

Synthesis, characterization and DFT studies of 1, 1'-Bis(diphenylphosphino)ferrocene substituted diiron complexes: Bioinspired [FeFe] hydrogenase model complexes

SANDEEP KAUR-GHUMAAN^{a,*}, A SREENITHYA^b and RAGHAVAN B SUNOJ^b

^aDepartment of Chemistry, University of Delhi, Delhi 110007, India

^bDepartment of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
e-mail: sandeepkaur.du@gmail.com; skaur@chemistry.du.ac.in

MS received 13 June 2014; revised 31 August 2014; accepted 16 September 2014

Abstract. The reaction of [Fe₂(CO)₆(μ-toluene-3, 4-benzenedithiolate)] **1** and bidentate diphosphine, 1, 1'-bis(diphenylphosphino)ferrocene (dppf) has been studied. New complexes obtained have been characterized by various spectroscopic techniques as bioinspired models of the iron hydrogenase active site. The crystal structure of [Fe₂(CO)₅(κ¹-dppfO)(μ-toluene-3, 4-benzenedithiolate)] **4** is reported.

Keywords. Bioinorganic chemistry; hydrogenase enzyme; bidentate phosphine; proton reduction; redox active ligands; density functional calculations.

1. Introduction

Hydrogen is attracting growing attention as the future energy source due to the steadily depleting fossil fuel sources. However, the wide application of hydrogen as a fuel is limited owing to the high cost associated with its production. Hence, scientists have been looking for new and alternative routes to prepare hydrogen. In this connection, highly efficient enzymes such as the [FeFe] hydrogenases (H₂ases) that catalyze the reversible reduction of protons to molecular hydrogen in biological systems, have been widely studied. Detailed structures of the [FeFe] hydrogenases have been determined using X-ray crystallographic^{1–3} and spectroscopic techniques.^{4,5} The investigations revealed that in the active site, the iron centres are coordinated by carbon monoxide, cyanide ligands and by a dithiolate bridging ligand between the two iron centres; one of the iron centres (Fe_p) is coordinated by a cysteinyl linked Fe₄S₄ cluster (figure 1).

Various models of the active site of the [FeFe] H₂ases have been designed and studied in order to get a detailed picture on the functional activity of these enzymes.^{6–9} Though a large number of mono- and bidentate phosphine substituted model complexes have been reported,^{10–21} there are only very few examples known in which the carbonyl ligand on the Fe-atom has been substituted by ferrocene phosphines. A

few such examples are: [Fe₂(μ-pdt)(CO)₅]₂[η⁵-Ph₂PC₅H₄)₂Fe],²² [Fe₂(μ-SCH₂XCH₂S-μ)(CO)₅]₂[η⁵-Ph₂PC₅H₄)₂Fe] (X = O, S),^{23,24} which contain the bidentate phosphine ligand 1, 1'-bis(diphenylphosphino)ferrocene (dppf), [Fe₂(μ-SCH₂XCH₂S-μ)(CO)₅]₂[η⁵-Ph₂PC₅H₄)₂Ru] (X = O, S)^{24,25} and [Fe₂(μ-pdt)(μ-dppf)CO]₄.²⁶ Rauchfuss and co-workers have also reported a [FeFe]-azadithiolate model complex in which they have tried to replicate the function of the ferredoxins by using redox-active ferrocene ligand Cp*Fe(C₅Me₄CH₂PEt₂)(FcP*).²⁷ The coupling of redox active centres in H₂ase biomimics is currently of significant interest.

So far all the reported complexes have an alkyl dithiolate as the bridging ligand. There has been no report yet on a ferrocene phosphine substituted complex with an aromatic dithiolate bridging ligand. The use of the rigid and unsaturated dithiolate linkers has been shown to lower the reduction potentials of the diiron complexes and also increase the stability of the reduced forms.^{28–38} This and the electron donor properties of ferrocene motivated the initiation of our studies on the reaction of [Fe₂(CO)₆(μ-toluene-3, 4-benzenedithiolate)] **1** with the bidentate ligand dppf.

Therefore, based on aforementioned considerations the following diiron complexes, [{Fe₂(μ-toluene-3, 4-benzenedithiolate)(CO)₅]₂(μ, κ²-dppf)] **2** and [Fe₂(μ-toluene-3, 4-benzenedithiolate)(CO)₅(κ¹-dppf)] **3** were successfully synthesized and characterized. [Fe₂(μ-toluene-3, 4-benzenedithiolate)(CO)₅(κ¹-dppfO)] **4** was obtained as one of the side products in the reaction.

