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# [FeFe]-Hydrogenase Models: Overpotential Control for Electrocatalytic $H_2$ Production by Tuning of the Ligand $\pi$ -Acceptor Ability

Fengwei Huo,<sup>[a]</sup> Jun Hou,<sup>\*[a,b]</sup> Guicai Chen,<sup>[b]</sup> Dongming Guo,<sup>[a]</sup> and Xiaojun Peng<sup>\*[b]</sup>

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In the search for synthetic competitive catalysts that function with hydrogenase-like capability, a series of (Pyrrol-1-yl)phosphane-substituted diiron complexes  $[(\mu-pdt)Fe_2(CO)_5L]$ [pdt = propanedithiolate, L = Ph<sub>2</sub>PPyr (**2**), PPyr<sub>3</sub> (**4**); Pyr = pyrrolyl] and  $[(\mu-pdt)Fe_2(CO)_4L_2]$  [L = Ph<sub>2</sub>PPyr (**3**), PPyr<sub>3</sub> (**5**)] were prepared as functional models for the active site of Feonly hydrogenase. The structures of these complexes were fully characterized by spectroscopy and X-ray crystallography. In the IR spectra the CO bands for complexes **2–5** are shifted to higher energy relative to those of complexes with "traditional" phosphane ligands, such as PPh<sub>3</sub>, PMe<sub>3</sub>, and PTA (1,3,5-triaza-7-phosphaadamantane), indicating that (pyrrol-1-yl)phosphanes are poor  $\sigma$ -donors and better  $\pi$ -acceptors. The electrochemical properties of complexes **2–5** were studied by cyclic voltammetry in CH<sub>3</sub>CN in the absence and presence of the the weak acid HOAc. The reduction potentials of these complexes show an anodic shift relative to other phosphane-substituted derivatives. All of the complexes can catalyze proton reduction from HOAc to H<sub>2</sub> in CH<sub>3</sub>CN at their respective Fe<sup>1</sup>Fe<sup>0</sup> level. Complex **4** is the most effective electrocatalyst, which catalytically generates H<sub>2</sub> from HOAc at –1.66 V vs. Fc<sup>+</sup>/Fc with only ca. 0.2 V overpotential in CH<sub>3</sub>CN.

### Introduction

Hydrogen has attracted remarkable interest as a clean and highly efficient energy carrier of the future.<sup>[1]</sup> However, presently expensive platinum-containing catalysts are used to efficiently catalyze hydrogen evolution from the reduction of protons and electrons.<sup>[2]</sup> Therefore, the search for less expensive and more efficient catalysts to replace platinum-based materials is an important goal for hydrogen energy applications.<sup>[3,4]</sup>

[FeFe]-hydrogenase ([FeFe]-H<sub>2</sub>ase) can efficiently catalyze the reversible reduction of protons to hydrogen with high rates up to 6000 molecules of H<sub>2</sub> per second per mmol.<sup>[5–7]</sup> The active site, which generates H<sub>2</sub>, consists of a 2Fe2S unit bridged to a 4Fe4S cluster by a cystein-S bridge, as revealed by X-ray structure determinations<sup>[8,9]</sup> and IR spectroscopic studies<sup>[10,11]</sup> illustrated in Figure 1A. The two Fe atoms in the 2Fe2S unit are coordinated by CO and CN<sup>-</sup>, as well as a bridging 1,3-dithiolato ligand.<sup>[12,13]</sup> Please note that the L ligand has not been identified with certainty, and it is possibly H<sub>2</sub>O, H or vacant based on different redox states.

Technology Dalian 116012, P. R. China E-mail: pengxj@dlut.edu.cn  $Fe_{4}S_{4}(S-cys)_{3}$   $Fe_{4}S_{4}(S-cys)_{4}$   $Fe_{4}S_{4}(S-cys)_$ 

Figure 1. Active site of  $[Fe]H_2ase$  (A) and the synthetic  $Fe^IFe^I$  electrocatalysts for  $H_2$  production (B).

Since the elucidation of the structures of  $[FeFe]-H_2ase$ , there have been numerous attempts aimed at the synthesis of diiron complexes that mimic the active site of  $[FeFe]-H_2ase$  in the past few years.<sup>[14–18]</sup> Mono- and disubstituted diiron complexes for electrocatalytic H<sub>2</sub> production were developed (Figure 1B).<sup>[19–24]</sup> However, the Fe<sup>I</sup>Fe<sup>I</sup> catalysts synthesized so far require the harsh conditions of either strong acids (i.e., HOTs or HClO<sub>4</sub>)<sup>[21–25]</sup> or a relatively high overpotential (0.5–1.0 V).<sup>[19,20]</sup> As is well known, [FeFe]-H<sub>2</sub>ase can generate H<sub>2</sub> at neutral pH and at low potential (ca. –0.8 V vs. Fc<sup>+</sup>/Fc). Thus, the major challenge now is to search for synthetic competitive catalysts with a low overpotential that function with [FeFe]-H<sub>2</sub>ase-like capability under mild conditions for both proton and electron sources.

Theoretic<sup>[26,27]</sup> and experimental<sup>[19,28–30]</sup> studies indicate that the ligands at the diiron core have an important influence on the electrocatalytic capabilities of the 2Fe2S com-

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<sup>[</sup>a] Key Laboratory for Precision & Non-traditional Machining of the Ministry of Education, Dalian University of Technology Dalian 116024, P. R. China Fax: +86-411-84706059 E-mail: junhou@dlut.edu.cn
[b] State Key Laboratory of Fine Chemicals, Dalian University of

plexes. In this context, numerous  $\sigma$ -donor-ligand-substituted diiron complexes, [(µ-pdt)Fe<sub>2</sub>(CO)<sub>5</sub>L] and [(µ-pdt)- $Fe_2(CO)_4L_2$  [L = PMe<sub>3</sub>, PMe<sub>2</sub>Ph, PPh<sub>3</sub>, P(OEt)<sub>3</sub>, CN<sup>-</sup>, 1,3,5-triaza-7-phosphaadamantane (PTA)] have been extensively investigated.<sup>[19,20,28-30]</sup> (Pyrrol-1-yl)phosphanes have been widely used to tune metal reactivity and selectivity in homogeneous catalysis because of their exceptional  $\pi$ -acceptor character.<sup>[31]</sup> Some (Pyrrol-1-yl)phosphane-substituted rhodium complexes, [Rh(acac)(CO)L] and [RhH-(CO)L (acac = acetylacetonato), were reported for hydroformylation with higher yields and better selectivity.<sup>[32,33]</sup> However, to the best of our knowledge, there is as yet no report on the use of (pyrrol-1-yl)phosphane-substituted diiron dithiolates as [FeFe]-H2ase model complexes. This led us to explore 2Fe2S synthetic catalysts with small overpotentials by tuning ligand  $\pi$ -acceptor ability using (pyrrol-1yl)phosphane ligands. Thus, we herein report on (pyrrol-1-yl)phosphane mono- and disubstituted diiron complexes formed by CO/L exchange reaction to study the influence of (pyrrol-1-yl)phosphanes on structure and electrochemical properties. The issue of overpotential in proton reduction by these complexes is also discussed.

