NOTE

Synthesis and Structural Characterization of Diiron Ethanedithiolate Complex $[(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_5]_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)$ Containing Bridging Diphosphine Ligand

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A diiron ethanedithiolate complex $[(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_5]_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)$ (**1**) has been prepared and characterized by spectroscopy. The title complex was synthesized by reaction of $[(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_6]$ (**A**) with dppb ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$) in the presence of the decarbonylating agent $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in MeCN at room temperature in 66 % yield. The new complex was characterized by IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy.

Keywords: Diiron ethanedithiolate, Dppb, Synthesis, Characterization.

[Fe-Fe]-hydrogenases are metalloenzymes that catalyze hydrogen metabolism in several microorganisms¹. X-ray crystallographic² and IR³ studies have revealed that the active site of [Fe-Fe]-hydrogenases consists of a butterfly $[2\text{Fe-2S}]$ cluster linked to a cubic $[4\text{Fe-4S}]$ cluster *via* the sulfur atom of a cysteinyl group. The bridging dithiolate could most likely be propane-dithiolate (PDT)⁴. Recently, many PDT model complexes⁵ for the active site of [Fe-Fe]-hydrogenases have been reported and characterized by various techniques⁶. In this paper, we report the synthesis and structural characterization of diiron ethanedithiolate complex containing a bridging diphosphine ligand dppb related to the active site of [Fe-Fe]-hydrogenases.

Reaction and operation was carried out under a dry, oxygen free nitrogen atmosphere with standard Schlenk and vacuumline techniques. MeCN was distilled with CaH_2 under N_2 . $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$, dppb and other materials were commercially available and used as received. Complex **A**⁷ was prepared according to the literature procedures. 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 $(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_6$ (0.186 g, 0.5 mmol) in CH_3CN (20 mL) was added a solution of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.056 g, 0.5 mmol) in CH_3CN (10 mL). The mixture was stirred at room temperature for 15 min and then was added dppb (0.107 g, 0.25 mmol). 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 $\text{CH}_2\text{Cl}_2/\text{petroleum ether}$ ($v/v = 1:2$) as eluent. Collecting the

main red band afforded 0.183 g (66 %) of **1** as a red solid. IR ($\text{KBr } \nu_{\text{max}}, \text{cm}^{-1}$): $\text{C}\equiv\text{O}$ 2043 (vs), 1975 (vs), 1923 (vs) ^1H NMR (500 MHz, CDCl_3): δ 7.54, 7.40 (2s, 10 H, $2\text{C}_6\text{H}_5$), 3.41 (s, 2H, PCH_2), 2.39 (s, 2H, PCH_2CH_2), 1.88 (s, 4H, 2SCH_2) ppm. ^{31}P NMR (200 MHz, CDCl_3 , 85 % H_3PO_4): δ 53.74 (s) ppm. ^{13}C NMR (125 MHz): δ 215.55, 215.47, 210.16 ($\text{C}\equiv\text{O}$), 136.43, 136.14, 132.07, 131.99, 130.26, 128.71, 128.64 (PhC), 34.92 (SCH_2), 33.68 (d, $J_{\text{P-C}} = 26.0$ Hz, PCH_2), 25.64 (d, $J_{\text{P-C}} = 14.1$ Hz, PCH_2CH_2) ppm.

As shown in **Scheme-I**, the title complex could be prepared by reaction of complex **A** with 0.5 equivalent of dppb in the presence of the decarbonylating agent $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in MeCN at room temperature in 66 % yield. The title complex **1** 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** showed three absorption bands in the range of 2043-1923 cm^{-1} for the terminal carbonyls and the $\nu(\text{C}\equiv\text{O})$ values are shifted toward lower frequencies relative to the parent complex **A** (2079, 2039, 2009, 1996 cm^{-1})⁷.

^1H NMR spectrum: As shown in Fig. 2, the ^1H NMR spectrum of **1** displayed two singlets at δ 7.54 and 7.40 ppm for its phenyl protons and two singlets at δ 3.41 and 2.39 ppm for the methylene protons of dppb.

^{31}P NMR spectrum: As shown in Fig. 3, the ^{31}P NMR spectrum of **1** exhibited a singlet at δ 53.74 ppm for the two phosphorus atoms of dppb, each one coordinated to one Fe of the diiron subsite.

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 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 215.51 ppm and a singlet at δ 210.16 ppm for the terminal carbonyls and two doublets at δ 33.68 and 25.64 ppm with coupling constants of $J_{P-C} = 26, 14.1$ Hz for the methylene carbons of dppb.

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

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