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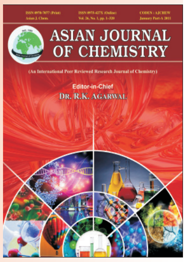

Synthesis and Structural Characterization of Diiron Dithiolate Complex $[(\mu\text{-}SCH_2)_2NCH_2PhFe_2(CO)_5]_2(Ph_2PCH_2CH_2CH_2PPh_2)$ with Bridging Diphosphine Ligand

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A novel diiron dithiolate complex $[(\mu\text{-}SCH_2)_2NCH_2PhFe_2(CO)_5]_2(Ph_2PCH_2CH_2CH_2PPh_2)$ (**1**), as the active site model of [FeFe]-hydrogenases, has been prepared and structurally characterized. The title complex could be prepared by reaction of $[(\mu\text{-}SCH_2)_2NCH_2Ph]Fe_2(CO)_6$ (**A**) with 1,3-*bis*(diphenylphosphinopropane) (DPPP) ($Ph_2PCH_2CH_2CH_2PPh_2$) in the presence of $Me_3NO{\cdot}2H_2O$ in MeCN at room temperature in 54 % yield. The new complex **1** was characterized by IR, ^1H NMR and ^{31}P NMR spectroscopy.

Keywords: Diiron dithiolate, 1,3-*bis*(diphenylphosphino)propane, Synthesis, Characterization.

INTRODUCTION

In recent years, diiron dithiolate complexes have been received considerable attention due to their structure very close to the active site of [FeFe]-hydrogenases[1]. [FeFe]-hydrogenases are natural enzymes that can catalyze the production and uptake of dihydrogen[2]. Many researchers reported a great number of monophosphine or diphosphine substituted diiron dithiolate complexes[3-5] in order to increase the electron density of diiron subsite and can easily to accept proton in catalytic process and their structures were characterized by various techniques[6]. We recently carried out a reaction of the parent complex **A** with 1,3-*bis*(diphenylphosphino)propane in the presence of the decarbonylating agent $Me_3NO{\cdot}2H_2O$. We have successfully prepared a new diiron dithiolate complex with a bridging diphosphine ligand.

EXPERIMENTAL

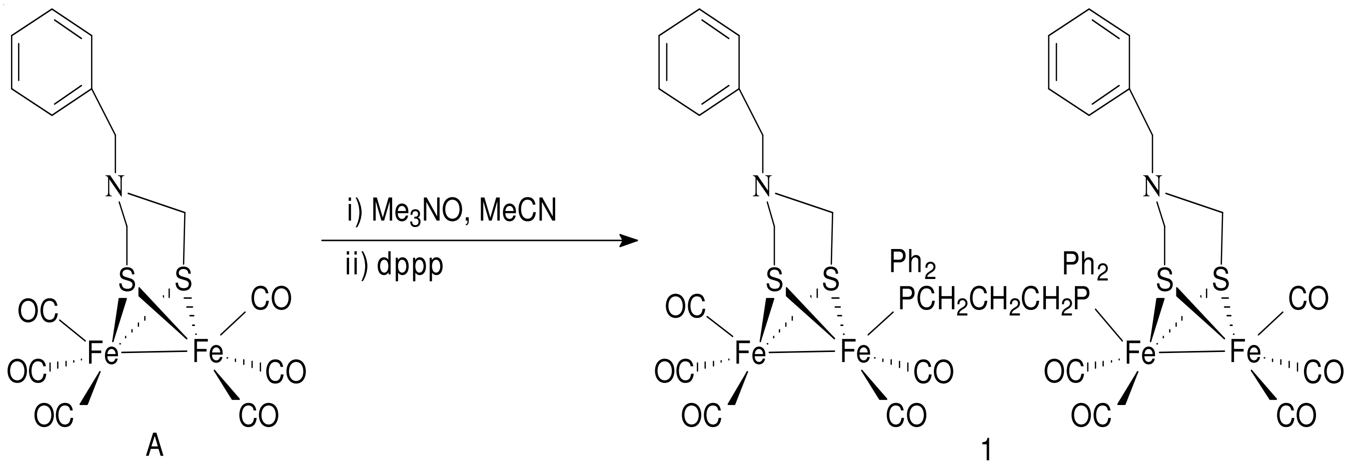
Reaction and operation was carried out under a dry, oxygen free nitrogen atmosphere with standard Schlenk and vacuum line techniques. Acetonitrile was distilled with CaH_2 under N_2. $Me_3NO{\cdot}2H_2O$, 1,3-*bis*(diphenylphosphino)propane and other materials were commercially available and used as received. Complex **A** was prepared according to the literature procedures[7]. IR spectra were recorded on a Nicolet 670 FTIR spectrometer. ^1H (^{31}P) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

