

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

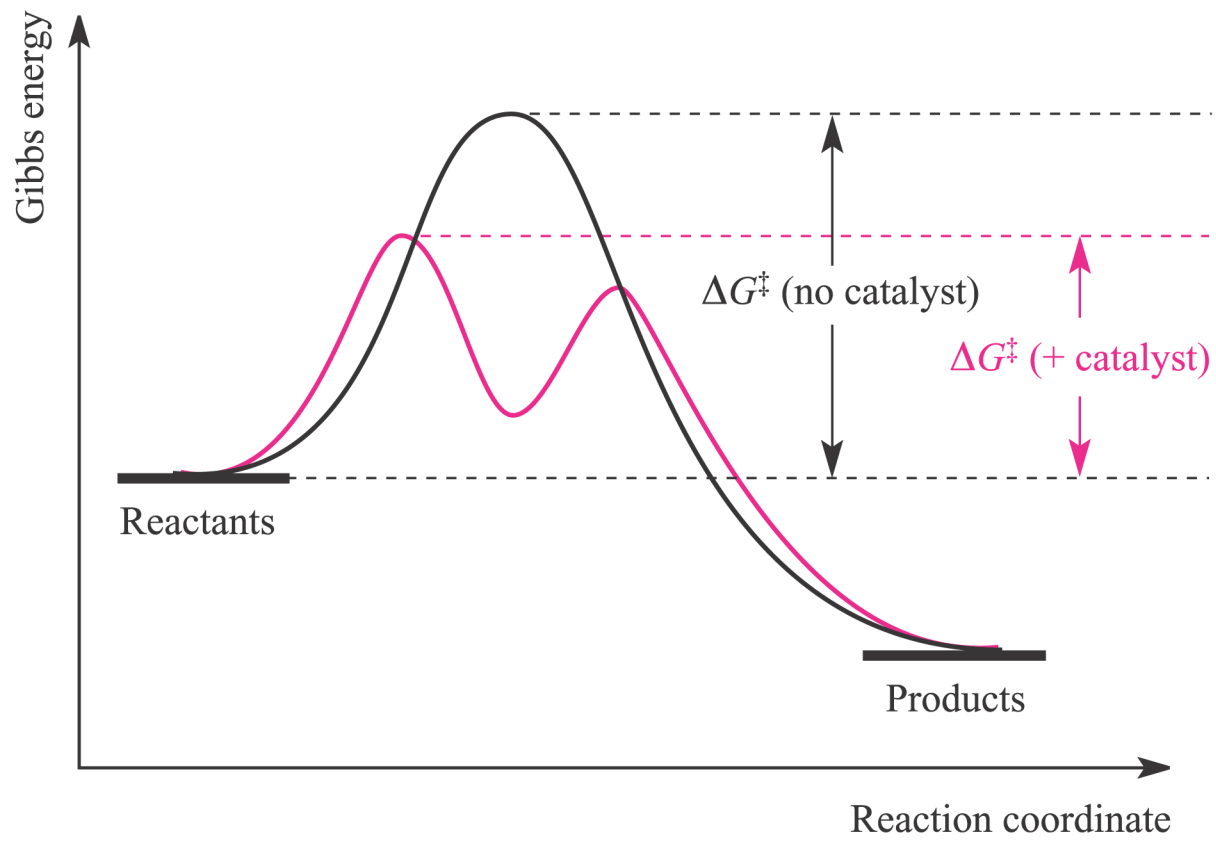
Nd, Tb, Dy, Pr

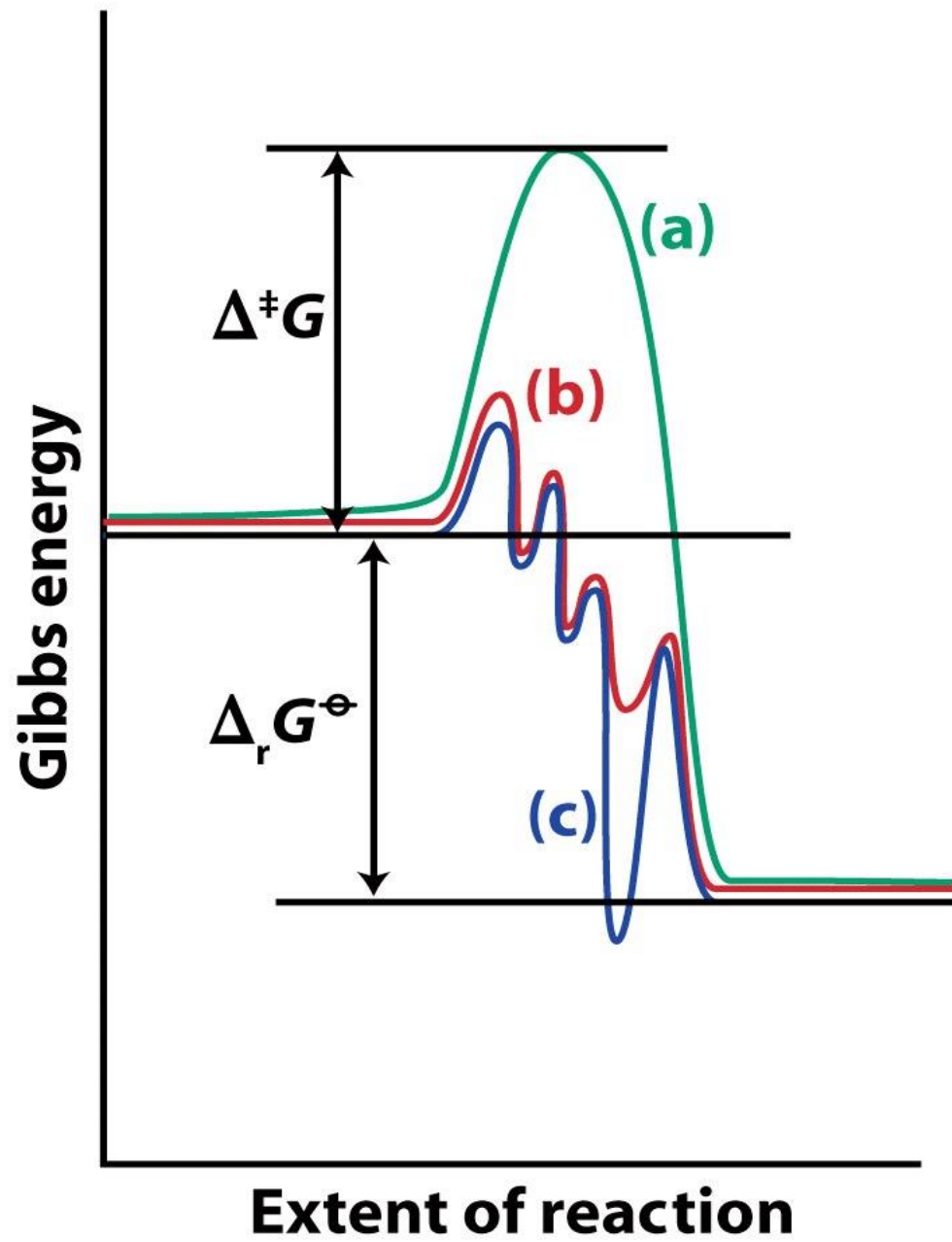


Alternative Energy

Ru, Nd, Tb, Dy, Pr

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

