# Synthesis, structure and reactivity of samarium complexes supported by Schiff-base ligands

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## ARTICLE INFO

## ABSTRACT

Three tris(salicyladiminato) samarium complexes $[3,5\text{-Bu}_2^t\text{-}2\text{-}(O)C_6H_2CH=NAr']_3Sm(THF)_n [Ar' = 4\text{-}ClC_6H_4$ (**1**), $4\text{-}CH_3C_6H_4$ (**2**), $8\text{-}C_9H_6N(\text{quinoline})$ (**3**)] were synthesized by the reaction of anhydrous $SmCl_3$ with the sodium salts of the Schiff-bases in THF in 3:1 molar ratio. X-ray diffraction studies revealed that the coordination geometry around samarium atom could be best described as a distorted pentagonal bipyramidal for complexes **1** and **2** and as a distorted tricapped trigonal prism for complex **3**. It was found that the coordination environment around samarium atom has significant effect on the catalytic activity of homoleptic Schiff-base complexes of lanthanide. The increasing order of the catalytic activity for the ring-opening polymerization of $\varepsilon$-caprolactone, as well as guanylation of aniline with *N,N*-diisopropylcarbodiimide is **3 < 2 < 1**.

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## 1. Introduction

In recent years the application of Schiff-base ligands in organometallic chemistry of main, transition and lanthanide metals have attracted much attention, in part because some of these complexes were reported to have fascinating catalytic reactivity. For example, chiral Schiff-base transition metal complexes are extensively used in a variety of chemical transformations such as oxidation, hydroxylation, aldol condensation, epoxidation and other related catalytic processes [1–3], bis(phenoxyimine) group 4 metal complexes and phenoxyimine Ni(II) complexes are excellent precatalysts or catalysts for olefin polymerization [1,4–7]. Lanthanide complexes bearing $N_2O_2$ tetradentate Schiff-base ligands are efficient catalysts for the asymmetric epoxidation of $\alpha,\beta$-unsaturated ketones [8], ring-opening polymerization of lactide and related cyclic esters [9–11]. Chiral yttrium–salen complexes are reported to be excellent catalysts for enantioselective acyl transfer reactions between eno-lesters and secondary alcohols [12], asymmetric Aldol–Tishchenko reactions [13] and the ring-opening of epoxides mediated by TMSCN and TMSN₃ [14]. Bis(salicyladiminato) scandium complexes can be used as efficient hydroamination of alkene catalysts [15]. In all the homogeneous catalyses these Schiff-base ligands are used as typically inert ancillary ligands to stabilize organometallic compounds, themselves do not participate in the transformations.

Only one research group concerns the chemistry of lanthanide-Schiff-base bond [16,17], although vast of non-aqueous lanthanide Schiff-base complexes have been reported [18–30].

Recently, we have reported that bis(salicyladiminato) lanthanide chlorides $[2\text{-}OC_6H_4CH=N(2,6\text{-}^iPr_2C_6H_3)]_2LnCl(THF)$ (Ln = Yb, Er) exhibit moderate catalytic activity for the ring-opening polymerization of $\varepsilon$-caprolactone ($\varepsilon$-CL) [31], indicating that the bond of lanthanide metal to salicyladiminato ligand is active for ring-opening of $\varepsilon$-caprolactone. The results encouraged us to further insight into the influence of coordination environment about the metal coursed by Schiff-base ligands on the reactivity of lanthanide-Schiff-base bond. Three Schiff-base ligands, $[3,5\text{-Bu}_2^t\text{-}2\text{-}(OH)\text{-}C_6H_2\text{-}CH=NAr']$ $[Ar' = 4\text{-}ClC_6H_4$, $4\text{-}CH_3C_6H_4$, $8\text{-}C_9H_6N$ (quinoline)], were chosen and the corresponding samarium complexes $[3,5\text{-Bu}_2^t\text{-}2\text{-}(O)C_6H_2CH=NAr']_3Sm(THF)_n [Ar' = 4\text{-}ClC_6H_4$ (**1**), $4\text{-}CH_3C_6H_4$ (**2**), $8\text{-}C_9H_6N(\text{quinoline})$ (**3**)] were synthesized. Preliminary results on their reactivity revealed that these new homoleptic samarium complexes showed moderate catalytic activity for the polymerization of $\varepsilon$-CL as well as guanylation of aniline with carbodiimide. The homoleptic Schiff-base complexes of samarium can also promote cyclotrimerization of phenyl isocyanate. Here we would like to report these results.

