

Organometallic Chemistry and Homogeneous Catalysis

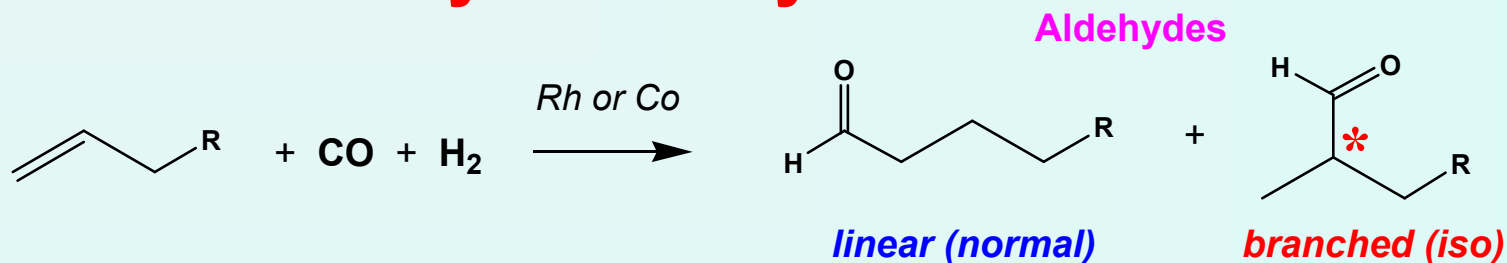
Dr. Alexey Zazybin

Lecture N10



Kashiwa Campus, January 8, 2010

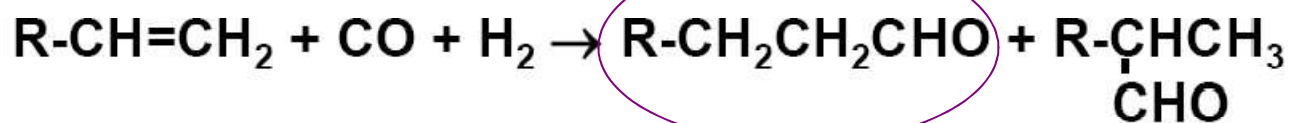
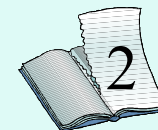
Hydroformylation



Homogeneous catalysis with transition metal complexes

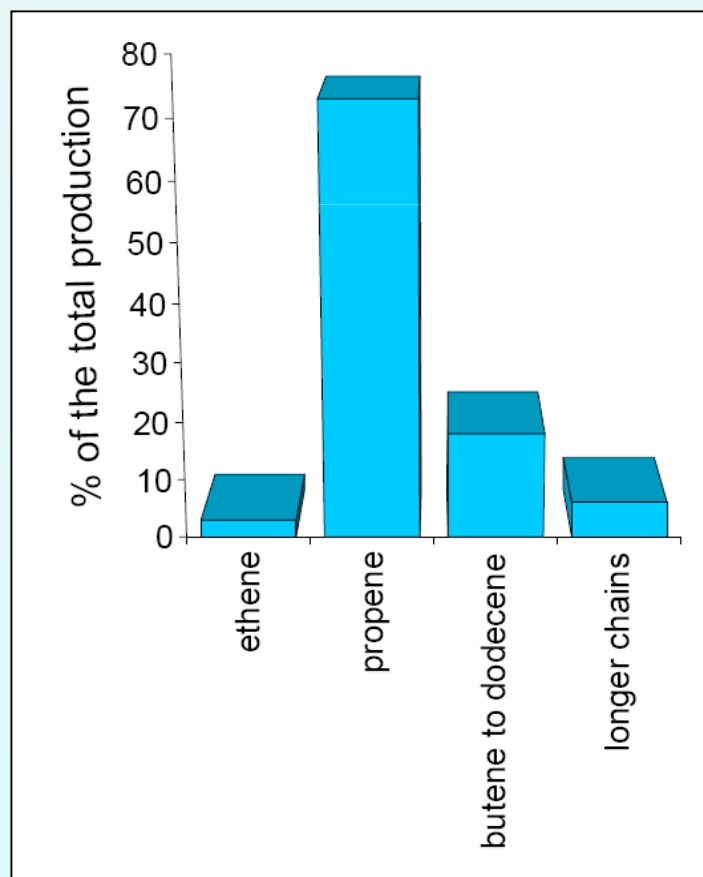
Name	Reaction	Catalyst metal	Capacity (Mio t/a)
RCH/RP, UCC, Shell, Exxon, BASF	olefine hydroformylation	Rh	6.2
Monsanto and Cativa Processes	methanol carbonylation	Rh, Ir	5.4
SHOP Process	ethene oligomerisation	Ni	1.0
Wacker-Hoechst Process	ethene oxidation	Pd + Cu	0.5

Hydroformylation



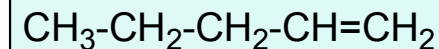
main product (anti-markovnikov)

Product distribution of industrial hydroformylation:

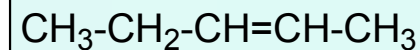


Reactivity (for unmodified Rh-catalysts):

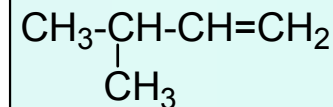
unbranched / end group



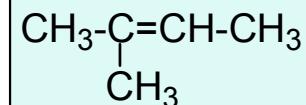
unbranched / internal



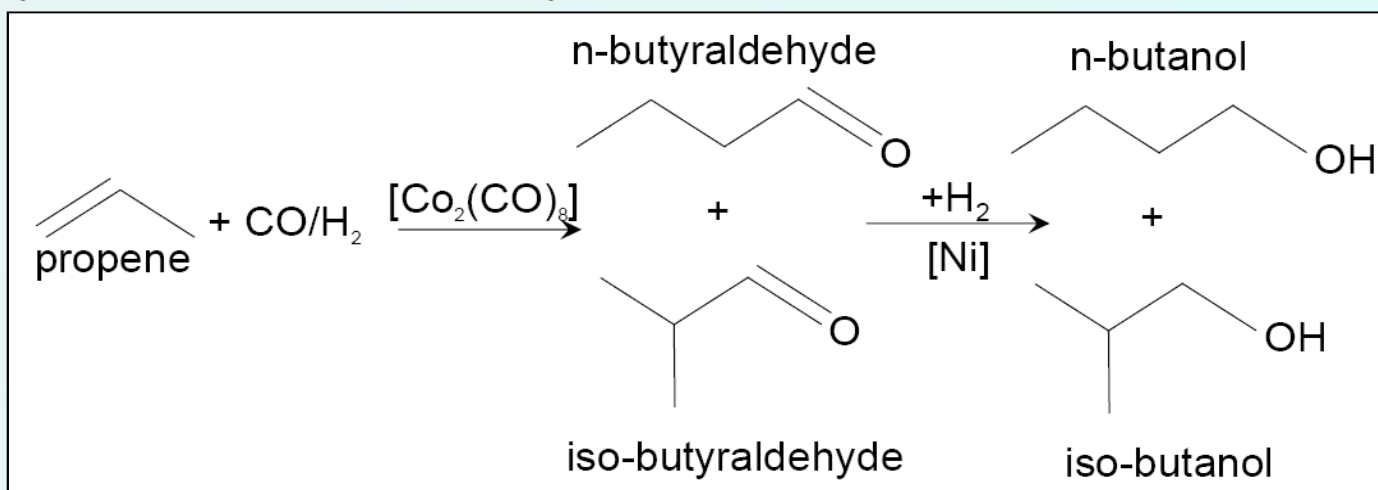
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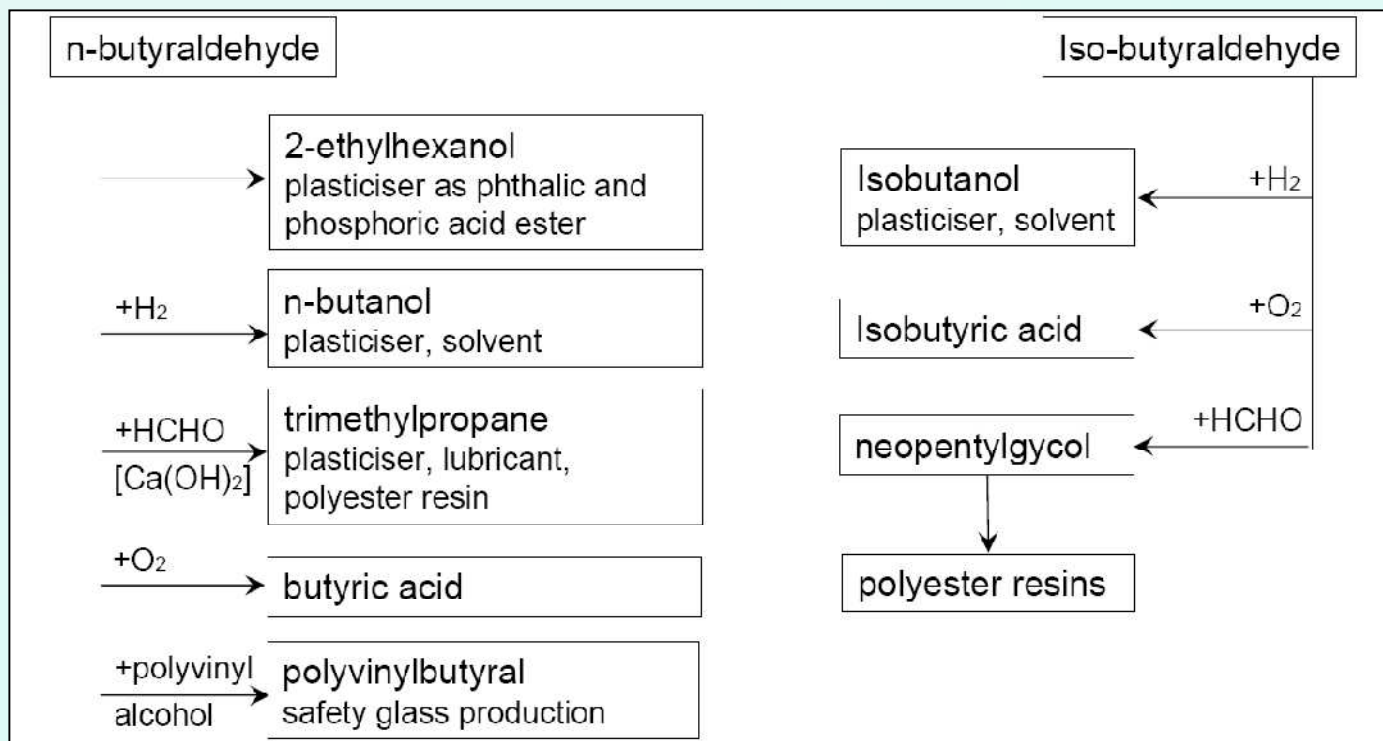
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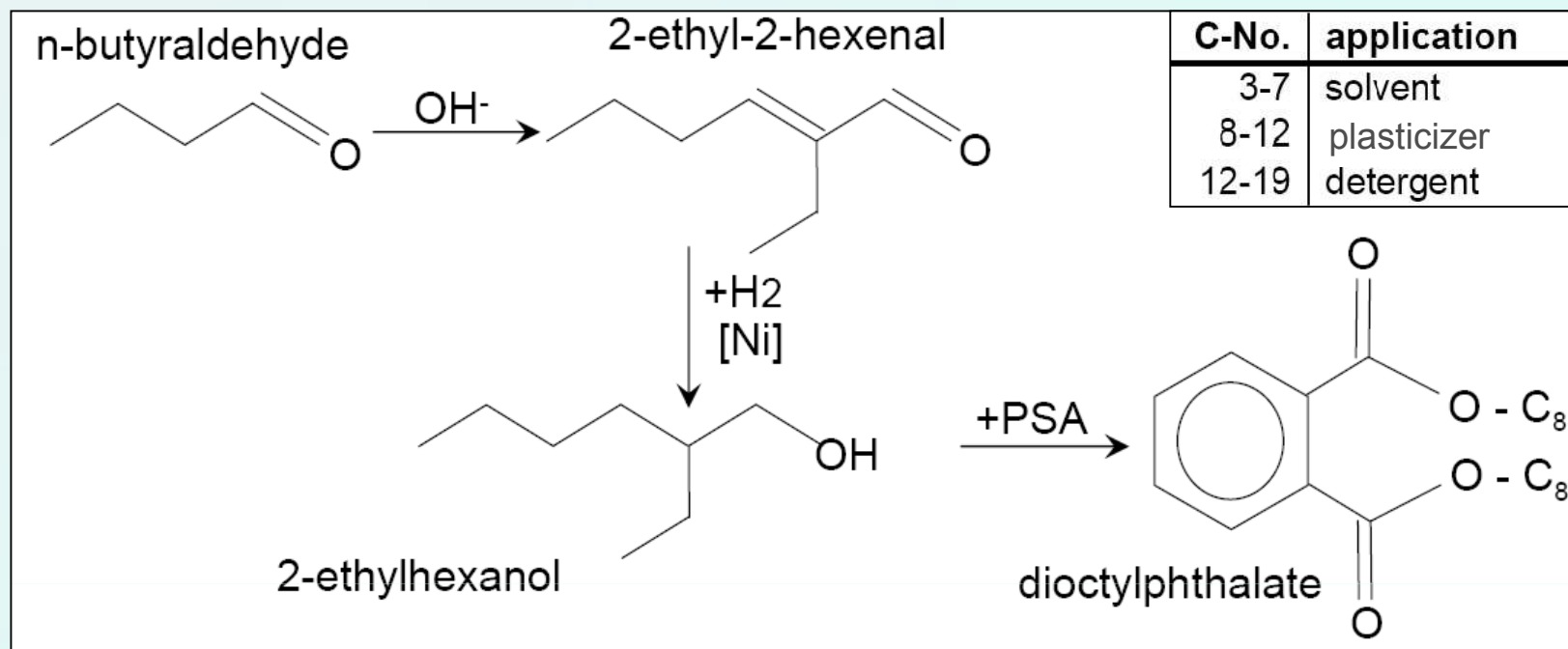
Hydroformylation of propene (oxo-synthesis)



