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# Synthesis, characterization and electrochemistry of phenyl-functionalized diiron propanedithiolate complexes

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ABSTRACT

A dinuclear [2Fe2S] mimic, [$\mu$-$(SCH_2)_2CHC_6H_5$]$Fe_2(CO)_6$ (**1**), of the active site of FeFe-hydrogenases has been synthesized from the reaction of 2-phenyl-1,3-propanedithiol with $Fe_3(CO)_{12}$. Displacement one or two carbonyls of complex **1** with triphenylphosphine ($PPh_3$) or bis(diphenylphosphino)methane (dppm) yielded [$\mu$-$(SCH_2)_2CHC_6H_5$]$Fe_2(CO)_5(PPh_3)$ (**2**), [$\mu$-$(SCH_2)_2CHC_6H_5$]$Fe_2(CO)_5$($\kappa$-dppm) (**3**) and [$\mu$-$(SCH_2)_2CHC_6H_5$]$Fe_2(CO)_4$($\mu$-dppm) (**4**). Complexes **1**–**4** have been fully characterized by elemental analysis, mass spectrometry, IR, $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopic techniques, and unequivocally determined by single crystal X-ray diffraction analysis. The phenyl groups are attached directly to the bridgehead–C atoms of the propanedithiolate bridge via equatorial bonds in chair conformation six-membered rings. The electrochemical behavior of **1**–**4** and the reduction of the proton of $CF_3COOH$ to hydrogen, catalyzed by **1** and **3**, were investigated by cyclic voltammetry.



## 1. Introduction

Clean fuel is becoming an urgent societal problem, due to diminishing fossil fuel resources and the deteriorating environment. Hydrogen is one source for perfect energy in that it is environmentally friendly and renewable [1,2]. Naturally, molecular hydrogen is produced from protons catalyzed by hydrogenases, especially FeFe-hydrogenases, in many microorganisms, reversibly and efficiently [3–5]. These enzymes have been under intense investigations due to the mimic active sites, which contain a butterfly [2Fe2S] structure, linked to a cubic [$Fe_4S_4$] cluster via a sulfur atom of cysteine, and a three-atom linker (–$CH_2XCH_2$–, X = $CH_2$, NH) bridged between the two S atoms (H-cluster) [6–8]. In order to simulate the structure and function of metal-sulfur sites in FeFe-hydrogenases, extensive researches [9] have been devoted to preparing synthetic models by either CO substitution or bridge variation based on the well-known diiron complexes [($\mu$-pdt)$Fe_2(CO)_6$] (pdt = $SCH_2CH_2CH_2S$) [10–12] and [($\mu$-adt)$Fe_2(CO)_6$] (adt = $SCH_2NHCH_2S$) [13]. In the bridge variation [($\mu$-adt)$Fe_2(CO)_6$] models, complexes [($\mu$–$SCH_2)_2NR$]$Fe_2(CO)_6$, where the R groups range from alkyl to aryl or heterocyclic groups, have been prepared [14–16], while in the bridge variation [($\mu$-pdt)$Fe_2(CO)_6$] models, [($\mu$-$SCH_2)_2CHR$]$Fe_2(CO)_6$, only the hydroxyl model (R = OH) [17] or carboxyl model, (R = COOH) [18] and their functional transformation derivatives have been synthesised [19,20]. To the best of our knowledge [21–25], no aryl rings or heterocyclic groups have been linked to the bridgehead C atom in the [($\mu$-pdt)$Fe_2(CO)_6$] model directly, apart from via an ester, ether or amide bond indirectly [19,20,26]. In order to extend this kind of FeFe-hydrogenase model, we herein report the synthesis, spectroscopic and crystallographic characterization of the phenyl functionalized [($\mu$-pdt)$Fe_2(CO)_6$] model, [$\mu$-$(SCH_2)_2CHC_6H_5$]$Fe_2(CO)_6$ (**1**), and its CO substitution derivatives [$\mu$-$(SCH_2)_2CHC_6H_5$]$Fe_2(CO)_5(PPh_3)$ (**2**), [$\mu$-$(SCH_2)_2CHC_6H_5$]$Fe_2(CO)_5$($\kappa$-dppm) (**3**) and [$\mu$-$(SCH_2)_2CHC_6H_5$]$Fe_2(CO)_4$($\mu$-dppm) (**4**), and investigate their electrochemical properties.

