

I Fundamental Organometallic Reactions

Following four reactions are important “formal” reaction patterns in organotransition metal complexes, which would conveniently explain the various transition metal catalyzed reaction mechanisms. Various electronic and steric factors control the activity and selectivity of the reactions.

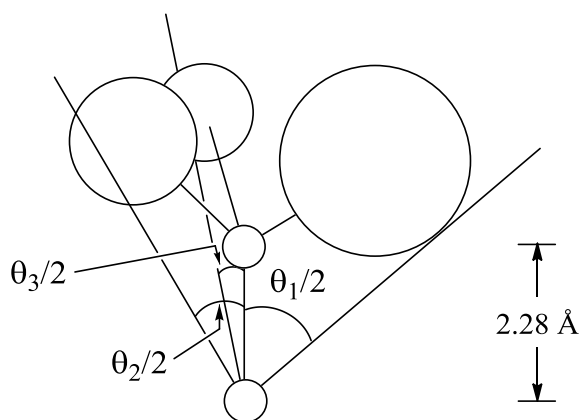
1. Coordination and Dissociation
2. Oxidative Addition and Reductive Elimination
3. Insertion and Elimination (De-insertion)
4. Reactions of Coordinated Ligands

(1) Coordination and Dissociation



How do you understand the difference between coordination bond and covalent single bond?

Steric and electronic effects on stability constant (coordination bond).



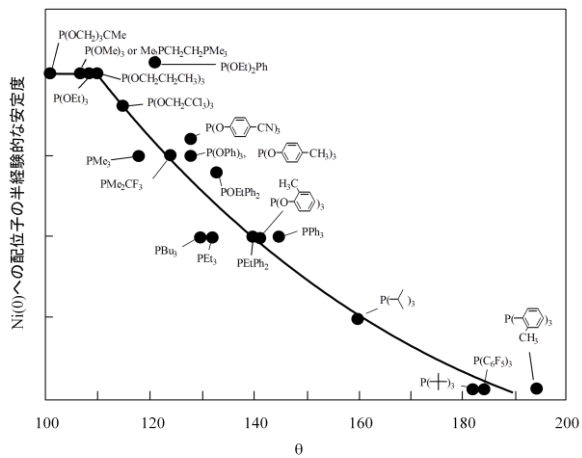


図3-2 NiL_4 錯体のLの配位に対する安定度定数とコーンアングル θ の関係

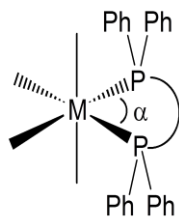


図3-3 α , ω -(ジフェニルホスフィノ)アルカンのバイトアングル

Steric effect is very important to control the stability, even in the prochiral olefin coordination. $\rightarrow \rightarrow \rightarrow$ ASYMMETRIC CATALYSIS??

Two opposite trend in stability of olefin-transition metal coordination bond is known. How do you understand?

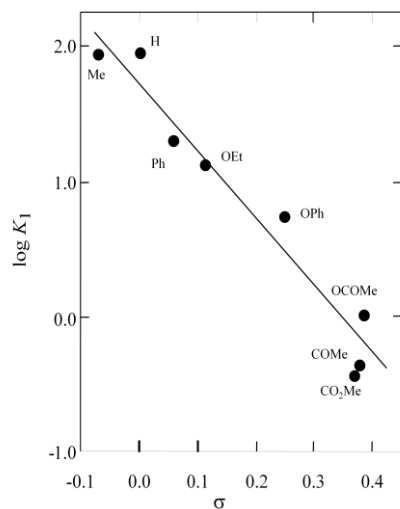
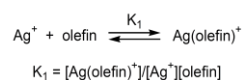


図3-4 Ag^+ へのオレフィンの配位平衡定数とオレフィンの置換基(R)のハメット定数 σ との関係



Cu ion is an important metal in relation to growth hormone.

Do you know ethylene molecule enhances the ripening of kiwi fruit? If you keep kiwi fruit with apple, very hard unripe kiwi fruit will be ready to eat quickly.

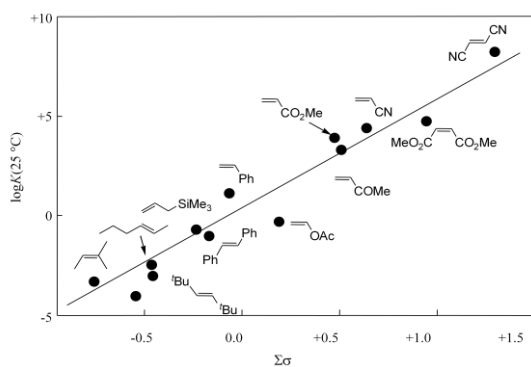
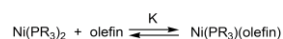


図3-5 $\text{Ni}(0)$ 錯体へのオレフィンの配位平衡定数とオレフィンの置換基のハメット定数 σ の関係

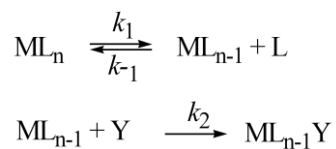


What kind of transition metal will favor electron deficient olefins?

(2) Mechanism of Ligand Exchange Processes.

Dissociative Mechanism (D)

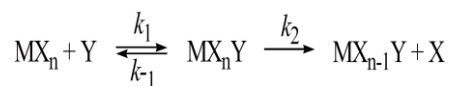
Associative Mechanism (A)



$$\text{速度} = \frac{k_1 k_2 [\text{ML}_n][\text{Y}]}{k_{-1}[\text{L}] + k_2[\text{Y}]}$$

$k_2 \gg k_1$ のとき、速度 = $k_1[\text{ML}_n]$ となる

スキーム3-1 解離的配位子交換反応機構



$$\text{速度} = \frac{k_1 k_2 [\text{MX}_n][\text{Y}]}{k_{-1} + k_2}$$

$k_2 \gg k_1$ のとき、速度 = $k_1[\text{MX}_n][\text{Y}]$

スキーム3-2 会合的配位子交換反応機構

(3) Ligand Exchange Reaction---Stereochemistry and Trans Effect
 Coordinatively Saturated Octahedral Complex

Square planar complex

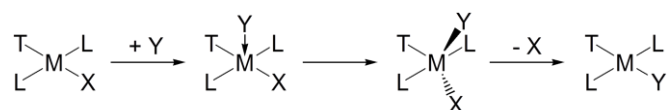


図3-6 平面四角形型錯体の会合的配位子交換反応

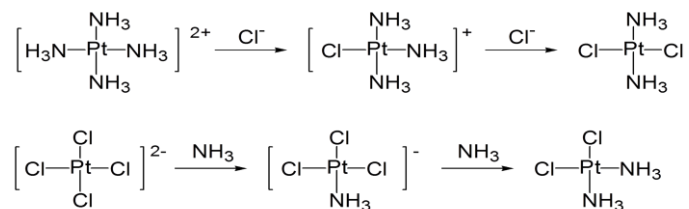
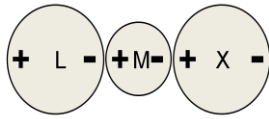


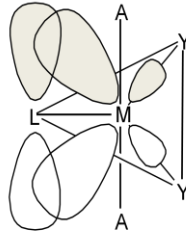
図3-7トランス効果を利用したシスおよびトランス - ジアンミンジクロロ白金(II)の選択的合成

The trend of trans effect is shown in page 49.

