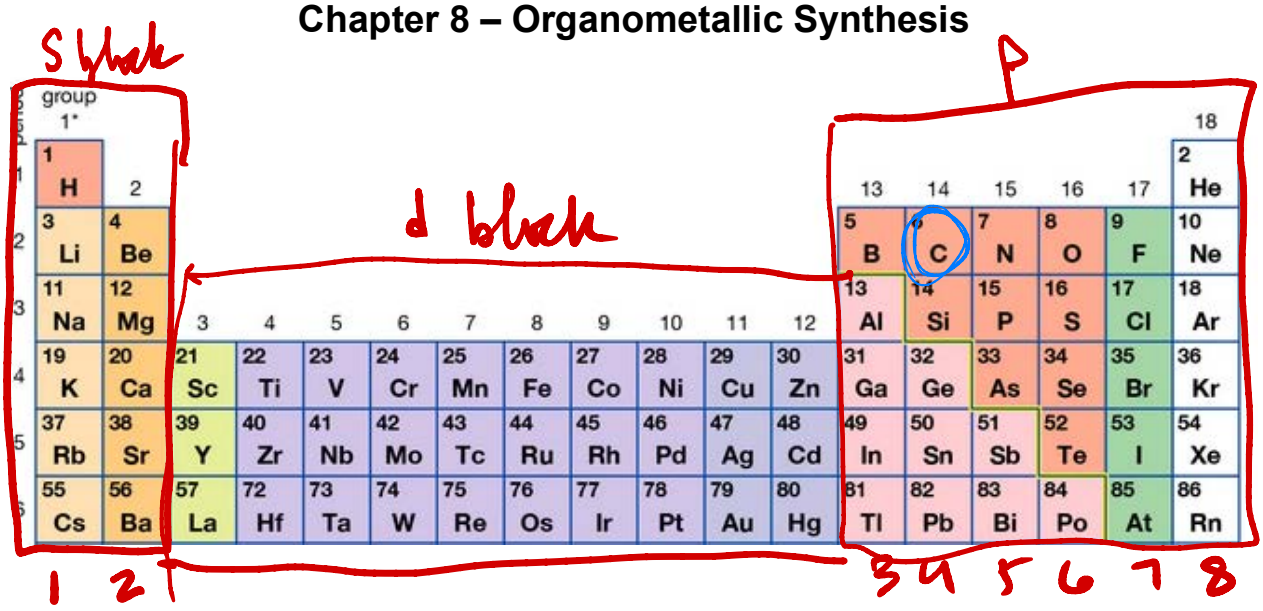
CHM 4220 Organic Synthesis, Cal Poly Pomona, Dr. Laurie S. Starkey

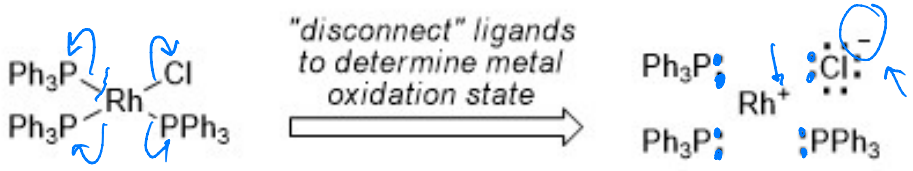
Chapter 8 – Organometallic Synthesis



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

Examples of Transition Metals Used in Synthesis

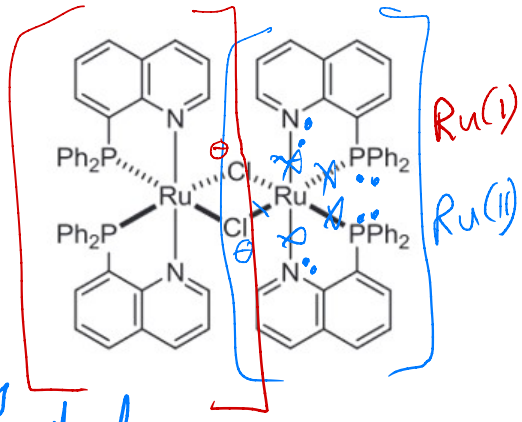
Metal	Sc	Ti Zr	V	Cr Mo W	Mn	Fe Ru Os	Co(I) Rh(I) Ir(I)	Ni Pd Pt	Cu(I)	Zn(II)
"d" electrons	3	4	5	6	7	8	8	10	10	10
electrons needed	15	14	13	12	11	10	10	8	8	8



