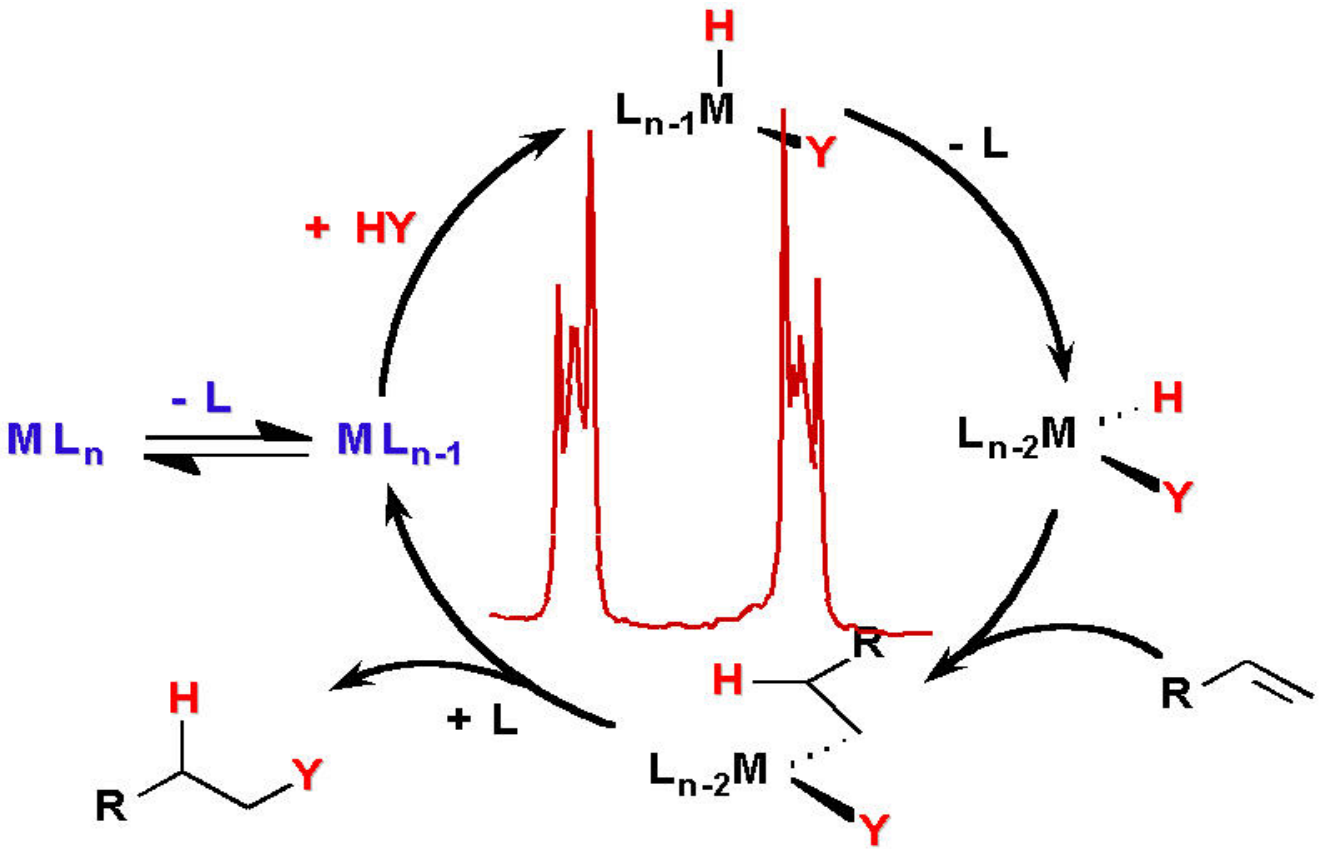
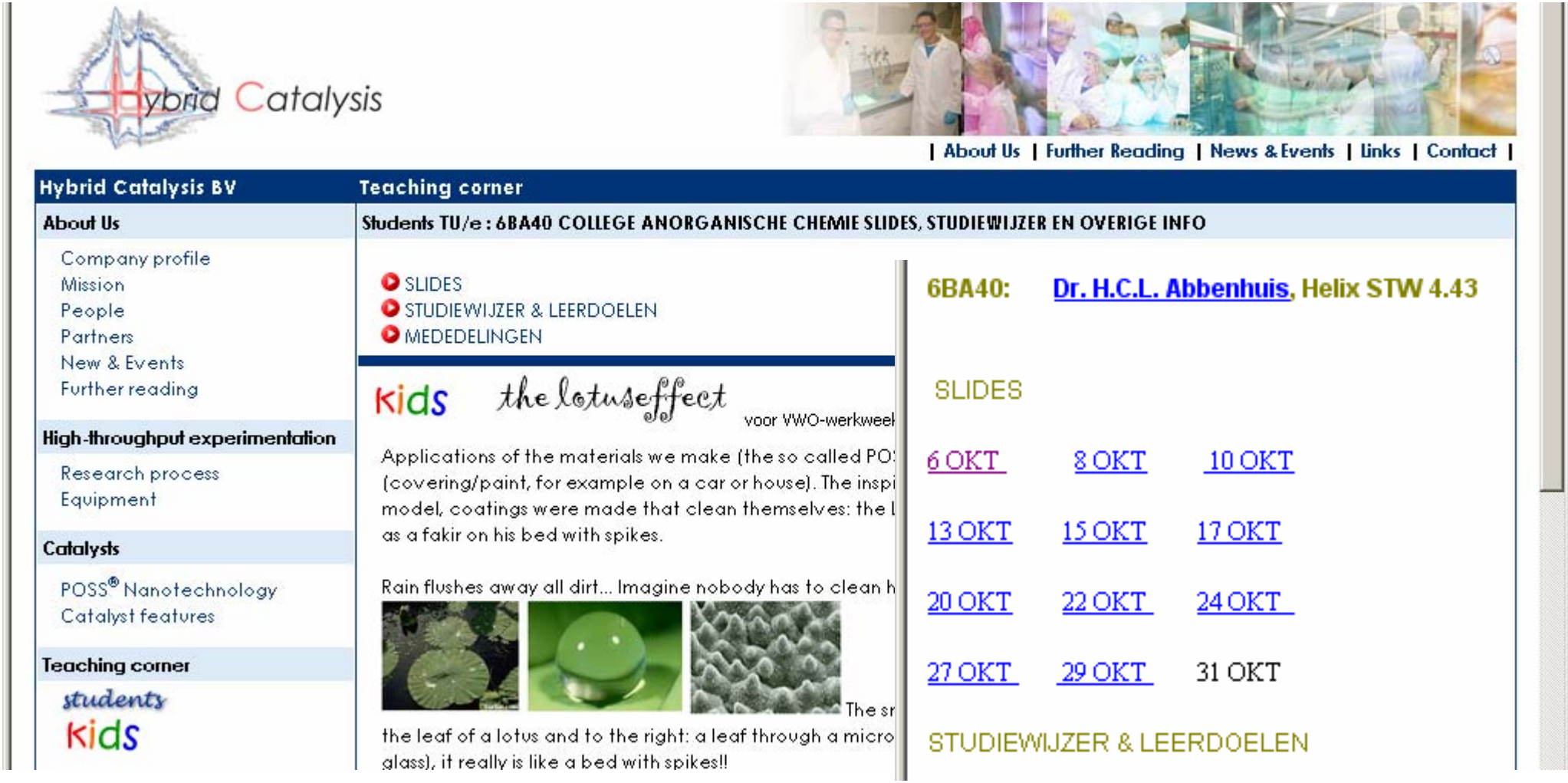
Inorganic Chemistry
6BA40



Catalysis
Ma, 03-11-2008, H27

Inorganic Chemistry 6BA40
Slides available:
http://www.hybridcatalysis.com/teachingcorner.htm



Gerealiseerde Leerdoelen

•de chemische binding van essentiële delen of van liganden in overgangsmetaal complexen en organometaalverbindingen beschrijven met behulp van kwalitatieve MO-diagrammen

•elektronenovergangen in overgangsmetaalcomplexen correleren met de eigenschappen van deze verbindingen

•de voornaamste reactiemechanismen in d-blok complexen weergeven

• voor d-blok organometaalverbindingen de basiseigenschappen en typerende chemische bindingen beschrijven

•kennis van chemische binding, reactie mechanismen en organometaalchemie

•eigenschappen van elementen en verbindingen daarvan aan de hand van de positie in het periodiek system uiteenzetten

•per d-blok metaal de meest optredende oxidatie toestanden noemen en typische verbindingen met hun reactiviteit

Nog te leren…

•Kennis toepassen op gecompliceerde (homogeen) katalytische systemen

Wetenschappelijke houding, het denken in overkoepelende termen, loslaten van het `hokjes denken', herkennen van de onderliggende principes

Inorganic Chemistry 6BA40
Leerdoelen

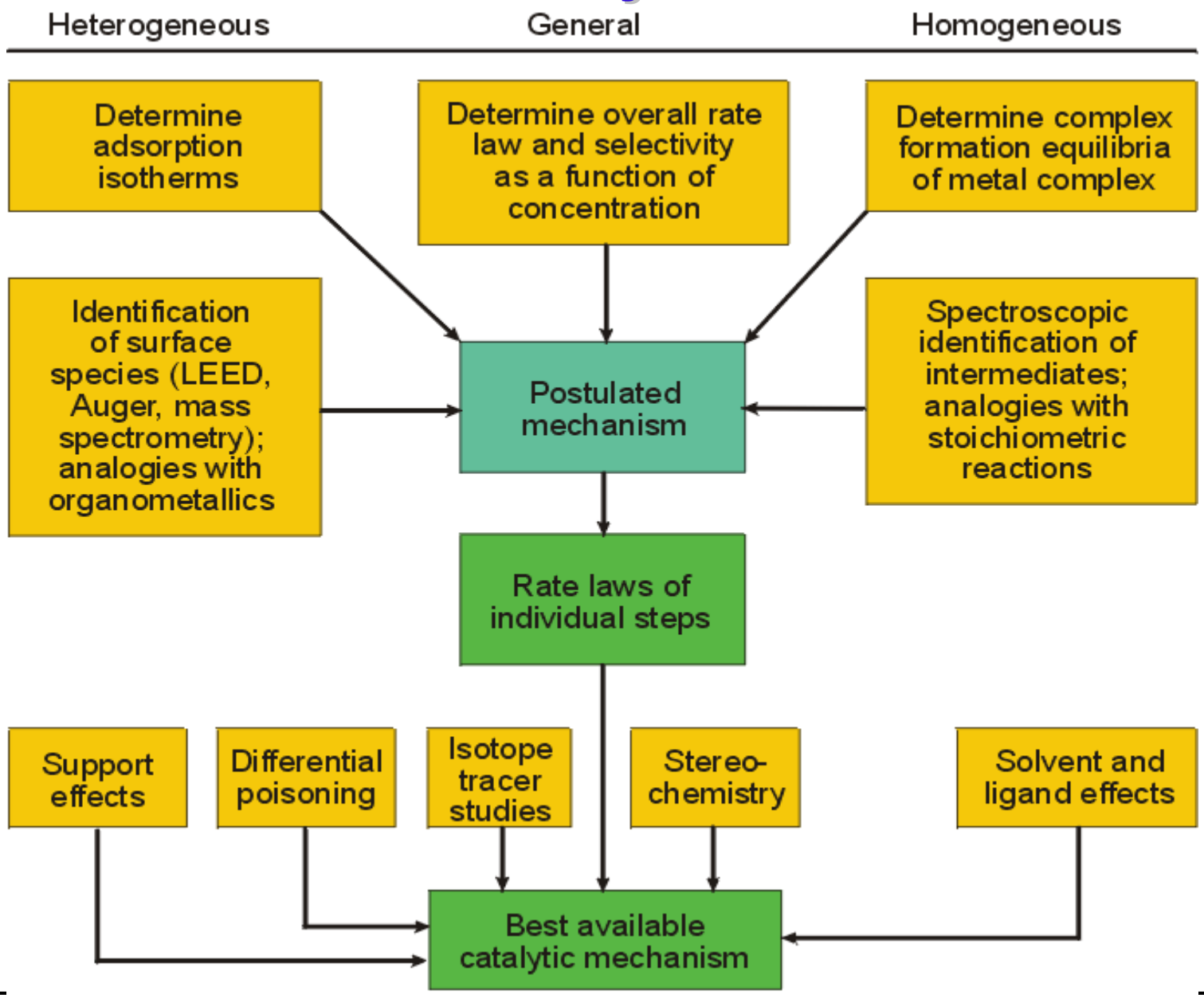
http://www.hybridcatalysis.com/teachingcorner.htm

