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Divalent Lanthanide Complexes: Highly Active Precatalysts for the Addition of N−H and C−H Bonds to Carbodiimides

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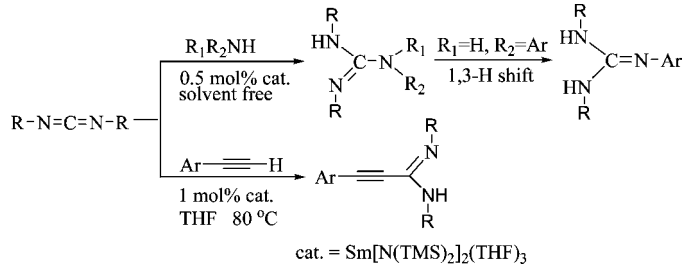

Various divalent lanthanide complexes with the formula $LnL_2(sol)_x$ (L = $N(TMS)_2$, sol = THF, $x = 3$, Ln = Sm (**I**), Eu (**II**), Yb (**III**); L = MeC_5H_4, sol = THF, $x = 2$, Ln = Sm (**IV**); L = ArO(Ar = [2,6-(^{t}Bu)$_2$-4-MeC_6H_2]), sol = THF, $x = 2$, Ln = Sm (**V**)), especially complexes **I**−**III**, serve as excellent catalyst precursors for catalytic addition of various primary and secondary amines to carbodiimides, efficiently providing the corresponding guanidine derivatives with a wide range of substrates under solvent-free condition. The reaction shows good functional groups tolerence. Complexes **I**−**III** are also excellent precatalysts for addition of terminal alkynes to carbodiimides yielding a series of propiolamidines. The active sequence of Yb < Eu < Sm for metal and MeC_5H_4 < ArO < $N(TMS)_2$ for ligand around the metal was observed for both reactions. The first step in both reactions was supposed to include the formation of a bimetallic bisamidinate samarium species originating from the reduction-coupling reaction of carbodiimide promoted by lanthanide(II) complex. The active species is proposed to be a lanthanide guanidinate and a lanthanide amidinate.

Introduction

The formation of C−C and C−N bonds catalyzed by lanthanide complexes is an active research area.[1] Guanidines and amidinates are important structural motifs found in many biologically and pharmaceutically active compounds.[2] Guanidinate and amidinate derivatives can also serve as ancillary ligands in the preparation of a variety of metal complexes, including those of the main, transition, and lanthanides metals.[3] Therefore, synthesis of guanidines and amidinates has attracted increasing attention. The direct guanylation of

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amine with carbodiimides provides a convenient and atom-economical approach to guanidines. However, the guanylation of amines without catalyst requires harsh conditions.[4] Recently, catalytic guanylation of amines with carbodiimides has been reported by using imido complexes of titanium and vanadium,[5] and metal amide complexes as precatalysts, including $LiN(SiMe_3)_2$,[6] lanthanide amides,[1g,h] and titanacarborane amide.[7] The former imido complexes are efficient catalysts only for the guanylation of primary aromatic amines with carbodiimides as the active species being an imido intermediate. The metal amide systems can catalyze guanylation of amines with carbodiimides to afford the corresponding substituted guanidines with a wide scope of amines including primary aromatic amines and aliphatic secondary amines. In those cases a metal guanidinate formed via nucleophilic addition of metal amide to carbodiimide is proved to be the active species. Half-sandwich lanthanide alkyl complexes were also reported to serve as another kind of precatalyst for efficient synthesis of substituted guanidines.[1b,c] The catalytic reaction proceeds through nucleophilic addition of an amide moiety formed in situ by acid−base reaction between a lanthanide alkyl bond and an amine N−H bond to a carbodiimide. The addition of terminal alkynes across carbodiimides has been first proven to be a straightforward route to propiolamidines by Hou's group using half-sandwich lanthanide alkyl complexes as precatalysts.[1a] Then, lithium amides and lanthanide amides were also found to be efficient precatalysts.[6,1g]

