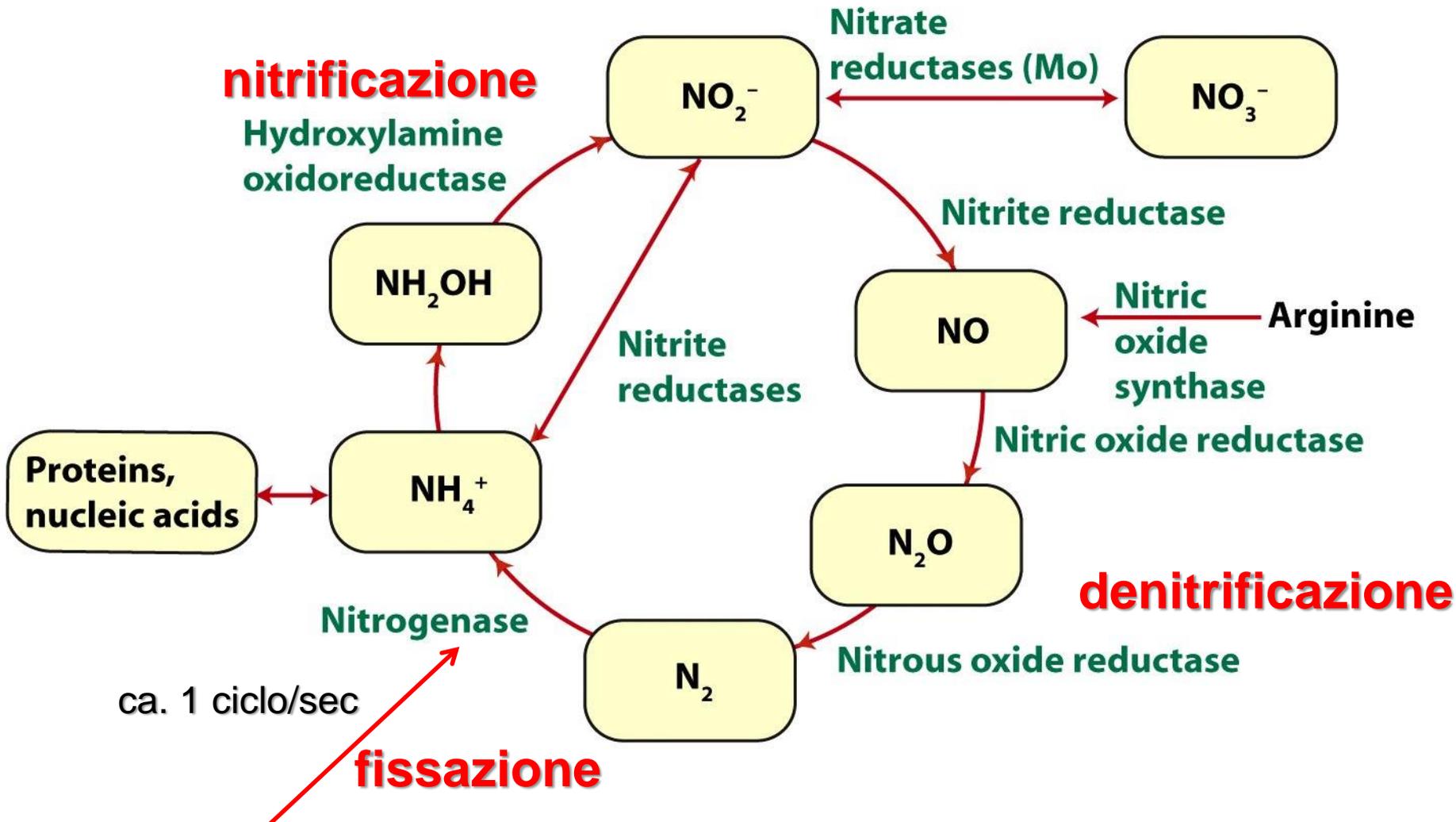


Metalli di inizio serie

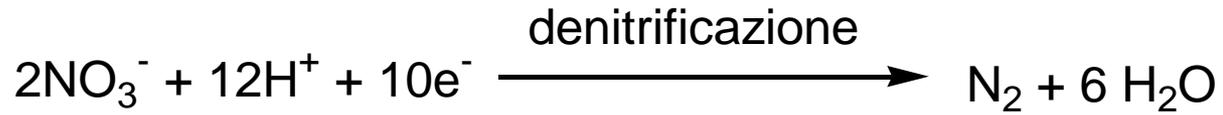
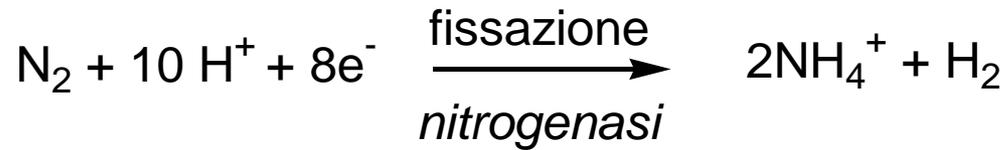
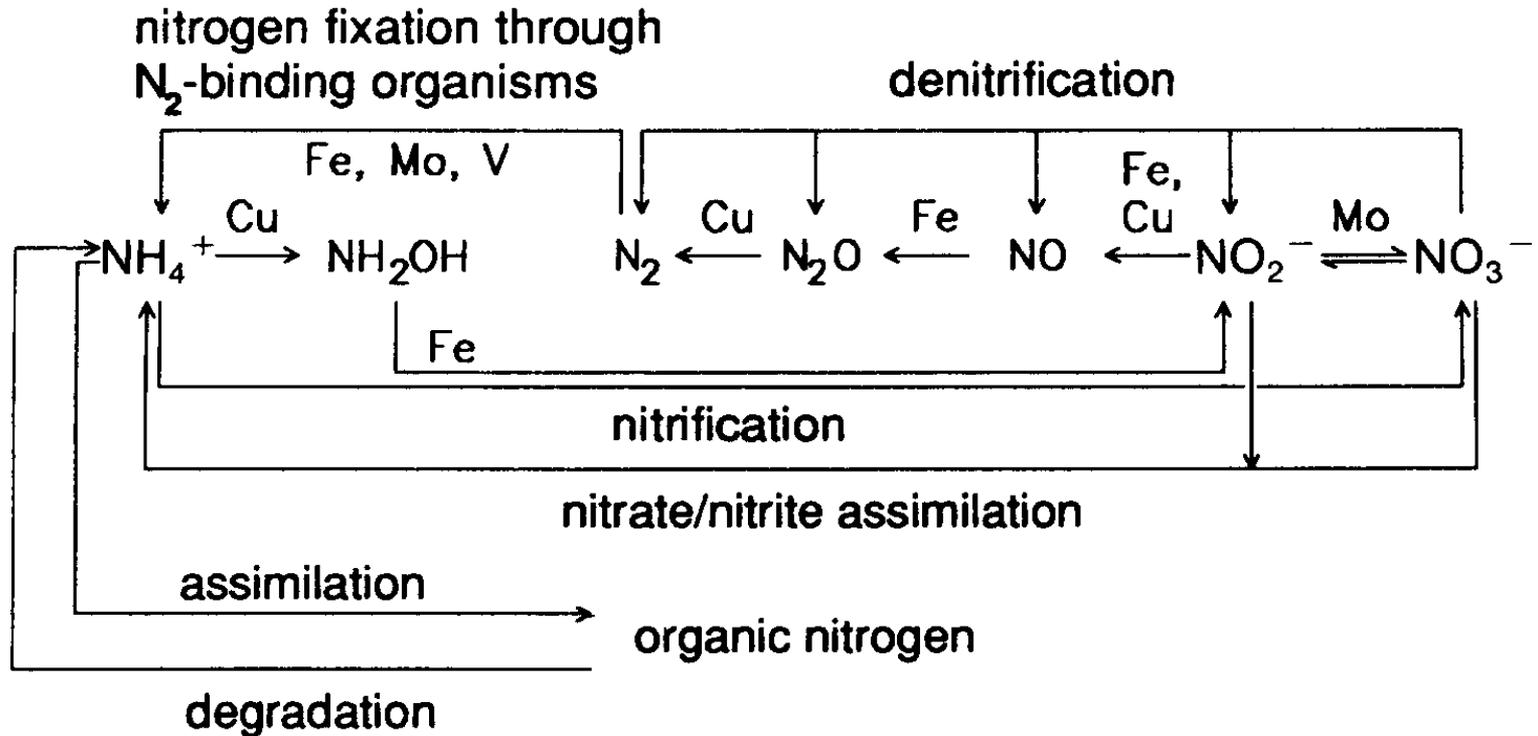


Il molibdeno è l'unico elemento del secondo periodo di transizione (4d) ad avere una funzione biologica. È biodisponibile sotto forma di molibdato MoO_4^{2-}

Ciclo dell'azoto



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

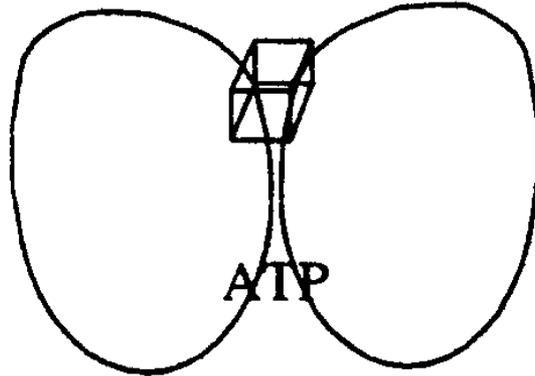


Nitrogenasi



1992

ca. 1 ciclo/sec

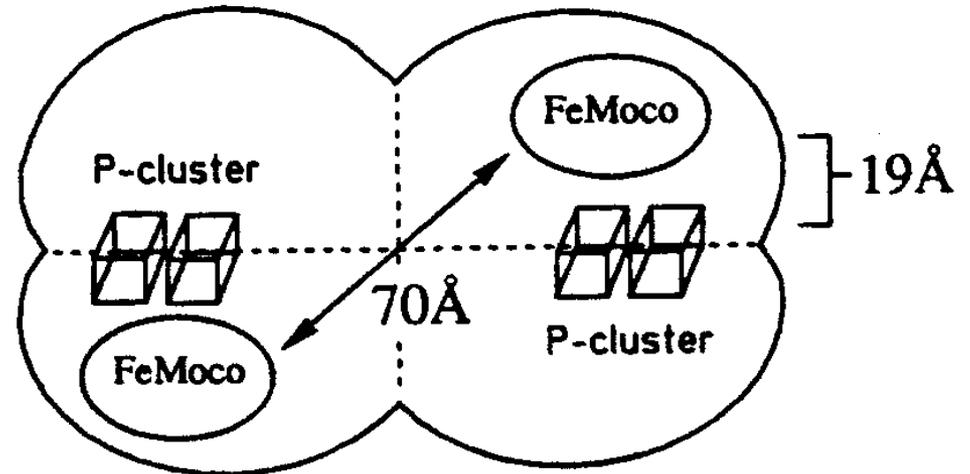


Fe protein

γ_2

60 kDa

+



FeMo protein

$\alpha_2\beta_2$

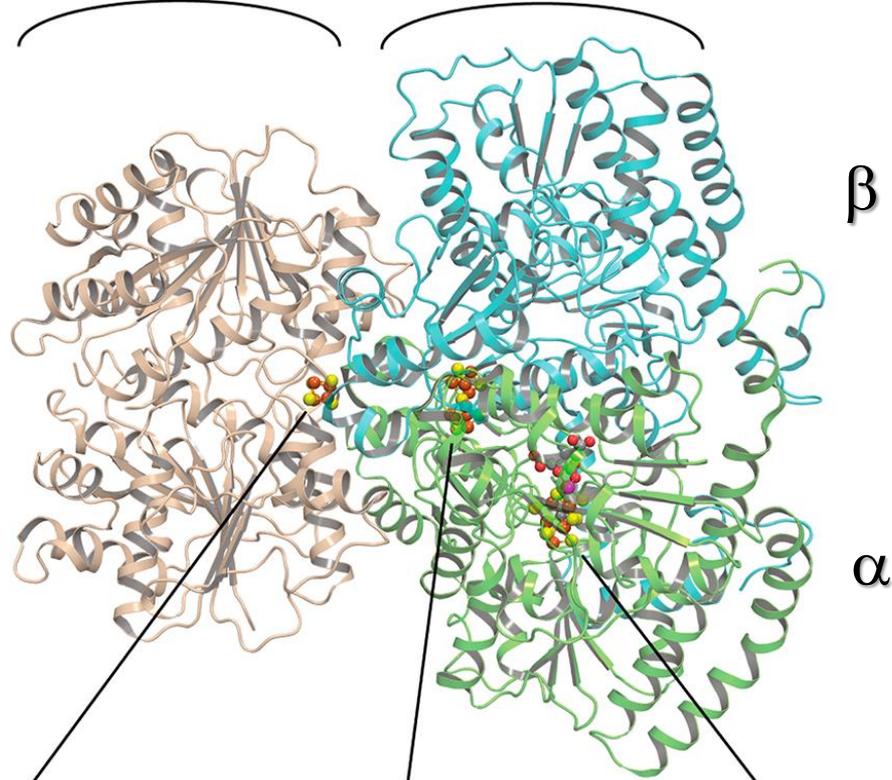
220 kDa

Nitrogenasi

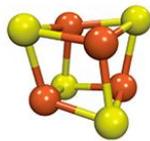
Fe protein

MoFe protein

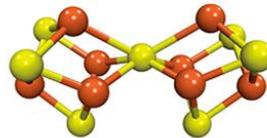
(A)



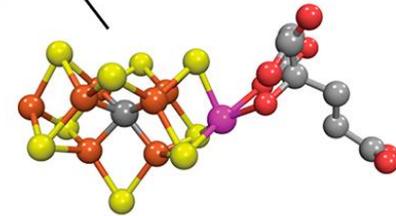
(B)



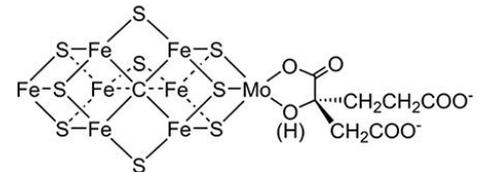
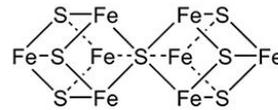
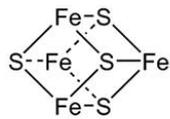
F cluster



