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Insertion of Nitriles into Zirconocene 1-aza-1,3-diene Complexes: Chemoselective Synthesis of N–H and N-Substituted Pyrroles  

**Zirconium-Mediated Synthesis of Pyrroles**

![Chemical diagram](image)

**Proposed mechanism:**

1. **Pathway A:**
   - Reaction of Cp₂ZrN with R₂CN (3 equiv) to form products A.  
   - Products A: 27–86% yield  
     - R³ = H or R², R³ = H
   - Products B: 61–87% yield
     - R² = H

2. **Pathway B:**
   - Reaction of Cp₂ZrN with R₂CN (3 equiv) to form products B.  
   - Products B: 61–87% yield
     - R² = H

**Selected examples:**

- **Products A:**
  - 78% yield
  - 86% yield
  - 27% yield
  - 46% yield

- **Products B:**
  - 80% yield
  - 61% yield
  - 87% yield
  - 74% yield

**Significance:** Liu and co-workers report the direct insertion of nitriles into zirconocene 1-aza-1,3-diene complexes for the synthesis of variously substituted N–H and N-substituted pyrroles in high yields.

**Comment:** The outcome of the reaction is determined by different cyclization patterns that depend on the relative stability and reactivity of the enamine–imine tautomers that are formed upon hydrolysis of the diazazirconacycles.