# Polyhedron 197 (2021) 115043

Contents lists available at ScienceDirect

# Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Spectroscopic and electrochemical comparison of [FeFe]-hydrogenase active-site inspired compounds: Diiron monobenzenethiolate compounds containing electron-donating and withdrawing groups



POLYHEDRON

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#### ARTICLE INFO

Article history: Received 26 July 2020 Accepted 14 January 2021 Available online 20 January 2021

Keywords: Iron-sulfur Hydrogenase model Electrocatalysis Proton reduction Monothiolates

#### 1. Introduction

The search for hydrogen-evolving catalysts [1] has frequently focused upon iron-based compounds [2] due to iron's established reactivity with hydrogen [3], its earth-abundance [4,5], and its presence in the active-site of hydrogenase enzymes [6]. The active site of [FeFe]-hydrogenase [7] enzymes (Fig. 1) [8] is responsible for efficient and reversible [3] redox chemistry associated with proton reduction [9]/dihydrogen activation [10,11]. Hence, a long synthetic history [12] has been paired with bio-mimicry [13] in the design of Fe<sub>2</sub>S<sub>2</sub> electrocatalysts [14].

Hexacarbonyl diiron dithiolate clusters are generally not electron rich enough to be protonated in their neutral forms and, therefore, require reduction as a first step in a catalytic mechanism (EC process) [15]. A recent review featured almost 200 examples of models with bridging aromatic dithiolates [16] (An S-R-S linker, where R is the aromatic group, Fig. 2) to ease reduction, particularly via using compounds containing electron withdrawing groups [17]. This approach is often accompanied with substitution of one or more carbonyls with electron donating ligands [18] to facilitate subsequent protonation and initiate a catalytic mechanism at

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# ABSTRACT

The novel compounds  $[Fe_2(\mu-SC_6H_4-p-NO_2)_2(CO)_6]$  (1),  $[Fe_2(\mu-SC_6H_4-p-t^Bu)(\mu-SC_6H_4-p-NO_2)(CO)_6]$  (2),  $[Fe_2(\mu-SC_6H_4-p-t^Bu)_2(CO)_6]$  (3),  $[Fe_2(\mu-SC_6H_4-p-t^Bu)(\mu-SC_6H_4-p-t^Bu)_2(CO)_6]$  (4) and  $[Fe_2(\mu-SC_6H_4-p-t^Bu)(\mu-S$ 

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lower overpotential [19]. "Unbridged" hexacarbonyl diiron dithiolate compounds lacking an S-linker-S bridge (although each S does form a bridge between the two Fe atoms), have been less studied for electrocatalytic reduction of protons, perhaps due to the presence of an aza-propane linker in the [FeFe]-hydrogenase active site. Yet, some unbridged alkyl [20–22], aromatic [23–26], and nitrogen-containing [27–29] bis(thiolate) systems have been explored. Additionally, unbridged systems have also had carbonyl ligands replaced by election donating ligands [30–33].

Considered herein are unbridged hexacarbonyl diiron dithiolate clusters with an electron-withdrawing aromatic thiolate ligand (to provide an easier initial reduction location) and an electron-donating aromatic thiolate (to enhance the basicity of the iron-sulfur core). The novel compounds  $[Fe_2(\mu-SC_6H_4-p-NO_2)_2(CO)_6]$  (1),  $[Fe_2(\mu-SC_6H_4-p-t^Bu)(\mu-SC_6H_4-p-NO_2)(CO)_6]$  (2),  $[Fe_2(\mu-SC_6H_4-p-t^-Bu)_2(CO)_6]$  (3),  $[Fe_2(\mu-SC_6H_4-p-t^-Bu)(\mu-SC_6H_4-p-CF_3)(CO)_6]$  (4) and  $[Fe_2(\mu-SC_6H_4-p-OCH_3)(\mu-SC_6H_4-p-CF_3)(CO)_6]$  (5) were synthesized, characterized and electrochemically tested for hydrogen-generation from weak acid sources to develop this hypothesis further. Comparisons are made to the well-known compound  $[Fe_2(\mu-SC_6-H_5)_2(CO)_6]$  (6) [34-37].

Three stereoisomers are possible for  $bis(\mu-RS)hexacarbonyldi$ iron complexes (Fig. 3). While the sterically hindered*syn-exo*isgenerally not observed for bulky R-groups, a mixture of*anti*and*syn-endo*exists in solution at room temperature [38], even if onlyone isomer is obtained in the solid/crystalline form.



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Fig. 1. [FeFe]-hydrogenase active site structure [8].



**Fig. 2.** [FeFe]-hydrogenase active site mimics frequently include some form of "linker" or bridge of either aromatic or non-aromatic nature. Unbridged compounds studied herein.



**Fig. 3.** Three isomers are possible for bis(µ-RS)hexacarbonyldiiron complexes, simplified structures shown looking down the Fe-Fe bond.

# 2. Experimental

#### 2.1. Synthesis and characterization

Preparation of the iron complexes evaluated in this study was under inert (argon atmosphere) conditions using standard Schlenk-line techniques. All reagents and solvents were purchased from commercial suppliers and used as received. Listed reagents were combined in 20 mL unstabilized anhydrous tetrahydrofuran (THF) and held at reflux for 1.5 h (allowing the reaction mixture to turn from dark green to deep red). The crude reaction mixture was filtered through Celite<sup>®</sup> and the solvent was removed under reduced pressure until near dryness. The complexes were isolated with silica preparative-scale TLC (without protection from air) using dichloromethane/hexane eluent. The resultant red/red–orange fraction/s were collected; the silica was removed by filtration, and the dichloromethane was removed under reduced pressure until complete dryness. NMR data was obtained on 300/400 MHz Bruker spectrometers. FTIR data was obtained from a Varian 3100 spectrometer and a Perkin Elmer 100 spectrometer, at 1.0 cm<sup>-1</sup> resolution. Elemental analysis was carried out by Atlantic Microlabs (Norcross, GA, USA).

