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A Comparative Study on the Reactivity of Tris-β-Diketiminate Ytterbium Complexes: Steric Effect of β-Diketiminato Ligands

Rui Jiao,[a] Mingqiang Xue,[a] Xiaodong Shen,[a] Yong Zhang,[a] Yingming Yao,[a] and Qi Shen*[a,b]

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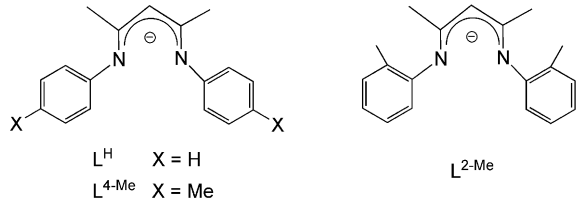
A series of tris-β-diketiminate ytterbium complexes with the general formula $[YbL_3]$ {L = $[N(C_6H_5)C(Me)]_2CH^-$, L^H (**1**); $[N(4\text{-}MeC_6H_4)C(Me)]_2CH^-$, $L^{4\text{-}Me}$ (**2**), and $[N(2\text{-}MeC_6H_4)C(Me)]_2CH^-$, $L^{2\text{-}Me}$ (**3**)} were synthesized and structurally characterized. All complexes have longer Yb–N bond lengths than other YbL-containing derivatives, and complex **3** has the longest average Yb–N bond length. A comparative study on the reactivity of complexes **1**–**3** revealed that complex **3** was a highly active catalyst for the polymerization of ε-caprolactone and L-lactide, as well as for the addition of amines to carbodiimides, whereas both complexes **1** and **2** were almost inactive under the same conditions. The active sequence is consistent with the distance of the Yb–N bond, which is reflected in the sterically induced activation of the bulky tris-β-diketiminate ytterbium complexes.

Introduction

Lanthanide derivatives bearing a β-diketiminato ancillary ligand have been well documented,[1] but the synthesis and chemistry of tris-β-diketiminate lanthanide complexes have been quite limited. To the best of our knowledge, only two kinds of complexes have been reported up to 2009: one is a homoleptic tris-β-diketiminate complex bearing a β-diketiminato ligand with a neighboring fused six-membered heterocyclic ring[2] and the other is the same complex bearing *N*,*N*-bisphenyl groups.[3] Recently, we studied the synthesis and reactivity of tris-β-diketiminate lanthanide complexes including $[LnL^{4\text{-}Cl}_3]$ {$L^{4\text{-}Cl}$ = $[N(4\text{-}ClC_6H_4)C(Me)]_2CH^-$; Ln = Pr, Nd, Sm}, $[NdL^H_3]$ {L^H = $[N(C_6H_5)C(Me)]_2CH^-$}, and $[NdL^{4\text{-}Me}_3]$ {$L^{4\text{-}Me}$ = $[N(4\text{-}MeC_6H_4)C(Me)]_2CH^-$} and found that these complexes can be synthesized in high yields. They were also proven to serve as catalysts for the ring-opening polymerization of ε-caprolactone (ε-CL) and L-lactide (L-LA) with high activity.[4]

It is well known that the reactivity of sterically demanding $[Ln(C_5Me_5)_3]$ complexes is very sensitive to steric factors, which can be tuned by changing the size of the metal or the ligand.[5] To further explore the chemistry of tris-β-diketiminate lanthanide complexes, the synthesis of various tris-β-diketiminate complexes with a small Yb metal was attempted; tris-β-diketiminate complexes with later lanthanide metals are not known. Considering the fact that a normal Ln–β-diketiminate moiety in β-diketiminate lanthanide dichlorides is inert for the ring-opening polymerization of ε-CL, whereas the same moiety in sterically demanding tris-β-diketiminate complexes is highly active,[4] the ring-opening polymerization of lactones including ε-CL and L-LA was chosen as a benchmark reaction to assess the reactivity of Ln–β-diketiminate species. The activity of tris-β-diketiminate ytterbium complexes towards the polymerization of ε-CL and L-LA was compared in an attempt to address the effect of the size of the β-diketiminato moiety on the reactivity of Ln–β-diketiminate species. To explore the potential application of these sterically demanding tris-β-diketiminate lanthanide complexes in organic synthesis, the addition of amines to carbodiimides was tested by using these ytterbium complexes for the first time, as this addition reaction is a direct approach to guanidines, which are important structural units in many biologically and pharmaceutically active compounds. It was found that the small metal ytterbium complexes $[YbL_3]$, where L was L^H, $L^{4\text{-}Me}$, and even more bulky $L^{2\text{-}Me}$ {$L^{2\text{-}Me}$ = $[N(2\text{-}MeC_6H_4)C(Me)]_2CH^-$} (Scheme 1), could be synthesized in good yields and that their reactivity depended greatly on the size



Scheme 1.

