Synthesis and Structural Characterization of Diiron Dithiolate Complex [(μ -SCH₂)₂NCH₂PhFe₂(CO)₅]₂(Ph₂PCH₂CH₂CH₂PPh₂) with Bridging Diphosphine Ligand

WEI GAO, LIAN-QI TIAN and JING YANG*

School of Pharmacy, Henan University of Traditional Chinese Medicine, Zhengzhou 450046, P.R. China

*Corresponding author: Email: weigao415@aliyun.com

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A novel diiron dithiolate complex [(μ -SCH₂)₂NCH₂PhFe₂(CO)₅]₂(Ph₂PCH₂CH₂CH₂PPh₂) (**1**), as the active site model of [FeFe]-hydrogenases, has been prepared and structurally characterized. The title complex could be prepared by reaction of [(μ -SCH₂)₂NCH₂Ph]Fe₂(CO)₆ (**A**) with 1,3-bis(diphenylphosphino)propane (DPPP) (Ph₂PCH₂CH₂CH₂PPh₂) in the presence of Me₃NO·2H₂O in MeCN at room temperature in 54 % yield. The new complex **1** was characterized by IR, ¹H NMR and ³¹P 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]-hydrogenases¹. [FeFe]-hydrogenases are natural enzymes that can catalyze the production and uptake of dihydrogen². Many researchers reported a great number of monophosphine or diphosphine substituted diiron dithiolate complexes³⁻⁵ 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 techniques⁶. We recently carried out a reaction of the parent complex **A** with 1,3-bis(diphenylphosphino)propane in the presence of the decarbonylating agent Me₃NO·2H₂O. 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 CaH₂ under N₂. Me₃NO·2H₂O, 1,3-bis(diphenylphosphino)propane 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 (³¹P) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

Synthesis: To a solution of [(μ -SCH₂)₂NCH₂Ph]Fe₂(CO)₆ (0.100 g, 0.21 mmol) in CH₃CN (10 mL) was added a solution of Me₃NO·2H₂O (0.034 g, 0.31 mmol) in CH₃CN (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 CH₂Cl₂ (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 CH₂Cl₂/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, CDCl₃): 7.53-7.03 (m, 30H, 6C₆H₅), 3.37 (s, 4H, 2PhCH₂N), 2.94 (d, *J*_{HeHa} = 11 Hz, 4H, 4NHeHaS), 2.45-2.40 (m, 8H, 2PCH₂ and 4NHeHaS), 1.62 (br. s, 2H, PCH₂CH₂CH₂P) ppm. ³¹P NMR (200 MHz, CDCl₃, 85 % H₃PO₄): 55.55 (s) ppm.

RESULTS AND DISCUSSION

As shown in **Scheme-I**, reaction of the starting material [(μ -SCH₂)₂NCH₂Ph]Fe₂(CO)₆ (**A**) with **1** equivalent of the decarbonylating agent Me₃NO·2H₂O 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 ³¹P 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. ^1H NMR spectrum of the title complex **1**

^1H NMR spectrum: As shown in Fig. 2, the ^1H 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 $J_{\text{HeHa}} = 11.0$ Hz for the equatorial hydrogen atoms in its NCH_2S groups and a multiplet at δ 2.45–2.40 ppm for the axial hydrogen atoms in its NCH_2S 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 δ 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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