Synthesis of trans-Cycloalkenes via Enantioselective Cyclopropanation and Skeletal Rearrangement


**Significance:** There are few ways to access chiral medium-sized rings possessing a trans double bond (for selected examples, see: A. Deiters et al. Chem. Eur. J. 2002, 8, 1833; X.-N. Wang et al. J. Am. Chem. Soc. 2014, 136, 9802). Such motifs often exhibit planar chirality and may find applications in the synthesis of complex polycyclic frameworks. The authors report an efficient procedure for the asymmetric synthesis of piperidine-fused trans-cycloalkenes 3 from triazoles 1 and methylenecyclopropanes 2.

**Comment:** The reaction is initiated by the in situ formation of an α-imino rhodium carbenoid from triazole 1. Cyclopropanation of the exocyclic methylene group of 2 leads to the formation of spiropentane A, which can then undergo a thermal rearrangement under microwave irradiation to give trans-cycloalkene 3. The authors propose a concerted mechanism, which draws similarities to the retro-Claisen [3,3]-sigmatropic rearrangement.