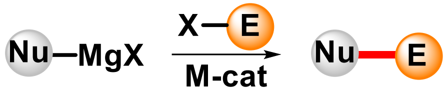
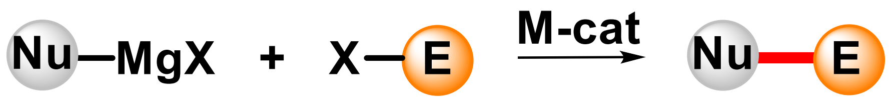
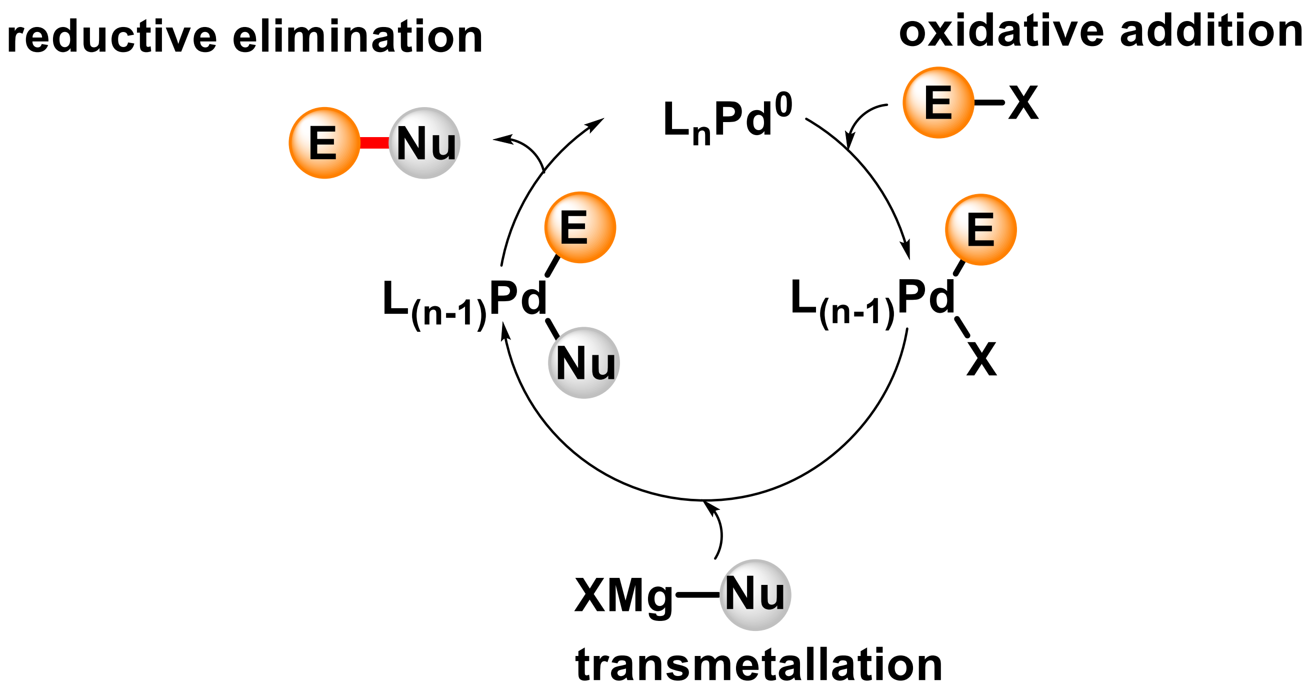
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

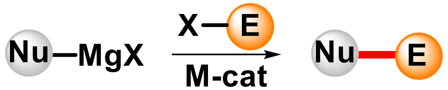


➢ The Kumada-Tamao-Corriu reaction (Kumada reaction)

- Mechanism of the Kumada-Tamao-Corriu reaction

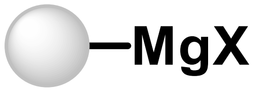




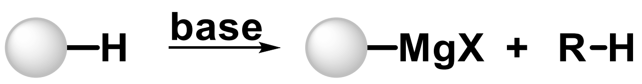


➢ The Kumada-Tamao-Corriu reaction (Kumada reaction)

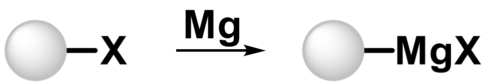
- Synthesis of funcionalized Grignard reagents



- Acid–base reaction

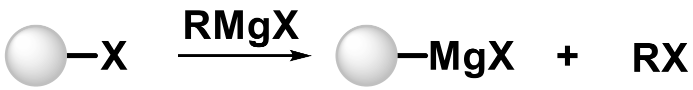


- Reaction with metal

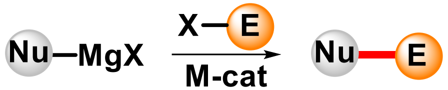


X = Cl, Br, I

- Halogen–Magnesium exchange reaction

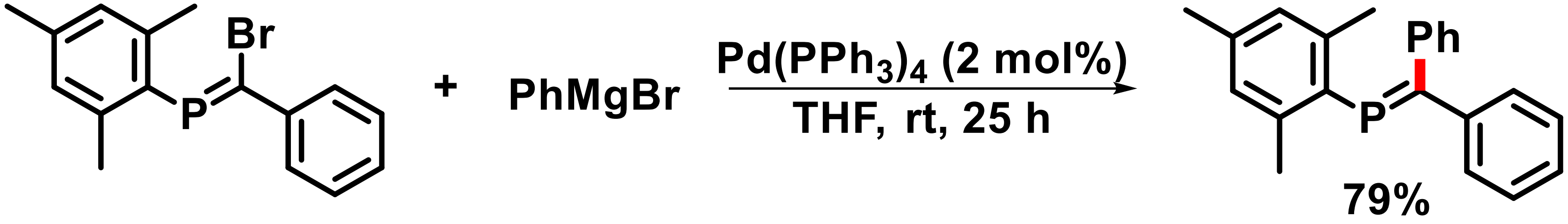


X = Cl, Br, I

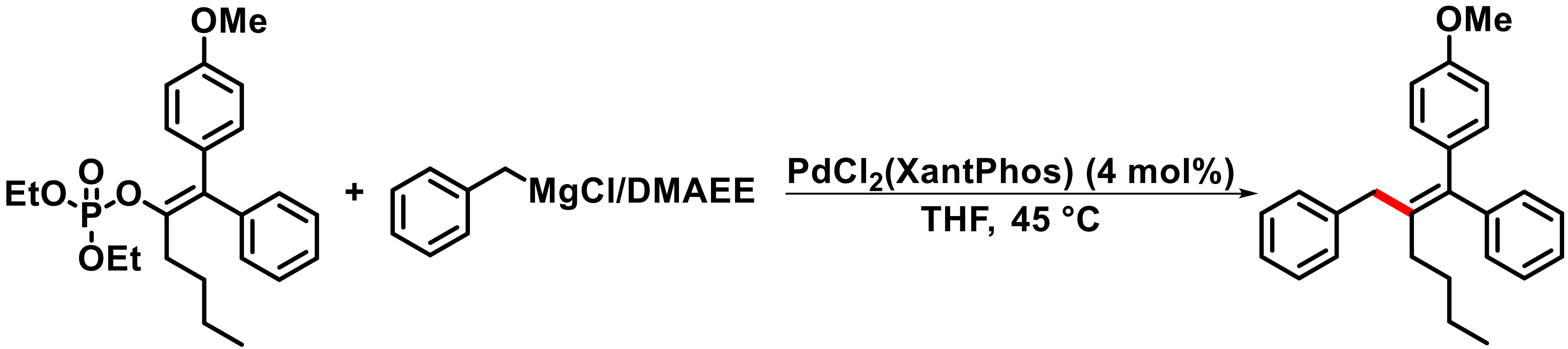


➢ The Kumada-Tamao-Corriu reaction (Kumada reaction)

- Selected examples: Palladium-catalyzed reactions

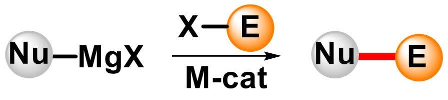


ChemistrySelect **2016**, *1*, 5260

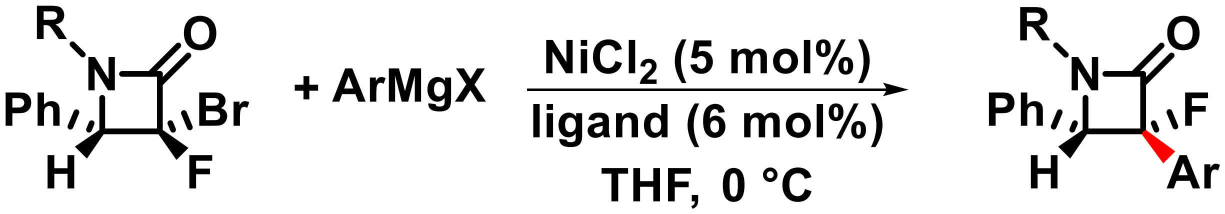


Org. Lett. **2015**, *17*, 608

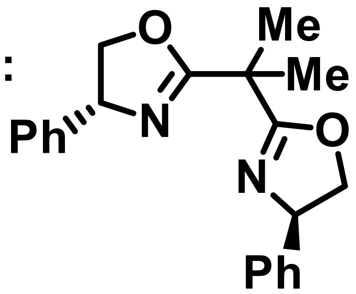
➢ The Kumada-Tamao-Corriu reaction (Kumada reaction)

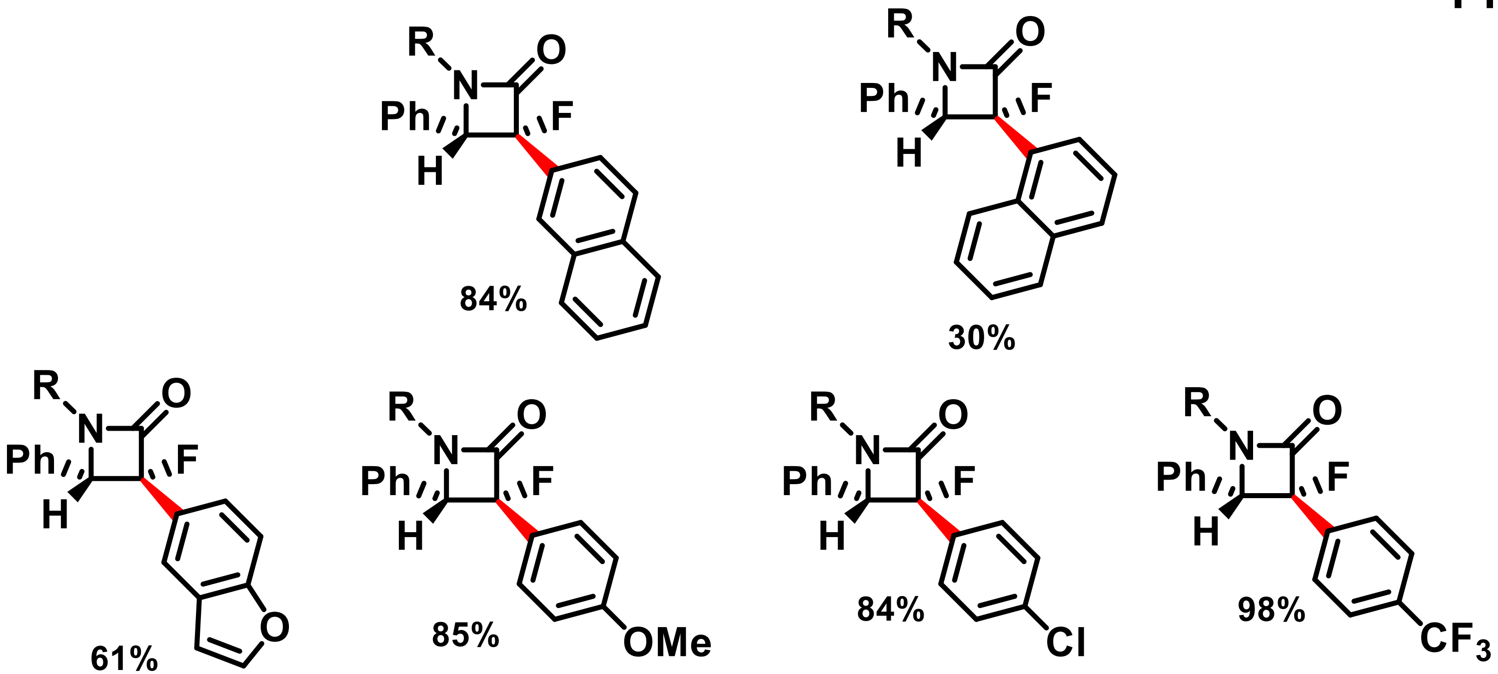


- Selected examples: Nickel-catalyzed reactions



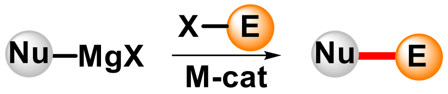
ligand:





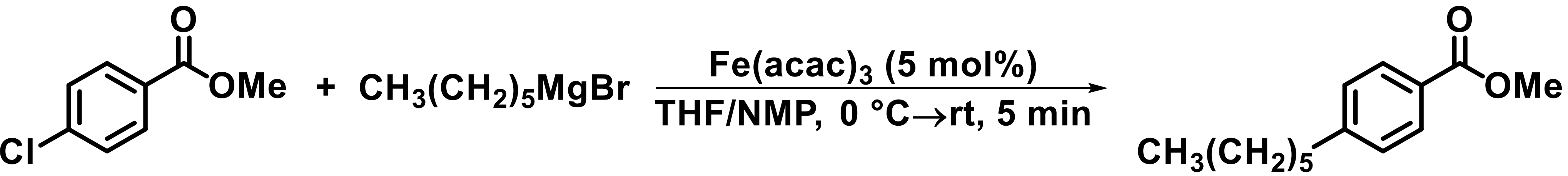
Tetrahedron **2013**, *69*, 1559

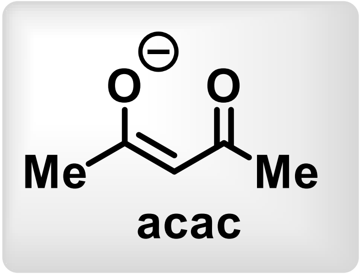
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

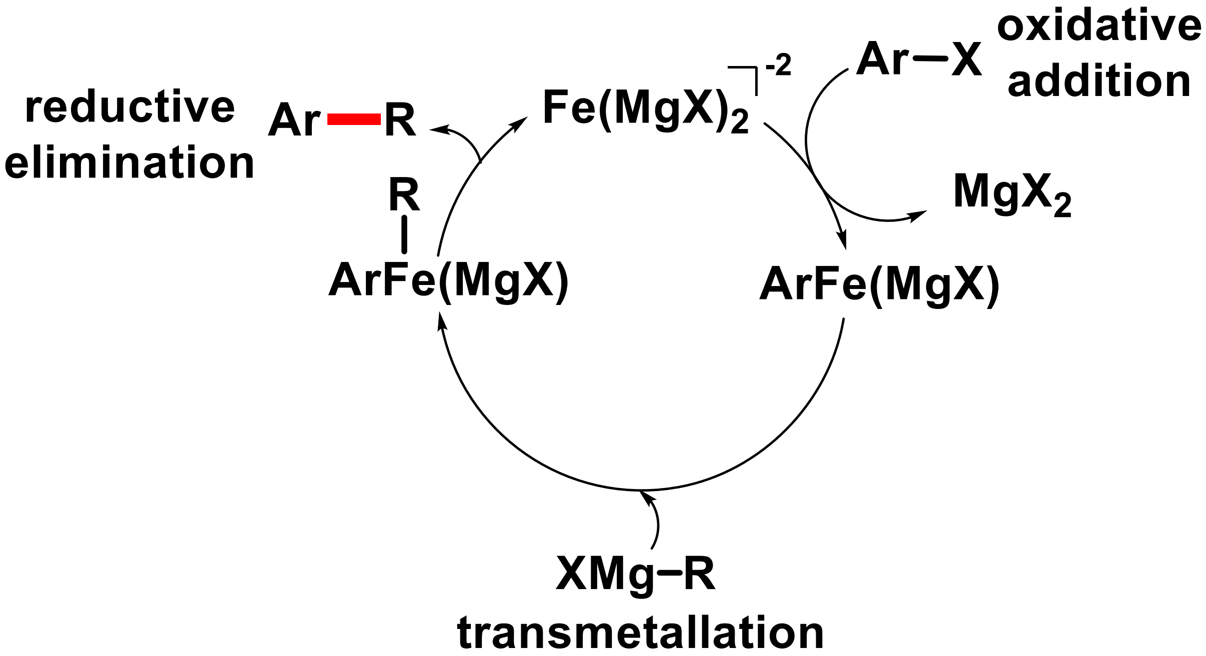


➢ The Kumada-Tamao-Corriu reaction (Kumada reaction)

- Selected examples: Iron-catalyzed reactions and proposed catalytic cycle



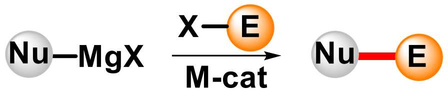




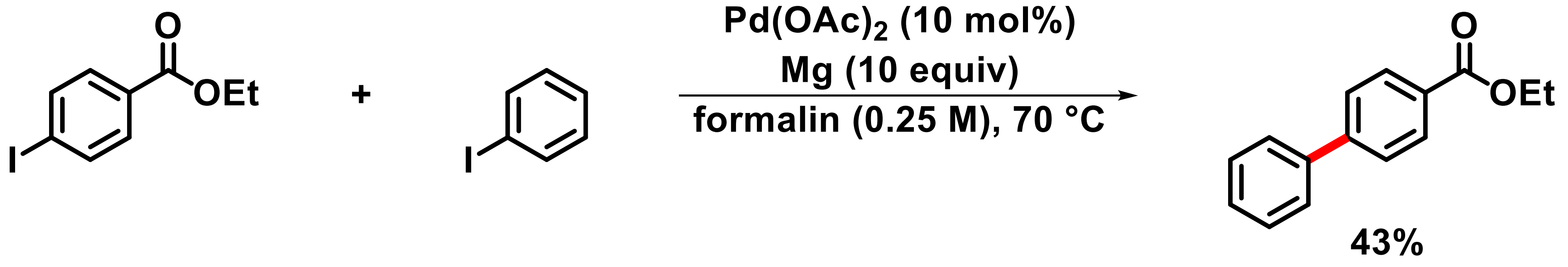
Angew. Chem. Int. Ed. **2002**, *41*, 609

Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

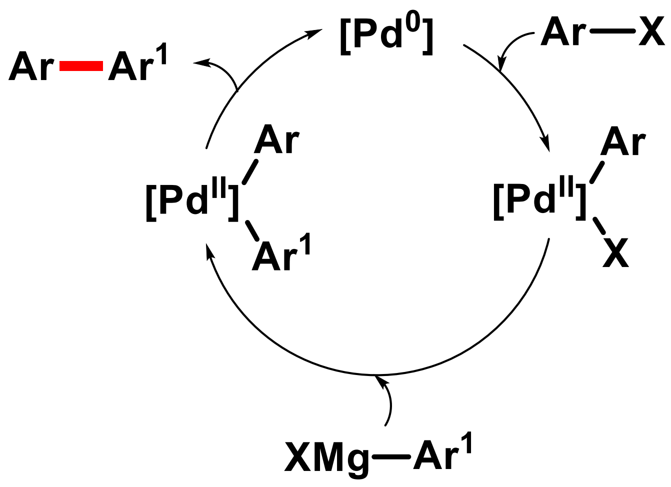
➢ The Kumada-Tasmao-Corriu reaction (Kumada reaction)



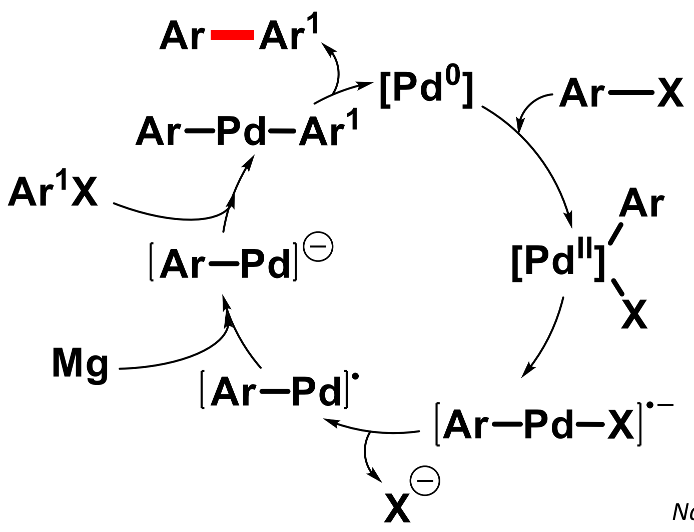
- Kumada reaction „on water“



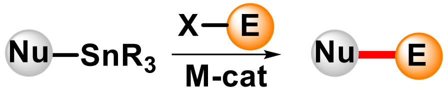
  - Traditional mechanism



  - Radical mechanism

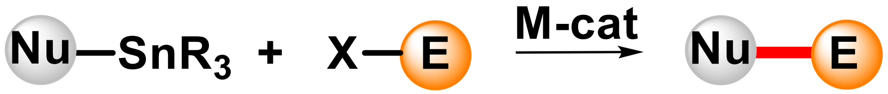


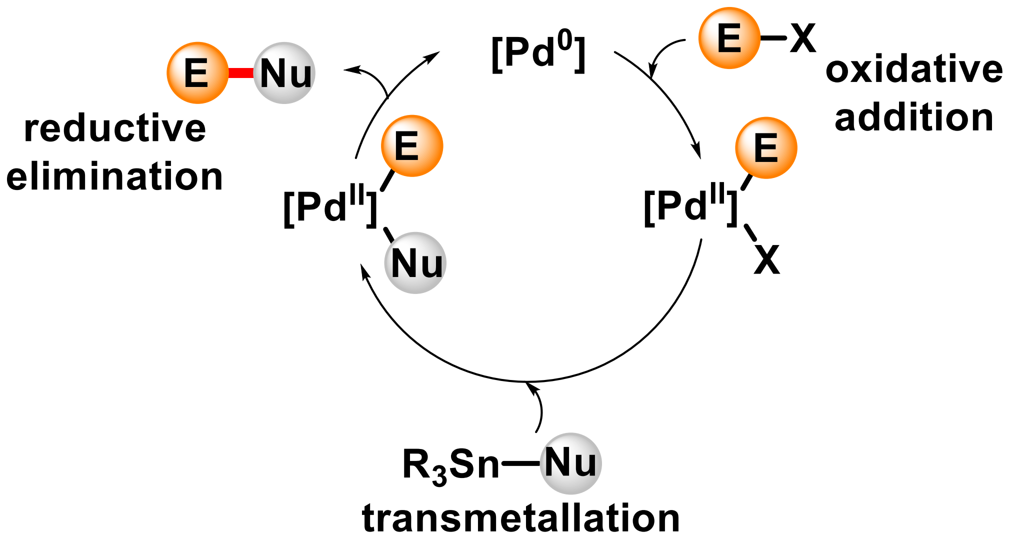
Nat. Commun. **2015**, *6*, 7401

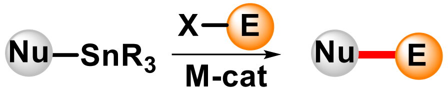


➢ The Migita-Kosugi-Stille(Stille reaction)