Reason for the trans effect:



σ -トランス効果:分極理論による
trans L-M-X軸方向の双極子の配列



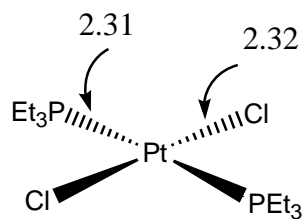
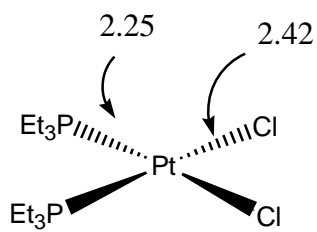
π -トランス効果:
5配位三方両錐型(*tp*)
活性中間体の安定化

図3-8 トランス効果の発現根拠

π - and σ -Orbitals of two mutually *trans*-ligands overlap with one of the transition metal d-orbitals also destabilize the bond of *trans* ligand.

Trans effect and trans influence. What is the difference?

Trans influence:



(2) Oxidative Addition and Reductive Elimination

2.1 Oxidative Addition

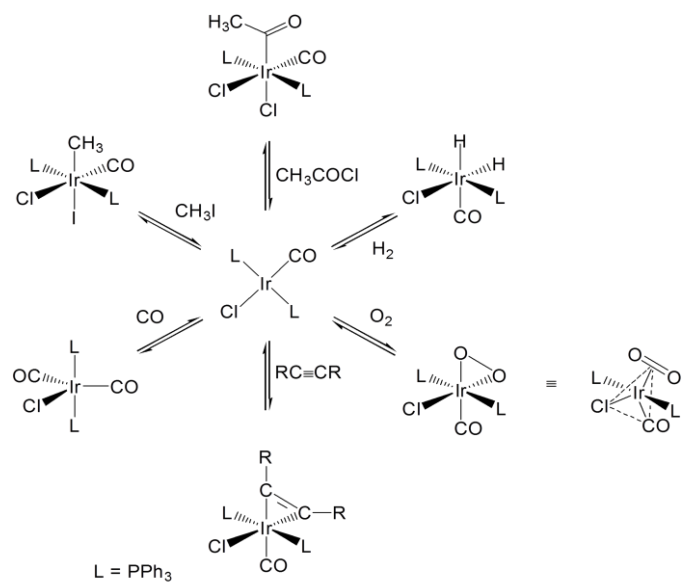
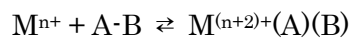


図3-9 Vaska錯体への酸化的付加と配位

(a) S_N2

(b) Radical(chain and non-chain processes)

(c) Concerted

Factors influencing on these processes?

Orthometallation

Oxidative Addition of Other Bonds such as C-O, C-S, HX etc.

Is it possible to cleave stable chemical bonds such as C-H and C-C?

By S_N2 and Radical process----merits and demerits

By concerted----Do you believe that methane C-H bond oxidatively adds to Rh?

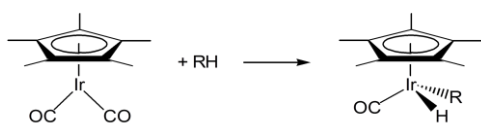


図3-10 イリジウム錯体へのアルカンの酸化的付加

cf: Other way to cleave CH bond

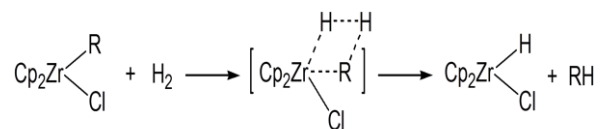


図3-12 σ ボンドメタセシス

How about C-C bond? It is well known that strained molecules such as cyclopropane shows high reactivity including C-C bond cleavage. Is it possible to cleave C-C bond of simple hydrocarbon such as hexane?

2.2 Reductive Elimination

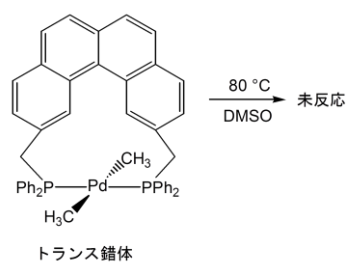
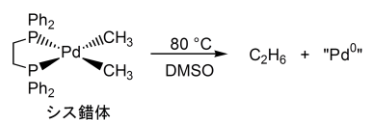
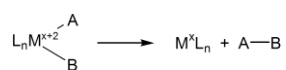


図3-13 シスおよびトランスジアルキルパラジウム(II)錯体の還元的脱離反応

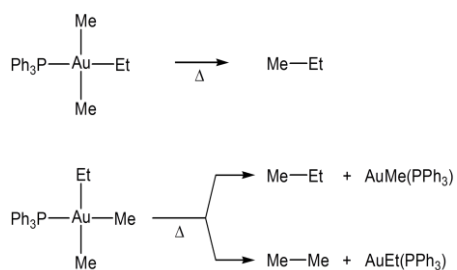


図3-14 有機金(III)錯体からの選択的還元的脱離反応

Dissociative Process is known.

T-Shape 3-coordinated intermediate is proposed.

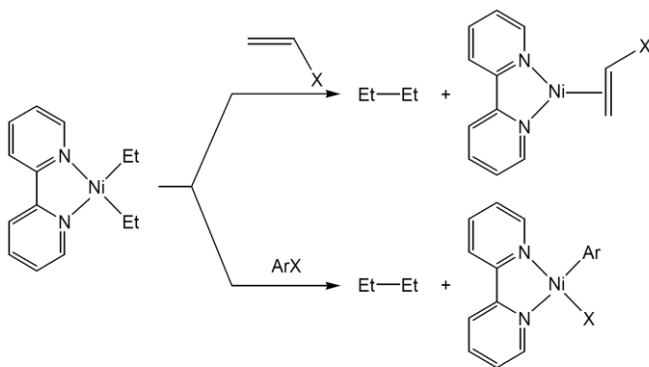


図3-15 電子不足型オレフィンまたはハロゲン化アリアルで促進されるジアルキルニッケル錯体の還元的脱離

Reductive elimination process involving C-C bond formation is enhanced by interaction with electron-deficient olefins such as acrylonitrile and aryl halides.