### **Results and Discussion**

# Preparation and Spectroscopic Characterization of Complexes 2–5

These new complexes were obtained in moderate yield by refluxing toluene solutions of 1 with (pyrrol-1-yl)phosphane. The preparation of these phosphane-substituted diiron complexes is summarized in Scheme 1.

The reaction of 1 with 1 mol-equiv. of Ph<sub>2</sub>PPyr in refluxing toluene for 48 h gave monosubstituted complex 2 in good yield. Disubstituted complex 3 as a major product together with a small amount of monosubstituted complex 2 was obtained by refluxing a solution of 1 with 2 equiv. of Ph<sub>2</sub>PPyr for 48 h. In a similar way, complexes 4 and 5 were prepared in refluxing toluene by treatment of 1 with 1 and 2 equiv. of PPyr<sub>3</sub>, respectively. However, the preparation of PPyr<sub>3</sub>-substituted complexes is relatively more difficult than that of Ph<sub>2</sub>PPyr-substituted derivatives, presumably because of the electronic effect. The reactivity of PPyr<sub>3</sub> is unusual as compared to that of alkylphosphanes. For instance, PPh<sub>3</sub> and PMe<sub>3</sub> can readily react with **1** to give mono- and disubstituted derivatives.<sup>[30]</sup> These observations are consistent with a greatly reduced nucleophilicity for the phosphorus atom in PPyr<sub>3</sub>, presumably due to aromatic delocalization of the nitrogen lone pair into the ring.<sup>[31]</sup>

The products obtained in analytically pure form are soluble in CH<sub>2</sub>Cl<sub>2</sub>, THF, and acetone. All complexes are airand thermally stable in the solid state but moderately sensitive in solution, and were characterized by IR and NMR spectroscopy as well as HR mass spectrometry, as detailed in the Experimental Section. The HR-MS analyses are in good agreement with the supposed molecular weight. The resonances of the 1,3-propanedithiolato methylene hydrogen and carbon atoms in their characteristic regions show a high-field shift as compared to the all-CO complex 1, because of the shield effects of the aromatic rings at the bulky tertiary phosphane ligands. The IR spectra of complexes 2–5 exhibit three major  $v_{CO}$  bands in the region 2056–1962 cm<sup>-1</sup>. All compounds were identified by X-ray structure determinations.

#### Molecular Structures of Complexes 2-5

The crystal structures of **2–5** were determined by X-ray crystallography and are shown in Figure 2. Selected bond lengths and bond angles are listed in Table 1.

The 2Fe2S centers of all complexes are six-coordinate and exhibit square-pyramidal geometries. The Fe–Fe distances [2.5222(10) Å in **2**, 2.5188(6) Å in **3**, 2.523(2) Å in **4**, and 2.5237(8) Å in **5**] are in good agreement with those found in tertiary phosphane-substituted diiron analogues.<sup>[19,20,30,34]</sup>

In monosubstituted derivatives **2** and **4**, the coordination configurations are nearly identical with the tertiary phosphane monosubstituted derivatives  $[(\mu-pdt)Fe_2(CO)_5L]$  [L =



Scheme 1. (a) for **2**,  $Ph_2PPyr$  (1 equiv.), toluene, reflux, 48 h; for **3**,  $Ph_2PPyr$  (2 equiv.), toluene, reflux, 72 h; (b) for **4**,  $PPyr_3$  (1 equiv.), toluene, reflux, 48 h; for **5**,  $PPyr_3$  (2 equiv.), toluene, reflux, 72 h.





Figure 2. ORTEP (ellipsoids at 30% probability level) view of 2 (a), 3 (b), 4 (c), and 5 (d).

	2	4		3	5
Bond lengths [Å]					
Fe(1)–Fe(2)	2.5222(10)	2.5188(6)	Fe(1)–Fe(2)	2.523(2)	2.5237(8)
Fe(1) - S(1)	2.2609(15)	2.2486(8)	Fe(1)-S(1)	2.274(3)	2.2768(12)
Fe(1)-S(2)	2.2594(15)	2.2584(8)	Fe(1) - S(2)	2.270(3)	2.2778(12)
Fe(2) - S(1)	2.2636(15)	2.2617(7)	Fe(2)-S(1)	2.268(3)	2.2733(12)
Fe(2)-S(2)	2.2635(15)	2.2563(8)	Fe(2)-S(2)	2.263(3)	2.2509(12)
Fe-Pap	2.2247(1)	2.1661(7)	Fe-P <sub>ap</sub> <sup>[c]</sup>	2.215(8)	2.1725(1)
Fe-C <sub>CO an</sub>	1.802(6)	1.801(3)	$Fe-C_{CO}ba^{[d]}$	1.767(6)	1.769(2)
Fe-C <sub>CO ba</sub> [a]	1.774(4)	1.783(1)	P–N	$1.746(2)^{[e]}$	$1.709(3)^{[f]}$
P–N	1.761(4)	$1.7096(2)^{[b]}$			
Bond angles [°]					
Fe(1)-S(1)-Fe(2)	67.76(4)	67.90(2)	Fe(1)–S(1)–Fe(2)	67.50(9)	67.37(3)
Fe(1)-S(2)-Fe(2)	67.79(5)	67.82(2)	Fe(1)-S(2)-Fe(2)	67.64(9)	67.73(4)
P(1) - Fe(2) - Fe(1)	156.96(5)	155.11(2)	P(1)-Fe(1)-Fe(2)	158.29(9)	160.60(4)
P(1)-Fe(2)-S(1)	110.99(5)	108.11(3)	P(2)-Fe(2)-Fe(1)	154.16(10)	154.01(4)
P(1)-Fe(2)-S(2)	106.94(6)	107.22(3)	P(1) - Fe(1) - S(1)	109.10(12)	110.74(4)
S(1) - Fe(2) - Fe(1)	56.07(4)	55.80(2)	P(1) - Fe(1) - S(2)	110.19(11)	111.86(5)
S(2) - Fe(2) - Fe(1)	56.03(4)	56.13(2)	S(1) - Fe(1) - Fe(2)	56.14(9)	56.25(3)
		(-)	S(2) - Fe(1) - Fe(2)	56.06(8)	55.63(3)

Table 1. Selected bond lengths and angles for 2–5.

