complex $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2(\mu\text{-SPh})\text{Pr}(\mu\text{-SPh})\text{Li}(\text{thf})_2]_\infty$ and a tetranuclear wine-cup-shaped complex $[\{(\text{Me}_3\text{Si})_2\text{N}\}_4(\mu_4\text{-Cl})\text{Sm}_4(\mu\text{-SPh})_4(\mu_3\text{-Cl})_4\text{Li}(\text{thf})]$, respectively, whereas the reaction of **1** with *t*BuSH or EtSH produced binuclear complexes **3** and **4** or tetranuclear cationic complexes **5** and **6**. The remarkable difference in the outcome of these reactions may be related to the steric effects of the R organic group ($i\text{Bu} > \text{Ph} > \text{Et}$) bound to the S atom in the resulting structures. It is assumed that in the case of thiols that bear larger

R groups (e.g. *t*Bu), the formation of a structure similar to that of the tetranuclear lanthanide thiolate complexes (e.g. **5** and **6**), described later in this paper, may cause the *t*Bu groups around the Ln_4 ring to become more crowded. Therefore, reactions of **1** or **2** with *t*BuSH seem to prefer the formation of smaller complexes **3** and **4**. Another reason for the formation of complexes with larger Ln nuclearity may be ascribed to the incorporation of Li^+ and/or Cl^- ions into their structures.^[6a] In the cases of **5** and **6**, the larger $[\text{Li}(\text{thf})_4]^+$ cation that is incorporated into their structures may to some extent stabilize the larger $[\{(\text{Me}_3\text{Si})_2\text{N}\}_4\text{Ln}_4(\mu_4\text{-SEt})(\mu\text{-SEt})_8]^-$ anion by ionic interactions.

Compounds **3–6** are extremely air- and moisture-sensitive, and they are readily soluble in dme, thf and toluene; they are also slightly soluble in *n*-hexane. Elemental analyses of **3–6** are consistent with the proposed formulas. The ^1H NMR spectra in C_6D_6 at room temperature shows the correct $(\text{Me}_3\text{Si})_2\text{N}^-/\text{S-}i\text{Bu}^-$ proton ratios for **3** and **4** and the correct $(\text{Me}_3\text{Si})_2\text{N}^-/\text{SEt}^-/\text{thf}$ proton ratio for **5**, though the proton signals of the $(\text{Me}_3\text{Si})_2\text{N}^-$ and SEt^- or $\text{S-}i\text{Bu}^-$ ligands are shifted significantly upfield owing to the paramagnetism of these complexes. The ^1H NMR spectrum of **6** contains broad uninterpretable signals that give no useful information about the solution behaviour of this paramagnetic complex. The identities of **3–6** were finally confirmed by X-ray crystallography.

Compound **3·2(thf)_{0.5}** crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit contains half of the $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Pr}(\mu\text{-S-}i\text{Bu})]_2$ molecule and two halves of solvated thf molecules, whereas **4** crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit contains half of the $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Sm}(\mu\text{-S-}i\text{Bu})]_2$ molecule. As the molecular structures of **3** and **4** are very similar, only that of **3** is showed in Figure 1. Their selected bond lengths and angles are compared in Table 1.

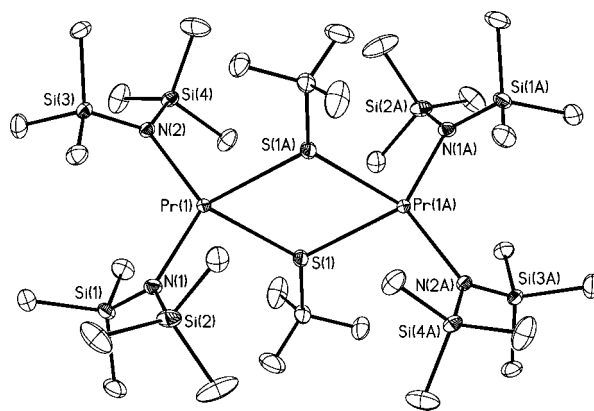


Figure 1. Perspective view of **3** with labelling scheme and 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

Compounds **3** or **4** consists of two $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Ln}]$ moieties interconnected by a pair of $\mu\text{-S-}i\text{Bu}$ anions to form a dimeric structure with a crystallographic centre of symmetry at the midpoint of the $\text{Ln}(1)$ and $\text{Ln}(1\text{A})$ atoms. Although the Pr_2S_2 core structure in **3** is uncommon in Pr^{III} thiolate complexes, the analogous Sm_2S_2 core structure in

Table 1. Selected bond lengths [Å] and angles [°] for **3** and **4**.^[a]

	Ln = Pr (3)	Ln = Sm (4)
Ln(1)–N(1)	2.292(3)	2.272(8)
Ln(1)–N(2)	2.303(3)	2.233(9)
Ln(1)–S(1)	2.8704(17)	2.786(3)
Ln(1)–S(1A)	2.8579(13)	2.844(3)
N(1)–Ln(1)–N(2)	114.43(13)	113.7(3)
N(1)–Ln(1)–S(1A)	131.27(10)	137.1(2)
N(2)–Ln(1)–S(1A)	103.28(9)	103.9(2)
N(1)–Ln(1)–S(1)	99.84(9)	103.2(2)
N(2)–Ln(1)–S(1)	135.75(9)	121.9(2)
S(1A)–Ln(1)–S(1)	69.61(5)	71.54(9)
C(13)–S(1)–Ln(1A)	119.97(15)	128.6(4)
C(13)–S(1)–Ln(1)	129.64(15)	122.9(4)
Ln(1)–S(1)–Ln(1A)	110.39(5)	108.46(9)

[a] Symmetry code: A: $-x+2, -y+2, -z+1$ for **3**; $-x, -y, -z+1$ for **4**.

4 is found in some known dinuclear Sm^{III} complexes such as $[(\text{thf})_3\text{I}_2\text{Sm}(\mu\text{-SC}_6\text{H}_4(\text{Me}_2\text{N})\text{-4})_2]_2$,^[8] $[(\text{C}_8\text{H}_8)\text{Sm}(\mu\text{-SPh})(\text{thf})_2]_2$,^[9] $[\text{Sm}(\text{C}_8\text{H}_8)(\text{thf})(\mu\text{-SC}_6\text{H}_2\text{iPr}_3\text{-2,4,6})_2]_2$,^[9] $[\text{Sm}(\text{SC}_6\text{H}_2\text{iPr}_3\text{-2,4,6})(\text{thf})_3(\mu\text{-SC}_6\text{H}_2\text{iPr}_3\text{-2,4,6})_2]^{[10]}$ and $[\text{Sm}(\text{SC}_6\text{F}_5)_2(\text{thf})(\mu\text{-SC}_6\text{F}_5)]_2$.^[11] The Ln(1)⋯Ln(1A) separation within the dimer in **3** or **4** is 4.703 or 4.568 Å, respectively, which is too long to include any metal–metal interaction. Each Ln centre in **3** or **4** is coordinated by two S atoms from two $\mu\text{-SiBu}^-$ anions and two N atoms from two $[\text{N}(\text{SiMe}_3)_2]^-$ anions to form a distorted tetrahedral geometry.

