Rhodium-Catalyzed Synthesis of Diaryl Sulfides Using S₈/Organopolysulfides

Significance: The rhodium-catalyzed reaction of sulfur or organopolysulfides with aryl penta- and monofluorides in the presence of tributylsilane is disclosed. The corresponding diaryl sulfides are obtained in moderate to good yield.

Comment: The mechanism is proposed to proceed via oxidative addition of the rhodium complex to the aryl fluoride and the SS–SS bond. After insertion of one sulfur atom, di-tert-butyl trisulfide is expelled and the rhodium–fluoride–aryl sulfide complex reacts with another aryl fluoride. The fluoride atoms are trapped with tributylsilane or triphenylphosphine and the corresponding diaryl sulfides are obtained after reductive elimination.

Selected examples:

- NO₂
  - S
  - NO₂
  - 42% yield (conditions A)

- Ph₂N
  - S
  - Ph₂N
  - 18% yield (conditions A)

- Cl
  - S
  - Cl
  - 53% yield (conditions B)

- NC
  - S
  - NC
  - 71% yield (conditions B)