[a] Average of five Fe– $C_{CO,ba}$  bonds. [b] Average of three P–N bonds. [c] Average of two Fe– $P_{ap}$  bonds. [d] Average of four Fe– $C_{CO,ba}$  bonds. [e] Average of two P–N bonds. [f] Average of six P–N bonds.

PMe<sub>3</sub>, PMe<sub>2</sub>Ph, PPh<sub>3</sub>, P(OEt)<sub>3</sub>].<sup>[30]</sup> The phosphane moieties Ph<sub>2</sub>PPyr and PPyr<sub>3</sub> occupy apical positions around the Fe atoms, and are roughly trans to the Fe-Fe bond. The Fe-P distance of 2.1661(7) Å in 4 is slightly shorter by 0.06 Å than that of 2.2247(14) Å in 2, consistent with the poor donor (or good acceptor) ability of the PPyr<sub>3</sub> ligand. One phenyl ring in 2 and one pyrrolyl ring in 4 are nearly facing the dithiaferracyclohexane ring similar to the PPh<sub>3</sub>-coordinating complex.<sup>[30]</sup> The angles of C(4)–S(1)–Fe(2)  $[113.13(11)^{\circ}]$  and C(6)–S(2)–Fe(2)  $[114.88(13)^{\circ}]$  for 4 are slightly larger than the corresponding angles of C(4)-S(1)-Fe(1)  $[111.37(16)^{\circ}]$  and C(6)–S(2)–Fe(1)  $[110.70(11)^{\circ}]$ . This indicates that the bulk ligand PPyr<sub>3</sub> around the diiron unit in 4 causes the dithiaferracyclohexane ring to slant towards the  $Fe(CO)_3$  unit. The larger differences between the C(6)-S(2)-Fe(2) [115.1(2)°] vs. C(6)-S(2)-Fe(1) [109.8(2)°] angles for 2 and C(4)–S(1)–Fe(2) [116.0(2)°] vs. C(4)–S(1)–Fe(2) [110.1(2)°] angles for 4 further confirm the steric interactions when PPyr<sub>3</sub> is replaced by Ph<sub>2</sub>PPyr. The angles of P(1)-Fe(2)-Fe(1) in 2 and 4 are ca. 8.1° and 6.1° larger than the C(3)-Fe(1)-Fe(2) angles, respectively. The average Fe(2)–C<sub>CO,ba</sub> distance of 1.781(2) Å for 4 is 0.02 Å longer than that of 2 [1.760(2) Å], and the corresponding length of C–O bonds [av. 1.139(13) Å] for 4 is shorter than that of 2 [av. 1.143(6) Å]. These features demonstrate that the introduction of the  $\pi$ -acceptor phosphane ligand decreases the electron donation of the iron centers and thereby leads to weaker  $\pi$ -back-bonding from the iron atoms to the carbonyl atoms. It is noteworthy that the average C-O bond length of 1.136 in 4 is in significant agreement with that reported for  $[(\mu-pdt)Fe_2(CO)_6]$  (av. 1.136 Å),<sup>[34]</sup> indicative of the similar electronic effects of both the PPyr<sub>3</sub> ligand and CO.

The average Fe–P bond lengths of 2.215(8) Å in 3 and 2.1725(12) Å in 5 are in good agreement with that in phosphane-disubstituted analogues; the Fe–P bond length of 5 is ca. 0.04 Å shorter than that of 3, further indicative of the better  $\pi$ -acceptor character of the PPyr<sub>3</sub> ligand relative to Ph<sub>2</sub>PPyr. In the case of 3 and 5, two aromatic rings face the propanedithiolato bridge, consistent with the fact that the <sup>1</sup>H NMR signals for the methylene protons of the 1,3-propanedithiolato bridge significantly shift to high field due to the shield effects of the aromatic rings.

An interesting structural feature of disubstituted complexes 3 and 5 is that the phosphane ligands are in apical/ apical (ap/ap) position and *trans* to the Fe-Fe bond, contrary to that of  $[(\mu-pdt)Fe_2(CO)_4(PTA)_2]$  featuring a ba/ba coordination mode.<sup>[20]</sup> This observation is identical to that found for PMe<sub>2</sub>Ph-<sup>[30]</sup> and tBuNC-disubstituted<sup>[35]</sup> derivatives. We note that PMe<sub>3</sub> and cyano-disubstituted complexes  $[(\mu-pdt)Fe_2(CO)_4(PMe_3)_2]$  and  $[(\mu-pdt)Fe_2(CO)_4 (CN)_2$ <sup>2-</sup> possess an ap/ba configuration.<sup>[36,37]</sup> It can be inferred that the steric interactions of bulk phosphane with the dithiaferracyclohexane ring are not the main factor in the rearrangement and that electronic effects probably play a key role. That is, the better electron-donating ligands favor rearrangements into the ba/ba or ap/ba configuration, whereas the ligands with better  $\pi$ -acceptor capability prefer the ap/ap coordination mode.



