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Protonation/Reduction of Carbonyl-Rich Diiron Complexes and the Direct Observation of Triprotonated Species: Insights into the Electrocatalytic Mechanism of Hydrogen Formation

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Abstract

Both the reduced and the protonated states of diiron dithiolate complexes, which are key intermediate species for the electrocatalytic production of hydrogen, are spectroscopically and theoretically investigated in this study. Five important states in the process of H₂ evolution are characterized. In the presence of a super acid, protonation occurs onto the Fe-Fe vector of $[(\mu$ xdt)Fe₂(CO)₆] (xdt = pdt, 1,3-propanedithiolate; edt, 1,2-ethanedithiolate; bdt, 1,2benzenedithiolate) to yield the cationic μ -H species (the C state). A single reduction at 193 K leads to the neutral species (the CE state), with similar structures for the pdt and edt bridgeheads. The CE species of the bdt analog is unstable under the same condition. An open structure resulting from the rupture of one Fe-S bond is suggested by DFT calculations. Subsequently, a second reduction induces a dramatic structural rearrangement in which the CEE state possesses an open structure exhibiting a μ -H and a μ -CO group. Protonation onto the terminal sulfur site of the CEE state affords the CEEC state, which readily converts to the parent hexacarbonyl complex accompanied by the liberation of H_2 at higher temperatures. In the presence of excess acid, the CEECC state is achieved and the third proton is coordinated to the Fe center. The Sproton and *Fe*-hydride are characterized by ¹H- and ²D-NMR spectroscopy. Electrocatalytic hydrogen production involving the CEEC and CEECC states is investigated by DFT calculation. In combination with the spectroscopic results, this information allows us to construct the possible catalytic routes and study the plausible role of the triply protonated species least explored in biomimetic catalysis.

Keywords: hydrogen evolution, electrocatalysis, hydrogenases, hydrides, protonation, iron complexes.

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Introduction

Iron hydride species have been implicated as key intermediates for energy transfer and storage in biocatalysis. For instance, in hydrogenases, the Fe hydride state is generated when the reductive production or heterolytic cleavage of molecular hydrogen takes place.¹⁻³ In biological nitrogen fixation, the FeMo cofactor stores reducing equivalents as Fe hydrides in the E₄ state,⁴⁻⁶ which are used for the subsequent activation of coordinated N₂ substrates.⁷ The Fe hydride states are transient and difficult to characterize because the enzymatic reactions involve rapid and efficient turnovers.⁸ The catalytic hydride intermediates have thus remained relatively unknown despite the substantial effort expended on their study.

Synthetic iron hydride complexes, in contrast, have been characterized and widely employed in organic syntheses since $Fe(H)_2(CO)_4$, the first transition-metal hydride complex, was prepared by Hieber in the 1930s.^{9,10} These complexes have proven to be attractive successors to homogeneous catalysts containing precious metals, as they display superior reactivity and chemo-/regio-selectivity compared to heterogeneous catalysts in a wide variety of catalytic reactions. Iron hydrido complexes play important roles in the hydrogenation,¹¹⁻¹⁵ hydrosilylation¹⁶⁻¹⁸ and hydroboration¹⁹⁻²¹ of unsaturated hydrocarbons, ketones and aldehydes, the hydrogenation of bicarbonates and carbon dioxide,²²⁻²⁴ and C-C/C-E (E = heteroatom) cross-coupling reactions.²⁵⁻²⁸

In the reversible biocatalytic cycle of proton reduction/hydrogen oxidation, three states have been characterized for [FeFe]hydrogenases with respect to the oxidation state of the Fe centers.²⁹ The most oxidized (H_{ox}) state possesses a mixed-valence Fe^IFe^{II} subset in the H-cluster.^{30,31} The reduced (H_{red}) state is achieved upon a one-electron reduction, in which an EPR inactive Fe^IFe^I configuration is realized.^{32,33} In both states, the attached [4Fe4S] subcluster in the H-cluster remains oxidized. A subsequent reduction event at a more negative potential converts the H_{red} state to the super-reduced (H_{sred}) state. In the transition, the Fe₂ subset maintains an invariant oxidation state while the [4Fe4S] cluster is singly reduced to +1.^{34,35} The H_{sred} state has been clearly identified only in eukaryotic [FeFe]hydrogenase (*Chlamydomonas reinhardtii*, *Cr*HydA1) but not in its prokaryotic homologs from *Desulfovibrio desulfuricans* (DdH) and *Clostridium pasteurianum* (CpI). It has been conjectured that the determining factor for the observation of the H_{sred} state is the inherent protein environment in distinct organisms, namely,

whether auxiliary iron-sulfur clusters (the F-cluster) are situated near the H-cluster.³⁶ In bacterial [FeFe]hydrogenases, the oxidized [4Fe4S] cluster is quickly reinstated by the neighboring F-cluster, affording the H_{red} state and making the H_{sred} state the transient species. [FeFe]hydrogenases in algae, which lack such auxiliary iron-sulfur clusters, instead terminate electron shuttling in and out of the H-cluster, making detection of the H_{sred} state possible. The H_{sred} state has been characterized as consisting of a {Fe₂} subunit bearing a bridging hydride based on recent infrared and site-selective X-ray absorption/emission spectroscopic measurements.³⁵⁻³⁷ The results of protein film voltammetry and chronoamperometry indicate that the catalytic current does not reveal a substantial decrease, and high turnover rates of hydrogen production are recorded at reduction potentials that are negative enough to reach the H_{sred} state.³⁸ These findings suggest the participation of the H_{sred} state in catalysis. Interestingly, this assignment is in sharp contrast to the common understanding that the related {Fe₂(µ-H)} moiety is energetically stable and less reactive for catalysis.³⁹⁻⁴³ Instead, the Fe₂ structure with a rotated geometry and a terminally bound hydride is responsible for H₂ production.⁴⁴

This finding regarding the H_{sred} state has rejuvenated the chemistry of synthetic bridging hydrido diiron complexes, which can be prepared by the protonation of the corresponding [(μ -xdt)Fe₂(CO)_{6-x}(L)_x]ⁿ (xdt = dithiolate linkers; L = ligands; n = number of the charge).⁴⁵⁻⁵² The {Fe^{II}(μ -H)Fe^{II}} synthetic mimics have been proposed to achieve the {Fe^I(μ -H)Fe^{II}} and {Fe^I(μ -H)Fe^{II}} states under reducing conditions, which have recently been characterized by spectroelectrochemical techniques.⁵³ These species are presumably capable of undergoing additional protonation steps to form doubly protonated⁵⁴⁻⁵⁸ and triply protonated products,^{59,60} and the subsequent liberation of H₂ from these species restores the parent Fe^IFe^I state. These proposed intermediates and mechanistic insights have only been established on the basis of electrochemical and DFT calculation results. None of them has been characterized by spectroscopy.

In this work, we describe the syntheses and characterization of a series of hydrido intermediate species possessing the {Fe₂(μ -H)} moiety. The corresponding stepwise reduced products, including the most reduced species with the {Fe^I(μ -H)Fe^I} core and its subsequent double- and triple-protonation products, were investigated by in-situ low-temperature NMR, UV-vis and FTIR spectroscopy combined with DFT calculations. The confirmation of H₂ release

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from these intermediates and recovery of the starting complexes demonstrated that all of them are active catalysts in electrocatalytic processes for hydrogen production.

Experimental Section

General Methods. All reactions were conducted using standard Schlenk and vacuum-line techniques under an atmosphere of purified nitrogen. All commercially available chemicals from Aldrich were of ACS grade and used without further purification. Solvents were of HPLC grade and were purified as follows: hexane was distilled from sodium; and dichloromethane was distilled from CaH2 under N2. Deuterated solvents obtained from Merck were distilled over 4 Å molecular sieves under N₂ prior to use. The complexes $[(\mu-xdt)Fe_2(CO)_6]$ (xdt = pdt, 1,3propanedithiolate, 1; edt, 1,2-ethanedithiolate, 2; bdt, 1,2-benzenedithiolate, 3) were prepared according to related procedures in the literature.^{61,62} [(Et₃Si)₂H][B(C₆F₅)₄] was prepared as described in the literature.⁶³ Infrared spectra were recorded on a Perkin Elmer Spectrum One using a 0.05-mm CaF₂ cell. In-situ FTIR measurements were performed using a Mettler Toledo ReactIR iC10 system equipped with a HgCdTe (MCT) detector and a 0.625-inch SiComp probe. ¹H, ¹³C{¹H}, ¹⁹F{¹H}, ²D and ¹¹B{¹H} NMR spectra were recorded on a Bruker AV-500 or DRX-500 spectrometer operating at 500, 125.7, 470.59, 76.8 and 160.46 MHz, respectively. UVvis-NIR spectra were recorded on a Varian Cary 5000 spectrophotometer using a 1-cm quartz cell. In-situ UV-vis spectra were recorded on a Varian Cary 5000 spectrophotometer equipped with a Hellma All-Quartz Immersion Probe (661.302) at a low temperature. Mass spectral analyses were performed on a Waters LCT Premier XE at the Mass Spectrometry Center in the Institute of Chemistry, Academia Sinica. Elemental analyses were performed on a Thermo Fisher EA1112 elemental analyzer. Continuous wave EPR measurements were performed at the X band using a Bruker E580 spectrometer equipped with a Bruker ELEXSYS super-high-sensitivity cavity. EPR spectra of 1μ H– 3μ H in frozen CH₂Cl₂ solution were obtained in a 4 mm JY-type EPR tube at 77 K. The following experimental conditions were used: for 1µH, a microwave power of 0.1917 mW, microwave frequency of 9.397 GHz, conversion time of 20.48 ms, receiver gain of 1002.374 and modulation amplitude of 10 G/100 kHz were used; for 2μ H, a microwave power of 0.1922 mW, microwave frequency of 9.439 GHz, conversion time of 20.48 ms, receiver gain of 10023.74 and modulation amplitude of 10 G/100 kHz were used; and for 3μ H, a microwave power of 19.14 mW, microwave frequency of 9.394 GHz, conversion time of 20.48 ms, receiver gain of 3990.525 and modulation amplitude of 10 G/100 kHz were used. EPR spectra were simulated using the WINEPR SimFonia program.

