

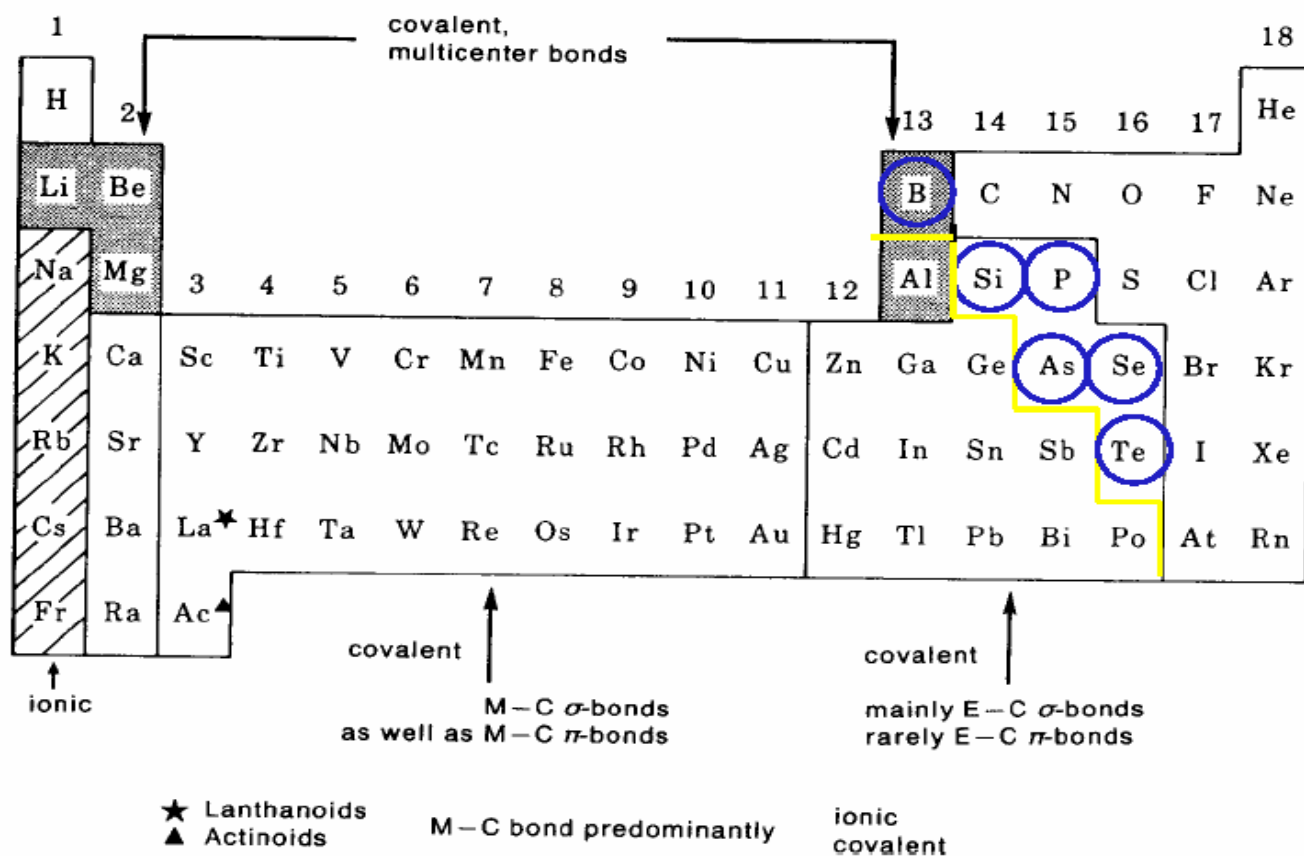
Organometallic Chemistry

Compounds that contain M-C bonds

- How strong or weak is a M-C bond?
- How stable are the organometallic compounds?

Organo-element Chemistry!

- What is a metal? :



• Electronegativity criteria? :

Tab. 2.1. Element electronegativities (X_M), ΔX differences and the percent of ionic character of the M—C bonds.

Li 0.97 1.53 44	Be 1.47 1.03 23	<table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>H</td> <td>← element</td> </tr> <tr> <td>2.1</td> <td>← electronegativity (x_M)</td> </tr> <tr> <td>0.4</td> <td>← difference $\Delta x = x_C - x_M$</td> </tr> <tr> <td>4</td> <td>← % ionic character of the E—C bond</td> </tr> </table>										H	← element	2.1	← electronegativity (x_M)	0.4	← difference $\Delta x = x_C - x_M$	4	← % ionic character of the E—C bond	B 2.01 0.49 6	C 2.50 0 0	N 3.07 0.57 8	O 3.50 1.00 22	F 4.10 1.60 47	Ne — — —
H	← element																								
2.1	← electronegativity (x_M)																								
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4	← % ionic character of the E—C bond																								
Na 1.01 1.49 42	Mg 1.23 1.27 33											Al 1.47 0.93 19	Si 1.74 0.76 13	P 2.06 0.44 5	S 2.44 0.06 1	Cl 2.83 0.33 2	Ar — — —								
K 0.91 1.59 46	Ca 1.04 1.46 41	Sc 1.20 1.30 34	Ti 1.32 1.18 29	V 1.45 1.05 24	Cr 1.56 0.94 20	Mn 1.60 0.90 18	Fe 1.64 0.86 16	Co 1.70 0.80 15	Ni 1.75 0.75 13	Cu 1.75 0.75 13	Zn 1.66 0.84 16	Ga 1.82 0.68 11	Ge 2.02 0.48 6	As 2.20 0.30 2	Se 2.48 0.02 0	Br 2.74 0.24 1	Kr — — —								
Rb 0.89 1.61 48	Sr 0.99 1.51 43	Y 1.11 1.39 38	Zr 1.22 1.28 33	Nb 1.23 1.27 33	Mo 1.30 1.20 30	Tc 1.36 1.14 28	Ru 1.42 1.08 26	Rh 1.45 1.05 24	Pd 1.35 1.15 28	Ag 1.42 1.08 28	Cd 1.46 1.04 24	In 1.49 1.01 22	Sn 1.72 0.78 15	Sb 1.82 0.68 12	Te 2.01 0.49 6	I 2.21 0.29 2	Xe — — —								
Cs 0.86 1.64 49	Ba 0.97 1.53 44	La* 1.08 1.42 39	Hf 1.23 1.27 33	Ta 1.33 1.17 29	W 1.40 1.10 26	Re 1.46 1.04 24	Os 1.52 0.98 22	Ir 1.55 0.95 20	Pt 1.44 1.06 24	Au 1.42 1.08 25	Hg 1.44 1.06 24	Tl 1.44 1.06 24	Pb 1.55 0.95 20	Bi 1.67 0.83 16	Po 1.76 0.74 13	At 1.90 0.60 8	Rn — — —								
Fr 0.86 1.64 49	Ra 0.97 1.53 44	Ac 1.0 1.5 43	Th 1.11 1.39 38	Pa 1.14 1.36 36	U 1.22 1.28 33																				

