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# A Carbonyl-Rich Bridging Hydride Complex Relevant to the Fe−Fe Hydrogenase Active Site

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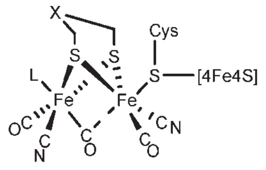
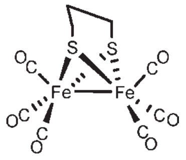
Protonation of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6$ with an acid derived from $[SiEt_3][B(C_6F_5)_4]$ and HCl affords a hydride-bridged dimer.

Hydrogenase enzymes catalyze the oxidation of dihydrogen and the reduction of protons in nature. X-ray crystallography of [FeFe]hydrogenases combined with IR spectroscopy has shown the active site to be comprised of a [2Fe2S] subunit linked to a [4Fe4S] cluster by a cysteinyl−S bridge[1,2] The two iron atoms in the [2Fe2S] subunit are linked by a bridging dithiolate ligand and are ligated by carbon monoxide and cyanide. This enzyme has been widely studied as a model for the generation/utilization of dihydrogen.[3]



Active site L = $H_2$ or $H_2O$; X = N?



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Many model complexes for this active site have been reported, several based on variants of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_6$ (**1**). Reduction leads to species that will catalyze proton reduction, but less progress has been made in the study of dihydrogen oxidation.[4] Both Darensbourg and Rauchfuss have reported the formation of mixed-valence species that may serve as models for the partially oxidized enzyme.[5]

Protonation of the Fe−Fe bond in models has been studied by several research groups as a pathway to more reactive complexes that mimic the oxidized enzyme. The electrochemical reduction of complex **1** in the presence of acid gives electrocatalytic dihydrogen evolution.[6] Building upon earlier work with more basic ligand sets,[7] protonation of $[Fe_2(\mu\text{-}S_2C_2H_4)(CN)_2(CO)_4]^{2-}$ gives an unstable bridging hydride species as a mixture of three isomers.[8] In contrast, $Fe_2(\mu\text{-}S_2C_3H_6)(PMe_3)_2(CO)_4$ affords a stable hydride-bridged cation as a single isomer.[9] Four isomers are observed upon protonation of $Fe_2(\mu\text{-}S_2C_3H_6)(CO)_4(CN\text{-}{}^tBu)_2$.[10] We sought to prepare model complexes by protonating less basic starting materials, which we anticipated would lead to more reactive (electrophilic) model complexes. We report our results on the protonation of the hexacarbonyl complex, **1**.

We found that complex **1** exhibits very low basicity. No reaction is observed when **1** is treated with excess $HBF_4 \cdot Et_2O$, suggesting that **1** is less basic than diethyl ether. With triflic acid, a protonation reaction is observed, but a clean product could not be isolated.[11]

We report two new methods for the protonation of **1** that rely on the high Lewis acidity of $[SiEt_3][B(C_6F_5)_4]$.[12] Our first method to prepare a strong Brönsted acid is analogous to a procedure reported by Reed for the preparation of $H_2[B_{12}Cl_{12}]$ and earlier work for preparing protonated benzenes (Scheme 1).[13]

The combination of equimolar quantities of **1** and $[SiEt_3][B(C_6F_5)_4]$, followed by dissolution in fluorobenzene and the addition of HCl gas, yields an orange solution. The $^1H$ NMR spectrum of this solution reveals the formation of a hydride-containing material and complete consumption of the starting

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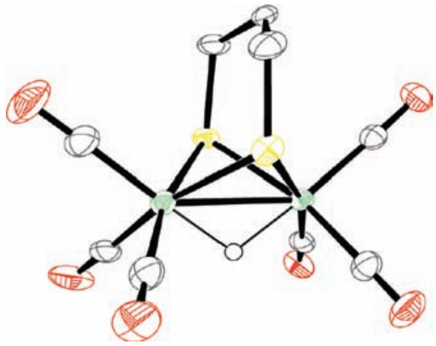
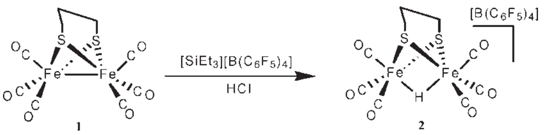


**Figure 1.** ORTEP of the cation of **2**. Counteranion and nonhydride hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