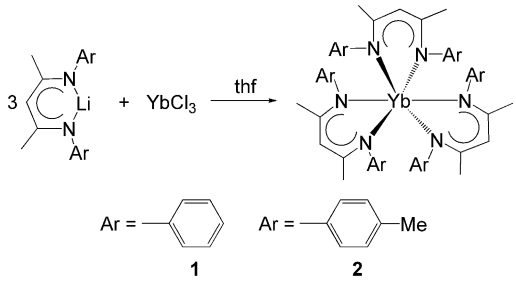
[a] Key Laboratory of Organic Synthesis, College of Chemistry, Chemical Engineering and Materials Science, Suzhou University, Dushu Lake Campus, Suzhou 215123, P. R. China
Fax: +86-512-65880305
E-mail: qshen@suda.edu.cn
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

of the ligands. Whereas complexes with the less bulky ligands L^H and $L^{4\text{-Me}}$ are almost inactive for the ring-opening polymerization of ε-CL or L-LA and for the addition of amines to carbodiimides, the more crowded complex $[YbL^{2\text{-Me}}_3]$ is a highly active catalyst for these reactions under the same reaction conditions. Here we report the results.

Results and Discussion

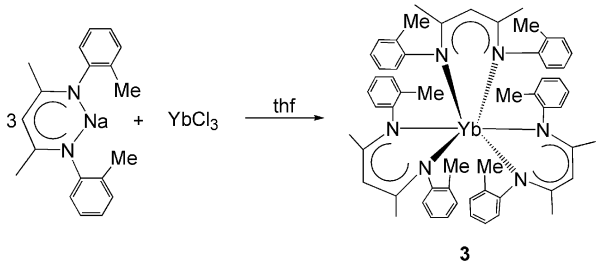
Syntheses and Molecular Structures of $[YbL^H_3]$ (1), $[YbL^{4\text{-Me}}_3]$ (2), and $[YbL^{2\text{-Me}}_3]$ (3)

The reaction of anhydrous $YbCl_3$ with LiL^H in a 1:3 molar ratio in thf went smoothly to afford the homoleptic complex $[YbL^H_3]$ (**1**) as orange-yellow crystals in 75% yield upon crystallization from toluene (Scheme 2).



Scheme 2.

The same reaction with 3 equivalents of the lithium salt $LiL^{4\text{-Me}}$, after workup, yielded the corresponding complex $[YbL^{4\text{-Me}}_3]$ (**2**) as orange-yellow crystals in good yield (Scheme 2). The structures of the two complexes were further confirmed by X-ray structural analysis. The success in the syntheses of complexes **1** and **2** spurred us to attempt the synthesis of a ytterbium complex with the more bulky ligand $L^{2\text{-Me}}$ to see whether the bulky complex $[YbL^{2\text{-Me}}_3]$ could be stabilized, as the deprotonation product was reported when the synthesis of the ytterbium complex $[YbL^{i\text{Pr}}_3]$ {$L^{i\text{Pr}}$ = $[N(2,6\text{-}i\text{Pr}_2C_6H_3)C(Me)]_2CH^-$} was tried by an oxidation approach.[6] Thus, the reaction of $YbCl_3$ with the lithium salt $LiL^{2\text{-Me}}$ in a 1:3 molar ratio was conducted at 50 °C in thf. Unfortunately, no definite complex could be isolated. Then, the same reaction with the sodium salt $NaL^{2\text{–Me}}$ was tried again in thf solution at 60 °C. We were pleased to observe that the reaction proceeded perfectly, after workup, to generate a red product in good yield. The product was further characterized by X-ray diffraction to be the target complex $[YbL^{2\text{–Me}}_3]$ (**3**; Scheme 3).



Scheme 3.

All the complexes are quite thermostable and decompose at 168–170, 150–153, and 175–176 °C for **1**, **2**, and **3**, respectively, but they are all moderately sensitive to air and moisture. They are freely soluble in donor solvents such as thf and dimethoxyethane (dme) and moderately soluble in toluene.

The IR spectra of complexes **1**, **2**, and **3** exhibited the strong absorptions near 1536, 1528, and 1512 cm^{-1}, respectively, which were consistent with partial C=N bond character.[7] These complexes did not provide any resolvable ^1H NMR spectra; the resonances are broad and shifted due to the strong paramagnetic nature of the Yb ion.

Crystals of **1** and **2** suitable for X-ray diffraction determination were obtained by crystallization from toluene, whereas crystals of **3** were obtained from a mixture of thf and hexane. The molecular structures of complexes **1**, **2**, and **3** are shown in Figures 1, 2, and 3 respectively. Selected bond lengths and angles and details of the crystal data collection are given in Tables 1 and 5.

