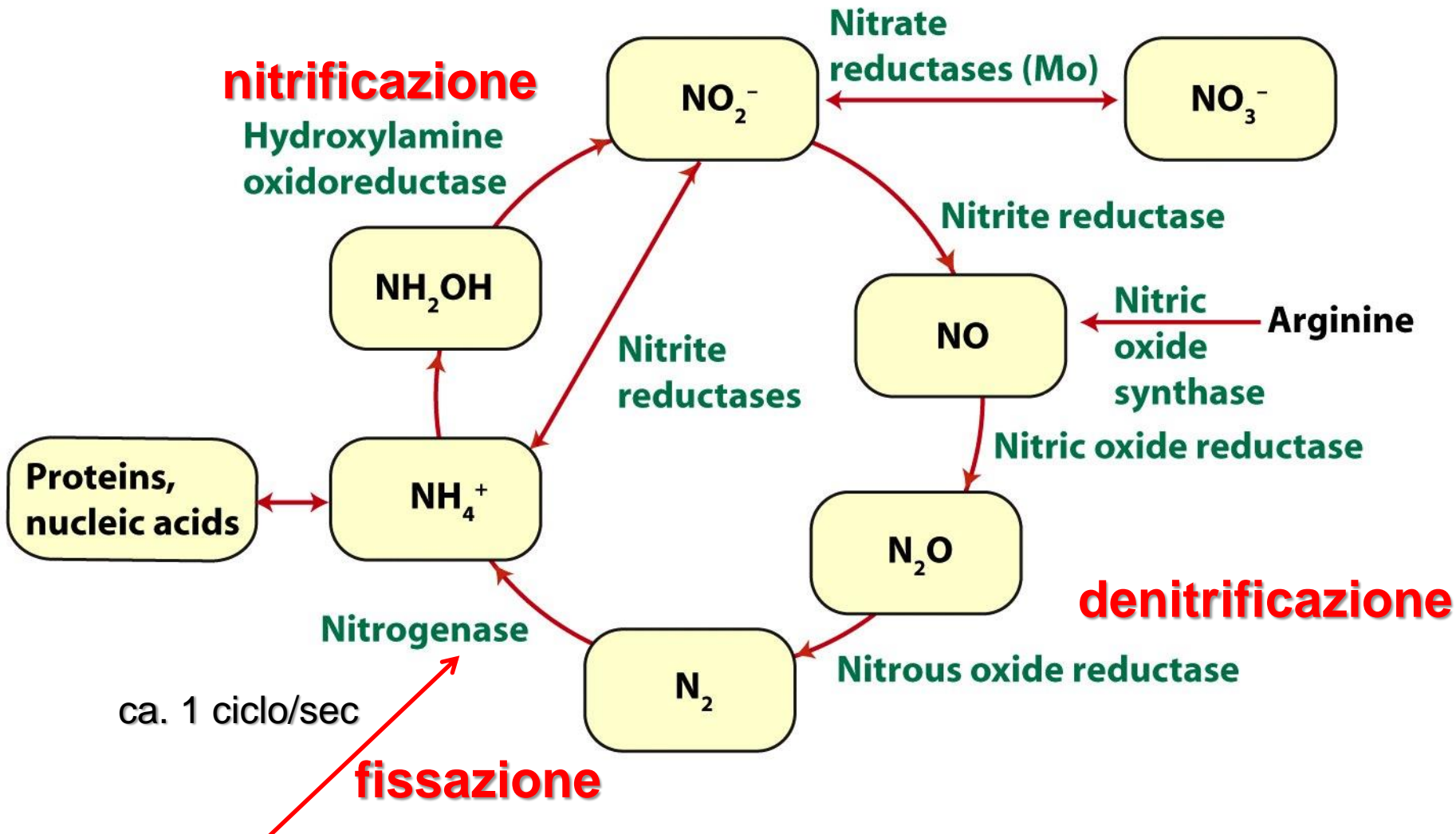


Metalli di inizio serie

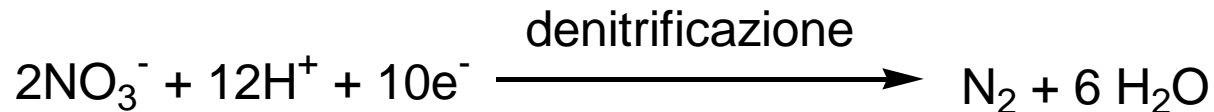
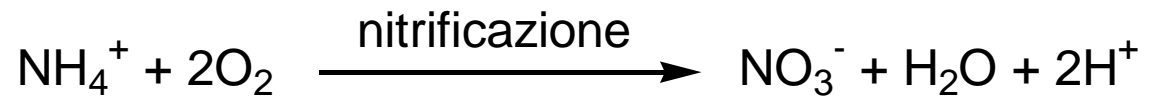
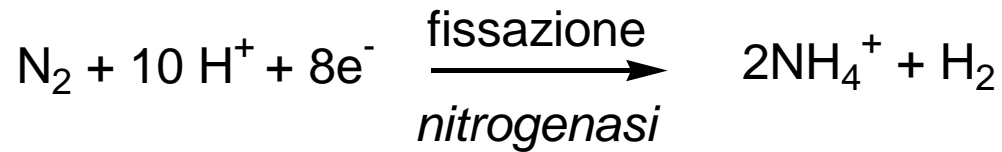
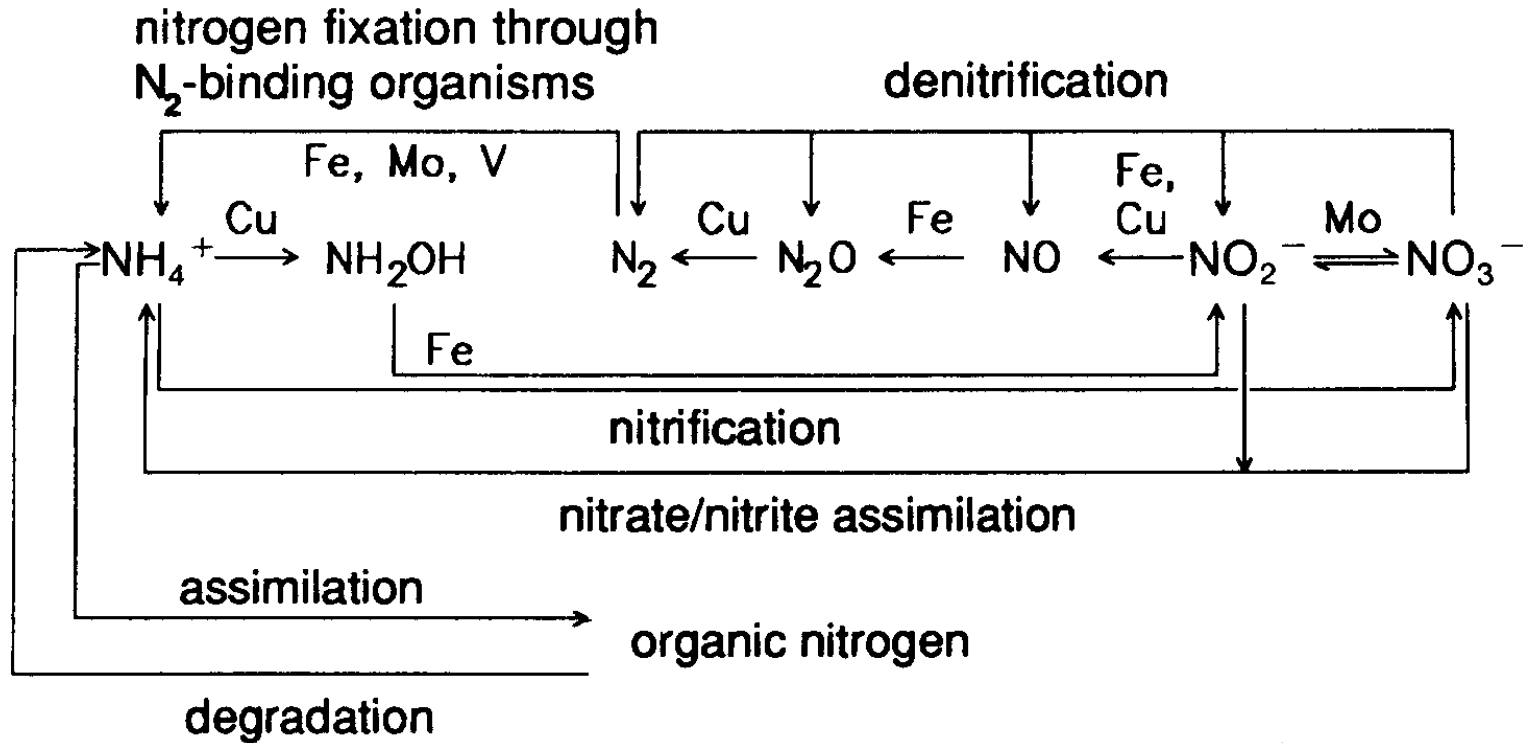


Il molibdeno è l'unico elemento del secondo periodo di transizione (4d) ad avere una funzione biologica

Ciclo dell'azoto



Batteri procarioti diazotropici (leguminose): 10⁸ ton N₂/y

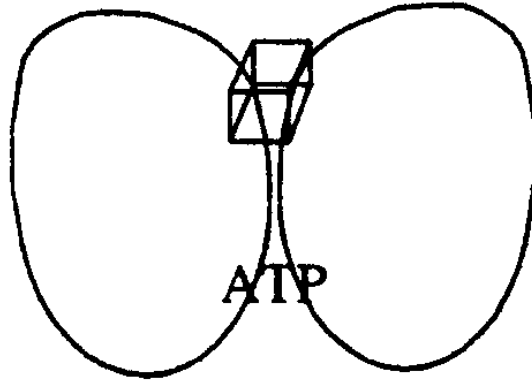


Nitrogenasi



1992

ca. 1 ciclo/sec

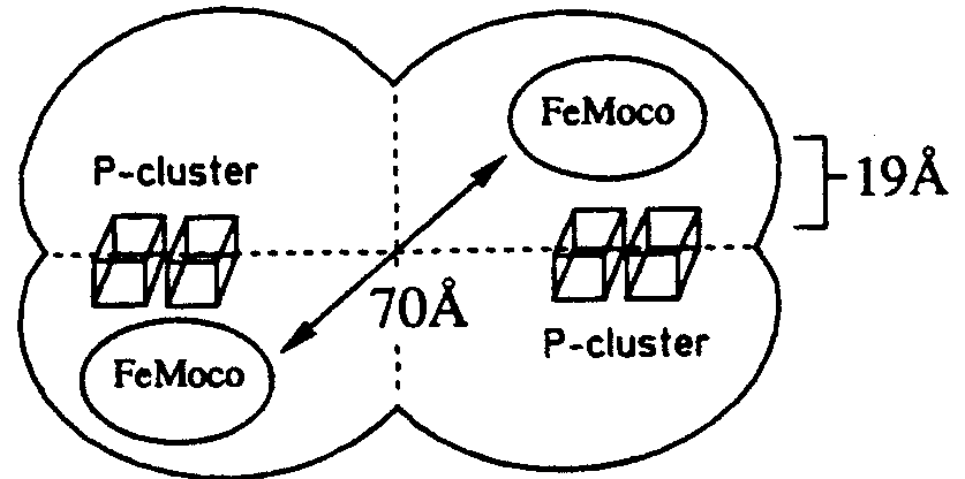


Fe protein

γ_2

60 kDa

+



FeMo protein

$\alpha_2\beta_2$

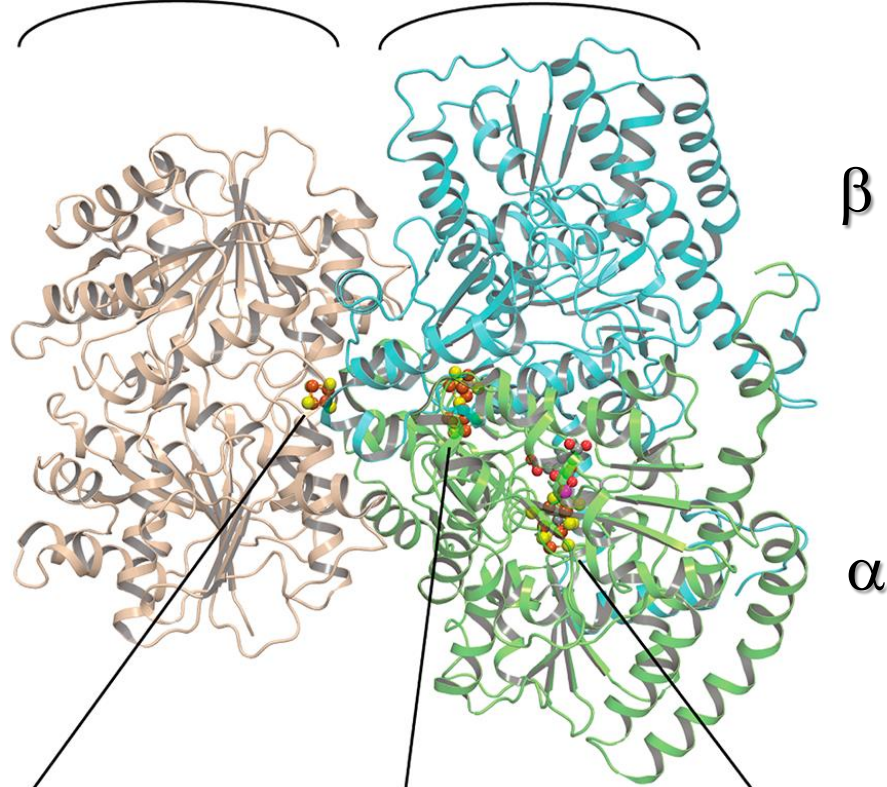
220 kDa

Nitrogenasi

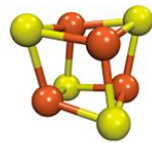
Fe protein

MoFe protein

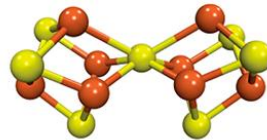
(A)