Molecular Structure Determinations. The X-ray single crystal crystallographic data collections for [1µH][B(C₆F₅)₄] (CCDC1424168), [2µH][B(C₆F₅)₄] (CCDC1424167), [3µH][B(C₆F₅)₄] (CCDC1424056) and [2µH][CF₃SO₃] (CCDC1424169) were performed at 200 (for the first three) or 150 K (for the last) on a Bruker SMART APEX CCD four-circle diffractometer with graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å) and outfitted with a low-temperature nitrogenstream aperture. The structures were solved using direct methods in conjunction with standard difference Fourier techniques and refined by full-matrix least-squares procedures. A summary of the crystallographic data for all complexes is shown in Table S1. Selected metric data of each structure are listed in the figure captions. The experimental data and the computed results are summarized in Table S2 for comparison. An empirical absorption correction (multi-scan) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically calculated positions using the riding model. All software used for diffraction data processing and crystal structure solution and refinement are contained in the SHELXTL97 program suite.⁶⁴ There are two asymmetric $1\mu H^+$ cations, two $[B(C_6F_5)_4]^-$ anions and one CH₂Cl₂ molecule in the unit cell of $[1\mu H][B(C_6F_5)_4]$. Only one of the complexes is discussed in the study. The C8 and C17 of the propane substituent on the bridging propanedithiolate group were disordered. There was one CH₂Cl₂ solvent molecule co-existing in the unit cell of $[2\mu H][B(C_6F_5)_4]$. The Cl₂ of the cosolvated CH₂Cl₂ molecule is disordered. There were two CF₃SO₃H molecules co-existing in the unit cell of [2µH][CF₃SO₃]. The F4–F6 and O8–O9 atoms of the co-solvated CF₃SO₃H molecule were disordered.

Electrochemistry. Electrochemical measurements were recorded on a CH Instruments 630C electrochemical potentiostat using a gastight three-electrode cell under N₂ at 298 K unless otherwise stated. A vitreous carbon electrode (1 or 3 mm in diameter) and a platinum wire were used as the working and auxiliary electrodes, respectively. The reference electrode was a nonaqueous Ag^+/Ag electrode (0.01 M AgNO₃/0.1 M [ⁿBu₄N][B(C₆F₅)₄]). All potentials were measured in CH₂Cl₂ solution containing 0.1 M [ⁿBu₄N][B(C₆F₅)₄]. The potentials are reported against the ferrocenium/ferrocene (Fc⁺/Fc) couple.

Computational Studies. All Kohn-Sham DFT calculations were performed using the Gaussian09 suite of the *ab initio* program⁶⁵ with a hybrid functional B3LYP^{66,67} to obtain the

geometry optimization and free energy. The Fe atom used the effective core potential and the associated basis set of LANL2DZ,⁶⁸ and the 6-31G(d,p) basis set was used for the O, S, C and H atoms. The computational solvent effect was applied using the polarizable continuum model $(PCM)^{69,70}$ for CH₂Cl₂ ($\epsilon = 8.93$) in all calculated results. All geometries were fully optimized and applied for harmonic vibrational frequency calculations under 298 K. Transition states were explored using a quasi-Newton algorithm⁷¹ to obtain a single imaginary frequency. The orbital contributions of atoms were analyzed by the QMForge program.⁷² Time-dependent DFT calculation^{73,74} was employed to investigate vertical electronic transitions using the functional/basis set combination. The first 50 excitations were calculated for the species. The computed transitions were analyzed by the SWizard program.⁷⁵ The half-bandwidths, $D_{1/2,I}$, were taken to be 3000 cm⁻¹. Validation of the proposed intermediates related to complex 2 and its derivatives based on the comparison of computed vibrational frequency with the experimental results was performed using both B3LYP and a GGA functional BP86^{76,77} with the same basis set. The results using BP86 were in agreement with the results using B3LYP. The computed IR spectra for the species, their optimized structures and the predicted vertical electronic transitions are displayed in either the main text or the supporting section.

Synthesis of $[(\mu-pdt)(\mu-H)Fe_2(CO)_6][B(C_6F_5)_4]$ ([1 μ H][B(C₆F₅)₄]). First, $[(\mu-pdt)Fe_2(CO)_6]$ (100 mg, 0.25 mmol) and [(Et₃Si)₂H][B(C₆F₅)₄] (470 mg, 0.51 mmol) were dissolved in CH₂Cl₂ (4 mL) solution at room temperature. The resulting red-orange solution was stirred for 1 hr, and the reaction was constantly monitored by FTIR spectroscopy until completion. The solution was and layered with hexane (15 mL). Orange-red crystals of $[(\mu-pdt)(\mu-pdt)]$ filtered H)Fe₂(CO)₆][B(C₆F₅)₄]·0.5CH₂Cl₂ suitable for X-ray crystallographic analysis were grown at 253 K. The yield was 210 mg (76 %). IR (CH₂Cl₂, cm⁻¹): vco 2132 (m), 2111 (vs), 2082 (s), 2069 (s), 2039 (sh); vBC 1645 (m). ¹H NMR (500 MHz, CD₂Cl₂, 298 K): -15.52 (s, 1H, FeHFe), 2.32 (q, 2H, ${}^{3}J_{HH} = 6.0$ Hz, SCH₂CH₂CH₂S), 2.77 (t, 4H, ${}^{3}J_{HH} = 6.0$ Hz, SCH₂CH₂CH₂S) ppm. ¹³C{¹H} NMR (125.77 MHz, CD₂Cl₂, 298 K): 21.73 (s, 2C, SCH₂CH₂CH₂S), 29.04 (s, 1C, SCH₂CH₂CH₂S), 123.23 (br, 4C, *ipso*-B(C_6F_5)₄), 135.84 (d, 8C, ¹ $J_{CF} = 242.5$ Hz, *m*-B(C_6F_5)₄), 137.77 (d, 4C, ${}^{1}J_{CF} = 243.1$ Hz, p-B($C_{6}F_{5}$)₄), 147.67 (d, 8C, ${}^{1}J_{CF} = 241.0$ Hz, o-B($C_{6}F_{5}$)₄), 195.88 (s, 4C, CO_{ba}), 199.98 (s, 2C, CO_{ap}) ppm. ¹⁹F{¹H} NMR (470.52 MHz, CD₂Cl₂, 298 K): -133.27 (br s, o-B(C₆F₅)₄), -164.37 (t, ³J_{FF} = 19 Hz, p-B(C₆F₅)₄), -167.58 (br s, m-B(C₆F₅)₄) ppm. ¹¹B{¹H} NMR (160.46 MHz, CD₂Cl₂, 298 K): -16.69 ppm. FAB⁺-MS: m/z 386.8 {M}⁺, 358.8

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 ${M - 1CO}^+$, 330.8 ${M - 2CO}^+$, 302.8 ${M - 3CO}^+$, 274.8 ${M - 4CO}^+$, 246.8 ${M - 5CO}^+$, 218.9 ${M - 6CO}^+$. Anal. Calcd for C₆₇H₁₆B₂Cl₂F₄₀Fe₄O₁₂S₄: C, 36.30; H, 0.73. Found: C, 36.27; H, 0.69.

Synthesis of $[(\mu-edt)(\mu-H)Fe_2(CO)_6][B(C_6F_5)_4]$ ($[2\mu H][B(C_6F_5)_4]$). First, $[(\mu-edt)Fe_2(CO)_6]$ (100 mg, 0.26 mmol) and $[(\text{Et}_3\text{Si})_2\text{H}][B(C_6F_5)_4]$ (490 mg, 0.53 mmol) were dissolved in CH₂Cl₂ (4 mL) solution at room temperature. The resulting red-orange solution was stirred for 2 hr, and the reaction was constantly monitored by FTIR spectroscopy until completion. The solution was with (18 mL). filtered and layered hexane Orange crystals of $[(\mu-edt)(\mu-$ H)Fe₂(CO)₆][B(C₆F₅)₄]·CH₂Cl₂ suitable for X-ray crystallographic analysis were grown at 253 K. The yield was 250 mg (89 %). IR (CH₂Cl₂, cm⁻¹): vco 2134 (m), 2113 (vs), 2084 (s), 2074 (s), 2036 (sh); vBC 1644 (m). ¹H NMR (500 MHz, CD₂Cl₂, 298 K): -17.93 (s, 1H, FeHFe), 3.25 (s, 4H, $S(CH_2)_2S$) ppm. ¹³C{¹H} NMR (125.77 MHz, CD₂Cl₂, 298 K): 39.08 (s, 2C, $S(CH_2)_2S$), 124.52 (br, 4C, *ipso*-B(C_6F_5)₄), 136.72 (d, 8C, ${}^1J_{CF} = 242.6$ Hz, *m*-B(C_6F_5)₄), 138.65 (d, 4C, ${}^1J_{CF}$ = 243.6 Hz, p-B(C₆F₅)₄), 148.55 (d, 8C, ${}^{1}J_{CF}$ = 240.5 Hz, o-B(C₆F₅)₄), 197.59 (s, 2C, CO_{ba}), 197.65 (s, 2C, CO_{ba}), 198.85 (s, 2C, CO_{ap}) ppm. ¹⁹F{¹H} NMR (470.52 MHz, CD₂Cl₂, 298 K): -133.95 (br s, o-B(C₆ F_5)₄), -164.56 (t, ${}^{3}J_{FF} = 19$ Hz, p-B(C₆ F_5)₄), -168.41 (br s, m-B(C₆ F_5)₄) ppm. ¹¹B{¹H} NMR (160.46 MHz, CD₂Cl₂, 298 K): -16.69 ppm. FAB⁺-MS: m/z 372.8 {M}⁺, 344.8 $\{M - 1CO\}^+, 316.8 \{M - 2CO\}^+, 288.8 \{M - 3CO\}^+, 260.8 \{M - 4CO\}^+, 232.8 \{M - 5CO\}^+, 260.8 \{M - 4CO\}^+, 200.8 \{M - 4CO\}^+$ 204.9 {M - 6CO}⁺. Anal. Calcd for C₃₃H₅BF₂₀Fe₂O₆S₂: C, 36.54; H, 0.48. Found: C, 36.69; H, 0.86.