Complex **3** crystallizes with one thf molecule in the unit cell. The molecular structures of complexes **1**–**3** are similar. The central Yb metal in each complex is ligated by six nitrogen atoms from three β-diketiminato groups in a distorted octahedral geometry, which are the same as those for other lanthanide metal analogues.[2–4] However, quite different binding modes of Ln–β-diketiminate and bond parameters among the three complexes were observed. Complexes **1** and **2** are isostructural, and each β-diketiminato ligand in **1** and **2** binds symmetrically to the central Yb atom. In contrast, each β-diketiminato ligand in complex **3** coordinates to the Yb atom in an asymmetrical binding mode. The β-diketiminato skeletal atoms of each β-diketiminate in **1** and **2** are almost coplanar, whereas the five atoms of the ligand $L^{2\text{-Me}}$ in complex **3** are not coplanar. All the Yb–N bond lengths and all the N–Yb–N bond angles in the β-diketiminato ligand are equal in complex **2** [2.360(5) Å for the Yb–N bond and 79.85(18)° for the N–Yb–N angle] and

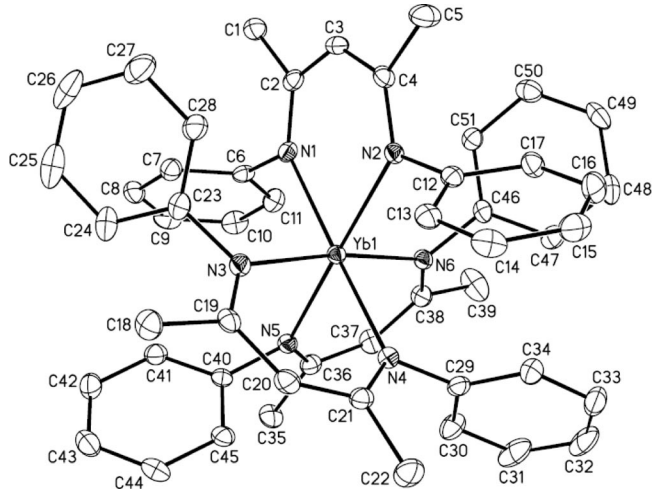


Figure 1. ORTEP diagram of **1** showing atom-numbering scheme; thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

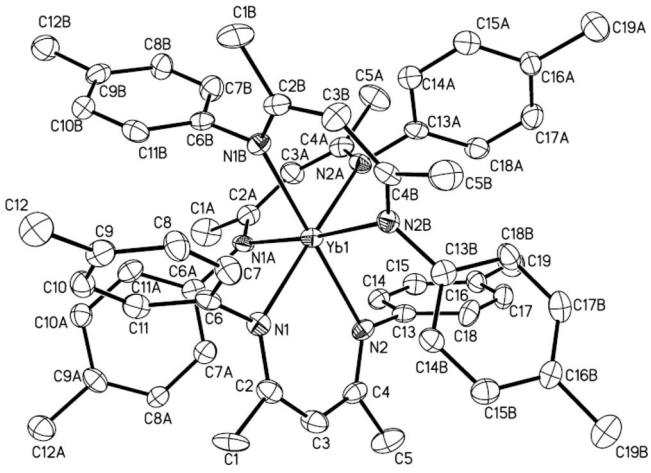


Figure 2. ORTEP diagram of **2** showing atom-numbering scheme; thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

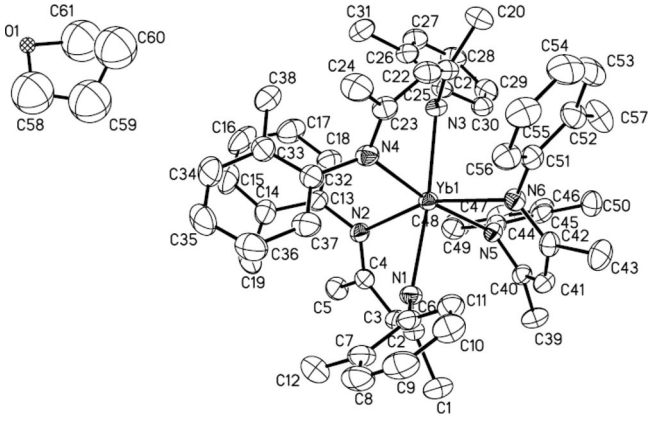


Figure 3. ORTEP diagram of **3** showing atom-numbering scheme; thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and bond angles (°) for complexes **1**–**3**.

	1	**3**		**2**
Yb1–N1	2.360(3)	2.442(3)	Yb1–N1	2.360(5)
Yb1–N2	2.360(3)	2.345(3)	Yb1–N2	2.361(5)
Yb1–N3	2.371(3)	2.403(3)	Yb1–N1A	2.360(5)
Yb1–N4	2.355(3)	2.369(3)	Yb1–N2A	2.361(5)
Yb1–N5	2.362(3)	2.438(3)	Yb1–N1B	2.360(5)
Yb1–N6	2.368(3)	2.387(3)	Yb1–N2B	2.361(5)
$(Yb–N)_{av.}$	2.363(3)	2.398(3)	$(Yb–N)_{av.}$	2.361(5)
N1–Ln1–N2	78.85(10)	75.49(12)	N1–Yb1–N2	79.85(18)
N3–Ln1–N4	79.55(11)	76.50(12)	N1B–Yb1–N2B	79.85(18)
N5–Ln1–N6	79.30(10)	76.82(11)	N1A–Yb1–N2A	79.85(18)
$(N–Ln–N)_{av.}$	79.23(10)	76.27(12)	$(N–Ln–N)_{av.}$	79.85(18)