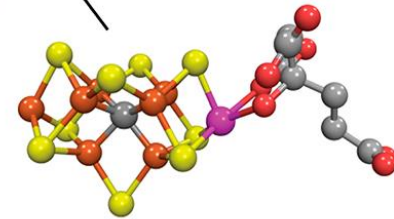
(B)



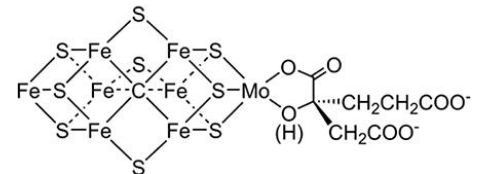
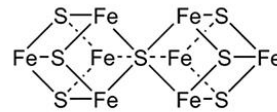
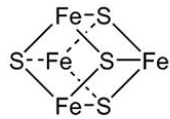
F cluster



P cluster

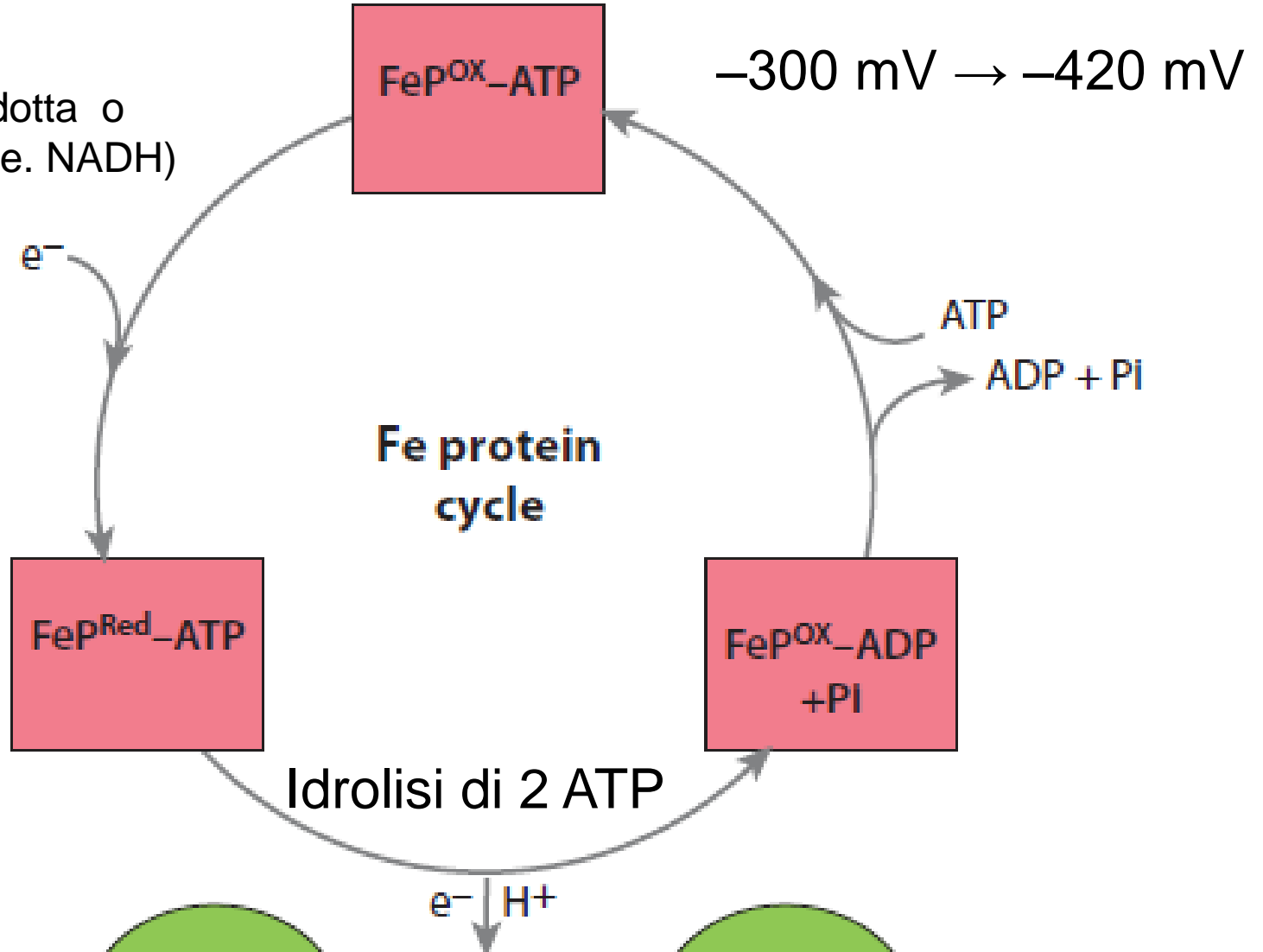


M cluster (FeMoco)

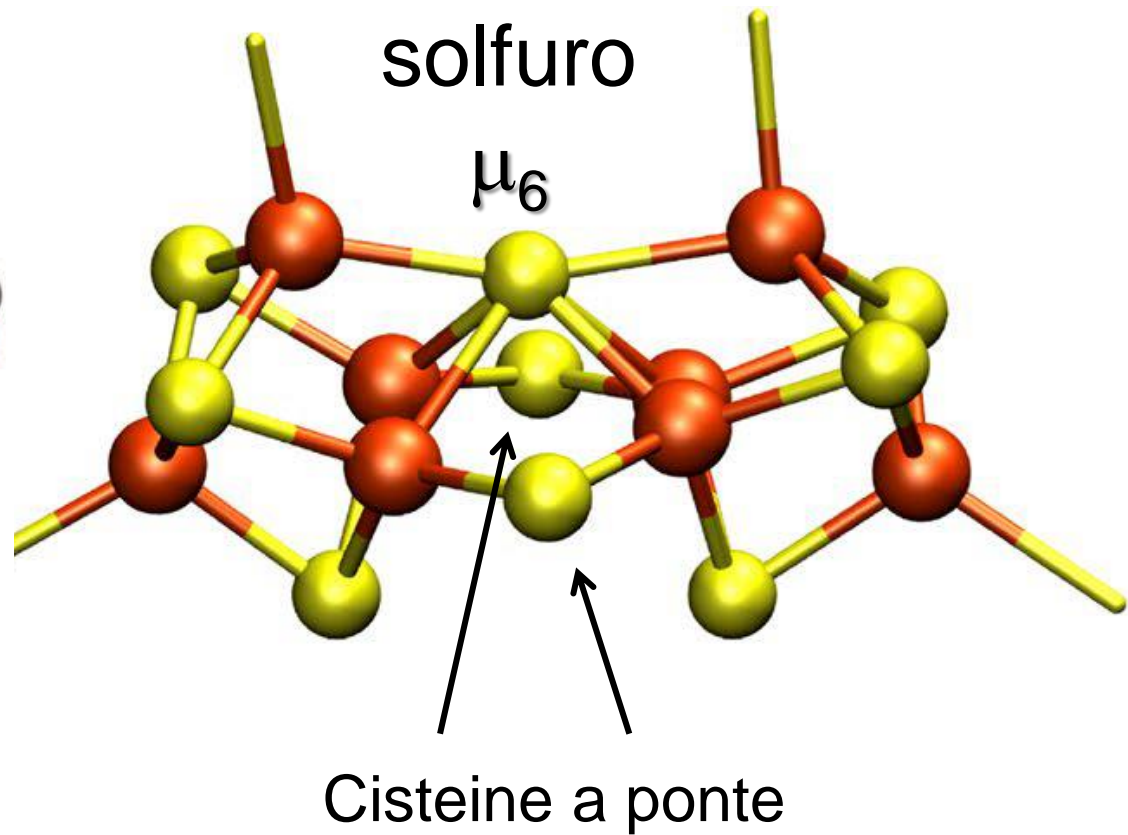
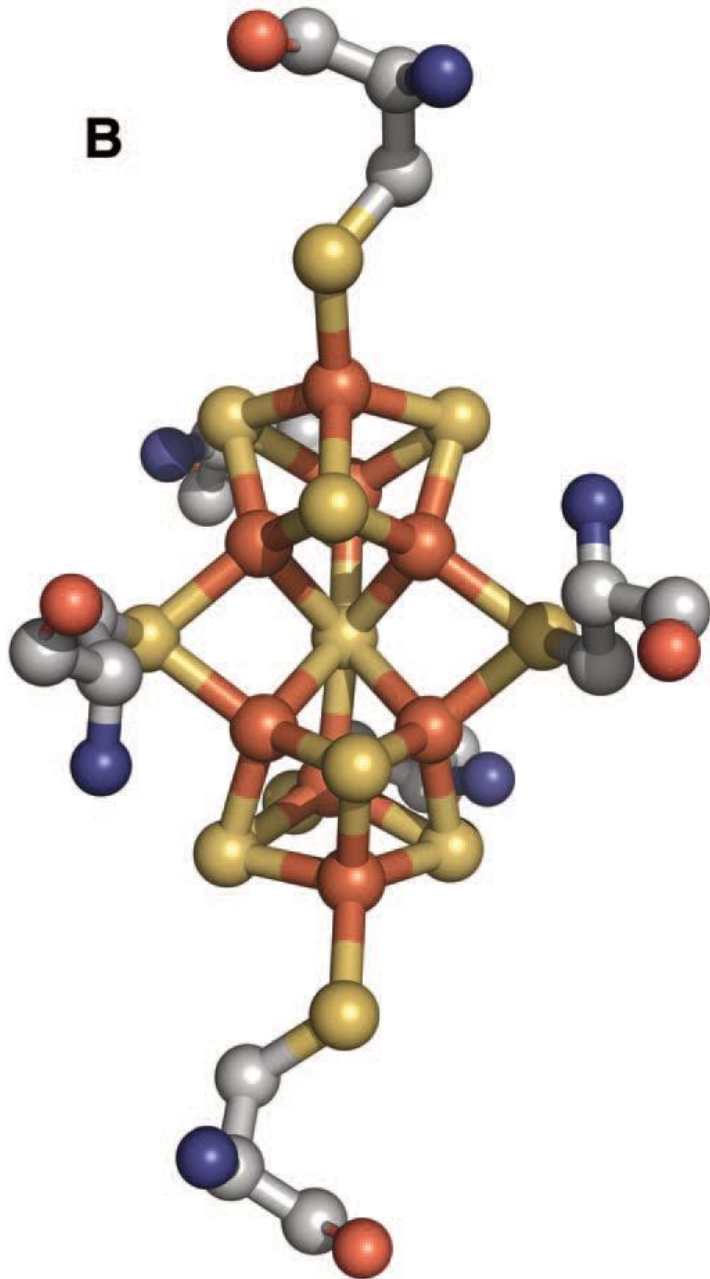


Fe-proteina

Ferridossina ridotta o flavodossina (i.e. NADH)

