# Diferrous Structural and Functional Models of the Iron-only Hydrogenases

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The Fe-only hydrogenases catalyze the interconversion between protons and dihydrogen. The H_2-binding center (H-cluster) in the Fe-only hydrogenases[1-5] adopts a face-shared bi-octahedral structure (Figure 1). The entire complement of ancillary ligands are unusual in the biological context.[6] Cyanide and CO are rarely observed in Nature, although they are also found in the NiFe hydrogenases.[7] Other unusual features include the dithiolate cofactor, the sulfur atoms of which bridge the iron atoms,[5, 8] and an $Fe_4S_4(SCys)_4$ cluster that is linked to the active site via a cysteinyl thiolate bridge. The oxidized, active form (H_{ox}, see below) of the binuclear active site can be described as $[Fe_2[(SCH_2)_2X](CN)_2(\mu\text{-}CO)(CO)_2(SR_2)(L)]^z$, where SR_2 represents the thiolato-bridged Fe_4S_4 ligand, X is speculated to be NH, and L is the H_x-binding site (x = 1, 2) that can also be occupied by CO (H_{ox}^{CO}) or possibly H_2O.[1, 9]
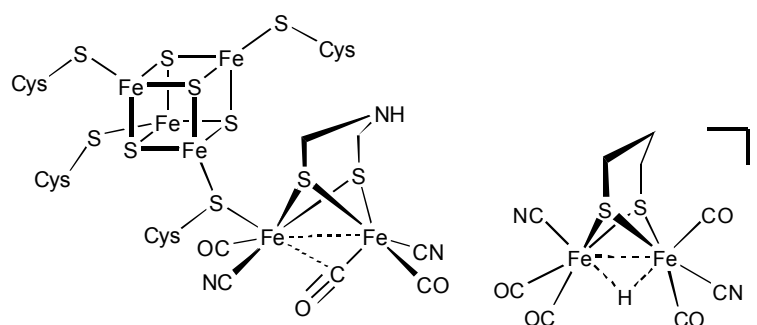

Figure 1. Hydrogenase active site, H_{red}(left) and $[HFe_2(S_2C_3H_6)(CN)_2(CO)_4]^-$ (right).

Oxidations of sub-ferrous compounds afford a new family of diferrous dithiolates. Low temperature oxidation of $Fe_2(S_2C_nH_{2n})(CNMe)_{6-x}(CO)_x$ (n = 2, 3; x = 2, 3) affords a family of mixed carbonyl-isocyanides of the type $[Fe_2(S_2C_nH_{2n})(CO)_x(CNMe)_{7-x}]^{2+}$.[10] The degree of substitution is controlled by the RNC/Fe ratio as well as the degree of initial substitution at iron, with tricarbonyl derivatives favoring more highly carbonylated products. The structures of the monocarbonyl derivatives $[Fe_2(S_2C_nH_{2n})(\mu\text{-}CO)(CNMe)_6](PF_6)_2$ (n = 2, 3) established crystallographically and spectroscopically, are quite similar, with Fe---Fe distances of ca. 2.5 Å, although the μ-CO is unsymmetrical in the propanedithiolate derivative. In the dicarbonyl species, $[Fe_2(S_2C_2H_4)(\mu\text{-}CO)(CO)(CNMe)_5](PF_6)_2$, the terminal CO ligand is situated at one of the basal sites, not trans to the Fe---Fe vector.

Oxidation of $(Et_4N)_2[Fe_2(S_2C_2H_4)(CN)_2(CO)_4]$ in the presence of cyanide and tertiary phosphines and of $Fe_2(S_2C_2H_4)(PMe_3)_2(CO)_4$ in the presence of cyanide affords a series of diferrous cyanide derivatives (Scheme 1)[11] that bear a stoichiometric, structural, and electronic relationship to the H_{ox}^{air} state of the Fe-only hydrogenases. With PPh3 as the trapping ligand, we obtained an unsymmetrical isomer of $Fe_2(S_2C_2H_4)(\mu\text{-}CO)(CN)_2(PPh_3)_2(CO)_2$, which was confirmed crystallographically. This diferrous cyanide features the *semi*bridging CO ligand with

