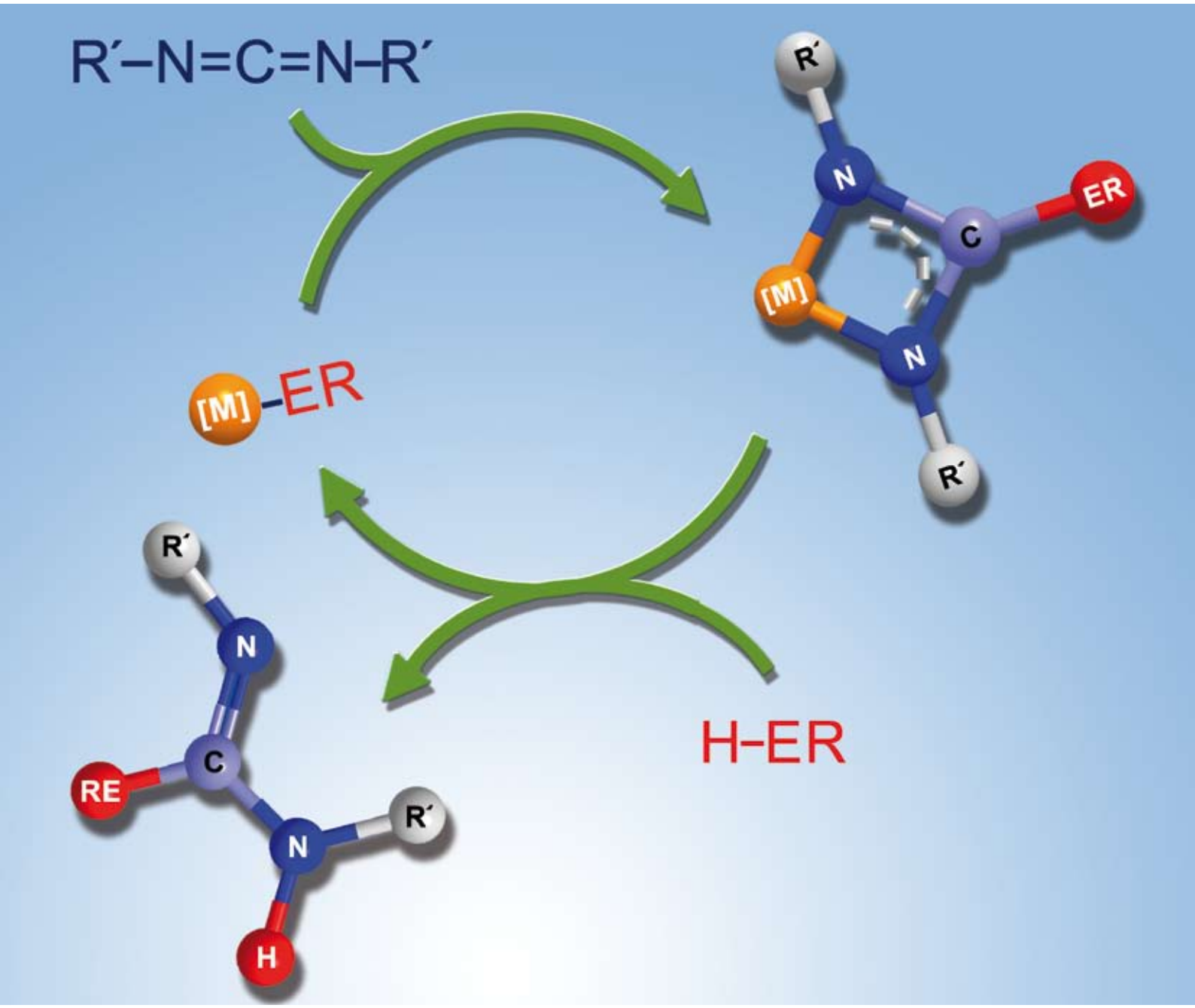
Organic & Biomolecular Chemistry

www.rsc.org/obc

Volume 6 | Number 10 | 21 May 2008 | Pages 1693–1856



ISSN 1477-0520

RSC Publishing

Catalytic addition of alkyne C–H, amine N–H, and phosphine P–H bonds to carbodiimides: an efficient route to propiolamidines, guanidines, and phosphaguanidines

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

Received 4th January 2008
First published as an Advance Article on the web 3rd April 2008
DOI: 10.1039/b800135a

Various metal complexes (*e.g.*, lanthanides, early transition metals, and alkali metals) can serve as catalyst precursors for the catalytic addition of alkyne C–H, amine N–H, and phosphine P–H bonds to carbodiimides, to give a new family of propiolamidines, guanidines, and phophaguanidines, some of which were difficult to prepare previously. The catalytic reaction proceeds generally through nucleophilic addition of an M–ER (E = CR^1R^2, NR^1, PR^1) bond, which is formed by an acid–base reaction between a catalyst precursor and a RE–H bond, to a carbodiimide compound, followed by protonolysis of the resultant amidinate–(phospha)guanidinate species "{R′NC(ER)NR′}M" with RE–H.

1 Introduction

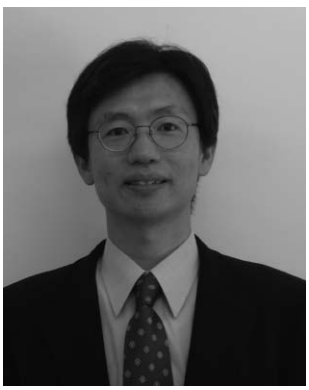
Multi-substituted amidines, guanidines, and phosphaguanidines of a general formula R′N=C(ER)NHR′ (E = CR^1R^2, NR^1, PR^1) are an important family of heteroatom-containing organic compounds, which can serve as building blocks for many biologically relevant compounds[1–3] and as stabilization ligands for various metal complexes.[4–12] Several routes are known for the synthesis of these compounds, but most of them are based on stoichiometric reactions. In contrast, catalytic approaches to these compounds are much less extensively studied.

[a]*Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan. E-mail: houz@riken.jp; Fax: 81 48 462 4665; Tel: 81 48 467 9393*
[b]*Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China. E-mail: wx_zhang@pku.edu.cn*

It is well known that the nucleophilic addition of metal–organic reagents "M–ER" (E = CR^1R^2, NR^1, PR^1) to carbodiimides R′N=C=NR′ can generally afford the corresponding amidinate–(phospha)guanidinate species "{R′NC(ER)NR′}M".[4–12] Although hydrolysis of "{R′NC(ER)NR′}M" could lead to stoichiometric formation of R′N=C(ER)NHR′, a catalytic transformation of "{R′NC(ER)NR′}M" to R′N=C(ER)NHR′ was thought difficult because of the strong chelation of the "NCN" unit to the metal center. Moreover, this hydrolysis approach is not suitable for the synthesis of the products having functional groups sensitive to hydrolysis. In 2005, we found that half-sandwich rare earth amidinate species can be protonated by terminal alkynes under appropriate conditions, which has thus led to the first catalytic addition of terminal alkynes to carbodiimides to give the corresponding amidine compounds.[13] This discovery encouraged us to investigate the catalytic addition of RE–H bonds to carbodiimides by use of rare earth and other metal catalysts. This article is intended to give an overview on our recent studies in this area. Related works by other groups are also described.

