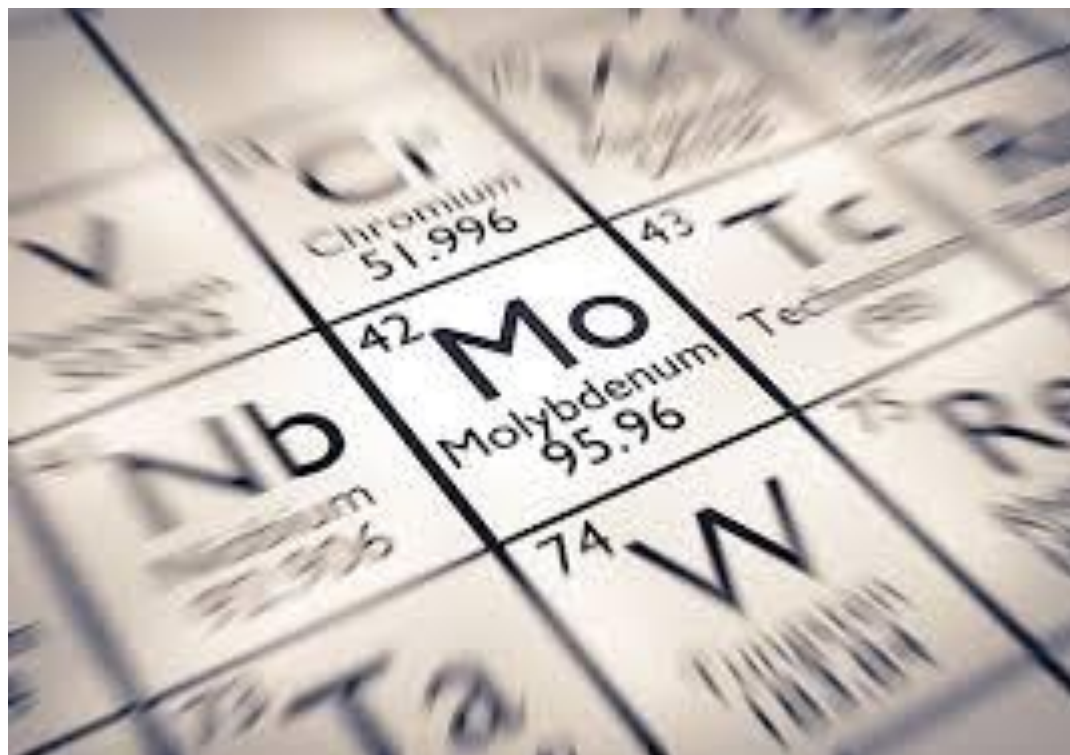
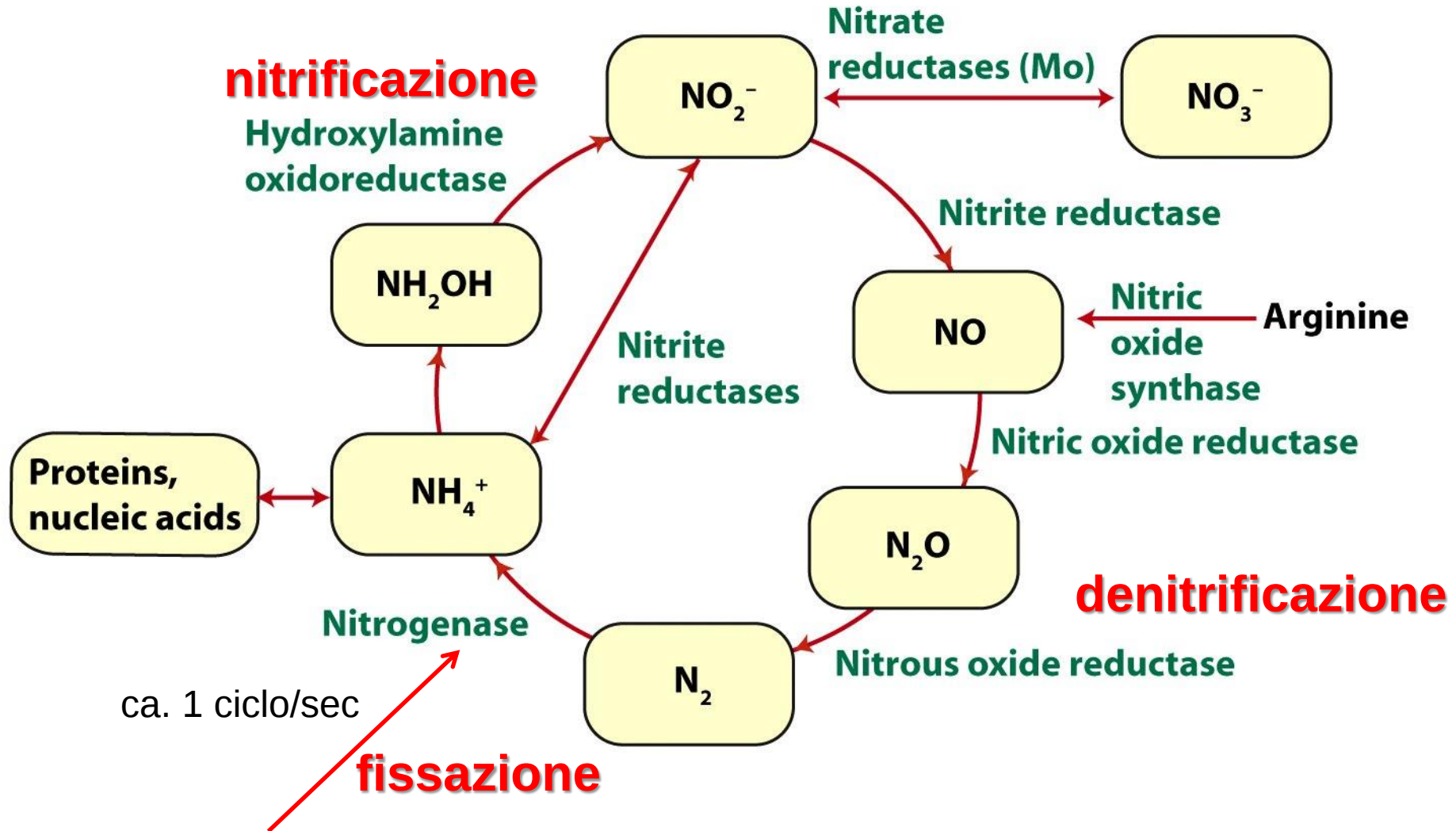
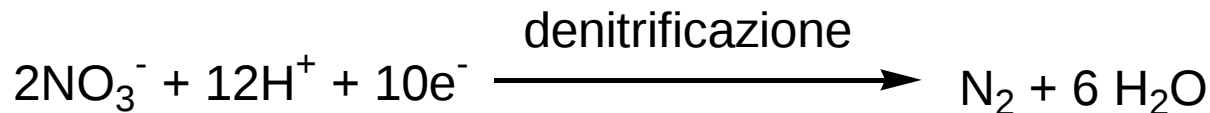
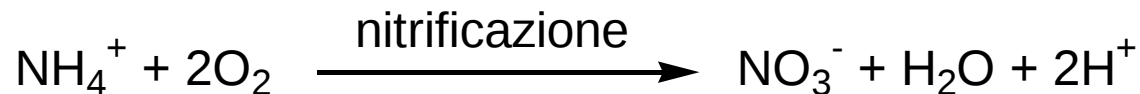
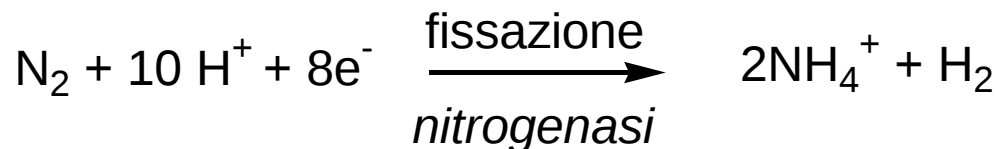
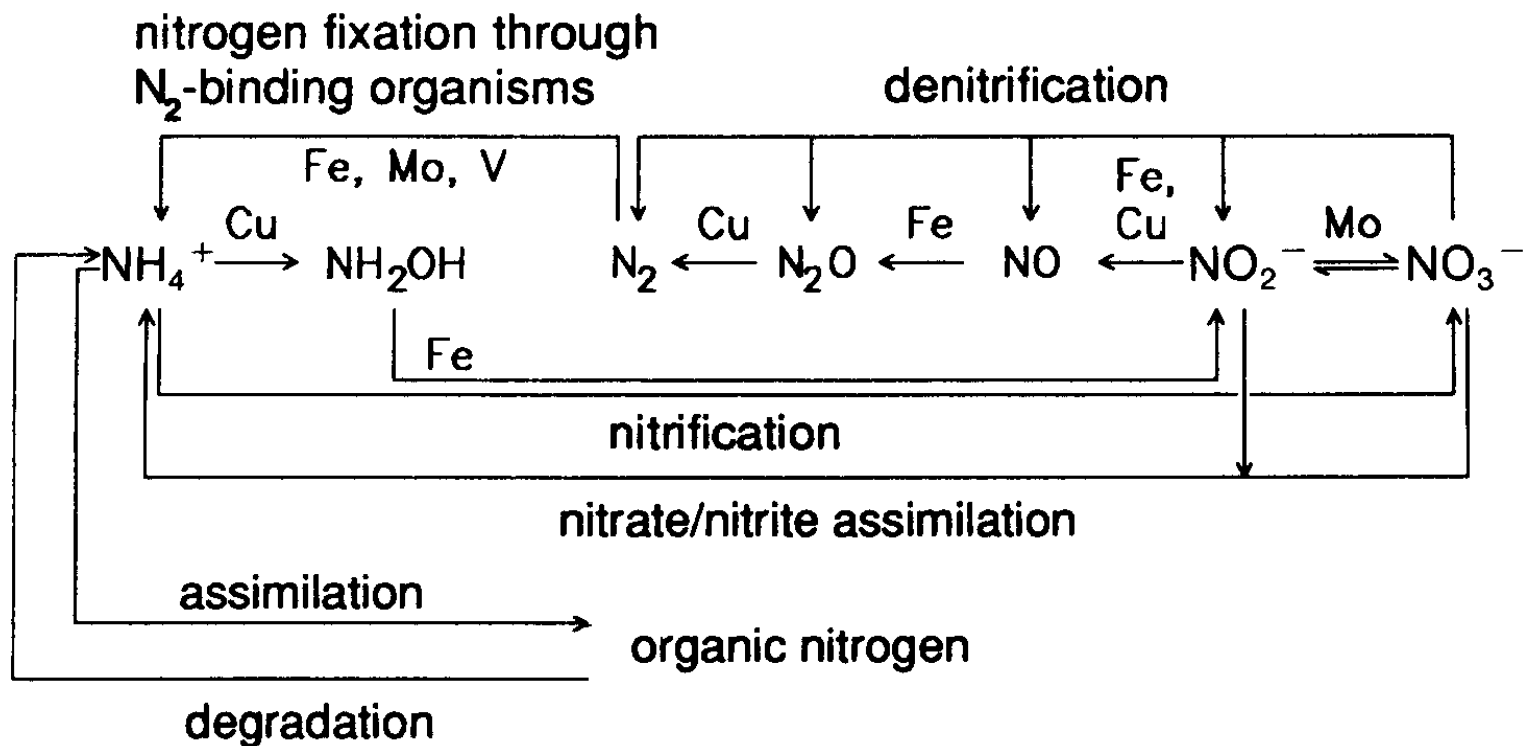




Ciclo dell'azoto



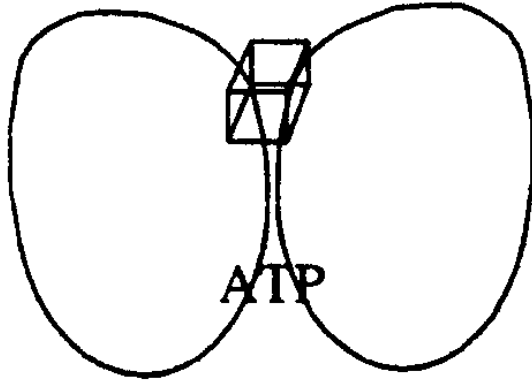
Batteri procarioti diazotropici: 10^8 ton N_2/y



