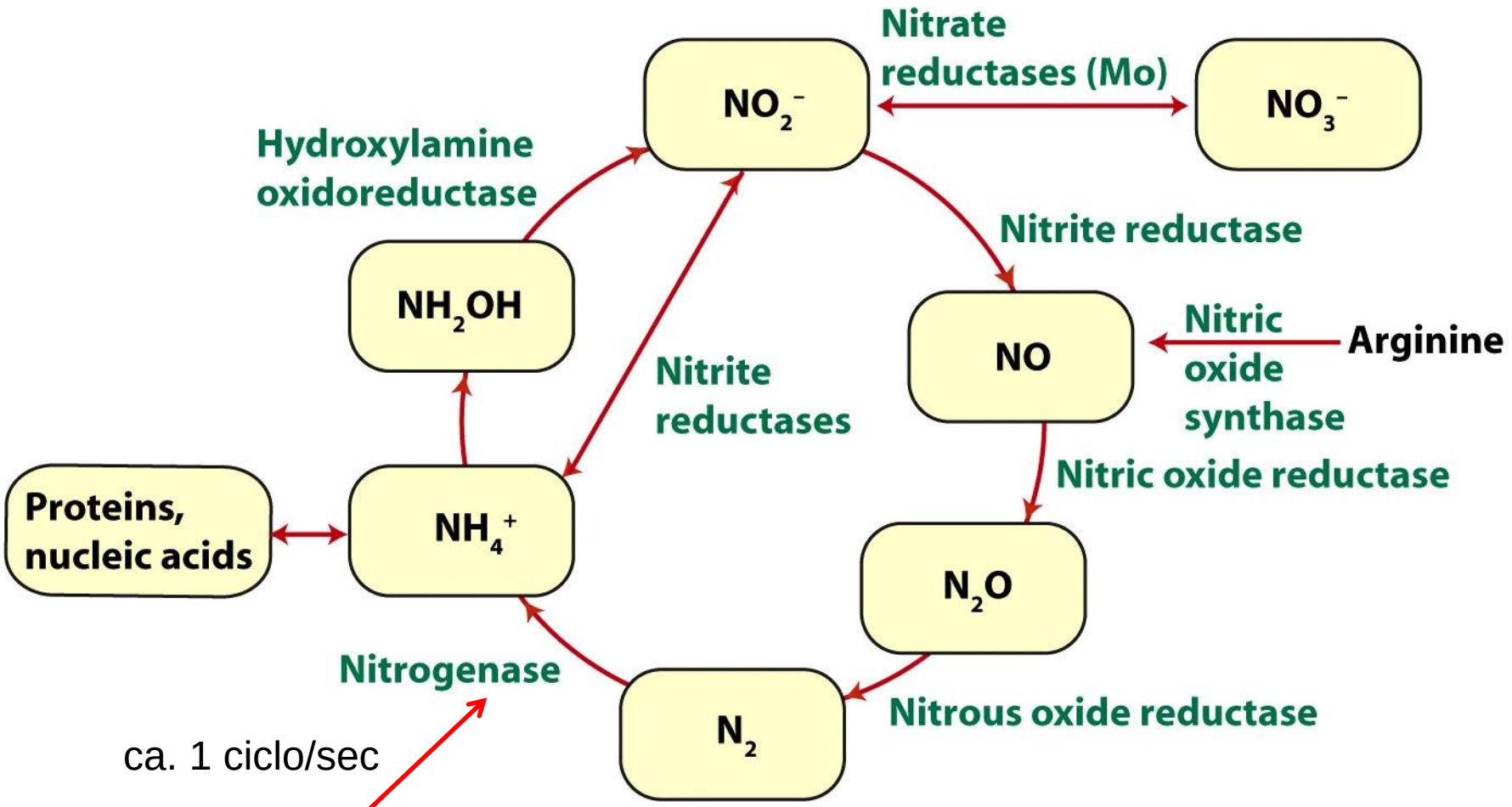
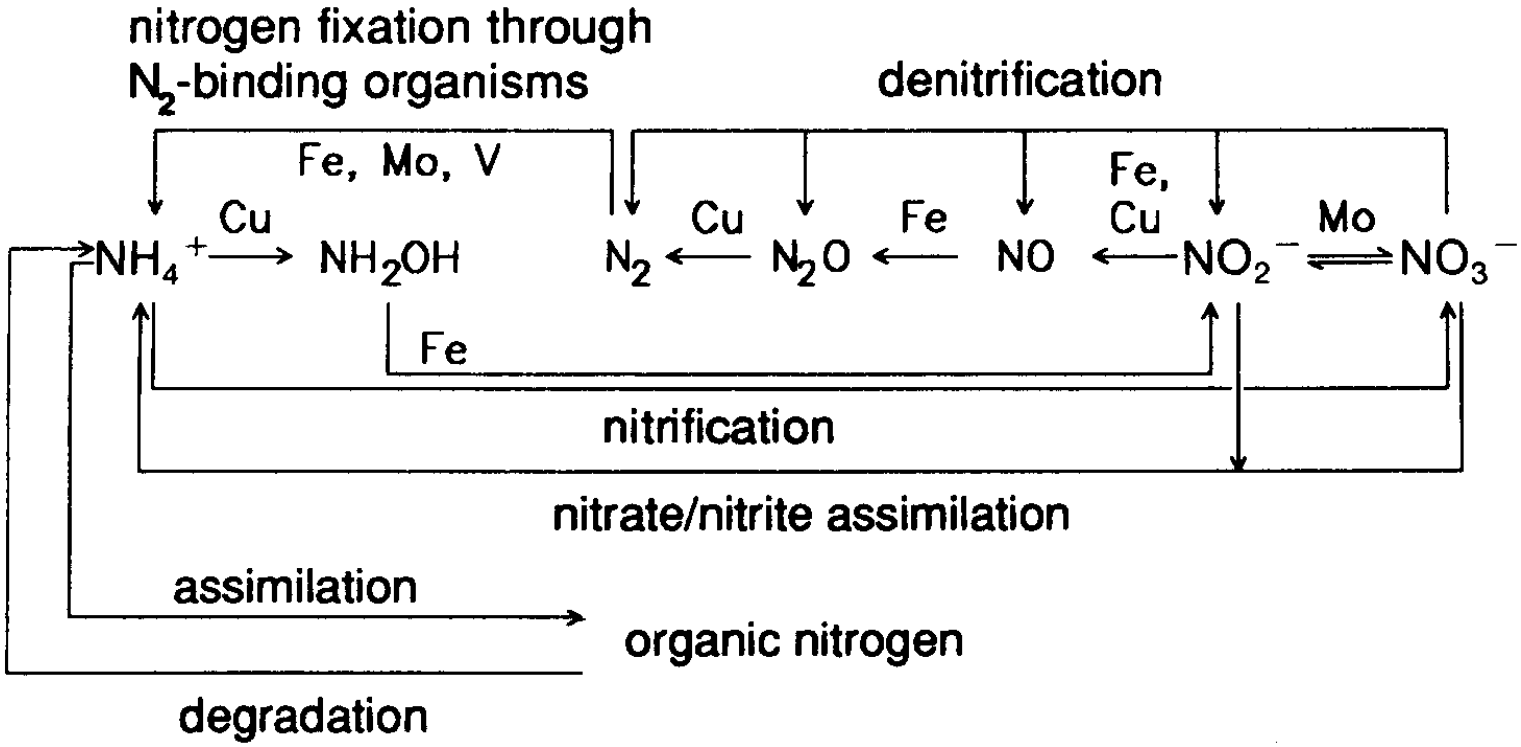
Ciclo dell'azoto



Batteri procarioti diazotropici: 10^8 ton N_2/y



$$N_2 + 10\,H^+ + 8e^- \xrightarrow[\textit{nitrogenasi}]{\text{fissazione}} 2NH_4^+ + H_2$$

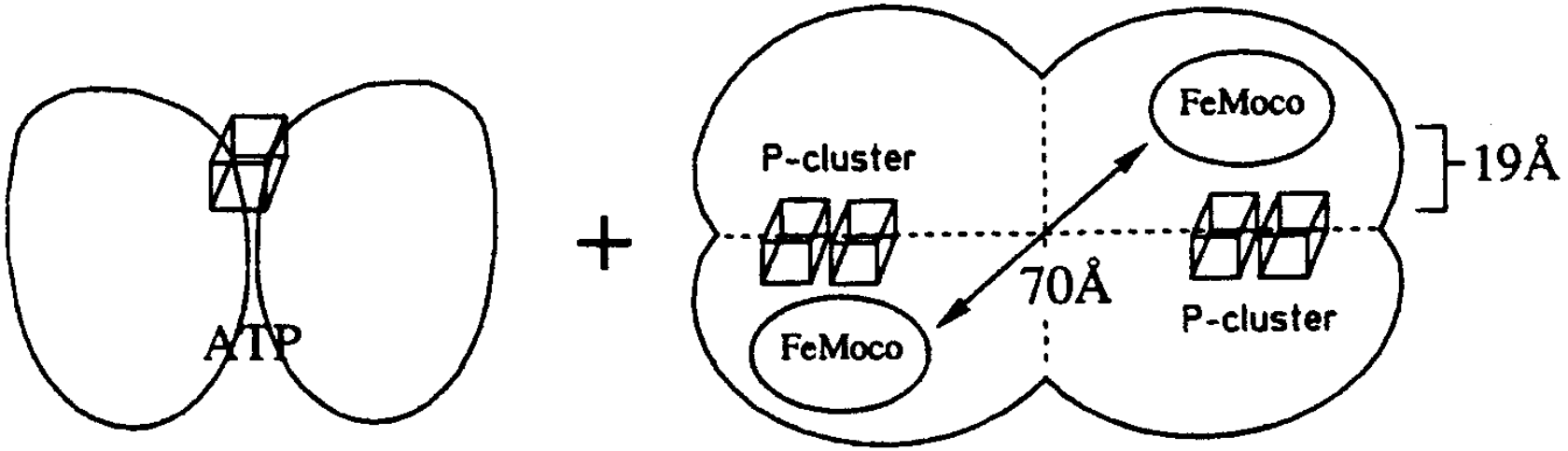
$$NH_4^+ + 2O_2 \xrightarrow{\text{nitrificazione}} NO_3^- + H_2O + 2H^+$$

