Organometallic compounds-IV

Organometallic Reactions and Catalysis

PG Semester I

Gauhati University

Lecture: 12, 13, 14, 15

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Contents

- Reactions of organometallic complexes
    - Ligand Substitution (dissociation/association)
    - Oxidative addition
    - Reductive elimination
    - Insertion and de-insertion
- Catalysis
    - Hydrogenation
    - Hydroformylation
    - Monsanto process
    - Wacker process
    - Alkene polymerization (Ziegler-Natta Catalyst)
    - Olefin metathesis
    - Suzuki coupling reaction

Reaction chemistry of complexes

Three general forms:

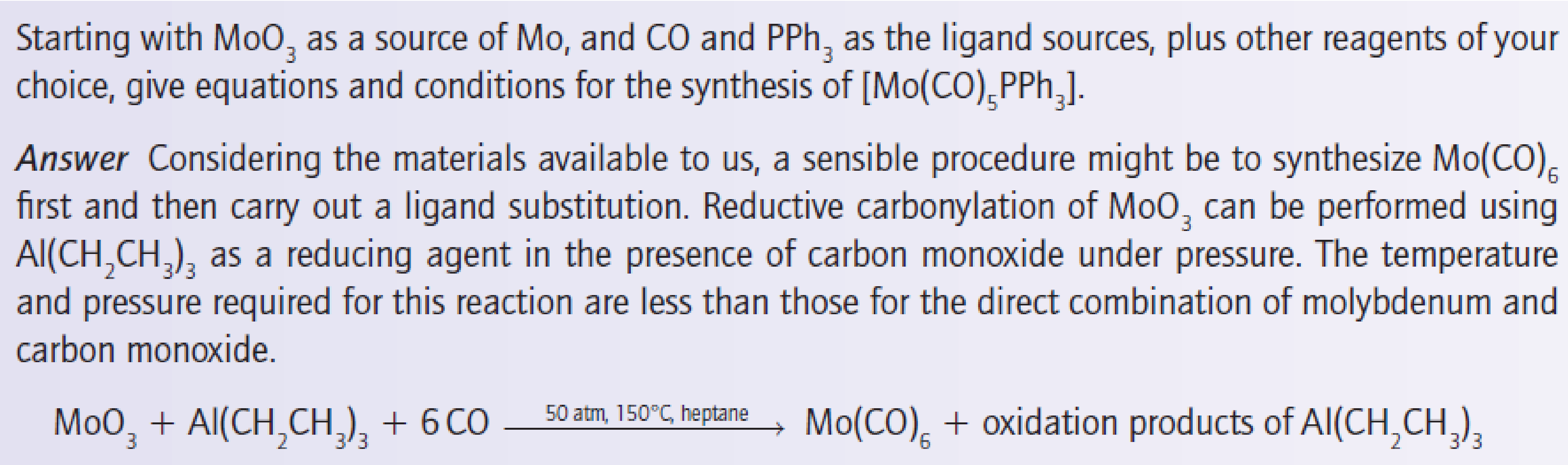
1. Reactions involving the gain and loss of ligands
    - a. Ligand Dissociation and Association
    - b. Oxidative Addition
    - c. Reductive Elimination
    - d. Nucleophilic displacement
2. Reactions involving modifications of the ligand
    - a. Insertion
    - b. Carbonyl insertion (alkyl migration)
    - c. Hydride elimination (equilibrium)
3. Catalytic processes by the complexes
    - a. Wilkinson, Monsanto
    - b. Carbon-carbon bond formation (Heck etc.)

Ligand Substitution (dissociation/association)

- Ligand substitution in organometallic complexes is similar to that of coordination complexes, with the restriction of maximum valence electron count of 18e
- Reactions can proceed via a dissociative, an associative, or an interchange pathway
- The replacement of CO by phosphine (electron donor ligand), possibly a dissociatively activated substitution.
- Associative activation require reaction intermediates with greater than 18e (not favourable)
- 16e organometallic compounds undergo associatively activated substitution because the 18e activated complex is energetically more favorable than 14e activated complex that occur in dissociative activation.
- The reactions of $[Ir(CO)Cl(PPh_3)_2]$ with PEt_3 are associatively activated

$$[Ir(CO)Cl(PPh_3)_2] + PEt_3 \rightarrow [Ir(CO)Cl(PPh_3)_2(PEt_3)] \rightarrow [Ir(CO)Cl(PPh_3)(PEt_3)] + PPh_3$$

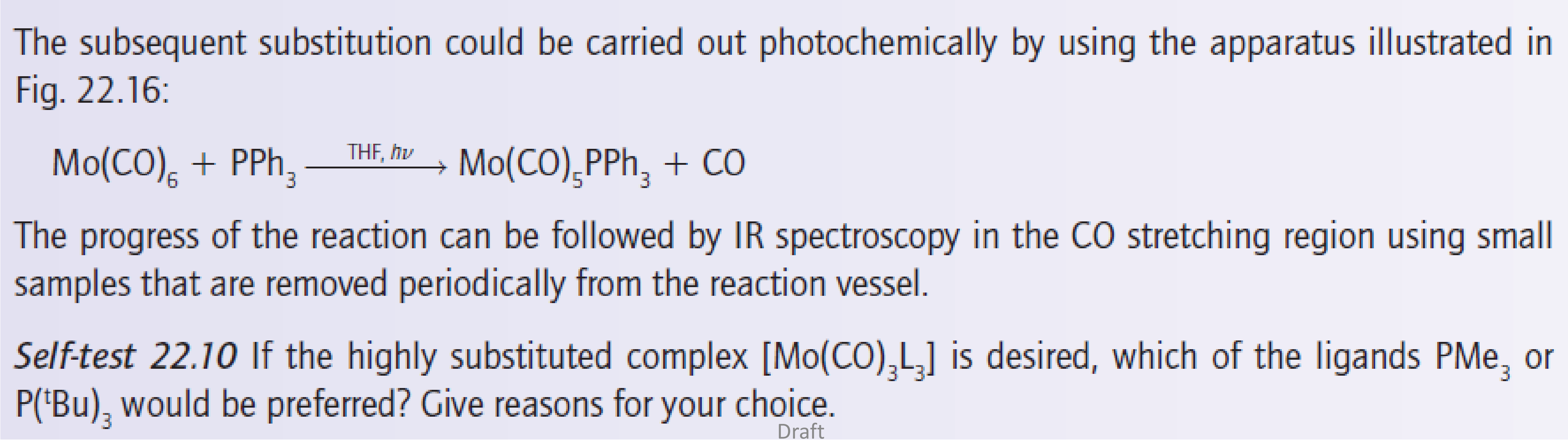
- Steric crowding between ligands to accelerate dissociative processes and to decrease the rates of associative processes
- The extent to which ligands crowd each other is approximated by the Tolman cone angle.
- Higher the cone angle (for bulky substituent) higher is the dissociation
- Electron count changes by -/+ 2 with no change in oxidation state
- Rate of CO substitution in six-coordinate metal carbonyls often decreases as more strongly basic ligands replace CO.
- With bulky PR_3 ligands, further substitution may be thermodynamically unfavorable due to ligand crowding.
- Increase in electron density on the metal center due to replacement of π-acceptor ligand by a donor ligand (such as PR_3) leads to stronger binding of the remaining CO ligands & thereby reducing the rate of CO dissociative substitution.
- The second carbonyl that is replaced is normally *cis* to the site of the first and that replacement of a third carbonyl results in a *fac*-complex. The reason for this regiochemistry is that CO ligands have very high *trans* effects.



Starting with MoO_3 as a source of Mo, and CO and PPh_3 as the ligand sources, plus other reagents of your choice, give equations and conditions for the synthesis of $[Mo(CO)_5PPh_3]$.

Answer Considering the materials available to us, a sensible procedure might be to synthesize $Mo(CO)_6$ first and then carry out a ligand substitution. Reductive carbonylation of MoO_3 can be performed using $Al(CH_2CH_3)_3$ as a reducing agent in the presence of carbon monoxide under pressure. The temperature and pressure required for this reaction are less than those for the direct combination of molybdenum and carbon monoxide.

$$MoO_3 + Al(CH_2CH_3)_3 + 6\,CO \xrightarrow{\text{50 atm, 150°C, heptane}} Mo(CO)_6 + \text{oxidation products of } Al(CH_2CH_3)_3$$



The subsequent substitution could be carried out photochemically by using the apparatus illustrated in Fig. 22.16:

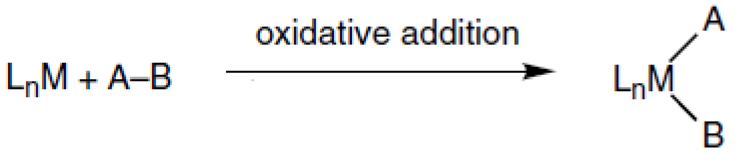
$$Mo(CO)_6 + PPh_3 \xrightarrow{\text{THF, } h\nu} Mo(CO)_5PPh_3 + CO$$

The progress of the reaction can be followed by IR spectroscopy in the CO stretching region using small samples that are removed periodically from the reaction vessel.

Self-test 22.10 If the highly substituted complex $[Mo(CO)_3L_3]$ is desired, which of the ligands PMe_3 or $P(^tBu)_3$ would be preferred? Give reasons for your choice.

Oxidative addition

- ➢ Addition of ligands (increase in CN. by 2) is accompanied by oxidation of the metal (by 2)

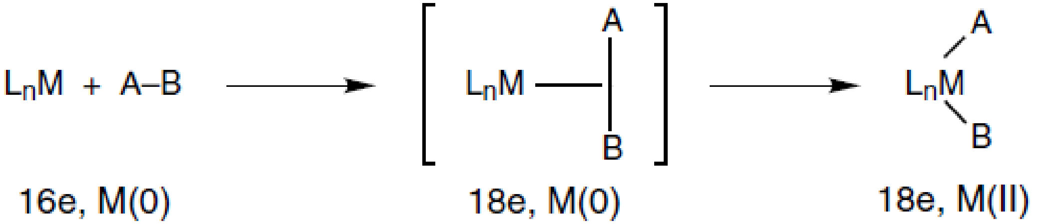


- ➢ In addition of AB to a metal atom, A-B bond should be weak enough to get cleaved and, both A and B are more electronegative than the metal (cis addition)
- ➢ d-electron count is reduced by two
- ➢ A σ-complex or TS (slow) is believed to form followed by electron transfer from the *d*-metal orbital into the antibonding σ*orbital of A-B initiates the cleavage of A-B bond (fast)

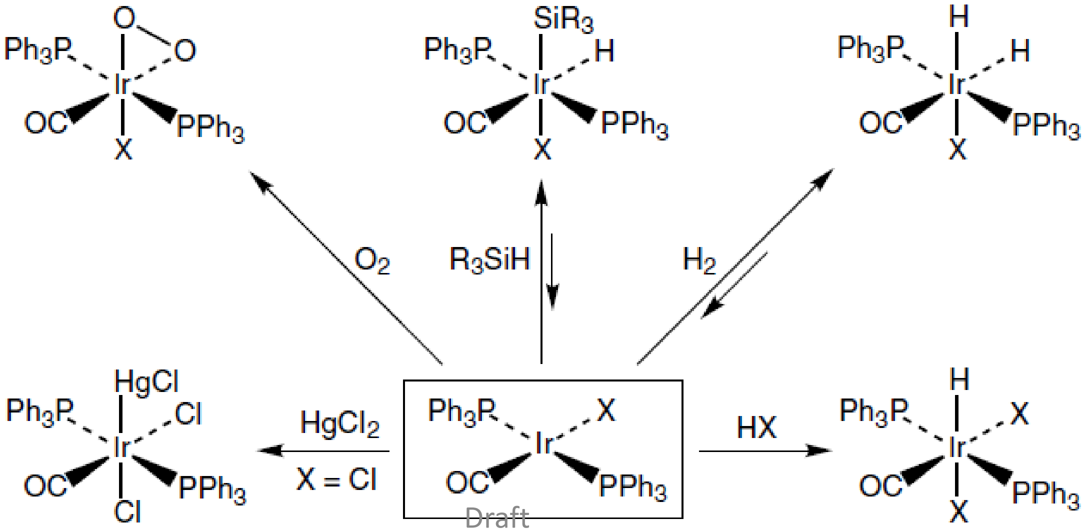
Requirements for oxidative addition

- ➢ Low OS of metal (electron rich/occupied) and stability of OS separated by two units (higher OS must be energetically accessible and stable)
- ➢ Two vacant coordination sites on metal (coordinatively unsaturated).
- ➢ Suitable orbitals available for bonding (must have non bonding electron pair).

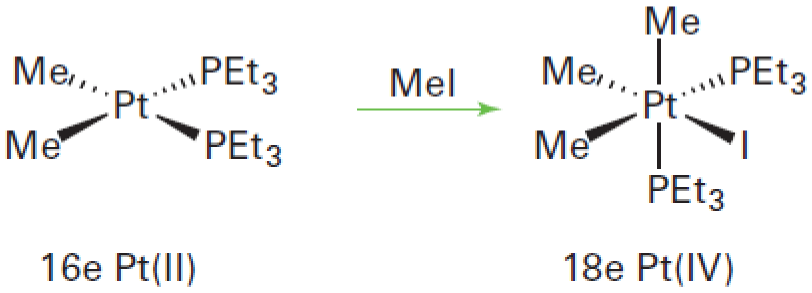
- Mechanism for oxidative addition vary according to the nature of A-B.
- If A-B in non polar like H_2, a concerted reaction leading to a three centered TS is most likely



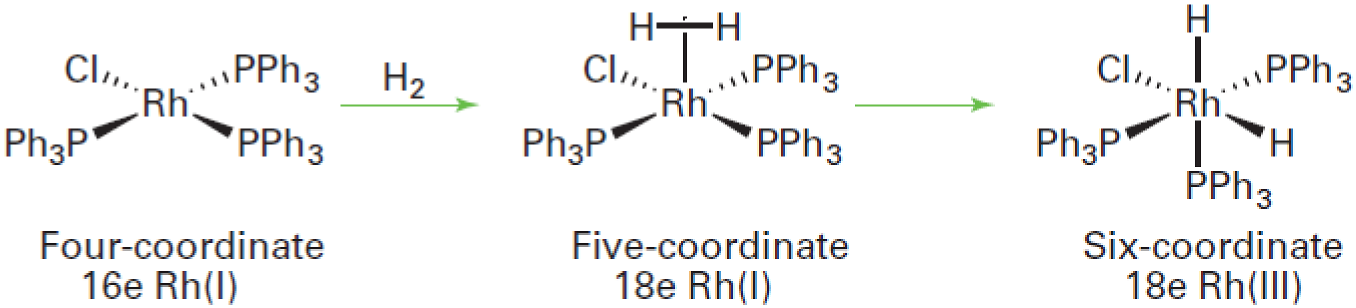
- Vaska’s complex (OS +1 → +3 & CN 4 → 6) undergoes several oxidative addition
- O_2 adds reversibly to Vaska’s complex, A-B bond is not broken, BO is reduced from 2 to 1
- If A-B is an electrophilic polar molecule such as CH_3I, oxidative addition tends to proceed via SN_2 mechanism involving 2e transfer or via radical via 1e transfer



- Oxidative addition reactions are particularly common for 16e square-planar metal complexes

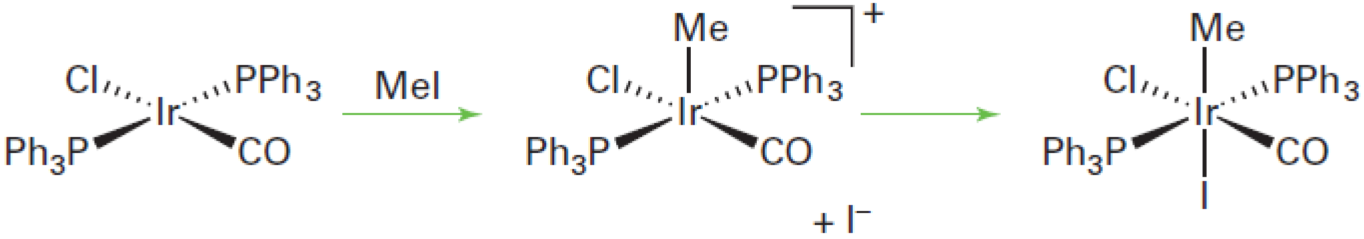


- The oxidative addition of hydrogen is a concerted reaction: dihydrogen coordinates to form a σ-bonded H_2 ligand, and then back bonding from the metal results in cleavage of the H-H bond and the formation of *cis* dihydrides



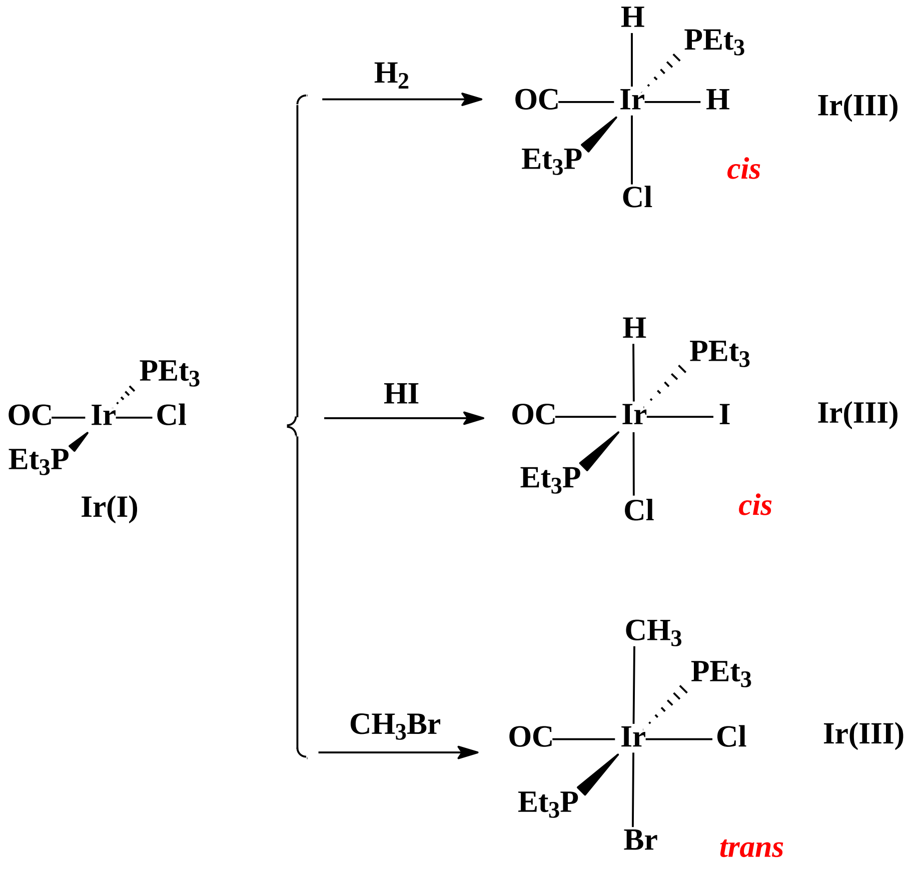
- Other molecules, such as alkanes and aryl halides, are known to react in a concerted fashion, and in all these cases the two incoming ligands end up *cis* to each other.

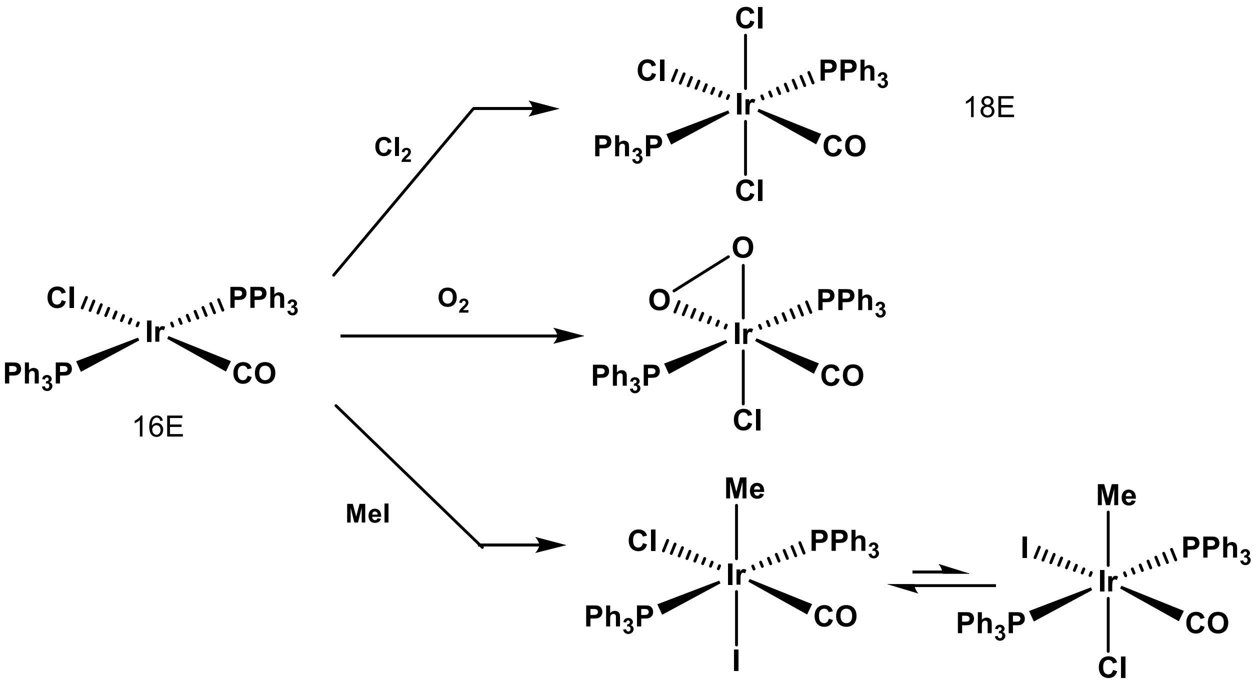
- All oxidative addition are not concerted, and either go through radical intermediates or as SN_2 displacement reactions.
- Radical oxidative addition reactions are rare.
- In an SN_2 oxidative addition reaction, a lone pair on the metal attacks the AB molecule displacing B (say), which subsequently bonds to the metal:



- There are two stereochemical consequences of this reaction.
- First, the two incoming ligands need not end up *cis* to each other
- Second, unlike the concerted reaction, any chirality at the A group is inverted.
- An SN_2-type oxidative addition is common for polar molecules such as alkyl halides
- Ease of oxidation (from d^8 to d^6), increases down the triad

Oxidative addition : Cis or trans?

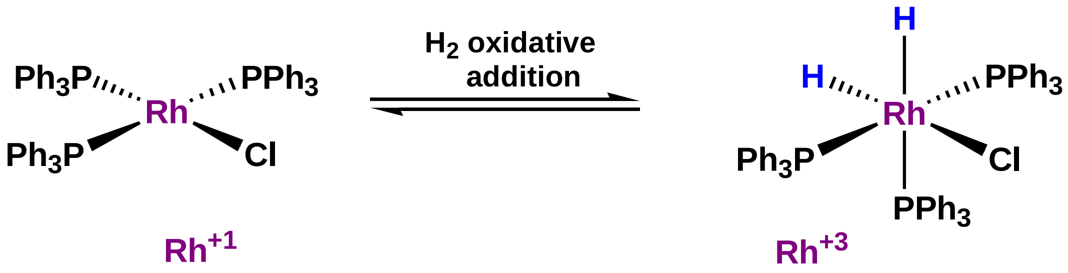




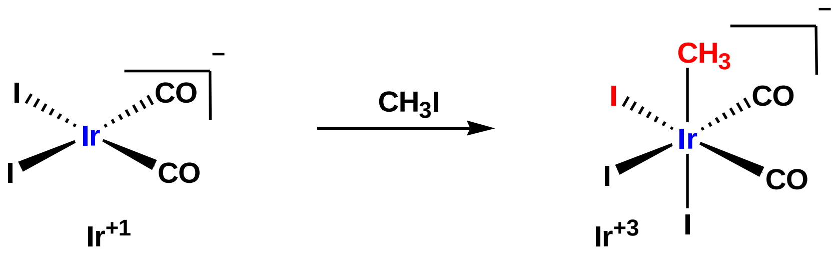
- ➢ Homonuclear systems (H_2, Cl_2, O_2, C_2H_2) Cis
- ➢ Heteronuclear systems (MeI) Cis or trans

An important step in many homogeneous catalytic cycles

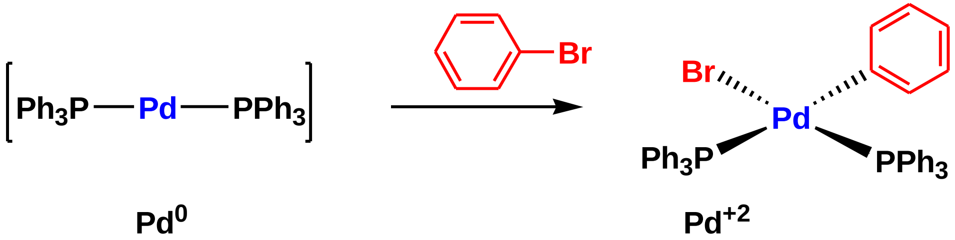
1. Hydrogenation of alkenes- Wilkinson catalyst



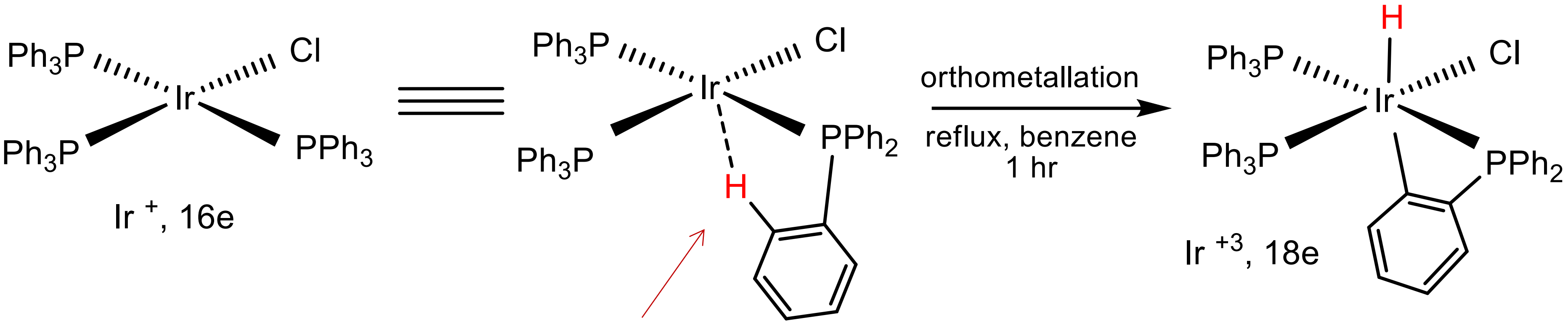
2. Methanol to acetic acid conversion-Cativa process



3. Pd catalyzed Cross coupling of Ar-B(OH)$_2$ and Ar-X–Suzuki Coupling



Oxidative addition involving C-H bonds and cyclo/orthometallation

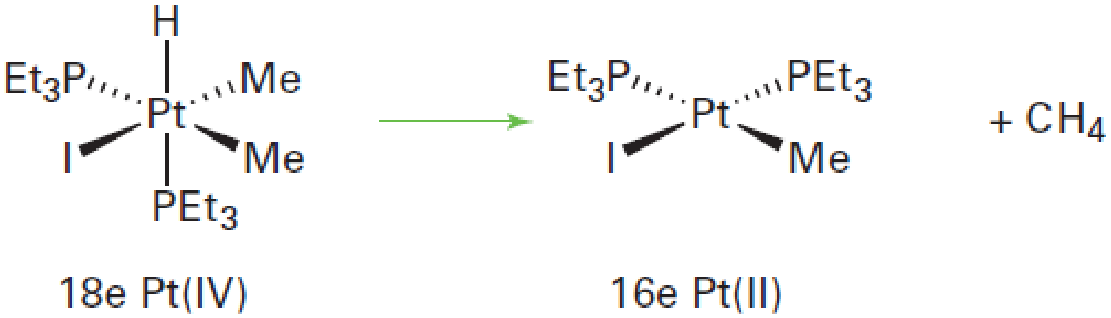


Agostic interaction (bivalent-H type)

- This type of reactions help to activate unreactive hydrocarbons such as methane - known as C-H activation
- H_2 is even also capable of nonclassical coordination to a metal (incomplete rapture of H-H bond)

Reductive elimination

- It is the reverse of oxidative addition.
- Two ligands couple and get eliminated from a metal center
- Oxidation state and coordination of metal decreases by 2 units
- Usually *cis* elimination takes place
- The concerted three-center mechanism is the most common.