- d-Metaal complexen, moleculaire vormen en isomerie, kristalveld- en Molecular Orbital Theorie (hoofdstuk 1.6-1.8; 2.8-9; 20, 21)
- Elektronen overgangen, magnetische eigenschappen en spectra in verbindingen van overgangsmetalen (hoofdstuk 21)
- Reactiemechanismen en kinetische aspecten (hoofdstuk 26)
- Organometaal verbindingen van de s-en p-blok elementen (hoofdstuk 19 / college slides)
- Organometaal verbindingen en hun voornaamste reacties (hoofdstuk 24 / college slides)
- Homogene Katalyse, basis kennis (hoofdstuk 27.1-27.6)

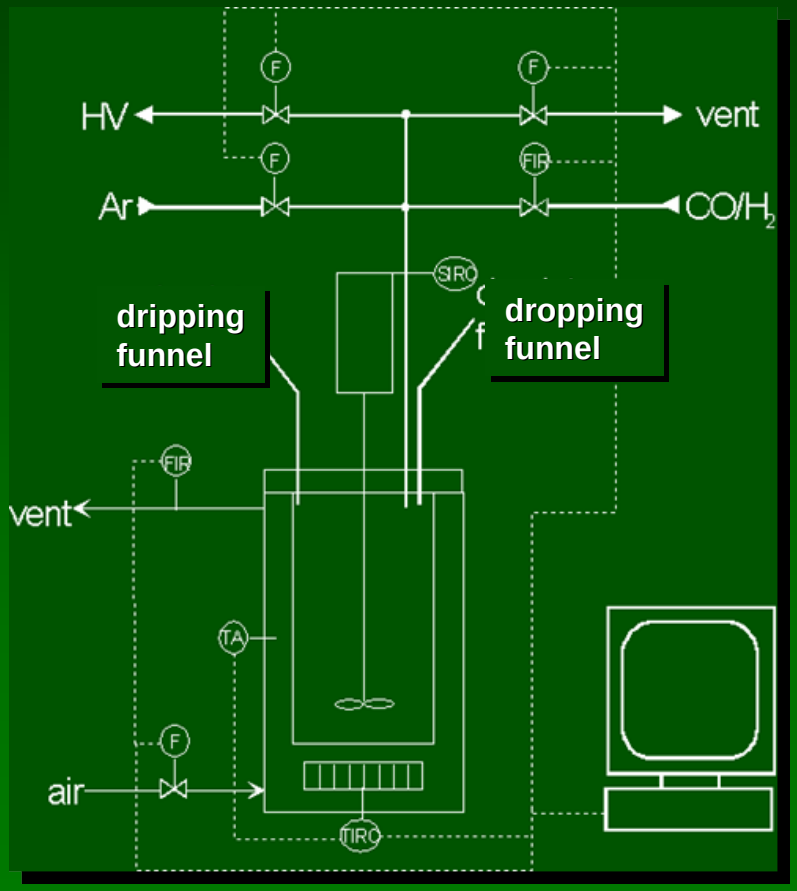
ZELFSTUDIE

- De eerste reeks overgangsmetalen (hoofdstuk 22)
- De tweede en derde reeks overgangsmetalen (hoofdstuk 23)

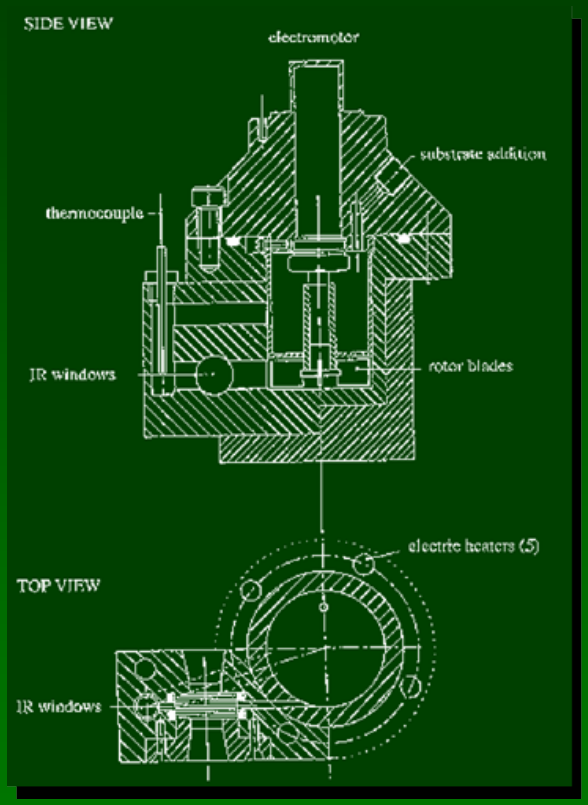
Catalysis

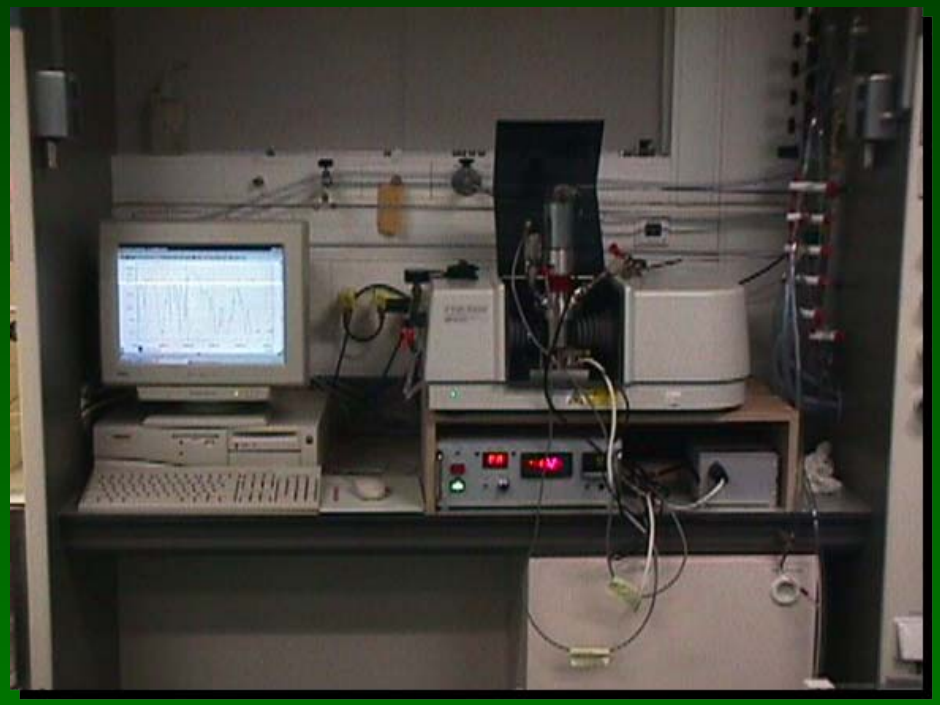

Heterogeneous
General
Homogeneous
Determine adsorption isotherms
Determine overall rate law and selectivity as a function of concentration
Determine complex formation equilibria of metal complex
Identification of surface species (LEED, Auger, mass spectrometry); analogies with organometallics
Postulated mechanism
Spectroscopic identification of intermediates; analogies with stoichiometric reactions
Rate laws of individual steps
Support effects
Differential poisoning
Isotope tracer studies
Stereo-chemistry
Solvent and ligand effects
Best available catalytic mechanism

Kinetics of Hydroformylation Reactions
Automated Autoclaves



High Pressure IR-Autoclave with Dedicated FT-IR Spectrometer





HP-IR autoclave

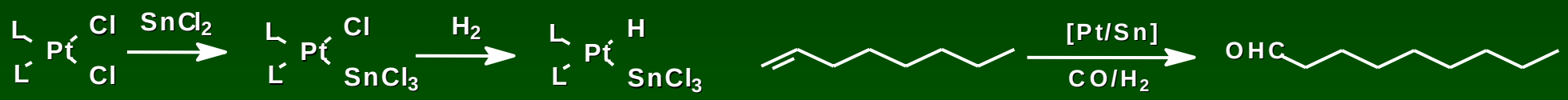
V = 55 ml ; V(side loop) = 0.6 ml ; p_{max} = 85 bar
T_{max} = 150°C ; stirring: 0 – 3000 rpm (800 rpm)
liquid velocity: 4-12 ml s^{-1} (max stirring)
IR windows: ZnS ø 10 mm ; d = 0.4mm

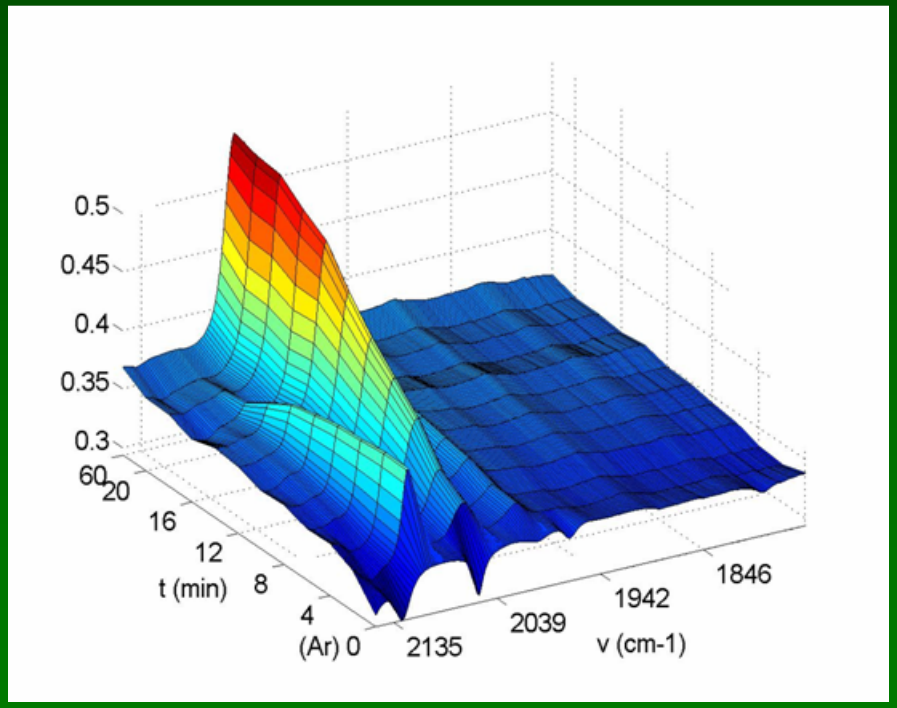
Fourier Transform IR (FTIR)

Shimadzu FT-IR 8300 ; 7800 cm^{-1} to 350 cm^{-1}
Resolution: 1, 2, 4, 8 and 16 cm^{-1}
Scanning speed: at 4 cm-1 from 2.0 s to 0.3 s
Beam: He-Ne laser ; Michelson interferometer

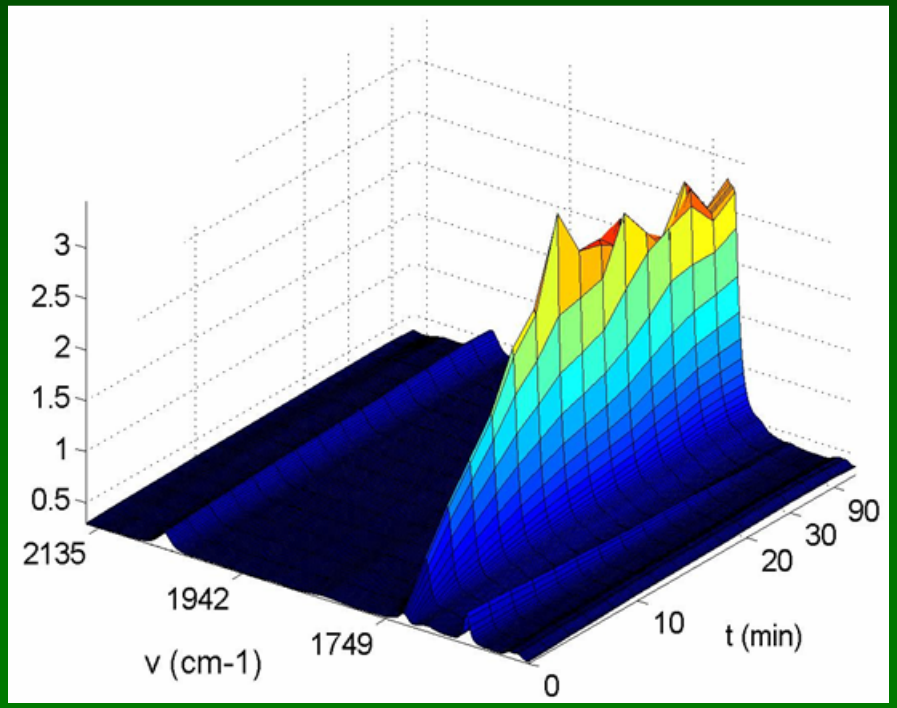
Mechanistic Investigations

- **Example for the use of high-pressure in situ IR in Pt/Sn catalyzed hydroformylation**





