



University of Lucknow | Centenary Year
लखनऊ विश्वविद्यालय | शताब्दी वर्ष



Homogeneous Catalysis

1895 Ostwald

A catalyst is a substance that changes the rate of a chemical reaction without itself appearing into the products.

Today We can define the catalyst as

A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved

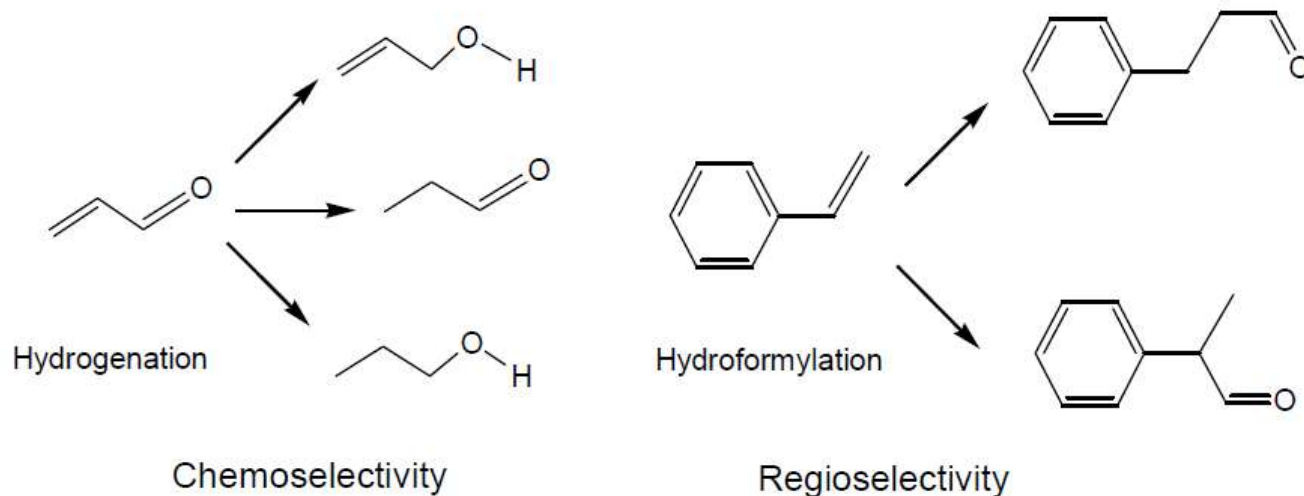
The "catalyst" may be added to the reactants in a different form, the catalyst precursor, which has to be brought into an active form ("activated"). During the catalytic cycle the catalyst may be present in several intermediate forms when we look more closely at the molecular level. An active catalyst will pass a number of times through this cycle of states; in this sense the catalyst remains unaltered. The number of times that a catalyst goes through this cycle is the turnover number.

The turnover number (TON) is the total number of substrate molecules that a catalyst converts into product molecules. The turnover frequency (TOF) is the turnover number in a certain period of time.

Homogeneous Catalysis

- Organometallic catalysts consist of a central metal surrounded by organic (and inorganic) ligands.
- Both the metal and the large variety of ligands determine the properties of the catalyst.
- The success of organometallic catalysts lies in the relative ease of catalyst modification by changing the ligand environment. Crucial properties to be influenced are the rate of the reaction and the selectivity to certain products.

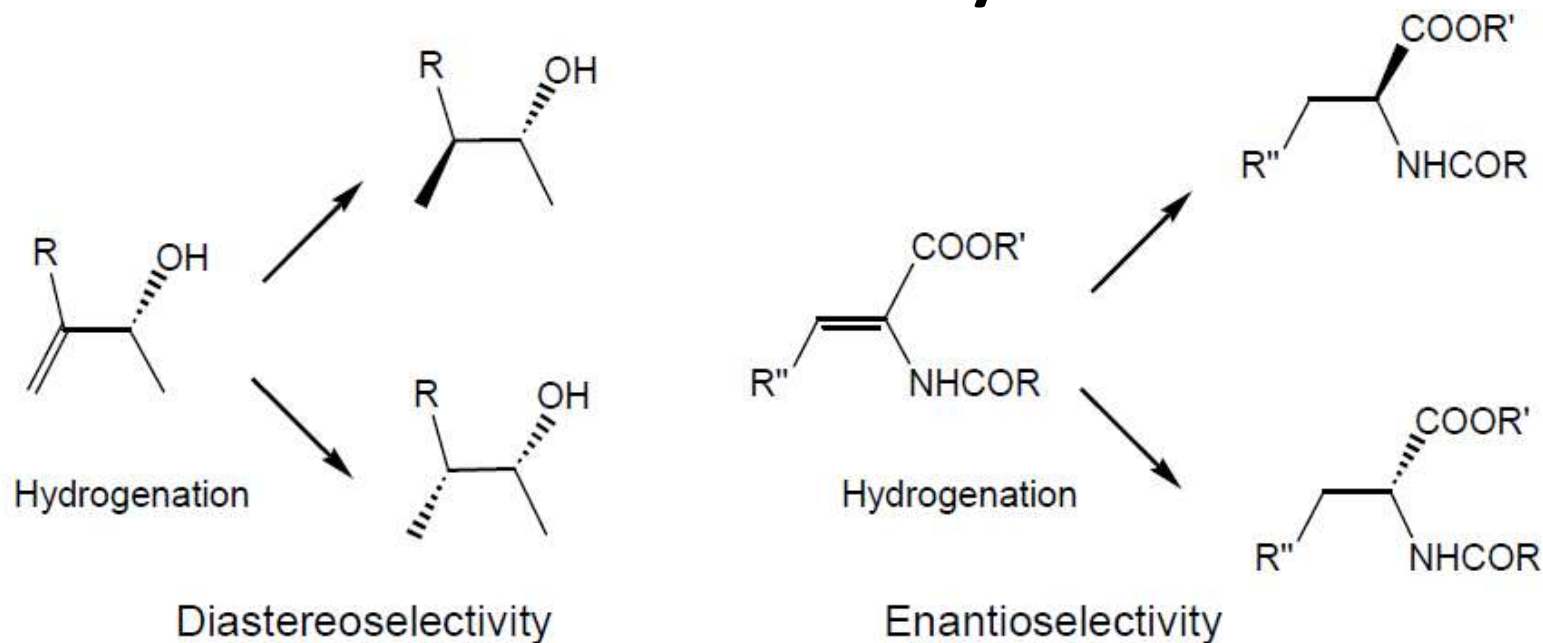
Selectivity



chemoselectivity, when two chemically different functionalities are present such as an alkene and an aldehyde which both can be hydrogenated, the chemoselectivity tells us whether the aldehyde or the alkene is being hydrogenated; or when more than one reaction can take place for the same substrate e.g. hydrogenation or hydroformylation;

regioselectivity, as in the example shown for the hydroformylation reaction, the formyl group can be attached to either the primary, terminal carbon atom or the secondary, internal carbon atom, which leads respectively to the linear and the branched product;

Selectivity



diastereoselectivity, the substrate contains a stereogenic centre and this together with the catalyst can direct the addition of dihydrogen in the example to give two diastereomers, the selectivity for either one is called the diastereoselectivity;

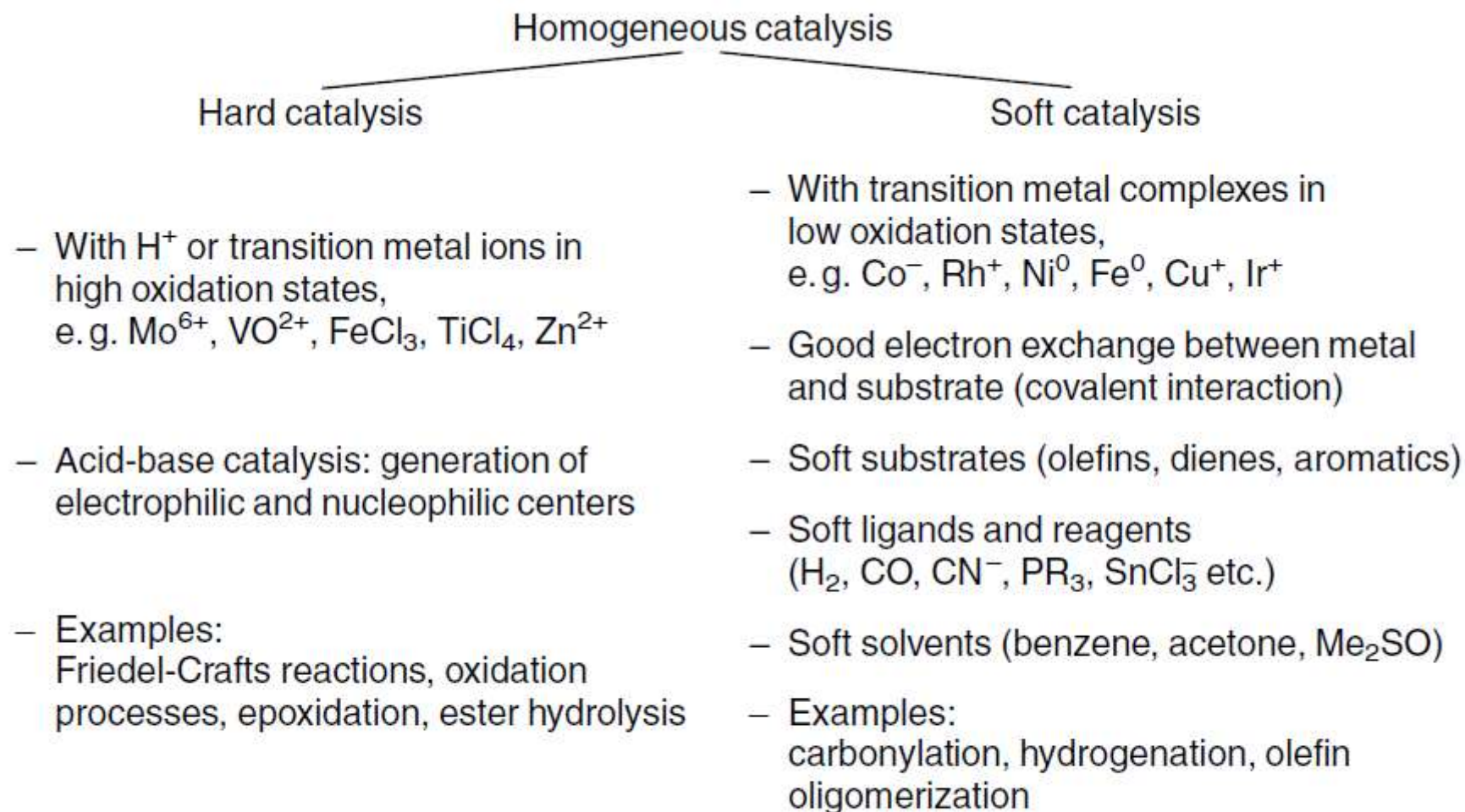
enantioselectivity, the substrate is achiral in this instance, but the *enantiopure* or *enantio-enriched* catalyst may give rise to the formation of one specific product enantiomer.

High selectivity is a means

- 1) to reduce waste,**
- 2) to reduce the work-up equipment of a plant, and**
- 3) to ensure a more effective use of the feedstocks.**

Rate enhancements of many orders of magnitude can be obtained in catalysis, often by very subtle changes. Rates represent a cost factor, higher rates allowing higher space-time yields (kg of product per time and reactor volume) and hence smaller reaction vessels.

Higher rates and higher overall catalyst yields (i.e. mass of product per unit mass of catalyst) reduce the incremental contribution of catalyst costs per unit mass of product generated: In the case of metallocene catalysts for olefin polymerisation for example the higher catalyst cost contribution of these catalysts (around \$0.04 per kg of polyolefin) has significantly reduced their impact and ability to displace Ziegler-Natta catalysts (where the catalyst cost contribution is only \$0.006-0.011 per kg of polymer).



Scheme 2-4 Hard and soft catalysis with transition metal compounds

Effective atomic number rule (EAN)

The rule is based on the observation that the well-characterized diamagnetic complexes of the transition metals in particular have 16 or 18 valence electrons. All ligands bound covalently to the metal center contribute two electrons to the valence shell, and the metal atom provides all the d electrons, corresponding to its formal oxidation state.

Examples:

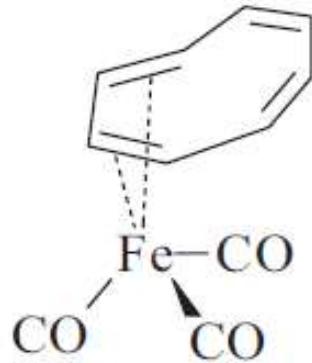
$[\text{Rh}^{\text{I}}\text{Cl}(\text{PPh}_3)_3]$ has $8 + (4 \times 2) = 16$ valence electrons
8 e

$[\text{CH}_3\text{Mn}^{\text{I}}(\text{CO})_5]$ has $6 + (6 \times 2) = 18$ valence electrons

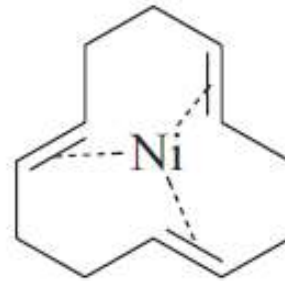
Tolman specified the following rules for organometallic complexes and their reactions:

- 1) Under normal conditions, diamagnetic organometallic complexes of the transition metals exist in measurable concentrations only as 16- or 18-electron complexes.
- 2) Organometallic reactions, including catalytic processes, proceed by elemental steps involving intermediates with 16 or 18 valence electrons.

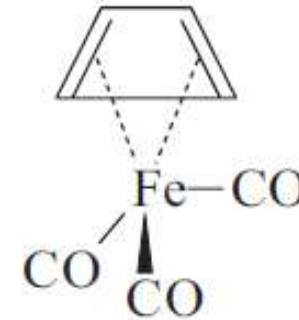
EAN Rule



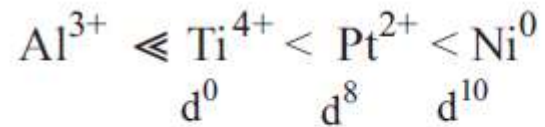
Cyclooctatetraene
iron tricarbonyl.
Formal Fe charge: 0.
Number of π electrons
involved: 4



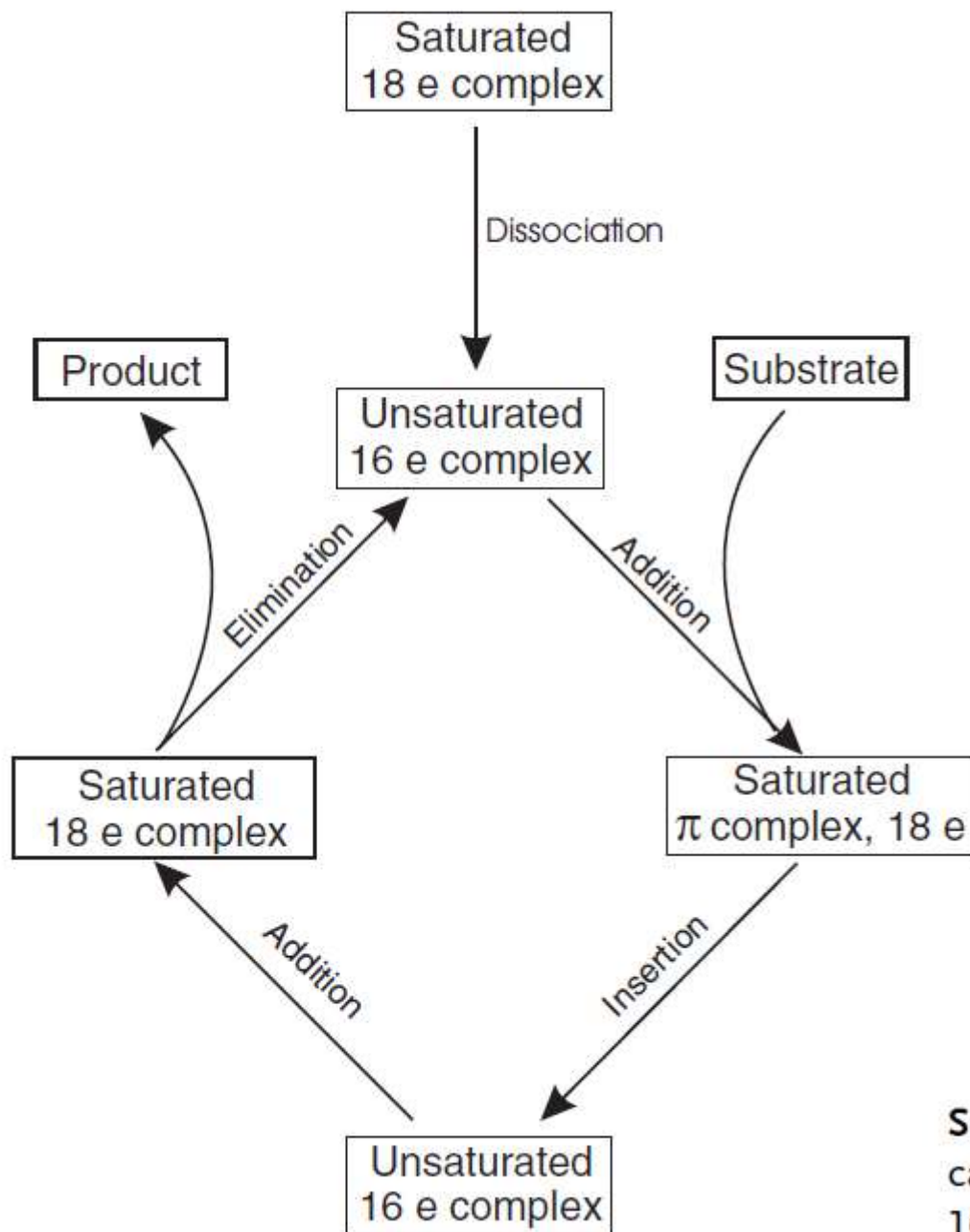
1,5,9-Cyclododecatriene
nickel.
Formal Ni charge: 0.
Number of π electrons
involved: 6



