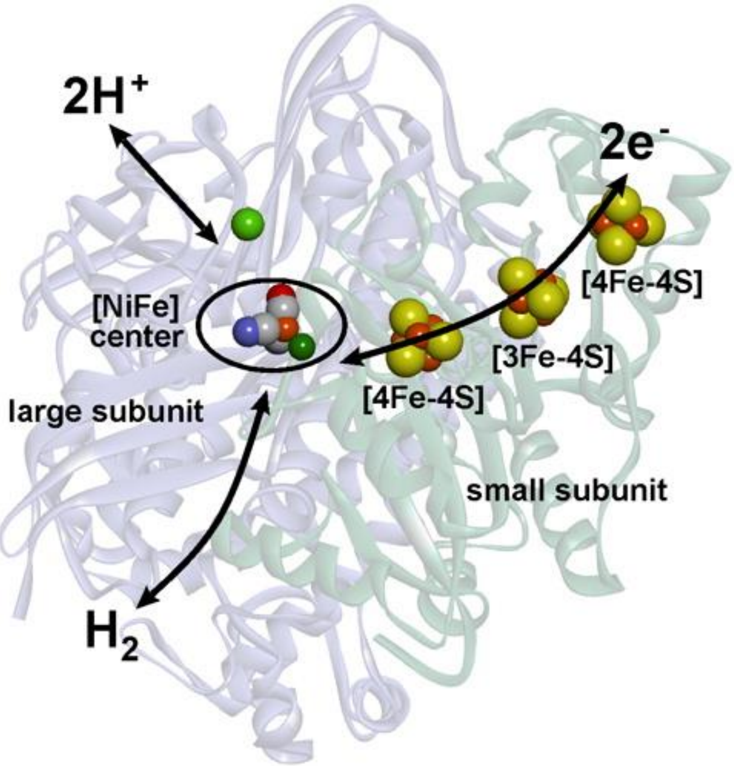
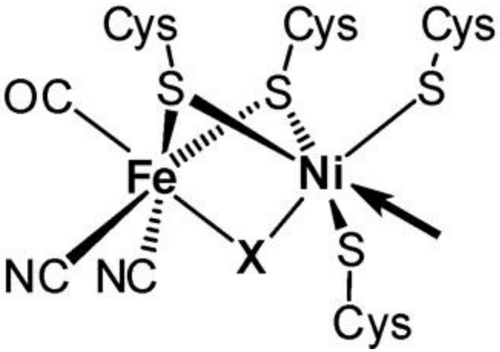
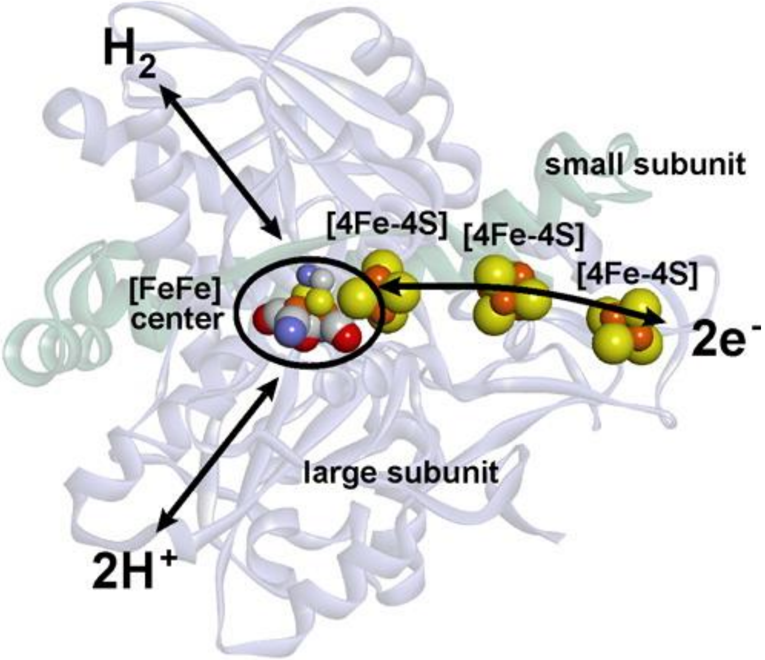
$$H_2 \leftrightarrows 2H^+ + 2e^-$$