# 2.1.1. Preparation of $[Fe_2(\mu - SC_6H_4 - p - NO_2)_2(CO)_6]$ (1)

Reagents: 0.0935 g (0.603 mmol) of 4-nitrothiophenol and 0.155 g (0.308 mmol) of triiron dodecacarbonyl. Yield 0.0800 g (0.136 mmol, 66%). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, ppm), δ: 8.26 (2H, d, 18.4 Hz), 8.13 (2H, d, 17.6 Hz), 7.87–7.68 (4H, m). IR (CH<sub>2</sub>-Cl<sub>2</sub>,  $\bar{v}_{CO}$ ): 2083, 2049, 2010 cm<sup>-1</sup>. Anal. Calc. for C<sub>18</sub>H<sub>8</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>: C, 36.76; H, 1.37, Found: C, 36.58; H, 1.52. Crystals (red–orange) suitable for X-ray diffraction were obtained by slow evaporation of dichloromethane at 4 °C, CCDC 1983686.

# 2.1.2. Preparation of $[Fe_2(\mu - SC_6H_4 - p^{-t}Bu)(\mu - SC_6H_4 - p^{-t}NO_2)(CO)_6]$ (2)

Reagents: 101 µL (0.0975 g, 0.600 mmol) of 4-tert-butylthiophenol, 0.0931 g (0.600 mmol) of 4-nitrothiophenol and 0.302 g (0.600 mmol) of triiron dodecacarbonyl. Yield: 0.0576 g (0.094 mmol, 24%). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, ppm), mixture of three isomers, δ: 8.26 (d, 16.0 Hz), 8.12 (m), 7.84 (m), 7.77 (m), 7.68 (m), 7.51-7.41 (m), 1.28, 1.26, 1.25 (s, overlapping). IR  $(CH_2Cl_2, \tilde{v}_{CO})$ : 2074 (m), 2034 (s), 1992 (s, br) cm<sup>-1</sup>. Anal. Calc. for C<sub>22</sub>H<sub>17</sub>Fe<sub>2</sub>NO<sub>8</sub>S<sub>2</sub>: C, 44.10; H, 2.86, Found: C, 44.31; H, 3.02. Crystals (red-orange) suitable for X-ray diffraction were obtained by slow evaporation of dichloromethane-heptane at 4 °C, CCDC 1983687. Preparation also yielded 0.0257 g (0.0429 mmol, 11%) of **1** and 0.0353 g (0.0568 mmol, 14%) of **3**. Additional preparations: 77.6 µL (0.0748 g, 0.450 mmol) of 4-tert-butylthiophenol, 0.0466 g (0.300 mmol) of 4-nitrothiophenol and 0.155 g (0.308 mmol) of triiron dodecacarbonyl (yield: 2, 0.0191 g, 0.0310 mmol, 16%; 1, 0.0115 g, 0.0192 mmol, 9.6%; 3, 0.0229 g, 0.0370 mmol, 18%). 51.7 µL (0.0499 g, 0.300 mmol) of 4-tert-butylthiophenol, 0.0698 g (0.450 mmol) of 4-nitrothiophenol, 0.155 g (0.308 mmol) of triiron dodecacarbonyl (yield: 2, 0.0360 g, 0.0590 mmol, 29%; 1, 0.0207 g, 0.0350 mmol, 17%; 3, 0.0104 g, 0.0170 mmol, 8.4%).

# 2.1.3. Preparation of $[Fe_2(\mu - SC_6H_4 - p^{-t}Bu)_2(CO)_6]$ (3)

Reagents: 400  $\mu$ L (0.386 g, 2.32 mmol) of 4-*tert*-butylthiophenol and 0.502 g (0.998 mmol) of triiron dodecacarbonyl. Yield 0.245 g (0.401 mmol, 60%). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, ppm),  $\delta$ : 7.46–7.31 (8H, m), 1.29 and 1.26 (18H, s, overlapping). IR (CH<sub>2</sub>Cl<sub>2</sub>,  $\bar{v}_{CO}$ ): 2070 (m), 2030 (s), 1987 (s) cm<sup>-1</sup>. Anal. Calc. for C<sub>26</sub>H<sub>26</sub>Fe<sub>2</sub>-O<sub>6</sub>S<sub>2</sub>: C, 51.17; H, 4.29, Found: C, 50.99; H, 4.16.

# 2.1.4. Preparation of $[Fe_2(\mu-SC_6H_4-p-{}^tBu)(\mu-SC_6H_4-p-CF_3)(CO)_6]$ (4)

Reagents: 52.0 μL (0.0515 g, 0.310 mmol) of 4-*tert*-butylthiophenol, 41.0 μL (0.0533 g, 0.299 mmol) of 4-(trifluoromethyl)thiophenol and 0.155 g (0.308 mmol) of triiron dodecacarbonyl. Yield: 0.0216 g (0.0341 mmol, 17%). <sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, ppm), isomer ratio unclear due to overlap, δ: 7.73–7.31 (m, 8H), 1.26 (s, 9H). IR (CH<sub>2</sub>Cl<sub>2</sub>,  $\bar{v}_{CO}$ ): 2075 (m), 2035 (s), 1994 (s) cm<sup>-1</sup>. Anal. Calc. for C<sub>23</sub>H<sub>17</sub>Fe<sub>2</sub>O<sub>6</sub>S<sub>2</sub>F<sub>3</sub> C, 44.40; H, 2.75, Found: C, 44.21; H, 2.62. Preparation also yielded 0.0579 g (0.0931 mmol, 45%) of **3** and 0.0211 g (0.0327 mmol, 16%) of [Fe<sub>2</sub>(μ-SC<sub>6</sub>H<sub>4</sub>-p-CF<sub>3</sub>)<sub>2</sub>(CO)<sub>6</sub>], IR (CH<sub>2</sub>Cl<sub>2</sub>,  $\bar{v}_{CO}$ ): 2077 (m), 2040 (s), 2000 (s) cm<sup>-1</sup> [38].