*For correspondence

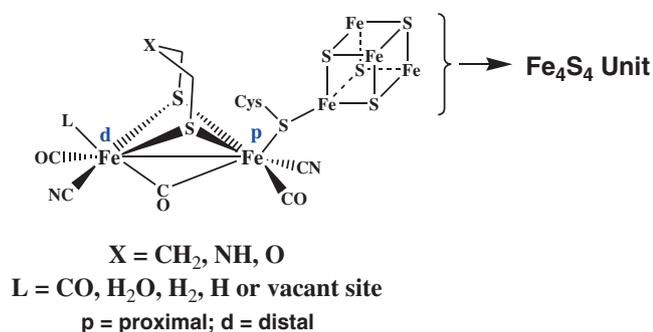


Figure 1. The [FeFe]-Hydrogenase active site.

The monooxidation of the diphosphine in complex **4** results from the decomposition process during the experiments. However, in this paper we also report the crystal structure of complex **4**, in which the uncoordinated phosphorus atom of the bidentate phosphine is present in its oxidized form (as P=O). Sun and co-workers have reported the crystal structure of a di-iron complex with P=S.¹¹ Similar P=O complexes have been reported by Hogarth and co-workers³⁹ but there was no report of the crystal structure for such complexes. Recently it has been reported that the P=O moiety in the complex [Fe₂(CO)₆][(μ -SCH₂)₂(Ph)P=O] can be protonated.⁴⁰

2. Experimental

2.1 General procedures

All the reagents and solvents were purchased from commercial sources and used as received. The starting dinuclear complex [Fe₂(CO)₆(μ -toluene-3,4-benzenedithiolate)] **1** was synthesized by the reported procedure.^{41–43} Elemental (C, H and N) analyses were performed on a Vario E L III elemental Analyser, elemental Analysensysteme GmbH. IR spectra were recorded from dichloromethane solutions of the samples over the range 400–4000 cm⁻¹ on a Perkin Elmer IR Spectrometer. ¹H and ³¹P NMR were recorded on a JEOL 400 MHz NMR Spectrometer. UV spectrum was recorded from dichloromethane solution on a Perkin Elmer UV-Spectrometer. Cyclic voltammogram was measured in dichloromethane using Autolab potentiostat.

2.2 Crystal structure analysis

X-ray diffraction data for complex **4** was collected using an Oxford XCALIBUR-S CCD single-crystal X-ray diffractometer (Mo-K α radiation, λ = 0.71073 Å) at 150(2) K. The structure was solved and refined

Table 1. Crystallographic data for **4**.

	4
Formula	C ₄₆ H ₃₄ Fe ₃ O ₆ P ₂ S ₂
<i>M_r</i>	976.34
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> (Å)	13.0962(4)
<i>b</i> (Å)	13.9516(6)
<i>c</i> (Å)	13.9861(6)
α (deg)	111.122(4)
β (deg)	105.019(3)
γ (deg)	107.055(3)
<i>V</i> (Å ³)	2079.50(14)
<i>Z</i>	2
<i>T</i> (K)	150(2)
λ (Å)	0.71073
<i>D</i> _{calc} (g cm ⁻³)	1.559
μ (mm ⁻¹)	1.260
<i>F</i> (000)	996
goodness-of-fit	0.989
R1 ^a /wR2 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0266/0.0645
R1 ^a /wR2 ^b (all data)	0.0357/0.0662
largest residuals (e Å ⁻³)	0.564/-0.287

by full-matrix least-squares techniques on *F*² using the *SHELX-97* program.⁴⁴ The absorption correction was done by the multiscan technique (SHELXTL program package). All data were corrected for Lorentz and polarization effects, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement process as per the riding model. The crystallographic data of **4** is summarized in table 1.

2.3 DFT calculations

All DFT calculations were performed using Gaussian 09⁴⁵ suite of quantum chemical program at the B3LYP^{46–48} level of theory. For geometry optimization, Los Alamos pseudopotential basis set (LANL2DZ)^{49–51} was employed for Fe in combination with 6-31G** basis set for other atoms. NMR calculations are done at the B3LYP/LANL2DZ (Fe), 6-31+G** level of theory using GIAO^{52,53} method.