In the Pr_2S_2 rhomb of **3**, the two Pr–S bond lengths are unsymmetrical with Pr(1)–S(1) of 2.870(17) Å and Pr(1)–S(1A) of 2.858(13) Å. The mean Pr–S bond length of 2.864(15) Å is comparable to that in $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2(\mu\text{-SPh})\text{-Pr}(\mu\text{-SPh})\text{Li}(\text{thf})_2]_n$ [2.831(5) Å].^[6a] The mean Pr–N bond length [2.298(3) Å] is close to that in $[\{(\text{Me}_3\text{Si})_2\text{N}\}_2(\mu\text{-SPh})\text{-Pr}(\mu\text{-SPh})\text{Li}(\text{thf})_2]_n$ [2.312(5) Å],^[6a] but slightly shorter than those found in $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Pr}(\mu\text{-Cl})\text{Li}(\text{thf})_3$ [2.359(3) Å]^[7b] and $[\text{Pr}\{\text{N}(\text{SiMe}_3)_2\}_4][\text{K}(\text{thf})_6]$ [2.428(5) Å].^[12]

In the Sm_2S_2 ring of **4**, the two Sm–S distances are also not equal [2.786(3) Å and 2.844(3) Å]. The average distance [2.815(3) Å] is close to those found in $[\text{Li}(\text{tmeda})_2][\text{Cp}^*\text{Sm}(\text{SC}\equiv\text{CPh})_2]$ [2.794(4) Å]^[5] and $\{(\text{Cp}_2\text{Sm})_2\text{Mo}(\mu\text{-S})_4\}(\text{PPh}_4)$ [2.785(3) Å],^[13] but slightly shorter than that in $[\text{Sm}(\text{C}_8\text{H}_8)(\text{thf})(\mu\text{-SC}_6\text{H}_2\text{iPr}_3\text{-2,4,6})_2]$ [2.881(5) Å].^[9] The mean Sm–N bond length [2.252(8) Å] is somewhat shorter than those in four-coordinate Sm^{III} complexes $\text{SmL}[\text{N}(\text{SiMe}_3)_2]_2$ {2.350(3) Å, L = *N*-*tert*-butyl-*N*-[2-(*tert*-butylamino)ethyl]imidazolyldiene}^[14] and $\text{Sm}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})_2$ [2.432(2) Å].^[15]

Having a common chemical formula $[\text{Li}(\text{thf})_4][\{(\text{Me}_3\text{Si})_2\text{N}\}_4\text{Ln}_4(\mu_4\text{-SEt})(\mu\text{-SEt})_8]$, **5**·0.5C₇H₈ and **6**·C₆H₆ crystallize in the monoclinic space group $P2_1/c$ with half of one toluene solvated molecule (**5**), and one benzene solvated molecule (**6**). As the structures of the $[\{(\text{Me}_3\text{Si})_2\text{N}\}_4\text{Ln}_4(\mu_4\text{-SEt})(\mu\text{-SEt})_8]^-$ anions in **5** and **6** are essentially identical, we only show the perspective view of the anion of **5** in Figure 2. The pertinent bond lengths and angles for **5** and **6** are compared in Table 2.

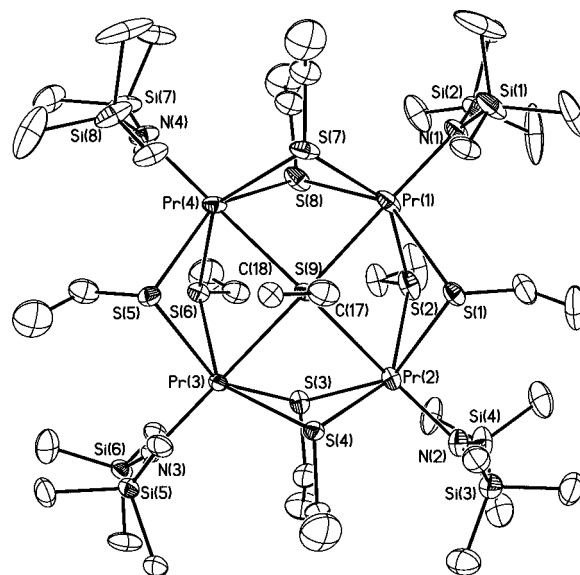


Figure 2. Perspective view of the anion of **5**, where only the disordered C(19)–C(20) atoms with a site occupancy factor of 0.45 are shown. The thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms are omitted for clarity.

