

Synthesis, characterization and electrochemistry of phosphine substituted derivatives with quinolyl-functionalized diiron



Na Wen^{a,*}, Jing Cao^a, Shao-Wu Du^b

^a College of Materials Science and Engineering, Fuzhou University, Fuzhou, Fujian 350116, PR China

^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

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ABSTRACT

Substitution reactions of the quinolyl-functionalized hydrogenase model complexes $[(\mu\text{-SCH}_2\text{C}_9\text{H}_6\text{N})_2\text{Fe}_2(\text{CO})_6]$ (**1**) or $[(\mu\text{-SCH}_2\text{C}_9\text{H}_6\text{N})(\mu\text{-SCH}_2\text{C}_9\text{H}_6\text{N-}\eta)\text{Fe}_2(\text{CO})_5]$ (**2**) by triphenylphosphine (PPh_3), bis (diphenylphosphino) methane (dppm) and trimethylphosphine (PMe_3) have been investigated. These reactions produced either the mono-substituted complexes $[(\mu\text{-SCH}_2\text{C}_9\text{H}_6\text{N})_2\text{Fe}_2(\text{CO})_5(\text{PPh}_3)]$ (**3**), $[(\mu\text{-SCH}_2\text{C}_9\text{H}_6\text{N})_2\text{Fe}_2(\text{CO})_5(\text{dppm})]$ (**4**), or the disubstituted one $[(\mu\text{-SCH}_2\text{C}_9\text{H}_6\text{N})_2\text{Fe}_2(\text{CO})_4(\text{PMe}_3)_2]$ (**5**). The three new phosphine substituted derivatives have been fully characterized by elemental analysis, mass spectrometry, IR, ^1H and ^{31}P NMR spectroscopic techniques. The molecular structures of **3–4** were further confirmed by single crystal X-ray diffraction analysis. The electrochemical behavior of **1–5** were investigated by cyclic voltammetry. The protonation study of complex **5** with $\text{HBF}_4\cdot\text{OEt}_2$ was also investigated by IR and low temperature NMR.

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1. Introduction

In nature, three types of hydrogenase (H_2ase) enzymes: [Fe], [FeFe] and [NiFe] catalyze the formation and oxidation of hydrogen [1–12]. Especially [FeFe]-hydrogenases, which is the most important hydrogenases can reversibly catalyze the reduction of proton to hydrogen with a high efficiency, in many microorganisms, reversibly and efficiently [13,14,5]. Until now, much work has focused on the synthesis, characterization and functional biomimics for the activity of [FeFe]-hydrogenases [15–23]. However, to better understand the chemical properties of the Fe-only model complexes active site for enzymatic H_2 production, various good donor ligands especially phosphine ligands, have been widely used in many all-CO parent complexes of the [FeFe]-hydrogenase by substituting the CO ligands in order to study the structure, electrochemistry and protonation properties of the substituted derivatives [24–27]. While extensive research has been devoted to studies concerning synthetic models of [FeFe]-hydrogenase by either CO substitution or thiolate bridge variation based on the well-known diiron model complexes $[(\mu\text{-SR})_2\text{Fe}_2(\text{CO})_6]$ [28–30], until now, there have been only a few studies focusing on the CO or quinoline-pendant arms ligated or proximal to a diiron site, which substitution by phosphine ligands at the diiron core that

can mimic the labile coordination site at Fe^{d} center in [FeFe]-hydrogenase enzyme. Herein, we would like to describe the synthesis and structural characterization of three new diiron phosphine-substituted complexes with pendant heterocyclic arms. In the presence of phosphine ligands, the parent complexes **1** and **2** are readily converted to their corresponding phosphine-substituted derivatives of **3**, **4** and **5**, formulated as $[(\mu\text{-SCH}_2\text{C}_9\text{H}_6\text{N})_2\text{Fe}_2(\text{CO})_5(\text{L})]$ (**3**, $\text{L} = \text{PPh}_3$; **4**, $\text{L} = \text{dppm}$), $[(\mu\text{-SCH}_2\text{C}_9\text{H}_6\text{N})_2\text{Fe}_2(\text{CO})_4(\text{PMe}_3)_2]$ (**5**) were synthesized and structurally characterized, especially electrochemistry, have been investigated. The protonation study of complex **5** with $\text{HBF}_4\cdot\text{OEt}_2$ investigated by IR was also discussed.

