

Chem 1310/2370 - 9/2/2009

Organometallics

→ The following table gives a brief summary of the reactions between major classes of functional groups and reducing, oxidizing, and organometallic agents (A/B = acid/base reaction = simple proton transfer; - = no reaction). Mechanisms of these processes are provided in lecture notes and in Vollhardt. Aldehydes are more reactive than ketones. Ester and acids are even less reactive. ↵

| Substrate → | <u>RCH₂OH</u> | <u>RR'CHOH</u> | <u>RR'R''COH</u> | <u>RCHO</u> | <u>RCOR'</u> | <u>RCO₂R'</u> | <u>RCO₂H</u> |
|--------------------------------------------------|--------------------------|----------------|------------------|---------------------|--------------|----------------------------|-------------------------|
| Reagent ↓ | | | | | | | |
| LAH | A/B | A/B | A/B | RCH ₂ OH | RR'CHOH | RCH ₂ OH + HOR' | RCH ₂ OH |
| NaBH ₄ | A/B | A/B | A/B | RCH ₂ OH | RR'CHOH | - | A/B |
| PCC | RCHO | RCOR' | - | - | - | - | - |
| CrO ₃ /H ₂ SO ₄ | RCOOH | RCOR' | - | RCOOH | - | - | - |
| R*-Li | A/B | A/B | A/B | RR*CHOH | RR'R*COH | RR'R*COH + HOR' | RCOR* |
| R*-MgX | A/B | A/B | A/B | RR*CHOH | RR'R*COH | RR'R*COH + HOR' | A/B |

See: V&S; Chapter 8.7-8.9

A. Organometallic Mechanisms

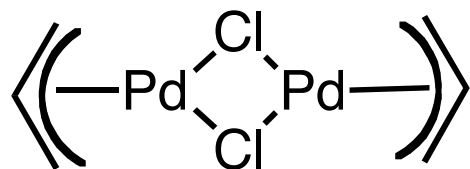
Oxidation State: The oxidation state of a metal is defined as the charge left on the metal after all ligands have been removed in their natural, closed-shell configuration. This is a formalism and not a physical property!

d-Electron Configuration: position in the periodic table *minus* oxidation state.

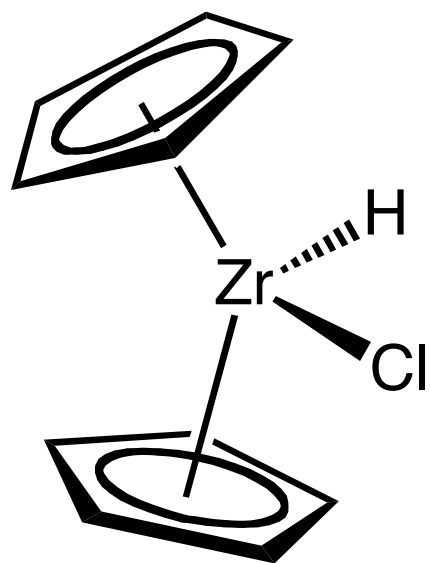
18-Electron Rule: In mononuclear, diamagnetic complexes, the total number of electrons never exceeds 18 (noble gas configuration). The total number of electrons is equal to the sum of d-electrons *plus* those contributed by the ligands.

18 electrons = coordinatively saturated

< 18 electrons = coordinatively unsaturated.

