DOI: 10.1002/chem.200601383

Catalytic Addition of Amine N–H Bonds to Carbodiimides by Half-Sandwich Rare-Earth Metal Complexes: Efficient Synthesis of Substituted Guanidines through Amine Protonolysis of Rare-Earth Metal Guanidinates

Wen-Xiong Zhang, Masayoshi Nishiura, and Zhaomin Hou*[a]

Abstract: Reaction of $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Y, Yb, and Lu) with one equivalent of $Me_2Si(C_5Me_4H)NHR'$ (R′ = Ph, 2,4,6-$Me_3C_6H_2$, *t*Bu) affords straightforwardly the corresponding half-sandwich rare-earth metal alkyl complexes $[\{Me_2Si(C_5Me_4)(NR')\}Ln(CH_2SiMe_3)(thf)_n]$ (**1**: Ln = Y, R′ = Ph, *n* = 2; **2**: Ln = Y, R′ = $C_6H_2Me_3$-2,4,6, *n* = 1; **3**: Ln = Y, R′ = *t*Bu, *n* = 1; **4**: Ln = Yb, R′ = Ph, *n* = 2; **5**: Ln = Lu, R′ = Ph, *n* = 2) in high yields. These complexes, especially the yttrium complexes **1**–**3**, serve as excellent catalyst precursors for the catalytic addition of various primary and secondary amines to carbodiimides, efficiently yielding a series of guanidine derivatives with a wide range of substituents on the nitrogen atoms. Functional groups such as C≡N, C≡CH, and aromatic C–X (X: F, Cl, Br, I) bonds can survive the catalytic reaction conditions. A primary amino group can be distinguished from a secondary one by the catalyst system, and therefore, the reaction of 1,2,3,4-tetrahydro-5-aminoisoquinoline with *i*PrN=C=N*i*Pr can be achieved stepwise first at the primary amino group to selectively give the monoguanidine **38**, and then at the cyclic secondary amino unit to give the biguanidine **39**. Some key reaction intermediates or true catalyst species, such as the amido complexes $[\{Me_2Si(C_5Me_4)(NPh)\}Y(NEt_2)(thf)_2]$ (**40**) and $[\{Me_2Si(C_5Me_4)(NPh)\}Y(NHC_6H_4Br\text{-}4)(thf)_2]$ (**42**), and the guanidinate complexes $[\{Me_2Si(C_5Me_4)(NPh)\}Y\{iPrNC(NEt_2)(NiPr)\}(thf)]$ (**41**) and $[\{Me_2Si(C_5Me_4)(NPh)\}Y\{iPrN\}C(NC_6H_4Br\text{-}4)(NHiPr)\}(thf)]$ (**44**) have been isolated and structurally characterized. Reactivity studies on these complexes suggest that the present catalytic formation of a guanidine compound proceeds mechanistically through nucleophilic addition of an amido species, formed by acid–base reaction between a rare-earth metal alkyl bond and an amine N–H bond, to a carbodiimide, followed by amine protonolysis of the resultant guanidinate species.

Keywords: amines · carbodiimides · guanidinates · guanidines · homogeneous catalysis · rare-earth metals

Introduction

Multi-substituted guanidines, RN=C(NR′R″)NHR, are an important class of ′CN_3′-core-containing compounds, which can serve as building blocks for many biologically relevant compounds,[1] and also as base catalysts in organic synthesis.[2] Typical methods for the preparation of substituted guanidines employ the reaction of an amine compound with a suitable electrophilic guanylating reagent[3] or functionalization of a pre-existing guanidine core.[4] Although addition of amine N–H bonds to carbodiimides (RN=C=NR) could, in principle, provide a straightforward and atom-economical route to guanidines, such catalytic reactions have been much less extensively explored. Primary aliphatic amines were known to undergo direct guanylation with carbodiimides to yield *N*,*N*′,*N*″-trialkylguanidines under rather forcing conditions.[5a] However, except for some activated carbodiimides,[6] less nucleophilic aromatic amines or secondary amines hardly react with carbodiimides under the same or harsher conditions.[5] Tetrabutylammonium fluoride was reported to promote the nucleophilic addition of some aromatic amines to carbodiimides.[7] Recently, titanium and vanadium imido complexes were reported to catalyze the addition of primary aromatic amines to carbodiimides to afford the corresponding guanidines,[5] but secondary amines could

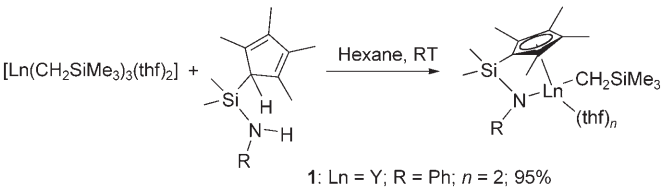
[a] Dr. W.-X. Zhang, Dr. M. Nishiura, Prof. Dr. Z. Hou
Organometallic Chemistry Laboratory
RIKEN (The Institute of Physical and Chemical Research)
Hirosawa 2–1, Wako, Saitama 351–0198 (Japan)
and
PRESTO, Japan Science and Technology Agency (JST) (Japan)
Fax: (+81) 48-462-4665
E-mail: houz@riken.jp

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

not be used in these reactions, because the formation of a "M=N" imido moiety is required for the catalytic process.

On the other hand, nucleophilic addition of metal amido reagents "(R′R″N)M" to carbodiimides to give the corresponding guanidinate species "[RNC(NR′R″)NR]M" is a well-established process.[8–11] The monoanionic guanidinate units are well known as stabilization ligands for various metal complexes, including those of lanthanide and early transition metals, because they can form strong chelating bonds with metal ions.[8–11] Catalytic transformation of a metal guanidinate species is rare and has remained unknown until very recently.[12,13]

We have recently found that half-sandwich rare-earth metal amidinates can be catalytically protonated by terminal alkynes under appropriate conditions, which led to the catalytic addition of terminal alkynes to carbodiimides to give a series of propiolamidine compounds previously unavailable with other means.[14] We report here that catalytic addition of amine N–H bonds to carbodiimides can be achieved analogously by the use of half-sandwich rare-earth metal alkyl complexes as catalyst precursors, yielding a new family of guanidines with various substituents. The corresponding rare-earth metal guanidinate complexes have been confirmed to be true catalyst species in this process. A portion of this work has been communicated previously.[12]



1: Ln = Y; R = Ph; *n* = 2; 95%
2: Ln = Y; R = $C_6H_2Me_3$-2,4,6; *n* = 1; 88%
3: Ln = Y; R = *t*Bu; *n* = 1; 93%
4: Ln = Yb; R = Ph; *n* = 2; 90%
5: Ln = Lu; R = Ph; *n* = 2; 92%

Scheme 1. Synthesis of half-sandwich yttrium, ytterbium, and lutetium alkyl complexes.

Table 1. Selected bond lengths [Å] and angles [°] for **1**, **4**, and **5**.

	1	**4**	**5**
Ln	Y	Yb	Lu
Ln–N	2.327(5)	2.285(4)	2.283(5)
Ln–O	2.382(3)	2.361(2)	2.349(3)
Ln–O*	2.382(3)	2.361(2)	2.349(3)
Ln–C(CH_2TMS)	2.481(6)	2.423(5)	2.423(7)
Ln–Cp(centroid)	2.336(6)	2.310(5)	2.296(7)
Ln–Cp(av)	2.628	2.607	2.595
N-Ln-Cp(centroid)	96.8(2)	97.8(2)	98.3(2)
N-Si-C(Cp)	98.1(3)	97.8(2)	97.9(3)
Si-N-Ln	102.7(2)	102.7(2)	102.6(3)
O-Ln-O*	138.0(2)	137.6(1)	138.0(2)

Results and Discussion

Synthesis of silylene-linked cyclopentadienyl-amido rare-earth metal alkyl complexes: The yttrium alkyl complex bearing the silylene-linked cyclopentadienyl-*tert*-butylamido ligand, [{$Me_2Si(C_5Me_4)(NtBu)$}$Y(CH_2SiMe_3)(thf)$] (**3**), has been reported previously.[15] The analogous cyclopentadienyl-arylamido rare-earth metal complexes [{$Me_2Si(C_5Me_4)(NR)$}$Ln(CH_2SiMe_3)(thf)_n$] (**1**: Ln = Y, R = Ph, *n* = 2; **2**: Ln = Y, R = $C_6H_2Me_3$-2,4,6, *n* = 1; **4**: Ln = Yb, R = Ph, *n* = 2; **5**: Ln = Lu, R = Ph, *n* = 2) were prepared similarly in high yields by the acid–base reactions between the rare-earth metal tris(alkyl) complexes [$Ln(CH_2SiMe_3)_3(thf)_2$] (Ln: Y, Yb, and Lu)[16] and the aryl amine ligands $(C_5Me_4H)SiMe_2NHR'$ (Scheme 1).[17,18] X-ray analyses revealed that complexes **1**, **4**, and **5** are isostructural and isomorphous. Their selected bond lengths and angles are summarized in Table 1, and only the ORTEP drawing of **1** is shown in Figure 1. It is noteworthy that the complex possesses a crystallographic mirror plane in the solid state, in which the whole phenyl ring, N1, Si2, C4, Y1, C1, Si1, and C2 are located. The C6–C6* bond of the Cp ring and the whole molecule are thus bisected by the mirror plane. The bond length of the Y1–N1 bond in the phenyl amido complex **1** (2.327(5) Å) is significantly longer than that in the analogous alkyl amido complex [{$Me_2Si(C_5Me_4)(NCMe_2Et)$}$Y(CH_2SiMe_3)(thf)$] (2.208(6) Å),[15a] even when the difference in coordination number between the metal centers of these two complexes is taken into account.[19] This is probably due to the weaker electron-donating power of

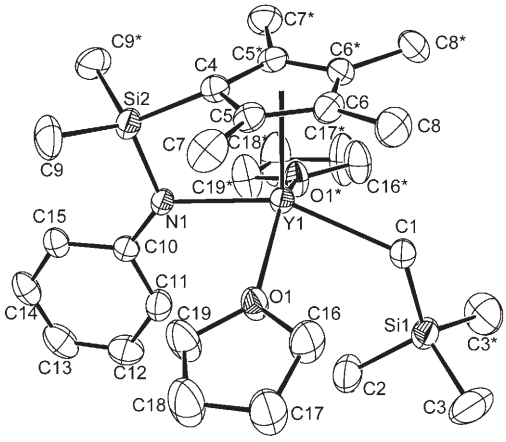


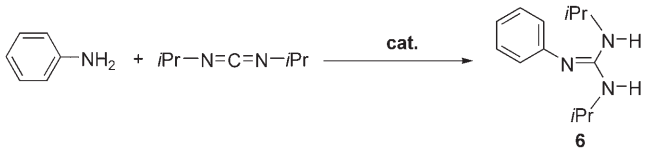
Figure 1. ORTEP drawing of **1** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

the phenyl amido ligand compared to that of the alkyl amido ligand. The bond lengths of the Y1–C1 (2.481(6) Å), Y1–Cp (centroid) (2.336(6) Å), and Y1–O1 (2.382(3) Å) bonds in **1** are comparable with those found in [{$Me_2Si(C_5Me_4)(NCMe_2Et)$}$Y(CH_2SiMe_3)(thf)$] (2.388(7), 2.333(7), and 2.319(5) Å), respectively.[15a]

Catalytic addition of primary aromatic amines to carbodiimides: The reaction of aniline $PhNH_2$ with *N*,*N*′-diisopropylcarbodiimide *i*PrN=C=N*i*Pr was first examined under various conditions. As a control experiment, *i*PrN=C=N*i*Pr

was heated with aniline in C_6D_6 at 80 °C or in C_6D_5Cl at 140 °C, but no reaction was observed in 24 h (Table 2, entries 1 and 2). In contrast, addition of a small amount (1–2 mol %) of the half-sandwich yttrium alkyl complex **1** at 80 °C led to rapid addition of aniline to *i*PrN=C=N*i*Pr to give the *N*,*N*′,*N*″-trisubstituted guanidine **6** in high yields (see Table 2, entries 3 and 12). Other complexes (**2**–**5**) were also effective for this catalytic reaction, although the activity of the Yb (**4**) and Lu (**5**) complexes was slightly lower than that of the Y analogue **1** (Table 2, entries 3–7). The R substituents on the amido unit in the Y complexes **1**–**3** did not show a significant influence on the catalytic activity in the present reaction (Table 2, entries 3–5). However, the bis(pentamethylcyclopentadienyl)yttrium complex $[(C_5Me_5)_2YCH(SiMe_3)_2]$ (Table 2, entry 8) showed much lower activity than those of the half-sandwich Y analogues **1**–**3**.

Table 2. Catalytic addition of an aniline to a *N*,*N*′-diisopropylcarbodiimide.[a]



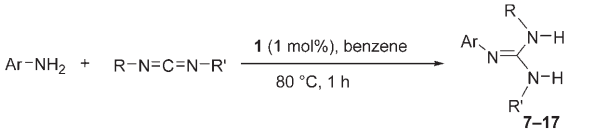
6

Entry	Catalyst (mol %)	Solvent	Temp [°C]	Time [h]	Yield [%][b]
1	0	C_6D_6	80	24	0
2	0	C_6D_5Cl	140	24	0
3	**1** (2)	C_6D_6	80	0.5	83
4	**2** (2)	C_6D_6	80	0.5	83
5	**3** (2)	C_6D_6	80	0.5	82
6	**4** (2)	C_6D_6	80	0.5	75
7	**5** (2)	C_6D_6	80	0.5	57
8	$[Cp^*_2YCH(TMS)_2]$ (2)	C_6D_6	80	0.5	32
9	**1** (2)	$[D_8]$THF	80	0.5	81
10	**1** (2)	$[D_8]$toluene	80	0.5	82
11	**1** (1)	C_6D_6	80	0.5	62
12	**1** (1)	C_6D_6	80	1	>99
13	**1** (0.5)	C_6D_6	80	1	60
14	**1** (0.5)	C_6D_6	80	3	96
15	**1** (1)	C_6D_6	RT	1	11
16	**1** (1)	C_6D_6	RT	24	62
17	**1** (1)	C_6D_6	50	1	33
18	**1** (1)	C_6D_6	50	24	92

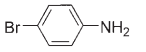
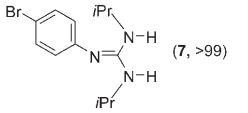
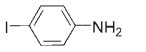
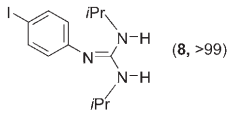
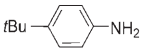
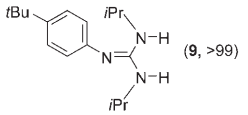
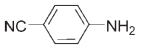
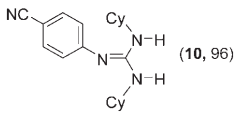
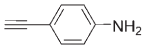
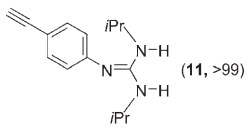
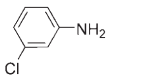
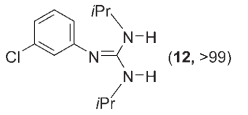
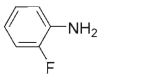
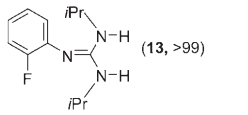
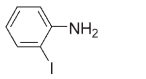
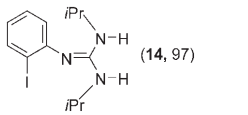
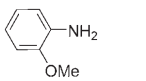
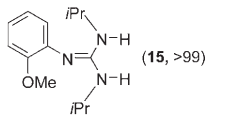
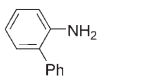
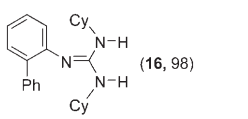
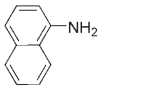
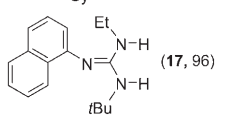
[a] Conditions: aniline, 0.51 mmol; *N*,*N*′-diisopropylcarbodiimide, 0.50 mmol. [b] Yields were determined by ^{1}H NMR spectroscopy by using 1,3,5-trimethylbenzene as an internal standard.