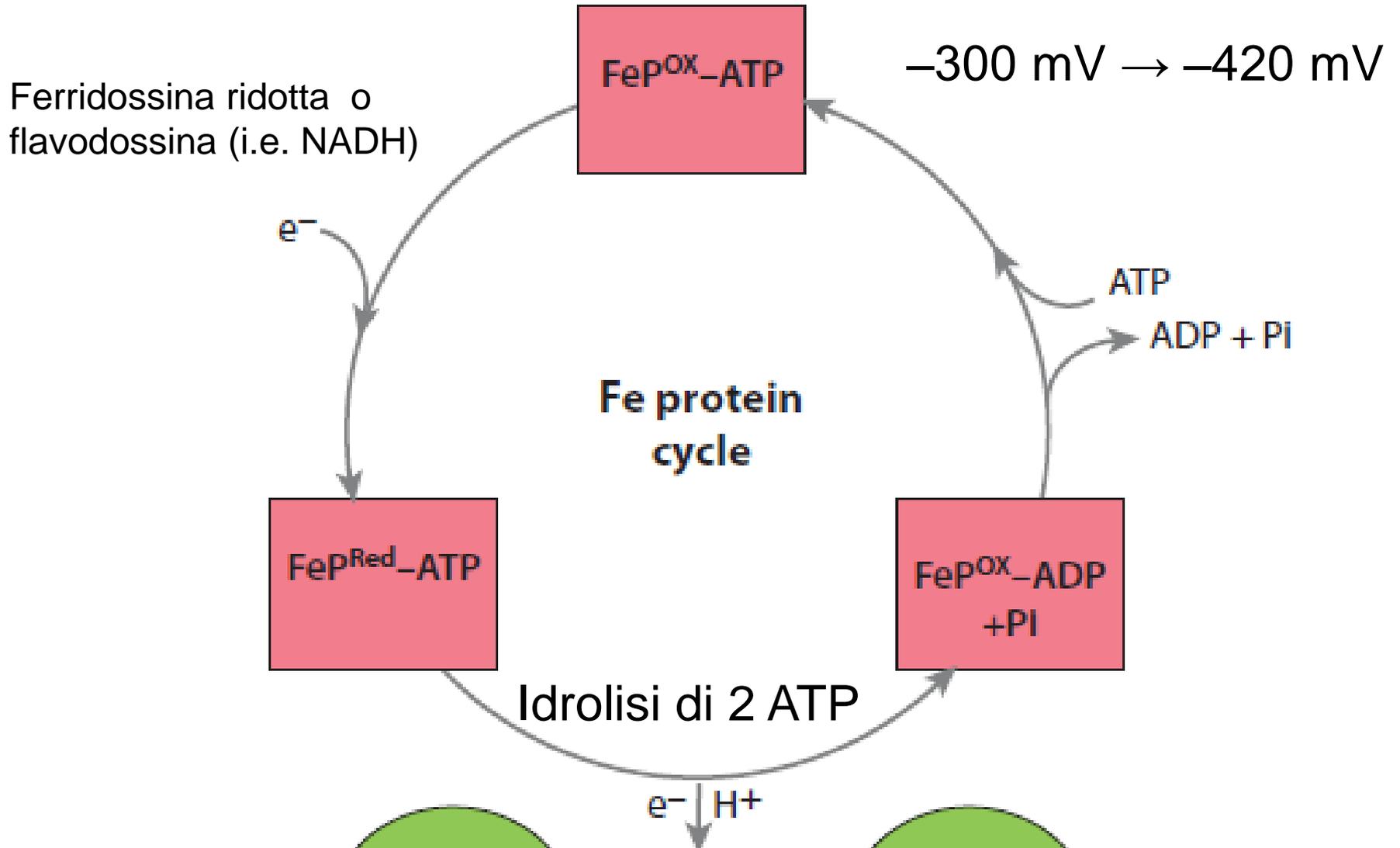
P cluster



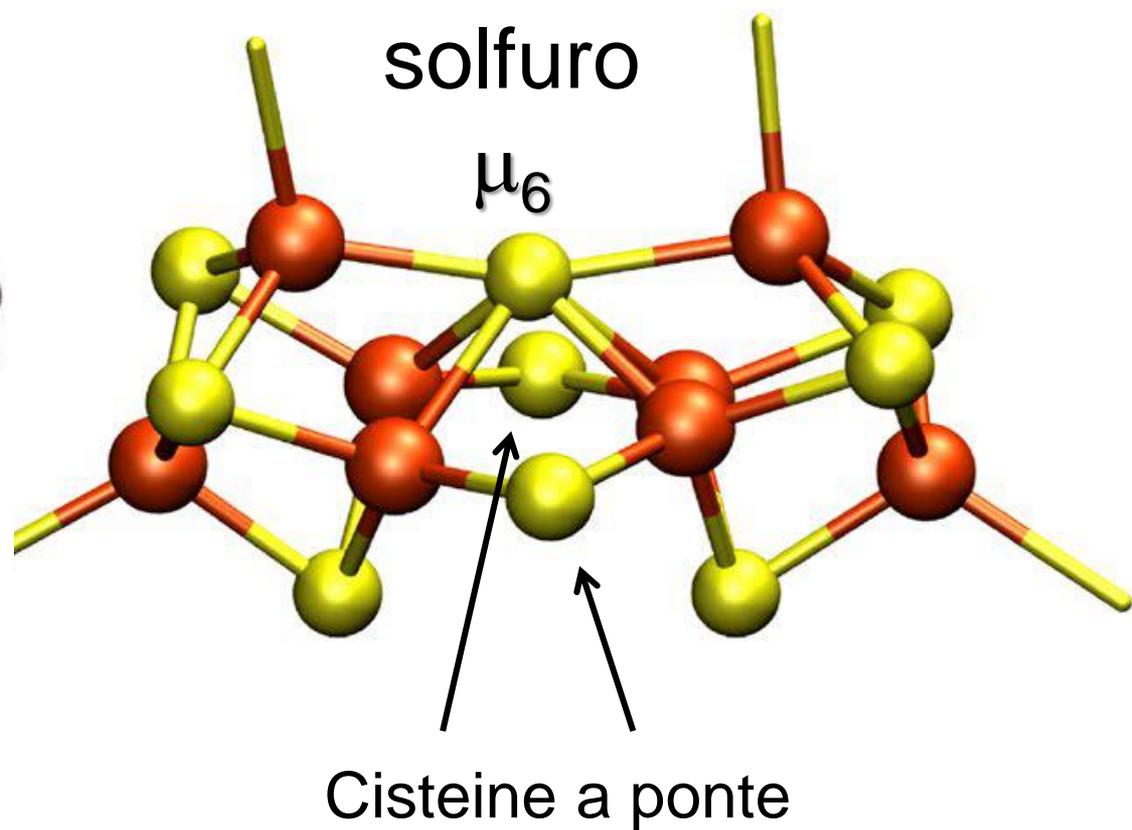
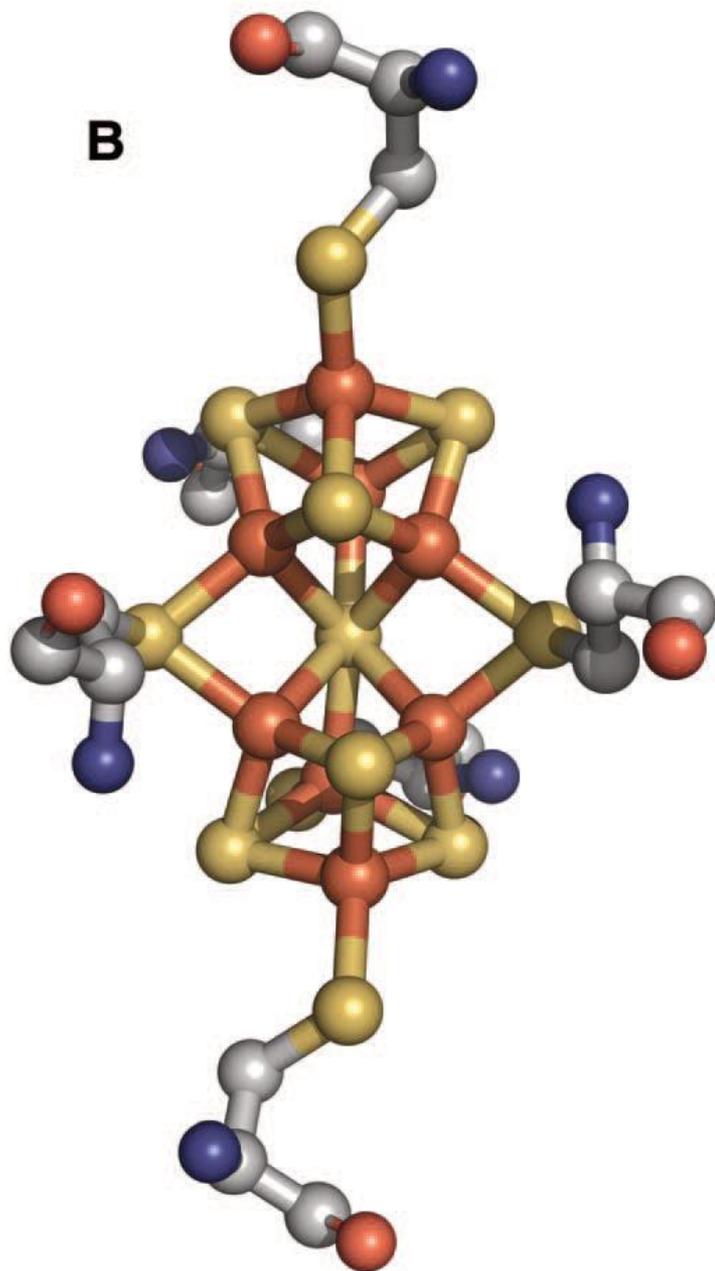
M cluster (FeMoco)

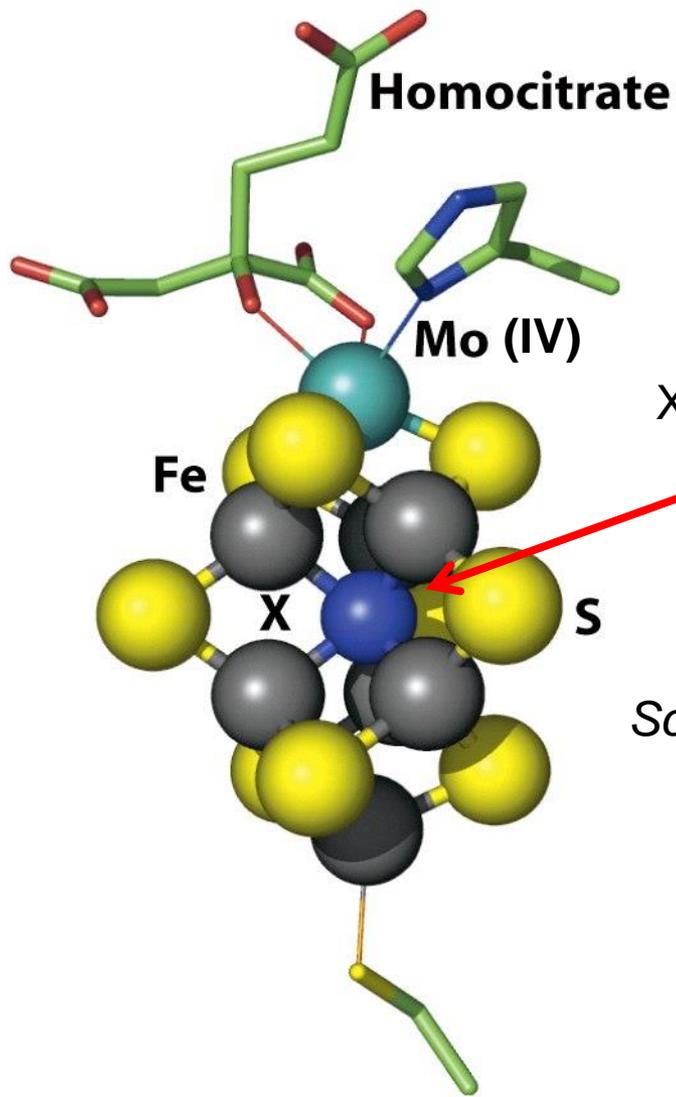


Fe-proteina



P-cluster 8Fe-7S





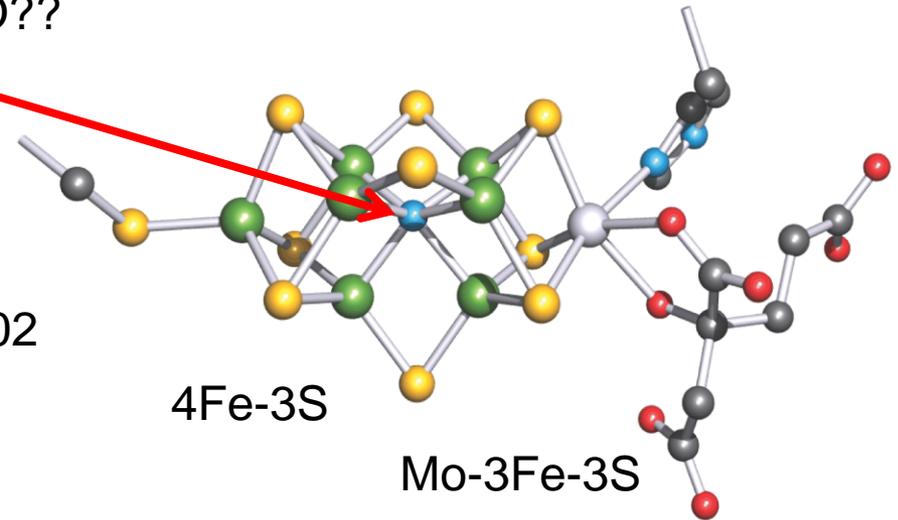
Nitrogenase FeMoCo

Cofattore FeMo

7Fe-9S-Mo-omocitrato

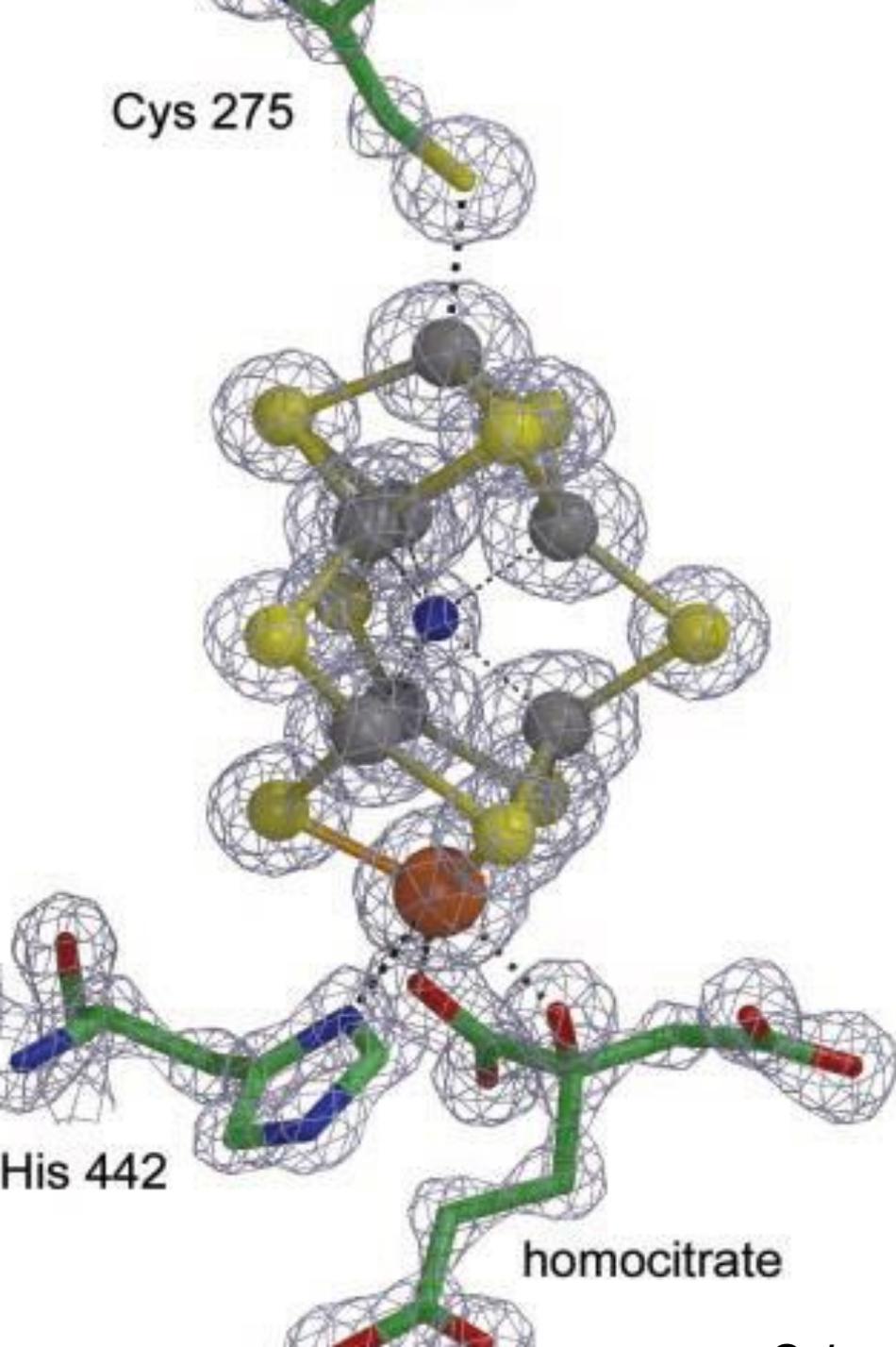
X = C, N, O??