Nitrogenasi



1992

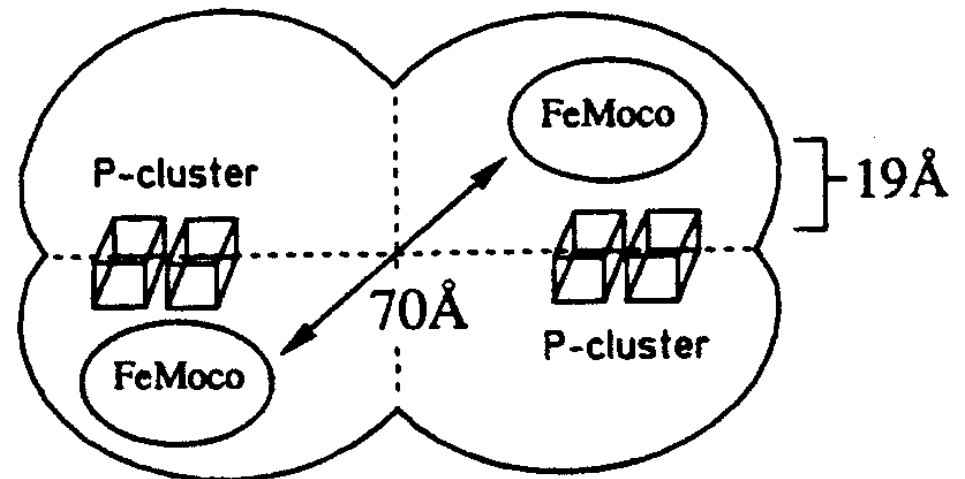


Fe protein

γ_2

60 kDa

+



FeMo protein

$\alpha_2\beta_2$

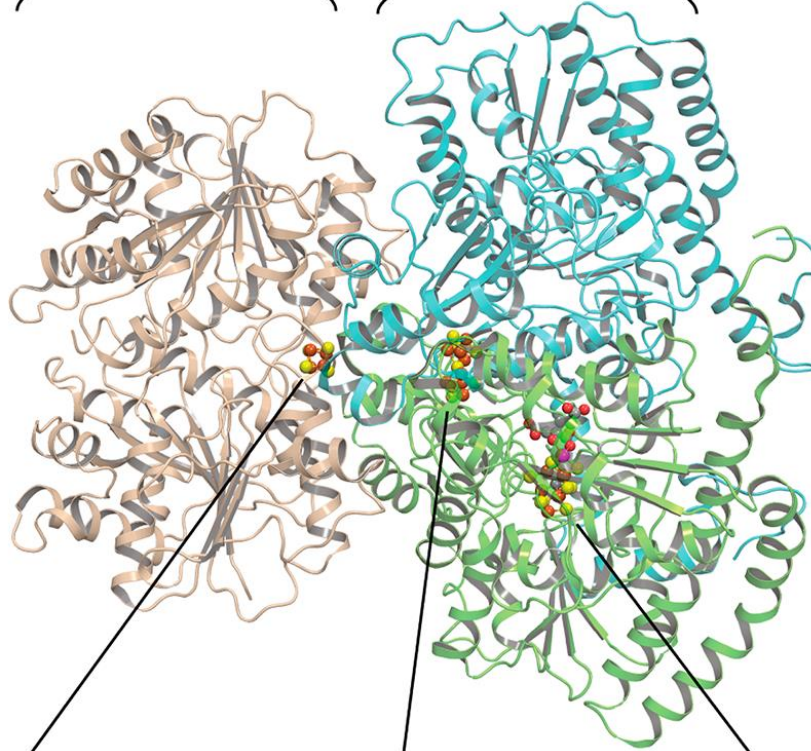
220 kDa

Nitrogenasi

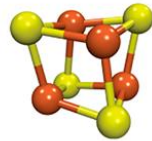
Fe protein

MoFe protein

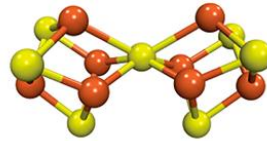
(A)



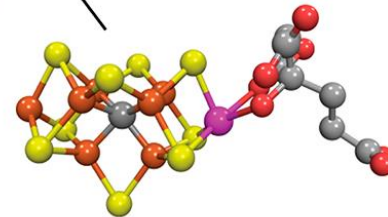
(B)



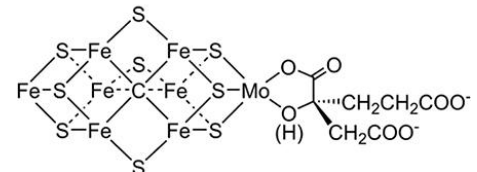
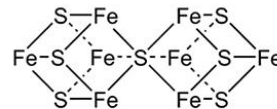
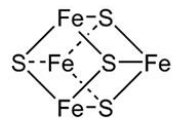
F cluster



P cluster

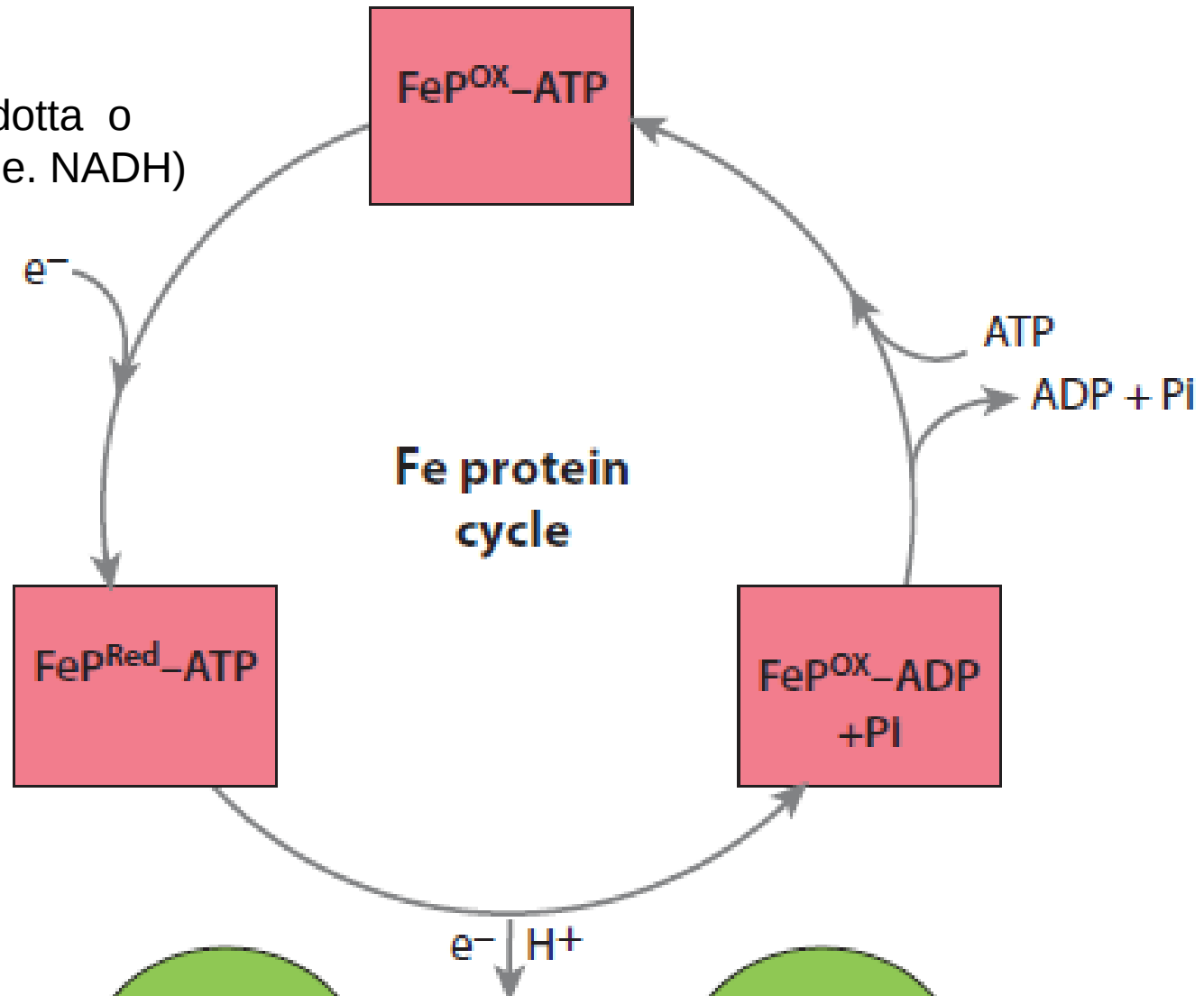


M cluster (FeMoco)

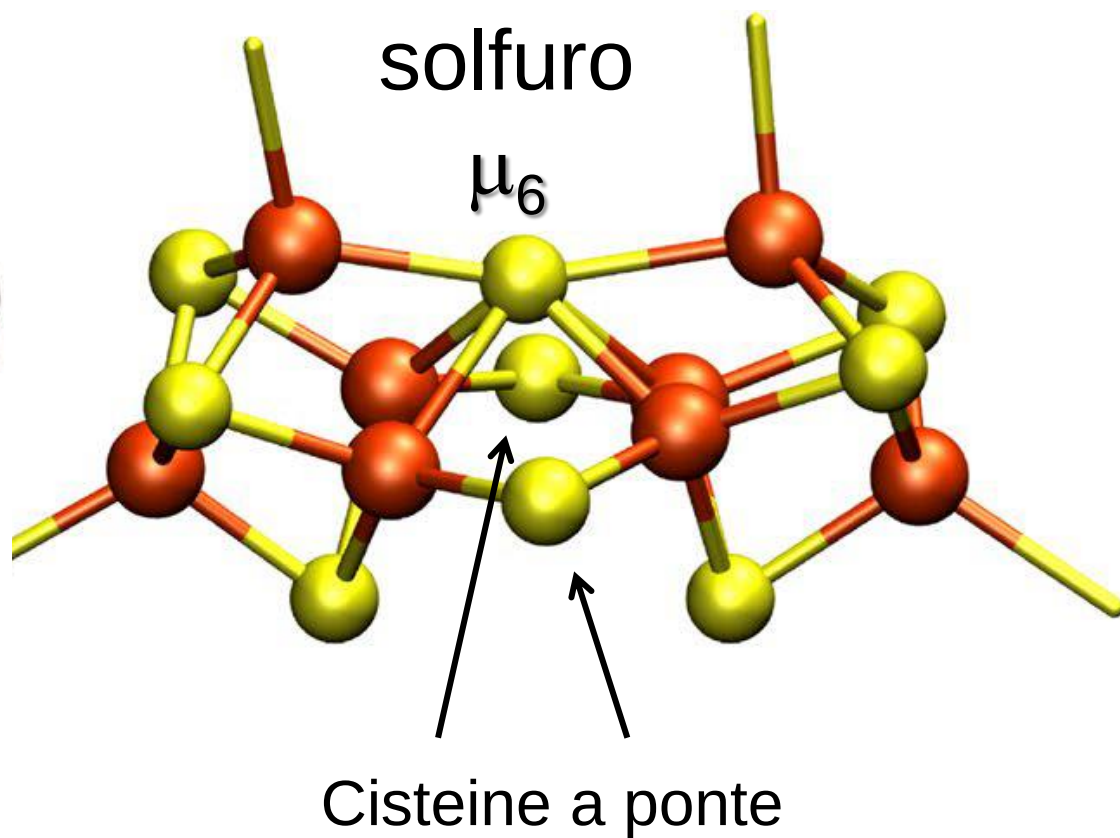
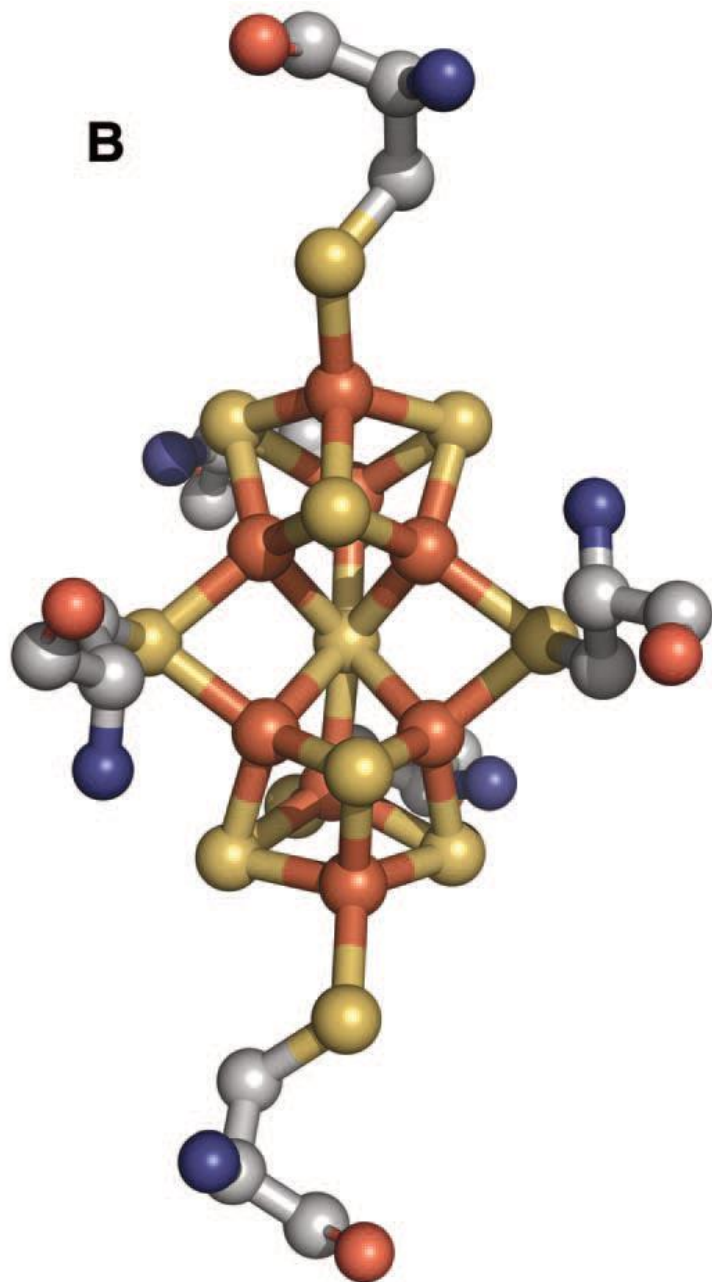


Fe-proteina

Ferridossina ridotta o
flavodossina (i.e. NADH)

