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.

Visit to LyondellBasell in Ferrara.

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

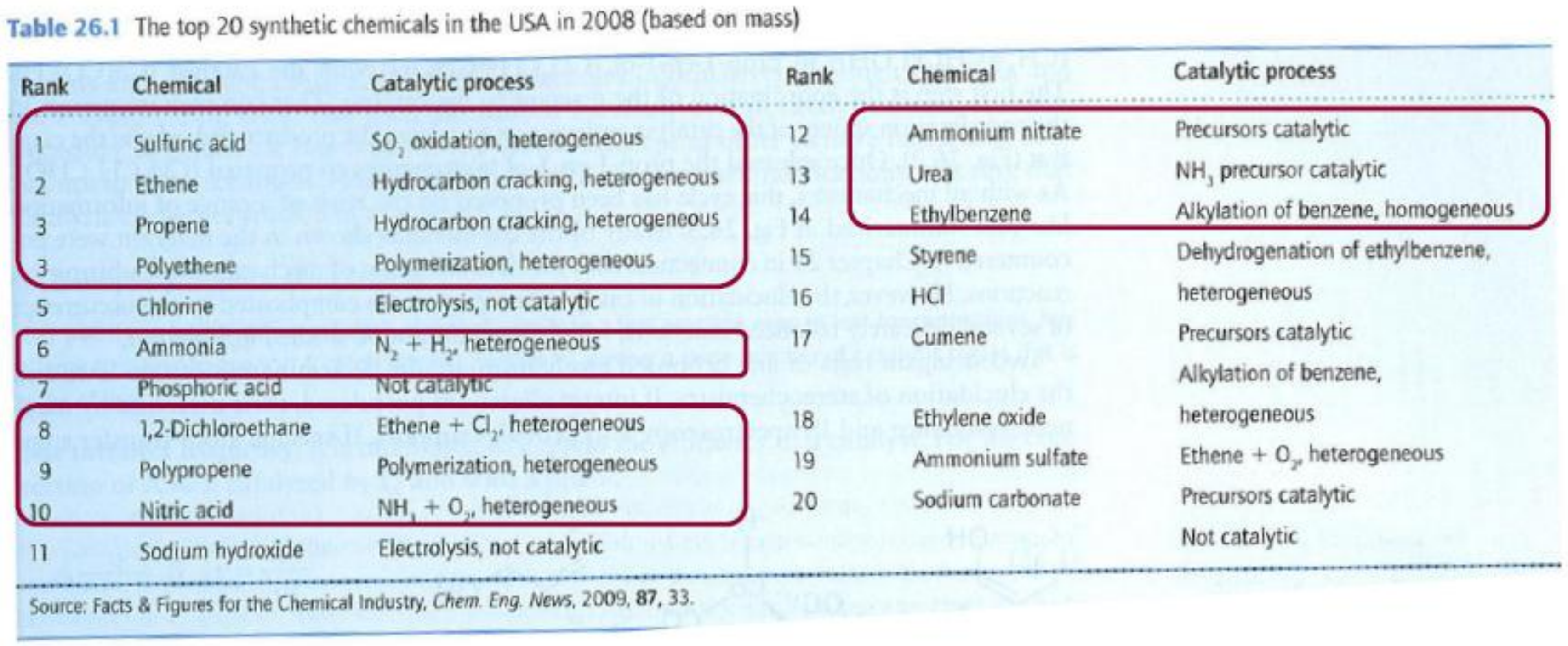


Table 26.1 The top 20 synthetic chemicals in the USA in 2008 (based on mass)

Rank	Chemical	Catalytic process
1	Sulfuric acid	SO_2 oxidation, heterogeneous
2	Ethene	Hydrocarbon cracking, heterogeneous
3	Propene	Hydrocarbon cracking, heterogeneous
3	Polyethene	Polymerization, heterogeneous
5	Chlorine	Electrolysis, not catalytic
6	Ammonia	$N_2 + H_2$, heterogeneous
7	Phosphoric acid	Not catalytic
8	1,2-Dichloroethane	Ethene + Cl_2, heterogeneous
9	Polypropene	Polymerization, heterogeneous
10	Nitric acid	$NH_3 + O_2$, heterogeneous
11	Sodium hydroxide	Electrolysis, not catalytic
12	Ammonium nitrate	Precursors catalytic
13	Urea	NH_3 precursor catalytic
14	Ethylbenzene	Alkylation of benzene, homogeneous
15	Styrene	Dehydrogenation of ethylbenzene, heterogeneous
16	HCl	Precursors catalytic
17	Cumene	Alkylation of benzene, heterogeneous
18	Ethylene oxide	Ethene + O_2, heterogeneous
19	Ammonium sulfate	Precursors catalytic
20	Sodium carbonate	Not catalytic

Source: Facts & Figures for the Chemical Industry, *Chem. Eng. News*, 2009, **87**, 33.

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

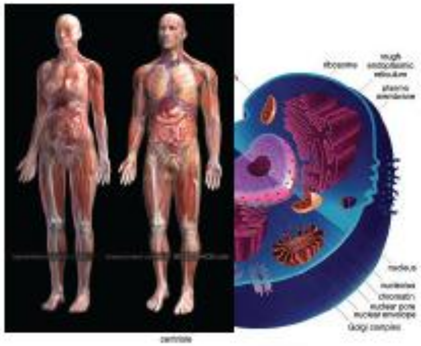
Fields of applications of catalysis

Construction Materials

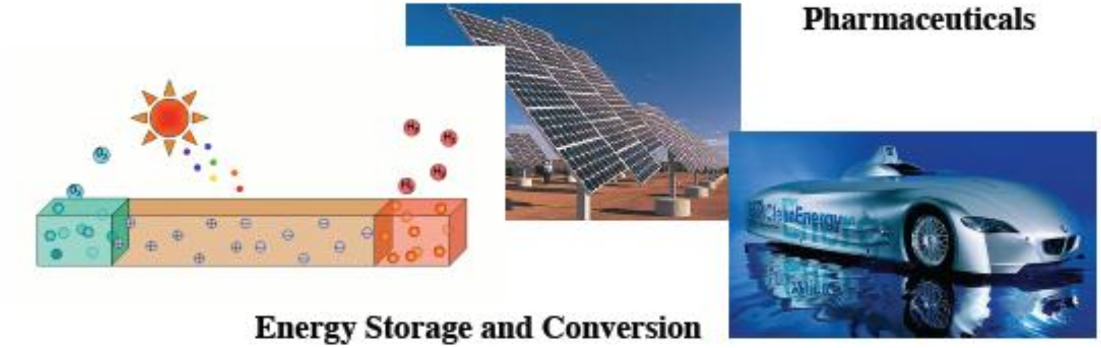
Fertilizers

Packaging Materials

Pharmaceuticals

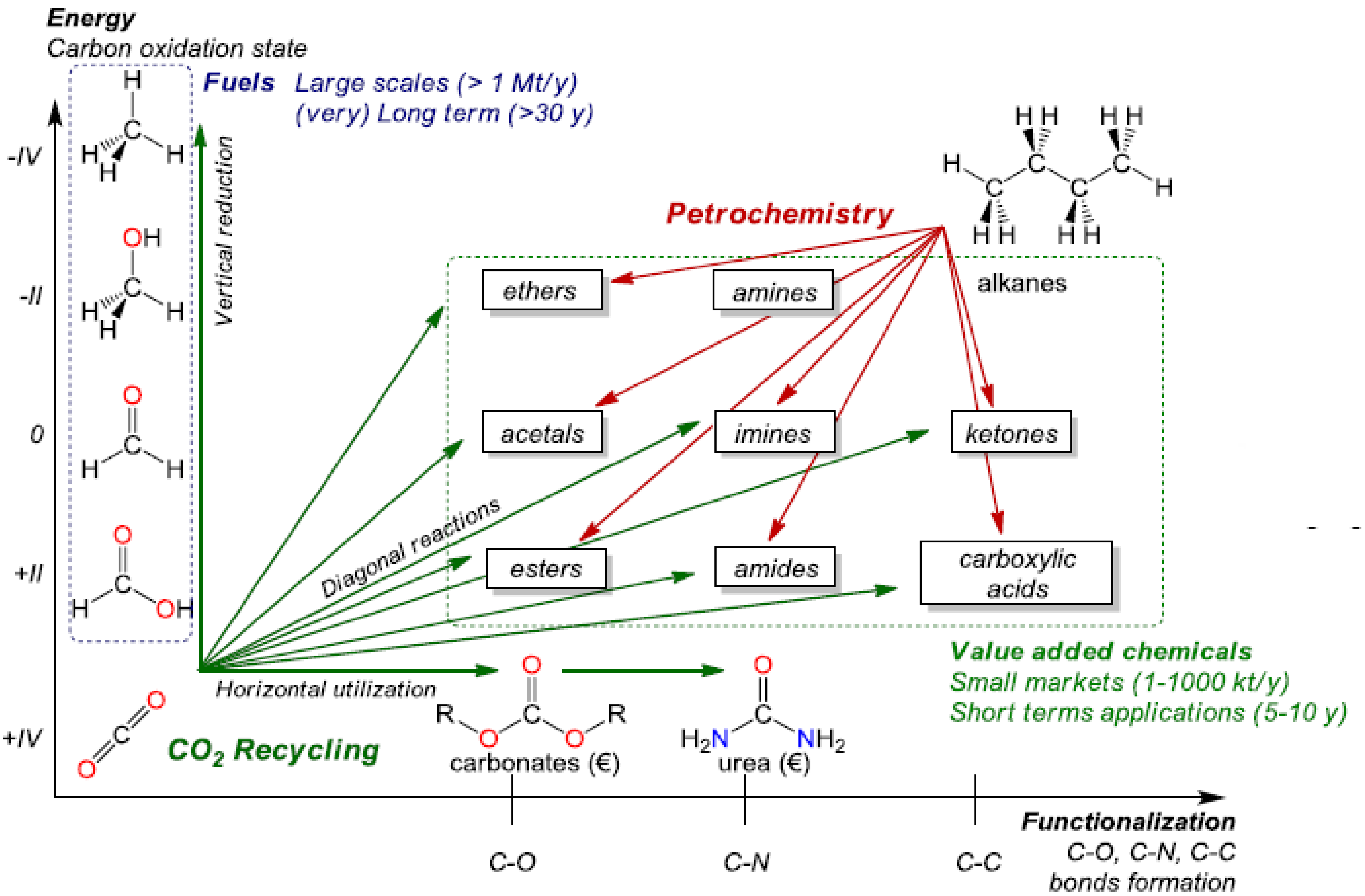


Biochemical Processes



Energy Storage and Conversion

CO_2 as a C_1 building block



Energy
Carbon oxidation state

-IV
-II
0
+II
+IV

Fuels Large scales (> 1 Mt/y)
(very) Long term (>30 y)

Vertical reduction

Petrochemistry

alkanes

ethers
amines
acetals
imines
ketones
esters
amides
carboxylic acids

Diagonal reactions

Horizontal utilization

CO_2 Recycling

carbonates (€)

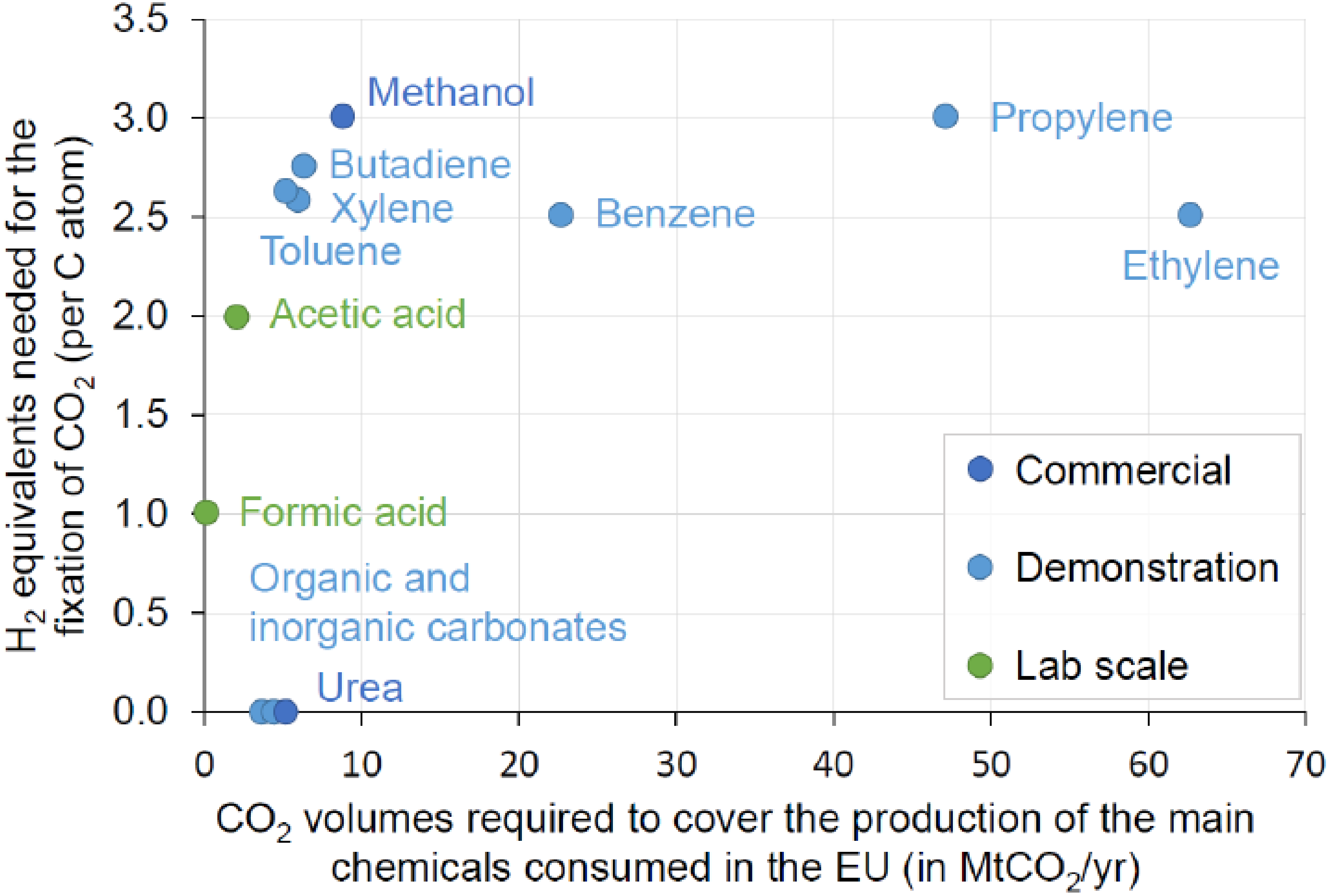
urea (€)

Value added chemicals
Small markets (1-1000 kt/y)
Short terms applications (5-10 y)

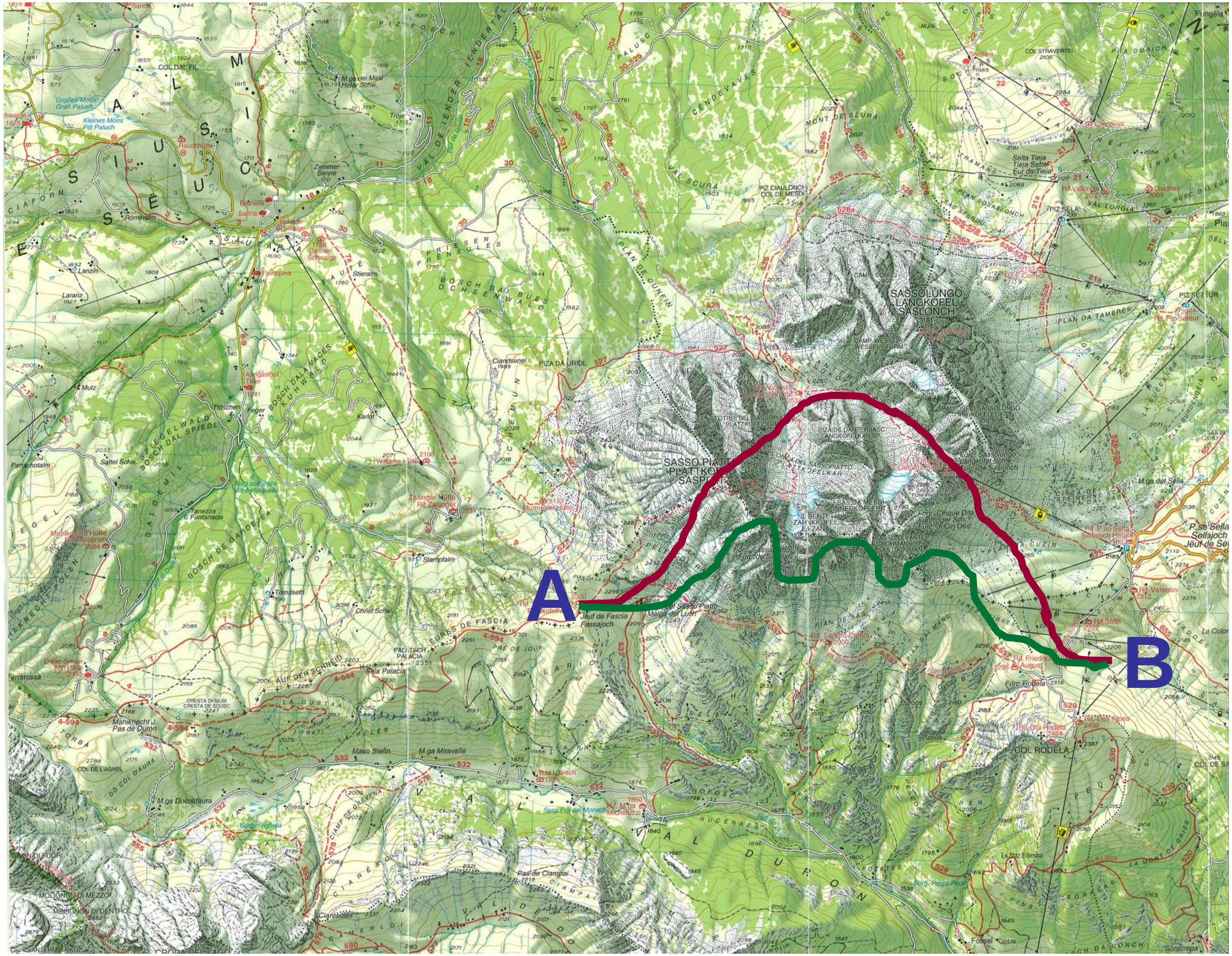
C-O
C-N
C-C

Functionalization
C-O, C-N, C-C
bonds formation

Carbon based products

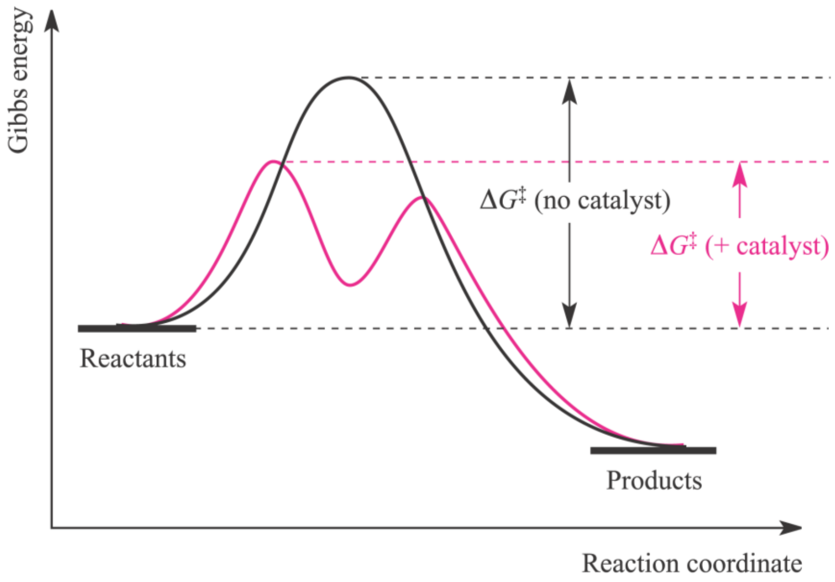


CATALYSIS: reduce the energy barriers



THE CATALYST

$$A \rightleftharpoons B$$



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.

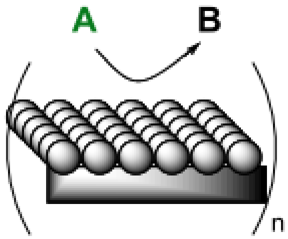
A catalyst does not modify the overall Gibbs free energy change in the reaction.

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

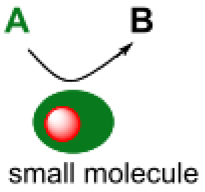
A catalyst is found unhaltered at the end of the catalytic cycle, it is NOT consumed during the catalytic reaction.