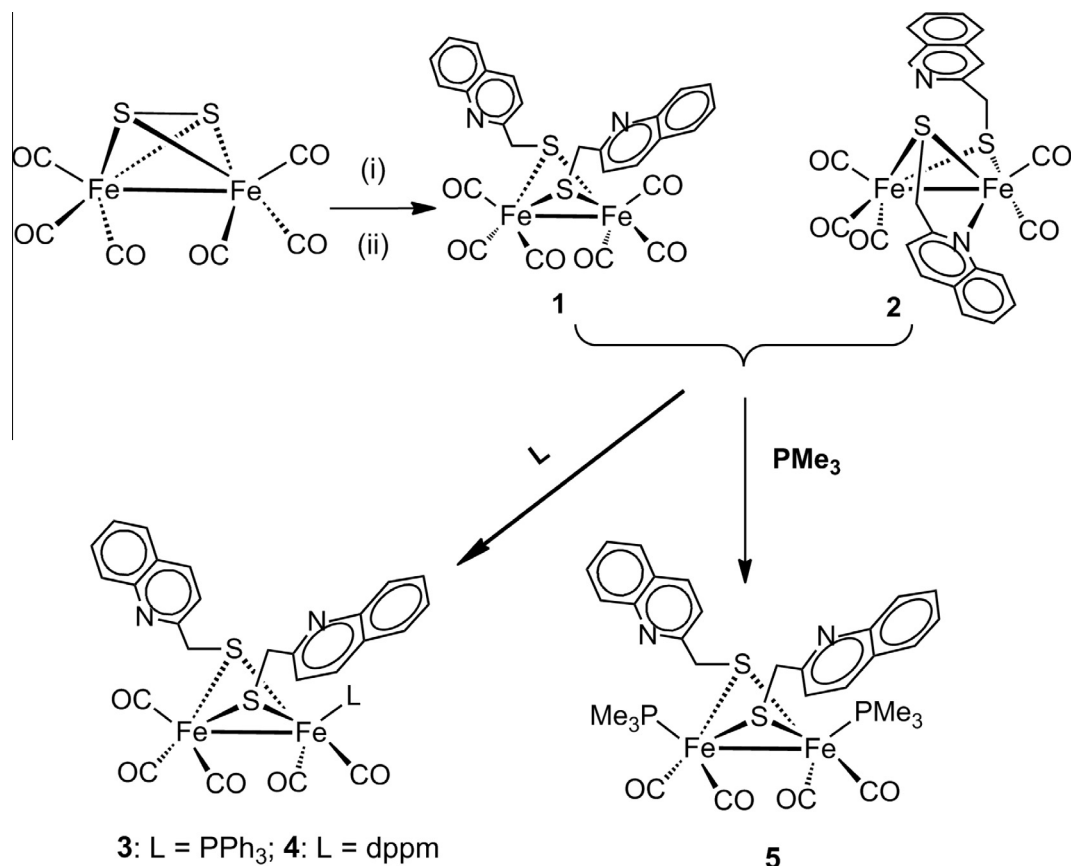
2. Experimental

2.1. Materials and methods

Unless otherwise indicated, all reactions and operations were performed under an atmosphere of dry, oxygen-free inert atmosphere using standard Schlenk-line techniques. Solvents were distilled from appropriate drying agents prior to use. Other chemicals in reagent grade were used without further purification. Parent complexes **1** and **2** were prepared according to previous work [31]. Infrared spectra were recorded on a Perkin–Elmer Spectrum-one FT-IR Spectrometer. Mass spectrum was obtained on a DECA-30000 LCQ Deca XP ion trap mass spectrometry. Elemental analysis

* Corresponding author. Tel.: +86 591 22866531.

