

HOMOGENEOUS CATALYSIS: INDUSTRIAL APPLICATIONS AND PHOTOCATALYSIS (4 CFU)

Targets:

- ❖ Knowledge of the fundamental principles of homogeneous catalysis.
- ❖ Relationship between the structure of the catalyst and the product of the catalytic reaction.
- ❖ Overview of some of the main catalytic systems applied in industry.
- ❖ Knowledge of the fundamental principles of homogeneous photocatalysis.

Final exam: one oral exam about both modules.

Topics:

- ❖ Fundamental principles of homogeneous catalysis.
- ❖ Carbonylation reactions.
- ❖ Hydrogenation reactions.
- ❖ Asymmetric catalysis.
- ❖ Hydroformylation reactions.
- ❖ Hydrocyanation reactions.
- ❖ Catalysis for polymerization.
- ❖ Basic principles of homogeneous photocatalysis.

May 7th: Visit to LyondellBasell in Ferrara.

**May 12th and 13th: Lectures from Prof. Martin Albrecht –
University of Bern**

Text books:

❖ Inorganic Chemistry Third Edition

Catherine E. Housecroft and Alan G. Sharpe

Pearson Prentice Hall

❖ Inorganic Chemistry Fourth Edition

Shriver & Atkins

Oxford University Press

❖ Homogeneous Catalysis: understanding the art

Autore: Piet W.N.M. van Leeuwen

Kluwer Academy Publisher

Springer: www.springer.com/chemistry

❖ Fundamentals of Organometallic Catalysis

Dirk Steinborn

Wiley-VCH (2012)

❖ Organometallics and Catalysis: an Introduction

Manfred Bochmann

Oxford University Press 2015

❖ Photochemistry and Photophysics

Vincenzo Balzani, Paola Ceroni, Alberto Juris

Wiley-VCH

The role of catalysis in chemical industry

More than **90%** of all chemicals are produced by **catalysis!**

Top 10 Industrial and Synthetic Chemicals (mid-2024):

Sulfuric acid	catalytic process
Nitrogen	not catalytic
Ethylene	catalytic process
Propylene	catalytic process
Ammonia	catalytic process
Chlorine	not catalytic
Sodium hydroxide	not catalytic
Benzene	catalytic process
Ethylene oxide	catalytic process
Methanol	catalytic process

Fields of applications of catalysis



Packaging Materials



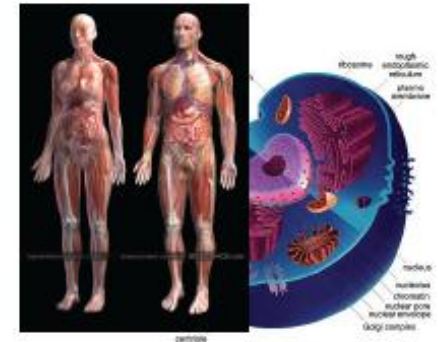
Construction Materials



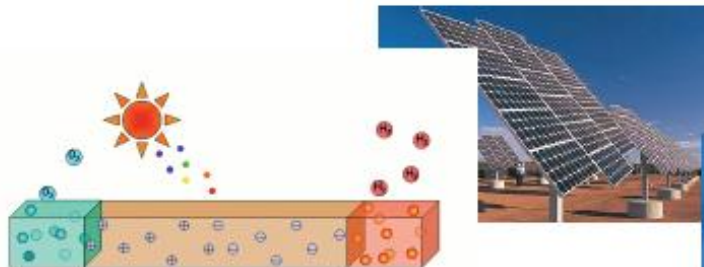
Pharmaceuticals



Fertilizers



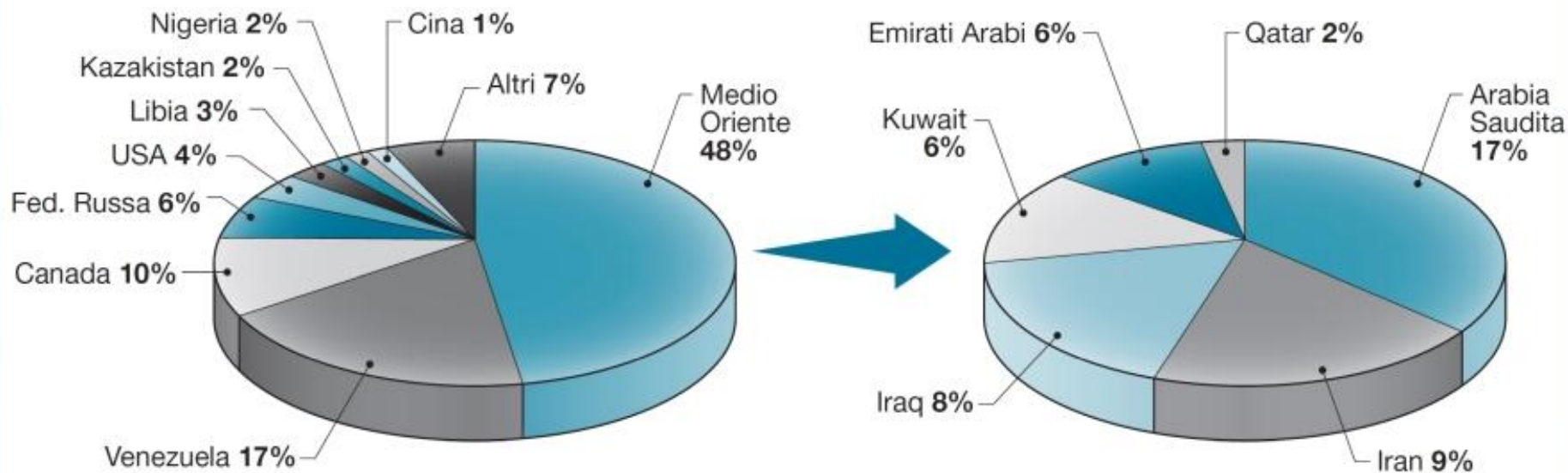
Biochemical Processes



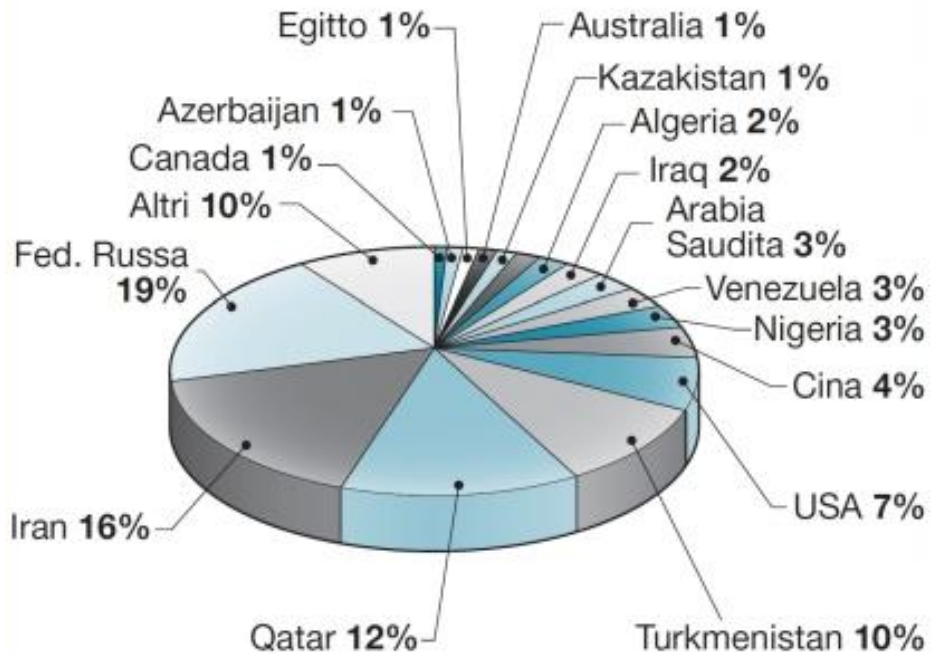
Energy Storage and Conversion



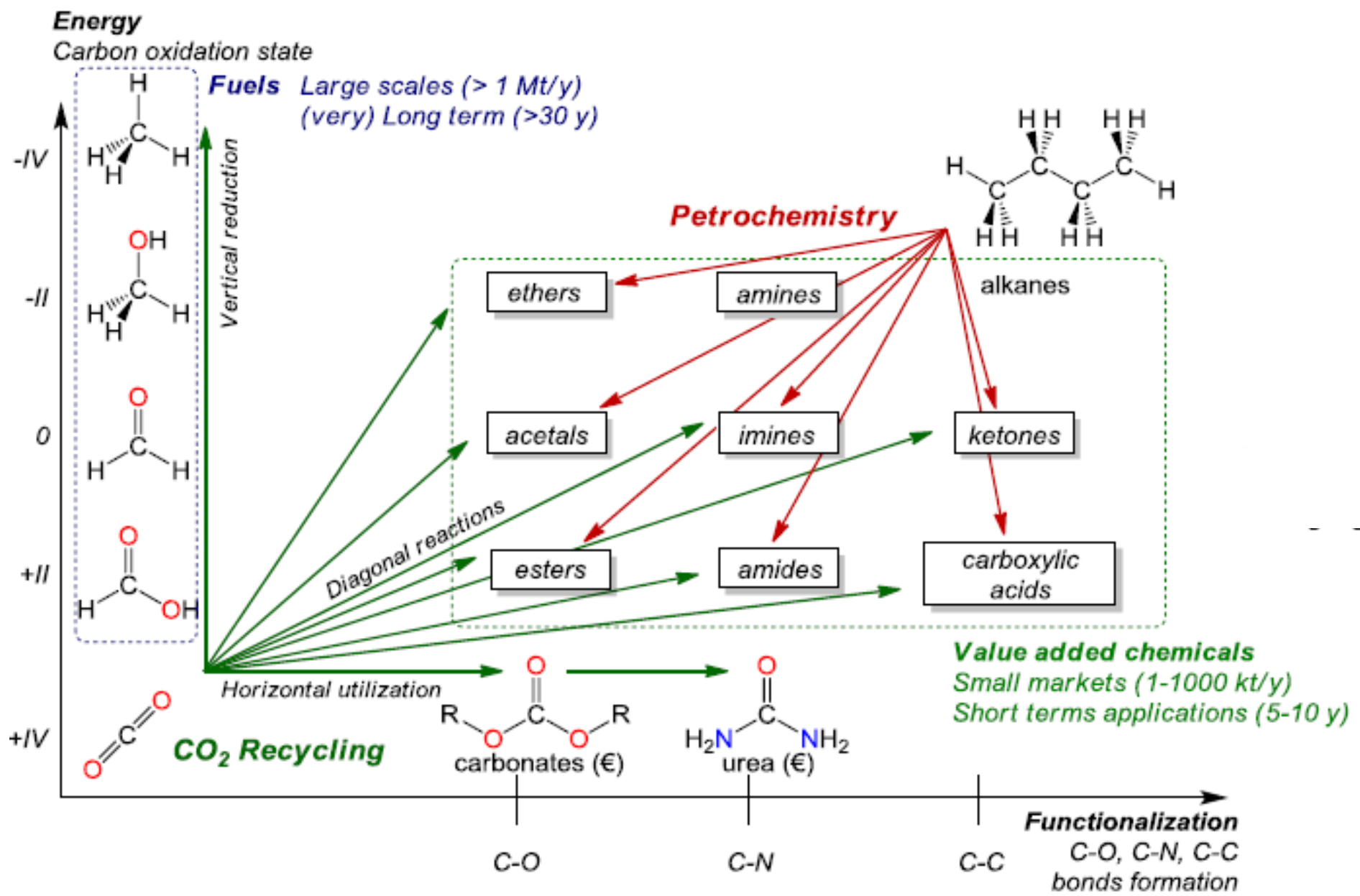
Geographical distribution of *oil reserves (in 2020)*



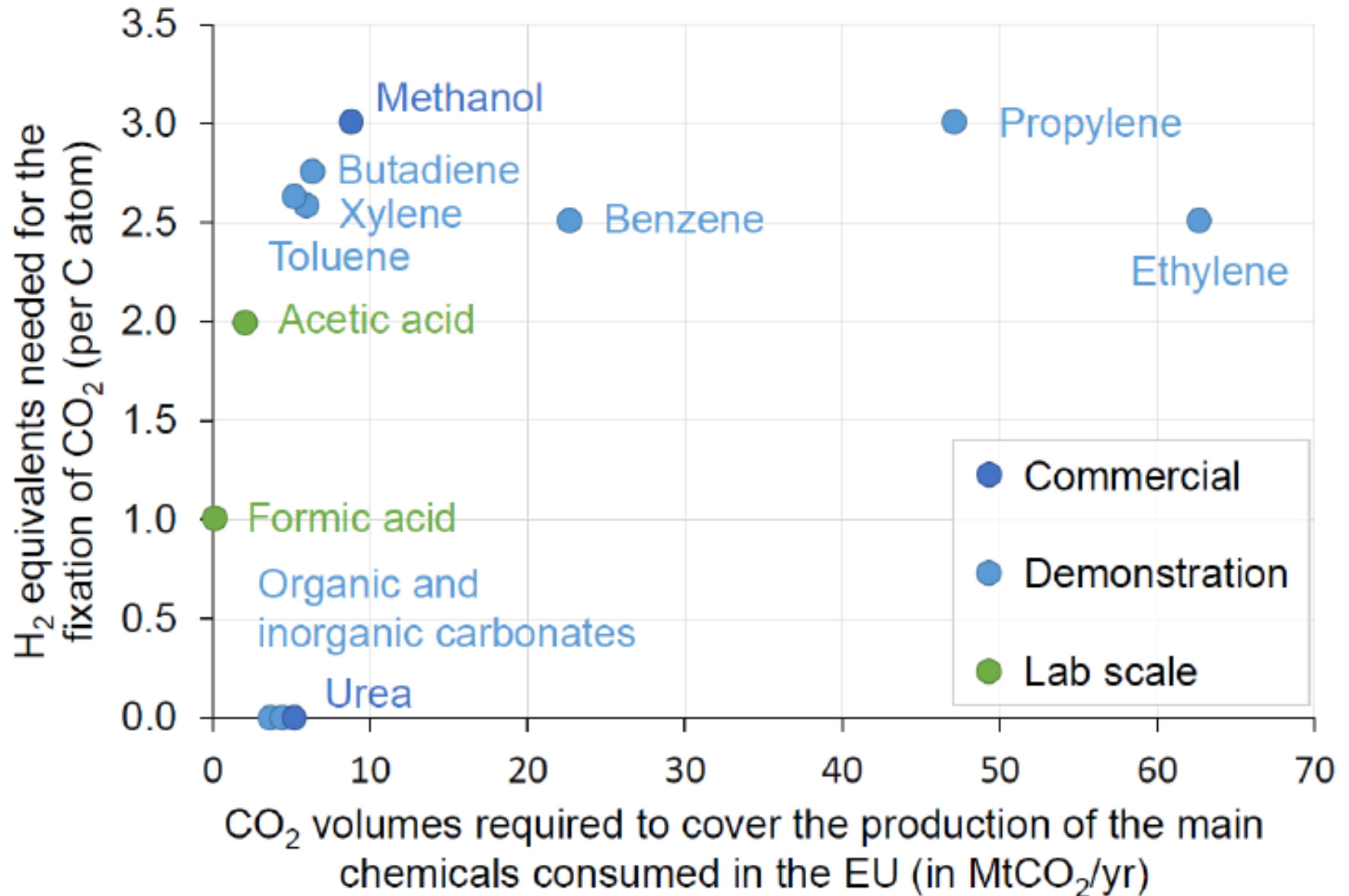
Geographical distribution of *natural gas reserves (in 2020)*



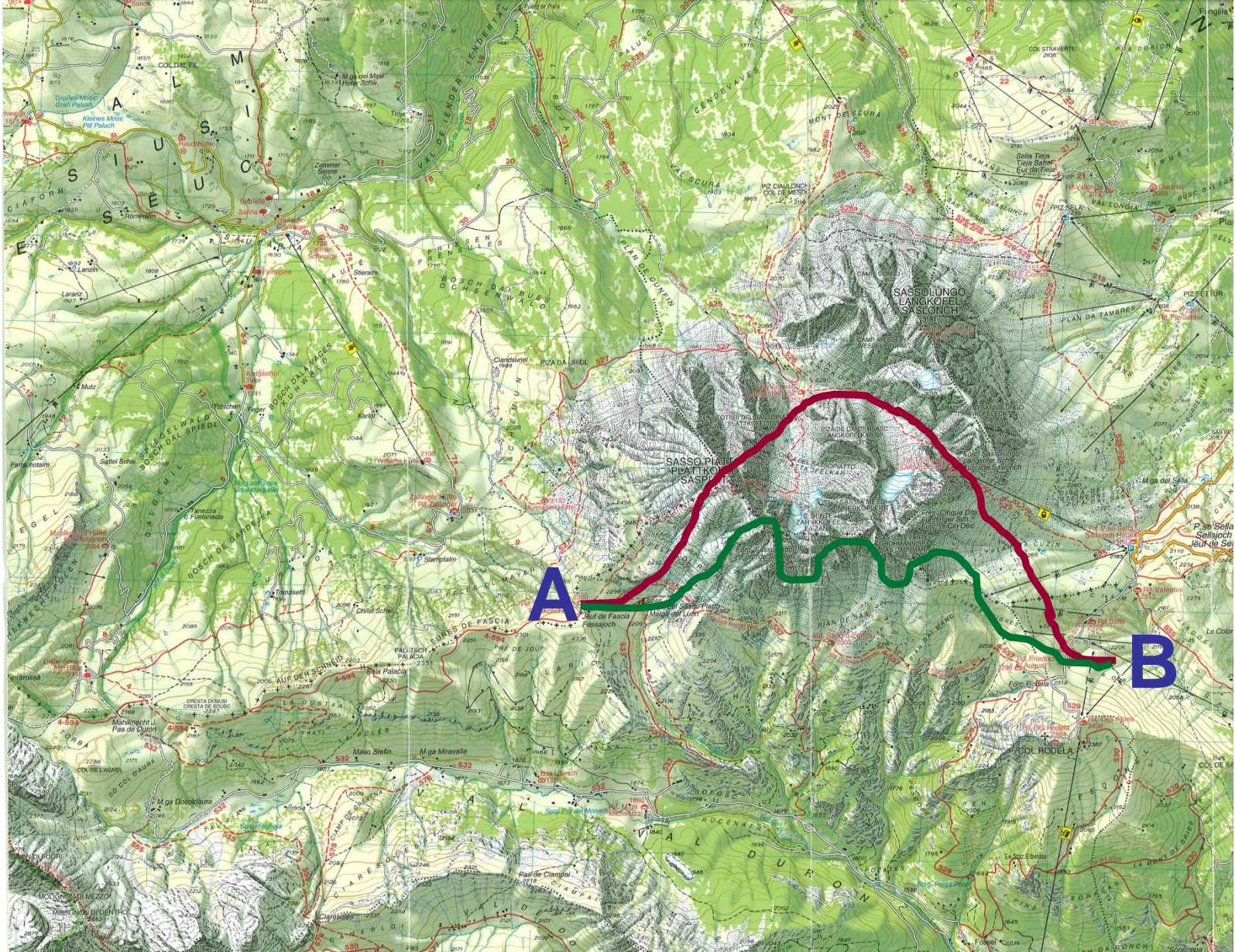
CO_2 as a C_1 building block



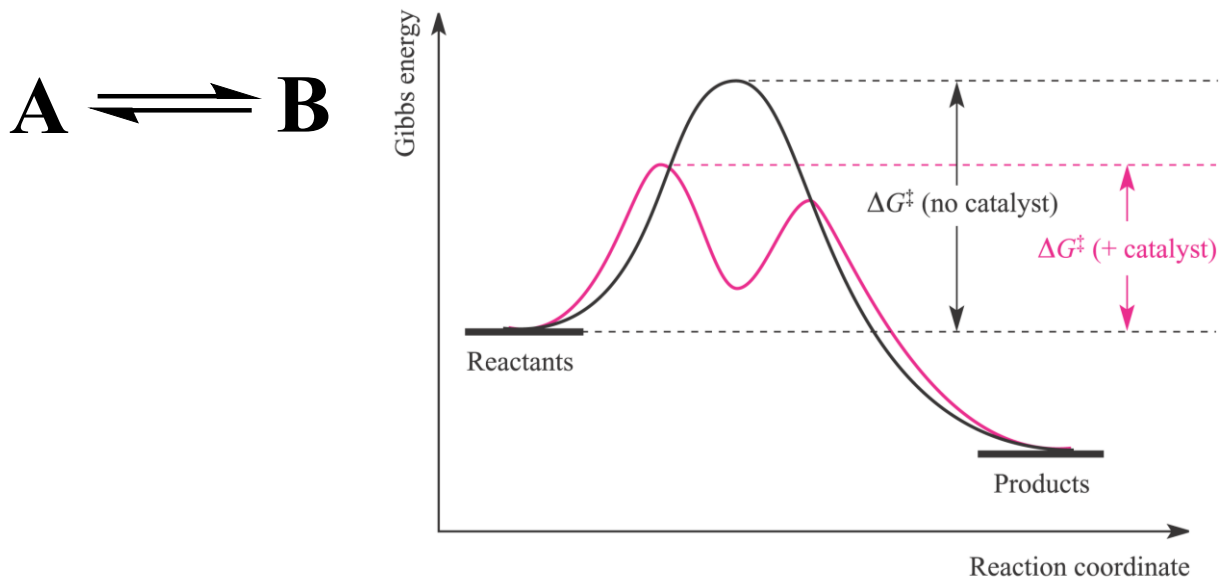
Carbon based products



CATALYSIS: reduce the energy barriers



THE CATALYST



A *catalyst* is any substance that, without appearing in the final product of a chemical reaction, *increases the rate* at which a chemical reaction approaches the equilibrium.

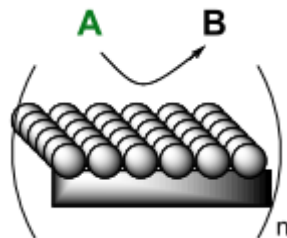
A *catalyst does not modify* the overall Gibbs free energy change in the reaction.

A *catalyst opens new reaction pathways* that are different and energetically favored with respect to those of the **NON** catalyzed reaction.

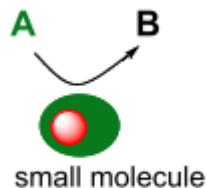
A *catalyst is found unaltered* at the end of the catalytic cycle, it is **NOT** consumed during the catalytic reaction.

CLASSES OF CATALYSTS

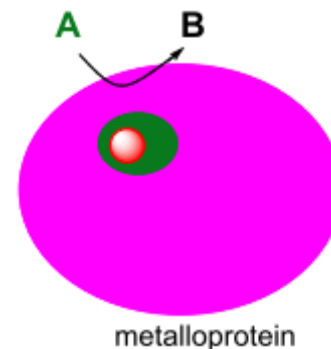
HETEROGENEOUS



HOMOGENEOUS



ENZYMES



- *heterogeneous catalysis: catalysts and reactants are present in different phases: i.e. the catalyst is a solid and reactants are present as gases or in solution;*
- *homogeneous catalysis: catalysts and reactants are present in the same phase: i.e. in solution;*
- *Enzymatic catalysis: is unique due to the special structure of proteins and the specificity in the action mode.*

HETEROGENEOUS vs HOMOGENEOUS Catalysis: a COMPARISON

HETEROGENEOUS

HOMOGENEOUS

Strength

Weakness

Strength

Weakness

Easy to be separated

Only the surface atoms are accessible

All the catalyst is accessible

Difficult to be separated

Easy to be recycled

Easy to be poisoned

Difficult to be recycled

High thermal stability

Difficult to be investigated

Easy to be studied

Low thermal stability

Limited possibility to be modified

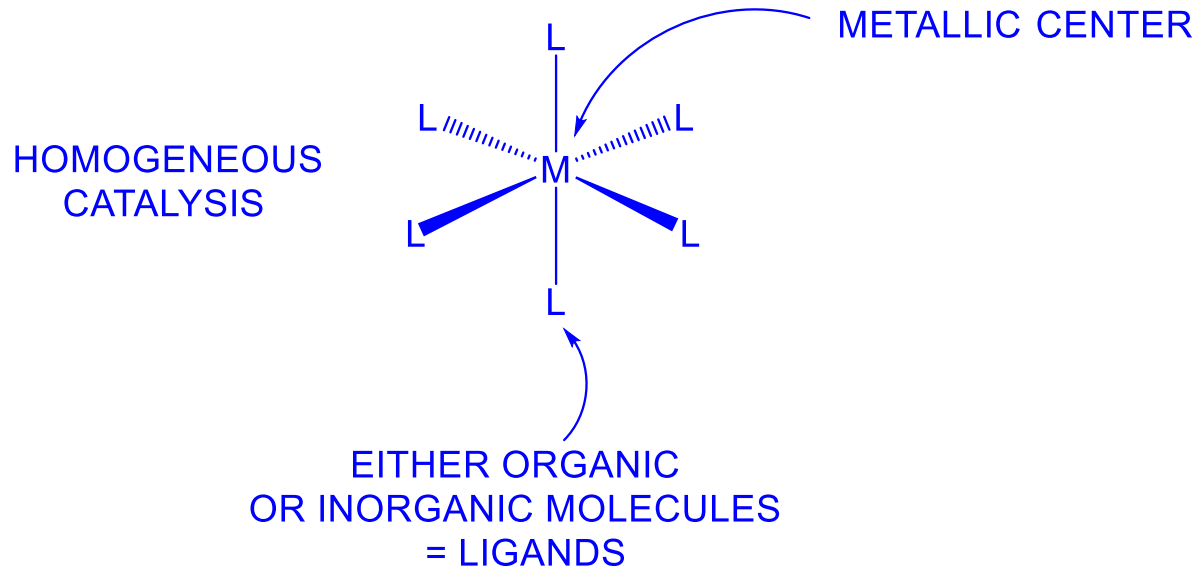
High versatility

Low selectivity

High selectivity

The catalysts of the two classes are active at very different reaction conditions.

