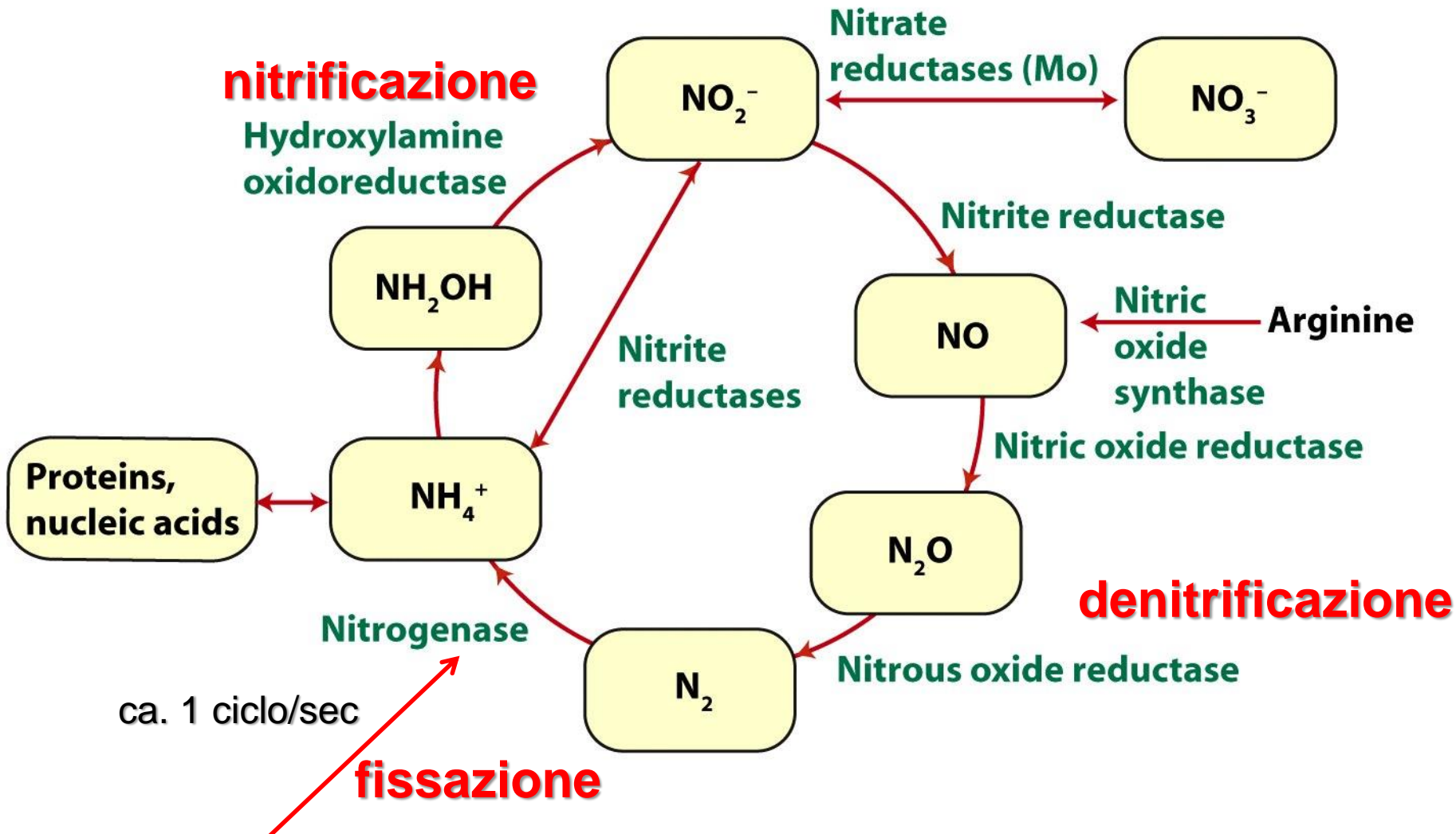


# Metalli di inizio serie

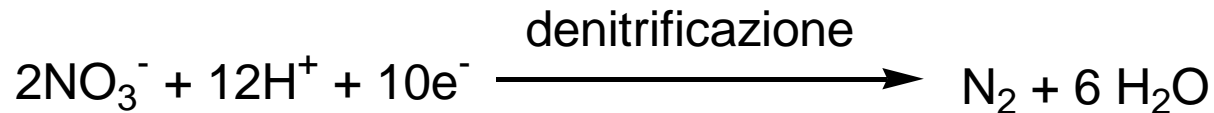
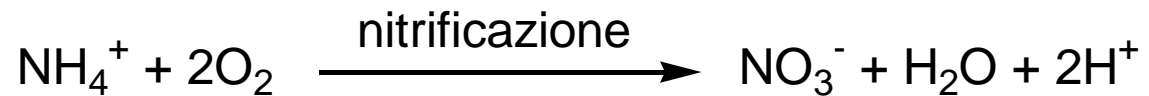
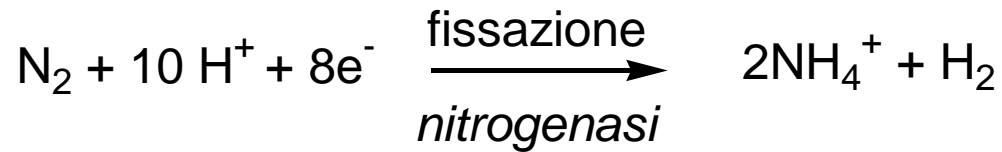
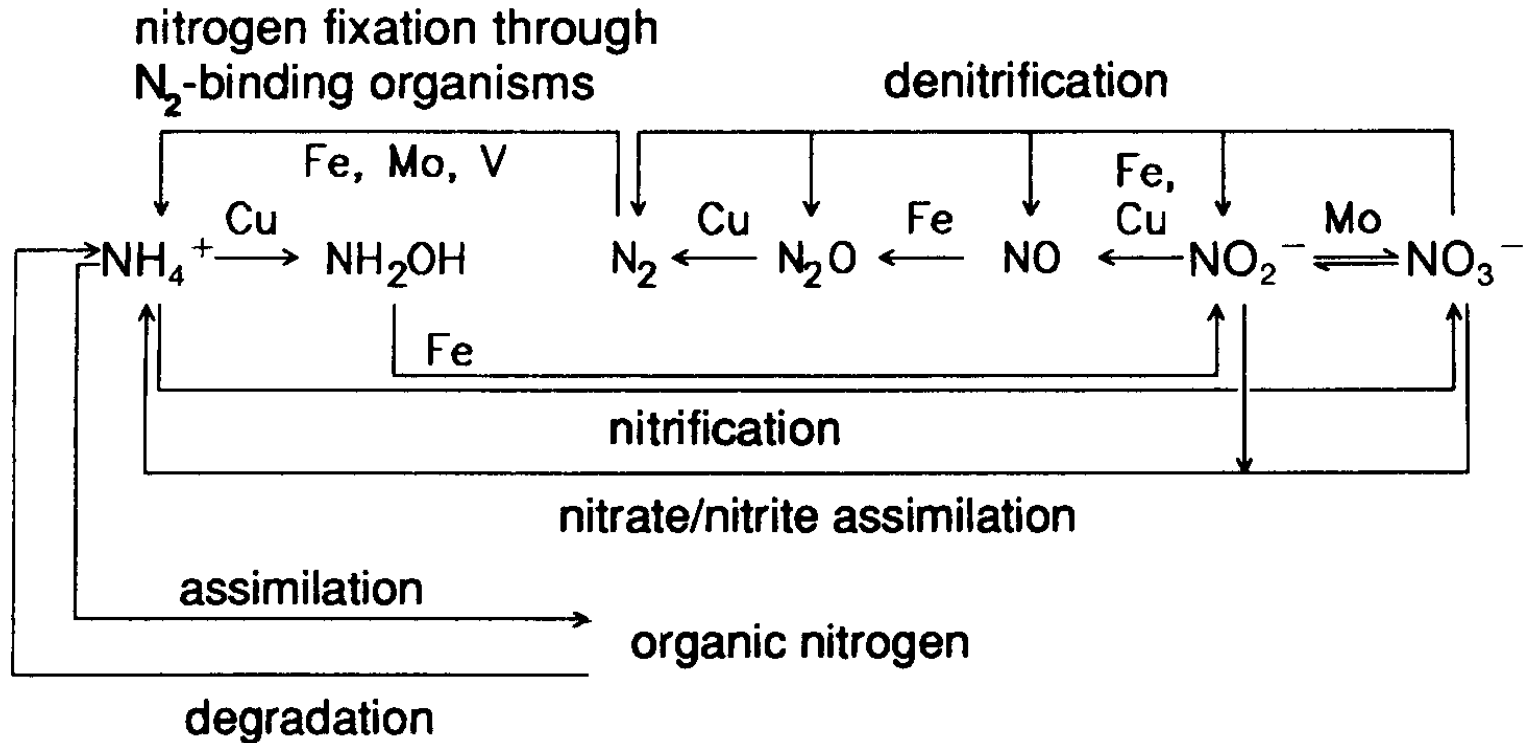


*Il molibdeno è l'unico elemento del secondo periodo di transizione (4d) ad avere una funzione biologica. È biodisponibile sotto forma di molibdato  $\text{MoO}_4^{2-}$*

# Ciclo dell'azoto



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

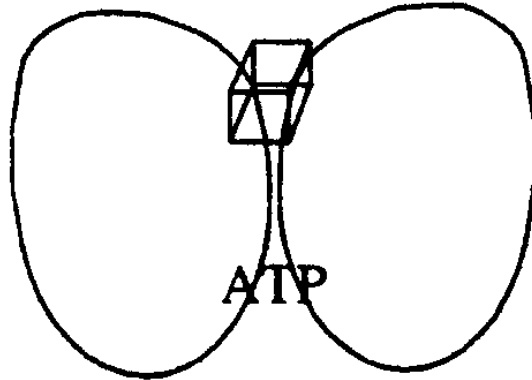


# Nitrogenasi



1992

ca. 1 ciclo/sec

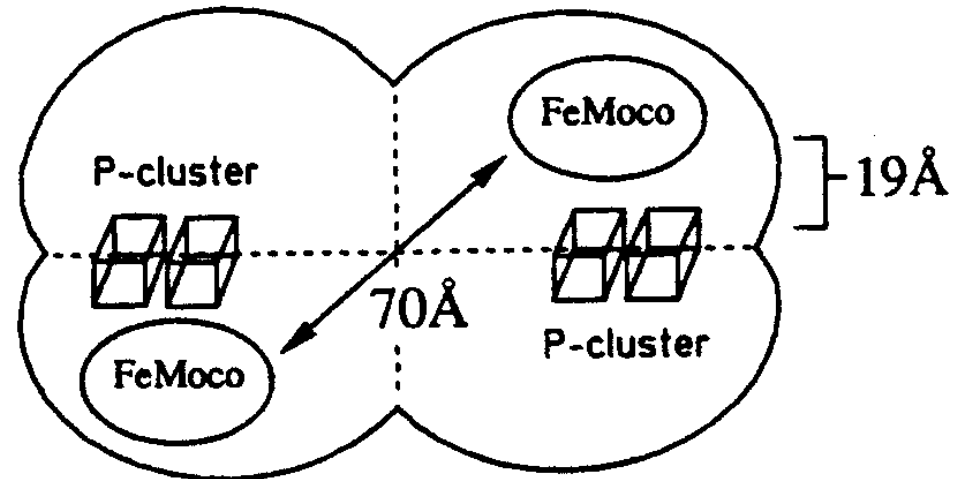


**Fe protein**

$\gamma_2$

60 kDa

+



**FeMo protein**

$\alpha_2\beta_2$

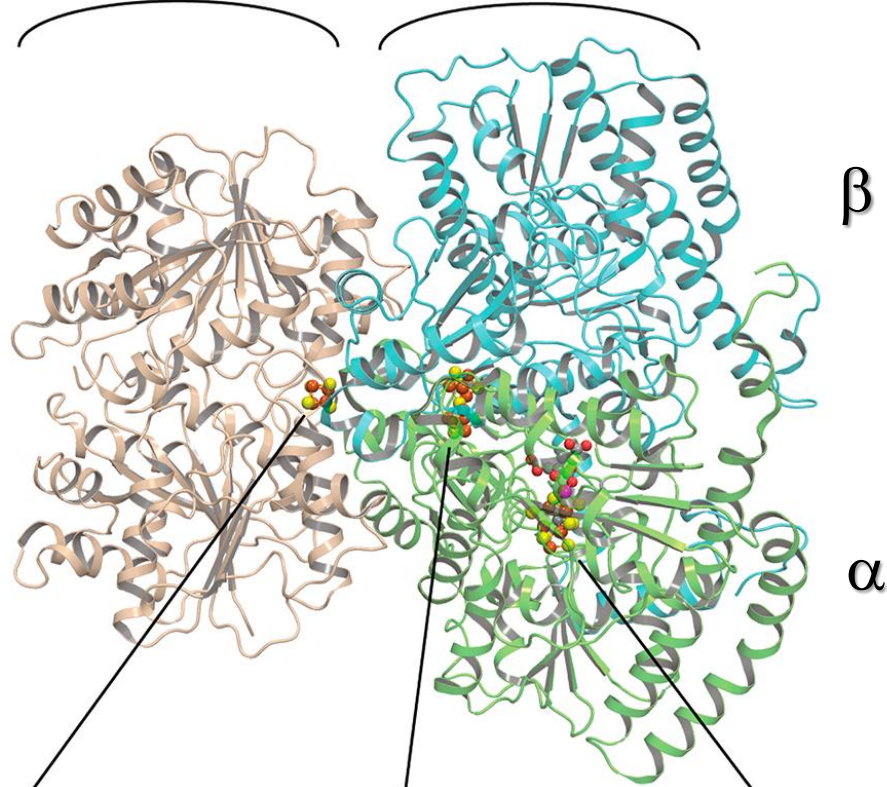
220 kDa

# Nitrogenasi

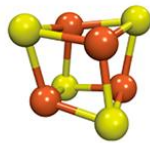
Fe protein

MoFe protein

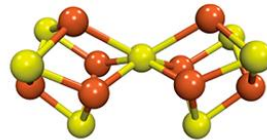
(A)



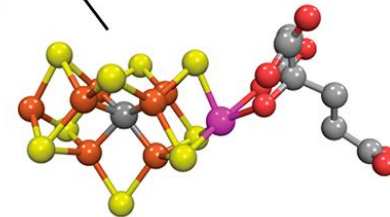
(B)



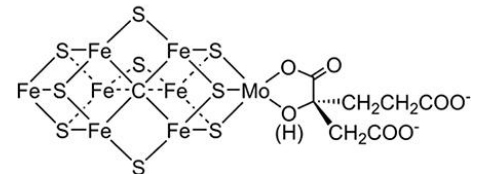
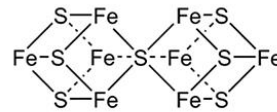
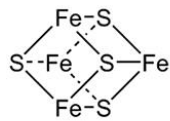
F cluster



