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

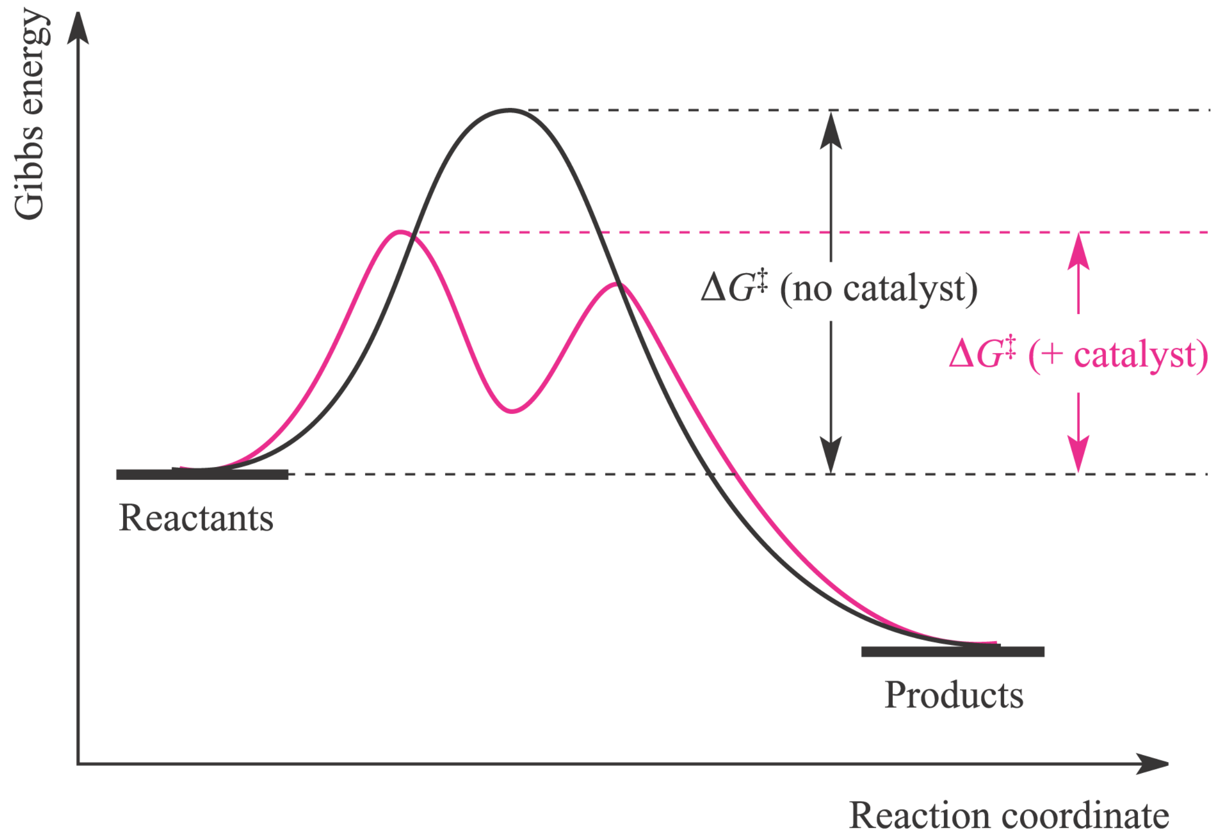
Hybrid/Electric Cars

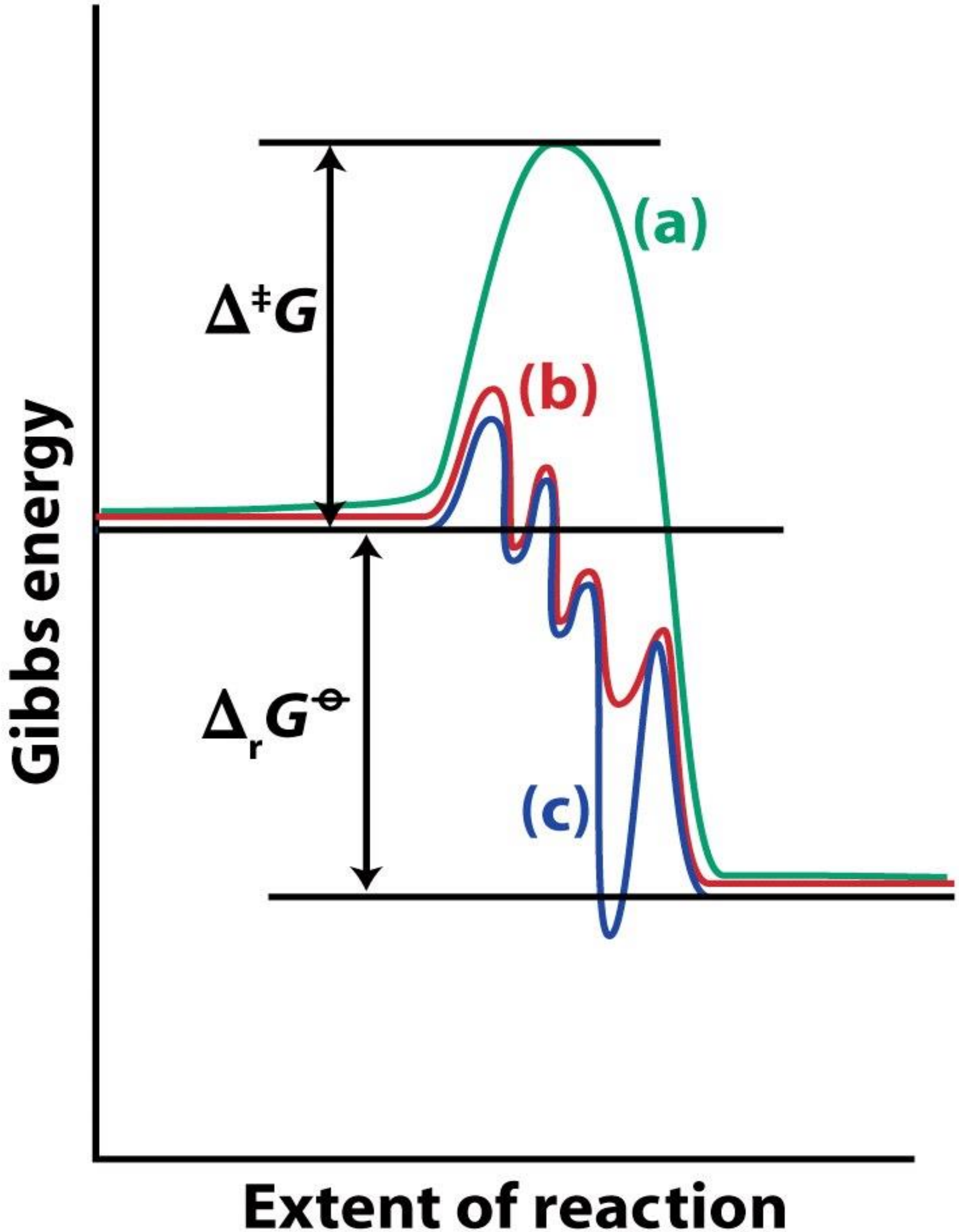
Nd, Tb, Dy, Pr

Alternative Energy

Ru, Nd, Tb, Dy, Pr

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


Gibbs energy
ΔG‡ (no catalyst)
ΔG‡ (+ catalyst)
Reactants
Products
Reaction coordinate



Gibbs energy
Extent of reaction
$\Delta^{\ddagger}G$
$\Delta_r G^{\ominus}$
(a)
(b)
(c)