Wen-Xiong Zhang

Wen-Xiong Zhang was born in 1972. He obtained his Ph.D. from Nankai University in 2002, and carried out postdoctoral research, first at Peking University and then at RIKEN. He returned to Peking University in 2007, where he is now an Associate Professor. His research focuses on active intermediates in metal-mediated synthetic reactions and activation of small molecules by rare earth compounds.



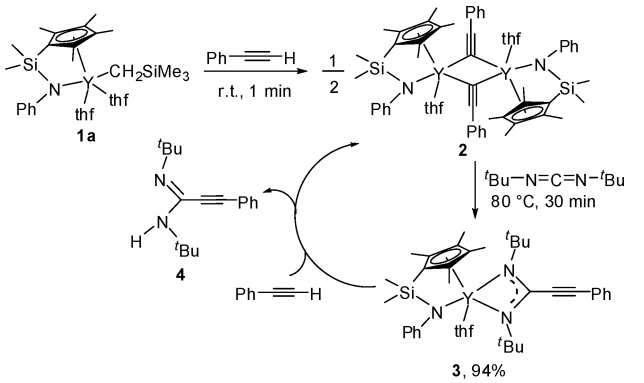
Zhaomin Hou

Zhaomin Hou was born in 1961. He obtained his Ph.D. from Kyushu University in 1989, and carried out postdoctoral research, first at RIKEN and then at the University of Windsor. He returned to RIKEN in 1993, where he is now Chief Scientist and Director of Organometallic Chemistry Lab. His research interests include development of new catalysts for efficient organic synthesis and materials innovation.

2 Addition of terminal alkyne C–H bonds to carbodiimides

The nucleophilic addition of alkali metal alkynides RC≡CM to carbodiimides was known to give easily the propiolamidinates {R′NC(C≡CR)NR′}M. However, the corresponding propiolamidines R′N=C(C≡CR)(NHR′), which contain a conjugated C–C triple bond, could hardly be obtained by hydrolysis of the propiolamidinate precursors because of their high sensitivity to hydrolysis.[13,14] During our studies on the catalytic dimerization of terminal alkynes by organo rare earth metal catalysts,[15] we examined the reactions of rare earth metal alkynides with carbodiimides. The reaction of the half-sandwich yttrium alkyl complex **1a** with 1 equiv of phenylacetylene in toluene yielded quantitatively the corresponding phenylacetylide **2**, which on reaction with 1,3-di-*tert*-butylcarbodiimide gave rapidly the propiolamidinate complex **3** at 80 °C (Scheme 1).[13] A reaction between the propiolamidinate **3** and phenylacetylene was not observed at room temperature in toluene-d_8. However, when a 1 : 1 mixture of **3** and phenylacetylene was heated to 80 °C, the propiolamidine **4** and the phenylacetylide **2** were formed almost quantitatively. Catalytic formation of **4** was achieved when excess phenylacetylene and 1,3-di-*tert*-butylcarbodiimide (1 : 1) were added to **3** in toluene-d_8 at 80 °C. Although a large number of amidinate complexes of various metals were previously reported, this was the first example of catalytic transformation of an amidinate species.

The use of an isolated amidinate complex such as **3** was not necessarily required for the present catalytic cross-coupling reaction. The alkyl complex **1a** also showed high catalytic activity under similar conditions (Table 1, entry 1). THF seemed to be a better solvent than benzene or toluene for this reaction (Table 1, entry 2). The Yb (**1c**) and Lu (**1d**) complexes were also effective, although their activity was slightly lower than that of the Y analogue **1a** (Table 1, entries 4–6). Formation of a

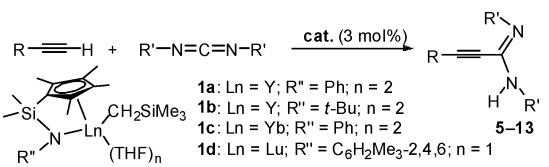


Scheme 1 Formation of an yttrium propiolamidinate and its reaction with phenylacetylene.

phenylacetylene homo-dimerization product was not observed under the present conditions, although these complexes were active for phenylacetylene homo-coupling in the absence of a carbodiimide.[15] A wide range of terminal alkynes could be used for this catalytic cross-coupling reaction. The reaction was not affected by either electron-withdrawing or -donating substituents or their positions at the phenyl ring of an aromatic alkyne (Table 1, entries 7–14). The aromatic C–Cl (entry 11) and C–Br (entry 10) bonds, which are known to be extremely susceptible to reductive cleavage by transition metals, survived in the present reactions. Heteroatom-containing alkynes such as pyridylacetylenes were also applicable (entry 13). In the case of an alkyl alkyne, the reaction became a little bit slower, probably owing to its weaker acidity (entry 14). *N*,*N*′-Diaryl-substituted carbodiimides were not suitable for this reaction, probably because the resulting amidines are too acidic.

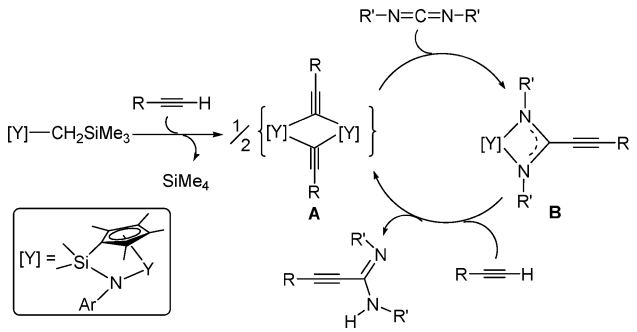
A catalytic cycle for the present cross-coupling reaction is shown in Scheme 2. The acid–base reaction between a half-sandwich

Table 1 Catalytic addition of terminal alkynes to carbodiimides by **1a**[a]



Entry	R	R′	Cat	Solvent	Temp/°C	Time/h	Yield (%)[b]
1	Ph	*i*-Pr	**1a**	C_6D_6	80	3	**5** (98)[c]
2	Ph	*i*-Pr	**1a**	THF-d_8	80	1	**5** (>99)[c]
3	Ph	*i*-Pr	**1b**	THF-d_8	80	1	**5** (98)[c]
4	Ph	*i*-Pr	**1a**	THF-d_8	80	0.5	**5** (93)[c]
5	Ph	*i*-Pr	**1c**	THF-d_8	80	0.5	**5** (84)[c]
6	Ph	*i*-Pr	**1d**	THF-d_8	80	0.5	**5** (76)[c]
7	4-MeC_6H_4	*t*-Bu	**1a**	Toluene	110	1	**6** (94)
8	4-$CF_3C_6H_4$	Cy	**1a**	THF	80	1	**7** (96)
9	4-$MeOC_6H_4$	*i*-Pr	**1a**	THF	80	1	**8** (96)
10	4-BrC_6H_4	*i*-Pr	**1a**	THF	80	1	**9** (93)
11	2-ClC_6H_4	*i*-Pr	**1a**	THF	80	1	**10** (97)
12	4-F-3-MeC_6H_3	*i*-Pr	**1a**	THF	80	1	**11** (95)
13	2-Py	Cy	**1a**	THF	80	1	**12** (98)
14	$CH_3(CH_2)_4$	*i*-Pr	**1a**	Toluene	110	2	**13** (70)

[a] Conditions: terminal alkynes, 2.07 mmol; carbodiimides, 2.01 mmol; catalyst **1a**, 0.06 mmol; solvent, 5 mL, unless otherwise noted. [b] Isolated yield. [c] Yields were determined by ^{1}H NMR using 1,3,5-trimethylbenzene as internal standard.



