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# Bis(phosphinimino)methanides as Ligands in Divalent Samarium Chemistry: Synthesis, Structures and Catalysis

Michal Wiecko,[a] Peter W. Roesky,*[a] Vladimir V. Burlakov,[b] and Anke Spannenberg*[b]

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The reaction of K{CH($PPh_2NSiMe_3$)$_2$} with samarium diiodide in a 1:1 molar ratio in thf affords the corresponding divalent samarium complex [{($Me_3SiNPPh_2$)$_2$CH}Sm(μ-I)(thf)]$_2$ (**1**), whereas treatment of K{CH($PPh_2NSiMe_3$)$_2$} with samarium diiodide in a 2:1 molar ratio in thf gives the homoleptic complex [{($Me_3SiNPPh_2$)$_2$CH}$_2$Sm] (**2**). When **1** is treated with $KNPh_2$ in toluene in a 2:1 molar ratio the mixed dimeric compound [({($Me_3SiNPPh_2$)CH}$_2$Sm)$_2$(μ-I)(μ-$NPh_2$)] (**3**) is obtained. The single-crystal X-ray structures of all these complexes have been determined. [{($Me_3SiNPPh_2$)$_2$CH}-Sm(μ-I)(thf)]$_2$ has also been successfully used as a catalyst for the polymerization of ε-caprolactone. Good activities and molecular masses are observed with this catalyst.

## Introduction

Over the past decade lanthanide reagents have become more and more recognized as useful reagents in organic synthesis.[1,2] Of the low-valent lanthanides, samarium has found the most widespread application.[3] In this context, the mild reducing agent $SmI_2$, introduced by Kagan and co-workers in the late 1970s, is still receiving much interest today.[4] Kagan showed that $SmI_2$ promotes the reduction of halides, aldehydes, ketones, and carboxylic acids, and reductive eliminations and deoxygenations. Although the use of other metals such as Yb, Eu, Tm, and Dy has been reported, $SmI_2$ has turned out to be the most versatile reagent with respect to the ease of preparation concomitant with a high redox potential. On the other hand, it is often necessary to enhance the reactivity by adding various salts and co-solvents such as the carcinogenic HMPTA. Other divalent samarium reagents such as [($\eta^5$-$C_5H_5$)$_2$Sm],[5] $SmBr_2$,[6] and [Sm{N($SiMe_3$)$_2$}$_2$(thf)$_2$][7] have also been used, although less frequently.

Beside $SmI_2$, the reactivity of the divalent samarocene [($\eta^5$-$C_5Me_5$)$_2$Sm(thf)$_2$][8] toward organic compounds has been extensively investigated by Evans and co-workers,[9,10] and it has also been shown that [($\eta^5$-$C_5Me_5$)$_2$Sm(thf)$_2$] is an active polymerization system for ε-caprolactone that maintains its activity after all of the initial batch of monomer is consumed.[11] An ε-caprolactone polymerization activity has also been observed for [($\eta^5$-$C_5H_5$)$_2$Sm],[12] $SmBr_2$, and [($\eta^5$-indenyl)$_2$Yb(thf)$_2$].[13] In this context, Yasuda and co-workers have investigated the efficiency of divalent lanthanide complexes such as [($\eta^5$-$C_5Me_5$)$_2$Yb(thf)$_2$], [($\eta^5$-$C_5Me_5$)$_2$-Sm(thf)$_2$], and [($\eta^5$-indenyl)$_2$Yb(thf)$_2$] as catalysts for the polymerization of methyl methacrylate (MMA).[14] Although the living polymerization of MMA is initiated by these complexes, their initiator efficiencies are much smaller than those obtained by organolanthanide(III) complexes.

