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Biomimetic Hydrogen Evolution Catalyzed by an Iron Carbonyl Thiolate

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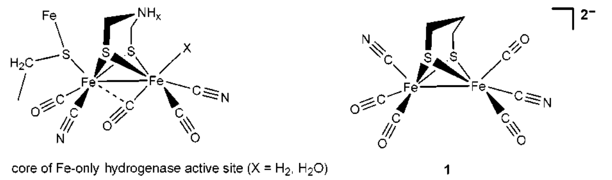
Homogeneous catalysts for proton reduction[1] are of interest because they are amenable to systematic manipulation, and they represent viable precursors to tailored heterogeneous catalysts, including those using more economically attractive base metals such as Fe. Hydrogenase enzymes represent a structurally unusual but highly efficient hydrogen-processing catalysts that rely on base metals (Ni, Fe).[2] The structures of both major families of hydrogenase enzymes, the Fe-only and the NiFe hydrogenases, are known at high resolution.[3] The active site of the Fe-only hydrogenases consists of an $Fe_2(\mu\text{-}SR)_2(CN)_2(CO)_3L_n$ core (L = H_2O/H_2 and a thiolate-linked $Fe_4S_4(SR)_4$ cluster, Scheme 1).[4] This core shares key structural features with organometallic complexes $Fe_2(\mu\text{-}SR)_2(CO)_6$ that have been known since the 1920s.[5] So stable are the $Fe_2(\mu\text{-}SR)_2(CO)_6$ derivatives that such compounds form under harsh conditions (e.g., 50−200 MPa at 250 °C) from primitive reagents (FeS, RSH, HCO_2H).[6]

We have reported that model complex $\{Fe_2[\mu\text{-}S_2(CH_2)_3](CN)_2(CO)_4\}^{2-}$ (**1**, Scheme 1) reacts with protons to give substoichiometric amounts of dihydrogen.[7] Unfortunately acid also converts **1** (and related dianions) into insoluble and catalytically inactive polymeric derivatives of unknown structure. The unsuitability of **1** as a catalyst is attributable to its highly reducing character, supported by the aforementioned ability to reduce protons directly as well as by electrochemical measurements.[8] This logic led us to investigate the complex $\{Fe_2[\mu\text{-}S_2(CH_2)_3](CN)(CO)_4(PMe_3)\}^-$ (**2**) which is less reducing than **1**. As described below, **2** is an active catalyst for proton reduction, and as such provides the first functional link between organometallic models and the Fe-only hydrogenases.

In evaluating the catalysis, we first examined the protonation of **2**. Dark red $HFe_2[\mu\text{-}S_2(CH_2)_3](CN)(CO)_4(PMe_4)$ (**3**) precipitates in analytical purity from MeCN solutions of **2** upon addition of excess aqueous H_2SO_4 (see Scheme 2). The ^1H NMR spectrum of this species shows a ^{31}P-coupled doublet signal at $\delta = -17$ ($J_{H-P} = 23$ Hz), consistent with protonation of the Fe−Fe bond. Amine bases do not convert **3** into **2**, probably reflecting the kinetic inertness of the hydride.[9] Complexes of the type $HFe_2(\mu\text{-}SR)_2(CO)_{6-x}L_x^+$ were first described by Poilblanc without examination of their redox properties.[10] It is significant that protonation of **2** occurs at Fe, not the N of cyanide, as both are basic sites.[11] Further treatment of **3** with toluenesulfonic acid (HOTs) gave a new and relatively air-stable species that exhibits ν_{CO} bands ca. 10 cm^{-1} higher in energy than **3** (Figure 1). In contrast, the conversion of **2** to **3** results in a shift in ν_{CO} of ca. 60 cm^{-1}. The new species generated by protonation of **3** is assigned as $\{HFe_2[\mu\text{-}S_2(CH_2)_3](CNH)(CO)_4(PMe_3)\}^+$ (**3**H^+).

