

## Synthesis and characterization of the diiron biomimics bearing phosphine borane for hydrogen formation

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### ABSTRACT

Eight new diiron carbonyl dithiolate complexes,  $[(\mu\text{-xdt})\text{Fe}_2(\text{CO})_5(\text{L})]$ ;  $\text{xdt} = \text{bdt}$ ,  $\text{L} = \text{dppmBH}_3$  (**2**),  $\text{dppeBH}_3$  (**2a**),  $\text{dppm}$  (**2b**),  $\text{xdt} = \text{edt}$ ,  $\text{L} = \text{dppmBH}_3$  (**4**),  $\text{dppeBH}_3$  (**4a**),  $\text{xdt} = \text{Bn-adt}$ ,  $\text{L} = \text{dppmBH}_3$  (**5**),  $\text{dppeBH}_3$  (**5a**), and  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_4(\mu\text{-dppm})]$ , (**3**), have been prepared and characterized by FTIR, NMR spectroscopy and X-ray single crystallography. Molecular structures of complexes **2–5** reveal that the  $\text{Fe}_2$  core exhibits a butterfly conformation and each Fe center is of the pseudo-square-pyramidal coordination geometry. For the mono-substituted species, the phosphine ligand is located in the axial position. For the di-substituted species, the phosphine ligand is spanned between two Fe sites, occupying the basal position. The attached borane unit exerts electronic withdrawing influence on the electron richness about the Fe center. When the phosphine pendant is not protected by borane, coordination to the adjacent Fe site occurs under the reducing condition. It allows synthesis of **3** from chemical or electrochemical reduction of **2b**. Electrocatalysis of acetic acid by complexes **2–5** is studied. The bdt derivatives are reduced at a potential 300 mV more positive than the edt and adt analogs. For the latter species, electrocatalytic events occur near the first reduction. In contrast, no catalysis is observed for **2** in the available electrochemical windows. The rate constant of the catalytic reaction by the species is measured. The adt derivative reveals the highest efficiency toward hydrogen production from acetic acid.

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### 1. Introduction

Among the isolated hydrogenases which can catalyze reversible processes between protons/electrons and molecular hydrogen [1], [FeFe] hydrogenase attracts more interests from chemists than the other two types: [NiFe] and hmd hydrogenase, due to its greater efficiency toward hydrogen generation (6000–9000  $\text{H}_2$  molecules per second) [2]. The structures of [FeFe] hydrogenase isolated from *Desulfovibrio desulfuricans* [3–5] and *Clostridium pasteurianum* [6,7] were characterized by high-resolution single crystal X-ray crystallography. The active site of [FeFe] hydrogenase composes of two units which are a diiron center and a [4Fe4S] cluster that is linked to the  $\text{Fe}_2$  core by a cysteine thiolate (Fig. 1). Three carbonyl groups are coordinated to the diiron center. Two of which as well as two cyanide groups are terminally ligated in the first coordination sphere about the metal sites. The third carbonyl is coordinated in

a semi-bridging fashion, which creates an inverted geometry and generates an empty site for catalysis.

Intensive studies have been focused on  $[(\mu\text{-xdt})\text{Fe}_2(\text{CO})_6]$  ( $\text{xdt} = \text{aliphatic dithiolates}$ ) due to that this type of the complex bears a similar structure to the active site of [FeFe] hydrogenase. Unfortunately, catalytic hydrogen formation by the complexes suffers from relatively negative reduction potentials. On the contrary, the bdt analog (**1**) ( $\text{bdt} = \text{benzene-1,2-dithiolate}$ ) shows an advantage on working potential [8,9]. It is reduced at around  $-1.3\text{ V}$ , which is at least 400 mV less than its counterparts [10–12]. Therefore, employment of **1** and its derivatives may facilitate electrocatalysis under lower applied potentials. In contrast to numerous examples about  $[(\mu\text{-x'dt})\text{Fe}_2(\text{CO})_{6-n}\text{L}_n]$  ( $\text{x'dt} = \text{aliphatic or aromatic dithiolates}$ ;  $\text{L} = \sigma\text{-donating ligands}$ ) [13–60], literatures concerning CO substitution by phosphines containing a phosphine borane end or a unprotected phosphine pendant are rare [61]. In this study,  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_5\text{L}]$  ( $\text{L} = \text{dppm-BH}_3$ , **2**;  $\text{dppe-BH}_3$ , **2a**;  $\text{dppm}$ , **2b**) and  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_4(\mu\text{-dppm})]$  (**3**) ( $\text{dppm} = \text{bis(diphenylphosphino)-methane}$ ;  $\text{dppe} = 1,2\text{-bis(diphenylphosphino)-ethane}$ ) are synthesized to examine their electrocatalytic ability toward hydro-

