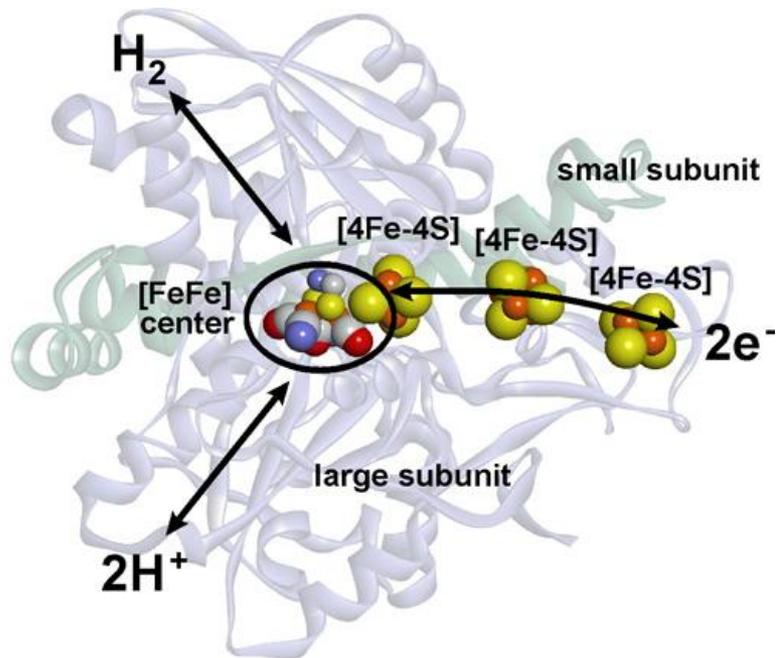
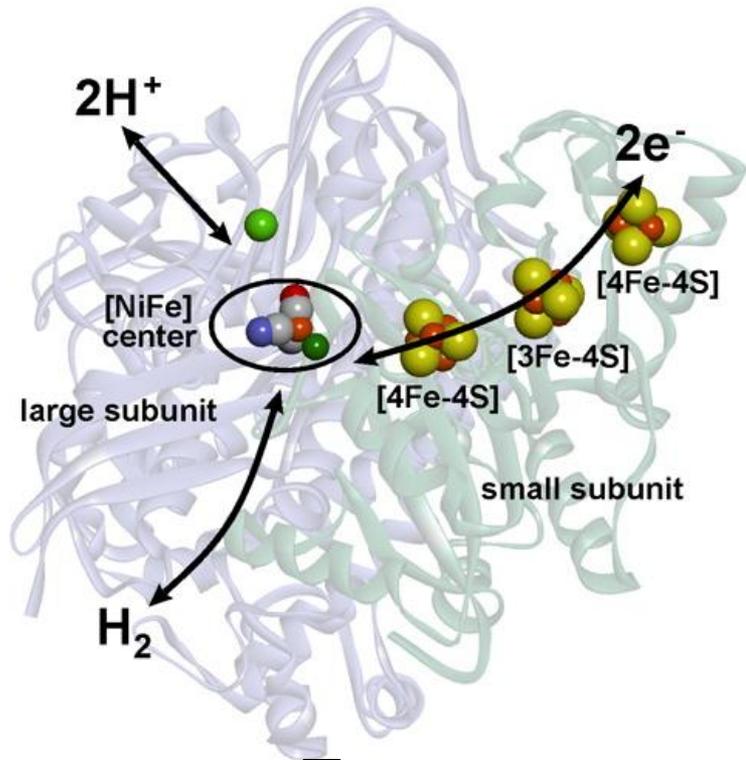


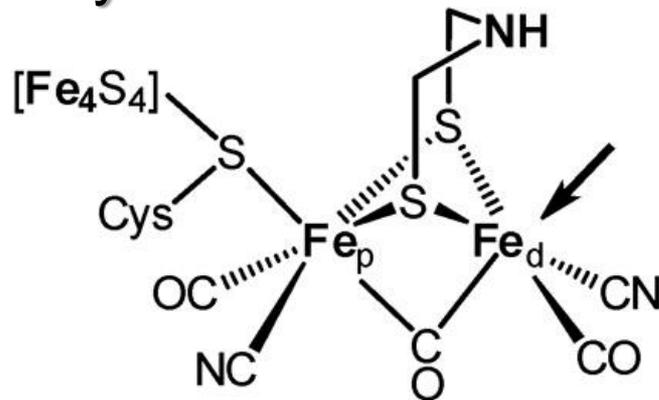
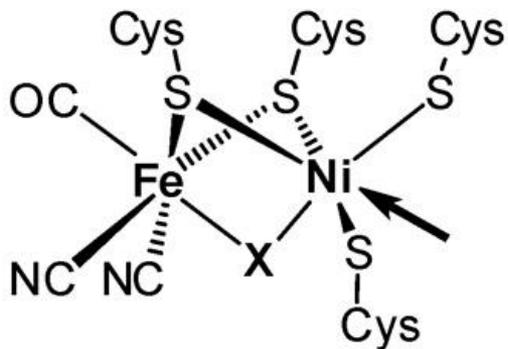


