Hydrogenase Models

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[FeFe]-Hydrogenase Models and Hydrogen: Oxidative Addition of Dihydrogen and Silanes**

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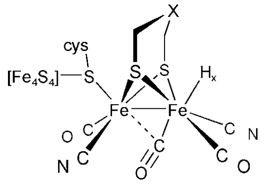
Intense interest has recently been focused on the biophysics[1] and synthetic models of [FeFe]-hydrogenases.[2] Such studies promise to contribute to the development of nonprecious metal catalysts[3] for the production and utilization of hydrogen.[4] A challenge in current research is the resistance of [FeFe]-hydrogenase models, diiron dithiolato carbonyl complexes, to form complexes directly from H_2, as well as related hydrogenic substrates. It is possible that the direct reaction of diiron dithiolates with hydrogen-rich substrates has been overlooked because it is considered too difficult or too obvious, or both. Although some diiron complexes promote isotopic H/D exchange under photochemical conditions,[5] such reactions yield no isolable hydrides. A mixture of the electron-rich diiron ethanedithiolate $[Fe_2(S_2C_2H_4)(CO)_4(PMe_3)_2]$ reacted with H_2 in the presence of $B(C_6F_5)_3$. In this case the borane activated H_2,[6] and the diiron center serves as a base [Eq. (1)].[7]

$$[Fe_2(S_2C_2H_4)(CO)_3(PMe_3)_2] + H_2 + B(C_6F_5)_3 \rightarrow [(\mu\text{-}H)Fe_2(S_2C_2H_4)(CO)_3(PMe_3)_2]HB(C_6F_5)_3 \tag{1}$$

We have now more directly examined the reactivity of diiron dithiolato carbonyl compounds with H_2 and with organosilanes as surrogate substrates.[8]

The active site of Fe-only hydrogenase enzymes can be described as $[Fe_2(SR)_2(\mu\text{-}CO)(CO)_2L_3]^{z+}$, wherein the three diatomic ligands on the distal iron atom (which are distal with respect to the {4Fe–4S} cluster) are "rotated" by approximately 60°, thereby opening a coordination site *trans* to the Fe–Fe bond (Scheme 1). Hydrogen binds to this active site, presumably as a σ complex, prior to the release and oxidation of H_2. To examine the reactions of hydrogen, silanes, and diiron dithiolato carbonyl compounds, we selected the recently described, unsymmetrically substituted diiron dithiolate complex $[Fe_2(S_2C_2H_4)(CO)_4(dppv)]$ (**1a**, dppv = *cis*-$C_2H_2(PPh_2)_2$) because of its enhanced reactivity toward ligand substitution.[9]



Scheme 1. Structure of the active site of the [FeFe]-hydrogenases.

Density functional theory (DFT) calculations indicated that substitution of CO by H_2 in **1a** is strongly disfavored by 29.2 kcal mol^{-1}. Assuming, however, that CO can be ejected (for example, photochemically), the subsequent binding of H_2 to the 32e$^-$ $[(dppv)(CO)Fe(S_2C_2H_4)Fe(CO)_2]$ complex (Figure 1) is exothermic by 19.5 kcal mol^{-1}. The initial stable product is predicted to feature an η^2-H_2 ligand (H–H 0.859 Å, compared to 0.74 Å for free H_2)[10] that would evolve to a dihydride species in which the H–H bond is fully cleaved. Oxidative addition to give a *cis*-dihydride species is, energetically, slightly uphill from the initial H_2 adduct. The subsequent step to give $[dppv(CO)Fe(S_2C_2H_4)(\mu\text{-}H)Fe(CO)_2H]$ is exothermic by 10.3 kcal mol^{-1}.

The energetics for the reaction of Ph_2SiH_2 with **1a** is initially quite similar to the case for H_2. The η^2-Ph_2SiH_2 complex is slightly activated (Si–H 1.665 Å compared to 1.417 Å for $SiH_2(Mes)_2$). Significant differences are detected in the oxidative cleavage of Ph_2SiH_2 compared to that for H_2, since oxidative addition is 3.3 kcal mol^{-1} less endothermic with the silane. The oxidative addition coupled to the isomerization of the *trans*-hydridosilyl derivative is strongly exothermic, by 10.4 kcal mol^{-1}, as it is for the H_2 case. Notably, the presence of donor ligands on the diiron center is crucial. Calculations indicate that neither Ph_2SiH_2 nor H_2 forms stable derivatives with analogous complexes when the diphosphine is replaced by two CO groups (see the Supporting Information).

