

Synthesis, Characterization, and Catalytic Activity of Rare Earth Metal Amides Supported by a Diamido Ligand with a CH₂SiMe₂ Link

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Received March 19, 2008

A series of four coordinate rare earth metal amides with general formula $\{(\text{CH}_2\text{SiMe}_2)[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}]_2\text{LnN}(\text{SiMe}_3)_2(\text{THF})\}$ [$\text{Ln} = \text{Yb}$ (**2**), Y (**3**), Dy (**4**), Sm (**5**), Nd (**6**)] containing a diamido ligand $(\text{CH}_2\text{SiMe}_2)[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}]_2^{2-}$ with a CH_2SiMe_2 link were synthesized in good yields via reaction of $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ with the corresponding diamine $(\text{CH}_2\text{SiMe}_2)[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NH}]_2$ (**1**). All compounds were fully characterized by spectroscopic methods and elemental analyses. The structures of complexes **2**, **3**, **4**, **5**, and **6** were determined by single-crystal X-ray analyses. Investigation of the catalytic properties of the complexes indicated that all complexes exhibited a high catalytic activity on the cyclotrimerization of aromatic isocyanates, which represents the first example of cyclopentadienyl-free rare earth metal complexes exhibiting a high catalytic activity and a high selectivity on cyclotrimerization of aromatic isocyanates. The temperatures, solvents, catalyst loading, and the rare earth metal effects on the catalytic activities of the complexes were examined.

Introduction

From an atom-economic perspective, the reactivity of isocyanates in the coordination sphere of various metal centers has received some renewed interest recently.¹ Such reactions are quite attractive because they can provide a very valuable access to various types of heterocycles as indicated by some investigations.² Among these investigations, much fewer have focused on cyclotrimerization reactions of the isocyanates, especially with rare earth metal complexes as

catalysts.³ Substituted aryl-functionalized isocyanurates are useful activators for anionic polymerization of ϵ -caprolactams to nylon-6 and are known to substantially enhance the stability of polyurethane networks and coating materials with respect to thermal resistance, flame retardation, chemical resistance, and film-forming characteristics.³ Different isocyanate trimerization catalytic systems have been reported, such as anions or neutral Lewis bases, organic acid salts and tertiary amines, and some metal-based systems.^{3a,b} Conventional catalysts for cyclotrimerization of isocyanates suffer from low activity, necessitating severe conditions, and poor selectivity resulting in byproducts.⁴

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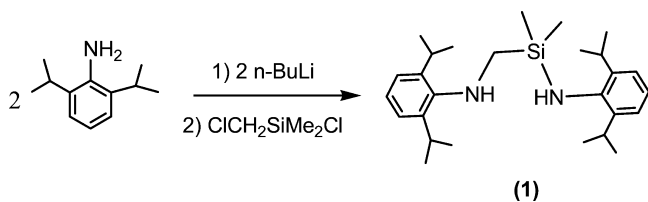
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Scheme 1. Preparation of the Ligand 1



During the past decades, a considerable attention has been given to the development of complexes supported by ligand systems other than cyclopentadienyl derivatives in lanthanide chemistry. A variety of cyclopentadienyl-free ligands have been found to be suitable for stabilizing rare earth metal species.⁵ Among these, amido ligands have attracted considerable attention in recent years because the electronic properties and steric effects of the ligands can be modified by variation of the substituents of nitrogen atoms.⁶ A variety of lanthanide complexes supported by monoamidinate ligands have been synthesized,^{5a,d,g} and some of them have been found to be effective initiators for the ring-opening polymerization of δ -caprolactone and other polar monomers.⁷ However, linked diamido ligands have been relatively seldom used in lanthanide chemistry.^{8,6a-g} Experimental results showed that the bridged diamido ligands significantly influence the chemical and physical properties of the resulting organometallic complexes.^{5b} In comparison with an unbridged ligand, a bridged diamido ligand will provide more open coordination environment around the metal center, which would be favorable for homogeneous catalysis.^{5g}

It has been documented that isocyanate can stoichiometrically insert into the rare earth metal–carbon and metal–nitrogen bonds to produce the corresponding insertion products.⁹ However, only reports on the $\text{Cp}'_2\text{LnN}^{\text{Pr}}(\text{THF})^{10a}$ ($\text{Cp}' = \text{MeC}_5\text{H}_4$, $\text{Ln} = \text{Y, Er, Yb}$) or $\text{Cp}_2\text{LnCl}/n\text{-BuLi}^{10b}$ as catalysts or catalytic system for cyclotrimerization of phenyl isocyanate are documented. The systematic study on the catalytic transformation of the isocyanates to isocyanurates with cyclopentadienyl-free rare earth metal amides as catalysts is far less explored.

We report here the synthesis and structural characterization of a series of novel rare earth metal amides incorporating a dimethylsilylmethylene-linked diamido ligand. Their catalytic activity on the cyclotrimerization of isocyanates will be for the first time reported.

Results and Discussion

Synthesis of the Ligand $(\text{CH}_2\text{SiMe}_2)[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NH}]_2$ (1). Treatment of $\text{ClSiMe}_2\text{CH}_2\text{Cl}$ with 2 equiv of $(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NHLi}$ in THF gave $(\text{CH}_2\text{SiMe}_2)[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NH}]_2$ (1) in 34% isolated yield as a white solid (Scheme 1, Figure 1). The compound was well characterized by spectroscopic methods and elemental analyses. It is soluble in THF, toluene, and nonpolar solvents such as *n*-hexane. ^1H NMR spectrum indicated that it decomposed upon exposure to air for a few days.

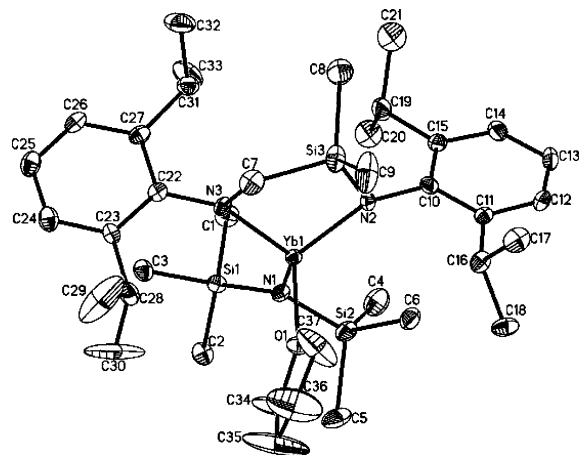
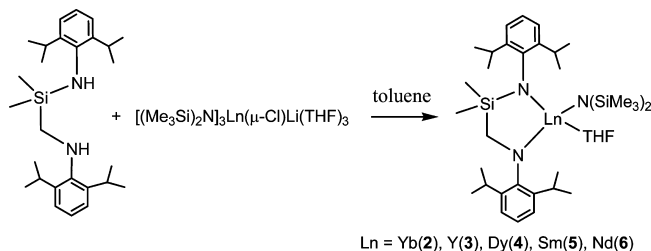


Figure 1. One of two asymmetrical molecular structures of complex 2, hydrogen atoms are omitted for clarity.