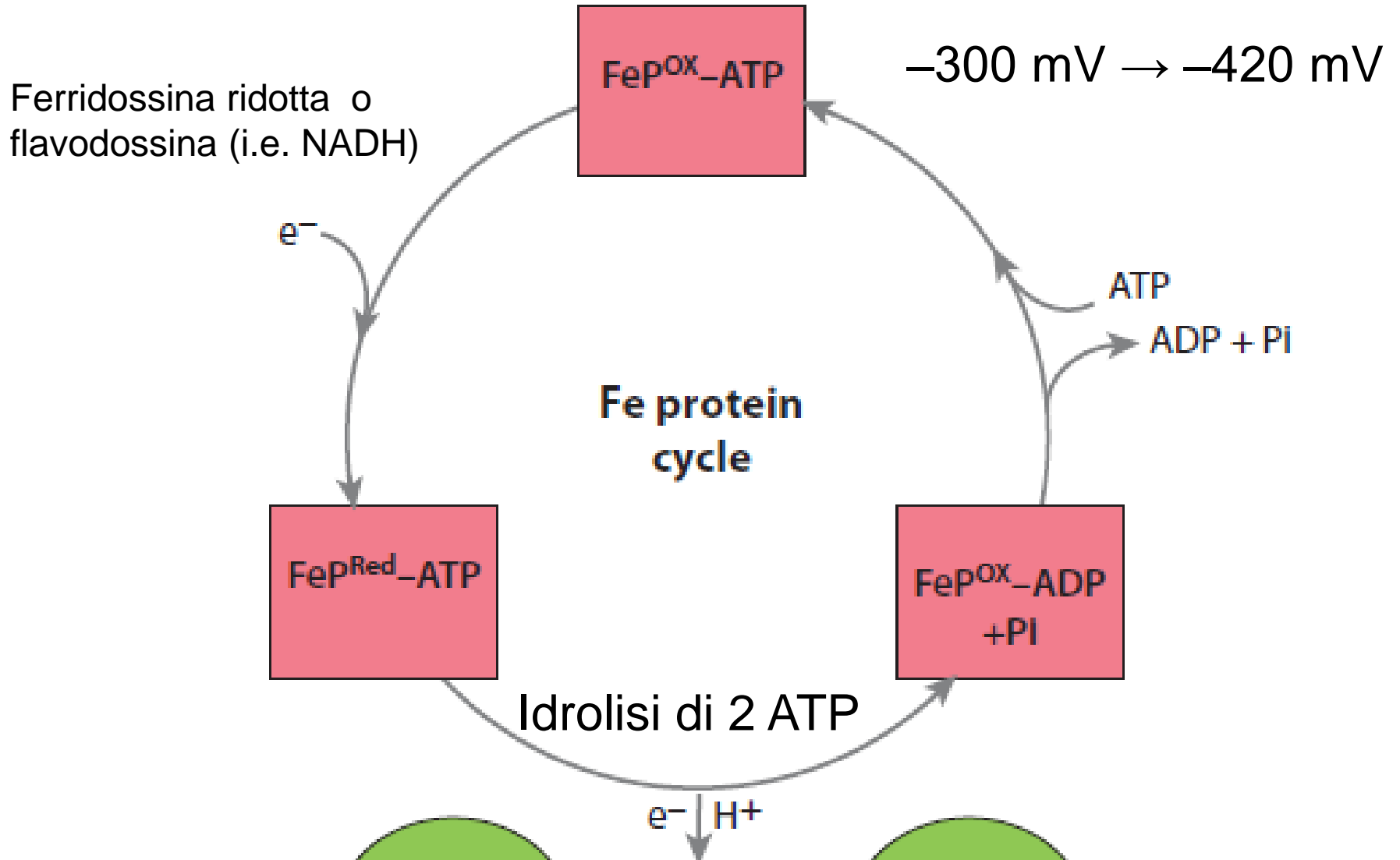
P cluster



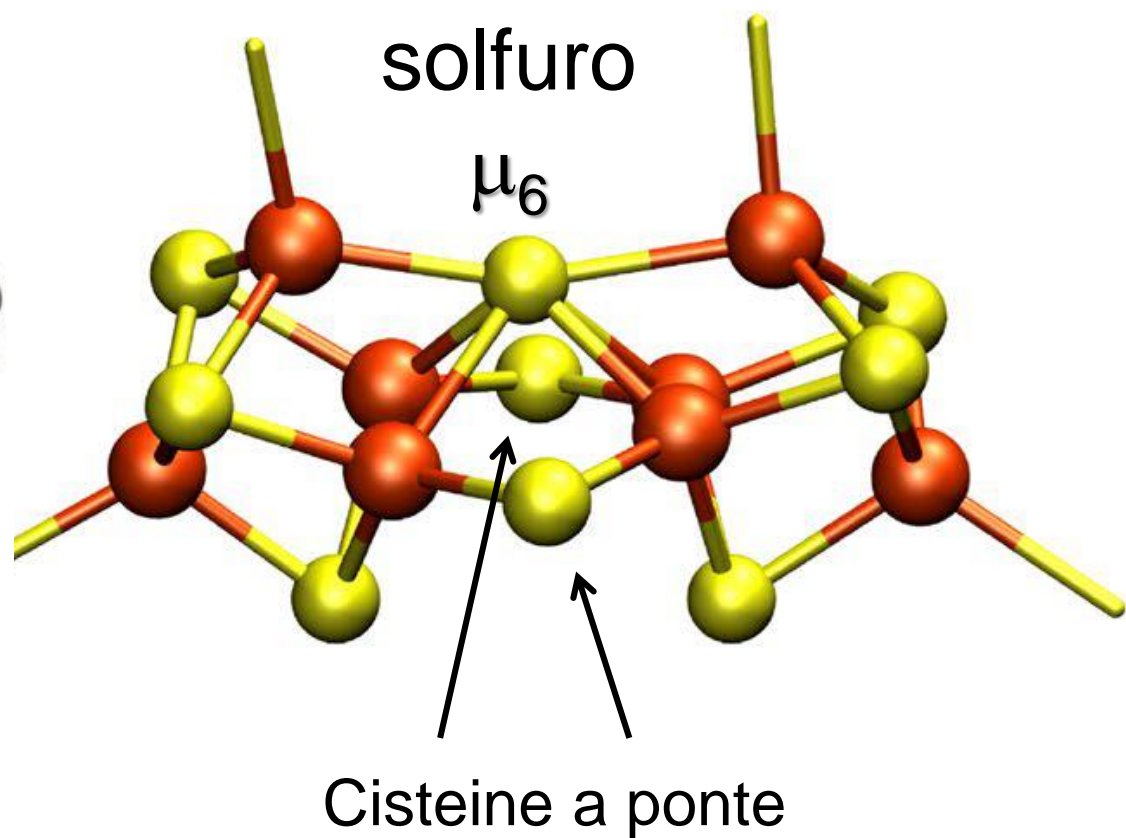
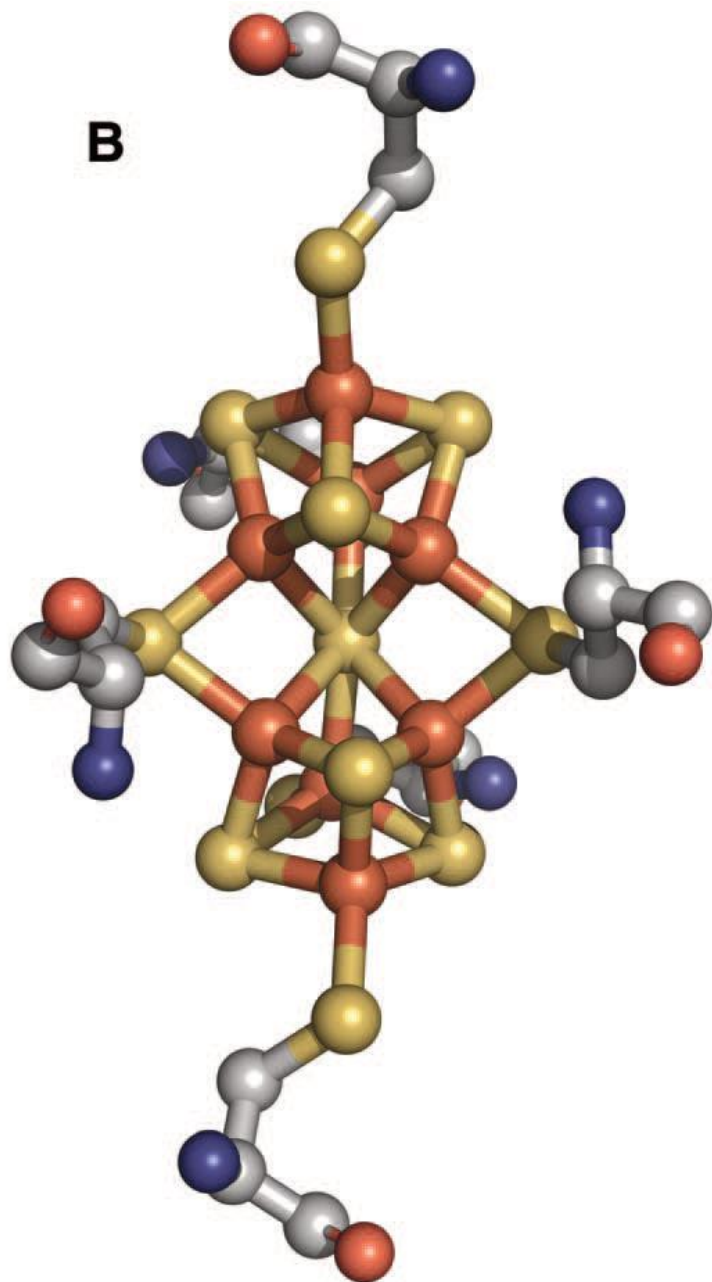
M cluster (FeMoco)



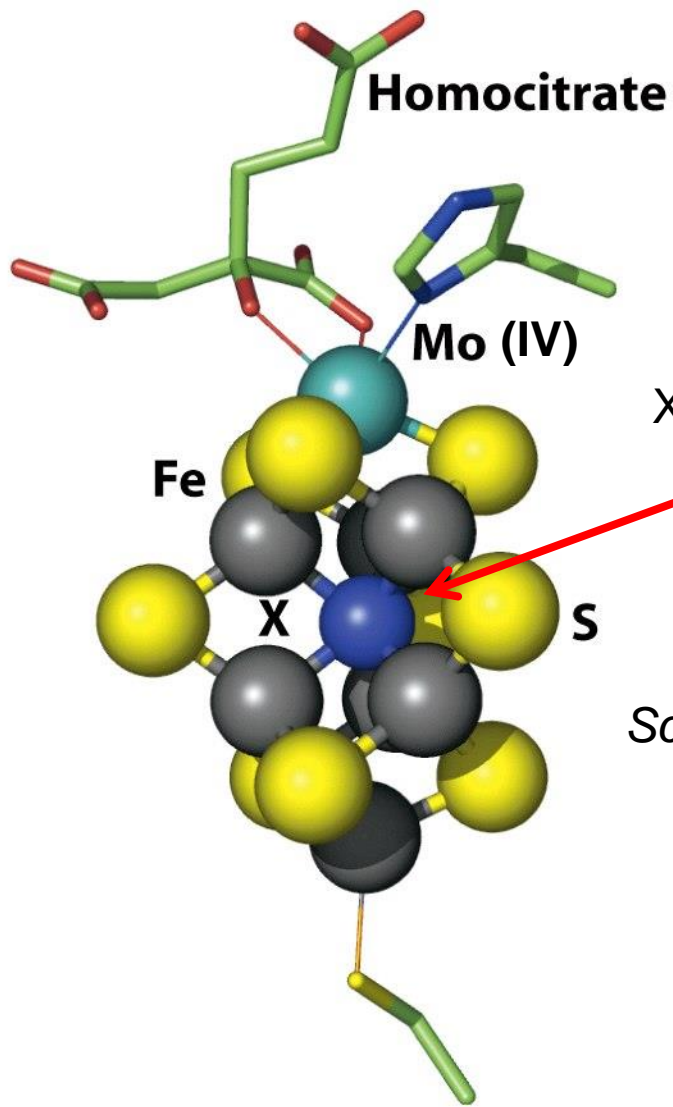
# Fe-proteina



# P-cluster 8Fe-7S







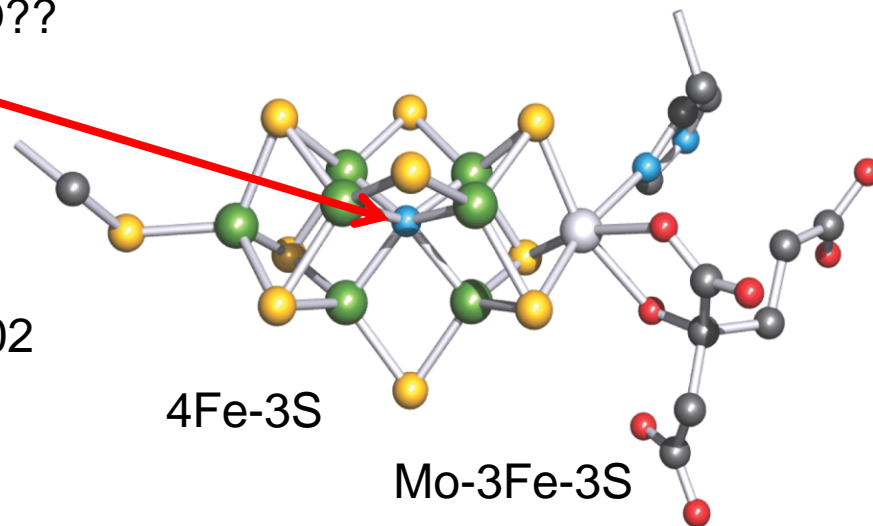
**Nitrogenase FeMoCo**

# Cofattore FeMo

## 7Fe-9S-Mo-omocitrato

X = C, N, O??