Synthesis of $[(\mu-bdt)(\mu-H)Fe_2(CO)_6][B(C_6F_5)_4]$ ($[3\mu H][B(C_6F_5)_4]$). First, $[(\mu-bdt)Fe_2(CO)_6]$ (100 mg, 0.24 mmol) and $[(Et_3Si)_2H][B(C_6F_5)_4]$ (450 mg, 0.49 mmol) were dissolved in CH₂Cl₂ (5 mL) solution at room temperature. The resulting red-orange solution was stirred for 4 hr, and the reaction was constantly monitored by FTIR spectroscopy until completion. The solution was filtered and layered with hexane (20 mL). Dark-red crystals of $[(\mu-bdt)(\mu-H)Fe_2(CO)_6][B(C_6F_5)_4]$ suitable for X-ray crystallographic analysis were grown at 253 K. The yield was 230 mg (88 %). IR (CH₂Cl₂, cm⁻¹): vco 2135 (m), 2116 (vs), 2084 (s), 2042 (sh); v_{BC} 1645 (m). ¹H NMR (500 MHz, CD₂Cl₂, 298 K): -13.44 (s, 1H, Fe*H*Fe), 7.06 (m, 2H, S₂C₆H₄), 7.55 (m, 2H, S₂C₆H₄) ppm. ¹³C{¹H} NMR (125.77 MHz, CD₂Cl₂, 298 K): 123.49 (br, 4C, *ipso*-B(C₆F₅)₄), 130.07 (s, 2C, S₂C₆H₄), 130.95 (s, 2C, S₂C₆H₄), 135.83 (d, 8C, ¹J_{CF} = 241.6 Hz, *m*-B(C₆F₅)₄), 137.76 (d, 4C,

 ${}^{1}J_{CF} = 243.7 \text{ Hz}, p-B(C_{6}F_{5})_{4}$), 143.10 (s, 2C, *ipso*-S₂C₆H₄), 147.68 (d, 8C, ${}^{1}J_{CF} = 243.5 \text{ Hz}, o-B(C_{6}F_{5})_{4}$), 195.39 (s, 4C, CO_{ba}), 198.88 (s, 2C, CO_{ap}) ppm. ${}^{19}F\{{}^{1}H\}$ NMR (470.52 MHz, CD₂Cl₂, 298 K): -133.86 (br s, *o*-B(C_{6}F_{5})_{4}), -164.57 (t, {}^{3}J_{FF} = 20 \text{ Hz}, p-B(C_{6}F_{5})_{4}), -168.33 (br s, *m*-B(C_{6}F_{5})_{4}) ppm. {}^{11}B\{{}^{1}H\} NMR (160.46 MHz, CD₂Cl₂, 298 K): -16.66 ppm. FAB⁺-MS: m/z 420.8 {M}⁺, 392.8 {M - 1CO}⁺, 364.8 {M - 2CO}⁺, 336.8 {M - 3CO}⁺, 308.8 {M - 4CO}⁺, 280.8 {M - 5CO}⁺, 252.8 {M - 6CO}⁺. Anal. Calcd for C₃₆H₅BF₂₀Fe₂O₆S₂: C, 39.31; H, 0.46. Found: C, 39.41; H, 0.80.

Reduction of $[2\mu H][B(C_6F_5)_4]$ by cobaltocene (Cp₂Co). To a CH₂Cl₂ solution (7 mL) of $[2\mu H][B(C_6F_5)_4]$ (80 mg, 0.076 mmol) was added a CH₂Cl₂ solution (0.5 mL) of Cp₂Co (14.5 mg, 0.076 mmol) under an N₂ atmosphere at 193 K. The resulting light green solution was stirred for 10 min and monitored by in situ FTIR spectroscopy. The formation of $2\mu H$ was confirmed according to the FTIR spectrum of the resultant solution. IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2074 (m), 2045 (vs), 1995 (s). To this solution was added a CH₂Cl₂ solution (0.5 mL) of Cp₂Co (19 mg, 0.1 mmol) under an N₂ atmosphere at 193 K. The solution species was converted to the doubly reduced species $2\mu H^{*-}$ according to the in-situ FTIR spectral results. IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2040 (m), 1991 (vs), 1960 (s), 1934 (sh), 1755 (w, br).

Reduction of $[1\mu$ H][B(C₆F₅)₄] **or** $[3\mu$ H][B(C₆F₅)₄] **by cobaltcene (Cp**₂Co). Similar synthetic procedures were applied for the reduction reactions of $[1\mu$ H][B(C₆F₅)₄] and $[3\mu$ H][B(C₆F₅)₄]. For 1 μ H: IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2072 (m), 2043 (vs), 1993 (s). For the species from oneelectron reduction of 3μ H⁺: IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2077 (m), 2041 (vs), 1999 (s). For the species from two-electron reduction of 3μ H⁺: IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2045 (w), 1995 (m), 1967 (s), 1917 (vs), 1866 (vs), 1850 (sh), 1751 (w, br), 1665 (w, br). For 1μ H^{*-}: IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2042 (m), 1992 (vs), 1972 (s), 1953 (s), 1934 (m), 1752 (w, br). For 3μ H^{*-}: IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2045 (m), 1996 (vs), 1979 (s), 1963 (s), 1935 (m), 1750 (w, br).

Protonation of 2µH*⁻ with HOTf. To the CH₂Cl₂ solution of the doubly reduced species **2µH***⁻ was added 1.1 equiv. of HOTf at 193 K. The resulting orange-brown solution was stirred for 10 min. The sulfur-protonated species **2µHSH*** was generated according to the in-situ FTIR spectral results. IR (CH₂Cl₂, cm⁻¹, 193 K): vco 2067 (m), 2020 (vs), 1990 (s), 1969 (sh), 1777 (w, br). Further protonation of **2µHSH*** occurred when an additional 6 equiv. of HOTf was added by microsyringe. The triply protonated species, **2µHtHSH***⁺, was generated after 20 min according

to the in-situ FTIR spectral results. IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2130 (s), 2097 (vs), 2082 (s), 2075 (s), 2046 (m), 2036 (m).

Protonation of 1µH*⁻ **or 3µH***⁻ **with HOTf.** Similar synthetic procedures were applied for the protonation reactions of **1µH***⁻ and **3µH***⁻. The species **1µHSH*** was extremely unstable at 193 K and its IR bands could not be clearly identified. For **3µHSH***: IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2070 (m), 2024 (vs), 2005 (s), 1973 (sh), 1780 (w, br). For **3µHtHSH***⁺: IR (CH₂Cl₂, cm⁻¹, 193 K): v_{CO} 2132 (s), 2097 (vs), 2078 (s, br), 2041 (m, br).

Results and discussion

Synthesis and characterization of [(µ-xdt)(µ-H)Fe₂(CO)₆]⁺ (1µH⁺-3µH⁺)

Diiron dithiolato hexacarbonyl complexes are generally inert upon contact with conventional acids, and protonation across the Fe-Fe vector of the Fe₂ core typically occurs when the basicity of the metal center has been enriched. It has been reported that the substitution of two CO groups by PMe₃ increases the rate constant of protonation by 2 orders.⁷⁸ Recent methods developed by Heinekey et al., which allow for the preparation of protonated species of the diiron hexacarbonyl complexes,⁷⁹ require the use of either HCl gas or arenium ions in the presence of [SiEt₃][B(C₆F₅)₄] to generate super strong Brønsted acids that are used to activate the Fe-Fe bond. We adopted a modified procedure based on this methodology to synthesize hexacarbonyl bridging hydride complexes [(μ -xdt)(μ -H)Fe₂(CO)₆][B(C₆F₅)₄] (*C* state, xdt = pdt, 1,3-propanedithiolate, [**1**µ**H**][B(C₆F₅)₄]; edt, 1,2-ethanedithiolate, [**2**µ**H**][B(C₆F₅)₄]; bdt, 1,2-benzenedithiolate, [**3**µ**H**][B(C₆F₅)₄]) from their corresponding parent molecules.



Scheme 1. Reaction scheme for the protonation-reduction processes involving the diiron hexacarbonyl complexes with different bridgeheads.

The CH₂Cl₂ solution of $[(\mu-xdt)Fe_2(CO)_6]$ (xdt = pdt, 1; edt, 2; bdt, 3) was reacted with [(Et₃Si)₂H)[B(C₆F₅)₄] to afford the protonated species in high yields (Scheme 1). The following synthetic discussion on the C state focuses on the edt and bdt analogs because the complex 1μ H⁺ has been reported by Heinekey et al. The resultant FTIR spectra exhibited carbonyl signature bands at 2134 m, 2113 vs, 2084 s, and 2074 s cm⁻¹ for 2μ H⁺ and 2135 m, 2116 vs, 2084 s cm⁻¹ for $3\mu H^+$ (Figures 1 and 6, Table 1). The shift of the v(CO) bands to higher energy by ca. 78 cm⁻ ¹ relative to the parent complexes suggested the formation of the {Fe(μ -H)Fe} core with two Fe^{II} centers. The high-field ¹H-NMR signals at -17.93 and -13.44 ppm were assigned to the bridging hydrides in $2\mu H^+$ and $3\mu H^+$, respectively (Figure S2). Two sets of ¹³C-NMR resonances were recorded for $3\mu H^+$: 195.39 and 198.88 ppm, which were assigned to the basal and apical carbonyls, respectively. Three distinct ¹³C-NMR singlets were observed in $2\mu H^+$, indicating two types of basal carbonyl groups. The protons in $1\mu H^+$ - $3\mu H^+$ are extremely labile and susceptible to instantaneous removal by THF or diethyl ether solvent residues to restore complexes 1-3. Attempts to prepare adt (adt = azadithiolate) derivatives failed. Similar synthetic procedures were applied to the reactions of $[(\mu-NR(CH_2S)_2)Fe_2(CO)_6]$ (R = H, ⁿPr), yielding the Nprotonated products. Further protonation of the Fe₂ core for the formation of bridging hydride did not occur in the presence of excess super acid.



Figure 1. In-situ FTIR spectra of $2\mu H^+$ (black), $2\mu H$ (red), $2\mu H^{*-}$ (blue), $2\mu HSH^*$ (olive green), $2\mu HtHSH^{*+}$ (brick red), and 2 (pink) in CH₂Cl₂ solution at 193 K. Asterisks represent 2 in-situ generated from deprotonation of $2\mu H^+$ by moisture residue. The spectrum of 2 was collected from the solution after the warm-up experiment of $2\mu HSH^*$.

The molecular structures of $1\mu H^+-3\mu H^+$ were characterized by X-ray crystallography and are displayed in Figures 2, S4 and S5, with selected corresponding metric parameters included in

 the figure captions. All three complexes possessed a {Fe₂S₂} unit that resembled the active site of [FeFe]hydrogenase. Each Fe center within the {Fe₂S₂} core was coordinated by 3 carbonyls and 2 thiolates, and the "bent" metal-metal bond was replaced by the bridging hydride to complete the distorted octahedral geometry. The Fe-Fe distances in three species were slightly elongated in comparison with the parent complexes. The hydride was asymmetrically coordinated to two Fe centers. The hydride of 2μ H⁺ was located close to one Fe site (1.59(5) vs. 1.81(4) Å). A similar result (1.54(6) vs. 1.70(6) Å) was observed in 1μ H⁺, and the Fe-H distances of 3μ H⁺ (1.63(4) vs. 1.66(4) Å) were relatively close. The Fe-H distance determined using X-ray single crystal diffraction is generally considered to be less accurate, but the values are still reliable references for comparison. The significant difference between the two Fe-H distances in 2μ H⁺ may have been the origin of two sets of chemically non-equivalent ¹³CO resonances.



