Cobalt

Cobalamins: Coenzyme B12 and its derivatives

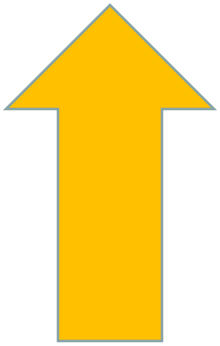
coenzyme
low molecular mass, determines the type of reaction

+

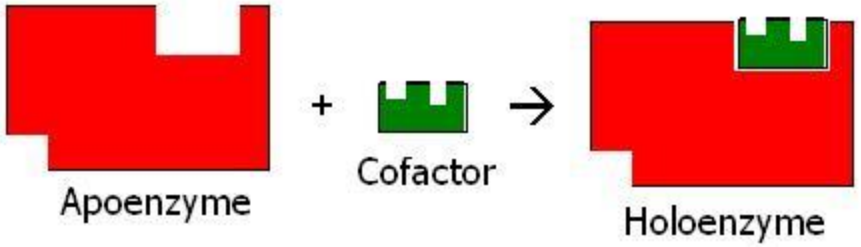
apoenzyme
high molecular mass (protein), determines substrate specifity (selectivity) and the reaction rate

→

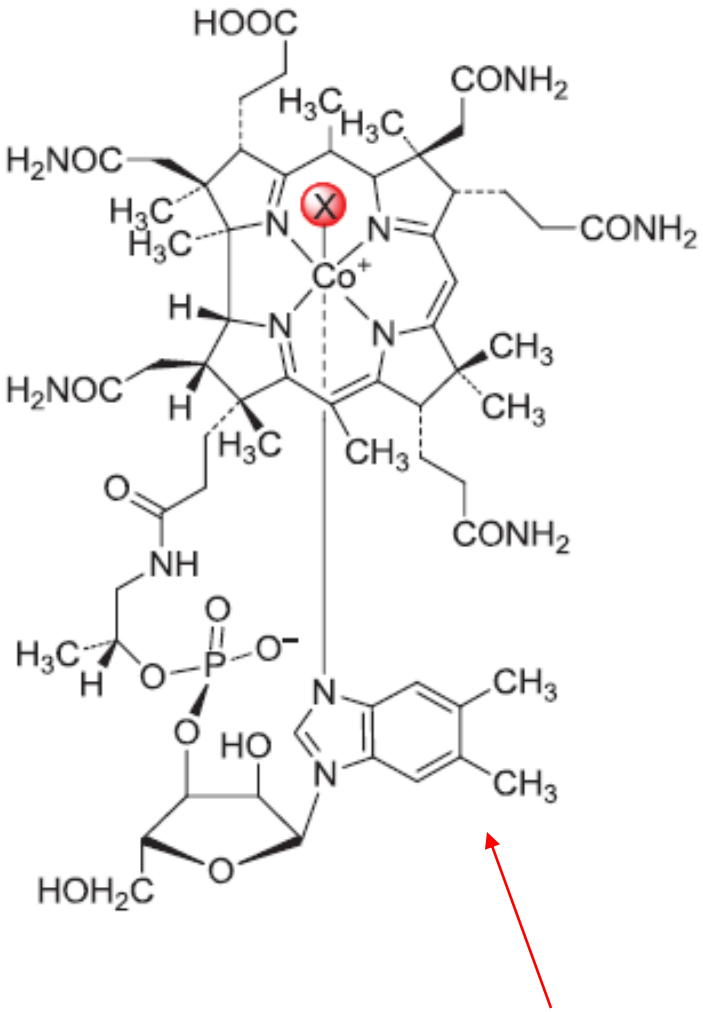
holoenzyme
complete enzyme, fully functional



Similar to prosthetic group (heme) but not covalently bound!



