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A *trans*-Selective Hydroboration of Internal Alkynes
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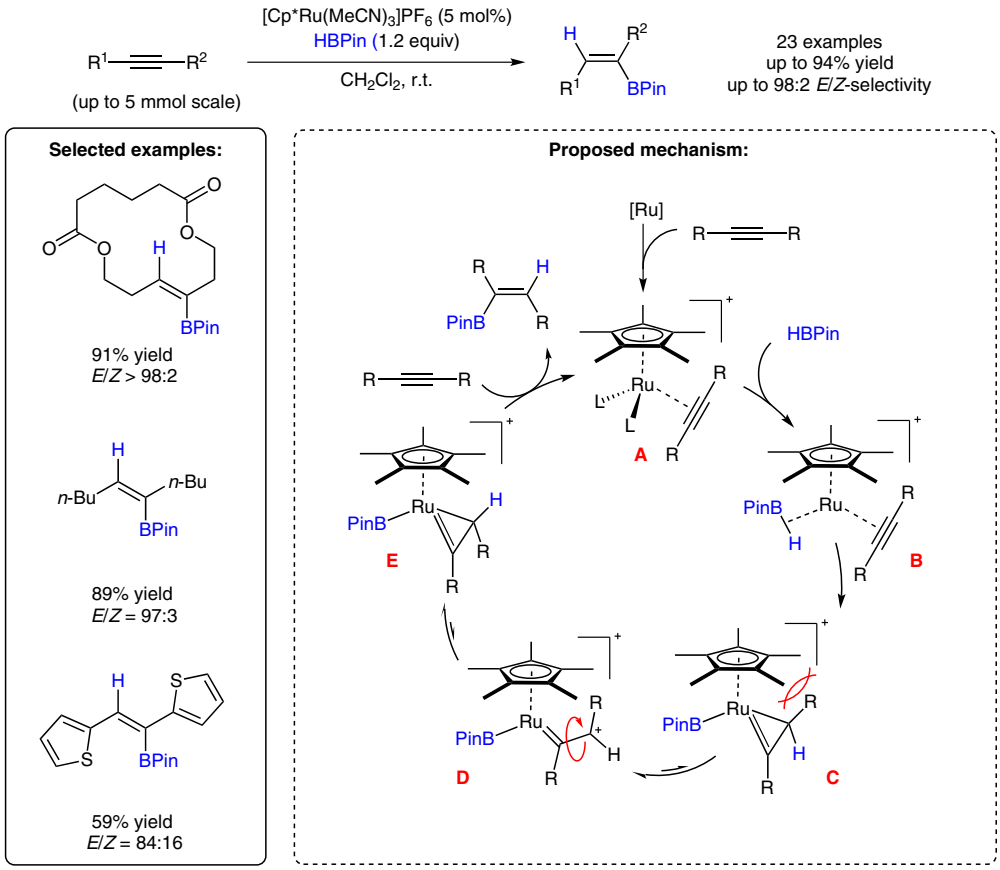
trans-Selective Hydroboration of Internal Alkynes Catalyzed by Ruthenium



Significance: Transition-metal-catalyzed hydroboration of alkynes is a reliable method for the synthesis of *Z*-alkenes due to the stereospecific requirement for *syn* addition of the B–H bond. Although access to the *E*-stereoisomer would be highly useful, transition-metal-catalyzed examples featuring *trans*-selective hydroboration necessitate the use of terminal alkynes (N. Miyaura and co-workers *J. Am. Chem. Soc*. **2000**, *122*, 4990; F. Pan, W. Leitner and co-workers *J. Am. Chem. Soc.* **2012**, *134*, 14349). Herein, the authors report a highly *trans*-selective ruthenium-catalyzed hydroboration of internal alkynes.

Comment: Both control and deuterium-labelling experiments provide support for a true *trans*-selective hydroboration, rather than an isomerization process. The proposed mechanism involves an inner-sphere hydride delivery to furnish metallocyclopropene **C**, which can relieve steric congestion about the Cp* ring via isomerization to metallocyclopropene **E**. The reductive elimination places the boron atom *anti* to the hydrogen atom, providing access to the *E*-configured olefin. While the method is highly functional-group-tolerant, modest regioselectivity is observed with unsymmetrical alkynes.

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Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

hydroboration

***trans*-selectivity**

ruthenium