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Synthesis of γ-amidine-functionalized dianionic β-diketiminato lanthanide amides and trianionic β-diketiminato Na/Sm heterobimetallic complexes and their reactivity in polymerization of L-lactide†

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The readily accessible dianionic β-diketiminato lanthanide amido complexes $LnLN(SiMe_3)_2(THF)$ ($L = \{(2,6\text{-}^iPr_2C_6H_3)NC(CH_2)CHC(CH_3)N(2,6\text{-}^iPr_2C_6H_3)\}^{2-}$) show an unprecedented reactivity toward carbodiimides. The reaction with *N*,*N*′-dicyclohexylcarbodiimide (DCC) led *via* [4 + 2] cycloaddition to γ-amidine-functionalized dianionic β-diketiminato lanthanide amido complexes, $LnL^1N(SiMe_3)_2$ ($L^1 = \{[(NHC_6H_{11})(NC_6H_{11})C]HC[C(CH_2)N(2,6\text{-}^iPr_2C_6H_3)]_2\}^{2-}$, Ln = Sm(**1**), Yb(**2**), Y(**3**), Gd(**4**)). Conversion of a mixture of $SmLN(SiMe_3)_2(THF)$ and $NaN(SiMe_3)_2$ with carbodiimide furnished the heterobimetallic complexes of Sm/Na with a novel amidinate-functionalized trianionic β-diketiminate ligand, $[Na(DME)_2](\mu\text{-}L^2)\text{-}[SmN(SiMe_3)_2]$ ($L^2 = \{[C(N^iPr)_2]HC[C(CH_2)N(2,6\text{-}^iPr_2C_6H_3)]_2\}^{3-}$, DME = dimethoxyethane) (**5**) for *N*,*N*′-diisopropylcarbodiimide (DIC) and $[Na(DME)_3]^+[SmL^3N(SiMe_3)_2]^-$ ($L^3 = \{[C(NCy)_2]HC[C(CH_2)N(2,6\text{-}^iPr_2C_6H_3)]_2\}^{3-}$) (**6**) for DCC. Molecular structures of complexes **1–6** were determined by an X-ray single crystal structure analysis. Complexes **1–4** were found to be highly active initiators of the ring-opening polymerization (ROP) of L-lactide (L-LA). The activity depended on the central metal with the increasing sequence of Yb < Y < Gd < Sm. Notably, the binary **1**/BnOH (benzyl alcohol) system exhibited an "immortal" nature and proved able to convert 2000 equivalents of L-LA with up to 100 equivalents of BnOH per initiator. All the polylactides (PLAs) obtained showed monomodal, narrow molar mass distributions (M_w/M_n = 1.08–1.13) with the M_n (average number molar mass) decreasing with increasing amount of BnOH proportionally.

Introduction

The dianionic β-diketiminate ligand in its metal complexes has been found to have a dipolar character,[1] which leads to a variety of remarkable transformations with various substrates. Examples include activation of N–H bonds of ammonia and/or the secondary amine $HN(C_6F_5)_2$,[1c,2a–c] nucleophilic addition with several reagents, such as RH (R = OH, PhO, C_6F_5O, $PhCO_2$,[1c,2d] or OTf[1b]), Me_3SiOTf,[2e–g] M–Cl (M = Si or Ge),[2h] $B(C_6F_5)_3$, $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$,[2g,i,j] $N_2CHSiMe_3$,[2j] and $BrCH_2CH_2Br$,[2e] and [4 + 2] cycloaddition of the C≡C bond of terminal alkynes as well.[2k] The striking reactivity makes them very useful in organometallic chemistry as readily available organometallic intermediates.

Recent investigations revealed that dianionic β-diketiminatolanthanide complexes are facilely prepared by either reduction of certain β-diketiminato ytterbium complexes[3] or deprotonation by the use of an external strong base[4] and self-deprotonation of the β-diketiminate ligand in sterically hindered lanthanide complexes.[5] Moreover, the dianionic β-diketiminatothulium complex was reported to be reactive and its protonation can be achieved by using an appropriate ammonium tetraarylborate, leading to the formation of salts containing a homoleptic bis-β-diketiminatothulium cation.[5a] More recently, we have succeeded in the synthesis of a series of dianionic β-diketiminatolanthanide amides $LnLN(SiMe_3)_2(THF)$ by the reaction of β-diketiminatolanthanide

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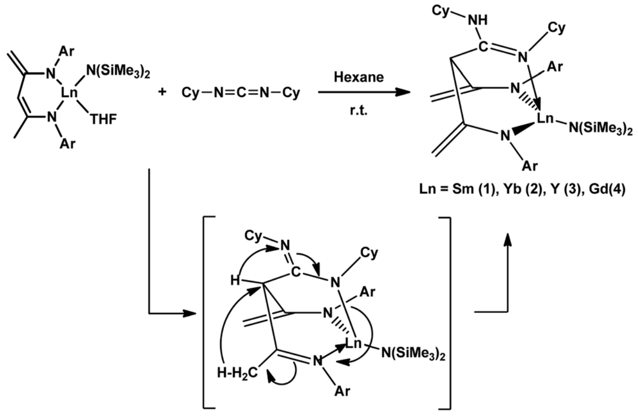
dichlorides with $NaN(SiMe_3)_2$ *via* sterically induced deprotonation, and a cationic β-diketiminatosamarium amide *via* protonation of $SmLN(SiMe_3)_2(THF)$ by $[HNEt_3][BPh_4]$.[6a] We have also demonstrated that $SmLN(SiMe_3)_2(THF)$ is highly reactive towards aromatic nitrile and ketene imine. The reaction with C_6H_5CN ($4\text{-}CH_3OC_6H_4CN$), and $(C_6H_5)_2C{=}C{=}N^tBu$, respectively, resulted in the formation of the corresponding modified dianionic β-diketiminatosamarium amides. In these complexes the skeleton of the original dianionic β-diketiminato ligand is entirely modified.[6b] The peculiar reactivity of $SmLN(SiMe_3)_2(THF)$ prompted us to probe the application of $LnLN(SiMe_3)_2(THF)$ as useful precursors in organolanthanide chemistry.