Cyclobutadiene
iron tricarbonyl.
Formal Fe charge: 0.
Number of π electrons
involved: 4



→
 π -Bonding contribution (softness),
stability of the metal olefin complex



Scheme 2-2 Course of a homogeneously catalyzed reaction according to the 16/18-electron rule

ELEMENTARY STEPS

Organometallic Chemistry

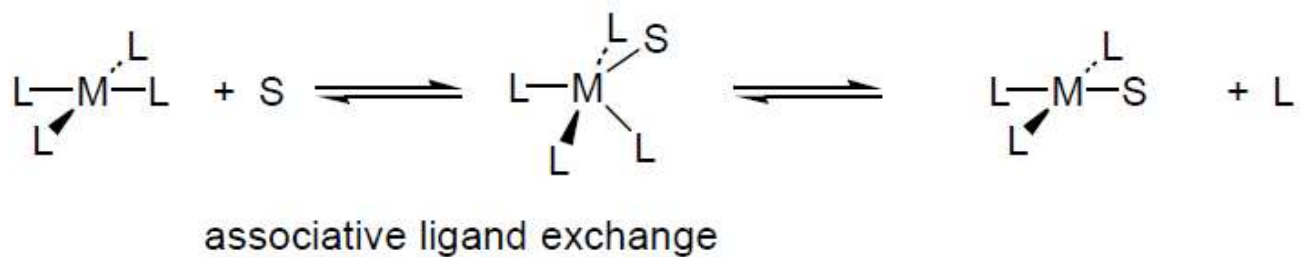
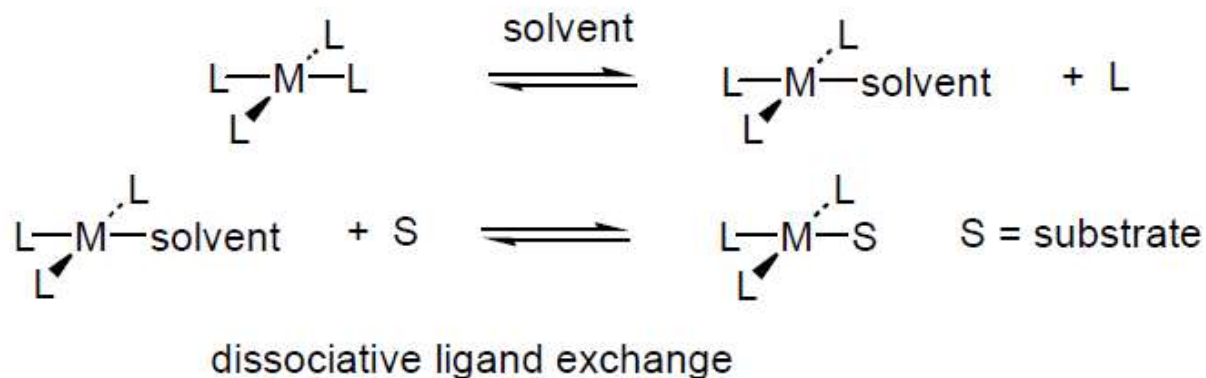


Figure 2.1. Dissociative and associative ligand exchange

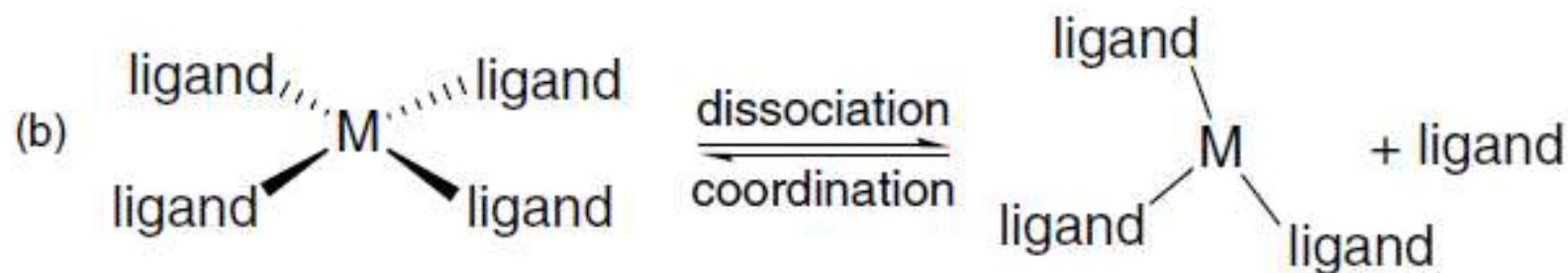
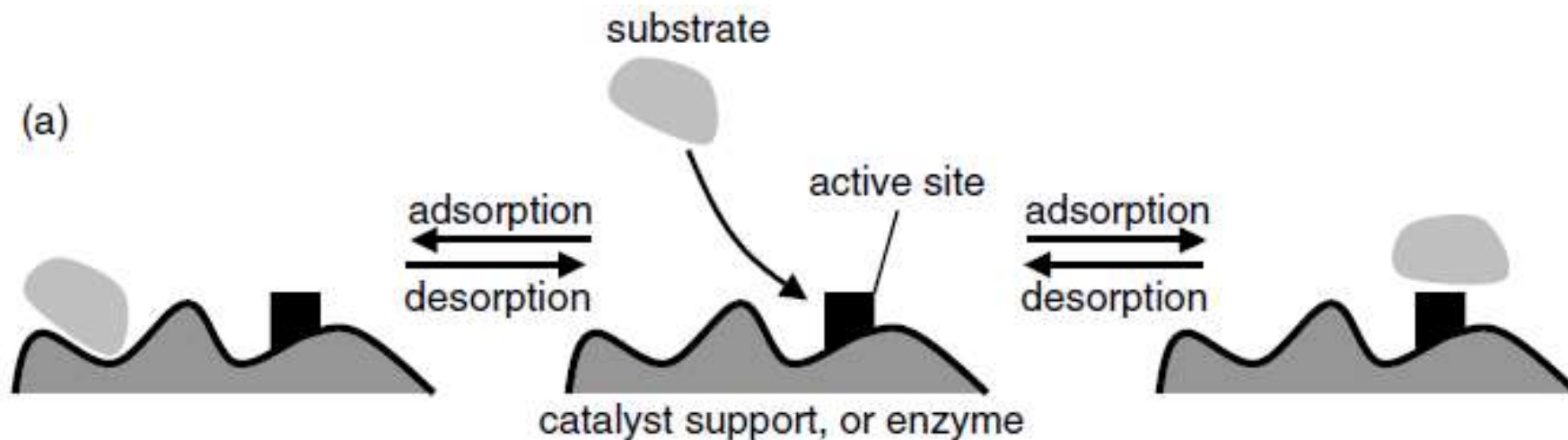


Figure 3.3 a Dynamic adsorption/desorption in heterogeneous catalysis and in enzymatic systems occurs both at active sites and elsewhere on the support; **b** similar coordination/dissociation occurs also in homogeneous complexes.

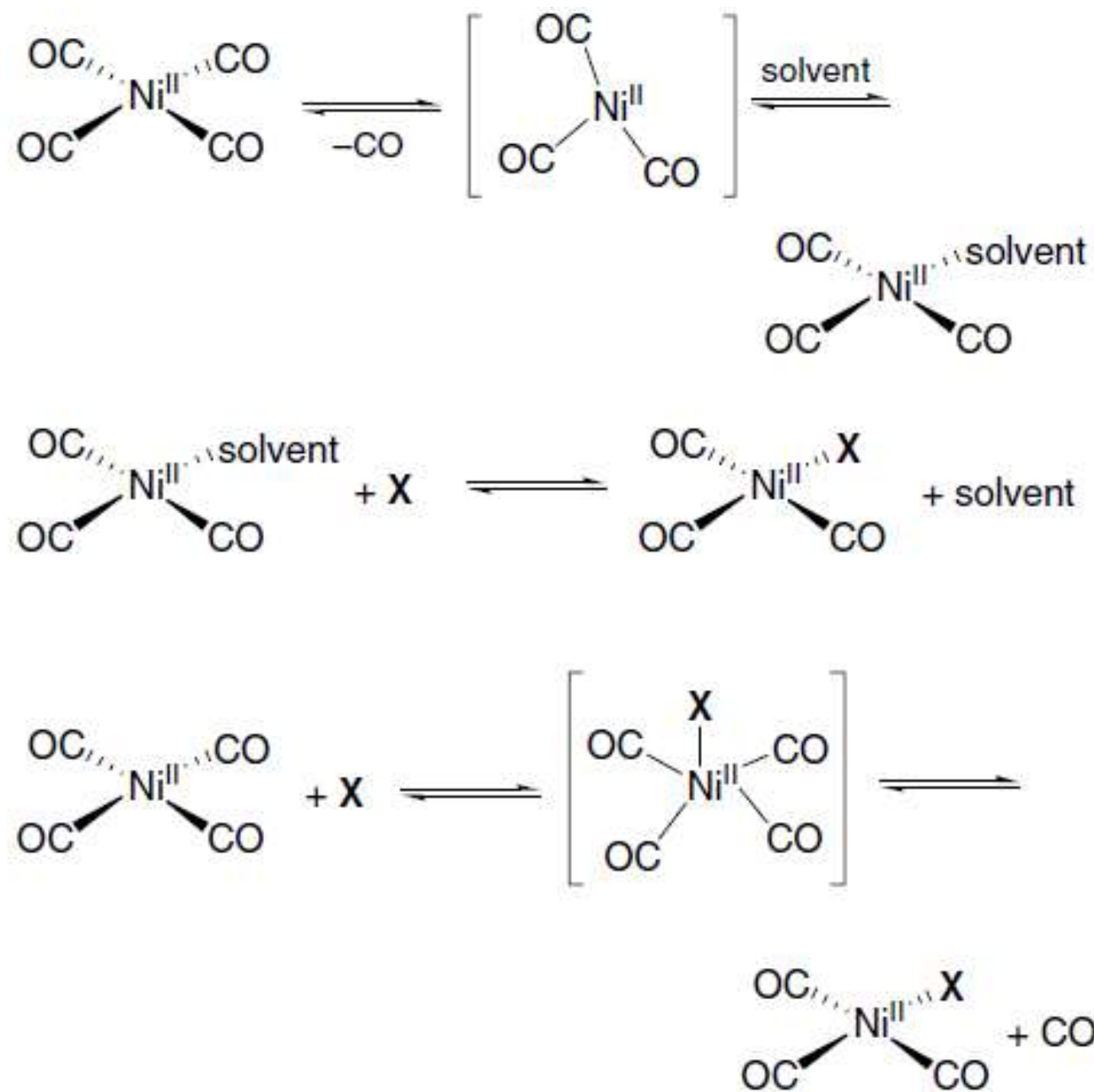


Figure 3.4 **a** Dissociative and **b** associative ligand exchange from $\text{Ni}(\text{CO})_4$.

Oxidative Addition

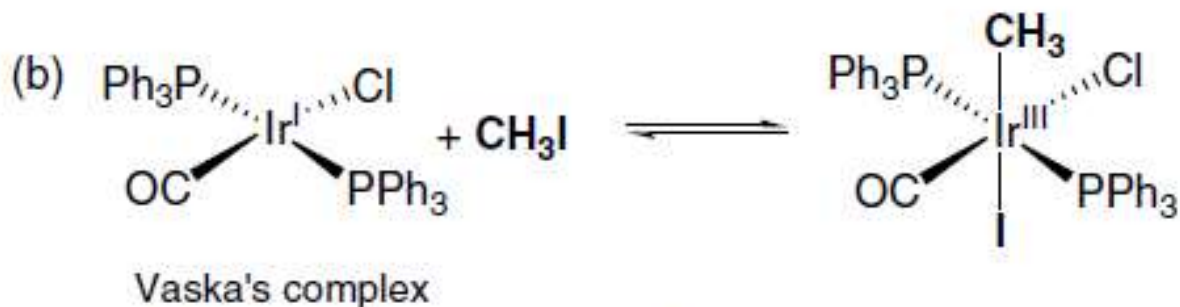
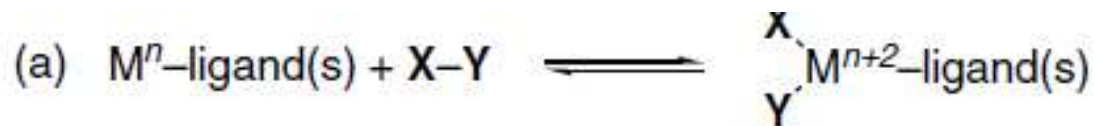


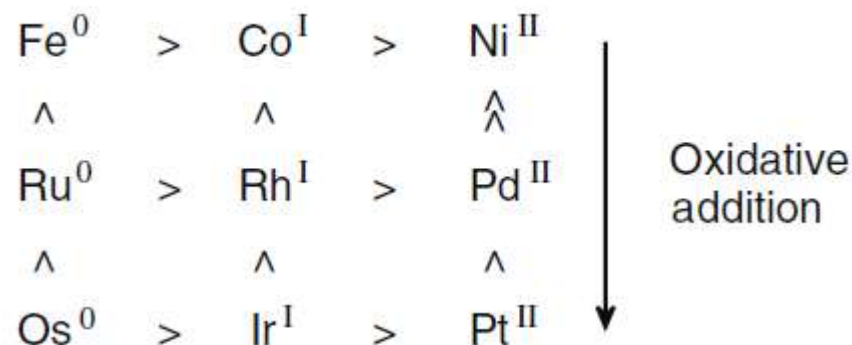
Figure 3.5 **a** General scheme for oxidative addition; **b** oxidative addition of CH_3I to Vaska's complex.

In oxidative addition, a metal M inserts into a covalent bond of a compound XY . The XY bond is broken and two new bonds form: MX and MY . The metal loses two valence electrons and gains two new ligands, X and Y . Oxidative addition is a key step in many catalytic cycles. Often, it is the slow (i.e., rate-determining) step, because a covalent bond (usually in the substrate) is broken. This creates a metastable species that easily reacts further in the cycle.

Oxidative Addition

Oxidative addition reactions can lead to both trans and cis products, depending on the compound added. The oxidative addition of alkyl halides, for example, leads most often to trans products, regardless of the reaction pathway. Dihydrogen, on the other hand, forms cis addition products with metal complexes. Note that the product can sometimes isomerize, making it difficult to distinguish between the pathways. The electron density at the metal center is a key parameter in oxidative addition reactions: σ -donor ligands, such as alkylphosphines or alkyl halides [increase the electron density at the metal center, and thus promote oxidative addition. Conversely, ligands that reduce the electron density at the metal center (e.g., phosphites, CO, or CN) will slow the oxidative addition reaction.