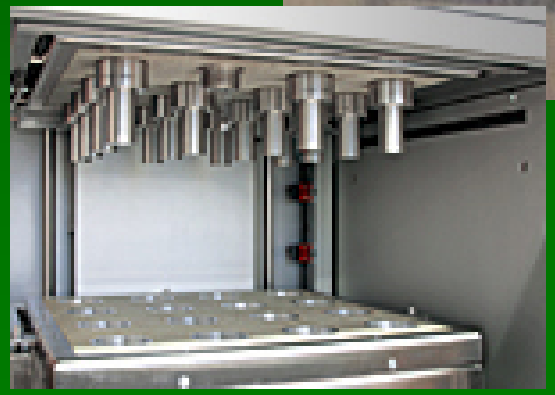
- Preformation of catalyst precursor



- Production of nonanal

R. v. Duren, 2002.

AMTEC Automated 16-Reactor System



- 15 ml reactors (stainless steel 316L)
- $p_{(max)}$ = 150 bar
- T(max) = 250˚C
- controlled stirrer speed 0-2000 rpm
- individual heating & pressure for each reactor
- liquid sampling, gas uptake measurement

Catalyst Characteristics

- **Turnover frequency**

  for a reaction $A + B \xrightarrow{[cat]} C$; $\nu = \frac{d[C]}{dt}$

  the turnover frequency *N* is defined as $N = \frac{\nu}{[cat]}$

- **Total turnover number and catalyst life-time**

  The total turnover number is the amount of product (mol) that can be formed by a certain amount of catalyst (mol) during it's life time.

- **Selectivity**

  The Selectivity of a catalyst is a measure for it's efficiency with which it distinguishes between different possible reaction pathways.

$$S = \frac{\text{yield desired product}}{\text{total conversion}}$$

Comparison of Catalytic Principles

Advantages and disadvantages of heterogeneous, homogeneous, and bio catalysis

	heterogeneous	homogeneous	biocatalysis
Conditions	generally harsh	mild	mild
Activity	changing	high	i.g. very high
Selectivity	changing	high	i.g. very high
Catalyst life-time	high	changing	i.g. low
Catalyst recycling	solved	expensive	expensive
Sensitivity agains poisons	high	low	high
Diffusion problems	possible	none	only whole cells
Mechanistic understanding	low	medium to good	medium

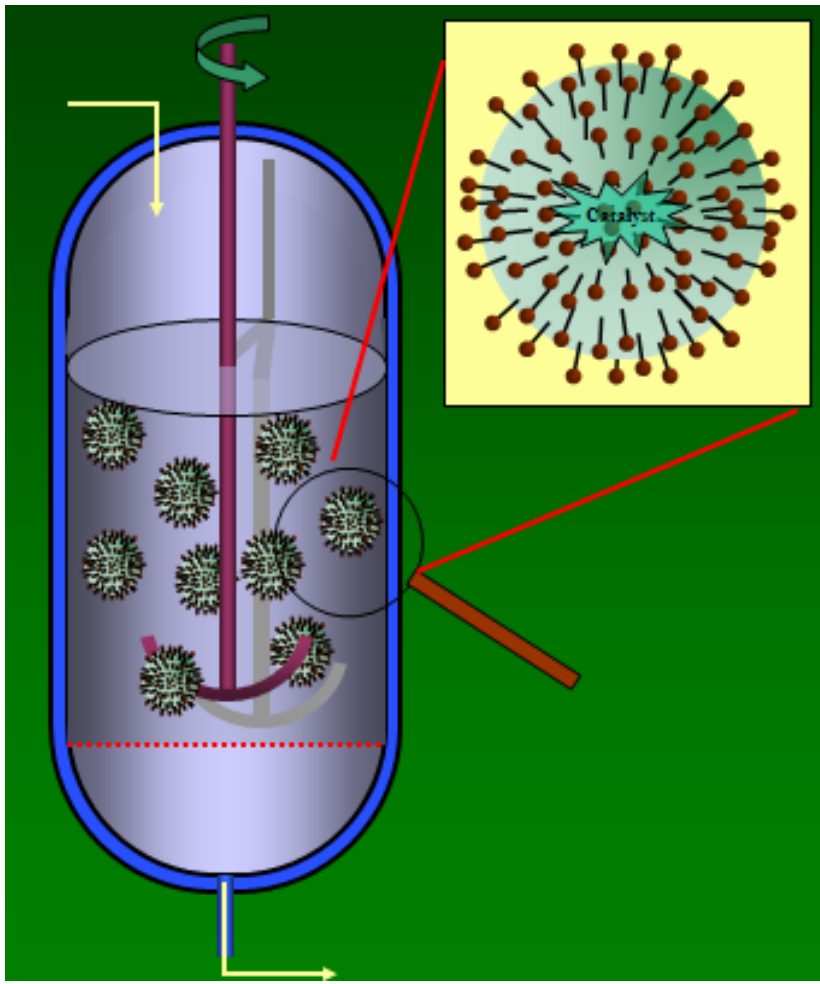
Homogeneous Catalysis

Homogeneous catalytic processes in industry

Process	Catalyst	Capacity / 1000 t/a
Hydroformylation	$HRh(CO)_n(PR_3)_m$	3690
	$HCo(CO)_n(PR_3)_m$	2445
Hydrocyanation (DuPont)	$Ni[P(OR_3)]_4$	~1000
Ethene-Oligomerization (SHOP)	Ni(P^O)-chelate complex	870
Acetic acid (Eastman Kodak)	$HRhI_2(CO)_2$ / HI / CH_3I	1200
Acetic acid anhydride (Tennessee-Eastman)	$HRhI_2(CO)_2$ / HI / CH_3I	227
Metolachlor (Novartis)	[Ir(ferrocenyldiphosphine]I / H_2SO_4	10
Citronellal (Takasago)	$[Rh(binap)(cod)]BF_4$	1,5
Indenoxide (Merck)	chiral Mn(salen)-complex	600 kg scale
Glycidol (ARCO, SIPSY)	$Ti(O^iPr)_4$ / diethyl tartrate	several tons

Integrated Catalysts

Nanoparticles for immobilization



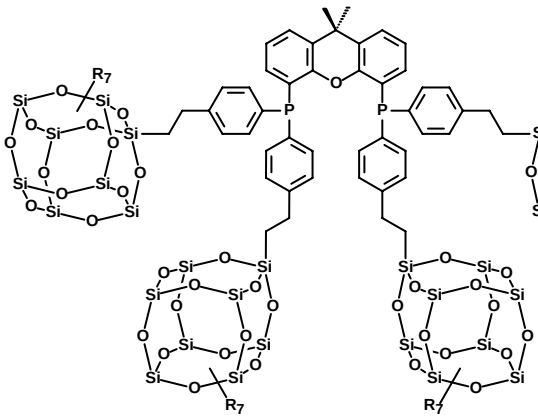
- Soluble or solubilized molecular particles
- Minimized diffusion limitations
- Dendrimers without functional groups for better metal compatibility
- Efficient recycling of expensive ligands