The yttrium complex **1** was then chosen as a catalyst for the addition reaction of various aromatic primary amines with carbodiimides. Representative results are summarized in Tables 3 and 4. As shown in Table 3, a wide range of substituted anilines could be used for this reaction. The reaction was not influenced by either electron-withdrawing or electron-donating substituents or the position of the substituents at the phenyl ring (Table 3, entries 1–11). Aromatic C–F (Table 3, entry 7), C–Cl (Table 3, entry 6), C–Br (Table 3, entry 1), and C–I (Table 3, entries 2 and 8) bonds survived in the present reactions. In the case of *p*-aminophenylacetylene, the reaction took place selectively at the amino group, but the terminal alkyne unit remained unchanged (Table 3, entry 5), although amino-free phenylacetylene can undergo

Table 3. Catalytic addition of various primary anilines to carbodiimides.[a]



7–17

Entry	$ArNH_2$	RN=C=NR	Product (Yield [%][b])
1		*i*PrN=C=N*i*Pr	 (**7**, >99)
2		*i*PrN=C=N*i*Pr	 (**8**, >99)
3		*i*PrN=C=N*i*Pr	 (**9**, >99)
4		CyN=C=NCy	 (**10**, 96)
5		*i*PrN=C=N*i*Pr	 (**11**, >99)
6		*i*PrN=C=N*i*Pr	 (**12**, >99)
7		*i*PrN=C=N*i*Pr	 (**13**, >99)
8		*i*PrN=C=N*i*Pr	 (**14**, 97)
9		*i*PrN=C=N*i*Pr	 (**15**, >99)
10		CyN=C=NCy	 (**16**, 98)
11		EtN=C=N*t*Bu	 (**17**, 96)

[a] Conditions: amines, 2.02 mmol; carbodiimides, 2.00 mmol; catalyst **1**, 0.02 mmol; benzene, 5 mL. [b] Yield of isolated product.

catalytic addition to carbodiimides under the similar conditions.[14]

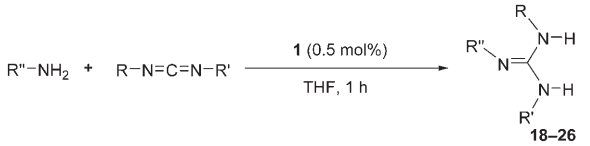
A variety of heterocyclic primary amines such as amino-substituted isoxazoles, pyrazoles, imidazoles, thiazoles, and pyridine could also be used for this reaction, as shown in Table 4. THF seemed to be a better solvent than benzene or toluene in this case, probably due to the better solubility of the heterocyclic amine compounds in THF. In the presence of 0.5 mol% of **1**, the reaction of 5-methylisoxazol-3-amine with *i*PrN=C=N*i*Pr was completed within one hour at room temperature in THF, yielding quantitatively the corresponding guanidine compound **18** (Table 4, entry 1). In the case of the bulkier 1-*tert*-butyl-3-ethylcarbodiimide, the reaction with 5-methylisoxazol-3-amine required a higher temperature (80°C) for completion in one hour (Table 4, entry 3). Consistent with this observation, the reaction between 5-methylisoxazol-3-amine and the further bulkier *N*,*N*′-di-*tert*-butylcarbodiimide did not occur under the same conditions, probably due to steric hindrance.

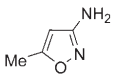
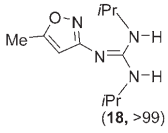
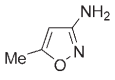
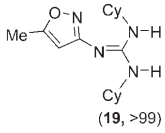
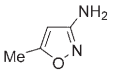
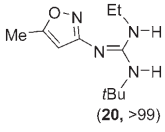
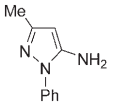
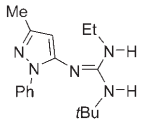
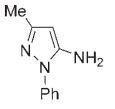
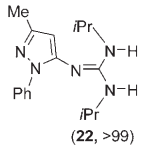
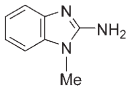
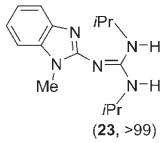
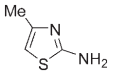
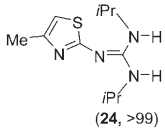
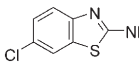
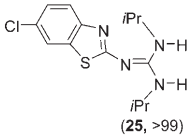
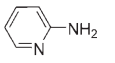
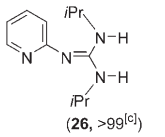
The ^{1}H and ^{13}C NMR spectra of the guanidine products **7**–**16**, **18**, **19**, and **22**–**26**, formed by the reactions of aromatic primary amines with the symmetric carbodiimides *i*PrN=C=N*i*Pr or CyN=C=NCy (Cy = cyclohexyl), all showed one set of signals for the *i*Pr or Cy groups, suggesting that the two *i*Pr or Cy groups in each guanidine product should be in a similar environment. An X-ray structure analysis of **10** revealed that both cyclohexylamino groups in **10** bear a proton on their nitrogen atoms, whereas the aromatic substituent C_6H_4CN-*p* is bonded to the imino-nitrogen atom (C=N) (Figure 2 and Table 3, entry 4). This is in agreement with the ^{1}H and ^{13}C NMR spectra in solution. The ^{1}H and ^{13}C NMR spectra of the guanidine products **17**, **20**, and **21**, which resulted from the reactions with the unsymmetrical carbodiimide EtN=C=N*t*Bu, also suggested the presence of only one isomer in solution. An X-ray structure analysis of **21** revealed that **21** adopts the *E* configuration, in which the bulkier N*t*Bu group is placed *trans* to the aromatic substituent around the C=N double bond (Figure 3 and Table 4, entry 4).

Diamines and triamines can also be applied in this catalytic reaction. In the presence of 1 mol% of **1**, the reaction of 1,3-diaminobenzene with two equivalents of *i*PrN=C=N*i*Pr gave quantitatively the corresponding biguanidine compound **27** (Scheme 2). Similarly, the reaction of 2,4,6-triaminopyrimidine with three equivalents of *i*PrN=C=N*i*Pr yielded the triguanidine compound **28** in high yield. These multiguanidine-functionalized compounds could serve as useful templates (or ligands) for the construction of further larger molecules.

Catalytic addition of secondary amines to carbodiimides: Secondary amines are generally less reactive than primary amines toward carbodiimides. However, in the presence of 3 mol% of **1**, various acyclic and cyclic secondary amines could be added to *i*PrN=C=N*i*Pr or CyN=C=NCy at 80°C or a higher temperature, to give the corresponding *N*,*N*′,*N*″,*N*″-tetrasubstituted guanidines in almost quantitative yields (Table 5). When a diamine such as piperazine was used to react with two equivalents of *i*PrN=C=N*i*Pr, the

Table 4. Catalytic addition of heterocyclic primary amines to carbodiimides.[a]



Entry	RNH_2	RN=C=NR	Temp [°C]	Product (Yield [%][b])
1		*i*PrN=C=N*i*Pr	RT	 (**18**, >99)
2		CyN=C=NCy	RT	 (**19**, >99)
3		EtN=C=N*t*Bu	80	 (**20**, >99)
4		EtN=C=N*t*Bu	RT	 (**21**, >99)
5		*i*PrN=C=N*i*Pr	RT	 (**22**, >99)
6		*i*PrN=C=N*i*Pr	80	 (**23**, >99)
7		*i*PrN=C=N*i*Pr	50	 (**24**, >99)
8		*i*PrN=C=N*i*Pr	80	 (**25**, >99)
9		*i*PrN=C=N*i*Pr	80	 (**26**, >99[c])

[a] Conditions: amines, 2.02 mmol; carbodiimides, 2.00 mmol; catalyst **1**, 0.01 mmol; THF, 5 mL, unless otherwise noted. [b] Yield of isolated product. [c] Conditions: Amine, 2.02 mmol; carbodiimide, 2.00 mmol; catalyst **1**, 0.02 mmol; benzene, 5 mL.

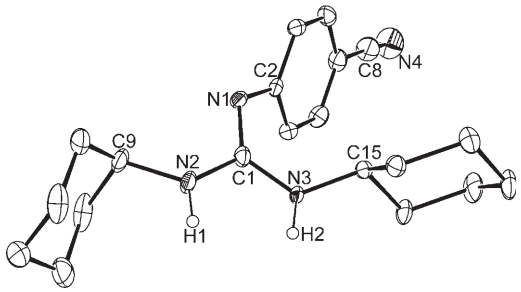


Figure 2. ORTEP drawing of **10** with 30% probability thermal ellipsoids. Hydrogen atoms, except those on the nitrogen atoms, are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1 1.324(3), N2–C1 1.352(3), N3–C1 1.366(3), N4–C8 1.131(3); N1-C1-N2 119.9(2), N1-C1-N3 125.8(2), N2-C1-N3 114.3(2).

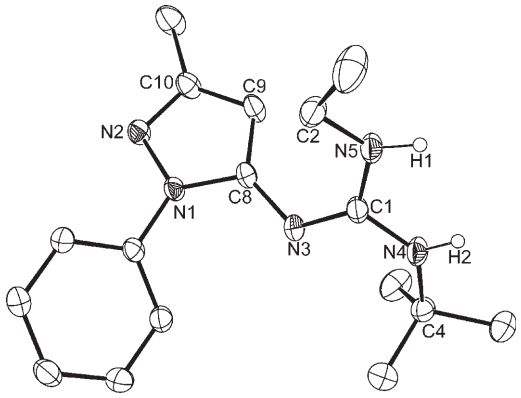
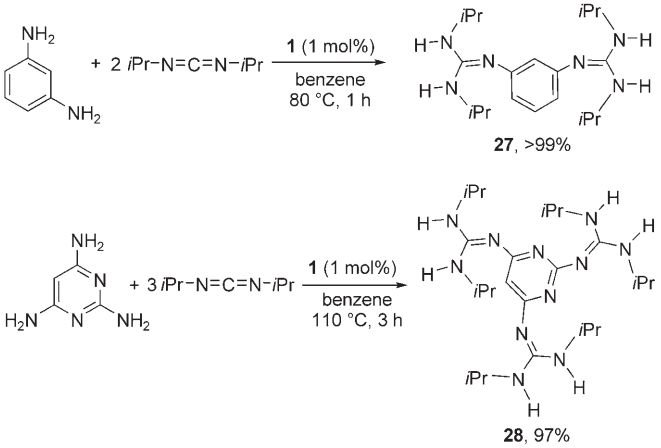


Figure 3. ORTEP drawing of **21** with 30% probability thermal ellipsoids. Hydrogen atoms, except those on the nitrogen atoms, are omitted for clarity. Selected bond lengths [Å] and angles [°]: N3–C1 1.3110(19), N4–C1 1.348(2), N5–C1 1.369(2), N3-C1-N4 120.5(1), N3-C1-N5 125.9(2), N4-C1-N5 113.6(1), C1-N3-C(8) 119.7(1).



Scheme 2. Catalytic addition of di- and triamines to a carbodiimide.

corresponding biguanidine **37** was formed in 99% yield by a double catalytic addition reaction (Table 5, entry 9).

Although tetrasubstituted guanidines could, in principle, have four possible isomers E_{anti}, E_{syn}, Z_{anti}, Z_{syn},[20] the ^{1}H and ^{13}C NMR spectra of the resulting guanidine compounds (**29**–**37**) in the present reactions suggested that only one isomer is present for each compound in solution. An X-ray structure analysis of **35** revealed that it is E_{anti} in the solid state (Figure 4 and Table 5, entry 7).

In the presence of 3 mol% of **1**, the reaction of 1,2,3,4-tetrahydro-5-aminoisoquinoline with one equivalent of *i*PrN=

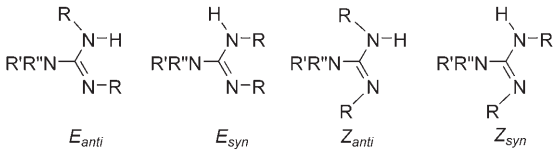
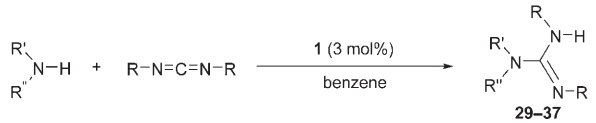
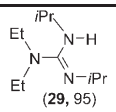
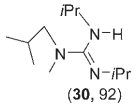
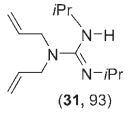
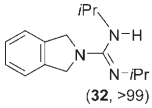
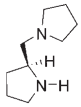
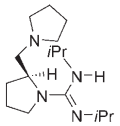
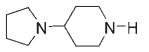
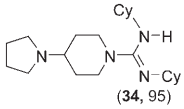
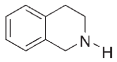
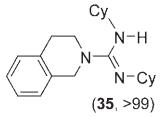
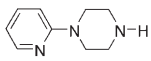
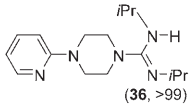
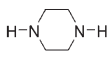
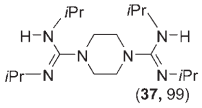


Table 5. Catalytic addition of secondary amines to carbodiimides.[a]



Entry	Amine	R	Temp [°C] (Time [h])	Product (Yield [%][b])
1		*i*Pr	80 (3)	 (**29**, 95)
2		*i*Pr	80 (3)	 (**30**, 92)
3		*i*Pr	80 (3)	 (**31**, 93)
4		*i*Pr	80 (0.5)	 (**32**, >99)
5		*i*Pr	110 (5)	 (**33**, 90)
6		Cy	80 (1)	 (**34**, 95)
7		Cy	80 (0.5)	 (**35**, >99)
8		*i*Pr	80 (1)	 (**36**, >99)
9		*i*Pr	80 (3)	 (**37**, 99)

[a] Conditions: amines, 2.00 mmol; carbodiimides, 2.00 mmol; catalyst **1**, 0.06 mmol; benzene, 5 mL. [b] Yield of isolated product.

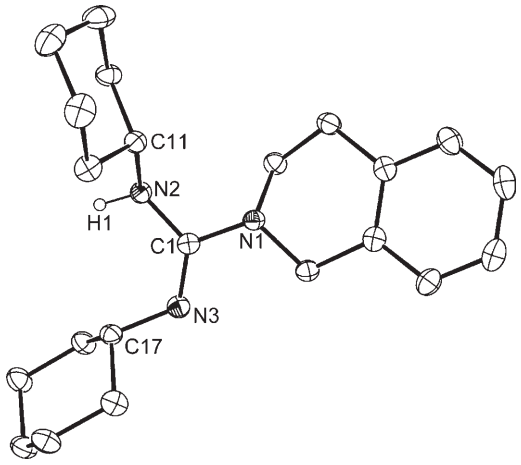
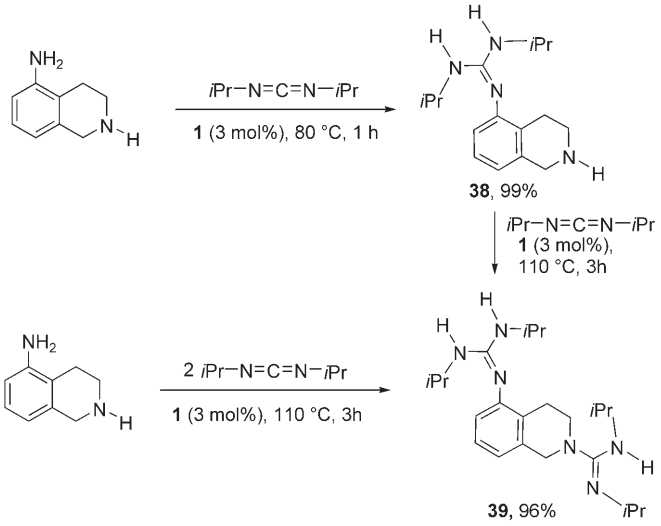


Figure 4. ORTEP drawing of **35** with 30% probability thermal ellipsoids. Hydrogen atoms, except that of the nitrogen atom N2, are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1 1.394(3), N2–C1 1.394(3), N3–C1 1.289(3); N1-C1-N2 113.0(2), N3-C1-N1 119.4(2), N3-C1-N2 127.6(2), C1-N3-C17 120.3(2).

C=N*i*Pr at 80 °C took place selectively at the primary amino group to give the monoguanidine compound **38** (Scheme 3), but no reaction was observed at the cyclic secondary N–H

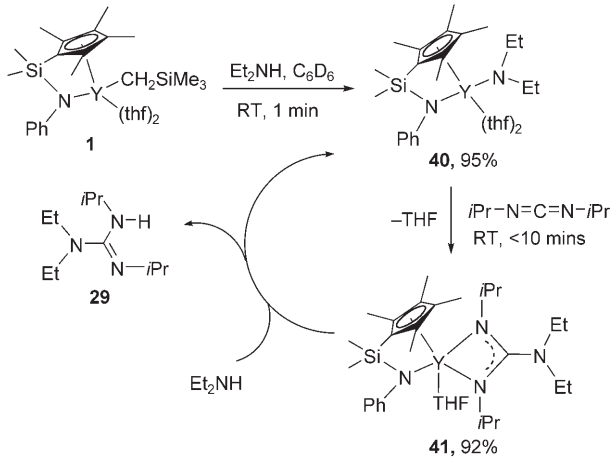


Scheme 3. Stepwise catalytic addition of 1,2,3,4-tetrahydro-5-aminoisoquinoline to *N,N'*-diisopropylcarbodiimide.

bond, showing that a primary amino group can be distinguished from a secondary one under the present catalytic conditions. Heating the reaction mixture with another equivalent of *i*PrN=C=N*i*Pr at 110 °C for three hours afforded the biguanidine **39** almost quantitatively. The biguanidine **39** could also be obtained alternatively by reaction of 1,2,3,4-tetrahydro-5-aminoisoquinoline with two equivalents of *i*PrN=C=N*i*Pr at 110 °C (Scheme 3).