Cobalamins: Coenzyme B12 and its derivatives



dimethylbenzimidazole + ribose 3-phosphate

X = CH_3: methylcobalamin (MeCbl or MeB_{12})

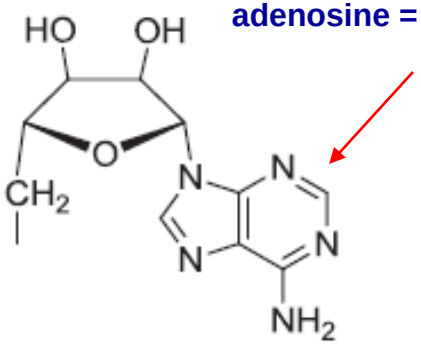
CN: cyanocobalamin (vitamin B_{12})

OH: hydroxycobalamin (vitamin B_{12a})

alkylcobalamins

R: 5´-deoxyadenosylcobalamin (coenzyme B_{12} or AdoCbl)

R = 5´-deoxyadenosyl

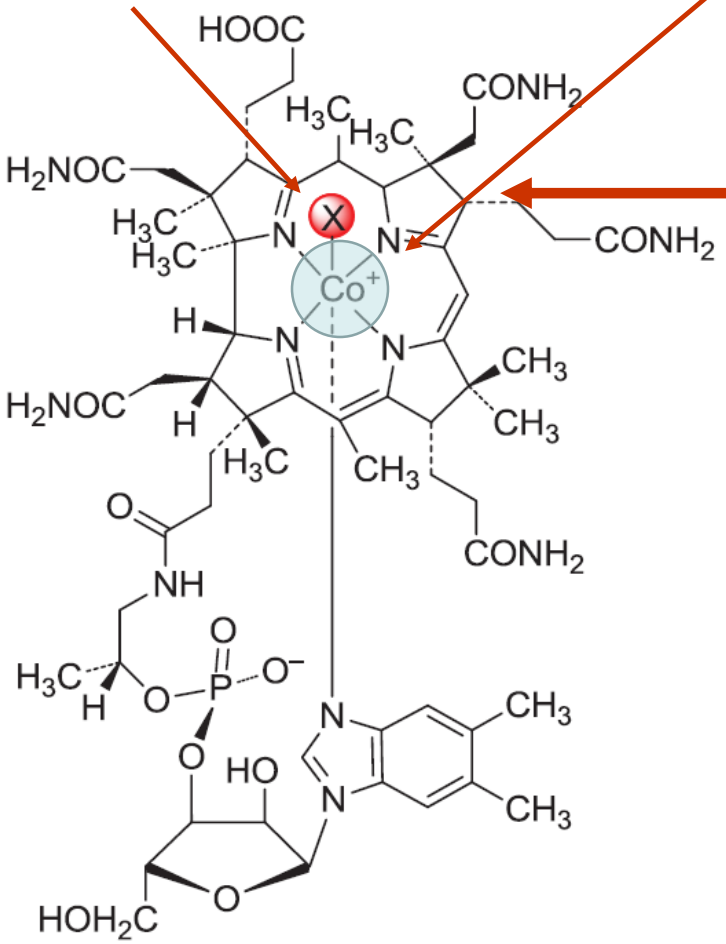


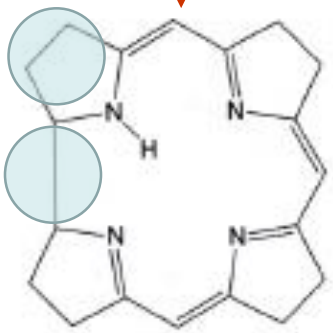
adenosine = adenine + ribose

Equatorial coordination through a corrin ring

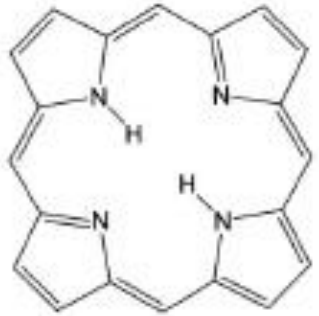
Me-Cobalamin and
Coenzime B_{12} NATURAL
organometallic compounds

