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NOTE

Synthesis and Structural Characterization of Diiron Ethanedithiolate Complex $[(\mu\text{-}SCH_2)_2Fe_2(CO)_4](PPh_3)_2$ Related to the Active Site of [Fe-Fe]-Hydrogenases

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A diiron ethanedithiolate complex $[(\mu\text{-}SCH_2)_2Fe_2(CO)_4](PPh_3)_2$ (**1**), as the active site of [Fe-Fe]-hydrogenases, has been prepared and characterized. The title complex was prepared by reaction of $[(\mu\text{-}SCH_2)_2]Fe_2(CO)_6$ (**A**) with PPh_3 at reflux in xylene in 50 % yield. The new complex was characterized by IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy.

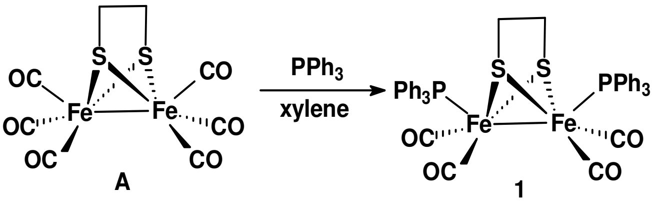
Keywords: Diiron ethanedithiolate, Triphenylphosphine, Synthesis, Characterization.

In recent years, butterfly [2Fe-2S] have received special attention due to their unique structure and close relationship with the natural enzymes of [Fe-Fe]-hydrogenases[1]. Protein crystallographic studies revealed that the active site of [Fe-Fe]-hydrogenases consists of a butterfly [2Fe-2S] cluster linked to a cubane-like [4Fe-4S] cluster *via* the sulfur atom of a cysteinyl group[2]. Based on structural information, a good number of diiron dithiolate complexes[3-5] were prepared and structurally characterized by various techniques[6] in order to mimic the natural properties of [Fe-Fe]-hydrogenases. In this paper, we report the synthesis and structural characterization of diiron ethanedithiolate complex 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 vacuum line techniques. Acetonitrile was distilled with CaH_2 under N_2.$Me_3NO{\cdot}2H_2O$, PPh_3 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, ^{13}C) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

Synthesis: A mixture of $(\mu\text{-}SCH_2)_2Fe_2(CO)_6$ (0.186 g, 0.5 mmol), PPh_3 (0.262 g, 1 mmol) and xylene (20 mL) was refluxed for 4 h to give a brown-red solution. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:1) as eluent. Collecting the main red band afforded 0.201 g (48 %) of **1** as a red solid. Anal. Calcd. for $C_{42}H_{34}O_4P_2S_2Fe_2$: C, 60.02; H, 4.08. Found: C, 60.31; H, 4.24. IR (KBr, ν_{max}, cm^{-1}): C≡O 1994 (vs), 1932 (vs). ^1H NMR (500 MHz, $CDCl_3$): 7.58, 7.39 (2s, 30 H, Ar-H), 1.57, 1.28 (2s, 4H, $2SCH_2$) ppm. ^{31}P NMR (200 MHz, $CDCl_3$, 85 % H_3PO_4): 60.03 (s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 216.78, 216.74 (C≡O), 136.93, 136.64, 133.21, 133.16, 133.12, 129.59, 128.34, 128.31 (Ar-C), 32.83 (CH_2) ppm.

As shown in **Scheme-I**, treatment of complex **A** with 2 equivalent of PPh_3 at reflux in xylene afforded the title complex **1** in 50 % 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.



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

Infrared spectrum: As shown in Fig. 1, the IR spectrum of **1** displayed two strong absorption bands at 1993 and 1933 cm^{-1} for the terminal carbonyls and the ν(C≡O) values of complex **1** are shifted toward lower frequencies relative to the parent complex **A** (2079, 2039, 2009, 1996 cm^{-1})[7] because PPh_3 is stronger electron donating than CO.

^1H NMR spectrum: As shown in Fig. 2, the ^1H NMR spectrum of **1** showed two singlets at δ 7.58 and 7.39 ppm for its phenyl protons and two singlets at δ 1.57 and 1.28 ppm for the methylene protons.

