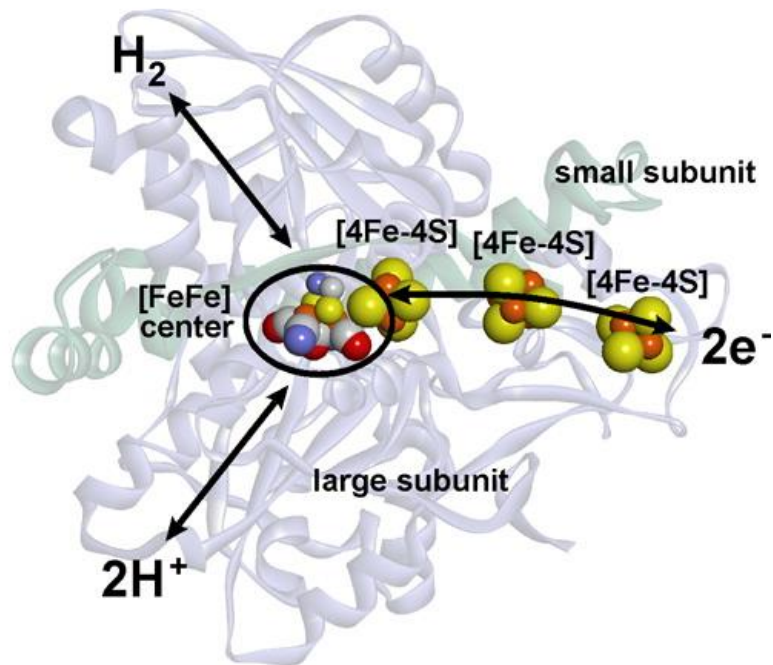
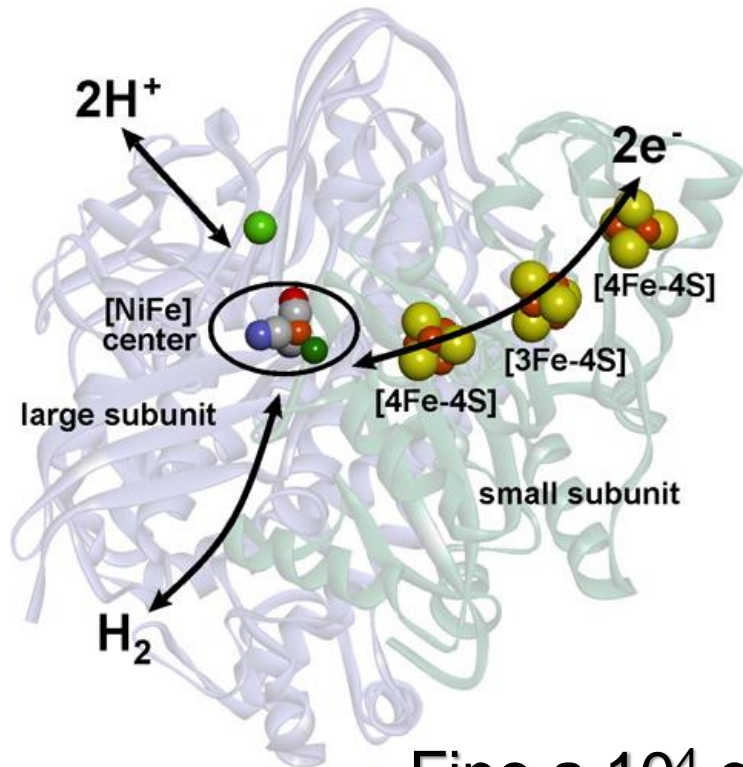
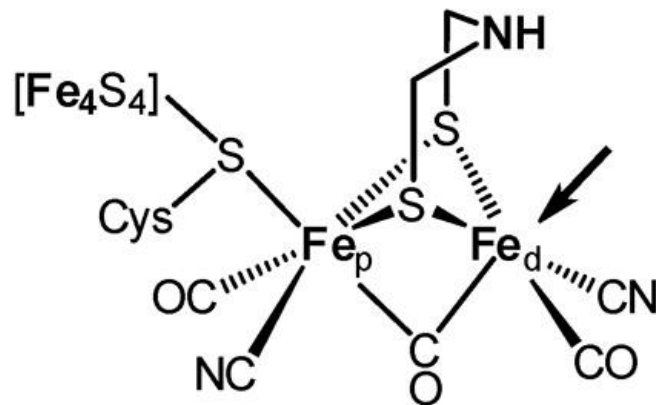
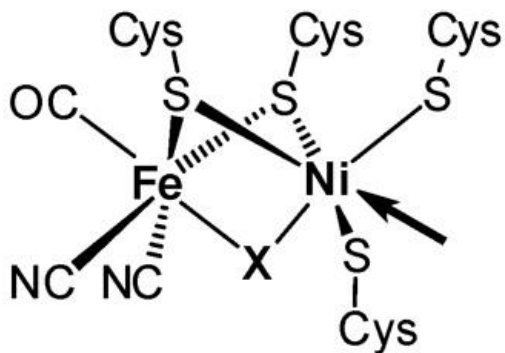