CLASSES OF CATALYSTS

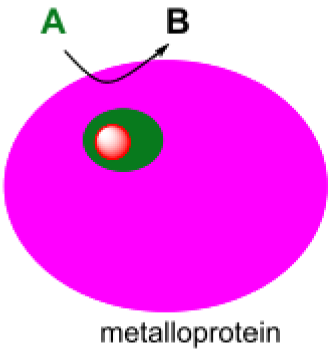
HETEROGENEOUS



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 is accessible	All the catalyst is accessible	Difficult to be separated
High thermal stabiity	Easy to be poisoned	Easy to be studied	Difficult to be recycled
Easy to be recycled	Difficult to be investigated	High selectivity	Low thermal stability
	Low selectivity		

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

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

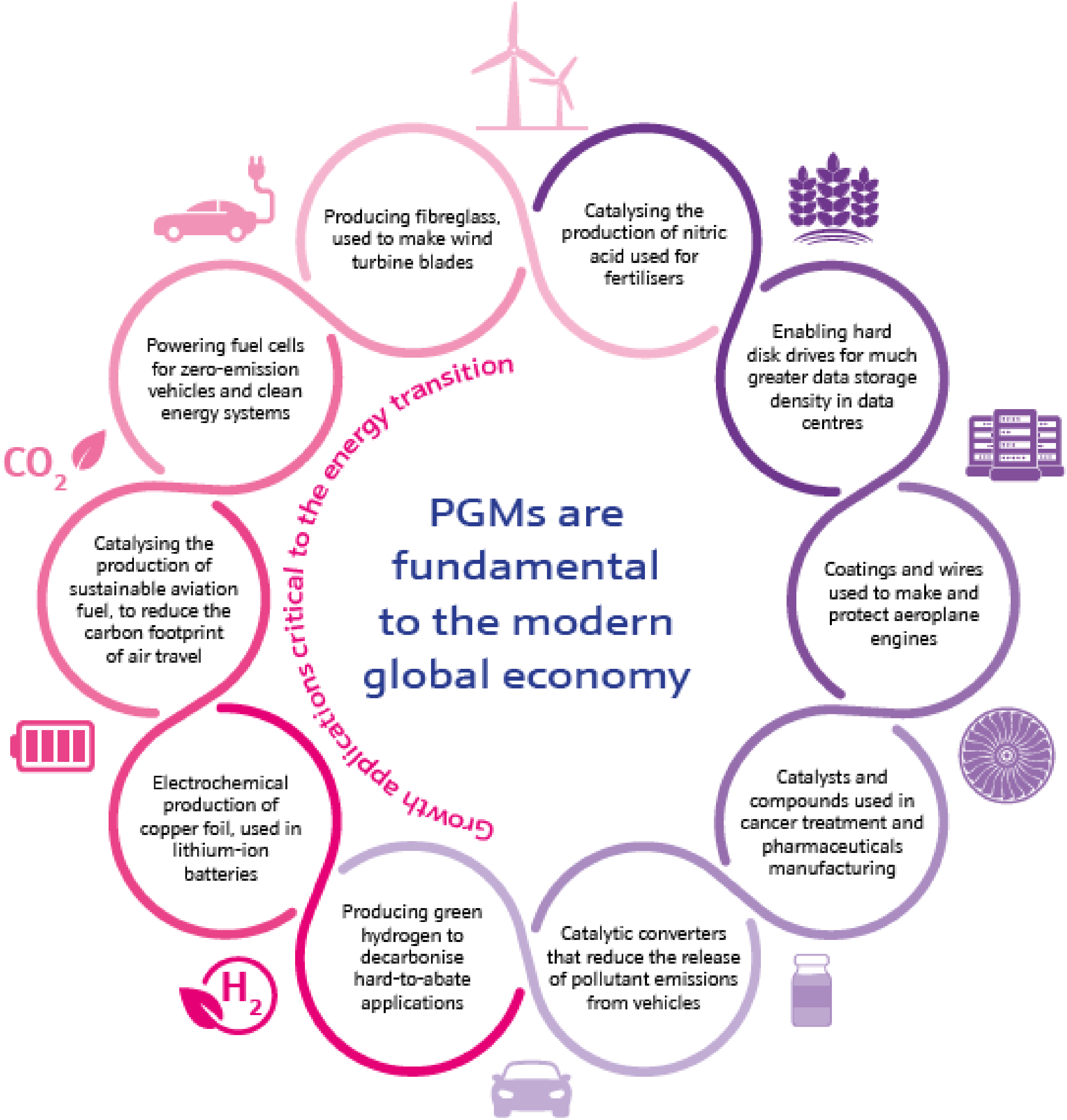
Hybrid/Electric Cars

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*



PGMs are fundamental to the modern global economy

Growth applications critical to the energy transition

Producing fibreglass, used to make wind turbine blades

Catalysing the production of nitric acid used for fertilisers

Enabling hard disk drives for much greater data storage density in data centres

Coatings and wires used to make and protect aeroplane engines

Catalysts and compounds used in cancer treatment and pharmaceuticals manufacturing

Catalytic converters that reduce the release of pollutant emissions from vehicles

Producing green hydrogen to decarbonise hard-to-abate applications

Electrochemical production of copper foil, used in lithium-ion batteries

Catalysing the production of sustainable aviation fuel, to reduce the carbon footprint of air travel

Powering fuel cells for zero-emission vehicles and clean energy systems

Cost

When does it matter?

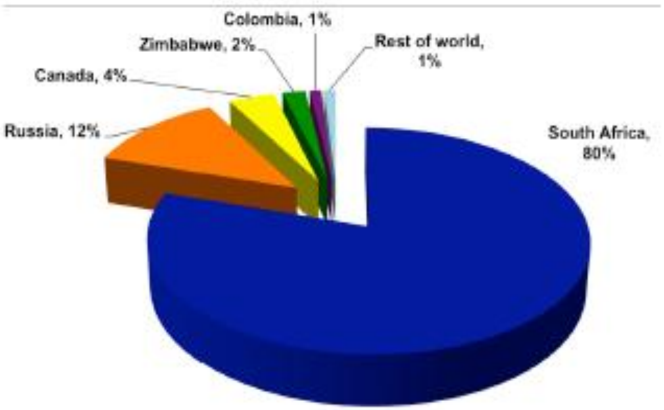
What defines expensive?

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

Platinum

\$12,400 per mol

CO_2: >7000 equiv per mol

Iron

\$0.02 per mol

CO_2: 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

Factors enabling PGMs recycling:

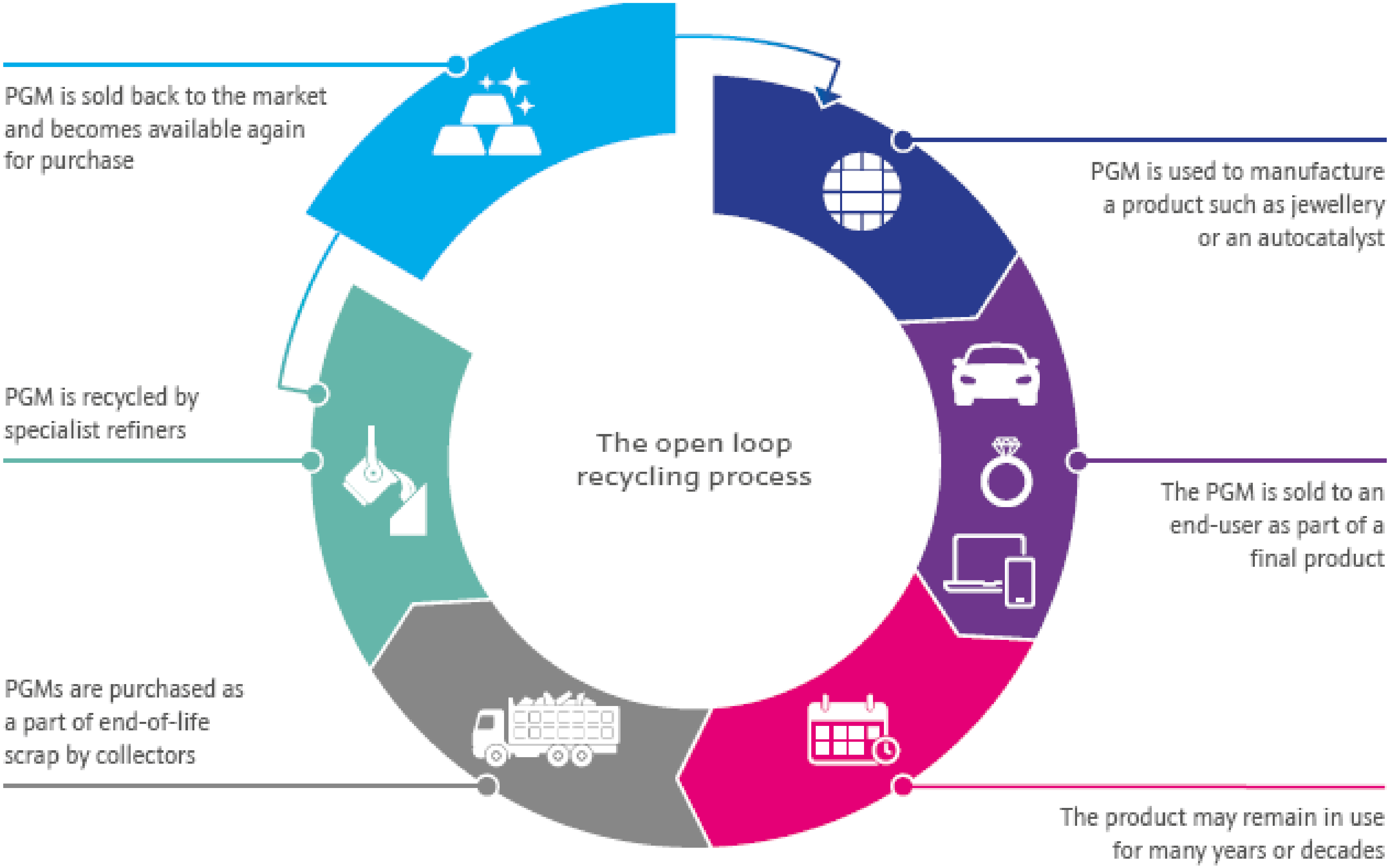
- ✓ **The value of the metals;**
- ✓ **Recycled PGMs are physically indistinguishable from "virgin" metal;**
- ✓ **PGMs can be recycled many times;**
- ✓ **Recycling does not change PGMs physical properties;**
- ✓ **Recycled PGMs have about 97 % lower global warming potential than newly mined metal.**

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

Open loop recycling



PGM is used to manufacture a product such as jewellery or an autocatalyst

The PGM is sold to an end-user as part of a final product

The product may remain in use for many years or decades

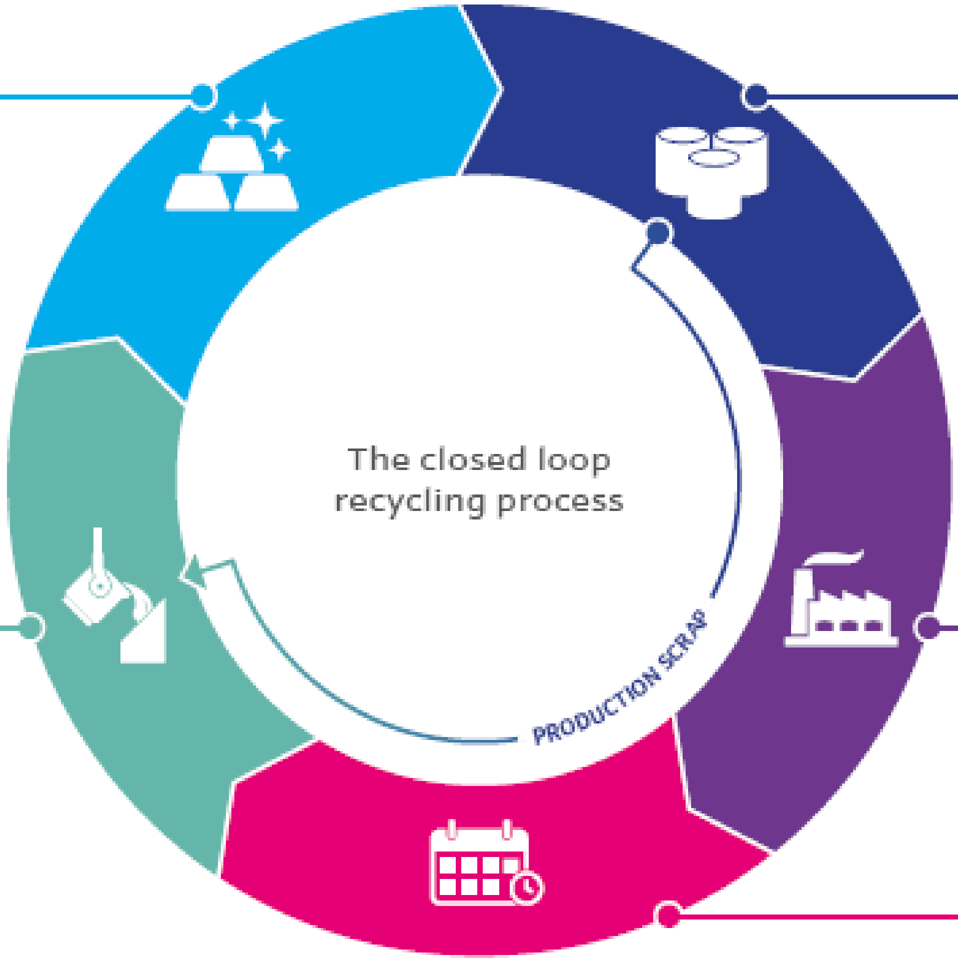
PGMs are purchased as a part of end-of-life scrap by collectors

PGM is recycled by specialist refiners

PGM is sold back to the market and becomes available again for purchase

TWO WAYS OF PGMS RECYCLING

Close loop recycling



Customer PGM is used to manufacture a product such as a process catalyst

The PGM-containing product is used in an industrial process

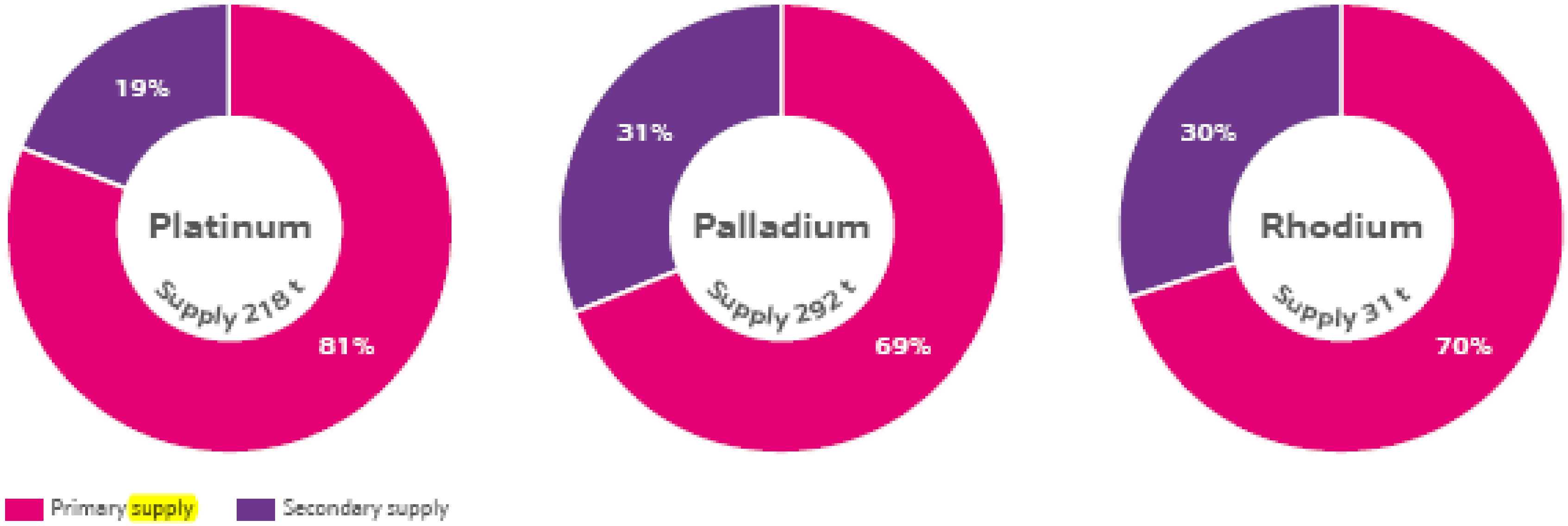
The PGM remains in use for a few months or years

PGM is recovered from scrap by specialist refiners

Refined PGM is credited to the customer's account

TWO WAYS OF PGMS RECYCLING

A case study



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

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

FIRST SERIES	**SECOND/THIRD SERIES**
Δ depends on ligands	Larger Δ
High-spin and low-spin states available	Preferentially low-spin states
Often unpaired e-	Preferentially paired e-
The highest oxidation state is not very stable (MnO_4^- is a strong oxidant)	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

$$\mathrm{Rh(I)} \rightleftharpoons \mathrm{Rh(III)} \rightleftharpoons \mathrm{Rh(V)}$$

FIRST SERIES

Oxidation states differ of one unit

$$\mathrm{Fe(0)} \rightleftharpoons \mathrm{Fe(I)} \rightleftharpoons \mathbf{Fe(II)} \rightleftharpoons \mathbf{Fe(III)} \rightleftharpoons \mathrm{Fe(IV)} \rightleftharpoons \mathrm{Fe(V)} \rightleftharpoons \mathrm{Fe(VI)}$$

THE GLOSSARY FOR CATALYSIS

- *Precatalysts are compounds from which the catalysts are generated. They are stable enough to be isolated in a pure form.*
- *Cocatalyst is any additional component required for the catalytic reaction; it may play different roles: activator, stabilizer. It is **not** catalytically active.*
- *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.*
- *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.*

THE GLOSSARY FOR CATALYSIS

- *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 main features applied to assess the catalyst performances are:*
  - *catalyst activity and productivity;*
  - *catalyst selectivity;*
  - *catalyst stability.*

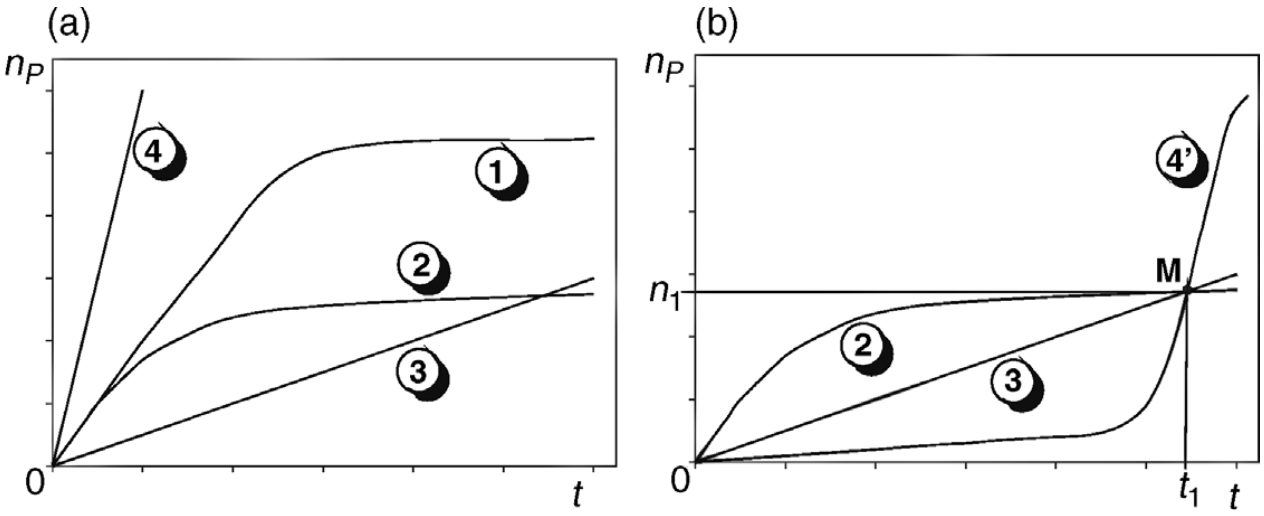
Catalyst activity is the parameter to evaluate the rate of the catalytic reaction with respect to the amount of catalyst. It is measured as **TON** and **TOF**.

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

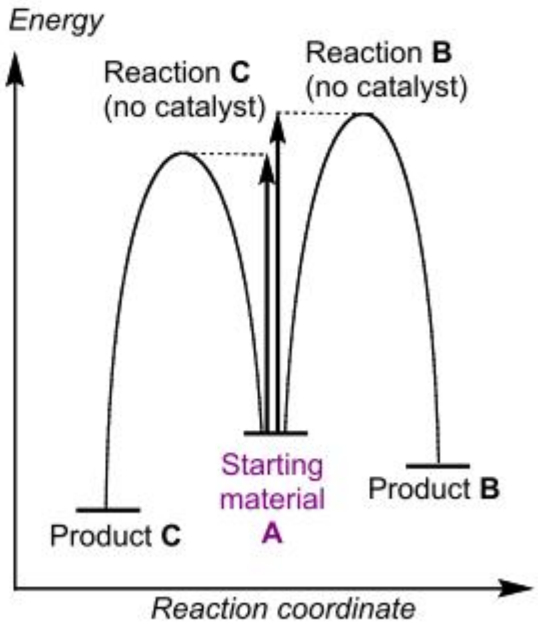
[sub]/[cat] or [sub]/[M]: a very important figure in catalysis.