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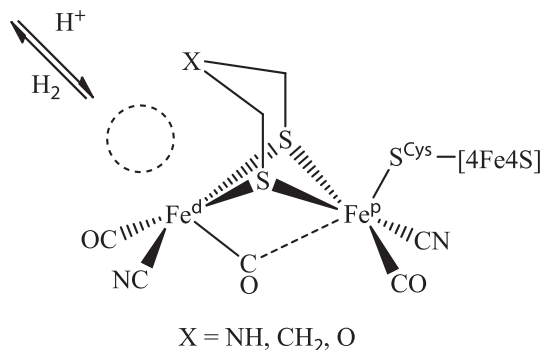


Fig. 1. The active site of [FeFe] hydrogenase.

gen production in the presence of acetic acid. For a sake of the comparison,  $[(\mu\text{-edt})\text{Fe}_2(\text{CO})_5\text{L}]$  ( $\text{L} = \text{dppm-BH}_3$ , **4**;  $\text{dppe-BH}_3$ , **4a**) ( $\text{edt} = \text{ethane dithiolate}$ ) and  $[(\mu\text{-adt})\text{Fe}_2(\text{CO})_5\text{L}]$  ( $\text{L} = \text{dppm-BH}_3$ , **5**;  $\text{L} = \text{dppe-BH}_3$ , **5a**) ( $\text{adt} = (\text{PhCH}_2\text{N}(\text{CH}_2\text{S})_2)^{2-}$ ) are also prepared.

## 2. Experimental

### 2.1. Reagents and instruments

All reactions were carried out using standard Schlenk and vacuum line techniques under an atmosphere of purified nitrogen. All commercially available chemicals were of ACS grade and used without further purification. Solvents were of HPLC grade and purified under  $\text{N}_2$  as follows: diethyl ether and THF were distilled from sodium/benzophenone. Hexane was distilled from sodium. Dichloromethane was distilled from  $\text{CaH}_2$ . Acetonitrile was distilled first over  $\text{CaH}_2$  and then from  $\text{P}_2\text{O}_5$ . Deuterated solvents obtained from Merck were distilled from 4 Å molecular sieves under  $\text{N}_2$  prior to use. Infrared spectra were recorded with a Perkin-Elmer Spectrum One using a 0.05 mm  $\text{CaF}_2$  cell.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded with a Bruker AV-500 or DRX-500 spectrometer operating at 500, 125.7, and 202.49 MHz. Spectra are referenced to tetramethylsilane (TMS) for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  and 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Mass spectral analyses were performed with a Waters LCT Premier XE at the Mass Spectrometry Center in the Institute of Chemistry, Academia Sinica. Elemental analyses were performed with an Elementar vario EL III elemental analyzer. Electrochemical measurements were recorded with a CH Instruments 630C electrochemical potentiostat using a gastight three-electrode cell under  $\text{N}_2$ . A glassy carbon electrode and a platinum wire were used as the working and auxiliary electrodes, respectively. The reference electrode was a nonaqueous  $\text{Ag}^+/\text{Ag}$  electrode (0.01 M  $\text{AgNO}_3/0.1$  M  $n\text{-Bu}_4\text{NPF}_6$ ). All potentials were measured in 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  solution in  $\text{CH}_2\text{Cl}_2$  solution and are reported against the  $\text{Fc}^+/\text{Fc}$  pair. The X-ray single crystal crystallographic data were collected at 150 K with a Bruker SMART APEX CCD four-circle diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å) outfitted with a low-temperature, nitrogen-stream aperture. The structures were solved by direct methods, in conjunction with standard difference Fourier techniques and refined by full-matrix least-squares procedures. An empirical absorption correction (multi-scan) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in geometrically calculated positions by the riding model. All software used for diffraction data processing and crystal structure solution and refinement are contained in the SHELXL-97 program suites [62]. A summary of all crystallographic data is shown in Table S1. In **2** and **3**, the co-solvent  $\text{CH}_2\text{Cl}_2$  molecule is disordered.