# 2.1.5. Preparation of [Fe<sub>2</sub>(µ-SC<sub>6</sub>H<sub>4</sub>-p-OCH<sub>3</sub>)(µ-SC<sub>6</sub>H<sub>4</sub>-p-CF<sub>3</sub>)(CO)<sub>6</sub>] (**5**)

Reagents: 41.0 μL (0.0467 g, 0.333 mmol) of 4-methoxythiophenol, 37.0 μL (0.0481 g, 0.270 mmol) of 4-(trifluoromethyl)thiophenol and 0.155 g (0.308 mmol) of triiron dodecacarbonyl. Yield: 0.0473 g (0.0778 mmol, 38%). <sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, ppm), isomer ratio unclear due to overlap, δ: 7.63 (m, 4H), 7.32 (m, 2H), 6.86 (m, 2H), 3.78 (s, 3H). IR (CH<sub>2</sub>Cl<sub>2</sub>,  $\tilde{v}_{CO}$ ): 2075 (m), 2037 (s), 1997 (s) cm<sup>-1</sup>. Anal. Calc. for C<sub>20</sub>H<sub>11</sub>Fe<sub>2</sub>O<sub>7</sub>S<sub>2</sub>F<sub>3</sub>: C, 40.30;

H, 1.86, Found: C, 40.02; H, 1.92. Preparation also yielded 0.0142 g (0.0220 mmol, 11%) of  $[Fe_2(\mu-SC_6H_4-p-CF_3)_2(CO)_6]$ , IR (CH<sub>2</sub>Cl<sub>2</sub>,  $\bar{v}_{CO}$ ): 2077 (m), 2040 (s), 2000 (s) cm<sup>-1</sup>[39]. and 0.0259 g (0.0455 mmol, 22%) of  $[Fe_2(\mu-SC_6H_4-p-OCH_3)_2(CO)_6]$ , IR (CH<sub>2</sub>Cl<sub>2</sub>,  $\bar{v}_{CO}$ ): 2073 (m), 2036 (s), 1995 (s) cm<sup>-1</sup> [24].

# 2.1.6. Preparation of $[Fe_2(\mu-SC_6H_5)_2(CO)_6]$ (6)

Reagents: 0.157 g (0.720 mmol) of diphenyl disulfide and 0.301 g (0.597 mmol) of triiron dodecacarbonyl. Yield 0.135 g (0.271 mmol, 68%). <sup>1</sup>H NMR (400 MHz,  $(CD_3)_2CO$ , ppm),  $\delta$ : 7.55 (2H, d, 7.6 Hz), 7.45–7.35 (4H, m), 7.34–7.24 ppm (4H, m). IR (CH<sub>2</sub>-Cl<sub>2</sub>,  $\bar{v}_{CO}$ ): 2075 (m), 2039 (s), 2000 (s) cm<sup>-1</sup>. IR (hexane,  $v_{CO}$ ): 2075 (m), 2038 (s), 2005 (s), 1998 (s) cm<sup>-1</sup>. Anal. Calc. for C<sub>18</sub>H<sub>10</sub>Fe<sub>2</sub>O<sub>6</sub>-S<sub>2</sub>: C, 43.40; H, 2.02, Found: C, 43.10; H, 1.74.

### 2.2. X-ray crystallography

Diffraction measurements for compounds **1** and **2** were carried out on either an Agilent Technologies SuperNova CRYSALISPRO or a Bruker SMART APEXII CCD diffractometer equipped with graphitemonochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Crystallographic data and data collection are summarized in the supplemental information file. Structural refinements were calculated from SHELXTL software using full-matrix least squares on F<sup>2</sup>.

#### 2.3. Cyclic voltammetry

All Cyclic Voltammograms (CV's) were obtained by using a CHI Model 600D Potentiostat 3-electrode cell with a glassy carbon 3.00 mm diameter working electrode, platinum wire counter electrode, and silver external reference electrode (10 mM AgNO3 in electrolyte solution). The electrolyte solution for all experiments was 0.100 M tetra-n-butylammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>) in anhydrous acetonitrile (Sigma-Aldrich). The potentials (E) at the working electrode in all CV's are reported with respect to the ferrocenium/ferrocene couple in electrolyte solution. The ferrocenium/ferrocene couple data was collected at the end of each experiment. All CV's reported are background corrected, i.e. the scan with only electrolyte present was subtracted from the raw data. All background scans confirmed the sufficient removal of O<sub>2</sub> as seen by the absence of a reduction peak ca. -1.2 V [39]. CV data was collected under the flow of ultra-high purity argon gas, with additional purging and confirmation of oxygen removal upon each addition of acetic acid to the cell.

# 3. Results and discussion

# 3.1. Synthesis

The general procedure combined the required benzenethiol with triiron dodecacarbonyl (1.5:1 thiol:iron) in anhydrous THF held at reflux, under an inert atmosphere, for ninety minutes. Yields were in the range of 50%–70%. In repeated syntheses of compound **2**, the two thiols were used in varied ratios, reacting in competition (Table 1). The thiol with the greater electron-donating benzenethiol appears to be slightly more reactive, such that an excess of the greater electron-withdrawing benzenethiol boosts the mixed product, compound **2**.

#### 3.2. Structure

Crystallographic characterization of compounds **1** and **2** confirms formation of the desired products. In both cases only the *anti* (ax,eq) isomer is seen, with the *ax*-Ph-*p*-NO<sub>2</sub> *eq*-Ph-*p*- $^{t}$ Bu isomer seen for compound **2** (Fig. 4). The *para*-groups on the phenyl rings lead to a negligible effect on the Fe-Fe bond length of compounds **1** 

#### Table 1

Reaction yields from varied ratios of competing thiols in syntheses of compound **2** ( $^{t}Bu = 4$ -*tert*-butylthiophenol, NO<sub>2</sub> = 4-nitrothiophenol).

Compound	<sup>t</sup> Bu:NO <sub>2</sub> 1.5:1	<sup>t</sup> Bu:NO <sub>2</sub> 1:1	<sup>t</sup> Bu:NO <sub>2</sub> 1:1.5
1	9.6%	11%	17%
2	16%	24%	29%
3	18%	14%	8.4%

(2.520 Å) and **2** (2.525 Å) compared to the *anti* (ax,eq) isomer of **4** (2.516 Å) [40]. The limited variation in Fe-Fe bond lengths comports with the long established structural stability of the butterfly-core feature [41,42]. The crystal data and structure refinement details for compounds **1** and **2** can be found in the supplementary information file.

