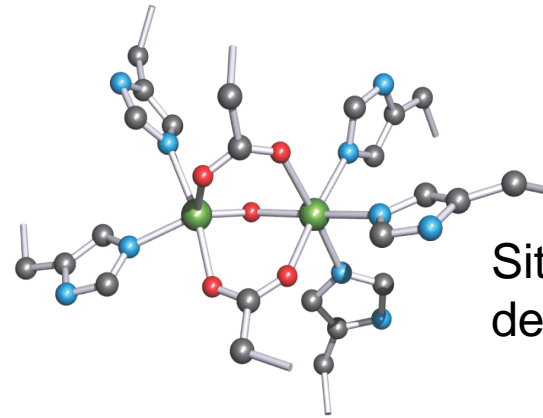
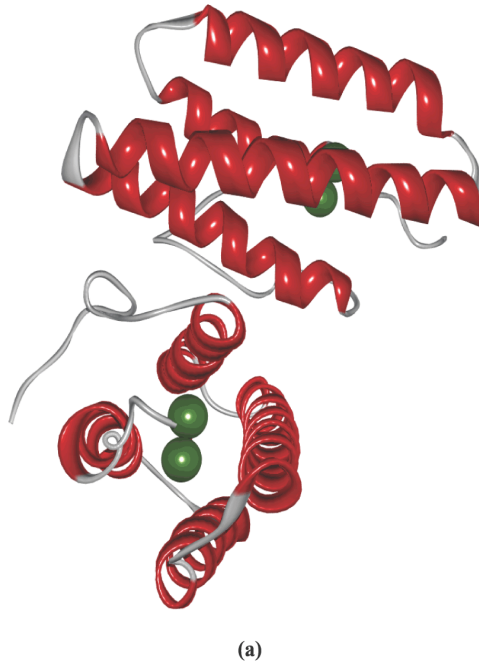


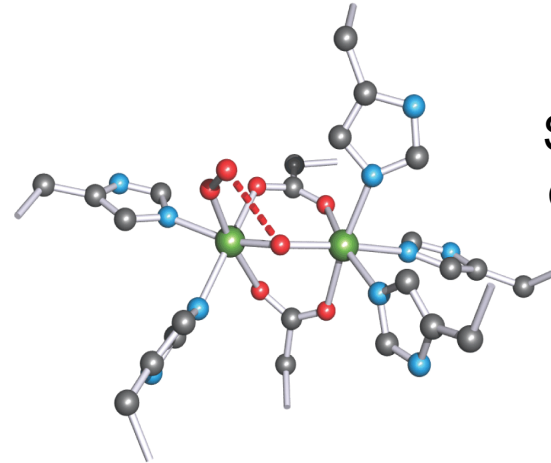
# Desossi-emeritrina

(2 di 8 sub-unità)

13,5 kDa  
113 a.a.

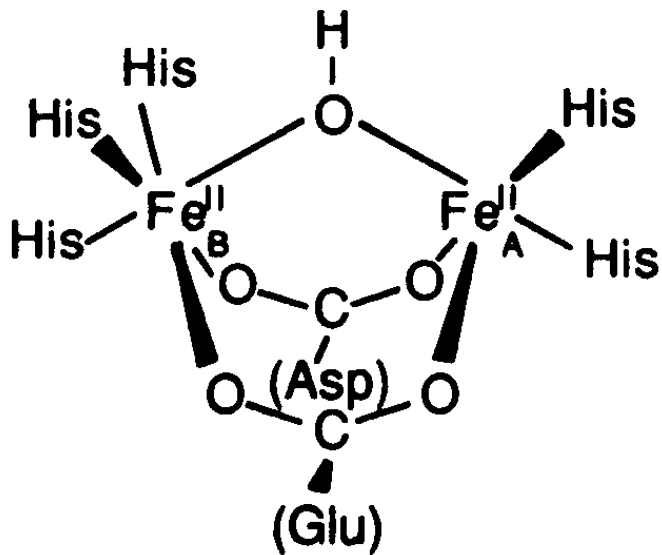


Sito attivo della  
desossi-emeritrina



Sito attivo della  
ossi-emeritrina

Trasporto O<sub>2</sub> in invertebrati marini, molluschi e ragni

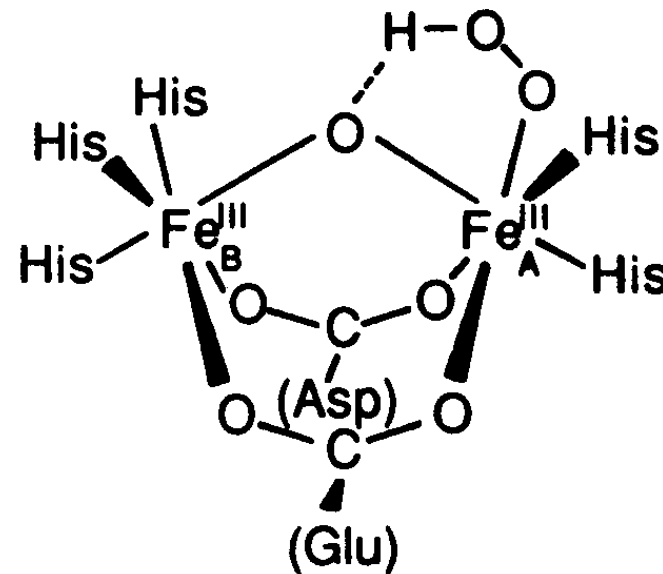
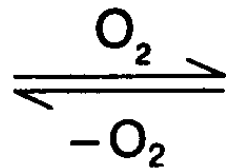


**deoxyhemerythrin**

Incolore

Fe(II) h.s. ( $S = 2$ , debole acc. antiferro)

Mossbauer: 2 Fe(II) indistinguibili



**oxyhemerythrin**

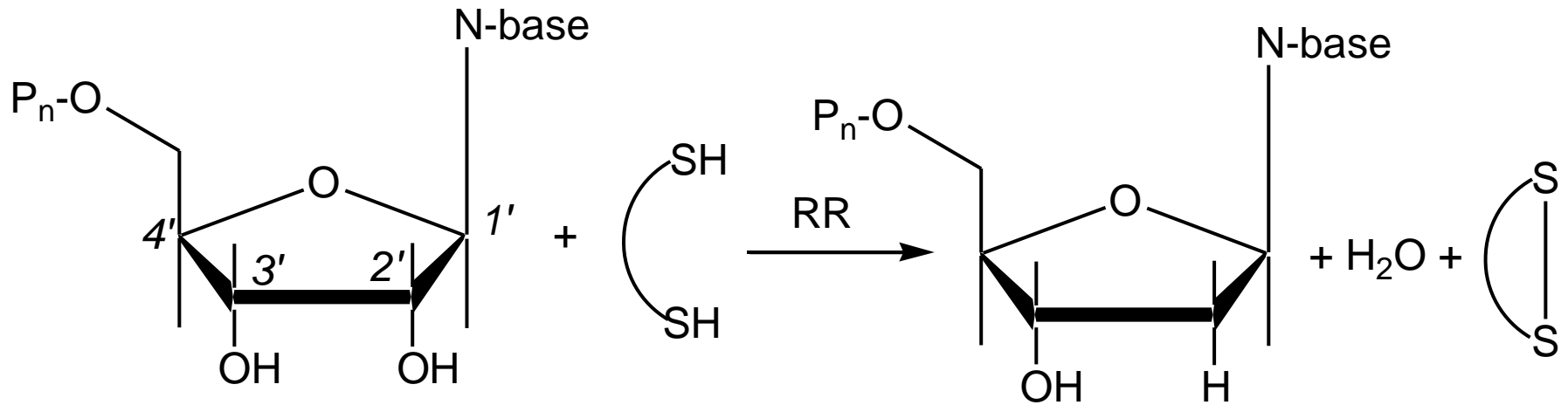
Viola (LMCT)

Fe(III) l.s. ( $S = \frac{1}{2}$ , forte acc. antiferro)

