Organometallics Study Meeting
Part 4. Reactions of Organometallic Complexes

2011/4/28 Yoshino (D1)

大学院講義有機化学 I. 10章

1. Basics

1-1. Ligand Exchange

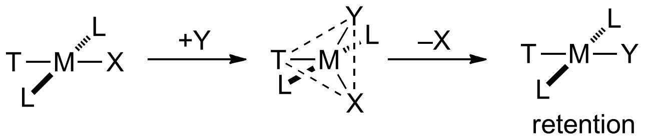
Dissosiative Mechanism

$ML_n \xrightarrow{-L} ML_{n-1} \xrightarrow{+L'} ML'L_{n-1}$ Reaction rate does not depend on the [L'].

$Fe(CO)_5$ (18e) : Photo-promoted dissociation of CO ligand

Associative Mechanism

Common in d^8 square planar 16e complex ($Pd(II)L_4$ etc.)



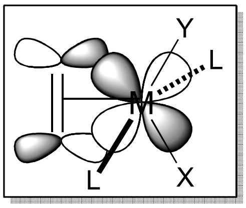
Trans Effect : Effect of T on ***rate*** of ligand exchange

CO, CN^-, C_2H_4 > PR_3, H^- > CH_3^- > $C_6H_5^-$, I^- > Br^-, Cl^- > NH_3, H_2O

Evaluated using Pt(II) complex

Trans Influence : Parameter indicating how weak T makes M-X bond

H^-, CH_3^-, $C_6H_5^-$ > PR_3, CN^- > CO, C_2H_4 > I^-, Br^- > Cl^- > NH_3, H_2O



π-Bonding ligands show strong trans effect by stabillizing 5-coordinated structure.

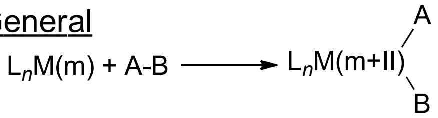
Transmetallation

$L_nM\text{-}X + R\text{-}M' \longrightarrow L_nM\text{-}R + M'X$

M = transition metal
M' = MgBr, BR'_2, SnR'_3, Cp_2ZrCl etc.
X = halides, OAc etc.

1-2. Oxidative Addition

General



$L_nM(m) + A\text{-}B \longrightarrow L_nM(m+II)(A)(B)$

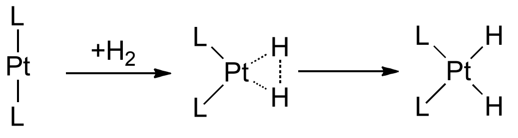
- Oxidation number increases by 2.
- Coordination number increases by 2.

Low valent, coordinatively unsaturated, electron rich complexes are active in oxidative addition.

Vaska's complex [*trans*-$Ir(CO)(PPh_3)_2Cl$, Ir(I), d^8, 16e]

ML_2 [Ni(0), Pd(0), Pt(0), d^{10}, 14e]

Oxidative Addition to H_2

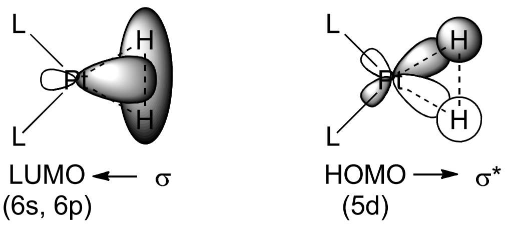


HOMO energy level increases when L-Pt-L bond bends (up to 90 °).

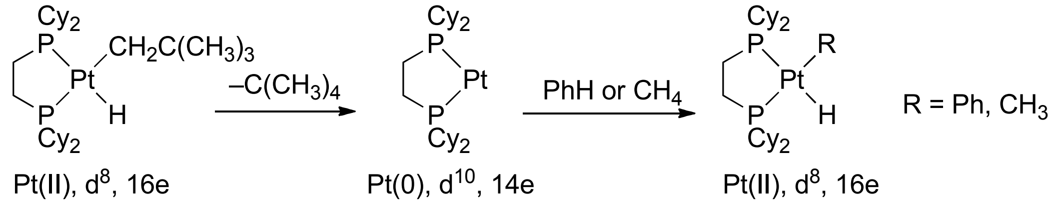
⇓

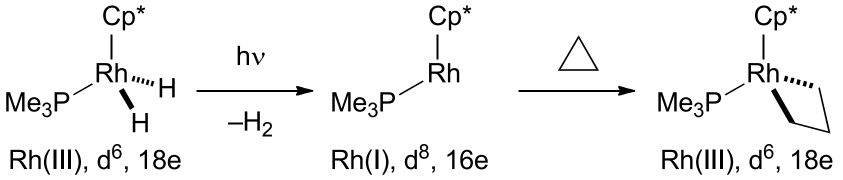
Bidentate phosphine ligand improve reactivity of oxidative addition.