[NiFe] Hydrogenase

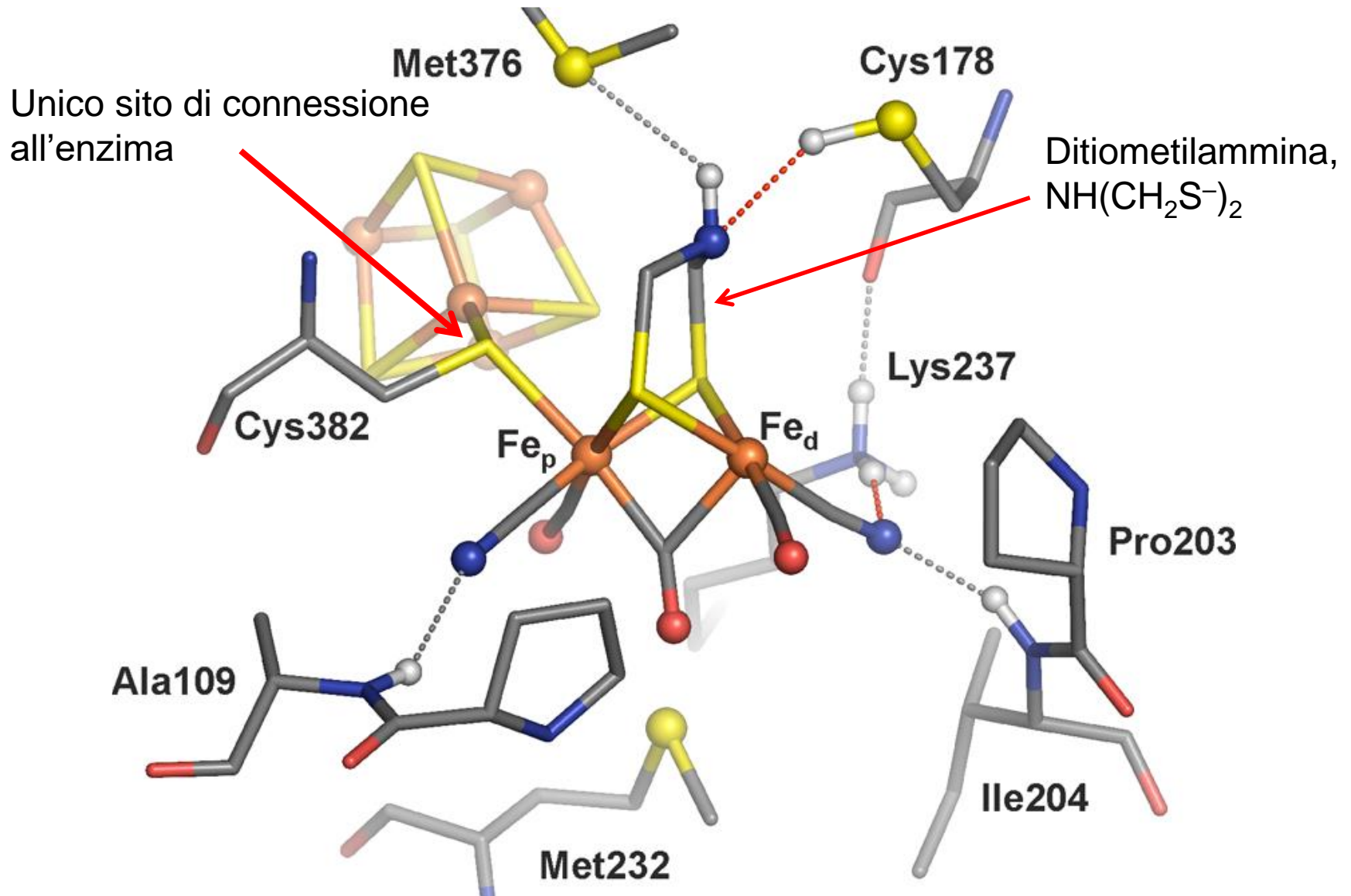
[FeFe] Hydrogenase

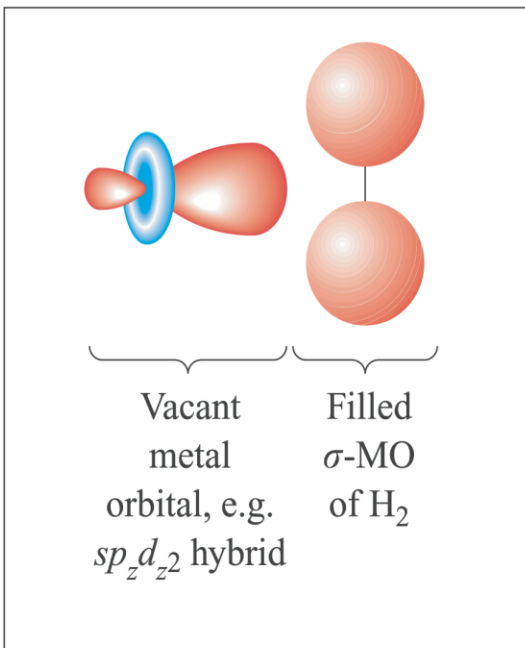
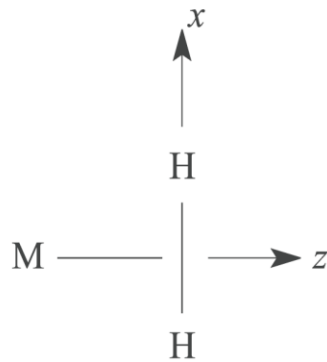


Fino a 10<sup>4</sup> cicli/secondo

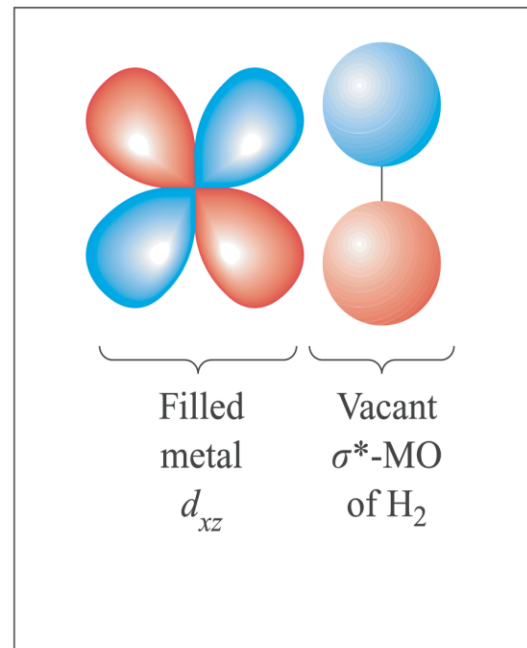


# [FeFe] Idrogenasi



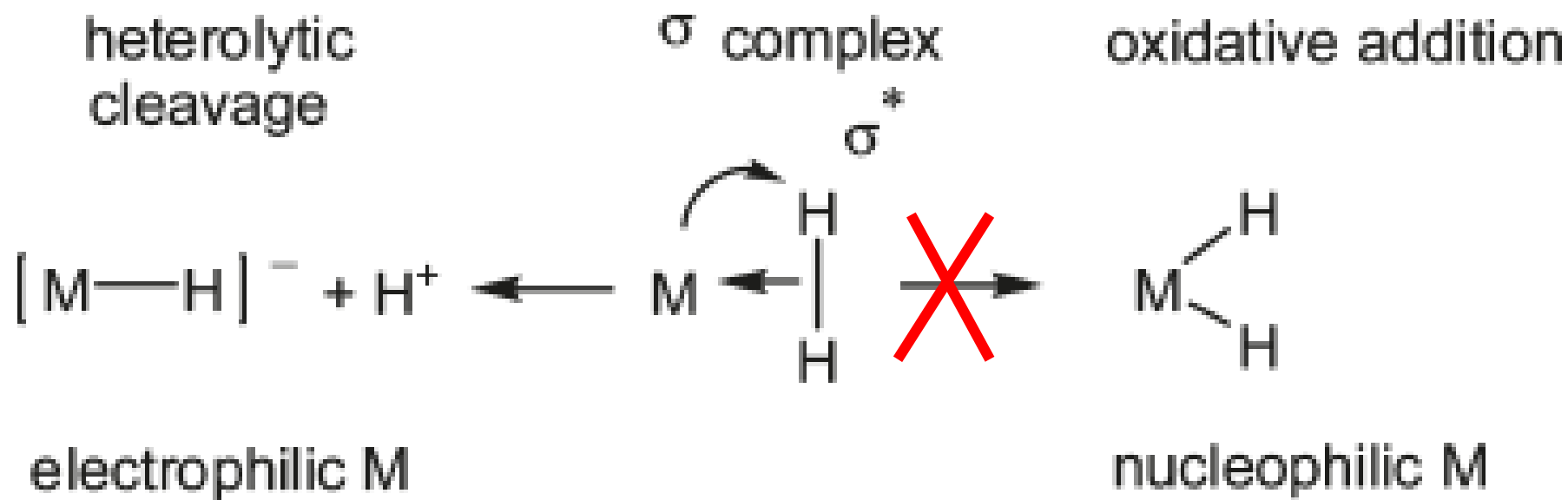


$H_2$ -to-M donation  
(a)

