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Directed ortho-meta'- and meta-meta'-Dimetalations: A Template Base Approach to Deprotonation *Science* **2014**, *346*, 834–837.

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

$$\begin{array}{c} DG \\ \hline \\ Na_4Mg_2(TMP)_6(nBu)_2 \end{array} \qquad \begin{array}{c} DG \\ \hline \\ [Mg] \end{array} \qquad \begin{array}{c} Electrophile \\ \hline \\ E \end{array}$$

DG = OAlk, CH_2OMe , CF_3 , $CONi-Pr_2$, oxazoline, carbamate

$$\begin{array}{c} DG \\ \hline \\ Na_4Mg_2(TMP)_6(n\text{-Bu})_2 \\ \hline \\ [Mg] \end{array} \begin{array}{c} DG \\ \hline \\ [Mg] \end{array}$$

 $DG = NMe_2, Ni-Pr_2, t-Bu$

Selected examples:

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.

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Metal-Mediated Synthesis

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