Carbodiimides are important substrates for metal-based reactivity studies. Various reaction modes, such as insertion reaction into Ln–N and Ln–C bonds, reductive coupling reaction *etc.*, were realized upon the metal complexes and carbodiimide used, which result in the formation of metal complexes with various skeletons.[7] Herein we report the reactions of $LnLN(SiMe_3)_2(THF)$ with carbodiimides that show a novel reaction mode, distinguishing from that found in the cases with nitrile and ketene imine reported,[6b] and the formation of both unpredictable amides **1–4** and Na/Sm heterobimetallic complexes **5** and **6**. The reactivity of complexes **1–4** in ROP of L-LA and an "immortal" polymerization with complex **1** and BnOH are also described.

Results and discussion

Reaction of $LnLN(SiMe_3)_2(THF)$ with *N*,*N*′-dicyclohexylcarbodiimide(DCC): synthesis and molecular structure of complexes 1–4

Addition of a hexane solution of DCC into a red *n*-hexane solution of $SmLN(SiMe_3)_2(THF)$[6a] in a molar ratio of 1 : 1 at room temperature resulted in a rapid color change to pale yellow. After workup, yellow crystals were isolated in 60% yield upon crystallization from *n*-hexane solution. The crystals were fully characterized to be complex **1** (Scheme 1).



Scheme 1 The synthesis of complexes **1–4**.

Complex **1** is very sensitive to air and moisture. It gave a satisfactory elemental analysis, consistent with the formula. IR spectra show the band at 1646 cm^{-1} assigned to the group of N═C from the CyNCNCy. However, the resolved ^1H NMR spectrum could not be obtained as the paramagnetic Sm(III). The identity of complex **1** was further confirmed by an X-ray structure determination.

Complex **1** crystallizes in triclinic $P\bar{1}$. The molecular structure is shown in Fig. 1, and the selected bond lengths and angles are listed in Table 1. Complex **1** consists of a bicyclo-[2,2,2]octane-like core with a LnC_5N_2 skeleton, and the γ-C atom and Sm metal as bridgehead atoms. The center Sm atom is bound to three nitrogen atoms from the newly formed ligand L^1 and one $-N(SiMe_3)_2$ group. Thus the original dianionic β-diketiminate ligand L has undergone modification and

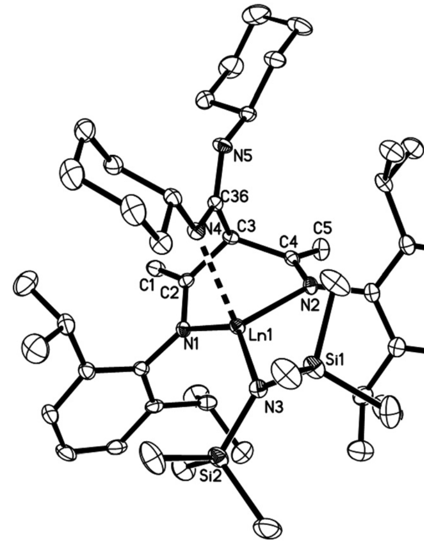


Fig. 1 ORTEP diagram of complexes **1–4** showing atom-numbering scheme.

Table 1 Selected bond lengths (Å) and bond angles (°) for complexes **1–4**

Bond lengths	**1**	**2**	**3**	**4**
Ln1–N1	2.388(3)	2.184(3)	2.248(2)	2.284 (2)
Ln1–N2	2.251(4)	2.209(3)	2.209(2)	2.239(2)
Ln1–N3	2.308(4)	2.193(3)	2.237(2)	2.275(2)
Ln1–N4	2.364(4)	2.314(3)	2.352(2)	2.3811(2)
N1–C2	1.338(5)	1.388(4)	1.384(3)	1.380(3)
N2–C4	1.383(5)	1.391(4)	1.380(3)	1.381(3)
C1–C2	1.399(6)	1.340(5)	1.334(4)	1.344(3)
C2–C3	1.539(5)	1.538(5)	1.543(3)	1.545(3)
C3–C4	1.533(6)	1.548(5)	1.544(3)	1.542(3)
C4–C5	1.334(6)	1.333(5)	1.340(3)	1.343(3)
C3–C36	1.543(6)	1.544(5)	1.536(3)	1.538(3)
C36–N4	1.335(6)	1.304(4)	1.307(3)	1.311(3)
C36–N5	1.328(5)	1.351(4)	1.354(3)	1.345(3)
N4–C36–N5	123.6(4)	124.0(3)	123.3(2)	123.37(2)
N1–Ln1–N2	88.76(12)	95.39(11)	93.59(7)	92.64(6)
N1–Ln1–N4	78.27(11)	83.63(10)	81.68(7)	80.87(6)
N2–Ln1–N4	85.44(13)	87.59(10)	86.57(7)	85.57(6)

the Sm and the γ-C atom are now in a non-planar LnN_2C_3 six-membered ring. The four-coordinate Sm atom adopts a distorted tetrahedral geometry.