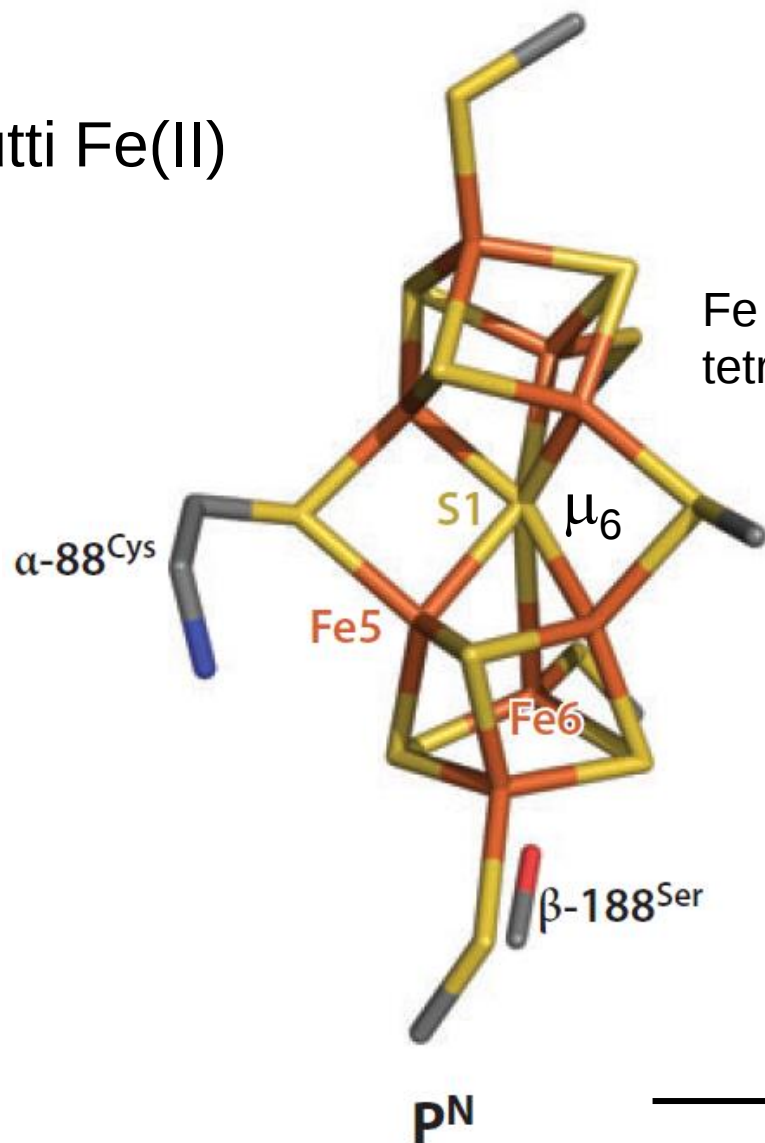


P-cluster 8Fe-7S



P-cluster 8Fe-7S

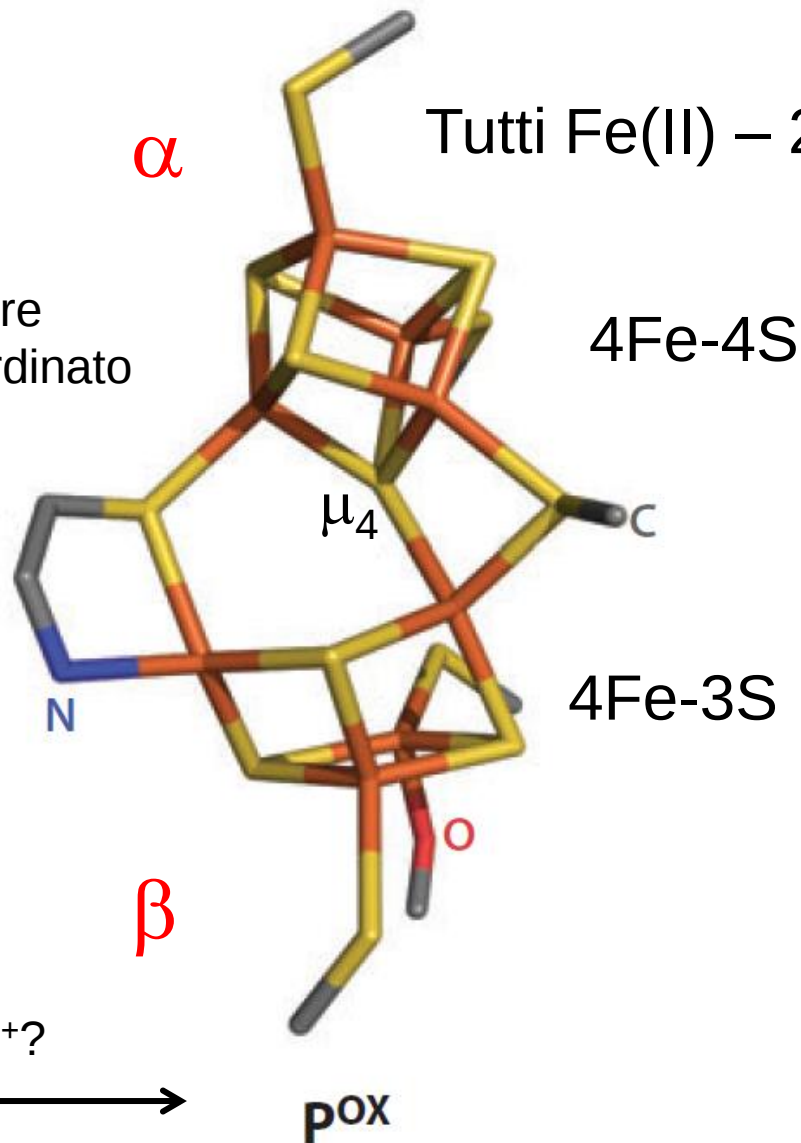
Tutti Fe(II)



Fe sempre
tetracoordinato

α

Tutti Fe(II) – 2e⁻



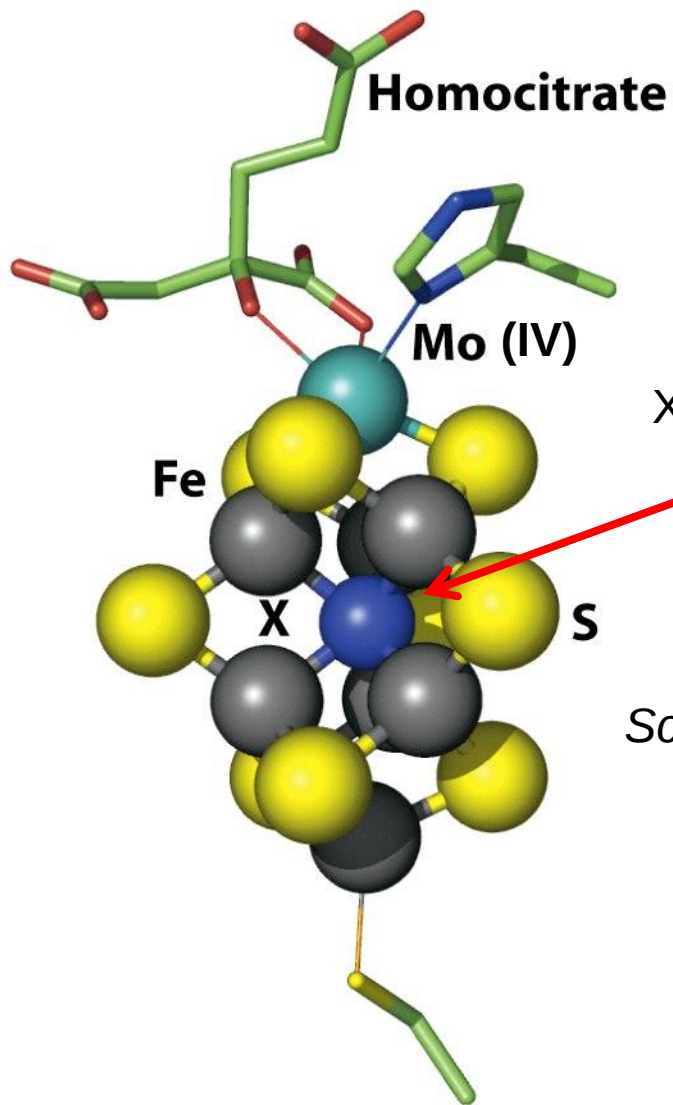
4Fe-4S

4Fe-3S

β

-2H⁺?





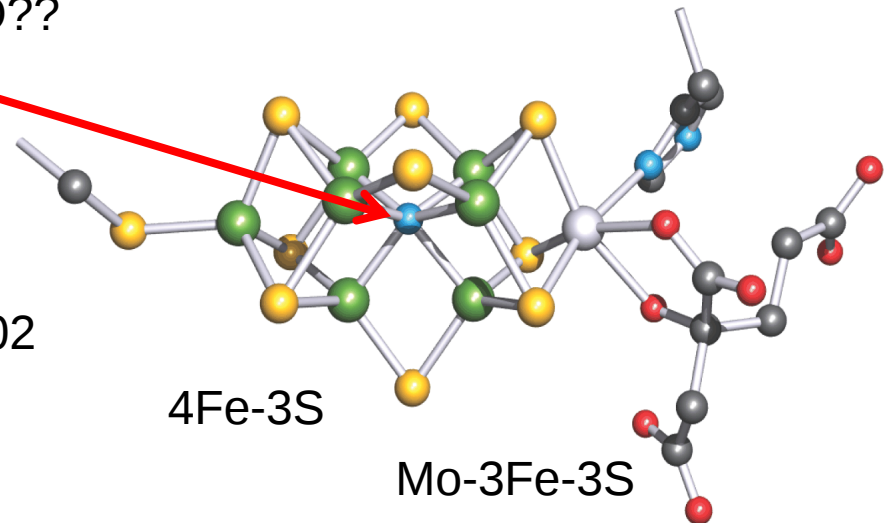
Nitrogenase FeMoCo

Cofattore FeMo

7Fe-9S-Mo-omocitrato

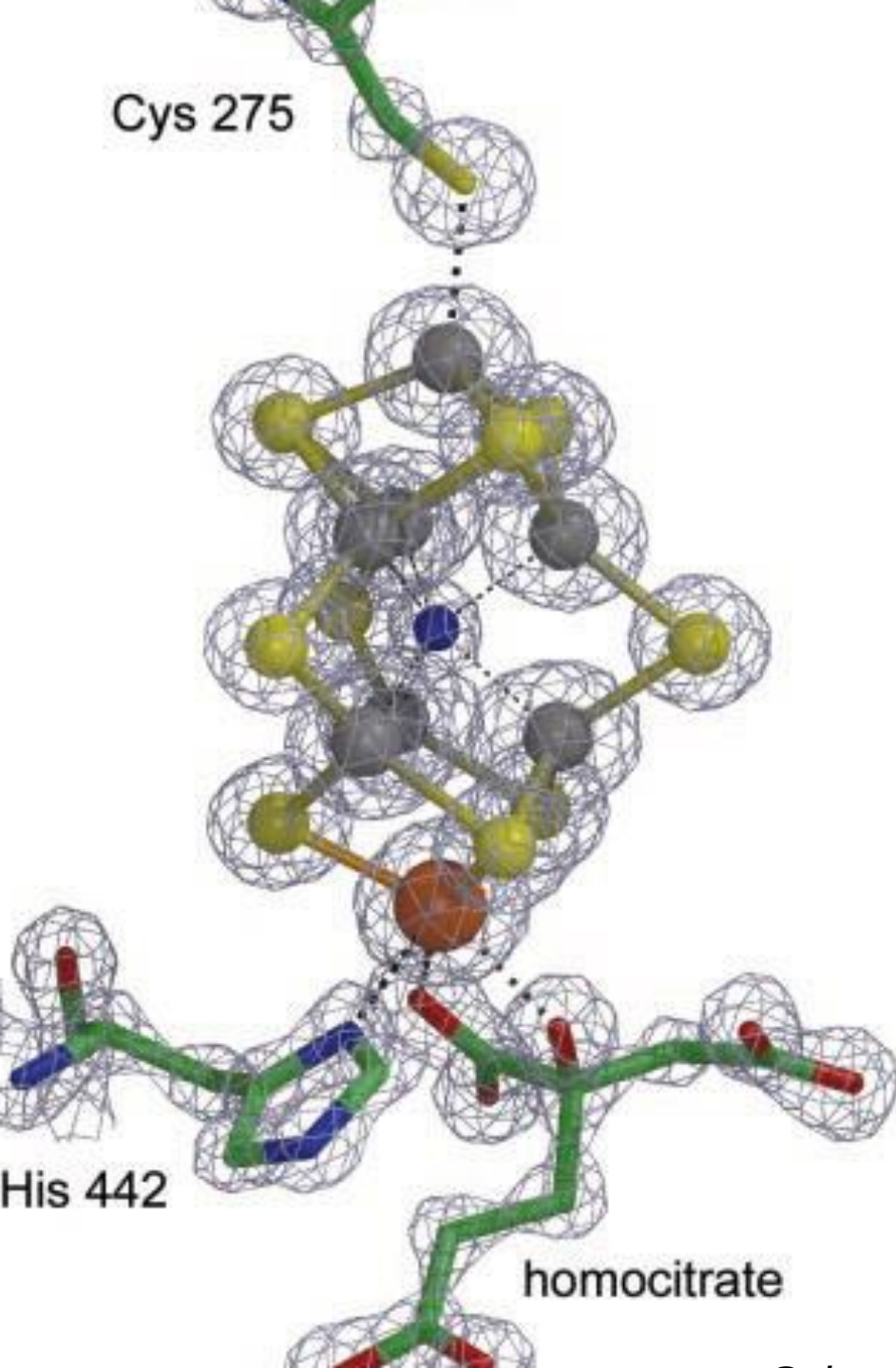
X = C, N, O??