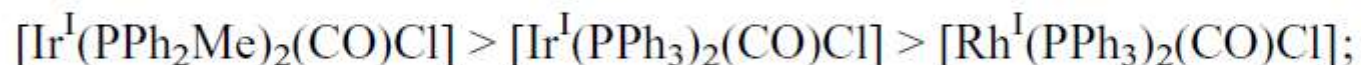
Oxidative addition



Oxidative addition

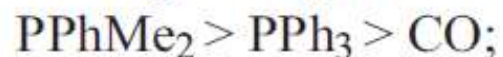
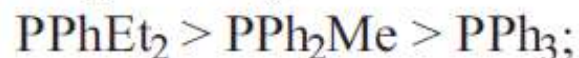
Scheme 2-1 Tendency to undergo oxidative addition for the metals of groups 8–10

The tendency to undergo oxidative addition increases from top to bottom in a group and from right to left in a period, as does the metal basicity. This is shown by numerous empirical orders of reactivity [10]:



Oxidative addition

Ligand effects are of major importance in oxidative addition reactions. Increasing donor character of a ligand increases the electron density at the metal center and favors oxidative addition. This means that electron-releasing (basic) ligands make the metal base stronger, while electron-withdrawing ligands weaken it. Some examples for ligand influences are given in the following:

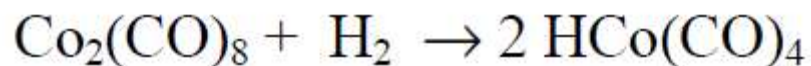
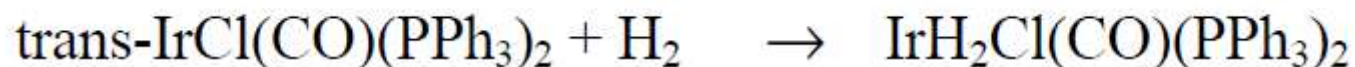


←
 σ -donor strength, oxidative addition

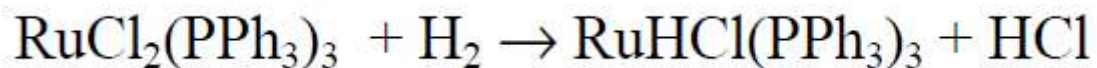
Reductive Elimination

1. Reductive elimination is the opposite of oxidative addition:
2. Starting from a metal M bonded to X and Y, a new XY bond forms and the MX and MY bonds break.
3. The free XY species leaves the complex, and the metal loses two ligands and gains two valence electrons.
4. Reductive elimination is observed mostly for transition elements, and especially for noble metals such as Pd, Pt, Rh, and Ir in their higher oxidation states (II, III, and IV).
5. In many catalytic cycles, the reactant enters the cycle in an oxidative addition step, and part of it leaves the intermediate in a reductive elimination step. Figure 3.8 shows a generic reductive elimination reaction, and an example of reductive elimination of HCN from a nickel complex.

Oxidative addition of dihydrogen commonly involves transformation of a d^8 square planar metal complex into a d^6 octahedral metal complex, or similar transformations involving $d^2 \rightarrow d^0$, $d^{10} \rightarrow d^8$ etc. The oxidative addition of dihydrogen to low-valent metal complexes is a common reaction



Heterolytic cleavage of dihydrogen



Reductive Elimination

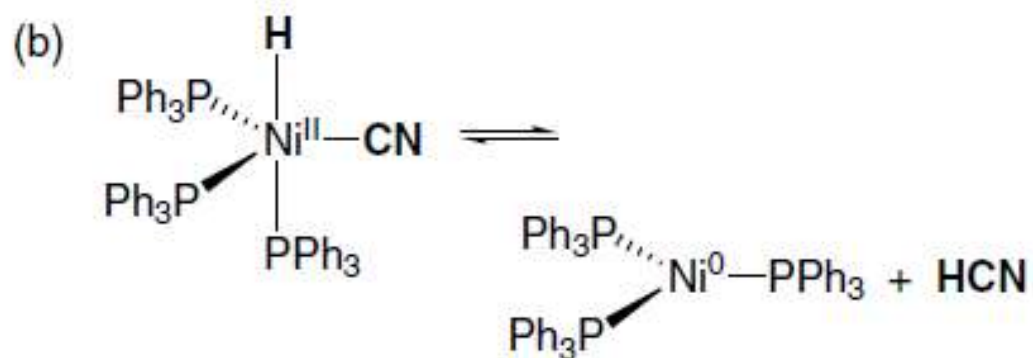
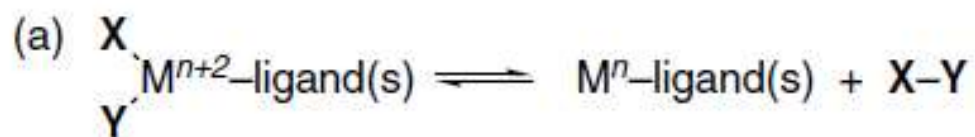


Figure 3.8 a Generic reductive elimination reaction; b reductive elimination of HCN from a nickel complex.

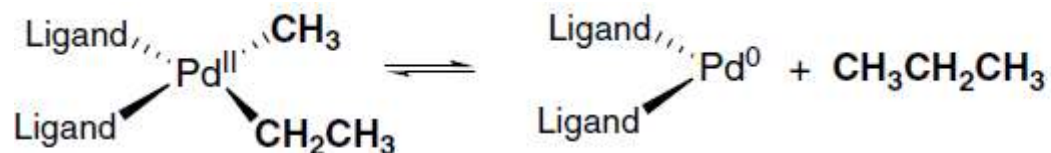


Figure 3.9 Carbon-carbon bond formation via reductive elimination from a palladium complex.

Insertion

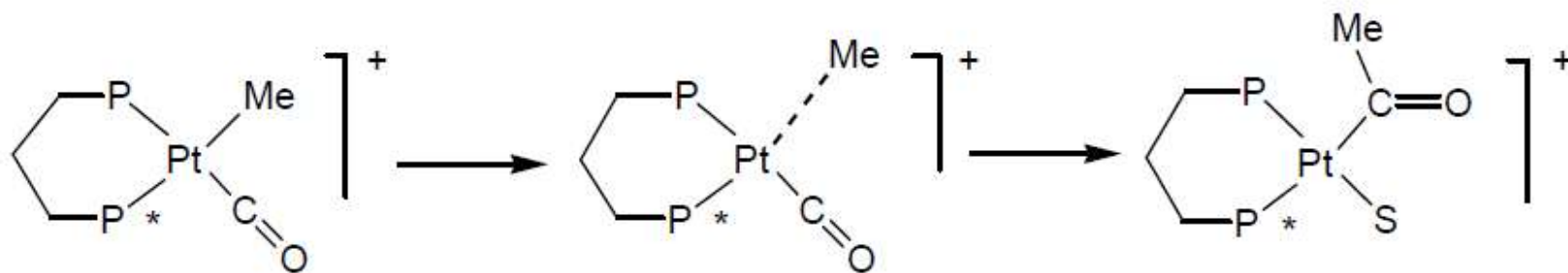
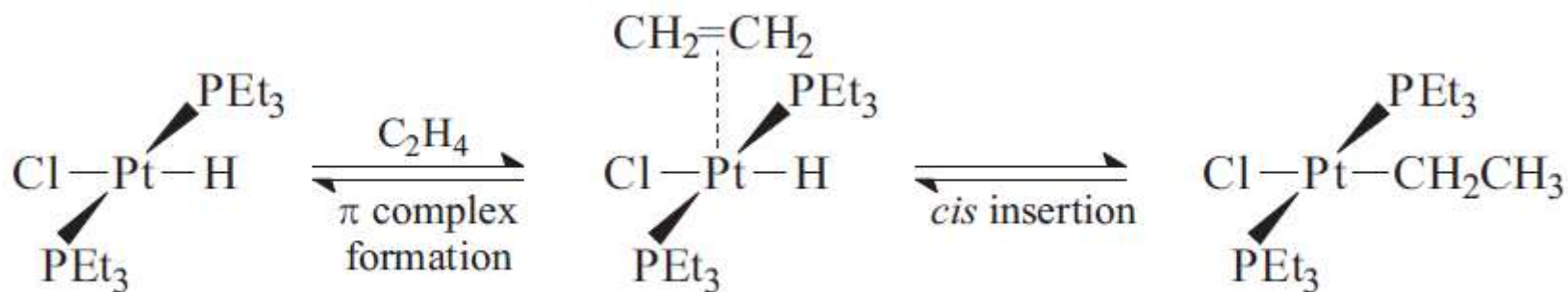


Figure 2.2. The insertion mechanism



Insertion and Migration

- An insertion or migration step involves the introduction of one unsaturated ligand into another metal–ligand bond on the same complex.
- Insertion and reductive elimination are common bond-forming steps, just as oxidative addition is a common bond-breaking step. The term .insertion. is somewhat problematic, because recent research has shown that in many cases it is the .end group. which migrates to the .inserting group.. The correct term therefore is migratory insertion, but many texts still use simply .insertion..
- There is a difference between migration and insertion products where chelating complexes are concerned: Insertion changes the positional geometry, migration does not. For example, for the square-planar Pd complex shown in Figure 3.10, CO insertion into the Pd–Me bond results in a cis configuration with the ligating P atom. Conversely, migration of the Me group will retain the original trans configuration.

Insertion and Migration

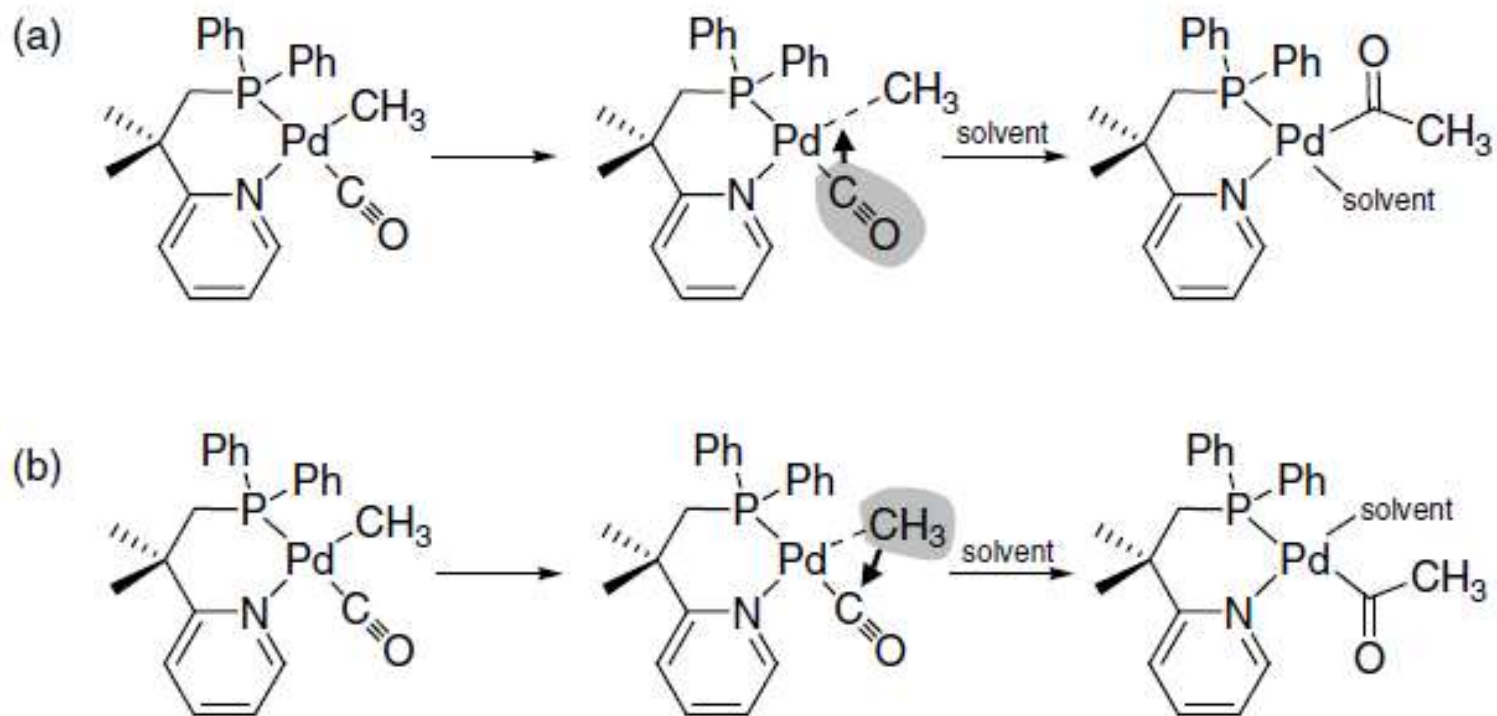


Figure 3.10 Examples of **a** CO insertion and **b** CH₃ migration, in a square-planar Pd complex with a P–N chelating ligand. Note that the migration mechanism retains the *cis* configuration between the CO group and the chelate nitrogen atom.

Insertion and Migration

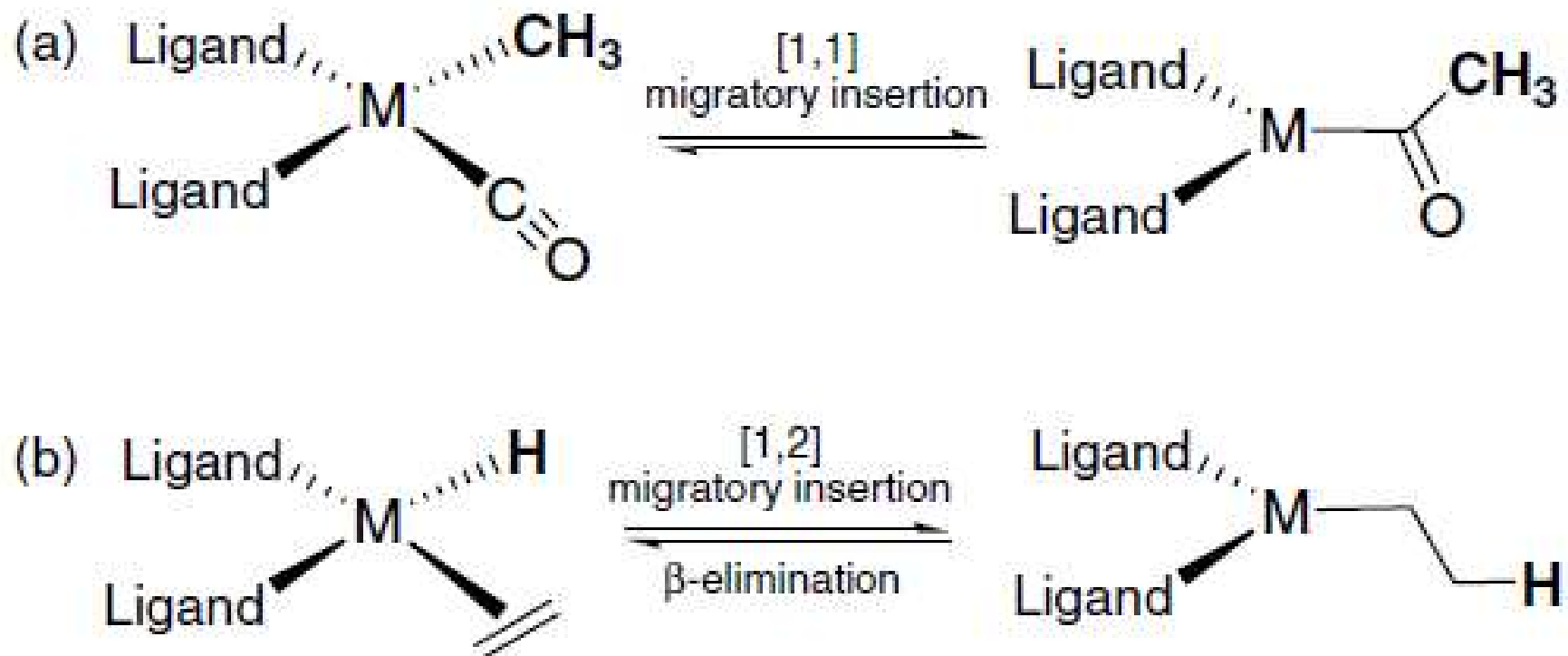


Figure 3.11 Examples of [1,1] and [1,2] migratory insertion reactions.

Insertion and migration

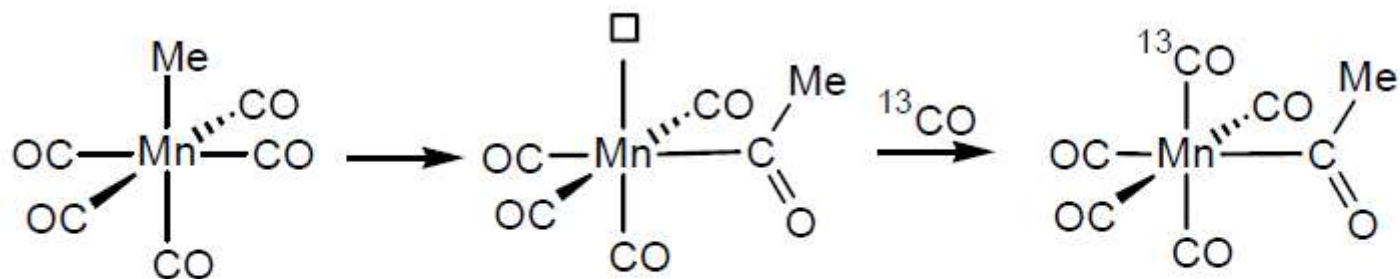


Figure 2.5. Disproval of "outersphere" insertion



Figure 2.6. Hydride migration to ethene

De-insertion and β -Elimination

- De-insertion is simply an insertion in reverse. In the special case where the deinserting group is an alkene, the reaction is known as a β -hydride elimination (or simply β elimination).
- A hydride is abstracted from the β -carbon, giving an alkene and a new MH or MR bond (Figure 3.12). Often the reaction proceeds via an agostic intermediate.
- The metal gains a new ligand (the hydride), and the electron count of the complex increases by two. Insertion creates a vacant site on the complex, while β -elimination requires one, and it must be *cis* to the eliminating group.
- Insertion and de-insertion reactions are always in equilibrium.