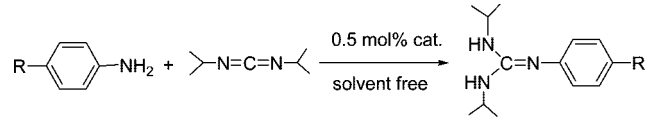
Divalent lanthanide complexes are efficient single-electron transfer reagents which have been widely used as precatalysts in organic synthesis.[8] Prompted by theses results, we considered that divalent lanthanide complexes might be used as efficient precatalysts in the addition of N−H and C−H bonds to carbodiimides, because the reduction-coupling of carbodiimides can be promoted by a divalent metallocene samarium complex $(MeC_5H_4)_2Sm(THF)_2$,[3k] and a divalent amide complex $Sm[N(TMS)_2]_2(THF)_3$,[9] to produce the corresponding bimetallic bisamidinate samarium complex. Herein, we report the high catalytic activity of divalent lanthanide complexes for addition of amines and terminal alkynes to carbodiimides. The lanthanide guandinate and lanthanide amidinate were supposed to generate in situ by insertion of carbodiimide into lanthanide amide or lanthanide alkynyl intermediate formed through protonation of the bisamidinate, which was produced through the reduction-coupling reaction of carbodiimides mediated by a divalent complex. The influence of ancillary ligand around the central metals on reactivity is also discussed.

SCHEME 1

$Sm[N(TMS)_2]_2(THF)_3$ (**I**) $Eu[N(TMS)_2]_2(THF)_3$ (**II**) $Yb[N(TMS)_2]_2(THF)_3$ (**III**)

$(MeC_5H_4)_2Sm(THF)_2$ (**IV**) $(ArO)_2Sm(THF)_2$ (**V** (Ar = [2,6-(^{t}Bu)$_2$-4-MeC_6H_2])) SmI_2 (**VI**)

TABLE 1. Catalytic Guanylation of an Aniline with an *N*,*N*′-Diisopropylcarbodiimide[a]



1 or 3

entry	cat.	catalyst loading (mol%)	R	temp/ °C	time/ min	product	yield (%)[b]
1	I	0.5	F	rt	3	1	98
2	I	0.5	H	rt	4	3	98
3[c]	**I**	0.5	H	rt	40	**3**	96
4	**II**	0.5	F	rt	6	**1**	80
5	**II**	0.5	H	rt	4	**3**	85
6	**III**	0.5	F	rt	60	**1**	87
7	**III**	0.5	H	rt	45	**3**	91
8[c]	**III**	1	H	60	180	**3**	97
9	**IV**	0.5	H	rt	120	**3**	82
10	**IV**	0.5	H	60	70	**3**	90
11	**V**	0.5	H	rt	80	**3**	87
12	**V**	0.5	H	60	52	**3**	88
13	**VI**	3	F	60	360	**1**	83
14	**VII**	0.5	F	rt	14	**1**	94
15[d]	**VIII**	1	H	60	240	**3**	95

[a] 1 mmol of **p**-flouroaniline or aniline, 1 mmol of *N*,*N*′-diisopropylcarbodiimide. [b] Isolated yields. [c] The reaction was run in THF, $C_{cat.}$ = 0.019 mmol/mL. [d] Reference 7.

Results and Discussion

Aromatic amines do not react with diisopropylcarbodiimide even with prolonged reaction time and raised reaction temperature to 100 °C without a catalyst. An addition of 0.5 mol % of $Sm[N(TMS)_2]_2(THF)_3$ (**I**)[10a] led to efficient catalytic guanylation of aniline with diisopropylcarbodiimide under solvent-free condition to afford a quantitative yield of guanidine **3** at room temperature in 4 min. The result prompted us to survey the reactivity of various divalent complexes. Thus, a series of divalent complexes were synthesized by metathesis reaction of LnI_2 with metal salts, including $Ln[N(TMS)_2]_2(THF)_3$ (Ln = Eu (**II**), Yb (**III**)),[10b,c] $Sm(MeC_5H_4)_2(THF)_2$ (**IV**),[11] $Sm(ArO)_2(THF)_2$ (Ar = [2,6-(^{t}Bu)$_2$-4-MeC_6H_2]) (**V**),[12] and SmI_2 (**VI**) (Scheme 1). For comparison, trivalent lanthanide amide complexes $Sm[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ (**VII**)[13] and $Yb[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ (**VIII**)[1h] were also prepared. The two reactions of aniline and *p*-flouroaniline with diisopropylcarbodiimide, respectively, were then conducted using these complexes. As shown in Table 1 all the complexes are effective. The reactivity depends greatly on the central metals with the active trend of Yb < Eu < Sm (Table 1 entries 1−7). The ligand

(4) (a) Tin, M. K. T.; Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *Dalton Trans.* **1999**, *17*, 2947–2950. (b) Tin, M. K. T.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **1998**, *37*, 6728–6730.

