

This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:29

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

### Diironhexacarbonyl clusters with imide and amine ligands: hydrogen evolution catalysts

Charles A. Mebi<sup>a</sup>, Derek S. Karr<sup>a</sup> & Ruixiao Gao<sup>a</sup>

<sup>a</sup> Department of Physical Sciences, Arkansas Tech University, Russellville, AR, USA

Published online: 05 Dec 2011.

To cite this article: Charles A. Mebi, Derek S. Karr & Ruixiao Gao (2011) Diironhexacarbonyl clusters with imide and amine ligands: hydrogen evolution catalysts, *Journal of Coordination Chemistry*, 64:24, 4397-4407, DOI: [10.1080/00958972.2011.638714](https://doi.org/10.1080/00958972.2011.638714)

To link to this article: <http://dx.doi.org/10.1080/00958972.2011.638714>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

## Diironhexacarbonyl clusters with imide and amine ligands: hydrogen evolution catalysts

CHARLES A. MEBI\*, DEREK S. KARR and RUIXIAO GAO

Department of Physical Sciences, Arkansas Tech University,  
Russellville, AR, USA

(Received 15 September 2011; in final form 21 October 2011)

The reaction of  $\text{Fe}_3(\text{CO})_{12}$  and *N*-(4-thiophenyl)-1,8-naphthalimide afforded a new diironhexacarbonyl complex (**3**). The integrity and electronic structure of **3** has been determined by elemental analysis and spectroscopy (NMR and infrared). Infrared spectrum of **3** shows peaks at 2000, 2040, and  $2075\text{ cm}^{-1}$  ascribed to stretching frequencies of the terminal metal carbonyls. Compound **4** was obtained from the reaction of  $\text{Fe}_3(\text{CO})_{12}$  and 4-aminothiophenol. A comparison of the electronic, electrochemical, and electrocatalytic properties of **3** and **4** are discussed. Cyclic voltammetric studies show that **3** and **4** catalyze the reduction of acetic acid to produce hydrogen at  $-2.19\text{ V}$  and  $-1.88\text{ V}$  versus  $\text{Fc}/\text{Fc}^+$ , respectively.

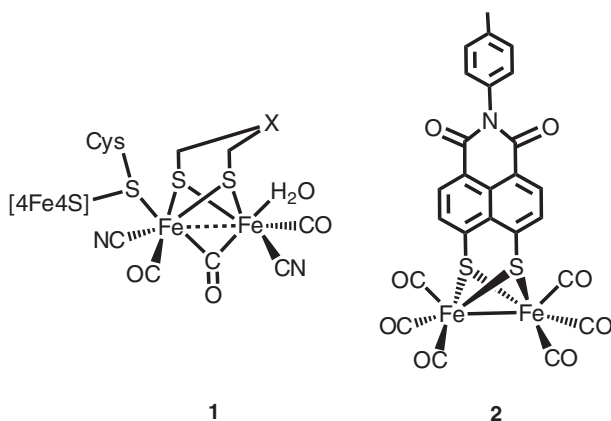
**Keywords:** Coordination compound; Electrocatalysis; Hydrogenase model; Iron carbonyl; Organometallic

### 1. Introduction

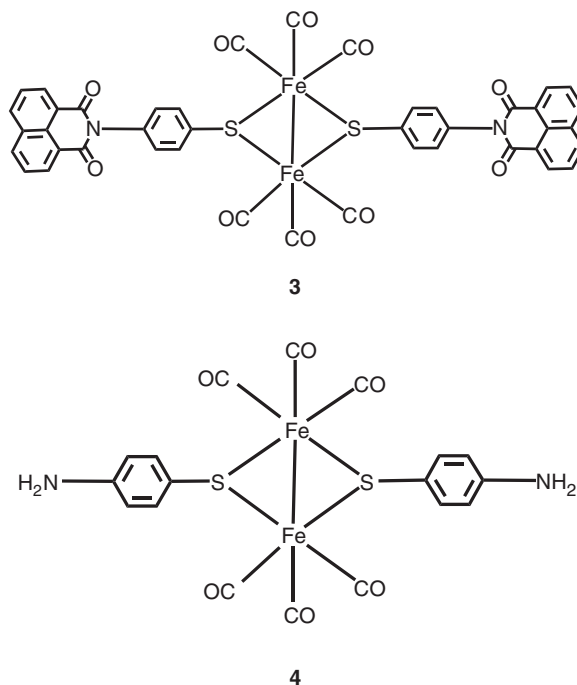
Syntheses of diironcarbonyl clusters as models for the active site of [Fe–Fe] hydrogenase enzyme have received great attention in recent years. These iron-clusters are potential catalysts for the production of hydrogen, a clean alternative to fossil fuels [1–51]. A representation of the active site of [Fe–Fe] hydrogenase is shown in compound **1** ( $\text{X} = \text{NH}, \text{CH}_2$ ). The active site is a diiron unit linked to an electron transport chain, [Fe4–S4] clusters [12, 13]. Diironcarbonyl complexes containing electroactive or electron-withdrawing groups have been reported to possess desirable electrochemical properties for effective models of **1** [47–51]. For example, Samuel *et al.* reported a new

\*Corresponding author. Email: cmebi@atu.edu

model containing naphthalene monoimide dithiolate, **2**, with one of the most positive reduction potentials for a diiron carbonyl complex [51].