The structures of the anions of **5** and **6** have a square-like Ln_4 array that is linked by four pairs of SEt^- ligands and is capped by a $\mu_4\text{-SEt}^-$ ligand above the Ln_4 plane (0.919 Å for **5** and 0.953 Å for **6**). This structure resembles that of $[(\text{thf})_6\text{Yb}_4(\mu_4\text{-S})(\mu\text{-}\eta^2\text{-}\eta^2\text{-S}_2)_4(\text{SC}_6\text{F}_5)_2]_2$,^[16a] $[(\text{thf})_6\text{Yb}_4(\mu_4\text{-S})(\mu\text{-}\eta^2\text{-}\eta^2\text{-S}_2)_4\text{I}_2]$,^[16b] and $[\text{Li}\{(\text{Me}_3\text{Si})_2\text{N}\}_4\text{Nd}_4(\mu_4\text{-Cl})(\mu\text{-SPh})_8\cdot\text{C}_6\text{H}_6]$,^[6a] which comprises a square array of Ln^{III} ions connected by four $\mu\text{-}\eta^2\text{-}\eta^2\text{-S}_2$ ligands or four pairs of SPh^- ligands and capped by a $\mu_4\text{-S}^{2-}$ or $\mu_4\text{-Cl}^-$ ion above the Ln_4 plane. It is noted that the symmetries of the structures of these compounds with the Ln_4 core are quite different owing to the different periphery bridging ligands and capping ligands. The structure of the anion of $[\text{Li}\{(\text{Me}_3\text{Si})_2\text{N}\}_4\text{Nd}_4(\mu_4\text{-Cl})(\mu\text{-SPh})_8\cdot\text{C}_6\text{H}_6]$ shows an approximate S_4 symmetry whereas those of $[(\text{thf})_6\text{Yb}_4(\mu_4\text{-S})(\mu\text{-}\eta^2\text{-}\eta^2\text{-S}_2)_4(\text{SC}_6\text{F}_5)_2]$ and $[(\text{thf})_6\text{Yb}_4(\mu_4\text{-S})(\mu\text{-}\eta^2\text{-}\eta^2\text{-S}_2)_4\text{I}_2]$ have an approximate C_{2v} symmetry. However, the symmetry of the anions of **5** and **6** is C_2 because of a $\mu_4\text{-SEt}^-$ ligand capping onto the Ln_4 core. Although thiolates serving as a quadruply bridging ligand are found in several transition- or main group metal–thiolate clusters such as $[\text{Ag}_8(\mu_4\text{-SC}_2\text{H}_4\text{-NH}_3)_6\text{Cl}_6\text{Cl}_2]_n$,^[17a] $[\text{Cu}_7\{\mu_4\text{-SCH}_2\text{CH}_2\text{NH}(\text{CH}_3)_2\}_6(\mu_3\text{-Cl})_2(\mu\text{-Cl})_{13}\text{Cl}_2]_n$,^[17b] $[\text{Cu}_4(\mu\text{-dppm})_4(\mu\text{-NS}_2)(\mu_4\text{-NS}_2)]\cdot\text{CH}_2\text{Cl}_2$,^[17c] and $[\{\text{Ti}_7(\mu_4\text{-Sthff})_6\}_2(\text{PF}_6)_2]_n$ (HStff = tetrahydrofurfuryl-thiol),^[17d] the existence of a $\mu_4\text{-SEt}^-$ ligand in **5** and **6** is unprecedented in the chemistry of lanthanide chalcogenolate complexes.

Each Ln centre in **5** and **6** is coordinated by one N atom from the $[\text{N}(\text{SiMe}_3)_2]^-$ anion and one $\mu_4\text{-S}$ atom and four $\mu\text{-S}$ atoms from the EtS^- ligands to form a distorted octahedral coordination geometry. The mean Ln– $\mu_4\text{-S}$ bond length, 3.089(3) Å for **5** and 3.029(3) Å for **6**, is much longer than the corresponding Ln– $\mu\text{-S}$ bonds, which correlates with the number of bonding interactions at the Ln centres.

Table 2. Selected bond lengths [Å] and angles [°] for **5** and **6**.

	Ln = Pr (5)	Ln = Sm (6)		Ln = Pr (5)	Ln = Sm (6)
Ln(1)–N(1)	2.317(10)	2.271(10)	Ln(3)–S(3)	2.895(3)	2.813(5)
Ln(2)–N(2)	2.314(12)	2.262(13)	Ln(3)–S(4)	2.916(3)	2.831(4)
Ln(3)–N(3)	2.303(9)	2.280(11)	Ln(3)–S(5)	2.871(3)	2.795(4)
Ln(4)–N(4)	2.316(12)	2.304(13)	Ln(3)–S(6)	2.860(3)	2.846(5)
Ln(1)–S(1)	2.892(4)	2.828(4)	Ln(4)–S(5)	2.859(4)	2.819(5)
Ln(1)–S(2)	2.865(5)	2.861(4)	Ln(4)–S(6)	2.872(3)	2.842(4)
Ln(1)–S(7)	2.892(5)	2.822(4)	Ln(4)–S(7)	2.902(4)	2.809(4)
Ln(1)–S(8)	2.865(4)	2.807(4)	Ln(4)–S(8)	2.869(4)	2.818(4)
Ln(2)–S(1)	2.870(3)	2.794(4)	Ln(1)–S(9)	3.057(3)	3.013(3)
Ln(2)–S(2)	2.866(4)	2.835(4)	Ln(2)–S(9)	3.163(3)	3.092(4)
Ln(2)–S(3)	2.851(3)	2.809(4)	Ln(3)–S(9)	3.079(3)	3.012(3)
Ln(2)–S(4)	2.894(3)	2.820(4)	Ln(4)–S(9)	3.058(3)	2.998(3)
N(1)–Ln(1)–S(1)	98.9(3)	112.2(3)	S(5)–Ln(3)–S(9)	74.58(9)	82.98(10)
N(1)–Ln(1)–S(2)	114.3(4)	101.2(3)	S(6)–Ln(3)–S(3)	80.07(10)	147.81(12)
N(1)–Ln(1)–S(7)	98.3(4)	96.2(3)	S(6)–Ln(3)–S(4)	138.74(9)	111.83(12)
N(1)–Ln(1)–S(8)	114.5(3)	117.0(3)	S(6)–Ln(3)–S(5)	70.06(10)	77.01(14)
N(1)–Ln(1)–S(9)	156.9(3)	157.3(3)	S(6)–Ln(3)–S(9)	77.69(8)	68.16(10)
S(1)–Ln(1)–S(9)	70.95(9)	84.62(10)	S(8)–Ln(4)–S(9)	81.65(11)	79.63(10)
S(2)–Ln(1)–S(1)	70.39(11)	77.61(11)	N(4)–Ln(4)–S(5)	95.4(3)	114.4(4)
S(2)–Ln(1)–S(7)	146.87(11)	114.69(11)	N(4)–Ln(4)–S(6)	120.1(3)	97.7(3)
S(2)–Ln(1)–S(9)	82.51(9)	66.46(9)	N(4)–Ln(4)–S(7)	98.0(3)	95.6(4)
S(8)–Ln(1)–S(2)	83.85(14)	141.11(11)	N(4)–Ln(4)–S(8)	115.2(3)	118.5(3)
S(7)–Ln(1)–S(1)	111.83(10)	146.70(12)	N(4)–Ln(4)–S(9)	156.0(3)	155.6(3)
S(7)–Ln(1)–S(9)	68.26(3)	73.88(10)	S(5)–Ln(4)–S(6)	70.05(9)	76.69(14)
S(8)–Ln(1)–S(1)	144.26(11)	81.06(12)	S(5)–Ln(4)–S(7)	115.85(11)	146.42(13)
S(8)–Ln(1)–S(7)	77.03(13)	70.38(11)	S(5)–Ln(4)–S(8)	145.65(12)	81.66(13)
S(8)–Ln(1)–S(9)	81.74(9)	79.54(10)	S(5)–Ln(4)–S(9)	75.07(9)	82.84(12)
S(4)–Ln(2)–S(9)	64.67(8)	69.94(10)	S(8)–Ln(4)–S(7)	76.81(12)	70.41(11)
N(2)–Ln(2)–S(1)	103.7(3)	106.5(3)	S(6)–Ln(4)–S(7)	141.31(12)	115.55(12)
N(2)–Ln(2)–S(2)	106.7(3)	106.6(4)	S(6)–Ln(4)–S(9)	77.85(8)	68.41(10)
N(2)–Ln(2)–S(3)	106.0(3)	106.9(4)	S(7)–Ln(4)–S(9)	68.10(9)	74.31(10)
N(2)–Ln(2)–S(4)	109.0(3)	102.8(3)	S(8)–Ln(4)–S(6)	80.69(11)	143.12(13)
N(2)–Ln(2)–S(9)	168.3(3)	166.2(3)	Ln(1)–S(9)–Ln(4)	84.90(7)	85.98(9)
S(1)–Ln(2)–S(4)	103.31(10)	147.93(12)	Ln(3)–S(9)–Ln(2)	83.08(7)	84.47(9)
S(1)–Ln(2)–S(9)	69.68(9)	83.73(10)	Ln(1)–S(9)–Ln(3)	146.84(10)	144.39(11)
S(2)–Ln(2)–S(1)	70.69(11)	78.61(11)	Ln(4)–S(9)–Ln(3)	86.41(8)	84.16(8)
S(2)–Ln(2)–S(4)	144.14(12)	105.36(11)	Ln(1)–S(9)–Ln(2)	85.35(8)	82.68(8)
S(2)–Ln(2)–S(9)	80.64(11)	65.69(9)	Ln(4)–S(9)–Ln(2)	143.93(9)	142.21(11)
S(3)–Ln(2)–S(1)	147.49(11)	88.04(13)	N(3)–Ln(3)–S(5)	95.8(2)	113.1(3)
S(3)–Ln(2)–S(2)	88.34(11)	146.31(13)	N(3)–Ln(3)–S(9)	158.7(2)	156.9(3)
S(3)–Ln(2)–S(4)	79.06(9)	71.00(12)	S(3)–Ln(3)–S(4)	77.99(9)	70.80(12)
S(3)–Ln(2)–S(9)	82.91(8)	82.32(12)	S(3)–Ln(3)–S(9)	83.69(9)	83.72(11)
N(3)–Ln(3)–S(3)	112.6(2)	113.2(4)	S(4)–Ln(3)–S(9)	65.54(8)	71.00(10)
N(3)–Ln(3)–S(4)	103.2(2)	98.8(3)	S(5)–Ln(3)–S(3)	146.00(10)	84.54(15)
N(3)–Ln(3)–S(6)	117.5(2)	98.4(4)	S(5)–Ln(3)–S(4)	114.51(10)	145.53(12)