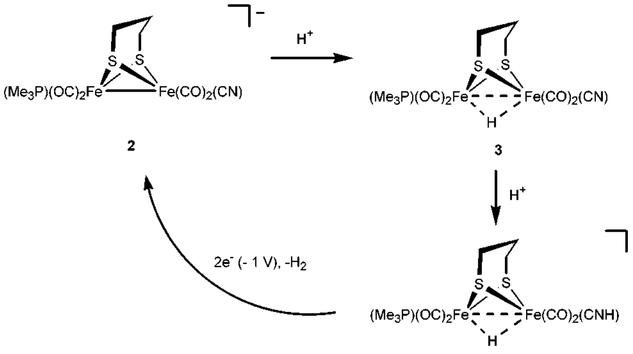
Scheme 1



core of Fe-only hydrogenase active site (X = H2, H2O)

1

Scheme 2



2

3

3H+

Proton reduction catalysis was demonstrated by cyclic voltammetry (CV) (Figure 2A). The voltammogram of a solution of **2** with 1 equiv of HOTs shows, in addition to the one-electron reduction of **2** ($E_p = -2.14$ V vs Ag|AgCl), two new reduction peaks at a potential ca. 1 V less negative. Shifts of reduction potential parallel the changes in the ν_{CO}.[12] These two peaks are ascribed to the reduction of **3**H^+ and **3** at $E_p = -1.03$ and $E_{1/2} = -1.13$ V, respectively. The value of ΔE_p (difference between the peak potentials for reduction and reverse oxidation) indicates that the reduction of **3** is a one-electron process (Figure 2B). With increasing acid concentration (HOTs, H_2SO_4, and HCl give similar results) the height of the first reduction peak increases, and its potential is shifted toward more negative potentials, as expected for catalytic proton reduction.[13] At more negative potentials the only significant electrochemical event observed is the reduction of **2**. In the presence of excess protons (≥3 equiv), solutions derived from **2** are completely stable under catalytic conditions for hours at room temperature. In a preparative-scale reaction, a solution of 10^{-3} M of **2** with 50 equiv H_2SO_4 was electrolyzed at −1.2 V (ca. −1 V vs NHE). Over the course of 15 min, 12 F per mol of **2** were passed. This corresponds to six turnovers for the bulk solution, close to the theoretical maximum because of the

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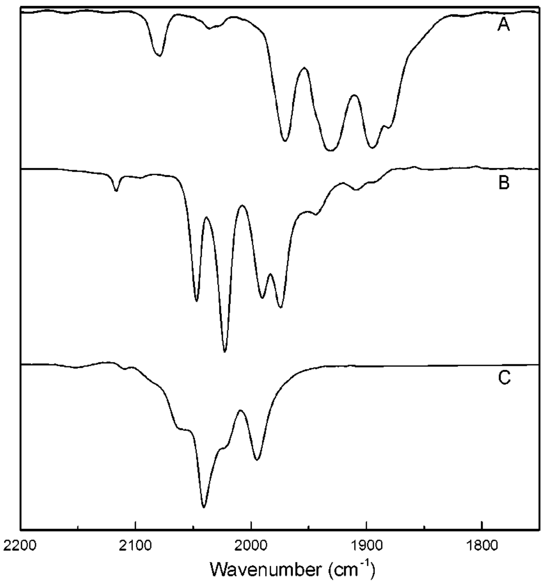

Figure 1. FT-IR spectra of (A) **2** (THF solution), (B) **3** (THF solution), and (C) **3**H$^+$ (MeCN solution).

