

Lecture “Modern Synthetic Methods”

Take-home messages from Week 10

3. (Transition) Metals in Organic Synthesis

3.1. Principles of Catalysis

Three main areas of catalysis:

- Heterogeneous catalysis
- Homogeneous catalysis
- Enzymatic catalysis

Definition of homogenous catalyst: “Concentration appears in the rate law to a higher power than indicated by its stoichiometric coefficient in the reaction equation”

Turnover number: $TON = M(\text{substrate converted}) / M(\text{catalysts})$

Turnover frequency: $TOF = M(\text{substrate converted}) / \text{time}$

Halpern principle:

- In ideal catalytic cycles all catalytically active species should be similar in energy separated by only small energetic barriers
- “If you can observe it - it’s probably not relevant in the catalytic cycle”

3.2. Palladium-catalyzed Reactions

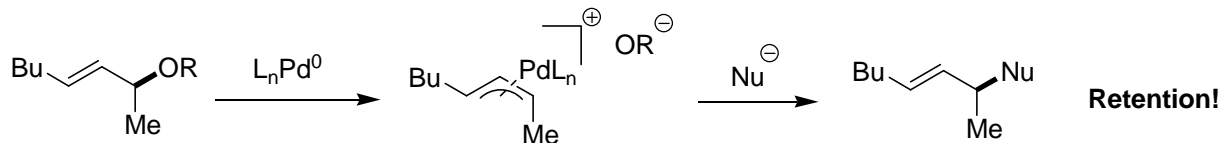
Most important oxidation states in catalysis:

- Pd^{II} : electrophilic
- Pd^0 : nucleophilic

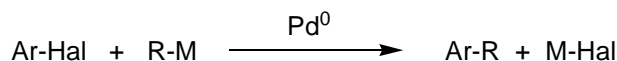
3.2.1. Wacker oxidation



3.2.2. Palladium-catalyzed allylic substitution



3.2.3. Palladium catalyzed cross-couplings



Kumada ($RMgX$), **Negishi** ($RZnX$), **Stille** ($RSnBu_3$), **Suzuki** ($RB(OR)_2$),

Hiyama (F_3Si-R/F^-), **Sonogashira** ($R-C\equiv$)