Science, 2002

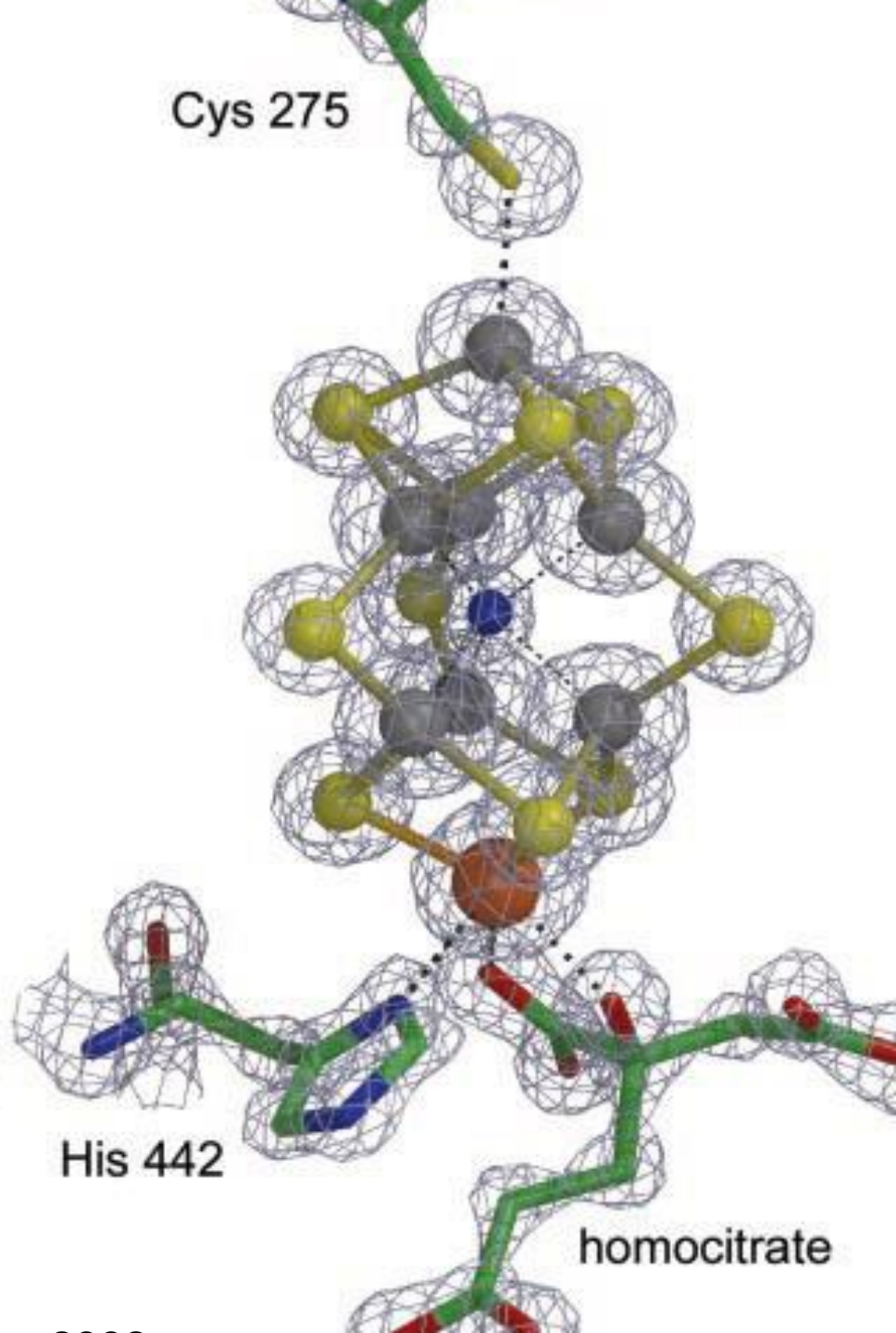


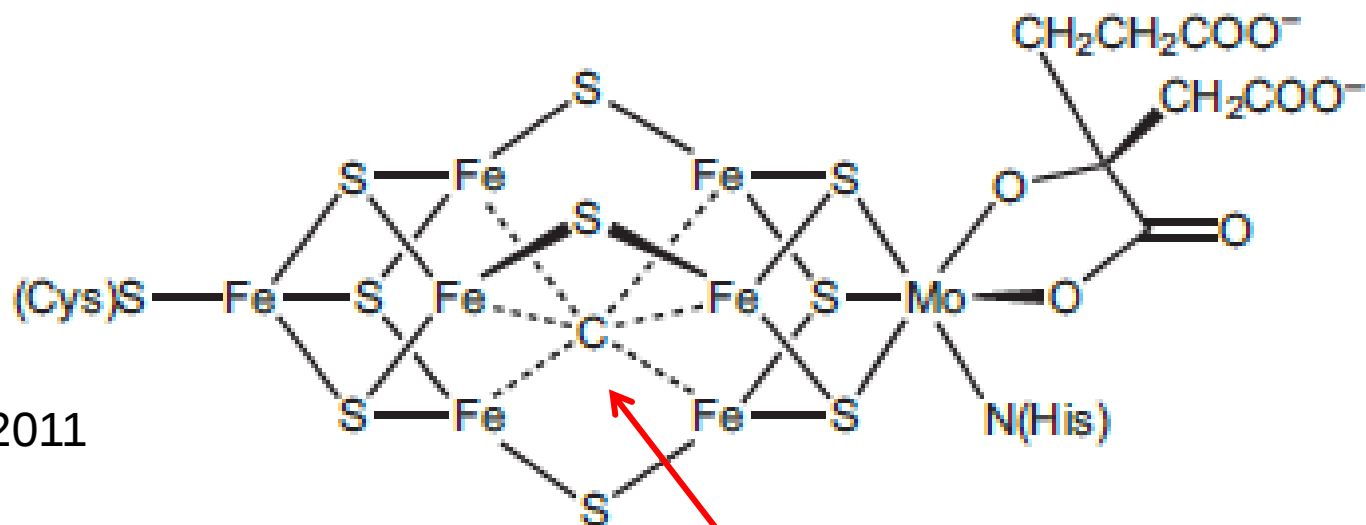
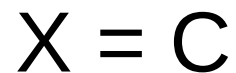
Tutto in α

Cys 275



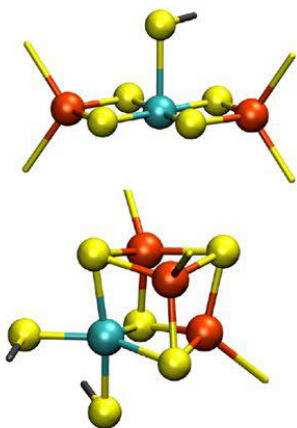
Cys 275





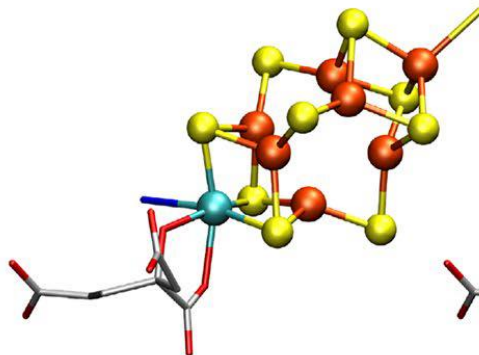
Science, 2011

Carburo, C⁴⁻



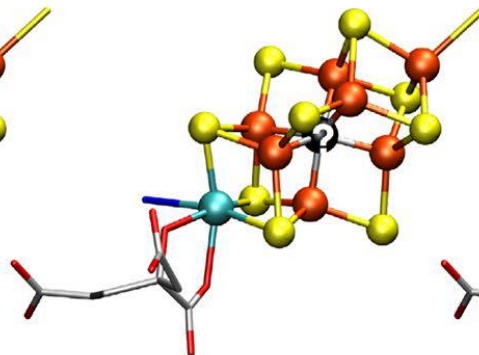
1978

First structural models from EXAFS



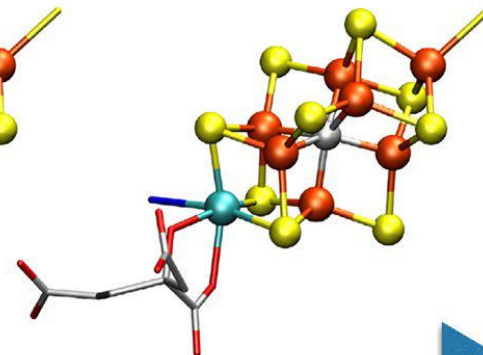
1992

First crystal structure (2.7Å)