Mechanistic studies:

a) Reaction of secondary amines: To gain information on the true catalyst species, the stoichiometric reaction of **1** with diethylamine was first carried out in benzene, which gave instantly the corresponding amido complex [{Me_2Si-(C_5Me_4)(NPh)}Y(NEt_2)$(thf)_2$] (**40**) in 95% yield at room temperature (Scheme 4). Nucleophilic addition of **40** to



Scheme 4. Formation of an yttrium guanidinate complex and its reaction with diethylamine.

*i*PrN=C=N*i*Pr took place rapidly to give the guanidinate complex [{$Me_2Si(C_5Me_4)$(NPh)}Y{*i*PrNC(NEt_2)(N*i*Pr)}(thf)] (**41**) in 92% yield. The reaction between the chelating Cp-anilido Y–N bond and *i*PrN=C=N*i*Pr was not observed even in the presence of an excess amount of *i*PrN=C=N*i*Pr. Both **40** and **41** have been structurally characterized by X-ray structure analyses (Figures 5 and 6).

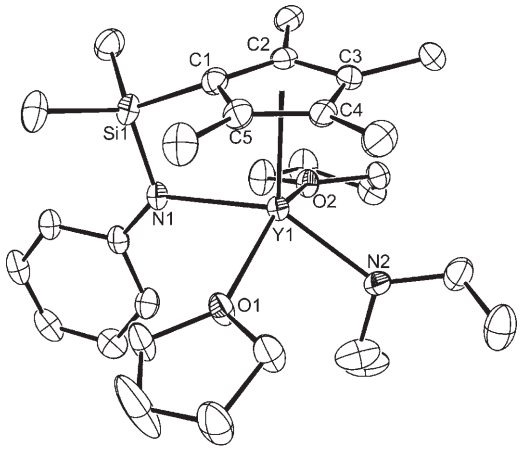


Figure 5. ORTEP drawing of **40** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.324(2), Y1–N2 2.199(3), Y1–O1 2.399(2), Y1–O2 2.398(2), Y1–C1 2.567(3), Y1–C2 2.635(3), Y1–C3 2.709(3), Y1–C4 2.693(3), Y1–C5 2.625(3), Y1–Cp(centroid) 2.358(3); N1-Y1-Cp(centroid) 96.2(1), N2-Y1-Cp(centroid) 142.9(1), N2-Y1-N1 142.94(10), O2-Y1-O1 142.10(7), N1-Si1-C1 99.12(14).

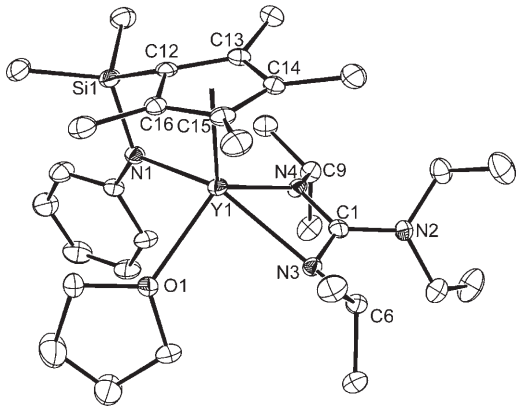
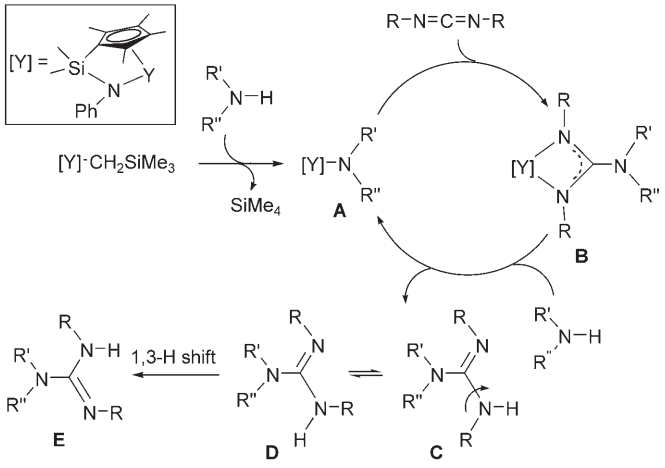


Figure 6. ORTEP drawing of **41** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.282(2), Y1–N3 2.462(2), Y1–N4 2.304(2), Y1–O1 2.4145(19), Y1–C12 2.573(3), Y1–C13 2.629(3), Y1–C14 2.743(3), Y1–C15 2.778(3), Y1–C16 2.673(3), Y1–Cp(centroid) 2.393(3), N2–C1 1.398(3), N3–C1 1.329(3), N4–C1 1.347(3); N1-Y1-Cp(centroid) 95.22(8), N3-Y1-Cp(centroid) 122.84(8), N4-Y1-Cp(centroid) 117.37(8), N1-Y1-N4 97.92(8), N1-Y1-N3 140.21(8), N4-Y1-N3 56.48(7), C1-N4-Y1 95.4(2), N3-C1-N4 115.1(3), N3-C1-N2 124.1(3), N4-C1-N2 120.8(3), N1-Si1-C12 96.6(1).

At room temperature, no reaction was observed between the guanidinate complex **41** and diethylamine. However, when a 1:1 mixture of **41** and diethylamine was heated to 80°C, the corresponding guanidine compound *i*PrN=C-(NEt_2)NH*i*Pr (**29**) and the amido complex **40** were formed almost quantitatively (Scheme 4). When excess diethylamine and *i*PrN=C=N*i*Pr (1:1) were added to **41** in C_6D_6 at 80°C, catalytic formation of **29** was achieved.

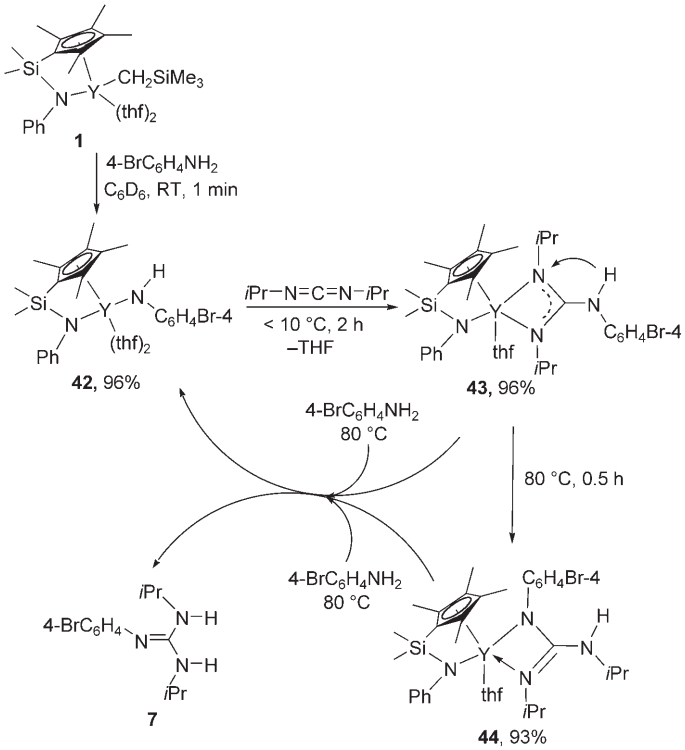
On the basis of the above observations, a possible catalytic cycle for the addition of secondary amines to carbodiimides could be proposed as shown in Scheme 5. The acid–base reaction between the yttrium alkyl complex **1** and an amine should simply yield an amido species such as **A**. Nucleophilic addition of the amido species to a carbodiimide



Scheme 5. A possible mechanism of catalytic addition of secondary amines to carbodiimides.

would afford directly the guanidinate species **B**. Protonation of **B** by another molecule of amine would regenerate the amido complex **A** and release the guanidine **C**. Rearrangement of **C** through C–N bond rotation to **D** and the subsequent 1,3-hydrogen shift would take place to give the more stable *E* isomer **E**. The isolation of the guanidinate **41** and its reaction with diethylamine to give guanidine **29** and the amido **41** (see Scheme 4) strongly support this mechanism.

b) Reaction of primary amines: The reaction of **1** with one equivalent of 4-bromoaniline at room temperature took place rapidly to afford the corresponding structurally characterizable amido complex **42** (Scheme 6 and Figure 7). The



Scheme 6. Formation of yttrium guanidinates and their reactions with 4-bromoaniline.

reaction of **42** with one equivalent of *i*PrN=C=N*i*Pr in C_6D_6 below 10°C gave the corresponding addition product **43** in 96% yield in two hours. The guanidinate complex **43** was not stable at room temperature in solution, and gradually changed to **44** through intramolecular proton transfer from the aryl amino nitrogen atom to an isopropyl amido nitrogen atom, followed by dissociation of the resultant isopropyl amino group from the metal center and formation of an aryl amido–Y bond (Scheme 6). This isomerization reaction probably occurs because the aryl amine proton in **43** is more acidic than the isopropylamine proton in **44**. The transformation of **43** to **44** took place more rapidly at higher temperatures. If the reaction of **42** with *i*PrN=C=N*i*Pr was carried out at 80°C, only the formation of **44** was observed,

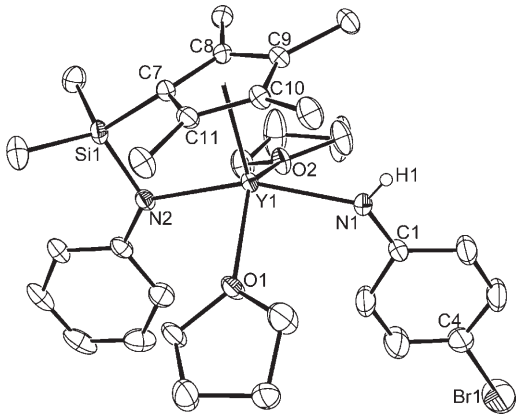


Figure 7. ORTEP drawing of **42** with 30% probability thermal ellipsoids. Hydrogen atoms, except that on the nitrogen atom N1, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.297(4), Y1–N2 2.337(4), Y1–O1 2.367(3), Y1–O2 2.383(4), Y1–C7 2.523(5), Y1–C8 2.597(5), Y1–C9 2.683(5), Y1–C10 2.688(5), Y1–C11 2.598(5), Y1–Cp-(centroid) 2.321(5); N1-Y1-Cp(centroid) 107.6(2), N2-Y1-Cp(centroid) 97.1(2), O1-Y1-O2 132.1(1), N1-Y1-N2 155.3(2), N2-Si1-C7 97.9(2).

whereas the reaction at room temperature gave a mixture of **43** and **44** at the early stage. A reaction between the chelating Cp-anilido Y–N bond and *i*PrN=C=N*i*Pr was not observed even in the presence of an excess of *i*PrN=C=N*i*Pr, as in the case of **41**. Complex **44** was structurally characterized by an X-ray analysis (Figure 8). The bond length of the N2–C18 bond (1.307(8) Å) is significantly shorter than that of the N1–C18 (1.376(8) Å) bond in the guanidinate unit, and the latter is the same as that of the N3–C18 bond (1.376(7) Å), suggesting that the C=N double bond of the guanidinate unit in **44** is highly localized between the N2 and C18 atoms.

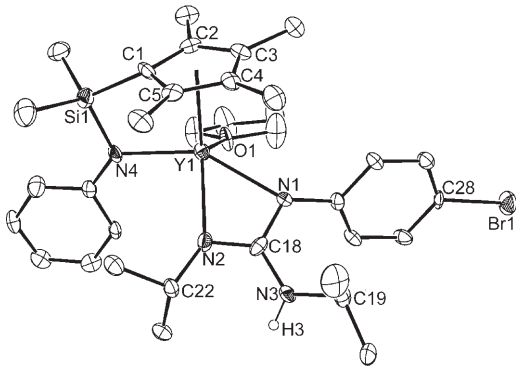
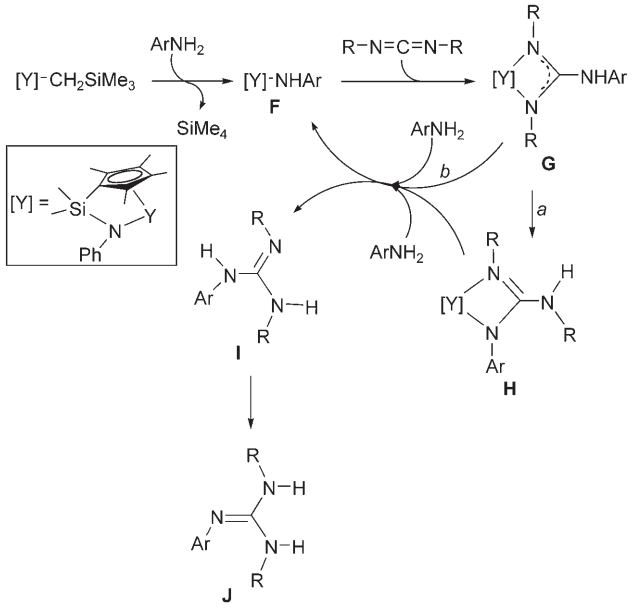


Figure 8. ORTEP drawing of **44** with 30% probability thermal ellipsoids. Hydrogen atoms, except that on the nitrogen atom N3, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–N1 2.370(5), Y1–N2 2.326(6), Y1–N4 2.283(5), Y1–O1 2.323(4), Y1–C1 2.527(7), Y1–C2 2.628(7), Y1–C3 2.733(7), Y1–C(4) 2.720(7), Y1–C5 2.581(6), Y1–Cp-(centroid) 2.349(7), N1–C18 1.376(8), N2–C18 1.307(8), N3–C18 1.376(7); N1-Y1-Cp(centroid) 112.6(2), N2-Y1-Cp(centroid) 128.4(2), N4-Y1-Cp(centroid) 96.8(2), N4-Y1-N2 96.2(2), N4-Y1-N1 148.6(2), N2-Y1-N1 57.0(2), C18-N1-Y1 92.8(4), C18-N2-Y1 96.7(5), C18-N3-C19 124.6(6), N2-C18-N3 124.3(7), N2-C18-N1 113.4(7), N3-C18-N1 122.4(6), N4-Si1-C1 97.5(3).

At room temperature, a reaction between **44** (or **43**) and 4-bromoaniline did not take place. However, when a 1:1 mixture of **44** (or **43**) and 4-bromoaniline was heated to 80 °C in C_6D_6, 4-BrC_6H_4N=C(NH*i*Pr)$_2$ (**7**) and **42** were formed almost quantitatively (Scheme 6). Rapid catalytic formation of **7** was achieved when excess 4-bromoaniline and *i*PrN=C=N*i*Pr (1:1) were added to **44** (or **43**) at 80 °C.

A possible catalytic cycle for the addition reaction of primary aromatic amines to carbodiimides is shown in Scheme 7. The acid–base reaction between a half-sandwich



Scheme 7. A possible mechanism of catalytic addition of primary aromatic amines to carbodiimides.

rare-earth metal alkyl and a primary amine yields an amido species such as **F**. Nucleophilic addition of the amido species to a carbodiimide would first afford the symmetrical guanidinate species **G**, which could then quickly be rearranged to the unsymmetrical guanidinate species **H** at high temperature through the intramolecular 1,3-hydrogen shift (path a). Protonolysis of **H** by another molecule of primay amine would regenerate the amido **F** and release the guanidine **I**. An intramolecular 1,3-hydrogen shift in **I** could give the more stable final product **J**. Formation of **I** through protonolysis of **G** (path b) could also be possible (see also Scheme 6).