The bonds of C1–C2 (1.399(6) Å) and C4–C5 (1.334(6) Å) both belong to a double bond, whereas the bonds of C2–C3 (1.539(5) Å) and C3–C4 (1.533(6) Å) are typical of single bonds, indicating the newly formed L^1 is an amidine-functionalized dianionic β-diketiminate ligand rather than an amidinate-functionalized monoanionic β-diketiminate ligand. Thus, the Sm1–N4 bond is a dative one. The Sm1–N2 bond length of 2.251(4) Å is comparable to that found in $SmLN(SiMe_3)_2(THF)$.[6a] The Sm1–N1 bond (2.388(3) Å) is much longer, even 0.024 Å longer than the dative Sm1–N4 bond. This may be because of the existence of the sterically hindered amidine group at the γ-C atom. The bond length of C3–C36 (1.543(6) Å) is typical of a single bond, whereas the C–N bond lengths (N4–C36, 1.335(6) Å; N5–C36, 1.328(5) Å) in the NCN unit are shorter and almost equal, indicating a typically delocalized amidino fragment. The Sm1–N3 (2.308(4) Å) bond length is comparable with that in the parent complex $SmLN(SiMe_3)_2(THF)$.[6a]

The formation of complex **1** is somewhat surprising. The unpredictable complex **1** may be formed by [4 + 2] cycloaddition reaction of $SmLN(SiMe_3)_2(THF)$ with DCC occurred at γ-C atom, followed by H-shift (Scheme 1). To the best of our knowledge the present reaction mode has not been found in the reaction chemistry of a dianionic β-diketiminate lanthanide derivative with an unsaturated small molecule. The [4 + 2] cycloaddition may be promoted by the electrophilic character of the lanthanide metal center and the nucleophilic character of the endocyclic γ-C atom in the LnN_2C_3 ring.

Complex **1** represents the first example of γ-C modified dianionic β-diketiminate stabilized lanthanide derivative formed by a direct reaction of a lanthanide metal complex with an organic molecule. To see the generality of the procedure, the same reaction with the analogous Yb, Y and Gd complexes were conducted. All the reactions went smoothly and the color change from dark green to purple for Yb and from orange to yellow for Y and Gd was observed. From these resulting solutions, the analogous complexes $LnL^1N(SiMe_3)_2$ (Ln = Yb(**2**), Y(**3**), Gd(**4**)) were isolated as purple crystals for complex **2**, yellow crystals for complexes **3** and **4** in moderate yields (70% for **2**, 62% for **3**, 60% for **4**) (Scheme 1).

All the bulk materials gave satisfactory elemental analyses. The room-temperature ^1H NMR spectrum of complex **3** in C_6D_6 showed that the resonances of the four methine groups from the isopropyl groups on the phenyl rings were two septets, suggesting restricted rotation about the *N*-dianionic β-diketiminate bond. The existence of two methylene groups on the ligand backbone is confirmed by the spectroscopic observation of two singlets at 4.04 and 3.49 ppm. The two singlets, not the geminal doublets, observed for the protons of CH_2 groups may be attributed to the delocalized property of the chemical bonds in both of the $CH_2{=}C–N$ units as confirmed by the bond parameters determined by X-ray structural analysis. No resolved ^1H NMR spectrum for **2** and **4** could be obtained, as paramagnetic Yb(III) and Gd(III). The identity of complexes **2–4** was confirmed by an X-ray structural determination. Complex **2** isolated as a solvate **2**·0.5(*n*-hexane). Complexes **2–4** all crystallize in triclinic $P\bar{1}$. The molecular structures of complexes **2–4** are shown in Fig. 1 as they and complex **1** are isostructural. The selected bond lengths and angles are listed in Table 1.

In each complex the bonds of C1–C2 and C4–C5 both belong to a double bond whereas the bonds of C2–C3 and C3–C4 are typical of single bonds (Table 1). These bond parameters demonstrate that the formed new ligand L^1 in **2–4** is a modified dianionic β-diketiminate ligand as in the case of complex **1**. The bond lengths of N1–C2 and N2–C4 in **2–4** range from 1.380–1.391 Å indicating a delocalized CH_2–C–N unit. The delocalized property of the chemical bonds in both of the CH2=C–N units led to the observation of two singlets for the protons of CH2 groups in the ^1H NMR spectrum of **3**. The bond lengths of Ln1–N1 (2.207(3) Å for **2**, 2.248(2) Å for **3** and 2.2841(17) Å for **4**) and Ln1–N2 (2.176(3) Å for **2**, 2.209(2) Å for **3** and 2.2749(17) Å for **4**) are well comparable with each other and the values can also be compared to those of their parent complexes reported.[6a] The bond lengths of Ln1–N4 in complexes **2–4** are in the range of a dative bond and are consistent with the difference in ionic radii of the center metals.

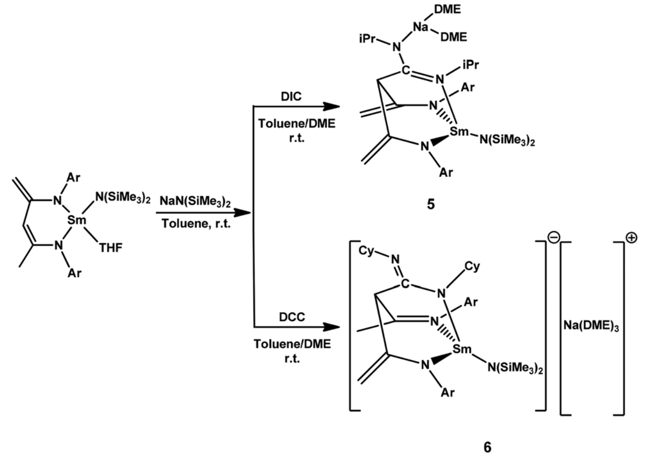
However, some definitely unusual bond parameters for **1** (Ln = Sm), compared to **2–4** (Ln = Yb, Y and Gd) were noticed. For example, the Ln1–N4 bond in **1** is about 0.045 Å shorter, implying a stronger donor character for N4 in **1**. The latter is consistent with pronounced elongation of the N4–C36 bond (1.335(6) Å) compared to those of the N4–C36 bond in **2–4** (1.304(4) Å in **2**; 1.307(3) Å in **3**; 1.311(3) Å in **4**). The C1–C2 bond is about 0.05 Å longer and the N1–C2 bond is 0.05 Å shorter than those found in **2–4**.