Orbital Interactiion



Oxidative Addition to C-H, C-C Bond

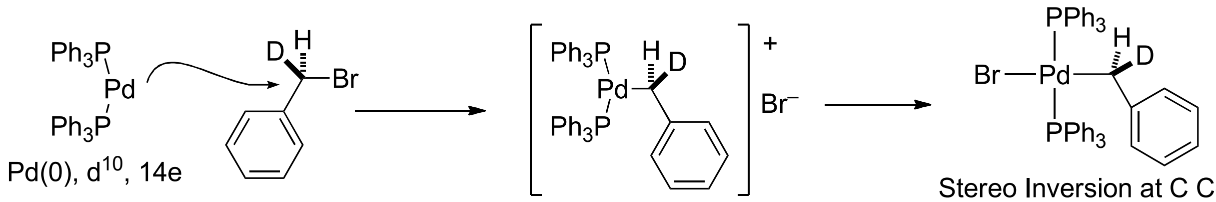




Oxidative Addition to C-X Bond through S_N2 Mechanism

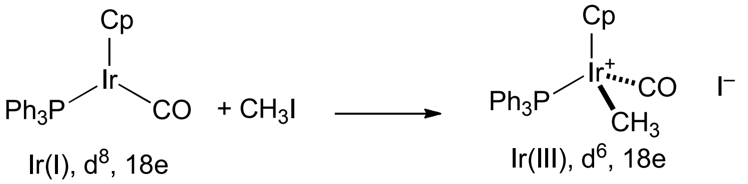
$L_nM + R\text{-}X \longrightarrow \left[L_nM\cdots R\cdots X\right]^{\ddagger} \longrightarrow [L_nM\text{-}R]^+ X^-$

Metal : Pd(0), $Pt(CH_3)_2$, Ir(I) etc.
Halides : Alkyl-X, Allyl-X (sp^3 C-X)

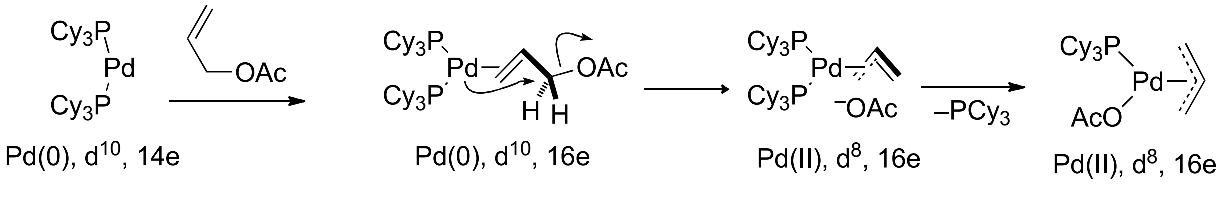


Stereo Inversion at C Center.
Trans Addition

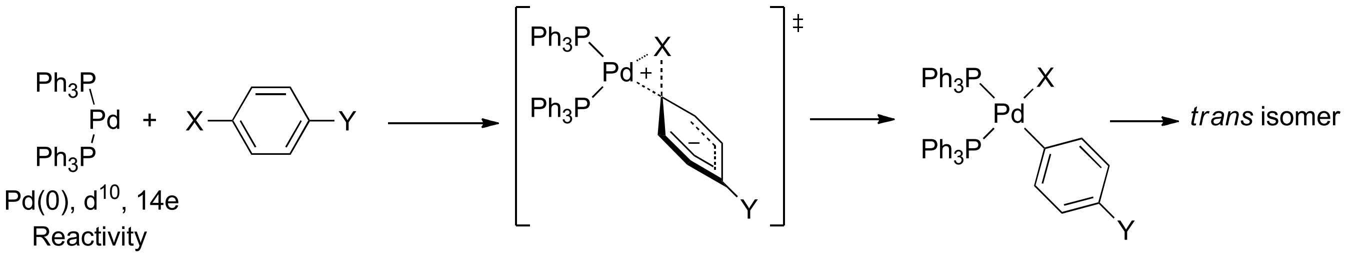
Even 18e complex can react thtough S_N2 mechanism.



Allyl-X shows higher reactivity and π-ally-complex is formed.



Oxidative Addition to sp^2 C-X bond



Reactivity
X : I > Br >> Cl
Y: Electron Withdrawing Group > Electron Donating Group

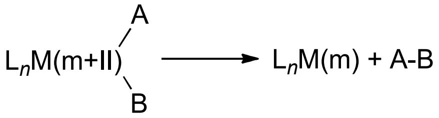
Alkenyl-X gives stereo-retained product.

Oxidative Addition through Radical Mechanism

$Alkyl\text{-}Br + Pt(PEt_3)$

1-3. Reductive Elimination

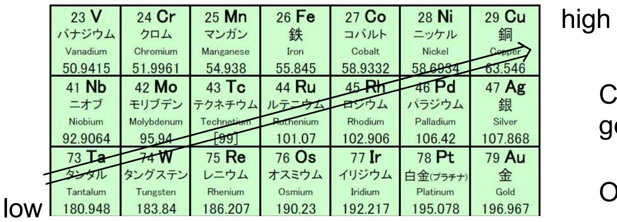
General



$$L_nM(m+II)(A)(B) \longrightarrow L_nM(m) + A\text{-}B$$

- Retro reaction of oxidative addition.
- 3-membered transition state.

