Synthesis, Structure, and Diverse Catalytic Activities of [Ethylenebis(indenyl)]lanthanide(III) Amides on N−H and C−H Addition to Carbodiimides and ε-Caprolactone Polymerization

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The simple silylamine elimination reaction of ethylenebis(indene) with the lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ produced the [ethylenebis(η^5-indenyl)][bis(trimethylsilyl)amido]lanthanide(III) complexes $(EBI)LnN(TMS)_2$ (Ln = Y (**1**), Sm (**2**), Yb (**3**)), which exhibited diverse catalytic activities on the addition of the N−H bond of amines and the C−H bond of terminal alkynes to the carbodiimides and on the ring-opening polymerization of ε-caprolactone as well. The new complexes **1** and **2** were fully characterized by spectroscopic methods, elemental analyses, and X-ray crystallographic analyses. This work offers a straightforward, highly atom efficient route for the syntheses of substituted guanidines and propiolamidines, and it represents the first application of readily accessible lanthanocene amides to these reactions.

Introduction

Many natural products and synthetic pharmaceuticals contain guanidine functional groups, which often play an essential role in their biological activity.[1] Guanidines have received considerable attention as ancillary ligands in the preparation of a variety of metal complexes, including those of early-transition-metals and lanthanide complexes.[2] Typical methods for the preparation of substituted guanidines employ the reaction of an amine with electrophilic guanylating reagent[3] or functionalization of a preexisting guanidine core.[4] On the other hand, the addition of the N−H bonds of the amines to carbodiimides (RN═C═NR) provides a direct and atom-efficient route to the guanidines; however, primary aliphatic amines are the only examples that can undergo direct guanylation with carbodiimides to yield the corresponding *N*,*N*′,*N*″-trialkylguanidines under rather forcing conditions.[5] Aromatic amines or secondary amines do not react with carbodiimides under the same or harsher conditions. Only a few works on the catalytic intermolecular hydroamination of the carbodiimides have provided direct methods for the construction of the CN-rich functionalized guanidines; for example, it has been reported that the lithium bis(trimethylsilyl) amide $LiN(TMS)_2$ can catalyze intermolecular hydroamination reaction of the aromatic amines and carbodiimides,[6] the half-sandwich yttrium alkyl complex $\{Me_2Si(C_5Me_4)(NR)\}Ln(CH_2SiMe_3)(THF)_n$ can catalyze the guanylation of aromatic amines and secondary amines,[7] and titanacarboranyl complexes or transition-metal−imido complexes can catalyze the guanylation of aromatic and secondary amines.[8] However, the synthesis of guanidines and propiolamidines using lanthanocene amido complexes as catalysts still remains to be examined.

Propiolamidines (RN═C(C≡CR′)(NHR)), which contain a conjugated C−C triple bond, could hardly be obtained because

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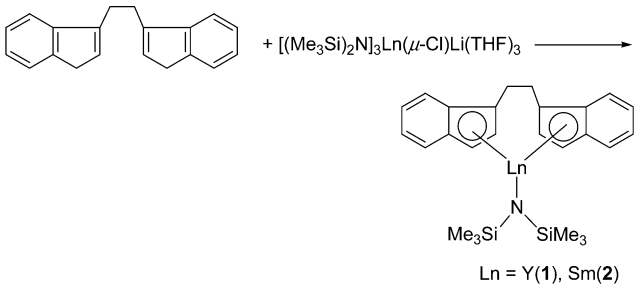
Scheme 1



of their high sensitivity to hydrolysis.[9] Although the addition of C−H bonds of terminal alkynes to carbodiimides could, in principle, provide a straightforward, atom-efficient route to propiolamidines, such a catalytic reaction has hardly been explored. The only clearly documented precedent for this reaction are the recent reports that a half-sandwich yttrium alkyl complex ({$Me_2Si(C_5Me_4)(NPh)$}$Y(CH_2SiMe_3)(THF)_2$)[9] and lithium bis(trimethylsilyl)amide ($LiN(TMS)_2$) act as catalysts.[6]

Hydroamination, the formal addition of an N−H bond across carbon−carbon unsaturated groups, has attracted much recent attention, because it offers an atom-efficient route to nitrogen-containing molecules which are important for fine chemicals and pharmaceuticals. Since Marks and co-workers have shown that the lanthanocene derivatives serve as excellent catalysts for the intramolecular hydroamination of alkenes and alkynes,[10] there has been a growing interest in developing new lanthanide complexes as catalysts of this transformation.[11] Livinghouse and co-workers found that the homoleptic lanthanide amides $Ln[N(TMS)_2]_3$ can catalyze the intramolecular hydroamination of aminoalkenes.[12] Gilbert and co-workers also found that the $(EBI)YbN(TMS)_2$ complex was an active catalyst for the intramolecular hydroamination of aminoalkenes.[13]

We report here an efficient and direct catalytic method for the guanylation of both aromatic and secondary amines, the addition of the terminal alkyne C−H bond to carbodiimides, and the ring-opening polymerization of ε-caprolactone using the lanthanocene amido complexes $(EBI)LnN(TMS)_2$ (Ln = Y, Sm, Yb) as catalysts. To the best of our knowledge, this represents the first example of the lanthanocene amido complexes as catalysts for the synthesis of substituted guanidines and propiolamidines.