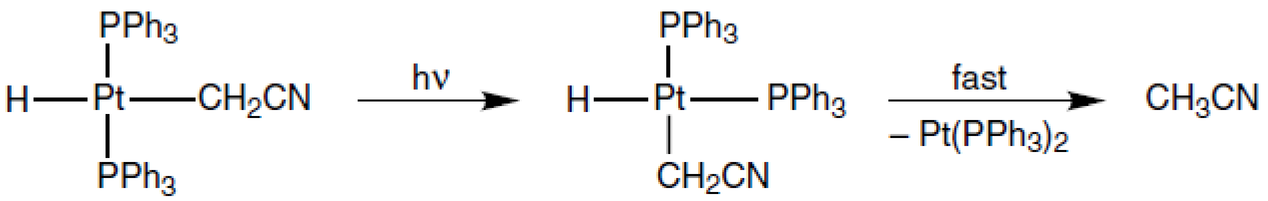


- Most facile for 3d-trandition metals (weak M-C bond, are smaller size results in pronounced steric effect), preferably late TM

Factors which facilitate reductive elimination

- A high formal positive charge on the metal (electron poor),
- The presence of bulky groups on the metal, and
- Both eliminating fragments/ligands to be *cis* to each other
- Facile if one of the ligand is H

- The two A and B ligands must be located in *cis* position in order to undergo the reductive elimination.

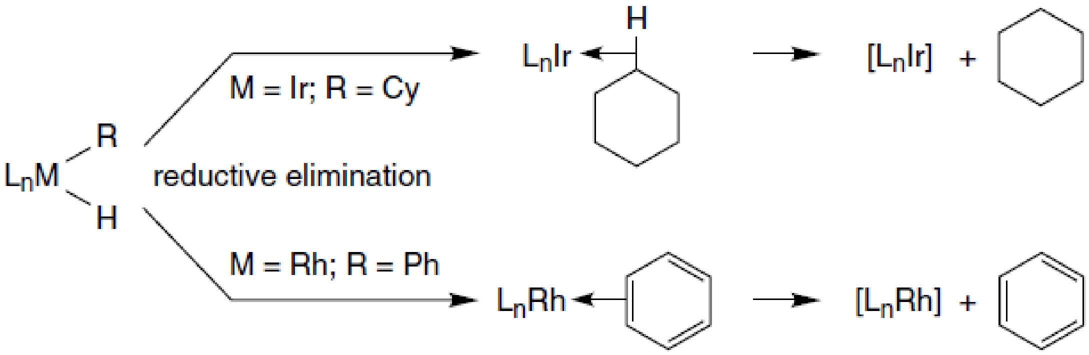


$$H{-}Pt(PPh_3)_2{-}CH_2CN \xrightarrow{h\nu} H{-}Pt(PPh_3)(PPh_3)(CH_2CN) \xrightarrow[-\,Pt(PPh_3)_2]{\text{fast}} CH_3CN$$

- Reductive elimination is favored by high oxidation states of the metal that can eventually be reached by oxidation

$$[Fe^{II}(bipy)_2Et_2] - 2\,e \longrightarrow [(Fe^{IV}(bipy)_2Et_2]^{2+} \longrightarrow n\text{-}C_4H_{10} + [(Fe^{II}(bipy)_2]^{2+}$$

- The reductive elimination from metal-alkyl-hydride complexes $L_nMR(H)$ (M=Ir, R= Cy or M=Rh, R=Ph) giving the alkane or arene occurs with inverse kinetic isotope effects which were taken into account by a preequilibrium with the - alkane or 2-arene complex.



Reductive elimination reactions involving the intermediacy of a σ-alkane or η^2-arene complex

- ➢ Radical mechanisms are also found in reductive elimination. An important example is the radical-chain mechanism of the dehydrogenation of cobalt carbonyl hydride.

$$2\,[HCo(CO)_4] \longrightarrow [Co_2(CO)_8] + H_2$$

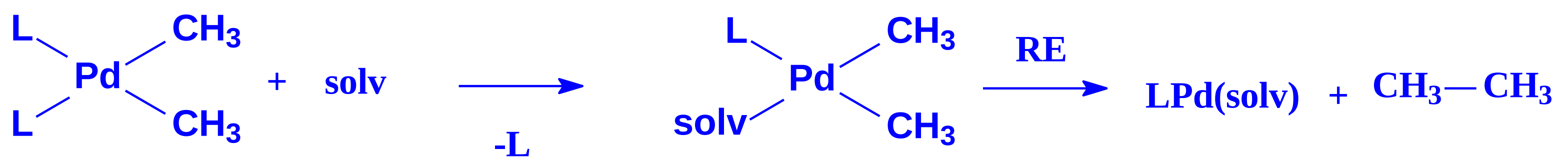
- ➢ The number of carbonyl atoms on cobalt being uncertain, the CO ligands are not represented in the following mechanistic scheme of the reductive elimination:
- ➢ The reductive elimination will most often be found in Part IV as the last step (irreversible) of catalytic mechanism

initiation: $$CoCo \rightleftharpoons 2\,Co^{\bullet}$$

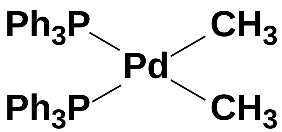
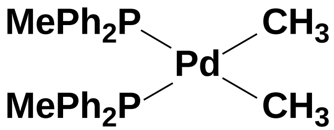
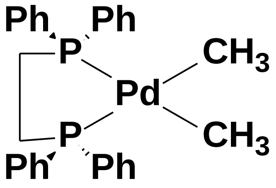
propagation: $$Co^{\bullet} + HCo \longrightarrow HCoCo^{\bullet}$$

$$HCoCo^{\bullet} + HCo \longrightarrow HCoCoH + Co^{\bullet} \xrightarrow{-H_2} CoCo \rightleftharpoons 2\,Co^{\bullet}$$

- Rate depends strongly on types of groups to be eliminated.



Relative rates of reductive elimination

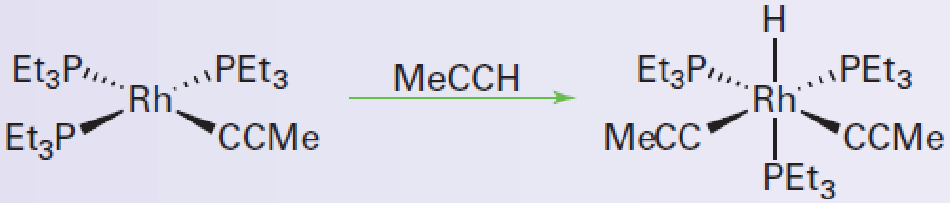
Complex	Rate Constant (s^{-1})	T(^oC)
	1.04×10^{-3}	60
	9.62×10^{-5}	60
	4.78×10^{-7}	80

Most crowded is the fastest reaction

RE is often assisted and accelerated by the addition of pi-acceptor such as olefines, acetylenes

EXAMPLE 22.12 Identifying oxidative addition and reductive elimination

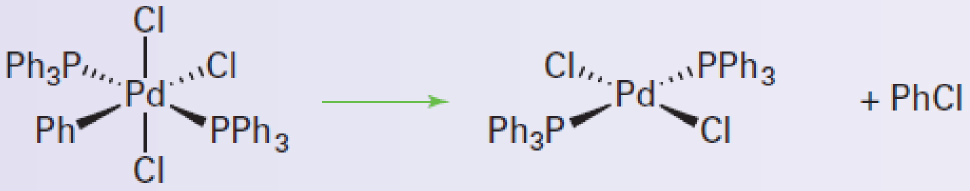
Show that the reaction



is an example of an oxidative addition reaction.

Answer In order to identify an oxidative addition reaction, we need to establish the valence electron counts and oxidation states of both the starting material and the product. The four-coordinate square-planar Rh starting material contains an η^1-alkynyl ligand as well as three neutral phosphine ligands; it is therefore a 16-electron Rh(I) species. The six-coordinate octahedral product contains two η^1-alkynyl ligands, a hydride ligand, and three neutral phosphine ligands; it is therefore an 18-electron Rh(III) species. The increase in both coordination number and oxidation number by 2 identifies it as an oxidative addition.

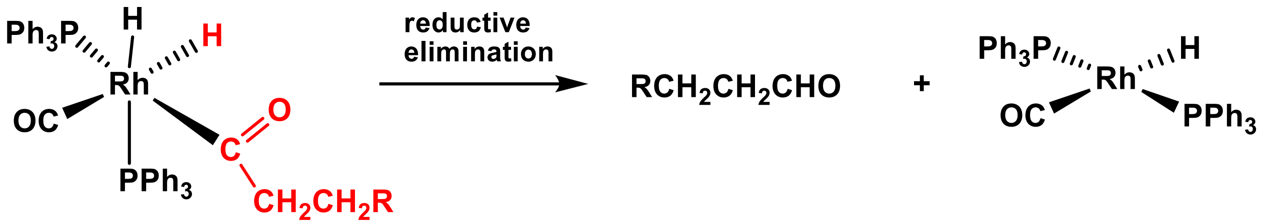
Self-test 22.12 Show that the reaction:



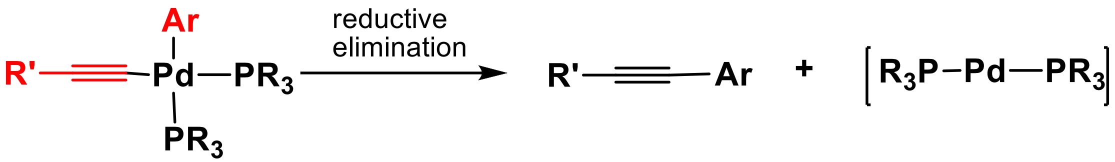
is an example of reductive elimination.

Final step in many catalytic cycles

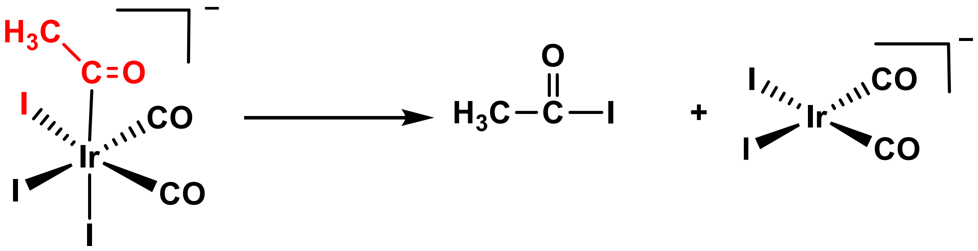
1. Hydroformylation (conversion of alkene to aldehyde)



2. Sonogashira Coupling (coupling of terminal alkyne to aryl group)

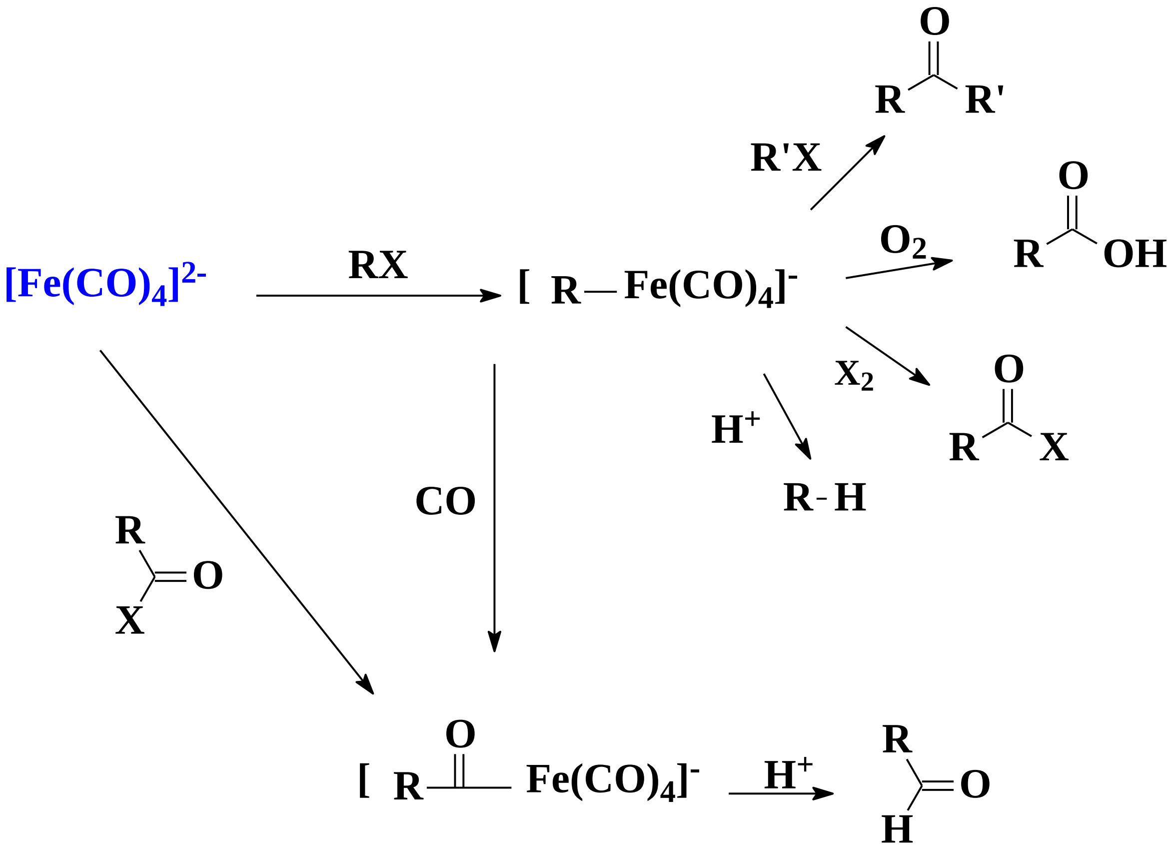


3. Cativa Process (Methanol to Acetic acid)



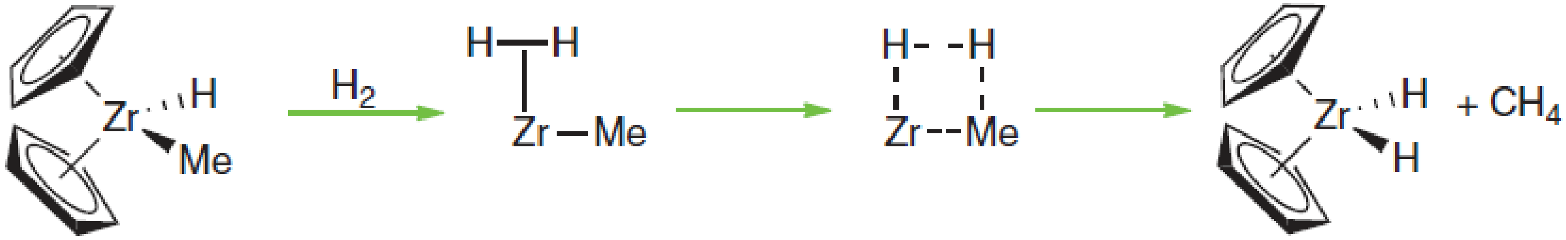
Nucleophilic displacement

- Ligand displacement can be described as nucleophilic substitutions
- Organometallic complexes with negative charges can behave as nucleophiles in displacement reactions
- Iron tetracarbonyl (anion) is very useful



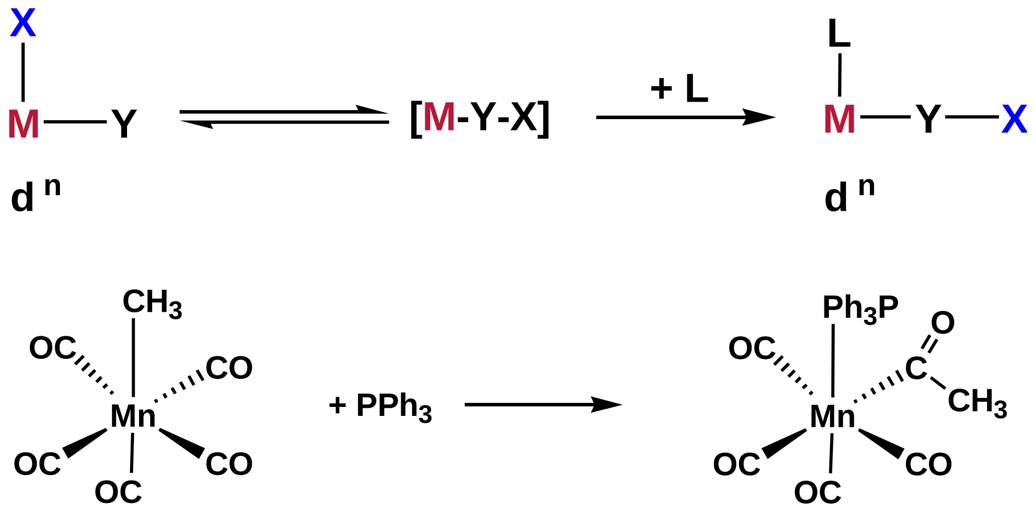
σ-Bond metathesis

- σ-bond metathesis reaction is a concerted process that sometimes occurs when oxidative addition cannot take place.
- A reaction sequence that appears to be an oxidative addition followed by a reductive elimination may in fact be the exchange of two species by a process known as **σ-bond metathesis**.
- σ -Bond metathesis reactions are common for early d-metal complexes where there are not enough electrons on the metal atom for it to participate in oxidative addition
- 16e compound [ZrHMe(Cp)$_2$] react with H_2 via formation of a four-membered transition state and, a concerted bond-making and bond-breaking step results in elimination of methane



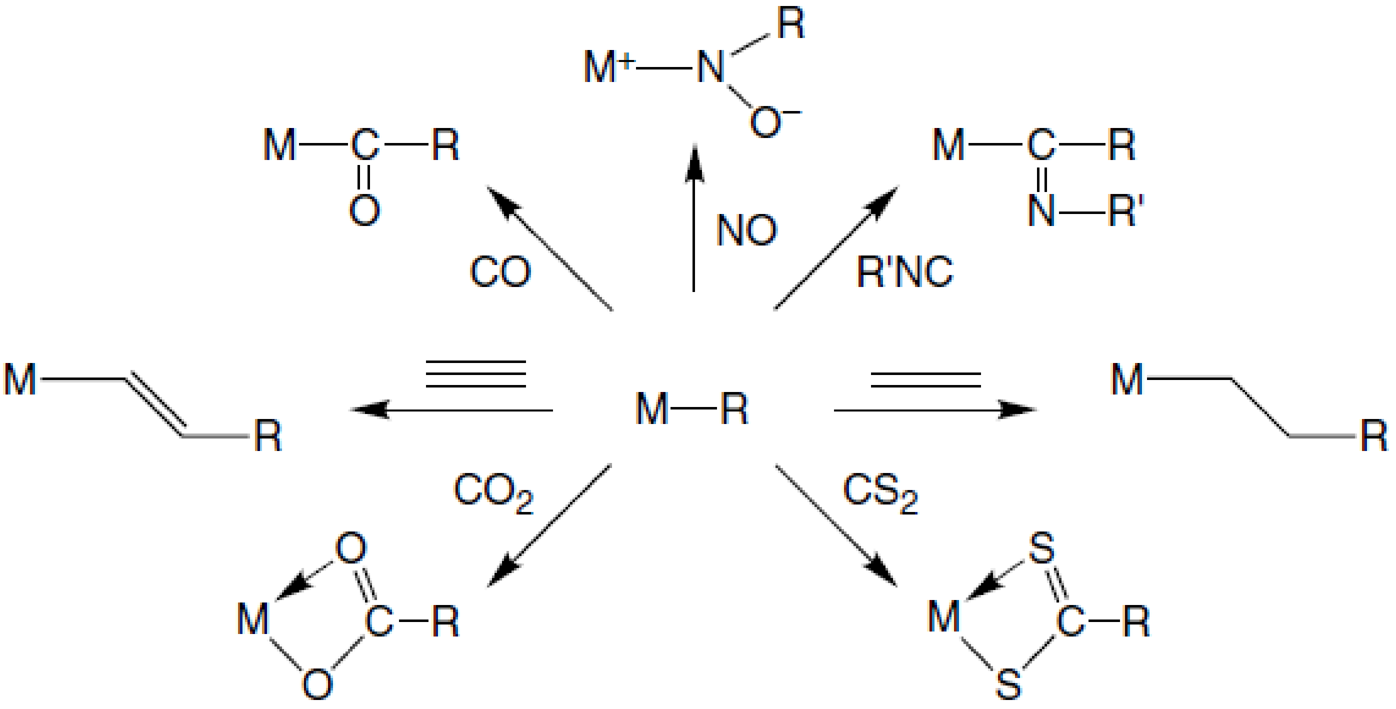
Migratory Insertion

- No change in the formal oxidation state of the metal
- A vacant coordination site is generated during a migratory insertion (*which gets occupied by the incoming ligand*)
- The groups undergoing migratory insertion must be *cis* to one another



- These reactions are enthalpy driven and although the reaction is entropy prohibited the large enthalpy term dominates
- Migratory insertion results in a decrease in the number of electrons on the metal atom by 2, with no change in the oxidation state.

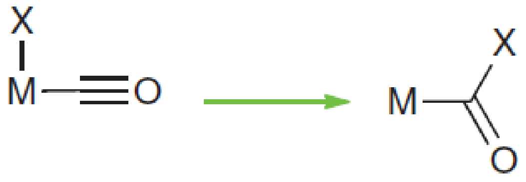
- The insertion of an unsaturated molecule (potentially L ligand) into an M-R bond (R= H, alkyl, hydroxy, alkoxy, amino, etc.), is very common



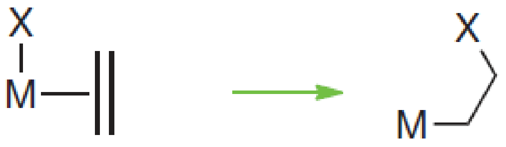
General scheme summarizing the insertion reactions (R = H or alkyl)

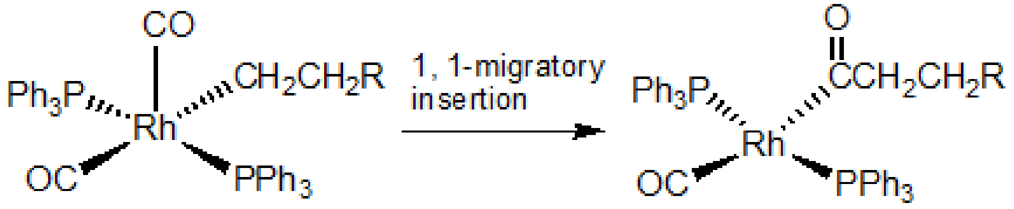
Types of Migratory Insertion

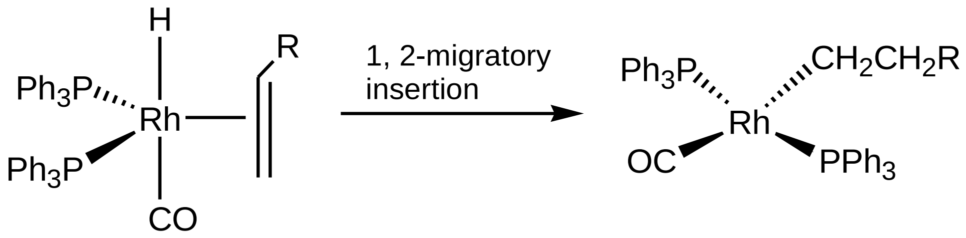
- **1,1-Migratory insertion:** because the X (= Me, Ar) group that was on the metal atom ends up on an atom that is one bond away from the metal atom (product is acyl group)



- **1,2-Migratory insertion:** because the X (H$^-$, Me, Ar) group that was on the metal atom ends up on an atom that is two bonds away from the metal atom (product is substituted alkyl)







- 1,1-Migratory insertion results from the migration of a species (hydride or alkyl group) to an adjacent ligand (carbonyl) to give a metal complex with two fewer electrons on the metal atom.

