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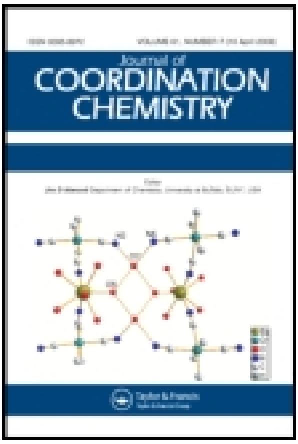

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Synthesis and structural characterization of diiron azadithiolate complexes relevant to the active site of [FeFe] hydrogenases

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Two N-functionally substituted diiron azadithiolate complexes, $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CH}_2\text{OC(O)C}_6\text{H}_4\text{I-}p]\text{Fe}_2(\text{CO})_6$ (**1**) and $\{[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CH}_2\text{OC(O)C}_6\text{H}_4\text{I-}p]\text{Fe}_2(\text{CO})_5\text{Ph}_2\text{PCH}\}_2$ (**2**) as models for the active site of [FeFe] hydrogenases, have been prepared and fully characterized. Complex **1** was prepared by the reaction of $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{Fe}_2(\text{CO})_6$ with *p*-iodobenzoic acid in the presence of 4-dimethylaminopyridine (DMAP) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) in 78% yield. Further treatment of **1** with 1 equiv. of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ followed by 0.5 equiv. of *trans*-1,2-bis(diphenylphosphino)ethylene (dppe) affords **2** in 60% yield. The new complexes **1** and **2** were characterized by IR and ^{1}H (^{13}C, ^{31}P) NMR spectroscopic techniques and their molecular structures were confirmed by X-ray diffraction analysis. The molecular structure of **1** has two conformational isomers, in one isomer its N-functional substituent is axial to its bridged nitrogen and in the other isomer its N-functional substituent is equatorial. The crystal structure of **2** revealed that its N-functional substituents are equatorial to its nitrogens and dppe occupies the two apical positions of the square-pyramidal irons.

Keywords: Diiron azadithiolate; [FeFe] hydrogenases; Synthesis; Crystal structure

1. Introduction

[FeFe] hydrogenases are metalloenzymes that catalyze hydrogen metabolism in several microorganisms [1–4]. X-ray crystallographic [5–8] and IR [9–11] studies have revealed that the active site of [FeFe] hydrogenases, so called H-cluster [12], consists of a butterfly [2Fe2S] cluster linked to a cubic [4Fe4S] cluster *via* the sulfur of a L-cysteinyl group. In addition, the two Fe atoms of the butterfly [2Fe2S] cluster are coordinated with CO and CN^-. The bridging dithiolate could most likely be an azadithiolate (ADT, $\text{SCH}_2\text{NHCH}_2\text{S}$) [7, 13], whose central nitrogen plays an important role in the heterolytic cleavage or in the formation of hydrogen [14] (scheme 1). Many ADT model complexes [15–25] for the active site of [FeFe] hydrogenases have been reported based on this structural information. In this article, we report the synthesis, characterization,

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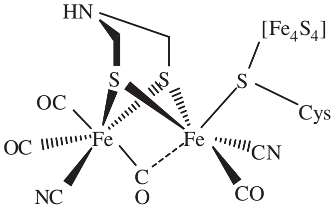


Scheme 1. H-cluster structure of [FeFe] hydrogenases.

and crystal structures of N-functionally substituted complex $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CH}_2\text{OC(O)C}_6\text{H}_4\text{I-}p]\text{Fe}_2(\text{CO})_6$ (**1**) and double butterfly complex $\{[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CH}_2\text{OC(O)C}_6\text{H}_4\text{I-}p]\text{Fe}_2(\text{CO})_5\text{Ph}_2\text{PCH}\}_2$ (**2**) related to the active site of [FeFe] hydrogenases. We introduce the iodo functionality to **1** because the complex could react with terminal alkyne [16, 17, 25] by the Sonogashira reaction [26], and further covalently link to a ruthenium photosensitizer [16, 17]. Phosphines are good surrogates for cyanide found in the natural enzymes [27], so we prepared the *trans*-1, 2-bis(diphenylphosphino)ethylene (dppe)-containing **2**.