## 2. Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. THF, toluene and hexane were

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dried and freed of oxygen by refluxing over sodium benzophenone ketyl and distilled under argon prior to use. ε-Caprolactone (ε-CL) was dried over $CaH_2$ for 4 days and stored over 3 Å molecular sieves under argon after distillation. Aniline was predried and distilled before use and N,N-diisopropylcarbodiimide was used after distillation. $3,5-Bu_2^t-2-(OH)-C_6H_2CH=N(4-ClC_6H_4)$, $[3,5-Bu_2^t-2-(OH)C_6H_2CH=N(4-CH_3C_6H_4)$ [32] and $3,5-Bu_2^t-2-(OH)C_6H_2-CH=N(8-C_9H_6N)$ [33] and anhydrous $SmCl_3$ [34] were prepared according to the literature procedures. Metal analyses were carried out by complexometric titration. Carbon, hydrogen and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. The IR spectra were obtained as KBr pellets on a Nicolet-550 FT-IR spectrometer. $^1H$ NMR and $^{13}C$ NMR spectrum were obtained on an INOVA-400 MHz apparatus. Molecular weight ($M_n$) and molecular weight distributions ($M_w/M_n$) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL-50 apparatus, and THF was used as an eluent at 40 °C.

### 2.1. Preparation of $[3,5-Bu_2^t-2-(O)C_6H_2CH=N(4-ClC_6H_4)]_3Sm(THF)$ (1)

A THF solution (20 mL) of $3,5-Bu_2^t-2-(OH)C_6H_2CH=N(2-ClC_6H_4)$ (2.06 g, 6.00 mmol) was added dropwise to a NaH suspension (0.17 g, 7.10 mmol) in THF at room temperature and stirred for 14 h. The mixture was then filtered. The resulting dark red solution was added to a suspension of $SmCl_3$ (0.51 g, 2.00 mmol) in THF (20 mL). The solution was stirred overnight at room temperature, and then the precipitate was separated from the reaction mixture by centrifugation. The solvent was removed under vacuum and the residue was dissolved in hexane. Complex 1 was isolated as yellow crystals at room temperature in a few days (1.82 g, 73%). Mp: 149–151 °C (dec). Anal. Calc. for $C_{67}H_{83}Cl_3N_3O_4Sm$: C, 64.32; H, 6.69; N, 3.36; Sm, 12.02. Found: C, 63.95; H, 6.91; N, 3.16; Sm, 11.92%. IR (KBr pellet, cm$^{-1}$): 2955 (s), 2909 (s), 2871 (s), 1605 (s), 1582 (s), 1535 (s), 1481 (s), 1435 (s), 1389 (s), 1319 (s), 1258 (s), 1165 (s), 1088 (m), 1026 (m), 980 (w), 926 (w), 872 (m), 833 (s), 787 (m), 725 (m), 640 (w), 602 (w), 517 (s).

### 2.2. Preparation of $[3,5-Bu_2^t-2-(O)C_6H_2CH=N(4-CH_3C_6H_4)]_3Sm(THF)$ (2)

The synthesis of complex 2 was carried out by the same way as that described above, but $3,5-Bu_2^t-2-(OH)C_6H_2CH=N(2-CH_3C_6H_4)$ (1.94 g, 6.00 mmol) was used instead of $3,5-Bu_2^t-2-(OH)C_6H_2-CH=N(2-ClC_6H_4)$. Yellow crystals were collected from hexane solution (1.72 g, 70%). Mp: 137–138 °C (dec). Anal. Calc. for $C_{70}H_{92}N_3O_4Sm$: C, 70.66; H, 7.79; N, 3.53; Sm, 12.64. Found: C, 70.80; H, 7.90; N, 3.39; Sm, 12.55%. IR (KBr pellet, cm$^{-1}$): 2955 (s), 2909 (s), 2871 (s), 1603 (s), 1589 (s), 1535 (s), 1505 (s), 1466 (s), 1435 (s), 1389 (s), 1319 (s), 1250 (s), 1196 (s), 1165 (s), 1026 (m), 980 (w), 926 (w), 872 (s), 833 (s), 740 (m), 679 (w), 640 (w), 517 (s).