Based on these results, we became interested in the synthesis of new samarium(II) complexes and their application as catalysts in the polymerization of polar monomers. Recently, we introduced the monoanionic bis(phosphinimino)-methanide {CH($PPh_2NSiMe_3$)$_2$}$^-$ as a versatile ligand in di- and trivalent lanthanide chemistry. We have previously reported the synthesis of a series of bis(phosphinimino)-methanide dichloride complexes of trivalent lanthanides, namely [{CH($PPh_2NSiMe_3$)$_2$}$LnCl_2$]$_2$ (Ln = Y, Sm, Dy, Er, Yb, Lu).[15] These compounds were obtained by the reaction of K{CH($PPh_2NSiMe_3$)$_2$}[16] with the corresponding yttrium or lanthanide trichloride. Further reactions of [{CH($PPh_2NSiMe_3$)$_2$}$LnCl_2$]$_2$ have led to the corresponding amido complexes [{CH($PPh_2NSiMe_3$)$_2$}Ln($NPh_2$)$_2$] (Ln = Y, Sm),[15] diphosphanylamido complexes [{CH($PPh_2NSiMe_3$)$_2$}Ln{($Ph_2P$)$_2$N}Cl] (Ln = Y, La, Nd, Yb),[17] cyclopentadienido complexes [{CH($PPh_2NSiMe_3$)$_2$}-Ln($\eta^5$-$C_5H_5$)$_2$] (Ln = Y, Sm, Er),[18] and cyclooctatetraene complexes [{CH($PPh_2NSiMe_3$)$_2$}Ln($\eta^8$-$C_8H_8$)] (Ln = Y, Sm, Er, Yb, Lu).[19] These derivatives have been used as homogeneous catalysts for a number of different catalytic applications. Thus, the complexes [{CH($PPh_2NSiMe_3$)$_2$}-Ln{($Ph_2P$)$_2$N}Cl] are active catalysts for the ring-opening polymerization of ε-caprolactone and the polymerization of MMA.[17]

In divalent lanthanide chemistry we have synthesized bis(phosphinimino)methanide complexes of composition [{($Me_3SiNPPh_2$)$_2$CH}Eu(μ-I)(thf)]$_2$ and [{($Me_3SiNPPh_2$)$_2$-

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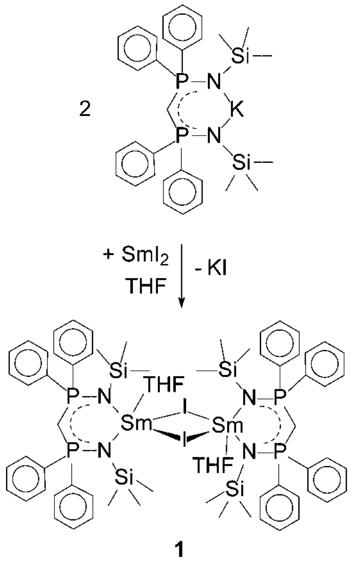
[a] Institut für Chemie und Biochemie, Freie Universität Berlin
Fabeckstraße 34-36, 14195 Berlin, Germany
[b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Straße 29a, 18059 Rostock, Germany

$CH\}YbI(thf)_2]$ by salt metathesis reactions from $K\{CH(PPh_2NSiMe_3)_2\}$ and $LnI_2$.[20] Further reaction of these complexes with $[K(thf)_nN(PPh_2)_2]$ has led selectively to the heteroleptic amido complexes $[\{(Me_3SiNPPh_2)_2CH\}Ln\{(Ph_2P)_2N\}(thf)]$ (Ln = Eu, Yb). The ytterbium complex can also be obtained by reduction of $[\{CH(PPh_2NSiMe_3)_2\}Yb\{(Ph_2P)_2N\}Cl]$. So far the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand has not been used in the more redox-sensitive chemistry of samarium(II). Only the homoleptic samarium(II) complex $[\{CH(PPh_2NC_6H_2\text{-}2,4,6\text{-}Me_3)_2\}_2Sm]$ of the related *N*-mesityl-substituted bis(phosphinimino)methanide has been reported recently by Hill and co-workers.[21] We report here on the synthesis of three bis(phosphinimino)methanide complexes of divalent samarium and their application in ε-caprolactone polymerization.

## Results and Discussion

### Synthesis and Structures

Reaction of $K\{CH(PPh_2NSiMe_3)_2\}$ with samarium diiodide in a 1:1 molar ratio in thf afforded the corresponding divalent samarium complex $[\{(Me_3SiNPPh_2)_2CH\}Sm(\mu\text{-}I)(thf)]_2$ (**1**) as crystals in good yields (Scheme 1).[22] The potassium reagent $K\{CH(PPh_2NSiMe_3)_2\}$, which was described earlier,[16] was used as starting material to avoid coordination of lighter alkali halides such as lithium chloride. The new complex was characterized by standard analytical and spectroscopic techniques, and its solid-state structure was established by single-crystal X-ray diffraction. The signals in the NMR spectra are broadened due to the presence of the paramagnetic metal. The signal of the $SiMe_3$ groups ($\delta$ = –0.16 ppm) is in the expected range. A similar shift is observed for the diamagnetic divalent complex $[\{(Me_3SiNPPh_2)_2CH\}YbI(thf)_2]$ ($\delta$ = 0.44 ppm). The signal of the methine proton in the $^1H$ NMR spectrum could not be clearly assigned, and those of the phenyl protons ($\delta$ = 7.05–7.70 ppm) are uncharacteristically broadened.



