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Using naphthalene-2-thiolate ligands in the design of hydrogenase models with mild proton reduction overpotentials

Charles A. Mebi [a,*], Derek S. Karr [a], Bruce C. Noll [b]

[a] Department of Physical Sciences, Arkansas Tech University, 1701 N. Boulder Ave., Russellville, AR 72801, USA
[b] Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711, USA

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ABSTRACT

Diiron–carbonyl complexes coupled to naphthalene-2-thiolate ligands, [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_6$] (**1**) and [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_5$PPh$_3$] (**2**), have been usefully prepared and structurally characterized. As models for the active site of hydrogenase enzymes, these compounds have been examined as electrocatalysts for the reduction of proton to produce molecular hydrogen. In the presence of acetic acid, **1** and **2** catalyze the electrochemical production of molecular hydrogen with mild overpotentials of −0.54 and −0.51 V versus Fc/Fc$^+$, respectively. The overpotential for compound **1** is 260 mV smaller than that of the analogous compound, [(μ-SPh)$_2$Fe$_2$(CO)$_6$].

1. Introduction

Iron–thiolato complexes are ubiquitous in biological systems. They are involved in electron transfer and biocatalytic processes [1]. For example, the active site (H-cluster, **A**: X = NH or CH_2) of the hydrogen producing enzyme, iron-only hydrogenase, contains a diiron carbonyl cluster with a bridging thiolato ligand [2–4]. Bioorganometallic chemistry focused on the study of models for the H-cluster is of great interest. This interest is due to the need to develop efficient and inexpensive catalysts for the generation of hydrogen, a clean alternative to fossil fuels [5–7]. Simple organometallic models of the H-cluster such as **B** and **C** have been investigated (Scheme 1). To modulate the stereoelectronic and electrocatalytic properties of models **B** and **C**, different thiolate ligands have been employed [8–40]. Of particular interest is the use of polyaromatic thiolate ligands providing π-electronic systems which may influence the stability and electrochemical properties of the [$Fe_2(CO)_6$] core [22–24].

This report contains a study of type **C** models containing naphthalene-2-thiolate ligands. The synthesis and spectroscopic (IR and NMR) characterization of [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_6$] (**1**) is described. The substitution of CO for triphenylphosphine in complex **1** to afford [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_5$PPh$_3$] (**2**) is reported. Compounds **1** and **2** are evaluated as electrocatalysts for the reduction of acetic acid to molecular hydrogen by cyclic voltammetry and the results are discussed.

2. Experimental

2.1. General methods

All syntheses were conducted under inert (N_2) atmosphere using Schlenk line techniques. The solvents, CH_2Cl_2, tetrahydrofuran (THF), and CH_3CN were purchased from VWR international and used as obtained. nBu$_4$NPF$_6$, naphthalene-2-thiol, triphenylphosphine, trimethylnitrogenoxide (Me_3NO), and triirondodecacarbonyl ($Fe_3(CO)_{12}$) were obtained from Aldrich and used without further purification. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained in $CDCl_3$ on a Bruker 300 MHz instrument. IR spectra in CH_2Cl_2 were recorded on a Nicolet FT/IR Magna spectrophotometer. Melting point determinations were conducted using an electro thermal melting point apparatus.

2.2. Electrochemistry

Electrochemical studies on the complexes were conducted using an Epsilon BAS potentiostat with glassy carbon working electrode, platinum auxiliary electrode and Ag/AgCl reference electrode. The glassy carbon and platinum electrodes were polished with alumina paste and rinsed with distilled water and acetone. The electrodes were connected to a cell that contains 10 mL of the catalytic mixture (1 mM). A 0.1 M CH_3CN solution of nBu$_4$NPF$_4$

* Corresponding author. Tel.: +1 4793562151; fax: +1 4799640837.
E-mail address: cmebi@atu.edu (C.A. Mebi).

