Lecture “Modern Synthetic Methods”

Take-home messages from Week 8

2.4.4. Allylation and crotylation reactions

- 3 different types: - Depends on the specific metal in the allyl/crotyl species

I: *E*/*Z*-crotylate geometry directly translates into *syn*/*anti*-ratio of the product

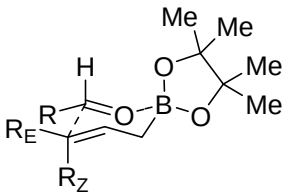
II: *E*/*Z*-crotylates give both *syn*-products

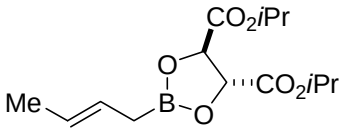
III: *E*/*Z*-crotylates give both *anti*-products

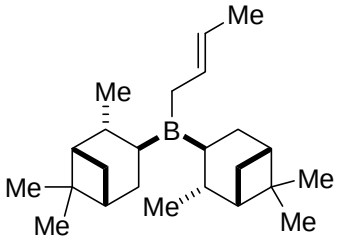
Type I: - Metals: **B**, **Al (***syn*- and *anti*-products)

- Closed Zimmermann-Traxler-type transition state

- Enantioselective allylation/crotylation by chiral ligands on the metal





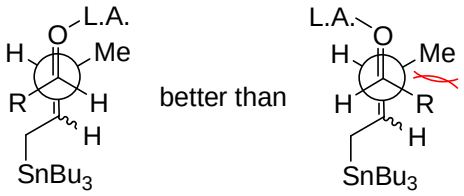


(Roush) (Brown)

Type II: - Metals: **Si**, **Sn (***syn*-products)

- Open (acyclic) transition state

- Requires use of additional Lewis acid



Type III: - Metals: **Ti**, **Zr**, **Cr (***anti*-products)

- Closed Zimmermann-Traxler-type transition state

- Rapid equilibrium of *E*/*Z*-metal crotylates