Scheme 2 A possible mechanism of catalytic addition of terminal alkynes to carbodiimides by **1a**.

rare earth metal alkyl and a terminal alkyne should yield straightforwardly an alkynide species such as **A**. Nucleophilic addition of the alkynide species to a carbodiimide affords the amidinate species **B**, which on abstraction of a proton from another molecule of alkyne would yield the corresponding amidine and regenerate the alkynide **A**.

More recently, lanthanocene silylamido complexes $[(CH_2)_2(\eta^5\text{-}C_9H_6)_2]LnN(SiMe_3)_2$ (Ln = Y, Sm),[16] and lithium silylamido $(Me_3Si)_2NLi$[17] were also reported to catalyze the addition of terminal alkynes to carbodiimides in an analogous way.

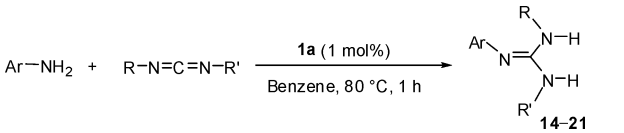
3 Addition of amine N–H bonds to carbodiimides

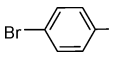
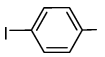
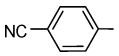
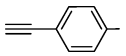
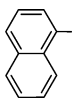
Primary aliphatic amines were known to undergo direct guanylation with carbodiimides to yield *N*,*N*′,*N*″-trialkylguanidines under rather forcing conditions.[18] However, less nucleophilic aromatic amines or secondary amines hardly react with carbodiimides under the same or harsher conditions, although tetrabutylammonium fluoride was previously reported to promote the nucleophilic addition of some aromatic amines to carbodiimides.[19] We recently found that half-sandwich rare earth metal alkyl complexes such as **1a** can serve as excellent catalysts for the catalytic addition of various aromatic primary amines and secondary amines to carbodiimides to afford the corresponding guanidines.[20]

Representative results of the addition of aromatic primary amines to carbodiimides catalyzed by **1a** are summarized in Tables 2 and 3.[20a] As shown in Table 2, a wide range of substituted anilines could be used for this reaction. The reaction was not influenced by either electron-withdrawing or -donating substituents or the position of the substituents at the phenyl ring (Table 2, entries 1–8). Aromatic C–F (entry 6), C–Cl (entry 5), C–Br (entry 1) and C–I (entry 2) bonds survived in the present reactions. In the case of *p*-aminophenylacetylene (entry 4), the reaction took place selectively at the amino group, while the terminal alkyne unit remained unchanged, although amino-free phenylacetylene could undergo catalytic addition to carbodiimides under conditions similar to those described above.

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 3. 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 **1a**, the reaction of 5-methylisoxazol-3-amine to ^{i}PrN=C=N^{i}Pr was completed within 1 h at room temperature in THF, yielding quantitatively the corresponding guanidine compound (Table 3, 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 1 h (Table 3, entry 2). In consistence with this observation, the reaction between 5-methylisoxazol-3-amine and the more bulky *N*,*N*′-di-*tert*-butylcarbodiimide did not occur under the same conditions, probably due to steric hindrance.

Table 2 Catalytic addition of various primary anilines to carbodiimides by **1a**[a]



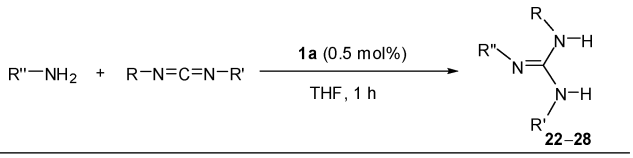
Entry	Ar	R	R′	Product (yield/%[b])
1		^{i}Pr	^{i}Pr	**14**(>99)
2		^{i}Pr	^{i}Pr	**15**(>99)
3		Cy	Cy	**16**(96)
4		^{i}Pr	^{i}Pr	**17**(>99)
5		^{i}Pr	^{i}Pr	**18**(>99)
6		^{i}Pr	^{i}Pr	**19**(>99)
7		^{i}Pr	^{i}Pr	**20**(>99)
8		Et	^{t}Bu	**21**(96)

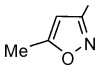
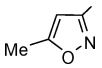
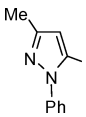
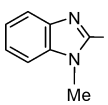
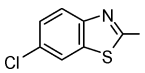
[a] Conditions: amines, 2.02 mmol; carbodiimides, 2.00 mmol; catalyst **1a**, 0.02 mmol; benzene, 5 mL. [b] Isolated yield.

Diamines and triamines are also applicable to this catalytic reaction. In the presence of 1 mol% of **1a**, the reaction of 1,3-diaminobenzene with 2 equiv of ^{i}PrN=C=N^{i}Pr gave quantitatively the corresponding biguanidine compound **29** (Scheme 3).[20a] Similarly, the reaction of 2,4,6-triaminopyrimidine with 3 equiv of ^{i}PrN=C=N^{i}Pr yielded the triguanidine compound **30** in high yield. These multiguanidine-functionalized compounds could serve as useful templates (or ligands) for the construction of further larger molecules.