In this study, we present the synthesis, spectroscopic, and electrochemical characterization of a new model; a design containing two naphthalimides linked to a diironhexacarbonyl unit (**3**). Naphthalimide, as an electroactive group [52–54], could mimic the electron transport chain of the hydrogenase enzyme. To investigate the electronic effect of the naphthalimide moiety on the iron-carbonyl unit in **3**, compound **4** has been synthesized and its electronic and electrochemical properties are compared to those of **3**. In addition, we report on the electrocatalytic reduction of acetic acid to produce molecular hydrogen by **3** and **4**.



## 2. Experimental

### 2.1. General

*N*-(4-Thiolphenyl)-1,8-naphthalimide was prepared following similar literature procedures [52–54]. An *N,N*-dimethylformamide solution containing equimolar amounts of 1,8-naphthalic anhydride and 4-aminothiolphenol was refluxed overnight. After cooling, water was added to afford *N*-(4-thiolphenyl)-1,8-naphthalimide as a pale yellow precipitate. All other chemicals and dry solvents were purchased from commercial sources and used without purification. The synthesis and electrochemical measurements were carried out under dinitrogen. Elemental analyses were performed by Columbia Analytical Services, Inc., Tucson, AZ, USA. Melting point determination was conducted using an Electrothermal Melting Point Apparatus.

### 2.2. Synthesis of 3

A THF solution of *N*-(4-thiolphenyl)-1,8-naphthalimide (3.03 g, 9.93 mmol) and  $\text{Fe}_3(\text{CO})_{12}$  (2.50 g, 4.96 mmol) was purged with nitrogen and stirred overnight at room temperature. A color change from green to red was observed. The solvent was removed using a rotary evaporator and the product was separated by column chromatography on silica gel with dichloromethane as eluent. Compound **3** was obtained as an orange solid in 22% yield (654 mg). IR ( $\text{CH}_2\text{Cl}_2$ ) ( $\text{cm}^{-1}$ ): ( $\nu_{\text{CO}}$ ) = 2075, 2040, 2000, 1780, 1740, 1710, and 1675.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  = 7.05–7.30 (m, 4H), 7.40–7.60 (m, 4H), 7.75–7.90 (m, 4H), 8.20–8.40 (m, 4H), 8.60–8.75 (m, 4H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  = 208.0, 164.0, 134.3, 132.4, 132.4, 131.4, 128.7, 128.1, 126.9, 122.5, 115.0. Elemental Analysis, Found: C: 56.65, H: 2.55, N: 3.29, S: 7.05; Calcd: C: 56.76, H: 2.25, N: 3.15, S: 7.21; m.p. 179–180°C.

### 2.3. Synthesis of 4

Compound **4** was prepared and isolated following the procedures described above for **3** using 4-aminothiolphenol (1.0 g, 7.96 mmol) and  $\text{Fe}_3(\text{CO})_{12}$  (1.0 g, 1.99 mmol). Compound **4** was obtained as an orange solid (426 mg) in 27% yield (based on  $\text{Fe}_3(\text{CO})_{12}$ ). IR ( $\text{CH}_2\text{Cl}_2$ ) ( $\text{cm}^{-1}$ ): ( $\nu_{\text{CO}}$ ) = 2070, 2035, and 1995.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  = 7.0–7.2 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 4H, ArH), 6.4–6.7 (d, 4H,  $^3J_{\text{HH}} = 7.5$  Hz, ArH), 3.7 (s, 4H,  $\text{NH}_2$ ).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ) (ppm):  $\delta$  = 209.0, 146.5, 135.0, 132.4, 115.0. Elemental Analysis, Found: C: 40.94, H: 2.69, N: 5.16, S: 11.76; Calcd: C: 40.92, H: 2.27, N: 5.30, S: 12.15; m.p. Dec 102°C.