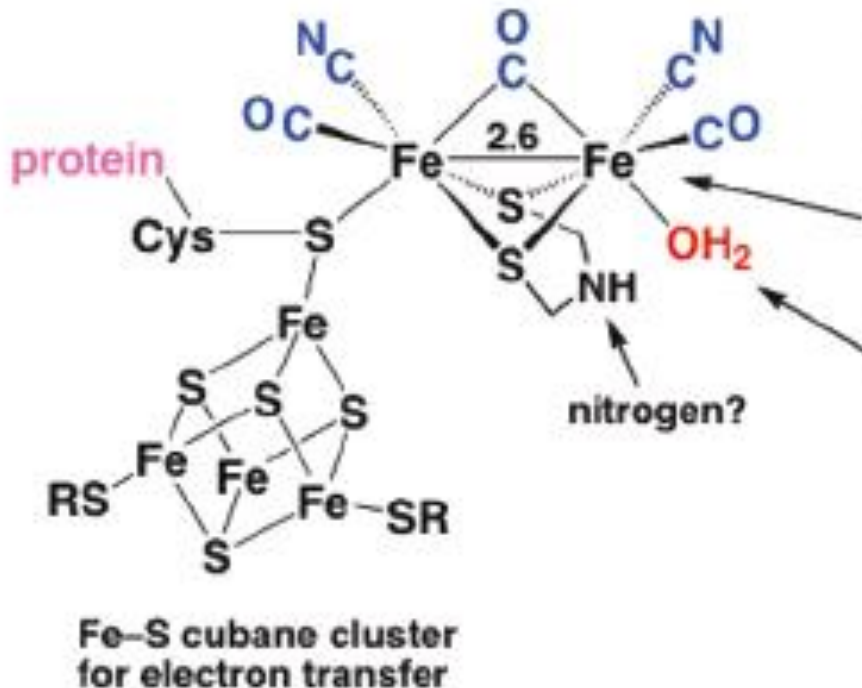


M-to- $H_2$  back-donation  
(b)

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



# Fe-Fe Hydrogenase

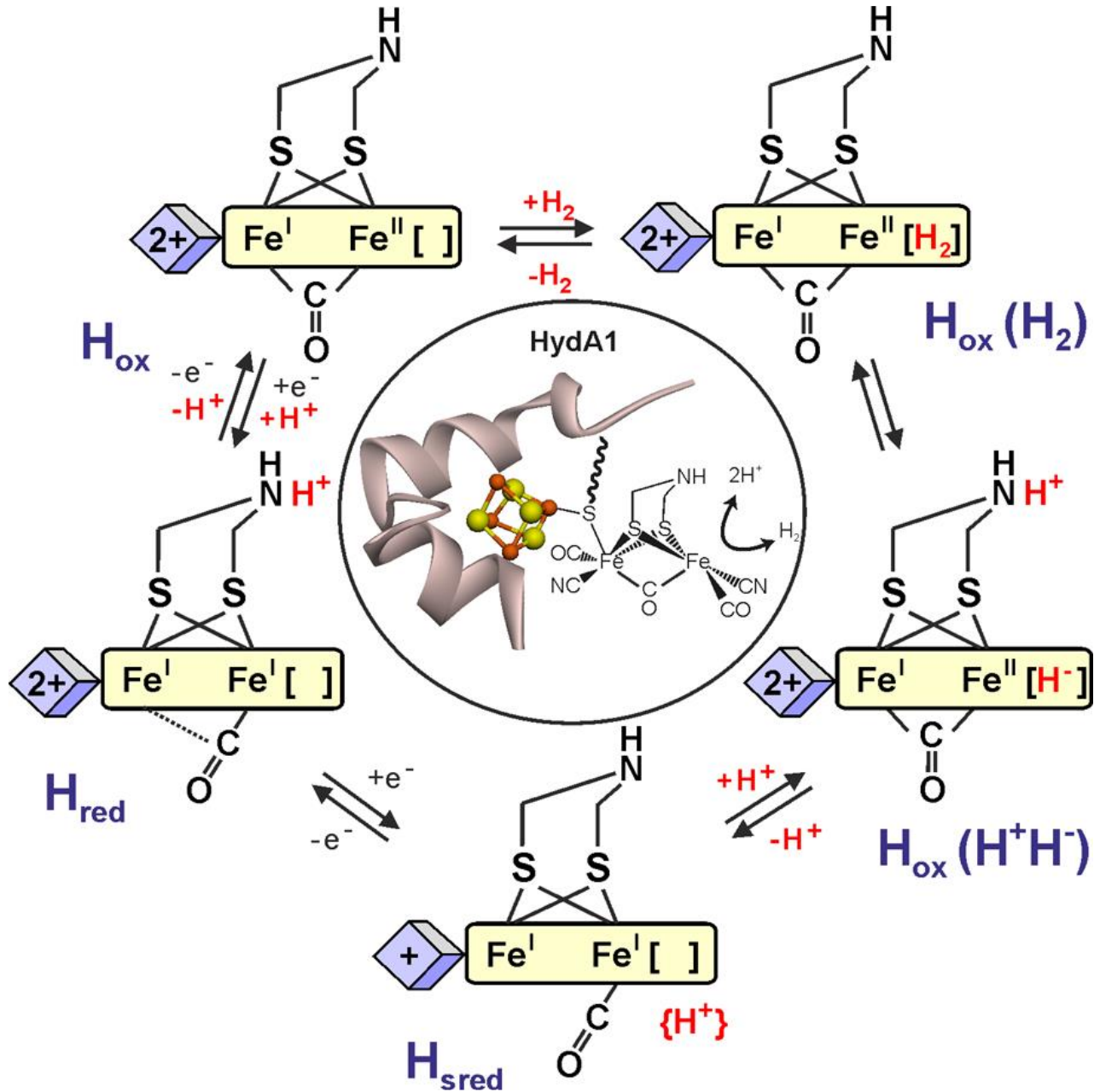


- Active site attached at only **one point**
- **CO** and **CN** ligands on low-spin Fe<sup>II</sup>
- Metal-metal bonds
- Intramolecular heterolysis of **H<sub>2</sub>** ostensibly at this site  
CO can displace **H<sub>2</sub>O**; can **H<sub>2</sub>**?  
**H<sub>2</sub>** is slightly stronger ligand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