Science, 2002

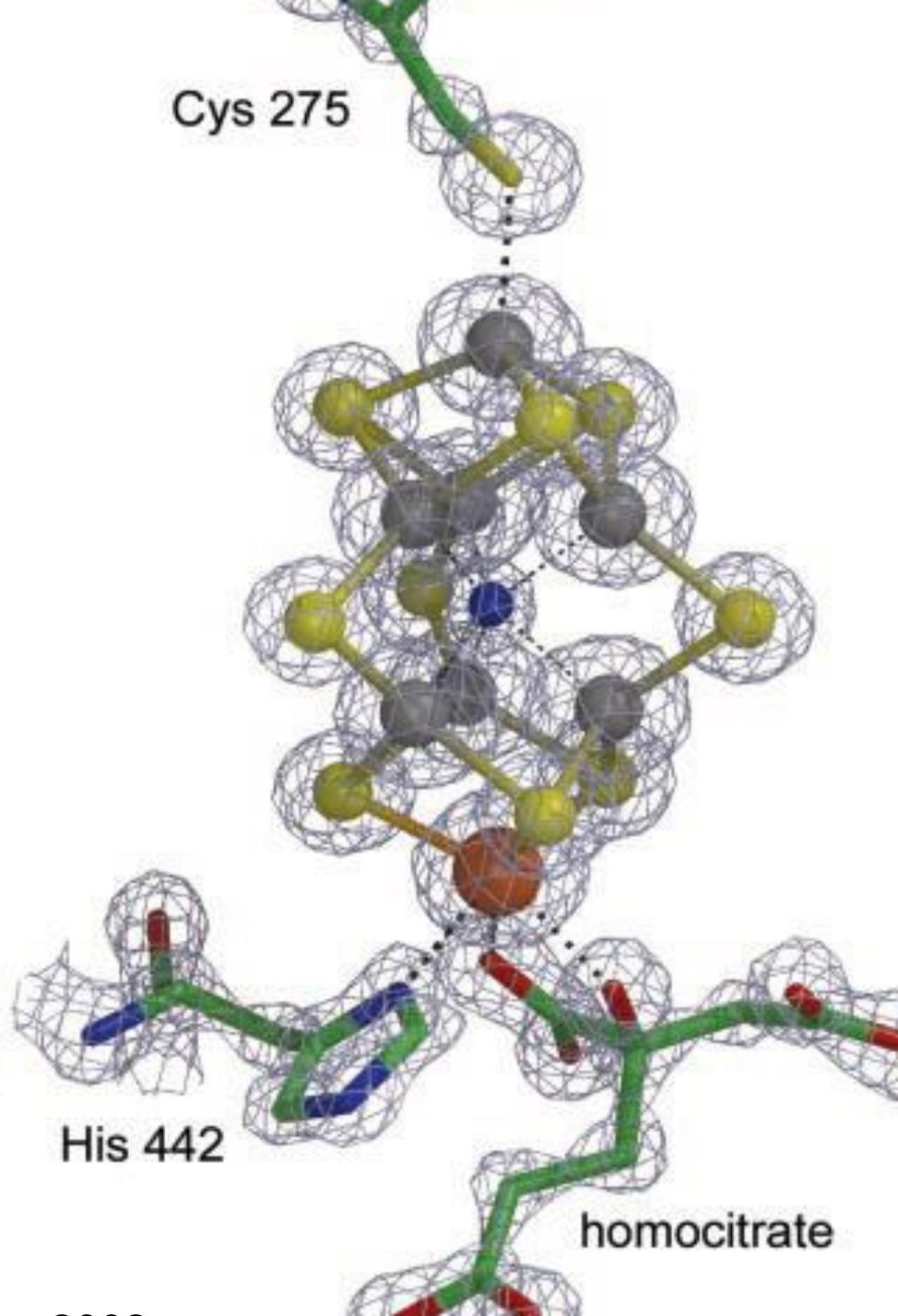


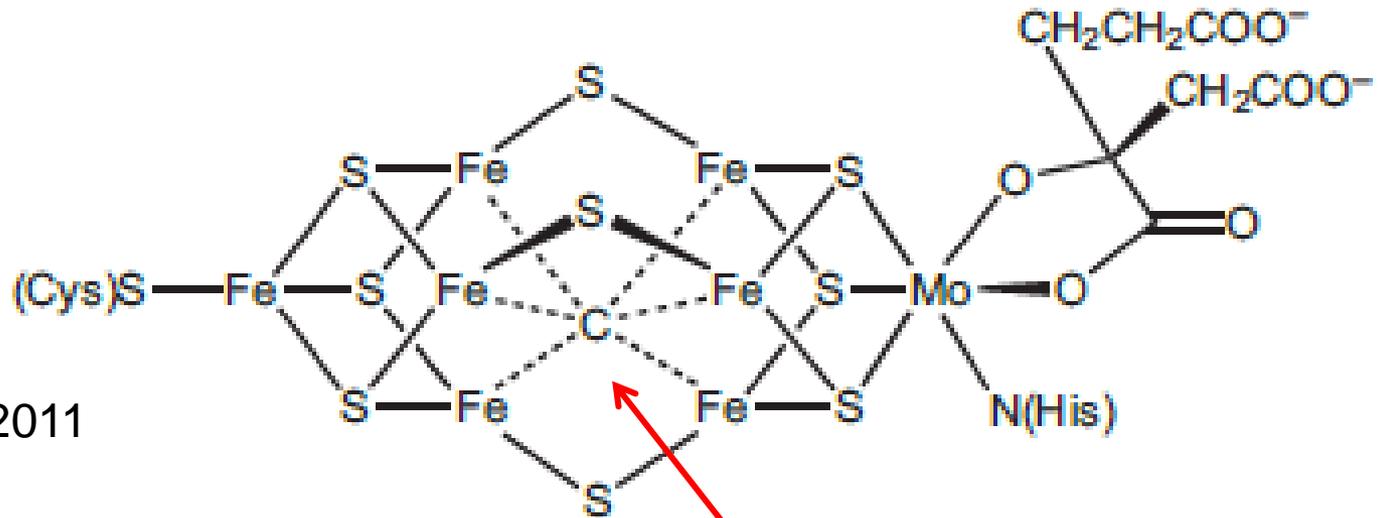
Tutto in α

Cys 275



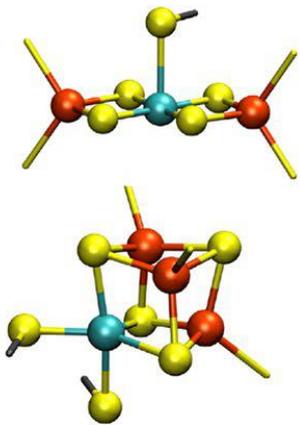
Cys 275





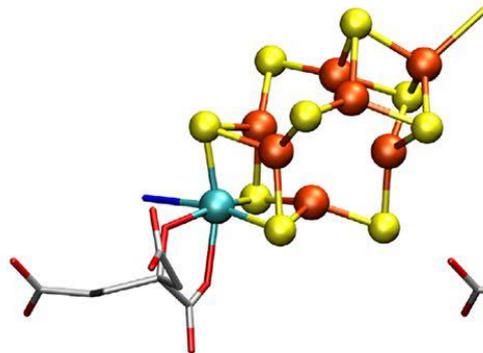
Science, 2011

Carburo, C⁴⁻



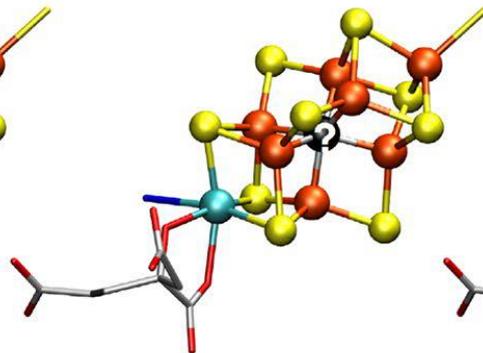
1978

First structural models from EXAFS



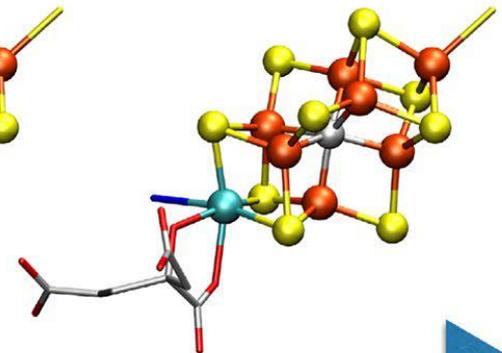
1992

First crystal structure (2.7Å)



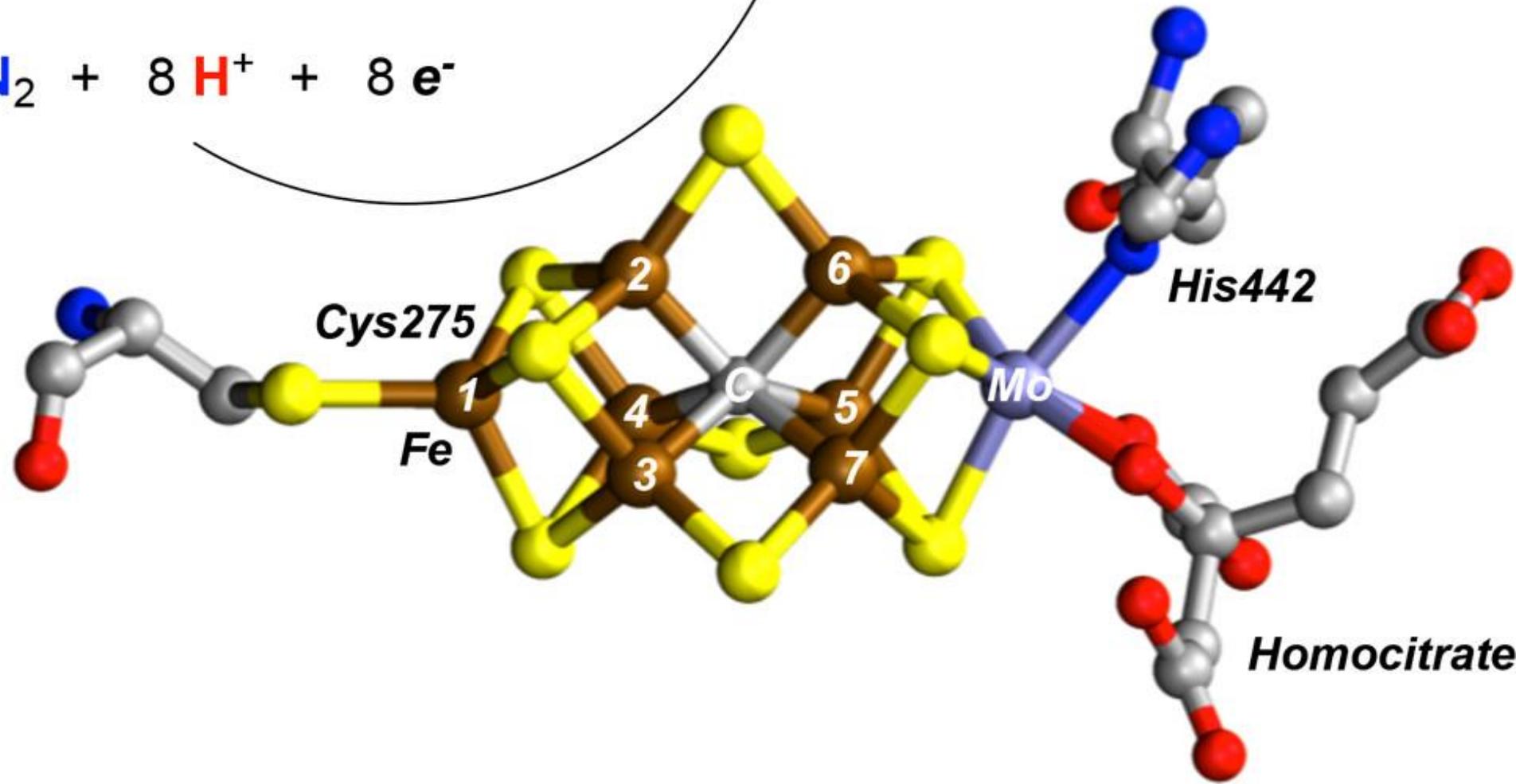
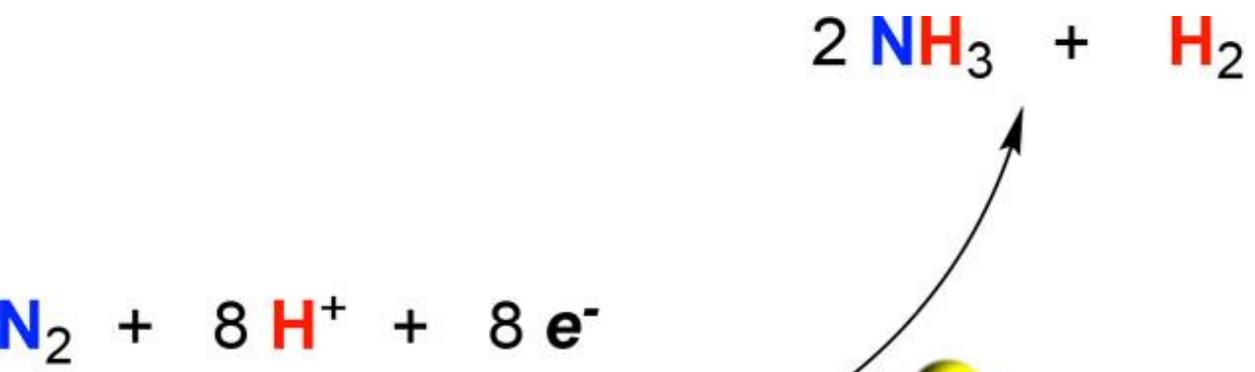
2002