The homogeneous catalyst



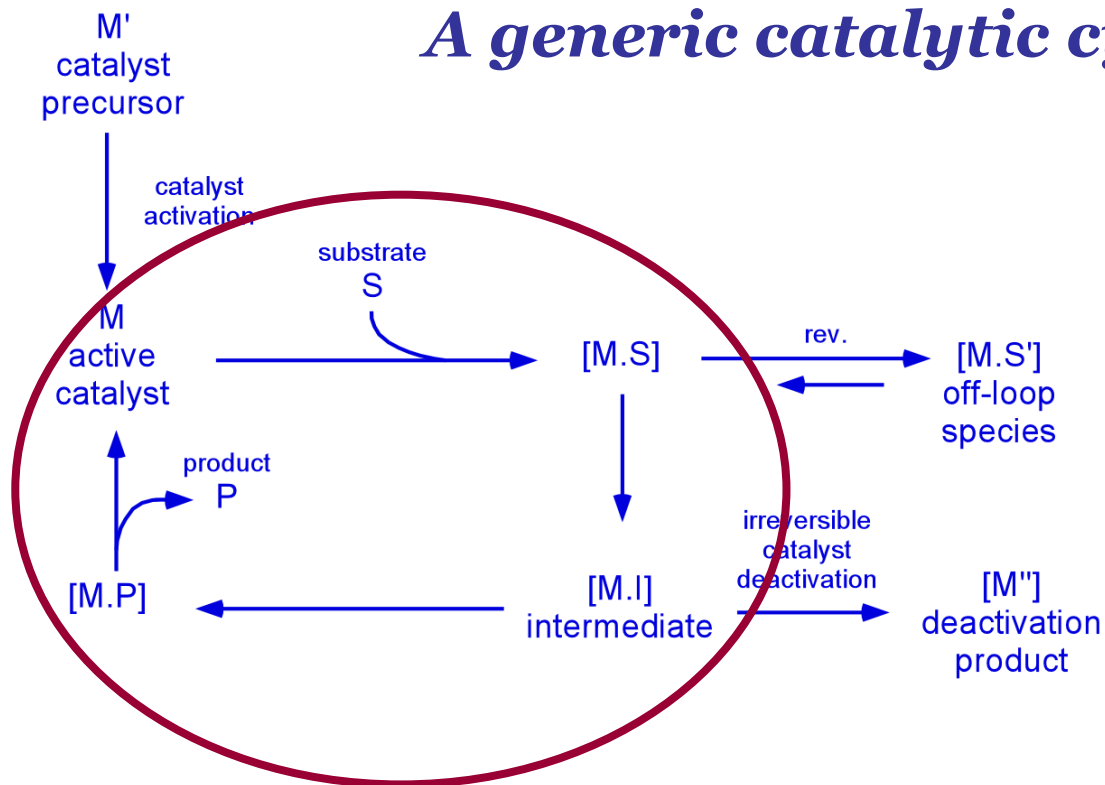
THE GLOSSARY FOR CATALYSIS

- *Precatalysts* (or *Catalyst Precursors*) are compounds from which the catalysts are generated. We can have either *in situ catalytic systems* or *preformed complexes*.
- *Cocatalyst* is any additional component required for the catalytic reaction; it may play different roles: activator, stabilizer. It is **not** catalytically active. It is added in lower amount with respect to the substrate, but in stoichiometric or in excess with respect to the precatalyst.
- *Catalytic system* is the combination of precatalyst, cocatalyst and solvent.
- *Inhibitor* is a substance that reduces the rate of a catalyzed reaction or blocks it (a *poison*).
- *Autocatalysis*: in autocatalytic reactions, a reaction product acts catalytically, so an acceleration of the reaction with increasing conversion can be observed.

THE GLOSSARY FOR CATALYSIS

➤ *The catalytic cycle is made by the set of reactions involving the catalyst and leading to the transformation of the substrate in the product. These reactions are called elementary steps.*

A generic catalytic cycle



THE GLOSSARY FOR CATALYSIS

- ***Activation step***: it is one reaction or the set of reactions needed to transform the precatalyst in the active species.
- ***Induction period***: it is a very slow initial phase of a chemical reaction, that, in later phases, proceeds at a higher reaction rate. An induction period can be caused by slow formation of catalyst.
- ***Rate-determining step***: it is the ***slowest step*** of the overall catalytic cycle, it decisively determines the rate of the overall reaction. In many cases it is the reaction step associated with the highest lying transition state in the reaction profile diagram.
- ***Resting state***: it is an organometallic complex that is present in ***significantly higher concentration*** than any other complex of the catalytic cycle. Not necessarily it is part of the catalytic cycle, but it is in equilibrium with a catalytically active species of the cycle itself. It is the catalyst in a «dormant» state.
- ***Die-out step***: it is a reaction external to the catalytic cycle that causes ***catalyst deactivation***.

THE PARAMETERS TO ASSESS THE CATALYST PERFORMANCE

➤ *The main parameters applied to assess the catalyst performances are:*

- ❖ *catalyst activity and productivity;*
- ❖ *catalyst selectivity;*
- ❖ *catalyst stability.*

➤ *Additional parameters applied to assess the industrial exploitation of a catalytic process*:*

- ❖ *cost;*
- ❖ *sustainability;*
- ❖ *Life Cycle Assessment.*

selectivity > stability > activity

* *Fondamenti di Chimica Industriale Cavani, Centi, Di Serio, Rossetti, Salvini, Strukul editore: Zanichelli*

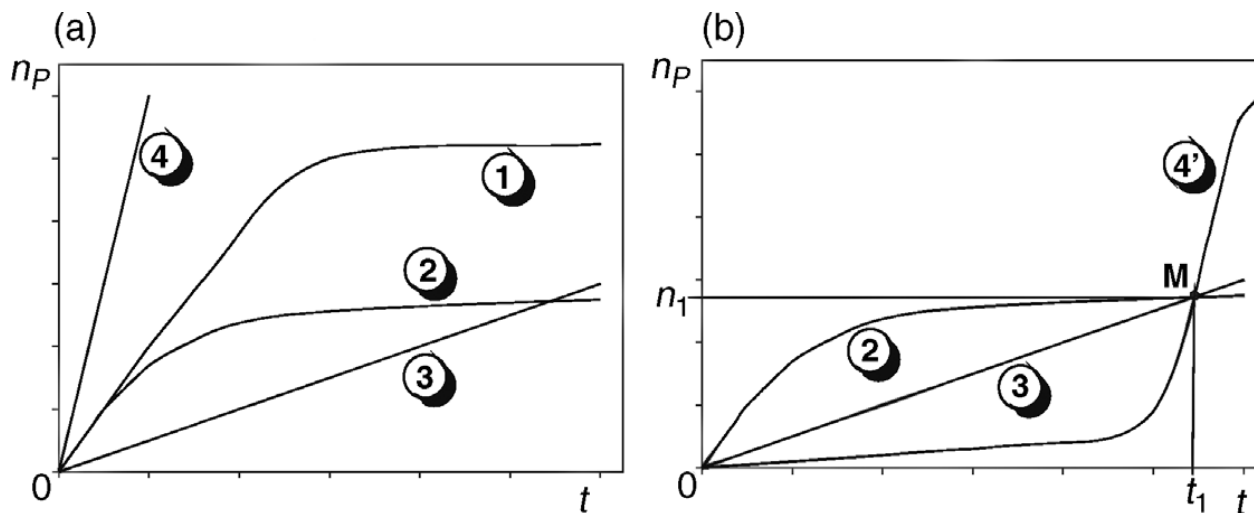
Catalyst activity is the parameter to evaluate the rate of the catalytic reaction with respect to the amount of catalyst. It is measured as **TON** and **TOF**.

TON is the turnover number = the **total number of substrate moles converted into the product by one mole of catalyst**. It is dimensionless. **PRODUCTIVITY**.

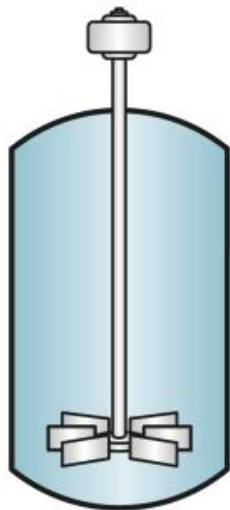
TOF is the turnover frequency, in other words the turnover number over a given time interval = the **total number of substrate moles converted into the product by one mole of catalyst in a certain period of time**; it has the dimension of 1/time i.g. h^{-1} . **ACTIVITY**

[sub]/[cat] or **[sub]/[M]**: a very important figure in catalysis.

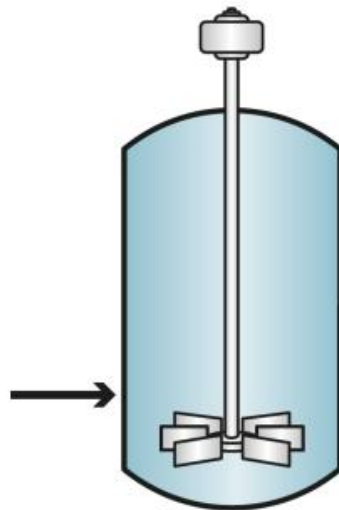
Plots of **conversion vs time**



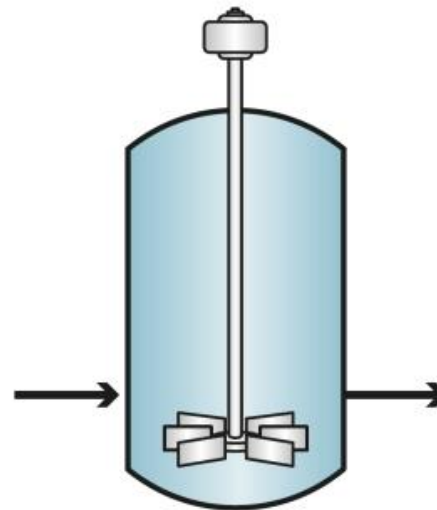
Catalyst activity: which is the best choice: a high TON or a high TOF?



Process in batch

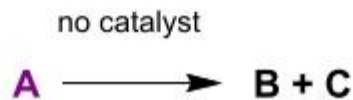
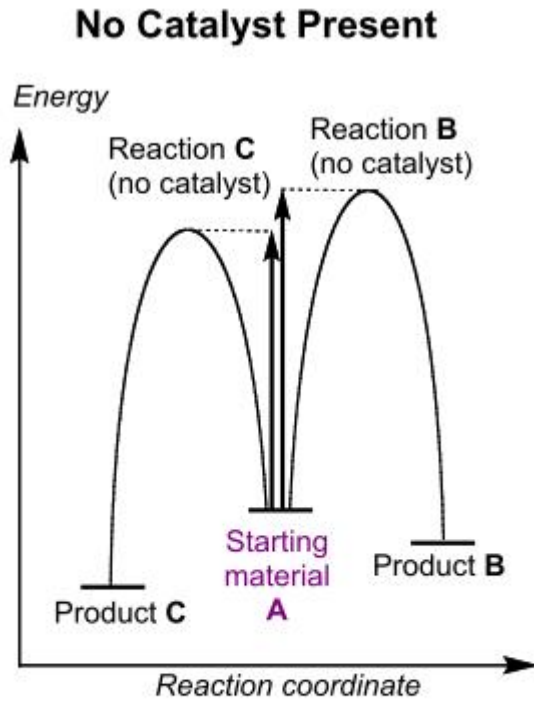


Process in fed-batch

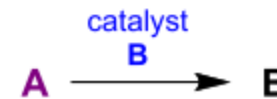
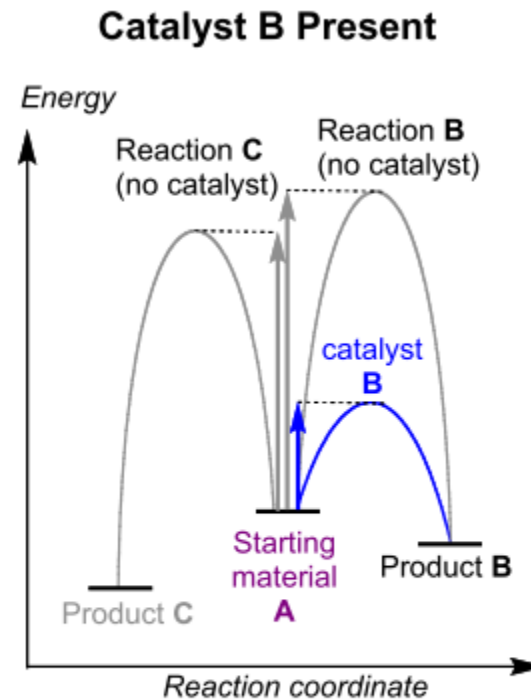


Process in continuous

CATALYSIS: selectivity in the target product



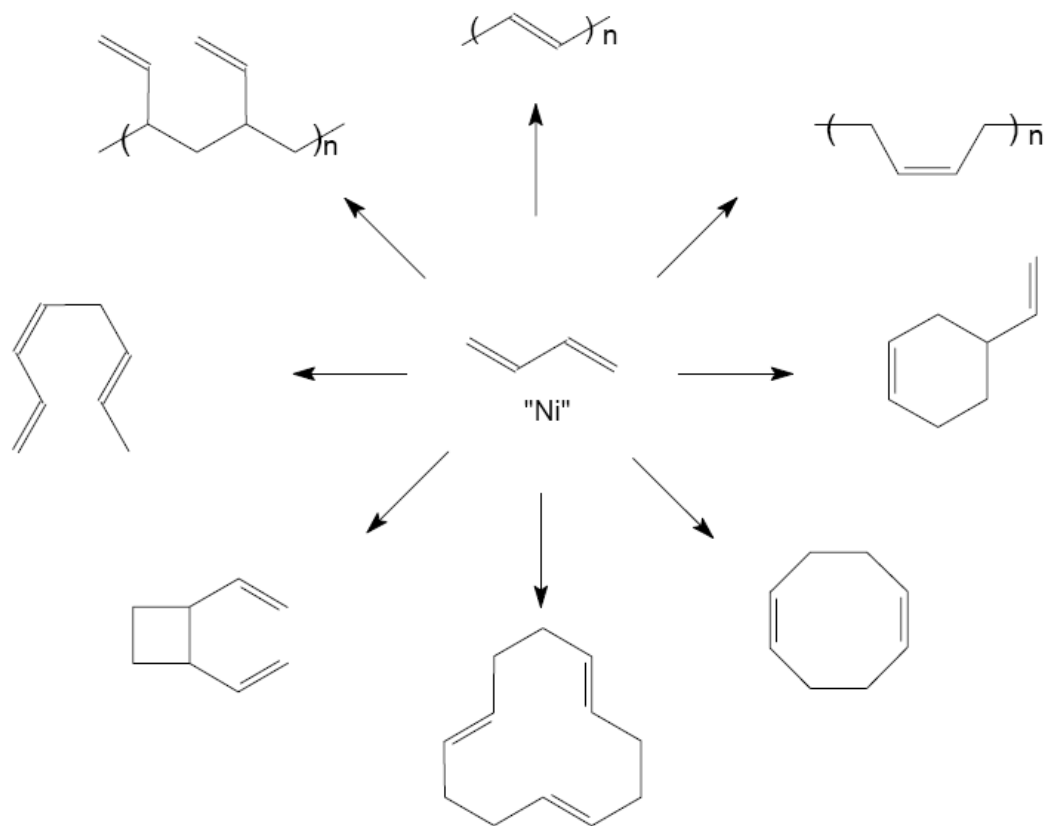
Several products
Separation process is required
Energetically unefficient
Low yield



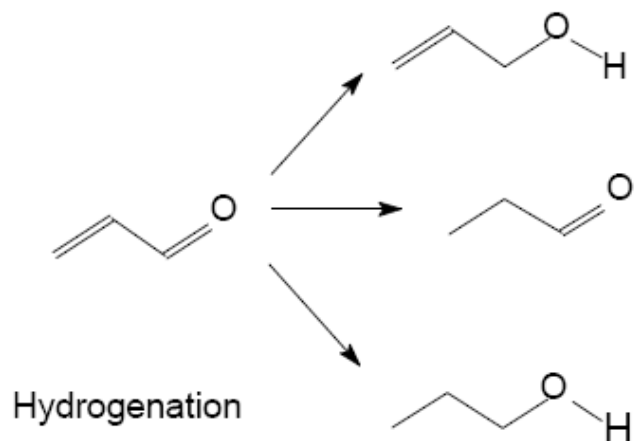
One product only
No separation process required
Energetically efficient
Yield 100%

Catalyst **SELECTIVITY**:

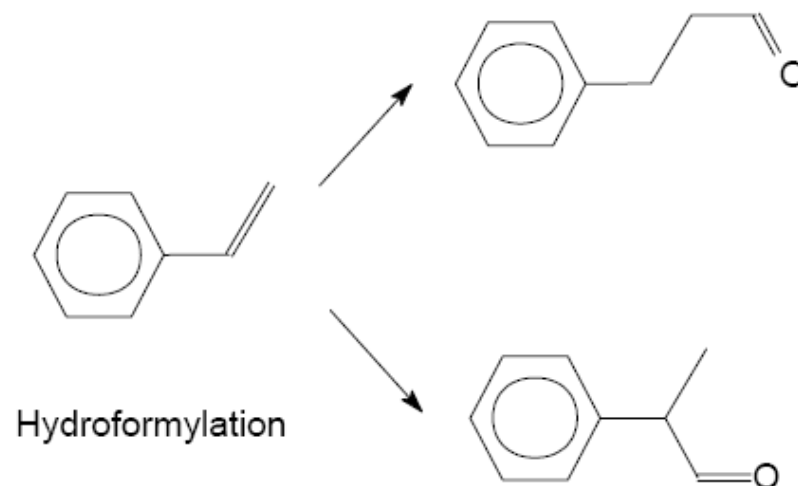
From the **same substrate** it is possible to obtain **different products** by using **different catalysts** based on the **same metal**



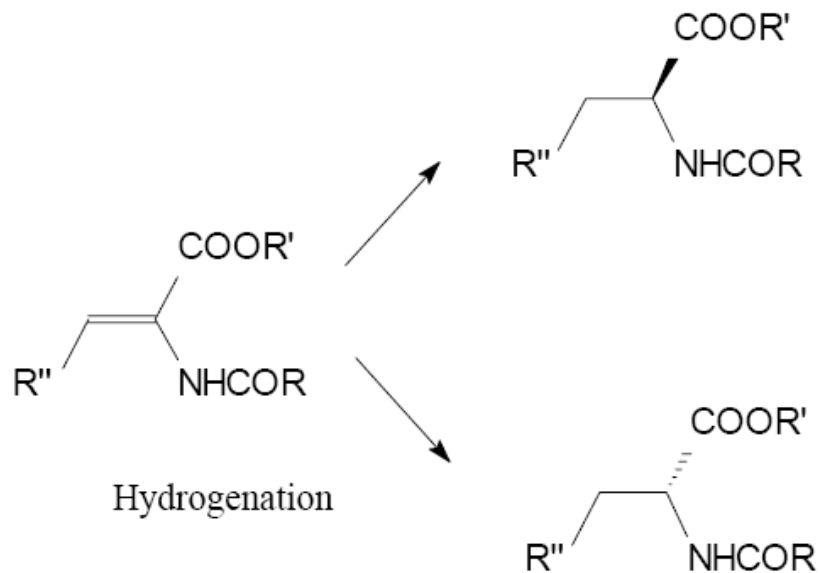
SELECTIVITY of chemical reactions:



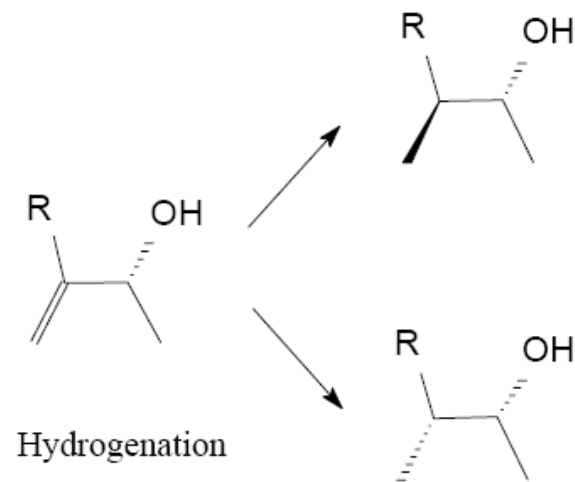
Chemoselectivity



Regioselectivity



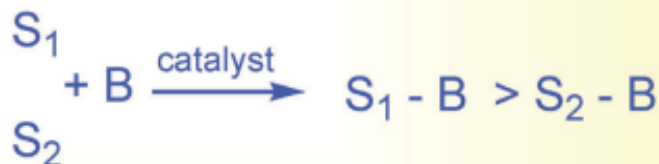
Enantioselectivity



Diastereoselectivity

SUBSTRATE-SELECTIVE CATALYSIS

The catalyst is able to choose only **one substrate** present in **an initial mixture of compounds** and to transform only that one into the desired product.



How the substrate selectivity is measured:

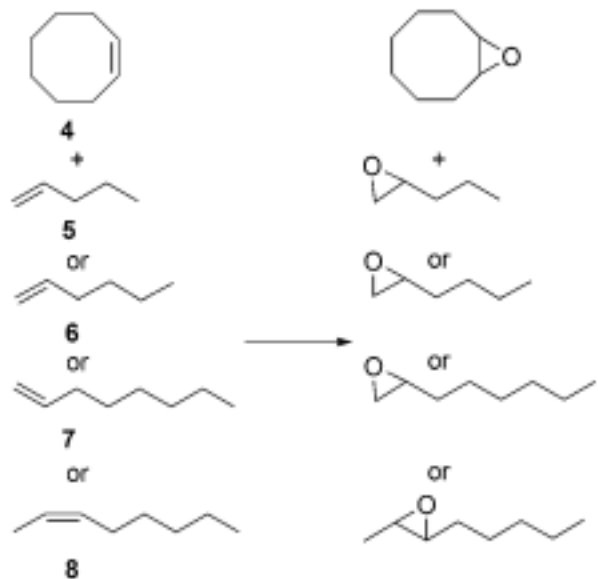
- 1) As the conversion of substrate or as the formation of product?
- 2) As yield or as rate constant?
- 3) In separate single experiments of one substrate at a time or in substrate-competing experiments?

The studied substrate contains the same reacting functionality.