Co abundance

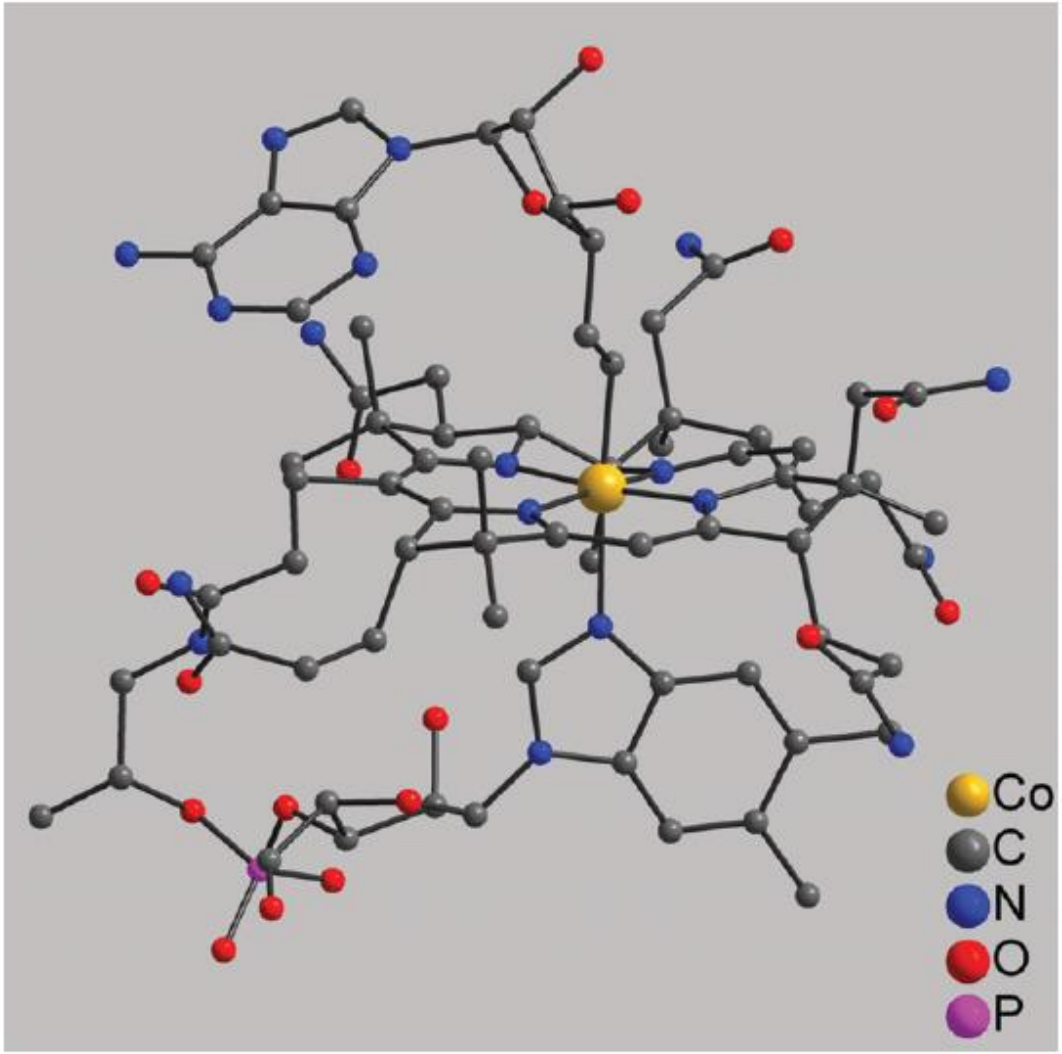


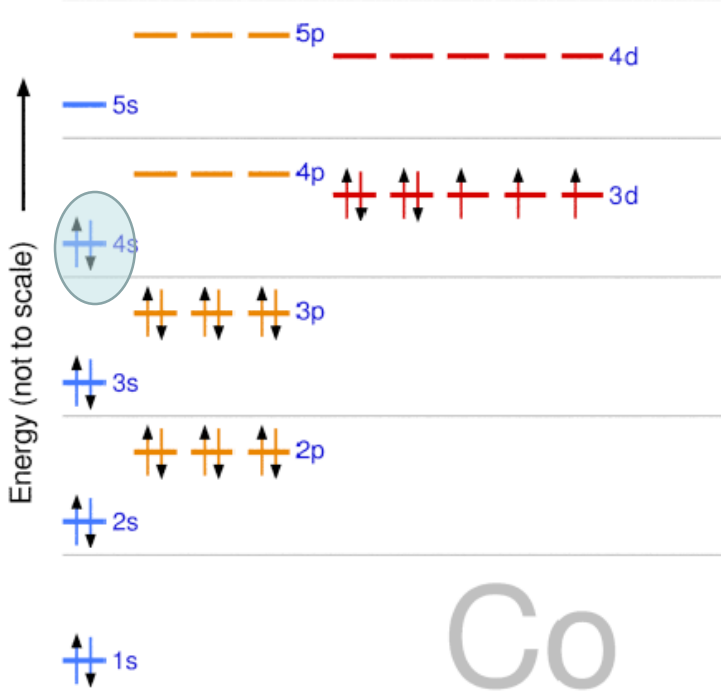


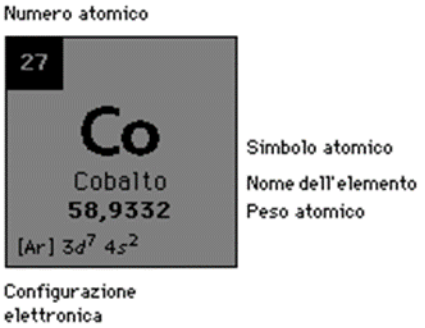
Corrin

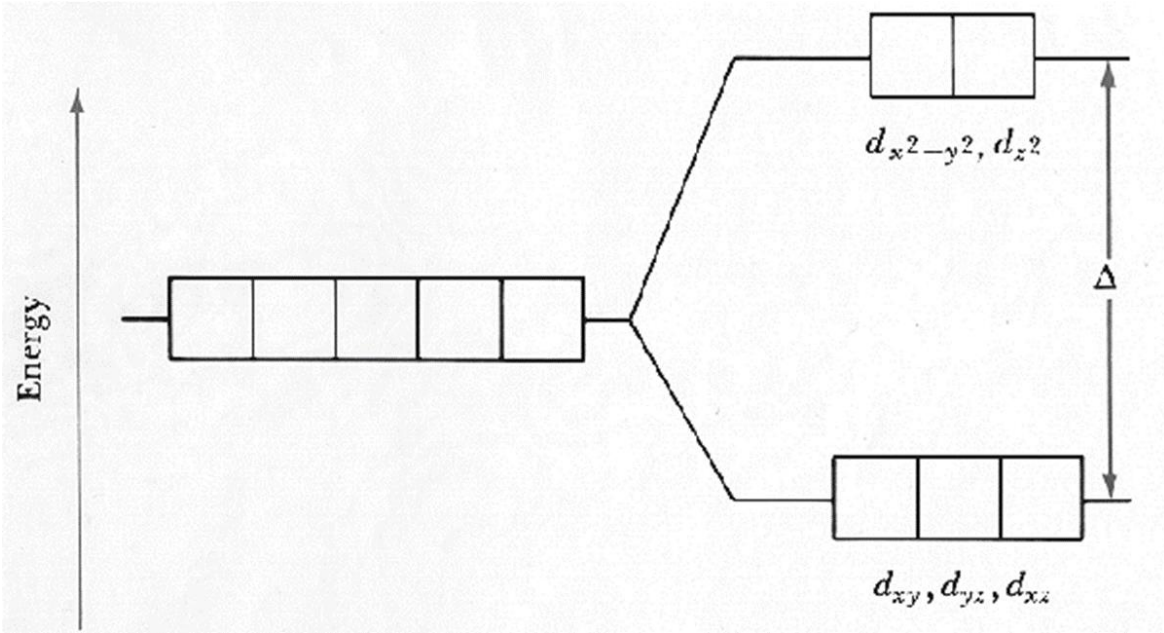


Porphyrin


Co
C
N
O
P


5p
4d
5s
4p
3d
4s
3p
3s
2p
2s
1s
Energy (not to scale)
Co


Numero atomico
27
Co
Cobalto
58,9332
[Ar] 3d7 4s2
Simbolo atomico
Nome dell'elemento
Peso atomico
Configurazione elettronica