De-insertion and β -Elimination

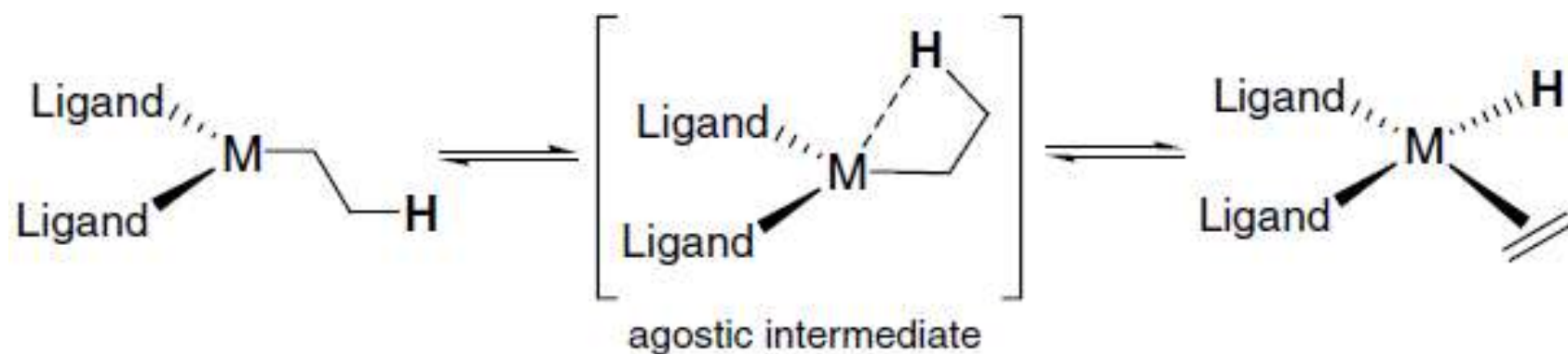


Figure 3.12 Generic equation for β -hydride elimination from a transition metal-alkyl complex.

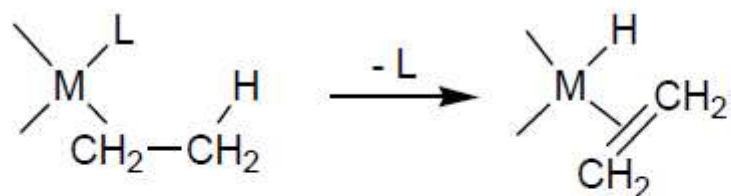


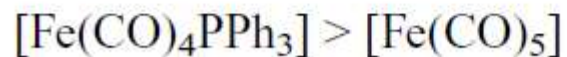
Figure 2.11. β -hydride elimination

General observations

- 1) Low oxidation states, especially negative ones or metal(0) complexes, increase the metal basicity. With increasing oxidation state, metals become more acidic.
- 2) Transition metal basicity increases from right to left in a period, and from top to bottom in a group; for example:

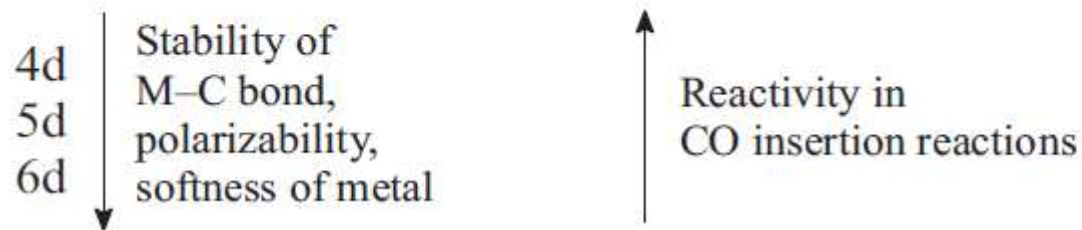


- 3) Electron-donor ligands such as phosphines increase the metal basicity:



General observations

If the stability and reactivity of the metal complexes in a triad of the periodic table are compared, two counteropposing trends become apparent [3]:



The harder metals at the top of the groups are more reactive towards carbonyl insertion. Thus iridium carbonyl complexes are less reactive than the rhodium and cobalt homologues. The following also applies:



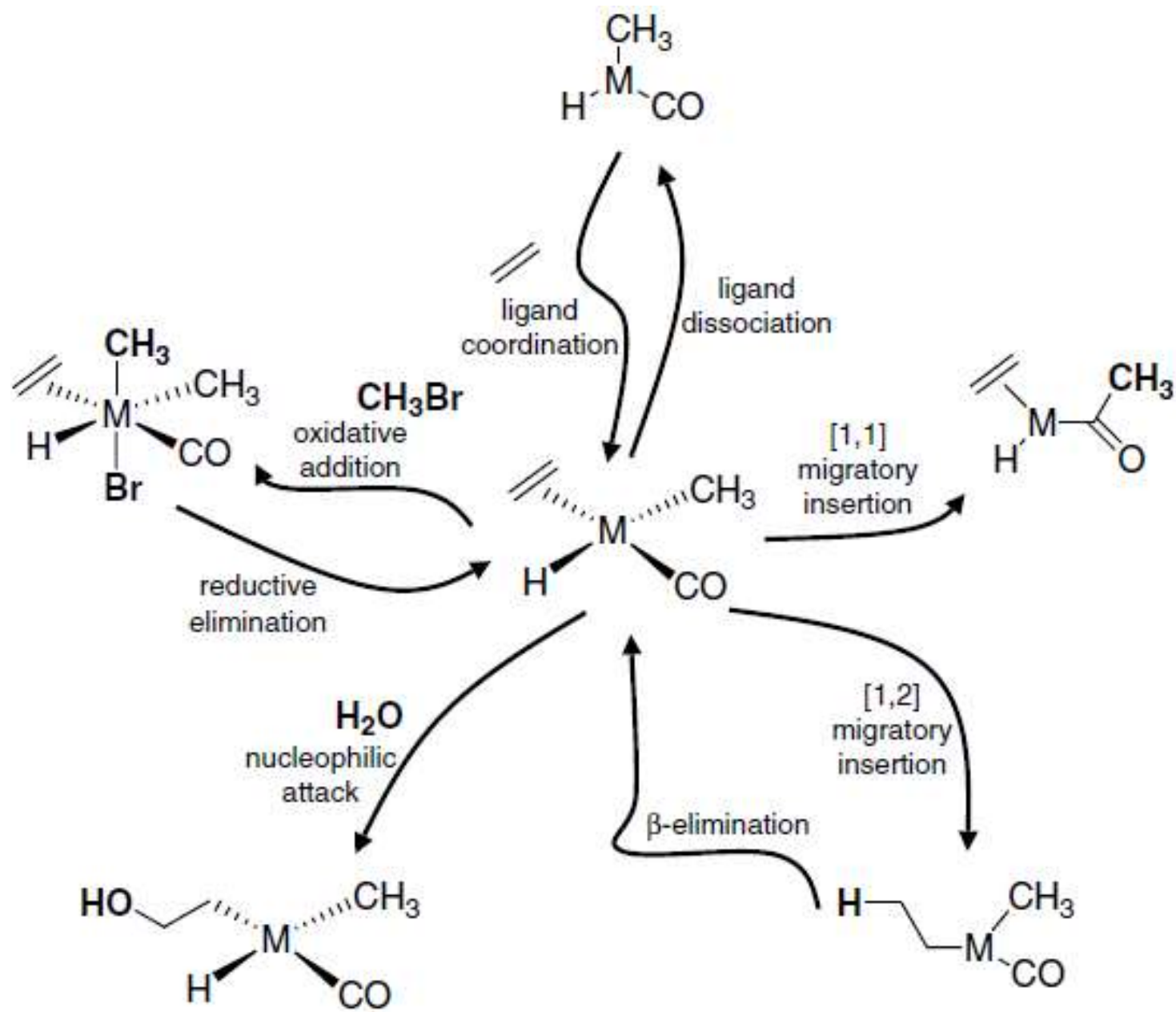
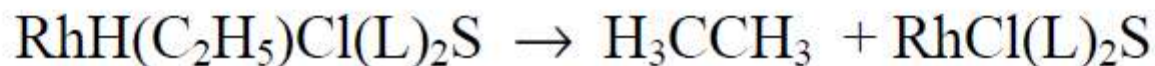
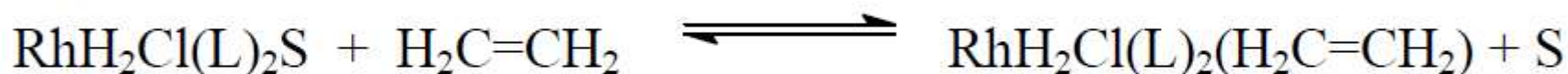
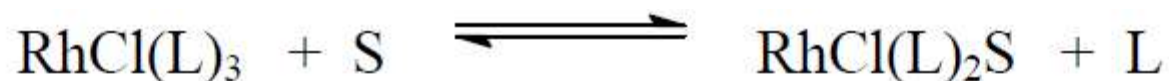


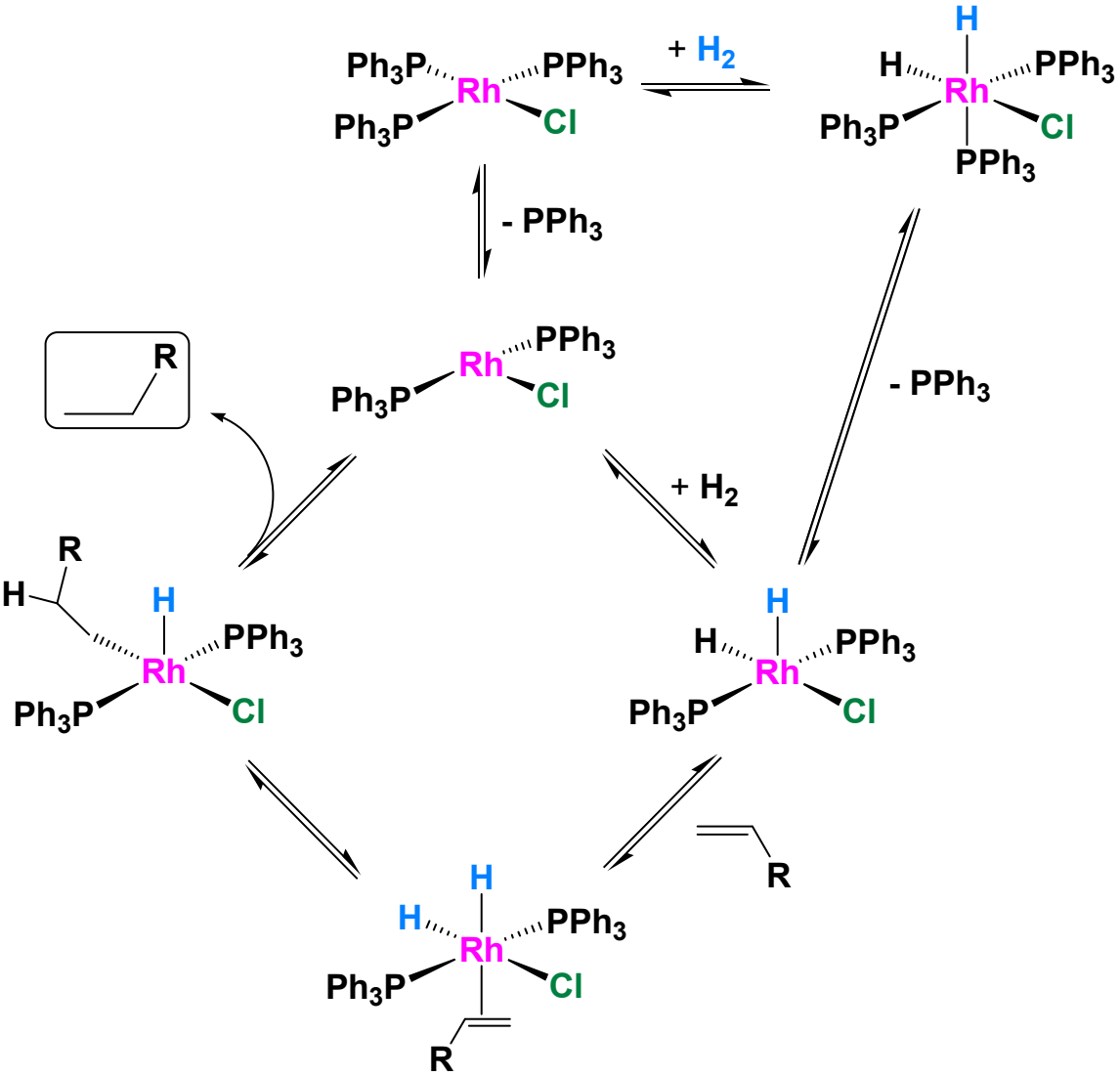
Figure 3.2 The main elementary steps in homogeneous catalysis.

HYDROGENATION

Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$



HYDROGENATION



HYDROGENATION

Ligand: Relative reactivity:

$(4\text{-ClC}_6\text{H}_4)_3\text{P}$ 1.7

Ph_3P 41

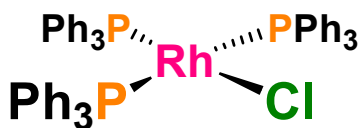
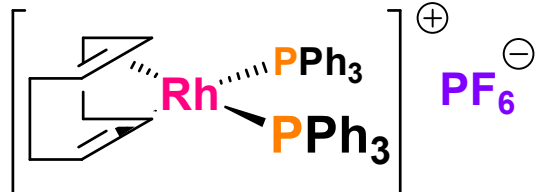
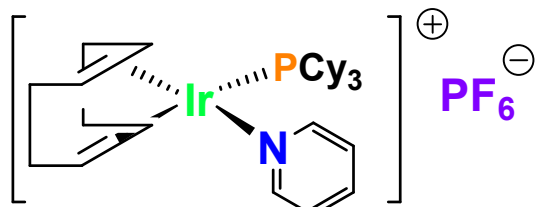
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$ 86

$(4\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}$ 100

Cationic Complexes are effective

Crabtree *Acc. Chem. Res.* **1979**, *12*, 331

TOF

Catalyst	1-Butene	Cyclohexene	1-Methylcyclohexene	2-Methyl-2-butene
 <i>Wilkinson's catalyst</i>	650	700	13	---
 <i>Schrock-Osborn catalyst</i>	4000	10	---	---
 <i>Crabtree's catalyst</i>	6400	4500	3800	4000