Scheme 1.

The solid-state structure of **1** is isostructural to the previously reported europium compound $[\{(Me_3SiNPPh_2)_2CH\}Eu(\mu\text{-}I)(thf)]_2$.[20] In **1**, which crystallizes in the monoclinic space group $P2_1/c$ the metal centers of the dimeric complexes are asymmetrically bridged by two iodine atoms [Sm–I 332.14(4) and Sm–I′ 335.74(4) pm; Figure 1]. A crystallographic inversion center is observed in the center of the Sm–I–Sm′–I′ plane. The bis(phosphinimino)methanide ligand forms a six-membered metallacycle (N1–P1–C1–P2–N2–Sm) by chelation of the two trimethylsilylimine groups to the lanthanide metal. The Sm–N distances [Sm–N1 259.2(3) and Sm–N2 256.3(3) pm] show an almost symmetrical attachment of the ligand to the metal center. The metallacycle adopts a twist-boat conformation in which the central carbon atom and the samarium atom are displaced from the $N_2P_2$ least-squares plane. As shown earlier, this displacement depends on the metal center and also on the packing in the solid state.[17]

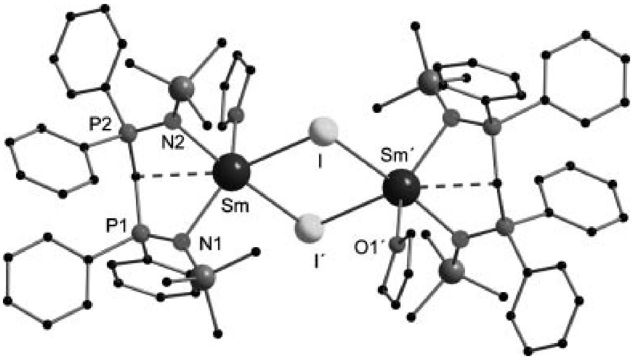
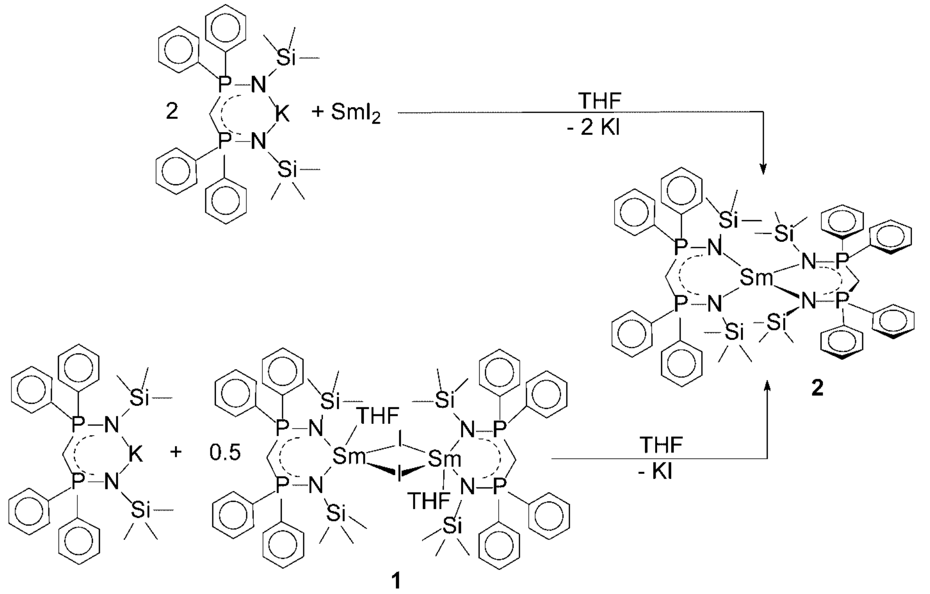


Figure 1. Solid-state structure of **1** showing the atom-labeling scheme. Hydrogen atoms have been omitted. Selected bond lengths [pm] and angles [°]: Sm–N1 259.2(3), Sm–N2 256.3(3), Sm–C1 297.7(4), Sm–I 332.14(4), Sm–I′ 335.74(4), Sm–O1 250.4(3), P1–N1 157.9(3), P2–N2 158.7(3); N1–Sm–N2 90.66(10), N1–Sm–C1 57.90(10), N2–Sm–C1 59.66(10), N1–Sm–I 133.19(8), N2–Sm–I 99.33(7), N1–Sm–I′ 95.02(7), N2–Sm–I′ 171.95(8), N1–Sm–O1 134.35(12), N2–Sm–O1 87.04(12), C1–Sm–I 158.36(6), C1–Sm–I′ 119.11(7), C1–Sm–O1 82.37(13), I–Sm–O1 92.01(9), I′–Sm–O1 84.92(9), I–Sm–I′ 80.896(10), Sm–I–Sm′ 99.104(10).