Uses of n- & iso-butyraldehyde

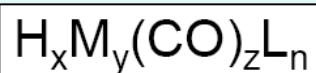


Important derivatives of *n*-butyraldehyde:



Catalysts

general structure:



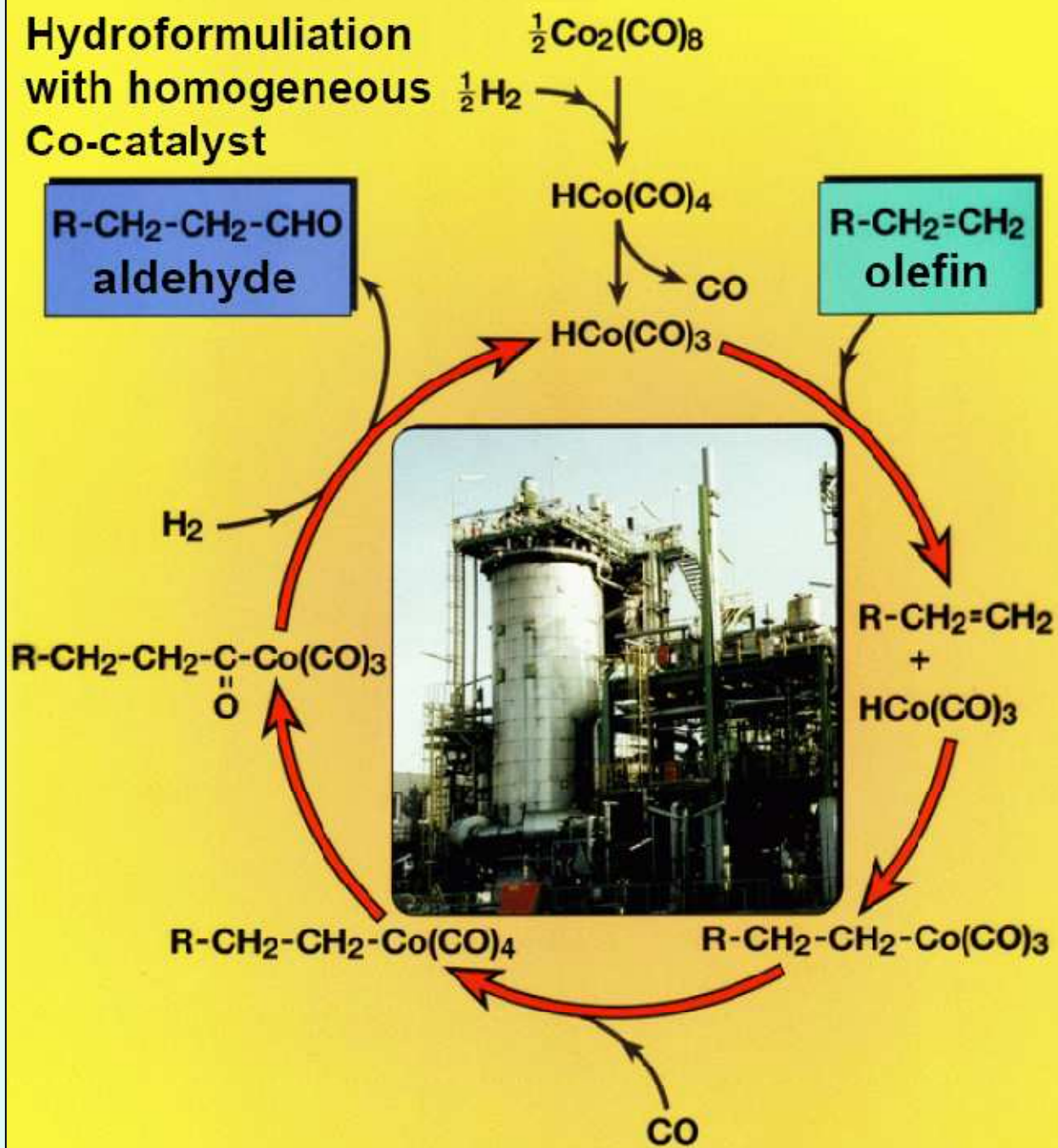
activity of non-modified metal catalysts:

$\text{Rh}(897\$/\text{mol}) \gg \text{Co}(2.83) > \text{Ir}(1554) > \text{Ru}(173) > \text{Os}(3161) > \text{Pt}(2369) > \text{Pd}(508)$

ligand modification: phosphines PR_3 ($\text{R}=\text{C}_6\text{H}_5, \text{n-C}_4\text{H}_9$) or phosphites $\text{P}(\text{OR})_3$

Mechanism:

Hydroformulation with homogeneous Co-catalyst

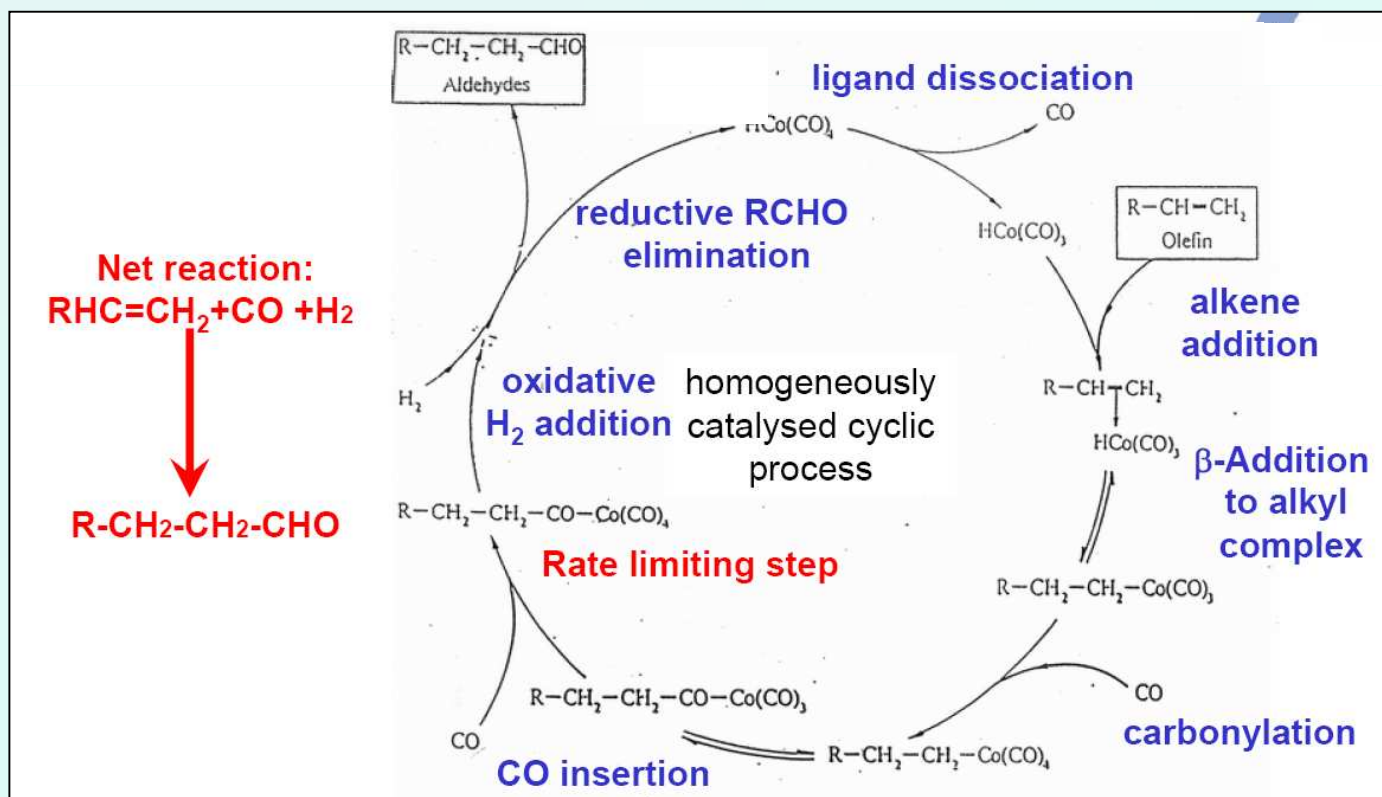


Unmodified Co catalysts (Catalytic cycle of Heck and Breslow, 1960's)

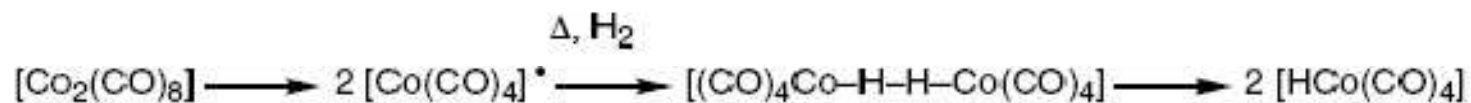


Elementary steps in the mechanism:

1. Reaction of the Co carbonyl $\text{Co}_2(\text{CO})_8$ with H_2 to form the catalyst $\text{HCo}(\text{CO})_3$
2. Dissociation of CO
3. Association of the olefin $\text{R-HC}=\text{CH}_2$
4. Formation of the alkyl Co carbonyl complex
5. Association of CO
6. Insertion of CO to form an alkyl Co carbonyl complex
7. Oxidative addition of H_2 and subsequent reductive elimination of the aldehyde



In the cobalt carbonyl catalysis, the catalytically active 16-electron species $[\text{HCo}(\text{CO})_3]$ is generated by binuclear oxidative addition of H_2 leading to $[\text{HCo}(\text{CO})_4]$:

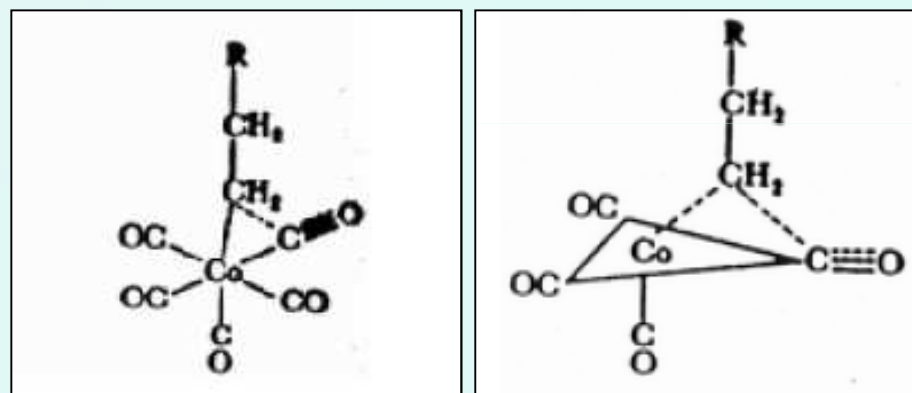


Selectivity

n/i ratio is influenced by:

- Catalyst concentration (*slight*)
- Temperature (*strong*)
- Partial pressure $p(\text{H}_2)$ (*slight*)
- Partial pressure $p(\text{CO})$ (*very strong*)

Transition state:

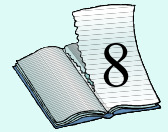


at high and low $p(\text{CO})$

Reaction rate:

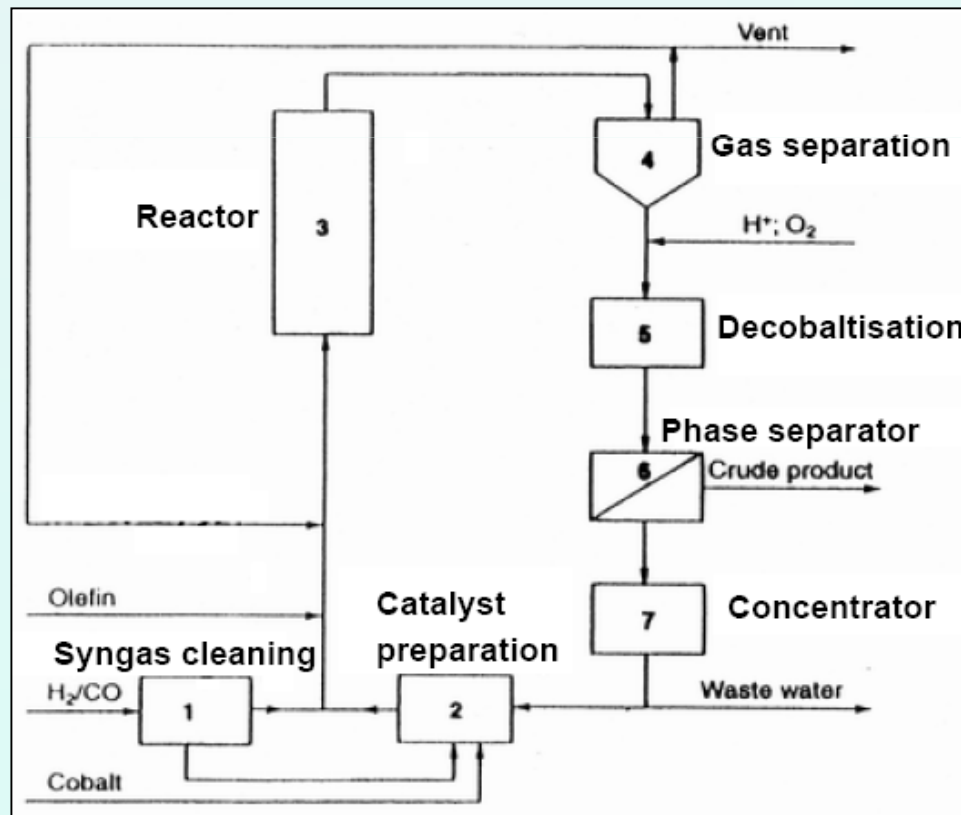
$$\frac{d[\text{aldehyde}]}{dt} \approx k[\text{substrate}][\text{Co}]p(\text{H}_2)p(\text{CO})^{-1}$$

1st generation of hydroformylation catalyst



1950's: Co as catalyst (BASF, Ruhrchemie)

- High-pressure process with unmodified Co catalyst
- Temperature 120 -160°C
- Pressure 270 –300 bar
- LHSV (liquid hourly space velocity) 0.1 -0.4/h
- max. n/i-ratio 4:1



Equipment:

1. Syngas cleaning
2. Catalyst preparation
3. Reactor
4. Gas separation
5. Decobaltisation
6. Phase separator
7. Concentrator

Phosphine modified cobalt catalysts: the Shell process

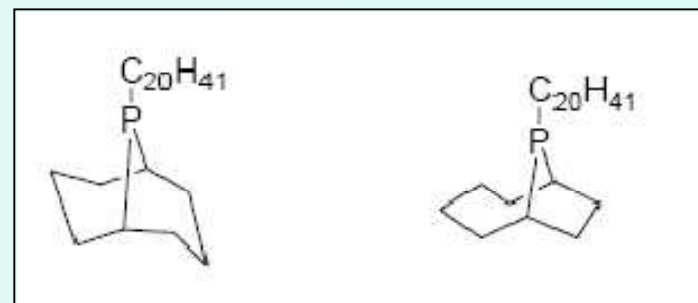
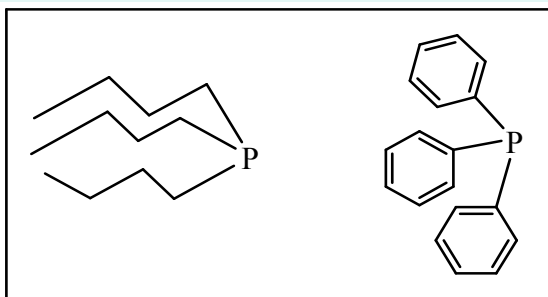
In the 60s it was recognised that ligand substitution on the cobalt carbonyl complex might influence the performance of the catalyst.

Tertiary alkyl phosphines have a profound influence:

- the reaction is a hundred times slower,
- 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.

Catalyst:

$\text{HCoL}(\text{CO})_3$, L =



Temperature 150 -190°C

Pressure 40 – 80 bar

LHSV 0.2/h

Co concentration 0.5 -1.0 weight-% of the feed

max. n/i-ratio 8:1

Order of activity (195 °C, 36 bar):



The linear : branched ratio:



High-pressure in-situ NMR spectroscopy have been reported about reactions of carbon monoxide with cobalt complexes of the type, $[\text{Co}(\text{CO})_3\text{L}]_2$.

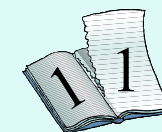
For $\text{L}=\text{P}(n\text{-C}_4\text{H}_9)_3$, high pressures of carbon monoxide cause CO addition and disproportionation of the catalyst to produce a catalytically inactive cobalt(I) salt with the composition $[\text{Co}(\text{CO})_3\text{L}_2]^+[\text{Co}(\text{CO})_4]^-$. Salt formation is favored by polar solvents

Main difference:

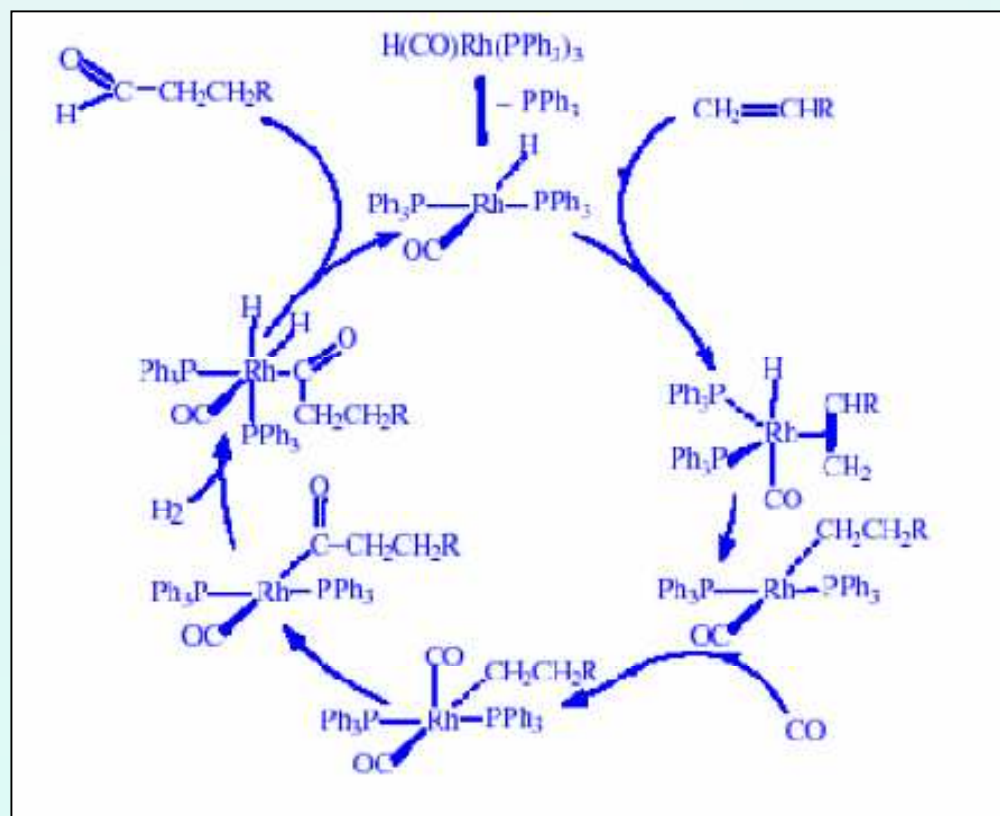
up to 80% alcohols (high hydrogenation activity)

H_2/CO ratio $\geq 2:1$

2nd generation of hydroformylation catalysts



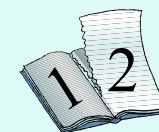
- Change from Co to Rh as catalyst
- 1974: Celanese builds the first plant in Bishop, Texas with ligand modified Rh-catalysts
- LPO (low-pressure oxo) introduced



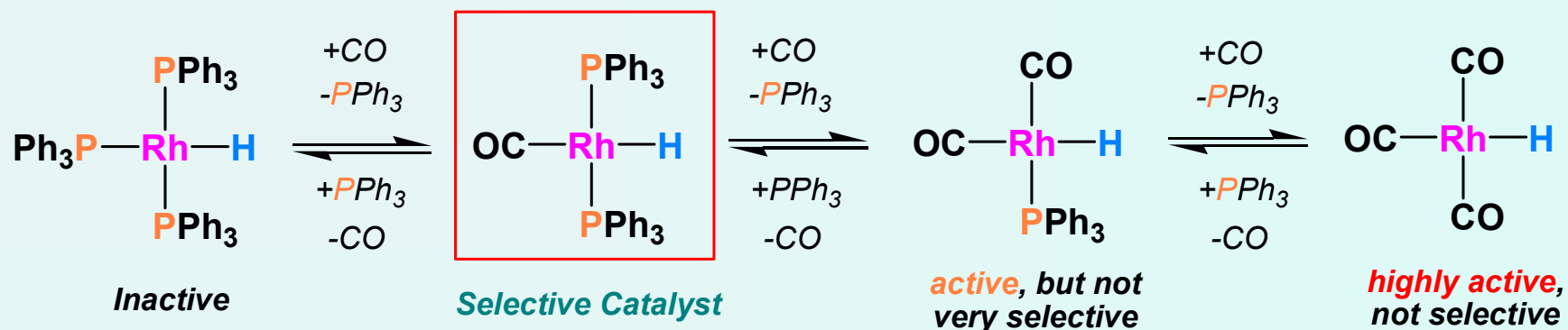
Elementary steps:

1. Dissociation of CO
2. Association of the olefine $\text{RHC}=\text{CH}_2$
3. Formation of the alkyl Co carbonyl complex
4. Association of CO
5. Insertion of CO
6. Oxidative addition of H_2
7. Reductive elimination of the aldehyde
8. Association of CO as regeneration of the $\text{HRh}(\text{CO})_2(\text{TPP})_2$

$\text{HRh}(\text{CO})(\text{PPh}_3)_3$ and $\text{Rh}(\text{acac})(\text{CO})_2$ – most widely used precatalysts



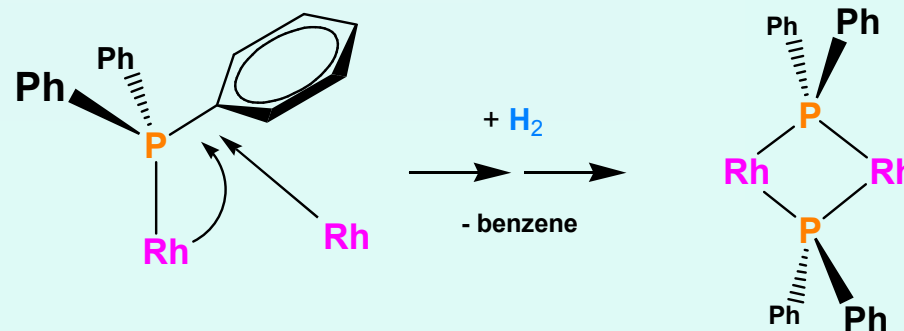
There is an interesting ratio between activity and selectivity of Rh catalysts with CO and PPh_3 ligands:



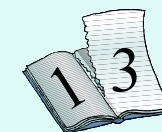
Reaction conditions: $T = 25 - 120^\circ\text{C}$, $P = 1 - 100$ atm

At low temperature selectivity is high ($n/i = 20$ at 25°C and 1 bar 1:1 H_2/CO), but the rate of the reaction is low. Increasing of temperature reduces selectivity ($n/i = 9$ at 50°C and 1 bar 1:1 H_2/CO)

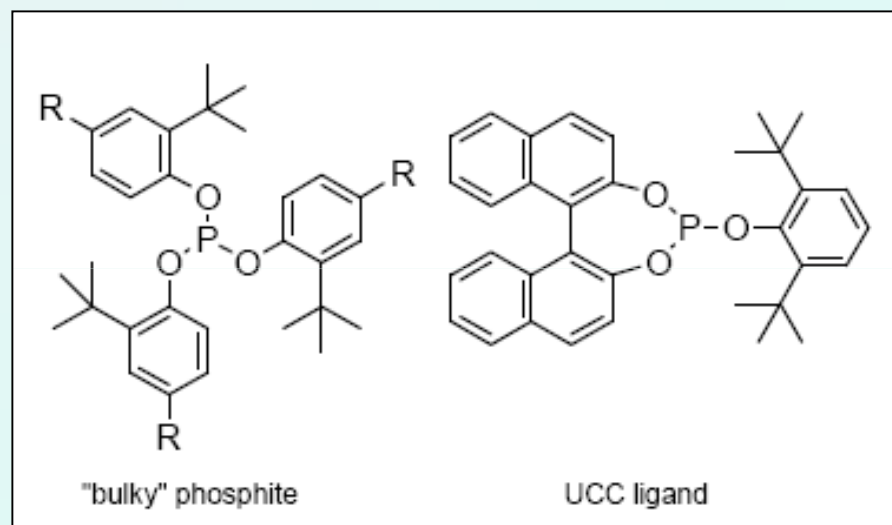
Important issue is catalyst's stability: usually large excess of PPh_3 is used (10 – 400)



While alkylphosphines are the ligands of choice for cobalt, they lead to slow reactions when applied in rhodium catalysis.