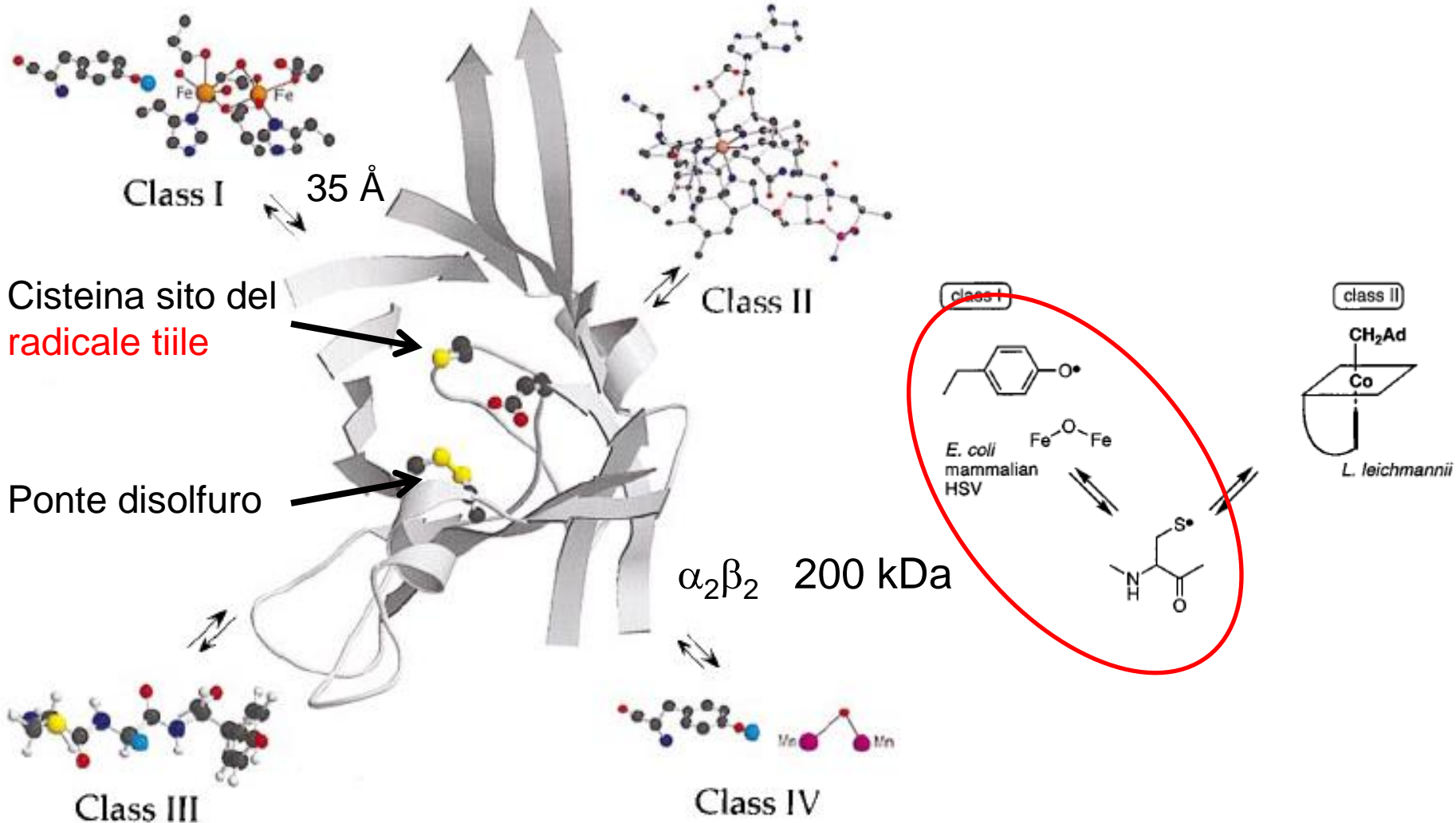
Raman risonante:  $848 \text{ cm}^{-1}$

Mossbauer: 2 Fe(III) diversi

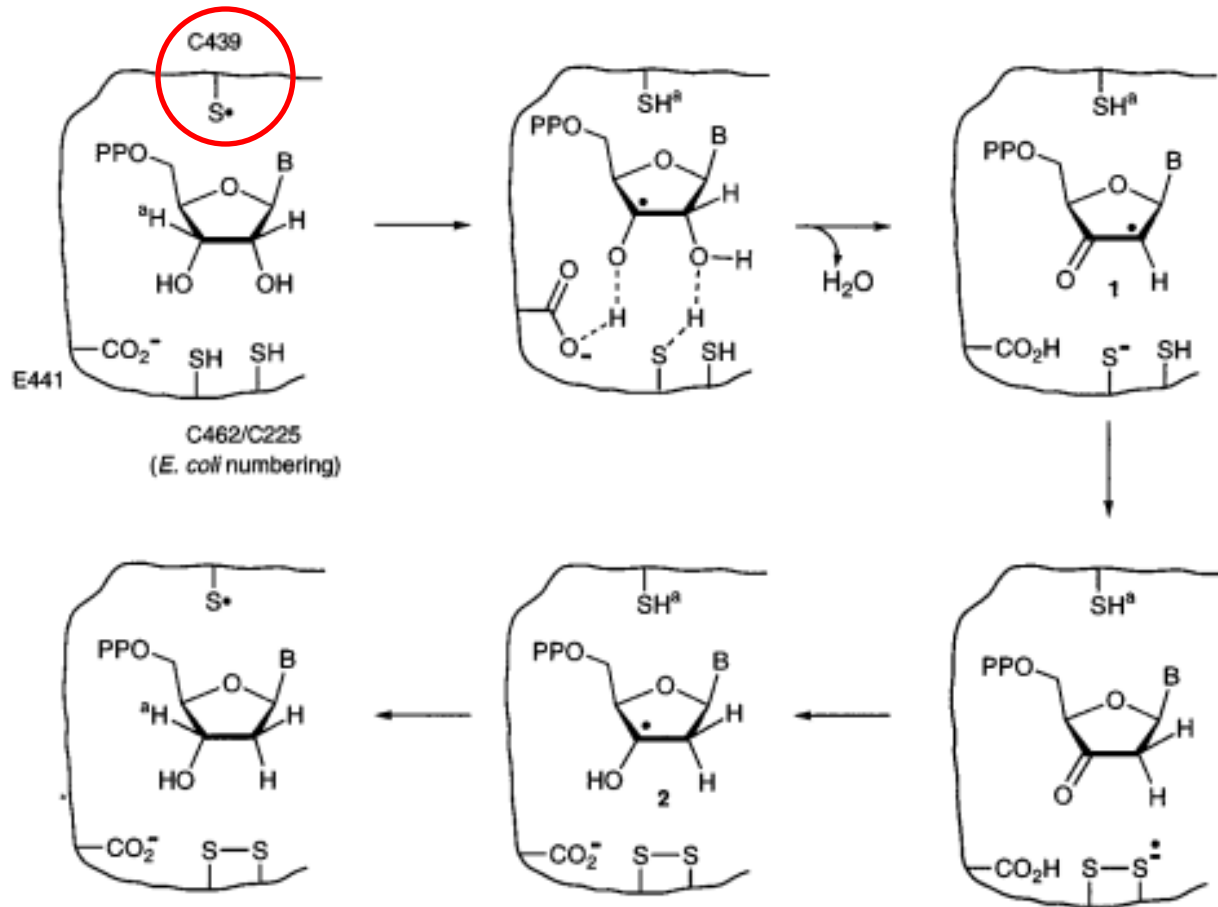
# Ribonucleotide Riduttasi (RNR)



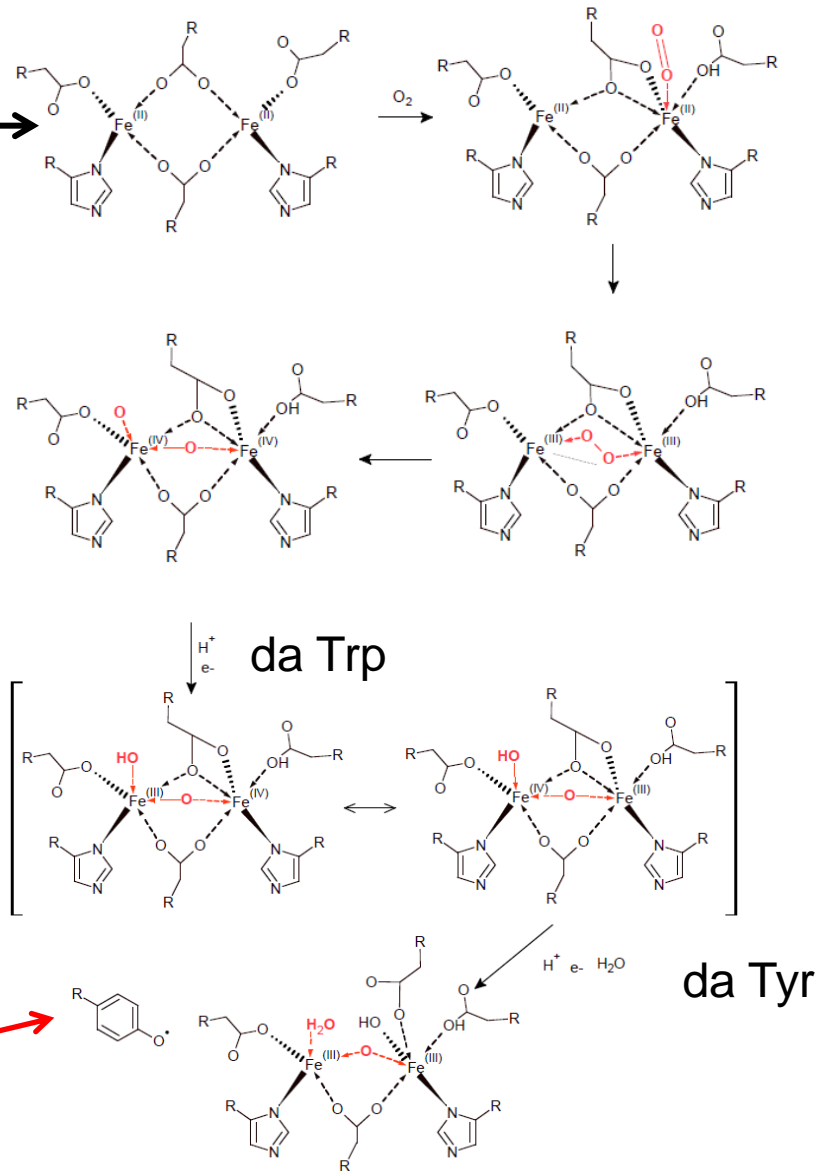
# Sito attivo e coenzimi metallici delle varie classi di Ribonucleotide Riduttasi