$$2NO_3^- + 12H^+ + 10e^- \xrightarrow{\text{denitrificazione}} N_2 + 6\,H_2O$$

Nitrogenasi

$N_2 + 10H^+ + 8e^- + 16MgATP \rightarrow 2NH_4^+ + H_2 + 16MgADP + 16PO_4^{3-}$

1992



Fe protein

γ_2

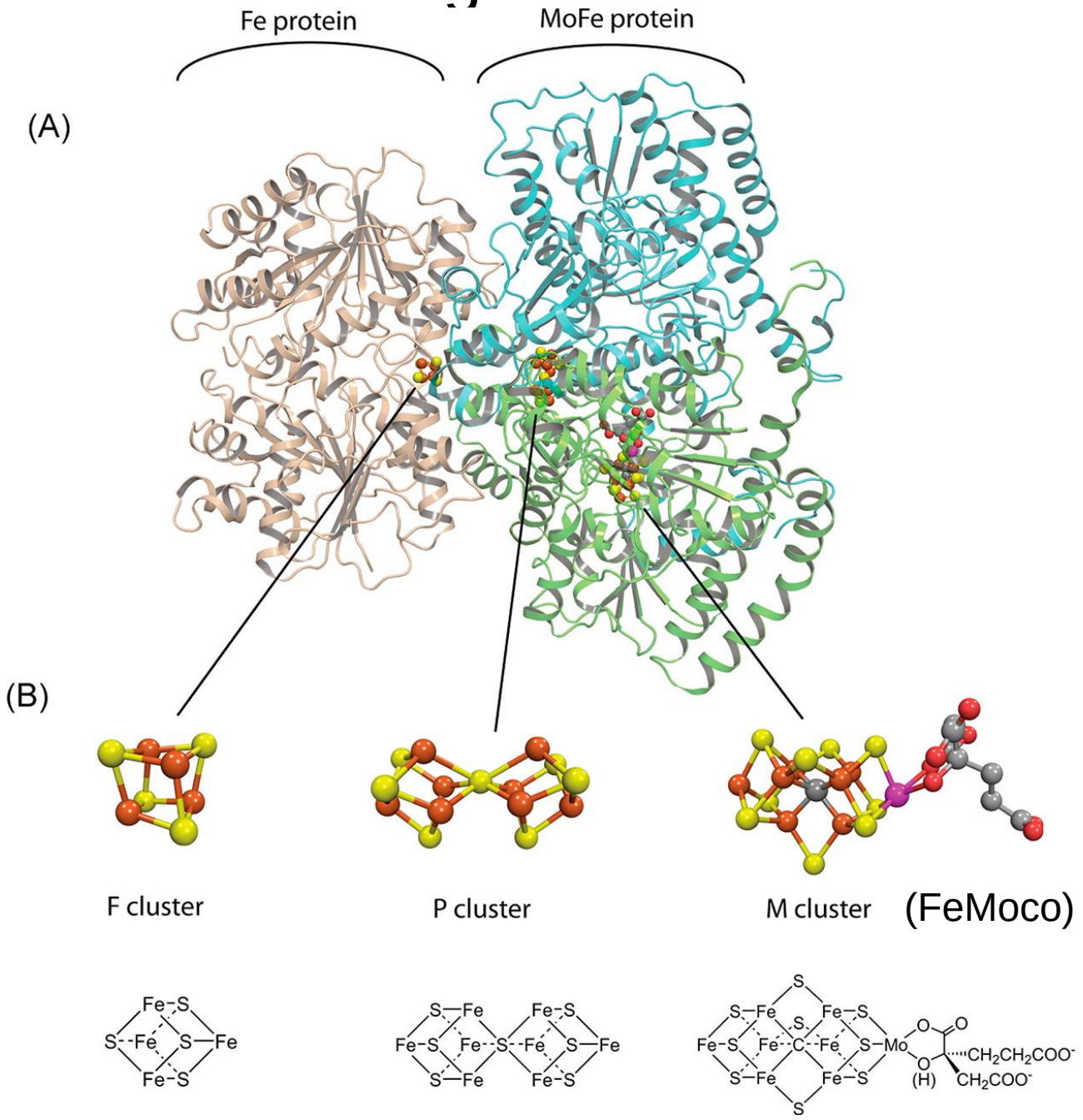
60 kDa

FeMo protein

$\alpha_2\beta_2$

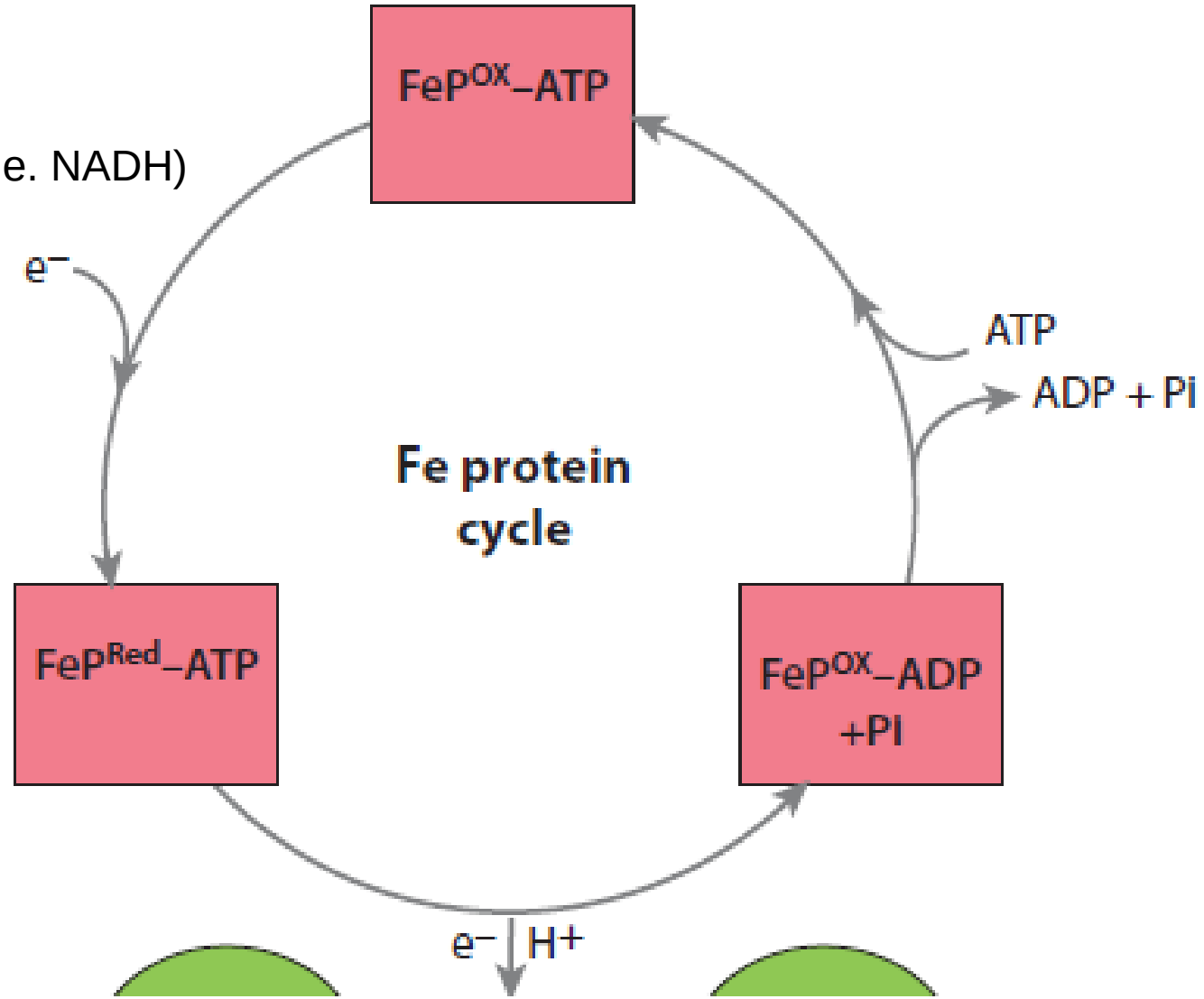
220 kDa

Nitrogenasi

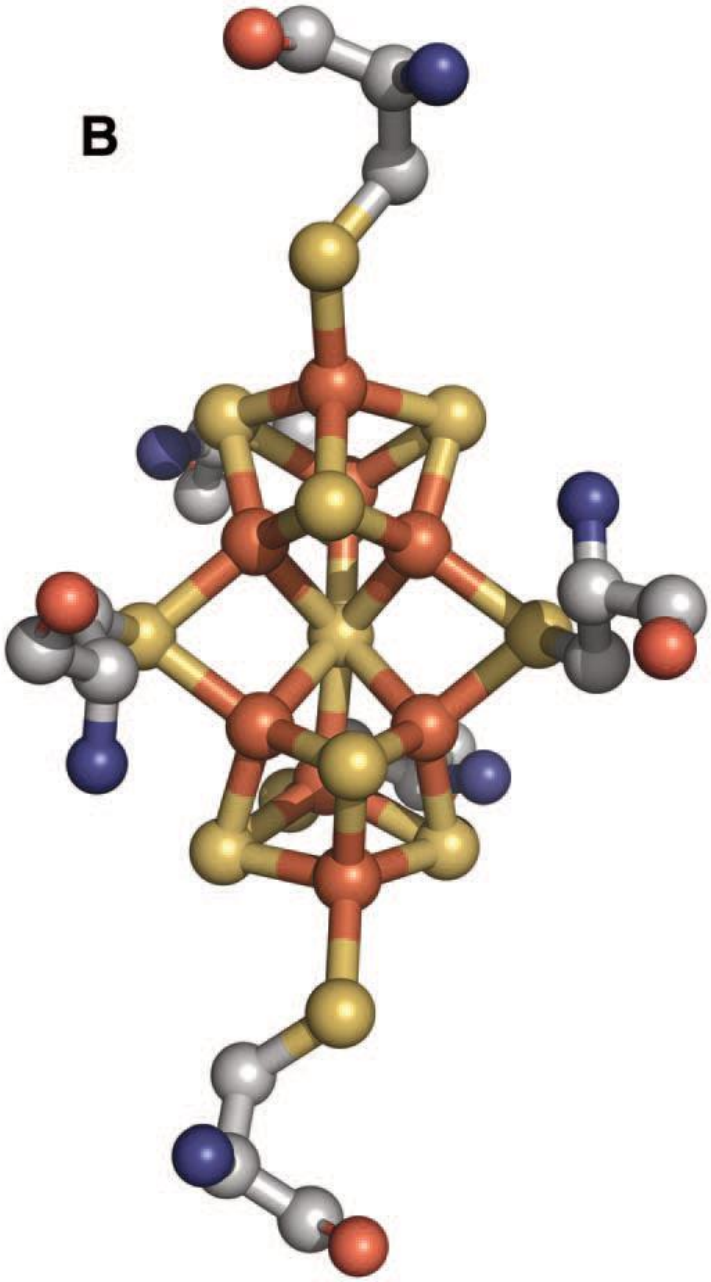


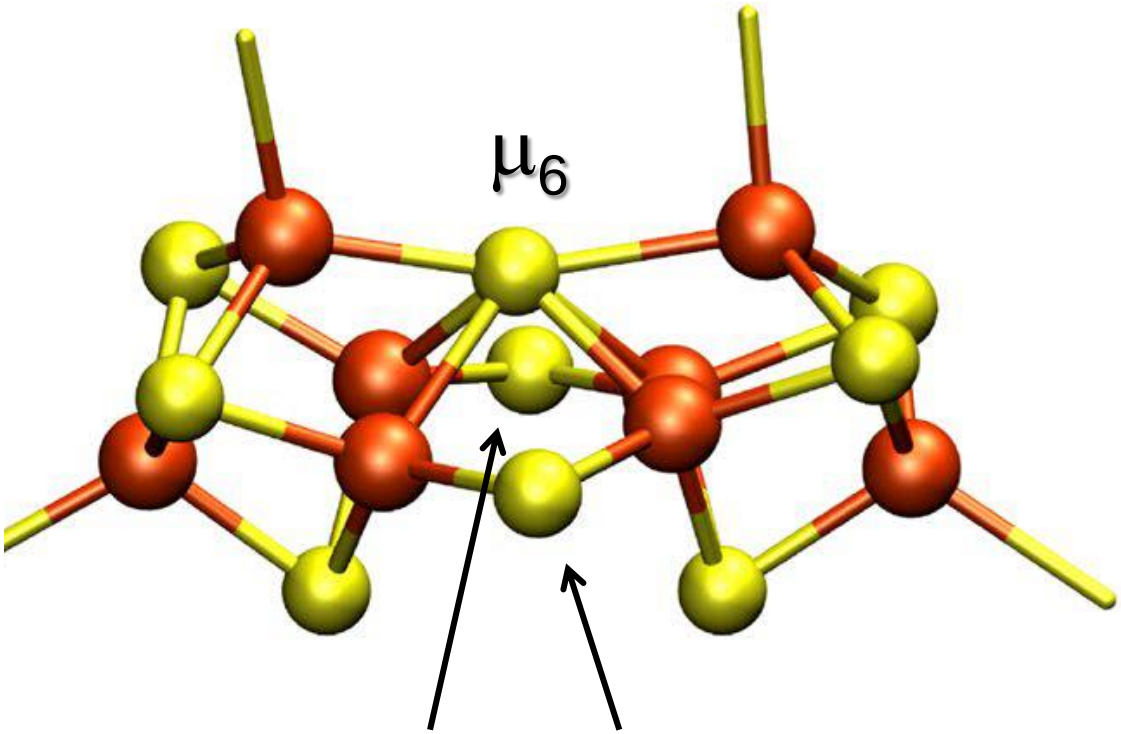
Fe-proteina

ferridossina o
flavodossina (i.e. NADH)