Plots of conversion vs time



CATALYSIS: selectivity in the target product

No Catalyst Present



$\mathbf{A} \xrightarrow{\text{no catalyst}} \mathbf{B + C}$

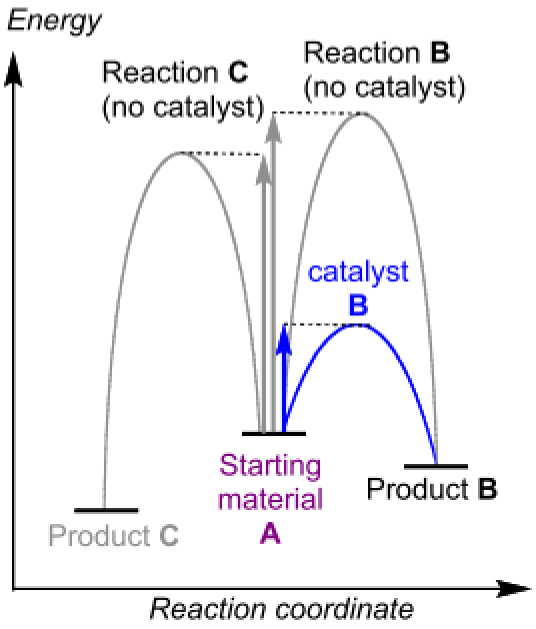
Several products

Separation process is required

Energetically unefficient

Low yield

Catalyst B Present



$\mathbf{A} \xrightarrow{\text{catalyst } \mathbf{B}} \mathbf{B}$

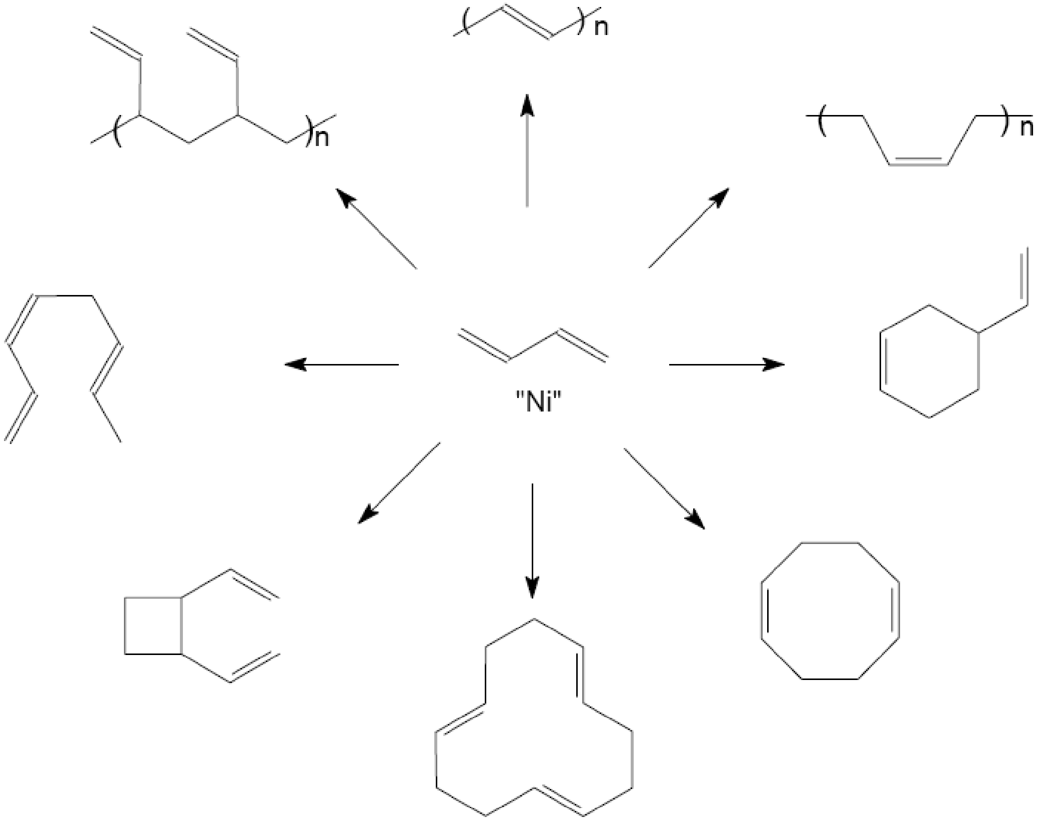
One product only

No separation process required

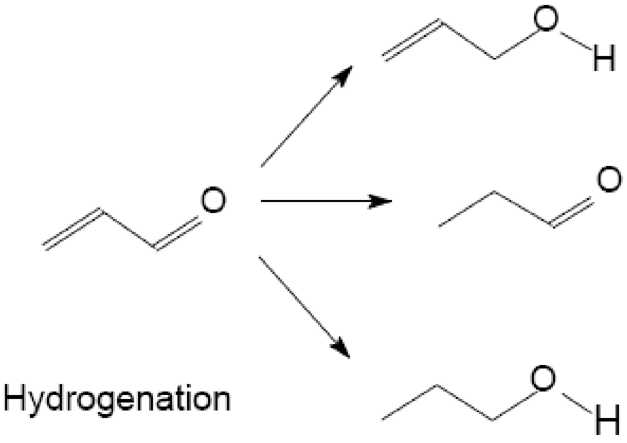
Energetically efficient

Yield 100%

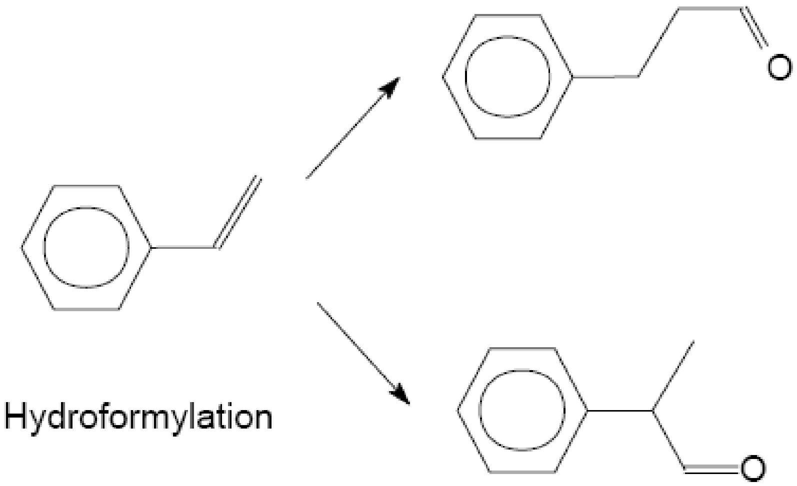
Catalyst SELECTIVITY:
From the same substrate it is possible to obtain different products by using different catalysts based on the same metal



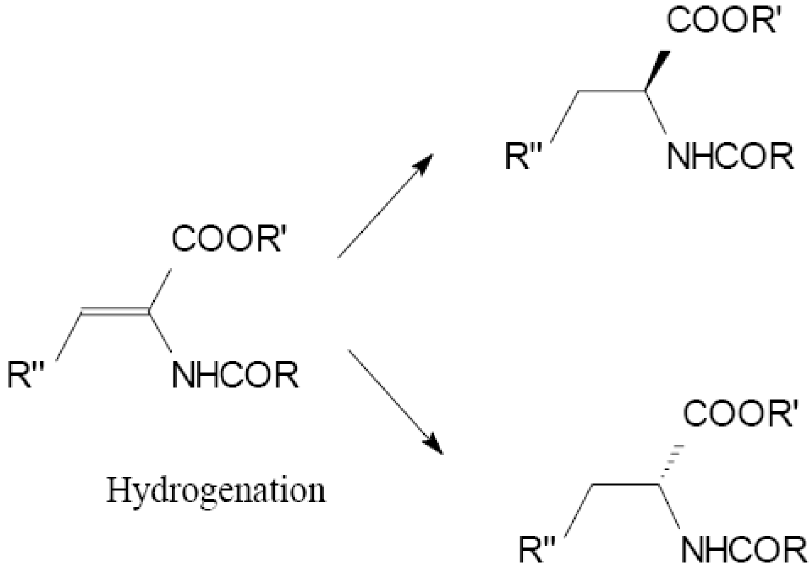
SELECTIVITY of chemical reactions:



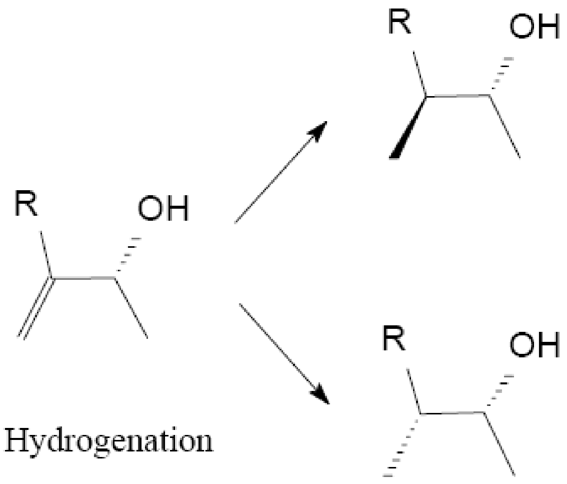
Chemoselectivity



Regioselectivity



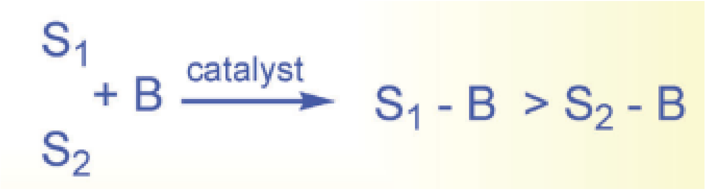
Enantioselectivity



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.



$$\begin{matrix} S_1 \\ \\ S_2 \end{matrix} + B \xrightarrow{\text{catalyst}} S_1 - B > S_2 - B$$

How the substrate selectivity is measured:

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

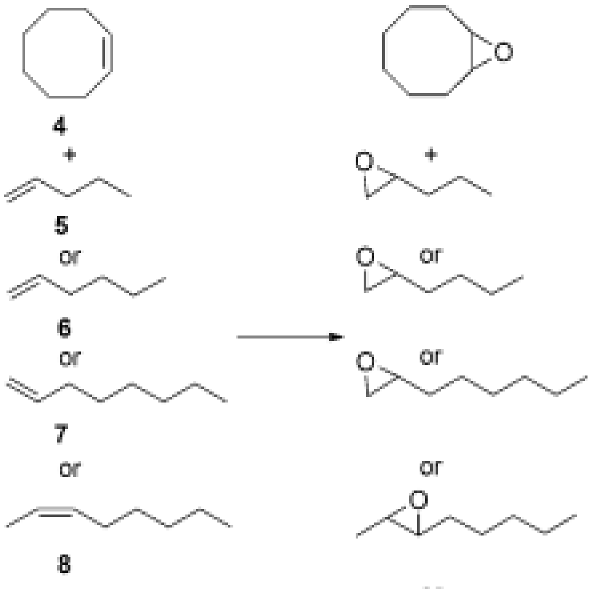
The studied substrate contains the same reacting functionality.

E. Lindbäck, S. Dawaigher, K. Wärnmarck *Chem. - Eur. J.* **2014**, *20*, 13432.

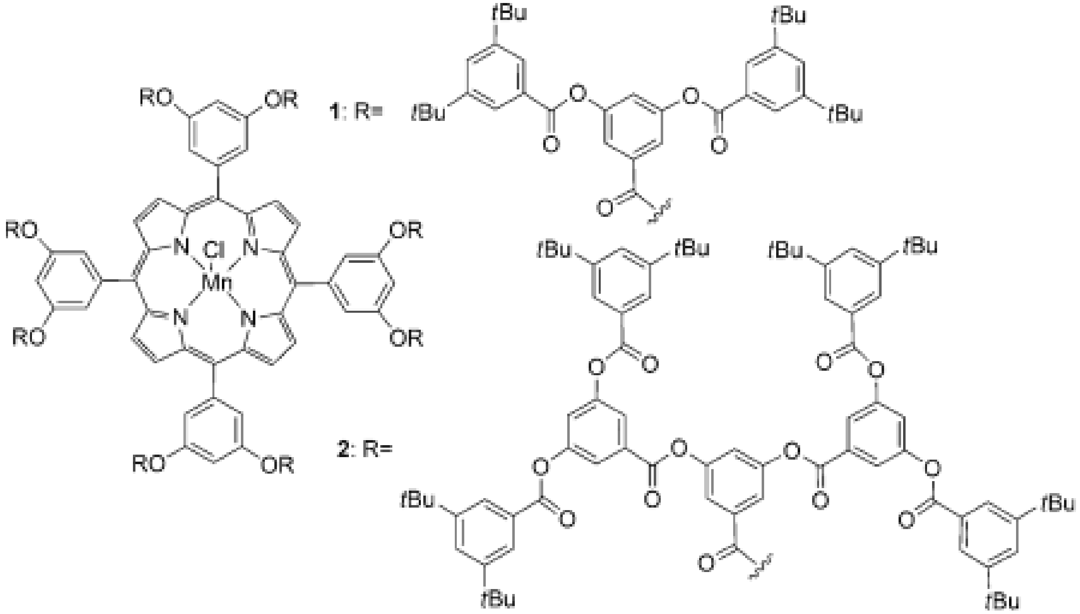
SUBSTRATE-SELECTIVE CATALYSIS

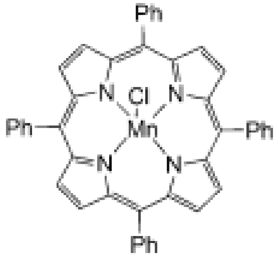
An example

Epoxidation of alkenes



The catalysts





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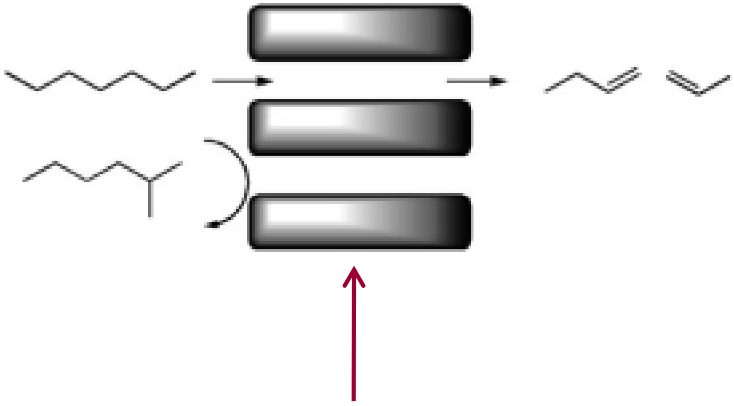
The investigated comparisons:
1 and 2 *vs* 3;
4 and 5 *vs* 4 and 6 *vs* 4 and 7;
1 *vs* 2 for 5, 6, 7;
4 and 7 *vs* 4 and 8.

SUBSTRATE-SELECTIVE CATALYSIS

Example of an industrial application: only heterogeneous catalysts

The steam cracking of hydrocarbons



Catalyst: Zeolites

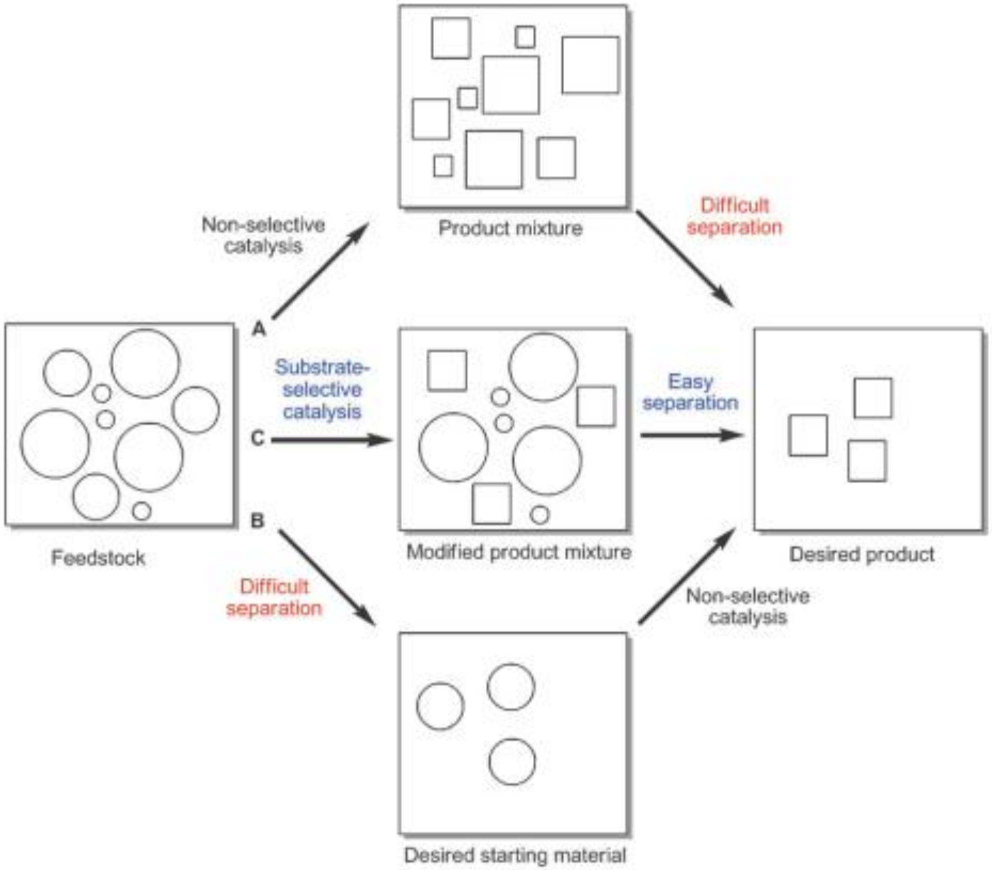
Only linear hydrocarbons are transformed into linear alkenes!

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:

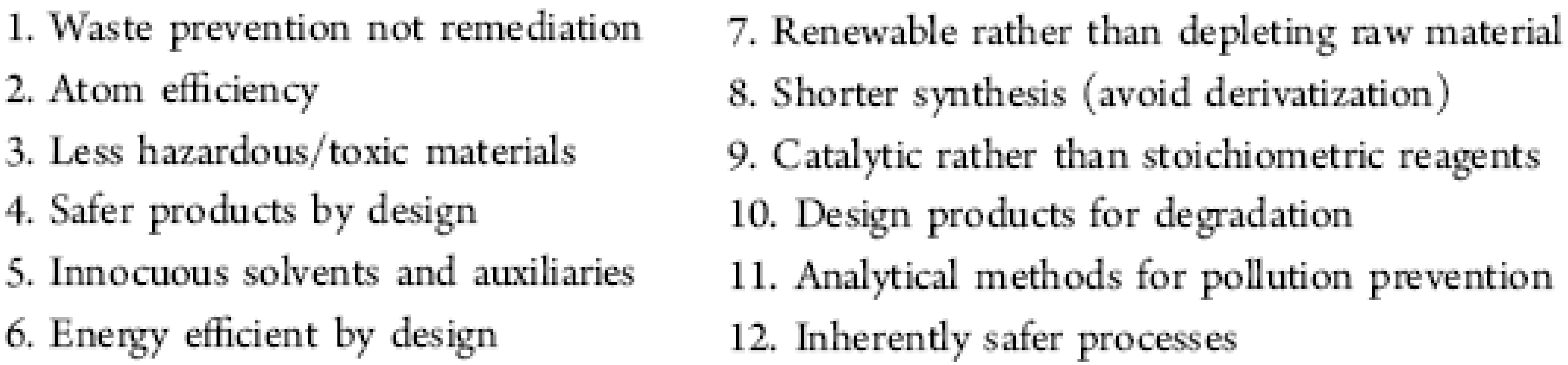


High SELECTIVITY in chemical reactions is a way to:

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

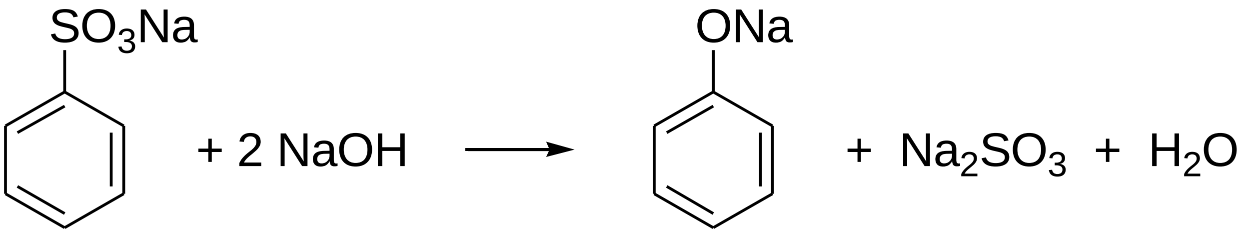
2. ATOM ECONOMY: synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.

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 e 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.



116 g **126 g** **18 g**

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 materials** in the stoichiometric equation.

i.g.: 116/260 = 44.9 %

High Atom Economy Processes

Hydrogenation

AE = 100 %

Oxidation

AE = 87 %

Carbonylation

AE = 100 %

Hydroformylation

AE = 100 %

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

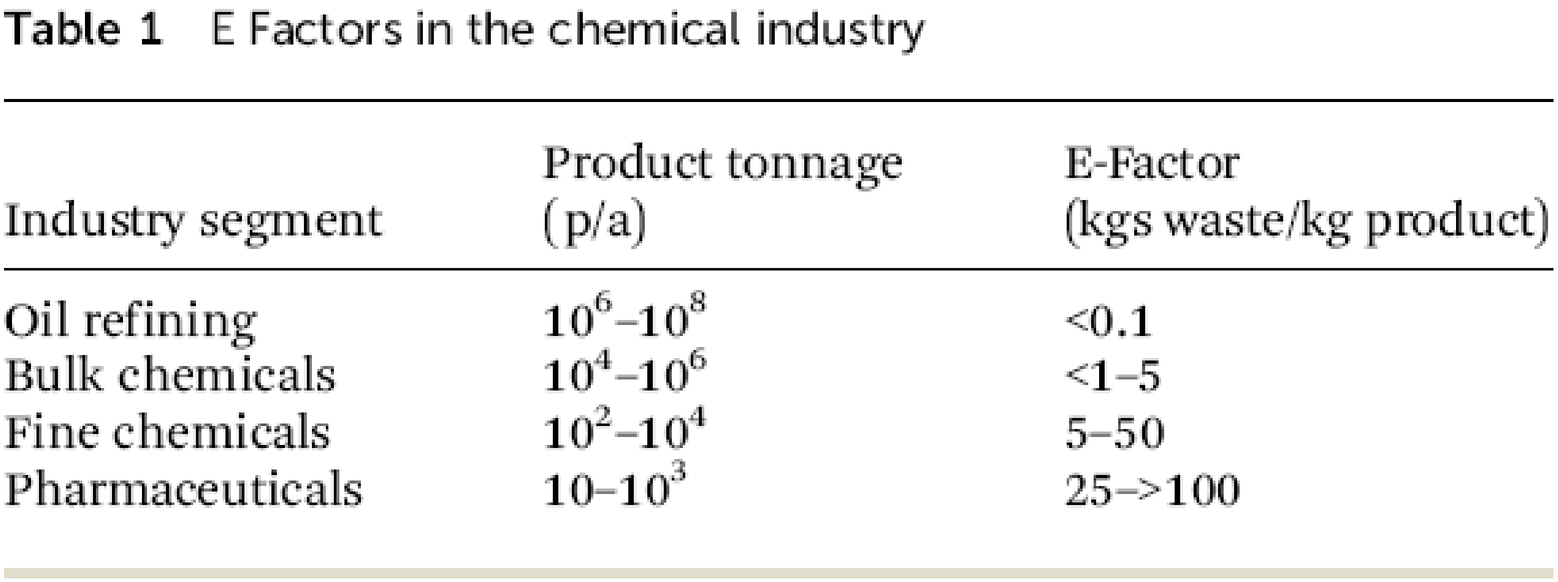
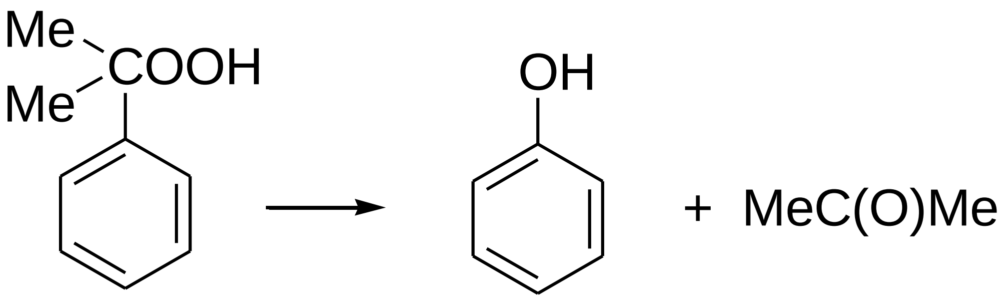


Table 1 E Factors in the chemical industry

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

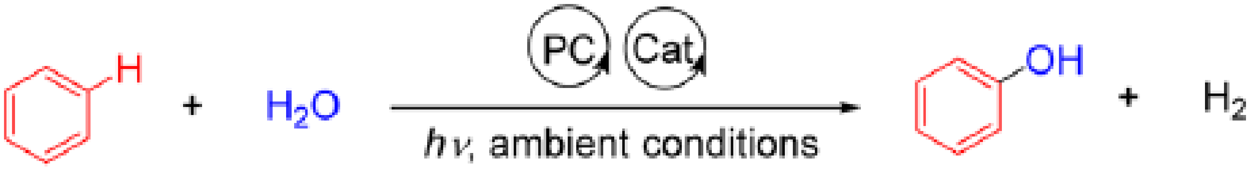
Current process industrially applied for the synthesis of phenol



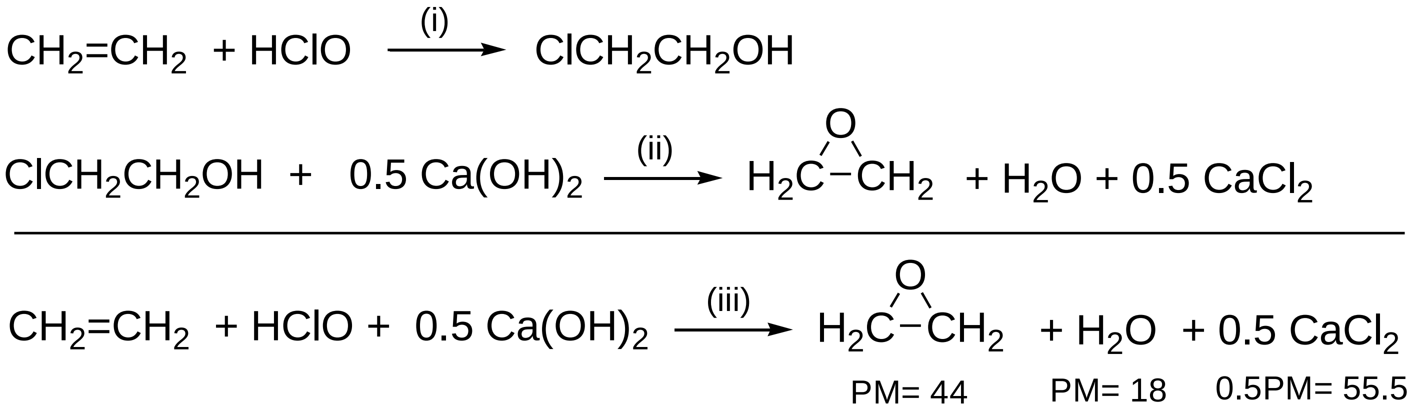
ATOM EFFICIENCY = 100 %

E FACTOR = 0

Process under investigation for the synthesis of phenol

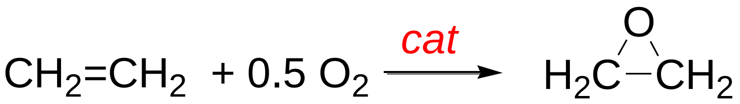


Traditional process industrially applied for ethylene oxide synthesis (chlorohydrin process):



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.