The bond lengths of Ln1–N3 are 2.193(3) Å for **2**, 2.237(2) Å for **3** and 2.2749(17) Å for **4**, which are consistent with that in **1**, when the differences in ionic radius among these metals are considered. The values are slightly longer than that in the parent $LnLN(SiMe_3)_2(THF)$.[6a] This may be because of the bulkier ligand L^1 in complexes **2–4** compared to the L ligand in $LnLN(SiMe_3)_2(THF)$.

An attempt to prepare a corresponding cationic complex by the reaction of complex **1** with $[HNEt_3][BPh_4]$, as the case with its parent complex,[6a] was not successful and complex **1** was recovered completely, reflecting complex **1** is not as active as its parent complex.

Reaction of a mixture of $SmLN(SiMe_3)_2(THF)$ and $NaN(SiMe_3)_2$ with carbodiimide: synthesis and molecular structures of complexes 5 and 6

It was unexpected that treatment of the *n*-hexane solution of $SmLN(SiMe_3)_2(THF)$ with an equivalent of *N*,*N*′-diisopropylcarbodiimide (DIC) solution in *n*-hexane at room temperature did not result in an isolable solid state, but instead a tar was obtained. Thus, the difficulty was met in the further purification and characterization of the product. To see whether an addition of $NaN(SiMe_3)_2$ into the reaction of



Scheme 2 The synthesis of complexes **5** and **6**.

$SmLN(SiMe_3)_2(THF)$ with DIC could catch the "product" of [4 + 2] cycloaddition, the reaction of a mixture of $SmLN(SiMe_3)_2(THF)$ and $NaN(SiMe_3)_2$ with DIC at a 1 : 1 molar ratio was then conducted at room temperature. Indeed, the reaction afforded yellow crystals in 30% yield upon crystallization from a mixture of DME and hexane. The crystals were characterized to be the heterobimetallic complex **5** (Scheme 2). The rather low yield of complex **5** could be attributed to the high solubility of complex **5** even in *n*-hexane. Complex **5** is sensitive to air and moisture, but is thermally stable. The molecular structure of complex **5** was determined by an X-ray crystal structure analysis.

Single crystals of complex **5** suitable for X-ray diffraction analysis were obtained by recrystallization from a mixture of DME and *n*-hexane at −10 °C. The molecular structure of complex **5** is shown in Fig. 2 with the selected bond lengths and angles. Complex **5** is an anionic heterobimetallic complex consisting of a bicyclo[2,2,2]octane-like core with a LnC_5N_2 skeleton and a Na ion coordinated to the formed amidinate group. The Sm atom and the γ-C atom locate at bridgeheads of the bicycle. The central Sm atom is coordinated by three nitrogen atoms from the newly formed trianionic ligand L^2 and one $-N(SiMe_3)_2$ group. The coordinated geometry around the four-coordinated Sm atom can be described as a distorted tetrahedron. The lengths of Sm1–N1 (2.299(8) Å) and Sm1–N2 bonds (2.270(8) Å) are almost consistent with the corresponding values in $SmLN(SiMe_3)_2(THF)$.[6b] The lengths of C1–C2 and C4–C5 bonds are 1.343(13) Å and 1.350(13) Å, respectively, indicating that both are double bonds. The C2–C3 (1.563(13) Å) and C3–C4 (1.552(13) Å) bonds both belong to single bonds. The length of the Sm1–N3 bond (2.315(7) Å) is almost consistent with that of the Sm1–N1 bond. These bond parameters indicate that L^2 is a trianionic ligand. The length of the Na1–N4 bond (2.458(9) Å) is much longer than those found in sodium amides reported and that of the Sm1–N3 bond, implying that the Na1–N4 bond is a dative one. The C3–C30 bond (1.566(13) Å) is typical of a single bond. The N4–C30 bond is shorter than a C–N single bond, whereas the N3–C30 bond is longer than a C═N double bond, indicating a significantly π-delocalized anionic N3CN4 fragment. Thus, the newly formed anionic amidinate group coordinates to both metals of Sm and Na as a bidentate species.

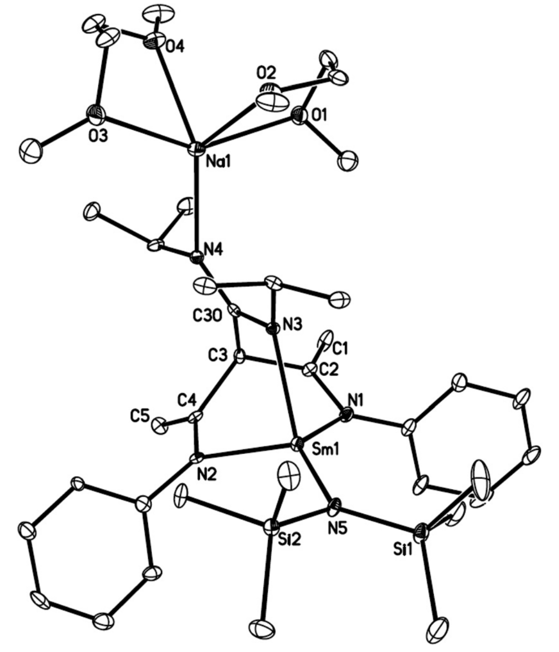


Fig. 2 ORTEP diagram of complex **5** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and ^{i}Pr substituents of L^2 are omitted for clarity. Selected bond lengths (Å)and angles (°): Sm(1)–N(1) 2.299(8), Sm1–N2 2.270(8), Sm1–N3 2.315(7), Sm1–N4 2.317(8), Na1–N5 2.458(9), N1–C2 1.377(12), C2–C3 1.563(13), C3–C4 1.552(13), C4–N2 1.385(11), C4–C5 1.350(13), C3–C30 1.566(13), C30–N4 1.354(11), C30–N5 1.315(12), N1–Sm1–N2 92.8(3), N1–Sm1–N3 84.7(3), N2–Sm1–N3 88.6(3), O1–Na1–O3 146.7(3), O2–Na1–N5 135.5(3), N5–Na1–O4 128.6(3), O2–Na1–O4 92.0(3).