* These values can be used for all the lanthanides.

Energy :

•The energy of the metal(M)-carbon(C) bond decreases within a main group with increasing atomic number.

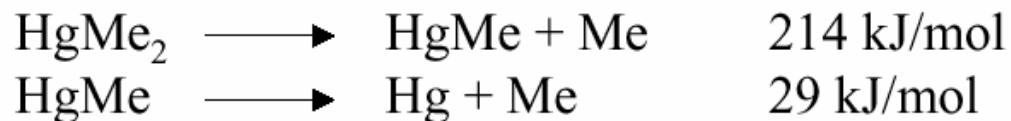
•Example:

for MMe ₃	B-C	365 kJ/mol
	Al-C	274 kJ/mol
	Ga-C	247 kJ/mol
	Tl-C	160 kJ/mol

•The bonds can be weak

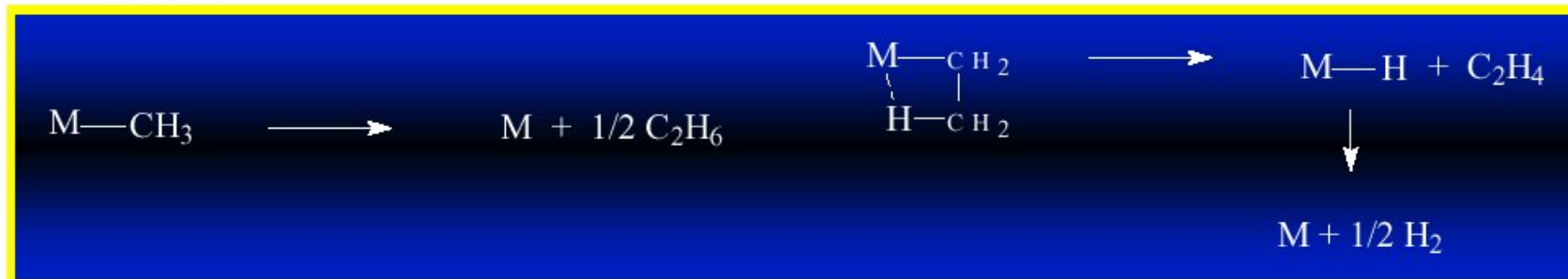
for HgMe ₂	Hg-C	121 kJ/mol
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•**Warning:** Those are average values:



Reactivity / Lability? :

- Influence of the thermal decomposition pathway: homolytic cleavage vs. β -elimination.



- Influence of the steric shielding: shielding \nearrow , reactivity \searrow
- Influence of the bond polarity: polarity \nearrow , reactivity toward H_2O \nearrow
- Available empty orbitals or reactive lone pairs at the metal center lead to an increase of the reactivity toward H_2O and/or O_2 .