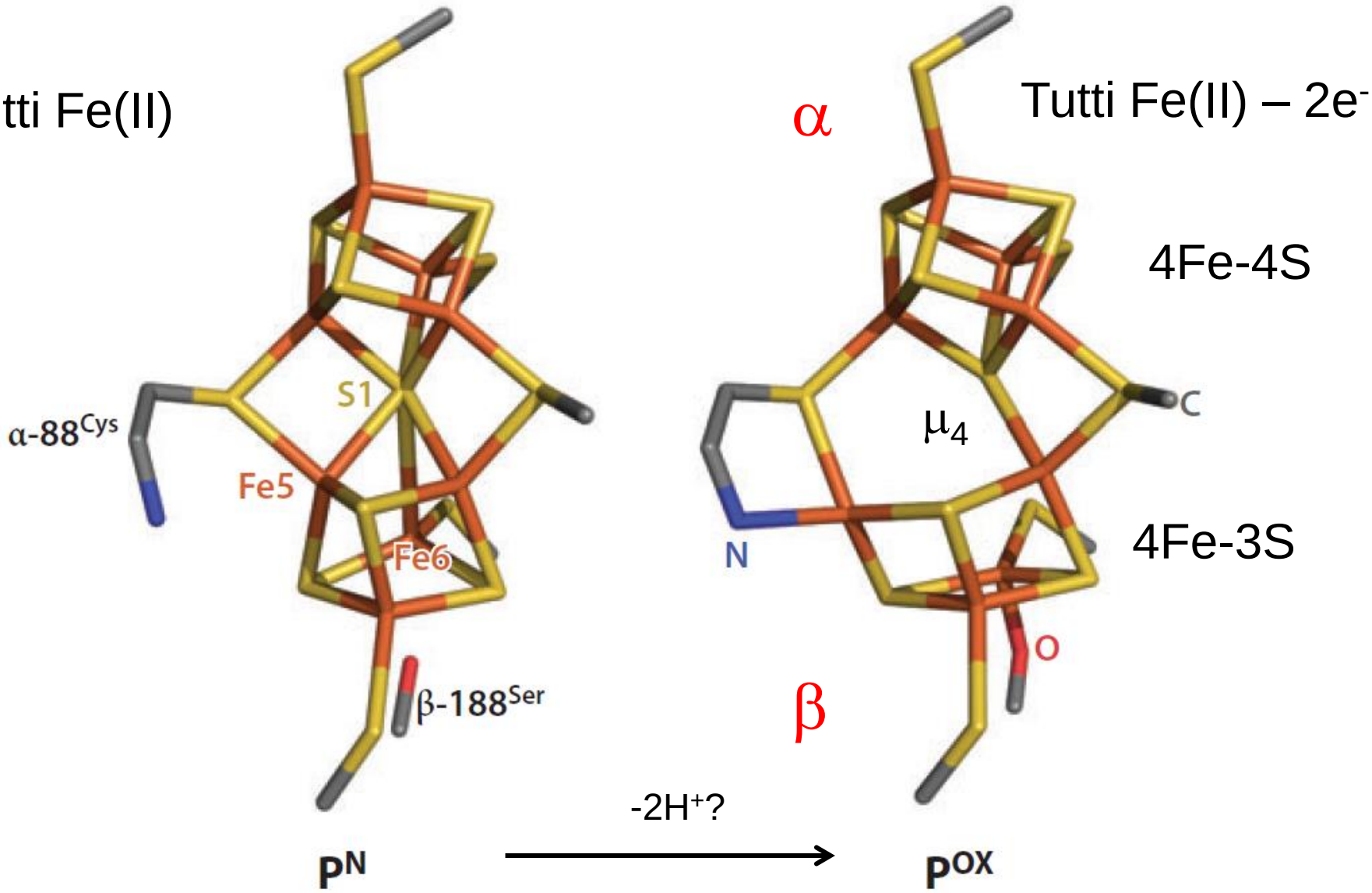


P-cluster 8Fe-7S



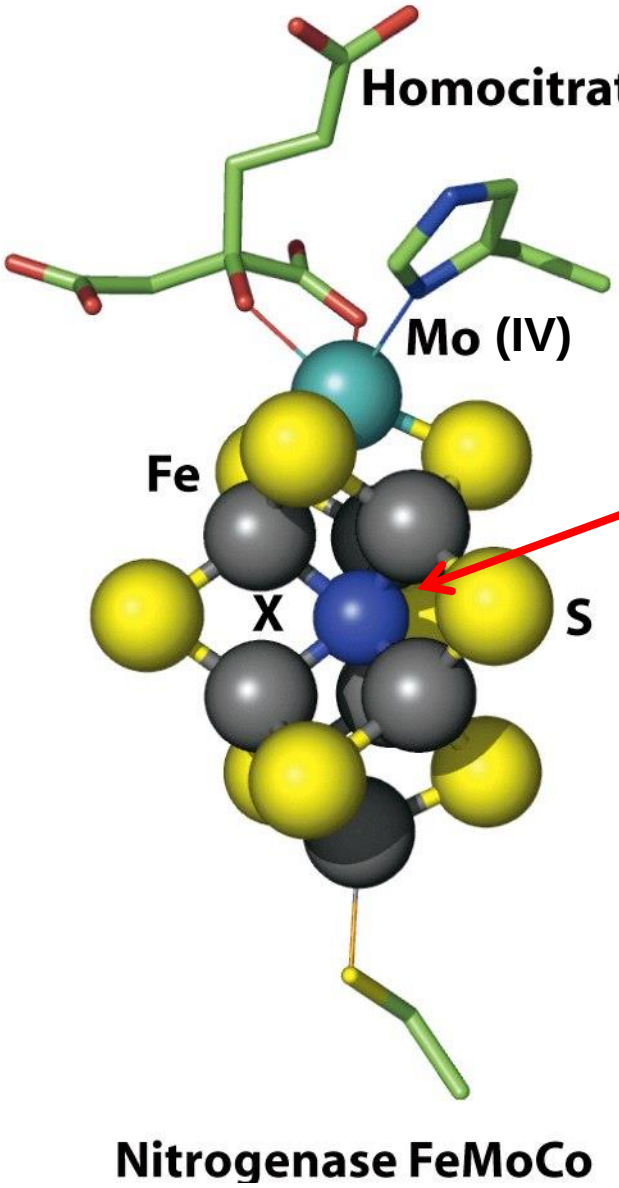


P-cluster 8Fe-7S



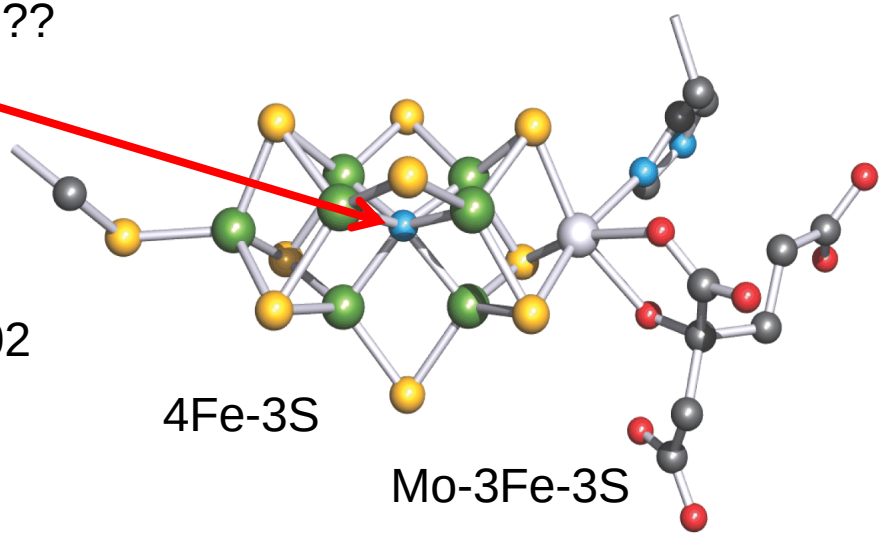
Cofattore FeMo

7Fe-9S-Mo-omocitrato



X = C, N, O??

