Journal of Organometallic Chemistry 769 (2014) 112–118

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Catalytic C–N bond formation in guanylation reaction by *N*-heterocyclic carbene supported magnesium(II) and zinc(II) amide complexes

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ARTICLE INFO

Article history:
Received 6 June 2014
Received in revised form
19 July 2014
Accepted 25 July 2014
Available online 4 August 2014

Keywords:
Catalysis
Guanidine
Magnesium
Neutral ligand
Zinc

ABSTRACT

The catalytic activity of *N*-heterocyclic carbene (NHC) supported magnesium(II) and a zinc(II) amide complex towards the addition of N–H bond of amine to carbodiimide was studied. Treatment of a free carbene *i.e.*, 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu) with magnesium and zinc bis(amide) *i.e.*, M $[N(SiMe_3)_2]_2$, M = Mg or Zn in toluene led to the formation of I^tBu:M$[N(SiMe_3)_2]_2$, M = Mg(**1**) and Zn(**2**) compounds, respectively. Both **1** and **2** were characterized by multinuclear (^1H, ^{13}C and ^{29}Si) NMR spectroscopy and single X-ray crystal structure analysis. Solid state structures revealed that both complexes are monomeric in nature and their magnesium and zinc atoms are three coordinated and distorted trigonal planar in geometries. Furthermore, compounds **1** and **2** were tested as catalysts for the guanylation reaction of addition of amine to carbodiimide and turned to be excellent catalysts.

Introduction

Metal catalyzed C–N bond formation reactions by the addition of amine to carbodiimide are important in guanidine synthesis [1]. Guanidines are used as bases as well as catalysts in organic synthesis [2]. And also, they are used as ancillary ligands [3] in a variety of main group [4], transition [5] and lanthanide [6] metal complexes. Moreover, guanidines are the important structural motifs found in many biologically and pharmaceutically active molecules [7]. Thus, synthesis of guanidines has attracted much attention in organic synthesis and coordination/organometallic chemistry. The synthesis of guanidines has been thoroughly examined by a variety of methods [8]. Among all methods, the convenient method is the direct addition of primary aliphatic amine to carbodiimide, but it requires very harsh reaction conditions [9]. In contrast to primary aliphatic amines, primary aromatic and secondary amines do not react with carbodiimide, even at harsh reaction conditions. Therefore, the catalytic hydroamination of carbodiimides is the most attractive method. This is an atom economical and most convenient approach for the synthesis of guanidines. In recent years, the construction of a new C–N bond in guanylation reaction (addition of amine N–H bond to carbodiimide) was achieved by the transition [10] and lanthanide [11] metal complexes. Additionally, there are few reports on the main group metal catalyzed hydroamination of carbodiimides. In 2006, Richeson's group reported the first example of the commercially available lithium amide catalyzed C–N bond formation in guanylation reaction [12]. Hill and coworkers have shown the heavier group 2 element catalyzed hydroamination of carbodiimides [13]. Alonso-Moreno et al., demonstrated the lithium alkyl and magnesium dialkyls catalyzed reaction of amines with carbodiimides [14]. Moreover, very recently, Bergman's group described the guanidinato stabilized aluminum(III) alkyl complex catalyzed hydroamination of carbodiimide. [15] And also, Zhang and coworkers have used commercially available $AlMe_3$ as catalyst for the guanylation reaction [16]. To the best of our knowledge there are no reports on *N*-heterocyclic carbene (NHC) stabilized magnesium and zinc bis(amides) as catalysts for guanylation reaction of both primary aromatic and cyclic secondary amines with carbodiimides.

