

Chapter 8 – Organometallic Synthesis

S block

d block

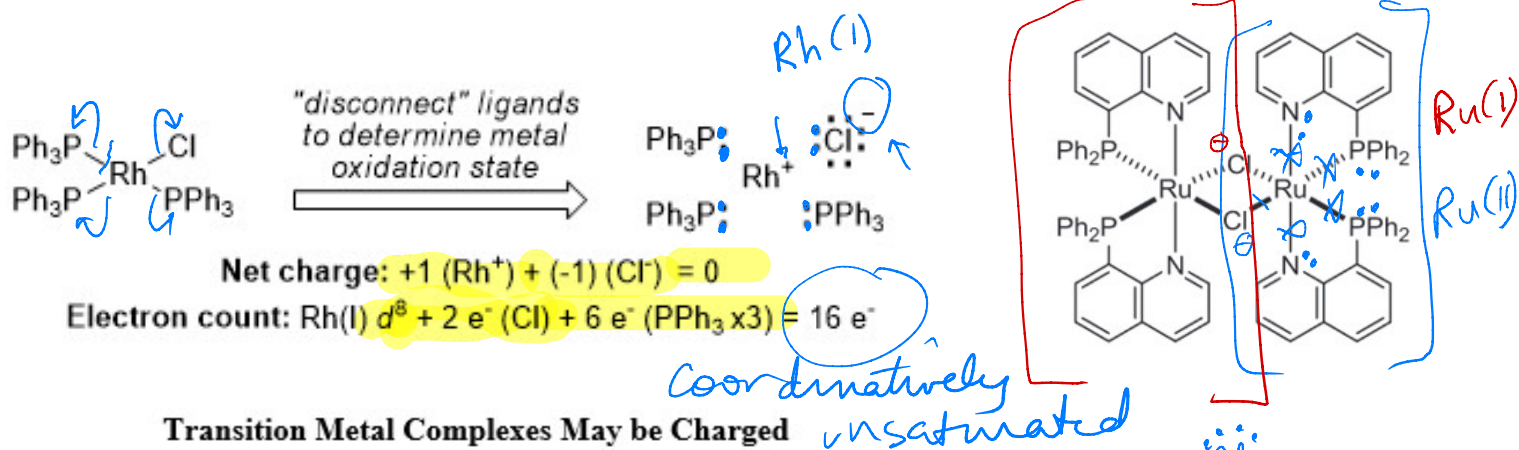
P

S²P⁶ octet 8e⁻

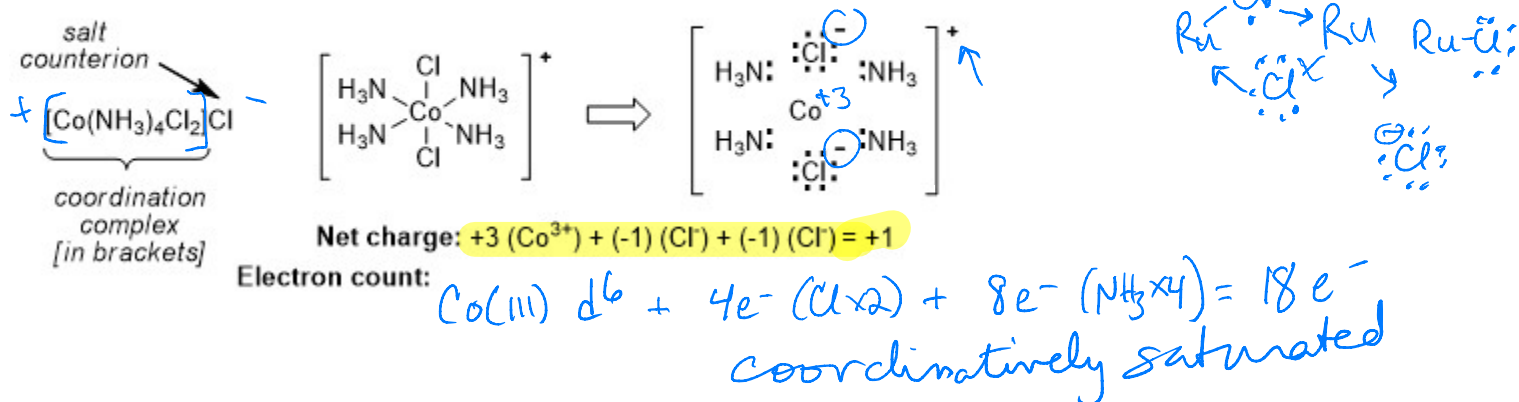
18-Electron Rule (or EAN, Effective Atomic Number, Rule)

Examples of Transition Metals Used in Synthesis

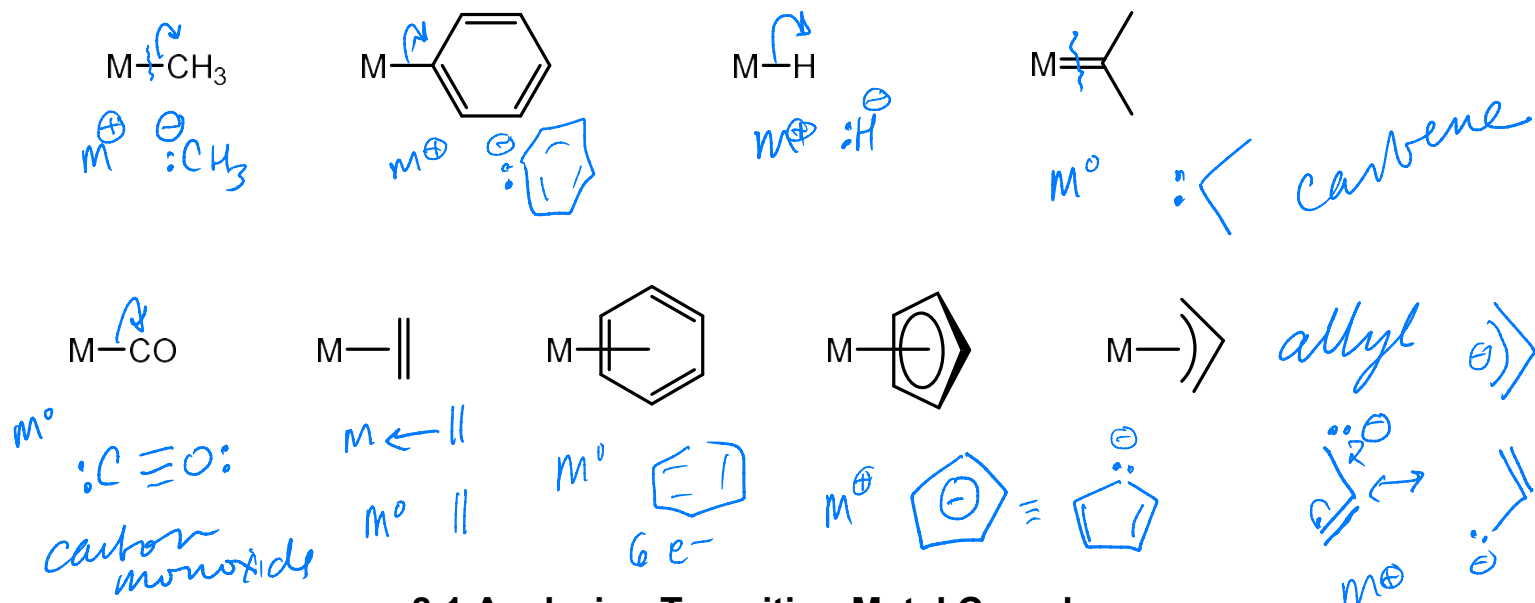
Metal	Sc	Ti Zr	V	Cr Mo W	Mn	Fe Ru Os	Co(I) Rh(I) Ir(I)	Ni Pd Pt	Cu(I)	Zn(II)
"d" electrons	3	4	5	6	7	8	8	10	10	10
electrons needed	15	14	13	12	11	10	10	8	8	8