Fe-μC bond lengths of 2.15 and 1.85 Å. Four isomers of $Fe_2(S_2C_2H_4)(\mu\text{-}CO)(CN)_2(PMe_3)_2(CO)_2$ were observed, the initial product again being unsymmetrical but more stable isomers are symmetrical. DFT calculations confirm that the most stable isomers of $Fe_2(S_2C_2H_4)(\mu\text{-}CO)(CN)_2(PMe_3)_2(CO)_2$ have cyanide trans to μ-CO. Oxidative decarbonylation also afforded the new tetracyanide $[Fe_2(S_2C_2H_4)(\mu\text{-}CO)(CN)_4(CO)_2]^-$. Insights into the oxidative decarbonylation mechanism of these syntheses comes from the spectroscopic characterization of the tetracarbonyl $[Fe_2(S_2C_2H_4)(\mu\text{-}CO)(CN)_3(CO)_3]^-$. This species reacts with PEt_3 to produce the stable adduct $[Fe_2(S_2C_2H_4)(\mu\text{-}CO)(CN)_3(CO)_2(PEt_3)]^-$.
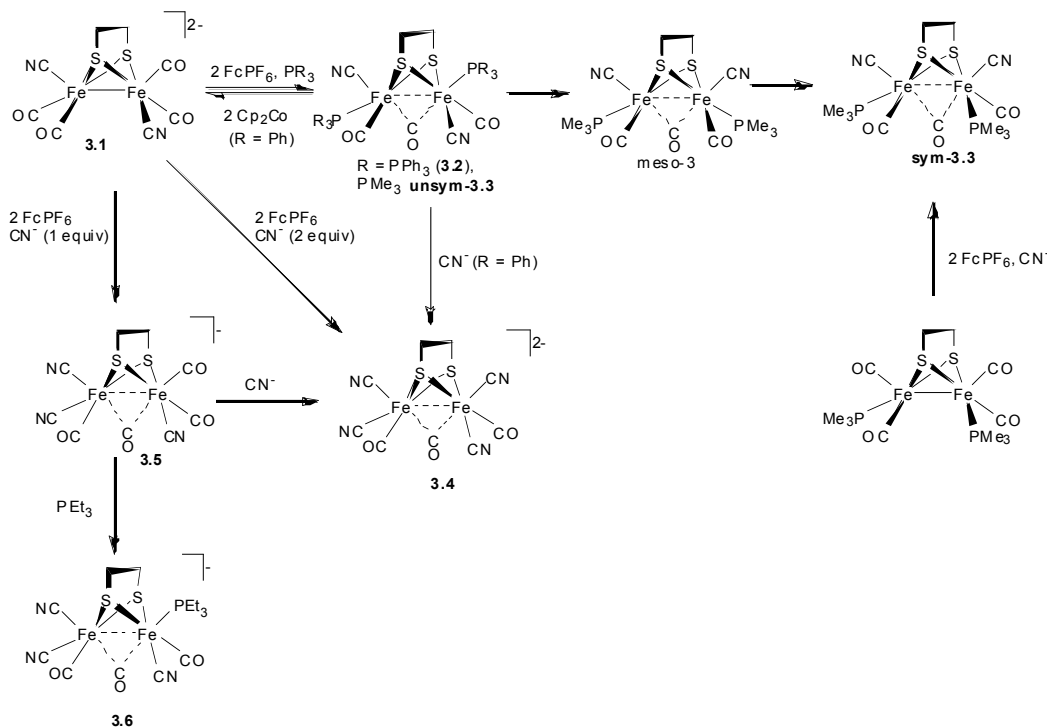
Scheme 1. Oxidative decarbonylation methodology for $(Et_4N)_2[Fe_2(S_2C_2H_4)(CN)_2(CO)_4]$.

The protonation of $(Et_4N)_2[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]$ has been further characterized. Low temperature IR spectroscopic studies show that the protonation of $(Et_4N)_2[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]$ with HOTs gave $Et_4N[Fe_2(S_2C_3H_6)(CN)(CNH)(CO)_4]$. The species, $Et_4N[Fe_2(S_2C_3H_6)(CN)(CNH)(CO)_4]$, undergoes an approximate first-order decay to the hydride $Et_4N[HFe_2(S_2C_3H_6)(CN)_2(CO)_4]$ (Figure 1). Addition of a second equiv of H^+ to $Et_4N[HFe_2(S_2C_3H_6)(CN)_2(CO)_4]$ resulted in protonation at the CN^- ligand to give $[HFe_2(S_2C_3H_6)(CN)(CNH)(CO)_4]$. $[HFe_2(S_2C_3H_6)(CN)(CNH)(CO)_4]$ was shown to catalyze the reduction of protons at -1.5 V vs Ag/AgCl. Decarbonylation of $Et_4N[HFe_2(S_2C_3H_6)(CN)_2(CO)_4]$ in the presence of PPh_3 resulted in $Et_4N[HFe_2(S_2C_3H_6)(CN)_2(CO)_3(PPh_3)]$ followed by $Et_4N[HFe_2(S_2C_3H_6)(CN)_2(CO)_2(PPh_3)_2]$, which exist as multiple isomers. MeCN solutions of $Et_4N[HFe_2(S_2C_3H_6)(CN)_2(CO)_4]$ in the absence of PPh_3 gave the solvolysis product, $Et_4N[HFe_2(S_2C_3H_6)(CN)_2(MeCN)(CO)_3]$ which reacts with PMe_3 and CN^- to produce $Et_4N[HFe_2(S_2C_3H_6)(CN)_2(PMe_3)(CO)_3]$ and $(Et_4N)_2[HFe_2(S_2C_3H_6)(CN)_3(CO)_3]$, respectively.

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