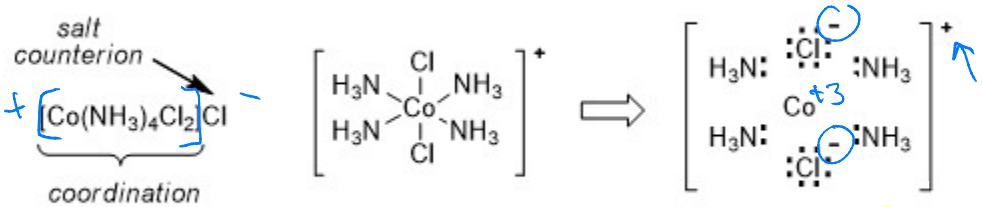
Net charge: +1 (Rh^+) + (-1) (Cl^-) = 0

Electron count: Rh(I) d^8 + 2 e^- (Cl) + 6 e^- (PPh_3 x3) = 16 e^-

coordinatively unsaturated



Transition Metal Complexes May be Charged

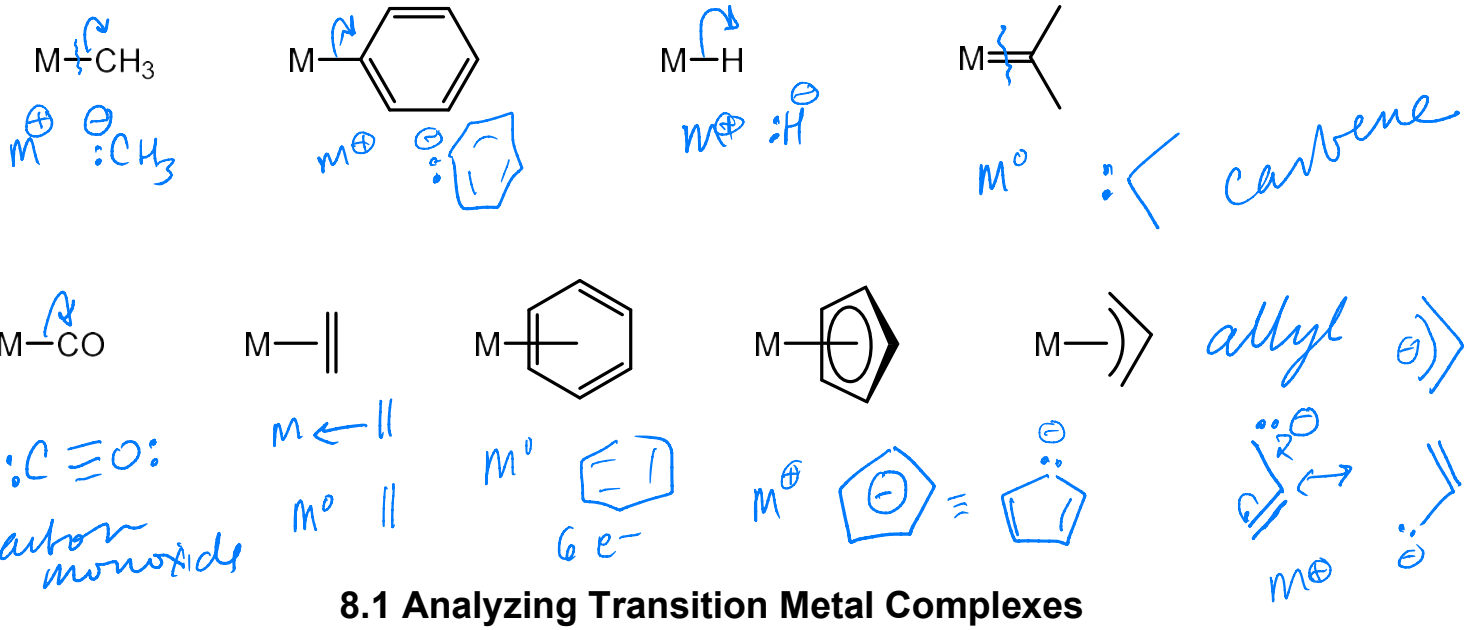


Net charge: +3 (Co^{3+}) + (-1) (Cl^-) + (-1) (Cl^-) = +1

Electron count: Co(III) d^6 + 4e⁻ (Cl x2) + 8e⁻ (NH_3 x4) = 18 e⁻

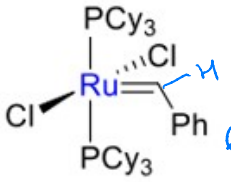
coordinatively saturated

Examples of carbon/hydrogen ligands

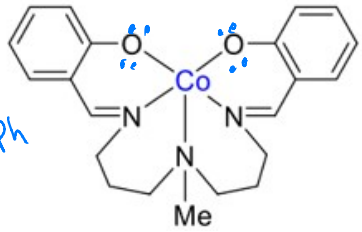


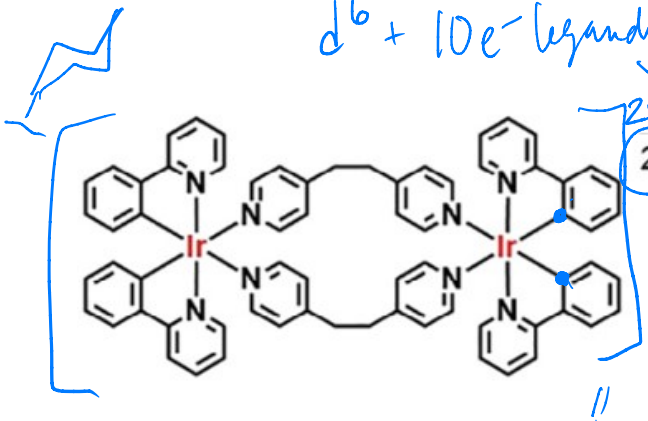
8.1 Analyzing Transition Metal Complexes

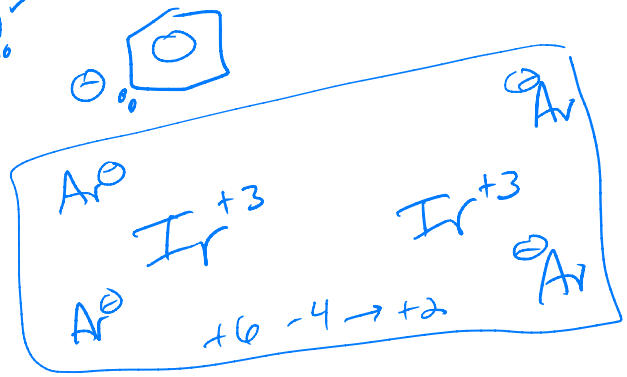
"Charge" on metal? Electron count on metal? Is it coordinatively saturated (i.e. 18 electrons)?

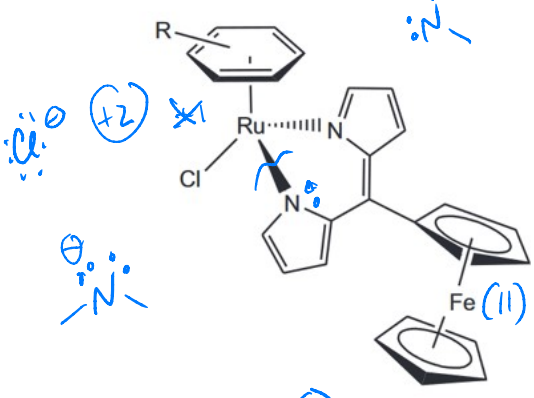


Grubbs catalyst





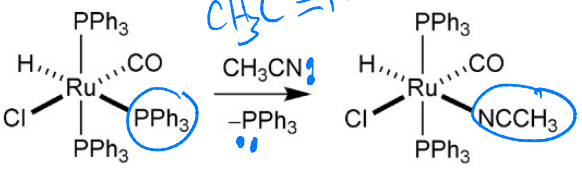




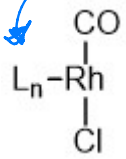
In 2014, the synthesis of half-sandwich Ru(II) dipyrrinato complexes containing 5-ferrocenyldipyrromethene (fcdpm) was reported (**53** in Fig. 17) [85]. The authors also described how these complexes bound to bovine serum albumin (BSA) and DNA, and had anticancer activity on Dalton's lymphoma (DL) cells. 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-

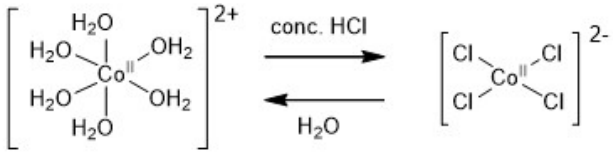
8.2 Organometallic Reaction Mechanisms

Ligand Exchange



some number of ligands (solvent)



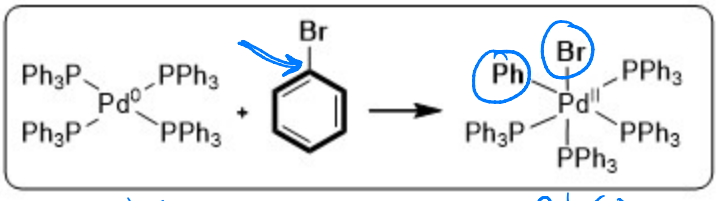


hexaaquacobalt(II) ion
pink solution

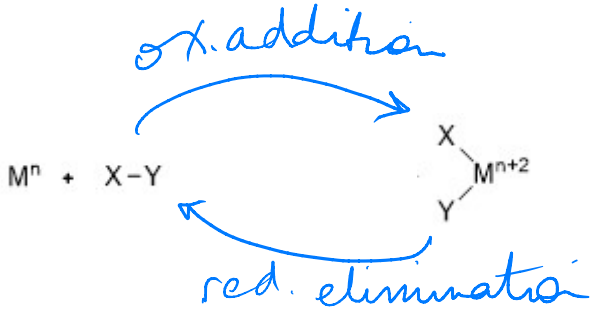
$[CoCl_4]^{2-}$ ion
blue solution

Drierite

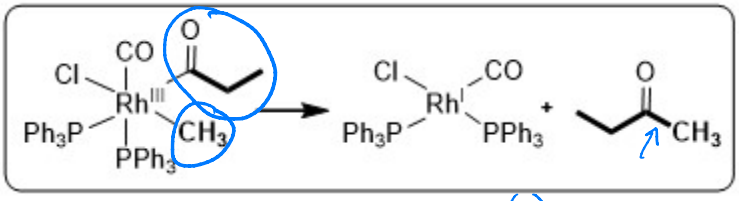
Oxidative Addition – results in +2 change in oxidation number