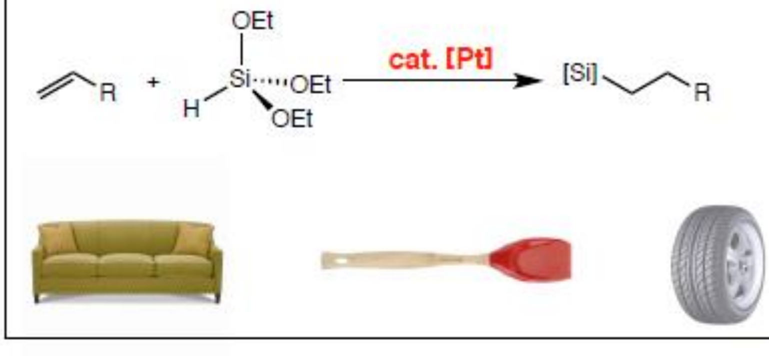
Esempi di processi catalitici eterogenei nella chimica di base

Industrial manufacturing process	Catalyst system
NH_3 synthesis (Haber process)	Fe on SiO_2 and Al_2O_3 support
Water–gas shift reaction	Ni, iron oxides
Catalytic cracking of heavy petroleum distillates	Zeolites
Catalytic reforming of hydrocarbons to improve octane number	Pt, Pt–Ir and other Pt-group metals on acidic alumina support
Methanation ($CO \longrightarrow CO_2 \longrightarrow CH_4$)	Ni on support
Ethene epoxidation	Ag on support
HNO_3 manufacture (Haber–Bosch process)	Pt–Rh gauzes

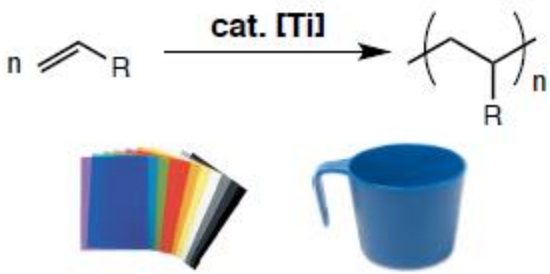
Transformative Organometallic Catalysis

Alkene Hydrogenation

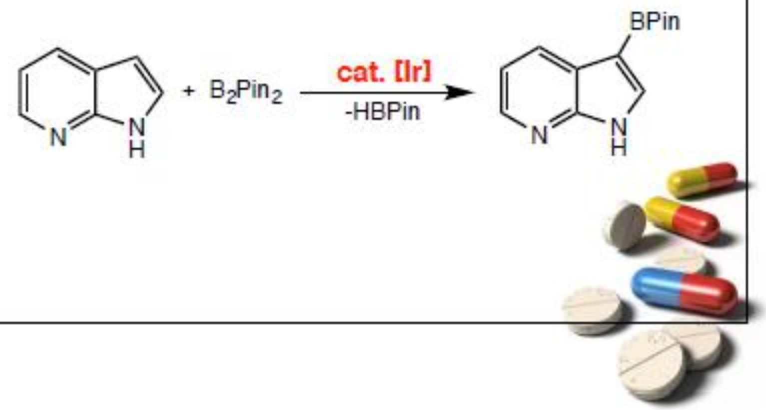
Hydrosilylation



Alkene Polymerization



C-H Functionalization Methods



Cost

When does it matter?

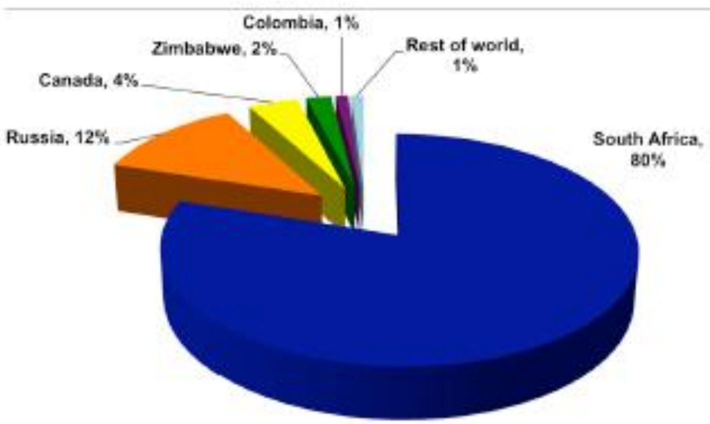
What defines expensive?