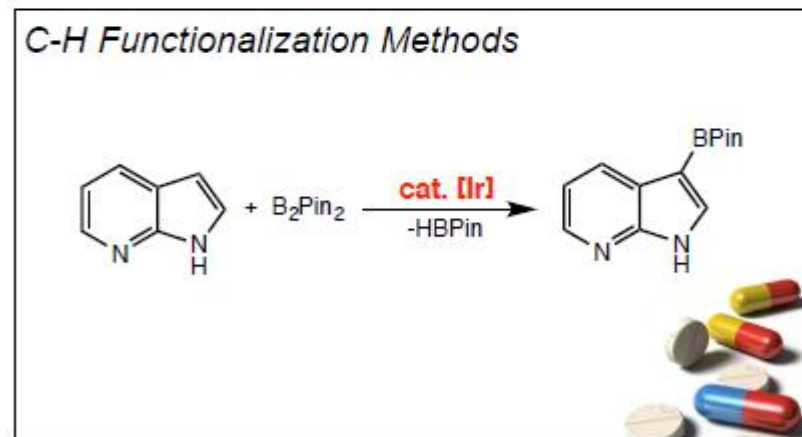
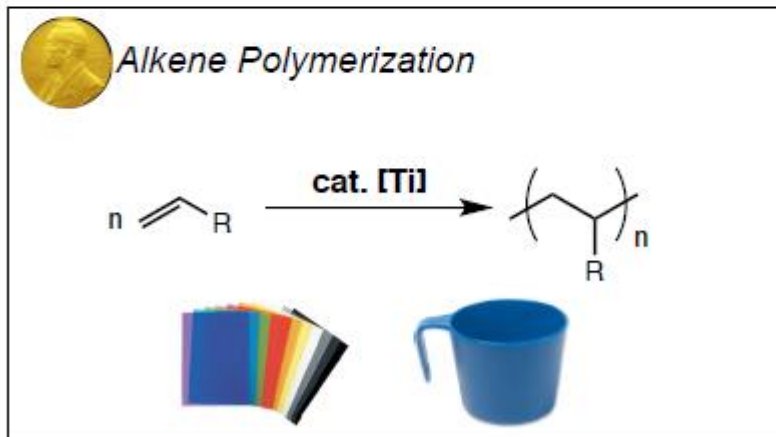
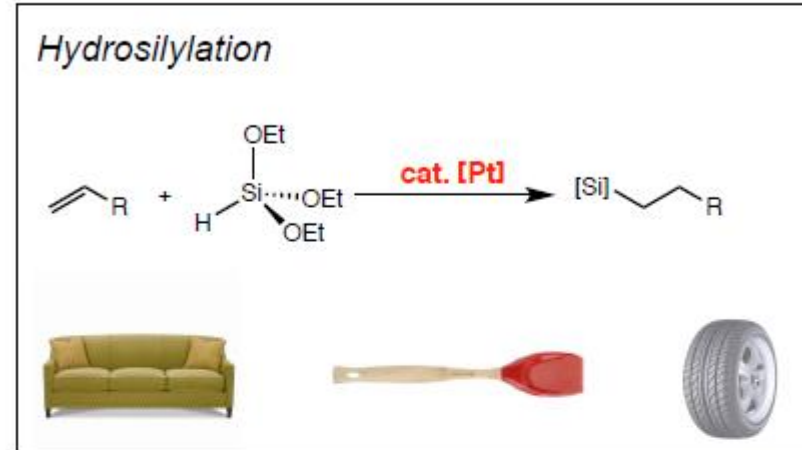
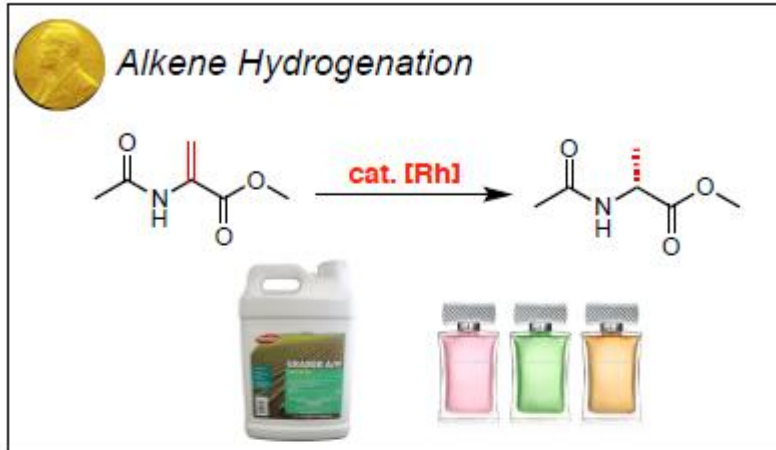




Esempi di processi catalitici eterogenei nella chimica di base

Industrial manufacturing process	Catalyst system
NH ₃ synthesis (Haber process)	Fe on SiO ₂ and Al ₂ O 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 → CO ₂ → CH ₄)	Ni on support
Ethene epoxidation	Ag on support
HNO ₃ manufacture (Haber-Bosch process)	Pt-Rh gauzes