Transition Metal Complexes May be Charged

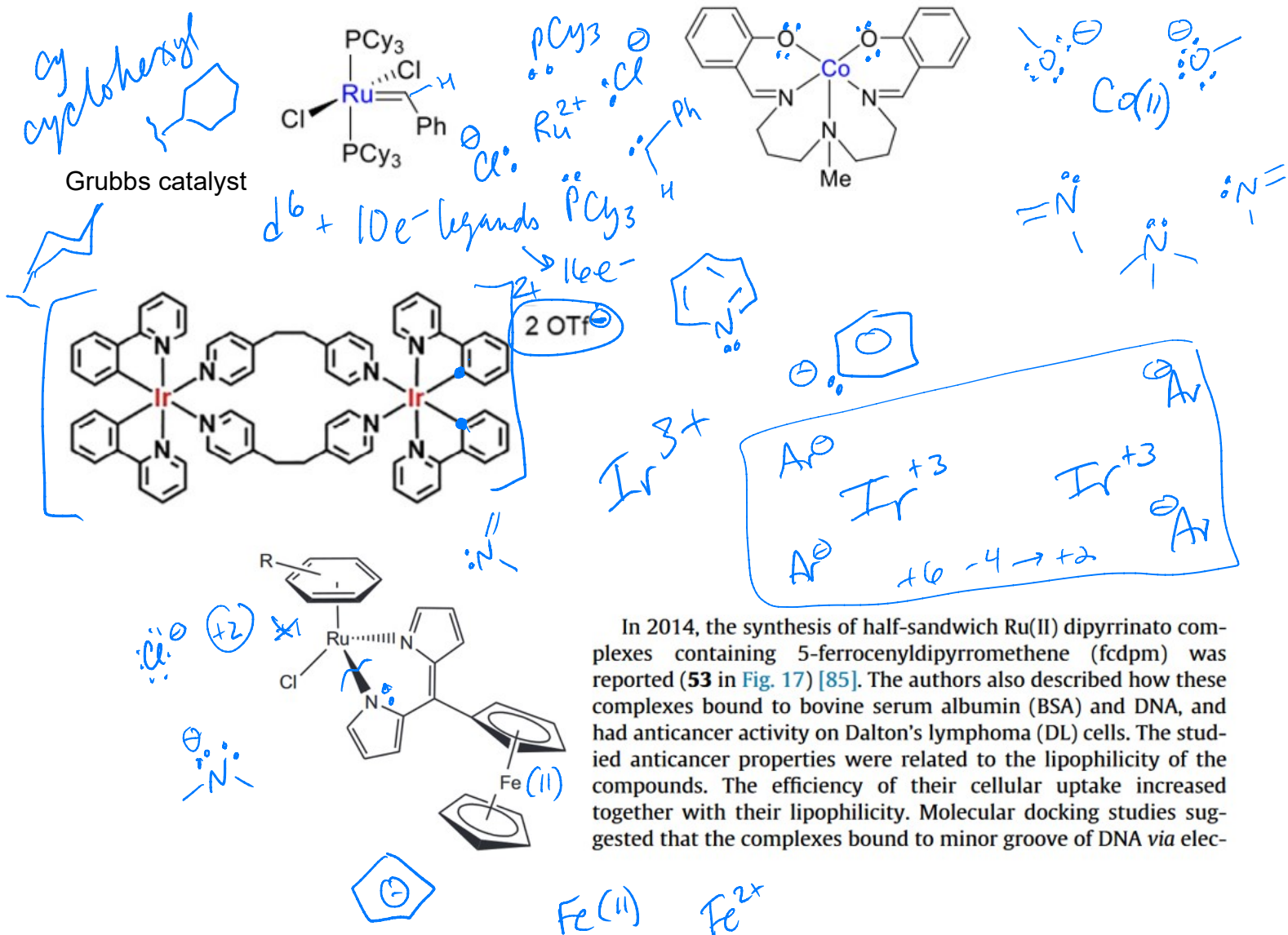


Examples of carbon/hydrogen ligands



8.1 Analyzing Transition Metal Complexes

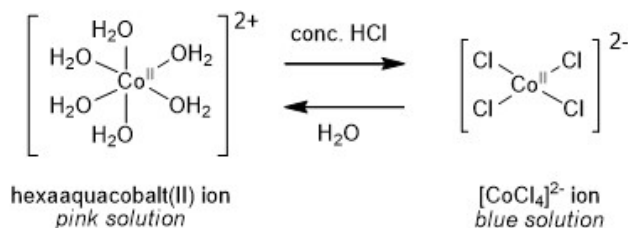
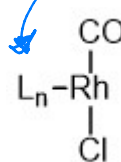
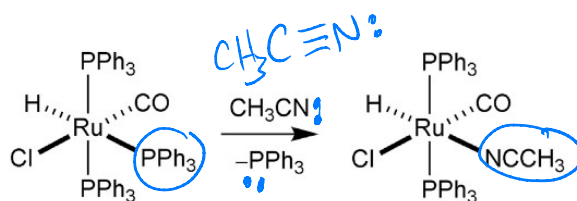
"Charge" on metal? Electron count on metal? Is it coordinatively saturated (i.e. 18 electrons)?