[NiFe] Hydrogenase

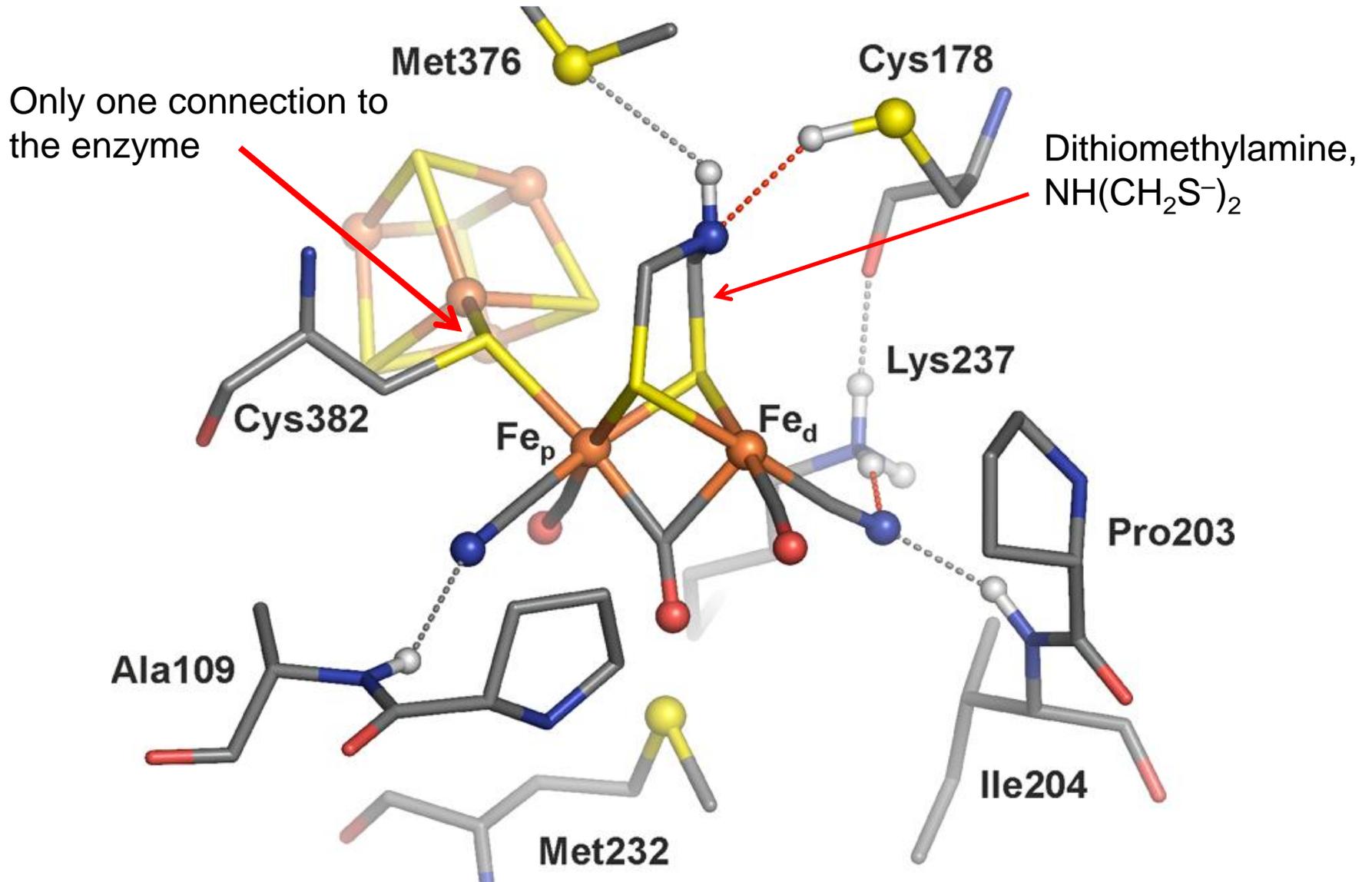
[FeFe] Hydrogenase

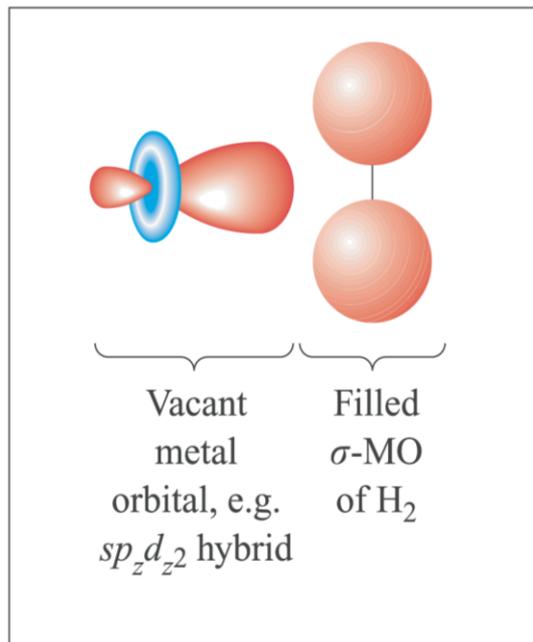
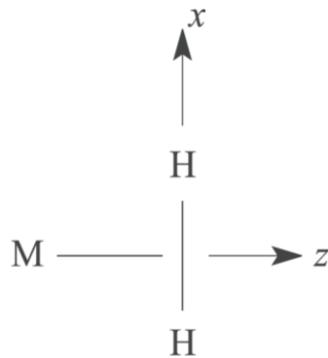