The average Pr–μ-S bond length [2.877(3) Å] in **5** is the same as that in Pr[S₂P(C₆H₁₁)₂]₃ [S₂P(C₆H₁₁)₂ = dicyclohexyldithiophosphinate, 2.877(4) Å].^[18] The mean Sm–μ-S bond length [2.822(4) Å] in **6** is comparable to those found in [(Me₃Si)₂N]₄(μ₄-Cl)Sm₄(μ-SPh)₄(μ₃-Cl)₄Li(thf)] [2.822(4) Å],^[6a] [(thf)Sm(SPh)₃]_{4n} [2.854(3) Å]^[19] and [Sm{O=P(NMe₂)₃}(SPh)₃] [2.830(2) Å].^[20] The mean Pr–N bond length [2.312(10) Å] in **5** is smaller than that reported in Pr[Et₂NCH₂CH₂NC(Me)CHC(Me)NCH₂CH₂Net₂]Cl₂ [2.5702(3) Å],^[21] whereas the length of the Sm–N bonds [2.279(12) Å] in **6** is between those of [(Me₃Si)₂N]₄(μ₄-Cl)Sm₄(μ-SPh)₄(μ₃-Cl)₄Li(thf)] [2.211(3) Å]^[6] and [(Me₃Si)₂-NSm(μ-Cl)₂Li(thf)₂](μ-Cl)₂ [2.284(4) Å].^[22]

Weak coordination of a soft-base sulfur atom to a hard-acid Ln centre in lanthanide thiolate complexes is known to be the cause for their catalytic behaviour in the ROP of ε-

caprolactone.^[23,6] Therefore, compounds **3–6** (Table 3) were employed to initiate the ROP of ε-caprolactone at ambient temperature. When the polymerization was performed in thf/toluene, a highly viscous product was observed to form in less than 10 min. After the resulting polymers were quenched by the addition of 1 M HCl in EtOH, the poly(ε-caprolactone)s were isolated as white solids and characterized by gel permeation chromatography. Compounds **3–6** were found to initiate the ROP of ε-caprolactone at room temperature to give relatively high molecular weight polymers (*M_n* > 13400) with narrow molecular weight distributions (*M_w*/*M_n* = 1.17–1.56) in good yields within a few minutes. For comparison, Table 3 lists the results for the ROP of ε-caprolactone initiated by **1–6** along with two known Pr^{III} and Sm^{III} benzenethiolate complexes, [(Me₃Si)₂N]₄(μ₄-Cl)Sm₄(μ-SPh)₄(μ₃-Cl)₄Li(thf)] (**7**) and [(Me₃Si)₂N]-

Table 3. Polymerization of ϵ -caprolactone catalyzed by **3–6**.

Entry ^[a]	Catalyst	Time [min]	[Monomer]/[cat.]	Yield ^[b]	M_n [$\times 10^4 \text{ g mol}^{-1}$]	M_w [$\times 10^4 \text{ g mol}^{-1}$]	M_w/M_n ^[c]	Ref.
1	1	20	400	59	2.71	5.55	2.05	[6b]
2	2	20	400	46	2.93	5.83	1.99	[6b]
3	3	1	400	100	6.31	9.12	1.44	this work
4	4	1	400	100	4.13	6.30	1.53	this work
5	4	2	100	100	1.77	2.76	1.56	this work
6	5	1	400	100	4.50	5.55	1.23	this work
7	5	2	800	100	1.34	1.70	1.27	this work
8	6	2	400	100	5.34	6.42	1.20	this work
9	6	9	600	100	2.42	2.83	1.17	this work
10	7	8	400	99	3.41	4.94	1.45	[6a]
11	7	15	600	75	3.33	5.09	1.53	[6a]
12	8	20	400	99	2.61	3.70	1.42	[6a]

[a] Temperature: 298 K; solvent: thf/toluene (1:4); $V_{\epsilon\text{-caprolactone}}:V_{\text{solvent}} = 1:5$. [b] Yield: weight of polymer obtained/weight of monomer used. [c] Determined by GPC analysis in thf, calibrated to a polystyrene standard.