### 2.3. Preparation of $[3,5-Bu_2^t-2-(O)C_6H_2CH=N(8-C_9H_6N)]_3Sm$ (3)

The synthesis of complex 3 was carried out by the same way as that described for complex 1, but $3,5-Bu_2^t-2-(OH)C_6H_2-CH=N(8-C_9H_6N)$ (2.16 g, 6.00 mmol) was used instead of $3,5-Bu_2^t-2-(OH)C_6H_2-CH=N(2-ClC_6H_4)$. Yellow crystals were obtained from hexane solution (2.05 g, 78%). Mp: 206–208 °C (dec). Anal. Calc. for $C_{72}H_{81}N_6O_3Sm$: C, 70.37; H, 6.64; N, 6.84; Sm, 12.24. Found: C, 70.50; H, 6.70; N, 6.69; Sm, 12.15%. IR (KBr pellet, cm$^{-1}$): 2955 (s), 2909 (s), 2871 (s), 1613 (s), 1497 (s), 1466 (s), 1427 (s), 1389 (s), 11366 (s), 1242 (s), 1157 (s), 1088 (m), 1049 (m), 1026 (m), 980 (m), 887 (m), 825 (m), 794 (s), 633 (s), 555 (m), 501 (s).

### 2.4. ε-Caprolactone polymerization

The procedures for the polymerization of ε-CL initiated by complexes 1–3 were similar, and a typical polymerization procedure is given below. A 50 ml Schlenk flask, equipped with a magnetic stirring bar, was charged with a toluene solution (3 mL) of ε-CL (0.6 mL, 5.4 mmol). To this solution was added the desired amount of initiator in toluene by syringe at the desired temperature. After the polymerization was carried out for a predefined time, 5 mL of ethanol containing 2% HCl solution was added to quench the reaction, and then the viscous solution was poured into a large excess of ethanol to induce the precipitation of the polymer. The polymer was washed with ethanol three times and dried at 30 °C under vacuum.

### 2.5. General procedure for guanylation of aniline with N,N-diisopropylcarbodiimide

A 30.0 mL Schlenk tube under dried argon was charged with complex 1 (0.11 g, 0.09 mmol) and aniline (0.16 mL, 1.8 mmol). To this mixture was added N,N-diisopropylcarbodiimide (0.28 mL, 1.8 mmol). The resulting mixture was stirred at 100 °C for 1 h. After the reaction was completed, the reaction mixture was hydrolyzed by water (3 mL), extracted with dichloromethane (310 mL), dried over anhydrous $Na_2SO_4$, and filtered. The solvent was removed under vacuum and the final product was obtained after washing with hexane (0.21 g, 53%). $^1H$ NMR (CDCl$_3$): δ 7.22 (2H), 6.95–6.91 (1H), 6.86–6.84(2H), 3.77 (2H), 3.61(2H), 1.17–1.15(12H). $^{13}C$ NMR (CDCl$_3$): δ 150.53, 150.41, 129.45, 123.75, 121.49, 43.42, 23.56.

### 2.6. Reaction of complex 3 with phenyl isocyanate

A mixture of PhNCO (0.35 g, 2.9 mmol), complex 3 (3.8 g, 2.9 mmol) and THF (15 mL) was stirred at 40 °C for 24 h. The solvent was then removed by vacuum and the resulting solid was extracted with toluene. Crystallization from toluene afforded [PhNCO]$_3 \cdot$ THF as light yellow crystals. Yield: 0.33 g (80%), mp 276 °C. Anal. Calc. for $C_{25}H_{23}N_3O_4$: C, 69.91; H, 5.40; N, 9.78. Found: C, 69.79; H, 5.32; N, 9.81%. IR (KBr pellet, cm$^{-1}$): 3060 (w), 1701 (s), 1590 (m), 1468 (s), 1445 (s), 1406 (s), 1288 (m), 1211 (m), 1146 (w), 1065 (s), 1025 (m), 818 (m), 745 (s), 690 (s), 579 (s).

### 2.7. X-ray structures determination

Suitable single-crystals of complexes 1–3 were sealed in a thin-walled glass capillary, and intensity data were collected on a Rigaku Mercury CCD equipped with a graphite-monochromotized Mo Kα radiation (λ = 0.71070 Å). Details of the intensity data collection and crystal data are given in Table 1. The crystal structures of these complexes were solved by direct methods using the SHELXS-97 program and expanded by Fourier techniques. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.95 Å) with assigned appropriate isotropic thermal parameters.

## 3. Results and discussion

### 3.1. Syntheses

Salt metathesis reaction of $LnCl_3$ with alkali metal salts of Schiff-bases is a useful method for the synthesis of lanthanide Schiff-base complexes in non-aqueous solution [18,19]. Thus, the