Conclusion

Rare-earth metal alkyl complexes bearing the silylene-linked cyclopentadienyl-amido ligands such as **1**–**5**, which can be easily prepared by the reactions of the rare-earth metal tris(alkyl) complexes [Ln(CH_2SiMe_3)$_3$(thf)$_2$] with the corresponding neutral ligands (C_5Me_4H)$SiMe_2NHR'$, can serve as excellent catalyst precursors for the catalytic addi-

tion of various amine N–H bonds to carbodiimides, leading to efficient formation of a series of guanidine derivatives with a wide range of substituents on the nitrogen atoms. Functional groups such as C≡N, C≡CH, and aromatic C–X (X = F, Cl, Br, I) bonds can survive the catalytic reaction conditions. A primary amino group can be distinguished from a secondary one by the catalyst system under appropriate conditions, and therefore, the reaction of 1,2,3,4-tetrahydro-5-aminoisoquinoline with *i*PrN=C=N*i*Pr can be achieved stepwise first at the primary amino group to selectively give the monoguanidine **38**, and then at the cyclic secondary amino unit to give the biguanidine **39**. The isolation and reactivity investigation of the amido (e.g., **40** and **42**) and guanidinate intermediates (e.g., **41** and **44**) suggest that the catalytic formation of a guanidine compound proceeds through nucleophilic addition of an amido species, formed by acid–base reaction between a rare-earth metal alkyl bond and an amine N–H bond, to a carbodiimide, followed by amine protonolysis of the resultant guanidinate species. These results have demonstrated that a guanidinate unit, though being often used as a supporting ligand for various metal complexes, does not always behave as a "spectator" ligand, and can itself participate in a reaction in a catalytic fashion under appropriate conditions.

Experimental Section

All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBRAUN glovebox. The argon was purified by passing it through a Dryclean column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieve catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (MBRAUN) to ensure both were always below 1 ppm. Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method (three times), and dried over fresh Na chips in the glovebox. [D_6]Benzene, [D_8]toluene, and [D_8]THF (all 99+ atom% D) were obtained from Acros and were dried over fresh Na chips in the glovebox for NMR reactions. All organic starting materials were purchased from TCI or Aldrich and were dried over molecular sieves (4Å) for two days, and when appropriate, were distilled prior to use. The ligands $(C_5Me_4H)SiMe_2NHR'$ (R′: Ph, *t*Bu) were prepared by the reaction of $(C_5Me_4H)SiMe_2Cl$ with R′NHLi (generated in situ from *n*BuLi with one equivalent of $R'NH_2$ in THF) as described previously.[17] $(C_5Me_4H)SiMe_2NH(C_6H_2Me_3$-2,4,6) was prepared analogously. [{$Me_2Si(C_5Me_4)(NtBu)$}$Y(CH_2SiMe_3)(thf)$] (**3**)[15a] and [$Cp^*_2YCH(TMS)_2$][21] were prepared according to published procedures.

IR spectra were obtained on a Shimadzu IRPrestige-21 spectrophotometer by using Nujol mulls between KBr disks. HRMS were recorded on a JEOL JMS-700 instrument operated in EF-FAB$^+$ mode. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) or a JEOL JNM-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C) at room temperature, unless otherwise noted. Micro elemental analyses were performed on a MICRO CORDER JM10 apparatus (J-Science Lab. Co.).

Preparation of $(C_5Me_4H)SiMe_2NH(C_6H_2Me_3$-2,4,6): A solution of $(C_6H_2Me_3$-2,4,6)NHLi (711 mg, 5.04 mmol) in THF (20 mL), which was prepared by reaction of *n*BuLi with one equivalent of $(C_6H_2Me_3$-2,4,6)NH_2 in THF was added to a solution of $(C_5Me_4H)SiMe_2Cl$ (1 g, 4.66 mmol) in THF (30 mL). The reaction mixture was stirred at room temperature for 12 h. After removal of the solvent under reduced pressure, the residue was extracted with hexane. Evaporation of hexane gave $(C_5Me_4H)SiMe_2NH(C_6H_2Me_3$-2,4,6) as a light yellow oil (1.4 g, 96% based on $(C_5Me_4H)SiMe_2Cl$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.28$ (s, 6H; $SiMe_2$), 1.98 (s, 6H; C_5Me_4), 2.15 (s, 6H; C_5Me_4), 2.27 (s, 6H; *o*-$C_6H_2(CH_3)_3$), 2.32 (s, 3H; *p*-$C_6H_2(CH_3)_3$), 2.43 (s, 1H; C_5Me_4H), 3.13 (s, 1H; NH), 6.88 ppm (s, 2H; $C_6H_2(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 0.3$, 11.4, 14.6, 19.7, 20.6, 56.7, 128.8, 130.0, 130.5, 133.0, 136.9, 140.2 ppm.

$(C_5Me_4H)SiMe_2NHtBu$: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.01$ (s, 6H; $SiMe_2$), 0.45 (br s, 1H; NH), 1.12 (s, 9H; $C(CH_3)_3$), 1.79 (s, 6H; C_5Me_4), 1.95 (s, 6H; C_5Me_4), 2.81 ppm (s, 1H; C_5Me_4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 0.9$, 11.1, 14.7, 33.7, 49.3, 56.9, 133.3, 135.3 ppm.

[{$Me_2Si(C_5Me_4)(NPh)$}$Y(CH_2SiMe_3)(thf)_2$] (1): A solution of $(C_5Me_4H)SiMe_2NHPh$ (544 mg, 2 mmol) in hexane (5 mL) was added to a solution of $[Y(CH_2SiMe_3)_3(thf)_2]$ (986 mg, 2 mmol) in hexane (10 mL) at room temperature. Immediate formation of a white precipitate was observed. After the mixture was stirred for 2 h, the precipitate was collected by decanting the solution and was washed with hexane to give **1** (1.2 g, 95%). Single crystals of **1**·0.5 hexane could be grown from a concentrated solution in hexane for one day at room temperature. ^{1}H NMR (300 MHz, C_6D_6): $\delta = -0.99$ (d, $J_{(Y,H)} = 2.5$ Hz, 2H; CH_2), 0.27 (s, 9H; $SiMe_3$), 0.86 (s, 6H; $SiMe_2$), 1.22 (s, 8H; β-CH_2, THF), 2.08 (s, 6H; C_5Me_4), 2.11 (s, 6H; C_5Me_4), 3.68 (s, 8H; α-CH_2, THF), 6.70 (t, $J = 8.2$ Hz, 1H; *p*-C_6H_5), 6.72 (d, $J = 8.2$ Hz, 2H; *o*-C_6H_5), 7.25 ppm (t, $J = 8.3$ Hz, 2H; *m*-C_6H_5); ^{13}C NMR (75 MHz, [D_8]THF): $\delta = 4.8$, 4.9, 11.8, 14.3, 23.1 (d, $J_{(Y,C)} = 38.6$ Hz), 26.4, 68.2, 106.2, 114.8, 120.5, 126.4, 127.6, 129.3, 157.2 ppm; elemental analysis calcd (%) for $C_{29}H_{50}NO_2Si_2Y$: C 59.06, H 8.54, N 2.37; found: C 59.66, H 8.62, N 2.37.

[{$Me_2Si(C_5Me_4)(NC_6H_2Me_3$-2,4,6)}$Y(CH_2SiMe_3)(thf)$] (2): Starting from $[Y(CH_2SiMe_3)_3(thf)_2]$ (986 mg, 2 mmol), complex **2** was obtained as a white powder (985 mg, 88% yield) in a manner analogous to that described for the synthesis of **1**. ^{1}H NMR (300 MHz, C_6D_6): $\delta = -0.88$ (d, $J_{(Y,H)} = 2.5$ Hz, 2H; CH_2), 0.28 (s, 9H; $SiMe_3$), 0.86 (s, 6H; $SiMe_2$), 1.25 (s, 4H; β-CH_2, THF), 2.07 (s, 6H; C_5Me_4), 2.12 (s, 6H; C_5Me_4), 2.38 (s, 6H; *o*-$C_6H_2(CH_3)_3$), 2.54 (s, 3H; *p*-$C_6H_2(CH_3)_3$), 3.32 (s, 4H; α-CH_2, THF), 6.92 ppm (s, 2H; $C_6H_2(CH_3)_3$); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 4.7$, 5.8, 6.4, 11.0, 11.7, 14.5, 14.6, 20.8, 21.1, 23.1 (d, $J_{(Y,C)} = 38.6$ Hz), 25.3, 71.0, 106.4, 110.5, 120.5, 126.4, 127.6, 129.3, 150.3 ppm; elemental analysis calcd (%) for $C_{28}H_{48}NO_2Si_2Y$: C 60.08, H 8.64, N 2.50; found: C 59.70, H 8.52, N 2.39.

[{$Me_2Si(C_5Me_4)(NPh)$}$Yb(CH_2SiMe_3)(thf)_2$](4): Starting from $[Yb(CH_2SiMe_3)_3(thf)_2]$ (1.15 g, 2 mmol), complex **4** was obtained as a red powder (124 mg, 90% yield) in a manner analogous to that described for the synthesis of **1**. Single crystals of **4**·0.5 hexane could be grown from a concentrated solution in hexane for one day at room temperature. Elemental analysis calcd (%) for $C_{29}H_{50}NO_2Si_2Yb$: C 51.68, H 7.48, N 2.08; found: C 51.99, H 7.59, N 1.82.

[{$Me_2Si(C_5Me_4)(NPh)$}$Lu(CH_2SiMe_3)(thf)_2$] (5): Starting from $[Lu(CH_2SiMe_3)_3(thf)_2]$ (581 mg, 1 mmol), complex **5** was obtained as a white powder (582 mg, 92% yield) in a manner analogous to that described for the synthesis of **1**. Single crystals of **5**·0.5 hexane could be grown from a concentrated hexane solution for one day at room temperature. ^{1}H NMR (300 MHz, C_6D_6): $\delta = -0.86$ (d, 2H; CH_2), 0.25 (s, 9H; $SiMe_3$), 0.84 (s, 6H; $SiMe_2$), 1.17 (s, 8H; β-CH_2, THF), 2.06 (s, 6H; C_5Me_4), 2.15 (s, 6H; C_5Me_4), 3.56 (s, 8H; α-CH_2, THF), 6.74 (t, $J = 7.5$ Hz, 1H; *p*-C_6H_5), 6.90 (d, $J = 7.6$ Hz, 2H; *o*-C_6H_5), 7.25 ppm (t, $J = 7.6$ Hz, 2H; *m*-C_6H_5); ^{13}C NMR (75 MHz, [D_8]THF): $\delta = 4.5$, 5.0, 11.8, 14.2, 26.3, 27.8, 68.2, 105.2, 114.7, 120.6, 126.1, 127.4, 129.2, 157.3 ppm; elemental analysis calcd (%) for $C_{29}H_{50}NO_2Si_2Lu$: C 51.54, H 7.46, N 2.07; found: C 52.06, H 7.63, N 1.98.

Typical procedures for the catalytic reaction of primary aromatic amines to carbodiimides: i) NMR tube reaction: In the glovebox, a J. Young valve NMR tube was charged with **1** (3 mg, 0.005 mmol), C_6D_6 (0.5 mL), aniline (48 mg, 0.51 mmol), *N,N′*-diisopropylcarbodiimide (63 mg, 0.50 mmol). The tube was taken outside the glovebox and heated at 80°C

in an oil bath. Formation of **6** was easily monitored by ^{1}H NMR spectroscopy. The reaction was quantitative and finished within 1 h.

ii) Preparative scale reaction: In the glovebox, a solution of aniline (188 mg, 2.02 mmol) in benzene (3 mL) was added to a solution of **1** (12 mg, 0.02 mmol) in benzene (2 mL) in a Schlenk tube. *N*,*N*′-Diisopropylcarbodiimide (252 mg, 2.00 mmol) was then added to the above reaction mixture. The Schlenk tube was taken outside the glovebox, and the mixture was stirred at 80 °C for 1 h. After the solvent was removed under reduced pressure, the residue was extracted with ether and filtered to give a clean solution. After removing the solvent under vacuum, the residue was recrystallized in ether to provide a colorless solid **6** in >99% yield.

1,3-Diisopropyl-2-phenylguanidine (6): Colorless solid, yield >99%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.91$ (d, $J=6.4$ Hz, 12H; CH_3), 3.52 (br, 2H; NH), 3.64–3.69 (m, 2H; CH), 6.90 (t, $J=7.6$ Hz, 1H; *p*-C_6H_5), 7.10 (d, $J=7.6$ Hz, 2H; *o*-C_6H_5), 7.25 ppm (t, $J=7.6$ Hz, 2H; *m*-C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): $\delta=23.4$, 43.4, 121.3, 123.7, 129.6, 149.7, 151.6 ppm; IR (Nujol): $\tilde{\nu}=3300$, 2956, 2924, 2854, 1648, 1617, 1591, 1462, 1378, 1262, 1124, 1019, 800, 694 cm^{-1}; HRMS: *m*/*z* calcd for $C_{13}H_{22}N_3$: 220.1814 $[M+H]^+$; found: 220.1795.

2-(4-Bromophenyl)-1,3-diisopropylguanidine (7): Colorless solid, yield >99%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.86$ (d, $J=6.4$ Hz, 12H; CH_3), 3.37 (br, 2H; NH), 3.55–3.60 (m, 2H; CH), 6.69 (d, $J=8.8$ Hz, 2H; *o*-C_6H_4), 7.30 ppm (d, $J=8.8$ Hz, 2H; *m*-C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): $\delta=23.3$, 43.4, 113.7, 125.4, 132.5, 149.6, 150.7 ppm; IR (Nujol): $\tilde{\nu}=3292$, 2953, 2924, 2853, 1632, 1605, 1578, 1535, 1462, 1377, 1263, 1072, 859, 806, 723 cm^{-1}; HRMS: *m*/*z* calcd for $C_{13}H_{21}BrN_3$: 298.0919 $[M+H]^+$; found: 298.0916.

2-(4-Iodophenyl)-1,3-diisopropylguanidine (8): Colorless solid, yield >99%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.86$ (d, $J=6.8$ Hz, 12H; CH_3), 3.40 (br, 2H; NH), 3.53–3.60 (m, 2H; CH), 6.68 (d, $J=8.8$ Hz, 2H; *o*-C_6H_4), 7.47 ppm (d, $J=8.8$ Hz, 2H; *m*-C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): $\delta=23.4$, 43.4, 83.8, 126.0, 138.5, 149.7, 151.3 ppm; IR (Nujol): $\tilde{\nu}=3304$, 2953, 2924, 2853, 1605, 1574, 1537, 1462, 1377, 1250, 1061, 841, 719 cm^{-1}; HRMS: *m*/*z* calcd for $C_{13}H_{21}N_3I$: 346.0780 $[M+H]^+$; found: 346.0799.

2-(4-*tert*-Butylphenyl)-1,3-diisopropylguanidine (9): Colorless solid, yield >99%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.90$ (d, $J=5.6$ Hz, 12H; CH_3), 1.27 (s, 9H; $C(CH_3)_3$), 3.49 (br, 2H; NH), 3.67 (br, 2H; CH), 7.13 (d, $J=$ 8.0 Hz, 2H; *o*-C_6H_4), 7.33 ppm (d, $J=8.0$ Hz, 2H; *m*-C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): $\delta=23.4$, 31.9, 34.4, 43.4, 123.2, 126.4, 143.5, 148.9, 149.7 ppm; IR (Nujol): $\tilde{\nu}=3312$, 2955, 2924, 2853, 1638, 1597, 1560, 1508, 1460, 1377, 1269, 742 cm^{-1}; HRMS: *m*/*z* calcd for $C_{17}H_{30}N_3$: 276.2440 $[M+H]^+$; found: 276.2431.

2-(4-Cyanophenyl)-1,3-dicyclohexylguanidine (10): Colorless single crystals suitable for X-ray analysis were grown in ether/hexane at room temperature overnight, yield 96%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.75$–1.82 (m, 20H; Cy), 3.31–3.38 (m, 2H; CH), 3.53 (d, 2H; NH), 6.82 (d, $J=$ 8.4 Hz, 2H; *o*-C_6H_4), 7.16 ppm (d, $J=8.4$ Hz, 2H; *m*-C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): $\delta=25.4$, 26.0, 33.9, 50.6, 103.6, 120.2, 123.9, 133.6, 149.7, 156.2 ppm; IR (Nujol): $\tilde{\nu}=3387$, 3290, 2953, 2924, 2853, 2216, 1585, 1570, 1551, 1460, 1377, 1165, 862, 719 cm^{-1}; HRMS: calcd for $C_{20}H_{29}N_4$: 325.2392 $[M+H]^+$; found: 325.2380.

2-(4-Ethynylphenyl)-1,3-diisopropylguanidine (11): Colorless solid, yield >99%; ^{1}H NMR (300 MHz, C_6D_6): $\delta=0.88$ (d, $J=6.3$ Hz, 12H; CH_3), 2.83 (s, 1H; C≡CH), 3.48 (br, 2H; NH), 3.52–3.63 (m, 2H; CH), 6.92 (d, $J=8.4$ Hz, 2H; *o*-C_6H_4), 7.48 ppm (d, $J=8.4$ Hz, 2H; *m*-C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): $\delta=23.1$, 43.2, 76.2, 85.0, 114.6, 123.6, 133.7, 149.7, 152.5 ppm; IR (Nujol): $\tilde{\nu}=3319$, 2955, 2924, 2853, 2106, 1630, 1589, 1500, 1458, 1377, 1267, 1167, 1125, 862, 723 cm^{-1}; HRMS: *m*/*z* calcd for $C_{15}H_{22}N_3$: 244.1814 $[M+H]^+$; found: 244.1817.

