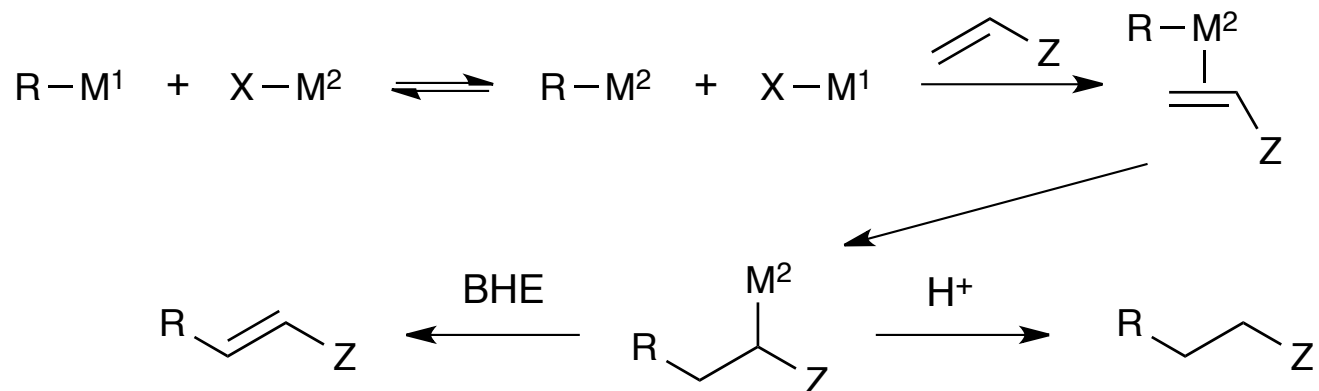


Conjugate Additions Involving Transmetalation

Access to highly functionalized organocupates can be tricky with "traditional" reagents like Grignards and organolithiums. This can be overcome by transmetalating from less reactive organometallic reagents. Many of these alternative organometallics do not react with carbonyls, so catalysis is possible.



$M^1 = \text{Li, Mg, Zn, Sn, Hg, B, Si, Al, Sb, Te, Zr}$

$M^2 = \text{Pd, Ni, Cu, Ru, Rh, Ir}$

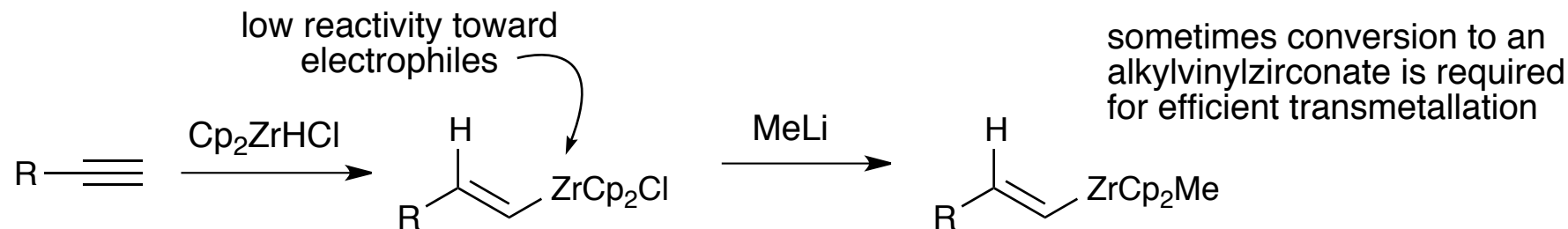
The transmetalation step is poorly understood. It generally proceeds with retention of configuration.

Processes involving a transmetalation step are quite common and we will see them again.

