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Synthesis of Guanidines from Amines and Carbodiimides Catalyzed by Mono-Indenyl-Ligated Rare Earth Metal Bis(silylamide) Complexes

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Nucleophilic addition of primary aromatic amines to carbodiimides in the presence of catalytic amount of the mono-indenyl-ligated rare earth metal bis(silylamide) complexes $(C_9H_6CMe_2CH_2C_5H_4N\text{-}\alpha)Ln[N(SiHMe_2)_2]_2$ at room temperature afforded efficiently a series of guanidines with a wide spectrum of substituents on the nitrogen atoms.

Keywords rare earth, amide complex, amine, carbodiimide, guanylation, catalysis

Introduction

Guanidines are important heteroatom-containing organic compounds which can serve as structural motifs for biological and pharmaceutical compounds, and as ancillary ligands in the coordination and organometallic chemistry.[1] Addition of amine N—H bonds to carbodiimides (R-N=C=N-R) provides a straightforward and atom-economical strategy to guanidines. However, without a catalyst such reaction requires harsh conditions.[2] Recently, imide complexes of titanium and vanadium,[3] amide complexes of main metals, rare earth metals and titanium,[4] alkyl complexes of half-sandwich rare earth metal alkyl complexes,[5] and commercially available metal alkyl complexes such as $ZnEt_2$,[6] *n*-BuLi,[6] AlR_3,[7] and $Zn(OTf)_2$[8] were found to be efficient catalysts for the addition of amines to carbodiimides to afford multi-substituted guanidines. Nevertheless, rare earth metal bis(amide) complexes as catalysts for the guanylation reaction of amines and carbodiimides remains unexplored to our knowledge.

During our investigation on the structure-reactivity relationship of rare earth metal complexes, we became interested in exploiting rare earth metal bis(amide) complexes as appropriately active catalyst precursors.[9] It was found that the half-sandwich rare earth metal bis(silylamide) complexes bearing the pyridylfunctionalized indenyl ligand $(C_9H_6CMe_2CH_2C_5H_4N\text{-}\alpha)Ln[N(SiHMe_2)_2]_2$ (Ln=Sc (**1**), Y (**2**), La (**3**), Sm (**4**), Nd (**5**), Er (**6**), Lu (**7**)) were highly active catalysts in the guanylation of primary amines and carbodiimides. Here we wish to report these results.

Experimental

Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and an argon-filled glovebox. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips in the glovebox. All carbodiimides and amines were pretreated before use. $CDCl_3$ and C_6D_6 were obtained from CIL. $(C_9H_6CMe_2CH_2C_5H_4N\text{-}\alpha)Ln[N(SiHMe_2)_2]_2$ (Ln= Sc (**1**), Y (**2**), La (**3**), Sm (**4**), Nd (**5**), Er (**6**), Lu (**7**))[9b] were prepared according to the literature.

NMR (^1H, ^{13}C) spectra were recorded on a Bruker AVANCE III spectrometer at 25 ℃. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument, quoted data are the average of at least two independent determinations. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer.

General procedures for synthesis of guanidines by reaction of aromatic amines with carbodiimides

The procedures for catalytic reactions promoted by these rare earth metal complexes were similar, and a typical procedure is given below. A 50 mL Schlenk tube was charged with **2** (10 mg, 0.005 mmol), *N*,*N*′-diisopropylcarbodiimide (0.42 g, 1 mmol), and aniline (0.31 g, 1 mmol), and 1 mL toluene in the glovebox. The resulting mixture was stirred at 20 ℃ for 30 min. Then the tube was taken out from the glovebox. The reaction

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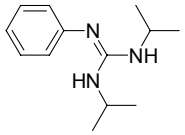
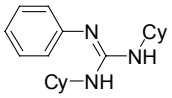
mixture was hydrolyzed by water (3.0 mL), extracted with CH_2Cl_2 (15 mL×3), dried over anhydrous Na_2SO_4, and filtered. The filtrate was dried, and the residue was purified by recrystallization from a mixture solution of ether and hexane to afford a white solid.

