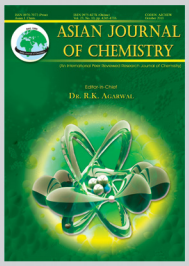
Asian Journal of Chemistry; Vol. 24, No. 1 (2012), 249-251

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Synthesis, Characterization, Protonation and Electrochemical Investigation of Diiron Tetracarbonyl Complex as a Model of [FeFe]-Hydrogenase

ZHIYIN XIAO[1,*], ZHIMEI LI[2,*], GUIFEN QIAN[2] and LI LONG[2]

[1]College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing 314001, P.R. China
[2]Department of Chemistry, Nanchang University, Nanchang 330031, P.R. China

*Corresponding author: Tel: +86 573 83640131; E-mail: zhiyin.xiao@mail.zjxu.edu.cn; lizhimei@ncu.edu.cn

(*Received*: 10 December 2010; *Accepted*: 15 September 2011) AJC-10410

As structural and functional relevancy to the active site in [FeFe]-hydrogenase, the diiron carbonyl complexes attracted our attentions. A phosphine-substituted complex (**2**) containing a pyridine group was synthesized by reaction of a diiron pentacarbonyl model complex (**1**) with triphenyl phosphine. Complex **2** was fully characterized by using FT-IR, NMR spectroscopies as well as elemental analysis. Protonation of the complex and electrochemical behaviours in the absence and presence of a strong acid were also investigated. The results showed that the bridging hydride was obtained and it catalyzed proton reduced at a rather positive potential, which was only about 0.15 V negative to the estimated standard potential.

Key Words: Diiron model complex, Electrochemistry, Hydrogen evolution, [FeFe]-Hydrogenase.

INTRODUCTION

As water is the only by-product in the process of oxidation of hydrogen, it has the potential to act as an alternative clean energy to replace fossil fuels. However, efficient catalysis to produce H_2 depends mostly on noble metals such as platinum. In nature, [FeFe]-hydrogenase possesses an active site of diiron center that coordinates with two pairs of terminal CO and CN^- ligands. This metalloenzyme exhibits high efficiency of catalyzing H_2 evolution under physiological conditions[1-4].

Due to structural similarity of complexes with $\{Fe_2(CO)_n\}$ core (n = 6, 5, 4) to the diiron sub-unit of the enzyme, they have attracted intense attention in the area of biological chemistry. In the catalytic conversion of proton to hydrogen catalyzed by the enzyme, one of the key steps is the protonation. Since phosphine ligands have electron-donating ability similar to that CN^-, a large number of phosphine-substituted derivatives have been prepared. However, in most cases, these phosphine-substituted derivatives show rather negative potential for their reduction and have significantly high over-potential in catalyzing proton reduction[5-10].

In this paper, we reported the synthesis, characterization, protonation and electrochemical investigation of a phosphine-substituted diiron complex, $[Fe_2(CO)_4(\mu\text{-}SCH_2)_2C(CH_3)(2\text{-}C_5H_4N)PPh_3]$ (**2**) by reaction of a diiron pentacarbonyl model complex (**1**) with triphenyl phosphine.

EXPERIMENTAL

All reactions and operations were carried out under dinitrogen or argon atmosphere with standard Schlenk techniques. Solvents were dried according to standard method. The ligand 2-methyl-2-(pyridin-2-yl) propane-1,3-dithiol and the model complex $[Fe_2(CO)_5(\mu\text{-}SCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]$ (**1**) were prepared according to a literature method[11]. $Fe_3(CO)_{12}$ was purchased from Sigma Aldrich, $HBF_4{\cdot}Et_2O$ and TfOH from Alfa Aesar. All chemicals were used as received.

Electrochemistry was carried out in Argon atmosphere in dry dichloromethane solvent at room temperature on Autolab Potentiostat 3.0. Conventional three-electrode system was employed in which vitreous carbon disk (ϕ = 1 mm) was used as working electrode, vitreous carbon strip as counter electrode and Ag/AgCl (Metrom) as reference electrode whose inner reference solution is composed of 0.05M $[NBu_4]Cl$ and 0.45M $[NBu_4]BF_4$ in dichloromethane, the electrolyte concentration is 0.5M $[NBu_4]BF_4$. 100 mV scanning rate was used unless otherwise stated. All potentials were quoted against ferrocenium/ferrocene couple, whose half-wave potential is 0.55 ± 0.01 V against the above Ag/AgCl reference electrode in dichloromethane.