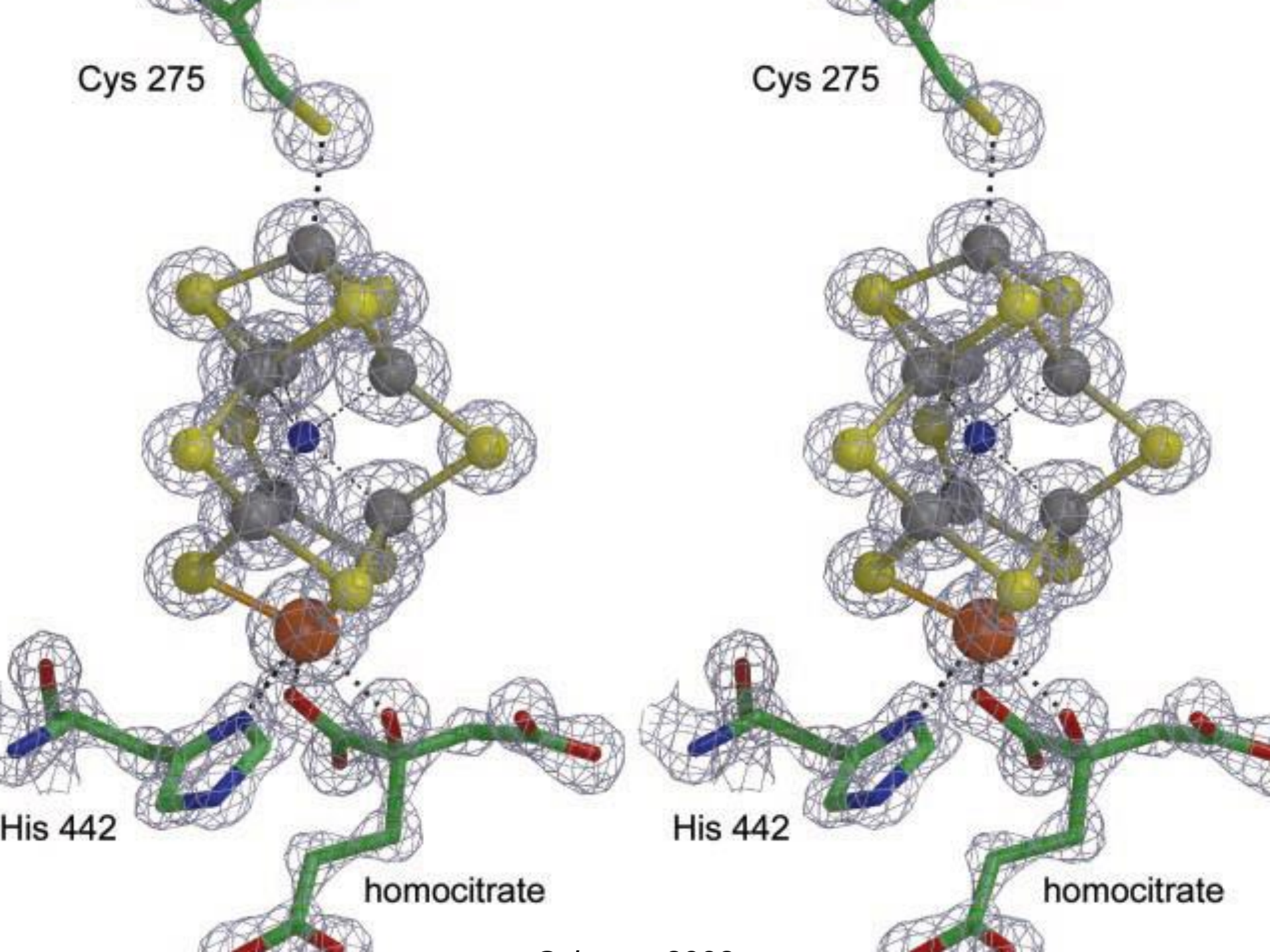
Science, 2002



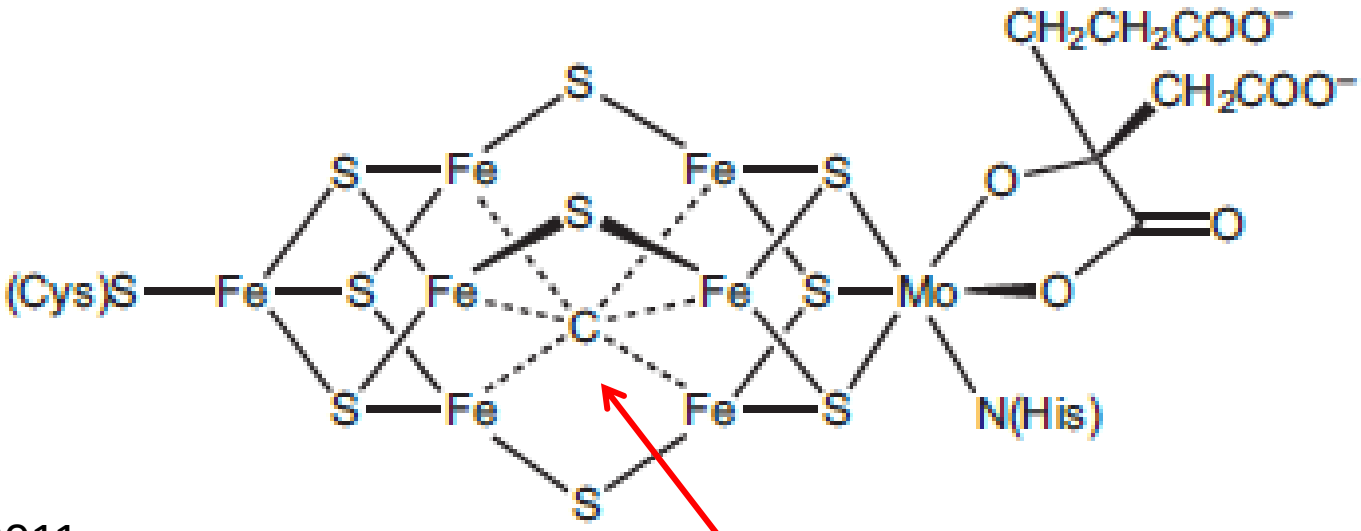
4Fe-3S

Mo-3Fe-3S

Tutto in α

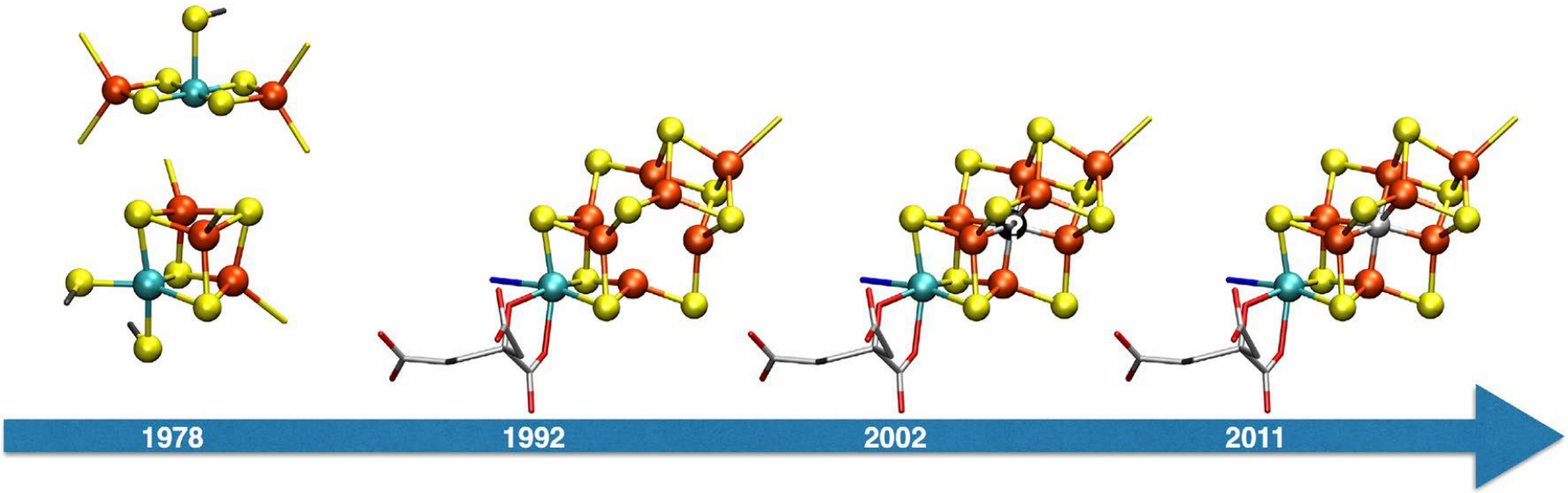

Cys 275
His 442
homocitrate
Cys 275
His 442
homocitrate

X = C

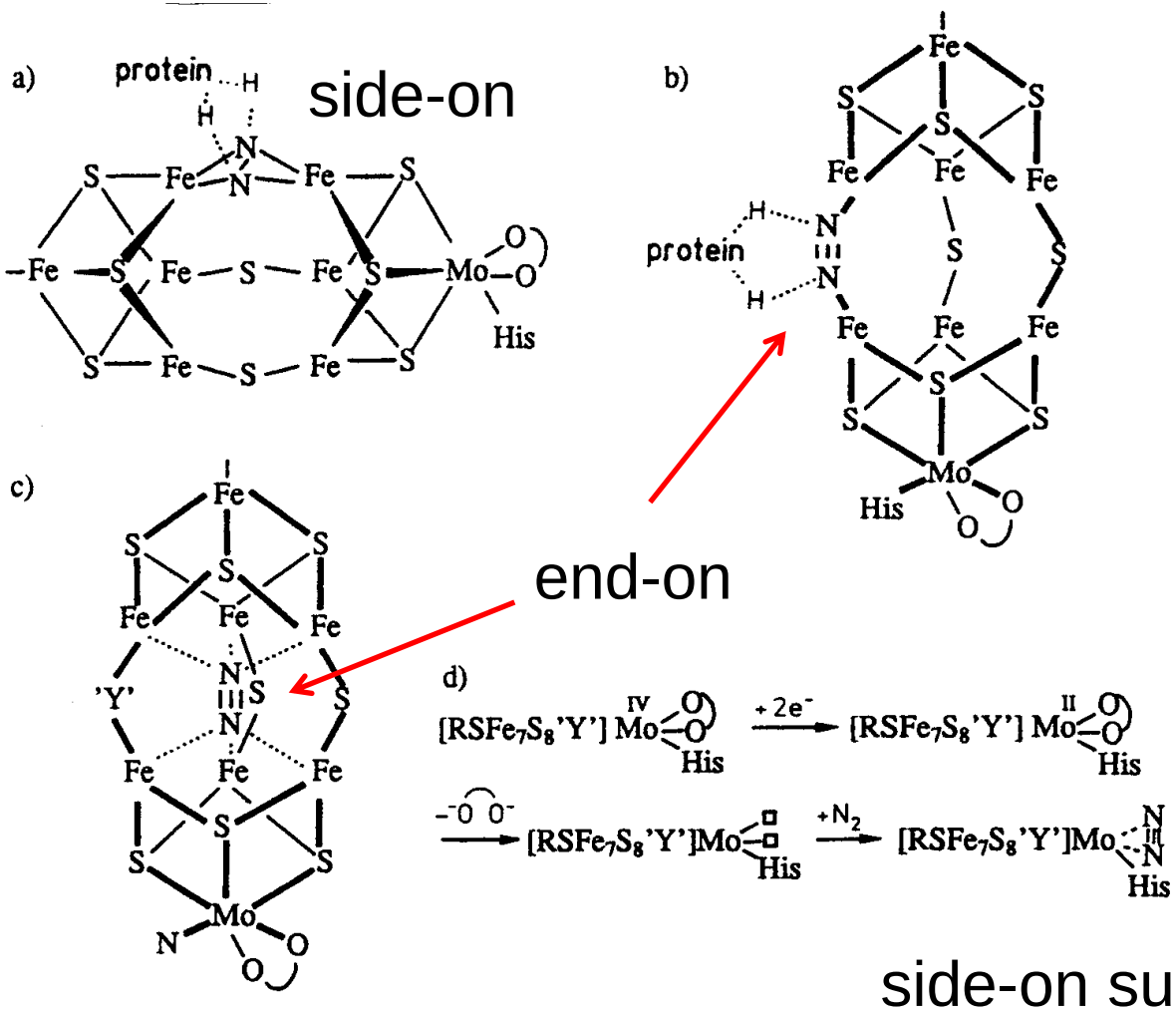


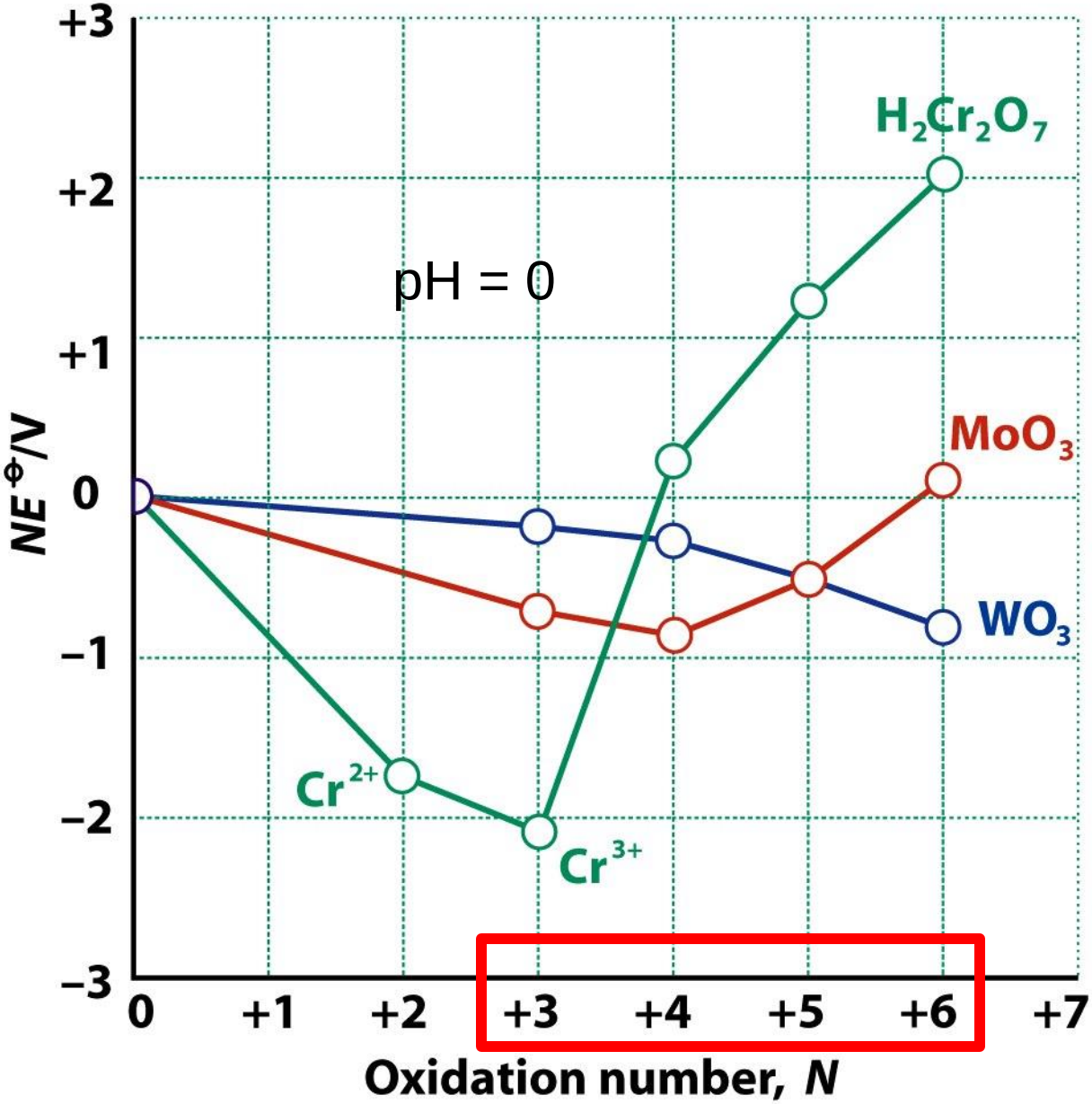
Science, 2011

Carburo, C^{4-}



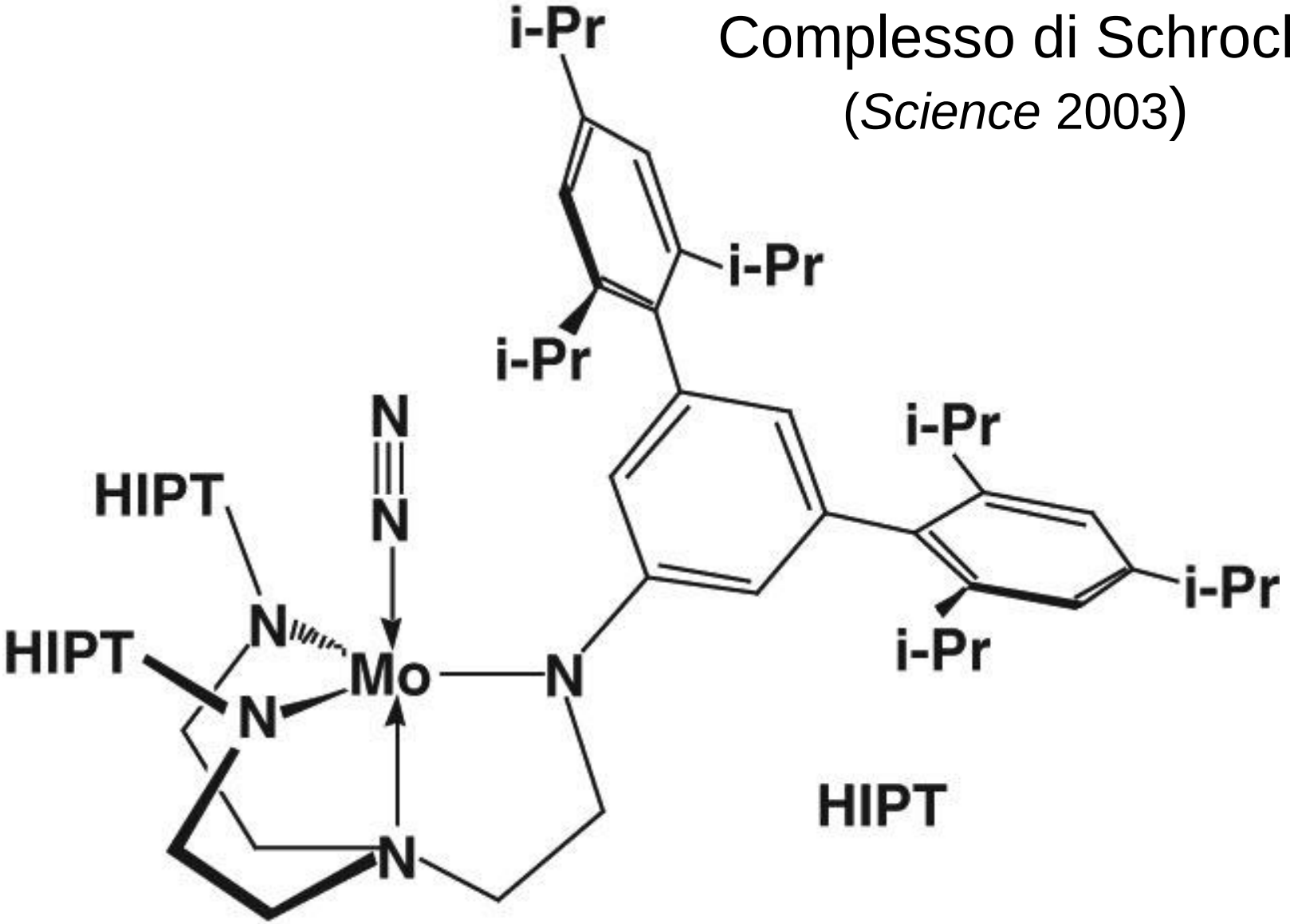
Ipotetici modi di coordinazione di N_2 al FeMoco