$(\mu\text{-SPh})\text{Pr}(\mu\text{-SPh})\text{Li}(\text{thf})_2)_n$ (**8**).^[6a] Complexes **3–6** showed better catalytic activity than their precursors, **1** and **2**, which may be ascribed to the weak Ln–S bonds in **3–6**.^[2g,2i,6] In addition, complexes **5** and **6** showed even better catalytic activity than complexes **3** and **4** under the same reaction conditions, which might be due to the fact that **3** and **4** have a less open coordination environment around the Ln metal (coordination number four) than **5** and **6**. Complex **3** and its Pr^{III} /benzenethiolate complex **8** had similar catalytic activity for the ROP of ϵ -caprolactone. In the case of [monomer]/[cat.] = 600, **6** initiated the polymerization of ϵ -caprolactone at a faster rate than its benzenethiolate analogue **7**. The former reaction was complete in 9 min with a 100% yield whereas the latter was complete in 15 min with a 75% yield. Therefore, we tentatively ascribed this difference to the fact that the SEt^- anions may be more easily dissociated from the Ln^{III} centres in **6** than the SPh^- and Cl^- anions in **7**.

Conclusions

In summary, the protonolysis reaction of **1** or **2** with an equimolar amount of *t*BuSH or EtSH was studied and amidolanthanide alkylthiolate complexes **3–6** were isolated in reasonable yields. Compounds **3–6** were characterized by elemental analysis, IR spectroscopy and X-ray analysis. Compounds **3** and **4** contain a Ln_2S_2 core structure whereas **5** and **6** consist of a square Ln_4 array with one SEt^- ligand capping above the mean Ln_4 plane. Occurrence of a $\mu_4\text{-SEt}^-$ ligand in the structures of **5** and **6** is rare in the chemistry of lanthanide chalcogenolate complexes. Compounds **3–6** showed better catalytic activity in the ROP of ϵ -caprolactone than their precursors **1** and **2** and their benzenethiolate analogues. It is anticipated that **1** or **2** could react with other thiols such as 1,2-diethanedithiol or cationic thiol TabHPF_6 [TabH = 4-(trimethylammonio)benzenethiol] to afford other lanthanide thiolate complexes with more interesting structural frameworks and better catalytic activities in the ROP of ϵ -caprolactone. Studies on these respects are underway in this laboratory.

Experimental Section

All manipulations were carried out under an atmosphere of argon by using standard Schlenk techniques. All solvents were heated at reflux and distilled from sodium benzophenone ketyl under an atmosphere of argon prior to use. $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{thf})_3$ (**1**: Ln = Pr; **2**: Ln = Sm),^[7] LnCl_3 ^[23] and $\text{Li}(\text{SiMe}_3)_2$ ^[24] were prepared according to literature methods. *t*BuSH and EtSH were obtained from commercial sources and used as received. ϵ -Caprolactone, purchased from ACROS Com, was dried by stirring with CaH_2 for 8 d and then distilled under reduced pressure. ^1H NMR spectra were recorded at ambient temperature with a Varian UNITYplus-400 spectrometer. ^1H NMR chemical shifts were referenced to the solvent signal in C_6D_6 . Elemental analyses for C, H and N were performed with a Carlo-Erbo CHNO-S microanalyzer. The IR spectra were recorded with a Nicolet MagNa-IR550 FTIR spectrometer (4000–400 cm^{-1}). Molecular weight and molecular weight distributions were determined against a polystyrene standard by gel permeation chromatography (GPC) with a Waters 1515 apparatus with three HR columns (HR-1, HR-2 and HR-4); thf was used as an eluent.

$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Pr}(\mu\text{-}i\text{Bu})_2$ (3**):** A solution of *t*BuSH (2.09 mmol) in thf (1.65 mL) was slowly added to a solution of **1** (1.31 g, 2.09 mmol) in thf (20 mL). The mixture was stirred at room temperature for 2 h, and then the solution was concentrated to dryness in vacuo. The resulting solid was extracted with *n*-hexane (10 mL) and toluene (20 mL) and then filtered. Compound **3**·2(thf)_{0.5} (1.05 g, 43%) was isolated as light yellow crystals by cooling the filtrate to 2 °C for 3 d. ^1H NMR (400 MHz, C_6D_6): $\delta = -7.17$ [br. s, $w_{1/2} = 40$ Hz, 18 H, $\text{C}(\text{CH}_3)_3$], -10.92 [br. s, $w_{1/2} = 200$ Hz, 72 H, $\text{Si}(\text{CH}_3)_3$] ppm. IR (KBr disc): $\tilde{\nu} = 2960$ (s), 2902 (m), 1635 (m), 1385 (m), 1260 (s), 1189 (s), 1079 (m), 938 (s), 845 (s), 608 (w) cm^{-1} . $\text{C}_{36}\text{H}_{98}\text{N}_4\text{Pr}_2\text{S}_2\text{OSi}_8$ (1173.86): calcd. C 36.83, H 8.42, N 4.77; found C 36.56, H 8.01, N 4.43.

$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sm}(\mu\text{-}i\text{Bu})_2$ (4**):** Compound **4** (0.78 g, 40%) was isolated as light yellow crystals from the reaction of **2** (1.12 g, 1.75 mmol) with *t*BuSH (1.75 mmol) in thf followed by a similar workup to that used in the isolation of **3**. ^1H NMR (400 MHz, C_6D_6): $\delta = -0.90$ [br. s, $w_{1/2} = 32$ Hz, 18 H, $\text{C}(\text{CH}_3)_3$], -2.00 [br. s, $w_{1/2} = 9$ Hz, 72 H, $\text{Si}(\text{CH}_3)_3$] ppm. IR: $\tilde{\nu} = 2962$ (s), 2903 (m), 1632 (m), 1385 (m), 1258 (s), 1185 (s), 1084 (m), 938 (s), 848 (s), 613 (w) cm^{-1} . $\text{C}_{32}\text{H}_{90}\text{N}_4\text{S}_2\text{Si}_8\text{Sm}_2$ (1120.66): calcd. C 37.89, H 8.42, N 4.42; found C 37.56, H 8.01, N 4.93.

