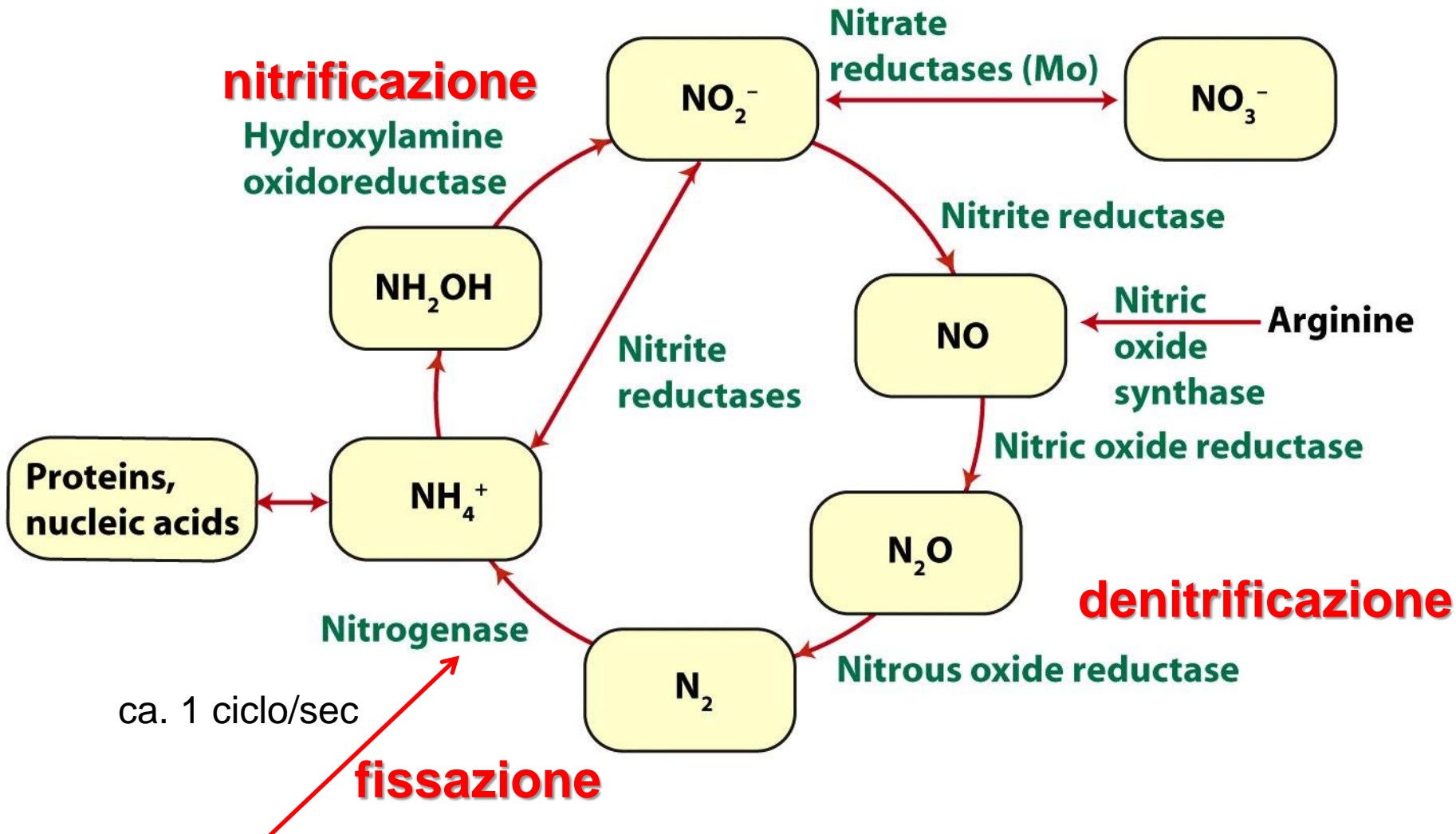
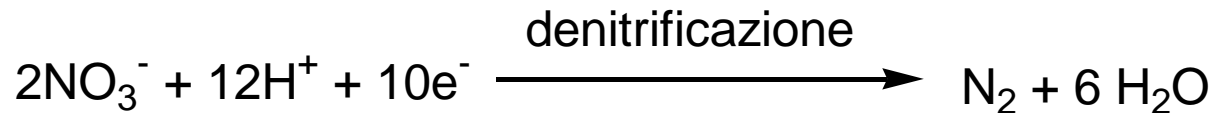
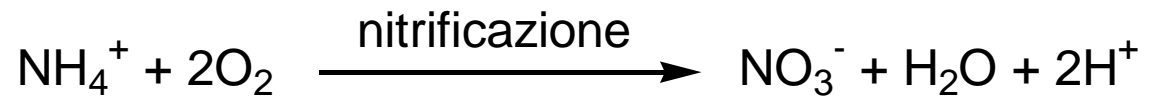
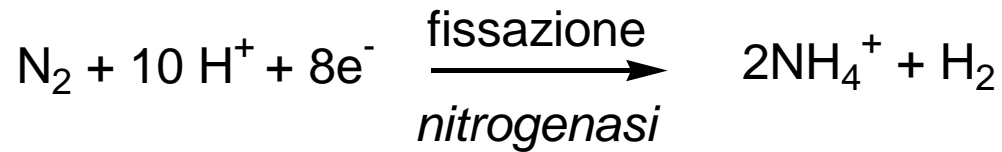
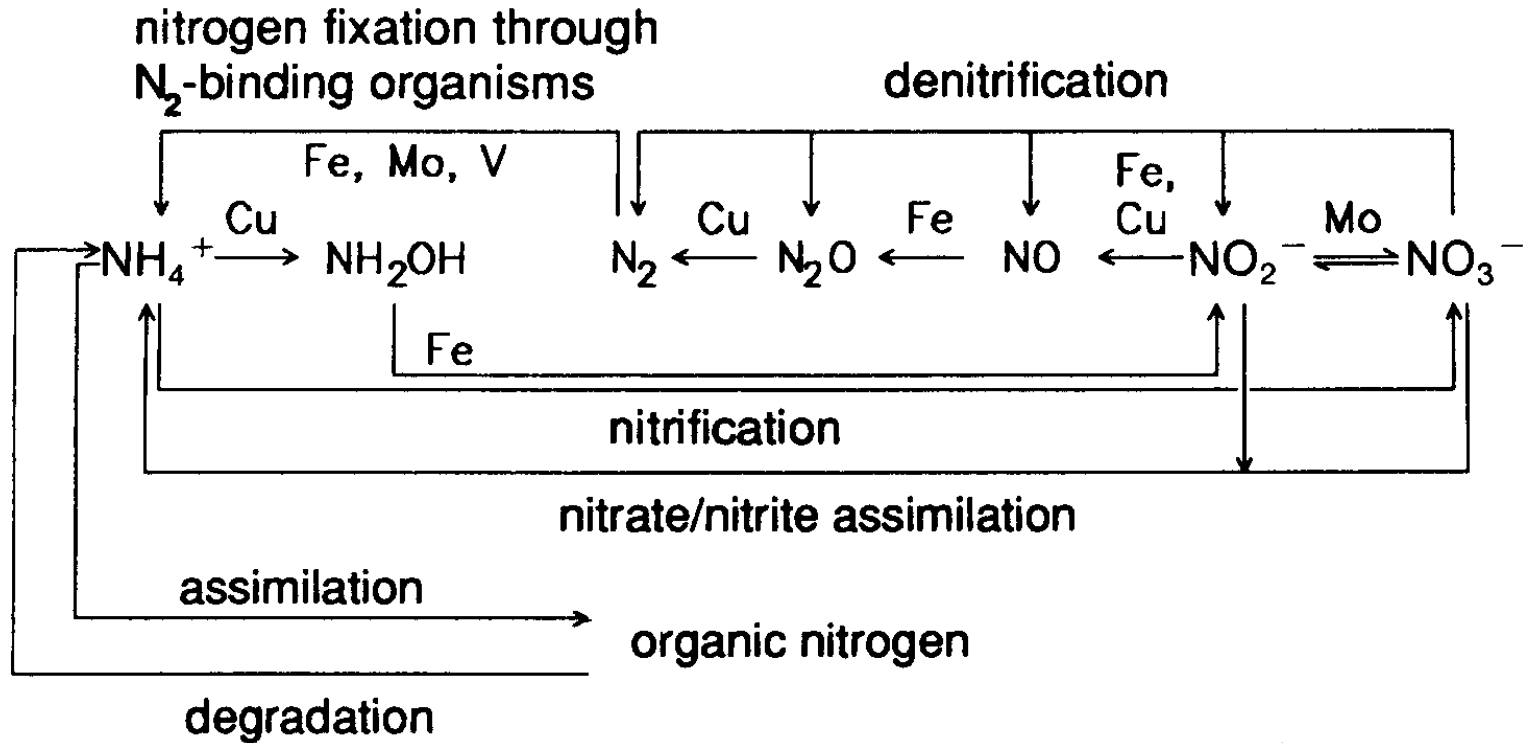


# Ciclo dell'azoto



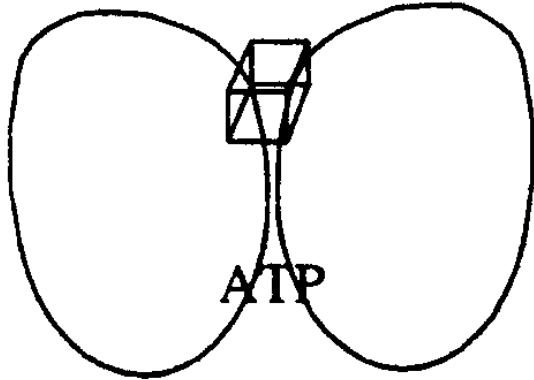
Batteri procarioti diazotropici: 10<sup>8</sup> ton N<sub>2</sub>/y



# Nitrogenasi



1992

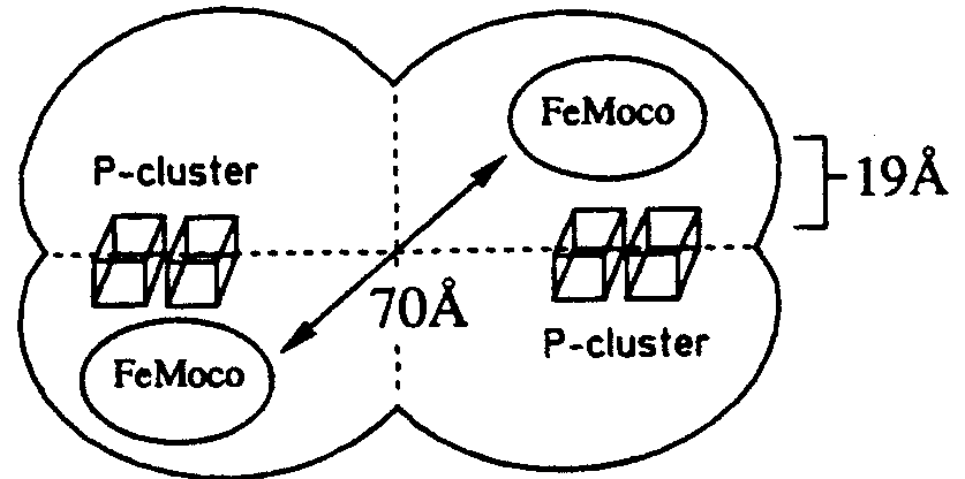


**Fe protein**

$\gamma_2$

60 kDa

+



**FeMo protein**

$\alpha_2\beta_2$

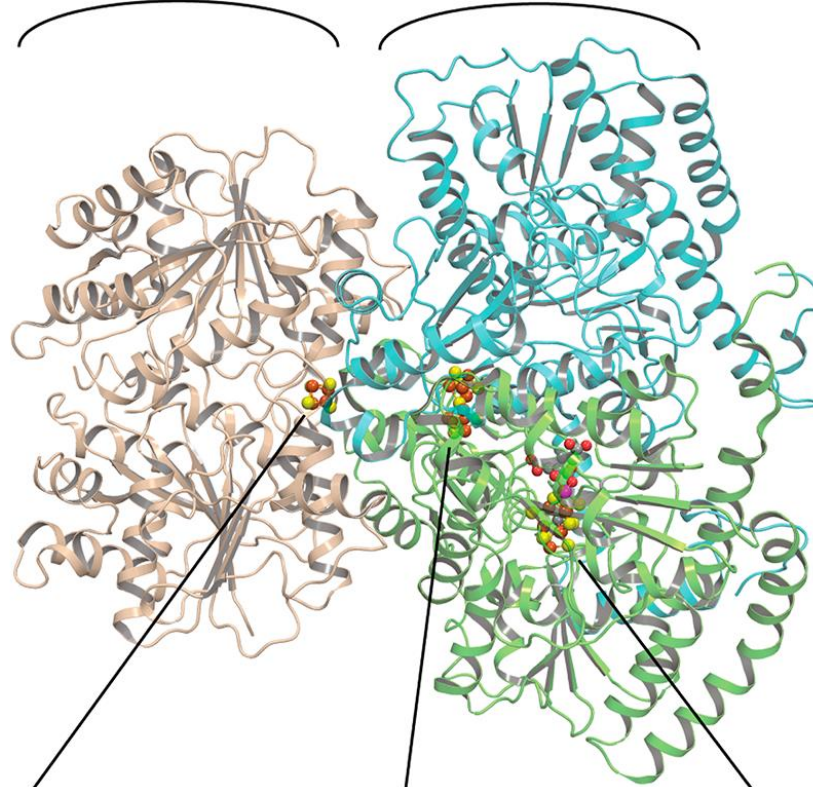
220 kDa

# Nitrogenasi

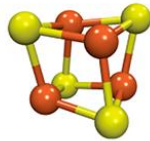
Fe protein

MoFe protein

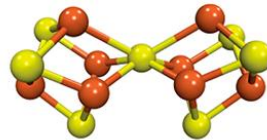
(A)