### 2.4. Electrochemistry

Electrochemical studies were conducted using an Epsilon BAS potentiostat. Cyclic voltammograms were obtained in a three-electrode cell under nitrogen at room temperature. The electrodes used are glassy carbon working electrode, platinum auxiliary electrode, and  $\text{Ag}/\text{AgCl}$  reference electrode. The potentials are converted to  $\text{Fc}/\text{Fc}^+$  reference by adding  $-0.44$  V to the recorded values [1]. The platinum and glassy carbon electrodes were polished with aluminum paste and rinsed with water and acetone.

A 0.1 mol L<sup>-1</sup> CH<sub>3</sub>CN solution of Bu<sub>4</sub>NPF<sub>4</sub> was used as supporting electrolyte. The concentration of compound used was 1 mmol L<sup>-1</sup> (10 mL) and the scan rate was 100 mV s<sup>-1</sup>. Glacial acetic acid was used as proton source.

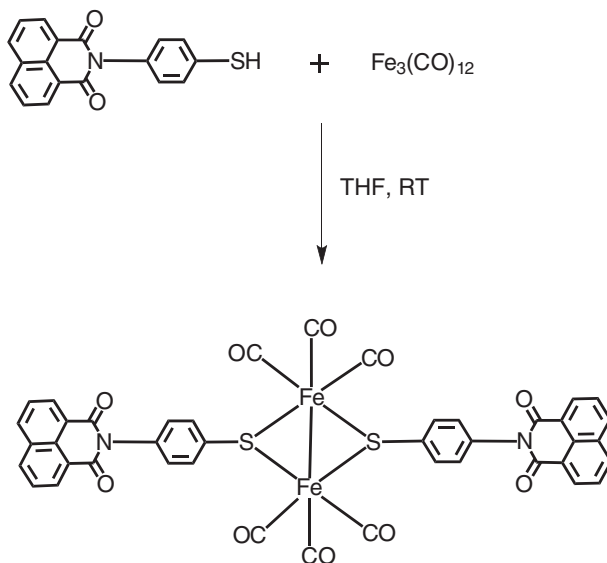
## 2.5. Spectroscopy

Infrared spectra were recorded on a Nicolet FT/IR Magna spectrophotometer using NaCl IR solution cell. Proton and carbon-13 NMR spectroscopic measurements were performed on a Bruker 300 MHz spectrometer. NMR spectra were referenced to residual solvent relative to TMS.

## 3. Results and discussion

### 3.1. Synthesis and spectroscopy

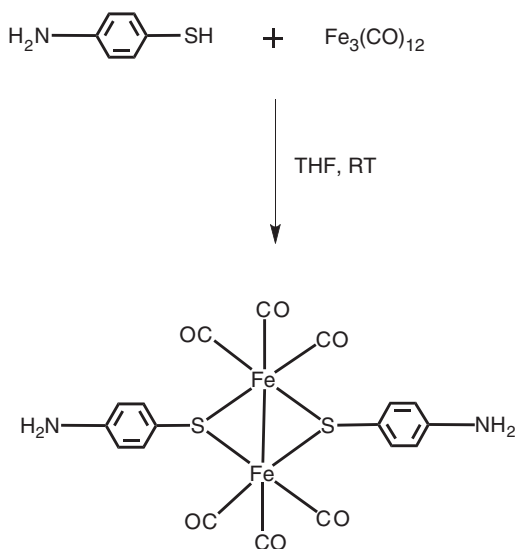
Preparation of **3** and **4** are described in Schemes 1 and 2, respectively. Reaction of *N*-(4-thiolphenyl)-1,8-naphthalimide and Fe<sub>3</sub>(CO)<sub>12</sub> carried out under nitrogen using Schlenk line techniques afforded **3** in 22% yield. A mixture of *N*-(4-thiolphenyl)-1,8-naphthalimide and Fe<sub>3</sub>(CO)<sub>12</sub> was stirred at room temperature overnight until a color change from green to red was observed. The product was purified by column chromatography on silica gel using dichloromethane as eluting solvent. The product was collected and, after the removal of solvent, afforded **3** as an orange powder. A similar procedure was utilized for the preparation, isolation, and purification of **4** (scheme 2). Four equivalents of 4-aminothiolphenol and one equivalent of Fe<sub>3</sub>(CO)<sub>12</sub>



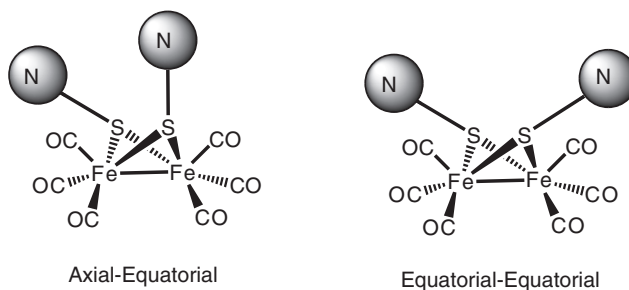
Scheme 1. Synthesis of **3**.

were dissolved in THF and stirred under nitrogen overnight. Compound **4** was obtained as an orange solid in 27% yield after chromatographic separation on silica gel using dichloromethane as solvent.