Transformative Organometallic Catalysis



Cost



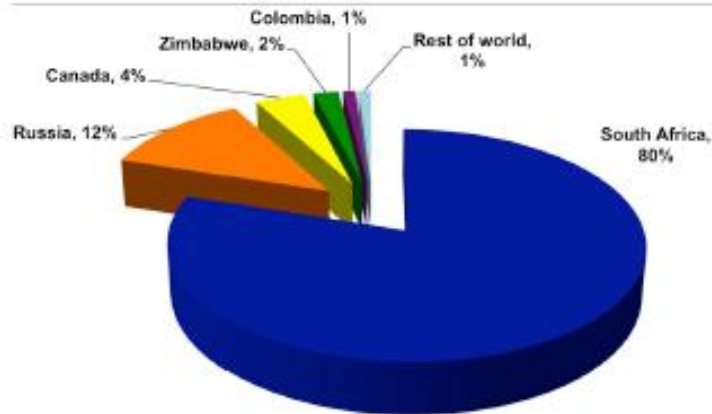
*When does it matter?
What defines expensive?*

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

CO₂: >7000 equiv per mol

Iron



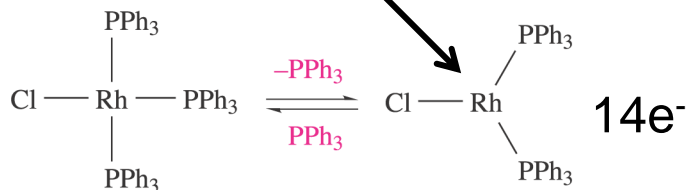
\$0.02 per mol

CO₂: 1 equiv per mol

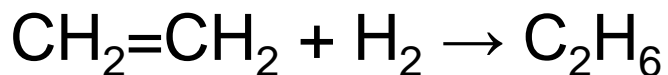
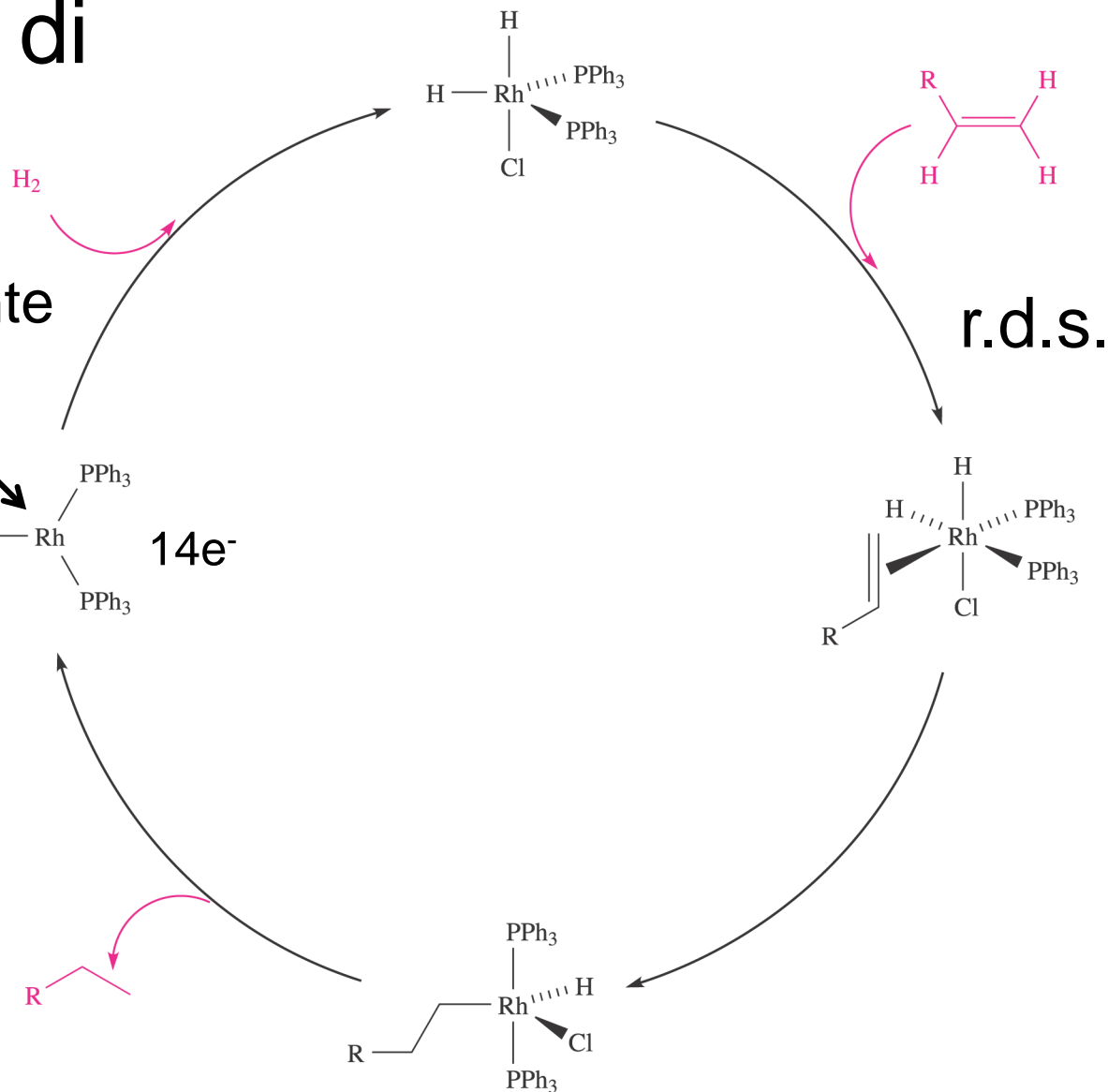
- temperatura e pressione
 - concentrazione del catalizzatore (rapporto substrato/catalizzatore)
 - *turnover* catalitico
1. **TON** (*catalytic turnover number*) = numero di moli di prodotto per mole di catalizzatore
 2. **TOF** (*catalytic turnover frequency*) = numero di moli di prodotto per mole 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