2002

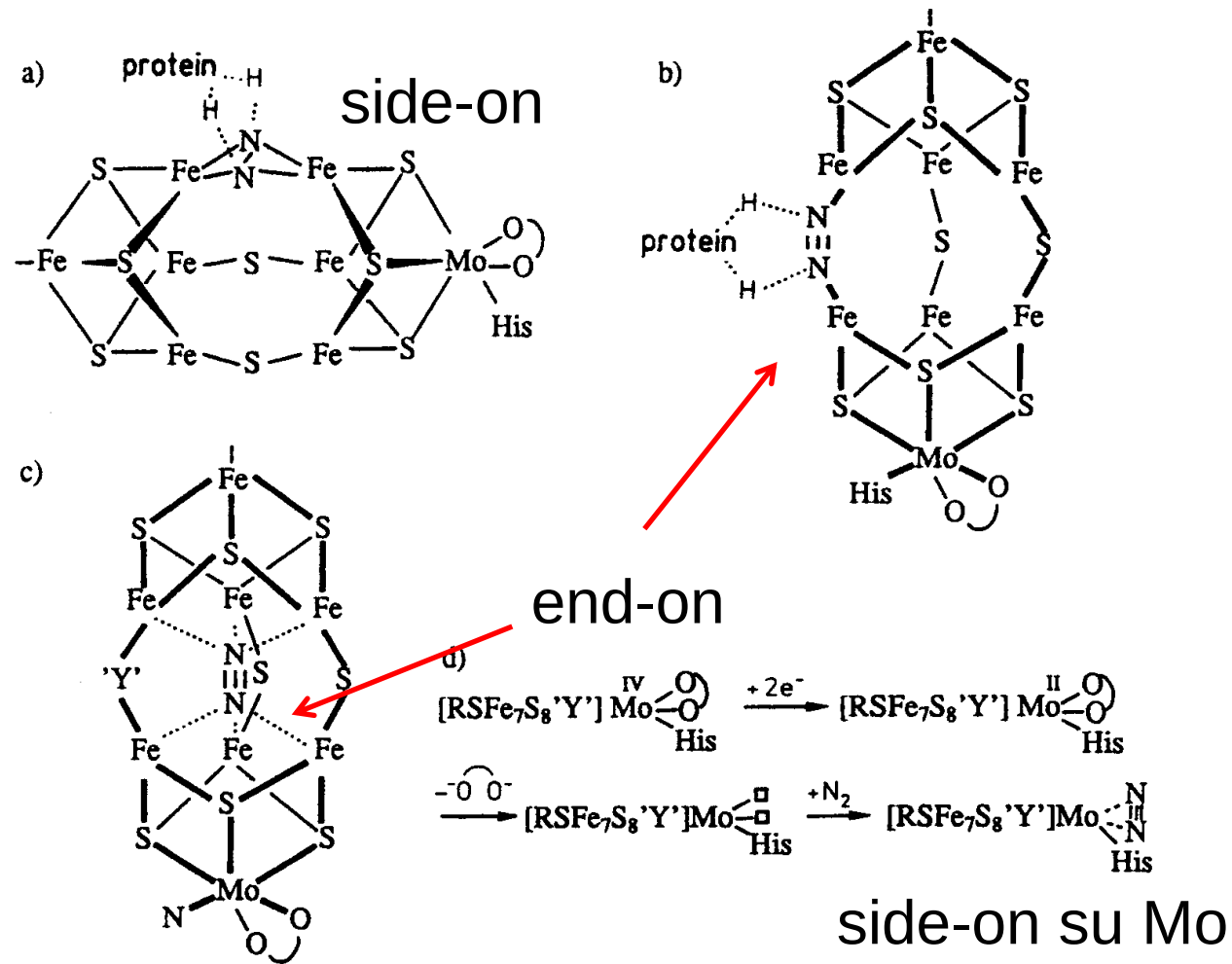
Discovery of interstitial atom



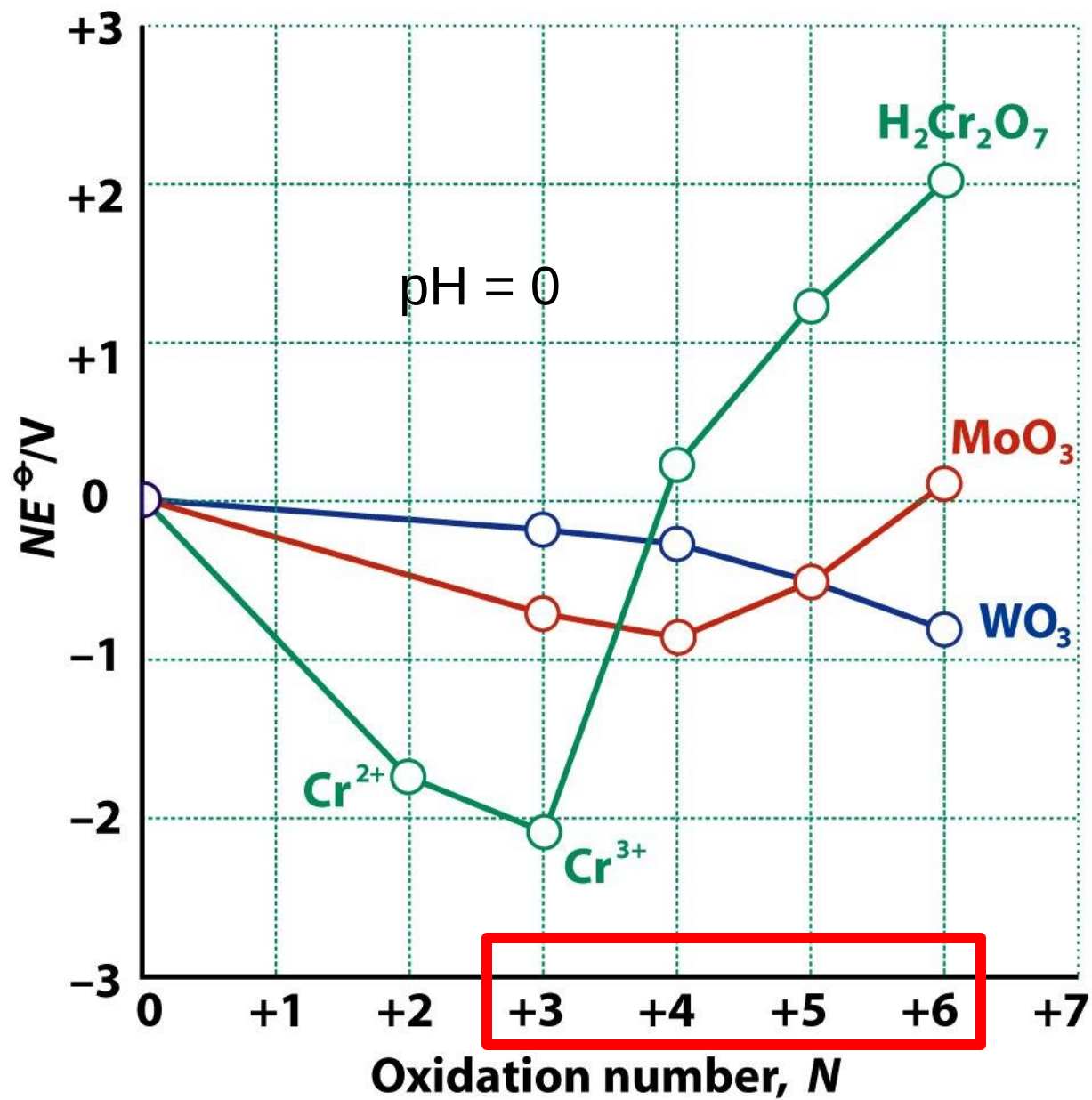
2011

Interstitial atom identified as carbon

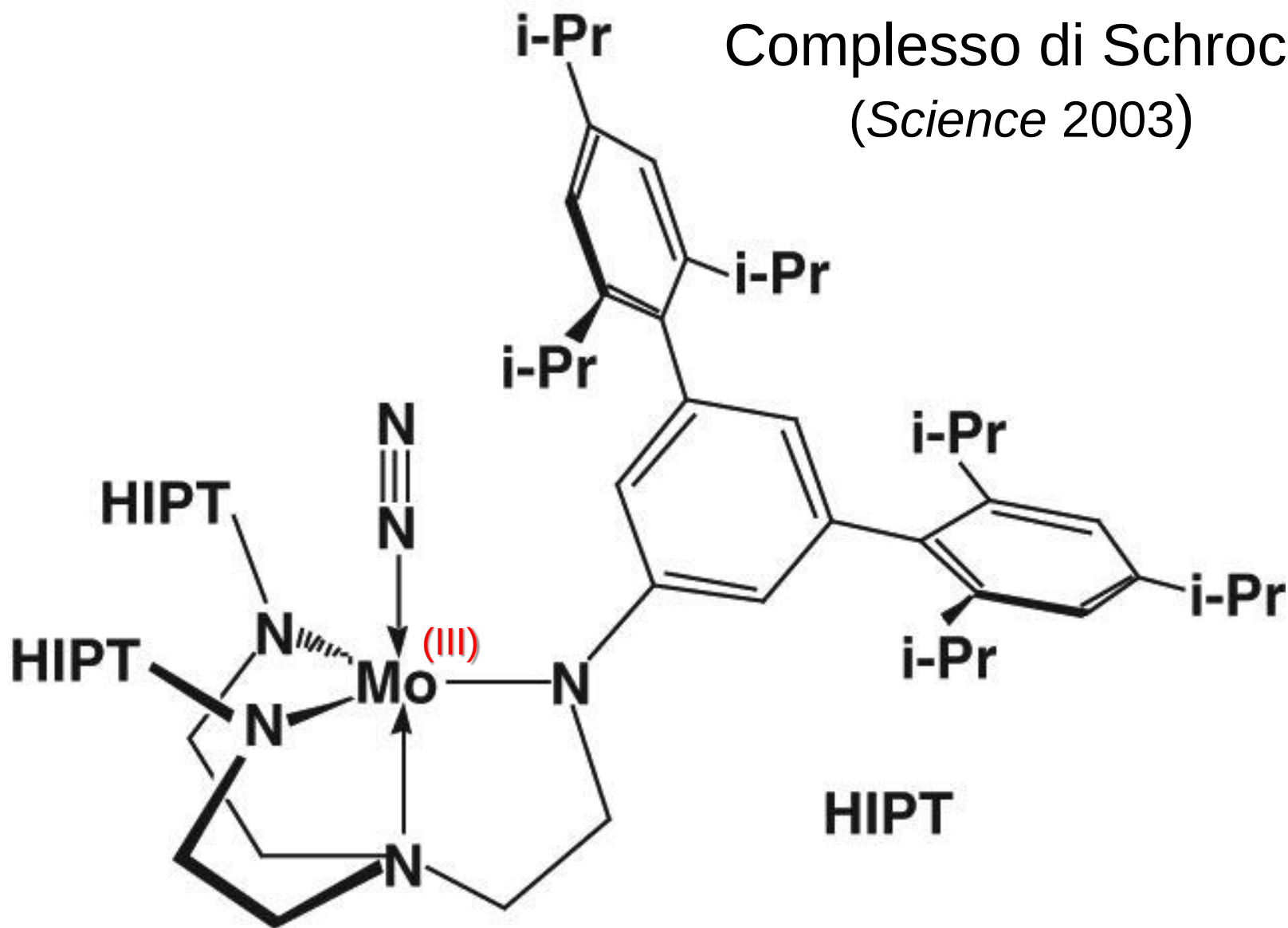
Ipotetici modi di coordinazione di N_2 al FeMoco



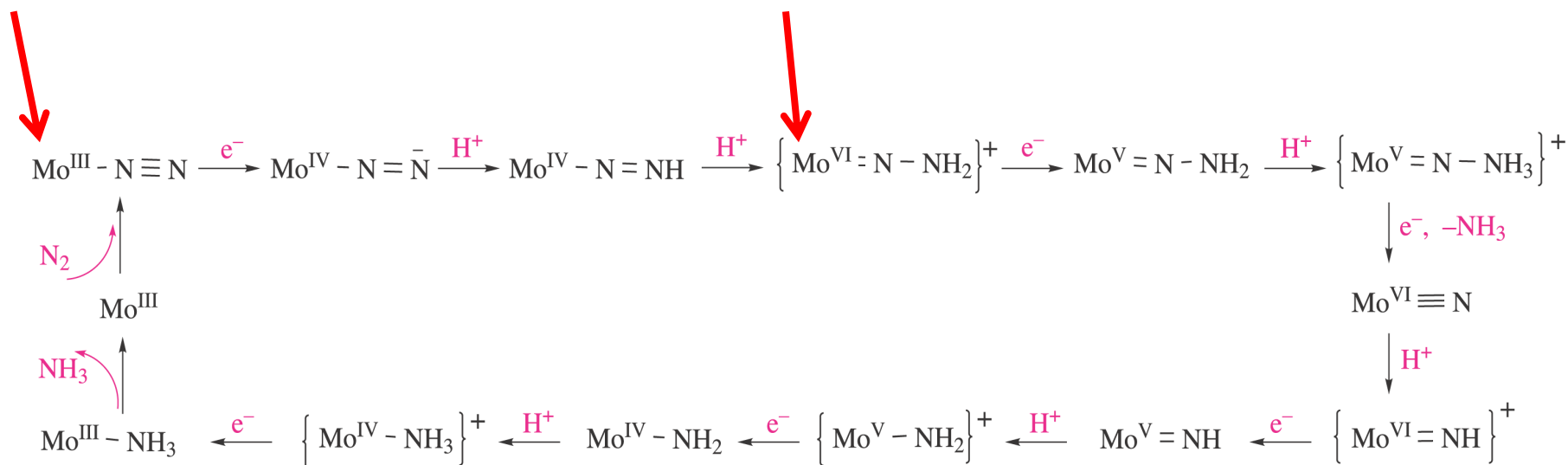
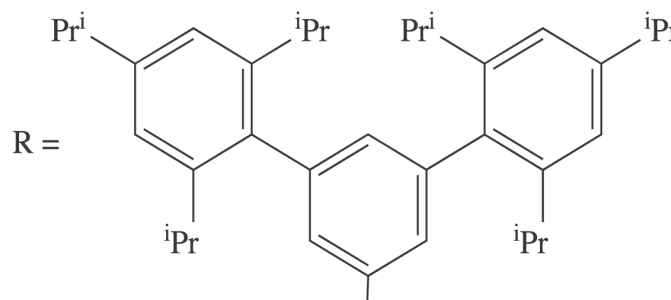
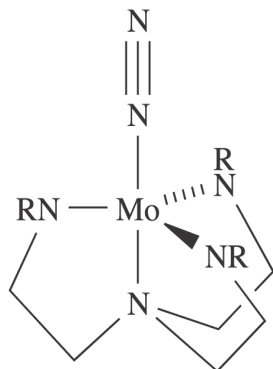
FeMo-co coordina N_2 solo dopo essere stato ridotto con 4 elettroni



Complesso di Schrock
(*Science* 2003)



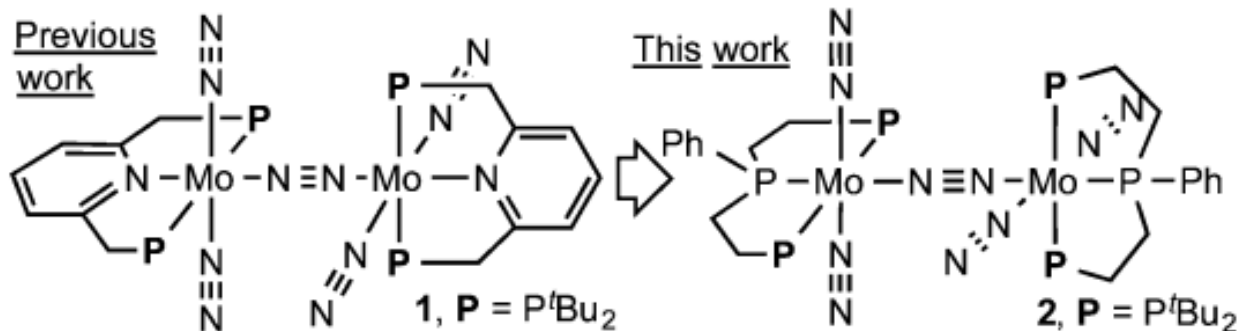
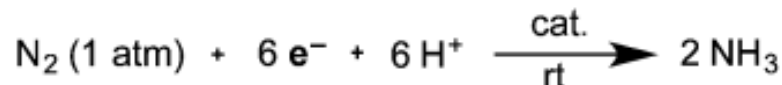
Schema della riduzione catalitica di N_2 a NH_3 su Mo



8 cicli catalitici, meccanismo *distale*

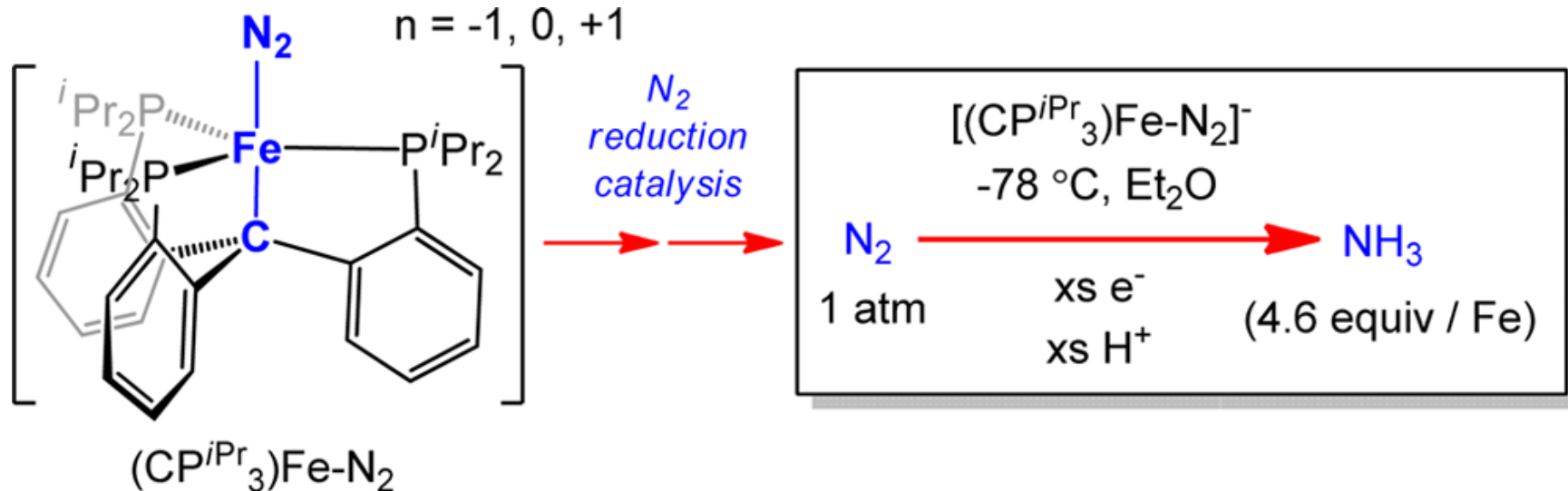
Complessi di Nishibayashi (2011 e 2015)

26 cicli catalitici, riducente CoCp^*_2



Complesso di Peters (2014)

4.6 cicli catalitici, riducente $\text{K}(\text{crown})$



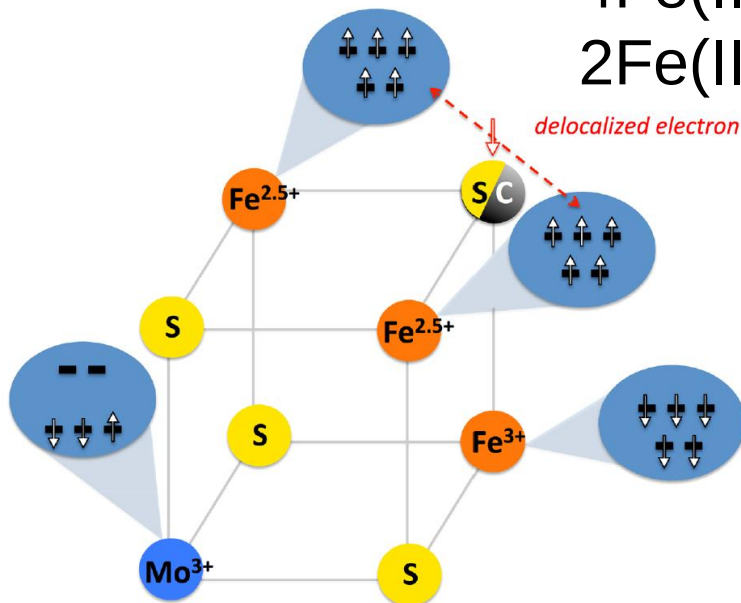
Struttura elettronica di FeMo-co

Resting state: $S = 3/2$

1) $[\text{MoFe}_7\text{S}_9\text{C}]^{3-}$	6Fe(II)1Fe(III)Mo(IV)	
2) $[\text{MoFe}_7\text{S}_9\text{C}]^{1-}$	4Fe(II)3Fe(III)Mo(IV)	Mo(IV), d^2 $S = 0$
3) $[\text{MoFe}_7\text{S}_9\text{C}]^{1+}$	2Fe(II)5Fe(III)Mo(IV)	