Compound **3** has been characterized by IR and NMR spectroscopy. The  $^1\text{H-NMR}$  spectrum of **3** shows five sets of multiplets between 7.0 and 8.8 ppm. The peaks are of equal integrated ratios corresponding to the five groups of aromatic protons on the naphthalimides. The spectrum is rather complex, an indication of the presence of isomers of **3** in solution. As reported for similar diironhexacarbonyl complexes [1, 55], the isomeric forms of **3** are based on the spatial orientation (axial or equatorial) of the naphthalimide groups (scheme 3).  $^1\text{H-NMR}$  spectrum of **4** recorded in chloroform contains three sets of peaks; a singlet at 3.7 ppm for the  $\text{NH}_2$  protons and multiplets at 6.5 and 7.1 ppm assigned to the aromatic protons.  $^{13}\text{C-NMR}$  spectra of **3** and **4** in chloroform contain, among other peaks, a peak at 208 ppm ascribed to the CO ligands.



Scheme 2. Synthesis of **4**.



Scheme 3. Possible isomers of **3** ( $N$  = naphthalimide).

The observed position of the  $^{13}\text{C}$ -signal for CO in **3** and **4** is similar to the values reported for other Fe–CO compounds [1–52].

Infrared spectroscopy is a very useful tool in ascertaining the structure and probing the electronic properties of iron-carbonyl complexes. The infrared spectra of **3** and **4** recorded in dichloromethane are represented in figure 1. Relevant IR data for **3** and **4** alongside those of **2** are presented in table 1. For **3**, we observe peaks at 2000, 2040, and 2075  $\text{cm}^{-1}$  ascribed to stretching frequencies of terminal metal carbonyls. The spectrum also contains four peaks at 1780, 1740, 1710, and 1675  $\text{cm}^{-1}$  attributed to naphthalimide [54]. The IR spectrum of **4** exhibits  $\nu_{(\text{CO})}$  peaks at 2070, 1995, and 2035  $\text{cm}^{-1}$  (table 1). These peaks are  $\sim 5\text{ cm}^{-1}$  lower than those observed for **3**. This small shift suggests the naphthalimides do not significantly influence the electronic properties of the Fe–CO core in **3**. Compound **2** was reported to have  $\nu_{(\text{CO})}$  values at 2005, 2043, and 2078  $\text{cm}^{-1}$  [51]. The IR results confirm the structures and integrity of **3** and **4**, further supported by elemental analysis data (*vide supra*).

### 3.2. Electrochemistry

To investigate the electrochemical and electrocatalytic properties of **3**, cyclic voltammetric studies were performed on **3** in acetonitrile under nitrogen. The cyclic

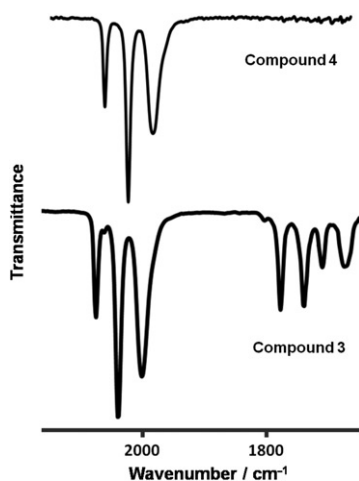


Figure 1. IR spectra of **3** and **4** in dichloromethane.

Table 1. Characteristic IR-frequencies for **2–4**.

Compound	$\nu_{(\text{CO})}$ ( $\text{cm}^{-1}$ )	Other peaks
<b>2</b> <sup>a</sup>	2005, 2043, 2078	Not reported
<b>3</b>	2000, 2040, 2075	1780, 1740, 1710, 1675
<b>4</b>	1995, 2035, 2070	1621, 1595

<sup>a</sup>Values obtained from ref. [51].