## 2. Experimental

### 2.1. Materials and methods

All reactions and operations were carried out under a dry, oxygen-free argon atmosphere with standard Schlenk and vacuum line techniques. $CH_2Cl_2$ and MeCN were distilled with $CaH_2$, while *n*-hexane and toluene were dried with sodium wire and diphenylmethanone under argon. $PPh_3$, dppm and $Me_3NO{\cdot}2H_2O$ were commercially available and used as received. 2-Phenyl-1,3-propanedithiol and $Fe_3(CO)_{12}$ were prepared according to literature methods [20,27]. Preparative TLC was carried out on glass plates (25 × 20 × 0.25 cm) coated with silica gel G (10–40 μm). IR spectra were recorded on a Bruker TENSOR 27 FTIR spectrometer. $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer. Elemental analyses were performed on an Elementar Vario EL β analyzer. The mass spectra were recorded

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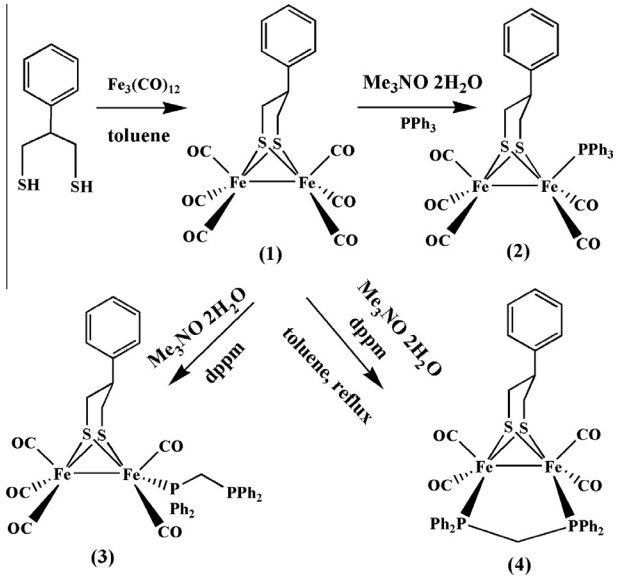


**Scheme 1.** Preparation of complexes **1**–**4**.

with a LC-MSD-Trap-XCT or GCT CA127 Micromass instrument. Melting points were determined on an X-4 apparatus and are uncorrected.

*2.1.1. Electrochemistry*

Electrochemical measurements were carried out using a CHI 620 Electrochemical Workstation (CH Instruments, Chenhua, Shanghai, China). A solution of 0.1 M *n*-$Bu_4NPF_6$ in $CH_3CN$ was used as the electrolyte and it was degassed by bubbling with dry nitrogen for 10 min before measurement. Cyclic voltammograms (CV) were obtained in a three-electrode cell with a glassy carbon electrode (3 mm diameter) as the working electrode, successively polished with 3 and 1 μm diamond pastes and sonicated in ion-free water for 10 min, a platinum wire as the counter electrode, and a non-aqueous $Ag/Ag^+$ electrode (1.0 mM $AgNO_3$ and 0.1 M *n*-$Bu_4NPF_6$ in $CH_3CN$) as the reference electrode. The potential scale was calibrated against the $Fc/Fc^+$ couple and reported versus this reference system.

*2.1.2. X-ray structure determination*

Single crystals of **1**–**4** suitable for X-ray diffraction analysis were grown by slow evaporation of a $CH_2Cl_2$/hexane solution at 5 °C. A suitable crystal was selected and recorded on an Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 291.15 K during data collection. Using Olex2, the structure was solved with the SHELXS structure solution program using direct methods and refined with the SHELXL refinement package using least squares minimisation.

*2.2. Synthesis of [(μ-$SCH_2$)$_2$$CHC_6H_5$]$Fe_2(CO)_6$ (**1**)*

2-Phenyl-1,3-propanedithiol (93 mg, 0.5 mmol) was dissolved in dry toluene (50 mL) and then $Fe_3(CO)_{12}$ (254 mg, 0.5 mmol) was added. The resulting solution was stirred, warmed up to 80 °C for 0.5 h under argon and then concentrated by evaporating the solvent in vacuo. The crude product was subjected to preparative TLC separation using $CH_2Cl_2$/petroleum ether (v/v = 1:10) as the eluent. From the main red band, complex **1** was obtained as a red solid (167 mg, 72%). Mp: 111.4–112.3 °C. IR (KBr disk, $cm^{-1}$): $\nu_{C\equiv O}$ 2071 (vs), 2032 (vs), 2008 (vs), 1977 (vs). $^1H$ NMR (300 MHz, $CDCl_3$, ppm): 1.828 (t, 2H, $^2J_{HaHe} = {}^3J_{HaHa'}$ = 13.2 Hz, 2 SC*Ha*He), 2.351 (m, 1H, CH), 2.688, 2.733 (dd, $^3J_{HeHa'}$ = 3.6 Hz, $^2J_{HeHa}$ = 13.5 Hz, 2 SCHa*He*), 7.015 (d, 2 *o*-PhH), 7.235–7.311 (m, 3H, 2 m-PhH, 1*p*-PhH). $^{13}C$ NMR (400 MHz, $CDCl_3$, ppm): 207.8, 207.5 (s, FeCO), 142.7, 128.9, 127.7, 126.7 (s, PhC), 49.8 (s, CH), 29.1 (s, $SCH_2$). HRMS (EI) (m/z): $M^+$, calcd 461.8618, found 461.8625. *Anal.* Calc. for $C_{15}H_{10}Fe_2O_6S_2$: C, 38.99; H, 2.18. Found: C, 38.83; H, 2.21%.