2.4 Synthesis

One portion of Me₃NO.2H₂O (0.051 g, 0.00046 mol) was added to a solution of 0.00046 mol of [Fe₂{ μ -L}(CO)₆] **1** (L = μ -toluene-3,4-benzenedithiolate) in MeCN (30 mL) under argon. The mixture was stirred at room temperature for 15 min followed by the addition of the dppf ligand (0.128 g, 0.00023 mol). After 1.5 h the volatiles were removed in vacuo. The resulting

respective solid was purified by column chromatography on silica gel with hexane/CH₂Cl₂ (1:4 v/v) as gradient eluent which gave **2** as a red-brown solid. Elution with CH₂Cl₂ gave **3** as a dark red-orange solid. Single crystals of **4** suitable for X-ray analysis were obtained by slow evaporation of the CH₂Cl₂/hexane solution of complex **3** at room temperature. The formation of complex **4** could be due to the presence of N-methyl amine oxide as O-atom source in the reaction mixture.

2.4a [*Fe*₂(μ-toluene-3,4-benzenedithiolate)(CO)₅]₂(μ, κ²-dppf)], **2**: Colour: red-brown. Yield: 24% (0.150 g). Anal. Calcd for C₅₈H₄₀Fe₅O₁₀P₂S₄: C, 50.98; H, 2.95. Found: C, 50.58; H, 3.00. IR (CH₂Cl₂, cm⁻¹): 2047, 1982, 1934. ¹H NMR (400 MHz, CDCl₃): δ 7.37 (s, 10H, Ph); 7.13 (s, 10H, Ph); 6.45 (m, 2H); 6.12 (s, 2H); 6.01 (m, 2H); 3.94–4.46 (s, 8H, Cp); 1.81 (s, 6H, CH₃) ppm. ³¹P NMR (161.8 MHz, CDCl₃): δ 52.51 (s, Fe – P) ppm.

2.4b [*Fe*₂(μ-toluene-3,4-benzenedithiolate)(CO)₅(κ¹-dppf)], **3**: Colour: dark red-orange. Yield: 37% (0.164 g). Anal. Calcd for C₄₆H₃₄Fe₃O₅P₂S₂: C, 57.53; H, 3.57. Found: C, 56.95; H, 3.70. IR (CH₂Cl₂, cm⁻¹): 2048, 1987, 1930. ¹H NMR (400 MHz, CDCl₃): δ 7.14–7.38 (s, 20H, Ph); 6.47 (m, 1H); 6.13 (s, 1H); 6.03 (m, 1H); 3.76–4.47 (s, 8H, Cp); 1.83, 1.82 (s, 3H, CH₃) ppm. ³¹P

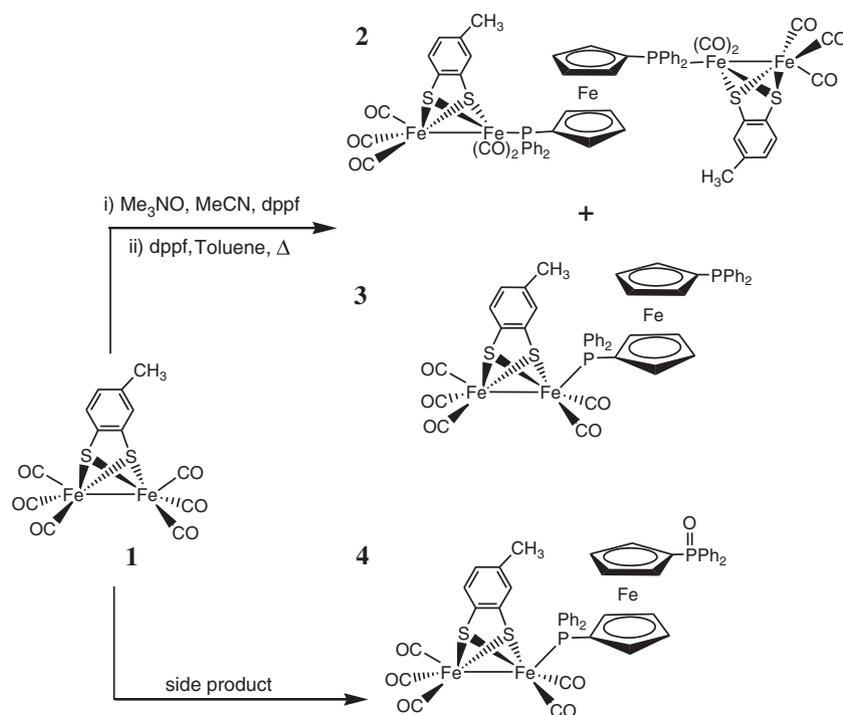
NMR (161.8 MHz, CDCl₃): δ 52.67, 52.53 (s, Fe – P); –16.68, –17.08 (s, P) ppm.