Reactivity : Complex with *lower d-orbital energy level shows higher reactivity.*



23 **V** バナジウム Vanadium 50.9415	24 **Cr** クロム Chromium 51.9961	25 **Mn** マンガン Manganese 54.938	26 **Fe** 鉄 Iron 55.845	27 **Co** コバルト Cobalt 58.9332	28 **Ni** ニッケル Nickel 58.6934	29 **Cu** 銅 Copper 63.546
41 **Nb** ニオブ Niobium 92.9064	42 **Mo** モリブデン Molybdenum 95.94	43 **Tc** テクネチウム Technetium [99]	44 **Ru** ルテニウム Ruthenium 101.07	45 **Rh** ロジウム Rhodium 102.906	46 **Pd** パラジウム Palladium 106.42	47 **Ag** 銀 Silver 107.868
73 **Ta** タンタル Tantalum 180.948	74 **W** タングステン Tungsten 183.84	75 **Re** レニウム Rhenium 186.207	76 **Os** オスミウム Osmium 190.23	77 **Ir** イリジウム Iridium 192.217	78 **Pt** 白金(プラチナ) Platinum 195.078	79 **Au** 金 Gold 196.967

Co(III), Rh(III) Ni(II), Pd(II) are
good species for reaductive elimination.

Only *cis*-ligands undergoes reductive elimination.

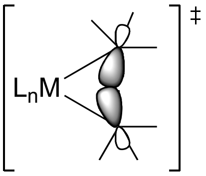
Reactivity (Ligands)

Alkyl (Me < Et < *n*Pr < *n*Bu) < Aryl, Alkenyl < H

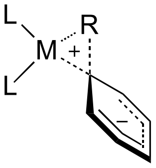
Elimination of alkyl group
requires strained TS.

Aryl, Alkenyl: π-orbital can particilate
n the formation of 3-membered TS.

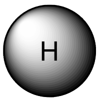
Hydride (H) has spherical symmetry
and form TS without strain,



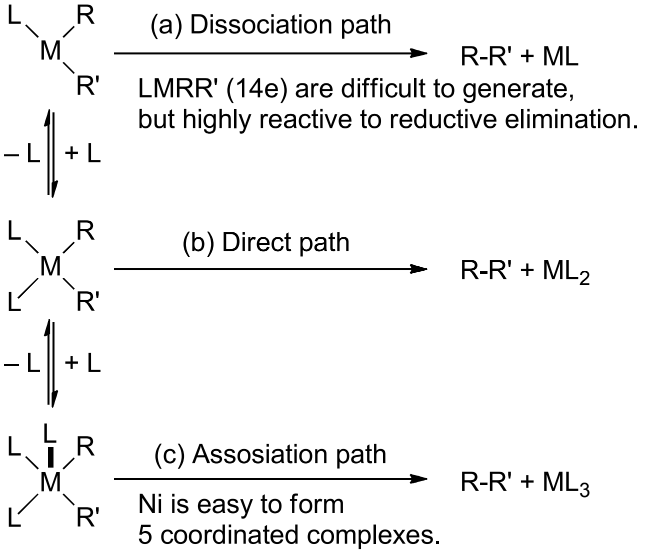
<



<



Reductive Elimination from Group 10 metal (II) Complex



(a) Dissociation path

LMRR' (14e) are difficult to generate,
but highly reactive to reductive elimination.

cis-L_2Pd-(alkyl)$_2$

(b) Direct path

Most Pd complexes

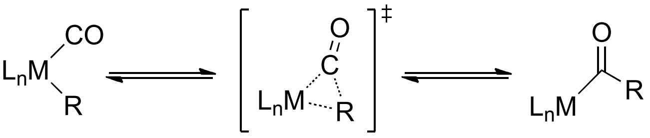
(c) Assosiation path

Ni is easy to form
5 coordinated complexes.

Most Ni complexes

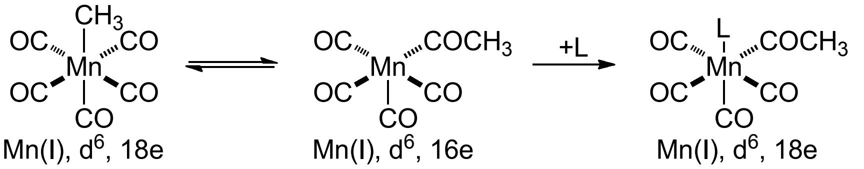
1-4. Insertion and Elimination

CO Insertion and Elimination



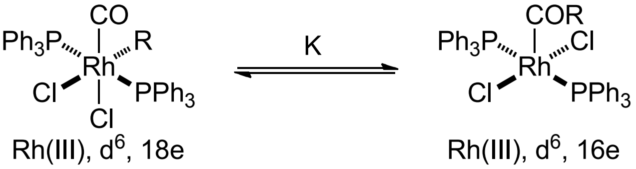
- R and CO must be *cis.*
- Reversible process.
- Attack of R^- to CO's LUMO.

CO does not move and R rearrange to CO group.



L = CO or PR_3

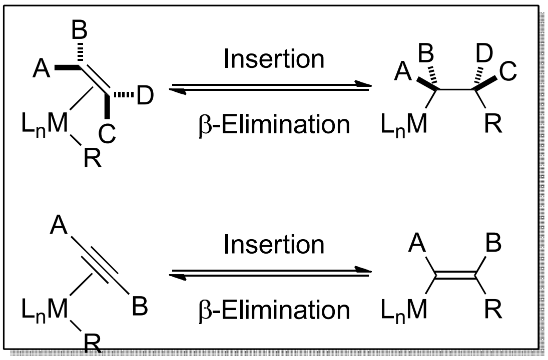
More σ-donating, nucleophilic group have large *K*.