- **Mechanism of the Stille reaction**

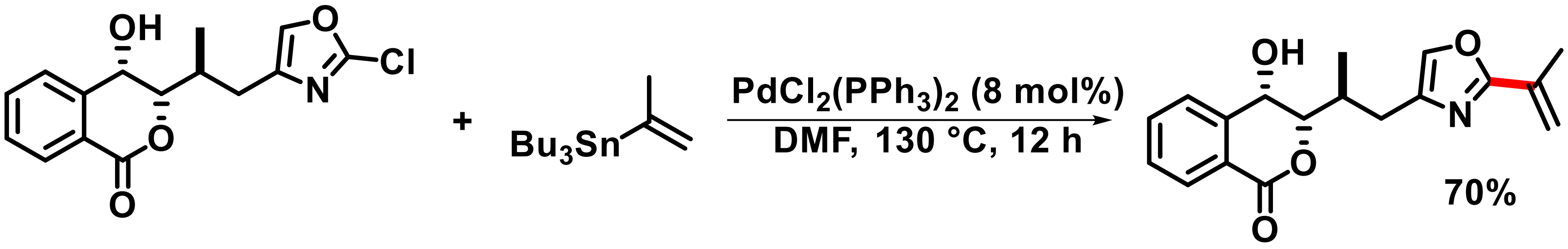




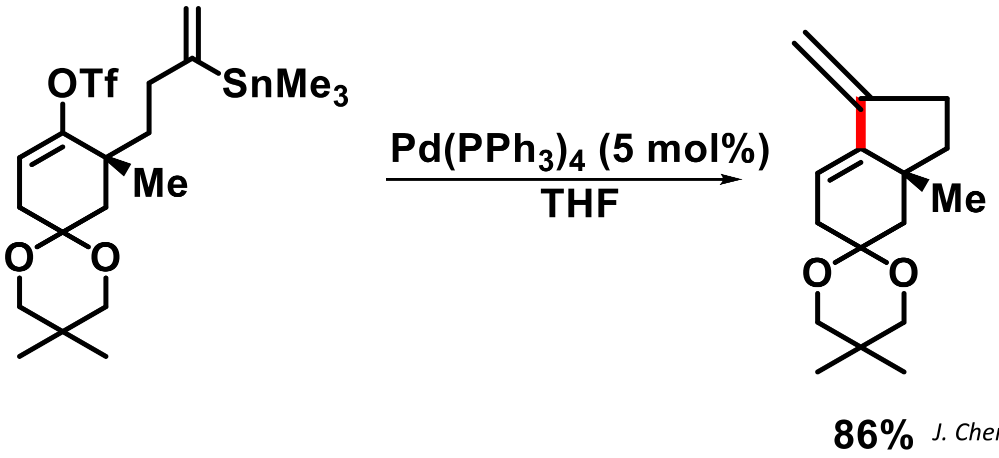


➢ The Stille reaction

- The Stille reaction – Selected examples



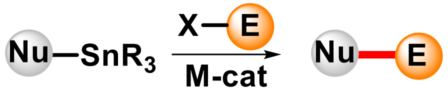
Tetrahedron **2011**, *67*, 9700



J. Chem. Soc., Chem. Commun., **1985**, 809

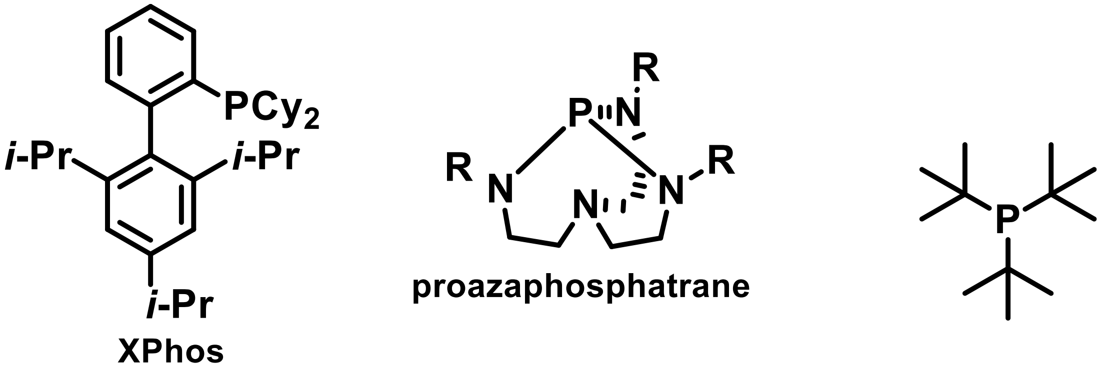
- Relative reactivity or organotributyltins ($RSnBu_3$) in the Stille reaction:
  alkynyl > alkenyl > aryl > allyl > alkyl

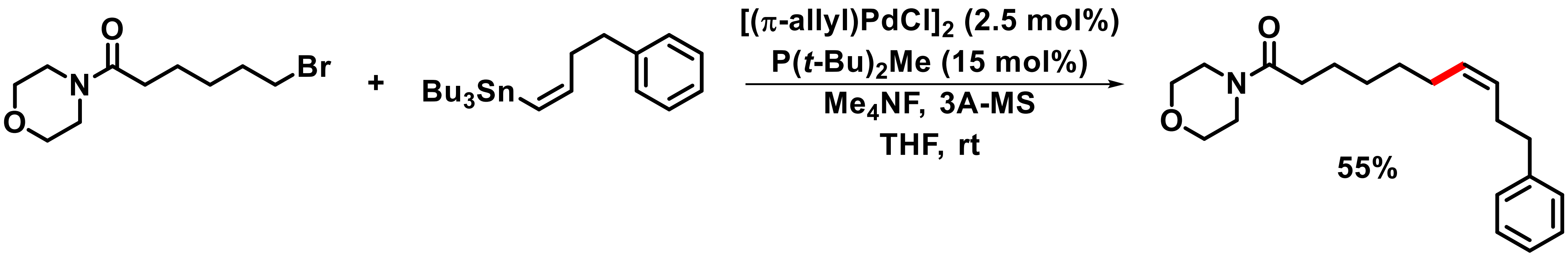
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions



➢ The Stille reaction

- Electron-rich bulky ligands are the best ligands for the Stille reaction



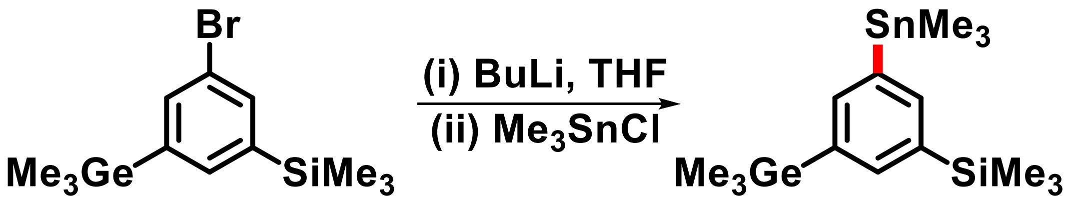


J. Am. Chem. Soc. **2003**, *125*, 3718

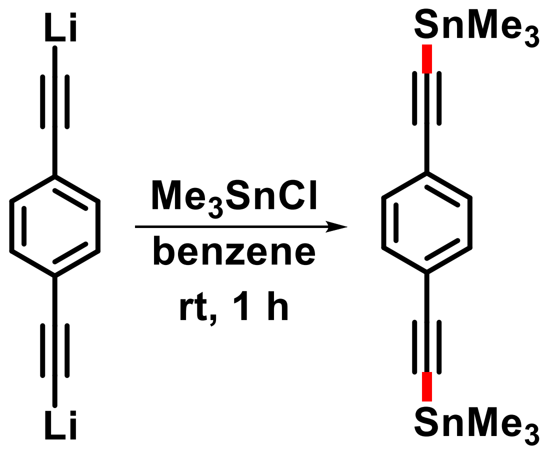
➢ The Stille reaction

- Synthesis of aryl- alkynylstannanes

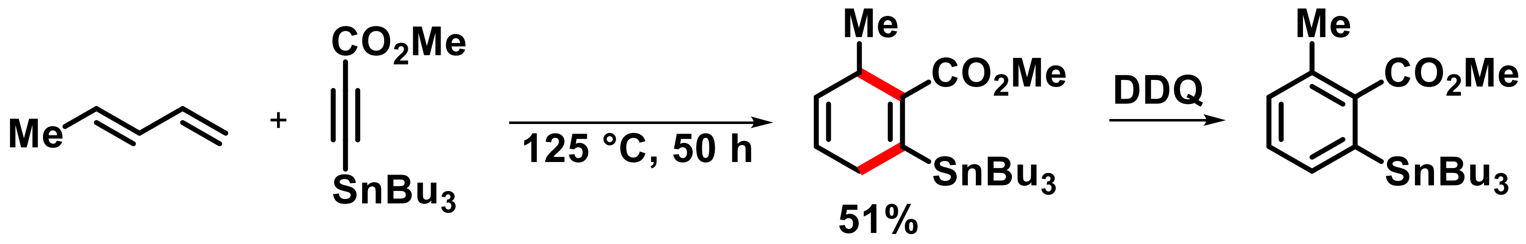
  - Lithiation



J. Organomet. Chem. **1983**, *251*, 149



  - Stannane modification



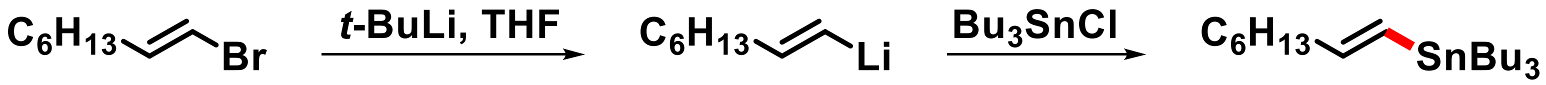
Tetrahedron **1989**, *45*, 1145

Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

➢ The Stille reaction

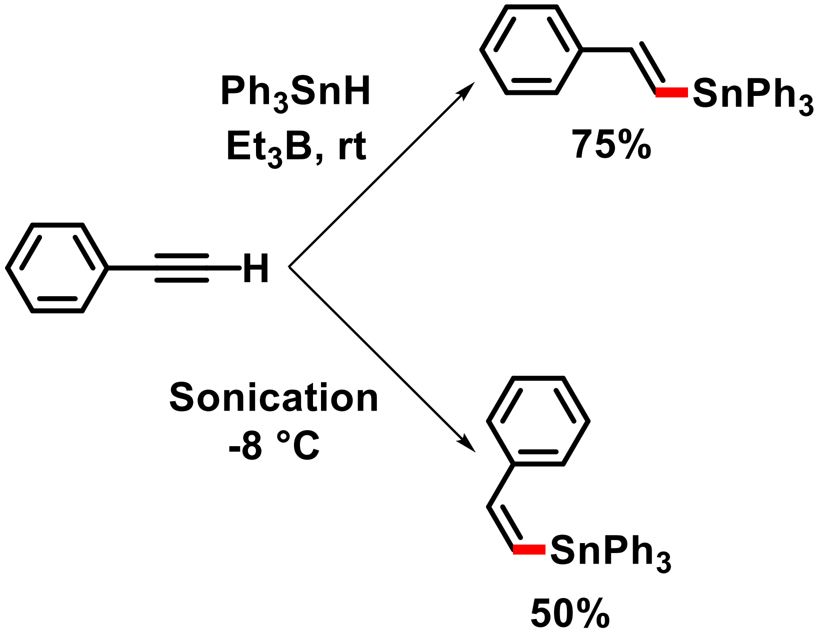
- Synthesis of alkenylstannanes

  - Lithiation

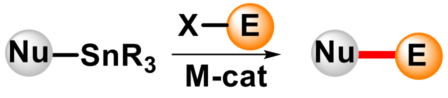


Organometallics **1991**, *10*, 2424

  - Hydrostannation



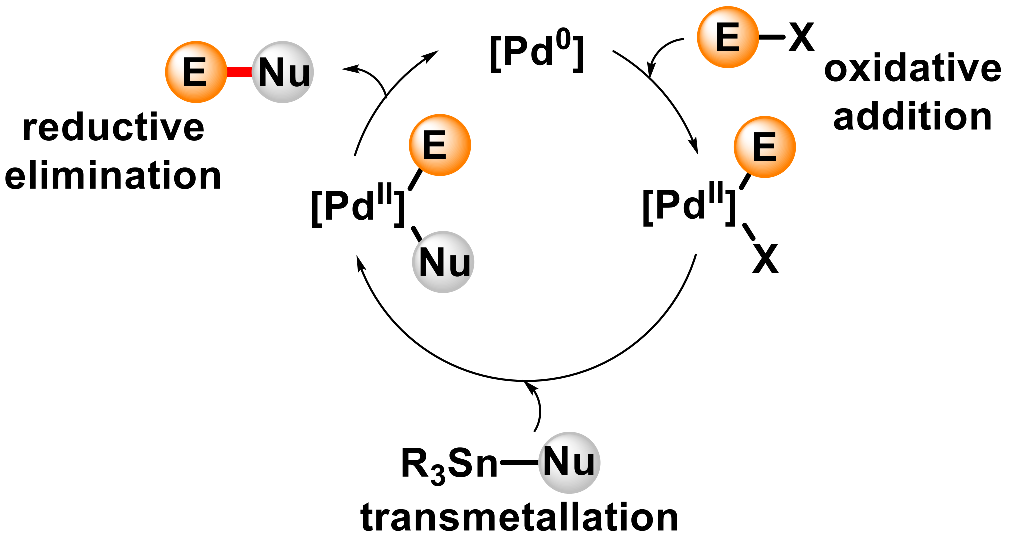
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions



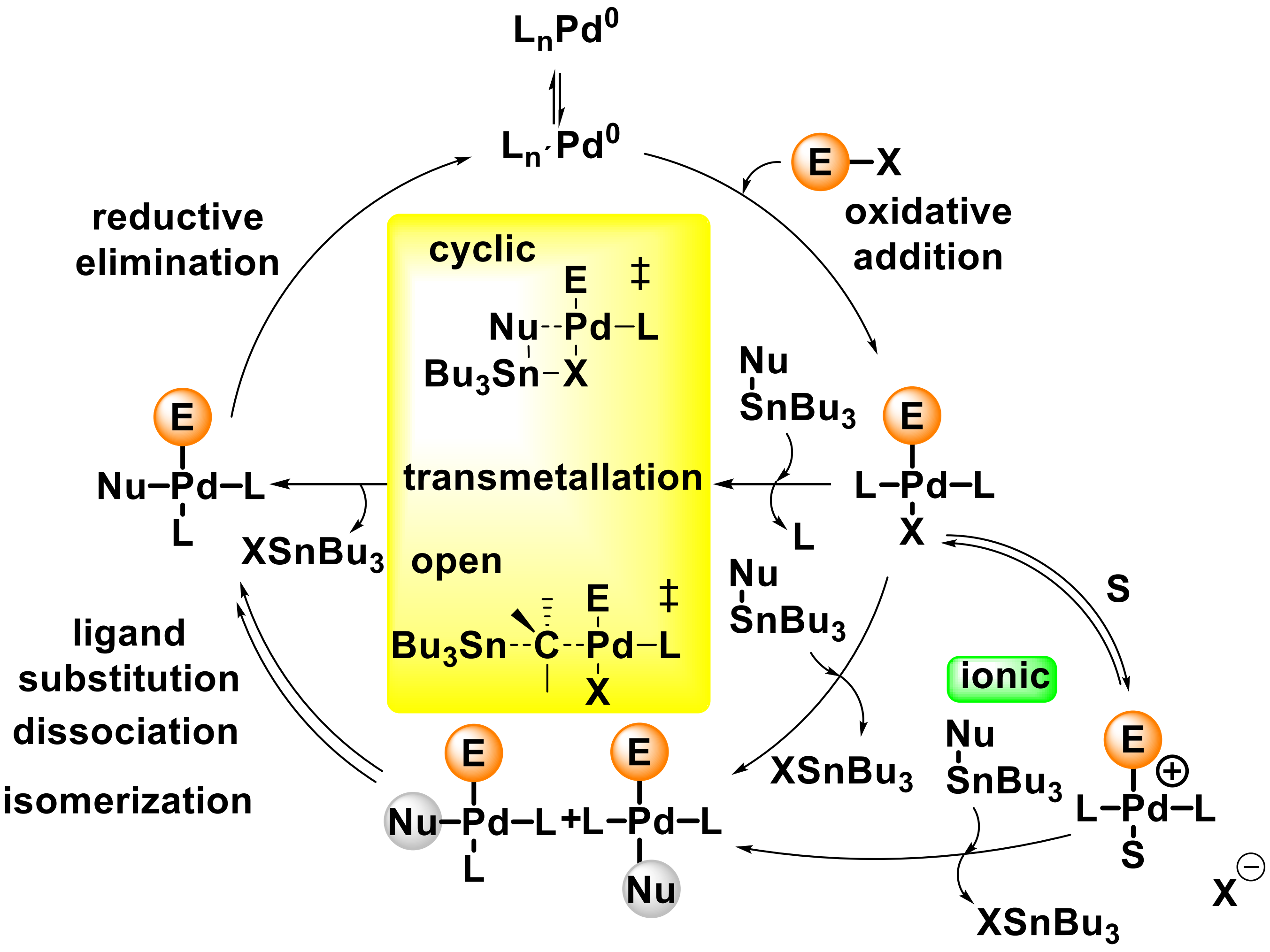
➢ The Stille reaction

- Advanced mechanism of the Stille reaction

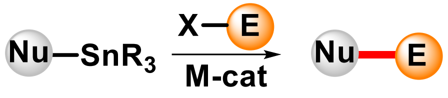
○ Simplified mechanism



○ Advanced mechanism

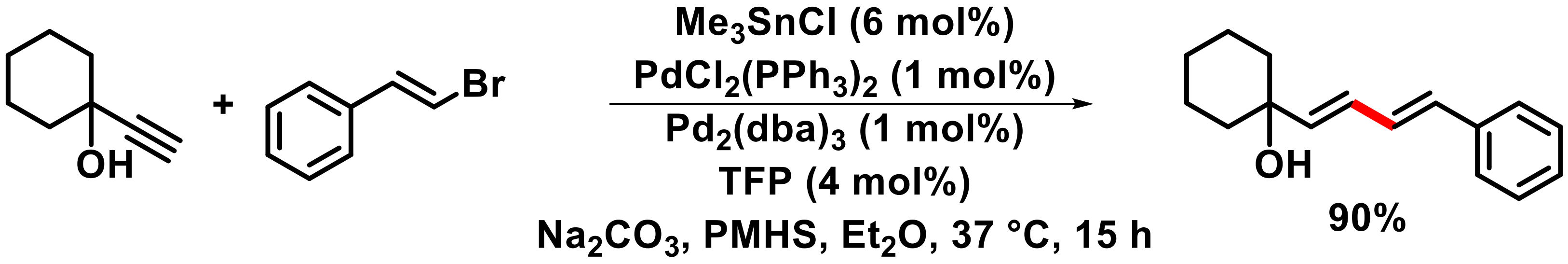


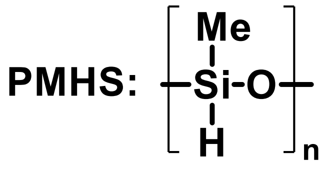
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

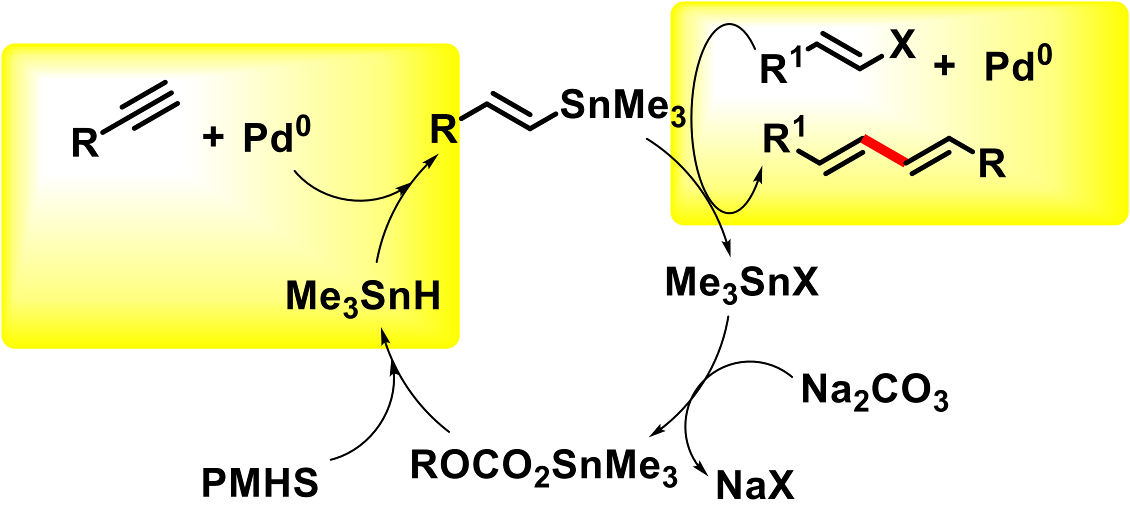


➢ The Stille reaction

- Greener Stille reaction
  - Catalytic in tin



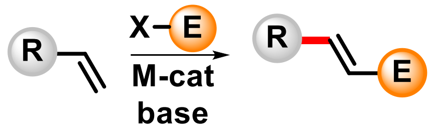


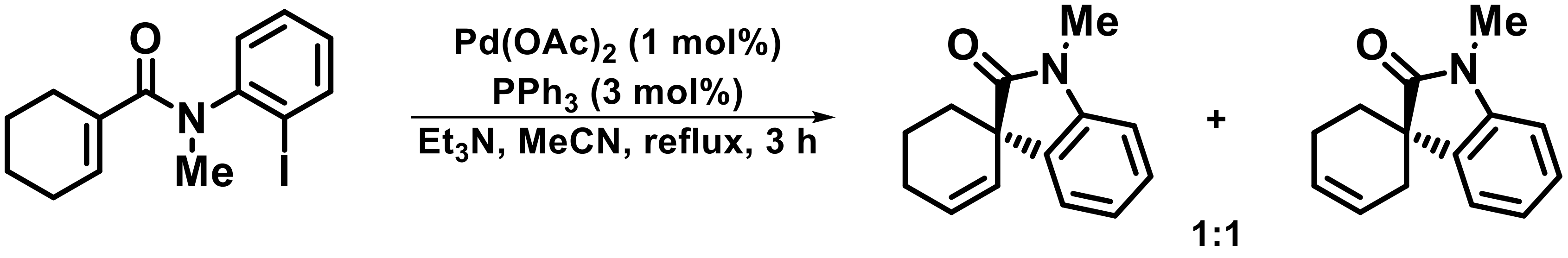


J. Am. Chem. Soc. **2000**, *122*, 384

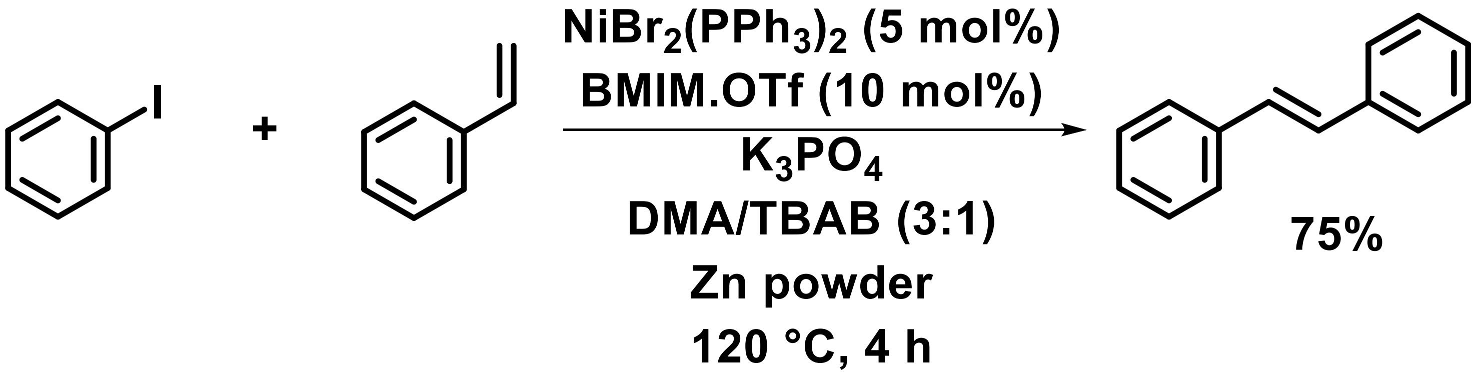
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