2-(3-Chlorophenyl)-1,3-diisopropylguanidine (12): Colorless solid, yield >99%; ^{1}H NMR (300 MHz, C_6D_6): $\delta=0.78$ (d, $J=6.3$ Hz, 12H; CH_3), 3.33 (br, 2H; NH), 3.46–3.52 (m, 2H; CH), 6.78–6.91 (m, 3H; C_6H_4), 7.08–7.11 ppm (m, 1H; C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): $\delta=23.3$, 43.4, 121.1, 121.9, 123.7, 130.5, 135.0, 149.8, 153.3 ppm; IR (Nujol): $\tilde{\nu}=3343$, 3231, 2955, 2924, 2853, 1636, 1609, 1580, 1547, 1499, 1464, 1383, 1366, 1265, 1125, 1070, 889, 775, 687 cm^{-1}; HRMS: *m*/*z* calcd for $C_{13}H_{21}ClN_3$: 254.1424 $[M+H]^+$; found: 254.1411.

2-(2-Fluorophenyl)-1,3-diisopropylguanidine (13): Colorless solid, yield >99%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.90$ (d, $J=6.4$ Hz, 12H; CH_3), 3.40 (br, 2H; NH), 3.61–3.70 (m, 2H; CH), 6.67–6.73 (m, 1H; C_6H_4), 6.90–6.94 (m, 1H; C_6H_4), 6.99–7.04 (m, 1H; C_6H_4), 7.11–7.15 ppm (m, 1H; C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): $\delta=23.3$, 43.5, 116.3 (d, $J_{(C,CF)}=$ 20.6 Hz), 122.0 (d, $J_{(C,CCF)}=7.4$ Hz), 124.9 (d, $J_{(C,CCF)}=3.3$ Hz), 126.3 (d, $J_{(C,CCF)}=3.3$ Hz), 139.1 (d, $J_{(C,CF)}=13.2$ Hz), 150.2, 156.1 ppm (d, $J_{(C,F)}=$ 243.2 Hz); IR (Nujol): $\tilde{\nu}=3254$, 2953, 2924, 2853, 1638, 1603, 1512, 1460, 1377, 1263, 1125, 864, 723 cm^{-1}; HRMS: *m*/*z* calcd for $C_{13}H_{21}FN_3$: 238.1720 $[M+H]^+$; found: 238.1713.

2-(2-Iodophenyl)-1,3-diisopropylguanidine (14): Colorless solid, yield 97%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.93$ (d, $J=6.8$ Hz, 12H; CH_3), 3.32 (br, 2H; NH), 3.59–3.68 (m, 2H; CH), 6.41–6.45 (m, 1H; C_6H_4), 6.94–6.96 (m, 1H; C_6H_4), 7.03–7.07 (m, 1H; C_6H_4), 7.84–7.87 ppm (m, 1H; C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): $\delta=23.7$, 43.5, 97.3, 122.9, 123.1, 129.3, 139.6, 149.3, 152.6 ppm; IR (Nujol): $\tilde{\nu}=3292$, 2953, 2924, 2853, 1602, 1572, 1535, 1458, 1377, 1271, 1015, 810, 762, 729 cm^{-1}; HRMS: *m*/*z* calcd for $C_{13}H_{21}N_3I$: 346.0780 $[M+H]^+$; found: 346.0748.

1,3-Diisopropyl-2-(2-methoxyphenyl)guanidine (15): Colorless solid, yield >99%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.95$ (d, $J=6.4$ Hz, 12H; CH_3), 3.48 (s, 3H; OCH_3), 3.55 (br, 2H; NH), 3.69–3.76 (m, 2H; CH), 6.77 (d, $J=8.0$ Hz, 1H; C_6H_4), 6.87–6.96 (m, 2H; C_6H_4), 7.10 ppm (d, $J=7.6$ Hz, 1H; C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): $\delta=23.5$, 43.5, 55.7, 113.2, 122.0, 122.1, 125.0, 140.8, 149.9, 152.7 ppm; IR (Nujol): $\tilde{\nu}=3312$, 3254, 2955, 2924, 2853, 1649, 1618, 1551, 1462, 1379, 1260, 1229, 1117, 1032, 741 cm^{-1}; HRMS: *m*/*z* calcd for $C_{14}H_{24}N_3O$: 250.1919 $[M+H]^+$; found: 250.1887.

2-(2-Biphenyl)-1,3-dicyclohexylguanidine (16): Colorless solid, yield 98%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.70$–1.78 (m, 20H; Cy), 3.31 (br, 2H; NH), 3.45–3.47 (m, 2H; CH), 6.99–7.03 (m, 1H; $C_{12}H_9$), 7.12–7.18 (m, 2H; $C_{12}H_9$), 7.21–7.30 (m, 3H; $C_{12}H_9$), 7.45–7.47 (m, 1H; $C_{12}H_9$), 7.74–7.77 ppm (m, 2H; $C_{12}H_9$); ^{13}C NMR (100 MHz, C_6D_6): $\delta=25.4$, 26.1, 34.1, 50.4, 122.1, 124.5, 126.4, 127.8, 128.7, 129.8, 131.1, 135.7, 142.0, 148.2, 148.8 ppm; IR (Nujol): $\tilde{\nu}=3374$, 3271, 2953, 2924, 2853, 1612, 1587, 1547, 1452, 1377, 889, 732, 698 cm^{-1}; HRMS: *m*/*z* calcd for $C_{25}H_{34}N_3$: 376.2753 $[M+H]^+$; found: 376.2740.

***tert*-Butyl-3-ethyl-2-(naphthalen-1-yl)guanidine (17)**: Colorless solid, yield 96%; ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.62$ (t, $J=7.2$ Hz, 3H; CH_2CH_3), 1.36 (s, 9H; $C(CH_3)_3$), 2.57–2.64 (m, 2H; CH_2CH_3), 3.52 (br, 2H; NH), 7.06 (d, $J=7.2$ Hz, 1H; $C_{10}H_7$), 7.31–7.40 (m, 3H; $C_{10}H_7$), 7.45 (d, $J=8.4$ Hz, 1H; $C_{10}H_7$), 7.74 (d, $J=7.6$ Hz, 1H; $C_{10}H_7$), 8.50 ppm (d, $J=8.4$ Hz, 1H; $C_{10}H_7$); ^{13}C NMR (100 MHz, C_6D_6): $\delta=15.2$, 30.1, 37.3, 50.9, 117.4, 121.3, 124.9, 125.2, 126.1, 126.9, 128.2, 130.3, 135.6, 148.1, 149.9 ppm; IR (Nujol): $\tilde{\nu}=3449$, 3412, 2953, 2924, 2853, 1634, 1570, 1521, 1458, 1379, 1211, 775 cm^{-1}; HRMS: *m*/*z* calcd for $C_{17}H_{24}N_3$: 270.1970 $[M+H]^+$; found: 270.1979.

Typical procedures for the catalytic reaction of heterocyclic primary amines to carbodiimides: In the glovebox, a solution of 5-methylisoxazol-3-amine (197 mg, 2.01 mmol) in THF (3 mL) was added to a solution of **1** (6 mg, 0.01 mmol) in THF (2 mL) in a Schlenk tube. *N*,*N*′-Diisopropylcarbodiimide (252 mg, 2.00 mmol) was then added to the above reaction mixture. The Schlenk tube was taken outside the glovebox and the mixture was stirred at room temperature for 1 h. After the solvent was removed under reduced pressure, the residue was extracted with ether and filtered to give a clean solution. After removing the solvent under vacuum, the residue was recrystallized in diethyl ether to provide colorless solid **18** (445 mg, 99% yield).

The ^{1}H NMR signals for the NH protons in **18**–**20** and **23**–**26** were not observed probably due to broadening.

1,3-Diisopropyl-2-(5-methylisoxazol-3-yl)guanidine (18): Colorless solid, yield >99%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.23$ (d, $J=6.4$ Hz, 12H; $CH(CH_3)_2$), 2.29 (s, 3H; CH_3), 3.86 (br, 2H; $CH(CH_3)_2$), 5.67 ppm (s, 1H; CH(isoxazolyl)); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=12.2$, 23.3, 43.0, 100.7, 153.1, 166.3, 168.1 ppm; IR (Nujol): $\tilde{\nu}=3382$, 3299, 3188, 2955, 2923, 2854, 1608, 1540, 1482, 1466, 1410, 1376, 1344, 1257, 1174, 1128,

1018, 811, 792 cm^{-1}; HRMS: *m/z* calcd for $C_{11}H_{21}N_4O$: 225.1715 $[M+H]^+$; found: 225.1712.

1,3-Dicyclohexyl-2-(5-methylisoxazol-3-yl)guanidine (19): Colorless solid, yield >99%; ^1H NMR (400 MHz, C_6D_6): $\delta=1.00$–1.96 (m, 23H; Cy and CH_3), 3.55–3.59 (m, 2H; CH(Cy)), 5.82 ppm (s, 1H; CH(isoxazolyl)); ^{13}C NMR (100 MHz, C_6D_6): $\delta=12.1$, 25.1, 26.1, 33.8, 50.1, 101.6, 153.5, 166.4, 169.1 ppm; IR (Nujol): $\tilde{\nu}=3409$, 3300, 2954, 2925, 2854, 1604, 1536, 1478, 1463, 1410, 1376, 1259, 1152, 1120, 890, 799 cm^{-1}; HRMS: *m/z* calcd for $C_{17}H_{29}N_4O$: 305.2341 $[M+H]^+$; found: 305.2344.

(*E*)-*tert*-Butyl-3-ethyl-2-(5-methylisoxazol-3-yl)guanidine (20): Colorless solid, yield >99%; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.20$ (t, $J=7.2$ Hz, 3H; CH_2CH_3), 1.39 (s, 9H; $C(CH_3)_3$), 2.25 (s, 3H; CH_3), 3.17–3.23 (m, 2H; CH_2CH_3), 5.62 ppm (s, 1H; CH(isoxazolyl)); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=12.3$, 14.9, 29.9, 36.5, 51.0, 100.9, 153.7, 166.3, 167.9 ppm; IR (Nujol): $\tilde{\nu}=3441$, 3298, 3189, 2962, 2923, 2854, 1603, 1555, 1475, 1410, 1376, 1354, 1331, 1256, 1238, 1217, 882, 791, 735 cm^{-1}; HRMS: *m/z* calcd for $C_{11}H_{21}N_4O$: 225.1715 $[M+H]^+$; found: 225.1714.

(*E*)-*tert*-Butyl-3-ethyl-2-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)guanidine (21): Colorless crystals, yield >99%. Single crystals suitable for X-ray analysis were grown in diethyl ether/hexane at room temperature for one day. ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.16$ (t, $J=7.2$ Hz, 3H; CH_2CH_3), 1.32 (s, 9H; $C(CH_3)_3$), 2.28 (s, 3H; CH_3), 3.12–3.19 (m, 2H; CH_2CH_3), 4.14 (br, 1H; NH), 4.38 (br, 1H; NH), 5.55 (s, 1H; CH(pyrazolyl)), 7.16 (t, $J=7.6$ Hz, 1H; *p*-C_6H_5), 7.33 (t, $J=7.6$ Hz, 2H; *m*-C_6H_5), 7.73 ppm (d, $J=7.6$ Hz, 2H; *o*-C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 14.4, 15.0, 30.0, 36.7, 51.0, 94.1, 123.4, 125.1, 128.0, 140.2, 148.6, 148.7, 151.7 ppm; IR (Nujol): $\tilde{\nu}=3321$, 3099, 2955, 2924, 2854, 1617, 1597, 1570, 1542, 1499, 1454, 1378, 1365, 1298, 1184, 1014, 906, 762, 693 cm^{-1}; HRMS: *m/z* calcd for $C_{17}H_{26}N_5$: 300.2188 $[M+H]^+$; found: 300.2181.

1,3-Diisopropyl-2-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)guanidine (22): Colorless solid, yield >99%; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.13$ (d, $J=6.4$ Hz, 12H; $CH(CH_3)_2$), 2.28 (s, 3H; CH_3), 3.72–3.80 (m, 2H; $CH(CH_3)_2$), 4.19 (br, 2H; NH), 5.55 (s, 1H; CH(pyrazolyl)), 7.15 (t, $J=$ 7.6 Hz, 1H; *p*-C_6H_5), 7.32 (dd, $J=7.6$, 8.0 Hz, 2H; *m*-C_6H_5), 7.77 ppm (d, $J=8.0$ Hz, 2H; *o*-C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.3$, 23.3, 43.0, 94.3, 122.9, 124.8, 127.8, 140.1, 148.5, 148.6, 150.9 ppm; IR (Nujol): $\tilde{\nu}=3363$, 3315, 2952, 2924, 2854, 1598, 1556, 1534, 1500, 1462, 1378, 1360, 1128, 1029, 907, 762, 719, 694 cm^{-1}; HRMS: *m/z* calcd for $C_{17}H_{26}N_5$: 300.2188 $[M+H]^+$; found: 300.2180.

1,3-Diisopropyl-2-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)guanidine (23): Colorless solid, yield >99%; ^1H NMR (300 MHz, C_6D_6): $\delta=1.16$ (d, $J=$ 6.3 Hz, 12H; $CH(CH_3)_2$), 3.32 (m, 3H; CH_3), 3.55 (br, 2H; $CH(CH_3)_2$), 6.99 (d, $J=7.8$ Hz, 1H; C_6H_4), 7.14–7.27 (m, 2H; C_6H_4), 7.86 ppm (d, $J=$ 8.4 Hz, 1H; C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): $\delta=23.1$, 27.7, 42.9, 107.7, 116.7, 119.8, 121.0, 134.4, 142.6, 154.6, 158.3 ppm; IR (Nujol): $\tilde{\nu}=3435$, 3230, 2956, 2924, 2854, 1623, 1610, 1510, 1466, 1383, 1317, 1286, 1120, 1009, 748 cm^{-1}; HRMS: *m/z* calcd for $C_{15}H_{24}N_5$: 274.2032 $[M+H]^+$; found: 274.2039.

1,3-Diisopropyl-2-(4-methylthiazol-2-yl)guanidine (24): Colorless solid, yield >99%; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.23$ (d, $J=6.4$ Hz, 12H; $CH(CH_3)_2$), 2.22 (s, 3H; CH_3), 3.87 (br, 2H; $CH(CH_3)_2$), 6.08 ppm (s, 1H; CH(thiazolyl)); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=17.6$, 23.2, 42.6, 102.5, 146.9, 152.4, 175.1 ppm; IR (Nujol): $\tilde{\nu}=3423$, 3232, 3103, 2955, 2924, 2854, 1606, 1560, 1465, 1408, 1384, 1340, 1261, 1176, 1126, 1058, 1013, 855, 800, 727 cm^{-1}; HRMS: *m/z* calcd for $C_{11}H_{21}N_4S$: 241.1487 $[M+H]^+$; found: 241.1480.

2-(6-Chlorobenzo[*d*]thiazol-2-yl)-1,3-diisopropylguanidine (25): Colorless solid, yield >99%; ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.26$ (d, $J=6.6$ Hz, 12H; CH_3), 3.91 (br, 2H; CH), 7.18 (d, $J=8.4$ Hz, 1H; C_6H_3), 7.38 (d, $J=8.4$ Hz, 1H; C_6H_3), 7.53 ppm (s, 1H; C_6H_3)); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=23.1$, 43.0, 119.3, 120.2, 125.3, 126.7, 132.6, 150.6, 153.7, 174.6 ppm; IR (Nujol): $\tilde{\nu}=3456$, 3236, 2953, 2924, 2854, 1606, 1555, 1488, 1445, 1378, 1330, 1273, 1174, 1126, 1100, 1048, 810, 731 cm^{-1}; HRMS: *m/z* calcd for $C_{14}H_{20}ClN_4S$: 311.1097 $[M+H]^+$; found: 311.1117.

1,3-Diisopropyl-2-(pyridin-2-yl)guanidine (26): Colorless solid, yield >99%; ^1H NMR (400 MHz, C_6D_6): $\delta=1.03$ (d, $J=6.4$ Hz, 12H; CH_3), 3.80 (br, 2H; CH), 6.40–6.44 (m, 1H; C_5H_4N), 7.18–7.20 (m, 2H; C_5H_4N), 8.18 ppm (m, 1H; C_5H_4N); ^{13}C NMR (100 MHz, C_6D_6): $\delta=23.7$, 42.7, 114.1, 121.3, 136.7, 145.4, 153.8, 164.6 ppm; IR (Nujol): $\tilde{\nu}=3454$, 3422, 2953, 2924, 2853, 1622, 1589, 1547, 1464, 1433, 1377, 1172, 785, 725 cm^{-1}; HRMS: *m/z* calcd for $C_{12}H_{21}N_4$: 221.1766 $[M+H]^+$; found: 221.1762.