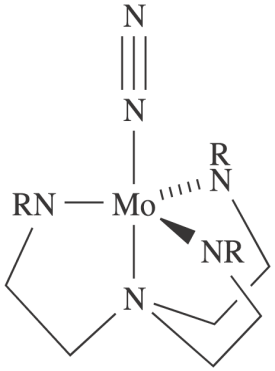

+3
+2
+1
0
−1
−2
−3
$NE^{\ominus}/V$
pH = 0
$H_2Cr_2O_7$
MoO_3
WO_3
Cr^{2+}
Cr^{3+}
0
+1
+2
+3
+4
+5
+6
+7
Oxidation number, *N*

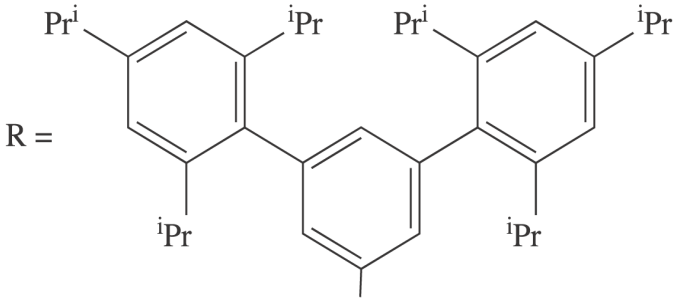
Complesso di Schrock

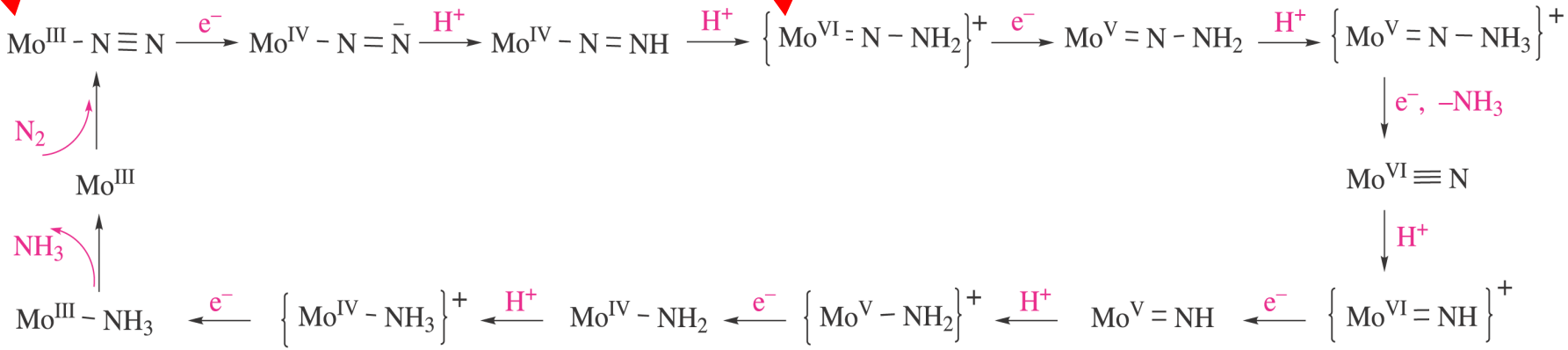
(*Science* 2003)



Schema della riduzione catalitica di N_2 a NH_3 su Mo

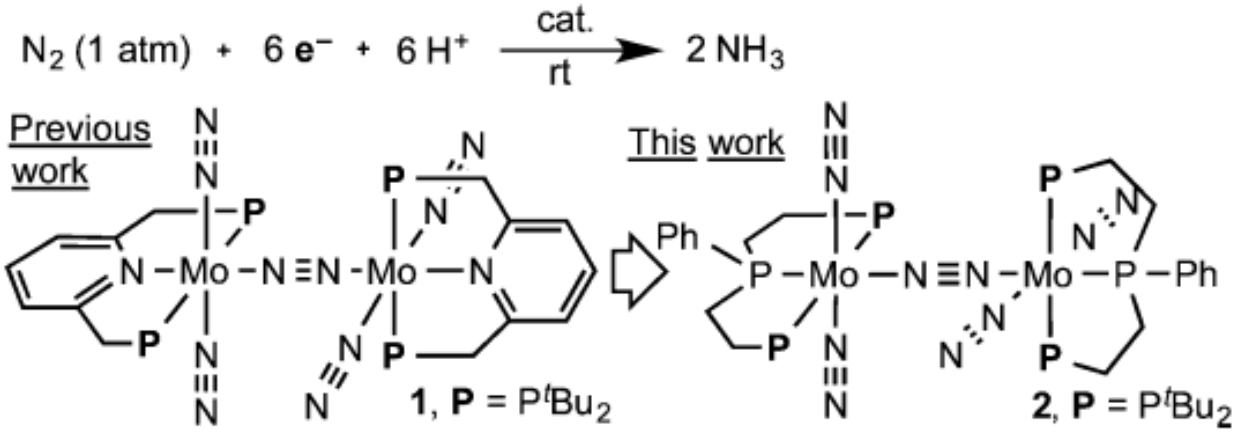




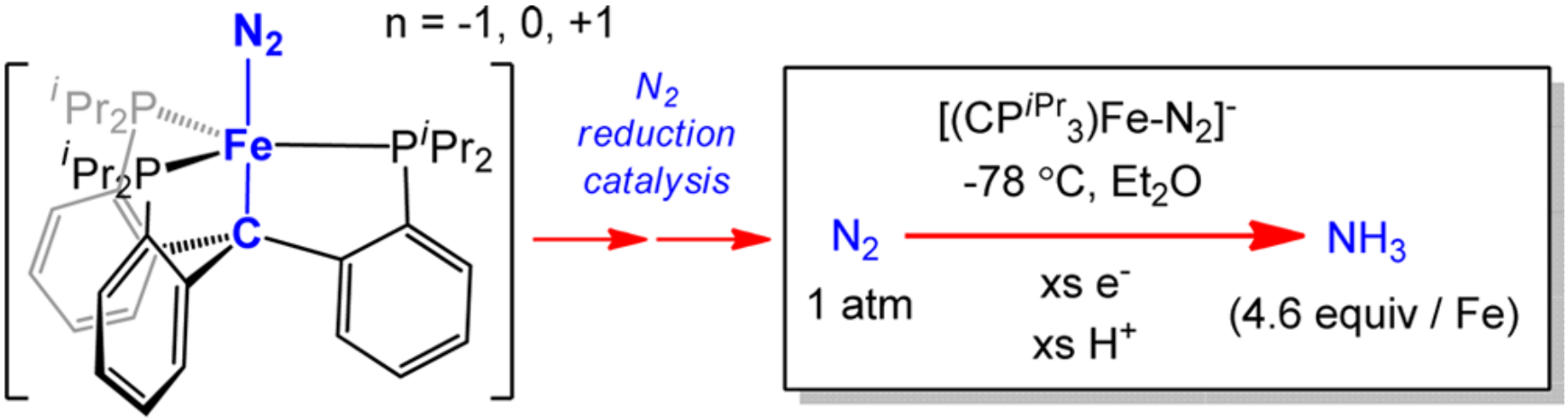


8 cicli catalitici, meccanismo *distale*

Complessi di Nishibayashi (2011 e 2015)
26 cicli catalitici, riducente $CoCp^*_2$



Complesso di Peters (2014)
4.6 cicli catalitici, riducente K



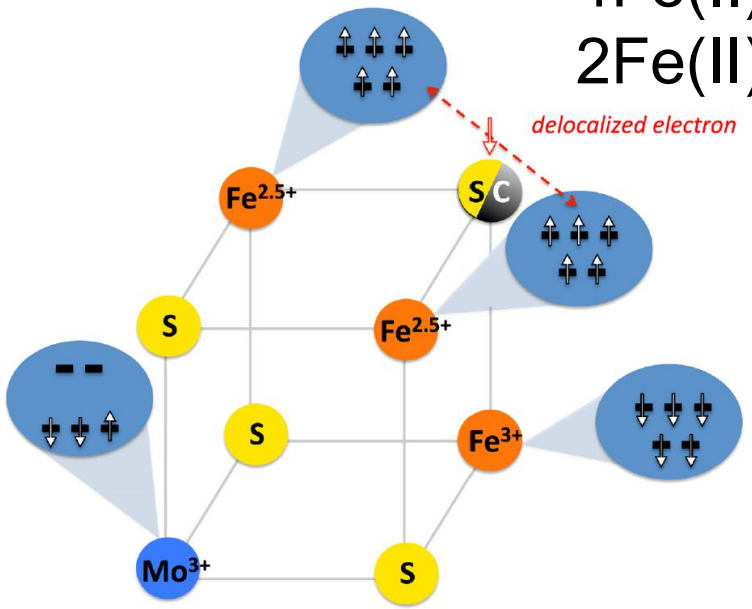
Struttura elettronica di FeMo-co

Resting state: *S* = 3/2

1) $[MoFe_7S_9C]^{3-}$ 6Fe(II)1Fe(III)Mo(IV)
2) $[MoFe_7S_9C]^{1-}$ 4Fe(II)3Fe(III)Mo(IV) Mo(IV), d^2 $S = 0$
3) $[MoFe_7S_9C]^{1+}$ 2Fe(II)5Fe(III)Mo(IV)

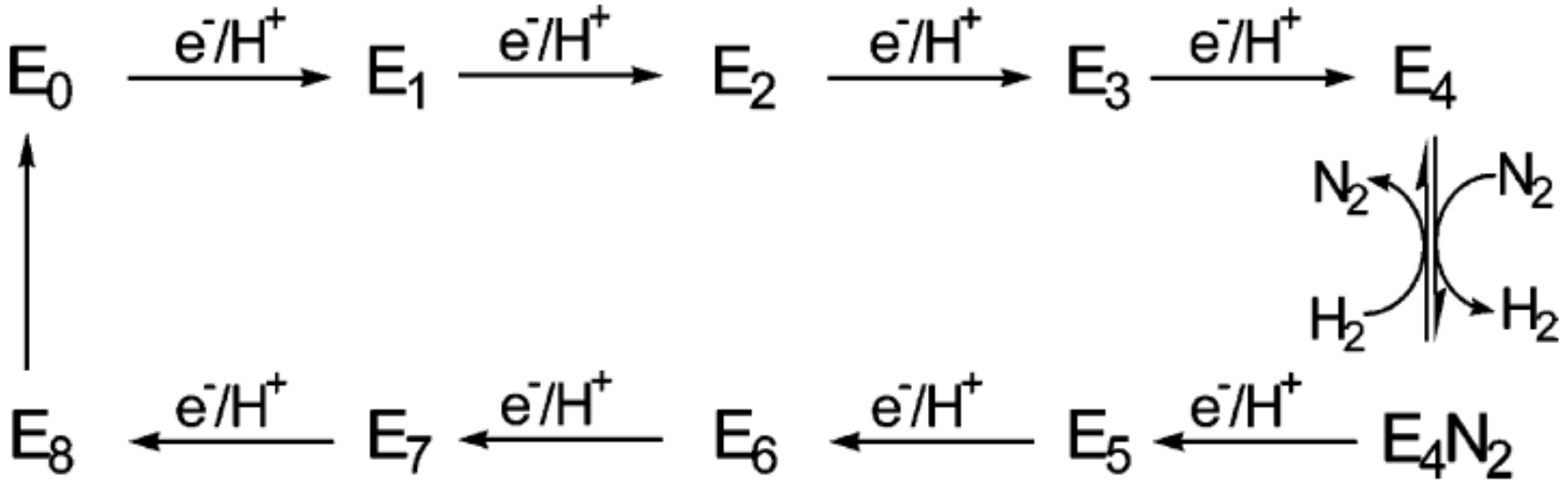
2014: Mo(III), d^3 basso spin (↑↑↓)? (violazione della regola di Hund)