In 1991, Arduengo and coworkers reported the synthesis and characterization of the first room temperature stable crystalline *N*-heterocyclic carbene (NHC) [17]. Since then NHC's have got enormous importance in both organometallic synthesis and catalysis [18]. Their strong σ donating properties led to the isolation of stable metal complexes that are usually resistant to decomposition. Despite the widely developed coordination chemistry of NHC's

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http://dx.doi.org/10.1016/j.jorganchem.2014.07.021
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with p-block elements, especially NHC supported unusual main group molecules [19], the chemistry of NHC as ligand to s-block elements is remain less widely considered. There are some reports on the NHC stabilized group 1 and group 2 metal complexes [20]. Monodentate and nonfunctionalized NHC stabilized zinc(II) alkyls, alkoxides, halides etc., are known in the literature [21]. Surprisingly, NHC stabilized zinc(II) bis(amide) complex is not known. In connection to our work, it is worthy of note that Hill and coworkers reported soluble magnesium hydride, which is prepared by the treatment IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)magnesiumbis(amide) adduct with phenylsilane [20b]. Very recently, Okuda and coworkers isolated dimeric zinc dihydride compounds, those are supported by IPr and IMes (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) ligands and soluble in organic solvents [22].

Herein, we report the synthesis and characterization of *N*-heterocyclic carbene supported magnesium(II) and zinc(II) amide complexes and their catalytic application towards the guanylation reaction of primary aromatic and cyclic secondary amines with *N,N′*-dialkyl carbodiimides.

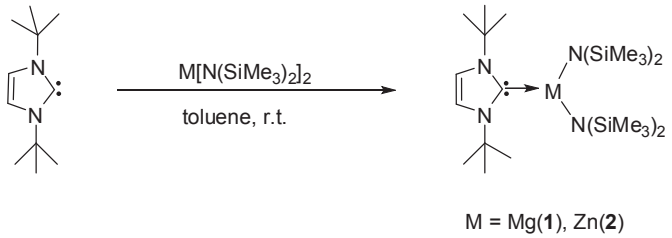
Results and discussion

Syntheses of N-heterocyclic carbene adducts of metal bis(amide)

The synthesis of NHC adducts of magnesium and zinc bis(amide) *i.e.* I^{t}Bu:M[N(SiMe$_3$)$_2$]$_2$, (I^{t}Bu = 1,3-di-*tert*-butylimidazol-2-ylidene) M = Mg(**1**), Zn(**2**), has been achieved by the treatment of I^{t}Bu with corresponding metal bis(amides) M[N(SiMe$_3$)$_2$]$_2$, in toluene at room temperature for 12 h (Scheme 1).

The crude compounds were recrystallized from toluene at −25 °C to give colorless crystals with moderate yields 68 and 62% for complexes **1** and **2** respectively. The isolated crystals of **1** and **2** are melting without any decomposition at temperatures 128 and 120 °C, respectively. The compounds **1** and **2** are freely soluble in organic solvents such as tetrahydrofuran, toluene, and benzene and sparingly soluble in hexane. Both compounds are sensitive toward air and moisture and require inert atmosphere for their stability. The compounds **1** and **2** were characterized by multinuclear (^{1}H, ^{13}C and ^{29}Si) NMR spectroscopic methods. Furthermore, the molecular structures of compounds **1** and **2** were confirmed by single crystal X-ray structural analysis.

^{1}H NMR spectrum of complex **1** in C_6D_6 exhibits three resonances as singlets, two singlet resonances for the NHC ligand at 6.35 and 1.42 ppm and one singlet for amide ligand *i.e.* N (SiMe$_3$)$_2$ at 0.38 ppm. Similarly, ^{1}H NMR spectrum for complex **2** shows two singlets for the NHC ligand at 6.41 and 1.44 ppm and a broad signal at 0.36 ppm for the amide ligand. ^{13}C {^{1}H} NMR signals appear at 178 and 176 ppm corresponding to carbene carbon of compounds **1** and **2**, respectively (in free I^{t}Bu, carbene carbon resonates at 213 ppm). In ^{29}Si {^{1}H} NMR complex **1** exhibits a peak at −17.12 ppm for the silyl group, where as a peak at −5.00 ppm for compound **2** was observed.



Scheme 1. Synthesis of **1** and **2**.

