

Chem 1140; Introduction to Organometallic Chemistry

- *General Mechanistic Principles*
- *Reactions with Wilkinson's Catalyst*

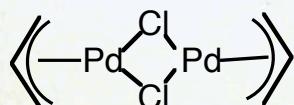
A. Organometallic Mechanisms

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!

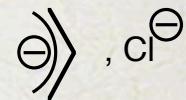
d-Electron Configuration: position in the periodic table *minus* oxidation state.

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.



for each Pd: Ox. state

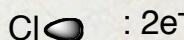


Pd(II)

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

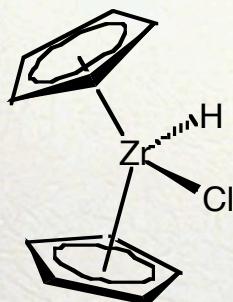
$$\text{d: } 10 \ (4\text{d}^{10} \ 5\text{s}^0) - 2 = \underline{8}$$

electron count:



$$\underline{8e^- + d^8 = 16e^-}$$

unsaturated



Ox. State: 2 Cp^- , 1 H^- , 1 Cl^-
 $\rightarrow \text{Zr(IV)}$

$$\text{d: } 4 \ (4\text{d}^2 \ 5\text{s}^2) - 4 = \underline{0}$$

electron count: 2 Cp^- : 12

H^- : 2

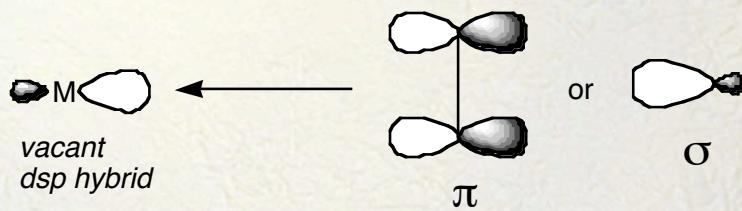
Cl^- : 2

Zr : 0

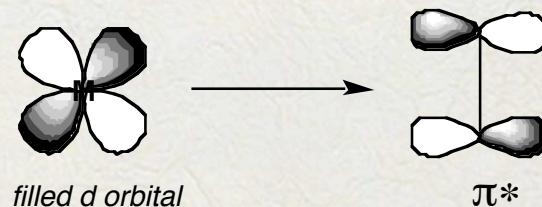
16 e⁻, unsaturated

Bonding considerations

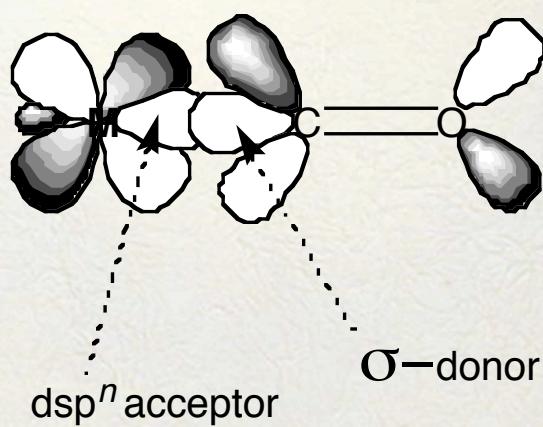
donation:



backdonation:

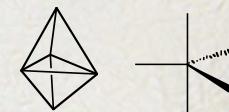


for M-CO:

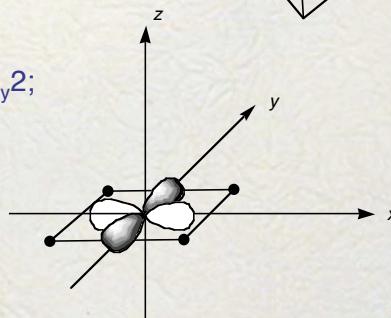


Structure

- saturated ($18 e^-$) complexes:
 - tetracoordinate: $\text{Ni}(\text{CO})_4$, $\text{Pd}(\text{PPh}_3)_4$ are tetrahedral
 - pentacoordinate: $\text{Fe}(\text{CO})_5$ is trigonal bipyramidal
 - hexacoordinate: $\text{Cr}(\text{CO})_6$ is octahedral



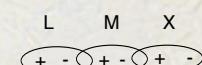
- unsaturated complexes have high $d_x^2 - y^2$; $16e^-$ prefers square planar