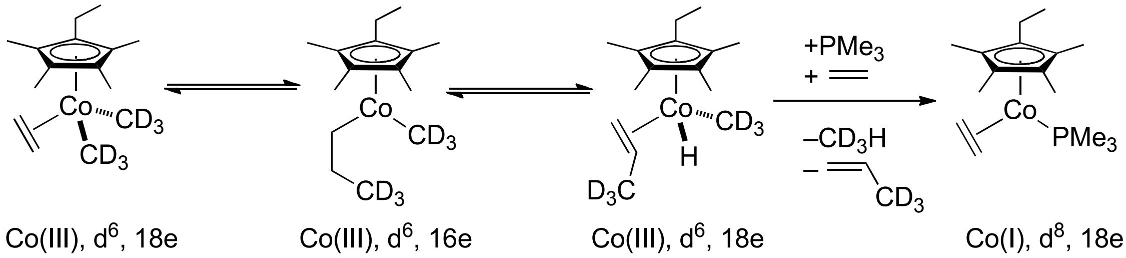
R	*K*
Et, *n*Pr, Bn	>50
$PhCH_2CH_2$	~17
CH_3	3.4±0.2
p$ClC_6H_4CH_2$	0.07
Ph	<0.05
$ClCH_2$, H	<0.02

Electronwithdrawing ligand more strongly coodinate to M.
Espcially, M-H bond is far stronger than M-C bond.
Also CO insertion to M-CO bond cannot proceed.

Insertion of Alkene, Alkyne and β-Hydride Elimination

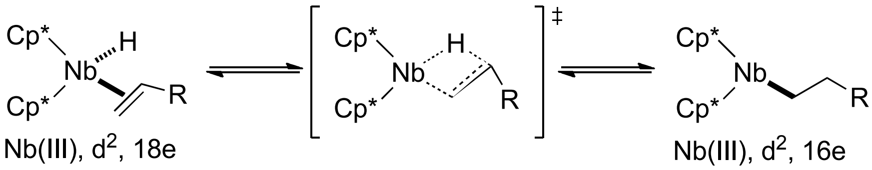


These processes are reversible.
Alkyl complexes are easy to undergo β-elimination.

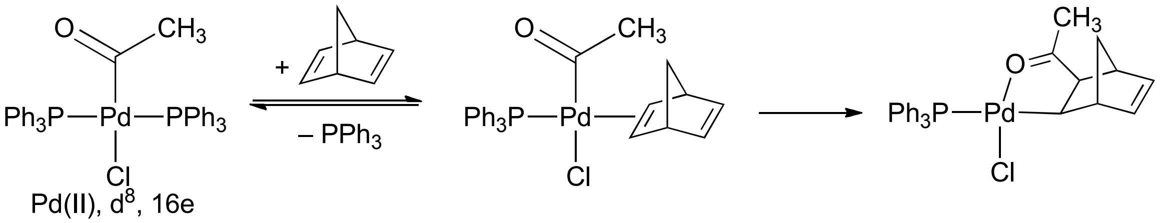


Only β-hydride eliminated product was observed.

Mechanism



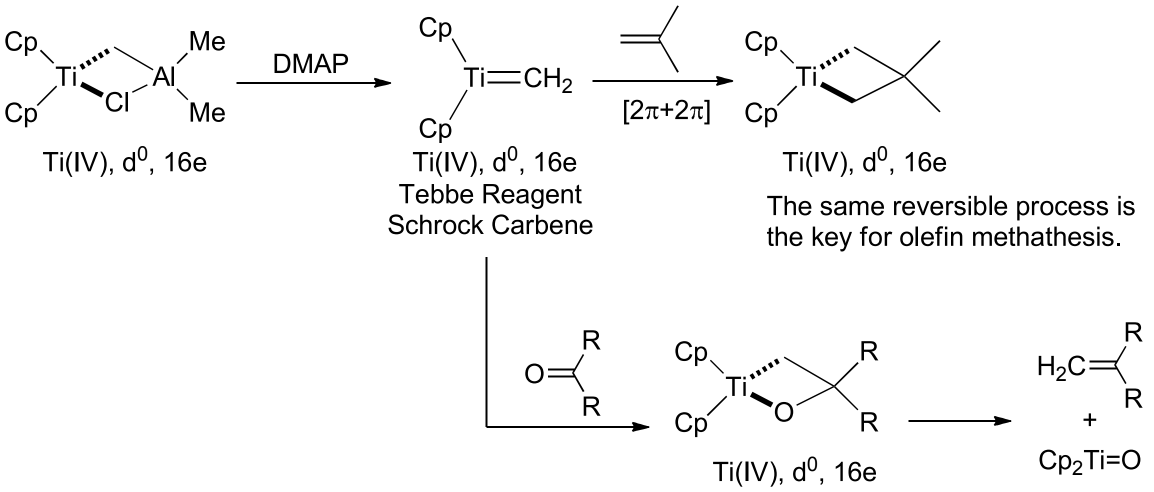
Reaction with Pd(II) Complex



Reaction proceeded dissociatively. Cationic (dppe)Pd(Ac)$(CH_3CN)^+$ complex shows higher reactivity.

