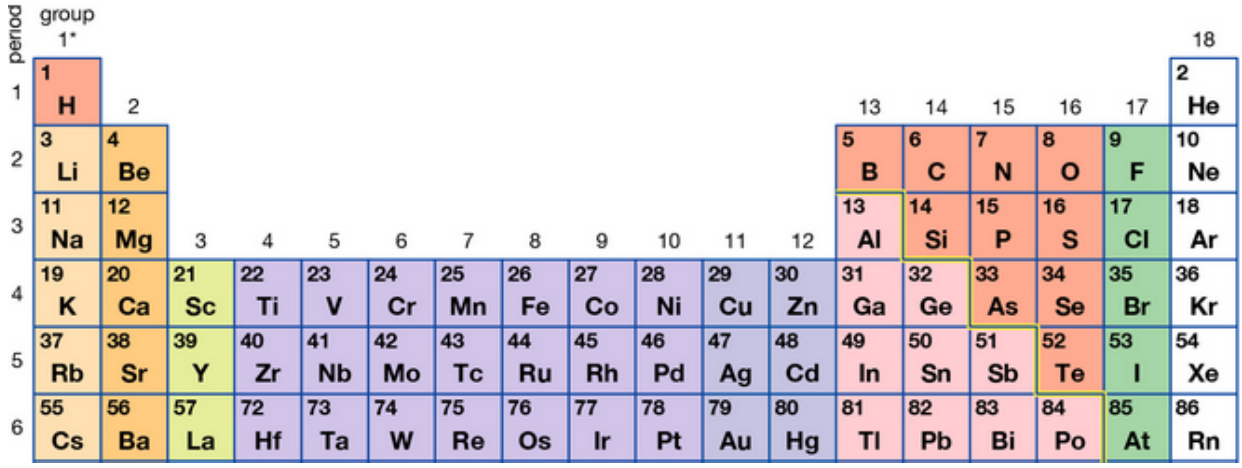
CHM 4220 Organic Synthesis, Cal Poly Pomona, Dr. Laurie S. Starkey

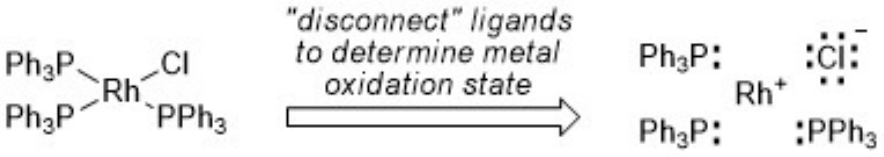
Chapter 8 – Organometallic Synthesis

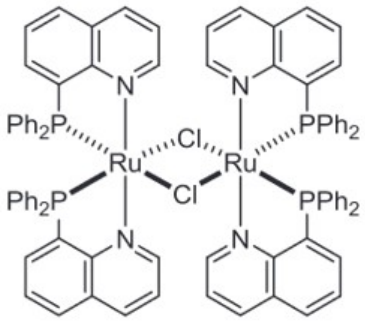


18-Electron Rule (or EAN, Effective Atomic Number, Rule)

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										





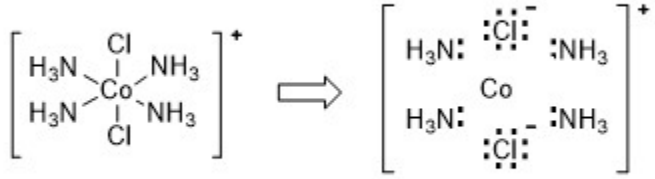
Net charge: +1 (Rh^+) + (-1) (Cl^-) = 0

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

Transition Metal Complexes May be Charged

salt counterion → $[Co(NH_3)_4Cl_2]Cl$

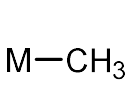
coordination complex [in brackets]

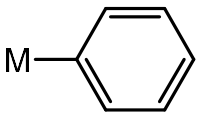


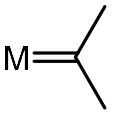
Net charge: +3 (Co^{3+}) + (-1) (Cl^-) + (-1) (Cl^-) = +1

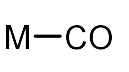
Electron count:

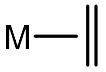
Examples of carbon/hydrogen ligands

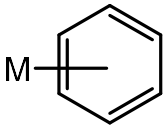


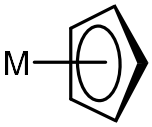


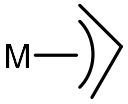






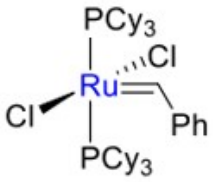




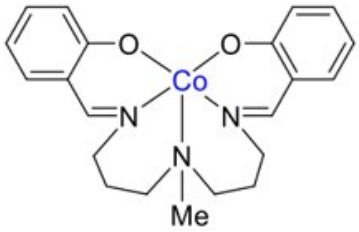


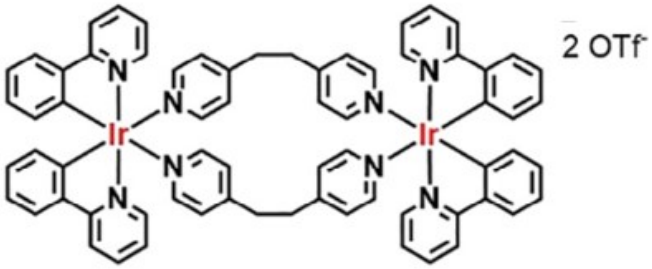
8.1 Analyzing Transition Metal Complexes

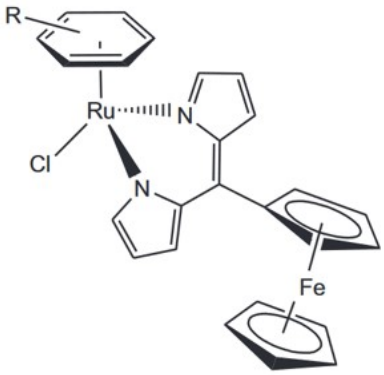
"Charge" on metal? Electron count on metal? Is it coordinatively saturated (i.e. 18 electrons)?



