

Synthesis and Structural Characterization of Diiron Dithiolate Complex $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{PhFe}_2(\text{CO})_5][(\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)_2\text{Fe}]$ Containing Diphosphine Ligand

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A novel diiron dithiolate complex $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{PhFe}_2(\text{CO})_5][(\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)_2\text{Fe}]$ (**1**), as the active site of [FeFe]-hydrogenases, has been prepared and structurally characterized. The title complex was prepared by treatment of $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{Ph}]_2\text{Fe}_2(\text{CO})_6$ (**A**) with 1,1'-bis(diphenylphosphino)-ferrocene (DPPF) $[(\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)_2\text{Fe}]$ in the presence of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in MeCN at room temperature in 53 % yield. The new complex **1** was characterized by IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy.

Keywords: Diiron dithiolate, 1,1'-bis(Diphenylphosphino)-ferrocene, Synthesis, Characterization.

INTRODUCTION

[FeFe]-hydrogenases are natural enzymes that catalyze the production and consumption of dihydrogen¹. X-ray crystallographic studies revealed that the active site of [FeFe]-hydrogenases contains a butterfly $[2\text{Fe}2\text{S}]$ cluster linked to a cubane $[4\text{Fe}4\text{S}]$ cluster *via* the sulfur atom of a cysteinyl group². The bridging dithiolate was supposed to be propane-dithiolate³ or azadithiolate⁴. Inspired by structural information, a large number of diiron dithiolate complexes⁵ related to the active site of [FeFe]-hydrogenases were prepared and characterized by various techniques⁶. In this paper, we report the synthesis and structural characterization of N-functionalized diiron azadithiolate complex related to the active site of [FeFe]-hydrogenases.

EXPERIMENTAL

Reaction and operation was carried out under a dry, oxygen free nitrogen atmosphere with standard Schlenk and vacuum line techniques. Acetonitrile was distilled with CaH_2 under N_2 . $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$, 1,1'-bis(diphenylphosphino)-ferrocene and other materials were commercially available and used as received. Complex **A** was prepared according to the literature procedures⁷. IR spectra were recorded on a Nicolet 670 FTIR spectrometer. ^1H (^{31}P , ^{13}C) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

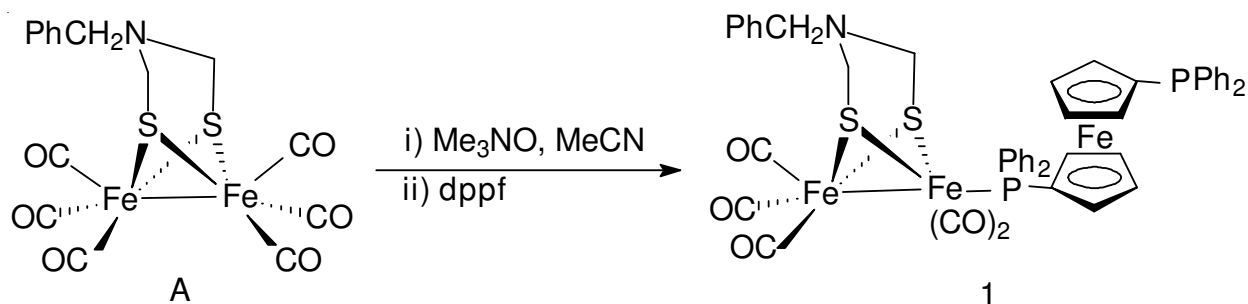
Synthesis: To a solution of $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{Ph}]_2\text{Fe}_2(\text{CO})_6$ (0.100 g, 0.21 mmol) in CH_3CN (10 mL) was added a solution of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.034 g, 0.31 mmol) in CH_3CN (5 mL). The mixture was stirred at room temperature for 15 min and then