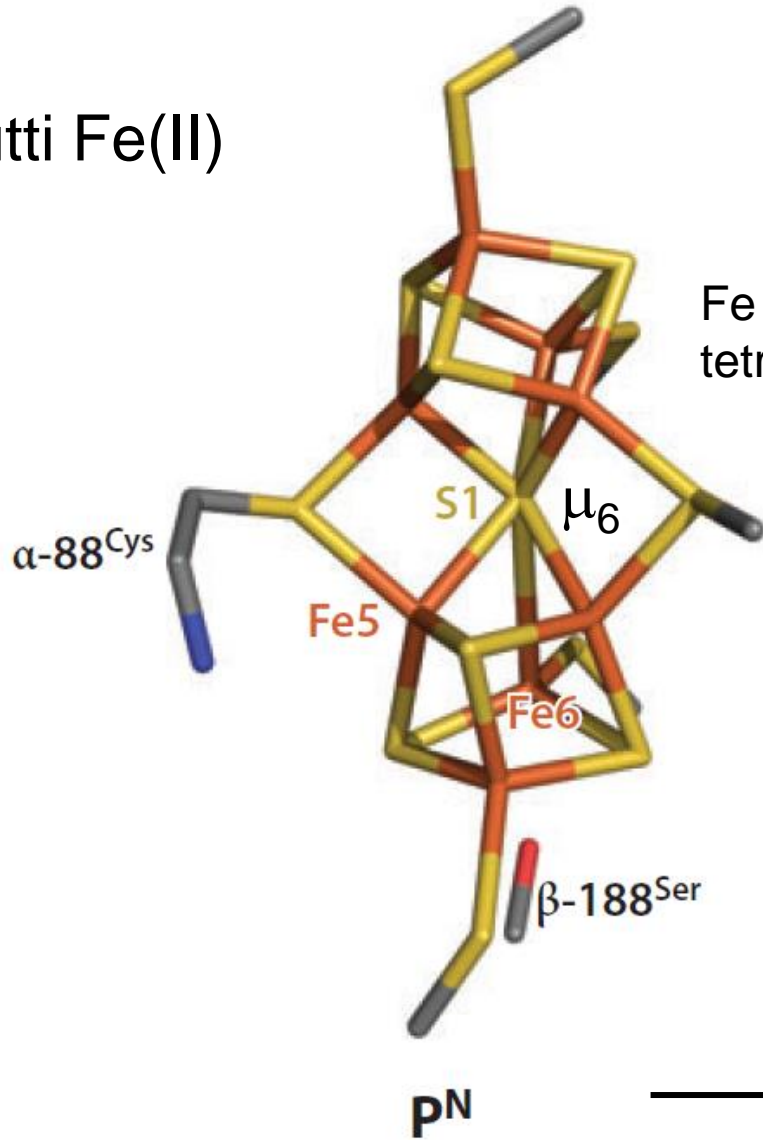


P-cluster 8Fe-7S



P-cluster 8Fe-7S

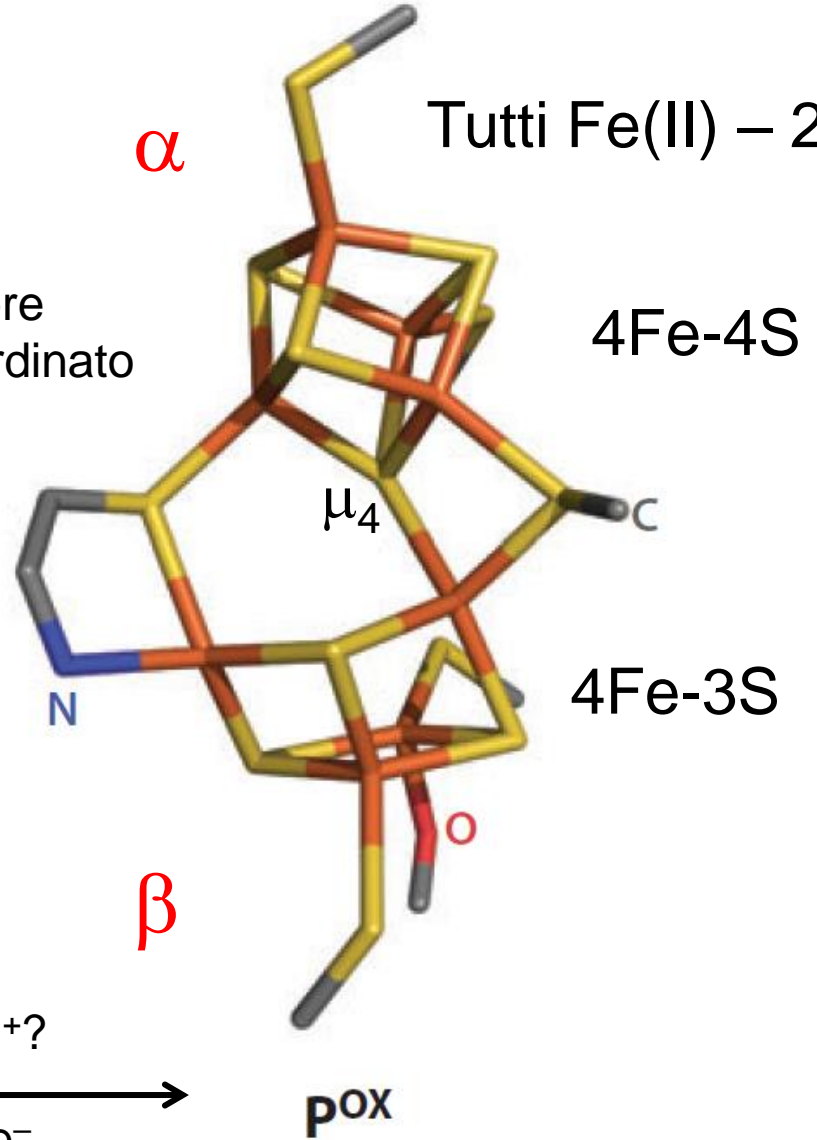
Tutti Fe(II)



Fe sempre
tetracoordinato

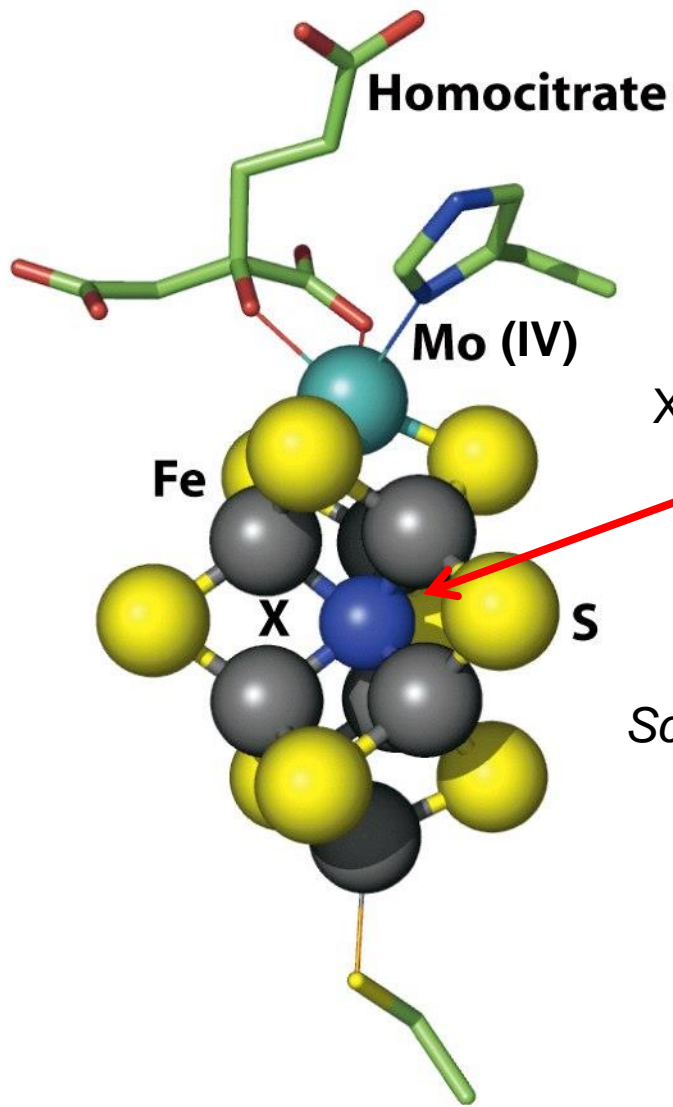
α

Tutti Fe(II) – 2e⁻



-2H⁺?

-2e⁻



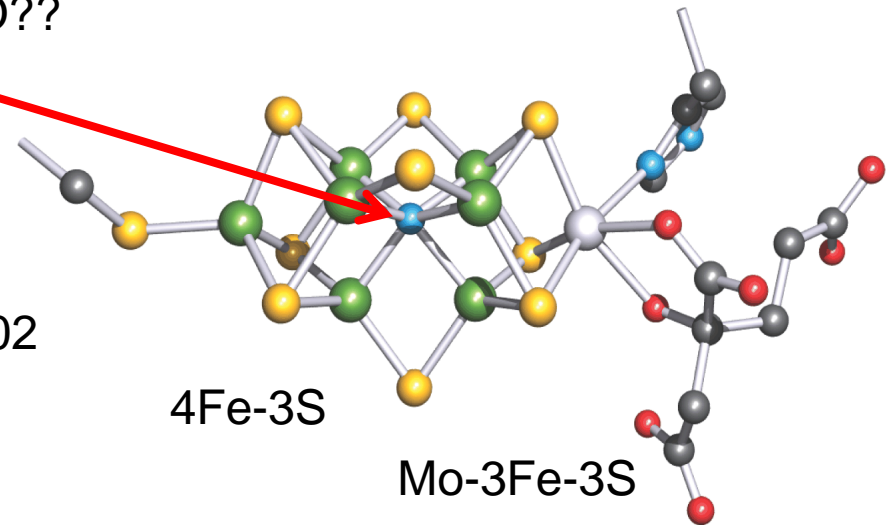
Nitrogenase FeMoCo

Cofattore FeMo

7Fe-9S-Mo-omocitrato

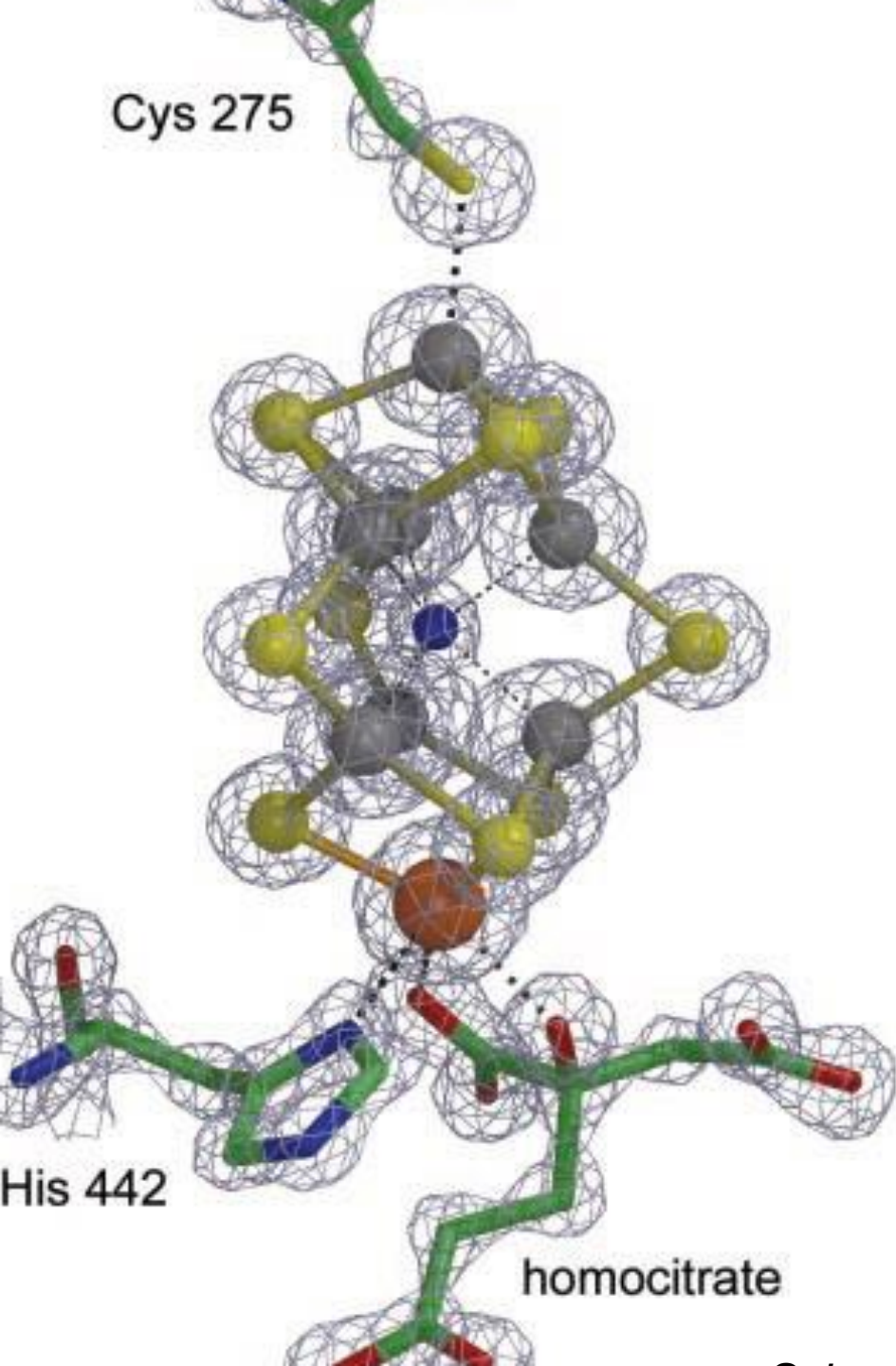
X = C, N, O??