specie cataliticamente attiva

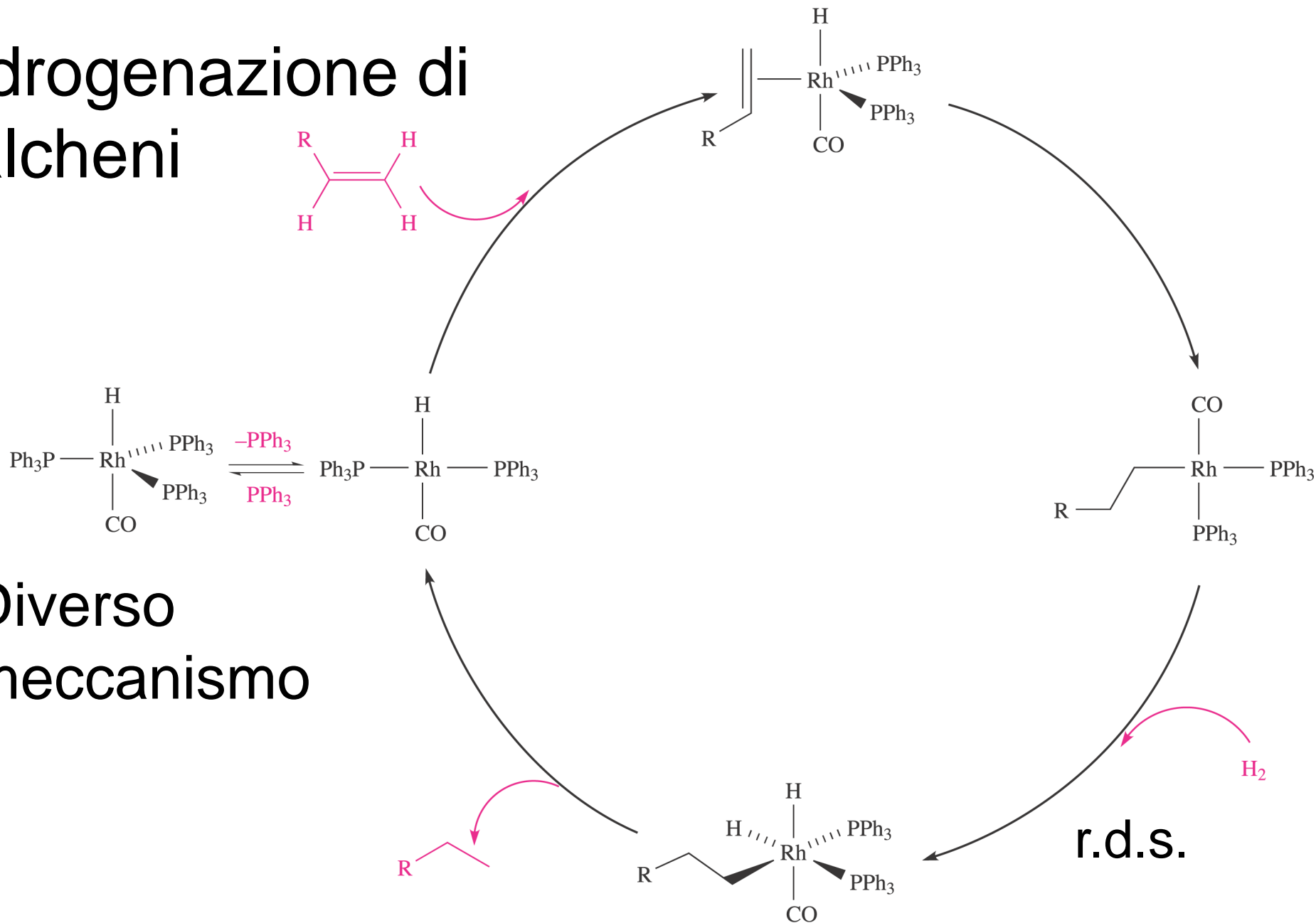


Catalizzatore di Wilkinson