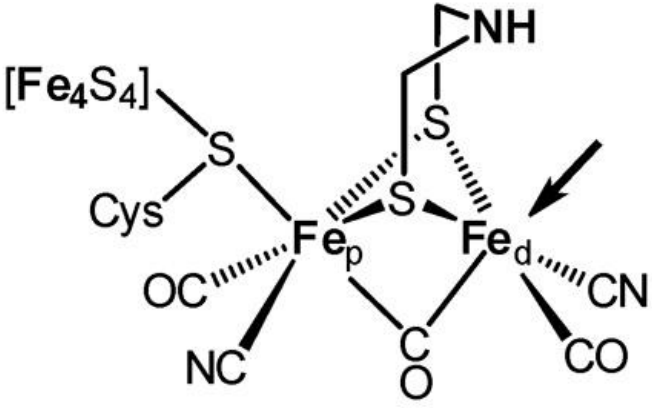
[NiFe] Hydrogenase



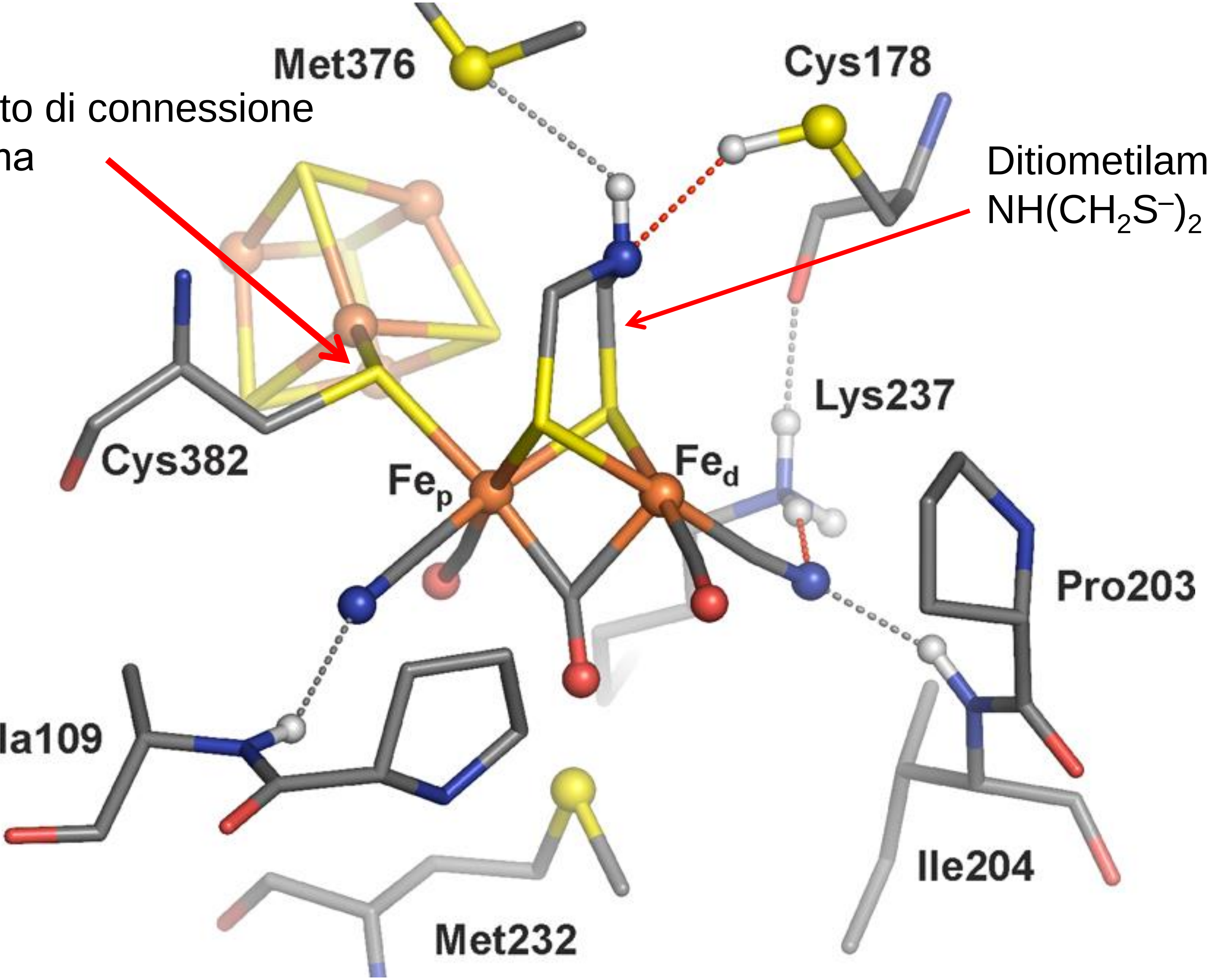


[FeFe] Hydrogenase





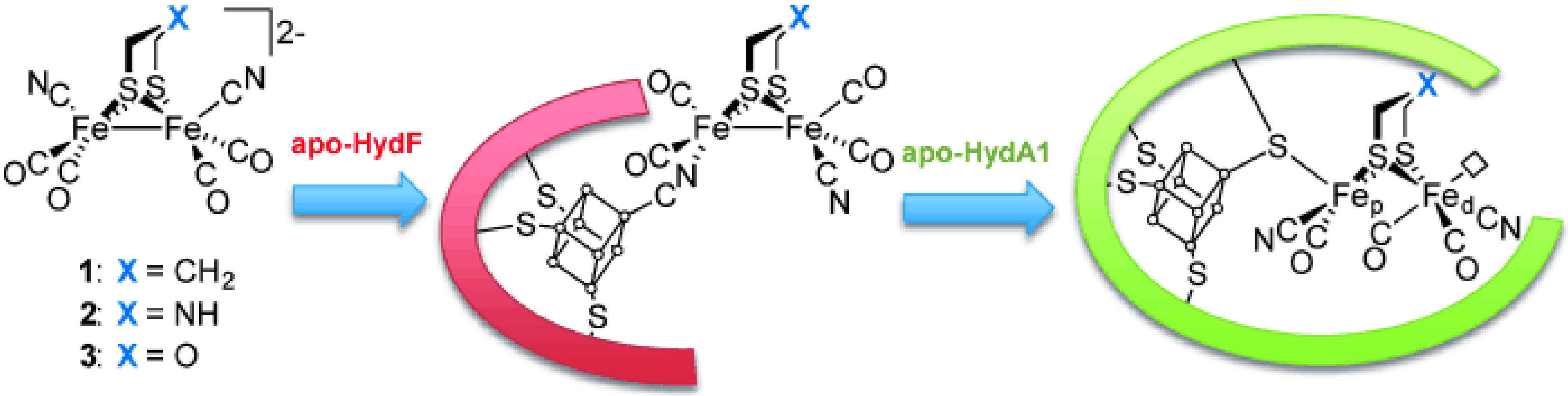
[FeFe] Idrogenasi



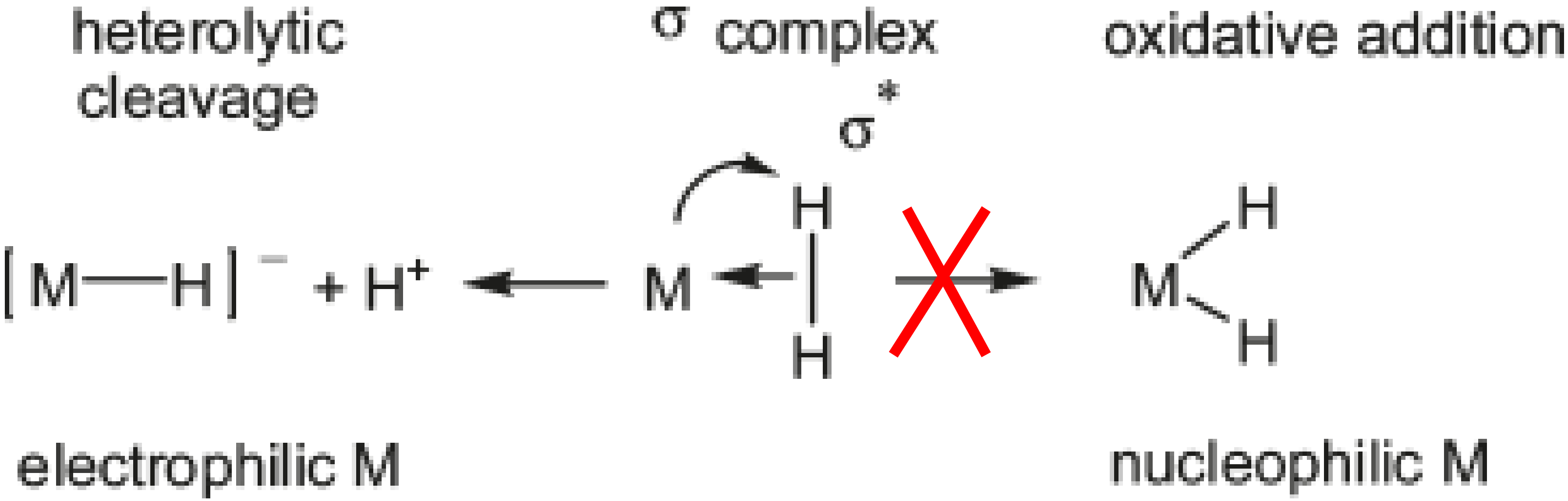
Unico sito di connessione all'enzima

Ditiometilammina, $NH(CH_2S^-)_2$

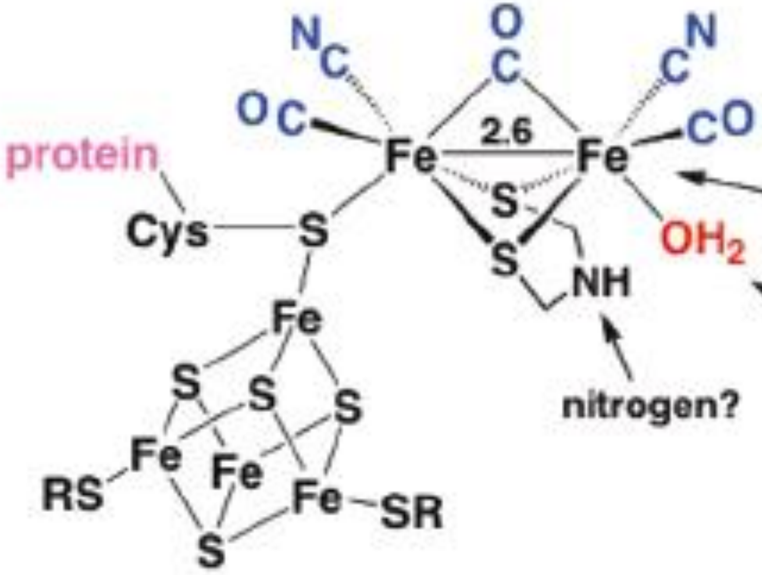
Soltanto l'enzima con X = NH è cataliticamente attivo