Reaction of **1** with a second equivalent of $K\{CH(PPh_2NSiMe_3)_2\}$ or treatment of $K\{CH(PPh_2NSiMe_3)_2\}$ with samarium diiodide in a 2:1 molar ratio in thf gave the homoleptic complex $[\{(Me_3SiNPPh_2)_2CH\}_2Sm]$ (**2**) as purple crystals (Scheme 2).[22] Compound **2** is similar to the *N*-mesityl-substituted bis(phosphinimino)methanide complex $[\{CH(PPh_2NC_6H_2\text{-}2,4,6\text{-}Me_3)_2\}_2Sm]$.[21] Dark purple crystals suitable for X-ray crystallographic studies formed in concentrated *n*-pentane. Compound **2**, which crystallizes in the triclinic space group $P\bar{1}$ forms discrete homoleptic monomers in the solid state (Figure 2). As observed for **1**, six-membered metallacycles (N1–P1–C1–P2–N2–Sm), which adopt a twist-boat conformation, are formed by the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligands and the samarium atom. The two $\{CH(PPh_2NSiMe_3)_2\}^-$ ligands act as tridentate donors. Thus, the samarium atom is six-coordinated. The distances



Scheme 2.

between the central carbon atom C1 and the samarium atom [Sm–C1 289.91(15) and Sm–C32 289.84(14) pm] are in the range of those for [$\{CH(PPh_2NC_6H_2\text{-}2,4,6\text{-}Me_3)_2\}_2$-Sm] [290.0(5) and 287.7(5) pm][21] and [Sm$\{C(SiMe_3)_2$-$(SiMe_2OMe)\}_2$(thf)] [278.7(5) and 284.5(5) pm][23] but significantly shorter than in **1** [297.7(4) pm]. On the other hand, the Sm–$C_{methine}$ bond lengths are significantly longer than in [($\eta^5$-$C_5Me_5$)Sm$\{CH_2(SiMe_3)_2\}$($\eta^5$-$C_5Me_5$)·K(thf)$_2$]$_n$ [265.2(9) pm].[24]

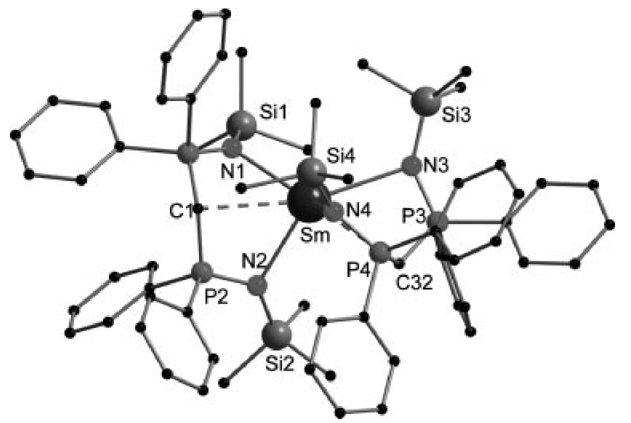
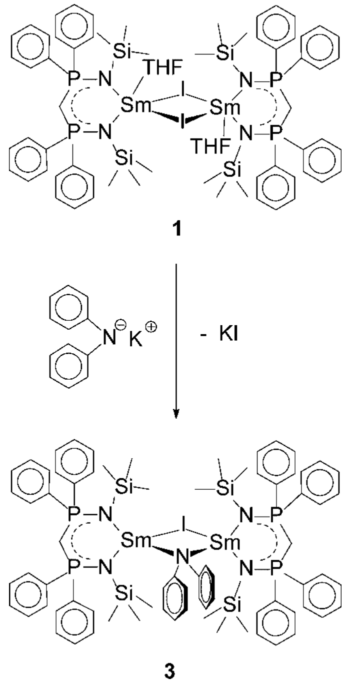