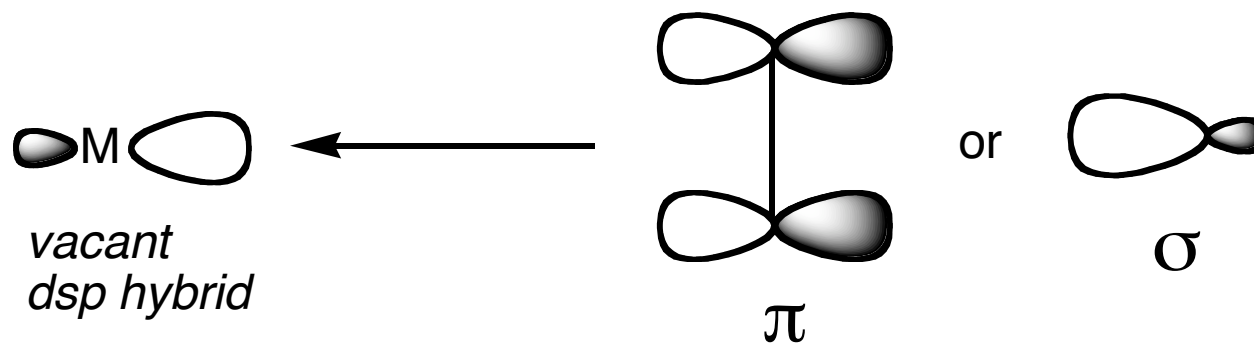


*bridging by lone
pairs on Cl;
each Cl acts as a
2-electron, mono-
negative ligand to
one of the Pd's,
and a 2-electron
neutral donor ligand
like PPh_3 to the other*

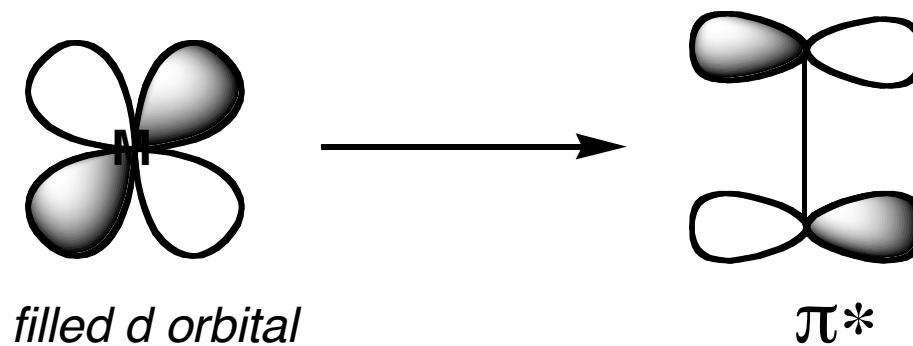


Bonding considerations

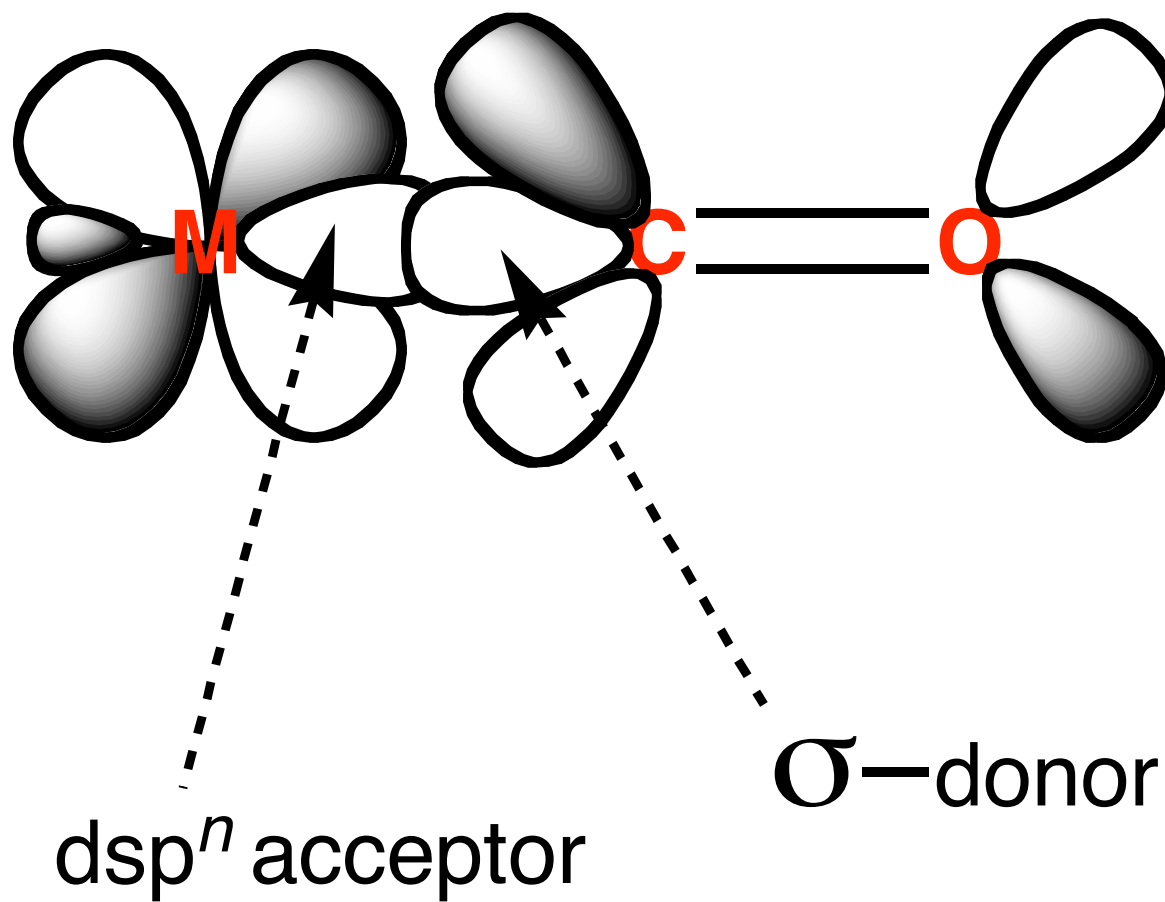
donation:



backdonation:



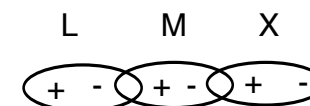
for M-CO:



Basic reaction mechanisms

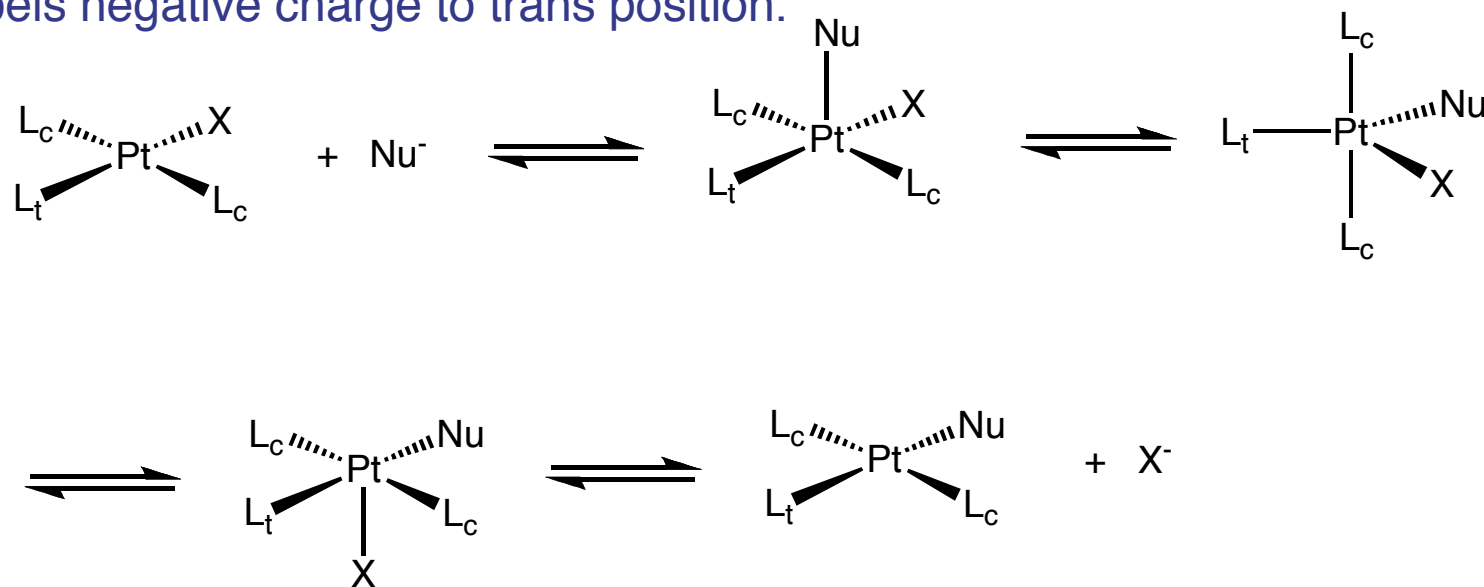
- **ligand substitution:** $M-L + L' \rightarrow M-L' + L$

can be associative, dissociative, or radical chain.