Il CO coordinato favorisce la rottura eterolitica di H_2



Fe–Fe Idrogenasi



Fe–S cubane cluster
for electron transfer

- **Active site attached at only one point**
- **CO and CN ligands on low-spin Fe^{II}**
- **Metal-metal bonds**
- **Intramolecular heterolysis of H_2 ostensibly at this site**

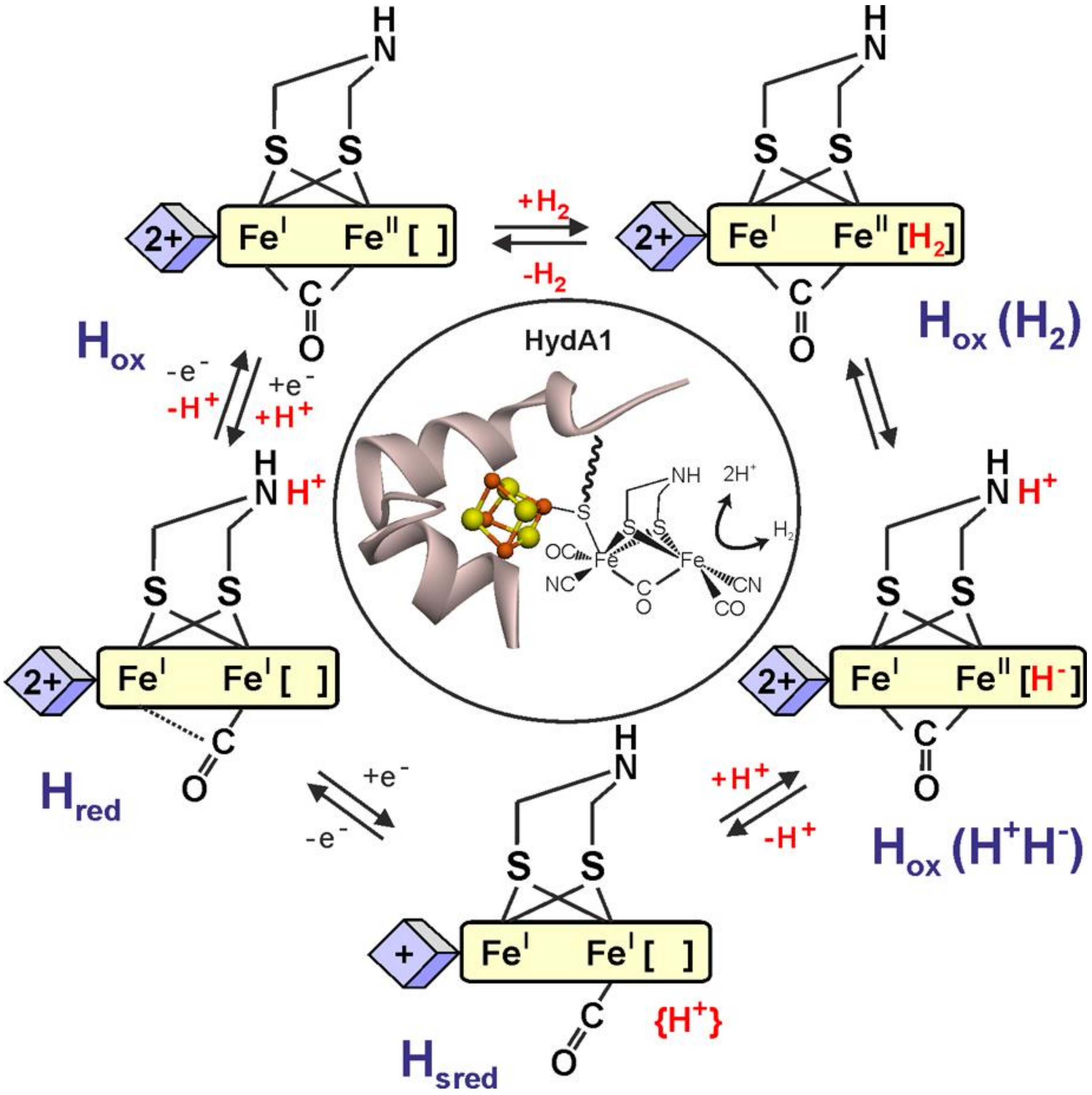
CO can displace H_2O; can H_2?

