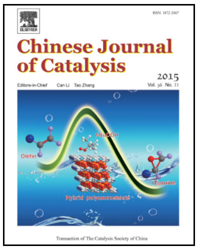
Chinese Journal of Catalysis 36 (2015) 2011–2019

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc



Article

Synthesis, characterization and catalytic reactivity of pentacoordinate iron dicarbonyl as a model of the [Fe]-hydrogenase active site

Tianyong Zhang [a,b], Liao Sheng [a], Qiusheng Yang [c], Shuang Jiang [a], Yanhong Wang [a], Chaohui Jin [a], Bin Li [a,*]

[a] Tianjin Key Laboratory of Applied Catalysis Science and Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China
[c] School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China

ARTICLE INFO

Article history:
Received 16 April 2015
Accepted 23 May 2015
Published 20 November 2015

Keywords:
Mono iron hydrogenase
Model complex
Catalytic transfer hydrogenation
Functional analogue
Benzoquinone

ABSTRACT

Two mono iron complexes $Fe(CO)_2PR_3(NN)$ (R = Cy (**3**), Ph (**4**), NN = *o*-phenylenediamine dianion ligand, $N_2H_2Ph^{2-}$) derived from the ligand substitution of $Fe(CO)_3I_2PR_3$ by the NN ligand were isolated and structurally characterized by single crystal X-ray diffraction. They have a similar first coordination sphere and oxidation state of the iron center as the [Fe]-hydrogenase active site, and can be a model of it. IR demonstrated that the effect of the NN ligand on the coordinated CO stretching frequencies was due to its excellent electron donating ability. The reversible protonation/deprotonation of the NN ligand was identified by infrared spectroscopy and density functional theory computation. The NN ligand is an effective proton acceptor as the internal base of the cysteine thiolate ligand in [Fe]-hydrogenase. The electrochemical properties of complexes **3, 4** were investigated by cyclic voltammograms. Complex **3** catalyzed the transfer hydrogenation of benzoquinone to hydroquinone effectively under mild conditions.

1. Introduction

[Fe]-Hydrogenase (Hmd) participates in the methanogenic process of the reduction of CO_2 to methane. In the presence of the substrate N^5,N^{10}-methenyl-tetrahydro-methnanopterin (methenyl-H_4MPT^+, or MPT^+), the enzyme catalyzes the heterolytic cleavage of H_2 (Scheme 1) [1,2].

Methenyl-H_4MPT^+ accepts H^+ ions and forms N^5,N^{10}-methylene-tetrahydromethanopterin (methylene-H_4MPT, or HMPT) [2]. The other proton from H_2 exchanges rapidly with the protons of the bulk water, while the immediate proton acceptor is unknown. In the active site of Hmd [3–8], the Fe ion has the ligands of one cysteine sulfur atom, two cis-CO ligands, and one bi-dentate donor atom of guanylylpyridinol cofactor through its nitrogen and acyl-carbon atoms (Fig. 1.) [6,9–11]. The coordination site *trans* to the acyl ligand was proposed to be the H_2-binding site. It is unclear whether this site is vacant or occupied by a solvent molecule, most likely a water molecule, in the resting state.

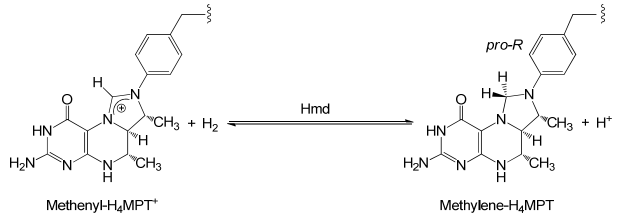
A mechanism based on the resting state model of wild-type Hmd [6,9] was proposed from DFT (density functional theory) calculations. The MPT^+ substrate triggers the H^+ release to re-

---

* Corresponding author. Tel/Fax: +86-22-27406610; E-mail: libin@tju.edu.cn

This work was supported by the National Natural Science Foundation of China (21103121, 21276187), Tianjin Municipal Natural Science Foundation (13JCQNJC05800) and the Specialized Research Fund for the Doctoral Program of Higher Education (20121317110009).

DOI: 10.1016/S1872-2067(15)60920-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 11, November 2015



Scheme 1. Reversible hydrogen transfer reduction catalyzed by Hmd.

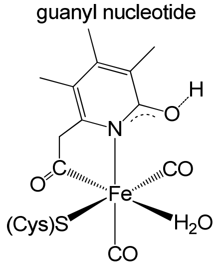


Fig. 1. The proposed active site of Hmd.

generate the resting state with the Fe-$H^{\delta+}\cdots H^{\delta-}$-O dihydrogen bond after the proton transfers from the Cys176-sulfur or 2-pydinol's oxygen [12]. The cysteine thiolate ligand in the open site which initially helps bind H_2 and then works as the internal base in the theory is the possible proton acceptor in the reaction. Some models have been developed to prove that the cysteine thiolate ligand has the reversible protonation property, but it is still a challenge to activate the dihydrogen [4–8]. This motivated us to develop more viable alternative ligands to focus on the function of hydrogenation.

