Dimeric FeFe-Hydrogenase Mimics Bearing Carboxylic Acids: Synthesis and Electrochemical Investigation.

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FeFe Hydrogenase Mimic, Electrochemical Degradation Mechanism

ABSTRACT: Hydrogen is expected to be important for future sustainable energy applications. Recent interest in adsorbing water splitting catalysts on a semiconductor surface for electrocatalytic hydrogen production warrants careful study of electrocatalysts with functional groups capable of binding to a surface. The monomeric complex $\text{Fe}_2(\mu\text{-S}_2(\text{CH}_2)_3)(\text{CO})_5\text{PPh}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ ($\text{S}_2(\text{CH}_2)_3 = 1,3\text{-propanedithiolate, pdt}$) and the dimeric complexes $[\{\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\}_2(\mu, \kappa^1, \kappa^1\text{-Ph}_2\text{PCH}_2\text{N}(\text{Ar})\text{CH}_2\text{PPh}_2)]$ ($\text{Ar} = p\text{-CO}_2\text{H-Ph, 3,5-CO}_2\text{HPh, } p\text{-CH}_2\text{CO}_2\text{HPh, } m\text{-CO}_2\text{H-Ph}$) bearing carboxylic acid functional groups have been prepared. The first electrochemical study of these dimeric FeFe complexes indicate that the complexes degrade upon reduction to form the species $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_4(\kappa^2\text{-Ph}_2\text{PCH}_2\text{N}(\text{Ar})\text{CH}_2\text{PPh}_2)]$. A route is proposed for the formation of $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_4(\kappa^2\text{-Ph}_2\text{PCH}_2\text{N}(\text{Ar})\text{CH}_2\text{PPh}_2)]$ from $[\{\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\}_2(\mu, \kappa^1, \kappa^1\text{-Ph}_2\text{PCH}_2\text{N}(\text{Ar})\text{CH}_2\text{PPh}_2)]$ and a crystal

structure of an intermediate in the proposed electrochemical degradation pathway is presented. The electrochemical study presented herein provides valuable insight into degradation pathways of FeFe hydrogenase mimics bearing carboxylic acids amenable to surface immobilization.

Introduction: In 1 hour the sun delivers enough energy to the earth's surface to sustain society's energy demand for an entire year. Solar energy is thus, the largest exploitable renewable energy resource [1]. The problem is energy generation from the sun is intermittent and fairly unpredictable. Therefore, an efficient method for storing this energy is essential for increased exploitation. Accordingly, many research groups have focused on developing integrated solar water splitting systems as a means to store solar energy chemically, in the form of H₂ [2–10].

The development of solar water splitting systems has benefited greatly from the work provided from the years of research on hydrogenases [11]. FeFe hydrogenases provide inspiration and knowledge on how an efficient proton reduction catalyst for water splitting systems may be designed [10,12]. Mimics of the FeFe hydrogenase active site have proved to be a promising class of molecular electrocatalysts for proton reduction in the presence of acids in non-aqueous media [11–14]. Understanding electron transfer chemistry of synthetic models was fundamental in guiding the design of newer, better systems for electrocatalytic hydrogen production for application in water splitting systems [15–17].

Recently, there has been great interest in adsorbing well-studied, water splitting catalysts on a semiconductor surface. In 2012, Ott and coworkers demonstrated light driven electron transfer between a photosensitizer and a proton reducing catalyst using a pentacoordinate iron complex as a functional model of the distal iron in FeFe hydrogenases [7,18]. Using this work as motivation, Sun and coworkers demonstrated visible light driven water splitting from a p-type dye-sensitized device [10]. Wu and coworkers improved on this system by linking the dye directly to the catalyst [2]. A carboxylic acid moiety was used as a group to bind to the semiconducting surface in all works described above.

The interest in immobilizing proton reducing catalysts onto semi-conductor surfaces warrants careful study of electrochemical processes of catalysts containing moieties capable of anchoring to surfaces. While there has been a great amount of electrochemical mechanistic studies on simpler FeFe hydrogenase models [12,15–17], investigations into models containing anchoring groups is lacking. Given the initial success of integrated solar water-splitting systems [2,7], it is important to develop and understand electrochemical properties of catalysts with the ability to be immobilized on a surface.