H_2 is slightly stronger ligand than H_2O on $W(CO)_3(PR_3)_2$

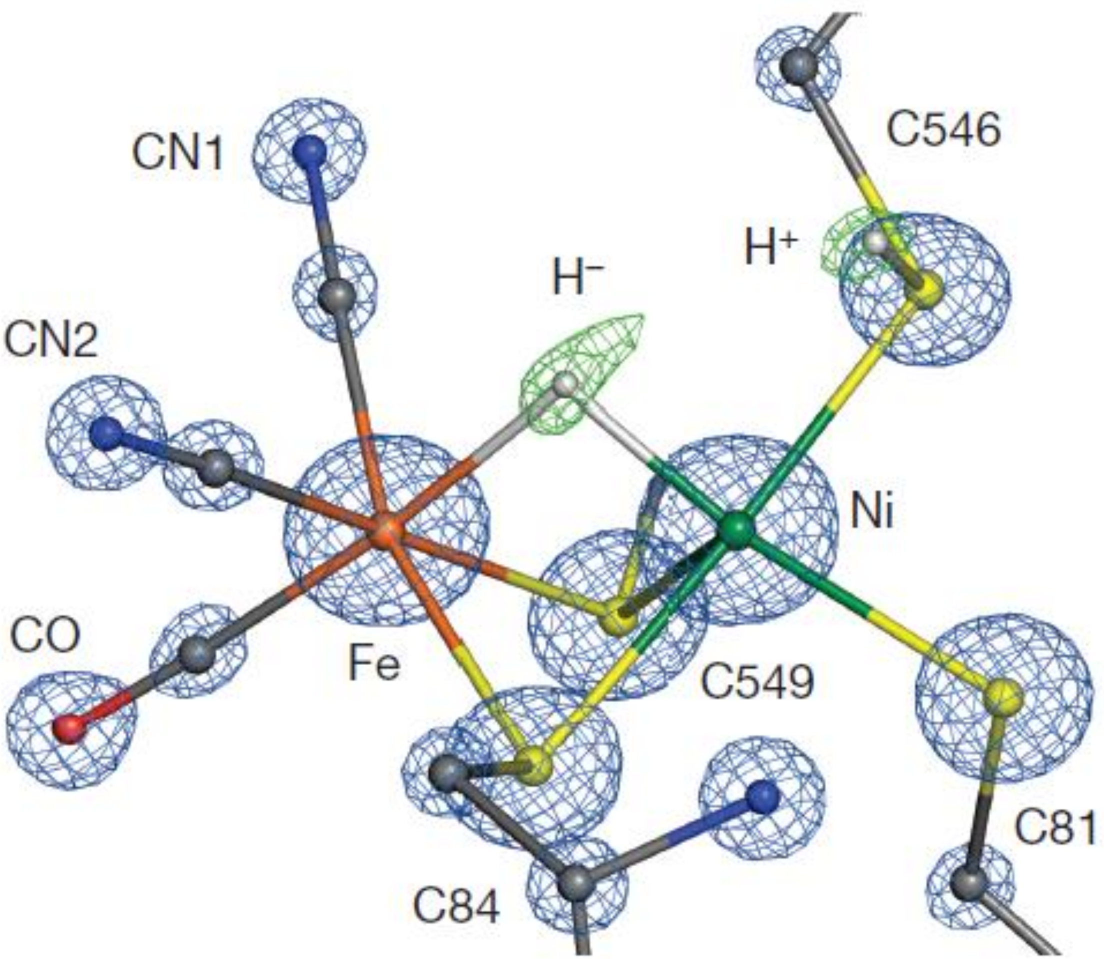
Trans CO ligand favors H_2 coordination and heterolysis

***High ligand-field strength* of CN may be needed to help maintain a *low-spin state* for Fe that is critical for strong CO binding. High-spin Fe^{II}-CO complexes are rare**