Catalytic hydrogenation via transition metal complexes has demonstrated in 1995 that the interaction of intermolecular and intramolecular M-H···H-N bonds were strong. Intermolecular H-bonds have been used to design the structure and catalytic activity of a transition metal complex in asymmetric hydrogenation reactions [13]. In the use of [FeFe]-hydrogenase [3], it is generally accepted that the coordination and subsequent heterolytic cleavage of dihydrogen occured at an iron center [14]. The reaction is likely facilitated by an amine of the proposed azadithiolate cofactor. In addition, a Noyori-type hydrogenation system based on the diamine-$RuCl_2$ complex functions by "metal-ligand bifunctional catalysis" for the hydride transfer to an outer sphere molecule [15], which is similar to the trigger mechanism of Hmd. Noyori [15] found that an unsubstituted diamine was critical and the catalyst would be ineffective when diamines without NH groups were used. The so-called "NH-effect" has been widely investigated and was proposed to stabilize an incoming ketone substrate [16]. A similar structure and catalytic mechanism have been found in a transition metal complex like tris(*o*-phenylenediamine) iron(II). Transition metal ions coordinated by a nitrogen ligand have a unique property in hydrogen transformation. Aromatic amines and hydroxides, such as phenylenediamine or hydroquinone derivatives, are widely known to possess $2H^+/2e^-$ pulling capability, which resembles the function of the internal base in the [Fe]-hydrogenase enzyme [17]. This inspired us to utilize an organic skeleton coordinated with a nitrogen or binitrogen ligand to mimic the hydrogenation to obtain a functional model of Hmd. In this paper, two new functional mono-iron hydrogenase active site models coordinated by a NN ligand were synthesised and characterized. The introduced NN ligand served as an internal base, which can undergo reversible protonation/deprotonation with the acid (HBF_4 or AcOH/ethanediamine). The developed models also catalyzed the hydrogenation of quinone under mild conditions.

2. Experimental

2.1. General procedures

All synthetic operations and measurements were conducted under a N_2 atmosphere using Schlenk line techniques because the precursors of these iron-series complexes are sensitive to light and air. Hence, the solvents, including *n*-hexane and tetrahydrofuran (THF), were distilled with Na metal to remove trace water, and were preserved with 4A sieves before use. Complexes $FeI_2(CO)_4$, $FeI_2(CO)_3PCy_3$ and $FeI_2(CO)_3PPh_3$ were prepared according to literature procedures. The following materials were reagent grade and used as purchased from Sigma-Aldrich: potassium *tert*-butoxide, *o*-phenylenediamine and *n*-Bu_4NPF_6. The $Fe(CO)_5$ was obtained as a gift from Jiangsu Tianyi Ultra-fine Metal Powder Co., Ltd (China).

The NMR spectra were measured on a Bruker AVANCE III 400MHz NMR spectrometer. ^1H NMR shifts were referenced to residual solvent resonances according to literature values. The solution IR spectra was recorded on a Shimadzu FTIR-8400 spectrometer using 0.1 mm KBr sealed cells. Quinone and hydroquinone samples were analyzed by reversed phase high performance liquid chromatography (C18, ϕ150 × 4.6mm) using an external standard method on an Agilent 1100 spectrometer. The mobile phase was CH_3CN/H_2O (30/70, *V*/*V*) and the flow rate was 1.0 mL/min. The measurement was performed at the wavelength of 298 nm.

2.2. Synthesis of complex **3** and **4**

Scheme 2 shows the synthetic route for the preparation of $Fe(CO)_2PR_3(NN)$. The precursors were obtained via the CO ligand substitution reaction of $FeI_2(CO)_4$ and PR_3 (1:1, R =PCy_3, PPh_3) following the procedure reported by Li et al [18]. First, a solution of $FeI_2(CO)_3PCy_3$ (500 mg, 0.742 mmol) dissolved in THF (100 mL) was prepared. Then, *o*-phenylenediamine (240 mg, 2.22 mmol) and *t*-BuOK (500 mg, 4.44 mmol) were mixed under stirring for 10 min in a flask, to which THF (50 mL) was added later. A bluish violet well-proportioned and stable solution was generated. The solution was transformed into a third Schlenk flask at the same ratio and intervals during 1 h and then keep stirred for 1.5 h. Afterwards 0.1 mL water was added into the system to react with the excess *o*-phenylenediamine dianion and then the solvent was removed in vacuo. After extraction with *n*-hexane and filtration through celite, the filtrate was dried in vacuo to yield the crude product including the target **3** (250 mg 30%) and byproduct *trans*-$[Fe(CO)_3(PCy_3)_2]$. The crude product can be used for single crystal growth by slow evaporation of the *n*-hexane solution of **3.** The purified