# Meccanismo radicalico della *RR*



# Ribonucleotide riduttasi da *escherichia coli*



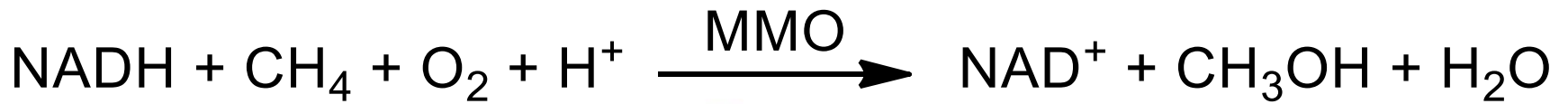
2e<sup>-</sup>  
da flavine

da Trp

da Tyr

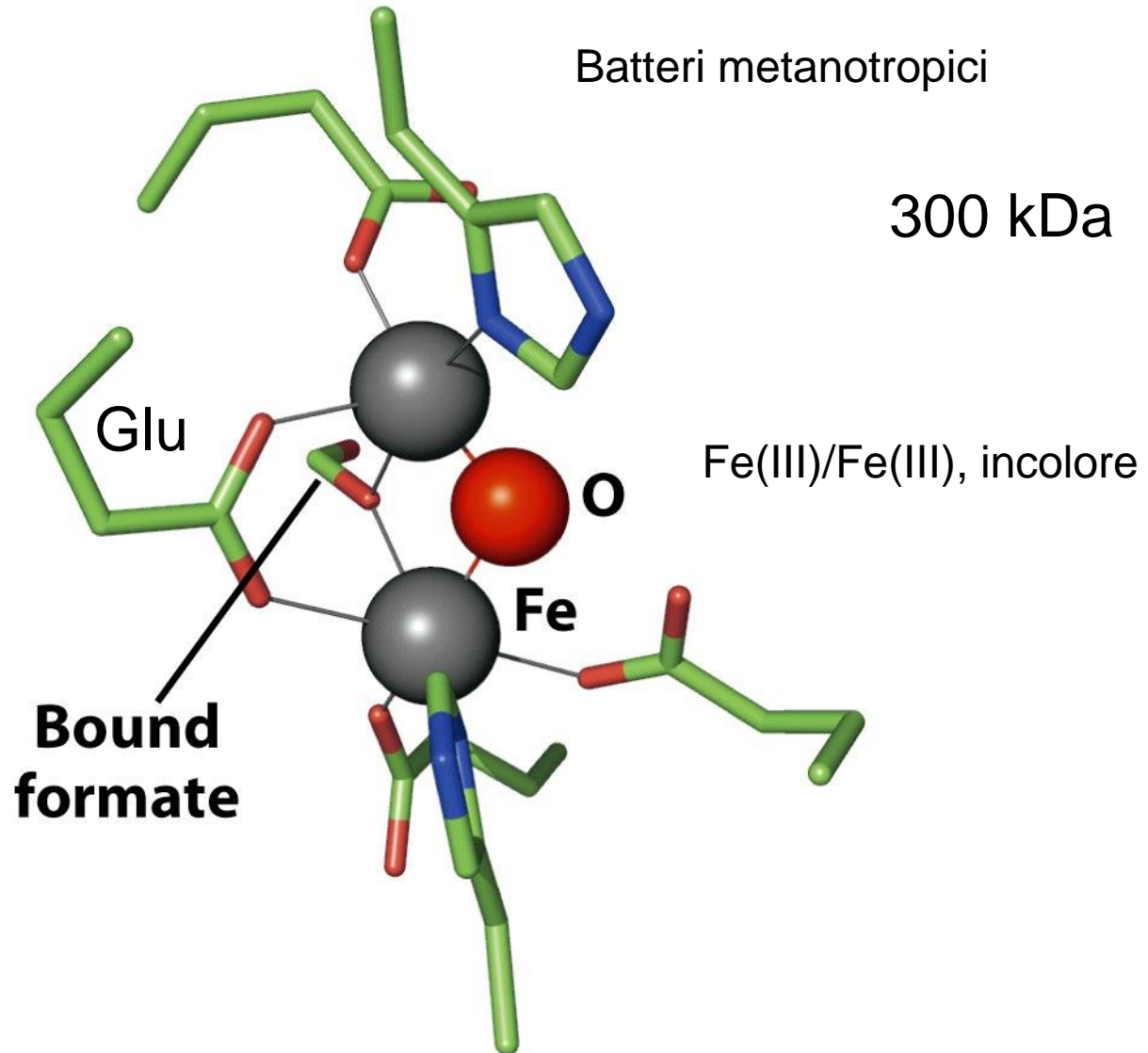
Radicale  
tirosina stabile

# Metano monoossigenasi solubile (sMMO)

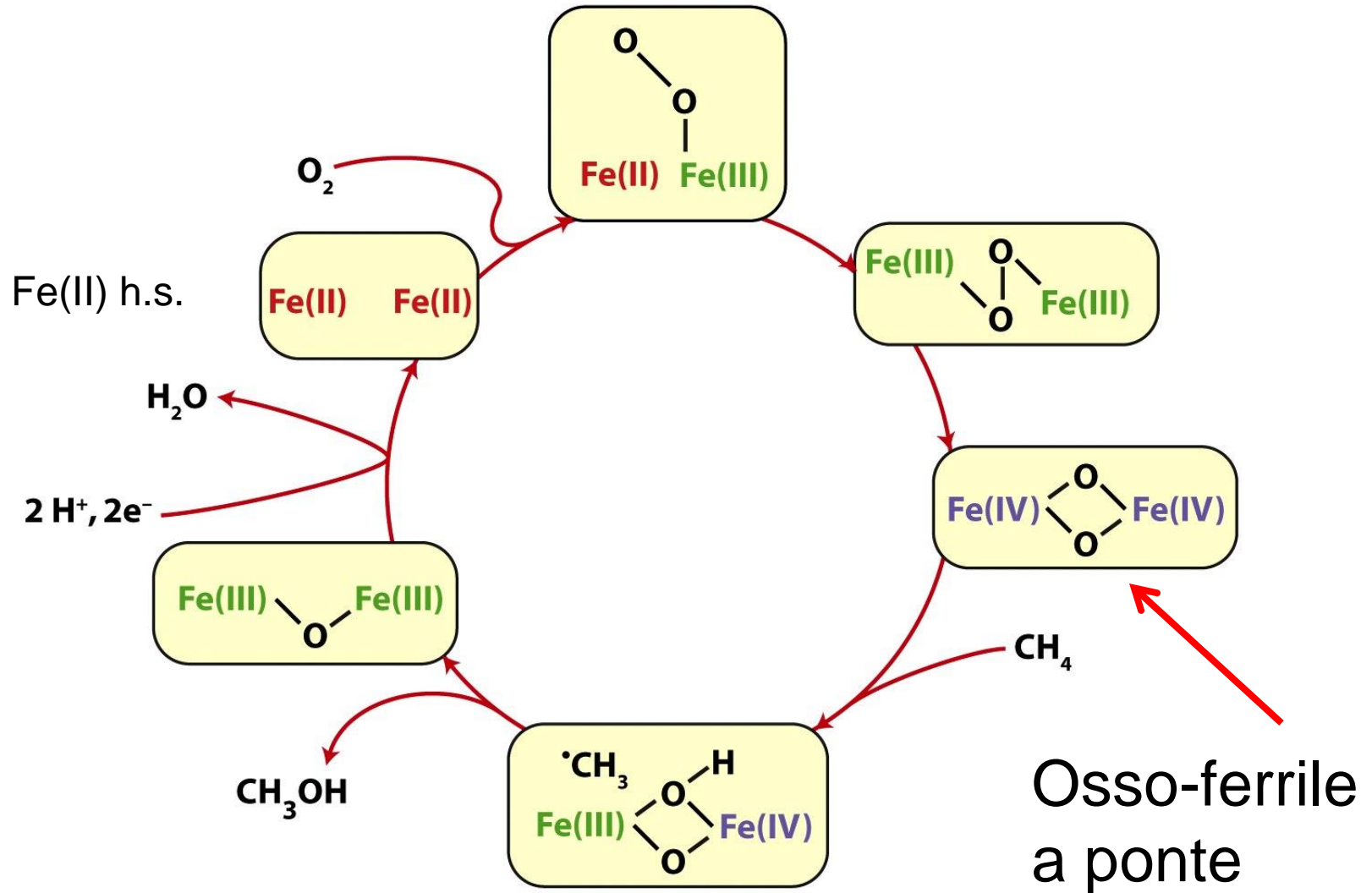