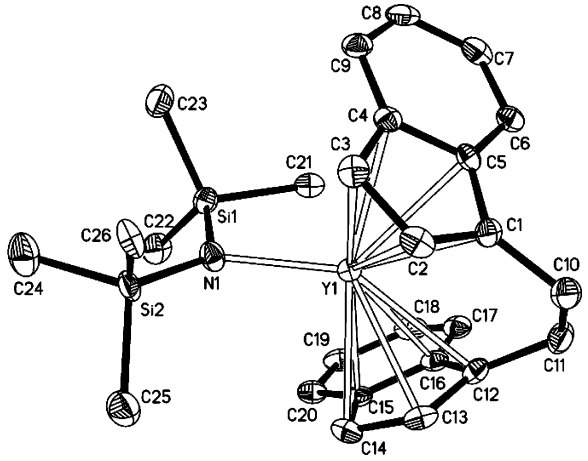


Figure 1. Molecular structure of $[\eta^5\text{-}(CH_2)_2(C_9H_6)_2]YN(TMS)_2$ (**1**). Selected bond distances (Å) and angles (deg): Y(1)−N(1) = 2.243(4), Y(1)−C(1) = 2.672(5), Y(1)−C(2) = 2.641(5), Y(1)−C(3) = 2.666(5), Y(1)−C(4) = 2.704(5), Y(1)−C(5) = 2.688(5), Y(1)−C(12) = 2.669(5), Y(1)−C(13) = 2.633(5), Y(1)−C(14) = 2.645(5), Y(1)−C(15) = 2.721(5), Y(1)−C(16) = 2.715(4); Si(1)−N(1)−Y(1) = 103.38(17), Si(2)−N(1)−Y(1) = 129.0(4).

Results and Discussion

Syntheses of *meso*-[Ethylenebis(η^5-indenyl)]lanthanide(III) Bis(trimethylsilyl)amido Complexes. The syntheses of the complexes $(EBI)LnN(TMS)_2$ (Ln = Y (**1**), Sm (**2**)) were achieved through the silylamine elimination reaction of ethylenebis(indene) with the lanthanide amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Y, Sm) in refluxing toluene (Scheme 1).[14] The complexes are sensitive to air and moisture and soluble in THF, DME, toluene, pyridine, and nonpolar solvents such as *n*-hexane. All of the complexes were fully characterized by spectroscopic methods and elemental analyses. The structures of the new complexes **1** and **2** were determined by single-crystal X-ray analyses.

X-ray analyses revealed that the central metal ions of the complexes **1** (Figure 1) and **2** (Figure 2) are η^5-bonded to each of the two indenyl groups and σ-bonded to the nitrogen atom of the $N(SiMe_3)_2$ ligand. There are two unique molecules in the unit cell, and X-ray analyses showed that morphologies of complexes **1** and **2** can be described as meso. An interaction between the lanthanide and the methyl is shown by the smaller angle formed between the interacting $Si(CH_3)_2$ group and the metal in complexes **1** and **2**.[14] The angles Si(1)−N(1)−Y(1) = 103.38(17)° in **1** and Si(1)−N(1)−Sm(1) = 105.9(3)° in **2** are obviously smaller than the angles Si(2)−N(1)−Y(1) = 129.0(4)° in **1** and Si(2)−N(1)−Sm(1) = 124.7(3)° in **2**, respectively. Similar results are also observed in other lanthanocene derivatives such as $(C_5Me_5)_2SmN(TMS)_2$, reported by Evans,[15] $Me_2Si(C_5Me_4)(C_{13}H_8)LnE(TMS)_2$ (Ln = Dy, Er; E = CH, N), reported by Qian,[16] and *meso*-$(EBI)Yb^{III}N(SiMe_3)_2$, reported by Gilbert.[13]

Guanylation of both Aromatic and Secondary Amines with Carbodiimides. In the absence of a catalyst, the aromatic amines do not react with the carbodiimides to any detectable degree, even with prolonged heating. However, addition of 2

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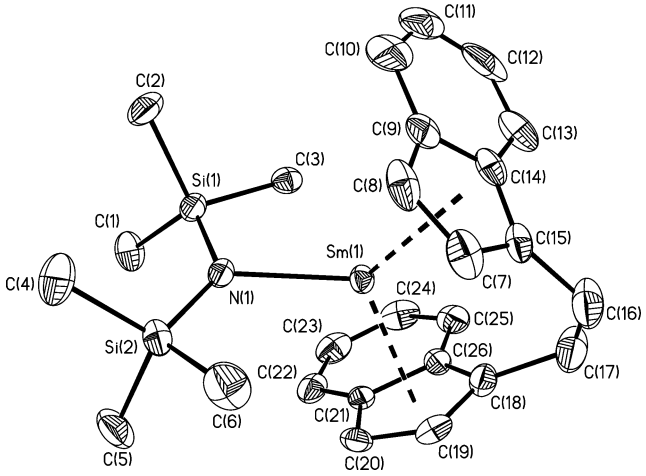


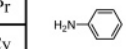
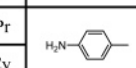
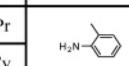
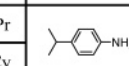
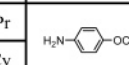
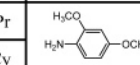
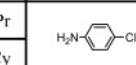
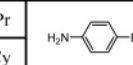
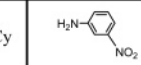
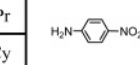
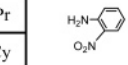
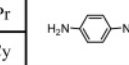
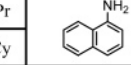
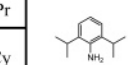
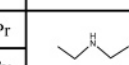
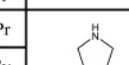
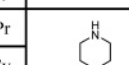
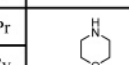
Figure 2. Molecular structure of $[\eta^5\text{-}(CH_2)_2(C_9H_6)_2]SmN(TMS)_2$ (**2**). Selected bond distances (Å) and angles (deg): Sm(1)−N(1) = 2.264(6), Sm(1)−C(7) = 2.676(9), Sm(1)−C(8) = 2.682(9), Sm(1)−C(9) = 2.744(9), Sm(1)−C(14) = 2.741(8), Sm(1)−C(15) = 2.722(8), Sm(1)−C(18) = 2.695(9), Sm(1)−C(19) = 2.662(8), Sm(1)−C(20) = 2.698(8), Sm(1)−C(21) = 2.746(8), Sm(1)−C(26) = 2.732(7); Si(1)−N(1)−Sm(1) = 105.9(3), Si(2)−N(1)−Sm(1) = 124.7(3).