2.4c [*Fe*₂(μ-toluene-3,4-benzenedithiolate)(CO)₅(κ¹-dppfO)], **4**: Colour: dark brown. Anal. Calcd for C₄₆H₃₄Fe₃O₆P₂S₂: C, 56.59; H, 3.51. Found: C, 56.90; H, 3.65. IR (CH₂Cl₂, cm⁻¹): 2050, 1988, 1931. ³¹P NMR (161.8 MHz, CDCl₃): δ 52.43 (s, Fe – P); 28.74 (s, P = O) ppm.

3. Results and Discussion

The disubstituted complex **2** and unsymmetrical mono-dppf substituted compound **3** were obtained in moderate yields in presence of equimolar amount of decarbonylating agent Me₃NO. 2H₂O with dppf in CH₃CN at room temperature (scheme 1). Complex **3** could also be synthesized on refluxing the toluene solutions of dppf and complex **1**. Complex **4** was obtained as one of the side products of the reaction of **1** and dppf. N-methyl amine oxide used in the synthesis could be the O-atom source for the formation of **4**. The complexes were purified by column chromatography on a silica gel column and characterized and studied by UV, IR, ¹H NMR, ³¹P NMR spectroscopies, satisfactory elemental analysis, X-ray crystallographic measurements and DFT calculations.

In complex **1**, ligand substitution with σ-donating dppf is facilitated due to the presence of the aromatic



Scheme 1. Synthesis of complexes 2–4.

sulphur bridge which decreases the electron density at the diiron core and thus makes the iron centres more electrophilic leading to complexes **2–4**. In the FTIR spectrum in dichloromethane, complex **1** shows bands at 2077, 2042, 2001, 1953 cm^{-1} . In comparison, complexes **2**, **3** and **4** exhibit strong absorption band frequencies in the region 1920–2050 cm^{-1} in their FTIR spectra (figure 2) corresponding to the terminal coordination of the carbonyl (CO) groups. Due to the incorporation of the electron donating dppf ligand into the butterfly Fe_2S_2 moiety, the absorption bands in the FTIR spectra of complexes **2–4** shift significantly towards lower wave numbers as compared to the hexacarbonyl analogue **1**, suggesting that dppf increases the electron density on the Fe(I)Fe(I) centres.^{54,55} This is further supported by the computed Mulliken atomic charges (see Supporting Information). The slight difference of the stretching frequencies in comparison to the reported diiron dithiolate complexes with bidentate phosphine ligands is due to the difference in the dithiolate linkers between the two iron; the aromatic dithiolate linker being a weaker donor in comparison to the aliphatic dithiolates.^{11,19} All the complexes were characterized by ^1H and ^{31}P NMR (see Supporting Information). Similar ^1H NMR spectrum was observed for complex **3**. The ^{31}P NMR spectrum for complex **2** displayed a signal at 52.51 ppm for the two phosphorus atoms of the bidentate phosphine ligand. This is because both the phosphorus atoms in complex **2** have an identical environment. In contrast, **3** showed signals at 52.67, 52.53 and -16.68 , -17.08 respectively. This indicates the presence of two isomers, apical and basal in the solution. The possibility of the existence of isomers in solution for bidentate phosphines has been reported previously.²⁷ Complex **4**, on the other hand displayed ^{31}P signals at 52.43 and 28.74 ppm. The signal at 28.74