Scheme 2. Preparation of the Lanthanide Complexes



Synthesis and Characterization of the Rare Earth Metal Complexes. Treatment of the diamine $(\text{CH}_2\text{SiMe}_2)[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NH}]_2$ (1) with 1 equiv of rare earth metal amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ in toluene produced the corresponding rare earth metal complexes with general formula $\{(\text{CH}_2\text{SiMe}_2)[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}]_2\}\text{LnN}(\text{SiMe}_3)_2(\text{THF})$ ($\text{Ln} = \text{Yb(2), Y(3), Dy(4), Sm(5), Nd(6)}$) (Scheme 2). The complexes are sensitive to air and moisture, they are soluble in solvents such as THF, toluene, CH_2Cl_2 , and even *n*-hexane. All complexes were fully characterized by spectroscopic

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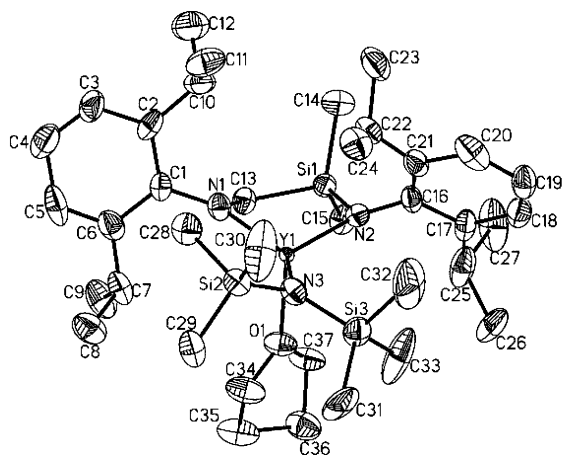


Figure 2. One of two asymmetrical molecular structures of complex **3**, hydrogen atoms are omitted for clarity.

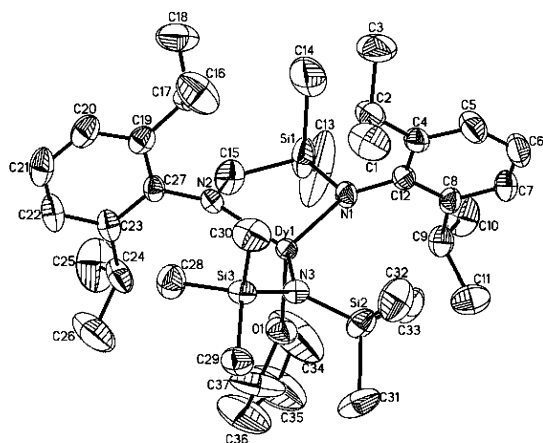


Figure 3. One of two asymmetrical molecular structures of complex **4**, hydrogen atoms are omitted for clarity.

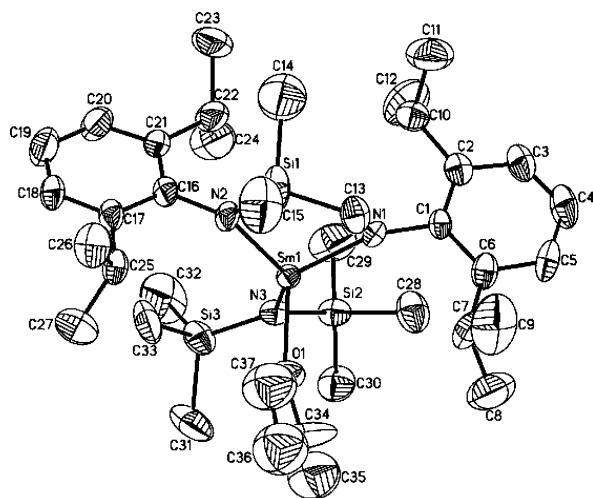


Figure 4. One of two asymmetrical molecular structures of complex **5**, hydrogen atoms are omitted for clarity.

methods and elemental analyses. The structures of all complexes were determined by single-crystal X-ray analyses.

Molecular Structures of the Complexes. To provide full structural information for these rare earth metal amides, single-crystal X-ray structural investigations were carried out for complexes **2–6** (Figures 1–5). Selected bond lengths and angles are listed in Table 1.

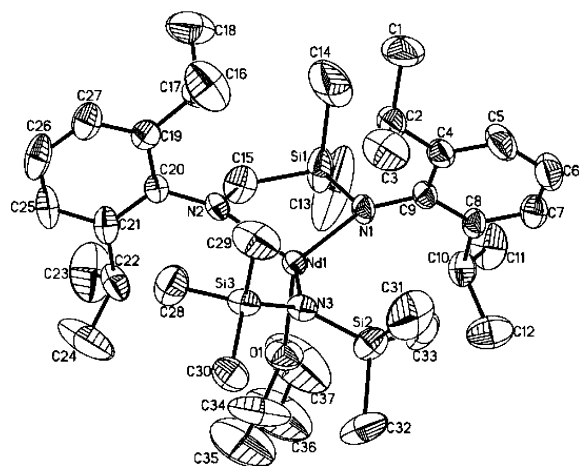


Figure 5. One of two asymmetrical molecular structures of complex **6**, hydrogen atoms are omitted for clarity.

The X-ray structure analyses revealed that the complexes **2–6** were all solvated monomeric structures crystallized in the orthorhombic system with space group $P2_12_12_1$; they are isostructural and isomorphous. Each of the central metal atoms of the above complexes is bonded with two unsymmetrical nitrogen atoms of the chelating diamido ligand, one nitrogen atom of the $N(\text{SiMe}_3)_2$ ligand and one oxygen atom of THF molecule. Thus, compounds chiral at central lanthanide metal were obtained; however, racemic compounds crystallized in the same unit cell. Comparison of the Ln–N bonds of the same molecule indicated that they are not identical, and also the N–Ln–N, and the N–Ln–O angles around the center metal are far from the ideal tetrahedral angles (Table 1), so the coordination geometry of the complexes can be described as distorted tetrahedral.