In 2014, the synthesis of half-sandwich Ru(II) dipyrinato complexes containing 5-ferrocenyldipyrromethene (fcdpm) was reported (53 in Fig. 17) [85]. The authors also described how these complexes bound to bovine serum albumin (BSA) and DNA, and had anticancer activity on Dalton's lymphoma (DL) cells. The studied anticancer properties were related to the lipophilicity of the compounds. The efficiency of their cellular uptake increased together with their lipophilicity. Molecular docking studies suggested that the complexes bound to minor groove of DNA via elec-

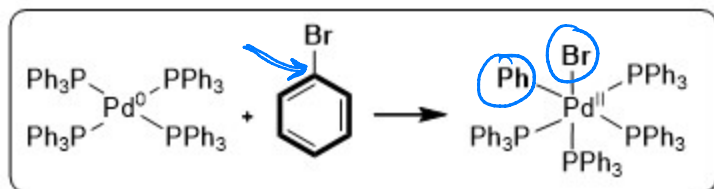
8.2 Organometallic Reaction Mechanisms

Ligand Exchange

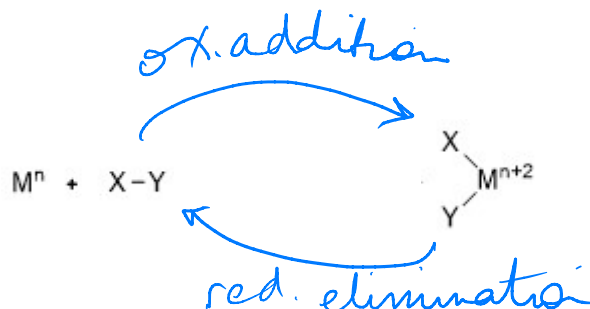


Write on

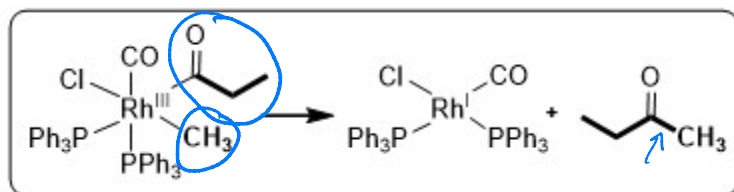
Oxidative Addition – results in +2 change in oxidation number



*Pd(0) → Pd(II)
↑ ox. no. oxidation*

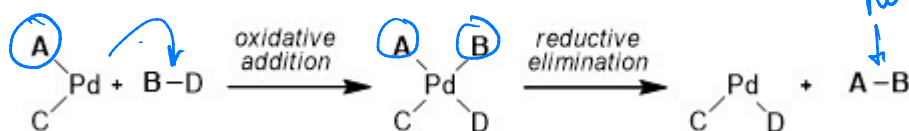


Reductive Elimination – results in -2 change in oxidation number



*Rh(III) → Rh(I)
↓ ox. no. reduction*

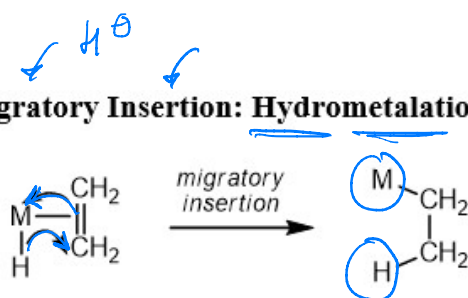
Palladium-Catalyzed Cross-Coupling Reaction



new C-C bonds!

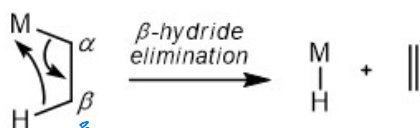
Migratory Insertion

1,2-Migratory Insertion: Hydrometalation of an Alkene

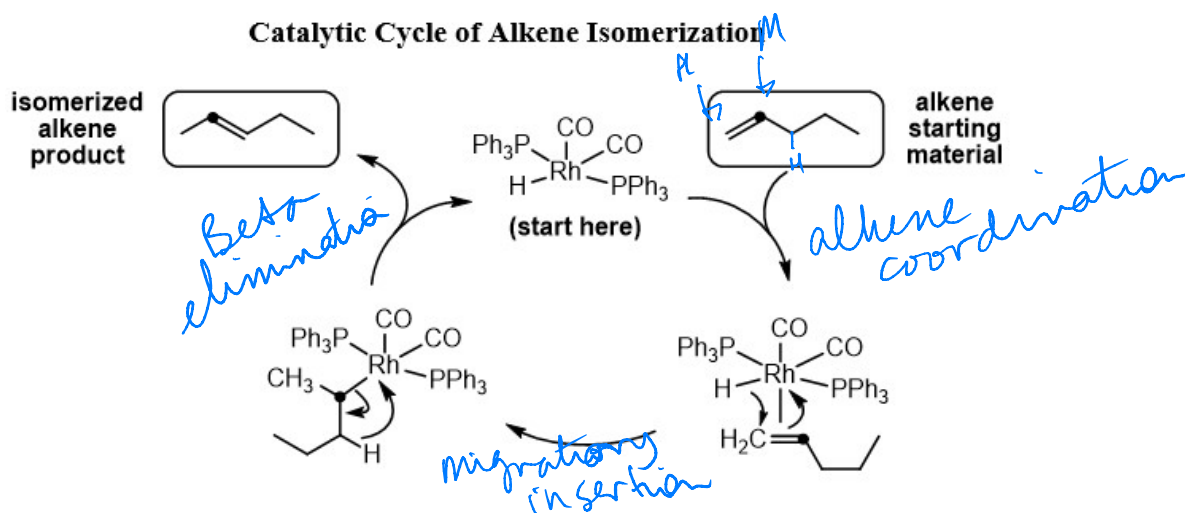


Beta Elimination

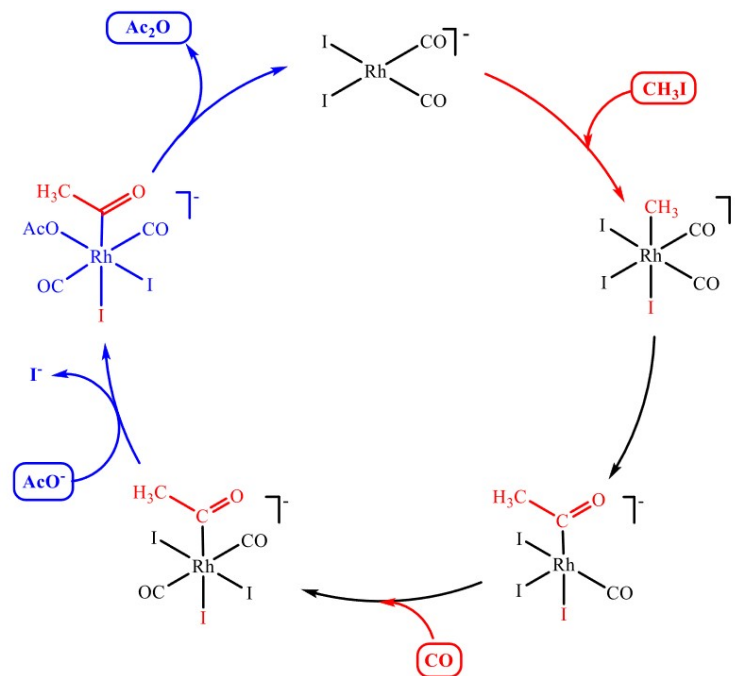
β -Hydride Elimination to Form an Alkene



Catalytic Cycle of Alkene Isomerization



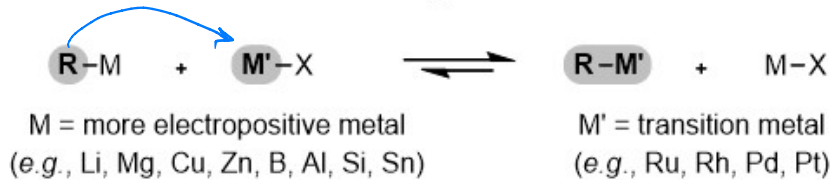
Describe each step, determine Rh oxidation state throughout:



Scheme 1. Catalytic cycle of $[RhI_2(CO)_2]^-$ at low water contents producing acetic anhydride.