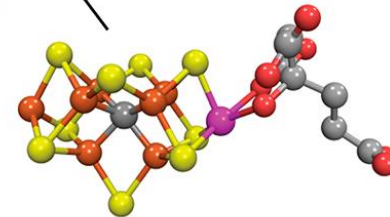
(B)



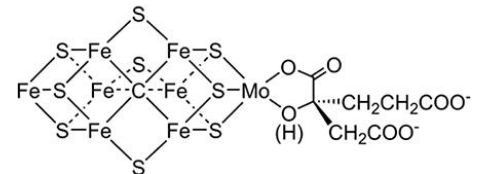
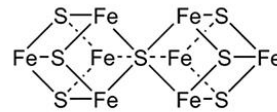
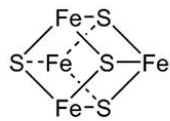
F cluster



P cluster

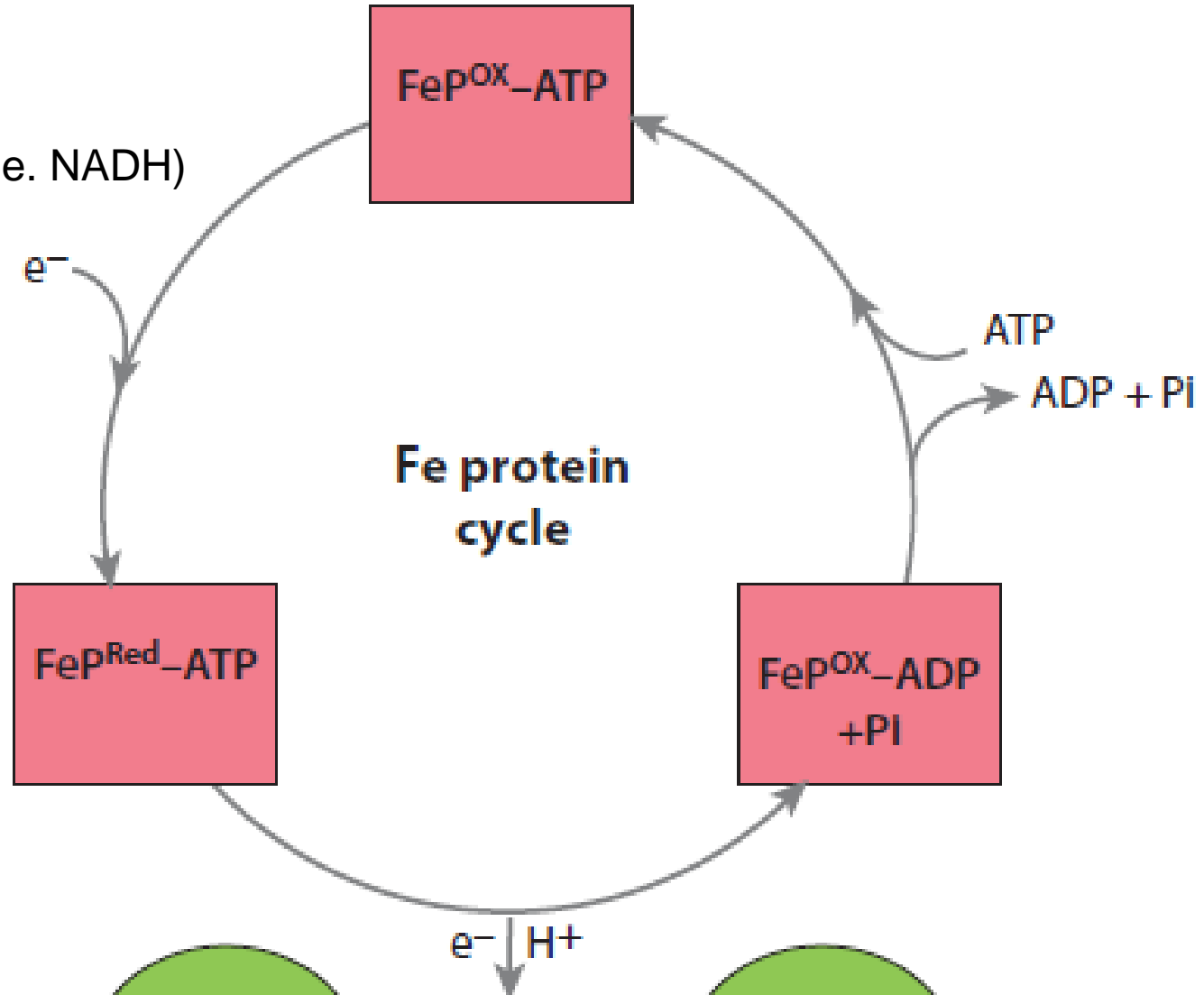


M cluster (FeMoco)

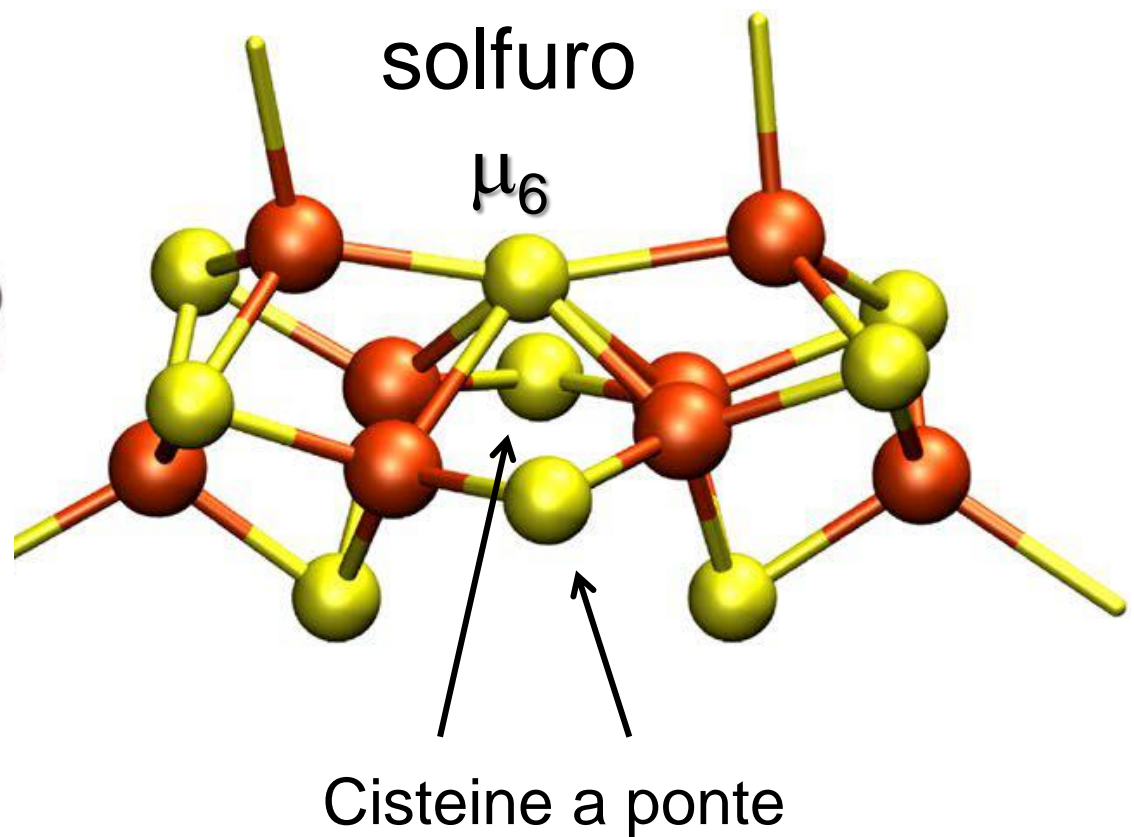
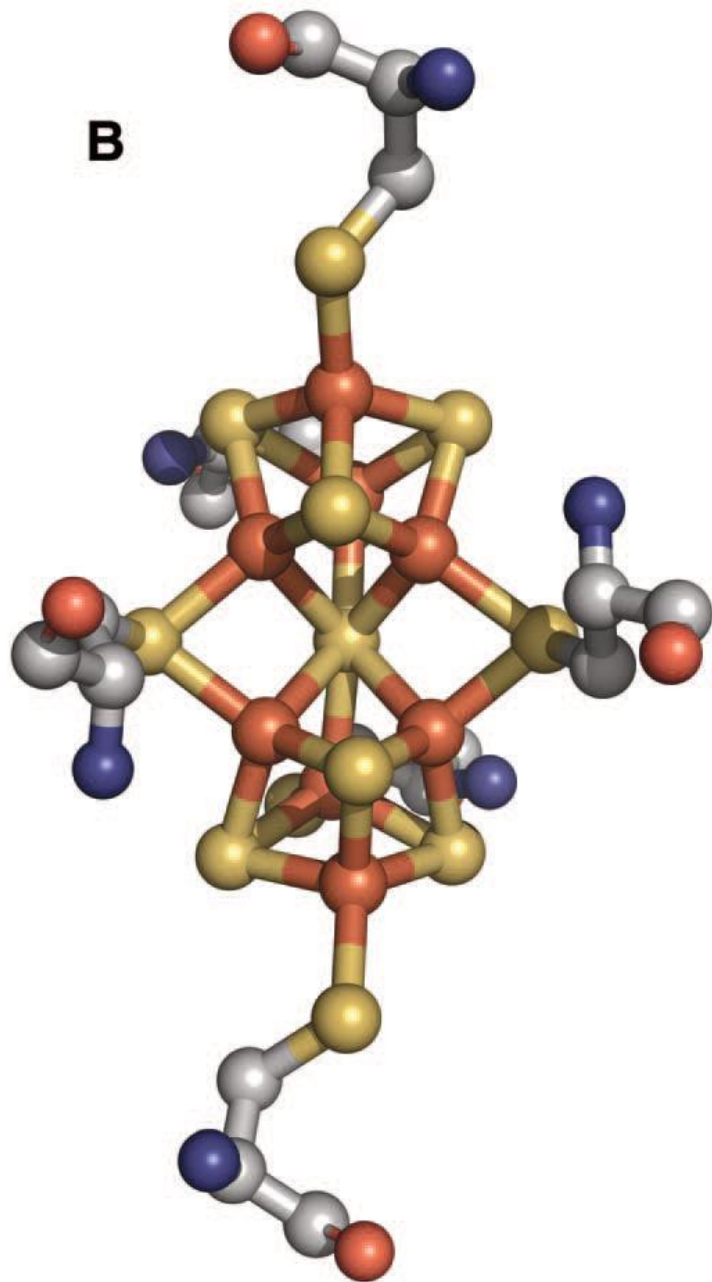


# Fe-proteina

ferridossina o  
flavodossina (i.e. NADH)