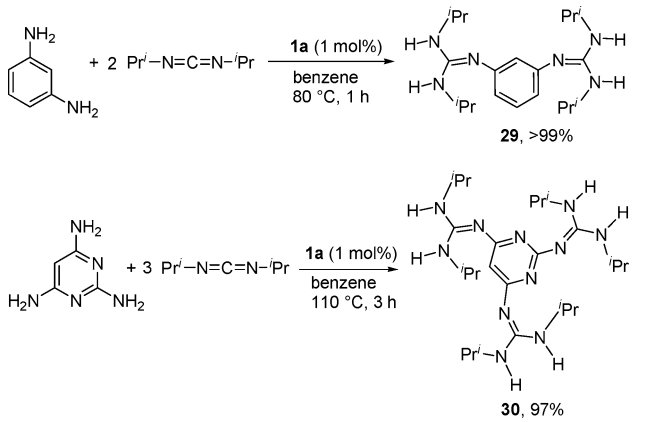
Secondary amines are generally less reactive than primary amines toward carbodiimides. However, in the presence of 3 mol% of **1a**, various acyclic and cyclic secondary amines could be added to ^{i}PrN=C=N^{i}Pr or CyN=C=NCy at 80 °C or a higher temperature, to give the corresponding *N*,*N*′,*N*″,*N*″-tetrasubstituted guanidines in almost quantitative yields (Table 4).[20] When a

Table 3 Catalytic addition of heterocyclic primary amines to carbodiimides by **1a**[a]



Entry	R″	R	R′	Temp/°C	Product (yield/%[b])
1		^{i}Pr	^{i}Pr	r.t.	**22**(>99)
2		Et	^{t}Bu	80	**23**(>99)
3		^{i}Pr	^{i}Pr	r.t.	**24**(>99)
4		^{i}Pr	^{i}Pr	80	**25**(>99)
5		^{i}Pr	^{i}Pr	50	**26**(>99)
6		^{i}Pr	^{i}Pr	80	**27**(>99)
7		^{i}Pr	^{i}Pr	80	**28**(>99[c])

[a] Conditions: amines, 2.02 mmol; carbodiimides, 2.00 mmol; catalyst **1a**, 0.01 mmol; THF, 5 mL, unless otherwise noted. [b] Isolated yield. [c] Conditions: amines, 2.02 mmol; carbodiimides, 2.00 mmol; catalyst **1a**, 0.02 mmol; benzene, 5 mL.



Scheme 3 Catalytic addition of di- and triamines to a carbodiimide by **1a**.

diamine such as piperazine was used to react with 2 equiv of ^{i}PrN=C=N^{i}Pr, the corresponding biguanidine **39** was formed in 99% yield by double catalytic addition reaction (Table 4, entry 9). Although tetrasubstituted guanidines could in principle have four possible isomers E_{anti}, E_{syn}, Z_{anti}, E_{syn},[21] NMR and X-ray analyses suggested that the guanidine products obtained in the present reactions may adopt exclusively the E_{anti} form.[20a]

The reaction of 1,2,3,4-tetrahydro-5-aminoisoquinodine with 1 equiv of ^{i}PrN=C=N^{i}Pr at 80 °C took place selectively at the primary amino group to give the monoguanidine compound **40**, and no reaction was observed at the cyclic secondary N–H bond, showing that a primary amino group can be distinguished from a secondary one under the present catalytic conditions (Scheme 4).[20a] Heating the reaction mixture with another equivalent of ^{i}PrN=C=N^{i}Pr at 110 °C for 3 h afforded the biguanidine **41** almost quantitatively. The biguanidine **41** could also be obtained alternatively by reaction of 1,2,3,4-tetrahydro-5-aminoisoquinodine with 2 equiv of ^{i}PrN=C=N^{i}Pr at 110 °C (Scheme 4).

The stoichiometric reaction of **1a** with diethylamine in benzene, gave instantly the corresponding amido complex **42** (Scheme 5).[20a] Nucleophilic addition of **42** to ^{i}PrN=C=N^{i}Pr took place rapidly to give the guanidinate complex **43**. At room temperature, no reaction was observed between the guanidinate complex **43** and diethylamine. However, when a 1 : 1 mixture of **43** and diethylamine was heated to 80 °C, the corresponding guanidine compound **31** and the amido complex **42** were formed almost quantitatively. When excess diethylamine and ^{i}PrN=C=N^{i}Pr (1 : 1) were added to **43** in C_6D_6 at 80 °C, catalytic formation of guanidine **31** was achieved.

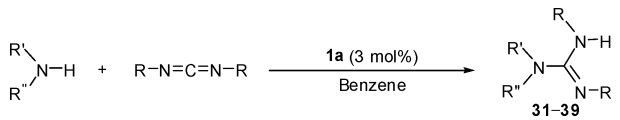
A possible catalytic cycle for the addition of secondary amines to carbodiimides is shown in Scheme 6. The acid–base reaction between the yttrium alkyl complex **1a** and an amine should yield straightforwardly an amido species such as **C**. Nucleophilic addition of the amido species to a carbodiimide would afford directly the guanidinate species **D**. Protonation of **D** by another molecule of amine would regenerate the amido complex **C** and release the guanidine **E**. Rearrangement of **E** through C–N bond rotation to **F** and the subsequent 1,3-hydrogen shift would take place to give the more stable *E*-isomer **G**.

The catalytic addition reaction between primary aromatic amines and carbodiimides could take place similarly (Scheme 7). In this case, however, the intramolecular 1,3-hydrogen shift in the initially formed symmetrical guanidinate species **I** could occur to give the unsymmetrical guanidinate species **J** (path a), because the aryl amine proton in **I** is more acidic than the alkyl amine proton in **J**. Protonolysis of **J** by another molecule of primary amine would regenerate the amido **H** and release the guanidine **K**. Intramolecular 1,3-hydrogen shift in **K** could give the more stable, final product **L**. Formation of **K** through protonolysis of **I** (path b) could also be possible.

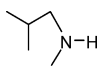
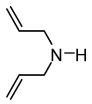
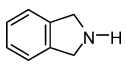
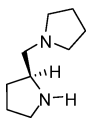
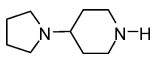
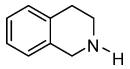
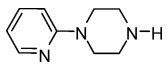
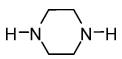
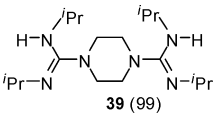
Wang and coworkers reported that lanthanocene amido complexes $[(CH_2)_2(\eta^5\text{-}C_9H_6)_2]LnN(SiMe_3)_2$ (Ln = Y, Sm)[16] and Cp-free lanthanide amido complexes $[\{(Me_3Si)_2N\}_3Ln(\mu\text{-}Cl)Li(thf)_3]$ (Ln = La, Sm, Eu, Y, and Yb)[22] and $\{(Me_3Si)_2N\}_3Ln$ (Ln = Y, and Yb)[22] could also act as good catalyst precursors for the catalytic addition of primary aromatic amines and secondary amines in an analogous fashion.