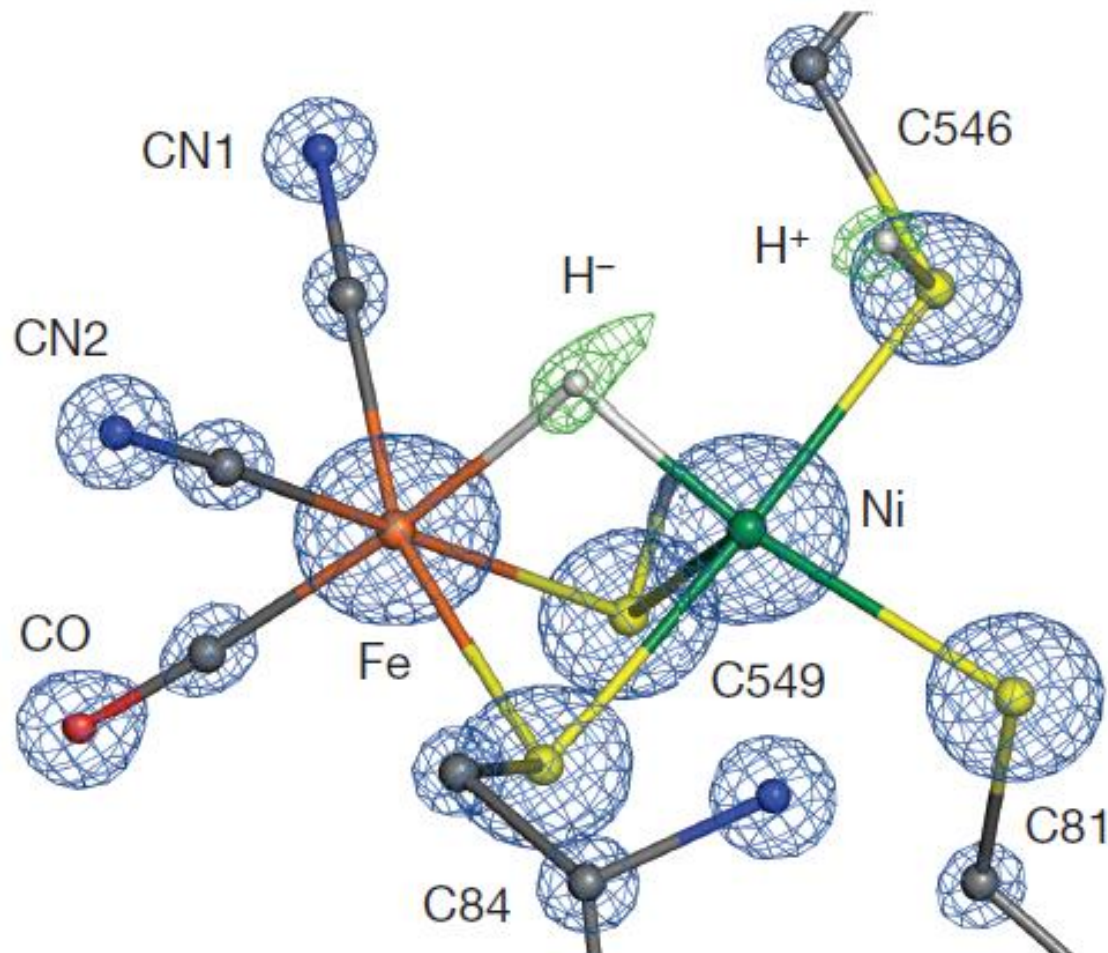
Trans **CO** ligand favors H<sub>2</sub> coordination and heterolysis

