



## Copper(I)–thiazol-2-ylidenes: highly reactive N-heterocyclic carbenes for the hydroboration of terminal and internal alkynes. Ligand development, synthetic utility, and mechanistic studies

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### Autorzy

Jin Zhang

Xue Li

Tao Li

Gaopeng Zhang

Kerou Wan

Yangmin Ma

Ran Fang

Roman Szostak

Michał Szostak

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In the last 15 years, copper-catalyzed borylative transformations utilizing boryl–copper have been established as a powerful activation mode in organic synthesis and catalysis, enabling direct transformations of various  $\pi$ -systems. Although many of these transformations use NHC (N-heterocyclic carbene) ligands, these studies have been almost exclusively limited to the derivatives of imidazol-2-ylidenes. However, the molecular properties of *N*-aryl-imidazol-2-ylidenes, such as IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), are limited by (1) the high degree of heteroatom stabilization and (2) symmetrical substitution of the nitrogen atoms. Herein, we report a study on Cu(I)–thiazol-2-ylidenes, thiazole analogues of imidazol-2-ylidenes, which (1) feature a distinct half-umbrella shape of the coordinating ligand and (2) exhibit lower heteroatom stabilization of the ancillary ligand through reduced  $\pi$ -donation from sulfur. We present the development of a family of stable Cu(I)–thiazol-2-ylidenes, where the combined sterics of thiazol-2-ylidenes lead to monomers [Cu(NHC)X] or bridged-halo dimers [Cu(NHC) ( $\mu$ -X)]<sub>2</sub>, their crystallographic characteristics, and application to the hydroboration of alkynes to afford trisubstituted vinylboronates by  $\beta$ -hydroboration of internal alkynes or terminal vinylboronates by  $\beta$ -hydroboration of terminal alkynes. Application to the late-stage modification and detailed mechanistic studies on the catalyst structure and activation are presented. Most crucially, Cu(I)–thiazol-2-ylidenes show a much higher  $\beta$ -selectivity in the hydroboration of alkynes than that of classical imidazol-2-ylidenes, affording vinylborons in excellent yields at ambient conditions. The unique “half-umbrella” shape of thiazol-2-ylidenes reverses the  $\alpha/\beta$  regioselectivity observed with imidazol-2-ylidenes in the hydroboration of terminal alkynes. Kinetic studies demonstrate that Cu(I)–thiazol-2-ylidenes supersede imidazol-2-ylidenes. Considering the significant utility of borylative transformations of  $\pi$ -systems, we anticipate that Cu(I)–thiazol-2-ylidenes will advance the synthetic transformations of boryl–copper in organic synthesis and catalysis.

#### Słowa kluczowe

copper catalysis, thiazol-2-ylidene, N-heterocyclic carbenes, hydroboration, DFT studies

Adres publiczny

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