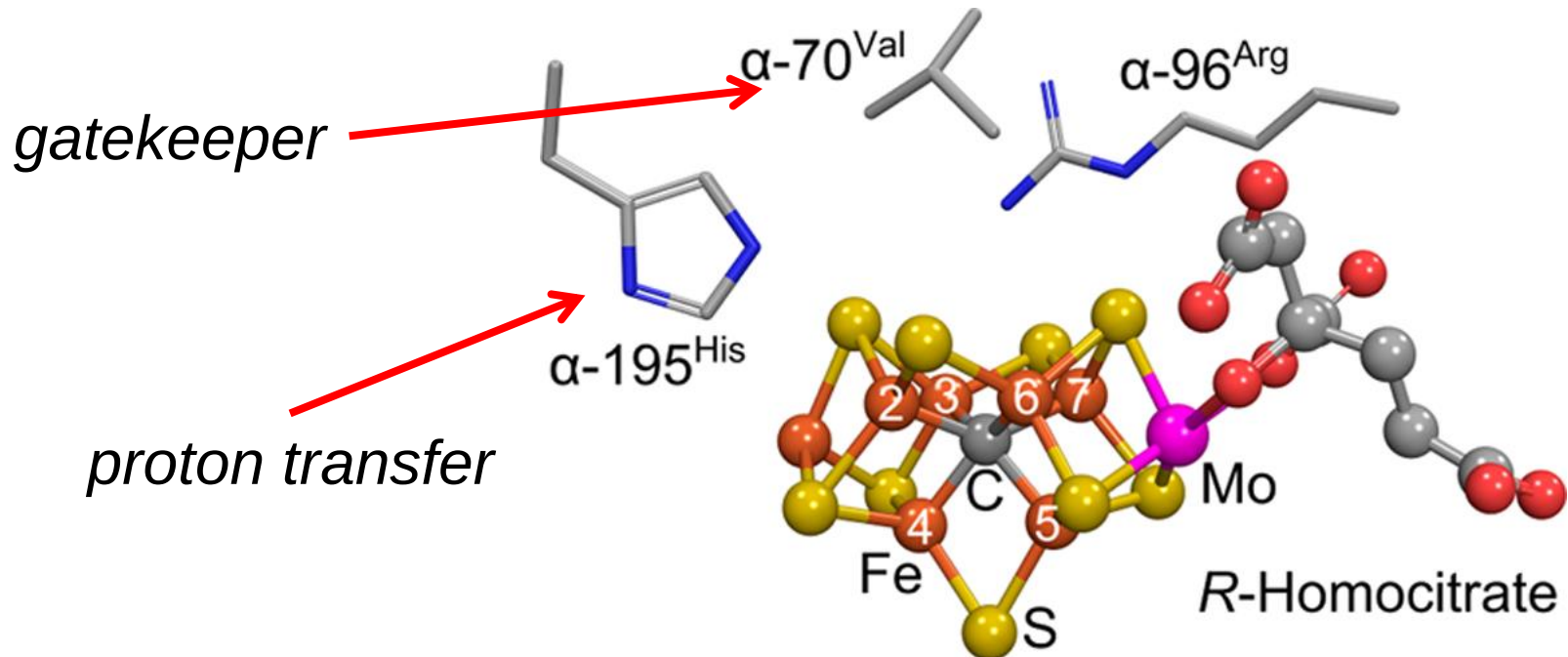
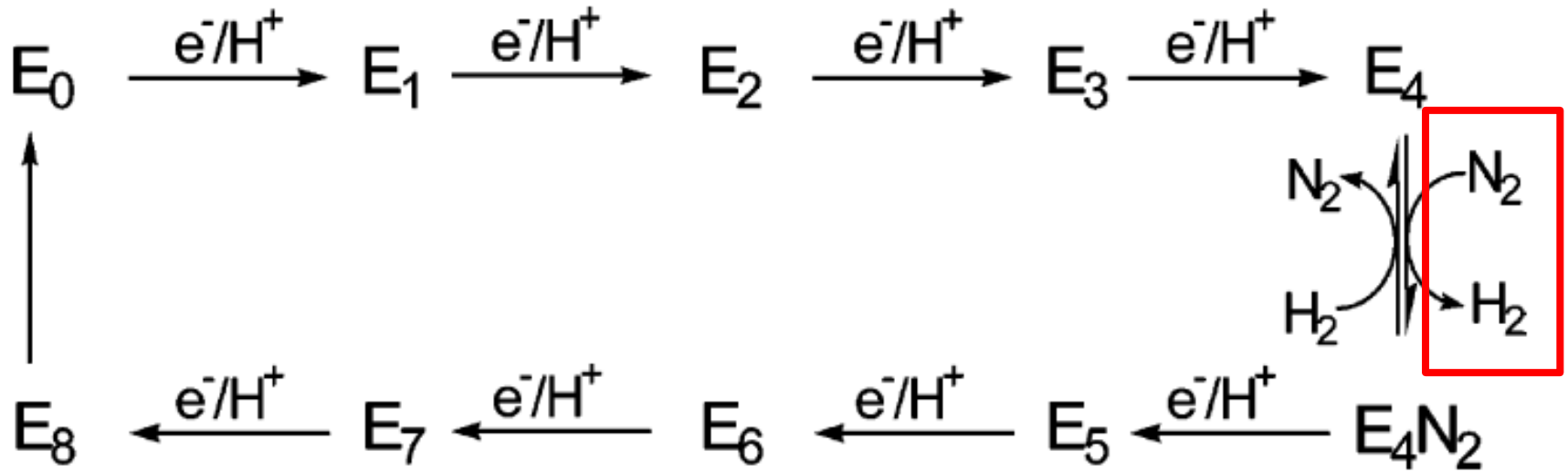
2014: Mo(III), d^3 basso spin ($\uparrow\uparrow\downarrow$)? (violazione della regola di Hund)

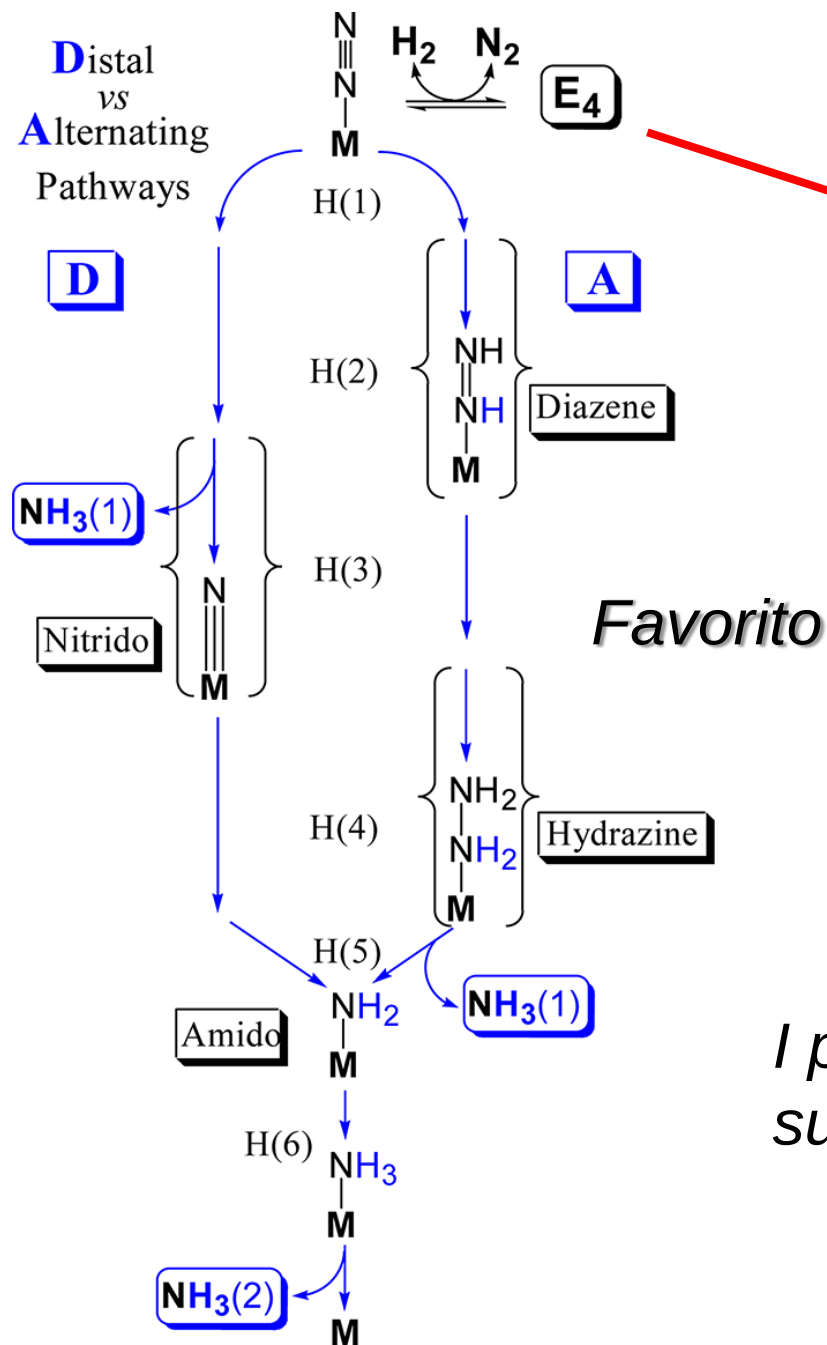
$6\text{Fe(II)}1\text{Fe(III)}\text{Mo(IV)} \rightarrow 5\text{Fe(II)}2\text{Fe(III)}\text{Mo(III)}$
 $4\text{Fe(II)}3\text{Fe(III)}\text{Mo(IV)} \rightarrow 3\text{Fe(II)}4\text{Fe(III)}\text{Mo(III)}$
 $2\text{Fe(II)}5\text{Fe(III)}\text{Mo(IV)} \rightarrow 1\text{Fe(II)}6\text{Fe(III)}\text{Mo(III)}$



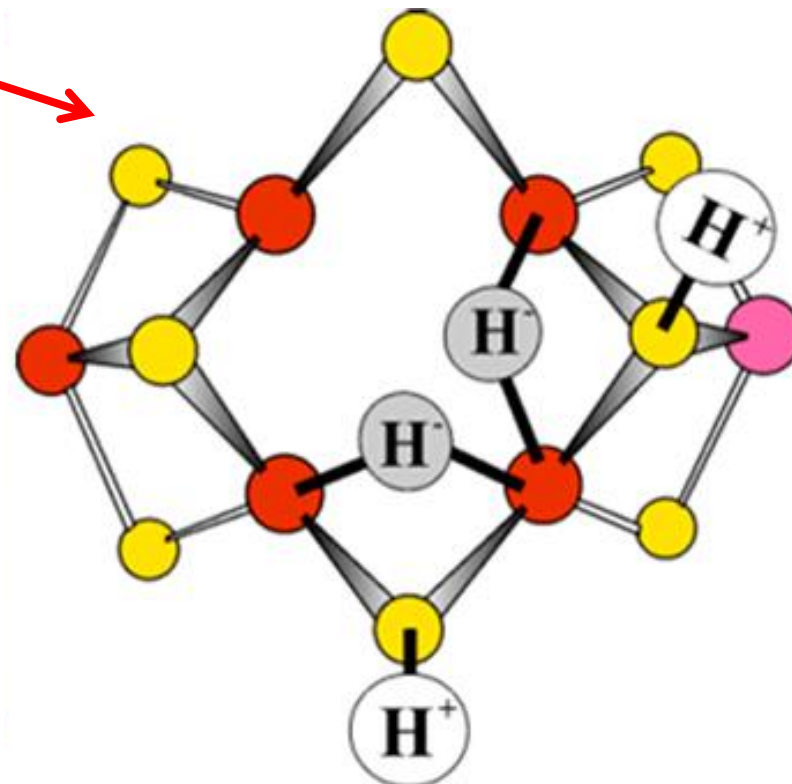
Cluster modello $[\text{MoFe}_3\text{S}_3\text{C}]^{1+}$ e $[\text{MoFe}_3\text{S}_4]^{3+}$