Basic reaction mechanisms

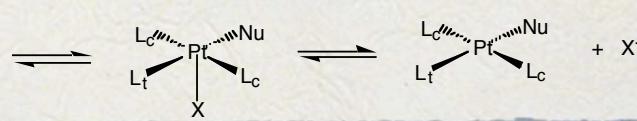
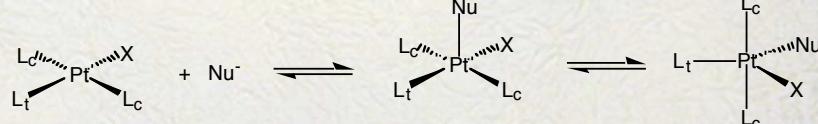
- **ligand substitution:** $\text{M}-\text{L} + \text{L}' \rightarrow \text{M}-\text{L}' + \text{L}$

can be associative, dissociative, or radical chain.

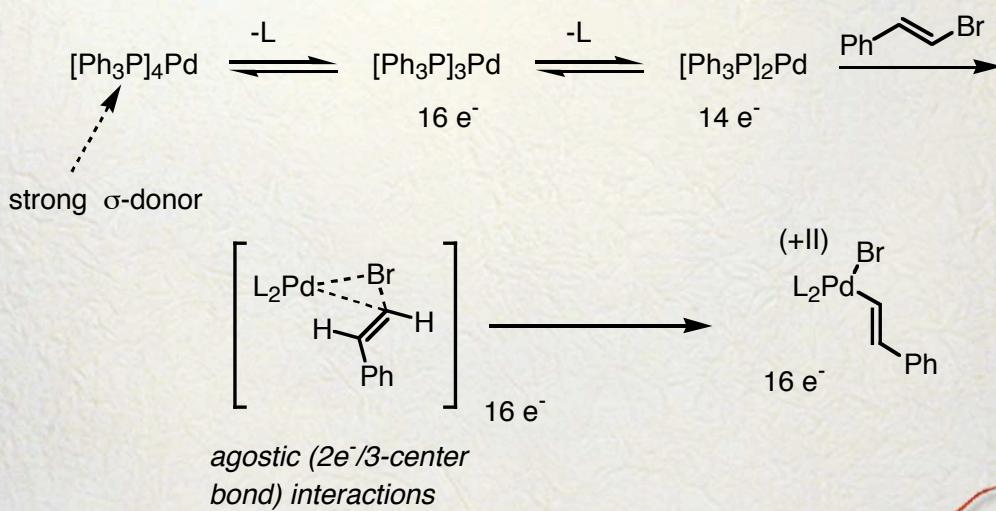


trans-effect: kinetic effect of a ligand on the rate of substitution at the position trans to itself in a square or octahedral complex (ground-state weakening of bond).

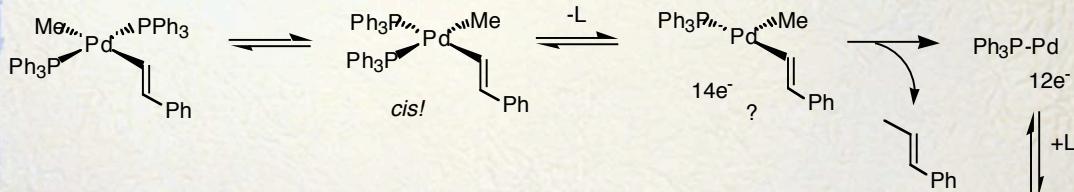
$\text{L} \rightarrow \text{M}$, repels negative charge to trans position.

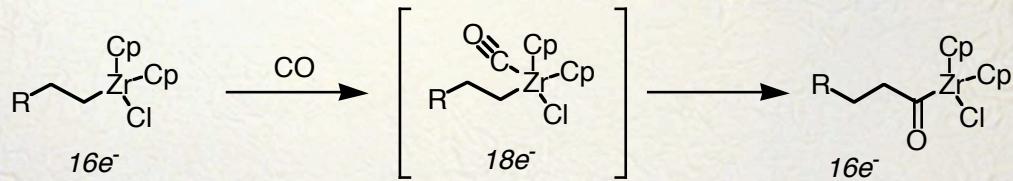
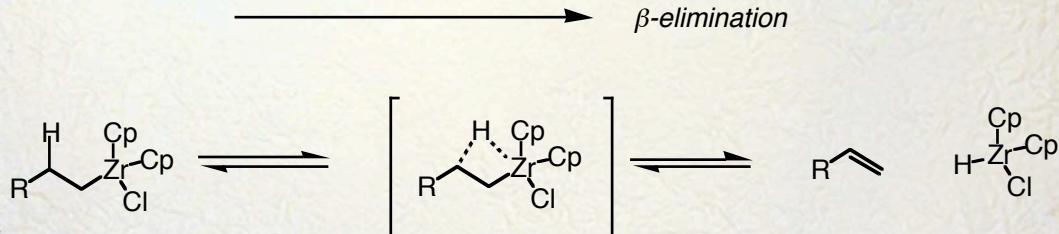


