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Hydrogen Activation by Biomimetic Diiron Dithiolates

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Using the thermally stable salts of $[Fe_2(SR)_2(CO)_3(PMe_3)(dppv)]BAr^F{}_4$, we found that the azadithiolates $[Fe_2(adtR)(CO)_3(PMe_3)(dppv)]^+$ react with high pressures of H_2 to give the hydride $[Fe_2(\mu\text{-H})(adtR)(CO)_3(dppv)(PMe_3)]BAr^F{}_4$. The related oxadithiolate and propanedithiolate complexes are unreactive toward H_2. Molecular hydrogen is proposed to undergo heterolysis assisted by the amine followed by isomerization of an initially formed terminal hydride. Use of H_2 and D_2O gave the deuteride as well as the hydride, implicating protic intermediates.

Hydrogenases are enzymes that catalyze the interconversion of H_2 with protons and reducing equivalents.[1] Understanding the reactivity of these enzymes via active-site models remains topical,[2] especially because these catalysts rely on inexpensive first-row transition metals.[3] Significant progress has been made in [FeFe]-hydrogenase models,[4,5] but nearly all studies to date have focused on *proton reduction*.[6] The opposite reaction, *hydrogen oxidation*, has proven elusive. This lack of reactivity is surprising because [FeFe]-hydrogenases are exceptionally active toward H_2 oxidation. The eventual translation of models to applications in fuel cells requires progress in hydrogen oxidation. Herein we report the first example of the activation of H_2 by a model for [FeFe]-hydrogenase, as well as the associated advances that have facilitated this progress.

Recently, we reported $[Fe_2(pdt)(CO)_3(PMe_3)(dppv)]BF_4$ ([**1**]BF_4, pdt = $S_2C_3H_6$), a paramagnetic ($S = {}^1/_2$) spin-localized species that represents a useful structural model for the H_{ox} state of the binuclear active site [dppv = *cis*-1,2-bis(diphenylphosphino)ethylene].[7,8] With a vacant coordination site, H_{ox} and its models are poised to activate H_2. Although $[\mathbf{1}]^+$ binds CO, it exhibits no discernible affinity toward H_2. The anticipated product of hydrogen activation, $[Fe_2(\mu\text{-H})(pdt)(CO)_3(PMe_3)(dppv)]BF_4$ ([**1**H]BF_4), was prepared independently by protonation of the corresponding Fe^IFe^I precursor; a terminal hydride is initially formed that rapidly isomerizes to bridging hydrides.[9]

The thermal sensitivity of [**1**]BF_4 severely limits studies of its reactivity toward H_2: it is unstable above 0 °C for more than a few seconds. We have found that the corresponding salt [**1**]$BAr^F{}_4$ is stable in solution for days at room temperature ($BAr^F{}_4{}^- = B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4{}^-$). The sensitivity of electrophilic iron carbonyls toward fluorinated counterions is precedented.[10] We confirmed that solutions of [**1**]$BAr^F{}_4$ rapidly decomposed upon treatment with $[Bu_4N]BF_4$. The robust salt [**1**]$BAr^F{}_4$, however, proved unreactive toward 1800 psi H_2, even upon addition of the bulky base 2,6-(^{t}Bu)$_2$pyridine. Many bases such as 2,6-dimethylpyridine are not compatible with [**1**]$BAr^F{}_4$, causing it to decompose to unidentified products. Apparently, H_2 activation by H_{ox} models is subject to a significant kinetic barrier.

The proposed azadithiolato cofactor has been shown to significantly affect the acid−base properties of diiron dithiolate complexes.[11] Furthermore, pendant amine bases dramatically affect the rate of H_2 uptake in Ni-based catalysts.[12] We therefore investigated azadithiolato analogues of [**1**]$BAr^F{}_4$. As described below, we present evidence that such mixed-valence azadithiolatodiiron complexes indeed activate H_2.