Complexes $\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\text{PPh}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ (**2**) and $[\{\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\}_2(\mu, \kappa^1, \kappa^1\text{-Ph}_2\text{PCH}_2\text{N}(\text{Ar})\text{CH}_2\text{PPh}_2)]$ (Ar = *p*-CO₂H-Ph (**3**), 3,5-CO₂HPh (**4**), *p*-CH₂CO₂HPh (**5**)) bearing carboxylic acid functional groups amenable to surface immobilization have been prepared. The synthetic strategy outlined affords a family of FeFe hydrogenase mimetic catalysts bearing carboxylic acid functionalities for anchoring on a semi-conductor surface. Cyclic voltammetry in *N,N*-dimethyl formamide (DMF) solutions indicate that complexes **3**, **4**, and **5** degrade upon reduction to form $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_4(\kappa^2\text{-Ph}_2\text{PCH}_2\text{N}(\text{Ar})\text{CH}_2\text{PPh}_2)]$. A route is proposed for the degradation product and a crystal structure of an intermediate in the proposed electrochemical degradation pathway is presented.

Materials and Methods

General Considerations. All reactions and operations were carried out under a dry argon atmosphere with standard Schlenk techniques. Solvents for syntheses were HPLC-grade and further purified using an alumina filtration system. All commercially available reagents (including $\text{Fe}_3(\text{CO})_{12}$, L1, HPPH_2) were of ACS grade and used without further purification. ¹H NMR spectra were recorded on 400 MHz Bruker spectrometers and are reported relative to TMS. ³¹P NMR spectra were recorded on 400 MHz Bruker spectrometers and are reported relative to H₃PO₄. High-resolution mass spectra were obtained on Bruker MicroTOF-II mass spectrometer from the mass spectrometry facility at The Ohio State University. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer.

X-ray Structure Determination. Details of x-ray structure determination and crystallographic data are summarized in the SI.

Electrochemistry. Cycling voltammetry measurements were performed using a Gamry Reference 600 Potentiostat. All voltammograms were obtained in a three-electrode cell under Ar atmosphere at room temperature. The working electrode was a glassy carbon disk (0.071 cm²), and a platinum mesh was used as the auxiliary electrode. The experimental reference electrode was Ag/AgNO₃, and measured potentials are reported vs NHE, as determined from recording with an internal reference of Cp₂Fe/Cp₂Fe⁺ = 0.69 V vs NHE in DMF. The supporting electrolyte was 0.1 M ⁿBu₄NPF₆ and the scan rate was 100 mV/s.

Representative synthesis of L2 and L3 [19]. To an oven dried round bottom flask was added diphenylphosphine (0.93 mL, 5.4 mmol) and paraformaldehyde (150 mg, 5.4 mmol) under an atmosphere of Ar. The slurry was heated for 1 h at 110 °C to afford a clear, colorless liquid. After allowing to cool, 10 mL of MeOH (dried over CaH₂) and the amine reagent (2.68 mmol, amine reagent = 4-aminobenzoic acid or 5-aminoisophthalic acid) was added to the flask to afford a yellow solution. The solution was heated at reflux for 2 h under Ar, during which time a solid precipitated out of solution. The solid was collected by filtration and washed with MeOH and Et₂O to afford crystalline solid.

Ph₂PCH₂N(*p*-CO₂H-Ph)CH₂PPh₂ (L2). Yield: 0.9 g (65%). ¹H NMR (d⁶-DMSO): δ 12.15 (s, 1H), 7.36 (m, 13H), 7.32 (m, 7H), 7.00 (m, 2H), 6.78 (m, 2H), 3.94 (d, 4H), 3.41 (s, 2H). ³¹P NMR (CDCl₃): δ -26.8.

Ph₂PCH₂N(3,5-CO₂H-Ph)CH₂PPh₂ (L3). Yield: 1 g (65%). ¹H NMR (d⁶-DMSO): δ 12.98 (s, 2H), 7.77 (m, 1H), 7.58 (m, 2H), 7.37 (m, 12H), 7.33 (m, 8H), 3.99 (m, 4H). ³¹P NMR (CDCl₃): δ -28.3.

Ph₂PCH₂N(*p*-CH₂CO₂H-Ph)CH₂PPh₂ (L4) [19]. To an oven dried round bottom flask was added diphenylphosphine (0.93 mL, 5.4 mmol) and paraformaldehyde (150 mg, 5.4 mmol) under an

atmosphere of Ar. The slurry was heated for 1 h at 110 °C to afford a clear, colorless liquid. After allowing to cool, MeOH (10 mL, dried over CaH₂) and 4-aminophenylacetic acid (2.68 mmol) was added to the flask to afford a clear, orange/yellow solution. The solution was heated at reflux for 3 h before solvent was removed by vacuum rotary evaporation to afford a gummy off white/yellow solid. The solid was crystallized by layering hexanes over a concentrated ethanol solution to afford an off white crystalline solid.