From Table 1, we can see that the usual consequences of the increase of the ionic radius of the Ln^{3+} ion when moving from Yb^{3+} to Nd^{3+} are clearly reflected by the average Ln–N distances of 2.178(4) Å found in **2**, 2.194(12) Å found in **3**, 2.219(3) Å found in **4**, 2.263(7) Å found in **5**, and 2.294(5) Å found in **6**. The usual lanthanide contraction is also reflected by the average Ln–O distances of 2.272(4) Å in **2**, 2.294(11) Å in **3**, 2.332(3) Å in **4**, 2.400(7) Å in **5**, and 2.446(5) Å in **6**. From Table 1, we can also find that the Ln–N bond distances for the metal to the chelating diamido ligand are generally shorter than those of the metal to the

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Table 1. Selected Bond Length (Å) and Bond Angle (°) of Complexes **2–6**

	2	3	4	5	6
Ln(1)–N(1)	2.132(4)	2.103(12)	2.177(3)	2.210(7)	2.233(5)
Ln(1)–N(2)	2.189(4)	2.193(12)	2.224(3)	2.270(6)	2.295(4)
Ln(1)–N(3)	2.217(4)	2.223(14)	2.256(3)	2.309(7)	2.354(5)
Ln(1)–O(1)	2.269(4)	2.294(11)	2.326(3)	2.392(7)	2.438(5)
Ln(2)–N(4)	2.122(4)	2.174(11)	2.160(3)	2.188(7)	2.216(5)
Ln(2)–N(5)	2.181(4)	2.222(12)	2.225(3)	2.266(6)	2.304(4)
Ln(2)–N(6)	2.224(4)	2.250(11)	2.274(4)	2.337(7)	2.359(5)
Ln(2)–O(2)	2.275(4)	2.294(11)	2.339(3)	2.407(7)	2.453(5)
Ln–N _{av.}	2.178(4)	2.194(12)	2.219(3)	2.263(7)	2.294(5)
Ln–O _{av.}	2.272(4)	2.294(11)	2.332(3)	2.400(7)	2.446(5)
N(2)–Ln(1)–N(1)	91.64(16)	92.1(5)	91.26(12)	90.0(2)	90.34(18)
N(3)–Ln(1)–N(1)	122.78(14)	122.9(4)	126.50(11)	127.6(2)	127.77(17)
N(3)–Ln(1)–N(2)	132.60(15)	132.4(4)	132.08(12)	132.6(2)	132.46(17)
N(1)–Ln(1)–O(1)	100.34(15)	100.6(4)	99.67(12)	98.7(3)	99.45(19)
N(2)–Ln(1)–O(1)	100.47(15)	100.6(5)	100.53(13)	100.7(3)	99.99(18)
N(3)–Ln(1)–O(1)	103.51(14)	102.8(4)	100.89(13)	101.1(3)	100.12(19)
N(5)–Ln(2)–N(4)	94.31(15)	94.8(4)	92.90(11)	91.7(2)	91.30(18)
N(6)–Ln(2)–N(4)	125.86(15)	126.7(5)	126.76(12)	128.7(2)	129.81(17)
N(6)–Ln(2)–N(5)	133.54(15)	131.5(5)	134.11(13)	134.0(3)	133.86(18)
N(4)–Ln(2)–O(2)	99.70(15)	101.8(5)	99.31(13)	99.1(3)	98.21(19)
N(5)–Ln(2)–O(2)	98.35(15)	98.9(4)	98.34(12)	97.8(2)	97.60(17)
N(6)–Ln(2)–O(2)	96.60(15)	95.9(5)	96.75(13)	96.2(3)	96.06(18)

N(SiMe₃)₂ ligand. For example, the Yb(1)–N(1) and Yb(1)–N(2) distances are 2.132(4) Å and 2.189(4) Å in **2**, which are shorter than the Yb(1)–N(3) distance of 2.217(4) Å. The similar results can also be found in other rare earth complexes **3** to **6**. This may be attributable to the steric effect of different ligands. It is also found that the N(2)–Ln(1)–N(1) angles decrease slightly as the ionic radii increase from Yb³⁺ to Nd³⁺. The other corresponding angles are also in the similar sequence.

The average Yb–N bond distance of 2.178(4) Å in **2** is comparable with the average Yb–N bond distance of 2.174(1) Å found in the cyclic binuclear Yb(III) complex {[μ-2-*p*-(Me₃SiN)₂C₆H₄]YbCl(THF)₂]₂},¹¹ but this average Yb–N distance is shorter than that of 2.211(5) Å found in [(Me₃Si)₂N]₃Yb^{III}(μ-Cl)Li(THF)₃,^{6h} 2.2376(5) Å found in the corresponding Yb(III) complex {[*o*-(Me₃SiN)₂C₆H₄]Yb(MeC₅H₄)₂}{Li(DME)₃},¹² 2.290(7) Å found in the anionic amido complex [Me₂Si(NPh)₂]₂Yb(THF)₂Li(THF)₄,¹³ and 2.334(4) Å found in the β-diketiminato supported lanthanide complex LYb(NPh)₂(THF) [L = (2,6-Me₂C₆H₃)NC(Me)-

CHC(Me)N(2,6-Me₂C₆H₃)].¹⁴ The average Sm–N bond distance of 2.263(7) Å in complex **5** is shorter than those of 2.322(5) to 2.334(5) Å found in complex {[*o*-(Me₃SiN)₂C₆H₄]Sm(MeC₅H₄)₂}{Li(DME)₃},¹² and 2.340(4) to 2.332(4) Å found in complex {[Me₂Si(NPh)₂]₂SmC₅H₅}{Li(DME)₃}.¹³ The average Nd–N bond distance of 2.294(5) Å in complex **6** is also shorter than that of 2.456 Å β-diketiminato supported neodymium complex LNd(NPh)₂(THF) [L = (2,6-Me₂C₆H₃)NC(Me)CHC(Me)N(2,6-Me₂C₆H₃)].¹⁴

The N(2)–Ln(1)–N(1) angles (formed by the chelating diamido ligand and the center metal) of 91.64(16)° in complexes **2**, 92.1(5)° in **3**, 91.26(12)° in **4**, 90.0(2)° in **5**, and 90.34(18)° in **6** are significantly larger than those found in {[Me₂Si(NPh)₂]₂Yb(MeC₅H₄)₂}{Li(DME)₃}(70.17(17)°), {[Me₂Si(NPh)₂]₂YbC₅H₅}{Li(DME)₃}(70.0(2)°),¹³ [Me₂Si(NPh)₂]₂Yb(THF)₂Li(THF) (89.31(11)°),¹³ LYbCl₂(THF)₂ (80.2(1)°) (L = *N*, *N*-bis(2,6-dimethylphenyl)-2,4-pentane-diiminato),¹⁴ {[*o*-(Me₃SiN)₂C₆H₄]Sm(MeC₅H₄)₂}{Li(DME)₃}(73.45(17)°),¹² and {[Me₂Si(NPh)₂]₂SmC₅H₅}{Li(DME)₃}(67.13(15)°).¹³

Catalytic Activities of the Complexes. During the study on the reactivity of the above complexes, it is found that the above complexes can function as catalysts for the cyclotrimerization of aromatic isocyanates to yield triaryl isocyanurates with a high activity and a high selectivity. To the best of our knowledge, it represents the first application of cyclopentadienyl-free rare earth metal complexes on catalytic cyclotrimerization of aryl isocyanates.