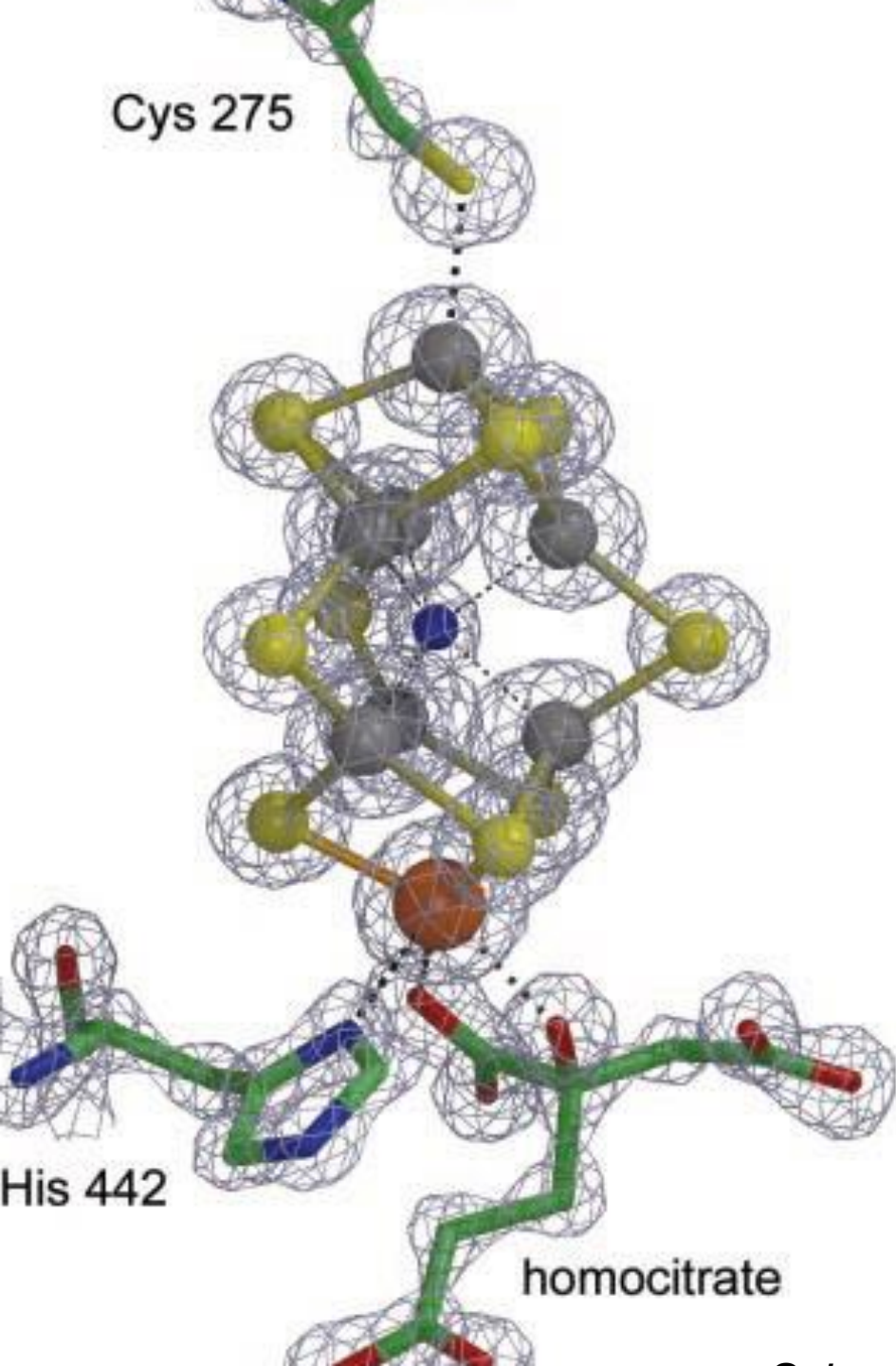
*Science*, 2002



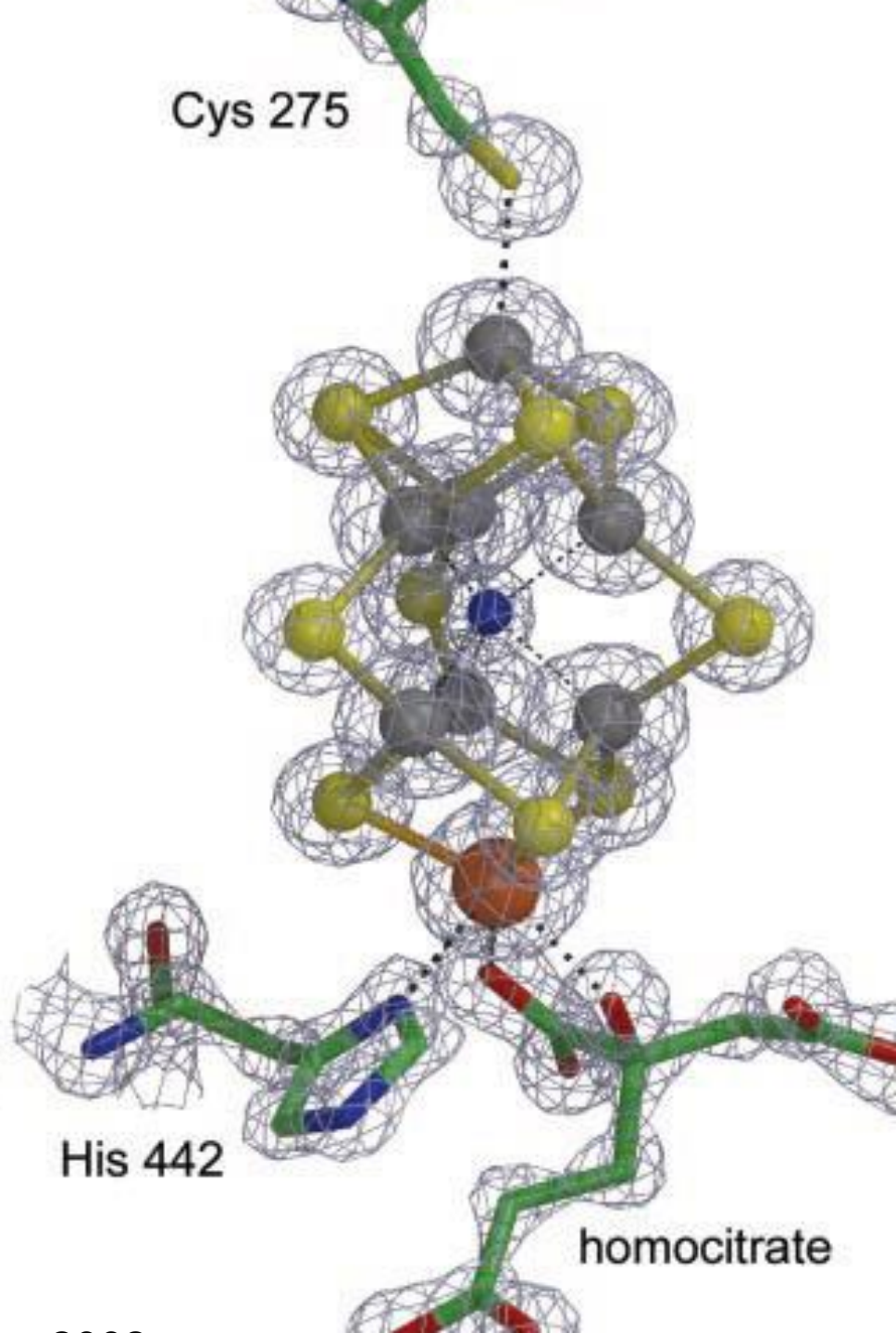
Tutto in  $\alpha$

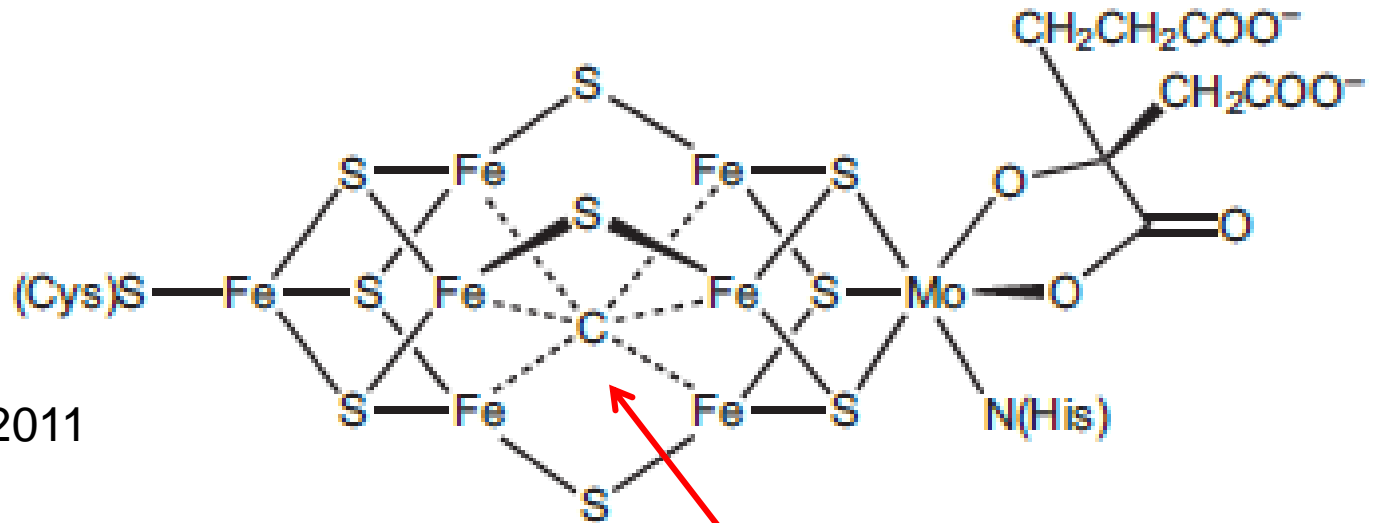
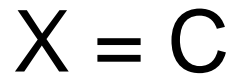


Cys 275



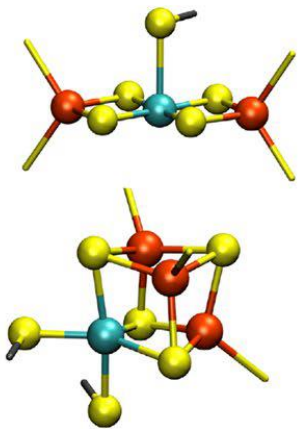
Cys 275





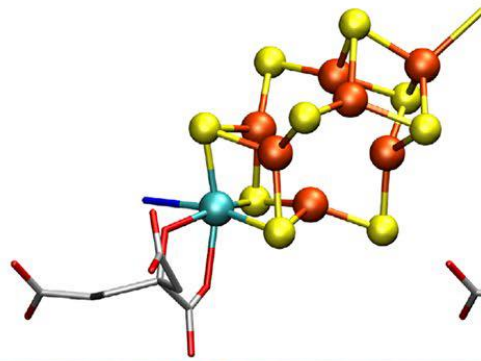
*Science*, 2011

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



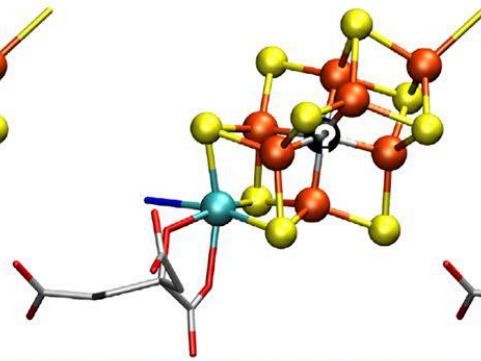
1978

First structural models from EXAFS



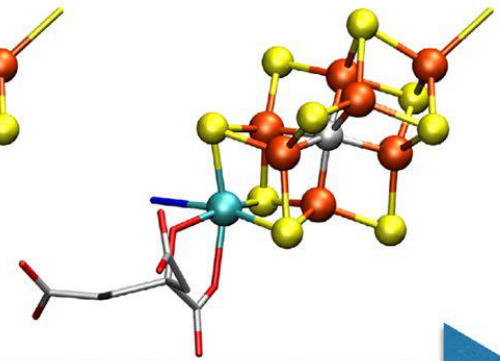
1992

First crystal structure (2.7Å)



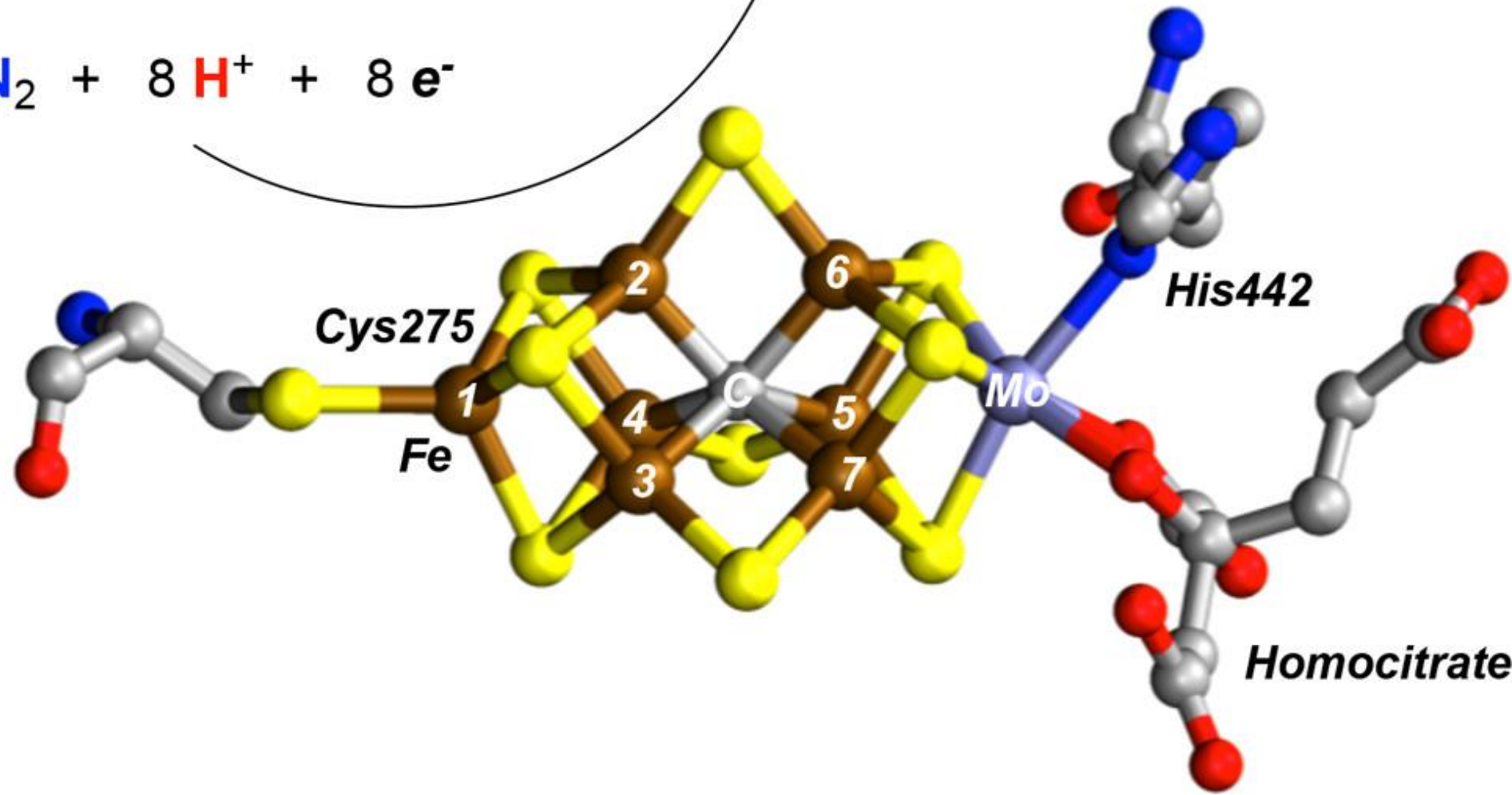
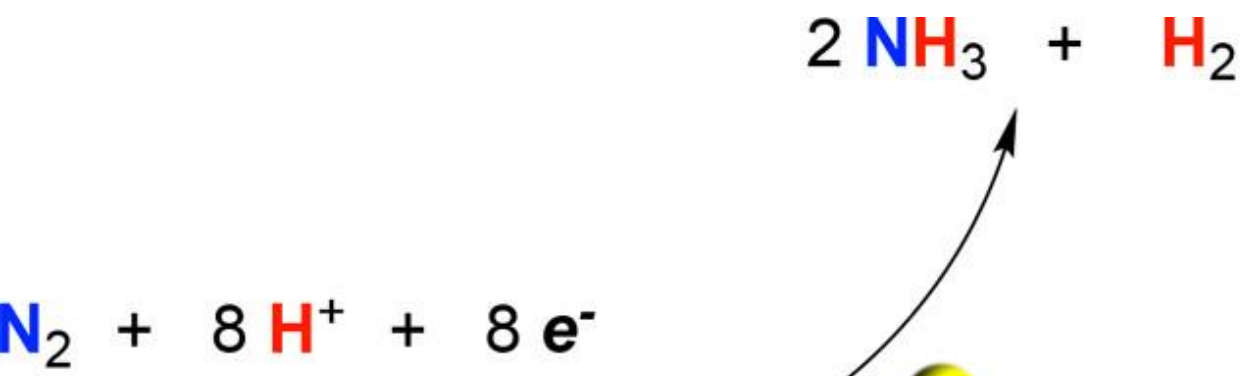
2002