1-5. Cycloaddition

Cycloaddition of Schrock Carbene



Ti(IV), d^0, 16e

Ti(IV), d^0, 16e
Tebbe Reagent
Schrock Carbene

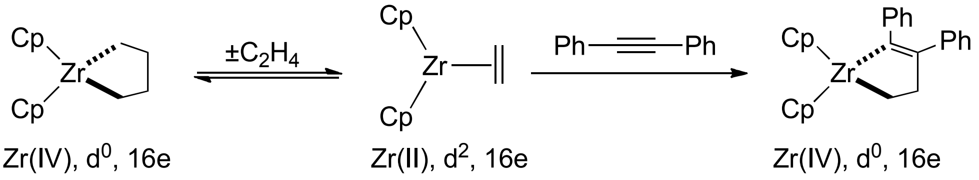
Ti(IV), d^0, 16e

The same reversible process is the key for olefin methathesis.

Ti(IV), d^0, 16e

$Cp_2Ti=O$

Oxidative Cyclization



Zr(IV), d^0, 16e

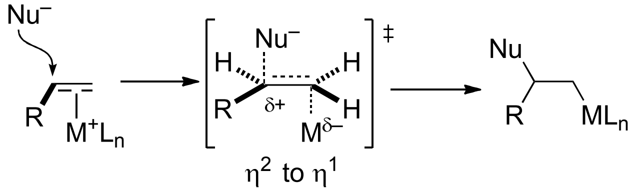
Zr(II), d^2, 16e

Zr(IV), d^0, 16e

Low valent alkene, alkyne complexes undergo this reaction.

1-6. Reactions at Ligands

Nucleophilic Attack to Metal-Alkene Complexes

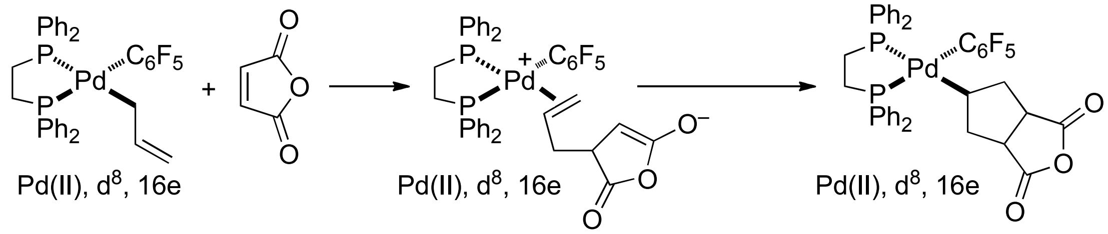


- Nucleophilic attack occured on opposite face to metal.
- Nucleophilic attack occured at more substituted carbon.
- Metal with high oxidation state

Pd(II)-alkene complexes have been well studied.
Nu: Alcohols, Amines, Enolates

Reactions of Allyl Ligands

η^1 -Allyl Complexes show nucleophilic reactivity.

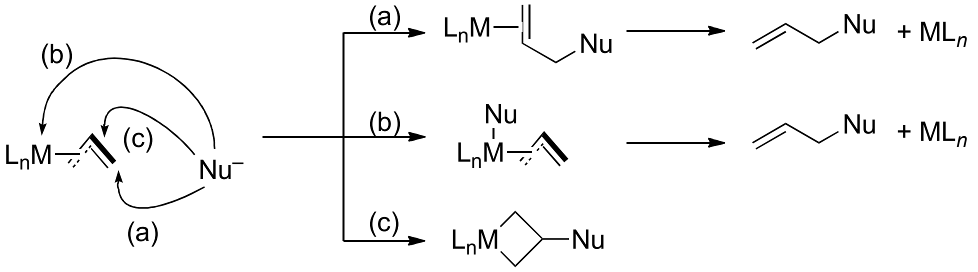


Pd(II), d^8, 16e

Pd(II), d^8, 16e

Pd(II), d^8, 16e

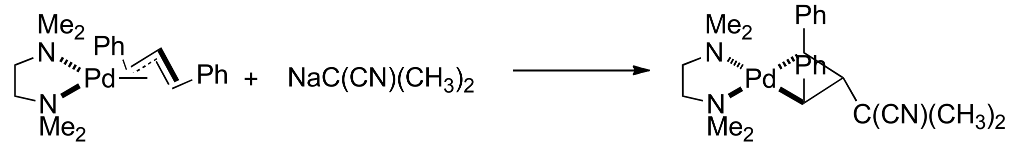
η^3 -Allyl Complexes show electrophilic reactivity.



Nu: Malonates, Amines

Nu: Grignard Reagents

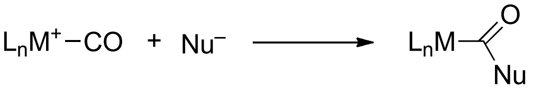
Example of Path (c)   Low valent Pd(0) is unstabilized by σ-donating N ligand.