Ipotesi di meccanismo

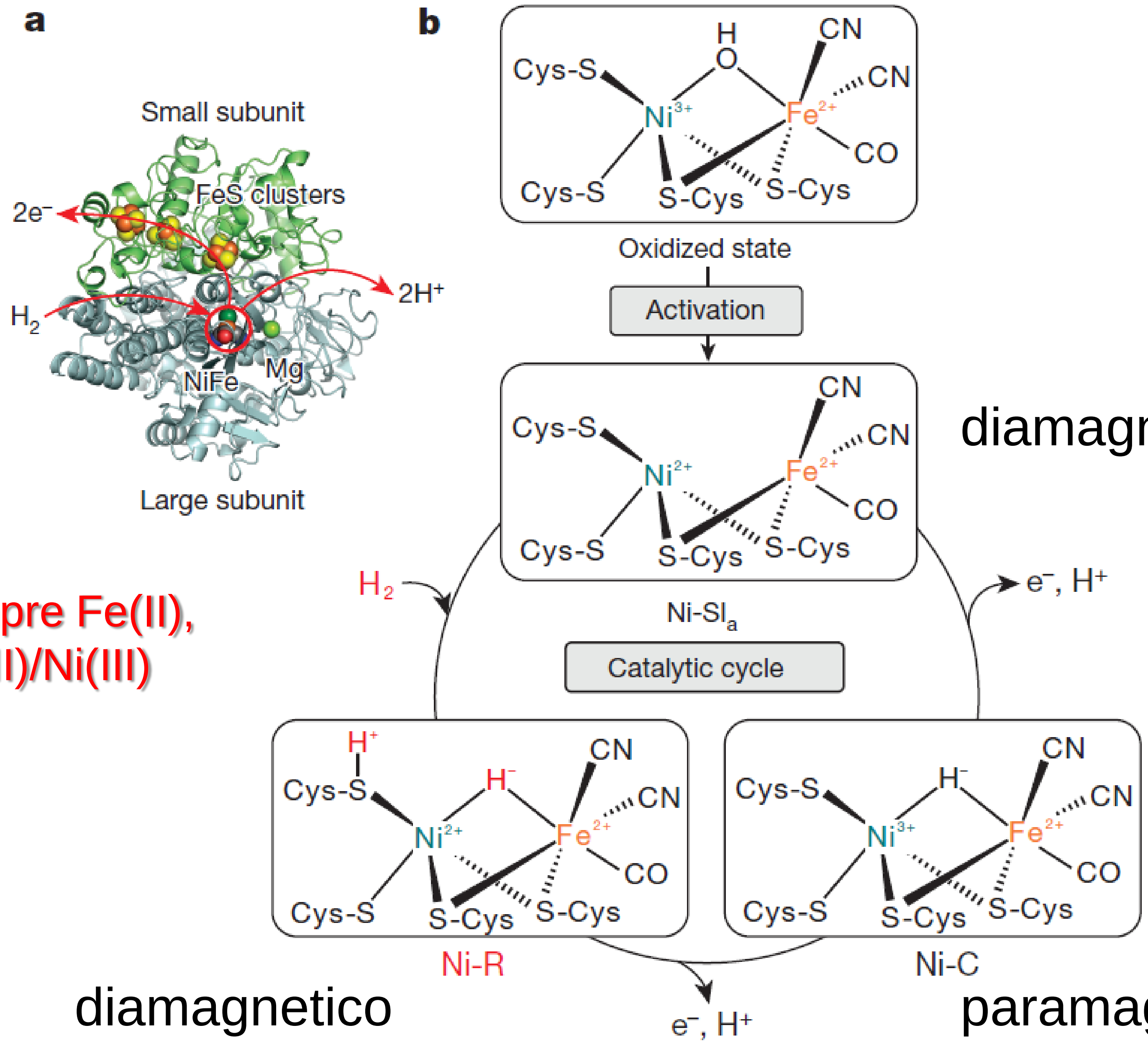


Fe–Ni Idrogenasi



Nature, **2015**

Ipotesi di meccanismo



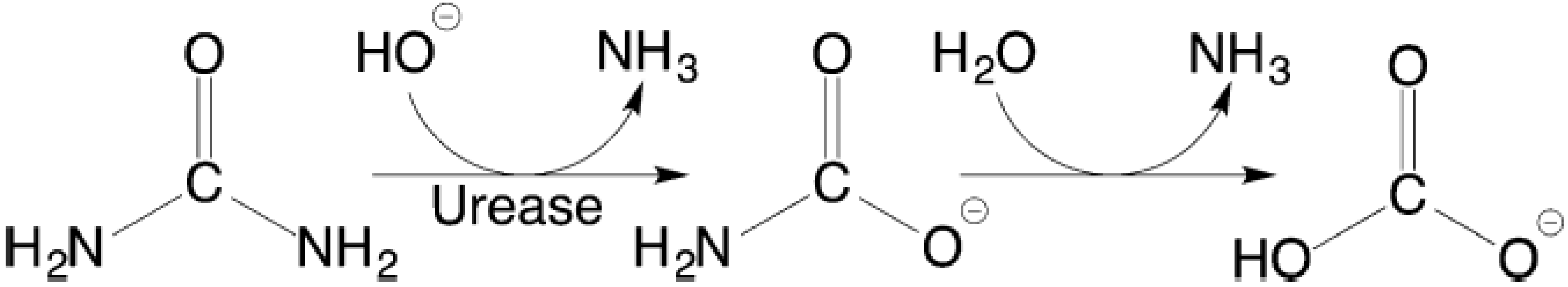
diamagnetico

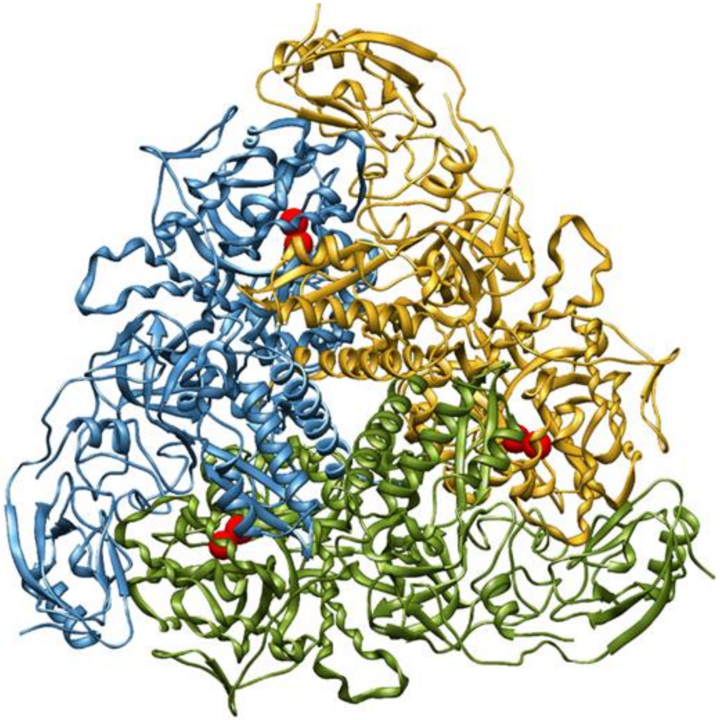
Ferro sempre Fe(II),
Nichel Ni(II)/Ni(III)