Discovery of interstitial atom

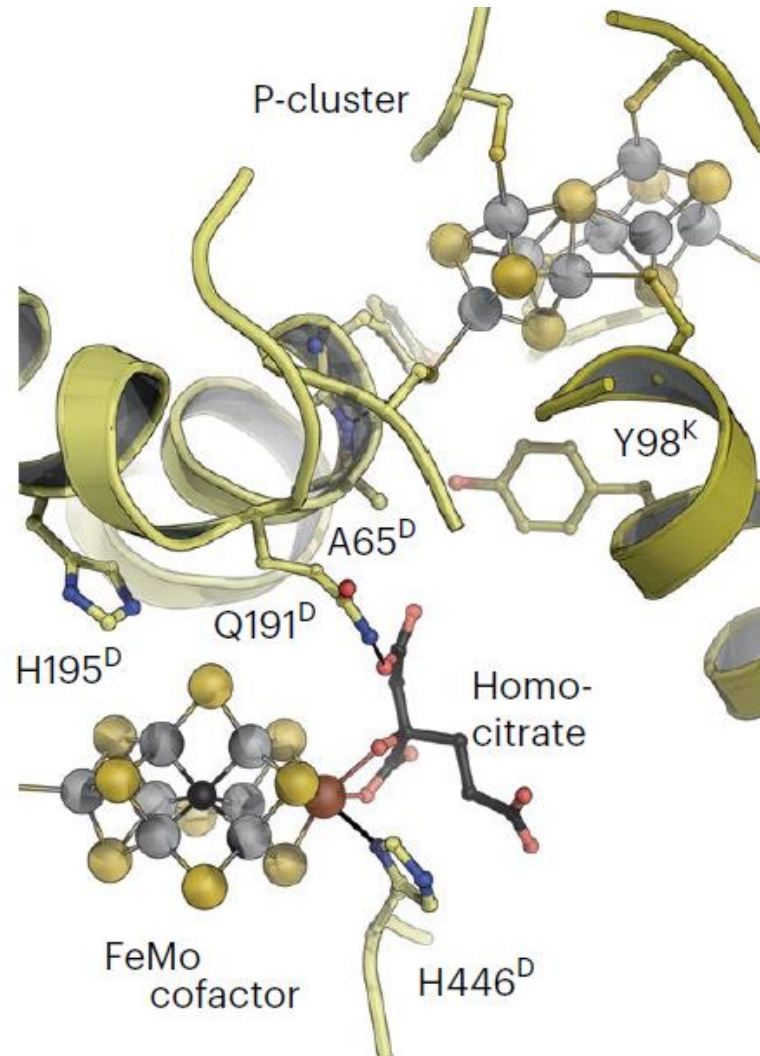


2011

Interstitial atom identified as carbon

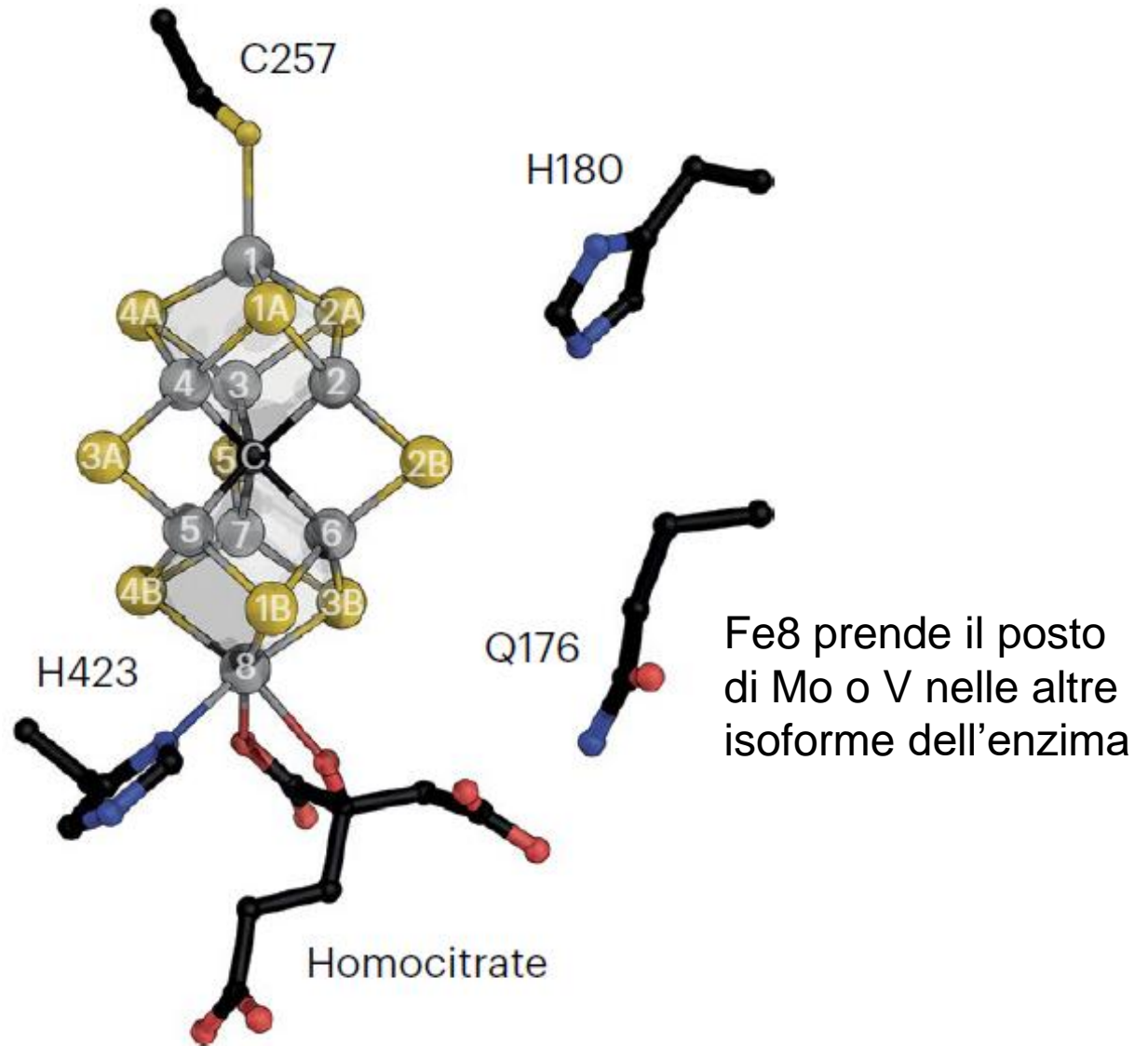


# Percorso del trasferimento elettronico tra P-cluster e il cofattore FeMo

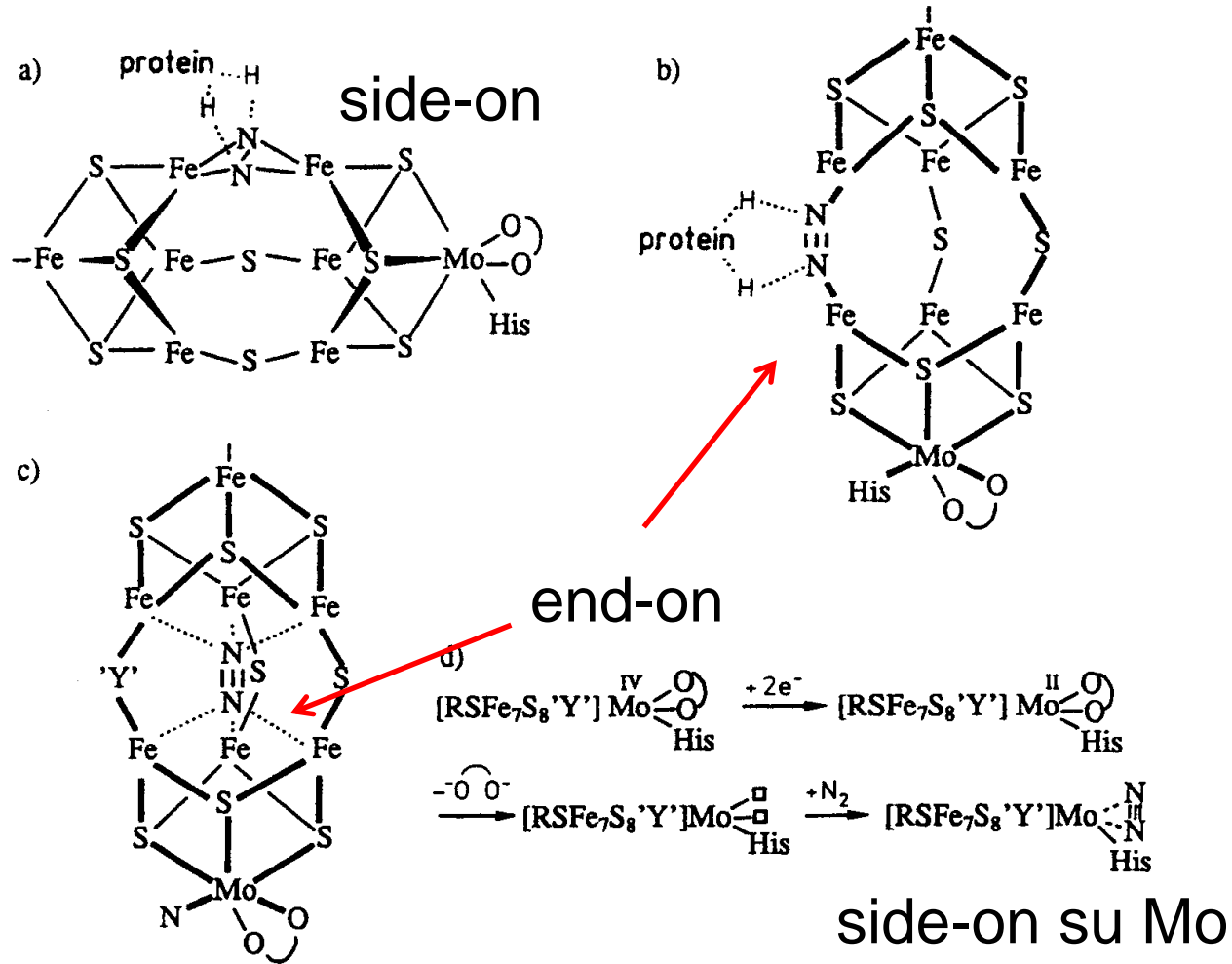




# Struttura del cofattore FeFe

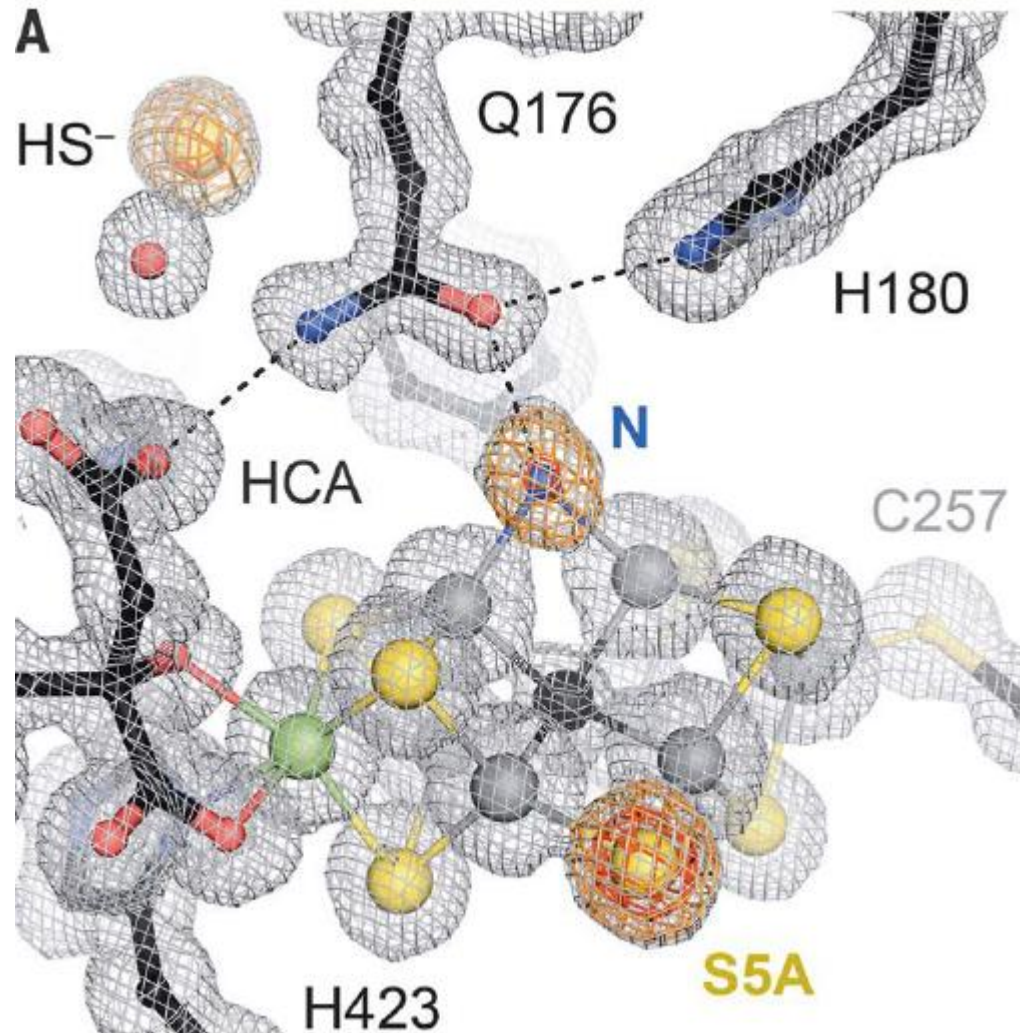


# Ipotetici modi di coordinazione di N<sub>2</sub> al FeMoco

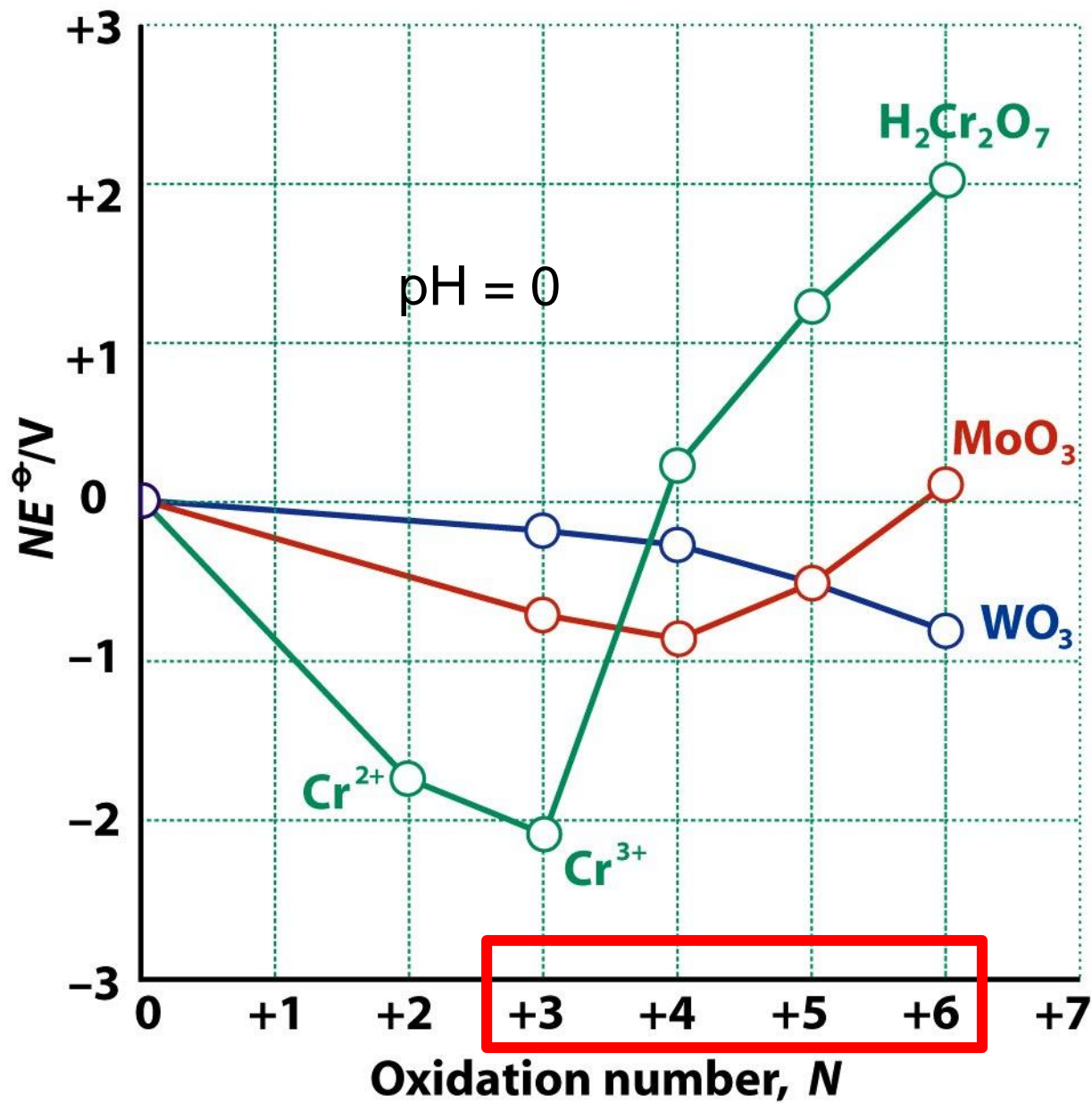


*FeMo-co coordina N<sub>2</sub> solo dopo essere stato ridotto con 4 elettroni*

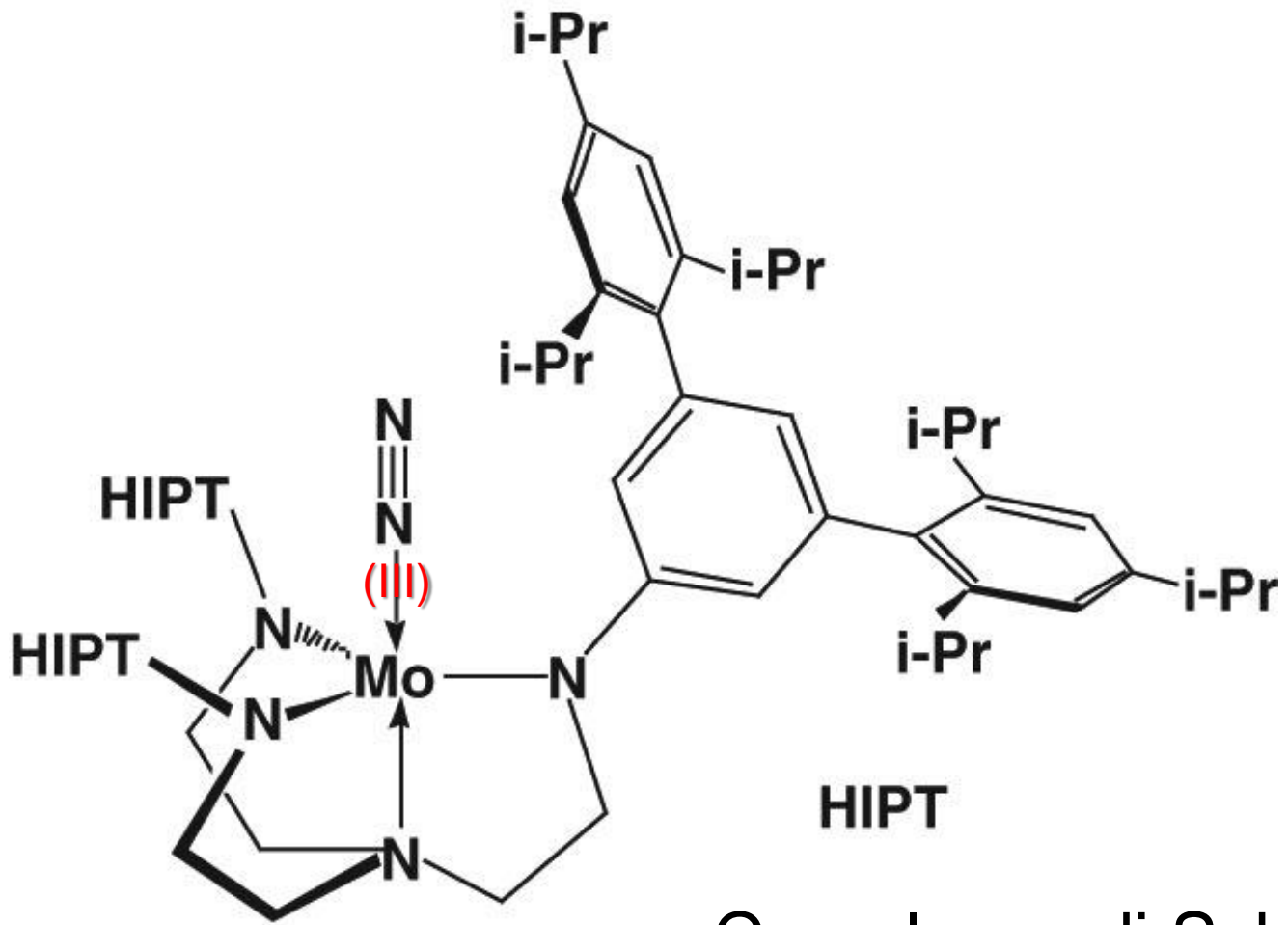
# Intermedio nel ciclo catalitico del cofattore FeV con (presumibilmente) un NH protonato nel sito attivo