voltammogram of **3** is presented in figure 2. Two quasi-irreversible redox events are observed at  $E_{1/2} = -1.60$  V ( $I_{pa}/I_{pc} = 0.5$ ,  $E_{pa} = -1.59$  V,  $E_{pc} = -1.61$  V) and  $E_{1/2} = -1.75$  V ( $I_{pa}/I_{pc} = 0.4$ ,  $E_{pa} = -1.76$  V and  $E_{pc} = -1.74$  V) versus Fc/Fc<sup>+</sup>. A tentative description of these electrochemical events is depicted in scheme 4. The event at  $-1.60$  V can be assigned to Fe<sup>I</sup>Fe<sup>I</sup>/Fe<sup>I</sup>Fe<sup>0</sup> couple and that at  $-1.75$  V to the Fe<sup>I</sup>Fe<sup>0</sup>/Fe<sup>0</sup>Fe<sup>0</sup> couple. An irreversible oxidation peak (Fe<sup>I</sup>Fe<sup>I</sup>/Fe<sup>II</sup>Fe<sup>I</sup>) at  $+0.47$  V versus Fc/Fc<sup>+</sup> was also observed. Compound **4** undergoes irreversible reduction (Fe<sup>I</sup>Fe<sup>I</sup>/Fe<sup>I</sup>Fe<sup>0</sup>) at  $-1.53$  V and oxidation (Fe<sup>I</sup>Fe<sup>I</sup>/Fe<sup>II</sup>Fe<sup>I</sup>) at  $+0.46$  V versus Fc/Fc<sup>+</sup>. A comparative examination of the cyclic voltammetric data for **2–4** is contained in table 2. Compounds **3** and **4** have similar iron-centered redox potentials attesting to the similarity in the electronic nature of the diiron cores. This is further confined by IR spectroscopy (*vide supra*).

Models with similar structures to **3** and **4** have been evaluated as electrocatalysts for the production of hydrogen atoms. Table 3 contains electrochemical data for four such

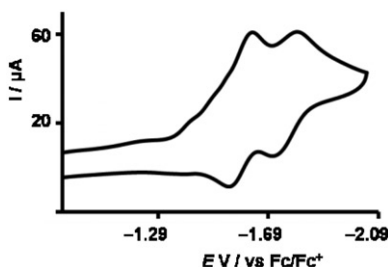
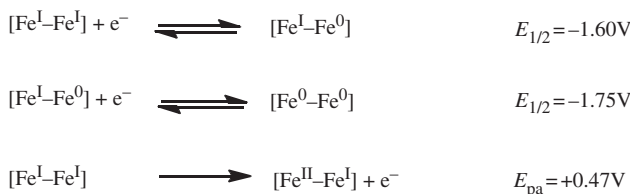


Figure 2. Cyclic voltammogram of **3** ( $1 \text{ mmol L}^{-1}$ ) recorded in  $\text{CH}_3\text{CN}$ ,  $0.1 \text{ mol L}^{-1}$   $\text{Bu}_4\text{NPF}_6$ , scan rate  $100 \text{ mV s}^{-1}$ .



Scheme 4. Electrochemical processes observed for **3**.

Table 2. Electrochemical data for **2–4**.<sup>a</sup>

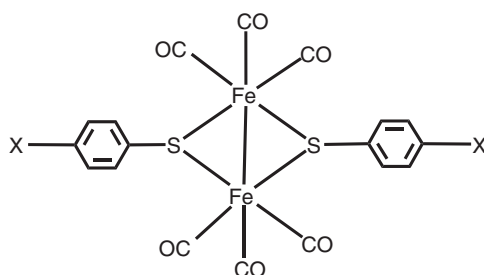
Compound	$E_{\text{pa}}$ (V)	$E_{1/2}$ (V)	$E_{\text{cat}}$ (V)	Overpotential
<b>2</b> <sup>b</sup>	–	–1.13, –1.49	–	–
<b>3</b>	+0.47	–1.60, –1.75	–2.19	–0.73
<b>4</b>	+0.46	–1.53 <sup>c</sup>	–1.88	–0.42

<sup>a</sup>Potentials referenced to Fc/Fc<sup>+</sup>.

<sup>b</sup>Values are obtained from ref. [51] and are reported vs. SCE. We converted the values to Fc/Fc<sup>+</sup> as described in ref. [1].

<sup>c</sup> $E_{\text{pc}}$  value.



Table 3. Electrochemical data for **3**, **4**, and similar compounds.<sup>a</sup>

X	$E_{pc}$ (V)	$E_{pa}$ (V)	$E_{cat}$ (V)
F	-1.19	+0.77	-1.7
Cl	-1.35	+0.79	-0.73
H	-1.44	+0.81	Not reported
MeO	-1.57	+0.93	Not reported
Naphthalimide ( <b>3</b> )	-1.60 <sup>b</sup>	+0.47	-2.19
NH <sub>2</sub> ( <b>4</b> )	-1.53	+0.46	-1.88

<sup>a</sup>Values obtained from ref. [1] except for **3** and **4** (this work). The values are referenced to Fe/Fe<sup>+</sup>.

<sup>b</sup> $E_{1/2}$  of first reduction process.

