Rhodium-Catalyzed Hydrothiolation of 1,3-Dienes

**Significance:** The development of reactions for the construction of C–S bonds is important because molecules essential to life contain this linkage. The addition of thiols to alkenes is a direct and atom-economical method for the formation of C–S bonds. The authors have developed an enantioselective addition of thiols to 1,3-dienes catalyzed by a rhodium–chiral bisphosphine ligand complex to give chiral secondary or tertiary allylic sulfides in good to high enantioselectivities.

**Comment:** The enantioselective hydrothiolation proceeds selectively at the more-substituted double bond. A broad range of functional groups are tolerated in this reaction, and the catalyst loading can be lowered to 0.1 mol%.

**Proposed mechanism:**

- **Path a:** 1,4-insertion
- **Path b:** 1,2-insertion

**Scope of substrate:**

- **1,3-diene:**
  - 95% yield, **rr > 20:1**
  - 95% yield, **rr = 99:1**
  - 99% yield, **rr = 98:2**
  - 67% yield, **rr = 96:4**
  - 93% yield, **rr = 99:1**

- **Thiol:**
  - 95% yield, **rr > 20:1**
  - 91% yield, **rr = 97:3**
  - 79% yield, **rr = 99:1**
  - 80% yield, **rr = 99:1**
  - 85% yield, **rr > 20:1**
  - 5% yield, **rr = 83:17**

- **Oligosubstituted dienes:**
  - 93% yield, **rr = 12:1**
  - 93% yield, **rr = 96:4**
  - 73% yield, **rr = 96:4**

**Proposed mechanism:**

- **R3** + **R4SH** → **L*RhI**
- **L*RhIII** → **SR4**
- **LnRhIII** → **SR4**
- **R1** + **R3** → **R2**
- **R1** + **R2** → **R3**
- **R1** + **R3** → **R4**

**Scope of substrate:**

- **95% yield, rr = 99:1**
- **96% yield, rr = 98:2**
- **67% yield, rr = 96:4**
- **93% yield, rr = 99:1**
- **95% yield, rr = 97:3**
- **84% yield, rr = 94:6**
- **86% yield, rr = 94:6**

**Key words:**

- Rhodium catalysis
- Hydrothiolation
- Thiols
- Dienes
- Sulfides