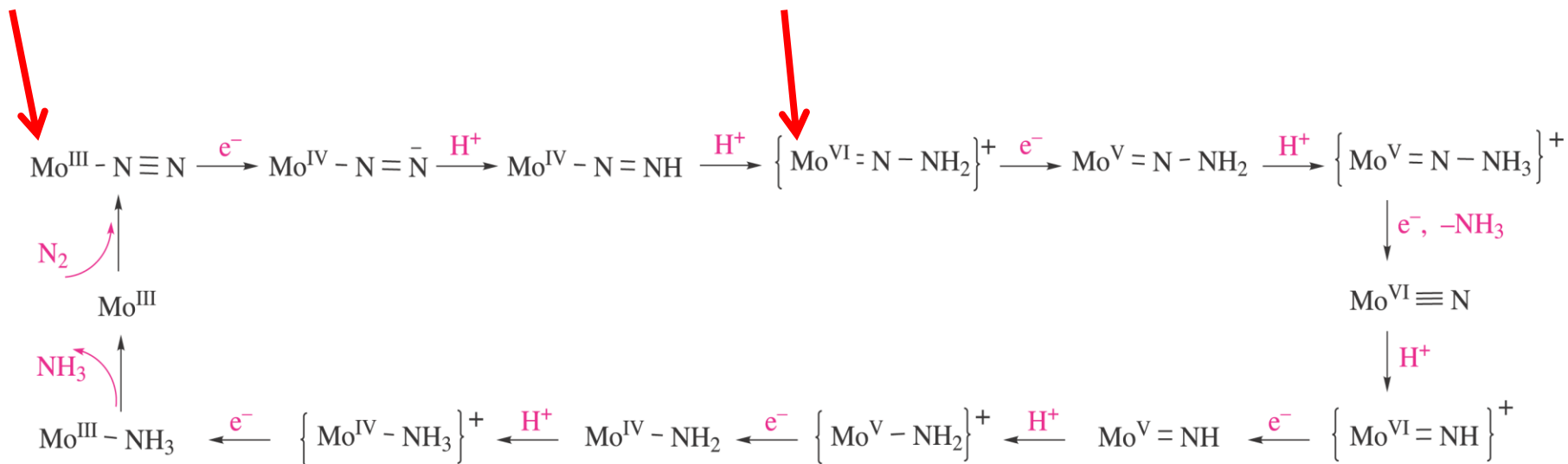
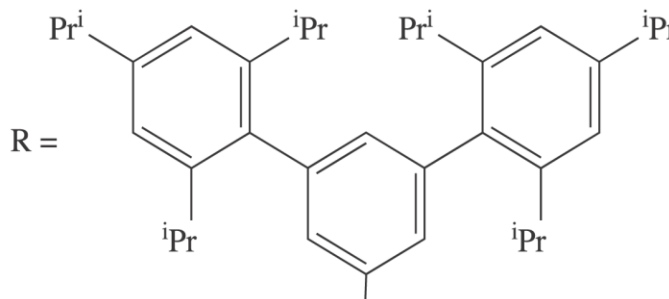
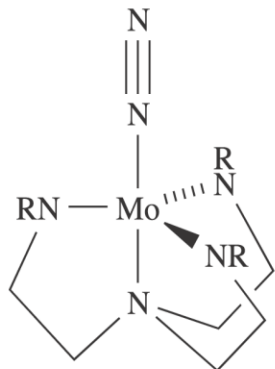


# Modelli



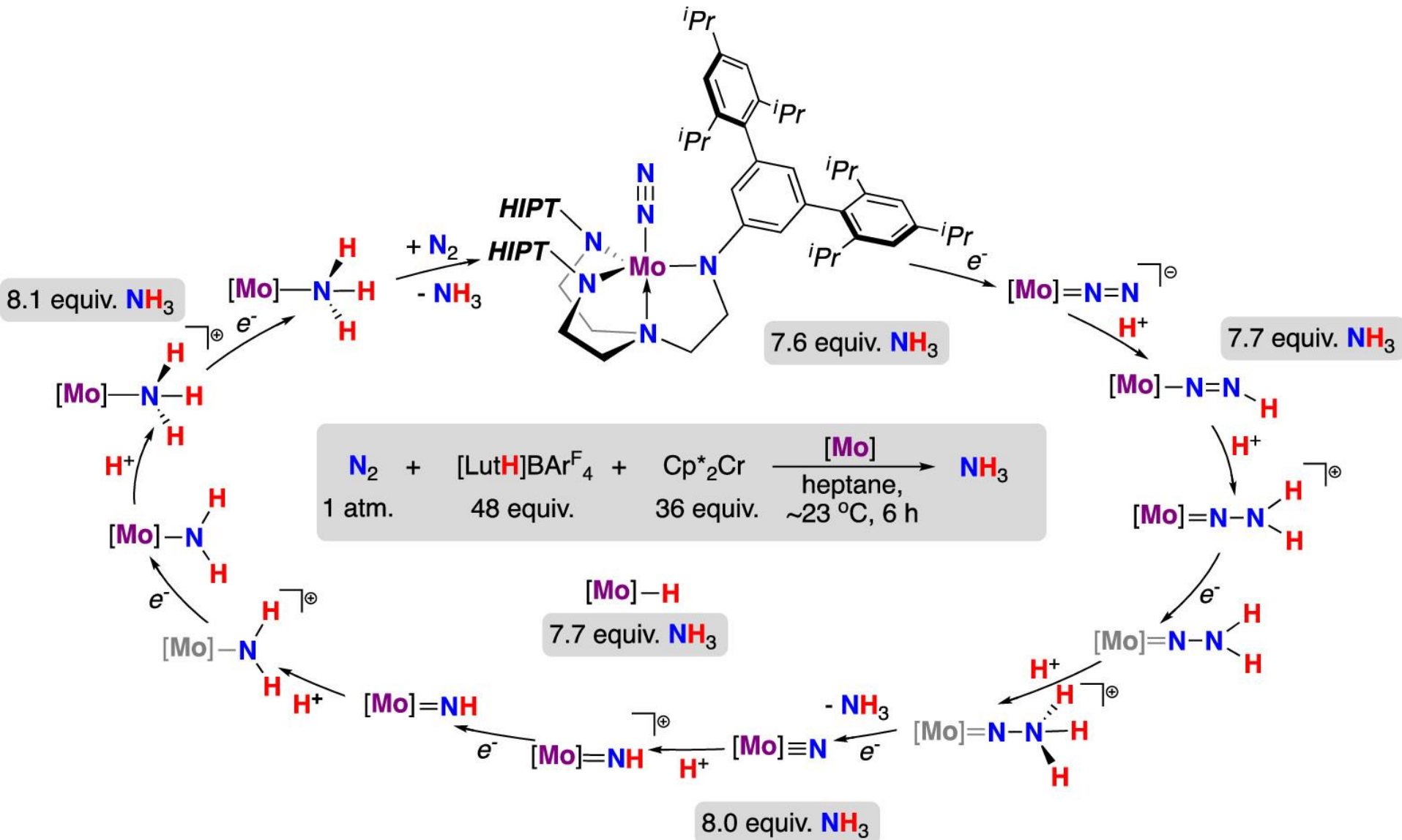
Complesso di Schrock  
(*Science* 2003)

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



8 cicli catalitici, meccanismo *distale*

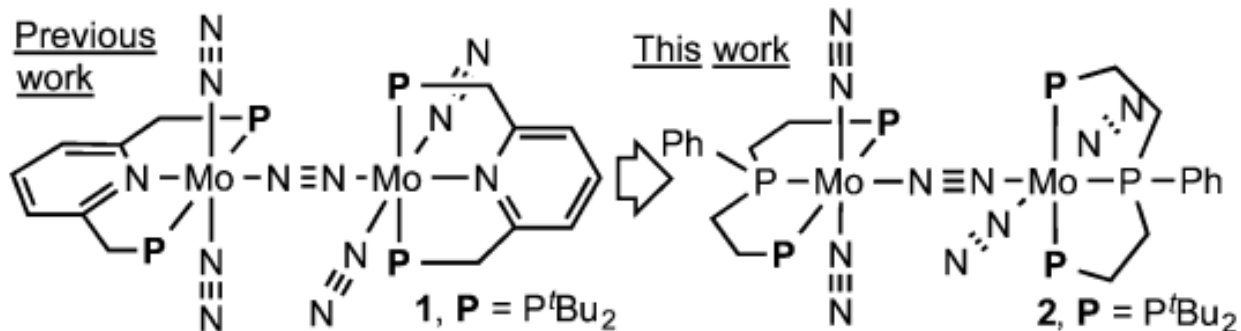
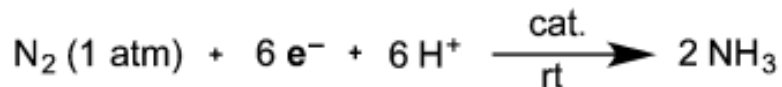
# Ciclo catalitico di Schrock



In viola i composti caratterizzati, in grigio quelli ipotizzati

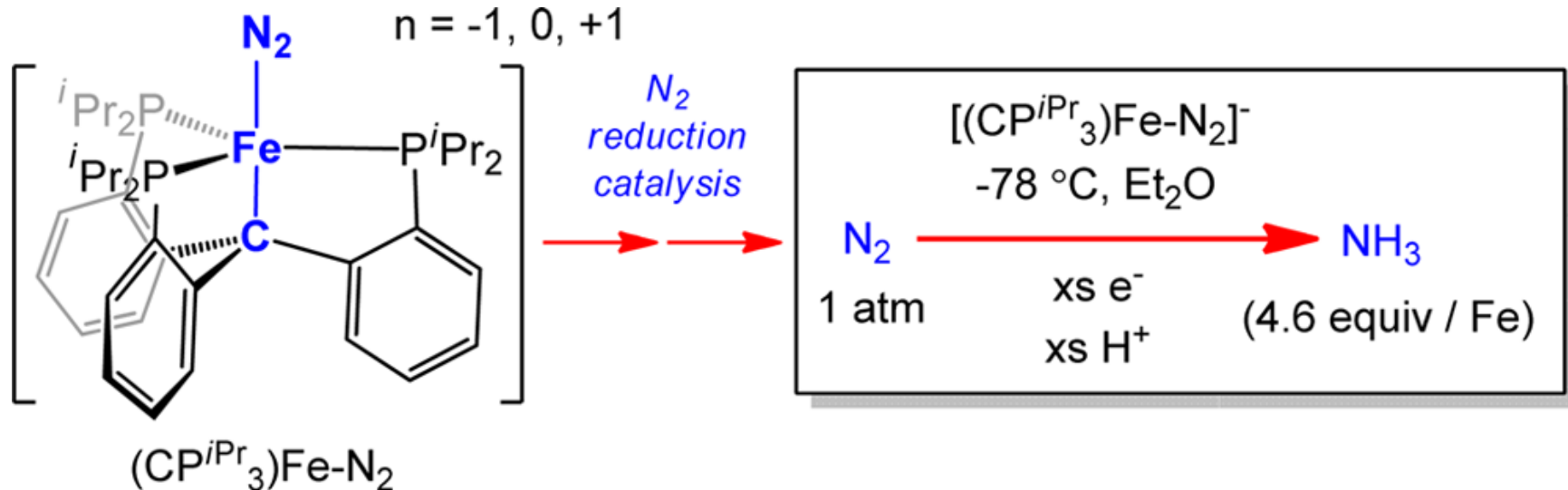
# Complessi di Nishibayashi (2011 e 2015)

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

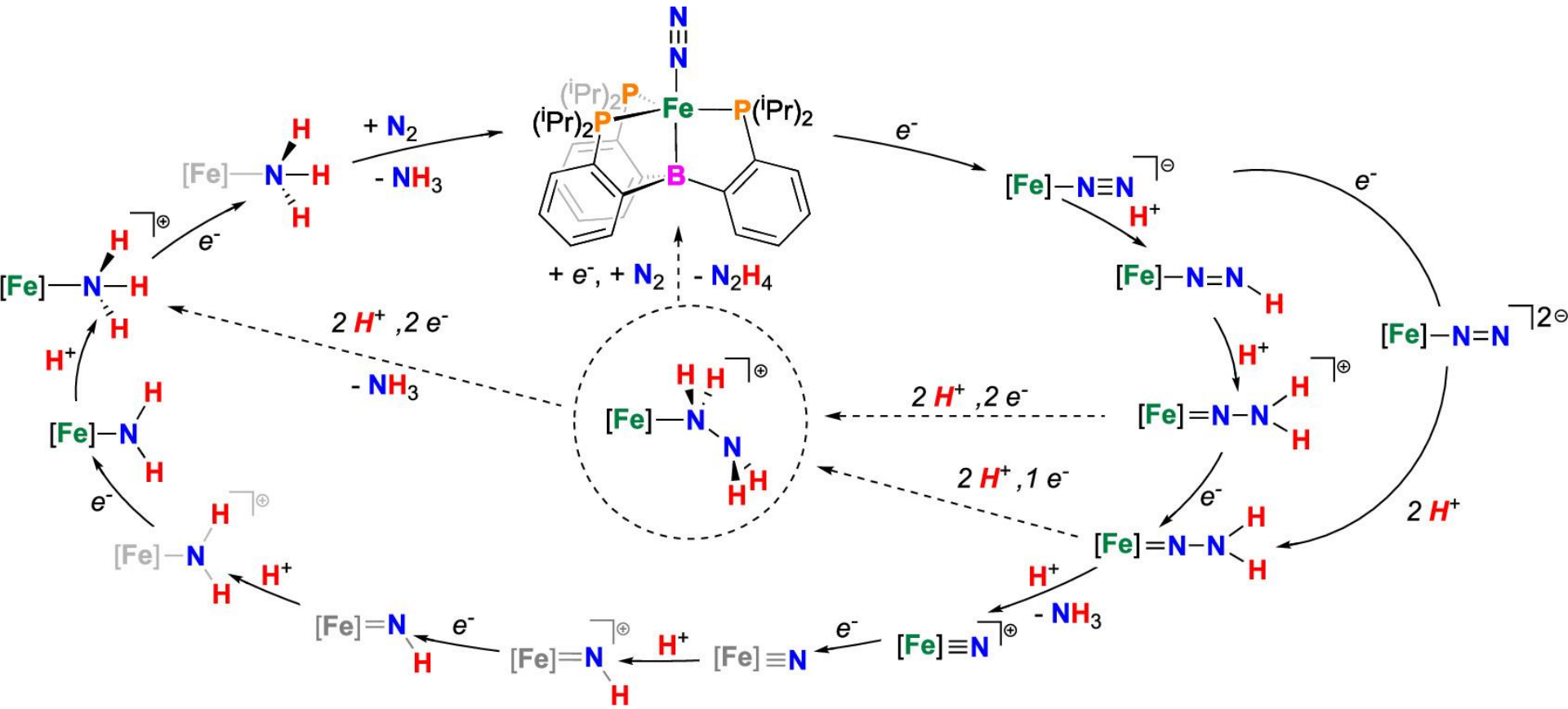


# Complesso di Peters (2014)

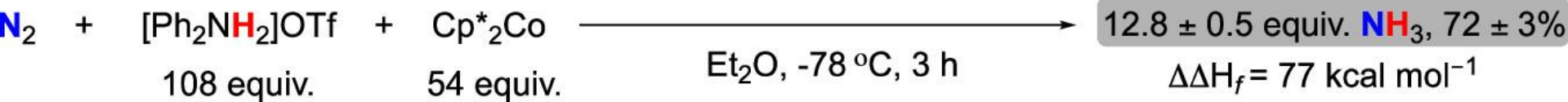
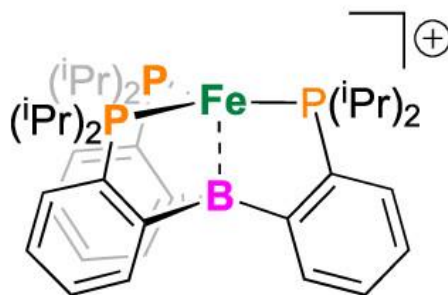
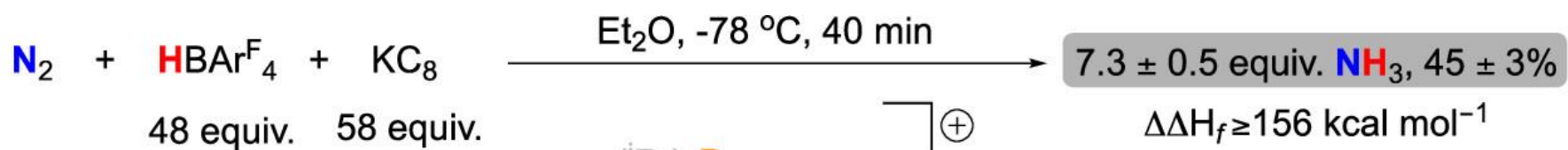
4.6 cicli catalitici, riducente  $\text{K}(\text{crown})$