*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

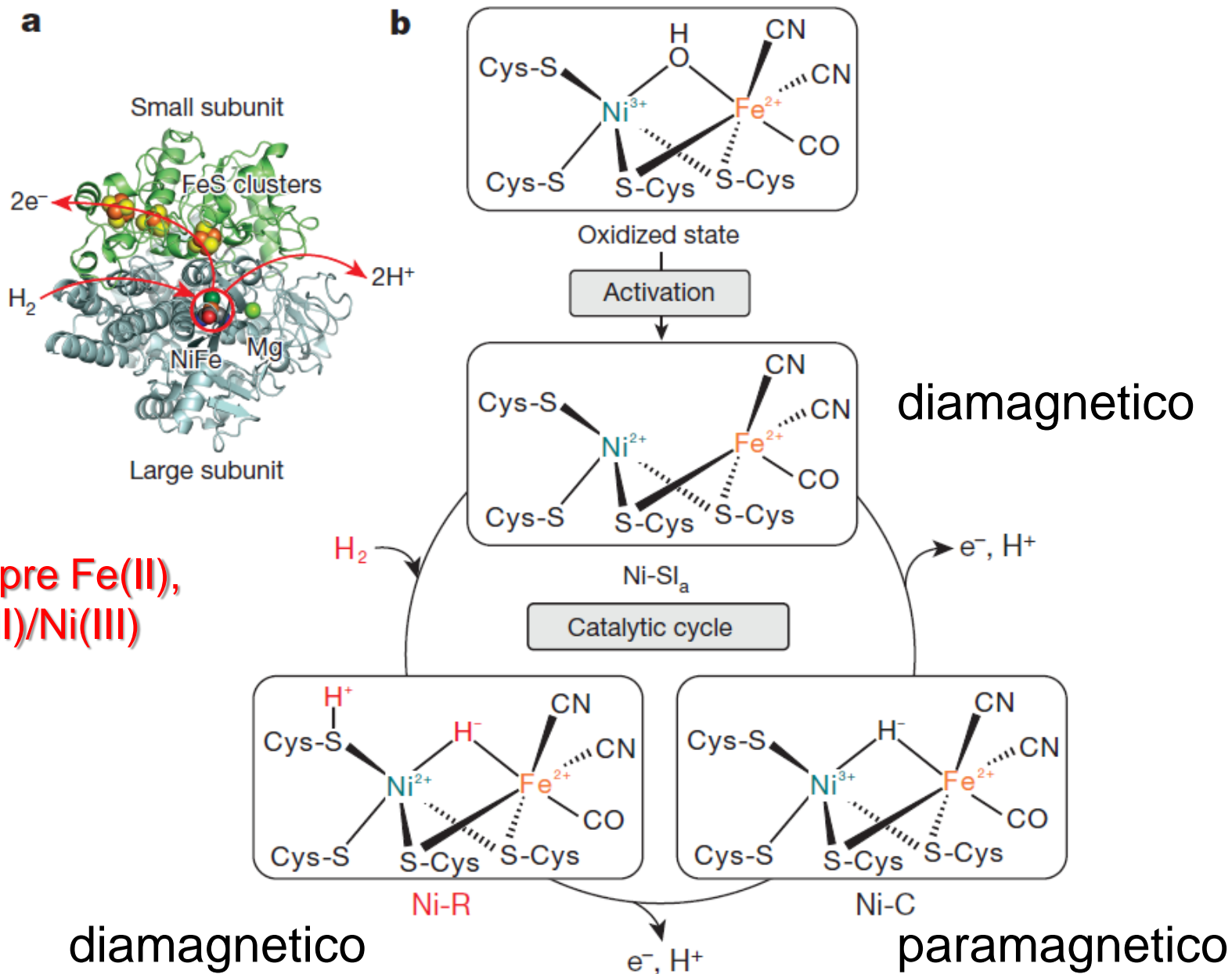


# Fe–Ni Idrogenasi

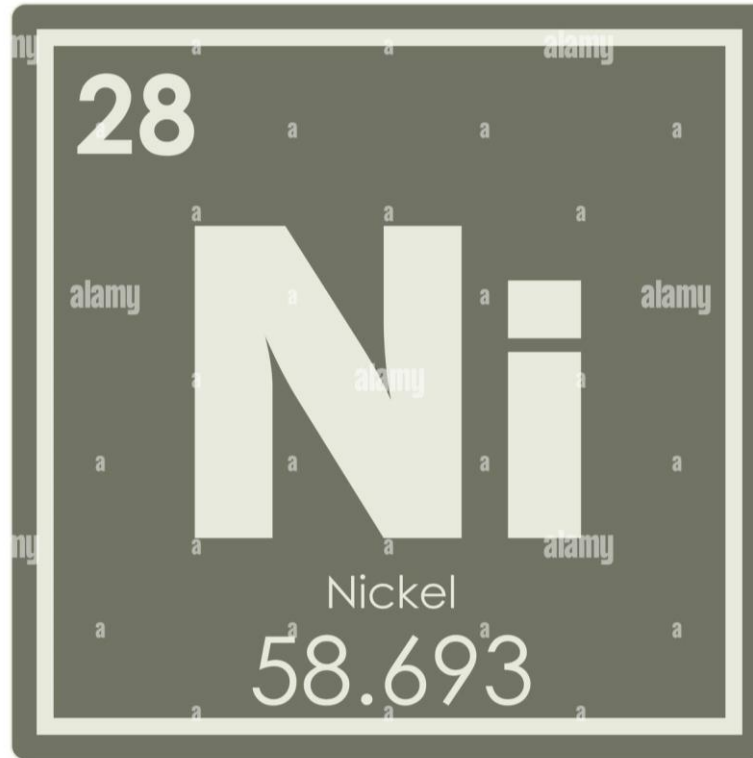


Risoluzione ultra-elevata; posizionati anche gli atomi di idrogeno.  
*Nature*, 2015

# Ipotesi di meccanismo







Enzimi al nichel svolgono ruoli cruciali in batteri, *archei*, funghi, alghe e piante. Al momento non sono noti Ni-enzimi nei mammiferi, e il nichel è classificato come “elemento possibilmente essenziale” per animali e uomini.

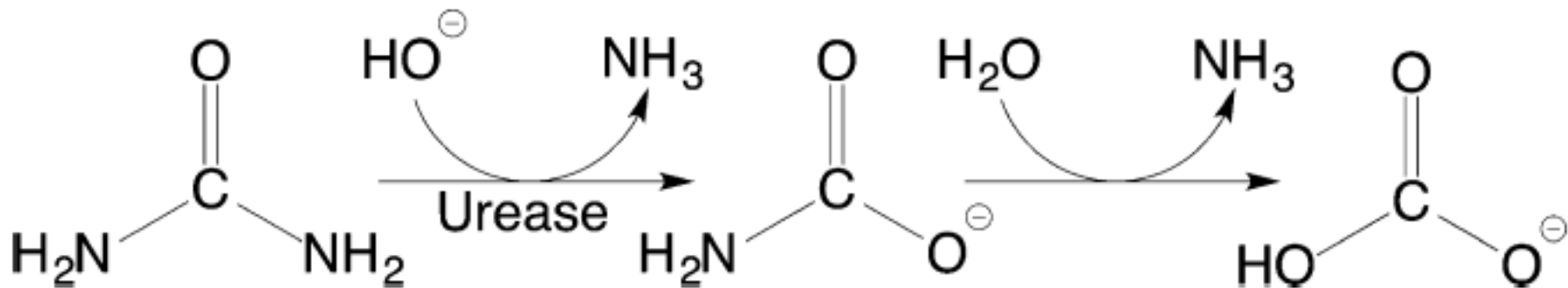
## Ni-Enzimi redox

- Leganti anionici allo zolfo (Cys<sup>-</sup> e S<sup>2-</sup>)
- Coppia redox Ni(II)/Ni(III)
- Insaturazione coordinativa
- Basso spin

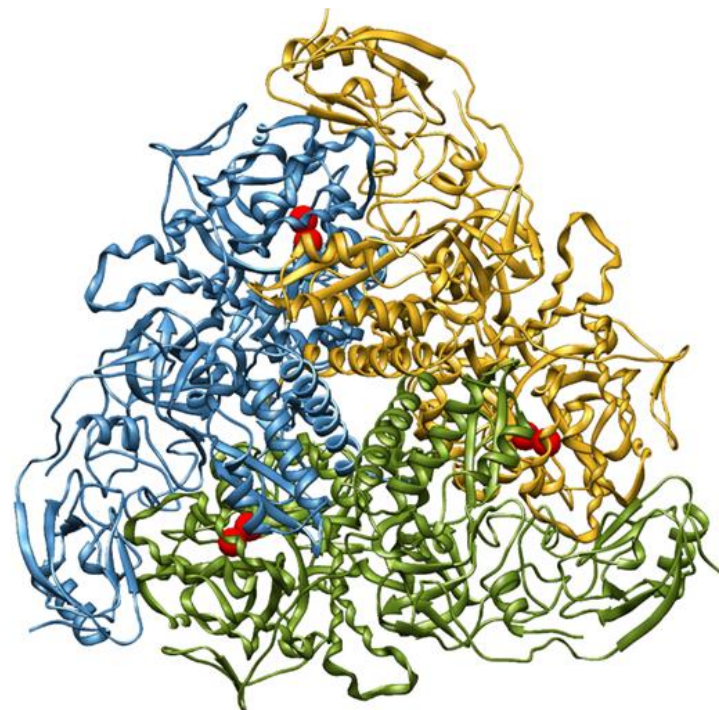
## Ni-Enzimi non-redox

- Sempre Ni(II), funzioni di acido di Lewis
- Leganti O/N
- Esacoordinato
- Alto spin