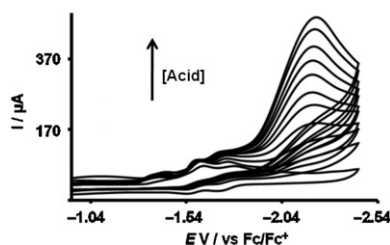


Figure 3. Cyclic voltammogram of **3** (1 mmol L<sup>-1</sup>, 10 mL) recorded in CH<sub>3</sub>CN, 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub>, scan rate 100 mV s<sup>-1</sup>; acetic acid added: 0, 7, 14, 21, 28, 35, 42, 49, 56, 63, and 70 mmol L<sup>-1</sup>.

models alongside those of **3** and **4** for comparison. The reduction potentials ascribed to the [Fe<sup>I</sup>-Fe<sup>I</sup>]/[Fe<sup>I</sup>-Fe<sup>0</sup>] couple for **3** and **4** (X = naphthalimide and NH<sub>2</sub>, respectively) are close to the value recorded for the model with X being methoxy. These reduction potentials are more negative than those observed for models with X: F, Cl, or H, suggesting that naphthalimide has less electron-withdrawing effect than fluorine and chlorine.

### 3.3. Electrocatalytic production of hydrogen

Compound **3** was examined as electrocatalyst for the reduction of proton to molecular hydrogen. The results are contained in figure 3. Cyclic voltammograms of **3** in the presence of acetic acid show a catalytic peak at -2.19 V with an overpotential of

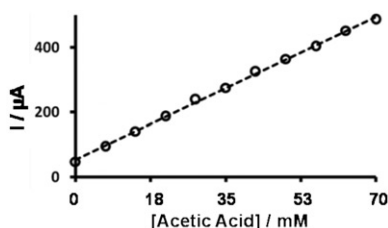


Figure 4. Plot of current vs. concentration of acetic acid added in the electrocatalytic reduction of proton to hydrogen atoms by **3**.

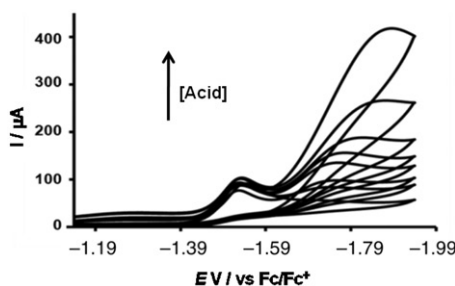


Figure 5. Cyclic voltammograms of **4** ( $1 \text{ mmol L}^{-1}$ ,  $10 \text{ mL}$ ) in the presence of acetic acid. Recorded in  $\text{CH}_3\text{CN}$ ,  $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ , scan rate  $100 \text{ mV s}^{-1}$ ; acetic acid added: 0, 4, 7, 9, 11, 14, 25, and  $30 \text{ mmol L}^{-1}$ .

$-0.73 \text{ V}$  versus  $\text{Fc/Fc}^+$ . The overpotential was calculated as described by Evans *et al.* [1]. The catalytic peak increases with increasing amount of acid added, as shown in figure 4. Figure 5 contains cyclic voltammograms of **4** in the presence of increasing concentration of acetic acid. A reduction peak at  $-1.88 \text{ V}$  versus  $\text{Fc/Fc}^+$  was observed. The current at this potential increases with acid concentration and is due to the reduction of proton to hydrogen [1]. The overpotential was calculated to be  $-0.42 \text{ V}$  versus  $\text{Fc/Fc}^+$ ,  $0.31 \text{ V}$  smaller than the value obtained for **3**.

#### 4. Conclusions

Two new diironhexacarbonyl complexes (**3** and **4**) containing imide and amine ligands have been synthesized. The structures, electronic, and electrochemical properties of the compounds have been probed with spectroscopic and electrochemical techniques. Both **3** and **4** are revealed by cyclic voltammetric studies in the presence of acetic acid to catalyze the reduction of proton to molecular hydrogen at relatively modest potentials ( $-2.19 \text{ V}$  and  $-1.88 \text{ V}$  vs.  $\text{Fc/Fc}^+$ , respectively).

#### Acknowledgments

Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for support of this research.