# Ciclo catalitico di Peters



In verde i composti caratterizzati, in grigio quelli ipotizzati



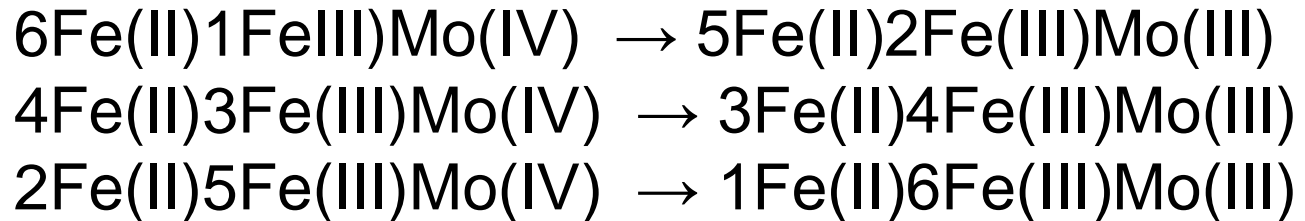


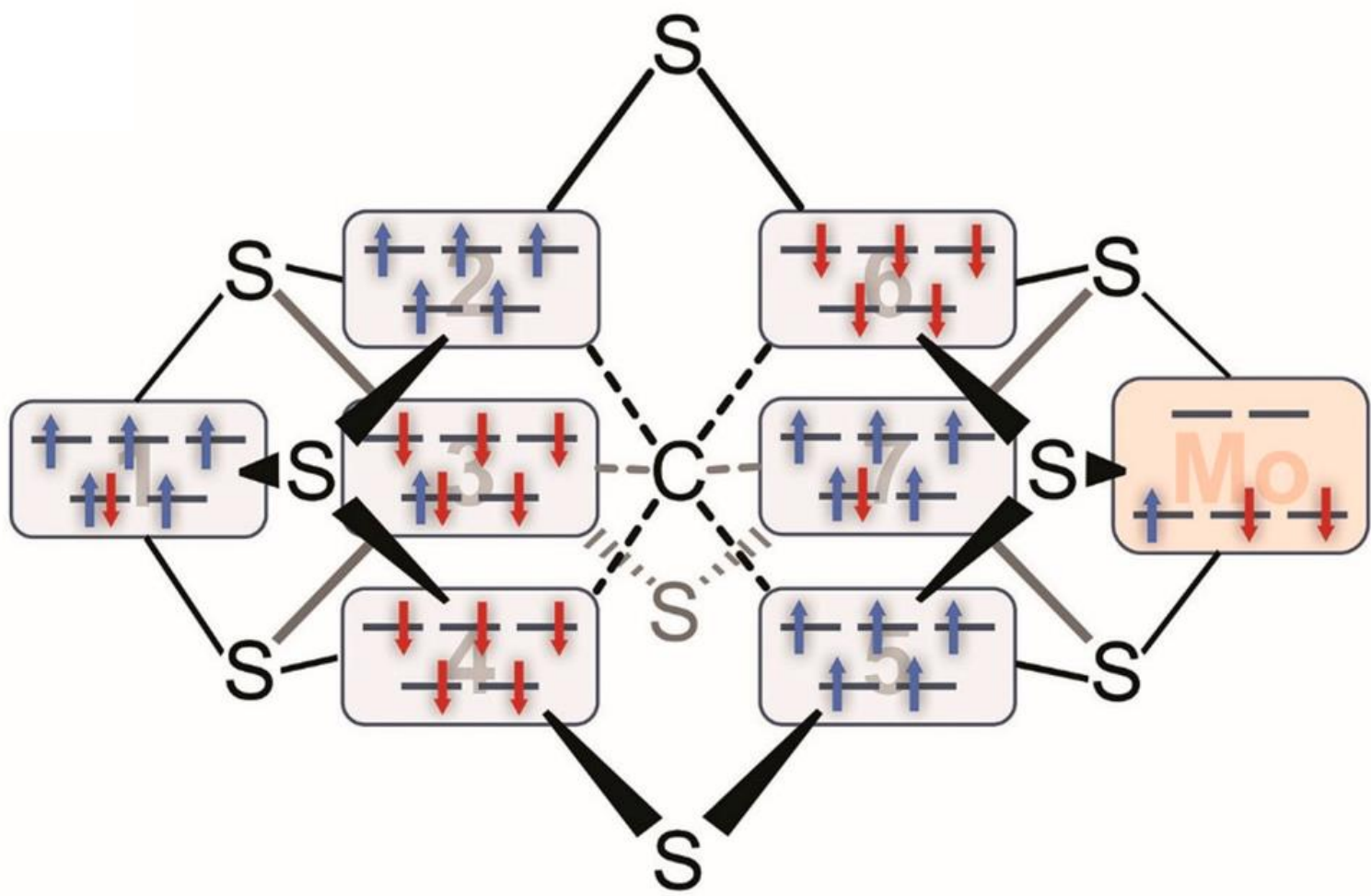
# Struttura elettronica e di spin di FeMo-co

Resting state:  $S = 3/2$

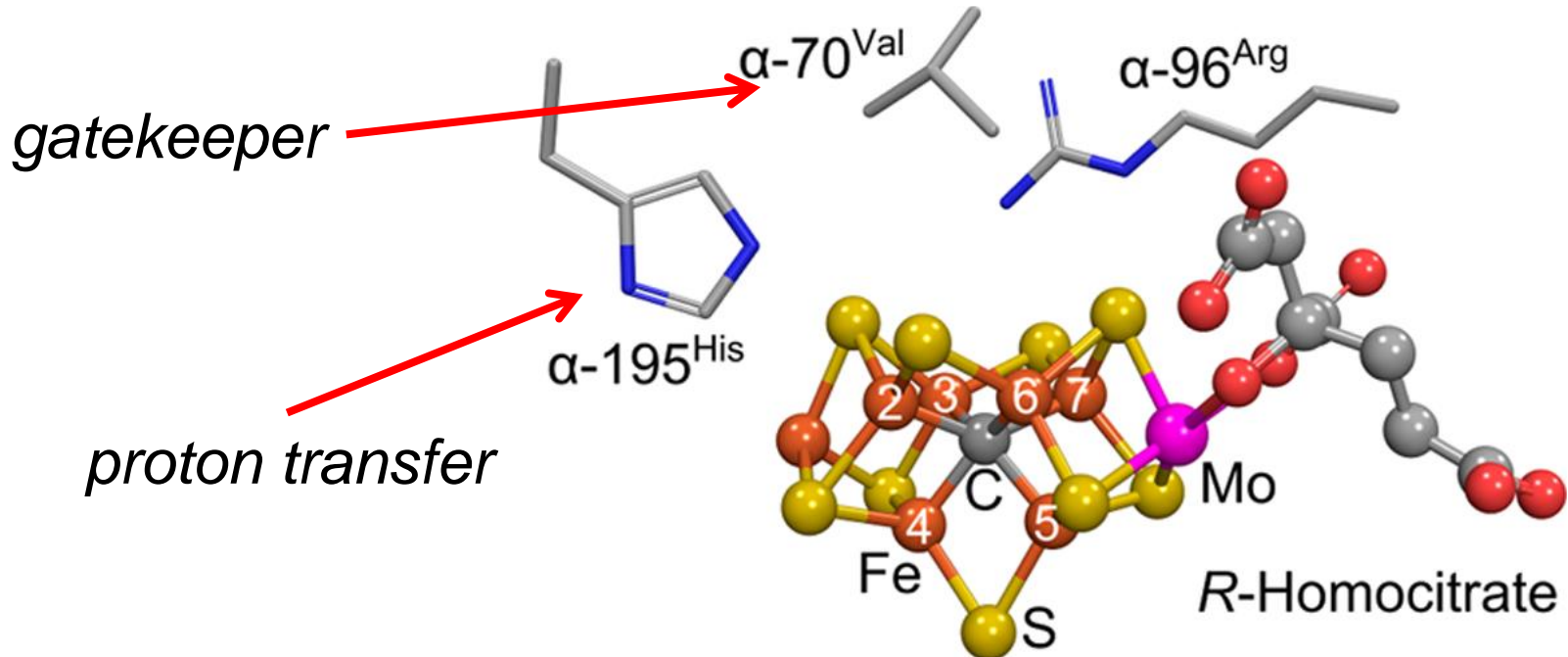
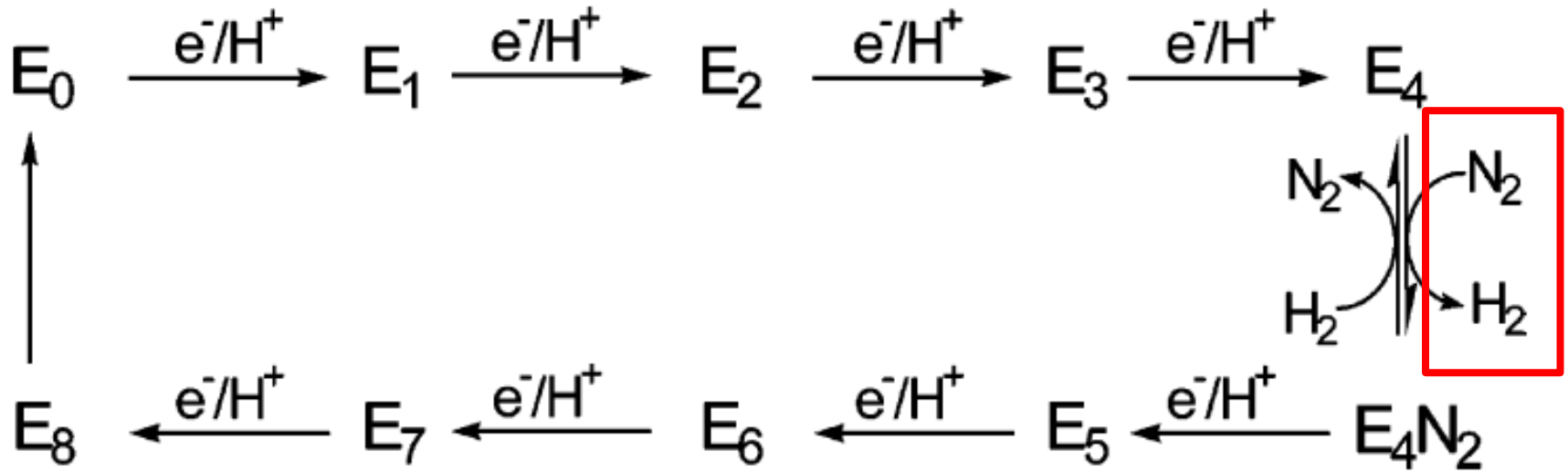
- |   |                       |                       |
|---|-----------------------|-----------------------|
| 1) $[\text{MoFe}_7\text{S}_9\text{C}]^{3-}$ | 6Fe(II)1Fe(III)Mo(IV) |                       |
| 2) $[\text{MoFe}_7\text{S}_9\text{C}]^{1-}$ | 4Fe(II)3Fe(III)Mo(IV) | Mo(IV), $d^2$ $S = 0$ |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

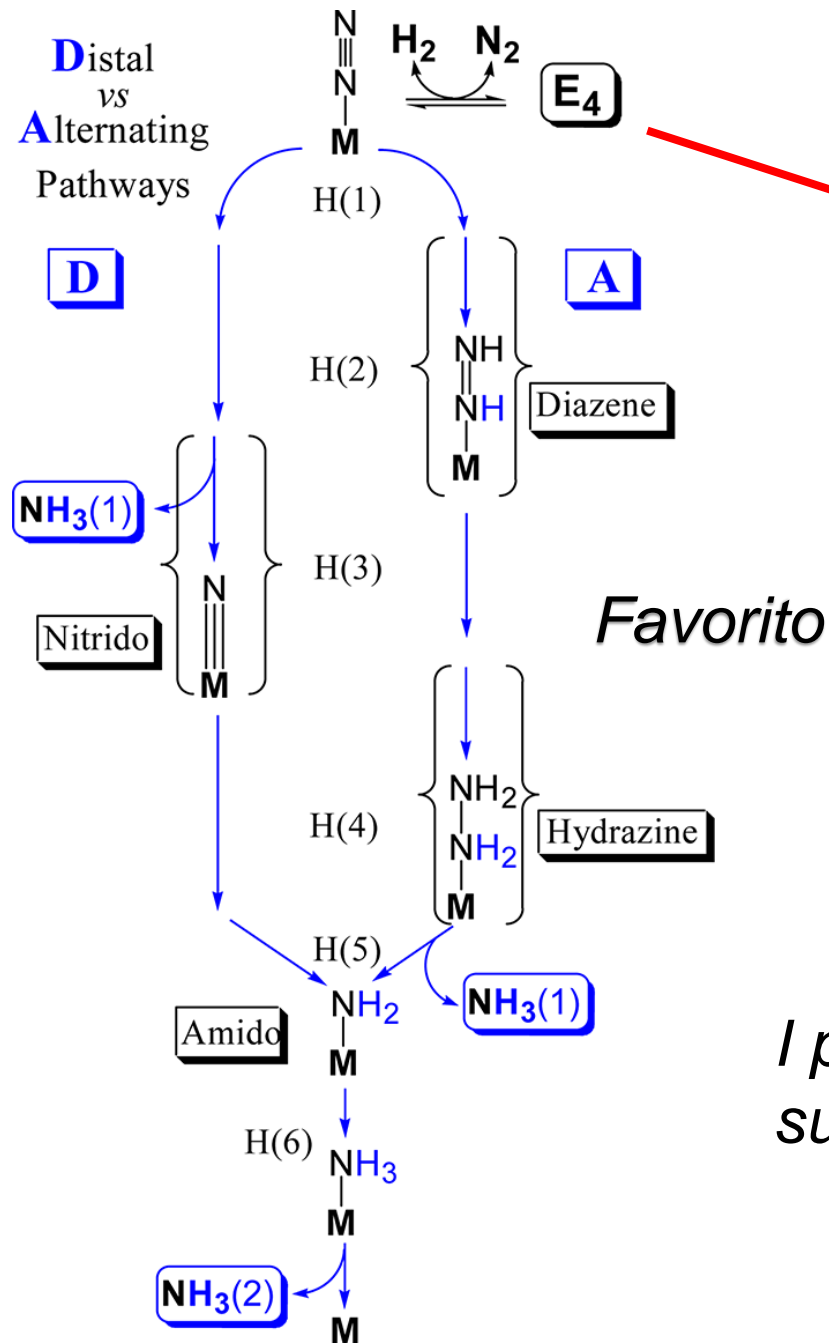
2014: Mo(III),  $d^3$  basso spin ( $\uparrow\uparrow\downarrow$ )? (violazione della regola di Hund)