Richeson and coworkers reported the addition of primary aromatic amines to carbodiimides catalyzed by titanium imido complexes **44**.[23] The proposed mechanism begins with [2 + 2] cycloaddition of a carbodiimide to the Ti=NAr bond. A proton-transfer reaction between an aromatic amine and the metal-bound

Table 4 Catalytic addition of secondary amines to carbodiimides by **1a**[a]



31–39

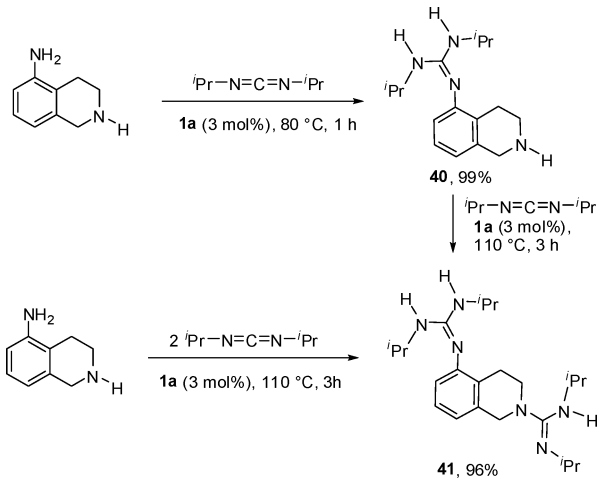
Entry	R′R″N–H	R	Temp/°C (Time/h)	Product (yield/%[b])
1		*i*-Pr	80(3)	**31**(95)
2		*i*-Pr	80(3)	**32**(92)
3		*i*-Pr	80(3)	**33**(93)
4		*i*-Pr	80(0.5)	**34**(>99)
5		*i*-Pr	110(5)	**35**(90)
6		Cy	80(1)	**36**(95)
7		Cy	80(0.5)	**37**(>99)
8		*i*-Pr	80(1)	**38**(>99)
9		*i*-Pr	80(3)	 **39** (99)

[a] Conditions: amines, 2.00 mmol; carbodiimides, 2.00 mmol; catalyst **1a**, 0.06 mmol; benzene, 5 mL. [b] Isolated yield.

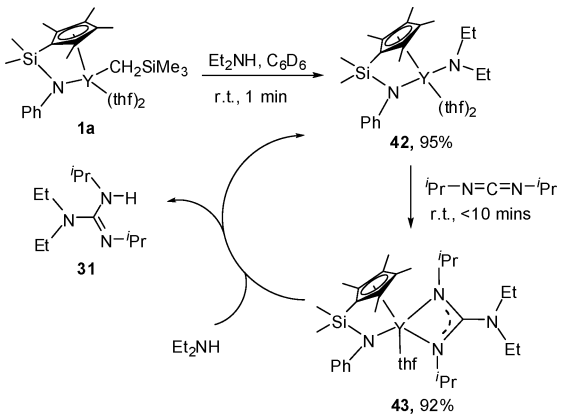
dianionic guanidate complex **45** then releases the neutral guanidine and reforms the Ti=NR bond (Scheme 8). Therefore, secondary amines could not be used in this reaction, because the formation of a "Ti=N" imido moiety is required for the catalytic process. In these catalyst systems, the resulting guanidine products **L** could be contaminated by that resulting from the initial imido species in the catalyst precursors.

Xie and coworkers reported that the carboranyl-alkoxy-ligated titanium amido complex could catalyze the addition of both primary aromatic amines and secondary amines to carbodiimides.[24] The reaction proceeded in a way analogous to that observed in the case of rare earth metal catalysts (Scheme 9). The reaction of the Ti–N amido bond in **M** with RN=C=NR yielded species **N** or **N′**. A protonolysis reaction between **N** or **N′** and an amine released the guanidine compound **G** and meanwhile regenerated **M**. No titanium imido species were observed in this catalytic process.

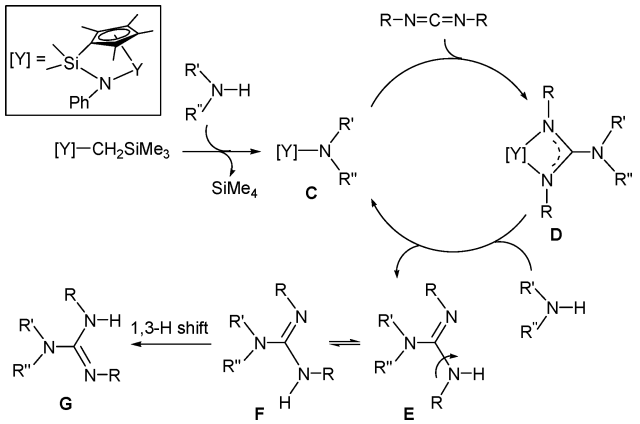
Montilla and coworkers reported that the vanadium imido chloride complex $Cl_3V{=}N(C_6H_3{}^iPr_2\text{-}2,6)$ can serve as a good catalyst precursor for the addition of both primary aromatic amines and secondary amines (Scheme 10).[25] There are two possible pathways for this reaction: (i) [2 + 2] carbodiimide addition to the V=N imido bond, a mechanism demonstrated by Richeson and coworkers for the formation of guanidines catalyzed by Ti=N imido complexes; (ii) carbodiimide insertion into a V–N amido bond, which was formed *in situ* by reaction of amines with the V–Cl bonds in $Cl_3V{=}N(C_6H_3{}^iPr_2\text{-}2,6)$. A DFT study revealed that the carbodiimide insertion into the V–N amido bond is more favorable than that into the V=N imido bond. A possible mechanism is shown in Scheme 11.[25] A reasonable intermediate **O** is proposed for the insertion of a primary V–N amido bond to carbodiimides to give the corresponding guanidinate intermediate **P**, which, after the amine protonolysis, gives a guanidine compound



Scheme 4 Stepwise catalytic addition of 1,2,3,4-tetrahydro-5-amino-isoquinodine to *N*,*N*′-diisopropylcarbodiimide by **1a**.



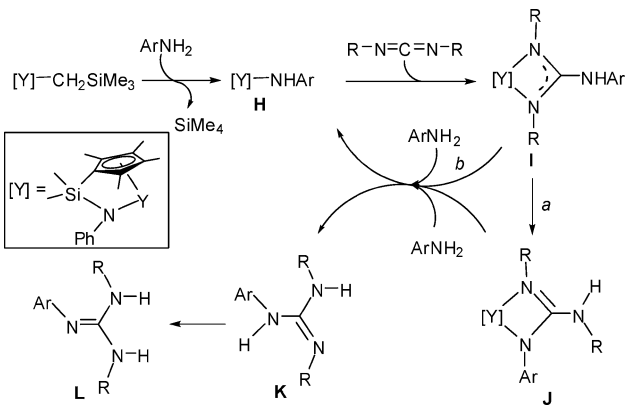
Scheme 5 Formation of an yttrium guanidinate and its reaction with diethylamine by **1a**.



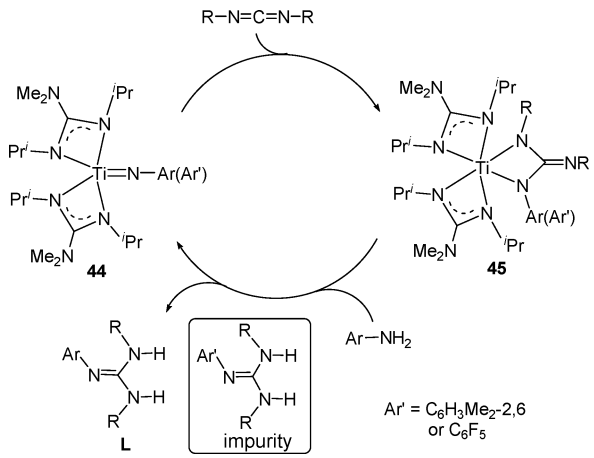
Scheme 6 A possible mechanism of catalytic addition of secondary amines to carbodiimides by **1a**.

and regenerates **O**, while the imido unit itself serves only as an ancillary ligand.