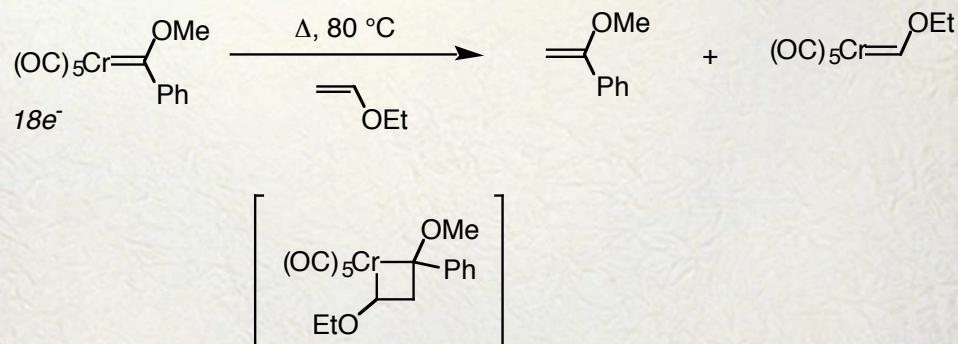
- oxidative addition:



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



- migratory insertion:**- β-elimination/hydrometalation:**

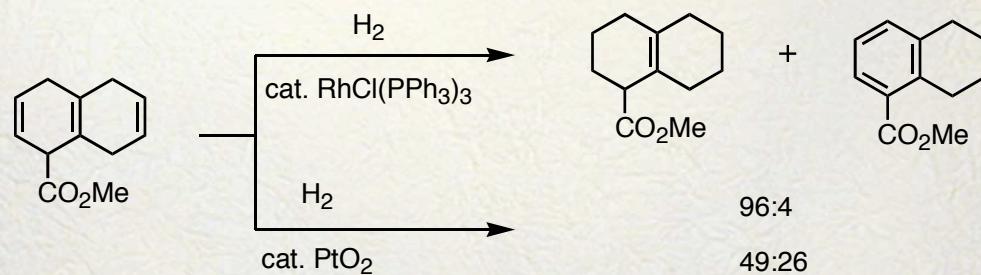
- olefin metathesis:*Fischer carbene complex***- transmetalation:**

Summary of Mechanisms:

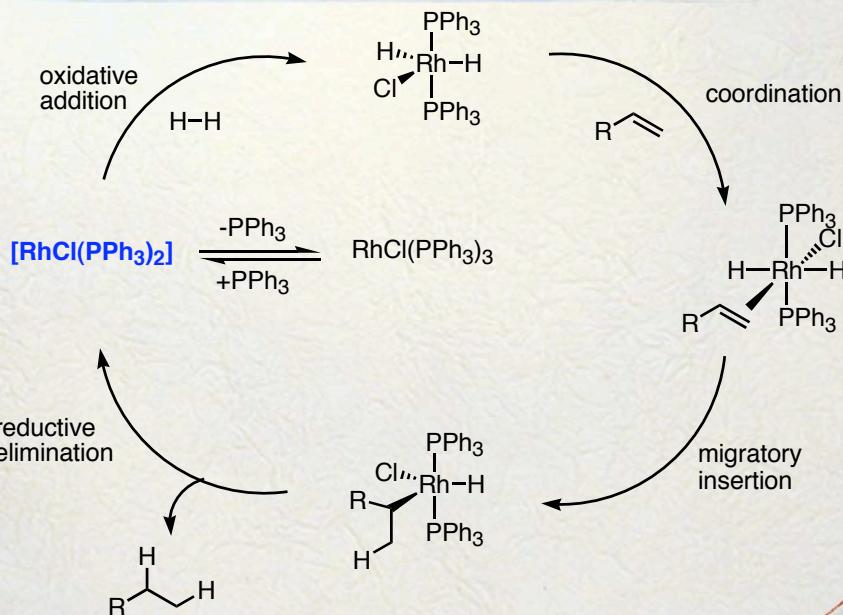
- ligand substitution
- oxidative addition/reductive elimination
- migratory insertion/β-elimination (carbo-, hydrometalation)
- alkene metathesis
- transmetalation

