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Research paper

Synthesis, characterisation and protonation of phosphate disubstituted derivatives with pyridyl-functionalized diiron

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ABSTRACT

Three new phosphine disubstituted derivatives of [2Fe2S] model complexes with pendant pyridine family, $[(\mu\text{-SEt})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{N})\text{Fe}_2(\text{CO})_4(\text{L})_2]$ (**2**, L = PPh_3; **3**, L = dppm; **4**, L = PMe_3), have been synthesized and the molecular structure of **2** was determinated by single crystal X-ray diffraction analysis. They were all characterized by MS, FT-IR, ^{31}P and ^{1}H NMR spectra and their electrochemical behaviors were also conducted. The protonation of complex **4** with $HBF_4{\cdot}Et_2O$ was also investigated by FT-IR, ^{31}P and ^{1}H NMR spectroscopies at variable temperature, which reveals the formations of both bridging and terminal hydride intermediates.

1. Introduction

The biohydrogenation enzyme exists widely in nature, because of the reversible reduction of protons to molecular hydrogen at high efficiency [1–6], especially [FeFe]-hydrogenases, which is the most important hydrogenases, can reversibly catalyze the reduction of proton to hydrogen with an extremely high efficiency (Chart 1a) [7–8]. Until now, much work has been focused on the synthesis, characterization and functional biomimics for the activity of sub-clusters {[4Fe4S] and [2Fe2S]} in [FeFe]-hydrogenases, such as the study for the combination of proton and generated hydrogen under electrochemical conditions [9–15]. To better understand the chemical properties of the active site in Fe-only model complexes for the production of enzymatic H_2, various good donor ligands especially phosphine ligands, have been widely used to substitute the carbonyl groups in many all-CO parent complexes of dirron hydrogenases in order to study the structure, electrochemistry and protonation properties of the as-formed substituted derivatives (Chart 1b, c). In addition, some model complexes featuring hemi-labile pendant N, S and O ligands have been synthesized [16], in which the pendant ligands are coordinated to Fe atoms at the apical position. On the other hand, a dynamic ligation of propylamine was observed in a diiron model complex $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_5(\text{H}_2\text{NPr})]$ in CH_3CN solution [17], which might have some relevance to the substrate and inhibitor binding at the [FeFe]-hydrogenase active site. In the meantime, although there is a broad consensus that an iron-bound bridging and terminal hydride species occur in the catalytic mechanism, such a species has rarely been directly observed experimentally (Chart 1d) [18–20]. Herein, we would like to describe the syntheses and structural characterization of three new diiron phosphine-substituted complexes with pendant heterocyclic arms. Complex **1** mentioned at this work refers to $[(\mu\text{-SEt})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{N})\text{Fe}_2(\text{CO})_5]$ [21], in which the pendant pyridine ring is loosely coordinated to the iron atom. In the presence of CO or phosphine ligands, complex **1** is readily converted to its corresponding hexacarbonyl complexes or corresponding phosphine-disubstituted derivatives. In this work, three phosphine-disubstituted derivatives of $[(\mu\text{-SEt})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{N})\text{Fe}_2(\text{CO})_5]$ were isolated via the chromatography technique, namely, $[(\mu\text{-SEt})(\mu\text{-SCH}_2\text{C}_6\text{H}_4\text{N})\text{Fe}_2(\text{CO})_4(\text{L})_2]$ (**2**, L = PPh_3; **3**, L = dppm; **4**, L = PMe_3). The experiment of complex **4** protonated by $HBF_4{\cdot}Et_2O$ which is characterized by FT-IR, ^{31}P and ^{1}H NMR spectra at variable temperature was also discussed.