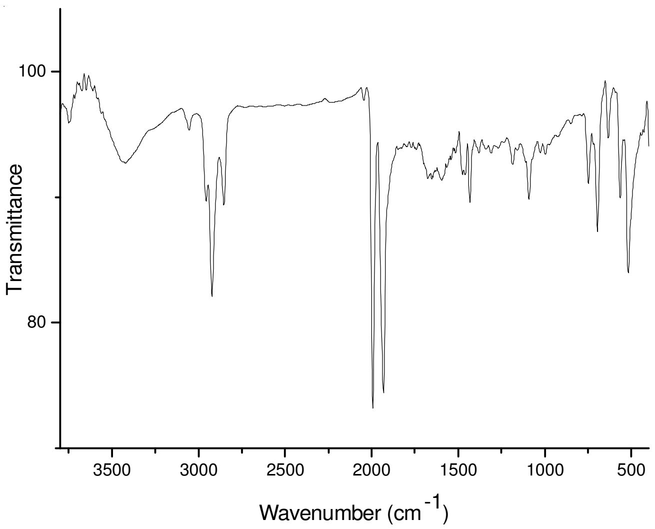


Fig. 1. IR spectrum of the title complex **1**

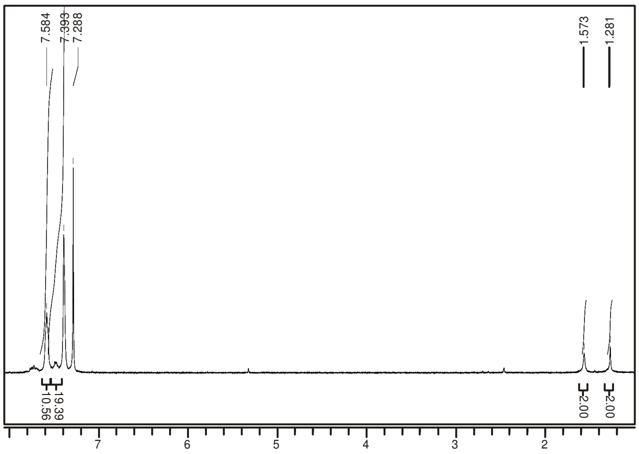


Fig. 2. ^{1}H NMR spectrum of the title complex 1

^{31}P NMR spectrum: As shown in Fig. 3, the ^{31}P NMR spectrum of **1** exhibited a singlet at δ 60.03 ppm for the phosphorus atom of PPh_3 coordinated to one Fe of the diiron subsite.

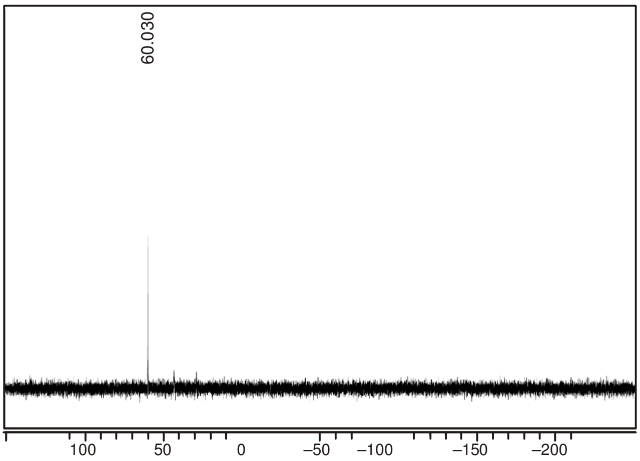


Fig. 3. ^{31}P NMR spectrum of the title complex **1**

^{13}C NMR spectrum. As shown in Fig. 4, the ^{13}C NMR spectrum of **1** demonstrated a doublet at δ 216.76 ppm for the terminal carbonyls and a singlet at δ 32.83 ppm for the methylene carbons.

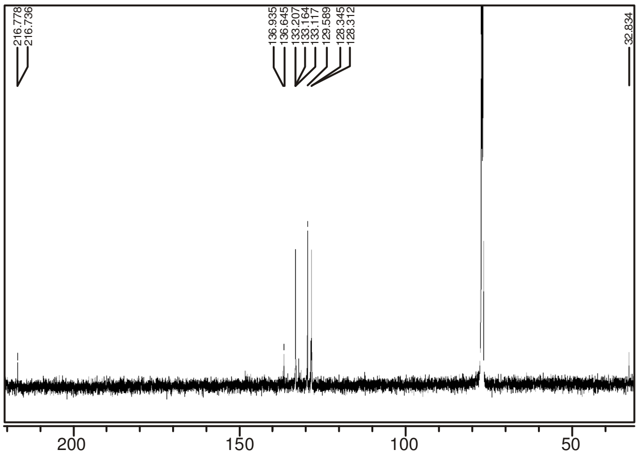


Fig. 4. ^{13}C NMR spectrum of the title complex **1**

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