In PPyr<sub>3</sub>-substituted diiron complexes **4** and **5**, as expected, the nitrogen geometries are planar, with a sum of angles at N ranging from  $358.6(9)^{\circ}$  to  $360.01(6)^{\circ}$ . The bond lengths within the pyrrole rings are also similar to those found in the free ligand.<sup>[38]</sup>

#### $\pi$ -Acceptor Ability of (Pyrrol-1-yl)phosphanes

In the IR spectra the  $v_{CO}$  bands in the CO region provide a powerful tool for evaluating the structural and electronic changes of carbonyl transition-metal complexes.<sup>[39]</sup> The IR data of the CO bands for complexes 2, 3, 4, and 5 are listed in Table 2. The spectra of the all-CO parent complex 1 and its PPh<sub>3</sub>-monosubstituted derivative  $[(\mu-pdt)Fe_2(CO)_5PPh_3]$ (6) are also included for comparison purposes. Compared with the all-CO parent complex 1, the  $v_{CO}$  bands of 2–5 shift to lower frequencies, indicating an increase of electron density on the iron cores when a CO ligand is replaced by a Ph<sub>2</sub>PPyr/PPyr<sub>3</sub> ligand. The monosustituted series of diiron complexes 2, 4, and 6 shows a steady increase of  $v_{CO}$  with an increasing degree of replacement of the phenyl groups by pyrrol-1-yl groups. It can be seen that the IR  $v_{CO}$  bands of 6 shift by an average of  $50 \text{ cm}^{-1}$  to lower frequencies, whereas the  $v_{CO}$  bands of complexes 2 and 4 shift to lower wavenumbers by ca. 32 cm<sup>-1</sup> and 18 cm<sup>-1</sup>, respectively. This indicates that the pyrrol-1-yl group plays a key role in decreasing the  $\pi$ -back-bonding of electrons from the metal cores to the CO ligands. The  $v_{CO}$  bands in 4 are higher than those of complexes 2 and 6, showing that complex 4 has a better  $\pi$ -acceptor ability and a poorer donor ability. In addition, the values of  $v_{CO}$  for 4 and 5 are significantly higher than those found for alkylphosphane-substituted derivatives,  $[(\mu-pdt)Fe_2(CO)_5L]$  and  $[(\mu-pdt)Fe_2(CO)_4L_2]$  (L = PMe<sub>3</sub>, PMe<sub>2</sub>Ph, PTA).<sup>[20,30]</sup> For instance, the CO stretching frequency of **5** is shifted to higher energy by nearly 45 cm<sup>-1</sup> upon replacement of PMe<sub>3</sub> by PPyr<sub>3</sub>. The shifts to higher frequencies for 4 and 5 indicate a significantly reduced degree of  $\pi$ -back-bonding donation from the iron atoms to the carbonyl ligands in these diiron complexes and therefore demonstrate either a strong  $\pi$ -acceptor ability or a poor  $\sigma$ donor character of the PPyr<sub>3</sub> ligand. As expected, the CO stretching frequencies of 4 are very close to those of 1, indicative of a similar  $\pi$ -acceptor ability of the PPyr<sub>3</sub> and CO ligands. This effect has also been observed in other PPyr<sub>3</sub>substituted carbonylmetal complexes.<sup>[40]</sup> Thus, the  $\pi$ -acceptor capabilities of these phosphane ligands exhibit the following trend: CO  $\approx$  PPyr<sub>3</sub> > PhPPyr > PPh<sub>3</sub>. As described for PPyr<sub>3</sub>-substituted carbonylmetal complexes by

Table 2. Summary of IR  $v_{CO}$  bands for diiron complexes.

Complex	$v_{\rm CO} \ [{\rm cm}^{-1}]$	
1	2072(m), 2034(s), 1997(s)	
2	2049(s), 1991(s), 1964(w)	
3	2008(s), 1964(m), 1947(s)	
4	2056(s), 2003(s), 1990(w)	
5	2028(s), 1984(m), 1970(s)	
6	2044(s), 1981(s), 1930(m)	

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Moloy et al., the good  $\pi$ -acceptor ability of PPyr<sub>3</sub> is attributed to the aromatic delocalization of the nitrogen lone pair into the five-membered rings.<sup>[31]</sup>

#### **Electrochemistry of Complexes 2–5**

The cyclic voltammograms of complexes 2–5 shown in Figure 3 were recorded in CH<sub>3</sub>CN solution (with 0.1 M  $nBu_4NPF_6$  as electrolyte), they were initiated from the open circuit potential and scanned in the cathodic direction as indicated in Figure 3. A summary of the redox potentials for 2-5 and the parent all-CO complex 1 and its PPh<sub>3</sub> derivatives,  $[(\mu-pdt)Fe_2(CO)_5PPh_3]$  (6), is given in Table 3. It has been demonstrated that complexes 2 and 3 display two irreversible oxidation peaks, whereas 4 and 5 show one irreversible oxidation peak. In publications, those reported for ADT-, PDT-, and ODT-bridged (ODT = oxadithiolato) analogs,<sup>[19-21,30,41,42]</sup> were assumed to be the oxidation events of Fe<sup>I</sup>Fe<sup>I</sup> to Fe<sup>II</sup>Fe<sup>I</sup> and Fe<sup>II</sup>Fe<sup>I</sup> to Fe<sup>II</sup>Fe<sup>II</sup>, respectively. In all cases discussed in this paper, it is noticeable that the 1st oxidation for complexes 2–5 exhibits a current intensity ca. twice that of the corresponding 1st reduction event, which was confirmed as a one-electron process by bulk electrolysis (vide infra).



Figure 3. Cyclic voltammograms of complexes 2, 3, 4, and 5 in CH<sub>3</sub>CN solution (0.1  $\times$  *n*Bu<sub>4</sub>NPF<sub>6</sub>) at a potential scan rate of 100 mVs<sup>-1</sup>.

Therefore, we assume the 1st oxidation of complexes 2– 5 is either a two-electron process of Fe<sup>I</sup>Fe<sup>I</sup> to Fe<sup>II</sup>Fe<sup>II</sup> or a combined result of two overlapping processes of Fe<sup>I</sup>Fe<sup>I</sup> to

Table 3. Redox potentials for phosphane derivatives of 1.

Complex	$E_{\rm pc}$ [V]	$E_{\rm pa}$ [V]	$E_{\rm pa}$ [V]
	Fe <sup>I</sup> Fe <sup>I</sup> /Fe <sup>0</sup> Fe <sup>I</sup>	Fe <sup>I</sup> Fe <sup>I</sup> /Fe <sup>II</sup> Fe <sup>I</sup>	Fe <sup>II</sup> Fe <sup>II</sup> Fe <sup>II</sup> Fe <sup>II</sup>
1	-1.62	0.84	_
2	-1.74	0.46	0.68
3	-1.92	0.32	0.72
4	-1.66	0.65	_
<b>5</b> <sup>[a]</sup>	-1.70	0.62	_
6	-1.84	-0.40	_

[a] Complex 5 was somewhat soluble in CH<sub>3</sub>CN.