was added a solution of 1,1'-bis(diphenylphosphino)-ferrocene (0.120 g, 0.21 mmol) in CH_2Cl_2 (2 mL). The new mixture was stirred for 1 h to give a red solution. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2 /petroleum ether (*v/v* = 1:2) as eluent. Collecting the main red band afforded 0.112 g (53 %) of **1** as a red solid. IR (KBr disk, cm^{-1}): $\nu(\text{C}\equiv\text{O})$ 2041 (vs), 1980 (vs), 1967 (vs), 1922 (vs). ^1H NMR (400 MHz, CDCl_3): 7.61, 7.48, 7.40, 7.33, 6.98 (5s, 25H, $5\text{C}_6\text{H}_5$), 4.74, 4.38, 4.31, 4.11 (s, 8H, $2\text{C}_5\text{H}_4$), 3.26 (s, 2H, NCH_2Ph), 2.83 (s, 2H, 2H_e), 2.20 (s, 2H, 2H_a) ppm. ^{31}P NMR (162 MHz, CDCl_3 , 85 % H_3PO_4): 55.70 (s), 40.81 (s) ppm. ^{13}C NMR (125 MHz, CDCl_3): 214.43, 214.35, 209.67 ($\text{C}\equiv\text{O}$), 138.47, 138.14, 135.84, 134.53, 133.84, 133.04, 132.95, 131.54, 131.46, 131.31, 129.78, 129.01, 128.40, 128.32, 128.22, 127.97, 127.89, 127.54 (PhC), 80.56, 80.22, 75.47, 75.38, 74.68, 74.60, 74.44, 74.38, 73.65, 73.55 (CpC), 63.20 (NCH_2Ph), 49.95 (NCH_2S) ppm.

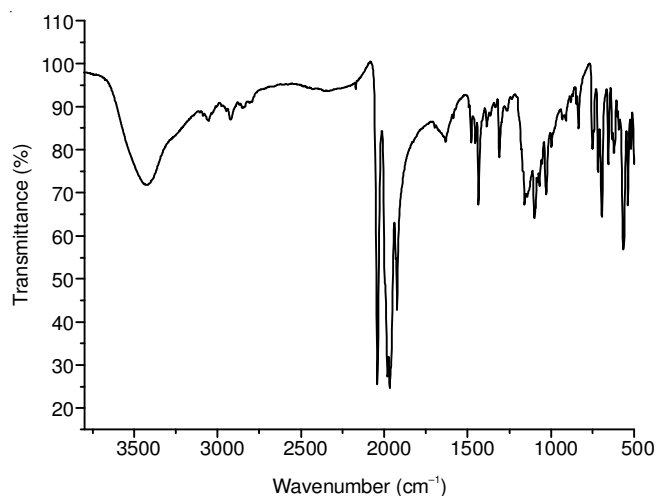
RESULTS AND DISCUSSION

As shown in **Scheme-I**, reaction of the starting material $[(\mu\text{-SCH}_2)_2\text{NCH}_2\text{Ph}]_2\text{Fe}_2(\text{CO})_6$ (**A**) with **1** equivalent of the decarbonylating agent $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ followed by addition of **1** equivalent of 1,1'-bis(diphenylphosphino)-ferrocene afforded the title complex **1** in 53 % yield. The title complex was air-stable red solids, which has been characterized by IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy.

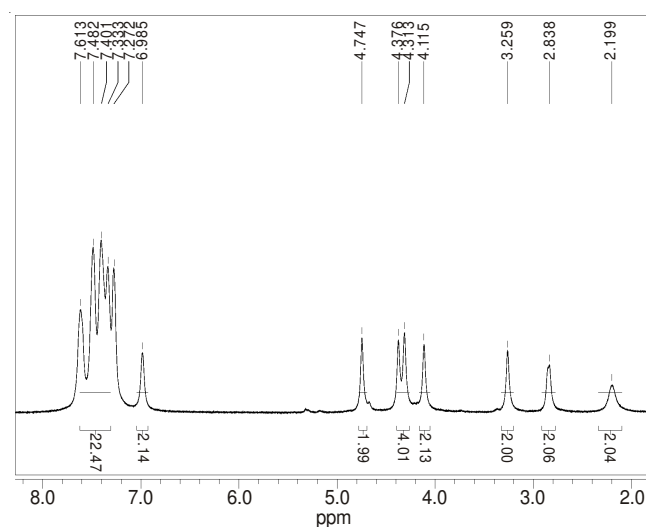
Infrared spectrum: As shown in Fig. 1, the IR spectrum of **1** displayed four strong absorption bands in the range of 2041-1922 cm^{-1} for the terminal carbonyls and the $\nu(\text{C}\equiv\text{O})$ values of complex **1** are shifted toward lower frequencies