(298 K, 1 bar)



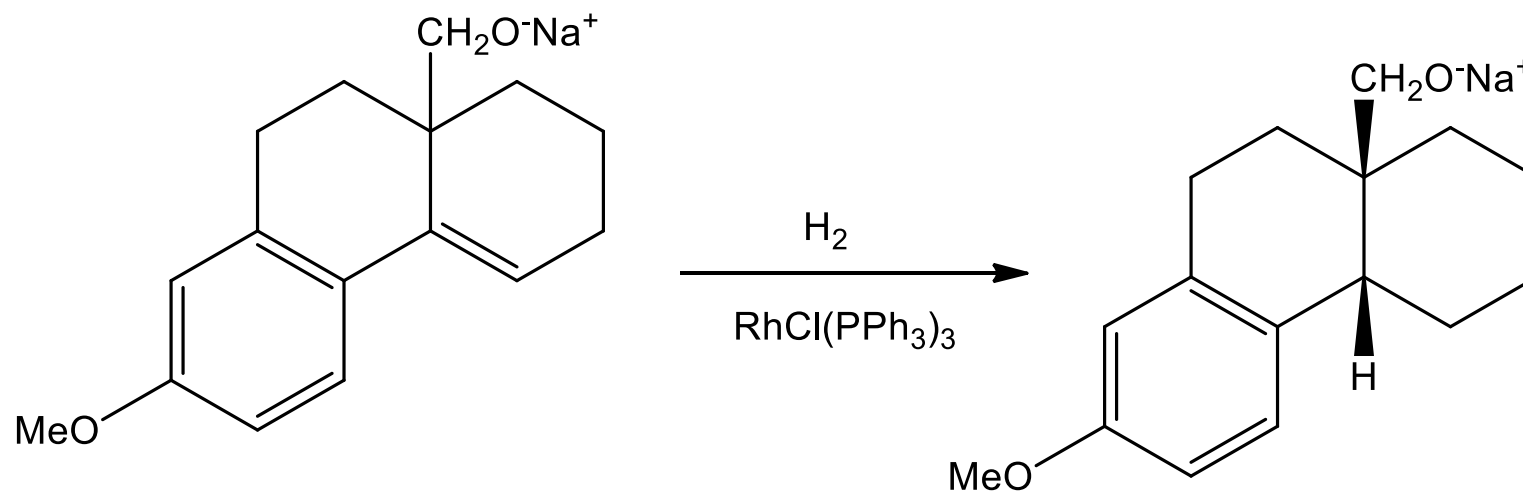
$$\Delta G^\circ = -101 \text{ kJ mol}^{-1}$$