they are almost equal in complex **1** (2.355–2.371 Å and 78.85–79.55°); the bond parameters in complexes **1** and **2** are well consistent with each other. However, the Yb–N bond lengths and the N–Yb–N bond angles in complex **3** are different and range from 2.345(3) to 2.442(2) Å and from 75.49(12) to 76.82(11)°, respectively. The average Yb–N bond length of 2.398(3) Å in complex **3** is about 0.036 Å longer than those for complexes **1** and **2** (2.363 Å in complex **1** and 2.361 Å in complex **2**). The average N–Yb–N bond angle in complex **3** is 76.27(12)°, which is about 3° smaller than those found in complexes **1** and **2**. In comparison with the average Yb–N bond length [2.243(3)–2.340(4) Å] for the trivalent LYb-containing complexes reported,[8] the average Yb–N bond length [2.398(3) Å] in complex **3** is 0.155–0.058 Å longer, whereas the average Yb–N bond length in complexes **1** and **2** is 0.116–0.022 Å longer. The average N–Yb–N angle in complexes **1**, **2**, and **3** is 79.23(10), 79.85(18), and 76.27(12)°, respectively, smaller than 85.43(13)–81.25(15)° found in the YbL-containing complexes mentioned above.[8] These bond parameters indicate that the coordination environment around the central metal Yb atom in tris-β-diketiminate ytterbium complexes is more crowded than those in the trivalent YbL-containing derivatives and complex **3**, with the most bulky β-diketiminato ligands, is the most sterically crowded.

Comparative Reactivity of Complexes 1–3

The difference in the sterically crowded coordination environment around the Yb atom between complex **3** and complex **1** or **2** might lead to the difference in reactivity of Yb–β-diketiminate species. Thus, the reactivity of **1**–**3** for the polymerization of lactones was examined.

Polymerization of ε-Caprolactone (ε-CL)

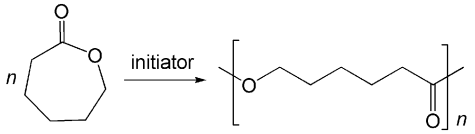
The activities of complexes **1** and **2** towards the ring-opening polymerization of ε-CL (500 equiv. of ε-CL per metal) were first assessed in a toluene solution at room temperature. It was found that even after 24 h no polymerization occurred for both systems, indicating that **1** and **2** were completely inactive under the present conditions (Table 2, Entries 6 and 8). However, a gradual increase in the viscosity of the toluene solution containing ε-CL and **1** or **2** was observed when the polymerization temperature was raised to 80 °C. For **1**, a 73% yield of poly(ε-CL) was obtained, and for **2**, a 72% yield was obtained after 4 h (Table 2, Entries 7 and 9). We have reported that the analogues of early and middle lanthanide metals can serve as highly active catalysts for this reaction at room temperature.[4] The observed large difference in activity demonstrates that the size of the central metal has a remarkable influence on the reactivity of these sterically demanding complexes.

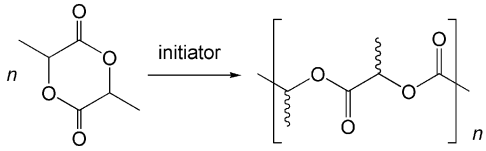
In contrast, a rapid polymerization of ε-CL was observed with the use of **3**; poly(ε-CL) was obtained in 87% yield after 15 min at room temperature with a molar ratio of 500 (monomer/catalyst; Table 2, Entry 1). When the molar ratio of monomer/catalyst was increased to 1000, the monomer conversion still reached 97% within 60 min (Table 2, Entry 4). Complex **3** is even more active than the reported β-diketiminate ytterbium aryloxo and amido chlorides $L^{iPr_2}L^1Yb(OAr)Cl(thf)$, $L^{Me_2}Yb(OAr)Cl(thf)$ {L^{Me_2} = $[N(2,6\text{-}Me_2C_6H_3)C(Me)]_2CH^-$}[9] and $L^{iPr_2}YbNR_2Cl$.[8a]

Table 2. Polymerization of ε-CL catalyzed by complexes **1**–**3**.[a]

Entry	Initiator	[M]/[I]	Time (min)	T (°C)	Yield (%)[b]	$M_{n,calcd} \times 10^{-4}$[c]	$M_{n,exp.} \times 10^{-4}$[d]	PDI
1	**3**	500	15	25	87	4.97	5.41	1.88
2	**3**	1000	15	25	43	4.91	5.11	1.58
3	**3**	1000	30	25	85	9.70	13.5	1.61
4	**3**	1000	60	25	97	11.1	21.7	1.54
5	**3**	1500	15	25	46	7.88	34.0	1.61
6	**1**	500	180	25	–	–	–	–
7	**1**	500	240	80	73	4.97	5.21	1.57
8	**2**	500	180	25	–	–	–	–
9	**2**	500	240	80	72	4.97	5.72	1.61

[a] Polymerization conditions: in toluene; [ε-CL] = 0.82 M. [b] Yield = weight of polymer obtained/weight of monomer used. [c] $M_{n,calcd.}$ = ([CL]/[I]) × 114.14 × (polymer yield). [d] Measured by GPC calibrated with standard polystyrene samples and corrected with the coefficient of 0.56.