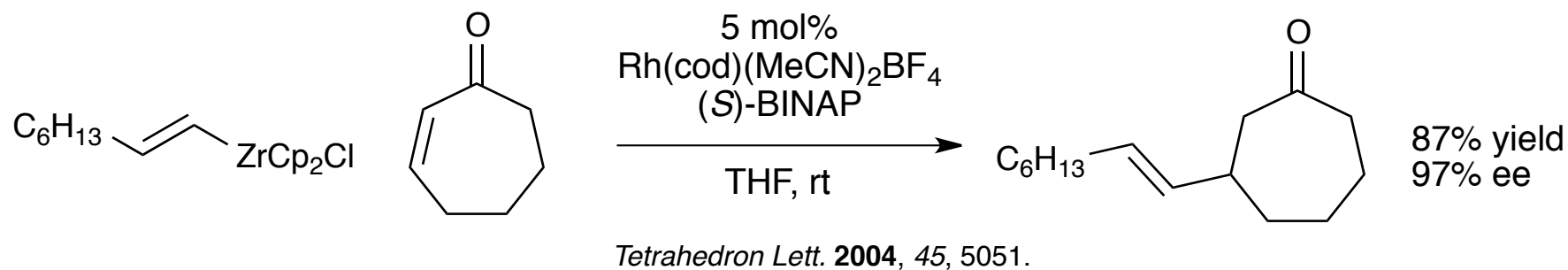
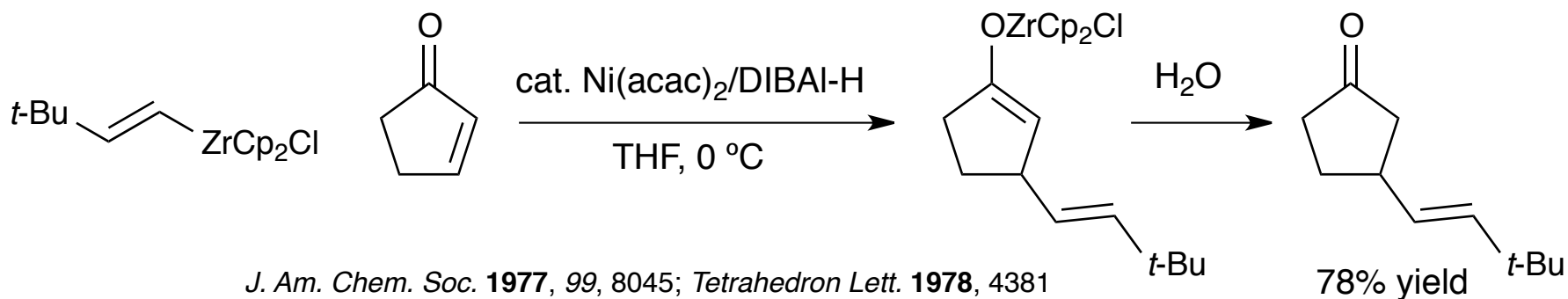
Most examples involve R groups with sp^2 carbons (alkenes, arenes), but alkyl groups can be transferred as well.

Conjugate Additions with Vinyl Zirconium Species

Facile synthesis by hydrozirconation of alkynes



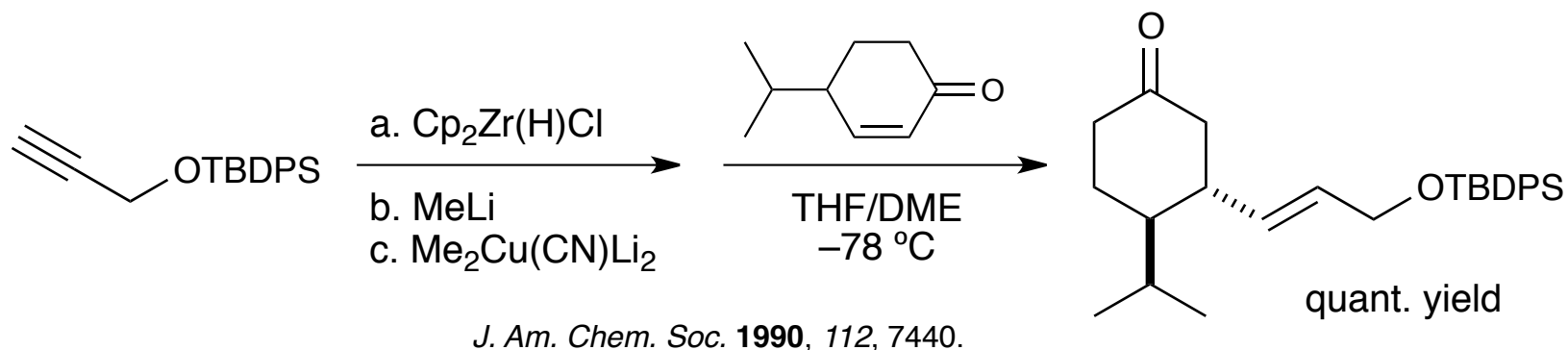
(*syn*-hydrozirconation to less substituted side)