- Application of membrane technology
- Combination with multi-phase catalysis

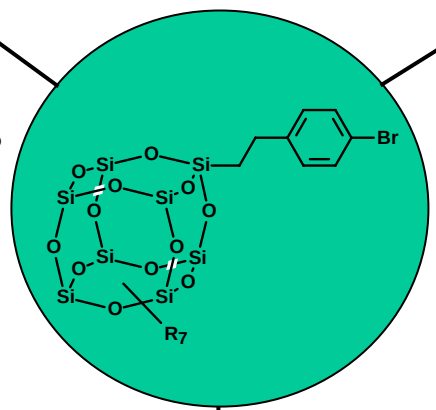
Nanoparticles

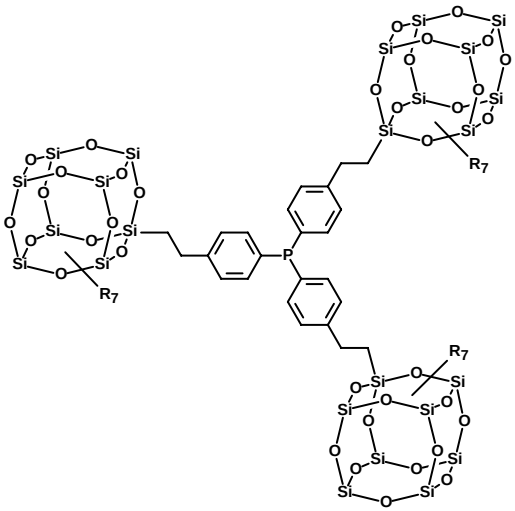
www.catalysis.nl

Molecular weight enlarged ligands

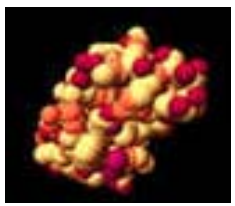


Xantphos-Derivative

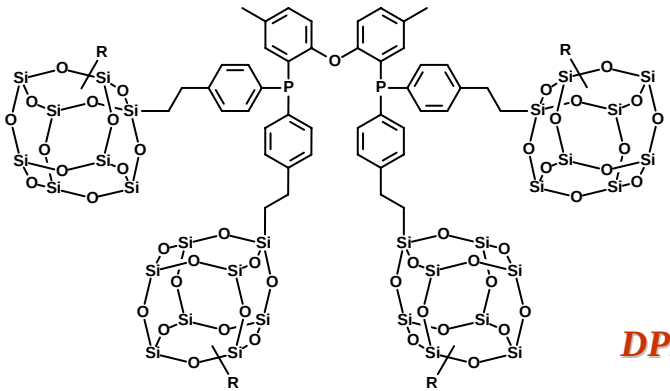




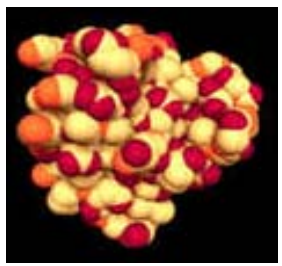
Triphenylphosphine-Derivative



Insulin 3 nm



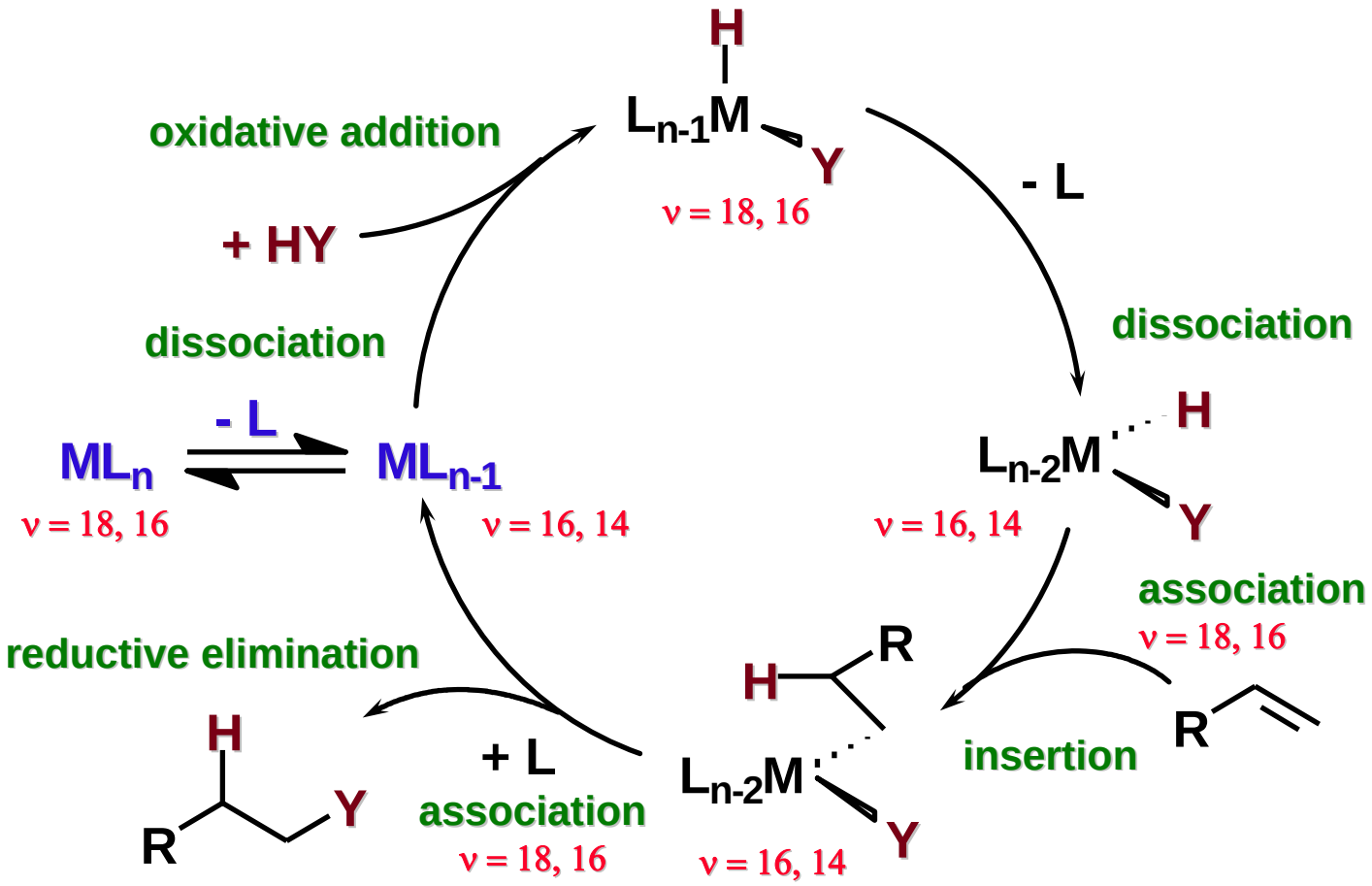
DPEphos-Derivative



cytochrome 4 nm

C. Muller, TU/e

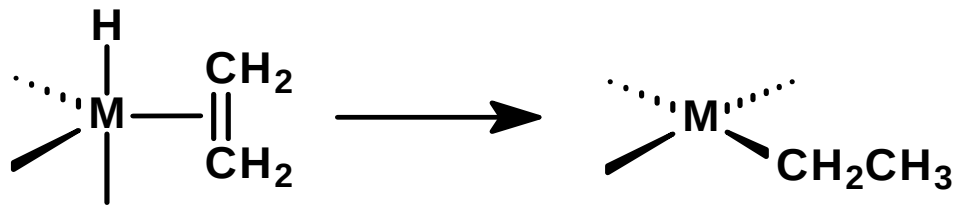
Catalytic Cycle and Elementary Steps



- Most elementary steps have been discussed in chapter 24 (reaction mechanisms)

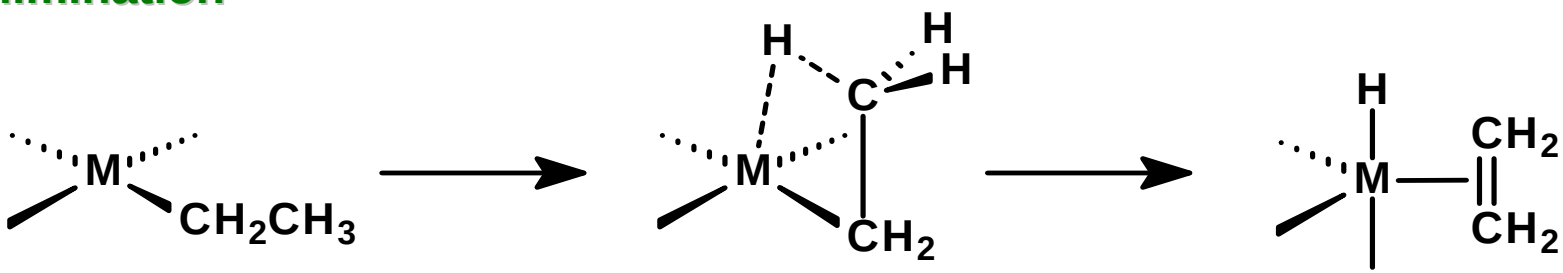
Homogeneous Catalysis
Elementary Steps

- **Migratory insertion**



alkene complex **metal alkyl complex**

- **β-Elimination**



➔ **β-Hydrogen is abstracted via a cyclic 4-membered transition state**

Homogeneous Hydrogenation

- **Wilkinson's catalyst 1965 $RhCl(PPh_3)_3$**

  1st homogeneous hydrogenation catalyst

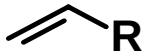
Synthesis of the catalyst

$$Rh^{III}Cl_3 * 3\,H_2O + \text{exc. } PPh_3 \xrightarrow[80°C]{EtOH} Rh^{I}Cl(PPh_3)_3 + 2\,HCl + Ph_3P{=}O$$

$d^6 4$

Reversible coordination of ethene

$$RhCl(PPh_3)_3 + \text{//} \underset{}{\overset{20°C}{\rightleftharpoons}} \textit{trans}\text{-}RhCl(C_2H_4)(PPh_3)_2 + PPh_3$$



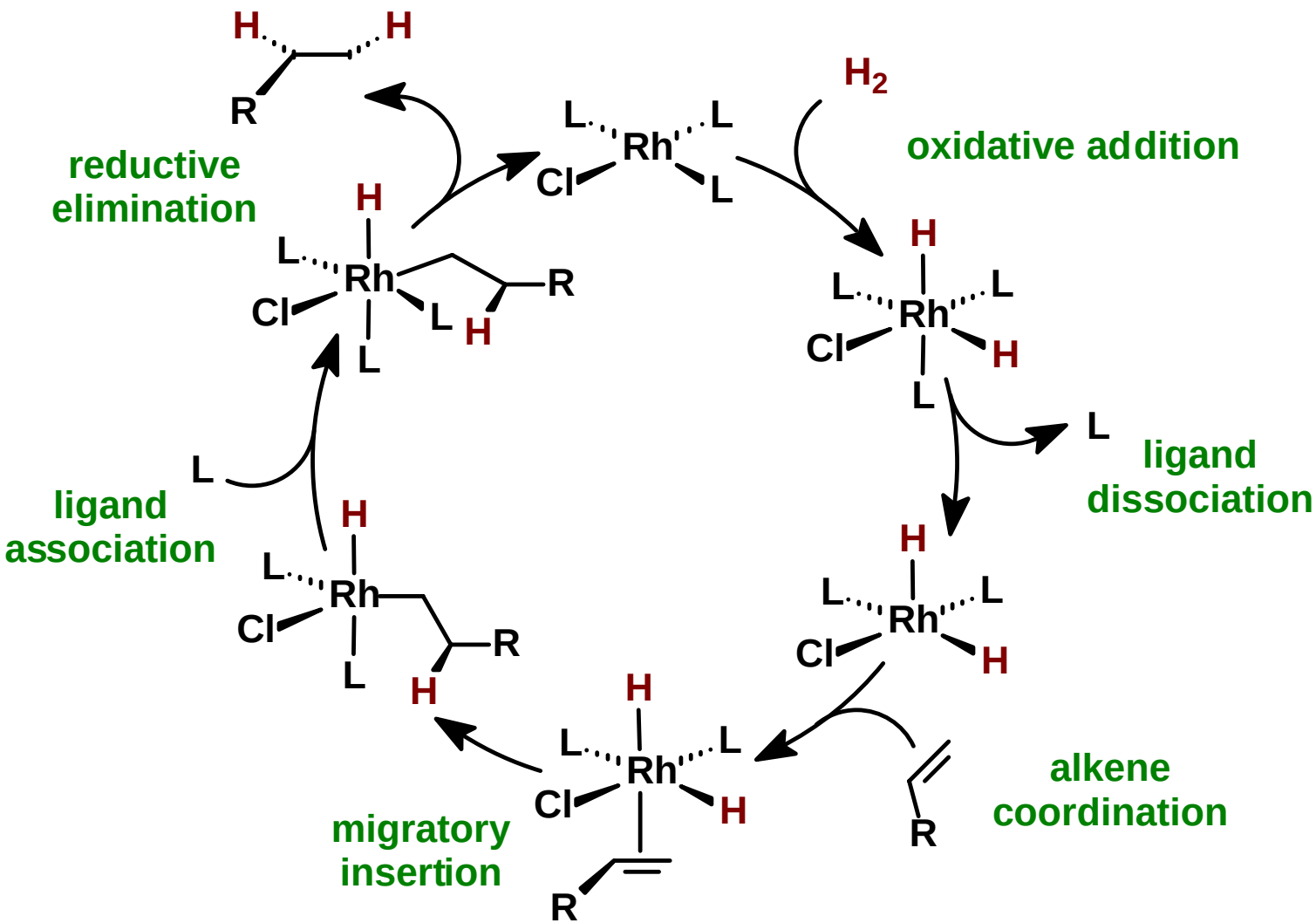
coordinates less by a factor of 2000

Irreversible coordination of CO

$$RhCl(PPh_3)_3 + CO \xrightarrow{20°C} \textit{trans}\text{-}RhCl(CO)(PPh_3)_2 + PPh_3$$

e.g. decarbonylation of aldehydes can lead to the deactivation of the catalyst

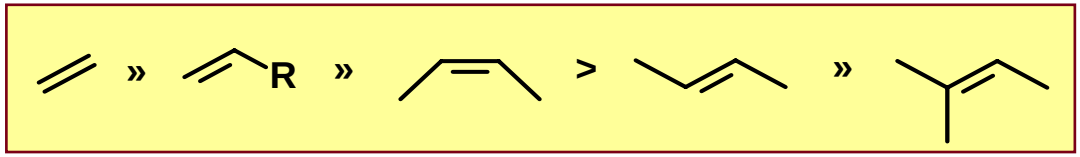
Homogeneous Hydrogenation



- H_2 activation is the rate limiting step

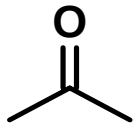
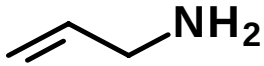
Homogeneous Hydrogenation