Batteri metanotropici

300 kDa

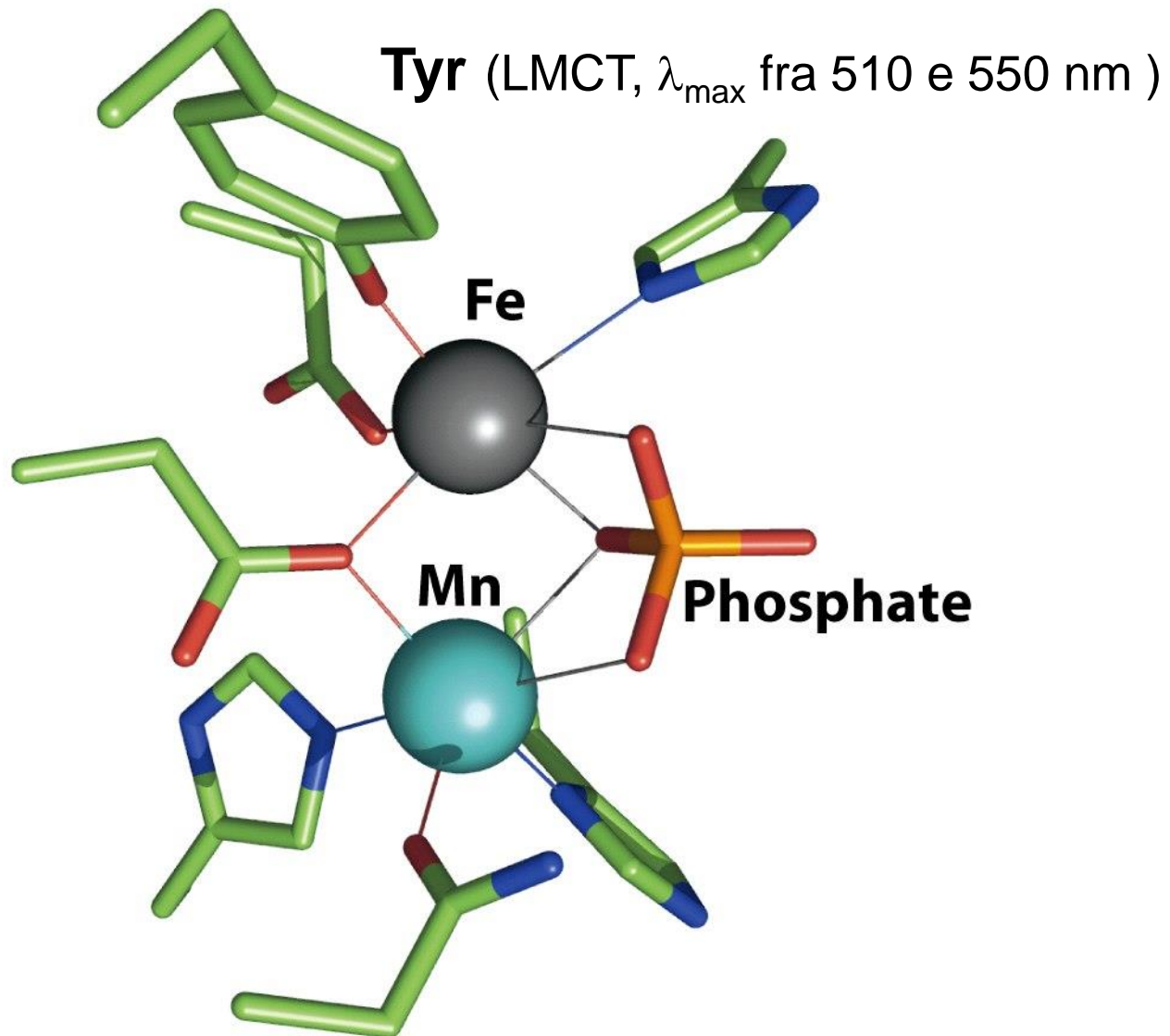


# Ipotesi di ciclo catalitico della MMO

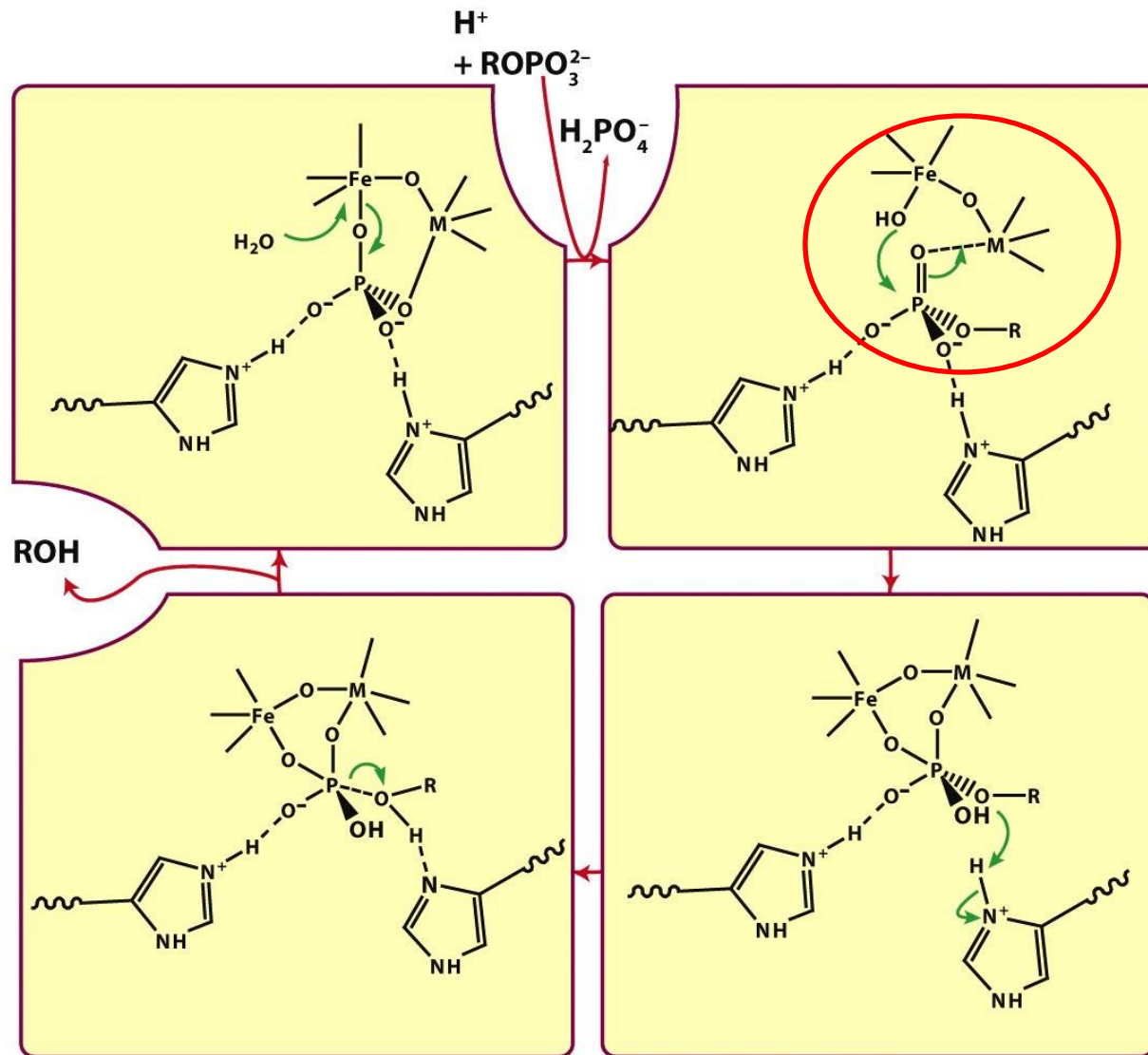




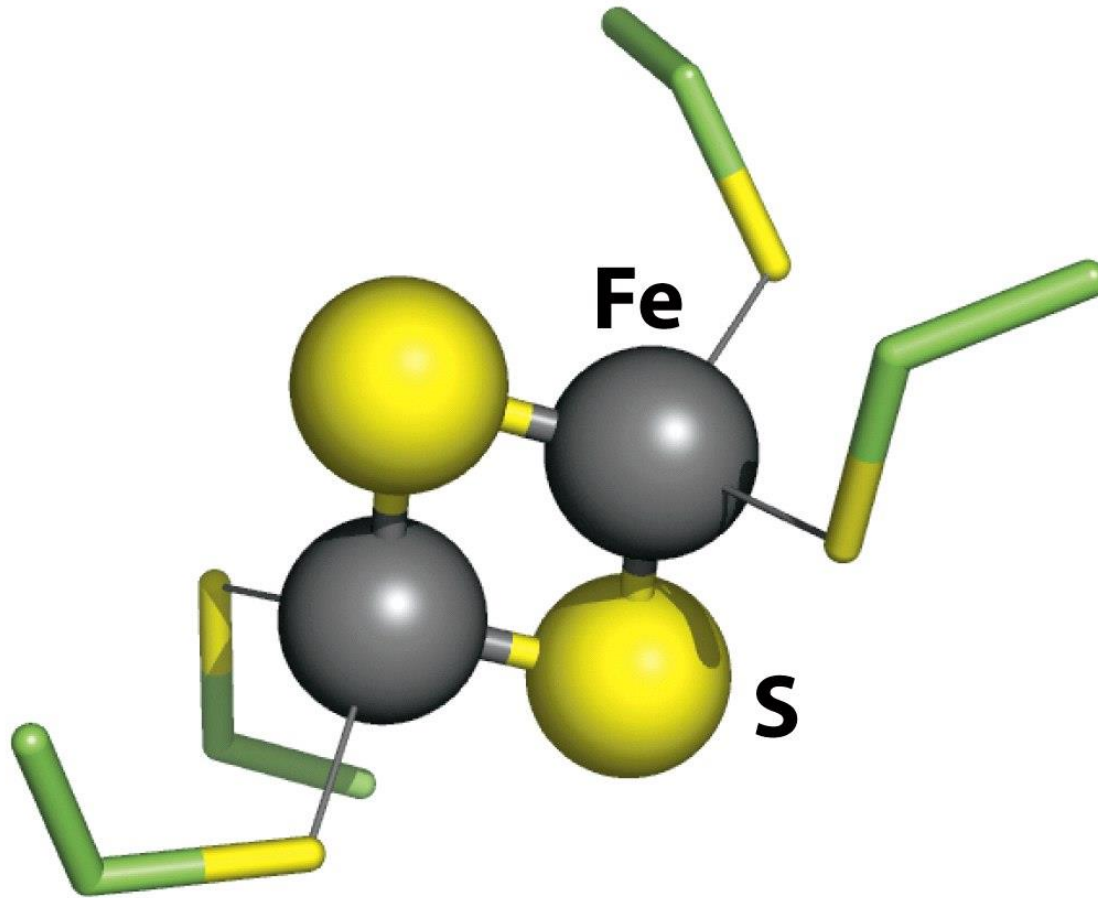
# Sito attivo di una fosfatasi acida



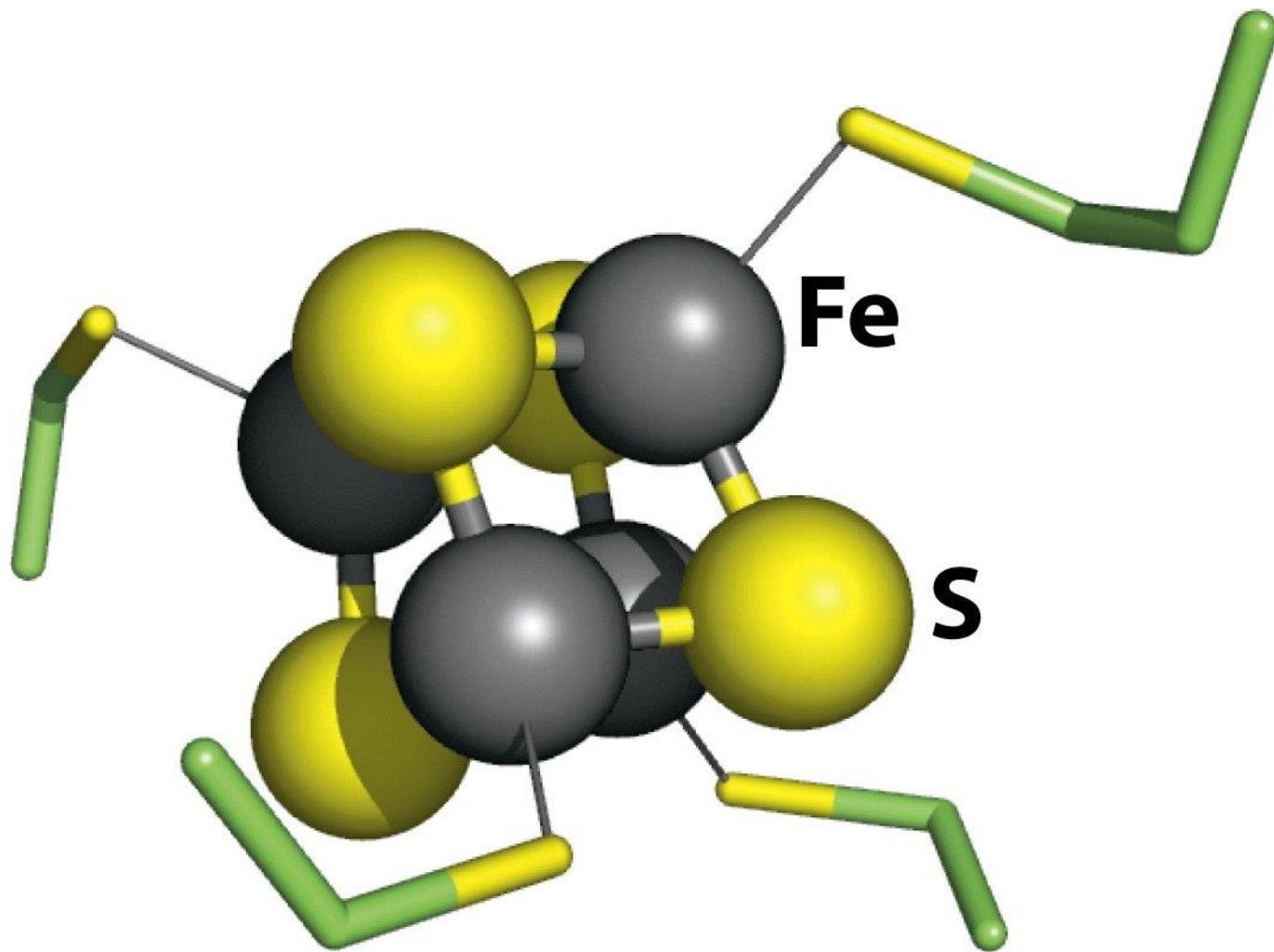
# Ciclo catalitico di una fosfatasi acida