(*i*PrNH)$_2$C{N-(1,3-C$_6$H$_4$)-N}C(*i*PrNH)$_2$ (27): In the glovebox, a solution of diamine (218 mg, 2.02 mmol) in benzene (3 mL) was added to a solution of **1** (12 mg, 0.02 mmol) in benzene (2 mL) in a Schlenk tube. Then *N,N'*-diisopropylcarbodiimide (505 mg, 4.00 mmol) was added to the above reaction mixture. The Schlenk tube was taken outside the glovebox and the mixture was stirred at 80°C for 1 h. After the solvent was removed under reduced pressure, the residue was extracted with diethyl ether and filtered to give a clean solution. After removing the solvent under vacuum, the residue was recrystallized in ether to provide a colorless solid **27**. Isolated yield >99%; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.14$ (d, $J=6.4$ Hz, 24H; CH_3), 3.54 (br, 4H; NH), 3.70–3.76 (m, 4H; CH), 6.38 (s, 1H; C_6H_4), 6.44 (d, $J=7.6$ Hz, 2H; C_6H_4), 7.12 ppm (t, $J=7.6$ Hz, 1H; C_6H_4); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=23.3$, 43.2, 117.0, 118.5, 129.7, 149.7, 151.1 ppm; IR (Nujol): $\tilde{\nu}=3378$, 2955, 2923, 2854, 1610, 1582, 1560, 1459, 1438, 1384, 1261, 1126, 801 cm^{-1}; HRMS: *m/z* calcd for $C_{20}H_{37}N_6$: 361.3080 $[M+H]^+$; found: 361.3062.

{(*i*PrNH)$_2$C=N}$_3$(2,4,6-C$_4$HN$_2$) (28): In the glovebox, a solution of triamine (253 mg, 2.02 mmol) in benzene (3 mL) was added to a solution of **1** (12 mg, 0.02 mmol) in benzene (2 mL) in a Schlenk tube. Then *N,N'*-diisopropylcarbodiimide (757 mg, 6.00 mmol) was added to the above reaction mixture. The Schlenk tube was taken outside the glovebox and the mixture was stirred at 110°C for 3 h. The isolation and purification processes were similar to those for **27**. Colorless solid, yield 97%; ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.18$–1.22 (m, 36H; CH_3), 3.49 (br, 6H; NH), 3.82–3.93 (m, 6H; CH), 5.82 ppm (s, 1H; C_4HN_2); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=23.4$, 23.5, 42.6, 42.7, 100.1, 153.3, 153.8, 163.3, 168.3 ppm; IR (Nujol): $\tilde{\nu}=3355$, 2955, 2924, 2854, 1617, 1507, 1462, 1378, 1170, 1126, 1019, 801, 721 cm^{-1}; HRMS: *m/z* calcd for $C_{25}H_{50}N_{11}$: 504.4251 $[M+H]^+$; found: 504.4278.

Typical procedures for catalytic addition of secondary amines to carbodiimides: i) NMR tube reaction: In the glovebox, a J. Young valve NMR tube was charged with **1** (12 mg, 0.02 mmol), C_6D_6 (0.5 mL), diethylamine (50 mg, 0.67 mmol), *N,N'*-diisopropylcarbodiimide (85 mg, 0.67 mmol). The tube was taken outside the glovebox and heated at 80°C in an oil bath. Formation of **29** was easily monitored by ^1H NMR spectroscopy and 1,3,5-trimethylbenzene used as an internal standard. The reaction was completed in 3 h. No other coupling products were observed.

ii) Preparative-scale reaction: In the glovebox, a solution of diethylamine (150 mg, 2.06 mmol) in benzene (3 mL) was added to a solution of **1** (36 mg, 0.06 mmol) in benzene (2 mL) in a Schlenk tube. Then *N,N'*-diisopropylcarbodiimide (252 mg, 2.00 mmol) was added to the above reaction mixture. The Schlenk tube was taken outside the glovebox 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 solution volume was reduced under vacuum to about 2 mL, and cooled to −30°C for two days. A colorless oil **29** of analytical purity was obtained after filtration and removing the solvent under vacuum. The guanidines **30** and **31** were purified analogously. Guanidines **32**–**37** were purified by recrystallization in hexane to provide a colorless solid.

(*E*)-Diethyl-2,3-diisopropylguanidine (29): Colorless oil, yield 95%; ^1H NMR (400 MHz, C_6D_6): $\delta=0.92$ (d, $J=6.4$ Hz, 6H; $NCH(CH_3)_2$), 1.07 (t, $J=6.8$ Hz, 6H; CH_2CH_3), 1.22 (d, $J=6.4$ Hz, 6H; $NHCH(CH_3)_2$), 2.97 (br, 1H; NH), 3.14 (q, $J=6.8$ Hz, 4H; CH_2CH_3), 3.30–3.43 ppm (m, 2H; CH); ^{13}C NMR (100 MHz, C_6D_6): $\delta=13.2$, 24.0, 25.7, 43.4, 46.3, 47.9, 153.1 ppm; IR (Nujol): $\tilde{\nu}=3396$, 2963, 2925, 2855, 1637, 1466, 1376, 1166, 1124, 1050, 800 cm^{-1}; HRMS: *m/z* calcd for $C_{11}H_{26}N_3$: 200.2127 $[M+H]^+$; found: 200.2119.

(*E*)-Isobutyl-2,3-diisopropyl(methyl)guanidine (30): Colorless oil, yield 92%; ^1H NMR (400 MHz, C_6D_6): $\delta=0.88$ (d, $J=6.8$ Hz, 6H; $CH(CH_3)_2$), 0.91 (d, $J=6.4$ Hz, 6H; $NCH(CH_3)_2$), 1.25 (d, $J=6.4$ Hz, 6H; $NHCH(CH_3)_2$), 1.86–1.93 (m, 1H; $CH(CH_3)_2$), 2.69 (s, 3H; CH_3), 2.97 (br, 1H; NH), 3.02 (d, $J=7.2$ Hz, 2H; CH_2), 3.30–3.36 ppm (m, 2H; CH);

^{13}C NMR (100 MHz, C_6D_6): δ = 20.8, 23.8, 25.8, 27.3, 37.9, 46.3, 47.9, 59.0, 154.9 ppm; IR (Nujol): $\tilde{\nu}$ = 3397, 2957, 2924, 2853, 1636, 1460, 1377, 1165, 1125, 1034, 953 cm^{-1}; HRMS: *m*/*z* calcd for $C_{12}H_{28}N_3$: 214.2283 $[M+H]^+$; found: 214.2282.

(*E*)-Diallyl-2,3-diisopropylguanidine (31): Colorless oil, yield 93%; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.88 (d, *J* = 6.4 Hz, 6H; NCH(CH_3)$_2$), 1.22 (d, *J* = 6.4 Hz, 6H; NHCH(CH_3)$_2$), 2.98 (br, 1H; NH), 3.29–3.41 (m, 2H; CH), 3.83 (d, *J* = 6.0 Hz, 4H; CH_2), 5.04–5.18 (m, 4H; −CH=CH_2), 5.91–6.01 ppm (m, 2H; −CH=CH_2); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.8, 25.7, 46.3, 47.9, 51.3, 116.1, 136.2, 153.3 ppm; IR (Nujol): $\tilde{\nu}$ = 3397, 2959, 2924, 2855, 1632, 1452, 1383, 1273, 1260, 1165, 1125, 916 cm^{-1}; HRMS: *m*/*z* calcd for $C_{13}H_{26}N_3$: 224.2127 $[M+H]^+$; found: 224.2134.

(*E*)-*N*,*N*′-Diisopropylisoindoline-2-carboxamidine (32): Colorless solid, yield >99%; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.95 (d, *J* = 6.4 Hz, 6H; NCH(CH_3)$_2$), 1.29 (d, *J* = 6.4 Hz, 6H; NHCH(CH_3)$_2$), 3.11 (br, 1H; NH), 3.30–3.36 (m, 1H; CH), 3.39–3.45 (m, 1H; CH), 4.69 (s, 4H; CH_2), 6.95–6.97 (m, 2H; C_6H_4), 7.02–7.05 ppm (m, 2H; C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ = 24.2, 26.2, 46.6, 47.9, 54.5, 122.6, 126.9, 138.9, 152.3 ppm; IR (Nujol): $\tilde{\nu}$ = 3387, 2957, 2924, 2853, 1632, 1462, 1384, 1346, 1163, 1124, 1089, 741 cm^{-1}; HRMS: *m*/*z* calcd for $C_{15}H_{24}N_3$: 246.1970 $[M+H]^+$; found: 246.1969.

(*E*)-*N*,*N*′-Diisopropyl-2-((pyrrolidin-1-yl)methyl)pyrrolidine-1-carboxamidine (33): Colorless solid, yield 90%; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.96 (d, *J* = 6.0 Hz, 3H; CH(CH_3)$_2$), 0.98 (d, *J* = 6.0 Hz, 3H; CH(CH_3)$_2$), 1.19 (d, *J* = 6.0 Hz, 3H; CH(CH_3)$_2$), 1.31 (d, *J* = 6.0 Hz, 3H; CH(CH_3)$_2$), 1.47–3.17 (m, 16H; CH_2), 3.31–3.43 (m, 3H; NH and CH(CH_3)$_2$), 4.46–4.52 ppm (m, 1H; CH); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.6, 24.3, 24.7, 25.1, 25.7, 26.4, 31.1, 46.0, 47.8, 50.2, 55.1, 56.4, 61.4, 152.2 ppm; IR (Nujol): $\tilde{\nu}$ = 3394, 3233, 2960, 2925, 2854, 1630, 1460, 1377, 1342, 1262, 1164, 1084, 1019, 950, 889, 800 cm^{-1}; HRMS: *m*/*z* calcd for $C_{16}H_{33}N_4$: 281.2705 $[M+H]^+$; found: 281.2725.

(*E*)-*N*,*N*′-Dicyclohexyl-4-(pyrrolidin-1-yl)piperidine-1-carboxamidine (34): Colorless solid, yield 95%; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.83–2.00 (m, 24H; CH_2(Cy) and CH_2(pyrrolidine ring)), 2.38 (br, 4H; CH_2(piperidine ring)), 2.75–2.80 (m, 4H; CH_2 (pyrrolidine ring)), 3.07–3.15 (m, 3H; CH), 3.24 (br, 1H; NH), 3.75–3.48 ppm (d, 4H; CH_2 (piperidine ring)); ^{13}C NMR (100 MHz, C_6D_6): δ = 24.0, 25.6, 26.0, 26.2, 26.8, 32.2, 35.0, 36.1, 47.5, 51.6, 54.0, 56.2, 62.6, 154.4 ppm; IR (Nujol): $\tilde{\nu}$ = 3397, 2953, 2924, 2853, 1630, 1454, 1377, 1260, 1231, 1020, 889, 802, 721 cm^{-1}; HRMS: *m*/*z* calcd for $C_{22}H_{41}N_4$: 361.3331 $[M+H]^+$; found: 361.3359.

(*E*)-*N*,*N*′-Dicyclohexyl-3,4-dihydroisoquinoline-2(1*H*)-carboxamidine (35): Colorless single crystals suitable for X-ray analysis were grown in ether/hexane at room temperature for one day, yield >99%; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.84–1.90 (m, 20H; CH_2(Cy)), 2.77 (t, *J* = 6.0 Hz, 2H; CH_2), 3.06–3.19 (m, 2H; CH), 3.31 (br, 1H; NH), 3.41 (t, *J* = 6.0 Hz, 2H; CH_2), 4.50 (s, 2H; CH_2), 6.91–7.02 ppm (m, 4H; C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ = 25.6, 25.9, 26.1, 26.8, 29.9, 35.0, 36.1, 46.9, 50.8, 53.9, 56.3, 126.0, 126.1, 126.9, 129.0, 135.2, 135.9, 154.0 ppm; IR (Nujol): $\tilde{\nu}$ = 3387, 2951, 2924, 2853, 1624, 1466, 1377, 1274, 1240, 1141, 1105, 1033, 887, 731 cm^{-1}; HRMS: *m*/*z* calcd for $C_{22}H_{34}N_3$: 340.2753 [M+H]$^+$; found: 340.2779.

(*E*)-*N*,*N*′-Diisopropyl-4-(pyridin-2-yl)piperazine-1-carboxamidine (36): Colorless solid, yield >99%; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.91 (d, *J* = 6.4 Hz, 6H; NCH(CH_3)$_2$), 1.21 (d, *J* = 6.4 Hz, 6H; NHCH(CH_3)$_2$), 3.00 (br, 1H; NH), 3.24 (t, *J* = 5.2 Hz, 4H; CH_2), 3.27–3.40 (m, 2H; CH), 3.47 (t, *J* = 5.2 Hz, 4H; CH_2), 6.27 (d, *J* = 8.8 Hz, 1H; C_5H_4N), 6.37–6.40 (m, 1H; C_5H_4N), 7.11–7.15 (m, 1H; C_5H_4N), 8.27–8.29 ppm (m, 1H; C_5H_4N); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.9, 25.6, 45.5, 46.4, 47.6, 48.5, 107.1, 113.2, 137.0, 148.3, 154.2, 160.0 ppm; IR (Nujol): $\tilde{\nu}$ = 3399, 2957, 2924, 2853, 1638, 1593, 1460, 1377, 1242, 1161, 775 cm^{-1}; HRMS: *m*/*z* calcd for $C_{16}H_{28}N_5$: 290.2345 $[M+H]^+$; found: 290.2351.

(1*E*,4*E*)-*N*1,*N*1′,*N*4,*N*4′-Tetraisopropylpiperazine-1,4-dicarboxamidine (37): Colorless solid, yield 99%; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.87 (d, *J* = 6.4 Hz, 12H; NCH(CH_3)$_2$), 1.23 (d, *J* = 6.0 Hz, 12H; NHCH(CH_3)$_2$), 2.96 (br, 2H; NH), 3.25 (s, 8H; CH_2), 3.27–3.41 ppm (m, 4H; CH); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.9, 25.7, 46.4, 47.5, 49.0, 154.6 ppm; IR (Nujol): $\tilde{\nu}$ = 3372, 2955, 2924, 2853, 1636, 1609, 1456, 1381, 1254, 1163, 1099, 1005, 930, 721 cm^{-1}; HRMS: *m*/*z* calcd for $C_{18}H_{39}N_6$: 339.3236 $[M+H]^+$; found: 339.3230.

Preparation of guanidines 38 and 39: In the glovebox, a solution of 1,2,3,4-tetrahydro-5-aminoisoquinodine (305 mg, 2.06 mmol) in benzene (3 mL) was added to a solution of **1** (36 mg, 0.06 mmol) in benzene (2 mL) in a Schlenk tube. Then *N*,*N*′-diisopropylcarbodiimide (252 mg, 2.00 mmol) was added to the above reaction mixture. The Schlenk tube was taken outside the glovebox and the mixture was stirred at 80°C for 1 h. After the solvent was removed under reduced pressure, the residue was extracted with ether and filtered to give a clean solution. After removing the solvent under vacuum, the residue was recrystallized in diethyl ether to provide colorless solid **38**. If two equivalents of *N*,*N*′-diisopropylcarbodiimide (504 mg, 4.00 mmol) were added and the reaction was carried out at 110°C for 3 h, the biguanidine **39** was obtained.

2-(1,2,3,4-Tetrahydroisoquinolin-5-yl)-1,3-diisopropylguanidine (38): Colorless solid, yield 99%; ^{1}H NMR (400 MHz, C_6D_6): δ = 0.90 (d, *J* = 6.0 Hz, 12H; CH_3), 2.81 (t, *J* = 6.0 Hz, 2H; $CH_2NCH_2CH_2$), 2.92–2.96 (m, 2H; $CH_2NCH_2CH_2$), 3.36 (d, 2H; $CH_2NCH_2CH_2$), 3.64 (br, 3H; NH), 3.86–3.87 (m, 2H; CH), 6.65 (d, *J* = 7.6 Hz, 1H; C_6H_3), 6.91 (d, *J* = 8.0 Hz, 1H; C_6H_3), 7.13 ppm (dd, *J* = 7.6, 8.0 Hz, 1H; C_6H_3); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.6, 26.7, 43.5, 45.1, 49.6, 119.8, 120.1, 126.4, 129.4, 138.0, 148.6, 149.6 ppm; IR (Nujol): $\tilde{\nu}$ = 3327, 3296, 2957, 2924, 2853, 1612, 1576, 1524, 1454, 1377, 1263, 1123, 1062, 808, 743 cm^{-1};HRMS: *m*/*z* calcd for $C_{16}H_{27}N_4$: 275.2236 $[M+H]^+$; found: 275.2225.