[Li(thf)₄][{(Me₃Si)₂N}₄Pr₄(μ₄-SEt)(μ-SEt)₈] (5): A solution of EtSH (1.85 mmol) in thf (0.88 mL) was added dropwise to a solution of **1** (1.12 g, 1.85 mmol) in thf (20 mL). After stirring at room temperature for 3 h, the volatile species were removed in vacuo, and the crude product was extracted with toluene (20 mL) and then filtered. The filtrate was kept at 2 °C for one week, which resulted in the formation of light yellow crystals of **5**·0.5C₇H₈ (0.440 g, 21%). ¹H NMR (400 MHz, C₆D₆): δ = 3.25 (s, 32 H, thf), 1.27 (br. s, w_{1/2} = 20 Hz, 27 H, CH₃), 0.71 (br. s, w_{1/2} = 36 Hz, 18 H, CH₂), -1.45 [br. s, w_{1/2} = 40 Hz, 72 H, Si(CH₃)₃] ppm. IR: ν̄ = 2961 (s), 2901 (m), 2184 (w), 1658 (m), 1520 (s), 1475 (s), 1385 (s), 1256 (s), 1179 (s), 1048 (m), 992 (m), 949 (s), 841 (s), 756 (m), 604 (s) cm⁻¹. C_{61.5}H₁₅₃LiN₄O₄Pr₄S₉Si₈ (2088.66): calcd. C 35.23, H 7.36, N 2.67; found C 35.58, H 7.42, N 2.19.

[Li(thf)₄][{(Me₃Si)₂N}₄Sm₄(μ₄-SEt)(μ-SEt)₈] (6): A solution of EtSH (2.02 mmol) in thf (0.96 mL) was added dropwise to a solution of **2** (1.29 g, 2.02 mmol) in thf (20 mL). After stirring at room temperature for 3 h, the volatile species were removed in vacuo, and the crude product was extracted with benzene (20 mL) and then filtered. The filtrate was kept at 2 °C for one week, which resulted in the formation of light yellow crystals of **6**·C₆H₆ (0.368 g, 17%). The ¹H NMR spectrum in C₆D₆ showed broad uninterpretable signals. IR: ν̄ = 2962 (s), 2905 (m), 2183 (w), 1655 (m), 1518 (s), 1482 (s), 1385 (s), 1248 (s), 1181 (s), 1053 (m), 995 (m), 937 (s), 841 (s), 753 (m), 610 (s) cm⁻¹. C₆₄H₁₅₅LiN₄O₄S₉Si₈Sm₄ (2158.59): calcd. C 36.61, H 6.86, N 2.60; found C 37.06, H 7.21, N 2.43.

Crystal Structure Determination and Refinement: All measurements were recorded with a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) at 193 K by using graphite monochromated Mo-K_α (λ = 0.71070 Å) light. X-ray quality crystals of **3**·2(thf)_{0.5}, **4**, **5**·0.5C₇H₈ and **6**·C₆H₆ were obtained directly from the above preparations. A light yellow chunk of **3**·2(thf)_{0.5} with dimensions 0.45 × 0.40 × 0.30 mm, a light yellow prism of **4** with dimensions 0.40 × 0.35 × 0.10 mm, a light yellow prism of **5**·0.5C₇H₈ with dimensions 0.22 × 0.47 × 0.30 mm and a light yellow prism of **6**·C₆H₆

with dimensions 0.14 × 0.50 × 0.30 mm were mounted in a sealed capillary, respectively. Diffraction data were collected with the ω mode with a detector distance of 35 mm to the crystals. A total of 720 oscillation images for each were collected in the range 6.04° < 2θ < 50.70° for **3**·2(thf)_{0.5}, 6.28° < 2θ < 50.70° for **4**, 6.10° < 2θ < 50.70° for **5**·0.5C₇H₈ and 6.18° < 2θ < 50.70° for **6**·C₆H₆. The collected data were reduced by using the program CrystalClear (Rigaku and MSC, ver. 1.3, 2001), and an absorption correction (multi-scan) was applied, which resulted in transmission factors ranging from 0.385 to 0.485 for **3**·2(thf)_{0.5}, from 0.406 to 0.799 for **4**, from 0.440 to 0.618 for **5**·0.5C₇H₈ and from 0.359 to 0.694 for **6**·C₆H₆. The reflection data were also corrected for Lorentz and polarization effects.

The structures of **3**·2(thf)_{0.5}, **4**, **5**·0.5C₇H₈, and **6**·C₆H₆ were solved by direct methods^[25] and refined by full-matrix least-squares on F².^[26] When crystals **3**·2(thf)_{0.5} and **5**·0.5C₇H₈ were taken away from their mother liquors, rapid evaporation of part of the solvated molecules in these crystals was observed. Although we made numerous attempts, these crystals were always weakly diffracting, especially at high angles, which made the final R value relatively higher. In addition, in the structures of **3**·2(thf)_{0.5}, **5**·0.5C₇H₈ and **6**·C₆H₆, serious disorder problems derived from the solvated molecules and methyl groups from bis(trimethylsilyl)amide anions also contributed greatly to the high R value. Therefore, the thf and C₇H₈ molecules in **3**·2(thf)_{0.5} and **5**·0.5C₇H₈ were fixed with constrained parameters and refined with an occupancy factor of 0.5. For **5**·0.5C₇H₈, three methyl groups bearing C(19), C(20) and C(21) atoms were found to be disordered over two positions with an occupancy ratio of 0.45:0.55 for C(19)/C(19A), C(20)/C(20A) and C(21)/C(21A). In the case of **6**·C₆H₆, a number of methyl groups were found to be disordered over two sites with an occupancy factor of 0.58:0.42 for C(12)/C(12A) and C(16)/C(16A) and 0.54:0.46 for C(19)/C(19A), C(25)/C(25A), C(28)/C(28A), C(31)/C(31A), C(34)/C(34A), C(35)/C(35A), C(36)/C(36A), C(38)/C(38A) and C(41)/C(41A). All non-hydrogen atoms, except for those from thf

Table 4. Summary of Crystallographic data for **3**·2(thf)_{0.5}, **4**, **5**·0.5C₇H₈ and **6**·C₆H₆.

	3 ·2(thf) _{0.5}	4	5 ·0.5C ₆ H ₅ CH ₃	6 ·C ₆ H ₆
Empirical formula	C ₃₆ H ₉₈ N ₄ OPr ₂ S ₂ Si ₈	C ₃₂ H ₉₀ N ₄ S ₂ Si ₈ Sm ₂	C _{61.5} H ₁₄₅ LiN ₄ O ₄ Pr ₄ S ₉ Si ₈	C ₆₄ H ₁₄₇ LiN ₄ O ₄ S ₉ Si ₈ Sm ₄
Formula mass	1173.86	1120.66	2088.66	2158.59
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P1̄	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a [Å]	11.396(2)	12.067(2)	15.024(3)	15.039(3)
b [Å]	12.160(2)	11.313(2)	25.455(5)	25.445(5)
c [Å]	12.366(3)	23.486(7)	26.689(5)	26.357(5)
α [°]	109.74(3)			
β [°]	99.50(3)	119.30(2)	99.60(3)	91.19(3)
γ [°]	99.763(3)			
V [Å ³]	1543.3(7)	2790.0(12)	10206(3)	10084(3)
Z	1	2	4	4
D _{calcd.} [g cm ⁻³]	1.263	1.331	1.359	1.422
F(000)	612	1156	4276	4392
μ [Mo-K _α [cm ⁻¹]]	18.1	23.5	21.9	26.1
Total no. of reflections	14972	25926	99290	97851
No. of unique reflections	5595 (R _{int} = 0.0206)	5104 (R _{int} = 0.0919)	18652 (R _{int} = 0.0779)	18439 (R _{int} = 0.0839)
No. of obsd. reflections	5405 [I > 2.00σ(I)]	4397 [I > 2.00σ(I)]	13470 [I > 2.00σ(I)]	12599 [I > 2.00σ(I)]
No. of variables	249	217	726	706
R ₁ ^[a]	0.033	0.084	0.095	0.107
wR ₂ ^[b]	0.095	0.171	0.231	0.245
GOF ^[c]	0.987	1.178	1.089	1.437
Residual peaks [e Å ⁻³]	2.53, -1.21	2.72, -1.70	1.51, -2.03	2.16, -2.70