InMe_3 , reacts H_2O and O_2

SnMe_4 , inert

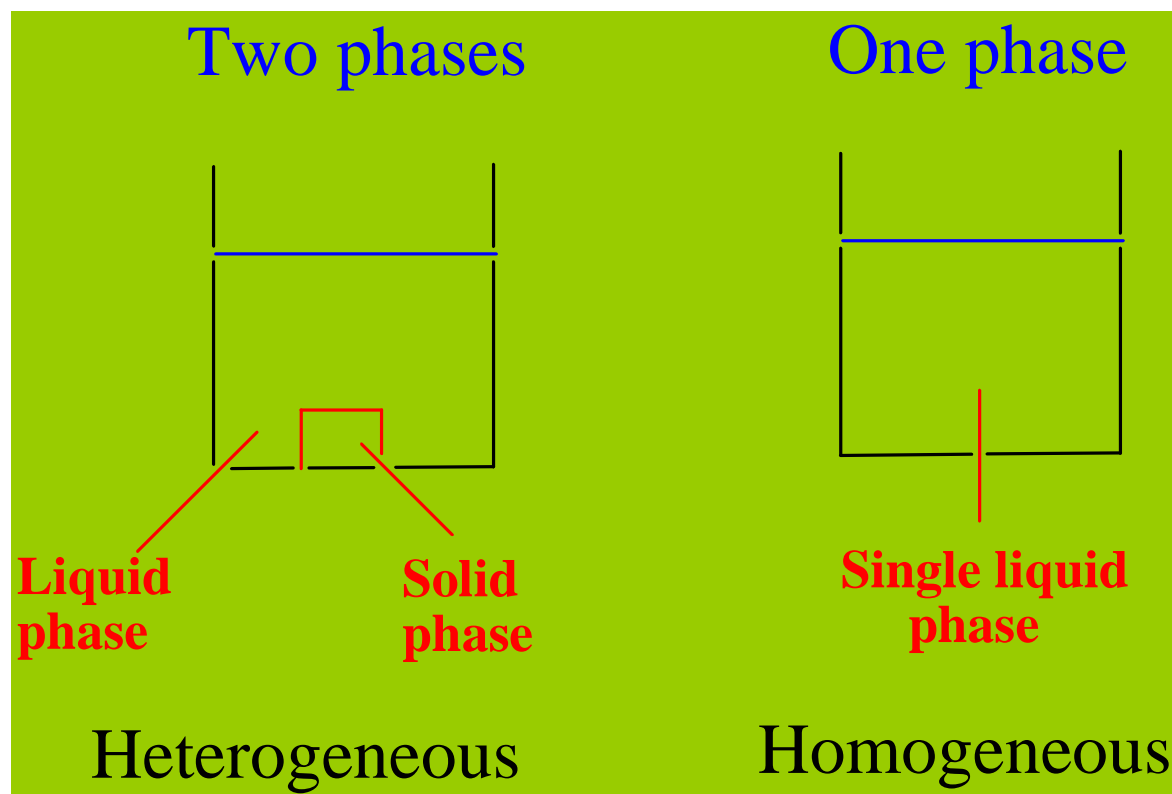
SbMe_3 , reacts with O_2

History of MGOMC

Catalysis

- A catalyst is a substance that increases the rate of a reaction but it is not itself consumed
- Catalysis plays a vital role in the production of fuels, commodity chemicals, fine chemicals and pharmaceuticals as well as providing the means for experimental safeguards all over the world
- More than 60% of all chemical products and 90% of all chemical processes are based on catalysis.
- A whole new technology appeared based on organometallic catalysis in olefin polymerization

- Nobel prizes for chemistry have been awarded to Ziegler and Natta (1963), Fischer and Wilkinson (1973) for their discoveries in Organometallic chemistry and homogeneous catalysis
- More recently, in 2005, Chauvin, Schrock, and Grubbs were awarded Nobel Prize for developing organometallic catalysts for olefin metathesis.
- Catalysis can be of two types Heterogeneous and Homogeneous



- Homogeneous Catalysis: They are present in the same phase as the reagents
- Heterogeneous Catalysts: They are present in a different phase from that of the reactants
- Of the two, heterogeneous catalysis has a much greater economic impact

Table 25.1 The top 20 synthetic chemicals in the USA in 2004 (based on mass)

Rank	Chemical	Catalytic process	Rank	Chemical	Catalytic process
1	Sulfuric acid	SO ₂ oxidation, heterogeneous	11	Urea	NH ₃ precursor catalytic
2	Ethene	Hydrocarbon cracking, heterogeneous	12	Ethylbenzene	Alkylation of benzene, homogeneous
3	Propene	Hydrocarbon cracking, heterogeneous	13	Styrene	Dehydrogenation of ethylbenzene, heterogeneous
4	Chlorine	Electrolysis, not catalytic	14	HCl	Precursors catalytic
5	1,2-Dichloroethane	Ethene + Cl ₂ , heterogeneous	15	Ethylene oxide	Ethene + O ₂ , heterogeneous
6	Phosphoric acid	Not catalytic	16	Cumene	Alkylation of benzene, heterogeneous
7	Ammonia	N ₂ + H ₂ , heterogeneous	17	Ammonium sulfate	Precursors catalytic
8	Sodium hydroxide	Electrolysis, not catalytic	18	Sodium carbonate	Not catalytic
9	Nitric acid	NH ₃ + O ₂ , heterogeneous	19	Butadiene	Dehydrogenation of butane, heterogeneous
10	Ammonium nitrate	Precursors catalytic	20	Titanium dioxide	Not catalytic

Source: Facts & Figures for the Chemical Industry, *Chem. Eng. News*, 2005, **83**, 67.

Table 25-1

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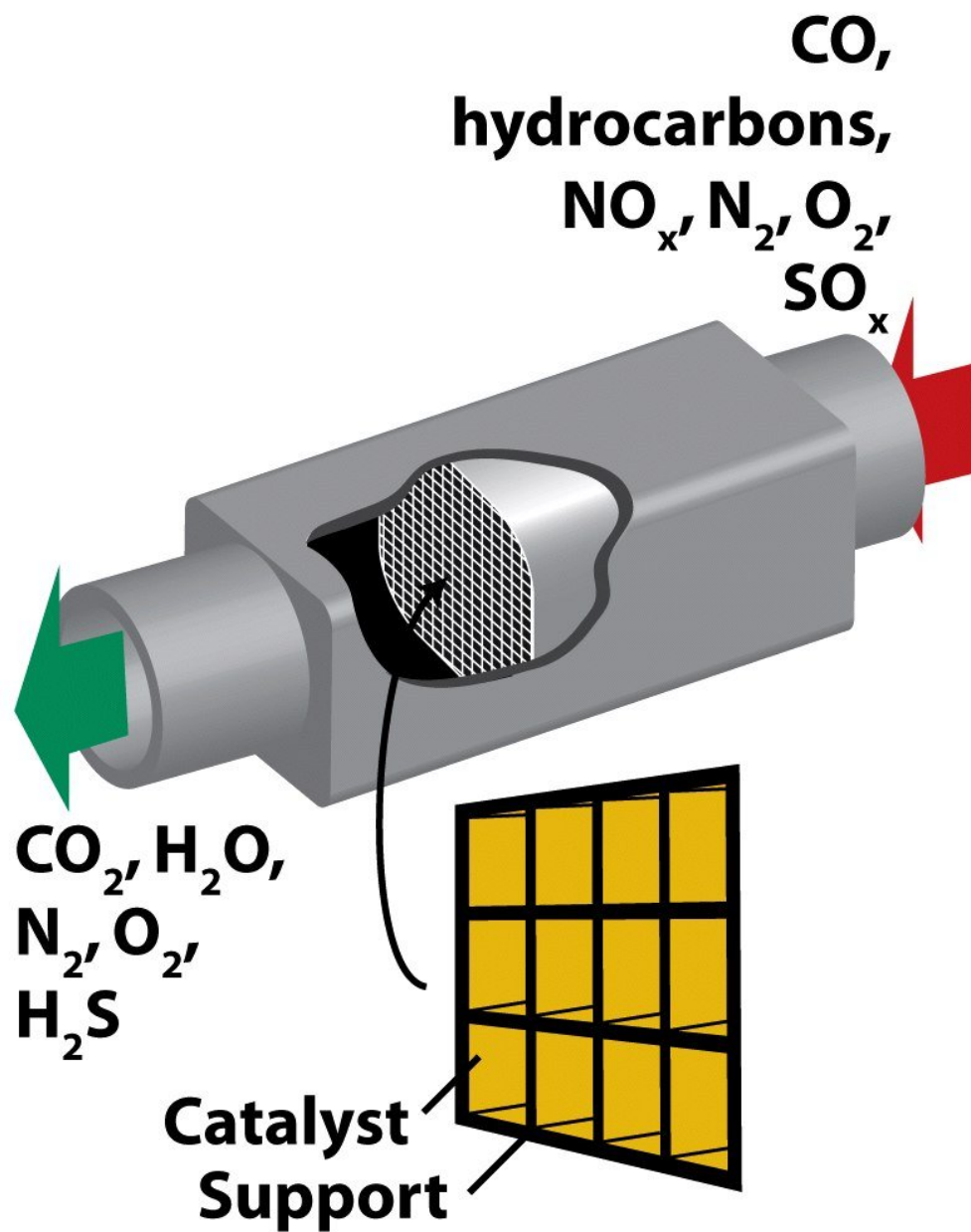