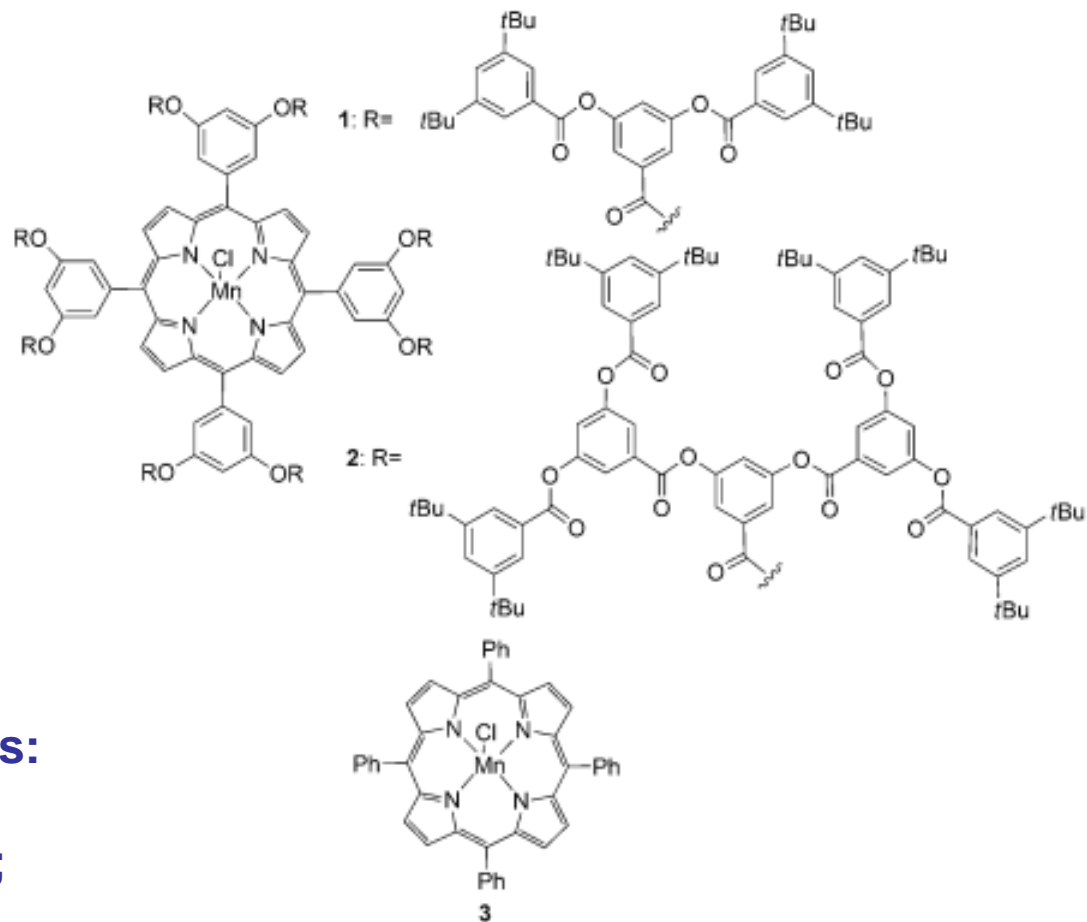
SUBSTRATE-SELECTIVE CATALYSIS

An example

Epoxidation of alkenes



The catalysts



The investigated comparisons:

1 and 2 vs 3;

4 and 5 vs 4 and 6 vs 4 and 7;

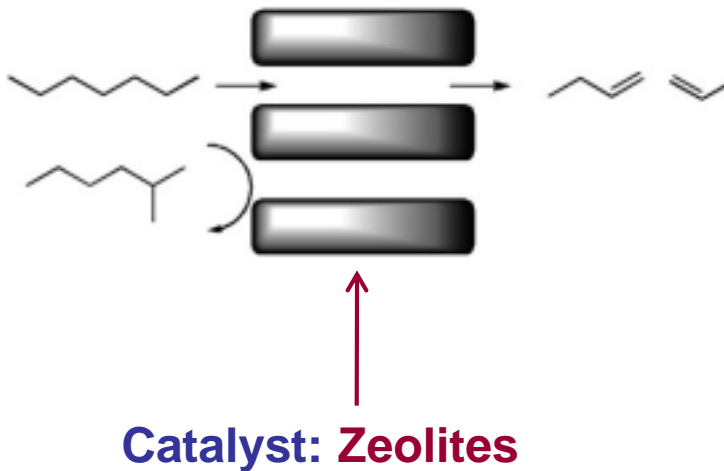
1 vs 2 for 5, 6, 7;

4 and 7 vs 4 and 8.

SUBSTRATE-SELECTIVE CATALYSIS

Example of an industrial application: only heterogeneous catalysts

The steam cracking of hydrocarbons



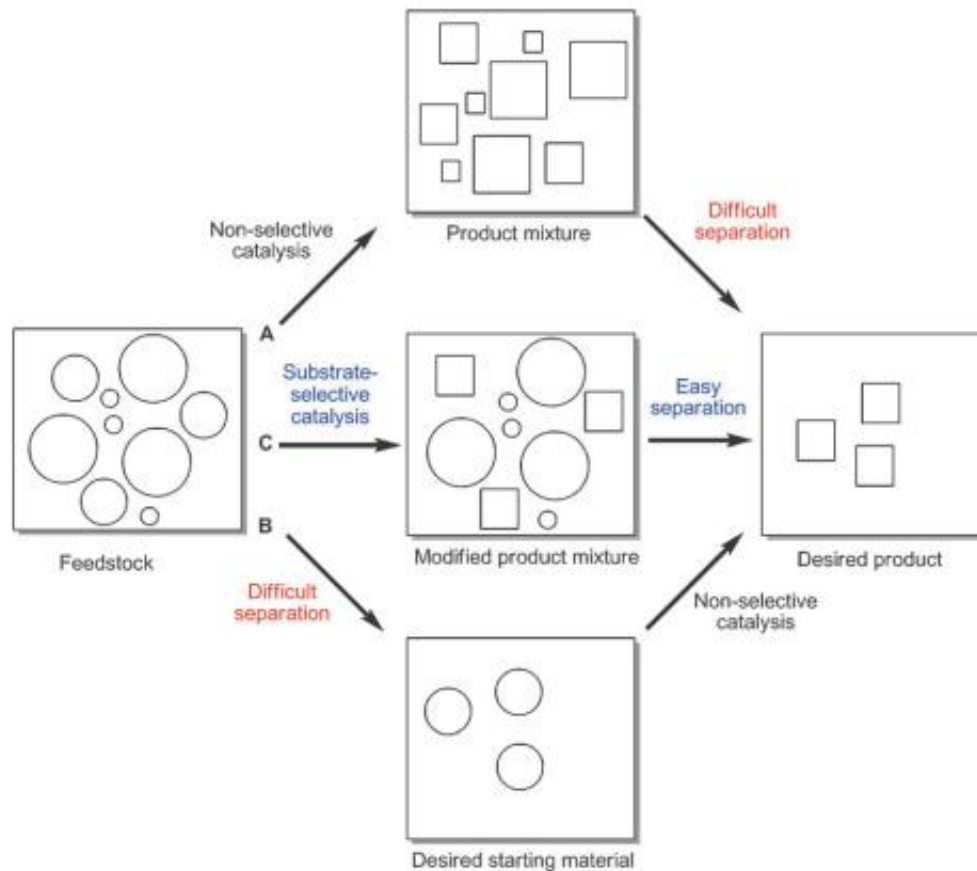
Only linear hydrocarbons are transformed into linear alkenes!

SUBSTRATE-SELECTIVE CATALYSIS

The way of discrimination is based on the following molecular properties:

Size; Shape; Hydrogen bonding; Polarity; Electronic effects due to substituents.

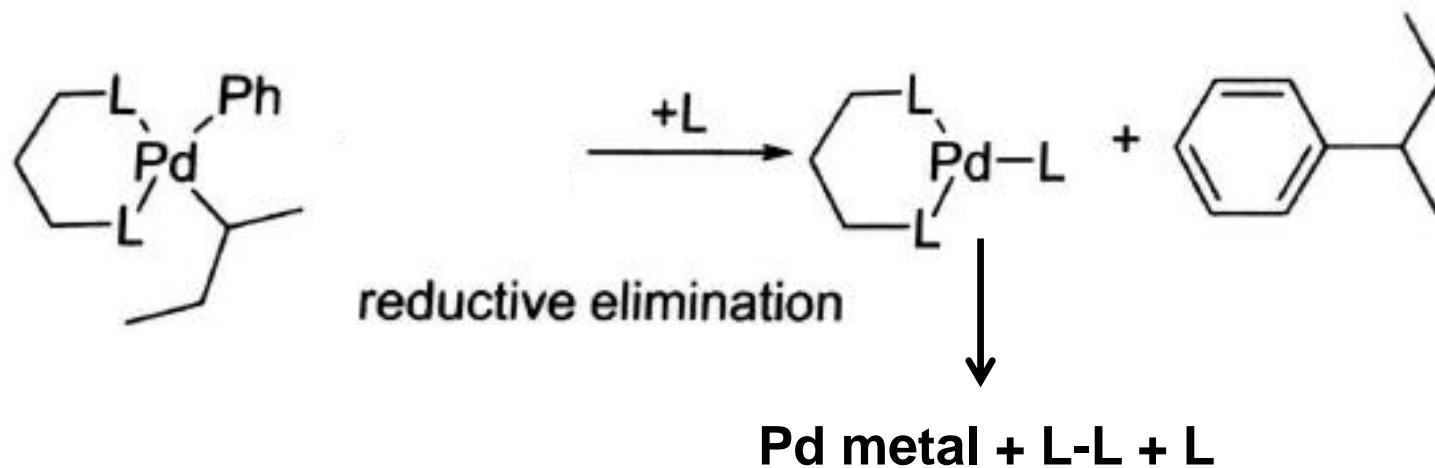
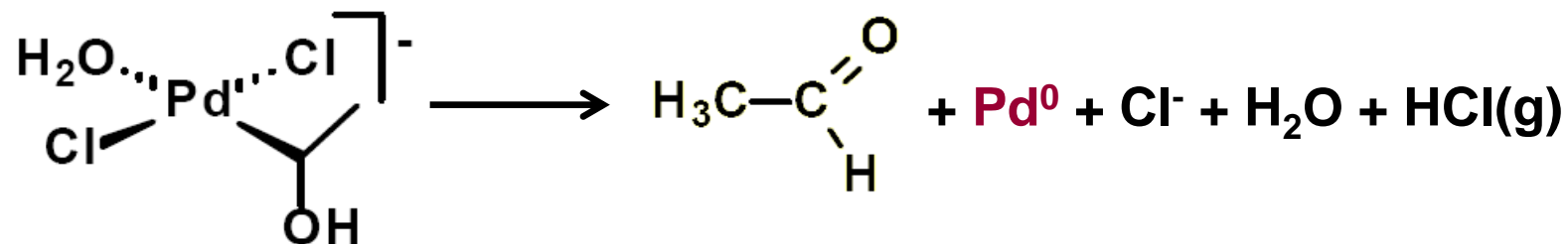
Substrate-selective catalysis in comparison with traditional approaches:



CATALYST STABILITY

METAL

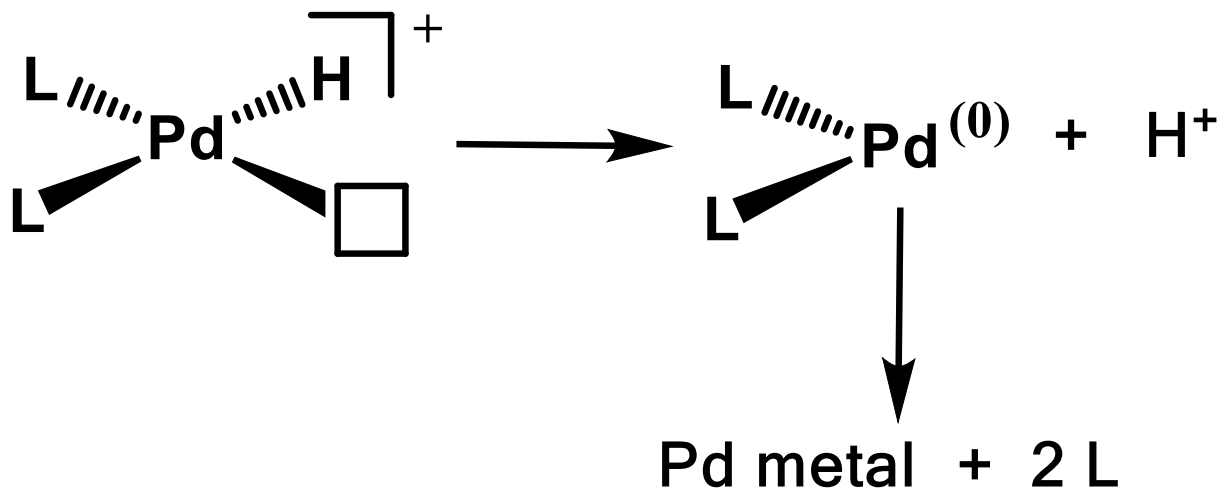
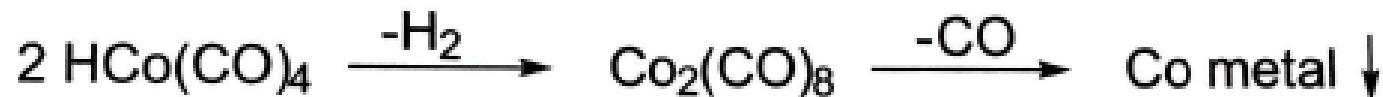
Deactivation through **metal deposition**



CATALYST STABILITY

METAL

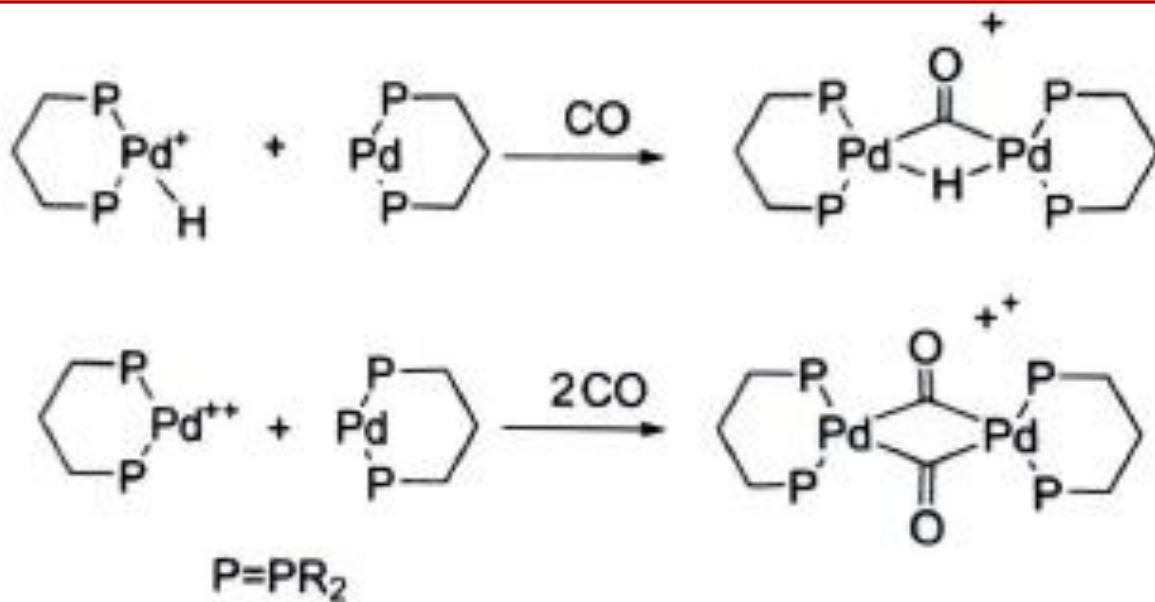
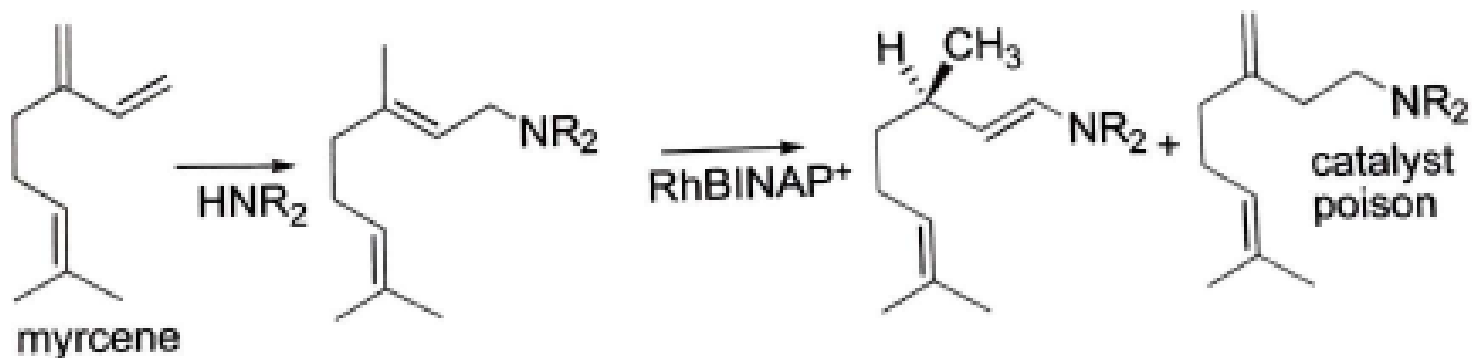
Deactivation through **metal deposition**



CATALYST STABILITY

METAL

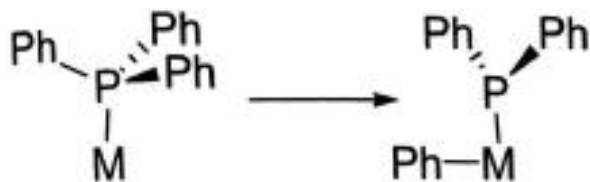
Deactivation through formation of inactive species



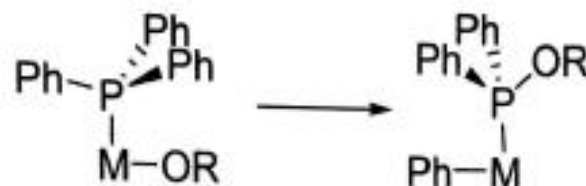
CATALYST STABILITY

LIGANDS

Deactivation through ligand decomposition



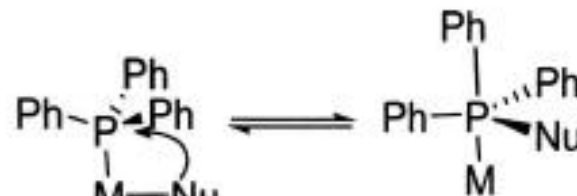
Oxidative addition



Nucleophilic attack



Phosponium ion formation

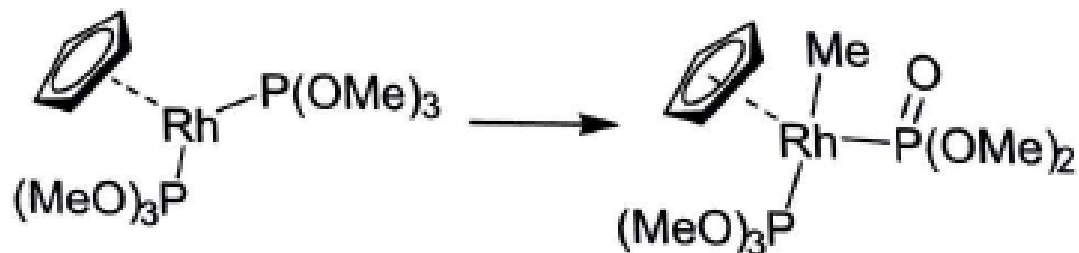
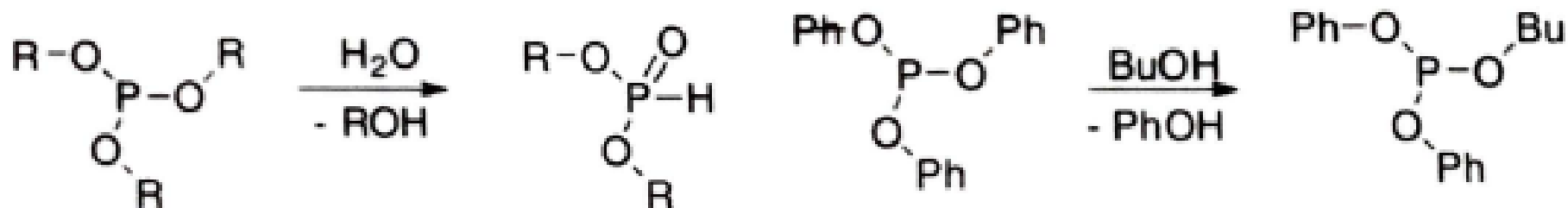


Phosphorane formation

CATALYST STABILITY

LIGANDS

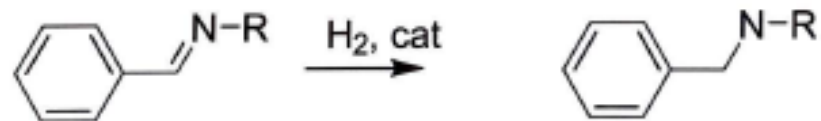
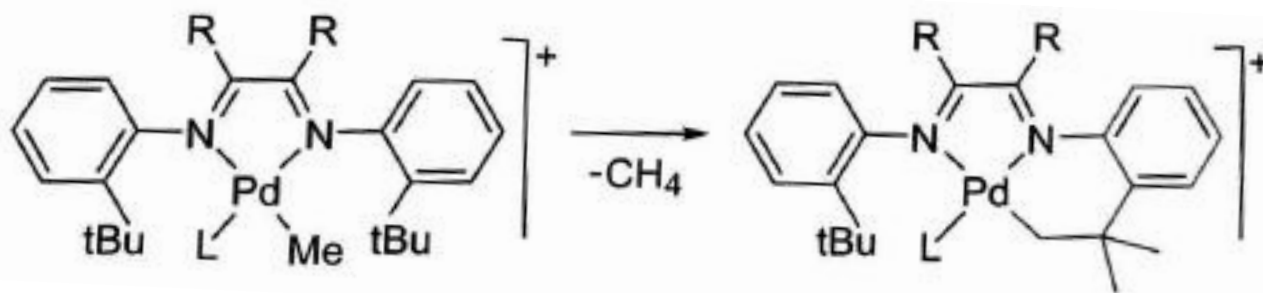
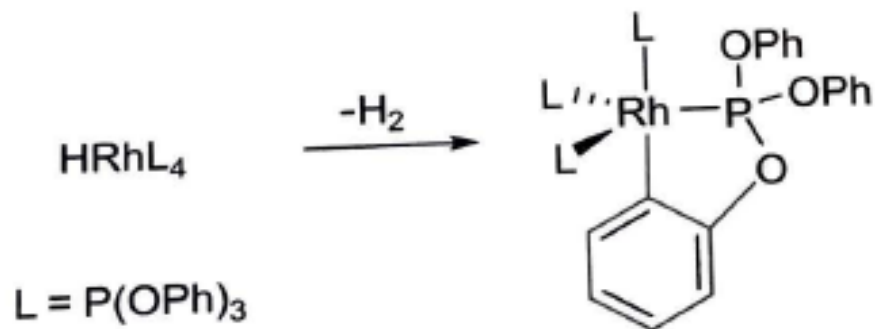
Deactivation through **ligand decomposition**



CATALYST STABILITY

LIGAND and METAL

Deactivation through cyclometalation of the ligand



SUSTAINABILITY

➤ *The main parameters applied to assess the catalyst performances are:*

- ❖ *catalyst activity and productivity;*
- ❖ *catalyst selectivity;*
- ❖ *catalyst stability.*

➤ *Additional parameters applied to assess the industrial exploitation of a catalytic process:*

- ❖ *Sustainability:*
 - ❖ *Metal present in the catalyst;*
 - ❖ *Catalyst recovery and recycling;*
 - ❖ *Selectivity.*

How Catalysis Relies on Exotic Elements

In the last 5 years, the average American (and likely European) has relied on **80** elements for quality of life.

General Electric uses **72** of the first **82** elements in its product line.



Pharmaceuticals

Pd, Rh, Os, Ir



Household Items

Rh, Pt



Refining

La, Pt



Hybrid/Electric Cars

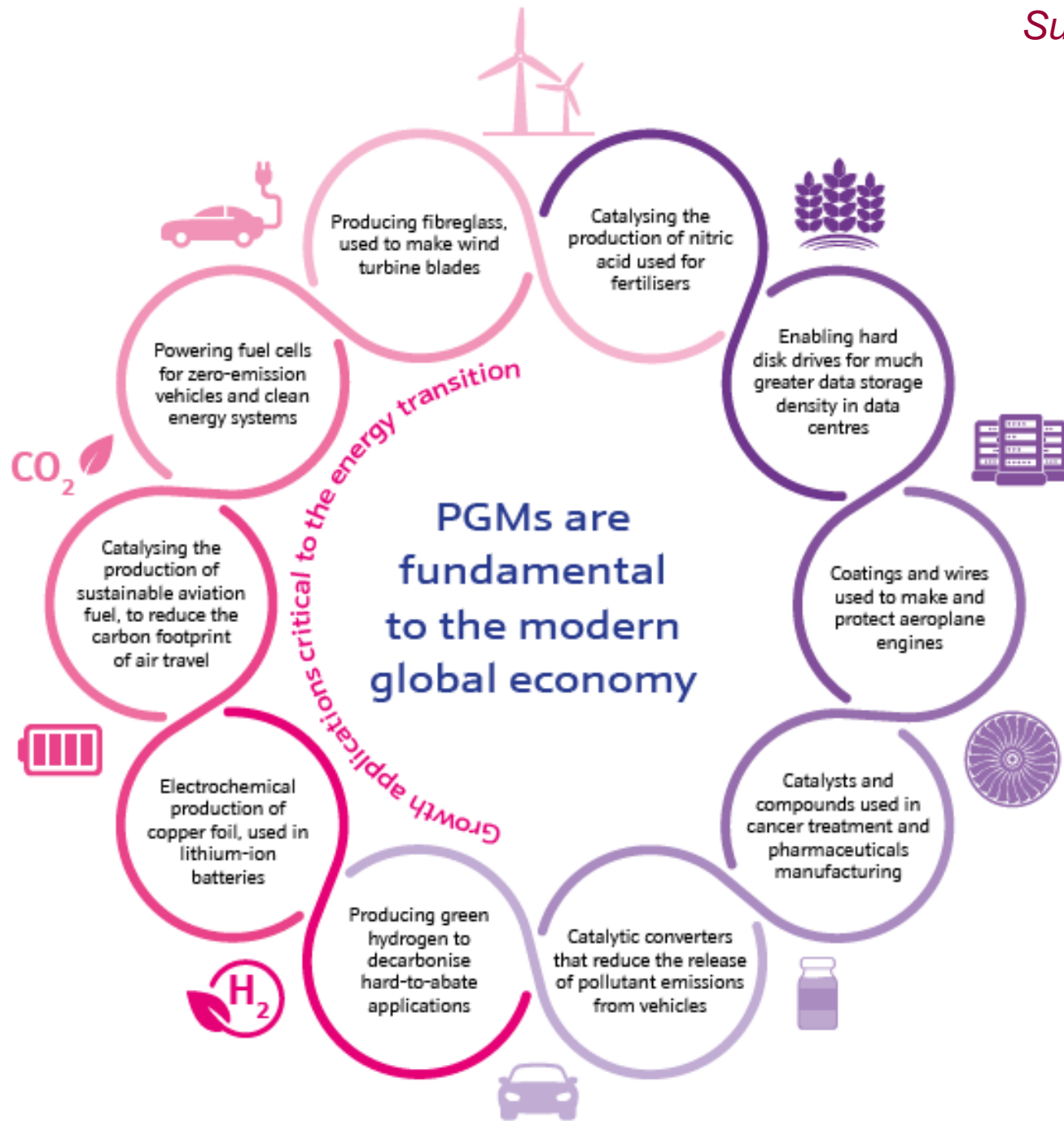
Nd, Tb, Dy, Pr



Alternative Energy

Ru, Nd, Tb, Dy, Pr

McGroarty, D. *Wall Street Journal* 1/31/13
Jaffe, R. *2011 APS-MRS Report*



Cost



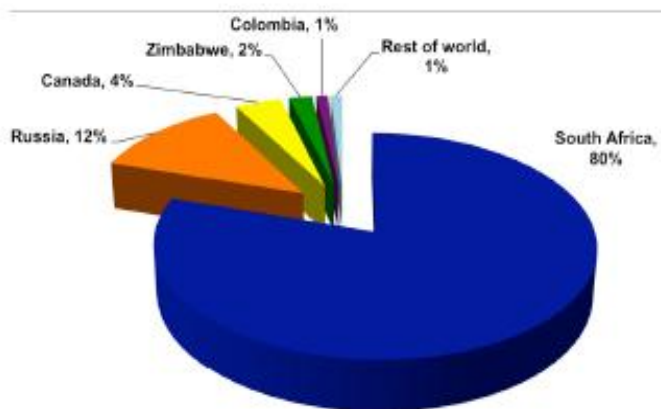
*When does it matter?
What defines expensive?*

Environmental Footprint



*What are the inputs for extraction?
1 ounce Pt = 10-30 tons of ore, 1 mile deep.*

Geopolitics



Who controls the critical elements?