Azadithiolate-containing analogues of $[\mathbf{1}]^+$ have proven to be particularly sensitive: attempts to generate

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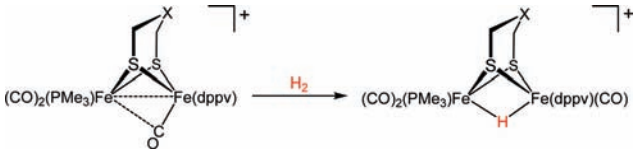
Table 1. Reactivity of $[Fe_2[(SCH_2)_2X](CO)_3(PMe_3)(dppv)]^+$ Derivatives toward H_2 (10 mM Toluene Solution, 1800 psi H_2, 26 h)



complex ($BAr^F{}_4^-$ salt)	yield of hydride (%)
$[Fe_2(pdt)(CO)_3(PMe_3)(dppv)]^+$ ($[\mathbf{1}]^+$)	< 5
$[Fe_2(adt)(CO)_3(PMe_3)(dppv)]^+$ ($[\mathbf{2}]^+$)	~30
$[Fe_2(adt\text{-}Bn)(CO)_3(PMe_3)(dppv)]^+$ ($[\mathbf{2'}]^+$)	~85
$[Fe_2(odt)(CO)_3(PMe_3)(dppv)]^+$ ($[\mathbf{3}]^+$)	< 5

$[Fe_2(adt)(CO)_3(PMe_3)(dppv)]BF_4$ ($[\mathbf{2}]BF_4$, where adt = $(SCH_2)_2(NH)$) by oxidation of **2** with $FcBF_4$ resulted in complex mixtures even at −78 °C. We found, however, that solutions of $[\mathbf{2}]BAr^F{}_4$, generated from the treatment of **2** with $FcBAr^F{}_4$,[13] are stable for days at room temperature. We also prepared the related benzyl derivative $[Fe_2[(SCH_2)_2NCH_2Ph](CO)_3(PMe_3)(dppv)]BAr^F{}_4$ ($[\mathbf{2'}]BAr^F{}_4$), which was used for the majority of our studies for reasons described below. The spectroscopies for $[\mathbf{1}]^+$, $[\mathbf{2}]^+$, and $[\mathbf{2'}]^+$ are very similar (see the Supporting Information) and indicate that one carbonyl is semibridging and the apical site on the Fe(dppv) center is vacant. In $[\mathbf{1}]^+$, $\nu_{\mu\text{-CO}}$ is ~30 cm^{-1} lower in energy, suggesting that the carbonyl has more bridging character. The unsaturated character of $[\mathbf{2'}]^+$ was confirmed by its rapid and reversible carbonylation to the adduct $[\mathbf{2'}(CO)]^+$.

The treatment of $[\mathbf{2}]BAr^F{}_4$ with 1800 psi H_2 for 26 h resulted in 30% conversion to the hydride $[\mathbf{2}(\mu\text{-H})]BAr^F{}_4$. The product $[\mathbf{2}(\mu\text{-H})]^+$ is spectroscopically identical with the hydride produced by protonation of **2** (see below). Analogous but more efficient reactivity was found for the tertiary amine $[\mathbf{2'}]BAr^F{}_4$, which gave $[\mathbf{2'}(\mu\text{-H})]BAr^F{}_4$ in high yield. The mixed-valence oxadithiolate $[Fe_2(odt)(CO)_3(PMe_3)(dppv)]^+$ ($[\mathbf{3}]^+$, where odt = $(SCH_2)_2O$) was also found to be thermally stable, being comparable to $[\mathbf{2'}]BAr^F{}_4$. It was, however, unreactive toward high pressures of H_2. Collectively, these results point to participation of the amine in the activation of H_2 by the cationic diiron complex (Table 1). Under otherwise identical conditions but using argon in place of hydrogen, $[\mathbf{2'}]^+$ remain unchanged.

A number of controls were conducted to verify the significance of our findings. ^1H and ^{19}F NMR analyses of reaction mixtures showed that $BAr^F{}_4^-$ and ferrocene remained unaffected. No deuteride was detected when the reaction was conducted in toluene-d_8. When toluene solutions of $[\mathbf{2'}]BAr^F{}_4$ were stored in the absence of H_2 for several days, only trace amounts of $[\mathbf{2'}(\mu\text{-H})]^+$ formed, probably from a reaction involving adventitious water. This interesting process was confirmed by the treatment of $[\mathbf{2'}]^+$ with D_2O to give small amounts of $[\mathbf{2'}(\mu\text{-D})]^+$. In the same way that the adt complexes $[\mathbf{2}]^+$ and $[\mathbf{2'}]^+$ exhibit greater reactivity toward H_2 than does $[\mathbf{1}]^+$, we found that $[Fe_2(adt)(CO)_2(dppv)_2]^+$ is reactive toward H_2 whereas the analogous propanedithiolate $[Fe_2(pdt)(CO)_2(dppv)_2]^+$ is not.