Figure 25-4

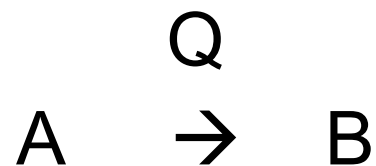
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- A catalyzed reaction is faster (or in some cases more specific) than an uncatalyzed version of the same reaction because the catalyst provide a different reaction pathway with a lower activation energy

Catalyst efficiency

- **Turnover frequency** : Commonly called the turnover number, N , and defined as molecules reacting per *active site* in unit time.
- [or] The number of moles of substrate that a mole of catalyst can convert before becoming inactivated. An ideal catalyst would have an infinite turnover number in this sense, because it wouldn't ever be consumed, but in actual practice one often sees turnover numbers which go from 100 to a million or more.



$$\gamma \text{ (rate)} = d[B]/dt$$

The turnover frequency, N is given by

$$N = \gamma / [Q]$$

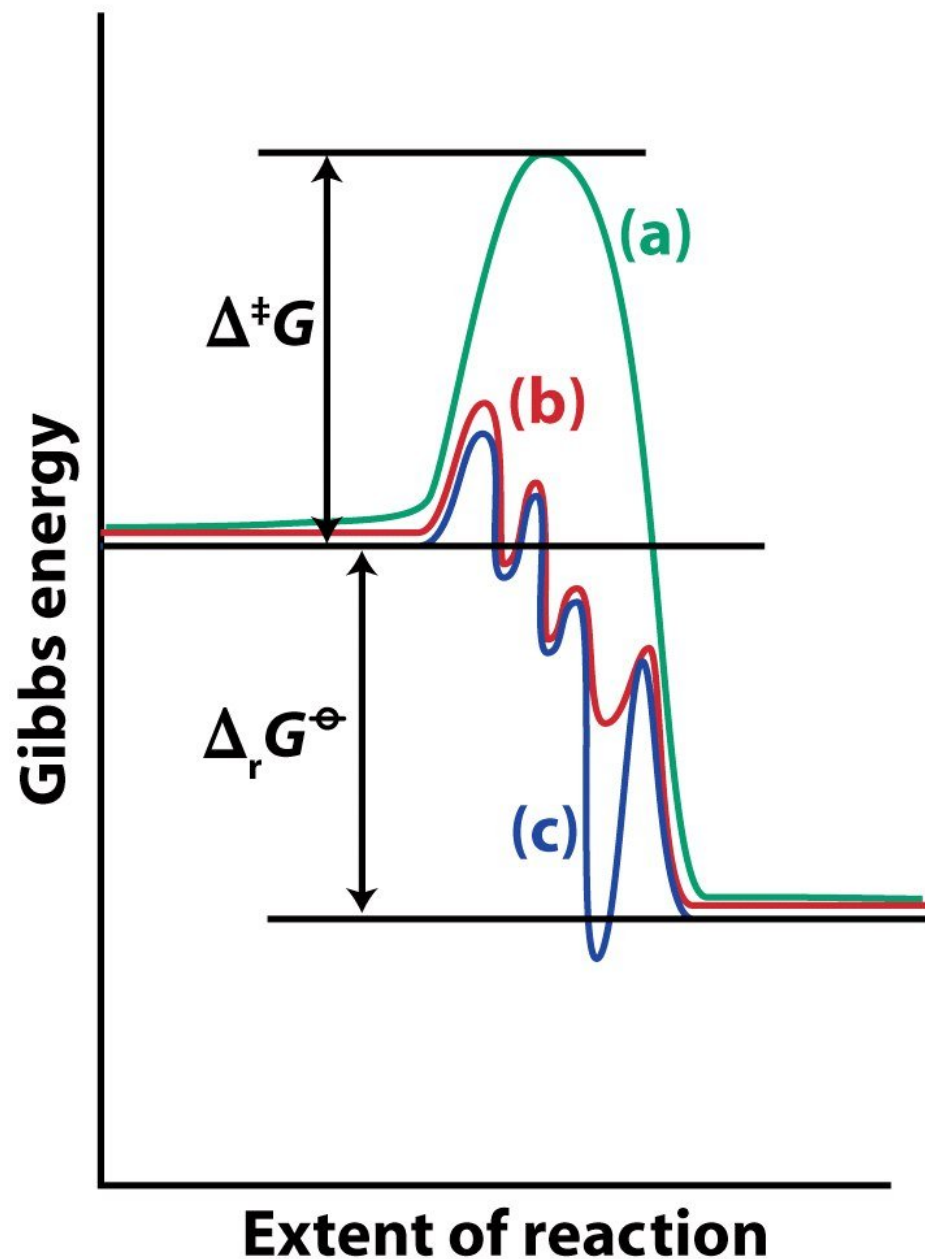
A highly active catalyst results in a fast reaction even in low concentrations and has a large turnover frequency

Catalytic Cycles

- The essence of catalysis is a cycle of reactions that consumes the reactants, forms products and regenerates the catalytic species
- The catalytic cycle operates in the principle of microscopic reversibility

Energetics

- A catalyst increases the rate of processes by introducing new pathways with lower energies of Activation