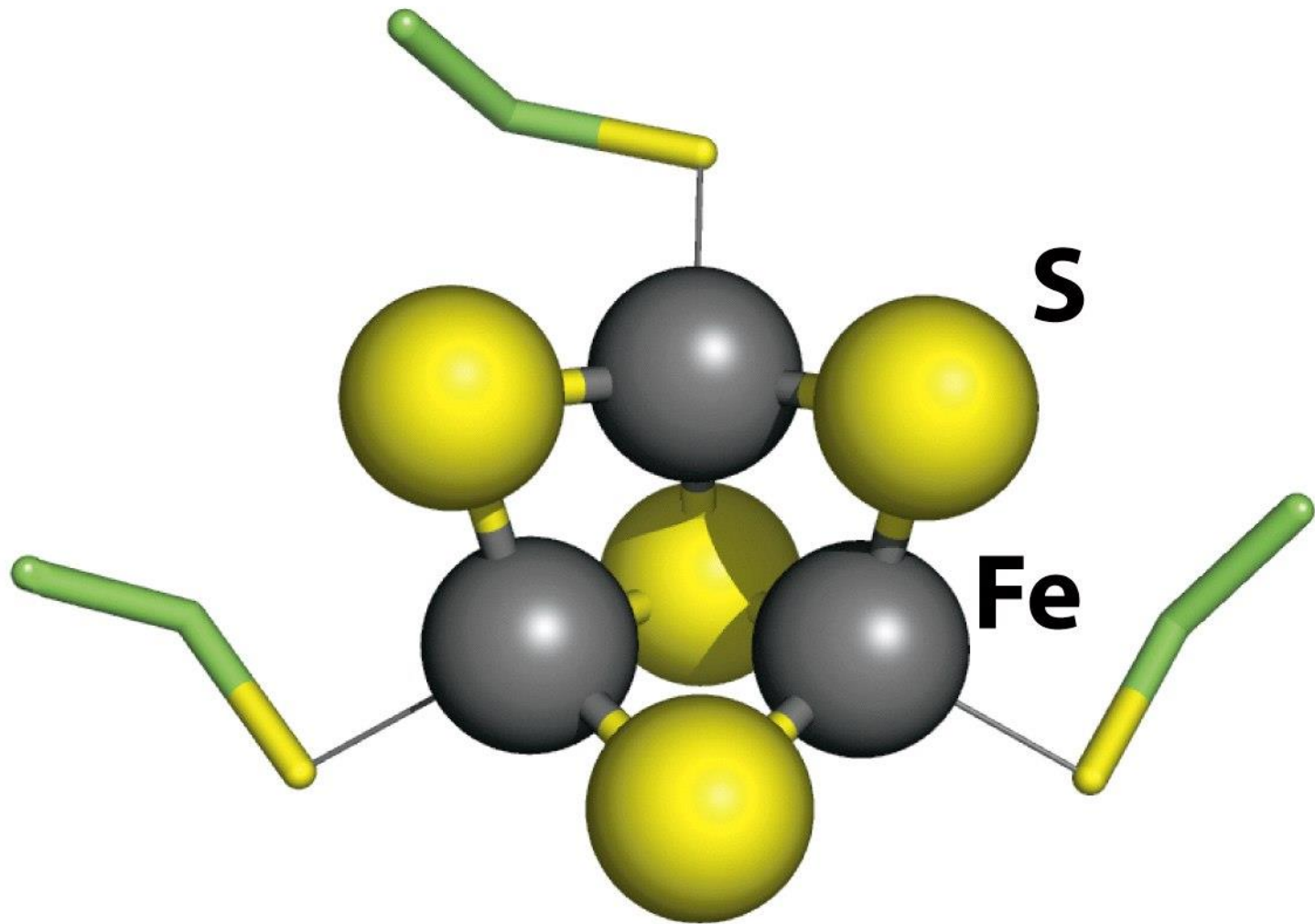
# Proteine Fe-S



**2Fe-2S]**

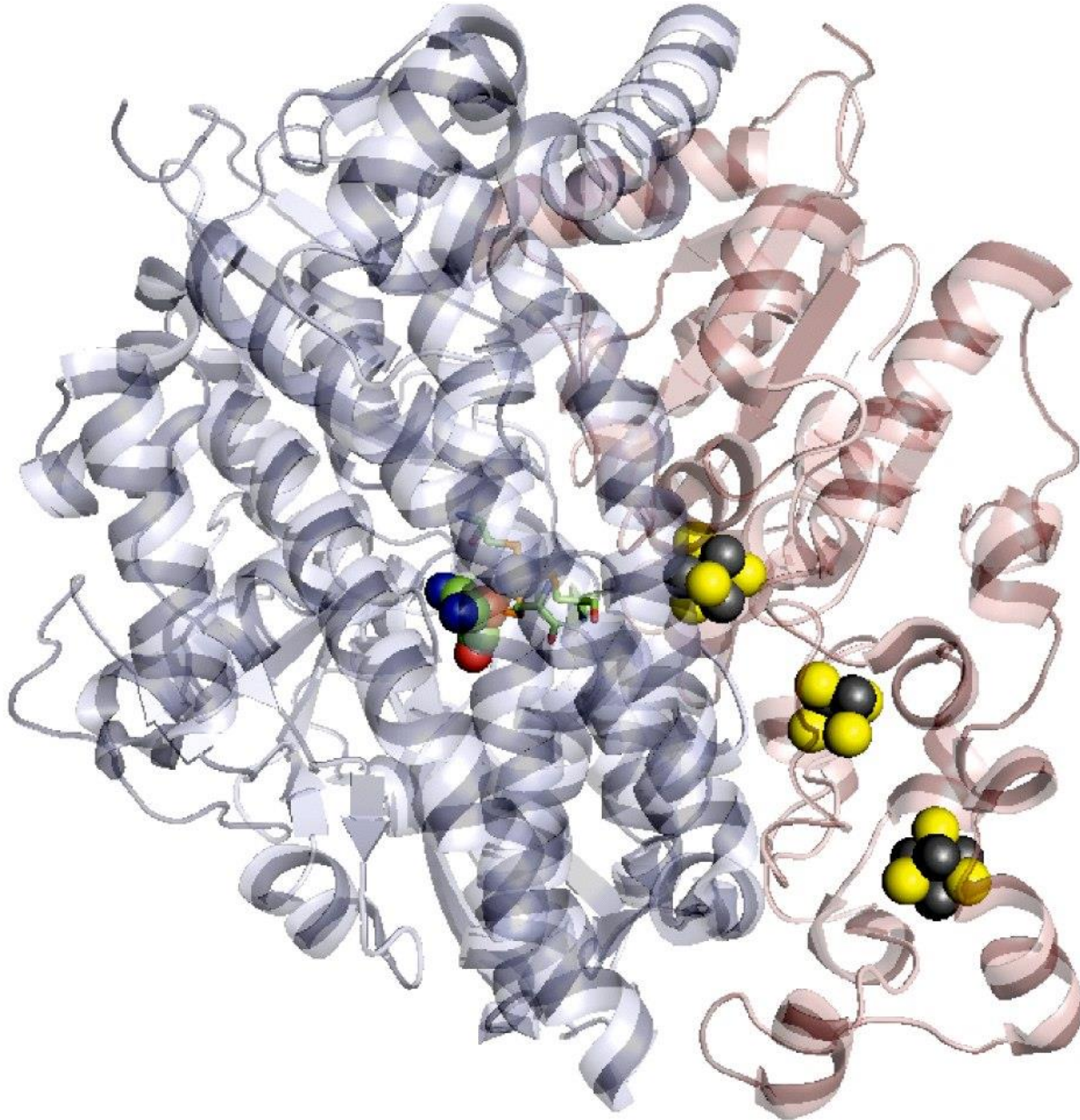


**[4Fe-4S]**



**[3Fe-4S]**

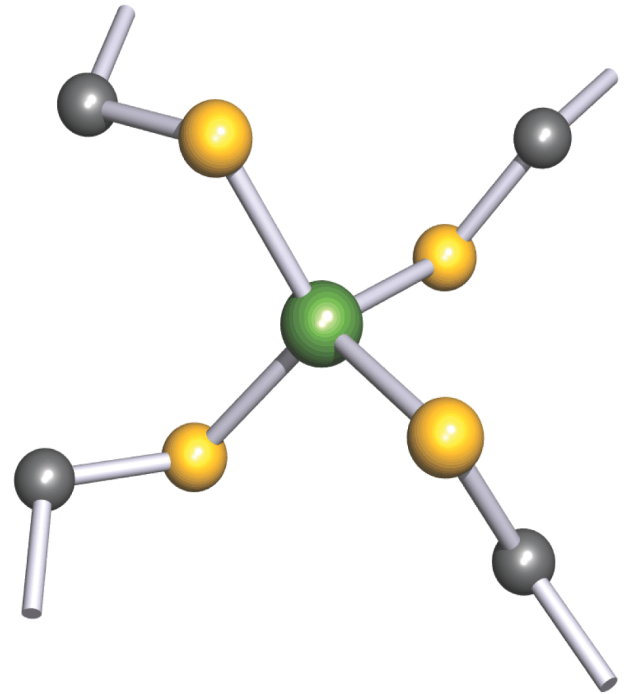
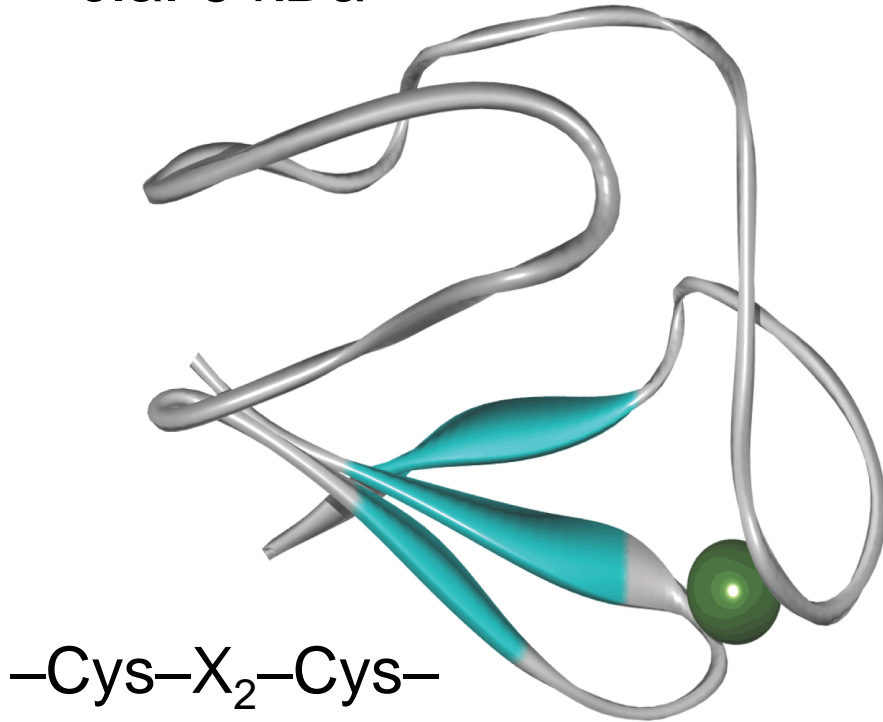
# [Ni-Fe]-idrogenasi



# Rubredossina da *clostridium pasteurianum*

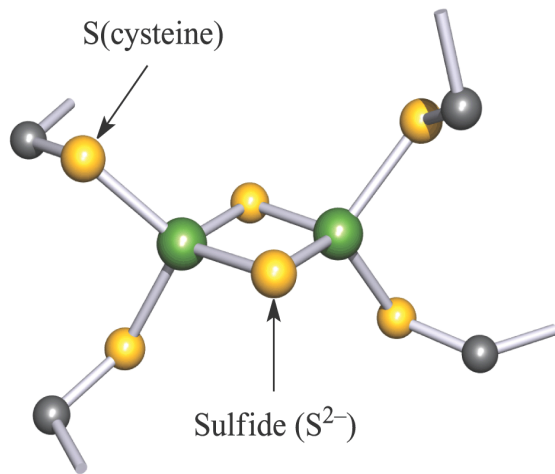
c.a. 6 kDa

$E^\circ \approx 0 \text{ V}$



# Unità ferro-zolfo da ferridossine

$E^\circ$  fra  $-250$  e  $-450$  mV

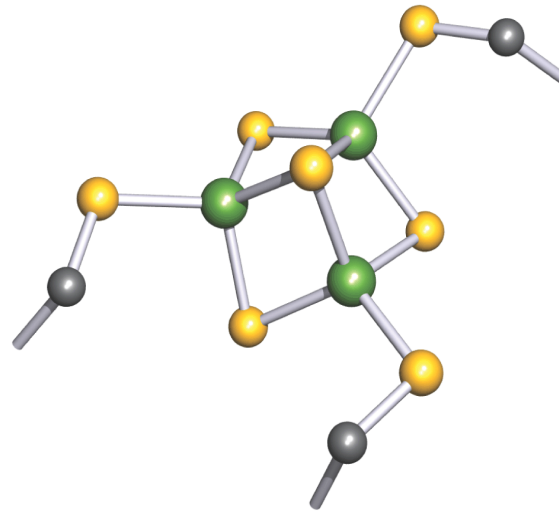


[2Fe-2S]

da spinaci

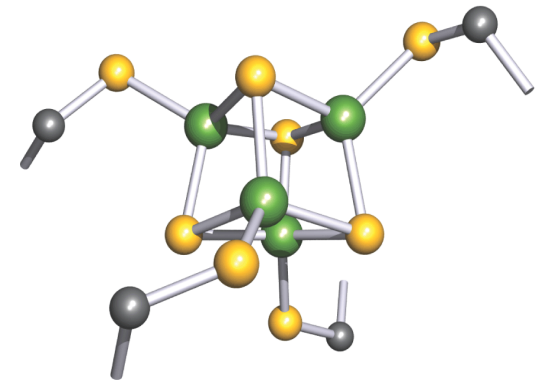
$E^\circ = -420$  mV

Fe(III)/Fe(III) – Fe(II)/Fe(III)



[3Fe-4S]

*azotobacter vinelandii*

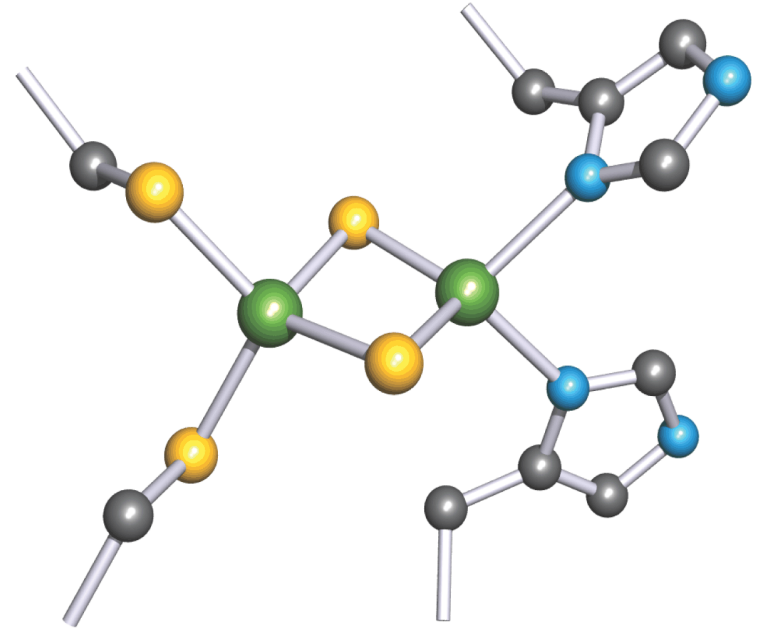
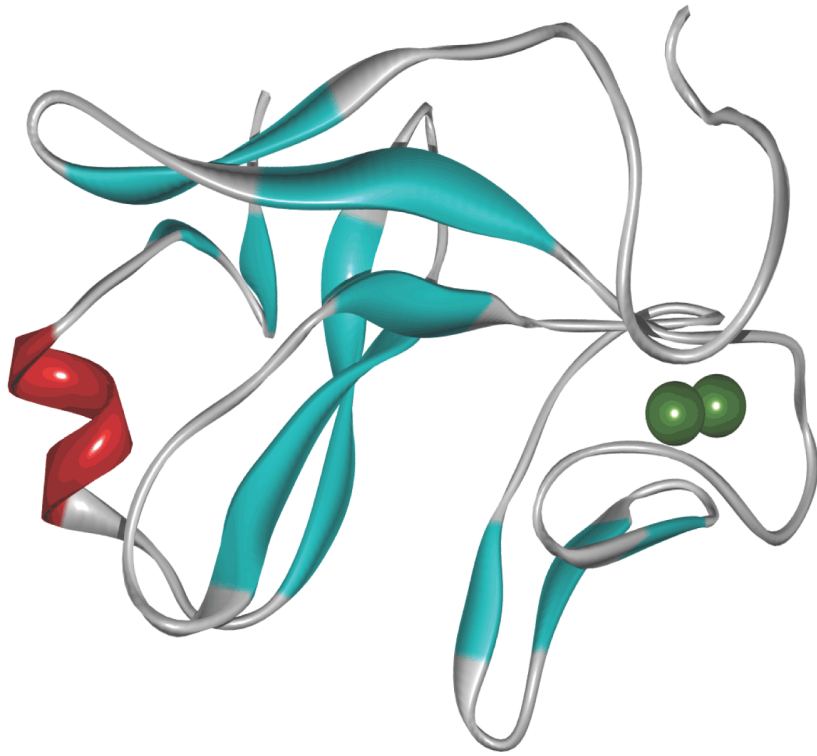


[4Fe-4S]

*chromatium vinosum*

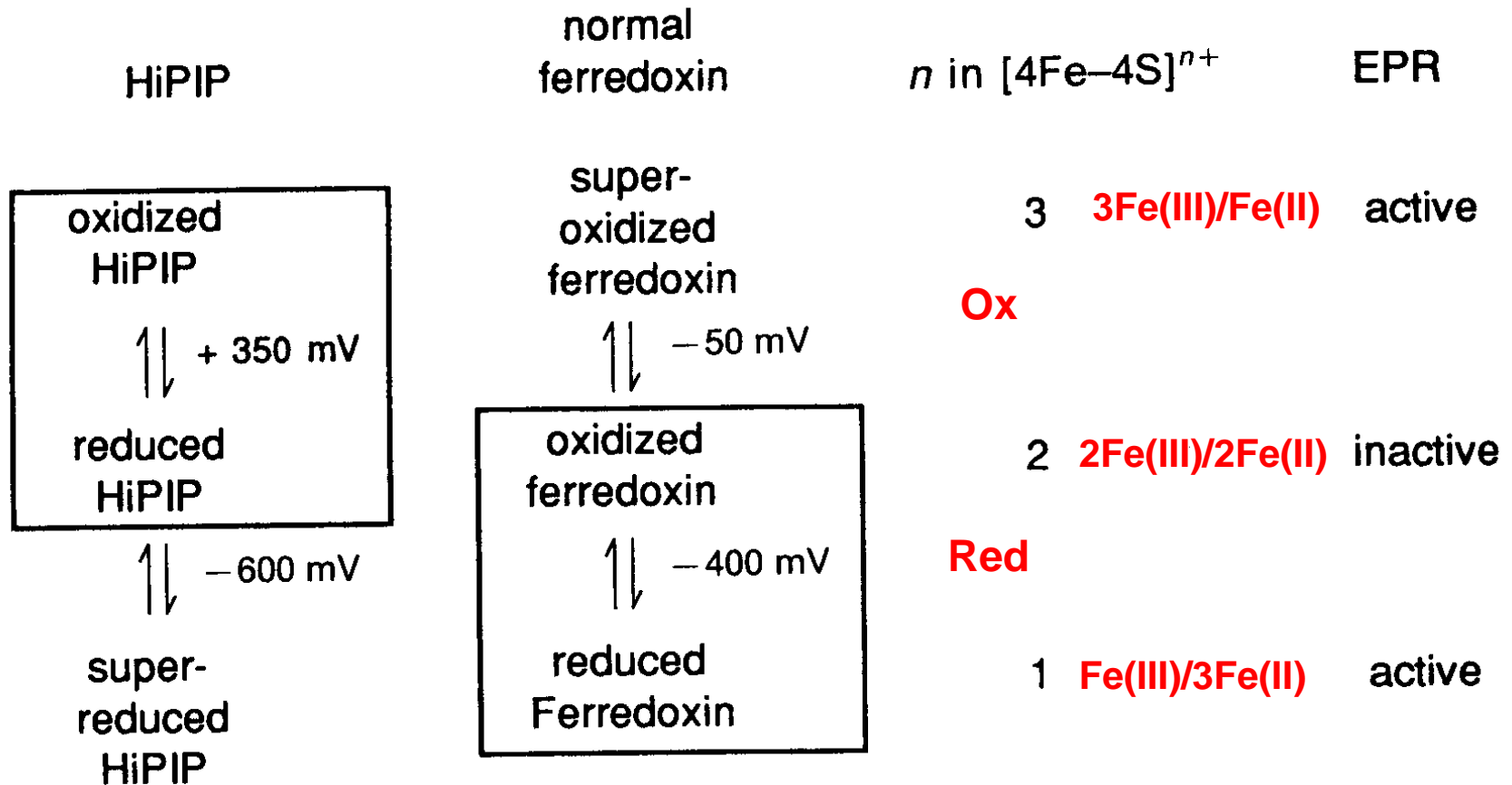


# Proteina Rieske da cloroplasti di spinaci



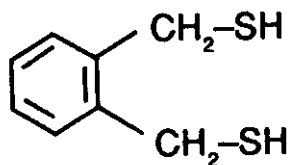
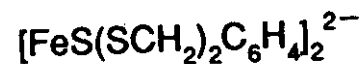
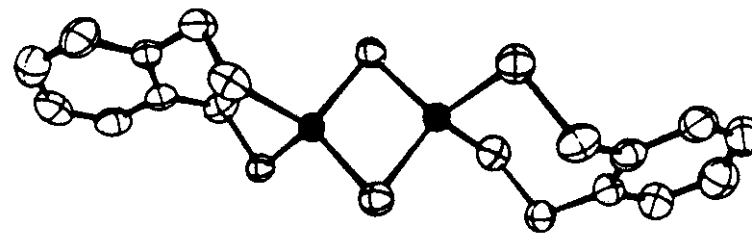
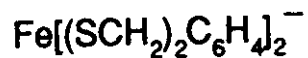
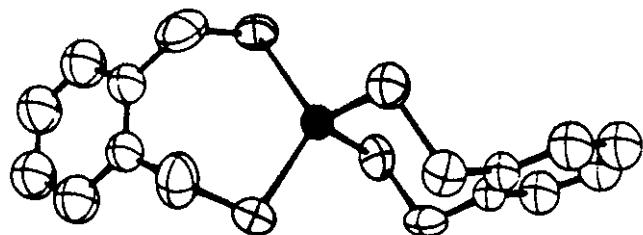
$$E^{\circ} = +290 \text{ mV}$$