Finding of this fundamental reactivity of organonickel complexes eventually led to “Cross coupling reaction” (Novel price to Prof. Suzuki and Negishi in 2010). The reaction is now commonly used in various organic syntheses. Finding of such new fundamental properties would open up new area in chemistry.

Oxidation state of the transition metal plays an important role in chemical reactivity of organotransition metal complex.

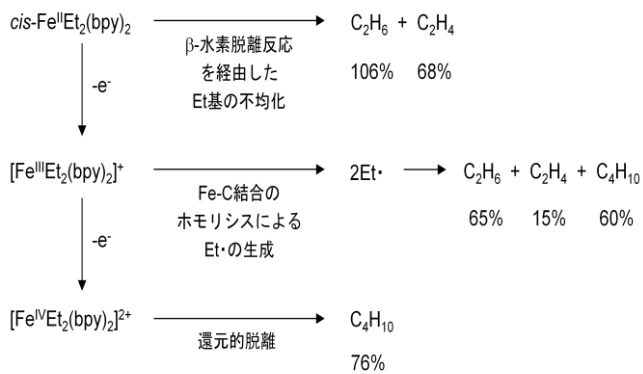
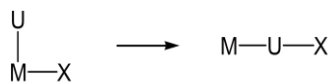


図3-16 金属の酸化数に依存したジエチル鉄錯体の分解経路

(4) Insertion Reaction



U = CO, C₂H₄, C₂R₂, NO, CR₂, CNR, RCN, O₂, CO₂

X = H, alkyl, aryl, OR, NR₂

図3-17 M-X結合への不飽和化合物Uの1, 1および1, 2挿入反応

4-1 CO Insertion mechanism in Mn-Me bond: alkyl migration

Principle of microscopic reversibility in chemical reaction: Forward and reverse reactions must have the same transition state.----Analysis of reverse reaction (de-insertion) gives information of transition state of insertion reaction.

(Similar fact is observed when you hike in the mountain. When one goes from one place to other place which locates over the mountain, easiest pathway (low energy path) is going the lowest mountain pass. On the way back to the original place, the same route is the easiest pathway (low energy path). The easiest pathway is like activation energy for chemical reaction.)

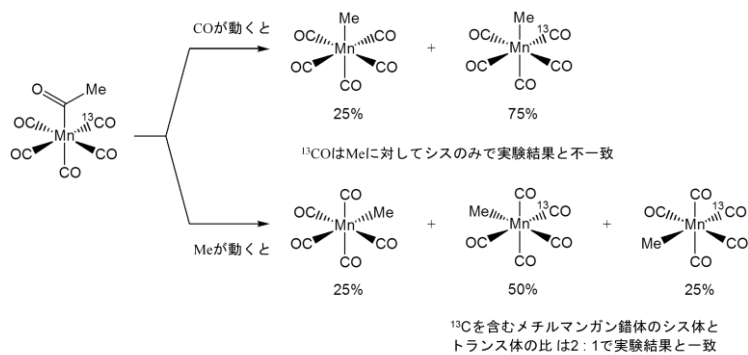


図3-18 Me移動によるMnCMeの脱カルボニル化

3-2 Another example of alkyl migration

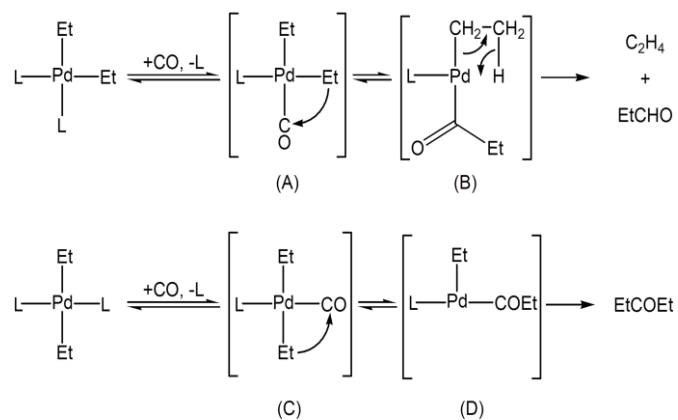


図3-19 シスおよびトランス-ジエチルパラジウム錯体のCO挿入反応

3-3 CO can insert in the CO insertion.

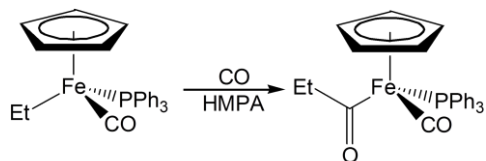


図3-20 COが移動する挿入反応

3-4 CO Insertion of early transition metal complex gave unusual reactivity.

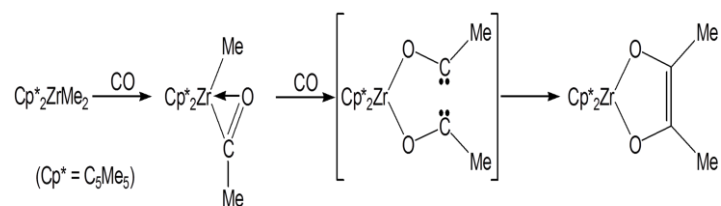


図3-21 前周期遷移金属錯体における特異なCO挿入反応

3-5 Olefin insertion into M-H bond: Peri-syn-planar transition state

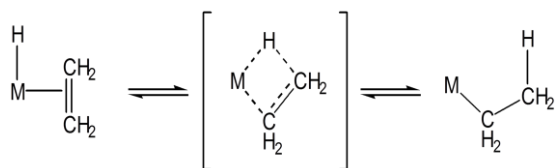


図3-22 エチレンの金属ヒドリド結合への挿入

3-6 Interesting reactivity change in Ni complex

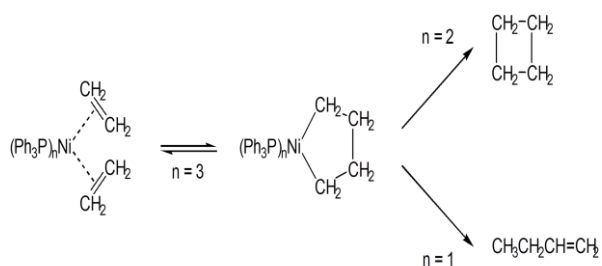


図3-24 配位数で制御されたニッケラシクロペンタンの反応

3-6 When all β -hydrogen atoms are replaced by Me, new reaction takes place:

α -hydrogen elimination

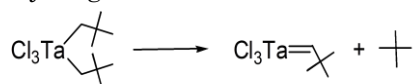


図3-25 α 水素脱離によるSchrock型カルベン錯体の生成

3-7 Acetylene also inserts to M-H bond: stereochemistry?