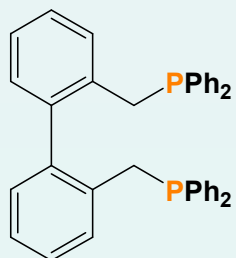
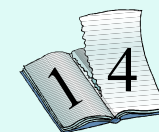


In the mid-60s the work of Wilkinson showed that **arylphosphines** should be used for rhodium and that even at mild conditions active catalysts can be obtained. The publications were soon followed by those of Prueett, in which **phosphites** were introduced:

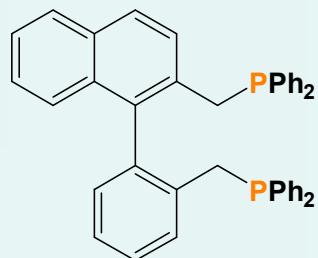


The first rhodium-catalysed, ligand-modified process came on stream in 1974 (Celanese) and more were to follow in 1976 (Union Carbide Corporation) and in 1978 (Mitsubishi Chemical Corporation), all using triphenylphosphine (tpp). The UCC (now Dow) process has been licensed to many other users and it is often referred to as the LPO process (Low Pressure Oxo process).

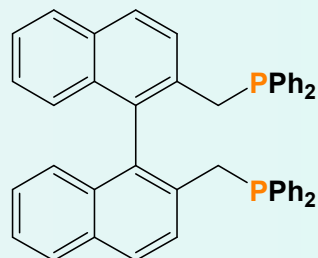
New Generation Rh Catalysts



Bisbi

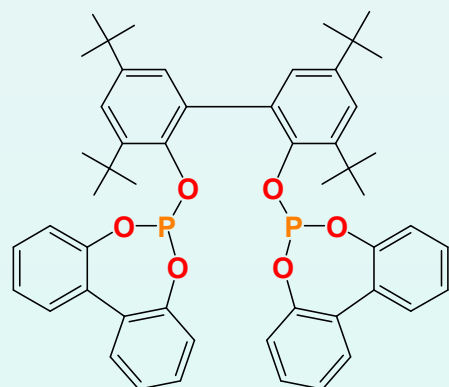


Bisbi*

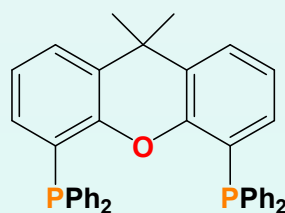


Naphos

If Rh/ PPh_3 catalysts give around an 8:1 ratio (n/i), Rh/bisphosphine complexes possess to reach 30:1 ratio



UC-44



Xantphos

If Rh/ PPh_3 ratio should be 1:400, (for the stability of catalytic system), Rh/bisphosphine ratio could be just 1:5

Catalyst (1 mM)	Init TOF (min^{-1})	Aldehyde n:i
Rh/ PPh_3 (1:400)	13	9:1
Rh/Bisbi (1:5)	25	70:1
Rh/Naphos (1:5)	27	120:1
Rh/Xantphos (1:5)	13	80:1

3rd generation of hydroformylation catalysts:

Ruhrchemie/Rhône-Poulenc process



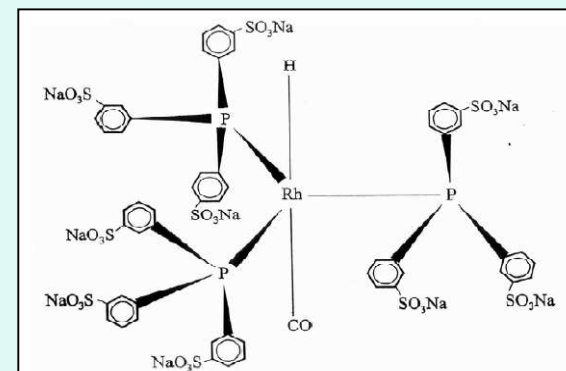
Two-phase variant

First plant in 1984 for *n*-butanals, 1995 extension for *n*-butene

Advantages:

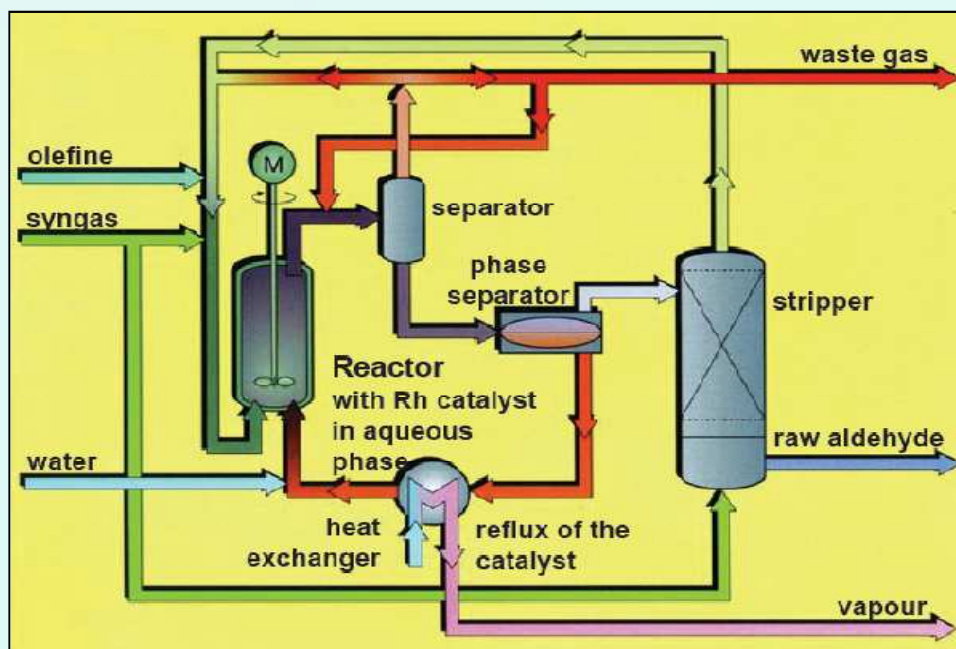
- simple catalyst cycle
- no side-reactions in the product processing

Catalyst: water soluble
Triphenylphosphine-
trisulfonate(TPPTS)



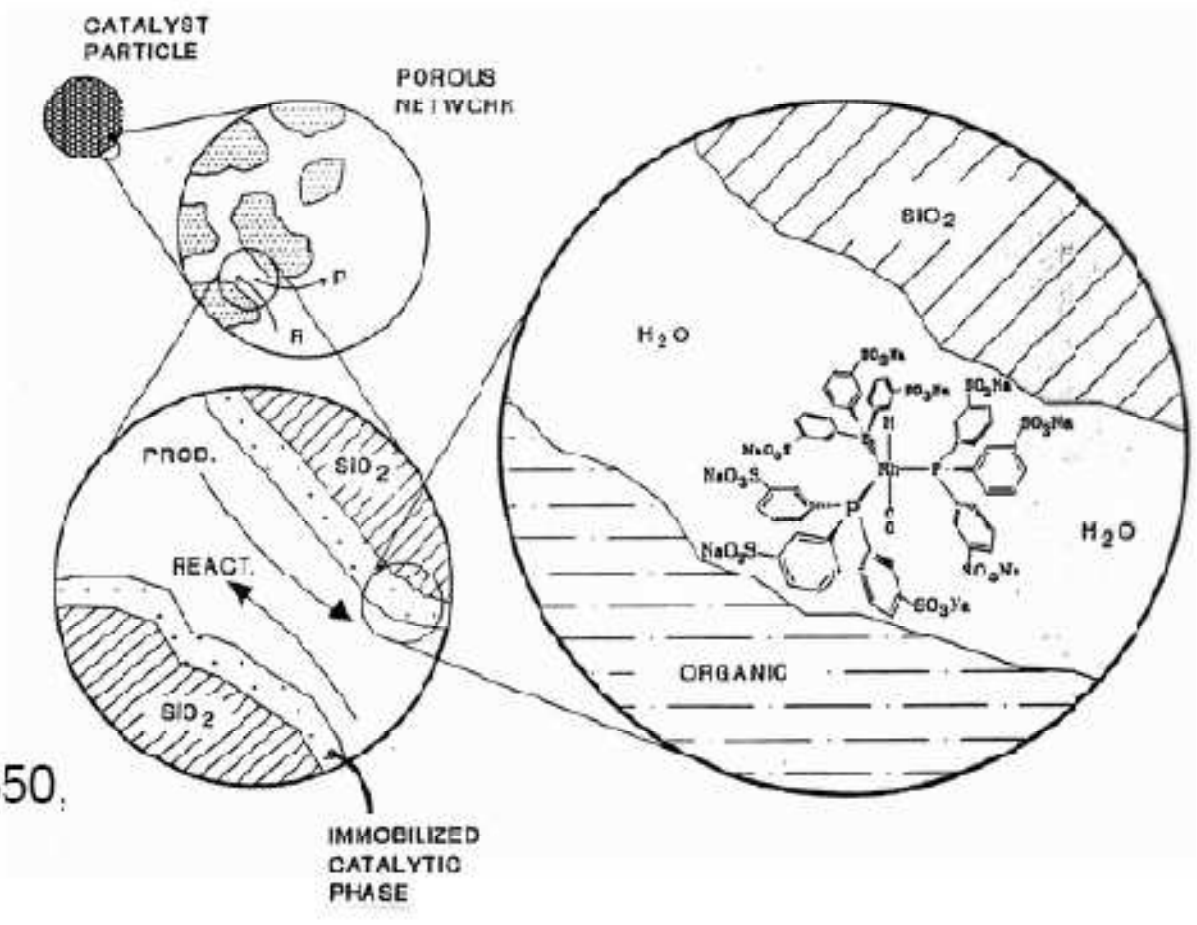
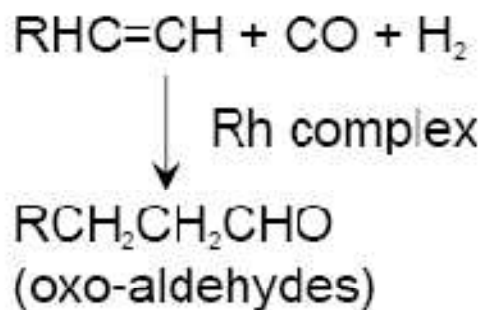
Equipment:

- 1.Continuous stirred tank
- 2.Phase separation
- 3.Heat exchanger
- 4.Stripper
- 5.Rectification
- 6.Raw product stream



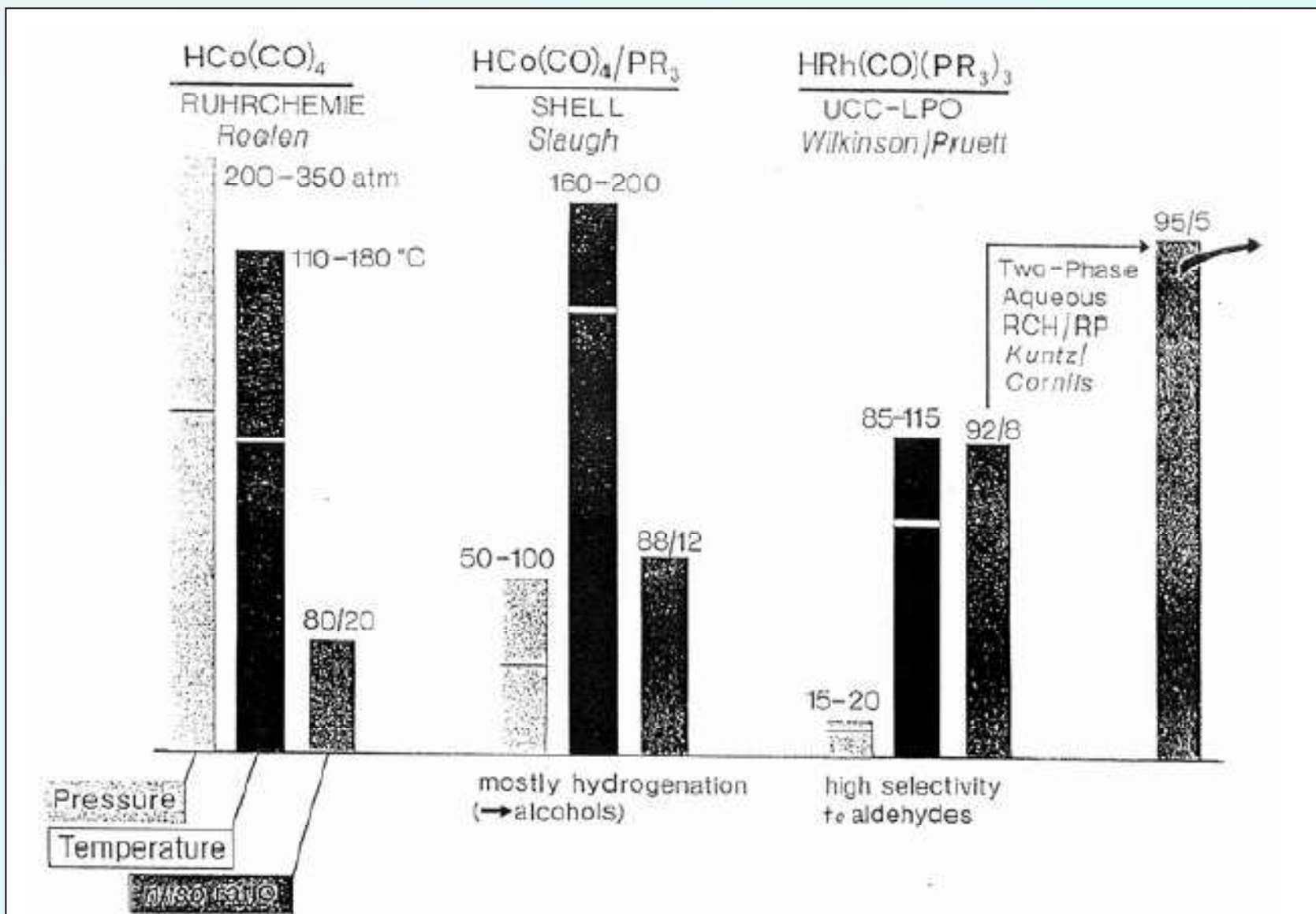
Hydrophilic support material for aqueous catalyst phases