Grubbs catalyst



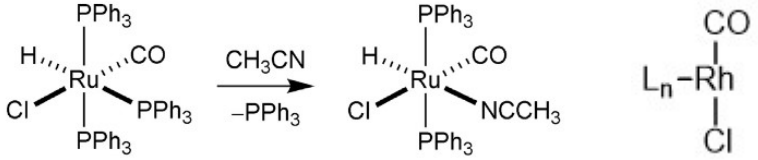


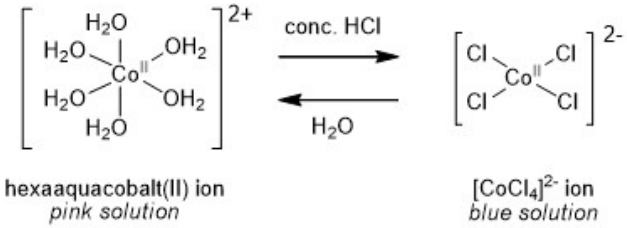


In 2014, the synthesis of half-sandwich Ru(II) dipyrrinato complexes containing 5-ferrocenyldipyrromethene (fcdpm) was reported (**53** in Fig. 17) [85]. The authors also described how these complexes bound to bovine serum albumin (BSA) and DNA, and had anticancer activity on Dalton's lymphoma (DL) cells.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

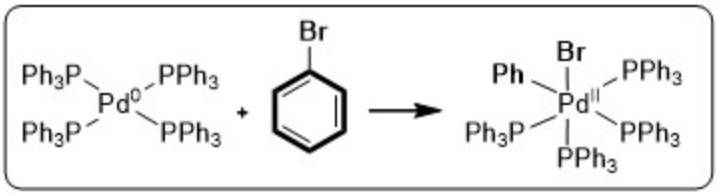




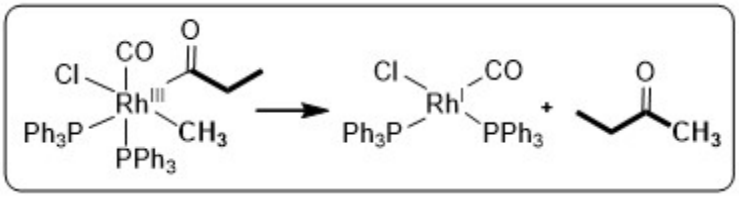
hexaaquacobalt(II) ion
pink solution

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

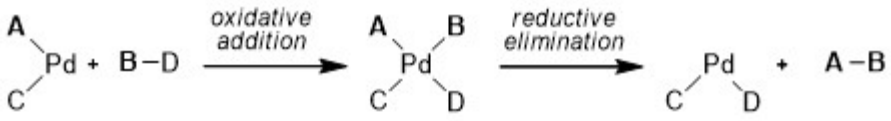
Oxidative Addition – results in +2 change in oxidation number