Socioeconomics



Working conditions? Stability of supply?

COST OF SOME TRANSITION METALS

Sustainability

Platinum



\$12,400 per mol

CO₂: >7000 equiv per mol

Iron



\$0.02 per mol

CO₂: 1 equiv per mol

Rh: 208 €/g in 2025

Pd: 31 €/g in 2025

Ru: 23 €/g in 2025

- Annual mining ~ 20 t
- 82 % from South Africa
- 80 % use in car exhaust catalysts

PLATINUM GROUP METALS RECYCLING

Sustainability

Factors enabling PGMs recycling:

- ✓ **The value of the metals;**
- ✓ **Recycled PGMs are physically indistinguishable from “virgin” metal;**
- ✓ **PGMs can be recycled many times;**
- ✓ **Recycling does not change PGMs physical properties;**
- ✓ **Recycled PGMs have about 97 % lower global warming potential than newly mined metal.**

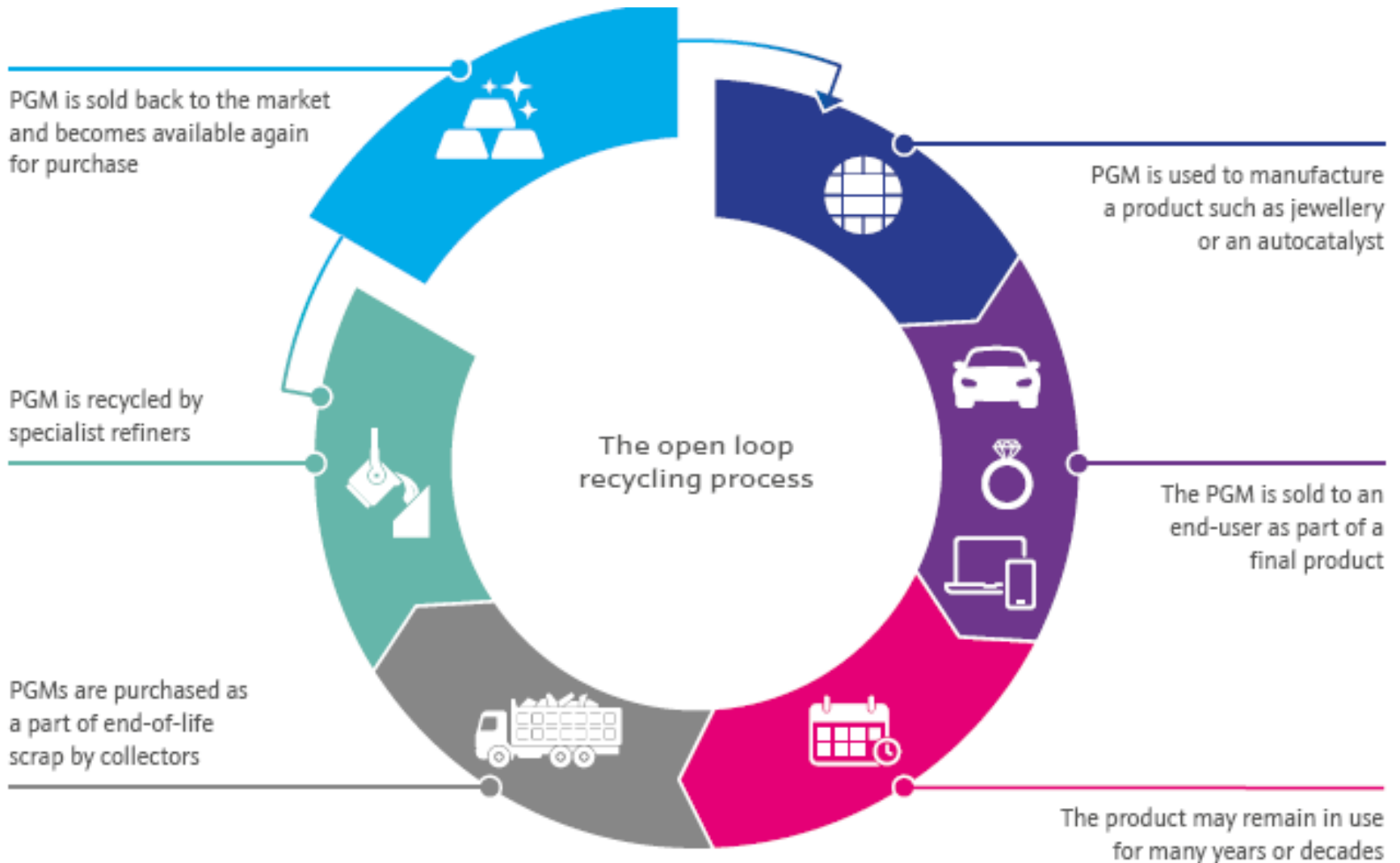
The recycling of PGMs is called urban PGM mine to differentiate it from the primary mining.

In terms of market supply, the recycled PGMs are referred to as secondary supply, whereas the mined PGMs are referred to as primary supply.

TWO WAYS OF PGMS RECYCLING

Sustainability

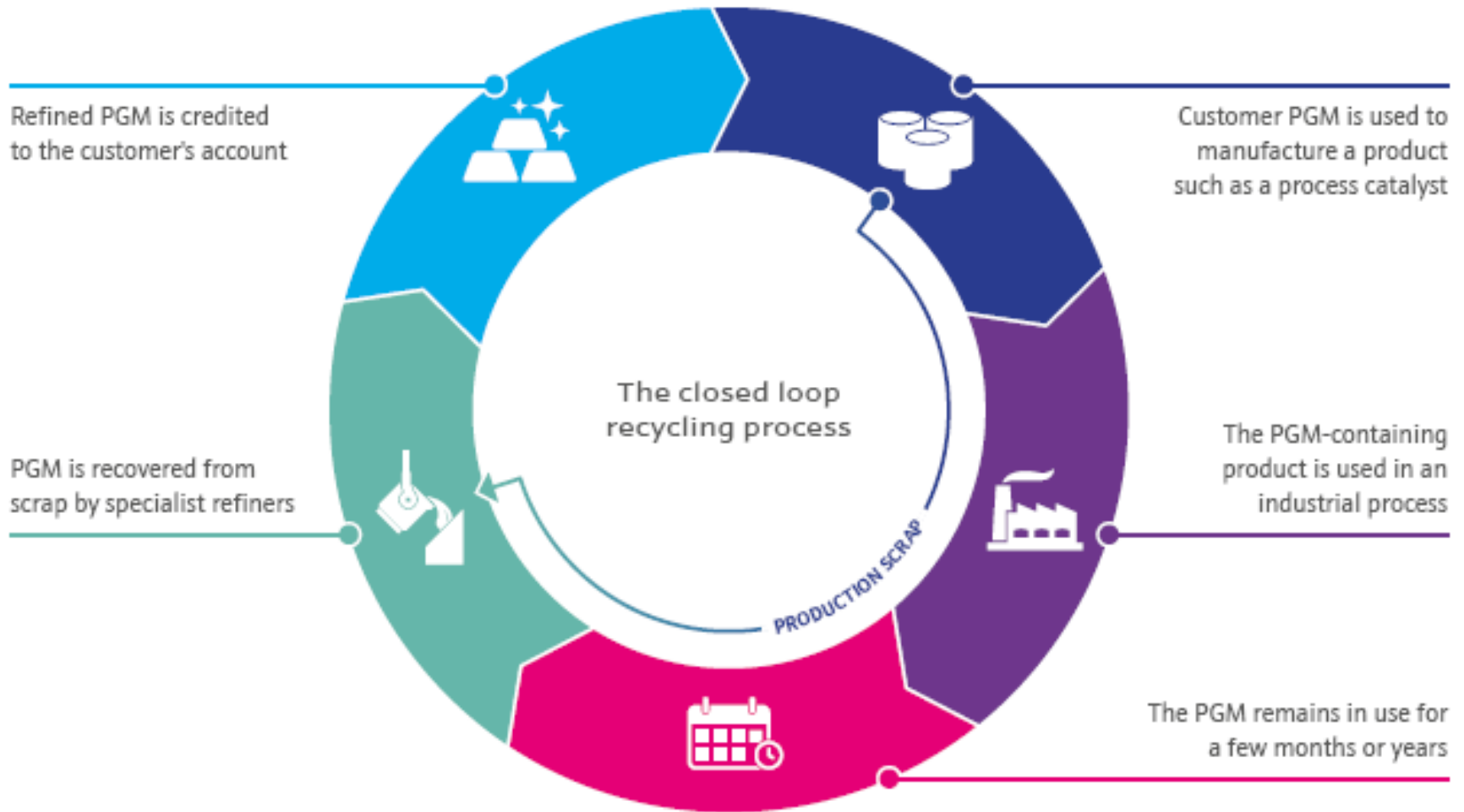
Open loop recycling



TWO WAYS OF PGMs RECYCLING

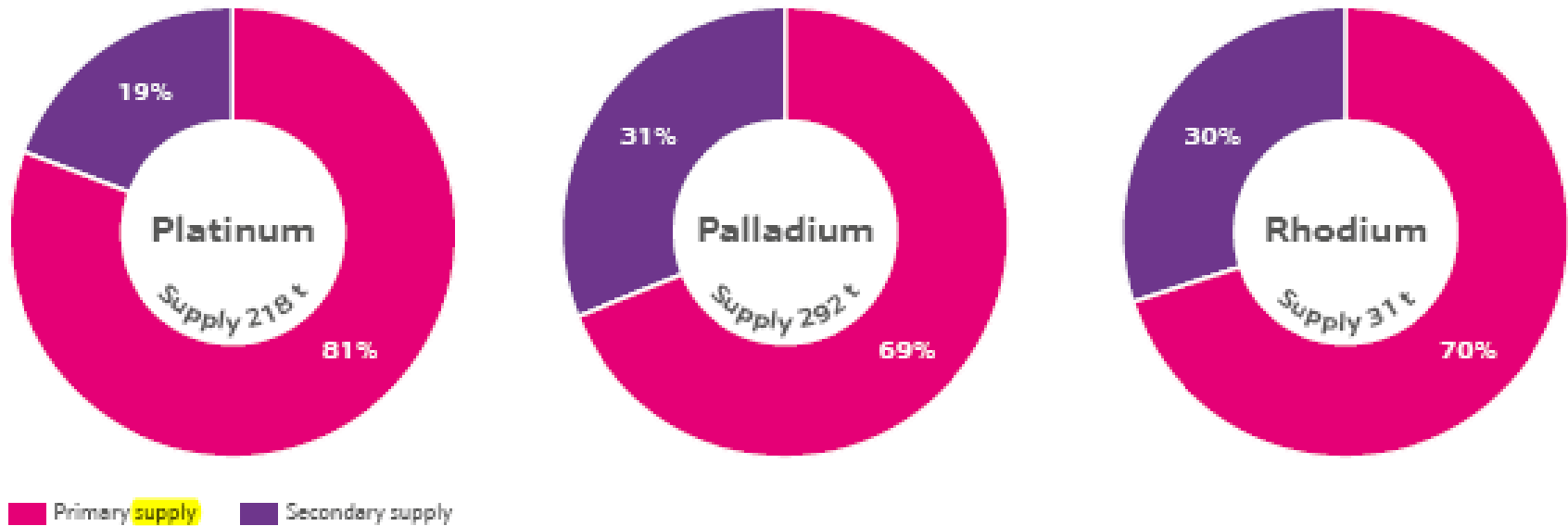
Sustainability

Close loop recycling

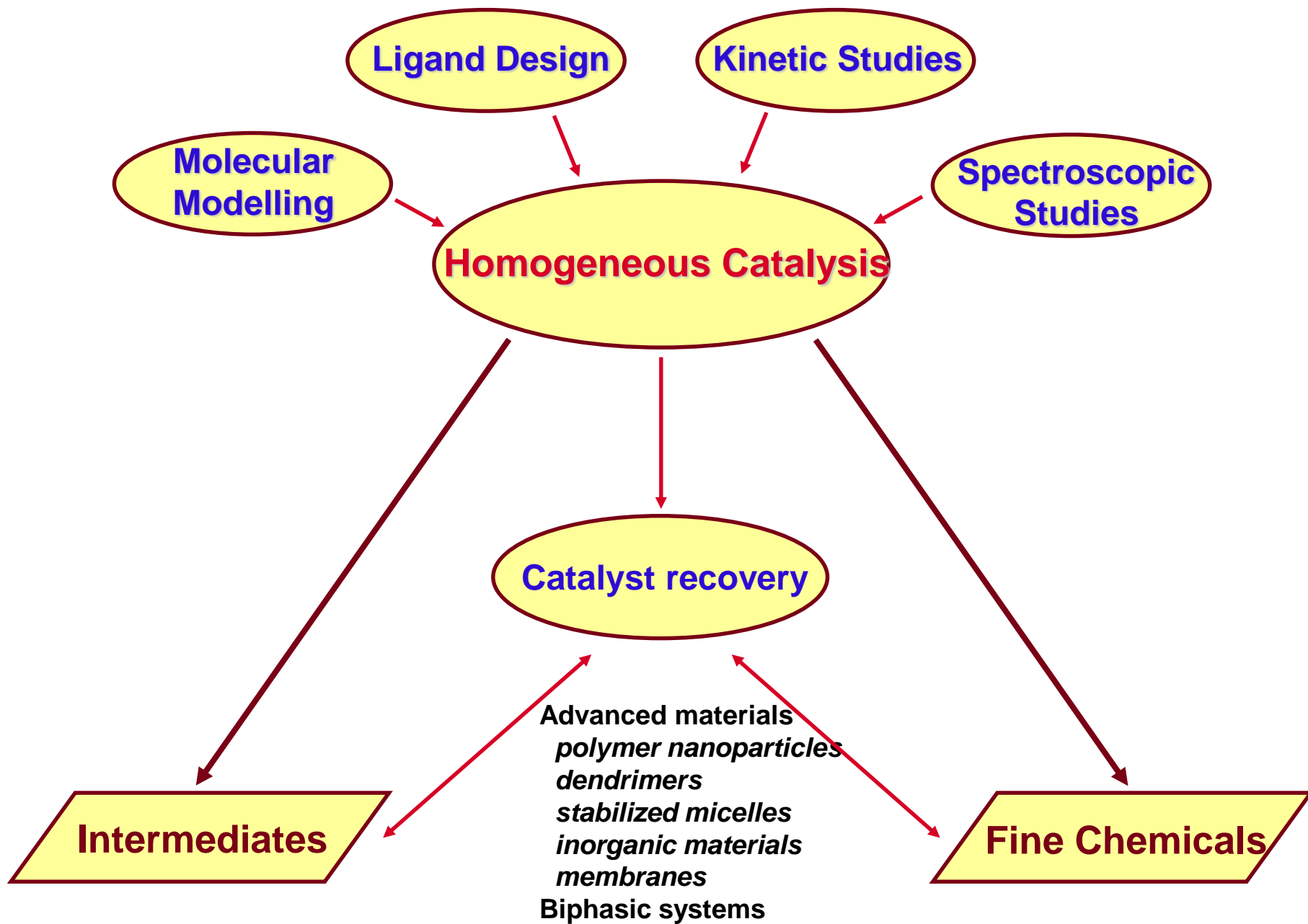


TWO WAYS OF PGMs RECYCLING

A case study

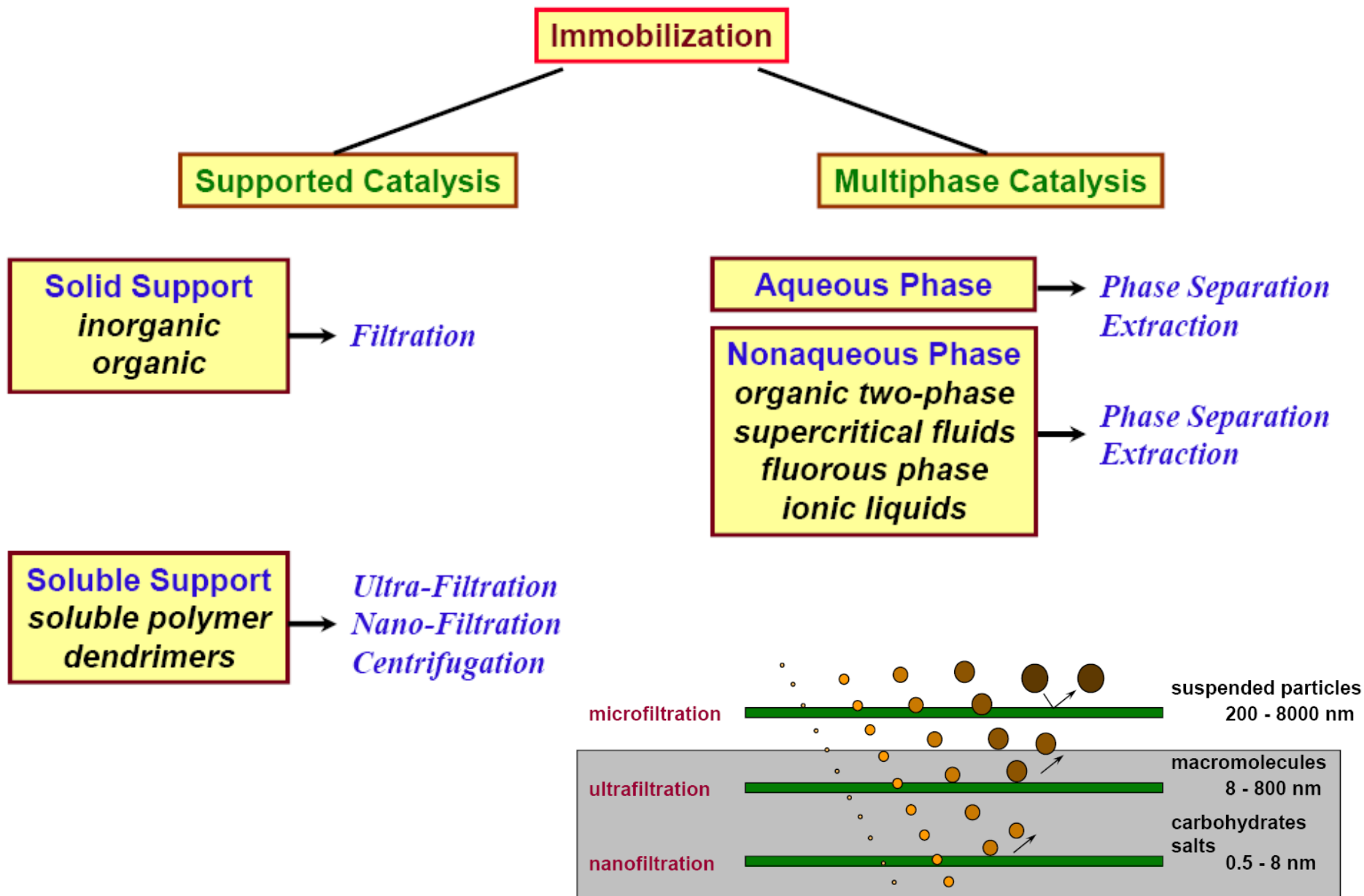


More general, **60 % of PGMs** used on new and replacement products is now **recycled metal**.