*Solid state crystal structures of compound **1** and **2***

The molecular structure of compounds **1** and **2** were further confirmed by single crystal X-ray diffraction analysis. Crystals of **1** and **2** suitable for X-ray structure determination were grown from a toluene solution by slow cooling to −25 °C. Molecular structures of **1** and **2** and selected bond lengths and bond angles are summarized in Figs. 1 and 2, respectively.

Compounds **1** and **2** were crystallized in the monoclinic P2(1)/n and monoclinic P2(1) space groups, respectively. Both compounds exist as monomers and their metal atoms are bonded to one carbenic carbon atom and two nitrogen atoms of the amido ligands. Thus, both magnesium and zinc atoms are three coordinated with a distorted structure from the trigonal planar by widening the angles between two silylamide groups (N4–Mg1–N5 = 128.42(7)) and N(4)–Zn(1)–N(3) 131.43(18) [°], in complexes **1** and **2** respectively. This is due the larger steric demands of the substitution.

The Mg–C$_{NHC}$ bond length in complex **1** is 2.241(2) Å, which is longer than that of Zn–C$_{NHC}$ bond distance in complex **2** (2.082(5) Å), this is due to the 0.19 Å longer covalent radii of magnesium element (1.41 Å) than that of zinc element (1.22 Å) [23]. The bond distance of Mg–C$_{NHC}$ of **1** (2.241(2) Å) is in good agreement with other NHC Mg (II) adducts (2.194–2.279 Å) [20a,20b,20e,20f]. And also, Zn–C$_{NHC}$ bond distance (2.082(5) Å) in **2** is matches well with recently reported Okuda's NHC stabilized zinc dihydride complexes ((IMes:ZnH$_2$)$_2$ 2.052(3) Å and (IPr:ZnH$_2$)$_2$ 2.054(3) Å) [22].

Catalytic activity

Guanylation of both primary aromatic and cyclic secondary amines with carbodiimides

The catalytic activity of NHC supported magnesium(II) and zinc(II) amide complexes **1** and **2** were investigated by performing the reaction of aniline with isopropyl carbodiimide (Table 1).

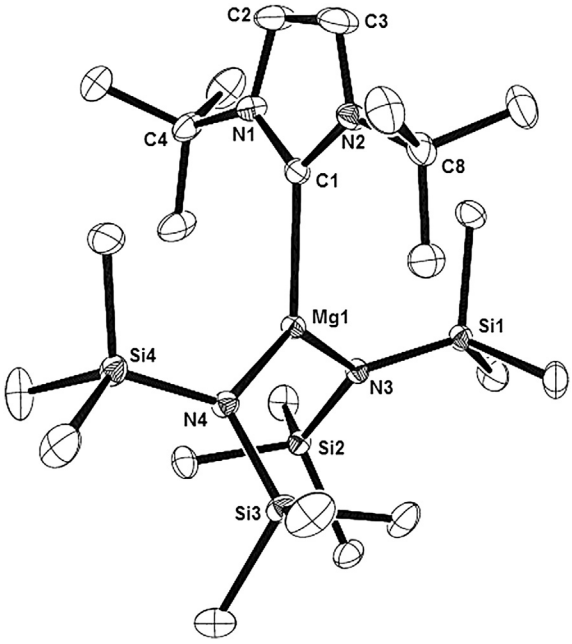


Fig. 1. Molecular structure of **1**. All hydrogen atoms are removed for the clarity. (Due to N4–Si4 rotation, positional disorder of three methyl groups attached to Si4 have been observed and that is solved by splitting of each methyl group by two) Selected bond lengths [Å] and angles [°]: Mg1–C1 2.241(2), Mg1–N4 2.0142(18), N1–C4 1.4895(28), C1–N1 1.3670(25); C1–Mg1–N4 116.97(7), C1–Mg1–N5 114.59(7), N4–Mg1–N5 128.42(7).