**Table 1**
Details of the crystallographic data and refinements for complexes **1**, **2** and **3**.

| Compound | **1** | **2** · 0.5C$_6$H$_{14}$ | **3** · C$_6$H$_{14}$ |
|---|---|---|---|
| Formula | C$_{67}$H$_{83}$Cl$_3$N$_3$O$_4$Sm | C$_{73}$H$_{99}$N$_3$O$_4$Sm | C$_{78}$H$_{95}$N$_6$O$_3$Sm |
| Formula weight | 1251.06 | 1232.90 | 1314.95 |
| $T$ (K) | 173(2) | 173(2) | 193(2) |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 12.6303(11) | 14.675(2) | 13.5940(10) |
| $b$ (Å) | 16.7540(8) | 16.238(3) | 15.9190(12) |
| $c$ (Å) | 17.4327(11) | 17.084(3) | 18.5734(18) |
| $\alpha$ (°) | 62.693(5) | 99.484(2) | 78.791(7) |
| $\beta$ (°) | 87.313(9) | 105.8090(10) | 85.690(8) |
| $\gamma$ (°) | 78.957(8) | 114.539(2) | 76.002(7) |
| $V$ (Å$^3$) | 3213.6(4) | 3378.9(9) | 3823.9(5) |
| $Z$ | 2 | 2 | 2 |
| $D_{calc}$ (g/cm$^{-3}$) | 1.293 | 1.212 | 1.142 |
| $\mu$ (mm$^{-1}$) | 1.086 | 0.917 | 0.814 |
| $F(000)$ | 1302 | 1304 | 1382 |
| Crystal size (mm) | 0.38 × 0.20 × 0.16 | 0.40 × 0.20 × 0.15 | 0.30 × 0.21 × 0.15 |
| $2\theta$ Range (°) | 50.7 | 50.0 | 50.7 |
| Reflections collected | 31888 | 32965 | 38374 |
| Independent reflections | 11713 | 12259 | 13936 |
| Reflections with $I \geqslant 2.0\sigma(I)$ | 8784 | 10066 | 11413 |
| Parameters refined | 746 | 737 | 806 |
| GOF | 1.089 | 1.093 | 1.123 |
| $R$ | 0.0748 | 0.0652 | 0.0760 |
| w$R$ | 0.1366 | 0.1263 | 0.1692 |



**Fig. 1.** Molecular structure of complex **1** drawn with 20% probability ellipsoids, the *t*-butyl atoms were not shown as ellipsoids and hydrogen atoms are omitted for clarity.



**Fig. 2.** Molecular structure of complex **2** drawn with 20% probability ellipsoids, the *t*-butyl atoms were not shown as ellipsoids and hydrogen atoms are omitted for clarity.

homoleptic lanthanide Schiff-base complexes were synthesized by the same method. Anhydrous SmCl$_3$ reacted with three equivalents of the sodium salts of the Schiff-bases formed *in situ* by the reaction of 3,5-Bu$_2^t$-2(OH)-C$_6$H$_2$CH=NAr′[Ar′ = 4-ClC$_6$H$_4$, 4-CH$_3$C$_6$H$_4$, 8-C$_9$H$_6$N(quinoline)] with NaH in THF, after workup, to give complexes **1–3** in good isolated yields (Scheme 1).

All these complexes have good solubility in THF, toluene and even in hexane. The compositions of these samarium species were confirmed by elemental analysis. In the IR spectra, the bands of stretching vibration of imine groups were observed at 1605 cm$^{-1}$ for complex **1**, 1603 cm$^{-1}$ for complex **2** and 1613 cm$^{-1}$ for complex **3**, respectively. Because of their paramagnetism, no resolvable NMR spectrum for these samarium Schiff-base complexes was obtained. The definitive molecular structures of complexes **1–3** were provided by a single-crystal X-ray structure determination.