Discovery of interstitial atom

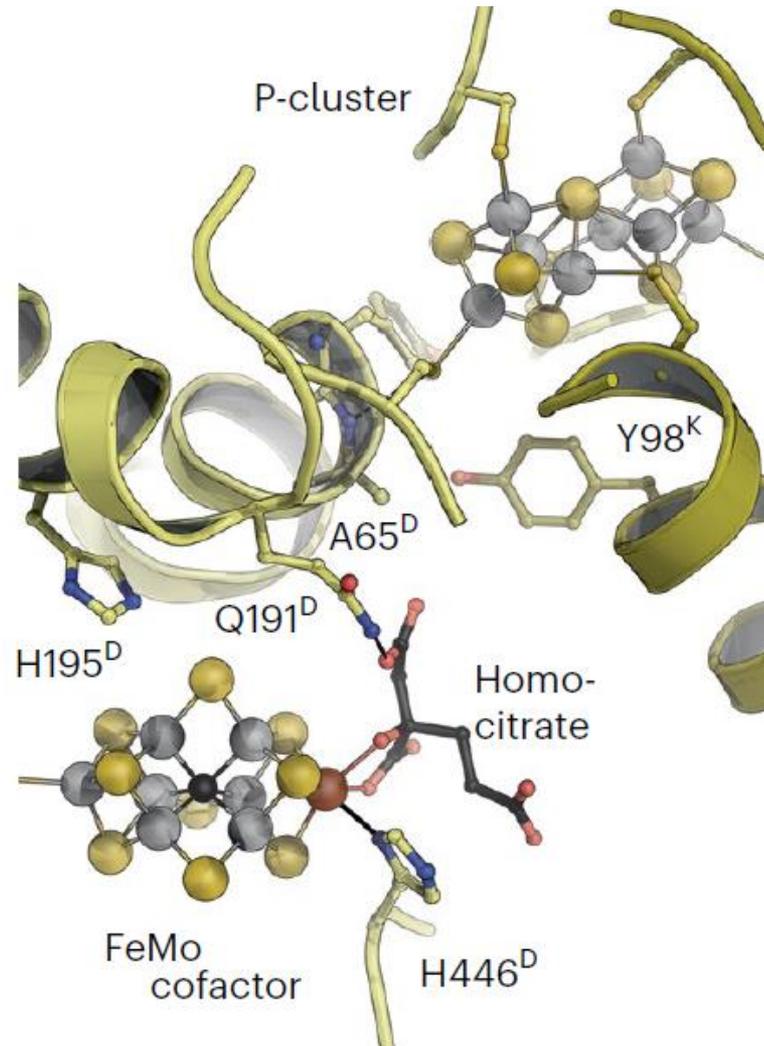


2011

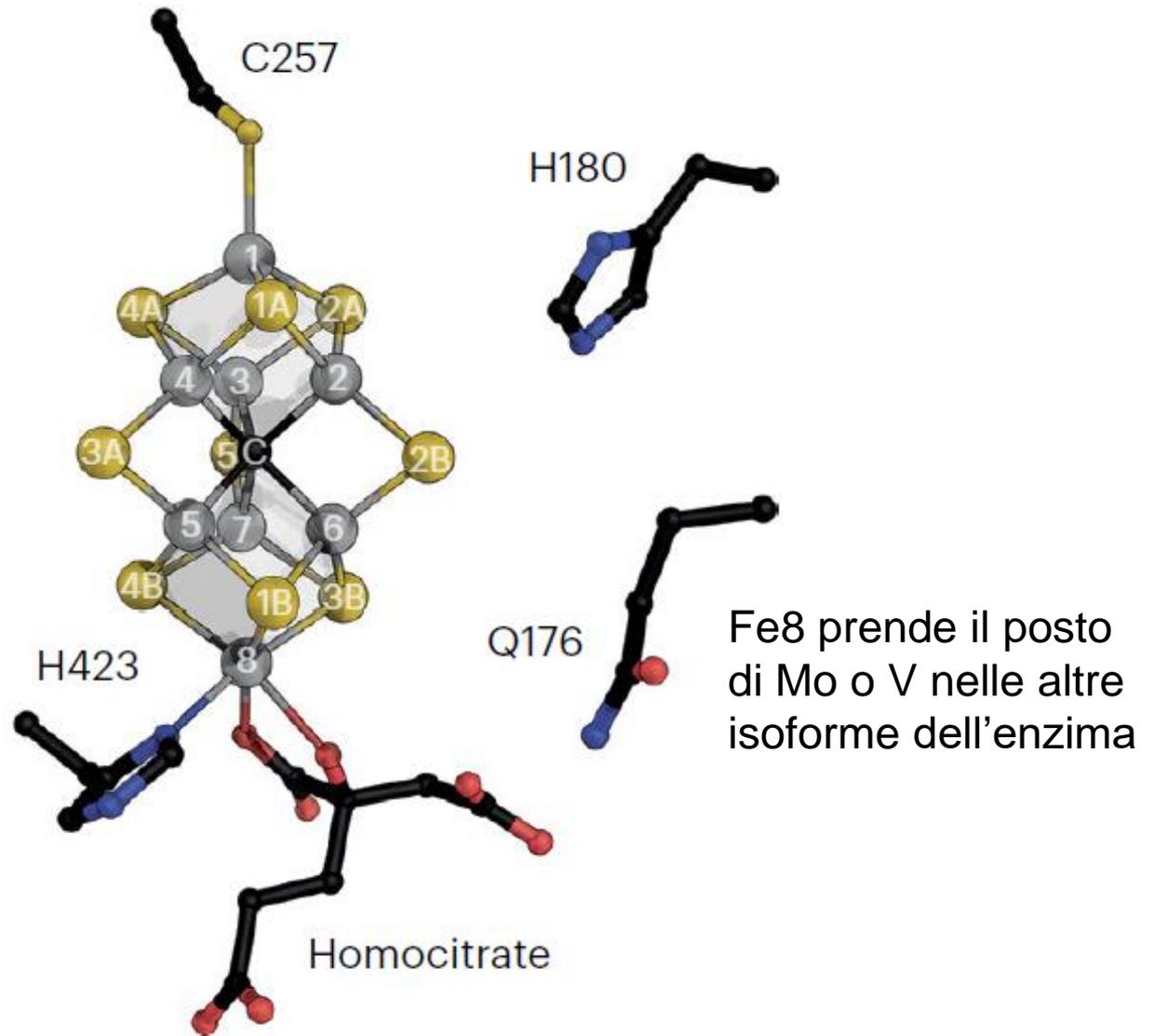
Interstitial atom identified as carbon



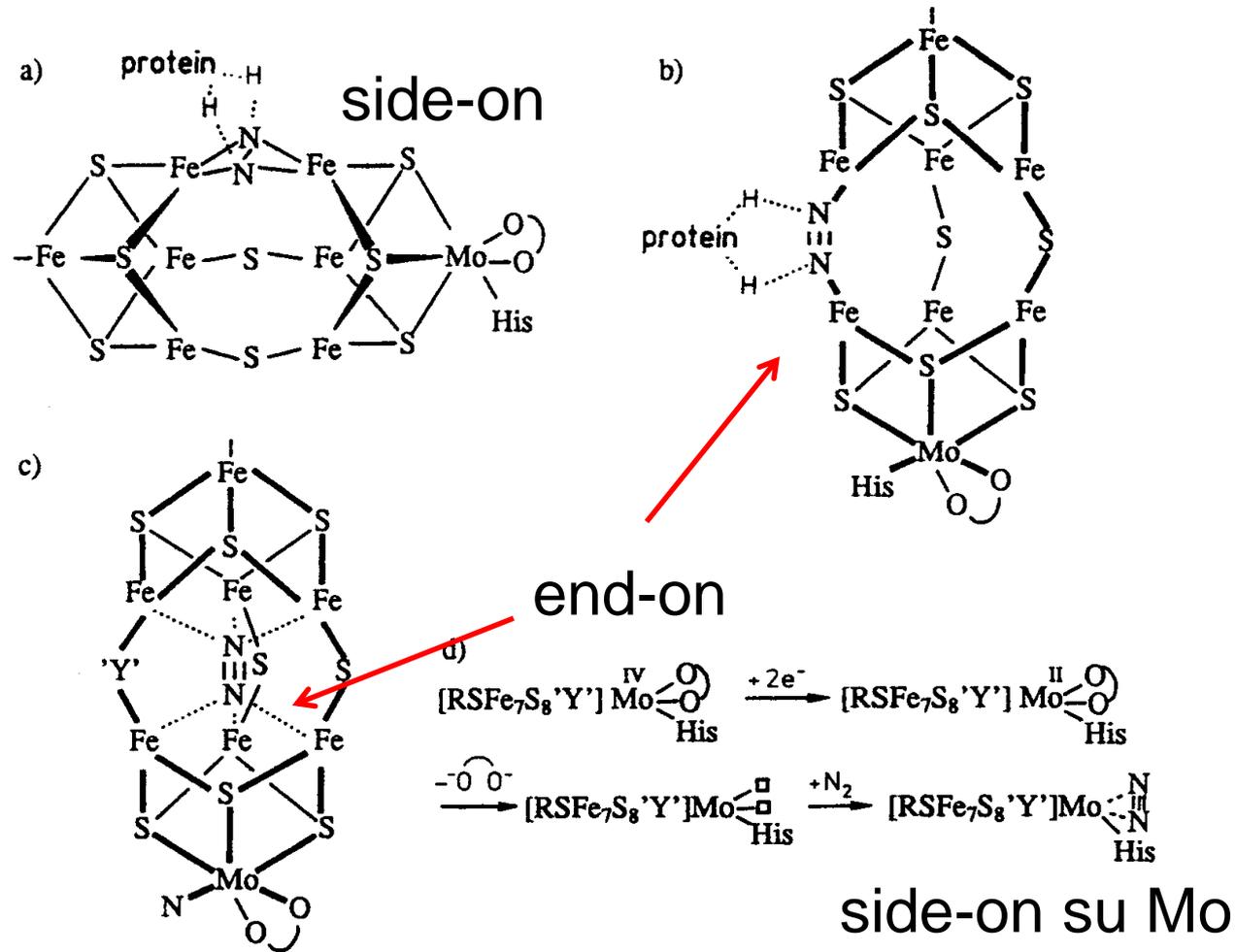
Percorso del trasferimento elettronico tra P-cluster e il cofattore FeMo



Struttura del cofattore FeFe

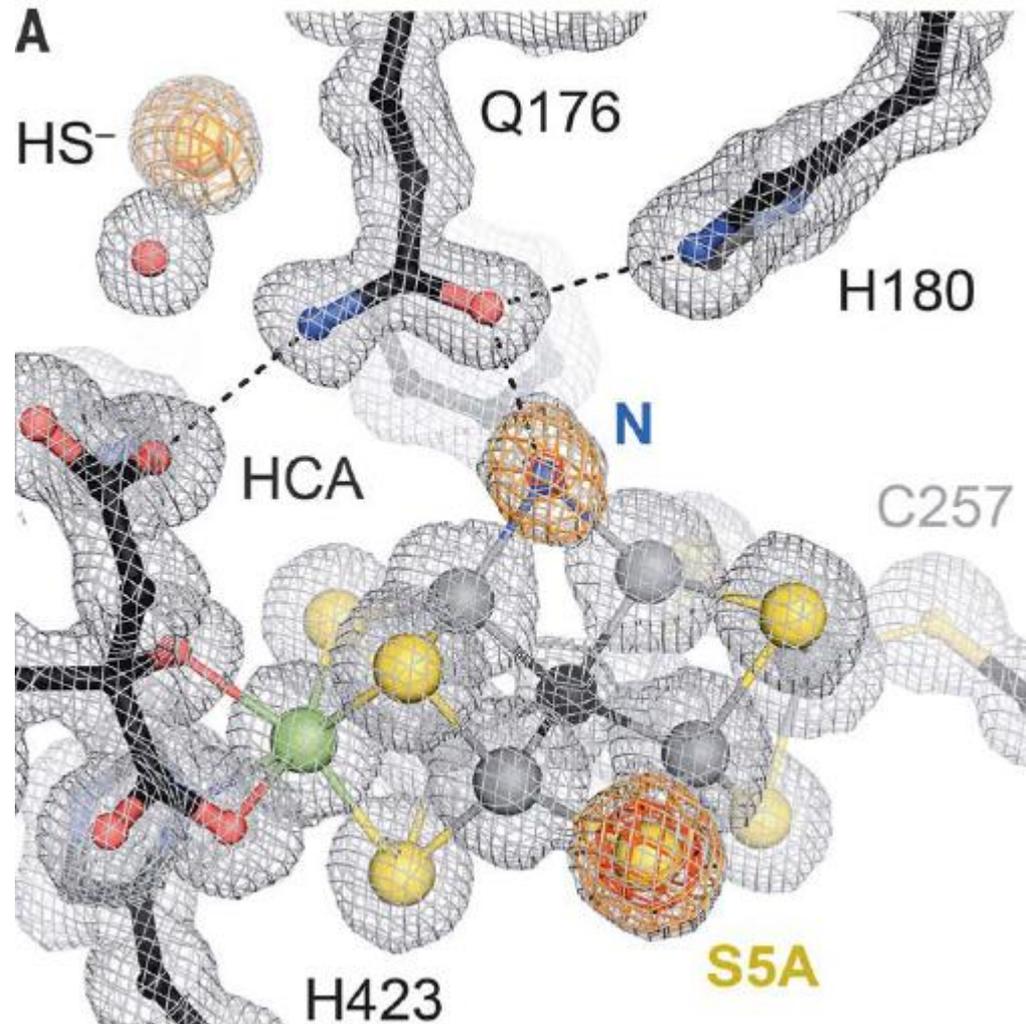


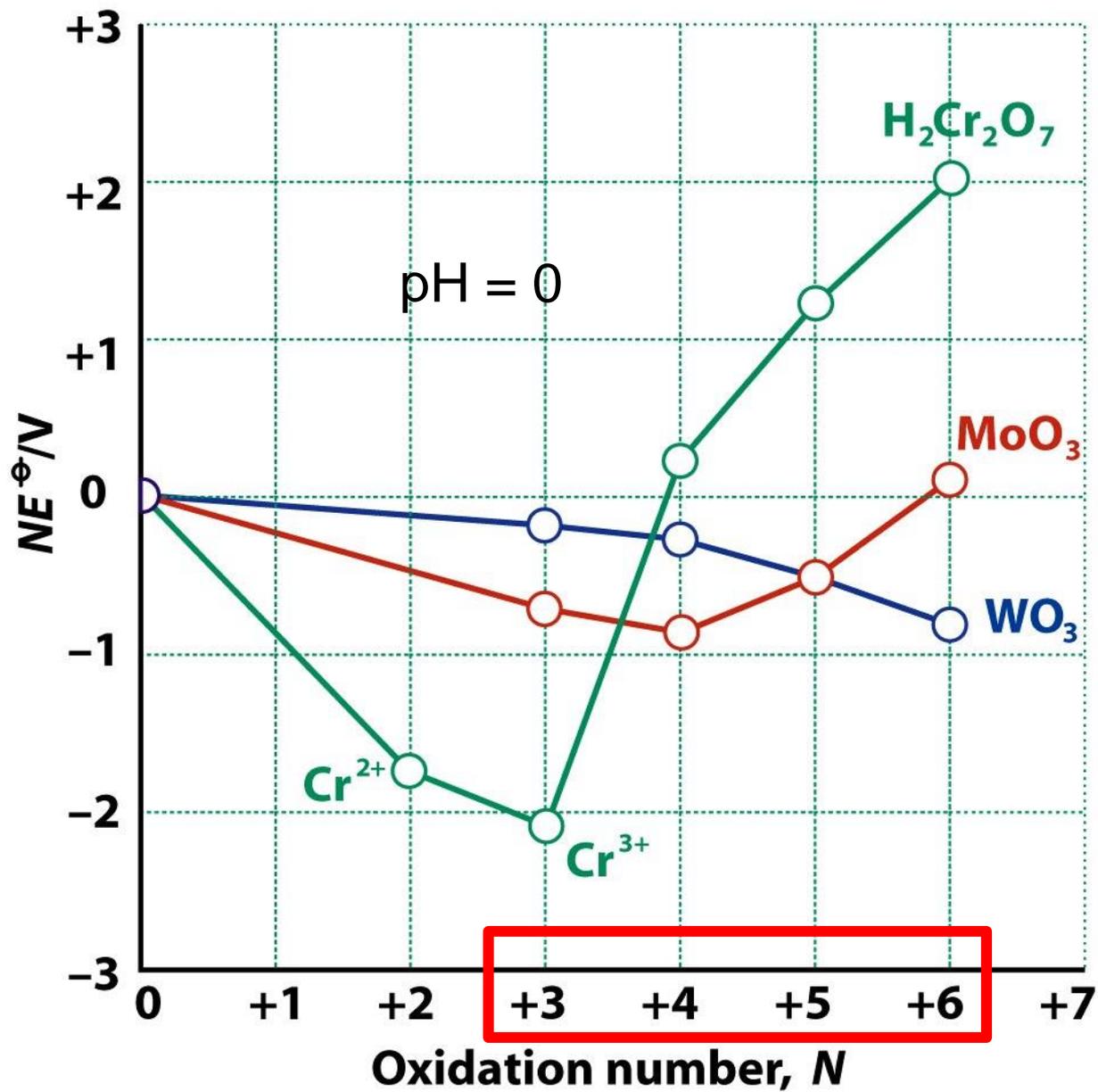
Ipotetici modi di coordinazione di N₂ al FeMoco