***N*-Phenyl-*N′*,*N″*-diisopropylguanidine**



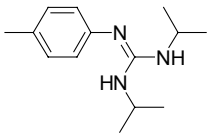
Known compound.[4d] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.16 (d, J=6.4 Hz, 12H, CHMe_2), 3.56 (br s, 2H, NH), 3.74—3.79 (m, 2H, CHMe$_2$), 6.85 (d, J=7.2 Hz, 2H, Ph-H), 6.92 (t, J=7.2 Hz, 1H, Ph-H), 7.24 (t, J=7.6 Hz, 2H, Ph-H).

***N*-Phenyl-*N′*,*N″*-dicyclohexylguanidine**



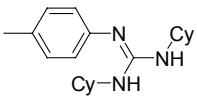
Known compound.[4d] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04—1.21 (m, 6H, Cy-H), 1.29—1.42 (m, 4H, Cy-H), 1.57—1.71 (m, 6H, Cy-H), 2.00 (d, J=9.2 Hz, 4H, Cy-H), 3.41 (br s, 2H, Cy-H), 3.62 (br s, 1H, NH, another NH was not observed), 6.85 (d, J=7.6 Hz, 2H, Ph-H), 6.91 (t, J=7.6 Hz, 1H, Ph-H), 7.23 (t, J=8.0 Hz, 2H, Ph-H).

***N*-*p*-Methylphenyl-*N′*,*N″*-diisopropylguanidine**



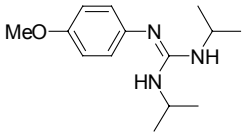
Known compound.[4c] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15 (d, J=6.4 Hz, 12H, NCHMe_2), 2.28 (s, 3H, Ar-CH_3), 3.54 (br s, 1H, NH, another NH was not observed), 3.76 (br s, 2H, NCHMe$_2$), 6.74 (d, J=8.0 Hz, 2H, Ar-H), 7.04 (d, J=8.0 Hz, 2H, Ar-H).

***N*-*p*-Methylphenyl-*N′*,*N″*-dicyclohexylguanidine**



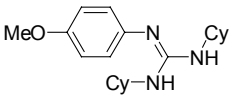
Known compound.[4c] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03—1.19 (m, 6H, Cy-H), 1.29—1.39 (m, 4H, Cy-H), 1.56—1.61 (m, 2H, Cy-H), 1.66—1.71 (m, 4H, Cy-H), 2.27 (s, 3H, Ar-CH_3), 3.40 (br s, 2H, Cy-H), 3.61 (br s, 1H, NH, another NH was not observed), 6.74 (d, J=8.0 Hz, 2H, Ar-H), 7.04 (d, J=8.4 Hz, 2H, Ar-H).

***N*-*p*-Methoxyphenyl-*N′*,*N″*-diisopropylguanidine**



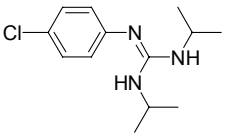
Known compound.[3a] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15 (d, J=6.0 Hz, 12H, NCHMe_2), 3.52 (br s, 1H, NH, another NH was not observed), 3.75 (br s, 2H, NCHMe$_2$), 3.77 (s, 3H, OCH_3), 6.75—6.83 (m, 4H, Ar-H).

***N*-*p*-Methoxyphenyl-*N′*,*N″*-dicyclohexylguanidine**



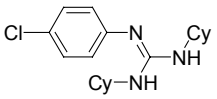
Known compound.[3a] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03—1.20 (m, 6H, Cy-H), 1.30—1.39 (m, 4H, Cy-H), 1.56—1.62 (m, 2H, Cy-H), 1.65—1.71 (m, 4H, Cy-H), 2.00 (d, J=10.4 Hz, 4H, Cy-H), 3.40 (br s, 2H, Cy-H), 3.59 (br s, 1H, NH), 3.77 (s, 3H, OCH_3), 6.75—6.82 (m, 4H, Ar-H).

***N*-*p*-Chlorophenyl-*N′*,*N″*-diisopropylguanidine**



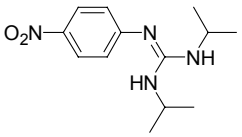
Known compound.[3a] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.16 (d, J=6.4 Hz, 12H, CHMe_2), 3.54 (br s, 2H, NH), 3.75 (sp, 2H, CHMe$_2$), 6.78 (d, J=8.8 Hz, 2H, Ar-H), 7.19 (d, J=8.4 Hz, 2H, Ar-H).