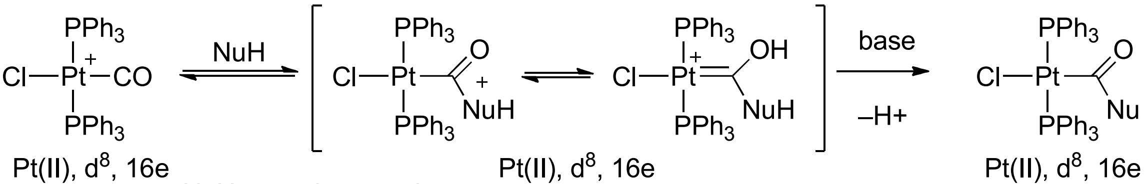
Hard nucleophiles, MeLi, H^-, favor path (c).

Metals which disfavor low valent states, Zr(IV), W(IV), Pt(II), tend to react through path (c).

Reactions of CO Ligands

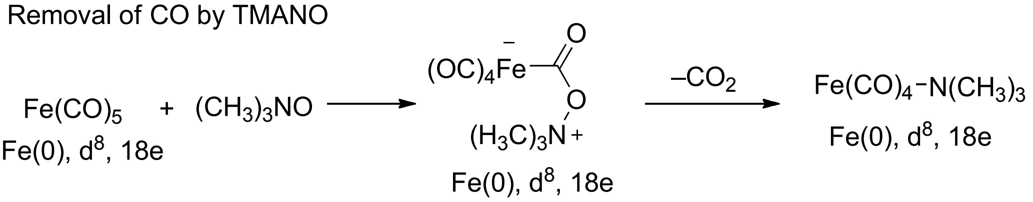


The weaker π-backdonation,
the higher reactivity of CO group.