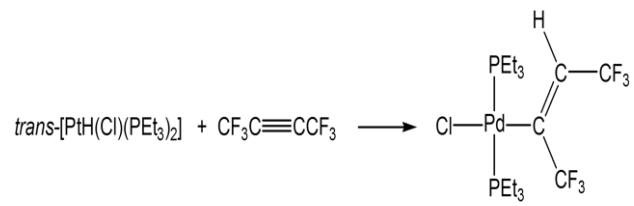


図3-26 遷移金属ヒドリド結合へのアルキンのシス挿入

3-8 Insertion of diene into M-H bond.

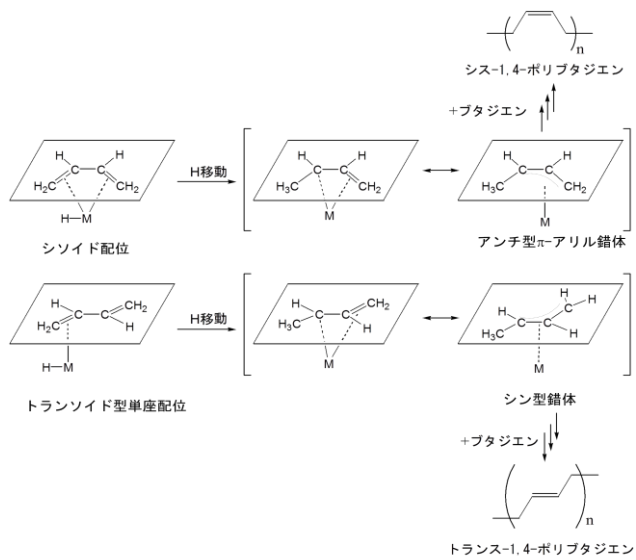


図3-27 遷移金属ヒドリド結合へのジエンの挿入

(4) Reaction of Coordinated Ligands

Coordinated ligands show different chemical reactivity depending on transition metal (electronic and steric effects).

4-1 How to control the property of coordinated olefins?

Nucleophile generally does not react with electron rich unsaturated molecules such as olefin. But nucleophile can attack the coordinated ethylene carbon from opposite side of high-valent transition metal. Why?

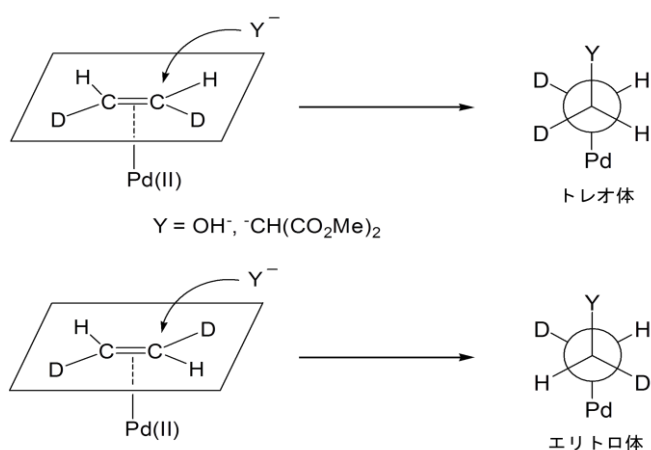


図3-28 Pd(II)に配位したエチレンへの求核試薬の反応の立体化学

What if it reacts directly with transition metal?

Allyl ligands show similar reaction pattern.

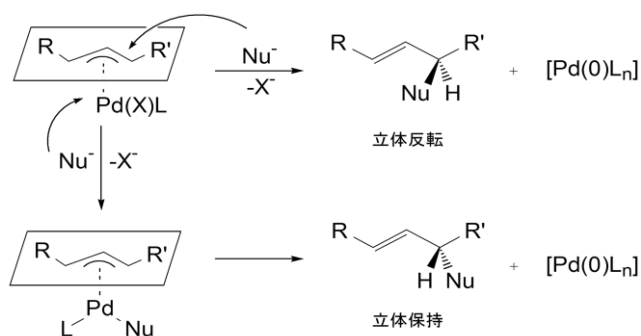


図3-11 π-アリルパラジウム錯体への求核
反応の立体化学

4-2 Carbonyl ligand has different chemical property from free carbon monoxide.

From CO to Me⁺---Model Reaction for Fischer Tropsch Hydrocarbon Synthesis

SASOL(South Africa): Fe-based catalysis for production of oil from coal (CO/H₂)

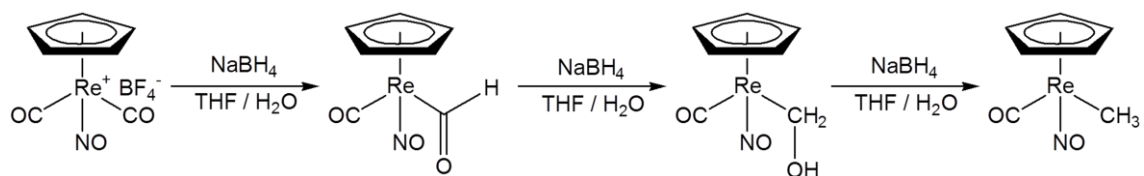


図3-30 配位カルボニルの段階的ヒドリド還元

II Transition Metal Complex-Mediated Catalyses and Organic Reactions

(1) Homogeneous Catalysis and Heterogeneous Catalysis

表4-1 均一系触媒と不均一系触媒

	均一系	不均一系
反応相	液相	気相／液相
温度	低い (200 °C以下)	高い (250–550°C)
形体	可溶性遷移金属錯体	金属又は金属酸化物／担体
熱的安定性	低い (200 °C以下)	高い
活性	低い	高い
選択性	高い	低い
触媒分離	困難	容易
反応機構研究	分子レベル	マクロ的, 速度論