Yttrium complex **3** was employed as a catalyst for selecting the favorable reaction conditions for the cyclotrimerization of phenyl isocyanate. The results were listed in Table 2. From the Table, we can see that the cyclotrimerization of phenyl isocyanate could be accomplished in solvents such as toluene, CH₂Cl₂, and THF in the presence of 1–3 mol % of catalyst. It is found that the outputs of the catalytic reaction were affected by the catalyst loading and

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Table 2. Influence of the Conditions on the Cyclotrimerization of Phenyl Isocyanate

entry	cat. (mol %) ^a	solvent	temp (°C)/time (h)	yield (%) ^b
1	3(3%)	toluene	r.t./12	99
2	3(2%)	toluene	r.t./12	83
3	3(1%)	toluene	r.t./12	66
4	3(1%)	toluene	80/12	99
5	3(2%)	THF	r.t./12	99
6	3(1%)	THF	r.t./12	92
7	3(1%)	THF	50/12	99
8	3(3%)	CH ₂ Cl ₂	r.t./12	71
9	3(2%)	CH ₂ Cl ₂	r.t./12	59
10	3(1%)	CH ₂ Cl ₂	r.t./12	43
11	3(3%)	CH ₂ Cl ₂	40/12	99
12	3(2%)	CH ₂ Cl ₂	40/12	74
13	3(1%)	CH ₂ Cl ₂	40/12	62

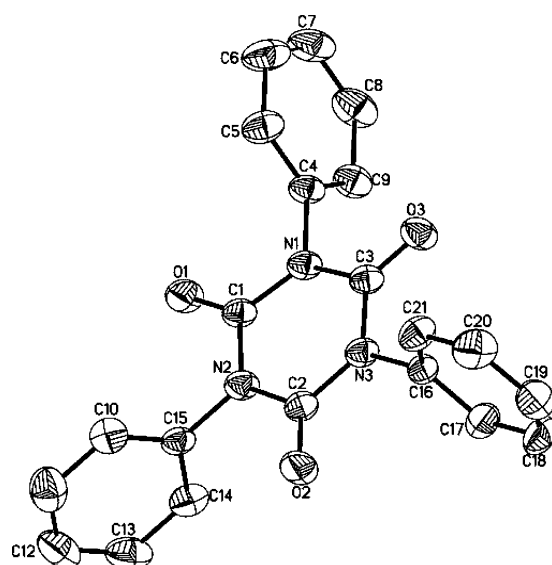
^a Catalyst: yttrium complex (**3**), catalyst to phenyl isocyanate mole ratio.^b Isolated yield.

reaction temperature when the reaction was carried out in toluene or CH₂Cl₂. For example, the outputs of the reactions decreased dramatically from 99% to 66%, and 71% to 43% when the catalyst loading was changed from 3 mol % to 1 mol % in toluene (Table 2, entries 1–3), and in CH₂Cl₂ (Table 2, entries 8–10). When the reaction was carried out at room temperature for 12 h in the presence of 1 mol % catalyst, the conversion of phenyl isocyanate to the final cyclotrimerization product was only 66% in toluene (Table 2, entry 3). A 99% yield of the cyclotrimerization product was obtained when the reaction was carried out at 80 °C for 12 h, (Table 2, entry 4). It is also found that the catalytic activity of the yttrium complex in THF was higher than that in toluene or CH₂Cl₂ in the presence of the same amount of catalyst loading (see Table 2, entries 2, 3; and entries 5, 6, 9, 10). It is notable that only the cyclotrimerization product was isolated, and no detectable dimerization or polymerization products were observed, indicating that the complex exhibited not only a high reactivity but also a higher selectivity on the reaction (Figure 6). Thus, 1 mol % catalyst loading was selected for the following study, and toluene and THF were selected as solvents for comparison of the catalytic activity of the catalysts.

To search for the generality of the above observation, and to search for the applications of other rare earth metal amides in this cyclotrimerization reaction, the catalytic activity and selectivity of the above different rare earth amides on cyclotrimerization of phenyl isocyanate were investigated. The results are listed in Table 3. It is found that all complexes **2**, **3**, **4**, **5**, and **6** exhibited a good to excellent catalytic activity on the cyclotrimerization of phenyl isocyanate, and all complexes showed a higher catalytic activity in THF than in toluene when the reaction was carried out at room temperature in the presence of 1 mol % catalyst. The cyclotrimerization compounds were the only products, indicating a high selectivity of the catalysts. The temperature has a great influence on the conversion of reaction when the catalytic reaction was carried out in toluene. The conversion could be improved when the reactions were carried out at 80 °C. For comparison, the catalytic activity of complex [(Me₃Si)₂N]₃Yb(μ-Cl)Li(THF)₃ (**7**) on the cyclotrimerization of phenyl isocyanate was studied (Table 3, entries 16, 17).