Gibbs energy profile of a catalyzed reaction contains no high peaks and no deep troughs

In a catalyzed reaction, no stable or non-labile catalytic intermediates are formed (shown by blue line)

The product must be released in a thermodynamically

favorable step

Figure 25-1

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Desired Properties of Catalysts

(i) Selectivity

- A selectivity catalyst yields a high proportion of the desired product with minimum amounts of side product. In industry there is considerable economic incentive to develop selective catalysts

(b) Lifetime

- A small amount of catalyst must survive through a large number of cycles of it is to be economically viable
- A catalyst may be destroyed by side reactions to the main catalytic cycle by the presence of small amounts of impurities in the starting material.
- For example, many alkene polymerization catalysts are destroyed by O_2 , so these polymerizations are carried out in absence of air

	Homogeneous	Heterogeneous
Form	Soluble metal complexes (usually mononuclear)	Metals, usually supported or oxide
Phase	Liquid	Solid/liquid; Solid/gas
Temperature	Low (< 250 °C)	High (250-500 °C)
Activity	Moderate	High
Selectivity	High	Low
Diffusion	Facile	Can be very important

	Homogeneous	Heterogeneous
Heat transfer	Facile	Can be problematic
Product separation	Liquid	Facile
Catalyst recycle	Expensive	Simple
Reaction Mechanism	Reasonably Well understood	Poorly Understood

Homogeneous Catalysis - Catalytic Steps

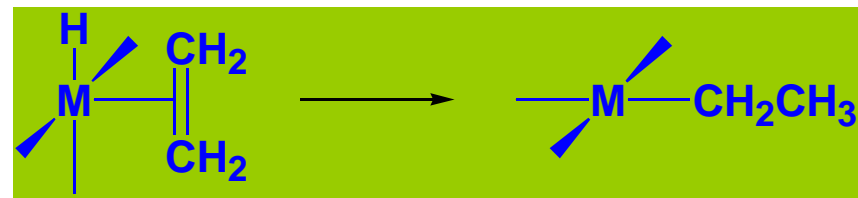
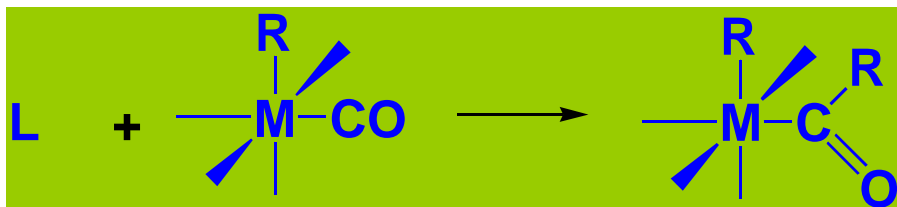
(a) Ligand coordination and dissociation: Catalysis steps often requires facile coordination of reactants to metal ions and equally facile loss of products. Both processes must occur with low Activation Energy. For this purpose, highly labile complexes are needed as they are coordinatively unsaturated (having an open coordination site or being weakly coordinated)

Square-planar 16-electron complexes are coordinatively unsaturated

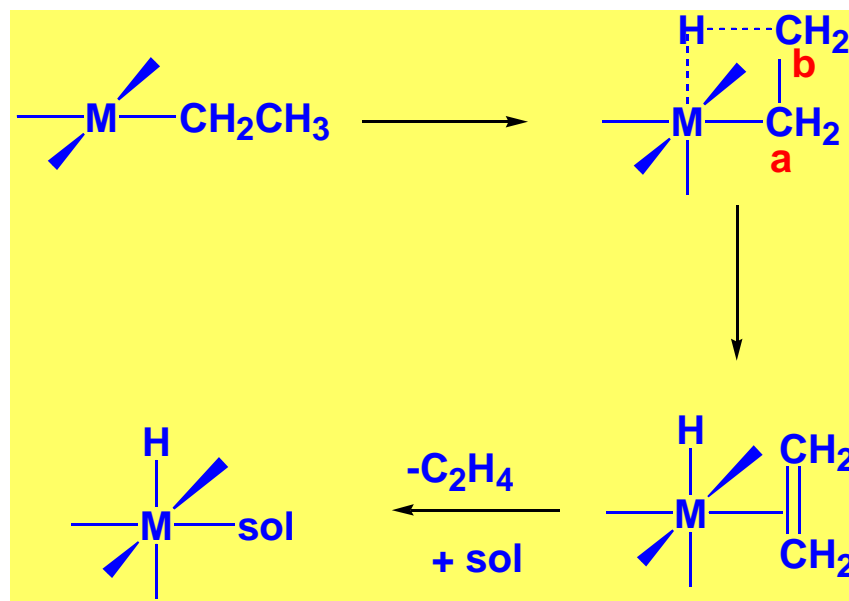
ML_4 complexes of Pd(II), Pt(II) and Rh(I)

$[RhCl(PPh_3)_3]$ – hydrogenation catalyst

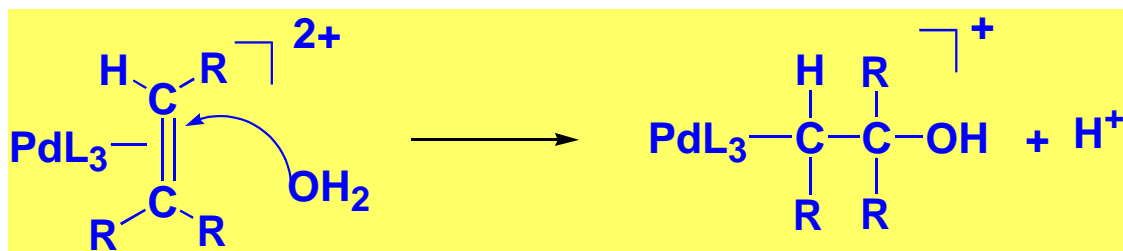
(b) Insertion and elimination: The migration of alkyl and hydride ligands to unsaturated ligands (Migratory insertion)



The reverse of insertion is elimination (β -hydrogen elimination)