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?

All of the Pt ever mined would fit in a box that is 25 cubic feet!

1 c.f. = 28.3 litri

Platinum

$12,400 per mol

CO_2: >7000 equiv per mol

Iron

$0.02 per mol

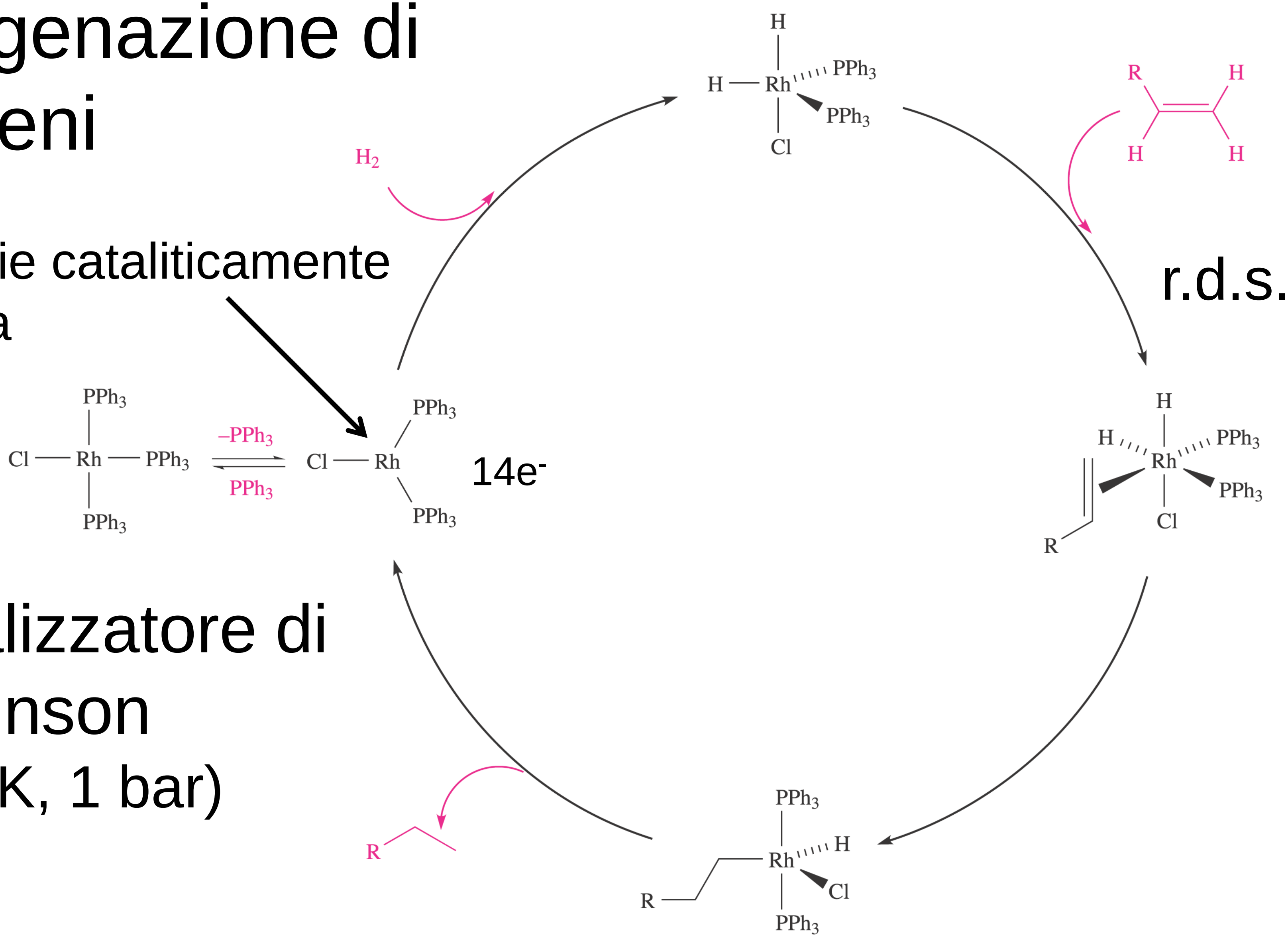
CO_2: 1 equiv per mol

- temperatura e pressione
- concentrazione del catalizzatore (rapporto substrato/catalizzatore)
- *turnover* catalitico

