Catalytic Conjunctive Cross-Coupling Enabled by Metal-Induced Metallate Rearrangement

**Significance:** Morken and co-workers report a catalytic conjunctive cross-coupling of organoborates, organolithium reagents and organotriflates for the synthesis of chiral boronic acids with high enantioselectivity.

**Comment:** The intermediate boronic ester ate-complex reacts in a palladium-induced metallate rearrangement, wherein 1,2-migration of an alkyl or aryl group from the boron atom to the vinyl α-carbon occurs simultaneously with C–Pd σ-bond formation.

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**Proposed catalytic cycle:**

1. Pd(II) → Pd(IV) transmetallation
2. Metal-induced metallate rearrangement
3. Conjunctive cross-coupling

**Selected examples:**

- **Ph**
  - 48% yield, er = 88:12
- **i-Pr**
  - 49% yield, er = 98:2
- **n-Bu**
  - 77% yield, er = 94:6
- **i-Bu**
  - 66% yield, er = 97:3
- **Me3SiPh**
  - 59% yield, er = 99:1
- **Ph**
  - 73% yield, er = 95:5
- **Ph**
  - 73% yield, er = 87:13
- **MeO**
  - 86% yield, er = 95:5
- **NMe2**
  - 73% yield, er = 94:6
- **Cl**
  - 77% yield, er = 94:6
- **B**
  - 59% yield, er = 99:1

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**SYNFACTS 01032016, 12(3), 0289 Published online: 16.02.2016 DOI: 10.1055/s-0035-1561257; Reg-No.: P00916SF