# High Potential Iron-sulfur Proteins (HiPIP)

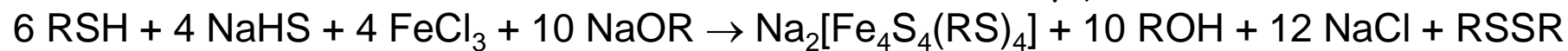
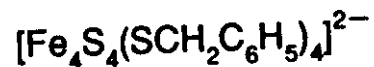
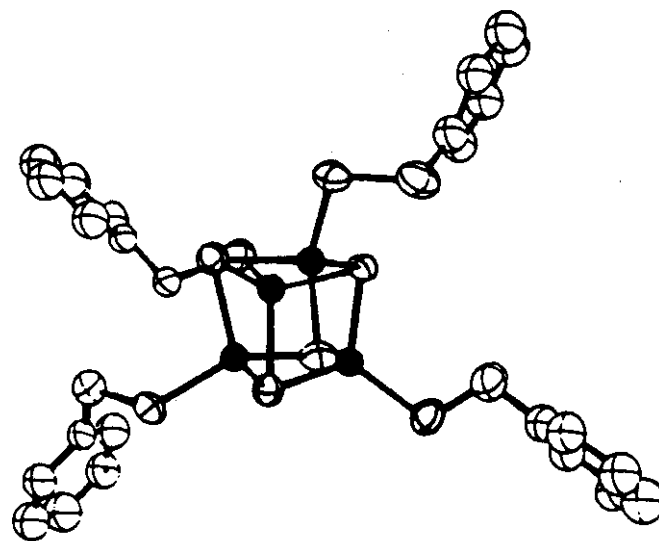


|           |   |
|-----------|---|
| [Rd]:     | -Cys-X <sub>2</sub> -Cys-X <sub>n</sub> -Cys-X <sub>2</sub> -Cys-   |
| [2Fe-2S]: | -Cys-X <sub>4</sub> -Cys-X <sub>2</sub> -Cys-X <sub>29</sub> -Cys-  |
| [4Fe-4S]: | -Cys-X <sub>2</sub> -Cys-X <sub>2</sub> -Cys-X <sub>n</sub> -Cys-   |
| HiPIP:    | -Cys-X <sub>2</sub> -Cys-X <sub>16</sub> -Cys-X <sub>13</sub> -Cys- |
| [3Fe-4S]: | -Cys-X <sub>5,7</sub> -Cys-X <sub>n</sub> -Cys-                     |