Ph₂PCH₂N(*p*-CH₂CO₂H-Ph)CH₂PPh₂ (L4). Yield: 1 g (70%). ¹H NMR (d⁶-DMSO): δ 12.15 (s, 1H), 7.36 (m, 13H), 7.32 (m, 7H), 7.00 (m, 2H), 6.78 (m, 2H), 3.94 (m, 4H), 3.41 (s, 2H). ³¹P NMR (CDCl₃): δ -27.5.

Fe₂(μ-pdt)(CO)₆ (1). The following procedure is adapted from previous methods [20]. A 50 mL schlenk flask was charged with toluene (10 mL). Under a strong flow of Ar was added Fe₃(CO)₁₂ (1.3 g, 2.6 mmol). To this green solution was added 1,3-propanedithiol (0.29 mL, 2.9 mmol). The green solution was heated at reflux for 3 h, turning red after 20 min. Solvent was removed by vacuum rotary evaporation and the crude product was subjected to silica gel chromatography (hexanes) to afford a red crystalline solid. Yield: 1.0 g (80%). ¹H NMR (CDCl₃): δ 2.14 (br t, 4H, SCH₂), 1.80 (m, CH₂). IR (CH₂Cl₂): νCO = 2071, 2032, 1998 cm⁻¹.

Representative synthesis of complexes 2-5. To round bottom flask was added **1** (100 mg, 0.259 mmol, 1.1 eq (2.2 eq for **3-5**)) followed by trimethylamine *N*-oxide hydrate (26.2 mg, 0.236 mmol (1:1 (CH₃)₃NO:Phosphine) and dry CH₃CN (10 mL). The flask was evacuated and refilled (Ar) and the resulting dark red solution was allowed to stir for 5 min at RT before PPh₂C₆H₄CO₂H (72.1 mg, 0.236 mmol) was added. The flask was again evacuated and refilled (Ar) and the mixture was then allowed to stir for 3 h at RT. The resulting suspension was diluted with DCM, washed with 1M HCl, water, and brine. The organic layer was dried over Na₂SO₄, filtered and solvent removed by vacuum rotary evaporation to afford a red solid. The solid was dissolved in DCM and the crude product was subjected

to silica gel chromatography, eluting first with DCM to remove **1** and then DCM:MeOH (9:1) to afford a red crystalline solid.

Yield(**2**): 100 mg (65%). ^{31}P NMR (CDCl_3): δ 65.7. IR (CH_2Cl_2): ν_{CO} = 2046, 1985, 1934, 1735 cm^{-1} . ESI-MS: m/z 662.9 $[\text{M-H}]^-$.

Yield(**2-1**): 100 mg (60%). ^{31}P NMR (CDCl_3): δ 64.9. IR (CH_2Cl_2): ν_{CO} = 2046, 1985, 1934, 1735 cm^{-1} .

$[\{\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\}_2(\mu, \kappa^1, \kappa^1\text{-Ph}_2\text{PCH}_2\text{N}(p\text{-CO}_2\text{H-Ph})\text{CH}_2\text{PPh}_2)]$ (**3**). Yield: 135 mg (90%). ^{31}P NMR (CDCl_3): δ 59.2. IR (CH_2Cl_2): ν_{CO} = 2045, 1981, 1925, 1712 cm^{-1} . ESI-MS: m/z 1247.84 $[\text{M-H}]^-$.

$[\{\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\}_2(\mu, \kappa^1, \kappa^1\text{-Ph}_2\text{PCH}_2\text{N(Ph)CH}_2\text{PPh}_2)]$ (**3-1**). Yield: 135 mg (90%). ^{31}P NMR (CDCl_3): δ 59.2. IR (CH_2Cl_2): ν_{CO} = 2045, 1981, 1925, 1712 cm^{-1} .

$[\{\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\}_2(\mu, \kappa^1, \kappa^1\text{-Ph}_2\text{PCH}_2\text{N(3,5-CO}_2\text{HPh)CH}_2\text{PPh}_2)]$ (**4**). Yield: 150 mg (80%). ^{31}P NMR (CDCl_3): δ 58.6. IR (CH_2Cl_2): ν_{CO} = 2044, 1980, 1928, 1732 cm^{-1} . ESI-MS: m/z 1291.82 $[\text{M-H}]^-$.