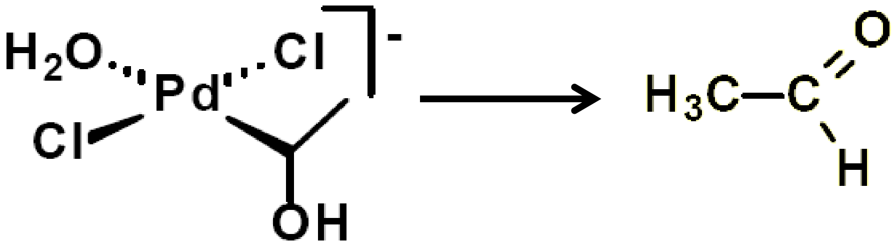
C FACTOR: Climate factor = total mass of CO_2 emitted/mass of product formed (kg CO_2 emitted /kg product).

It is the sum total of kg CO_2 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.

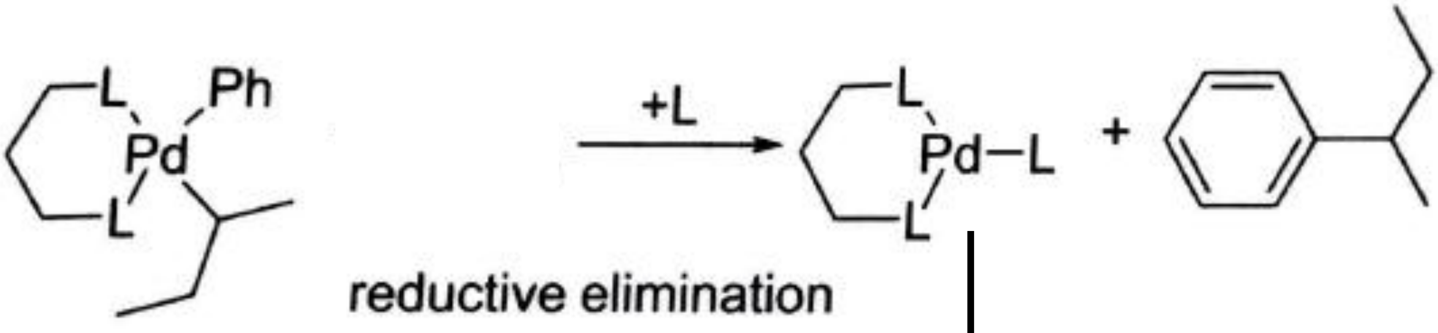
CATALYST STABILITY

METAL

Deactivation through metal deposition



+ Pd^0 + Cl^- + H_2O + HCl(g)



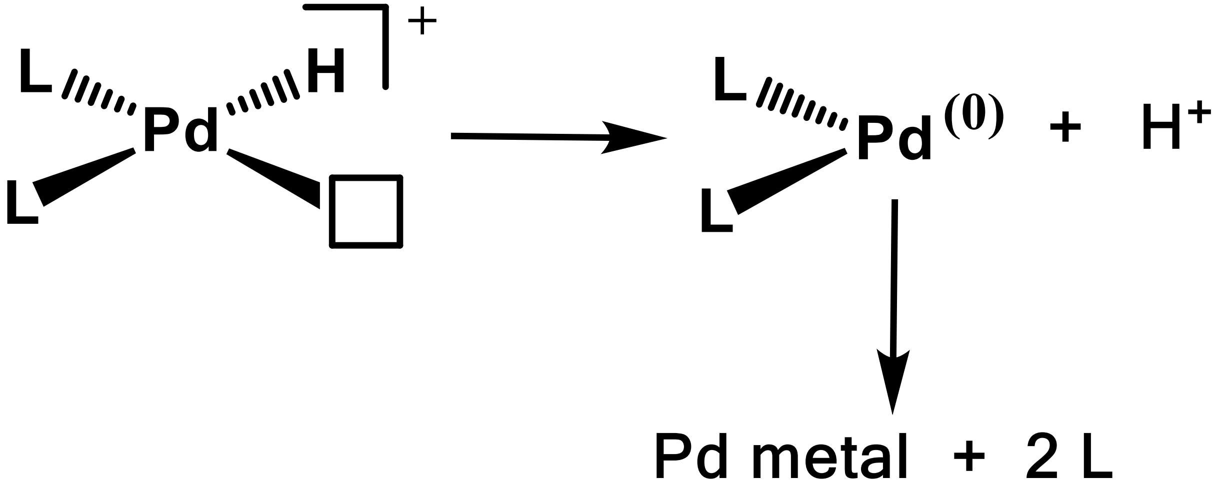
Pd metal + L-L + L

CATALYST STABILITY

METAL

Deactivation through metal deposition

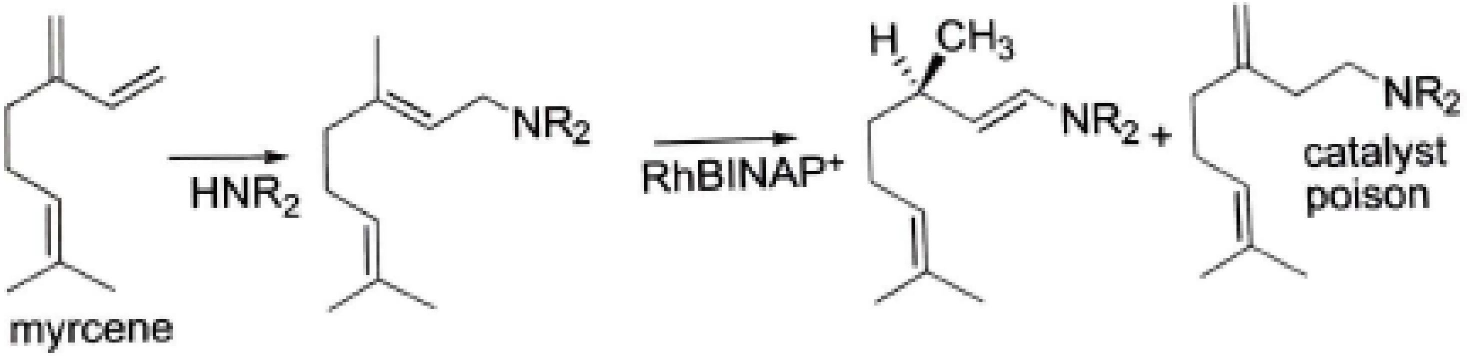
$$2\ \mathrm{HCo(CO)_4} \xrightarrow{-\mathrm{H_2}} \mathrm{Co_2(CO)_8} \xrightarrow{-\mathrm{CO}} \text{Co metal} \downarrow$$

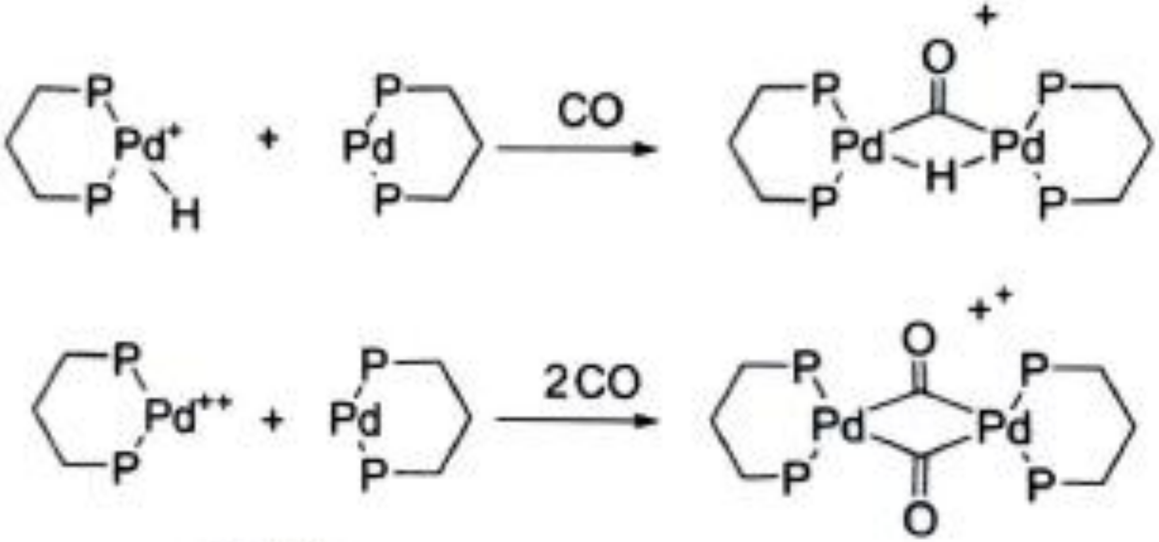


CATALYST STABILITY

METAL

Deactivation through formation of inactive species





P=PR₂

CATALYST STABILITY

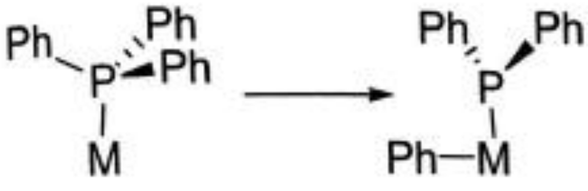
LIGANDS

Deactivation through ligand decomposition

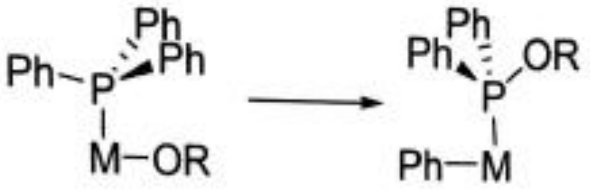
$$PR_3 + 1/2\ O_2 \longrightarrow O{=}PR_3$$

$$PR_3 + H_2O \longrightarrow H_2 + O{=}PR_3$$

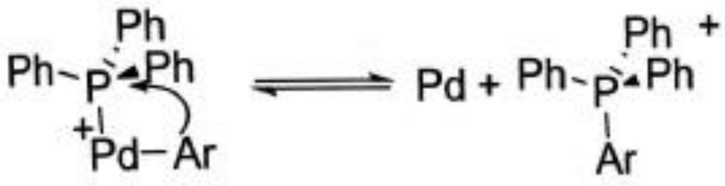
$$PR_3 + CO_2 \longrightarrow CO + O{=}PR_3$$



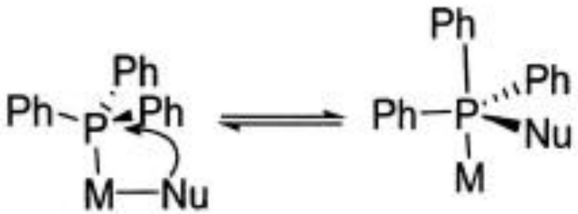
Oxidative addition



Nucleophilic attack



Phosphonium ion formation

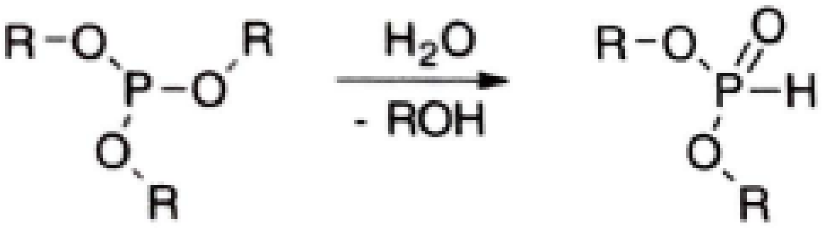


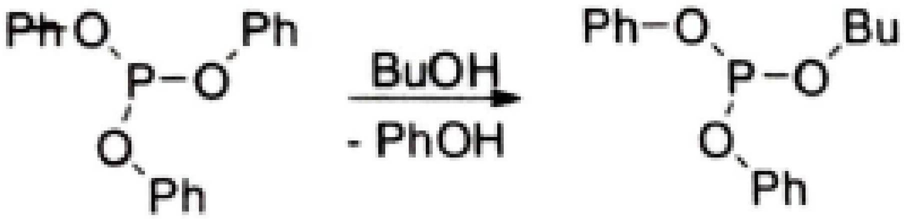
Phosphorane formation

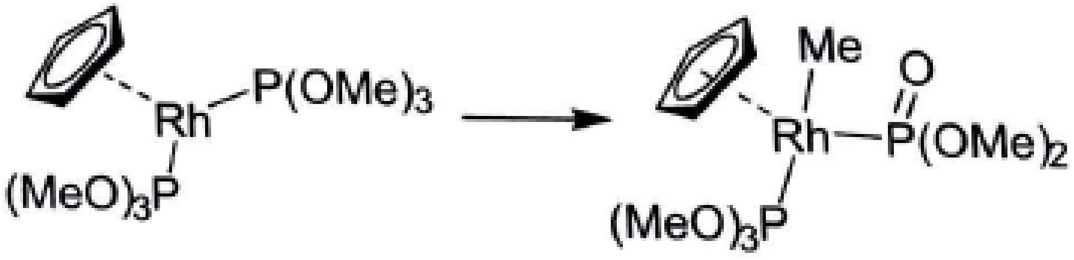
CATALYST STABILITY

LIGANDS

Deactivation through ligand decomposition



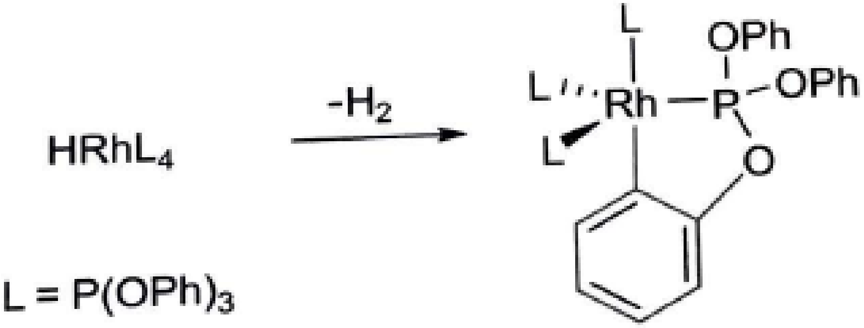


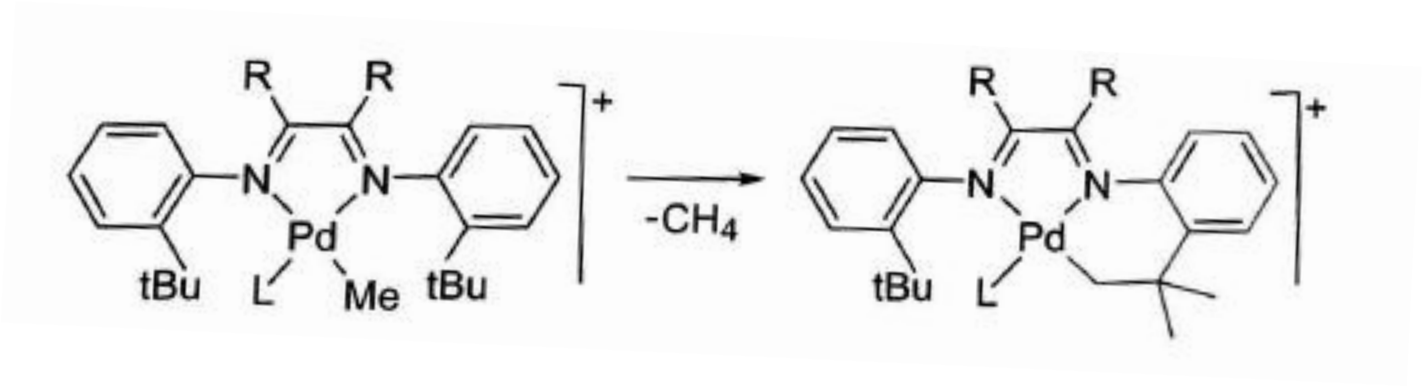


CATALYST STABILITY

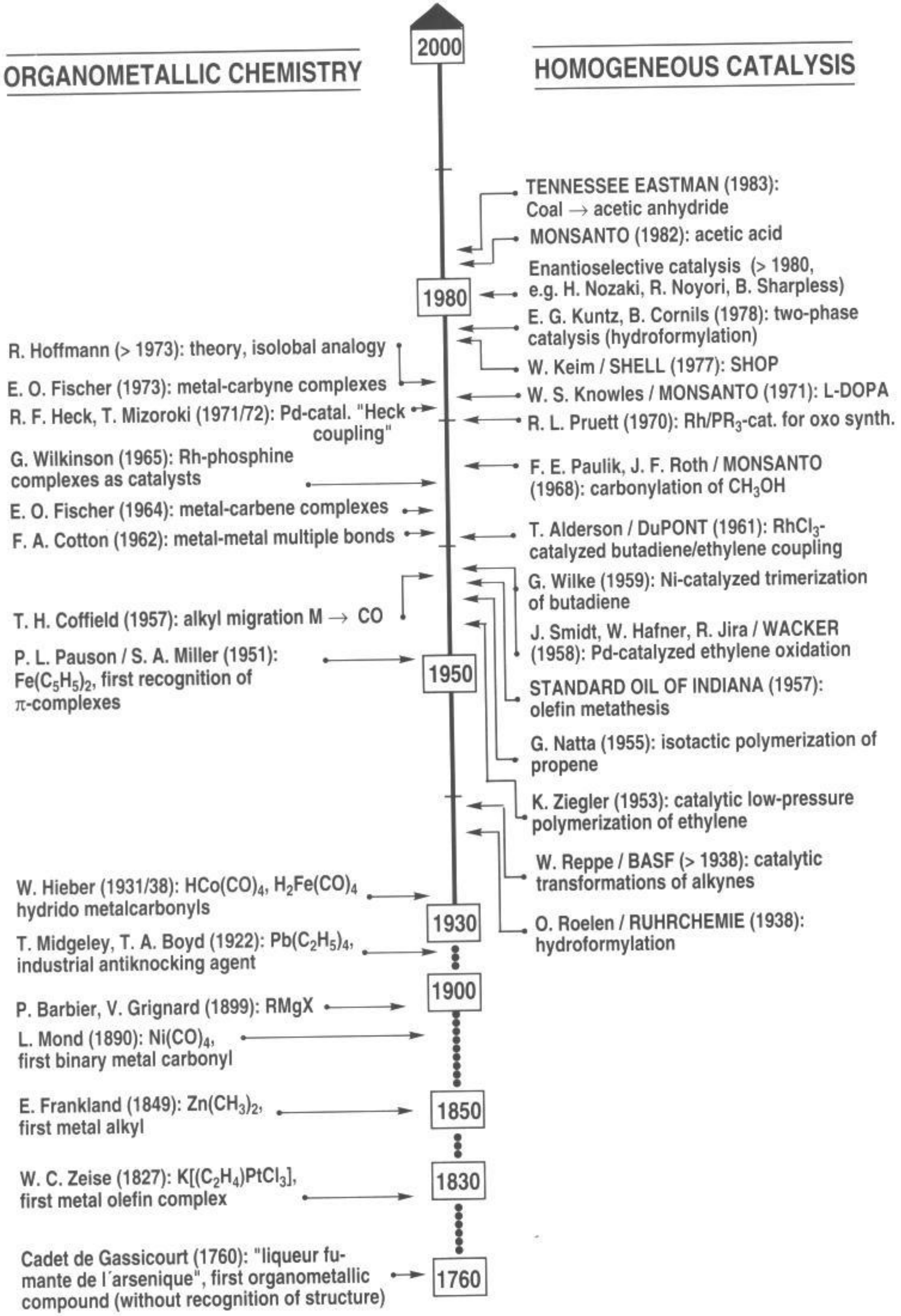
LIGANDS

Deactivation through cyclometalation of the ligand





Historical development of organometallic chemistry and homogeneous catalysis



ORGANOMETALLIC CHEMISTRY

R. Hoffmann (> 1973): theory, isolobal analogy

E. O. Fischer (1973): metal-carbyne complexes

R. F. Heck, T. Mizoroki (1971/72): Pd-catal. "Heck coupling"

G. Wilkinson (1965): Rh-phosphine complexes as catalysts

E. O. Fischer (1964): metal-carbene complexes

F. A. Cotton (1962): metal-metal multiple bonds

T. H. Coffield (1957): alkyl migration M → CO

P. L. Pauson / S. A. Miller (1951): $Fe(C_5H_5)_2$, first recognition of π-complexes

W. Hieber (1931/38): $HCo(CO)_4$, $H_2Fe(CO)_4$ hydrido metalcarbonyls

T. Midgeley, T. A. Boyd (1922): $Pb(C_2H_5)_4$, industrial antiknocking agent

P. Barbier, V. Grignard (1899): RMgX

L. Mond (1890): $Ni(CO)_4$, first binary metal carbonyl

E. Frankland (1849): $Zn(CH_3)_2$, first metal alkyl

W. C. Zeise (1827): $K[(C_2H_4)PtCl_3]$, first metal olefin complex

Cadet de Gassicourt (1760): "liqueur fumante de l´arsenique", first organometallic compound (without recognition of structure)

