Enantioselective Palladium/Organo-Catalyzed Additions to Unsaturated Aldehydes

**Significance:** Synergistic catalysis has recently been gaining attention because the two separate catalysts can be optimized independently (see Review below). The authors present a palladium/chiral secondary amine catalyzed reaction between azaarenes and unsaturated aldehydes.

**Comment:** Although diastereoselectivity was poor (highest ratio 2.7:1), good enantioselectivities were observed for both major and minor isomers. The palladium acts as a Lewis acid to activate the azaarene, whereas the proline-derived organocatalyst activates the aldehyde towards 1,4-addition.

**Selected examples:**

- 99% yield, dr = 2.7:1
  - 99% ee (major)/56% ee (minor)
- 69% yield, dr = 1.6:1
  - 85% ee (major)/53% ee (minor)
- 68% yield, 89% ee

**Proposed mechanism:**

**References:**


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