Reductive Elimination – results in -2 change in oxidation number

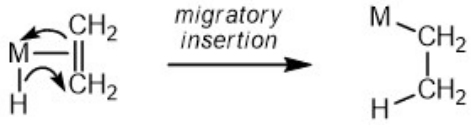


Palladium-Catalyzed Cross-Coupling Reaction



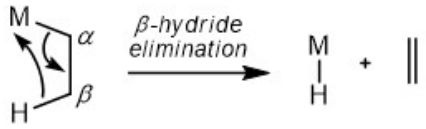
Migratory Insertion

1,2-Migratory Insertion: Hydrometalation of an Alkene

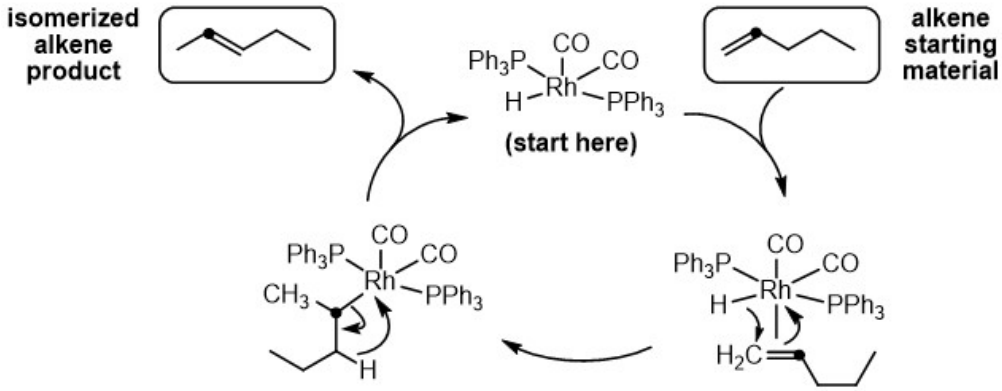


Beta Elimination

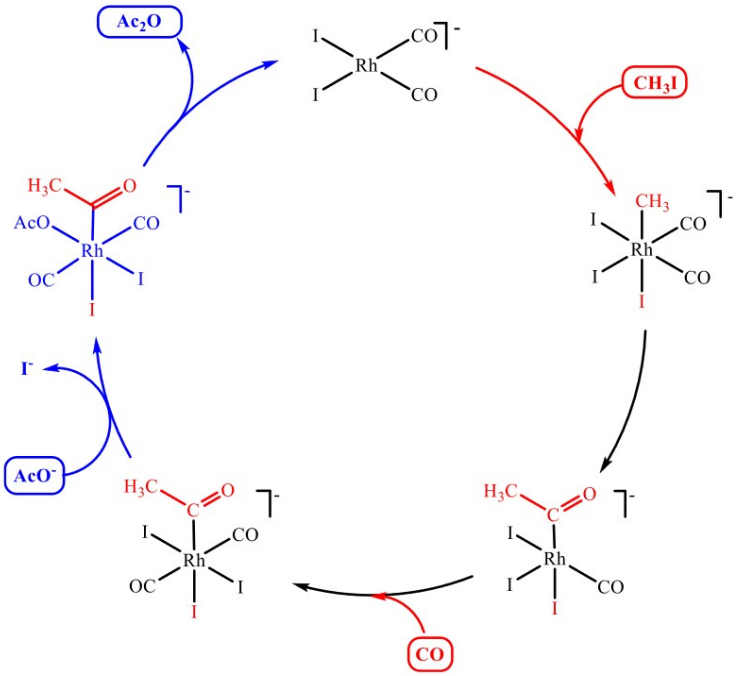
β-Hydride Elimination to Form an Alkene



Catalytic Cycle of Alkene Isomerization



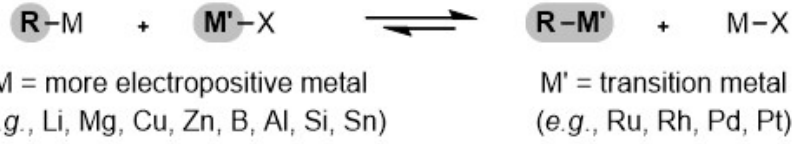
Describe each step, determine Rh oxidation state throughout:



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

Transmetalation

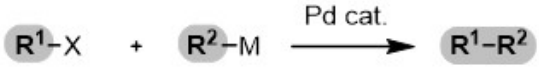
Transmetalation Exchanges Coordinated Metal Atoms



M = more electropositive metal
(*e.g.*, Li, Mg, Cu, Zn, B, Al, Si, Sn)

M' = transition metal
(*e.g.*, Ru, Rh, Pd, Pt)

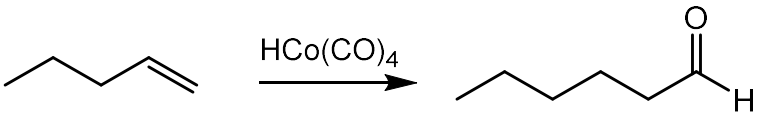
Reaction	Metal (M)
Hiyama	Si
Suzuki-Miyaura	B
Stille	Sn
Negishi	Zn
Sonogashira	Cu
Kumada	Mg

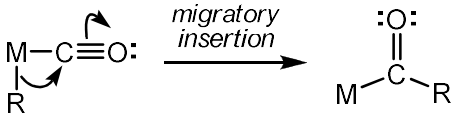


Transmetalation is involved in cross-coupling reactions

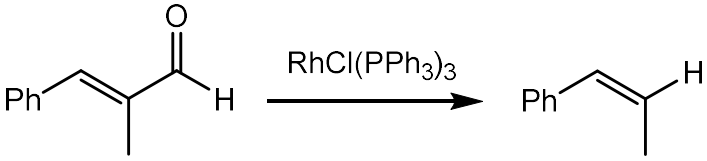
Transition Metal-Mediated Synthetic Transformations

