Unit 4
Stereocontrolled 1,2-Addition to Carbonyl Groups

★ Addition of "Unstabilized" Carbon Nucleophiles
★ Reagent Control: Organozinc and Related Addition Reactions
   Alkyl, Alkenyl, and Alkynyl Metal Compounds

General Reviews on Organozinc Chemistry

"Preparation and Applications of Functionalized Organozinc Compounds"


General Methods for the Preparation of Organozinc Compounds

<table>
<thead>
<tr>
<th>Oxidative Addition</th>
<th>R-I → R-ZnI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn, Me₃SiCl</td>
<td>BrCH₂CH₂Br</td>
</tr>
<tr>
<td>THF</td>
<td>or</td>
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<tr>
<td>LiNaph, ZnCl₂</td>
<td></td>
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</tbody>
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<table>
<thead>
<tr>
<th>Halogen-Zinc Exchange</th>
<th>R-I → R₂Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-5 equiv Et₂Zn</td>
<td>cat Cul or CúCN</td>
</tr>
<tr>
<td>Et₁, Et₂Zn (volatile)</td>
<td></td>
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</tbody>
</table>

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<thead>
<tr>
<th>Transmetalation</th>
<th>RLi or RMgX + ZnBr₂ or ZnCl₂ → R-ZnX</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-BEt₂ + 2 equiv Et₂Zn, rt (neat) → R₂Zn + Et₃B (volatile)</td>
<td></td>
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</tbody>
</table>
Asymmetric Addition of Dialkylzinc Compounds to Aldehydes

**Review:** "Catalytic Asymmetric Organozinc Additions to Carbonyl Compounds"

Photograph removed due to copyright reasons.

Ryoji Noyori in Stockholm (2001)

Proposed Mechanism for the Catalytic Dimethylzinc Addition to Benzaldehyde

Figure removed to due copyright reasons.
Asymmetric Addition of Alkenylmetal Compounds to Aldehydes

Asymmetric Vinylation of Ketones


*modified Yoshioka ligand* Figure removed due to copyright reasons.

Jamison Vinylation


Figure removed due to copyright reasons.

*J. D. Morrison ligand*

Asymmetric Addition of Alkynylzinc Compounds to Aldehydes

**Reviews:** "Asymmetric Alkynylzinc Additions to Aldehydes and Ketones"

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Erick M. Carreira