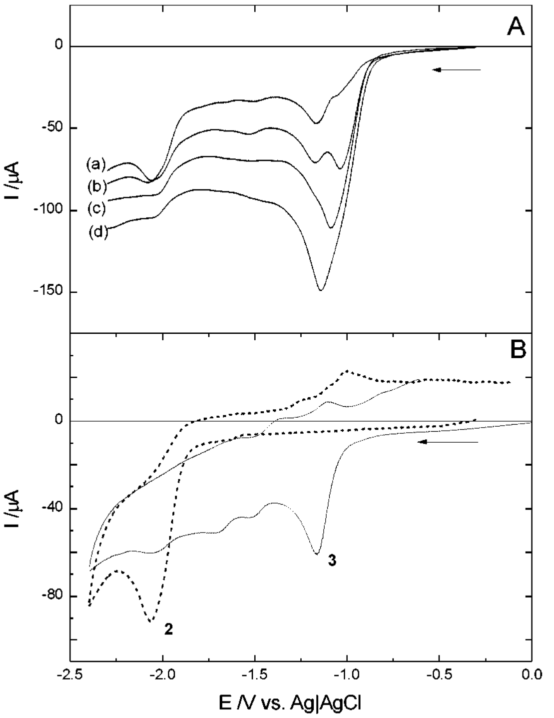

Figure 2. (A) Effect of x equiv of toluenesulfonic acid (HOTs) on the cyclic voltammetry of **2**, (a) x =1, (b) x = 2, (c) x = 3, (d) x = 4. (B) Cyclic voltammetry of **2** and **3**. *Conditions:* 2.3 mM **2** or 2.8 mM **3** in MeCN−Bu$_4$NPF$_6$; potential scan rate = 200 mV s^{-1}; glassy carbon working electrode of surface area 0.0701 cm^2.

time constant of the electrolysis cell. In such large-scale experiments, bubbles of H$_2$ are obvious. Gas chromatographic analysis showed that the dihydrogen yield was 100 (±10)%. A simplified catalytic cycle is presented in Scheme 2.

Having uncovered the catalytic behavior of **3**, we examined the catalytic properties of structurally related species. The monocyanide $\{Fe_2[\mu\text{-}S_2(CH_2)_3](CN)(CO)_5\}^-$ (**4**)[8b,14] is inactive catalytically. IR measurements show that this species only protonates at the N of cyanide, not at the Fe−Fe bond, emphasizing that the PMe$_3$ ligand in **2** enhances the basicity of the Fe−Fe bond. The diphosphine derivative $Fe_2[S_2(CH_2)_3](CO)_4(PMe_3)_2$ (**5**, $E_{1/2} = -1.86$ V), is protonated (HOTs) to give $\{HFe_2[S_2(CH_2)_3](CO)_4(PMe_3)_2\}^+$.[10] Although this hydrido species undergoes a reduction at $E_{1/2} = -0.98$ V (vs −1.13 V for **3**), the voltammetric response does not exhibit catalytic features with increased [HOTs]. It is clear that catalysis is quite sensitive to subtle electronic effects such that replacement of one PMe$_3$ by CNH (the difference between **3**H$^+$ and **4**H$^+$) significantly alters the catalytic properties of this bimetallic unit. We conclude that the catalytic properties of **3** could be due to its ability to both sustain protonation at the Fe−Fe bond[15] and carry a proton at the terminal cyanide. The diiron complex $Cp_2Fe_2(SC_2H_5)_2(CO)_2$,[16] which has no Fe−Fe bond, is catalytically inactive.

Much effort has focused on homogeneous proton reduction by metalloporphyrin catalysts.[1,13,17] The complex [Fe(tetraphenylporphyrinate)]$^{2-}$ is particularly active, although it is electrochemically generated and operates at −1.6 V versus SCE in DMF, which is ∼500 mV more negative than for **3**. The extractable cofactor of nitrogenase (FeMoco) requires only a modest overpotential of −0.5 V, but this catalyst is unstable in acid,[18] in contrast to our organometallic catalyst, and can generate only micromolar amounts of dihydrogen.[19] Previous catalysts proceed via an initial reduction which generates a basic center that accepts a proton.[13,17,19,20] In the present case protonation precedes reduction. Protonation enhances the ability of the dimetal center to accept electrons, which explains the rather modest overpotentials observed in this work.

Further studies are underway to more thoroughly describe mechanistic details, but this work shows that relatively simple analogues of the Fe-only hydrogenases can be effective catalysts for the reduction of protons to dihydrogen, beginning with protonation at the Fe−Fe bond. These systems are amenable to modification so that it should be possible to prepare immobilized and water-soluble catalysts, as well as derivatives featuring the recently proposed azadithiolate cofactor.[4e] Whereas the Fe-hydrogenases are proposed to bind protons at a single Fe center, our catalyst protonates at the metal−metal bond. Understanding this difference between the synthetic and natural catalyst is of continuing interest.

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Supporting Information Available: Experimental procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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