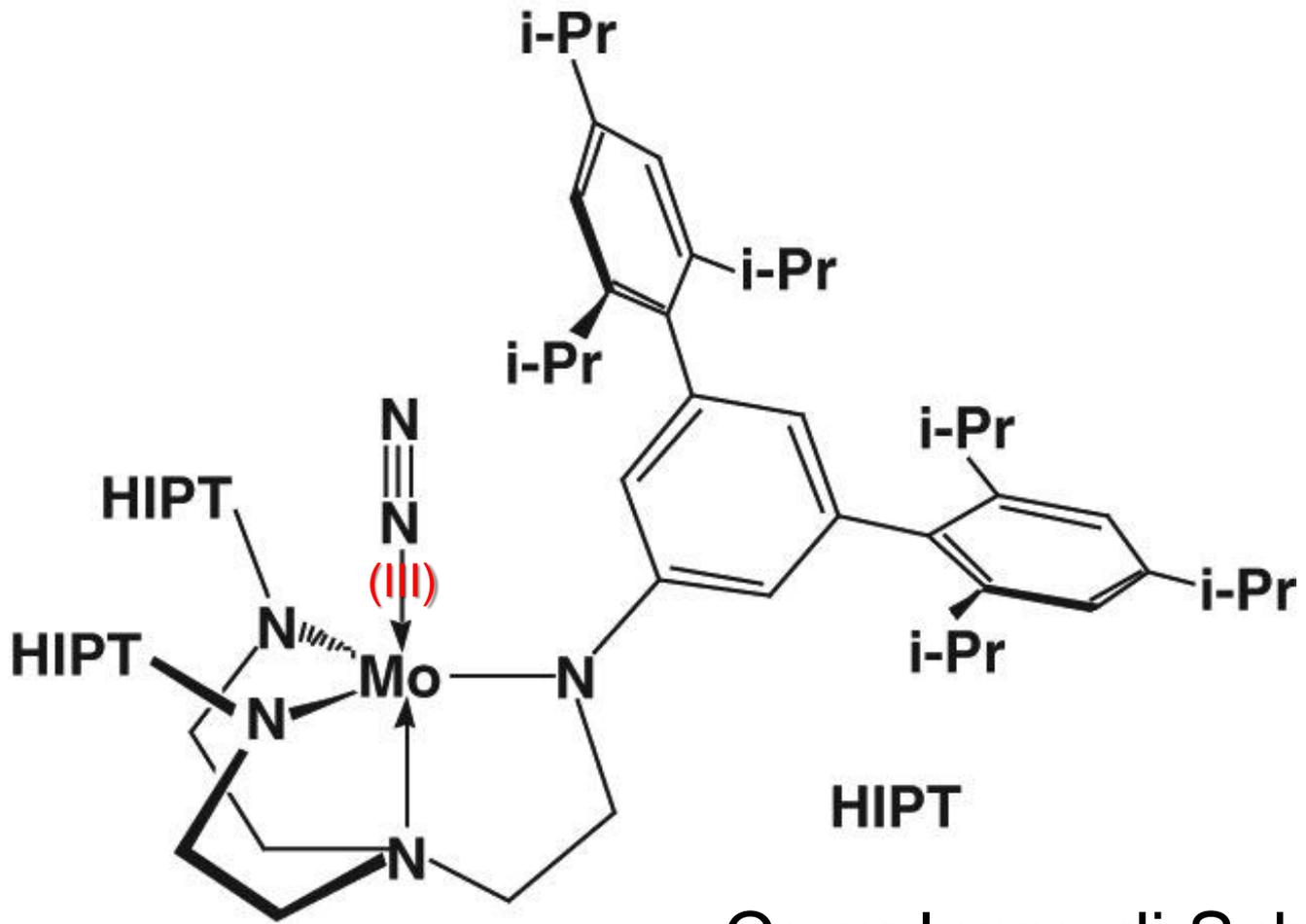
FeMo-co coordina N₂ solo dopo essere stato ridotto con 4 elettroni

Intermedio nel ciclo catalitico del cofattore FeV con (presumibilmente) un NH protonato nel sito attivo



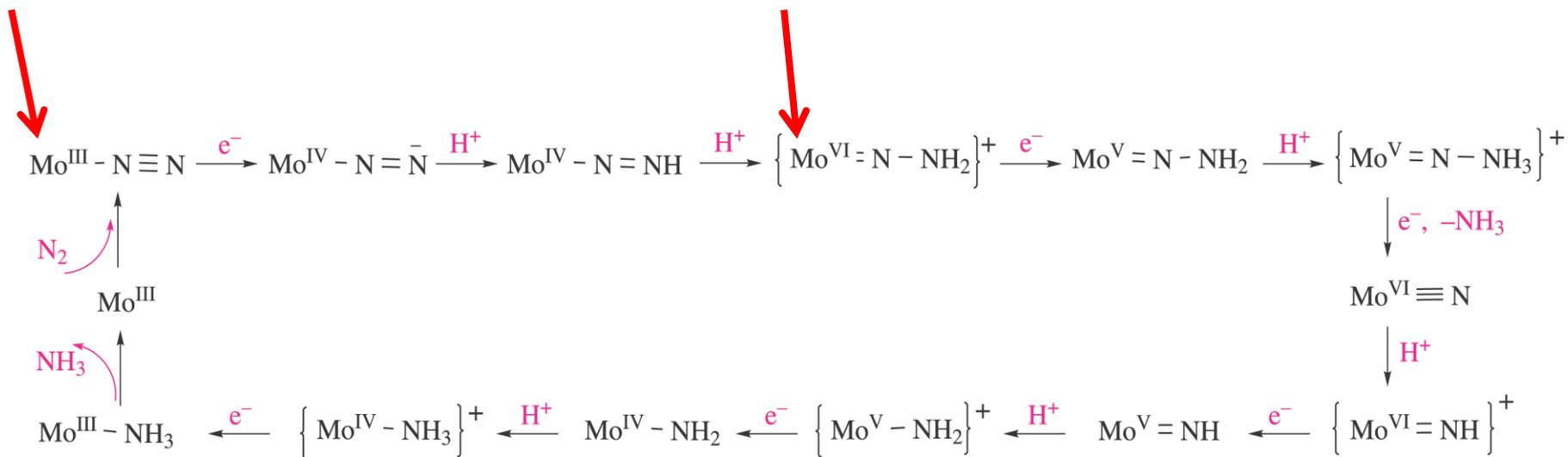
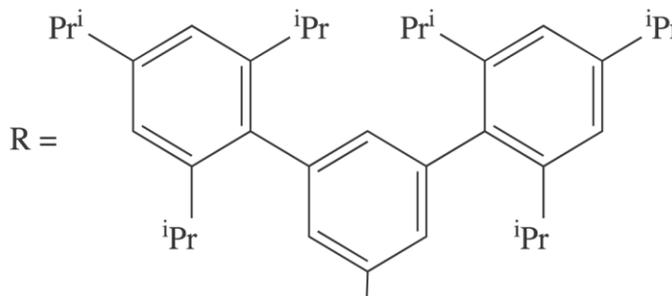
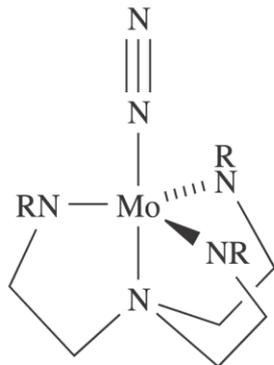


Modelli



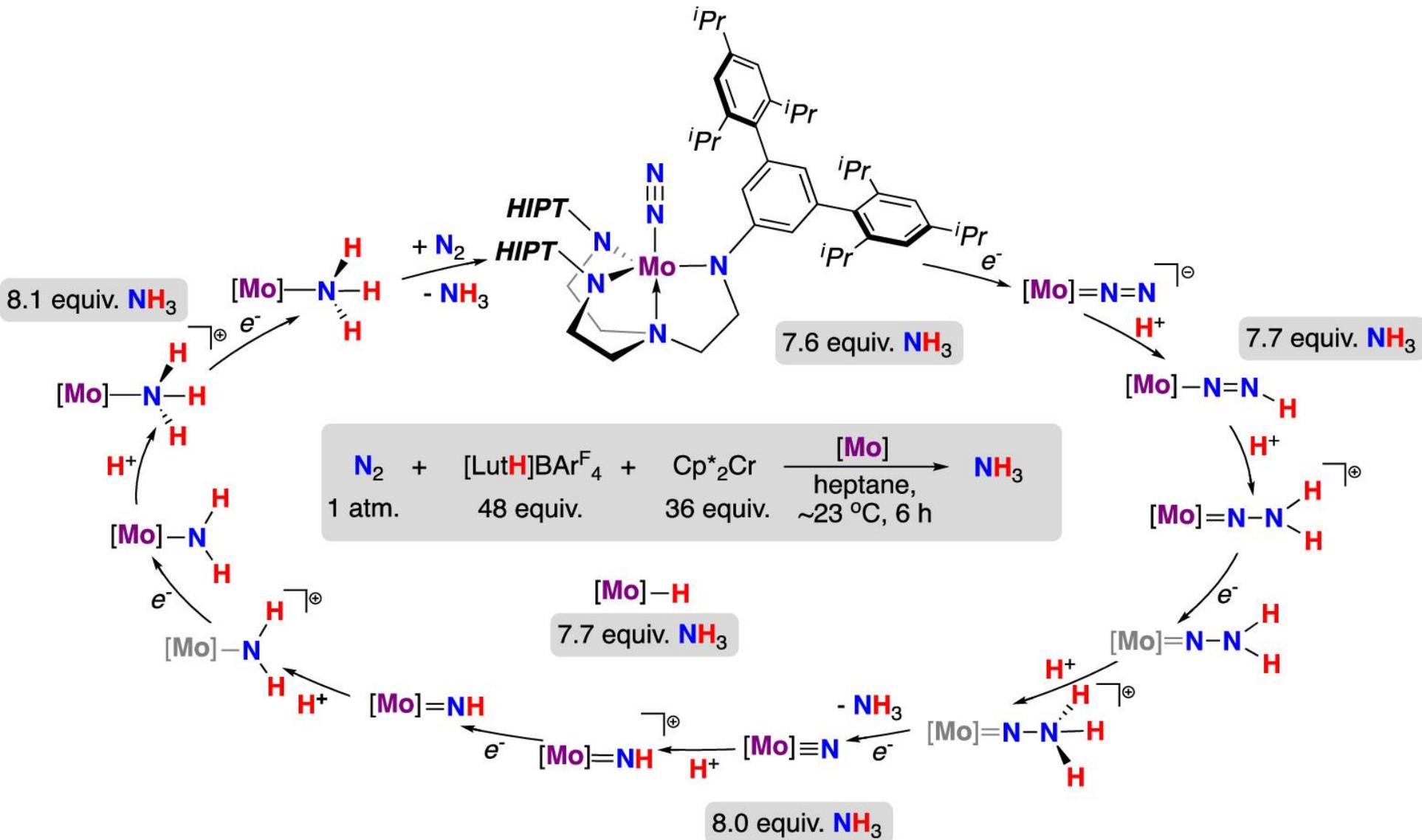
Complesso di Schrock
(*Science* 2003)

Schema della riduzione catalitica di N₂ a NH₃ su Mo



8 cicli catalitici, meccanismo *distale*

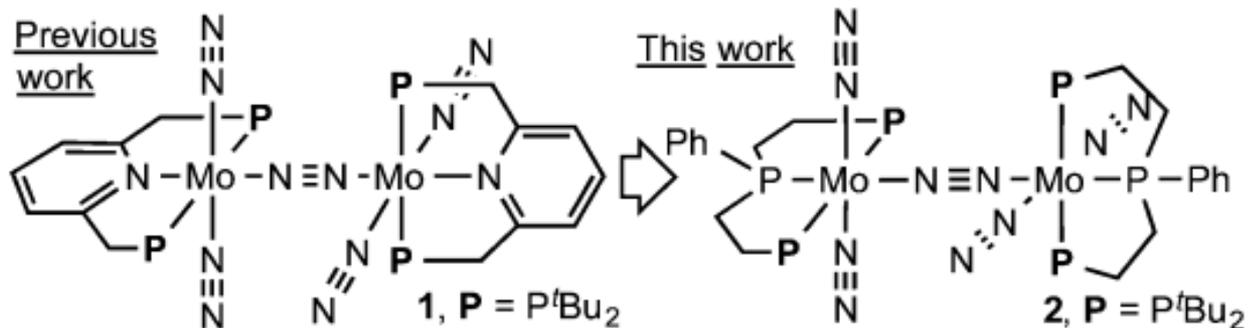
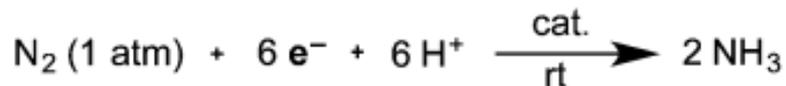
Ciclo catalitico di Schrock



In viola i composti caratterizzati, in grigio quelli ipotizzati

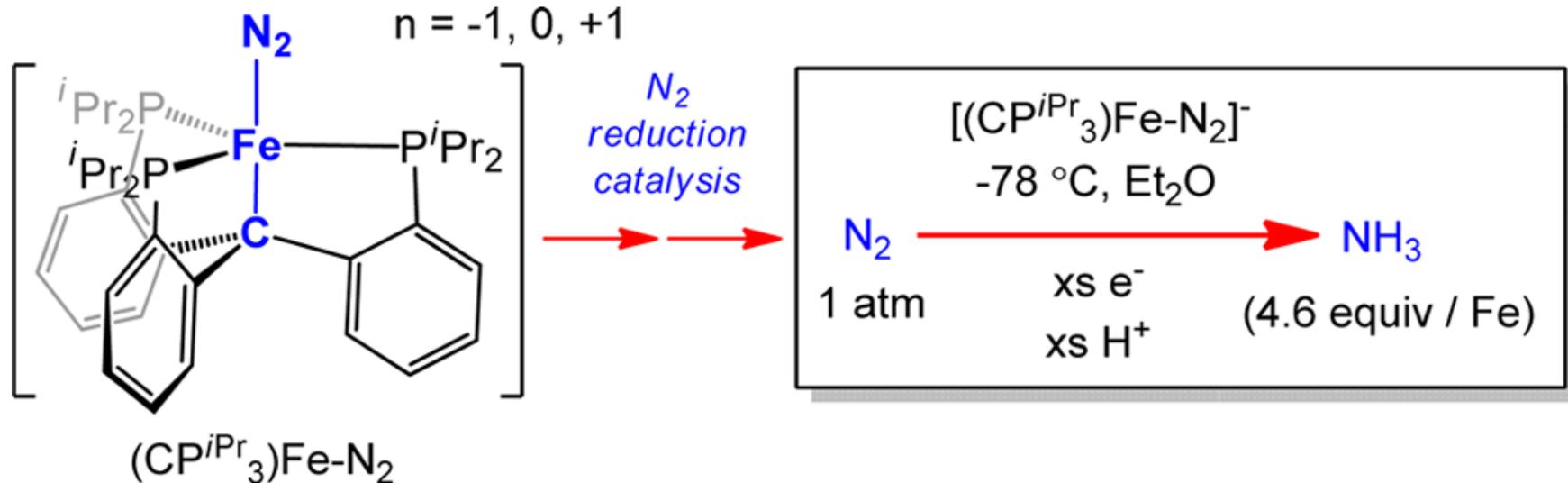
Complessi di Nishibayashi (2011 e 2015)

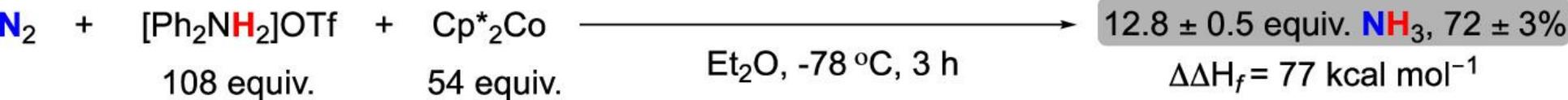
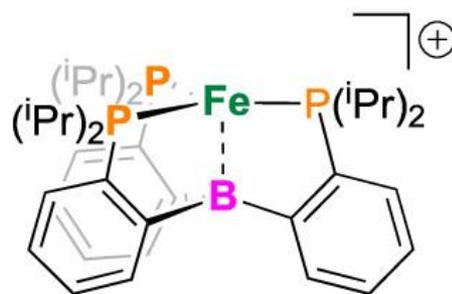
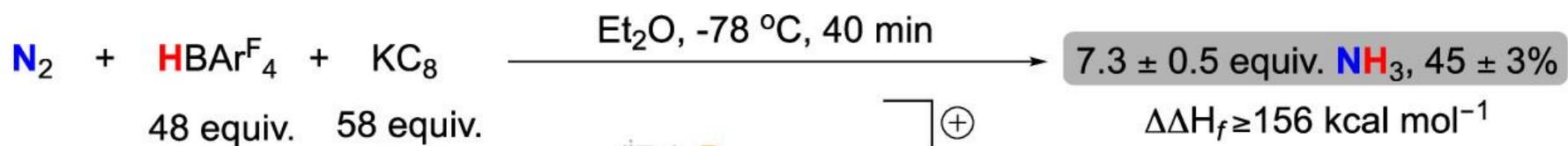
26 cicli catalitici, riducente CoCp^*_2



Complesso di Peters (2014)

4.6 cicli catalitici, riducente K(crown)