Turnover up to 10⁴ cycles/second

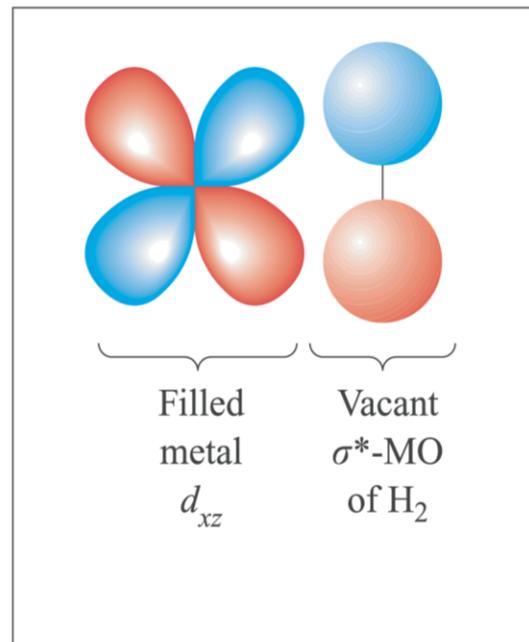


[FeFe] hydrogenase



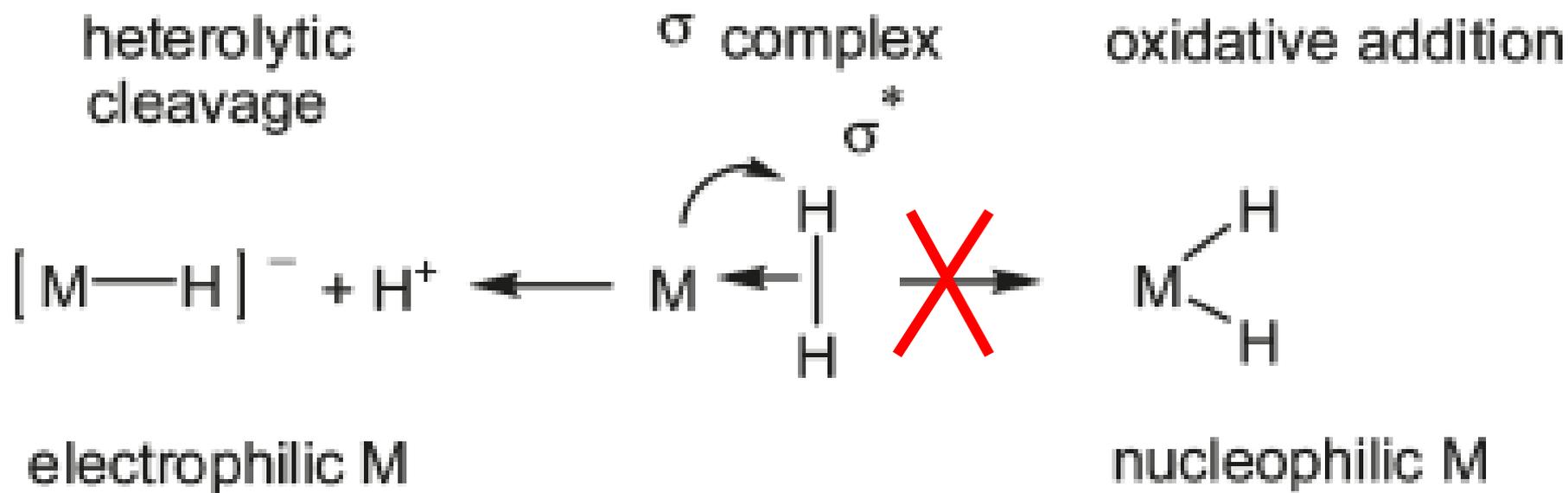


H₂-to-M donation

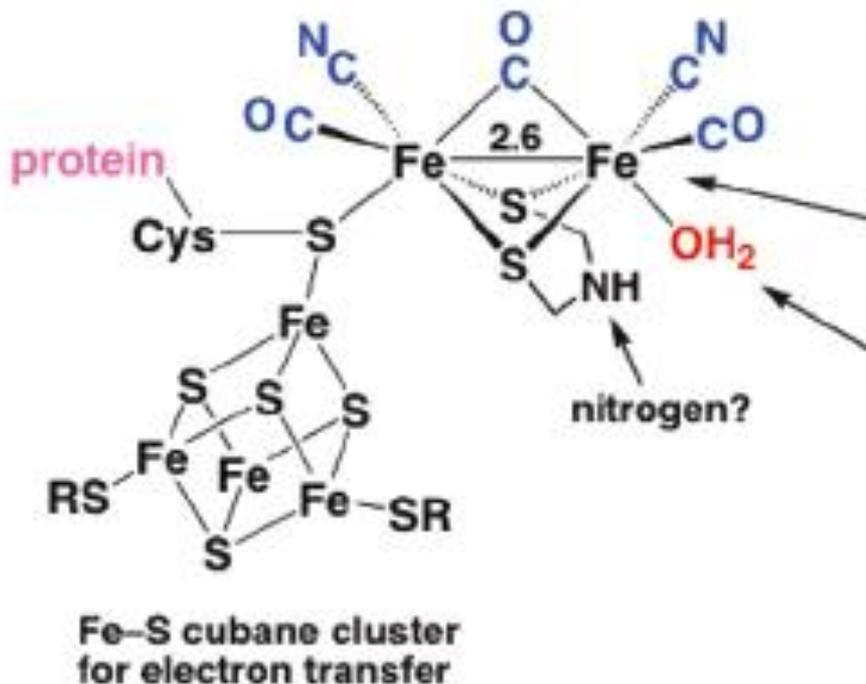


M-to-H₂ back-donation

The CO ligand favors the heterolytic cleavage of H₂



Fe-Fe hydrogenase

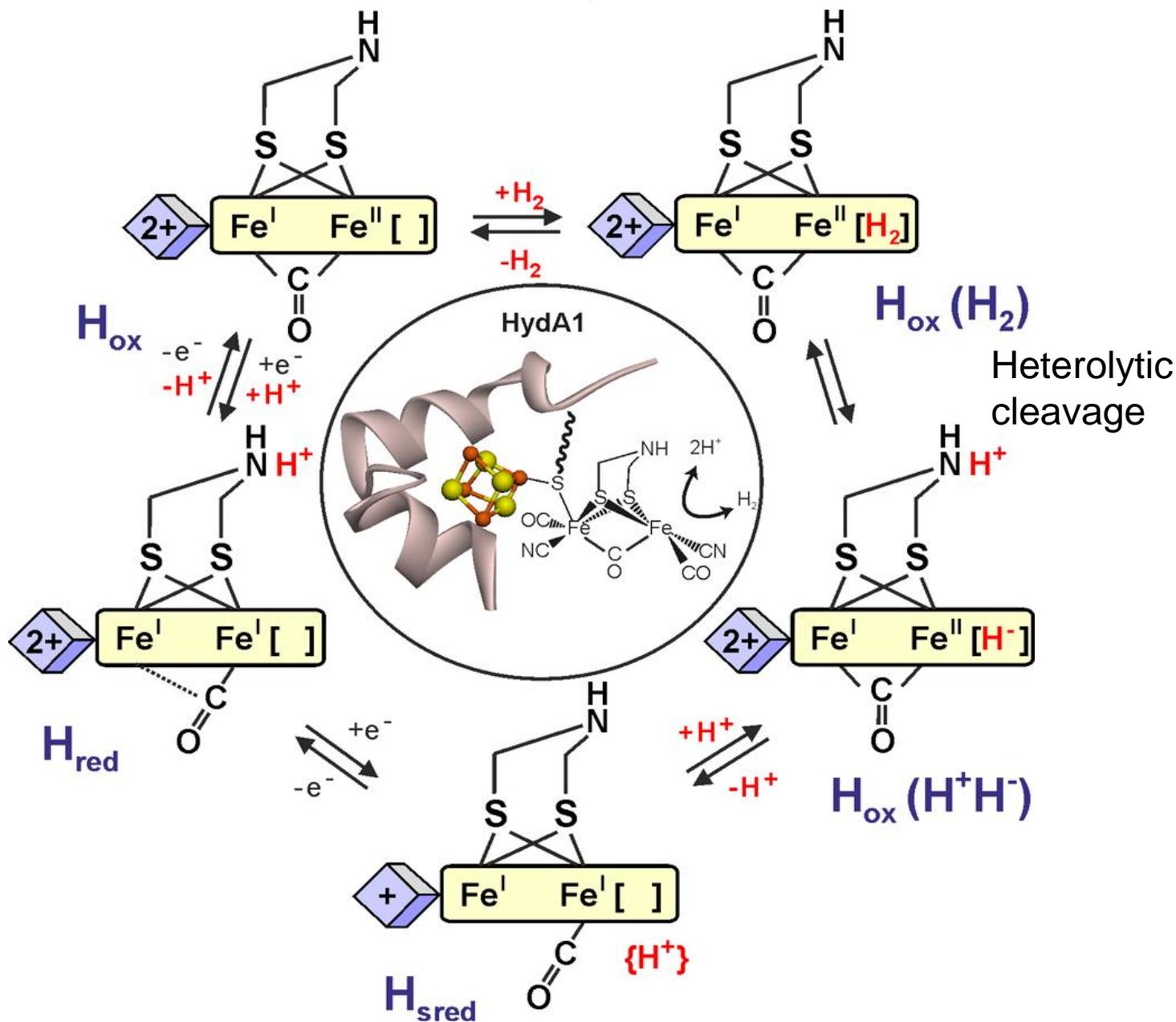


- Active site attached at only **one point**
- **CO** and **CN** ligands on low-spin Fe^{II}
- Metal-metal bonds
- Intramolecular heterolysis of **H₂** ostensibly at this site
CO can displace **H₂O**; can **H₂**?
H₂ is slightly stronger ligand than **H₂O** on W(CO)₃(PR₃)₂