A linear increase in the corrected molecular weights (M_n) of the polymers with conversion and almost no changed polydispersity indexes during the polymerization were observed (Table 2, Entries 2–4). However, the values of M_n of the resulting polyesters with complex **3** by 0.56[10] are much larger than the calculated data for one polymer chain growing per metal center, and the polydispersity indexes of the polymers (PDIs, evaluated by gel permeation chromatography, GPC) are rather broad, ranging from 1.54 to 1.88. This may be because of slow initiation and fast propagation, which result in low efficiency of the catalyst and rather broad molecular weight distributions.

Polymerization of L-Lactide (L-LA)

Complex **3** also showed very high L-LA polymerization activity. For instance, almost complete conversion of L-LA was obtained within 5 min at 80 °C in toluene with a monomer/**3** molar ratio of 300 (Table 3, Entry 1). When the molar ratio of monomer/**3** was increased to 500, the conversion of the monomer was still as high as 96.2% after 5 min (Table 3, Entry 2). The polymers obtained had corrected molecular weights[11] close to the calculated values and a narrow polydispersity (1.18–1.30; Table 3, Entries 1–4). In contrast, both complexes **1** and **2** are inactive under the same conditions (Table 3, Entries 5 and 6).

No end group was assigned to the β-diketiminato group, but the signals for the ε-CL or L-LA polymer were detected by end-group analysis of ε-CL or L-LA oligomers. The same situation was also found in the cases of the tris-β-diketiminate lanthanide complex as the catalyst.[4] Normally, no end-group detection was attributed to the formation of cyclic polymers through intramolecular attack of the Ln–O bond in an active species to the N-bonded acyl carbon atom.[3b,12] Another possibility for no end-group detection may be because the molecular weights of the oligomers obtained are too large to be detected by ^{1}H NMR spectroscopy.

Addition of Amines to Carbodiimides

To further explore the reactivity of tris-β-diketiminate ytterbium complexes, the addition of amines to carbodiimides was examined by using complexes **1**–**3** for the first time.

Taking the reaction of aniline with diisopropylcarbodiimide as a model reaction, the activities of complexes **1**–**3** were tested at 60 °C under solvent-free conditions. As shown in Table 4, a great difference in the activities of **1**, **2**, and **3** was observed. The reaction with complex **3** as the catalyst afforded the product in almost quantitative yield, whereas the reaction with complex **1** or **2** yielded the product in a very low yield of 5 or 18%, respectively, at 1 mol-

Table 3. Polymerization of L-LA by complexes **1**–**3**.[a]

Entry	Initiator	[M]/[I]	Time (min)	T (°C)	Yield (%)[b]	$M_{n,calcd} \times 10^{-4}$[c]	$M_{n,exp.} \times 10^{-4}$[d]	PDI
1	**3**	300	5	80	98.3	4.25	5.39	1.30
2	**3**	500	5	80	96.2	6.93	7.63	1.21
3	**3**	700	30	80	54.0	5.45	6.94	1.26
4	**3**	800	60	80	29.6	3.41	4.66	1.18
5	**2**	300	300	80	–	–	–	–
6	**1**	300	300	80	–	–	–	–

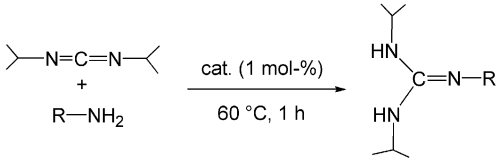
[a] Polymerization conditions: in toluene; [L-LA] = 1.0 M. [b] Yield = weight of polymer obtained/weight of monomer used. [c] $M_{n,calcd.}$ = ([LA]/[I]) × 144.13 × (polymer yield). [d] Measured by GPC calibrated with standard polystyrene samples and corrected with the coefficient of 0.58.

Table 4. Addition of amines to carbodiimides by complexes **1**–**3**.[a]

Entry	Amine	Catalyst	Cat. loading (mol-%)	Yield[b] (%)
1	$C_6H_5NH_2$	**3**	1	96
2	$C_6H_5NH_2$	**3**	0.25	88
3	$C_6H_5NH_2$	**1**	1	5
4	$C_6H_5NH_2$	**2**	1	18
5	2-$MeC_6H_4NH_2$	**3**	1	94
6	2,6-$Me_2C_6H_3NH_2$	**3**	1	NR
7	4-$FC_6H_4NH_2$	**3**	1	98
8	2-$CH_3OC_6H_4NH_2$	**3**	1	96
9	2-$ClC_6H_4NH_2$	**3**	1	96
10	4-$ClC_6H_4NH_2$	**3**	1	100
11	1-naphthylamine	**3**	1	89
12	morpholine	**3**	1	NR

[a] The reaction was performed by treating the amine (1 equiv.) with the carbodiimide (1 equiv.) at 60 °C for 1 h. [b] Isolated yields; NR = no reaction.