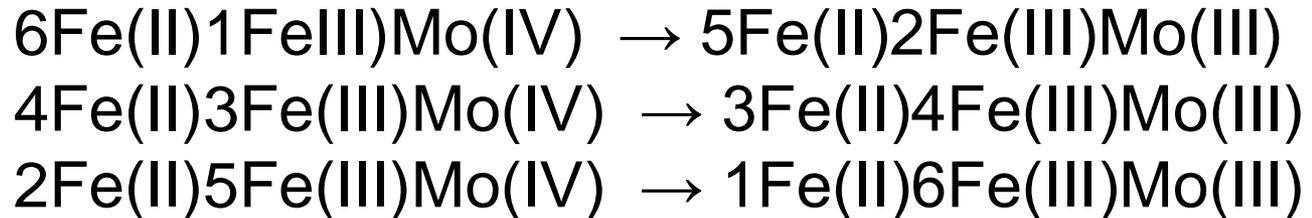


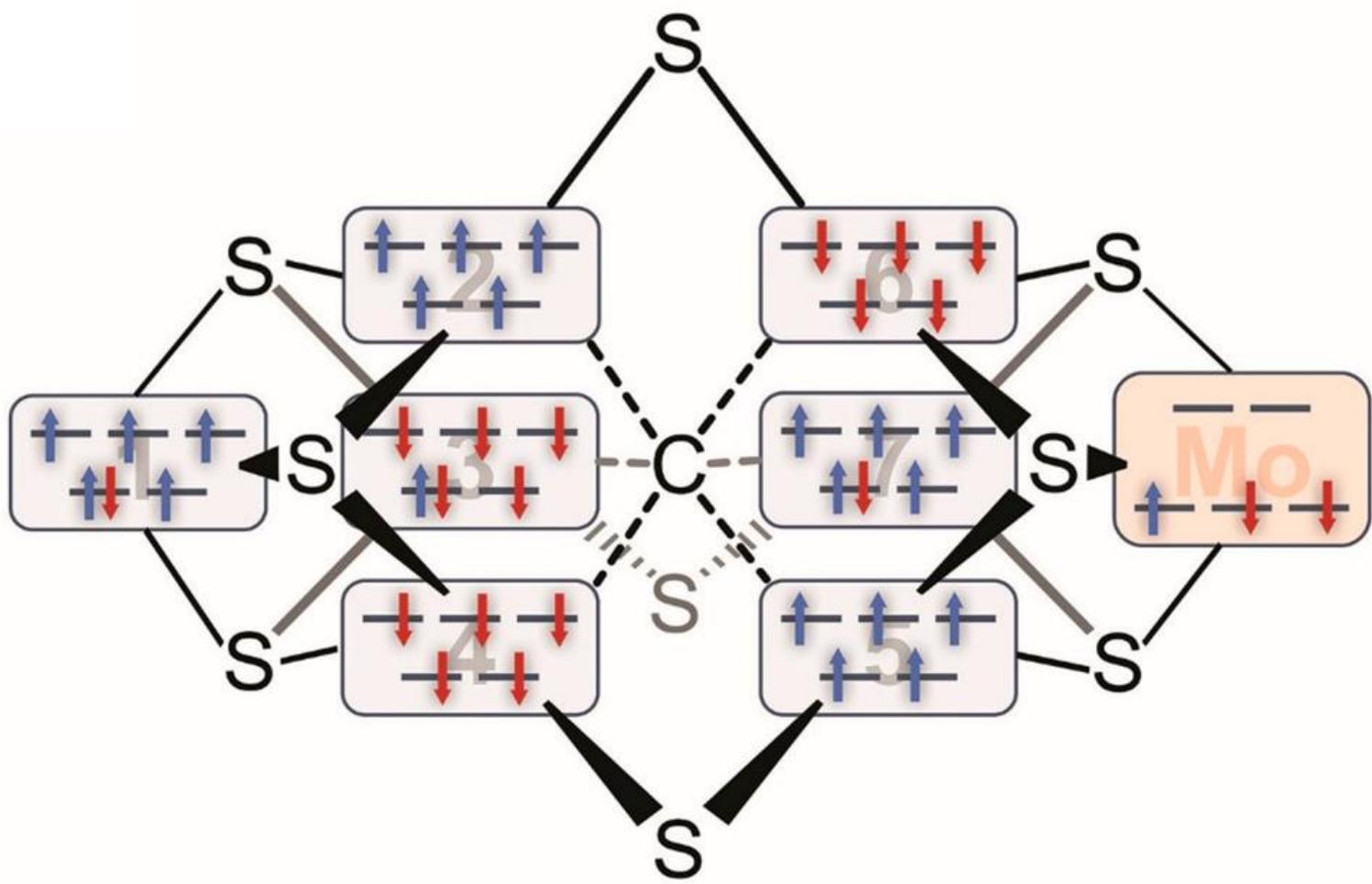
Struttura elettronica e di spin di FeMo-co

Resting state: $S = 3/2$

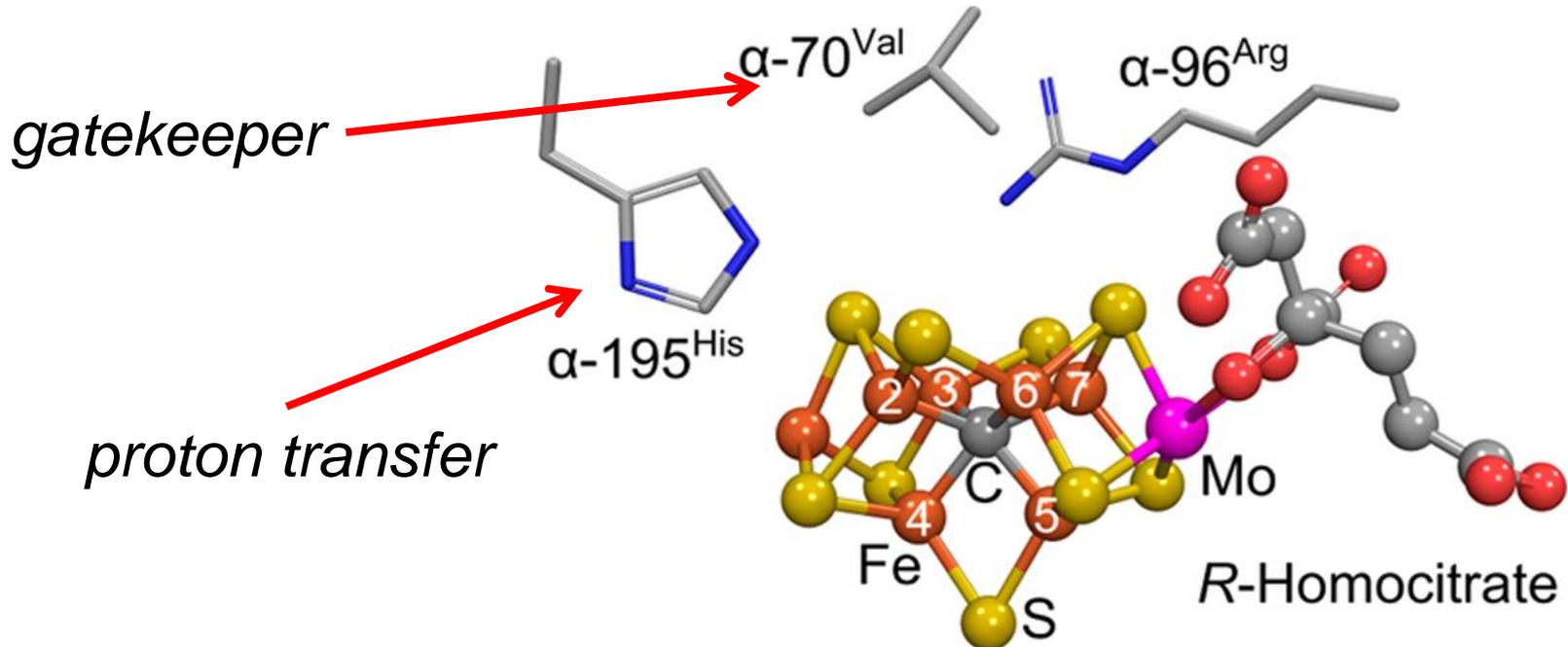
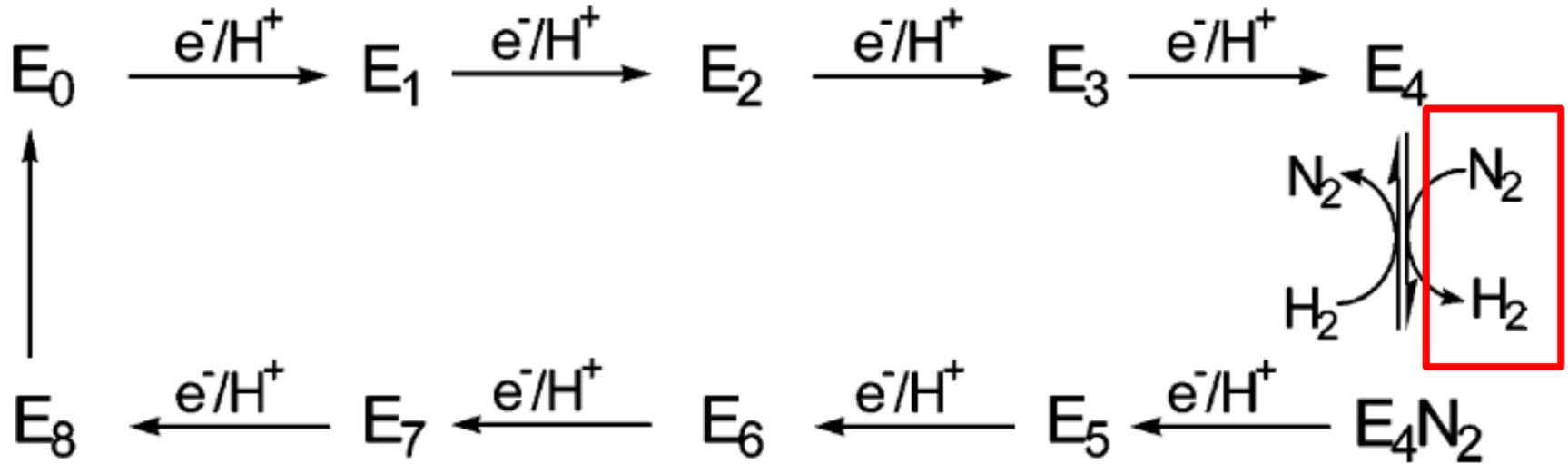
- | | | |
|---|-----------------------|-----------------------|
| 1) $[\text{MoFe}_7\text{S}_9\text{C}]^{3-}$ | 6Fe(II)1Fe(III)Mo(IV) | |
| 2) $[\text{MoFe}_7\text{S}_9\text{C}]^{1-}$ | 4Fe(II)3Fe(III)Mo(IV) | Mo(IV), d^2 $S = 0$ |
| 3) $[\text{MoFe}_7\text{S}_9\text{C}]^{1+}$ | 2Fe(II)5Fe(III)Mo(IV)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

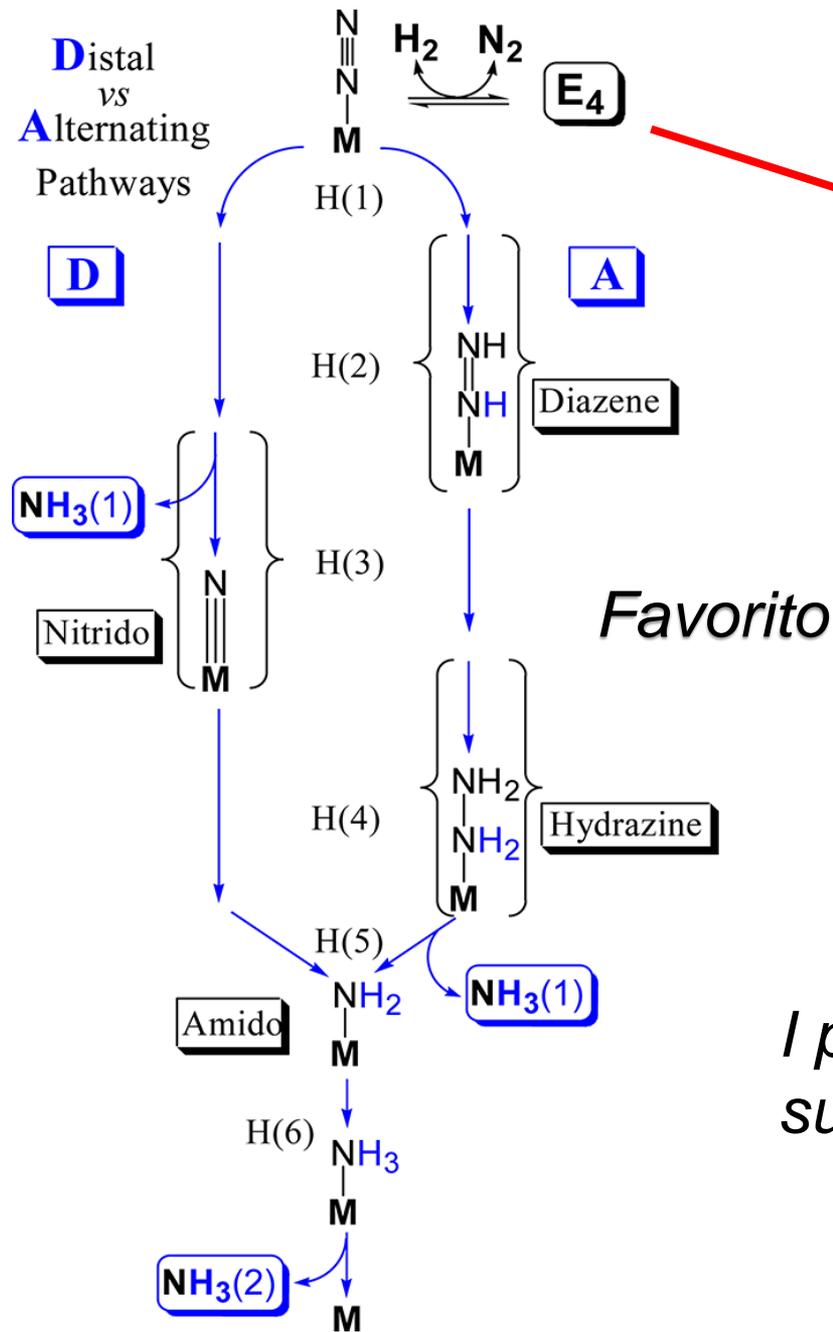
2014: Mo(III), d^3 basso spin ($\uparrow\uparrow\downarrow$)? (violazione della regola di Hund)



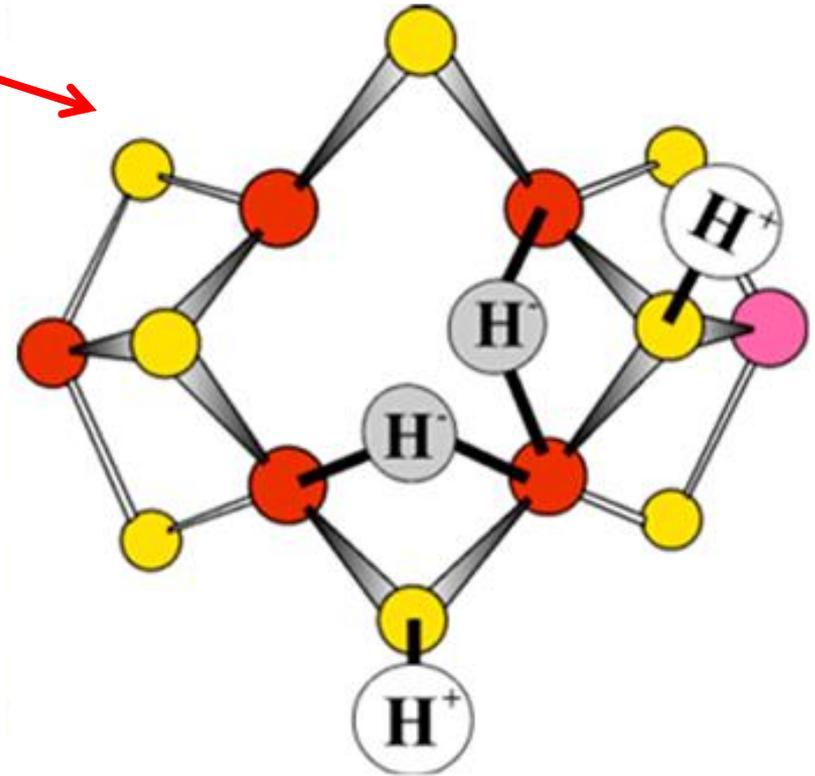


Ciclo catalitico



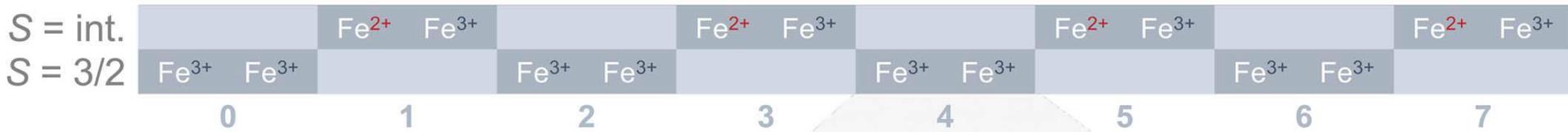
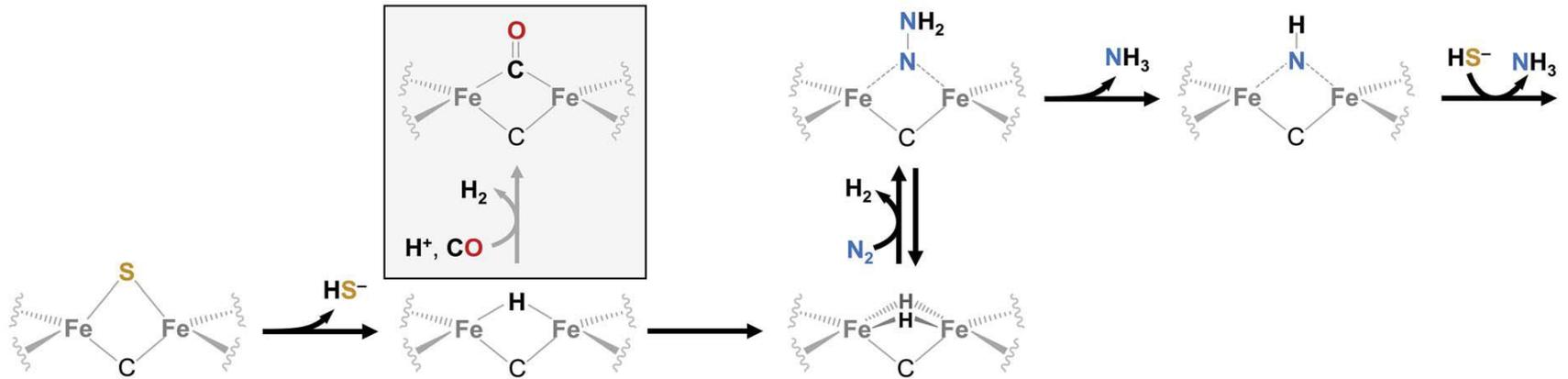