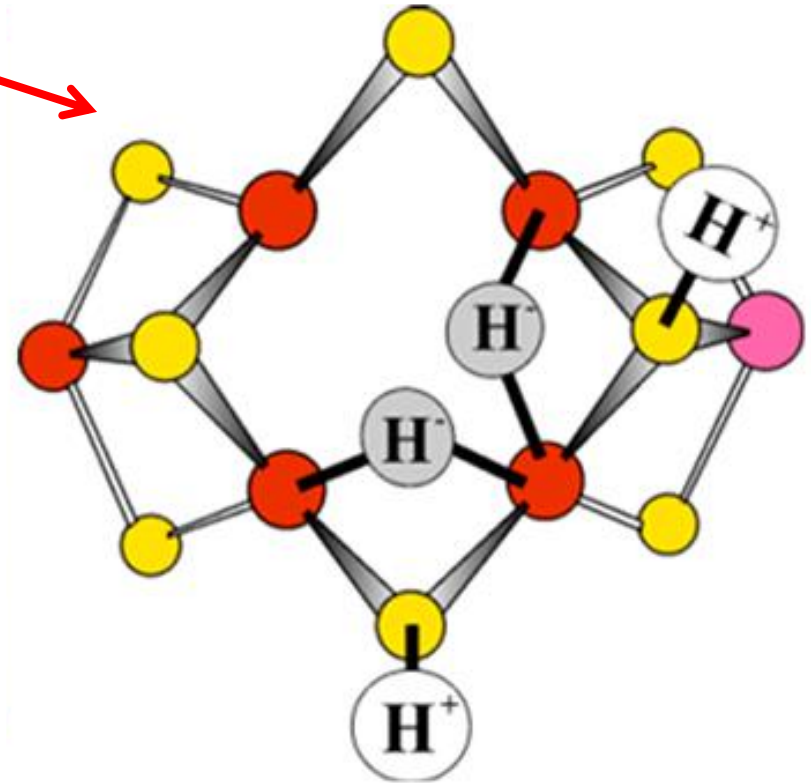


# Ciclo catalitico



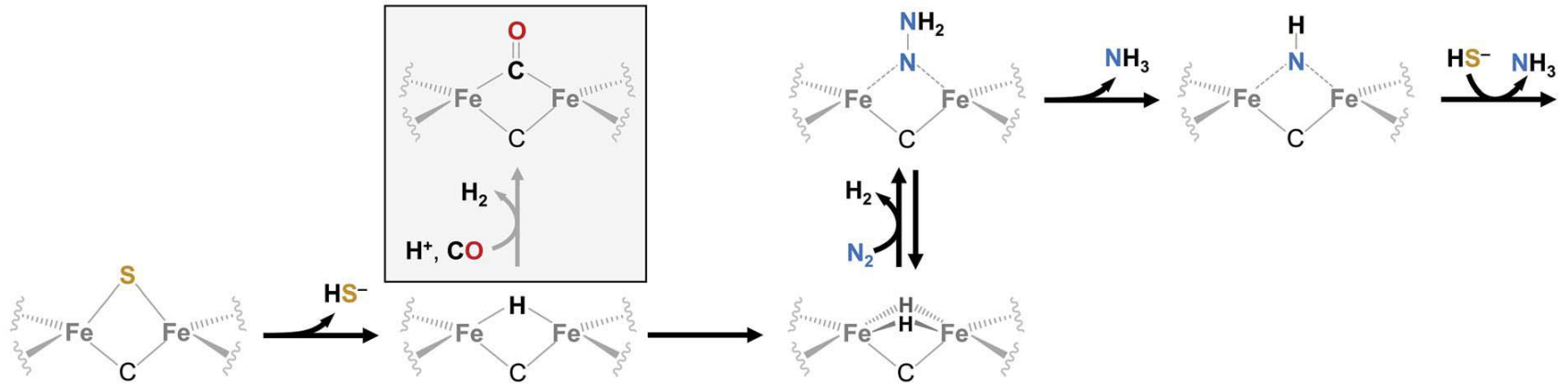


## Modello di E<sub>4</sub>

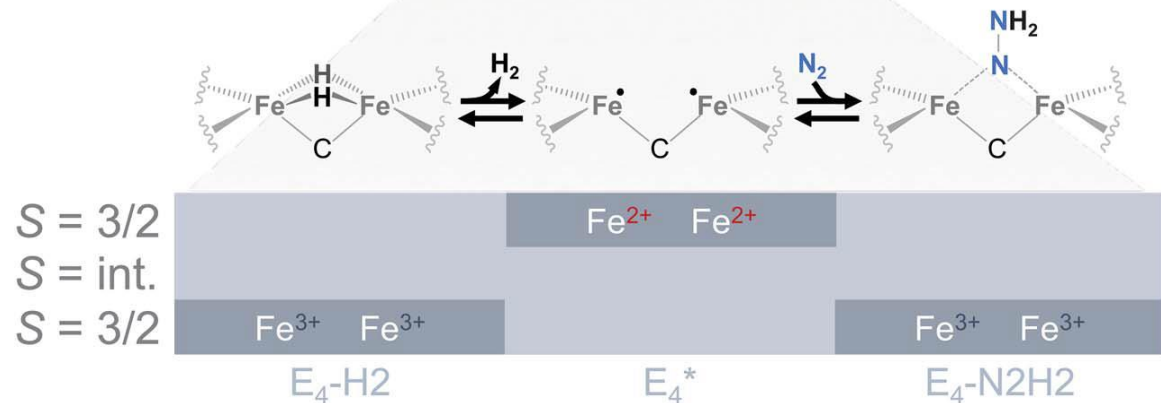


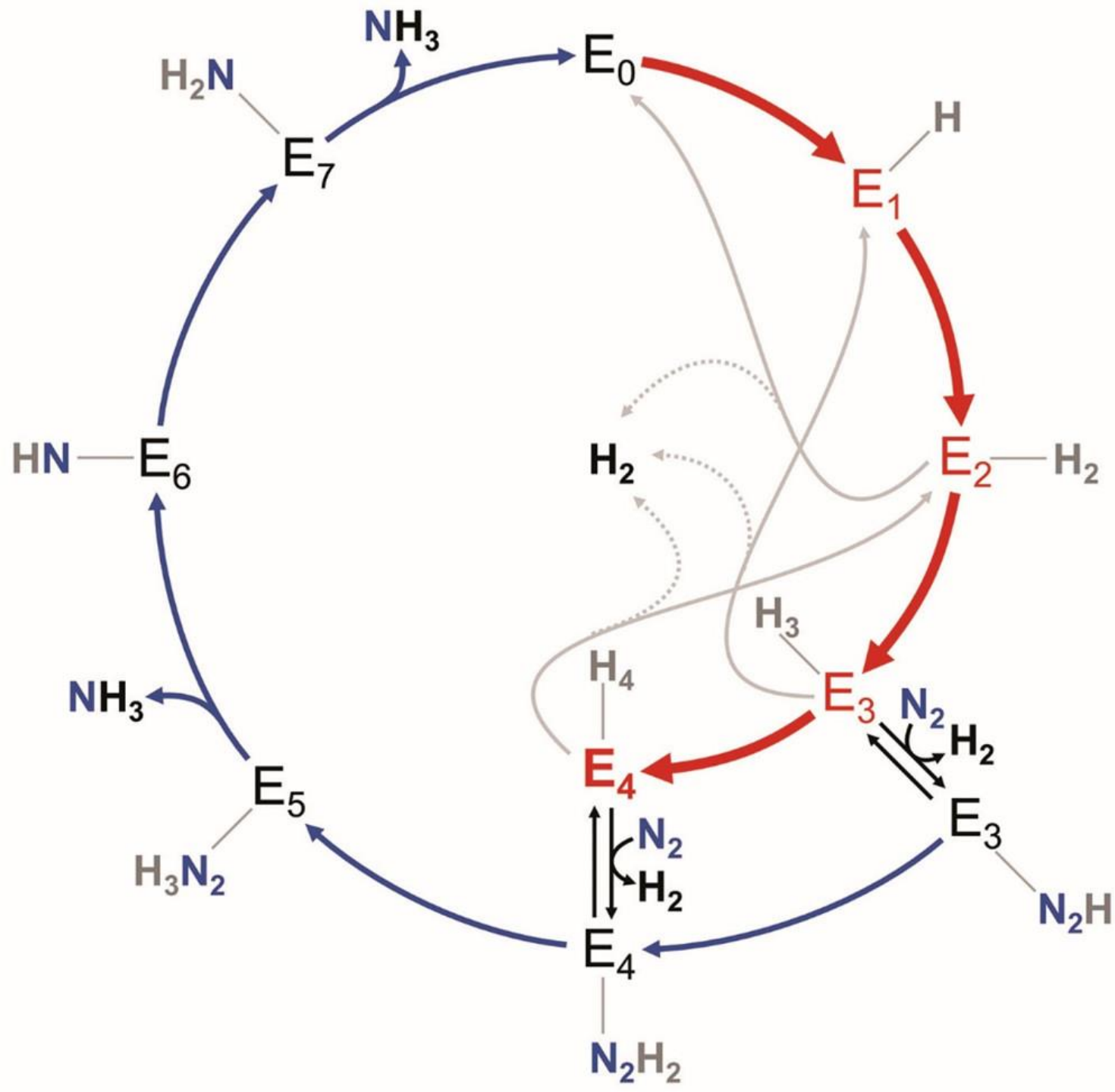
*I primi 4 elettroni si accumulano sugli idruri e non sugli atomi di ferro*

# Ipotesi di trasferimento elettronico

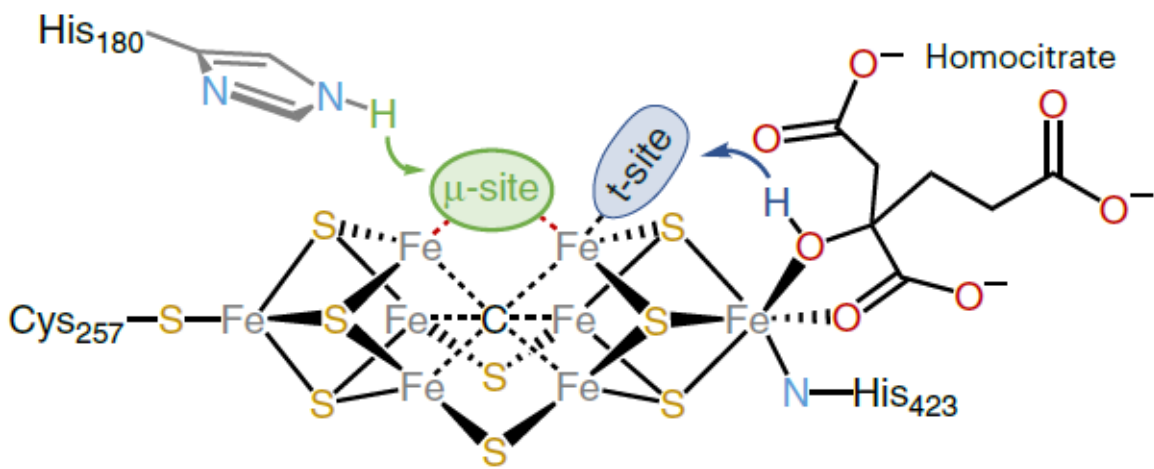
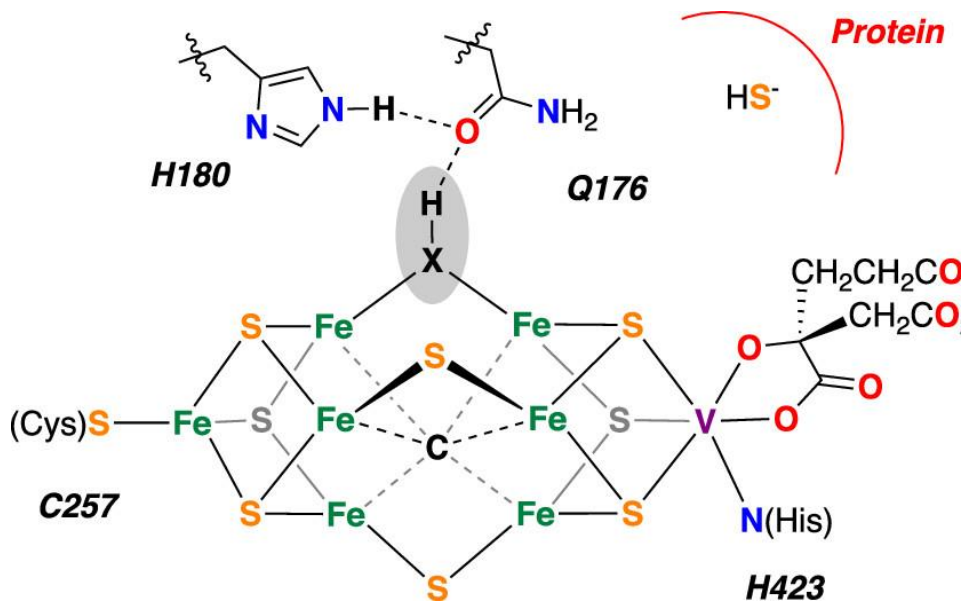


Nel ciclo catalitico il FeMoco cambia di una sola unità il suo stato di ossidazione complessivo ( $E_n$  dispari)

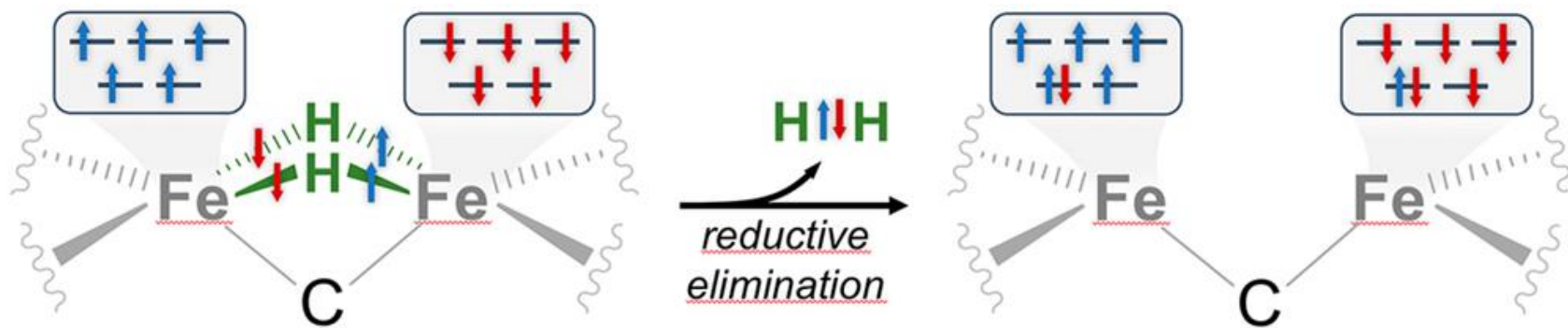




# Ipotesi di sito catalitico tra Fe2 e Fe6, dopo spostamento del solfuro a ponte

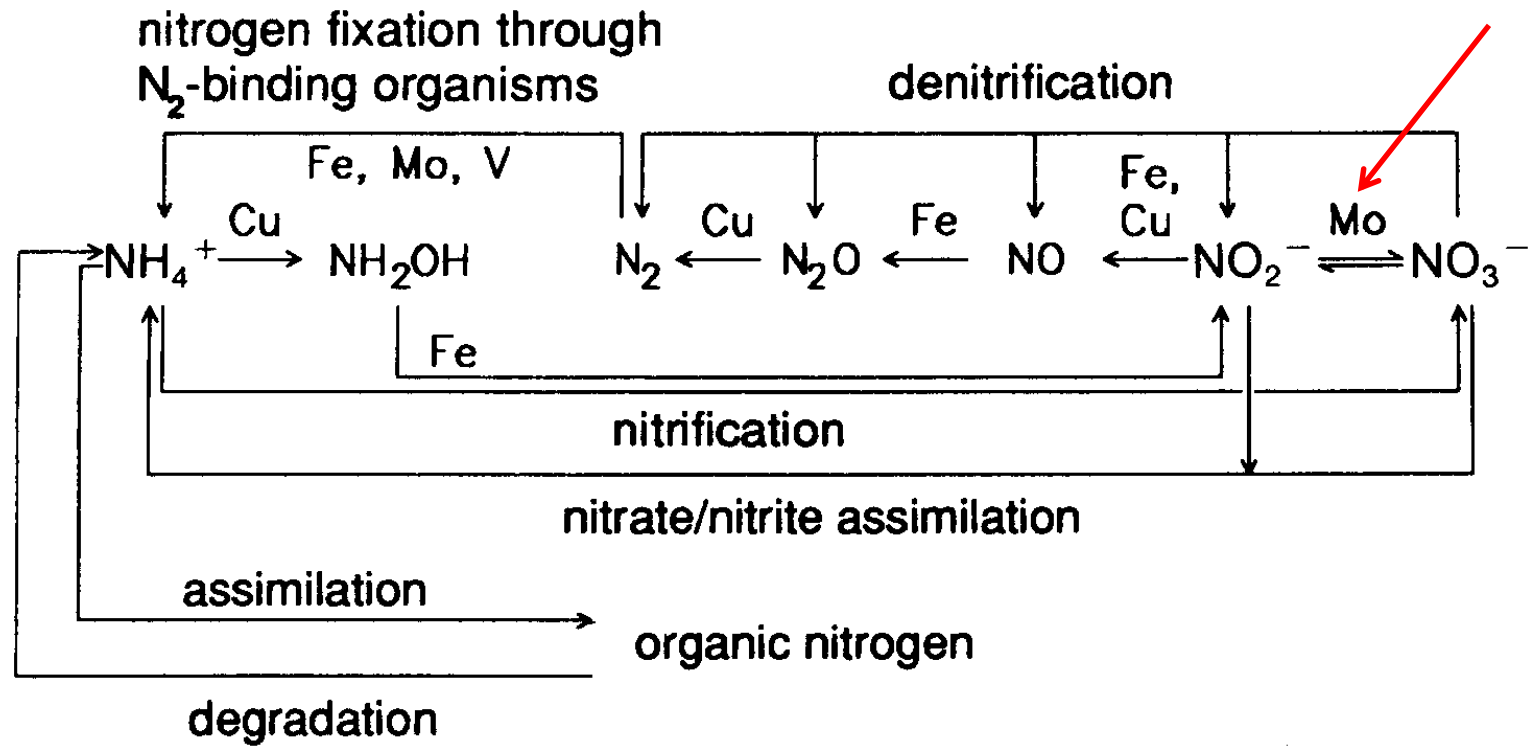






# Altri enzimi al molibdeno

*catalizzano la ossidazione o la riduzione di piccole molecole*

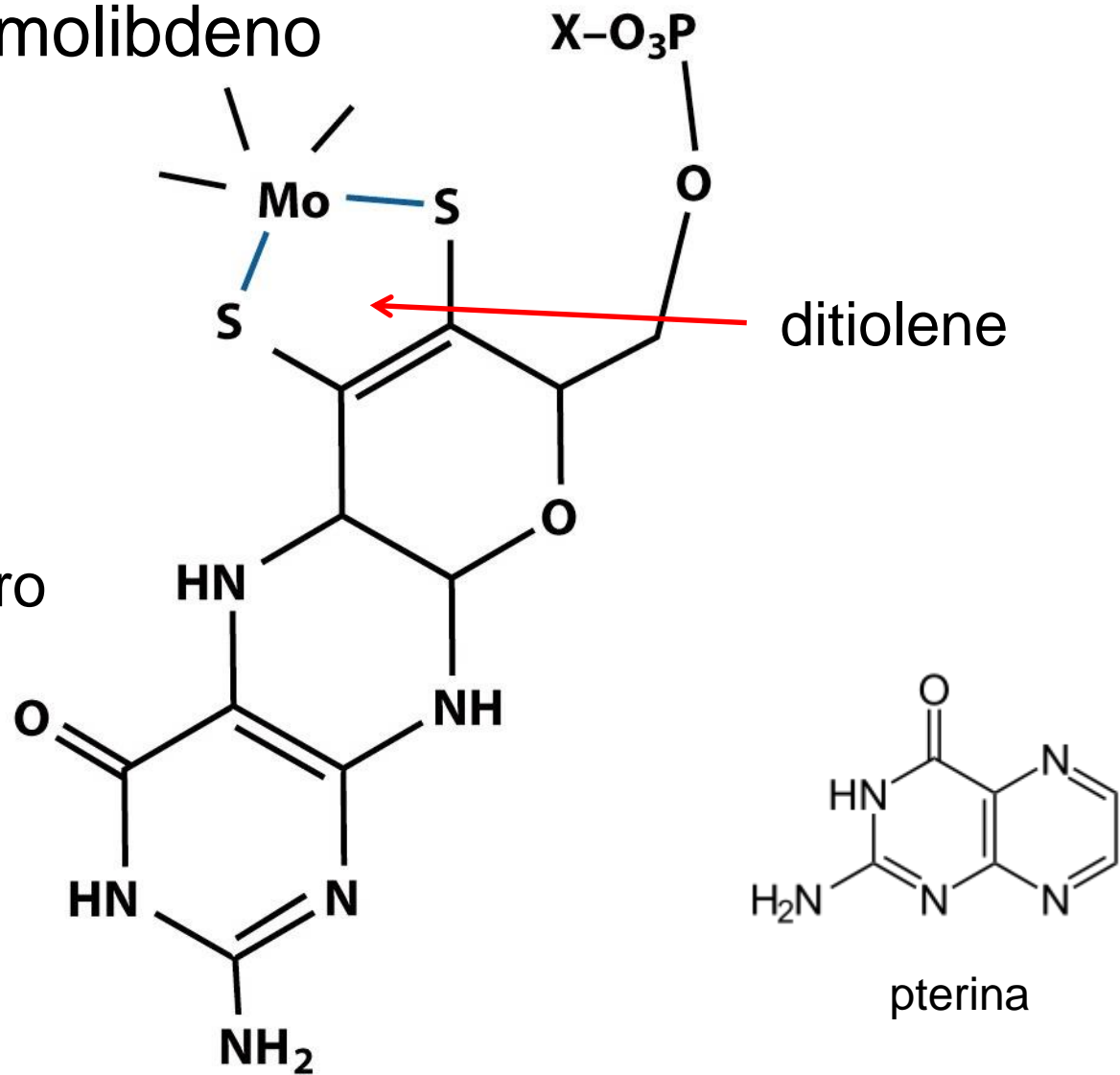


Tre famiglie di enzimi al Mo (*osso-trasferasi*)