Figure 2. Solid-state structure of **2** showing the atom labeling scheme. Hydrogen atoms have been omitted. Selected bond lengths [pm] and angles [°]: Sm–N1 278.51(12), Sm–N2 260.70(10), Sm–N3 277.41(12), Sm–N4 261.25(11), Sm–C1 289.91(15), Sm–C32 289.84(14), N1–P1 157.81(15), N2–P2 158.30(14), N3–P3 157.86(13), N4–P4 158.13(14); N1–Sm–N2 85.34(3), N1–Sm–N3 116.48(4), N1–Sm–N4 136.31(4), N2–Sm–N3 135.46(4), N2–Sm–N4 105.16(4), N3–Sm–N4 85.69(4), N1–Sm–C32 163.78(4), N2–Sm–C32 90.27(4), N3–Sm–C32 57.63(4), N4–Sm–C32 59.90(4), N1–Sm–C1 57.09(4), N2–Sm–C1 59.97(4), N3–Sm–C1 164.50(4), N4–Sm–C1 91.23(4), C1–Sm–C32 132.66(4).

Earlier attempts to synthesize a heteroleptic complex of composition [$\{CH(PPh_2NC_6H_2\text{-}2,4,6\text{-}Me_3)_2\}$Sm$\{N(SiMe_3)_2\}$] did not succeed.[21] Therefore, to obtain another heteroleptic amido complex, **1** was treated with $KNPh_2$ in toluene in a 2:1 molar ratio. Surprisingly, we did not obtain the desired complex [$\{(Me_3SiNPPh_2)_2CH\}$Sm$(NPh_2)_2$] but instead repeatedly isolated the mixed dimeric compound [($\{(Me_3SiNPPh_2)_2CH\}$Sm)$_2$($\mu$-I)($\mu$-$NPh_2$)] (**3**) in high yields (Scheme 3).[22] Compound **3** was characterized by elemental analysis and Raman spectroscopy. The solid-state structure of **3** was also determined by single-crystal X-ray diffraction (Figure 3). It crystallizes in the monoclinic space group *C*2/*c* with one molecule of toluene and forms a dimer in the solid state in which the metal centers are symmetrically bridged by one iodine atom and the nitrogen atom of the



Scheme 3.

$Ph_2N^-$ group. A crystallographic $C_2$ axis is observed along I and N3. As a result of the bridging nature of the nitrogen atom, the Sm–N3 bond length [259.4(3) pm] is longer than in $[Sm\{N(SiMe_3)_2\}(thf)_2]$ [244.2(9) and 242.4(9) pm],[25] in which the $\{N(SiMe_3)_2\}^-$ groups are terminally bonded. The Sm–I bond length of 328.33(4) pm is a bit shorter than in $[Sm\{N(SiMe_3)_2\}(\mu\text{-}I)(DME)(thf)]_2$ [e.g. 334.14(9) and 335.53(9) pm].[25] As observed for **1** and **2**, the six-membered N1–P1–C1–P2–N2–Sm ring in **3**, which is formed by the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand and the samarium atom, adopts a twist-boat conformation. The distance between the central carbon atom C1 and the lanthanide atom [292.2(4) pm] lies between the values observed for **1** [297.7(4) pm] and **2** [Sm–C1 289.91(15) and Sm–C32 289.84(14) pm]. The Sm–N1 and Sm–N2 distances are 255.0(3) and 253.8(3) pm, respectively; and indicate an almost symmetrical attachment of the ligand at the metal center.

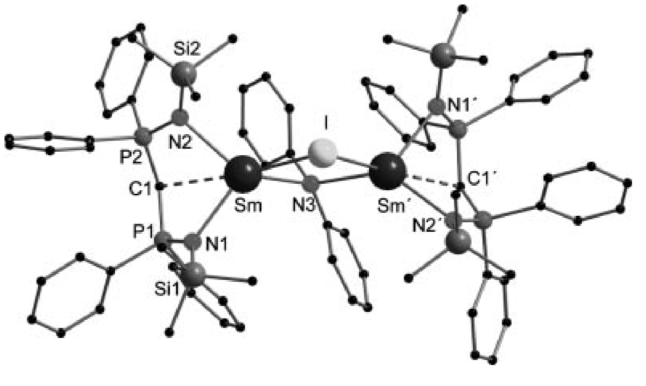


Figure 3. Solid-state structure of **3** showing the atom labeling scheme. Hydrogen atoms have been omitted. Selected bond lengths [pm] and angles [°]: Sm–N1 255.0(3), Sm–N2 253.8(3), Sm–N3 259.4(3), Sm–C1 292.2(4), Sm–I 328.33(4), N1–P1 159.1(3), N2–P2 158.4(3); N1–Sm–N2 94.24(10), N1–Sm–N3 118.45(8), N2–Sm–N3 135.65(8), N1–Sm–C1 59.33(9), N2–Sm–C1 60.46(10), N3–Sm–C1 109.64(11), N1–Sm–I 117.43(7), N2–Sm–I 109.95(7), N3–Sm–I 82.14(8), C1–Sm–I 168.06(7), Sm–N3–Sm 113.19(17), Sm–I–Sm 82.521(14).