Encouraged by the theoretical results, we attempted the reaction of **1a** with H_2. No reaction occurred when a toluene solution of **1a** was treated with 1 atm H_2 under reflux or photolysis conditions. In THF, however, under photolysis conditions, a sealed NMR sample of **1a** and 1 atm H_2 partially converted into two hydride derivatives, exhibiting strongly upfield resonances in the ^{1}H NMR spectrum (see the Supporting Information). The main product, **2a**, is characterized by a coupled doublet ($\delta = -12.8$ ppm, $J = 18.4$ Hz,) and doublet of triplets ($\delta = -14.9$ ppm, $J = 18.4$, 31.2 Hz). This species exhibits a single ^{31}P NMR signal. We assign **2a** as the *trans*-dihydride (Scheme 2). A second product, charac-

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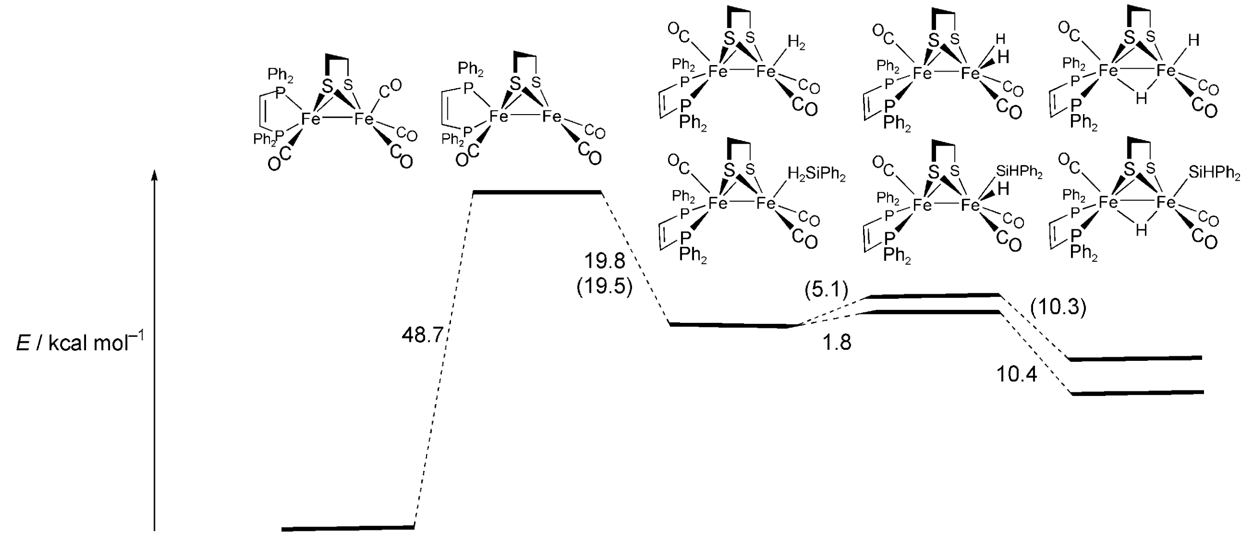
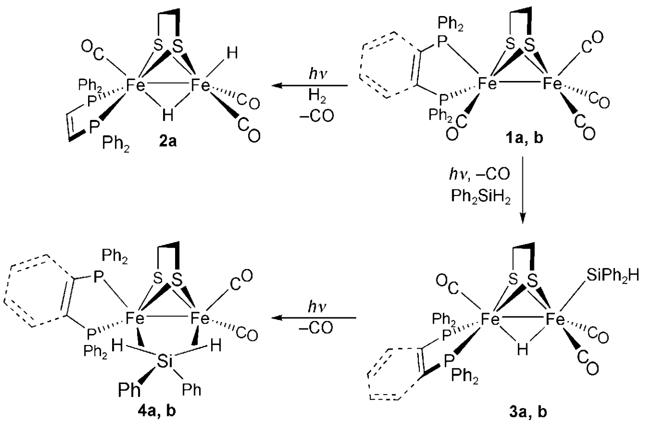


Figure 1. Energetic profile for the gas-phase conversion of [$Fe_2(S_2C_2H_4)(CO)_4$(dppv)] into the dihydride (values in parentheses) and the diphenylsilyl hydride. Reaction energy values (kcal mol^{-1}) have been computed using density functional calculations at the BP86/TZVP level (see the Supporting Information for details).