The Na atom is ligated by one nitrogen atom of the ligand L^2 and four oxygen atoms from the two DME molecules. The Na atom is five coordinate and adopts a distorted-trigonal–bipyramidal geometry.

Replacement of DIC by DCC in the above reaction led to the color change from red to yellow. However, crystallization from the resulting solution did not give the analogue, but a discrete ion-pair complex **6** (Scheme 2). The molecular structure of complex **6** was determined by X-ray crystallography technique. The skeleton of the solid state structure of complex **6** can be clearly observed as shown in Fig. 3. The detailed bond parameters could not be obtained because of the poor quality of the crystals. Complex **6** consists of an disconnected anion $[L^3SmN(SiMe_3)_2]^-$ and a cation $[Na(DME)_3]^+$. The center Sm atom in the anion is coordinated by one L^3 and one amido group being four coordinate. The coordinate geometry can be described as a distorted tetrahedron, which is similar to that of complex **6**. Efforts to isolate fine single-crystals were unsuccessful.

ROP of L-LA by complexes 1–4

Polyesters, such as poly(lactide), poly(glucol), poly(ε-caprolactone), and related copolymers, have wide applications in the

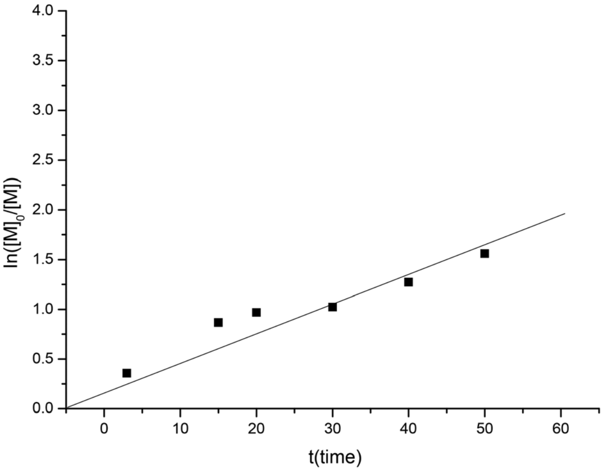


Fig. 3 Plot of $\ln([M]_0/[M])$ *versus* time for the polymerization of L-LA by **1**. Conditions: $[M]_0/[I]_0 = 3000$, $[\text{L-LA}]_0 = 1.0$ M, in toluene, 25 °C.

medical field as biodegradable surgical sutures or as a delivery medium for controlled release of drugs due to their biodegradable, biocompatible, and permeable properties.[8] The ROP of cyclic esters promoted notably (but not only) by single-site metal-based initiators/catalysts, is definitely the most useful route for the synthesis of aliphatic polyesters with predictable molecular weight and low polydispersity index.[9]

The complexes **1–4** present new candidates for studying the ROP of cyclic esters. This is because each of them contains a highly electropositive metal, an active group of $–N(SiMe_3)_2$ and a stationary spectator ligand (L^1). Thus, complexes **1–4** were evaluated for the ROP of L-LA in toluene at room temperature with a molar ratio of monomer to initiator of 2000 ($[M]_0$ = 1.0 M). Representative results are summarized in Table 2. Of the catalysts investigated, complex **1** (entry 3) was the most effective with a 90% yield of PLA within 1.5 min. The resulting PLA had the M_n as high as 25.7×10^4 with M_w/M_n of 1.37. Complex **4** was also effective, but was less active than **1** (entry 10). Complex **2** showed the lowest activity and a 10% yield of PLA was obtained (entry 4). Even with elongation of the polymerization time to 60 min, only 47% yield could be obtained (entry 6). The polymerization with **3** gave a 25% yield within 1.5 min and a 96% yield after 60 min (entries 7–9). The active sequence of **2** < **3** < **4** < **1** observed here is consistent with the increasing order of ion radii of metals. Such an active order is often observed in the systems with lanthanide metal initiators.[10] Polymerization in THF is less active than that in toluene (Table 2, entry 15). This may be because of the competitive coordination of THF.

Complexes **5** and **6** are much less active than complex **1** (entries 11–14).

The polymerization of L-LA with complex **1** proceeded smoothly in toluene at the molar ratios of monomer-to-complex **1** ranging from 1000 to 3000 (entries 1–3, 16–19). The M_n(obsd) of the resulting PLAs increased almost linearly with the ratio and were in close agreement with the M_n(calcd) values calculated for one chain growing per metal center. All PLAs obtained in the present polymerizations showed a unimodal molar mass distribution as revealed by SEC (size

Table 2 Polymerization of L-LA by complexes **1–6**[a]