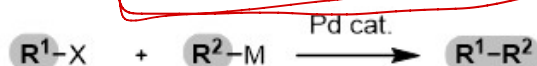
Transmetalation

Transmetalation Exchanges Coordinated Metal Atoms



↑
Grignard

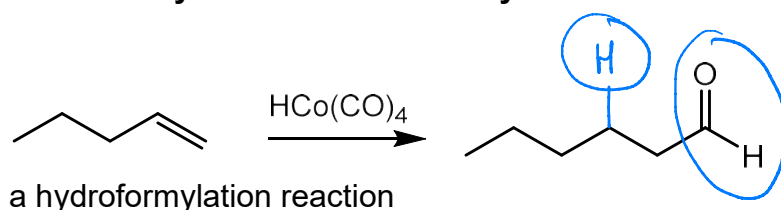
Reaction	Metal (M)
Hiyama	Si
Suzuki-Miyaura	B
Stille	Sn
Negishi	Zn
Sonogashira	Cu
Kumada	Mg



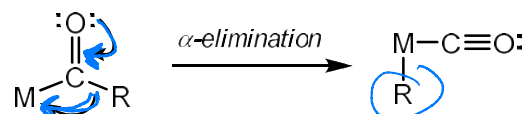
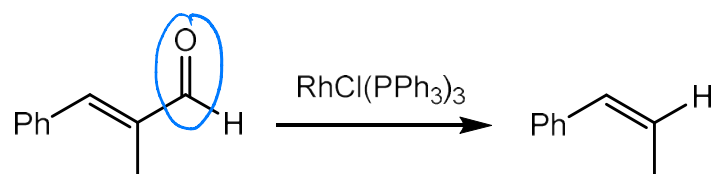
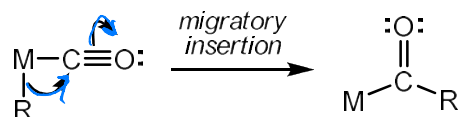
Transmetalation is involved in cross-coupling reactions