2. Experimental

2.1. *Materials and methods*

All reactions and operations were carried out under a dry, oxygen-free nitrogen atmosphere with standard Schlenk and vacuum-line techniques. CH_2Cl_2 and MeCN were distilled with CaH_2 under N_2. *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), *p*-iodobenzoic acid, $Me_3NO \cdot 2H_2O$, dppe, and other materials were commercially available and used as received. $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{Fe}_2(\text{CO})_6$ [21, 22] was prepared according to the literature procedures. Preparative TLC was carried out on glass plates (26 cm × 20 cm × 0.25 cm) coated with silica gel H (10–40 µm). IR spectra were recorded on a Nicolet 670 FTIR spectrometer. ^{1}H (^{13}C, ^{31}P) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer. Melting points were determined on a YRT-3 apparatus and are uncorrected.

2.2. *Synthesis of 1*

DCC (0.055 g, 0.27 mmol) and DMAP (0.017 g, 0.24 mmol) were added to a solution of *p*-iodobenzoic acid (0.057 g, 0.23 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at 0°C for 1.5 h. To this mixture $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{Fe}_2(\text{CO})_6$ (0.100 g, 0.23 mmol) was added, and the new mixture was stirred at room temperature for 3 h until TLC showed that $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{CH}_2\text{OH}]\text{Fe}_2(\text{CO})_6$ was completely consumed and gave a red solution. The solvent was removed under reduced pressure and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 2 : 1) as eluent. From the main red band, **1** (0.118 g) was obtained as a red solid. Yield: 78%; m.p. 84–86°C. IR (KBr disc): $\nu_{C\equiv O}$ 2069 (vs), 2032 (vs), 2006 (vs), 1970 (s) cm^{-1}; $\nu_{C=O}$ 1716 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): 7.81 (d, 2H, $J = 8.0$ Hz, 2*m*-COPh*H*), 7.66 (d, 2H, $J = 8.0$ Hz, 2*o*-COPh*H*), 4.19 (t, 2H, $^3J = 5.0$ Hz, $\mathrm{NCH_2}\mathit{CH_2}\mathrm{O}$), 3.65 (s, 4H, $\mathrm{2NC}\mathit{H_2}\mathrm{S}$), 3.11 (t, 2H, $^3J = 5.0$ Hz, $\mathrm{NC}\mathit{H_2}\mathrm{CH_2O}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): 207.63 (s, Fe*C*O), 165.77 (s, O*C*O), 137.91 (s, *m*-COPh*C*), 130.92 (s, *o*-COPh*C*), 129.14 (s, *i*-COPh*C*), 101.15 (s, *p*-COPh*C*), 62.82 (s, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2O}$), 55.66 (s, $\mathrm{N}\mathit{C}\mathrm{H_2CH_2O}$), 53.27 (s, $\mathrm{N}\mathit{C}\mathrm{H_2S}$) ppm.