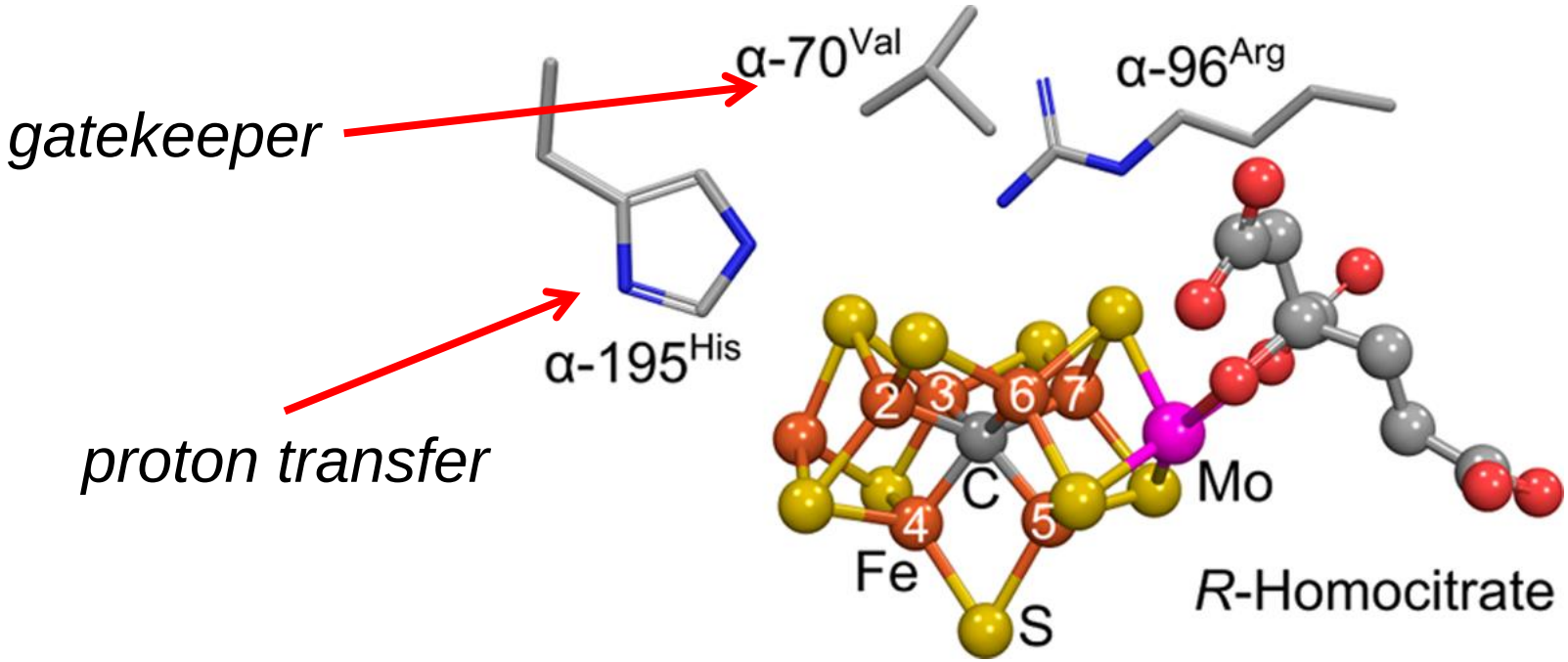
6Fe(II)1FeIII)Mo(IV) → 5Fe(II)2Fe(III)Mo(III)
4Fe(II)3Fe(III)Mo(IV) → 3Fe(II)4Fe(III)Mo(III)
2Fe(II)5Fe(III)Mo(IV) → 1Fe(II)6Fe(III)Mo(III)

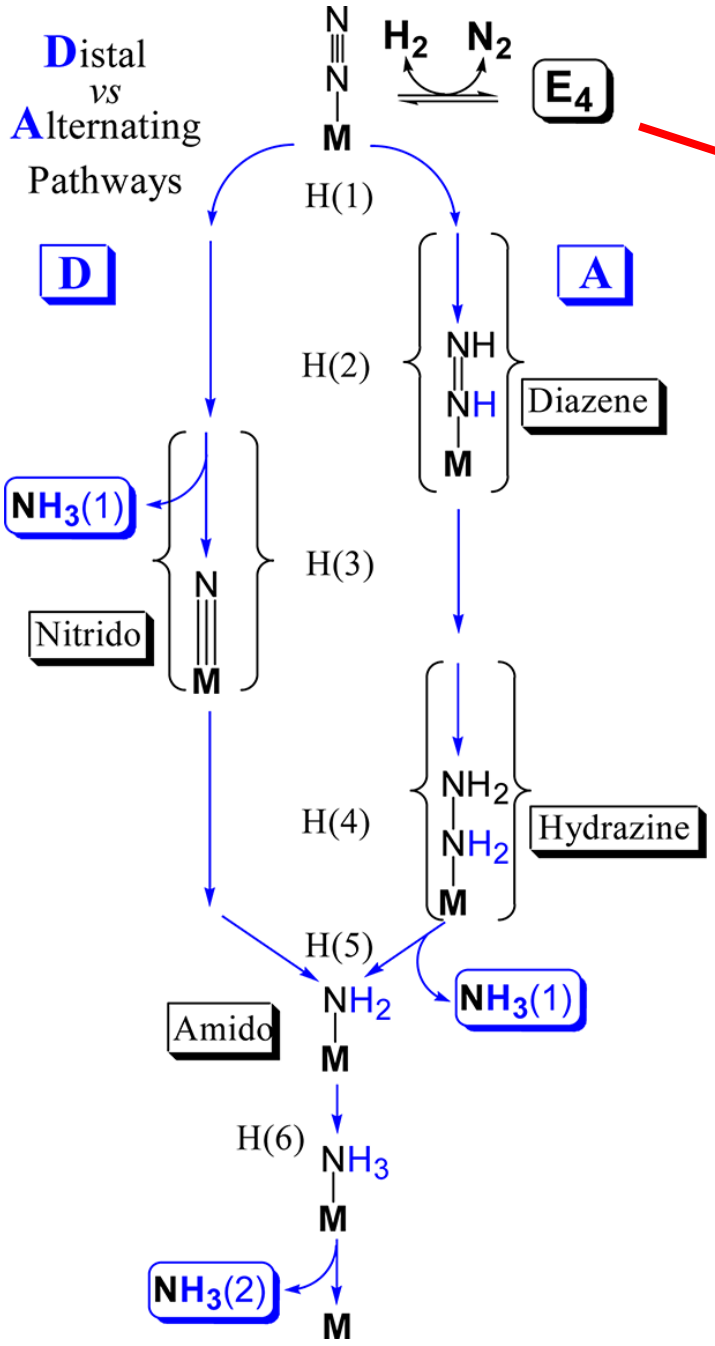


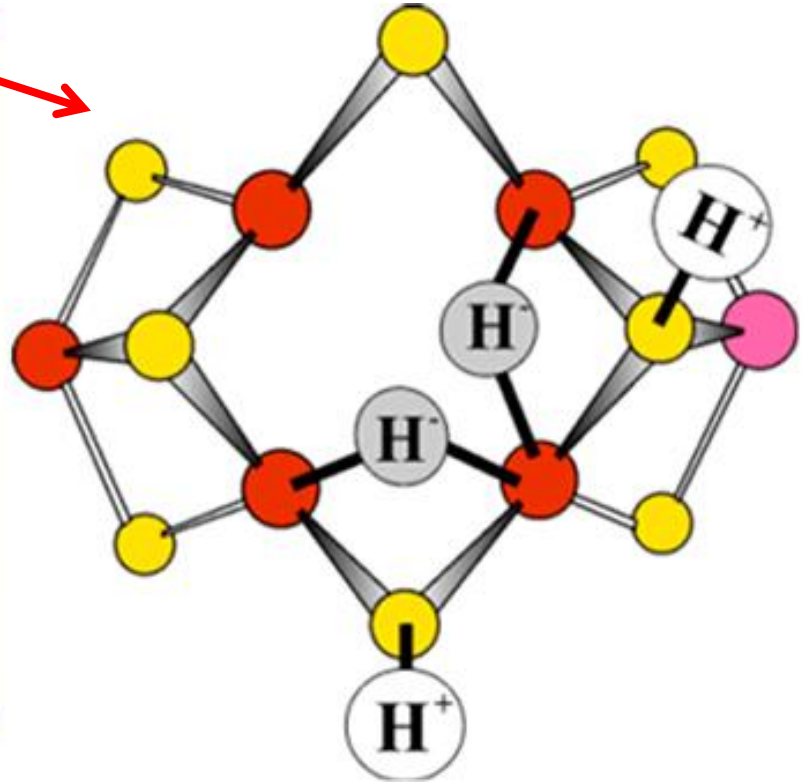
Cluster modello $[MoFe_3S_3C]^{1+}$ e $[MoFe_3S_4]^{3+}$