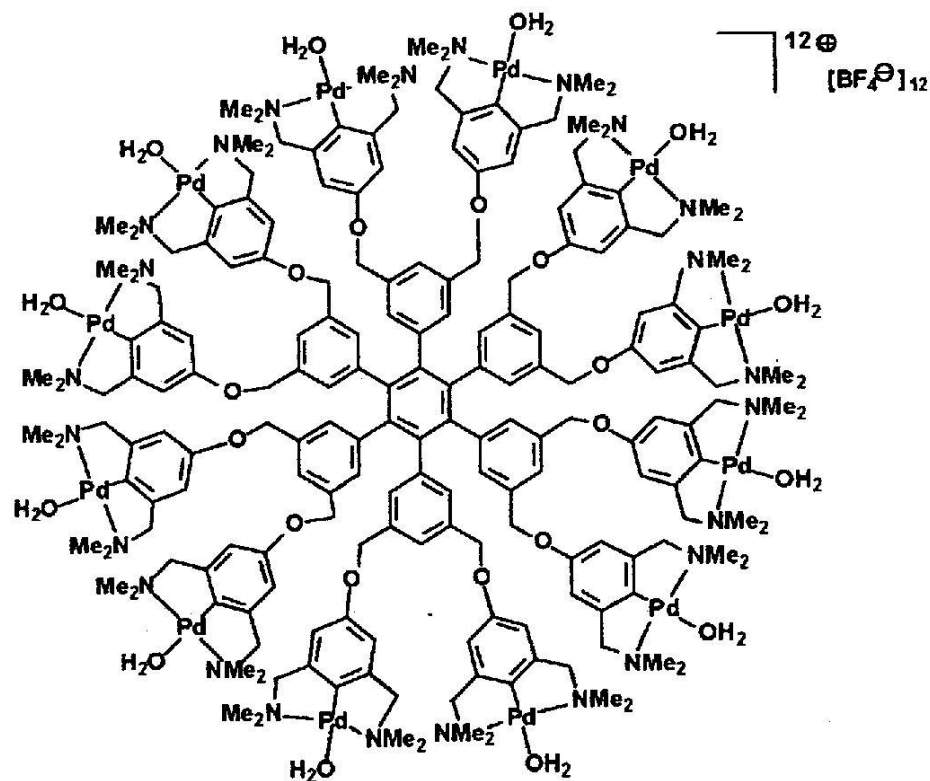
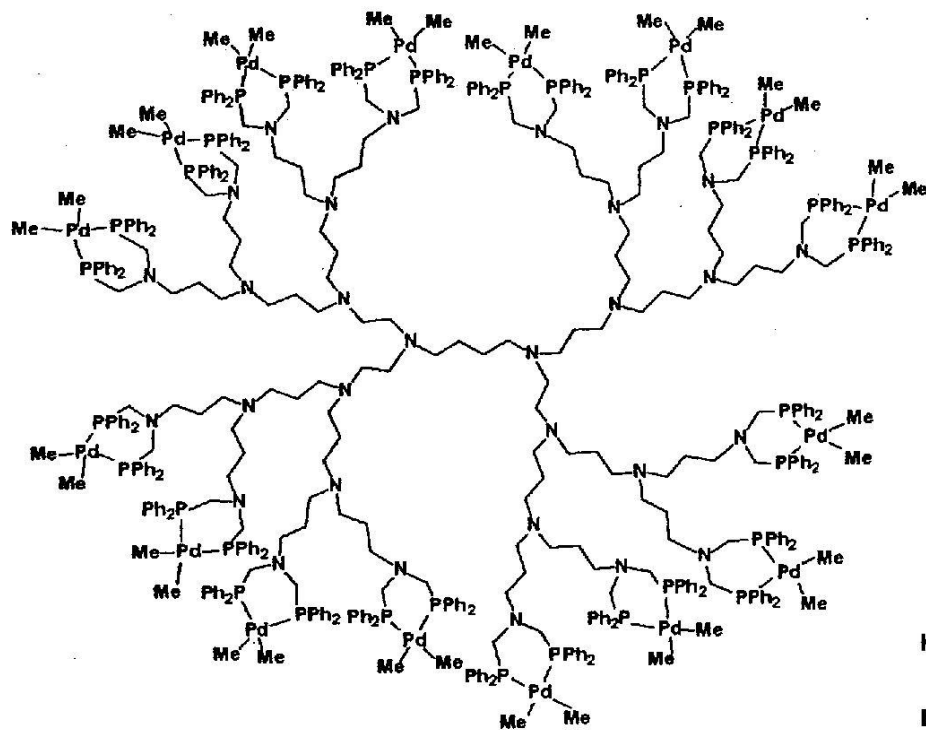


Immobilization of homogeneous catalysts

Sustainability

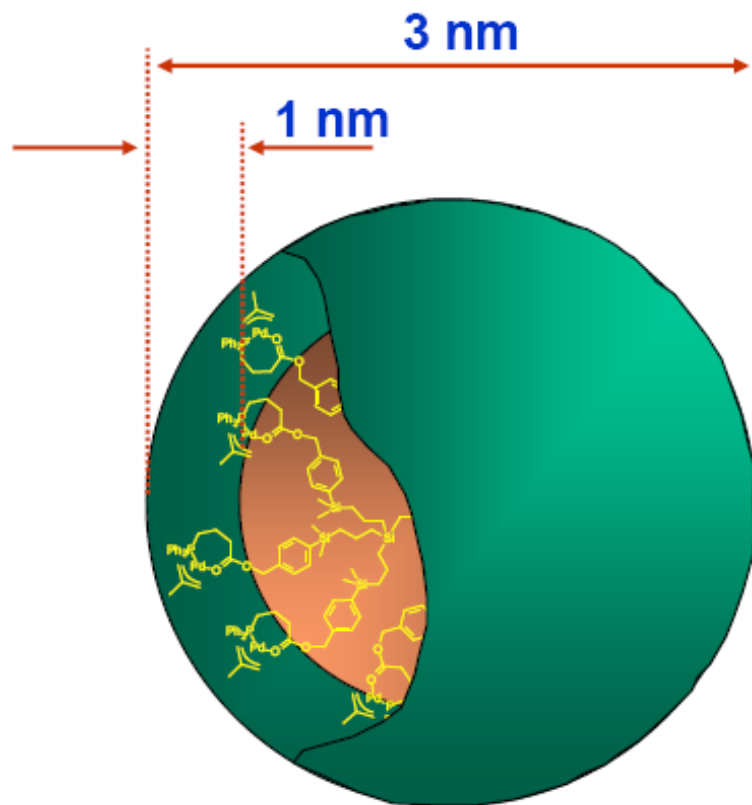


Dendrimers as an example of soluble supports



Dendritic Effect

High local concentration of active sites



12 Pd complexes concentrated within a shell of 9.95 nm^3



$[\text{Pd}] = 2 \text{ mol/L}$

In normal catalytic runs in solution



$[\text{Pd}] = 5 \text{ mmol/L}$

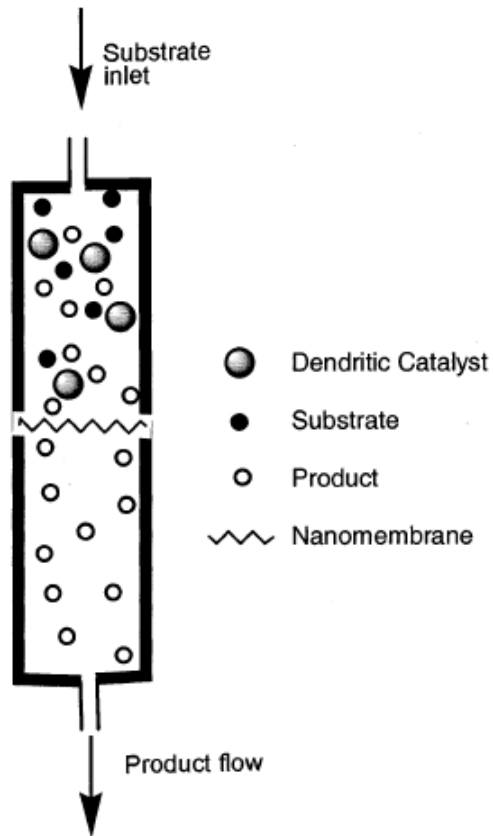
Dendrimers in continuous homogeneous catalysis

❑ Process in
“batch”

❑ Continuous Flow Membrane
Reactor CFMR

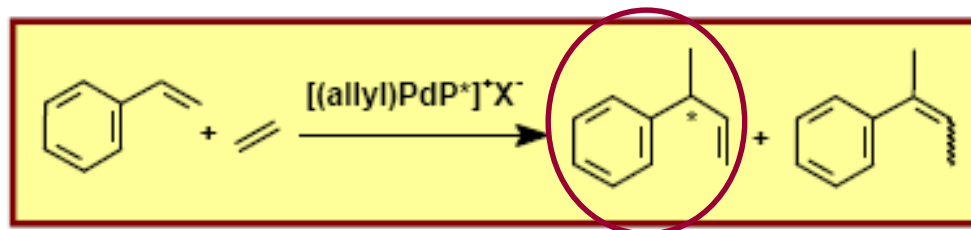
Drawbacks:

- ❑ Leakage of the catalyst through the membrane;
- ❑ the metal leaves the ligand and goes through the membrane;
- ❑ Dendrimers synthetic procedure;
- ❑ Characterization of the dendrimer and the metal-dendrimer system.

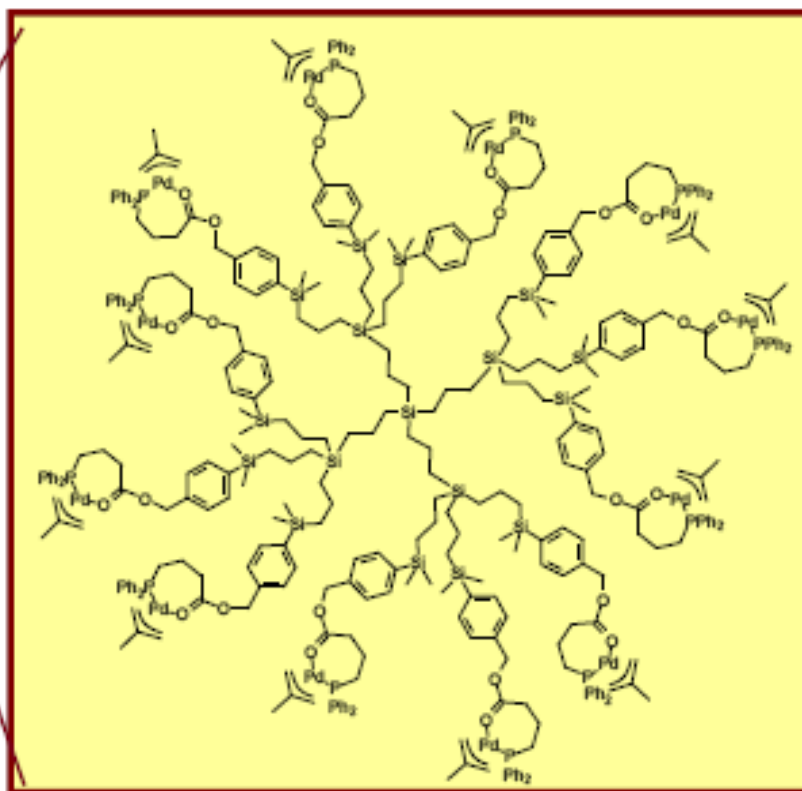


Dendrimers as an example of soluble supports

Hydrovinylation of Styrene

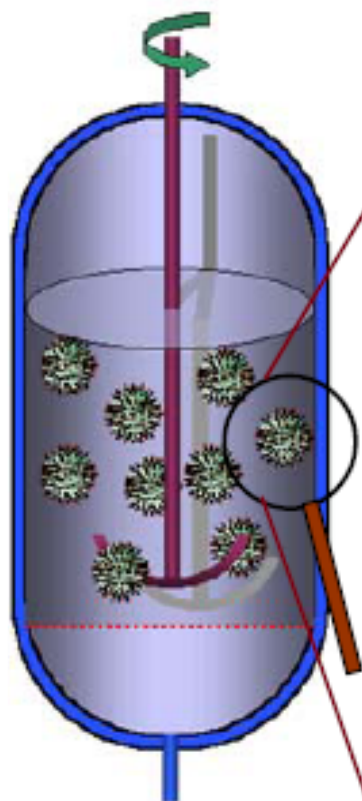


Carbosilane Dendrimer



Higher selectivity in the product with respect to the model compound.

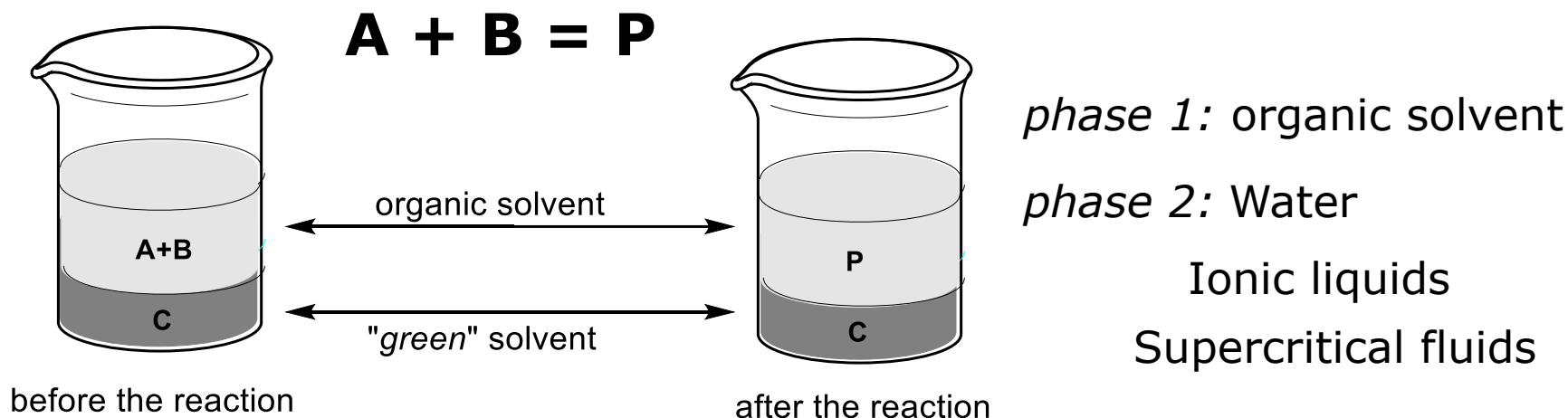
High retention (98 %) of G₁-dendrimer.



Homogeneous catalysis in biphasic system *Sustainability*

The catalyst is dissolved in one liquid phase and reactants and products are dissolved in a second liquid phase, selectively.

The reaction takes place either at the interface or inside one phase, only.

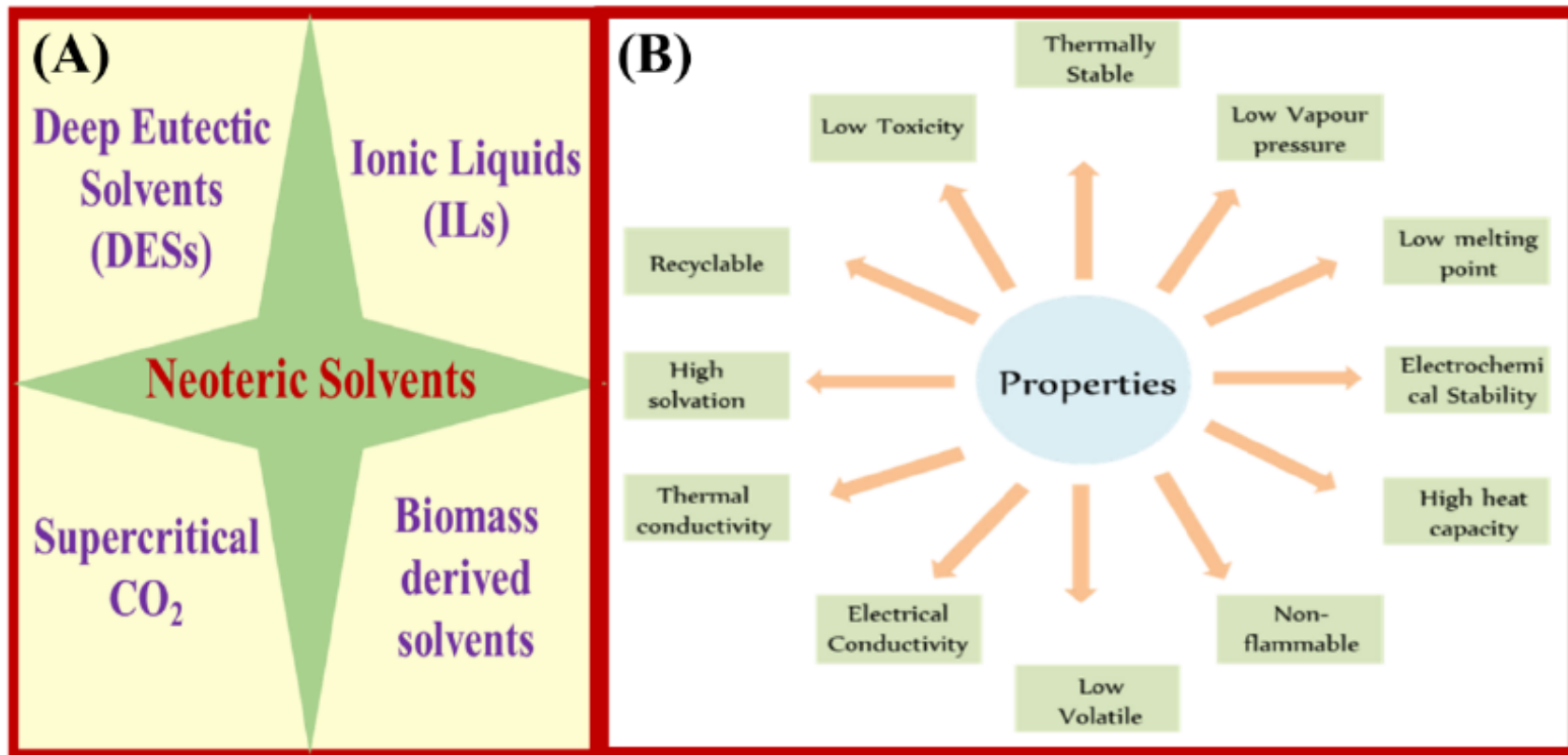


Requirements:

- the two solvents do not have to be miscible;
- A proper transfer of compounds between the two phases;
- Catalyst and product need to have a different solubility in the two phases.

New class of solvents

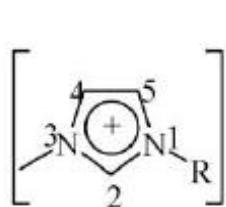
Their properties



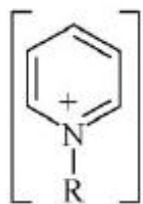
Ionic Liquids

Sustainability

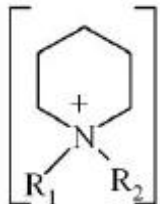
They are **anhydrous salts**; melting temperature $< 100\text{ }^\circ\text{C}$; negligible vapor pressure; thermally stable; recyclability; toxicity?



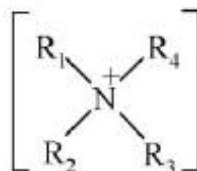
1-alkyl-3-methylimidazolium



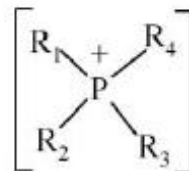
N-alkylpyridinium



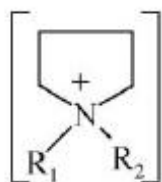
N-alkyl-N-methylpiperidinium



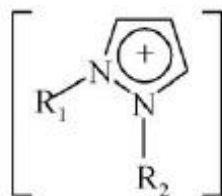
Tetraalkylammonium



Tetraalkylphosphonium



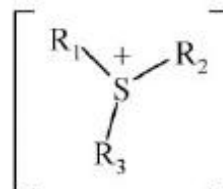
N-alkyl-N-methylpyrrolidinium



1,2-dialkylpyrazolium



N-alkylthiazolium



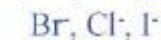
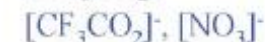
Trialkylsulfonium

$R_{1,2,3,4} = \text{CH}_3(\text{CH}_2)_n$, ($n = 1, 3, 5, 7, 9$); aryl; etc.

water-immiscible



water-miscible

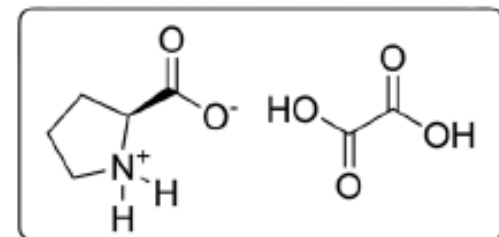
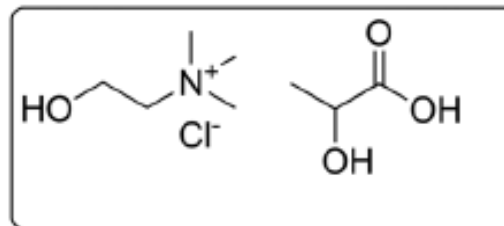
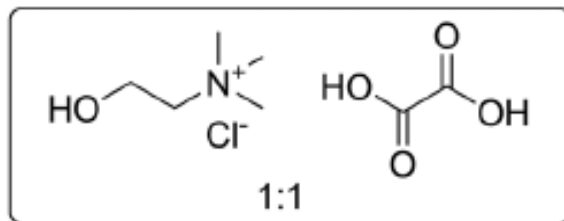
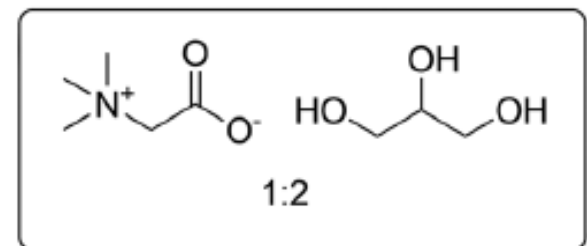
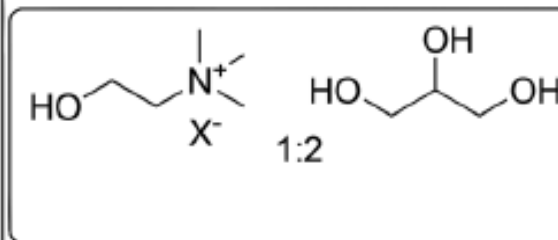
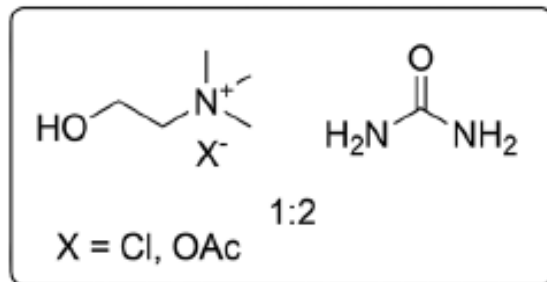


Deep eutectic solvents

Sustainability

They are formed by mixing a **hydrogen bond donor (HBD)** with an **ammonium or phosphonium salt**.

easy to be synthesized; low melting temperature;
negligible vapor pressure; thermally stable;
recyclability; non-toxic and biodegradable.



METALS OF FIRST TRANSITION ROW VS METALS OF SECOND AND THIRD SERIES

Sustainability

FIRST SERIES

Δ depends on ligands

High-spin and low-spin states available

Often unpaired e-

The highest oxidation state is not very stable (MnO_4^- is a strong oxidant)

SECOND/THIRD SERIES

Larger Δ

Preferentially low-spin states

Preferentially paired e-

The highest oxidation state is rather stable (ReO_4^- is not a strong oxidant)

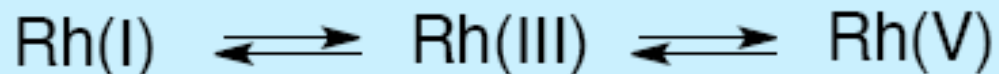
Similar atomic radii

Second series more reactive than the third one.

METALS OF FIRST TRANSITION ROW VS METALS OF SECOND AND THIRD SERIES

SECOND/THIRD SERIES

Oxidation states differ of two units



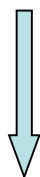
FIRST SERIES

Oxidation states differ of one unit



High **SELECTIVITY** in chemical reactions is a way to:

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



12 principles of **GREEN CHEMISTRY**

1. Waste prevention not remediation
2. Atom efficiency
3. Less hazardous/toxic materials
4. Safer products by design
5. Innocuous solvents and auxiliaries
6. Energy efficient by design
7. Renewable rather than depleting raw material
8. Shorter synthesis (avoid derivatization)
9. Catalytic rather than stoichiometric reagents
10. Design products for degradation
11. Analytical methods for pollution prevention
12. Inherently safer processes

Two of the 12 principles of **GREEN CHEMISTRY**

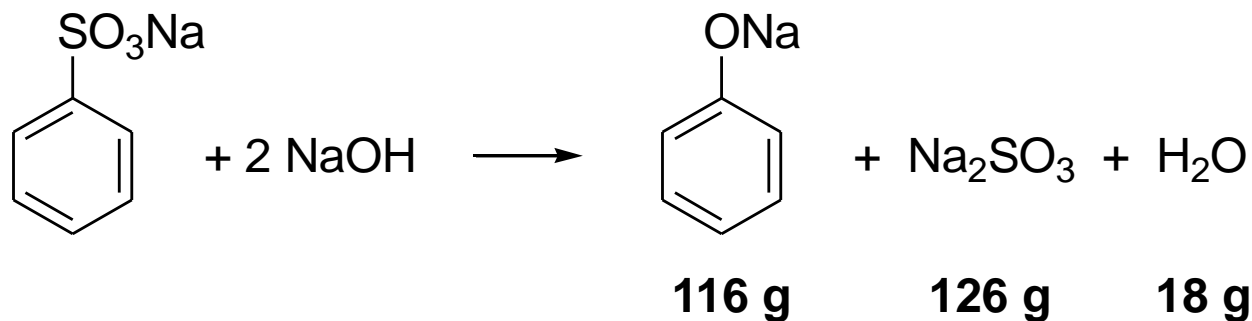
2. ATOM ECONOMY/EFFICIENCY: synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.

9. CATALYSIS: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Catalysis as a tool for small molecules activation:

H_2	source of H
O_2	source of O
CO_2 and CO	source of C
N_2	source of N

ATOM ECONOMY: synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product. In other words, most of the atoms of reagents should be found in the target product.



Atom efficiency with respect to C: 100 %;

Atom efficiency with respect to S: 0 %.

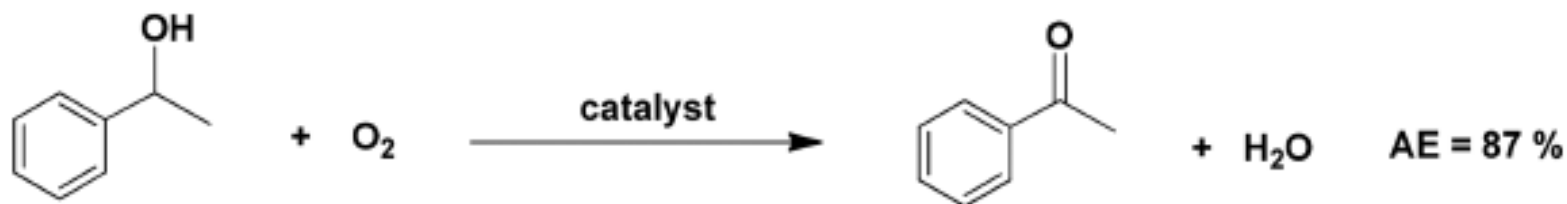
ATOM ECONOMY: molecular weight of the target product divided by the sum of the molecular weights of **all the products** in the stoichiometric equation.

i.g.: $116/260 = 44.9 \%$

Hydrogenation



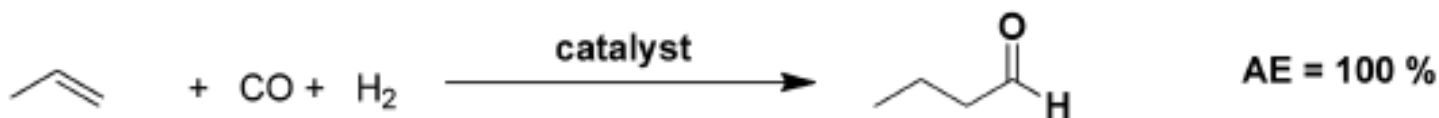
Oxidation



Carbonylation



Hydroformylation



E FACTOR : the total mass of waste formed per mass of target product (kg waste/kg product).

Reaction yield is taken into account;

WATER is excluded, it is not considered as a waste;

Solvent is included if it is not fully recycled.