### 2.2. Synthesis of $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_5(\text{dppmBH}_3)]$ (**2**)

To a 10 mL  $\text{CH}_2\text{Cl}_2$  solution of  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_6]$  (100 mg, 0.23 mmol) was added  $\text{Me}_3\text{NO}$  (20.7 mg, 0.28 mmol) which was dissolved in 1 mL MeCN and the solution was stirred for 15 min. The ligand  $\text{dppm-BH}_3$  (91.5 mg, 0.23 mmol) was added and the reaction mixture was allowed to stir for additional 30 min at room temperature. The resulted solution was evaporated under reduced pressure. The residue was purified by chromatography on silica gel with dichloromethane/hexane (1:2 v/v) as eluent to give  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_5(\text{dppmBH}_3)]$  (**2**) (163.5 mg, 90% yield) as a red solid. Crystals of  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_5(\text{dppmBH}_3)] \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{CH}_3\text{OH}$  suitable for X-ray crystallographic analysis were grown from  $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{OH}$  solution at  $-20$  °C. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  2052 (s), 1994 (s), 1985 (sh), 1938 (w).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K): 3.37 (dd,  $J_{\text{PH}} = 11$  Hz,  $J_{\text{PC}} = 6.5$  Hz, 2H,  $\text{PCH}_2\text{PBH}_3$ ), 6.40 (m, 2H,  $\text{S}_2\text{C}_6\text{H}_4$ ), 6.70 (m, 2H,  $\text{S}_2\text{C}_6\text{H}_4$ ), 7.00–7.70 (m, 20H,  $\text{PC}_6\text{H}_5$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CDCl}_3$ , 298 K): 29.18 (m, 1C,  $\text{PCH}_2\text{PBH}_3$ ), 126.24 (s, 2C,  $\text{S}_2\text{C}_6\text{H}_4$ ), 128.36 (d,  $J_{\text{PC}} = 9.4$  Hz, 4C,  $\text{PC}_6\text{H}_5$ ), 128.40 (m, 2C,  $\text{S}_2\text{C}_6\text{H}_4$ ), 129.11 (d,  $J_{\text{PC}} = 9.7$  Hz, 4C,  $\text{PC}_6\text{H}_5$ ), 130.40 (d,  $J_{\text{PC}} = 53.2$  Hz, 2C, *ipso*- $\text{PC}_6\text{H}_5$ ), 130.60 (s, 2C, *para*- $\text{PC}_6\text{H}_5$ ), 131.37 (s, 2C, *para*- $\text{PC}_6\text{H}_5$ ), 132.19 (d,  $J_{\text{PC}} = 8.9$  Hz, 4C,  $\text{PC}_6\text{H}_5$ ), 133.26 (d,  $J_{\text{PC}} = 10.8$  Hz, 4C,  $\text{PC}_6\text{H}_5$ ), 134.29 (d,  $J_{\text{PC}} = 41.9$  Hz, 2C, *ipso*- $\text{PC}_6\text{H}_5$ ), 149.24 (s, 2C, *ipso*- $\text{S}_2\text{C}_6\text{H}_4$ ), 209.30 (s, 3C, CO), 213.78 (d,  $J_{\text{PC}} = 4.9$  Hz, 2C, CO) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CDCl}_3$ , 298 K): 13.68 (br, 1P,  $\text{CH}_2\text{PBH}_3$ ), 52.30 (d,  $J_{\text{PP}} = 18$  Hz, 1P,  $\text{FePCH}_2$ ) ppm. FAB-MS:  $m/z$  789.0  $\{2\text{-H}^+\}^+$ . Anal. Calc. for  $\text{C}_{37.5}\text{H}_{32.5}\text{BFe}_2\text{O}_{5.5}\text{P}_2\text{S}_2\text{Cl}$ : C, 52.70; H, 3.77. Found: C, 52.69; H, 3.73%.