Science, 2002

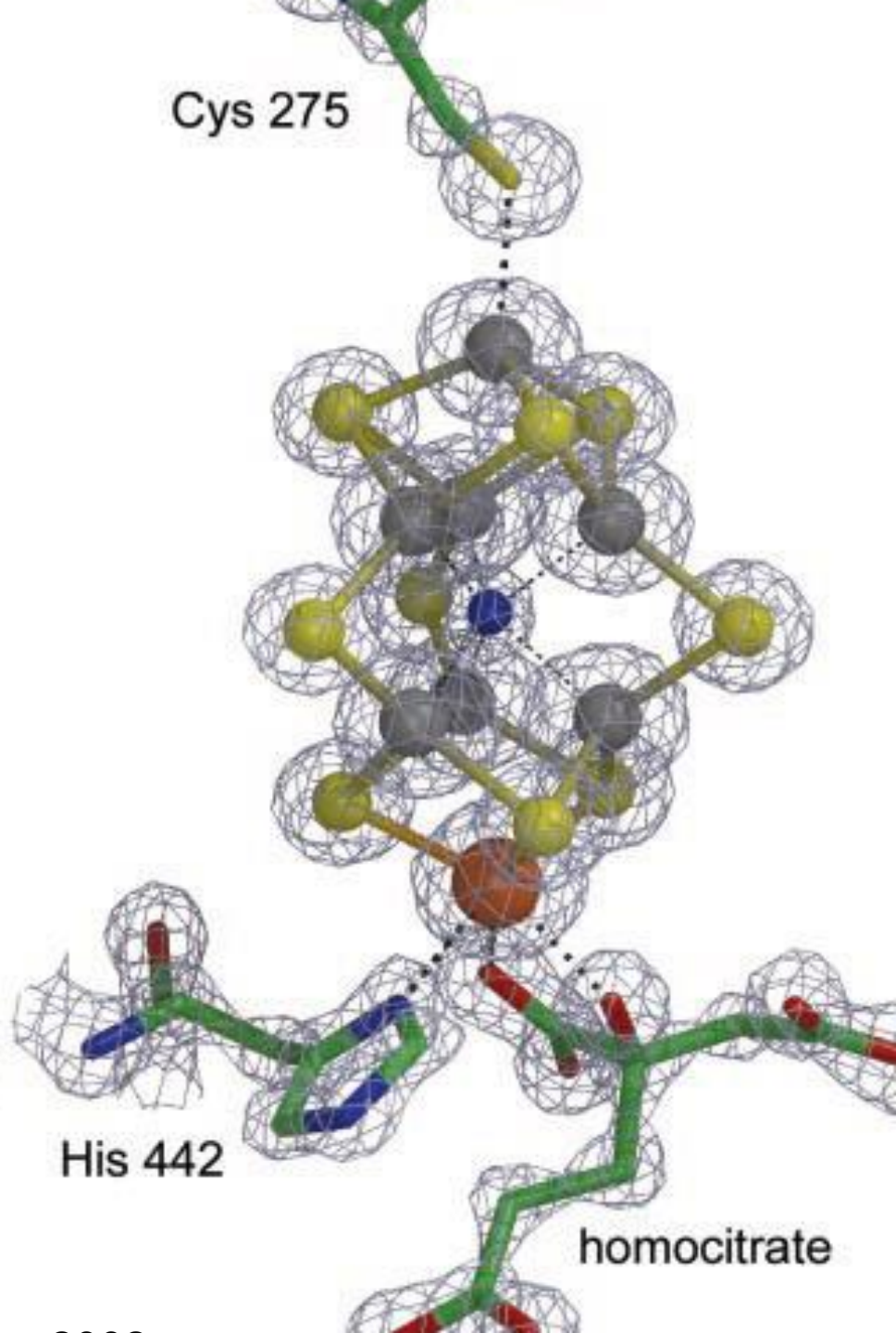


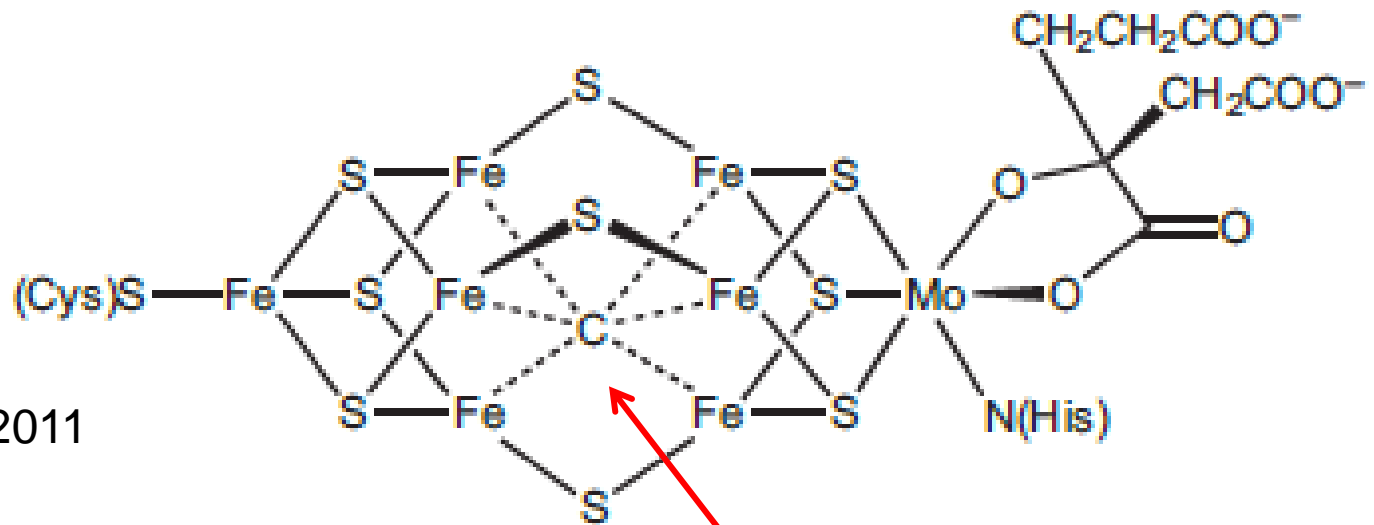
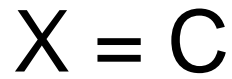
Tutto in α

Cys 275



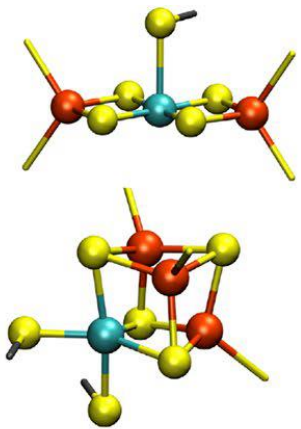
Cys 275





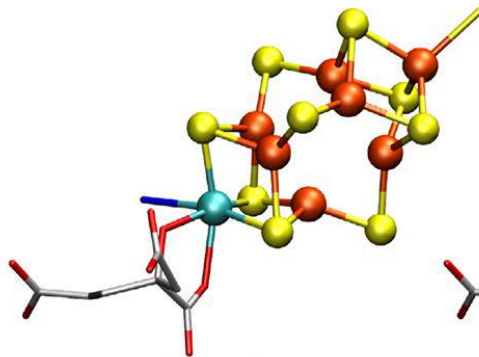
Science, 2011

Carburo, C⁴⁻



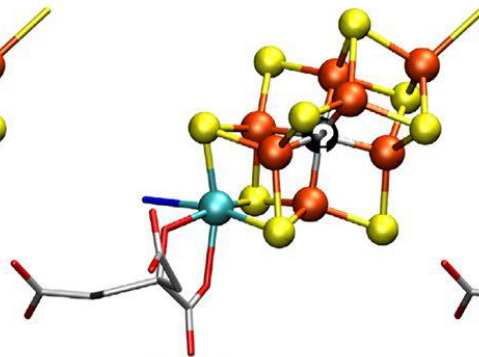
1978

First structural models from EXAFS



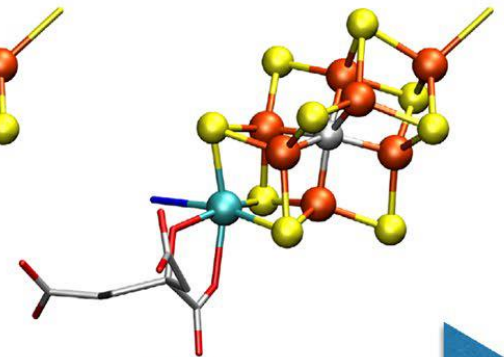
1992

First crystal structure (2.7Å)