Synthesis: To a solution of $[(\mu\text{-}SCH_2)_2NCH_2Ph)]Fe_2(CO)_6$ (0.100 g, 0.21 mmol) in CH_3CN (10 mL) was added a solution of $Me_3NO{\cdot}2H_2O$ (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 1,3-*bis*(diphenylphosphino)propane (0.045 g, 0.11 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 0.075 g (54 %) of **1** as a red solid. IR (KBr disk, cm^{-1}): ν(C=O) 2042 (vs), 1979 (vs), 1923 (vs). ^1H NMR (400 MHz, $CDCl_3$): 7.53-7.03 (m, 30H, $6C_6H_5$), 3.37 (s, 4H, $2PhCH_2N$), 2.94 (d, J_{HeHa} = 11 Hz, 4H, 4NHeHaS), 2.45-2.40 (m, 8H, $2PCH_2$ and 4NHeHaS), 1.62 (br. s, 2H, $PCH_2CH_2CH_2P$) ppm. ^{31}P NMR (200 MHz, $CDCl_3$, 85 % H_3PO_4): 55.55 (s) ppm.

RESULTS AND DISCUSSION

As shown in **Scheme-I**, reaction of the starting material $[(\mu\text{-}SCH_2)_2NCH_2Ph]Fe_2(CO)_6$ (**A**) with **1** equivalent of the decarbonylating agent $Me_3NO{\cdot}2H_2O$ followed by addition of 0.5 equivalent of 1,3-*bis*(diphenylphosphino)propane afforded the title complex **1** in 54 % yield. The title complex was air-stable red solids, which has been characterized by IR, ^1H NMR and ^{31}P NMR spectroscopy.

Infrared spectrum: As shown in Fig. 1, the IR spectrum of **1** displayed three strong absorption bands in the range of 2042-1923 cm^{-1} for the terminal carbonyls. The ν(C=O) values of complex **1** are shifted toward lower frequencies relative to the parent complex **A** (2076, 2038, 2004, 1998, 1983 cm^{-1})[7] because the diphosphine ligand 1,3-*bis*(diphenylphosphino)-propane is stronger electron donor than carbonyl.