1. **TON** (*catalytic turnover number*) = numero di moli di prodotto per mole di catalizzatore
2. **TOF** (*catalytic turnover frequency*) = numero di moli di prodotto per mole di catalizzatore nell'unità di tempo

- selettività del catalizzatore nei riguardi del prodotto desiderato
- frequenza con la quale il catalizzatore deve essere rinnovato
- facilità di separazione del catalizzatore omogeneo dai prodotti di reazione.

Idrogenazione di alcheni



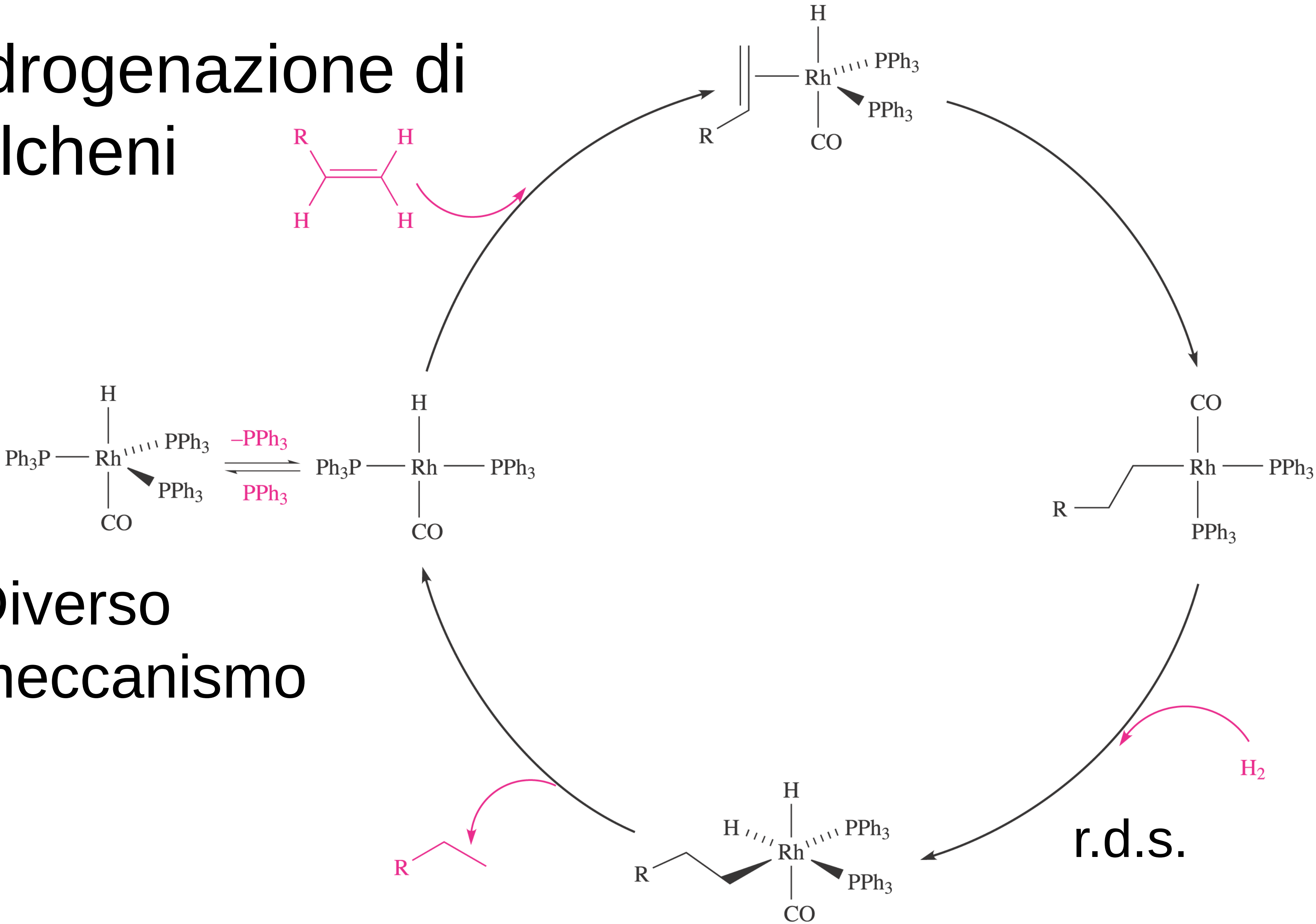
Catalizzatore di Wilkinson

(298 K, 1 bar)

$CH_2{=}CH_2 + H_2 \rightarrow C_2H_6$

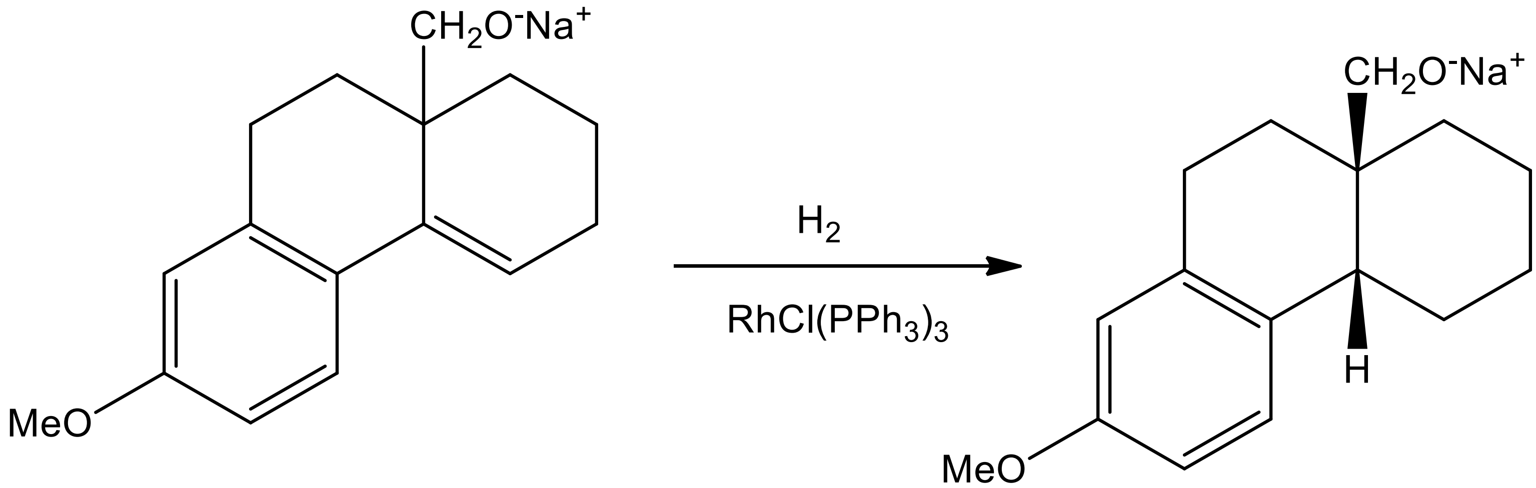
$\Delta G^\circ = -101\ \mathrm{kJ\ mol^{-1}}$