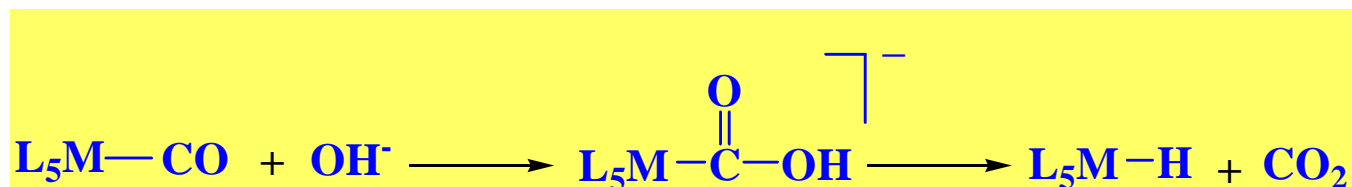


(c) Nucleophilic attack on coordinated ligands: The coordination of ligands (CO, alkenes) to metals in positive oxidation states results in the activation of coordinated C atoms towards attack by nucleophile.

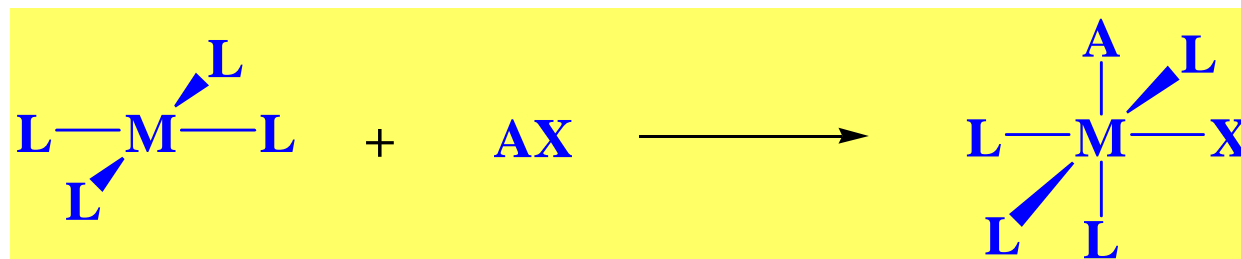


e.g. Stereochemical evidence indicates that the reaction occurs by direct attack on the most highly substituted C atom of the coordinated olefin.

Similarly a coordinated CO ligand is attacked by an OH⁻ ion at the C atom forming -CO(OH) ligand



(d) Oxidative addition and reductive elimination: Oxidative addition of a molecule AX to a complex brings about dissociation of the A – X bond and coordination of the two fragments

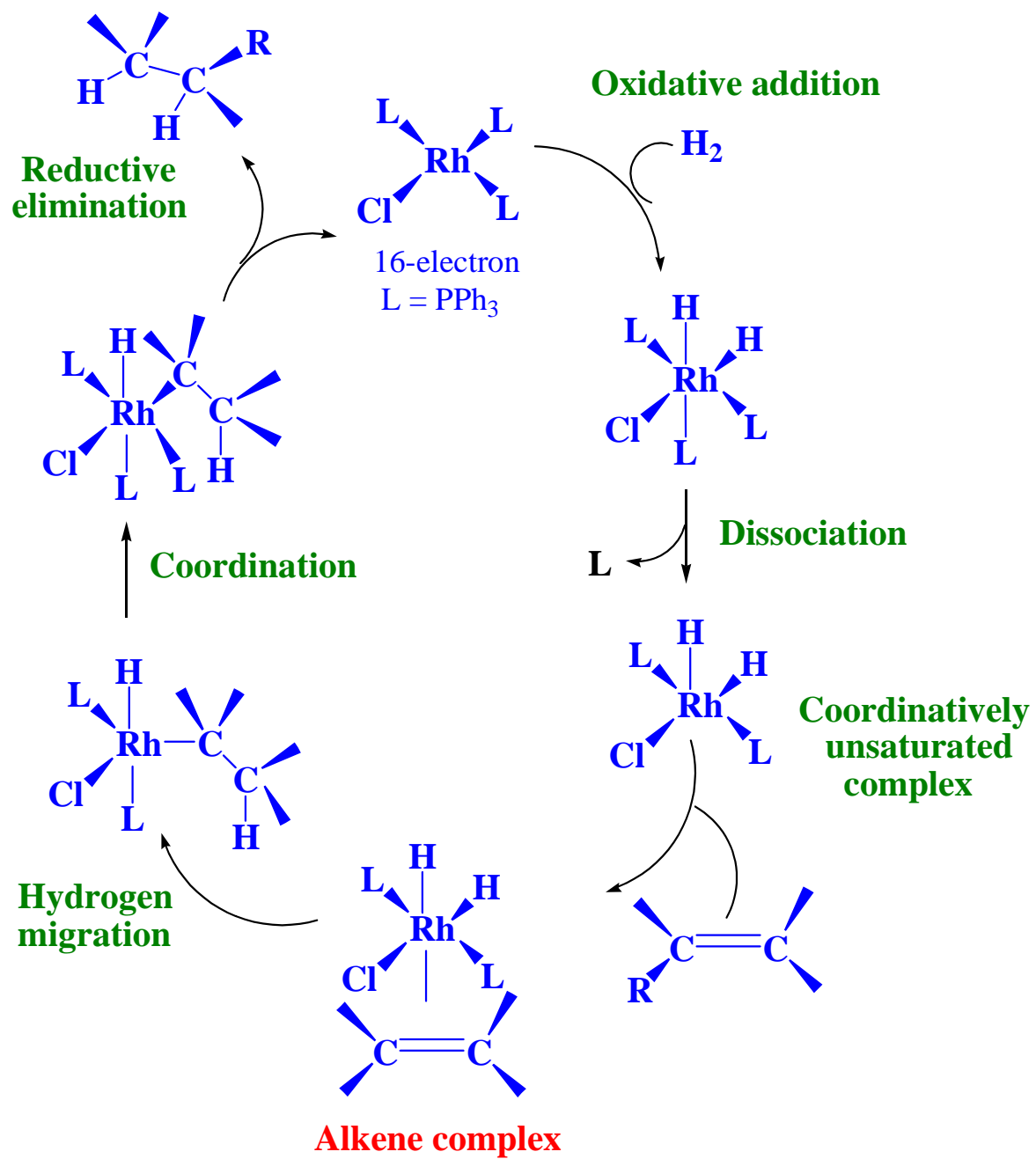


Reductive elimination is the reverse of oxidative addition and often follows it in a catalytic cycle