2.3. *Synthesis of 2*

To a solution of **1** (0.080 g, 0.12 mmol) in MeCN (10 mL) was added $Me_3NO \cdot 2H_2O$ (0.014 g, 0.12 mmol). The mixture was stirred at room temperature for 15 min to give a brown-black solution. After dppe (0.024 g, 0.06 mmol) was added, the new mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 2 : 1) as eluent. From the main red band, **2** (0.060 g) was obtained as a dark red solid. Yield: 60%; m.p. 164°C (dec). IR (KBr disc): $\nu_{C\equiv O}$ 2040 (vs), 1982 (vs), 1959 (w), 1938 (s) cm^{-1}; $\nu_{C=O}$ 1726 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): 7.81 (d 4H, $J = 8.5$ Hz, 4*m*-COPh*H*), 7.60 (d, $J = 8.0$ Hz, 4H 4*o*-COPh*H*), 7.70–7.38 (m, 20 H, $4C_6\mathit{H}_5$), 6.48 (t, 2H, $J = 21.0$ Hz, 2PC*H*), 3.83 (s, 4H, $\mathrm{2NCH_2}\mathit{CH_2}\mathrm{O}$), 2.81 (d, 4H, $J_{\mathrm{HeHa}} = 10.5$ Hz, $\mathrm{4NCH_a}\mathit{H_e}\mathrm{S}$), 2.50 (s, 4H, $\mathrm{4NC}\mathit{H_a}\mathrm{H_eS}$), 2.04 (s, 4H, $\mathrm{2NC}\mathit{H_2}\mathrm{CH_2O}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, TMS): 213.75 (t, $J = 5.1$ Hz, PFe*C*O), 209.14 (s, Fe*C*O), 165.48 (s, O*C*O), 141.29 (d, $J = 25.9$ Hz, P*C*H), 137.94 (s, *m*-COPh*C*), 134.59 (d, $J = 41.0$ Hz, *i*-PPh*C*), 133.13 (t, $J = 5.1$ Hz, *o*-PPh*C*), 130.86 (s, *o*-COPh*C*), 130.61 (s, *p*-PPh*C*), 129.06 (s, *i*-COPh*C*), 128.86 (t, $J = 4.3$ Hz, *m*-PPh*C*), 101.22 (s, *p*-COPh*C*), 61.48 (s, $\mathrm{NCH_2}\mathit{C}\mathrm{H_2O}$), 56.90 (s, $\mathrm{N}\mathit{C}\mathrm{H_2CH_2O}$), 51.55 (s, $\mathrm{N}\mathit{C}\mathrm{H_2S}$) ppm. ^{31}P NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 59.51 (s) ppm.

2.4. *X-ray structure determination*

Single crystals of $\mathbf{1} \cdot 0.25CH_2Cl_2$ and $\mathbf{2} \cdot 2CH_2Cl_2$ suitable for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2/hexane solution of **1** and **2** at −10°C. A single crystal of $\mathbf{1} \cdot 0.25CH_2Cl_2$ or $\mathbf{2} \cdot 2CH_2Cl_2$ was mounted on a Rigaku MM-007 CCD diffractometer equipped with a Saturn 70CCD. Data were collected at low temperature (113 K) by using a graphite monochromator with Mo-Kα radiation ($\lambda = 0.71073$ Å) in ω–φ scanning mode. Data collection, reduction, and absorption correction were performed by the CRYSTALCLEAR program [28]. The structures were solved by direct methods using SHELXS-97 [29] and refined by full-matrix least-squares (SHELXL-97) [30] on F^2. Hydrogens were located by using the geometric method. Complete crystal data and parameters for data collection and refinement are listed in table 1.

3. Results and discussion

3.1. *Synthesis and characterization*

The synthetic route to **1** and **2** is illustrated in scheme 2. We carried out the reaction of $[(\mu\text{-}SCH_2)_2NCH_2CH_2OH]Fe_2(CO)_6$ with 1 equiv. *p*-iodobenzoic acid in the presence of

Table 1. Crystal data and structure refinement details for $\mathbf{1} \cdot 0.25CH_2Cl_2$ and $\mathbf{2} \cdot 2CH_2Cl_2$.