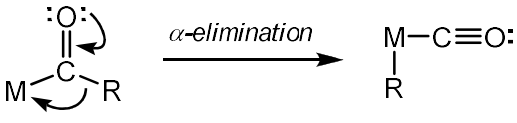
8.3 Carbonylation and Decarbonylation



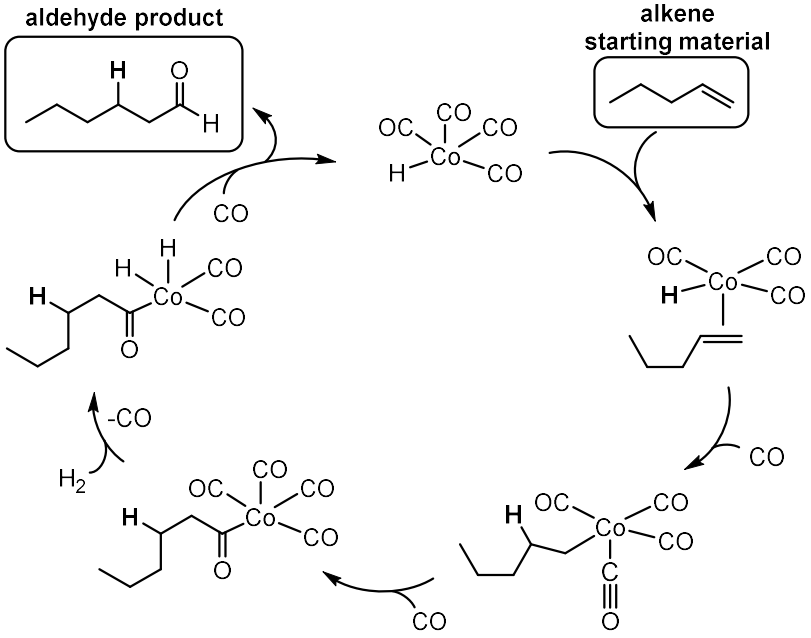


a hydroformylation reaction

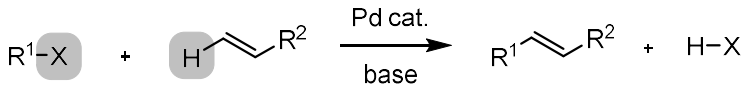




convert aldehydes to alkanes (RCHO → RH), or
acid chlorides to alkyl halides (RCOCl → RCl)

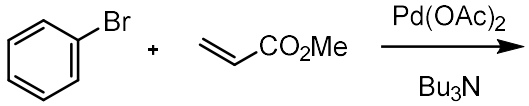


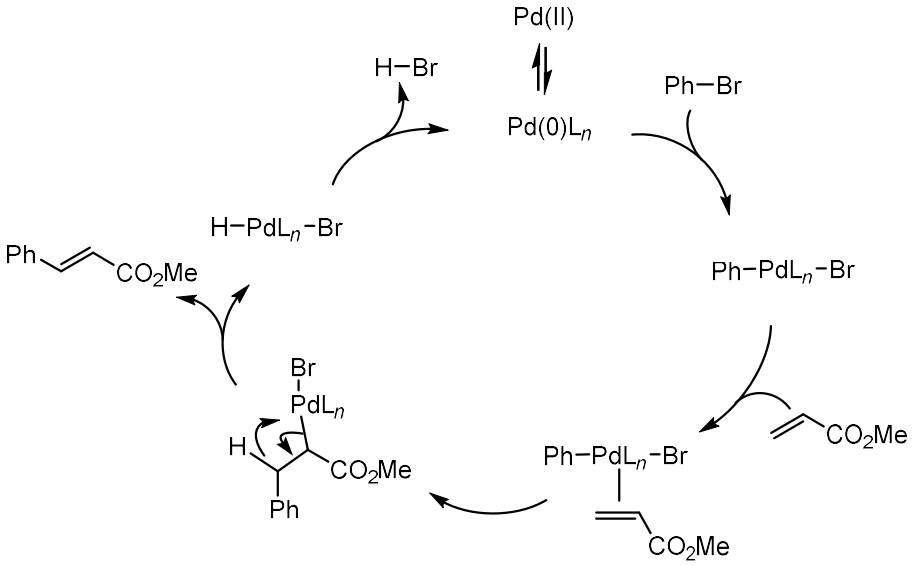
8.4 The Heck Reaction



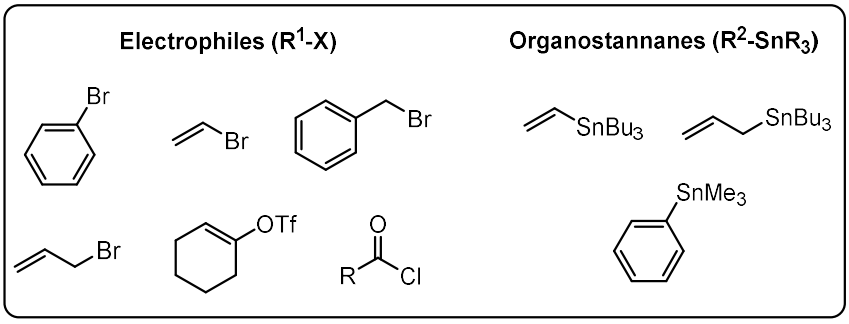
R^1 = aryl or vinyl; R^2 = EWG or EDG (Ar, CO_2R, CN, R, H); X = I, Br, OTf

Example:

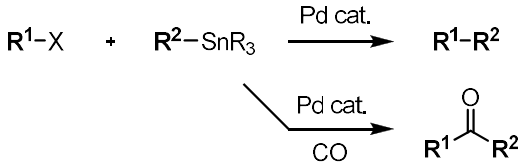




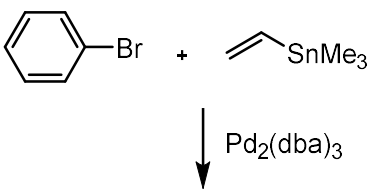
8.5 Pd-Catalyzed Cross-Coupling Reactions