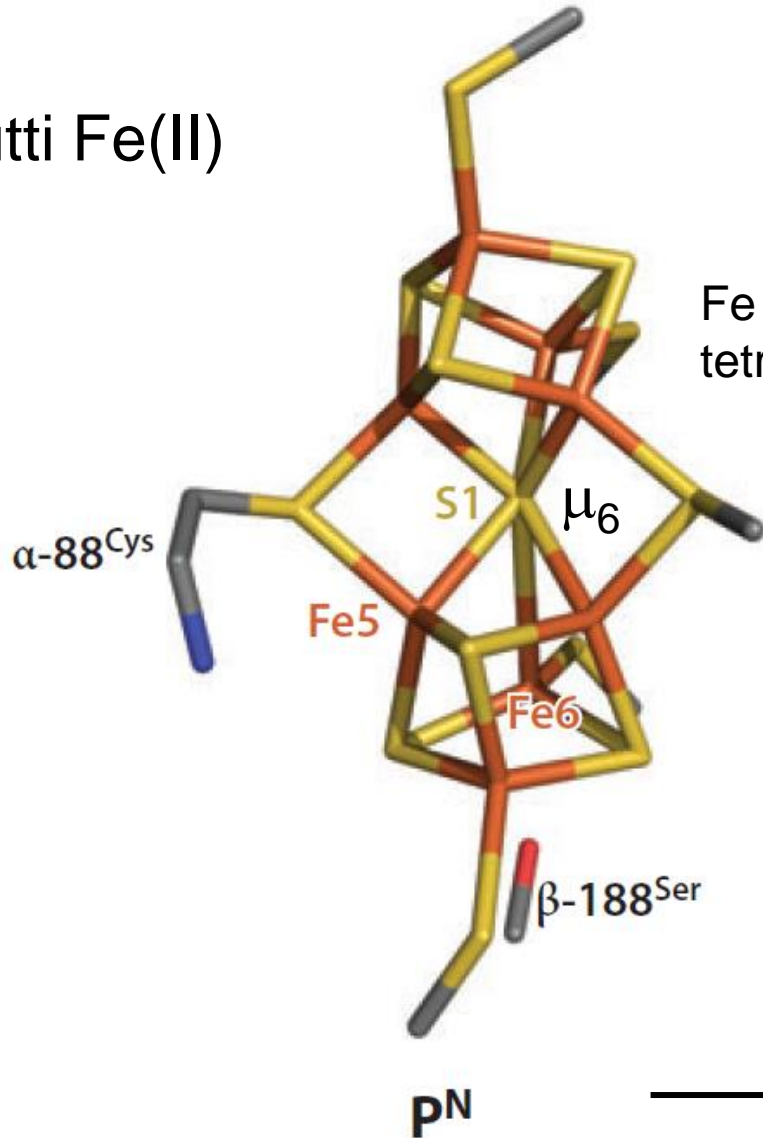


# P-cluster 8Fe-7S



# P-cluster 8Fe-7S

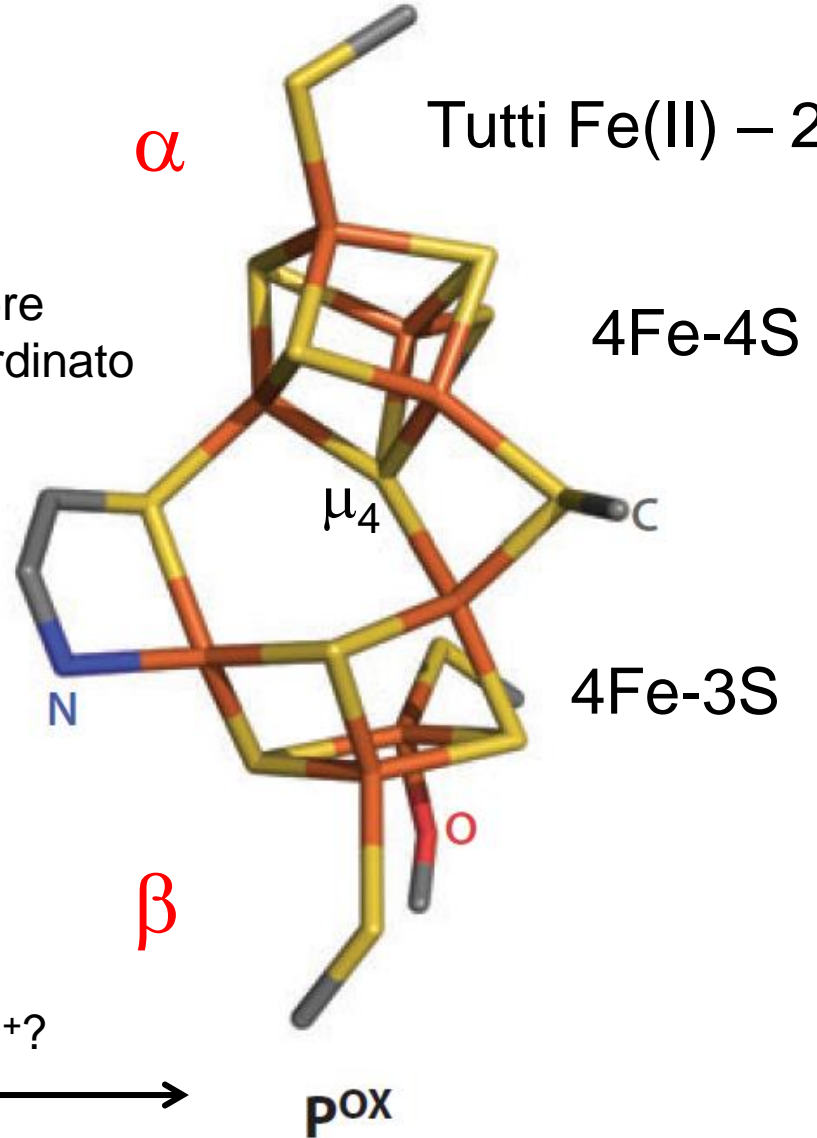
Tutti Fe(II)



Fe sempre tetracoordinato

$\alpha$

Tutti Fe(II) – 2e<sup>-</sup>



4Fe-4S

4Fe-3S

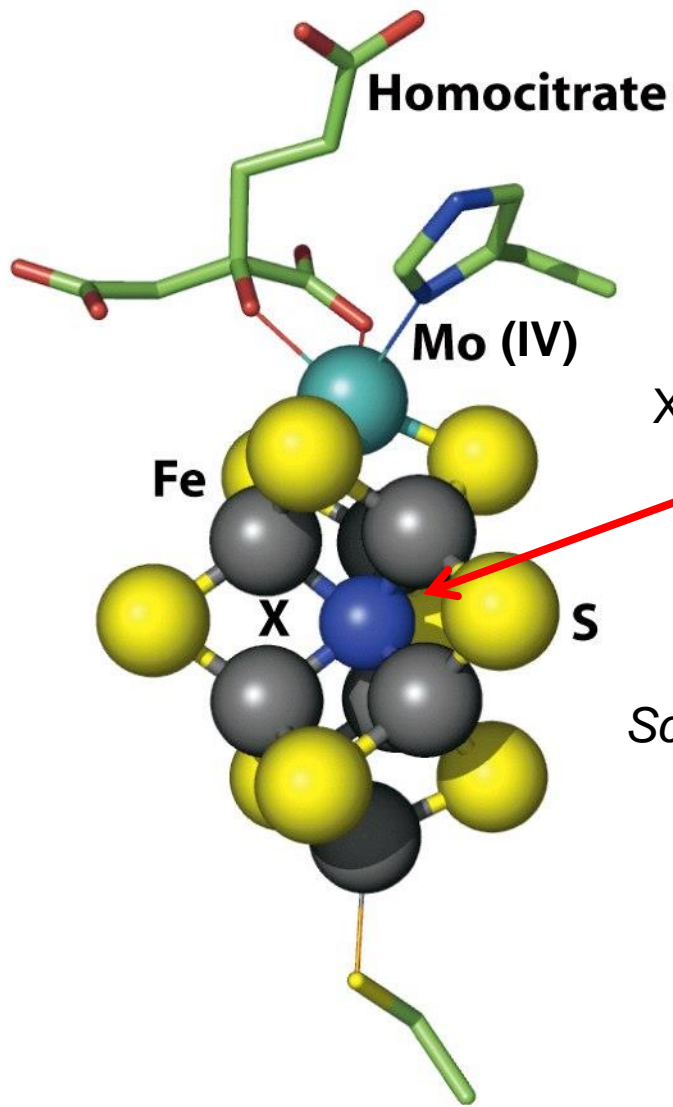
$\beta$

-2H<sup>+</sup>?

PN

POX





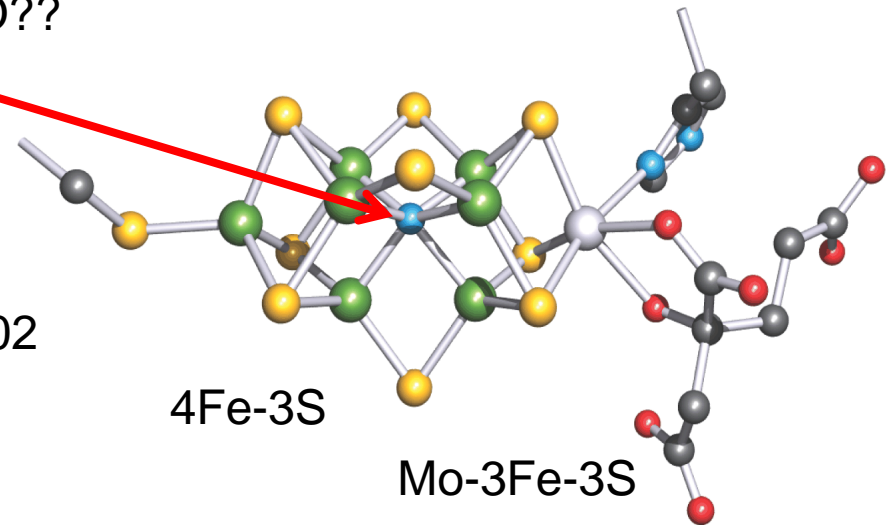
**Nitrogenase FeMoCo**

# Cofattore FeMo

## 7Fe-9S-Mo-omocitrato

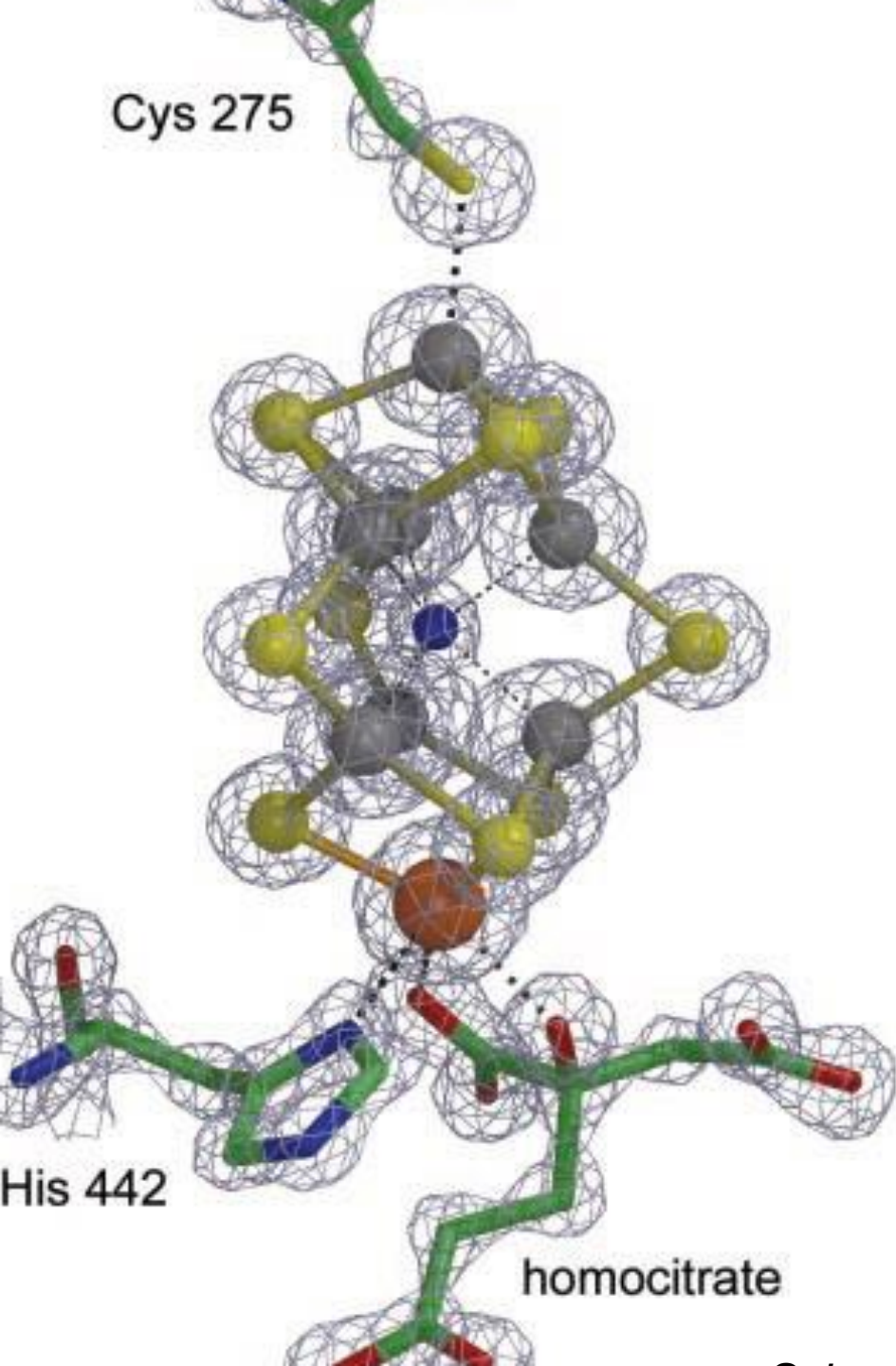
X = C, N, O??