***N*-*p*-Chlorophenyl-*N′*,*N″*-dicyclohexylguanidine**



Known compound.[4c] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03—1.19 (m, 6H, Cy-H), 1.28—1.39 (m, 4H, Cy-H), 1.57—1.62 (m, 2H, Cy-H), 1.66—1.71 (m, 4H, Cy-H), 1.96—2.00 (m, 4H, Cy-H), 3.38 (br s, 2H, Cy-H), 3.60 (br s, 2H, NH), 6.77 (d, J=8.4 Hz, 2H, Ar-H), 7.18 (d, J=8.8 Hz, 2H, Ar-H).

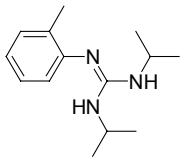
***N*-*p*-Nitrophenyl-*N′*,*N″*-diisopropylguanidine**



Known compound.[4d] This compound was isolated as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (d,

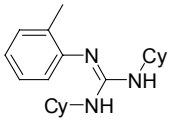
J=6.0 Hz, 12H, CHMe_2), 3.76−3.80 (m, 4H), 6.89−6.91 (m, 2H, Ar-*H*), 8.10−8.13 (m, 2H, Ar-*H*).

N-*o*-Methylphenyl-*N′*,*N″*-diisopropylguanidine



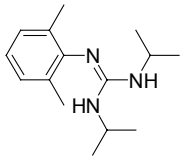
Known compound.[4c] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.16 (d, J=6.4 Hz, 12H, CHMe_2), 2.14 (s, 3H, Ar-CH_3), 3.43 (br s, 1H, N*H*, another N*H* was not observed), 3.76 (br s, 2H, C*H*Me$_2$), 6.76 (d, J=8.0 Hz, 1H, Ar-*H*), 6.87 (dt, J=1.2, 7.2 Hz, 1H, Ar-*H*), 7.09 (t, J=7.6 Hz, 1H, Ar-*H*), 7.14 (d, J=7.6 Hz, 1H, Ar-*H*).

N-*o*-Methylphenyl-*N′*,*N″*-dicyclohexylguanidine



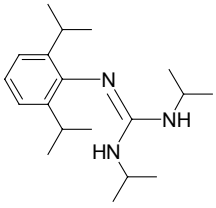
Known compound.[4c] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02−1.18 (m, 6H, Cy-*H*), 1.29−1.39 (m, 4H, Cy-*H*), 1.57−1.62 (m, 2H, Cy-*H*), 1.66−1.70 (m, 4H, Cy-*H*), 2.01 (d, J=10.4 Hz, 4H, Cy-*H*), 2.13 (s, 3H, Ar-CH_3), 3.40 (br s, 2H, Cy-*H*), 3.48 (br s, 1H, N*H*, another N*H* was not observed), 6.76 (d, J=7.6 Hz, 1H, Ar-*H*), 6.86 (t, J=7.6 Hz, 1H, Ar-*H*), 7.08 (t, J=7.6 Hz, 1H, Ar-*H*), 7.13 (d, J=7.2 Hz, 1H, Ar-*H*).

***N*,*N′*-Diisopropyl-*N″*-2,6-dimethylphenylguanidine**



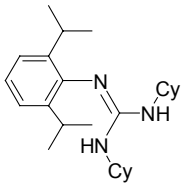
Known compound.[3a] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.16 (br s, 12H, CHMe_2), 2.10 (s, 6H, Ar-CH_3), 3.32 (br s, 2H, C*H*Me$_2$), 3.96 (br s, 2H, N*H*), 6.79 (t, J=7.6 Hz, 1H, Ar-*H*), 6.99 (d, J=7.6 Hz, 2H, Ar-*H*).