### 3.2. Description of the structures

The molecular structures of complexes **1–3** are shown in Figs. 1–3, respectively, and selected bond lengths and angles are outlined in Table 2. Both complexes **1** and **2** are monomer in the solid state and have similar molecular structure. Each samarium ion in **1**
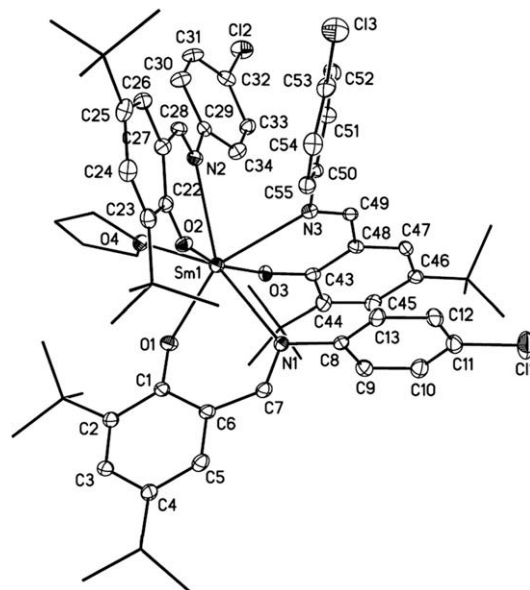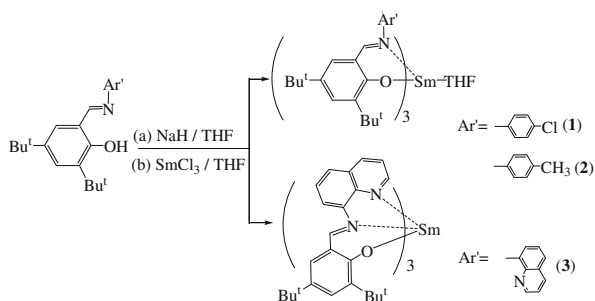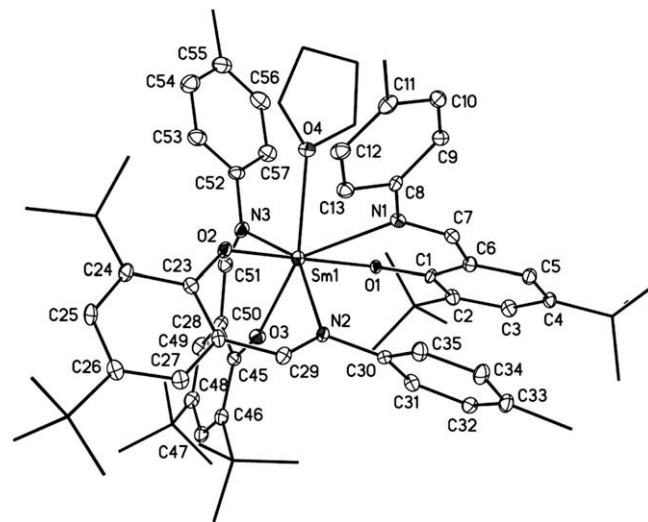


**Scheme 1.**

and **2** is ligated by three salicyladiminato moieties and a THF molecule. The geometry about the seven-coordinate samarium metal center can be best described as a distorted pentagonal bipyramidal, with two oxygen atoms (O2, O3 for complex **1** and O1, O2 for complex **2**) from Schiff-base ligands occupying the axial positions. The Sm–N(Schiff-base) distances in complexes **1** and **2** range from 2.579(4) to 2.709(4) Å, which are comparable with each other and also with those in {N[CH$_2$CH$_2$NCH(2-O-3, 5-Bu$_2^t$C$_6$H$_2$)]$_3$}Sm (**4**) [2.552(5), 2.555(5) and 2.560(5) Å] [21] and ($\eta^5$-C$_5$H$_5$)Sm($\mu$-OC$_{20}$H$_{20}$N$_2$O)]$_2$($\mu$-THF) · (THF)$_2$ (**5**) [2.55(5), 2.56(5), 2.65(5) and 2.67(5) Å] [26] published previously. The Sm–O(Ar) bond lengths vary from 2.193(4) to 2.233(3) Å, giving the average 2.214 and 2.231 Å in complexes **1** and **2**, respectively. These distances are comparable to the corresponding values observed in other lanthanide Schiff-base complexes: complex **4**, 2.232(4), 2.222(4), 2.218(3) Å; {N[CH$_2$CH$_2$NCH(2-O-3, 5-Bu$_2^t$C$_6$H$_2$)]$_3$}Nd, 2.241(6),
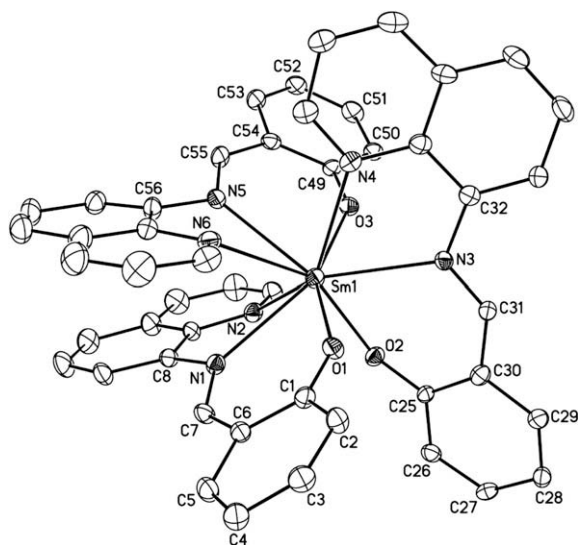
**Fig. 3.** Molecular structure of complex **3** drawn with 30% probability ellipsoids, *t*-butyl groups on the arene rings and hydrogen atoms are omitted for clarity.