# Ureasi (enzima non-redox)

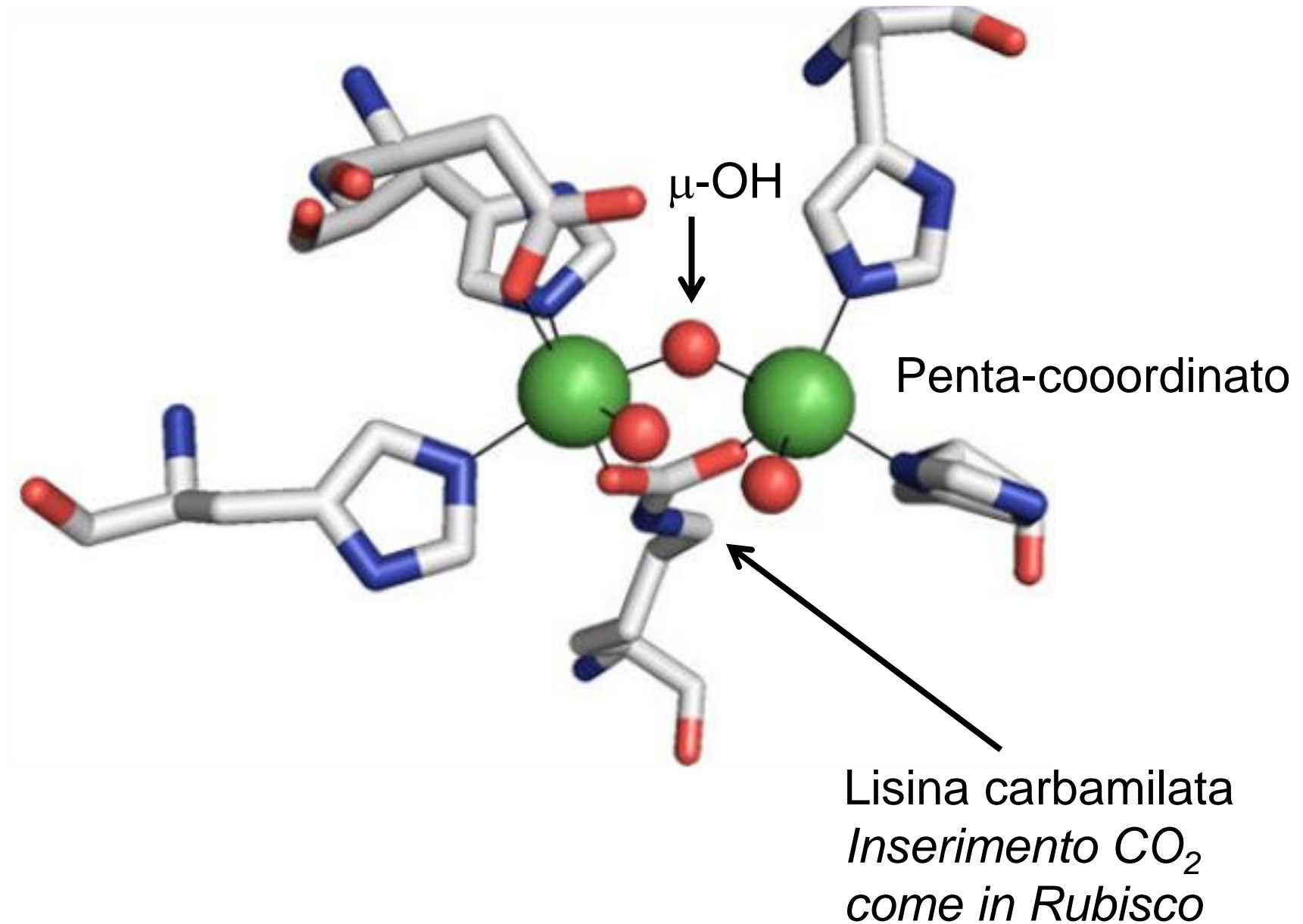


*l'ureasi è la più efficiente tra le idrolasi note, induce un aumento di velocità rispetto alla reazione non catalizzata di  $3 \times 10^{15}$  volte (da centinaia di anni a microsecondi)*