#### 3.3. NMR spectroscopy

Compounds 1–5 were characterized by <sup>1</sup>H NMR in acetone- $d_{6}$ , with peaks attributed to aromatic protons in the 8.26-7.31 ppm region, representing downfield shifts from the corresponding thiol reagents (due to an increase in electronegativity from H-S to Fe-S bonds). Purified compounds 1 and 3 display NMR patterns matching a predominantly anti isomeric form in deuterated acetone at room temperature, while the NMR pattern for compound **2** is suggestive of a mixture of three isomers in that three overlapping singlet peaks (of the <sup>t</sup>Bu protons) are seen between 1.28 and 1.25 ppm.[43] This pattern is assigned to a mixture of the two anti isomers (ax-Ph-p-NO<sub>2</sub>, eq-Ph-p-<sup>t</sup>Bu and eq-Ph-p-NO<sub>2</sub>, ax-Ph-p-<sup>t</sup>Bu) and the syn-endo isomer. Due to overlap, it was not possible to assign an in-solution isomer equilibrium ratio. There is an equilibrium between the syn-endo and anti isomer for many (RS)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> compounds [44], when the R group is aromatic the *anti isomer* is strongly (>10:1) favored [38,45]. Longer timescale THF reflux was used herein to promote isomer ratio equilibration. Compounds 4 and 5 also displayed this apparent mixture of isomers in solution, but the exact ratio could not be determined due to overlap in the aromatic region. Well known compound **6** was characterized by <sup>1</sup>H NMR in acetone- $d_{6}$ , with peaks attributed to aromatic protons in the 7.57–7.24 ppm region, representing upfield shifts of the ortho protons from the corresponding diphenyl disulfide reagents (due to a decrease in electronegativity from sulfur-sulfur to Fe-sulfur bonds). An assignment of a predominantly anti (ax,eq) product isomer for compound **6** is achieved by comparison to the literature NMR [38].

# 3.4. IR spectroscopy

IR spectroscopy of complexes 1-6 were recorded in dichloromethane and reveal three distinct carbonyl stretching peaks, with the lowest energy carbonyl vibration being somewhat broadened (or split into two peaks with weakly interacting non-polar hexane as a solvent), consistent with hexacarbonyl diiron dithiolate compounds. The  $Fe_3(CO)_{12}$  starting material only displays one intense CO band, owing to its high degree of symmetry, the presence of three CO stretching bands indicate the formation of a Fe<sub>2</sub>(CO)<sub>6</sub> subunit. The trend (Table 2) in CO stretching aligns with the increasing electron density on the Fe<sub>2</sub>-core from compound 1 to compound 3. Electron density is withdrawn from the Fe-Fe bond due to the electron-withdrawing nitro group of compound **1**, which diminishes the electron density available to be donated to the carbonyl  $\pi^*$ orbital, resulting in higher energy CO stretching vibrations. The opposite effect is observed in complex 3, which contains the electron-donating <sup>t</sup>Bu substituent. Compound **2** represents a competition between electron-donating and electron-withdrawing components, with carbonyl stretching values closer to those of compound **1**. A Hammett [46] constant of +0.78 for  $p-NO_2$  and

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Fig. 4. ORTEP diagram of 1 and 2 with 50% probability thermal ellipsoids.

Table 2	
Reduction potentials and infrared data of <b>1–6</b> . IR absorption peaks are attributed to CO stretching modes.	

Complex	$E_{pc1}$ (V) <sup>a</sup>	$\tilde{v}_{CO} (cm^{-1})^b$	Mean $\tilde{v}_{CO}$ (cm <sup>-1</sup> )	Mean Hammett constant <sup>c</sup>
1	-1.29	2080, 2044, 2003	2042	+0.78
2	$-1.33/-1.53^{d}$	2078, 2041, 2001	2040	+0.30
3	-1.59	2074, 2034, 1993	2034	-0.19
4	-1.49	2075, 2035, 1994	2035	+0.18
5	-1.44	2075, 2037, 1997	2036	+0.14
6	-1.55	2074, 2038, 1999	2037	0.00

<sup>a</sup> Potential at peak of first reduction wave vs.  $Fc/Fc^*$  at 0.100 V s<sup>-1</sup> in 0.100 M  $n-Bu_4NPF_6$  in anhydrous acetonitrile.

<sup>b</sup> Recorded in dichloromethane.

<sup>c</sup> The mean Hammett constant is calculated by averaging the values of the R-groups used: NO<sub>2</sub> (+0.78), CF<sub>3</sub> (+0.54), H (0.00), <sup>1</sup>Bu (-0.19) and OCH<sub>3</sub> (-0.27) [46].

<sup>d</sup> There are two peaks in the region of the first reduction wave of the other compounds listed.

-0.19 for *p*-<sup>t</sup>Bu for the substituents used in compound **2** yields a response akin to a combined Hammett constant of +0.30. A mean  $\bar{v}_{CO}$  value of 2040 cm<sup>-1</sup> for compound **2** indicates reduced electron density on the Fe<sub>2</sub>-core compared to that seen in compound **4** (where the Hammett constant for H is 0), which has a mean  $\bar{v}_{CO}$  value of 2037 cm<sup>-1</sup>. Slightly positive mean Hammett constants for compounds **4** and **5** suggest slightly greater electron-density of the Fe<sub>2</sub>-core compared to that seen in compound **6**, however, slightly lower mean  $\bar{v}_{CO}$  values are attributed to the 1 cm<sup>-1</sup> instrument resolution (Table 2).

