Iron-Catalyzed Asymmetric Hydrosylation of 1,1-Disubstituted Alkenes

**Significance:** Chiral organosilicon compounds have important applications in selective C–C bond-forming reactions. While an asymmetric alkene hydrosilylation provides a direct route to such scaffolds, the use of 1,1-disubstituted alkenes is rather elusive. For a racemic example, see: *J. Am. Chem. Soc.* 2004, 126, 13794. Herein, Bart et al. present a highly enantioselective method for the anti-Markovnikov hydrosilylation of 1,1-disubstituted alkenes catalyzed by an iron complex.

**Comment:** The substrate scope is quite broad with a variety of ortho-, meta- and para-substituted aryl rings tolerated on the alkene. Sensitive aldehyde and ketone functionalities must first be protected as the acetal or ketal. In addition to the use of styrene derivatives, aliphatic 1,1-disubstituted olefins could be applied. The authors demonstrate that the products can be further functionalized to yield chiral 3-substituted Si- or O-containing rings.

**Selected examples:**

- R1 R2 Ph2SiH2
  - R1 R2 SiHPh2
  - Fe catalyst (1–5 mol%) NaBHEt3 (3–15 mol%)
  - neat or in PhMe (1.0 M), r.t., 12 h
  - anti-Markovnikov selectivity up to 99% yield up to 99% ee

- Further derivatizations:
  - [Ir(OMe)(cod)]2 (4 mol%), dtbpy (8 mol%) norbornene (1.2 equiv)
  - THF, 80 °C, 12 h
  - 89% yield

- OH
  - HO
  - Ph3P, DIAD
  - THF, r.t., 4 h
  - 62% yield

- Me3N
  - SiHPh2
  - 95% yield 98% ee

- F
  - 96% yield 94% ee

- OMeth
  - 90% yield 78% ee

- Further derivatizations:
  - t-BuOK, t-BuOOH, TBAF
  - THF, 70 °C, 12 h
  - 86% yield

- 91% ee

- 99% yield 98% ee

- 87% yield 91% ee

- 92% yield 93% ee

- 99% yield 91% ee

- 95% yield 98% ee

- 90% yield 78% ee

- 85% yield 96% ee

- 92% yield 93% ee

- 99% yield 98% ee

- 96% yield 94% ee