Idrogenazione di alcheni



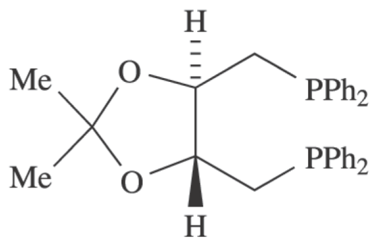
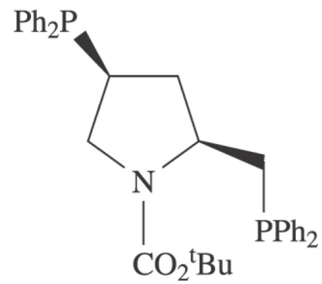
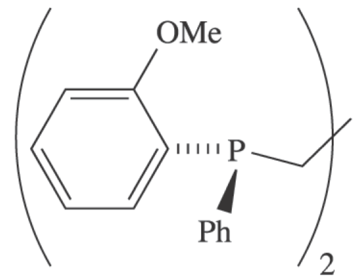
Diverso meccanismo

Idrogenazione catalitica regioselettiva



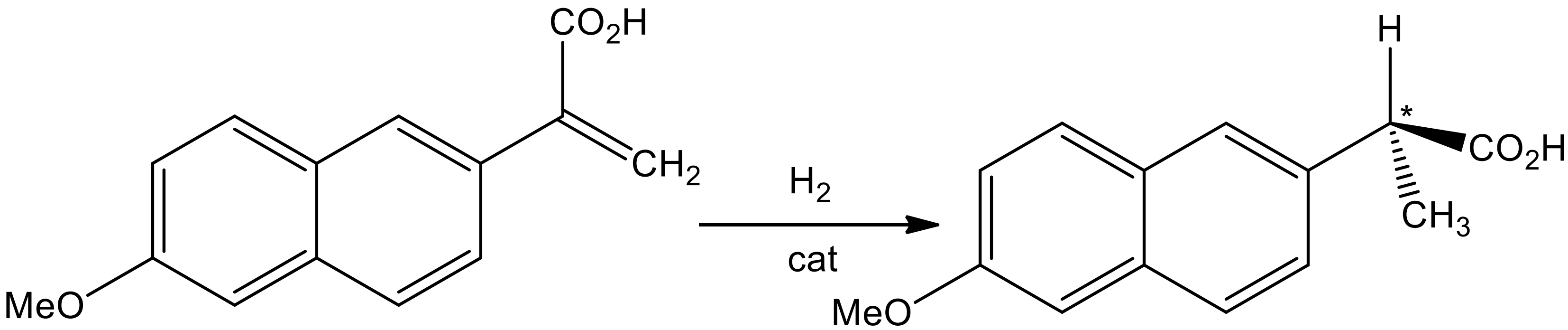
Fosfine chirali per catalisi asimmetrica

Idrogenazione di CH_2=C(COOH)(NHCOMe) usando catalizzatori di Rh(I) con diverse difosfine chirali

Bisphosphine	 (*R*,*R*)-DIOP	 (*S*,*S*)-BPPM	 (*R*,*R*)-DIPAMP
% ee (selective to enantiomer *R* or *S*)	73 (*R*)	99 (*R*)	90 (*S*)

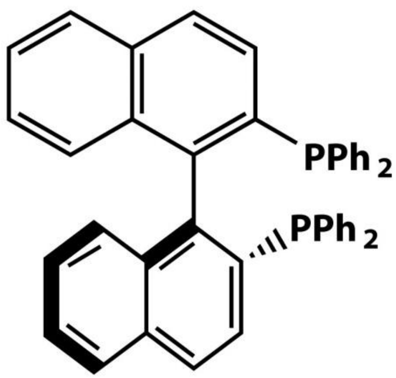
$$\% \text{ ee} = \left(\frac{|R-S|}{|R+S|}\right) \times 100$$

Idrogenazione catalitica asimmetrica di olefine prochirali



Naproxen

cat = Ru[(*S*)-BINAP]Cl_2



2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, BINAP

Processo Wacker

$$CH_2{=}CH_2 + 1/2O_2 \xrightarrow{[PdCl_4]^{2-}} CH_3CHO$$