Ciclo catalitico

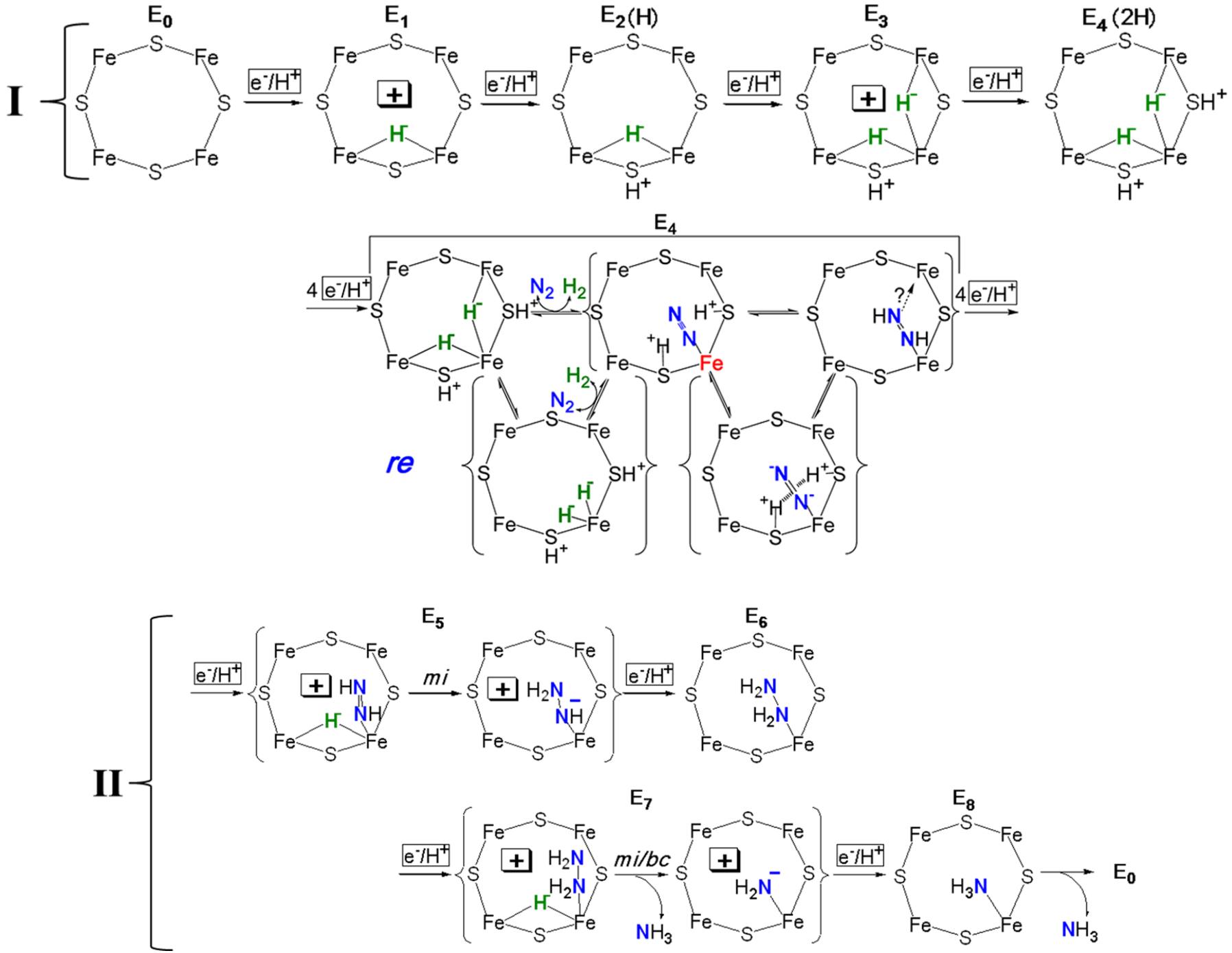


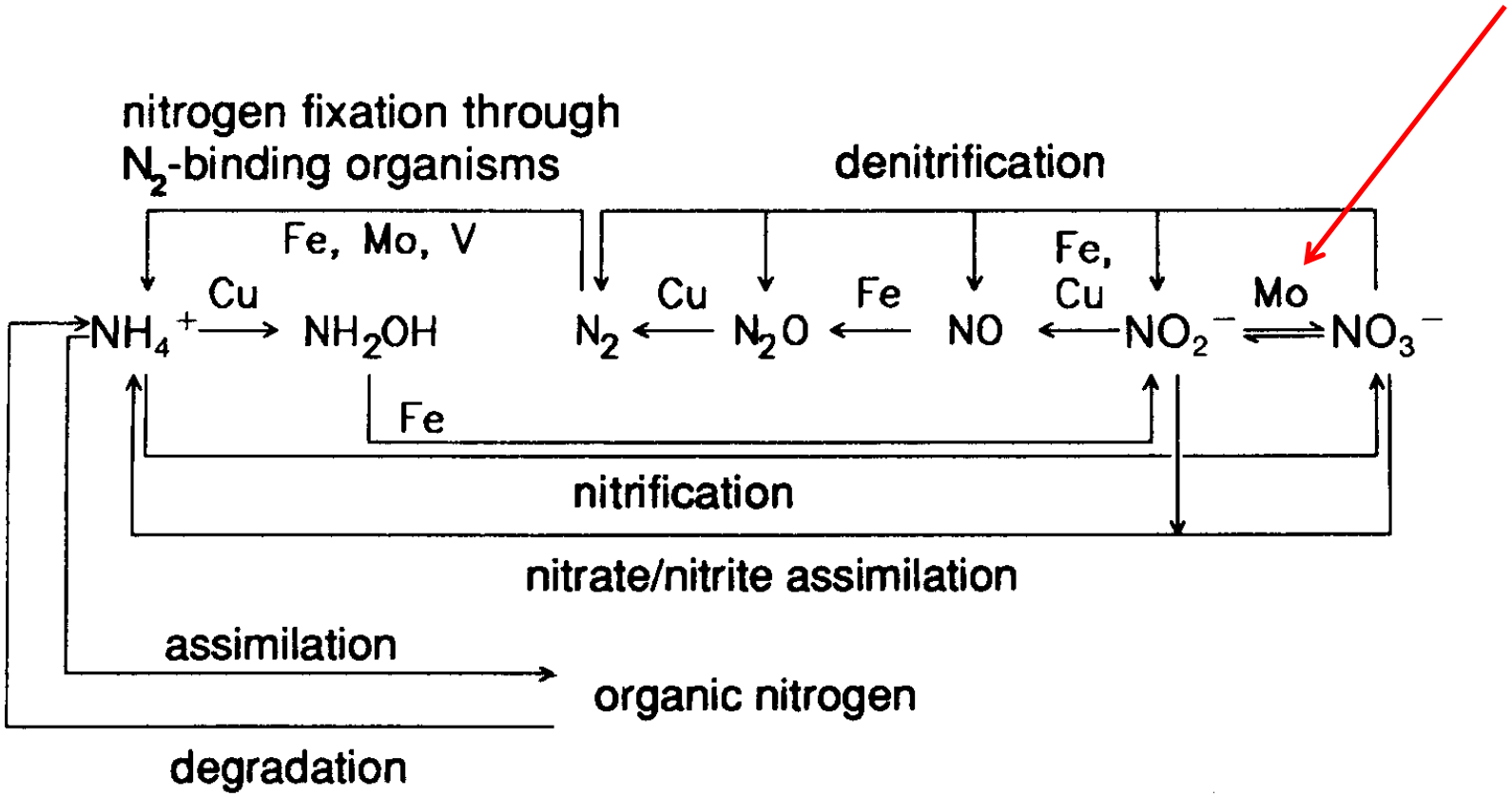






I primi 4 elettroni si accumulano sugli idruri e non sugli atomi di ferro

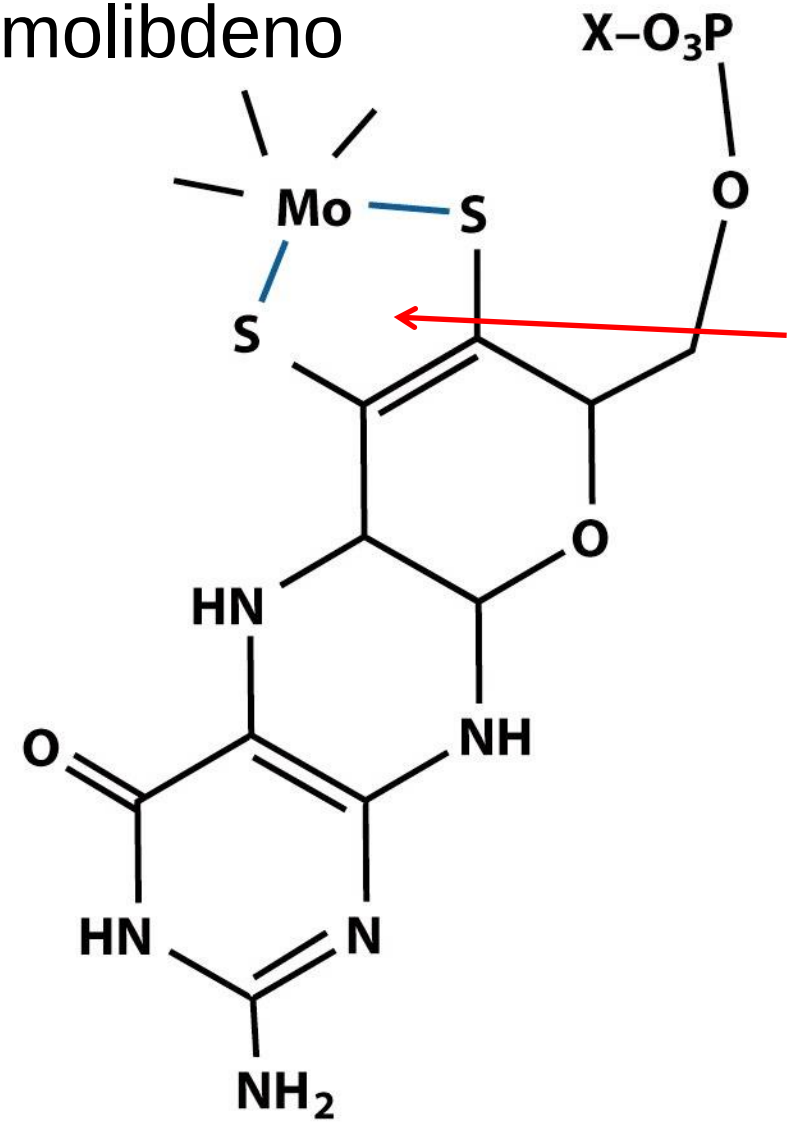

I
E0
E1
E2(H)
E3
E4 (2H)
e-/H+
E4
4 e-/H+
re
II
E5
E6
E7
E8
mi
mi/bc
NH3
E0

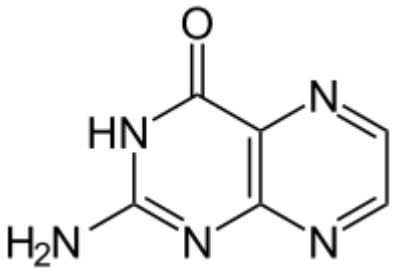


Tre famiglie di enzimi al Mo (*osso-trasferasi*)