E Factor is an **additive metric**: E Factor for multi-step processes is obtained by adding the E Factor of individual steps.

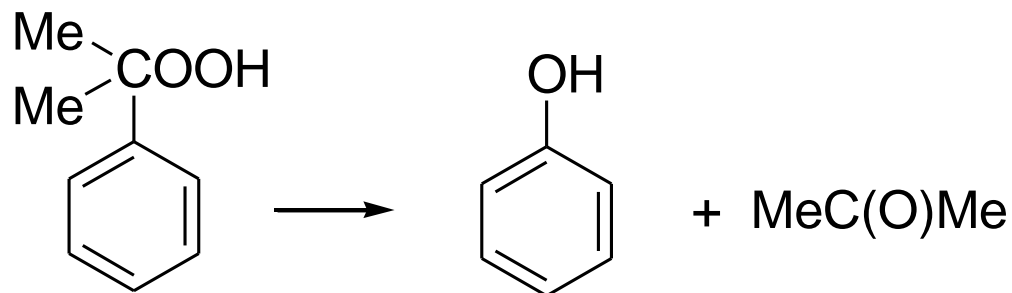
E Factor for an **ideal process** is.....?

In the example for a yield of 100 %, the E factor is $126/116 = 1.09$

Table 1 E Factors in the chemical industry

Industry segment	Product tonnage (p/a)	E-Factor (kgs waste/kg product)
Oil refining	10^6 – 10^8	<0.1
Bulk chemicals	10^4 – 10^6	<1–5
Fine chemicals	10^2 – 10^4	5–50
Pharmaceuticals	10 – 10^3	25–>100

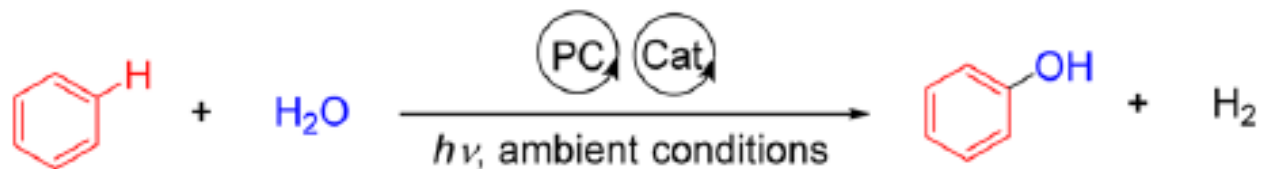
Current process industrially applied for the synthesis of phenol: the **cumene** process



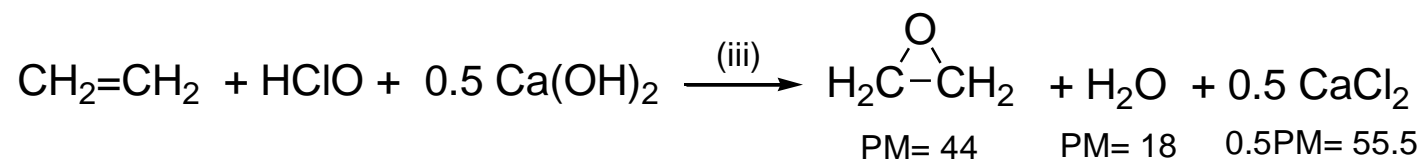
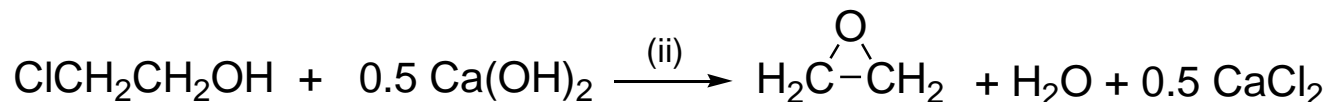
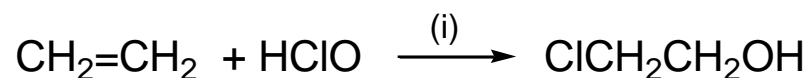
ATOM EFFICIENCY = 100 %

E FACTOR = 0

Process under investigation for the synthesis of phenol

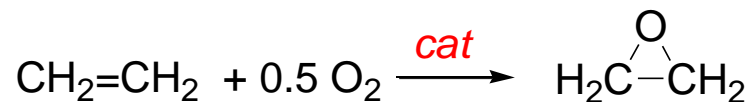


Traditional process industrially applied for ethylene oxide synthesis (chlorohydrin process):



ATOM EFFICIENCY = 37 %

Innovative process industrially applied for ethylene oxide synthesis:



ATOM EFFICIENCY = 100 %

EQ FACTOR: Environmental Quotient; it considers the environmental impact of waste.

EQ is obtained by multiplying the E factor by an **arbitrarily** assigned unfriendliness **quotient Q**: the higher it is, the most hazardous is the material.

The **quotient Q** for the same compound varies on the basis of the produced amount of the compound itself.

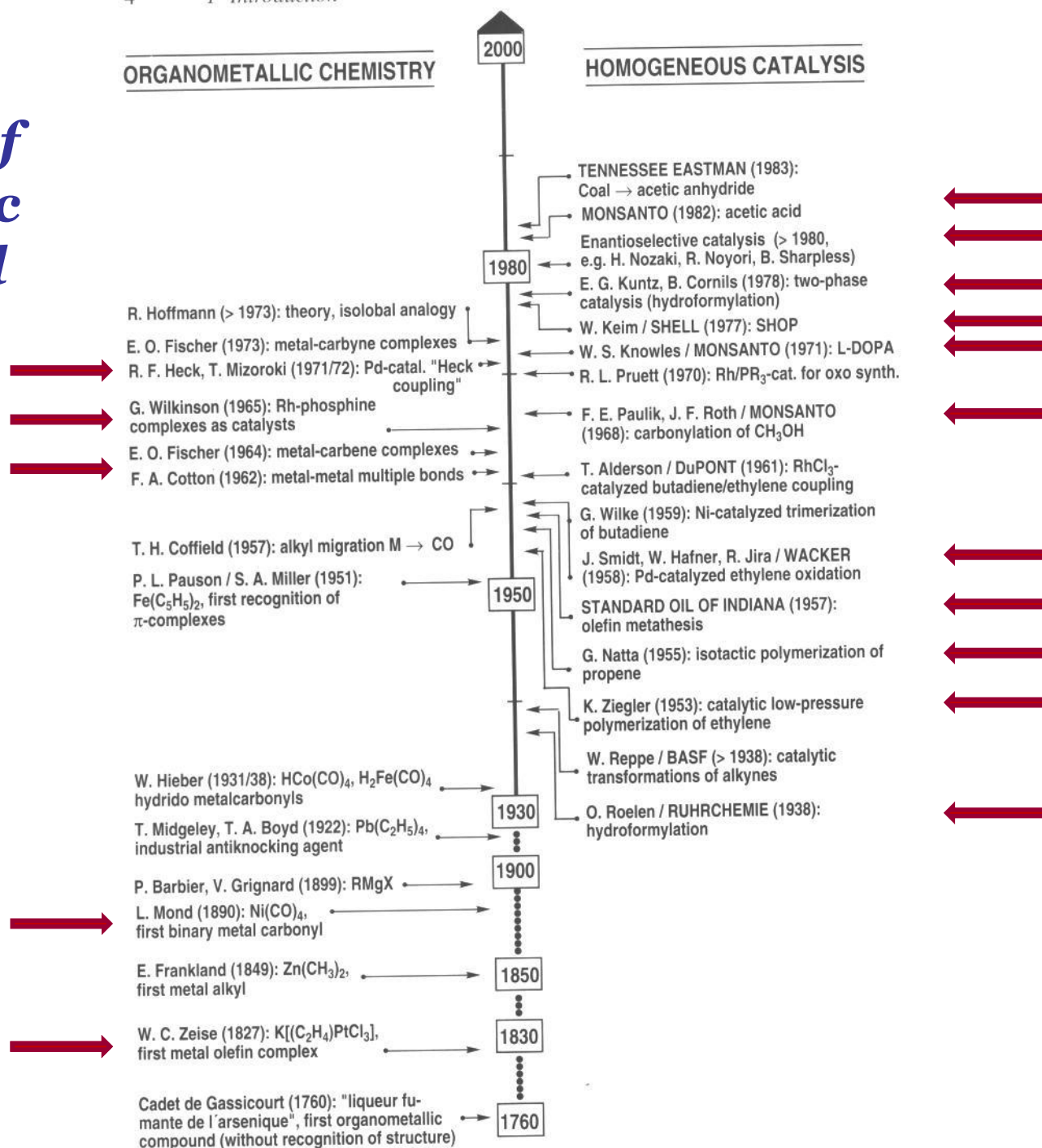
C FACTOR: Climate factor = total mass of CO₂ emitted/mass of product formed (**kg CO₂ emitted /kg product**).

It is the sum total of kg CO₂ emitted in the production of the raw materials and in their conversion to the products. It is the so-called **carbon footprint** of the process.

Historical development of organometallic chemistry and homogeneous catalysis

ORGANOMETALLIC CHEMISTRY

HOMOGENEOUS CATALYSIS



Historical evolution of homogeneous catalysis and the main scientists involved



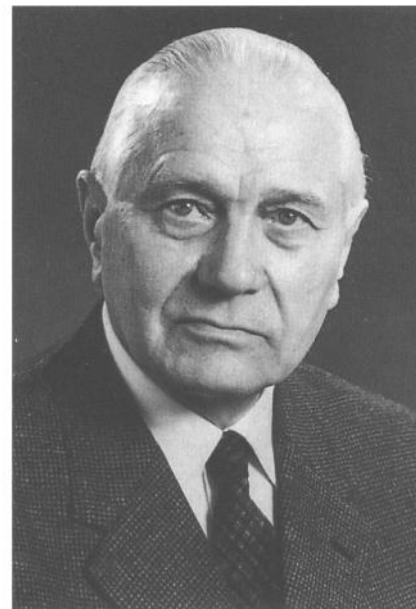
William ZEISE
1789 - 1847

A Danish apothecary and professor in Copenhagen;
He synthesized the first metal-olefin complex.



Walter REPPE
1892 - 1969

The research director of the R&D department in BASF;
He introduced the first catalyst for carbonylation reactions.



Otto ROELEN
1897 - 1993

A chemist at Ruhrchemie;
He introduced the first catalyst for hydroformylation of olefins (oxo-synthesis).

Historical evolution of homogeneous catalysis and the main scientists involved



Karl ZIEGLER
1898 - 1973

Director of one Max-Planck-Institute;

He discovered the first catalyst for polyethylene synthesis.

Nobel Prize in 1963

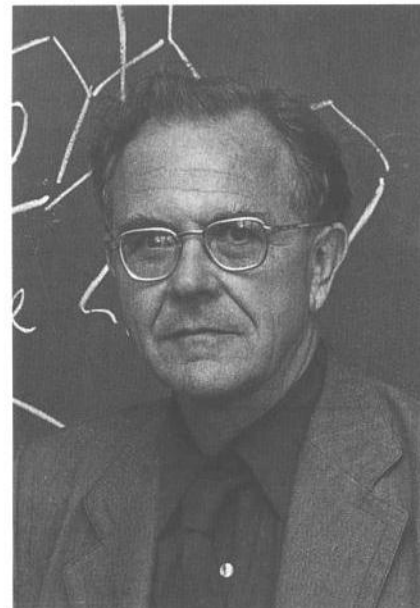


Giulio NATTA
1903 - 1979

Professor at Milan and Turin Universities;

He discovered the first catalyst for the synthesis of isotactic polypropylene.

Nobel Prize in 1963



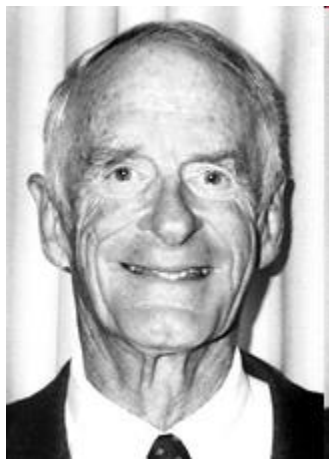
Geoffrey WILKINSON
1921 - 1996

Professor at Imperial College in Londra;

He discovered the first catalyst for hydrogenation reactions.

Nobel Prize in 1973

Historical evolution of homogeneous catalysis and the main scientists involved



William KNOWLES
1917- 2012



Ryoji NOYORI
1938



Barry SHARPLESS
1941

Their research interest was asymmetric catalysis and its applications.

Awarded by Nobel Prize in 2001

**Sharpless: awarded for the second time by Nobel Prize in 2022
for click chemistry**

Historical evolution of homogeneous catalysis and the main scientists involved



Yves CHAUVIN
1930 – 2015



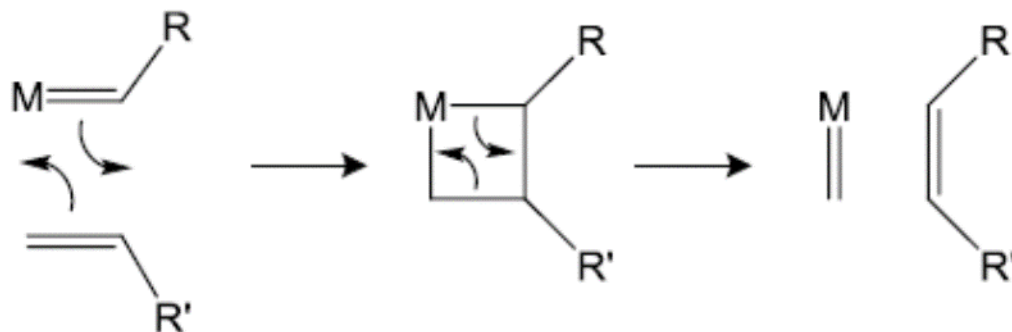
Richard SCHROCK
1945



Robert GRUBBS
1945 - 2021

**Their research interest was catalysis in metathesis reactions
and their applications.**

Awarded by Nobel Prize in 2005



Historical evolution of homogeneous catalysis and the main scientists involved



Richard HECK
1931 - 2015



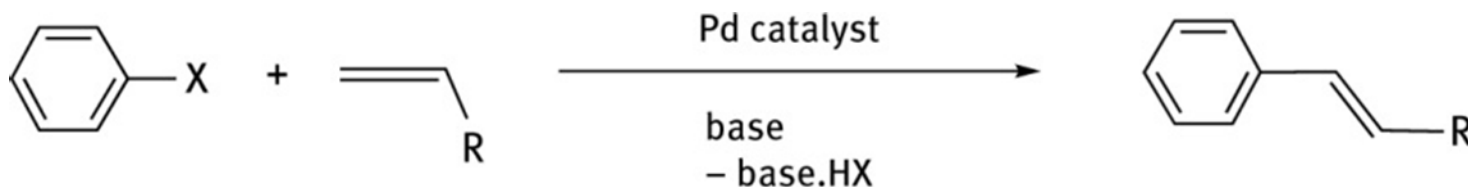
Ei-ichi NEGISHI
1935 - 2021



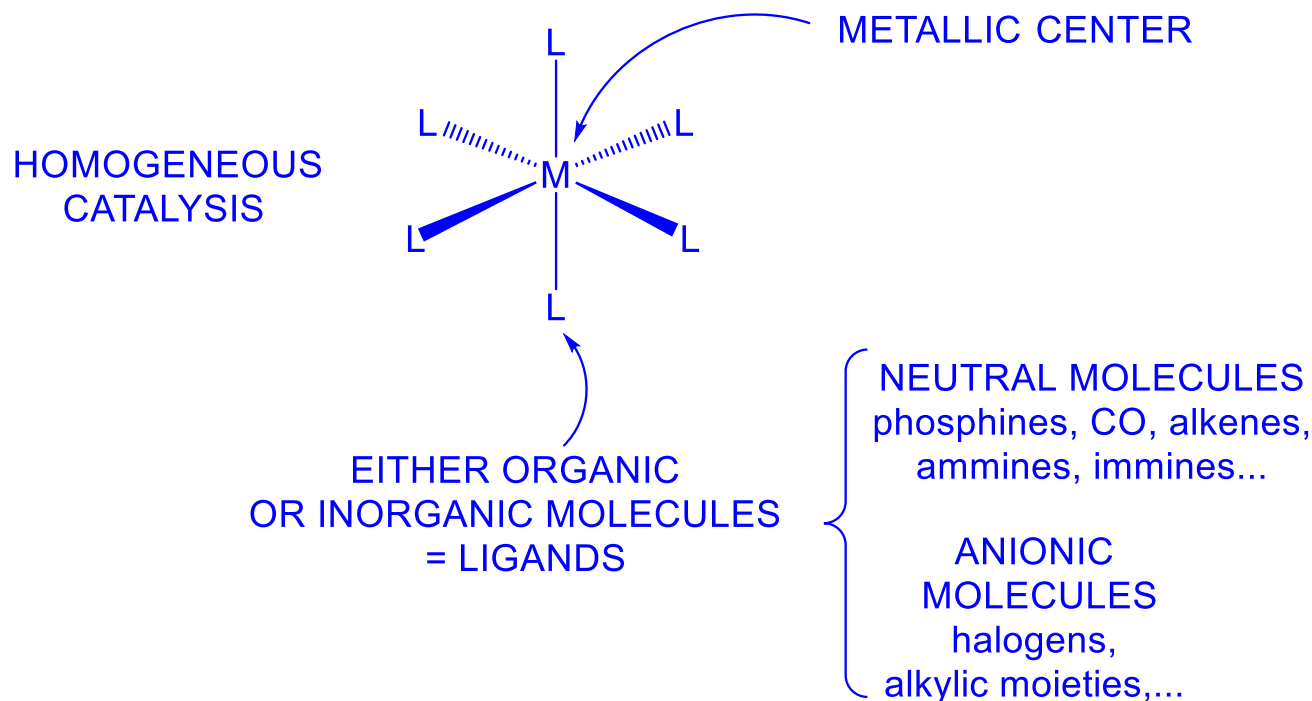
Akira SUZUKI
1930

Their research interest was C-C coupling reactions catalyzed by palladium complexes.

Awarded by Nobel Prize in 2010



The homogeneous catalyst



Metal and **ligands** dictate the catalyst performances.

Ligands are classified in:

SPECTATOR or ANCILLARY Ligands

They remain unchanged during the catalytic cycle. They play these roles:

- make soluble the complexes in the reaction medium;
- block a number of coordination sites of a defined geometry and leave available other sites for the substrates;
- avoid the leaching of the metal;
- tune the electronic and steric properties of the complex itself.

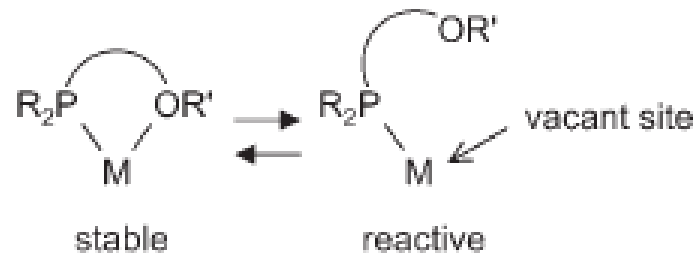
ACTIVE Ligands

The substrates of the reaction.

UNCONVENTIONAL Ligands

- NON-innocent ligands.
- Ligands from weak interactions

HEMILABILE Ligands



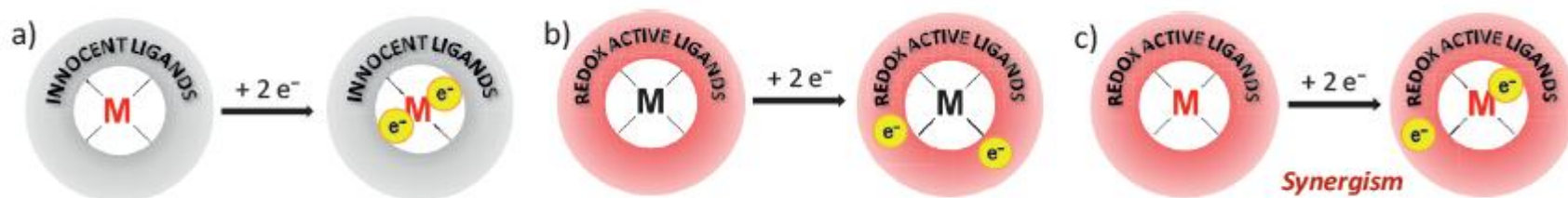
Slight modifications on **ancillary ligands** significantly affect the chemistry of the complex and, therefore, the properties of the catalyst.

Ancillary ligands affect catalyst **ACTIVITY** and catalyst **SELECTIVITY**.

A FEW EXAMPLES OF NON-INNOCENT LIGANDS

Redox-active ligands

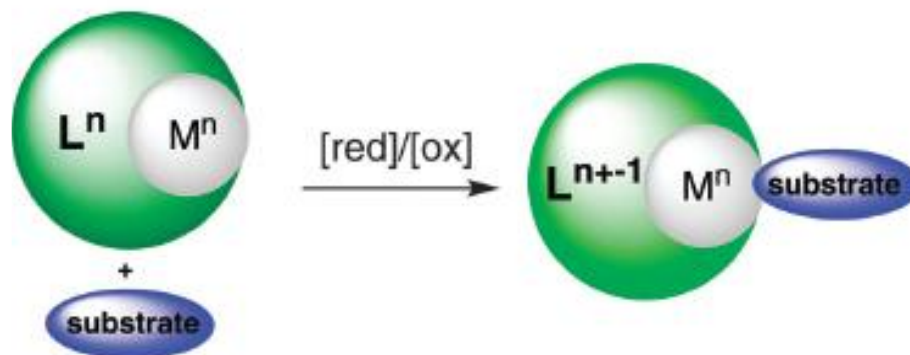
Redox-active ligands have frontier orbitals at energetically more accessible levels than classical spectator ligands, to allow easier electron transfers.



The four main ways of action of redox-active ligands

1. The oxidation/reduction of the ligand modifies the **Lewis acidity/basicity of the metal**.

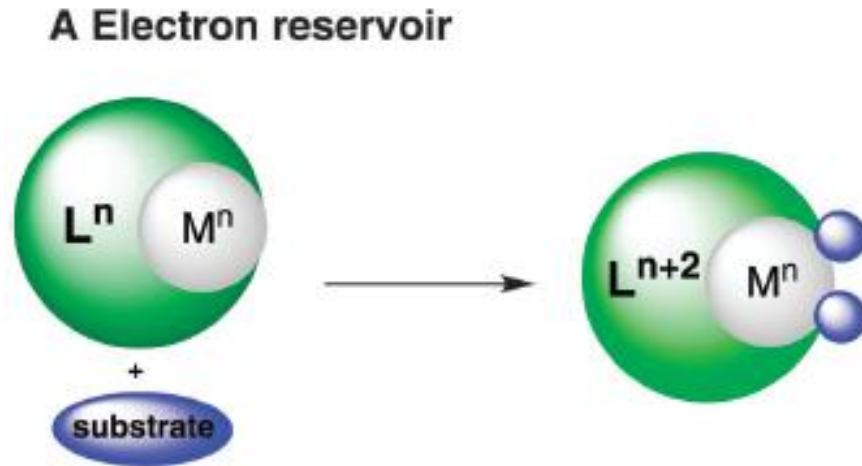
B Enhanced Lewis acidity/basicity



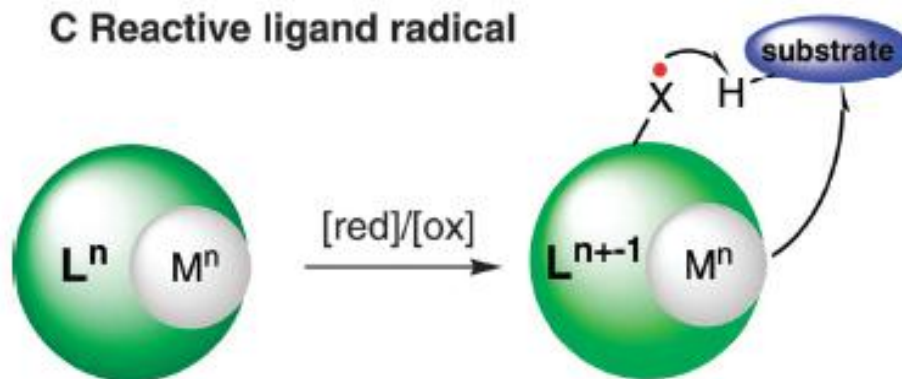
Redox-active ligands

The four main ways of action of redox-active ligands

2. The ligand acts as an **electron reservoir**.



3. The ligand might become a **radical species**, which is actively involved in bond-making and bond-breaking with the metal.