The mechanisms of oxidative additions can vary depending upon reaction conditions and the nature of the reactants

- concerted reaction
- heterolytic (ionic) addition of A^+ and X^-
- radical addition of A and X
- Despite diversity of mechanism, the rates of oxidative addition of alkyl halides
- primary alkyl < secondary alkyl < tertiary alkyl < F < Cl < Br < I

- Principle of Microscopic Reversibility
- If a certain series of steps constitutes the mechanism of a forward reaction, the mechanism of the reverse reaction is given by the same steps traversed backwards. (applies only to thermal reactions and not-photochemical reactions)
- The sequence of transition states and relative intermediates in the mechanism of a reversible reaction must be the same but in reverse order for the backward reaction as for the forward reaction



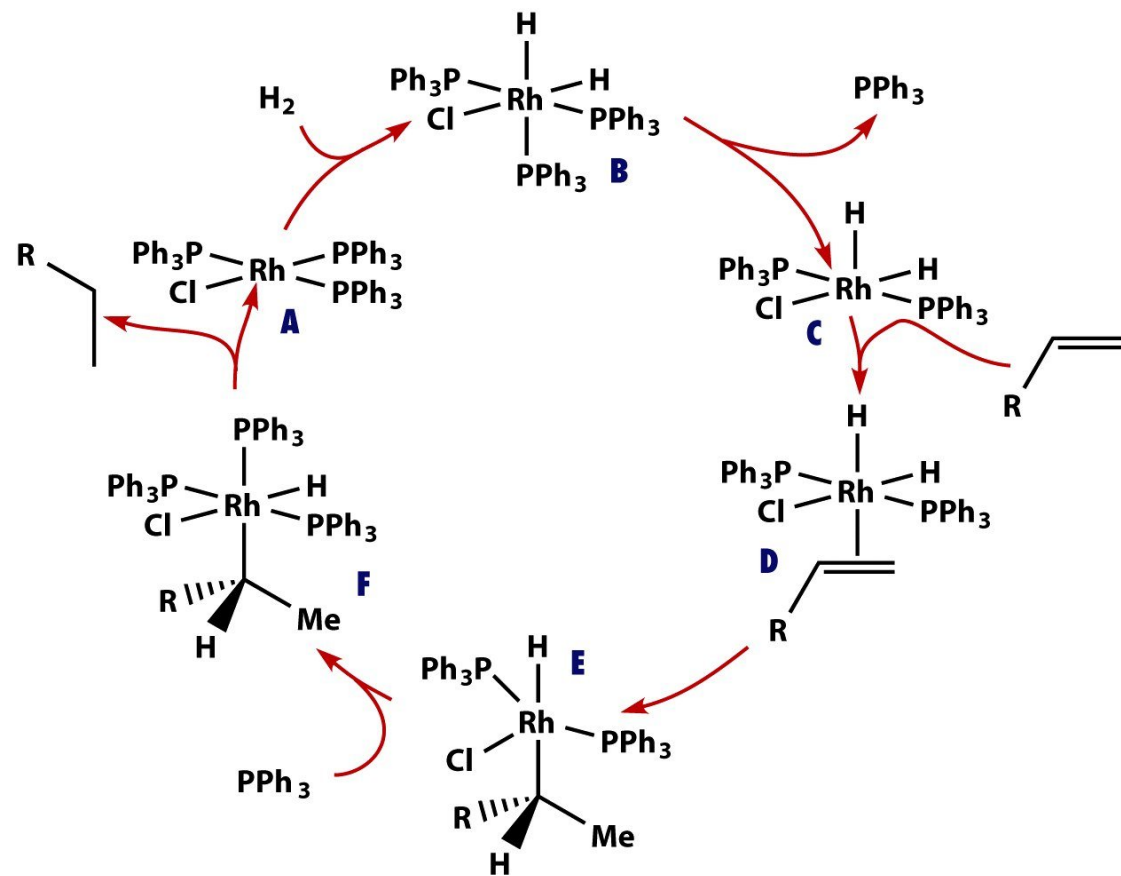
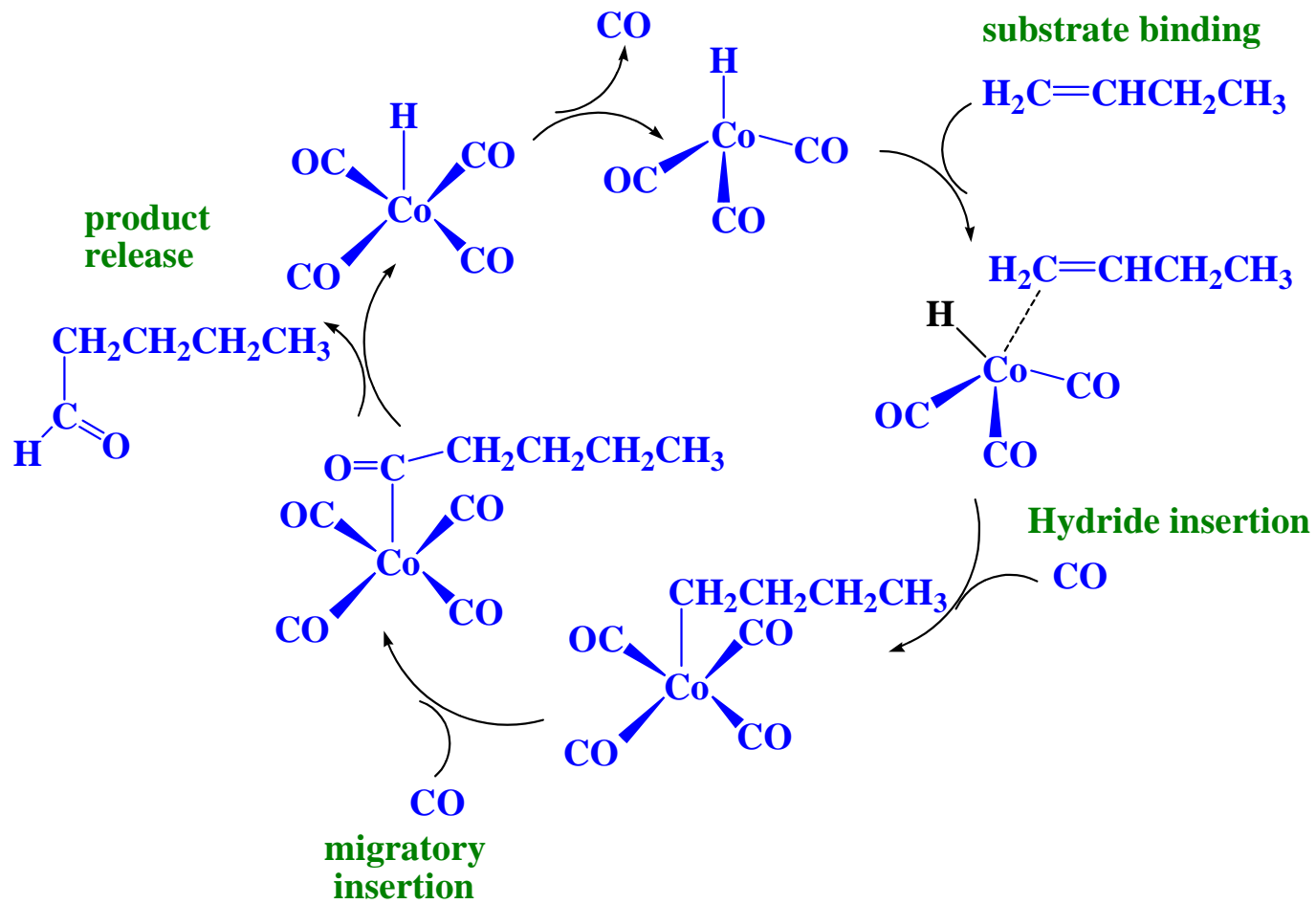