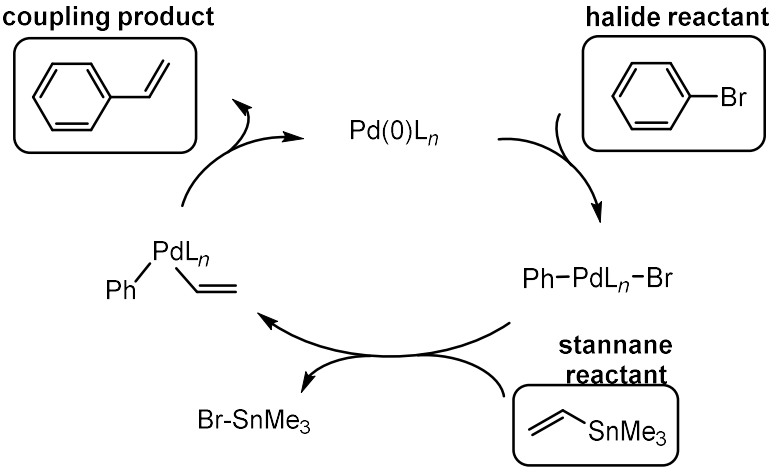


Stille Reaction

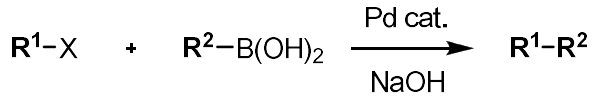


Example:

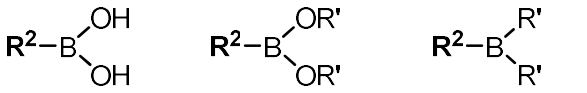




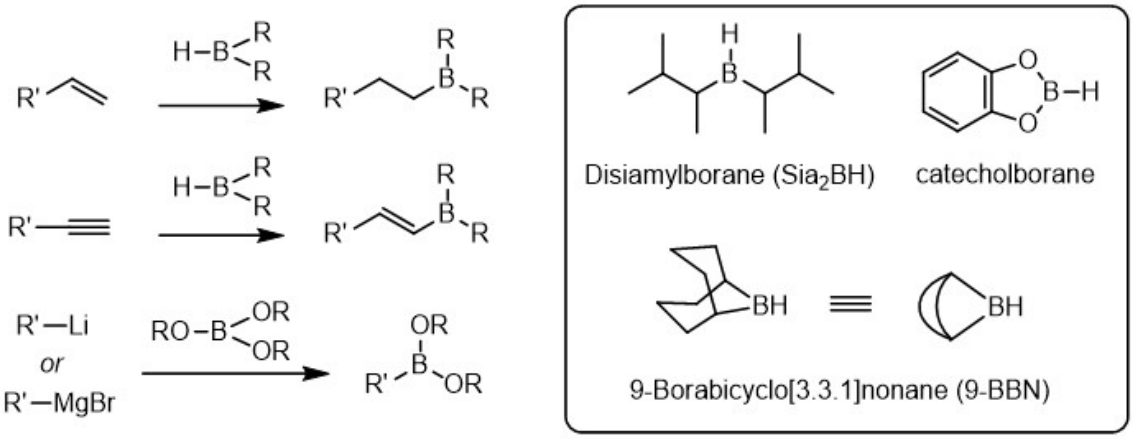
Suzuki-Miyaura Reaction



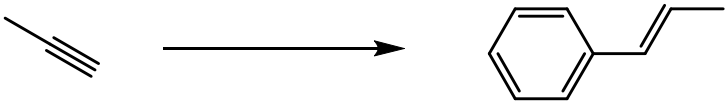
R^1 = aryl, vinyl, alkynyl; R^2 = aryl, vinyl, allyl, alkyl

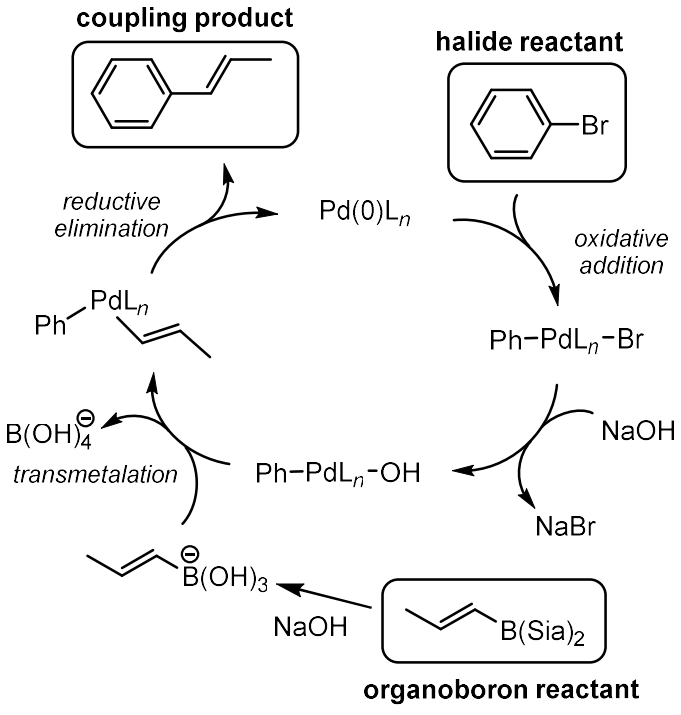


boronic acid | boronic ester | organoborane



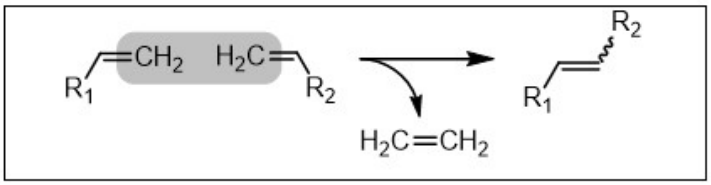
Use a Suzuki-Miyaura Coupling Reaction to achieve the following transformation:



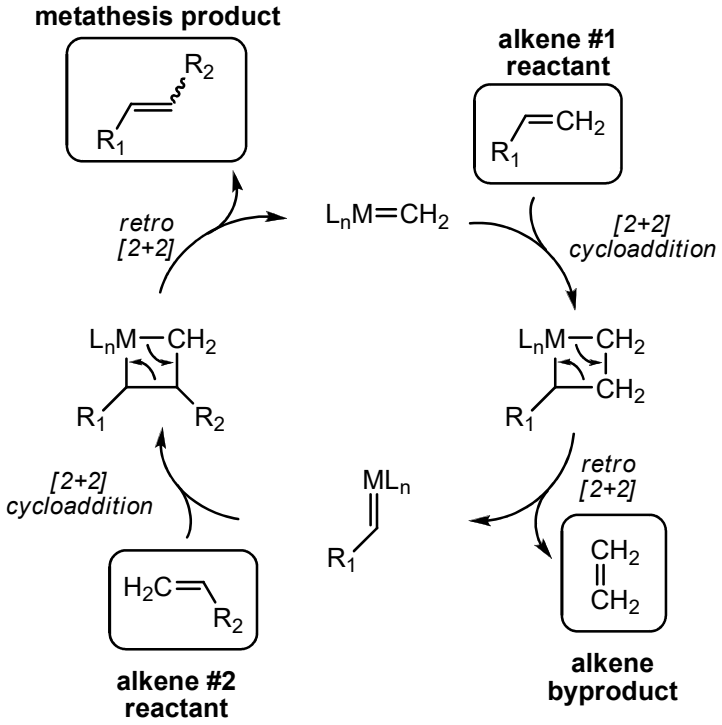


8.6 Olefin Metathesis Reactions

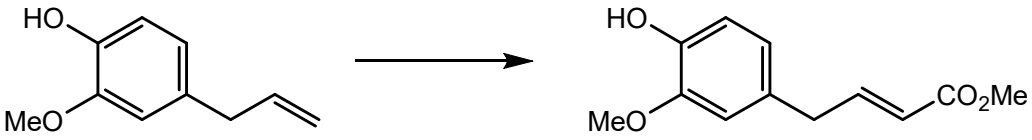
General Alkene Metathesis Reaction



Cross-Metathesis

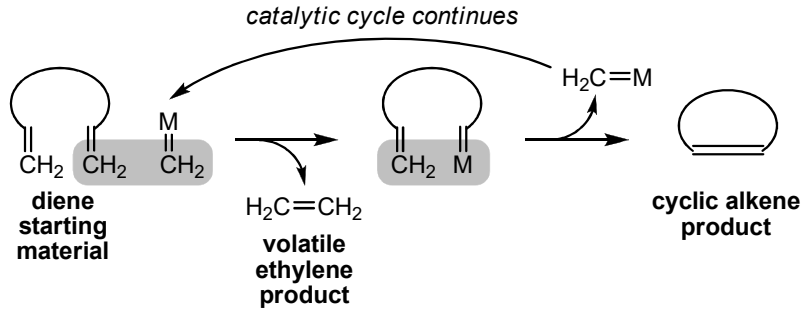


Use a Cross-Metathesis Reaction to achieve the following transformation:



eugenol

Ring-Closing Metathesis (RCM)



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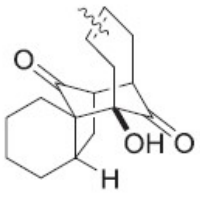

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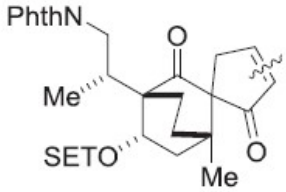

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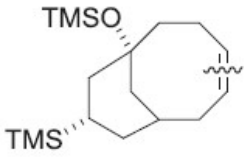

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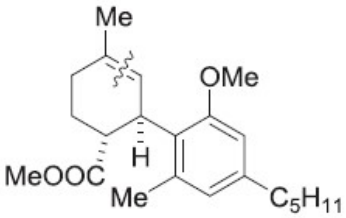

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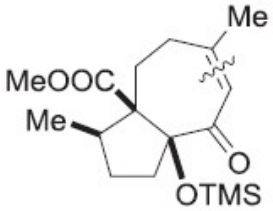

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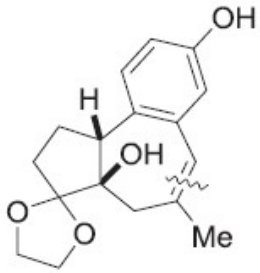

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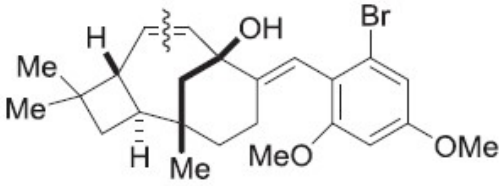

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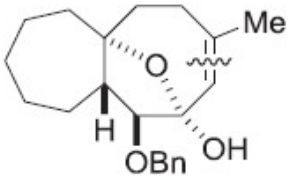