### 2.3. Synthesis of $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_5(\text{dppeBH}_3)]$ (**2a**)

To a 10 mL  $\text{CH}_2\text{Cl}_2$  solution of  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_6]$  (100 mg, 0.23 mmol) was added  $\text{Me}_3\text{NO}$  (20.7 mg, 0.28 mmol) which was dissolved in 1 mL MeCN and the solution was stirred for 15 min. The ligand  $\text{dppeBH}_3$  (94.8 mg, 0.23 mmol) was added and the reaction mixture was allowed to stir for additional 30 min at room temperature. The resulted solution was evaporated under reduced pressure. The residue was purified by chromatography on silica gel with dichloromethane/hexane (1:2 v/v) as eluent to give  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_5(\text{dppeBH}_3)]$  (**2a**) (120.2 mg, 65% yield) as a red solid. Crystals of  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_5(\text{dppeBH}_3)]$  suitable for X-ray crystallographic analysis were grown from  $\text{CH}_2\text{Cl}_2\text{-hexane}$  solution at  $-20$  °C. IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  2052 (s), 1991 (s), 1982 (sh), 1933 (w).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K): 2.37 (m, 4H,  $\text{P}(\text{CH}_2)_2\text{PBH}_3$ ), 6.27 (m, 2H,  $\text{S}_2\text{C}_6\text{H}_4$ ), 6.35 (m, 2H,  $\text{S}_2\text{C}_6\text{H}_4$ ), 7.20–7.58 (m, 20H,  $\text{PC}_6\text{H}_5$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.79 MHz,  $\text{CDCl}_3$ , 298 K): 20.54 (d,  $J_{\text{PC}} = 34.6$  Hz, 1C,  $\text{P}(\text{CH}_2)_2\text{PBH}_3$ ), 26.30 (d,  $J_{\text{PC}} = 22.1$  Hz, 1C,  $\text{P}(\text{CH}_2)_2\text{P}$ ), 125.57 (s, 2C,  $\text{S}_2\text{C}_6\text{H}_4$ ), 127.85 (s, 2C,  $\text{S}_2\text{C}_6\text{H}_4$ ), 128.51 (d,  $J_{\text{PC}} = 9.4$  Hz, 4C,  $\text{PC}_6\text{H}_5$ ), 128.61 (d,  $J_{\text{PC}} = 54.1$  Hz, 2C, *ipso*- $\text{PC}_6\text{H}_5$ ), 128.93 (d,  $J_{\text{PC}} = 9.8$  Hz, 4C,  $\text{PC}_6\text{H}_5$ ), 129.98 (s, 2C, *para*- $\text{PC}_6\text{H}_5$ ), 131.36 (s, 2C, *para*- $\text{PC}_6\text{H}_5$ ), 131.98 (m, 8C,  $\text{PC}_6\text{H}_5$ ), 136.38 (d,  $J_{\text{PC}} = 39.1$  Hz, 2C, *ipso*- $\text{PC}_6\text{H}_5$ ), 148.05 (s, 2C, *ipso*- $\text{S}_2\text{C}_6\text{H}_4$ ), 208.97 (s, 3C, CO), 214.47 (d,  $J_{\text{PC}} = 7.3$  Hz, 2C, CO) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.48 MHz,  $\text{CDCl}_3$ , 298 K): 18.94 (br, 1P,  $\text{CH}_2\text{PBH}_3$ ), 55.84 (d,  $J_{\text{PP}} = 44.8$  Hz, 1P,  $\text{FePCH}_2$ ) ppm. FAB-MS:  $m/z$  803.0  $\{2a\text{-H}^+\}^+$ . Anal. Calc. for  $\text{C}_{37}\text{H}_{31}\text{BFe}_2\text{O}_5\text{P}_2\text{S}_2$ : C, 55.26; H, 3.89. Found: C, 55.53; H, 3.99%.

### 2.4. Synthesis of $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_5(\text{dppm})]$ (**2b**)

To a 10 mL  $\text{CH}_2\text{Cl}_2$  solution of  $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_6]$  (100 mg, 0.23 mmol) was added  $\text{Me}_3\text{NO}$  (20.7 mg, 0.28 mmol) which was dissolved in 1 mL MeCN and the solution was stirred for 15 min. The ligand  $\text{dppm}$  (88.4 mg, 0.23 mmol) was added and the reaction mixture was allowed to stir for additional 30 min at room temperature. The resulted solution was evaporated under reduced pressure. The residue was purified by chromatography on silica gel

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