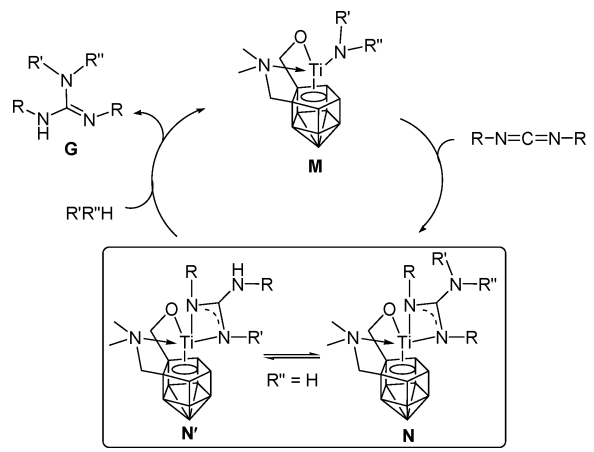
Richeson and coworkers reported that lithium silyl amido compound $(Me_3Si)_2NLi$ can also serve as a good catalyst precursor for the addition of amines to carbodiimides.[17] Efficient guanylations of 2,3-dimethylindole and acetamide could be achieved



Scheme 7 A possible mechanism of catalytic addition of primary aromatic amines to carbodiimides by **1a**.

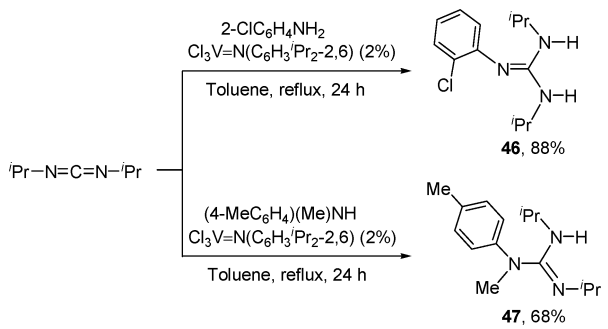


Scheme 8 A proposed mechanism for the addition of primary aromatic amines to carbodiimides catalyzed by titanium imido complexes.

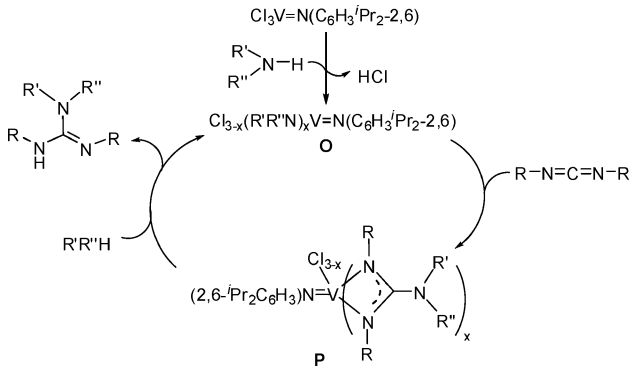


Scheme 9 A possible mechanism of catalytic addition of amines to carbodiimides by a titanacarborane amido complex.

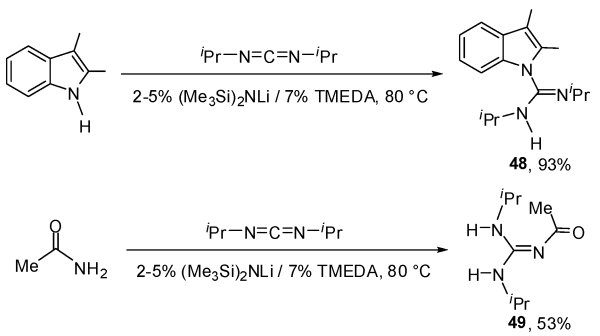
(Scheme 12). In these cases, efficient catalysis required the addition of tetramethylethylenediamines (TMEDA), which increased the reactivity of this catalyst system presumably through modulation of the lithium coordination sphere. An unsymmetric guanidinate intermediate $[Li\{^iPrNC(NH^iPr)NPh\}(thf)]_2$, which was formed by reaction of $(Me_3Si)_2NLi$ with $PhNH_2$ and $^iPrN{=}C{=}N^iPr$, was



Scheme 10 Addition of amines to *N*,*N*′-diisopropylcarbodiimide catalyzed by a vanadium imido complex.



Scheme 11 A proposed mechanism for the addition of amines to carbodiimides catalyzed by a vanadium imido complex.



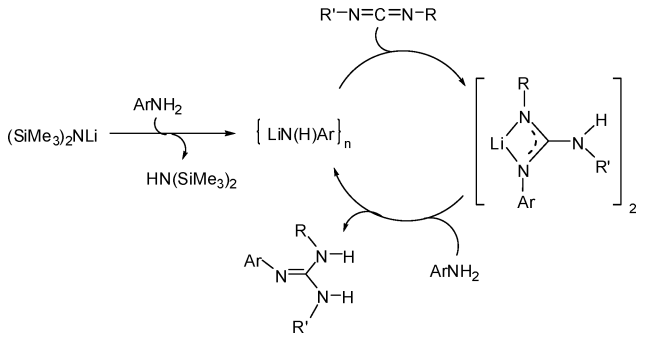
Scheme 12 Catalytic addition of 2,3-dimethylindole and acetamide to *N*,*N*′-diisopropylcarbodiimide by $(Me_3Si)_2NLi$.

isolated and confirmed to be a dimeric species by X-ray analysis. A possible catalytic cycle is shown in Scheme 13.

4 Addition of phosphine P–H bonds to carbodiimides

The half-sandwich rare earth metal alkyl complexes such as **1a**–**e** and **50a**–**h** are also active for the catalytic addition of phosphine P–H bonds to carbodiimides to give a new family of phosphaguanidines with various substituents.[26] Among the lanthanide *o*-dimethylaminobenzyl complexes **50a**–**f**, the activity increased as the metal size became larger (Lu < Gd < Sm < Nd < Pr < La) (Table 5), and the largest lanthanum complex La (**50a**) showed the highest activity.

Table 6 summarizes representative results of the catalytic addition of various phosphines to carbodiimides by complex



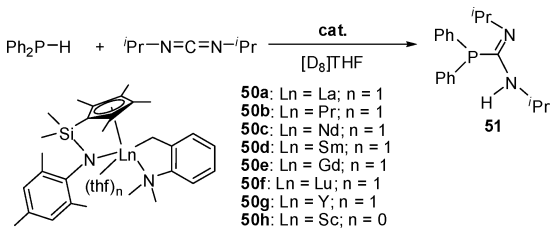
Scheme 13 A possible mechanism of catalytic addition of primary aromatic amines to carbodiimides by $(Me_3Si)_2NLi$.