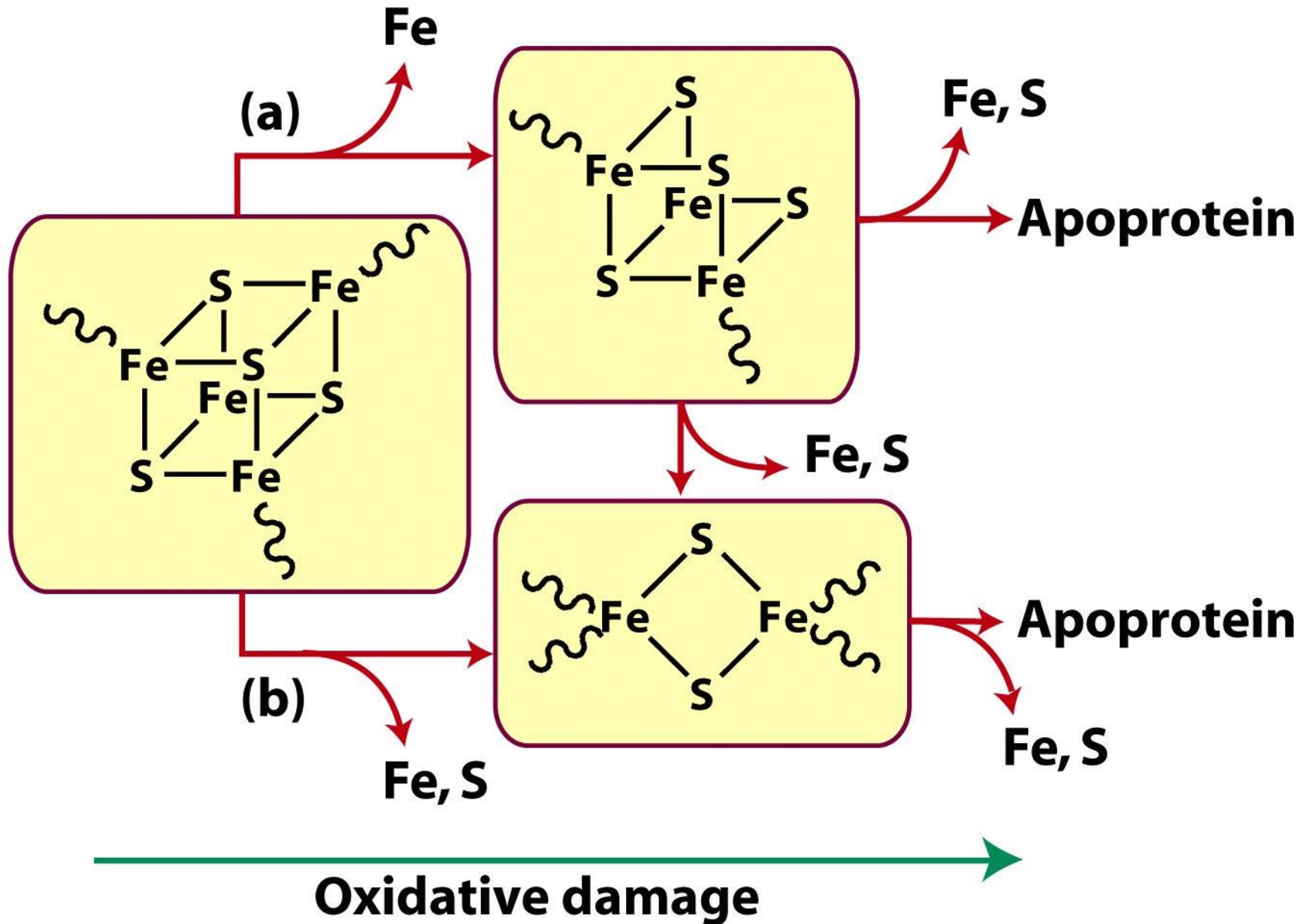
# Complessi modello



*o*-xylene- $\alpha, \alpha'$ -dithiol,  $(\text{HSCH}_2)_2\text{C}_6\text{H}_4$

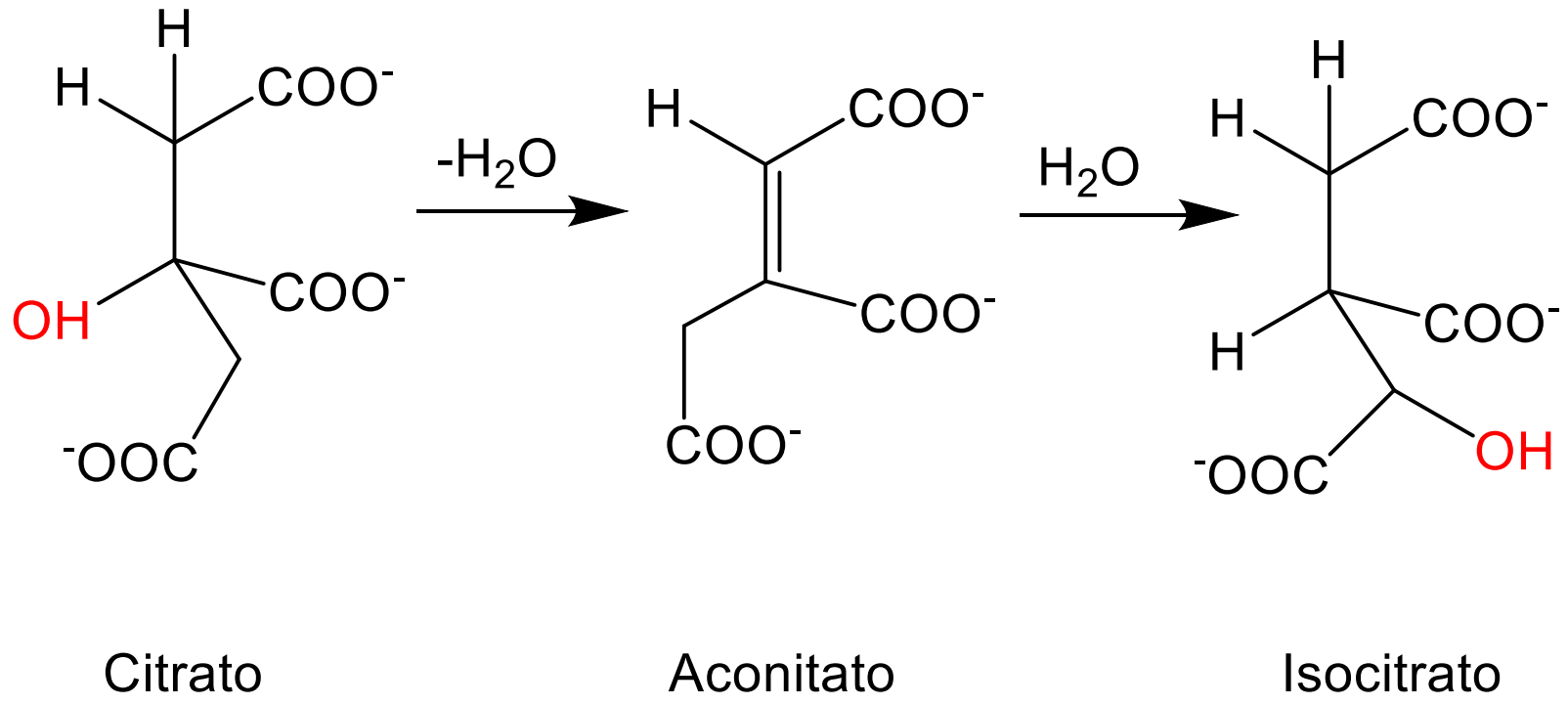


# Proteine Fe-S come sensori di O<sub>2</sub>

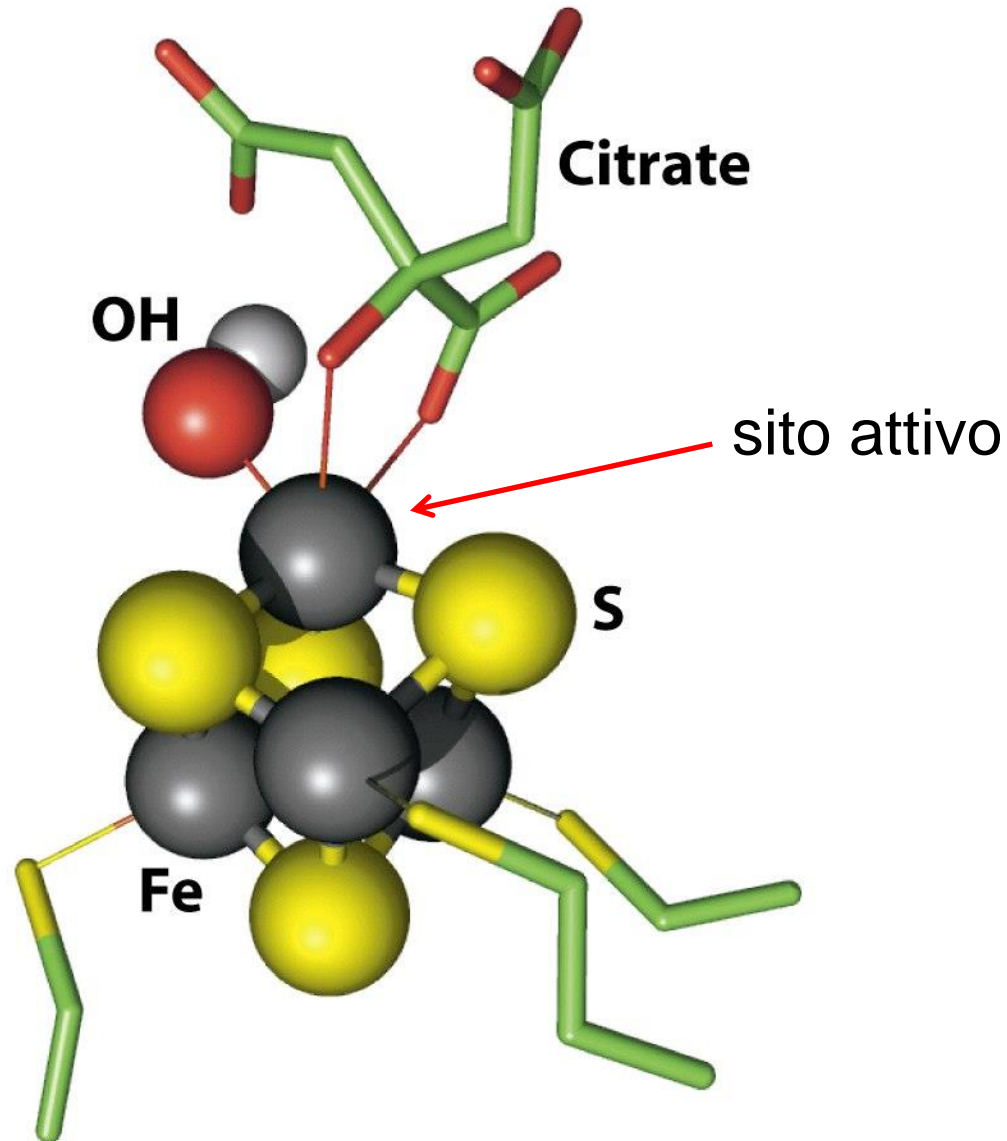


# Enzima Aconitasi

catalizza interconversione del citrato in isocitrato



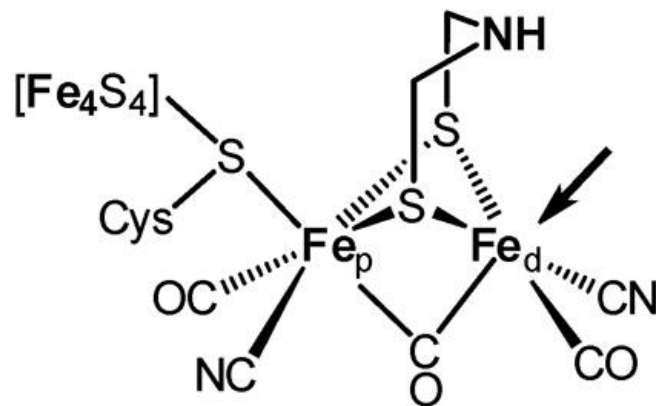
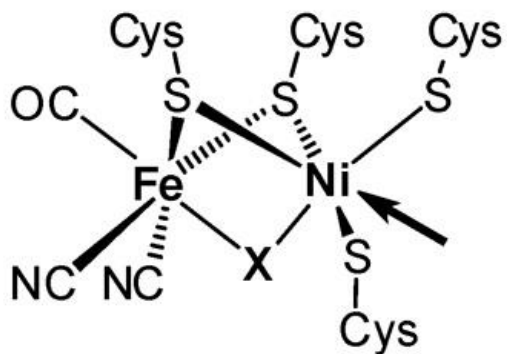
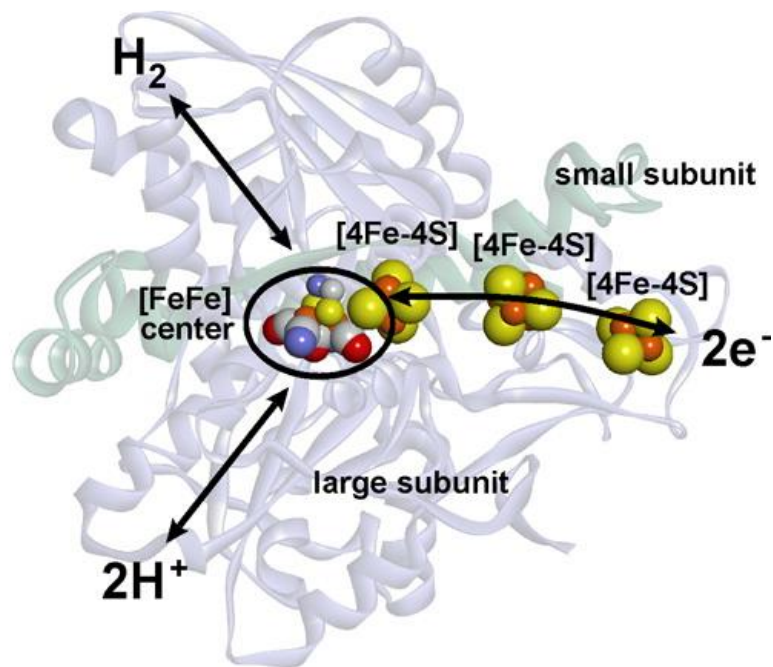
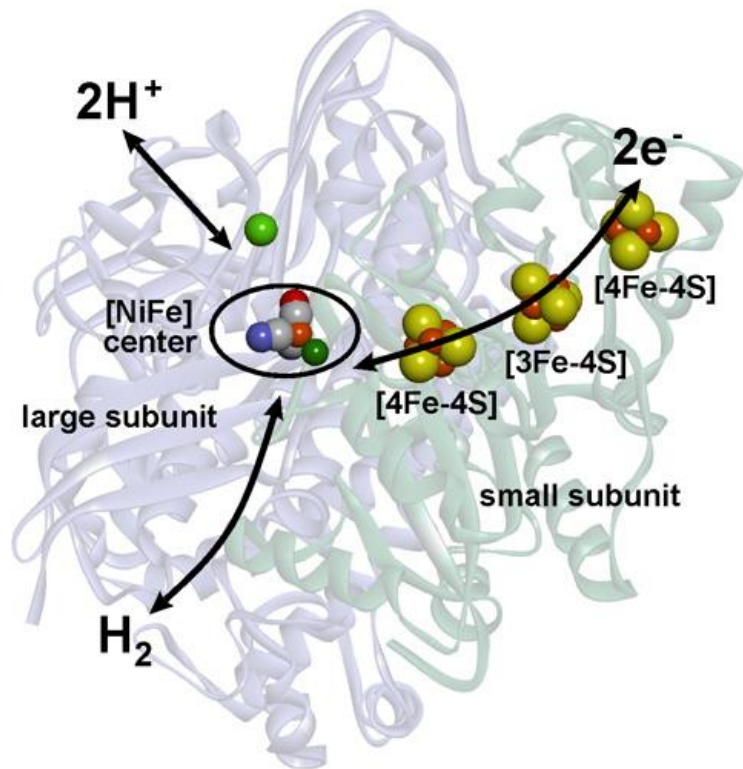
# Sito catalitico dell'aconitasi