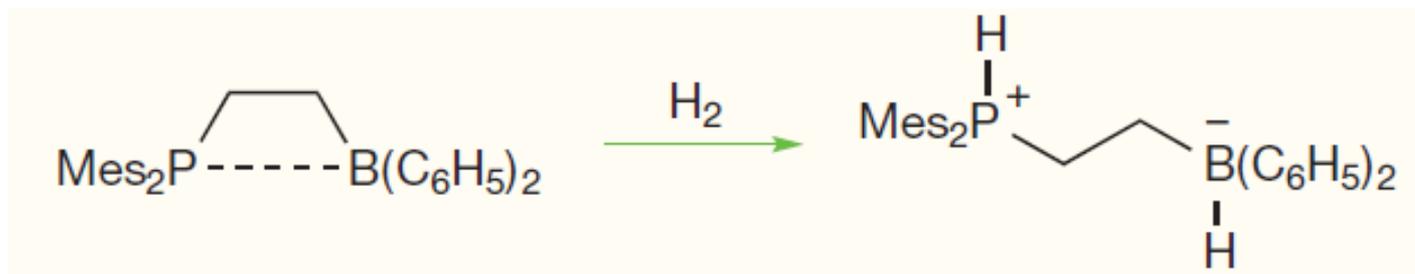
Trans **CO** ligand favors H₂ coordination and heterolysis

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^{II}-CO complexes are rare

mechanism hypothesis

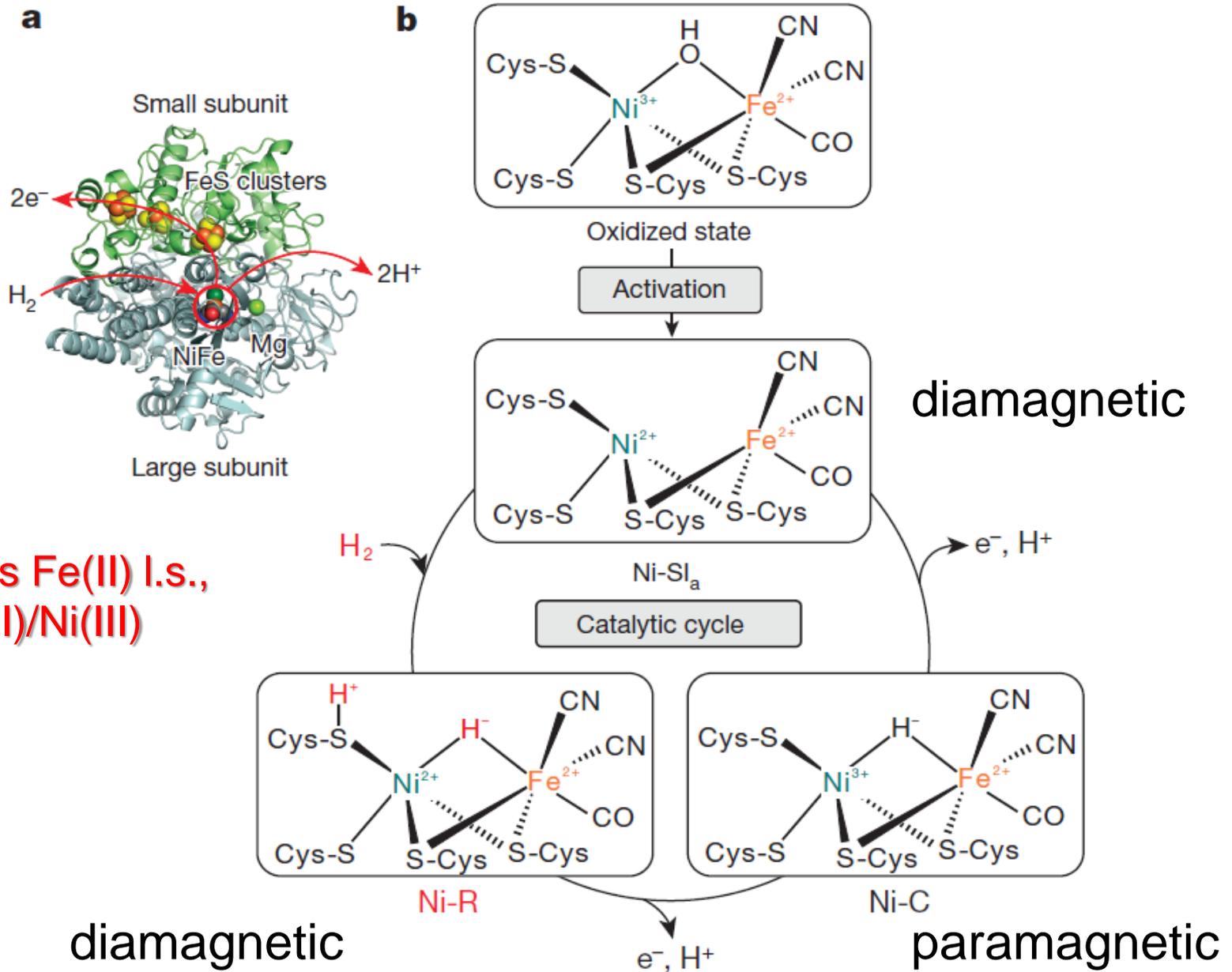


The acidic Fe(II) atom and the basic NH group of the bridging dithiomethylamine behave as a *frustrated Lewis pair*, FLP, leading to the heterolytic cleavage of the H–H bond.