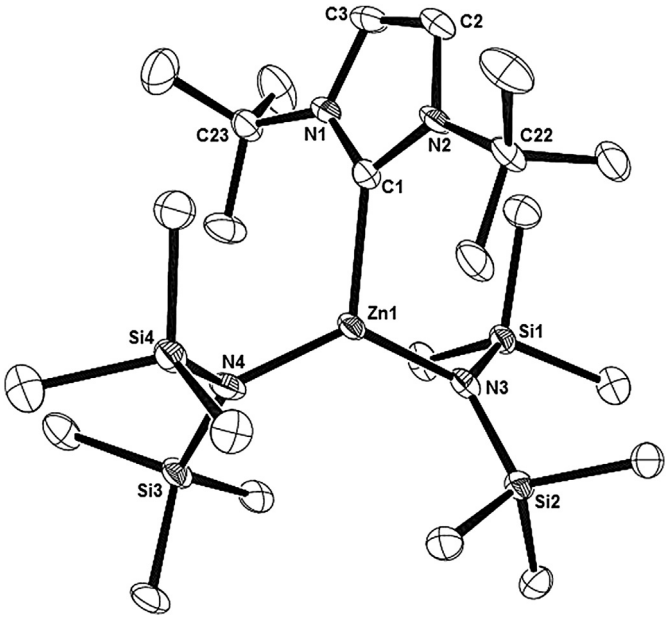


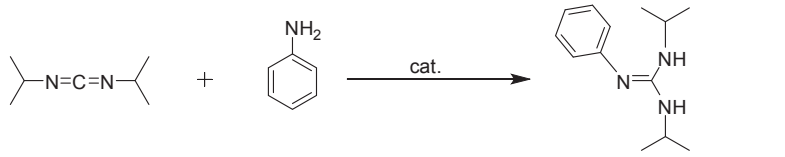
Fig. 2. Molecular structure of **2**. All hydrogen atoms are removed for the clarity. Selected bond lengths [Å] and angles [°]: Zn(1)–C(1) 2.082(5), Zn(1)–N(3) 1.958(5), C1–N1 1.3612(66), N1–C23 1.4943(67), Zn(1)–N(4) 1.956(5); C(1)–Zn(1)–N(3) 110.90(19), C(1)–Zn(1)–N(4) 117.66(19), N(3)–Zn(1)–N(4) 131.43(18).

The addition of aniline to isopropyl carbodiimide in the presence of 1 mol % either compound **1** or **2** at room temperature without solvent, immediate formation of the *N*,*N*′,*N*″-trisubstituted guanidine product was occurred (Table 1, Entry 1 and 2). To know the effect of I^{t}Bu, which is coordinated to the metal bis(amide), alternatively another reaction performed by using Mg[N(SiMe$_3$)$_2$]$_2$ as catalyst (at same reaction conditions) led to no change in the product yield (Table 1, Entry 3). Furthermore, compounds Mg[N(SiMe$_3$)$_2$]$_2$ and **1** were tested with less catalyst load of 0.1% at reaction temperature 50 °C in thf (Table 1, Entry 4 and 6) and also 0.5% catalyst load at reaction temperature 60 °C without any solvent (Table 1, Entry 5 and 7). From the above reactions, it is indicated that compound **1** slightly better catalyst than that of Mg[N(SiMe$_3$)$_2$]$_2$. In addition to this compound **1** catalyzed (1 mol %) guanylation reaction was performed in toluene and thf solvents at room temperature led to the formation of product in quantitative yield (Table 1, Entry 8 and 9).

The scope of compound I^{t}Bu:Mg[N(SiMe$_3$)$_2$]$_2$ (**1**) catalyzed addition of amines to carbodiimides was examined by taking examples of a wide variety of primary aromatic and cyclic secondary amines. The results are given in Tables 2 and 3. Herewith, worthy to mention that considering the same catalytic activities of both compounds **1** and **2** in the reaction of aniline with 1,3-diisopropyl carbodiimide (Table 1, Entries 9,10 and 7 & 11) for further reactions, selection of only compound **1** is justified.

