Cooperative Transition-Metal and Chiral Brønsted Acid Catalysis

**Significance:** The authors report a protocol for the enantioselective hydrogenation of various ketimines in the presence of a chiral Brønsted catalyst and a well-defined nonchiral iron catalyst. This work demonstrates that enantioselective reduction reactions with hydrogen can be performed without employing precious-metal catalysts and chiral ligands yielding products with high yields and enantioselectivities.

**Comment:** NMR spectroscopic studies revealed the formation of complex 1 when a 1:1 mixture of TRIP and the Knölker iron complex (cat. 1) were mixed. Upon addition of a ketimine to the reaction mixture, the formation of complex 2 was observed. These results suggest that a cooperative catalytic system is operative for this transformation.

**Selected examples:**

- HNPh
  - 80% yield
  - 94% ee

- MeO
  - 60% yield
  - 93% ee

- HN-PMP
  - 91% yield
  - 93% ee

- HN-PMP
  - 91% yield
  - 83% ee

**Proposed reaction intermediates:**

- complex 1
- complex 2