50a.[26] A wide range of diarylphosphines could be used as the nucleophiles. Aromatic C–Cl (entry 5) and C–Br (entry 6) bonds survived in the catalytic conditions to yield selectively the corresponding halogen-substituted phosphaguanidines **56** and **57**, a new class of phosphaguanidine building blocks that could be useful for construction of further larger phosphaguanidine derivatives. The reaction of an alkyl/aryl phosphine such as ethylphenylphosphine (entry 7) with ^{i}PrN=C=N^{i}Pr required a longer time for completion, however, a dialkyl phosphine could not be utilized in this reaction, probably owing to the weaker acidity of these phosphines compared to that of diaryl phosphines. The reaction of $PhPH_2$ with ^{i}PrN=C=N^{i}Pr afforded selectively the mono-addition product **59** (entry 8), while in the case of $CyPH_2$, the bis-addition product **61** was also obtained as a minor product (12%) in addition to the mono-addition product **60** (70%) (entry 9).

The stoichiometric reaction between **50a** and diphenylphosphine in THF at room temperature gave the monomeric phosphide complex **62** (Scheme 14). Recrystallization of **62** in benzene afforded a phosphido bridged dimeric complex **63**. The reaction of **62** or **63** with ^{i}PrN=C=N^{i}Pr in THF at room temperature gave the phosphaguanidinate complex **64**. Recrystallization of **64** in ether at room temperature yielded the ether-coordinated complex **65** as light-orange crystals suitable for X-ray analysis. A reaction between **64** and diphenylphosphine was not observed at room temperature in $[D_8]$THF. However, when a 1 : 1 mixture of **64** and diphenylphosphine was heated to 80 °C, the phosphaguanidine **51** and **62** were formed almost quantitatively. The catalytic formation of **51** was achieved when excess amounts of diphenylphosphine and ^{i}PrN=C=N^{i}Pr (1 : 1) were added to **64** in $[D_8]$THF and heated at 80 °C. The analogous reaction between **65** and diphenylphosphine afforded **51** and **62** similarly. These results clearly demonstrate that a lanthanide phosphaguanidinate species can be protonated by a phosphine P–H bond.

A possible reaction mechanism for the catalytic addition of a phosphine P–H bond to a carbodiimide compound by **50a** is shown in Scheme 15. The acid–base metathesis reaction between a phosphine P–H bond and the La–benzyl bond should yield straightforwardly a phosphide species such as **Q**. Nucleophilic addition of the phosphide species to a carbodiimide would afford the phosphaguanidinate species **R**, which on abstraction of a proton from another molecule of phosphine, would yield the phosphaguanidine product and regenerate the phosphide **Q**.

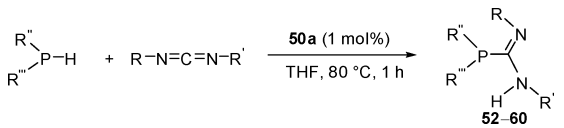
Table 5 Catalytic addition of diphenylphosphine to *N*,*N*′-diisopropylcarbodiimide by lanthanide *o*-dimethylaminobenzyl alkyl complexes[a]



Entry	Catalyst (Ln, mol%)	Ionic radius of Ln^{3+}/Å[b]	Temp/°C	Time/h	Yield[c] (%)
1	**50h** (Sc, 3)	0.745	80	1	15
2	**50g** (Y, 3)	0.900	80	1	86
3	**50f** (Lu, 3)	0.861	80	1	50
4	**50e** (Gd, 3)	0.938	80	1	65
5	**50d** (Sm, 3)	0.958	80	1	69
6	**50c** (Nd, 3)	0.983	80	1	93
7	**50b** (Pr, 3)	0.990	80	1	94
8	**50a** (La, 3)	1.032	80	0.5	>99
9	**50a** (La, 1)	1.032	80	1	>99

[a] Conditions: diphenylphosphine, 0.35 mmol; *N*,*N*′-diisopropylcarbodiimide, 0.34 mmol; Ln catalyst. [b] The ionic radius of six-coordination.[27] [c] Yields were determined by ^{31}P NMR.

Table 6 Catalytic addition of phosphines to carbodiimides by **50a**[a]



Entry	R″R‴PH	R, R′	Yield (%)[b]
1	Ph_2PH	*t*-Bu, Et	**52** (95)
2	Ph_2PH	Cy	**53** (95)
3	$(2\text{-}MeC_6H_4)_2PH$	*i*-Pr	**54** (99)
4	$(4\text{-}MeOC_6H_4)_2PH$	*i*-Pr	**55** (99)
5	$(3,5\text{-}Cl_2C_6H_3)_2PH$	*i*-Pr	**56** (95)
6	$(4\text{-}BrC_6H_4)_2PH$	*i*-Pr	**57** (97)
7	PhEtPH	*i*-Pr	**58** (86)[c]
8	$PhPH_2$	*i*-Pr	**59** (96)[c]
9	$CyPH_2$	*i*-Pr	**60** (70)[d]

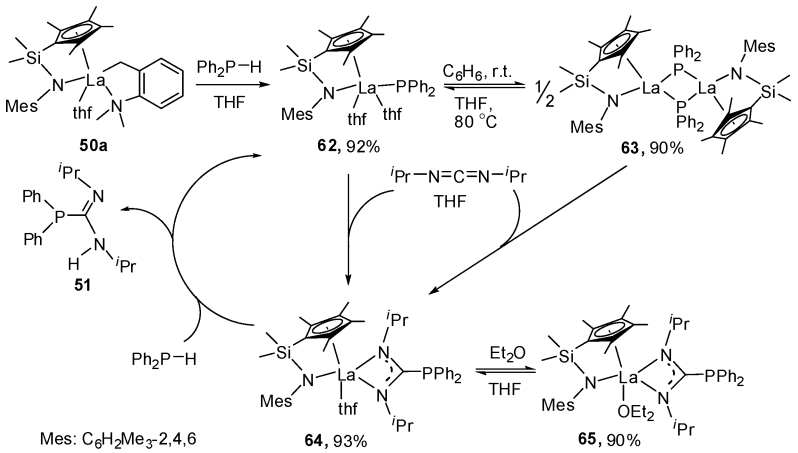
[a] Conditions: phosphine, 2.02 mmol; carbodiimide, 2.00 mmol; catalyst, 0.02 mmol; solvent, 5 mL, unless otherwise noted. [b] Isolated yield. [c] Toluene, 110 °C, 12 h. [d] (^{i}PrN=CNH^{i}Pr)$_2$(PCy) (**61**) (12%, determined by ^{31}P NMR) was also observed.