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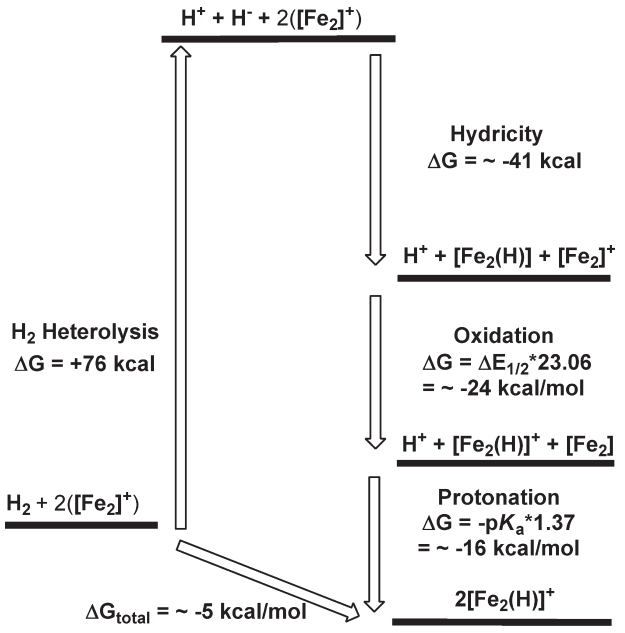
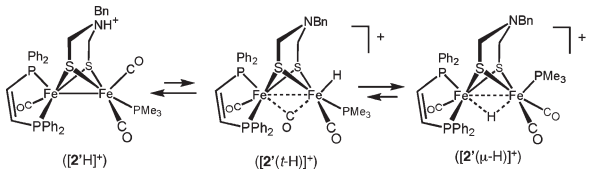
Scheme 1. Thermodynamic Cycle for the Reaction $2[Fe_2(SR)_2(CO)_3(PR_3)_3]^+ + H_2 \rightarrow 2[HFe_2(SR)_2(CO)_3(PR_3)_3]^+$



The formation of the μ-hydride $[\mathbf{2'}(\mu\text{-H})]^+$ requires explanation because the mechanism for H_2 activation should produce a terminal hydride adjacent to the adt.[14,15] In an independent experiment, protonation of **2'** with $[H(OEt_2)]BAr^F{}_4$ was found to afford the ammonium salt $[\mathbf{2'}H]^+$, which was characterized by IR and ^{31}P NMR spectroscopies.[16] This ammonium compound was found to convert to $[\mathbf{2'}(\mu\text{-H})]^+$ via a first-order process ($k = 3.9 \times 10^{-4}\ s^{-1}$, 23 °C, CH_2Cl_2; eq 1).



(1)

This tautomerization is assumed to occur via the terminal hydride ($[\mathbf{2'}(t\text{-H})]^+$), which is not observed. The related terminal hydride $[\mathbf{1}(t\text{-H})]^+$, which is observable, isomerizes to $[\mathbf{1}(\mu\text{-H})]^+$ (see the Supporting Information).[14] Thus, under the conditions of hydrogenation (hours, 25 °C), $[\mathbf{2'}(\mu\text{-H})]^+$ is the *expected* product.

The hydrogenation points to the stoichiometry shown in eq 2.

$$2[Fe_2(adtR)(CO)_3(PMe_3)(dppv)]^+ + H_2 \rightarrow 2[HFe_2(adtR)(CO)_3(PMe_3)(dppv)]^+ \quad (2)$$

Although this reaction appears homolytic on the basis of the stoichiometry, the finding that it requires azadithiolate indicates a heterolytic mechanism. A thermodynamic cycle highlights the key steps; although the heterolytic cleavage of H_2 is expected to