*Science*, 2002

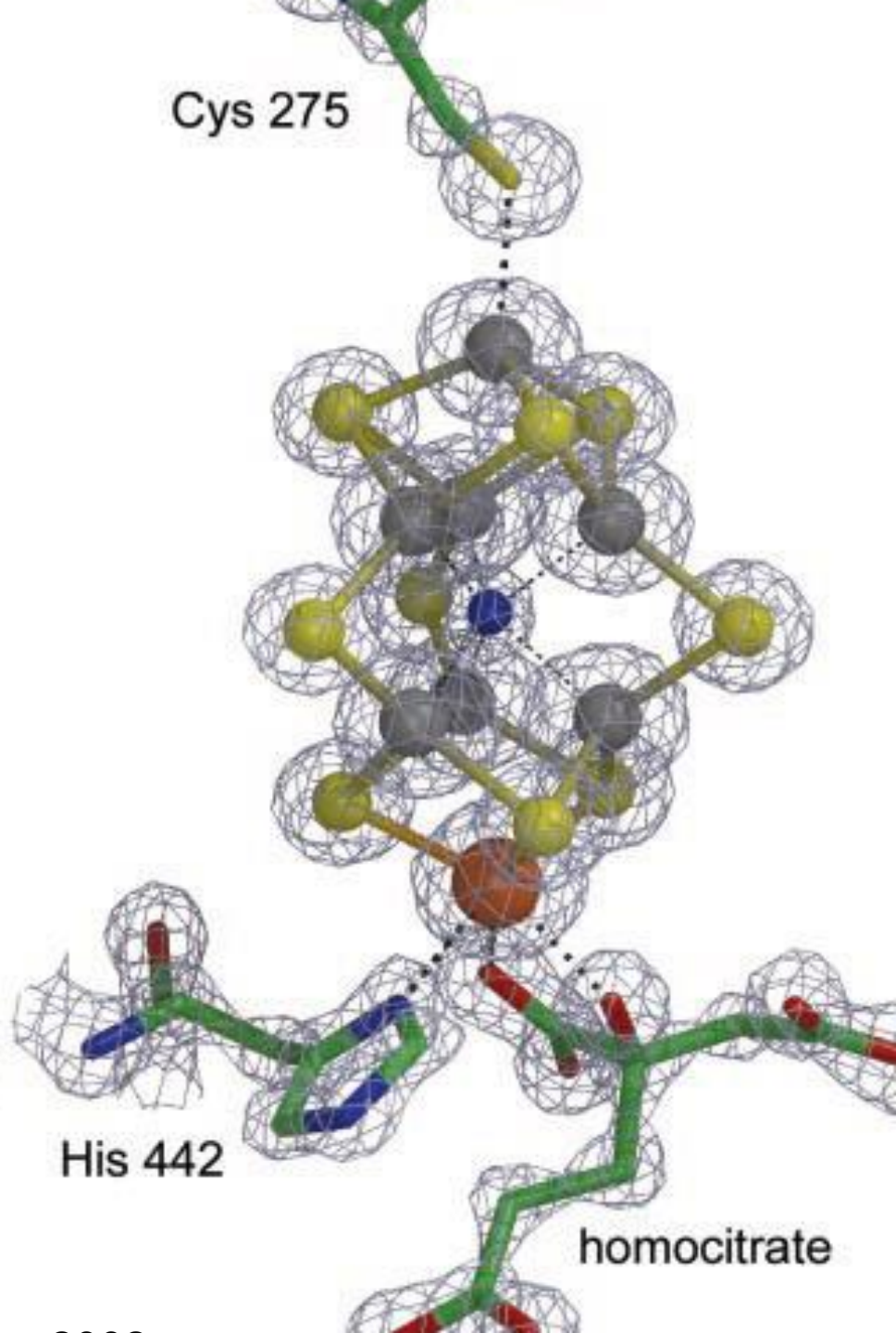


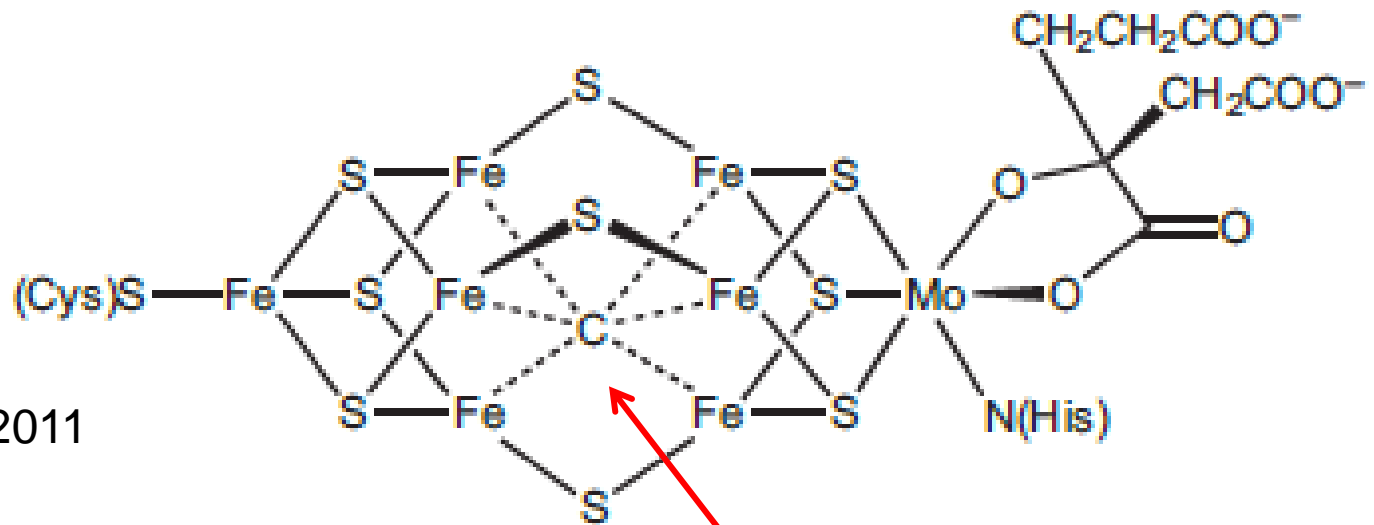
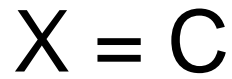
Tutto in  $\alpha$

Cys 275



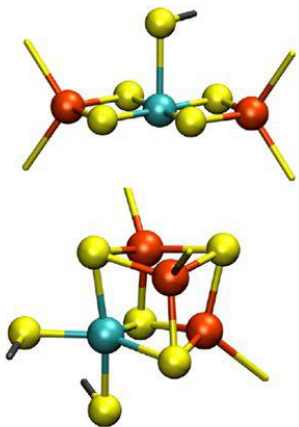
Cys 275





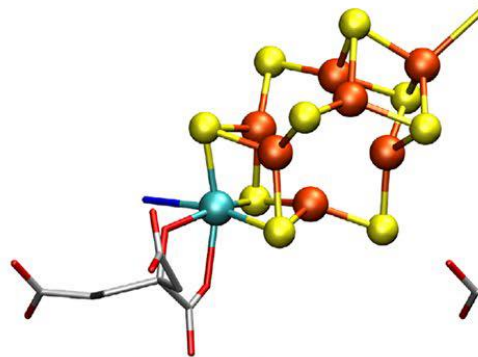
*Science*, 2011

Carburo, C<sup>4-</sup>



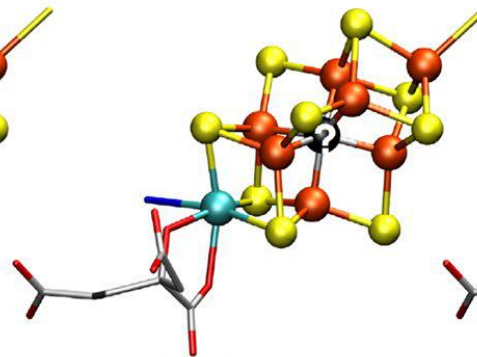
1978

First structural models from EXAFS



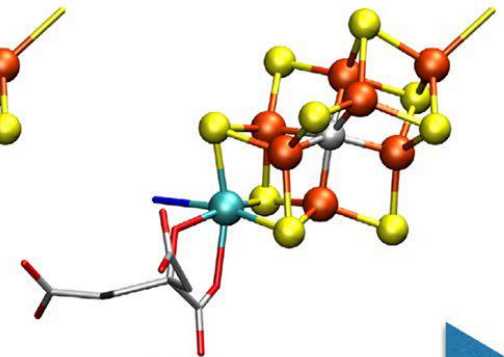
1992

First crystal structure (2.7Å)