mol % of (EBI)LnN(TMS)$_2$ (Ln = Y (**1**), Sm (**2**), Yb (**3**)) led to an efficient guanylation of aniline with dicyclohexylcarbodiimide, to give the expected products **5** in 95%, 95%, and 92% yields using the catalysts **2**, **1**, and **3** (Table 1, entry 2), respectively, indicating that the central metals of the complexes have little influence on the catalytic activity of the complexes on the guanylation reaction of aniline. Therefore, complex **2** was selected as the catalyst for the examination of the following guanylation of aromatic amines and complex **1** as the catalyst for the guanylation of secondary amines (Scheme 2).

To examine the scope of the guanylation reaction catalyzed by the complexes (EBI)LnN(TMS)$_2$, a variety of aromatic amines and secondary amines were evaluated. The results are given in Table 1. From this table, we can see that catalyst **2** is compatible with a wide range of substituents on the phenyl ring, regardless of the electronic nature or the steric effects of the substituents on the aryl groups. When the substituents on the phenyl ring are electron-donating groups such as CH_3O-, CH_3-, and *i*-Pr, excellent yields (>90%) of the compounds **6**−**15** (Table 1, entries 3−12) were obtained at room temperature. When the substituents on the phenyl ring are electron-withdrawing ones such as Cl−, Br−, and O_2N-, good yields of the compounds **16**−**19** can be isolated from the reactions of 4-chloroaniline and 4-bromoaniline with carbodiimides at room temperature (Table 1, entries 13−16), while the reactions of 3-nitroaniline with carbodiimides required 36 h at 110 °C with moderate isolated yields of compound **20** (80% and 82%) (Table 1, entry 17). No products can be isolated from the reactions of 2-nitroaniline and 4-nitroaniline with carbodiimides, even using catalysts **1**−**3** over 36 h at 110 °C (Table 1, entries 18−21), indicating that electronic effects have a great influence on the catalytic reaction. It is also found that steric effects have a great influence on the catalytic reaction: for example, the reactions of 4-isopropylaniline with carbodiimides produced almost quantitative amounts of products in 12 h at room temperature (Table 1, entries 7 and 8), while the interactions of 2,6-diisopropylaniline with carbodiimides gave only 81% and 85% yields over 24 h at 110 °C (Table 1, entries 26 and 27). The fact that the reactions of α-naphthylamine with carbodiimides (Table 1, entries 24 and 25) required temperatures higher than those of reactions of aniline with carbodiimides (Table 1, entries 1 and 2) may be due to the combined steric and electronic effects. The requirement of high temperature for reactions of 1,4-phenylenediamine with carbodiimides may be due to the bis-guanylation processes, while the products obtained were mixtures of the biguanidines and the monoguanidines from the same reactions at room temperature.

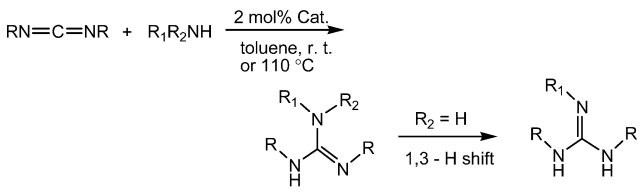
Examination of the reactivity of secondary amines with carbodiimides catalyzed by catalyst **1** gave satisfactory results (Table 1, entries 28−35); the amines can be other chain or cyclic

Table 1. Catalytic Addition of the Amines to Carbodiimides

entry	Cata.	R	Amine	*T*p (°C) / time (h)	Product	Yield (%)[a]
1	**2**	^{i}Pr		r.t. / 12	4	93
2	**2**	Cy		r.t. / 12	5	95 (95)[b] (92)[c]
3	**2**	^{i}Pr		r.t. / 12	6	93
4	**2**	Cy		r.t. / 12	7	95
5	**2**	^{i}Pr		r.t. / 12	8	92
6	**2**	Cy		r.t. / 12	9	94
7	**2**	^{i}Pr		r.t. / 12	10	95
8	**2**	Cy		r.t. / 12	11	96
9	**2**	^{i}Pr		r.t. / 12	12	96 (92)[c]
10	**2**	Cy		r.t. / 12	13	95
11	**2**	^{i}Pr		r.t. / 12	14	92
12	**2**	Cy		r.t. / 12	15	91
13	**2**	^{i}Pr		r.t. / 12	16	93
14	**2**	Cy		r.t. / 12	17	92
15	**2**	^{i}Pr		r.t. / 12	18	92 (88)[c]
16	**2**	Cy		r.t. / 12	19	93 (95)[b]
17	**2**	Cy		110 / 36	20	80 (82)[b]
18	**2**	^{i}Pr		110 / 36		No reaction[a, b, c]
19	**2**	Cy		110 / 36		No reaction[a, b, c]
20	**2**	^{i}Pr		110 / 36		No reaction[a, b, c]
21	**2**	Cy		110 / 36		No reaction[a, b, c]
22	**2**	^{i}Pr		110 / 12	21	91[d]
23	**2**	Cy		110 / 12	22	92[d]
24	**2**	^{i}Pr		110 / 12	23	95
25	**2**	Cy		110 / 12	24	97
26	**2**	^{i}Pr		110 / 24	25	81 (84)[b]
27	**2**	Cy		110 / 24	26	85
28	**1**	^{i}Pr		110 / 36	27	77 (71)[e]
29	**1**	Cy		110 / 36	28	68
30	**1**	^{i}Pr		110 / 24	29	88
31	**1**	Cy		110 / 24	30	94
32	**1**	^{i}Pr		110 / 24	31	95
33	**1**	Cy		110 / 24	32	93
34	**1**	^{i}Pr		110 / 24	33	96
35	**1**	Cy		110 / 24	34	91