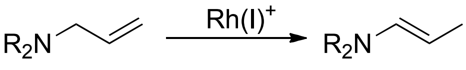
NuH = alcohols, amines

Removal of CO by TMANO

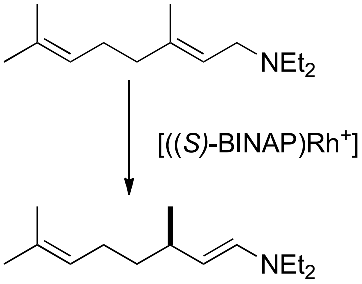


2. Homogenious Catalysis

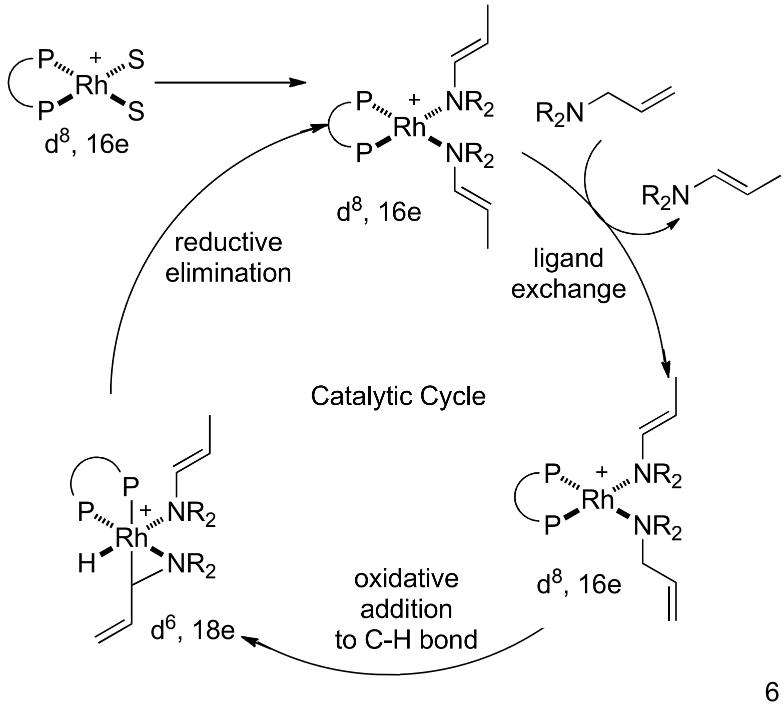
2-1. Isomerization of Olefin



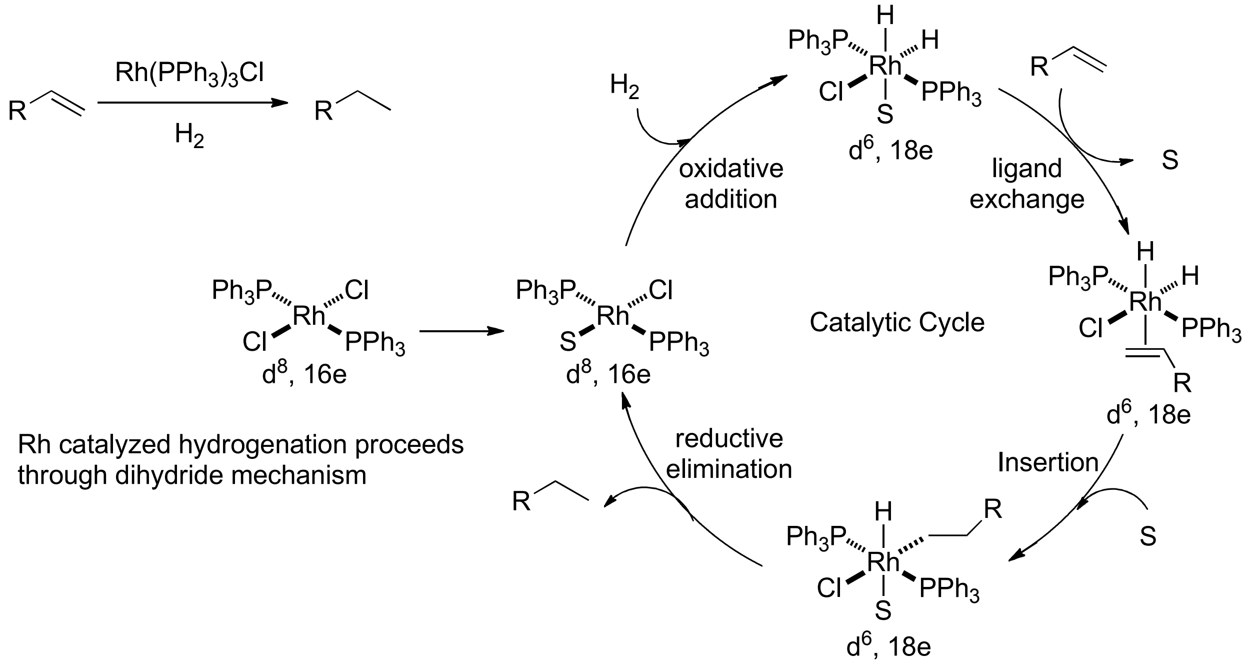
Takasago's Menthol Synthesis



96-99% ee

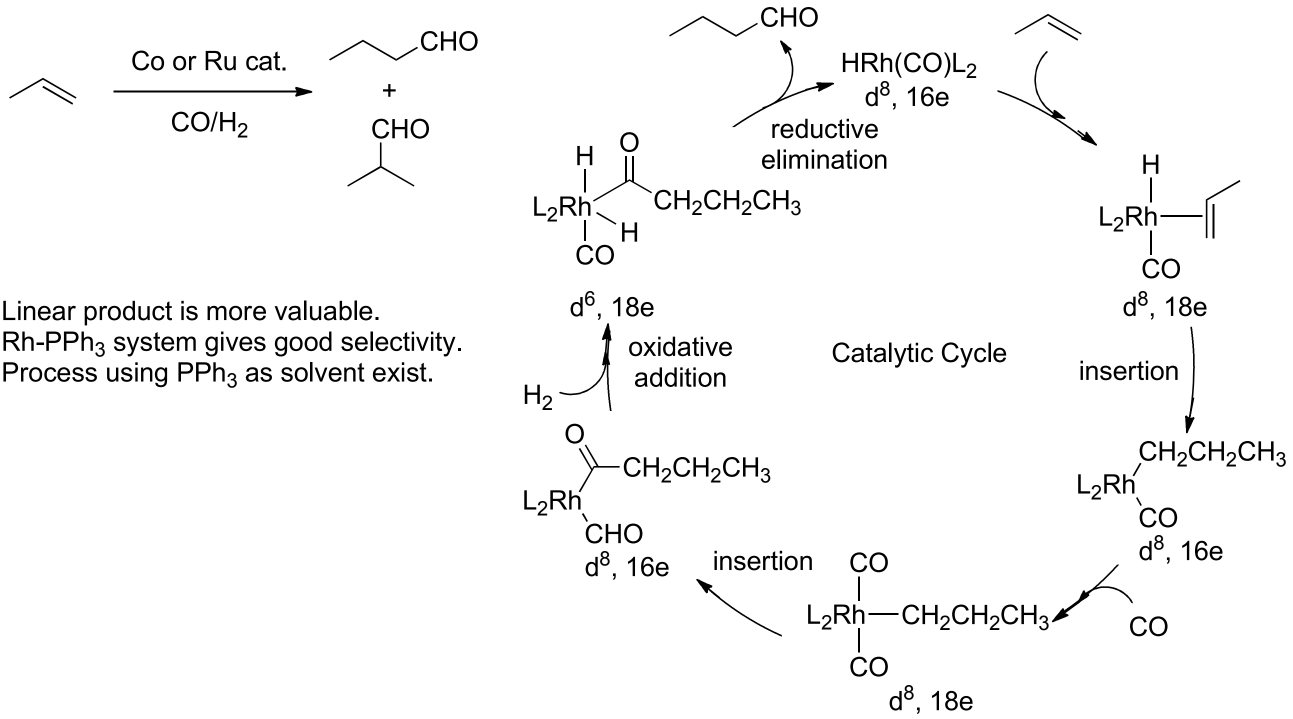


2-2. Hydrogenation



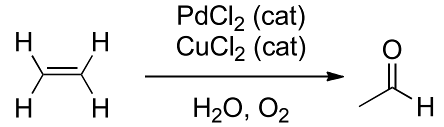
Rh catalyzed hydrogenation proceeds through dihydride mechanism