2002

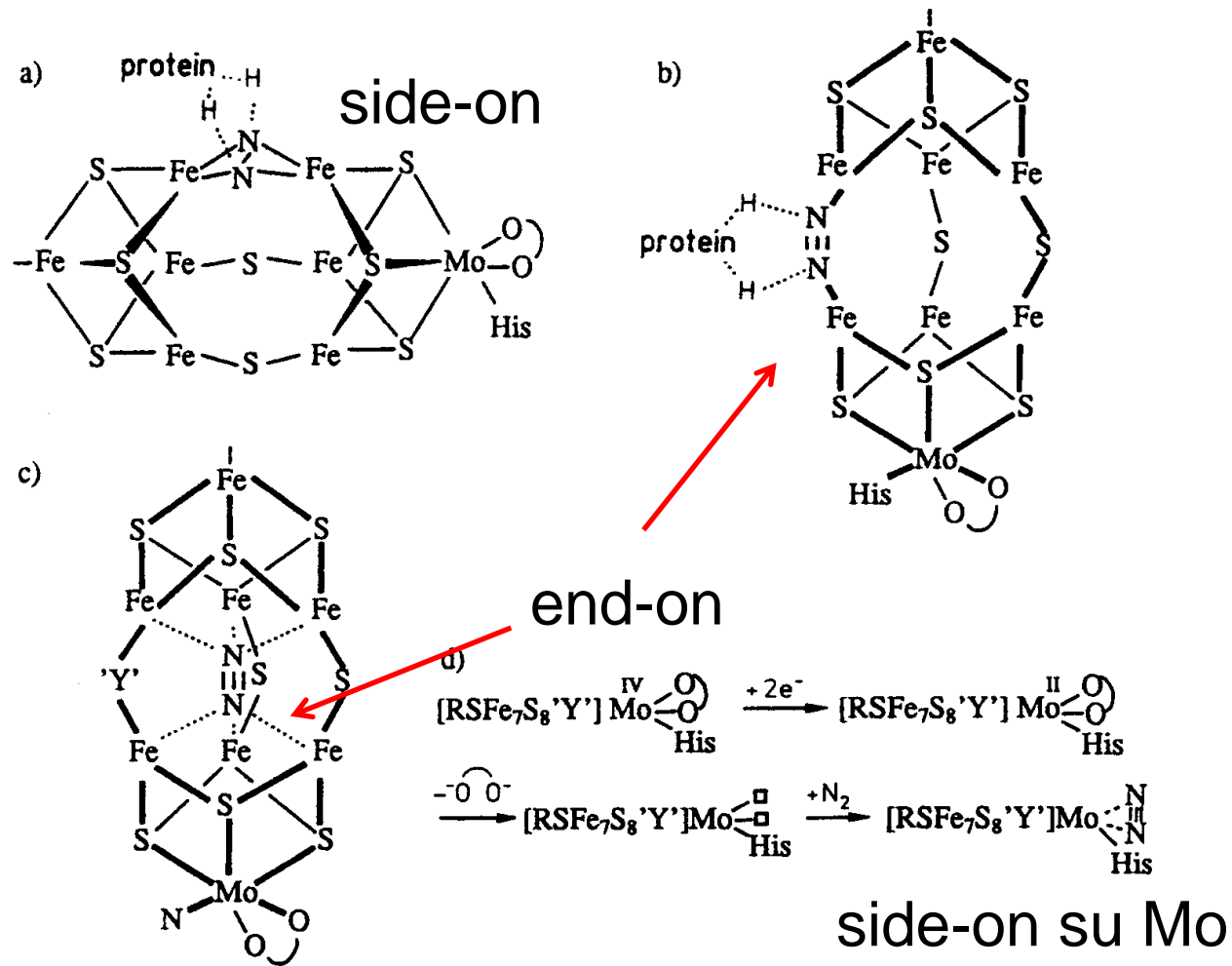
Discovery of interstitial atom



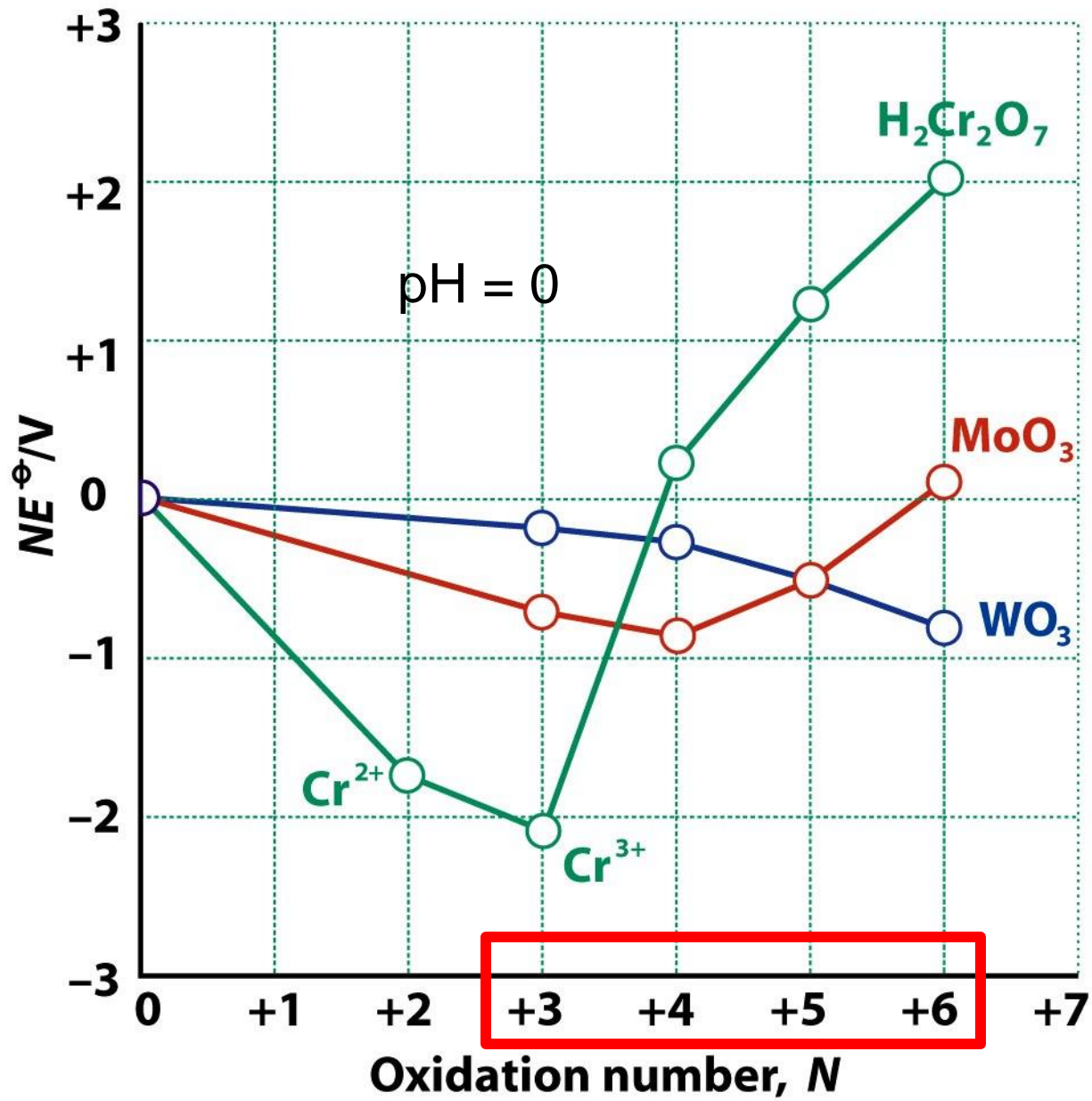
2011

Interstitial atom identified as carbon

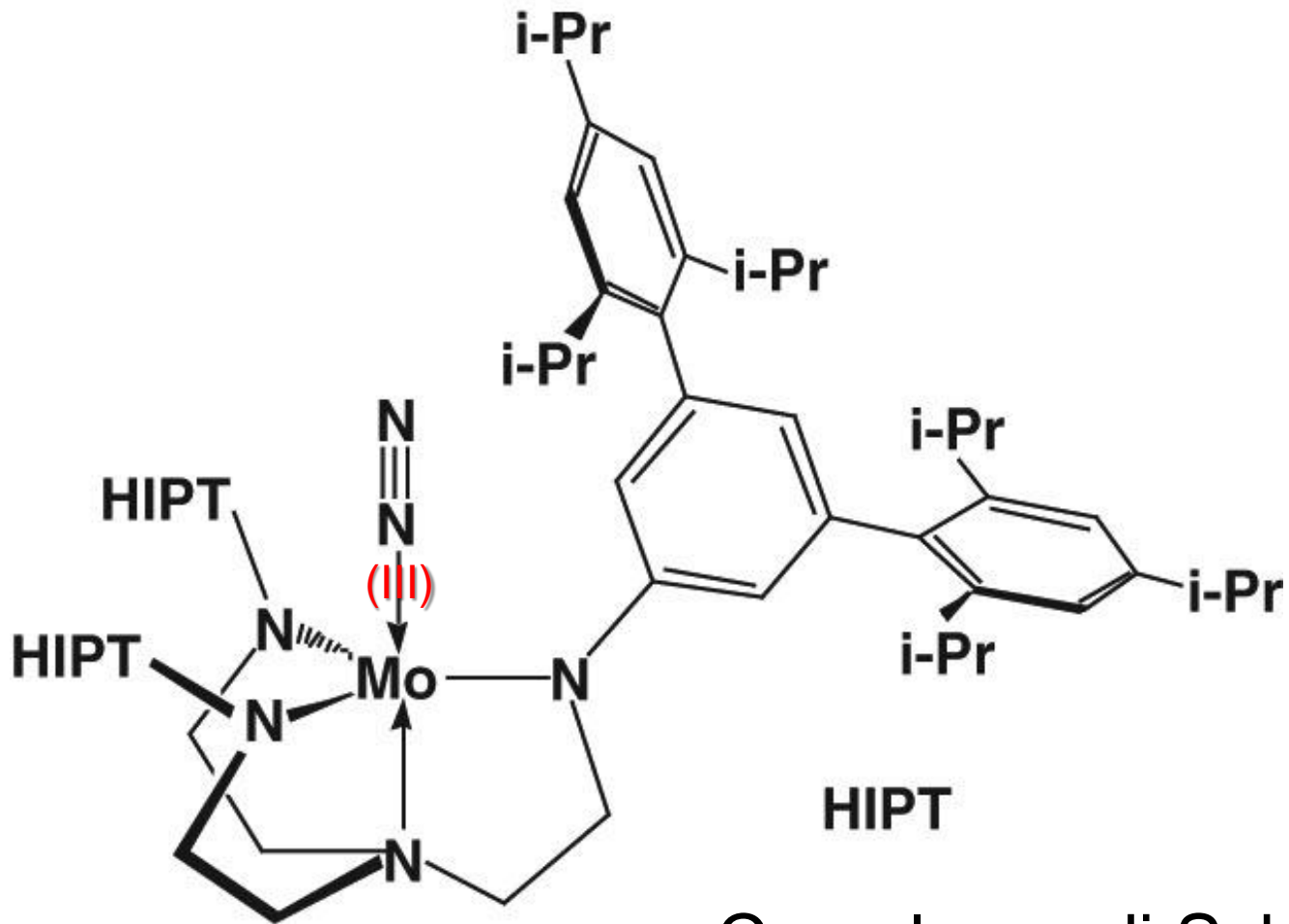
Ipotetici modi di coordinazione di N₂ al FeMoco



FeMo-co coordina N₂ solo dopo essere stato ridotto con 4 elettroni

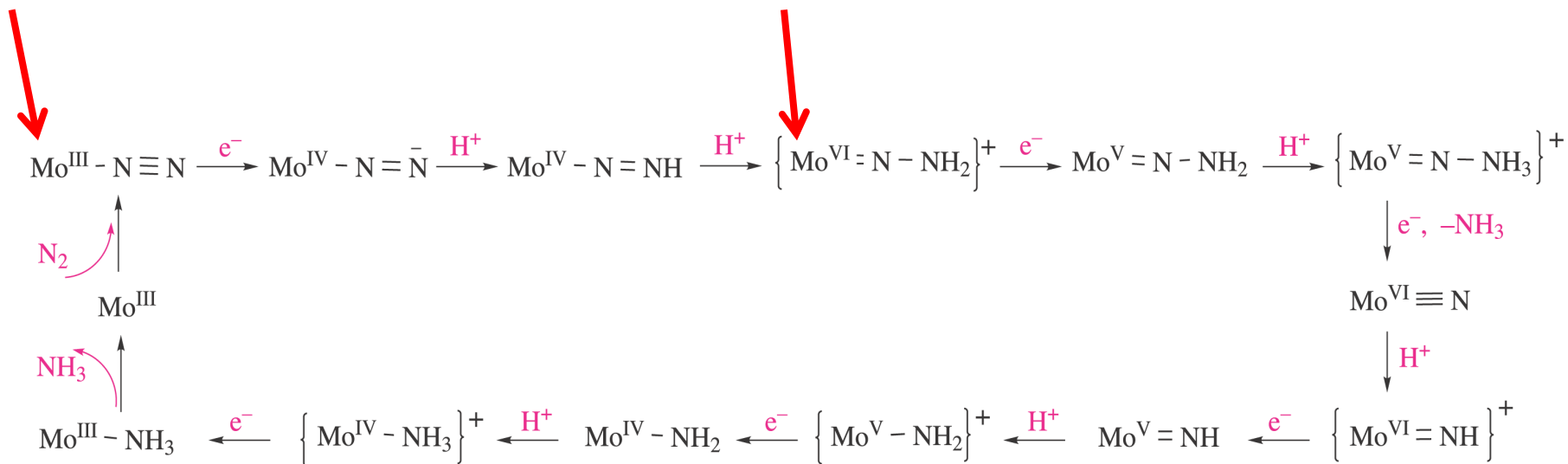
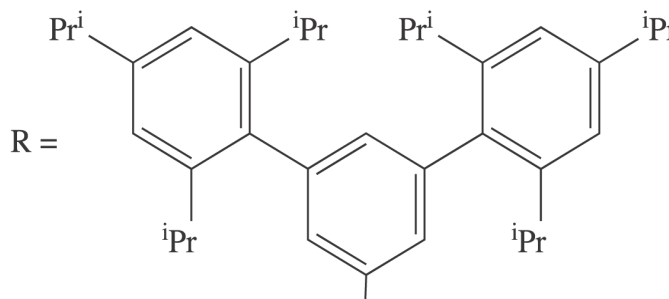
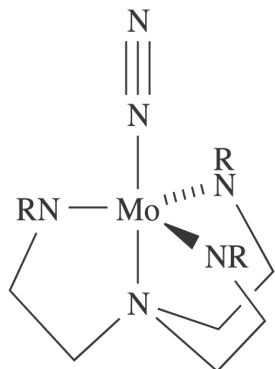


Modelli



Complesso di Schrock
(*Science* 2003)

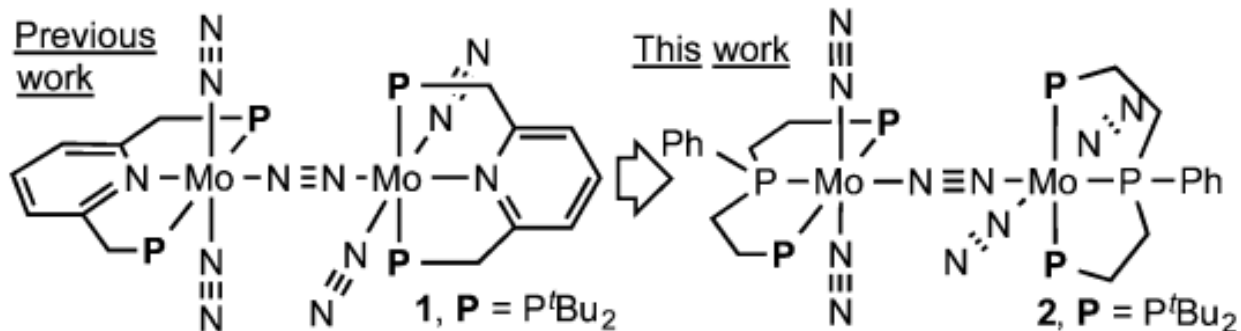
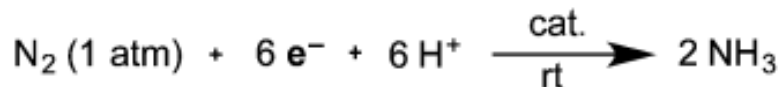
Schema della riduzione catalitica di N₂ a NH₃ su Mo



8 cicli catalitici, meccanismo *distale*

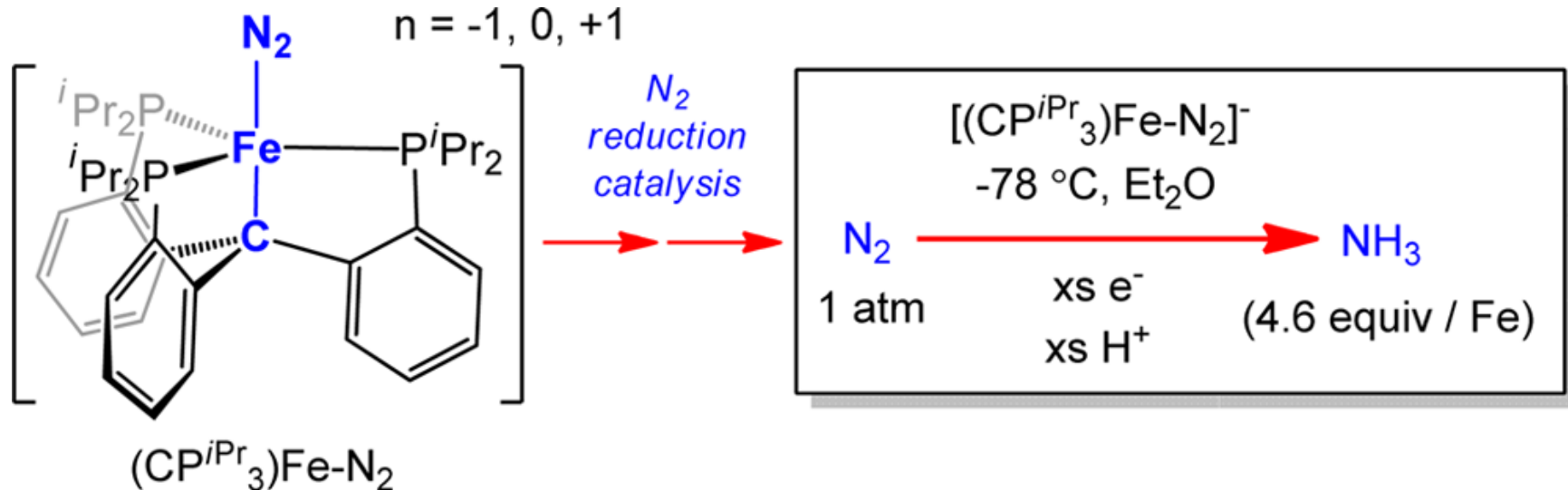
Complessi di Nishibayashi (2011 e 2015)

26 cicli catalitici, riducente CoCp^*_2



Complesso di Peters (2014)