$[\{\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\}_2(\mu, \kappa^1, \kappa^1\text{-Ph}_2\text{PCH}_2\text{N}(p\text{-CH}_2\text{CO}_2\text{HPh)CH}_2\text{PPh}_2)]$ (**5**). Yield: 110 mg (70%). ^{31}P NMR (CDCl_3): δ 58.87. IR (CH_2Cl_2): ν_{CO} = 2044, 1978, 1922, 1710 cm^{-1} . ESI-MS: m/z 1261.85 $[\text{M-H}]^-$.

$[\{\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\}_2(\kappa^2\text{-(Ph}_2\text{PCH}_2)_2\text{N(Ph)})]$ (**6**). ^{31}P NMR (CDCl_3): δ 53.07. IR (CH_2Cl_2): ν_{CO} = 2021, 1947, 1892 cm^{-1} .

Results and Discussion

Synthesis and Characterization. Previous work has shown when $(\text{Ph}_2\text{PCH}_2)_2\text{N(Ph)}$ was used for the CO-displacement of $\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6$ (**1**) in the presence of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in CH_3CN at room temperature, the dimeric complex $[\{\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\}_2(\mu, \kappa^1, \kappa^1\text{-Ph}_2\text{PCH}_2\text{N(Ph)CH}_2\text{PPh}_2)]$ (**6**) was the sole product [21]. Furthermore, a family of ligands (L2-L4, scheme 1) bearing carboxylic acid

functional groups has also been described [19]. Combining these two synthetic strategies, two equivalents of **1** in the presence of CO-removing reagent $\text{Me}_3\text{NO} \cdot 2 \text{H}_2\text{O}$ afforded the monosubstituted complexes **3**, **4**, and **5** (65-90%) (Scheme 1). All new complexes presented herein were characterized by MS, IR and ^{31}P NMR spectra. Furthermore, x-ray crystal structures were obtained for complexes **3** and **4**. The results of the mass spectra for all complexes are in good agreement with the previously reported diiron complexes [21].

Each complex displays three νCO stretches comparable to those reported for analogous diiron complexes, along with an additional stretch at $\sim 1700 \text{ cm}^{-1}$ for the carboxylic acid moiety [21]. The νCO stretches of the monomeric complex **2** display a red shift from 25 cm^{-1} to 64 cm^{-1} in comparison with the all-CO diiron complex **1** indicating the strong donating character of the phosphine (L2). The νCO stretches of **2** shows very little difference with the $\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5\text{PPh}_3$ (**2-1**) indicating little effect in electronic environment of the iron centers with PPh_3 or $\text{PPh}_2(\text{p-C}_6\text{H}_4\text{CO}_2\text{H})$ (**L2**, **2**) as ligands. Similar changes in the νCO bands as in **2** and **2-1** were observed for complexes **3-5**. The stretching frequencies of all complexes are summarized in Table 1, and the spectra are presented in the SI.

The molecular structures of **3** and **4** were determined by X-ray diffraction studies of single crystals, which are shown in Figure 1. Similar to that of previously reported complexes [21], the central $[\text{Fe}_2\text{S}]$ structure of all complexes has a butterfly framework, and each iron atom is coordinated with a pseudosquare-pyramidal geometry. The main framework of **3** and **4** are similar to each other and to previously reported dimeric complexes [21]. Complexes **3** and **4** are of the type $\text{Fe}_2(\text{SR})_2(\text{CO})_5(\text{PR}_3)$ with the formal oxidation state of the Fe centers as +1. Complexes of this type were reported as diamagnetic as early as 1973 [22]. The metal-metal bonding was used to explain the diamagnetism and how to satisfy the 18-electron rule on each iron. Furthermore, the Fe—Fe bond distances in complexes **3** and **4** in our work were $2.502 \text{ \AA}$ and $2.511 \text{ \AA}$ respectively, which is similar to the Fe—Fe bond distance in similar complexes [12,21]. Therefore, given the bond distances and oxidation state in our

complexes, an Fe—Fe bond is shown in each of our molecular structures. Crystallographic details of each complex are outlined in the SI.

Electrochemistry. The redox behavior of the diiron complexes in solution was investigated using cyclic voltammetry (CV). CV data were collected for **2-5** for comparison with the analogous unfunctionalized complexes, **2-1** and **3-1**. Redox potentials are summarized in Table 1. Initial CVs were recorded in dichloromethane (DCM), as is typical for CV measurements of FeFe hydrogenase mimics [23]. Due to the low solubility of the carboxylic acid derivatives in DCM, follow up experiments were carried out in DMF. A restricted region of the CV was used in order to simplify the analysis of the reducing region ($-0.5\text{ V} \rightarrow -2.0\text{ V}$ vs NHE). When a wider range was used, CVs matched other previously reported monosubstituted FeFe hydrogenase mimics, and the full range CVs are presented in the SI [23].