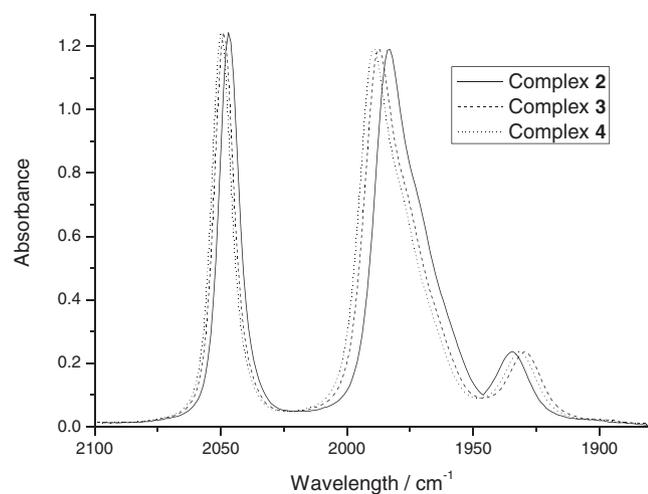


Figure 2. IR spectra for complexes **2–4** in dichloromethane.

ppm indicates the presence of oxidized phosphorus ($\text{P} = \text{O}$), which is also evidenced by X-ray analysis of a crystal of **4**. Further the UV-Visible spectrum of complex **2** in dichloromethane showed bands at 263 (sh), 368 and 500 (sh) nm (see Supporting Information). The transitions are mainly from Fe(2) , Fe(3) to the dithiolate linker or to the ferrocene phosphine ligand.

The molecular structure of complex **4** was further confirmed by X-ray crystallography (figure 3). The crystallographic parameters, data collection and structure refinement of the compound **4** are given in table 1. Dark orange coloured crystal of complex $[\text{Fe}_2(\mu\text{-toluene-3,4-benzenedithiolate})(\text{CO})_5(\kappa^1\text{-dppfO})]$ **4** suitable for X-ray structure analysis, could be grown from the slow evaporation of the $\text{CH}_2\text{Cl}_2/\text{hexane}$ solution of complex **3** at room temperature. The crystal structure analyses show that the crystal of complex **4** crystallizes in Triclinic space group P-1. The geometry around the iron centres has been found to be distorted square pyramidal, which is common in $[\text{FeFe}] \text{H}_2\text{ase}$ model complexes.^{56–58} In the crystal structure, two Fe atoms and two S atoms form a butterfly conformation as shown in the thermal ellipsoid plots (figure 3).

Iron-sulphur distances of 2.2826(7) and 2.2856(6) are slightly more than that reported for this class of compounds.¹¹ The Fe – Fe distance in **4** (2.4930(5) Å) is close to those found in similar other complexes (2.49–2.51 Å);^{11,12} but relatively shorter than that found in *Desulfovibrio desulfuricans* and *Clostridium pasteurianum* (ca. 2.55–2.62 Å).^{1–3} The phosphine group of the dppf ligand occupies an apical position. The $\text{Fe(2)} - \text{P(2)}$ bond distance of 2.2419(6) agrees well

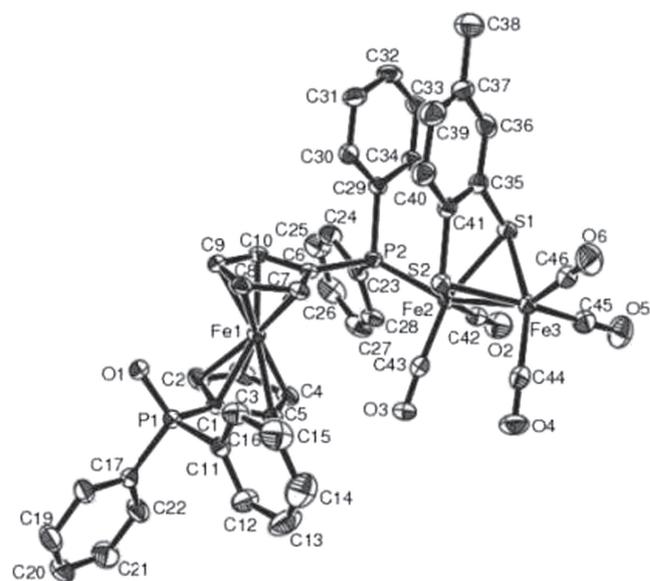


Figure 3. Solid state structure of **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$] are given in table S2 in the SI.