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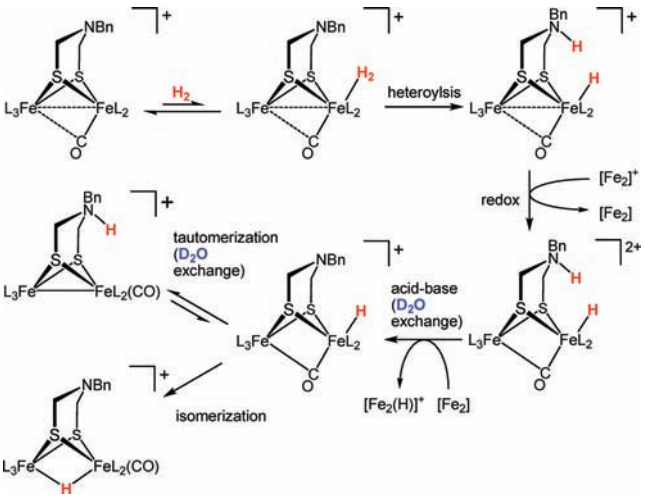
Scheme 2. Proposed Mechanism of H_2 Activation by $[Fe_2[(SCH_2)_2NR](CO)_3(PMe_3)(dppv)]^+$



be endergonic, this process can be driven if the diiron cation is a strong hydride acceptor. In this case, subsequent protonation and redox events are required to make the overall process energetically downhill (Scheme 1). In the protein, the stoichiometry, of course, differs from that in eq 2 because the initial heterolysis is coupled to oxidation by an Fe−S cluster and one proton is released to the protein. In our system, the diiron complexes can interact; half of $[\mathbf{2}']^+$ serves sequentially as an oxidant and then a proton acceptor.

The proposed mechanism invokes the initial formation of the adduct $[\mathbf{2}'(H_2)]^+$ (Scheme 2). Because exogenous CO binds only weakly to $[\mathbf{2}']^+$,[8,17] coordination of H_2 is expected[18] to be unfavorable. Binding of H_2 initiates the heterolytic activation sequence as implied by the requirement for the amine-containing dithiolate. We have shown that the redox couple for the CO adduct $[Fe_2[(SCH_2)_2X](CO)_4(PMe_3)(dppv)]^{+/2+}$ is ∼250 mV more positive than the $[Fe_2[(SCH_2)_2X](CO)_3(PMe_3)(dppv)]^{0/+}$ couple.[7] Thus, we anticipate that $[\mathbf{2}'(H_2)]^+$ would be unable to reduce $[\mathbf{2}']^+$. The ammonium hydride $[H\mathbf{2}'(t\text{-}H)]^+$ is, however, expected[19] to be a powerful reductant (∼−1.6 V vs $Fc^{0/+}$). Heterolysis of $[\mathbf{2}'(H_2)]^+$ is apparently irreversible because $[\mathbf{2}']^+$ was not observed to catalyze the formation of HD from H_2 and D_2O under the conditions of the experiment. We thus propose that heterolysis induces rapid electron transfer to give the ammonium hydride $[H\mathbf{2}'(t\text{-}H)]^{2+}$ and $\mathbf{2}'$, the latter of which rapidly deprotonates the former.

When a solution of $[\mathbf{2}']^+$ was treated with H_2 (2000 psi) in the presence of D_2O, we obtained $[\mathbf{2}'(\mu\text{-}D)]^+$ and $[\mathbf{2}'(\mu\text{-}H)]^+$ in a ratio of ∼4:1. Comparable results were obtained for the corresponding reaction involving D_2 and H_2O, which gives both $[\mathbf{2}'(\mu\text{-}D)]^+$ and $[\mathbf{2}'(\mu\text{-}H)]^+$. Control experiments confirmed that $[\mathbf{2}'(\mu\text{-}H)]^+$ does *not* exchange with D_2O. Proton transfer from an initial dihydrogen complex $[\mathbf{2}'(H_2)]^+$ would account for 50% of the exchange. The high degree of exchange is consistent with tautomerization between $[\mathbf{2}'(\mu\text{-}H)]^+$ and $[\mathbf{2}'(t\text{-}H)]^+$ (see eq 1). We have shown that terminal hydrides are also kinetically inert in the absence of the amine cofactor as indicated by the behavior of $[\mathbf{2}'(t\text{-}H)]^+$.[11]

The results presented in this Communication establish that biomimetic diiron dithiolato complexes can thermally activate hydrogen. The findings point to a mechanism that involves a coupling of the electron and proton transfers. Optimized models will require manipulation of the steps in Scheme 1, as well as suppressing the formation of the μ-hydride, which is a thermodynamic sink. The present results highlight the importance of the amine in the activation of H_2 by the diiron center.[12,20]

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Supporting Information Available: Preparative and spectroscopic details, including EPR, IR, NMR, and electrospray ionization mass spectrometry spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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