2-((*E*)-2-Amidino-1,2,3,4-tetrahydroisoquinolin-5-yl)-1,3-diisopropylguanidine (39): Colorless solid, yield 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.8 Hz, 6H; CH_3), 1.12 (d, *J* = 6.4 Hz, 6H; CH_3), 1.17 (d, *J* = 6.4 Hz, 12H; CH_3), 2.68 (t, *J* = 5.6 Hz, 2H; $CH_2NCH_2CH_2$), 3.34–3.38 (m, 3H; $CH_2NCH_2CH_2$ and CH), 3.43–3.50 (m, 1H; CH), 3.73–3.80 (m, 2H; CH), 4.26 (s, 2H; $CH_2NCH_2CH_2$), 6.62 (d, *J* = 7.6 Hz, 1H; C_6H_3), 6.75 (d, *J* = 7.6 Hz, 1H; C_6H_3), 7.04 ppm (t, *J* = 7.6 Hz, 1H; C_6H_3); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.4, 23.7, 25.0, 26.1, 43.1, 46.1, 46.3, 47.3, 49.9, 119.8, 119.9, 125.9, 128.7, 136.2, 147.8, 148.6, 154.9 ppm; IR (Nujol): $\tilde{\nu}$ = 3314, 3275, 2953, 2924, 2853, 1643, 1605, 1578, 1535, 1454, 1377, 1258, 1165, 1126, 1043, 721 cm^{-1}; HRMS: *m*/*z* calcd for $C_{23}H_{41}N_6$: 401.3393 $[M+H]^+$; found: 401.3385. The ^{1}H NMR signals for the NH protons in **39** were not observed probably due to broadening.

Isolation of the amido complex [{Me$_2$Si(C$_5$Me$_4$)(NPh)}Y(NEt$_2$)(thf)$_2$] (40): In the glovebox, a solution of diethylamine (36 mg, 0.485 mmol) in benzene (3 mL) was added to a solution of **1** (286 mg, 0.485 mmol) in benzene (2 mL) in a flask. After 10 min, the solvent was removed under reduced pressure. The residue was extracted with THF and filtered to give a clean solution. The solution volume was reduced under vacuum to precipitate **40** as colorless crystalline powder (265 mg, 0.461 mmol, 95% yield). Single crystals of **40** suitable for X-ray analysis were grown in THF at −30°C for 3 d. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.92 (s, 6H; $SiMe_2$), 1.16 (t, *J* = 6.8 Hz, 6H; CH_2CH_3), 1.32 (br, 8H; β-CH_2, THF), 2.14 (s, 6H; C_5Me_4), 2.16 (s, 6H; C_5Me_4), 3.15 (q, *J* = 6.8 Hz, 4H; CH_2CH_3), 3.61 (br, 8H; α-CH_2, THF), 6.68 (t, *J* = 7.6 Hz, 1H; *p*-C_6H_5), 6.76 (d, *J* = 7.6 Hz, 2H; *o*-C_6H_5), 7.25 ppm (t, *J* = 7.6 Hz, 2H; *m*-C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ = 5.1, 11.7, 14.3, 16.4, 25.8, 44.3, 69.3, 106.1, 114.3, 120.0, 121.6, 126.5 (d, $J_{(Y,C)}$ = 2.5 Hz), 129.7, 157.0 ppm; IR (Nujol): $\tilde{\nu}$ = 2954, 2923, 2854, 1587, 1479, 1460, 1377, 1293, 1251, 1178, 1076, 1026, 918, 829, 800, 759, 691 cm^{-1}; elemental analysis calcd for $C_{29}H_{49}N_2O_2SiY$: C 60.61, H 8.59, N 4.87; found: C 60.22, H8.37, N 5.19.

Isolation of the guanidinate complex [{Me$_2$Si(C$_5$Me$_4$)(NPh)}Y{*i*PrNC(NEt$_2$)(N*i*Pr)}(thf)] (41): In the glovebox, a solution of diethylamine (31 mg, 0.429 mmol) in benzene (3 mL) was added to a solution of **1** (253 mg, 0.429 mmol) in benzene (2 mL) in a flask. Then *N*,*N*′-diisopropylcarbodiimide (54 mg, 0.429 mmol) was added to the above reaction mixture. After 0.5 h, the solvent was removed under reduced pressure. The residue was extracted with hexane and filtered to give a clean solution. The solution volume was reduced under vacuum to precipitate **41** as colorless crystalline powder (248 mg, 0.395 mmol, 92% yield). Single crystals of **41** suitable for X-ray analysis were grown in THF/hexane at −30°C for one week. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.96 (s, 6H; $SiMe_2$), 0.99 (t, *J* = 7.2 Hz, 6H; CH_2CH_3), 1.07 (d, *J* = 6.4 Hz, 12H; CH(CH_3)$_2$), 1.16 (br, 4H; β-CH_2, THF), 2.11 (s, 6H; C_5Me_4), 2.38 (s, 6H; C_5Me_4),

2.88 (q, $J=7.2$ Hz, 4H; CH_2CH_3), 3.47–3.54 (m, 2H; $CH(CH_3)_2$), 3.71 (br, 4H; α-CH_2, THF), 6.68 (t, $J=7.6$ Hz, 1H; *p*-C_6H_5), 6.74 (d, $J=7.6$ Hz, 2H; *o*-C_6H_5), 7.18 ppm (t, $J=7.6$ Hz, 2H; *m*-C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): $\delta=5.1$, 12.2, 14.0, 15.7, 25.3, 26.2, 44.7, 47.1, 71.2, 107.4, 115.3, 121.0, 122.2, 127.2 (d, $J_{(Y,C)}=1.7$ Hz), 129.0, 156.4, 172.6 ppm (d, $J_{(Y,C)}=1.6$ Hz); IR (Nujol): $\tilde{\nu}=2956$, 2923, 2854, 1587, 1491, 1457, 1410, 1377, 1291, 1179, 1017, 921, 831, 801, 760 cm^{-1}; elemental analysis calcd for $C_{32}H_{55}N_4OSiY$: C 61.12, H 8.82, N 8.91; found: C 60.75, H 8.44, N 9.09.

Isolation of the amido complex [{$Me_2Si(C_5Me_4)$(NPh)}Y(NHC$_6$H$_4$Br-4)(thf)$_2$] (42): In the glovebox, a solution of 4-bromoaniline (83 mg, 0.485 mmol) in benzene (3 mL) was added to a solution of **1** (286 mg, 0.485 mmol) in benzene (2 mL) in a flask. After 10 min, the solvent was removed under reduced pressure. The residue was extracted with benzene/hexane (1:1) mixed solvent and filtered to give a clean solution. The solution volume was reduced under vacuum to precipitate **42** as colorless crystalline powder (314 mg, 0.466 mmol, 96% yield). Single crystals of **42**·0.5 THF suitable for X-ray analysis were grown in THF/hexane at room temperature for three days. ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.91$ (s, 6H; $SiMe_2$), 1.14 (br, 8H; β-CH_2, THF), 2.05 (s, 6H; C_5Me_4), 2.06 (s, 6H; C_5Me_4), 3.57 (br, 8H; α-CH_2, THF), 4.06 (s, 1H; NH), 6.17 (d, $J=8.8$ Hz, 2H; C_6H_5), 6.69–6.75 (m, 3H; C_6H_5 and C_6H_4), 7.24–7.28 ppm (m, 4H; C_6H_5 and C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): $\delta=5.0$, 11.4, 14.0, 25.5, 70.4, 103.0, 107.5, 115.1, 116.5, 120.0, 123.0, 126.8 (d, $J_{(Y,C)}=1.6$ Hz), 129.9, 132.5, 156.6, 157.9 ppm; IR (Nujol): $\tilde{\nu}=3420$, 2953, 2922, 2853, 1584, 1476, 1462, 1377, 1288, 1246, 1177, 1015, 910, 810, 752, 692 cm^{-1}; elemental analysis calcd for $C_{31}H_{44}BrN_2O_2SiY$: C 55.28, H 6.58, N 4.16; found: C 54.79, H 6.21, N 4.36.

Isolation of the guanidiate complex [{$Me_2Si(C_5Me_4)$(NPh)}Y{*i*PrNC(NHC$_6$H$_4$Br-4)(N*i*Pr)}(thf)] (43): In the glovebox, a solution of 4-bromoaniline (69 mg, 0.40 mmol) in THF (3 mL) was added to a solution of **1** (236 mg, 0.40 mmol) in THF (2 mL) in a flask at −30 °C. Then *N*,*N*′-diisopropylcarbodiimide (50 mg, 0.40 mmol) was added to the above reaction mixture. The reaction mixture was stirred at −30 °C for 2 h. After the solvent was removed under reduced pressure, the residue was extracted with cold hexane and filtered to give a clean solution. The solution volume was reduced under vacuum to precipitate **43** as colorless crystalline powder (279 mg, 0.384 mmol, 96% yield). The guanidinate compound **43** was stable at low temperature in solid state. At room temperature, it gradually changed to **44** in 15 h in C_6D_6. ^{1}H NMR (400 MHz, C_6D_6, 6 °C): $\delta=0.98$ (s, 6H; $SiMe_2$), 0.99 (d, $J=6.4$ Hz, 12H; NCH(CH_3)$_2$), 1.27 (br, 4H; β-CH_2, THF), 2.13 (s, 6H; C_5Me_4), 2.38 (s, 6H; C_5Me_4), 3.24–3.30 (m, 2H; NCH(CH_3)$_2$), 3.61 (br, 4H; α-CH_2, THF), 5.13 (s, 1H; NH), 6.55 (d, $J=8.8$ Hz, 2H; C_6H_4), 6.71 (t, $J=7.2$ Hz, 1H; C_6H_5), 6.80 (d, $J=8.4$ Hz, 2H; C_6H_5), 7.20 (dd, $J=7.2$, 8.4 Hz, 2H; C_6H_5), 7.26 ppm (d, $J=8.8$ Hz, 2H; C_6H_4); ^{13}C NMR (100 MHz, C_6D_6, 6 °C): $\delta=5.2$, 12.4, 15.3, 25.3, 25.6, 46.8, 69.7, 108.1, 113.4, 115.4, 118.6, 120.7, 122.9, 127.0 (d, $J_{(Y,C)}=1.6$ Hz), 129.2, 132.4, 142.2, 156.5, 163.2 ppm (d, $J_{(Y,C)}=1.7$ Hz); ^{1}H NMR (400 MHz, [D$_8$]THF, 0 °C): $\delta=0.61$ (s, 6H; $SiMe_2$), 0.98 (d, $J=6.4$ Hz, 12H; NCH(CH_3)$_2$), 2.10 (s, 6H; C_5Me_4), 2.23 (s, 6H; C_5Me_4), 3.36–3.43 (m, 2H; NCH(CH_3)$_2$), 3.57 (br, 1H; NH), 6.32 (t, $J=7.2$ Hz, 1H; C_6H_5), 6.48 (d, $J=8.4$ Hz, 2H; C_6H_5), 6.79 (d, $J=9.2$ Hz, 2H; C_6H_4), 6.84–6.90 (m, 2H; C_6H_5), 7.31 ppm (d, $J=9.2$ Hz, 2H; C_6H_4); ^{13}C NMR (100 MHz, [D$_8$]THF, 0 °C): $\delta=4.8$, 12.2, 14.4, 25.3, 26.3, 47.0, 68.1, 107.8, 111.7, 114.9, 118.0, 120.8, 122.8, 126.6 (d, $J_{(Y,C)}=2.4$ Hz), 128.7, 132.3, 143.7, 156.6, 164.3 ppm (d, $J_{(Y,C)}=1.6$ Hz); IR (Nujol): $\tilde{\nu}=3417$, 2956, 2924, 2854, 1587, 1530, 1488, 1462, 1378, 1285, 1177, 1017, 992, 918, 803, 760 cm^{-1}; elemental analysis calcd for $C_{34}H_{50}BrN_4OSiY$: C 56.12, H 6.93, N 7.70; found: C 55.65, H 6.70, N 7.32.

Isolation of the guanidiate complex [{$Me_2Si(C_5Me_4)$(NPh)}Y{*i*PrN=C(NC$_6$H$_4$Br-4)(NH*i*Pr)}(thf)] (44): In the glovebox, a solution of 4-bromoaniline (61 mg, 0.354 mmol) in benzene (3 mL) was added to a solution of **1** (209 mg, 0.354 mmol) in benzene (2 mL) in a Schlenk tube. Then *N*,*N*′-diisopropylcarbodiimide (45 mg, 0.354 mmol) was added to the above reaction mixture. The Schlenk tube was taken outside the glovebox and the mixture was stirred at 80 °C for 0.5 h. After the solvent was removed under reduced pressure, the residue was extracted with hexane and filtered to give a clean solution. The solution volume was reduced under vacuum to precipitate **44** as colorless crystalline powder (239 mg, 0.329 mmol, 93% yield). Single crystals of **44**·THF suitable for X-ray analysis were grown in THF at room temperature for one week. ^{1}H NMR (400 MHz, C_6D_6): $\delta=0.73$ (d, $J=6.4$ Hz, 6H; NCH(CH_3)$_2$), 0.94 (s, 6H; $SiMe_2$), 1.08 (d, $J=6.4$ Hz, 6H; NHCH(CH_3)$_2$), 1.19 (br, 4H; β-CH_2, THF), 2.01 (s, 6H; C_5Me_4), 2.24 (s, 6H; C_5Me_4), 3.04–3.11 (m, 1H; NCH(CH_3)$_2$), 3.20–3.25 (m, 1H; NHCH(CH_3)$_2$), 3.51 (br, 4H; α-CH_2, THF), 3.55 (s, 1H; NH), 6.68–6.81 (m, 5H; C_6H_5 and C_6H_4), 7.16–7.22 ppm (m, 4H; C_6H_5 and C_6H_4); ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta=0.56$ (s, 6H; $SiMe_2$), 0.98 (d, $J=6.4$ Hz, 6H; NCH(CH_3)$_2$), 1.07 (d, $J=6.4$ Hz, 6H; NHCH(CH_3)$_2$), 1.88 (s, 6H; C_5Me_4), 2.03 (s, 6H; C_5Me_4), 3.30–3.40 (m, 2H; CH(CH_3)$_2$), 4.33 (br, 1H; NH), 6.29 (t, $J=7.2$ Hz, 1H; C_6H_5), 6.48 (d, $J=8.0$ Hz, 2H; C_6H_5), 6.72 (d, $J=8.8$ Hz, 2H; C_6H_4), 6.82 (t, $J=8.0$ Hz, 2H; C_6H_5), 7.13 ppm (d, $J=8.8$ Hz, 2H; C_6H_4); ^{13}C NMR (100 MHz, THF-d_8): $\delta=5.2$, 11.8, 14.8, 23.4, 25.0, 26.6, 45.7, 46.4, 68.4, 107.8, 111.1, 115.2, 120.7, 123.5, 123.8, 126.9 (d, $J_{(Y,C)}=1.7$ Hz), 129.1, 132.1, 151.2, 156.9, 165.3 ppm (d, $J_{(Y,C)}=2.5$ Hz); IR (Nujol): $\tilde{\nu}=3387$, 2953, 2922, 2853, 1585, 1531, 1479, 1462, 1377, 1280, 1179, 1150, 991, 916,

Table 6. Crystallographic data and structure refinement details for **1**, **4**, **5**, and **40**.

	1·0.5 hexane	**4**·0.5 hexane	**5**·0.5 hexane	**40**
formula	$C_{32}H_{57}NO_2Si_2Y$	$C_{32}H_{57}NO_2Si_2Yb$	$C_{32}H_{57}LuNO_2Si_2$	$C_{29}H_{49}N_2O_2SiY$
M_w	632.88	717.01	718.94	574.70
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Ibam*	*Ibam*	*Ibam*	*Pbca*
a [Å]	19.770(3)	19.703(2)	19.720(3)	19.274(3)
b [Å]	22.883(4)	22.817(3)	22.839(3)	15.952(2)
c [Å]	15.523(2)	15.5323(19)	15.5108(19)	19.581(3)
β [°]	90	90	90	90
V [Å^3]	7022.4(19)	6982.7(15)	6986.0(15)	6020.4(14)
Z	8	8	8	8
ρ_{calcd} [g cm^{-3}]	1.197	1.364	1.367	1.268
μ [mm^{-1}]	1.755	2.773	2.921	2.004
F(000)	2712	2960	2968	2448
θ range [°]	1.36–25.06	1.37–25.56	1.36–25.57	1.96–25.07
no of reflns collected	19356	20235	20098	29247
no of indep reflns	3239	3415	3418	5325
no of variables	191	191	193	323
GOF	1.036	1.011	0.965	1.027
R [$I>2\sigma(I)$]	0.0433	0.0248	0.0278	0.0372
Rw	0.0888	0.0592	0.0614	0.0753

Table 7. Crystallographic data and structure refinement details for **41**, **42**, and **44**.