## References

- [1] G.N. Felton, C.A. Mebi, B.J. Petro, A.K. Vannucci, D.H. Evans, R.S. Glass, D.L. Lichtenberger. *J. Organomet. Chem.*, **694**, 2681 (2009).
- [2] F. Gloaguen, T.B. Rauchfuss. *Chem. Soc. Rev.*, **38**, 100 (2009).
- [3] J.-F. Capon, F. Gloaguen, F.Y. Petillon, P. Schollhammer, J. Talarmin. *Coord. Chem. Rev.*, **253**, 1476 (2009).
- [4] (a) E.J. Lyon, I.P. Georgakaki, J.H. Reibenspies, M.Y. Darensbourg. *Angew. Chem.*, **111**, 3373 (1999); (b) *Angew. Chem. Int. Ed.*, **38**, 3178 (1999).
- [5] A. Le Cloirec, S.C. Davies, D.J. Evans, D.L. Hughes, C.J. Pickett, S.P. Best, S. Borg. *Chem. Commun.*, 2285 (1999).
- [6] M. Schmidt, S.M. Contakes, T.B. Rauchfuss. *J. Am. Chem. Soc.*, **121**, 9736 (1999).
- [7] P.I. Volkers, C.A. Boyke, J. Chen, T.B. Rauchfuss, C.M. Whaley, S.R. Wilson, H. Yao. *Inorg. Chem.*, **47**, 7002 (2008).
- [8] C. Tard, C.J. Pickett. *Chem. Rev.*, **109**, 2245 (2009).
- [9] M.L. Singleton, D.J. Crouthers, R.P. Duttweiler III, J.H. Reibenspies, M.Y. Darensbourg. *Inorg. Chem.*, **50**, 5015 (2011).
- [10] J.D. Lawrence, H. Li, T.B. Rauchfuss, M. Benard, M.-M. Rohmer. *Angew. Chem. Int. Ed.*, **40**, 1768 (2001).
- [11] H. Li, T.B. Rauchfuss. *J. Am. Chem. Soc.*, **124**, 726 (2002).
- [12] J.W. Peters, W.N. Lanzilotta, B.J. Lemon, L.C. Seefeldt. *Science*, **282**, 1853 (1998).
- [13] Y. Nicolet, C. Piras, P. Legrand, C.E. Hatchikian, J.C. Fontecilla-Camps. *Structure*, **7**, 13 (1999).
- [14] J.D. Lawrence, H. Li, T.B. Rauchfuss. *Chem. Commun.*, 1482 (2001).
- [15] T. Liu, M. Wang, Z. Shi, H. Cui, W. Dong, J. Chen, B. Akermark, L. Sun. *Chem. Eur. J.*, **10**, 4474 (2004).
- [16] W. Dong, M. Wang, X. Liu, K. Jin, G. Li, F. Wang, L. Sun. *Chem. Commun.*, 305 (2006).
- [17] J. Hou, X. Peng, J. Liu, Y. Gao, X. Zhao, S. Gao, K. Han. *Eur. J. Inorg. Chem.*, 4679 (2006).
- [18] S. Jiang, J. Liu, L. Sun. *Inorg. Chem. Commun.*, **9**, 290 (2006).
- [19] L.-C. Song, J.-H. Ge, X.-F. Liu, L.-Q. Zhao, Q.-M. Hu. *J. Organomet. Chem.*, **691**, 570 (2006).
- [20] L.-C. Song, J.-H. Ge, X.-G. Zhang, Y. Liu, Q.-M. Hu. *Eur. J. Inorg. Chem.*, 3204 (2006).
- [21] H.-G. Cui, M. Wang, W.-B. Dong, L.-L. Duan, P. Li, L.-C. Sun. *Polyhedron*, **26**, 904 (2007).
- [22] S. Jiang, J. Liu, Y. Shi, Z. Wang, B. Akermark, L. Sun. *Dalton Trans.*, 896 (2007).
- [23] Y. Si, C. Ma, M. Hu, H. Chen, C. Chen, Q. Liu. *New J. Chem.*, **31**, 1448 (2007).
- [24] L.C. Song, B.-S. Yin, Y.-L. Li, L.-Q. Zhao, J.-H. Ge, Z.-Y. Yang, Q.-M. Hu. *Organometallics*, **26**, 4921 (2007).
- [25] V. Vijaikanth, J.-F. Capon, F. Gloaguen, F.Y. Petillon, P. Schollhammer, J. Talarmin. *J. Organomet. Chem.*, **692**, 4177 (2007).
- [26] L.-C. Song, Z.-Y. Yang, H.-Z. Bian, Q.-M. Hu. *Organometallics*, **23**, 3082 (2004).
- [27] L.-C. Song, Z.-Y. Yang, H.-Z. Bian, Y. Liu, H.-T. Wang, X.-F. Liu, Q.-M. Hu. *Organometallics*, **24**, 6126 (2005).
- [28] L.-C. Song, Z.-Y. Yang, Y.-J. Hua, H.-T. Wang, Y. Liu, Q.-M. Hu. *Organometallics*, **26**, 2106 (2007).
- [29] D. Seyferth, R.S. Henderson, L.C. Song. *Organometallics*, **1**, 125 (1982).
- [30] F. Gloaguen, J.D. Lawrence, M. Schmidt, S.R. Wilson, T.B. Rauchfuss. *J. Am. Chem. Soc.*, **123**, 12518 (2001).
- [31] Q.-Q. Zhang, R.S. Dickson, G.D. Fallon, R. Mayadunne. *J. Organomet. Chem.*, **627**, 201 (2001).
- [32] X. Zhao, I.P. Georgakaki, M.L. Miller, R. Mejia-Rodriguez, C.-Y. Chiang, M.Y. Darensbourg. *Inorg. Chem.*, **41**, 3917 (2002).
- [33] J.W. Tye, M.Y. Darensbourg, M.B. Hall. *Inorg. Chem.*, **45**, 1552 (2006).
- [34] S.P. Best, S.J. Borg, J.M. White, M. Razavet, C.J. Pickett. *Chem. Commun.*, 4348 (2007).
- [35] A.K. Justice, G. Zampella, L. De Gioia, T.B. Rauchfuss, J.I. van der Vlugt, S.R. Wilson. *Inorg. Chem.*, **46**, 1655 (2007).
- [36] A. Winter, L. Zsolnai, G. Huttner. *Z. Naturforsch B*, **37**, 1471 (1982).
- [37] J.A. Cabeza, M.A. Martinez-Garcia, V. Riera, D. Ardura, S. Garcia-Granda. *Organometallics*, **17**, 1471 (1998).
- [38] J.-F. Capon, F. Gloaguen, P. Schollhammer, J. Talarmin. *J. Electroanal. Chem.*, **566**, 241 (2004).
- [39] R.S. Glass, M.S. Singh. *ARKIVOC*, 185 (2005).
- [40] J.-F. Capon, F. Gloaguen, P. Schollhammer, J. Talarmin. *J. Electroanal. Chem.*, **595**, 47 (2006).
- [41] G.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. *J. Am. Chem. Soc.*, **129**, 12521 (2007).
- [42] F. Gloaguen, D. Morvan, J.-F. Capon, P. Schollhammer, J. Talarmin. *J. Electroanal. Chem.*, **603**, 15 (2007).
- [43] J.S. McKennis, E.P. Kyba. *Organometallics*, **2**, 1249 (1983).