- 1,2-Migratory insertions are observed with η^2-ligands (alkenes, alkynes) and result in the formation of an η^1-ligand with no change in oxidation state of the metal

- Insertion reaction is important in catalytic cycle (insertion of CO into M-C bond and insertion of ethylene into M-H bond)
- For example, CO insertion (migratory insertion) in $Mn(CO)_5$-CH_3
- Although the name is CO insertion, actually it is methyl migration.
- The reverse of insertion is called elimination
- Insertion reduces the electron count, elimination increases it
- Neither insertion nor elimination causes a change in oxidation state

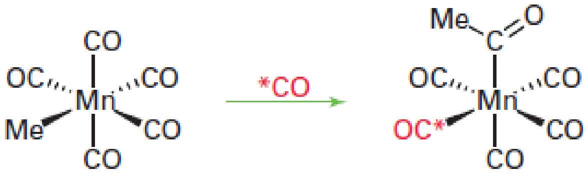
Criteria for CO-insertion:

1. It involves ligands that are cis to each other
2. During the course of the reaction, a vacant coordination becomes available
3. The reverse reaction cannot occur unless a ligand is first eliminated

1,1-Migratory insertion

- The migratory insertion of CO with [$CH_3Mn(CO)_5$] illustrates several key features of 1,1-insertion reaction

$$[Mn(CH_3)(CO)_5] + {}^{13}CO \rightarrow [Mn(CH_3CO)(CO)_4({}^{13}CO)]$$



- The incoming CO (labelled) is *cis* to the newly formed acyl (CH_3CO) group, indicating a kinetically controlled reaction
- The incoming CO group does not insert into the Mn-CH_3 bond, reaction is intramolecular
- Either the Me-group migrates to an adjacent CO ligand, or a CO ligand adjacent to the Me-group inserts into the Mn-CH_3 bond.

$$\text{cis-}[Mn(CH_3CO)(CO)_4({}^{13}CO)] \rightarrow [Mn(CH_3)(CO)_5] + CO$$

- The reverse reaction (decarbonylation or deinsertion, broadly elimination) helps to predict whether Me-migration or CO-insertion occurs.
- For the reaction to take place, *cis*-[$Mn(CH_3CO)(CO)_4({}^{13}CO)$] must lose a CO ligand *cis* to the acyl group.

Possible mechanisms

- The insertion of CO into a M-C bond in alkyl complexes is of particular interest for its potential applications to organic synthesis and catalysis
- Three plausible mechanisms have been suggested

Mechanism 1: CO Insertion

Direct insertion of CO into a M-C bond.

Mechanism 2: CO Migration

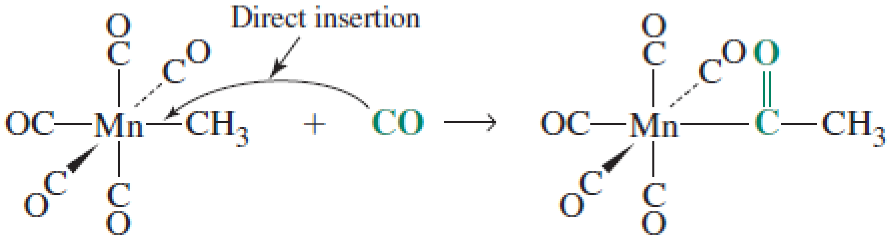
Migration of a CO ligand to give intramolecular CO insertion. This would yield a 5-coordinate intermediate, with a vacant site available for attachment of an incoming CO.

Mechanism 3: Alkyl Migration

In this case, the alkyl group would migrate, rather than the CO, and attach itself to a CO *cis* to the alkyl. This would also give a 5-coordinate intermediate with a vacant site available for an incoming CO.

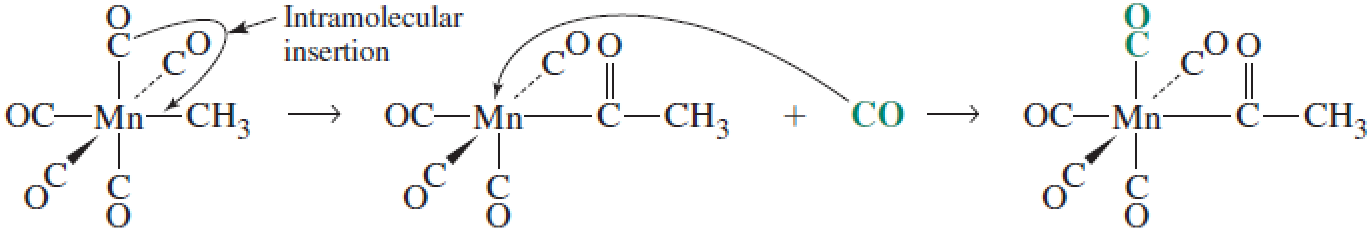
CO Insertion Reactions

Mechanism 1



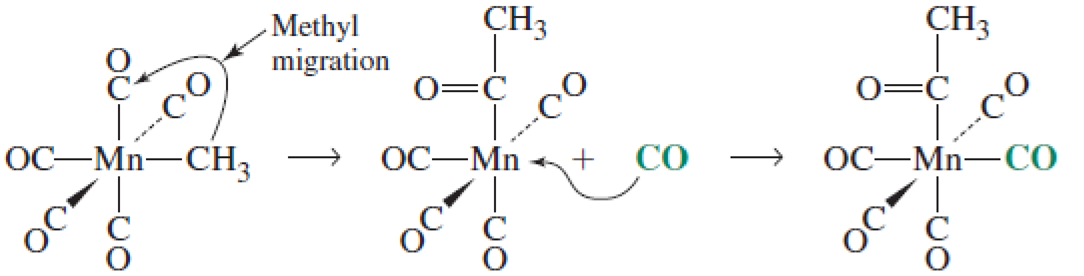
New CO in the acyl group

Mechanism 2



New CO *cis* to $\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3}$

Mechanism 3

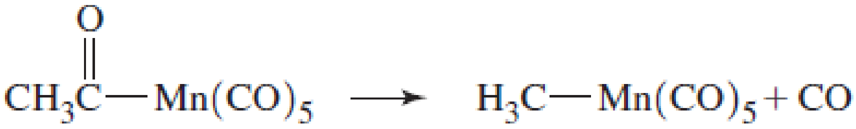


New CO *cis* to $\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_3}$

- In both mechanisms 2 and 3, the intramolecular migration is considered to occur to one of the migrating group’s nearest neighbors, located in *cis* positions.

- Reaction of $CH_3Mn(CO)_5$ with ^{13}CO gives a product with the labeled CO in carbonyl ligands only; *none* is found in the acyl position

- The reverse reaction ^{13}C in the acyl position, the product $CH_3Mn(CO)_5$ has the labeled CO entirely *cis* to CH_3. No labeled CO is lost in this reaction.



$$CH_3\overset{\overset{O}{\|}}{C}-Mn(CO)_5 \longrightarrow H_3C-Mn(CO)_5 + CO$$

- The reverse reaction, when carried out with ^{13}C in a carbonyl ligand *cis* to the acyl group, gives a product that has a 2:1 ratio of *cis* to *trans* product (*cis* and *trans* refer to the position of labeled CO relative to CH_3 in the product). Some labeled CO also dissociates from the Mn in this reaction

- The mechanisms can now be evaluated. Mechanism 1 is definitely ruled out by the first experiment. Direct insertion of ^{13}CO must result in ^{13}C in the acyl ligand, but none is found. Mechanisms 2 and 3 are both compatible with the results of this experiment.

- If the forward reaction is carbonyl migration (mechanism 2), the reverse reaction must proceed by loss of a CO ligand, followed by migration of CO from the acyl ligand to the empty site. Because this migration is unlikely to occur to a *trans* position, all the product should be *cis* .

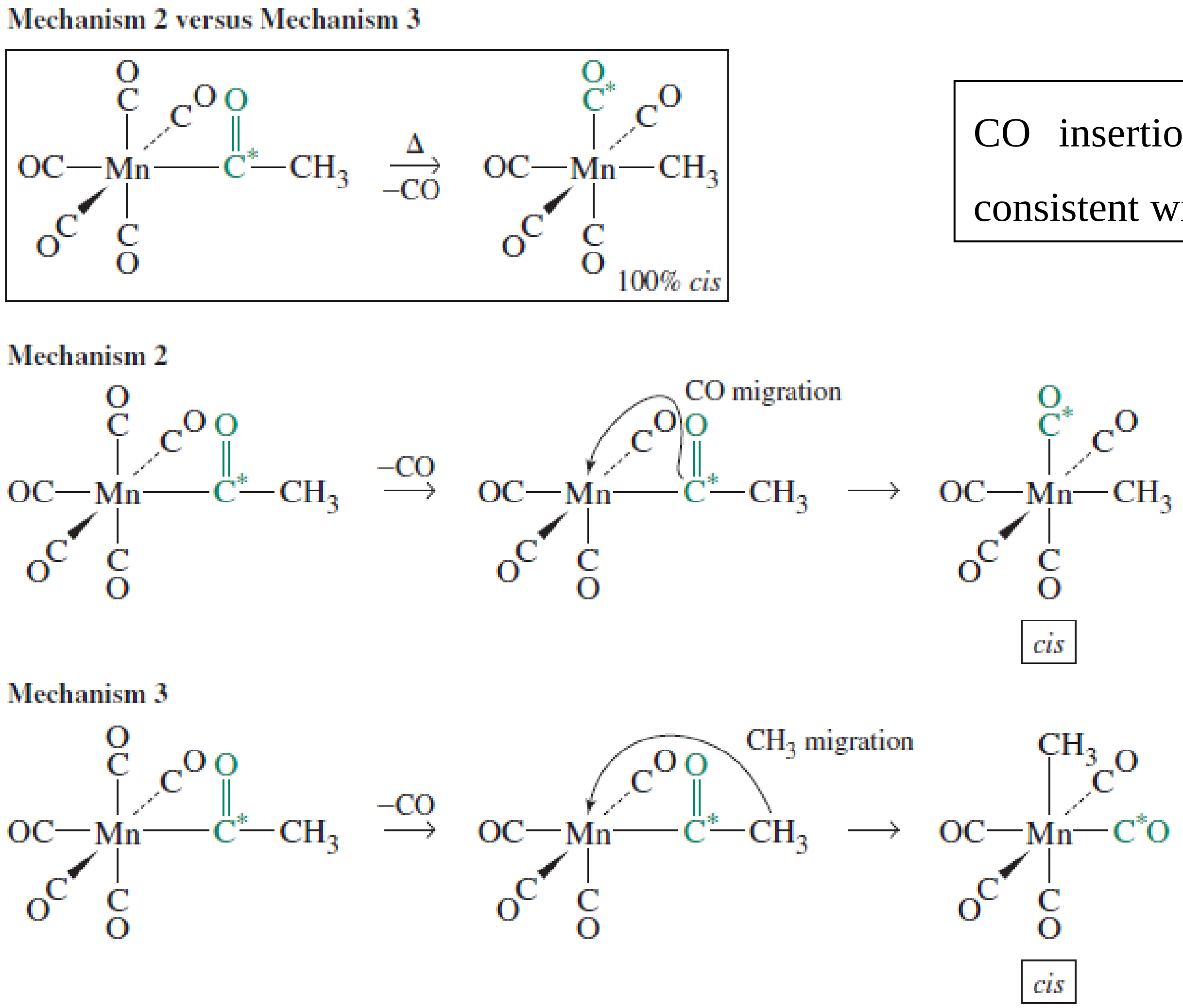
- If the mechanism is alkyl migration (mechanism 3), the reverse reaction must proceed by loss of a CO ligand, followed by migration of the methyl group of the acyl ligand to the vacant site. Again, all the product should be *cis*.

- Both mechanisms 2 and 3 would transfer labeled CO in the acyl group to a *cis* position and are therefore consistent with the experimental data for the second experiment

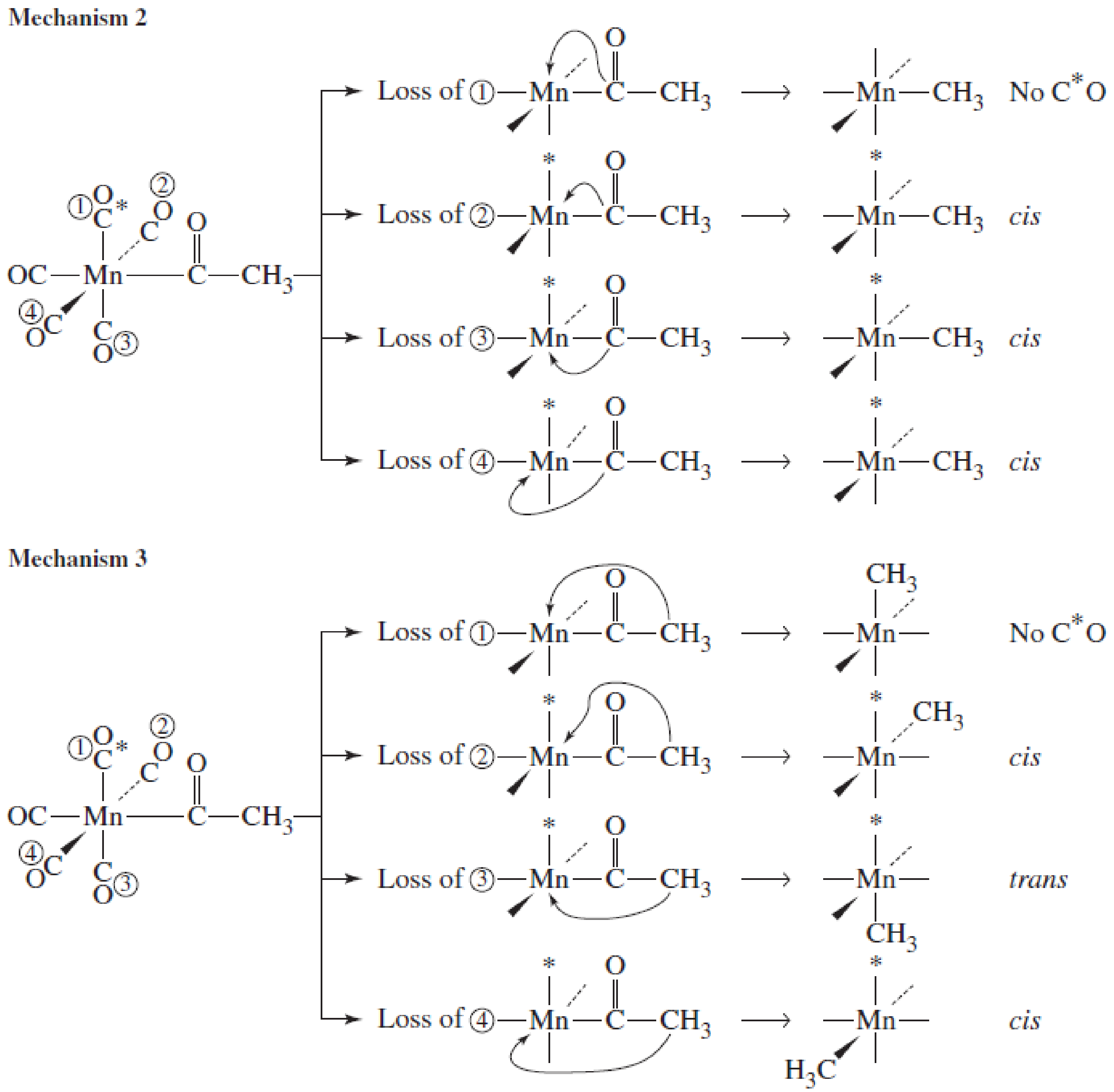
- The third experiment differentiates conclusively between mechanisms 2 and 3. The CO migration of mechanism 2, with ^{13}CO *cis* to the acyl ligand, requires migration of CO from the acyl ligand to the vacant site.

- As a result, 25% of the product should have no ^{13}CO label and 75% should have the labeled CO *cis* to the alkyl.

- On the other hand, alkyl migration (mechanism 3) should yield 25% with no label, 50% with the label *cis* to the alkyl, and 25% with the label *trans* to the alkyl. Because this is the ratio of *cis* to *trans* found in the experiment, the evidence supports mechanism 3, the accepted reaction pathway.



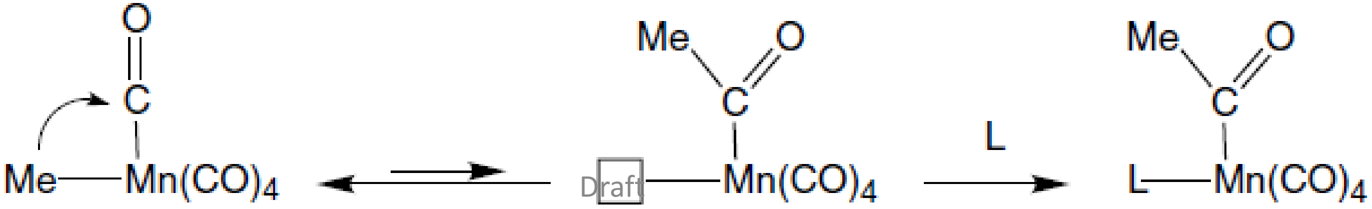
CO insertion is not possible, Me-migration is consistent with the experimental results.



Mechanisms of Reverse Reactions for CO Migration and Alkyl Insertion (2). C* indicates the location of ^{13}C

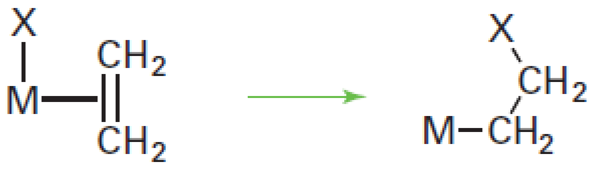
- The σ-bound group *migrates* to the π-system
- It looks like that a π-system has inserted into the M-X bond, hence the name insertion
- Mostly X (-Me) group that moves (migrates), the term migratory insertion is used
- The relative positions of the other groups on the migrating atom are left unchanged, stereochemistry at the X (Me) group is preserved.
- Things to keep in mind for such types of reaction

1. It involves ligands which are cis to each other
2. In the course of the reaction a vacant coordination site becomes available
3. The reverse reaction cannot occur unless a ligand is first eliminated.
4. Insertion reduces the electron count, no change in oxidation state

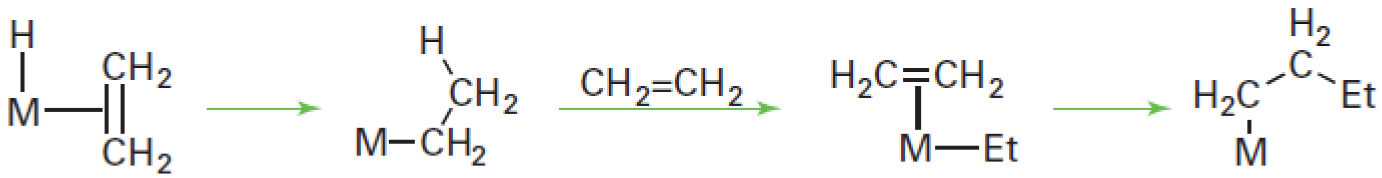


1,2-Migratory insertion

- Insertion of ethylene into M-H bond
- 1,2-Insertion reactions are commonly observed with η2-ligands



- If, in the above reaction with XH, another ethene molecule were to coordinate, the resultant ethyl group could migrate to give a butyl group



- Repetition of this process gives polyethene.
- Catalytic reactions of this kind are of considerable industrial importance

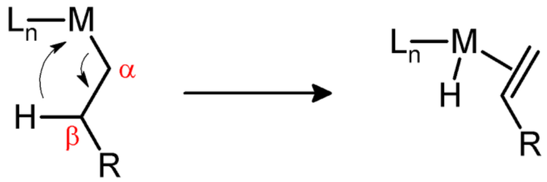
β-Hydride elimination

- In β-hydride elimination an alkyl group having a β hydrogen, σ -bonded to a metal center is converted into the corresponding metal-bonded hydride and a π bonded alkene.

- The alkyl must have hydrogens on the β-carbon. For instance butyl groups can undergo this reaction but methyl, $PhCH_2$, Me_3CCH_2, Me_3SiCH_2 groups cannot.

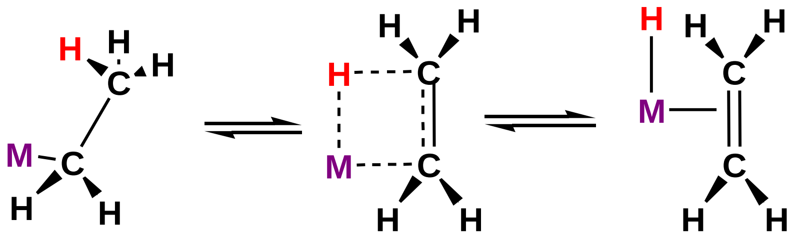
- The metal complex must have an empty (or vacant) site cis to the alkyl group.

- β-hydride elimination is the reverse of 1,2-insertion.



No change in the formal oxidation state of the metal

Mechanism

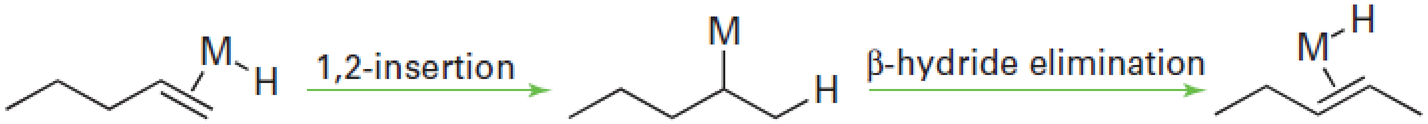


Can either be a vital step in a reaction or an unwanted side reaction

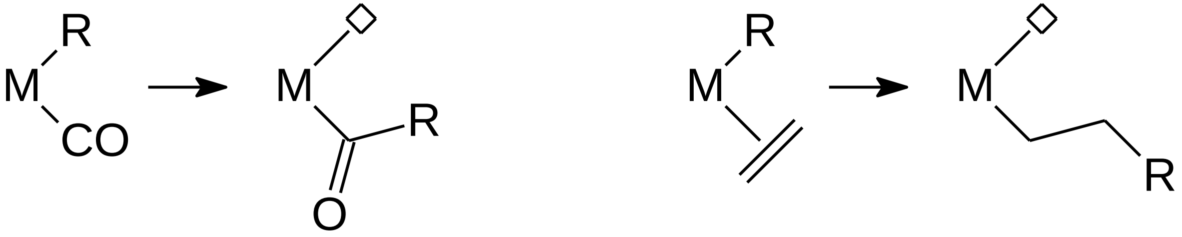
- Both 1,2-insertion and β-hydride elimination proceed through a *syn* intermediate

- β-hydride elimination can provide a facile route for decomposition of alkyl-containing compounds

- The 1,2-insertion reaction, coupled with the β-hydride elimination, can also provide a low-energy route to alkene isomerization

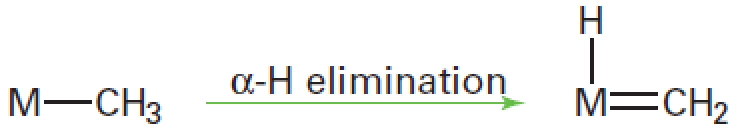


- If at a metal center have a σ-bound group (hydride, alkyl, aryl) a ligand containing a π-system (olefin, alkyne, CO, nitriles), the σ-bound group can *migrate* to the π-system

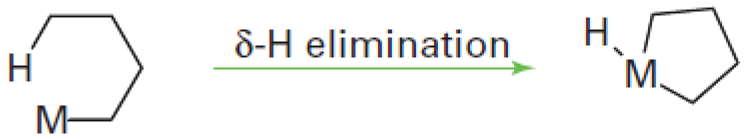


α, γ, δ-Hydride elimination and cyclometallation

- α-Hydride eliminations are occasionally found for complexes that have no β-hydrogens and the reaction gives rise to a highly reactive carbene



- γ and δ-Hydride eliminations are more common. Because the product contains a **metallocycle**, a cyclic structure incorporating a metal atom, these reactions are normally described as **cyclometallation** reactions



- Cyclometallation reactions, in which a metal inserts into a remote CH bond, are equivalent to hydride elimination reactions.