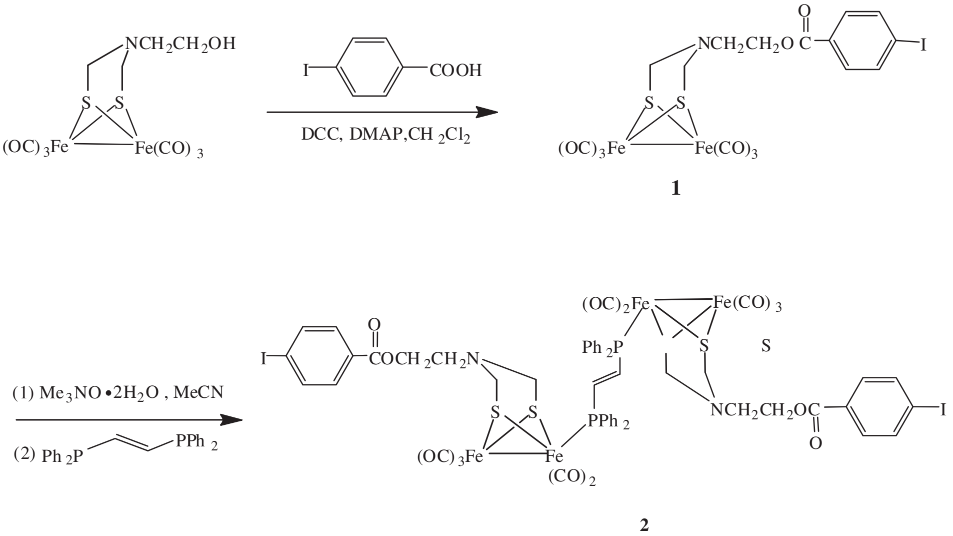
Compound	$\mathbf{1} \cdot 0.25CH_2Cl_2$	$\mathbf{2} \cdot 2CH_2Cl_2$
Empirical formula	$C_{34.50}H_{25}ClFe_4I_2N_2O_{16}S_4$	$C_{60}H_{50}Cl_4Fe_4I_2N_2O_{14}P_2S_4$
Formula weight	1364.46	1832.20
Temperature (K)	113(2)	113(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	7.4600(1)	11.809(6)
b	18.853(4)	12.836(7)
c	34.612(7)	12.884(9)
α	90	89.25(4)
β	95.55(3)	85.75(4)
γ	90	63.47(3)
Volume (Å^3), Z	4845.2(2), 4	1742.0(2), 1
Calculated density (g cm^{-3})	1.870	1.747
Absorption coefficient (mm^{-1})	2.741	2.084
F(000)	2660	908
Crystal size (mm^3)	$0.30 \times 0.24 \times 0.16$	$0.16 \times 0.14 \times 0.06$
θ range for data collection (°)	2.08–25.02	1.59–27.83
Limiting indices	$-8 \leq h \leq 8$; $-22 \leq k \leq 21$; $-41 \leq l \leq 41$	$-15 \leq h \leq 15$; $-16 \leq k \leq 15$; $-15 \leq l \leq 16$
Reflections collected/unique	38,471/8483	18,031/8125
Completeness to θ	99.3	98.2
Max. and min. transmission	0.6682/0.4936	0.8852/0.7316
Data/restraints/parameters	8483/147/641	8125/70/443
Goodness-of-fit on F^2	1.045	1.015
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0503$, $wR_2 = 0.1353$	$R_1 = 0.0377$, $wR_2 = 0.0779$
R indices (all data)	$R_1 = 0.0661$, $wR_2 = 0.1427$	$R_1 = 0.0576$, $wR_2 = 0.0827$
Largest difference peak and hole (e Å^{-3})	1.180 and −0.952	0.981 and −1.128

DMAP and DCC in CH_2Cl_2 from 0°C to room temperature, resulting in **1** in 78% yield. Treatment of **1** with 1 equiv. of decarbonylating agent $Me_3NO \cdot 2H_2O$ in MeCN at room temperature, followed by the addition of 0.5 equiv. of dppe, gave the double butterfly model complex **2**.

