Iron-Catalyzed Asymmetric Carboazidation of Styrenes

**Significance:** The authors report the use of a NON-pincer ligand for the asymmetric iron-catalyzed carboazidation reaction of styrenes. A variety of alkyl halides generating stabilized radicals were used.

**Comment:** A complex system involving synergistic effects of both van der Waals and π-interactions were found to be responsible for the stereocontrol of the reaction.

**Proposed mechanism:**

\[
\begin{align*}
\text{Ar}^+ + \text{TMSN}_3 + \text{R}^X & \xrightarrow{\text{Fe(OTf)}_2 (1 \text{ mol\%})} \text{ArN}_3^+ \\
\text{L}^* \text{FeX}_2 & \xrightarrow{\text{lauroyl peroxide (2.0 equiv)}} \text{ArN}_3^+ \\
\text{Ar} = 4-t\text{BuC}_6\text{H}_4
\end{align*}
\]

**Selected examples:**

- **74% yield**
  - er = 95:5
- **72% yield**
  - er = 90:10
- **76% yield**
  - R = CO_2Et, er = 90:10
  - R = F, er = 92:8
- **87% yield**
  - R = CO_2Et, er = 94:6
- **68% yield**
  - R = F, er = 92:8

**Proposed mechanism:**

1. **Iron(II) Complex:** \(\text{L}^*\text{FeX}_2\)
2. **Addition of TMSN₃:** \(\text{L}^*\text{FeX}_2 + \text{TMSN}_3 \rightarrow \text{L}^*\text{FeX}_2\text{N}_3\)
3. **Radical Formation:** \(\text{RX} \rightarrow \text{R}^*\)
4. **Coupling:** \(\text{R}^* + \text{R}' \rightarrow \text{R}^* \text{R}'\)
5. **Reduction:** \(\text{L}^*\text{FeX}_2\text{N}_3 \rightarrow \text{L}^*\text{FeX}_2\text{N}_3^{-}\)
6. **Stabilization:** \(\text{Ar}^+ + \text{TMSN}_3 \rightarrow \text{ArN}_3^+\)

**Category:** Metals in Synthesis

**Key words:** iron catalysis, asymmetric synthesis, difunctionalization, azides