HOMOGENEOUS CATALYSIS

TENNESSEE EASTMAN (1983): Coal → acetic anhydride

MONSANTO (1982): acetic acid

Enantioselective catalysis (> 1980, e.g. H. Nozaki, R. Noyori, B. Sharpless)

E. G. Kuntz, B. Cornils (1978): two-phase catalysis (hydroformylation)

W. Keim / SHELL (1977): SHOP

W. S. Knowles / MONSANTO (1971): L-DOPA

R. L. Pruett (1970): Rh/PR_3-cat. for oxo synth.

F. E. Paulik, J. F. Roth / MONSANTO (1968): carbonylation of CH_3OH

T. Alderson / DuPONT (1961): $RhCl_3$-catalyzed butadiene/ethylene coupling

G. Wilke (1959): Ni-catalyzed trimerization of butadiene

J. Smidt, W. Hafner, R. Jira / WACKER (1958): Pd-catalyzed ethylene oxidation

STANDARD OIL OF INDIANA (1957): olefin metathesis

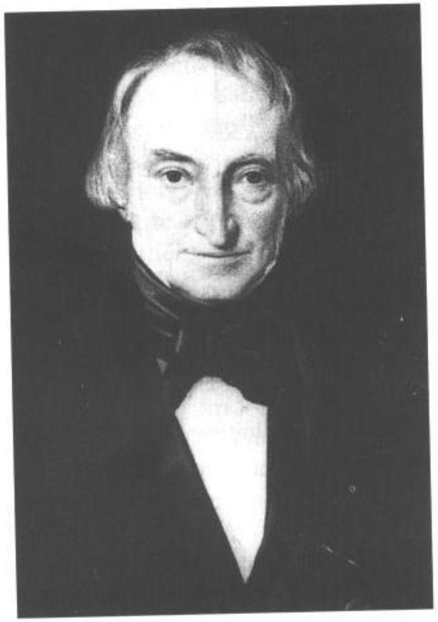
G. Natta (1955): isotactic polymerization of propene

K. Ziegler (1953): catalytic low-pressure polymerization of ethylene

W. Reppe / BASF (> 1938): catalytic transformations of alkynes

O. Roelen / RUHRCHEMIE (1938): hydroformylation

Historical evolution of homogeneous catalysis and the main scientists involved



William ZEISE
1789 - 1847

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

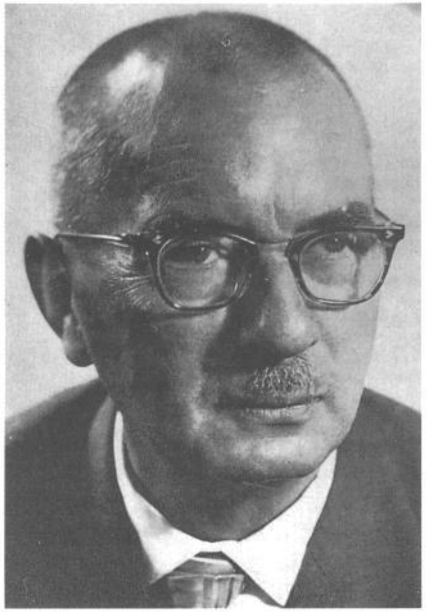
Walter REPPE
1892 - 1969

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

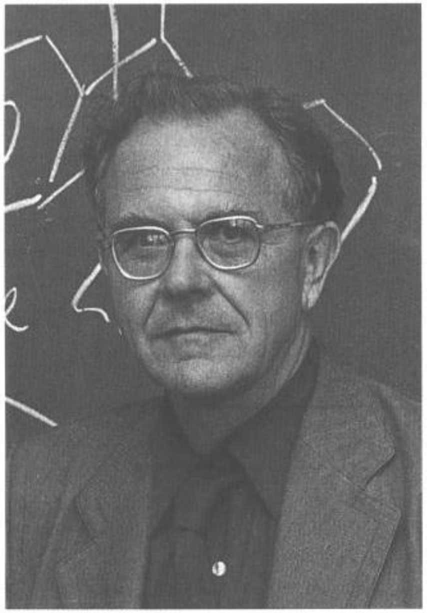


Karl ZIEGLER
1898 - 1973

Director of one Max-Planck-Institute;
He discovered the first catalyst for polyethylene synthesis.
Nobel Prize in 1963

Giulio NATTA
1903 - 1979

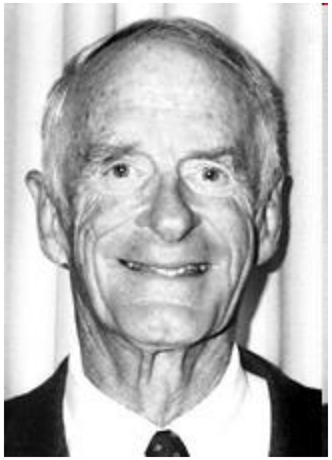
Professor at Milan and Turin Universities;
He discovered the first catalyst for the synthesis of isotactic polypropylene.
Nobel Prize in 1963



Geoffrey WILKINSON
1921 - 1996

Professor at Imperial College in Londra;
He discovered the first catalyst for hdrogentation 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

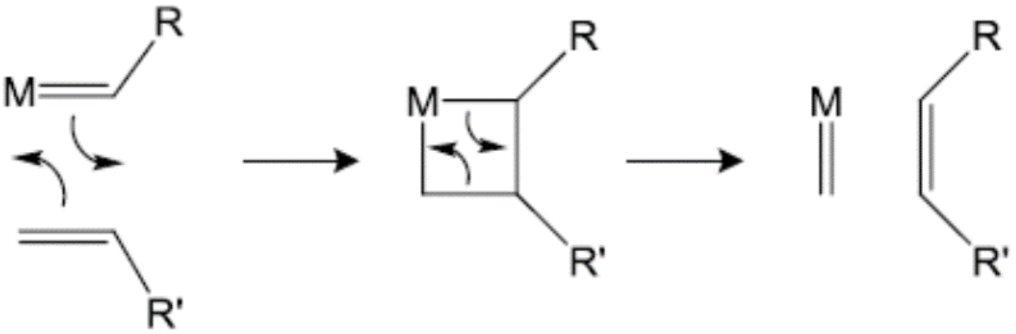
Yves CHAUVIN
1930 – 2015

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

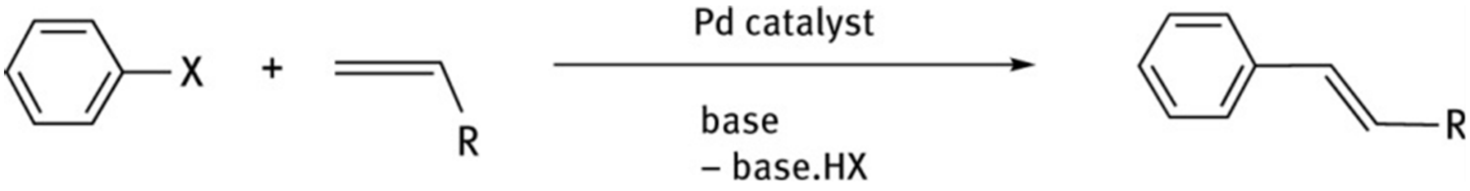
Richard HECK
1931 - 2015

Ei-ichi NEGISHI
1935 - 2021

Akira SUZUKI
1930

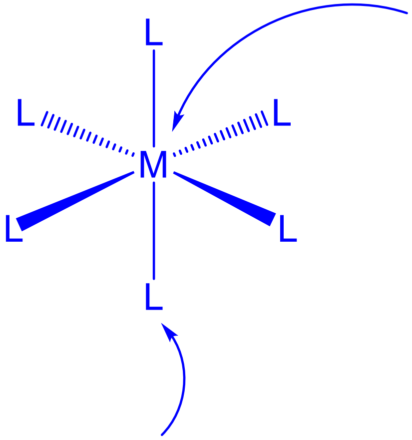
Their research interest was C-C coupling reactions catalyzed by palladium complexes.

Awarded by Nobel Prize in 2010



The homogeneous catalyst

HOMOGENEOUS
CATALYSIS



METALLIC CENTER

EITHER ORGANIC
OR INORGANIC MOLECULES
= LIGANDS

NEUTRAL MOLECULES
phosphines, CO, alkenes,
ammines, immines...

ANIONIC
MOLECULES
halogens,
alkylic moieties,...

Metal and ligands dictate the catalyst performances.

Ligands are classified in:

ACTIVE Ligands

The substrates of the reaction.

SPECTATOR or ANCILLARY Ligands

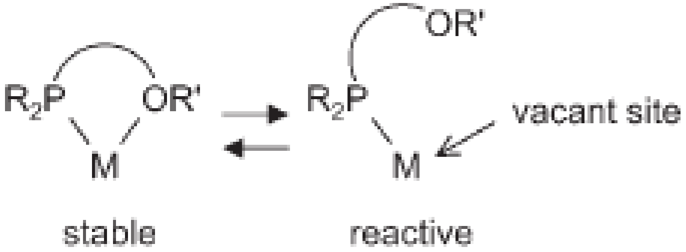
They remain unchanged during the catalytic cycle. They play these roles:

- 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.

UNCONVENTIONAL Ligands

- NON-innocent ligands.
- Ligands from weak interactions

HEMILABILE Ligands



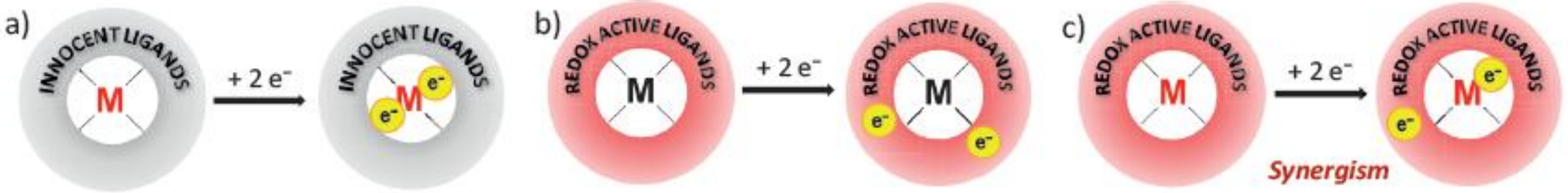
Slight modifications on ancillary ligands significantly affect the chemistry of the complex and, therefore, the properties of the catalyst.

Ancillary ligands affect catalyst ACTIVITY and catalyst SELECTIVITY.

A FEW EXAMPLES OF NON-INNOCENT LIGANDS

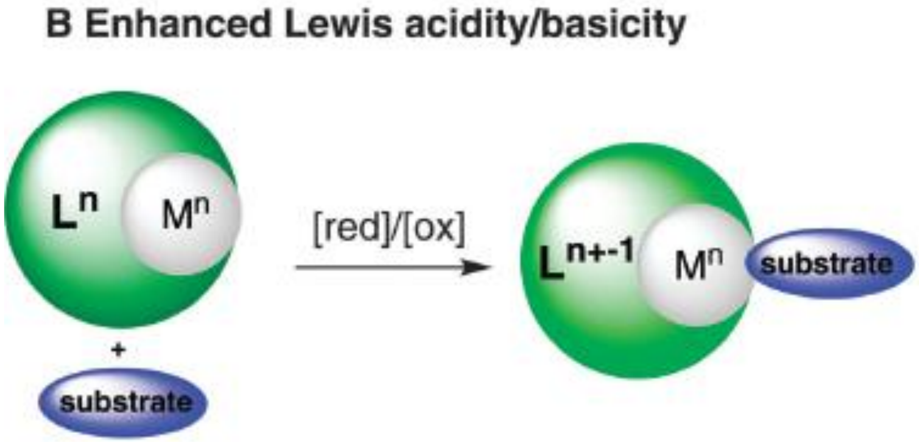
Redox-active ligands

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

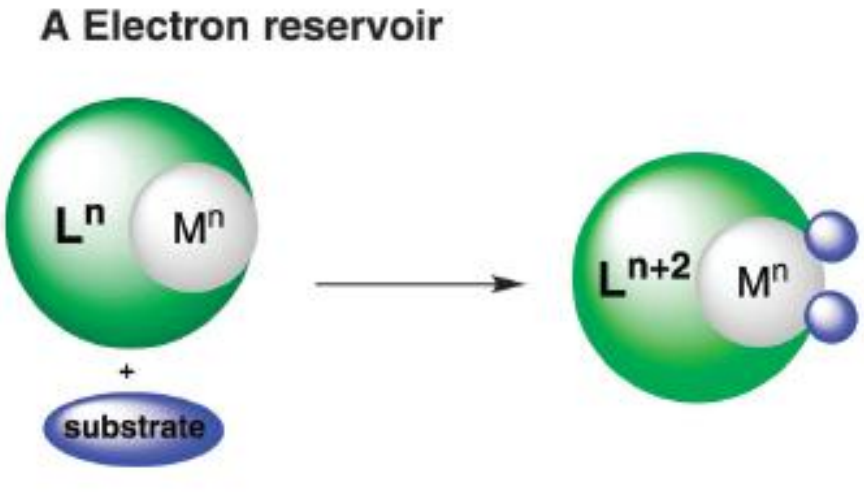
1. The oxidation/reduction of the ligand modifies the Lewis acidity/basicity of the metal.



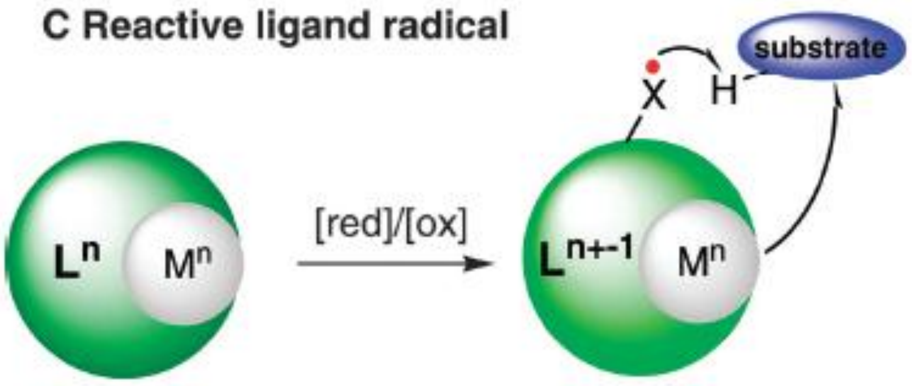
Redox-active ligands

The four main ways of action of redox-active ligands

2. The ligand acts as an electron reservoir.



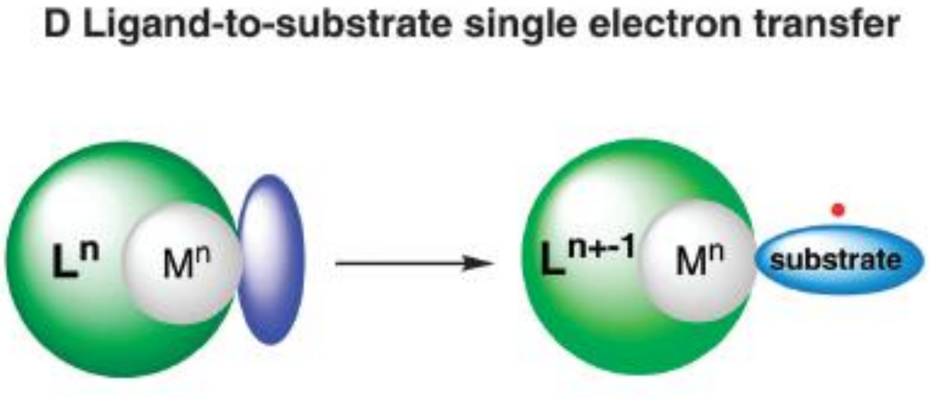
3. The ligand might become a radical species, which is actively involved in bond-making and bond-breaking with the metal.



Redox-active ligands

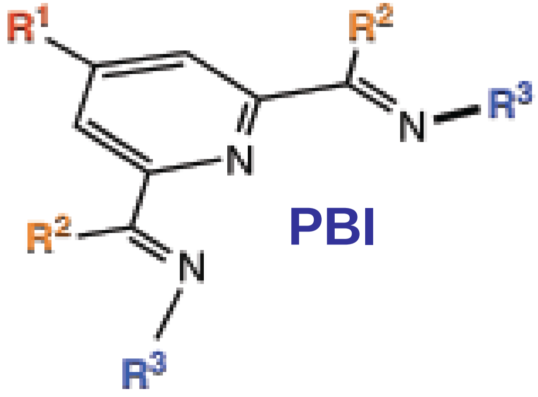
The four main ways of action of redox-active ligands

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

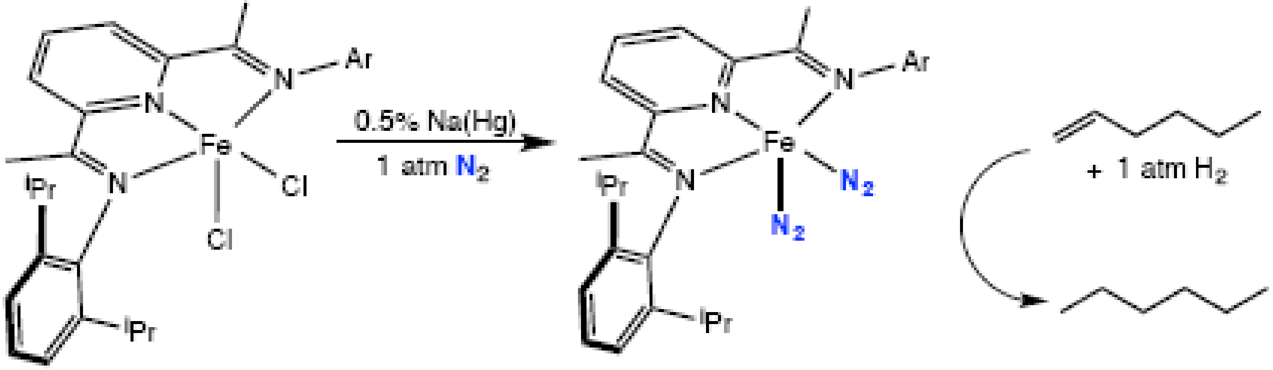


A FEW EXAMPLES OF NON-INNOCENT LIGANDS

BIS(IMMINO) PYRIDINES (Paul Chirik)



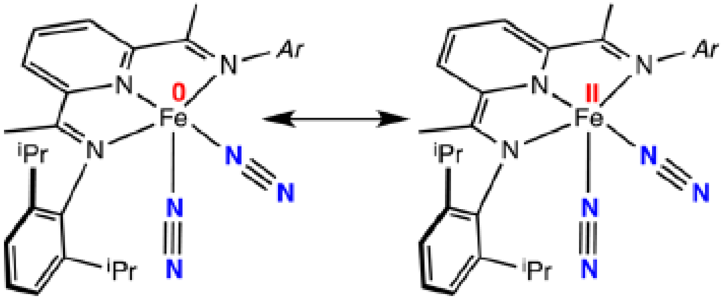
PBI



High activity @ 0.3 mol% [Fe], 23 ºC

POSSIBLE ELECTRONIC STRUCTURES FOR BIS(IMMINO) PYRIDINES

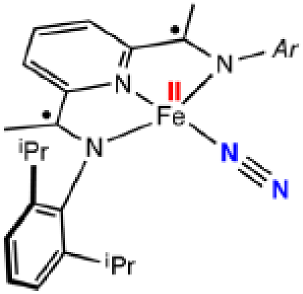
Redox Non-Innocent



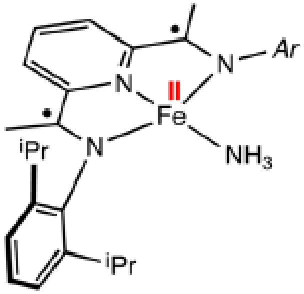
$(^{iPr}PDI)Fe(N_2)_2$ $(^{iPr}PDI)Fe(N_2)_2$