2.248(4), 2.242(6) Å [21]; [(salen′)Y(μ-Cl)(THF)]₂ (salen′ = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine), 2.143(2), 2.16 Å [19]; (salen′)Y(C₅Me₅), 2.141(2), 2.148(2) Å [22]; [3,5-Bu$^t_2$-2-(O)C₆H₂CH=N(8-C₉H₆N)]YbCl₂(DME), 2.115(2) Å [29] when corrections are made for trivalent seven-coordinate ionic radii [35].

Complex **3** has an unsolvated monomeric structure, and the coordination sphere of the samarium center is composed of the six nitrogen atoms and three oxygen atoms from three tridentate Schiff-base ligands. The coordination geometry about the nine-coordinate samarium metal center can be viewed as a distorted tri-capped trigonal prism. The two triangular faces of the prism are constituted by O1, O2, N1 and O3, N4, N5, while N2, N3 and N6 are in the capping positions. The three dihedral angles between the O1O2N1 and N2N3N6 planes, the O1O2N1 and O3N4N5 planes and the O3N4N5 and N2N3N6 planes are 12.89°, 7.63° and 5.25°, respectively. The average Sm–N(imino) distance in complex **3** is 2.635 Å, and the average Sm–O interaction is 2.304 Å. These distances are consistent with the Sm–N and Sm–O distances in complexes **1** and **2** if substraction of the differences between se-

ven- and nine-coordinate Sm³⁺ in radii is made. However, the Sm–N(quinoline) distances range from 2.671(5) to 2.817(5) Å, with an average of 2.724 Å, which is slightly longer than the Sm–N(imino) distances, indicating that the interaction between samarium atom and nitrogen atom of the quinoline ring is somewhat weaker than that between samarium atom and nitrogen atom of imino groups.

### 3.3. The ring-opening polymerization of ε-CL

The catalytic activity of complexes **1–3** for the ring-opening polymerization of ε-CL was tested and the preliminary results are shown in Table 3. It can be seen that the Schiff-base ligands around the central metal atom have significant effect on the catalytic activity of the samarium complexes. For example, the yield reached as high as 100% at 60 °C for 35 min in the case of [M]/[I] = 100 (mole ratio) using complex **1** as the initiator, and 90% yield can also be obtained when the molar ratio of [M]/[I] increased to 300 after 140 min (Table 3, entries 1 and 7). Complex **2** showed a somewhat lower activity than that for complex **1** (Table 3, entries 1, 3 and 9, 10). This might be attributed to the difference in electronic effect between the two ligands, and the presence of an electron-withdrawing group on the Schiff-base ligand could increase the activity of the corresponding samarium complex. Similar results have been observed in the polymerization of propylene with bis(phenoxyimine) titanium catalyst [5,6]. The activity of both complexes **1** and **2** is lower than that of samarium aryloxide complex [36], but higher than that for phenyl compound (C₆H₅)₃Sm [37] and bis(salicyladiminato) lanthanide chlorides [2-OC₆H₄CH=N(2,6-$^i$Pr₂C₆H₃)]₂LnCl(THF) (Ln = Yb, Er) [31], due to the difference in central metals and ligands. In contrast, complex **3** is inactive under the same polymerization conditions. No activity shown by complex **3** might be attributed to that three of tridentate Schiff-base ligands with quinoline ring around the samarium atom make the coordination sphere about the central metal much more crowded and the coordination of an additional nitrogen atom from quinoline to samarium makes the nine-coordinated samarium metal being much more stable, which results in the difficulty in coordination and insertion of ε-CL to initiator. The polymers obtained by complexes **1** and **2** have high molecular weight ($M_n > 10^4$) and rather narrow molecular weight distributions ($M_w/M_n$ range from 1.20 to 1.60). However, complexes **1** and **2** showed low initiation efficiency (20–88%) (Table 3). Additionally, the observed molecular weights [$M_n$(obsd)] (GPC values corrected with the coefficient