Figure 2. Molecular structure of 2μ H⁺. All hydrogen atoms except for the hydride are omitted for clarity. Selected bond length (Å) and angles (deg): Fe–Fe, 2.5477(7); Fe–S, ave. 2.2461(10); Fe–C_{CO,ap}, ave. 1.819(4); Fe–C_{CO,ba}, ave. 1.832(4); Fe1–H1, 1.81(4); Fe2–H1, 1.59(5); S–Fe–S, ave. 80.35(4); S–Fe–Fe, ave. 55.45(3); Fe–S–Fe, ave. 69.11(3).

Electrochemistry and chemical reductions of 1µH⁺-3µH⁺

The electrochemical properties of 1μ H⁺- 3μ H⁺ were investigated in CH₂Cl₂ solution. Cyclic voltammograms of 1μ H⁺ showed a quasi-reversible one-electron reduction event ($i_{pa}/i_{pc} = 0.9$) at $E_{1/2}^{red} = -0.69$ V ($E_{pc} = -0.74$ V, $E_{pa} = -0.64$ V) at 200 K and a fully irreversible reduction process at 298 K, as shown in Figures 3 and S6. Similar electrochemical behaviors were recorded for the analogs, for which the reductions occurred at -0.68 V ($E_{1/2}^{red}$; $E_{pc} = -0.72$ V, $E_{pa} = -0.64$ V) at 210 K for 2μ H⁺ and -0.67 V (E_{pc}) at 213 K for 3μ H⁺. The redox process was less reversible for the latter ($i_{pa}/i_{pc} = 0.61$) because 3μ H was relatively unstable and readily regenerated 3 during hydrogen production (vide infra). There is a significant concept to be addressed here: in contrast to the corresponding parent complexes, the protonated complexes displayed insignificant variations in reduction potentials despite their different bridgeheads. Given the electron-withdrawing ability of the bdt unit, the potential for electron addition to 3 was decreased by at least 300 mV relative to the pdt and edt analogs. The current electrochemical results, however, suggested that the Fe^{II}₂ core in 1μ H⁺- 3μ H⁺ stemming from the formation of the hydride group played a greater role in the reduction than the bridgehead.



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Figure 3. Cyclic voltammograms of 1μ H⁺ (blue line, 200 K), 2μ H⁺ (red line, 210 K) and 3μ H⁺ (black line, 213 K) in CH₂Cl₂ solution under N₂ atmosphere ([complex] 1 mM, v = 100 mV s⁻¹, 1 mm vitreous carbon electrode, 0.1 M [*n*-Bu₄N][B(C₆F₅)₄]).

The chemical reduction of $2\mu H^+$ by 1 equiv. of Cp₂Co (cobaltocene) in CH₂Cl₂ solution at 193 K afforded $[(\mu-edt)(\mu-H)Fe_2(CO)_6]$ (2µH, the *CE* state). The IR profile of 2µH exhibited three carbonyl bands at 2074 m, 2045 vs and 1995 s cm⁻¹ (Figure 1), which was closely similar to the IR profile of complex 2 (2073 m, 2033 vs, 1996 s, 1989 s cm^{-1} at 193 K) with a slight energy shift. Similar FTIR spectral results were observed regardless of the bridgehead identity. At 193 K, a set of v(CO) peaks for 1μ H was recorded at 2072 m, 2043 vs and 1993 s cm⁻¹. For the one-electron reduction of $3\mu H^+$, these peaks were observed at 2077 m, 2041 vs and 1999 s cm⁻¹. These carbonyl vibrational bands were comparable to the ones for the corresponding parent molecules at 193 K: 2075 m, 2034 vs, 1999 s, 1993 s cm⁻¹ for 1; and 2079 m, 2041 vs, 2002 s cm^{-1} for 3. The affirmative evidence for the formation of $2\mu H$ and $1\mu H$ was a color change from orange-yellow to green. The electronic spectrum of $2\mu H^+$ at 193 K revealed one visible band at 458 ($\varepsilon = 500 \text{ M}^{-1} \text{ cm}^{-1}$) nm, which was readily replaced by two new transitions at 451 ($\varepsilon = 1.700$ M^{-1} cm⁻¹) and 625 ($\varepsilon = 740 M^{-1} cm^{-1}$) nm upon contact with the reducing agent (Figure 4). Similarly, 1µH exhibited two visible transitions at 457 ($\varepsilon = 2,700 \text{ M}^{-1} \text{ cm}^{-1}$) and 666 ($\varepsilon = 1,300$ M^{-1} cm⁻¹) nm. Figure 5 displays the 77 K EPR spectra of 1μ and 2μ in frozen CH₂Cl₂ solution. A rhombic signal with hyperfine interactions with hydride was recorded, in which g_{XYZ} = 2.0083, 1.9776, 1.9705, A_{xyz} = 2.1, 2.1, 3.9 G for 1µH and g_{xyz} = 1.9924, 1.9696, 1.9637, A_{xyz} = 5, 5, 4.1 G for **2µH**.



Figure 4. Electronic spectra of 1μ H (blue line) and 2μ H (red line) in CH₂Cl₂ solution at 193 K under N₂ atmosphere.



Figure 5. CW X-band EPR spectra (black line) of 1μ H (left panel) and 2μ H (right panel) recorded in frozen CH₂Cl₂ solution at 77 K. The red line represents the simulation result.

Lomoth et al. recently derived a conclusion from the photolysis results of $[(\mu-bdt)Fe_2(CO)_6]$ in the presence of sensitizers and acids with $pK_a \leq 12.7$ that $[Fe_2(bdt)(CO)_6]$ and $[Fe_2(bdt)(CO)_6H]$ exhibit similar IR and UV-vis spectra.⁸⁰ $[Fe_2(bdt)(CO)_6H]$ possesses a similar structure to **1µH** and **2µH**. From our initial in-situ FTIR results, it is tempting to state that the one-electron reduced species of **3µH**⁺ could be **3µH**, though the DFT calculations suggested that **3µH**^{*} was thermodynamically more favorable. The species **3µH**^{*} was formulated as $[(\mu,\kappa^2-bdt)(\mu-H)Fe_2(CO)_6]$ with the rupture of one Fe-S bond, and the optimized structure exhibited the bridging hydride. The details of the calculation results are discussed in the following paragraph.

The species $3\mu H^*$ was not as stable as $1\mu H$ or $2\mu H$, which exhibited no detectable decomposition in CH₂Cl₂ solution at 193 K. Under the same conditions, $3\mu H^*$ partially converted to 3 and produced gas bubbles (Figure 6); such evolution did not occur until higher temperatures for the pdt and edt analogs. In addition, trace amount of $3\mu H^{*-}$ possibly generated via disproportionation was detected. The formation of molecular hydrogen was confirmed by GC

analysis, and the yield of H_2 was estimated to be approximately 60 % after the resulting solution was kept at 193 K for 5 minutes. The yield was increased to approximately 98 % in 30 minutes, indicating that the temperature was not low enough to prevent $3\mu H^*$ from decomposing. The conversion could be obscured in the in-situ FTIR spectra. A prominent difference was observed in the electronic and EPR spectra for the one-electron reduction of $3\mu H^+$ relative to $1\mu H$ and 2μ H. The solution from the singly reduced reaction of 3μ H⁺ exhibited only one detectable visible band at 459 ($\varepsilon = 1.200 \text{ M}^{-1} \text{ cm}^{-1}$) nm in addition to one UV absorption at 333 ($\varepsilon = 11,400$ M^{-1} cm⁻¹) nm (Figure S8). These two transitions were close to the energy transitions of **3**: 333 (ϵ $= 20,600 \text{ M}^{-1} \text{ cm}^{-1}$) and 457 ($\varepsilon = 1,000 \text{ M}^{-1} \text{ cm}^{-1}$) nm. The absence of the band at ~ 650 nm in the observed electronic spectra may have suggested that 3 was the dominant species in solution even at 193 K. The single reduction of $3\mu H^+$ displayed a weak EPR signal at 77 K relative to the strong EPR signals for 1µH and 2µH (Figure S9), which supports the suggestion based on the UV-vis results. Figure S10 compares the IR and UV-vis spectra of the optimized structures of 3, $3\mu H^+$ and $3\mu H^*$. Both species, 3 and $3\mu H^*$, possessed similar vibrational patterns with similar energies. This result suggests that it was difficult to characterize $3\mu H^*$, especially when the major species in solution was 3. Time-dependent DFT (TD-DFT) calculations of the geometry of the ground state predicted electronic excitations between 550 and 800 nm for 3μ H*. By contrast, **3** did not possess noticeable transitions in the same region. No distinct assignment upon the single reduction of $3\mu H^+$ could be made based on the experimental observations. Failure to observe the excitation signature of $3\mu H^*$ at approximately 650 nm in the experiments can be rationalized by the small extinction coefficient and the short lifetime of $3\mu H^*$ in solution at 193 K.





Figure 6. In-situ FTIR spectra of $3\mu H^+$ (black), the single reduction of $3\mu H^+$ (red), the double reduction of $3\mu H^+$ (blue), and $3\mu H^{*-}$ (olive green) in CH₂Cl₂ solution at 193 K. The species from the double reduction of $3\mu H^+$ contain $3\mu H^{*-}$ and $[(\mu,\kappa^2-bdt)(\mu-CO)Fe_2(CO)_5]^{2-}$. The asterisks denote $[(\mu,\kappa^2-bdt)(\mu-CO)Fe_2(CO)_5]^{2-}$. The signal of 1645 cm⁻¹ is from $[B(C_6F_5)_4]^-$.

The 35-electron complex $2\mu H$ was susceptible to additional reduction at 193 K for the formation of a new species (the CEE state) that possessed an IR profile of 2040 m, 1991 vs, 1960 s, 1934 sh and 1755 w cm⁻¹ (Figure 1). This new species could also be yielded by the reaction of $2\mu H^+$ with 2 equiv. of Cp₂Co. The product was deduced to be a doubly reduced complex. The magnitude of the red shift of the carbonyl bands due to the single reduction of 2μ H was smaller than the magnitude of the shift from the conversion of $2\mu H^+$ to $2\mu H$ ($\Delta v \approx 34$ vs. 58 cm⁻¹). In association with the presence of the bridging CO peak at 1755 cm⁻¹, the molecular structure of the doubly reduced $2\mu H^+$, which was designated as $2\mu H^{*-}$, was assigned to a {Fe₂S₂} core in which one thiolate, one hydride and one carbonyl spanned between two metal sites and one thiolate was terminally coordinated to one Fe site. The $\{(\mu,\kappa^2-\text{edt})(\mu-\text{CO})(\mu-\text{H})\text{Fe}_2\}$ skeleton of $2\mu H^{*-}$ resembled the structural feature in $[(\mu,\kappa^2-bdt)(\mu-PPh_2)(\mu-H)Fe_2(CO)_5]$ with a PPh₂ bridging group instead of the bridging CO.⁸¹ Both species revealed similar IR signatures in the terminal CO region, though the IR signature was blue shifted for 2µH*-. The formulation of the complex $2\mu H^{*-}$ was supported by computational studies as $[(\mu,\kappa^2-edt)(\mu-H)(\mu-CO)Fe_2(CO)_5]^{-}$ (vide infra). Similar IR profiles were recorded for the singly reduced 1μ and 3μ . The resulting species, $1\mu H^{*-}$ and $3\mu H^{*-}$, had identical structures to $2\mu H^{*-}$. The electronic spectra of $1\mu H^{*-}-3\mu H^{*-}$ were featureless in the region of 550–800 nm. The species $1\mu H^{*-}-3\mu H^{*-}$ were degraded to 1–3, respectively, and molecular hydrogen when the temperature was raised to room temperature.