Modello di E₄

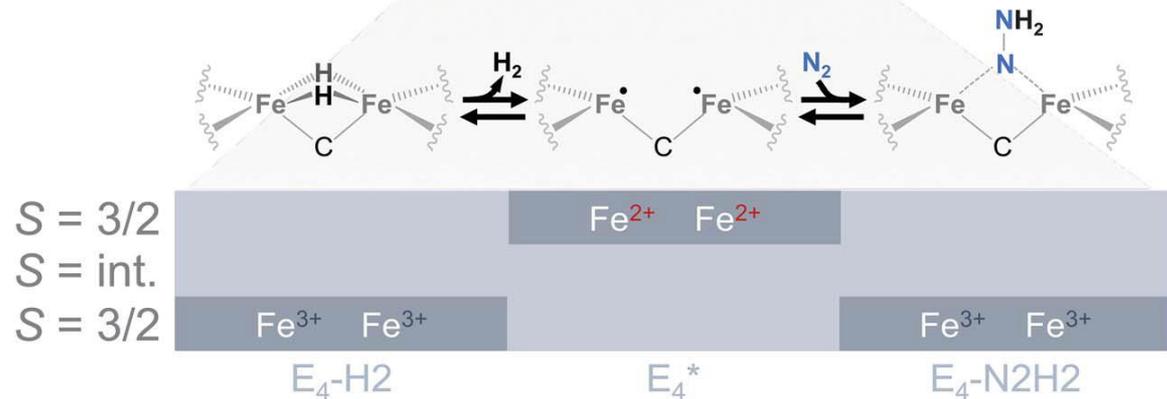


I primi 4 elettroni si accumulano sugli idruri e non sugli atomi di ferro

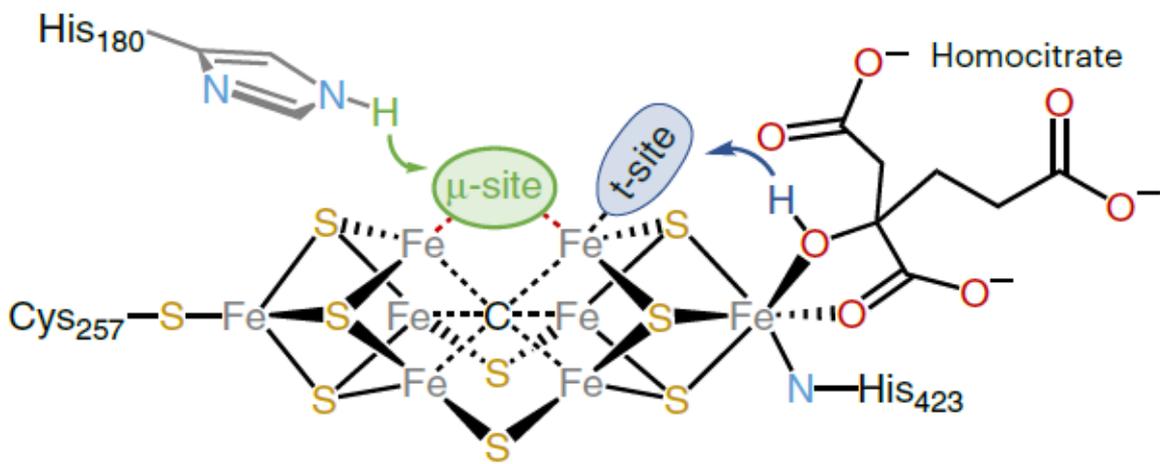
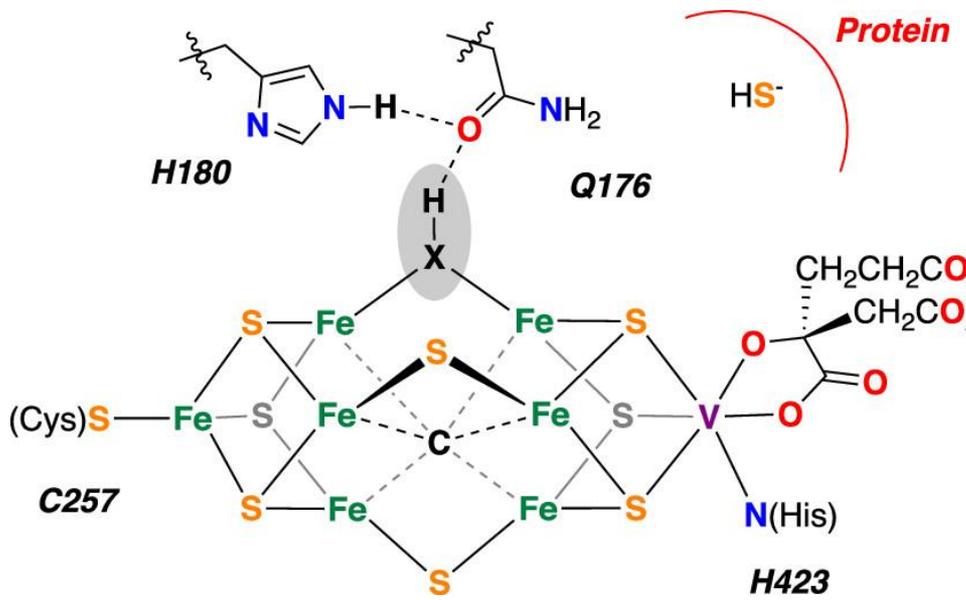
Ipotesi di trasferimento elettronico

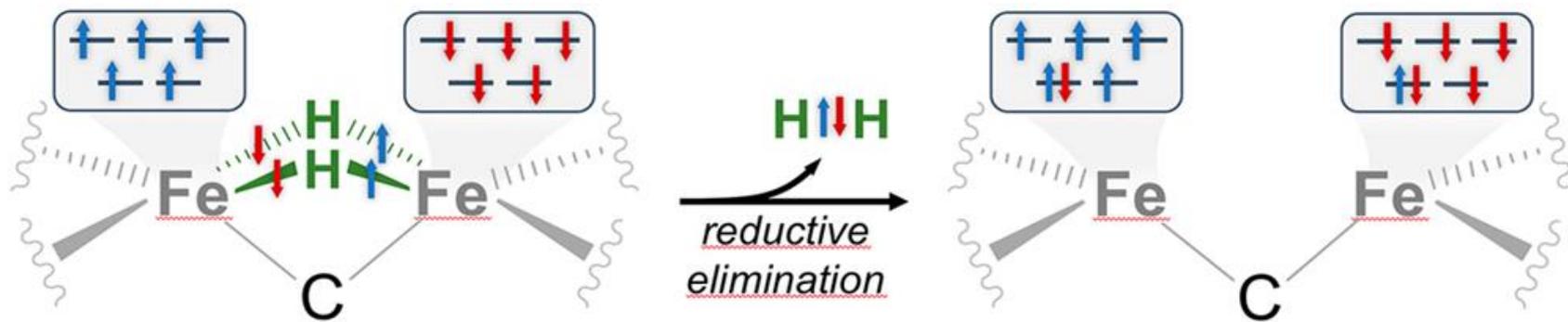


Nel ciclo catalitico il FeMoco cambia di una sola unità il suo stato di ossidazione complessivo (E_n dispari)



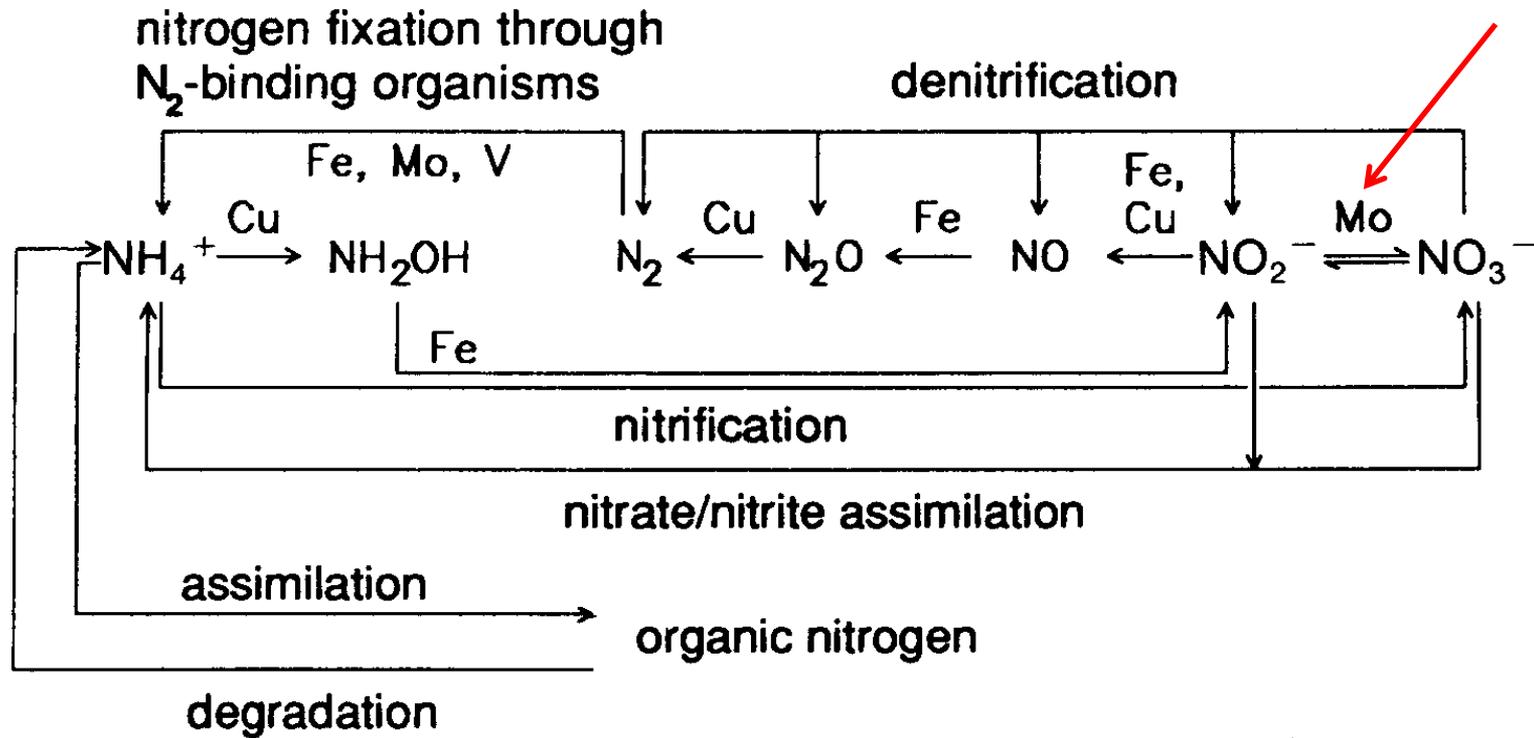
Ipotesi di sito catalitico tra Fe2 e Fe6, dopo spostamento del solfuro a ponte





Altri enzimi al molibdeno

catalizzano la ossidazione o la riduzione di piccole molecole

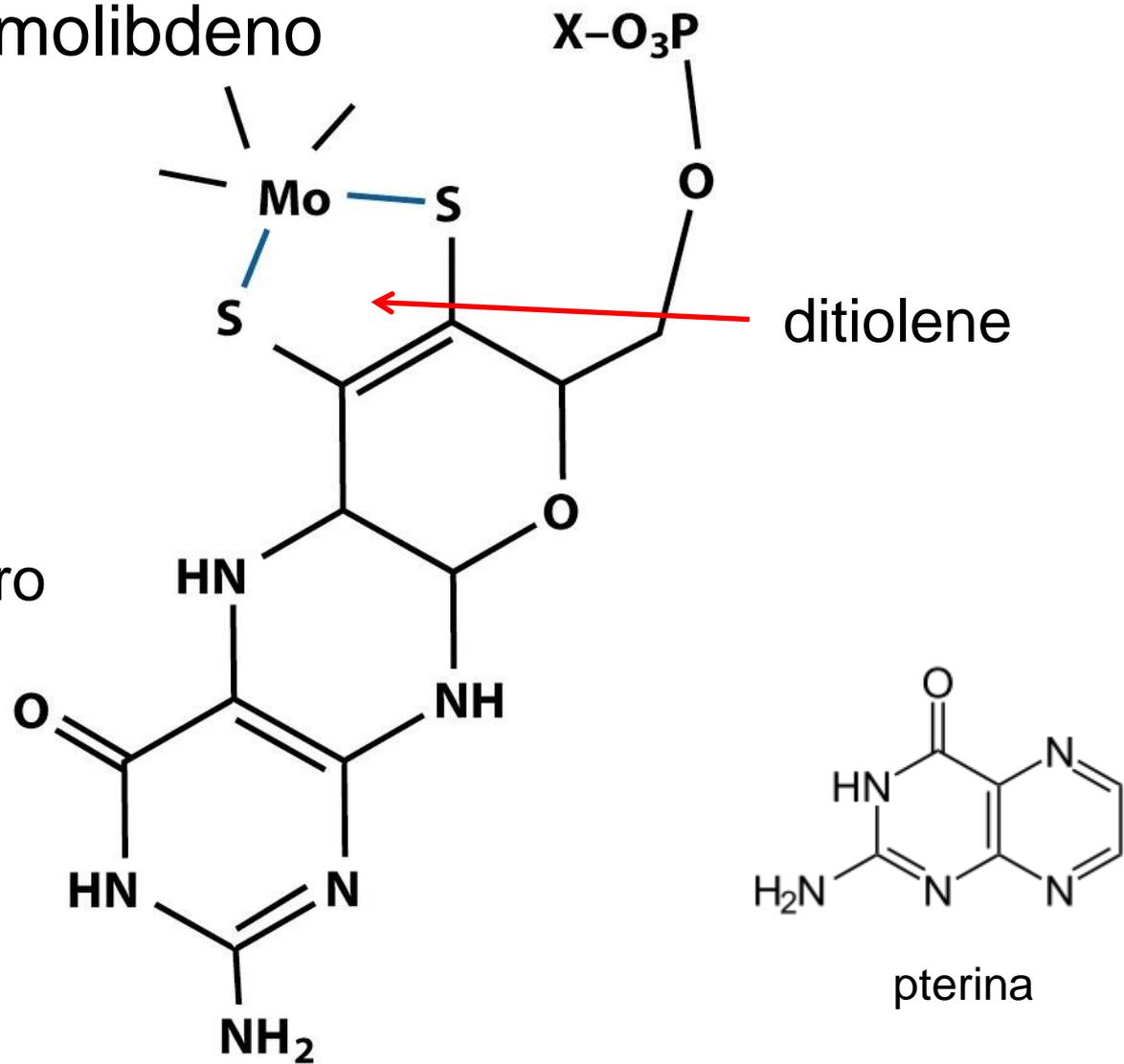


Tre famiglie di enzimi al Mo (*osso-trasferasi*)