#### 3.5. Cyclic voltammetry

Complexes 1-6 have been studied in acetonitrile by cyclic voltammetry. An irreversible reduction event, ascribed to [Fe<sup>1</sup>- $Fe^{I} \rightarrow [Fe^{I}-Fe^{0}]$ , is observed for all six complexes from -1.29 V to -1.59 V vs Fc<sup>+</sup>/Fc (all potentials are reported vs Fc<sup>+</sup>/Fc). A lack of reversibility has been observed with other unbridged thiolate systems and has been attributed to the irreversible cleavage of one thiolate upon reduction [47]. In contrast, models containing bridging dithiolates may exhibit increased reversibility as the close proximity of the cleaved thiolate allows for later re-coordination [48]. The electron density on the metal centers (indicated by their CO stretching modes) broadly correlates with the observed reduction potentials (Table 2), where the compound with the greatest electron density is the hardest to reduce (compound 3 requiring -1.59 V) and the compound with least electron density is easiest to reduce (compound 1 requiring -1.29 V). As the irreversibility of this reduction is ascribed to a following chemical step, this correlation is suggestive that the post-reductive chemical step [49] is insufficiently rapid [50] to affect the observed reduction potential [51] of the process. The reduction potentials of compounds **1–6** strongly correlates with the mean Hammett constants of the substituents (Table 2), providing evidence that the reductive event is located upon the Fe<sub>2</sub>-core. Multiple cycles through the first reduction wave do not indicate decomposition/surface passivation. An irreversible oxidative process is seen for all compounds between 0.75 and 0.95 V (Fig. 5). Complex **1** and **2** also display substantial subsequent reductions, in each case including a quasi-reversible peak at *ca.* -1.9 V (tentatively ascribed to a reduction of the nitro substituent), along with an irreversible peak at *ca.* -2.6 V for compound **1** and *ca.* -2.4 V for compound **2** (Figure SI-1 and Fig. 6).

Complexes 1-6 were evaluated in acetonitrile for their ability to reduce protons to molecular hydrogen, as observed by an increase in current upon addition of a proton source. Cyclic voltammograms of 1.00 mM with 0-50 equivalents of acetic acid were collected for the six complexes studied. The two nitro-containing compounds display complex electrochemical responses, Figure SI-1 and Fig. 6. The nitro group has been seen to form a pre-wave in the presence of protons [52], and an increase in reduction current has been reported to be due to the following functional group reaction:  $-NO_2 + 4H^+ + 4e^- \rightarrow -NHOH + H_2O$ , for nitrobenzene [53]. There are limited examples of nitro-group containing hydrogenase active site mimics being tested for proton reduction. However, the examples that we are aware of, involve a nitro group located either on a benzene ring [54] or on a phenylacetylene [55], which is itself attached to the nitrogen atom of an azadithiolate bridge, and display increased current at the first reduction in the presence of protons. A similar current enhancement with increasing acetic acid concentration is displayed for 1 and 2 at the potential of the first reduction ( $E_{pc1}$  = -1.29 V to -1.53 V). This increased current cannot be attributed to proton reduction, however, due to the inability of an acid to be reduced at a potential less negative than its standard reduction potential in a given solvent ( $\vec{E}_{HOAc} = -1.46$  V in MeCN) [56]. The current enhancement of this first reduction peak is therefore assigned to a multi-proton multi-electron reduction of the nitro group to a hydroxylamine group. The quasi-reversible



**Fig. 5.** Cyclic Voltammetry overlays of compounds **1–5** (top to bottom) recorded in 0.100 M  $Bu_4NPF_6$  in dry acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc<sup>+</sup>/Fc at 0.100 V/s under Ar.



**Fig. 6.** Cyclic voltammetry of 1.00 mM of compound **2** with added acetic acid added: 1.0 mM, 2.0 mM, 5.0 mM, 10.0 mM, 20.0 mM, 50.0 mM. Recorded in 0.100 M  $Bu_4NPF_6$  in dry acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc<sup>+</sup>/ Fc at 0.100 V/s under Ar.

reduction feature of compounds **1** and **2** at *ca.* -1.9 V also see an increase in current with added acid, but only up to a five-fold acetic acid excess, above which the reduction feature is no longer present.

All complexes display increased currents at very negative potentials beyond -2.2 V, primarily in the potential region of



**Fig. 7.** Linear sweep voltammetry of 1.00 mM of compounds **1** (orange), **2** (green), **3** (purple), **4** (blue), **5** (red), **6** (black), with 10.0 mM acetic acid added to each. Recorded in 0.100 M Bu<sub>4</sub>NPF<sub>6</sub> in dry acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc<sup>+</sup>/Fc at 0.100 V/s under Ar. Direct response of 10.0 mM acetic acid shown in dotted grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

direct reduction [56,57] and, therefore, electrocatalysis via direct acetic acid reduction on the glassy carbon working electrode competes with that from the complexes studied. It is not clear that the current enhancement is simply additive, given that 6 displays less current than acetic acid alone (Fig. 7). Compounds 1, 2 and 5 show enhanced currents modestly greater than that observed via direct reduction of acetic acid alone in this potential region. Using an  $E_{1/2}^{red}$  of -2.14 V for compound **2** yields an overpotential of 0.68 V (assuming that  $E_{1/2}^{red} \approx E^{\circ}$  for irreversible processes) [57], marginally better than the 0.76 V overpotential for compound **3** ( $E_{1/2}^{red}$  of -2.22 V). Which indicates that the electrocatalytic [58] peak is shifted very slightly anodically for compound 2, suggestive that the reduction potential of the protonated iron compound is slightly decreased by the presence of the nitro group. Yet, the electrondonating *t*-butyl group keeps the electron density of the iron-core great enough to allow for protonation upon initial reduction. Representing marginal support of this paper's hypothesis: An electronwithdrawing aromatic thiolate ligand provides an easier initial reduction while an electron-donating aromatic thiolate enhances the basicity of the iron-sulfur core. Furthermore, Compound 5 displays an additional reductive event in the presence of acetic acid at a less cathodic potential of *ca*.  $E_{1/2}^{red}$  of -1.72 V (Fig. 8), crucially



Fig. 8. Cyclic voltammetry of 1.00 mM of compound 5 with added acetic acid added: 1.0 mM, 2.0 mM, 5.0 mM, 10.0 mM, 20.0 mM, 50.0 mM. Recorded in 0.100 M  $Bu_4NPF_6$  in dry acetonitrile on a 3.00 mm diameter glassy carbon electrode vs. Fc<sup>+</sup>/ Fc at 0.100 V/s under Ar.

prior to the onset reduction of competing direct reduction (Fig. 7). Catalytic reduction of acetic acid to molecular hydrogen at this potential would represent an overpotential of just 0.26 V. Again, the combination of the electron-withdrawing aromatic thiolate ligand (trifluoromethyl substituent) provides an easier initial reduction while an electron-donating aromatic thiolate (methoxy substituent) enhances the basicity of the iron-sulfur core. An alternative interpretation is that the methoxy group is involved in a homoassociative [59] process with the acetic acid, enhancing the acidity of the acetic acid.