Ciclo catalitico

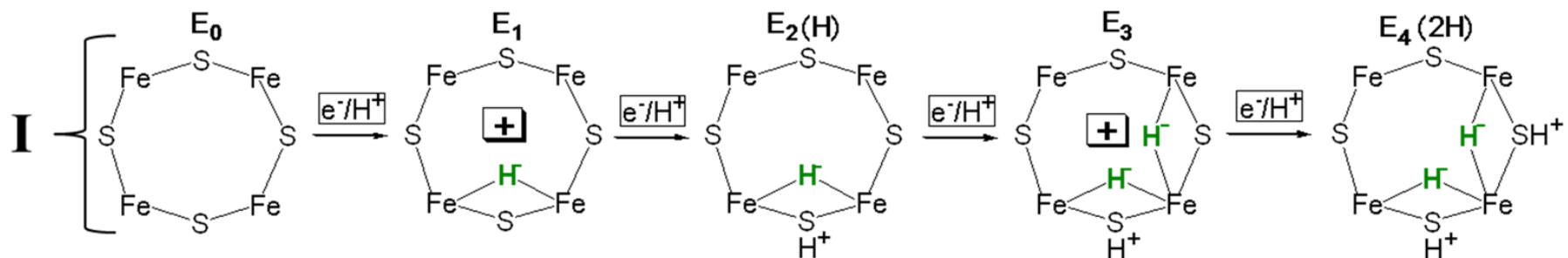




Modello di E₄

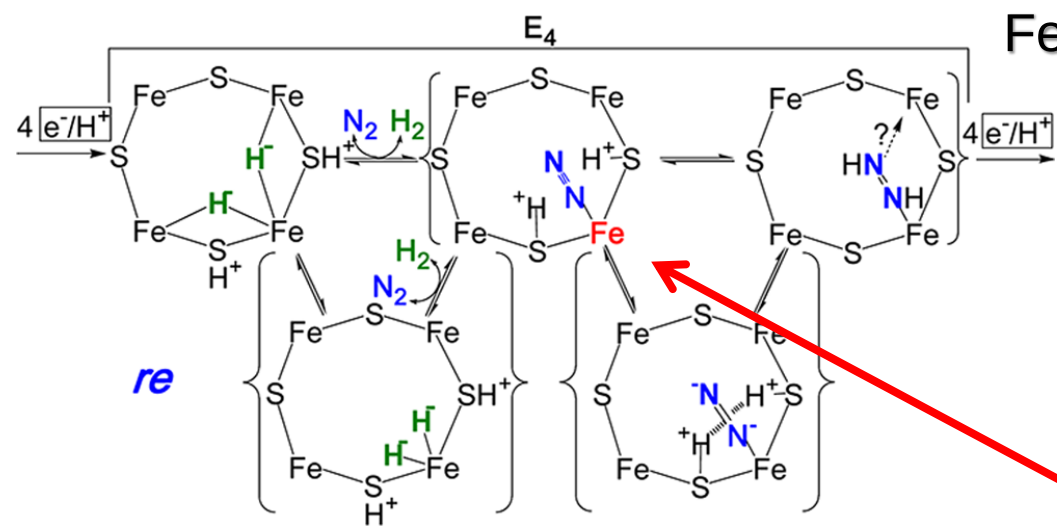


*I primi 4 elettroni si accumulano
sugli idruri e non sugli atomi di ferro*

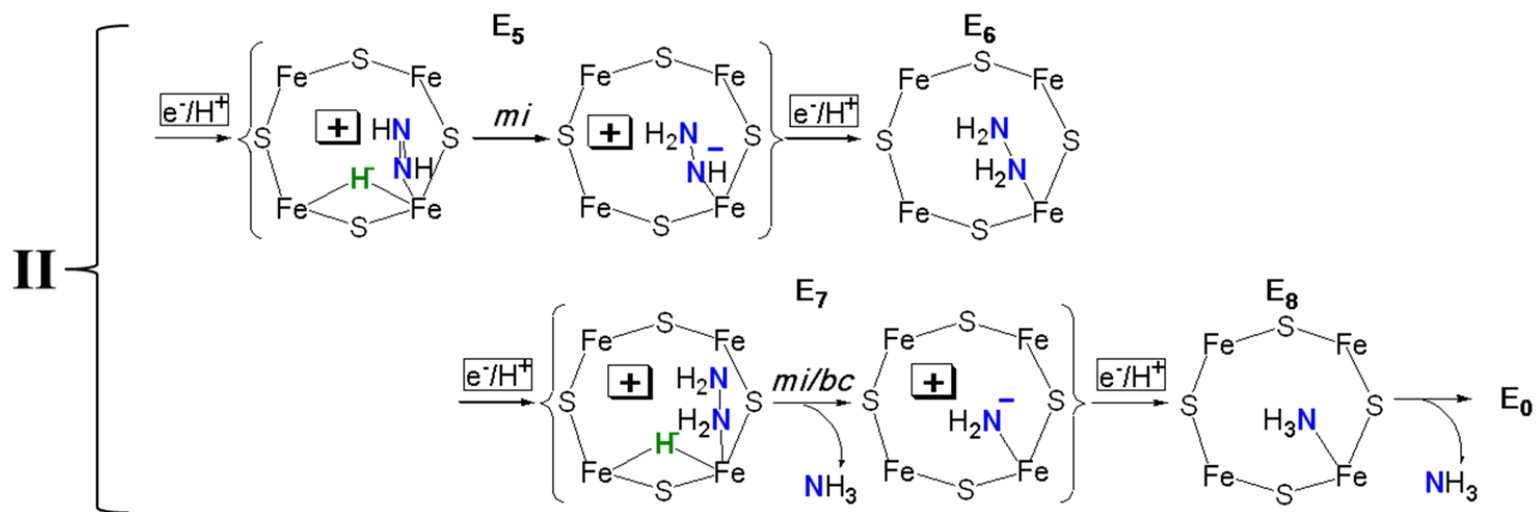


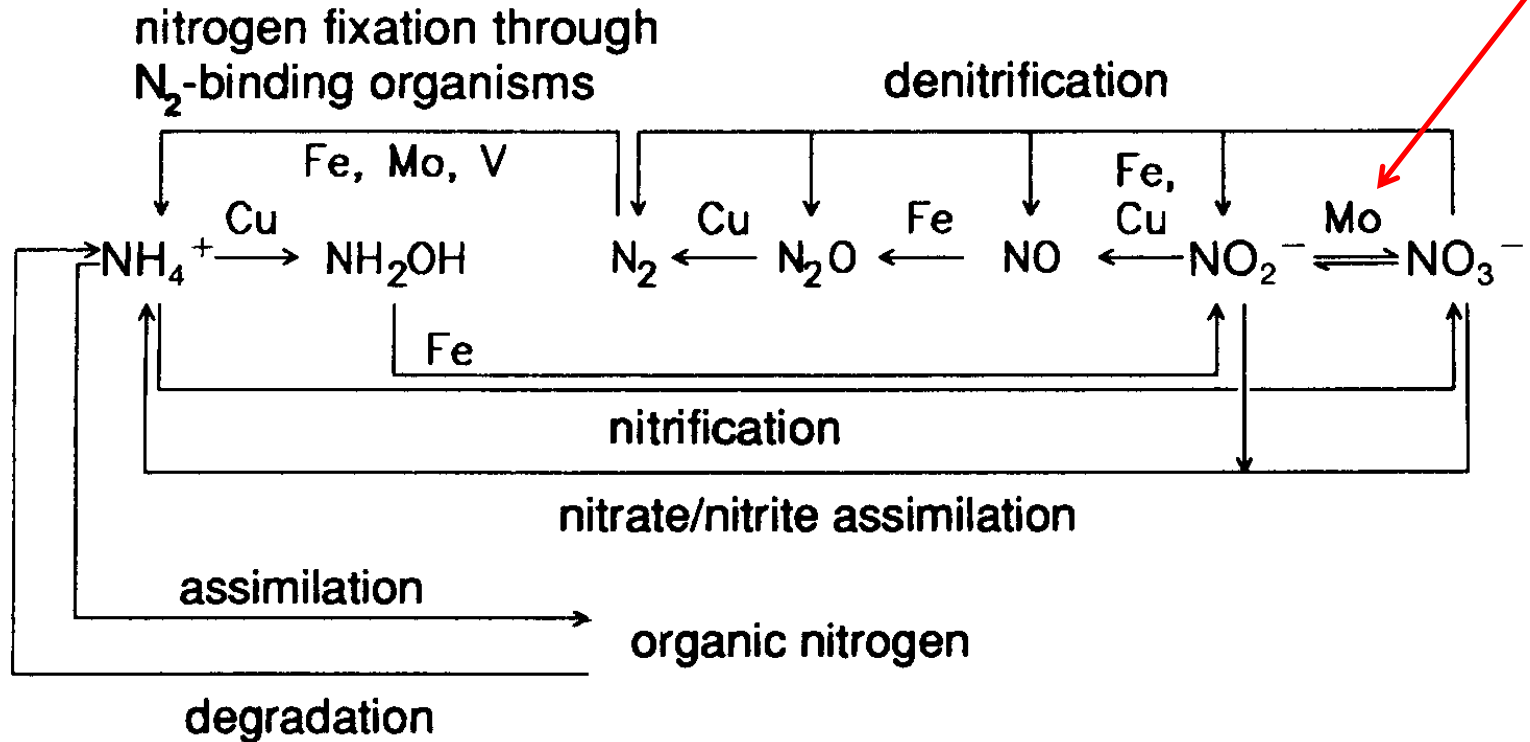
FeMoco attivato

Nel ciclo catalitico il FeMoco cambia di una sola unità il suo stato di ossidazione complessivo (E_n dispari)



$Fe(0)?$

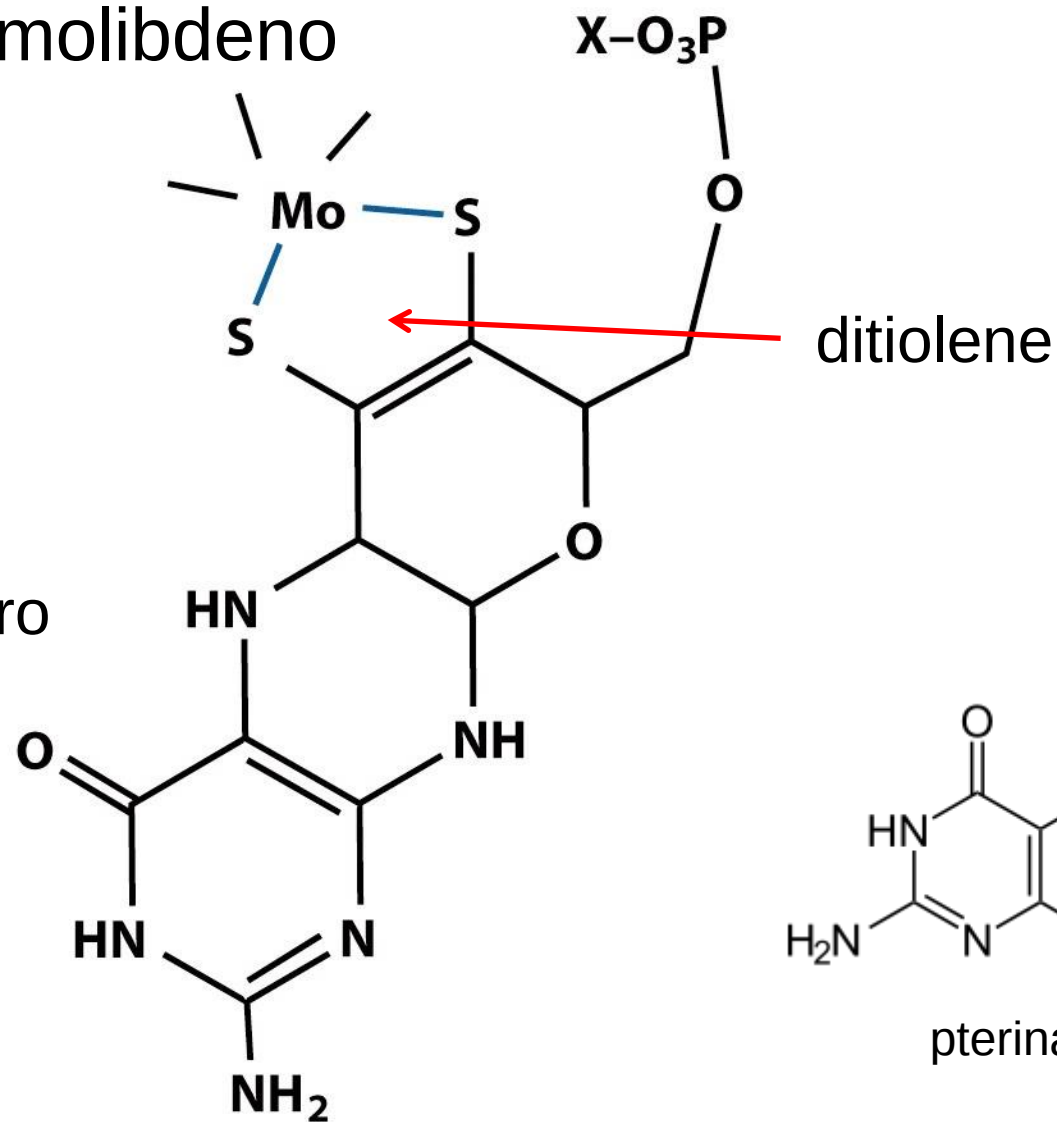




Tre famiglie di enzimi al Mo (*osso-trasferasi*)