We found that the readily available alkali metal compounds such as $(Me_3Si)_2NM$ (M = Li, Na, K) and RLi (R = *n*-Bu, CH_2SiMe_3) can also act as excellent catalyst precursors for the catalytic addition of various primary and secondary phosphines to carbodiimides to afford cleanly the corresponding phosphaguanidines (Table 7, entries 1–13).[28,29] The alkali metal catalysts are even more active than the lanthanide catalysts and can catalyze the reaction at room temperature. It is also noteworthy that aromatic C–Cl (entry 8) and C–Br (entry 9) bonds remained unchanged even when *n*-BuLi was used as a catalyst, which is in sharp contrast with the stoichiometric reactions between $(4\text{-}XC_6H_4)_2PH$–*n*-BuLi and ^{i}PrN=C=N^{i}Pr, which yielded a mixture of the X-containing phosphaguanidines and the X-free phosphaguanidines (X = Cl, Br) after protonolysis with [HNEt$_3$][Cl]. The present catalytic reaction could also be carried out under solvent-free conditions on a larger preparative scale, demonstrating its practical usefulness well (Scheme 16).

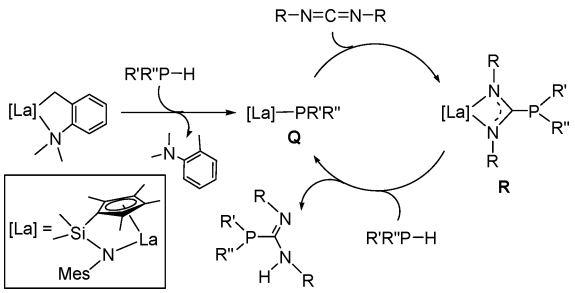
In a 1 : 1 : 1 reaction of $(Me_3Si)_2NK$, Ph_2PH, and CyN=C=NCy, the potassium phosphaguanidinate complex $[Ph_2PC(NCy)_2K(OEt_2)]_2$ (**69**) was isolated quantitatively from a diethyl ether solution and confirmed by an X-ray diffraction analysis.[28] Complex **69** adopts an "inverse sandwich" dimeric structure, in which the two K atoms are bridged by two coplanar guanidinate units in a μ-η^2,η^2-fashion through the nitrogen atoms. Addition of 2 molar equiv of Ph_2PH to a THF solution of **69** yielded guanidine CyN=C(PPh$_2$)(NHCy) and $KPPh_2$ quantitatively. A possible reaction mechanism for the potassium-catalyzed addition of phophines to carbodiimides is shown in Scheme 17.

Conclusion

Catalytic addition of terminal alkyne C–H, amine N–H, and phosphine P–H bonds to carbodiimides (R′N=C=NR′) can be achieved by use of various metal catalysts, including lanthanides, early transition metals, and alkali metals. These reactions have provided a general efficient route to a new family of propiolamidines, guanidines, and phophaguanidines, some of which were difficult to prepare previously. The catalytic reaction proceeds generally through nucleophilic addition of the M–ER (E = CR^1R^2, NR^1, PR^1) bond, which is formed by acid–base reaction between a catalyst precursor and an RE–H (E = CR^1R^2, NR^1, PR^1) bond, to a carbodiimide compound, followed by protonolysis of the resultant "(R′NC(ER)NR′)M" species with RE–H. These reactions have demonstrated that an amidinate–(phopha)guanidinate unit, though often used as an ancillary ligand for various organometallic complexes, can participate in a catalytic reaction under appropriate conditions. Future challenges in this area could include expansion of the catalytic transformation

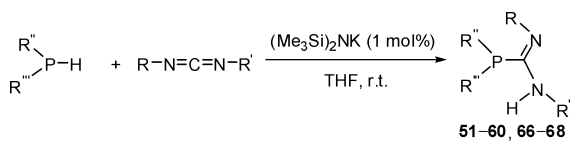


Scheme 14 Formation of a lanthanum phosphaguanidinate and its reaction with diphenylphosphine.



Scheme 15 A possible mechanism of catalytic addition of phosphines to carbodiimides by **50a**.

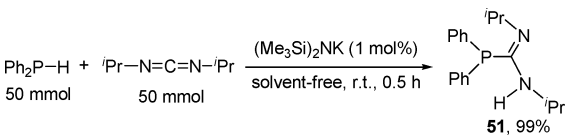
Table 7 Catalytic addition of phosphines to carbodiimides by $(Me_3Si)_2NK$[a]



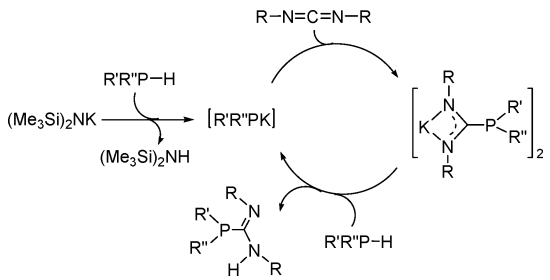
Entry	$R''^2R'''PH$	R, R′	Time	Yield (%)[b]
1	Ph_2PH	*i*-Pr	5 min	**51** (99)
2	Ph_2PH	*t*-Bu, Et	5 min	**52** (98)
3	Ph_2PH	Cy	5 min	**53** (99)
4	Ph_2PH	Ph, Cy	5 min	**66** (99)
5	Ph_2PH	*p*-Tolyl	5 min	**67** (99)
6	$(2\text{-}MeC_6H_4)_2PH$	*i*-Pr	5 min	**54** (99)
7	$(4\text{-}MeOC_6H_4)_2PH$	*i*-Pr	5 min	**55** (99)
8	$(3,5\text{-}Cl_2C_6H_3)_2PH$	*i*-Pr	5 min	**56** (98)
9	$(4\text{-}BrC_6H_4)_2PH$	*i*-Pr	5 min	**57** (97)
10	PhEtPH	*i*-Pr	4 h	**58** (96)[c]
11	$(i\text{-}Bu)_2PH$	*i*-Pr	12 h	**68** (95)[d]
12	$PhPH_2$	*i*-Pr	1 h	**59** (97)
13	$CyPH_2$	*i*-Pr	1 h	**60** (80)[e]

[a] Conditions: phosphine, 2.02 mmol; carbodiimide, 2.00 mmol; catalyst, 0.02 mmol; solvent, 5 mL, unless otherwise noted. [b] Isolated yield. [c] Catalyst, 3% mol, toluene, 110 °C. [d] Catalyst, 3% mol. [e] $(^iPrN{=}CNH^iPr)_2(PCy)$ (**61**) (15%, determined by ^{31}P NMR) was also observed.

of an amidinate–(phopha)guanidinate species beyond protonolysis.



Scheme 16 Catalytic addition of diphenylphosphine to *N*,*N*′-diisopropylcarbodiimide by $(Me_3Si)_2NK$ under solvent-free conditions.



Scheme 17 A possible mechanism of catalytic addition of phosphines to carbodiimides by $(Me_3Si)_2NK$.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 18065020, "Chemistry of Concerto Catalysis") from the Ministry of Education, Culture, Sports, Science and Technology of Japan, a Grant-in-Aid for Scientific Research (A) (No. 18205010) from the Japan Society for the Promotion of Science, and the National Natural Science Foundation of China (No. 20702003).

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