Asymmetric hydrogenation

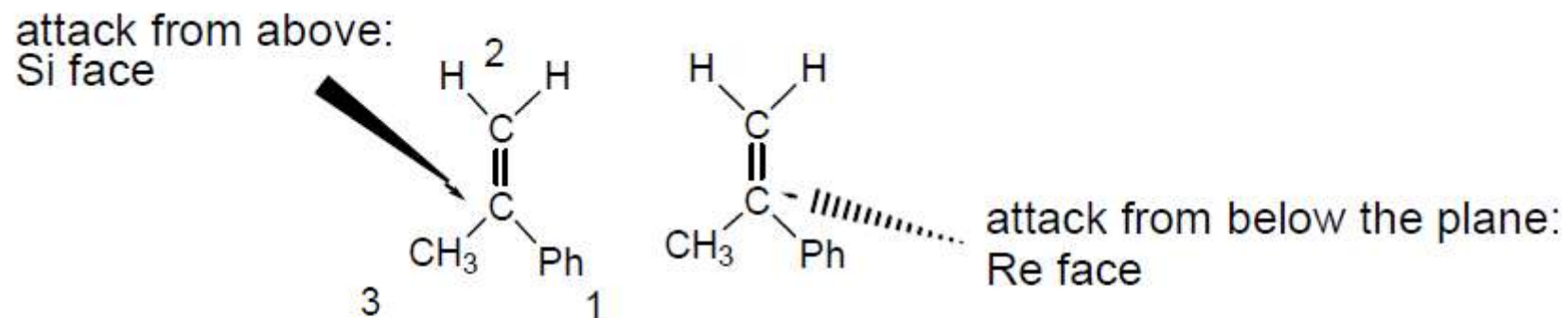


Figure 4.2. Re and Si faces of a 1,1-disubstituted substituted alkene

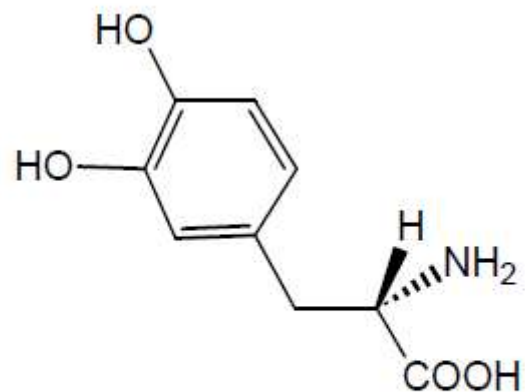


Figure 4.3. L-Dopa

Asymmetric hydrogenation

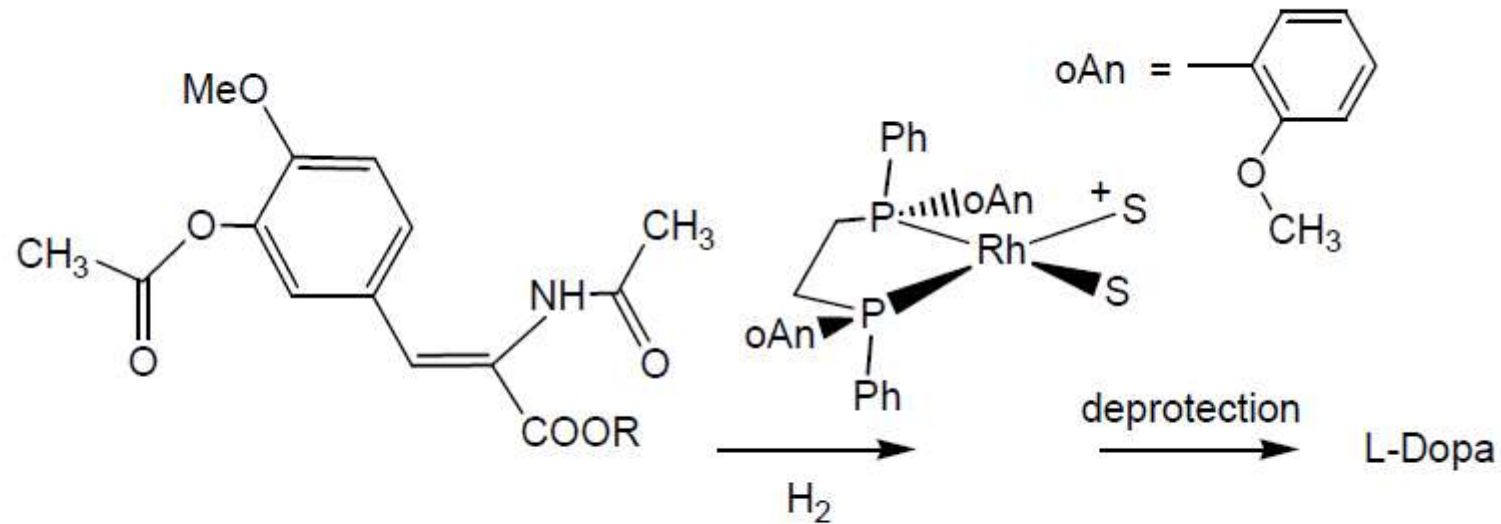


Figure 4.4. Synthesis of L-Dopa

Asymmetric hydrogenation

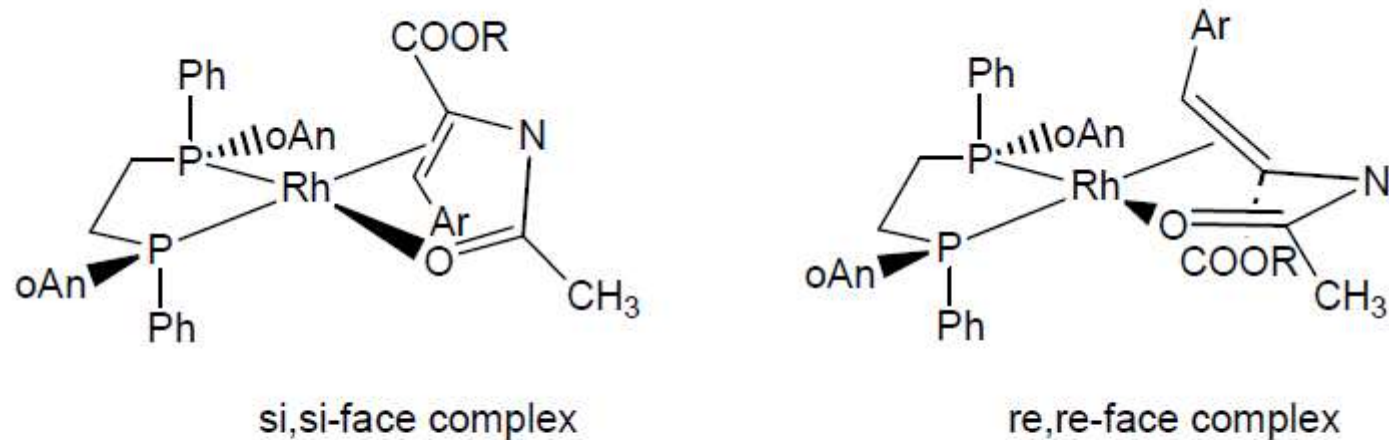
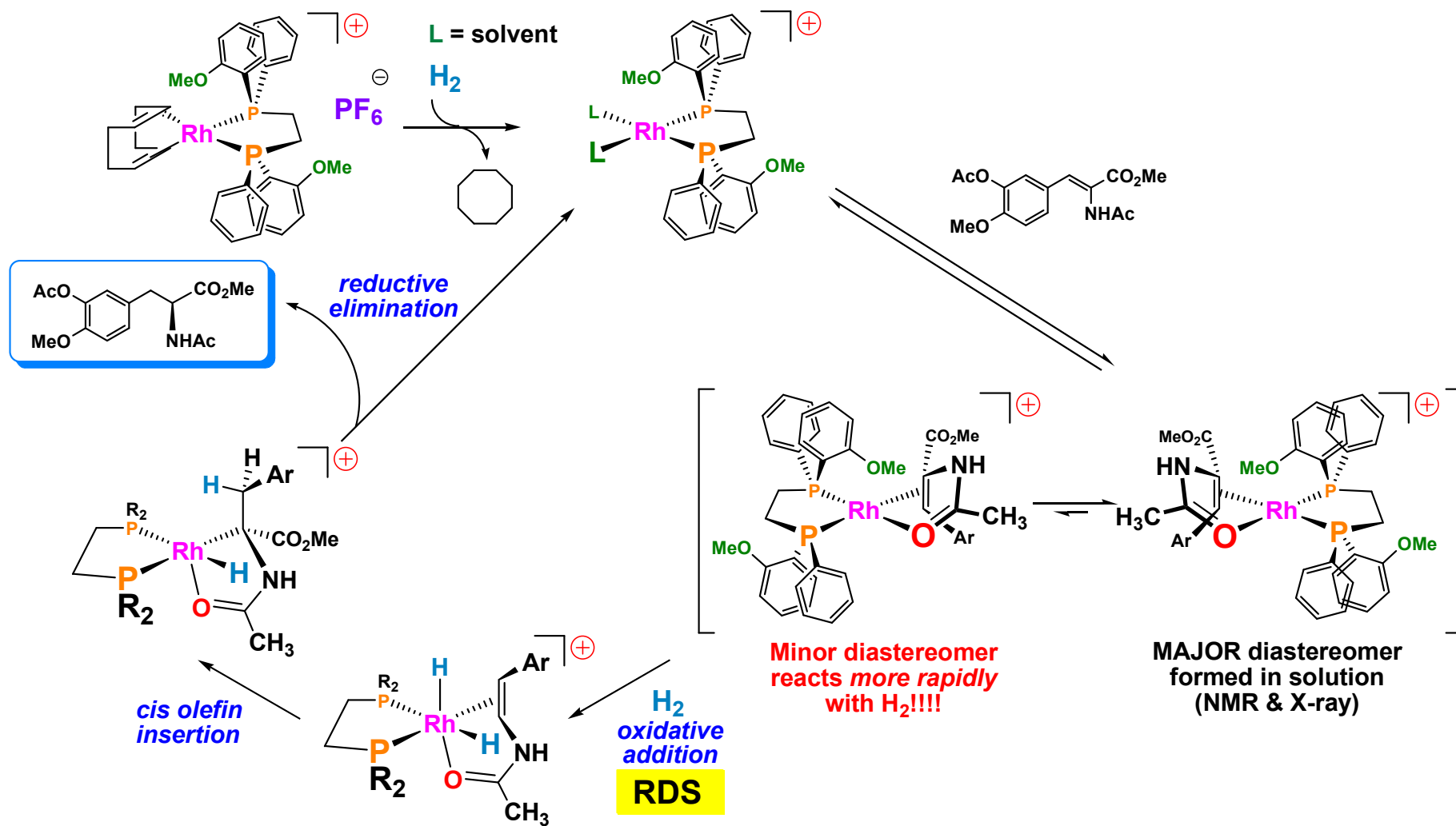


Figure 4.5. Diastereomeric alkene complexes with DIPAMP-Rh

Halpern Science 1982, 217, 401



ISOMERISATION

The way to menthol

Insertion and β -elimination. A catalytic cycle that involves only one type of elementary reaction must be a very facile process. Isomerisation is such a process since only migratory insertion and its counterpart β -elimination are required.

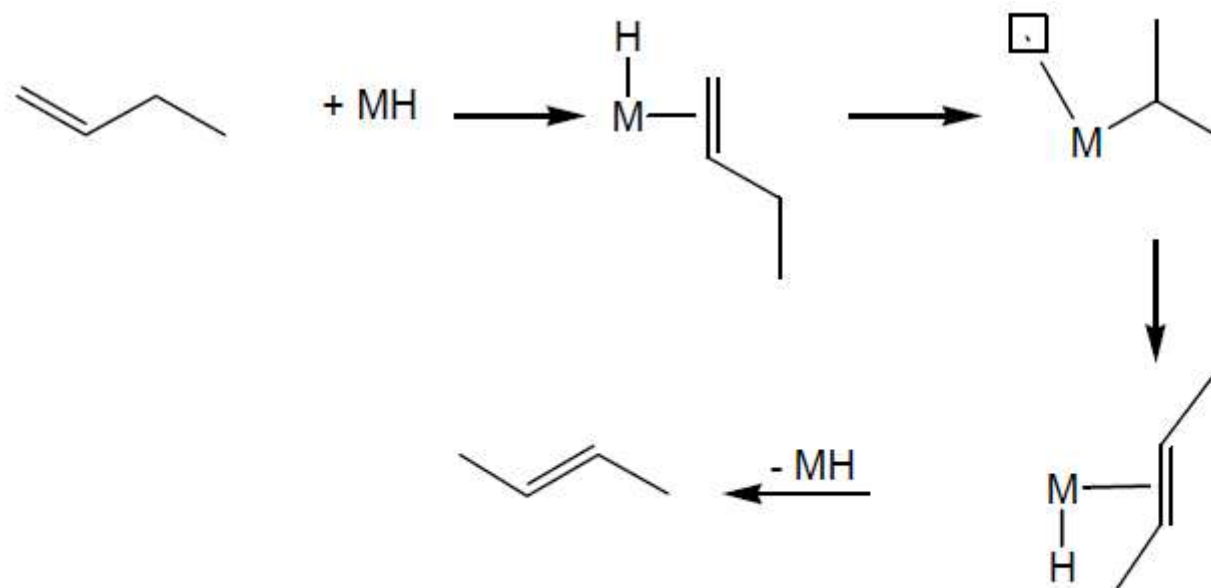


Figure 5.1. Simplified isomerisation scheme involving β -elimination

Takasago Process for (-) menthol

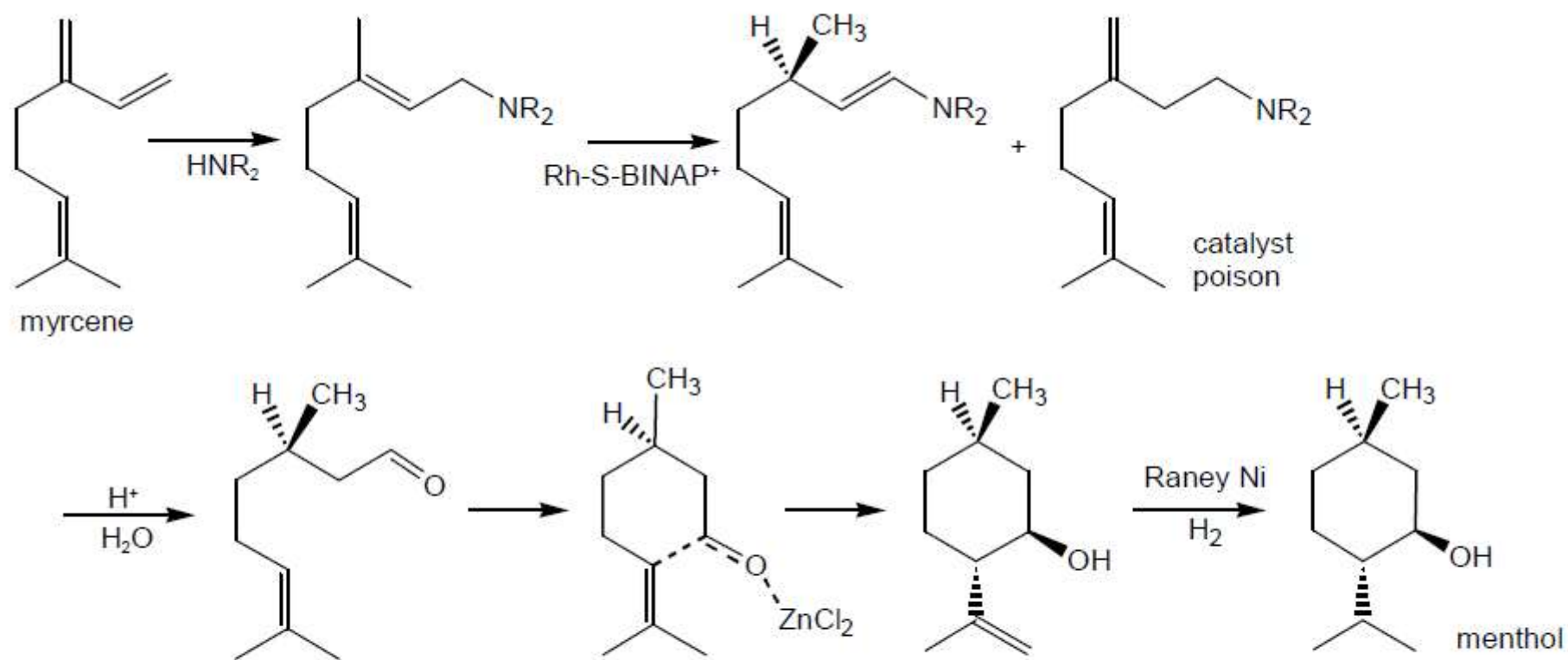


Figure 5.6. The Takasago process for (-)menthol

CARBONYLATION OF METHANOL AND METHYL ACETATE

Monsanto developed the rhodium-catalysed process for the carbonylation of methanol to produce acetic acid in the late sixties. It is a large-scale operation employing a rhodium/iodide catalyst converting methanol and carbon monoxide into acetic acid. At standard conditions the reaction is thermodynamically allowed,



but without a catalyst, as so many carbonylation reactions, it would not take place at all.