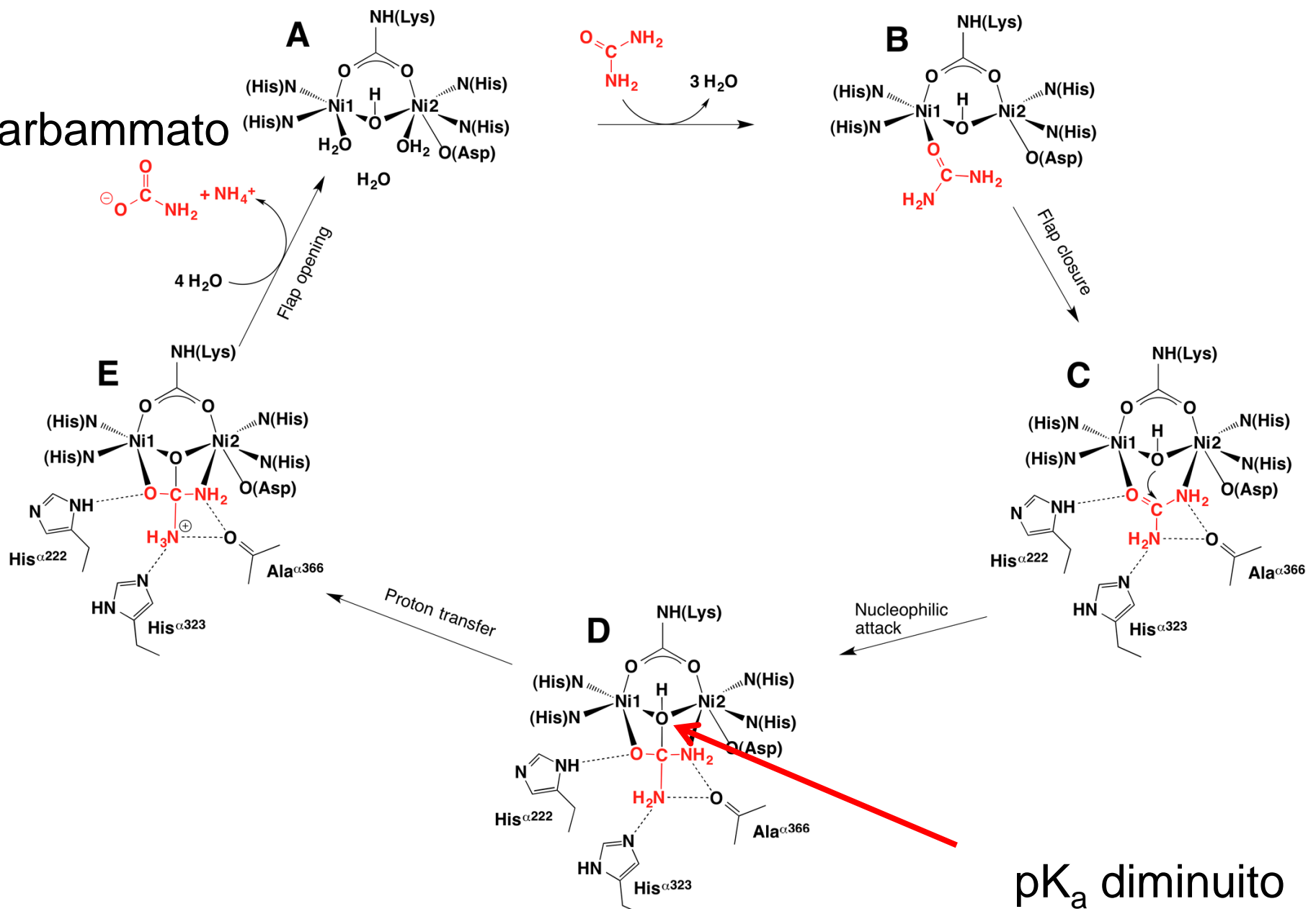


trimero di trimeri del tipo  $(\alpha\beta\gamma)_3$

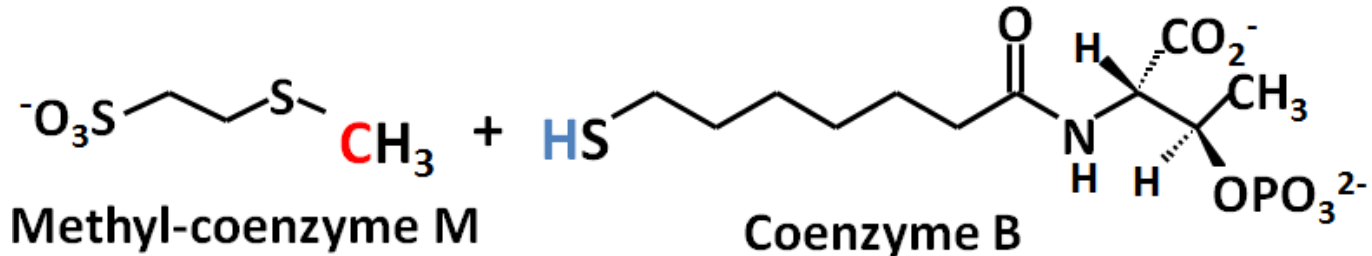
# Sito attivo di ureasi



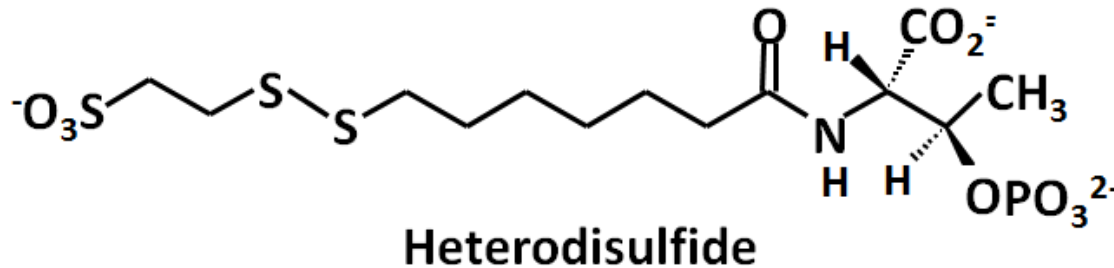
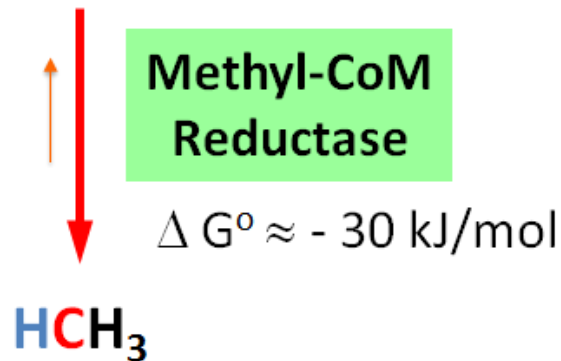
carbammato



# metil-coenzima M riduttasi (MCR) enzima redox (*archei* metanogenici)

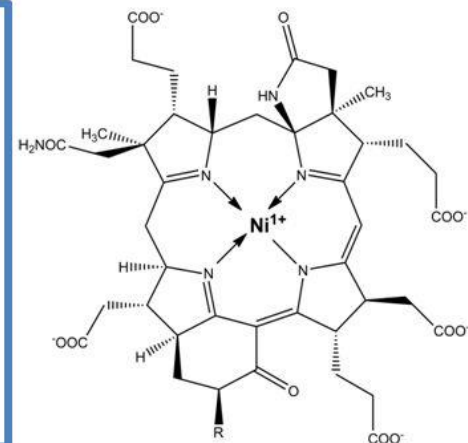
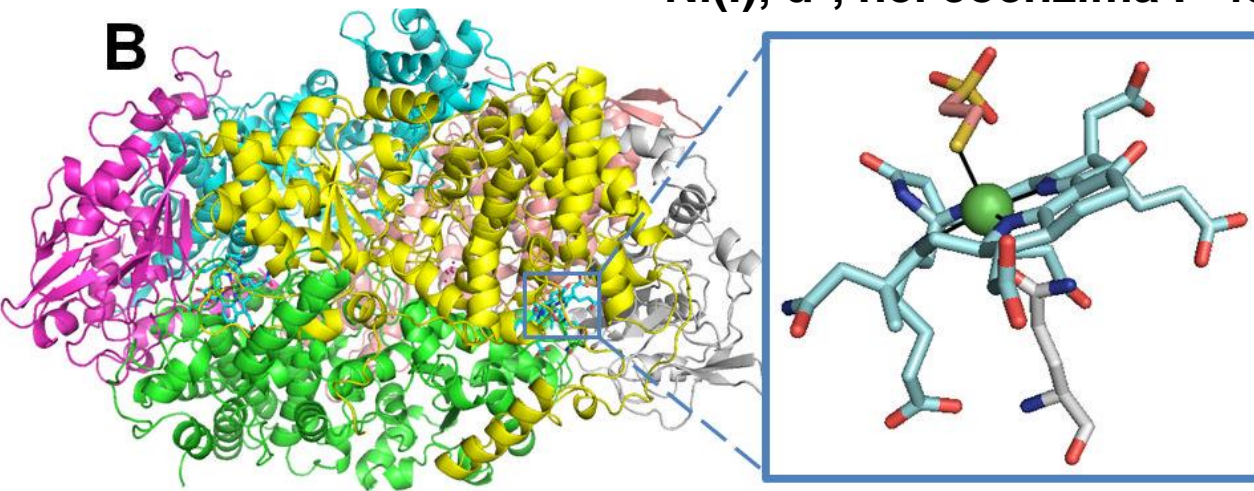