- **The least substituted C=C bond is hydrogenated fastest**



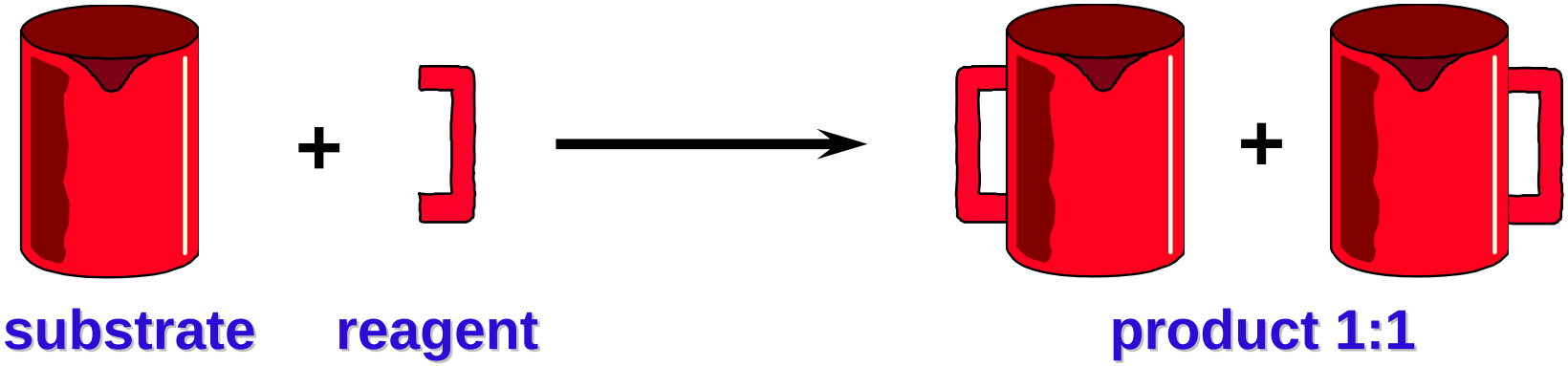
- **For simple alkenes manly steric factors determine the reactivity**

terminal > internal
cis* > *trans

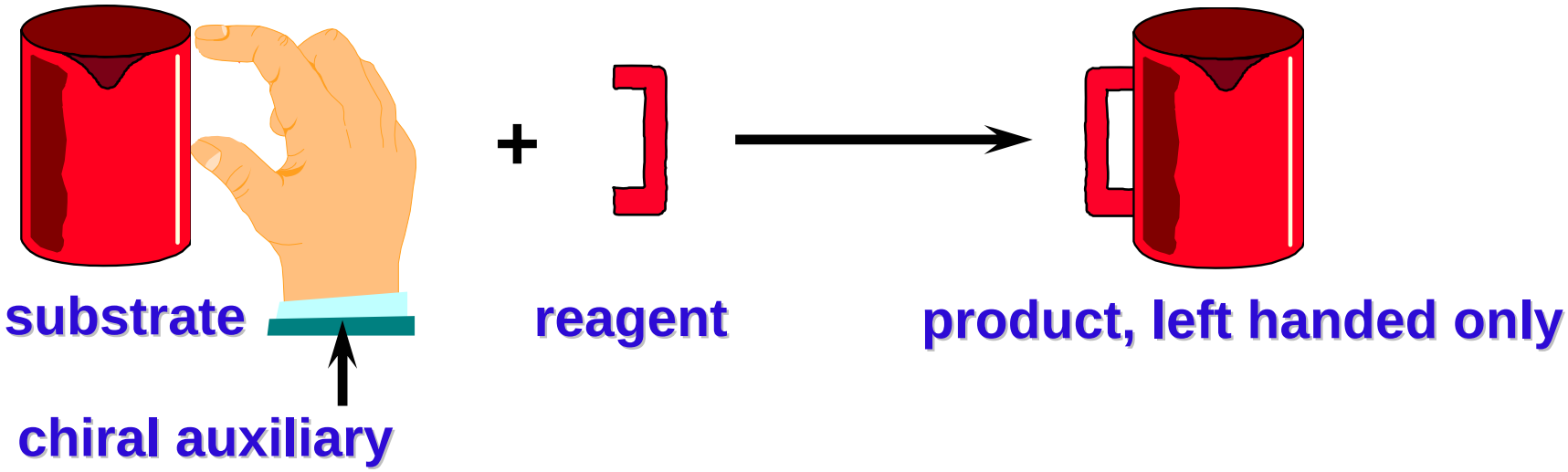
- **hydrogenation is stereospecific *cis***
- **low tendency towards isomerization**
- **tolerated functional groups:** **COOH, COOR, CN, NO_2,** 
- **strongly coordinating substrates inhibit:**  **;**

Asymmetric Synthesis

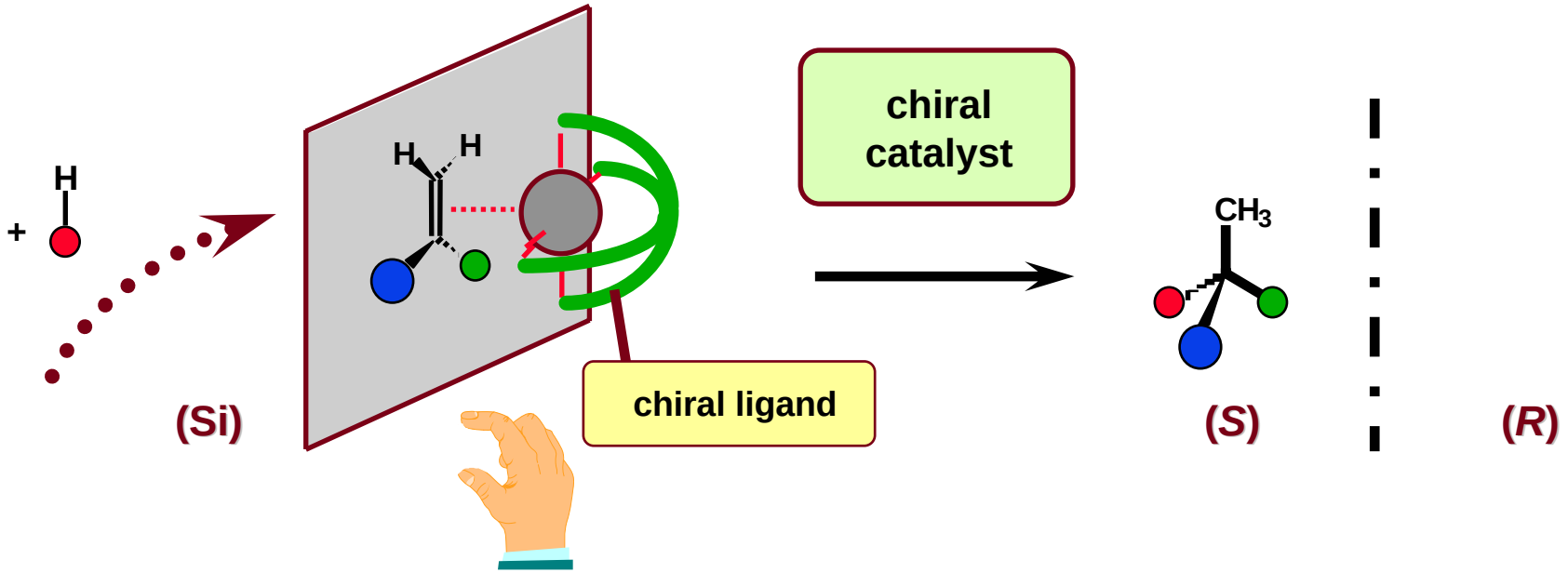
- **classical synthesis**



- **stereoselective synthesis**



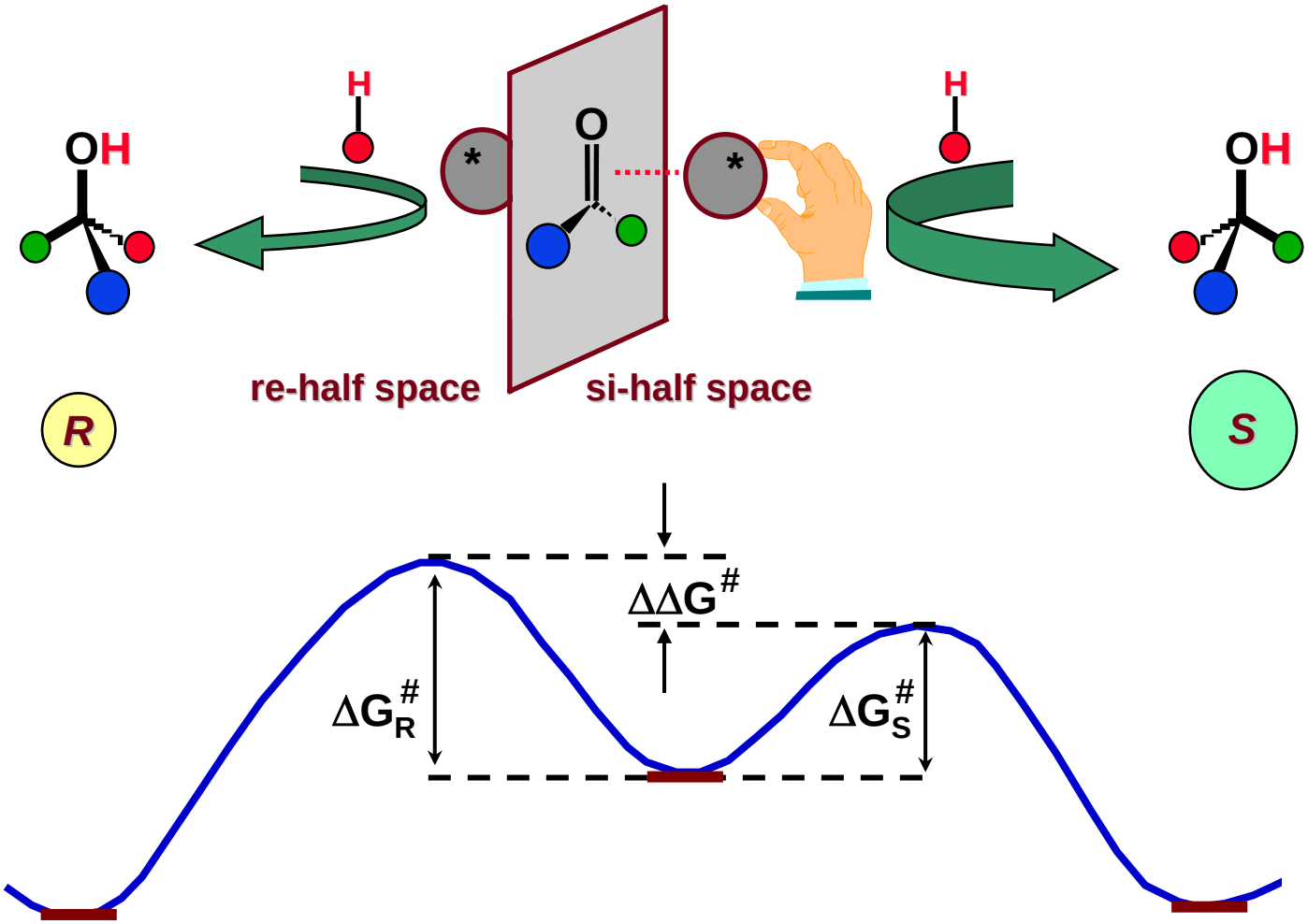
Conversion of a Substrate Using a Chiral Catalyst

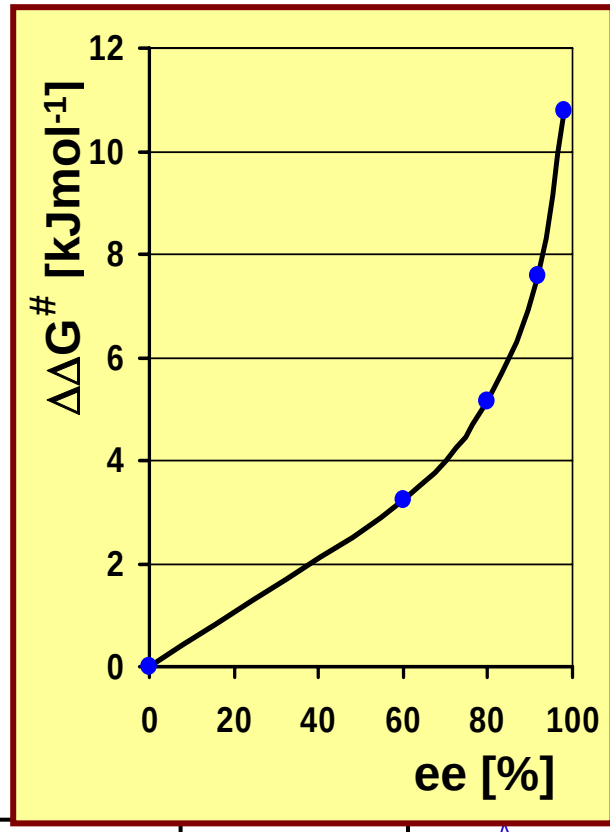


→ A **chiral catalyst** favors one face of the substrate

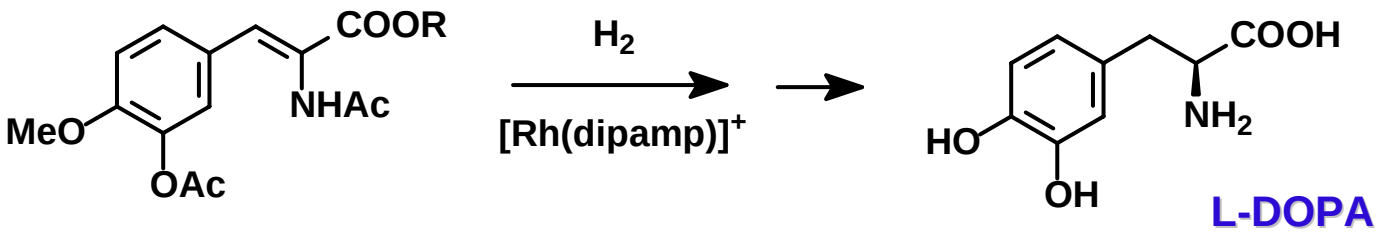
One product **enantiomer** is formed **predominantly**