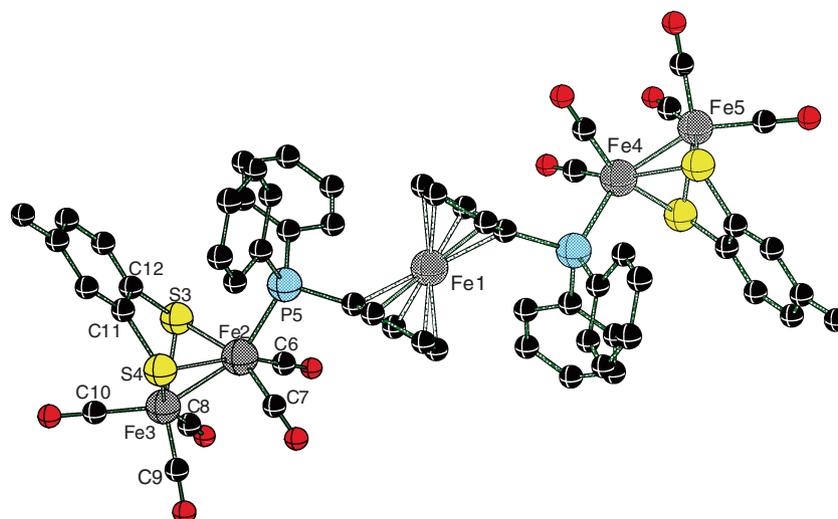


Figure 4. Optimized geometry of complex **2**.

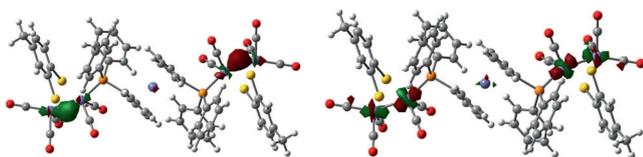


Figure 5. HOMO (left) and LUMO (right) for complex **2**.

with similar other reported phosphine complexes.^{11,12} The P = O bond distance of 1.4803(15) Å is much less than the reported P = S bond distance of 1.9445(18) Å.¹¹ Moreover, the P = O group points away from the iron carbonyl core.

In the absence of crystals of **2** suitable for X-ray analysis, we have carried out computational studies in order to get structural insights. Optimized geometry of complex **2** is given in figure 4 and important structural parameters are provided in the Supporting Information. Calculations were done for the other complexes (**1**, **3** and **4**) as well (see Supporting Information). Analysis of molecular orbitals show that HOMO and LUMO of complex **2** (figure 5) are predominantly centred on the metal atoms (iron atoms directly attached to the dithiolate ligand, i.e., Fe2, Fe3, Fe4 and Fe5, (figure 4)) which implies that reduction is metal centred (see Supporting Information). The cyclic voltammogram (scan rate = 0.1 V/s) of complex **2** in dichloromethane indeed showed a metal-centred (iron atom attached to the dithiolate bridge) one-electron reduction at -1.58 V and three oxidations at 0.57, 0.97 and 1.45 V vs. Fc/Fc⁺ couple which is set at 0.00 V (figure 6). The oxidations are irreversible and are associated with dppf and iron atoms attached to the dithiolate bridge. The smaller anodic peak at -1.16 V is probably due to a chemical process occurring after reduction to form a new species

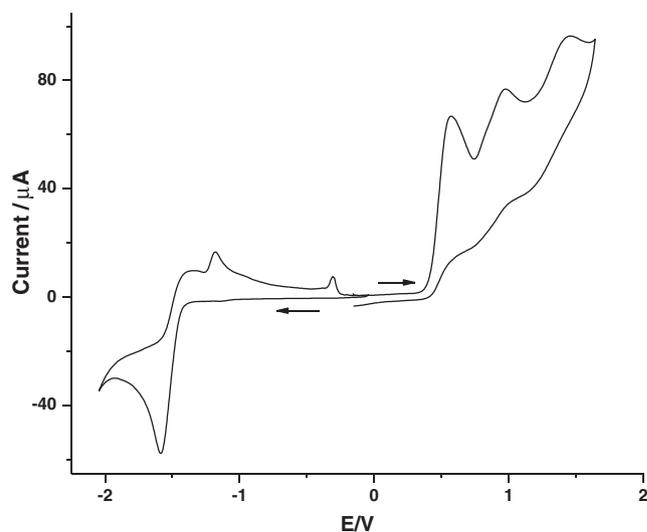


Figure 6. Cyclic voltammogram of complex **2** (1.08 mM) in dichloromethane. Potentials are vs. Fc/Fc⁺ couple.