% catalyst loading (Table 4, Entries 1, 3, and 4). It is worth noting that complex **3** is a highly active precatalyst for the addition reaction. For example, the yield of the product still reached 88% when the catalyst loading was decreased to 0.25 mol-% (Table 4, Entry 2). Preliminary results showed that the reaction with aromatic amines bearing either electron-withdrawing or electron-donating groups, except for the reaction performed with the bulky aromatic amine 2,6-$Me_2C_6H_3NH_2$, went smoothly (Table 4, Entries 5–10) to give the corresponding guanidines in excellent yields.



The catalytic reaction was supposed to proceed by the active amide intermediate [L_2YbNHR] formed in situ by the reaction of YbL_3 with amines directly, followed by insertion of the carbodiimine to the amide and the protonation of guanidinate by amine.[13] Thus, the formation of the amide intermediate should be the key point for guanylation. The amination of YbL_3 with a bulky amine might be not favored. This may be the reason why the reaction with the bulky amine 2,6-$Me_2C_6H_3NH_2$ was sluggish. The reaction of **3** with aniline was monitored by ^1H NMR spectroscopy in [D_6]benzene, and new signals for free $HL^{2\text{-Me}}$ (at about 13.01, 2.19, and 1.78 ppm) appeared during the period of the reaction, indicating the occurrence of the amination of **3**. Attempts to isolate the amide have not yet been successful.

The results obtained from the reactions tested revealed that the chemical behavior of complexes **1** and **2** is quite similar: the ligands L^H and $L^{4\text{-Me}}$ in **1** and **2** are both inert, whereas complex **3** is highly active, and the normally inert ligand $L^{2\text{-Me}}$ in **3** can act as an active group. The remarkable difference in the reactivities of complexes **3** and **1** and/or **2** can only be attributed to the difference in amount of steric crowding resulting from the different sizes of the ligands, as no difference in the electronic factors of complexes **3** and **2** was observed. In complex **3**, the three more bulky ligands $L^{2\text{-Me}}$ around the Yb metal make the coordination sphere more crowded than those in complexes **1** and **2**, as confirmed by structural analysis. Extreme steric saturation could have limited the reactivity of **3**. However, as a substrate would not be able to approach the Yb metal, the much longer length of the Yb–N bond observed in **3** in comparison to that observed in complexes **1** and **2** (see the Molecular Structure section) can provide a basis for the high hemilability of the β-diketiminato ligand, as neither the β-diketiminate nor the ytterbium receive the normal electrostatic stabilization from each other at this distance. Thus, a normally inert β-diketiminato ligand could be activated by "steric-induced activation"; that is, in an extremely sterically crowded tris-β-diketiminate lanthanide complex the metal–ligand bond can be elongated to such an extent as to activate the ligand. Such an activation of ancillary ligands was well documented in [$Ln(C_5Me_5)_3$].[5]

If the activities of complexes **1** and **2** are compared to those of larger metal analogues (Pr, Nd, Sm),[3b,4] it can be found that for a given less bulky ligand L^H or $L^{4\text{-Me}}$ the complexes containing large metals (Pr, Nd) showed high catalytic activity. This may be because the factor that appears to drive the reactivity of these complexes in the ring-opening polymerization of lactones is the amount of coordination unsaturation, not the amount of steric crowding. In complexes **1** and **2** the small size of the Yb metal surrounded by three of the ligands L^H and/or $L^{4\text{-Me}}$ makes the coordination sphere more crowded, which does not favor the coordination of the substrate, whereas for large-metal analogues there is still a room for coordination of the substrate.

Conclusions

In conclusion, we have synthesized and structurally characterized the first tris-β-diketiminate ytterbium complexes with various β-ketiminato ligands. Further examination of their reactivities in the ring-opening polymerization of caprolactone and lactide and in the addition of amines to carbodiimides revealed that the catalytic activities of the tris-β-diketiminate ytterbium complexes were greatly affected by the steric bulk of the β-diketiminato ligands. The most sterically crowded complex **3** was found to be the most active among the three complexes. Moreover, complex **3** was first explored to be a highly active precatalyst for the addition of amines to carbodiimides. The results indicate that a normally inert β-ketiminate ligand can become an active group by steric-induced activation. Further study on the chemistry of tris-β-diketiminate lanthanide complexes is ongoing in our laboratory.