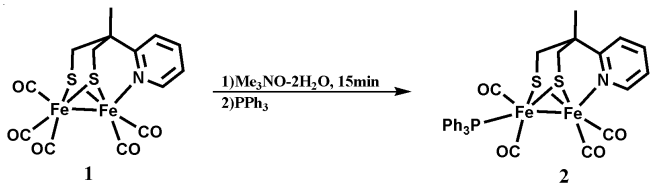
Synthesis of $[Fe_2(CO)_4(\mu\text{-}SCH_2)_2C(CH_3)(2\text{-}C_5H_4N)PPh_3]$ (2): To a solution of the complex $[Fe_2(CO)_5(\mu\text{-}SCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]$ (**1**) (27 mg, 0.06 mmol) in dry MeCN (10 mL) was added $Me_3NO{\cdot}2H_2O$ (7 mg, 0.06 mmol) under argon. After

15 min, triphenyl phosphine (16 mg, 0.06 mmol) was added. The reaction was stirring for 4 h and a green grass solid was obtained. After removal of solvent, the solid was purified using flash chromatography (silica gel 25 g, first washed by a volume mixture of ethyl acetate (20 %) and *n*-hexane (80 %) and than a mixture of acetone (40 %) and petroleum ether (60 %)). Yield: 82 %. FT-IR (CH_2Cl_2, ν/cm^{-1}): 1995, 1946, 1927, 1894 (-CO). ^{1}H NMR (δ (ppm), $CDCl_3$): 0.98 (s, 3H, -CH_3), 1.41 (d, *J* = 17.7Hz, 2H, -SCH_2), 1.65 (d, *J* = 17.6Hz, 2H, -SCH_2), 7.07 (s, 1H, Py-H), 7.23 - 7.76 (m, 17H, Ar-15H + Py-2H), 9.58 (s, 1H, Py-H). ^{31}P NMR (δ (ppm), $CDCl_3$): 58.77(s). Microanalysis for $C_{31}H_{26}NO_4PS_2Fe_2$ (m.w. = 683.34), found (calcd.) (%): C, 54.18 (54.49); H, 3.52 (3.84); N, 2.37 (2.05).

Protonation of complex 2 to form [(μ-H)Fe_2(CO)$_4$-(μ-SCH_2)$_2$C(CH_3)(2-C_5H_4N)PPh_3]BF_4 3: To a solution of complex **2** (9.5 mg, 0.014 mmol) in dichloromethane (4 mL) at room temperature was added 1 equivalent of trifluoromethanesulfonic acid (TfOH) (1.3 μL) under argon. With a colour change from dark green to dark red, a hydride (**3**) was formed conformed by IR spectroscopy. FT-IR (CH_2Cl_2, ν/cm^{-1}): 2063, 2041, 2009 (-CO).

RESULTS AND DISCUSSION

Synthesis and characterization of complex 2: Complex **2** was synthesized by reacting one equivalent of triphenyl phosphine under the aid of decarbonylating agent ($Me_3NO{\cdot}2H_2O$), **Scheme-I**. The substitution reaction afforded a green solid. This reaction was followed by IR spectroscopy and TLC. Compared to complex **1**, infrared absorption frequencies of complex **2** was 41 cm^{-1} lower (Fig. 1). The complex **2** was fully characterized by using FT-IR, ^{1}H and ^{31}P NMR (Fig. 2) spectroscopies and elemental analysis. These analytical data confirmed unambiguously the composition proposed in **Scheme-I**. Further substitution by a second PPh_3 turned out to be difficult, which was attributed to steric effect of complex **2**.