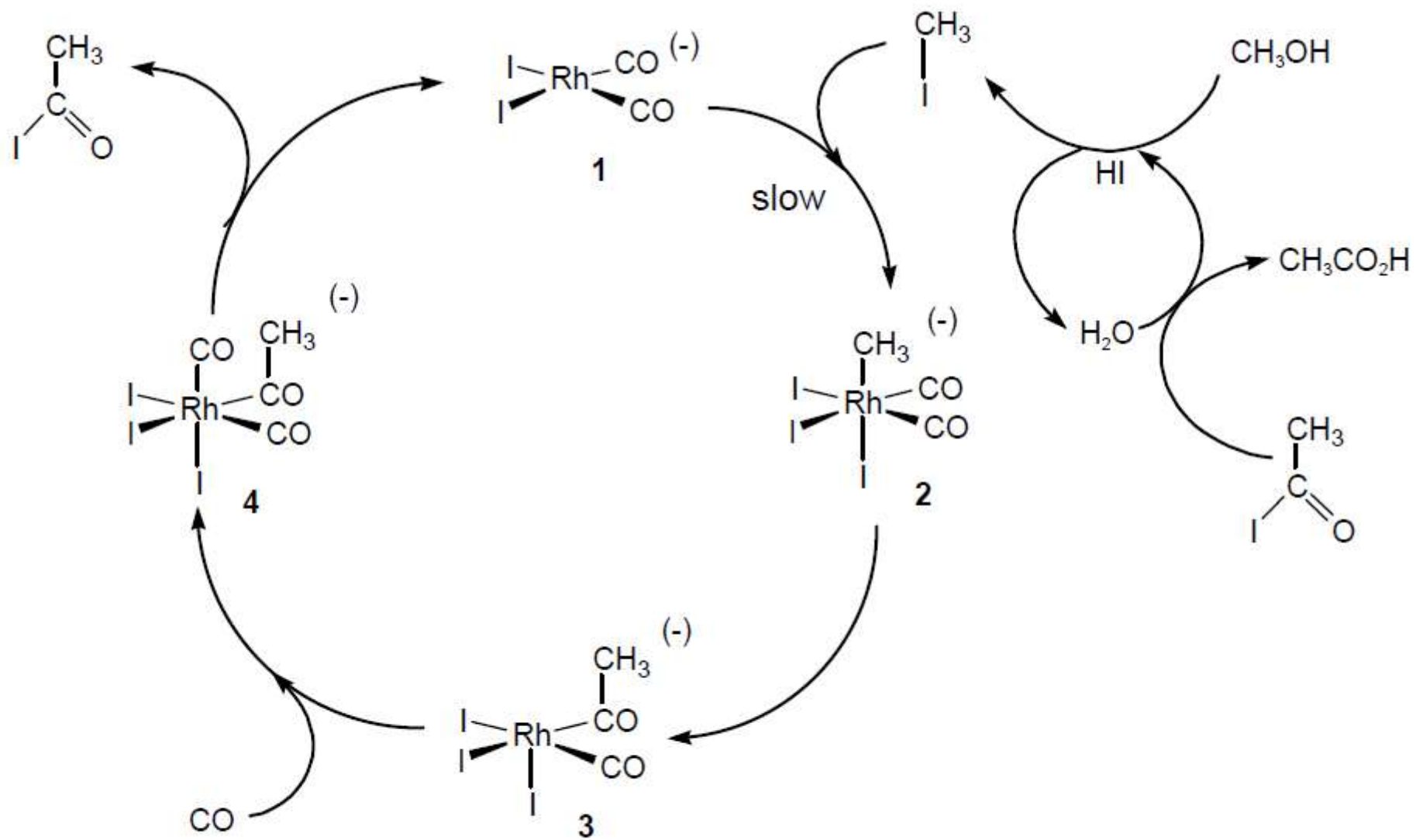


Figure 6.1. Monsanto carbonylation of methanol

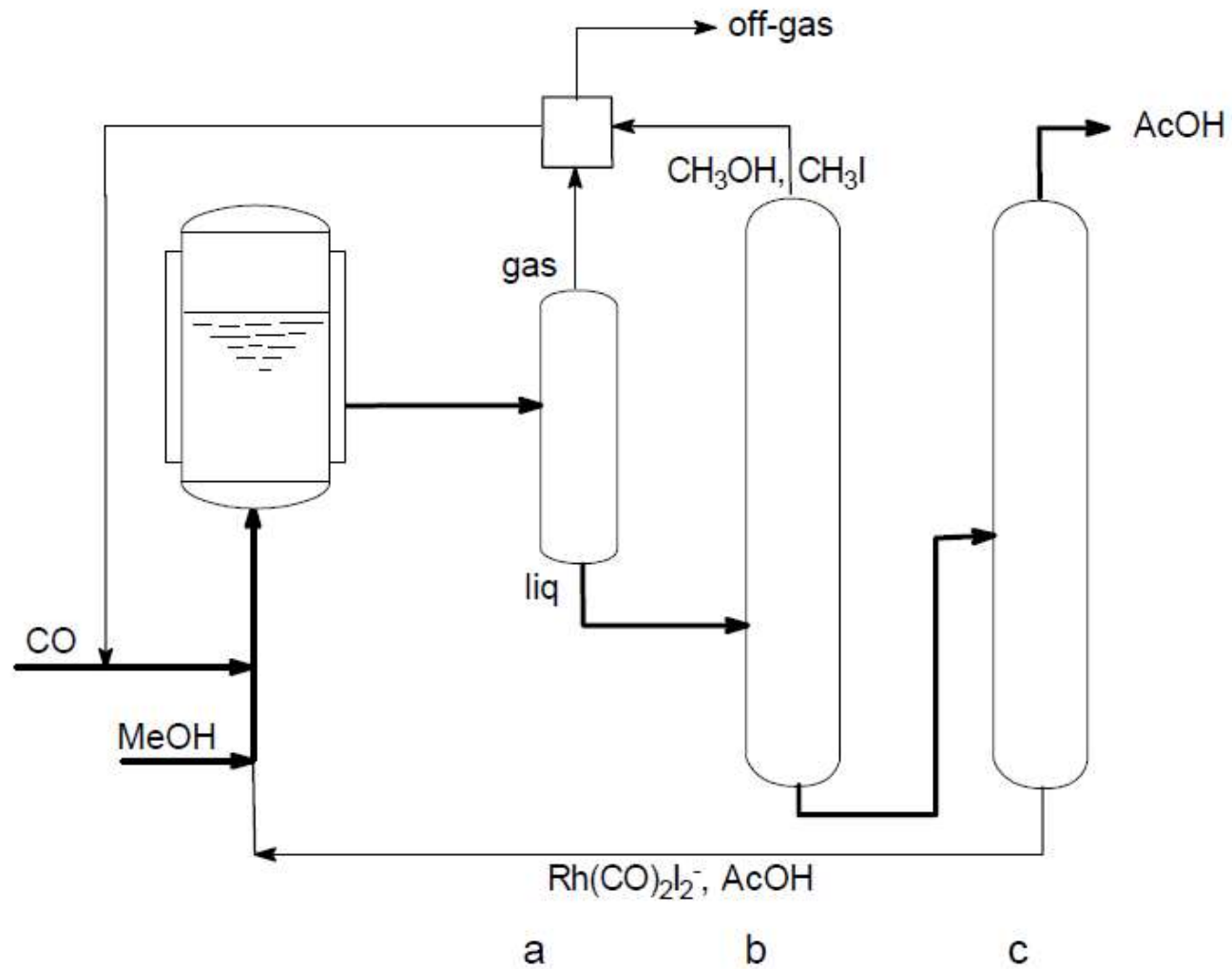


Figure 6.4. Process scheme Monsanto a= depressurisation, b= light ends removal, c= acetic acid distillation

Carbonylation process

Stripping has the technical advantage that the expensive rhodium catalyst remains in the reactor and the disadvantage that the least volatile component (acetic acid) has the lowest concentration of all components in the gas removed by stripping. Distillation as a separation method has the advantage that acetic acid is the most abundant component in the liquid, but now rhodium will be circulated in the system and will remain in the bottom of the distillation unit and it should not precipitate anywhere!

For a process it is very attractive if the reaction rate is independent of the concentrations of the educts. The conversion rate is constant over a wide range of concentrations, and the high rate is retained at a high conversion level. This means that distillation is carried out with a liquid with a very high product content.

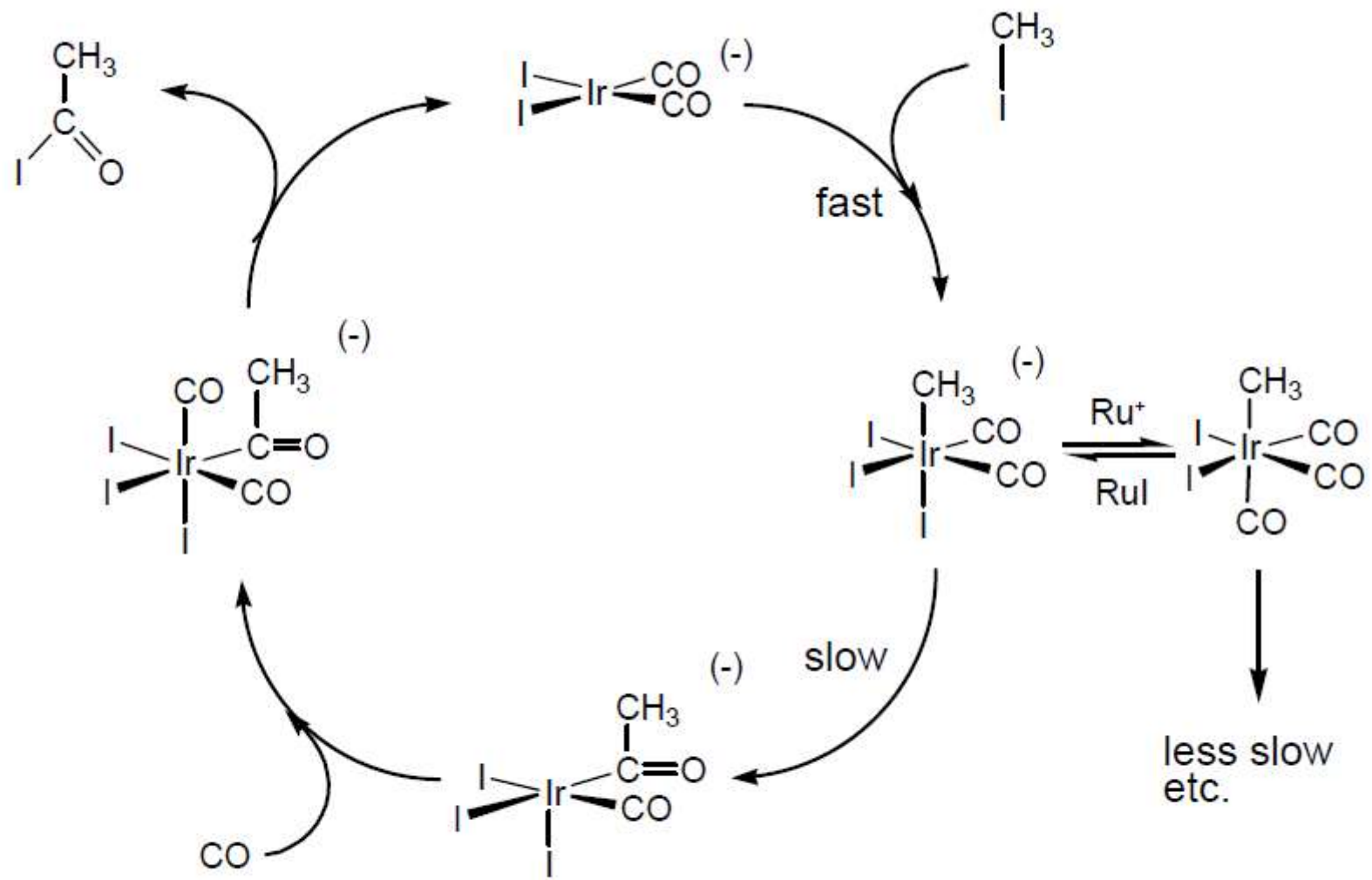
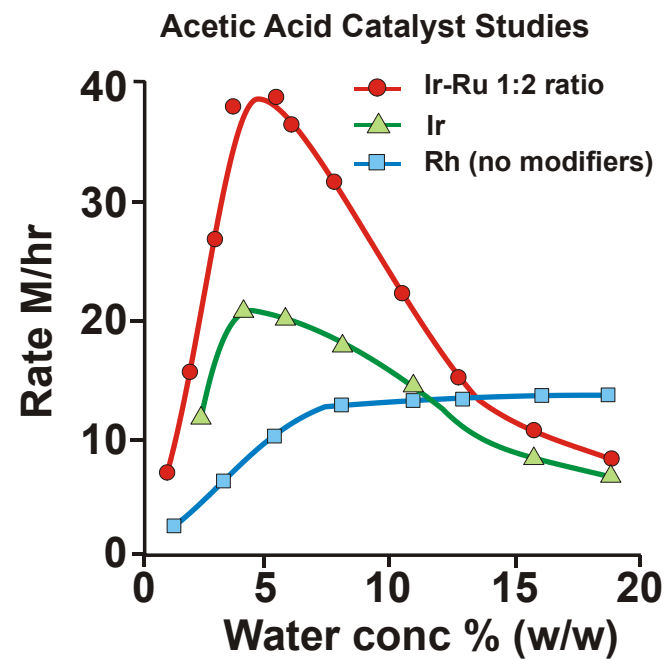
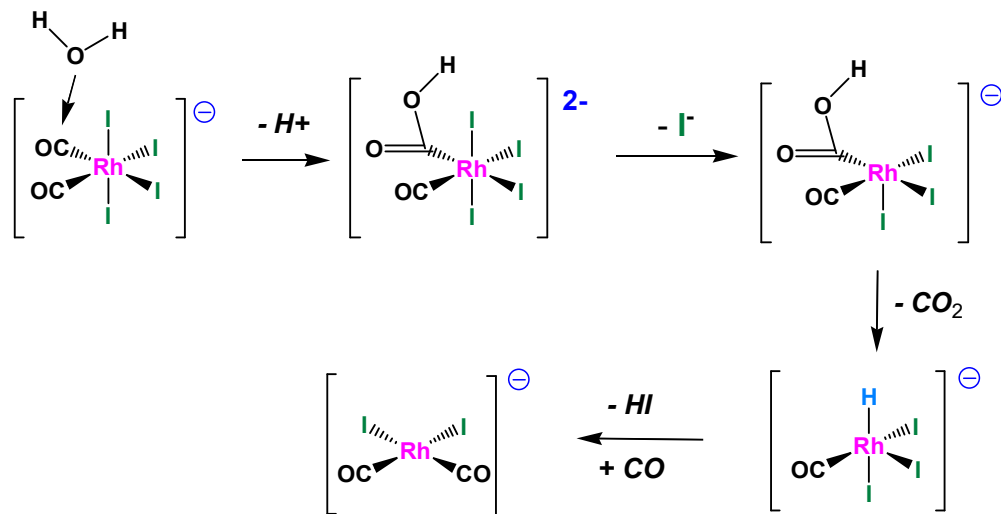