Highly active, easily separable organo-metallic catalysts for hydroformulation



hydrophilised SiO₂, CPG-350,
pore size 34.3nm,
pore surface 0.97mL/g

Hydroformylation catalysis

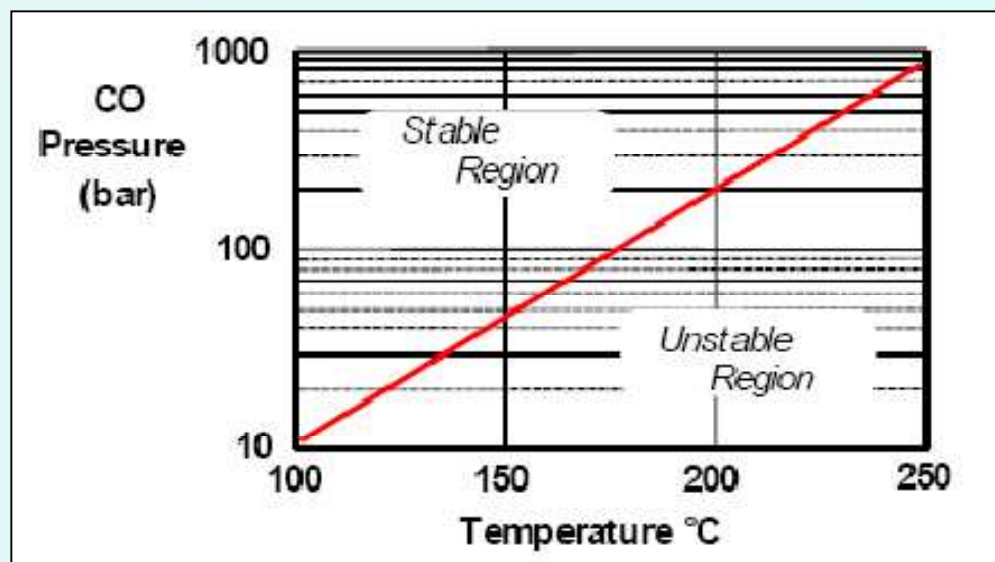


Typical data of performance of the most important catalyst systems for oxosynthesis:



catalyst characteristics	HCo(CO)_4	$\text{Co(CO)}_3\text{PR}_3$	$\text{HRh(CO)(PR}_3)_3$	
		$\text{R} = n\text{C}_4\text{H}_9$	$\text{R} = \text{C}_6\text{H}_5$	$\text{R} = m\text{-C}_6\text{H}_4\text{SO}_3\text{Na}$
p / bar	200 - 350	50 - 100	15 - 20	10 - 100
T / °C	10 - 180	160 - 200	85 - 115	50 - 130
n/iso ratio	80/20	88/12	92/8	
selectivity	low	middle	high	very high
hydrogenation activity	middle	high	low	low

The reaction conditions for HCo(CO)_4 hydroformylation are largely governed by the thermal instability of HCo(CO)_4 , which produces metallic cobalt if the CO partial pressure is not kept high enough.



Trends

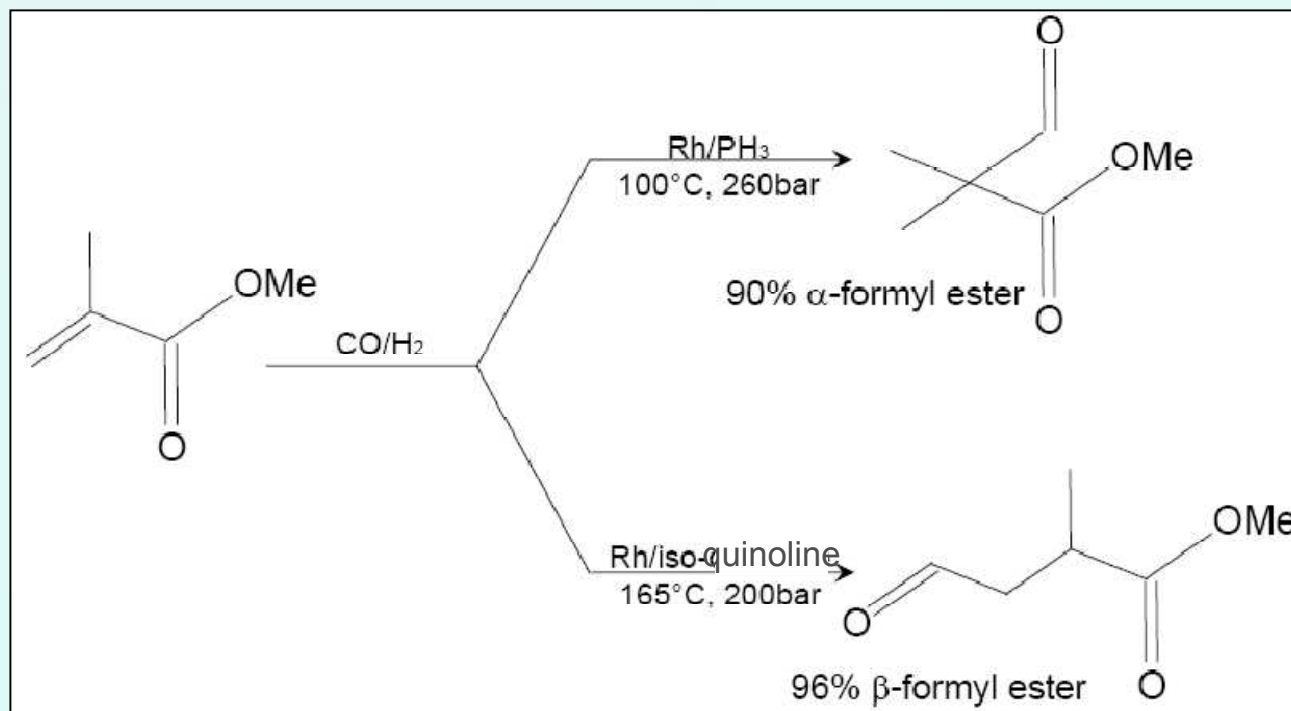


Developments mainly in two areas:

- Simplification of the process
- Higher propene turn-over

both can be achieved using improved ligands

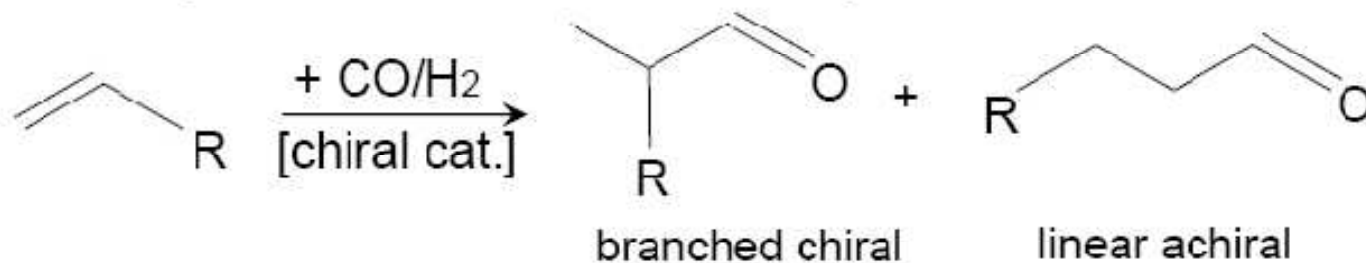
Influencing the regio-selectivity of the hydroformylation of methacrylic acid methyl ester



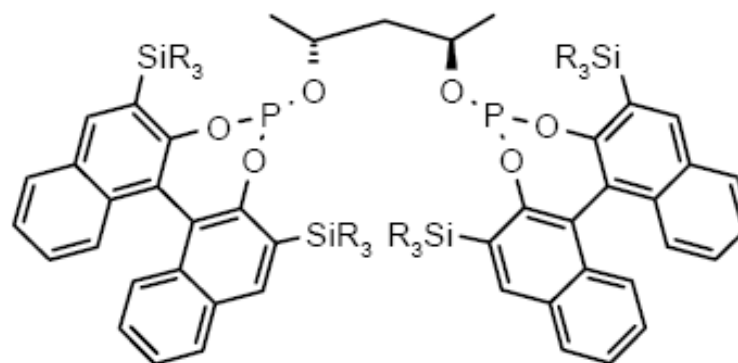
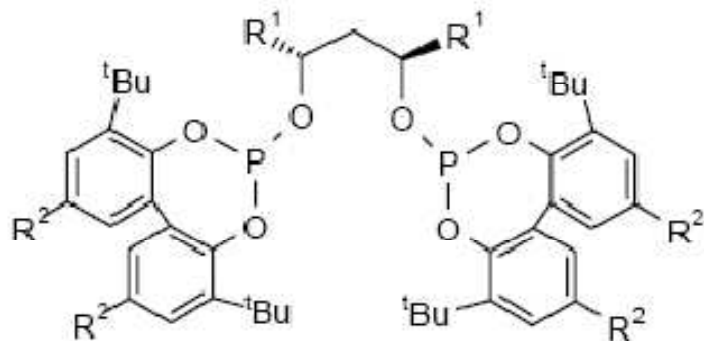
Asymmetric hydroformylation

20

- Synthesis of chiral precursors for pharmaceuticals and agrochemicals
- potential market for synthetic chiral molecules (start of 21st century)
- ⇒ 2 billion US\$
- desired product is the branched aldehyde with chiral C-atom



- chelate ligand

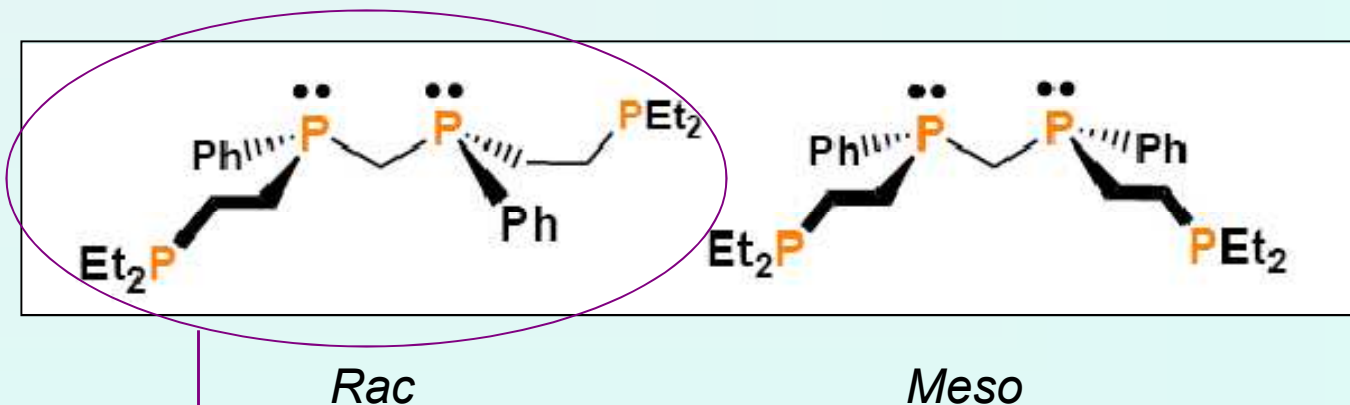


Bimetallic Hydroformylation



A unique bimetallic rhodium complex that provides a very strong example of bimetallic cooperativity in homogeneous catalysis has been reported by Stanley and coworkers (1993)

They designed a novel binucleating tetraphosphine ligand that can both bridge and chelate two transition metal centers, producing bimetallic complexes that only have a single, conformationally flexible bridging group.