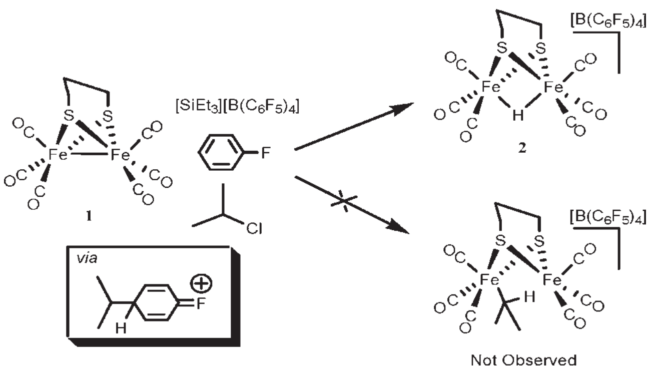
**Scheme 1**



material.[14] A sharp singlet is observed at $\delta$ −15.9, and signals for new propanedithiolate protons are observed at $\delta$ 2.14 (4H, t) and 1.75 (2H, quint). The $^{13}C$ NMR spectrum contains the propyl carbons at $\delta$ 29.6 (1C) and 22.1 (2C) as well as distinct apical and basal carbonyls at $\delta$ 200.6 (2C) and 196.9 (4C). The carbonyl resonances suggest that the fluxionality of complex **1** has been reduced upon protonation. These new signals are attributed to the hydride-bridged dimer $[Fe_2(\mu\text{-}H)(\mu\text{-}S_2C_3H_6)(CO)_6][B(C_6F_5)_4]$ (**2**; Figure 1). An orange solid is isolated by removal of all volatiles under reduced pressure and washing with heptane. The IR spectrum of **2** shows new bands for an oxidized species at 2132, 2112, and 2082 cm$^{-1}$ (KBr) versus complex **1**, which has bands at 2072, 2033, and 1993 cm$^{-1}$.[15] The shift to higher frequencies upon protonation is similar to that of earlier reports on related complexes.[7−9]

An alternative preparation of **2** avoids the use of HCl gas. We had hoped that alkylation of **1** would occur, with the carbocation formed via chloride abstraction from 2-chloropropane (Scheme 2). The prompt addition of 1 equiv of 2-chloropropane to stoichiometric amounts of $[SiEt_3][B(C_6F_5)_4]$ and **1** in protio fluorobenzene gives clean formation of **2**. These experiments in protio solvent were analyzed by NMR spectroscopy with solvent suppression.[16] The formation of $ClSiEt_3$ was confirmed by $^1H$ and $^{29}Si$ NMR data. New signals are also identified for *o*- and *p*-isopropylfluorobenzene, which we attribute to substitution of the solvent by the isopropyl cation; the nucleophilicity of fluorobenzene is anomalously high.[17] The arenium ions formed are presumed to be acidic enough to protonate complex **1**.[18] A control reaction using $C_6D_5F$ yields the same

**Scheme 2**



propanedithiolate signals for **2**, but the hydride intensity observed is only 6% of that in the $C_6H_5F$ experiment, consistent with the formation of **2**-$d_1$. Analogous experiments in chlorobenzene also produce stoichiometric quantities of **2**. In addition, when isolated **2** is dissolved in $C_6D_5F$, it slowly converts to **2**-$d_1$.

Crystals of **2** suitable for diffraction studies were obtained by layering a fluorobenzene solution with pentane. The structure obtained contains one $B(C_6F_5)_4$ anion for each iron dimer. A bridging hydride was located in the electron density map and was refined isotropically.

Protonation of **1** results in the formal oxidation of the iron atoms. However, the Fe−Fe distance in **2** is elongated only slightly to 2.5540(4) Å (vs 2.5103(11) Å in **1**[19]). Protonation of the Fe−Fe bond in hydrogenase models had been observed previously, but only with anionic complexes or those with a more basic ligand set.[20] Darensbourg and coworkers reported similar changes in the Fe−Fe separation upon protonation of $Fe_2(\mu\text{-}S_2C_3H_6)(PMe_3)_2(CO)_4$.[21]

In our preliminary assessment of the reactivity of **2**, we find that **2** is a strong acid. Treatment of **2** with $Et_2O$ (10 equiv) gives complete conversion to **1** over several minutes. This observation is consistent with the low basicity of **1** noted. The reaction of **2** with stronger bases such as pyridine gives the immediate formation of **1**. A solution of **2** under an atmosphere of deuterium gas exhibited no formation of HD, even upon standing for a week at room temperature. Complex **2** does not lose CO at room temperature.

Observations by Rauchfuss et al. have suggested that strong $\sigma$-donor ligands are required in ferrous species to inhibit carbonyl lability.[22] In the case of **2**, carbonyl loss is not significant despite the $\pi$-acidic ligand set. The reactivity of **2** is dominated by deprotonation.

We have been able to protonate a neutral hydrogenase model to give a hydride-bridged complex. Protonation appears to have very little effect on the Fe−Fe separation. In

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[14] $^1H$ NMR for **1** (500 MHz, $C_6H_5F$): $\delta$ 1.66 (4H, t), 1.34 (2H, quint).

[15] We have been unable to prepare a sample of **2** for IR analysis free of traces of **1** because of extremely facile deprotonation.

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addition, the product does not react with hydrogen gas, apparently because CO dissociation does not take place. This lack of lability is in contrast to the ferrous tricarbonyl $CpFe(CO)_3^+$, where CO loss has been demonstrated.[23] The methodology described here allows for isolation of a salt with a noncoordinating anion; we believe this to be widely applicable for the protonation of weakly basic substrates.

**Supporting Information Available:** Experimental details, characterization data, NMR and IR spectra, and X-ray diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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