Reactions with Wilkinson's Catalyst

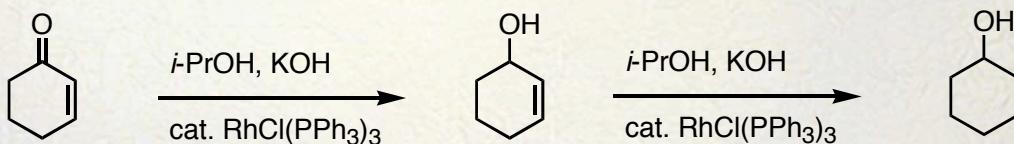
Alkene Hydrogenation



Mechanism

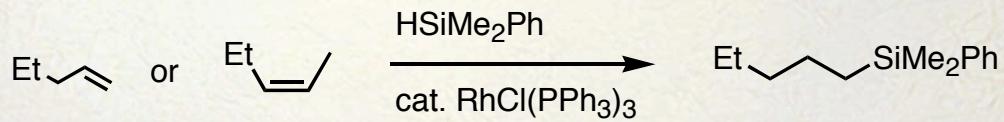


Reductions

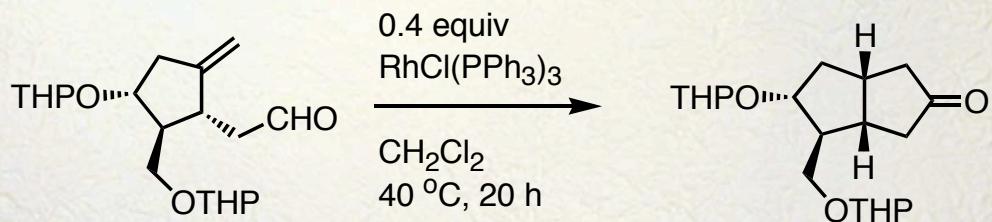


Where does the hydrogen come from????

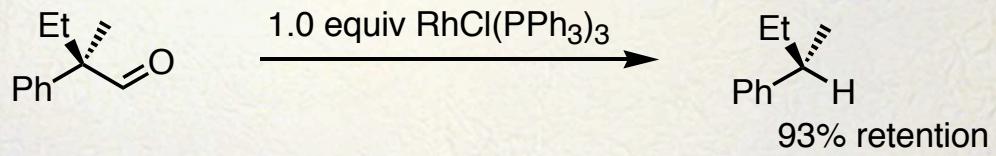
Hydrosilylation



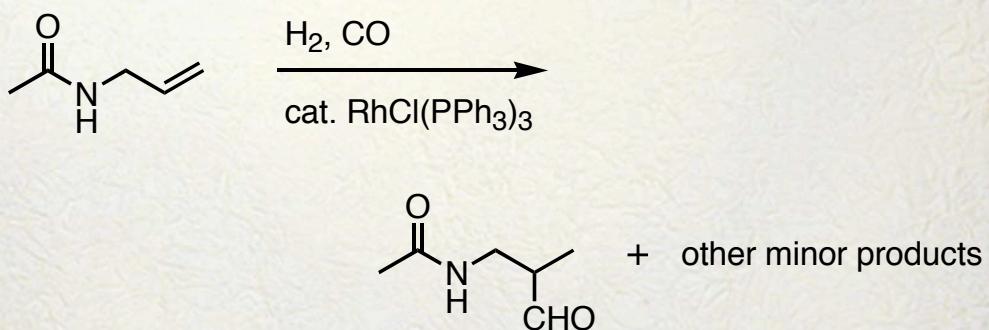
Hydrocarbonylation



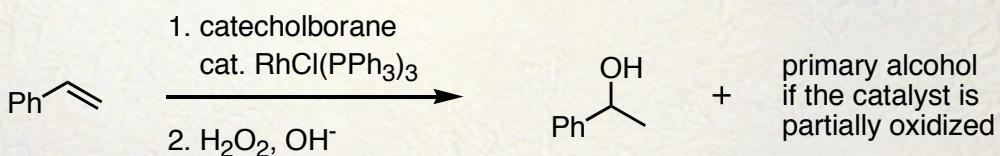
Decarbonylation



Hydroformylation



Markownikow Hydroboration



Cycloisomerization