[a] Isolated yield. T_p = reaction temperature. [b] Isolated yield using catalyst **1**. [c] Isolated yield using catalyst **3**. [d] Two equivalents of RN=C=NR was used, and the products are the bis-guanidines. [e] Isolated yield by running the reaction for 24 h.

Scheme 2



Catalyst = $[\eta^5\text{-}(CH_2)_2(C_9H_6)_2]LnN(SiMe_3)_2$ (Ln = Y (**1**); Sm (**2**); Yb (**3**))

Scheme 3

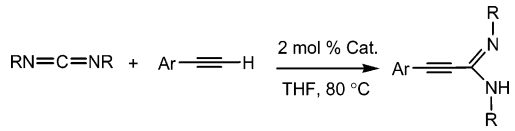


Table 2. Catalytic Addition of Alkynes to Carbodiimides

entry	cat.	R	Ar	T_p (°C)/ time (h)	product	yield (%)[a]
1	**1**	^{i}Pr	Ph	80/3	**35**	92
2	**2**	^{i}Pr	Ph	80/3	**35**	90
3	**3**	^{i}Pr	Ph	80/3	**35**	90
4	**1**	Cy	Ph	80/3	**36**	89
5	**2**	Cy	Ph	80/3	**36**	85
6	**3**	Cy	Ph	80/3	**36**	86
7	**1**	^{i}Pr	4-$MeOC_6H_4$	80/3	**37**	85
8	**1**	Cy	4-$MeOC_6H_4$	80/3	**38**	83
9	**3**	Cy	4-$MeOC_6H_4$	80/3	**38**	81
10	**1**	^{i}Pr	4-FC_6H_4	80/3	**39**	94
11	**1**	^{i}Pr	4-ClC_6H_4	80/3	**40**	95
12	**1**	Cy	4-ClC_6H_4	80/3	**41**	93

[a] Isolated yield. Catalyst: 2 mol %. T_p = reaction temperature.

species, indicating that the catalyst is compatible for not only the aromatic amines but also the secondary amines. However, the reactions generally required a slightly longer time to be completed.

Catalytic Addition of the Terminal Alkynes to Carbodiimides. The satisfactory results obtained for the construction of C−N bonds encouraged an effort to expand the scope of this catalytic process into the realm of C−C coupling. The addition of terminal alkynes to carbodiimides could, in principle, provide a straightforward route to propiolamidines. In fact, synthetic routes to propiolamidines remain scarce, and the only clearly documented precedents for this reaction are the recent reports that half-sandwich rare-earth-metal complexes bearing silylene-linked cyclopentadienyl−amido ligands[9] and $LiN(SiMe_3)_2$ act as catalysts.[6] Initial screens were conducted at 80 °C for the reactions of diisopropylcarbodiimide and phenylacetylene with 2 mol % (EBI)$LnN(TMS)_2$ (Ln = Y (**1**), Sm (**2**), Yb (**3**)) loading (Scheme 3). The propiolamidine **35** was obtained over 3 h in 92%, 90%, and 90% yields using the catalysts **1**−**3** (Table 2, entries 1−3), respectively, indicating that the central metal of the complexes has little influence on the catalytic activities of the addition of terminal alkynes to carbodiimides. ^{1}H NMR analyses of the C−H addition products gave no information about the microstructure of the compounds, probably due to the fast 1,3-hydrogen shift in solution. The solid-state structure of **35** revealed that the isopropyl and isopropylamino groups were trans to the C=N double bond in the final addition product (Figure 3), which is identical with the propiolamidines in the literature.[9] The yields of the propiolamidine **36** obtained from the similar reactions of dicyclohexylcarbodiimide and phenylacetylene were slightly lower than those in the above reactions under the same conditions, probably due to the steric effects arising from the larger cyclohexyl group in carbodiimide (Table 2, entries 4−6).

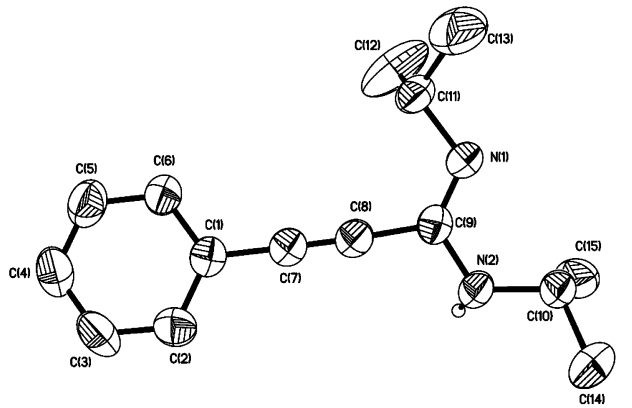


Figure 3. Molecular structure of (*E*)-*N*,*N*′-diisopropyl-3-phenylpropiolamidine (**35**). Selected bond distances (Å) and angles (deg): C(9)−N(1) = 1.266(4), C(9)−N(2) = 1.373(4), C(8)−C(9) = 1.453(4), C(8)−C(7) = 1.189(4); N(1)−C(9)−N(2) = 123.1-(3).