### Catalysis

Since it is known that divalent lanthanide complexes such as $[(\eta^5\text{-}C_5H_5)_2Sm]$,[12] $[(\eta^5\text{-}C_5Me_5)_2Sm(thf)_2]$,[11] and $[(\eta^5\text{-indenyl})_2Yb(thf)_2]$[13] are efficient catalysts for the polymerization of ε-caprolactone (CL),[14] we were interested in using compound **1** as a precatalyst for this polymerization. Complex **1** showed high activity in polymerization of CL at room temperature. Monomer/initiator molar ratios of 1/2000 and 1/10000 afforded the corresponding poly(caprolactone)s with excellent yields (92–95%) within short reaction times. The molecular weights obtained depend strongly on the amount of initiator. Poly(caprolactone) with a $\bar{M}_n$ of 723000 was obtained in toluene with a [CL]/[**1**] ratio of 10000/1 in one hour with complete conversion at room temperature (Table 1, entry 2). The molecular weights decrease at elevated temperature (Table 1, entries 3 and 4). Moderate $\bar{M}_w/\bar{M}_n$ values (1.81–2.75) were observed.

## Conclusions

In summary, a series of bis(phosphinimino)methanide complexes of divalent samarium have been reported. Reaction of $K\{CH(PPh_2NSiMe_3)_2\}$ with samarium diiodide in a 1:1 molar ratio in thf affords the corresponding divalent samarium complex $[\{(Me_3SiNPPh_2)_2CH\}Sm(\mu\text{-}I)(thf)]_2$ (**1**). Reaction of **1** with a second equivalent of $K\{CH(PPh_2NSiMe_3)_2\}$ or treatment of $K\{CH(PPh_2NSiMe_3)_2\}$ with samarium diiodide in a 2:1 molar ratio in thf gives the homoleptic complex $[\{(Me_3SiNPPh_2)_2CH\}_2Sm]$ (**2**). When **1** is treated with $KNPh_2$ in toluene in a 2:1 molar ratio the mixed dimeric compound $[(\{(Me_3SiNPPh_2)_2CH\}_2Sm)_2(\mu\text{-}I)(\mu\text{-}NPh_2)]$ (**3**) is obtained. The single-crystal X-ray structures of all three complexes show that the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand is bound in an uncommon coordination mode to the metal atom. A six-membered N1–P1–C1–P2–N2–Sm metallacycle, which adopts a pseudo-boat conformation, is formed by chelation of the two trimethylsilylimine groups to the metal center. The heteroleptic complex **1** is an efficient catalyst for the polymerization of CL. Good polydispersity and molecular masses are obtained with this catalyst.

## Experimental Section

**General Considerations:** All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried, Schlenk-type glassware either on a dual-manifold Schlenk line interfaced with a high vacuum ($10^{-3}$ Torr) line, or in an argon-filled MBraun glove box. Thf was pre-dried with Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade or Euriso-Top GmbH (99 atom% D). NMR spectra were recorded with

Table 1. Polymerization of ε-CL initiated by **1** in toluene.

| CL:**1**[a] | $T$ [°C] | $t$ [h] | Yield[b] [%] | $\bar{M}_{n(theor.)}$[c] [g mol$^{-1}$] | $\bar{M}_{n(obsd.)}$ [g mol$^{-1}$] | $\bar{M}_w/\bar{M}_n$[d] | $\bar{M}_{n(corr.)}$[e] [g mol$^{-1}$] |
|---|---|---|---|---|---|---|---|
| 2000:1 | room temp. | 1 | 93 | $2.12\cdot10^5$ | $1.07\cdot10^5$ | 2.47 | $0.6\cdot10^5$ |
| 10000:1 | room temp. | 1 | 95 | $10.8\cdot10^5$ | $7.23\cdot10^5$ | 2.52 | $4.05\cdot10^5$ |
| 2000:1 | 75 | 1 | 94 | $2.15\cdot10^5$ | $2.58\cdot10^4$ | 1.81 | $1.44\cdot10^4$ |
| 10000:1 | 75 | 1 | 92 | $10.5\cdot10^5$ | $3.85\cdot10^4$ | 2.75 | $2.16\cdot10^4$ |