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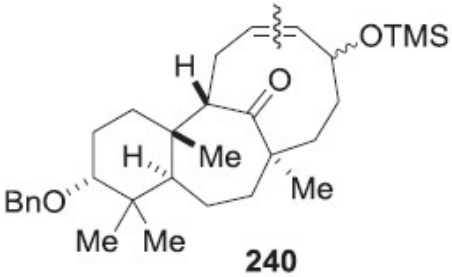

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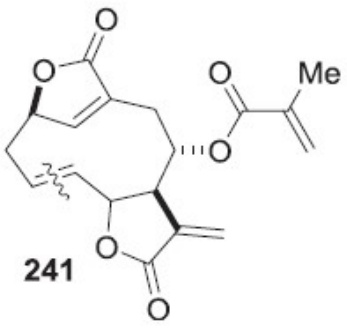

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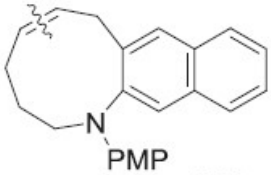

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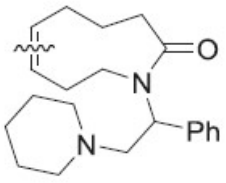

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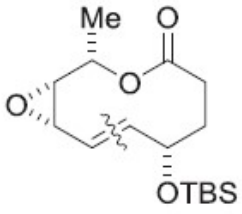

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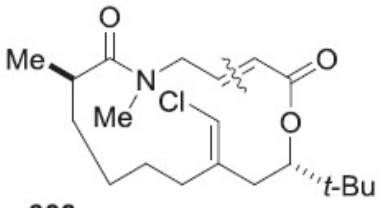

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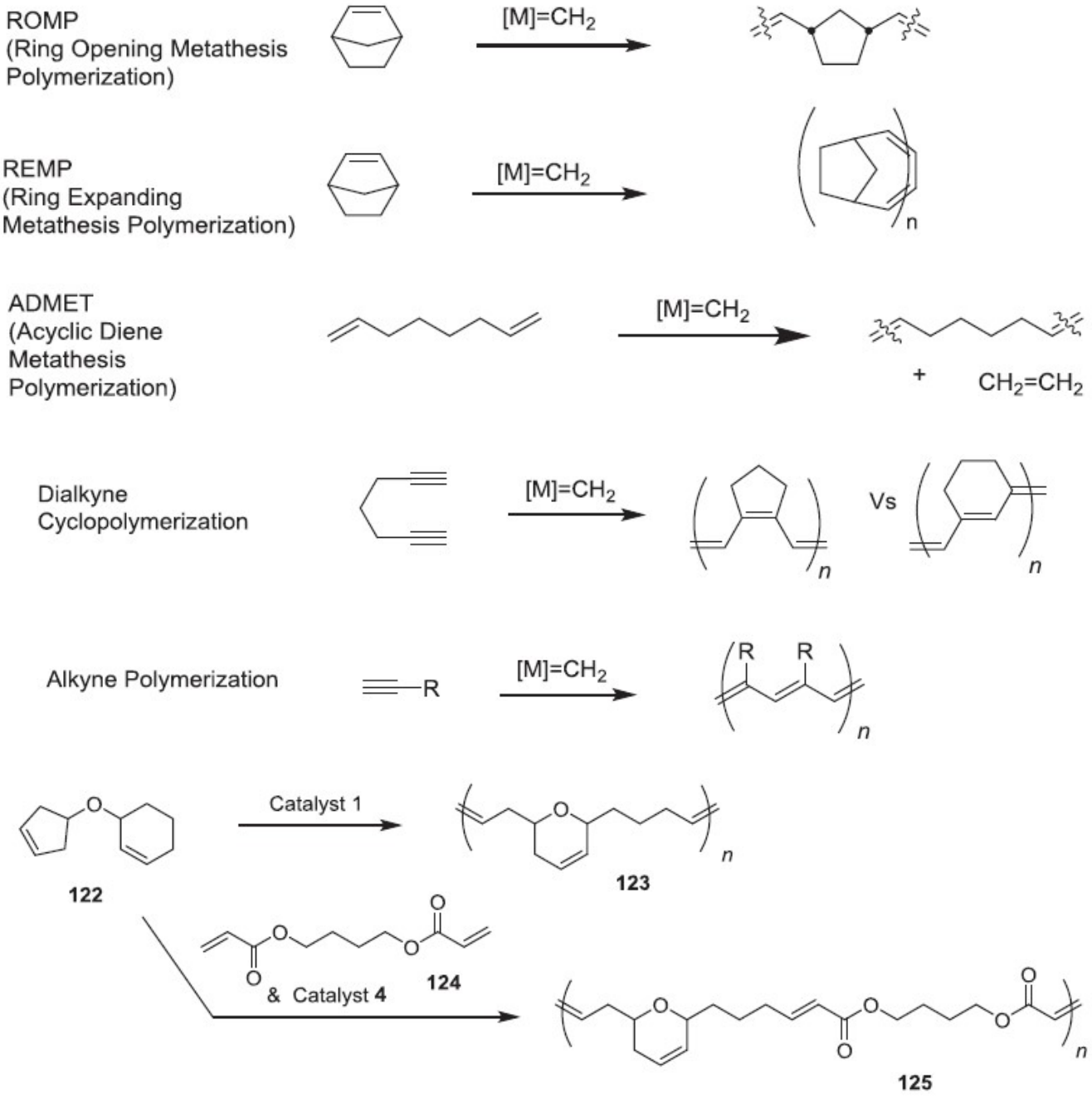
Polymerization



