Directed Regioselective 2,5- and 3,5-Dimagnesiations of Substituted Arenes

**Significance:** The regioselective deprotonation of a directing group substituted arene substrate generally takes place in the ortho position, adjacent to the substituent. The authors developed a protocol by which the metalating agent deprotonates the arene at the more distant arene sites. Depending on the nature of the directing group, 2,5- or 3,5-dimetalation is observed. The dimagnesiated species were quenched with electrophiles.

**Comment:** Interestingly, the used disodium monomagnesium alkylamide forms a template that is responsible for the metalation at the more distant arene sites. The next challenge is the rational design of a range of template bases.

**Selected examples:**

- **Na₄Mg₂(TMP)₆(nBu)₂**
  - DG = OAlk, CH₂OMe, CF₃, CON-i-Pr₂, oxazoline, carbamate

- **I₂**
  - DG = NMe₂, N-i-Pr₂, t-Bu

**Yields:**
- 78% yield
- 65% yield
- 67% yield
- 65% yield
- 77% yield
- 71% yield
- 66% yield
- 67% yield