Hydrogen Production from Model Complexes of the [FeFe]- and [NiFe]-Hydrogenase Active Sites

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Many chemists have envisioned molecular hydrogen as an efficient and environmentally friendly fuel of the future. However, for the hydrogen economy to become viable new hydrogen-processing catalysts are needed to replace platinum, which is costly and of limited supply. Nature offers direction toward this goal, as enzymes called hydrogenases evolved several billion years ago to utilize molecular hydrogen as a fuel. The [FeFe]-hydrogenases predominately function to produce hydrogen from protons and electrons, while the [NiFe]-hydrogenases function to oxidize hydrogen.[1] The active sites of both enzymes contain first-row transition metals and biologically exotic ligands. When assayed for their rates and efficiencies of hydrogen processing, the hydrogenase enzymes are directly comparable to platinum.[2] Unfortunately, despite several crystal structures and a wealth of spectroscopic techniques, the mechanism of hydrogen processing remains speculative. Our goals as synthetic chemists have focused on the reactivity of models for the [FeFe]- or [NiFe]-hydrogenases in hopes of understanding of how Nature tunes these first-row transition metals into phenomenal catalysts.

Active site models for the [FeFe]-hydrogenases were unknowingly present before the first crystal structure in 1999. In fact, diiron dithiolates had been investigated since the 1920's and had well-established chemistry.[3] However, unique compared to all other diiron dithiolates, the active-site structure of [FeFe]-hydrogenase features a rotated diiron dithiolate core, exposing a vacant terminal position. Thus, the mechanism of hydrogen processing is thought to occur by substrate (H_2, H^+) binding in the terminal position. To properly model the biological mechanism of [FeFe]-hydrogenase, we sought terminal hydrides of diiron dithiolates. After the first terminal hydride complex, $[HFe_2(edt)(CO)_2(PMe_3)_4]^+$,[4] was published from our group others quickly followed.[5] This new class of diiron dithiolate terminal hydrides were derived by the biologically relevant pathway of protonation of a Fe(I)Fe(I) precursor. Unfortunately, the terminal hydrides derived in this fashion were unstable, and when warmed above –80 °C quickly isomerized to isomeric bridging hydrides.

To understand and control the selective formation of terminal hydride species and the following isomerization pathway, a series of diiron dithiolates were investigated. All diiron dithiolates explored showed the kinetic formation of a terminal hydride species that subsequently isomerized via a series of turnstile rotations to bridging hydrides.[6] We learned that these turnstile rotations were controlled by a combination of electronic and steric effects, as the 1,3-propanedithiolate derivatives were vastly more stable than their corresponding 1,2-ethanedithiolate derivatives. Additionally, more phosphine ligands generally resulted in a more stable terminal hydride. Thus, protonation of $Fe_2(pdt)(CO)_2(dppv)_2$ provided the terminal hydride complex $[(t\text{-}H)Fe_2(pdt)(CO)_2(dppv)_2]^+$, which isomerized at room temperature ($t_{1/2} \sim 10$ min) to the bridging hydride $[(\mu\text{-}H)Fe_2(pdt)(CO)_2(dppv)_2]^+$.[7] With a pseudo-stable terminal hydride complex in hand, we sought to explore the catalytic mechanism of proton reduction via the terminal hydride. To our surprise, although the mechanism was very similar to that proposed in biology, the catalytic efficiency suffered greatly when compared to the bridging hydride complex. We continued the research focusing our efforts on proton relay.

The active site of [FeFe]-hydrogenase is speculated to contain a 2-azapropane-1,3-dithiolate as the bridging dithiolate ligand, although the exact identity of the bridgehead atom could be either carbon, nitrogen, or oxygen. Recent work on mononuclear nickel phosphines led to the impression that an azadithiolate (adt) could function as a proton relay lowering the kinetic barrier of proton transfers to and from the terminal hydride position. Due to the significant amount of steric congestion in $[(H)Fe_2(pdt)(CO)_2(dppv)_2]^+$, the iron hydride does not deprotonate with tetramethylguanidine (pK_a = 26) and requires the strong acid HBF_4•Et_2O (pK_a = -2) for its formation. Upon incorporation of the proposed azadithiolate cofactor, $[(H)Fe_2(adt)(CO)_2(dppv)_2]^+$ was observed to have a significantly smaller barrier to proton transfer to and from the terminal position, and enables the oxidation of H_2 (Figure 1).[8,9] In addition, $[(H)Fe_2(adt)(CO)_2(dppv)_2]^+$ was observed to be a remarkably fast and efficient catalyst for proton reduction, with turnover frequencies approaching that of the enzyme.[10]

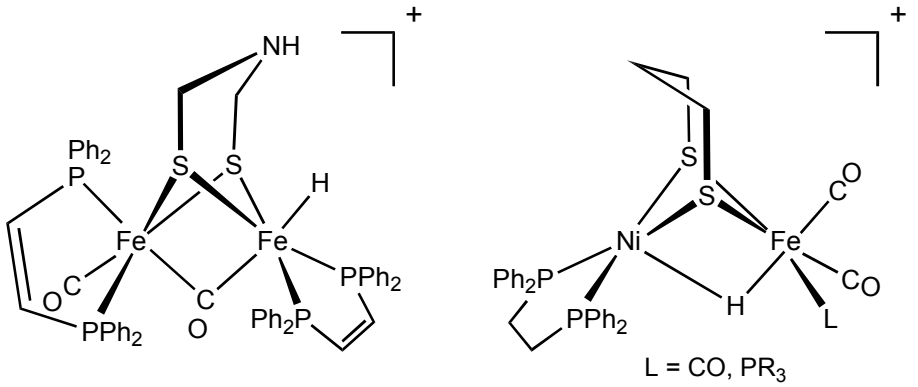

Figure 1: Model complexes for the active sites of [FeFe]- and [NiFe]-Hydrogenase.

Unlike the [FeFe]-hydrogenases, model complexes for the [NiFe]-hydrogenases were unknown prior to the crystal structure in 1996. However, most synthetic efforts focused on structural models for the active site, and neglected the catalytically imperative hydride ligand. Thus, we sought a nickel-iron hydride complex to explore the relevant reactivity of the first (μ-H)Ni(μ-SR)$_2$Fe complex. We found that the previously reported (dppe)Ni(μ-pdt)Fe(CO)$_3$, a Ni(I)Fe(I) complex, reacted with acid to provide $[(dppe)Ni(\mu\text{-}H)(\mu\text{-}pdt)Fe(CO)_3]^+$, the first nickel-iron hydride (Figure 1).[11] After protonation, the hydride complex is amenable to substitution chemistry at the Fe(CO)$_3$ subunit. Further derivatives altering the Ni(diphosphine)(SR)$_2$ subunit have been achieved through a new synthetic procedure to the Ni(I)Fe(I) complex.[12] All nickel-iron hydrides investigated are active catalysts for the reduction of protons.[13] As the catalytic mechanism of [NiFe]-hydrogenase is widely speculative, the reactivity of this new class of nickel-iron hydrides offers insight into Nature's catalytic mechanism.

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