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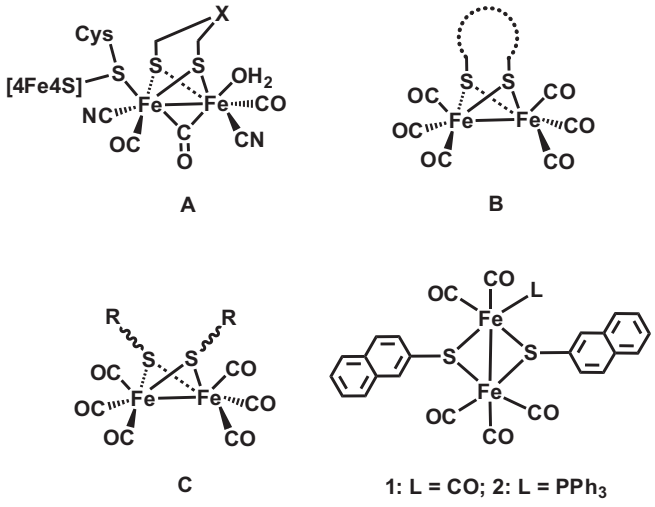


Scheme 1.

was used as supporting electrolyte. Anhydrous solvent (acetonitrile) from Aldrich was used and purged with nitrogen before each measurement. Electrocatalytic studies were conducted using glacial acetic acid.

2.3. Synthesis of [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_6$] (**1**)

Triirondodecarbonyl (1.57 g, 3.12 mmol) and naphthalene-2-thiol (1.00 g, 6.25 mmol) contained in a 100 mL flask were treated with THF and refluxed for 1 h or until the color of the mixture changed from green to red. The solvent of the solution was removed by rotary evaporation affording an orange solid. Separation of the residue by silica gel chromatography using hexanes as eluent gave [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_6$] in 90% yield (1.68 g, R_f: 0.3). IR (CH_2Cl_2, $_{CO}$) 2075, 2039, 2001 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.60–7.86 (m); 7.27–7.52 (m). ^{13}C NMR ($CDCl_3$): 209, 140–126 ppm. Elemental *Anal.* Calc.: C, 52.20; H, 2.36; S, 10.72. Found: C, 52.21; H, 2.36; S, 11.24%. Melting point: decomposes at 164 °C.

2.4. Synthesis of [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_5$PPh$_3$] (**2**)

A dichloromethane solution of **1** (101 mg, 0.168 mmol, 15 mL) was transferred into an acetonitrile solution of Me_3NO (18.7 mg, 0.168 mmol, 15 mL) and stirred for 10 min under nitrogen atmosphere. To the dark red solution was added triphenylphosphine (44.0 mg, 0.168 mmol) dissolved in 5 mL of CH_2Cl_2 to afford an orange mixture. The solution was stirred at room temperature for 1 h and the solvent removed by rotary evaporation. The residue was separated by chromatography on preparative silica gel TLC plate (solvent: Hexanes/CH_2Cl_2; 1:1, R_f: 0.6). Compound **2** was obtained as red solid in 40% yield (55.7 mg). IR (CH_2Cl_2, $_{CO}$) 2050, 1990, 1960 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.61–7.98 (m); 7.31–7.50 (m), 7.0–7.12 (m). ^{13}C NMR ($CDCl_3$): 210, 140–126 ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): 56.7 (s) ppm. Elemental *Anal.* Calc.: C, 62.03; H, 3.52; S, 7.70. Found: C, 61.85; H, 4.1; S, 7.78%. Melting point: decomposes at 140 °C.

2.5. Crystal structure determination

Red block-like specimen of **2**, approximate dimensions 0.250 × 0.250 × 0.400 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker SMART X2S benchtop diffractometer system equipped with a doubly curved silicon crystal monochromator and a Mo Kα microfocus sealed tube (λ = 0.71073 Å). The structure was solved and refined using the Bruker SHELXTL Software Package [41].