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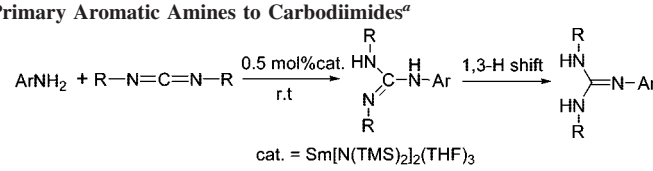
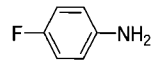
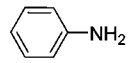
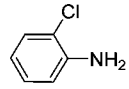
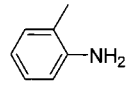
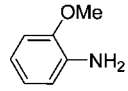
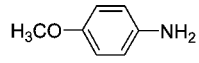
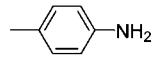
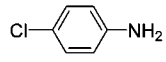
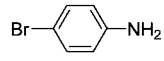
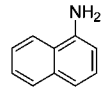
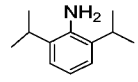
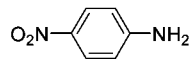
(11) Evans, W. J.; Gonzales, S.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2600–2608.

(12) Jiang, T.; Shen, Q.; Lin, Y.; Jin, S. J. *Organomet. Chem.* **1993**, *450*, 121–124.

(13) Zhou, S. L.; Wang, S. W.; Yang, G. S.; et al. *Polyhedron* **2003**, *22*, 1019–1024.

TABLE 2. Catalytic Addition of Primary Aromatic Amines to Carbodiimides[a]



entry	R	$ArNH_2$	time / min.	product	yield (%)[b]
1	*i*-Pr		3	**1**	98
2	Cy		8	**2**	99
3	*i*-Pr		4	**3**	98
4	Cy		10	**4**	99
5	*i*-Pr		2	**5**	99
6	Cy		15	**6**	99
7	*i*-Pr		5	**7**	95
8	Cy		20	**8**	98
9	*i*-Pr		35	**9**	98
10	Cy		39	**10**	92
11	*i*-Pr		8	**11**	95
12	*i*-Pr		4	**12**	90
13	*i*-Pr		8	**13**	98
14	*i*-Pr		20	**14**	99
15	*i*-Pr		10	**15**	96
16[c]	*i*-Pr		720	**16**	95
17	*i*-Pr		300	**17**	95

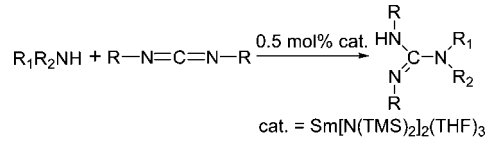
[a] The reaction was performed by treating 1 equiv of amines with 1 equiv of carbodiimides at rt. [b] Isolated yields. [c] 60 °C.

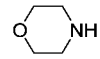
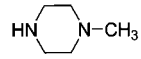
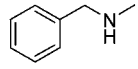
around the central metal shows a significant influence. The active sequence of $-I < -MeC_5H_4 < -OAr < -N(TMS)_2$ was observed, which indicated a combination of Lewis acidic metal with a stronger basic ligand led to a more active complex (Table 1, entries 1, 4, 6, 9, 11, and 13). It was noticed that divalent amide complex is even more active than the trivalent amide $Ln[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ (Ln = Sm (**VII**) and Yb[7] (**VIII**)) (Table 1 entries 14 and 15). For example, the reaction of aniline with diisopropylcarbodiimide catalyzed by **III** afforded the product **3** in 97% yield for 3 h in THF solution at 60 °C, while the same reaction with $Yb[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ gave **3** in 95% yield for 4 h (Table 1 entries 8 and 15). Besides, the reaction of *p*-flouroaniline with diisopropylcarbodiimide by **I** yielded the product **1** in 98% yield at room temperature in 3 min without solvent, while the same reaction with **VII** gave **1** in 22% for 3 min and 94% for 14 min, respectively. This may be because of the presence of a coordinated LiCl.

The reaction went much faster under solvent-free condition than that in THF solvent (Table 1, entries 2 and 3), Thus, **I** was then chosen as the precatalyst for the guanylation of various primary aromatic amines with carbodiimides under solvent-free condition. Representative results are summarized in Table 2.