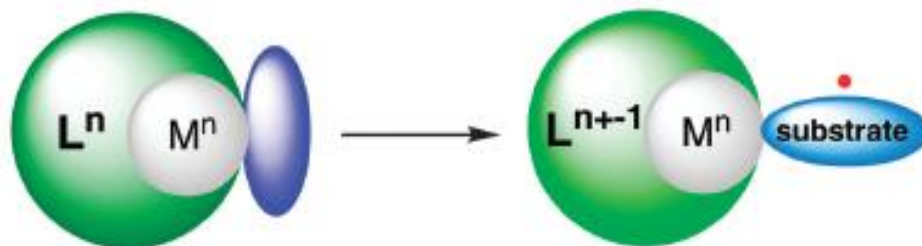


Redox-active ligands

The four main ways of action of **redox-active ligands**

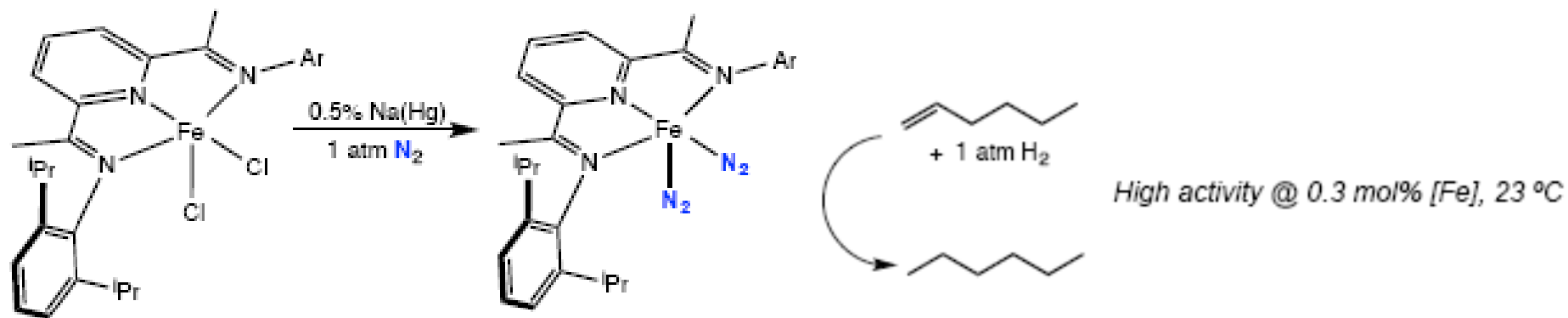
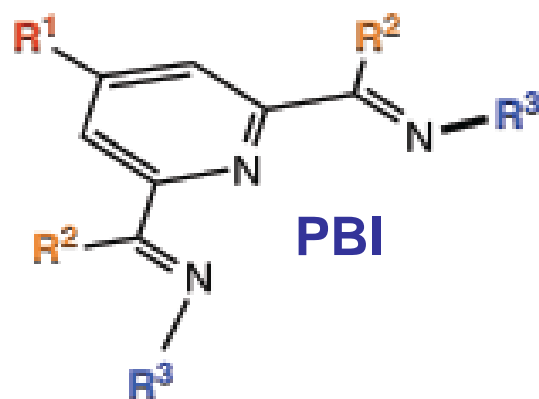
4. The ligand might allow the substrate activation through **single electron transfer**.

D Ligand-to-substrate single electron transfer

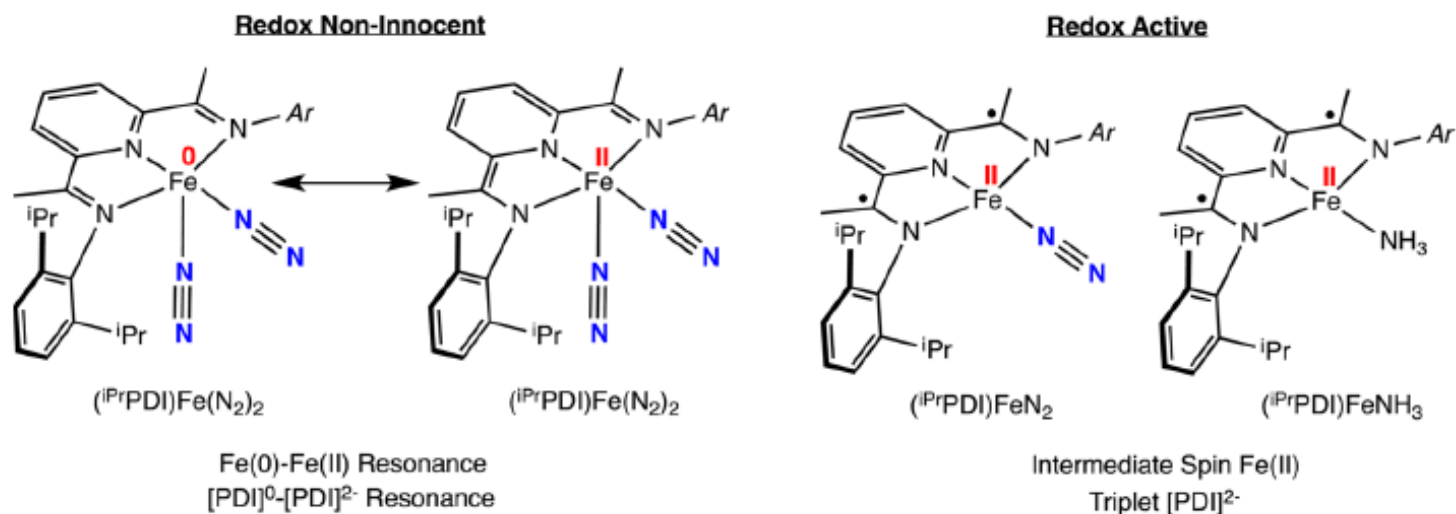


A FEW EXAMPLES OF NON-INNOCENT LIGANDS

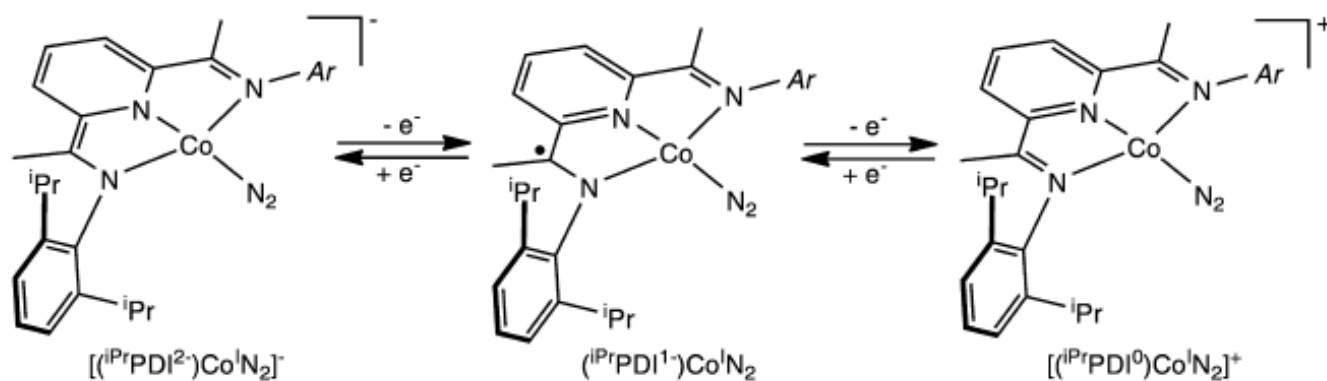
BIS(IMMINO) PYRIDINES (Paul Chirik)



POSSIBLE ELECTRONIC STRUCTURES FOR BIS(IMMINO) PYRIDINES



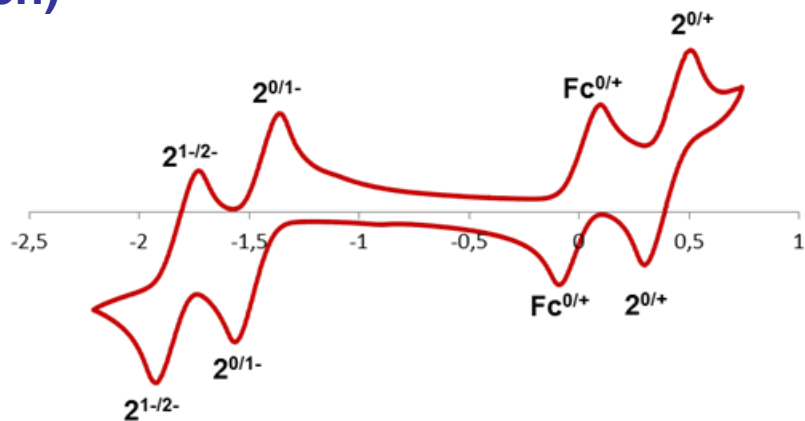
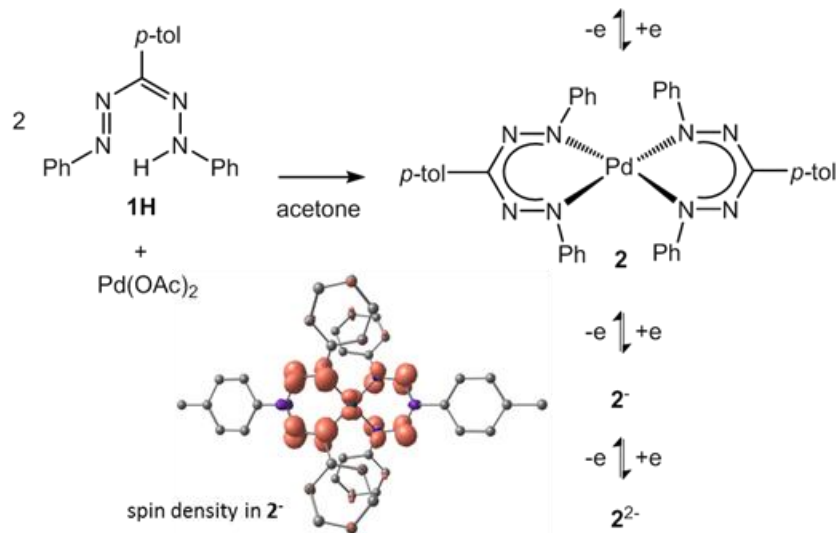
Cobalt Dinitrogen Series



A FEW EXAMPLES OF NON-INNOCENT LIGANDS

FORMAZANS or Formazanate ligands

(Edwin Otten)

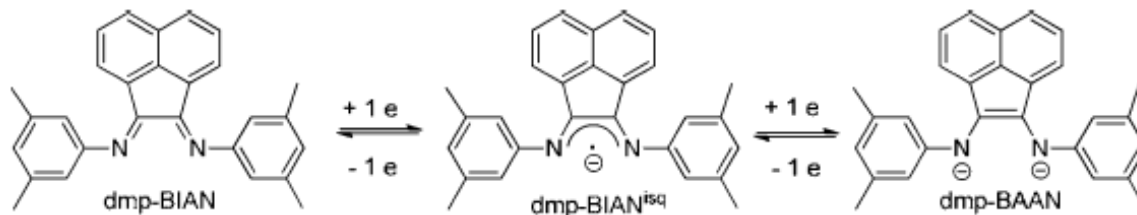


Cyclic voltammogram of compound 2 (ca. 1.50 mM solution of 2 in THF; 0.1 M [nBu₄N][PF₆] electrolyte; scan rate = 0.5 V·s⁻¹)

BIS(ARYL)ACENAPHTHENE α -DIIMINES (Ar-BIAN)

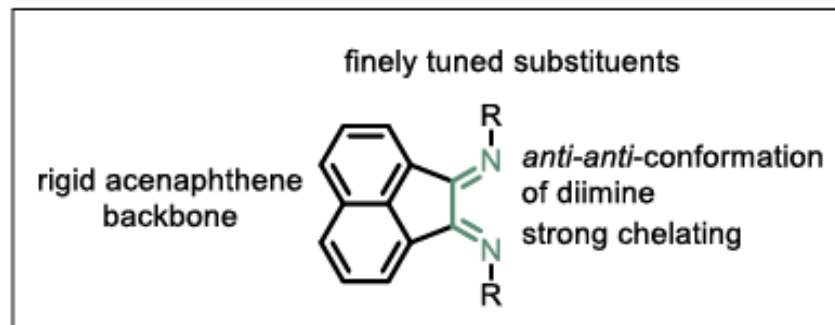
(Fabio Ragaini, Kensha Marie Clarke)

Scheme 1. First Three Oxidation Levels of the BIAN Ligand

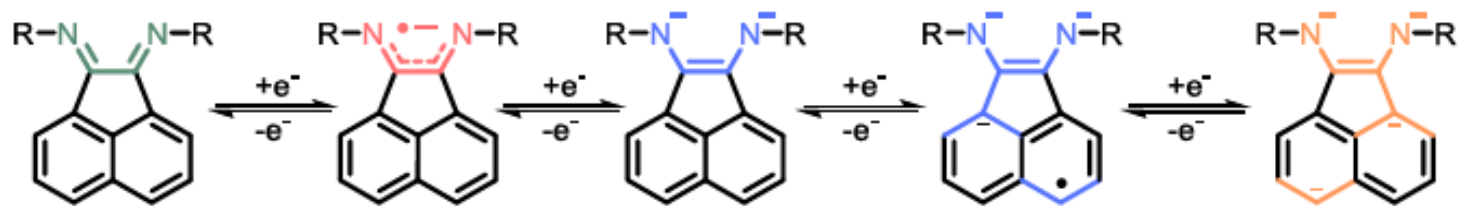


A FEW EXAMPLES OF NON-INNOCENT LIGANDS

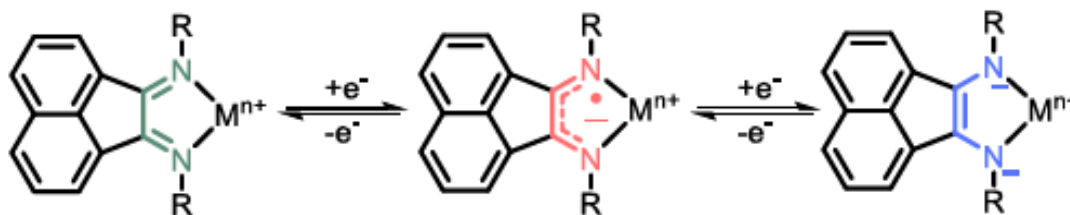
BIS(ARYL)ACENAPHTHENE α -DIIMINES (Ar-BIAN)



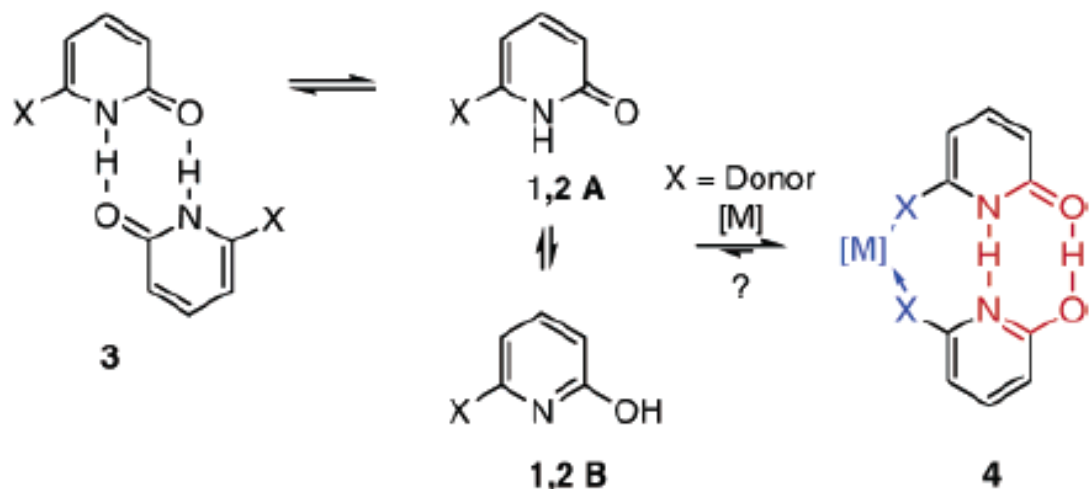
Extended redox properties of BIAN



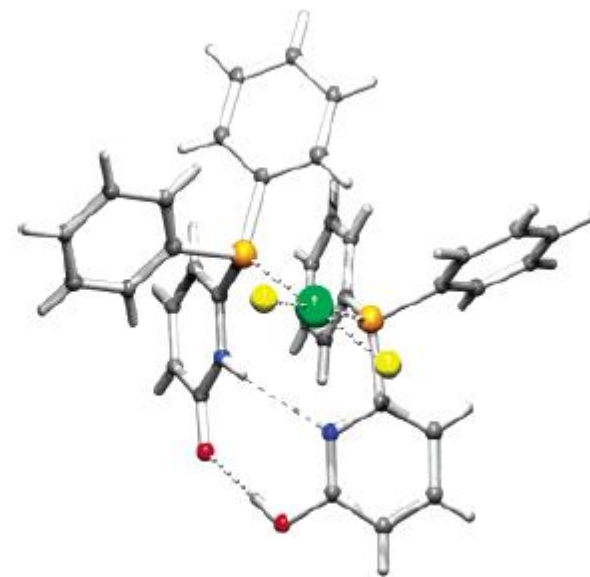
Redox properties of metal/BIAN complexes



IN SITU GENERATION OF BIDENTATE DONOR LIGANDS: A SUPRAMOLECULAR APPROACH



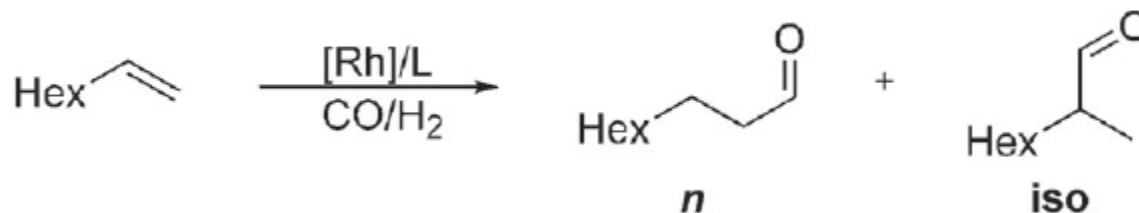
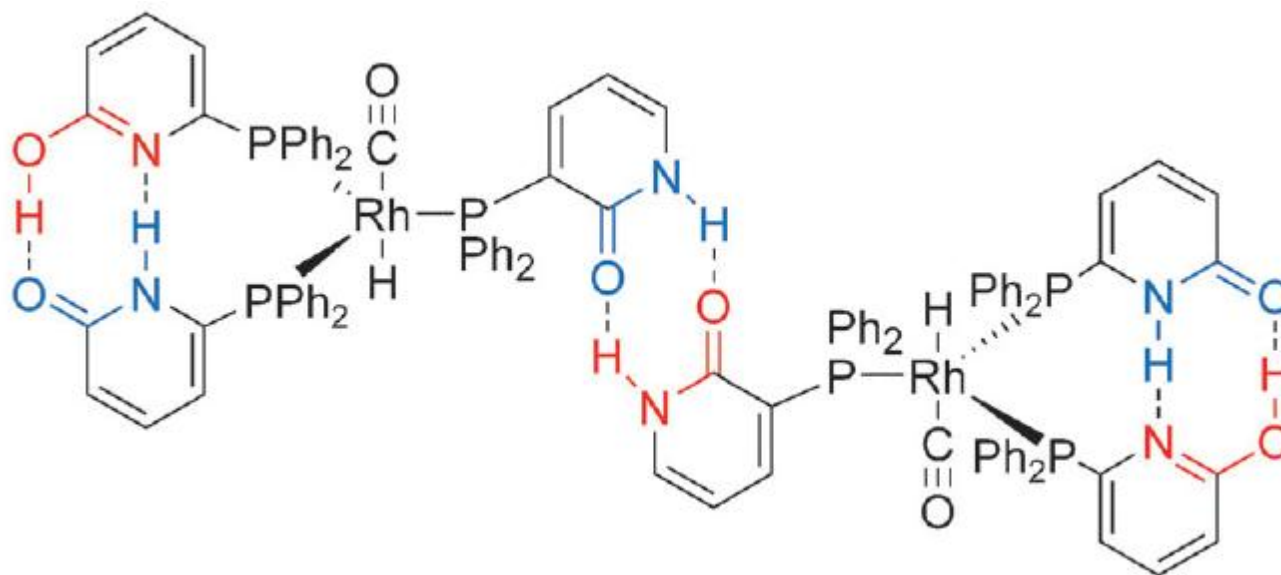
- 1: X = H
- 2: X = PPh₂



X-ray plot of *cis*-[PtCl₂(6-DPPon)₂] 5.

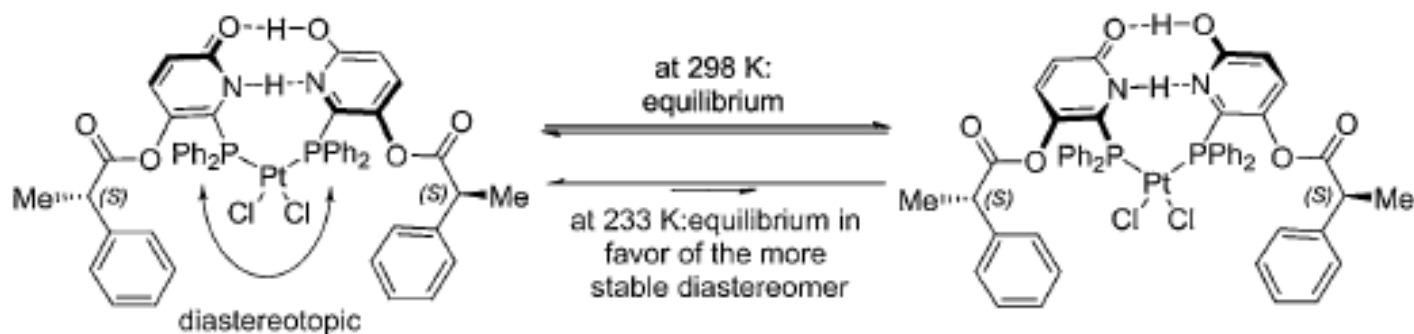
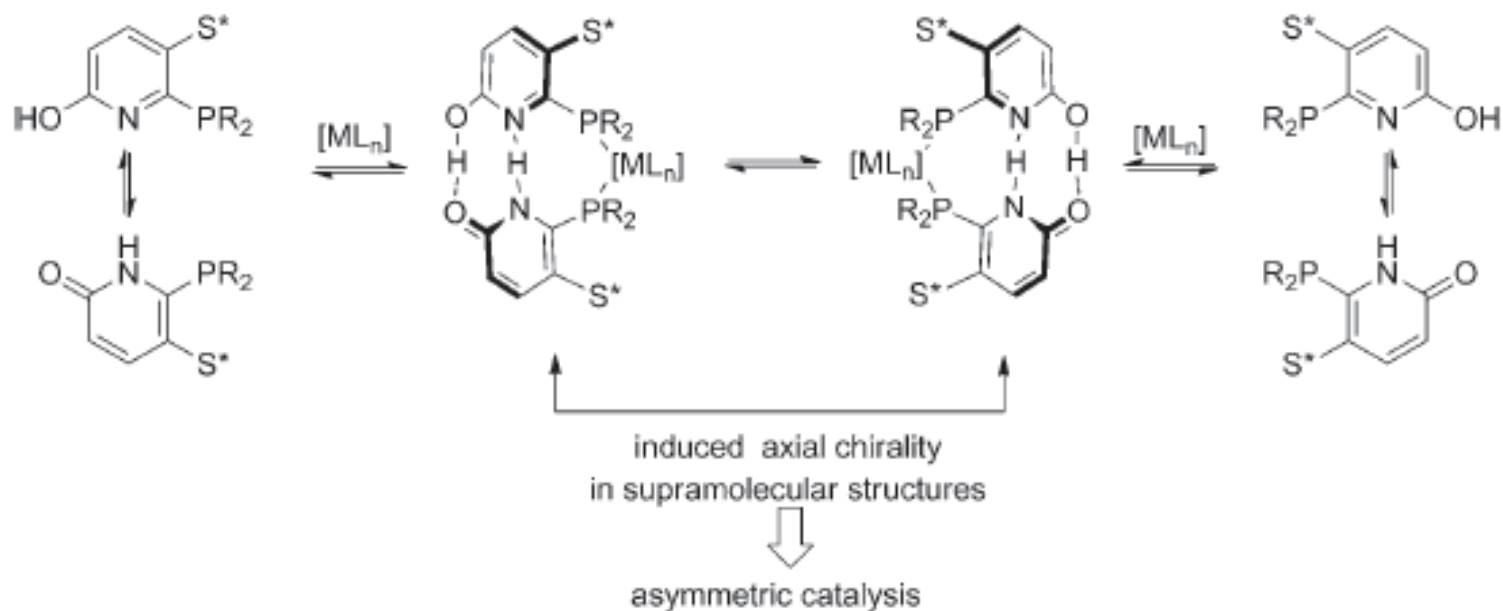
Breit B.; Seiche, W. *J. Am. Chem. Soc.* 2003, 125, 6608.