Complexes **1** and **2** have been characterized by IR and NMR spectroscopies. The IR spectra of **1** and **2** showed four absorptions in the range 2069–1938 cm^{-1} for their terminal carbonyls and one absorption at 1716 or 1726 cm^{-1} for their ester carbonyls. The $\nu_{C\equiv O}$ values of **2** are much lower than those of **1**, due to the increased back-bonding in **2** caused by the CO substitution of **1** with the stronger electron-donating dppe [31]. The ^{1}H NMR spectrum of **1** displayed a singlet at 3.65 ppm for its identical protons in each of its two NCH_2S groups, whereas **2** exhibited a doublet and a singlet at 2.81 and 2.50 ppm for its different protons in each NCH_2S group. The ^{13}C NMR spectrum of **1** exhibited a singlet at 207.63 ppm for its terminal carbonyls, whereas **2** exhibited a triplet at 213.75 ppm for its PFeCO carbonyls and a singlet at 209.14 ppm for its FeCO carbonyls. The ^{31}P NMR spectrum of **2** displayed a singlet at 59.51 ppm.

3.2. *X-ray crystal structure*

The molecular structures of $\mathbf{1} \cdot 0.25CH_2Cl_2$ and $\mathbf{2} \cdot 2CH_2Cl_2$ have been unequivocally confirmed by single-crystal X-ray diffraction analysis. The ORTEP diagrams of



Scheme 2. Preparation of **1** and **2**.

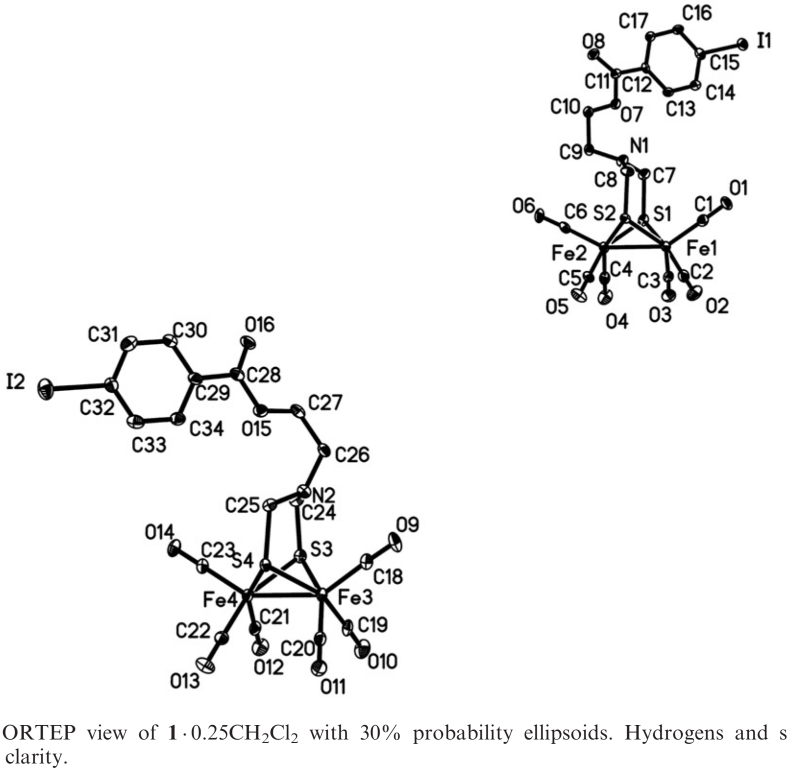


Figure 1. ORTEP view of $\mathbf{1} \cdot 0.25CH_2Cl_2$ with 30% probability ellipsoids. Hydrogens and solvent are omitted for clarity.