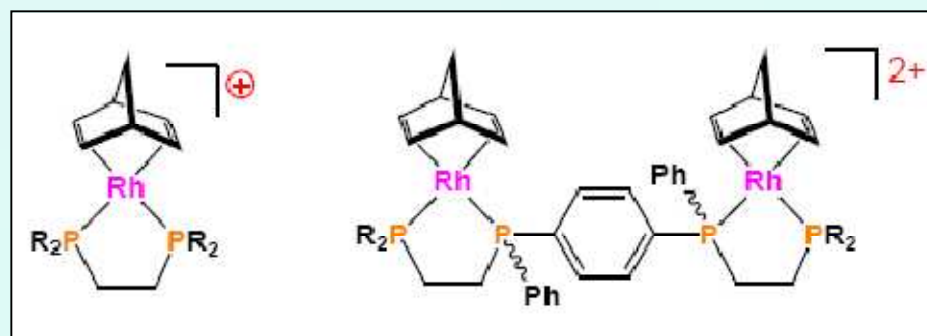
$[Rac-Rh_2(nbd)_2(P_4)](BF_4)_2$ (nbd = norbornadiene) is a catalyst precursor to a highly active and regioselective hydroformylation catalyst for 1-alkenes under mild conditions

A comparison between $[rac\text{-Rh}_2(\text{nbd})_2(\text{P}_4)](\text{BF}_4)_2$ and some of the best monometallic catalysts is shown in the table below (90°C, 6.2 bar 1:1 H_2/CO , 1000 eq. 1-hexene, acetone solvent).

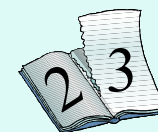
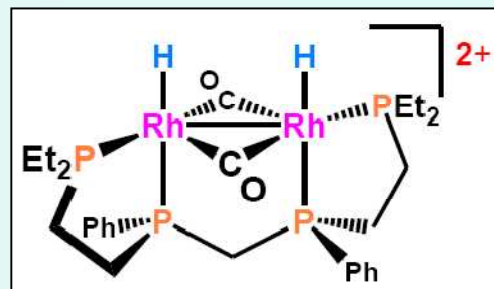
It was also discovered that adding 30% water to the acetone solvent dramatically reduces catalyst degradation rxns, increasing both the rate and selectivity

Catalyst (1 mM)	Init TOF (min^{-1})	Aldehyde L:B	% iso
$[rac\text{-Rh}_2\text{P}_4]^{2+}$	20(1)	25:1	2.5
$[rac\text{-Rh}_2\text{P}_4]^{2+}$ (30% H_2O)	30(1)	33:1	< 0.5
Rh/ PPh_3 (1:400)	13(1)	9:1	< 0.5
Rh/Bisbi (1:5)	25(2)	70:1	< 0.5
Rh/Naphos (1:5)	27(1)	120:1	1.5
Rh/Xantphos (1:5)	13(2)	80:1	5.0

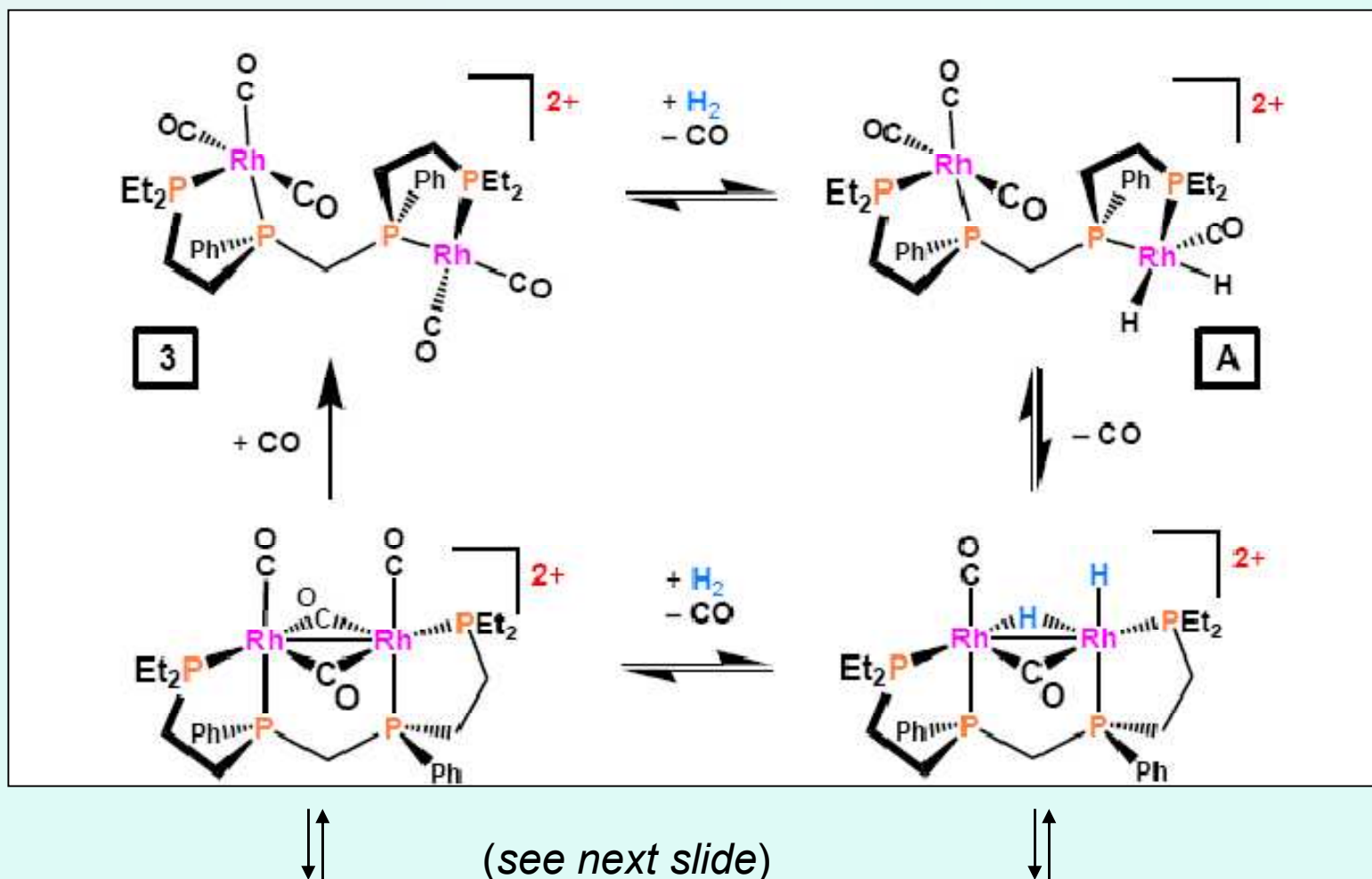
The hydroformylation activity of a series of monometallic complexes and spaced bimetallic complexes was very bad

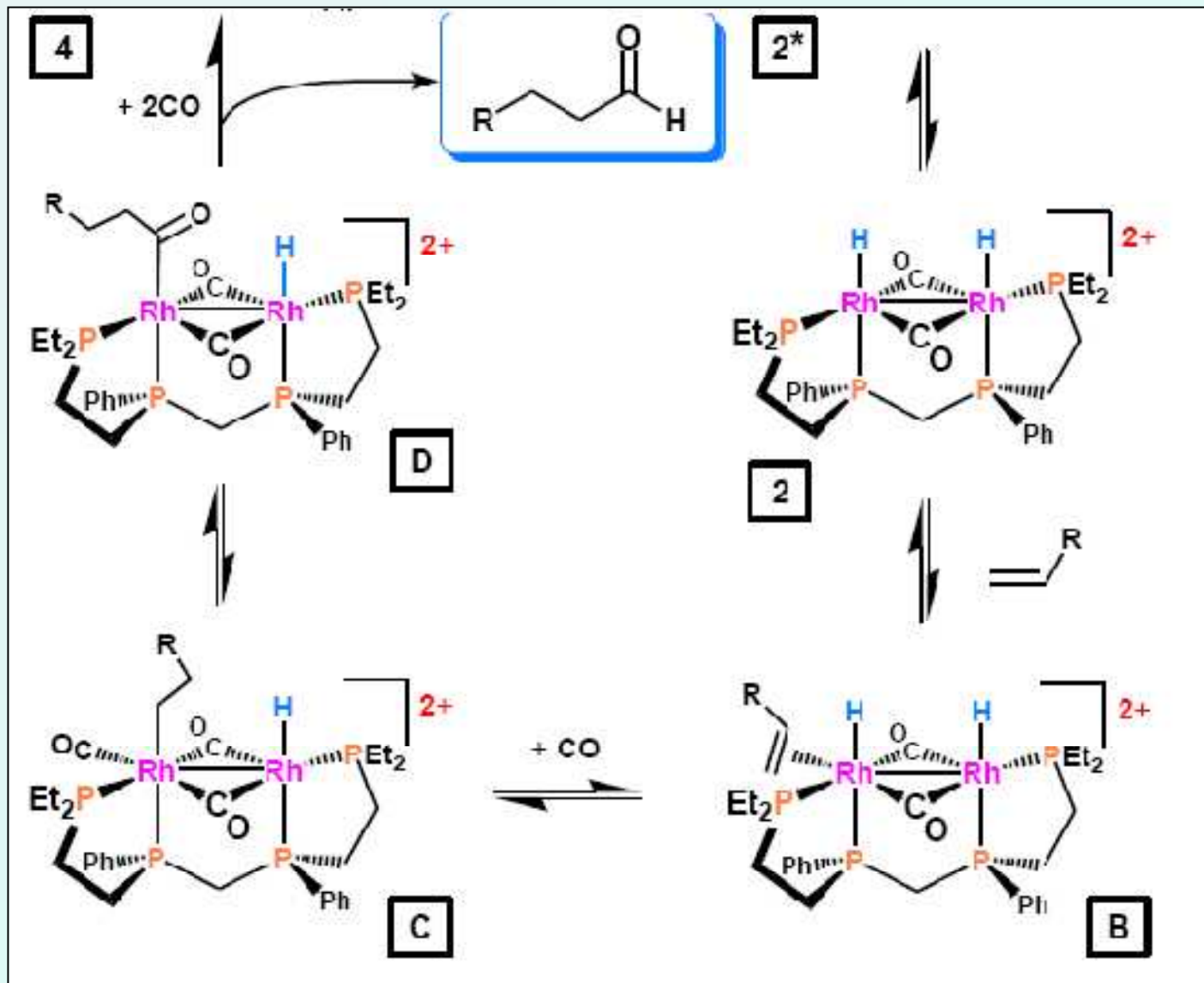


Proposed active dirhodium catalyst:



The proposed mechanism:

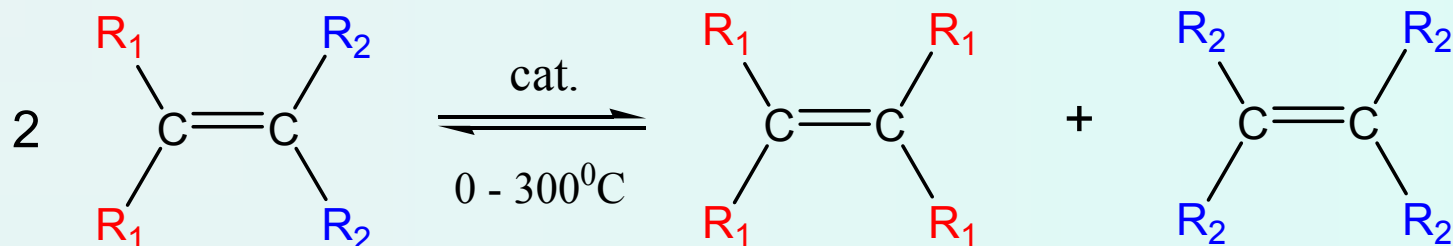




Olefin metathesis



1961, Banks and Bailey:



In 1964 this process was applied in industry

Note: whichever catalyst is used it can only bring the system to the equilibrium

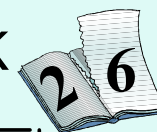
In the absence of steric hindrance the forthcoming (statistic) distribution should be 50% of $(R_1)_2C=C(R_2)_2$, 25% of $(R_1)_2C=C(R_1)_2$ and 25% $(R_2)_2C=C(R_2)_2$

Total number of bonds before and after the metathesis reaction does not change, so $\Delta S_{\text{reaction}} = 0$

$\Delta H_{\text{reaction}}$ is close to 0, but not equal to zero

That is why the equilibrium between the reagents and products is not controlled by statistic distribution

Equilibrium distribution of different olefins in metathesis reaction at 298 K

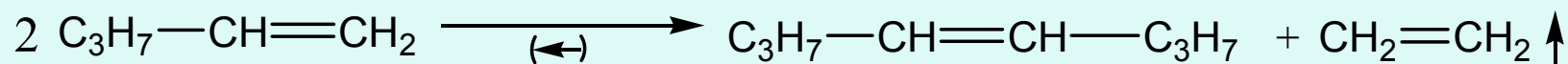


Substrate (S)	Product 1 (P1)	Product 2 (P2)	ΔH_r , kJ/mole	Distribution, %		
				S	P1	P2
$\text{CH}_3\text{-CH=CH-CH}_2\text{-CH}_3$	$\text{CH}_3\text{-CH=CH-CH}_3$	$\text{CH}_3\text{-CH}_2\text{-CH=CH-CH}_2\text{-CH}_3$	-0.58	48	26	26
$\text{CH}_3\text{-CH}_2\text{-CH=CH}_2$	$\text{CH}_2\text{=CH}_2$	$\text{CH}_3\text{-CH}_2\text{-CH=CH-CH}_2\text{-CH}_3$	1.07	53	23.5	23.5
$\text{CH}_3\text{-CH=CH}_2$	$\text{CH}_2\text{=CH}_2$	$\text{CH}_3\text{-CH=CH-CH}_3$	1.28	58	21	21
$\text{CH}_3\text{-C(CH}_3\text{)=CH-CH}_3$	$\text{CH}_3\text{-CH=CH-CH}_3$	$\text{CH}_3\text{-C(CH}_3\text{)=C(CH}_3\text{)-CH}_3$	10.39	85	7.5	7.5
$\text{CH}_3\text{-C(CH}_3\text{)=CH}_2$	$\text{CH}_2\text{=CH}_2$	$\text{CH}_3\text{-C(CH}_3\text{)=C(CH}_3\text{)-CH}_3$	19.53	97	1.5	1.5

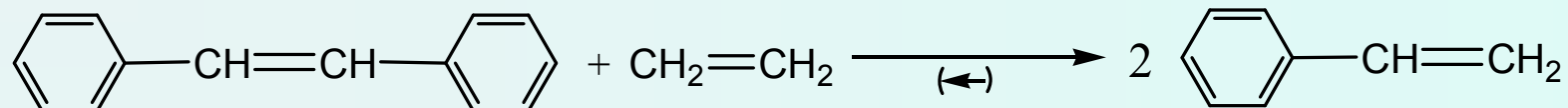
Is it possible to **shift the equilibrium**?