It is notable from Table 2 that the catalyst **1** is compatible with various substituents on the phenyl ring such as –OCH$_3$, CH$_3$, Cl, etc., and formation of corresponding *N*,*N*′,*N*″-trisubstituted guanidine products (**1a**–**17a**) in high yields, except **9a**. When the substituents on the phenyl ring are electron donating such as –CH$_3$, –OCH$_3$, excellent yields were obtained at room temperature (Table 2, Entries 3, 4 and 5, 6). In case of electron withdrawing substituent as Cl, on the phenyl ring, good yield (Table 2, Entry 8) was obtained at room temperature. No product could be isolated from the reaction of 4-NO$_2$ aniline with isopropyl carbodiimide at 60 °C for 24 h (Table 2, Entry 9) in presence of catalyst **1**. This indicates that the electronic factor has a great influence on the catalytic activity of the reaction. The steric effect also shows influence on the catalytic reaction. The reaction of 2-methyl aniline with isopropyl carbodiimides produced almost quantitative yield (96%) (Table 2, Entry 10), while the reaction with 2,6 dimethyl aniline gave a good yield 81% over room temperature stirring for 2 h (Table 2, Entry 12). Interestingly, if the methyl substituent at both ortho positions of the phenyl ring and more bulky alkyl group such as *tert*-butyl group at the para position of the phenyl ring led to the formation of expected product in quantitative yields (Table 2, Entries 13–16). In fact the reaction of more bulky aniline, 2,6-diisopropylphenylamine with isopropyl carbodiimide requires higher temperature (Table 2, Entry 17).

Table 1
Metal catalyzed reaction of aniline with *N*,*N*′-diisopropylcarbodiimide.

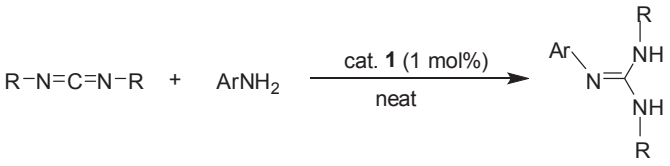


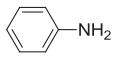
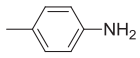
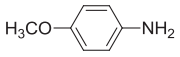
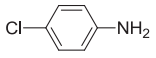
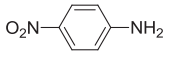
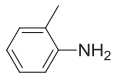
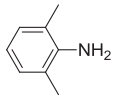
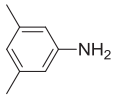
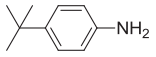
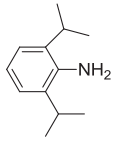
1,3-diisopropylcarbodiimide aniline 1,3-diisopropylphenylguanidine

Entry	Catalyst	Catalyst load [mol%]	Temp. [°C]	Solvent	Time [min]	Yield [%][a]
1	**1**	1	25	–	1	Quant.
2	**2**	1	25	–	1	Quant.
3	Mg[N(SiMe$_3$)$_3$]$_2$	1	25	–	1	Quant.
4	Mg[N(SiMe$_3$)$_3$]$_2$	0.1	50	thf(d_8)	720	73[a]
5	Mg[N(SiMe$_3$)$_3$]$_2$	0.5	60	–	120	80
6	**1**	0.1	50	thf(d_8)	120	88[b]
7	**1**	0.5	60	–	5	94
8	**1**	1	25	thf	120	Quant.
9	**1**	1	25	Toluene	120	Quant.
10	**2**	1	25	Toluene	120	Quant.
11	**2**	0.5	60	–	5	92

The reaction was performed by treating 1 equiv of aniline with 1 equiv of *N*,*N*′-diispropyl carbodiimide.
[a] Isolated yield.
[b] NMR yield measured by integration of consumption of starting material relative to the formation of product.

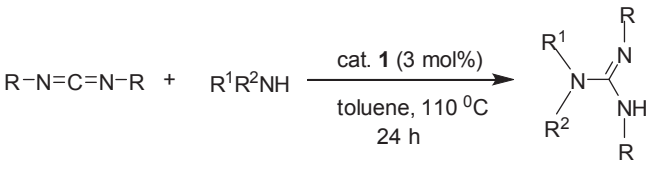
Table 2
Results of reaction of various anilines with *N,N′*-dialkyl carbodiimides catalyzed by $I^tBu:Mg[N(SiMe_3)_2]_2$ (**1**).