	41	**42**·0.5 THF	**44**·THF
formula	$C_{32}H_{55}N_4OSiY$	$C_{66}H_{96}Br_2N_4O_5Si_2Y_2$	$C_{38}H_{58}BrN_4O_2SiY$
M_w	626.80	1419.29	799.79
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2(1)/c$	$C2/c$	$P2(1)/c$
a [Å]	9.0094(14)	37.755(7)	17.800(5)
b [Å]	21.103(3)	9.2298(17)	9.853(3)
c [Å]	17.645(3)	19.745(4)	22.577(6)
β [°]	90.151(3)	96.211(2)	96.444(4)
V [Å^3]	3354.8(9)	6840(2)	3934.6(19)
Z	4	4	4
ρ_{calcd} [g cm^{-3}]	1.245	1.378	1.350
μ [mm^{-1}]	1.803	2.940	2.565
F(000)	1344	2944	1672
θ range [°]	1.50–26.02	2.08–25.04	1.82–25.01
no of reflns collected	18822	16027	16355
no of indep reflns	6587	5991	6688
no of variables	364	359	409
GOF	1.005	0.959	1.009
R [$I>2\sigma(I)$]	0.0392	0.0492	0.0621
Rw	0.0558	0.1159	0.1018

827, 754 cm^{-1}; elemental analysis calcd for $C_{34}H_{50}BrN_4OSiY$: C 56.12, H 6.93, N 7.70; found: C 55.72, H 6.91, N 7.22.

X-ray crystallographic studies: Crystals for X-ray analyses of **1**, **4**, **5, 10**, **21, 35**, **40**, **41**, **42**, and **44** were obtained as described in the preparations. The crystals were manipulated in the glovebox and were sealed in thin-walled glass capillaries. Data collections were performed at −100 °C on a Bruker CCD APEX diffractometer with a CCD area detector, by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed by using SAINT and SADABS to yield the reflection data file. The structures were solved by the use of the SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection, and processing parameters for the rare-earth metal complexes **1**, **4**, **5**, **40**–**42**, and **44** are summarized in Tables 6 and 7, whereas those for organic compounds **10**, **21**, and **35** were given only in the Supporting Information. CCDC-622021 (**1**·0.5 hexane), CCDC-622022 (**4**·0.5 hexane), CCDC-622023 (**5**·0.5 hexane), CCDC-622024 (**10**), CCDC-622025 (**21**), CCDC-622026 (**35**), CCDC-622027 (**40**), CCDC-610669 (**41**), CCDC-622028 (**42**·0.5 THF), and CCDC-622029 (**44**·THF) contains the supplementary crystallographic data for this paper. Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 14078224, "Reaction Control of Dynamic Complexes") from the Ministry of Education, Culture, Sports, Science, and Technology of Japan and by the National Natural Science Foundation of China (No. 20328201).

[1] a) *Guanidines: Historical, Biological, Biochemical and Clinical Aspects of the Naturally Occurring Guanidino Compounds* (Eds.: A. Mori, B. D. Cohen, A. Lowenthal), Plenum Press, New York, **1985**; b) *Guanidines 2: Further Explorations of the Biological and Clinical Significance of Guanidino Compounds* (Eds.: A. Mori, B. D. Cohen, A. Lowenthal), Plenum Press, New York, **1987**; c) R. G. S. Berlinck, M. H. Kossuga, *Nat. Prod. Rep.* **2005**, 22, 516–550; d) R. G. S. Berlinck, *Nat. Prod. Rep.* **2002**, *19*, 617–649.

[2] a) T. Ishikawa, T. Kumamoto, *Synthesis* **2006**, 737–752; b) J. C. McManus, T. Genski, J. S. Carey, R. J. K. Taylor, *Synlett* **2003**, 369–371; c) J. C. McManus, J. S. Carey, R. J. K. Taylor, *Synlett* **2003**, 365–368; d) T. Ishikawa, T. Isobe, *Chem. Eur. J.* **2002**, *8*, 552–557; e) B. Kovacevic, Z. B. Maksic, *Org. Lett.* **2001**, *3*, 1523–1526; f) M. Costa, G. P. Chiusoli, D. Taffurelli, G. Dalmonego, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1541–1546.

[3] a) A. R. Katritzky, B. V. Rogovoy, *Arkivoc* **2005**, *4*, 49–87; b) J. C. Manimala, E. V. Anslyn, *Eur. J. Org. Chem.* **2002**, 3909–3922; c) L. Peterlin-Mašic, D. Kikelj, *Tetrahedron* **2001**, *57*, 7073–7105; d) J. Li, Z. Zhang, E. Fan, *Tetrahedron Lett.* **2004**, *45*, 1267–1269; e) E. Convers, H. Tye, M. Whittaker, *Tetrahedron Lett.* **2004**, *45*, 3401–3404; f) T. Gers, D. Kunce, P. Markowski, J. Izdebski, *Synthesis* **2004**, 37–42; g) Y. Yu, J. M. Ostresh, R. A. Houghten, *J. Org. Chem.* **2002**, *67*, 3138–3141; h) Y.-Q. Wu, S. K. Hamilton, D. E. Wilkinson, G. S. Hamilton, *J. Org. Chem.* **2002**, *67*, 7553–7556; i) M. Tamaki, G. Han, V. J. Hruby, *J. Org. Chem.* **2001**, *66*, 1038–1042; j) H.-J. Musiol, L. Moroder, *Org. Lett.* **2001**, *3*, 3859–3861; k) P. López-Cremades, P. Molina, E. Aller, A. Lorenzo, *Synlett* **2000**, 1411–1414; l) D. R. Kent, W. L. Cody, A. M. Doherty, *Tetrahedron Lett.* **1996**, *37*, 8711–8714.

[4] a) G. Evindar, R. A. Batey, *Org. Lett.* **2003**, *5*, 133–136; b) D. A. Powell, P. D. Ramsden, R. A. Batey, *J. Org. Chem.* **2003**, *68*, 2300–2309; c) A. K. Ghosh, W. G. J. Hol, E. Fan, *J. Org. Chem.* **2001**, *66*, 2161–2164.

[5] a) T.-G. Ong, G. P. A. Yap, D. S. Richeson, *J. Am. Chem. Soc.* **2003**, *125*, 8100–8101; b) F. Montilla, A. Pastor, A. Galindo, *J. Organomet. Chem.* **2004**, *689*, 993–996.

[6] T. P. Hopkins, J. M. Dener, A. M. Boldi, *J. Comb. Chem.* **2002**, *4*, 167–174.

[7] a) P. Molina, E. Aller, A. Lorenzo, *Synlett* **2003**, 714–716; b) P. Molina, E. Aller, A. Lorenzo, *Synthesis* **1998**, 283–287.

[8] For reviews of the coordination chemistry of guanidines and guanidinates, see: a) M. P. Coles, *Dalton Trans.* **2006**, 985–1001; b) P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, *214*, 91–141.

[9] For examples of Group 3 and lanthanide guanidinate complexes, see: a) A. A. Trifonov, D. M. Lyubov, G. K. Fukin, E. V. Baranov, Y. A. Kurskii, *Organometallics* **2006**, *25*, 3935–3942; b) A. A. Trifonov, D. M. Lyubov, E. A. Fedorova, G. K. Fukin, H. Schumann, S. Mühle, M. Hummert, M. N. Bochkarev, *Eur. J. Inorg. Chem.* **2006**, 747–756; c) X. Pang, H. Sun, Y. Zhang, Q. Shen, H. Zhang, *Eur. J.*

Inorg. Chem. **2005**, 1487–1491; d) L. Zhou, Y. Yao, Y. Zhang, H. Sheng, M. Xue, Q. Shen, *Appl. Organomet. Chem.* **2005**, *19*, 398–399; e) L. Zhou, Y. Yao, Y. Zhang, M. Xue, J. Chen, Q. Shen, *Eur. J. Inorg. Chem.* **2004**, 2167–2172; f) J. Chen, Y. Yao, Y. Luo, L. Zhou, Y. Zhang, Q. Shen, *J. Organomet. Chem.* **2004**, *689*, 1019–1024; g) Y. Yao, Y. Luo, J. Chen, Z. Zhang, Y. Zhang, Q. Shen, *J. Organomet. Chem.* **2003**, *679*, 229–237; h) Y. Luo, Y. Yao, Q. Shen, K. Yu, L. Weng, *Eur. J. Inorg. Chem.* **2003**, 318–323; i) Y. Luo, Y. Yao, Q. Shen, *Macromolecules* **2002**, *35*, 8670–8671; j) J. Zhang, X. Zhou, R. Cai, L. Weng, *Inorg. Chem.* **2005**, *44*, 716–722; k) J. Zhang, R. Cai, L. Weng, X. Zhou, *Organometallics* **2004**, *23*, 3303–3308; l) J. Zhang, R. Cai, L. Weng, X. Zhou, *Organometallics* **2003**, *22*, 5385–5391; m) J. Zhang, R. Cai, L. Weng, X. Zhou, *J. Organomet. Chem.* **2003**, *672*, 94–99; n) A. A. Trifonov, E. A. Fedorova, G. K. Fukin, M. N. Bochkarev, *Eur. J. Inorg. Chem.* **2004**, 4396–4401; o) M. P. Coles, P. B. Hitchcock, *Inorg. Chim. Acta* **2004**, *357*, 4330–4334; p) Z. Lu, G. P. A. Yap, D. S. Richeson, *Organometallics* **2001**, *20*, 706–712; q) G. R. Giesbrecht, G. D. Whitener, J. Arnold, *J. Chem. Soc. Dalton Trans.* **2001**, 923–927; r) Y. Zhou, G. P. A. Yap, D. S. Richeson, *Organometallics* **1998**, *17*, 4387–4391.

[10] For examples of main group metal guanidinate complexes, see: a) M. P. Coles, P. B. Hitchcock, *Chem. Commun.* **2005**, 3165–3167; b) C. N. Rowley, G. A. DiLabio, S. T. Barry, *Inorg. Chem.* **2005**, *44*, 1983–1991; c) A. P. Kenney, G. P. A. Yap, D. S. Richeson, S. T. Barry, *Inorg. Chem.* **2005**, *44*, 2926–2933; d) F. Feil, S. Harder, *Eur. J. Inorg. Chem.* **2005**, 4438–4443; e) M. L. Cole, P. C. Junk, *Dalton Trans.* **2003**, 2109–2111; f) G. R. Giesbrecht, A. Shafir, J. Arnold, *J. Chem. Soc. Dalton Trans.* **1999**, 3601–3604; g) C.-C. Chang, C.-S. Hsiung, H.-L. Su, B. Srinivas, M. Y. Chiang, G.-H. Lee, Y. Wang, *Organometallics* **1998**, *17*, 1595–1601; h) P. J. Bailey, R. O. Gould, C. N. Harmer, S. Pace, A. Steiner, D. S. Wright, *Chem. Commun.* **1997**, 1161–1162.

[11] For examples of transition-metal guanidinate complexes, see: a) C. B. Wilder, L. L. Reitfort, K. A. Abboud, L. McElwee-White, *Inorg. Chem.* **2006**, *45*, 263–268; b) J. Vicente, J. A. Abad, M.-J. López-Sáez, P. G. Jones, *Organometallics*, **2006**, *25*, 1851–1853; c) C. J. Carmalt, A. C. Newport, S. A. O'Neill, I. P. Parkin, A. J. P. White, D. J. Williams, *Inorg. Chem.* **2005**, *44*, 615–619; d) M. P. Coles, P. B. Hitchcock, *Eur. J. Inorg. Chem.* **2004**, 2662–2672; e) S. J. Birch, S. R. Boss, S. C. Cole, M. P. Coles, R. Haigh, P. B. Hitchcock, A. E. H. Wheatley, *Dalton Trans.* **2004**, 3568–3574; f) M. P. Coles, P. B. Hitchcock, *Organometallics* **2003**, *22*, 5201–5211; g) T.-G. Ong, G. P. A. Yap, D. S. Richeson, *Organometallics* **2003**, *22*, 387–389; h) S. R. Foley, G. P. A. Yap, D. S. Richeson, *Inorg. Chem.* **2002**, *41*, 4149–4157; i) T.-G. Ong, G. P. A. Yap, D. S. Richeson, *Organometallics* **2002**, *21*, 2839–2841; j) M. K. T. Tin, G. P. A. Yap, D. S. Richeson, *Inorg. Chem.* **1999**, *38*, 998–1001; k) N. Thirupathi, G. P. A. Yap, D. S. Richeson, *Chem. Commun.* **1999**, 2483–2484; l) F. A. Cotton, C. A. Murillo, X. Wang, C. C. Wilkinson, *Inorg. Chem.* **2006**, *45*, 5493–5500; m) J. F. Berry, F. A. Cotton, P. Huang, C. A. Murillo, X. Wang, *Dalton Trans.* **2005**, 3713–3715; n) F. A. Cotton, L. M. Daniels, C. A. Murillo, D. J. Timmons, C. C. Wilkinson, *J. Am. Chem. Soc.* **2002**, *124*, 9249–9256; o) F. A. Cotton, L. M. Daniels, P. Huang, C. A. Murillo, *Inorg. Chem.* **2002**, *41*, 317–320; p) M. D. Irwin, H. E. Abdou, A. A. Mohamed, J. P. Fackler Jr., *Chem. Commun.* **2003**, 2882–2883; q) A. W. Holland, R. G. Bergman, *J. Am. Chem. Soc.* **2002**, *124*, 9010–9011; r) A. P. Duncan, S. M. Mullins, J. Arnold, R. G. Bergman, *Organometallics* **2001**, *20*, 1808–1819; s) S. M. Mullins, A. P. Duncan, R. G. Bergman, J. Arnold, *Inorg. Chem.* **2001**, *40*, 6952–6963; t) I. M. Muller, R. Robson, *Angew. Chem.* **2000**, *112*, 4527–4530; *Angew. Chem. Int. Ed.* **2000**, *39*, 4357–4359.

[12] Catalytic protonolysis of half-sandwich rare-earth metal guanidinates by secondary amines was recently communicated. See: W.-X. Zhang, M. Nishiura, Z. Hou, *Synlett* **2006**, 1213–1216.

[13] a) During the preparation of this manuscript, a report on lithium-catalyzed addition of amines to carbodiimides appeared. See: T.-G. Ong, J. S. O'Brien, I. Korobkov, D. S. Richeson, *Organometallics* **2006**, *25*, 4728–4730. b) For alkali-metal-catalyzed addition of phosphine P–H bonds to carbodiimides, see: W.-X. Zhang, M. Nishiura, Z. Hou, *Chem. Commun.* **2006**, 3812–3814.

[14] W.-X. Zhang, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2005**, *127*, 16788–16789.

[15] a) K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228–243; b) S. Arndt, P. Voth, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 4690–4700; c) K. C. Hultzsch, T. P. Spaniol, J. Okuda, *Angew. Chem.* **1999**, *111*, 163–165; *Angew. Chem. Int. Ed.* **1999**, *38*, 227–230.

[16] a) M. F. Lappert, R. Pearce, *J. Chem. Soc. Chem. Commun.* **1973**, 126–127; b) G. K. Barker, M. F. Lappert, *J. Organomet. Chem.* **1974**, *76*, C45–C46; c) P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Bartlett, P. P. Power, *J. Chem. Soc. Chem. Commun.* **1988**, 1007–1009.

[17] Z. Hou, T. Koizumi, M. Nishiura, Y. Wakatsuki, *Organometallics* **2001**, *20*, 3323–3328.

[18] M. Nishiura, Z. Hou, Y. Wakatsuki, T. Yamaki, T. Miyamoto, *J. Am. Chem. Soc.* **2003**, *125*, 1184–1185.

[19] The coordination number of the Y center in **1** is seven, whereas that in $[\{Me_2Si(C_5Me_4)(NCMe_2Et)\}Y(CH_2SiMe_3)(thf)]$ is six. The ionic radius of seven-coordinate Y^{3+} (0.96 Å) is usually 0.06 Å larger than that of six-coordinate Y^{3+} (0.90 Å). See: R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.

[20] a) J. Grundy, M. P. Coles, P. B. Hitchcock, *Dalton Trans.* **2003**, 2573–2577; b) R. T. Boeré, V. Klassen, G. Wolmershäuser, *J. Chem. Soc. Dalton Trans.* **1998**, 4147–4154.

[21] K. H. den Haan, J. L. de Boer, J. H. Teuben, A. L. Spek, B. Kojić-Prodić, G. R. Hays, R. Huis, *Organometallics* **1986**, *5*, 1726–1733.

Received: September 27, 2006
Published online: March 9, 2007