Asymmetric Synthesis

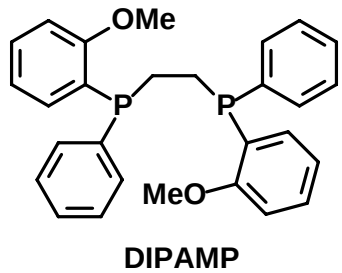


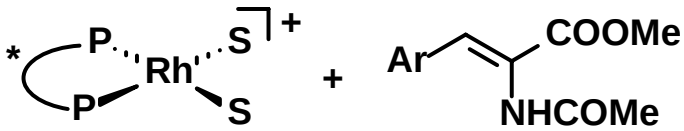


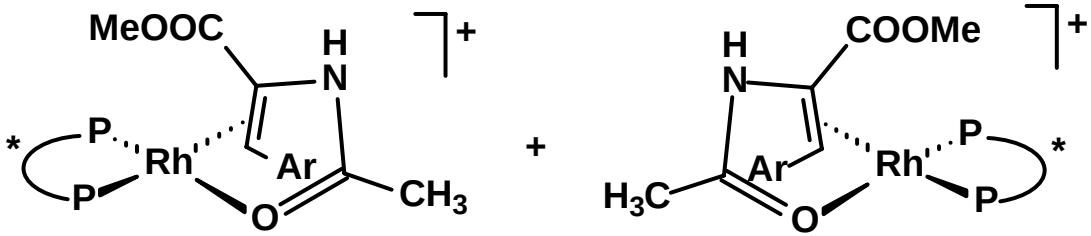
Asymmetric Hydrogenation



- **Monsanto's L-DOPA process**
  L-DOPA is an agent against Parkinson's disease







major diastereomer

minor diastereomer

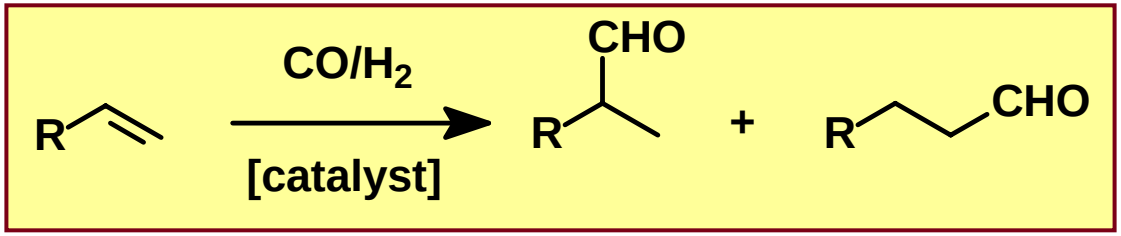
k_R

k_S

$k_S \gg k_R$

(*S*)-product formed predominantly

Hydroformylation



- The hydroformylation reaction was found by O. Roelen in 1938 during his work on Fischer-Tropsch synthesis

- Very important reaction for the production of softeners for plastics and detergent alcohols.

- Bulky substituents increase the linearity of the product.

- Acceptor ligands increase the rate of the reaction by accelerating ligand and CO dissociation and olefin coordination.

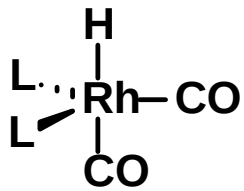
Industrial Hydroformylation Overview

Catalyst	$Co(CO)_4H$	$Co(PBu_3)(CO)_3H$	$Rh(CO)_4H$	$Rh(TPP)_3(CO)H$	$Rh(TPPTS)_3(CO)H$
T	110-180°C	160-200°C	100-140°C	85-115°C	50-130°C
p	200-350 bar	30-100 bar	200-300 bar	15-20 bar	10-100 bar
Products	aldehydes	alcohols	aldehydes	aldehydes	aldehydes
l/b (propene)	80:20	88:12	50:50	92:8	95:5
Byproducts	medium	high	low	low	low
Poisoning	low	medium	high	-	high
Feed stocks	C_2-C_{20}	Higher alkenes	spec. alkenes, ethene	lower alkenes	lower alkenes
Processes	Ruhrchemie BASF Kuhlmann	Shell	-	LPO	Ruhrchemie/Rhône Poulenc
Separation cat./product	several	distillation under increased pressure	-	distillation	phase separation
Catalyst recycling	several	in residue	-	cat. remains in reactor	in aqueous phase

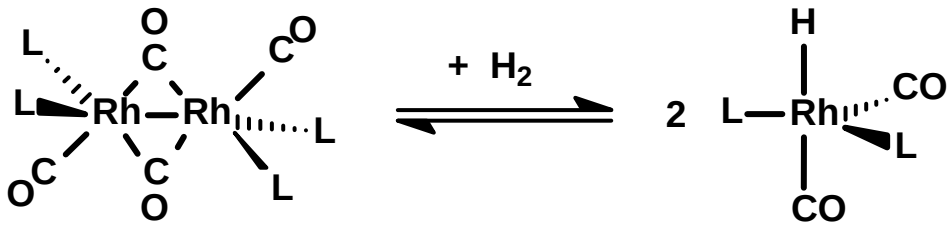
Hydroformylation

- **Formation of the catalyst complex**

- **Cobalt systems:** $Co_2(CO)_8 \xrightarrow{H_2} 2\ HCo(CO)_4$

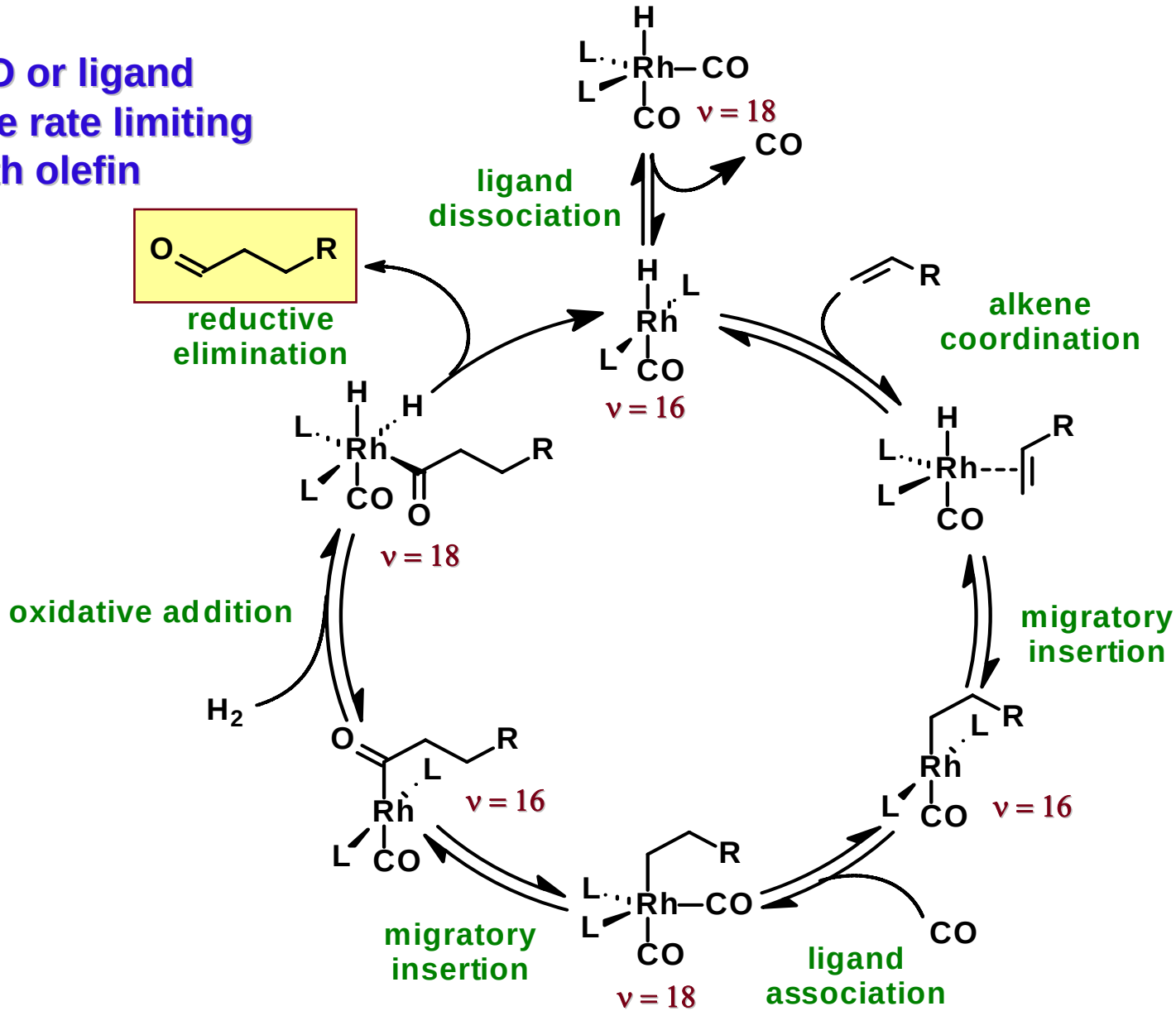
- **Rhodium systems:** $(acac)Rh(CO)_2 \xrightarrow[-\ Hacac]{CO/H_2\ ;\ L}$ 

- **At high Rh concentration and low pressure there is an equilibrium between catalytically inactive dimeric species and the active hydride.**



Hydroformylation

- In most cases CO or ligand dissociation is the rate limiting step, together with olefin coordination.

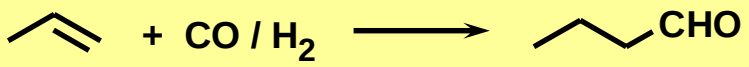


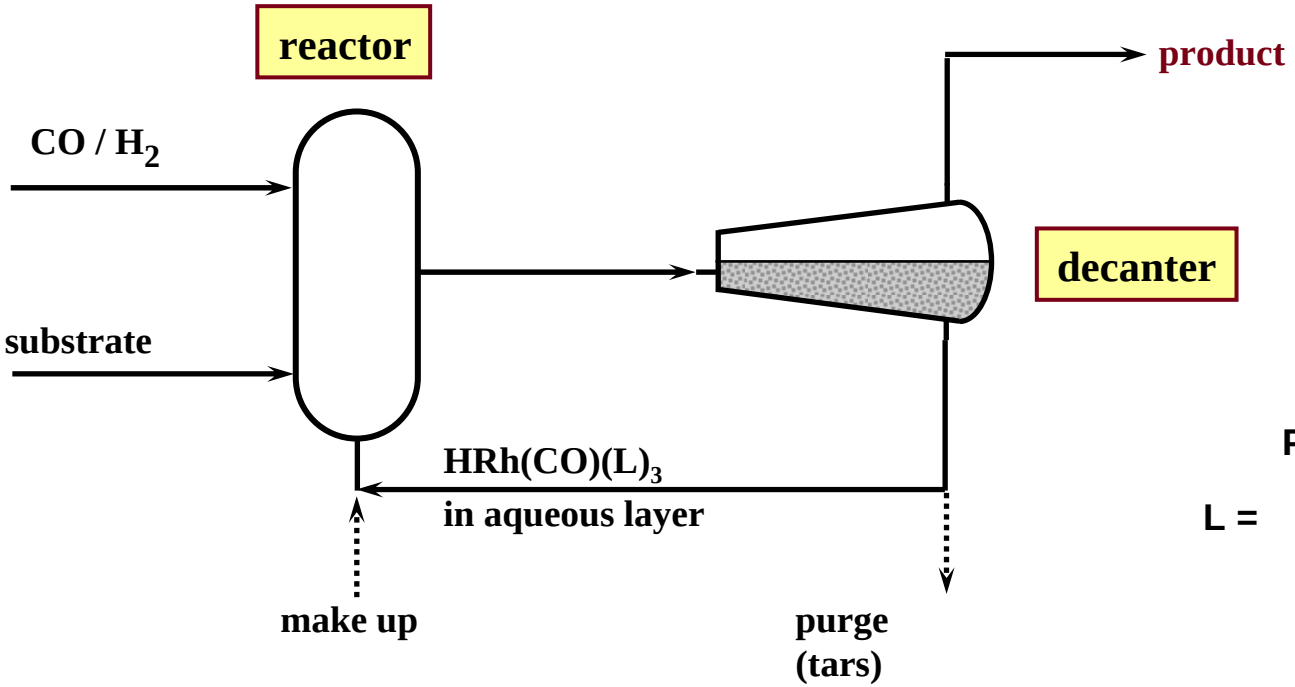
Type I rate law:

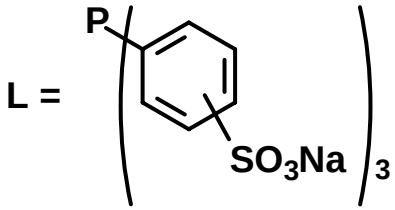
$$r = \frac{A[\text{alkene}][Rh]}{B + [L]}$$

Hydroformylation Processes

Ruhrchemie/Rhône Poulenc,
Rhodium + Phosphine
two Phase Process



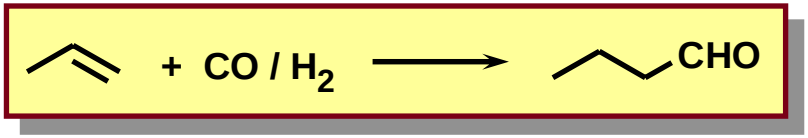


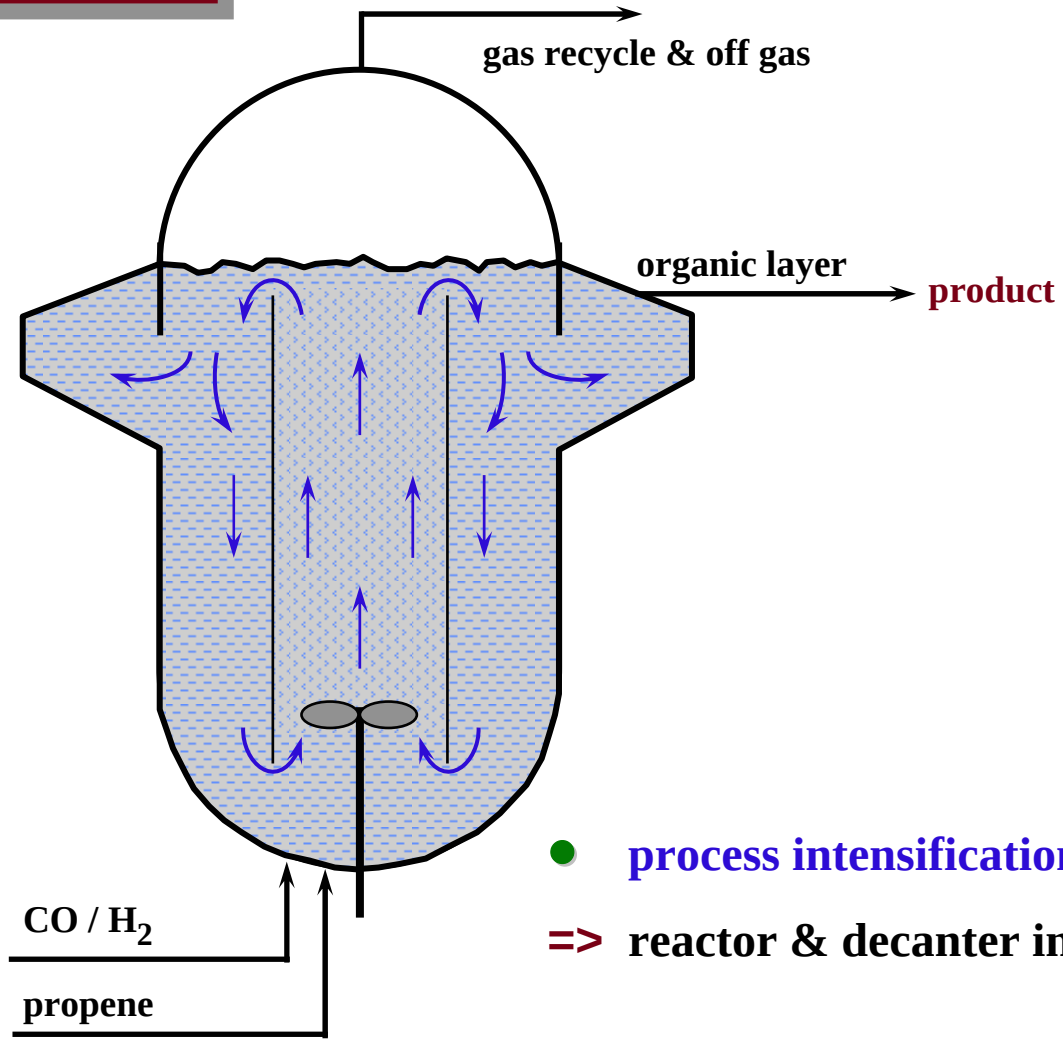


- **limited by alkene solubility in water**

Hydroformylation Processes

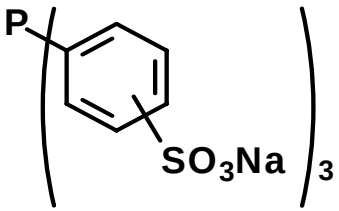
Ruhrchemie/Rhône Poulenc, two Phase Process





hydrophilic ligand: TPPTS

L =



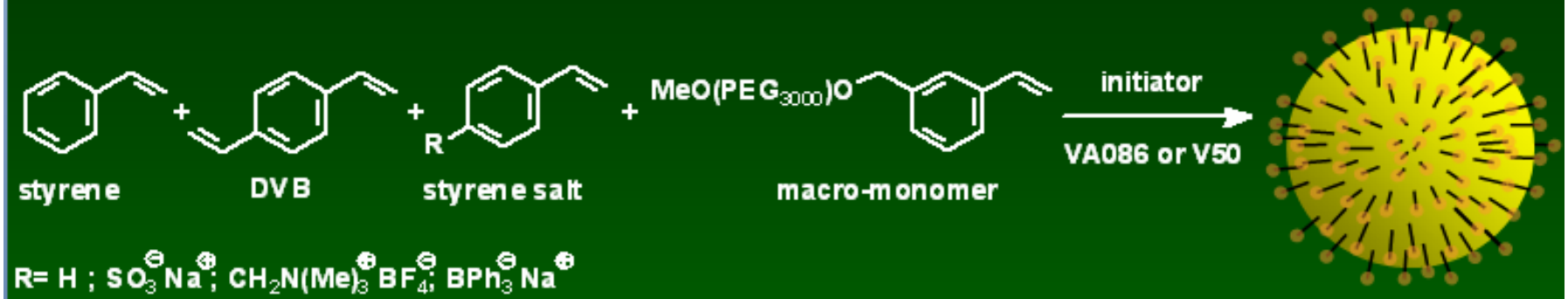
solubility: > 1 kg / l H_2O

- **process intensification**

=> reactor & decanter in one unit

Nanoparticles

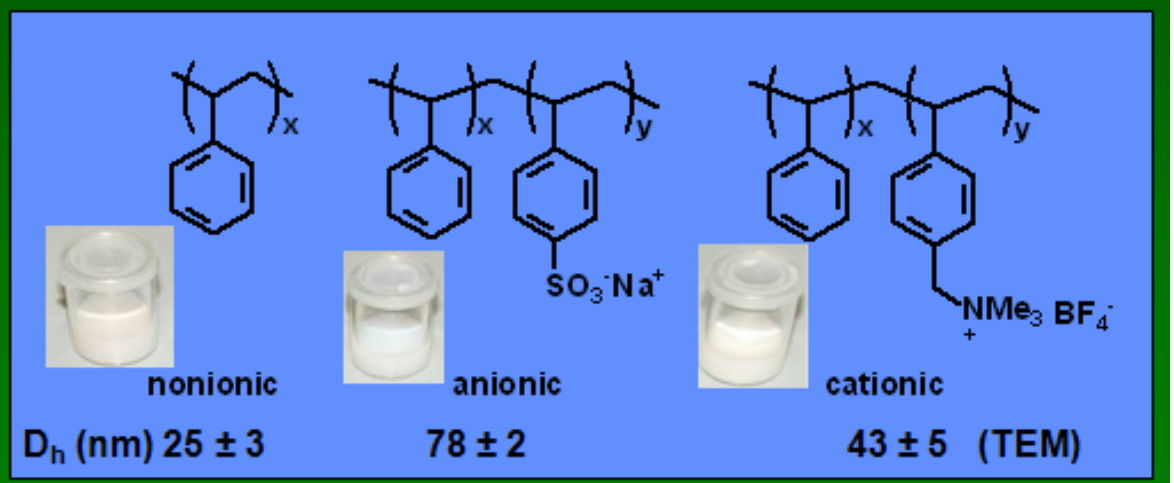
Latices as Phase-Transfer Agents



Typical latex composition

styrene	73%
styrene salt	20%
DVB	4%
PEG_{3000}	2%
initiator V50	1%

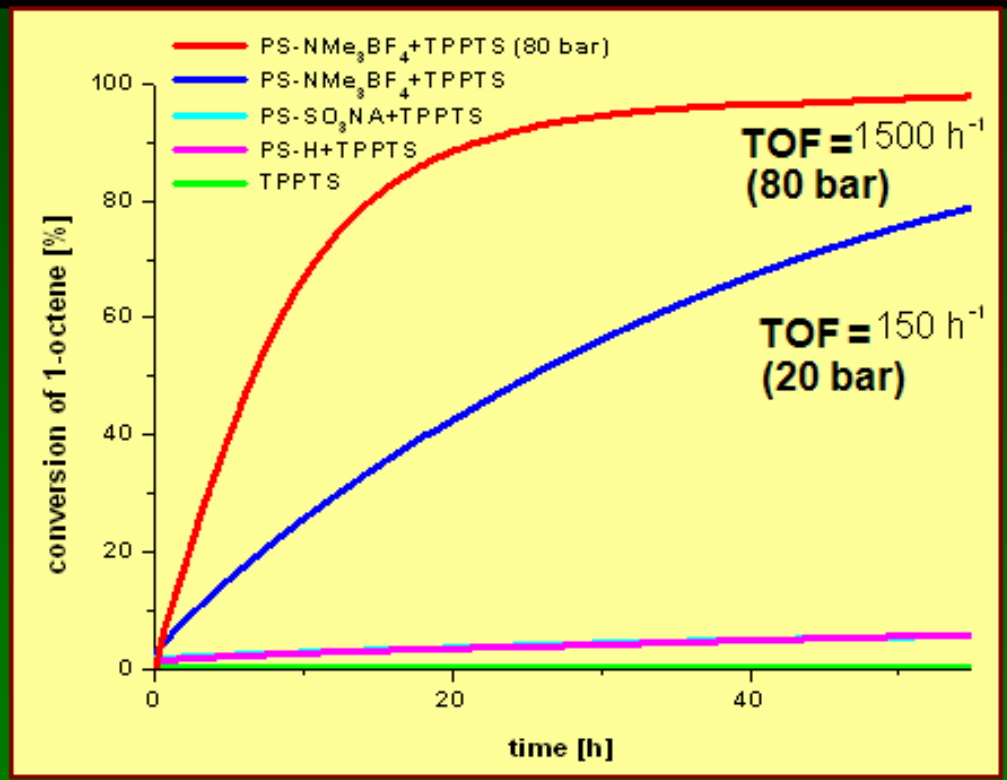
V50 = 2,2'-Azobis(2-methylpropionamide)dihydrochloride