Pd(0) ↑ox.no. oxidation Pd(II)

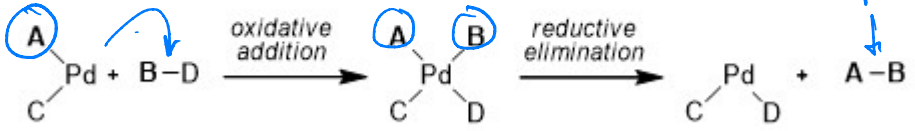


Reductive Elimination – results in -2 change in oxidation number



Rh(III) ↓ox.no. reduction Rh(I)

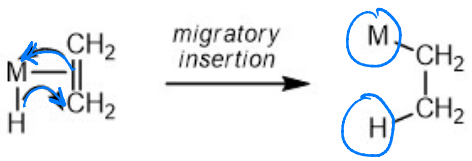
Palladium-Catalyzed Cross-Coupling Reaction



new C–C bonds!

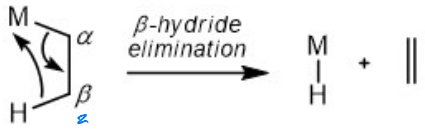
Migratory Insertion

1,2-Migratory Insertion: Hydrometalation of an Alkene

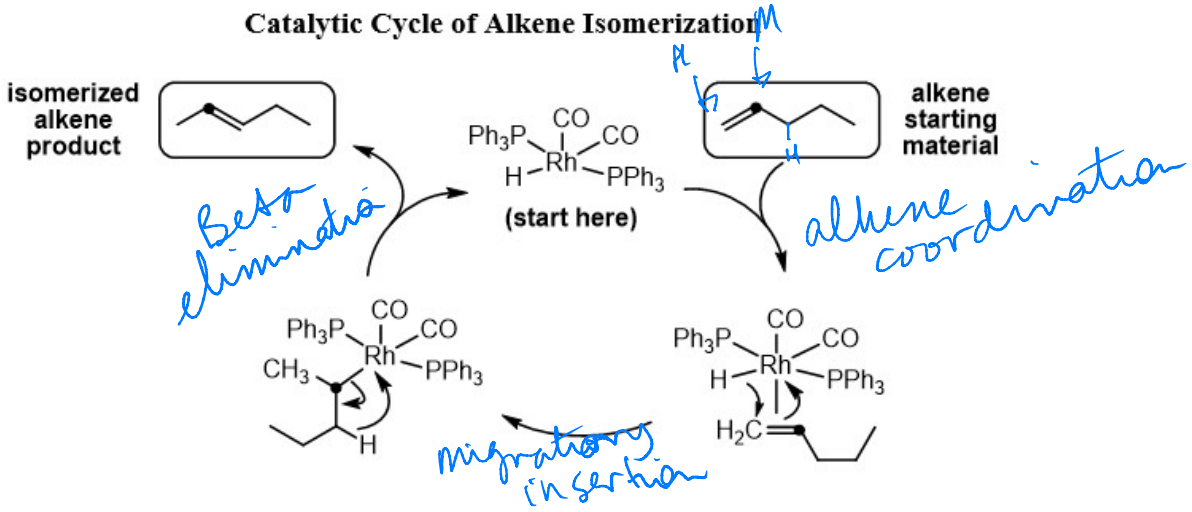


Beta Elimination

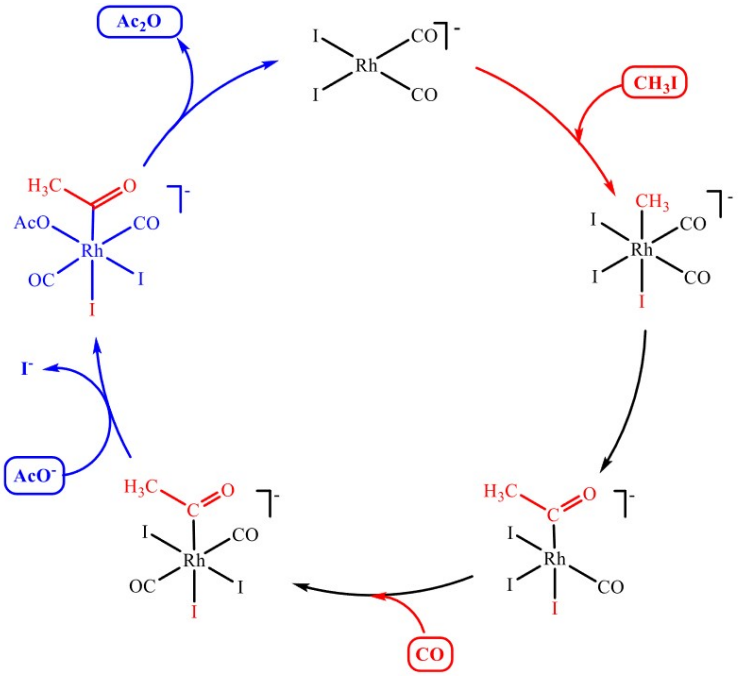
β-Hydride Elimination to Form an Alkene



Catalytic Cycle of Alkene Isomerization



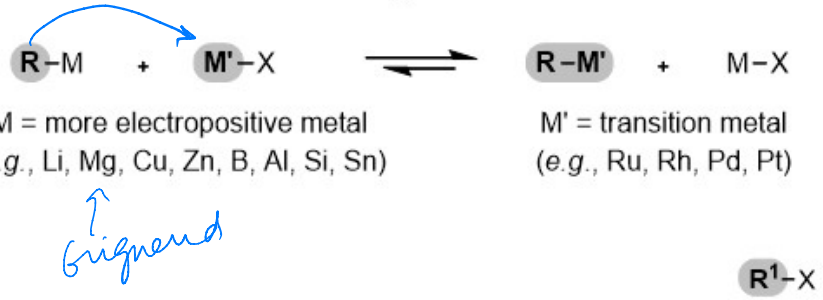
Describe each step, determine Rh oxidation state throughout:



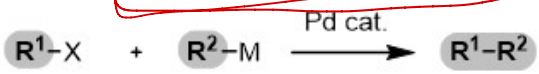
Scheme 1. Catalytic cycle of $[RhI_2(CO)_2]^-$ at low water contents producing acetic anhydride.