It was not possible to quantitatively generate $3\mu H^{*-}$ from $3\mu H^+$ under reducing conditions at low temperature. The in-situ FTIR spectra for the two consecutive one-electron reduction reactions of $3\mu H^+$ at 193 K revealed the presence of $3\mu H^{*-}$, which was masked by $[(\mu,\kappa^2-bdt)(\mu-CO)Fe_2(CO)_5]^{2-}$. The latter was the major species (~80 %) in solution. We used an alternative procedure to obtain the distinct IR profile of $3\mu H^{*-}$. The complex $[(\mu,\kappa^2-bdt)(\mu-CO)Fe_2(CO)_5]^{2-}$ was synthesized first in CH₂Cl₂ solution at 193 K and reacted with HOTf

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(trifluoromethanesulfonic acid) to afford $3\mu H^{*-}$. The resulting carbonyl bands at 2045 m, 1996 vs, 1979 s, 1963 s, 1935 m and 1750 w cm⁻¹ were similar to the bands of $1\mu H^{*-}$ and $2\mu H^{*-}$, suggesting that $3\mu H^{*-}$ had enhanced stability relative to $3\mu H^{*}$ in CH₂Cl₂ solution at 193 K.

Protonation of 1µH*--3µH*-

The presence of the terminally coordinated thiolate (the S^t site) in $1\mu H^{*-}-3\mu H^{*-}$ provided an opportunity to examine the capability of the S^t site for proton attachment as it occurred in $[(\mu,\kappa^2-bdt)(\mu-PPh_2)(\mu-H)Fe_2(CO)_5]$.^{81,82} The reaction of $1\mu H^{*-}-3\mu H^{*-}$ with one equiv. of HOTf at 193 K afforded an *S*-protonated product $[(\mu,\kappa^2-xdtH)(\mu-H)(\mu-CO)Fe_2(CO)_5]$ ($1\mu HSH^*-3\mu HSH^*$, the *CEEC* state), which was characterized by in-situ FTIR spectroscopy. Species $1\mu HSH^*$ was extremely unstable even at this temperature. Complexes $2\mu HSH^*-3\mu HSH^*$ exhibited similar IR patterns to $2\mu H^{*-}-3\mu H^{*-}$ but were shifted by an average of 28 cm⁻¹ to a higher energy. These results were consistent with previous observations on the protonation of the S^t site.

The consecutive protonation of $2\mu HSH^*$ occurred in the presence of extra amounts of acid at 193 K, leading to a new species (the "3H" species, the CEECC state) possessing v(CO) bands at 2130 s, 2097 vs, 2082 s, 2075 s, 2046 m, 2036 m cm⁻¹. The disappearance of the CO band in the lower energy region indicated a structural rearrangement upon the addition of the third proton. All carbonyl groups were thus assigned to be terminally ligated. Compared to 2μ HSH*, the shift of the IR profile to higher energy by ca. 63 cm⁻¹ suggested that two Fe centers were converted to the Fe^{II}Fe^{II} state due to the formation of an additional Fe-hydride. The S-proton and the 2 Fe-hydrides were characterized by NMR spectroscopy. The SD resonance of 2µHSD* was observed at 2.3 ppm at 193 K in CH₂Cl₂ solution (Figure S11). This signal retained the same chemical shift when additional DOTf was injected into a CH_2Cl_2 solution of $2\mu HSD^*$ at 193 K, while an up-fielded ²D-NMR signal located at -12.98 ppm replaced the μ H of **2µHSD*** at -12.38 ppm. Additionally, a ¹H-NMR signal of -13.0 ppm was identified for the same species. The ${}^{1}\text{H}/{}^{2}\text{D-NMR}$ resonances at ~ -13 ppm for the multi-hydride species, which are displayed in Figure 7, may have originated from the hydride in either bridging or terminal fashion.⁸³ We assigned the "3H" species to $[(\mu,\kappa^2-\text{edtH})(\mu-H)(t-H)Fe_2(CO)_6]^+$ (2µHtHSH*+) with the assistance of computational studies (vide infra). These results suggested that the exchange between the terminal and bridging hydrides/deuterides was fast on the NMR time scale at this

temperature. The species 2μ HtDSD^{*+} was also characterized by electrospray ionization mass spectrometry (ESI-MS) analysis. High-resolution ESI-MS (positive mode) revealed a prominent peak at m/z = 1056.8368 (Figure S12), which corresponded to $[(\mu,\kappa^2-\text{edtD})(\mu-\text{H})(\text{t-}D)\text{Fe}_2(\text{CO})_6]^+ \cdot \text{HB}(\text{C}_6\text{F}_5)_4$ (calcd = 1056.8389). The observed isotopic pattern of $[(\mu,\kappa^2-\text{edtD})(\mu-\text{H})(\text{t-}D)\text{Fe}_2(\text{CO})_6]^+ \cdot \text{HB}(\text{C}_6\text{F}_5)_4$ was in excellent agreement with the simulated one.





Figure 7. Variable-temperature (A) 2 D and (B) 1 H NMR spectra from the in-situ reaction of 2μ HSD* with DOTf in CH₂Cl₂ solution. The solvent signal is indicated as an asterisk.

It was observed that 2μ HtHSH^{*+} had higher stability in solution at low temperature compared to 2μ HSH^{*}, which slowly transformed at 203 K. In contrast, for 2μ HtHSH^{*+}, no detectable change was observed for days under the same conditions. We attempted to crystallize 2μ HtHSH^{*+} and successfully grew orange-red crystals at 193 K over the course of 2 months. These crystals were structurally characterized as [(μ -edt)(μ -H)Fe₂(CO)₆][OTf] ([2μ H][OTf]), as shown in Figure S13. The species 2μ H⁺ in OTf salt was extremely unstable and was readily deprotonated to 2 when dissolved in CH₂Cl₂ solution at 205 K. This result was consistent with the understanding that the Fe₂ core in a hexacarbonyl complex is electronically deficient and cannot accept protons unless a super acid is employed.

Computational studies

Theoretical studies were undertaken to make better assignments, although the spectroscopic evidence provided a data point for conjecturing the structures of the intermediates. The calculation work mainly focused on the protonation/reduction intermediates of complex 2, as similar intermediates were generated for its analogous complexes. A summary of the solvent-corrected free energy for all computed species and transition states is provided in the supporting materials.

DFT calculations were employed to obtain the optimized structures and free energies of all possible intermediates from the *C* to the *CEECC* species. Herein, we defined $2\mu H^+$ as the *C* species resulting from protonation (the chemical step) of the parent complex 2, $2\mu H$ as the *CE* species resulting from the initial protonation and subsequent reduction (referred to as the related electrochemical step in cyclic voltammetry) of complex 2, and so forth. We initially compared the experimental structural parameters of 2 and $2\mu H^+$ with the corresponding calculated values because the structures of both species have been characterized by X-ray single crystallography. Consistent results were obtained, suggesting that the applied functional/basis set was valid for this purpose. The energetically lowest-lying species were used as the reference ground to make an initial guess for the following state. In addition, a validation check was performed between the experimental and computational carbonyl stretching frequencies, resulting in a linear relationship⁸⁴ that indicated that the calculated models made reliable claims regarding the corresponding intermediate species. Finally, mechanisms of two hydrogen-evolution processes are discussed in detail.

Computed structures and relative stabilities of potential intermediates

The *CE* state: For the one-electron reduced species of $2\mu H^+$, several isomers were proposed. Only two of them, $2\mu H$ and $2\mu H^*$, were investigated, as shown in Figure 8. The plausible third species with a terminal hydride and a μ -CO group was eliminated on the basis of the experimental FTIR data. Complex $2\mu H$ retained the structure of $2\mu H^+$, though the Fe-Fe bond was elongated by 0.17 Å. The μ -H was slightly displaced from the symmetric position to one Fe

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center. Complex $2\mu H^*$ was a species featuring an open structure with one thiolate terminally coordinated to one Fe center, which resulted from the rupture of one Fe-S bond. The assumption of $2\mu H^*$ is still under consideration because the Fe-S bond breakup or elongation has been experimentally observed or theoretically predicted, respectively, in the reduced products of [(μ -xdt)Fe₂(CO)₆] (xdt = thiolate bridges).⁸⁵⁻⁹³ A comparison of the free energy of the optimized structures indicated that the species $2\mu H$ was thermodynamically more stable than $2\mu H^*$ by +10.28 kcal mol⁻¹. We therefore assigned the *CE* state as $2\mu H$, which was consistent with the previous conclusion concerning the protonated species of [(μ -xdt)Fe₂(CO)₆]^{-.57,94} Earlier, based on the DFT calculations, De Gioia et al. and Hall et al. later proposed the best candidate for the *EC* product in proton binding of the mono-reduced complex to be [(μ -xdt)(μ -H)Fe₂(CO)₆], which preserves the typical {(μ -xdt)Fe₂} core observed in $2\mu H$. For the pdt analog, a similar result was obtained in favor of $1\mu H$ by +10.09 kcal mol⁻¹ (Figure S14). In contrast, the open structure of $3\mu H^*$, designated [(μ , κ^2 -bdt)(μ -H)Fe₂(CO)₆], was more stable than the structure of $3\mu H$ by +9.48 kcal mol⁻¹.



Figure 8. Computed structures of the *CE* species for the edt and bdt analogs. The free energy difference is reported in kcal mol^{-1} . All hydrogen atoms except for the hydride are omitted for clarity. Color scheme: Fe, dark green; S, yellow; O, red; C, grey and H, white.