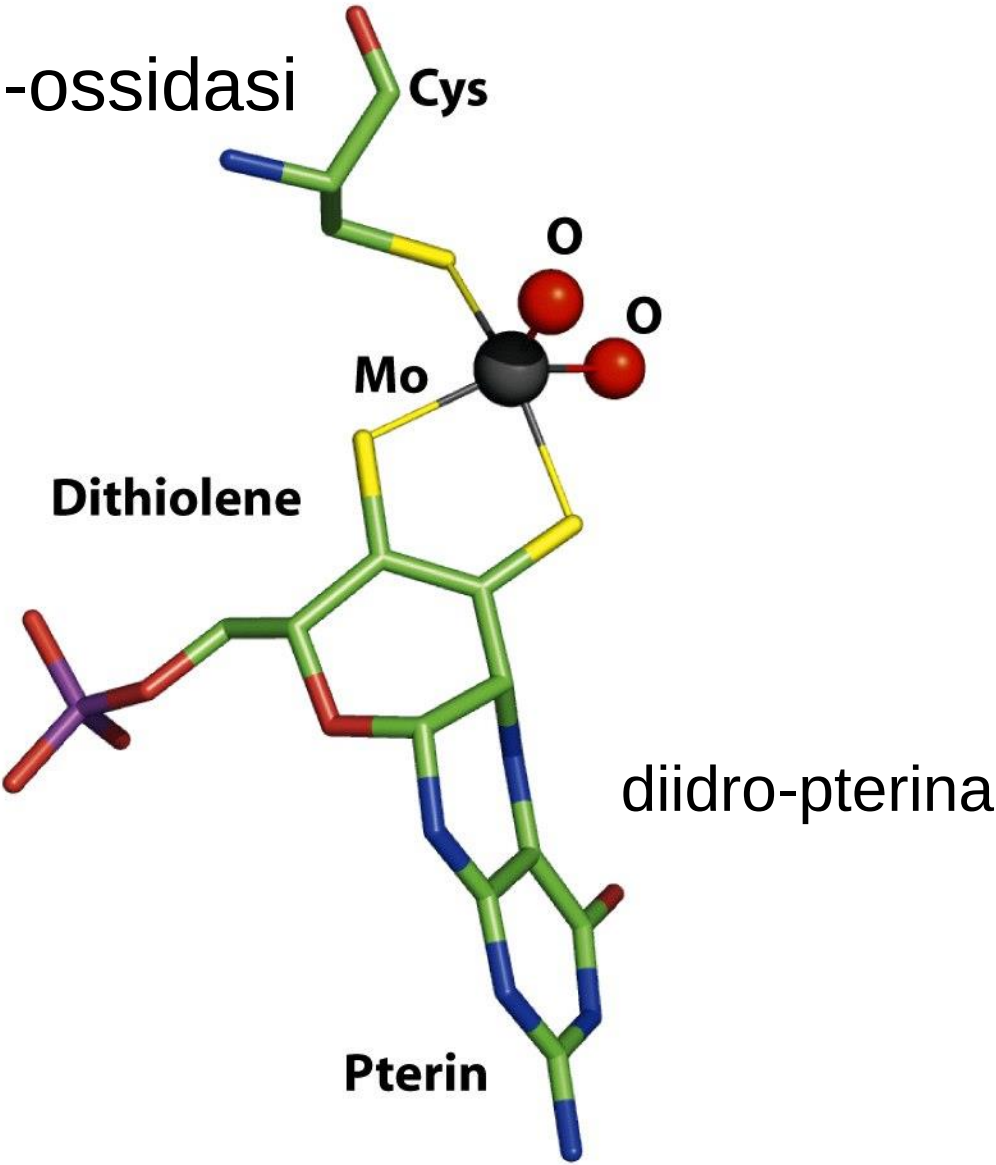
- xantina-ossidasi
- solfito-ossidasi
- DMSO-riduttasi

Cofattore del molibdeno



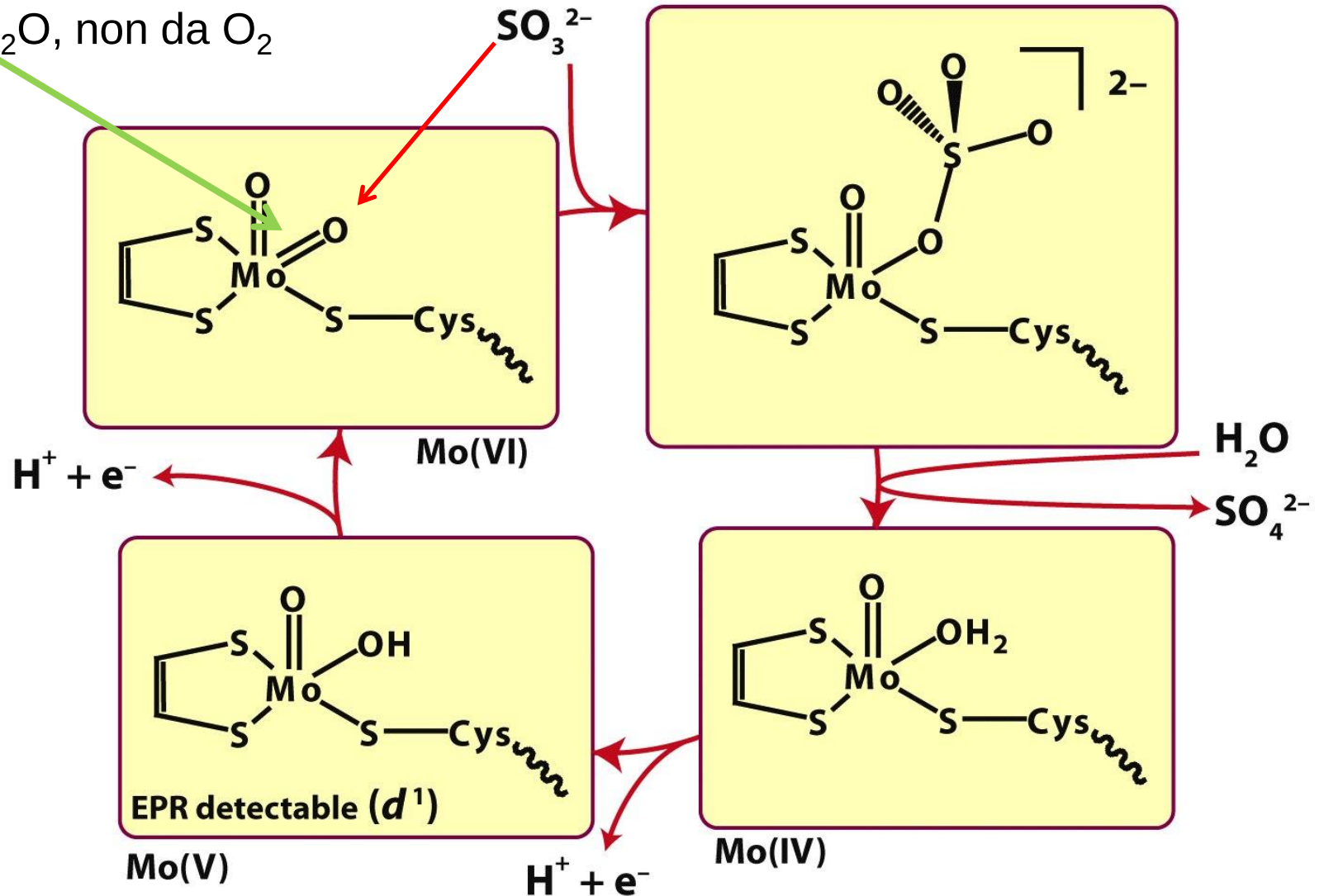
Molybdopterin as ligand

Sito della solfito-ossidasi



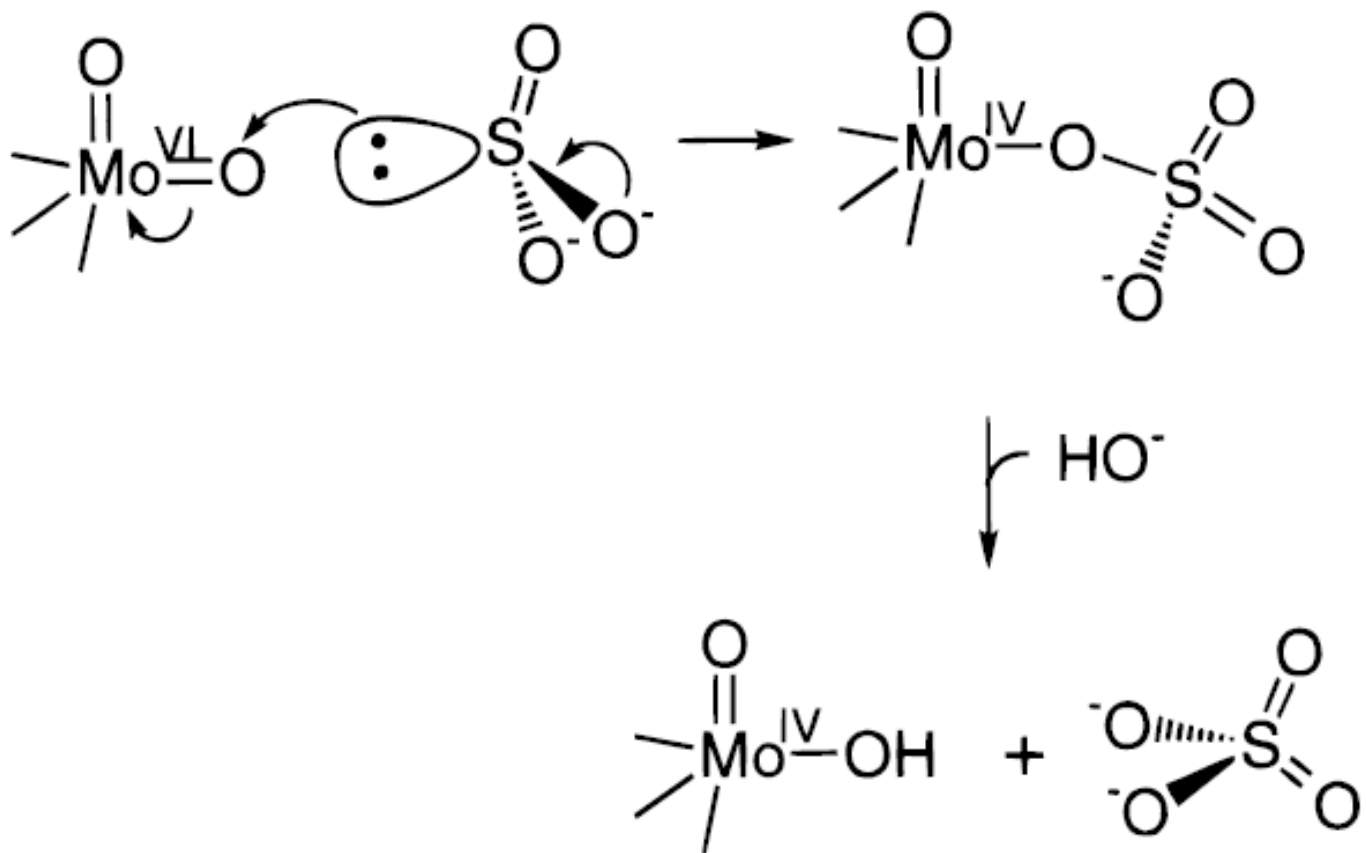
Ciclo catalitico della solfito-ossidasi

O da H₂O, non da O₂

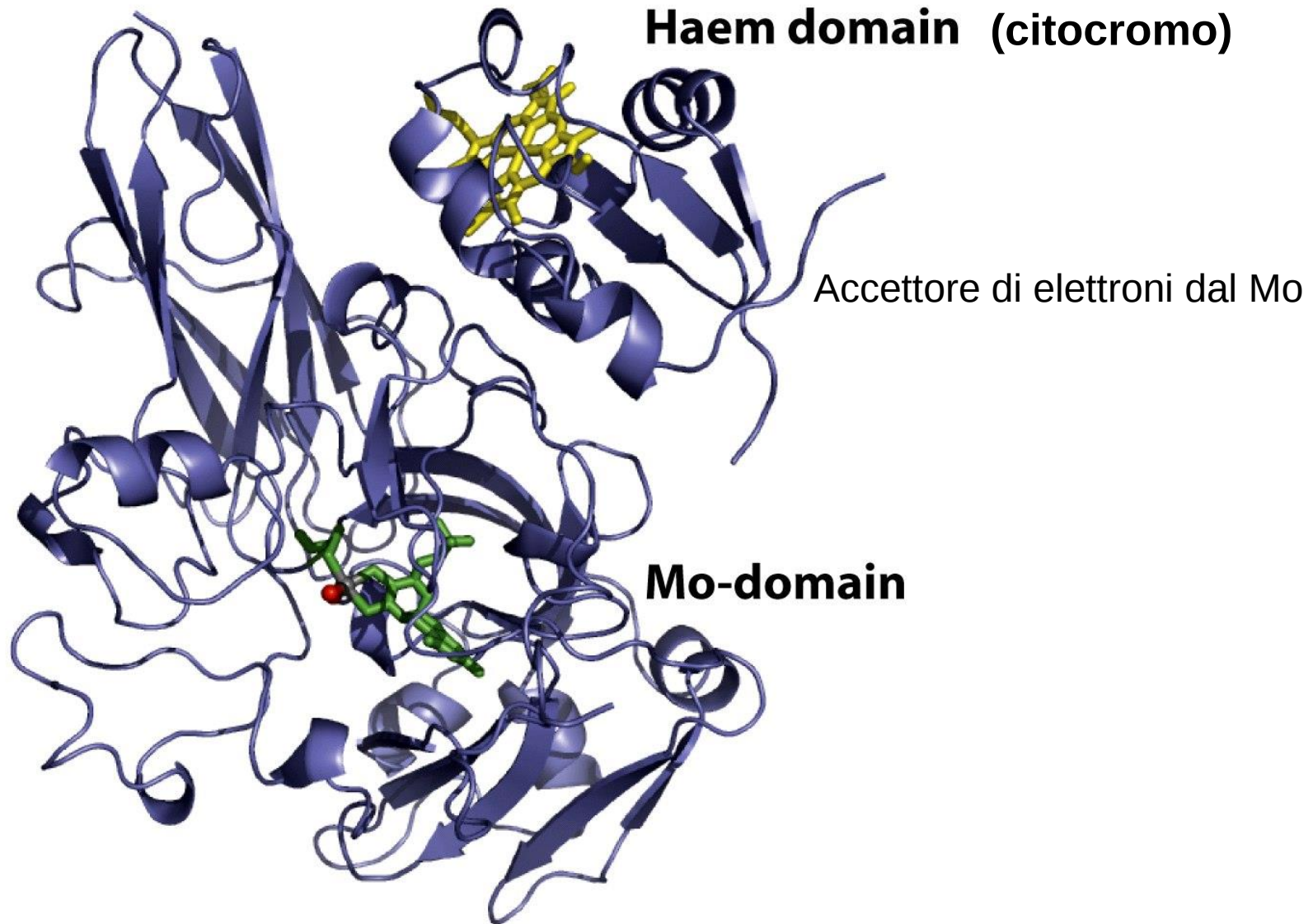


Mo possiede tre stati di ossidazione stabili, Mo(IV), Mo(V) e Mo(VI)

Dettaglio del meccanismo di trasferimento di ossigeno



Struttura della solfito-ossidasi



Scala di entalpia delle reazioni di trasferimento di atomi di ossigeno