Run	Initiator	$[M]_0/[I]_0/[BnOH]$	t (min)	Yield[b] (%)	M_n (calcd)[c] (10^4 g mol^{-1})	M_n (obsd)[d] (10^4 g mol^{-1})	PDI
1	**1**	1000 : 1 : 0	1.5	95	13.7	15.3	1.45
2	**1**	1500 : 1 : 0	1.5	95	20.5	22.3	1.38
3	**1**	2000 : 1 : 0	1.5	90	25.9	25.7	1.37
4	**2**	2000 : 1 : 0	1.5	10	2.88	3.46	1.46
5	**2**	2000 : 1 : 0	30	20	5.77	6.80	1.39
6	**2**	2000 : 1 : 0	60	47	13.5	12.3	1.42
7	**3**	2000 : 1 : 0	1.5	25	7.21	6.89	1.43
8	**3**	2000 : 1 : 0	30	75	21.6	18.7	1.30
9	**3**	2000 : 1 : 0	60	96	27.7	30.2	1.42
10	**4**	2000 : 1 : 0	1.5	70	20.2	20.8	1.42
11	**5**	2000 : 1 : 0	1.5	—	—	—	—
12	**5**	2000 : 1 : 0	20	25	7.21	5.89	1.35
13	**6**	2000 : 1 : 0	1.5	—	—	—	—
14	**6**	2000 : 1 : 0	10	33	9.51	7.42	1.45
15[e]	**1**	2000 : 1 : 0	1.5	78	22.5	21.2	1.46
16	**1**	2500 : 1 : 0	1.5	60	21.6	20.1	1.41
17	**1**	2500 : 1 : 0	30	96	34.6	31.6	1.42
18	**1**	3000 : 1 : 0	3	30	13.0	15.7	1.43
19	**1**	3000 : 1 : 0	50	80	34.6	32.7	1.33
20[f]	**1**	2000 : 1 : 2	1.5	98	14.1	14.8	1.13
21[f]	**1**	2000 : 1 : 5	3	99	5.71	5.30	1.12
22[f]	**1**	2000 : 1 : 10	15	99	2.85	2.94	1.08
23[f]	**1**	2000 : 1 : 20	20	98	1.41	1.36	1.13
24[f]	**1**	2000 : 1 : 50	30	98	0.57	0.59	1.09
25[f]	**1**	2000 : 1 : 100	30	96	0.28	0.27	1.11

[a] General polymerization conditions: in toluene, [LLA] = 1 mol L^{-1}. T = 25 °C. [b] Yield: weight of polymer obtained/weight of monomer used. [c] M_n value calculated from the relation: molecular weight of M × conv. × [M]/[Ln]. [d] Determined by GPC against polystyrene standards in THF, multiplied by 0.58.[12] [e] THF as solvent. [f] [LLA] = 2 mol L^{-1}, time is not optimized.

exclusion chromatography) calibration and had moderate molar mass distributions (M_w/M_n 1.37–1.46, entries 1–3 and 16–19); inflecting the polymerization with complex **1** has a limited transesterification reaction.

It should be noted that complex **1** is much more active than the previously reported monoanionic β-diketiminatolanthanide complexes.[11] This is probably due to the more open coordination sphere around the center metal by the L^1 ligand compared to those by the two mixture ligands of monoanionic β-diketiminato and an another ancillary ligand, and/or by two monoanionic β-diketiminato ligands.[11]

The polymerization kinetics of L-LA with complex **1** at a molar ratio of monomer to **1** of 3000 was further investigated at room temperature in toluene. The conversion increases with time, and a first order dependence on the monomer concentration was observed (Fig. 3). The M_n of the polymers increased linearly with the monomer conversion, while the values of M_w/M_n remained relatively narrow (M_w/M_n = 1.31–1.43) (Fig. 4), which demonstrated that the polymerization in this system occurs in a living manner. The end groups analysis of the oligomer of L-LA, which was prepared from the polymerization of L-LA using complex **1** in a 1/10 molar ratio and quenched by wet *n*-hexane, were determined by ^{1}H NMR. The ^{1}H NMR spectrum (see ESI†) exhibited the quartet characteristic of a –C*H*-(Me)OH terminal group at *δ* 4.35 ppm. The –CH(Me)OH group was formed by hydrolysis of the metal–silylamido bond. An additional resonance at *δ* 4.18 ppm assigned to the C*H*$_2$OH end group[12] was also observed. The results indicate that the present polymerization could be supposed to proceed by a coordination insertion mechanism.

The polymerization with complex **1** in the presence of two equivalents of BnOH gave the PLA with narrower molar mass distribution (M_w/M_n 1.13, entry 20, compared to that obtained by the system without BnOH M_w/M_n 1.37, entry 3) and the M_n close to the calculated one, indicating the binary system of **1**/BnOH had a living character.

To address the possibility of achieving immortal polymerization using these systems by introducing several equivalents of a chain-transfer agent, detailed polymerizations with complex **1** and BnOH were conducted. Representative results are summarized in Table 2. Immortal polymerization with complex **1** and BnOH could be realized at room temperature (Table 2, entries 20–25). Remarkably, the binary **1**/BnOH system was able to almost quantitatively convert 2000 equivalents of L-LA with up to 100 equivalents of BnOH per metal initiator. The obtained PLAs at various BnOH/**1** ratios (from 2 to 100) showed monomodal, narrow molar mass distributions (M_w/M_n = 1.08–1.13) with M_n values decreasing proportionally with increasing amounts of BnOH. Thus, the amidino-modified dianionic β-diketiminato ligand L^1 appears to be a good ligand for stabilizing the oxophilic samarium center, preventing irreversible decomposition in the presence of a large excess of free alcohol, thereby initiating a living chain transfer polymerization to give the PLAs with a chain end caped by the OH group.

The end-group of the resulting PLA was measured by ^{1}H NMR. The results (see ESI†) revealed that the resulting PLA macromolecular chain is capped with the OH group at one end, and with the PhCH$_2$O– group at the other end (PhCH$_2$O– is overlapped by the methyl group in the polymer chain at about 5.12 ppm and at 2.62 ppm for the OH group).