表4-2 反応機構を考える際に役立つ概念

機能	概念
触媒の活性化	配位不飽和、酸化的付加
金属中心での反応	アルキル移動 / 移動挿入 求核的、求電子的付加と引抜き
生成物の脱離	還元的脱離、β-脱離

(2) Catalysis of Alkene

(2-1) Hydrogenation of Alkene

Dihydride Mechanism

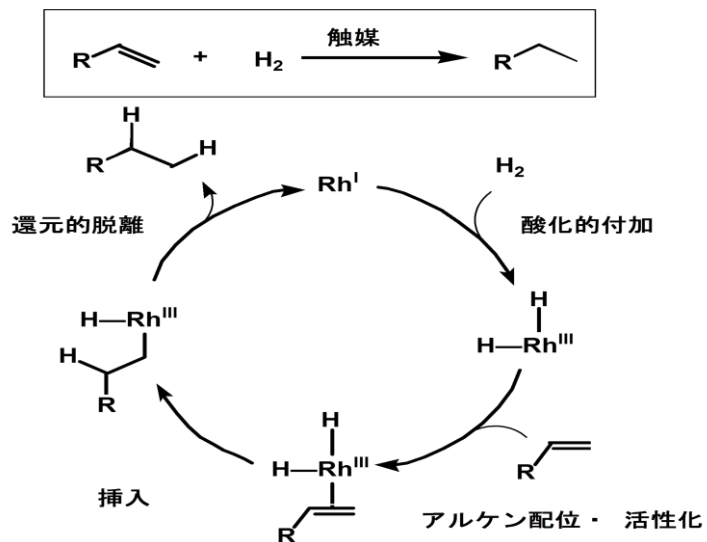
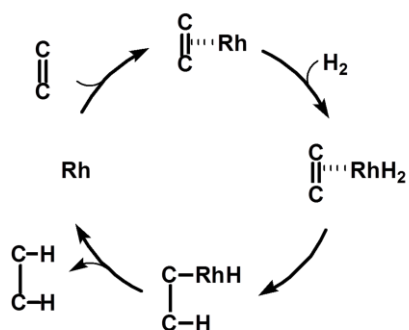


図4-1 水素化

■ ジヒドリド機構



■ モノヒドリド機構

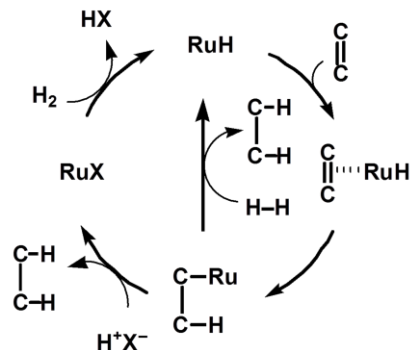


図4-5 モノヒドリドとジヒドリド機構

(2-2) Isomerization of Alkene (Double bond shift)

Insertion Mechanism

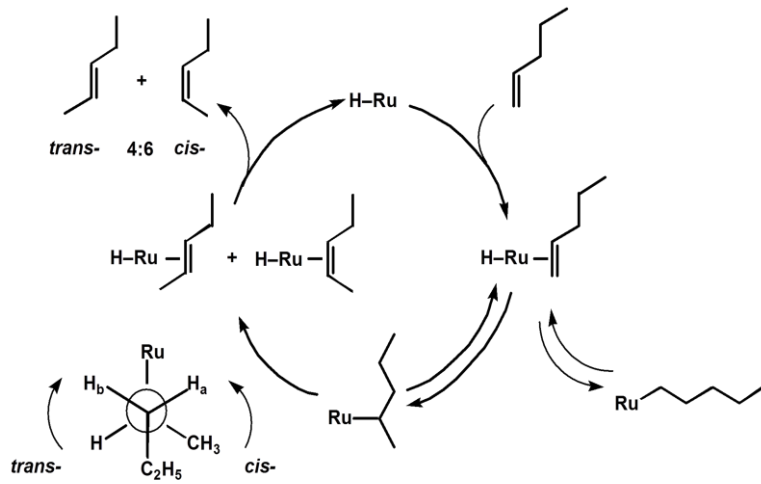


図4-2 アルケンの異性化

π -Allyl Mechanism

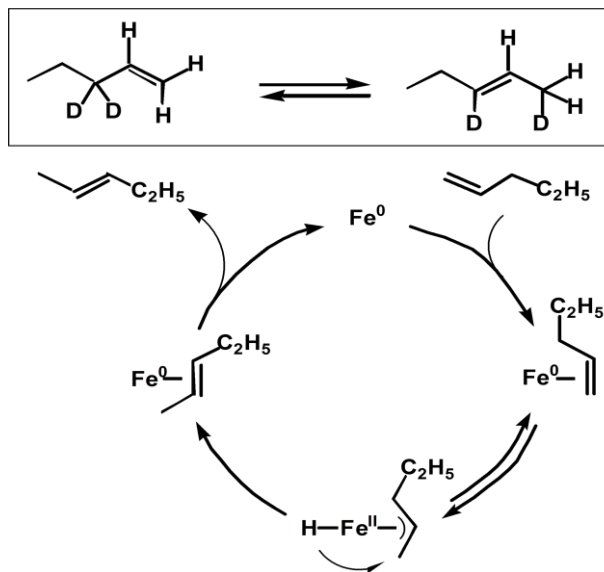


図4-3 π アリル中間体を経るアルケンの異性化反応

(2-3) Polymerization

1. Ziegler-Natta Catalyst

How Ziegler catalyst was found? Lazy student's contribution is important.

Secret story of new finding:-----, and Natta's contribution to polypropylene. Nobel prize was give to Ziegler and Natta.!

Polypropylene by Ziegler catalyst was highly crystalline material with high melting point and was easy to mold and dye. Many application in daily life such as blue plastic bucket etc. Microstructure of the polypropylene was found to be isotactic by NMR!