Figure 25-5
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- Wilkinson's catalyst
- Useful for the hydrogenation of a wide variety of alkenes at pressure of hydrogen close to 1 atm or less
- Wilkinson's catalyst is highly sensitive to the nature of phosphine ligand and alkene substrate
- Analogous alkyl phosphine ligands are inactive because they are strongly bound to the metal and do not readily dissociate

- Hydroformylation
- Co and Rh are employed as catalysts
- Aldehydes produced by hydroformylation are normally reduced to alcohols that are used as solvents, plasticizers and in the synthesis of detergents
-
- The scale of production is enormous amounting to millions of tones per year



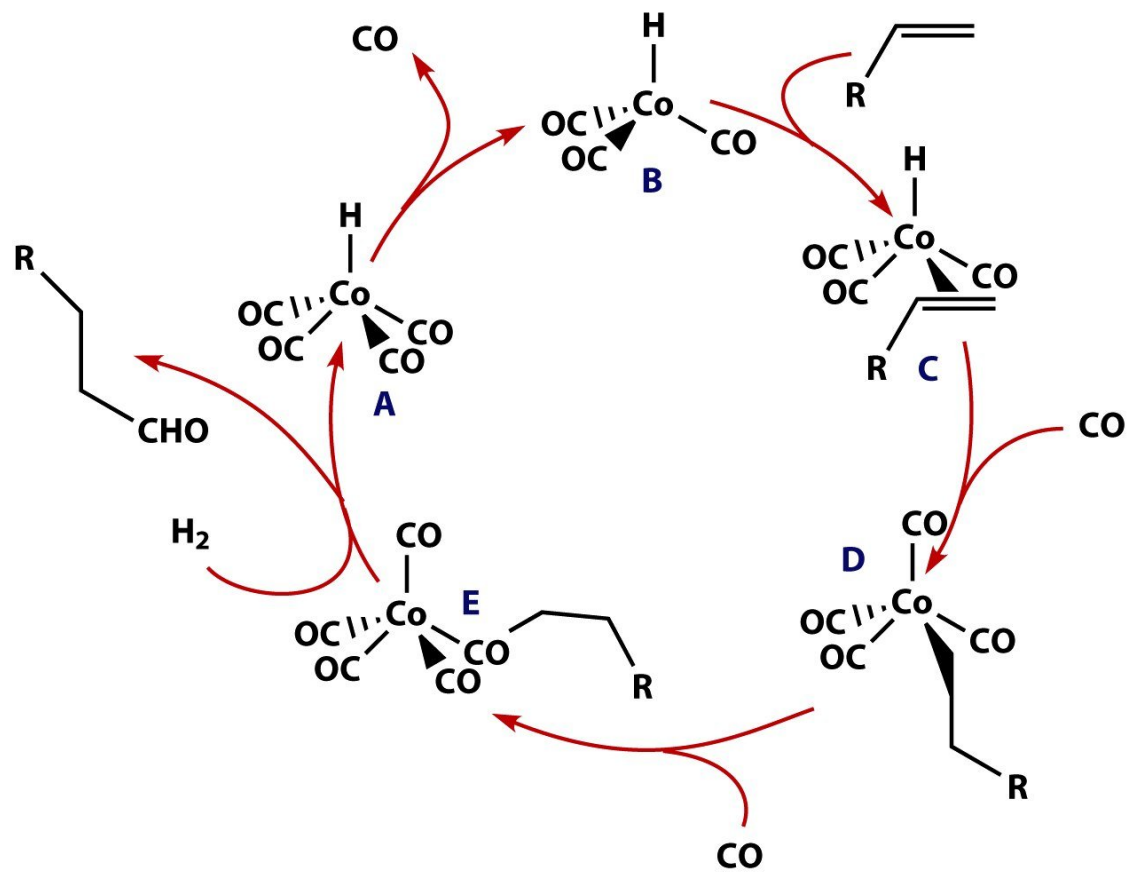


Figure 25-8
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