

Catalytic Addition of Terminal Alkynes to Carbodiimides by Half-Sandwich Rare Earth Metal Complexes

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Nucleophilic addition of organometallic reagents “RM” to carbodiimides ($R'N=C=NR'$) to give the corresponding amidinates “($R'NC(R)NR'$)M” is a well established process. The amidinate units have long been used as ancillary ligands for stabilization of various metal complexes, including those of early transition metals and lanthanides.^{1–4} However, catalytic transformation of a metal amidinate species has not been reported previously. Hydrolysis of a metal amidinate species could be a convenient, albeit stoichiometric route to amidines $R'N=C(R)NHR'$. However, propiolamidines $R'N=C(C\equiv CR)(NHR')$ which contain a conjugated C–C triple bond could hardly be obtained in this way because of their high sensitivity to hydrolysis.⁵ On the other hand, although addition of terminal alkyne C–H bonds across carbodiimides could, in principle, provide a straightforward, atom-economic route to propiolamidines, such a catalytic reaction has hardly been explored.⁶ In fact, although various amidines have been reported, little information about propiolamidines could be found in the literature, and in particular, isolated propiolamidines remained elusive.^{5,6}

We report here that half-sandwich rare earth metal complexes bearing silylene-linked cyclopentadienyl–amido ligands can act as an excellent catalyst for the addition of terminal alkynes to carbodiimides, which yields efficiently the corresponding N,N' -disubstituted propiolamidines. A rare earth metal amidinate species has been confirmed to be a true catalytic species in this process. As far as we are aware, this is the first example of catalytic transformation of a metal amidinate species and also the first example of efficient preparation of well-defined propiolamidines,^{5,6} a new family of amidines which may show unique reactivity that differs from those of the previously known amidines.⁷

The reaction of $\{Me_2Si(C_5Me_4)(NPh)\}Y(CH_2SiMe_3)(THF)_2$ (**1a**) with 1 equiv of phenylacetylene in toluene yielded quantitatively the corresponding phenylacetylide **2** (Scheme 1).⁸ Nucleophilic addition of **2** to 1,3-di-*tert*-butylcarbodiimide took place rapidly at 80 °C to give the propiolamidinate complex **3** (Scheme 1 and Figure 1). A reaction between **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 **4b** and the phenylacetylide **2** were formed almost quantitatively. More remarkably, catalytic formation of **4b** was achieved when excess phenylacetylene and 1,3-di-*tert*-butylcarbodiimide (1:1) were added to **3** in toluene-*d*₈ at 80 °C. These results are in striking contrast with what was observed previously for other amidinate complexes, such as $\{PhC(NSiMe_3)_2\}_2YCH(SiMe_3)_2$,^{4b} in which the amidinate ligands remained intact even in the presence of an excess amount of terminal alkynes at high temperatures. Although a large number of amidinate complexes of various metals have been reported,^{1–4} catalytic transformation of an amidinate species is, to the best of our knowledge, unprecedented.

The use of an isolated amidinate complex, such as **3**, was not necessarily required for the present catalytic cross-coupling reaction.

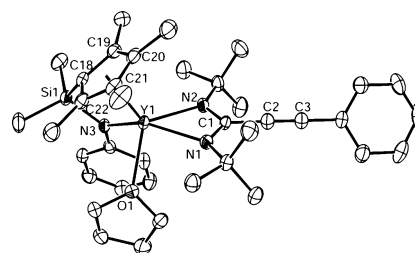
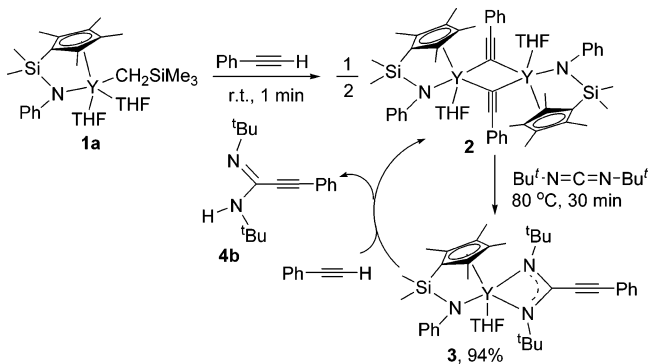


Figure 1. ORTEP drawing of **3**. Selected bond lengths (Å): Y(1)–N(1) 2.393(5), Y(1)–N(2) 2.339(5), N(1)–C(1) 1.322(7), N(2)–C(1) 1.325(7), C(1)–C(2) 1.449(8), C(2)–C(3) 1.182(8).

Scheme 1. Formation of an Yttrium Propiolamidinate and Its Reaction with Phenylacetylene



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 phenylacetylene homodimerization product was not observed under the present conditions, although these complexes were active for phenylacetylene homocoupling in the absence of a carbodiimide.⁸

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 9–18). The aromatic C–Cl (entries 12 and 14) and C–Br (entries 13 and 15) bonds survived in the present reactions. Heteroatom-containing alkynes, such as pyridylacetylenes (entries 19 and 20), were also applicable. In the case of an alkyl alkyne (entry 21), the reaction became a little bit slower probably owing to its weaker acidity. N,N' -Diaryl-substituted carbodiimides were not suitable for this reaction, probably because the resulting amidines are too acidic. The tris(alkyl) complex $Y(CH_2SiMe_3)_3(THF)_2$ showed no catalytic activity under the same conditions, suggesting that the Cp–amido ligands also play an important role.