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



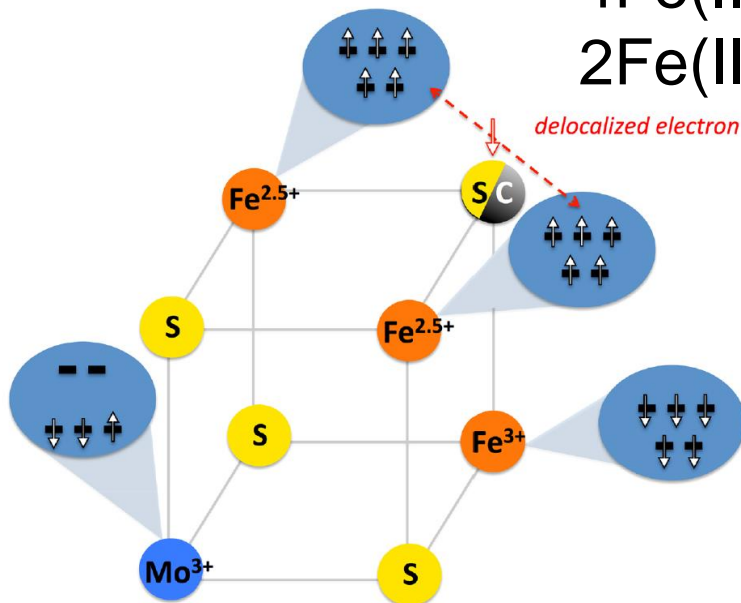
Struttura elettronica di FeMo-co

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) | |

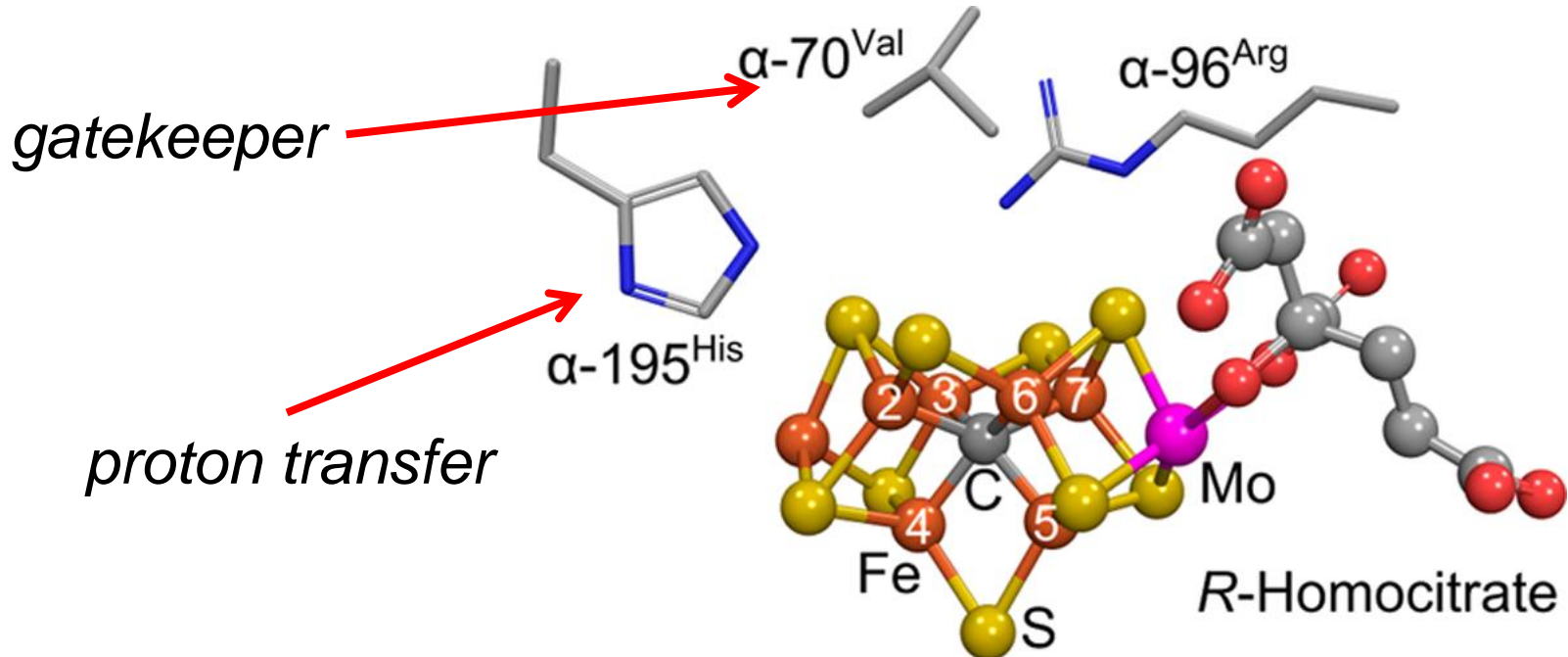
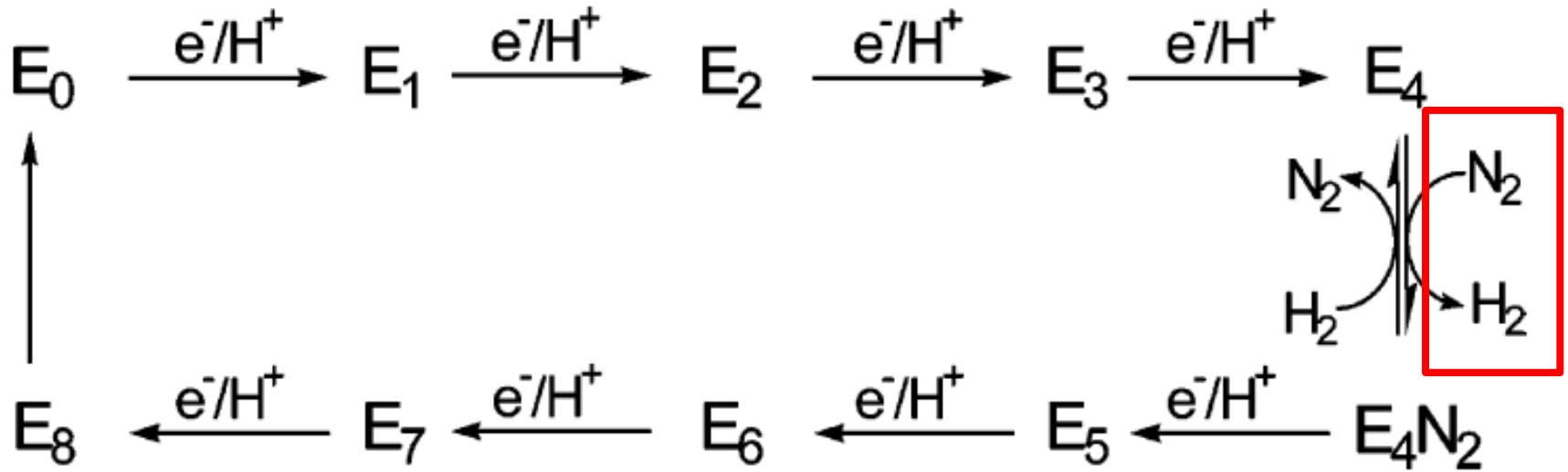
2014: Mo(III), d^3 basso spin ($\uparrow\uparrow\downarrow$)? (violazione della regola di Hund)

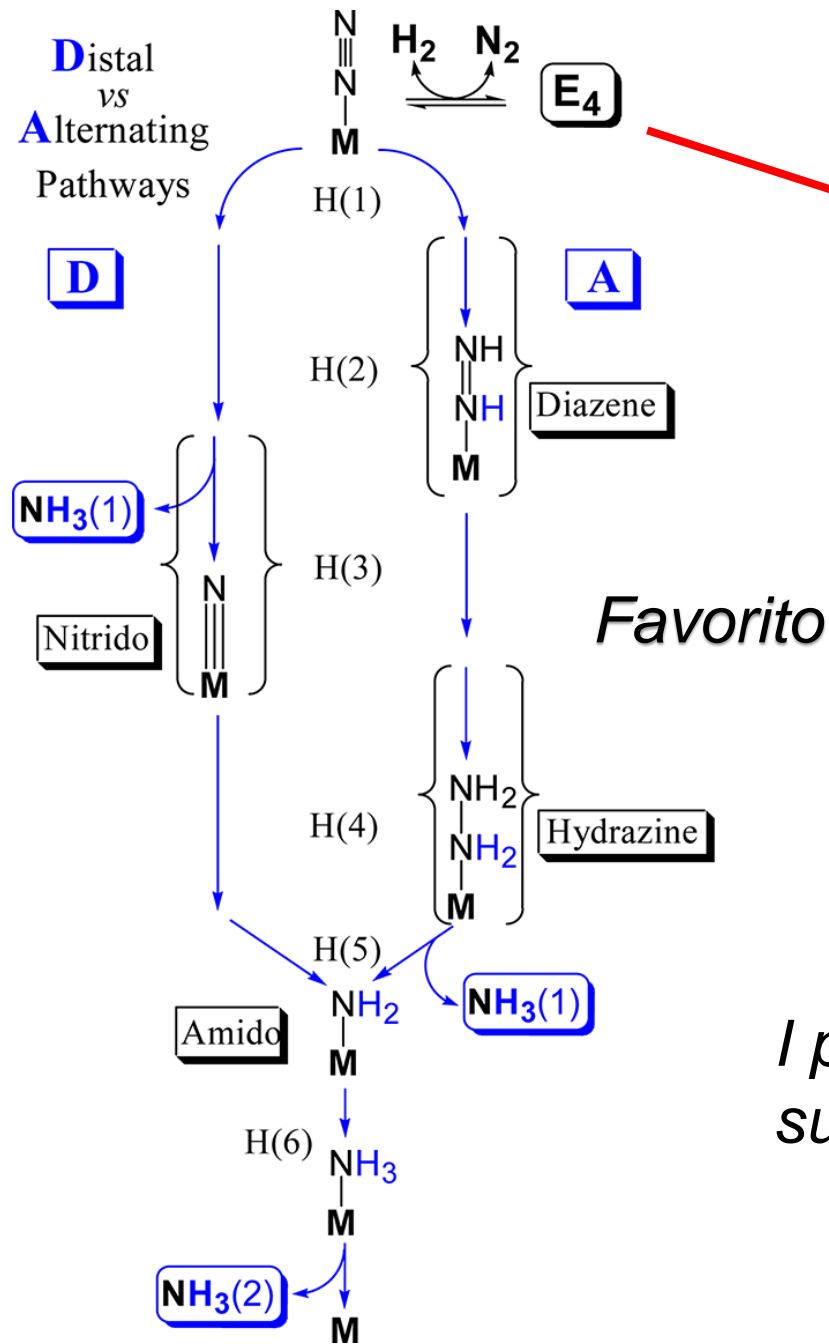
- | | | |
|-----------------------|---------------|------------------------|
| 6Fe(II)1Fe(III)Mo(IV) | \rightarrow | 5Fe(II)2Fe(III)Mo(III) |
| 4Fe(II)3Fe(III)Mo(IV) | \rightarrow | 3Fe(II)4Fe(III)Mo(III) |
| 2Fe(II)5Fe(III)Mo(IV) | \rightarrow | 1Fe(II)6Fe(III)Mo(III) |



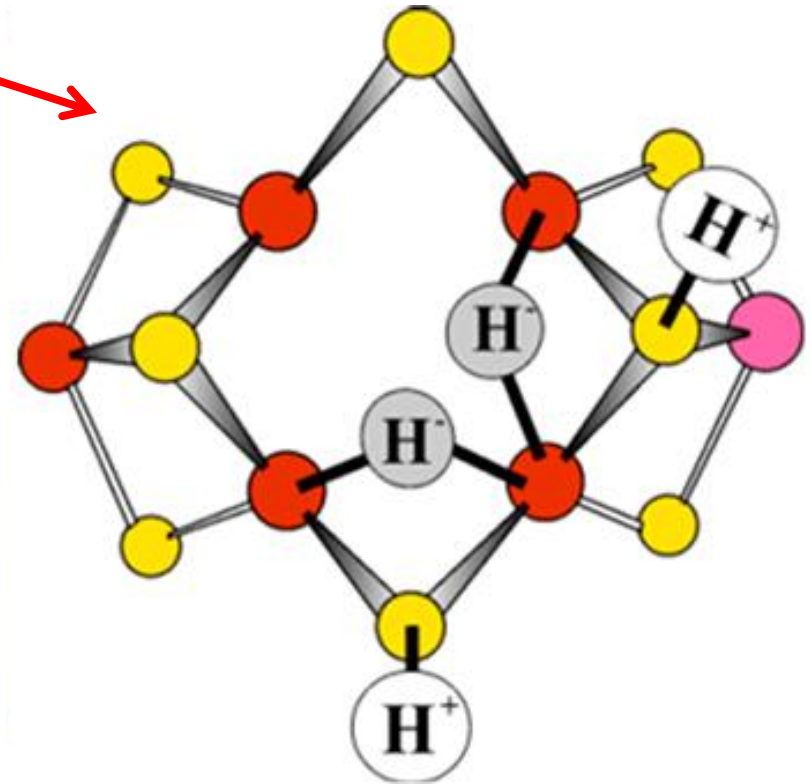
Cluster modello $[\text{MoFe}_3\text{S}_3\text{C}]^{1+}$ e $[\text{MoFe}_3\text{S}_4]^{3+}$

