Subscriber access provided by American Chemical Society

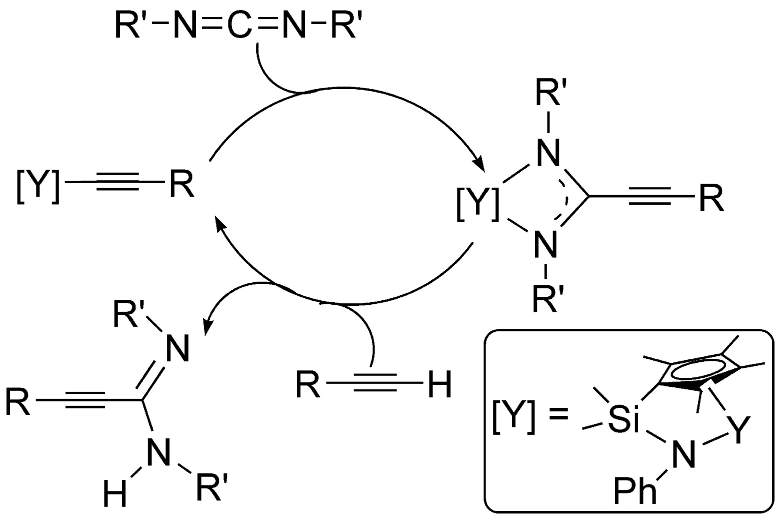
Communication

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

Wen-Xiong Zhang, Masayoshi Nishiura, and Zhaomin Hou

*J. Am. Chem. Soc.*, **2005**, 127 (48), 16788-16789• DOI: 10.1021/ja0560027 • Publication Date (Web): 10 November 2005

**Downloaded from http://pubs.acs.org on March 25, 2009**



## More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 15 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 11/10/2005

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

Wen-Xiong Zhang, Masayoshi Nishiura, and Zhaomin Hou*

*Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan, and PRESTO, Japan Science and Technology Agency (JST), Japan*

Received August 31, 2005; E-mail: houz@riken.jp

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≡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 illusive.[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 $\{PhC(NSiMe_3)_2\}_2YCH(SiMe_3)_2$,[4n] 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.

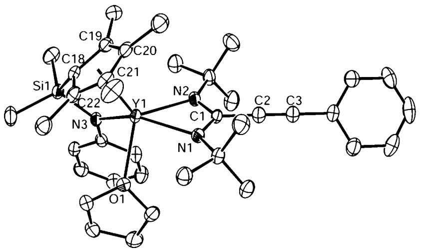
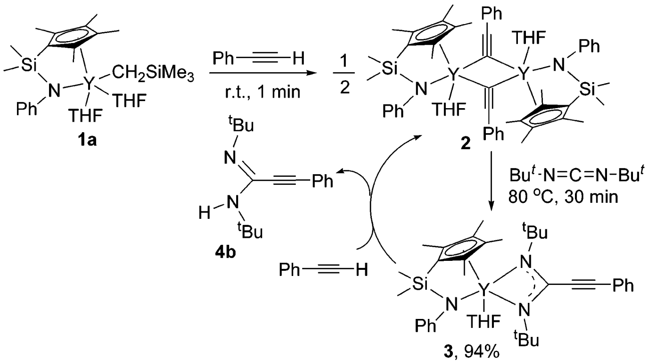


***Figure 1.*** ORTEP drawing of **3**. Selected bond lengths (Å): Y(1)−N(1) 2.393(5), Y(1)−N(2) 2.339(5), N(1)−C(1) 1.322(7), N(2)−C(1) 1.325(7), C(1)−C(2) 1.449(8), C(2)−C(3) 1.182(8).

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

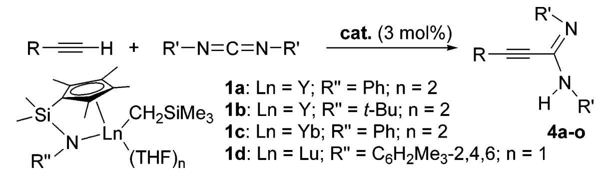


The alkyl complex **1a** also showed high catalytic activity under similar conditions (Table 1, entry 1). THF seemed to be a better solvent than benzene or toluene for this reaction (Table 1, entry 2). The Yb (**1c**) and Lu (**1d**) complexes were also effective, although their activity was slightly 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.