Scheme-I: Synthesis of complex **2**

Protonation of complex 2: In complex **2**, there are two positions which can possibly be protonated, the pyridine-N and the Fe-Fe bond. We attempted to protonate the complex in a stepwise manner without success. Upon protonation, only a μ-hydride product was observed. The reaction of **2** with one equivalent of TfOH was performed in dichloromethane at room temperature. When the acid was added, the colour of the solution turned quickly from dark green to red. Infrared absorption of the resultant product shifted significantly to higher frequencies by about 99 cm^{-1} (Fig. 3). In light of this significant shift, the protonation is expected to occur at the Fe-Fe bond. Additionally, the spectral profile of the protonated product possesses characteristic spectral pattern of diiron tetracarbonyl complex[12-14]. Thus, we believe that the protonated product is a bridging hydride. In an early work, protonation of complex **1** gave eventually a diiron hexacarbonyl complex[11,15]. In this case, however, we obtained a μ-hydride rather than a product containing a pendant pyridinium, **Scheme-II**. This is probably due to the strong electron-donating ability which increases significantly the electron density of the Fe-Fe bond and thus it is preferably protonated.

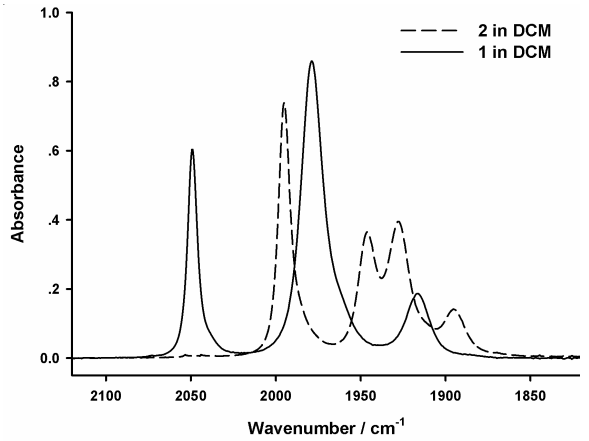


Fig. 1. IR spectra of complexes **1** (solid line) and **2** (dashed line) in CH_2Cl_2

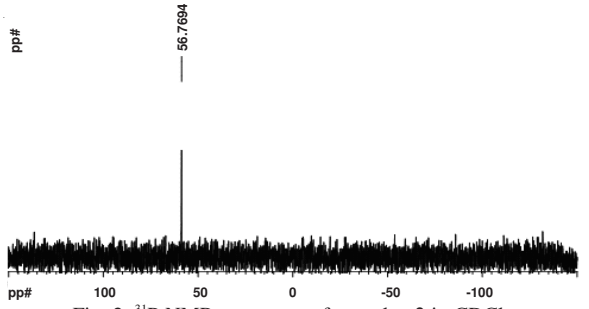


Fig. 2. ^{31}P NMR resonance of complex **2** in $CDCl_3$

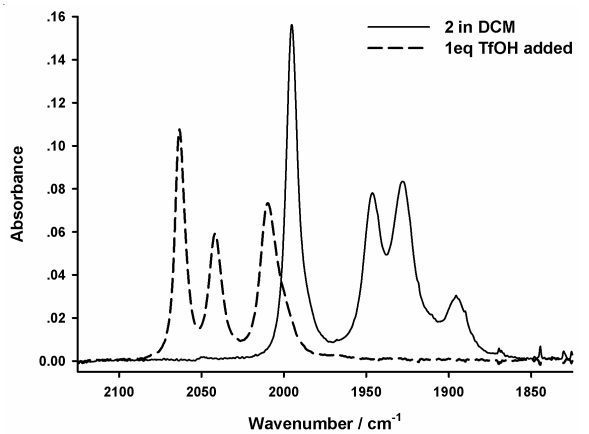
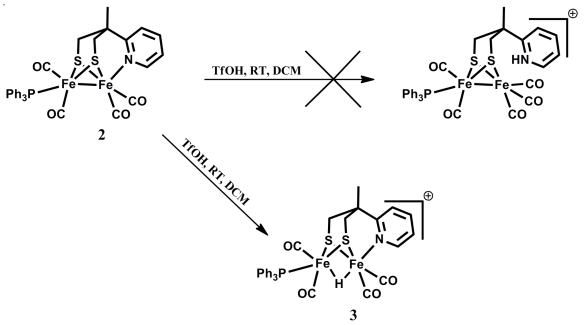