CVs of the **2** and **2-1** in DCM and DMF show an irreversible reductive process at -1.15 V vs NHE indicative of the reduction of a monophosphinated Fe center (Figure 2) [23]. CVs of **3-5** in DMF also show a similar irreversible reductive process at -1.15 V vs NHE. However, a second, semi-reversible reductive process at -1.48 V occurs in **3-5** (Figure 3). Therefore, there is an unexpected difference in redox chemistry between the complexes **2** and **3-5**. An early study of $\text{Fe}_2(\mu\text{-pdt})(\text{CO})_6$ type complexes demonstrated that CO substitution with $\text{P}(\text{OMe})_3$ occurs upon reduction [24]. Furthermore, the large amount of literature on the electrochemistry of $\text{Fe}_2(\text{pdt})(\text{CO})_5\text{L}$ and $\text{Fe}_2(\text{pdt})(\text{CO})_4\text{L}_2$ ($\text{L} = \text{PX}_3 - \text{PPh}_3$ for example) allowed us to hypothesize that the second reduction peak may be the di-substituted complex **6** (Figure 4) [23]. We therefore synthesized **6** according to the reported procedure and a CV was recorded in DMF [25]. When the CV of **3-1** and **6** are compared (Figure 5), one can see the excellent agreement in the second reductive process which indicates that the reductive degradation of **3-1** to form **6** is underway.

A complex where the $\text{Ph}_2\text{PCH}_2\text{N}(\text{Ar})\text{CH}_2\text{PPh}_2$ ligand binds in a P—Fe—P (**6** for example) fashion could be present in the starting material. The presence of such a complex may result in the second reduction wave at -1.45 V vs NHE, without going through a degradative pathway as shown in Figure 4. The IR stretching frequencies of **6** show a significant red shift relative to IR stretching frequencies of **2-5** (Table 1). No indicative peaks of bidentate complexes (such as **6**) are found in any of the dimeric structures. As an example, Figure 6 shows an IR spectra of **3-1** and **6**, clearly showing that there is no **6** present in the starting material. Therefore **6** is being formed in-situ.

Degradative Route. We hypothesized that the reductive degradation pathway from **3-1** to **6** may proceed through a route outlined in Figure 7. Upon reduction of an Fe center, dissociation of phosphorous on one of the FeFe centers occurs to afford intermediate (**I**). Association of the free phosphorous to the remaining FeFe center followed by dissociation of a CO ligand affords **6**, which is then reduced in solution (Figure 7).

Evidence for a similar pathway, but without an applied potential was found when growing crystals for these structures. We found that when crystals were grown from a tetrahydrofuran (THF) solution (coordinating environment), two distinct crystals structures were apparent. Red, square platelets and red needles were obtained. The needle structures found were determined to be **3** (Figure 1). The platelets were determined to be $[\text{Fe}_2(\mu\text{-pdt})(\text{CO})_5(\kappa^1\text{-Ph}_2\text{PCH}_2\text{N}(p\text{-CO}_2\text{H-Ph})\text{CH}_2\text{PPh}_2)]$ (intermediate **I**, Figure 8). ^{31}P NMR confirmed that **I** was not present in the starting material. The ^{31}P NMR of all complexes synthesized may be found in the SI. Again, no indicative peaks of **I** were found in any of the dimeric structures.

The presence of **I** in a coordinating solvent suggests that the first step of the degradative pathway to form **I** does not require reduction to proceed. However, it has been demonstrated previously that when the Fe center is reduced, the process of ligand dissociation is more facile [24]. When crystals were

grown from a DCM:Ethanol mixture (50:1), where only a small portion of the solvent is coordinating, only one crystal structure was apparent – red needles, complex **3**.

Improved stability of 4. Complexes **2**, **3** and **5** all showed similar CV responses in the reductive region -1.15 V and -1.48 V vs NHE (Figure 3). Complex **4** does show a slight peak at -1.48 V, however the reductive peak is significantly smaller (Figure 9). The smaller second reductive peak indicates that **4** may be more stable to ligand dissociation relative to the other complexes. The improved stability may be because the carboxylic acid moieties in the 3,5 positions may protect the iron centers from the coordinating solvents, which is thought to initiate the degradation [24]. The carboxylic acids may also contribute an inductive effect, where the electron-withdrawing nature of the carboxylic acids contributes to better P—Fe interactions.