Figure 6.3. BP's CATIVA process

Water effect in carbonylation



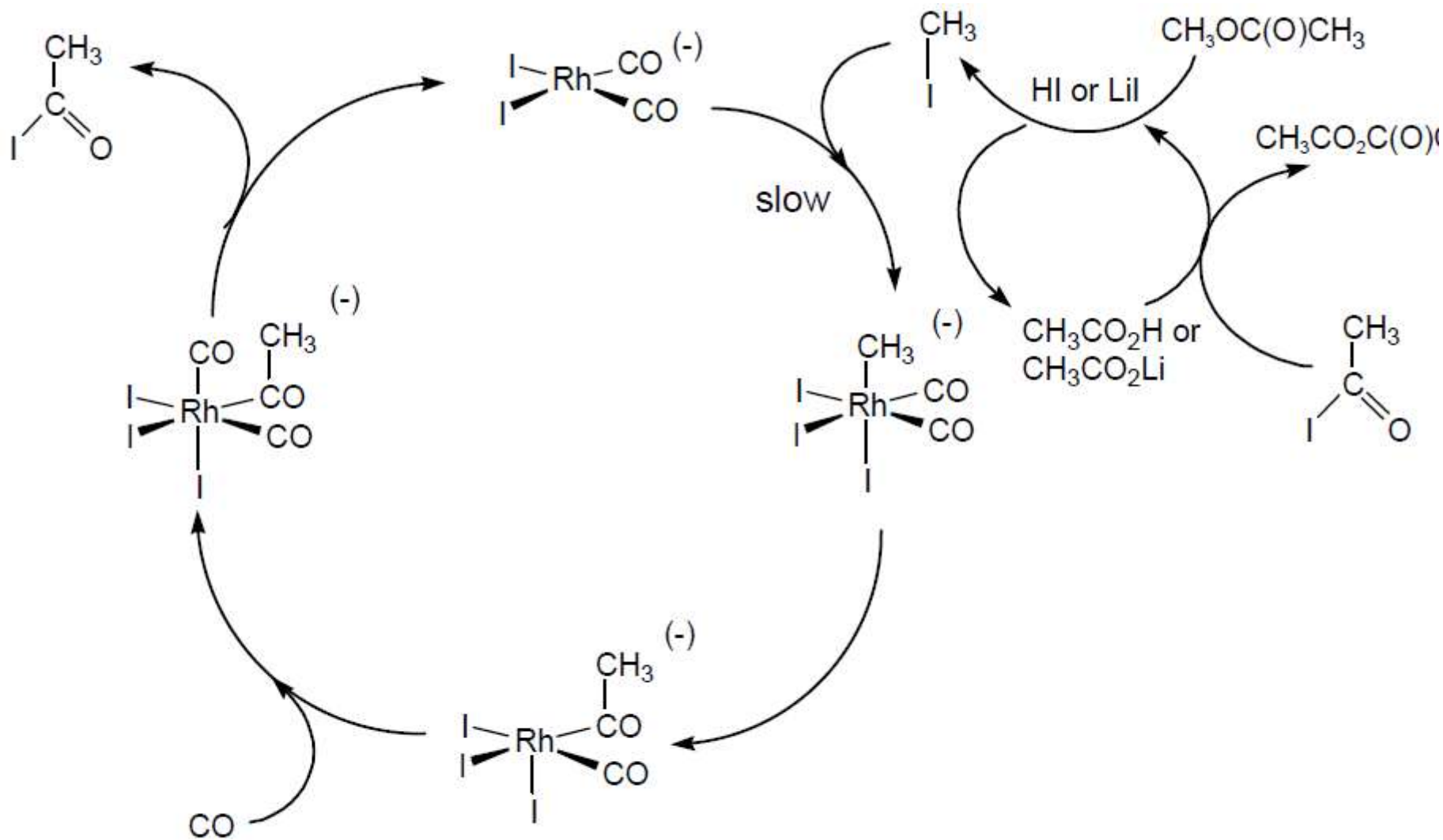
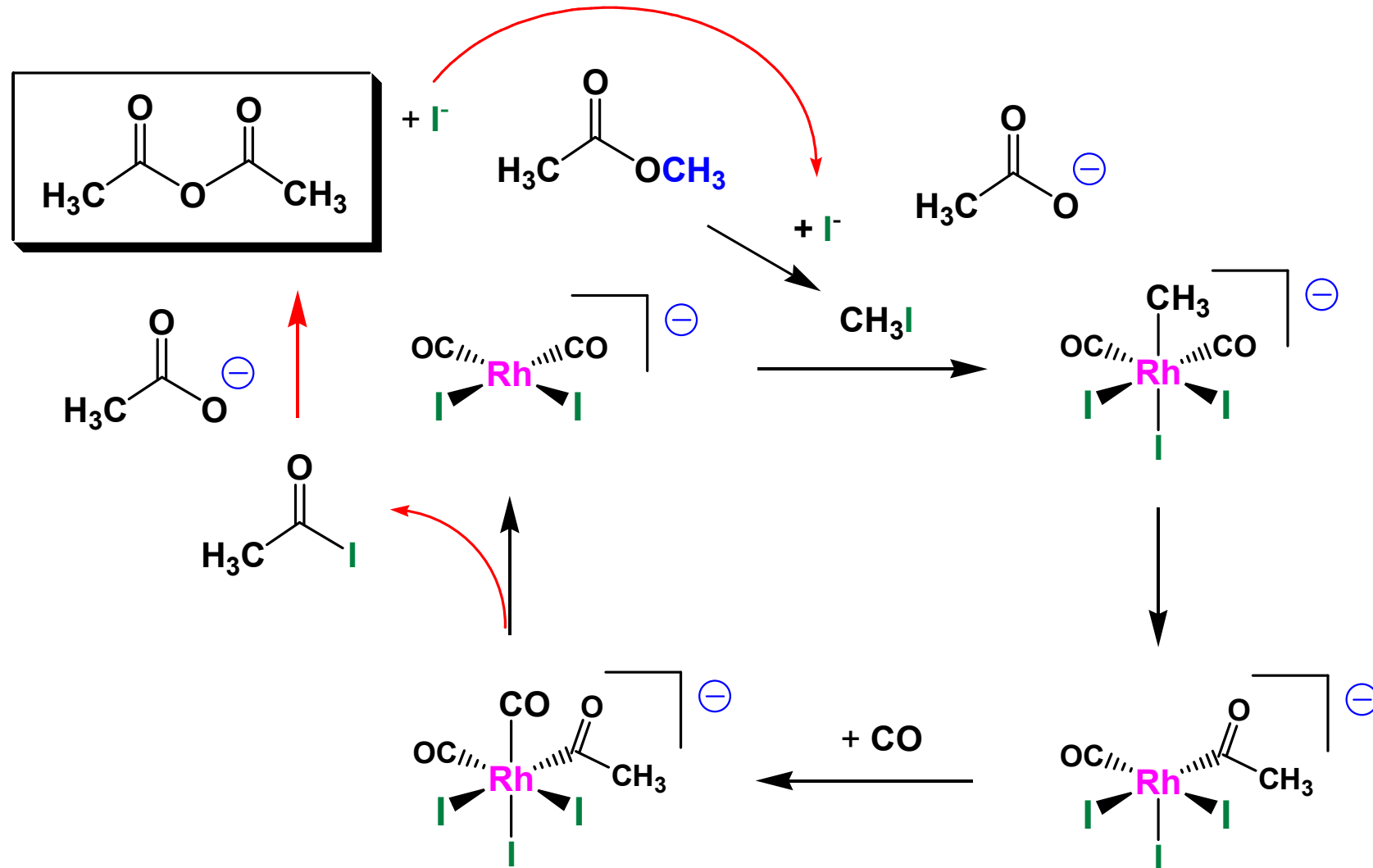
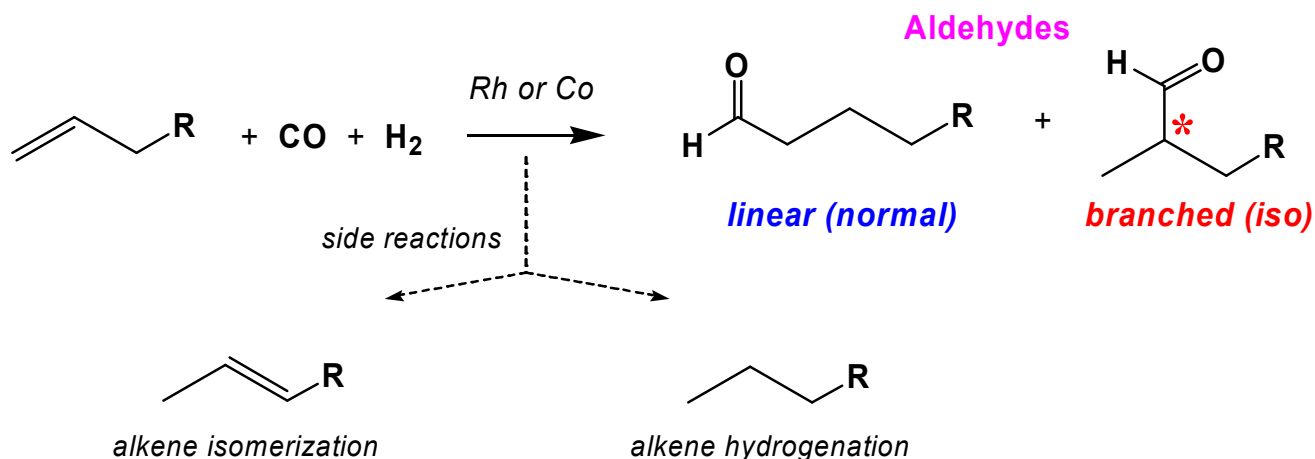


Figure 6.5. Eastman carbonylation of methyl acetate

Eastman Chemical Acetic Anhydride Process

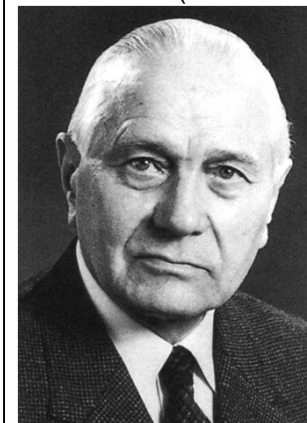


Hydroformylation (Oxo) Catalysis



- * Largest homogeneous catalytic process
- * > 15 billion pounds of aldehydes (alcohols) per year
- * Commercial catalysts are complexes of Co or Rh
- * Selectivity to linear (normal) or branched (iso) products is important

Otto Roelen (1897-1993)



Thermodynamics

Thermodynamics of hydroformylation and hydrogenation of propene at standard conditions are as follows:



$$\begin{array}{l} \Delta G \quad 63 \quad -138 \quad -117 \text{ (l)} \quad = -42 \text{ kJ.mol}^{-1} \\ \Delta H \quad 21 \quad -109 \quad -238 \quad = -150 \text{ kJ.mol}^{-1} \end{array}$$



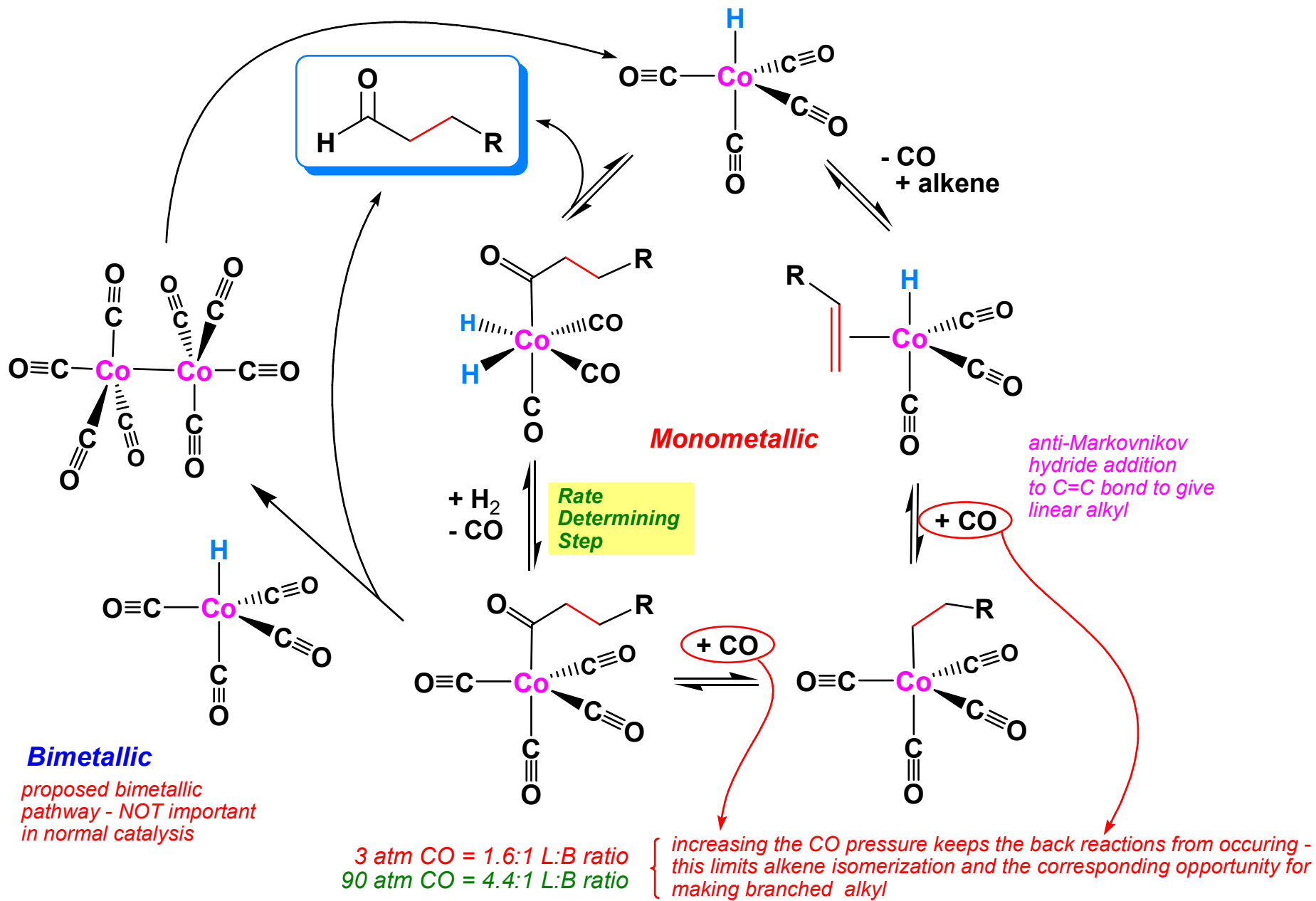
$$\begin{array}{l} \Delta G \quad 63 \quad -25 \quad = -88 \text{ kJ.mol}^{-1} \\ \Delta H \quad 21 \quad -105 \quad = -126 \text{ kJ.mol}^{-1} \end{array}$$

Thermodynamics

At higher temperatures the entropy loss becomes more important and ΔG will be less negative.

The thermodynamically favoured product of a hydroformylation reaction is not the aldehyde but the alkane. Yet the product is the aldehyde because “kinetic” control occurs.

The reaction is highly exothermic. Thus, if the reaction is conducted under adiabatic conditions the temperature rises and ΔG approaches zero, at which point the reaction reaches equilibrium and the temperature will not increase further, preventing further escalation!



Cobalt catalyzed hydroformylation reaction

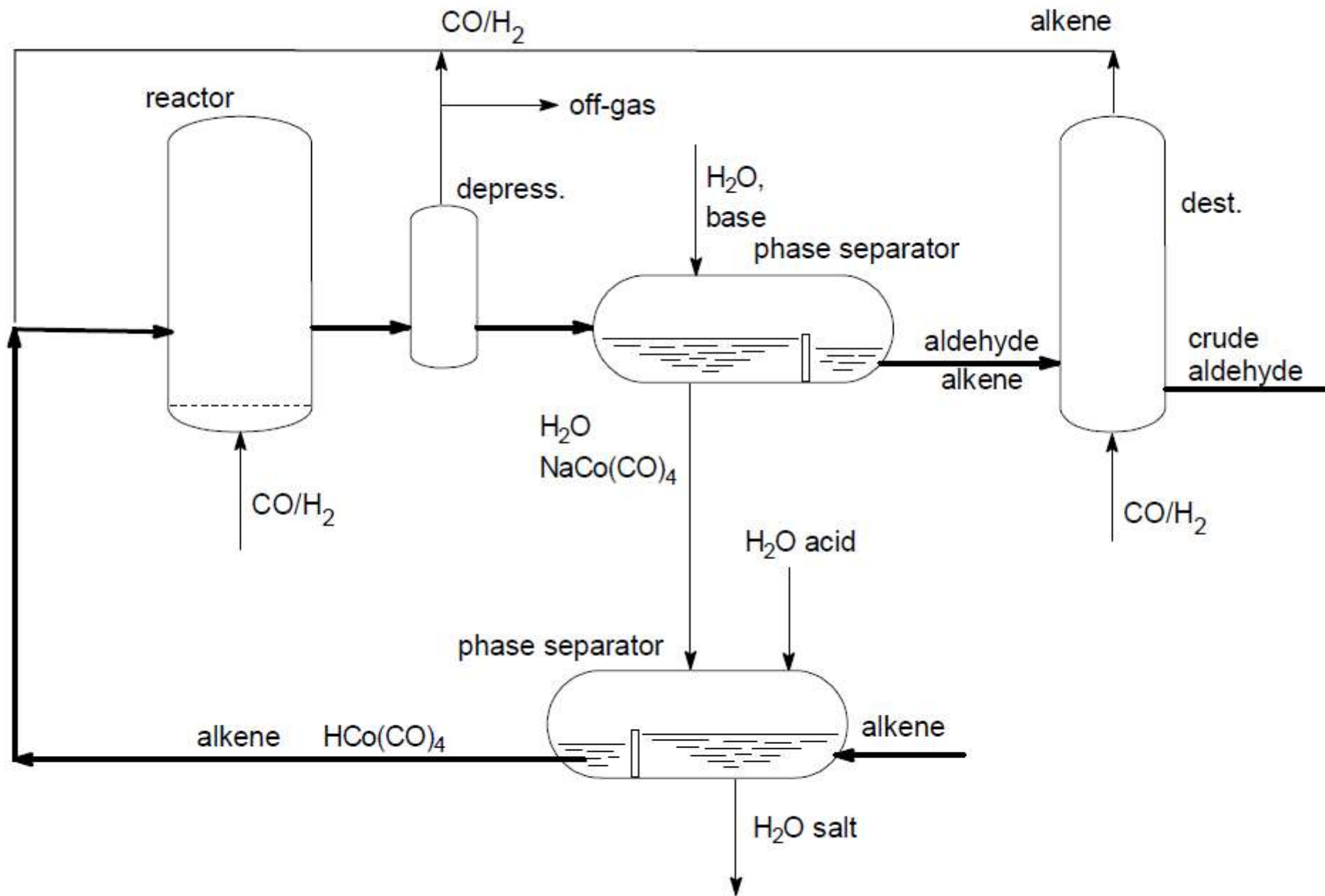


Figure 7.4. Kuhlmann hydroformylation process

Phosphine modified cobalt catalysts: the Shell process

In the sixties it was recognised that ligand substitution on the cobalt carbonyl complex might influence the performance of the catalyst. Tertiary alkyl phosphines have a profound influence:

- the reaction is a hundred times slower [4,5],
- the selectivity to linear products increases,
- the carbonyl complex formed, $\text{HCoL}(\text{CO})_3$, is much more stable, and
- the catalyst acquires activity for hydrogenation.

As a result of the higher stability the process can be (and must be!) operated at lower pressure (25-100 bar versus 200-300 bar for $\text{HCo}(\text{CO})_4$). The higher stability can be explained by the electron donation of the phosphine to the electron deficient cobalt carbonyl thus strengthening the Co-CO bonds. The phosphine complex is less active than the tetracarbonyl complex and therefore the reaction is carried out at higher temperatures (170 °C versus 140 °C). The temperature is "dictated" by the rate required; the high pressures in the tetracarbonyl system are needed to prevent decomposition of the carbonyls to metal and CO.