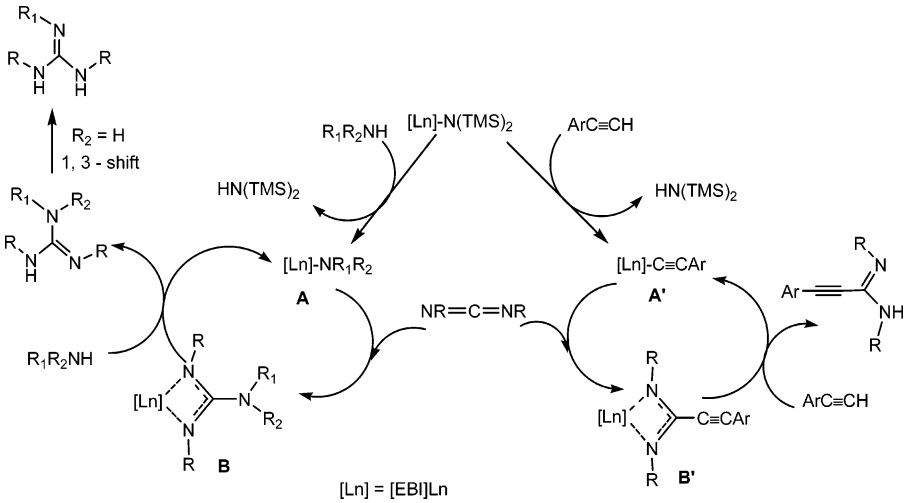
The results of the catalytic additions of other terminal alkynes having an electron-donating group on the phenyl ring, such as 4-ethynylanisole, or terminal alkynes having an electron-withdrawing group on phenyl ring, such as 1-ethynyl-4-fluorobenzene or 1-ethynyl-4-chlorobenzene, to carbodiimides are summarized in Table 2. The results indicated that the reaction can proceed smoothly, producing the corresponding propiolamidines regardless of either electron-withdrawing or electron-donating substituents on the phenyl ring of the aromatic alkyne (Table 2, entries 7−12). However, reactions of alkynes substituted with electron-withdrawing groups, 1-ethynyl-4-fluorobenzene and 1-ethynyl-4-chlorobenzene, with carbodiimides (Table 2, entries 10−12), became somewhat easier than the reaction of the electron-rich substituted alkyne 4-ethynylanisole with carbodiimides (Table 2, entries 7−9), probably owing to the stronger acidity of the former, which may favor the alkyne−amido exchange process in the catalytic initiation step. These results indicated that the catalytic activity of the lanthanocene amides on the addition of alkynes to carbodiimides can be compared with those of half-sandwich yttrium alkyl complexes[9] and the lithium amide $LiN(TMS)_2$.[6]

Proposed Mechanism for the Addition of Amines and Terminal Alkynes to Carbodiimides. The reaction mechanism is proposed as follows (Scheme 4): interaction of the amines or the terminal alkynes with lanthanocene amides gave the new amido intermediate **A** (or **A**′) through an acid−base exchange reaction,[10] and then the intermediate **A** (or **A**′) reacted with carbodiimide, producing a metal guanidinate or amidinate species **B** (or **B**′) through an insertion reaction.[17] Transfer of a proton then releases the product (as shown in Figure 3) with concomitant regeneration of the catalytic active species. A 1,3-H shift produced the final guanylation products when the amines were the aromatic species. This process can be verified by the crystal structure of the final product of **25** (Figure 4), which showed a double-bond character for the N(1)−C(1) bond with a distance of 1.294(2) Å.

Ring-Opening Polymerization of ε-Caprolactone. In order to further reveal the catalytic activity of the [ethylenebis-(indenyl)]lanthanide(III) amido complexes, the ring-opening polymerization of ε-caprolactone using complexes **1** and **2** as catalysts was studied (Table 3). From this table, we can see

(17) (a) Zhang, J.; Cai, R.; Weng, L.; Zhou, X. *Organometallics* **2004**, *23*, 3303−3308. (b) Zhang, J.; Cai, R.; Weng, L.; Zhou, X. *J. Organomet. Chem.* **2003**, *672*, 94−99.

Scheme 4. Proposed Mechanism for the Catalytic Addition of N−H and C−H Bonds to Carbodiimides



that complexes **1** and **2** showed high catalytic activities in toluene, THF, and DME. It was found that the molecular weights of the polymers obtained in toluene and THF were higher than those obtained in DME at the same temperature, probably due to the coordination of the two oxygen atoms of DME, which may disfavor the propagation process. In particular, the molecular weights (M_n) of the polymers obtained with complex **1** as catalyst in THF and toluene at −30 °C reach values of 4.0×10^5 and 5.2×10^5, respectively, indicating the central metal and solvent effects on the chain propagation process. The polydispersities of the polymers in the range of 1.3−2.0 can be compared with the those of polymers obtained by the hindered lanthanide allyl complexes $[Li(OEt_2)(THF)_3][Ln\{3\text{-}(\eta^3\text{-}C_3H_3\text{-}SiMe_3\text{-}1)_2SiMe_2\}_2]$.[18]