2002

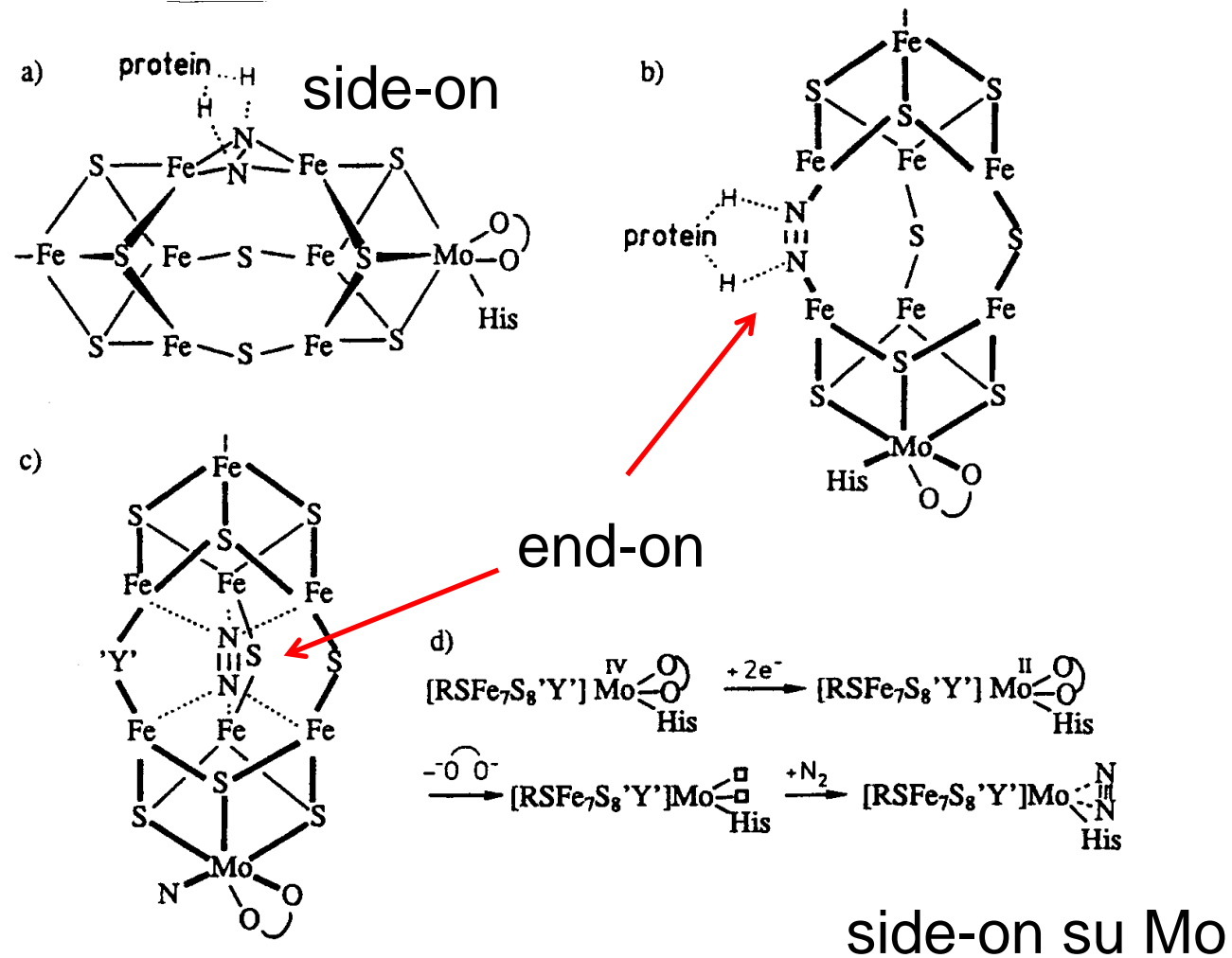
Discovery of interstitial atom

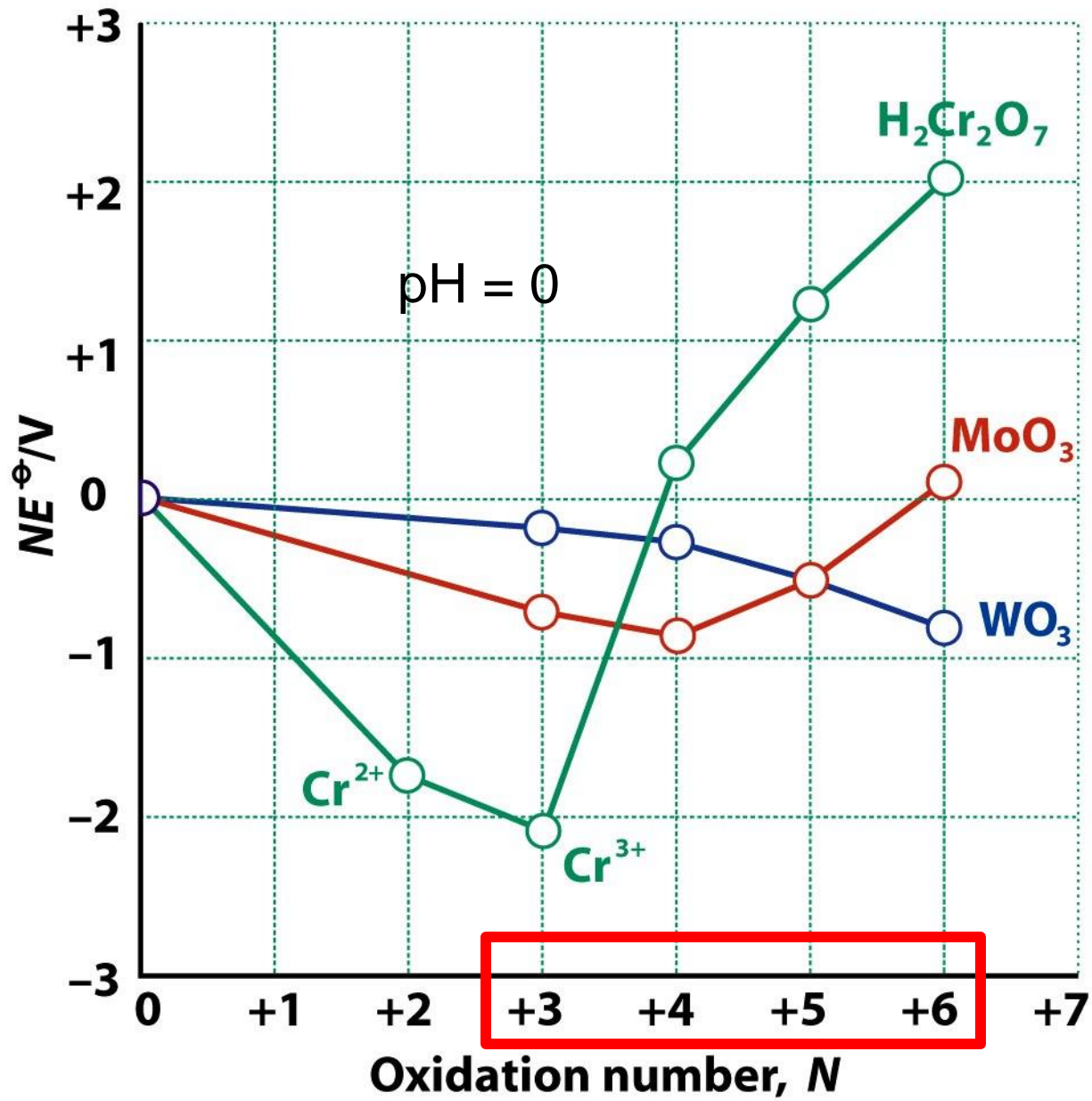


2011

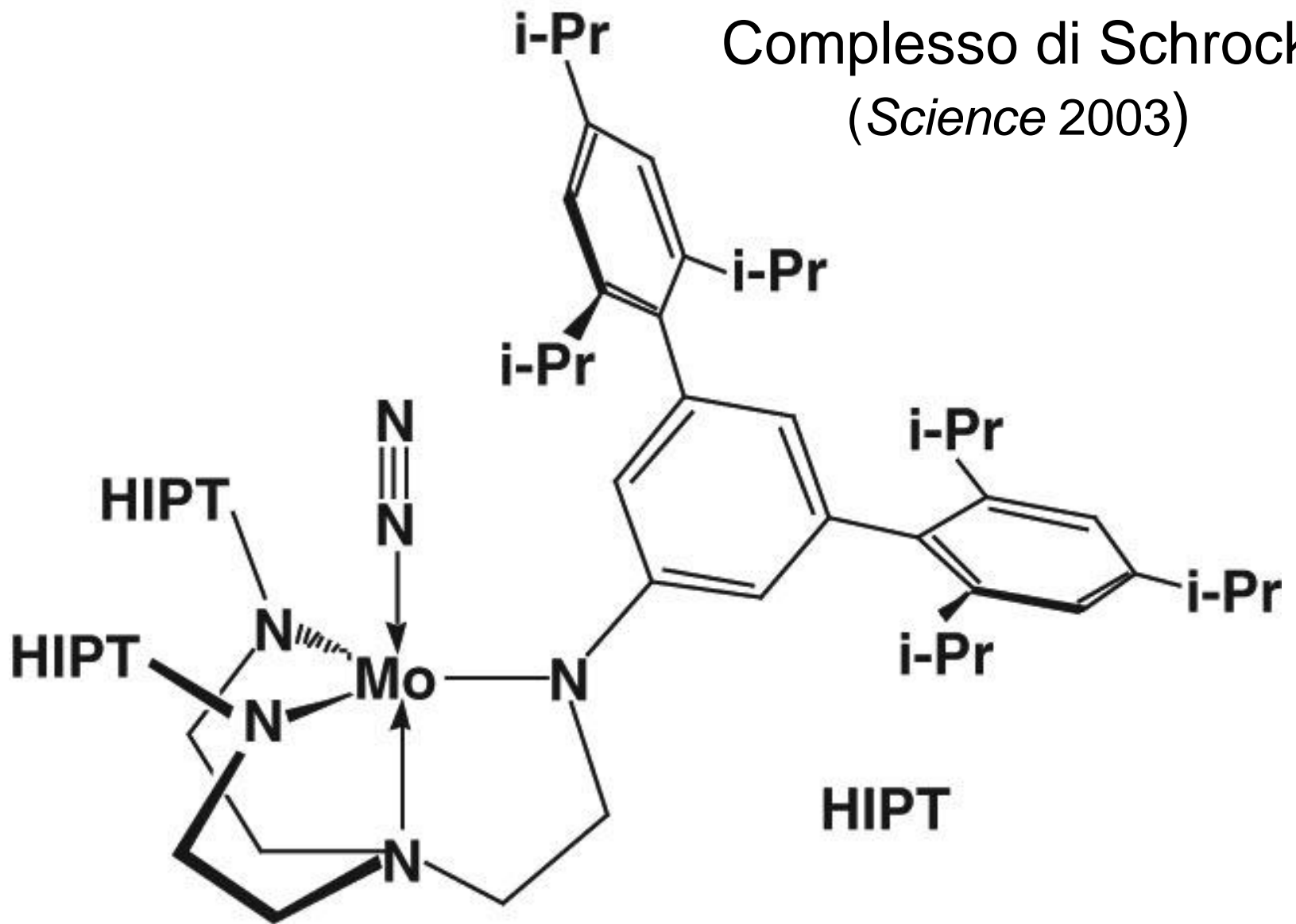
Interstitial atom identified as carbon

# Ipotetici modi di coordinazione di N<sub>2</sub> al FeMoco

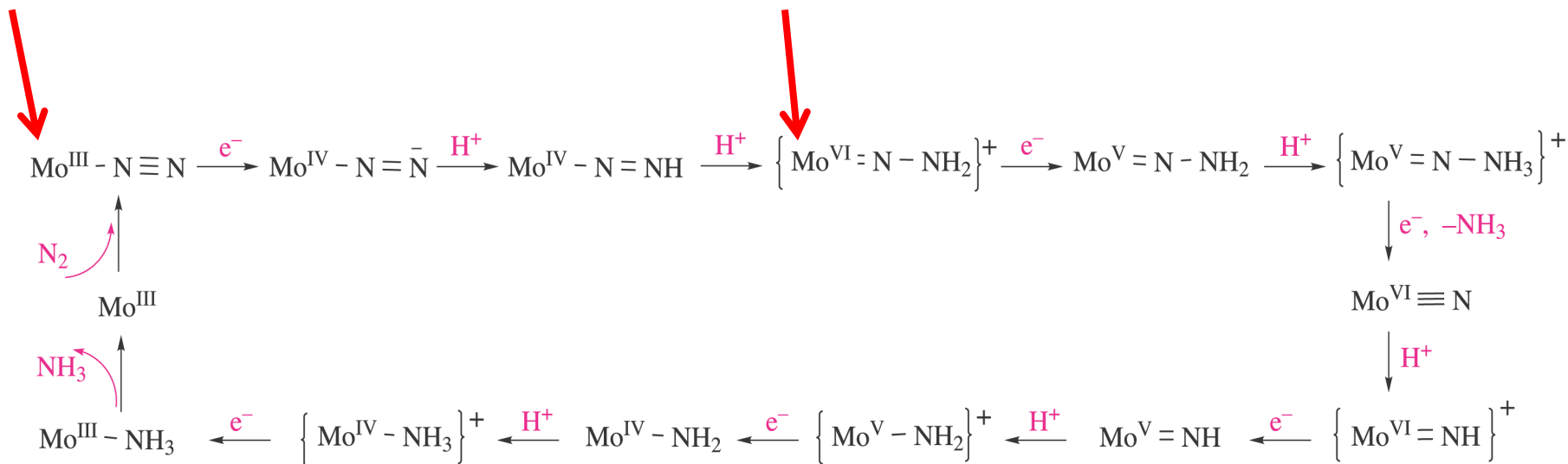
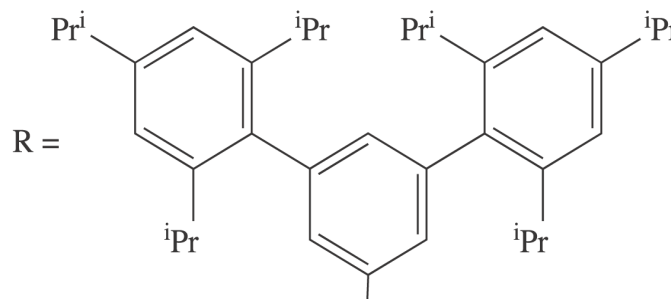
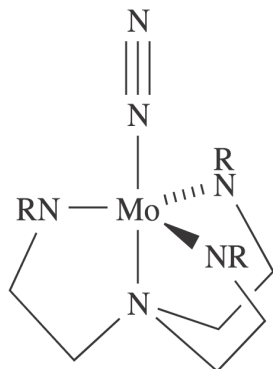




Complesso di Schrock  
(*Science* 2003)



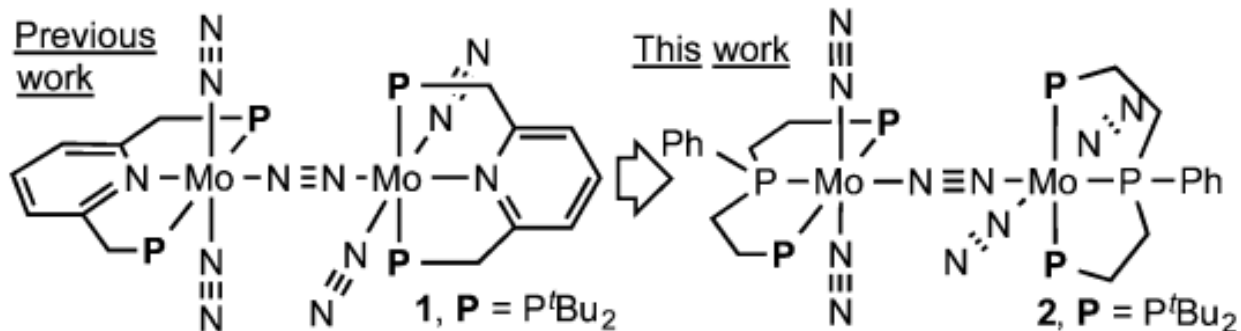
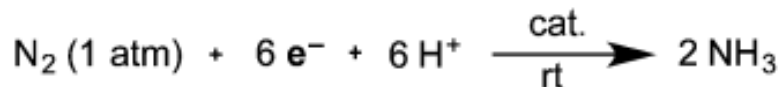
# Schema della riduzione catalitica di N<sub>2</sub> a NH<sub>3</sub> su Mo



8 cicli catalitici, meccanismo *distale*

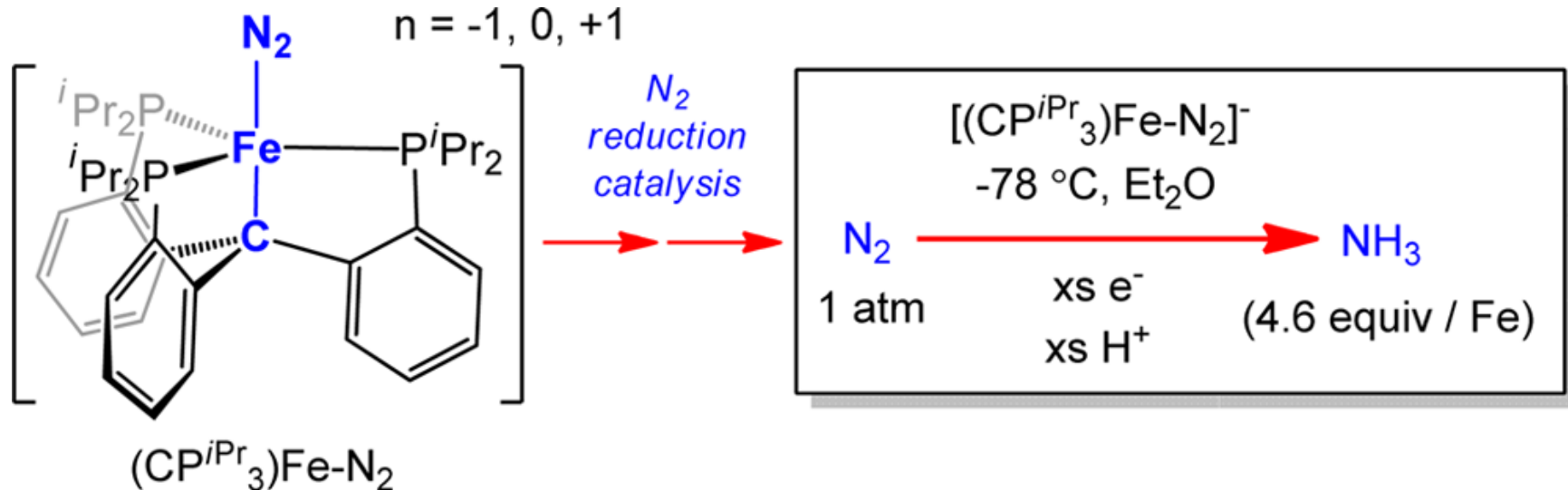
# Complessi di Nishibayashi (2011 e 2015)