- [44] M.K. Harb, U.-P. Apfel, J. Kübel, H. Görls, G.N. Felton, T. Sakamoto, D.H. Evans, R.S. Glass, D.L. Lichtenberger, M. El-khateeb, W. Weigand. *Organometallics*, **28**, 6666 (2009).
- [45] K. Charreteur, M. Kdider, J.-F. Capon, F. Gloaguen, F.Y. Pétillon, P. Schollhammer, J. Talarmin. *Inorg. Chem.*, **49**, 2496 (2010).
- [46] B.J. Petro, A.K. Vannucci, L.T. Lockett, C.A. Mebi, R. Kottani, N.E. Gruhn, G.S. Nichol, P.J. Goodyer, D.H. Evans, R.S. Glass, D.L. Lichtenberger. *J. Mol. Struct.*, **890**, 281 (2008).
- [47] R.J. Wright, C. Lim, T.D. Tilley. *Chem. Eur. J.*, **15**, 8518 (2009).
- [48] P.S. Singh, H.C. Rudbeck, P. Huang, S. Ezzaher, L. Eriksson, M. Stein, S. Ott, R. Lomoth. *Inorg. Chem.*, **48**, 10883 (2009).
- [49] C.A. Mebi, B.C. Noll, R. Gao, D. Karr. *Z. Anorg. Allg. Chem.*, 2550 (2010).
- [50] J. Chen, A.K. Vannucci, C.A. Mebi, N. Okumura, S.C. Borowski, M. Swenson, L.T. Lockett, D.H. Evans, R.S. Glass, D.L. Lichtenberger. *Organometallics*, **29**, 5330 (2010).
- [51] A.S. Samuel, D.T. Co, C.L. Stern, M.R. Wasielewski. *J. Am. Chem. Soc.*, **132**, 8813 (2010).
- [52] D. Kolosov, V. Adamovich, P. Djurovich, M.E. Thompson, C. Adachi. *J. Am. Chem. Soc.*, **124**, 9945 (2002).
- [53] R.J. Sarma, C. Tamuly, N. Barooah, J.B. Baruah. *J. Mol. Struct.*, **829**, 29 (2007).
- [54] N. Barooah, C. Tamuly, J.B. Baruah. *J. Chem. Sci.*, **117**, 117 (2005).
- [55] R.S. Glass, N.E. Gruhn, E. Lorange, M.S. Singh, N.T. Stessman, U.I. Zakai. *Inorg. Chem.*, **44**, 5728 (2005).