As can be seen from Table 2, **I** is a very robust and efficient catalyst. All these reactions with primary aromatic amines could take place at room temperature with use of only 0.5 mol % of **I** to yield the corresponding *N*,*N*′,*N*″-trisubstituted guanidines in excellent yields (Table 2, entries 1−17). The reaction was not influenced by either electron-withdrawing or electron-donating substituents at the phenyl group. The catalyst system showed good functional group tolerance. The

TABLE 3. Catalytic Addition of Aliphatic Amines to Carbodiimides[a]



entry	R	R_1R_2NH	product	yield (%)[b]
1	*i*-Pr		**18**	98
2	Cy		**19**	98
3	*i*-Pr		**20**	97
4	Cy		**21**	98
5	*i*-Pr		**22**	93
6	Cy		**23**	99
7	*i*-Pr		**24**	87
8	Cy		**25**	90
9	*i*-Pr		**26**	95
10	*i*-Pr	n-$BuNH_2$	**27**	94

[a] The reaction was performed by treating 1 equiv of amines with 1 equiv of carbodiimides at 80 °C for 3 h. [b] Isolated yields.

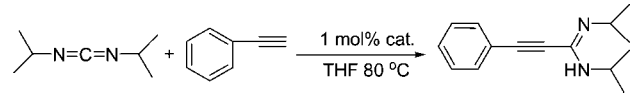
group of Cl, Br, and even NO_2 at the phenyl ring remained unchanged in the present reactions (Table 2, entries 13, 14, and 17). Notably, the reaction of diisopropylcarbodiimide with an aromatic amine bearing two bulky substituents on both ortho positions at the phenyl ring can also occur smoothly to give the corresponding guanidine in excellent yield, although the reaction requires a higher reaction temperature (60 °C) and prolonged reaction time (12 h) due to steric hindrance (Table 2, entry 16).

The reactions with secondary aliphatic amines also went smoothly, even though secondary amines are generally less active than primary amines. In the presence of 0.5 mol % of **I**, various acyclic and cyclic secondary amines could react with diisopropylcarbodiimide and dicyclohexylcarbodiimide at 80 °C to afford the corresponding guanidines in excellent yields after 3 h (Table 3, entries 1−9). The reaction with 1-methylpiperazine can still give good yield, even if it is less active than other cyclic secondary amines (Table 3, entries 7 and 8). Examination of the reactivity of n-$BuNH_2$ with diisopropylcarbodiimide gave satisfactory yield (94%, entry 10).

The excellent results obtained in addition of amines to carbodiimides encouraged us to further survey the catalytic reactivity of divalent lanthanide complexes for addition of terminal alkynes to carbodiimides. The reactions of phenylacetylene with 1,3-diisopropylcarbodiimide were first examined at 80 °C with complexes **I**−**V** at 1 mol % loading under various conditions. The results are listed in Table 4. All reactions went smoothly providing propiolamidine **28** in good to excellent yields depending both on the central metals and the ligand around the metal. The same active sequences as those found for guanylation were observed: Yb < Eu < Sm (Table 4, entries 1−3) and $-MeC_5H_4$ < −OAr < $-N(TMS)_2$ (Table 4, entries 1, 4, and 5). In contrast to the addition of amines to carbodiimides, the present reaction in THF is more active than that in solvent-free condition (Table 4, entries 1 and 6).

With reaction conditions optimized (Table 4, entry 1), we then examined the scope of this divalent lanthanide amide-catalyzed addition with selected alkynes and carbodiimides

TABLE 4. Catalytic Addition of a Phenylacetylene with an *N*,*N*′-Diisopropylcarbodiimide[a]



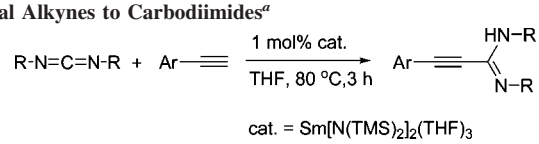
entry	cat.	catalyst loading (mol%)	temp/°C	time/h	yield (%)[b]
1	**I**	1	80	3	94
2	**II**	1	80	3	90
3	**III**	1	80	3	86
4	**IV**	1	80	3	81
5	**V**	1	80	3	83
6[c]	**I**	1	80	3	82

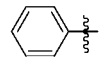
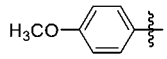
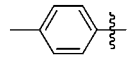
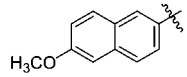
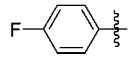
[a] 1 mmol of phenylacetylene, 1 mmol of *N*,*N*-diisopropylcarbodiimide, in THF, $C_{cat.}$ = 0.013 mmol/mL. [b] Isolated yields. [c] The reaction was conducted under solvent-free condition.