1) It is possible to change concentration of one or several substances

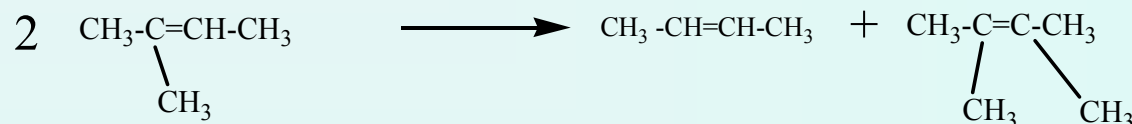
a) Ethylene formation:



b) Ethylene under pressure applies to the reaction:



2) It is possible to change the temperature (ΔH_r and ΔG_r depend on temp.)



T, K	ΔH_r , kJ/mole	Distribution, %		
		S	P1	P2
300	19.53	97.2	1.4	1.4
500	18.25	88.3	5.85	5.85
800	17.08	77.4	11.3	11.3
1000	16.94	72.5	13.75	13.75



So, different types of alkenes can undergo metathesis reaction:

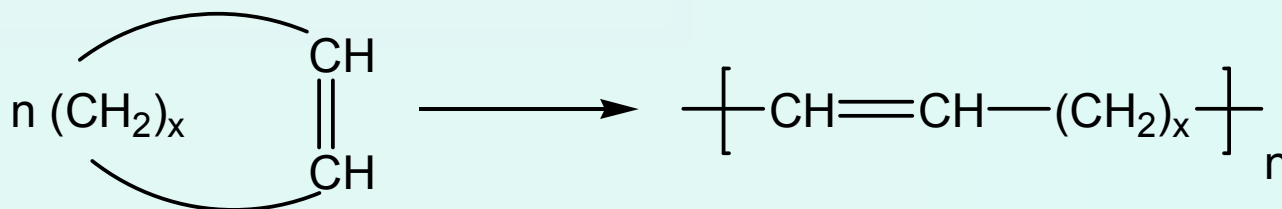
- Ethylene
- Terminal alkenes
- Internal alkenes
- Arylalkenes
- With 1 or 2 substituents at one or both ends of the double bond



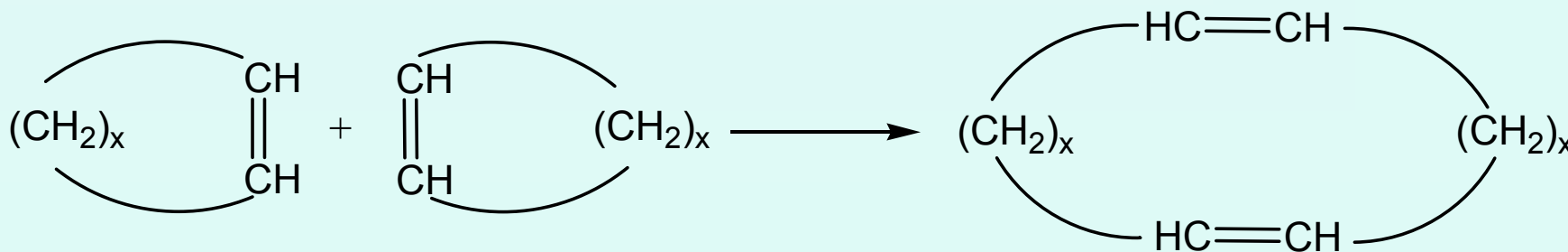
How about cycloalkenes?

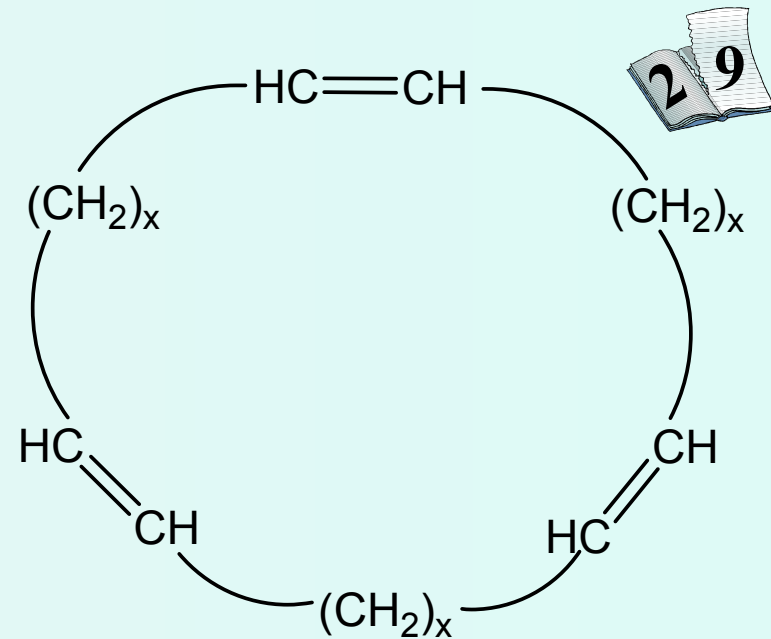
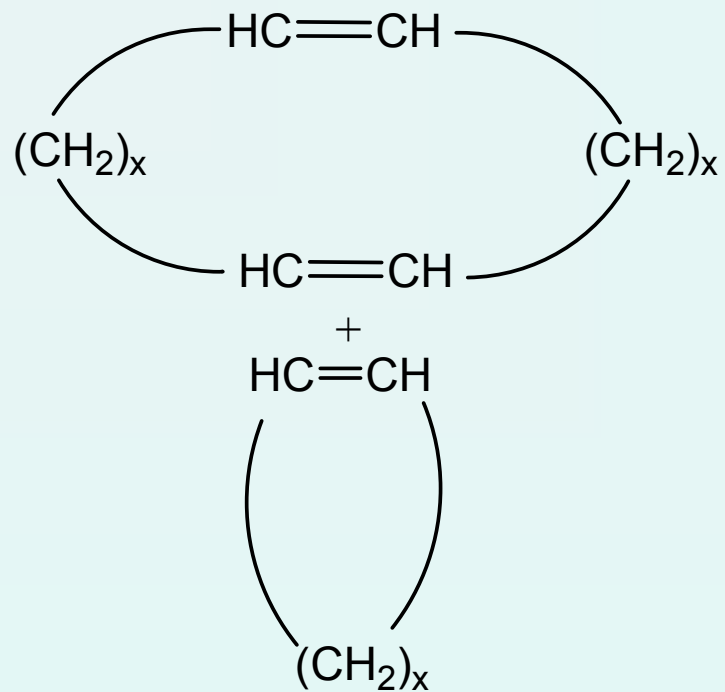
To main pathways:

1) Polymers formation

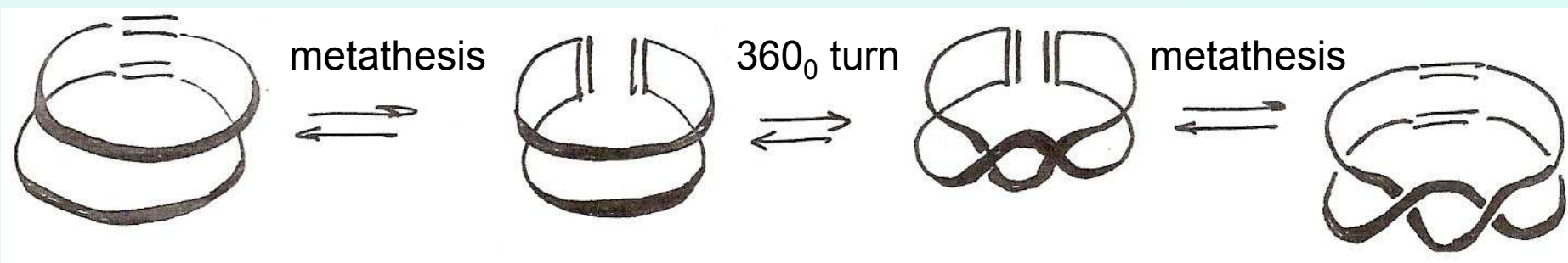


2) Formation of cyclic oligomers





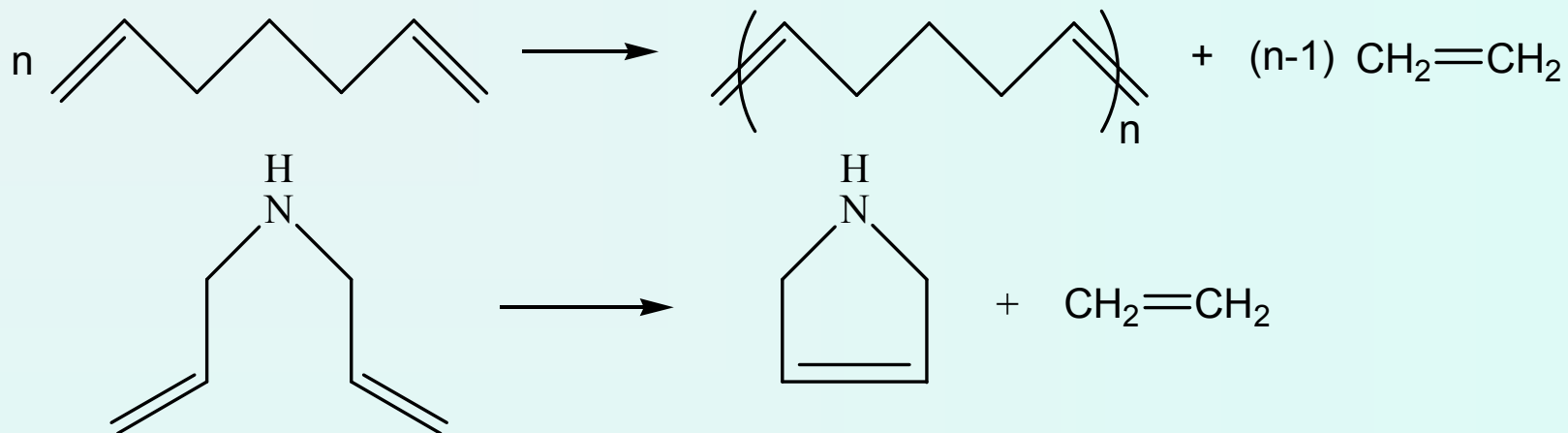
But the most interesting is metathesis of cycloalkenes with large cycle (e.g. C₁₂)



How about dienes?

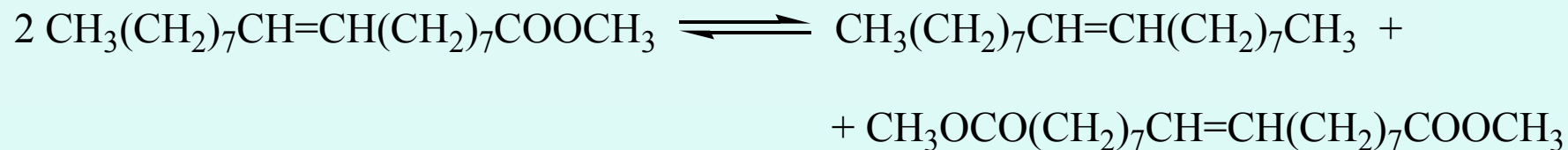


Dienes with terminal double bonds can form products of polycondensation or cycloalkenes:



How about functionalized alkenes?