Fig. 3. IR spectra of complex **2** (solid line) and its protonated product after addition of 1 eq. of TfOH (dashed line)

Electrochemistry of complex 2: From cyclic voltammograms of complex **2** presented in Fig. 4, the complex **2** exhibits one irreversible reduction process at -2.07 V. The phosphine-substituted diiron complexes have been reported to undergo a two-electron reduction to give the corresponding dianion at moderately negative potentials[16-18]. It is assumed that complex **2** could be reduced to $\mathbf{2}^{2-}$ in the reduction.

Upon addition of HBF_4 to a solution of complex **2** in dichloromethane triggers the appearance of three new reduction peaks noted as I (-1.09 V), II (-1.49 V) and III (-2.07 V) in



Scheme-II: Protonation procedure of **2** in dichloromethane at room temperature by TfOH acid

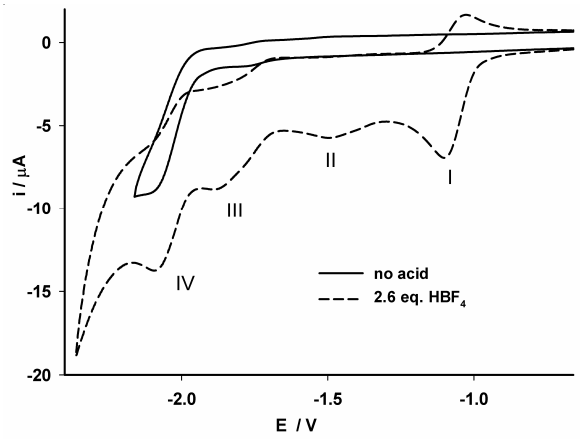


Fig. 4. Cyclic voltammograms of complex **2** (1.6 mM) in free acid solution (solid line) and in the presence of 2.6 eq. HBF_4 (dashed line)

Fig. 4. The peak IV in the curve is corresponding to the reduction process of complex **2**. The three new peaks occur at less negative than the potentials of complex **2**. The peak I is corresponding to the quasi-reversible reduction and is less negative than of $[HFe_2(bdt)(CO)_5(P(OMe)_3)]^+$ about 100 mV, the latter potential is only 0.25 V negative to the estimated standard potential as reported[7]. As mentioned above, complex **2** was transformed to complex **3** in acid solution determined by FT-IR, it indicates that the peak I is associated with complex **3** to $\mathbf{3}^-$. The higher positive shift of reduction potential is associated with the bridging hydride.

As shown in Fig. 5, the peak current of the process I and II increases steadily with the addition of acid. But the current increasing rate of peak I is much slower than peak II, especially when the addition of acid is over 2.6 equivalents and finally the current levels off nearly. This is a characteristic feature for a kinetically controlled process of reduction I[19]. For the second catalytic-wave, two features are particularly noteworthy. Firstly, the profiles of the cyclic voltammograms alter with the concentration of acid. Secondly, with concentration of added acid at 6.5 equivalents, this catalytic wave starts to left shift. These experimental observations suggest that the process II is not the only one contributing to this catalysis.

Conclusion

In this paper, we synthesized a phosphine-substituted complex **2** containing pyridine ligand and it was fully characterized by FTIR, NMR, element analysis. Upon addition strong acid to a solution of complex **2**, a bridging hydride was obtained.

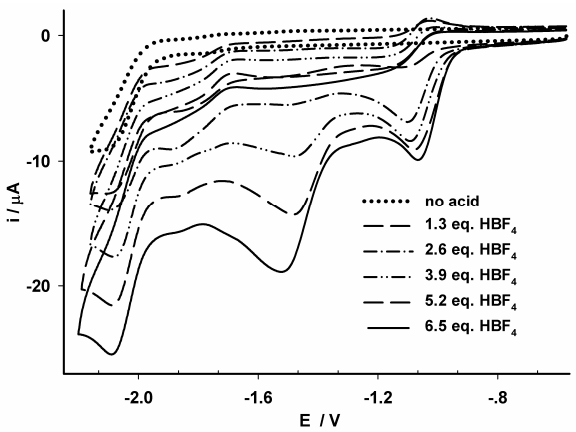


Fig. 5. Cyclic voltammograms of complex **2** (1.6 mM) in the presence of HBF_4

The result of electrochemical experiments showed that complex **2** catalyzed proton reduction at a rather positive potential in strong acid media.