26 cicli catalitici, riducente  $\text{CoCp}^*_2$



# Complesso di Peters (2014)

4.6 cicli catalitici, riducente K





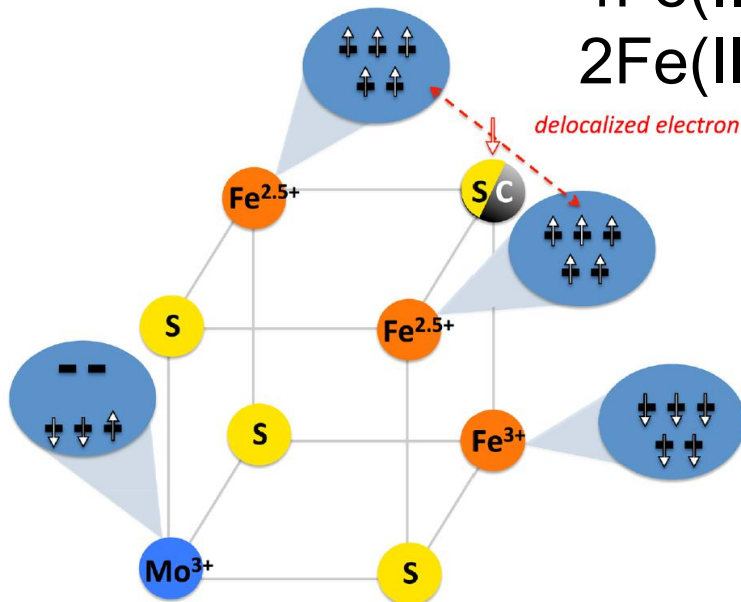
# Struttura elettronica di FeMo-co

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) |                       |

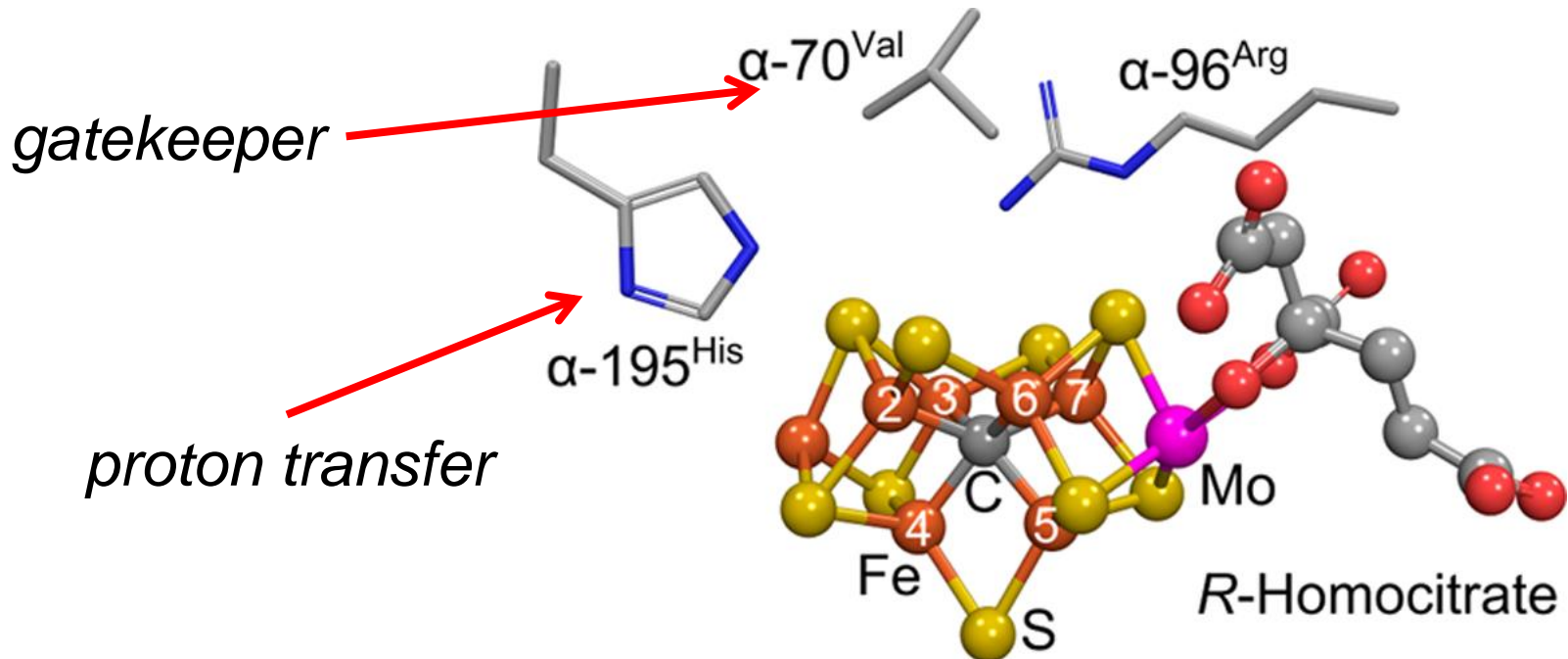
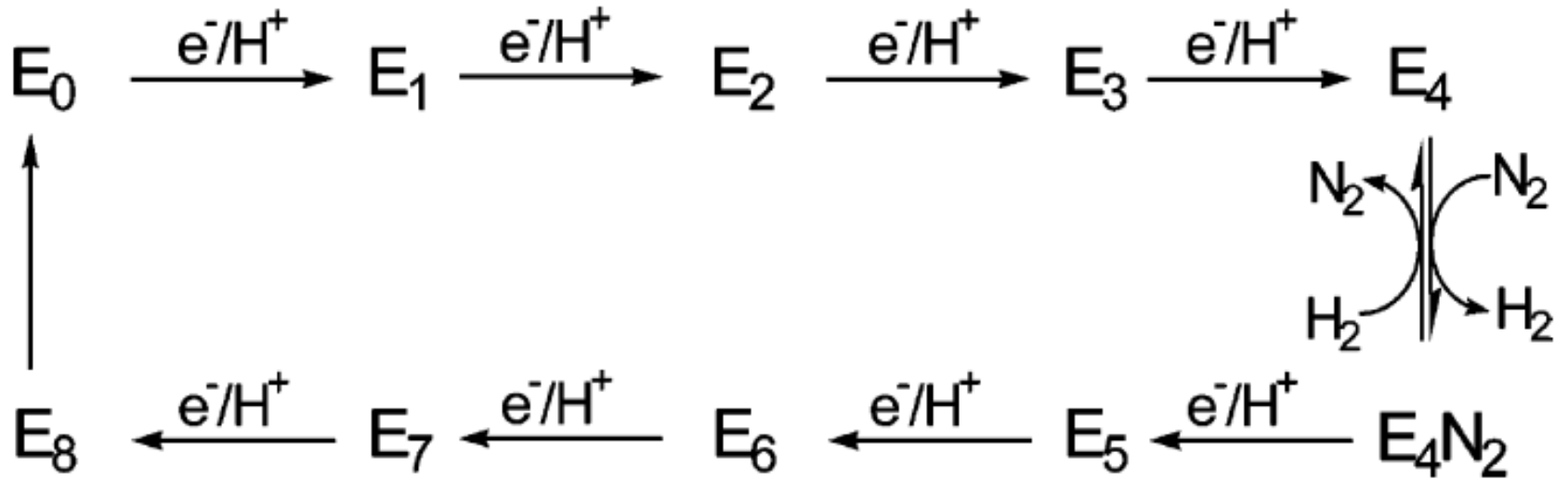
2014: Mo(III),  $d^3$  basso spin ( $\uparrow\uparrow\downarrow$ )? (violazione della regola di Hund)

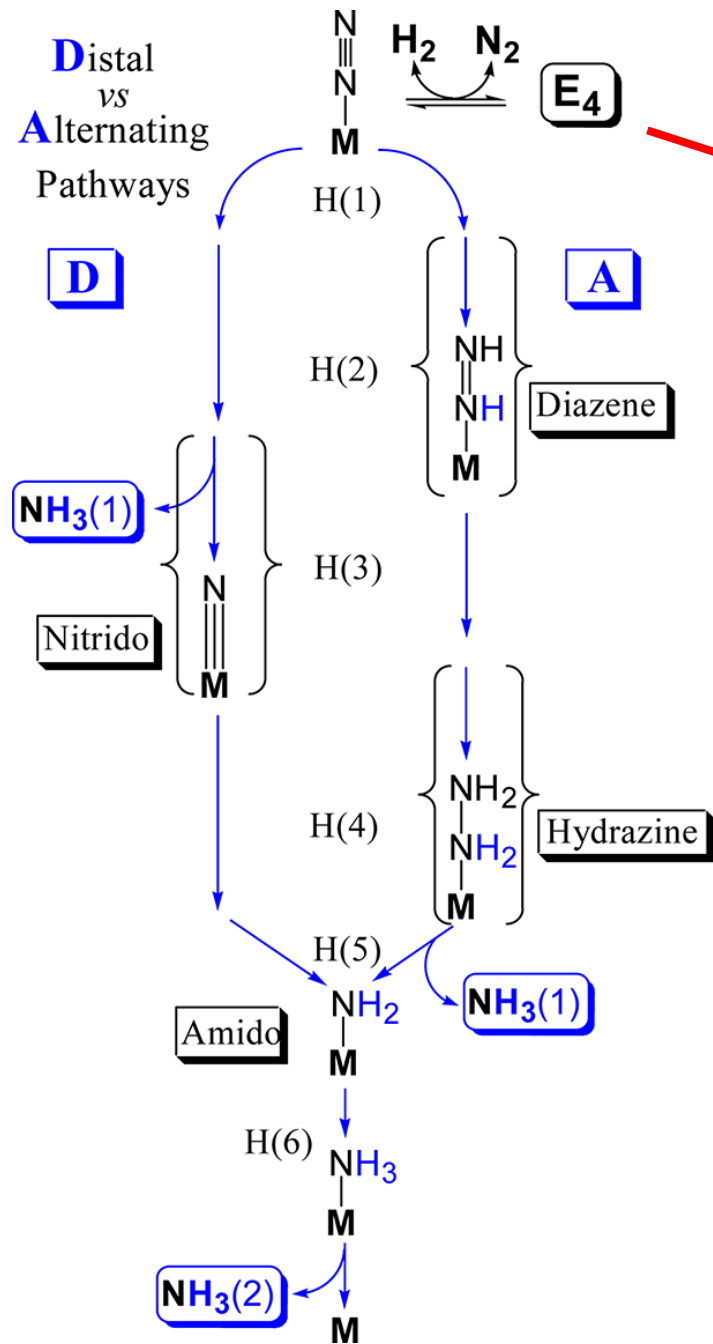
|                       |               |                        |
|-----------------------|---------------|------------------------|
| 6Fe(II)1Fe(III)Mo(IV) | $\rightarrow$ | 5Fe(II)2Fe(III)Mo(III) |
| 4Fe(II)3Fe(III)Mo(IV) | $\rightarrow$ | 3Fe(II)4Fe(III)Mo(III) |
| 2Fe(II)5Fe(III)Mo(IV) | $\rightarrow$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



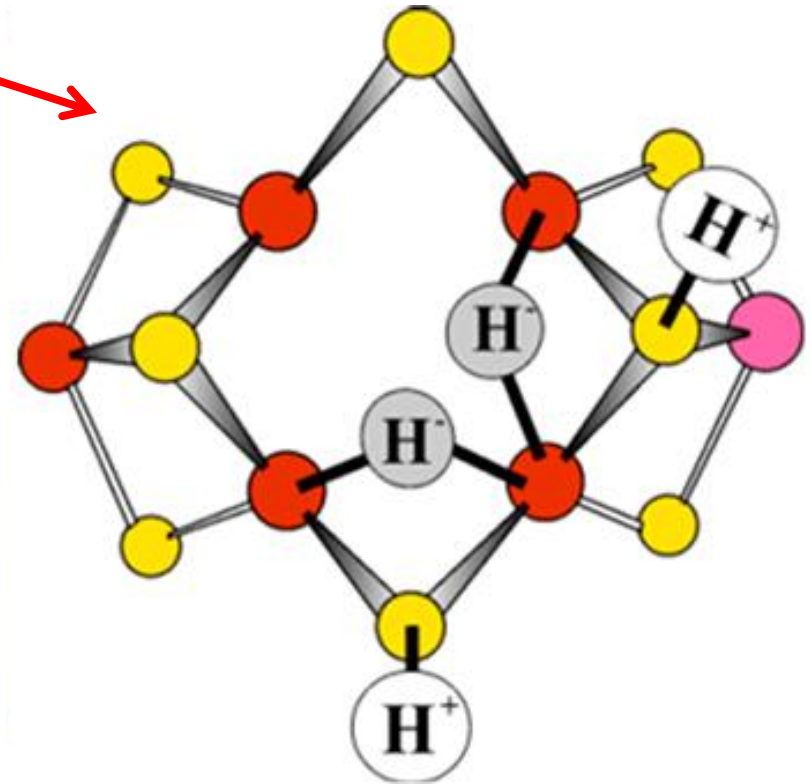
Cluster modello  $[\text{MoFe}_3\text{S}_3\text{C}]^{1+}$  e  $[\text{MoFe}_3\text{S}_4]^{3+}$