(Table 5). In general, the addition reaction proceeds efficiently at 80 °C to provide the desired product in excellent yields, regardless of electron-donating substituents on the phenyl ring. The results can be compared with those of half-sandwich yttrium alkyl complexes[1a] and are somewhat better than those found by indenyl lanthanide amides.[1g]

To understand the real active species, stoichiometric reactions of **I** and **IV** respectively with *N*,*N*′-diisopropylcarbodiimide were conducted. After workup a light yellow powder was obtained for both reactions. The powder was supposed to be **A** and **A**′ as shown in eq 1. An attempt to obtained the crystals of **A** and **A**′ suitable for X-ray analysis was unsuccessful. Moreover, the ^1H NMR data for the Sm(III) complex **A** and **A**′ are not valuable. Therefore, the further examination of **A** and **A**′ was conducted by the in situ reaction of **A** and **A**′ with aniline. A small amount of biamidine together with aniline and a trace of diketone from the hydrolysis of the biamidine by contaminated water in the system was obtained. But purifying the biamidine is very difficulty because it is more polar and sensitive. Therefore the hydrolysis of the reaction mixture of **A** and aniline, and

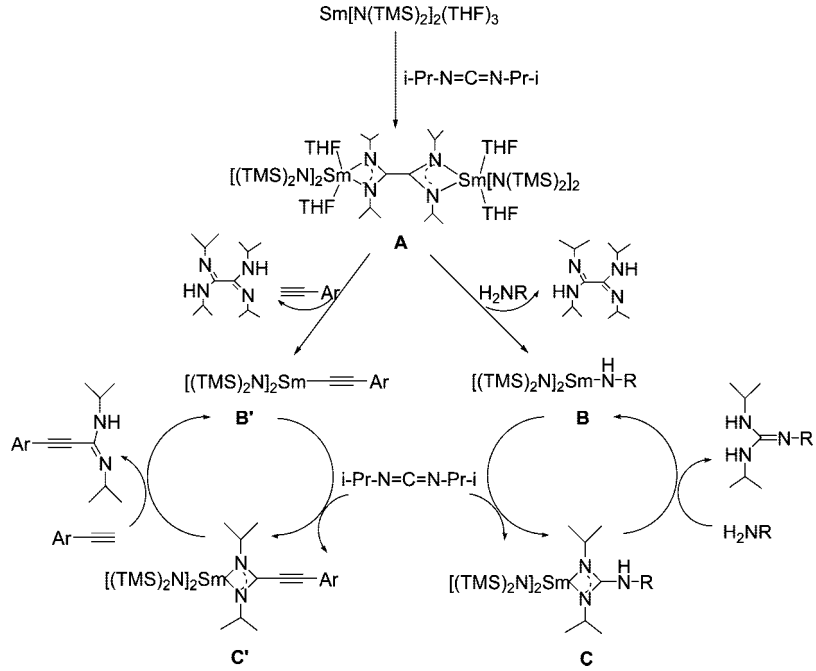
TABLE 5. Catalytic Addition of Terminal Alkynes to Carbodiimides[a]



entry	R	Ar	product	yield (%) [b]
1	*i*-Pr		**28**	94
2	Cy		**29**	95
3	*i*-Pr		**30**	96
4	*i*-Pr		**31**	95
5	Cy		**32**	90
6	*i*-Pr		**33**	98
7	Cy		**34**	97
8	*i*-Pr		**35**	90

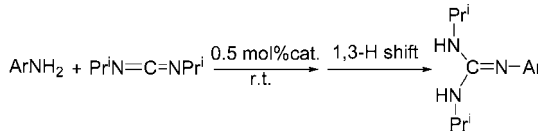
[a] The reaction was performed by treating 1 equiv of alkynes with 1 equiv of carbodiimides at 80 °C. [b] Isolated yields.