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

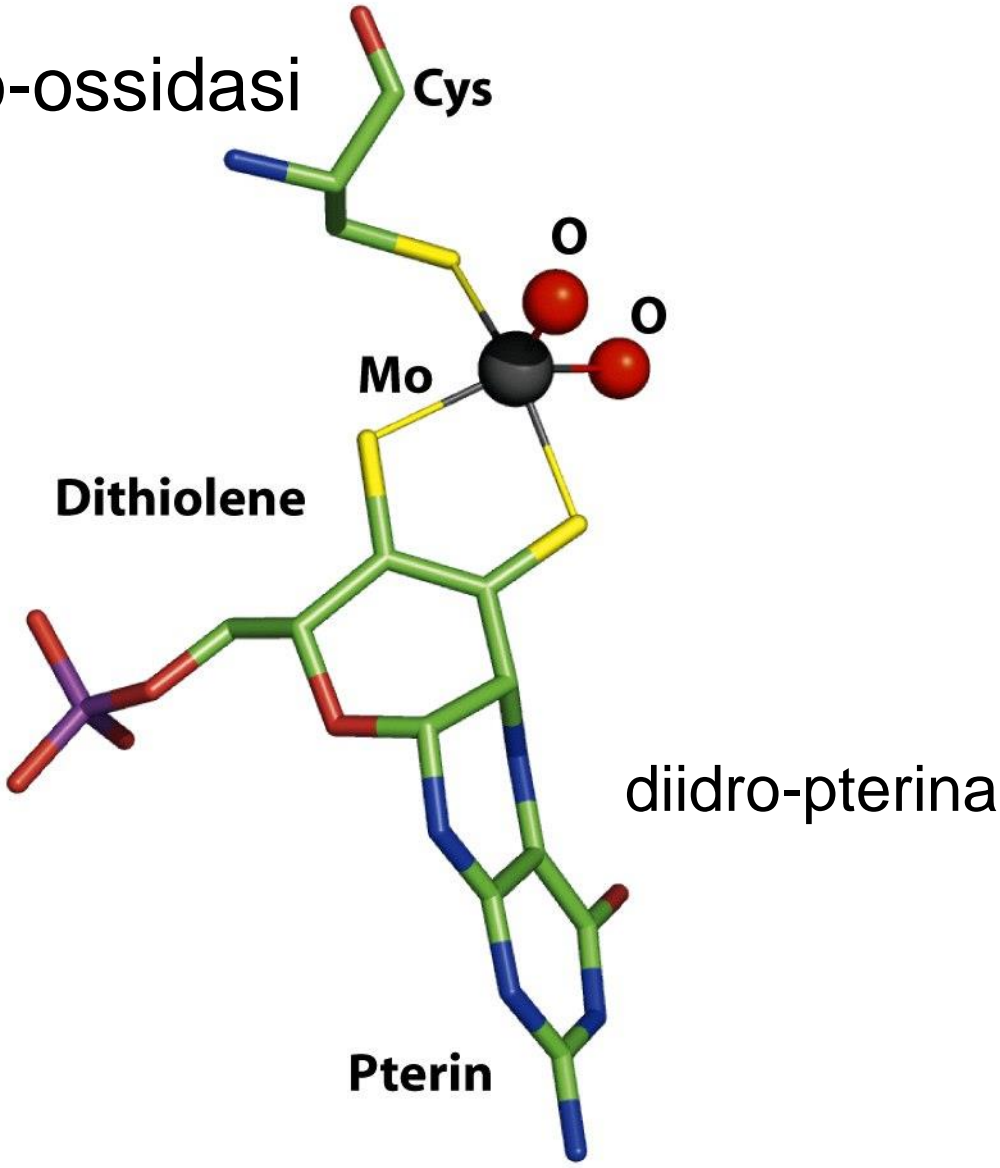
# Cofattore del molibdeno

di-idro o tetra-idro  
pterina

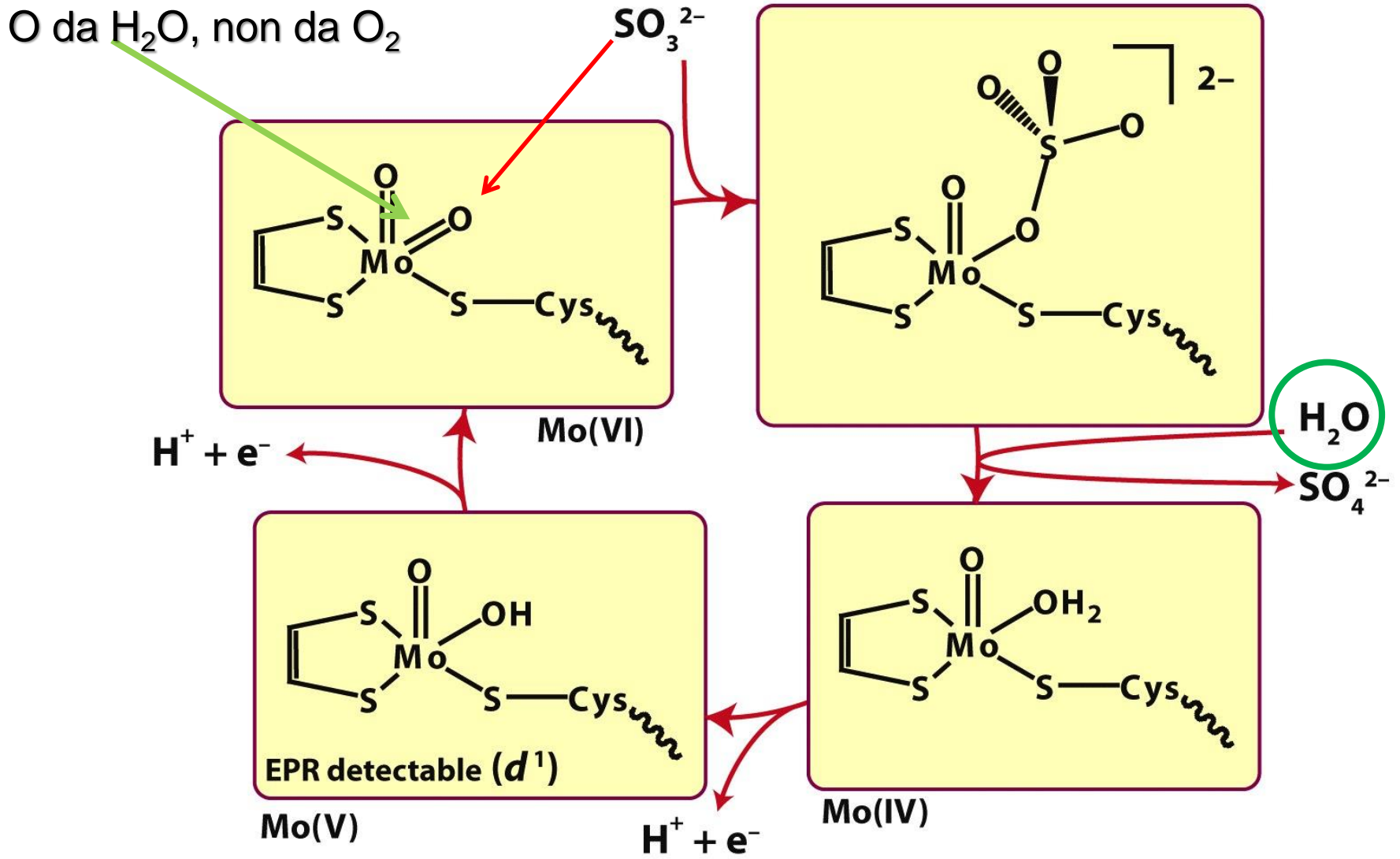


**Molybdopterin as ligand**

# Sito della solfito-ossidasi

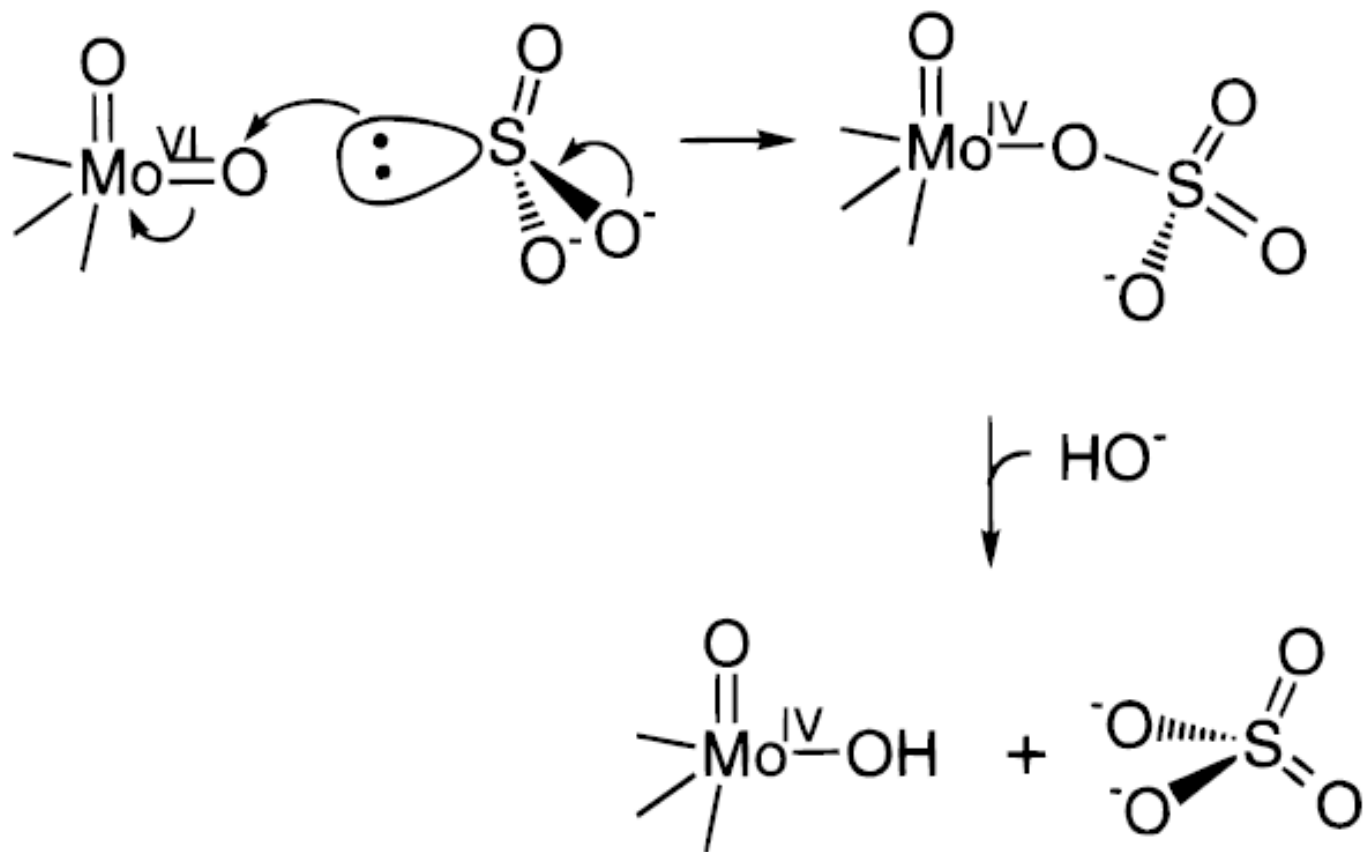


# Ciclo catalitico della solfito-ossidasi

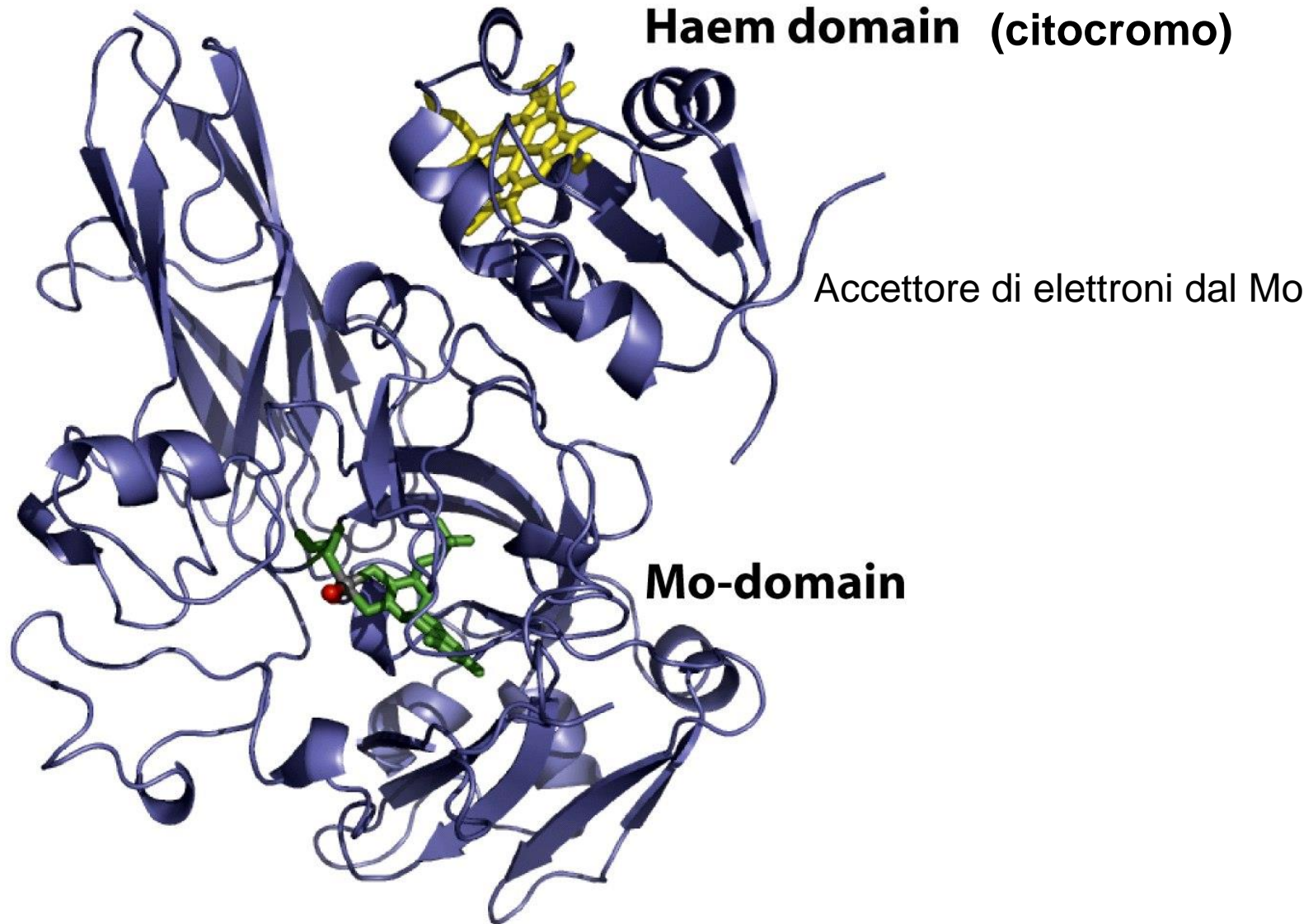


Mo possiede tre stati di ossidazione stabili, Mo(IV), Mo(V) e Mo(VI)

# Dettaglio del meccanismo di trasferimento di ossigeno



# Struttura della solfito-ossidasi





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