**Table 2**
Selected bond distances (Å) and angles (°) for complexes **1**, **2** and **3**.

| 1 | | 2 | | 3 | |
|---|---|---|---|---|---|
| Sm(1)–O(1) | 2.23(5) | Sm(1)–O(1) | 2.23(3) | Sm(1)–O(1) | 2.32(4) |
| Sm(1)–O(2) | 2.19(4) | Sm(1)–O(2) | 2.23(3) | Sm(1)–O(2) | 2.29(4) |
| Sm(1)–O(3) | 2.22(4) | Sm(1)–O(3) | 2.23(3) | Sm(1)–O(3) | 2.31(4) |
| Sm(1)–N(1) | 2.61(5) | Sm(1)–N(1) | 2.71(4) | Sm(1)–N(1) | 2.62(5) |
| Sm(1)–N(2) | 2.67(5) | Sm(1)–N(2) | 2.58(4) | Sm(1)–N(2) | 2.68(5) |
| Sm(1)–N(3) | 2.63(5) | Sm(1)–N(3) | 2.65(4) | Sm(1)–N(3) | 2.62(5) |
| Sm(1)–O(4) | 2.52(4) | Sm(1)–O(4) | 2.49(4) | Sm(1)–N(4) | 2.67(5) |
| | | | | Sm(1)–N(5) | 2.67(5) |
| | | | | Sm(1)–N(6) | 2.82(5) |
| | | | | | |
| O(2)–Sm(1)–O(3) | 165.3(2) | O(1)–Sm–O(2) | 171.5(1) | O(1)–Sm–O(2) | 84.1(2) |
| O(1)–Sm–O(4) | 79.9(2) | O(3)–Sm–N(2) | 82.2(1) | O(1)–Sm–N(1) | 71.2(2) |
| O(1)–Sm–N(1) | 71.1(2) | O(3)–Sm–N(3) | 70.4(1) | O(2)–Sm–N(1) | 89.0(2) |
| N(1)–Sm–N(3) | 79.0(2) | O(4)–Sm–N(3) | 76.4(1) | N(2)–Sm–N(3) | 133.6(2) |
| N(3)–Sm–N(2) | 71.0(2) | O(4)–Sm–N(1) | 68.8(1) | N(2)–Sm–N(6) | 105.7(2) |
| O(4)–Sm–N(2) | 69.9(2) | N(2)–Sm–N(1) | 70.5(1) | N(3)–Sm–N(6) | 120.4(2) |
| | | | | N(4)–Sm–N(5) | 78.9(2) |
| | | | | O(3)–Sm–N(4) | 73.1(2) |
| | | | | O(3)–Sm–N(5) | 69.8(2) |

**Table 3**
Polymerization of ε-caprolactone initiated by complexes **1**, **2** and **3**.[a]

| Entry | Init. | [M]/[I][b] | Temperature (°C) | Time (min) | Yield (%) | $M_n$(calcd)[c] ($\times 10^4$) | $M_n$(obsd)[d] ($\times 10^4$) | $M_w/M_n$[d] | Efficiency[e] (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 100 | 60 | 35 | 100 | 1.1 | 2.2 | 1.60 | 50 |
| 2 | 1 | 200 | 40 | 35 | 26 | 0.6 | 3.0 | 1.20 | 20 |
| 3 | 1 | 200 | 60 | 35 | 80 | 1.8 | 2.5 | 1.39 | 72 |
| 4 | 1 | 200 | 80 | 35 | 87 | 2.0 | 3.8 | 1.40 | 53 |
| 5 | 1 | 300 | 60 | 35 | 53 | 1.8 | 2.7 | 1.37 | 67 |
| 6 | 1 | 300 | 60 | 70 | 82 | 2.8 | 3.2 | 1.37 | 88 |
| 7 | 1 | 300 | 60 | 140 | 90 | 3.1 | 3.9 | 1.37 | 79 |
| 8 | 1 | 500 | 70 | 180 | 98 | 5.6 | 7.2 | 1.85 | 78 |
| 9 | 2 | 100 | 60 | 35 | 92 | 1.0 | 2.1 | 1.40 | 48 |
| 10 | 2 | 200 | 60 | 35 | 74 | 1.7 | 3.2 | 1.24 | 53 |
| 11 | 2 | 500 | 70 | 180 | 97 | 5.5 | 6.4 | 2.18 | 86 |
| 12 | 3 | 100 | 60 | 35 | 0 | – | – | – | – |

[a] Polymerization conditions: solvent, toluene; solvent/monomer = 5 v/v.
[b] [M]/[I] = [Monomer]/[Initiator].
[c] $M_n$(calcd) = 114 × [M]/[I] × yield (calculated for one polymer chain per samarium atom).
[d] Measured by GPC calibrated with standard polystyrene samples and corrected by the Mark–Houwink equation [$M_n$(obsd) = 0.56$M_n$ (GPC)] [38].
[e] Initiation efficiency = $M_n$(calcd)/$M_n$(obsd).