- A cyclometallation reaction is often also thought of as the oxidative addition to an adjacent C-H bond

Problem solving

Q. Classify the following reactions as oxidative addition, reductive elimination, (1,1/1,2) migratory insertion, β-H elimination, ligand coordination change or simple addition

(a) $[RhI_3(CO)_2CH_3]^- \rightarrow \{RhI_3(CO)(\text{ solvent})[C(O)CH_3]\}^-$

(b) $Ir(PPh_2Me)_2(CO)Cl + CF_3I \rightarrow Ir(I)(CF_3)(PPh_2Me)_2(CO)Cl$

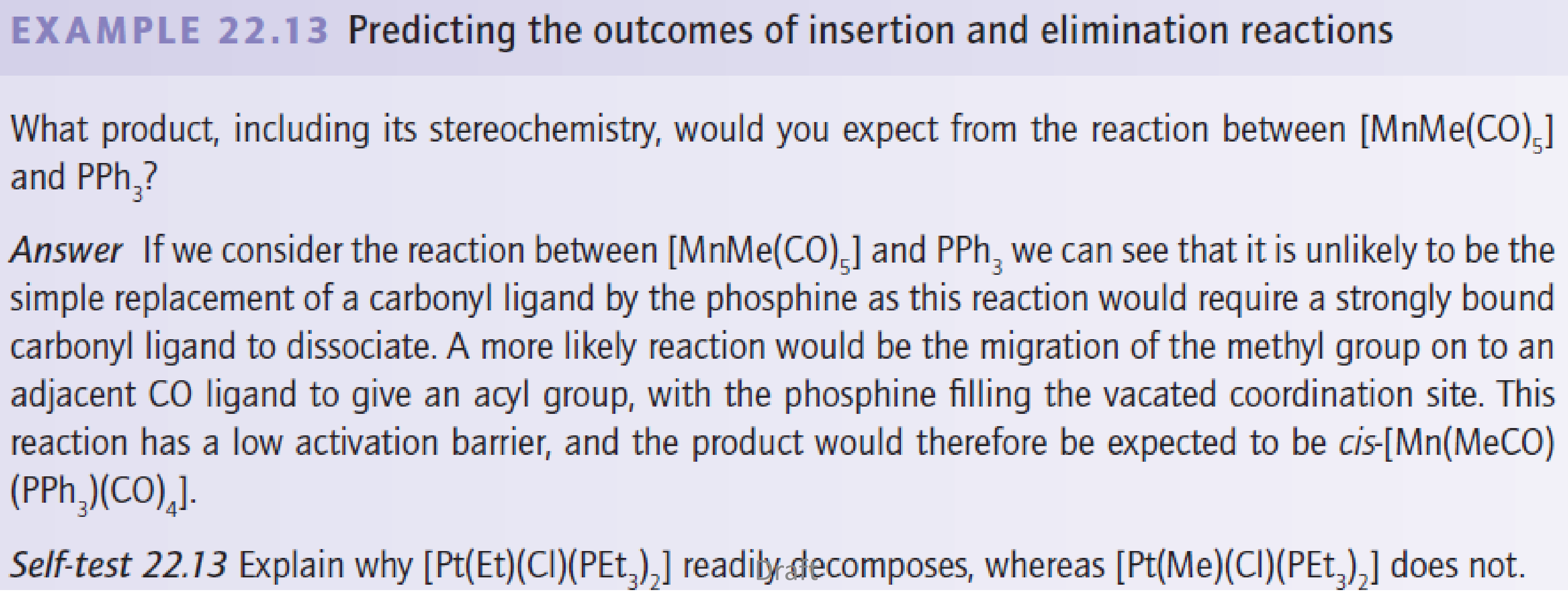
(c) $TiCl_4 + 2\ Et_3N \rightarrow TiCl_4(NEt_3)_2$

(c) $HCo(CO)_3(CH_2{=}CHCH_3) + CO \rightarrow CH_3CH_2CH_2Co(CO)_4$

Step 1. Determine the oxidation state of the metal in reactant and product

Step 2. Count the electrons for reactant and product

Step 3. See if any ligand in the reactant has undergone change



EXAMPLE 22.13 Predicting the outcomes of insertion and elimination reactions

What product, including its stereochemistry, would you expect from the reaction between $[MnMe(CO)_5]$ and PPh_3?

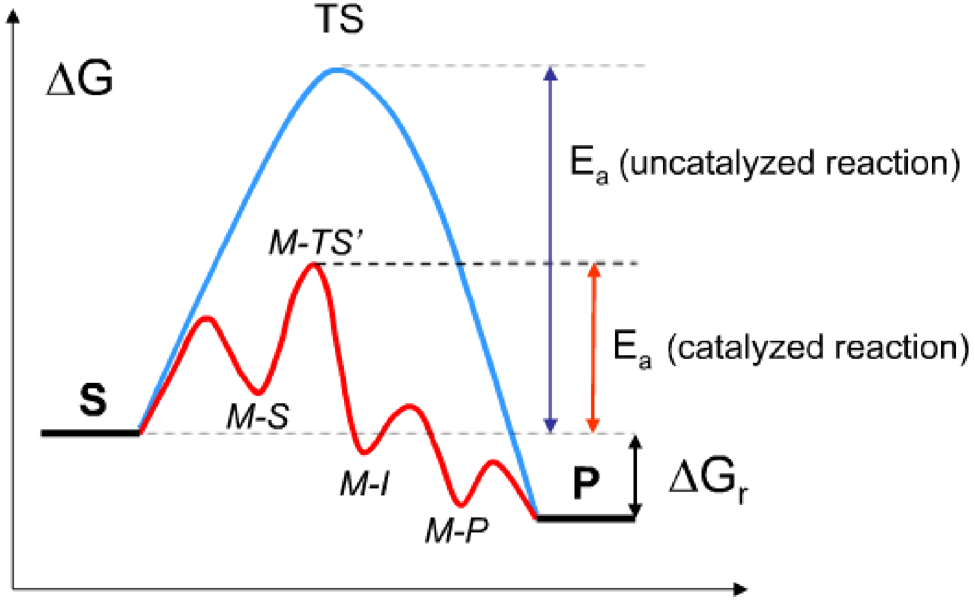
Answer If we consider the reaction between $[MnMe(CO)_5]$ and PPh_3 we can see that it is unlikely to be the simple replacement of a carbonyl ligand by the phosphine as this reaction would require a strongly bound carbonyl ligand to dissociate. A more likely reaction would be the migration of the methyl group on to an adjacent CO ligand to give an acyl group, with the phosphine filling the vacated coordination site. This reaction has a low activation barrier, and the product would therefore be expected to be *cis*-$[Mn(MeCO)(PPh_3)(CO)_4]$.

Self-test 22.13 Explain why $[Pt(Et)(Cl)(PEt_3)_2]$ readily decomposes, whereas $[Pt(Me)(Cl)(PEt_3)_2]$ does not.

Basis for catalysis

- Catalysis is a chemical process where a catalyst is involved
- A catalyst alters (accelerates) the rate of a reaction without itself being consumed.
- A catalyst influences (preferably lowers) the activation energy and controls the rate (lower Gibbs free energies of activation) .
- Catalyzed reaction proceeds by multistep mechanism where the metal stabilizes intermediates that are stable only when bound to metal.

Catalysis is kinetic not thermodynamics



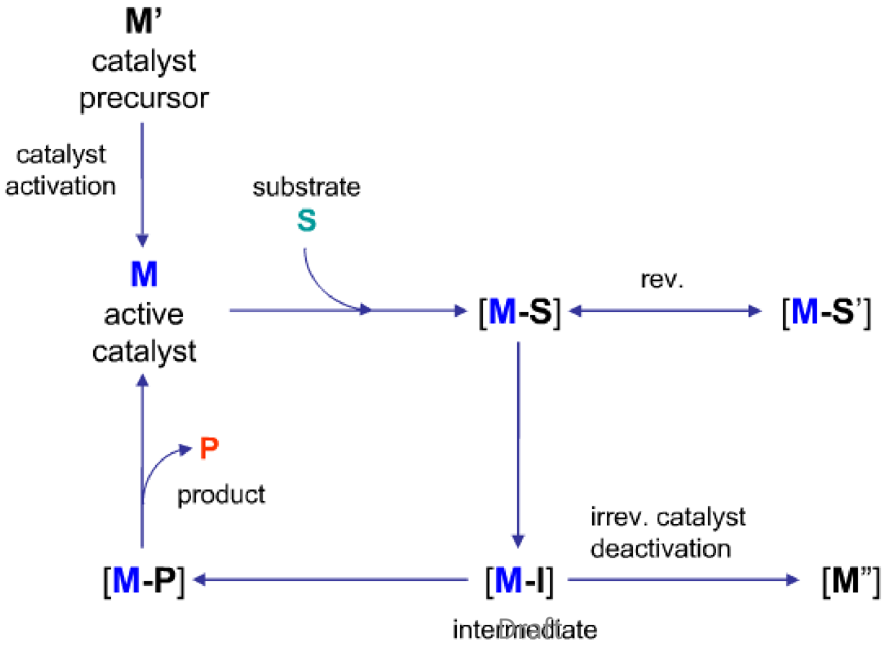
Importance of catalysis

- Many major industrial chemicals are prepared with the aid of catalysts
- Many fine chemicals are also made with the aid of catalysts
- Reduce cost of production
- Lead to higher selectivity and less waste

Synthetic chemicals	**Catalytic Process**
Ethene, propene	Hydrocarbon cracking, heterogenous
Sulfuric acid	SO_2 oxidation, heterogenous
NH_3	$N_2 + H_2$, heterogenous
Polyethene	Polymerization, heterogeneous
Nitric acid	$NH_3 + O_2$, heterogeneous
Urea	NH_3 precursor catalytic

Catalytic Cycle

- A catalyzed reaction pathway is usually represented by a catalytic cycle
- A catalytic cycle consists of a series of stoichiometric reactions (often reversible) that form a closed loop
- The catalyst must be regenerated so that it can participate in the cycle of reactions more than once
- For a catalytic cycle to be efficient, the intermediates must be short-lived.
- Catalytically active species must have a vacant coordination site (to coordinate substrate)
- One of the catalytic steps in the cycle is rate-determining



M'
catalyst
precursor

catalyst
activation

substrate
S

M
active
catalyst

[M-S]

rev.

[M-S']

P
product

irrev. catalyst
deactivation

[M-P]

[M-I]
intermediate

[M"]

Mechanistic Concept

- The fundamental reactions are involved the following steps of mechanistic cycle

Function	**Concept**
Activation of catalyst	Coordinative unsaturation – generation of vacant site to accommodate reactant Oxidative addition Non classical coordination of small molecules
Reaction on metal center	Alkyl migration/migratory insertion Carbene, metallacycle formation and rearrangement Nucleophilic and electrophilic addition and subtraction
Release of the product from metal center	Reductive elimination β-elimination

Homogeneous versus Heterogeneous Catalysis

- **Homogeneous:** Homogeneous catalysts are present in the same phase as the reagents, and are often well defined
- **Heterogeneous:** Heterogeneous catalysts are present in a different phase from the reagents
- Heterogeneous catalysts are used very extensively in industry and have a much greater economic impact than homogeneous catalysts.

Parameter	**Heterogeneous**	**Homogeneous**
Phase	Gas/solid	Usually liquid/solid
Solubility	Insoluble in reaction medium	Soluble in reaction medium
Temperature & pressure	High	Low
Catalyst Activity	Low	High
Product selectivity	Low (often mixtures)	Good
Catalyst recycling	Simple and cost effective	Expensive and complex
Reaction mechanism	Poorly understood	Reasonably well understood
Product & catalyst separation	Easy	Elaborate and problematic
Fine tuning of catalyst	Difficult	Easy

Comparing different catalysts: Catalyst life and Catalyst efficiency

Turnover Number (TON)

- TON is defined as the amount of reactant (in moles) divided by the amount of catalyst (in moles) times the percentage yield of product
- A large TON indicates a stable catalyst with a long life

Turnover Frequency (TOF)

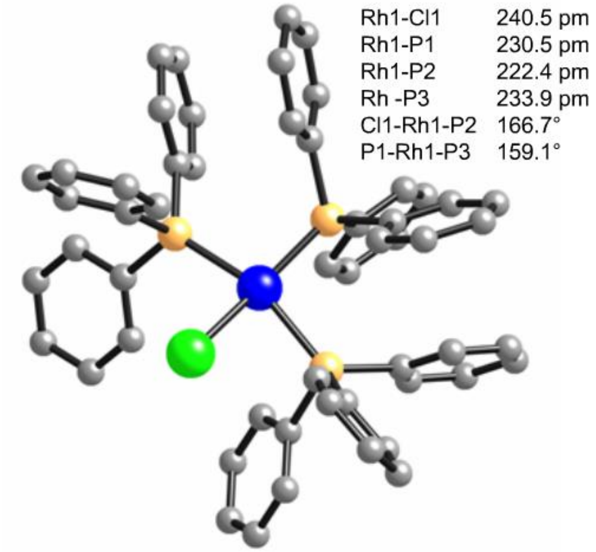
- It is the number of passes through the catalytic cycle per unit time (often per hour). Effectively this is dividing the TON by the time taken for the reaction. The units are just *time*$^{-1}$.
- A higher TOF indicates better efficiency for the catalyst

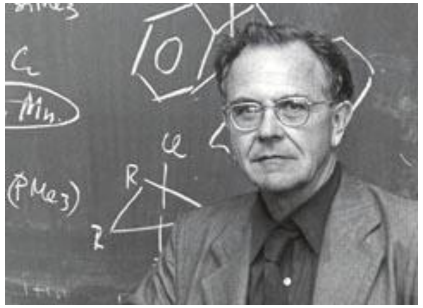
Catalytic steps in homogeneous reactions

- Most catalytic process can be built up from several different types of step

  - Association/dissociation of a ligand: requires labile complexes
  - Insertion and elimination reactions
  - Nucleophilic attack on a coordinated ligand
  - Oxidation and reduction of a metal center
  - Oxidative addition/reductive elimination

Alkene hydrogenation: Wilkinson's catalyst





Nobel prize winner for Ferrocene

- Discovered by G. Wilkinson as well as by R. Coffey around 1964-65

$$RhCl_3(H_2O)_3 + CH_3CH_2OH + 3PPh_3 \rightarrow RhCl(PPh_3)_2 + CH_3CHO + 2HCl + 3H_2O$$

- Square planar 16e d^8 complex, $(Ph_3P)_3RhCl$ chlorotris(triphenylphosphine)rhodium(I)
- Widely undergoes oxidative addition and attain 18e configuration
- Wilkinson's catalyst is the first example of an effective and rapid homogeneous catalyst for hydrogenation of alkenes, active at room temperature and atmospheric pressure.

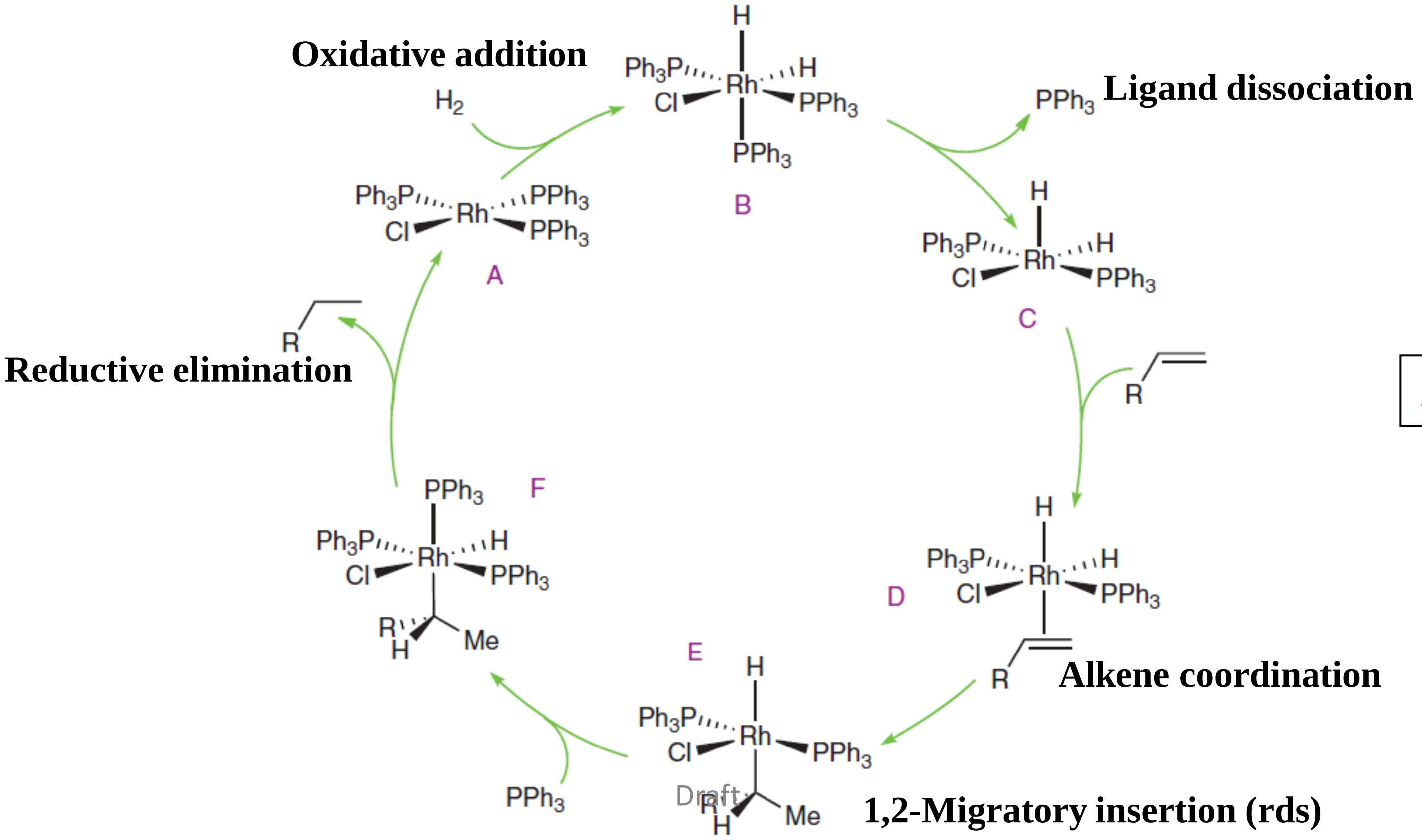
Catalytic cycle for hydrogenation with Wilkinson's catalyst

- Although addition of H_2 to a double bond is thermodynamically favorable, the kinetic barrier is high and does not take place at room temperature and pressure

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3\text{-}CH_3\ ,\ \Delta H = -131\ kJmol^{-1}\ \&\ \Delta H = -101\ kJmol^{-1}$$

- A catalyst is required for the reaction to occur at viable rate without the need for high temperatures and pressures
- Metallic Ni, Cu, Pd or Pt surface (heterogenous) can be used as catalyst
- In presence of Wilkinson's catalyst alkene hydrogenation (homogenous) can be carried out at 298K and 1 bar H_2 pressure
- Evidence in favor of dissociation of one PPh_3 ligand (gives T shaped tricoordinate complex)
- For complexes with less sterically hindered phosphines such as Et_3P, the catalytic effect disappears (no steric repulsion, no dissociation)
- With corresponding Ir-complex, the stronger Ir-P bond restricts the dissociation (no catalysis)

- Oxidative addition of H_2 to the 16e $[RhCl(PPh_3)_3]$ (A), to form 18e dihydrido complex (B).
- Dissociation of a PPh_3 ligand from (B) results in a coordinatively unsaturated complex (C)
- Alkene coordination results in the formation of the complex (D).
- H-transfer from Rh atom in (D) to coordinated alkene gives a transient 16e alkyl complex (E).
- Complex (E) binds phosphine ligand to produce (F)
- H-migration to C-atom results in the reductive elimination of alkane & regeneration of the catalyst (A)


Oxidative addition

Ligand dissociation

Alkene coordination

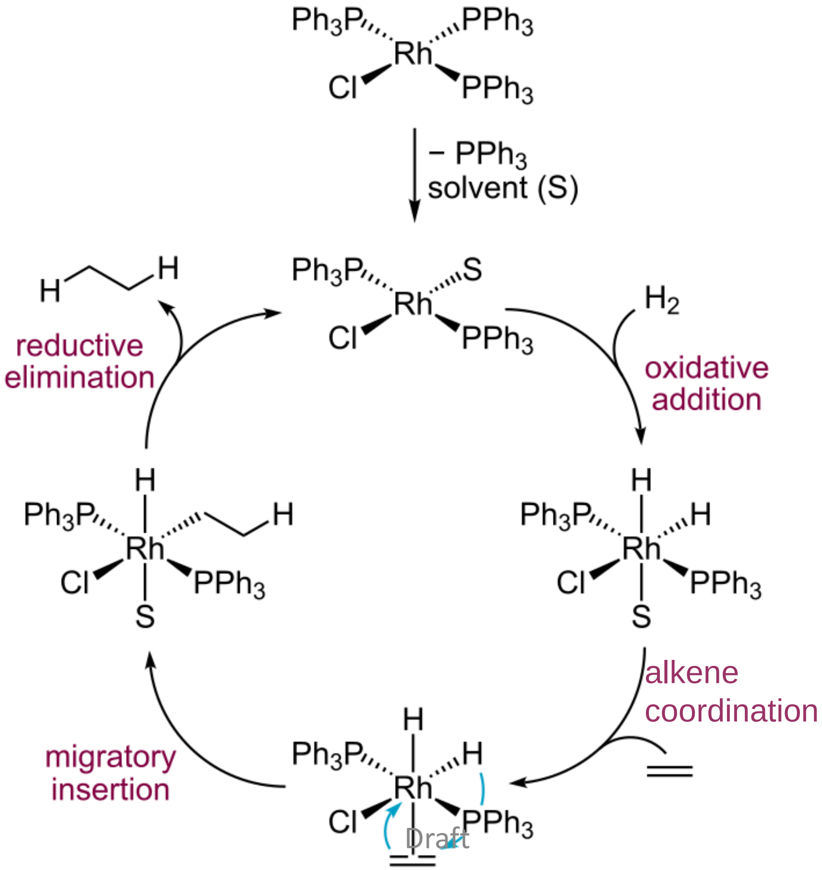
1,2-Migratory insertion (rds)

Reductive elimination

Ref: S.Atkins

- Loss of a PPh_3 to generate T-shaped three coordinate 14e intermediate $(PPh_3)_2RhCl$, stabilized by solvent
- Oxidative addition of H_2 molecule.
- An alkene can then coordinates and reacts with H_2 molecule to form an alkyl group
- This involves H-migration from metal to C-atom in the coordinated alkene.
- Reductive elimination of the product alkane (proceeds through three centered TS)

Rh oscillates between Rh(I) (d^8 square planar) and Rh(III) (d^6 octahedral) species



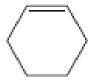
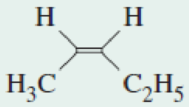
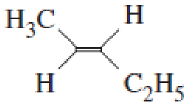
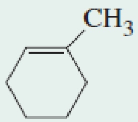
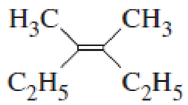
Ref:
1.Huheey, Keiter, Huheey, Medhi
2. Bochmannn

- Wilkinson’s catalyst is highly sensitive to the nature of the phosphine ligand and the alkene substrate (selective hydrogenations of sterically unhindered C=C bonds)
- Analogous complexes with alkylphosphine ligands are inactive (strong M-alkylphosphine bond do not readily dissociate)
- Sterically hindered alkenes are not hydrogenated, presumably because steric hindrance prohibits effective coordination.
- Alkenes with multiple double bonds, the least hindered double bonds are reduced lower activation barriers)
- The selectivity of Wilkinson’s catalyst is a consequence of the bulky triphenylphosphine ligands
- The selectivity can be tuned by phosphines with different cone angles than PPh_3

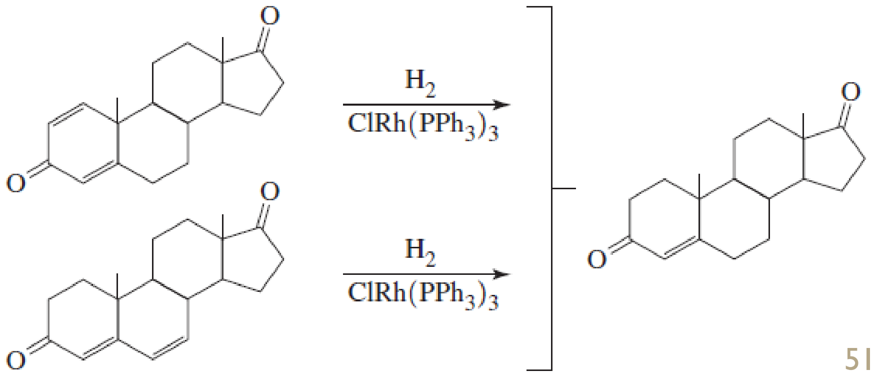
Relative reactivity of alkenes for hydrogenation

- Cis alkenes undergo hydrogenation more readily than trans alkenes
- Internal and branched alkenes undergo hydrogenation more slowly than terminal ones
- A polar functional group accelerates the catalysis
- Conjugate dienes react slower
- Hydrogenation of internal and branched alkenes are slowest

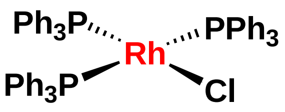
Relative Rates of Hydrogenation Using Wilkinson's Catalyst at 25 °C

Compound Hydrogenated	Rate Constant × 100 ($L\ mol^{-1}s^{-1}$)
	31.6
	9.9
	1.8
	0.6
	< 0.1

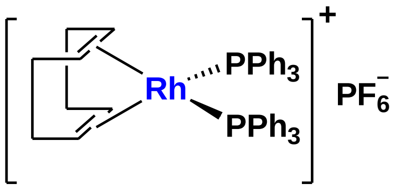
Data from A. J. Birch, D. H. Williamson, *Org. React.*, **1976**, *24*, 1.