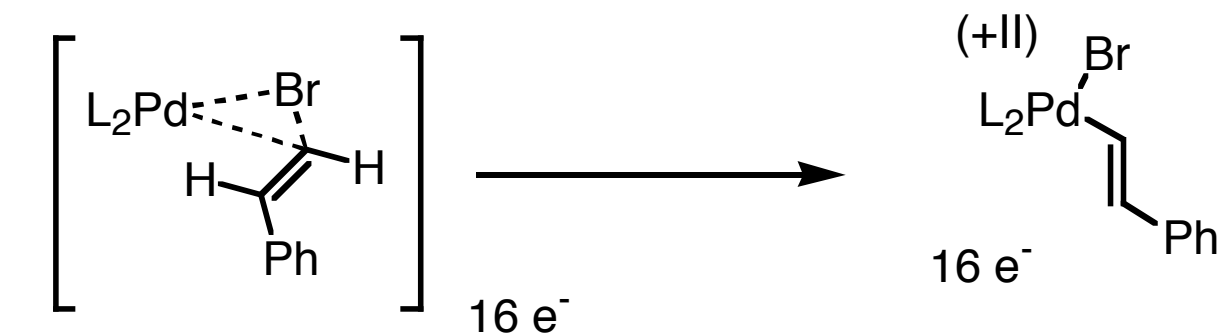
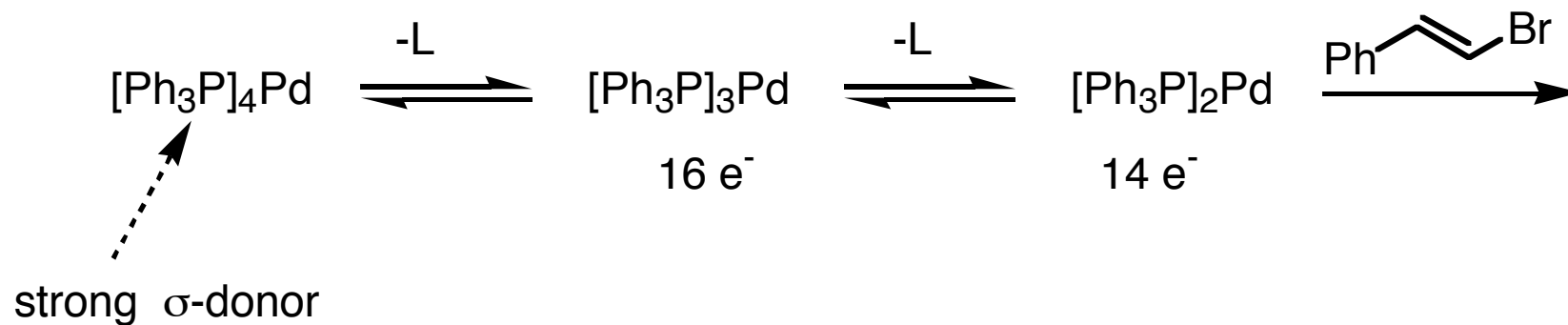


trans-effect: kinetic effect of a ligand on the rate of substitution at the position trans to itself in a square or octahedral complex (ground-state weakening of bond).

$L \rightarrow M$, repels negative charge to trans position.