Table 3. Influence of Different Rare Earth Metal Amides on the Cyclotrimerization of Phenyl Isocyanate

entry	cat.(mol%) ^a	solvent	temp (°C)/time (h)	yield (%) ^b
1	2(1%)	toluene	r.t./12	62
2	2(1%)	toluene	80/12	99
3	2(1%)	THF	r.t./12	99
4	3(1%)	toluene	r.t./12	66
5	3(1%)	toluene	80/12	99
6	3(1%)	THF	r.t./12	92
7	4(1%)	toluene	r.t./12	62
8	4(1%)	toluene	80/12	99
9	4(1%)	THF	r.t./12	99
10	5(1%)	toluene	r.t./12	61
11	5(1%)	toluene	80/12	99
12	5(1%)	THF	r.t./12	99
13	6(1%)	toluene	r.t./12	56
14	6(1%)	toluene	80/12	99
15	6(1%)	THF	r.t./12	99
16	12 ^c (1%)	toluene	r.t./12	75
17	12 ^c (1%)	THF	r.t./12	99

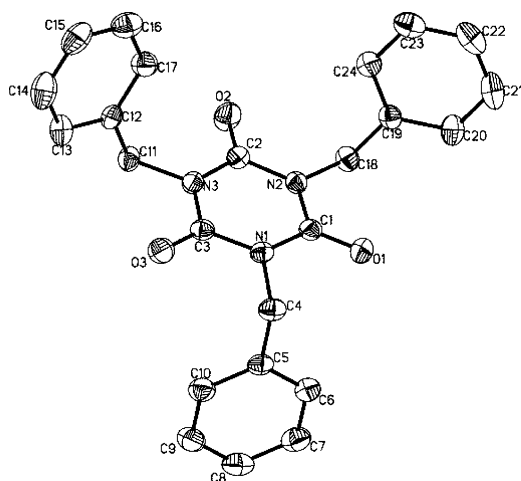
^a Catalyst to phenyl isocyanate mole ratio. ^b Isolated yield. ^c **12**: [(Me₃Si)₂N]₃Yb(μ-Cl)Li(THF)₃.**Figure 6.** Molecular structure of the compound **7**, hydrogen atoms are omitted for clarity.

Its catalytic activity on the cyclotrimerization of phenyl isocyanate is comparable with those of all the new complexes **2** to **6**. As indicated in Table 3, all the above new complexes and [(Me₃Si)₂N]₃Yb(μ-Cl)Li(THF)₃ (**12**) exhibited a similar high catalytic activity on the cyclotrimerization of isocyanate, so complexes **2** and **3** were selected for the following study on cyclotrimerization of different isocyanates. The results are compiled in Table 4.

From Table 4, we can see that complexes **2** and **3** exhibited a high catalytic activity for the cyclotrimerization of aromatic isocyanates. The aromatic isocyanates could be phenyl isocyanate, benzyl isocyanate, 4-isopropylbenzyl isocyanate (Table 4, entries 1–7, Figure 7). It is strange that all the complexes showed no catalytic activity on the cyclotrimerization of the 4-nitrophenylisocyanate (Table 4, entries 8, 9), which needs to be further investigated. It is notable that other byproducts such as dimerization products or polymerization products were not observed in the reactions, indicating a high selectivity of the complexes. The structures

Table 4. Data for the Cyclotrimerization of Different Isocyanates

entry	cat	R-	solvent	temp (°C)/time (h)	product	yield (%) ^a	t (°C) /time (h)	yield (%) ^a
1	2	phenyl	THF	r.t./12	7	99	50/12	
2	3	phenyl	THF	r.t./12	7	92	50/12	99
3	2	benzyl	THF	r.t./12	8	99	50/12	
4	3	benzyl	THF	r.t./12	8	99	50/12	
5	2	4-isopropylphenyl	THF	r.t./12	9	99	50/12	
6	3	4-isopropylphenyl	THF	r.t./12	9	46	50/12	81
7	3	4-isopropylphenyl	toluene	r.t./12	9	54	80/12	99
8	2	4-nitrophenyl	THF	r.t./12	0	0	50/12	0
9	3	4-nitrophenyl	THF	r.t./12	0	0	50/12	0
10	2	cyclohexyl	THF	r.t./12	10	0	50/12	11
11	2	cyclohexyl	toluene	r.t./12	10	0	80/12	26
12	3	cyclohexyl	toluene	r.t./12	10	0	80/12	28
13	2	isopropyl	THF	r.t./12	11	8	50/12	15
14	2	isopropyl	toluene	r.t./12	11	0	80/12	25
15	3	isopropyl	toluene	r.t./12	11	0	80/12	24
16	2	allyl	THF	r.t./12	0	0	50/12	0
17	3	allyl	THF	r.t./12	0	0	50/12	0

^a Isolated yield.**Figure 7.** Molecular structure of the compound **8**, hydrogen atoms and the solvated THF molecule are omitted for clarity.

of cyclotrimerization products **7** and **8** have been determined (Figures 6 and 7).

When we move our study on the catalytic activity of the above complexes to the cyclotrimerization of aliphatic isocyanates, such as the isopropyl isocyanate, cyclohexyl isocyanate, allyl isocyanate, it is found that all these complexes exhibited a relatively low catalytic activity on the cyclotrimerization of the corresponding aliphatic isocyanates. For example, no cyclotrimerization products could be obtained when the reaction was carried out with cyclohexyl isocyanate at room temperature in THF or in toluene. This transformation could be achieved but with low conversion by raising the reaction temperature (Table 4, entries 10, 11 and 12). Similar results have been obtained with isopropyl isocyanate (Table 4, entries 13, 14 and 15), but allyl isocyanate cannot be cyclotrimerized to the product even at 80 °C.

On the basis of the proposed mechanism for cyclotrimerization of isocyanates catalyzed by zirconium compounds^{9h} or calcium complexes,¹⁵ the catalytic cycle is proposed as follows (Schemes 3 and 4): Coordination of the isocyanate to the rare earth metal led to dissociation of THF and to formation of the intermediate **I**; migration insertion of the

isocyanate into the Ln–N(SiMe₃)₂ bond produced the intermediate **II**. **II** reacted with another molecule of isocyanate through insertion reaction and gave intermediate **III**, which further reacted with another molecule of isocyanate to produce the final cyclotrimerization products and furnished a catalytic cycle.

Conclusion

A series of novel lanthanide amides with general formula {(CH₂SiMe₂)[(2,6-ⁱPr₂C₆H₃)N]₂}LnN(SiMe₃)₂(THF) were synthesized via reaction of [(Me₃Si)₂N]₃Ln^{III}(μ-Cl)Li(THF)₃ (Ln = Yb, Y, Dy, Sm, Nd) with the corresponding diamine (CH₂SiMe₂[(2,6-ⁱPr₂C₆H₃)NH]₂). All complexes were fully characterized by spectroscopic methods and elemental single-crystal X-ray analyses. These complexes exhibited an excellent catalytic activity on the cyclotrimerization of aromatic isocyanates to yield the corresponding isocyanurates, which represents the first example to be reported in this field of the function of cyclopentadienyl-free rare earth metal complexes as highly efficient selective catalysts. These catalysts have the advantages of easy preparation and manipulation, compatibility with different solvents, and an excellent activity and selectivity on the cyclotrimerization of aromatic isocyanates. These advantages of the complexes imply the potential applications of other cyclopentadienyl-free rare earth metal amides in this field. Extension works on this field are now in progress in our laboratory.