10.1021/ja0560027 CCC: $30.25 © 2005 American Chemical Society

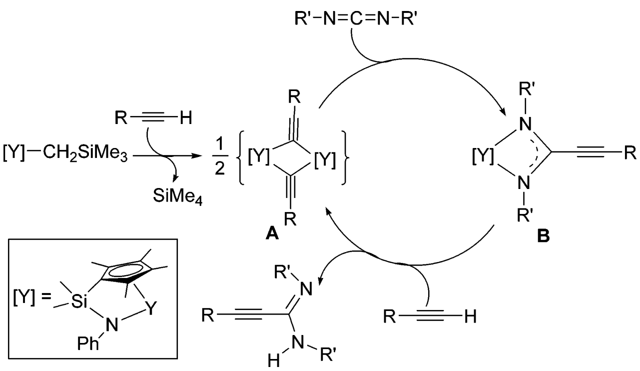
***Table 1.*** Catalytic Addition of Terminal Alkynes to Carbodiimides[a]



| entry | R | R′ | cat. | solvent | temp (°C) | time (h) | yield[b] (%) |
|---|---|---|---|---|---|---|---|
| 1 | Ph | *i*-Pr | **1a** | $C_6D_6$ | 80 | 3 | **4a** (98)[c] |
| 2 | Ph | *i*-Pr | **1a** | THF-$d_8$ | 80 | 1 | **4a** (>99)[c] |
| 3 | Ph | *i*-Pr | **1b** | THF-$d_8$ | 80 | 1 | **4a** (98)[c] |
| 4 | Ph | *i*-Pr | **1a** | THF-$d_8$ | 80 | 0.5 | **4a** (93)[c] |
| 5 | Ph | *i*-Pr | **1c** | THF-$d_8$ | 80 | 0.5 | **4a** (84)[c] |
| 6 | Ph | *i*-Pr | **1d** | THF-$d_8$ | 80 | 0.5 | **4a** (76)[c] |
| 7 | Ph | *t*-Bu | **1a** | toluene | 110 | 1 | **4b** (94) |
| 8 | Ph | Cy | **1a** | THF | 80 | 1 | **4c** (95) |
| 9 | 4-$MeC_6H_4$ | *t*-Bu | **1a** | toluene | 110 | 1 | **4d** (94) |
| 10 | 4-$CF_3C_6H_4$ | Cy | **1a** | THF | 80 | 1 | **4e** (96) |
| 11 | 4-$MeOC_6H_4$ | *i*-Pr | **1a** | THF | 80 | 1 | **4f** (96) |
| 12 | 4-$ClC_6H_4$ | *t*-Bu | **1a** | toluene | 110 | 1 | **4g** (95) |
| 13 | 4-$BrC_6H_4$ | *i*-Pr | **1a** | THF | 80 | 1 | **4h** (93) |
| 14 | 2-$ClC_6H_4$ | *i*-Pr | **1a** | THF | 80 | 1 | **4i** (97) |
| 15 | 2-$BrC_6H_4$ | *i*-Pr | **1a** | THF | 80 | 1 | **4j** (94) |
| 16 | 2-$MeC_6H_4$ | *i*-Pr | **1a** | THF | 80 | 1 | **4k** (97) |
| 17 | 3-$MeC_6H_4$ | *i*-Pr | **1a** | THF | 80 | 1 | **4l** (97) |
| 18 | 4-F-3-$MeC_6H_3$ | *i*-Pr | **1a** | THF | 80 | 1 | **4m** (95) |
| 19 | 3-Py | *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*-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 alkynide species such as **A**.[8] Nucleophilic addition of the alkynide species to a carbodiimide would afford 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**. 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.

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

**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.

## References

(1) Review: Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300.

(2) For examples of main group metal amidinate complexes, see: (a) Rowley, C. N.; DiLabio, G. A.; Barry, S. T. *Inorg. Chem.* **2005**, *44*, 1983−1991. (b) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2000**, *39*, 924−929. (c) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274−289. (d) Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1998**, *17*, 4042−4048. (e) Kennedy, A. R.; Mulvey, R. E.; Bowlings, R. B. *J. Am. Chem. Soc.* **1998**, *120*, 7816−7824.