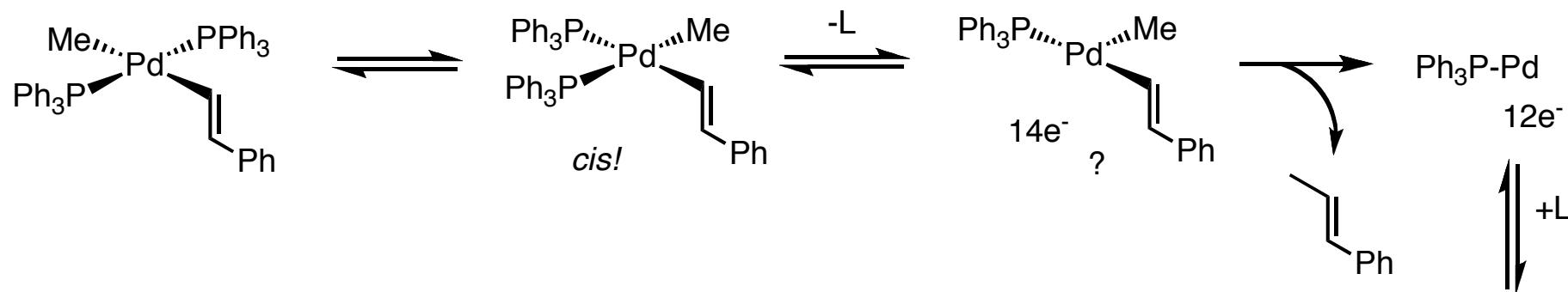


- oxidative addition:



*agostic ($2e^-/3$ -center
bond) interactions*

- **reductive elimination:** the major way in which transition metals are used to make C,C- and C,H-bonds!

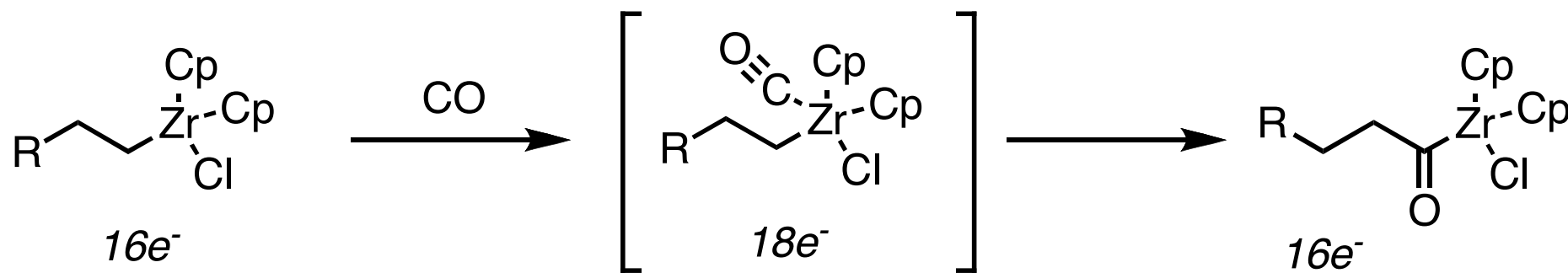


Complex geometry and ligand effects on rate: Amatore, C.; Jutand, A.; Suarez, A., "Intimate mechanism of oxidative addition to zerovalent palladium complexes in the presence of halide ions and its relevance to the mechanism of palladium-catalyzed nucleophilic substitutions." *J. Am. Chem. Soc.* **1993**, *115*, 9531-9541.