K. Kunna, C. Müller, J. Loos, D. Vogt, *Angew. Chem. Int. Ed.* **2006**, 45, 7289-7292.

Nanoparticles

Latex Enhanced Aqueous Phase Catalysis



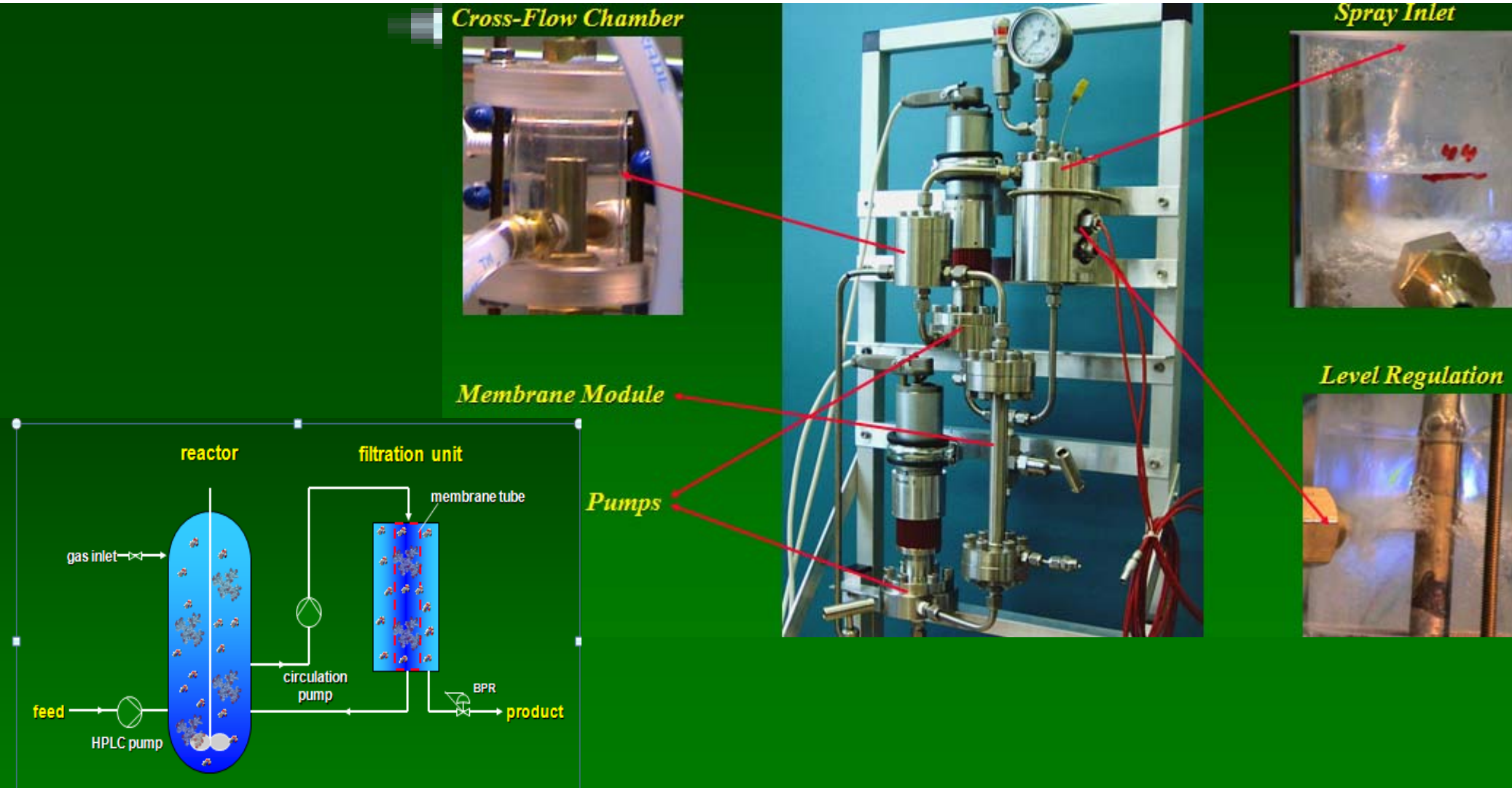
1-octene (150 mmol); ligand (0.21 mmol); [Rh(acac)(CO)$_2$] (0.035 mmol); latex: 100 mg solid content; S:P:Rh 5000:6:1; water phase : org. phase 1:2.3; CO/H2 1:1; p = 20 bar; T = 80°C; stirring: 600 rpm.

K. Kunna, C. Müller, J. Loos, D. Vogt, *Angew. Chem. Int. Ed.* **2006**, 45, 7289-7292.

Novel reaction engineering

www.catalysis.nl

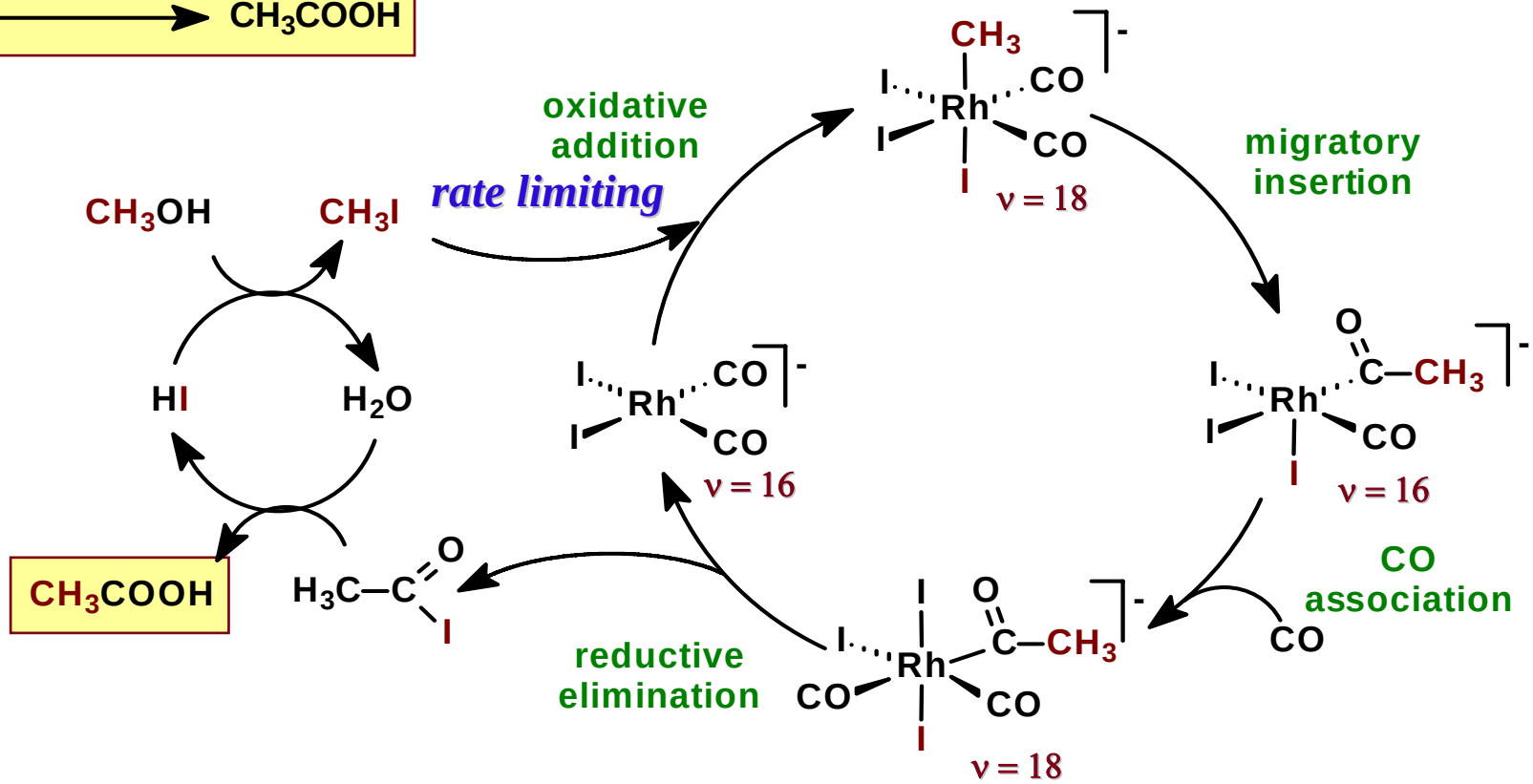
Membrane Loop reactor

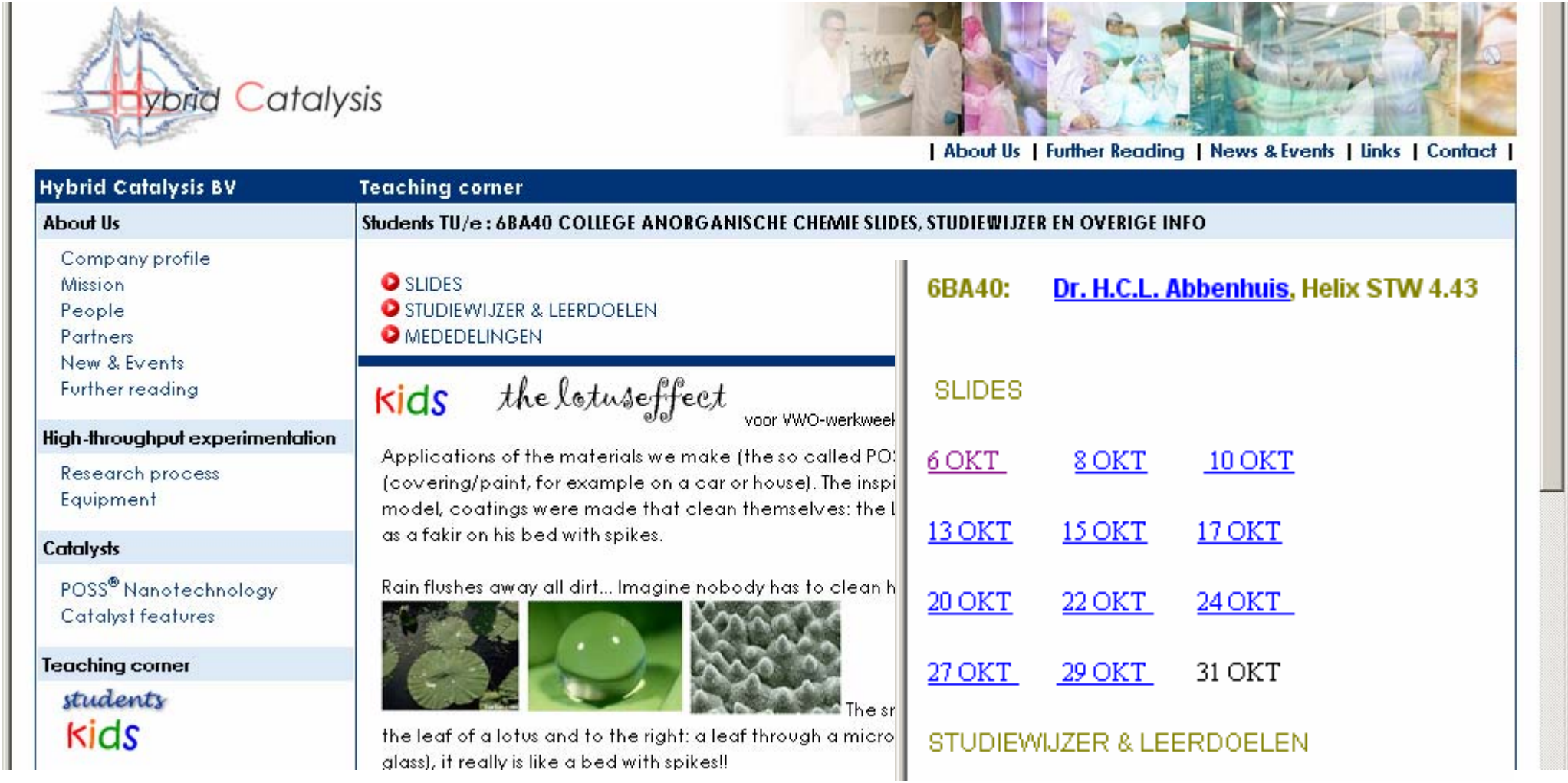


Monsanto Acetic Acid Process

Carbonylation of Methanol

$$CH_3OH + CO \xrightarrow{[RhI_2(CO)_2]^-} CH_3COOH$$



- Currently ~ 3.5 Mt/a produced worldwide, 60% of all acetyl compounds based on this process.
- New BP process uses $[IrI_2(CO)_2]^-$ with $Ru_2(CO)_6I_2(\mu\text{-}I)_2$ as cocatalyst

Inorganic Chemistry 6BA40
Slides available:
http://www.hybridcatalysis.com/teachingcorner.htm