***N*,*N″*-Diisopropyl-*N′*-2,6-diisopropylphenylguanidine**



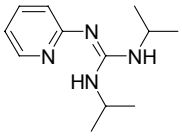
Known compound.[4c] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15 (d, J=7.2 Hz, 12H, ArCHMe_2), 1.15 (br s, 12H, NCHMe_2), 3.09 (sept, 2H, ArC*H*Me$_2$), 3.40 (br s, 2H, NC*H*Me$_2$), 4.19 (br s, 1H, N*H*, another N*H* was not observed), 6.96 (t, J=7.6 Hz, 1H, Ar-*H*), 7.07 (d, J=7.6 Hz, 1H, Ar-*H*).

***N*,*N″*-Dicyclohexyl-*N′*-2,6-diisopropylphenylguanidine**



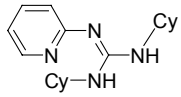
Known compound.[4c] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81−2.35 (m, 20H, Cy-*H*), 1.15 (d, J=6.8 Hz, 12H, CHMe_2), 3.08 (sept, 2H, C*H*Me$_2$), 3.89 (br s, 1H, N*H*, another N*H* was not observed), 6.95 (t, J=7.6 Hz, 1H, Ar-*H*), 7.06 (d, J=7.6 Hz, 2H, Ar-*H*).

1,3-Diisopropyl-2-(pyridin-2-yl)guanidine



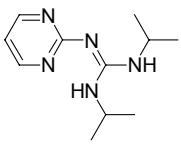
Known compound.[11] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1. 25 (d, J=6.4 Hz, 12H, CHMe_2), 3.93 (br s, 2H, C*H*Me$_2$), 6.61 (t, J=5.6 Hz, 1H, Py-*H*), 6.83 (d, J=8.4 Hz, 1H, Py-*H*), 6.87−7.20 (br s, 1H, N*H*), 7.41 (dt, J=2.2, 7.6 Hz, 1H, Py-*H*), 8.07 (dd, J=1.6, 5.2 Hz, 1H, Py-*H*).

1,3-Dicyclohexyl-2-(pyridin-2-yl)guanidine



Known compound.[12] This compound was isolated as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.24−1.32 (m, 6H, Cy-*H*), 1.35−1.45 (m, 4H, Cy-*H*), 1.58−1.63 (m, 2H, Cy-*H*), 1.71−1.77 (m, 4H, Cy-*H*), 1.98−2.03 (m, 4H, Cy-*H*), 3.61 (br s, 2H, Cy-*H*), 6.60 (t, J=6.4 Hz, 1H, Py-*H*), 6.83 (d, J=8.4 Hz, 1H, Py-*H*), 7.41 (dt, J=2.4, 4.0 Hz, 1H, Py-*H*), 8.06 (dd, J=1.6, 5.2 Hz, 1H, Py-*H*).

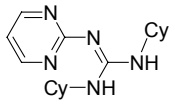
1,3-Diisopropyl-2-(pyrimidin-2-yl)guanidine



New compound. This compound was isolated as a white solid. m.p. 127−128 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.24 (d, J=6.4 Hz, 12H, NCHMe_2), 4.05 (br s, 2H, NC*H*Me$_2$), 6.55 (t, J=4.8 Hz, 1H, Py-*H*), 6.62−7.23 (br s, 1H, N*H*), 8.38 (d, J=4.8 Hz, 2H, Py-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.4 (CHMe_2), 42.6 (*C*HMe$_2$), 111.1 (Py-*C*), 155.2 (N=*C*NH), 157.1 (Py-*C*),

166.4 (Py-*C*). FT-IR (KBr) *v*: 3350 (s), 3170 (s), 2780 (w), 2680 (w), 1650 (s), 1560 (s), 1480 (s), 1360 (m), 1220 (w), 1180 (w), 802 (m) cm^{-1}; GC-MS (EI) *m*/*z*: $C_{11}H_{19}N_5^+$ 221. Anal. calcd for $C_{11}H_{19}N_5$: C 59.70, H 8.65, N 31.65; found C 59.64, H 8.61, N 31.75.

