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 metallocyclopentene C, which can relieve steric congestion about the Cp* ring via isomerization to metallocyclopentene 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 alkyynes.

**Selected examples:**

- 91% yield
  - E/Z > 98:2

- 89% yield
  - E/Z = 97:3

- 59% yield
  - E/Z = 84:16

**Proposed mechanism:**

[Diagram showing the proposed mechanism for the trans-selective hydroboration reaction.]