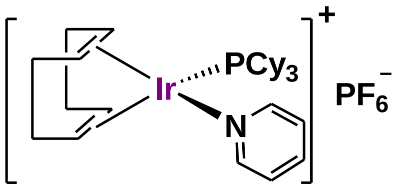
Fine tuning of a catalyst: More efficient than Wilkinson's catalyst



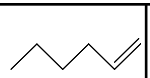
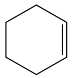
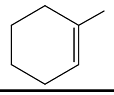
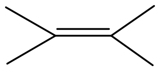
Wilkinson's catalyst



Schrock-Osborn's catalyst



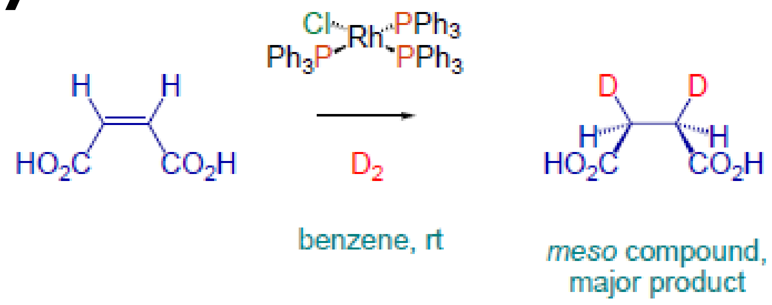
Crabtree's catalyst

Catalyst 25°C, 1 atm H_2	Turnover frequency (TOF) in h^{-1} for hydrogenation of alkenes			
				
Wilkinson's catalyst	650	700	13	NA
Schrock–Osborn catalyst	4000	10	NA	NA
Crabtree's catalyst	6400	4500	3800	4000

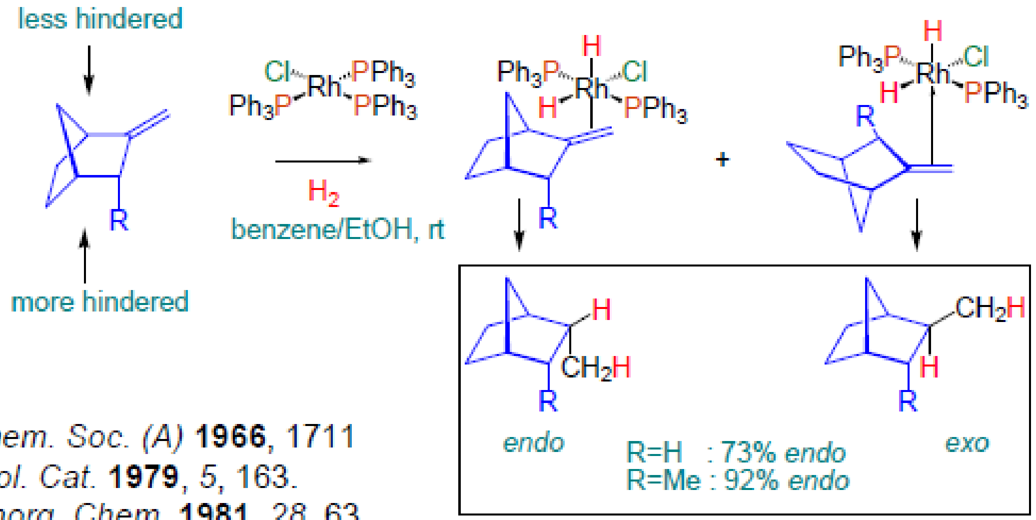
- The cationic metal centre is relatively more electrophilic than neutral metal centre and thus favours alkene coordination.
- Cationic catalysts are the most active homogeneous hydrogenation catalysts till date

Wilkinson's catalyst selectivity

Hydrogenation is stereoselective

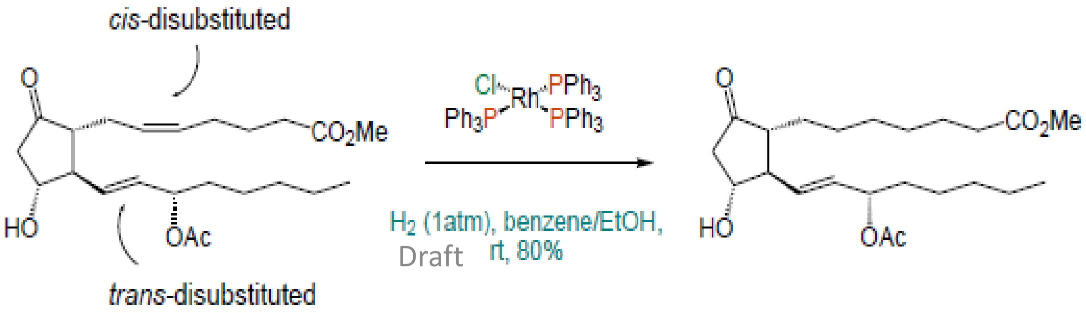


Rh preferentially binds to the least sterically hindered face of the olefin



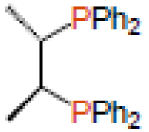
Wilkinson, *J. Chem. Soc. (A)* **1966**, 1711
Rousseau, *J. Mol. Cat.* **1979**, *5*, 163.
Jardine, *Prog. Inorg. Chem.* **1981**, *28*, 63.

Cis-disubstituted C=C react faster than *trans*-disubstituted C=C

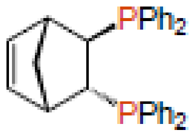


Asymmetric hydrogenation

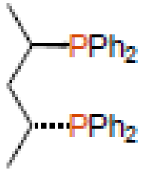
- Homogenous catalysis is quite dominant in asymmetric hydrogenation.
- It involves the use of chiral catalyst and prochiral alkenes, generating chiral carbon on hydrogenation
- A variety of bidentate chiral diphosphines have been synthesized and used to make amino acids by hydrogenation of enamides:



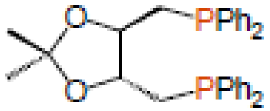
Chiraphos



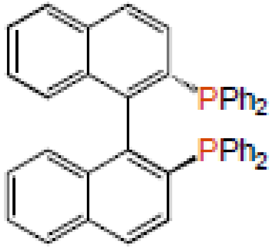
NORPHOS



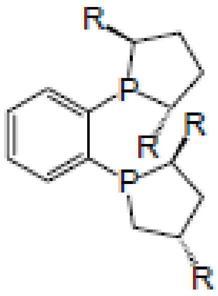
SKEWPHOS



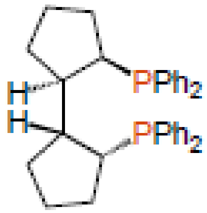
DIOP



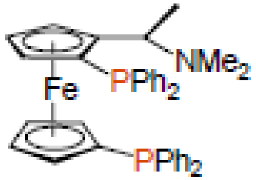
BINAP



DuPHOS



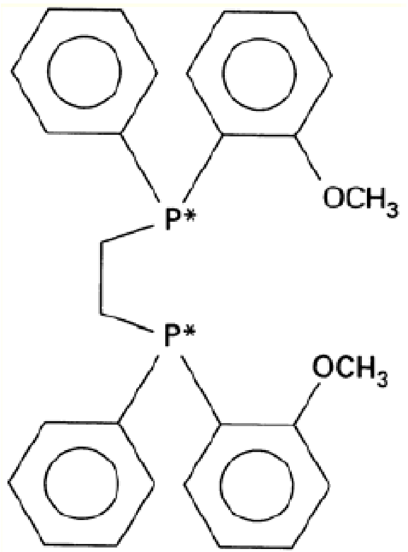
BICP



JOSIPHOS

Burk, *Acc. Chem. Res.* **2000**, *33*, 363.

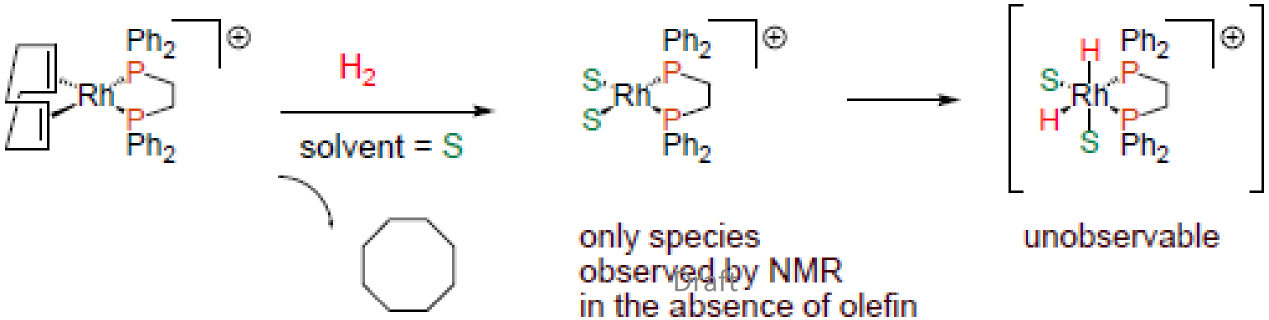
Chiral hydrogenation catalysts



- Catalysts similar to Wilkinson’s but using chiral phosphine ligands have been used for the asymmetric hydrogenation of small molecules
- Important in the fine chemicals/pharmaceutical industry
- Noles and Nyori received the 2001 chemistry Nobel prize for the development of asymmetric hydrogenation catalysis

Catalytically active species

- With bidentate ligands, olefin coordination can precede oxidative addition of H_2 (S = methanol, ethanol, acetone)

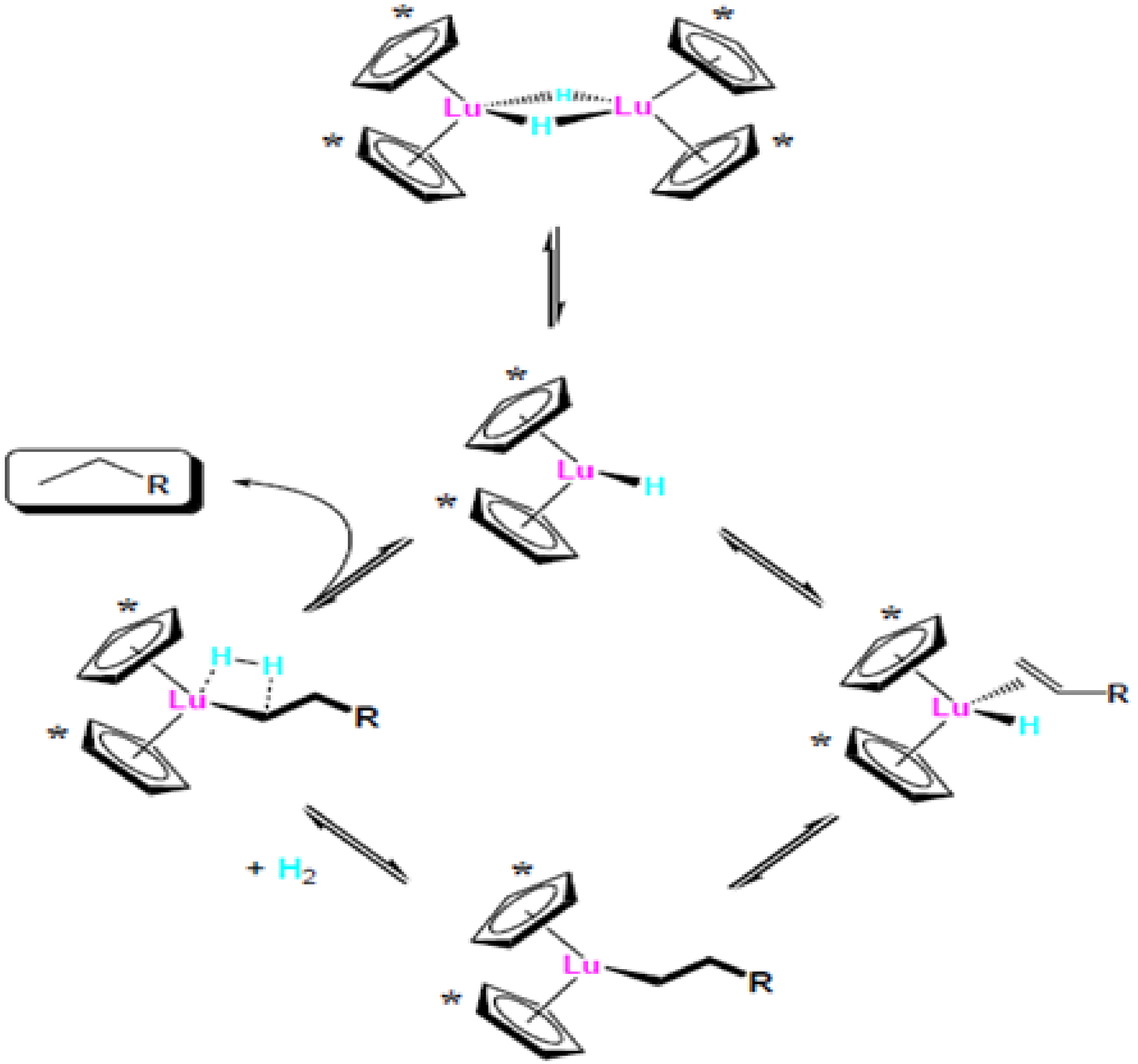


only species observed by NMR in the absence of olefin

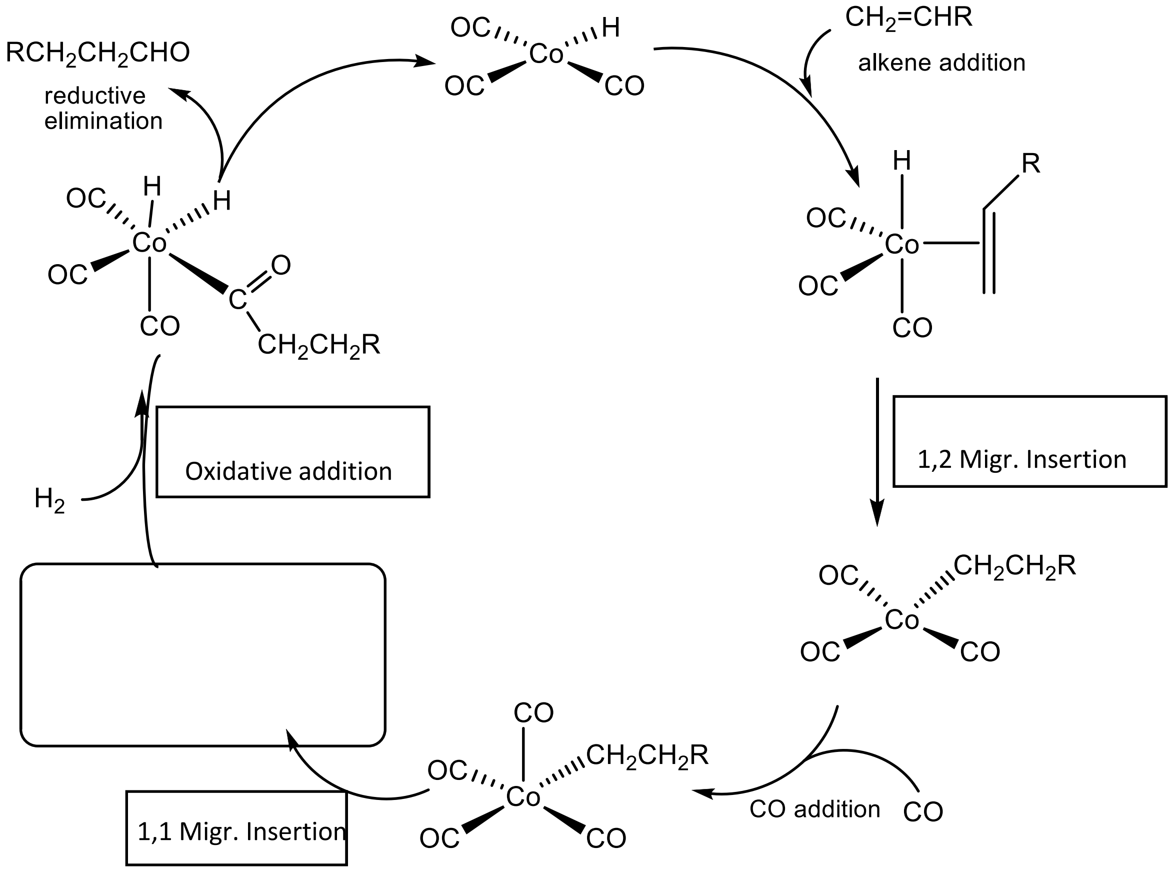
unobservable

Lanthanide Hydrogenation Catalysts

- Tobin Marks reported the extraordinary activity of $(Cp^*{}_2LuH)_2$ for the hydrogenation of alkenes and alkynes.
- The monometallic complex catalyzes the hydrogenation of 1-hexene with a TOF = 120,000/hr at 1 atm H_2, 25ºC. This is one of the most active hydrogenation catalysts known.



Problem solving - fill in the blanks

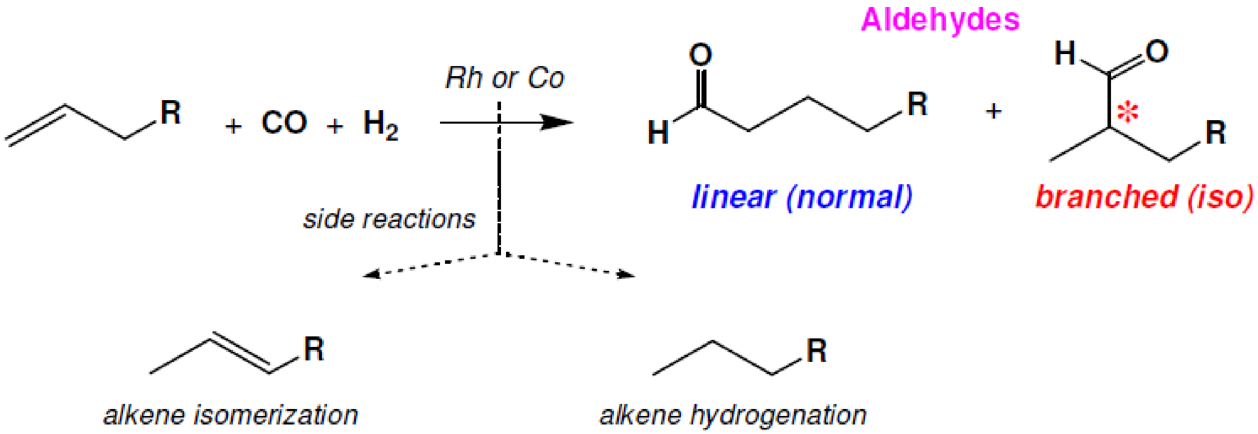


Hydroformylation

- Hydroformylation was discovered by Otto Roelen in 1938
- A less common, more appropriate name is hydrocarbonylation. Also known as oxo reaction (older name)
- The reaction of an alkene with CO and H_2, catalyzed by cobalt or rhodium salts to form an aldehyde is called hydroformylation

Otto Roelen (1897-1993)

$$RCH{=}CH_2 + CO + H_2 \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}CHO \qquad \text{(one C-more)}$$



- Aldehydes produced are reduced to alcohols that are used as solvents and plasticizers, in detergent synthesis

- The first hydroformylation catalyst were based on [$HCo(CO)_4$] (still widely used), requires high temperature (~ 450 K) and pressure (> 200atm)

- It is used in converting terminal alkenes into aldehydes and other organic products (carbon chain increased by one)

- Mixture of products are formed, roughly 3:1 of both linear and branched chain aldehyde and alcohols are formed.

- The general mechanism of the reaction was proposed in 1961 by Heck and Breslow

- Under pressure of CO and H_2, the cobalt catalyst precursor [($Co_2(CO)_8$] is transformed into $HCo(CO)_4$ (A)

$$Co_2(CO)_8 + H_2 \rightarrow 2[HCo(CO)_4]$$

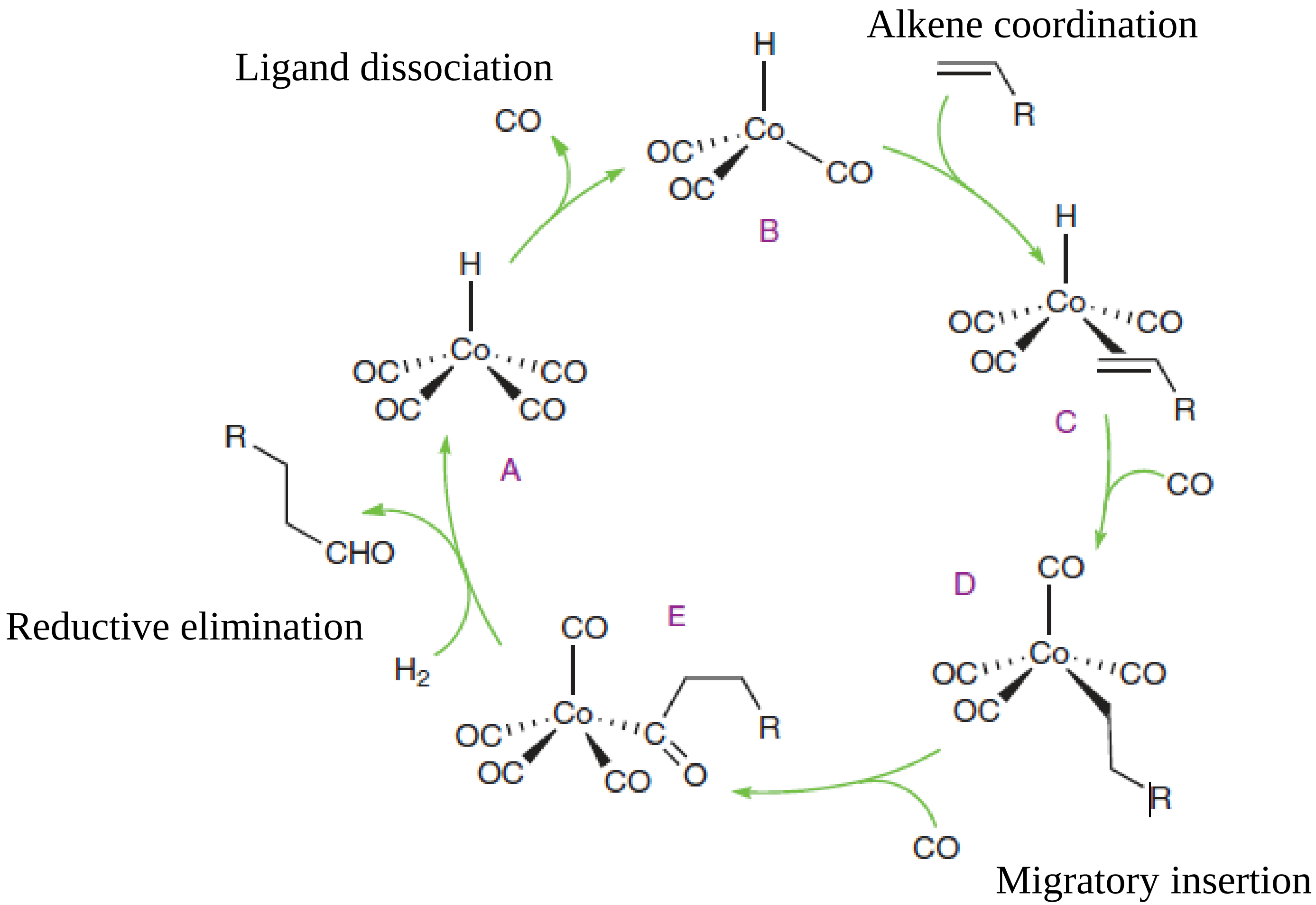
- $HCo(CO)_4$ to looses CO to produce the coordinatively unsaturated complex [$HCo(CO)_3$] (B, 16e species)

$$[HCo(CO)_4] \rightarrow [HCo(CO)_3] + CO$$

- [$HCo(CO)_3$] then coordinates an alkene, producing (C), whereupon the coordinated hydrido ligand migrates onto the alkene, and CO re-coordinates to give a normal alkyl complex (D).