[a] Initial molar CL/catalyst ratio. [b] Determined gravimetrically. [c] Calculated from $M_{monomer}\times[M]/[I]\times$ yield. [d] Measured by SEC. [e] SEC values multiplied by 0.56.[29]

a Jeol JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane or 85% phosphoric acid ($^{31}$P). Raman spectra were recorded with a Bruker RFS 100. Elemental analyses were performed with an Elementar vario EL. $SmI_2(thf)_2$,[26] $K\{CH(PPh_2NSiMe_3)_2\}$,[16] and $\{CH_2(PPh_2NSiMe_3)_2\}$[27] were prepared according to literature procedures.

**$[\{(Me_3SiNPPh_2)_2CH\}Sm(\mu\text{-}I)(thf)]_2$ (1):** $SmI_2(thf)_2$ (1.20 g, 2.2 mmol) and $K\{CH(PPh_2NSiMe_3)_2\}$ (1.20 g, 2.0 mmol) were placed in a flask and 15 mL of thf was condensed onto the mixture. The mixture was stirred for 16 h at room temperature and filtered. The thf was removed from the resulting dark-purple solution in vacuo. The obtained dark solid was washed with 10 mL of cold toluene yielding 1.72 g (95%) of **1**. Crystals of **1** suitable for X-ray crystallographic studies were obtained by concentrating a hot thf/toluene (2:1) solution. $^1$H NMR ([D$_8$]THF, 400 MHz): $\delta$ = –0.16 (s, 36 H, SiMe$_3$), 4.97 (br. s), 6.75 (br. s) 7.05–7.70 (m, 40 H, Ph) ppm. $^{13}$C{H} NMR ([D$_8$]THF, 100.4 MHz): $\delta$ = 4.0 (SiMe$_3$), 128.5, 129.6, 130.4, 131.9 (Ph) ppm. Raman (solid): $\tilde{\nu}$ = 604 cm$^{-1}$ (s), 618 (m), 1000 (s), 1027 (m), 1104 (w), 1157 (w), 1573 (w), 1588 (m), 2889 (br), 3049 (s), 3059 (m). $C_{70}H_{92}I_2N_4O_2P_4Si_4Sm_2$ (1812.3): calcd. C 46.39, H 5.12, N 3.09; found C 46.77, H 4.47, N 2.67.

**$[\{(Me_3SiNPPh_2)_2CH\}_2Sm]$ (2):** $SmI_2(thf)_2$ (273 mg, 0.5 mmol) and $K\{CH(PPh_2NSiMe_3)_2\}$ (597 mg, 1.0 mmol) were placed in a flask and 15 mL of thf was condensed onto the mixture. The mixture was stirred for 16 h at room temperature. The solvent was removed in vacuo and the resulting residue was suspended in 15 mL of *n*-pentane and filtered. The obtained solution was concentrated at 35 °C. Dark crystals suitable for X-ray crystallographic studies formed after several hours. By further concentration of the mother liqueur an overall yield of 560 mg (89%) of **2** was obtained. Raman (solid): $\tilde{\nu}$ = 609 cm$^{-1}$ (m), 617 (w), 999 (s), 1027 (m), 1103 (w), 1156 (w), 1182 (w), 1572 (w), 1587 (m), 2897 (br), 2952 (br), 3055 (m). $C_{62}H_{78}N_4P_4Si_4Sm\cdot\frac{1}{2}C_5H_{12}$ (1265.91 + 36.08): calcd. C 59.50, H 6.50, N 4.30; found C 59.90, H 6.59, N 4.09.

**$[(\{(Me_3SiNPPh_2)_2CH\}Sm)_2(\mu\text{-}I)(\mu\text{-}NPh_2)]$ (3):** Freshly prepared **1** (453 mg, 0.25 mmol) and $KNPh_2$ (104 mg, 0.50 mmol) were suspended in 15 mL of toluene. The dark mixture was stirred for 6 h at about 70 °C and another 10 h at room temperature. Filtration and concentration of the resulting solution yielded 676 mg (79%) of **3** as very dark purple crystals. $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 161.7 MHz, 25 °C): $\delta$ = 341.7 ppm. Raman (solid): $\tilde{\nu}$ = 607 cm$^{-1}$ (s), 617 (m), 987 (m), 999 (s), 1026 (m), 1102 (w), 1157 (w), 1572 (w), 1588 (m), 2891 (br), 2944 (br), 3056 (m). $C_{74}H_{88}IN_5P_4Si_4Sm_2$ (1711.4): calcd. C 51.93, H 5.18, N 4.09; found C 52.10, H 5.14, N 3.73.