The *CEE* **state:** The subsequent reduction of the *CE* state led to a Fe(I)Fe(I) species, for which we considered two electronic states: the diamagnetic state (the singlet state) and the paramagnetic state (the triplet). Throughout the discussion, the multiplicity of this species was one if not otherwise specified. The geometry of the resulting species was distorted to a structure featuring a lengthened Fe-Fe distance of 3.352 Å when the reduced $2\mu H$ was optimized. The

hydride was converted to the terminal mode from the bridging mode and remained in the location underneath the Fe-Fe vector, as displayed in Figure 9. The new species was thus designated as $2tH^-$. For the electronic isomer $2\mu H^-$ (M = 3), the optimized structure was similar to $2\mu H$. Next, two electronic isomers of $2\mu H^*$ were also investigated. A Fe₂ core bearing asymmetric bridging hydride and carbonyl groups was obtained for $2\mu H^{*-}$. A one-electron addition to $2\mu H^*$ increased the Fe-S distances by 0.04 Å while decreasing the Fe-Fe distance by 0.12 Å. Optimization of $2\mu H^{*-}$ (M = 3) resulted in the related {(μ -H)Fe₂S₂} skeleton of $2\mu H^-$ (M = 3) due to restoring the Fe-S bond, which had an almost identical energy. Among these four possible isomeric products, $2\mu H^{*-}$ was the most favorable species. The species $2\mu H^-$ (M = 3) and $2tH^-$ were less stable by +7.97 and +15.74 kcal mol⁻¹, respectively.

We also considered two less plausible scenarios. First, $2\mu H(CO)_5^-$, a high-energy, mono-CO-eliminated species with $\Delta G^{CEE} = +12.23$ kcal mol⁻¹, was produced. For the triplet state, an open structure resulting from splitting the Fe-S bond, which was designated as $2\mu H(CO)_5^{*-}$ (M = 3), was found by convergence. This structure was more thermodynamically favorable than its electronic congener but was still destabilized by +2.34 kcal mol⁻¹ compared to $2\mu H^{*-}$. The attractive characteristic of both species was the presence of an apical vacant site, which could facilitate succeeding protonation steps. The plausible presence of $2\mu H(CO)_5^-$ and $2\mu H(CO)_5^{*-}$ (M = 3) in solution was excluded because these species did not exhibit the μ -CO signature observed in the experiments.



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Figure 9. Computed structures of the *CEE* species for the edt analog. The free energy difference is reported in kcal mol⁻¹. All hydrogen atoms except for the hydride and formyl hydrogen are omitted for clarity. Color scheme: Fe, dark green; S, yellow; O, red; C, grey and H, white.

Exploration of the formyl species $[(\mu-edt)Fe_2(CO)_5(C(O)H)]^-$ (2H^{CO-}) proved fruitless. First, to produce the formyl species, an intramolecular rearrangement from its anionic hydride analogs was attempted. De Gioia et al. previously reported that the conversion from $[(\mu-pdt)(\mu-pdt)]$ H)Fe₂(CO)₆]⁻ to its formyl tautomer requires overcoming an energy barrier of +11.4 kcal mol^{-1,57} suggesting a slow conversion. It could be reasonably assumed that the kinetic barrier of the possible related transformation for the edt analog was as high as in the pdt species, although the calculated free energy of $2H^{CO-}$ was only +3.24 kcal mol⁻¹ higher than $2\mu H^{*-}$. Second, it has been reported that the formyl complex of the pdt analog is solely synthesized from the reaction between the hexacarbonyl complex and metal hydrides.⁵⁴ It was thus reasonable to propose that 2H^{CO-} could be prepared via a similar synthetic procedure. From the experiments, it was found that $2\mu H^{*-}$ did not react by hydrogen evolution when exposed to excess HOTf in solution. This result revealed the acidic character of the bridging hydride in the species. Consequently, the hydride attack of the carbonyl group to form the formyl species was not favored. The last piece of evidence is that the FTIR data lacked the corresponding formyl vibrational band. In the current study, it was concluded in light of theoretical and experimental evidence that the intramolecular isomerization of $2\mu H^{*-}$ to $2H^{CO-}$ was not feasible.

The *CEEC* state: Figure S15 displays the highest occupied molecular orbital (HOMO) of $2\mu H^{*-}$, with significant contributions from the Fe₂ (44.2 %), terminal thiolate (S^t, 18.9 %) and bridging CO (CO^b, 17.6 %). These electron-rich sites are prone to protonation. The initial models bearing two hydrides attached to the Fe₂ core ultimately converged to structures consisting of one μ -H and one terminal hydride (t-H) in 2μ HtH^{s*} and 2μ HtH^{a*} (Figure 10). The species with the t-H and S^t groups on the same side relative to the plane of the FeS^µFeH^µ rhomb was designated 2μ HtH^{s*} and the opposite side was designated 2μ HtH^{a*}. The t-H group, along with 2 CO and the μ -S groups, was coordinated in the equatorial position about the distal Fe with respect to the S^t site. One another isomer composed with a t-H and a S^t-proton was designated 2tHSH^{in*}. Protonation onto the μ -CO group afforded the formyl species 2μ HtH^{CO} and restored the compact

structure with 2 bridging thiolates. These 34-electron species 2μ HtH* (2 isomers), 2tHSH^{in*} and 2μ HH^{CO} were not as stable as the other isoelectronic isomer 2μ HSH*, the structure of which possessed a protonated S^t site. It has been shown that the terminal thiolate in complexes with structural resemblance to 2μ H*⁻ exhibits enhanced nucleophilicity⁹⁵ and facilitates the coordination of the S^t site to metal ions and substrates. The predicted S^t-protonation was in good agreement with the FTIR data that showed the same band pattern as in 2μ H*⁻ but hypsochromically shifted by ca. 29 cm⁻¹. The protonated 2μ H*⁻ (i.e., the *CEEC* state) was accordingly assigned to 2μ HSH*.



Figure 10. Computed structures of the CEEC species for the edt analog. The free energy difference is reported in kcal mol⁻¹. All hydrogen atoms except for the hydride, sulfur proton and formyl hydrogen are omitted for clarity. Color scheme: Fe, dark green; S, yellow; O, red; C, grey and H, white.

The *CEECC* **state:** The last step to the formation of the "3H" species was the subsequent protonation of the doubly reduced di-protonated neutral complex. The existence of triply protonated species in electrocatalytic cycles has been proposed by Talarmin^{59,60} and Jones et al.,⁵⁸ but none of these species have been experimentally characterized to date. De Gioia et al. performed a survey of the possible structures using DFT calculations.⁶⁰ The optimized structures with the highest stability for both of the cationic and neutral tri-protonated pdt species consisted

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of a $\{Fe_2S\}$ moiety, as shown in Figure S16, in which one thiolate group bridged 2 Fe centers and the other was protonated as well as detached from the Fe₂. Regarding the ligation mode of the hydrides, both were coordinated to the metals in the bridging mode in the cationic species, while one of them was the terminal hydride in the neutral species.

Taking De Gioia's models as valuable references, we first investigated several potential candidates bearing the Fe_2 core with oxidation states other than Fe(I)Fe(I), as the observed spectroscopic data indicate that the Fe centers are oxidized upon addition of the third proton (Figure 11). Two species, 2µHtH^sSH^{*+} and 2µHtH^aSH^{*+}, were of similar free energy, although the former was slightly stabilized by +1.58 kcal mol⁻¹. The structural variation between these species arose from the positions of the t-H and S^t-H groups relative to the plane of the FeS^µFeH^µ rhomb. The species with both H entities on the same side was designated 2µHtH^sSH^{*+} and the opposite side was designated 2µHtH^aSH^{*+}. All S-protonated complexes other than 2µHtHSH^{*+} were high-energy species. The protonated thiolate retained the bridging functionality in $2(tH)_2SH^+$ and was detached from the Fe₂ core in $2\mu HtHSH^{\#+}$. The relative free energy for both species was greater than +23 kcal mol⁻¹. Though one species, $2(\mu H)_2 SH^{\#+}$, had improved stability and a structure containing a protonated thiolate pendant and 2 µ-H ligands, it was less favorable by +9.2 kcal mol⁻¹. The singly terminal hydride-hydrogen adduct species, $2tH_2tH^+$, was comparatively disfavored by +21.78 kcal mol⁻¹. For the sake of comparison, we also estimated the free energy of the optimized geometry of $2\mu HSH_2^{*+}$, which contained the S^t site with 2 proton attachments. The highest free energy value of $2\mu HSH_2^{*+}$ relative to the other analogs strongly argued against double protonation onto the S^t site. A similar implication could be drawn from the previous observation: the mono-protonated S^t group in $[(\mu,\kappa^2-bdtH)(\mu-$ PPh₂)(µ-H)Fe₂(CO)₅] was highly acidic and readily de-protonated by exogenous THF molecules in CH₂Cl₂ solution.⁸¹



Figure 11. Computed structures of the *CEECC* species for the edt analog. The free energy difference is reported in kcal mol⁻¹. All hydrogen atoms except for the hydride, sulfur proton and coordinated hydrogen are omitted for clarity. Color scheme: Fe, dark green; S, yellow; O, red; C, grey and H, white.

Validation of the computed intermediates via vibrational frequency comparison

The accurate assignment of every state during the process of H₂ evolution was performed based on the combined results of the in-situ spectroscopic and DFT calculation studies: the *CE* state was 2μ H, the *CEE* state was 2μ H^{*-}, the *CEEC* state was 2μ HSH^{*} and the *CEECC* state was 2μ HtH^sSH^{*+} (Figure S17). All associated species were of the lowest free energy among the potential candidates for each state. The IR vibrational profiles of the carbonyls for the selected optimized structures were consistent with the corresponding results of the in-situ measurements. In addition, the calculated frequencies of the vibrational bands exhibited high correlations with the experimental data. Figure S19 displays a linear relationship ($R^2 = 0.9953$) between the computed and measured data for all species in the catalytic cycle. We also used BP86 to validate the results concerning complex **2** and its related species. These results are summarized in Table S8. Figure S20 shows a linear relationship between the experimental and computed data of the IR vibrational profiles. The results were consistent with the findings obtained using B3LYP. For the remaining isomers at each state, the averaged values of their

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calculated vibrational bands in energy may have been similar, though the number and intensity of peaks in the IR profiles did not correspond to the experimental results (Figure S18). A linear correlation could not be achieved.