Ciclo catalitico

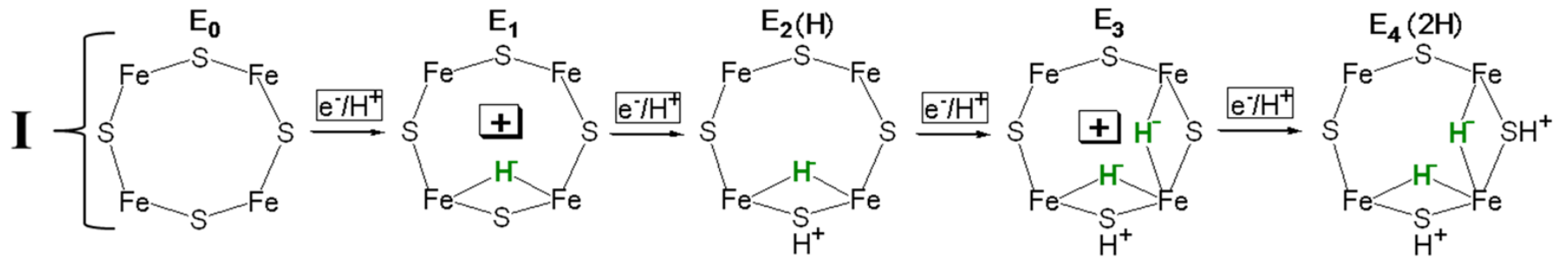




Modello di E₄

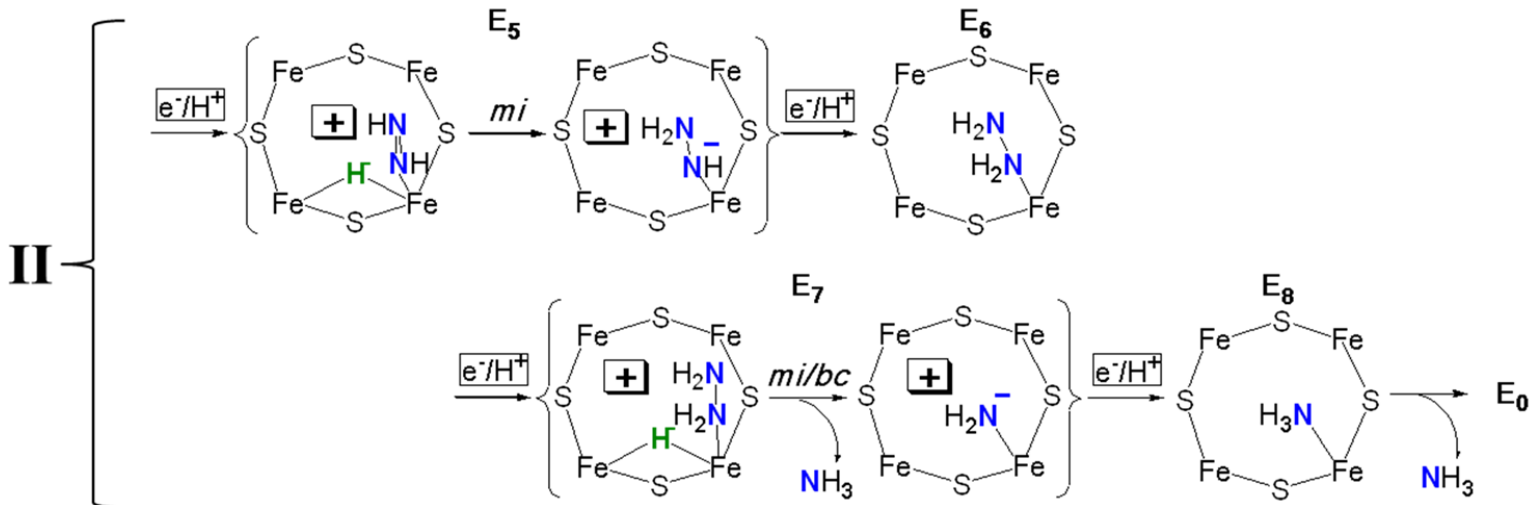
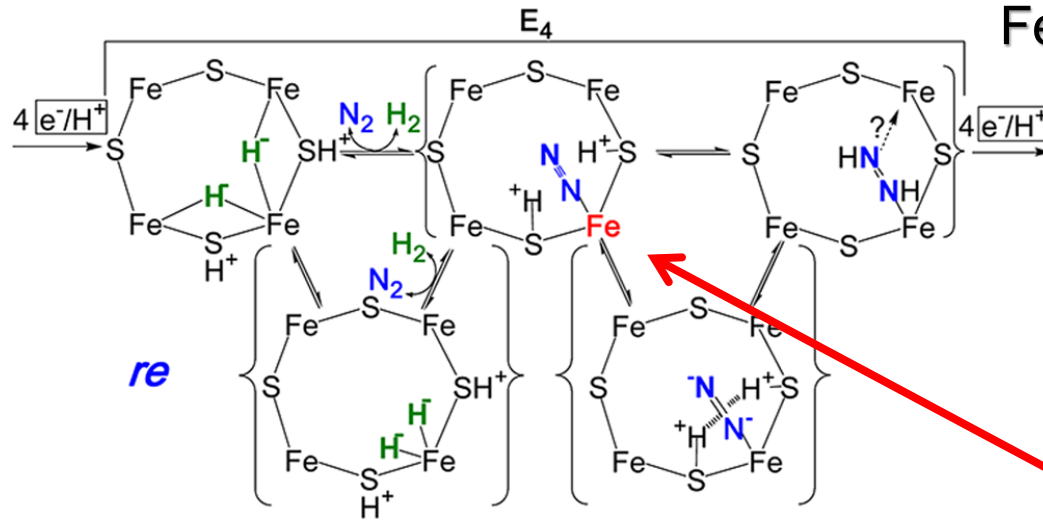


I primi 4 elettroni si accumulano sugli idruri e non sugli atomi di ferro



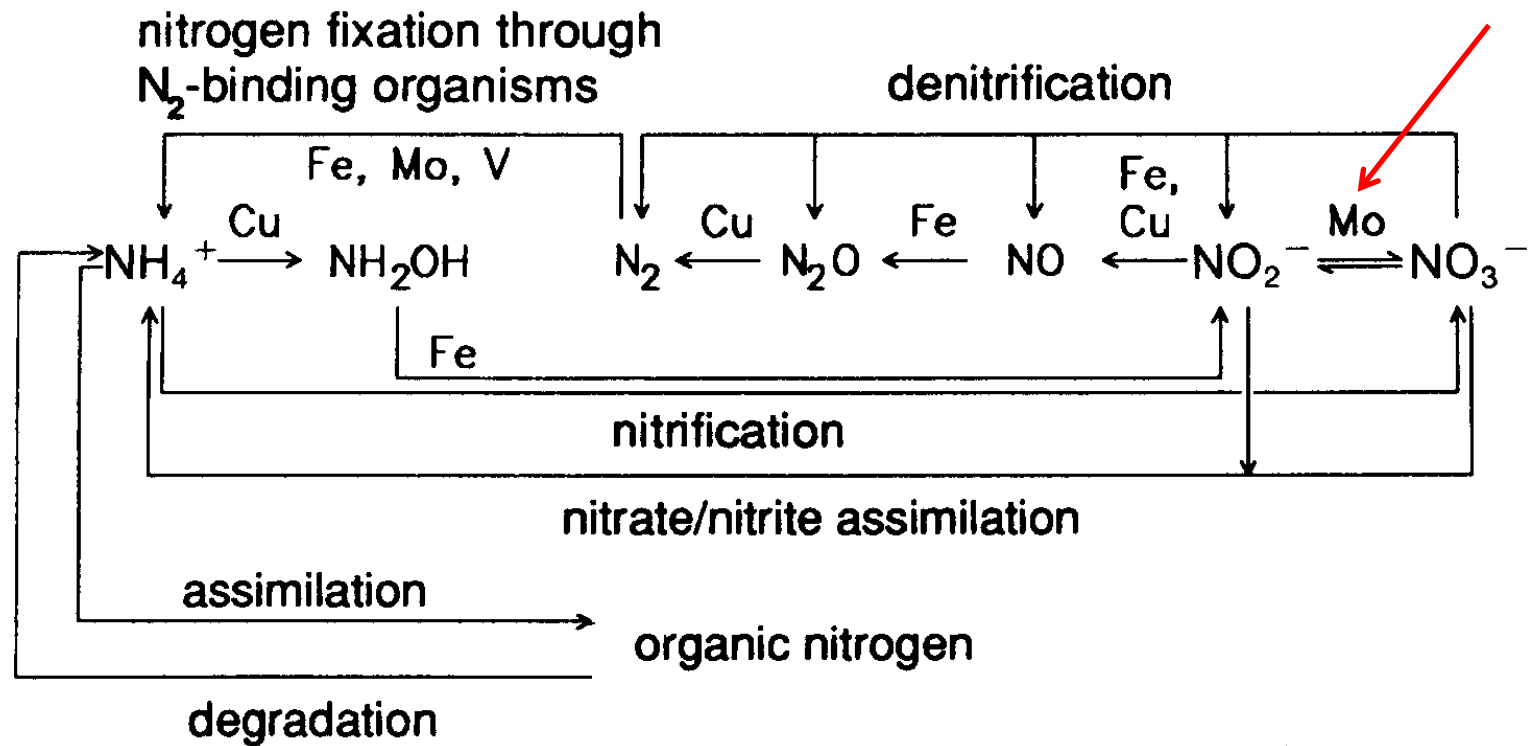
FeMoco attivato

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



Altri enzimi al molibdeno

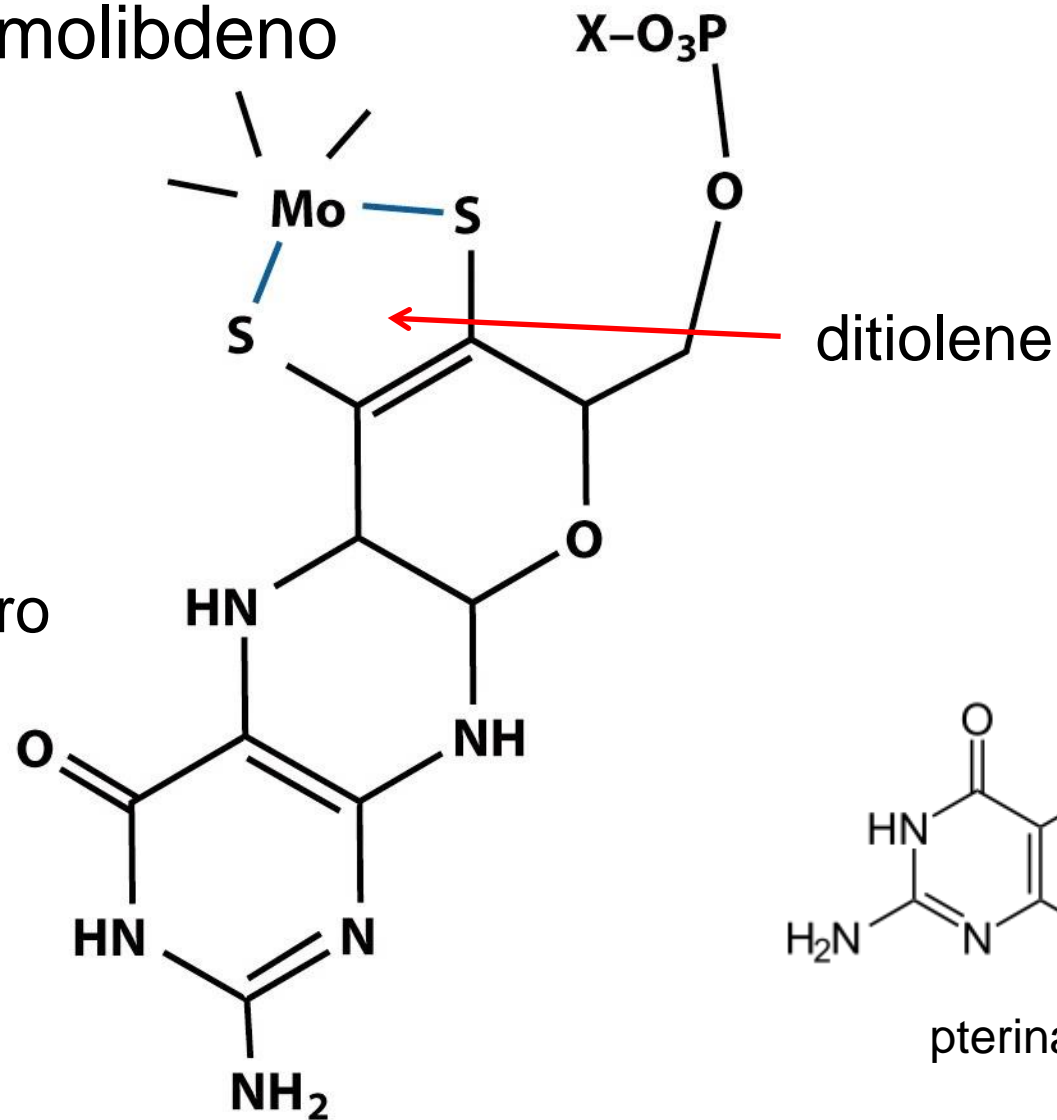
catalizzano la ossidazione o la riduzione di piccole molecole



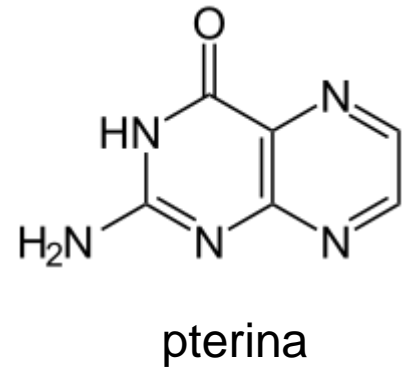
Tre famiglie di enzimi al Mo (*osso-trasferasi*)