in solution.³⁶ On chemical oxidation of complex **2** by 1 equivalent of FcPF₆ (ferrocenium hexafluorophosphate) in dichloromethane, the IR bands were blue-shifted to 2050 and 1987 cm⁻¹ in comparison to the parent complex (2047 and 1982 cm⁻¹) (see Supporting Information) This indicates that the first oxidation is due to the dppf moiety. A similar peak pattern for **2** and [**2**]⁺ also suggests that the first oxidation does not lead to any change in the molecular structures of the species. The remaining two oxidations at two separate potentials can be assigned to the Fe centres in the {Fe₂S₂} units. Moreover, DFT calculations (HOMO and LUMO localized on the Fe centres of the {Fe₂S₂} units) indicate that there is weak communication between the Fe centres of the two {Fe₂S₂} units.

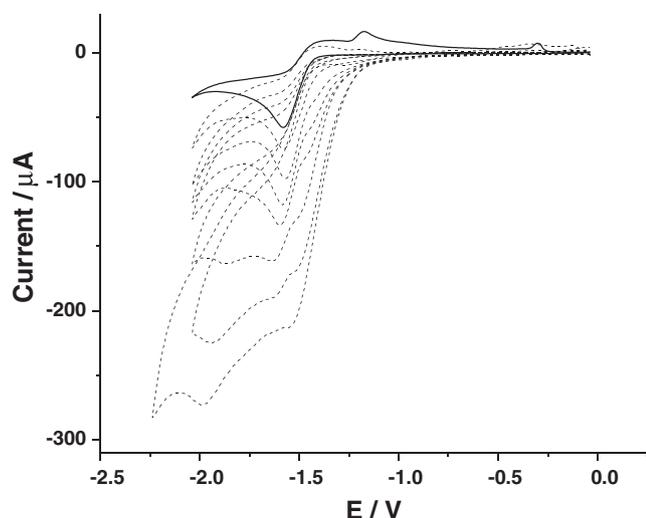


Figure 7. Cyclic voltammograms of complex **2** in the absence (—) and presence (.....) of 2, 4, 6, 8, 12, 16 and 20 molar equivalents of acetic acid (1.08 mM solution in dichloromethane, supporting electrolyte $[\text{NBu}_4][\text{PF}_6]$, scan rate 0.1 V s^{-1} , glassy carbon electrode, potentials are vs. Fc/Fc^+ couple).

Addition of acetic acid (upto 8 molar equivalents) to a dichloromethane solution of **2** initially resulted in current increase at a potential (-1.59 V) close to the reduction potential observed in the absence of acid (figure 7). This peak disappeared slowly with increase in the amount of acid. In addition, a shoulder was observed at -1.43 V which shifts towards more negative potential with increase in the concentration of acid in the solution. A new reduction wave appeared at -1.88 V in presence of 12 molar equivalents of acid in the solution. This peak also showed a cathodic shift with increase in the amount of acid. No increase of current was observed beyond 20 molar equivalents of acid. These results suggest that the complex may be catalytically active towards proton reduction. Due to the complicated nature of the cyclic voltammograms attempts have not been made to predict the catalytic mechanism. The calculated UV-Visible spectrum and the calculated NMR spectrum show good agreement with the experimental values, which could be regarded as an additional validation of the optimized geometries (see Supporting Information).

4. Conclusions

Two new model complexes related to the $[\text{FeFe}]-\text{H}_2$ ases (**2** and **3**) have been synthesized from substitution of CO ligand in complex **1** by redox active electron-rich dppf ligand. The oxidized phosphine complex **4** was obtained as a side product. In the complexes reported

by Ghosh *et al.* and Camara *et al.* based on IR studies, the first oxidation was assigned to the Fe centres of the $\{\text{Fe}_2\text{S}_2\}$ units. While for complex **2**, the first oxidation is associated with the dppf moiety as indicated by small shifts of the IR absorption bands. The Density functional results indicate that HOMO and LUMO of complex **2** are localized on the Fe centres of the $\{\text{Fe}_2\text{S}_2\}$ units leading to weak communication between the centres. Complex **2** was found to be catalytically active in presence of acetic acid. The catalysis was observed at lower reduction potential in comparison to the complexes reported by Ghosh *et al.* and Liu *et al.* The electron delocalization in the oxidized species and the mechanism of proton reduction by complex **2** are the subject of ongoing investigations.