1,3-Dicyclohexyl-2-(pyrimidin-2-yl)guanidine



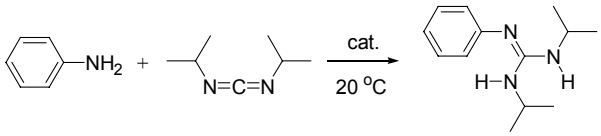
New compound. This compound was isolated as a white solid. m.p. 125－126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.23－1.32 (m, 6H, Cy-*H*), 1.37－1.47 (m, 4H, Cy-*H*), 1.57－1.63 (m, 2H, Cy-*H*), 1.69－1.75 (m, 4H, Cy-*H*), 1.98－2.03 (m, 4H, Cy-*H*), 3.74 (br s, 2H, Cy-*H*), 6.54 (t, *J*=4.4 Hz, 1H, Py-*H*), 8.38 (d, *J*=4.8 Hz, 2H, Py-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.6, 25.7, 33.5, 49.2 (Cy-*C*), 111.0 (Py-*C*), 155.2 (N=*C*NH), 157.1 (Py-*C*), 166.5 (Py-*C*). FT-IR (KBr) *v*: 3330 (s), 3170 (s), 2930 (m), 2850 (m), 2780 (w), 2680 (w), 1650 (s), 1560 (s), 1480 (s), 1360 (m), 1220 (w), 1180 (w), 804 (m) cm^{-1}. Anal. calcd for $C_{17}H_{27}N_5$: C 67.73, H 9.03, N 23.24; found C 67.66, H 8.96, N 23.38.

Results and Discussion

The catalytic reaction of aniline $PhNH_2$ with *N*,*N*′-diisopropylcarbodiimide ^{i}PrN=C=N^{i}Pr was first examined under various conditions. The results were summarized in Table 1. It is noteworthy that, in the absence of $(C_9H_6CMe_2CH_2C_5H_4N\text{-}\alpha)Ln[N(SiHMe_2)_2]_2$ (Ln=Sc (**1**), Y (**2**), La (**3**), Sm (**4**), Nd (**5**), Er (**6**), Lu (**7**)), the reaction of ^{i}PrN=C=N^{i}Pr with aniline did not take place under the present conditions. In contrast, addition of a small amount (0.5 mol%) of **2** at 20 ℃ induced rapidly the nucleophilic addition of aniline to ^{i}PrN=C=N^{i}Pr to afford quantitatively *N*,*N*′,*N*″-trisubstituted guanidine in 30 min (Table 1, run 5). Even when the catalyst loading decreased to 0.2 mol%, the isolated yield still reached upon to 92% using **2** as the catalyst (Table 1, run 6). The other mono-indenyl-ligated rare earth metal bis(silylamide) complexes **1**, **3**－**7** were also effective for this catalytic reaction. The catalytic activity is shown in Figure 1. Obviously, among these rare earth metal catalysts, **2** exhibited the highest activity. In contrast, **1** showed rather poor activity, only 9% isolated yield was obtained at the expense of 0.5 mol% catalyst loading in 30 min (Table 1, run 2). The catalytic activity of **2** was comparable with that by tris(guanidinate) rare earth metal complexes.[10]

Therefore, **2** was chosen as the catalyst for the addition reaction of various primary aromatic amines with carbodiimides. As shown in Table 2, a wide range of substituted anilines could be applied for this reaction. *N*,*N*′-diisopropylcarbodiimide ^{i}PrN=C=N^{i}Pr and *N*,*N*′-dicyclohexylcarbodiimide CyN=C=NCy showed similar activity in these reactions. The catalytic reaction

Table 1 Reaction of aniline with *N*,*N*′-diisopropylcarbodiimide catalyzed by $(C_9H_6CMe_2CH_2C_5H_4N\text{-}\alpha)Ln[N(SiHMe_2)_2]_2$[a]



Run	cat.	Catalyst loading/ mol%	*t*/min	Isolated yield/%
1	**1** (Sc)	2	30	64
2	**1** (Sc)	0.5	30	9
3	**2** (Y)	2	30	99
4	**2** (Y)	1	30	99
5	**2** (Y)	0.5	30	99
6	**2** (Y)	0.2	30	92
7	**3** (La)	0.5	30	62
8	**4** (Sm)	2	30	95
9	**4** (Sm)	0.5	30	35
10	**5** (Nd)	0.5	30	53
11	**6** (Er)	0.5	30	84
12	**7** (Lu)	0.5	30	71

[a] The reaction was performed by treating 1 equiv. of aniline with 1 equiv. of *N*,*N*′-diisopropylcarbodiimide with **1**－**7** as the catalyst.