Scheme-I: Synthesis of the title complex **1**

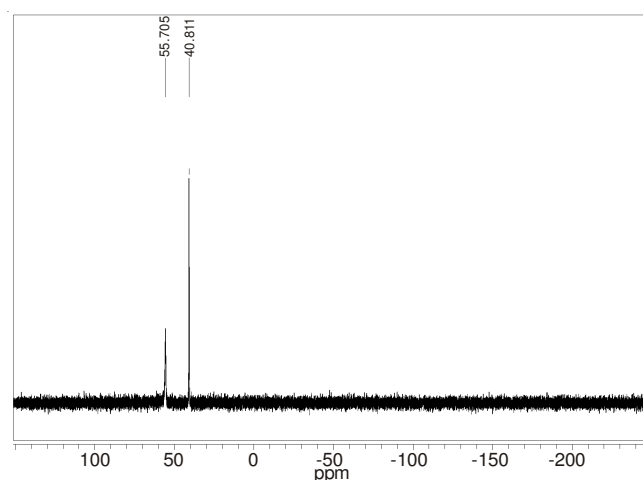
relative to the parent complex **A** (2076, 2038, 2004, 1998, 1983 cm^{-1})⁷ due to the stronger electron donating properties of 1,1'-bis(diphenylphosphino)-ferrocene than carbonyl.

Fig. 1. IR spectrum of the title complex **1**

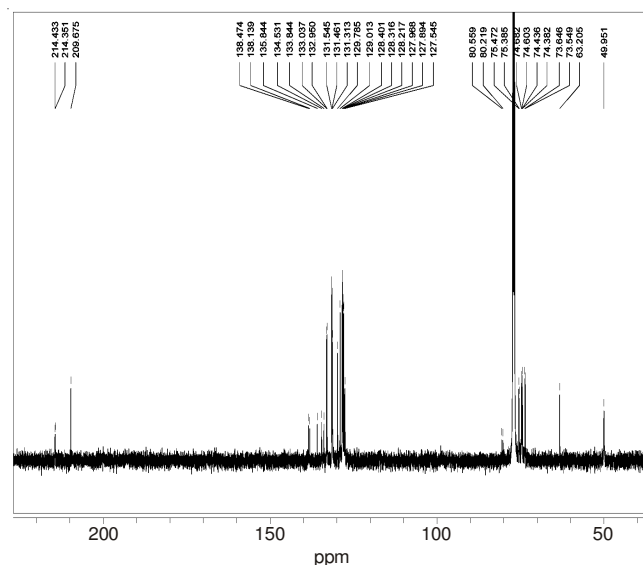
¹H NMR spectrum: As shown in Fig. 2, the ¹H NMR spectrum of **1** showed four singlets at δ 4.74, 4.38, 4.31 and 4.11 ppm for its two cyclopentadienyl ring protons, a singlet at δ 3.26 ppm for the methylene protons of benzyl group and two singlets at δ 2.83 and 2.20 ppm for the equatorial and axial hydrogen atoms in its NCH_2S groups.

Fig. 2. ¹H NMR spectrum of the title complex **1**

³¹P NMR spectrum: As shown in Fig. 3, the ³¹P NMR spectrum of **1** exhibited two singlets at δ 55.70 and 40.81 ppm for the two phosphorus atoms of 1,3-bis(diphenylphosphino propane), only one coordinated to one Fe of the diiron subsite.

Fig. 3. ³¹P NMR spectrum of the title complex **1**

¹³C NMR spectrum: As shown in Fig. 4, the ¹³C NMR spectrum of **1** demonstrated a doublet at δ 214.39 ppm and a singlet at δ 209.67 ppm for the terminal carbonyls and five doublets at δ 80.39, 75.42, 74.64, 74.41 and 73.60 ppm for its cyclopentadienyl ring carbons.

Fig. 4. ¹³C NMR spectrum of the title complex **1**

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