Table 1. Catalytic Addition of Terminal Alkynes to Carbodiimides^a

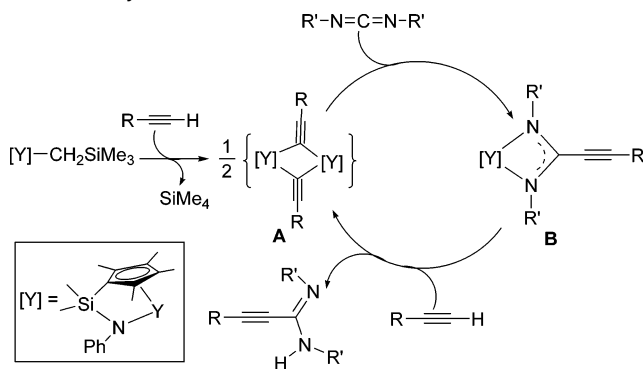
$$\text{R}-\text{C}\equiv\text{H} + \text{R}'-\text{N}=\text{C}=\text{N}-\text{R}' \xrightarrow{\text{cat. (3 mol\%)}} \text{R}-\text{C}\equiv\text{N}=\text{C}(\text{R}')-\text{N}-\text{R}'$$

1a: Ln = Y; R'' = Ph; n = 2
1b: Ln = Y; R'' = *t*-Bu; n = 2
1c: Ln = Yb; R'' = Ph; n = 2
1d: Ln = Lu; R'' = C₆H₂Me₃-2,4,6; n = 1

4a-o

entry	R	R'	cat.	solvent	temp (°C)	time (h)	yield ^b (%)
1	Ph	<i>i</i> -Pr	1a	C ₆ D ₆	80	3	4a (98) ^c
2	Ph	<i>i</i> -Pr	1a	THF- <i>d</i> ₈	80	1	4a (>99) ^c
3	Ph	<i>i</i> -Pr	1b	THF- <i>d</i> ₈	80	1	4a (98) ^c
4	Ph	<i>i</i> -Pr	1a	THF- <i>d</i> ₈	80	0.5	4a (93) ^c
5	Ph	<i>i</i> -Pr	1c	THF- <i>d</i> ₈	80	0.5	4a (84) ^c
6	Ph	<i>i</i> -Pr	1d	THF- <i>d</i> ₈	80	0.5	4a (76) ^c
7	Ph	<i>t</i> -Bu	1a	toluene	110	1	4b (94)
8	Ph	Cy	1a	THF	80	1	4c (95)
9	4-MeC ₆ H ₄	<i>t</i> -Bu	1a	toluene	110	1	4d (94)
10	4-CF ₃ C ₆ H ₄	Cy	1a	THF	80	1	4e (96)
11	4-MeOC ₆ H ₄	<i>i</i> -Pr	1a	THF	80	1	4f (96)
12	4-ClC ₆ H ₄	<i>t</i> -Bu	1a	toluene	110	1	4g (95)
13	4-BrC ₆ H ₄	<i>i</i> -Pr	1a	THF	80	1	4h (93)
14	2-ClC ₆ H ₄	<i>i</i> -Pr	1a	THF	80	1	4i (97)
15	2-BrC ₆ H ₄	<i>i</i> -Pr	1a	THF	80	1	4j (94)
16	2-MeC ₆ H ₄	<i>i</i> -Pr	1a	THF	80	1	4k (97)
17	3-MeC ₆ H ₄	<i>i</i> -Pr	1a	THF	80	1	4l (97)
18	4-F-3-MeC ₆ H ₃	<i>i</i> -Pr	1a	THF	80	1	4m (95)
19	3-Py	<i>i</i> -Pr	1a	THF	80	1	4n (98)
20	2-Py	Cy	1a	THF	80	1	4o (98)
21	CH ₃ (CH ₂) ₄	<i>i</i> -Pr	1a	toluene	110	2	4p (70)

^a Conditions: terminal alkynes, 2.07 mmol; carbodiimides, 2.01 mmol; catalyst, 0.06 mmol; solvent, 5 mL, unless otherwise noted. ^b Isolated yield. ^c Conditions: terminal alkynes, 0.35 mmol; carbodiimides, 0.34 mmol; catalyst, 0.01 mmol. Yields were determined by ¹H NMR using 1,3,5-trimethylbenzene as an internal standard.

Scheme 2. A Possible Mechanism of Catalytic Addition of Terminal Alkynes to Carbodiimides

A catalytic cycle for the present cross-coupling reaction is shown in Scheme 2. The acid–base reaction between a half-sandwich rare earth metal alkyl and a terminal alkyne should yield straightforwardly an alkyne species such as **A**.⁸ Nucleophilic addition of the alkyne species to a carbodiimide would afford the amidine species **B**, which on abstraction of a proton from another molecule of alkyne would yield the corresponding amidine and regenerate the alkyne **A**. The isolation of **3** and its reaction with phenylacetylene to give **2** and **4b** (see Scheme 1) strongly support this mechanism.

In summary, the catalytic addition of terminal alkynes to carbodiimides has been achieved for the first time by use of half-sandwich rare earth metal complexes as a catalyst, which offers a straightforward, atom-economic route to *N,N'*-disubstituted propiolamidines, a new family of amidines that were difficult to access by other means. Moreover, the results observed in this work

demonstrate that an amidinate unit, though being often used as an ancillary ligand for various organometallic complexes, can itself participate in a catalytic reaction under appropriate conditions.

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Supporting Information Available: Experimental details, X-ray data for **3**, **4g**, and **4i**, and scanned NMR spectra of all products (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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