# 4. Conclusion

Models of the [FeFe]-hydrogenase active site featuring monobenzenethiolate groups have been spectroscopically and electrochemically compared. The Hammett constants of the substituents on the thiolate moieties strongly correlate with the reduction potentials and IR spectroscopy of the compounds studied. While all six compounds show varied degrees of electrocatalytic activity, only compound **5**,  $[Fe_2(\mu-SC_6H_4-p-OCH_3)(\mu-SC_6H_4$  $p-CF_3)(CO)_6]$ , provides a low overpotential of proton reduction (0.26 V), at a potential where direct reduction does not compete.

#### **CRediT** authorship contribution statement

**Ryan J. Day:** Investigation, Data curation. **Anthony J. Gross:** Investigation. **Elizabeth S. Donovan:** Investigation, Methodology. **Kyle D. Fillo:** Investigation. **Gary S. Nichol:** Formal analysis. **Greg A.N. Felton:** Conceptualization, Investigation, Visualization, Supervision, Writing - original draft, Writing - review & editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgement

The authors acknowledge the financial support of Eckerd College start-up funds.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115043.

#### References

- M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q. Mi, E.A. Santori, N.S. Lewis, Solar water splitting cells, Chem. Rev. 110 (11) (2010) 6446–6473.
- [2] T. Agarwal, S. Kaur-Ghumaan, HER catalysed by iron complexes without a  $Fe_2S_2$  core: a review, Coord. Chem. Rev. 397 (2019) 188–219.
- [3] G.J. Kubas, Fundamentals of  $H_2$  binding and reactivity on transition metals underlying hydrogenase function and  $H_2$  production and storage, Chem. Rev. 107 (10) (2007) 4152–4205.
- [4] M. Wang, L. Chen, L. Sun, Recent progress in electrochemical hydrogen production with earth-abundant metal complexes as catalysts, Energy Environ. Sci. 5 (5) (2012) 6763.
- [5] S. Fukuzumi, Y.-M. Lee, W. Nam, Thermal and photocatalytic production of hydrogen with earth-abundant metal complexes, Coord. Chem. Rev. 355 (2018) 54–73.
- [6] W. Lubitz, H. Ogata, O. Rüdiger, E. Reijerse, Hydrogenases, Chem. Rev. 114 (8) (2014) 4081–4148.
- [7] C. Tard, C.J. Pickett, Structural and Functional Analogues of the Active Sites of the [Fe]-, [NiFe]-, and [FeFe]-Hydrogenases, Chem. Rev. 109 (6) (2009) 2245– 2274.
- [8] J.C. Fontecilla-Camps, A. Volbeda, C. Cavazza, Y. Nicolet, Structure/Function Relationships of [NiFe]- and [FeFe]-hydrogenases, Chem. Rev. 107 (10) (2007) 4273–4303.