Experimental Section

Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere using standard Schlenk techniques. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. [(Me₃Si)₂N]₃Ln^{III}(μ-Cl)Li(THF)₃ (Ln = Yb, Y, Dy, Sm, and Nd) were prepared according to literature methods.^{6h,m,n} Elemental analyses data were obtained on a Perkin-Elmer 2400 Series II elemental analyzer. ¹H NMR and ¹³C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ¹H; 75.0 MHz for ¹³C) in C₆D₆ for lanthanide complexes and in CDCl₃ for organic compounds. Chemical shifts

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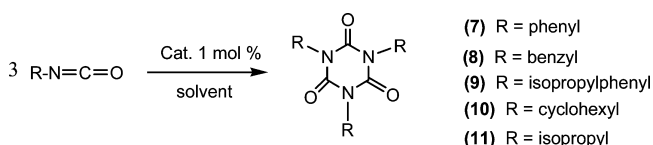
Table 5. Crystallographic Data for Compounds 2–8

	2	3	4	5
empirical formula	C ₃₇ H ₆₈ N ₃ OSi ₃ Yb	C ₃₇ H ₆₈ N ₃ OSi ₃ Y	C ₃₇ H ₆₈ N ₃ OSi ₃ Dy	C ₃₇ H ₆₈ N ₃ OSi ₃ Sm
formula weight	828.25	744.12	817.71	805.56
T(K)	113(2)	293(2)	293(2)	294(2)
wavelength (Å)	0.71070	0.71073	0.71073	0.71073
cryst system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
a(Å)	11.037(8)	11.029(2)	11.2552(9)	11.2846(14)
b(Å)	21.149(14)	21.200(4)	21.0568(16)	21.076(3)
c(Å)	36.69(2)	36.909(7)	37.425(3)	37.567(5)
V(Å ³)	8565(10)	8630(3)	8869.8(12)	8934.8(19)
Z	8	8	4	8
D _{calcd} (g cm ⁻³)	1.285	1.145	1.222	1.198
μ (mm ⁻¹)	2.297	1.464	1.794	1.423
F(000)	3448	3200	3400	3384
θ range for data collcn (deg)	1.47–27.93	1.10–25.02	1.46–27.60	1.08–25.02
reflens collcd/unique	76435/20420, [R _{int} = 0.074]	51730/8384, [R _{int} = 0.100]	77014/20459, [R _{int} = 0.025]	46718/8674, [R _{int} = 0.081]
data/restns/params	20420/0/833	8384/33/840	20459/0/844	8674/72/843
obsd reflens [I > 2σ(I)]	19049	7571	18661	6640
Goodness-of-fit F ²	1.067	1.102	1.057	1.028
R ₁ , wR ₂ [I > 2σ(I)]	0.042, 0.074	0.086, 0.221	0.030, 0.072	0.041, 0.082
R ₁ , wR ₂ (all data)	0.047, 0.076	0.093, 0.230	0.035, 0.074	0.067, 0.094
largest diff peak/hole (e Å ⁻³)	0.840 and -0.790	3.047 and -0.729	0.574 and -1.037	0.432 and -0.686
	6	7	8	
empirical formula	C ₃₇ H ₆₈ N ₃ OSi ₃ Nd	C ₂₅ H ₂₃ N ₃ O ₄	C ₂₄ H ₂₁ N ₃ O ₃	
formula weight	799.45	429.46	399.44	
T(K)	293(2)	293(2)	293(2)	
wavelength (Å)	0.71073	0.71073	0.71073	
cryst system	orthorhombic	triclinic	monoclinic	
space group	P2 ₁ 2 ₁ 2 ₁	P $\bar{1}$	Pn	
a(Å)	11.3055(16)	11.2432(17)	11.4057(9)	
b(Å)	21.110(3)	11.3103(17)	4.5668(4)	
c(Å)	37.690(5)	11.493(3)	18.9688(14)	
α (deg)	90	91.117(2)	90	
β (deg)	90	115.099(2)	90.0100(10)	
γ (deg)	90	119.092(2)	90	
V(Å ³)	8995(2)	1108.5(4)	988.04(14)	
Z	4	2	2	
D _{calcd} (g cm ⁻³)	1.178	1.287	1.343	
μ (mm ⁻¹)	1.262	0.089	0.090	
F(000)	3356	452	420	
θ range for data collcn (deg)	1.45–27.56	2.04–27.61	2.08–27.55	
no. of reflens collcd/unique	76032/20558, [R _{int} = 0.064]	8412/4852, [R _{int} = 0.040]	8049/4114, [R _{int} = 0.020]	
data/restns/params	20558/0/844	4852/0/290	4114/2/272	
obsd reflens [I > 2σ(I)]	14476	2487	3861	
Goodness-of-fit F ²	1.063	1.086	1.043	
R ₁ , wR ₂ [I > 2σ(I)]	0.051, 0.088	0.069, 0.227	0.029, 0.078	
R ₁ , wR ₂ (all data)	0.091, 0.101	0.19, 0.331	0.031, 0.080	
largest diff peak/hole (e Å ⁻³)	0.989 and -1.263	0.438 and -0.486	0.121 and -0.101	

(δ) were reported in ppm. *J* values are reported in Hz. IR spectra were recorded on a Shimadzu FTIR-8400s spectrometer (KBr pellet). Mass spectra were performed on a Micromass GCT-MS spectrometer. Melting points were determined in capillaries, and were uncorrected.

Preparation of (CH₂SiMe₂)[(2,6-¹Pr₂C₆H₃)NH]₂ (1). To a solution of (2,6-¹Pr₂C₆H₃)NH₂ (10.0 mL, 53.02 mmol) in THF (50.0 mL) was slowly added a 1.43 M *n*-BuLi solution (37.10 mL, 53.02 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature and was then cooled to 0 °C again. To the reaction mixture was added ClSiMe₂CH₂Cl (3.50 mL, 26.51 mmol) in one portion. The reaction mixture was stirred for 12 h at 50 °C. The solvents were pumped off under reduced pressure. The residue was extract with *n*-hexane (2 × 20.0 mL), and the extractions were