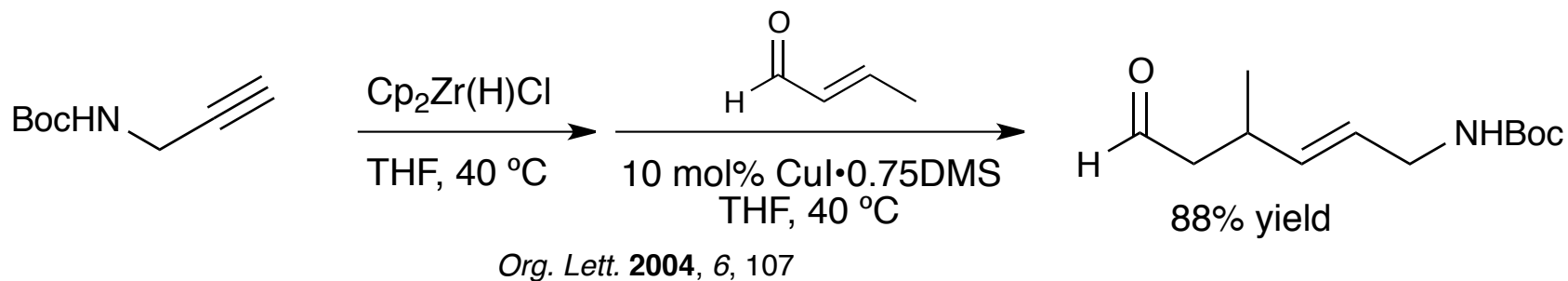
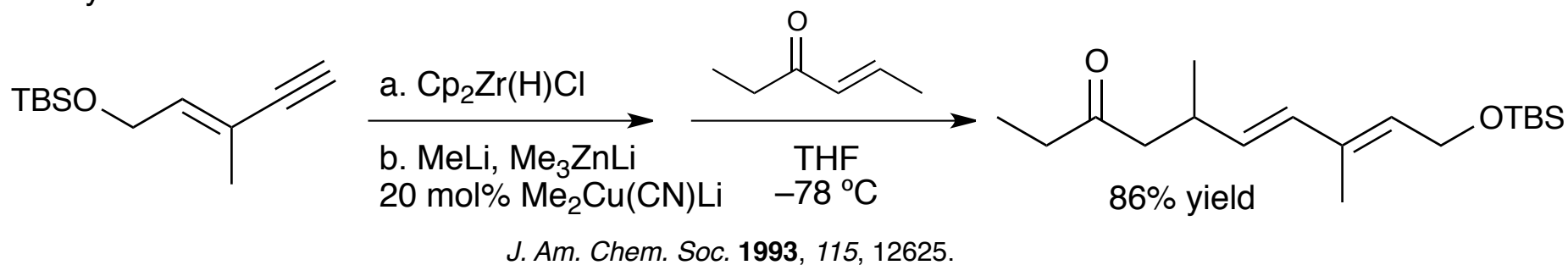
Conjugate Additions with Copper

Conducting reactions with copper have taken a while to develop, but can now be run catalytically.

Initial conditions required addition of MeLi to vinylZrCl and Me₂CuCNLi₂



catalytic conditions



Conjugate Additions with Palladium & Rhodium

Conjugate addition reactions can also be carried out with Pd and Rh catalysts. In these cases boronic acids/esters and siloxanes can be used. Most conditions use protic conditions to minimize β -hydride elimination.