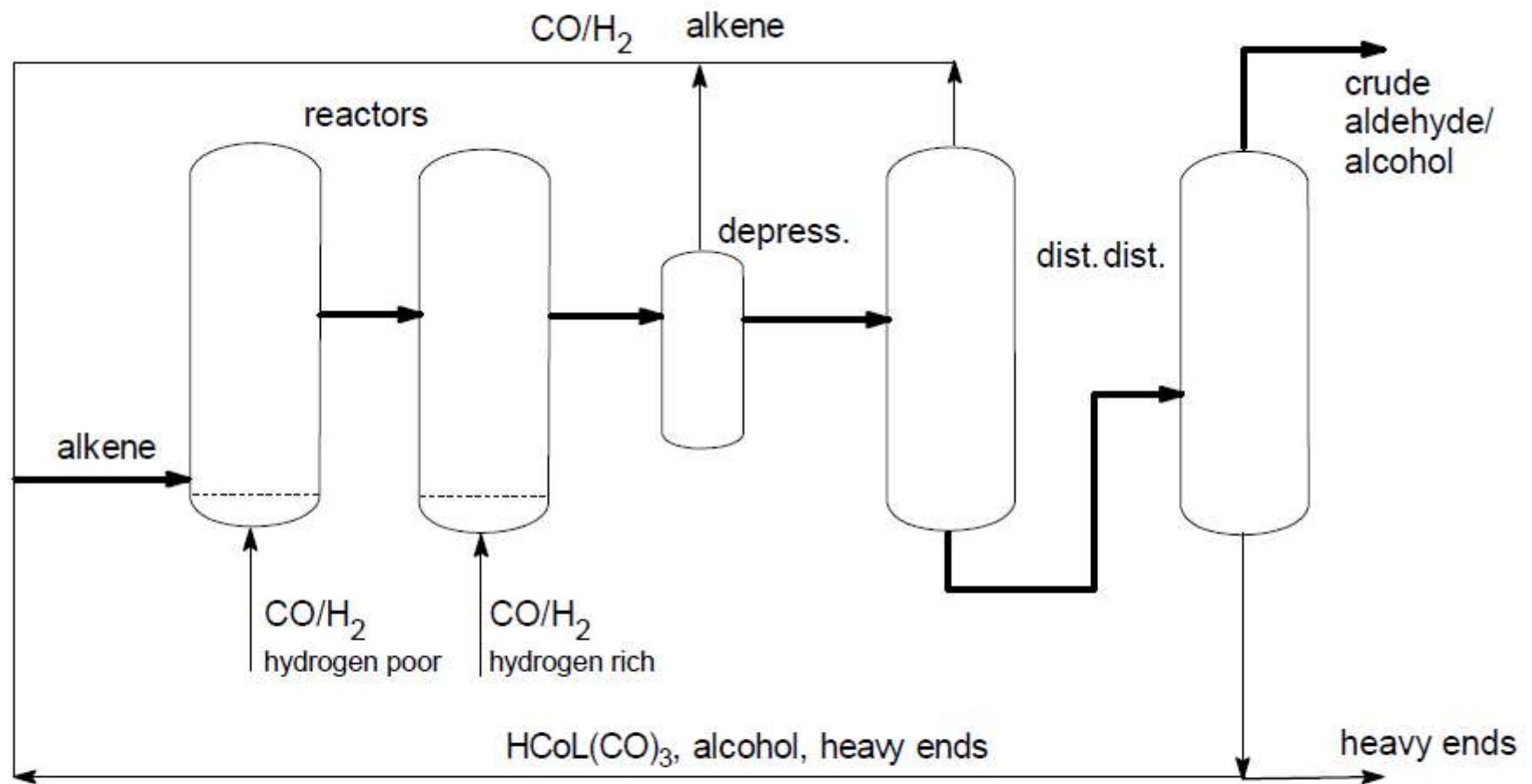
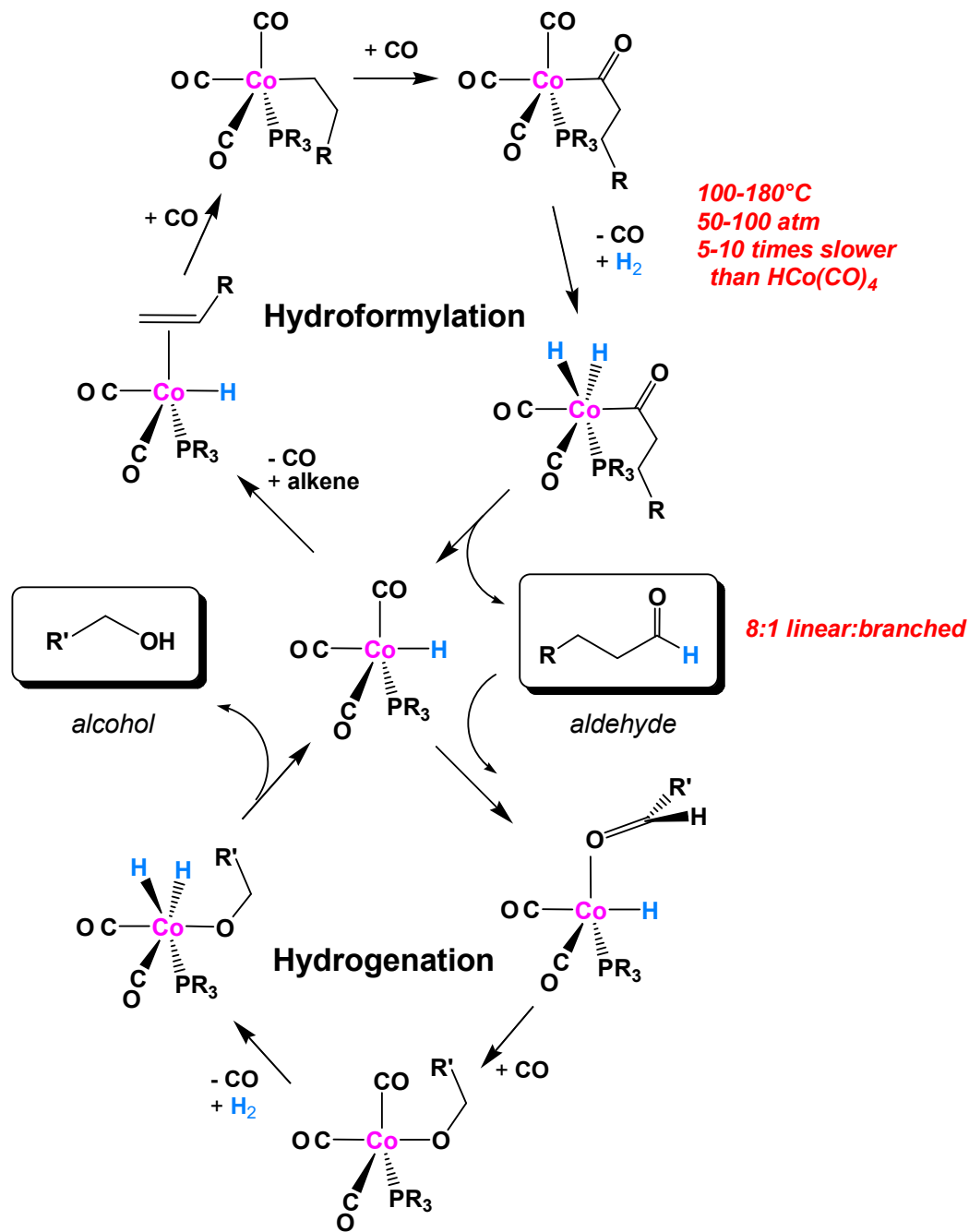
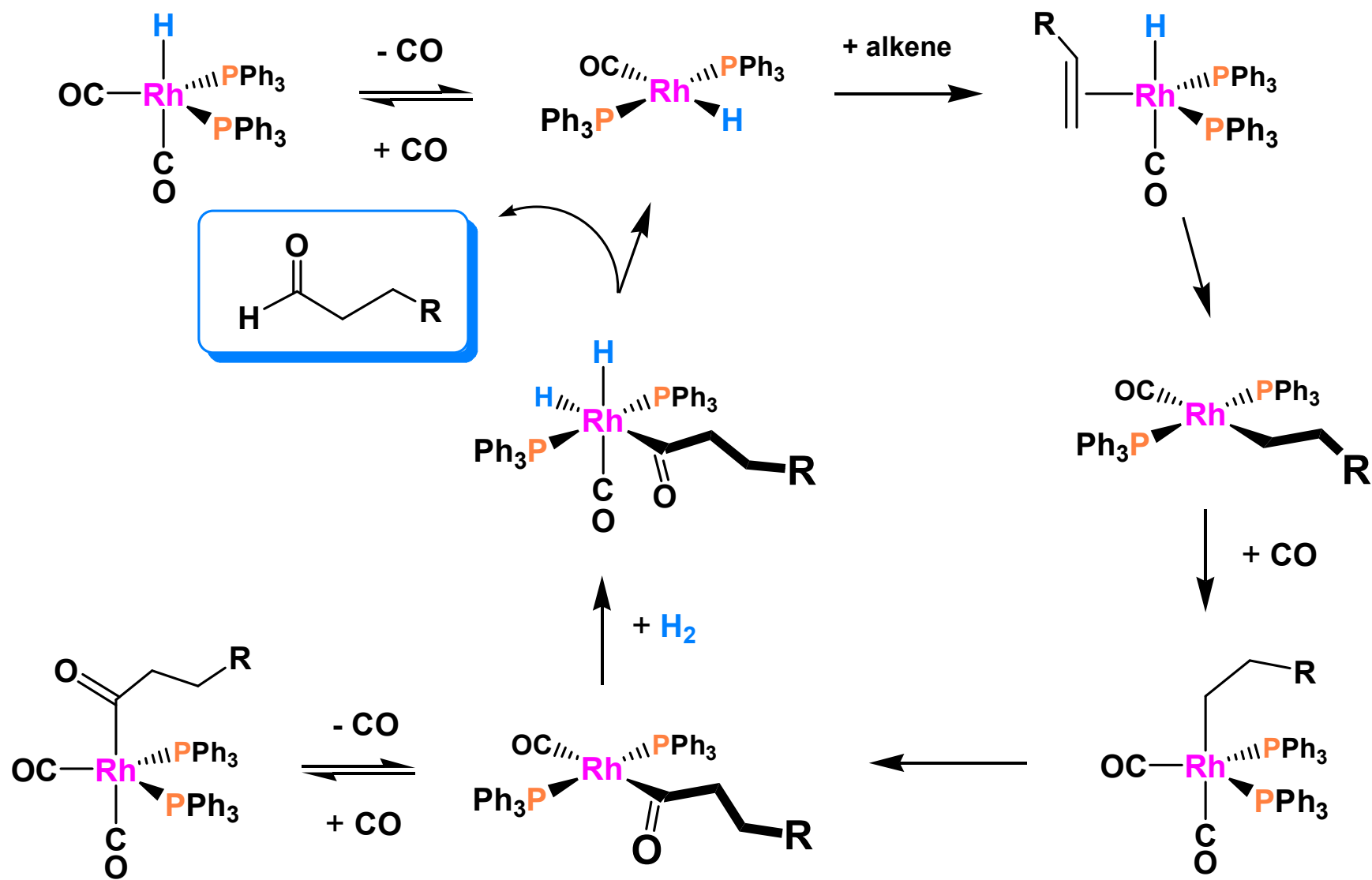


Figure 7.6. Flow scheme of the Shell process



Phosphine modified
 Cobalt catalyzed
 Hydroformylation Reaction

RHODIUM CATALYSED HYDROFORMYLATION



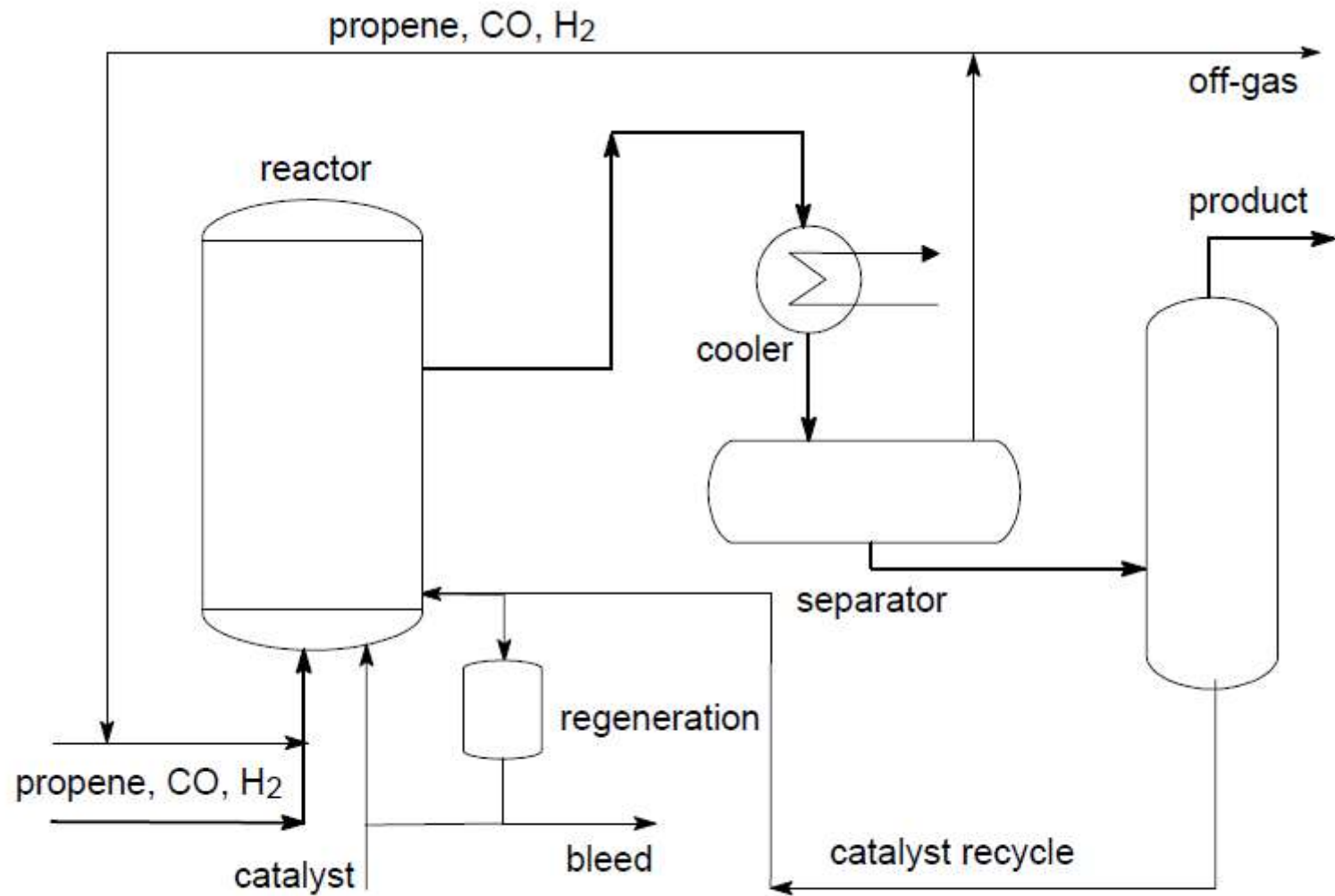
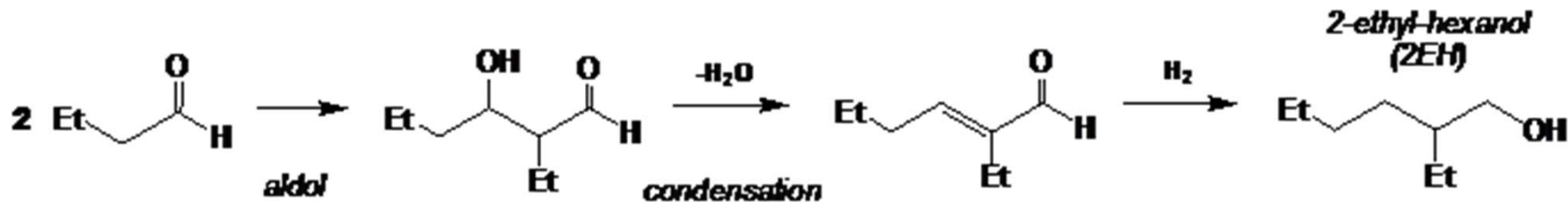


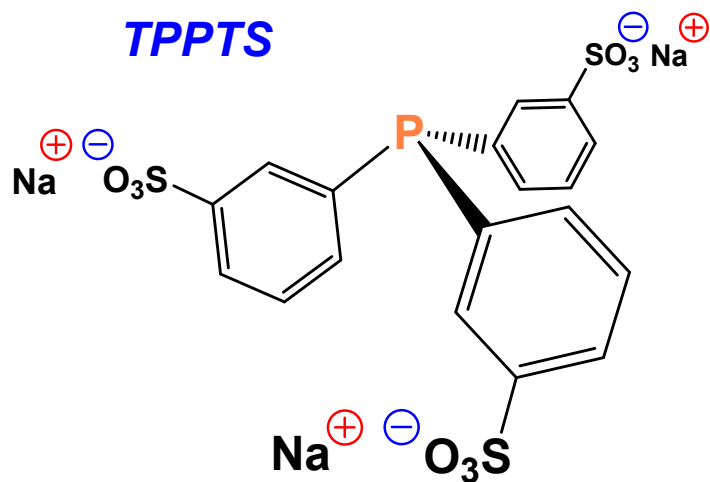
Figure 8.5. LPO process scheme with removal of product in liquid phase

2-ethyl-1-hexanol Product

- Rh/PPh₃ catalyzed hydroformylation is responsible for just over 50% of all oxo alcohols produced. Propylene is the largest single alkene hydroformylated to produce butylaldehyde, which can be hydrogenated to produce butanol, or dimerized by an aldol condensation and then hydrogenated to form 2-ethyl-1-hexanol (2EH), the largest single product produced by hydroformylation (over 5 billion lbs a year). 2-ethyl-1-hexanol is usually reacted with phthalic anhydride to produce dialkyl phthalic esters that are used as plasticizers to keep polyvinyl chloride plastics soft and flexible.



Aqueous-Phase Rh Hydroformylation



Hydrocyanation (addition of H-CN)

Hydrocyanation is used industrially to prepare adiponitrile from butadiene.

Adiponitrile is the key intermediate in synthesizing Nylon-6,6.