$10^9$  t/y di metano biologico

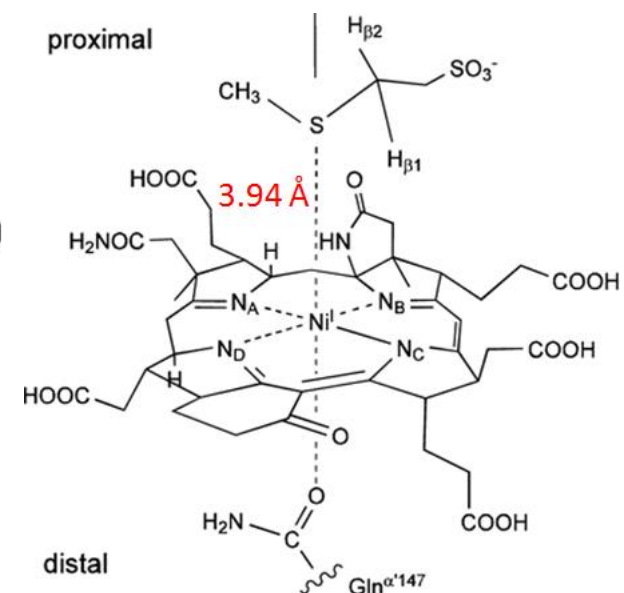
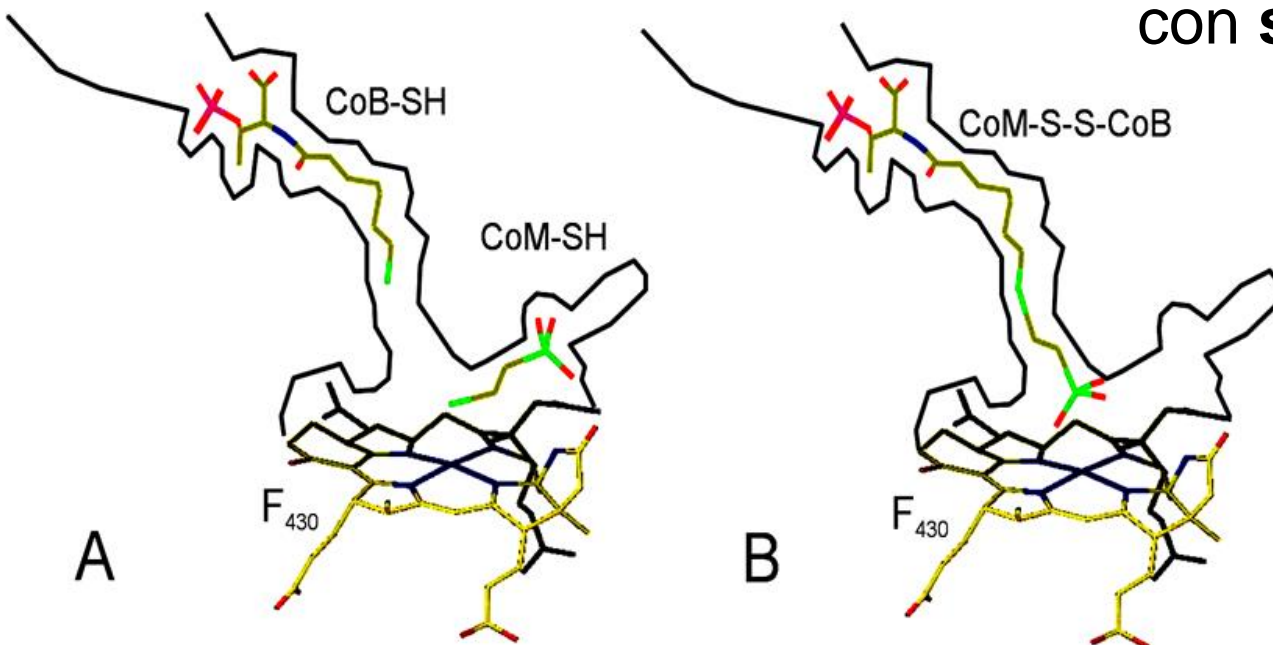


Gli *archei* metanogenici utilizzano  $H_2$  e  $CO_2$  come uniche fonti di energia e di carbonio

# Ni(I), $d^9$ , nel coenzima F-430

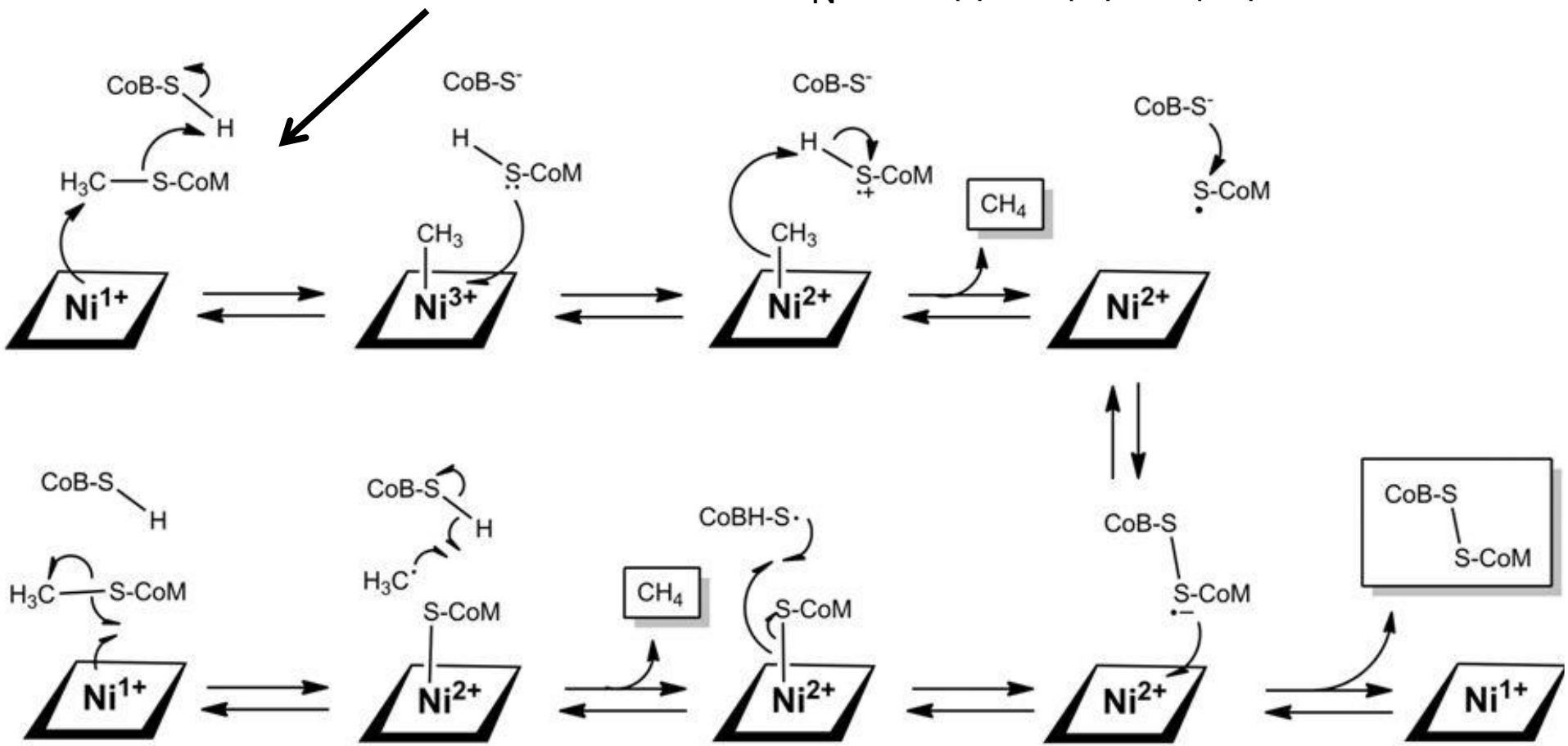


Macrocielo tetrapirrolico  
con **solo 5 doppi legami**



glutamina

# Meccanismo S<sub>N</sub>2, Ni(I)/Ni(II)/Ni(III)



$$E^{\circ}_{\text{Ni(II)F-430/Ni(I)F-430}} < -600 \text{ mV}$$

Meccanismo radicalico, Ni(I)/Ni(II)