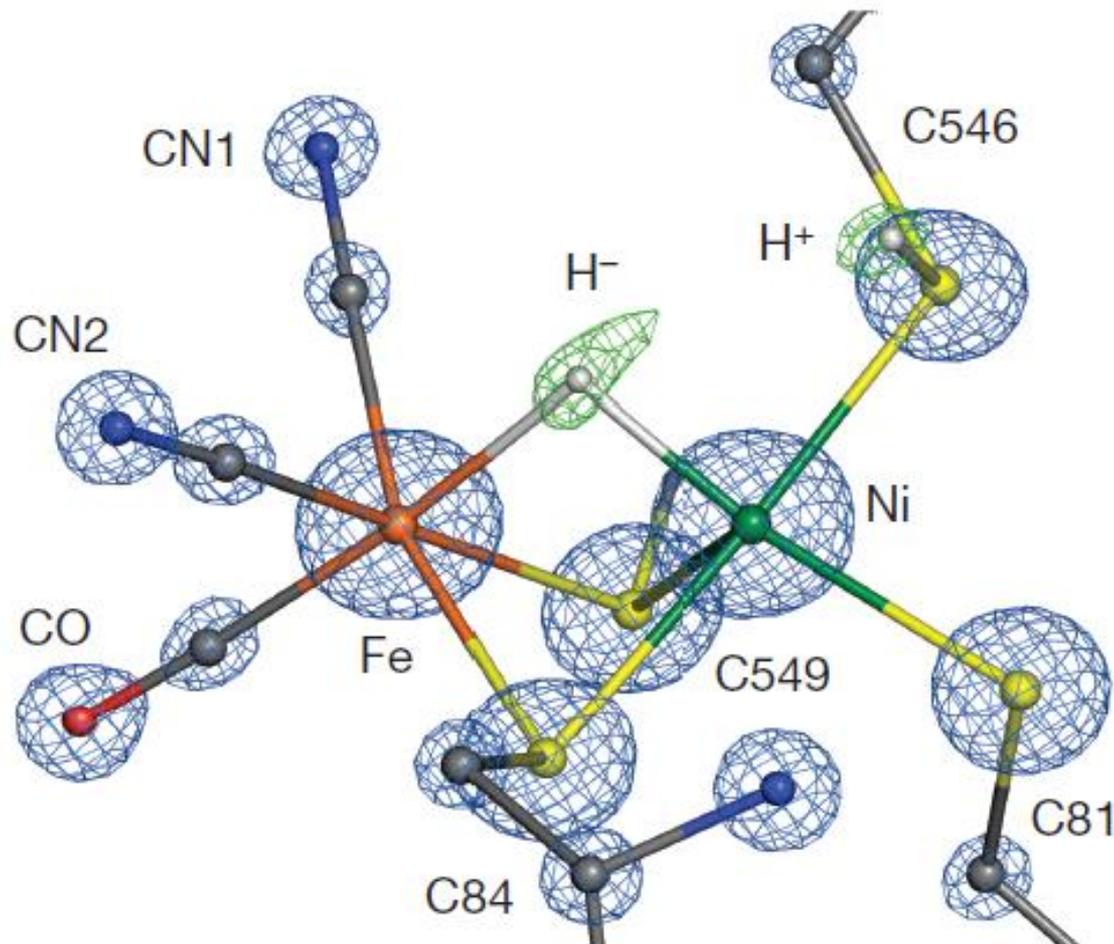


FLP (*frustrated Lewis pair*)

mechanism hypothesis

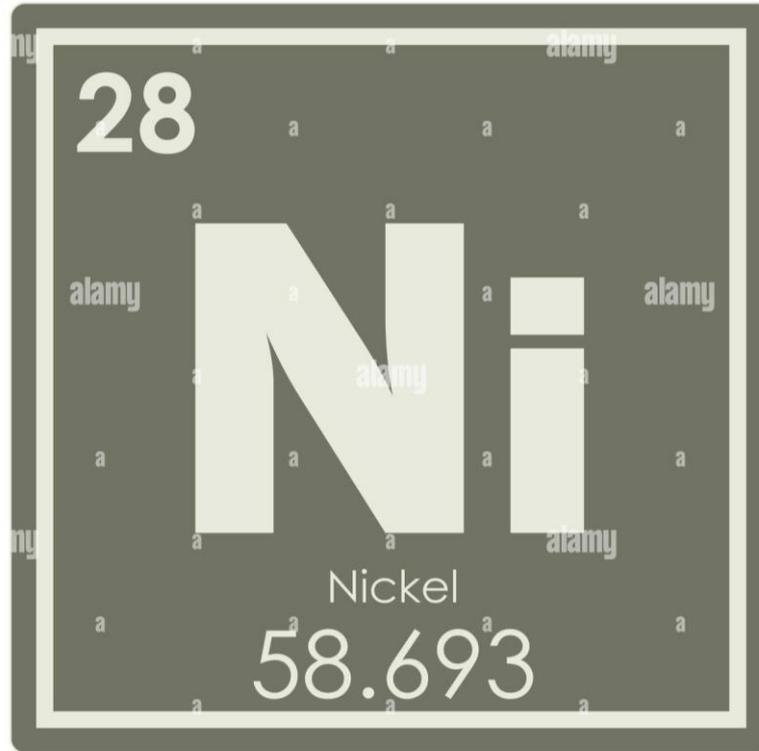


Fe–Ni hydrogenase



Ultra-high resolution X-ray structure allowed to position also the H atoms.

Nature, **2015**



Nickel enzymes play crucial roles in bacteria, *archaea*, fungi, algae and plants. There are currently no known Ni-enzymes in mammals, and nickel is classified as a “possibly essential element” for animals and humans (estimated need: 25 – 35 $\mu\text{g}/\text{day}$).

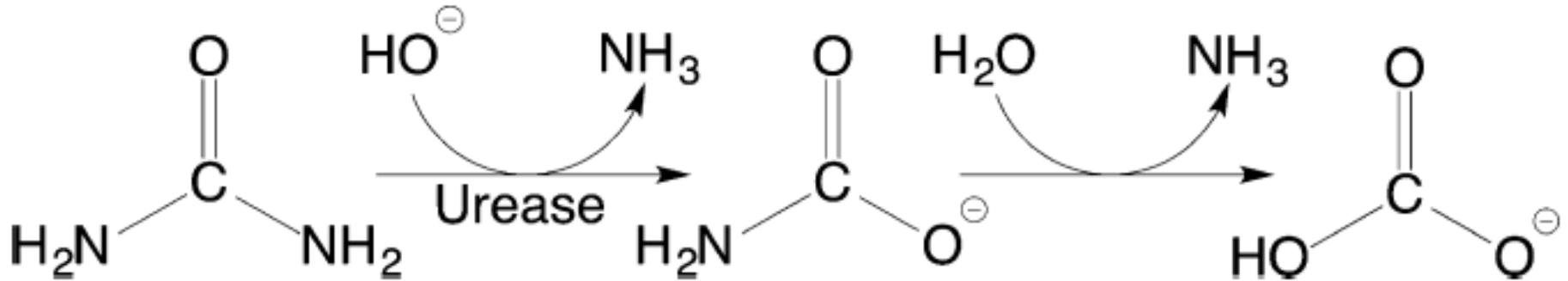
Redox Ni-enzymes

- Anionic sulfur ligands (Cys⁻ e S²⁻)
- Redox pair Ni(II)/Ni(III)
- Coordinatively unsaturated
- Low spin