Transition Metal-Mediated Synthetic Transformations

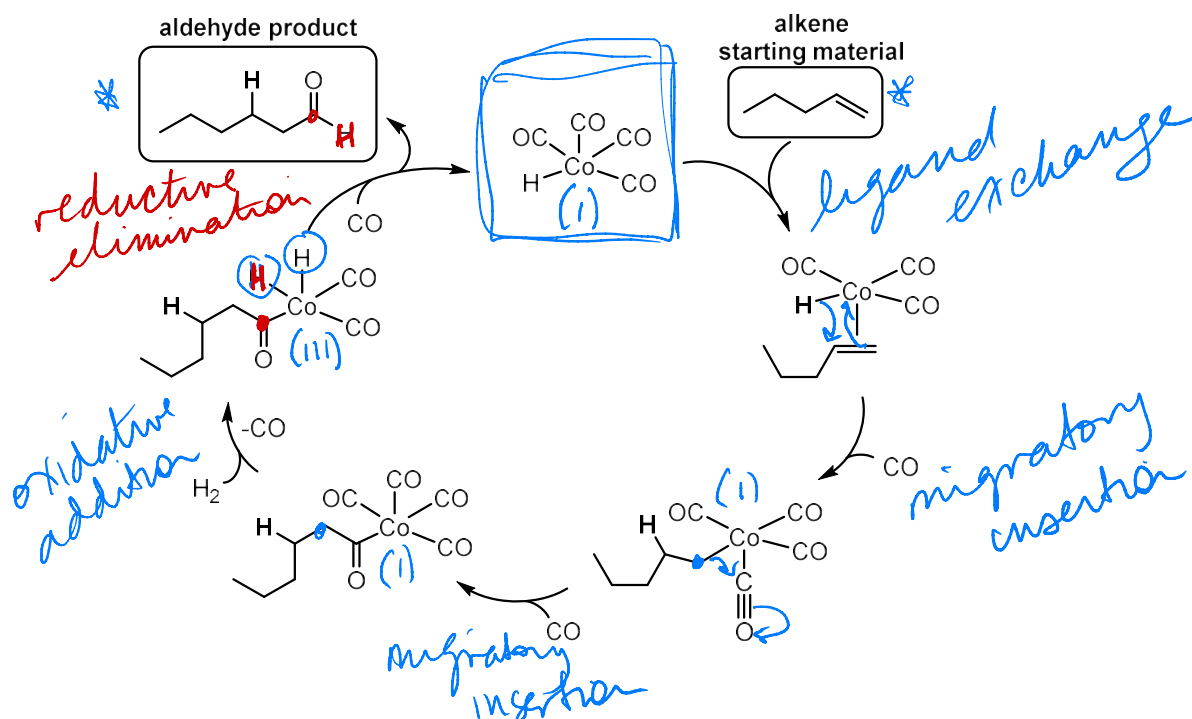
8.3 Carbonylation and Decarbonylation



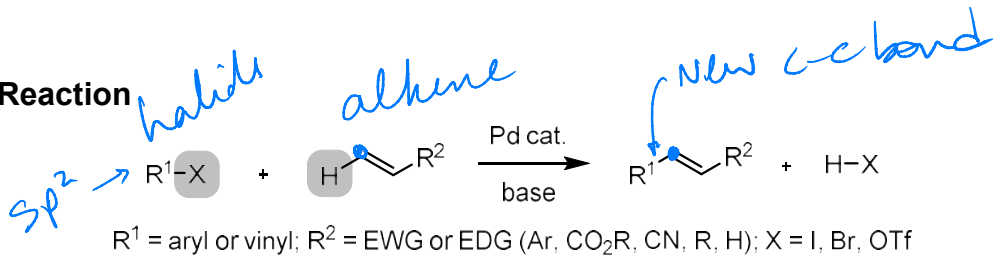
a hydroformylation reaction



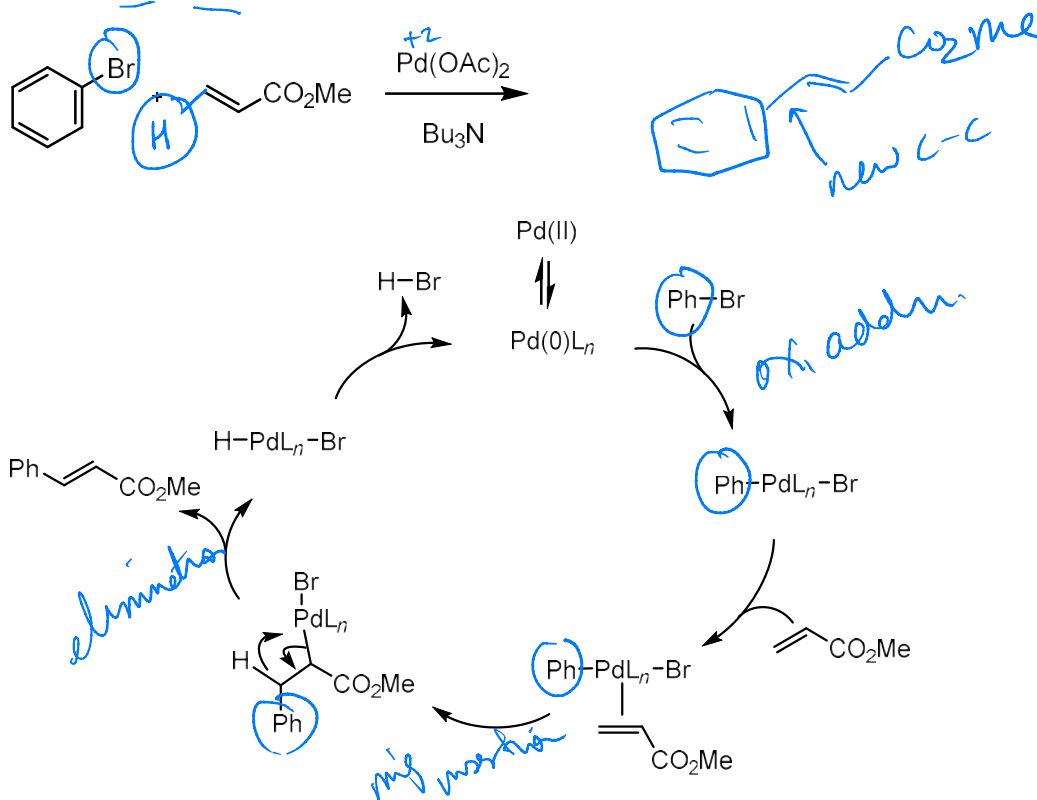
- convert aldehydes to alkanes ($\text{RCHO} \rightarrow \text{RH}$), or
- acid chlorides to alkyl halides ($\text{RCOCl} \rightarrow \text{RCl}$)



8.4 The Heck Reaction

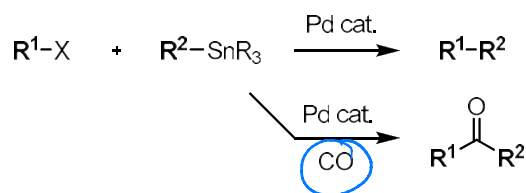


Example:

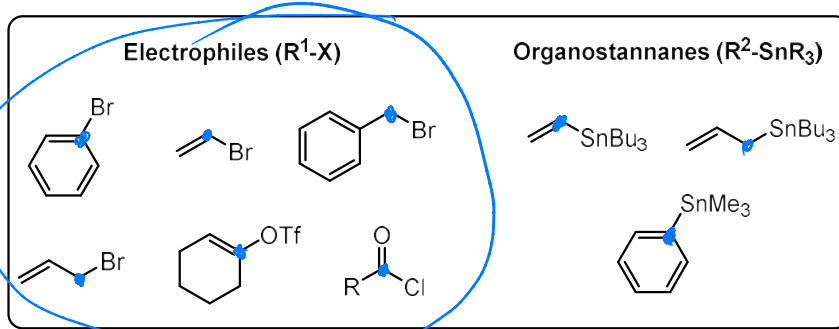
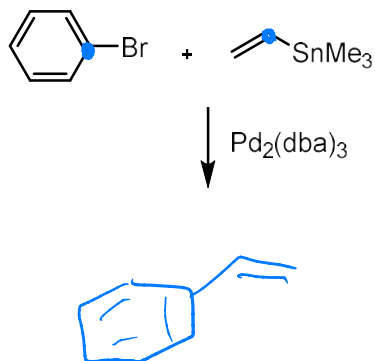


8.5 Pd-Catalyzed Cross-Coupling Reactions

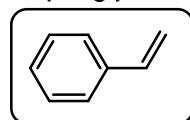
Stille Reaction



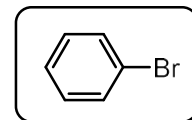
Example:



coupling product



halide reactant



Pd(0)L_n

$\text{Ph-PdL}_n\text{-Br}$

stannane reactant

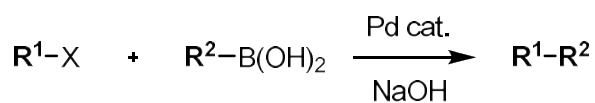


Br-SnMe_3

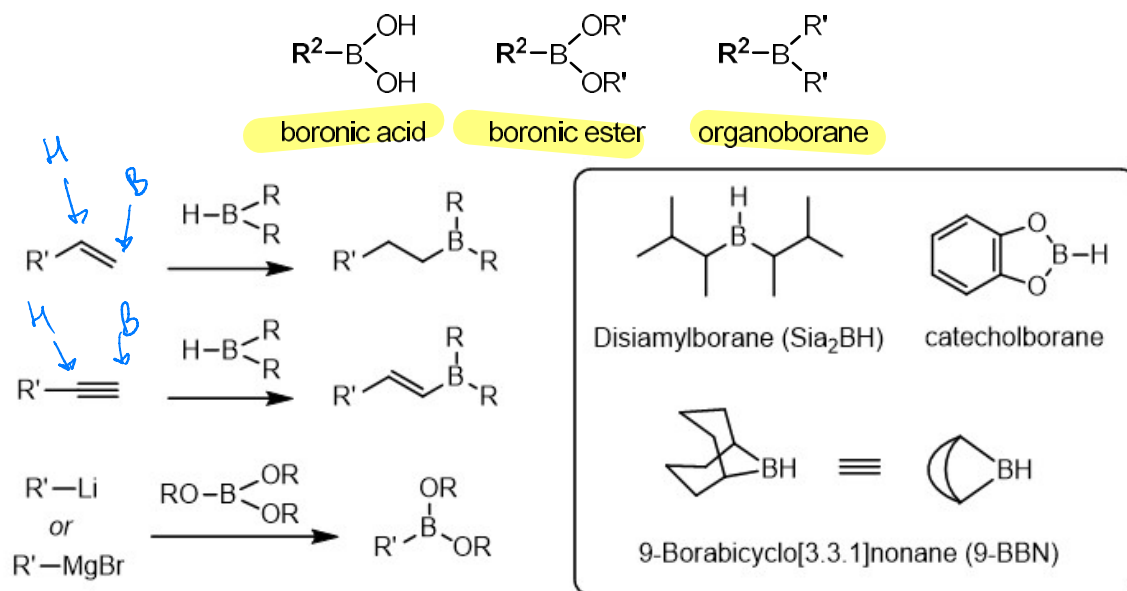
transmetalation

red elimination

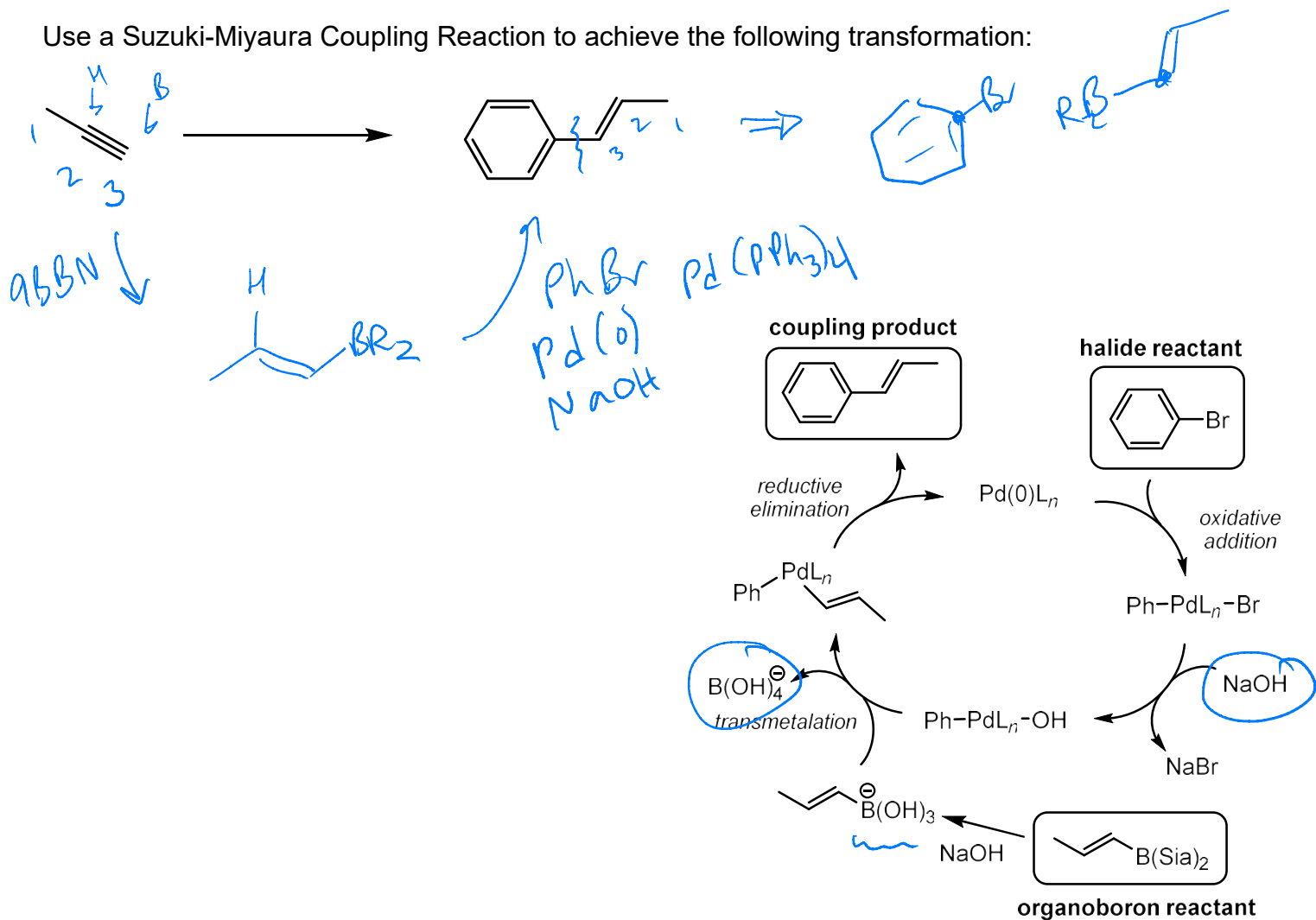
Suzuki-Miyaura Reaction



R^1 = aryl, vinyl, alkynyl; R^2 = aryl, vinyl, allyl, alkyl



Use a Suzuki-Miyaura Coupling Reaction to achieve the following transformation:



alkene

The diagram illustrates a Diels-Alder reaction. On the left, a diene (represented by a box containing R_1 and CH_2) reacts with a dienophile (represented by a box containing H_2C and R_2). An arrow points to the right, leading to the product, a cyclohexene derivative. The product is shown as a six-membered ring with a double bond, and the substituents R_1 and R_2 are attached to the ring. A wavy line indicates the stereochemistry of the product.

ethylene (g)

The diagram illustrates the metathesis of two alkenes via a metallacyclobutane intermediate. The reaction proceeds through two parallel pathways:

- Left Pathway:** An alkene with substituents R_1 and R_2 (labeled **alkene #2 reactant**) undergoes $[2+2]$ cycloaddition with a metal-carbene complex $L_nM=CH_2$ to form a metallacyclobutane intermediate. This intermediate then undergoes $retro [2+2]$ cycloaddition to yield the **metathesis product**, an alkene with substituents R_1 and R_2 in a different configuration.
- Right Pathway:** An alkene with substituent R_1 (labeled **alkene #1 reactant**) undergoes $[2+2]$ cycloaddition with the same metal-carbene complex $L_nM=CH_2$ to form a metallacyclobutane intermediate. This intermediate then undergoes $retro [2+2]$ cycloaddition to yield an **alkene byproduct** (ethylene, $CH_2=CH_2$) and a metal-alkene complex ($R_1-CH=CH-L_nM$).

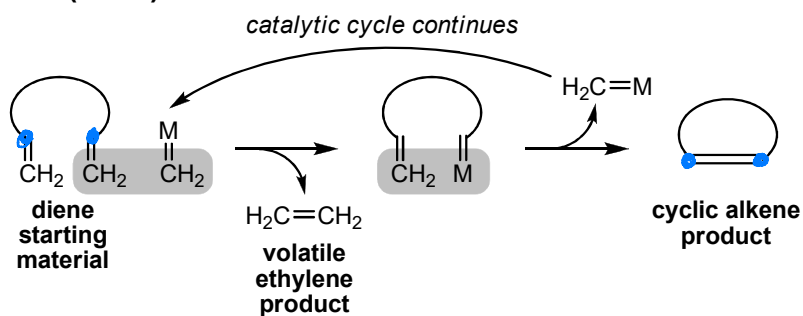
Blue circles and arrows highlight the cycloaddition and retrocycloaddition steps in both pathways.