➢ The Heck reaction



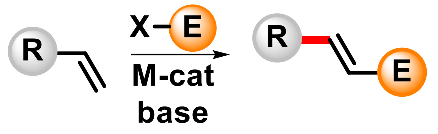


J. Org. Chem. **1987**, *52*, 4133



ChemistrySelect **2019**, *4*, 6913

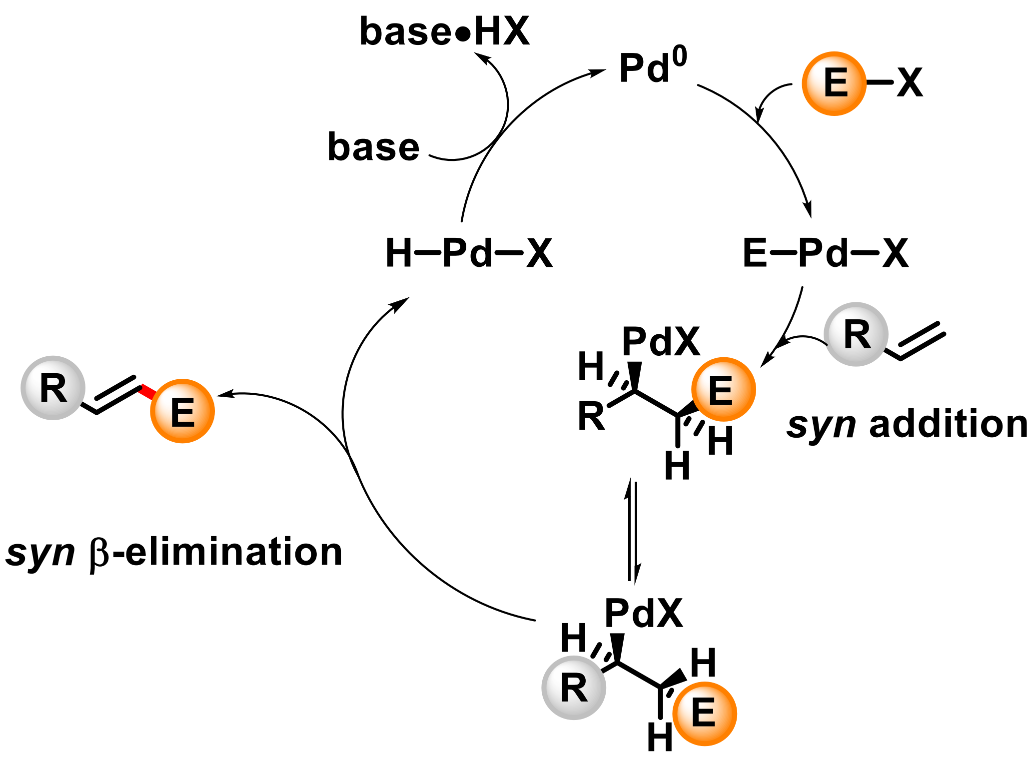
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions



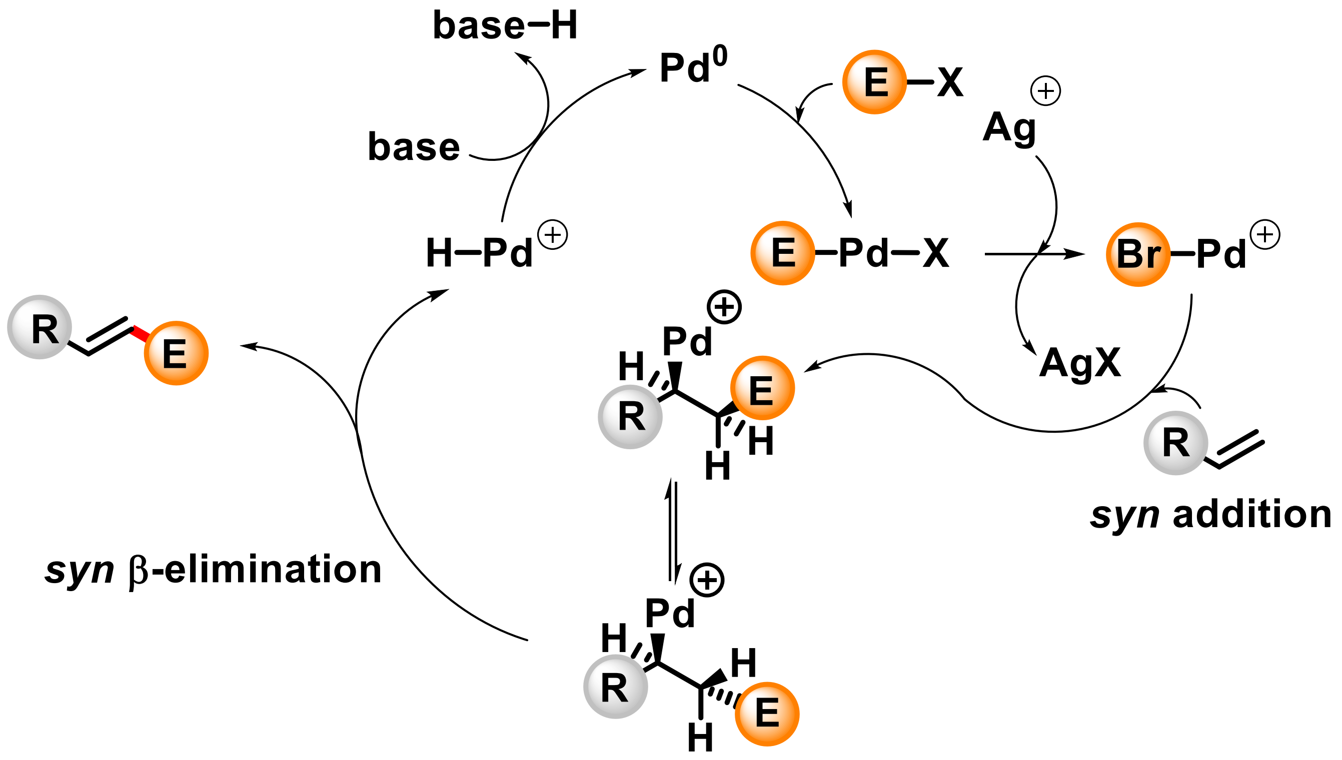
➢ The Heck reaction

- Mechanisms of the Heck reaction

  - Neutral mechanism



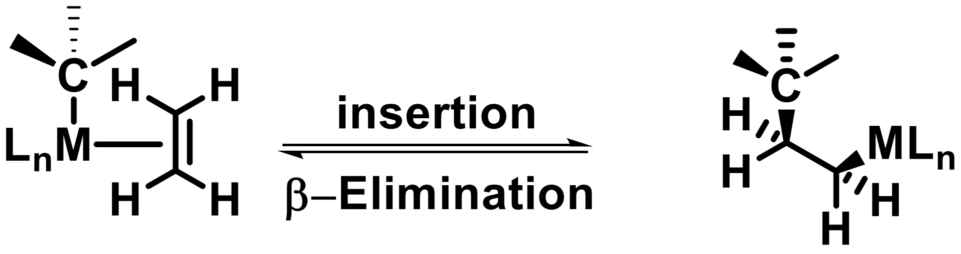
  - Cationic mechanism



Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

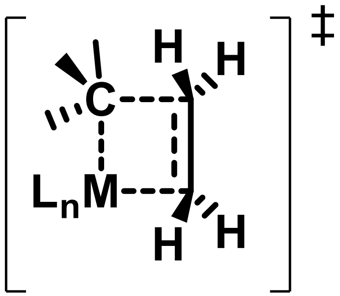
➢ Migratory insertion

- **Insertion of alkenes into metal-carbon bonds**

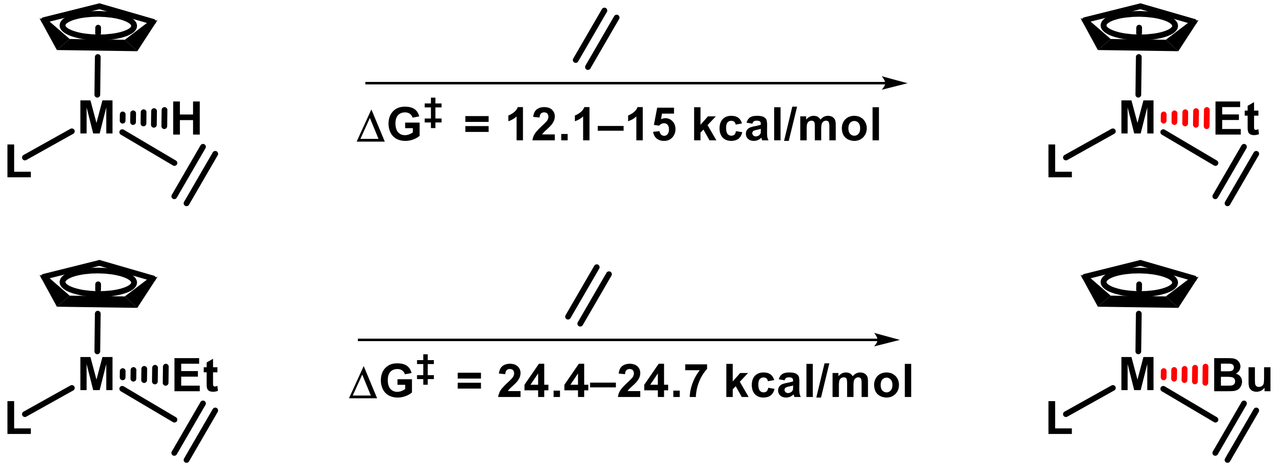


syn addition/elimination

○ **Concerted transition state**



○ **Thermodynamically favorable but kinetically unfavorable**

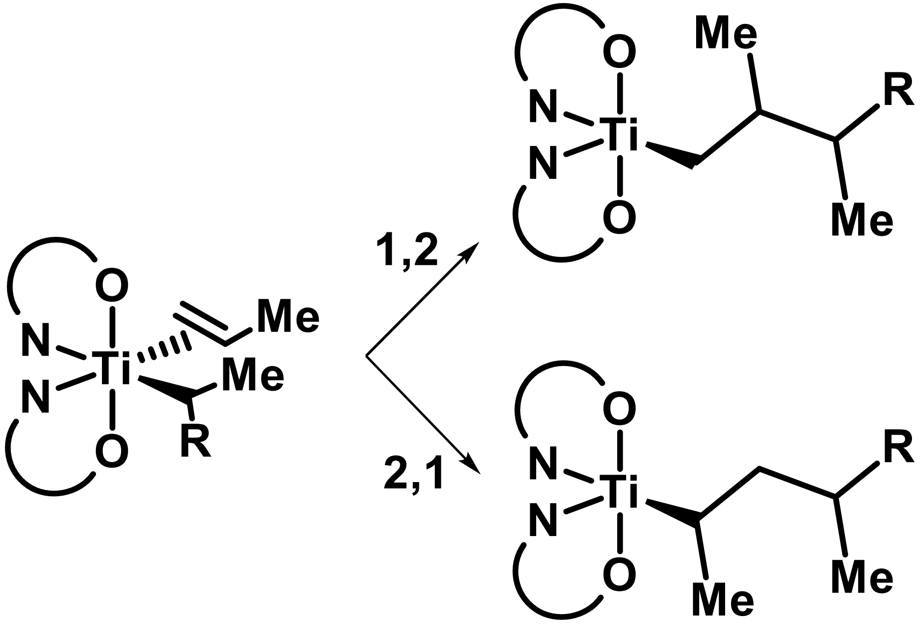


J. Am. Chem. Soc. **1992**, *114*, 10394

Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

➢ Migratory insertion

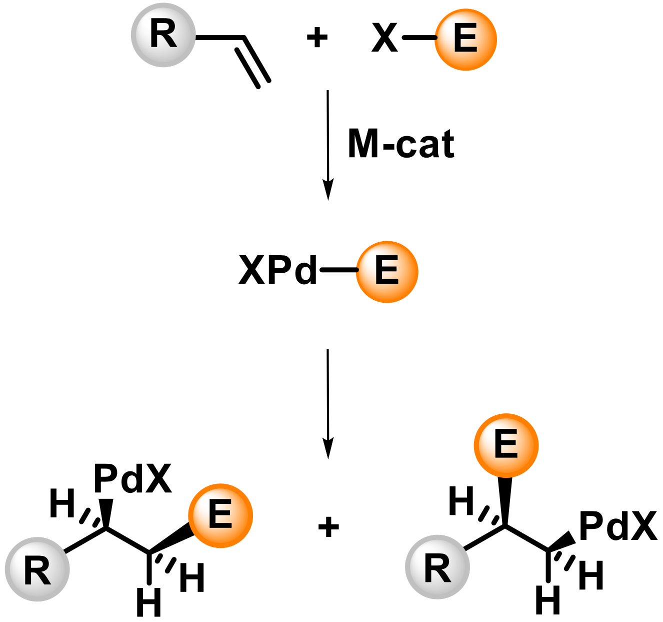
- Insertion of alkenes into metal-carbon bonds
  - Markovnikov (2,1) or anti-Markovnikov (1,2) regioselectivity



Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

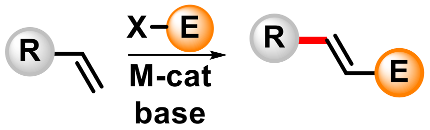
➢ The Heck reaction

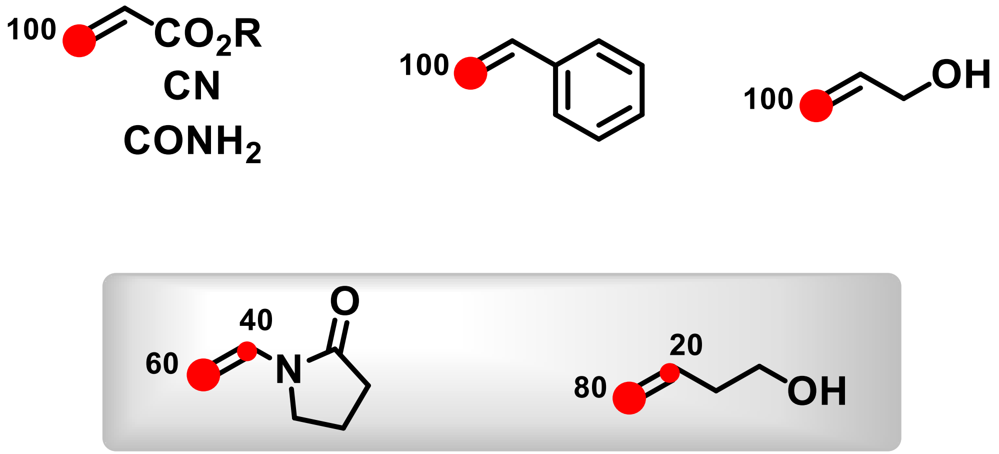
- **Regioselectivity of the Heck reaction**



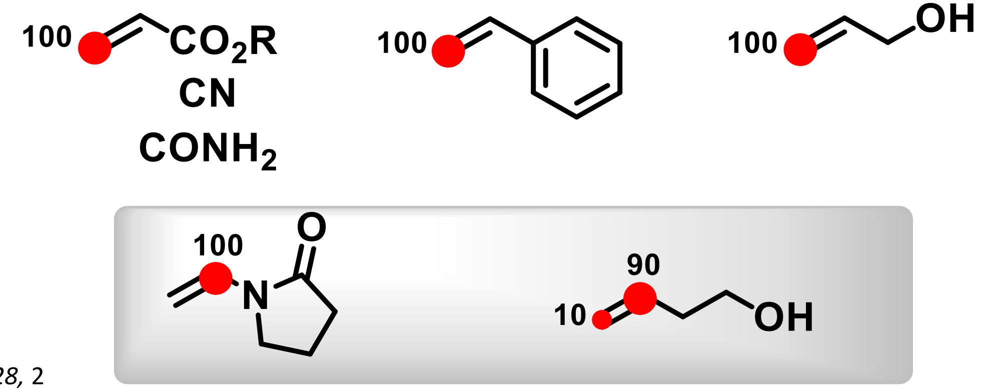
two possible regioisomers

○ **Affected by steric reasons**



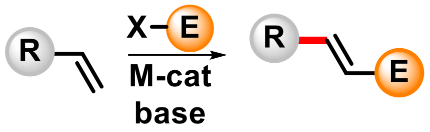


○ **Affected by electronic reasons**



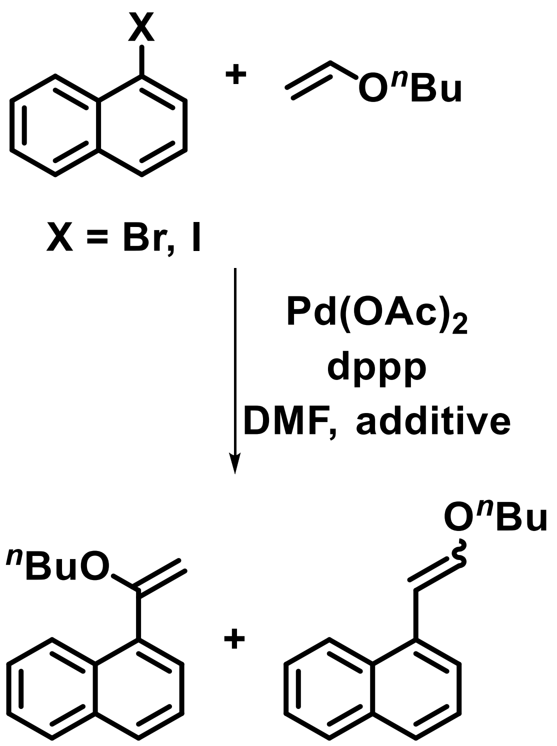
Acc. Chem. Res. **1995**, *28*, 2
J. Org. Chem. **1992**, *57*, 1481

Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions



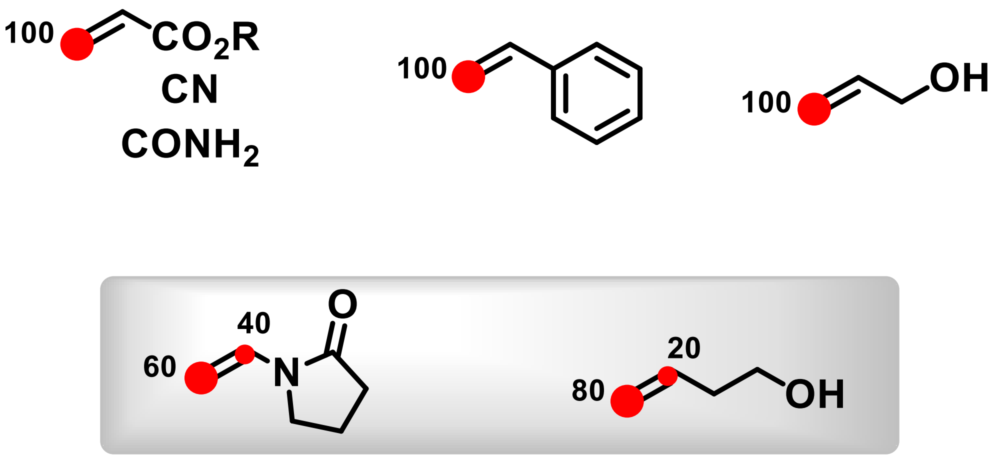
➢ The Heck reaction

- **Regioselectivity of the Heck reaction**

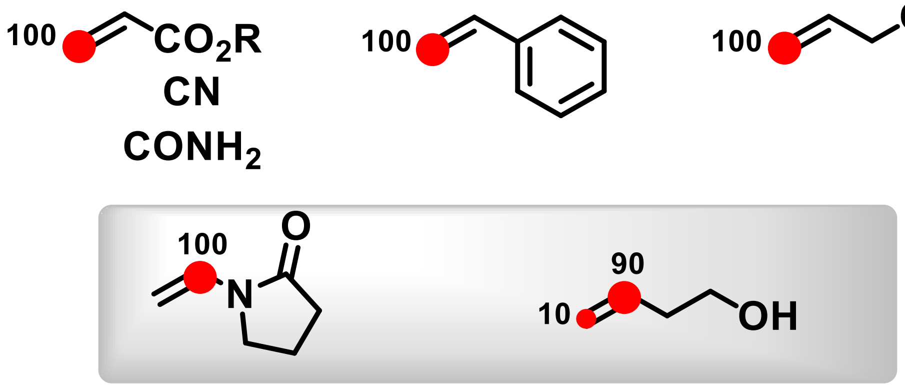


Et_3N, 100 °C	67/33
TlOAc, 100 °C	>99/1

○ **Affected by steric reasons**



○ **Affected by electronic reasons**

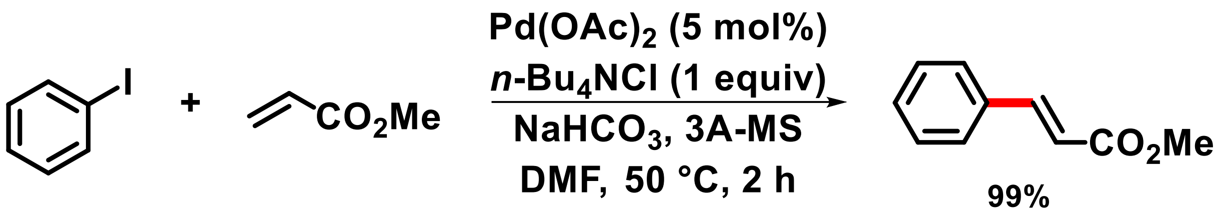


Acc. Chem. Res. **1995**, *28*, 2
J. Org. Chem. **1992**, *57*, 1481

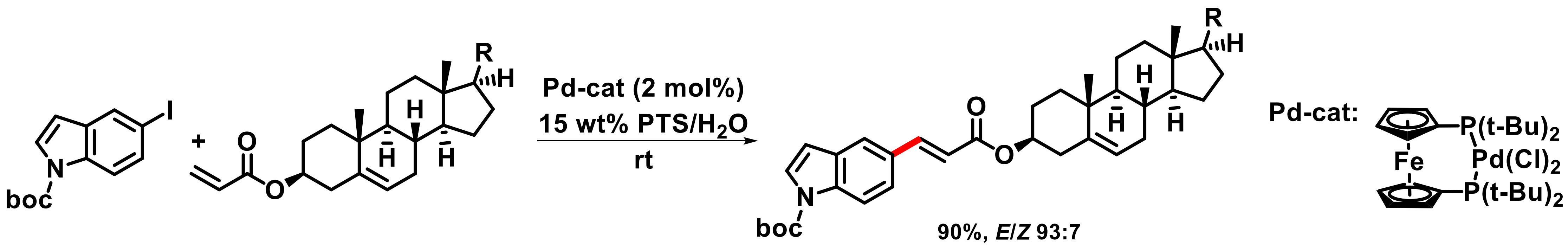
➢ The Heck reaction

- The Heck reaction under mild reaction conditions

  - Jeffery conditions – use of ammonium salts



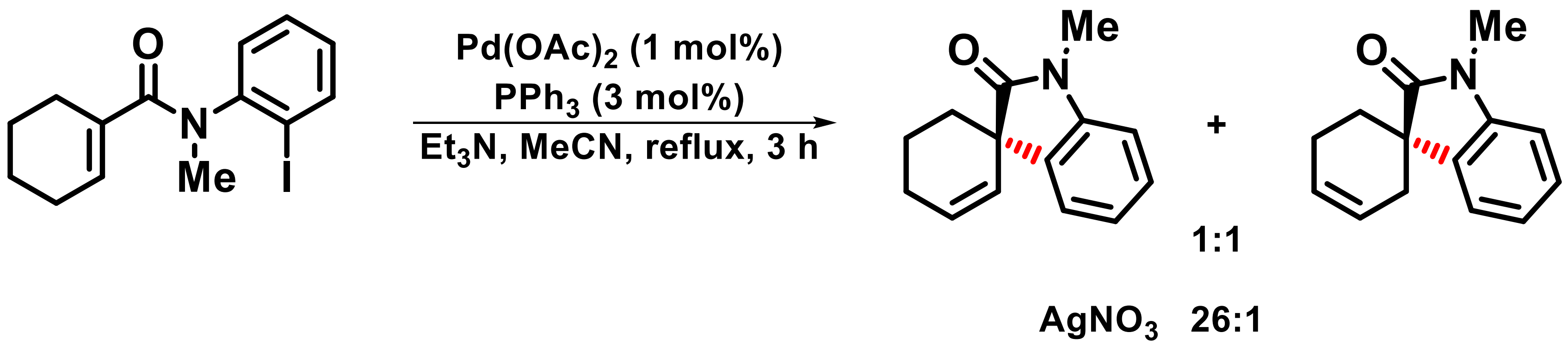
Tetrahedron **1996**, *52*, 10113



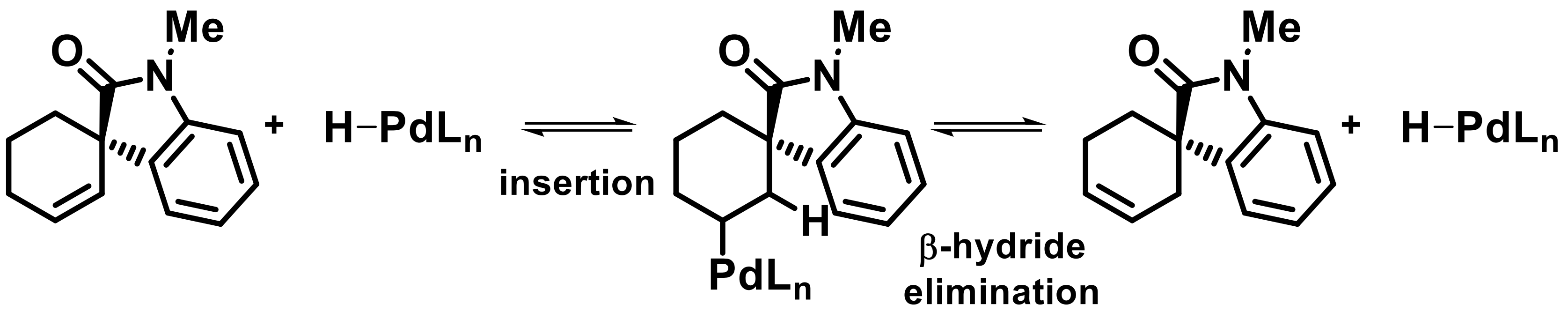
Org. Lett. **2008**, *10*, 1329

➢ The Heck reaction

- Double bond isomerization

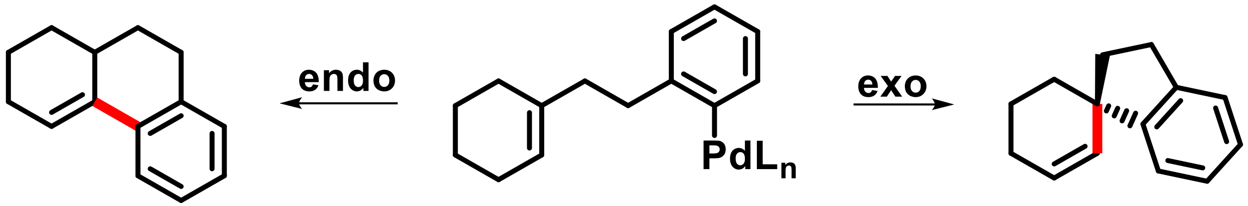


J. Org. Chem. **1987**, *52*, 4133

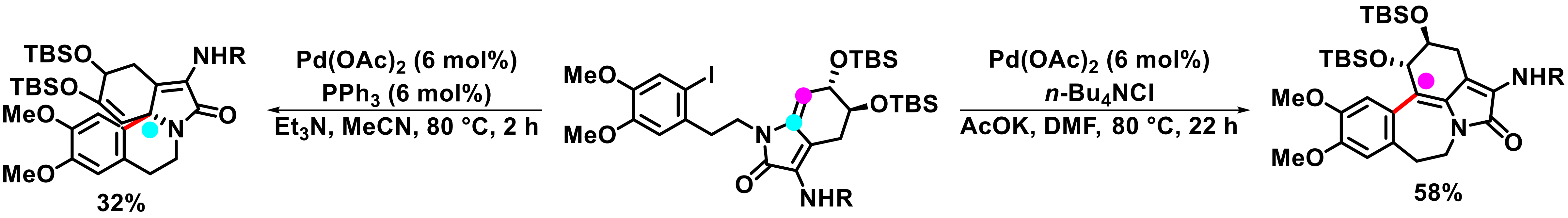


➢ The Heck reaction

- **Intramolecular Heck reaction – exo x endo cyclization**



- **Influenced by reaction conditions and substrate structure**

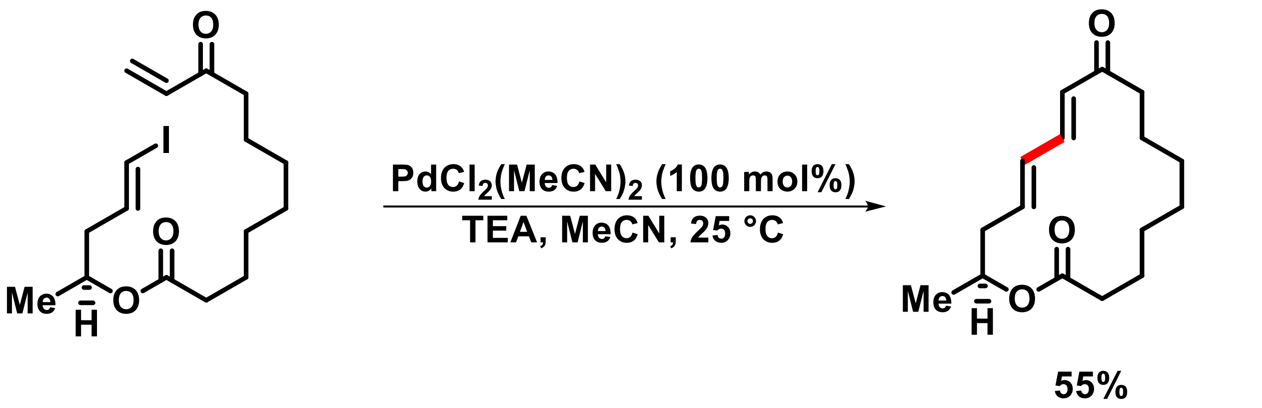


J. Am. Chem. Soc. **1995**, *117*, 7834

Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

➢ The Heck reaction

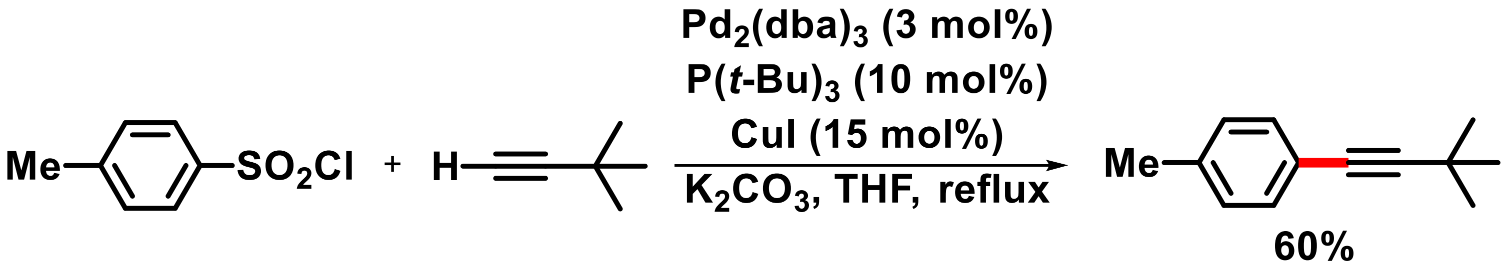
- Intramolecular Heck reaction – excelent tool for macrolactonization



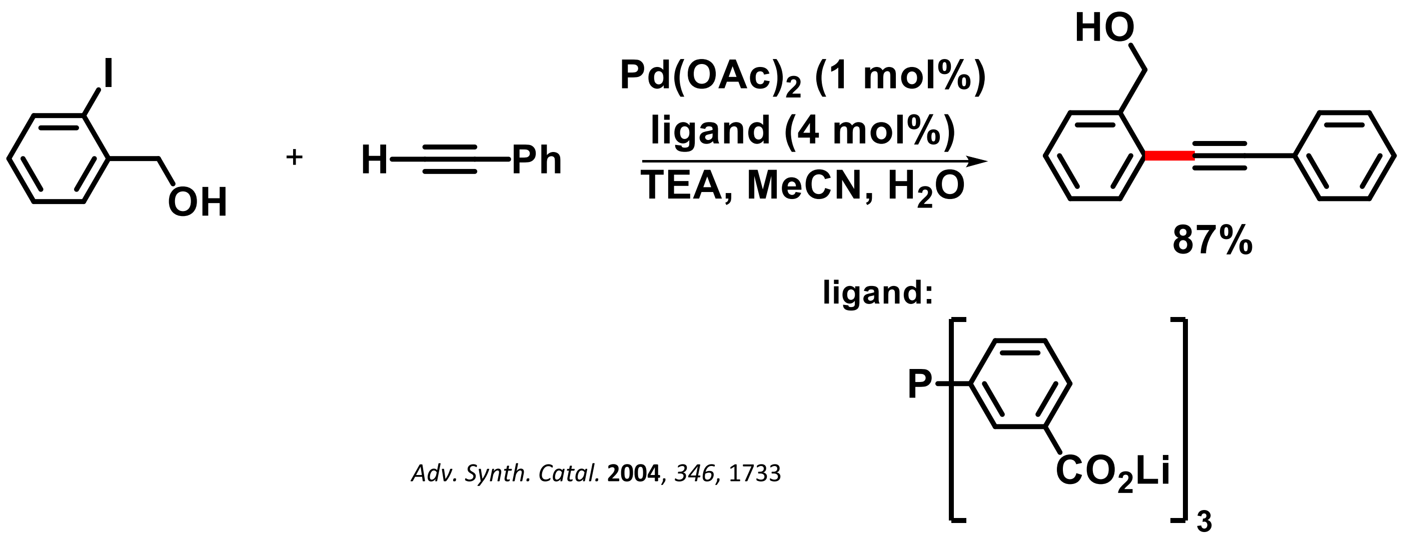
Tetrahedron **1981**, *37*, 4035

Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

➢ The Sonogashira reaction

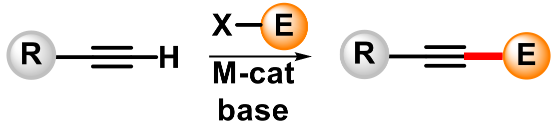


Adv. Synth. Catal. **2004**, *346*, 1793

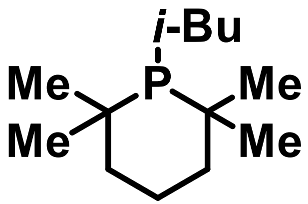


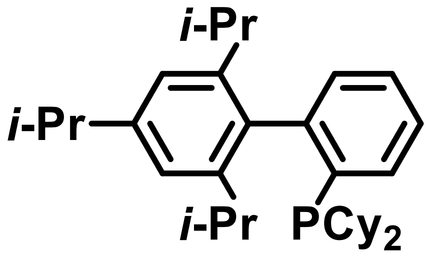
Adv. Synth. Catal. **2004**, *346*, 1733