Cossee機構

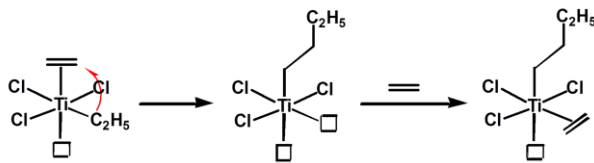
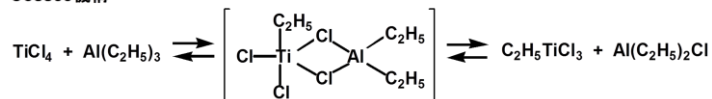


図4-7 Ziegler-Natta触媒によるアルケンの重合

2. Kaminsky catalyst: A trace of water impurity gives alumoxane.

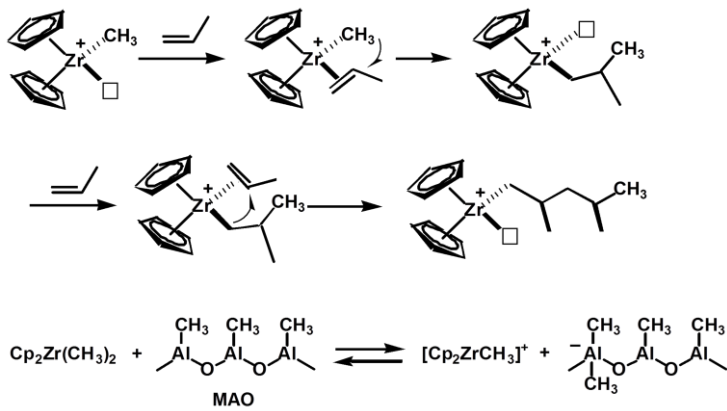


図4-8 Kaminsky触媒による立体規則重合

(2-4) Oligomerization

1. Dimerization of Alkene

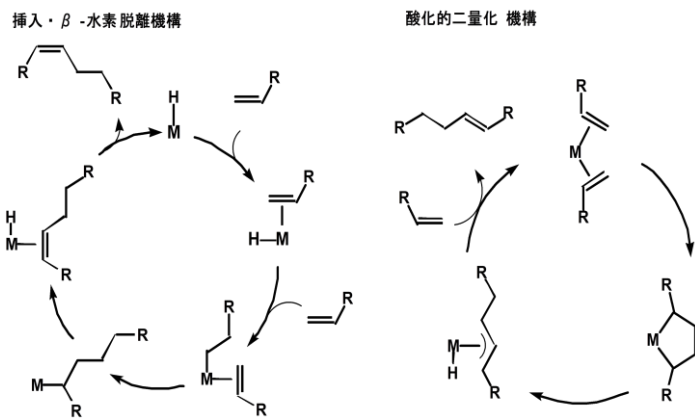


図4-10 アルケンの二量化

2. Trimerization of Butadiene giving Cyclododecatriene

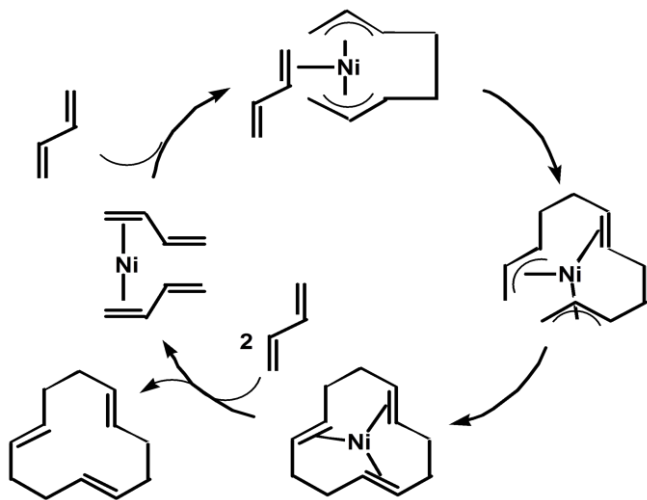


図4-12 ニッケル触媒によるブタジエンの三量化

Active nickel catalyst has no stabilizing ligand such as tertiary phosphine: Wilke was a person who introduced sex in catalysis.

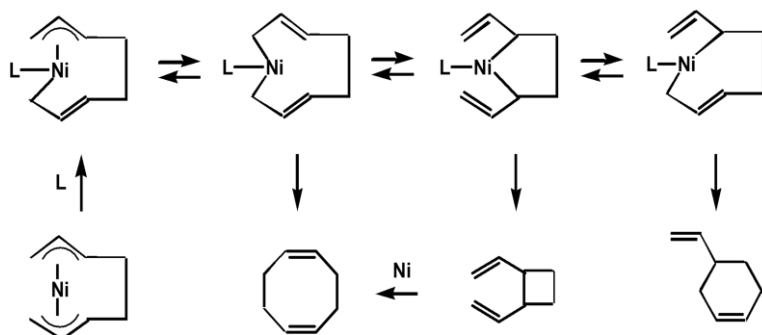


図4-13 ブタジエンの二量化

Dimerization mechanism was shown as if you can see the changing butadiene molecules on nickel active intermediate.

(2-5) Olefin Metathesis Reaction

Strong C=C double bond was easily cleaved on W complex, but how?

Symmetry forbidden cyclobutane mechanism to carbene mechanism.

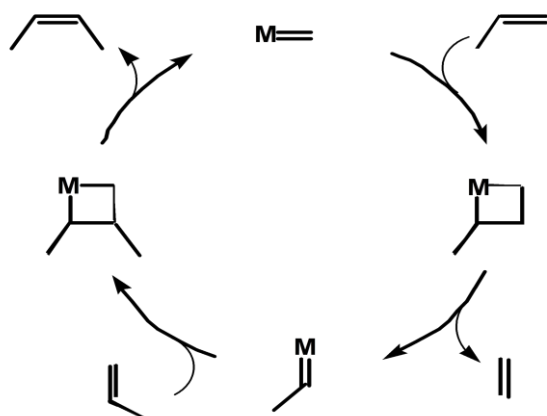
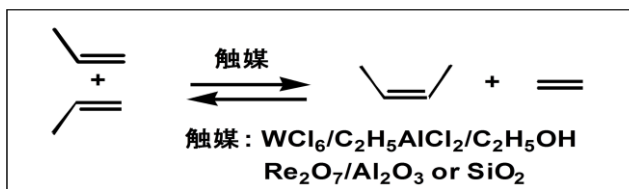


図4-15 アルケンのメタセシス反応

(3) Catalysis using CO

(3-1) Hydroformylation (Oxo process)

ブチルアルデヒド合成

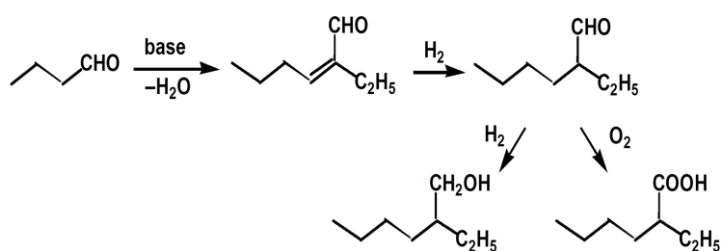
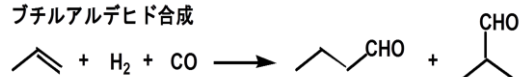


図4-16 プロピレンのヒドロホルミル化

Mechanism:

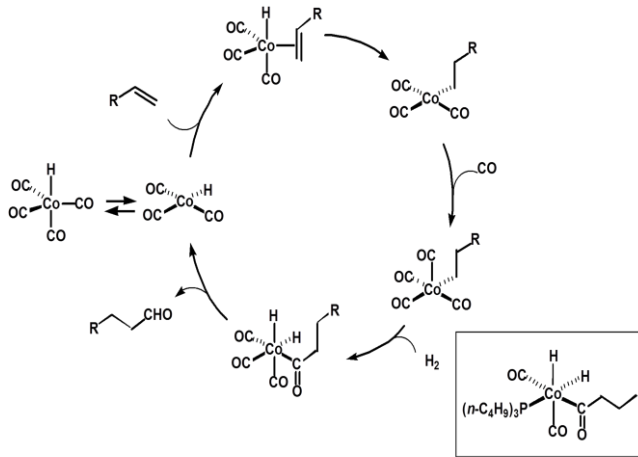


図4-17 コバルト触媒によるアルケンのヒドロホルミル化

Group 9 transition metals such as Co and Rh show high catalytic activity in combination with tertiary phosphine ligands.

Many applications:

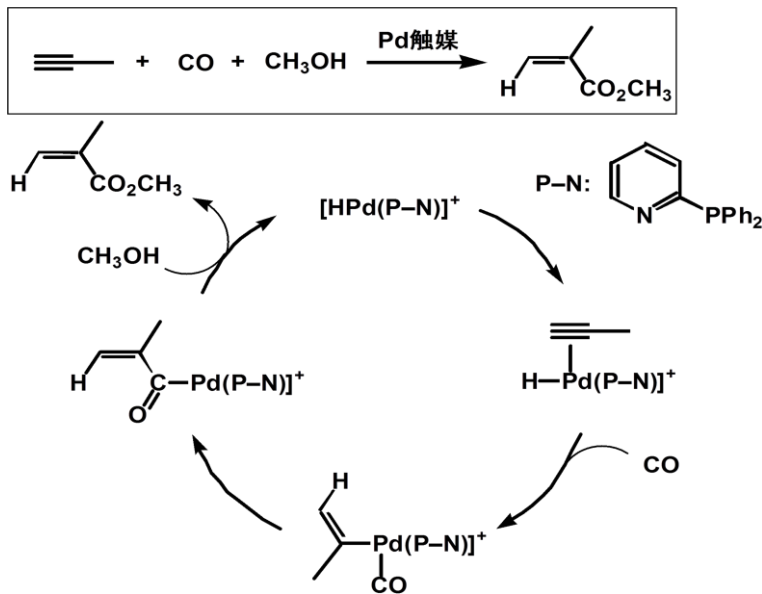


図4-19 メチルアセチレンのカルボニル化反応

(4) Role of transition metal catalysts in industrial acetic acid synthesis.

Acetic acid is one of the most important chemicals and was produced by (destructive distillation of coal. History of acetic acid production revealed importance of transition metal catalysts.

(4-1) Hydration of acetylene---Mercury catalyst was excellent but caused fatal environmental pollution, Minamata disease.

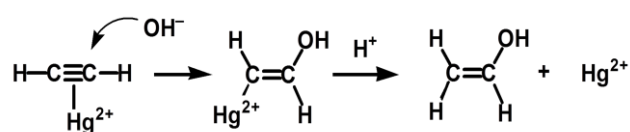
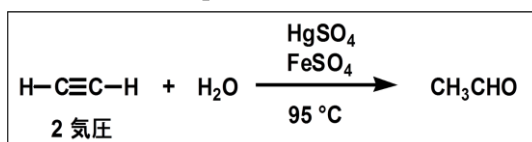


図4-21 アセチレンの水和反応

(4-2) Wacker Oxidation (Pd catalyst)

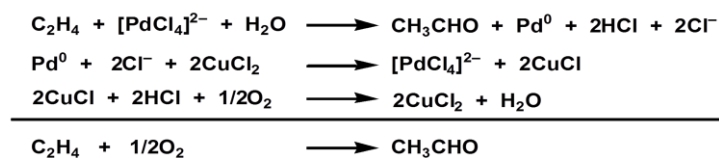


図4-22 パラジウム触媒によるエチレンのワッカー型酸化反応

Key step: nucleophilic attack of water (OH⁻) to the coordinated ethylene.

Reactivity change of ethylene on coordination to high-valent palladium metal.

Oil shock came to warn to use too much oil-----New procedure without alkene.

The reaction is very important oxidation reaction to produce aldehyde from alkene.

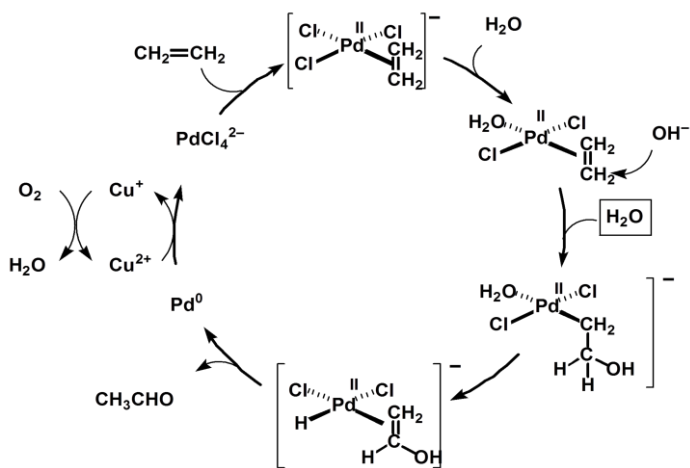


図4-23 ワッカー反応の触媒サイクル

(4-3) Monsanto Synthesis: acetic acid synthesis from methanol and CO by Rh catalyst