**Polymerization of ε-Caprolactone:** A 5 M solution of the ε-caprolactone in toluene (4 mL for 1:2000 or 20 mL for 1:10000) was added to **1** (0.018 g, 0.01 mmol). The mixture was stirred and left at room temperature or warmed to 75 °C. After one hour the reaction mixture was treated with an excess of methanol. After 2–3 h the polymer was separated from the mother liquor by decanting and dried in vacuo. The residue was dissolved in 20 mL (1:2000) or in 60 mL (1:10000) of toluene and the solution was transferred to a beaker and treated with an excess of methanol. The poly-ε-caprolactone was separated and dried in vacuo until the weight remained constant.

The molecular masses of poly(ε-caprolactone)s were measured by the GPC method on a Hewlett–Packard liquid chromatograph 1090 HP [SDV column $10^4 \times 10^3 \times 100$ Å (Polymer Standard Service); eluent: thf] and were corrected by calibration relative to polystyrene standards.

**X-ray Crystallographic Studies of 1–3:** Suitable crystals of **1**–**3** were covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold N$_2$ stream (–73 °C) of a Stoe IPDS 2T diffractometer. Subsequent computations were carried out with an Intel Pentium IV PC. Data collection and refinement were performed with SHELXS-97[28a] and SHELXL-97.[28b]

**$[\{(Me_3SiNPPh_2)_2CH\}Sm(\mu\text{-}I)(thf)]_2$ (1):** Monoclinic, space group $P2_1/c$ (no. 14); lattice constants $a$ = 1970.31(13), $b$ = 996.34(6), $c$ = 2366.4(2) pm, $\beta$ = 113.216(6)°, $V$ = 4269.3(5) × 10$^6$ pm$^3$, $Z$ = 2; $\mu$(Mo-$K_\alpha$) = 2.259 mm$^{-1}$; $2\theta_{max.}$ = 58.8°; 11260 ($R_{int}$ = 0.0423) independent reflections measured, of which 6555 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.946 and –1.140 e A$^{-3}$; 405 parameters (all non-hydrogen atoms except the thf molecules were calculated anisotropic; the positions of the H atoms were calculated for idealized positions) $R1$ = 0.0350; w$R2$ = 0.0750.

**$[\{(Me_3SiNPPh_2)_2CH\}_2Sm]$ (2):** Triclinic, space group $P\bar{1}$ (no. 2); lattice constants $a$ = 1182.45(6), $b$ = 1555.64(7), $c$ = 1994.55(10) pm, $\alpha$ = 75.270(4)°, $\beta$ = 81.858(4)°, $\gamma$ = 77.736(4)°, $V$ = 3452.4(3) × 10$^6$ pm$^3$, $Z$ = 1; $\mu$(Mo-$K_\alpha$) = 2.259 mm$^{-1}$; $2\theta_{max.}$ = 58.5°; 18523 ($R_{int}$ = 0.0803) independent reflections measured, of which 13118 were considered observed with $I > 2\sigma(I)$; max. residual electron density 1.072 and –1.361 e A$^{-3}$; 705 parameters (all non-hydrogen atoms except the pentane molecules were calculated anisotropic; the positions of the H atoms were calculated for idealized positions) $R1$ = 0.0491; w$R2$ = 0.1091.

**$[(\{(Me_3SiNPPh_2)_2CH\}Sm)_2(\mu\text{-}I)(\mu\text{-}NPh_2)]$ (3):** Monoclinic, space group $C2/c$ (no. 15); lattice constants $a$ = 2144.9(3), $b$ = 1730.74(13), $c$ = 2445.1(3) pm, $\beta$ = 112.308(11)°, $V$ = 8397(2) × 10$^6$ pm$^3$, $Z$ = 4; $\mu$(Mo-$K_\alpha$) = 1.929 mm$^{-1}$; $2\theta_{max.}$ = 50.0°; 7408 ($R_{int}$ = 0.0490) independent reflections measured, of which 5877 were considered observed with $I > 2\sigma(I)$; max. residual electron density 1.490 and –0.726 e A$^{-3}$; 428 parameters (all non hydrogen atoms except the toluene molecules were calculated anisotropic; the positions of the H atoms were calculated for idealized positions) $R1$ = 0.0339; w$R2$ = 0.0779.

CCDC-622744 to -622746 (for **1**–**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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