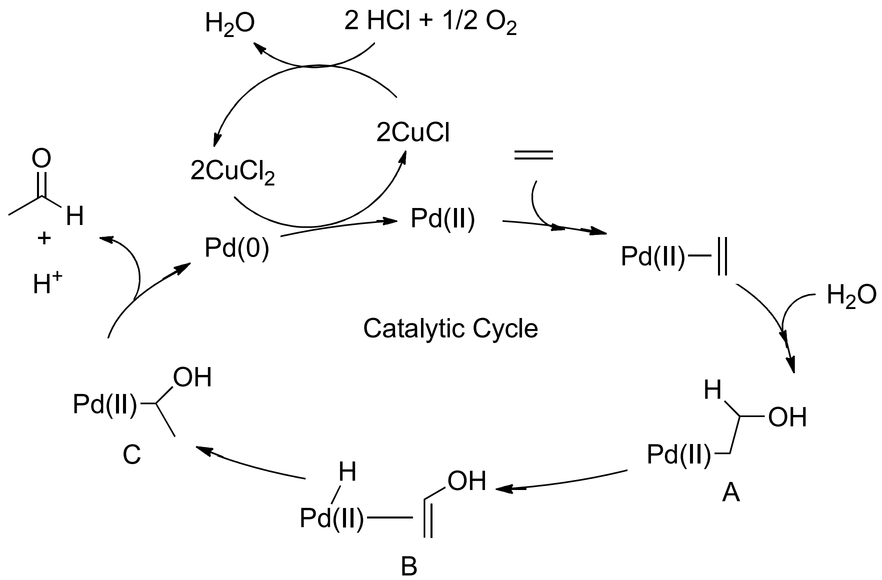
2-3. Hydroformylation



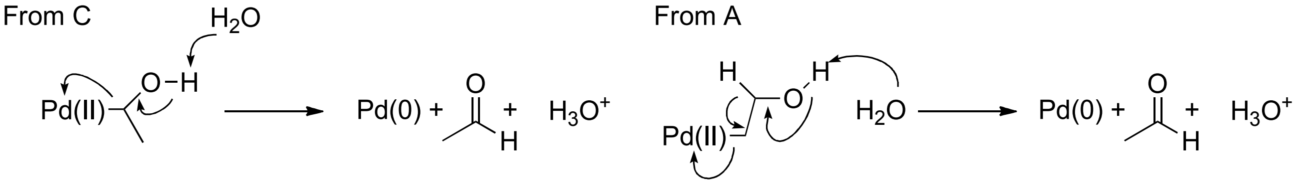
Linear product is more valuable.
Rh-PPh_3 system gives good selectivity.
Process using PPh_3 as solvent exist.

2-4. Hoechst-Wacker Oxidation





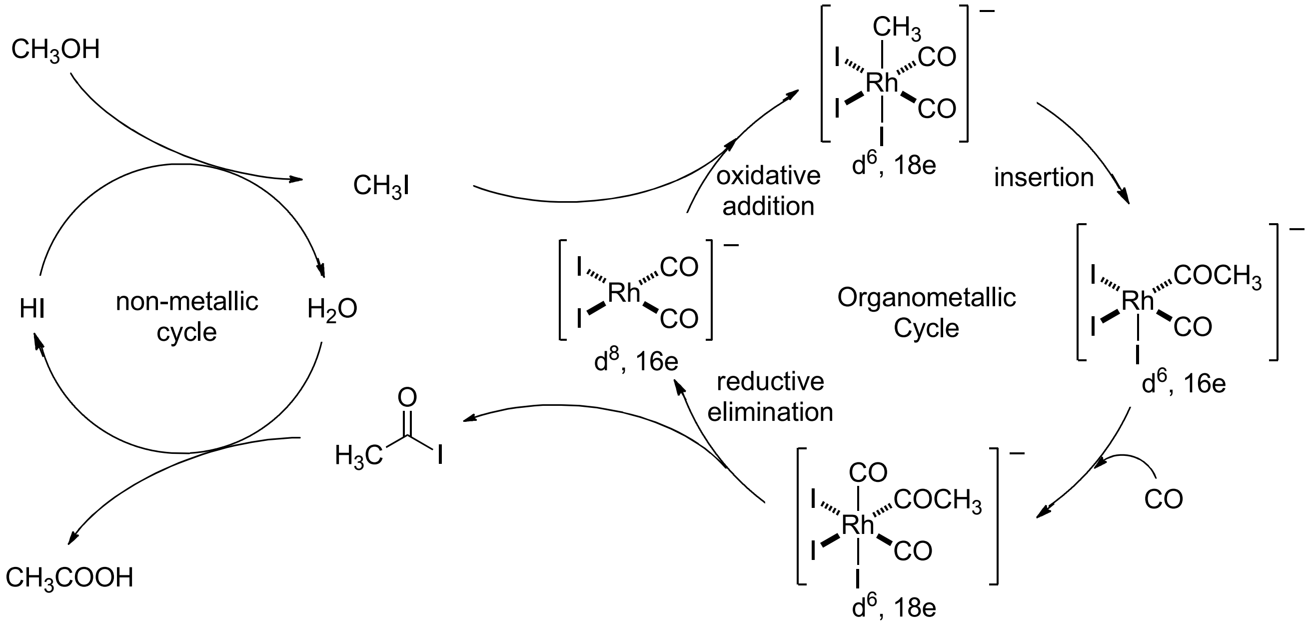
2 Proposal Pathways to Give Product



Reaction using D_2O instead of H_2O gave no deuterated aldehyde.
So pathway of non-Pd-catalyzed isomerization from B was denied.

2-5. Carbonylation of Methanol

$$CH_3OH \xrightarrow[\text{}]{\text{Rh cat.}\ \text{HI, CO}} CH_3COOH$$



2-6. Other Reactions

Heck Reaction, Cross Coupling, Olefin Methathesis etc.