Energy
$d_{x^2-y^2}, d_{z^2}$
Δ
d_{xy}, d_{yz}, d_{xz}

Octahedral

Numero atomico

27

Co

Cobalto

58,9332

[Ar] $3d^7\ 4s^2$

Simbolo atomico

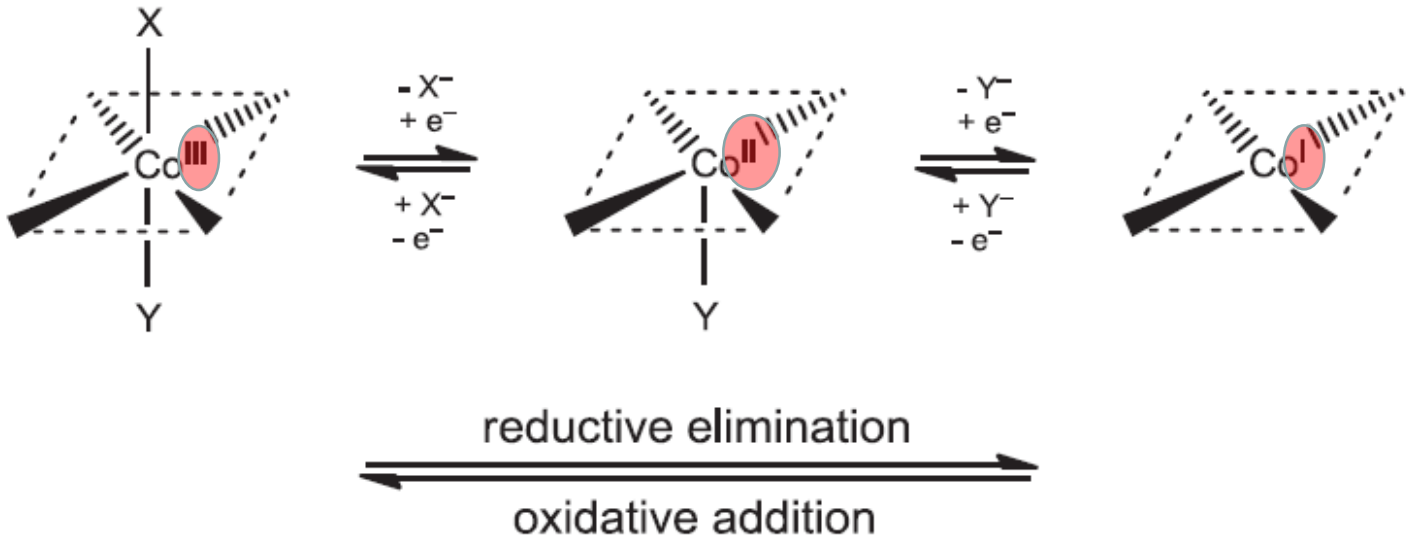
Nome dell'elemento

Peso atomico

Configurazione elettronica

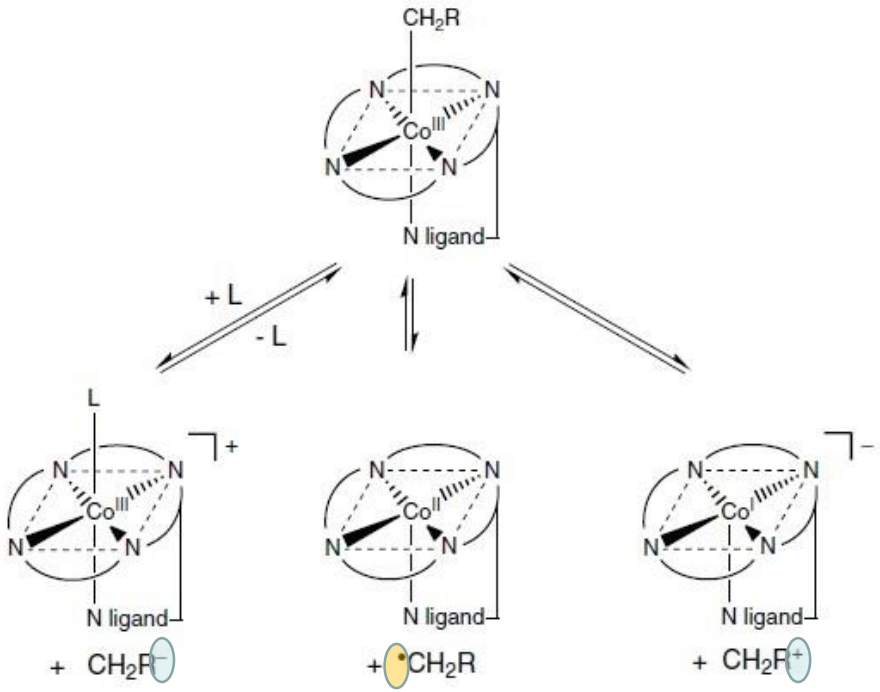
Reactions of the alkylcobalamins

One-electron reduction and oxidation



Co configuration changes from d^6 to d^8

Co-C Bond Cleavage in Alkylcobalamins

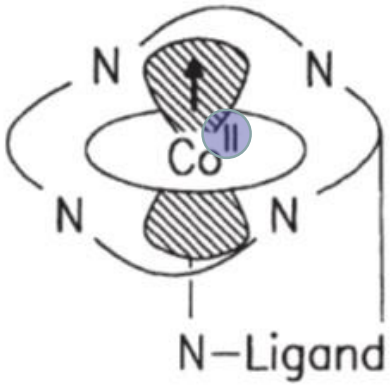


type of reaction:	heterolysis	homolysis	heterolysis