- In presence of CO at high pressure, (D) undergoes migratory insertion & coordinates another CO, giving the acyl complex (E)

- The formation of aldehyde occurs by the attack of H_2 along with the formation of $[HCo(CO)_4]$
- $[HCo(CO)_4]$ will regenerate the coordinatively unsaturated $[HCo(CO)_3]$



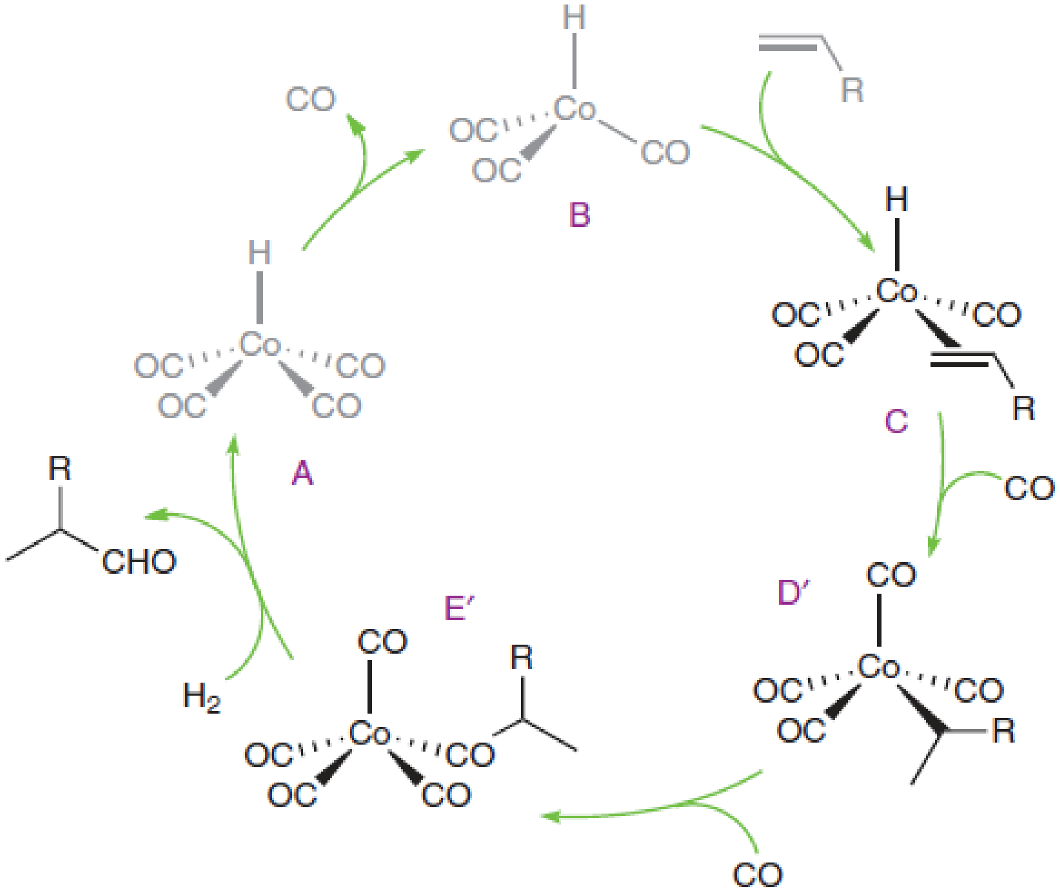
Ligand dissociation

Alkene coordination

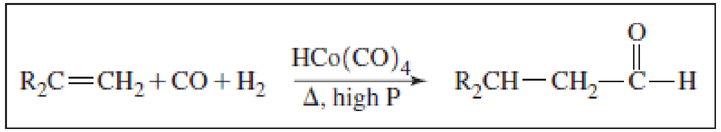
Migratory insertion

Reductive elimination

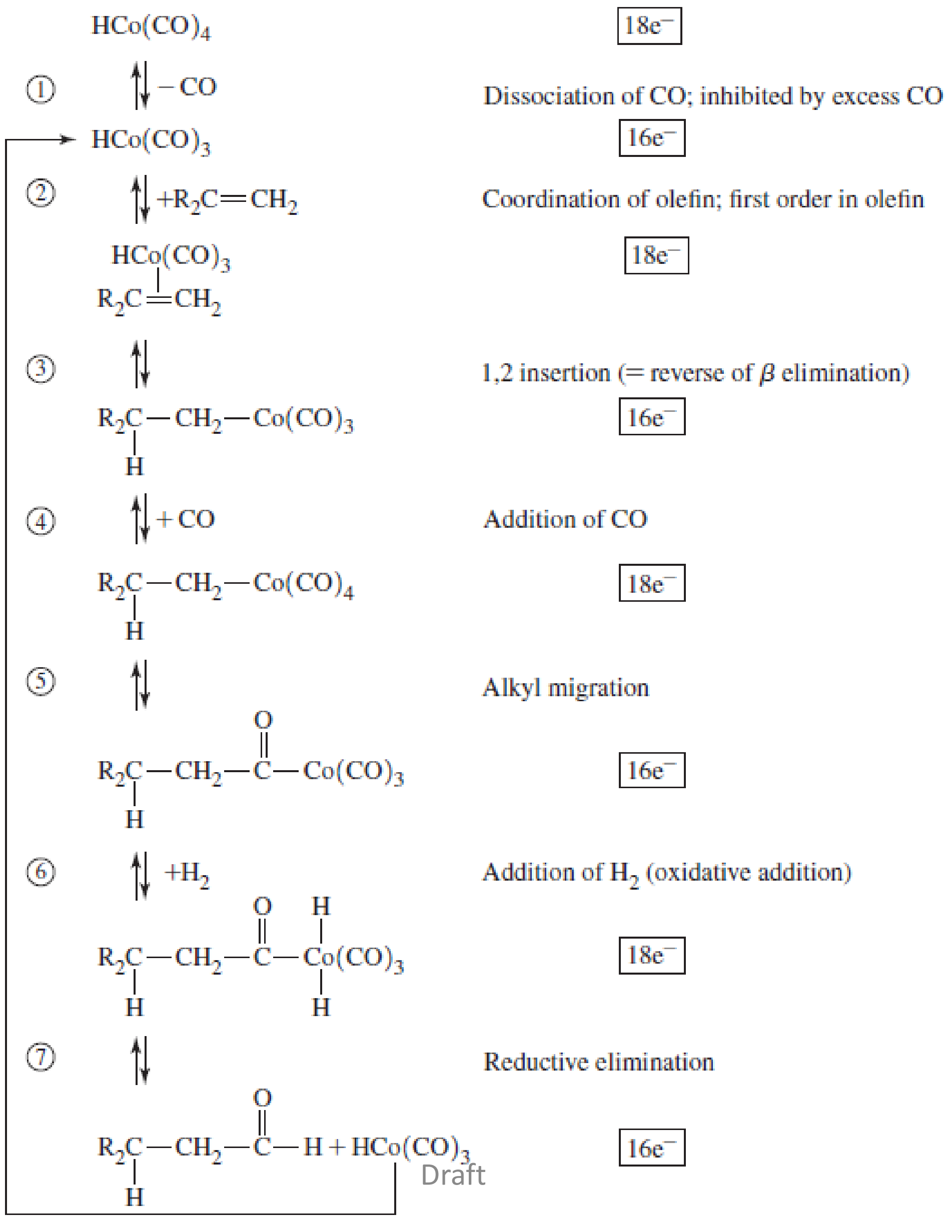
- A significant portion of branched aldehyde is also formed in the cobalt catalyzed hydroformylation.
- This product may result from a 2-alkylcobalt intermediate formed when reaction of (C) leads to an isomer of (D), with hydrogenation then yielding a branched aldehyde



Hydroformylation (Oxo) Process



$$R_2C{=}CH_2 + CO + H_2 \xrightarrow[\Delta,\ \text{high P}]{HCo(CO)_4} R_2CH{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$



$HCo(CO)_4$ $\boxed{18e^-}$

① $-CO$ Dissociation of CO; inhibited by excess CO

$HCo(CO)_3$ $\boxed{16e^-}$

② $+R_2C{=}CH_2$ Coordination of olefin; first order in olefin

$\boxed{18e^-}$

③ 1,2 insertion (= reverse of β elimination)

$\boxed{16e^-}$

④ $+CO$ Addition of CO

$\boxed{18e^-}$

⑤ Alkyl migration

$\boxed{16e^-}$

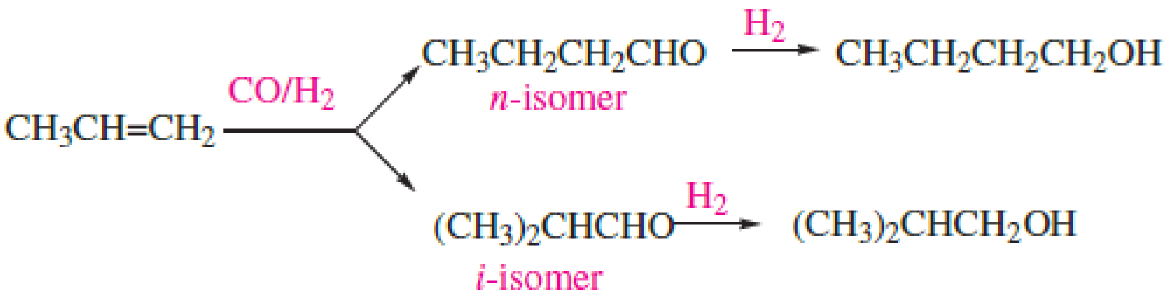
⑥ $+H_2$ Addition of H_2 (oxidative addition)

$\boxed{18e^-}$

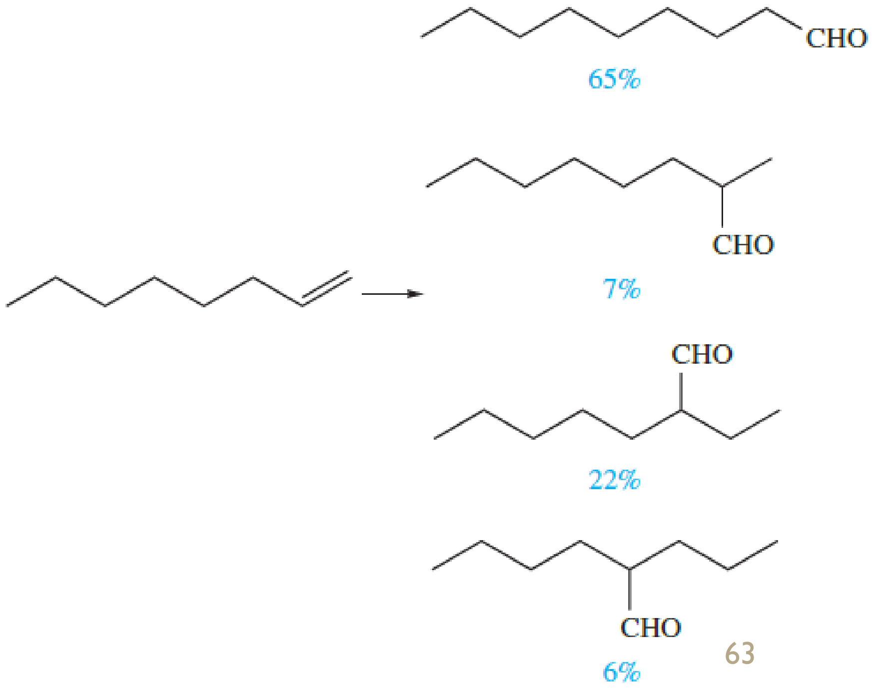
⑦ Reductive elimination

$R_2CH{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + HCo(CO)_3$ $\boxed{16e^-}$

- Two major complications in the process are the hydrogenation of aldehydes to alcohols, and alkene isomerization
- The first of these problems can be controlled by using H_2 :CO ratios greater than 1:1.



- The isomerization problem (regioselectivity) can be addressed by using other catalysts.
- Distribution of products formed when oct-1-ene undergoes hydroformylation at 423K, 200 bar, and with a 1:1 H_2:CO ratio



- The rate of hydroformylation was hindered by sterically demanding alkenes

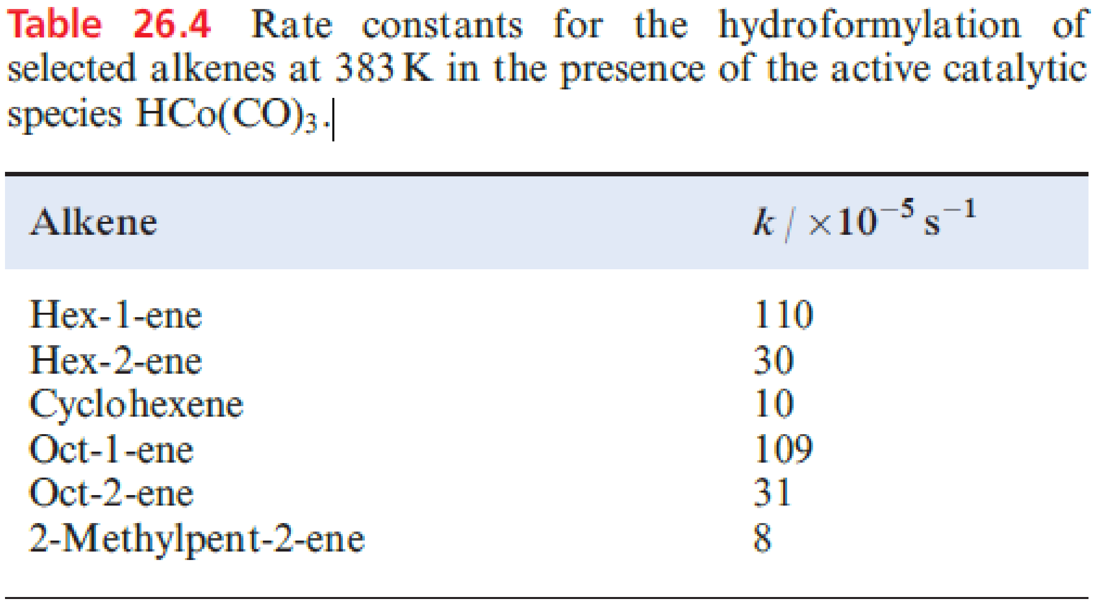


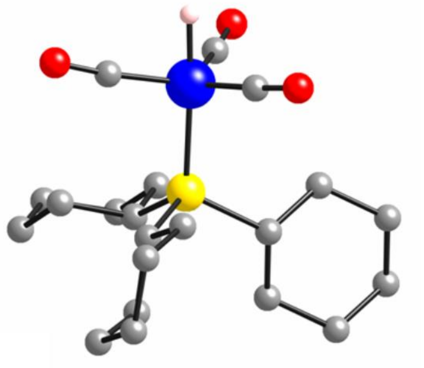
Table 26.4 Rate constants for the hydroformylation of selected alkenes at 383 K in the presence of the active catalytic species $HCo(CO)_3$.

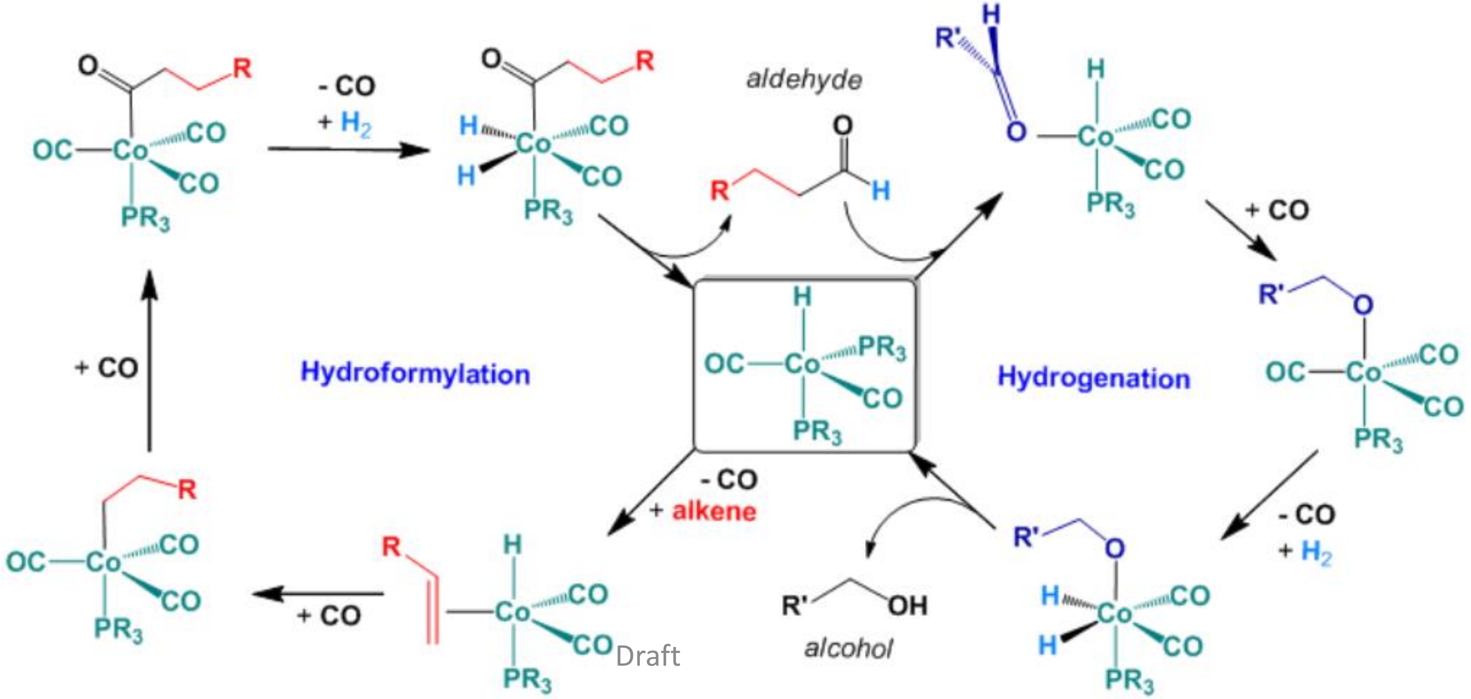
Alkene	k / $\times 10^{-5}$ s^{-1}
Hex-1-ene	110
Hex-2-ene	30
Cyclohexene	10
Oct-1-ene	109
Oct-2-ene	31
2-Methylpent-2-ene	8

- Other hydroformylation Co-catalysts (industrial) that are used are $[HCo(CO)_3(PBu_3)]$ (must lose CO to become coordinatively unsaturated) and $[HRh(CO)(PPh_3)_3]$ (loses PPh_3 to give the catalytically active $[HRh(CO)(PPh_3)_2]$)
- The Co-process is difficult to operate partly because of high pressure involved and partly because of the need to recycle the volatile Co-carbonyl.
- Loss of 15% of products due to additional reactions such as hydrogenation, condensation

Cobalt Phosphine modified catalyst

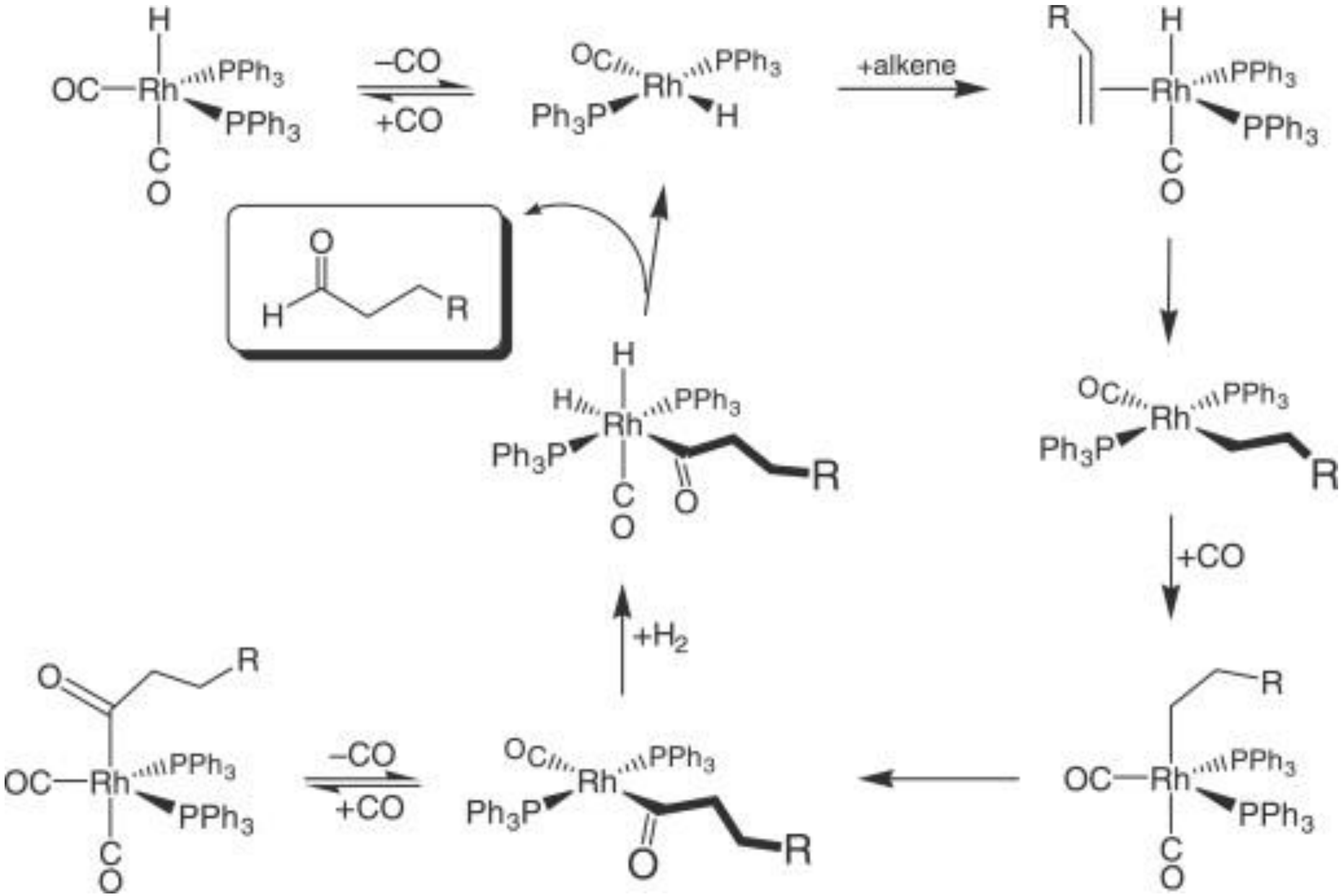
- Use of phosphines in Co-catalyzed hydroformylation makes the reaction slower
- Addition of phosphine stabilizes the catalyst and reduces the pressure requirement to some extent
- Selectivity to linear products increases
- The carbonyl complex [$HCoL(CO)_3$], is much more stable
- The catalyst is active for hydrogenation

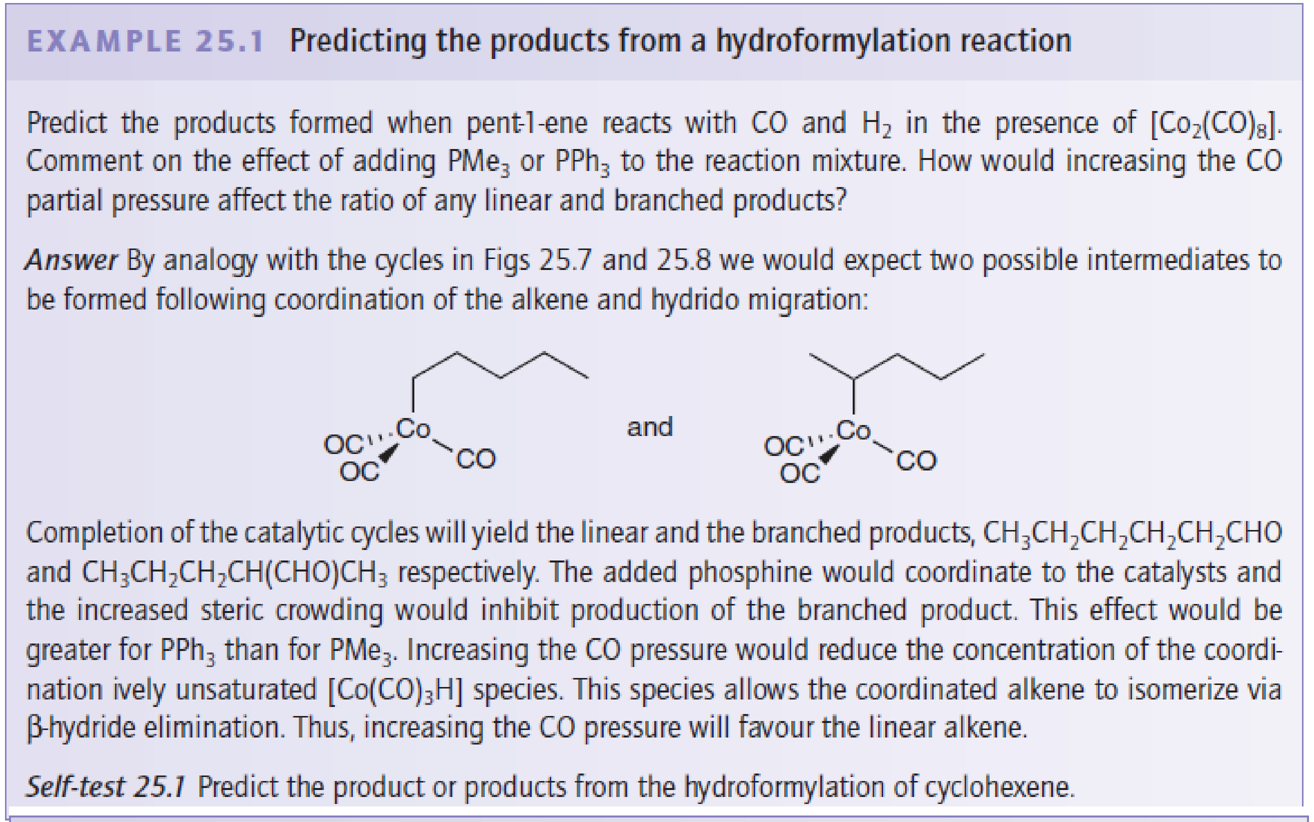




Rh-catalyst

- Hydroformylation catalyst precursor $[Rh(CO)H(PPh_3)_3]$ loses a PPh_3 ligand to form the coordinatively unsaturated 16e complex $[Rh(CO)H(PPh_3)_2]$ & thereby promoting hydroformylation at moderate temperatures and 1 atm pressure
- Excess of PPh_3 prevents the reactions which occur in the presence of CO, terminal product predominates (20:1)
- Initial step is generation of a 16e square planar intermediate for 18e precursor
- Next step is alkene coordination and hydrogen transfer to give alkyl species
- Alkyl undergoes CO addition and insertion to give acyl derivative
- Acyl derivative undergoes oxidative addition of H2 to give hydridoacyl complex
- Next, change in OS of Rh (rate determining step)
- Finally, another H-transfer to C-atom of acyl group, reductive elimination of aldehyde, followed by dissociation of the product and regeneration of active species


–CO
+CO
+alkene
+CO
+H$_2$
–CO
+CO



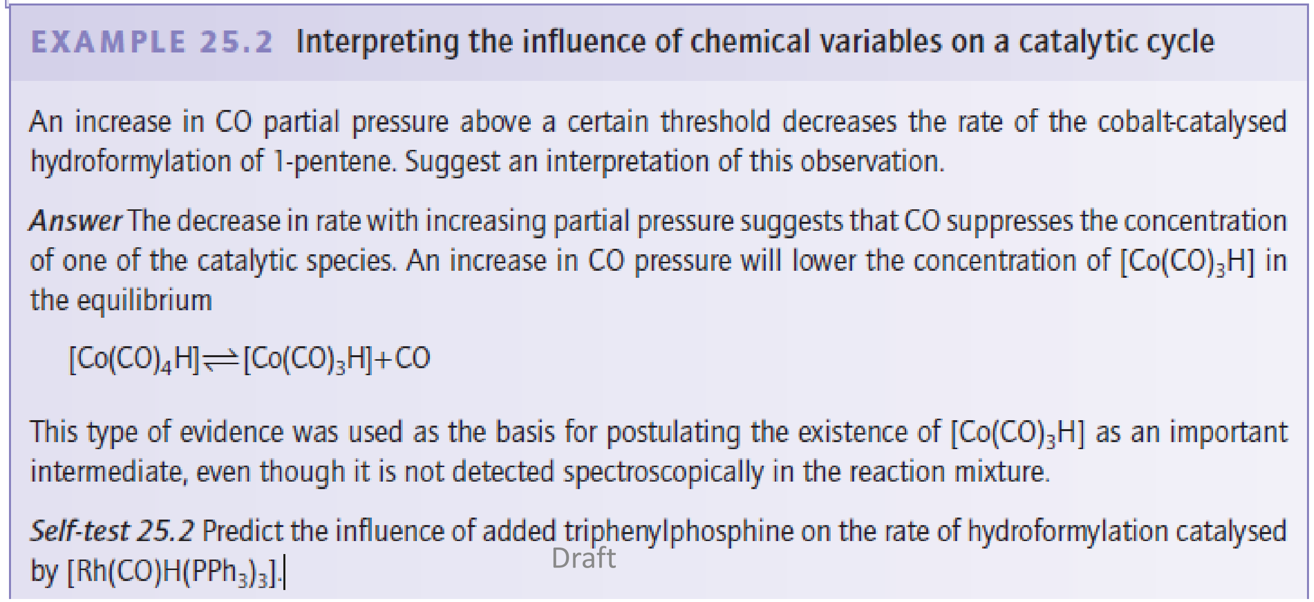
EXAMPLE 25.1 Predicting the products from a hydroformylation reaction

Predict the products formed when pent-1-ene reacts with CO and H_2 in the presence of $[Co_2(CO)_8]$. Comment on the effect of adding PMe_3 or PPh_3 to the reaction mixture. How would increasing the CO partial pressure affect the ratio of any linear and branched products?