Conclusion

Complexes **2-5** bearing carboxylic acid functional groups have been prepared. Cyclic voltammetry in a DMF solution indicates that the intermolecular bridged complexes degrade upon reduction to form $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-Ph}_2\text{PCH}_2\text{N}(\text{Ar})\text{CH}_2\text{PPh}_2)]$. A route is proposed for this degradation product and a crystal structure of an intermediate in the proposed electrochemical degradation pathway is presented. The complexes presented in this work may potentially be used in the design of heterogeneous hydrogen evolution catalysts. Therefore, understanding the electrochemical processes is important. Thus, the electrochemical degradation pathway presented here may provide valuable insight in the future designs of heterogeneous hydrogen evolution catalysts.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data of complexes **3**, **4** and **I** are presented in CIF format. IR and ^{31}P NMR Spectra are detailed. Crystallographic data for **3** were collected through the SCrALS (Service Crystallography at the Advanced Light Source) program at Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The ALS is supported by the

U.S. Department of Energy, Office of Energy Sciences Materials Sciences Division, under contract DE-AC02-05CH11231. CCDC <1404584>, CCDC <1404585>, and CCDC <1404586> contain the supplementary crystallographic data for complexes **3**, **4** and **I**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk

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Scheme 1. Reaction scheme of **1-5**.

Complexes	$\nu(\text{CO})(\text{cm}^{-1})$ (CH_2Cl_2)	$\text{Fe}^{\text{I}}/\text{Fe}^{\text{0}}$ V vs NHE(DMF)
1	2071, 2032, 1998	-
2	2046, 1981, 1960, 1925, 1713	-1.13
2-1	2046, 1985, 1960, 1933	-1.12
3	2046, 1981, 1960, 1926, 1712	-1.14, -1.50
3-1	2045, 1981, 1960, 1925	-1.20, -1.49
4	2045, 1982, 1958, 1925, 1745, 1707	-1.21
5	2045, 1981, 1959, 1927, 1747, 1709	-1.16, -1.5
6	2021, 1947, 1892	-1.45

Table 1. FTIR stretching frequencies for complexes in the carbonyl region and selected reduction potentials (-0.5 V $\rightarrow$ -2.0 V vs NHE).

Figure 1. X-ray crystal structures of **3** and **4**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms, solvent molecules and disorder at the propane dithiolate bridge are omitted for clarity.

Figure 2. Cyclic voltammograms of **2** and **2-1** (1 mM) in 0.1 M $n\text{Bu}_4\text{NPF}_6$ in dichloromethane and N,N -dimethylformamide under an Ar atmosphere.

Figure 3. Cyclic voltammograms of complexes **3**, **3-1**, and **5**, (1 mM) in 0.1 M $n\text{Bu}_4\text{NPF}_6$ in DMF under an Ar atmosphere.

Figure 4. Proposed reduced species observed in a selected region of the CV ($-0.5 \text{ V} \rightarrow -2.0 \text{ V}$ vs NHE).

Figure 5. Cyclic voltammograms of **3-1** and **6** (1 mM) in 0.1 M $n\text{Bu}_4\text{NPF}_6$ in DMF under an Ar atmosphere.

Figure 6. Select regions of the IR spectra of **3-1** and **6**. The spectra show the clear shift of **6** relative to **3-1**.

Figure 7. Proposed degradative route of **3-1** to **6**. The route is believed to be operating during the reduction of **3-5**.

Figure 8. X-ray crystal structures of **I**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. The crystal structure of **I** is partially oxidized at atom P(2), where oxygen atom O(8) is present 14% of the time. As a result, this crystal consists of a mixture of oxidized (14%) and non-oxidized (86%) Fe dimer molecules. Both structures are presented in the SI.

Figure 9. Cyclic voltammograms of **3-1** and **4** (1 mM) in 0.1 M $n\text{-Bu}_4\text{NPF}_6$ in DMF under an Ar atmosphere.

The electrochemical study presented provides valuable insight into degradation pathways of FeFe hydrogenase mimics. The first electrochemical study of dimeric FeFe complexes indicate that the intermolecular bridged complexes degrade upon reduction to form the bidentate species $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-Ph}_2\text{PCH}_2\text{N}(\text{Ar})\text{CH}_2\text{PPh}_2)]$. A route for the electrochemical degradation pathway is presented.