Most metathesis catalysts are unstable in the presence of carboxylic acids and alcohols but sometimes it is possible to proceed a metathesis reaction:



Catalysts

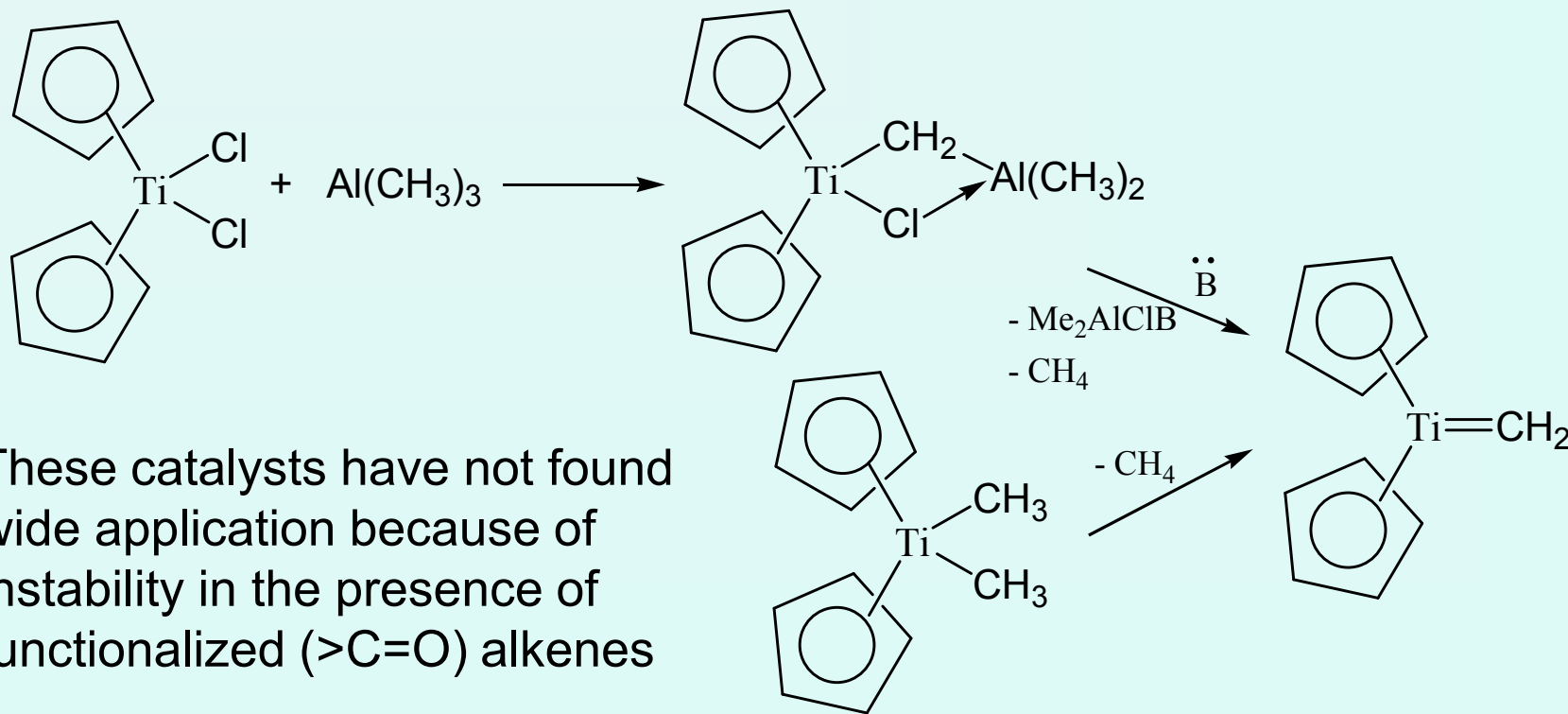


1. **Heterogeneous** catalysts consisted of **halogenides, oxides and oxyhalogens**. Usually co-catalysts, as zinc and aluminium alkyls are used:



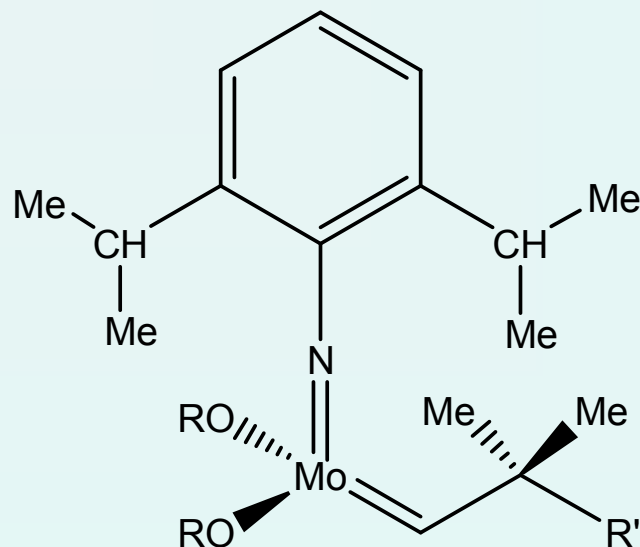
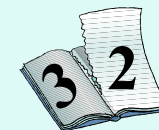
Most of this catalysts can be dissolved in benzene. But the question about whether these catalysts are homogeneous or heterogeneous is open. The nature of active centers of these catalysts is also not clear.

2. **Titanocene** catalysts. Starting materials are Cp_2TiCl_2 or $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$:

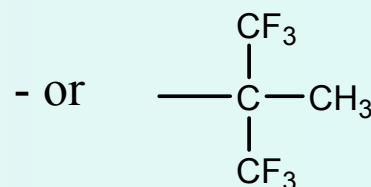
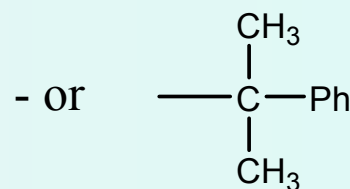
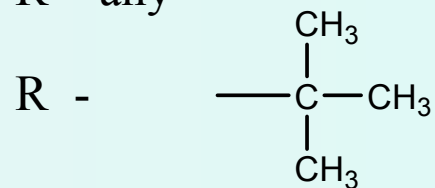


These catalysts have not found wide application because of instability in the presence of functionalized ($>\text{C}=\text{O}$) alkenes

3. Schrock's catalysts based on W, Mo and Re



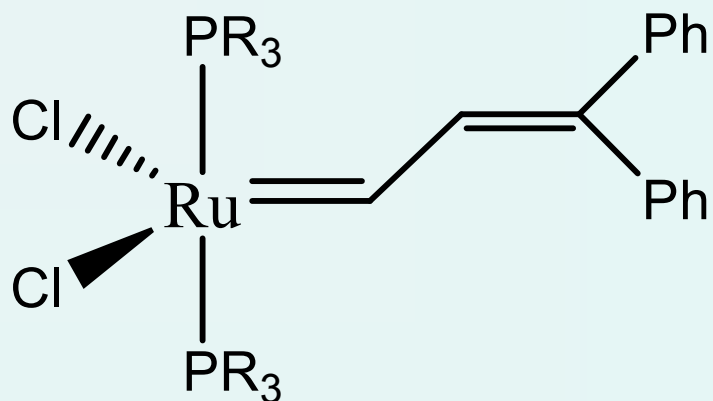
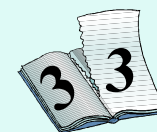
R' - any



This catalyst is very active: 1 mole of the catalyst transforms 1000 mole of cis-pentene-2 over 1 minute. This catalyst is stable in the presence of $>\text{C}=\text{O}$ groups in substrate but it is unstable in the presence of moisture and O_2

4. Grubb's catalysts based on Ru

Opposite to the above mentioned catalyst Grubb's catalysts do not comprise TM with high oxidation state and stabilized with phosphine ligands

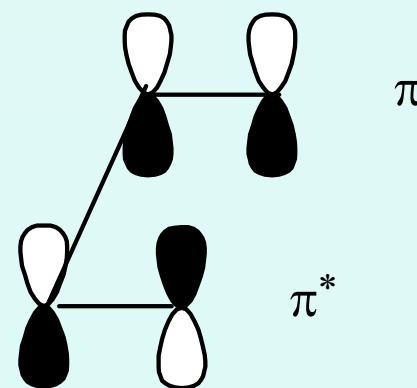
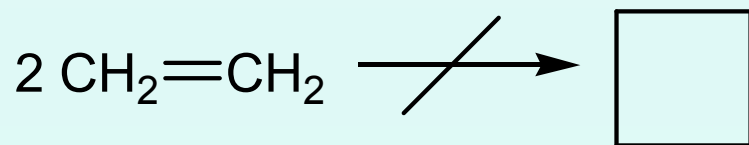


These catalysts are very stable in the presence of $>C=O$ groups and are active even in the presence of water. However, they are less active in compare to Scrock's catalysts

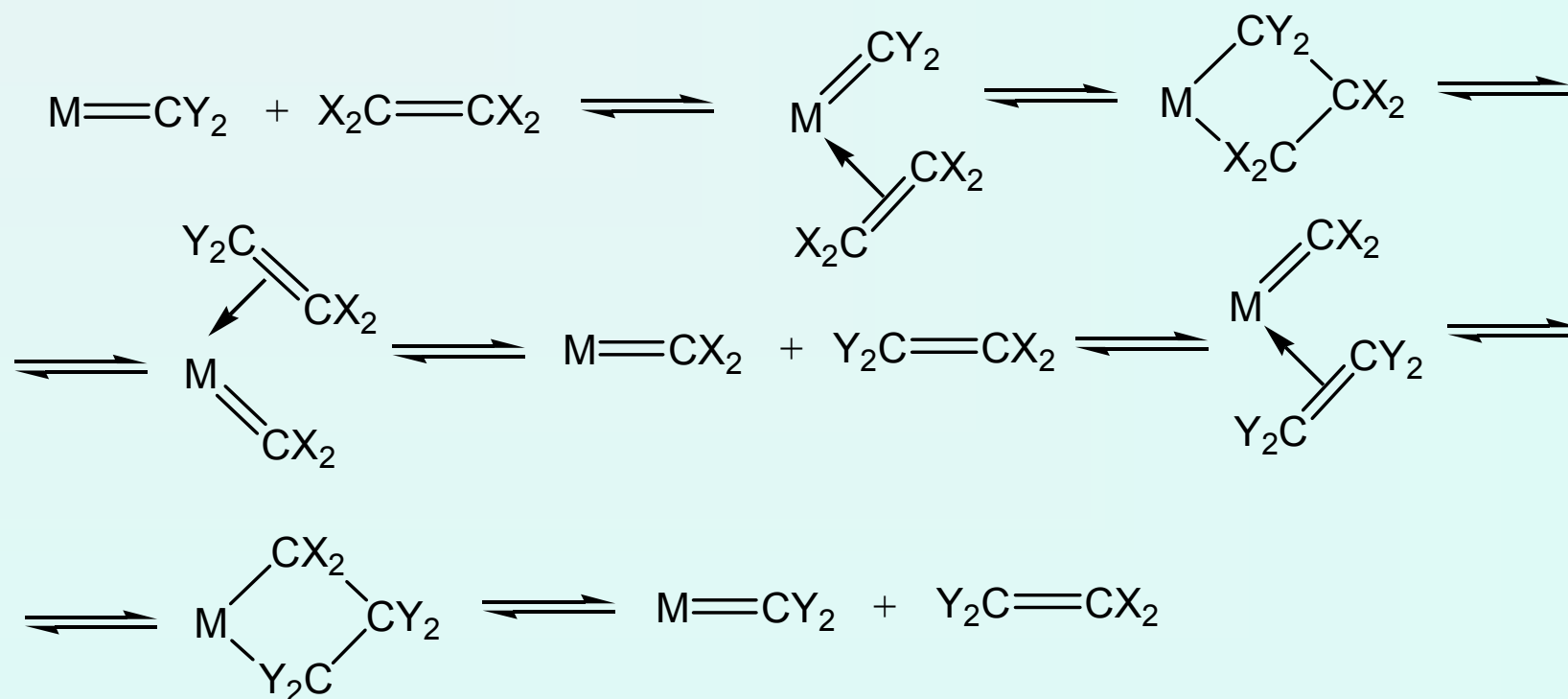
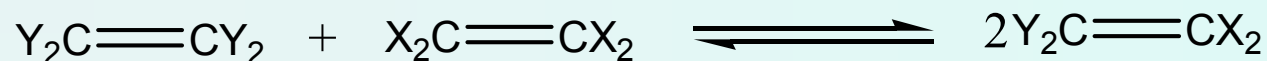
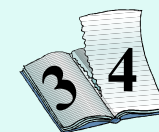
Reaction mechanism

Reaction takes place as [2+2] addition. Without catalyst the reaction does not take place because it is a ban on symmetry.

For example, heating of ethylene will never results in cyclobutane formation:



In the case of catalytic reaction carbene complexes helps to avoid this ban:



4-centered transition state is possible
now due to the metal d-orbitals