Studies of the effects of temperature on the catalytic activities of the complexes **1** and **2** indicated that these activities obviously decrease as the polymerization temperature goes below 0 °C (Table 3). These results are different from those for the catalytic activity of organolanthanide(II) complexes with furfuryl- and tetrahydrofurfuryl-functionalized indenyl ligands, which showed high catalytic activities in a broad temperature range of +30 to −60 °C.[19] The fact that the molecular weights of the polymers obtained by catalysts **1** and **2** generally increase as the polymerization temperatures decrease is probably due to trace amounts of impurities included in the system, which were more active at elevated temperatures, thus terminating the propagation process.[20]

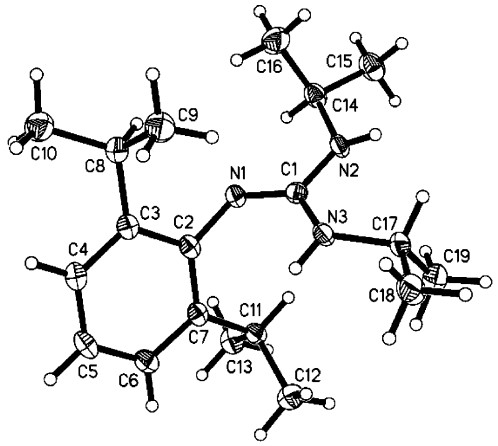


Figure 4. Molecular structure of *N*-2,6-diisopropylphenyl-*N*′,*N*″-diisopropylguanidine (**25**). Selected bond distances (Å) and angles (deg): N(1)−C(1) = 1.294, N(1)−C(2) = 1.413(2), N(2)−C(1) = 1.373(2), N(3)−C(1) = 1.374(2); C(1)−N(1)−C(2) = 120.70(15), N(1)−C(1)−N(2) = 119.11(17), N(1)−C(1)−N(3) = 125.08(17), N(2)−C(1)−N(3) = 115.81(17).

Table 3. Data for the Polymerizations of ε-Caprolactone (ε-CL)

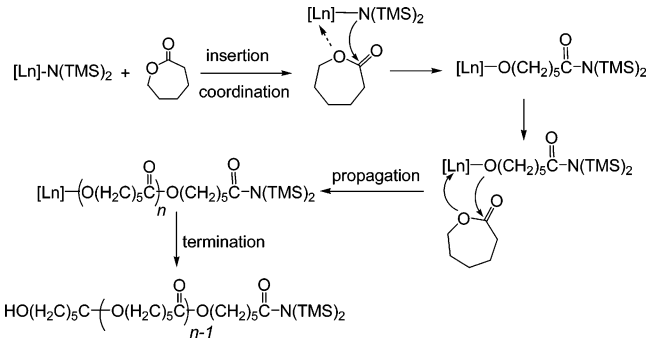
solvent	T_p (°C)	time (min)	$10^{-4}M_n$	$10^{-4}M_w$	M_w/M_n	conversn (%)	$10^{-6}\times$ activity
			Catalyst **1**				
toluene	60	1	2.05	3.78	1.9	92	3.14
	30	1	2.22	3.70	1.7	93	3.15
	0	5	3.23	5.87	1.8	87	0.60
	−30	30	40.06	64.31	1.6	46	0.054
THF	60	1	2.58	3.98	1.5	99	3.40
	30	1	4.59	6.70	1.5	95	3.24
	0	5	5.08	9.90	2.0	78	0.54
	−30	30	52.36	78.71	1.5	51	0.057
DME	60	1	1.88	3.15	1.7	92	3.10
	30	1	1.77	2.30	1.3	85	2.92
	0	5	2.14	3.47	1.6	64	0.16
	−30	30				39	0.044
			Catalyst **2**				
toluene	30	1	1.63	2.98	1.8	99	3.04
	0	1	4.51	7.21	1.6	72	2.21
	−15	5	4.59	7.59	1.7	58	0.36
	−30	20	5.80	9.19	1.6	25	0.039
THF	30	1	2.17	2.88	1.3	96	2.78
	0	1	1.78	2.60	1.5	75	2.32
	−15	5	1.87	2.73	1.5	79	0.49
	−30	20	3.98	7.16	1.8	19	0.029
DME	30	1	1.26	1.57	1.3	88	2.72
	0	15	1.43	1.90	1.3	65	0.13
	−15	20	2.05	3.36	1.6	55	0.093
	−30	20	3.04	4.99	1.6	26	0.041

Condition: Solvent/ε-CL (V/V) = 3:1; Cat./ε-CL (mol/mol) = 1:500; Activity: g Polymer·mol^{-1}(cat)·h^{-1}; *T*p: Polymerization temperature.

^{1}H NMR analyses of the polymers obtained from different catalytic systems indicated that there is a silyl group connected to the polymers, suggesting that the silylamido group of the catalysts migrated to the polymer ends. Thus, the ε-CL polymerization mechanism is proposed as being a coordination−insertion process (Scheme 5).[21]

(18) Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2004**, *23*, 2972−2979.
(19) Wu, Y.; Wang, S.; Qian, C.; Sheng, E.; Xie, M; Sheng, G.; Feng, Q.; Zhang, L.; Tang, X. *J. Organomet. Chem.* **2005**, *690*, 4139−4149.
(20) Knjazhanski, S. Y.; Elizalde, L.; Cadenas, G.; Bulychev, B. M. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1599−1606.
(21) Deng, X.; Yuan, M.; Xiong, C.; Li, X. *J. Appl. Polym. Sci.* **1999**, *73*, 1401−1408.