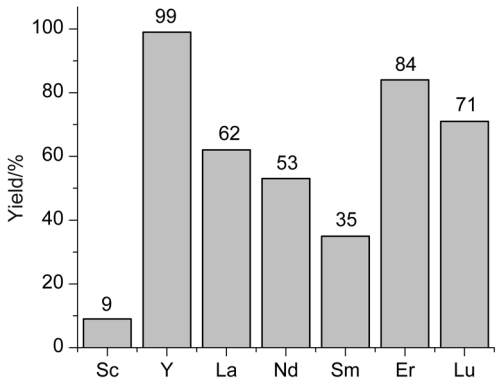
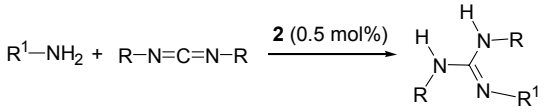
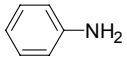
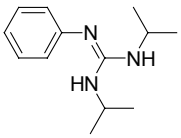
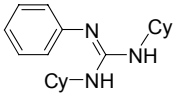
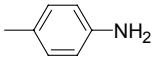
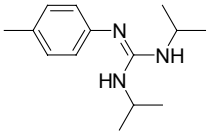
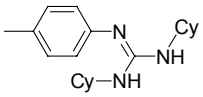
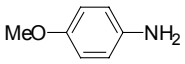
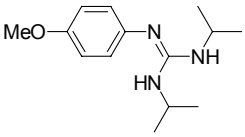
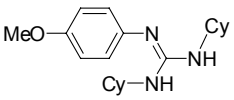
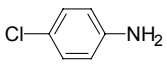
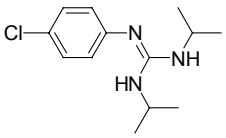
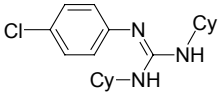
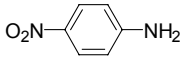
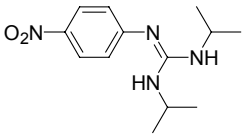
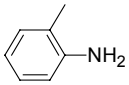
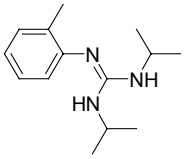
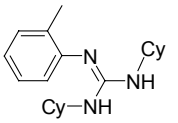


Figure 1 The comparison of catalytic activity using $(C_9H_6CMe_2CH_2C_5H_4N\text{-}\alpha)Ln[N(SiHMe_2)_2]_2$ as catalysts.

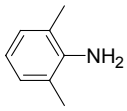
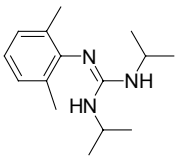
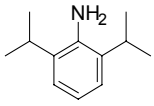
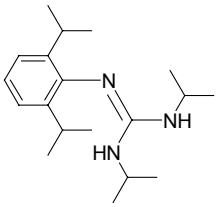
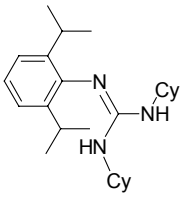
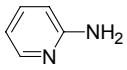
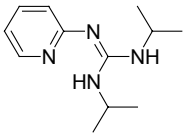
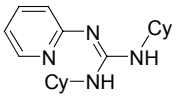
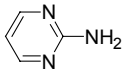
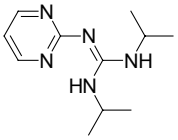
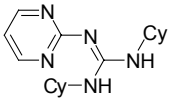
was hardly dependent on the electron-donating substituents at the phenyl ring (Table 2, runs 1－6). However, it was strongly influenced by the electron-withdrawing substituents at the phenyl ring. For example, the reaction of 4-nitrophenylamine with diisopropylcarbodiimide at 20 ℃ for 24 h only gave 26% yield (Table 2, run 9). In comparison, under the same conditions the electron-donating group substituted aromatic amines showed much higher activity than the electron-withdrawing substituted aromatic amines. This finding is somewhat different to the results obtained from tris(guanidinate) rare earth metal complexes, in-which the reaction was not influenced by either electron-withdrawing or electron-donating substituents at