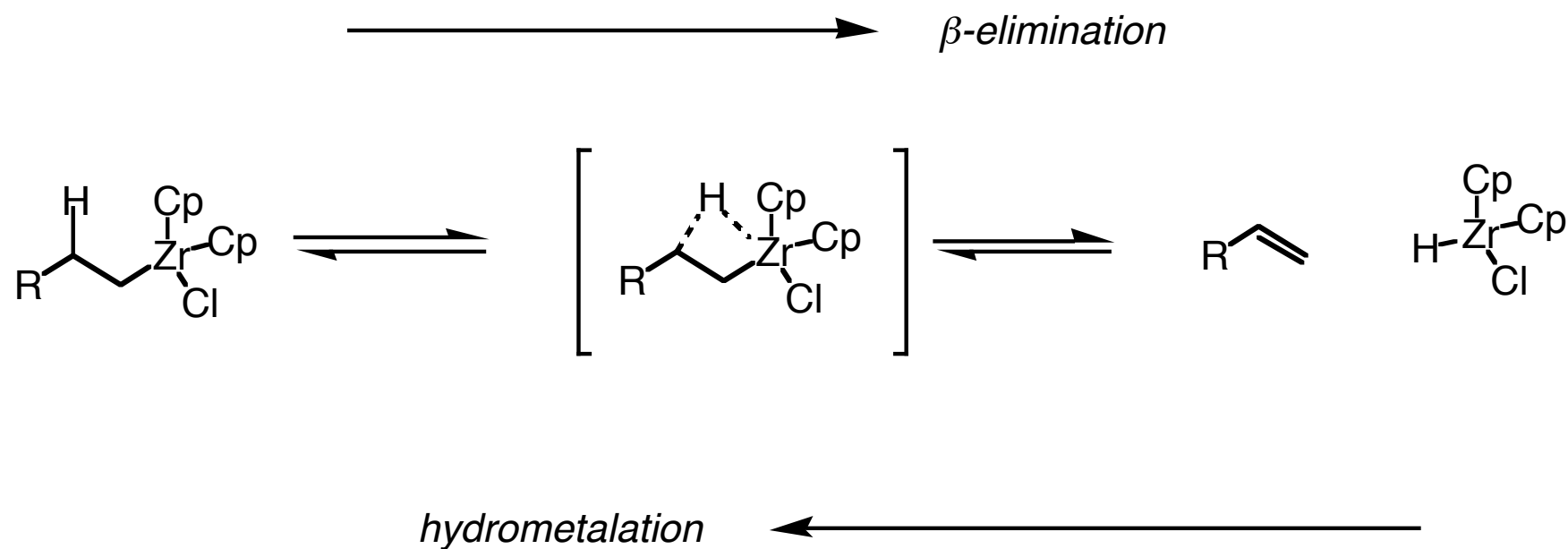
The Ligand. Among the phosphines used for the Heck reaction are PPh₃, P(*o*-tol)₃, P(furyl)₃, PCy₃, 2-(di-*t*-butylphosphanyl)biphenyl, dppe, dppp, dppb, and dppf as well as AsPh₃. PCy₃ is very effective for aromatic chlorides. Most phosphines favor the *trans*-complex and thus slow down the catalytic cycle. Bidentate phosphines are used when monodentate ligands are ineffective or to influence stereoselectivity in combination with triflates (cationic pathway).

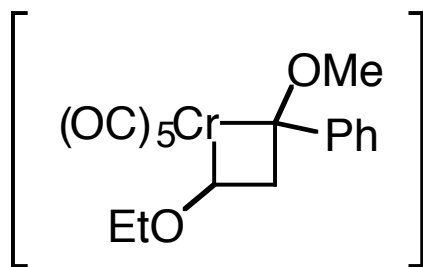
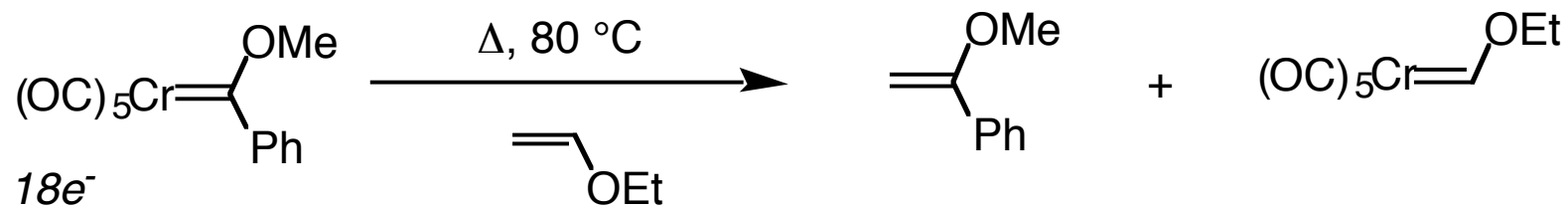
N-heterocyclic carbene ligands (for example with N,N'-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMES•HCl)) provide useful, highly reactive catalytic systems.

- migratory insertion:



- β -elimination/hydrometalation:



- olefin metathesis:*Fischer carbene complex*

- **transmetalation:**



Summary of Mechanisms:

- ligand substitution
- oxidative addition/reductive elimination
- migratory insertion/ β -elimination (carbo-, hydrometalation)
- alkene metathesis
- transmetalation