# Ciclo catalitico

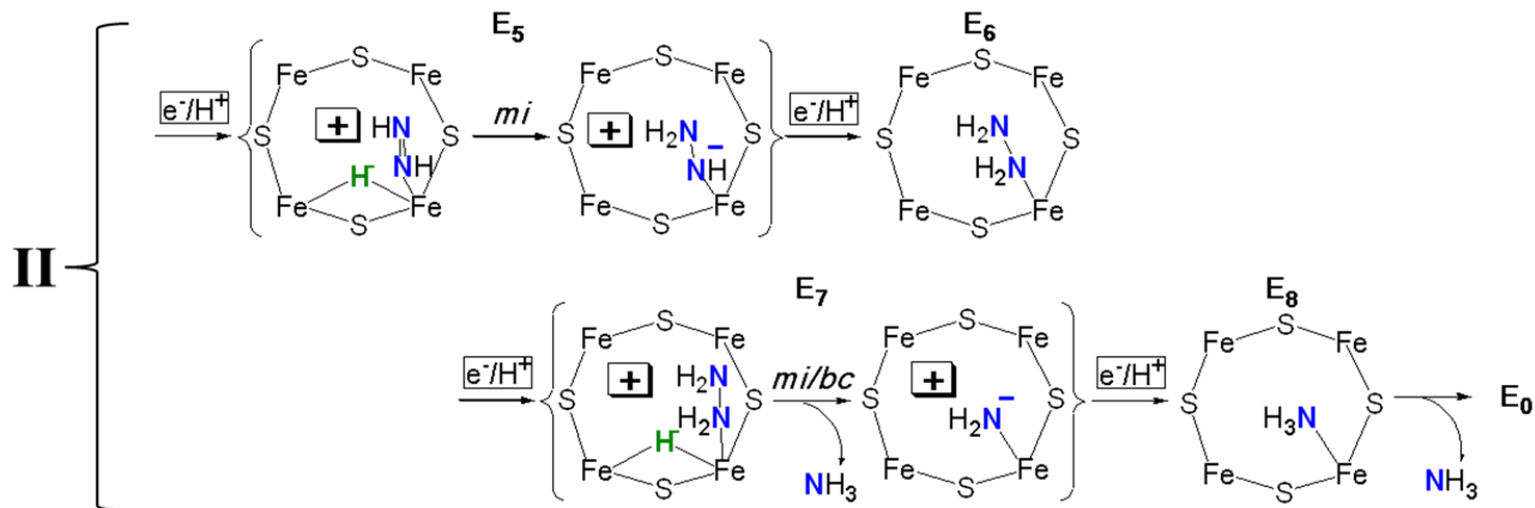
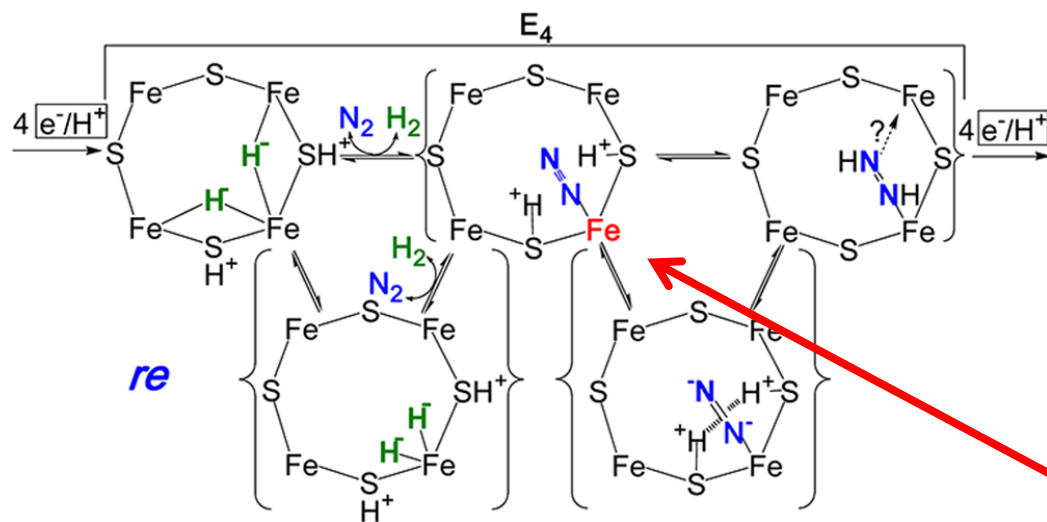
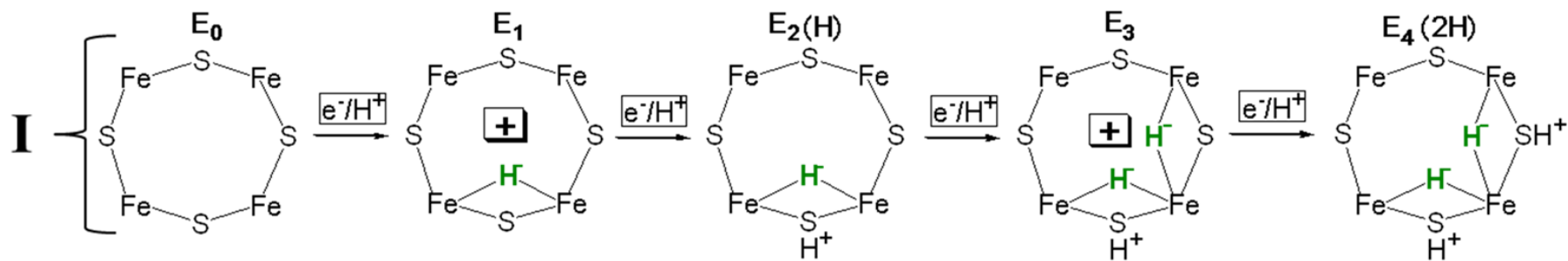


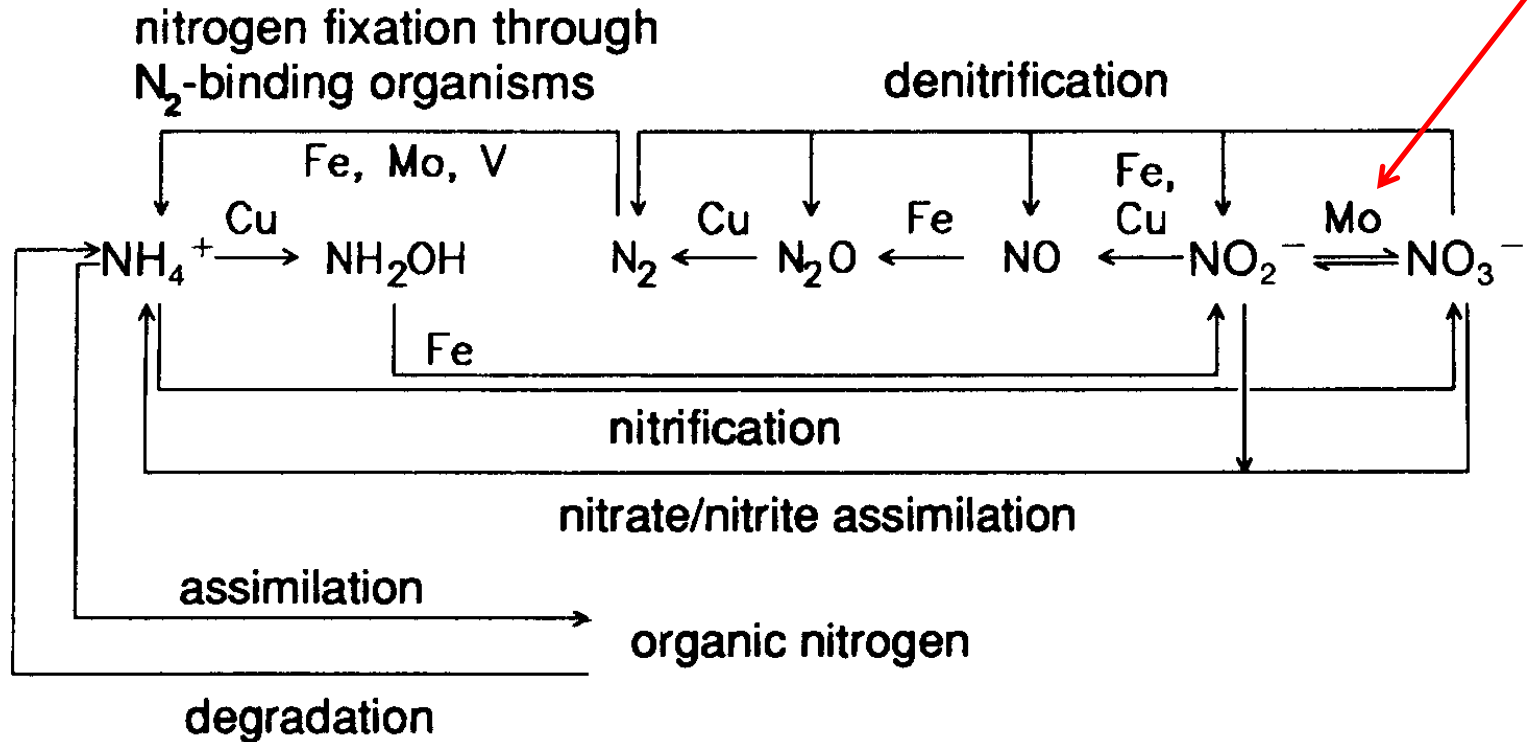


Modello di E<sub>4</sub>



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

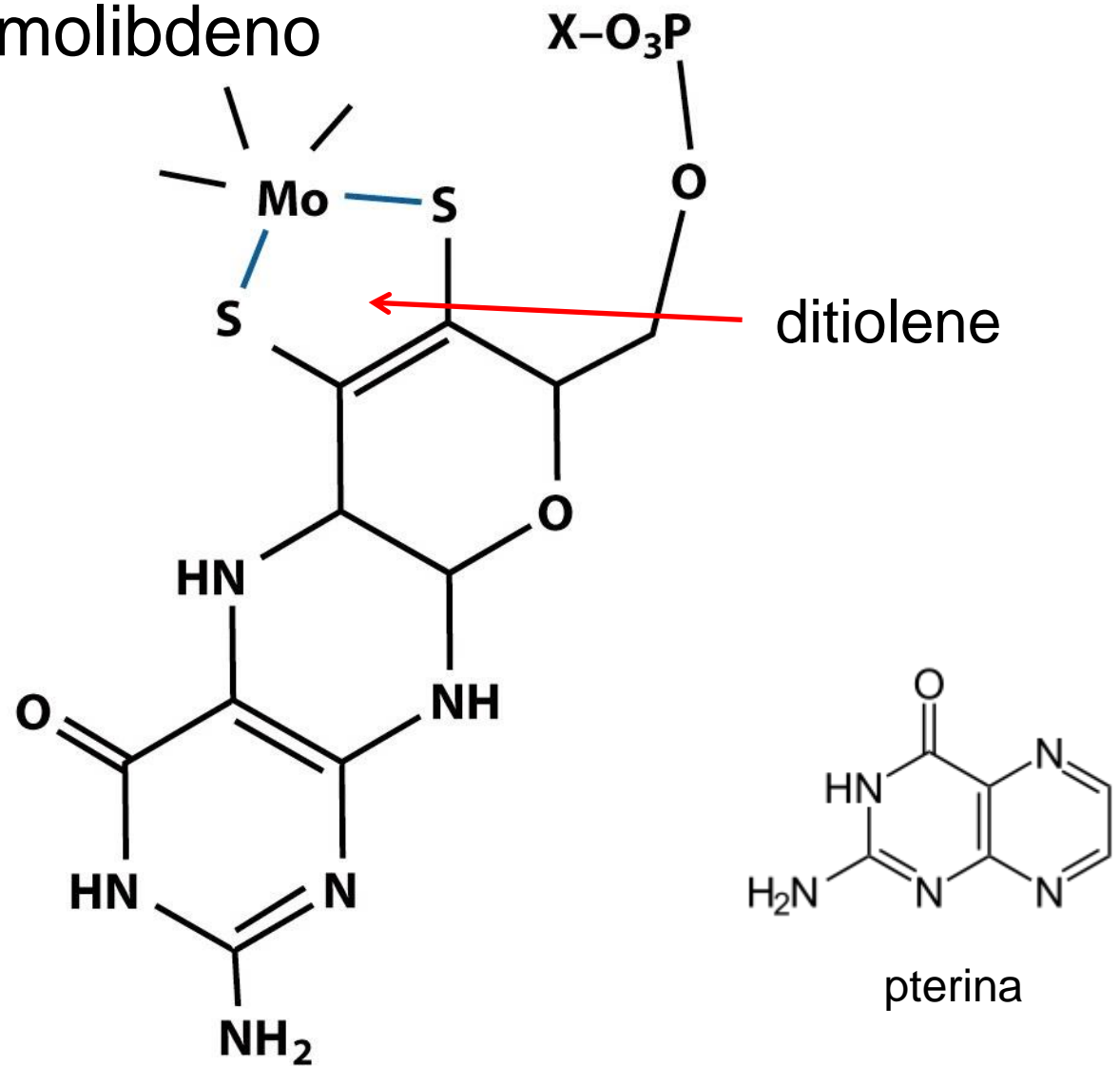




Tre famiglie di enzimi al Mo (*osso-trasferasi*)

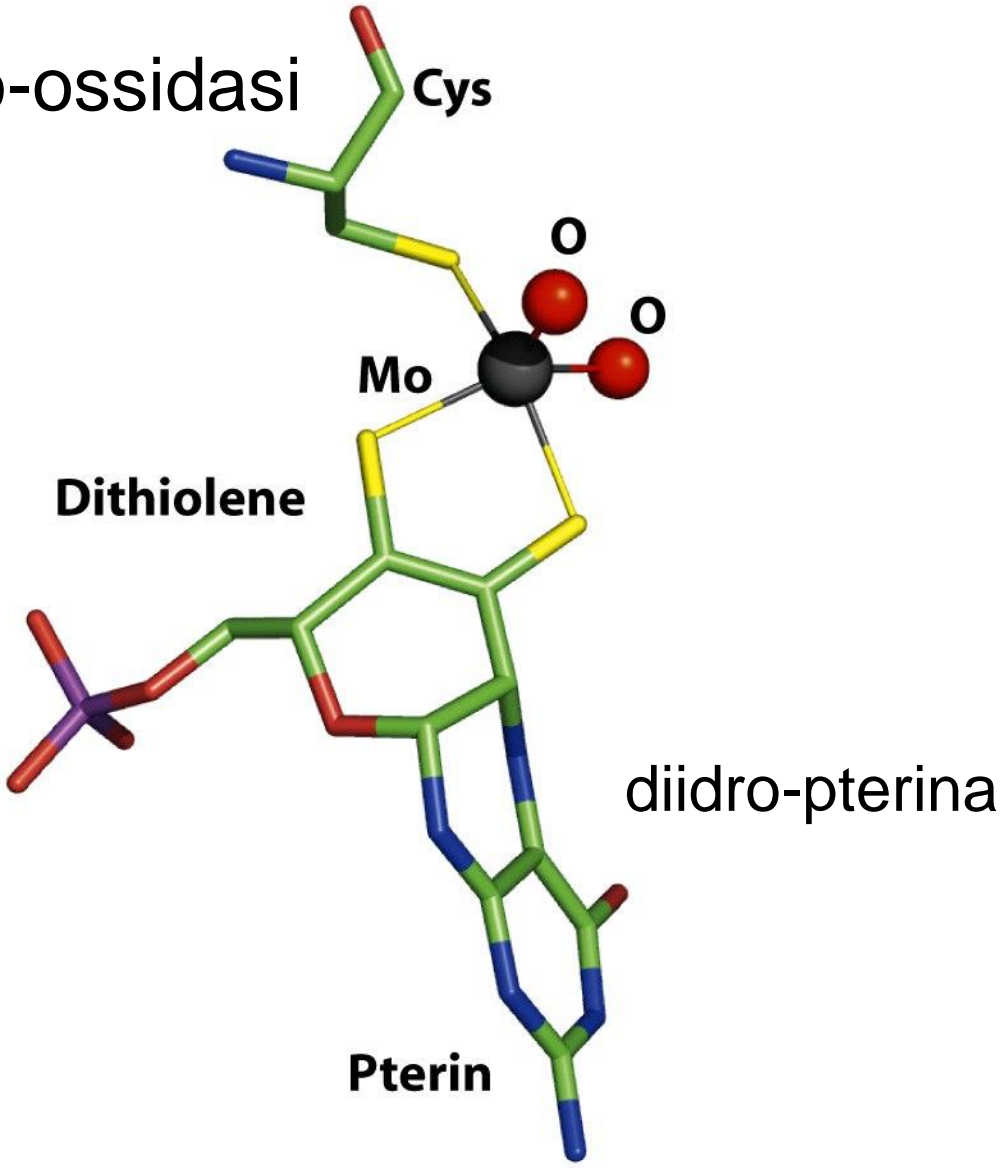
- xantina-ossidasi
- solfito-ossidasi
- DMSO-riduttasi