Mechanistic studies on H₂ evolution

H₂ evolution via 2µHSH* (the "2H" species) and 2µHtH^sSH^{*+} (the "3H" species). The complex 2µHSH* is one of the key intermediates in catalysis, as rapid gas evolution was observed from the CH₂Cl₂ solution of 2µHSH* when the temperature was higher than 208 K. The only FTIR-detectable species in solution was ultimately complex 2 (Figure 12), and the gas content analyzed by GC was molecular hydrogen. We employed DFT calculation to elucidate the plausible mechanism. Two intramolecular pathways are initially investigated for the reaction. As shown in Scheme S1, one intermediate and two transition states were anticipated in the transition to a plausible η^2 -H₂ adduct species **2tH₂***. To facilitate the formation of the transient intermediate, the S^t-H and µ-H groups are required to be in close proximity. The large kinetic barrier (25.62 kcal mol⁻¹) suggested a slow rate for the H₂ evolution and the regeneration of 2. The similar results were reported for the related species involving this type of the pathway with the energy barrier of 17.8-25.85 kcal mol⁻¹.^{57,94} We found out that the other pathway with the participation of **2tHSH**ⁱⁿ* was the more feasible route, depicted in Figure 13. A smaller energy barrier of 16.95 kcal mol⁻¹ was estimated. In the transition to **2tHSH**^{in*}, the μ -H and μ -CO groups were changed to the terminal fashion. It has to be noted here that aside from $2\mu HSH^*$, 2μ HtH^{S*} (i.e. [2H₂(f)] in the literature)⁹⁴ generated via the CEEC or ECEC mechanism was proposed to be the other possible intermediate for H₂ formation according to the corresponding lower energy transition state. It was indicated that a lower energy pathway for the intramolecular mechanism could be achieved if $[2H_2(f)]$ was present. Based on our low temperature spectral results of the CEEC routes, 2µHtH^S* was not observed except for 2µHSH*. In the conversion of 2µHSH* to 2 at 213 K (Figure S22), we did not detect CO signals in higher energy (> 2090 cm⁻ ¹). The energy barrier for tautomerization of $2\mu HSH^*$ to $2\mu HtH^{S*}$ was not reported in the literature and not found in this work. It is suggested that the catalytic proton reduction does not carry out via the $2\mu HSH^* \rightarrow 2\mu HtH^{S*} \rightarrow 2$ route. Consequently, we suggest that $2\mu HtH^{S*}$ does not participate in the catalysis.



Figure 12. In-situ FTIR spectra of the conversion from 2μ HSH* (blue line) to 2 (red line) in CH₂Cl₂ solution upon temperature increase from 193 K to 298 K. The grey traces show the progressing of the spectral changes.



Figure 13. Free energy profile for hydrogen formation from 2µHSH* to 2 via 2tHSH^{in*}.

Temperature-sensitive H₂ evolution behavior was also experimentally observed for the "3H" species. The species 2μ HtH^sSH^{*+}, in contrast to 2μ HSH^{*} (the "2H" species), remained stable in CH₂Cl₂ solution for hours when the temperature was kept below 220 K. The species 2μ H⁺ was characterized as the end product in solution when 2μ HtH^sSH^{*+} was completely depleted (Figure 14). Several mechanisms via the intramolecular pathway are possible for the H₂ evolution with the involvement of 2μ HtH^sSH^{*+}. They are discussed in the supporting information section (Scheme S2) except for the most thermodynamically and kinetically feasible route as depicted in Figure 15. The key species 2μ HtH₂^{in*+} that accounted for the formation of H₂ was formed from bond formation between t-H and *S*-H within the FeS^µFeS^tH^µ packet via the energetically high-lying transition states. Similar to 2μ HtSH^{*+}, the hydrogen formation from 2μ HtH^sSH^{*+} to 2μ H⁺ was kinetically hindered.



Figure 14. In-situ FTIR spectra of the conversion of 2μ HtH^sSH^{*+} (blue line) in CH₂Cl₂ solution upon temperature increase from 193 K to 298 K. The grey traces show the progressing of the spectral changes. The red line represents the spectrum of the resultant solution. It contains 2μ H⁺ and 2 as the minor and major species, respectively. The symbols of star (*) and triangle (Δ) denote 2μ H⁺ and 2, respectively. The solution contains OTf⁻ anions that readily deprotonate 2μ H⁺, which depletes its concentration.



Figure 15. Free energy profile for hydrogen formation from 2µHtH^sSH^{*+} to 2µH⁺.

It should be noted that both H₂ evolution processes involving **2µHSH*** and **2µHtH*SH***+ via the intramolecular pathway showed a relatively high barrier of ~ 17 and ~ 24 kcal mol⁻¹, respectively, which corresponds to a rate constant of 2.65 and 2.13×10^{-5} s⁻¹, respectively, at 300 K. These small rate constants are inconsistent with the fast reactions in the experiments. Therefore, an alternative involving the bimolecular pathway is more likely. It has been proposed based on electrochemical studies that the one-electron reduced species of [Fe₂(µpdt)(CO)₅(P(OMe)₃)(µ-H)]^{+,96} [Fe₂(µ-bdt)(CO)₅(P(OMe)₃)(µ-H)]^{+ 97} and [Fe₂(CO)₄(κ^2 -dppe)(µpdt)(µ-H)]^{+ 98} might be involved in bimolecular reactions. In addition, H₂ formation from the photogenerated [Fe₂(bdt)(CO)₆H] has been recently proposed to occur via a bimolecular pathway.⁸⁰ Despite the proposals based on the experimental observations, this issue concerning Fe₂ catalysts has not been addressed by any computational study. Taking the catalysis of H₂ evolution by the Co-diglyoxime complexes [Co(dpgBF₂)₂] and [Co(dmgBF₂)₂] (dpg = difluoroboryl-diphenylglyoxime, dmg = difluoroboryl-dimethylglyoxime) as an example,⁹⁹ a homolytic pathway associated with two Co^{III}H species is favored based on the results of laser

flash-quench kinetics experiments.¹⁰⁰ Later, extensive theoretical analysis on mechanistic pathways¹⁰¹ and kinetic measurements using NMR spectroscopy lent support to the statement.¹⁰² In the current work, the energy barrier might render intramolecular H₂ evolution unfavorable, suggesting the plausibility of a bimolecular route for the catalysis. Further studies on this aspect are underway.

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Concluding remarks

In this work, we investigate $[(xdt)(\mu-H)Fe_2(CO)_6]^+$ (the C state) and its daughter species in the subsequent reduction/protonation events, $[(xdt)(\mu-H)Fe_2(CO)_6]$ (the CE state), $[(xdt)(\mu-H)Fe_2(CO)_6]$ (the H)(μ -CO)Fe₂(CO)₅]⁻ (the CEE state), [(xdtH)(μ -H)(μ -CO)Fe₂(CO)₅] (the CEEC state), and $[(xdtH)(\mu-H)(t-H)Fe_2(CO)_6]^+$ (the *CEECC* state) using in-situ spectroscopy (FTIR, UV-vis, ¹H-²D-NMR), electrochemistry, MS and DFT calculation. There are a few points to be addressed here. First, the C state $(1\mu H^+ - 3\mu H^+)$ display a reduction event at ca. -0.65 V at 200 K regardless of the bridgehead identity. However, its redox stability depends on the bridgehead. Fully reversible processes are observed for the pdt and edt species, while the partial oxidative return wave of the bdt analog indicates that stability of the reduced $3\mu H^+$ is strongly decreased relative to its alkyl counterparts. This decomposition reaction restores the parent complex $[(\mu$ xdt)Fe₂(CO)₆] by releasing molecular hydrogen. In fact, four of the characterized species (the *CE–CEECC* states) represent the active states for the formation of molecular hydrogen (Scheme 2). These species as well as the C state are therefore considered to be the catalytic intermediates. Complexes 2μ H, 2μ HSH^{*} and 2μ HtHSH^{*+} involve clean reactions, with the quantitative formation of 2 for the first two species and $2\mu H^+$ for the latter. The regeneration of a decreased amount of 2 after the catalytic cycle of $2\mu H^{*-}$, as determined from the magnitude of the IR signals, suggests the occurrence of side reactions.



Scheme 2. The reaction routes and the intermediates (the *C*–*CEECC* states) in the catalytic cycle of H_2 evolution. The pathways for ET, PT, deprotonation, H_2 -evolution and H_2 -evolution-deprotonation are displayed in red, olive-green, black, blue and cyan, respectively. The dashed line indicates a non-stoichiometric reaction.

All of the complexes in the catalytic cycle (Scheme 2) are 34-electron species except for the CE state, which is an odd-number electron derivative. Single-electron transfer to the closedshell species leads to the paramagnetic $[Fe^{II}(\mu-H)Fe^{I}]$ core, which is characterized by the rhombic EPR signal. Reduction of the Fe₂ dithiolato carbonyl complexes increases the energies of the Fe d orbitals, leading to a smaller energetic separation from the unoccupied CO π^* orbitals.¹⁰³ In addition, the difference between the Fe d and S 3p orbitals is increased. These changes in the molecular orbitals enhance the Fe-C_{co} bond strength and diminish the Fe-S covalency. Based on our calculated results, the C \equiv O and Fe-S bond distances are elongated by ~ 0.01 and 0.05 Å, respectively, when $2\mu H^+$ accepts one electron to become $2\mu H$. The Fe-C_{CO} bond length is shortened by ~ 0.01 Å due to enhanced π -backdonation. Weakening the Fe-S bond is the primary net effect of the reduction. Consequently, a further one-electron addition to the 35electron species 2μ H causes the rupture of one Fe-S bond and the generation of the 34-electron species $2\mu H^{*-}$, resulting in an open structure. One of the terminal carbonyls rearranges to the bridging mode to fulfill the 18-electron rule, leading to distorted geometry about the Fe center. This type of 34-electron complex is thermodynamically favored, while the 36-electron species is presumed to be initially formed but short-lived, undergoing prompt structural rearrangement. The 35- or 33-electron analogs in the current study are also high in energy and thus are not detectable except at very low temperatures. In the experimental study of the model system, the single reduction of $[NBu_4]_2[{Fe_4S_4(L)}{Fe_2(CH_3C(CH_2S)_3)(CO)_5}]$ (L = 1,3,5-tris(4,6-dimethyl-3-mercaptophenylthio)-2,4,6-tris(p-tolylthio)benzene) causes dissociation of the alkylthiolate group, which connects the Fe₂ moiety to the [4Fe4S] subset, from the Fe₂ unit.¹⁰⁴ Computational results using different models have also shown that $[(\mu,\kappa^2-pdtH)(\mu-H)(\mu-CO)(\kappa^2-dppe)Fe_2(CO)_3]$ $(dppe = Ph_2P(CH_2)_2PPh_2)$ and $[(\mu-S(CH_2)_3SH)(\mu-H)(\kappa^2-dppe)Fe_2(CO)_4]^-$ (Figure S24) are optimized as the lowest energy species along the successive reductive routes.⁶⁰ One bridging thiolate is converted to the terminal ligand in the former, and this sulfur ligand then becomes a

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pendent end away from the metal site in the latter. By contrast, the starting complex, $[(\mu-pdt)(\mu-H)(t-H)(\kappa^2-dppe)Fe_2(CO)_4]^+$, exhibits a dithiolate bridge spanning two Fe centers.