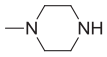
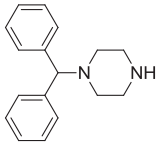


Entry	R	$ArNH_2$	Temp [°C]	Time [min]	Product[a]	Yield [%][b]
1	*i*-Pr		25	1	**1a**	94
2	Cy		25	40	**2a**	99
3	*i*-Pr		25	1	**3a**	97
4	Cy		25	60	**4a**	98
5	*i*-Pr		25	1	**5a**	97
6	Cy		25	10	**6a**	96
7	*i*-Pr		25	240	**7a**	97
8	Cy		60	720	**8a**	66
9	*i*-Pr		60	1440	**9a**	No reaction
10	*i*-Pr		25	60	**10a**	96
11	Cy		25	20	**11a**	96
12	*i*-Pr		25	120	**12a**	81
13	*i*-Pr		25	1	**13a**	94
14	Cy		25	10	**14a**	95
15	*i*-Pr		25	10	**15a**	96
16	Cy		25	5	**16a**	96
17	*i*-Pr		100	720	**17a**	86[c]

[a] The reaction was performed by treating 1 equiv of aromatic amine with 1 equiv of *N,N′*-dialkyl carbodiimide.
[b] Isolated yield.
[c] The reaction was done in toluene at 100 °C for 12 h.

Table 3
Results of reaction of various cyclic secondary amines with *N,N′*-dialkyl carbodiimides catalyzed by $I^tBu:Mg[N(SiMe_3)_2]_2$ (**1**).



Entry	R	R^1R^2NH	Product[a]	Yield [%][b]
1	*i*-Pr		**1b**	96
2	Cy		**2b**	96
3	*i*-Pr		**3b**	92
4	Cy		**4b**	95
5	*i*-Pr		**5b**	93
6	Cy		**6b**	96
7	*i*-Pr		**7b**	86
8	*i*-Pr		**8b**	97
9	*i*-Pr		**9b**	93

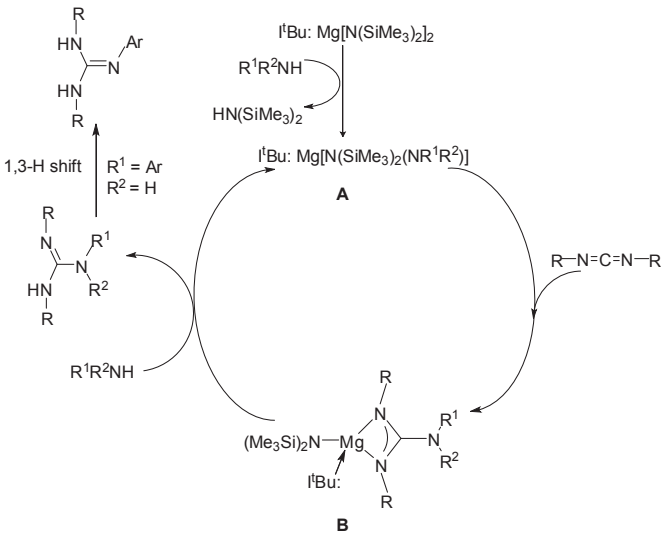
[a] Reaction was performed by treating 1 equiv of cyclic secondary amine with 1 equiv of *N,N′*-dialkyl cabodiimide.
[b] Isolated yield.

Furthermore, we examine catalytic activity of compound **1** towards the addition of a various cyclic secondary amines with carbodiimides (Table 3). *N,N′,N″*-trisubstituted guanidine products (**1b**–**9b**) were obtained in good to excellent yields. However, the reaction generally requires a higher temperature 110 °C and longer reaction time 24 h for the completion. From the above results (Tables 2 and 3), it indicates that catalyst **1** is compatible towards hydroamination of various amines.