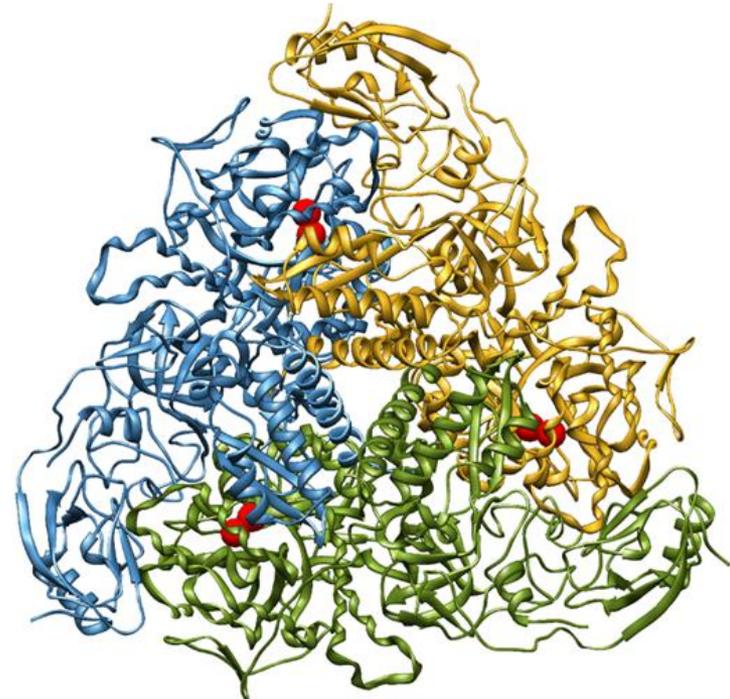
Non-redox Ni-enzymes

- O/N ligands
- Always as Ni(II), Lewis acid behavior
- Six-coordinate
- High spin

Urease (non-redox enzyme)

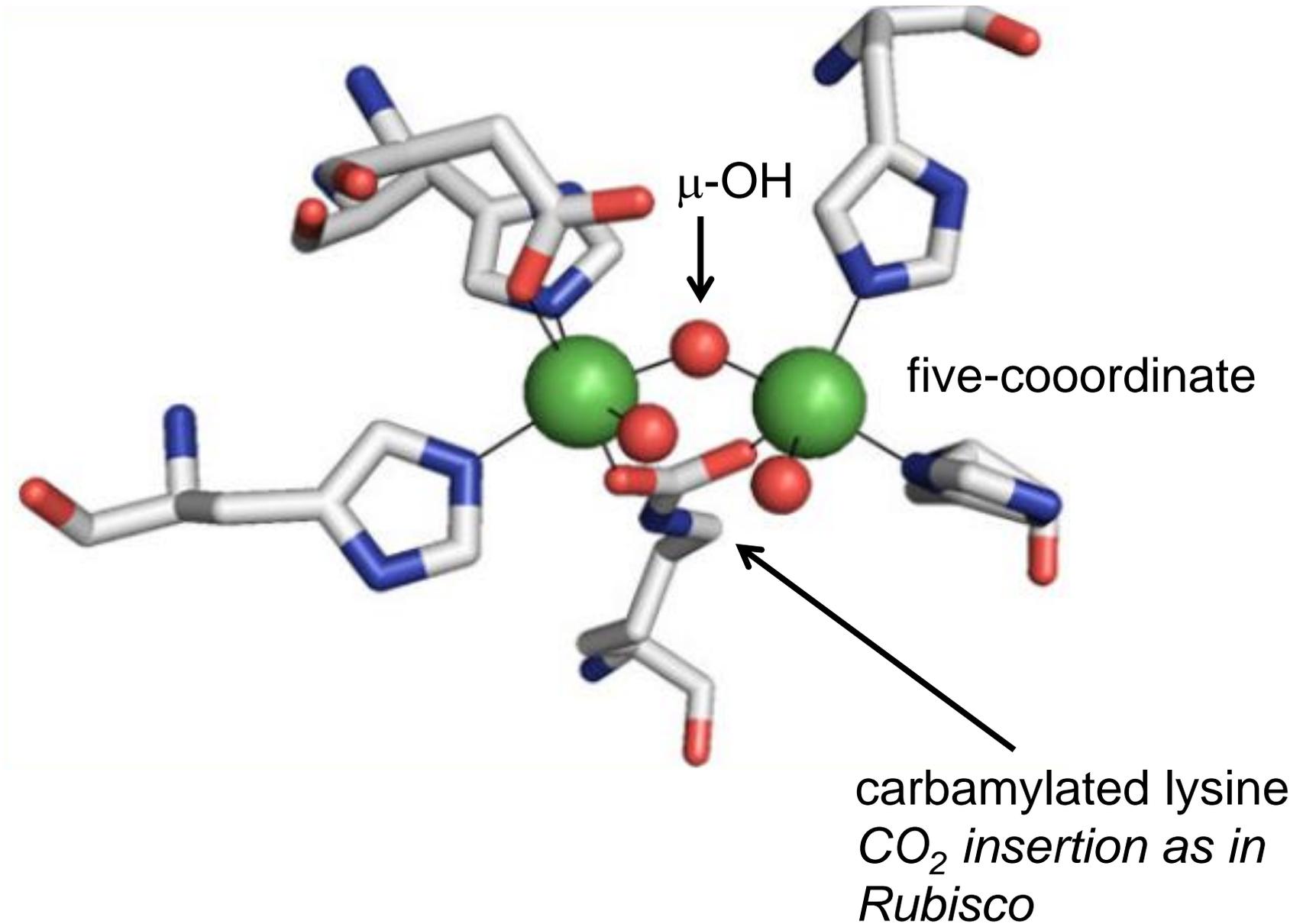


urease is the most efficient of the known hydrolases, inducing a 3×10^{15} fold increase in speed over the uncatalyzed reaction (from hundreds of years to microseconds)