The most important point is that the effective charge at the Fe center for all six species throughout the catalytic cycle of H_2 production remains practically invariant (Table 2). In contrast, the NPA (natural population analysis) charges of the dithiolate linkers and CO groups reveal significant changes. These units, which are located in the first coordination sphere, act as surrogates for excess electron density as well as donors upon electron removal. Compared with the species studied here, the Fe₂ subset in the H-cluster is coordinated by 3 CO, 2 CN⁻ and one S^{cys} ligands, leaving it 3 CO groups short. Considering that the σ -donating ability is more greatly enhanced than the π -accepting ability in cyanides, the ligation of the [4Fe4S] unit, which has good electron-withdrawing ability, can buffer the excess electron density to keep the electronic changes of the Fe_2 core low via extensive delocalization. In addition to redox tunability, this electronic functionality of the attached [4Fe4S] cofactor provides the other rationale for its presence in the composition of the H-cluster. It has been suggested based on X-ray absorption spectra that $[(\mu-xdt)Fe_2(CO)_4(PMe_3)_2]$ (xdt = pdt, Bn-adt) and its protonated product $[(\mu-xdt)(\mu-xdt)]$ H)Fe₂(CO)₄(PMe₃)₂]⁺ exhibit almost unchanged effective oxidation states.^{105,106} We have extended this observation to all intermediates in the catalysis: their effective Fe charges are not altered upon reduction and/or protonation.

The conversion of $2 \rightarrow 2\mu H^+ \rightarrow 2\mu H$ is reminiscent of the biocatalytic pathway with the participation of the H_{sred} state for H₂ evolution. The H_{sred} state initially has been spectroscopically characterized to possess the {Fe^IFe^I} subset (H_{sred}-A, Scheme 3).³⁶ Recently, the structure of the H_{sred} state (H_{sred}-B) is proposed computationally to match experimental X-ray absorption and narrow-band emission (XAE).³⁷ Like 2 and $2\mu H^+$, both H_{sred}-A and H_{sred}-B are the 34-electron species, and H_{sred}-B, which is similar to $2\mu H^+$, exhibits the bridging hydride. The presence of the μ -H group might infer a different catalytic route for the proton reduction. According to the recent DFT calculations of the H-cluster, the structure with a μ -H is more stable by at least +8 kcal mol⁻¹ than the structure featuring a terminal hydride.¹⁰⁷ A significant barrier larger than +23 kcal mol⁻¹ due to the salt bridge between Lys358 and the coordinated cyanide has been estimated,¹⁰⁸ suggesting that structural rearrangement to the t-H is kinetically hindered. It is, therefore, reasonable to state that H_{sred}-C retains the {Fe(μ -H)Fe} core in which the mixed-

valence Fe_2 unit is achieved due to the electron transfer from the $[4Fe4S]^+$ cofactor upon second protonation.¹⁰⁷ This type of 35-electron species exhibits one structural feature: the extended Fe-S bond according to our results. In the protonation-reduction route of $2 \rightarrow 2\mu H^+ \rightarrow 2\mu H$, the Fe-S bond is extended from 2.306 (DFT; 2.239(2) exp¹⁰⁹) Å to 2.318 (DFT; 2.2461(10) exp) Å and ultimately 2.368 (DFT) Å. This result indicates that the Fe-S bond order is decreased regardless of whether protonation or reduction occurs. Electronic redistribution occurs upon the reduction of $2\mu H^+$, as reflected in the decrease in the NPA charge of the S site by 36% compared to 1.4% for the Fe center. It is therefore suggested that the electron density surplus in H_{sred} -C relative to H_{sred} -B is accommodated by the groups coordinated to the Fe center, not by the metal itself. Consequently elongation of the Fe-S bond might occur in the H_{sred} state (designated H_{sred} -D), enhancing the nucleophilicity of the thiolate site and thus offering a possible protonation site. The presence of a protonated four-coordinate S in Fe₂ dithiolato model complexes has been proposed according to spectroscopic¹¹⁰⁻¹¹⁴ and theoretical^{115,116} investigations. The isolation and structural characterization of $[(\mu-edt-Et)Fe_2(CO)_4(PMe_3)_2]^{+117}$ and $[(\mu-pdt-O)Fe_2(CO)_{6-x}(P)_x]$ (x = 0; x = 1, P = PPh₃; x = 2, P = PMe₃),¹¹⁸ in which the μ -S is ethylated and a sulfenato bridge is formed, respectively, provide direct evidences for accessibility of the thiolate bridge toward the electrophilic attack. In H_{sred}-C, the proton on the adt (i.e., aza-N) site is not close to the Fehydride. The S site with proton accessibility in H_{sred}-D replaces the aza nitrogen bridgehead in terms of its functional role in catalysis.



Scheme 3. The structures of the H_{sred} state (\mathbf{H}_{sred} - \mathbf{A}), suggested by the EPR and FTIR results, the H_{sred} state (\mathbf{H}_{sred} - \mathbf{B}), suggested by the XAE (X-ray absorption and emission spectroscopy) and computational results,¹¹⁹ and the putative H_{sred} states (\mathbf{H}_{sred} - \mathbf{C} and \mathbf{H}_{sred} - \mathbf{D}). The [H⁺] in \mathbf{H}_{sred} - \mathbf{A} is proposed to be bound to a nearby amino acid residue. The blue dashed lines indicate the plausible weakened Fe-S interaction.

In summary, the experimental characterization and theoretical investigation of the Fe₂ dithiolato carbonyl complexes and their daughter species in the subsequent protonation and reduction reactions offer valuable information on the catalytic mechanism of H₂ production. The chemistry of these biologically relevant complexes assists in the better design of artificial catalysts and reveals the reaction species at the active site.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.

The results of spectroscopy, structural determinations, MS and computational chemistry

(PDF)

X-ray single crystallography (CIF)

Notes

The authors declare no competing financial interest.

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Table	1.	Spectroscopic [§]	and	electrochemical	properties	of	1–3	and	the	corresponding
protona	ated	/reduced derivati	ves in	n CH ₂ Cl ₂ solution						

	pdt	edt	bdt
Parent (1–3)	vco: 2075 m, 2034 vs, 1999 s, 1993 s	vco: 2073 m, 2033 vs, 1996 s, 1989 s	vco: 2079 m, 2041 vs, 2002 s
	λex: 328 (18,100), 459 (1,400)	λ _{ex} : 322 (18,200), 450 (1,500)	λex: 333 (20,600), 457 (1,000)
С	v _{C0} : 2132 m, 2111 vs, 2082 s, 2069 s	v _{co} : 2134 m, 2113 vs, 2084 s, 2074 s	v _{co} : 2135 m, 2116 vs, 2084 s
	$E_{1/2}^{\text{red}^+_+} = -0.69$	$E_{1/2}^{\text{red}\ddagger} = -0.68$	$E_{ m pc}^{\ddagger} = -0.67$
	λ _{ex} : 331, (3,900), 443 (500), 486 (500)	λex: 308 (4,000), 367 (1,300), 458 (500)	λ _{ex} : 341 (7,500), 383 (2,800), 508 (1,500)
CE	v _{CO} : 2072 m, 2043 vs, 1993 s	v _{CO} : 2074 m, 2045 vs, 1995 s	ν_{CO}^{\diamond} : –
	λex: 457 (2,700), 666 (1,300)	λex: 451 (1,700), 625 (740)	$\lambda_{\mathrm{ex}}^{\diamond}\!\!:-$
	<i>g</i> _{xyz} [†] : 2.0083, 1.9776, 1.9705; <i>A</i> _{xyz} : 2.1, 2.1, 3.9	g _{xyz} [†] : 1.9924, 1.9696, 1.9637; A _{xyz} : 5, 5, 4.1	$g_{\exp}^{\dagger \diamond}$: 2.0122
CEE	vco: 2042 m, 1992 vs, 1972 s, 1953 s, 1934 m, 1752 w, br	vco: 2040 m, 1991 vs, 1960 s, 1934 sh, 1755 w, br	vco: 2045 m, 1996 vs, 1979 s, 1963 s, 1935 m, 1750 w, br
CEEC	_	vco: 2067 m, 2020 vs, 1990 s, 1969 sh, 1777 w, br	vco: 2070 m, 2024 vs, 2005 s, 1973 sh, 1780 w, br
CEECC	_	vco: 2130 s, 2097 vs, 2082 s, 2075 s, 2046 m, 2036 m	vco: 2132 s, 2097 vs, 2078 s, br, 2041 m, br

Units for v_{CO}: cm⁻¹; for *E* (vs. Fc⁺/Fc): V; for λ_{ex} (ϵ): nm (M⁻¹ cm⁻¹); for *A*: G. The species **1µHSH*** was extremely unstable at 193 K and its IR bands could not be clearly identified. [§]193 K. [‡]200 K for pdt, 210 K for edt and 213 K for the bdt species. [†]77K. The simulated results. For the bdt derivative, the experimental value is reported. [◊]contains [(μ -bdt)Fe₂(CO)₆] as a major species in the single reduction of **3µH**⁺. Physical properties of the CE state are largely unknown due to fast decomposition.

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Table 2. NPA	charges	of species	2 and	its derivatives.
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	2	$2\mu H^+$	2μΗ	2μH*-	2µHSH*	2µHtH ^S SH*+	$\Delta\left(\% ight)^{\diamond}$
Fe1 (Fe ^t) [§]	-1.429	-1.422	-1.410	-1.395	-1.356	-1.386	5.1
Fe2	-1.429	-1.422	-1.451	-1.578	-1.552	-1.544	10.9
$S1 (S^t)^{\$}$	+0.356	+0.442	+0.285	-0.198	+0.246	+0.342	179.8
S2	+0.356	+0.442	+0.285	+0.297	+0.321	+0.414	44.1
H^{μ}	_	+0.166	+0.177	+0.164	+0.148	+0.135	25.3
H^{S}	—	_	_	_	+0.185	+0.203	9.7 *
\mathbf{H}^{t}	_	—	_	—	_	+0.134	_
CO [‡]	+2.253	+2.853	+2.237	+1.877	+2.088	+2.715	43.3
edt ^{‡†}	-0.107	-0.060	-0.124	-0.167	-0.081	-0.013	143.9
sum	0	+1	0	-1	0	+1	—

[§]Fe^t and S^t denote the Fe ligated by the S^t and the terminal sulfur site, respectively. [‡]Given values represent the sum over the respective atoms or groups. [†]edt = the bridging ligand without the S atoms. [◊] Δ (%) = (max. value – min. value)/(value of species 2) × 100 %. [¶]It is referenced to 2µH⁺. [•]It is referenced to 2µHSH^{*}.

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20 27	(110) The reviewer pointed out that Hand initially group and by Lubitz et al. has a
28	(119) The reviewer pointed out that Hsred initially proposed by Lubitz et al. has a
20	[4Fe4S]+/Fe(1)Fe(1) state without bridging H attached. Once the proton is transferred to the 2Fe
30	as a hydride, inevitably two electrons are consumed by the proton and the oxidation state has to
31	change into [4Fe4S]+/Fe(II)Fe(II) with a bridging hydride attached.
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