2. Experimental

2.1. General procedures and materials

Unless otherwise indicated, all reactions and operations were performed under an atmosphere of dry, oxygen-free inert

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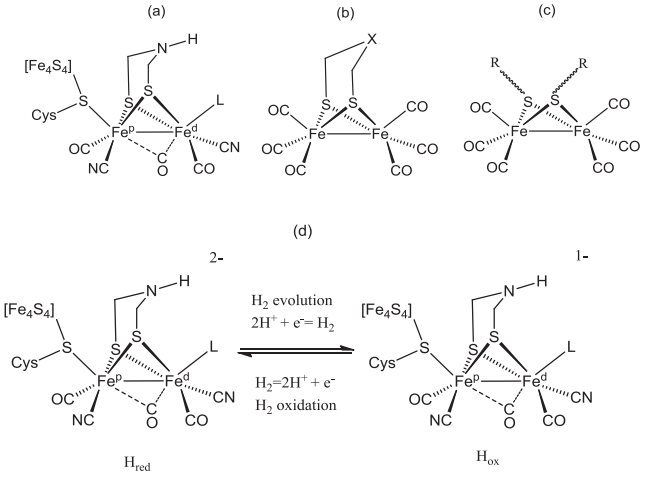


Chart 1. (a) An active center of [FeFe]-hydrogenase as determined experimentally from *D. desulfuricans*. (b) Simple all-CO model complexes of the active site (H-cluster, X = NH, CH_2 or O) of the hydrogen producing enzyme. (c) Model complexes with pendant ligands. (d) the H_{red} (L = H^+ (Fe^IFe^I) or H^- ($Fe^{II}Fe^{II}$) and H_{ox} = vacant or H_2O ($Fe^{II}Fe^I$) states of the [FeFe]-hydrogenase active site.

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. Complex **1** was prepared according to our previous literature. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR Spectrometer. Mass spectra were obtained on a DECAX-30000 LCQ Deca XP ion trap mass spectrometry. Elemental analyses were carried out with an Elementar Vario Micro Elemental Analyzer. ^{1}H and ^{31}P NMR spectra were collected on a Bruker Biospin Avance III 400 NMR spectrometer.

2.2. Single crystal X-ray structural determination

X-ray diffraction data were collected on a Rigaku diffractometer with a Mercury CCD area detector (Mo $K\alpha$; λ = 0.71073 Å). Empirical absorption correction was applied to the data using the *CrystalClear* program [22]. The structure was solved by direct method using SHELXS-97 [23] and refined by full-matrix least-squares on F^2 using the SHELXL-2016 programme [24]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all treated by geometrical positions.

2.3. Electrochemistry

Electrochemistry test was carried out under an argon atmosphere on a CHI600D electrochemical potentiostat. A solution of 0.1 M *n*-Bu_4NPF_6 (Aldrich, spectroscopy grade) in CH_3CN was used as the electrolyte. The electrolyte solution was degassed by bubbling with dry argon for 10 min before measurement. Cyclic voltammetry experiments were carried out in a three-electrode cell configuration consisting of a glassy carbon disc (diameter 2 mm) which is successively polished with 3- and 1-μm diamond pastes and sonicated in ion-free water for 10 min, a platinum counter electrode and a Ag/AgCl reference electrode. The energy level of the Ag/AgCl reference electrode was calibrated against by ferrocence/ferrocenium (Fc/Fc^+) redox system (just as the internal standard).

2.4. Syntheses of [(μ-SEt)(μ-$SCH_2C_6H_4N$)$Fe_2(CO)_4(L)_2$] (2, L = PPh_3; 3, L = dppm; 4, L = PMe_3)

Complex **2** was prepared *via* the reaction of **1** and PPh_3. In detail, a mixture of **1** (0.03 g, 0.05 mmol) and PPh_3 (0.025 g, 0.20 mmol) was stirred in toluene (20 mL) at room temperature under N_2 for 3 h, and then the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate (4:1 v/v) as eluent. Finally, complex **2** was obtained as a red solid (22 mg, 40%). Complexes **3** (14 mg, 33%) and **4** (8 mg, 26%) were synthesized in a way similar to that described for **2**, except that dppm and PMe_3 were employed instead of PPh_3, respectively.