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$. [c] $GOF = \{\sum w(|F_o| - |F_c|)^2 / (n - p)\}^{1/2}$, where n is the number of reflections and p is total number of parameters refined.

solvent molecule in **3**·2(thf)_{0.5}, and those from C₆H₆ solvent molecule in **6**·C₆H₆, and those disordered C atoms in **5**·0.5C₇H₈, and part of disordered C atoms [C(12), C(16), C(19), C(25), C(28), C(31), C(38), C(41)] in **6**·C₆H₆ were refined anisotropically. Hydrogen atoms on C(43)–C(46) atoms in **5**·0.5C₆H₅CH₃ and C(43)–C(46) atoms in **6**·C₆H₆ were not located. All other hydrogen atoms were placed in geometrically idealized positions (C–H = 0.98 Å for methyl groups, C–H = 0.99 Å for methylene groups or C–H = 0.95 Å for phenyl groups) and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{C})$ for methyl groups. All the calculations were performed with a Dell workstation by using the CrystalStructure crystallographic software package (Rigaku and MSC, Ver.3.60, 2004). Crystal and data collection parameters for **3**·2(thf)_{0.5}, **4**, **5**·0.5C₇H₈ and **6**·C₆H₆ are summarized in Table 4.

CCDC-624794 (for **3**), -624795 (for **4**), -624796 (for **5**) and -624797 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

A Typical Procedure for the ROP of ϵ -Caprolactone: A 50-mL Schlenk flask equipped with a magnetic stir bar was charged with thf (0.33 mL), toluene (1.32 mL) and **5** (0.011 g). To this light yellow solution, ϵ -caprolactone (0.33 mL) was added at room temperature by using a syringe and with vigorous magnetic stirring. The stirring was ceased in a few minutes due to the viscosity. The reaction mixture was quenched by the addition of 1 M HCl in EtOH after a fixed interval. The solution was then poured into petroleum ether (20 mL) to precipitate the white oligomer. The resulting oligomer was washed with methanol three times, collected and dried in vacuo.