# Cofattore del molibdeno

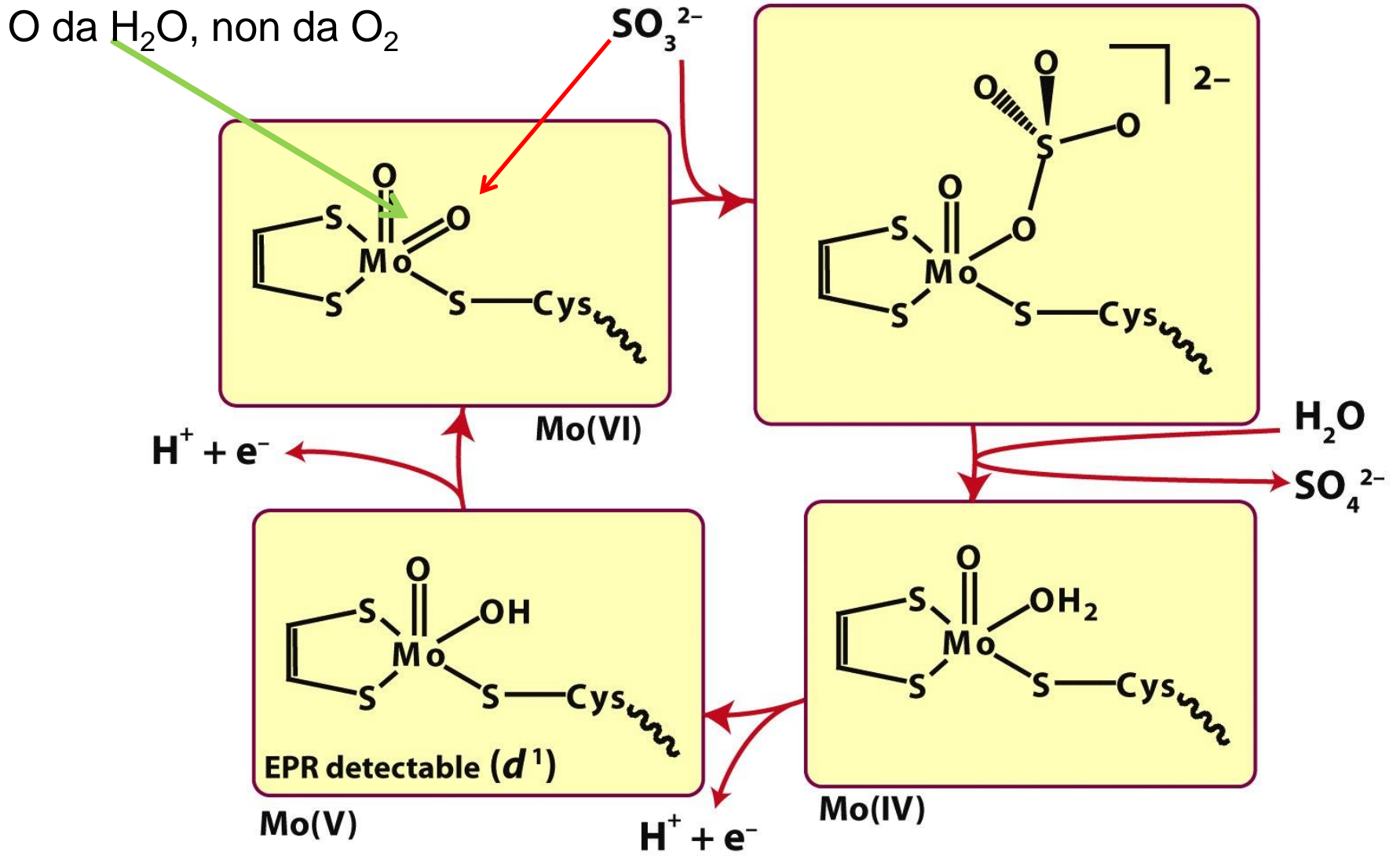


**Molybdopterin as ligand**

# Sito della solfito-ossidasi

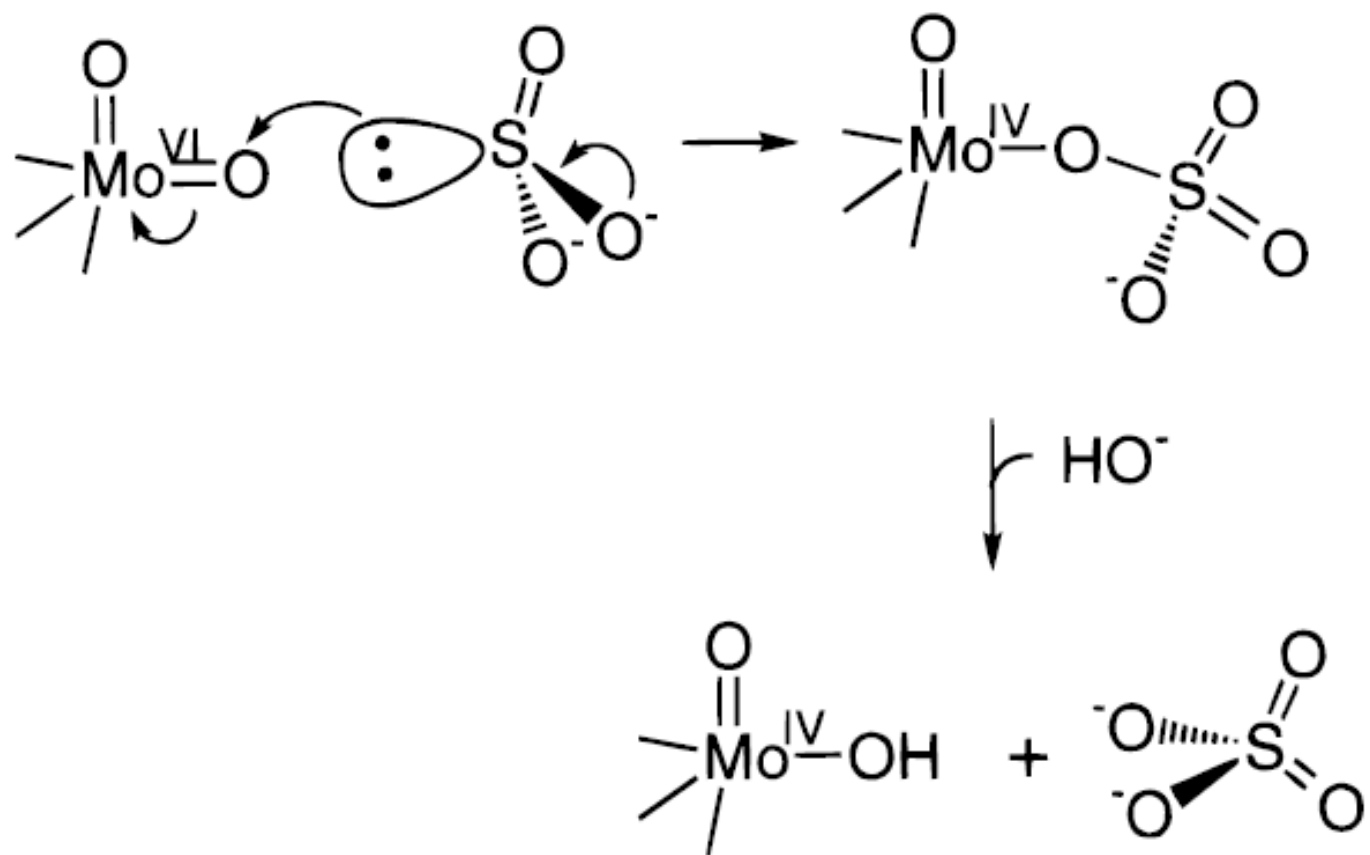


# Ciclo catalitico della solfito-ossidasi

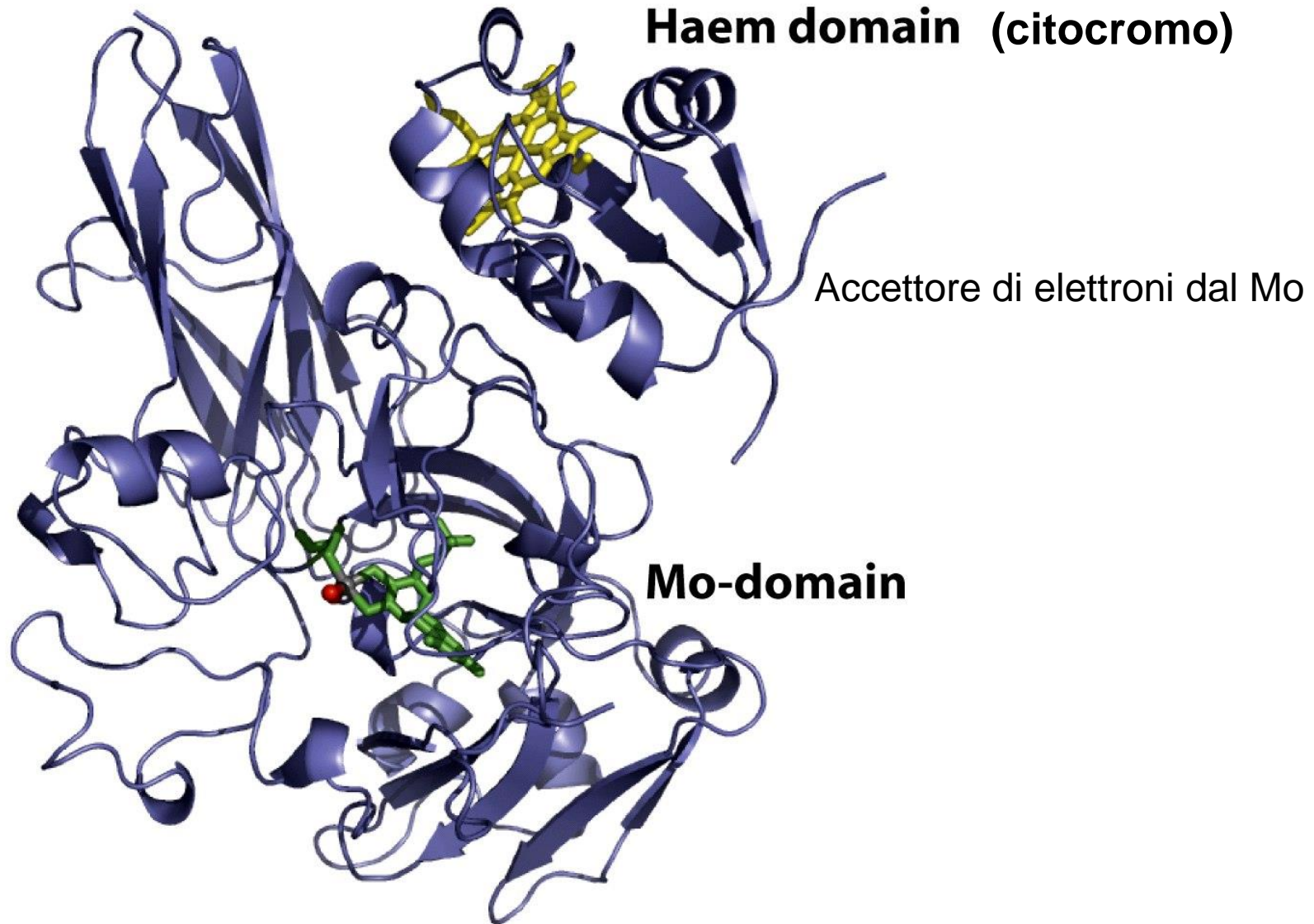


Mo possiede tre stati di ossidazione stabili, Mo(IV), Mo(V) e Mo(VI)





# Struttura della solfito-ossidasi



# Scala di entalpia delle reazioni di trasferimento di atomi di ossigeno