Reaction scheme showing the synthesis of methyl eugenyl acrylate from eugenol and methyl acrylate:

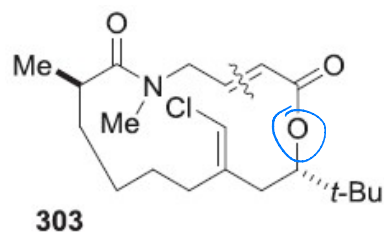
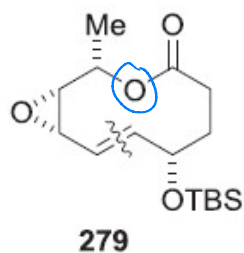
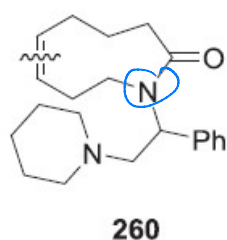
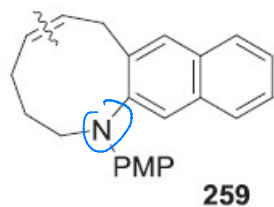
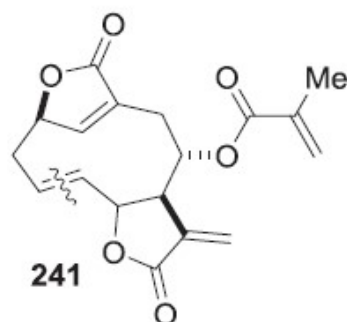
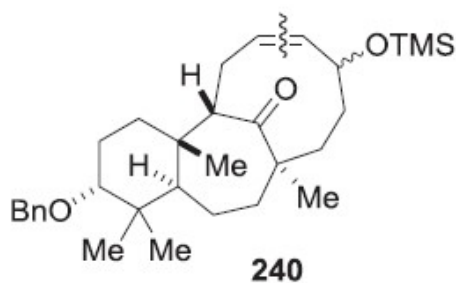
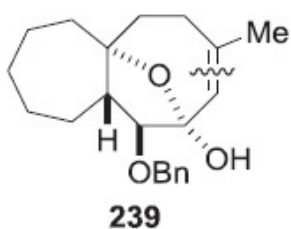
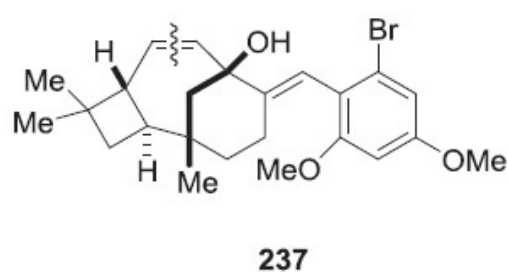
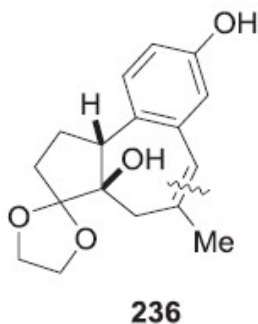
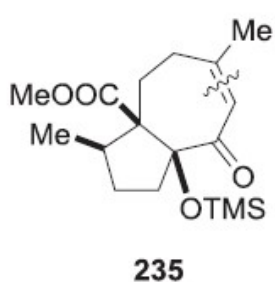
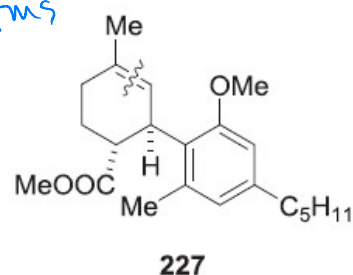
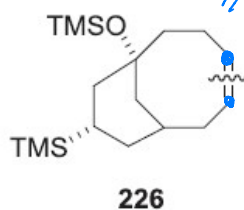
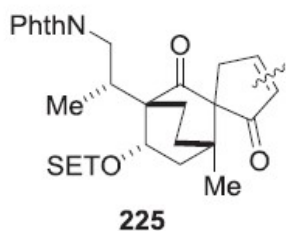
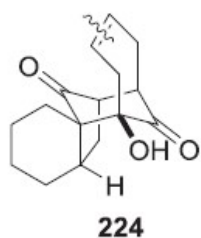
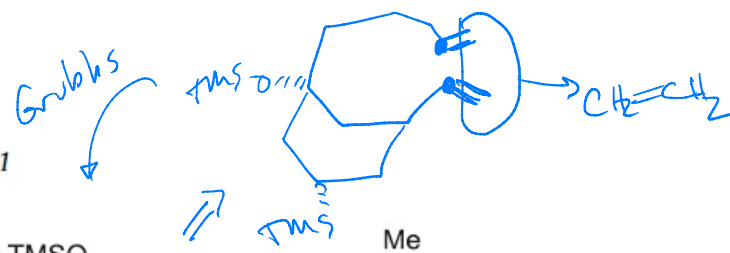
Eugenol (4-allyl-2-methoxyphenol) reacts with **methyl acrylate** ($\text{CH}_2=\text{CHCO}_2\text{Me}$) to form **methyl eugenyl acrylate** ($\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OMe}$).

The reaction is catalyzed by $\text{H}_2\text{C}=\text{CH}_2$ (ethylene) and $\text{CH}_2=\text{CH}_2$ (ethylene).