Proposed mechanism for guanylation reaction

Based on the above results, a possible catalytic cycle for the addition of primary aromatic or cyclic secondary amines to carbodiimides is proposed in Scheme 2.

The reaction of primary/secondary amine with NHC metal bis(amide) adduct gave the new bis(amido) intermediate **A** through an elimination of $HN(SiMe_3)_2$. The postulated intermediate **A** further reacts with carbodiimide to produce metal guanidinate intermediate **B** through an insertion reaction. Interaction of metal guanidinate species **B** with amines releases the guanidine product along with the regeneration of the catalytically active species. For primary aromatic amines, a 1,3-H shift occurs to give the final stable guanylation product. Efforts were made to isolate and characterize the intermediates **A** and **B** and turned to be unsuccessful.



Scheme 2. Proposed mechanism for the guanylation reaction catalyzed by the ItBu:Mg $[N(SiMe_3)_2]_2$ (**1**).

Conclusion

In summary, we have synthesized nonfunctionalized monodentate NHC supported magnesium(II) and zinc(II) amide complexes by simple addition of 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu) to the metal bis(amide). These NHC metal bis(amide) adduct exhibited catalytic activity toward addition of primary aromatic and cyclic secondary amines with carbodiimide. Moreover, compound **1** is compatible to a wide range of substrates and solvents. Further studies are underway aimed at the catalytic addition of terminal alkynes and phosphines to carbodiimides, and also complex **1** catalyzed ring opening of cyclic esters.

Experimental section

General

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of dinitrogen. NMR reactions were conducted in Young valve NMR tubes and sealed in a glovebox. NMR spectra were recorded on Bruker AV 400 MHz spectrometer for ^1H NMR ($^{13}C\{^1H\}$ NMR 100 MHz and $^{29}Si\{^1H\}$ NMR 80 MHz). Solvents (toluene, benzene, and hexane) were collected from MBraun Solvent Purification System. Solvent thf was dried over sodium and stored in Na wire. C_6D_6 was purchased from Sigma–Aldrich and dried over sodium before distillation under nitrogen and storage over molecular sieves. I^tBu [24] and Mg $[N(SiMe_3)_2]_2$ [25] were prepared according to reported literature procedures. All amines were predried or distilled before use. Zn $[N(SiMe_3)_2]_2$, *N,N′*-diisopropylcarbodiimide and *N,N′*-dicyclohexylcarbodiimide were purchased from Sigma–Aldrich and used without further purification.

*Synthesis and characterization of complexes **1** and **2***

*Synthesis of I^tBu:Mg[N(SiMe$_3$)$_2$]$_2$ (**1**)*

1,3-Di-*tert*-butylimidazol-2-ylidene (I^tBu) (1.27 g and 7.07 mmol) and $Mg[N(SiMe_3)_2]_2$ (2.44 g and 7.07 mmol) were dissolved in toluene and stirred at room temperature for 12 h. Upon concentration and cooling to −25° the formation of compound **1** as colorless crystals yielded. Yield: 2.516 g (68%). M. p. 128 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 6.35$ (s, 2H, C*H*), 1.42 (s, 18H, C(CH_3)$_3$), 0.38 (s, 36H, N{Si(CH_3)$_3$}$_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): $\delta = 177.7$ (carbene *C*), 119.1 (*C*H), 57.5 (*C*(CH_3)$_3$), 31.0 (CH_3), 6.9 (SiCH_3) ppm. $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 25 °C): $\delta = -17.12$ N(*Si*Me$_3$)$_2$ ppm.