Fe<sup>II</sup>Fe<sup>I</sup> and Fe<sup>II</sup>Fe<sup>I</sup> to Fe<sup>II</sup>Fe<sup>II</sup>. Further oxidation of these complexes probably arises from the degradation of oxidized species or the ligand redox process, which is beyond the scope of this article.

Complexes 2, 3, 4, and 5 exhibit an electrochemically irreversible reduction at -1.74 V, -1.92 V, -1.66 V, and -1.70 V, respectively. Bulk electrolysis of complexes 2–5 at each reduction potential shows a net consumption of ca. 0.95 electrons per molecule, demonstrating these reduction events are one-electron reduction processes from Fe<sup>I</sup>Fe<sup>I</sup> to Fe<sup>0</sup>Fe<sup>I</sup>. However, for the electron counting of the 1st reduction process of the parent complex 1, whether it is a one-electron process or a two-electron process, is disputable.<sup>[19–21,30,41–44]</sup> For most model complexes including ADT, PDT, and ODT derivatives, the concerned reduction event was considered to be a one-electron process.

In comparison to complex 1, the first reduction potentials of complexes 2–5 are shifted to a relatively more negative value, consistent with the increase of electron density at the diiron core upon replacement of CO by the better donor ligands. Noticeably, the reduction potentials of 4 and 5 show a minor negative shift by only 40 mV and 80 mV, respectively, as compared to complex 1. The minor shift suggests that the PPyr<sub>3</sub> ligand is a somewhat weaker  $\pi$ -acceptor in comparison to CO and therefore, slightly affects the redox capability of these diiron complexes. On the other hand, the reduction shifts are smaller than those observed for complex 6 and other reported phosphane-substituted diiron complexes.<sup>[19,20,30,42]</sup> Within the series of 2, 4, and 6, we can see that the reduction potentials gradually shift to more positive potentials with displacement of the phenyl ring by the pyrrol-1-yl group, consistent with the change trends of the IR  $v_{CO}$  bands.

In all cases, a linear dependence of the peak currents  $(i_p)$  on the square root of the scan rate  $(v^{1/2})$  in CH<sub>3</sub>CN solution indicates the electron-transfer reactions are diffusion-controlled.<sup>[45]</sup>

#### Electrocatalytic Proton Reduction to H<sub>2</sub>

The behavior of electrocatalytic proton reduction to  $H_2$  by 2–5 has been investigated by cyclic voltammetry in the absence and presence of the weak acid HOAc. The cyclic voltammograms recorded in CH<sub>3</sub>CN solutions with different acetic acid concentrations (0–20 mM) are shown in

Figure 4. As can be seen, when 1 mM of HOAc was added, an obvious increase in the current intensity of the first reduction peak at -1.74 V, -1.92 V, -1.66 V, and -1.70 V for 2-5, respectively, was observed. The height of the reduction peak in each CV shows a further increase with the sequential increments of acid concentration. The current height change at their respective reduction peak displays a good linear dependence on the concentrations of HOAc. In addition, the reduction potentials slightly move to more cathodic values with increasing acid concentration. All of these features are clearly indicative of a catalytic proton reduction process.<sup>[19-21,30,41-43,46]</sup> The CVs of complexes 2-5 indicate they are electrocatalytically active at the first reduction potentials for proton reduction from HOAc. The electrocatalytic properties of complexes 2-5 are very similar to that of [(µ-pdt)Fe<sub>2</sub>(CO)<sub>5</sub>PTA] reported by Darensbourg and coworkers,<sup>[20]</sup> which also shows the first reduction peak is catalytically active in the presence of a weak acid (HOAc). To further confirm the evolution of hydrogen at the first reduction peak, bulk electrolyses in CH<sub>3</sub>CN solutions for 2-5 were performed in a gas-tight H-type cell as described in the Experimental Section. The electrolysis of complexes 2, 3, 4, and 5 was carried out at -1.80 V, -1.98 V, -1.72 V, and -1.76 V, respectively, in the presence of HOAc (50 mm). When 12 C of charge had passed through the cell, a sample of gas was collected and analyzed by gas chromatography, showing hydrogen is the sole gaseous product.

By using the standard potential  $(-1.46 \text{ V vs. Fc}^+/\text{Fc})$  reported by Evans et al. for the HOAc reduction in

CH<sub>3</sub>CN,<sup>[47]</sup> the overpotentials of complexes 2–5 are 0.28, 0.46, 0.2, and 0.24 V, respectively. Darensbourg and coworkers reported H<sub>2</sub> evolution by electrolysis catalyzed by complex [(µ-pdt)Fe<sub>2</sub>(CO)<sub>5</sub>PTA] at -1.94 V vs. Fc<sup>+</sup>/Fc with ca. 0.48 V overpotential for H<sub>2</sub>/H<sup>+</sup> (HOAc).<sup>[20,48]</sup> It is noteworthy that complex 4 can electrocatalytically generate  $H_2$ in weak acid at -1.66 V with only ca. 0.2 V overpotential. This potential is quite similar to that of  $[(\mu-S-2 RCONHC_6H_4)_2Fe_2(CO)_6$  (R = 4-FC<sub>6</sub>H<sub>4</sub>) reported by Sun and co-workers.<sup>[49]</sup> Although hexacarbonyldiiron azadithiolate complexes,  $[{(\mu-SCH_2)_2N(2-C_4H_3O)}Fe_2(CO)_6]$  and  $[{(\mu-SCH_2)_2N(4-BrC_6H_4)}Fe_2(CO)_6]$ , can catalyze the H<sub>2</sub> production at lower potentials (ca. -1.13 to -1.48 V vs. Fc<sup>+</sup>/ Fc),<sup>[24,25]</sup> a strong acid (HClO<sub>4</sub>) is needed. A summary of the overpotentials for 2-5 and diiron dithiolates is given in Table 4. To the best of our knowledge, in terms of reduction overpotential, complex 4 is the most energy-efficient diiron electrocatalyst for the H<sub>2</sub> production in the presence of a weak acid (HOAc) based on ligand-substituted 2Fe2S biomimics. Complex 4 with the best catalytic capability for proton reduction displays a catalytic potential very close to that of the noble metal Pt. In our previous work, we reported (pyrrolidin-1-yl)phosphane monosubstituted complex  $[(\mu-pdt)Fe_2(CO)_5P(NC_4H_8)_3]$  can also catalyze the H<sub>2</sub> production in the presence of HOAc at -1.98 V with a relatively high overpotential (ca. 0.52 V).<sup>[29]</sup> However, its peak current is higher than that of 4. Thus, it seems that a low overpotential is achieved at the cost of low rates of catalysis. Further experiments will be performed to confirm this in



Figure 4. Successive cyclic voltammograms of 1.0 mM solution of 2 (a), 3 (b), 4 (c), 5 (d) with HOAc (0, 1, 5, 10, and 20 mM) in CH<sub>3</sub>CN (0.1 M  $nBu_4NPF_6$  as supporting electrolyte) at a potential scan rate of 100 mV s<sup>-1</sup>.