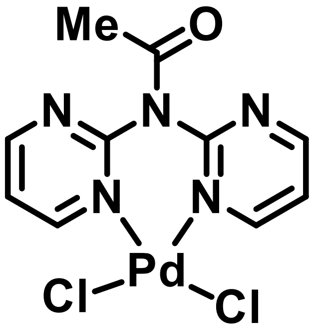
➢ The Sonogashira reaction

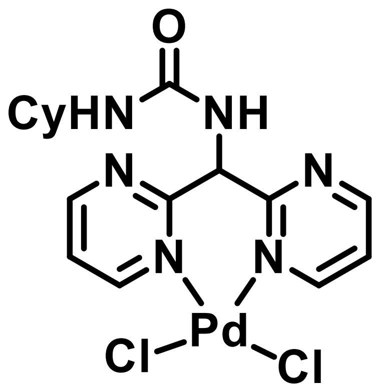


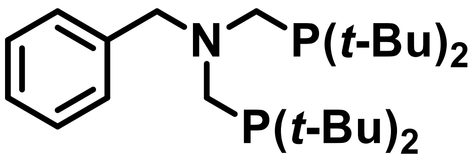
- Ligands for the Sonogashira reaction

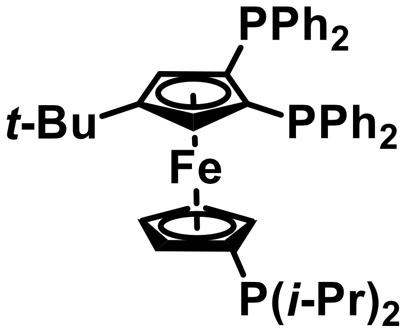


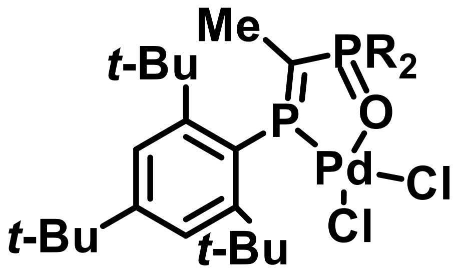


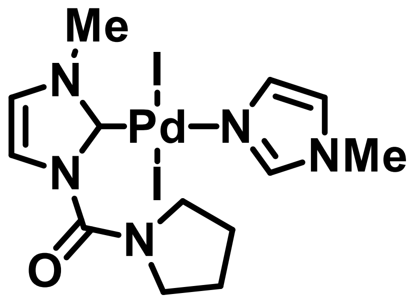








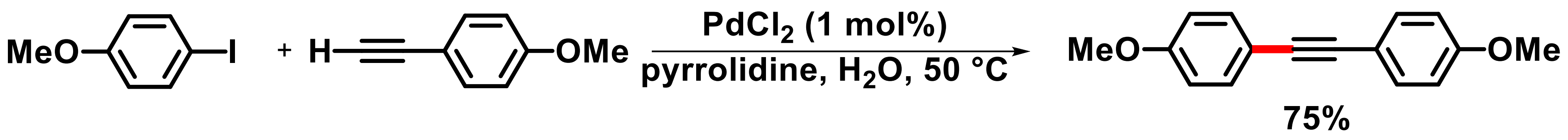




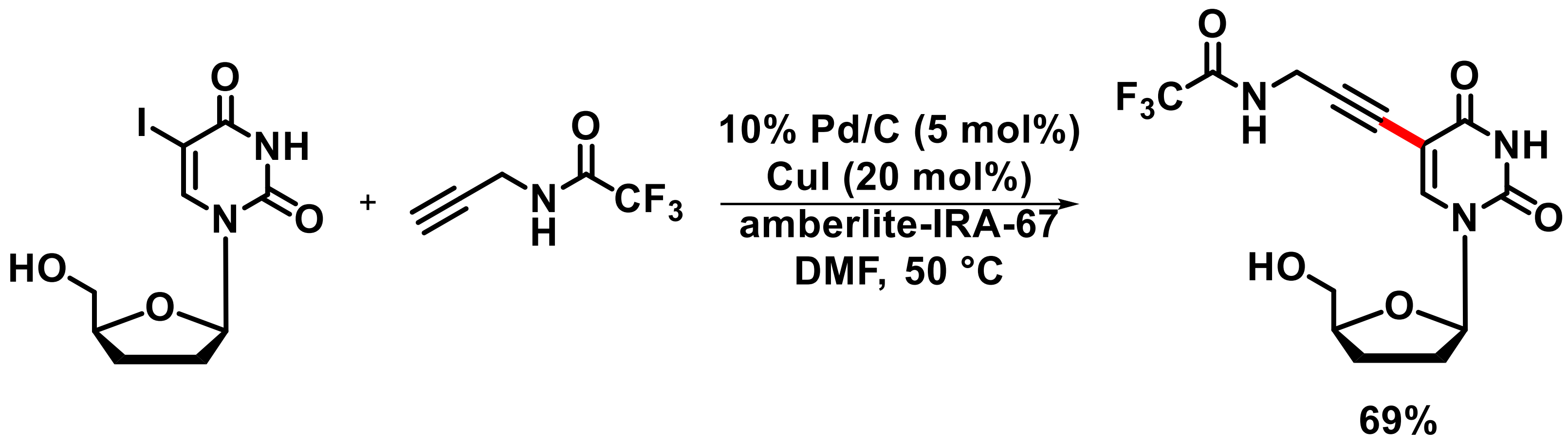
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

➢ The Sonogashira reaction

- Ligands-free Sonogashira reaction



J. Org. Chem. **2005**, *70*, 391

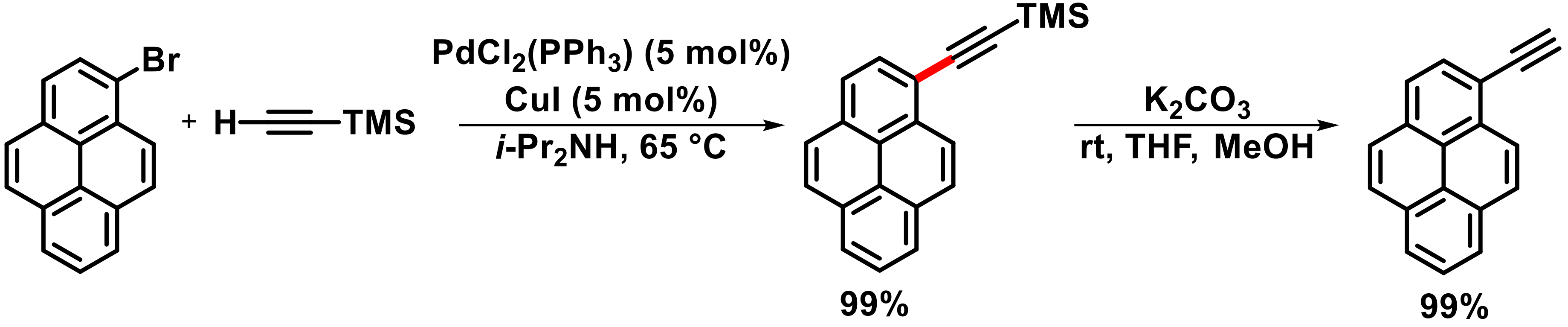


Chem. Commun. **2005**, 4551

Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

➢ The Sonogashira reaction

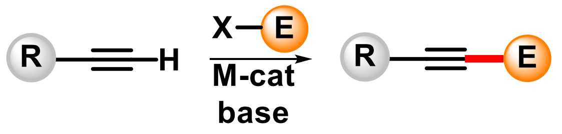
- Synthesis of terminal alkynes



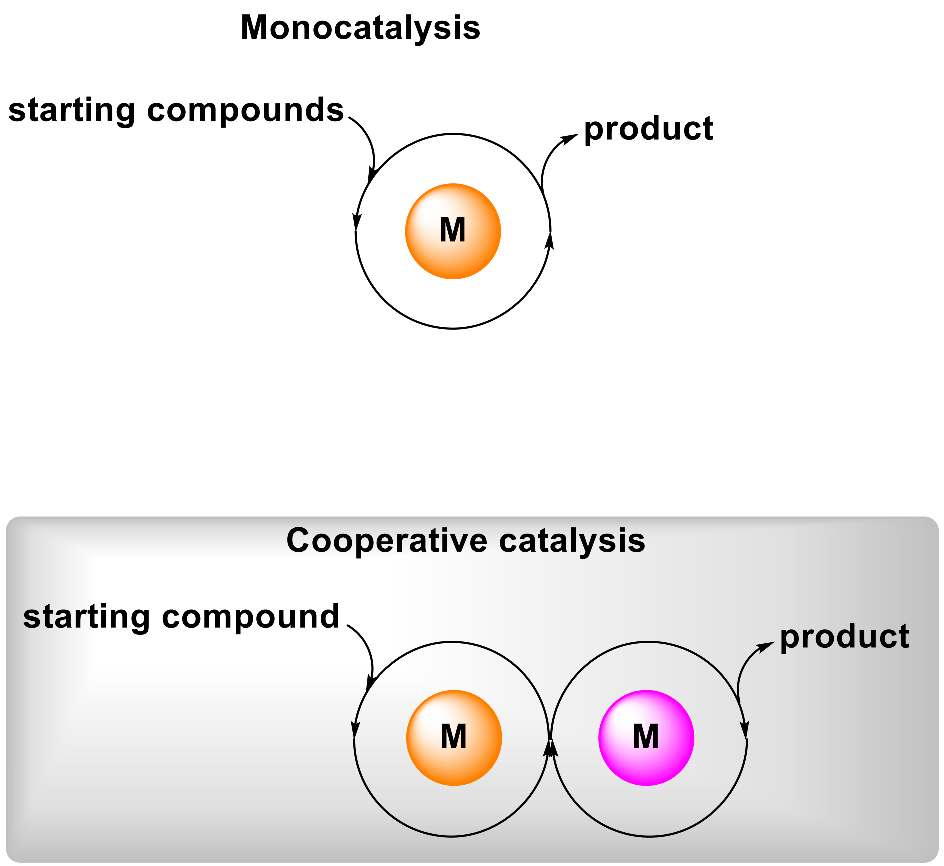
Chem. Commun. **2015**, 12088

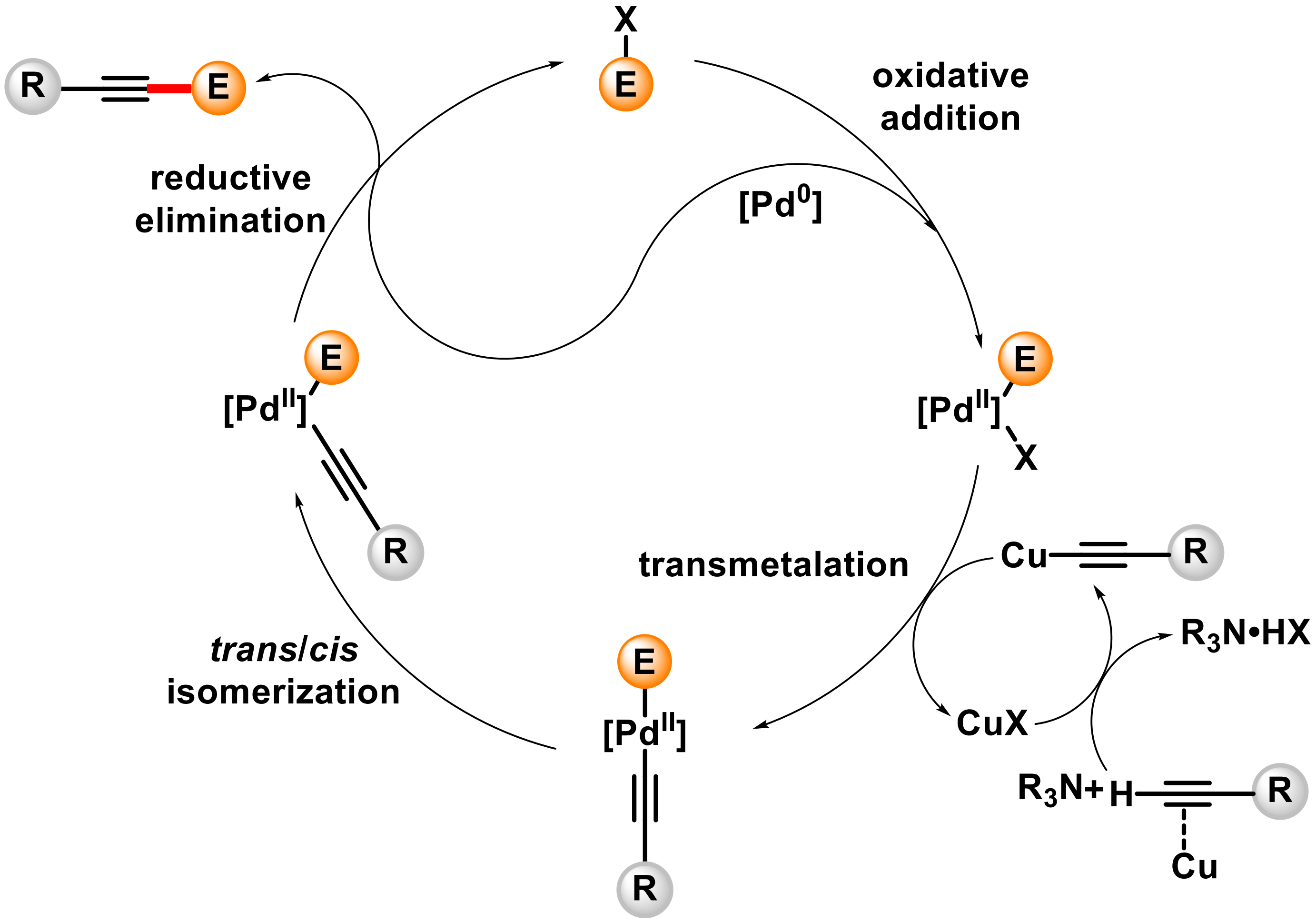
Formation of C–C Bond by Transtion-Metal-Catalyzed Reactions

➢ The Sonogashira reaction

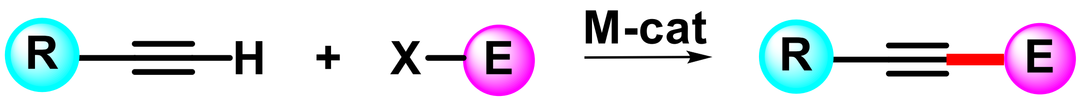


- Mechanism of the Sonogashira reaction





➢ The Sonogashira reaction



- Mechanism of the copper-free Sonogashira reaction