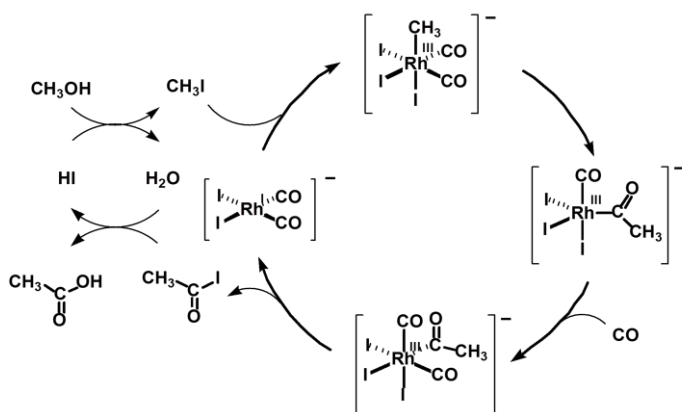


図4-24 ロジウム触媒によるメタノールのカルボニル化による酢酸合成

(5) C-C Bond Coupling Reaction

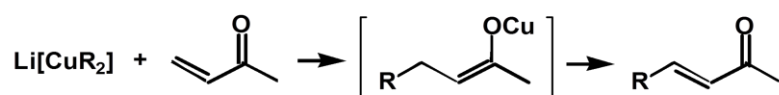
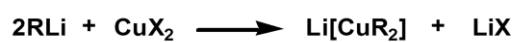
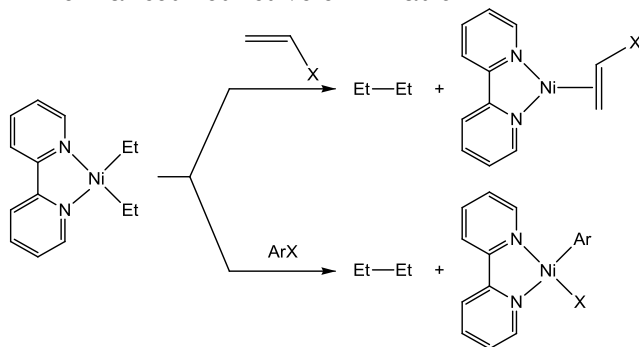


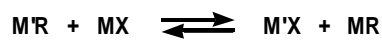
図5-1 有機銅アート錯体による炭素-炭素結合形成反応

Dr. Tamao's inspiration!!!

ArX enhanced reductive elimination



Transmetalation



$\text{M}' = \text{Li, Mg, Zn, Sn, Hg, B, Si, Ge, Al, Zr(IV)}$

$\text{M} = \text{遷移金属}$

Ni complex must be a good catalyst for cross coupling reaction of ArX and Grignard reagent!!!! -----Nobel prize of Suzuki and Negishi

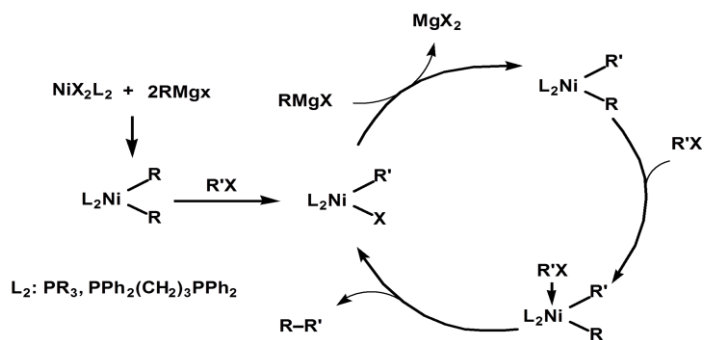


図5-4 ニッケル触媒によるクロスカップリング反応

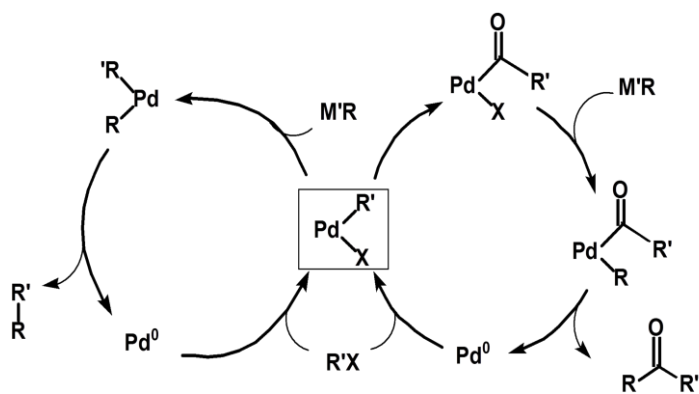
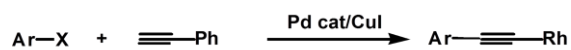
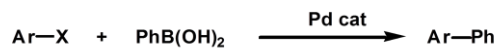


図5-5 パラジウム触媒による炭素-炭素結合形成反応

■ 菌頭反応



■ 鈴木-宮浦反応



■ 小杉-右田-Stille 反応

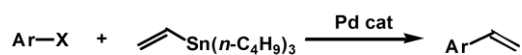


図5-6 パラジウム触媒によるクロスカップリング反応

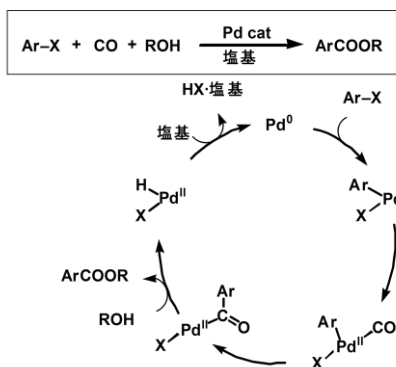


図5-7 パラジウム触媒によるハロゲン化物のカルボニル化反応

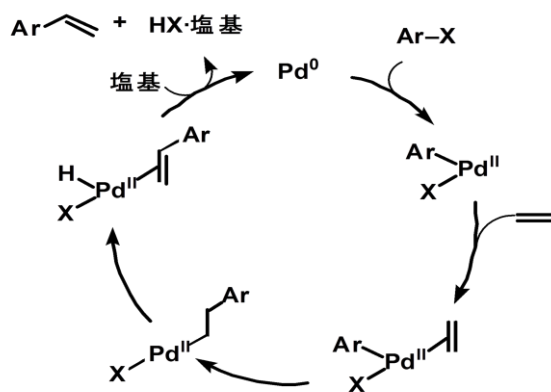
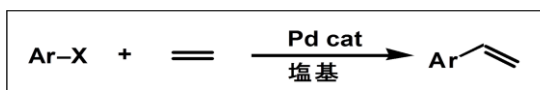
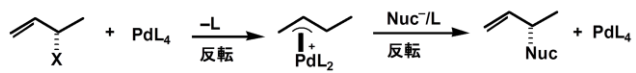


図5-8 溝呂木—Heck反応



$X = \text{Br, Cl, OAc, OCOOR, OPh, N}^+\text{R}_3, \text{SO}_2\text{Ph}$
 $\text{Nuc}^- = \text{CH}(\text{CO}_2\text{R})_2, \text{CH}(\text{COR})(\text{CO}_2\text{R}), \text{CH}(\text{COR})_2, \text{CH}(\text{SO}_2\text{Ph})(\text{CO}_2\text{R})$

図5-10 パラジウム触媒によるアリル化反応