Fe(0)-Fe(II) Resonance
$[PDI]^0$-$[PDI]^{2-}$ Resonance

Redox Active



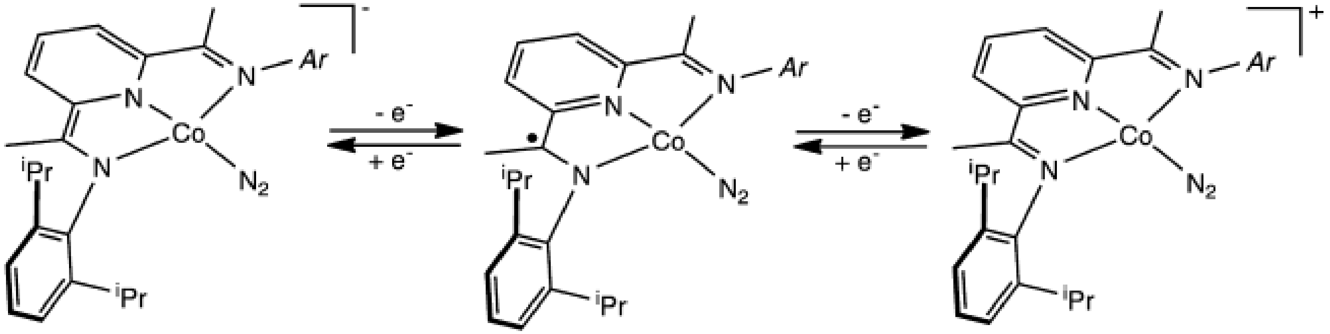
$(^{iPr}PDI)FeN_2$



$(^{iPr}PDI)FeNH_3$

Intermediate Spin Fe(II)
Triplet $[PDI]^{2-}$

Cobalt Dinitrogen Series

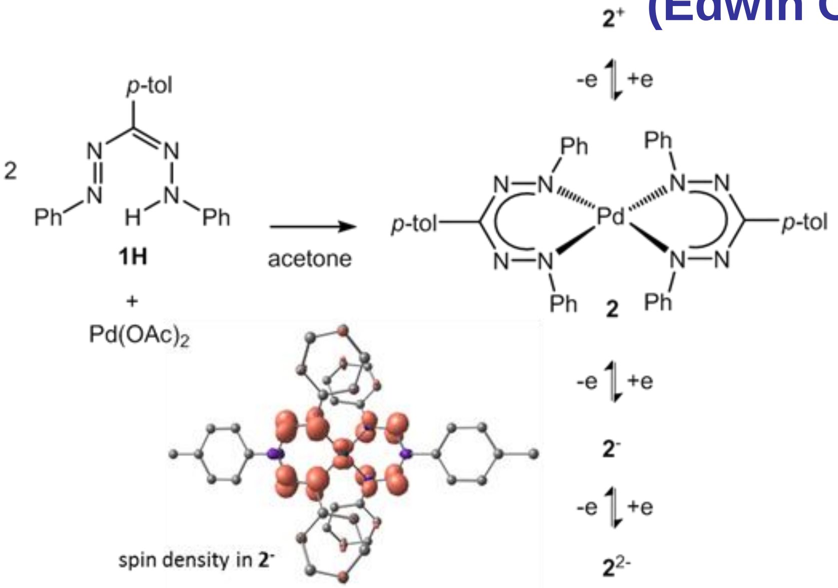


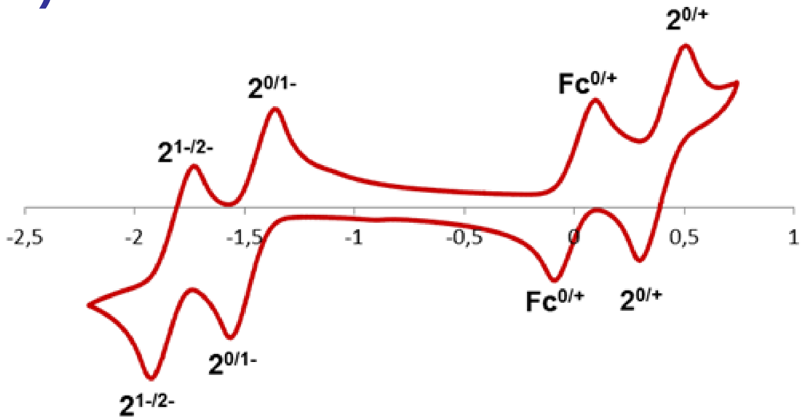
$[(^{iPr}PDI^{2-})Co^{I}N_2]^-$ $(^{iPr}PDI^{1-})Co^{I}N_2$ $[(^{iPr}PDI^{0})Co^{I}N_2]^+$

A FEW EXAMPLES OF NON-INNOCENT LIGANDS

FORMAZANS or Formazanate ligands

(Edwin Otten)



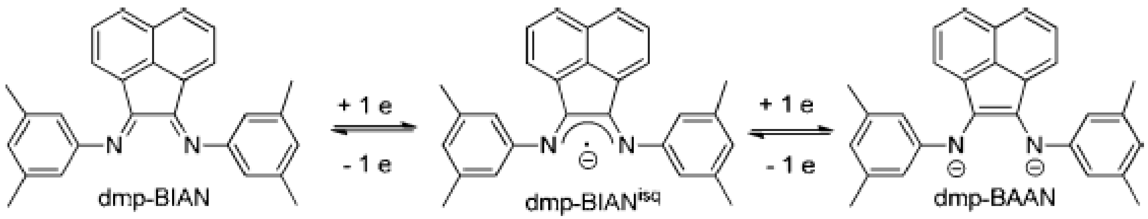


Cyclic voltammogram of compound 2 (ca. 1.50 mM solution of 2 in THF; 0.1 M [nBu4N][PF6] electrolyte; scan rate = 0.5 V·s-1)

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

(Fabio Ragaini, Kensha Marie Clarke)

Scheme 1. First Three Oxidation Levels of the BIAN Ligand

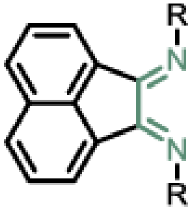


A FEW EXAMPLES OF NON-INNOCENT LIGANDS

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

finely tuned substituents

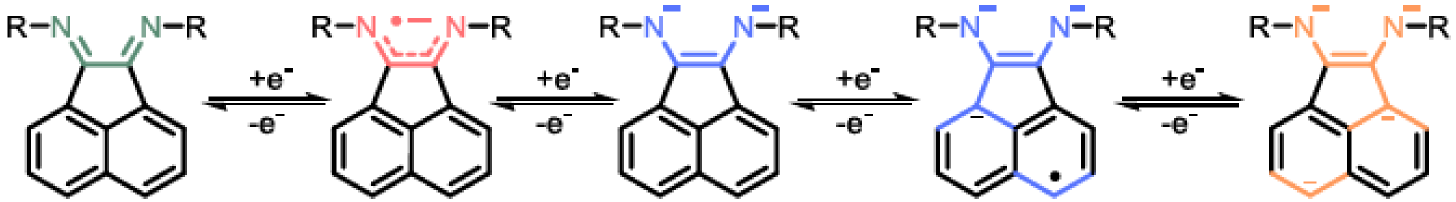
rigid acenaphthene backbone



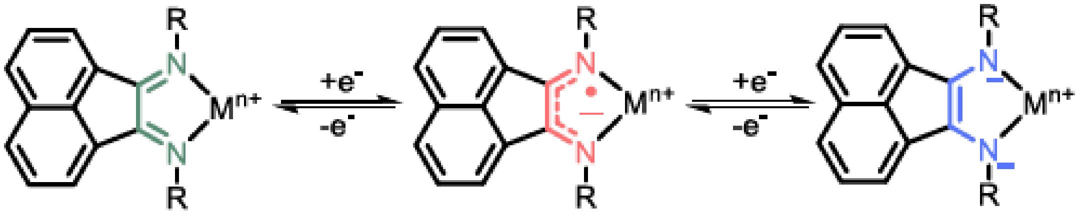
anti-anti-conformation of diimine

strong chelating

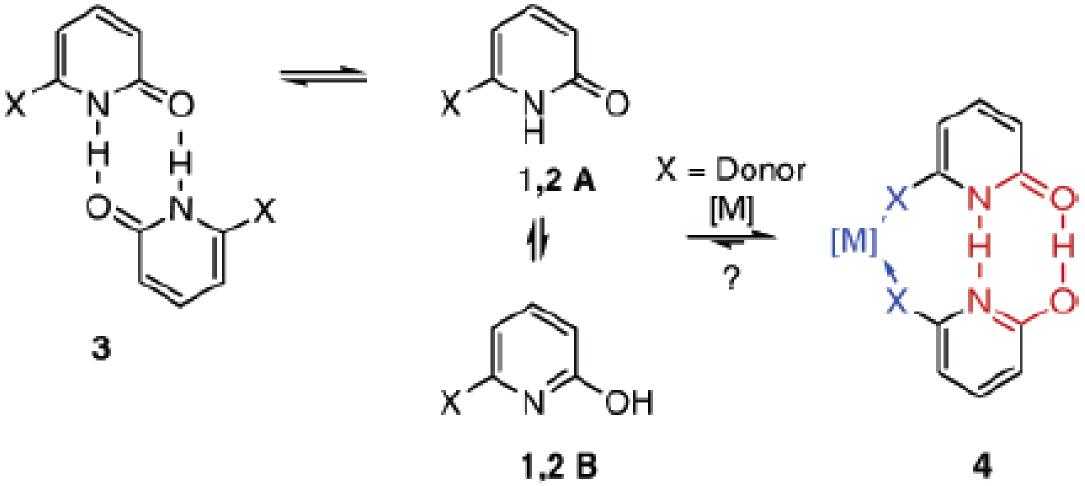
Extended redox properties of BIAN



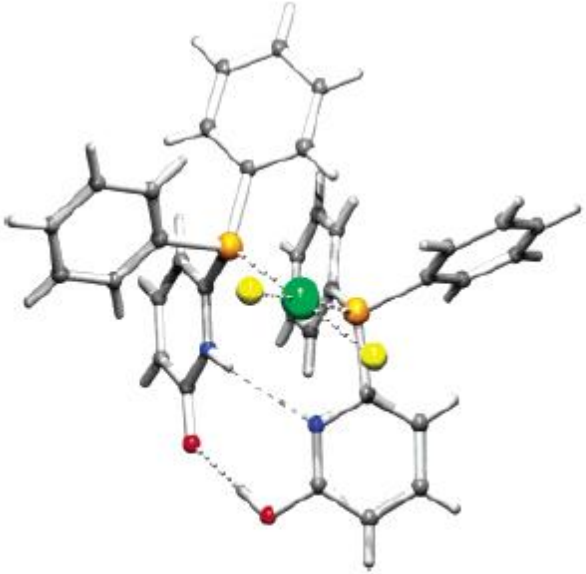
Redox properties of metal/BIAN complexes



IN SITU GENERATION OF BIDENTATE DONOR LIGANDS: A SUPRAMOLECULAR APPROACH



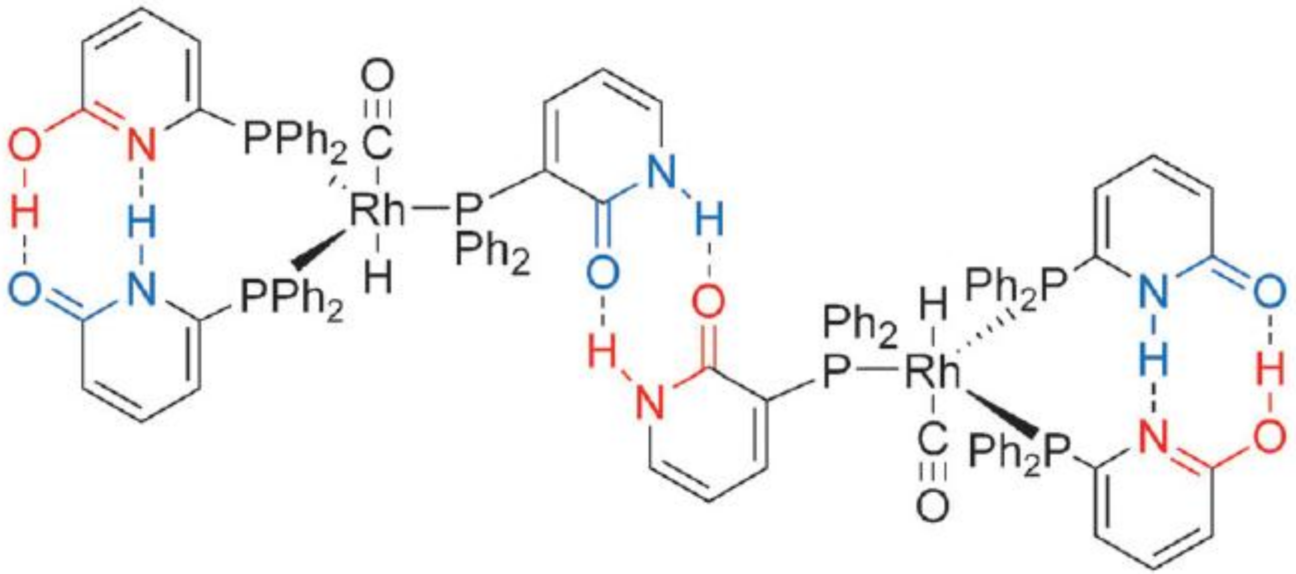
1: X = H
2: X = PPh_2

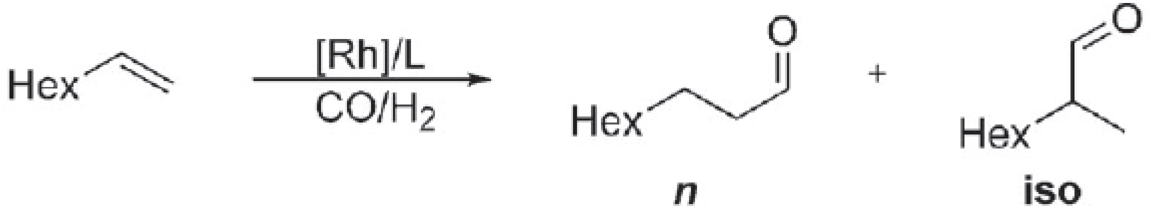


X-ray plot of *cis*-$[PtCl_2(6\text{-}DPPon)_2]$ **5**.

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

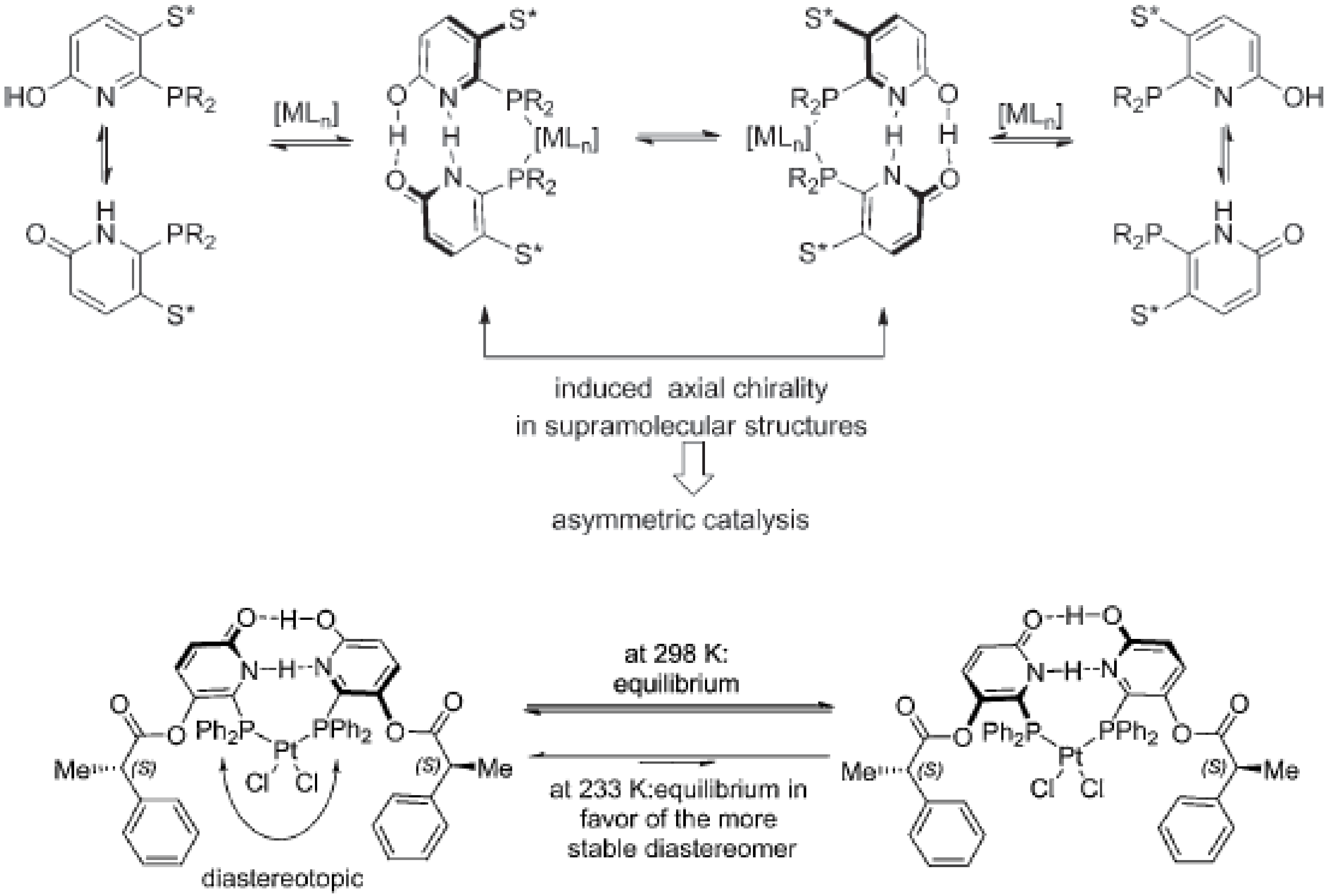
IN SITU GENERATION OF BIDENTATE DONOR LIGANDS: A SUPRAMOLECULAR APPROACH





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.**

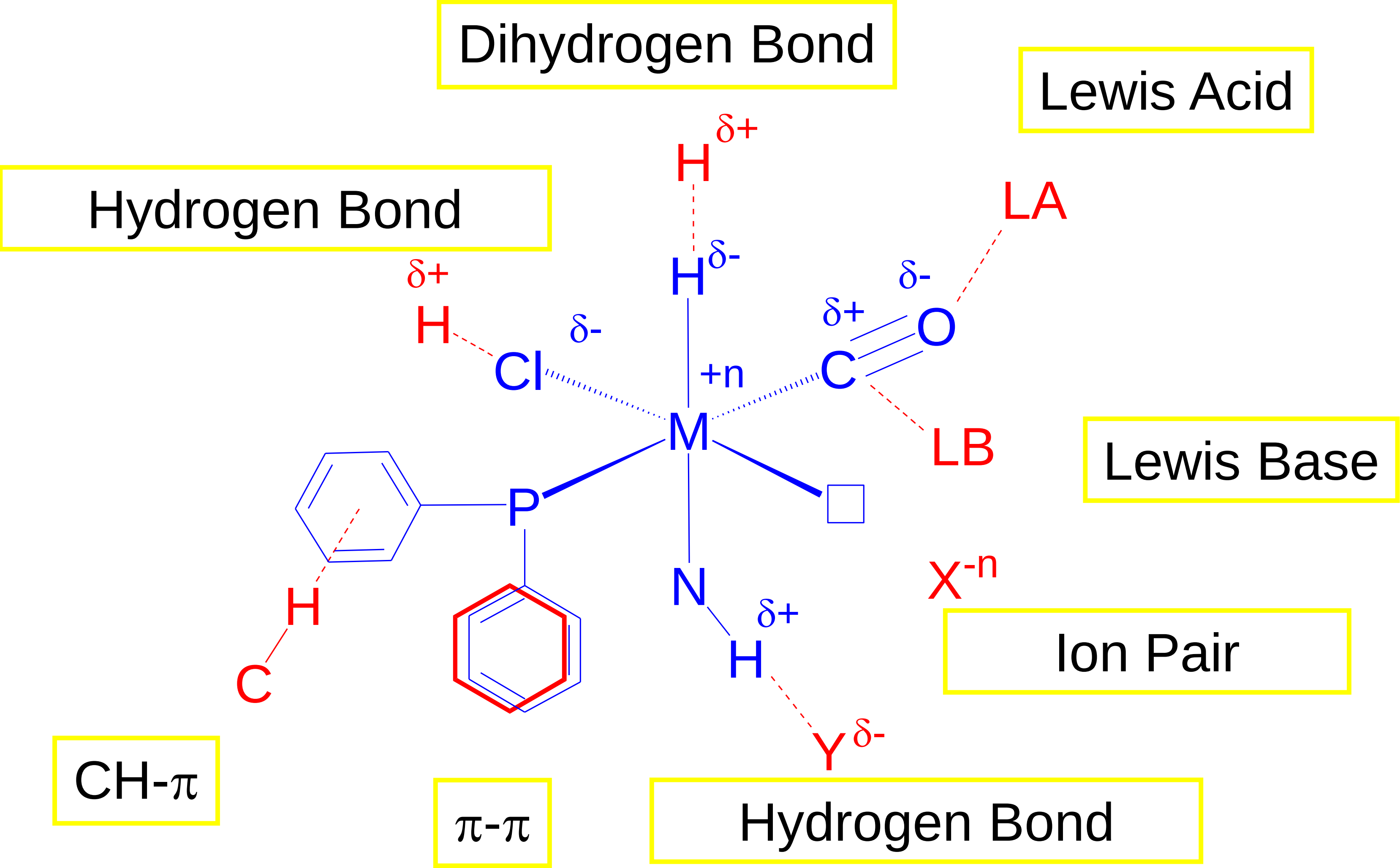
FACTORS AFFECTING CATALYTIC ACTIVITY IN HOMOGENEOUS CATALYSIS

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:



Dihydrogen Bond

Lewis Acid

Hydrogen Bond

Lewis Base

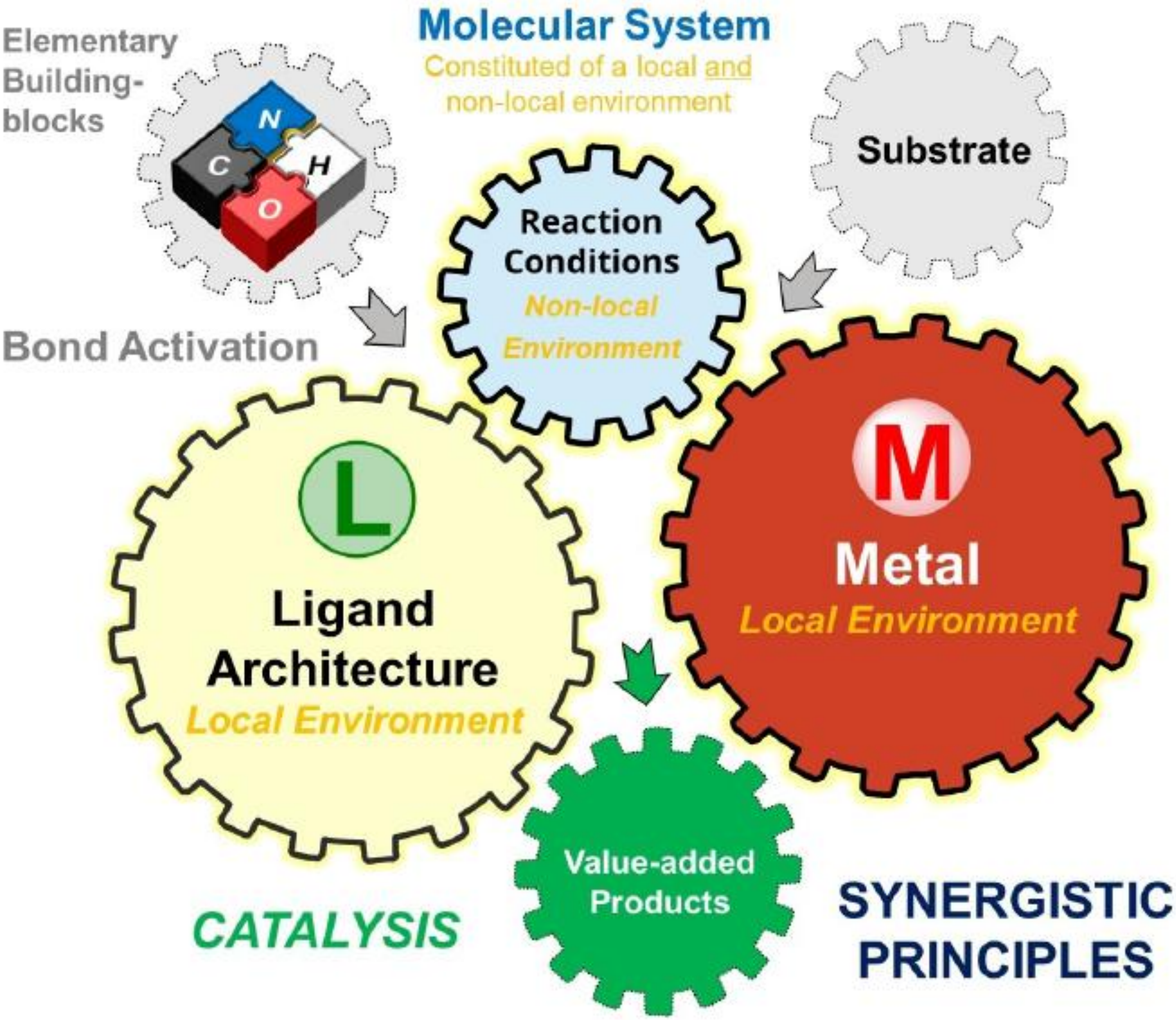
Ion Pair

CH-π

π-π

Hydrogen Bond

THE HOMOGENEOUS CATALYTIC SYSTEM



Werle C. et al. *ChemCatChem* 2021, *13*, 1659.