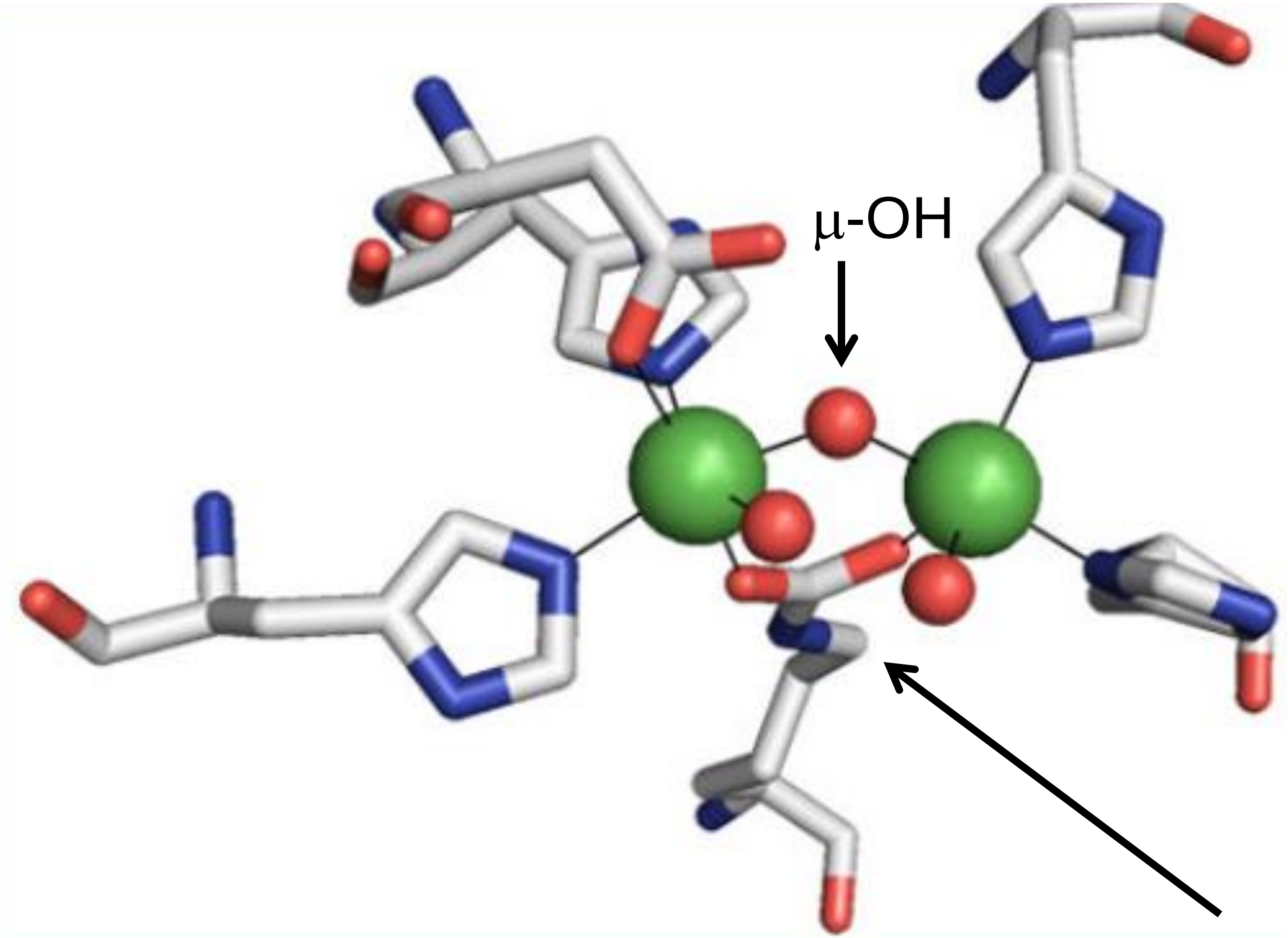
diamagnetico

paramagnetico

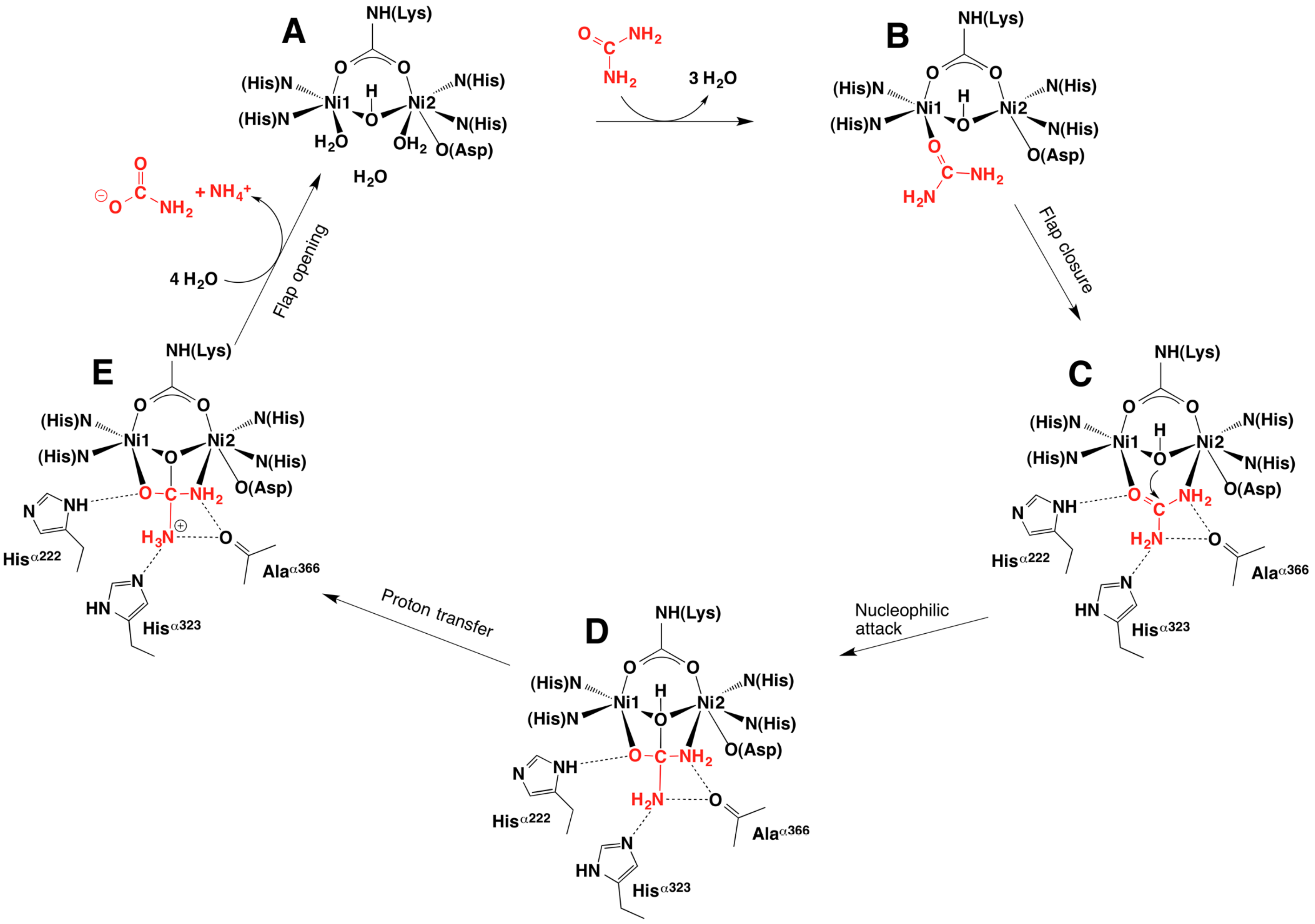
Ureasi



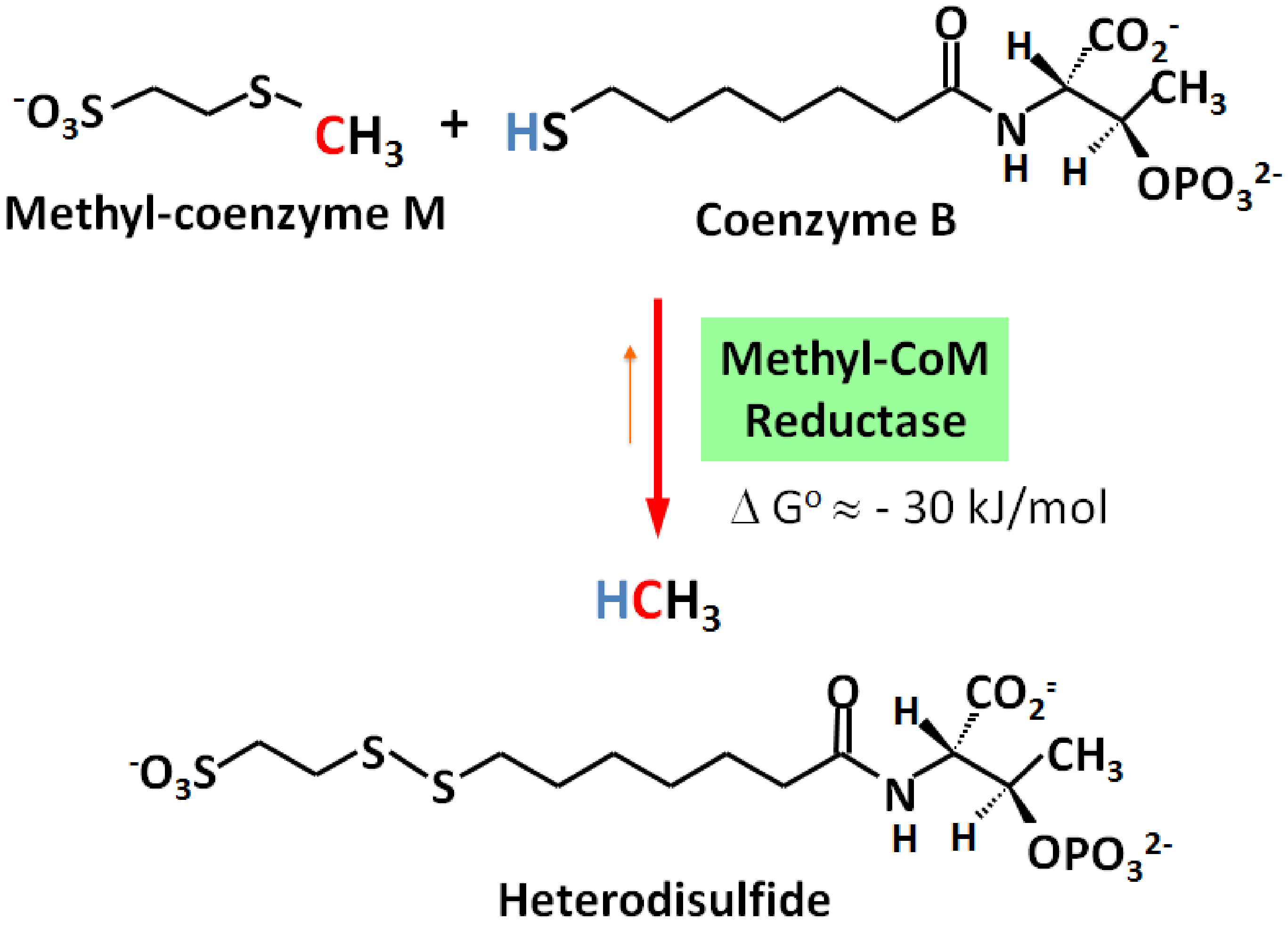


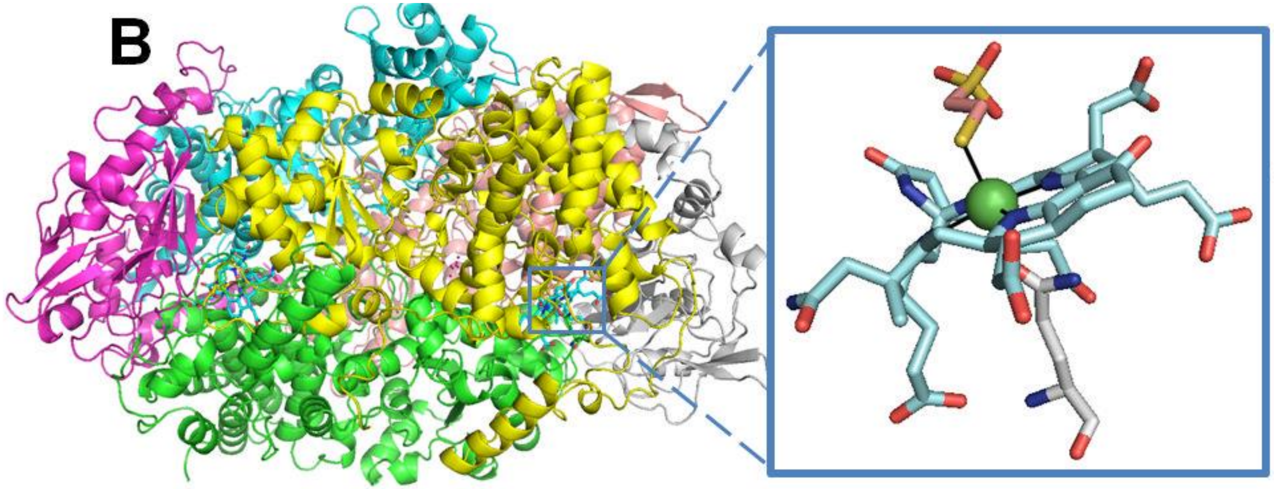


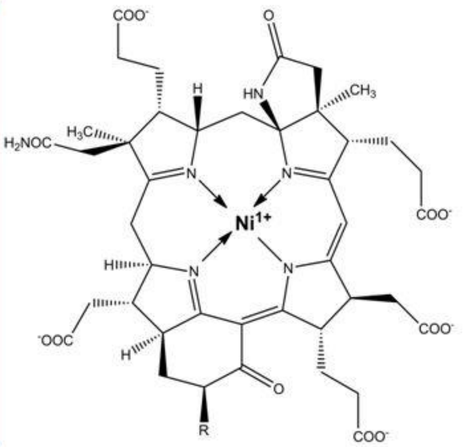
Lisina carbamilata