- [9] J.-F. Capon, F. Gloaguen, F.Y. Pétillon, P. Schollhammer, J. Talarmin, Electron and proton transfers at diiron dithiolate sites relevant to the catalysis of proton reduction by the [FeFe]-hydrogenases, Coord. Chem. Rev. 253 (9-10) (2009) 1476–1494.
- [10] J.C. Gordon, G.J. Kubas, Perspectives on how nature employs the principles of organometallic chemistry in dihydrogen activation in hydrogenases, Organometallics 29 (21) (2010) 4682–4701.
- [11] M.Y. Darensbourg, A. Llobet, Preface for small molecule activation: from biological principles to energy applications. Part 3: small molecules related to (artificial) photosynthesis, Inorg. Chem. 55 (2) (2016) 371–377.
- [12] Y. Li, T.B. Rauchfuss, Synthesis of Diiron(I) dithiolato carbonyl complexes, Chem. Rev. 116 (12) (2016) 7043–7077.
- [13] D.M. Heinekey, Hydrogenase enzymes: recent structural studies and active site models, J. Organomet. Chem. 694 (2009) 2671–2680.
- [14] G.A.N. Felton, C.A. Mebi, B.J. Petro, A.K. Vannucci, D.H. Evans, R.S. Glass, D.L. Lichtenberger, Review of electrochemical studies of complexes containing the Fe<sub>2</sub>S<sub>2</sub> core characteristic of [FeFe]-hydrogenases including catalysis by these complexes of the reduction of acids to form dihydrogen, J. Organomet. Chem. 694 (17) (2009) 2681–2699.
- [15] S.L. Matthews, D.M. Heinekey, A carbonyl-rich bridging hydride complex relevant to the Fe–Fe hydrogenase active site, Inorg. Chem. 49 (21) (2010) 9746–9748.
- [16] S. Gao, Y. Liu, Y. Shao, D. Jiang, Q. Duan, Iron carbonyl compounds with aromatic dithiolate bridges as organometallic mimics of [FeFe] hydrogenases, Coord. Chem. Rev. 402 (2020) 213081, https://doi.org/10.1016/j. ccr.2019.213081.
- [17] E.S. Donovan, J.J. McCormick, G.S. Nichol, G.A.N. Felton, Cyclic voltammetric studies of chlorine-substituted diiron benzenedithiolato hexacarbonyl electrocatalysts inspired by the [FeFe]-hydrogenase active site, Organometallics 31 (2012) 8067–8070.
- [18] E.S. Donovan, H.M. Plummer, A. Sosa Parada, G.S. Nichol, G.A.N. Felton, Pnictogen ligand coordination to an iron-sulfur compound, Inorg. Chim. Acta 487 (2019) 387–394.
- [19] R. Kositzki, S. Mebs, N. Schuth, N. Leidel, L. Schwartz, M. Karnahl, F. Wittkamp, D. Daunke, A. Grohmann, U.-P. Apfel, F. Gloaguen, S. Ott, M. Haumann, Electronic and molecular structure relations in diiron compounds mimicking the [FeFe]-hydrogenase active site studied by X-ray spectroscopy and quantum chemistry, Dalton Trans. 46 (37) (2017) 12544–12557.
- [20] D. Chong, I.P. Georgakaki, R. Mejia-Rodriguez, J. Sanabria-Chinchilla, M.P. Soriaga, M.Y. Darensbourg, Electrocatalysis of hydrogen production by active site analogues of the iron hydrogenase enzyme: structure/function relationships, Dalton Trans. (21) (2003) 4158–4163.
- [21] C.M. Thomas, O. Rüdiger, T. Liu, C.E. Carson, M.B. Hall, M.Y. Darensbourg, Synthesis of carboxylic acid-modified [FeFe]-hydrogenase model complexes amenable to surface immobilization, Organometallics 26 (16) (2007) 3976– 3984.
- [22] S.J. Borg, S.K. Ibrahim, C.J. Pickett, S.P. Best, Electrocatalysis of hydrogen evolution by synthetic diiron units using weak acids as the proton source: Pathways of doubtful relevance to enzymic catalysis by the diiron subsite of [FeFe] hydrogenase, C. R. Chimie 11 (8) (2008) 852–860.
- [23] Y. Si, M. Hu, C. Chen, Diiron models for active site of FeFe-hydrogenase with aromatic thiolate bridges: Structures and electrochemistry, C. R. Chimie 11 (8) (2008) 932–937.
- [24] Y. Tang, Z. Wei, W. Zhong, X. Liu, Diiron complexes with pendant phenol group (s) as mimics of the diiron subunit of [FeFe]-hydrogenase: synthesis, characterisation, and electrochemical investigation, Eur. J. Inorg. Chem. (2011) 1112–1120.
- [25] F. Ridley, S. Ghosh, G. Hogarth, N. Hollingsworth, K.B. Holt, D.G. Unwin, Fluorinated models of the iron-only hydrogenase: an electrochemical study of the influence of an electron-withdrawing bridge on the proton reduction overpotential and catalyst stability, J. Electroanal. Chem. 703 (2013) 14–22.
- [26] A.L. Haley, L.N. Broadbent, L.S. McDaniel, S.T. Heckman, C.H. Hinkle, N.N. Gerasimchuk, J.C. Hershberger, C.A. Mebi, [Fe-Fe] hydrogenase models: iron (I)-carbonyl clusters coupled to *alpha* and *para*-toluenethiolate ligands, Polyhedron 114 (2016) 218–224.
- [27] Z Yu, M. Wang, P. Li, W. Dong, F. Wang, L. Sun, Diiron dithiolate complexes containing intra-ligand NH···S hydrogen bonds: [FeFe] hydrogenase active site models for the electrochemical proton reduction of HOAc with low overpotential, Dalton Trans. (18) (2008) 2400.
- [28] C.A. Mebi, D.S. Karr, R. Gao, Diironhexacarbonyl clusters with imide and amine ligands: hydrogen evolution catalysts, J. Coord. Chem. 64 (24) (2011) 4397– 4407.
- [29] F. Wen, X. Wang, L. Huang, G. Ma, J. Yang, C. Li, A Hybrid photocatalytic system comprising ZnS as light harvester and an [Fe<sub>2</sub>S<sub>2</sub>] hydrogenase mimic as hydrogen evolution catalyst, ChemSusChem 5 (2012) 849–853.
- [30] C.A. Mebi, D.S. Karr, B.C. Noll, Using naphthalene-2-thiolate ligands in the design of hydrogenase models with mild proton reduction overpotentials, Polyhedron 50 (1) (2013) 164–168.
- [31] M. Natarajan, I.K. Pandey, S. Kaur-Ghumaan, Synthesis and electrocatalysis of diiron monothiolate complexes: small molecule mimics of the [FeFe] hydrogenase enzyme, Chem. Select 2 (2017) 1637–1644.
- [32] I.K. Pandey, M. Natarajan, H. Faujdar, F. Hussain, M. Stein, S. Kaur-Ghumaan, Intramolecular stabilization of a catalytic [FeFe]-hydrogenase mimic investigated by experiment and theory, Dalton Trans. 47 (14) (2018) 4941– 4949.