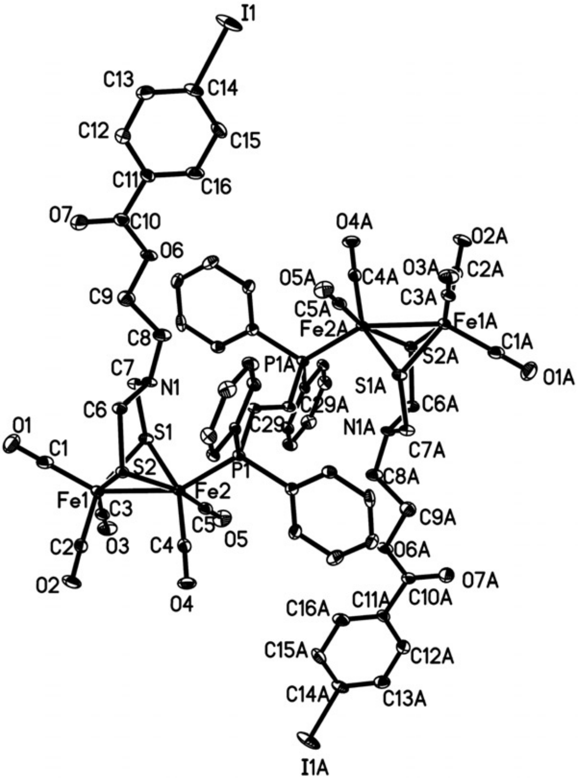


Figure 2. ORTEP view of **2** · $2CH_2Cl_2$ with 30% probability ellipsoids. Hydrogens and solvent are omitted for clarity.

1 · $0.25CH_2Cl_2$ and **2** · $2CH_2Cl_2$ are shown in figures 1 and 2 and selected bond lengths and angles are given in tables 2 and 3, respectively. Complex **1** has two conformational isomers, each containing a substituted ADT bridged between two irons of $Fe(CO)_3$ to form two fused six-membered rings, in one isomer the N-substituted functionality is attached to its bridged nitrogen by an axial bond of its two fused six-membered rings and in the other by an equatorial bond. The six-membered rings Fe1–S1–C7–N1–C8–S2 and Fe4–S3–C24–N2–C25–S4 have chair conformations, but the six-membered rings Fe2–S1–C7–N1–C8–S2 and Fe3–S3–C24–N2–C25–S4 have boat conformations. All irons in **1** have distorted square-pyramidal geometry with each Fe displaced by about 0.40 Å from the pyramidal base toward the apical ligand. The Fe1–Fe2 bond length is 2.5148(1) Å and Fe3–Fe4 bond length is 2.5078(1) Å, in good agreement with Fe–Fe bond lengths found in other all-CO diiron complexes, such as $[(\mu\text{-}SCH_2)_2NCH_2CH_2OC(O)C_4H_3S\text{-}2]Fe_2(CO)_6$ [2.5096(8) Å] [22], $[(\mu\text{-}SCH_2)_2NMe]Fe_2(CO)_6$ [2.4924(7) Å] [32], $[(\mu\text{-}SCH_2)_2CH_2]Fe_2(CO)_6$ [2.5103(1) Å] [33], $[(\mu\text{-}SCH_2)_2CHO_2CCH_2CO_2Et]Fe_2(CO)_6$ [2.5148(6) Å] [34], and $[(\mu\text{-}SCH_2)_2S]Fe_2(CO)_6$ [2.5159(1) Å] [35], but shorter than those in natural enzymes of *Clostridium pasteurianum* and *Desulfovibrio desulfuricans* (2.55–2.62 Å) [5, 6]. All carbons of carbonyls are about 1.80 Å from the Fe in their equatorial and axial positions.

Table 2. Selected bond lengths (Å) and angles (°) for $\mathbf{1} \cdot 0.25CH_2Cl_2$.

I(1)–C(15)	2.098(6)	Fe(3)–Fe(4)	2.5078(1)
Fe(1)–C(1)	1.803(7)	Fe(4)–S(4)	2.2482(2)
Fe(1)–S(1)	2.2531(2)	Fe(4)–S(3)	2.2489(2)
Fe(1)–S(2)	2.2576(2)	S(1)–C(7)	1.871(6)
Fe(1)–Fe(2)	2.5148(1)	N(1)–C(8)	1.406(8)
Fe(2)–S(2)	2.2484(2)	N(1)–C(9)	1.476(7)
Fe(2)–S(1)	2.2650(2)	O(1)–C(1)	1.155(7)
Fe(3)–S(4)	2.2499(2)	O(8)–C(11)	1.211(7)
Fe(3)–S(3)	2.2597(2)	O(16)–C(28)	1.199(7)
S(1)–Fe(1)–S(2)	84.66(7)	S(1)–Fe(2)–Fe(1)	55.95(5)
S(1)–Fe(1)–Fe(2)	56.40(5)	Fe(1)–S(1)–Fe(2)	67.64(6)
S(2)–Fe(1)–Fe(2)	55.90(5)	Fe(2)–S(2)–Fe(1)	67.85(6)
S(2)–Fe(2)–S(1)	84.59(6)	O(8)–C(11)–O(7)	122.3(6)
S(2)–Fe(2)–Fe(1)	56.25(5)	C(7)–N(1)–C(8)	116.2(5)