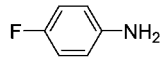
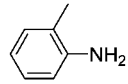
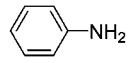
SCHEME 2. Proposed Mechanism for Addition of Amines and Terminal Alkynes to Carbodiimides



A′ and aniline was conducted and led to the isolation of pure diketone derived from biamidine. The isolation of diketone indicates the bimetallic bisamidinate complexes **A** and **A′** were really the product of the first reaction step in the reaction process of carbodiimide with amine by **I** and **IV**, respectively (Scheme 2). To confirm the formation of **A** and **A′** is essential for the catalytic reactions by **I** and **IV**, the reactions of *p*-fluoroaniline and *o*-methylaniline with *N*,*N*′-diisopropylcarbodiimide using **A** respectively, and the reaction of aniline with *N*,*N*′-diisopropylcarbodiimide using **A′** were further examined. As shown in Table 6, **A** or **A′** is really a more efficient catalyst related to **I** or **IV**, as the reaction with **I** or **IV** required longer time versus those with **A** or **A′** for obtaining the same yields. On the basis of the above results, a possible catalytic cycle by **I** for addition of amines and terminal alkynes to carbodiimides is proposed in Scheme 2.

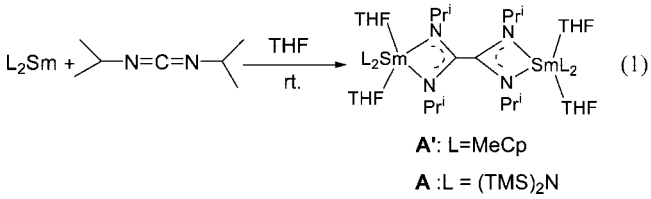
TABLE 6. Catalytic Addition of Amines to Carbodiimides with I (IV) and A (A′)[a]



entry	cat	$ArNH_2$	Time / min.	product	yield (%)[b]
1	**I**		3	**1**	98
2	**A**		2	**1**	98
3	**I**		15	**7**	95
4	**A**		7	**7**	99
5	**IV**		120	**3**	82
6	**A'**		52	**3**	94

[a] The reaction was performed by treating 1 equiv of amines with 1 equiv of carbodiimides at rt. [b] Isolated yields.

Reaction of **I** with RN═C═NR affords a bimetallic bisamidinate complex **A** via reduction-coupling of RN═C═NR. The protonolysis of **A** by an amine and alkyne releases a biamidine and two amide and alkynyl species **B** and **B′**, respectively. Nucleophilic addition of **B** and **B′** to a carbodiimide affords the corresponding species **C** and **C′**. The protonolysis of **C** and **C′** by another amine and alkyne molecule releases the product and generates **B** and **B′**.



(1)

Conclusions

Divalent lanthanide complexes **I**−**V** were first found to be highly active precatalysts for catalytic guanylation of amines with carbodiimides under solvent-free condition with a wide scope of amines. Complexes **I**−**V** are also efficient catalyst precursors for addition of terminal alkynes to carbodiimides. The active sequences of −I < $-MeC_5H_4$ < −ArO < $-N(TMS)_2$ for ligands and Yb < Eu < Sm for metals were observed for both reactions. The first step for both reactions was supposed to include the formation of a bimetallic bisamidinate samarium species originating from the reduction-coupling reaction of carbodiimide promoted by a samarium(II) complex. The active species is proposed to be a lanthanide guanidinate for addition of amines and a lanthanide amidinate complex for addition of terminal alkynes. Further studies on the applications of divalent complexes in C−N bond formation are now underway.

Experimental Section

General Procedure 1: For the Direct Synthesis of Guanidines from Reaction of Aromatic Amines with Carbodiimides Catalyzed by I (Product 3 as an Example). A 30 mL Schlenk tube was charged with **I** (0.006 g, 0.009 mmol). To the flask were added *N*,*N*′-diisopropylcarbodiimide (0.239 g, 1.90 mmol) and aniline (0.177 g, 1.90 mmol). The resulting mixture was stirred at room temperature for 3 min. The reaction mixture was then hydrolyzed with water (0.5 mL), extracted with dichloromethane (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under reduced pressure, the residue was recrystallized in hexane to provide a white solid **3** (98% yield). ^{1}H NMR ($CDCl_3$) δ 7.22 (2H), 6.95−6.91 (1H), 6.86−6.84 (2H), 3.77 (2H), 3.61 (2H), 1.17−1.15 (12H). ^{13}C NMR ($CDCl_3$) δ 150.5, 150.4, 129.4, 123.7, 121.5, 43.4, 23.6.