Transmetalation

Transmetalation Exchanges Coordinated Metal Atoms



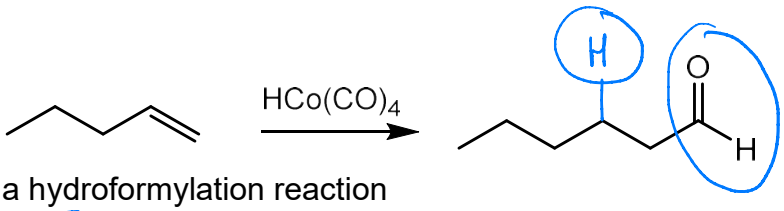
Reaction	Metal (M)
Hiyama	Si
Suzuki-Miyaura	B
Stille	Sn
Negishi	Zn
Sonogashira	Cu
Kumada	Mg

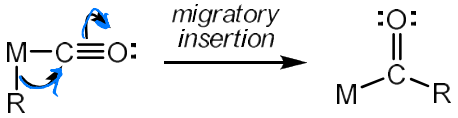


Transmetalation is involved in cross-coupling reactions

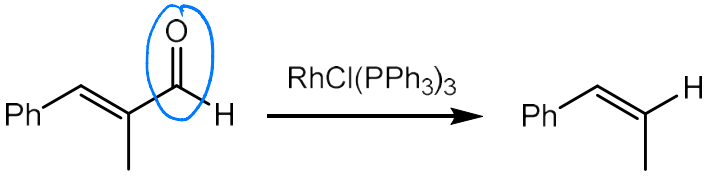
Transition Metal-Mediated Synthetic Transformations

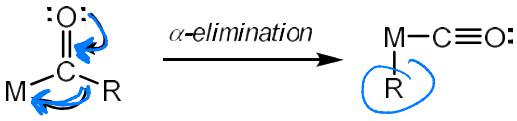
8.3 Carbonylation and Decarbonylation



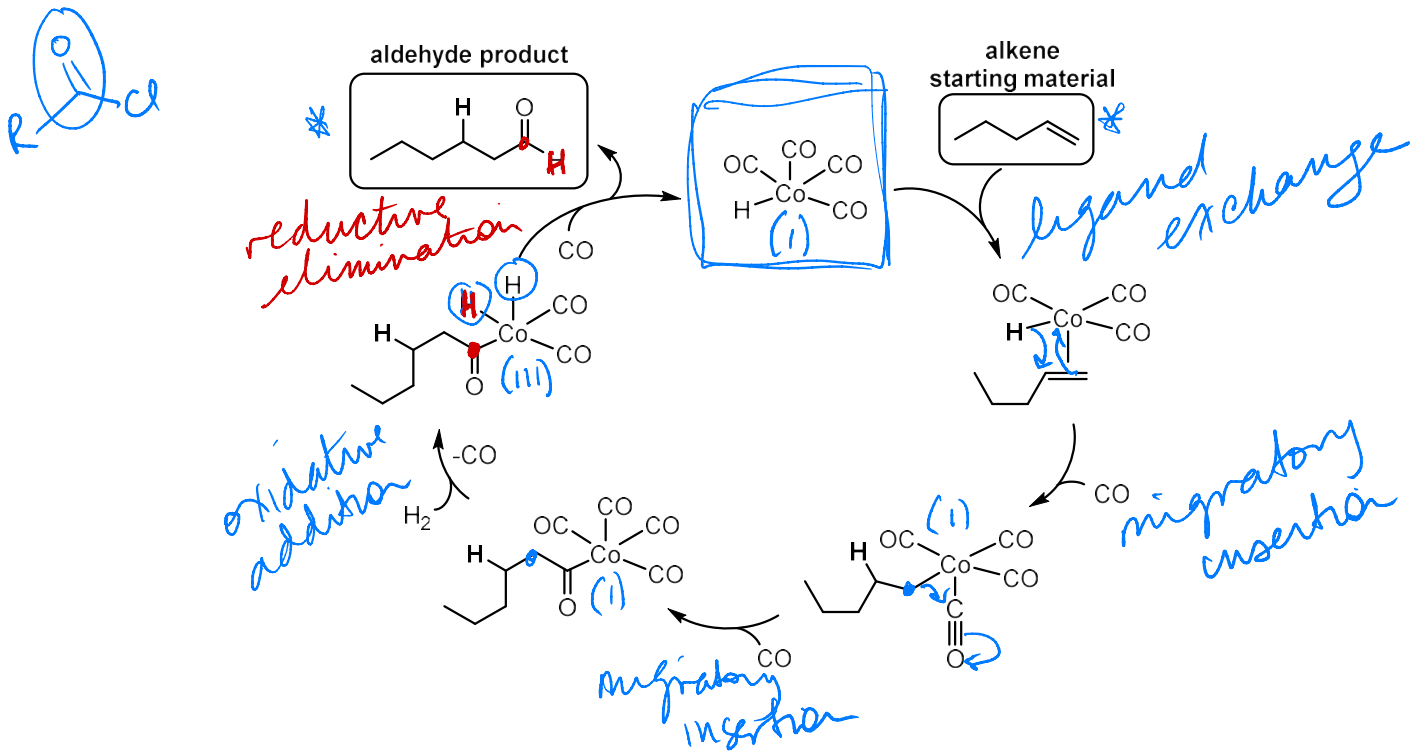


a hydroformylation reaction

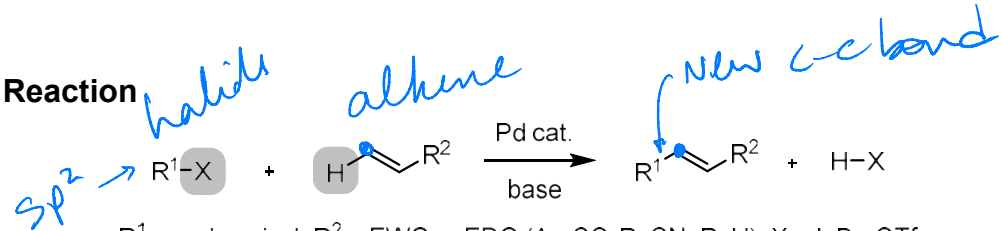




- convert aldehydes to alkanes (RCHO → RH), or
- acid chlorides to alkyl halides (RCOCl → RCl)

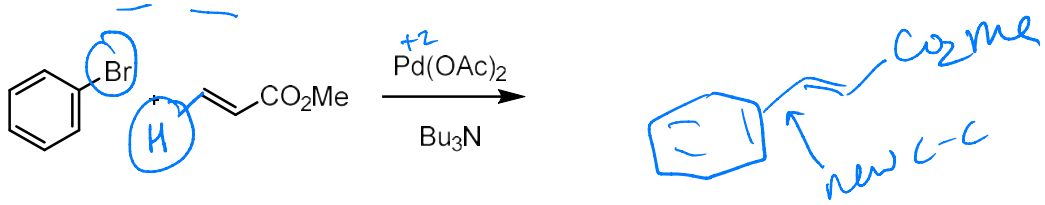


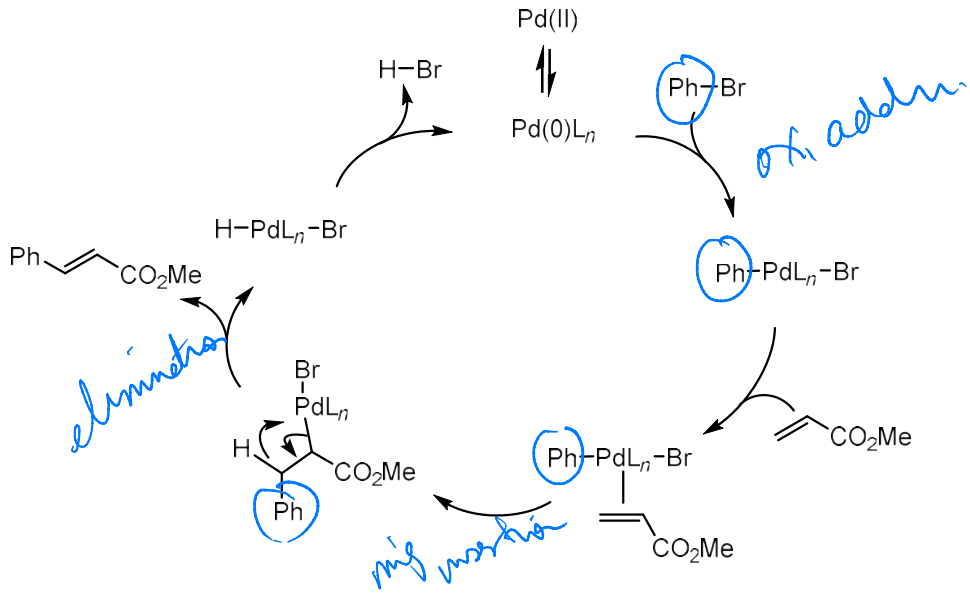
8.4 The Heck Reaction



R^1 = aryl or vinyl; R^2 = EWG or EDG (Ar, CO_2R, CN, R, H); X = I, Br, OTf

Example:

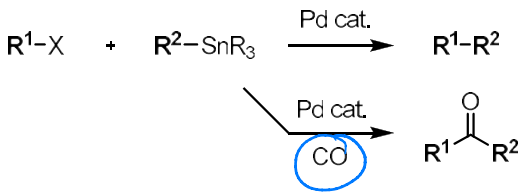


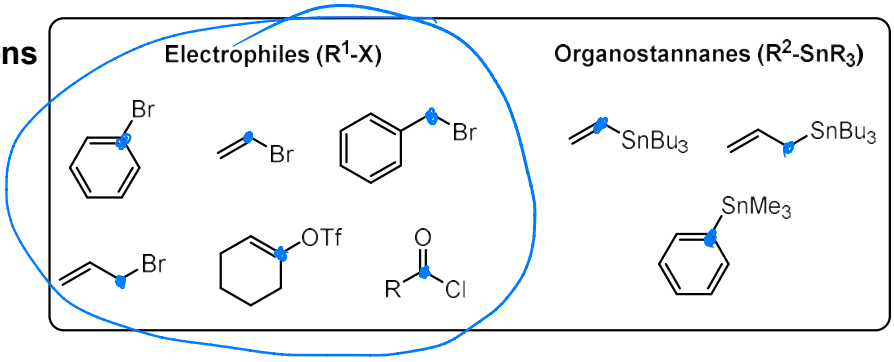


8.5 Pd-Catalyzed Cross-Coupling Reactions

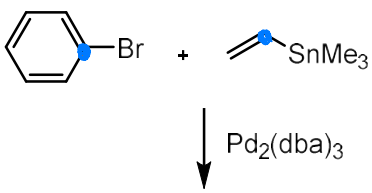
Stille Reaction

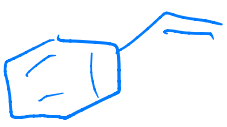
Tin

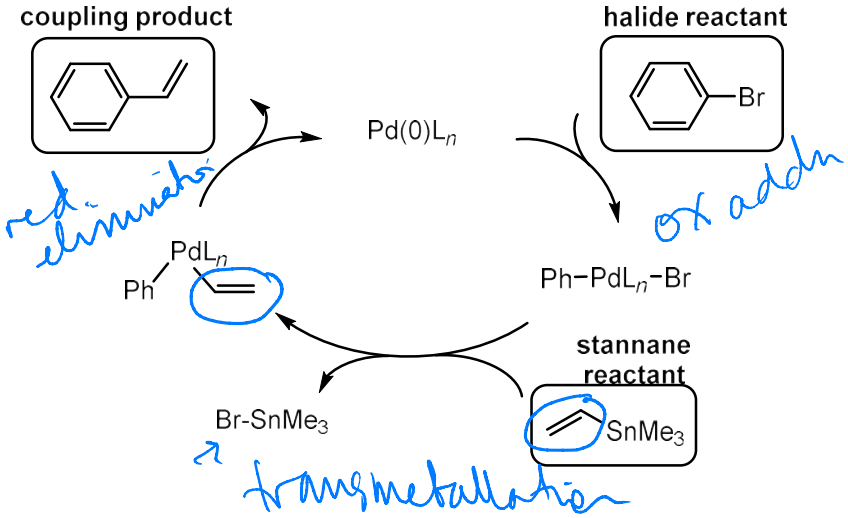




Example:



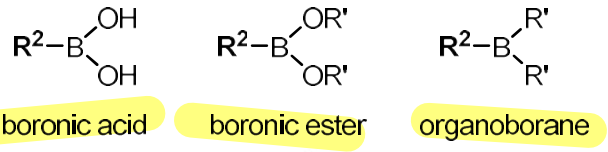


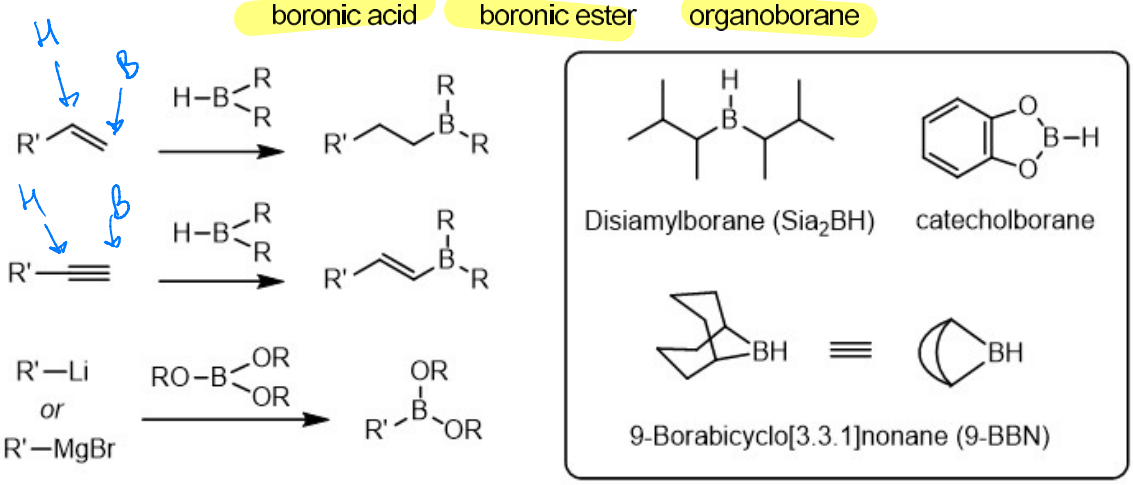


Suzuki-Miyaura Reaction

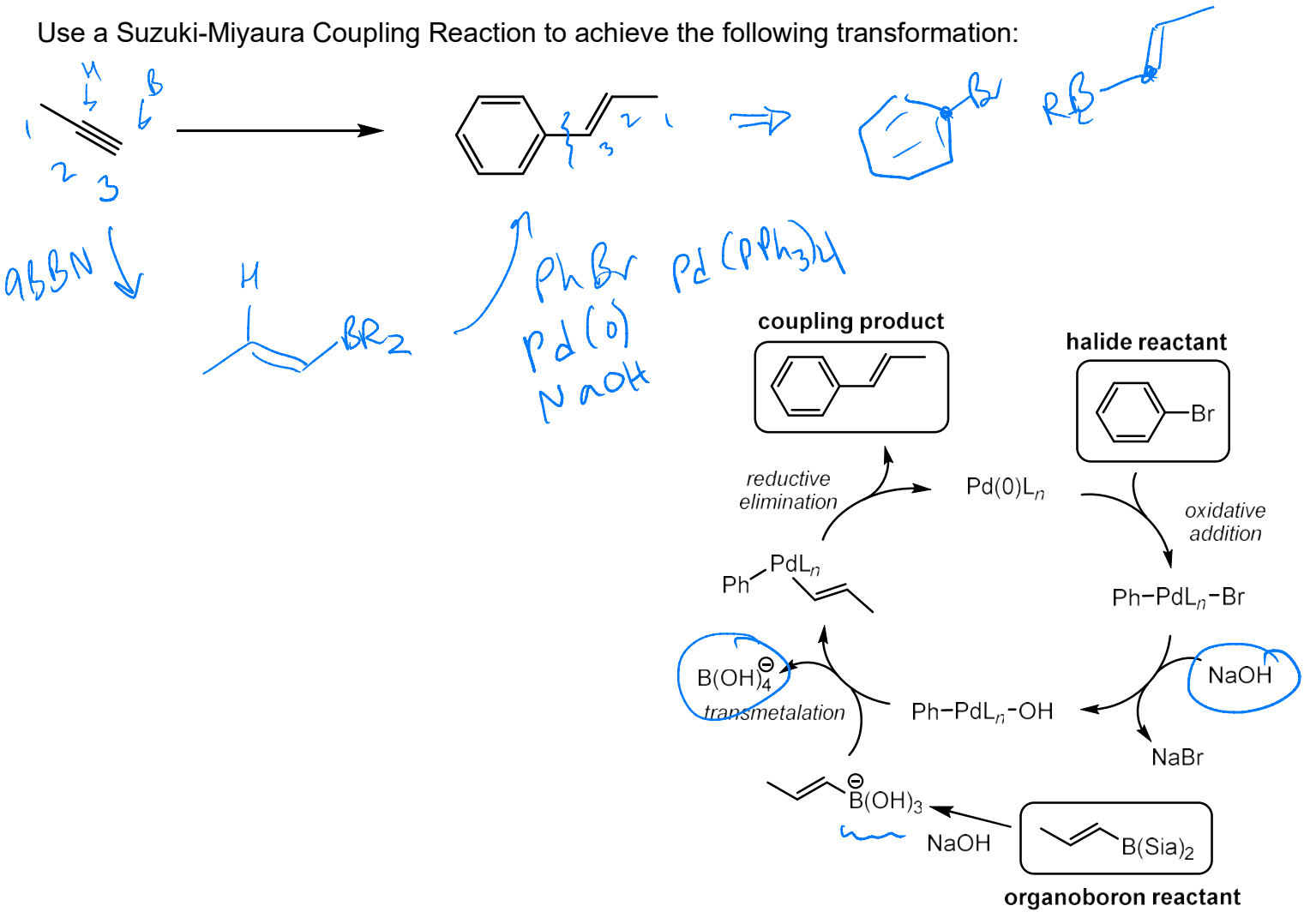
$$R^1\text{–X} + R^2\text{–B(OH)}_2 \xrightarrow[\text{NaOH}]{\text{Pd cat.}} R^1\text{–}R^2$$

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



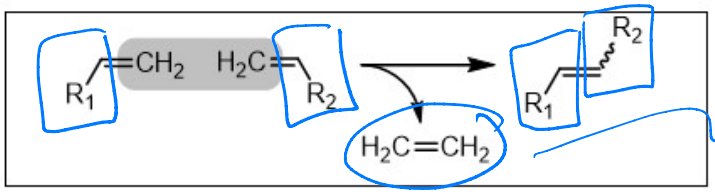


Use a Suzuki-Miyaura Coupling Reaction to achieve the following transformation:

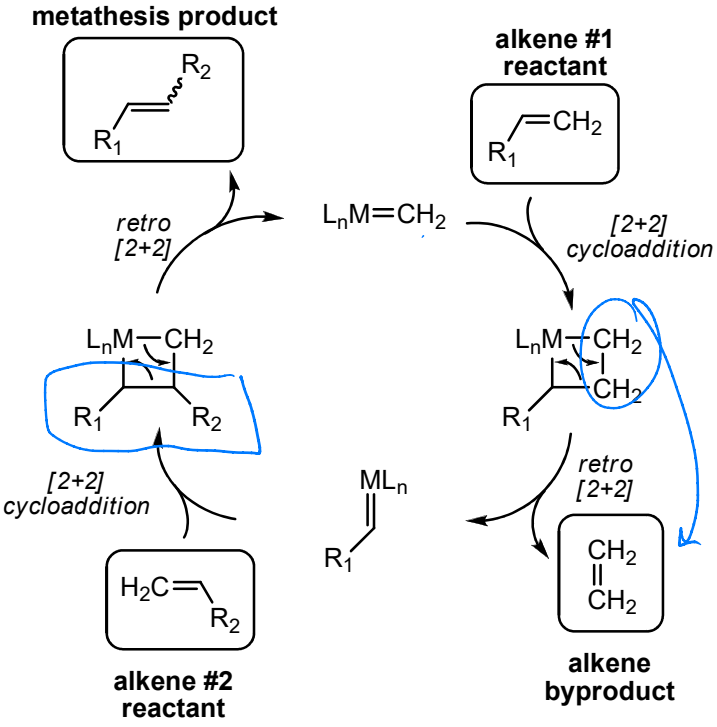


8.6 Olefin Metathesis Reactions

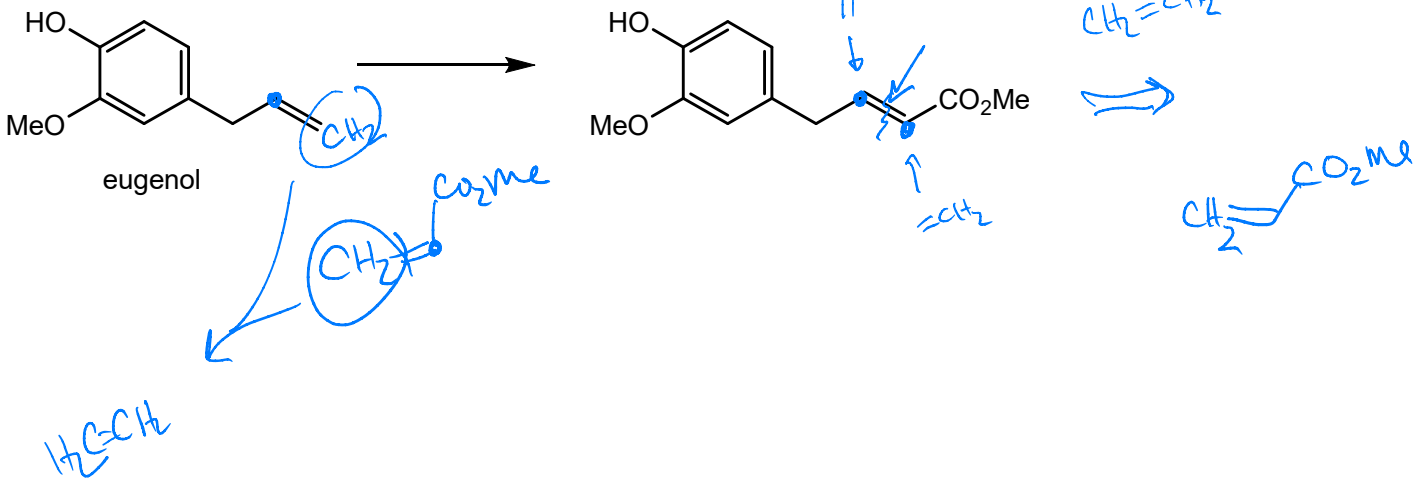
General Alkene Metathesis Reaction



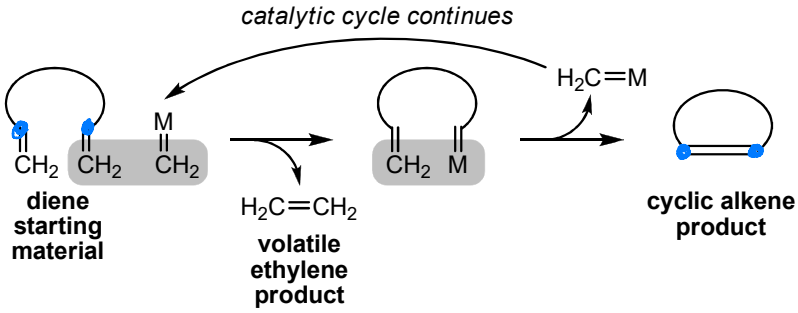
Cross-Metathesis

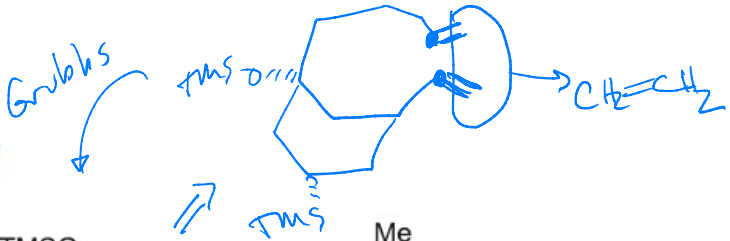


Use a Cross-Metathesis Reaction to achieve the following transformation:



Ring-Closing Metathesis (RCM)





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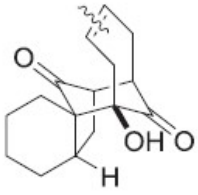

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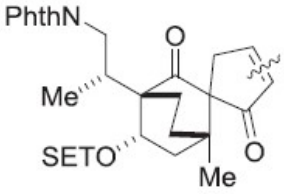

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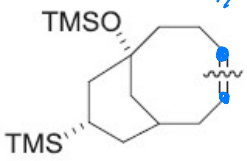

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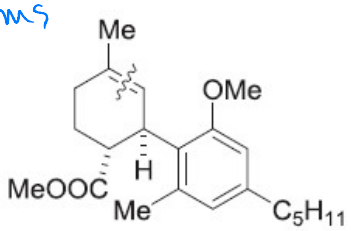

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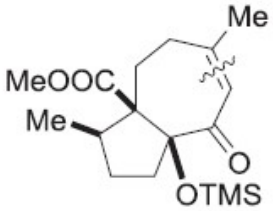

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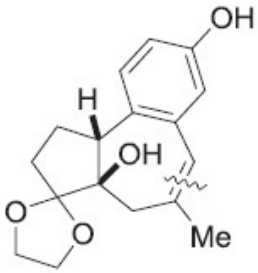

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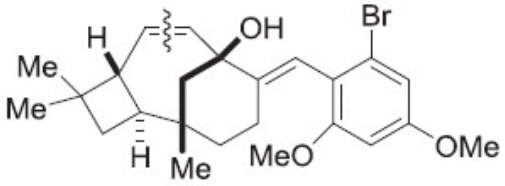

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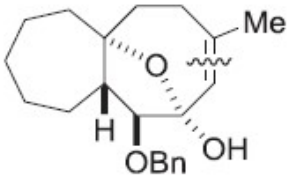

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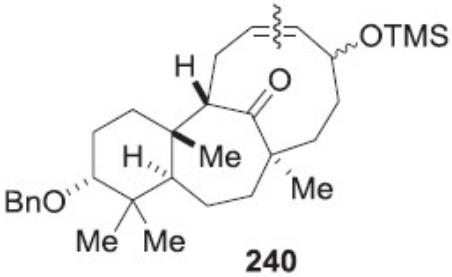

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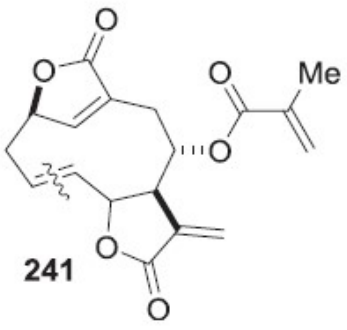

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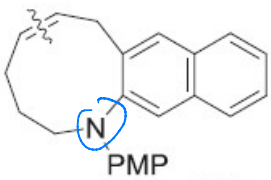

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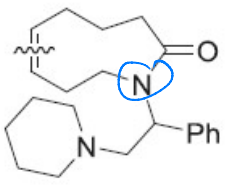

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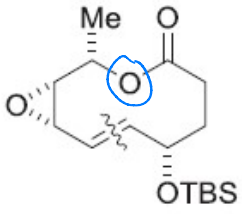