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future work. This significant electrocatalytic feature of **4** as well as of the analogues **2**, **3**, and **5** are interpreted as follows. On replacement of the CO ligand by the PPyr<sub>3</sub> ligand (or PPyr<sub>2</sub>Ph and PPyrPh<sub>2</sub>), the low potential at the first reduction is maintained due to the small donating ability of the phosphane ligands relative to the CO ligand. The reduced species (Fe<sup>I</sup>Fe<sup>0</sup> level) of **4** provides a strong base for proton uptake, whereas that of **1** at its Fe<sup>I</sup>Fe<sup>0</sup> level is not a strong enough nucleophile to react with the proton, because the six strongly  $\pi$ -accepting CO ligands decrease the nucleophilicity of the diiron core. In contrast, the PPyr<sub>3</sub> ligand (or PPyr<sub>2</sub>Ph and PPyrPh<sub>2</sub>) with a smaller  $\pi$ -acceptor ability modulates the nucleophilicity of the diiron core of the reduced species (Fe<sup>I</sup>Fe<sup>0</sup> level) of **4** at a functional level for H<sub>2</sub> production.

Table 4. Summary of overpotential for phosphane-substituted 2Fe2S complexes.

Complex	E <sub>pc</sub> [V] Fe <sup>I</sup> Fe <sup>I</sup> /Fe <sup>0</sup> Fe <sup>I</sup>	$E_{\rm overpotential}$ [V]
1	-1.62	0.16
2	-1.74	0.28
3	-1.92	0.46
4	-1.66	0.20
5	-1.70	0.24
6	-1.84	0.38
[(µ-pdt)Fe <sub>2</sub> (CO) <sub>5</sub> PTA]	-1.94	0.48
$[(\mu-S-2-RCONHC_6H_4)_2Fe_2(CO)_6]^{[a]}$	-1.66	0.20

[a]  $R = 4 - FC_6H_4$ .

On the basis of the electrochemical observations described above and similar cases of phosphane-substituted 2Fe2S complexes previously reported,<sup>[19–21,30,41–43]</sup> an ECCE (electrochemical/chemical/electrochemical) mechanism for the electrocatalytic proton reduction process by **2–5** could be proposed, as presented in Scheme 2. The Fe<sup>I</sup>Fe<sup>I</sup> complex initially undergoes an electrochemical reduction to generate a one-electron reduced intermediate Fe<sup>I</sup>Fe<sup>0</sup>, which is singly protonated to form a hydride species Fe<sup>I</sup>Fe<sup>II</sup>H in the presence of HOAc. After a further proton-



 $L = CO, Ph_2PPyr or PPyr_3$ 

Scheme 2. Proposed ECCE mechanism for catalytic proton reduction to  $H_2$  by complexes 2–5.

ation of  $Fe^{I}Fe^{II}H$  and a second electroreduction event, hydrogen is evolved, and the starting material is reclaimed to fulfill the catalytic cycle. Our results also show that the oneelectron reductive level  $Fe^{0}Fe^{I}$  is electrocatalytically active.

### Conclusions

In the search for synthetic competitive catalysts that function with [Fe]-H<sub>2</sub>ase-like capability, a series of  $\pi$ -acceptor (pyrrol-1-yl)phosphane-substituted diiron complexes **2–5** were prepared as functional models for the Fe-only hydrogenase. This work explored the derivative chemistry of the precursor [( $\mu$ -S<sub>2</sub>R)Fe<sub>2</sub>(CO)<sub>6</sub>] by replacement of CO with the exceptional  $\pi$ -acceptor (pyrrol-1-yl)phosphane ligands and developed applications of (pyrrol-1-yl)phosphanes in bio-organometallic chemistry and catalysis.

In the presence of the weak acid HOAc complexes 2-5 can catalyze proton reduction to H<sub>2</sub> at the first reduction level Fe<sup>I</sup>Fe<sup>0</sup>. The most effective electrocatalyst is the PPyr<sub>3</sub>substituted complex 4. As compared to that of other  $\sigma$ donor phosphane-substituted diiron complexes (most of them catalyze proton reduction at the Fe<sup>0</sup>Fe<sup>0</sup> level with high overpotentials), the introduction of (pyrrol-1-yl)phosphane ligands maintains the reduction of 2–5 at relatively positive potentials due to the ligand  $\pi$ -acceptor character and improves the electrocatalytic ability. Since minor ligand  $\pi$ acidity modulation has a significant influence on the proton reduction of these diiron models, the approach as exemplified by complexes 2–5 is worthy of further investigation in future functional biomimetic designs of [FeFe]-H2ase. In contrast to electron-rich diiron models supported by multiple donors, diiron models with an appropriate  $\pi$ -acidity ligand have two main advantages: (a) enhanced stability towards  $O_2$  and, therefore, easy operation; (b) in terms of thermodynamics, small overpotentials for electrocatalytic H<sub>2</sub> production.

Electrocatalytic proton reduction to  $H_2$  at moderate overpotentials in the presence of the weak acid HOAc was achieved through replacement of CO by moderate  $\pi$ -acceptor (pyrrol-1-yl)phosphanes. Ligand PPyr<sub>3</sub> may be utilized as a surrogate for CO in the diiron systems. The pyrrol-1-yl groups are amenable to further modification so that it should be possible to prepare water-soluble electrocatalysts. Further investigations are underway to improve the proton affinity of the diiron complexes by a built-in proton relay site and to develop more advanced and effective electrocatalysts for proton reduction.