General Procedure 2: For the Direct Synthesis of Guanidines from Reaction of Secondary Amines with Carbodiimides Catalyzed by I (Product 18 as an Example). A 30 mL Schlenk tube was charged with **I** (0.011 g, 0.018 mmol). To the flask were added *N*,*N*′-diisopropylcarbodiimide (0.441 g, 3.50 mmol) and pyrrolidine (0.248 g, 3.50 mmol). The resulting mixture was stirred at 80 °C for 3 h. The reaction mixture was then hydrolyzed with water (0.5 mL), extracted with hexane (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under vacuum, the final product **18** was obtained as a white powder (98% yield). ^{1}H NMR ($CDCl_3$) δ 3.38 (2H), 3.26 (4H), 1.80 (4H), 1.11−1.10 (12H). ^{13}C NMR ($CDCl_3$) δ 153.7, 47.9, 46.8, 26.3, 24.8.

General Procedure 3: For the Direct Synthesis of Propiolamidines from Reaction of Terminal Alkynes with Carbodiimides Catalyzed by I (Product 28 as an Example). A 30.0 mL Schlenk tube in a drybox under dried argon was charged with **I** (0.010 g, 0.015 mmol), phenylacetylene (0.153 g, 1.500 mmol), and THF (1.20 mL). To the mixture was added *N*,*N*′-diisopropylcarbodiimide (0.189 g, 1.5 mmol). The Schlenk tube was taken outside and the mixture was stirred at 80 °C for 3 h. After the solvent was removed under reduced pressure, the residue was extracted with hexane and filtered to give a clean solution. The solvent was evaporated under vacuum; recrystallization of the crude from *n*-hexane afforded the product as a yellow solid (94%). ^{1}H NMR ($CDCl_3$) δ 7.51−7.48 (2H), 7.39−7.33 (3H), 3.99−3.93 (2H), 1.17−1.16 (12H). ^{13}C NMR ($CDCl_3$) δ 141.0, 131.7, 129.1, 128.2, 121.2, 91.6, 91.4,.79.1, 45.8, 23.7.

General Procedure 4: For Synthesis and Characterization of A and A′ (A = [{$(Me_3Si)_2N$}$_2$Sm(μ-$C_2N_4{}^iPr_4$)Sm{$N(SiMe_3)_2$}$_2$] as an Example). Synthesis: A solution of *N*,*N*′-diisopropylcarbodiimide (0.204 g, 2 mmol) in THF (20 mL) was added at ambient temperature with stirring to a purple solution of [Sm{$N(SiMe_3)_2$}$_2$($THF)_3$] (0.1 M, 20 mL, 2 mmol) in hexane. The color turned gradually to light yellow, and the mixture was stirred continuously for 1 h. The volume of solvent was reduced to 20 mL and stored at −10 °C for 2 days. Light-yellow powders of **A** were collected (1.03 g, 43%).

Characterization: Element Analysis and IR of A = [{$(Me_3Si)_2N$}$_2$Sm(μ-$C_2N_4{}^iPr_4$)Sm{$N(SiMe_3)_2$}$_2$]. Found: C, 37.59; H, 8.26; N, 9.11. Anal. Calcd for $C_{38}H_{102}N_8Si_8Sm_2$: C, 38.14; H, 8.59; N, 9.36. IR (KBr) 2966 (s), 1646 (s), 1630 (s), 1496 (m), 1384 (m), 1364 (m), 1248 (w), 1176 (m), 1128 (w), 843 (w) cm^{-1}.

Isolation of Diketone $O_2C_2H_2N_2{}^iPr_2$ from the Mixture of A and 2 equiv of Aniline. A solution of **A** (1.196 g, 1 mmol) in THF (10 mL) was added to aniline (0.186 g, 2 mmol) in THF (5 mL) with stirring at room temperature. After stirring for 1 h, distilled water (10 mL) was added to the system and extracted with dichloromethane (3 × 10 mL), then the organic phase was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure, then washed with OEt_2 to obtain a white solid (0.160 g, 93%). ^{1}H NMR ($CDCl_3$) δ 1.12−1.13 (12H), 3.78−3.88 (2H), 4.07−4.08 (2H). ^{13}C NMR ($CDCl_3$) δ 157.4, 42.5, 24.0.

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Supporting Information Available: Experimental procedures and characterizations and copies of ^{1}H NMR and ^{13}C NMR of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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