IN SITU GENERATION OF BIDENTATE DONOR LIGANDS: A SUPRAMOLECULAR APPROACH



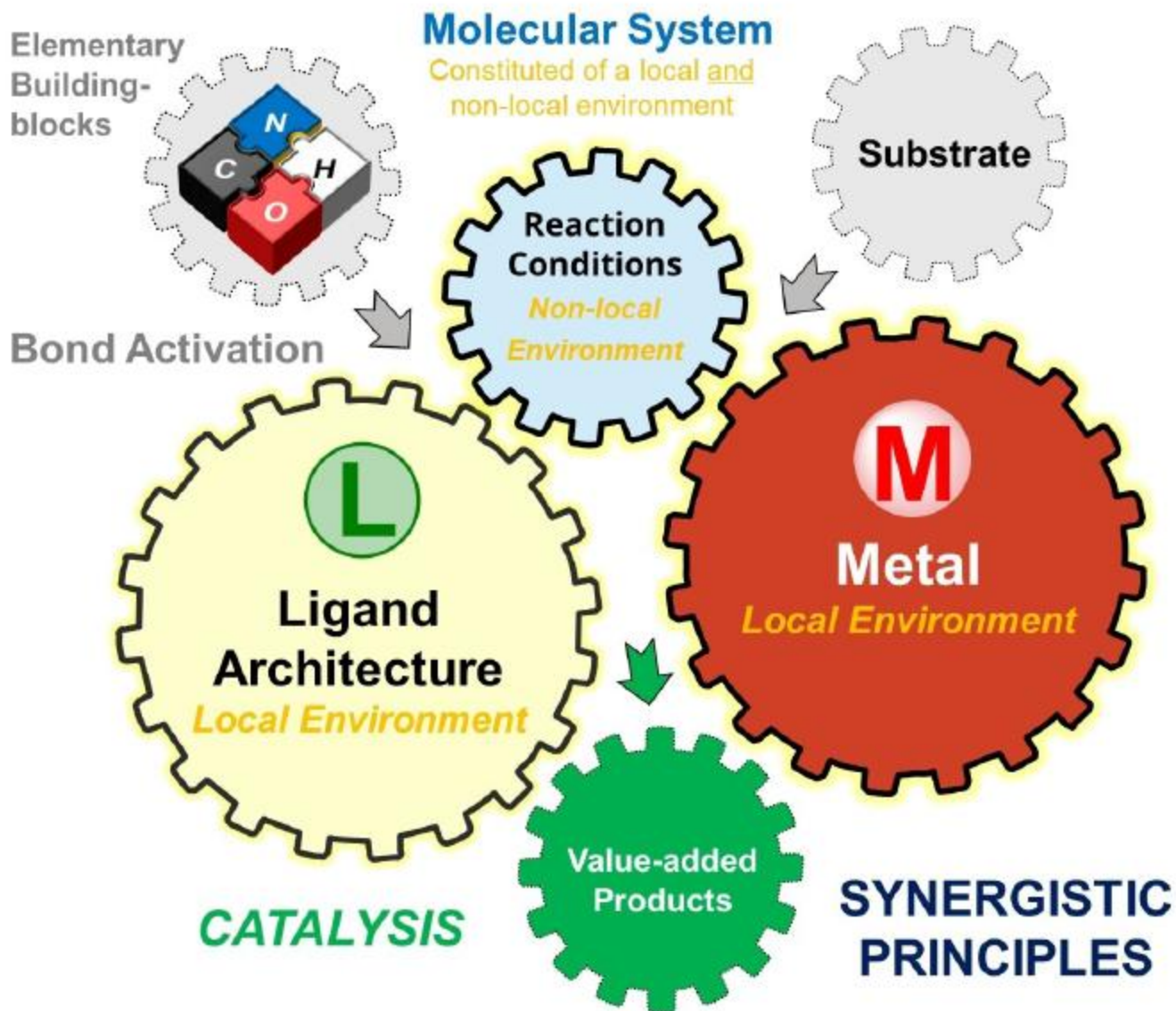
Breit B.; Seiche, W. *Angew. Chem. Int. Ed.* 2012, 51, 11033.

IN SITU GENERATION OF BIDENTATE DONOR LIGANDS: AXIAL CHIRALITY INDUCED BY SELF-ASSEMBLY



Breit B. et al. *Angew. Chem. Int. Ed.* 2018, 57, 5100.

THE HOMOGENEOUS CATALYTIC SYSTEM



FACTORS AFFECTING CATALYTIC ACTIVITY IN HOMOGENEOUS CATALYSIS

- 1) Interaction among catalyst and reactants;
- 2) Transfer of **reagents** inside the phase where the reaction takes place from other phases;
- 3) Transfer of **products** from the phase where the reaction takes place to other phases;

Chemical properties of the catalyst

Acid-base properties

Easy to be oxidized or reduced

Capability of bonding the substrates

Solvent

Solvating ability

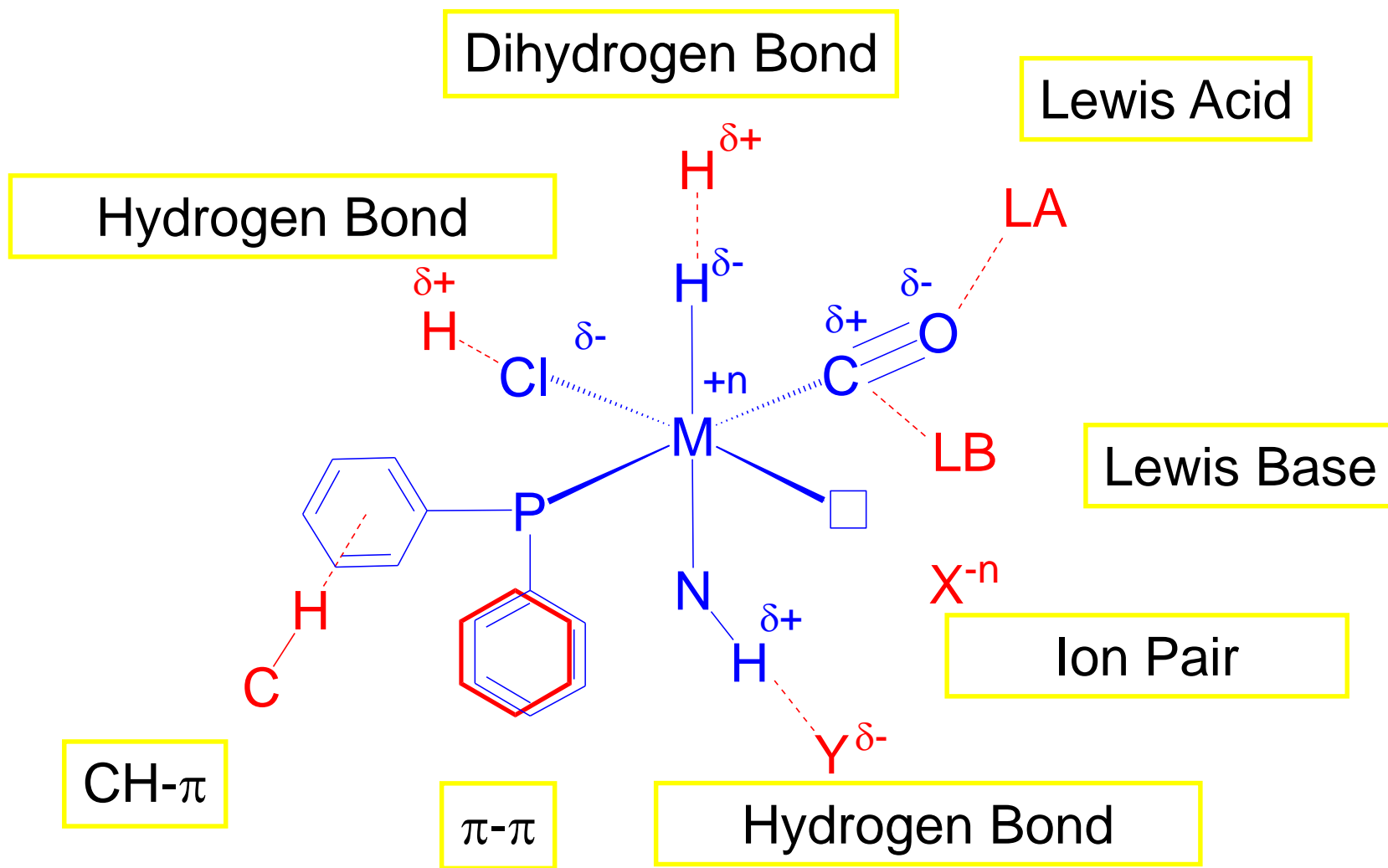
Physical-chemical properties: density, ϵ_r , surface tension, volatility, thermal stability

Easy to allow separation

Cost

Toxicity

PRIMARY AND SECONDARY COORDINATION SPHERE:



The elementary steps of the catalytic cycle

The role of the catalytic center: (1) substrates bonded to the metal centre are «closer» and have a specific orientation
(2) lower the activation energy of the reaction

The elementary steps taking place on the metal centre during a catalytic reaction are studied through model reactions on organometallic complexes in homogeneous phase. We assume that analogous elementary steps might take place on ion metals on surfaces.

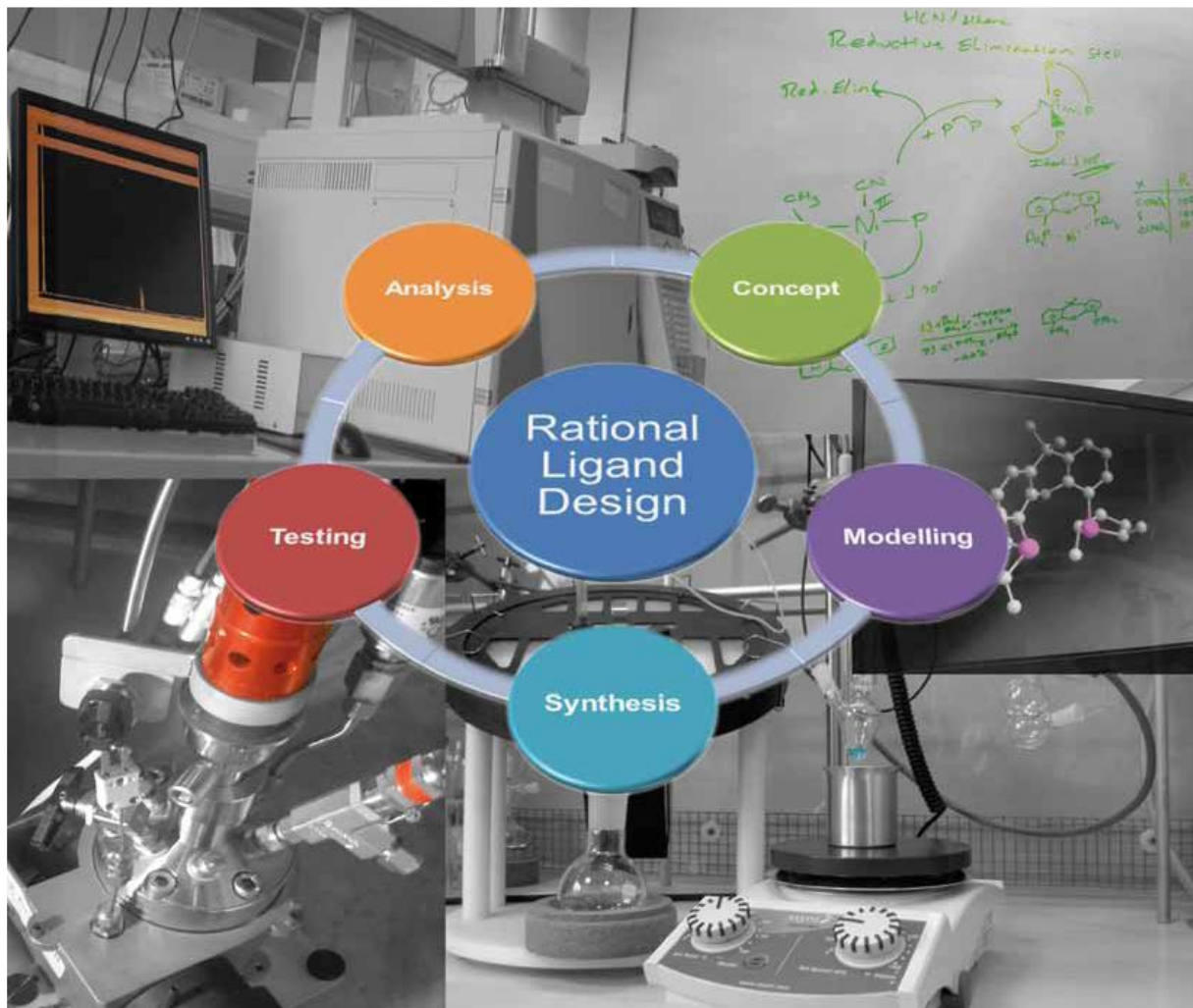
Creation a vacant coordination site followed by substrate coordination:
substitution reactions.

Oxidative addition reactions vs reductive elimination reactions;

Migratory insertion reactions vs β -elimination reactions;

α -elimination reactions.

Key steps in the investigation of homogeneous catalysts



Investigation of homogeneous catalysts

The **catalytic process** is monitored with time with the usual analytical techniques: gas-chromatography, liquid-chromatography, gas flow registration, etc. to build the **kinetic profile** of the reaction.

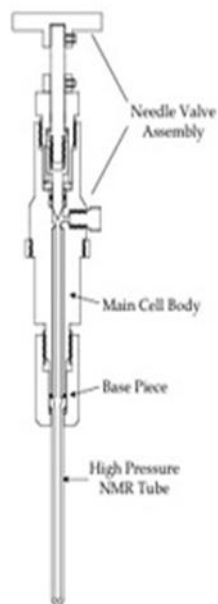
Investigation of homogeneous catalysts is divided into two parts:

1. Investigation of the **ongoing catalytic reaction**;
2. Investigation of the **intermediates** of the catalytic cycle.

The analytical techniques preferentially applied are:

IR and NMR

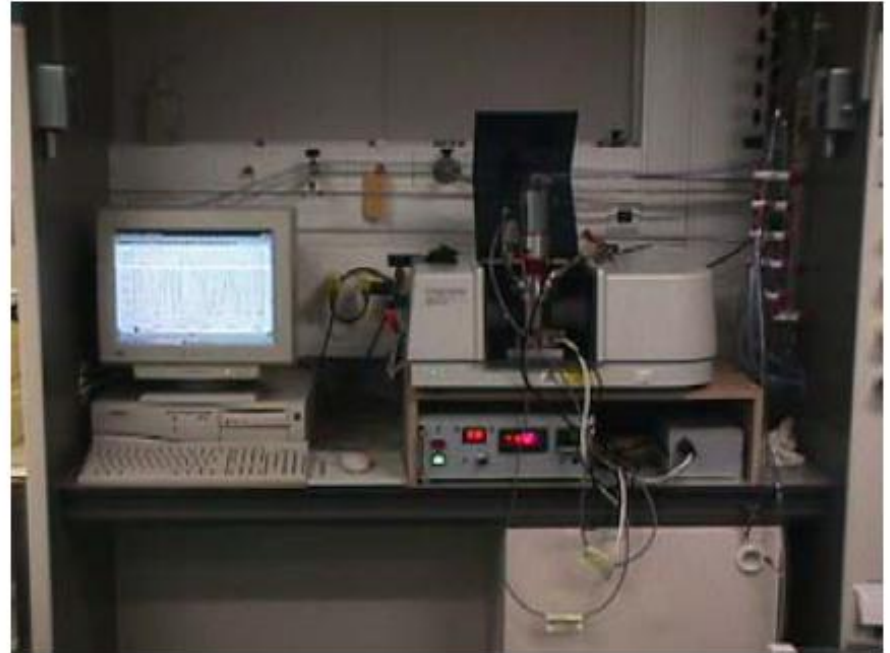
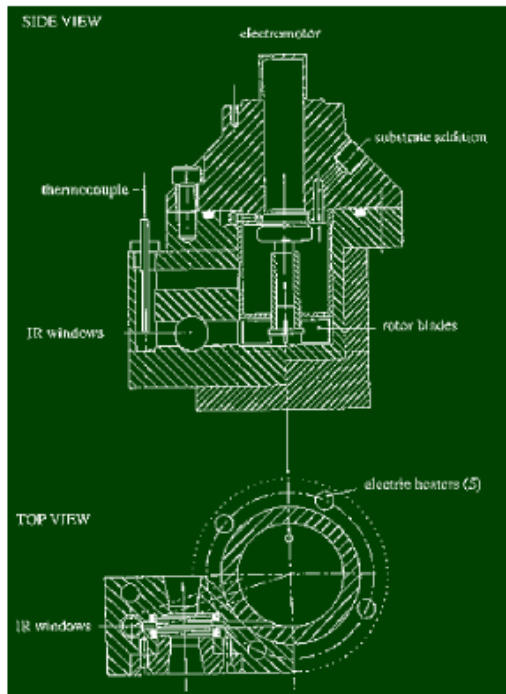
High pressure NMR



- ✓ Simple setup;
- ✓ Suitable if no gas is consumed;
- ✓ Up to 50 atm;
- ✓ Suitable for labeled gasses;
- ✓ Detailed structural information.

- ↓ High concentration with respect to catalysis;
- ↓ Sapphire tubes;
- ↓ Pure Ti valve head;
- ↓ Safety issues.

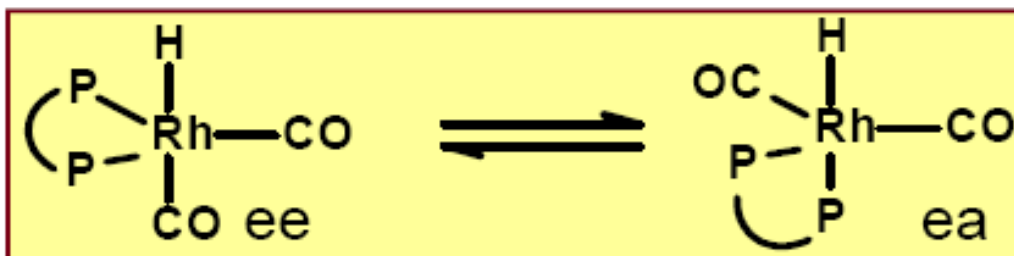
High pressure IR-Reactors with dedicated FT-IR Spectrometers



- ✓ in situ studies;
 - ✓ Concentrations comparable to those applied in catalysis;
 - ✓ Up to 85 atm.
- ↓ Poor structural information.

High pressure *in situ* NMR in hydroformylation reactions

- ✓ Ideal situation because all atoms involved in the 1st coordination sphere are NMR active: ^1H , ^{13}C , ^{31}P , ^{103}Rh ;
- ✓ easy exchange and marking with ^2D , ^{13}CO .

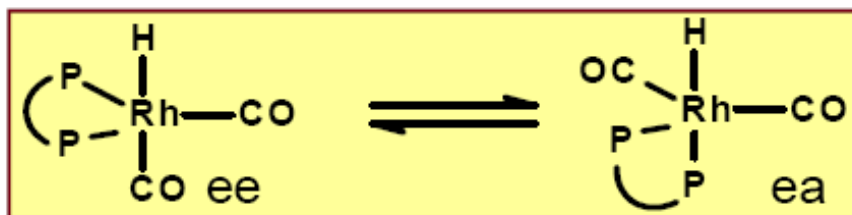


- **equatorial-equatorial** coordination, **ee**
- *cis*-relation of hydride and P-atoms
- small $J_{(\text{P-H})} < 10 \text{ Hz}$
- large $J_{(\text{P-P})} \sim 250 \text{ Hz}$

- **equatorial-apical** coordination, **ea**
- *trans*-relation of hydride and P-atoms
- large $J_{(\text{P-H})} \sim 180 - 200 \text{ Hz}$
- small $J_{(\text{P-P})} < 70 \text{ Hz}$

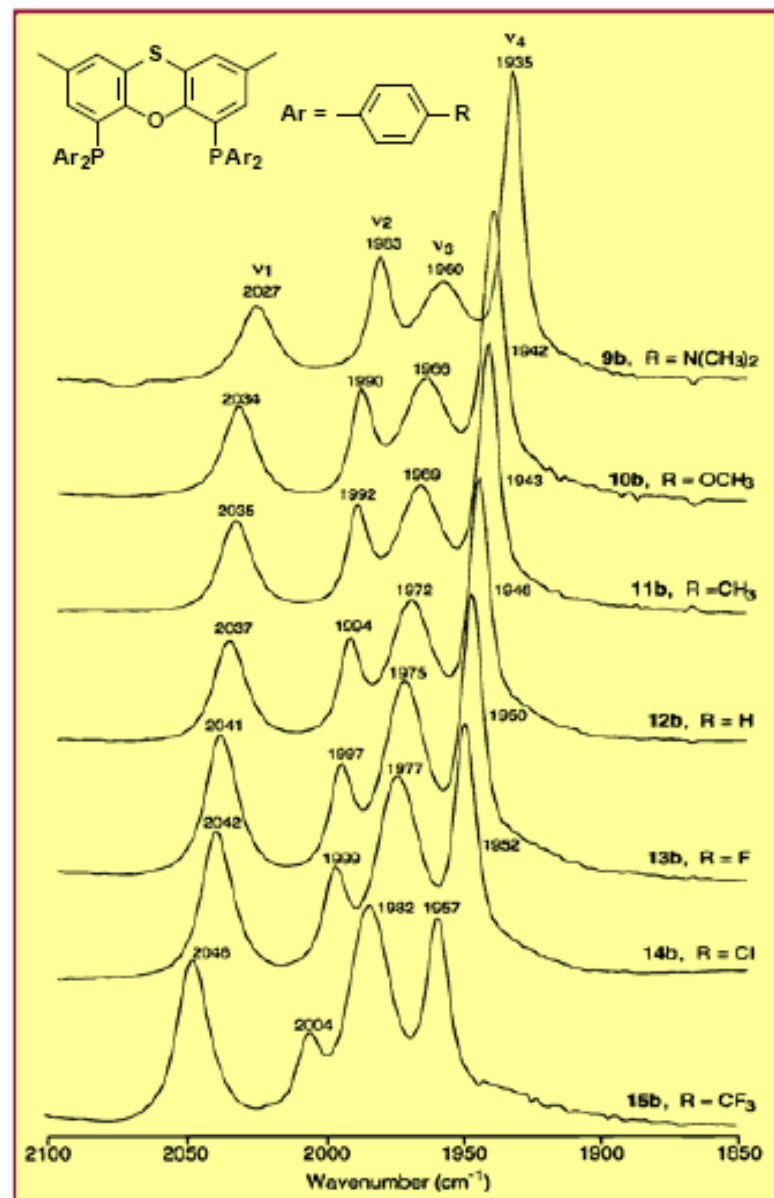
- rapid exchange of P-atoms observed for both, ee and ea complexes

High pressure in situ IR in hydroformylation reactions



HP-IR helps to distinguish ee and ea coordination

- ee coordinated ligands: $\nu_{(\text{CO})} = 1970, 2030 \text{ cm}^{-1}$
- ea coordinated ligands: $\nu_{(\text{CO})} = 1950, 2000 \text{ cm}^{-1}$



Instrumentation diagram for *Flow-NMR* spectroscopy

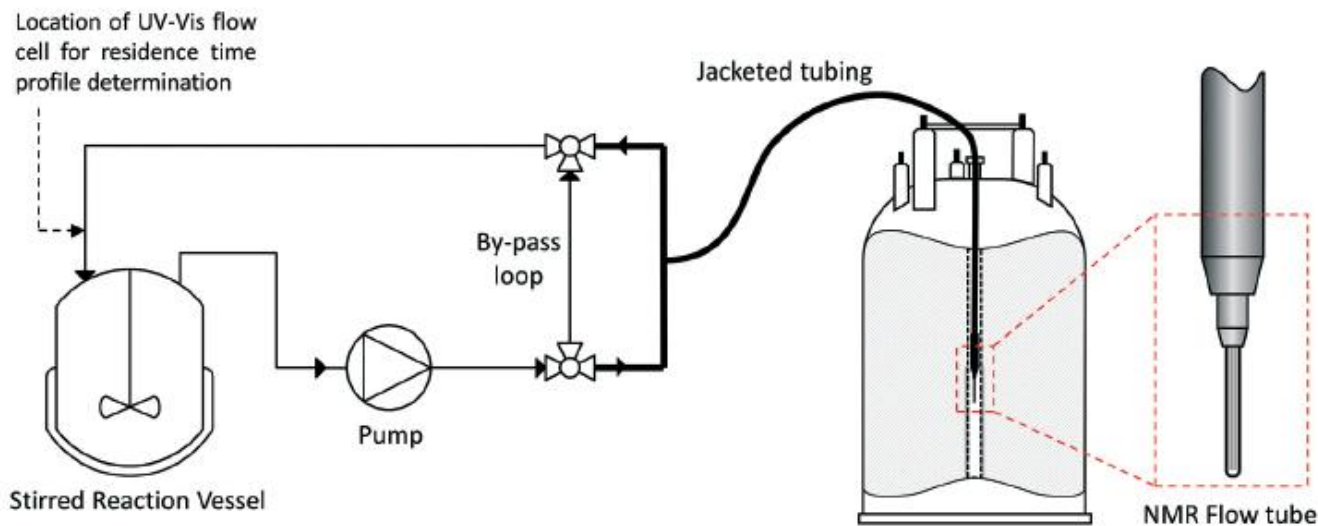


Fig. 1 Flow scheme and instrumentation diagram for the FlowNMR reaction monitoring apparatus (not to scale; for details see the Experimental section).

Lowe, J. P.; et al. *Catal. Sci. Technol.* 2016, 6, 8406.