3. Results and Discussion

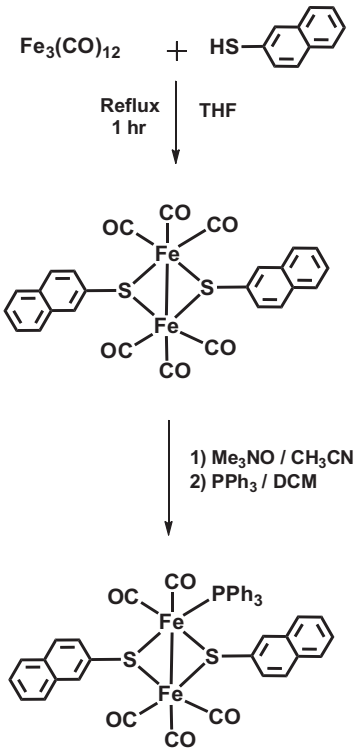
3.1. Preparation

The synthesis of [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_6$] is presented in Scheme 2. A 100 mL round bottom flask containing naphthalene-2-thiol and $Fe_3(CO)_{12}$ was purged with nitrogen and 60 mL of freshly distilled THF added. The mixture was stirred under reflux conditions for 1 h or until there was a change in color from dark green to deep red. Removal of the solvent by rotary evaporation followed by chromatographic separation on silica gel using hexanes as eluent gave **1** in 90% yield. Red crystalline plates of **1** were obtained from hexanes solution of [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_6$] at −20 °C.

Scheme 1 also describes the substitution of one of the CO ligands on **1** for electron-donating triphenylphosphine to afford [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_5$PPh$_3$] (**2**). A dichloromethane solution of **1** was added to an acetonitrile solution of Me_3NO and stirred for 10 min under nitrogen atmosphere. The resultant dark red solution was then treated with triphenylphospine and stirred for 40 min affording a red solution. Compound **2** was obtained in 40% yield as a red solid after removal of solvent followed by chromatographic separation on silica gel (Hexanes/CH_2Cl_2; 1:1). Recrystalization of **2** was accomplished from hexanes solution of [(μ-naphthalene-2-thiolato)$_2$Fe$_2$(CO)$_5$PPh$_3$] in a freezer at −20 °C overnight affording red block crystals of **2**.

3.2. Spectroscopy

Compounds **1** and **2** were characterized using spectroscopic methods (IR and NMR). ^{1}H NMR spectra of **1** and **2** in chloroform



Scheme 2. Synthesis of compounds **1** and **2**.

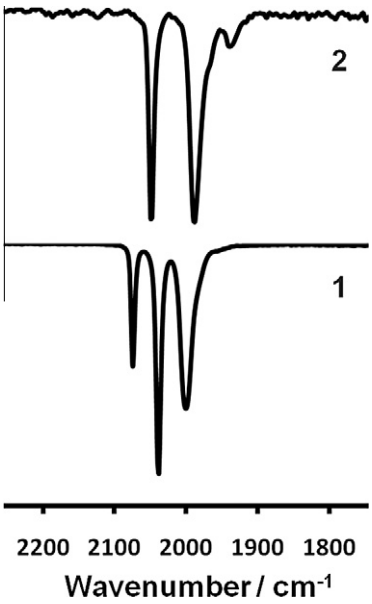


Fig. 1. IR spectra of **1** and **2** in CH_2Cl_2.

Table 1
Infrared data for **1** and **2**.

Compound	Infrared[a]	
	ν(co)/cm^{-1}	$\bar{\nu}$(co)/cm^{-1}[b]
1	2075, 2039, 2001	2038
2	2050, 1990, 1960	2000(38)[c]

[a] Recorded in DCM.
[b] $\bar{\nu}$ is average of IR values.
[c] $\Delta\bar{\nu}$ is average shift = $\bar{\nu}_1 - \bar{\nu}_2$.

show peaks for the aromatic protons (8.0–7.3 ppm). ^{31}P NMR spectrum of **2** confirms the presence of the PPh_3 ligand in complex **2** with a chemical shift at 56.7 ppm as a singlet. The ^{13}C NMR spectra of **1** and **2** show peaks ascribed to the CO ligands at ~210 ppm including a set of peaks between 140 and 126 ppm.