0.56) [38] are higher than the theoretical ones [$M_n$(calcd)] (calculated for one polymer chain per samarium atom) and the value of $M_n$(calcd)/$M_n$(obsd) could give the average number of efficient Schiff-base ligands per samarium atom during the polymerization. It is obvious that this average number is lower than 1. Therefore, we can suggest that only one of the three Schiff-base ligands in the samarium complex could initiate the ring-opening polymerization of ε-CL. In order to clarify the polymerization mechanism, oligomers of ε-CL, terminated by 2-propanol or methanol, have been prepared from the oligomerization of ε-CL with a [ε-CL]/[complex **2**] molar ratio of 10 according to the literature procedures [17,36]. However, the ^{1}H NMR spectra show no signal of an isopropyl group or an Schiff-base ligand. This might be attributed to that initiation efficiency of complex **2** is rather low and the oligomers with low molecular weight are difficult to be obtained.

The influence of reaction conditions on the polymerization was also examined using complex **1** as the single component initiator. In the case of [M]/[I] = 300 (mole ratio), the yields and the molecular weights of the polymers obtained increased with the increase of the reaction time at 60 °C, whereas the molecular weight distributions of the polymers remained almost unchanged (Table 3, entries 5–7). The polymerization temperature also has great effect on the catalytic activity of the samarium complexes. When the polymerization temperature increased from 40 to 80 °C, the yields increased from 26% to 87% (Table 3, entries 2–4), and the molecular weight distributions ($M_w/M_n$) of the resulting polymers will be slightly broadened.

### 3.4. Guanylation of aniline with N,N-diisopropylcarbodiimide

Recently, catalytic guanylation of amines with carbodiimides provides a convenient approach to guanidines and has attracted increasing attention [39–47]. Therefore, in order to further reveal the catalytic activity of homoleptic Schiff-base complexes of lanthanides, we tested the catalytic activity of complexes **1–3** for guanylation of aniline with N,N-diisopropylcarbodiimide with 5 mol% catalyst loading (Table 4). The results showed that the reaction could take place under solvent-free conditions to give the expected product (N-phenyl-N′,N′-diisopropylguanidine) in 53%, 43%, and 10% yields using the catalysts **1**, **2** and **3**, respectively (Table 4, entries 1–3). The active order, **1** > **2** > **3**, which agrees with that for ε-caprolactone polymerization, was observed. Under the same reaction condition the reaction of amine with carbodiimine does not occur without the presence of samarium complex. The results indicate that homoleptic Schiff-base complexes can serve as a cat-

**Table 4**
Catalytic addition of the aniline to N,N-diisopropylcarbodiimide.
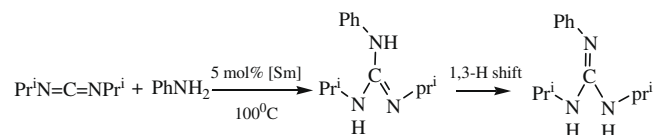


| Entry | Cat. | Temperature (°C) | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | 1 | 100 | 1 | 53 |
| 2 | 2 | 100 | 1 | 43 |
| 3 | 3 | 100 | 1 | 10 |
| 4 | 1 | 100 | 4 | 84 |
| 5 | 1 | 60 | 0.5 | 5 |

[a] Isolated yield.

alyst even if the activity is rather low, and the activity depends on the ligands.

### 3.5. Reaction of complex **3** with phenyl isocyanate

Lanthanide complexes were reported to serve as the catalyst for polymerization of alkyl isocyanate [48] and alkyl isocyanates are well-known to be able to insert into Ln–C, Ln–N and Ln–S bond to give the corresponding insertion products [49–51]. Thus, the reaction of complex **3** with phenyl isocyanate in 1:1 molar ratio was tried. After workup, the cyclotrimer of phenyl isocyanate $(PhNCO)_3$ was isolated in 80% yield, which indicating complex **3** might be an active promoter for cyclotrimerization of phenyl isocyanate.

## 4. Conclusion

Three of homoleptic Schiff-base samarium complexes with the formula $[3,5-Bu^t_2-2-(O)C_6H_2CH=NAr']_3Sm(THF)_n$ [Ar′ = 4-ClC₆H₄ (**1**), 4-CH₃C₆H₄ (**2**), 8-C₉H₆N(quinoline) (**3**)] were prepared by metathesis reactions of anhydrous $SmCl_3$ with Schiff-base salt in good yields, and structurally characterized. The Schiff-base ligands around the central metal ion have significant effect on the catalytic behavior of the homoleptic Schiff-base samarium complexes: complexes **1** and **2** showed moderate activity for the ring-opening polymerization of ε-caprolactone, as well as guanylation of aniline with N,N-diisopropylcarbodiimide, whereas complex **3** was almost inactive under the same reaction conditions.

## Acknowledgement

## Appendix A. Supplementary material

CCDC 670747, 670748 and 670749 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.024.

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