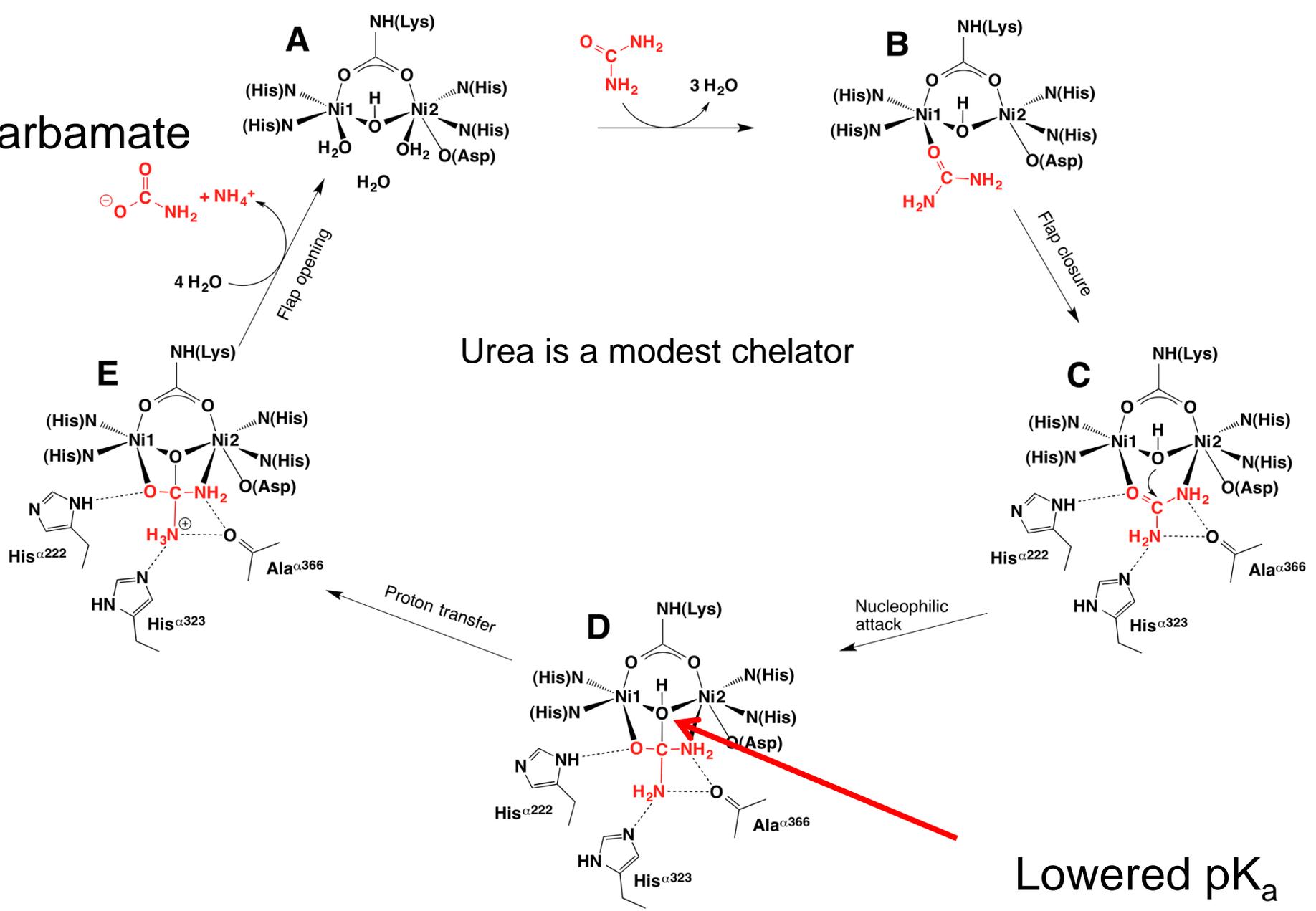


Trimer of trimers of the type $(\alpha\beta\gamma)_3$

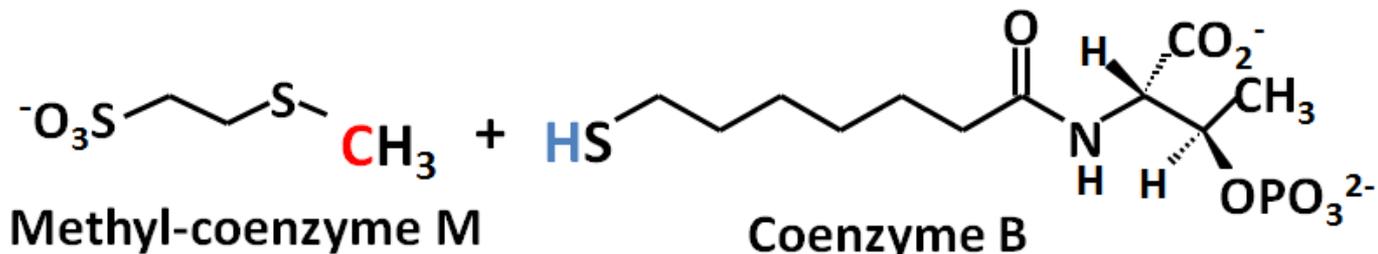
Dinuclear active site in urease



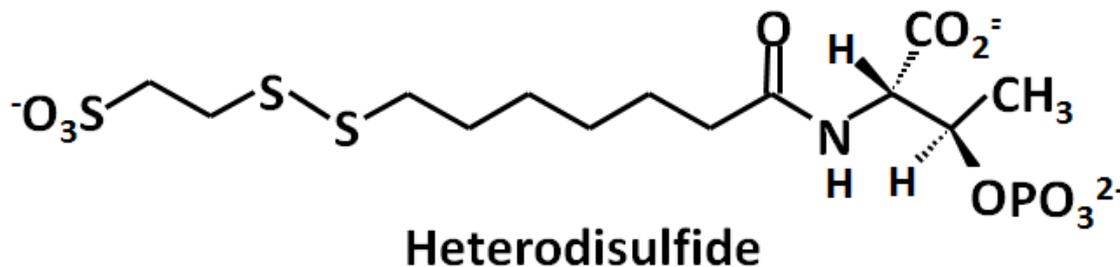
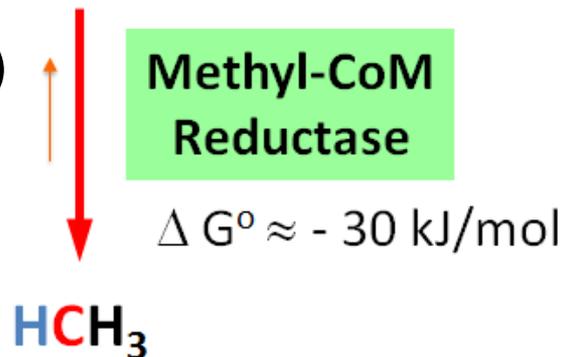
carbamate