The infrared spectra of **1** and **2** recorded in dichloromethane are reported in Fig. 1. IR spectrum of **1** contains three peaks at 2075, 2039 and 2001 cm^{-1} characteristic of stretching vibrational modes of terminal metal carbonyls. These bands are consistent with those reported [8–34] for similar organometallic compounds indicating the presence of $Fe_2(CO)_6$ unit. Compound **2** also shows three IR peaks at 2050, 1990 and 1960 cm^{-1}. These peaks are shifted to lower wavenumbers compared to **1** as a result of the electron-donating property of PPh_3 ligand (enhanced back-donation into the π^* orbital of CO in **2**). The average shift ($\Delta\bar{\nu}$) was determined to be ~38 cm^{-1} (see Table 1).

3.3. X-ray crystallography

The spectroscopic data obtained for the products in Scheme 1, allow for the assignment of the suggested structures for **1** and **2**. Their compositions and structures were further ascertained by elemental analyses and X-ray crystallographic study. Red crystals of **1** and **2** were obtained from hexanes solutions of the compounds at −20 °C. Block-like crystals **2** suitable for X-ray diffraction were obtained and subjected to X-ray diffraction studies. Crystallographic data for **2** are presented in Table 2 and structural parameters are contained in Table 3. The Fe–Fe bond length for **2** is 2.5215(4). This value is close to that reported for the active site of the hydrogenase enzyme (2.6 Å) [2]. The X-ray diffraction analysis of **2** reveals a butterfly structure (Fig. 2) with equatorial–axial spatial orientation of the naphthyl groups tethered to the iron–carbonyl moiety.

Table 2
Summary of data collection, solution, and refinement parameters for **2**.

	2
Empirical formula	$C_{43}H_{29}Fe_2O_5PS_2$
Formula weight	832.45
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.2438(5)
b (Å)	11.4387(5)
c (Å)	16.7992(8)
α (°)	79.708(2)
β (°)	74.0790(10)
γ (°)	65.2540(10)
V (Å^3)	1881.90(15)
Z	2
D_{calc} (Mg/cm^3)	1.469
Absorption coefficient (mm^{-1})	0.970
F(000)	852
Reflections collected	18479
θ (°)	2.23–25.01
Index ranges	$-13 \leqslant h \leqslant 13$, $-13 \leqslant k \leqslant 13$, $-19 \leqslant l \leqslant 19$
Independent reflections (R_{int})	6561 (0.0274)
Coverage of independent reflections	98.8%
Absorption correction	Multiscan
Largest difference peak and hole	0.299 and −0.256 e Å^{-3}
Maximum and minimum transmission	0.7935 and 0.6976
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0269, wR_2 = 0.0660
R indices (all data)	R_1 = 0.0329, wR_2 = 0.0698
Goodness-of-fit (GOOF) on F^2	1.035
CCDC	898238

Table 3
Selected bond lengths [Å] and bond angles [°] for **2**.

Bond lengths (Å)		Bond angles (°)			
Fe1–Fe2	2.5215(4)	S1–Fe1–Fe2	56.865(15)	Fe2–S1–Fe1	66.814(16)
Fe1–S1	2.2827(6)	S1–Fe2–Fe1	56.321(15)	Fe2–S2–Fe1	67.518(16)
Fe1–S2	2.2705(5)	S2–Fe2–Fe1	56.306(14)	P1–Fe2–S2	103.835(19)
Fe2–S1	2.2970(5)	S2–Fe1–Fe2	56.176(14)	P1–Fe2–S1	112.08(2)
Fe2–S2	2.2671(5)	S1–Fe1–S2	80.141(18)	P1–Fe2–Fe1	156.670(18)
Fe2–P	2.2540(5)	S1–Fe2–S2	79.909(19)		