## **Experimental Section**

Materials and Techniques: Unless noted otherwise, all reactions and operations were carried out under nitrogen by using standard Schlenk techniques. All solvents were dried and distilled prior to use according to standard methods. Pyrrole and  $Et_3N$  were distilled from Na and stored under nitrogen. The following materials were commercial chemicals and used without further purification: 1,3-propanedithiol, PCl<sub>3</sub>, Ph<sub>2</sub>PCl, and [Fe(CO)<sub>5</sub>]. The starting materials P(pyrrol-1-yl)<sub>3</sub> (PPyr<sub>3</sub>), Ph<sub>2</sub>P(pyrrol-1-yl) (Ph<sub>2</sub>PPyr), and [( $\mu$ -



pdt)Fe<sub>2</sub>(CO)<sub>6</sub>] were synthesized according to literature procedures.<sup>[31,50]</sup> [( $\mu$ -pdt)Fe<sub>2</sub>(CO)<sub>5</sub>PPh<sub>3</sub>] (6) was prepared according to the literature<sup>[30]</sup> as an IR and electrochemistry reference complex. Infrared spectra were recorded with a Nicolet FT-IR spectrophotometer as solutions with CaF<sub>2</sub> plates. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR were collected with a Varian INOVA 400 M NMR spectrometer. The <sup>1</sup>H and <sup>13</sup>C spectra were normally referenced to TMS, and the <sup>31</sup>P spectra were referenced to 85% H<sub>3</sub>PO<sub>4</sub>. HR-MS data acquisition was carried out with a GCT-MS instrument (Micromass, England). Elemental analysis was performed with a PE 2400 II Elemental Analyzer (Perkin–Elmer).

Synthesis of [(µ-pdt)Fe<sub>2</sub>(CO)<sub>5</sub>L] (2) (L = Ph<sub>2</sub>PPyr): PPh<sub>2</sub>(pyrrol-1yl) (0.83 g, 3.3 mmol) in toluene (30 mL) was added to a red solution of [(µ-pdt)Fe<sub>2</sub>(CO)<sub>6</sub>], 1 (1.27 g, 3.3 mmol) in toluene (50 mL) through a syringe. The reaction mixture was refluxed until TLC indicated there was no remaining carbonyl complex of the starting material. The solvent was removed under vacuum, and the resultant dark red residue was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5, v/v). A red solid was obtained by recrystallization from *n*-pentane/CH<sub>2</sub>Cl<sub>2</sub> at -30 °C. Yield: 1.20 g (68%). Crystals suitable for X-ray studies were grown from a mixed CH<sub>2</sub>Cl<sub>2</sub>/hexane solution. C<sub>24</sub>H<sub>20</sub>Fe<sub>2</sub>NO<sub>5</sub>PS<sub>2</sub> (608.92): calcd. C 47.32, H 3.31, N 2.30; found C 47.51, H 3.20, N 2.48. IR (in CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{v}_{CO} = 2049$ , 1991, 1964 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta =$ 1.53 (m, 4 H), 1.84 (m, 2 H), 6.44 (s, 2 H), 7.19 (s, 2 H), 7.52 (m, 10 H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 212.6, 209.2, 137.4, 137.0, 131.6, 131.5, 131.1, 128.9, 128.8, 126.5, 112.6, 29.9, 22.1 ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  = 116.25 ppm. HR-MS (EI): calcd. for [M]<sup>+</sup> 608.9247; found 608.9219.

Synthesis of  $[(\mu-pdt)Fe_2(CO)_4L_2]$  (3) (L = Ph<sub>2</sub>PPyr): PPh<sub>2</sub>(pyrrol-1-yl) (1.40 g, 5.6 mmol) in toluene (50 mL) was added to a red solution of  $[(\mu-pdt)Fe_2(CO)_6]$ , 1 (1.07 g, 2.8 mmol) in toluene (50 mL) through a syringe. The reaction mixture was refluxed until TLC indicated there was no remaining carbonyl complex of the starting material. The solvent was removed under vacuum, and the resultant dark red residue was purified by column chromatography on silica gel eluting with CH2Cl2/hexane (1:2, v/v). A red solid was obtained by recrystallization from *n*-pentane/CH<sub>2</sub>Cl<sub>2</sub> at -30 °C. Yield: 1.4 g (61%). Crystals suitable for X-ray studies were grown from a mixed CH<sub>2</sub>Cl<sub>2</sub>/hexane solution. C<sub>39</sub>H<sub>34</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub> (832.01): calcd. C 56.27, H 4.12, N 3.37; found C 56.16, H 4.28, N 3.56. IR (in CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{v}_{CO}$  = 2008, 1964, 1947 cm<sup>-1</sup>. <sup>1</sup>H NMR  $(400 \text{ MHz}, \text{CDCl}_3)$ :  $\delta = 0.81$  (br., 6 H), 6.35 (s, 4 H), 7.19 (s, 4 H), 7.42 (m, 20 H) ppm. <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 213.8, 138.0, 137.6, 131.5, 130.7, 128.7, 126.6, 112.2, 29.8, 19.6 ppm. <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 113.17 ppm. HR-MS (EI): calcd. for [M]<sup>+</sup> 832.0134; found 832.0156.

Synthesis of  $[(\mu-pdt)Fe_2(CO)_5L]$  (4) (L = PPyr<sub>3</sub>): Complex 4 was prepared acording to a procedure similar to that described above for 2. A mixture of 1 (1.0 g, 2.58 mmol) with P(pyrrol-1-yl)<sub>3</sub> (0.591 g, 2.58 mmol) in toluene (80 mL) was refluxed for 72 h. After solvent evaporation, the resultant dark red residue was purified by column chromatography on silica gel. The monosubstituted complex 4 was obtained after eluting with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:10, v/v). Following further recrystallization from *n*-pentane/CH<sub>2</sub>Cl<sub>2</sub> at -30 °C, a dark red solid was obtained. Yield: 0.95 g (63%). Crystals suitable for X-ray studies were grown from a mixed CH<sub>2</sub>Cl<sub>2</sub>/hexane solution. C<sub>20</sub>H<sub>18</sub>Fe<sub>2</sub>N<sub>3</sub>O<sub>5</sub>PS<sub>2</sub> (586.91): calcd. C 40.91, H 3.09, N 7.16; found C 41.02, H 3.15, N 7.05. IR (in CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{v}_{CO}$  = 2056, 2003, 1990 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.64 (m, 4 H), 1.92 (m, 2 H), 6.40 (s, 6 H), 6.90 (s, 6 H) ppm. <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 210.5, 210.4, 208.4, 123.7, 123.6 113.7, 113.6, 29.5, 22.6 ppm. <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.58 ppm. HR-MS (EI): calcd. for [M]<sup>+</sup> 586.9124; found 586.9153.