Scheme 2. Reactivity of [$Fe_2(S_2C_2H_4)(CO)_4(P_2)$], where P_2 = dppv (a) or dppbz (b), with H_2 and diphenylsilane.

terized by a broad singlet at $\delta = -14.4$ ppm, was also detected. Relative to toluene, THF is advantageous for this photoreaction because it aids the initial decarbonylation step.[11] As shown by the calculations, decarbonylation is required for H_2 reactivity, as CO binds more strongly than H_2. The same dihydride products formed more efficiently when NH_3BH_3 was used instead of H_2 (see the Supporting Information).

The inefficient reactivity of H_2 toward **1a** led us to investigate corresponding reactions involving silanes. DFT analysis indicated that this process would be more favorable (see above). No reaction occurred under reflux conditions, even in the presence of the decarbonylation agent Me_3NO. Solutions of **1a** in toluene were indeed found to readily react with silanes upon photolysis. In the case of diphenylsilane, the ^{1}H NMR spectrum of the crude product showed three hydride resonances, indicating the formation of multiple products. The reaction rate and product distribution ratio were unaffected by the presence of an atmosphere of CO.

Similar photoreactions occurred, starting with the related complex [$Fe_2(S_2C_2H_4)(CO)_4$(dppbz)] (**1b**). The dppbz ligand, 1,2-bis(diphenylphosphino)benzene, is virtually isosteric with dppv but is more rigid and, as a result, its derivatives crystallized more readily. Irradiation of a toluene solution containing Ph_2SiH_2 for 16 h resulted in the precipitation of an orange solid. NMR and IR spectroscopic analysis indicated that this species (**3b**) had a bridging hydride with a chemical shift and P–H coupling constant ($J_{P\text{-}H} = 28.5$ Hz) similar to the value for the main product obtained from **1a** in the presence of Ph_2SiH_2.

Crystallographic analysis confirmed the structure of a silyl hydrido complex with idealized C_s symmetry (Figure 2). The hydride ligand, which was located crystallographically, bridges the two metal centers and is slightly off center (closer to the {Fe(dppbz)(CO)} site by 0.05 Å). The silyl ligand is apical, and the remaining Si–H group is not bonded to the iron atom. We assume that **3b** arises from the decarbonylation of the tetracarbonyl precursor **1b**, followed by formation of a transient σ complex, which undergoes intramolecular oxidative addition. The structure demonstrates that the reactions are localized on the {$Fe(CO)_3$} center, not on the more electron rich {Fe(dppbz)(CO)} site. The localization of reactivity on the unsubstituted Fe center is also seen for the protonation[12] and the ligand substitution[9] of this family of compounds.

As for **2a**, we assume that **3b** arises from formation of a transient σ complex, which undergoes intramolecular oxidative addition. The selective formation of **3b** arises from its low solubility in toluene. Photolysis of solutions of **1b** (in the presence of Ph_2SiH_2) or **3b** (in the absence of Ph_2SiH_2) in THF afforded a new product, **4b** (Scheme 2). The ^{1}H NMR spectrum of the hydride region of **4b** displayed two signals, a doublet and a doublet of triplets, integrating to 1:1, and again these signals match those seen for the crude product of photolysis of **1a** and Ph_2SiH_2.