3.4. Electrochemistry

Cyclic voltammograms (CVs) of compounds **1** and **2** were recorded in acetonitrile. The relevant parameters are contained in Table 4. The CVs of compounds **1** and **2** contain two interesting electrochemical events; an irreversible reduction (**1**, E_{pc} = −1.33 V; **2**, E_{pc} = −1.49 V versus Fc/Fc$^+$) assigned to [Fe^I–Fe^I] → [Fe^I–Fe^0] and an irreversible oxidation (**1,** E_{pa} = +0.61 V versus Fc/Fc$^+$; **2,** E_{pa} = +0.31 V versus Fc/Fc$^+$) ascribed to [Fe^I–Fe^I] → [Fe^I–Fe^{II}]. The reduction of compound **1** occurs at a less negative potential and its oxidation at a more positive potential than compound **2**. This is in accord with the substitution of CO for PPh_3 making the [Fe–Fe] center of **2** more electron-rich than **1**. The assignments and shifts in potentials are consistent with results of similar models reported in the literature [9]. The effect of the naphthalene rings on the redox property of compound **1** can be clearly seen in comparison with the complexes, [(μ-naphthalene-1,8-dithiolate)Fe_2CO_6] and [(μ-SPh)$_2Fe_2(CO)_6$]. The first reduction potential of complex **1** exhibits an anodic shift of about 190 mV in comparison to that of [(μ-naphthalene-1,8-dithiolate)Fe_2CO_6] complex [8] and a positive shift (110 mV) to that of [(μ-SPh)$_2Fe_2(CO)_6$] [25b].

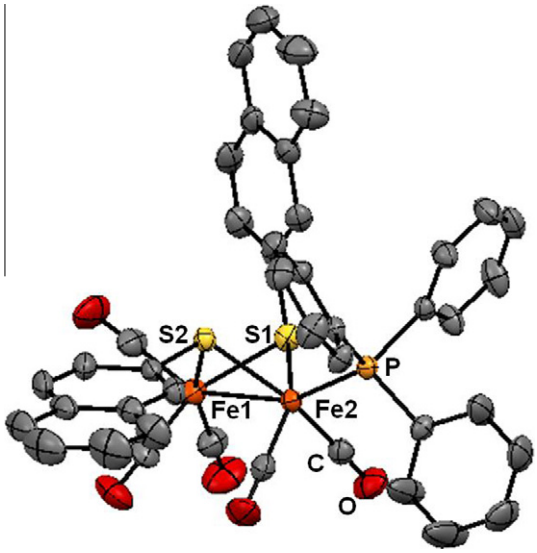


Fig. 2. Thermal ellipsoid representation of **2**. Thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table 4
Electrochemical data for **1** and **2**.

Compound	E_{pc}/V	E_{pa}/V	E_{cat}	Overpotential
1	−1.33	+0.61	−2.00	−0.54
2	−1.49	+0.31	−1.97	−0.51
3[a]	−1.52	+0.87	−2.00	−0.54
4[b]	−1.44	+0.81	−2.26	−0.80

[a] **3** is [(μ-naphthalene-1,8-dithiolate)$Fe_2(CO)_6$], Refs. [8] and [23].
[b] **4** is [(μ-SPh)$_2Fe_2(CO)_6$], Refs. [9] and [25b].

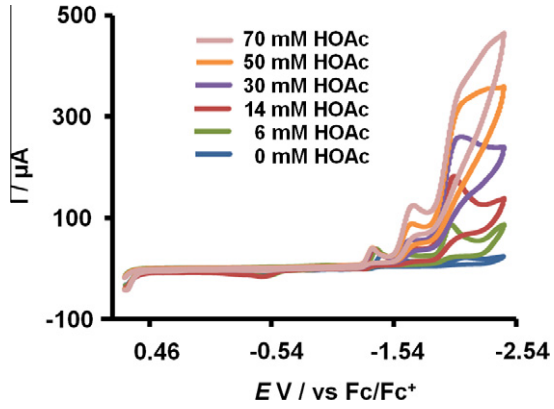


Fig. 3. Cyclic voltammograms of **1** (1 mM) in 0.1 M Bu_4NPF_6/CH_3CN at 100 mV/s in the presence of increasing amounts of acetic acid (0, 6, 14, 30, 50, 70 mM).