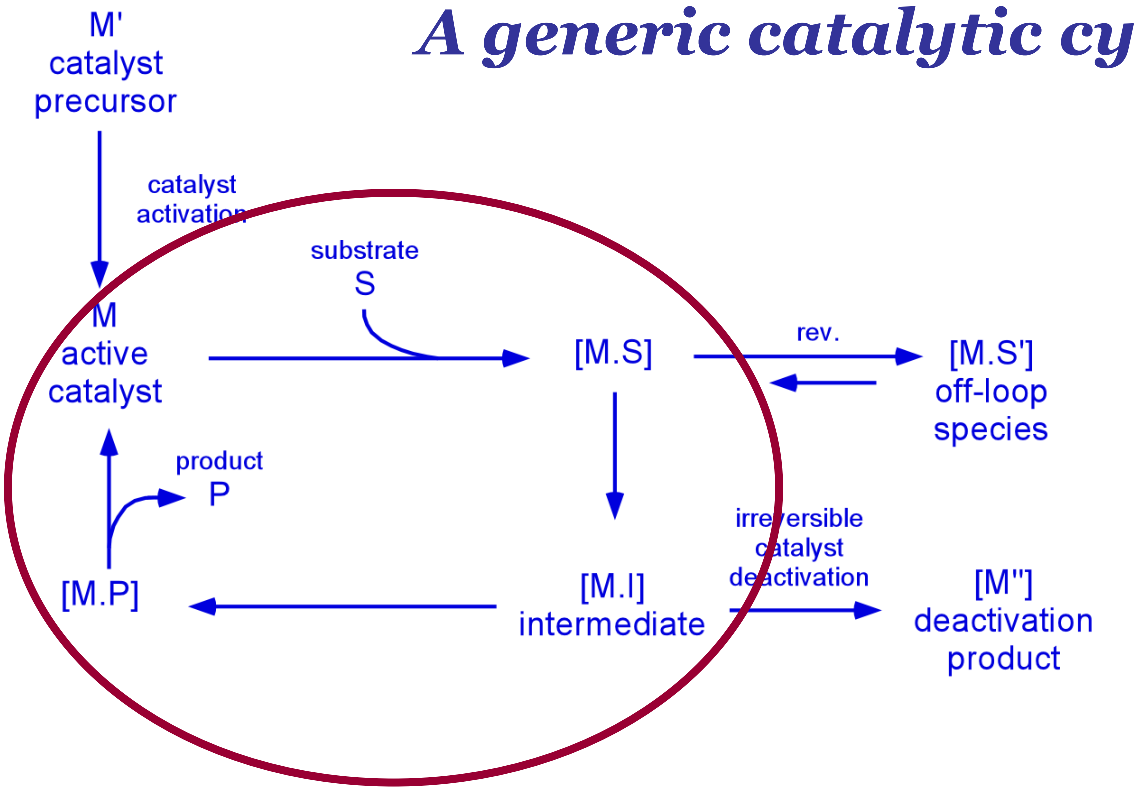
The CATALYTIC SYSTEM is formed by different components:

The catalyst precursor (or precatalyst): is the added complex, which has to be brought into the active form, the catalytically active species;

the solvent;

the cocatalysts: compounds added in lower amount with respect to the substrate, but in stoichiometric or in excess with respect to the precatalyst. They can play different roles, i.e. activator, stabilizer, etc.

A generic catalytic cycle



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.

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.

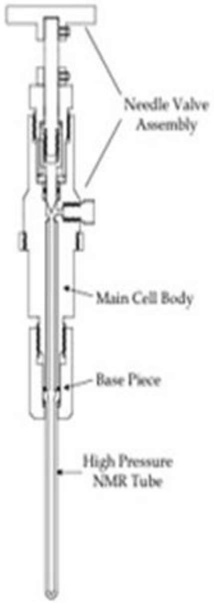
Investigation of homogeneous catalysts is divided into two parts:

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

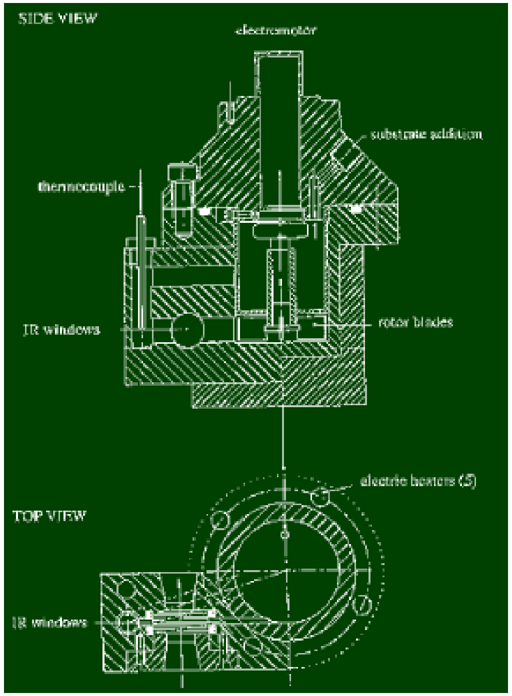
High pressure NMR

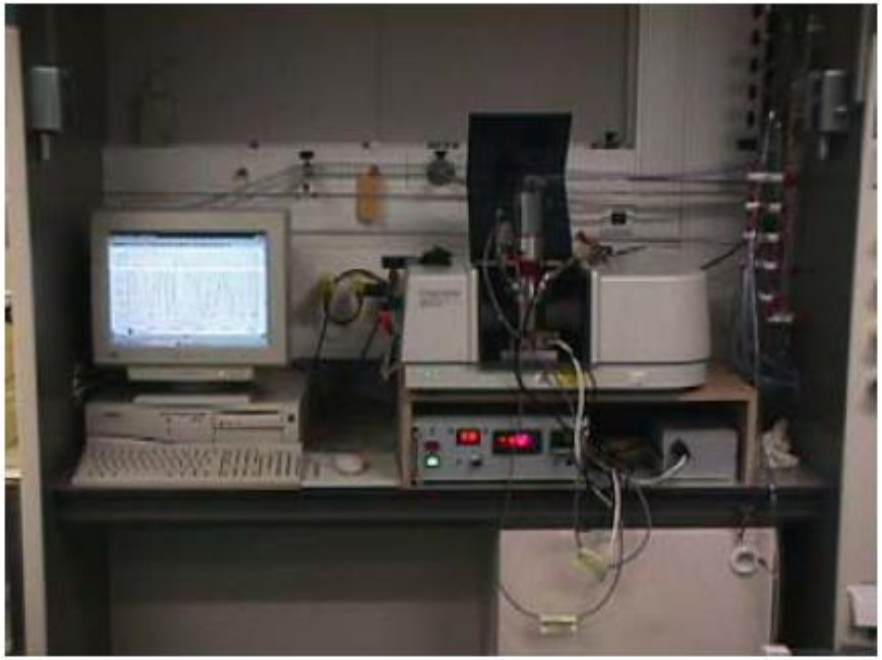


- ✓ **Simple setup;**
- ✓ **Suitable if no gas is consumed;**
- ✓ **Up to 50 atm;**
- ✓ **Suitable for labled gasses;**
- ✓ **Detailed structural information.**

- ↓ **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;**

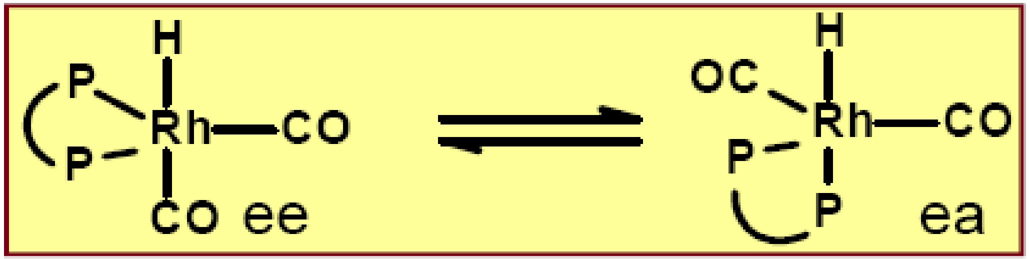
✓ **Concentrations comparable to those applied in catalysis;**

✓ **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: ^{1}H, ^{13}C, ^{31}P, ^{103}Rh;
- ✓ easy exchange and marking with ^{2}D, ^{13}CO.

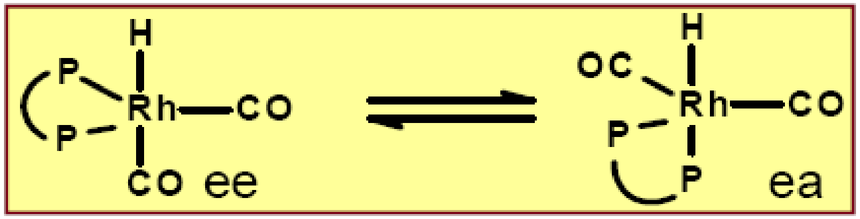


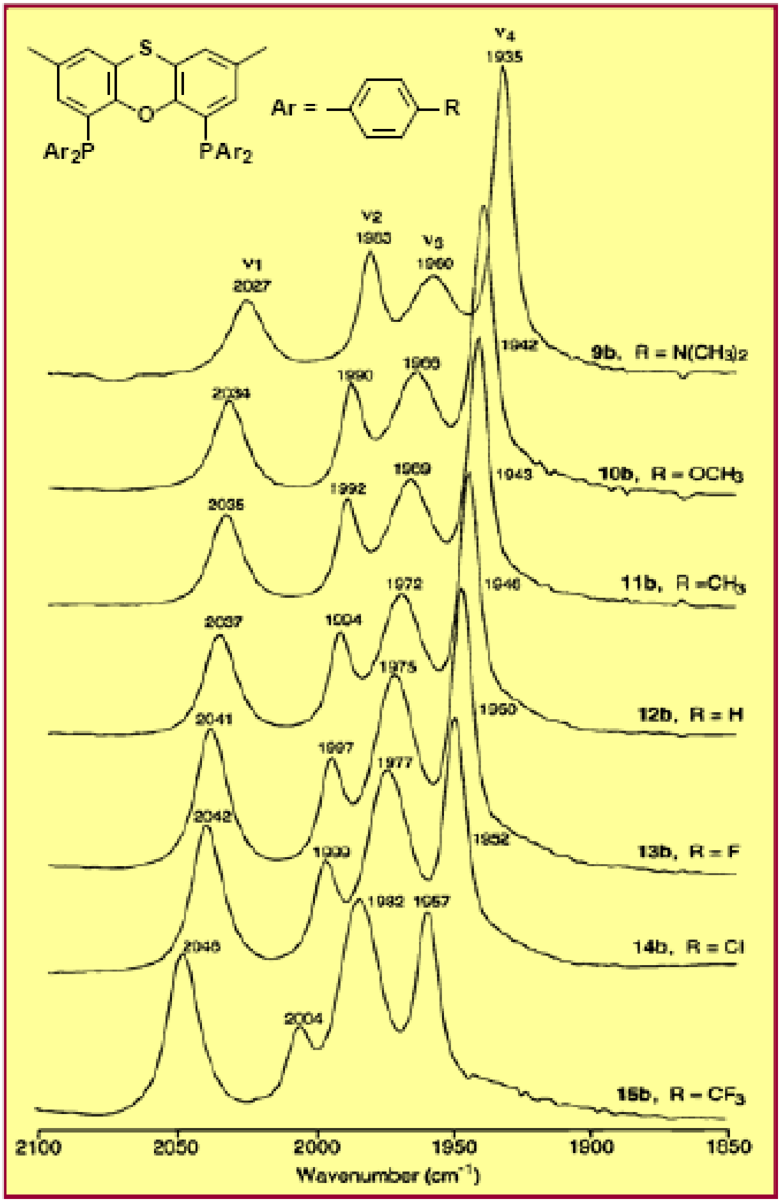
- **equatorial-equatorial coordination, ee**
- ***cis*-relation of hydride and P-atoms**
- **small $J_{(P-H)}$ < 10 Hz**
- **large $J_{(P-P)}$ ~ 250 Hz**

- **equatorial-apical coordination, ea**
- ***trans*-relation of hydride and P-atoms**
- **large $J_{(P-H)}$ ~ 180 - 200 Hz**
- **small $J_{(P-P)}$ < 70 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: $\nu_{(CO)}$ = 1970, 2030 cm^{-1}
- ea coordinated ligands: $\nu_{(CO)}$ = 1950, 2000 cm^{-1}

Instrumentation diagram for Flow-NMR spectroscopy

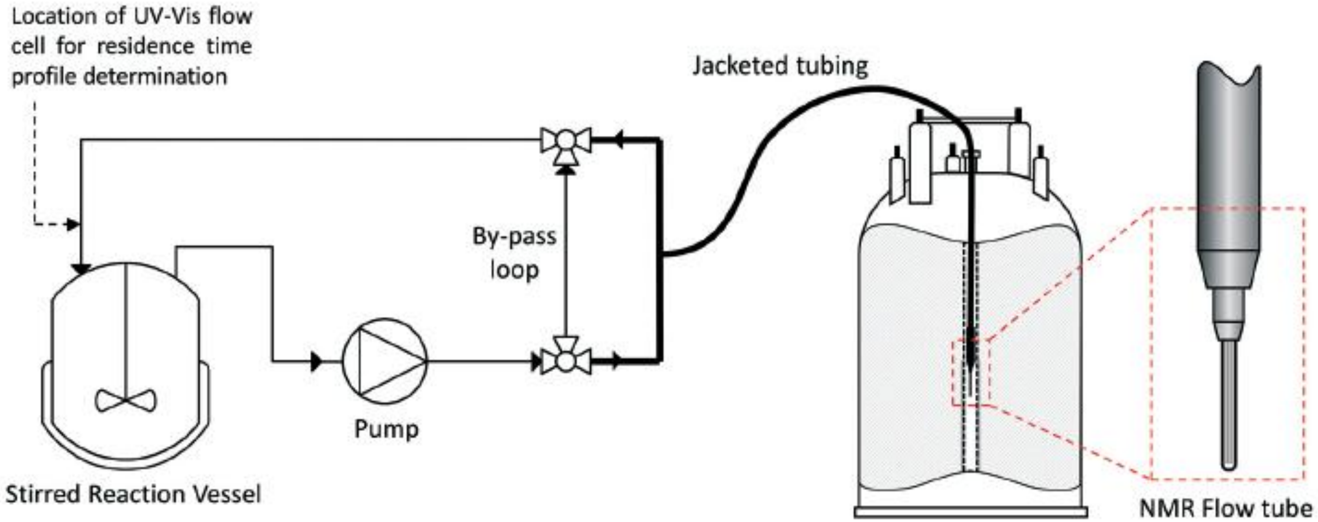
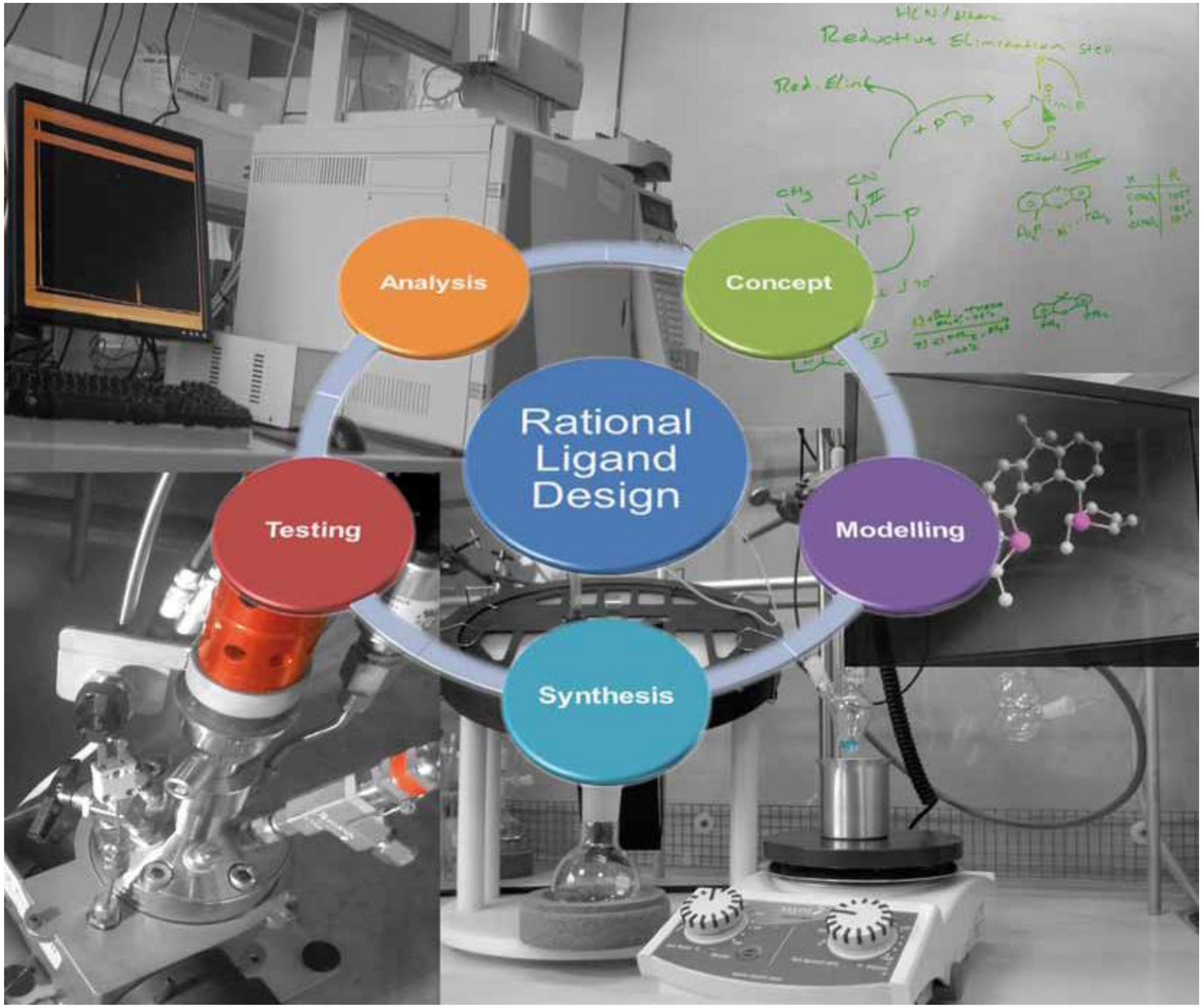
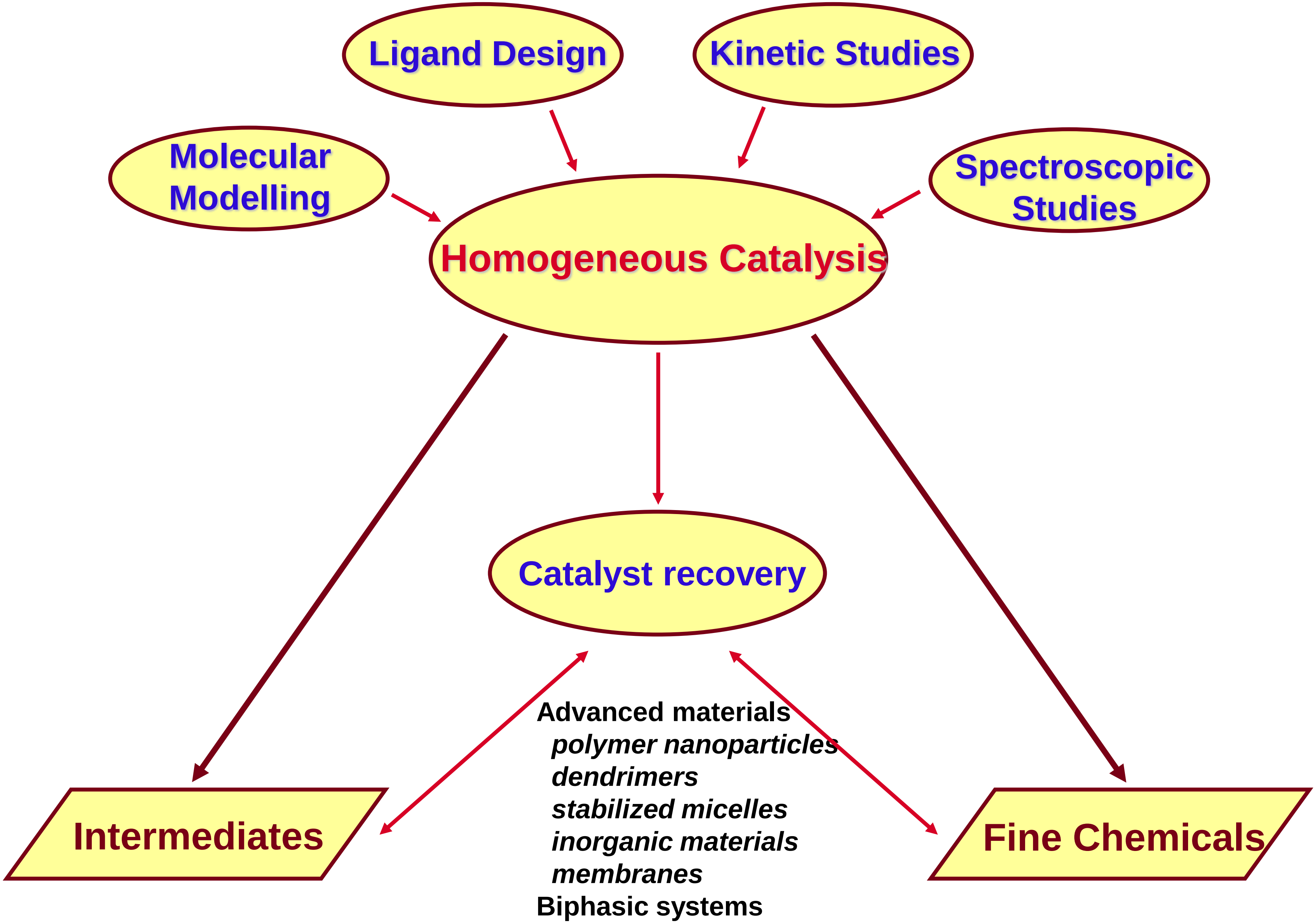


Fig. 1 Flow scheme and instrumentation diagram for the FlowNMR reaction monitoring apparatus (not to scale; for details see the Experimental section).