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

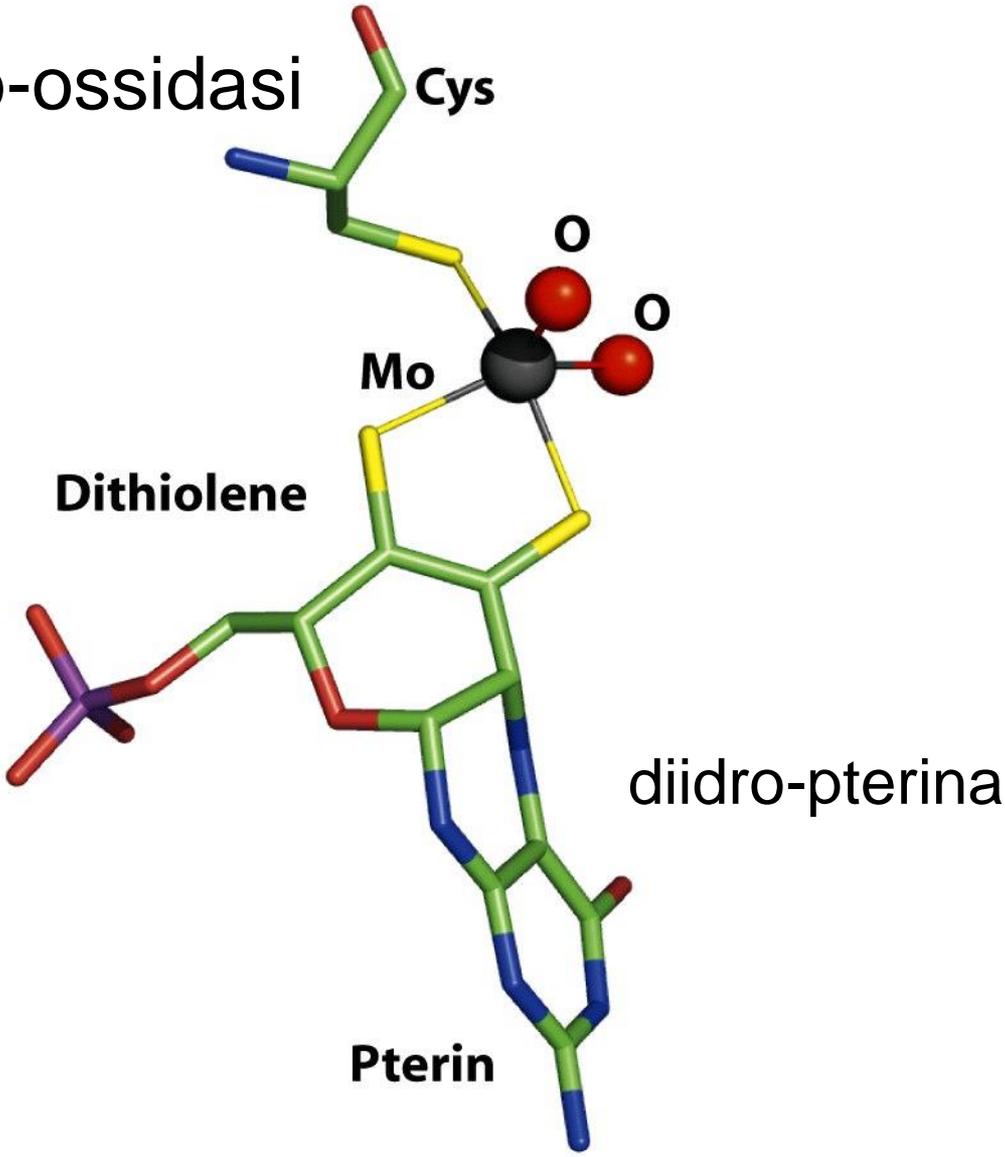
Cofattore del molibdeno

di-idro o tetra-idro
pterina

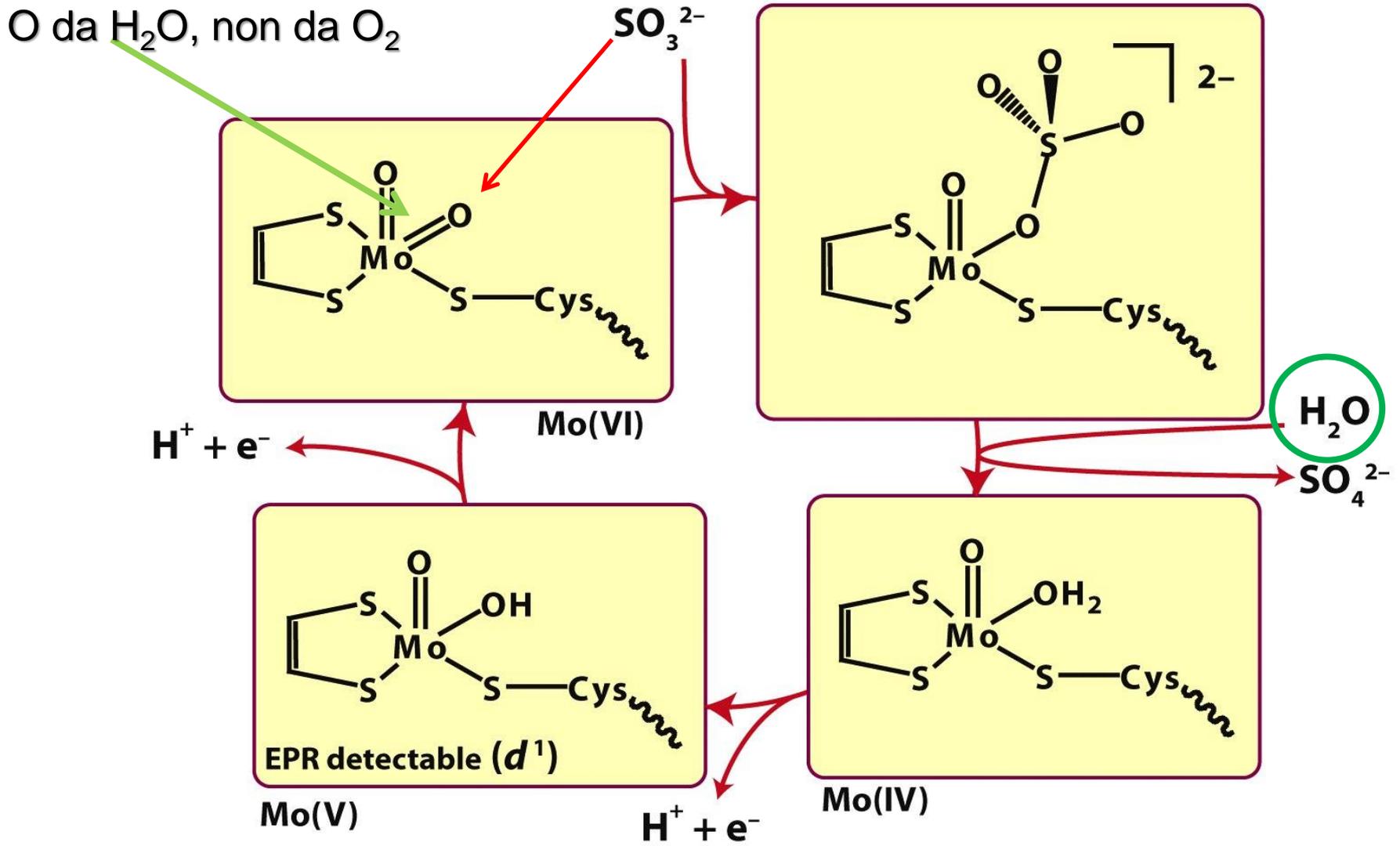


Molybdopterin as ligand

Sito della solfito-ossidasi

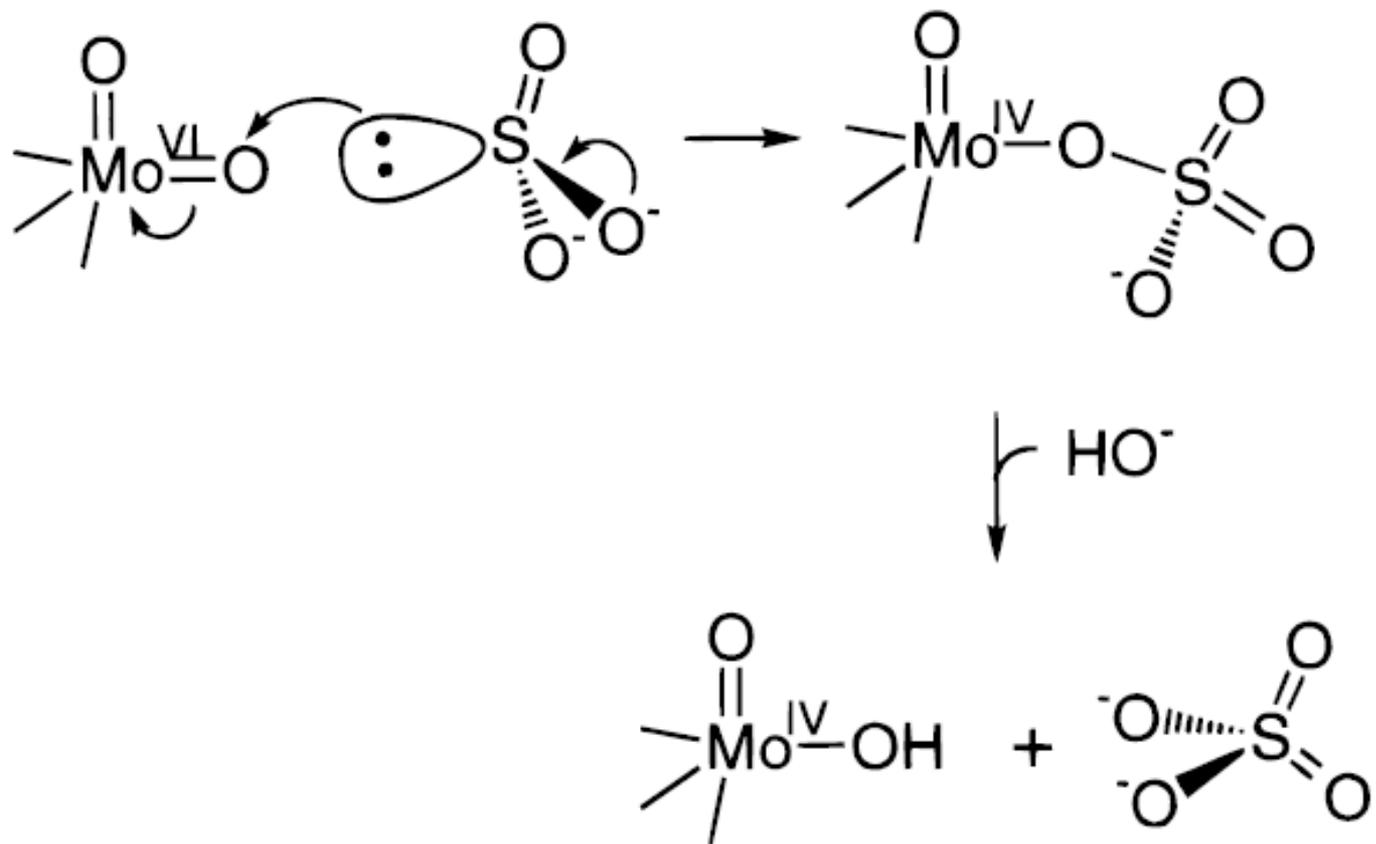


Ciclo catalitico della solfito-ossidasi

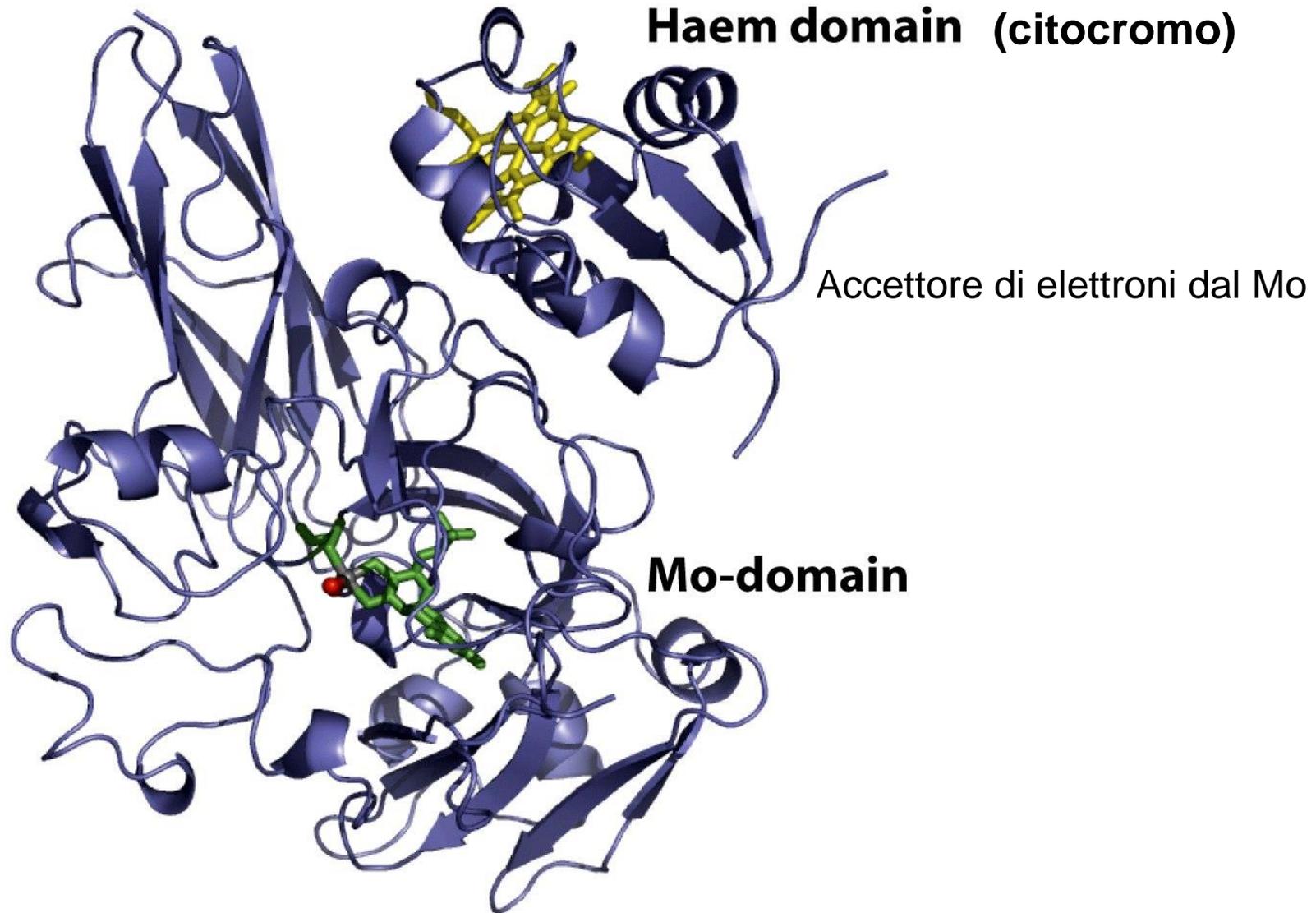


Mo possiede tre stati di ossidazione stabili, Mo(IV), Mo(V) e Mo(VI)

Dettaglio del meccanismo di trasferimento di ossigeno



Struttura della solfito-ossidasi



Scala di entalpia delle reazioni di trasferimento di atomi di ossigeno