Idrogenazione di alcheni



Diverso
meccanismo

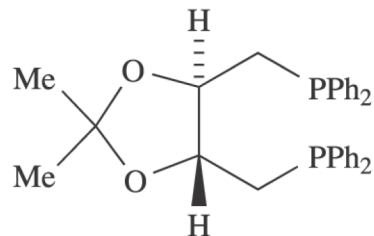
Idrogenazione catalitica regioselettiva



Fosfine chirali per catalisi asimmetrica

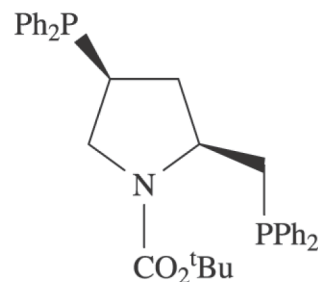
Idrogenazione di $\text{CH}_2=\text{C}(\text{COOH})(\text{NHCOMe})$ usando catalizzatori di Rh(I) con diverse difosfine chirali

Bisphosphine



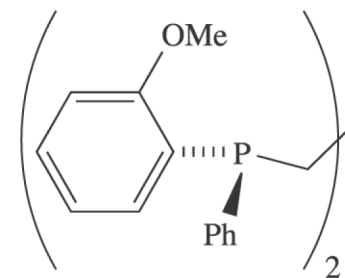
(*R,R*)-DIOP

73 (*R*)



(*S,S*)-BPPM

99 (*R*)



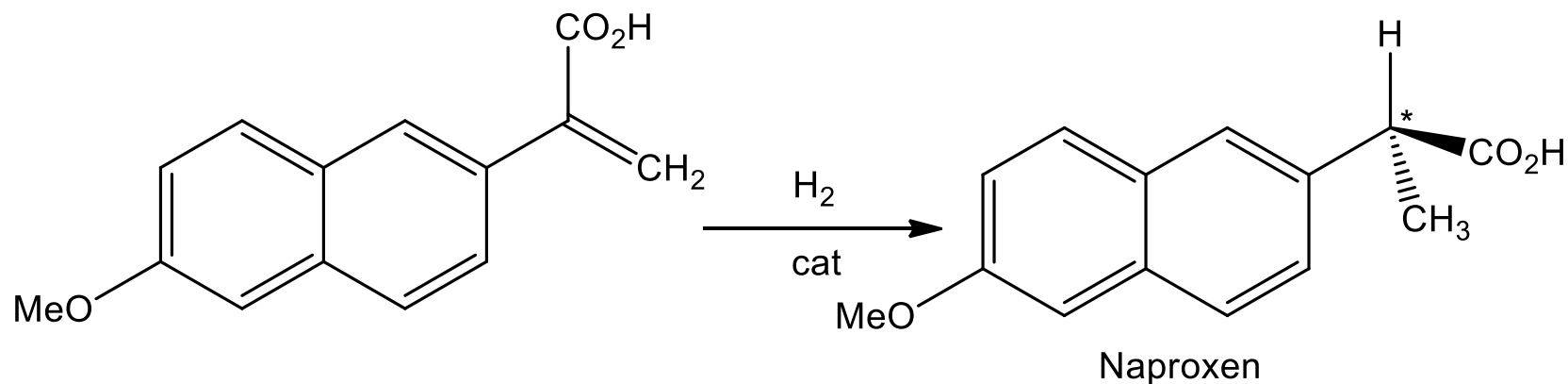
(*R,R*)-DIPAMP

90 (*S*)

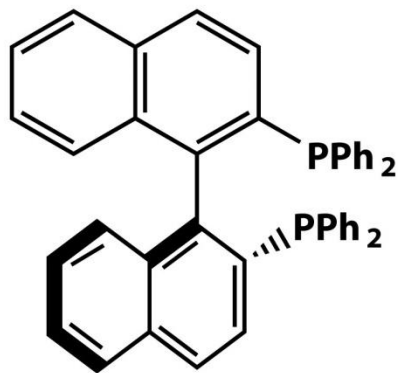
% ee (selective to enantiomer *R* or *S*)

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

Idrogenazione catalitica asimmetrica di olefine prochirali



cat = Ru[(S)-BINAP]Cl₂



**2,2'-bis(diphenylphosphino)-
1,1'-binaphthyl, BINAP**

Processo Wacker