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- [33] T. Agarwal, S. Kaur-Ghumaan, Mono- and dinuclear mimics of the [FeFe] hydrogenase enzyme featuring bis(monothiolato) and 1,3,5-triaza-7phosphaadamantane ligands, Inorg. Chim. Acta 504 (2020) 119442.
- [34] S.F.A. Kettle, L.E. Orgel, Alkyl- and Aryl-thio-iron tricarbonyls, J. Chem. Soc. (1960) 3890–3891.
- [35] P.C. Ellgen, J.N. Gerlach, Kinetics and mechanism of the substitution reactions of bis(mercaptotricarbonyliron) complexes, Inorg. Chem. 12 (11) (1973) 2526– 2532.
- [36] R. Mathieu, R. Poilblanc, P. Lemoine, M. Gross, Electrochemical behaviour and chemical oxidation study of the thio- and phosphido-bridge binuclear iron complexes, J. Organomet. Chem. 165 (2) (1979) 243–252.
- [37] J.A. Adeleke, Y.W. Chen, L.K. Liu, Preparation and crystal structures of iron complexes syn-[(μ-SPh)Fe(CO)<sub>3</sub>]<sub>2</sub>, (C<sub>5</sub>H<sub>4</sub>SPh)<sub>2</sub>Fe, Organometallics 11 (1992) 2543–2550.
- [38] B. Suchland, A. Malassa, H. Görls, S. Krieck, M. Westerhausen, Iron(I)-Based Carbonyl Complexes with Bridging Thiolate Ligands as Light-Triggered CO Releasing Molecules (photoCORMs), Z. Anorg. Allg. Chem. 646 (3) (2020) 125– 132.
- [39] E.S. Donovan, G.A.N. Felton, Electrochemical analysis of cyclopentadienylmetal carbonyl dimer complexes: Insight into the design of hydrogen-producing electrocatalysts, J. Organomet. Chem. 711 (2012) 25–34.
- [40] W. Henslee, R.E. Davis, Phenylthio iron tricarbonyl dimer, Cryst. Struct. Comm. 1 (1972) 403–406.
- [41] D. Seyferth, R.S. Henderson, L.-C. Song, Chemistry of μ-dithio-bis (tricarbonyliron), a mimic of inorganic disulfides.1. Formation of Di-μthiolato-bis(tricarbonyliron) Dianion, Organometallics 1 (1982) 125–133.
- [42] L.-C. Song, Investigations on butterfly Fe/S cluster S-centered anions (μ-S<sup>-</sup>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>, (μ-S<sup>-</sup>)(μ-RS)Fe<sub>2</sub>(CO)<sub>6</sub>, and related species, Acc. Chem. Res. 38 (1) (2005) 21–28.
- [43] S. Lü, R.-F. Zhang, Q.-L. Li, J. He, Y.-L. Li, Synthesis, characterization and electrochemical properties of two isomers of Diiron Diselenolato complexes and a new pathway to the μ4-Se twin cluster, J. Organomet. Chem. 873 (2018) 66–72.
- [44] S. Aime, L. Milone, R. Rossetti, P.L. Stanghellini, Solution structures and dynamic behaviour of some iron chalcogen derivatives, Transition Met. Chem. 4 (5) (1979) 322–325.
- [45] L. Maresca, F. Greggio, G. Sbrignadello, G. Bor, The anti-syn equilibria of the organothio bridged derivatives of iron carbonyl, (μ-RS)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>, and of their monosubstitution products with some phosphines, (μ-RS)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>5</sub>(PR'<sub>3</sub>), Inorg. Chim. Acta 5 (1971) 667–674.
- [46] C. Hansch, A. Leo, R.W. Taft, A survey of Hammett substituent constants and resonance and field parameters, Chem. Rev. 91 (2) (1991) 165–195.
- [47] O. In-noi, K.J. Haller, G.B. Hall, W.P. Brezinski, J.M. Marx, T. Sakamoto, D.H. Evans, R.S. Glass, D.L. Lichtenberger, Electrochemical, Spectroscopic, and Computational Study of Bis(μmethylthiolato)diironhexacarbonyl:

Homoassociative Stabilization of the Dianion and a Chemically Reversible

- Reduction/Reoxidation Cycle, Organometallics 33 (2014) 5009–5019.
  [48] E.S. Donovan, G.S. Nichol, G.A.N. Felton, Structural effects upon the durability of hydrogenase-inspired hydrogen-producing Electrocatalysts: Variations in the (μ-edt) [Fe<sub>2</sub>(CO)<sub>6</sub>] system, J. Organomet. Chem. 726 (2013) 9–13.
- [49] R.S. Nicholson, I. Shain, Theory of Stationary Electrode Polarography, Anal. Chem. 36 (1964) 706–723.
- [50] N. Elgrishi, D.A. Kurtz, J.L. Dempsey, Reaction parameters influencing cobalt hydride formation kinetics: implications for benchmarking H<sub>2</sub>-Evolution Catalysts, J. Am. Chem. Soc. 139 (1) (2017) 239–244.
- [51] D.A. Kurtz, B. Dhakal, L.T. McDonald, G.S. Nichol, G.A.N. Felton, Inter-ligand intramolecular through-space anisotropic shielding in a series of manganese carbonyl phosphorous compounds, Dalton Trans. 48 (39) (2019) 14926–14935.
- [52] B. Kwiatek, M.K. Kalinowski, Electrochemical reduction of substituted nitrobenzenes in N,N-dimethylformamide containing proton donating agents, J. Electroanal. Chem. Interfacial Electrochem. 226 (1-2) (1987) 61–67.
- [53] H. Li, C. Huang, Y. Li, W. Yang, F. Liu, Electrocatalytic reduction of trace nitrobenzene using a graphene-oxide@polymerized-manganese-porphyrin composite, RSC Adv. 9 (39) (2019) 22523–22530.
- [54] T. Liu, M. Wang, Z. Shi, H. Cui, W. Dong, J. Chen, B. Åkermark, L. Sun, Synthesis, structures and electrochemical properties of nitro- and amino-functionalized Diiron Azadithiolates as active site models of Fe-Only hydrogenases, Chem. – Eur. J. 10 (18) (2004) 4474–4479.
- [55] a) G. Si, L.-Z. Wu, W.-G. Wang, J. Ding, X.-F. Shan, Y.-P. Zhao, C.-H. Tung, M. Xu, Synthesis, structure and electrochemical property of diphenylacetypene-substituted Diiron Azadithiolates as active site of Fe-only hydrogenases, Tetrahedron Lett. 48 (2007) 4775-4779;
  b) G. Si, W.-G. Wang, H.-Y. Wang, C.-H. Tung, L.-Z. Wu, Facile synthesis and functionality-dependent electrochemistry of Fe-only hydrogenase mimics, Inorg. Chem. 47 (2008) 8101–8111.
- [56] G.A.N. Felton, R.S. Glass, D.L. Lichtenberger, D.H. Evans, Iron-only hydrogenase mimics. thermodynamic aspects of the use of electrochemistry to evaluate catalytic efficiency for hydrogen generation, Inorg. Chem. 45 (23) (2006) 9181–9184.
- [57] B.D. McCarthy, D.J. Martin, E.S. Rountree, A.C. Ullman, J.L. Dempsey, Electrochemical reduction of Brønsted acids by glassy carbon in acetonitrile–implications for electrocatalytic hydrogen evolution, Inorg. Chem. 53 (16) (2014) 8350–8361.
- [58] G.A.N. Felton, Electrocatalytic reactions: anion radical cyclobutanation reactions and electrogenerated base reactions, Tetrahedron Lett. 49 (2008) 884–887.
- [59] G.A.N. Felton, A.K. Vannucci, J. Chen, L.T. Lockett, N. Okumura, B.J. Petro, U.I. Zakai, D.H. Evans, R.S. Glass, D.L. Lichtenberger, Hydrogen generation from weak acids: electrochemical and computational studies of a diiron hydrogenase mimic, J. Am. Chem. Soc. 129 (2007) 12521–12530.