Table 2 Reactions of different aromatic and heterocyclic amines with carbodiimides catalyzed by ($C_9H_6CMe_2CH_2C_5H_4N$-α)Ln-[$N(SiHMe_2)_2$]$_2$ (**2**)[a]



Run	R^1–NH_2	R	*T*/°C	*t*/h	Product	Isolated yield/%
1		^{i}Pr	20	0.5		99
2		Cy	20	0.5		98
3		^{i}Pr	20	0.5		99
4		Cy	20	0.5		99
5		^{i}Pr	20	1		95
6		Cy	20	1		96
7		^{i}Pr	20	1		95
8		Cy	20	1		95
9		^{i}Pr	20	24		26
10		^{i}Pr	20	4		93
11		Cy	20	7		91

Continued

Run	R^1-NH_2	R	*T*/℃	*t*/h	Product	Isolated yield/%
12		^{i}Pr	20	18		91
13		^{i}Pr	20 (80)	24		43 (91)
14		Cy	20 (80)	24		32 (90)
15		^{i}Pr	20	3		95
16		Cy	20	3		92
17		^{i}Pr	20	0.5		95
18		Cy	20	0.5		97

[a] The reaction was performed by treating 1 equiv. of aromatic or heterocyclic amines with 1 equiv. of carbodiimides with 0.05 equiv. (10 mg) of **2** as the catalyst in toluene (1 mL).

the phenyl ring.[10] Meanwhile, the position and bulky of the substituents at the phenyl ring also dramatically affect the reactivity. In the case of 2,6-diisopropylphenyl amine, the reaction with carbodiimides required a higher temperature (80 ℃) and longer reaction time (24 h) for *ca.* 90% isolated yield, probably due to the steric hindrance of isopropyl group (Table 2, runs 13 and 14). Remarkably, aromatic C—Cl bond survived in the present reaction (Table 2, runs 7 and 8), and heterocyclic primary amines such as 2-pyridinyl amine and 2-pyrimidinyl amine could also be used for this reaction.

A proposed mechanism for the present catalytic reaction is illustrated in Scheme 1. Amide exchange of the rare earth metal amide complex with an amine yielded straightforwardly an aromatic amide species (**i**). Nucleophilic addition of the amide species (**i**) to a carbodiimide gave the mixed-ligated rare earth metal guanidinate species (**ii**). Protonation of **ii** by another molecule of amine regenerated the rare earth metal amide complex (**i**) with the release of the guanidine (**iii**). Rearrangement of **iii** through 1,3-hydrogen shift afforded the more stable guanidine isomer.

Conclusions

In summary, nucleophilic addition of primary aromatic amines to carbodiimides took place efficiently in the presence of catalytic amount of the mono-indenyl-ligated rare earth metal bis(silylamide) complexes, and afforded a series of guanidines with a wide spectrum of

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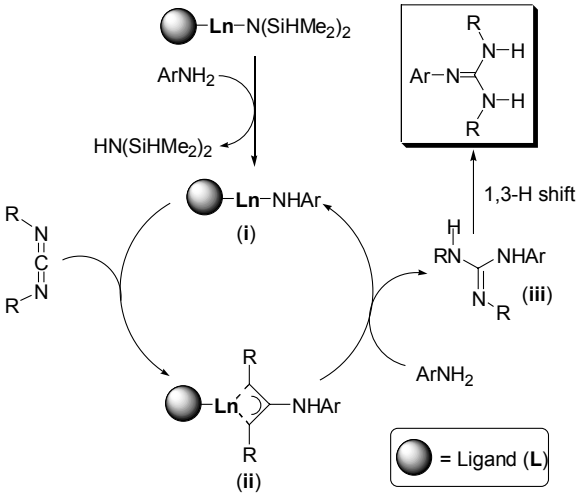
Scheme 1 Proposed mechanism for the guanylation reaction of amines and carbodiimides



substituents on the nitrogen atoms. Among these rare earth metal bis(amide) complexes, the yttrium species showed the highest activity. The catalytic activity was influenced by the electronic effect, the steric effect and the position of the substituents at the phenyl ring.

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(Cheng, F.)