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

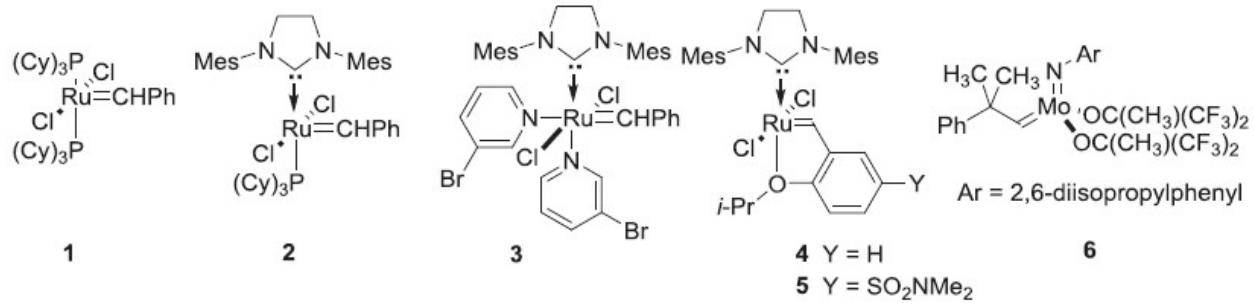
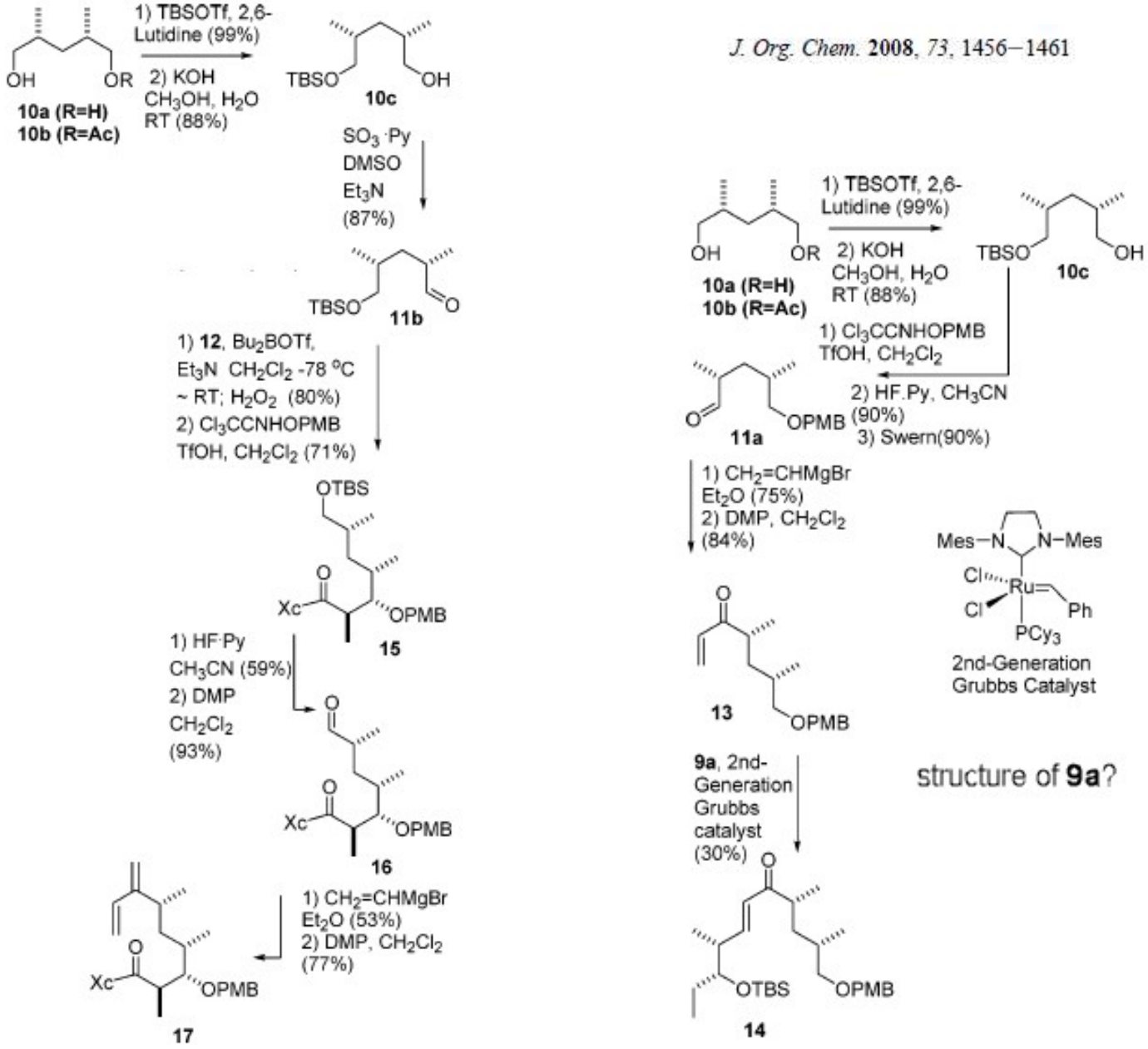


Fig. 1. Structures of classic general-purpose alkene metathesis catalysts **1–6**.



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