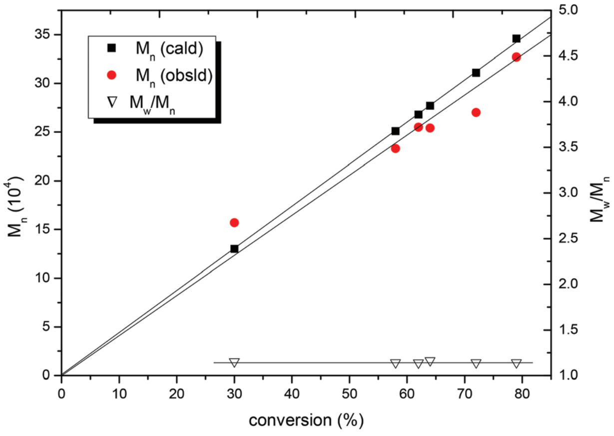


Fig. 4 Relationship between conversion and M_n and M_w/M_n for the polymerization of L-LA by **1**. For the conditions, see Fig. 3.

Conclusion

Reaction of LnLN(SiMe$_3$)$_2$(THF) with DCC led to the formation of complexes **1–4** with a γ-amidine-functionalized dianionic β-diketiminato ligand, which represents a novel reaction mode of LLnN(SiMe$_3$)$_2$(THF) in reaction with unsaturated substrates. The heterobimetallic complexes **5** and **6** with a γ-amidinate-functionalized trianionic β-diketiminato ligand could also be accessed by reaction of a mixture of SmLN(SiMe$_3$)$_2$(THF) and NaN(SiMe$_3$)$_2$ with carbodiimides. Complexes **1–4** were highly active in the ROP of L-LA. Notably, "immortal" polymerization could be achieved using a binary system of complex **1** and BnOH, demonstrating the modified L^1 ligand was suitable for designing well defined single-site lanthanide catalyst.

Experimental section

General procedures

All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl before use. Anhydrous LnCl$_3$ was prepared according to the literature procedure.[13] Complexes LnLN(SiMe$_3$)$_2$(THF) were prepared by the methods reported.[6a] Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument. The IR spectra were recorded on a Nicolet-550 FT-IR spectrometer as KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on an INOVA-400 MHz apparatus and processed using MestReNova software. The number-average molar masses (M_n) and molar mass distributions (M_w/M_n)

were determined against a polystyrene standard by size exclusion chromatography (SEC) on a PL-50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL min^{-1} at 40 °C.

Synthesis of complexes (1–6)

$SmL^1N(SiMe_3)_2$ (1). Into a stirred red solution of $SmLN(SiMe_3)_2(THF)$ (0.89 g, 1.00 mmol) in *n*-hexane (30 mL) was added dropwise a THF solution of DCC (2 mL, 1.00 mmol) at room temperature. During this period, the color of the reaction mixture changed from red to yellow. The reaction mixture was stirred for another four hours. The solvent was partly removed under vacuum, and the remaining solution was kept at room temperature for crystallization. The yellow crystals of **1** suitable for X-ray crystal structure analysis were obtained after several days (0.56 g, 60%). Anal. calcd for $C_{48}H_{79}N_5Si_2Sm$ (933.70): C, 61.81; H, 8.54; N, 7.51. Found: C, 62.00; H, 8.26; N, 7.42%. IR (KBr, cm^{-1}): 3446(m), 2961(w), 2929(m), 2350(vs), 1646(m), 1546(m), 1514(m), 1457(w), 1381(m), 1159(w), 934(w), 762(w), 680(m).

$YbL^1N(SiMe_3)_2\cdot0.5$(*n*-hexane) (2·0.5(*n*-hexane)). The synthesis of complex **2**·0.5(*n*-hexane) was carried out in the same way as that described for complex **1**; but $YbLN(SiMe_3)_2(THF)$ (0.92 g, 1.00 mmol) and DCC (2 mL, 1.00 mmol) were used. Violet crystals of **2** suitable for X-ray crystal structure analysis were obtained at room temperature (0.68 g, 70%). Anal. calcd for $C_{51}H_{87}N_5Si_2Yb$ (999.48): C, 61.23; H, 8.71; N, 7.01. Found: C, 61.08; H, 8.60; N, 7.02. IR (KBr, cm^{-1}): 3446(s), 2960(s), 2929(vs), 2854(m), 2360(m), 1646 (s), 1546(m), 1514(m), 1457(w), 1381(m), 1159(w), 934(w), 762(w), 680(m).

$YL^1N(SiMe_3)_2$ (3). The synthesis of complex **3** was carried out in the same way as that described for complex **1**; but $YLN(SiMe_3)_2(THF)$ (0.83 g, 1.00 mmol) and DCC (2 mL, 1.00 mmol) were used. Yellow crystals of **3** suitable for X-ray crystal structure analysis were obtained from *n*-hexane (0.54 g, 62%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.48–7.54 (m, 6 H, 2,6-^{i}Pr$_2$C$_6$*H*$_3$), 4.78 (s, 1 H, γ-C*H*), 4.45–4.46 (d, $^3J_{HH}$ = 4 Hz, 1 H, –N*H*), 3.80 (s, 2 H, NCC*H*$_2$), 3.60–3.67 (m, 3 H, C*H*Me$_2$+–C*H* of Cp), 3.25 (s, 2 H, NCC*H*$_2$), 3.17 (sept, $^3J_{HH}$ = 7 Hz, 2 H, C*H*Me$_2$), 3.00 (m, 1 H, –C*H* of Cp), 1.67–1.84 (m, 6 H, C*H*$_2$ of Cp), 1.56–1.57 (d, $^3J_{HH}$ = 4 Hz, 6 H, CH*Me*$_2$), 1.52–1.54 (d, $^3J_{HH}$ = 4 Hz, 6 H, CH*Me*$_2$), 1.39–1.41 (d, $^3J_{HH}$ = 4 Hz, 6 H, CH*Me*$_2$), 1.37–1.38 (d, $^3J_{HH}$ = 4 Hz, 6 H, CH*Me*$_2$), 1.15–1.23 (m, 6 H, C*H*$_2$ of Cp), 0.89–1.07 (m, 6 H, C*H*$_2$ of Cp), 0.03 (s, 18 H, Si*Me*$_3$); ^{13}C NMR (101 MHz, C_6D_6): 163.5, 155.5, 154.7, 153.0, 147.3, 144.9, 124.9, 124.8, 124.7, 84.8, 57.0, 56.1, 52.6, 33.8, 30.0, 28.1, 27.0, 26.8, 26.6, 26.5, 25.9, 25.6, 25.3, 24.7, 24.3. Anal. calcd for $C_{48}H_{79}N_5Si_2Y$ (872.26): C, 66.17; H, 9.14; N, 8.04. Found: C, 65.98; H, 9.12; N, 8.10. IR (KBr, cm^{-1}): 3446(s), 2960(s), 2929(vs), 2854(m), 2360(m), 1646 (s), 1546(m), 1513(m), 1457(w), 1380(m), 1159(w), 934(w), 762(w), 681(m).