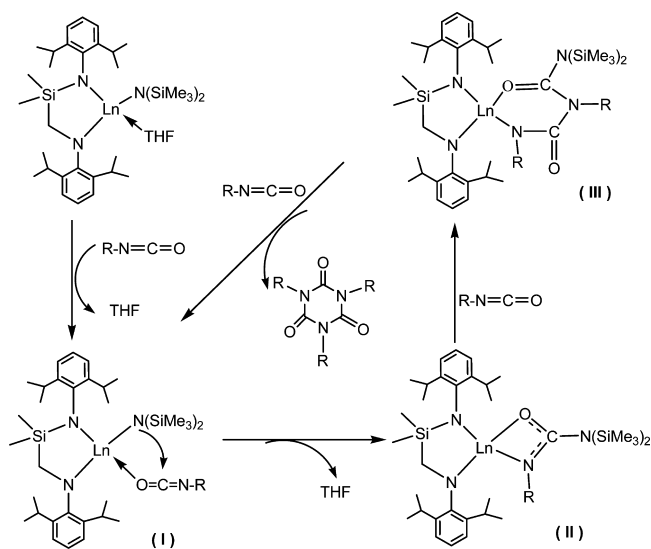
Scheme 3. Catalytic Cyclotrimerization of Isocyanate



combined. The solution was reduced in volume under reduced pressure and cooled at -10 °C to give (CH₂SiMe₂)[(2,6-¹Pr₂C₆H₃)NH]₂ (1) as white crystals (3.82 g, 34% yield). m.p.: 89 °C-91 °C. ¹H NMR (CDCl₃, ppm): δ 7.12–7.07 (m, 6H, aromatic CH), 3.48 (br, 2H, CH(CH₃)₂), 3.16 (br, 2H, CH(CH₃)₂), 2.64 (br, 2H, NH), 2.48 (d, *J* = 7.3, 2H, CH₂), 1.25 (d, *J* = 6.8, 24H, CH₃), 0.30 (s, 6H, Si(CH₃)). ¹³C NMR (CDCl₃, ppm): δ 146.3, 142.3, 140.2, 132.4, 123.6, 123.5, 122.8, 118.5 (C₆H₃), 43.5 (CH₂), 27.9 (CH(CH₃)₂), 27.5 (CH(CH₃)₂), 24.2 (CH₃), 22.4 (CH₃). IR (KBr pellet, cm⁻¹): ν 3356 (s), 3059 (m), 2932 (s), 2870 (s), 2801 (s), 1620 (m), 1589 (m), 1439 (s), 1381 (s), 1362 (s), 1327 (s), 1254 (s), 1196 (s), 1177 (m), 1107 (s), 1045 (s), 910 (s), 879 (m), 864 (w), 837 (m), 802 (m), 756 (m), 737 (m), 691 (m), 652 (w), 613 (w), 567 (w), 556 (w), 525 (w). HRMS (EI) *m/z*: calcd for C₂₇H₄₄N₂Si: 424.3274; Found: 424.3271. Anal. Calcd for C₂₇H₄₄N₂Si: C, 76.35; H, 10.44; N, 6.60. Found: C, 76.70; H, 10.16; N, 6.49.

Preparation of {(CH₂SiMe₂)[(2,6-¹Pr₂C₆H₃)N]₂}YbN(SiMe₃)₂-(THF) (2). To a toluene (10.0 mL) solution of (CH₂SiMe₂)[(2,6-¹Pr₂C₆H₃)NH]₂ (1) (1.35 g, 3.17 mmol) was added a toluene (50.0 mL) solution of [(Me₃Si)₂N]₃Yb^{III}(μ-Cl)Li(THF)₃ (2.897 g, 3.17

Scheme 4. Catalytic Cycle of Cyclotrimerization of Isocyanate



mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was then refluxed for 12 h, the color of the solution was gradually changed from yellow to dark red. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (2 × 15.0 mL). The extractions were combined and concentrated to about 10.0 mL. The red crystals were obtained by cooling the concentrated solution at 0 °C for several days (2.336 g, 89% yield). IR (KBr pellet, cm⁻¹): ν 3059 (m), 3020 (m), 2963 (s), 2866 (s), 2797 (w), 2361 (s), 2342 (s), 1624 (m), 1439 (s), 1381 (s), 1327 (s), 1254 (s), 1107 (m), 1045 (m), 968 (w), 914 (s), 841 (s), 799 (s), 737 (s). Anal. Calcd for C₃₃H₆₀N₃Si₃Yb (2-THF): C, 52.42; H, 8.00; N, 5.56. Found: C, 52.79; H, 7.94; N, 5.23.

Preparation of {(CH₂SiMe₂)[(2,6-*i*-Pr₂C₆H₃)N]₂}YN(SiMe₃)₂- (THF) (3). This compound was prepared as white crystals in 49% (0.995 g) yield by treatment of (CH₂SiMe₂)[(2,6-*i*-Pr₂C₆H₃)NH]₂ (1) (1.16 g, 2.73 mmol) with [(Me₃Si)₂N]₃Y^{III}(μ-Cl)Li(THF)₃ (2.263 g, 2.73 mmol) using the procedures similar to those described above for preparation of 2. ¹H NMR (C₆D₆, ppm): δ 7.25–7.10 (m, 6H) (C₆H₃), 4.11 (s, 4H, OC₄H₈), 3.78 (m, 2H, CH(CH₃)₂), 3.57–3.49 (m, 2H, CH(CH₃)₂), 3.28–3.23 (m, 2H, CH₂), 3.01–2.53 (m, 4H, OC₄H₈), 1.61–1.26 (s, 24H, CH₃), 0.35–0.17 (s, 24H, Si(CH₃)₃). ¹³C NMR (CDCl₃, ppm): δ 123.3, 122.7, 120.9, 71.8, 45.5, 27.3, 26.2, 24.5, 24.0, 23.7, 23.2, 4.0, 2.0, 0.8. IR (KBr pellet, cm⁻¹): ν 3067 (m), 2963 (s), 2932 (s), 2870 (s), 2187 (s), 1674 (m), 1632 (m), 1497 (s), 1466 (m), 1443 (m), 1385 (m), 1362 (s), 1319 (m), 1254 (s), 1053 (s), 934 (m), 907 (m), 841 (s), 806 (s), 745 (s), 644 (w), 540 (w). Anal. Calcd for C₃₇H₆₈N₃OSi₃Y: C, 59.72; H, 9.21; N, 5.65. Found: C, 59.77; H, 9.03; N, 5.73.

Preparation of {(CH₂SiMe₂)[(2,6-*i*-Pr₂C₆H₃)N]₂}DyN(SiMe₃)₂- (THF) (4). This compound was prepared as colorless crystals in 81% yield following the procedure described for complex 2 from the reaction of (CH₂SiMe₂)[(2,6-*i*-Pr₂C₆H₃)NH]₂ (1) (0.879 g, 2.07 mmol) with [(Me₃Si)₂N]₃Dy^{III}(μ-Cl)Li(THF)₃ (1.87 g, 2.07 mmol). IR (KBr pellet, cm⁻¹): ν 2959 (s), 2866 (m), 2361 (s), 2342 (s), 1458 (m), 1439 (m), 1254 (s), 914 (s), 841 (m), 799 (m). Anal. Calcd for C₃₇H₆₈N₃OSi₃Dy: C, 54.35; H, 8.38; N, 5.14. Found: C, 54.44; H, 8.07; N, 5.45.