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

Key steps in the investigation of homogeneous catalysts





Ligand Design

Kinetic Studies

Molecular Modelling

Spectroscopic Studies

Homogeneous Catalysis

Catalyst recovery

Intermediates

Fine Chemicals

Advanced materials
- *polymer nanoparticles*
- *dendrimers*
- *stabilized micelles*
- *inorganic materials*
- *membranes*

Biphasic systems

Immobilization of homogeneous catalysts

Immobilization

Supported Catalysis

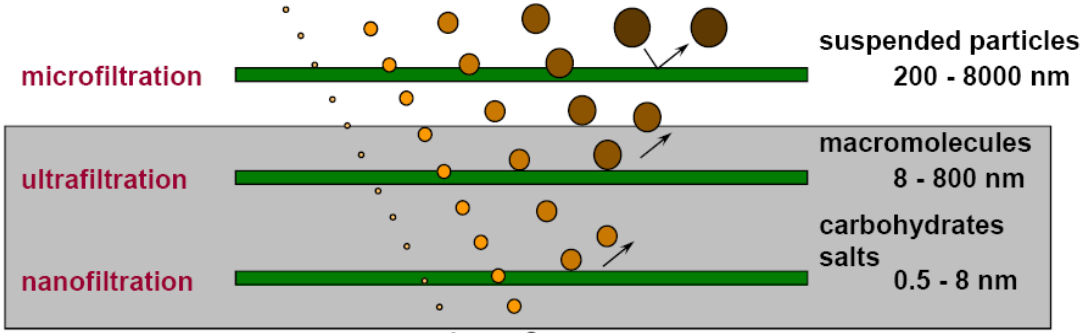
Solid Support
inorganic
organic
→ *Filtration*

Soluble Support
soluble polymer
dendrimers
→ *Ultra-Filtration*
Nano-Filtration
Centrifugation

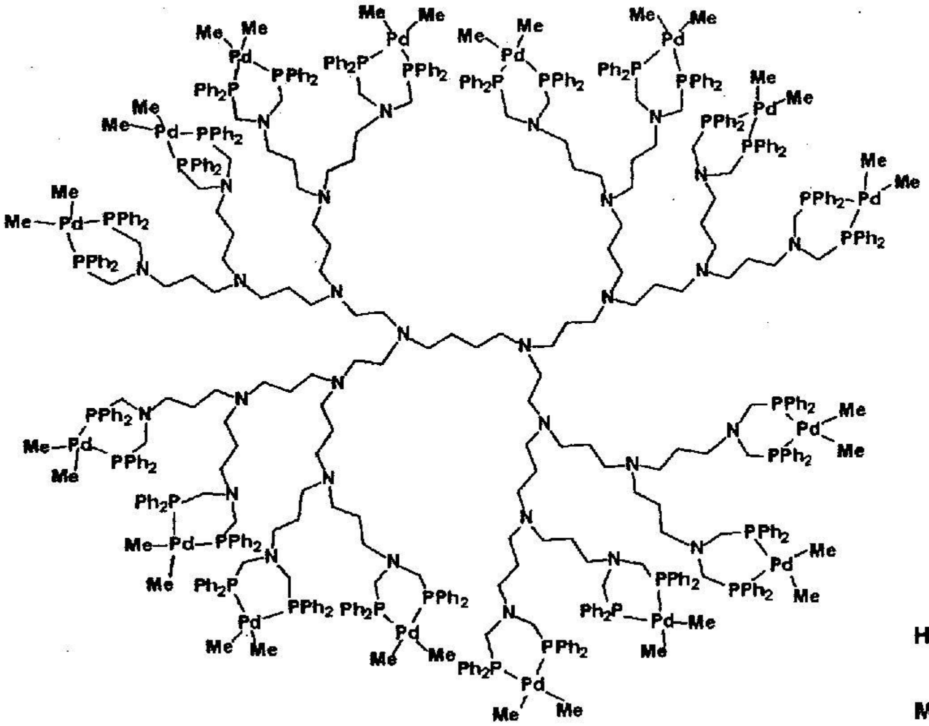
Multiphase Catalysis

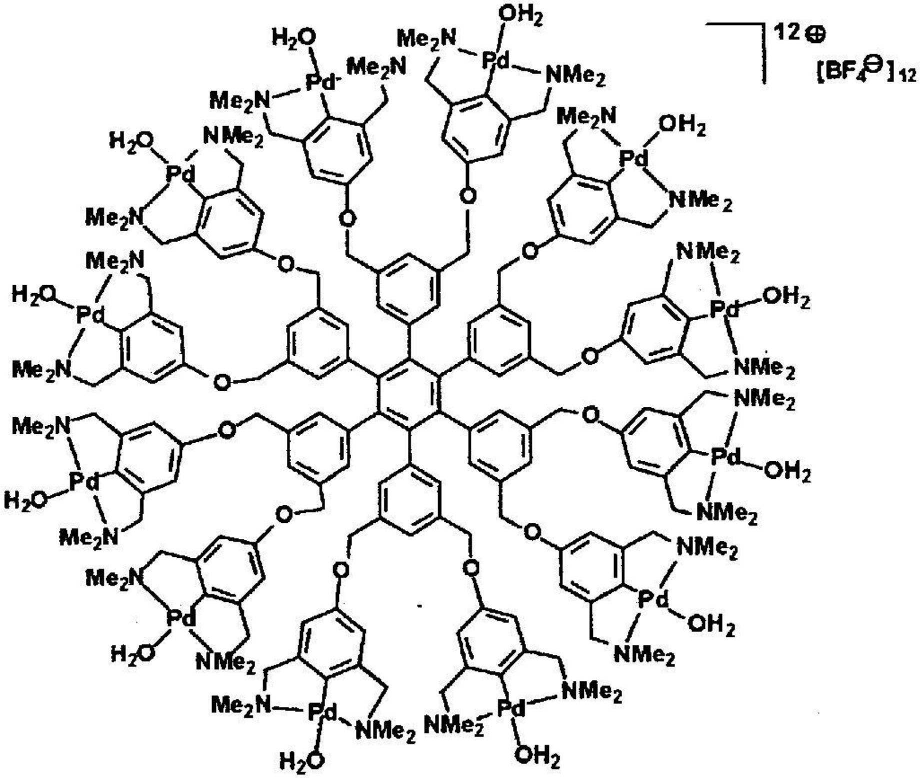
Aqueous Phase → *Phase Separation*
Extraction

Nonaqueous Phase
organic two-phase
supercritical fluids
fluorous phase
ionic liquids
→ *Phase Separation*
Extraction



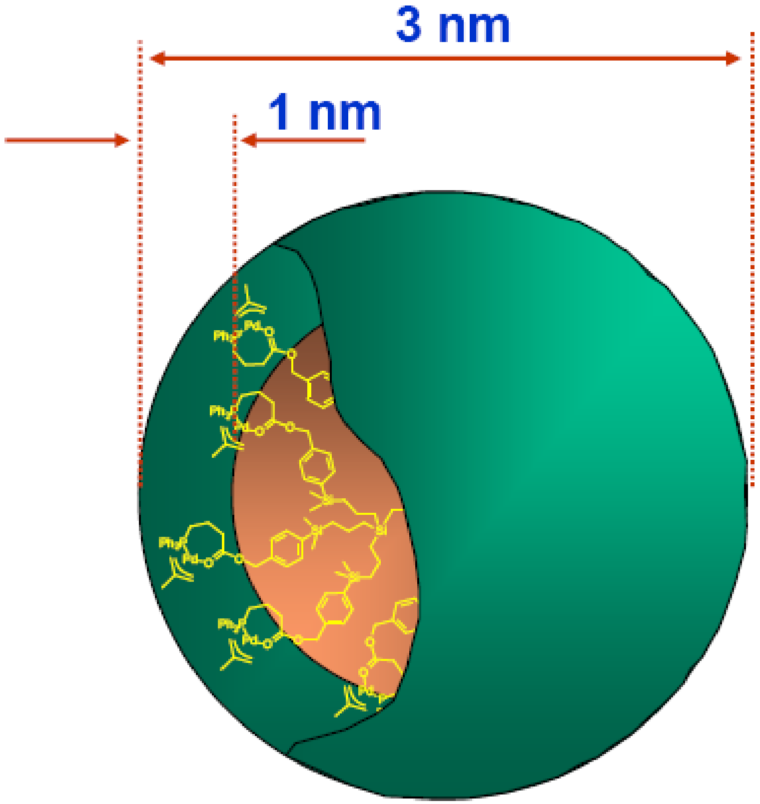
Dendrimers as an example of soluble supports





Dendritic Effect

High local concentration of active sites



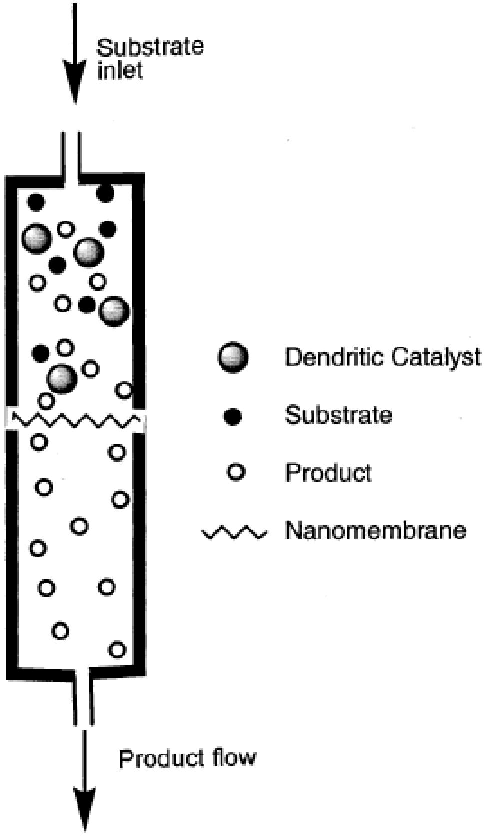
12 Pd complexes concentrated within a shell of 9.95 nm^3 → [Pd] = 2 mol/L

In normal catalytic runs in solution → [Pd] = 5 mmol/L

Dendrimers in continuous homogeneous catalysis

- Process in "batch"

- Continuous Flow Membrane Reactor CFMR

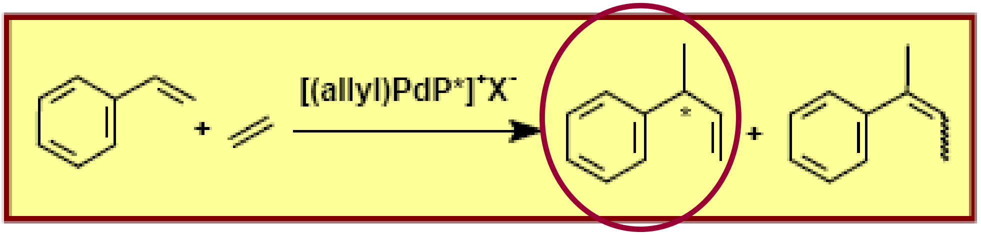


Drawbacks:

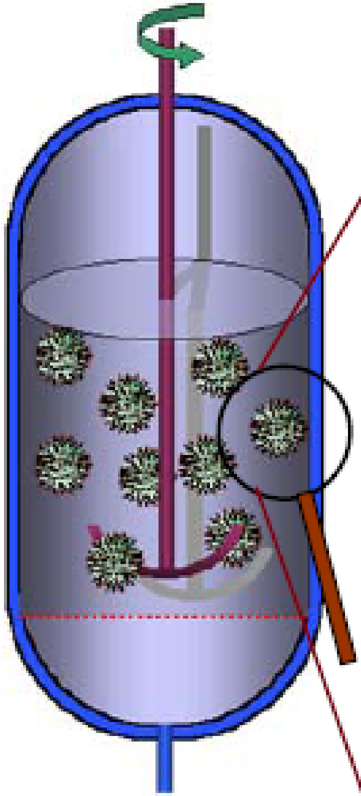
- Leackage of the catalyst through the membrane;
- the metal leaves the ligand and goes through the membrane;
- Dendrimers synthetic procedure;
- Characterizzation of the dendrimer and the metal-dendrimer system.

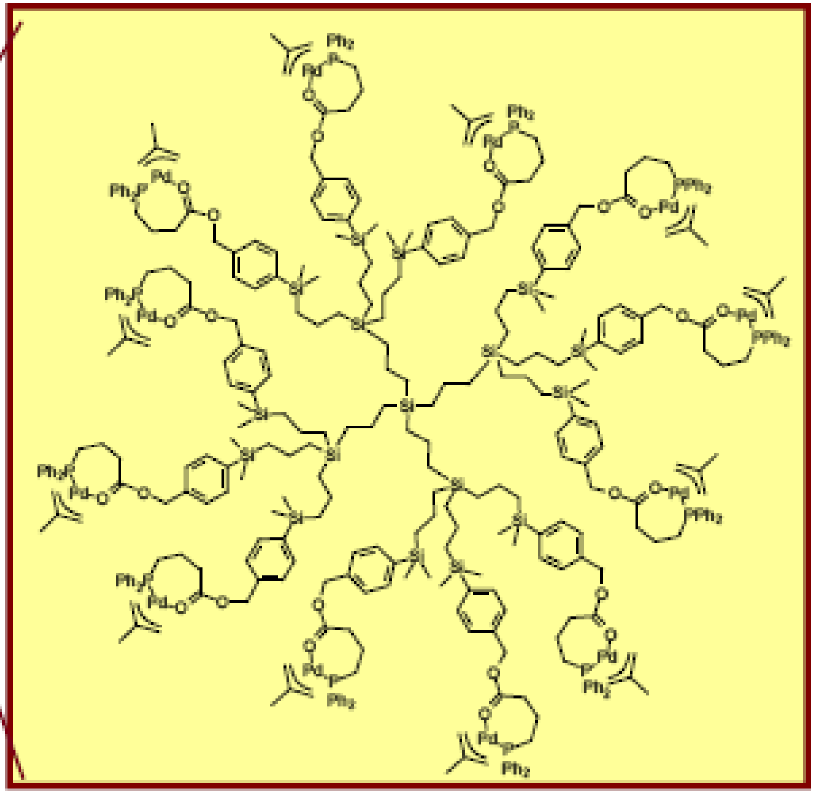
Dendrimers as an example of soluble supports

Hydrovinylation of Styrene



Carbosilane Dendrimer





Higher selectivity in the product with respect the model compound.

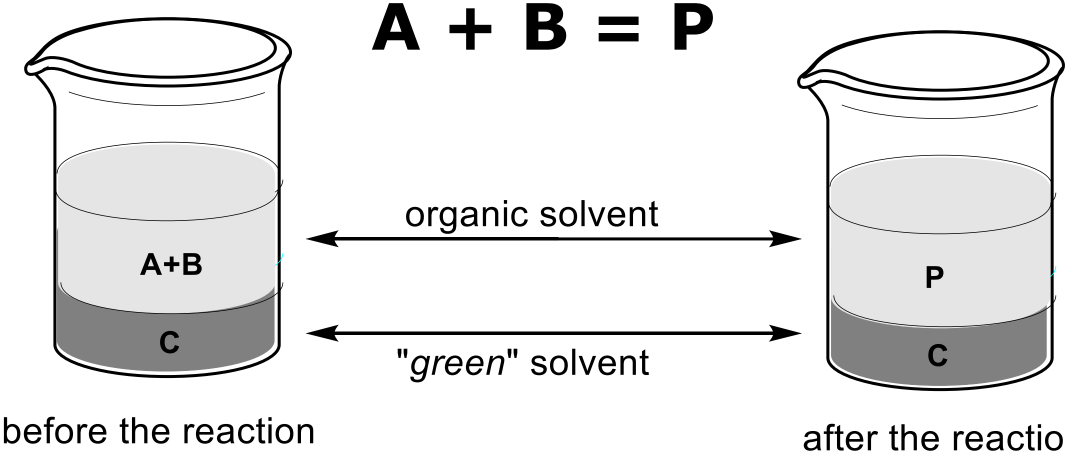
High retention (98 %) of G_1-dendrimer .

Homogeneous catalysis in biphasic system

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.

A + B = P



phase 1: organic solvent

phase 2: Water

Ionic liquids

Supercritical fluids

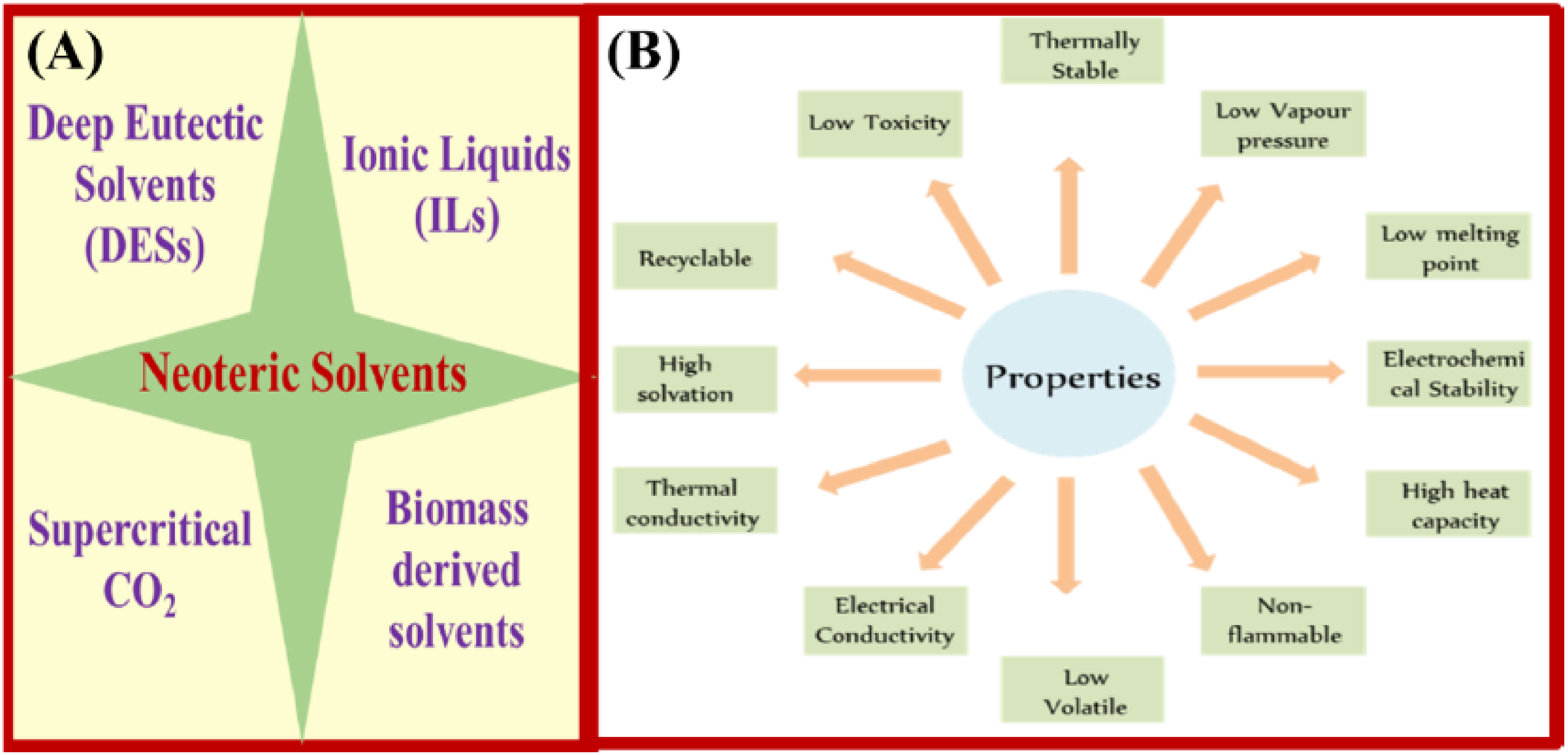
Requirements:

- **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.**

Neoteric solvents

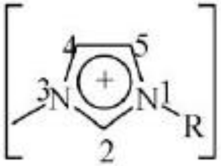
New class of solvents

Their properties

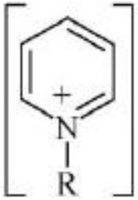


Ionic Liquids

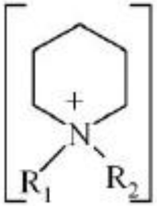
They are anhydrous salts; melting temperature < 100 °C; negligible vapor pressure; thermally stable; recyclability; toxicity?



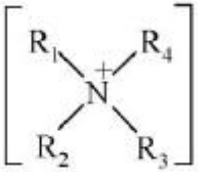
1-alkyl-3-methyl-imidazolium



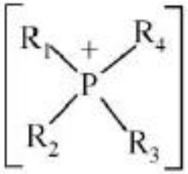
N-alkyl-pyridinium



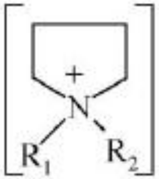
N-alkyl-*N*-methyl-piperidinium



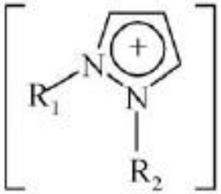
Tetraalkyl-ammonium



Tetraalkyl-phosphonium

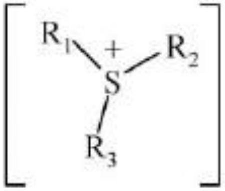


N-alkyl-*N*-methyl-pyrrolidinium



1,2-dialkyl-pyrazolium

N-alkyl-thiazolium



Trialkyl-sufonium

$R_{1,2,3,4} = CH_3(CH_2)_n$, *(n* = 1, 3, 5, 7, 9); aryl; *etc.*

water-immiscible	→	water-miscible
$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO_2]^-$
$[NTf_2]^-$	$[OTf]^-$	$[CF_3CO_2]^-$, $[NO_3]^-$
$[BR_1R_2R_3R_4]^-$	$[N(CN)_2]^-$	Br^-, Cl^-, I^-
		$[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

Deep eutectic solvents

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.