$GdL^1N(SiMe_3)_2$ (4). The synthesis of complex **4** was carried out in the same way as that described for complex **1**; but $GdLN(SiMe_3)_2(THF)$ (0.90 g, 1.00 mmol) and DCC (2 mL, 1.00 mmol) were used. Yellow crystals of **4** suitable for X-ray crystal structure analysis were obtained from *n*-hexane (0.56 g, 60%). Anal. calcd for $C_{48}H_{79}N_5Si_2Gd$ (940.60): C, 61.36; H, 8.48; N, 7.45. Found: C, 61.79; H, 8.19; N, 7.28%. IR (KBr, cm^{-1}): 3445(s), 2961(s), 2929(vs), 2854(m), 2360(m), 1645 (s), 1546(m), 1514(m), 1457(w), 1381(m), 1159(w), 934(w), 763(w), 680(m).

$[Na(DME)_2]\{\mu\text{-}L^2\}[SmN(SiMe_3)_2]$ (5). Into a stirred solution of $SmLN(SiMe_3)_2(THF)$ (0.89 g, 1.00 mmol) was added a toluene solution of $NaN(SiMe_3)_2$ (5 mL, 1.00 mmol) at room temperature. The mixture was stirred for two hours. Into this reaction solution was added a toluene solution of DIC (2 mL, 1.00 mmol). During this period, the color of the reaction mixture was observed to change from red to yellow. The reaction mixture was stirred for another four hours. Removing the solution by centrifugation to dry and extracting the yellow residues with *n*-hexane led to a yellow solution. Into this solution was added a small amount of DME for crystallization at −10 °C. Complex **5** was isolated as yellow crystals after several days. Yield: 0.32 g (30%). Anal. calcd for $C_{50}H_{91}N_5NaO_4Si_2Sm$ (1055.8): C, 56.83; H, 8.62; N, 6.63. Found: C, 57.00; H, 8.36; N, 6.42%. IR (KBr, cm^{-1}): 2960(m), 2878(w), 2180(m), 1627(m), 1545(m), 1378(m), 1221(vs), 1164(vs), 927(w), 759(w), 631(m), 508(m).

$[Na(DME)_3]^+[SmL^3N(SiMe_3)_2]^-$ (6). Into a stirred solution of $SmLN(SiMe_3)_2(THF)$ (0.89 g, 1.00 mmol) was added a toluene solution of $NaN(SiMe_3)_2$ (5 mL, 1.00 mmol) at room temperature. The mixture was stirred for two hours, then a toluene solution of DCC (2 mL, 1.00 mmol) was added. During this period, the color of the reaction mixture changed from red to yellow. The reaction mixture was stirred for another four hours. Removing the solution by centrifugation led to yellow solids. The solids were extracted with *n*-hexane and a small amount of DME was then added. The solution was kept at −10 °C for crystallization. Complex **6** was isolated as yellow crystals after several days. Yield: 0.44 g (36%). $C_{54}H_{101}N_5NaO_6Si_2Sm$ (1226.054): C, 52.90; H, 8.30; N, 5.71. Found: C, 53.40; H, 8.42; N, 5.52%. IR (KBr, cm^{-1}): 2960(m), 2878(w), 2180(m), 1626(m), 1545(m), 1378(m), 1220(vs), 1164(vs), 928(w), 759(w), 631(m), 509(m).

General procedure for the polymerization of L-LA

The procedures for the polymerization of L-LA initiated by complexes **1–4** are similar, and a typical procedure is given below. To a stirred solution of L-LA in toluene was added a toluene solution of the initiator using a syringe. The polymerization mixture was stirred for a definite time at the desired temperature and then quenched with an ethanol solution containing a small amount of hydrochloric acid (5%). The polymer was precipitated from ethanol and washed with ethanol three times and dried under a vacuum and weighed.

A typical procedure for immoral polymerization is given below

To a stirred solution of L-LA and BuOH in toluene was added a toluene solution of the initiator using a syringe. The polymerization mixture was stirred for a definite time at the desired temperature and then quenched with an ethanol solution containing a small amount of hydrochloric acid (5%). The solvent was removed under vacuum and the polymer was dried under vacuum and weighed.

X-Ray crystallographic structure determinations

Crystals of complexes **1–6** suitable for X-ray diffraction were sealed in a thin-walled glass capillary filled under argon. Diffraction data were collected on an Agilent Xcalibur CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71070 Å) for complexes **2–4** and on a Rigaku Saturn CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71075 Å) for complexes **1**, **5** and **6**. The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. Collection and crystal data are given in ESI.† The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELXL-97 programs. CCDC 976986 (for **1**), 976987 (for **2**), 976988 (for **3**), 916989 (for **4**), 976990 (for **5**) contain the supplementary crystallographic data for this paper.

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