2.5. Analytical data for complexes 2–4

For **2:** Anal.Calcd for $C_{48}H_{41}Fe_2NO_4P_2S_2$ (933.62): C 61.70, H 4.39, N 1.50; Found: C 61.30, H 4.01, N 1.31. MS (ESI): *m/z* 955.5 $[M + Na]^+$. IR (CH_2Cl_2, cm^{-1}): 1991 (s), 1950 (m), 1931 (w). ^{1}H NMR ($CDCl_3$): δ 7.39–7.19 (m, 34H, C_6H_5 and C_5H_4), δ 3.14 (m, 2H, CH_2), 1.98 (s, 2H, CH_2), 1.12 (m, 3H, CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ 49.90 (s) ppm.

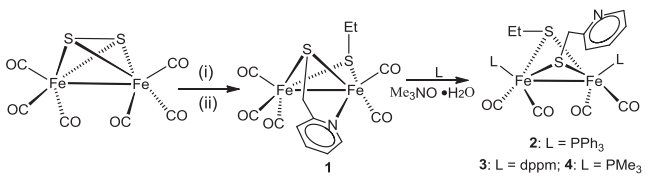
For **3**: Anal. Calcd for $C_{62}H_{55}Fe_2NO_4P_4S_2$ (1176.70): C 63.23; H 4.67; N 1.19; Found: C 63.14; H 4.51; N 1.07. MS (ESI): *m/z* 1177.1 [M]. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1990 (s), 1946 (m), 1928 (m). ^{1}H NMR ($CDCl_3$): δ 7.43–7.09 (m, 44H, C_6H_5 and C_5H_4), 3.16 (m, 2H, CH_2), 2.74 (s, 4H, CH_2), 1.75 (m, 2H, CH_2), 1.19 (m, 3H, CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ 44.70 ppm (d, *J* = 130.8 Hz), −25.72 (d, *J* = 140.4 Hz) ppm.

For **4**: Anal. Calcd for $C_{18}H_{29}Fe_2NO_4P_2S_2$ (561.0): C 38.50, H 5.17, N 2.50. Found: C 38.34, H 5.21, N 2.30. MS (ESI): *m/z* 562.5 $[M + H]^+$. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 1979 (s), 1938 (m), 1910 (s). ^{1}H NMR ($CDCl_3$): δ 7.55–6.99 (m, 4H, C_5H_4), 3.47 (m, 2H, CH_2), 2.17 (m, 2H, CH_2), 1.38 (m, 18H, CH_3), 1.18(m, 3H, CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ = 8.19 (s) ppm.

3. Results and discussion

3.1. Synthesis and characterization of compounds 2–4

Treatments of **1** with excess PPh_3 or dppm in toluene at room temperature afford the disubstituted complexes [(μ-SEt)(μ-$SCH_2C_6H_4N$)$Fe_2(CO)_4(L)_2$] (**2**, L = PPh_3; **3**, L = dppm; **4**, L = PMe_3) (Scheme 1). The substitution of **1** with phosphine ligands in MeCN with the aid of Me_3NO, resulted in a higher yields. This correlates well the fact that in complex **1** the pendant pyridine ring is loosely coordinated to the iron atom. Complexes **2**–**4** all display three absorption bands in the carbonyl region from 1910 to 1991 cm^{-1}. The ÿ$_{CO}$ bands shift to a much lower energy compared with those of the parent complex (1925–2072 cm^{-1}). This correlates well with the fact that the phosphine-disubstituted complex may have a much more significant increase in electron density of the diiron center [25–29]. The average value of the Δν(CO) bands of **4** shifts *ca.* 92 cm^{-1} to lower frequency compared with that of the all-CO parent complex (Table 1). The average values of the three ν_{CO} bands for the PMe_3-disubstituted complex **4** (1951 cm^{-1}) is, as expected, larger than those for the PPh_3 and dppm-disubstituted homologues **2** and **3** (1957 and 1954 cm^{-1}), which results from the good electron donating capability of PMe_3 ligand.



Scheme 1. Synthesis of complexes **2**–**4**. (i) $LiBEt_3H$, THF, −78 °C; (ii) 2-(chloromethyl)pyridine hydrobromide, Et_3N.