*Synthesis of I^tBu:Zn[N(SiMe$_3$)$_2$]$_2$ (**2**)*

This compound was synthesized following the same procedure as described above with starting materials 1,3-di-*tert*-butylimidazol-2-ylidene (0.190 g and 1.1 mmol) and $Zn[N(SiMe_3)_2]_2$ (0.427 g and 1.1 mmol). Colorless crystalline solid compound **2** was obtained from toluene. Yield: 0.367 g (62%). M. p. 120 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): $\delta = 6.41$ (s, 2H, C*H*), 1.44 (s, 18H, CH_3), 0.36 (br, 36H, N(SiCH_3)$_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): $\delta = 175.7$ (carbene *C*), 119.2 (*C*H), 58.6 (*C*(CH_3)$_3$), 31.4 (CH_3), 6.9 (SiCH_3) ppm. $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6, 25 °C): $\delta = -5.00$ N(*Si*Me$_3$)$_2$ ppm.

X-ray crystallography

Suitable crystals of complexes **1** and **2** were mounted on a glass fiber. The crystallographic data for these compounds are summarized in Table 4.

Geometry and intensity data were collected with a Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an INCOATEC micro source (Mo-Kα radiation, $\lambda = 0.71073$ Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+ [26] and corrected for absorption with SADABS [27]. The structures were solved by direct methods and refined on F^2 with SHELXL-97 [28]. Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

*General procedure for the direct synthesis of guanidines from the reaction of primary aromatic amines with carbodiimides catalyzed by **1***

A 30 mL Schlenk tube under inert atmosphere (N2-glovebox) was charged with the catalyst I^tBu:Mg$[N(SiMe_3)_2]_2$ (0.01 equiv), aromatic amine (1 equiv). To the above mixture carbodiimide

Table 4
Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{23}H_{56}MgN_4Si_4$	$C_{23}H_{56}ZnN_4Si_4$
Formula weight	525.39	566.45
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)
a (Å)	11.949(5)	11.334(5)
b (Å)	23.325(9)	12.060(5)
c (Å)	12.104(5)	11.995(5)
β (°)	95.190(5)	96.655(5)
V (Å^3)	3360(2)	1628.5(12)
T (K)	100	100
Density (calc.) mg/m^3	1.039	1.155
Z	4	2
F(000)	1160	616
No. of reflections collected	58,716	18,736
No. of independent reflections	10,229 [R(int) = 0.0423]	6046 [R(int) = 0.1017]
λ (Å)	0.71073	0.71069
Absorption coefficient (mm^{-1})	0.212	0.918
Theta range (deg)	2.51–30.66	1.71–25.50
Goodness-of-fit on F^2	1.041	0.859
R [$I > 2\delta$ (*I*)]	*R*1 = 0.0442, *wR*2 = 0.0940	*R*1 = 0.0538, *wR*2 = 0.1268
Largest diff. peak and hole (e Å^{-3})	0.503, −0.290	1.268, −0.716

(1 equiv) was added. The resulting mixture was stirred at room temperature or heated at 60 °C for a fixed interval. The reaction mixture was then hydrolyzed with water (1 mL) and extracted with dichloromethane (3 × 10 mL). The extracts were combined and dried over anhydrous Na_2SO_4. The solvent was removed to get crude compound. The pure product could be obtained by washing the crude product with hexane or diethyl ether.

General procedure for the direct synthesis of guanidine from cyclic secondary amine with alky carbodiimides catalyzed by ***1***

A 30 mL Schlenk tube under inert atmosphere (N2-glovebox) was charged with the catalyst I^tBu:Mg[$N(SiMe_3)_2$]$_2$ (0.03 equiv), secondary amine (1.0 equiv), and toluene (5 mL). To this mixture carbodiimides (1.0 equiv) was added. The flask was then closed to prevent evaporation of amines with low boiling points, and the resulting mixture was heated to 110 °C for the desired time. The solvent was removed under reduced pressure; the residue was extracted with hexane (3 × 15 mL) and filtered to give a clean solution. After removing the hexane under reduced pressure, the final products were obtained.

Acknowledgments

S.N. acknowledges Science and Engineering Research Board (SERB), Department of Science and Technology (DST) for the research grant No. SR/S1/IC-52/2012. A.B. and T.P. acknowledge University Grant Commission (UGC) for their fellowships.

Appendix A. Supplementary material

CCDC 985052 and 985053 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.07.021.

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