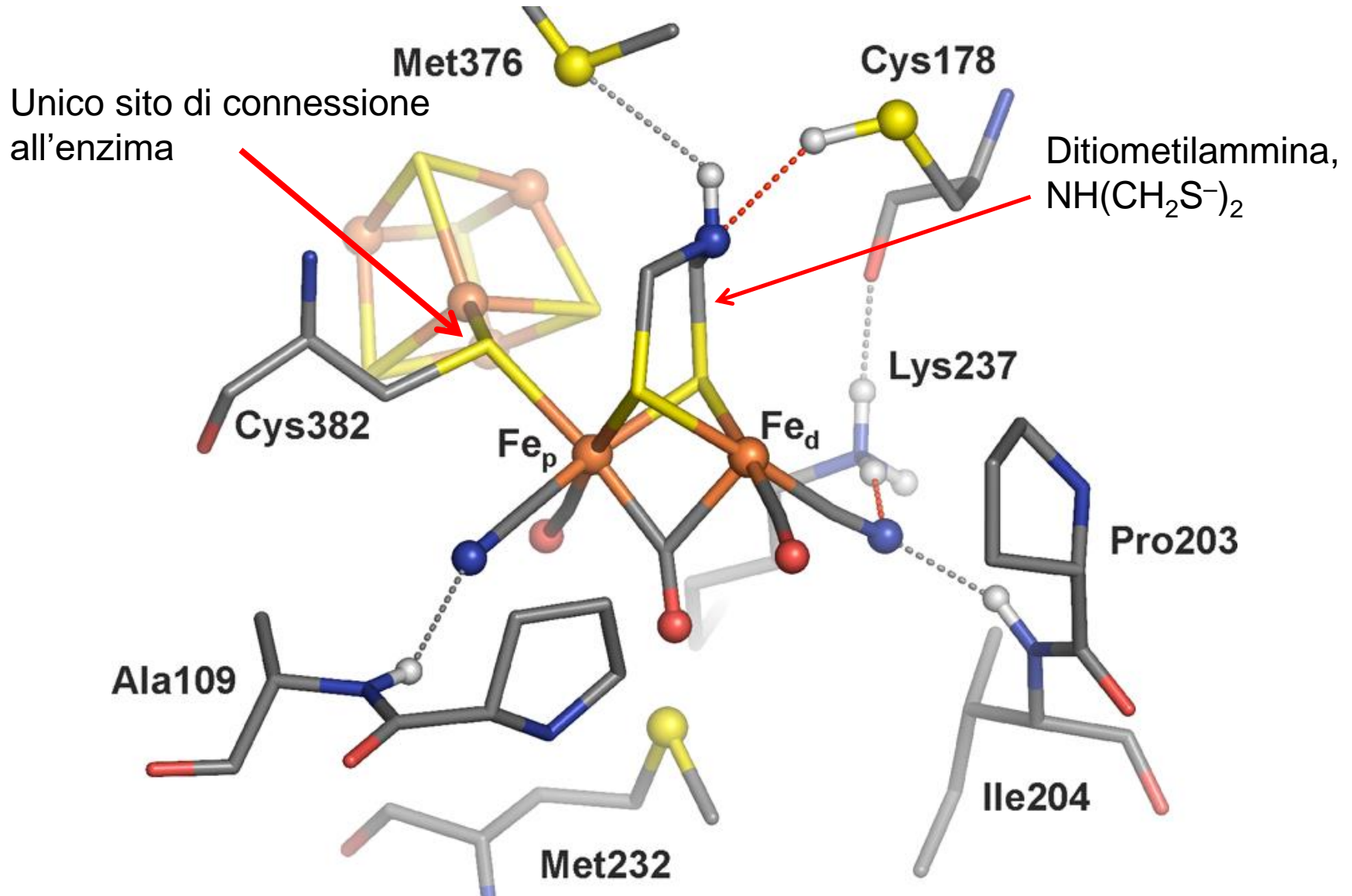


[NiFe] Hydrogenase

[FeFe] Hydrogenase

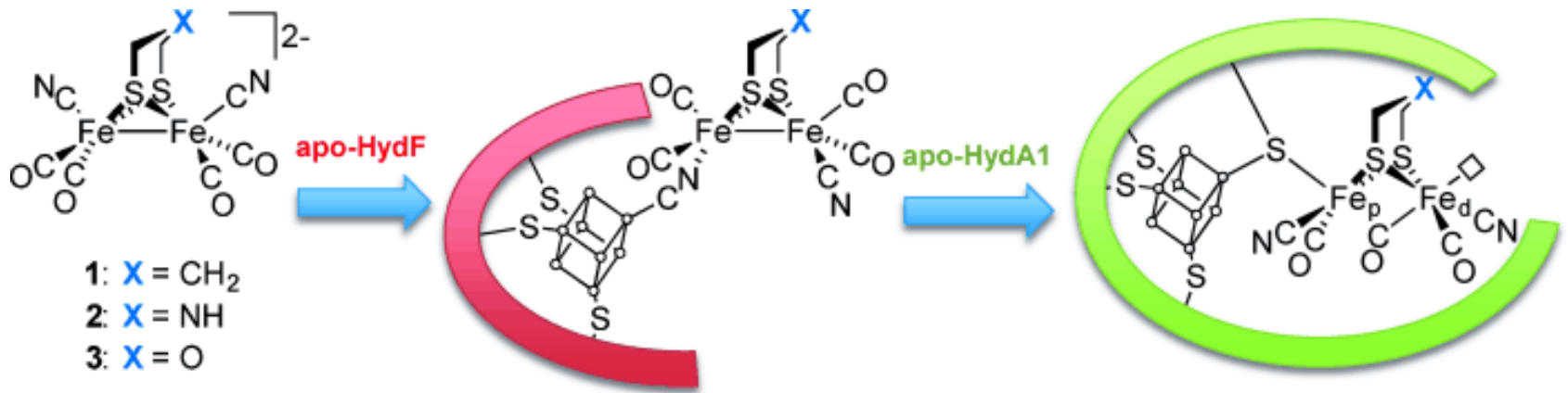


# [FeFe] Idrogenasi

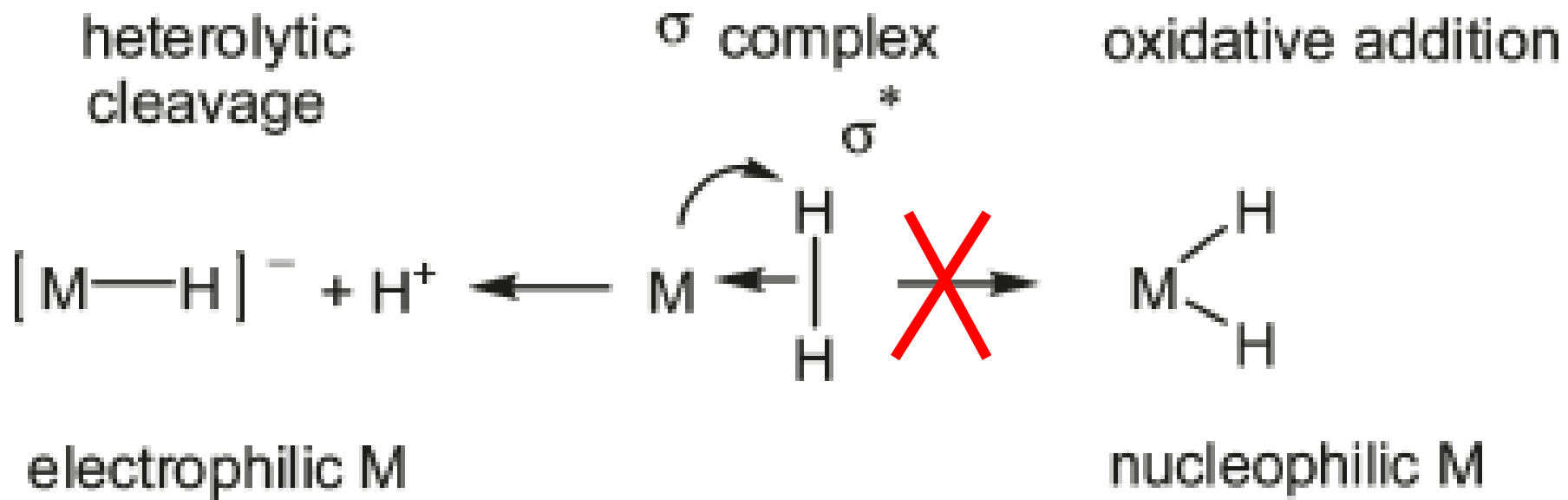




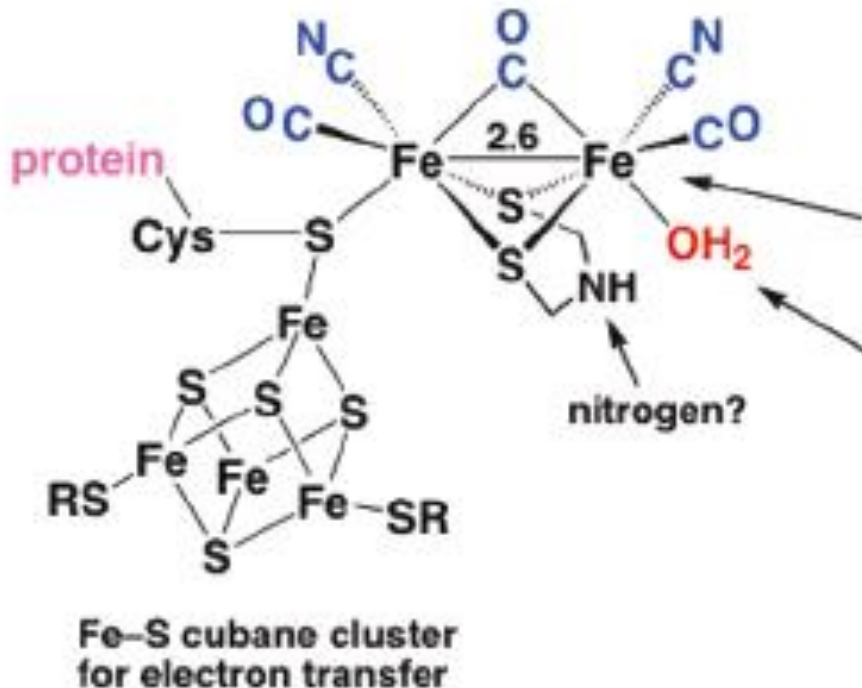
*Soltanto l'enzima con X = NH è cataliticamente attivo*



Il CO coordinato favorisce la rottura eterolitica di H<sub>2</sub>



# Fe-Fe Hydrogenase

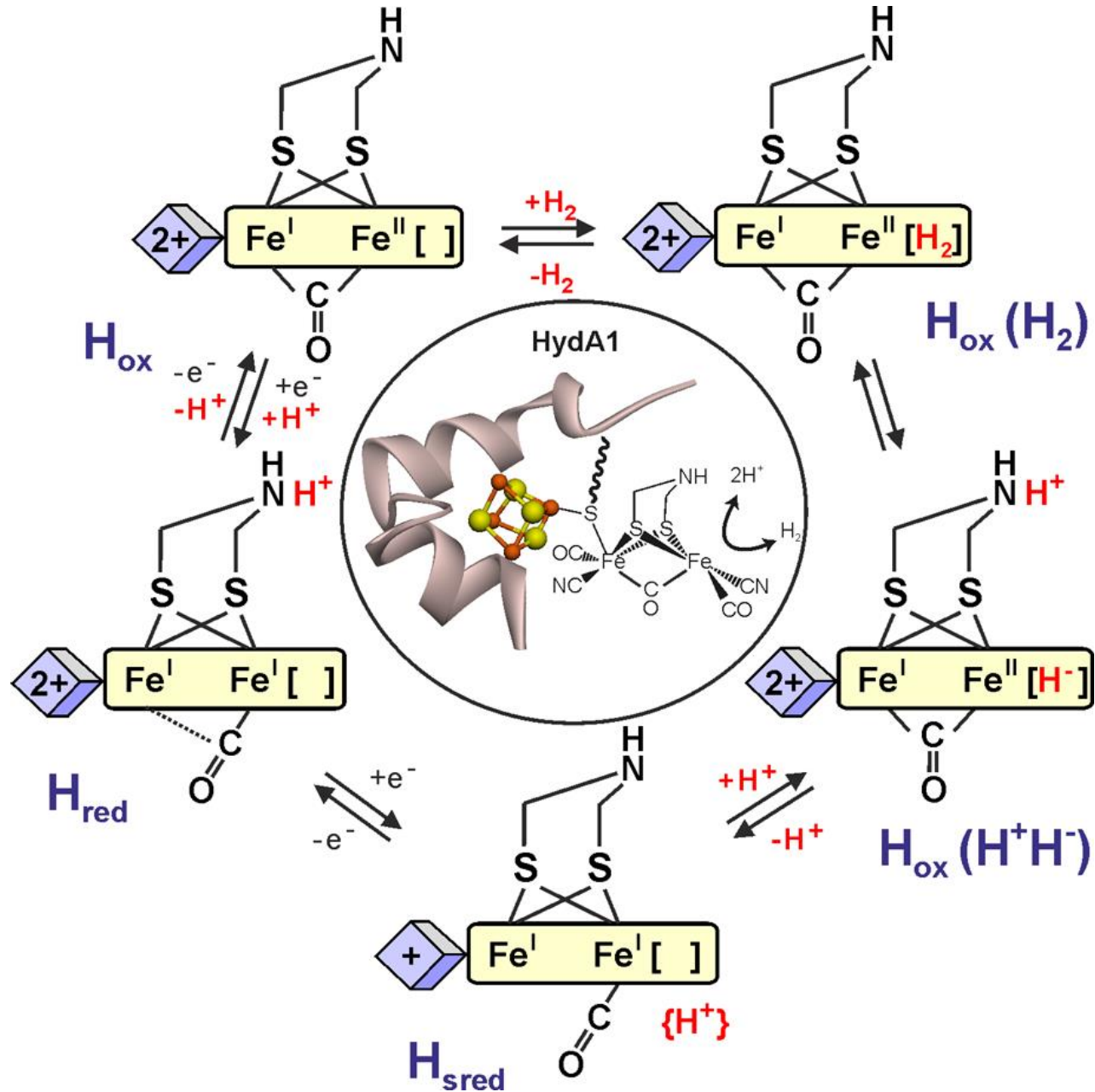


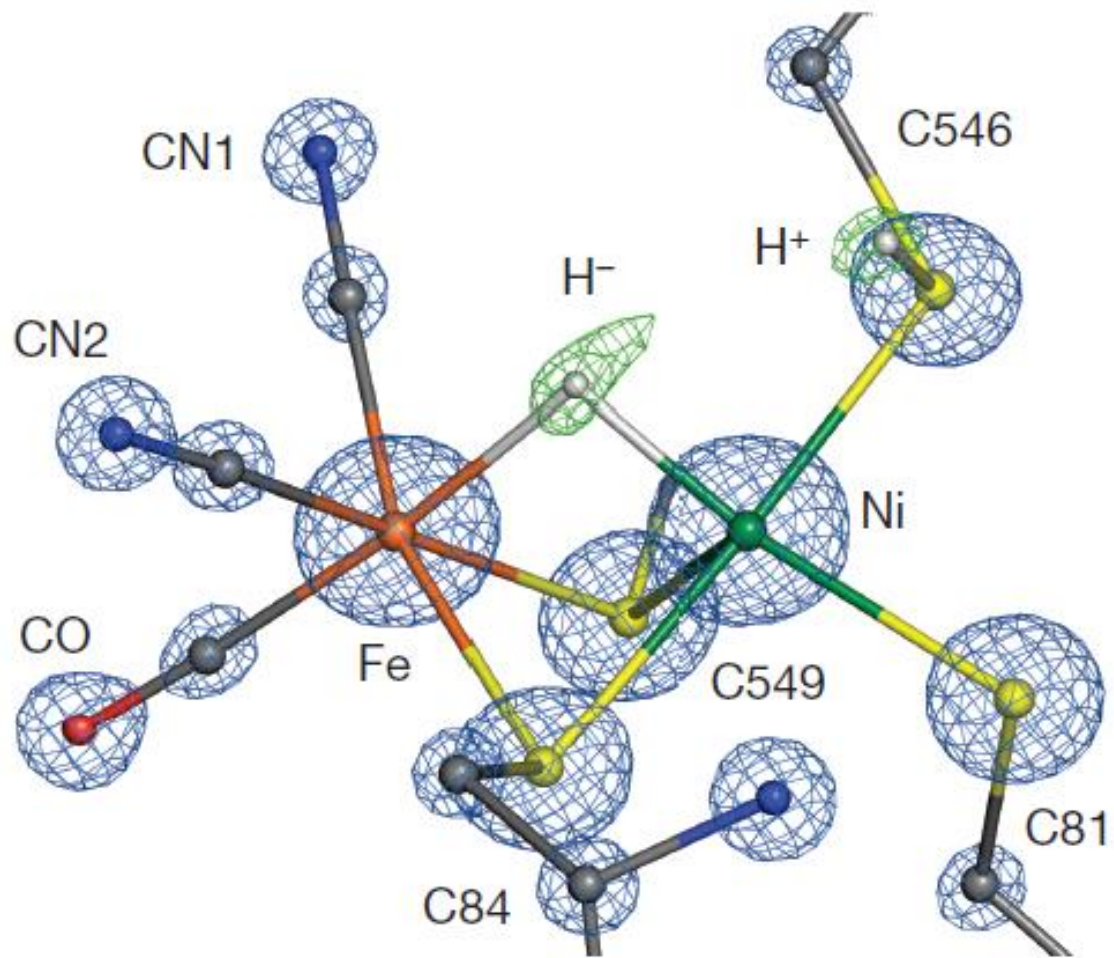
- Active site attached at only **one point**
- **CO** and **CN** ligands on low-spin Fe<sup>II</sup>
- Metal-metal bonds
- Intramolecular heterolysis of **H<sub>2</sub>** ostensibly at this site  
CO can displace **H<sub>2</sub>O**; can **H<sub>2</sub>**?  
**H<sub>2</sub>** is slightly stronger ligand than **H<sub>2</sub>O** on W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>

Trans **CO** ligand favors H<sub>2</sub> coordination and heterolysis

*High ligand-field strength* of **CN** may be needed to help maintain a *low-spin state* for Fe that is critical for strong CO binding. High-spin Fe<sup>II</sup>-CO complexes are rare

# Ipotesi di meccanismo





*Nature*, 2015

# Ipotesi di meccanismo