3.5. Electrocatalytic production of hydrogen

Compounds **1** and **2** were examined as electrocatalyts for the reduction of proton to molecular hydrogen. The results are presented in Figs. 3 and 4. Cyclic voltammograms of **1** and **2** in the presence of acetic acid show a new peak at −2.00 V and −1.97 V versus Fc/Fc^+. The current at these reduction potentials increases with the amount of acetic acid added. This is attributed to the reduction of proton to molecular hydrogen [9]. Interestingly, the cyclic voltammogram of **1** in the presence of acid show another

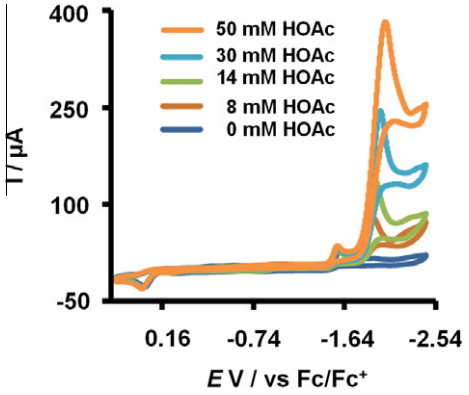


Fig. 4. Cyclic voltammograms of **2** (1 mM) in 0.1 M Bu_4NPF_6/CH_3CN at 100 mV/s in the presence of increasing amounts of acetic acid (0, 8, 14, 30, 50 mM).

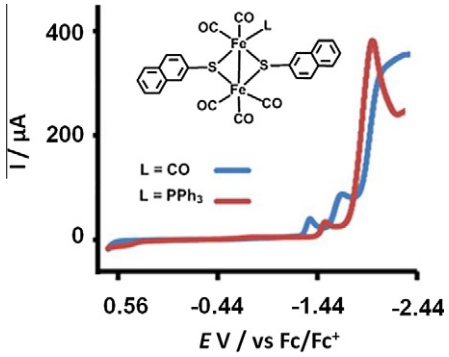


Fig. 5. Cyclic voltammograms of **1** (blue) **2** (red) recorded under the same conditions: (1 mM) in 0.1 M Bu_4NPF_6/CH_3CN at 100 mV/s in the presence of 50 mM acetic acid. (Colour online.)

peak at −1.66 V versus Fc/Fc^+. This peak may be due a new complex formed by the substitution of CO in **1** for acetonitrile. The overpotential of the catalysts have been calculated as described by Evans et al. [9] and presented in Table 4. Compounds **1** and **2** have overpotentials of −0.54 and −0.51 V (versus Fc/Fc^+) respectively. These values compare favourably with those reported for similar models [(naphthalene-1,8-dithiolate)$Fe_2(CO)_6$] (−0.54 V versus Fc/Fc^+) [23] and [(μ-SPh)$_2Fe_2(CO)_6$] (−0.80 V versus Fc/Fc^+) [9,25b]. As observed in Fig. 5, although the reduction of **1** occurs at a less negative potential than **2**, compound **2** catalyzes the reduction of protons at a slightly less negative potential.

4. Conclusion

We have synthesized and structurally characterized two diiron–carbonyl complexes containing polyaromatic thiolate ligands, [(μ-naphthalene-2-thiolato)$_2Fe_2(CO)_6$] and [(μ-naphthalene-2-thiolato)$_2Fe_2(CO)_5PPh_3$]. The reduction of [(μ-naphthalene-2-thiolato)$_2Fe_2(CO)_6$] produced a new species attributed to the substitution of CO by solvent molecule. Upon reduction, [(μ-naphthalene-2-thiolato)$_2Fe_2(CO)_5PPh_3$] is shown to be more stable to CO substitution and generate hydrogen from acetic acid at a slightly lower overpotential than [(μ-naphthalene-2-thiolato)$_2Fe_2(CO)_6$]. Our results also show that the proton reduction overpotential for [(μ-naphthalene-2-thiolato)$_2Fe_2(CO)_6$] is 260 mV smaller than that of the analogous compound, [(μ-SPh)$_2Fe_2(CO)_6$]. This study illustrates the potential of naphthalene-2-thiolate ligand to modulate redox and electrocatalytic properties of the iron–carbonyl moiety.

Acknowledgements

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Appendix A. Supplementary data

CCDC 898238 contains the supplementary crystallographic data for compound **2**. 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 e-mail: deposit@ccdc.cam.ac.uk.

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