methyl-coenzyme M reductase redox enzyme in methanogenic *archei*

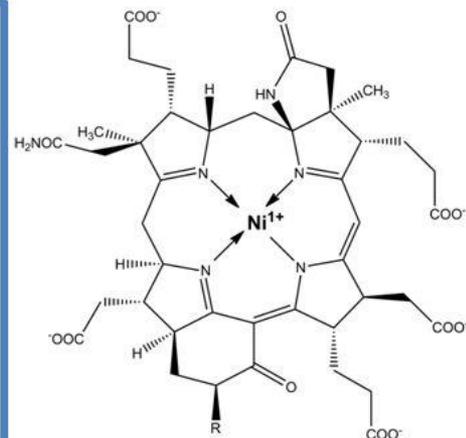
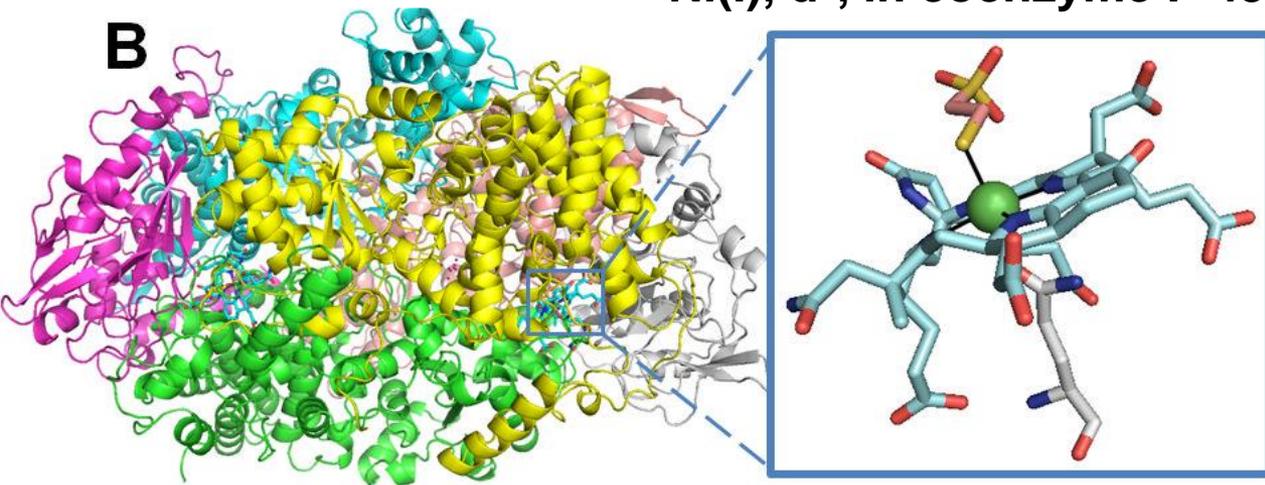


All biological methane (est. 10^9 t/y)
is produced by these *archea*



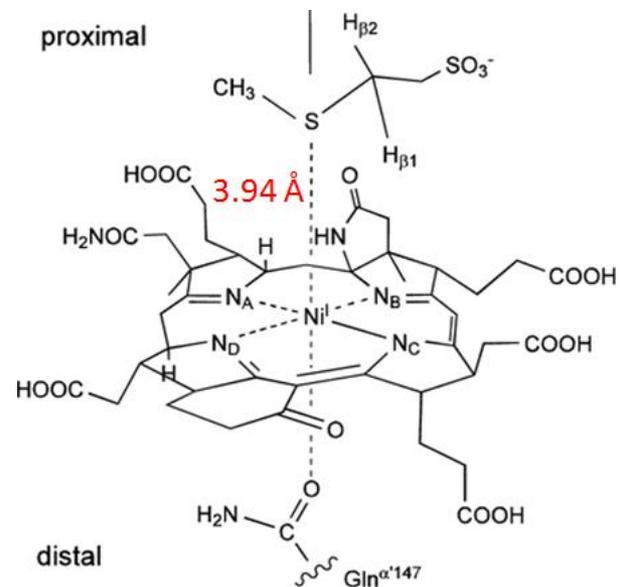
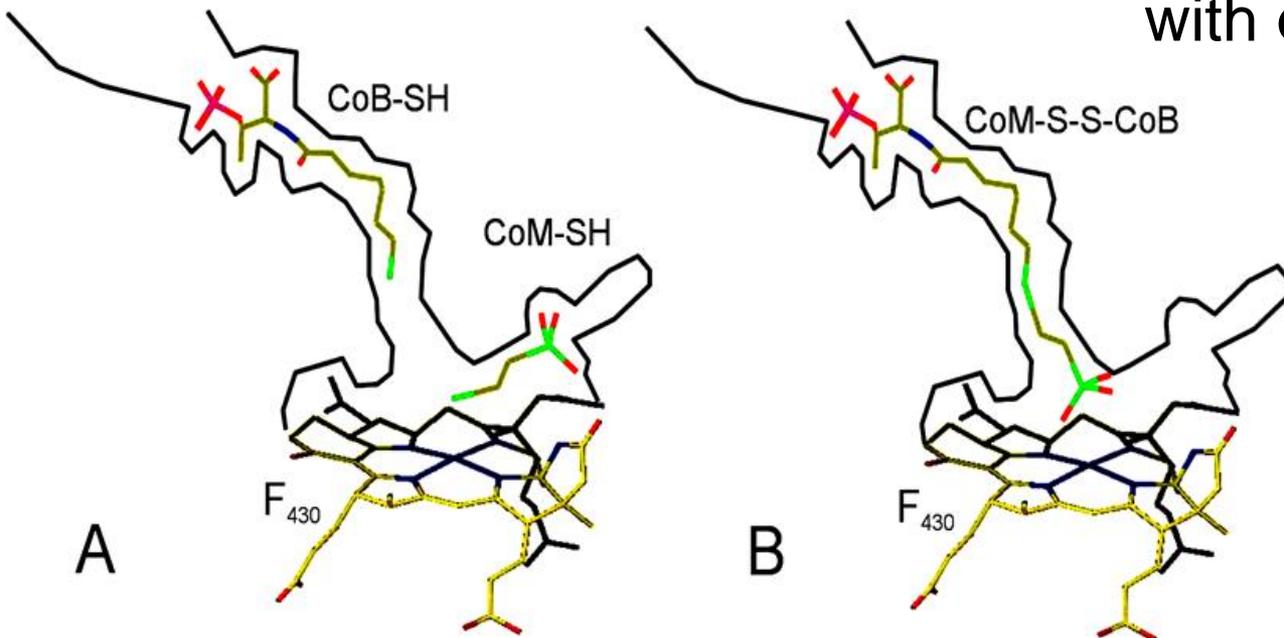
Methanogenic *archea* utilize H_2 and CO_2 as unique sources for energy and carbon

Ni(I), d^9 , in coenzyme F-430



$\alpha_2\beta_2\gamma_2$

tetrapyrrole macrocycle
with **only 5 double bonds**



glutamine