Answer By analogy with the cycles in Figs 25.7 and 25.8 we would expect two possible intermediates to be formed following coordination of the alkene and hydrido migration:

Completion of the catalytic cycles will yield the linear and the branched products, $CH_3CH_2CH_2CH_2CH_2CHO$ and $CH_3CH_2CH_2CH(CHO)CH_3$ respectively. The added phosphine would coordinate to the catalysts and the increased steric crowding would inhibit production of the branched product. This effect would be greater for PPh_3 than for PMe_3. Increasing the CO pressure would reduce the concentration of the coordination ively unsaturated $[Co(CO)_3H]$ species. This species allows the coordinated alkene to isomerize via β-hydride elimination. Thus, increasing the CO pressure will favour the linear alkene.

Self-test 25.1 Predict the product or products from the hydroformylation of cyclohexene.



EXAMPLE 25.2 Interpreting the influence of chemical variables on a catalytic cycle

An increase in CO partial pressure above a certain threshold decreases the rate of the cobalt-catalysed hydroformylation of 1-pentene. Suggest an interpretation of this observation.

Answer The decrease in rate with increasing partial pressure suggests that CO suppresses the concentration of one of the catalytic species. An increase in CO pressure will lower the concentration of $[Co(CO)_3H]$ in the equilibrium

$$[Co(CO)_4H] \rightleftharpoons [Co(CO)_3H] + CO$$

This type of evidence was used as the basis for postulating the existence of $[Co(CO)_3H]$ as an important intermediate, even though it is not detected spectroscopically in the reaction mixture.

Self-test 25.2 Predict the influence of added triphenylphosphine on the rate of hydroformylation catalysed by $[Rh(CO)H(PPh_3)_3]$.

EXERCISE 14.4

Show how $(CH_3)_2CHCH_2CHO$ can be prepared from $(CH_3)_2C{=}CH_2$ by the hydroformylation process.

A shortcoming of the cobalt carbonyl-based hydroformylation process is that it produces only about 80 percent of the much more valuable linear aldehydes, with the remainder having branched chains. Modifying the catalyst by replacing one of the CO ligands of the starting complex by PBu_3 (Bu = *n*-butyl) to give $HCo(CO)_3(PBu_3)$ increases the selectivity of the process to give an approximately 9:1 ratio of linear to branched aldehydes.[26] The effect of phosphines on the thermodynamics of this cobalt-catalyzed hydroformylation system has been explored.[27] Finally, replacing the cobalt with rhodium yields far more active catalysts (much less catalyst needs to be present) that can function with higher linear to branched selectivity at significantly lower temperatures and pressures than cobalt-based catalysts.[28] A proposed mechanism for an example of such a catalytic process using $HRh(CO)_2(PPh_3)_2$ is in **Figure 14.19**.*

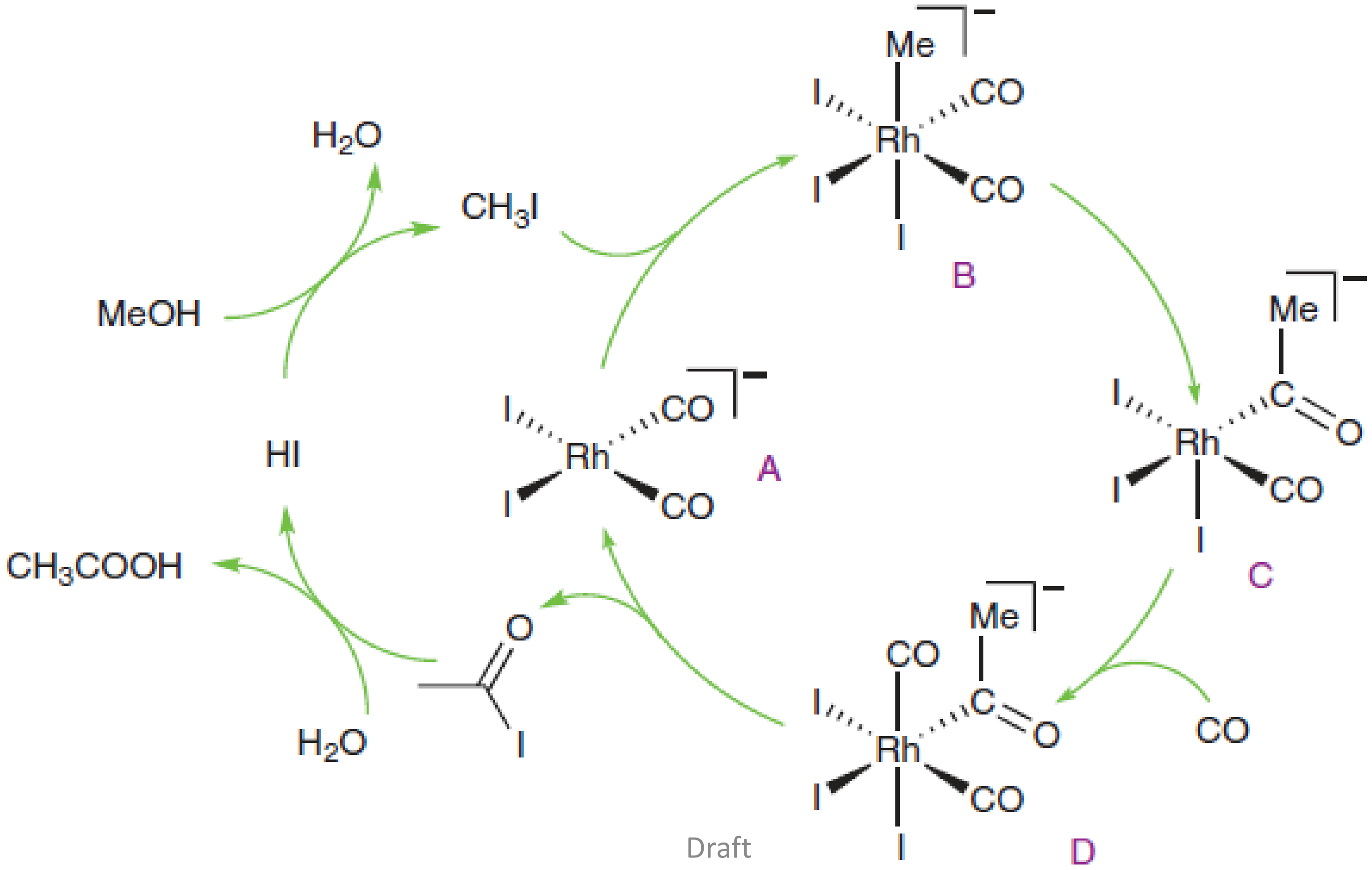
Monsanto Acetic acid Process (1966)

- Monsanto developed the Rh-catalyzed process for the carbonylation of methanol to produce acetic acid.

$$CH_3OH + CO \rightarrow CH_3COOH; \qquad \Delta G = -75 kJ/mol$$

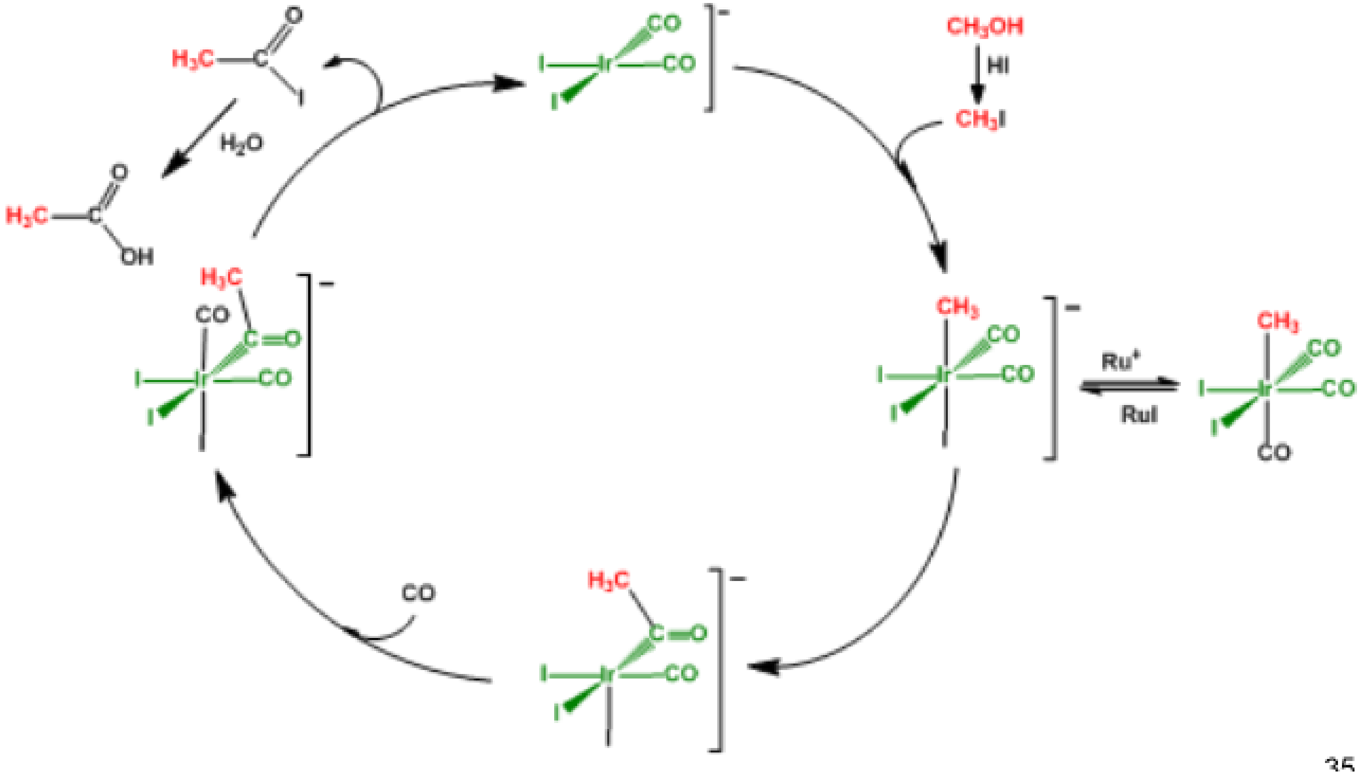
- It operates at 30-60 bar and 150-200 ºC, Zr-reactor are used due to corrosive nature of reagent.
- Under the conditions used, iodide ions react with methanol to set up an appreciable concentration of iodomethane in the first step of the reaction.
- Starting with the four-coordinate, 16-electron complex $[Rh(CO)_2I_2]^-$ (A), the next step is the oxidative addition of iodomethane to produce the six-coordinate, 18-electron complex $[Rh(Me)(CO)_2I_3]^-$ (B)
- Both Monsanto and Cativa processes are highly selective and generate ethanoic acid of sufficient purity that it can be used in human food.
- This step is followed by methyl migration, yielding a 16-electron acyl complex (C)

- Coordination of CO restores an 18e complex (D), which is then set to undergo reductive elimination of acetyl iodide with the regeneration of $[Rh(CO)_2I_2]^-$
- Water then hydrolyses the acetyl iodide to acetic acid and regenerates HI.
- Under normal conditions, the rate-determining step for the Rh-based system is the oxidative addition of iodomethane



Cativa Process

- Cativa processes follow essentially the same reaction sequence (Monsanto process), which uses Ir-catalyst
- In this process, the migration of the methyl group is the rate determining step (differs from Monsanto process).
- Methyl migration on Ir is favored by formation of a neutral intermediate, & I^- accepting promoters help facilitate substitution of an I^- ligand by CO in the Ir-analogue of complex (B).



Wacker's Process (oxidation of alkene)

- **Wacker process** is used to produce ethanal (acetaldehyde) from ethene and oxygen
- It is the most successful system that uses a palladium catalyst to oxidize the alkene, with the palladium being re-oxidized via a secondary copper catalyst.

$$CH_2=CH_2 + 1/2O_2 \rightarrow CH_3\text{-}CHO; \qquad \Delta G = -197 kJ/mol$$

- It is the combination of three well known reactions viz.

1. The oxidation of ethene is known to be caused by a palladium(II) salt

$$CH_2=CH_2 + PdCl_2 + H_2O \rightarrow CH_3\text{-}CHO + Pd(0) + HCl$$

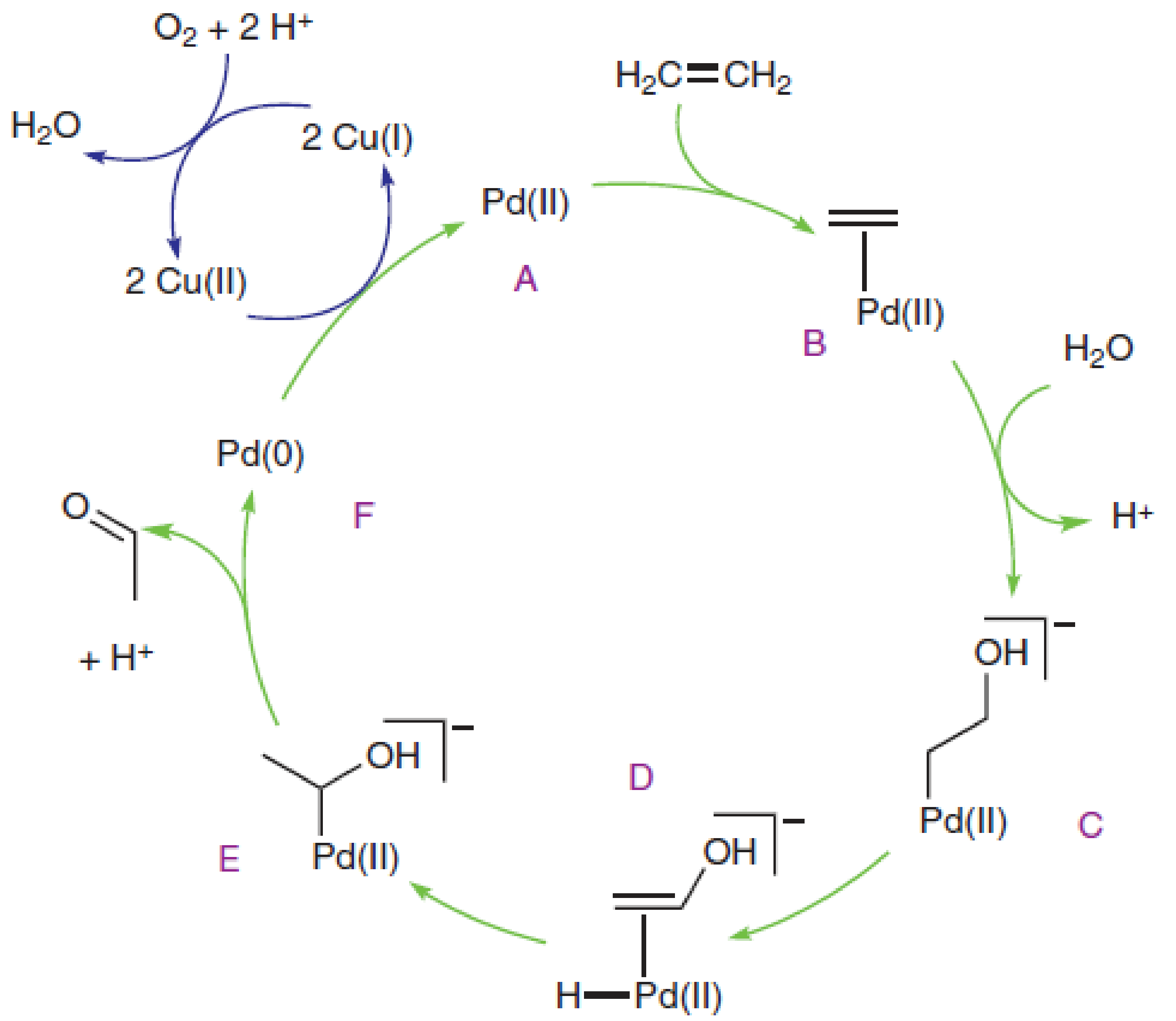
2. The Cu (II) catalyzed oxidation of Pd(0) back to Pd(II) by oxygen

$$Pd(0) + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$$

3. The air oxidation of Cu(I) to Cu(II)

$$2CuCl + 1/2O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

- The hydration of the alkene/Pd(II) complex (B) occurs by the attack of H_2O from the solution on the coordinated ethene rather than the insertion of coordinated OH.
- Hydration, to form (C), is followed by two steps that isomerize the coordinated alcohol.
- First, β-hydrogen elimination leading to the formation of (D), & then migration of a hydride resulting the formation of (E).
- Elimination of the ethanal and an H^+ ion then leaves Pd(0), which is converted back to Pd(II) by the auxiliary copper(II)-catalyzed air oxidation cycle.
- Alkene ligands coordinated to Pt(II) are also susceptible to nucleophilic attack, but only palladium leads to a successful catalytic system (due to the greater lability of 4d Pd(II) complexes & more favorable potential for oxidation of Pd(0) to Pd(II))



- The Pd/Cu catalyzed oxidation of olefins can be applied to many substrates.
- If acetate is used as the nucleophile instead of water, stereo selectively alkenyl is resulted

Ziegler-Natta Catalysis (Polymerization of olefins)

- K. Ziegler (Germany) discovered in 1953 that when $TiCl_4$(s) and $AlEt_3$ are combined together they produced an extremely active **heterogeneous catalyst** for the polymerization of ethylene at atmospheric pressure.
- G. Natta (Italy) extended the method to other olefins like propylene and developed variations of the Ziegler catalyst based on his findings on the mechanism of the polymerization reaction.
- The Ziegler-Natta catalyst family includes halides of titanium, chromium, vanadium, and zirconium, typically activated by alkyl aluminum compounds

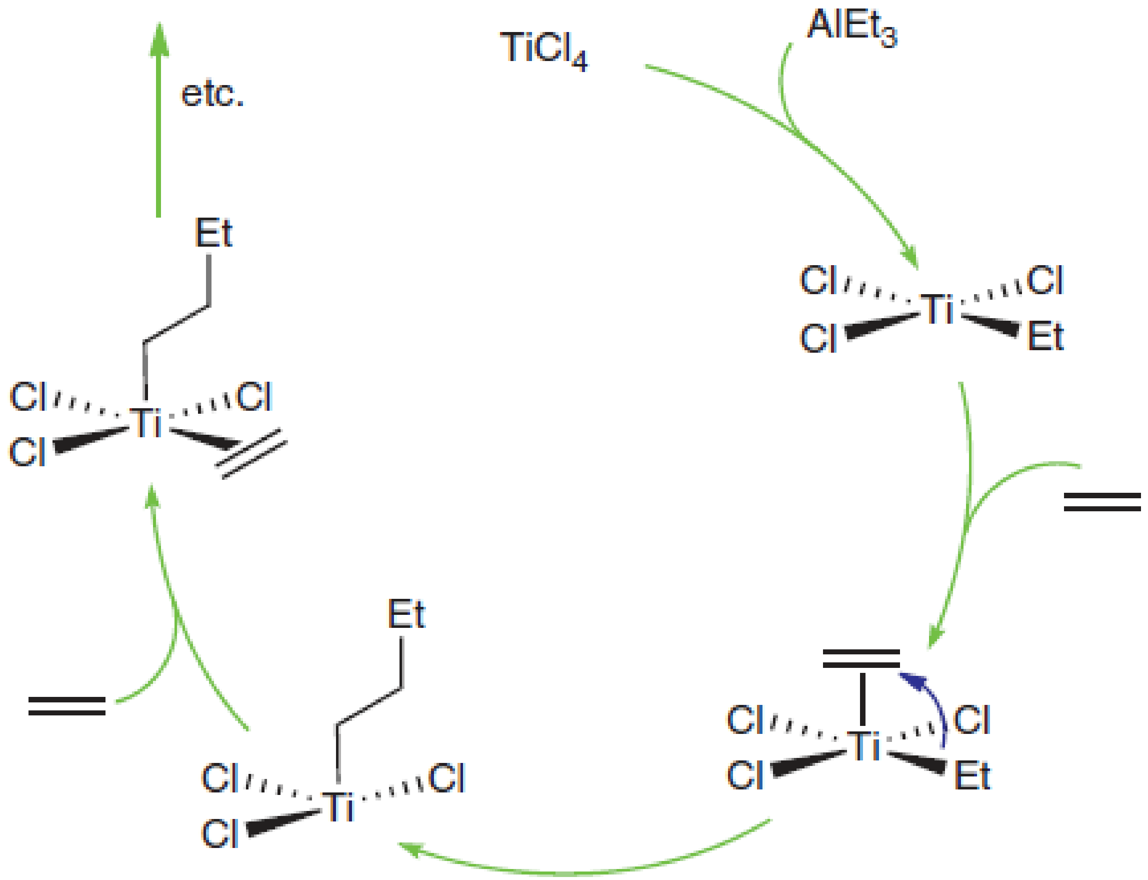
Ziegler and Natta received the Nobel Prize in Chemistry for their work in 1963

Mechanism

- Details of the mechanism of Ziegler-Natta catalysis are still uncertain
- Cossee–Arlman mechanism is regarded as highly plausible
- The catalyst is prepared from $TiCl_4$ and $Al(C_2H_5)_3$, which react to give polymeric $TiCl_3$ mixed with $AlCl_3$ in the form of a fine powder.
- The alkylaluminium alkylates a Ti atom on the surface of the solid and an ethene molecule coordinates to the neighboring vacant site.
- In the propagation steps for the polymerization, the coordinated alkene undergoes a migratory insertion reaction.
- This migration opens up another neighboring vacancy, and so the reaction can continue and the polymer chain can grow.
- The release of the polymer from the metal atom occurs by β-hydrogen elimination, and the chain is terminated.
- Some catalyst remains in the polymer, but the process is so efficient that the amount is negligible.

- Three different steps in polymerization

- **Initiation** (generation of active catalyst from less active or precursor),
- **Propagation** (polymer chain growth over repeated steps) and
- **Termination** (stops the polymer chain growth)



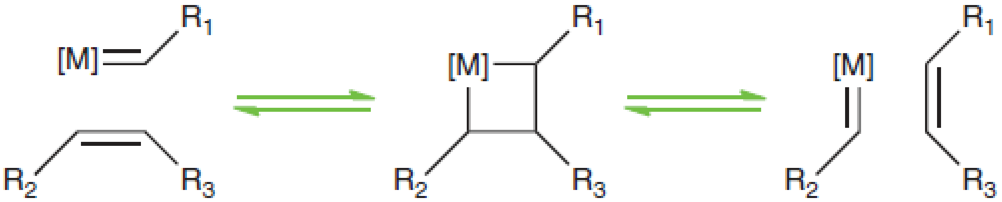
Function of aluminium alkyl

1. Alkylate the transition metal
2. Acts as Lewis acid and create a vacant coordination site by abstracting a halide or alkyl ligand from the transition metal
3. Acts as cleaning role, by mopping up impurities from the monomer and the reaction medium

- Metallocene complexes of Ti, Zr and Hf (Cp_2MR_2) have also been used for the same purpose with $[Cp_2MR]^+$ being the 14e active species
- The active species has a pseudo-tetrahedral structure with vacant site suitable for alkene coordination

Olefin Metathesis (dismutation reaction)

- Alkene (olefin) metathesis are metal-catalyzed reactions in which C=C bonds are redistributed (discovered in 1950s)
- Alkene metathesis reactions are catalyzed by homogeneous organometallic complexes that allow considerable control over product distribution
- A key step in the reaction mechanism is the dissociation of a ligand from a metal center to allow an alkene to coordinate
- Alkene metathesis reactions proceed through a metallacyclobutane intermediate

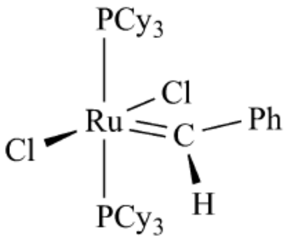


- Chauvin, Grubbs, and Schrock for their work in Olefin metathesis were awarded Nobel Prize in 2005
- In the case of Grubbs' catalyst, it is known that the dissociation of a PCy_3 (Cy = cyclohexyl) ligand from the Ru metal center is crucial in allowing the alkene molecule to coordinate prior to metallacyclobutane formation.
- The metathesis of alkene is reversible and can be extremely rapid

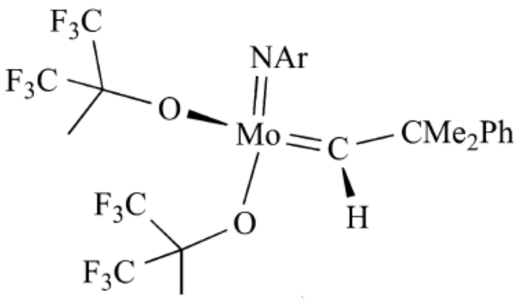
- In this transformation, the C=C bond of an alkene such as RCH=CHR′ is broken with the resulting RHC and R′HC fragments being redistributed

$$\begin{matrix}\text{RHC}\\ \| \\ \text{R'HC}\end{matrix} + \begin{matrix}\text{CHR'}\\ \| \\ \text{CHR}\end{matrix} \xrightleftharpoons{\text{cata.}} \begin{matrix}\text{RHC}=\text{CHR'}\\ + \\ \text{R'HC}=\text{CHR}\end{matrix}$$

- To make catalysts more tolerant of functionality, a move to the right in the periodic table became necessary
- Mo and W catalysts are intermediate in character, while soft Ru catalysts prefer C=C bonds over heteroatoms
- Grubbs’ Ru catalysts have proved to be the easiest to handle, but some applications require Schrock’s more reactive Mo catalysts. Both contain the critical metal carbene unit required for catalysis

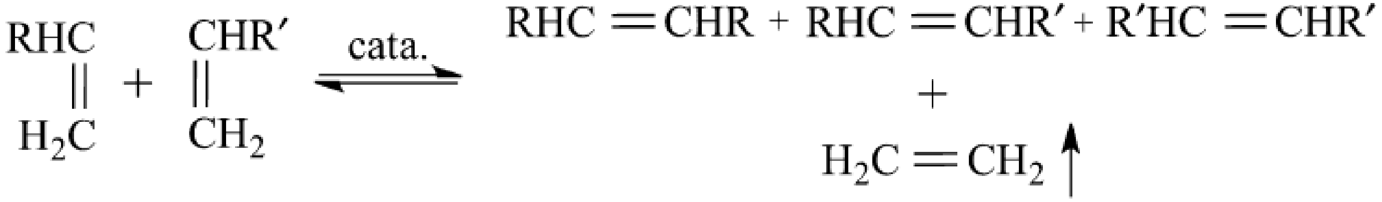


Grubbs catalyst



Schrock catalyst

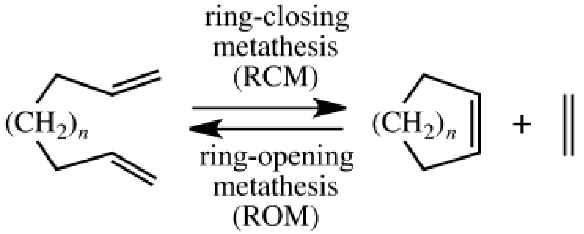
- Metatheses naturally divide into two types depending on the substrates and products.
- *Simple metathesis* (shown above) involving a single alkene as reactant
- *Cross metathesis* (CM), where two different alkenes react.
- In a common variant of CM, one product is removed, such as volatile C_2H_4, to drive the reaction to the right.
- With some choices of R and R′, the cross product RCH=CHR′ can be strongly favored kinetically.
- This happens when R is a electron donor alkyl or aryl and R′ is an electron withdrawing group, stabilizing the mixed product by a push-pull effect.