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

Cofattore del molibdeno

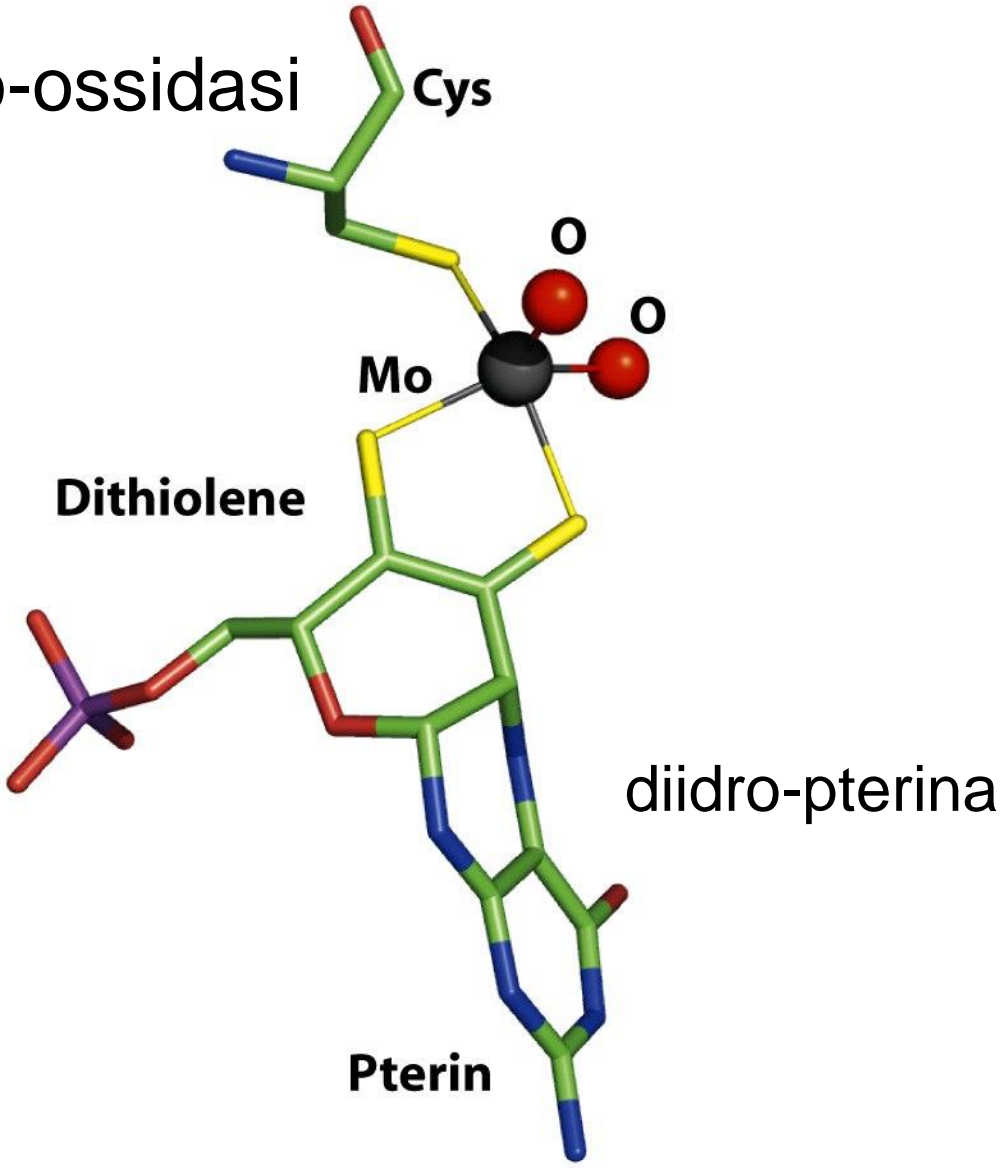


di-idro o tetra-idro
pterina

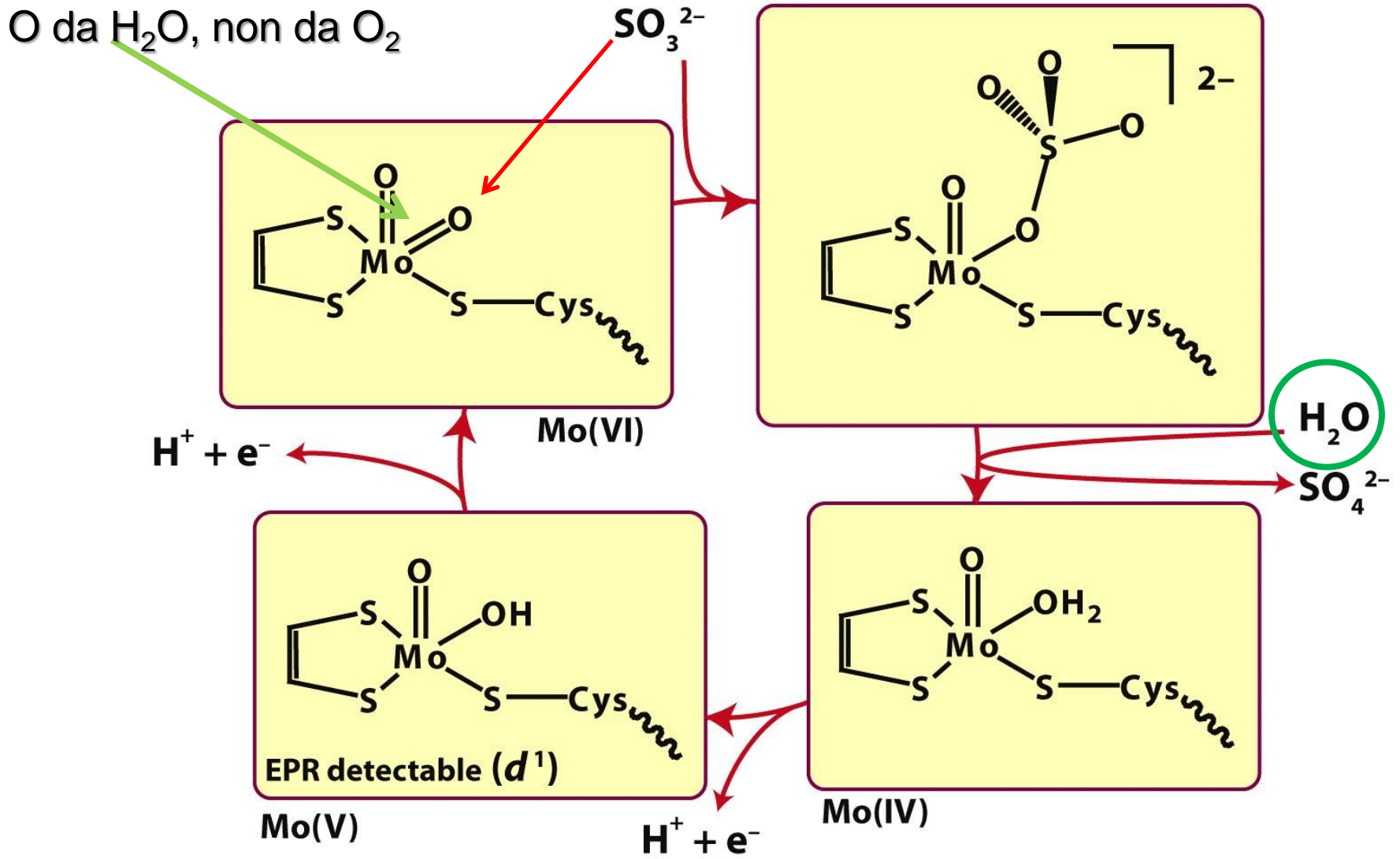


Molybdopterin as ligand

Sito della solfito-ossidasi

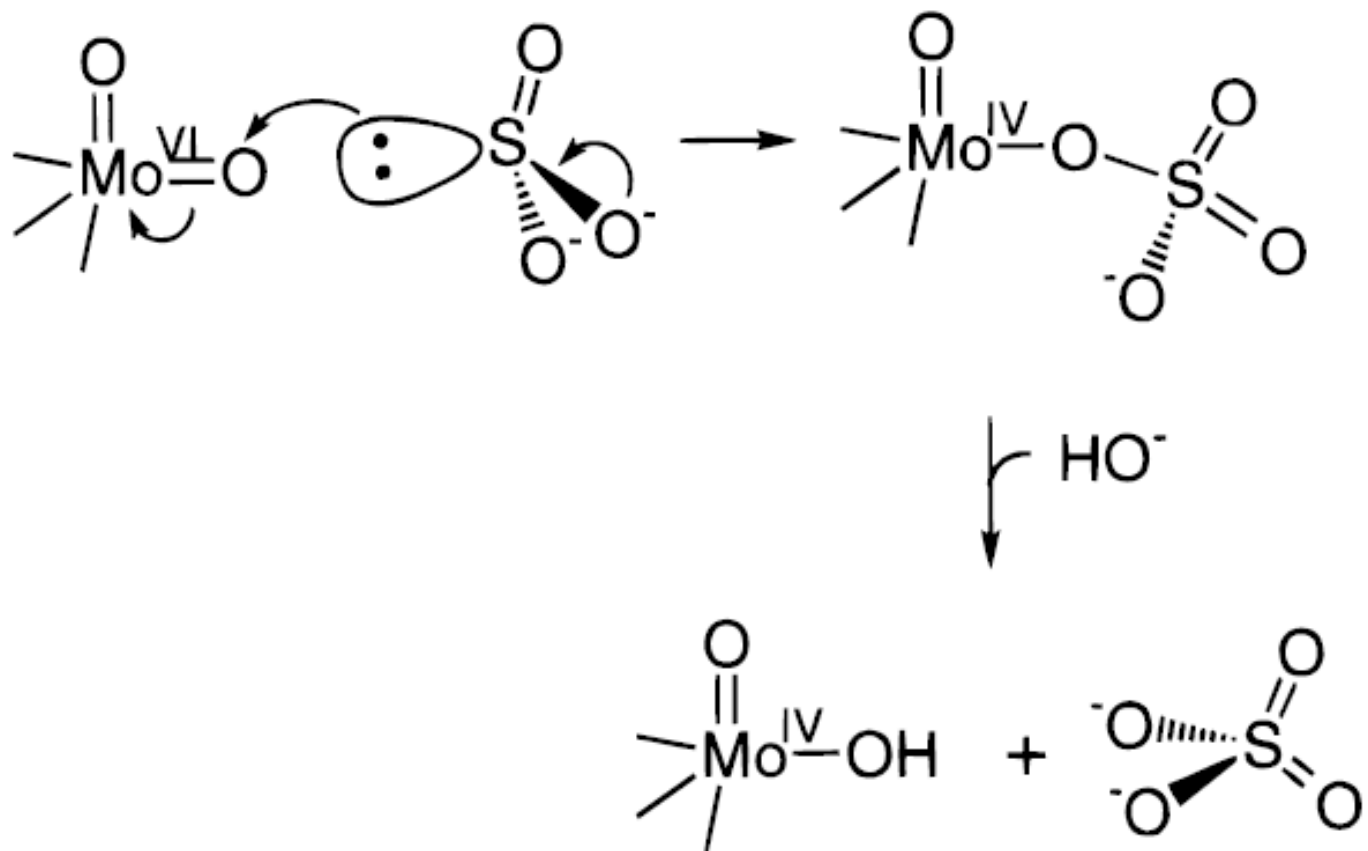


Ciclo catalitico della solfito-ossidasi

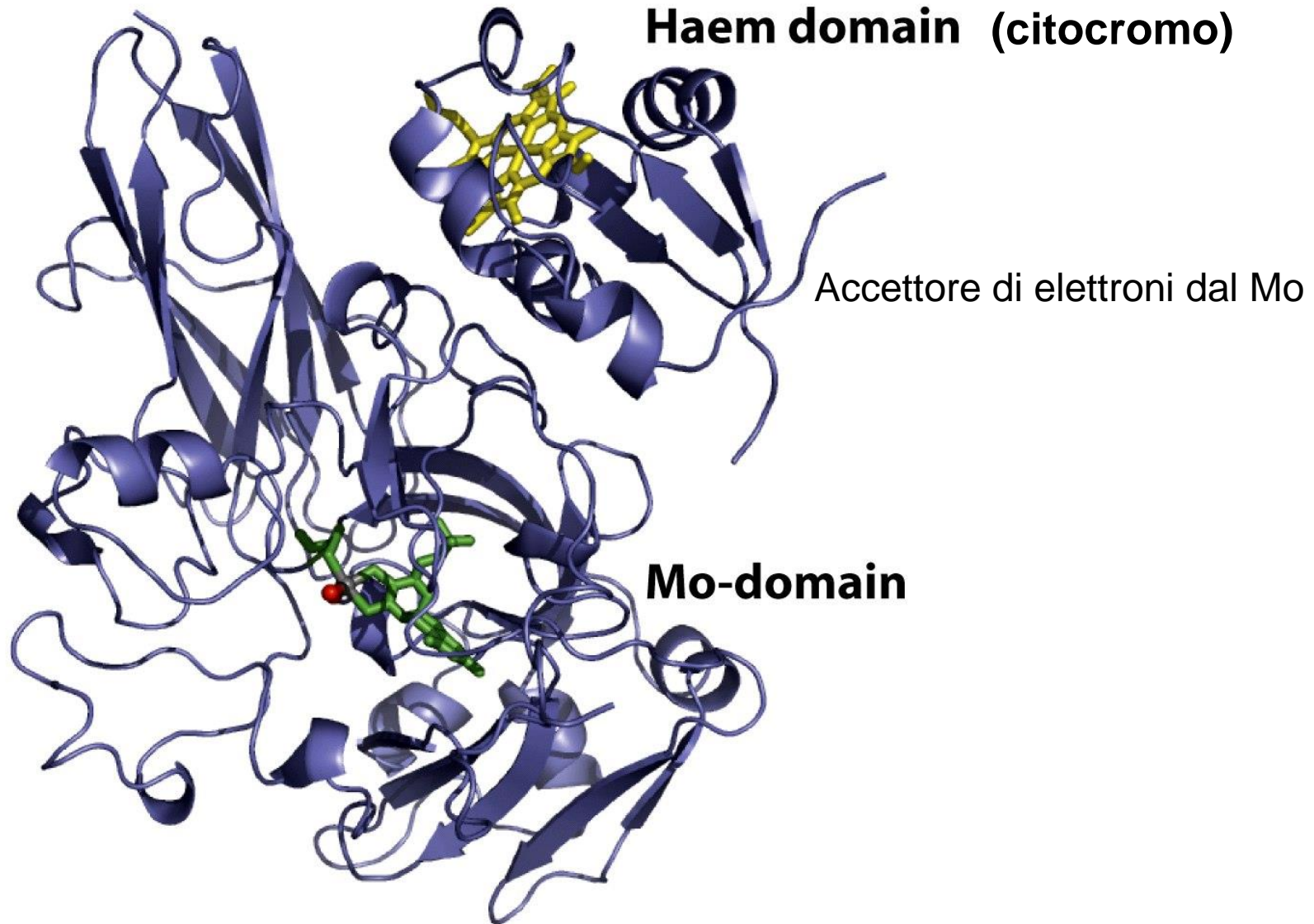


Mo possiede tre stati di ossidazione stabili, Mo(IV), Mo(V) e Mo(VI)

Dettaglio del meccanismo di trasferimento di ossigeno



Struttura della solfito-ossidasi



Scala di entalpia delle reazioni di trasferimento di atomi di ossigeno