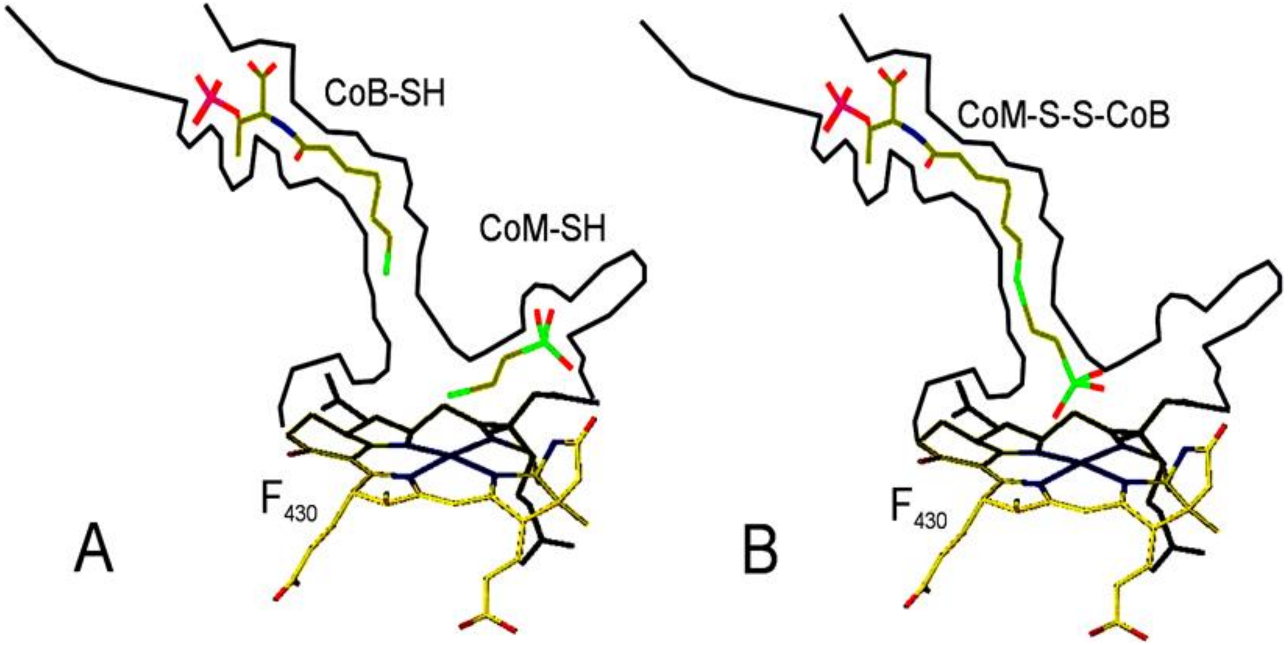

A
B
C
D
E
NH(Lys)
(His)N
Ni1
Ni2
N(His)
O(Asp)
H₂O
OH₂
3 H₂O
4 H₂O
+ NH₄⁺
Flap closure
Nucleophilic attack
Proton transfer
Flap opening
Hisα222
Hisα323
Alaα366

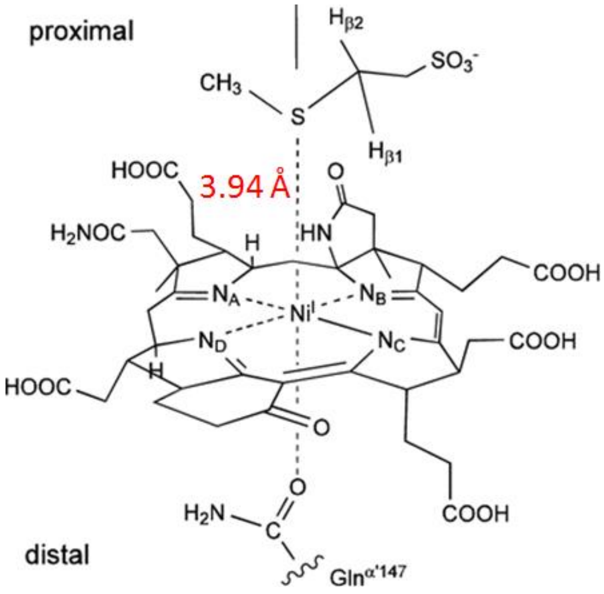
metil-coenzima M riduttasi (MCR)




B


COO-
O
H
HN
CH3
H2NOC
H3C
N
N
Ni1+
COO-
H
N
N
-OOC
COO-
H
O
R
COO-


CoB-SH
CoM-SH
F430
A
CoM-S-S-CoB
F430
B


proximal
Hβ2
SO3-
CH3
S
Hβ1
HOOC
3.94 Å
O
H2NOC
H
HN
COOH
NA
Ni
NB
ND
NC
COOH
HOOC
H
O
O
H2N
C
COOH
distal
Glnα'147

Meccanismo S_N2