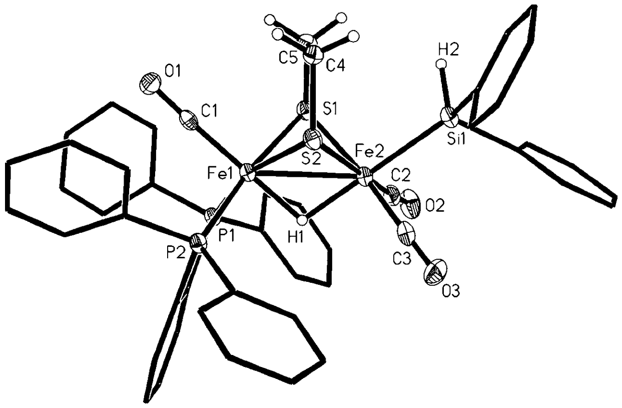


Figure 2. Structure of $[Fe_2(S_2C_2H_4)(\mu\text{-}H)(SiPh_2H)(CO)_3(dppbz)]$ (**3b**), with thermal ellipsoids set at 35% probability. Phenyl thermal ellipsoids and phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], and angles [°]: Fe1–Fe2 2.6058(11), Fe1–H1 1.6416(381), Fe1–S1 2.2697(11), Fe1–S2 2.2612(11), Fe1–P1 2.1991(11), Fe1–P2 2.2115(11), Fe1–C1 1.7459(41), Fe2–H1 1.7094(375), Fe2–Si1 2.3025(12), Fe2–C2 1.7630(44), Fe2–C3 1.7553(44); Fe2-Fe1-P1 109.14(4), Fe2-Fe1-P2 118.21(4), Fe2-Fe1-C1 140.09(12), Fe1-Fe2-Si1 141.12(4), P1-Fe1-P2 86.78(4), P1-Fe1-C1 95.87(12), P2-Fe1-C1 93.10(12), Si1-Fe2-C2 87.11(12), Si1-Fe2-C3 86.31(13).

Crystallographic analysis revealed that **4a** is formed from **3a** by decarbonylation, reformation of Si–H bonds, and a pair of Fe–H–Si σ interactions spanning the diiron center. The Fe–H–Si σ interactions occupy two basal sites[13] of the $[Fe_2(SR)_2L_6]$ framework (Figure 3). Bridging silanes are known in organoruthenium and organoiron complexes, for example, $[Cp^*{}_2Ru_2(tBu_2SiH_2)(CO)_2]$ and $[Cp^*{}_2Fe_2(tBu_2SiH_2)(H)_2]$ ($Cp^* = C_5Me_5$).[14] Variable-temperature NMR spectroscopic analysis of **4a** and **4b** indicated that these species are stereochemically rigid over the range −80 to 20°C. Relaxation-time (T_1) measurements of the hydride signals of complex **4a** were found to be similar to those reported for Fe–H complexes at 1.34 and 0.71 s for the hydride signals at $\delta = -11.81$ and −14.52, respectively.[15] Complexes spectroscopically similar to **3a** and **4a** were detected when $PhSiH_3$ was used in place of Ph_2SiH_2 and when $[Fe_2(S_2C_3H_6)(CO)_4(dppv)]$ was substituted for **1a** (see the Supporting Information).

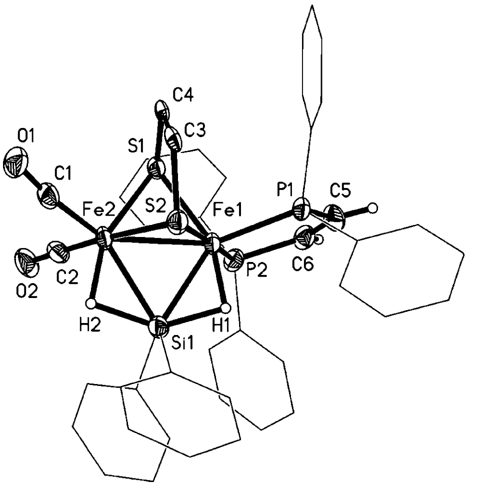


Figure 3. Structure of $[Fe_2(S_2C_2H_4)(\eta^2{:}\eta^2\text{-}SiPh_2H_2)(CO)_2(dppv)]$ (**4a**) with thermal ellipsoids set at 35% probability. Phenyl thermal ellipsoids and phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], and angles [°]: Fe1–Fe2 2.512(2), Fe1–H1 1.512(10), Fe1–S1 2.228(3), Fe1–S2 2.266(4), Fe1–P1 2.188(3), Fe1–P2 2.196(4), Fe1–Si1 2.308(4), Fe2–C1 1.786(12), Fe2–H2 1.511(10), Fe2–Si1 2.355(4), Fe2–C2 1.745(12), Si1–H1 1.625(19), Si1–H2 1.626(19); Fe2-Fe1-P1 149.36(12), Fe2-Fe1-P2 117.54(12), Fe2-Fe1-C1 141.68(39), Fe1-Fe2-Si1 58.31(10), Fe2-Fe1-Si1 56.49(10), Fe1-Si1-Fe2 65.20(11), P1-Fe1-P2 86.51(13), H1-Si1-H2 145.52(57).

In summary, this work provides the first evidence on the product of the reaction of H_2 with diiron dithiolato complexes (Scheme 2). The reactivity is readily modeled computationally and the overall patterns are confirmed using organosilanes. The results demonstrate that the diiron dithiolato carbonyl complexes, which are robust and readily prepared,[16] represent promising platforms for transformations of hydrogen-rich substrates.

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