Synthesis of  $[(\mu-pdt)Fe_2(CO)_4L_2]$  (5) (L = PPyr<sub>3</sub>): Complex 5 was prepared according to a procedure similar to that described above for 3. A mixture of 1 (2.4 g, 6.20 mmol) with  $P(pyrrol-1-yl)_3$  (3.0 g, 13.1 mmol) in toluene (120 mL) was refluxed for 72 h. TLC showed the main product was the disubstituted complex 5 with a small amount of a mixture with the starting material 1 and the monosubstituted complex 4. Following solvent evaporation, the resultant dark red residue was purified by column chromatography on silica gel. The starting material 1 was eluted with hexane, and the monosubstituted complex 4 was obtained after eluting with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:10, v/v). The disubstituted complex 5 was obtained with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:4, v/v) as elute. Following further recrystallization from n-pentane/CH2Cl2 at -30 °C, an orange solid was obtained. Yield: 2.5 g (51%). Crystals suitable for X-ray studies were grown from a mixed CH<sub>2</sub>Cl<sub>2</sub>/hexane solution. C<sub>31</sub>H<sub>30</sub>Fe<sub>2</sub>N<sub>6</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub> (787.99): calcd. C 47.23, H 3.84, N 10.66; found C 47.41, H 3.71, N 10.82. IR (in CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{v}_{CO}$  = 2028, 1984, 1970 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.90 (s, 2 H), 1.31 (s, 4 H), 6.40 (s, 12 H), 6.94 (s, 12 H) ppm. <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 211.0, 123.7, 113.6, 29.0, 21.2 ppm. <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 138.60 ppm. HR-MS (EI): calcd. for [M]<sup>+</sup> 787.9944; found 787.9967.

X-ray Structure Determinations: The single-crystal X-ray data were collected with a Siemens SMART CCD diffractometer. The data were collected at 293 K by using graphite-monochromated Mo- $K_{\alpha}$ radiation ( $\lambda = 0.71073$  Å) with the  $\omega$ -2 $\theta$  scan mode. Data processing was accomplished with the SAINT processing program.<sup>[51]</sup> Intensity data were corrected for absorption with empirical methods. The structure was solved by direct methods and refined on  $F_0^2$ against full-matrix least squares using the SHELXTL-97 program package.[52] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by geometrical calculation, but their positions and thermal parameters were fixed during the structure refinement. A summary of the crystallographic data and structural determinations is provided in Table 5. CCDC-617988 (for 2), -617989 (3), -617990 (4), and -617991 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data\_request/cif

Electrochemistry: Acetonitrile used for electrochemical measurements was distilled from P2O5 and freshly distilled from CaH2 under N<sub>2</sub>. Measurements were made with a BAS 100 B/W electrochemical workstation controlled by a PC running BAS 100W 2.0 software.<sup>[??]</sup> ((<=AUTHOR: Please add reference for software!)) The working electrode was glassy carbon (Bioanalytical Systems) of diameter 3 mm, successively polished with 3 µm and 1 µm alumina and sonicated in ion-free water for 15 min prior to use. The counter electrode was a platinum wire. The experimental reference electrode was a non-aqueous Ag/Ag+ electrode (0.01 м AgNO<sub>3</sub>/ 0.1 м *n*Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN). The supporting electrolyte was 0.1 м nBu<sub>4</sub>NPF<sub>6</sub> (Fluka, electrochemical grade). Ferrocene was used as an internal reference. All potentials are reported relative to Fc<sup>+</sup>/Fc. During the electrocatalytic experiments under argon, increments of acid were added by microsyringe. Bulk electrolysis experiments were performed under argon with a BAS 100 B/W electrochemical analyzer, and carried out on a glassy carbon rod ( $A = 3.14 \text{ cm}^2$ ) in a gas-tight H-type electrolysis cell containing ca. 18 mL of CH<sub>3</sub>CN solution. Gas chromatography was performed with a GC 920 instrument equipped with a thermal conductivity detector (TCD) under isothermal conditions with argon as a carrier gas.

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	2	3	4	5
Empirical formula	C <sub>24</sub> H <sub>20</sub> Fe <sub>2</sub> NO <sub>5</sub> PS <sub>2</sub>	C <sub>39</sub> H <sub>34</sub> Fe <sub>2</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>20</sub> H <sub>18</sub> Fe <sub>2</sub> N <sub>3</sub> O <sub>5</sub> PS <sub>2</sub>	$C_{31}H_{30}Fe_2N_6O_4P_2S_2$
$M_r$ [gmol <sup>-1</sup> ]	609.20	832.44	587.16	788.37
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	tetragonal
Space group	$P2_1/c$	P2(1)	$P\overline{1}$	P4(3)
a [Å]	9.2405(17)	9.373(3)	9.2604(19)	19.042(3)
b [Å]	17.439(3)	16.816(5)	9.646(2)	19.042(3)
c [Å]	16.549(3)	12.407(4)	14.459(3)	9.6956(19)
	90	90	91.520(3)	90
β[°]	102.025(3)	98.333(5)	100.732(3)	90
γ [°]	90	90	106.683(3)	90
V Å <sup>3</sup>	2608.3(8)	1934.9(10)	1211.2(4)	3515.8(10)
Z	4	2	2	4
<i>T</i> [K]	293	293	293	293
$\rho_{\rm calcd}$ [g cm <sup>-3</sup> ]	1.551	1.429	1.610	1.489
$\mu \text{ [mm^{-1}]}$	1.369	0.982	1.472	1.079
F [000]	1240	856	596	1616
Total reflections	6099	6542	5394	7226
Reflections observed	3296	3938	4545	5019
Parameters	316	460	298	424
Goodness-of-fit on $F^2$	0.947	1.011	1.092	1.017
$R_1^{[a]} [I > 2\sigma (I)]$	0.0653	0.0800	0.0398	0.0426
$wR2^{[b]} [I > 2\sigma(I)]$	0.1240	0.1444	0.1127	0.0619
Max. peak/hole [eÅ-3]	0.860/-0.574	0.782/-0.326	0.569/-0.739	0.322/-0.251

Table 5. X	-ray crysta	llographic	data	for	2–5
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[a]  $R_1 = (\Sigma ||F_o| - |F_c||)/(\Sigma |F_o|)$ . [b]  $wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$ .

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