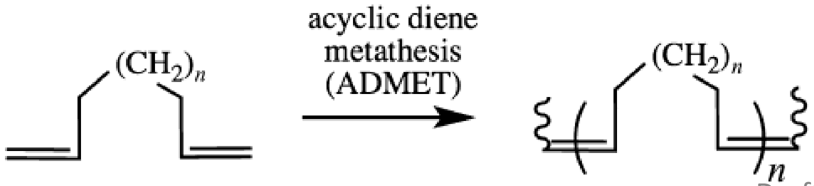
$$\begin{matrix}\mathrm{RHC}\\ \| \\ \mathrm{H_2C}\end{matrix} + \begin{matrix}\mathrm{CHR'}\\ \| \\ \mathrm{CH_2}\end{matrix} \xrightleftharpoons{\text{cata.}} \mathrm{RHC{=}CHR} + \mathrm{RHC{=}CHR'} + \mathrm{R'HC{=}CHR'} + \mathrm{H_2C{=}CH_2}\uparrow$$

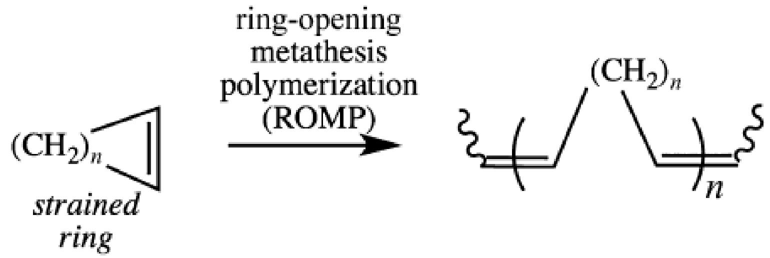
$$\begin{matrix}\mathrm{PhHC}\\ \| \\ \mathrm{H_2C}\end{matrix} + \begin{matrix}\mathrm{CHCOOEt}\\ \| \\ \mathrm{CH_2}\end{matrix} \xrightleftharpoons{\text{cata.}} \mathrm{PhHC{=}CHCOOEt} + \mathrm{H_2C{=}CH_2}\uparrow$$

- With an unconjugated diene, ring-closing metathesis (RCM) is possible, a reaction that is particularly good for forming medium and large rings.
- The reverse of the equation is ring-opening metathesis (ROM), favored by ring strain or a large excess of C_2H_4.
- The outcome is governed by the thermodynamics of the given equation, together with the possibility of driving off the volatile C_2H_4 in RCM.

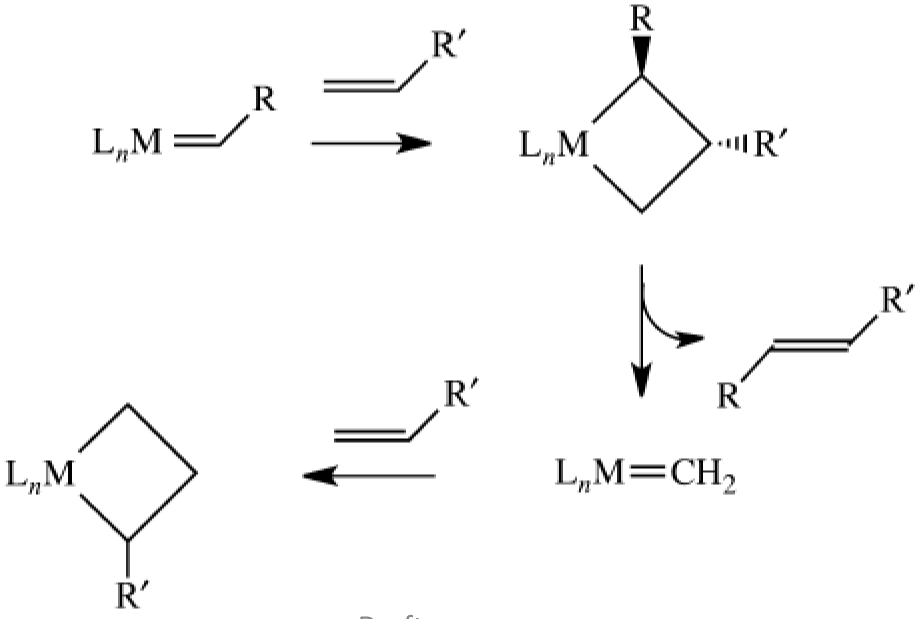


- The efficiency of the best catalysts is high enough for polymer formation.
- The two best known cases are acyclic diene metathesis (ADMET) and ring-opening metathesis polymerization, or ROMP, driven by ring strain

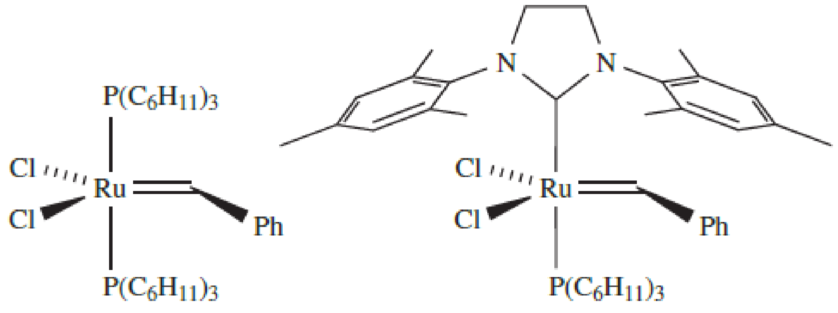




- **Chauvin mechanism** for metal-catalysed alkene metathesis involves a metal alkylidene species and a series of [2+2]-cycloadditions and cyclo-reversions.
- A metallacyclobutane is formed from an initial carbene reacting with an incoming alkene and then cleaving in a different direction to give the new alkene and a different carbene.
- The tendency of R and R/ to occupy different faces of the metallacyclobutane as a result of mutual steric repulsion translates into preferential formation of trans (*E*) alkenes



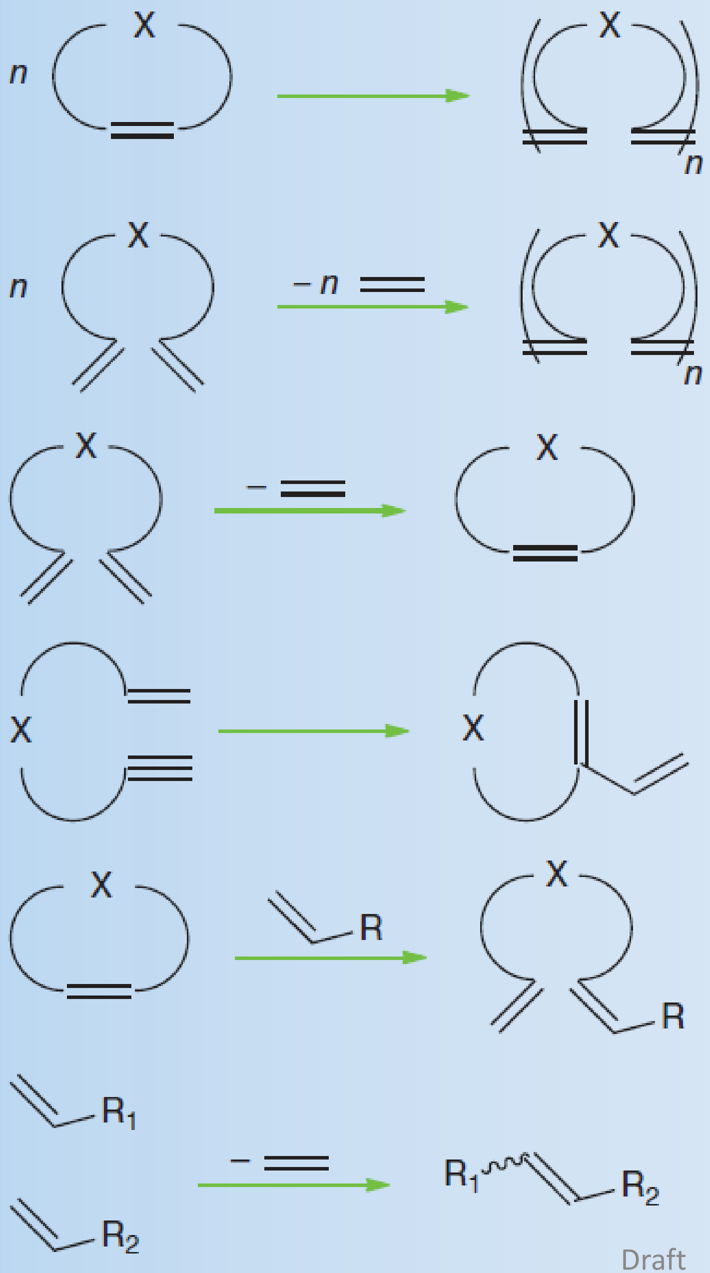
- The Schrock and Grubbs catalysts that have played a dominant role in the development of this area of chemistry
- Grubbs catalyst 1 is commercially available and second generation of it 2 exhibits higher catalytic activities in alkene metathesis reactions
- In Grubbs' catalysts, tricyclohexylphosphine is chosen in preference to other PR_3 ligands because its steric hindrance and strongly electron-donating properties lead to enhanced catalytic activity.



C_6H_{11} = cyclohexyl

- A great advantage of Grubbs' catalysts is that they are tolerant of a large range of functional groups, thus permitting their widespread application
- The stronger σ-donor and poorer π-acceptor ability of the NHC ligand would both encourage PCy_3 dissociation and stabilize the alkene complex, more active.

The scope of the alkene metathesis reaction



Ring-opening metathesis polymerization (ROMP)

Acyclic diene metathesis polymerization (ADMET)

Diene ring-closing metathesis (RCM)

Enyne ring-closing metathesis (RCM)

Ring-opening metathesis (ROM)

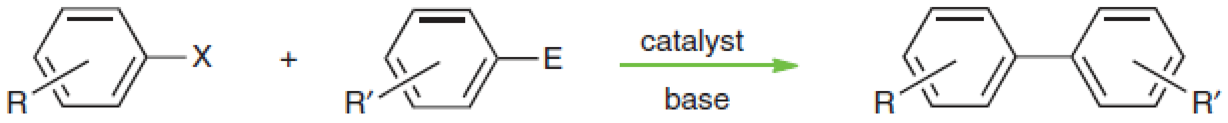
Cross-metathesis (CM or XMET)

Suzuki Coupling

- The Suzuki reaction allows the coupling of vinyl and arylboranes, *via* boronates, with vinyl or aryl halides, using a Pd(0) catalyst.

$$\mathrm{RI} + \mathrm{R'BR''_2} \xrightarrow[\text{base}]{\mathrm{Pd^0}} \mathrm{R\text{-}R'} + \mathrm{BR''_2I}$$

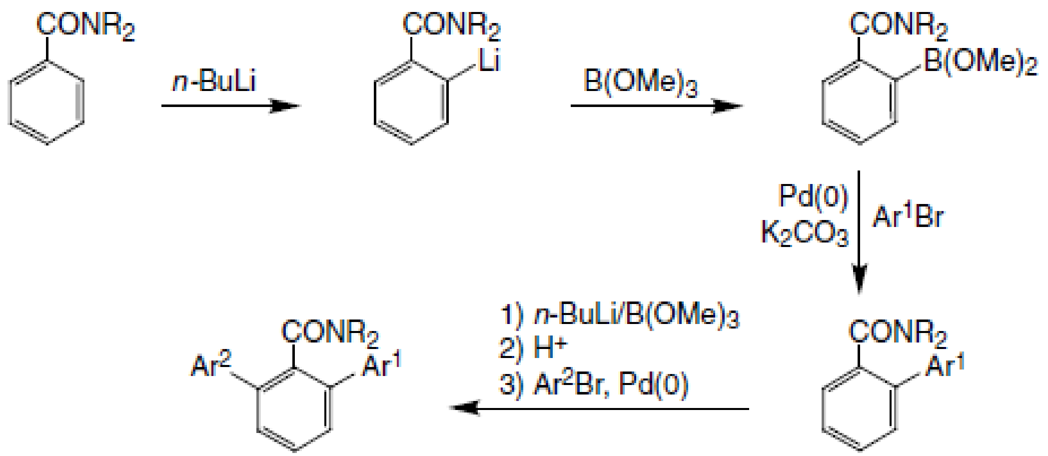
R, R' = vinyl or aryl; R" = OH, OR"' or alkyl (9-BBN)

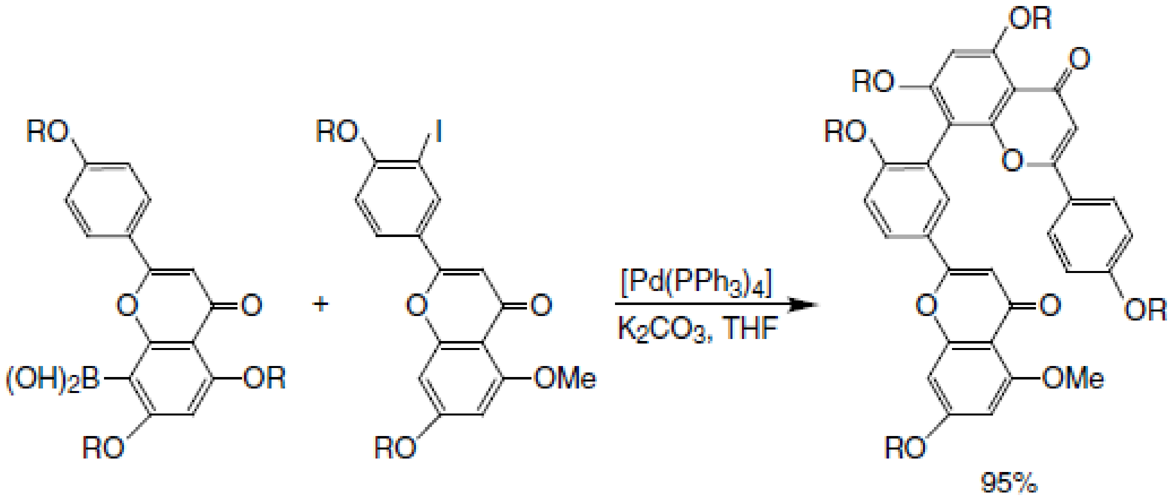


Suzuki: E = $B(OH)_2$

- The Suzuki reaction allows the introduction of alkenes, alkynes and arenes in C-C coupling processes, the hydroboration of alkenes and alkynes being very well known
- It is the addition of a base in the medium of the Suzuki reaction that leads to the transformation of a borane BR_3 into a boronate $BR_3(OH)^-$ that is the active species for transmetallation towards Pd

Examples:

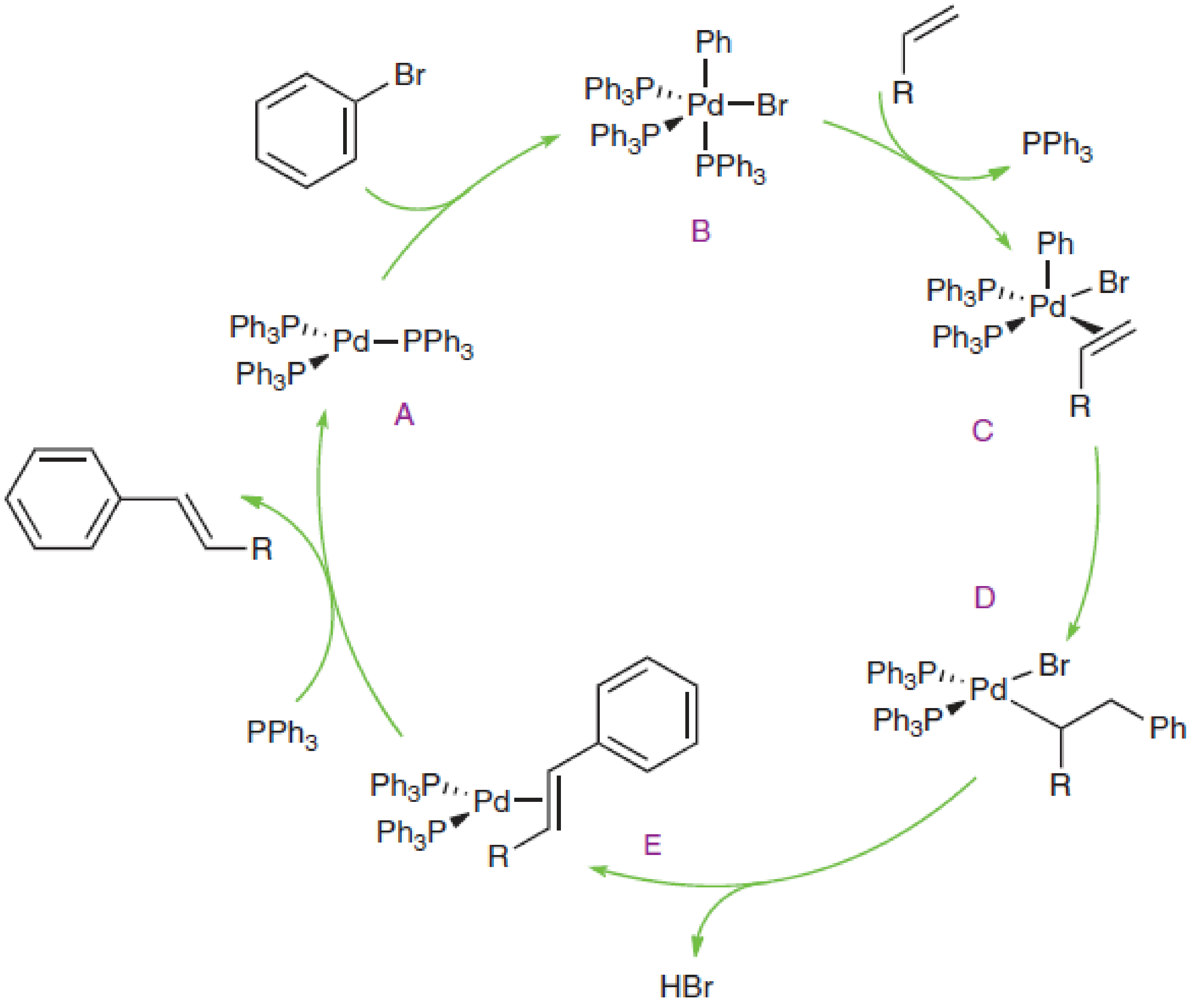




- ➢ The above examples are restricted to aryl iodides for which oxidative addition on Pd(0) is much more facile than with aryl chlorides (the most difficult to activate among the aryl halides) or even aryl bromides

Mechanism

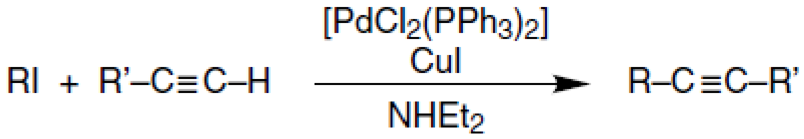
- Either a Pd(II) complex, such as [$PdCl_2(PPh_3)_2$], in the presence of additional PPh_3 or a Pd(0) compound, such as [$Pd(PPh_3)_4$] is used as the catalyst.
- Mechanism is unclear (and probably differs with each Pd/ligand/substrate combination)
- An idealized catalytic cycle for the coupling of an ethenyl group with an aryl halide is shown
- An initial oxidative addition of an aryl–halogen bond to an unsaturated Pd(0) complex (A) results in a Pd(II) species (B).
- Coordination of an alkene results in complex (C); 1,2-insertion results in an alkyl complex (D), which can be deprotonated with the loss of the halide to give the organic product attached to the palladium atom (E).
- In all palladium-catalyzed coupling reactions, the two coupling fragments must be *cis* to each other at the metal center before insertion or reductive elimination can take place



- Palladium-catalyzed coupling reactions are tolerant to a wide range of substitution on both fragments

The Sonogashira reaction

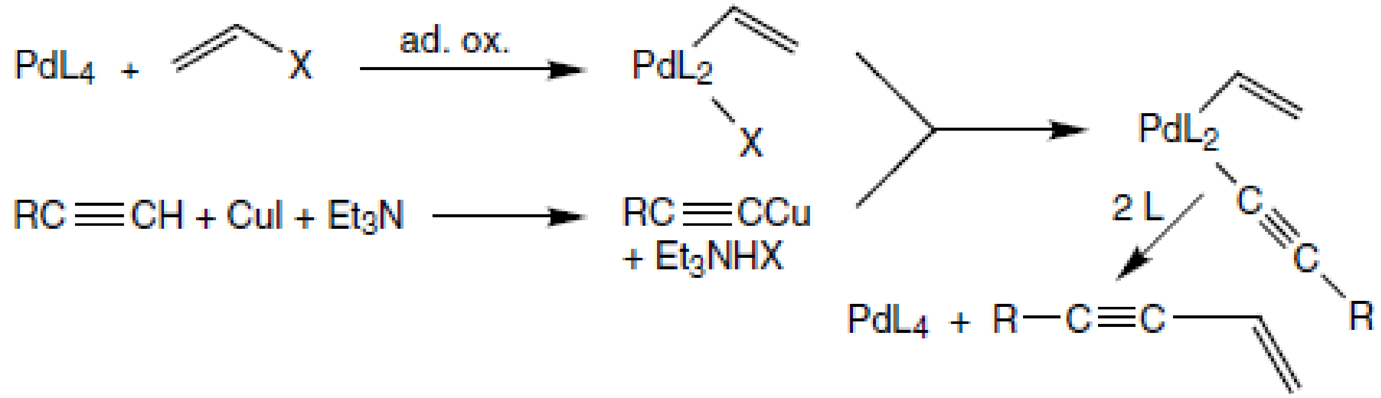
- Coupling terminal alkynes with halides catalyzed by Cu(I) & Pd(0) or Pd(0) alone
- Metalation of alkynes in situ before coupling
- Sonogashira reaction allows to couple a vinyl or aryl halide with a terminal alkyne.

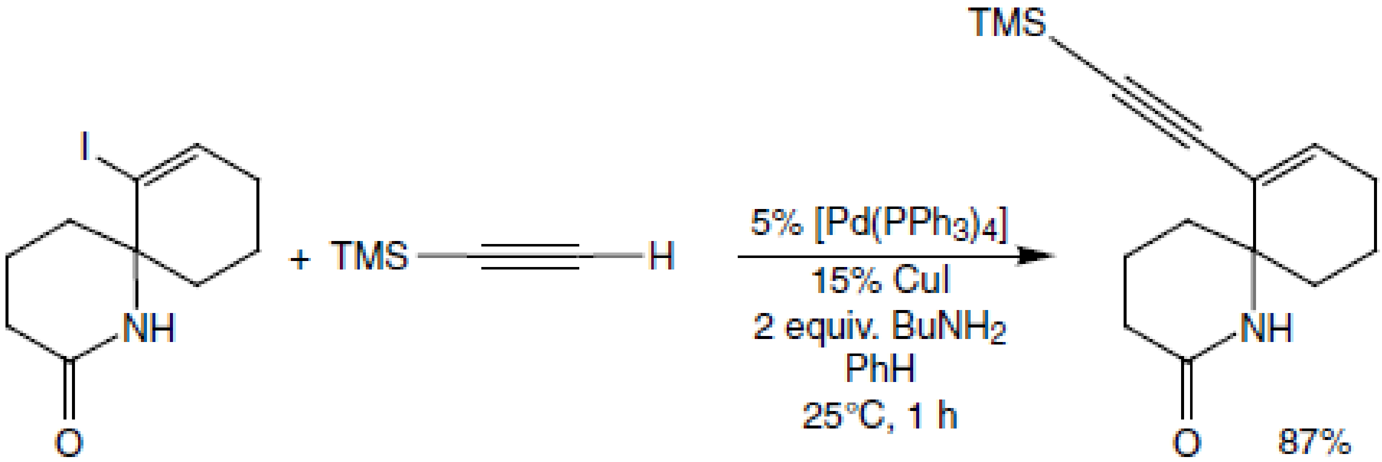


R = vinyl or aryl; R' = many functional groups

- In the Sonogashira reaction, the C-C coupling involves the usual mechanism, but the trans metallating agent (Cu(I) or Pd(0) itself) plays a catalytic role
- Two catalysts are a Pd(0) complex, such as [$PdCl_2(PPh_3)_2$], and a Cu(I) halide.
- This reaction is used in the synthesis of many pharmaceuticals, including treatments for psoriasis, Parkinson's disease, Tourette's syndrome, and Alzheimer's disease

Mechanism and examples:





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