Preparation of {(CH₂SiMe₂)[(2,6-*i*-Pr₂C₆H₃)N]₂}SmN(SiMe₃)₂- (THF) (5). Following the procedures described for the preparation of complex 2, complex 5 was prepared as yellow crystals in 79% yield from the reaction of (CH₂SiMe₂)[(2,6-*i*-Pr₂C₆H₃)NH]₂ (1)

(0.796 g, 1.88 mmol) with [(Me₃Si)₂N]₃Sm^{III}(μ-Cl)Li(THF)₃ (1.67 g, 1.88 mmol) in toluene. IR (KBr pellet, cm⁻¹): ν 3059 (m), 2959 (m), 2866 (m), 2797 (m), 1937 (w), 1859 (w), 1632 (w), 1589 (w), 1443 (m), 1381 (m), 1362 (m), 1327 (m), 1254 (s), 1196 (s), 1177 (m), 1107 (m), 1045 (m), 934 (w), 912 (m), 802 (w), 737 (w), 571 (w). Anal. Calcd for C₃₃H₆₀N₃Si₃Sm (5-THF): C, 54.04; H, 8.25; N, 5.73. Found: C, 54.33; H, 8.31; N, 5.48.

Preparation of {(CH₂SiMe₂)[(2,6-*i*-Pr₂C₆H₃)N]₂}NdN(SiMe₃)₂- (THF) (6). This compound was prepared as blue crystals in 76% yield from the reaction of (CH₂SiMe₂)[(2,6-*i*-Pr₂C₆H₃)NH]₂ (1) (0.974 g, 2.30 mmol) with [(Me₃Si)₂N]₃Nd^{III}(μ-Cl)Li(THF)₃ (2.03 g, 2.30 mmol) in toluene. IR (KBr pellet, cm⁻¹): ν 2959 (s), 2866 (m), 2797 (m), 2361 (s), 2342 (s), 1458 (m), 1439 (s), 1254 (s), 1196 (s), 914 (s), 841 (s), 799 (s). Anal. Calcd for C₃₃H₆₀N₃Si₃Nd (6-THF): C, 54.49; H, 8.31; N, 5.78. Found: C, 54.68; H, 8.37; N, 5.42.

X-ray Structure Determination. A suitable crystal of the complex 2, 3, 4, 5, 6, 7, and 8 was mounted in a sealed capillary. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer using the graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); temperature 294(2) K; ψ and ω scan technique; SADABS effects and empirical absorption were applied in the data corrections. All structures were solved by direct methods (SHELXL-97), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on F² (SHELXL-97). Crystal data and details of the data collection are given in Table 5. Further details are included in the Supporting Information.

General Procedure for the Cyclotrimerization of Isocyanates (8¹⁶ As an Example). To a solution of THF (5 mL) in a 30.0 mL Schlenk tube under dried argon was added complex 2 (0.018 g, 0.022 mmol) and benzyl isocyanate (0.29 g, 2.2 mmol). The resulting mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction mixture was hydrolyzed by water (1 mL), extracted with diethyl ether (3 × 10 mL), dried over anhydrous Na₂SO₄, and filtered. After the solvent was removed under the reduced pressure, the final products were further purified by recrystallization from THF. Compound 8 was isolated as colorless crystals (99%). White solid. Mp: 160.0–160.5 °C. ¹H NMR (CDCl₃, ppm): δ 7.48–7.31(m, 15H, aromatic CH); 5.04(6H, CH₂). ¹³C NMR (CDCl₃, ppm): δ 148.8, 135.4, 128.7, 128.3, 127.8, 45.9. HRMS (EI) *m/z*: calcd for C₂₄H₂₁N₃O₃ 399.1583; Found: 399.1580.

Compound 7:^{3b} White solid. Mp: 280.8–281.3 °C. ¹H NMR (CDCl₃, ppm): δ 7.43–7.15(m, 15H, aromatic CH). ¹³C NMR (CDCl₃, ppm): δ 148.4, 133.3, 129.1, 128.1. HRMS (EI) *m/z*: calcd for C₂₁H₁₅N₃O₃ 357.1113; Found: 357.1116.

Compound 9: White solid. Mp: 287.5–288.0 °C. ¹H NMR (CDCl₃, ppm): δ 7.35–7.28 (m, 12H, aromatic CH); 2.99–2.91(3H, CH); 1.27–1.25 (d, *J* = 6.9, 18H, CH₃). ¹³C NMR (CDCl₃, ppm): δ 149.6, 130.8, 127.7, 127.0, 33.5, 23.5. HRMS (EI) *m/z*: calcd for C₃₀H₃₃N₃O₃ 483.2522; Found: 483.2520.

Compound 10:¹⁷ White solid. Mp: 227.0–227.5 °C. ¹H NMR (CDCl₃, ppm): δ 4.08–4.06 (3H, NCH), 1.95–1.04 (30H, CH₂). ¹³C NMR (CDCl₃, ppm): δ 48.8, 33.6, 25.3, 24.5. HRMS (EI) *m/z*: calcd for C₂₁H₃₃N₃O₃ 375.2522; Found: 375.2527.

Compound 11:¹⁸ White solid. Mp: 98.5–99.0 °C. ¹H NMR (CDCl₃, ppm): δ 4.88–4.84 (3H, CH); 1.33–1.30(18H, CH₃). ¹³C

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Rare Earth Metal Amides Supported by a Diamido Ligand

NMR (CDCl₃, ppm): δ 148.3, 47.3, 19.2. HRMS (EI) m/z : calcd for C₁₂H₂₁N₃O₃ 255.1583; Found: 255.1579.

Acknowledgment. This work was co-supported by the National Natural Science Foundation of China (Grants 20672002, 20702001), the program for the NCET (Grant NCET-04-0590), and the grant from Anhui Province, and the Anhui Education Department (Grants 2007Z016, TD200707).

We are also grateful for the assistance of Prof. Baohui Du and Jiping Hu in running the IR and NMR spectra.

Supporting Information Available: CIF file giving crystal data for complexes **2**, **3**, **4**, **5**, **6**, and compounds **7**, **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC800496D