Scheme 5. Proposed Mechanism for ε-Caprolactone Polymerization



Conclusion

In summary, the [ethylenebis(indenyl)]lanthanide(III) amido complexes (EBI)LnN(TMS)$_2$ (Ln = Y, Sm, Yb) can be synthesized by the simple silylamine elimination reaction of ethylenebis(indenyl) with the lanthanide amides [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$. These lanthanocene amides exhibited versatile catalytic activities with high efficiency toward the addition of N−H and C−H bonds to carbodiimides and ring-opening polymerization of ε-caprolactone. The results indicated that the catalysts were compatible for a wide range of substrates, regardless of the electronic nature of the substituents. The results also suggested that the lanthanocene amides exhibit potential applications as catalysts in the synthesis of functionalized guanidines and propiolamidines. To the best of our knowledge, this is the first report of the application of readily accessible lanthanocene amides to these reactions. Extensive studies are now in progress in our laboratory.

Experimental Section

General Remarks. All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and an oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over either finely divided $LiAlH_4$ or sodium benzophenone ketyl under argon prior to use, unless otherwise noted. THF-d_8 was distilled under argon from Na/K alloy. All amines and alkynes were predried, sublimed, recrystallized, or distilled before use. *N*,*N*′-Dicyclohexylcarbodiimide and *N*,*N*′-diisopropylcarbodiimide were used without further purification. ε-Caprolactone (ε-CL) was dried over finely divided CaH_2 and distilled before use. $C_9H_7CH_2CH_2C_9H_7$,[22] [η^5-$(CH_2)_2(C_9H_6)_2$]YbN(TMS)$_2$,[23] and [(Me$_3$Si)$_2$N]$_3$Ln^{III}(μ-Cl)Li(THF)$_3$ (Ln = Y, Sm,[24] Yb[23]) were prepared according to the literature methods. Elemental analysis data were obtained on a Perkin-Elmer 2400 Series II elemental analyzer. IR spectra were recorded on a Perkin-Elmer 983(G) spectrometer (CsI crystal plate, Nujol mulls). ^{1}H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer in THF-d_8 for the lanthanide complexes and in $CDCl_3$ for the organic compounds. Gel permeation chromatography (GPC) analyses of the polymer samples were carried at 30 °C using THF as an eluent on a Waters-2414 instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 mL min^{-1}.

Synthesis of [η^5-$(CH_2)_2(C_9H_6)_2$]YN(TMS)$_2$ (1). To a toluene (20.0 mL) solution of $C_9H_7CH_2CH_2C_9H_7$ (0.387 g, 1.50 mmol) was added a toluene (50.0 mL) solution of [(Me$_3$Si)$_2$N]$_3$Y(μ-Cl)Li(THF)$_3$ (1.243 g, 1.50 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, it was then refluxed for 12 h. The solvent was evaporated under reduced pressure. The resulting solid was extracted with *n*-hexane (2 × 15.0 mL). The extracts were combined and concentrated to about 15.0 mL. Pale yellow crystals were obtained by cooling the concentrated solution to 0 °C for several days (0.636 g, 84% yield). Mp: 150−152 °C. ^{1}H NMR (THF-d_8): δ 7.07−6.69 (m, 8H), 6.34 (d, J = 3.3 Hz, 2H), 6.15 (d, J = 3.0 Hz, 2H), 3.87−3.37 (m, 4H). ^{13}C NMR (C_6D_6): δ 145.8, 144.8, 144.6, 126.5, 125.2, 125.0, 124.5, 124.1, 123.9, 122.2, 121.8, 120.7, 120.4, 119.3, 118.9, 117.1, 100.4, 100.0, 37.9, 27.8, 26.7, 4.6, 3.5, 2.6, 1.8, 1.4. IR (Nujol mull, cm^{-1}): ν 3064 (m), 3016 (m), 2962 (m), 2895 (m), 1606 (m), 1462 (m), 1396 (m), 1261 (m), 1091 (m), 1016 (w), 966 (m), 800 (m), 767 (s), 736 (m), 713 (w). Anal. Calcd for $C_{26}H_{34}NSi_2Y$: C, 61.76; H, 6.78; N, 2.77. Found: C, 61.41; H, 6.64; N, 2.62.

Synthesis of [η^5-$(CH_2)_2(C_9H_6)_2$]SmN(TMS)$_2$ (2). This compound was prepared as orange crystals in 81% yield from the reaction of $C_9H_7CH_2CH_2C_9H_7$ (0.309 g, 1.20 mmol) with a toluene (50.0 mL) solution of [(Me$_3$Si)$_2$N]$_3$Sm(μ-Cl)Li(THF)$_3$ (1.068 g, 1.20 mmol) by employing procedures similar to those used for the preparation of **1**. Mp: 160−161 °C. IR (Nujol mull, cm^{-1}): ν 2923 (s), 2855 (s), 2334 (w), 2293 (w), 1691 (w), 1460 (m), 1377 (m), 1246 (w), 1160 (m), 1015 (w), 967 (m), 767 (m), 617 (w), 412 (w), 335 (w), 206 (w). Anal. Calcd for $C_{26}H_{34}NSi_2Sm$: C, 55.07; H, 6.04; N, 2.47. Found: C, 55.36; H, 5.75; N, 2.27.

X-ray Crystallography. Suitable crystals of complexes **1**, **2**, **25**, and **35** were mounted in sealed capillaries. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å); the temperature was 113(2) K for compounds **1** and **25** and 293(2) K for compounds **2** and **35**. φ and ω scan techniques were used; SADABS effects and empirical absorption were applied in the data corrections. All structures were solved by direct methods (SHELXTL-97),[25] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares calculations based on F^2 (SHELXTL-97).[25] See Table 4 for crystallographic data.

