Rhodium-Catalyzed cis-Selective Hydrogenation of Fluoroarenes

**Significance:** All-cis-polyfluorinated cycloalkanes exhibit attractive electronic properties due to their high dipole moments. However, multistep syntheses from diastereoselectively fluorinated precursors are generally required. The authors report a rhodium/cyclic (alkyl)(amino)(carbene) complex catalyzed cis-selective hydrogenation of fluorinated arenes to provide a variety of highly diastereoselectively fluorinated cycloalkanes.

**Comment:** To suppress the formation of hydrodefluorinated byproducts, the choice of a less-polar solvent such as hexane is important.

**Selected examples:**

- 90% yield, dr = 17:1
- 96% yield, dr = 6:1
- 81% yield, dr = 6:1
- 60% yield, dr = 20:1
- 60% yield, dr = 20:1
- 26% yield, dr = 20:1
- 42% yield, dr > 20:1
- 93% yield, dr = 13:1
- 88% yield, dr = 9:1
- 91% yield, dr = 6:1
- 81% yield, dr = 6:1
- 80% yield, dr = 6:1
- 83% yield, dr = 1:5:1

**Application of the fluorinated cycloalkane:**

- **N,N-diBoc**
  - 92% yield, dr > 20:1

- **ICy HBF₄ analog**
  - 52% yield (2 steps), dr > 20:1

- **Lomustine analog**
  - 75% yield, dr > 20:1

- **Bromhexine analog**
  - 90% yield (2 steps)