Experimental Section

General Procedures: All manipulations were performed under a purified argon atmosphere by using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone

ketyl before use. [D_6]Benzene used for NMR reactions was dried with Na and vacuum-transferred immediately prior to use. ε-Caprolactone was purchased from Acros, dried with CaH_2 for 48 h, and distilled under reduced pressure. L-Lactide was recrystallized twice with dry toluene. L^HH and $L^{4\text{-Me}}H$ were prepared according to a literature method.[4] Anhydrous $YbCl_3$ was prepared according to a literature procedure.[14] Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and a hexamine buffer.[15] Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo–Erba EA-1110 instrument. IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. ^{1}H NMR spectra were obtained in $CDCl_3$ for the ligands by using a Unity Inova-400 spectrometer. Melting points of the crystalline samples were determined in sealed Ar-filled capillaries. Molecular weights and molecular weight distributions were determined against polystyrene standards by gel permeation chromatography (GPC) at 30 °C with a Waters 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4) by using thf as the eluent.

$L^{2\text{-Me}}H$: A mixture of 2-toluidine (10.9 g, 0.1 mol), 2,4-pentanedione (5.1 g, 0.05 mol), and 4-toluenesulfonic acid (9.6 g) in toluene (250 mL) was heated at reflux for 24 h in a Dean–Stark apparatus. The toluene was then decanted off, and the white solid residue was treated with diethyl ether (250 mL), water (100 mL), and Na_2CO_3 (12 g). After stirring for 30 min, the ether layer was separated, dried with $MgSO_4$, and evaporated in vacuo. The residue was dried in vacuo (10^{-2} bar) at 100 °C for 6 h to remove any remaining free 2-toluidine, then crystallized from hexane, and recrystallized from anhydrous ethanol to give the ligand.[16] Yield: 12.1 g (87%). M.p. 35.9–36.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.54 (s, 1 H, NH), 7.16 (d, 4 H, ArH), 6.97 (d, 4 H, ArH), 4.91 (s, 1 H, β-CH), 2.20 (s, 6 H, *o*-CH_3), 1.91 (s, 6 H, α-CH_3) ppm.

YbL^H_3 (1): To a slurry of anhydrous $YbCl_3$ (1.12 g, 4.01 mmol) in thf (25 mL) was slowly added a solution of LiL^H (12.0 mmol) in thf (12.0 mL) at room temperature. The reaction mixture was stirred at 50 °C for 48 h, the solvents were stripped off in vacuo, and toluene was added to extract the product. The precipitate was removed by centrifugation, and the orange-yellow supernatant was then concentrated and cooled to 0 °C to give orange-yellow crystals. Yield: 2.77 g (75%). M.p. 168–170 °C (dec.). $C_{51}H_{51}N_6Yb$ (921.02): calcd. C 66.51, H 5.58, N 9.12, Yb 18.79; found C 66.99, H 5.53, N 9.07, Yb 18.82. IR (KBr): $\tilde{\nu}$ = 3056 (s), 2925 (m), 1628 (w), 1590 (m), 1536 (vs), 1482 (s), 1451 (s), 1389 (vs), 1273 (s), 1189 (m), 1073 (w), 1027 (m), 934 (w), 818 (m), 749 (m), 702 (s), 648 (w), 509 (w) cm^{-1}.

$YbL^{4\text{-Me}}_3$ (2): Prepared in a manner similar to that used for the preparation of **1**, but $YbCl_3$ (0.28 g, 1.00 mmol) and $LiL^{4\text{-Me}}$ (15.0 mL, 3.00 mmol) were used instead. Orange-yellow crystals of **2** were obtained. Yield: 0.73 g (73%). M.p. 150–153 °C (dec.). $C_{57}H_{63}N_6Yb$ (1005.17): calcd. C 68.11, H 6.32, N 8.36, Yb 17.21; found C 68.73, H 6.15, N 8.01, Yb 17.21. IR (KBr): $\tilde{\nu}$ = 3025 (m), 2925 (m), 2354 (m), 1996 (m), 1628 (s), 1528 (vs), 1505 (vs), 1447 (vs), 1273 (s), 1186 (s), 1027 (m), 857 (m), 741 (m) cm^{-1}.

$YbL^{2\text{-Me}}_3$ (3): To a slurry of anhydrous $YbCl_3$ (0.60 g, 2.14 mmol) in thf (20 mL) was slowly added a solution of $NaL^{2\text{-Me}}$ (0.264 M in thf, 24.4 mL, 6.44 mmol) at room temperature. The reaction mixture was stirred at 60 °C for 24 h. After the solvents were stripped off in vacuo, the product was extracted with toluene (30 mL). The toluene was then stripped off in vacuo, and hexane (20 mL) and thf (1 mL) were added for crystallization at room temperature. Red crystals were isolated. Yield: 1.14 g (53%). M.p. 175–176 °C (dec). $C_{57}H_{63}N_6Yb$ (1005.17): calcd. C 68.11, H 6.32, N 8.36, Yb 17.21; found C 67.42, H 6.00, N 8.29, Yb 15.92. IR (KBr): $\tilde{\nu}$ = 1512 (w), 1446 (w), 1369 (w), 1307 (w), 1229 (m), 1288 (m), 1099 (m), 1061 (m), 1022 (m), 965 (m), 887 (m), 779 (s), 659 (s), 459 (vs), 409 (vs) cm^{-1}.