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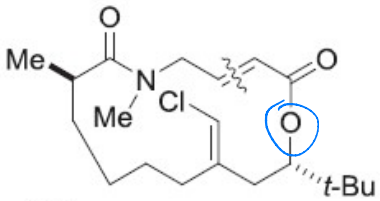
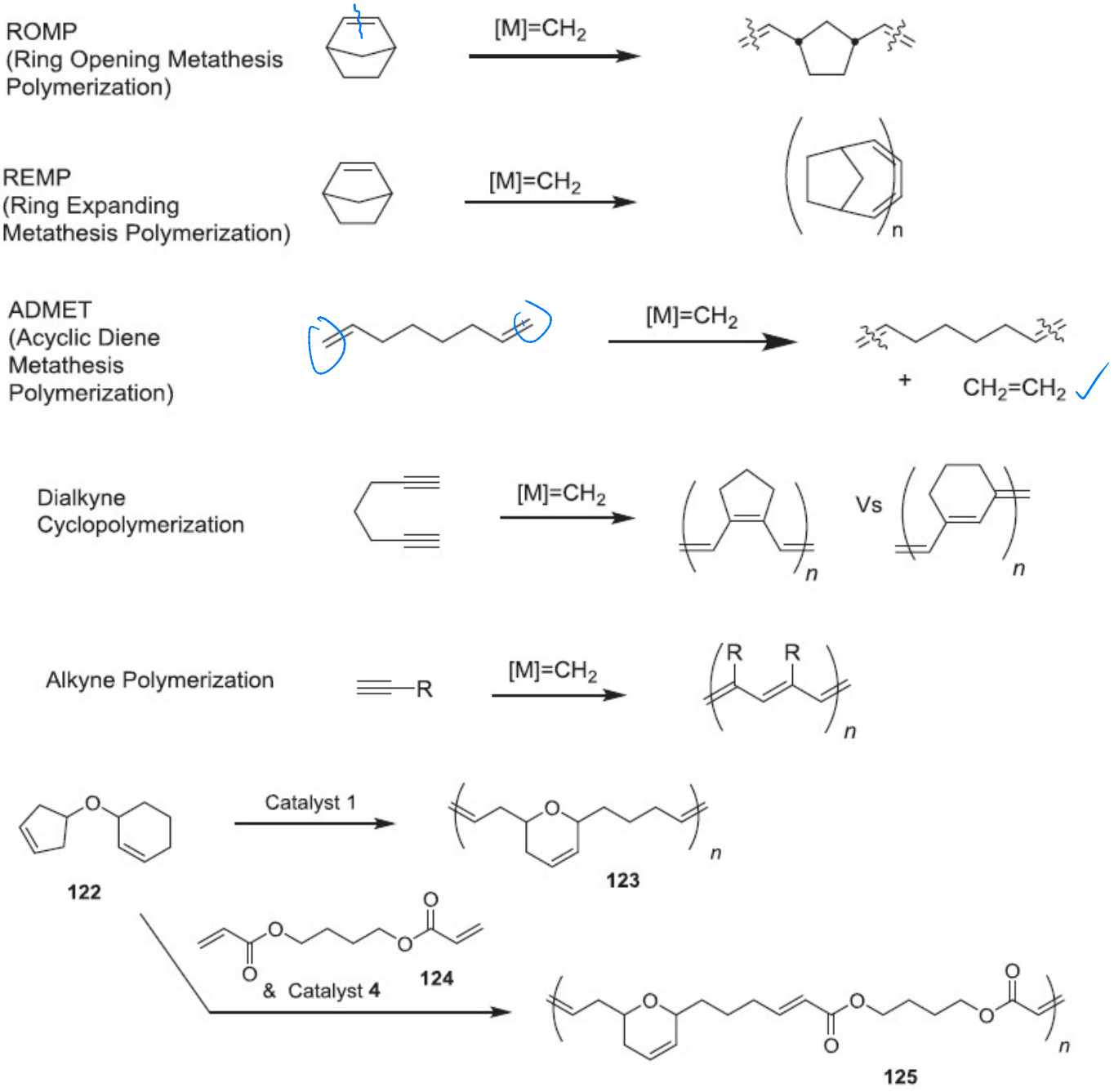
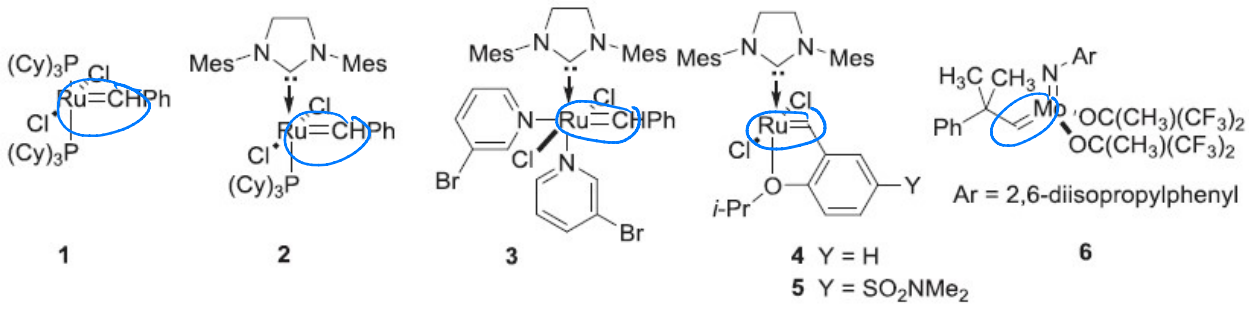


303

Polymerization



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



1 2 3 4 Y = H 5 Y = SO_2NMe_2 6

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

PG on/off red/ox new C–C bond

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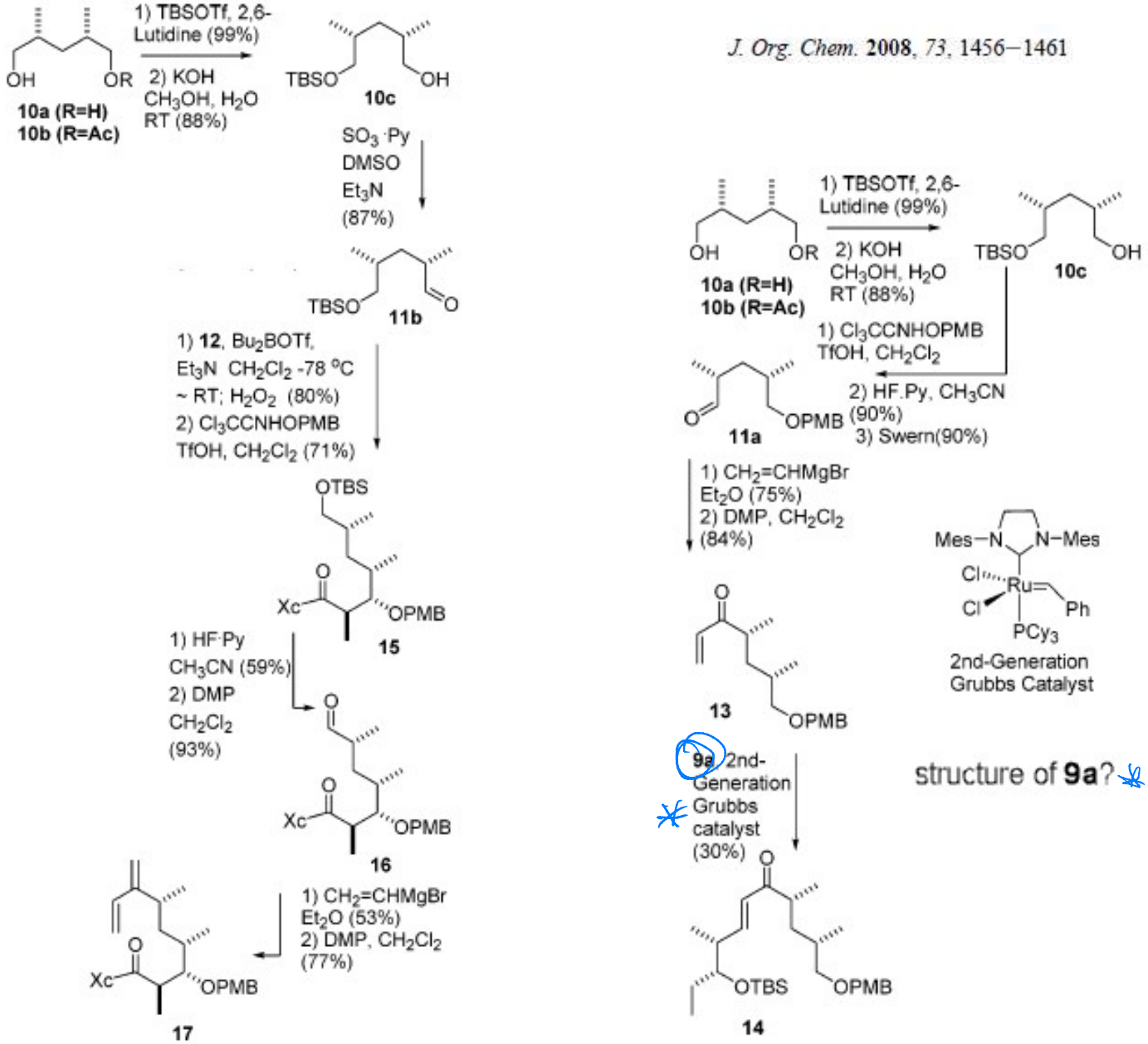

structure of **9a**?