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

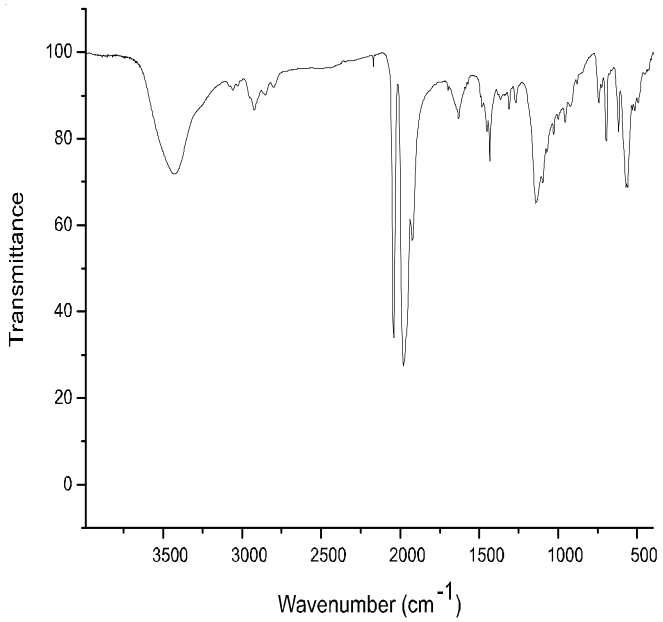


Fig. 1. IR spectrum of the title complex **1**

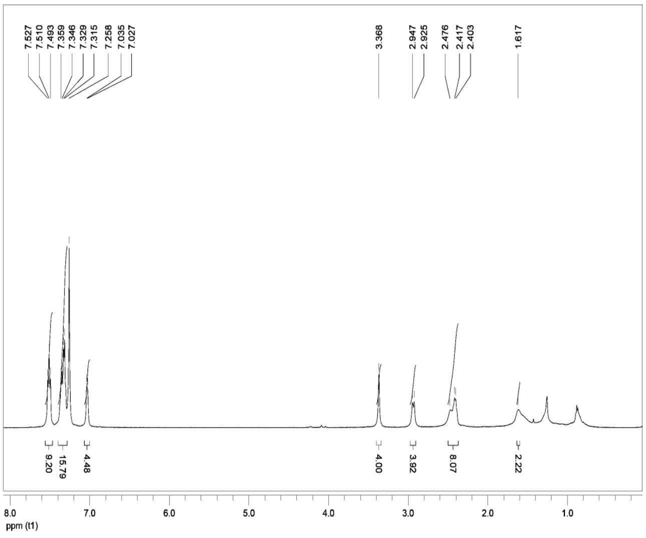


Fig. 2. ^{1}H NMR spectrum of the title complex **1**

^{1}H NMR spectrum: As shown in Fig. 2, the ^{1}H NMR spectrum of **1** showed a singlet at δ 3.37 ppm for the methylene protons of benzyl group and a doublet with a coupling constant of J_{HeHa} = 11.0 Hz for the equatorial hydrogen atoms in its NCH$_2$S groups and a multiplet at δ 2.45-2.40 ppm for the axial hydrogen atoms in its NCH$_2$S groups and two methylene protons of 1,3-*bis*(diphenylphosphino)propane.

^{31}P NMR spectrum: As shown in Fig. 3, the ^{31}P NMR spectrum of **1** exhibited a singlet at d 55.55 ppm for the two phosphorus atoms of 1,3-*bis*(diphenylphosphino)propane, each one coordinated to one Fe of the diiron subsite.

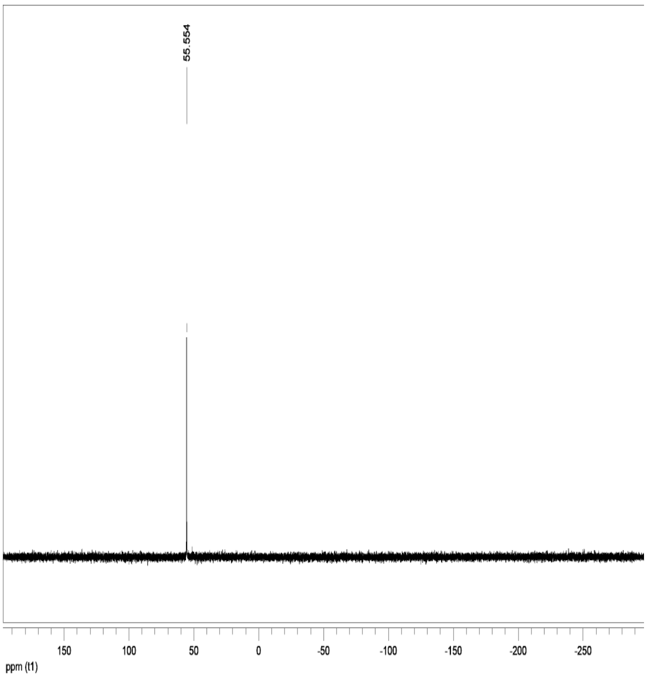


Fig. 3. ^{31}P NMR spectrum of the title complex **1**

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