Typical Procedure for the Polymerization of L-Lactide: A 50-mL Schlenk flask, equipped with a magnetic stirring bar, was charged with L-lactide (0.50 g, 3.47 mmol) and toluene (3.47 mL). The contents of the flask were then stirred at 80 °C until L-lactide was dissolved, and then a toluene solution (2.00 mL) of complex **3** (11.24 mg, 0.0104 mmol, [LA]/[Yb] = 300:1, [LA] = 1.00 M) was added by syringe. The mixture was stirred vigorously at 80 °C for the desired time. The reaction mixture was quenched by ethanol and precipitated in ethanol, filtered, washed with ethanol, and dried in vacuo and weighed.

Typical Procedure for the Polymerization of ε-Caprolactone: A 50-mL Schlenk flask, equipped with a magnetic stirring bar, was charged with a solution of the initiator in toluene. To this solution was added the desired amount of ε-caprolactone by syringe. The contents of the flask were then stirred vigorously at the desired temperature for a fixed time. The reaction mixture was quenched by the addition of ethanol and then poured into ethanol to precipitate the polymer. The polymer was dried in vacuo and weighed.

Typical Procedure for Addition of Amines to Carbodiimides Catalyzed by Complexes 1–3: Taking the reaction of aniline with diisopropylcarbodiimide as an example, A 30-mL Schlenk flask was charged with complex **3** (0.0082 g, 0.0076 mmol). To the flask was added *N*,*N*′-diisopropylcarbodiimide (0.12 mL, 0.76 mmol) and aniline (0.07 mL, 0.76 mmol). The resulting mixture was stirred at 60 °C for a fixed time, then hydrolyzed with water (0.5 mL), extracted with dichloromethane (3 × 10 mL), dried with anhydrous Na_2SO_4, and filtered. After the solvent was removed under reduced pressure, the residue was recrystallized from hexane to provide a white solid *N*-phenyl-*N*′,*N*″-diisopropylguanidine. Yield: 0.1604 g (96%). ^{1}H NMR ($CDCl_3$): δ = 7.22 (2 H), 6.95–6.91 (1 H), 6.86–6.84 (2 H), 3.77 (2 H), 3.61 (2 H), 1.17–1.15 (12 H) ppm.

NMR-Scale Reaction: In a glove box, complex **3** (13.7 mg, 0.0127 mmol), C_6D_6 (0.5 mL), and aniline (25 mg, 0.2688 mmol) were loaded into a J. Young NMR tube equipped with a Teflon valve. The tube was closed and then removed from the glove box, and the reaction was monitored by ^{1}H NMR spectroscopy at room temperature for the desired time.

X-ray Crystallography: A suitable crystal was sealed in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected with a Rigaku Mercury CCD area detector in the ω scan mode by using graphite-monochromated Mo-K_α radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. The structures were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using the SHELXL-97 programs. Table 5 contains the crystallographic data for complexes **1**–**3**. CCDC-765303 (for **1**), -765304 (for **2**), and -765305 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 5. Crystallographic data for complexes **1**–**3**.

	1	**2**	**3·thf**
Empirical formula	$C_{51}H_{51}N_6Yb$	$C_{57}H_{63}N_6Yb$	$C_{61}H_{71}N_6OYb$
Formula weight	921.02	1005.17	1077.28
Temperature (K)	193(2)	223(2)	293(2)
Crystal system	monoclinic	trigonal	triclinic
Space group	P 21/c	$P\bar{3}$	$P\bar{1}$
Crystal size (mm)	$0.43\times0.17\times0.10$	$0.36\times0.30\times0.12$	$0.60\times0.50\times0.38$
a (Å)	18.5059(15)	19.022(2)	12.1778(14)
b (Å)	10.5351(7)	19.022(2)	12.5956(15)
c (Å)	22.9125(19)	23.977(2)	17.704(2)
α (°)	90	90	95.185(3)
β (°)	103.715(2)	90	95.506(3)
γ (°)	90	120	96.273(3)
V (Å^3)	4339.7(6)	7513.1(14)	2672.8(5)
Z	4	6	2
$D_{calcd.}$ (mg cm^{-3})	1.410	1.333	1.339
μ (mm^{-1})	2.197	1.910	1.796
F_{000}	1876	3102	1114
θ range (°)	3.06–27.48	3.00–25.50	3.02–25.35
Reflections collected/unique	47470/9948 (R_{int} = 0.0458)	19321/9279 (R_{int} = 0.0413)	25863/9700 (R_{int} = 0.0317)
Data/restraints/parameters	9948/0/530	9279/0/589	9700/11/621
Goodness-of-fit on F^2	1.198	1.156	1.109
Final R [$I>2\sigma(I)$]	0.0440	0.0626	0.0382
wR_2 (all data)	0.0704	0.1182	0.0947

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