E-mail address: wennaa@fzu.edu.cn (N. Wen).



Scheme 1. Synthetic routes to complexes **1–5**. (i) LiEt₃H, THF, –78 °C. (ii) 2-(chloromethyl)quinoline hydrochloride, Et₃N.

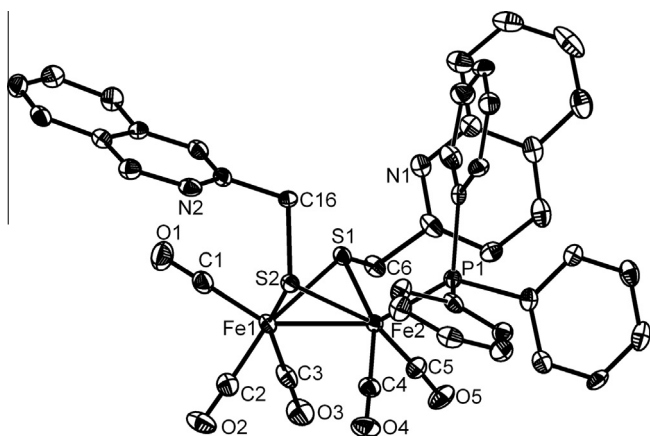


Fig. 1. Molecular structure of **3** with thermal ellipsoid set at 50% probability. Hydrogen atoms are omitted for clarity.

was carried out with an Elementar Vario Micro Elemental Analyzer. ¹H, ³¹P NMR spectrum was gained from a Bruker Biospin Avance III spectrometer.

2.1.1. Electrochemistry

Electrochemistry test was carried out under Ar atmosphere on a CHI600D electrochemical potentiostat. A solution of 0.1 M *n*-Bu₄NPF₆ (Aldrich, spectroscopy grade) in CH₃CN or CH₂Cl₂ was used as the electrolyte. The electrolyte solution was degassed by bubbling with dry Ar for 10 min before measurement. Cyclic voltammograms were obtained in a three-electrode cell under Ar. The working electrode was a glassy carbon disc (diameter 2 mm),

successively polished with 3- and 1-μm diamond pastes and sonicated in ion-free water for 10 min. A Ag|AgCl electrode was used as the reference electrode and a platinum wire as the auxiliary electrode.

2.1.2. Structure determination

X-ray diffraction data were collected on a Rigaku diffractometer with a Mercury CCD area detector (Mo Kα; λ = 0.71073 Å). Single crystals of **3–5** suitable for X-ray diffraction analysis were grown by slow evaporation of a CH₂Cl₂/hexane solution at 5 °C. Empirical absorption correction was applied to the data using the

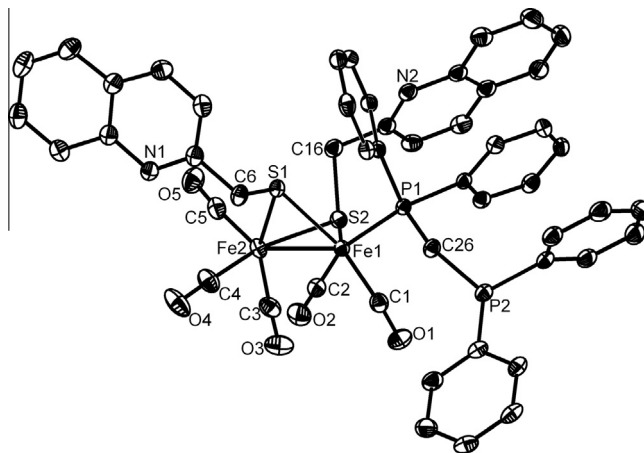


Fig. 2. Molecular structure of **4** with thermal ellipsoid set at 50% probability. Hydrogen atoms and the labels for benzene rings are omitted for clarity.

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