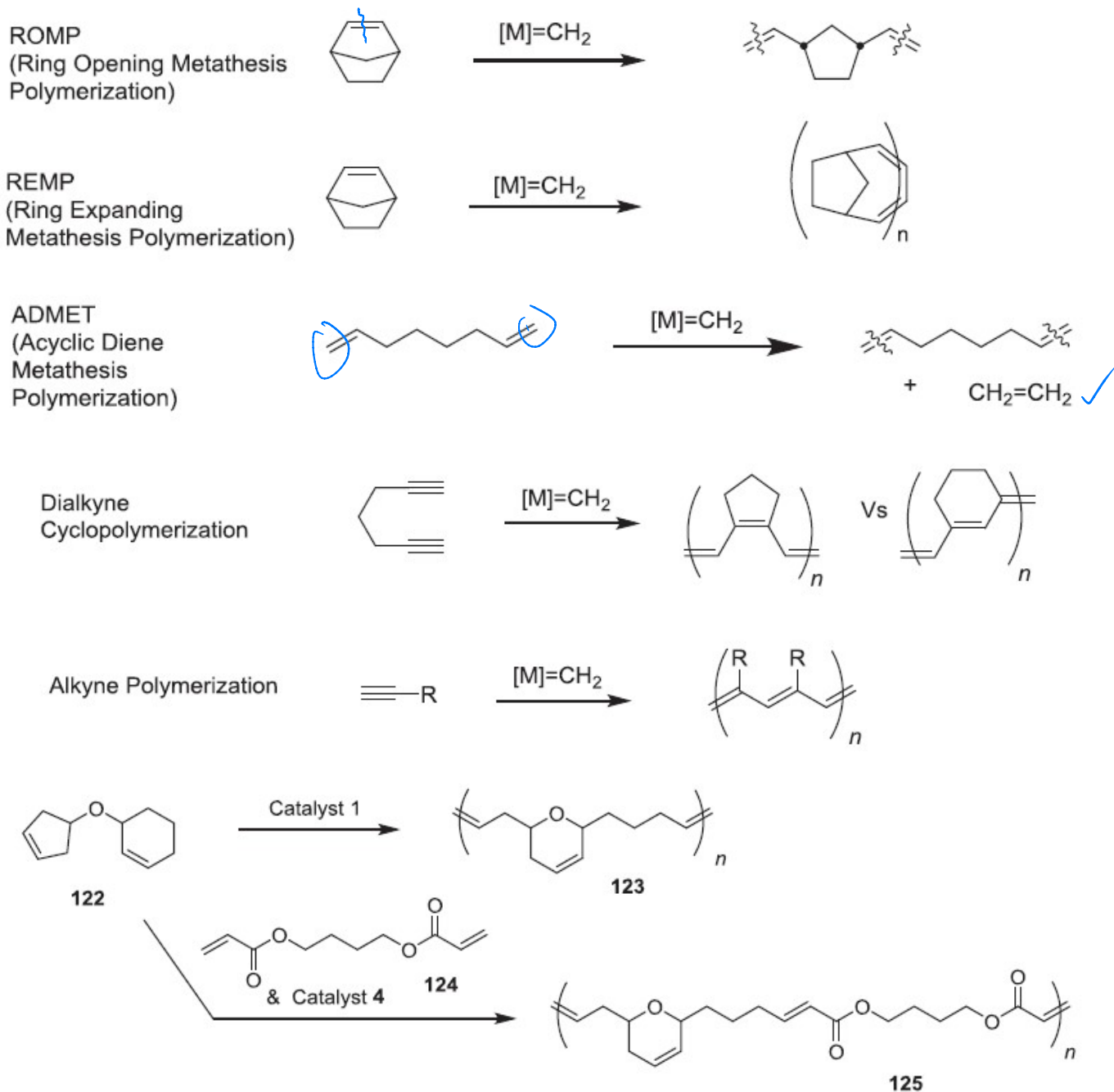
Ring-Closing Metathesis (RCM)



J.W. Herndon / Coordination Chemistry Reviews 401 (2019) 213051



Polymerization



Scheme 5. Ring rearranging ADMET polymerization and multiple olefin metathesis polymerization (MOMP).

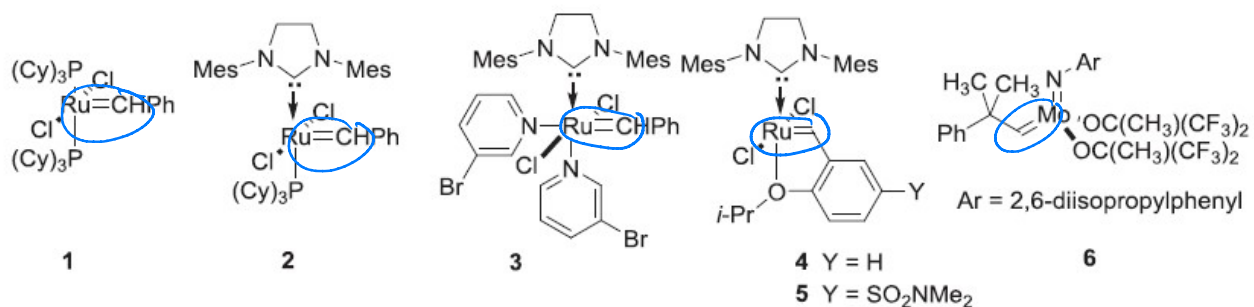
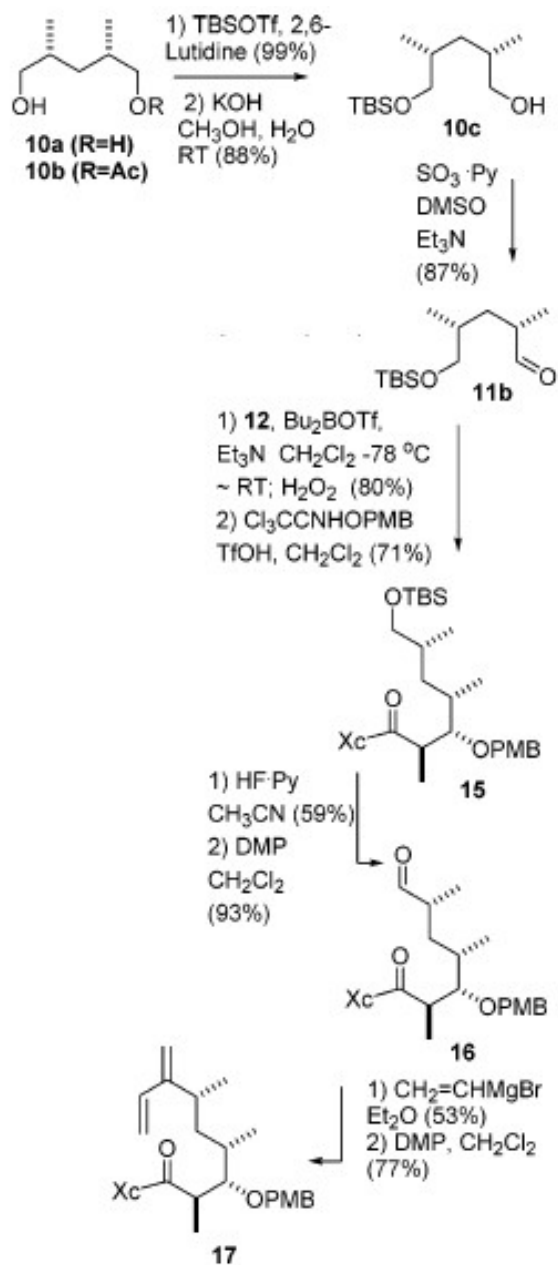


Fig. 1. Structures of classic general-purpose alkene metathesis catalysts 1–6.

PGA on/off red lot new C-C bond



J. Org. Chem. **2008**, *73*, 1456–1461