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- [1] a) F. Nief, *Coord. Chem. Rev.* **1998**, *13*, 178–179; b) Z. M. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1–22; c) A. Kornienko, T. J. Emge, G. A. Kumar, R. E. Riman, J. G. Brennan, *J. Am. Chem. Soc.* **2005**, *127*, 3501–3505; d) H. X. Li, Y. J. Zhu, M. L. Cheng, Z. G. Ren, J. P. Lang, Q. Shen, *Coord. Chem. Rev.* **2006**, *250*, 2059–2092.
- [2] a) E. Downing, L. Hesselink, J. Ralston, R. M. Macfarlane, *Science* **1996**, *273*, 1185–1189; b) A. Goldbach, M. L. Saboungi, *Acc. Chem. Res.* **2005**, *38*, 705–712; c) G. A. Kumar, R. E. Riman, L. A. D. Torres, O. B. Garcia, S. Banerjee, A. Kornienko, J. G. Brennan, *Chem. Mater.* **2005**, *17*, 5130–5135; d) G. S. Pomrenke, P. B. Klein, D. W. Langer, *Rare Earth Doped Semiconductors: MRS Symposium*, vol. 301, Materials Research Society, Pittsburgh, PA, **1993**; e) Q. Shen, H. R. Li, C. S. Yao, Y. M. Yao, L. L. Zhang, K. B. Yu, *Organometallics* **2001**, *20*, 3070–3073; f) J. Zhang, L. P. Ma, R. H. Cai, L. H. Weng, X. G. Zhou, *Organometallics* **2005**, *24*, 738–742; g) J. Y. Kim, T. Livinghouse, *Org. Lett.* **2005**, *7*, 1737–1739; h) Y. Nakayama, T. Shibahara, H. Fukumoto, A. Nakamura, K. Mashima, *Macromolecules* **1996**, *29*, 8014–8016; i) X. Y. Yu, G. X. Jin, N. H. Hu, L. H. Weng, *Organometallics* **2002**, *21*, 5540–5548; j) Z. Hou, Y. Zhang, H. Tezuka, P. Xie, O. Tardif, T. Koizumi, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* **2000**, *122*, 10533–10543; k) D. R. Cary, G. E. Ball, J. Arnold, *J. Am. Chem. Soc.* **1995**, *117*, 3492–3501.
- [3] a) H. C. Aspinall, S. A. Cunningham, *Inorg. Chem.* **1998**, *37*, 5396–5398; b) H. Sugiyama, Y. Hayashi, H. Kawaguchi, K. Tatsumi, *Inorg. Chem.* **1998**, *37*, 6773–6779; c) K. Tatsumi, T. Amemiya, H. Kawaguchi, K. Tani, *J. Chem. Soc., Chem. Commun.* **1993**, 773–774; d) S. D. Stults, R. A. Andersen, A. Zalkin, *Organometallics* **1990**, *9*, 1623–1629; e) Z. Z. Wu, W. W. Ma, Z. E. Huang, R. F. Cai, *Polyhedron* **1996**, *15*, 3427–3432; f) Z. Z. Wu, Z. E. Huang, R. F. Cai, X. G. Zhou, Z. Xu, X. Z. You, X. Y. Huang, *J. Organomet. Chem.* **1996**, *506*, 25–30; g) S. M. Cendrowski-Guillaume, G. L. Gland, M. Nierlich, M. Ephritikhine, *Organometallics* **2000**, *19*, 5654–5660; h) Y. R. Li, C. F. Pi, J. Zhang, X. G. Zhou, Z. X. Chen, L. H. Weng, *Organometallics* **2005**, *24*, 1982–1988.
- [4] H. C. Aspinall, D. C. Bradley, M. B. Hursthouse, K. D. Sales, N. P. C. Walker, *J. Chem. Soc., Chem. Commun.* **1985**, 1585–1586.
- [5] a) H. Schumann, I. Albrecht, E. Hahn, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 985–986; b) H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, *J. Organomet. Chem.* **1988**, *349*, 103–115.
- [6] a) H. X. Li, Z. G. Ren, Y. Zhang, W. H. Zhang, J. P. Lang, Q. Shen, *J. Am. Chem. Soc.* **2005**, *127*, 1122–1123; b) H. X. Li, Z. G. Ren, M. L. Cheng, W. H. Zhang, J. P. Lang, Q. Shen, *Inorg. Chem.* **2006**, *45*, 1885–1887.
- [7] a) S. L. Zhou, S. W. Wang, G. S. Yang, X. Y. Liu, E. H. Sheng, K. H. Zhang, L. Cheng, Z. X. Huang, *Polyhedron* **2003**, *22*, 1019–1024; b) M. H. Xie, X. Y. Liu, S. W. Wang, L. Liu, Y. Y. Wu, G. S. Yang, S. L. Zhou, E. H. Shen, Z. X. Huang, *Chin. J. Chem.* **2004**, *22*, 678–682.
- [8] H. X. Li, Y. Zhang, Z. G. Ren, M. L. Cheng, J. Wang, J. P. Lang, *Chin. J. Chem.* **2005**, *23*, 1499–1502.
- [9] K. Mashima, Y. Nakayama, N. Kanehisa, Y. Kai, A. Nakamura, *J. Chem. Soc., Chem. Commun.* **1993**, 1847–1848.
- [10] K. Mashima, Y. Nakayama, H. Fukumoto, N. Kanehisa, Y. Kai, A. Nakamura, *J. Chem. Soc., Chem. Commun.* **1994**, 2523–2524.
- [11] J. H. Melman, T. J. Emge, J. G. Brennan, *Inorg. Chem.* **2001**, *40*, 1078–1081.
- [12] W. J. Evans, D. S. Lee, D. B. Rego, J. M. Perotti, S. A. Kozimor, E. K. Moore, J. W. Ziller, *J. Am. Chem. Soc.* **2004**, *126*, 14574–14582.
- [13] W. J. Evans, M. A. Ansari, J. W. Ziller, S. I. Kham, *Organometallics* **1995**, *14*, 3–4.
- [14] P. L. Arnold, S. A. Mungur, A. J. Blake, C. Wilson, *Angew. Chem. Int. Ed.* **2003**, *42*, 5981–5984.
- [15] W. J. Evans, D. K. Drummond, H. M. Zhang, J. L. Atwood, *Inorg. Chem.* **1988**, *27*, 575–579.
- [16] a) M. Fitzgerald, T. J. Emge, J. G. Brennan, *Inorg. Chem.* **2002**, *41*, 3528–3533; b) J. H. Melman, M. Fitzgerald, D. Freedman, T. J. Emge, J. G. Brennan, *J. Am. Chem. Soc.* **1999**, *121*, 10247–10248; c) A. Kornienko, L. Huebner, D. Freedman, T. J. Emge, J. G. Brennan, *Inorg. Chem.* **2003**, *42*, 8476–8480; d) D. Freedman, S. Sayan, T. J. Emge, M. Croft, J. G. Brennan, *J. Am. Chem. Soc.* **1999**, *121*, 11713–11719; e) A. Kornienko, J. H. Helman, T. J. Emge, J. G. Brennan, *Inorg. Chem.* **2002**, *41*, 121–126; f) A. Y. Kornienko, T. J. Emge, J. G. Brennan, *J. Am. Chem. Soc.* **2001**, *123*, 11933–11939; g) D. Freedman, T. J. Emge, J. G. Brennan, *Inorg. Chem.* **2002**, *41*, 492–500.
- [17] a) W. P. Su, R. Cao, M. C. Hong, J. T. Chen, J. X. Lu, *Chem. Commun.* **1998**, 1389–1390; b) R. G. Prichard, R. V. Arish, Z. Salehi, *J. Chem. Soc., Dalton Trans.* **1999**, 243–250; c) H. Xu, J. H. K. Yip, *Inorg. Chem.* **2003**, *42*, 4492–4494; d) J. E. Barclay, D. J. Evans, S. C. Davies, D. L. Hughes, P. Sobota, *J. Chem. Soc., Dalton Trans.* **1999**, 1533–1534; e) X. J. Wang, T. Lange-tepe, D. Fenske, B. S. Z. Kang, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1158–1167; f) M. D. Janssen, A. L. Spek, D. M. Grove, G. van Koten, *Inorg. Chem.* **1996**, *35*, 4078–4081; g) Y. Agnus, R. Louis, R. Weiss, *J. Chem. Soc., Chem. Commun.* **1980**, 867–

- 869; h) R. V. Parish, Z. Saleh, R. G. Pritchard, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 251–253; i) K. L. Tang, T. B. Xia, X. L. Jin, Y. Q. Tang, *Polyhedron* **1993**, *12*, 2895–2898; j) B. Krebs, A. Brommelhaus, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1682–1683; k) B. Krebs, A. Brommelhaus, *Z. Anorg. Allg. Chem.* **1991**, *595*, 167–182.
- [18] Y. Meseri, A. A. Pinkerton, G. Chapuis, *J. Chem. Soc., Dalton Trans.* **1977**, 725–729.
- [19] J. Lee, D. Freedman, J. H. Melman, M. Brewer, L. Sun, T. J. Emge, F. H. Long, J. G. Brennan, *Inorg. Chem.* **1998**, *37*, 2512–2519.
- [20] K. Mashima, Y. Nakayama, T. Shibahara, H. Fukumoto, A. Nakamura, *Inorg. Chem.* **1996**, *35*, 93–99.
- [21] D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, H. G. Schmidt, M. Noltemeyer, *J. Organomet. Chem.* **2002**, *643*, 47–52.
- [22] H. X. Li, Q. F. Xu, J. X. Chen, M. L. Cheng, Y. Zhang, W. H. Zhang, J. P. Lang, Q. Shen, *J. Organomet. Chem.* **2004**, *689*, 3438–3448.
- [23] M. D. Taylor, C. P. Carter, *J. Inorg. Nucl. Chem.* **1962**, *24*, 387–393.
- [24] J. S. Ghotra, M. B. Hursthouse, A. J. Welch, *J. Chem. Soc., Chem. Commun.* **1973**, 669–670.
- [25] G. M. Sheldrick, *SHELXS-97: Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [26] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *PATY: The DIRDIF Program System*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1992**.

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