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

Cofattore del molibdeno

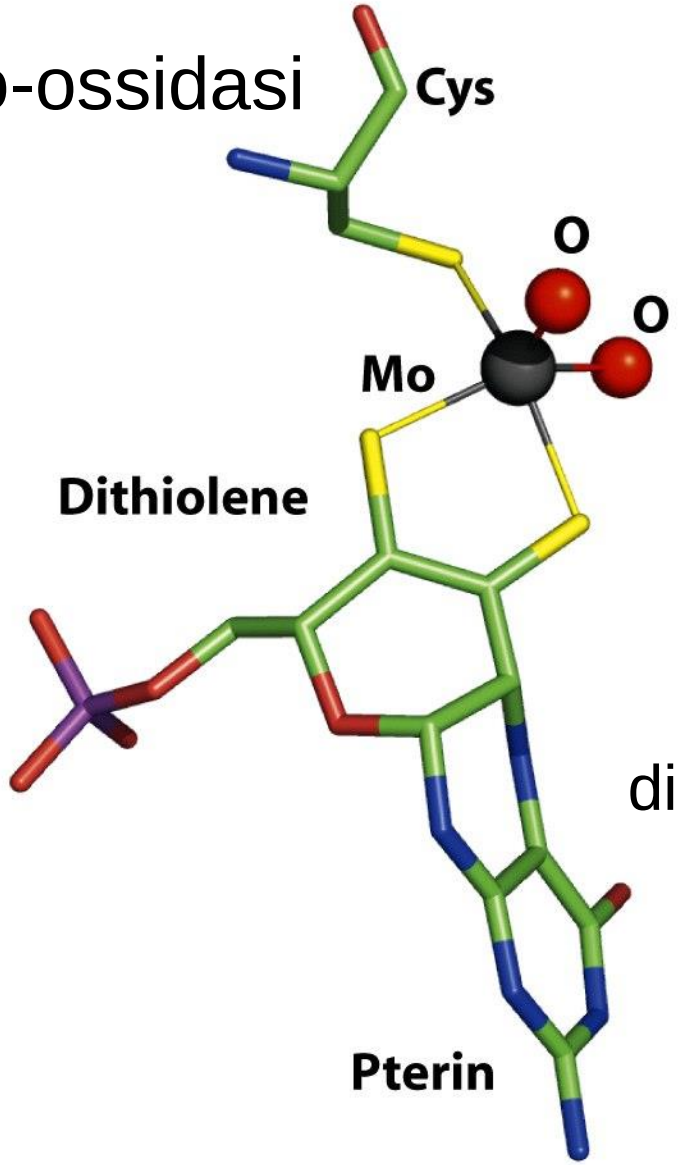




pterina

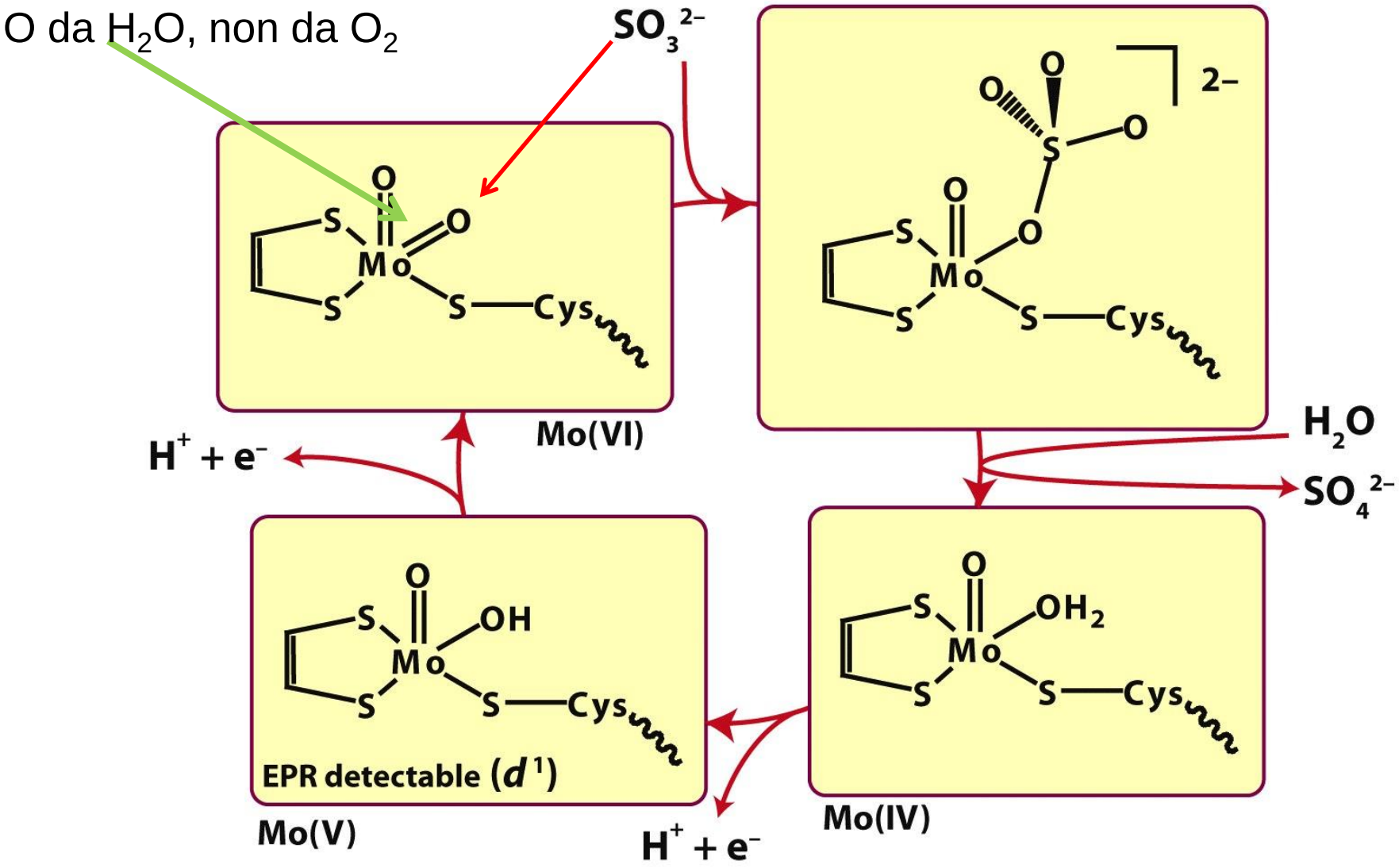
Molybdopterin as ligand

Sito della solfito-ossidasi

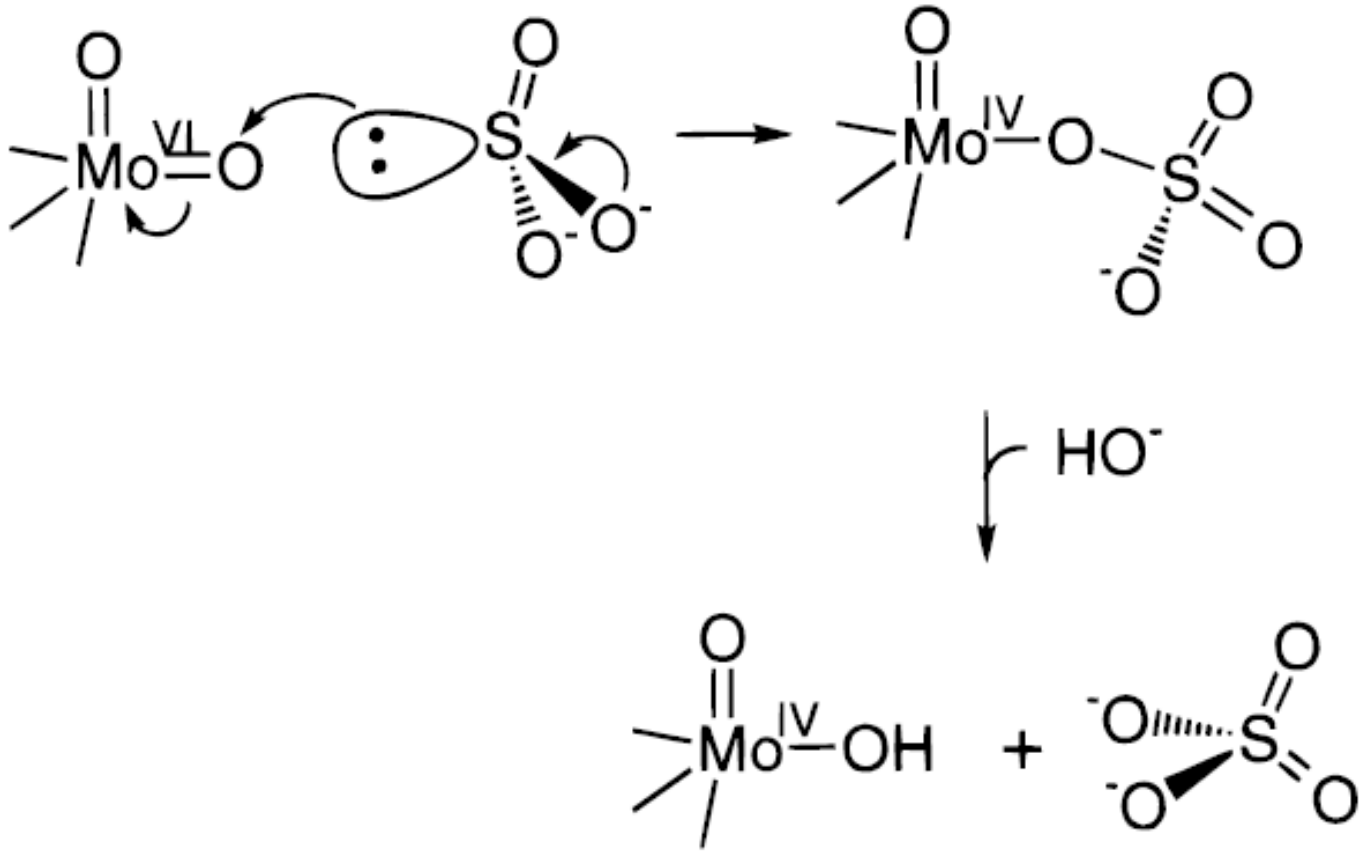


diidro-pterina

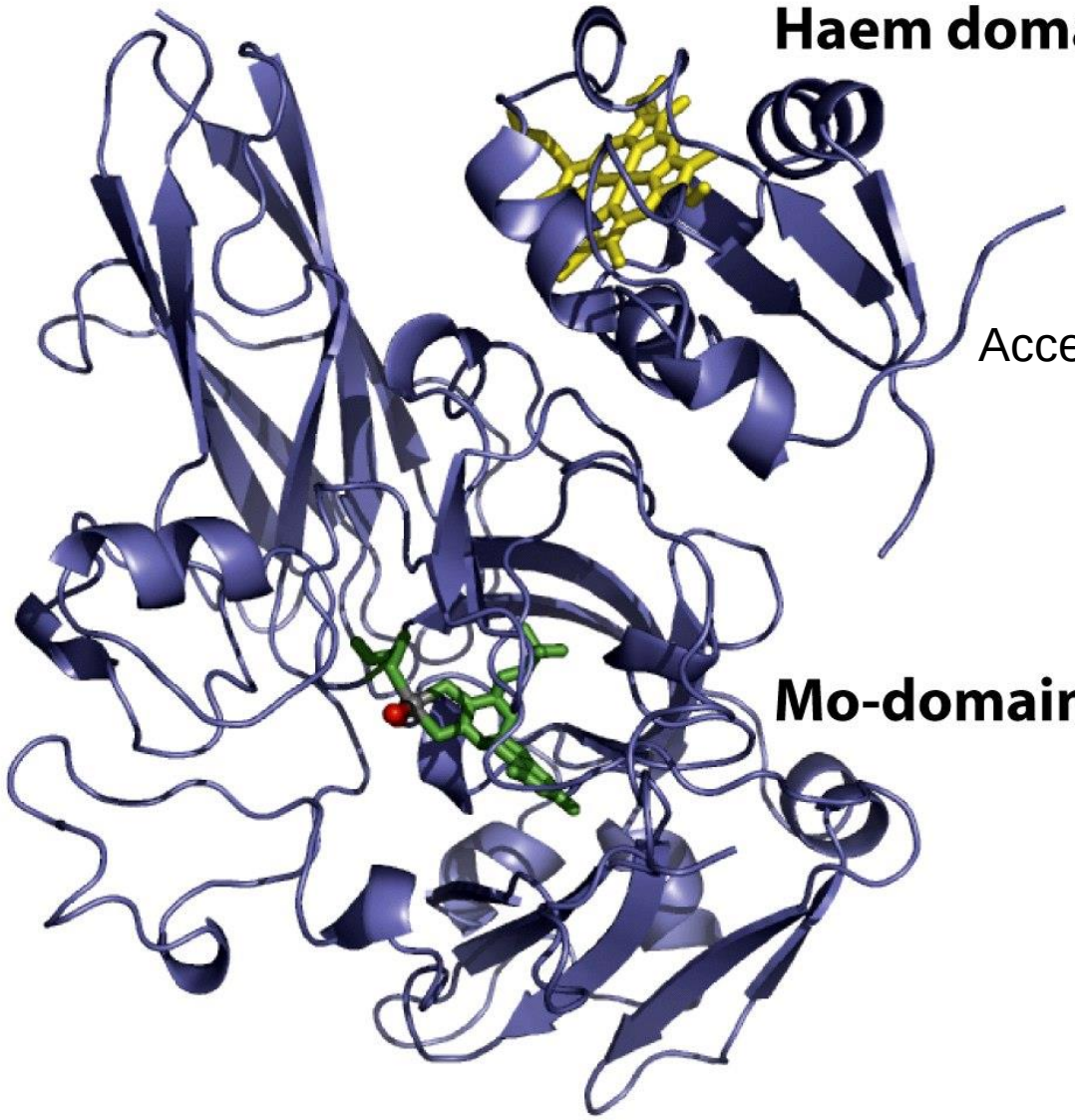
Ciclo catalitico della solfito-ossidasi



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

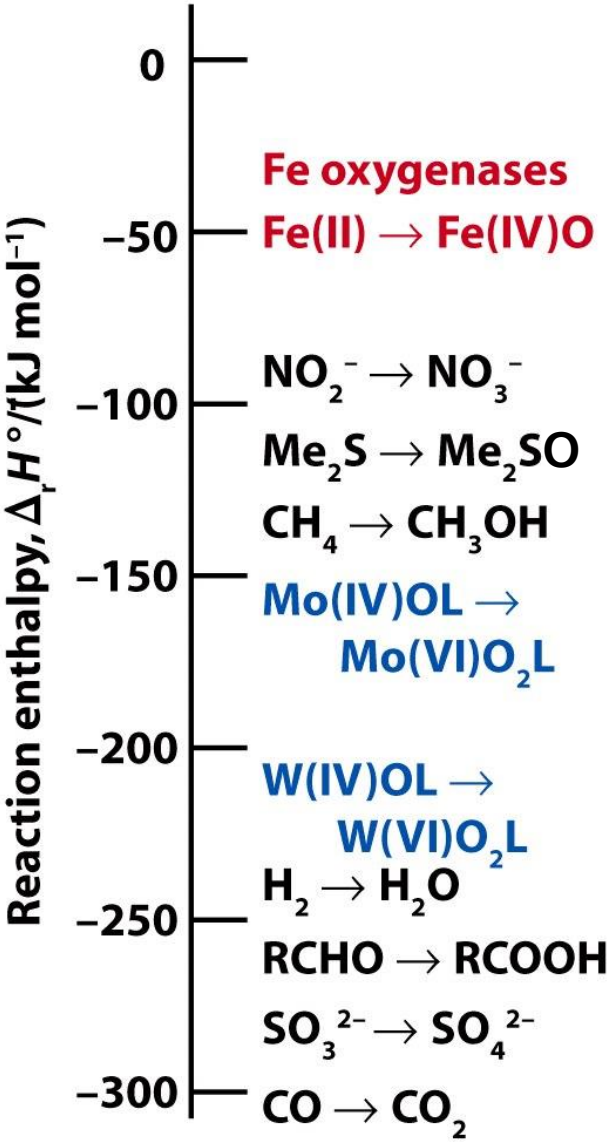

O
Mo
VI
O
S
O
O
O
Mo
IV
O
S
O
O
O
HO-
O
Mo
IV
OH
+
O
S
O
O
O

Struttura della solfito-ossidasi



Accettore di elettroni dal Mo

Scala di entalpia delle reazioni di trasferimento di atomi di ossigeno



osso-ferrile