General Procedure for the Direct Synthesis of Guanidines from the Reaction of Aromatic Amines with Carbodiimides Catalyzed by (EBI)LnN(TMS)$_2$. A 30.0 mL Schlenk tube under dried argon was charged with the lanthanocene amides (EBI)LnN(TMS)$_2$ (Ln = Y, Sm, Yb) (0.02 equiv), aromatic amines (1.0 equiv), and toluene (5 mL). To the mixture was added carbodiimides (1.0 equiv). The resulting mixture was stirred at room temperature or was heated to 110 °C for a fixed interval, as shown in Table 1. After the reaction was completed, the reaction mixture was hydrolyzed by water (3 mL), extracted with dichloromethane (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under reduced pressure, the final products were further purified by washing with diethyl ether or hexane.

General Procedure for the Direct Synthesis of Guanidines from the Reaction of Secondary Amines with Carbodiimides Catalyzed by (EBI)YN(TMS)$_2$. A 30.0 mL Schlenk tube under dried argon was charged with the lanthanocene amides (EBI)YN(TMS)$_2$ (0.02 equiv), secondary amines (1.0 equiv), and toluene (5 mL). To this mixture was added carbodiimides (1.0 equiv). The flask was then closed to prevent evaporation of amines with low boiling points, and the resulting mixture was stirred at room temperature or was heated to 110 °C for the desired time, as shown in Table 1. After the solvent was removed under reduced pressure, the residue was extracted with hexane (3 × 15 mL) and filtered to give a clean solution. After the solvent was removed under vacuum, the final products were obtained.

(22) Robert, B. G.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501−1505.
(23) Sheng, E.; Wang, S.; Yang, G.; Zhou, S.; Cheng, L.; Zhang, K.; Huang, Z. *Organometallics* **2003**, *22*, 684−692.
(24) Zhou, S.; Wang, S.; Yang, G.; Liu, X.; Sheng, E.; Zhang, K.; Cheng, L.; Huang, Z. *Polyhedron* **2003**, *22*, 1019−1024.
(25) Sheldrick, G. M. SHELXTL, version 5.10; Bruker Analytical X-ray Systems, Madison, WI, 1997.

Table 4. X-ray Experimental Data for Complexes 1 and 2, 35, and 25

	1	2	35	25
empirical formula	$C_{26}H_{34}NSi_2Y$	$C_{26}H_{34}NSi_2Sm$	$C_{15}H_{20}N_2$	$C_{19}H_{33}N_3$
formula wt	505.63	567.07	228.33	303.48
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$Pca2_1$	$P2_1/n$
a (Å)	10.548(6)	9.618(3)	8.5537(11)	8.8510(11)
b (Å)	21.289(11)	17.742(7)	16.863(2)	14.2184(18)
c (Å)	23.140(12)	30.754(10)	10.0178(13)	14.9359(17)
β (deg)	91.923(8)	91.96(3)	90	95.772(5)
V (Å^3)	5193(5)	5245(3)	1445.0(3)	1870.1(4)
T (K)	113(2)	293(2)	293(2)	113(2)
D_{calcd} (g cm^{-3})	1.293	1.436	1.050	1.078
Z	8	8	4	4
F(000)	2112	2296	496	672
no. of rflns collected	41 851	10 831	9838	13 705
no. of unique rflns	10 170 ($R_{int} = 0.1088$)	10 205 ($R_{int} = 0.0317$)	2354 ($R_{int} = 0.0366$)	3290 ($R_{int} = 0.0588$)
no. of params	623	541	155	216
λ(Mo Kα) (Å)	0.710 70	0.710 73	0.710 73	0.710 73
μ (mm^{-1})	2.351	2.343	0.062	0.064
θ range (deg)	1.30−26.00	1.75−25.97	2.42−25.00	1.98−25.00
goodness of fit	1.071	1.055	1.005	1.122
R1 ($I > 2\sigma(I)$)	0.0655	0.0597	0.0477	0.059
wR2	0.134	0.120	0.127	0.132
largest diff peak, hole (e Å^{-3})	0.801, −0.878	1.599, −0.848	0.218, −0.202	0.402, −0.256

Typical Procedures for the Catalytic Addition of Terminal Alkynes to Carbodiimides. A 30.0 mL Schlenk tube under dried argon was charged with the lanthanocene amides (EBI)LnN(TMS)$_2$ (Ln = Y, Sm, Yb) (0.02 equiv), alkynes (1.0 equiv), and THF (5 mL). To this mixture was added carbodiimides (1.0 equiv). The Schlenk tube was taken outside, and the mixture was stirred at 80 °C for 3 h. After the solvent was removed under reduced pressure, the residue was extracted with hexane and filtered to give a clean solution. The solvent was evaporated under vacuum; recrystallization of the crude solid from *n*-hexane afforded the products.

ε-Caprolactone Polymerization. ε-CL polymerization reactions were performed in a 50.0 mL Schlenk flask, placed in an external temperature-controlled bath, on a Schlenk line. In a typical procedure, the catalyst (20−50 mg) was loaded into the Schlenk flask and the solvent was added. ε-CL was added through a gastight syringe after the external bath temperature was stabilized. The polymeric product was precipitated into hydrochloric acid (0.1 M, 50.0 mL), washed with 0.1 M hydrochloric acid, and then dried to a constant weight in a vacuum oven at 50 °C. The molecular weights of the polymers were analyzed by GPC techniques.

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Supporting Information Available: Text and figures giving experimental details and characterization data for the reaction products and CIF files giving crystal data for complexes **1**, **2**, **25**, and **35**. This material is available free of charge via the Internet at http://pubs.acs.org.

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