metal configuration in the product	d^6 low-spin, stable, inert	d^7 low-spin, 1 unpaired electron $(d_{z^2})^1$	d^8, "super-nucleophilic" $(d_{z^2})^2$
alkyl ligand, eliminated as:	"carbanion", nucleophilic	primary alkyl radical very reactive	"carbocation", electrophilic
app. electrochemical potential equivalent[a]:	> 0 V	0 to -0.4 V	< -0.9 V

After homolysis

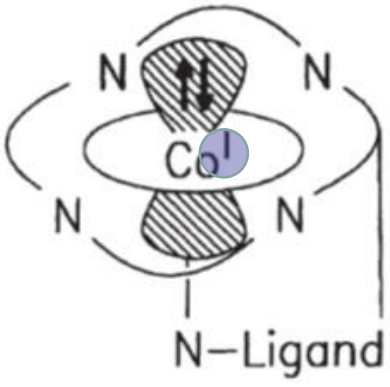
After heterolysis

Radical Scavenger

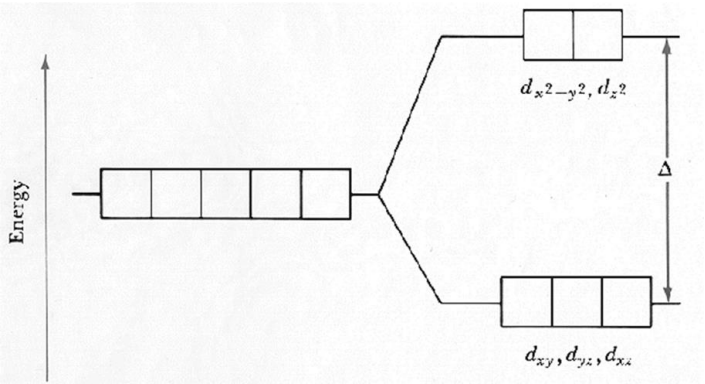


$(d_{z^2})^1$

Supernucleophile

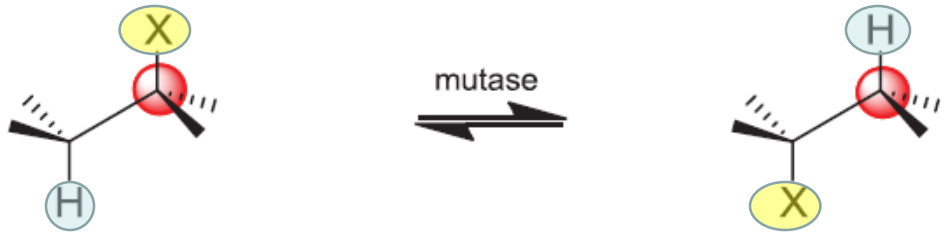


$(d_{z^2})^2$

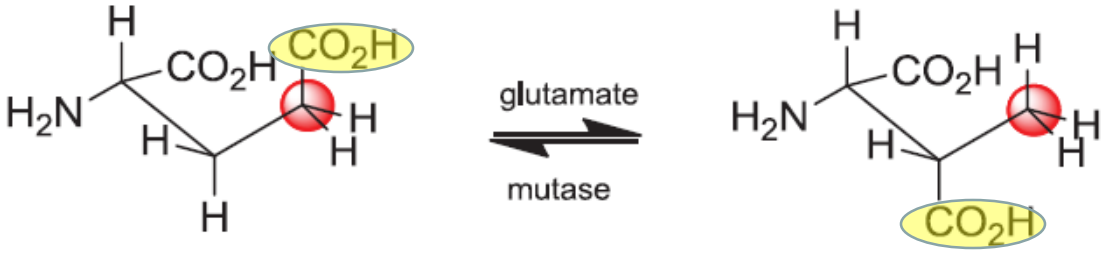


Mutase* activity of Coenzyme B12

in general:



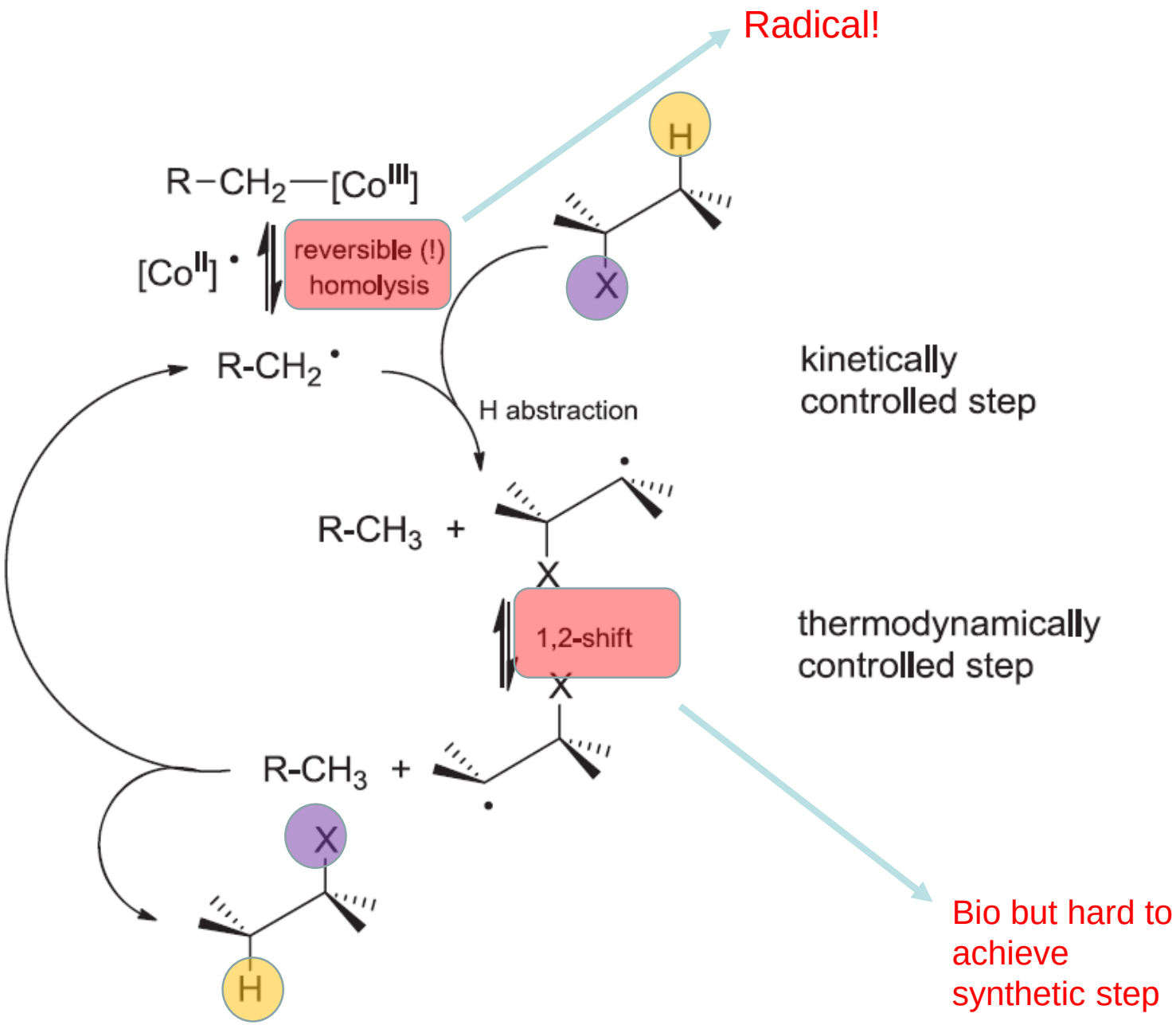
example:



glutamic acid

β-methylaspartic acid

*** Isomerases are one of the three enzyme classes connected with B_{12} cofactors**


Radical!
R−CH2—[CoIII]
[CoII] •
reversible (!) homolysis
R-CH2 •
H abstraction
kinetically controlled step
R-CH3 +
1,2-shift
thermodynamically controlled step
R-CH3 +
Bio but hard to achieve synthetic step
H
X