(3) For examples of transition metal amidinate complexes, see: (a) van Meerendonk, W. J.; Schröder, K.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Eur. J. Inorg. Chem.* **2003**, 427−432. (b) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197−6198. (c) Kondo, H.; Yamaguchi, Y.; Nagashima, H. *J. Am. Chem. Soc.* **2001**, *123*, 500−501. (d) Kondo, H.; Yamaguchi, Y.; Nagashima, H. *Chem. Commun.* **2000**, 1075−1076. (e) Döhler, T.; Görls, H.; Walther, D. *Chem. Commun.* **2000**, 945−946. (f) Yamaguchi, Y.; Nagashima, H. *Organometallics* **2000**, *19*, 725−727. (g) Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 4183−4190. (h) Whitener, G. D.; Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1249−1255. (i) Averbuj, C.; Eisen, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 8755−8759. (j) Decker, J. M.; Geib, S. J.; Meyer, T. Y. *Organometallics* **1999**, *18*, 4417−4420.

(4) For examples of lanthanide amidinate complexes, see: (a) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182−9183. (b) Deng, M.; Yao, Y.; Zhang, Y.; Shen, Q. *Chem. Commun.* **2004**, 2742−2743. (c) Villiers, C.; Thuéry, P.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2004**, 4624−4632. (d) Richter, J.; Feiling, J.; Schmidt, H.-G.; Noltemeyer, M.; Brüser, W.; Edelmann, F. T. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1269−1275. (e) Bambirra, S.; Leusen, D. v.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2003**, 522−523. (f) Zhang, J.; Ruan, R.; Shao, Z.; Cai, R.; Weng, L.; Zhou, X. *Organometallics* **2002**, *21*, 1420−1424. (g) Luo, Y.; Yao, Y.; Shen, Q.; Sun, J.; Weng, L. *J. Organomet. Chem.* **2002**, *662*, 144−149. (h) Bambirra, S.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, *20*, 782−785. (i) Aubrecht, K. B.; Chang, K.; Hillmyer, M. A.; Tolman, W. B. *J. Polym. Sci. A* **2001**, *39*, 284−293. (j) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197−3204. (k) Doyle, D.; Gun’ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **2000**, 4093−4097. (l) Schmidt, J. A. R.; Arnold, J. *Chem. Commun.* **1999**, 2149−2150. (m) Kincaid, K.; Gerlach, C. P.; Giesbrecht, G. R.; Hagadorn, J. R.; Whitener, G. D.; Shafir, A.; Arnold, J. *Organometallics* **1999**, *18*, 5360−5366. (n) Duchateau, R.; Wee, C. T. v.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291−2302. (o) Hagadorn, J. R.; Arnold, J. *Organometallics* **1996**, *15*, 984−991. (p) Duchateau, R.; Wee, C. T. v.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931−4932.

(5) Although formation of propiolamidines by hydrolysis of alkali metal propiolamidates was reported, the spectral data provided could not be unambiguously assigned to the claimed amidines. See: Fujita, H.; Endo, R.; Aoyama, A.; Ichii, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1846−1852. It is now rather skeptical that the moisture-sensitive propiolamidines could survive the given hydrolysis conditions. Under similar conditions, we obtained an amide product rather than an amidine. See Supporting Information for more details.

(6) It was previously claimed that addition of a terminal alkyne to a carbodiimide was achieved in the presence of $Co_2(CO)_8/H_4Ru_4(CO)_{12}$. However, the spectral data provided for the product were obviously indicative of an amide, but were mistakenly assigned to an amidine. See: Schmidt, G. F.; Süss-Fink, G. *J. Organomet. Chem.* **1988**, *356*, 207−211. See also Supporting Information for more details.

(7) (a) Boyd, G. V. In *The Chemistry of Amidines and Imidates*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Vol. 2, Chapter 8. (b) Greenhill, J. V.; Lue, P. *Prog. Med. Chem.* **1993**, *30*, 203−326.

(8) (a) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc*. **2003**, *125*, 1184−1185. (b) Nishiura, M.; Hou, Z. *J. Mol. Catal. A* **2004**, *213*, 101−106.

JA0560027