Table 3. Selected bond lengths (Å) and angles (°) for $\mathbf{2} \cdot 2CH_2Cl_2$.

I(1)–C(14)	2.102(3)	Fe(2)–S(1)	2.2719(1)
Fe(1)–C(1)	1.793(4)	S(1)–C(7)	1.836(3)
Fe(1)–S(2)	2.2620(2)	P(1)–C(29)	1.809(3)
Fe(1)–S(1)	2.2628(1)	O(6)–C(10)	1.328(4)
Fe(1)–Fe(2)	2.5130(2)	O(6)–C(9)	1.449(4)
Fe(2)–C(5)	1.768(3)	O(7)–C(10)	1.216(4)
Fe(2)–C(4)	1.777(3)	N(1)–C(7)	1.443(4)
Fe(2)–P(1)	2.2230(2)	N(1)–C(6)	1.444(3)
Fe(2)–S(2)	2.2614(2)	N(1)–C(8)	1.465(4)
S(2)–Fe(1)–S(1)	84.63(5)	S(2)–Fe(2)–Fe(1)	56.26(5)
S(2)–Fe(1)–Fe(2)	56.24(5)	S(1)–Fe(2)–Fe(1)	56.17(4)
S(1)–Fe(1)–Fe(2)	56.52(4)	Fe(1)–S(1)–Fe(2)	67.31(5)
P(1)–Fe(2)–S(2)	102.65(6)	Fe(2)–S(2)–Fe(1)	67.50(6)
P(1)–Fe(2)–S(1)	105.98(5)	O(7)–C(10)–O(6)	123.8(3)
S(2)–Fe(2)–S(1)	84.43(6)	C(7)–N(1)–C(6)	112.8(3)

The main framework of **2** is composed of a zigzag structure with one [2Fe2S] butterfly unit attached to each end of the dppe bridge. Each [2Fe2S] subunit has a square pyramidal structure. The [2Fe2S] cores in the tetranuclear **2** and the parent **1** are geometrically similar. In **2,** the N-substituted functionalities are attached to bridgehead nitrogens by an equatorial bond and point toward the bulky dppe. The P1–Fe2–Fe1 plane is parallel to that of P1A–Fe2A–Fe1A. The midpoint of the CH=CH double bond of dppe is an inversion center. The phosphine in **2** occupies only the two apical positions, consistent with the behavior of monophosphine [34, 36] and diphosphine [19, 20, 37] ligands. The Fe1–Fe2 bond length of **2** is 2.5130(2) Å and is almost equal to that in **1**, showing that the ligand exchange has no effect on the Fe–Fe bond length.

4. Conclusions

Two [FeFe] hydrogenase model complexes, $[(\mu\text{-}SCH_2)_2NCH_2CH_2OC(O)C_6H_4I\text{-}p]Fe_2(CO)_6$ (**1**) and $\{[(\mu\text{-}SCH_2)_2NCH_2CH_2OC(O)C_6H_4I\text{-}p]Fe_2(CO)_5Ph_2PCH\}_2$ (**2**), have been prepared in high yields. These compounds were fully characterized by IR and NMR spectroscopic techniques and their molecular structures were confirmed by X-ray diffraction analysis.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 798278 and 809331 for **1** $\cdot$ 0.25CH_2Cl_2 and **2** $\cdot$ 2CH_2Cl_2, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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