*2.3. Synthesis of [(μ-$SCH_2$)$_2$$CHC_6H_5$]$Fe_2(CO)_5(PPh_3)$ (**2**)*

The parent complex **1** (92 mg, 0.20 mmol) was dissolved in dry MeCN under argon and then $Me_3NO{\cdot}2H_2O$ (22 mg, 0.20 mmol) was added. After stirring at room temperature for 0.5 h, the resulting brown solution was mixed with $PPh_3$ (52 mg, 0.20 mmol) and stirred for 2 h at the room temperature. The solvent was removed on a rotary evaporator and the residue was subjected to preparative TLC separation using $CH_2Cl_2$/petroleum ether (v/v = 1:8) as the eluent. From the main red band, complex **2** was obtained as a red solid (74 mg, 53%). Mp: 175.3–175.9 °C. IR (KBr disk, $cm^{-1}$): $\nu_{C\equiv O}$ 2046 (vs), 1994 (vs), 1980 (vs), 1958 (vs), 1939 (vs) .$^1H$ NMR (400 MHz, $CDCl_3$, ppm): 1.667–1.697 (m, 3H), 2.192 (m, 2H), 6.351 (s, 2H, PhH), 7.071 (s, 3H, PhH), 7.441 (s, 9H, PhH), 7.701 (s, 6H, PhH). $^{13}C$ NMR (400 MHz, $CDCl_3$, ppm): 213.7, 213.6, 209.3 (s, FeCO), 143.6, 136.2, 135.8, 133.4, 133.3, 130.4, 128.8, 128.7, 128.4, 127.0, 126.4 (s, PhC), 48.2 (s, CH), 29.7, 29.3 (s, $SCH_2$). $^{31}P$ NMR (161.9 MHz, $CDCl_3$, 85% $H_3PO_4$, ppm): 64.46 (s). ESI-MS (m/z): 697 ($[M+H]^+$). *Anal.* Calc. for $C_{32}H_{25}Fe_2O_5PS_2$: C, 55.20; H, 3.62. Found: C, 55.12; H, 3.74%.

*2.4. Synthesis of [(μ-$SCH_2$)$_2$$CHC_6H_5$]$Fe_2(CO)_5$(κ-dppm) (**3**)*

A similar process was performed as for the synthesis of complex **2**, but with dppm instead of $PPh_3$. After the preparative TLC separation using $CH_2Cl_2$/petroleum ether (v/v = 1:6) as the eluent, complex **3** was acquired as a red solid (131 mg, 80%). Mp: 134.3–134.4 °C. IR (KBr disk, $cm^{-1}$): $\nu_{C\equiv O}$ 2042 (vs), 1980 (vs), 1924 (vs). $^1H$ NMR (400 MHz, $CDCl_3$, ppm): 1.794 (t, 2H, $^2J_{HaHe} = {}^3J_{HaHa'}$ = 12.4 Hz, 2 SC*Ha*He), 2.256 (m, 1H, CH), 2.395 (d, $^2J_{HeHa}$ = 12.4 Hz, 2 SCHa*He*), 3.470 (d, 2H, P–$CH_2$–P), 6.759

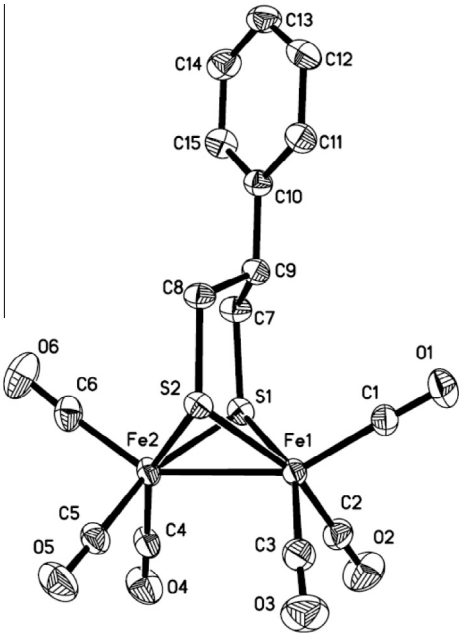


**Fig. 1.** Molecular structure of **1** with thermal ellipsoids at 30% probability.