



NOTE

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

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A diiron ethanedithiolate complex $(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_4[(\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)_2\text{Fe}]$ (**1**), as the active site of [FeFe]-hydrogenases, has been prepared and characterized by spectroscopy. The title complex could be prepared by reaction of $(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_6$ (**A**) with 1,1'-bis(diphenylphosphino)ferrocene (dppf) $[(\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)_2\text{Fe}]$ at reflux in xylene in 26 % yield. The new complex was characterized by IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy.

Keywords: Diiron ethanedithiolate, 1,1'-bis(Diphenylphosphino)ferrocene.

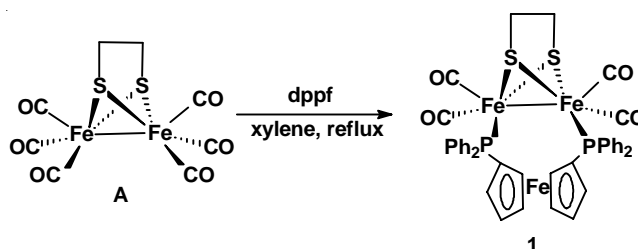
Since the discovery of the active site of [FeFe]-hydrogenases, the butterfly diiron dithiolate clusters have received special attention¹⁻³. In recent years, many researchers have reported a large number of diiron dithiolate complexes⁴⁻⁶. In order to extend the study on diiron dithiolate complexes related to the active site of [FeFe]-hydrogenases, we carried out the reaction of complex **A** with a bidentate phosphine ligand dppf at reflux in xylene. In this paper, we report the synthesis and structural characterization of diiron ethanedithiolate complex containing a bridging diphosphine ligand 1,1'-bis(diphenylphosphino)ferrocene (dppf) relevant to the active site of [FeFe]-hydrogenases.

Reaction and operation was carried out under a dry, oxygen free nitrogen atmosphere with standard Schlenk and vacuumline techniques. Acetonitrile was distilled with CaH_2 under nitrogen atmosphere. $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$, dppf 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: A mixture of $(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_6$ (0.186 g, 0.5 mmol), dppf (0.278 g, 0.5 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 0.113 g (26 %) of **1** as a red solid. IR (KBr disk, cm^{-1}): $\nu(\text{C}\equiv\text{O})$ 2044 (ν_s), 1982 (ν_s),

1958 (ν_s), 1934 (ν_s). ^1H NMR (500 MHz, CDCl_3): 7.35 (s, 20 H, $4\text{C}_6\text{H}_5$), 4.41, 4.21, (2s, 8H, $2\text{C}_5\text{H}_4$), 1.81 (s, 4H, 2SCH_2) ppm. ^{31}P NMR (200 MHz, CDCl_3 , 85 % H_3PO_4): 52.56 (s) ppm. ^{13}C NMR (125 MHz, CDCl_3): 215.70, 215.63, 209.97, 209.85 ($\text{C}\equiv\text{O}$), 138.77, 138.44, 132.47, 132.38, 129.93, 128.10, 129.03 (PhC), 80.10, 79.76, 74.74, 74.65, 74.07, 74.02 (CpC), 34.83, 29.68 (CH_2) ppm.

As shown in **Scheme-I**, treatment of complex **A** with 1 equivalent of dppf at reflux in xylene afforded the title complex in 26 % 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-I: Synthesis of the title complex **1**

Infrared spectrum: The IR spectrum of **1** showed four absorption bands in the range of 2044-1934 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: The ¹H NMR spectrum of **1** displayed two singlets at δ 4.41 and 4.21 ppm for its Cp ring protons and a singlet at δ 1.81 ppm for methylene protons.

³¹P NMR spectrum: The ³¹P NMR spectrum of **1** exhibited a singlet at δ 52.56 ppm for the two phosphorus atoms of dppf, each one coordinated to one Fe of the diiron subsite.

¹³C NMR spectrum: The ¹³C NMR spectrum of **1** demonstrated two doublets at δ 215.66 and 209.91 ppm for the terminal carbonyls, three doublets at δ 79.93, 74.69 and 74.04 ppm for its Cp ring carbons and two singlets at δ 34.83 and 29.68 ppm for methylene carbons.

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