ACKNOWLEDGEMENTS

The authors thank the Natural Science Foundation of China (Grant No. 20871064), Innovation fund for postgraduate students (Z Li, Grant No. YC07A019) and Centre of Analysis and Testing at Jiaxing University for supporting this work.

REFERENCES

1. D.J. Evans and C.J. Pickett, *Chem. Soc. Rev*., **32**, 268 (2003).
2. F. Gloaguen and T.B. Rauchfuss, *Chem. Soc. Rev.*, **38**, 100 (2009).
3. X.M. Liu, S.K. Ibrahim, C. Tard and C.J. Pickett, *Coord. Chem. Rev.*, **249**, 1641 (2005).
4. J.W. Peters, W.N. Lanzilotta, B.J. Lemon and L.C. Seefeldt, *Science*, **282**, 1853 (1998).
5. F.I. Adam, G. Hogarth, S.E. Kabir and D. Richards, *Comp. Rendus Chim.*, **11**, 890 (2008).
6. S. Ezzaher, J.F. Capon, F. Gloaguen, F.Y. Petillon, P. Schollhammer and J. Talarmin, *Inorg. Chem.*, **46**, 3426 (2007).
7. J.F. Capon, F. Gloaguen, P. Schollhammer and J. Talarmin, *J. Electroanal. Chem.*, **595**, 47 (2006).
8. S. Jiang, J.H. Liu, Y. Shi, Z. Wang, B. Akermark and L.C. Sun, *Dalton Trans*., 896 (2007).
9. Z. Wang, W.F. Jiang, J.H. Liu, W.I. Jiang, Y. Wang, B. Akermark and L.C. Sun, *J. Organomet. Chem.*, **693**, 2828 (2008).
10. S. Jiang, J.H. Liu, Y. Shi, Z. Wang, B. Akermark and L.H. Sun, *Polyhedron*, **26**, 1499 (2007).
11. F.F. Xu, C. Tard, X.F. Wang, S.K. Ibrahim, D.L. Hughes, W. Zhong, X.R. Zeng, Q.Y. Luo, X.M. Liu and C.J. Pickett, *Chem. Commun.*, 606 (2008).
12. G. Eilers, L. Schwartz, M. Stein, G. Zampella, L. de Gioia, S. Ott and R. Lomoth, *Chem. Eur. J.*, **13**, 7075 (2007).
13. F.J. Wang, M. Wang, X.Y. Liu, K. Jin, W.B. Donga and L.C. Sun, *Dalton Trans.*, 3812 (2007).
14. X. Zhao, I.P. Georgakaki, M.L. Miller, J.C. Yarbrough and M.Y. Darensbourg, *J. Am. Chem. Soc.*, **123**, 9710 (2001).
15. Z.Y. Xiao, F.F. Xu, L. Long, Y.Q. Liu, G. Zampella, L. De Gioia, X.R. Zeng, Q.Y. Luo and X.M. Liu, *J. Organomet. Chem.*, **695**, 721 (2010).
16. J.F. Capon, S. Ezzaher, F. Gloaguen, F.Y. Petillon, P. Schollhammer and J. Talarmin, *Chem. Eur. J.*, **14**, 1954 (2008).
17. M.H. Cheah, S.J. Borg and S.P. Best, *Inorg. Chem.*, **46**, 1741 (2007).
18. J.F. Capon, S. Ezzaher, F. Gloaguen, F.Y. Petillon, P. Schollhammer, J. Talarmin, T.J. Davin, J.E. McGrady and K.W. Muir, *New J. Chem.*, **31**, 2052 (2007).
19. C. Tard, X.M. Liu, D.L. Hughes, C.J. Pickett, *Chem. Commun*., 133 (2005).