Supplementary Information

Supplementary data related to this article can be found on the journal website: www.ias.ac.in/chemsci. CCDC 887865 contains the crystallographic data for **4**. Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgements

The author thanks Department of Science & Technology (DST), India for financial support (SR/S1/IC-28/2011). Dr. S. M. Mobin is gratefully acknowledged for crystallographic measurements of complex **4**. SKG is thankful to University of Delhi for providing R & D grant. RBS and AS are grateful to IIT Bombay computer centre for computational resources.

References

- Peters J W, Lanzilotta W N, Lemon B J and Seefeldt L C 1998 *Science* **282** 1853
- Nicolet Y, Piras C, Legrand P, Hatchikian C E and Fontecilla-Camps J C 1999 *Structure* **7** 13
- Nicolet Y, de Lacey A L, Vernéde X, Fernandez V M, Hatchikian E C and Fontecilla Camps J C 2001 *J. Am. Chem. Soc.* **123** 1596
- De Lacey A L, Stadler C, Cavazza C, Hatchikian E C and Fernandez V M 2000 *J. Am. Chem. Soc.* **122** 11232
- Chen Z, Lemon B J, Huang S, Swartz D J, Peters J W and Bagley K A 2002 *Biochemistry* **41** 2036
- Tard C and Pickett C J 2009 *Chem. Rev.* **109** 2245
- Simmons T R, Berggren G, Bacchi M, Fontecave M and Artero V 2014 *Coord. Chem. Rev.* **270–271** 127
- Wang N, Wang M, Chen L and Sun L 2013 *Dalton Trans.* **42** 12059
- Li H and Rauchfuss T B 2002 *J. Am. Chem. Soc.* **124** 726

10. Cloirec A L, Best S P, Borg S, Davies S C, Evans D J, Hughes D L and Pickett C J 1999 *Chem. Commun.* 2285
11. Gao W, Ekström J, Liu J, Chen C, Eriksson L, Weng L, Åkermark B and Sun L 2007 *Inorg. Chem.* **46** 1981
12. Song L C, Li C G, Ge J H, Yang Z Y, Wang H T, Zhang J and Hu Q M 2008 *J. Inorg. Biochem.* **102** 1973
13. Liu T and Darenbourg M Y 2007 *J. Am. Chem. Soc.* **129** 7008
14. Ezzaher S, Capon J F, Gloaguen F, Pétilion F Y, Schollhammer P and Talarmin J 2009 *Inorg. Chem.* **48** 2
15. Barton B E, Olsen M T and Rauchfuss T B 2008 *J. Am. Chem. Soc.* **130** 16834
16. Wang N, Wang M, Liu J, Jin K, Chen L and Sun L 2009 *Inorg. Chem.* **48** 1155
17. Ott S, Borgström M, Kritikos M, Lomoth R, Bergquist J, Åkermark B, Hammarström L and Sun L 2004 *Inorg. Chem.* **43** 4683
18. Song L-C, Gao W, Luo X, Wang Z-X, Sun X-J and Song H-B 2012 *Organometallics* **31** 3324
19. Karnahl M, Orthaber A, Tschierlei S, Nagarajan L and Ott S 2012 *J. Coord. Chem.* **65** 2713
20. Lounissi S, Capon J F, Gloaguen F, Matoussi F, Pétilion F Y, Schollhammer P and Talarmin J 2011 *Chem. Commun.* **47** 878
21. Durgaprasad G, Bolligarla R and Das S K 2011 *J. Organomet. Chem.* **696** 3097
22. Liu X-F and Yin B-S 2010 *J. Coord. Chem.* **63** 4061
23. Song L-C, Yang Z-Y, Bian H-Z and Hu Q-M 2004 *Organometallics* **23** 3082
24. Song L-C, Li Q-S, Yang Z-Y, Hua Y-J, Bian H-Z and Hu Q-M 2010 *Eur. J. Inorg. Chem.* 1119
25. Song L-C, Yang Z-Y, Bian H-Z, Liu Y, Wang H T, Liu X F and Hu Q-M, 2005 *Organometallics* **24** 6126
26. Ghosh S, Hogarth G, Hollingsworth N, Holt K B, Kabir S E and Sanchez B E 2014 *Chem. Commun.* **50** 945
27. Camara J M and Rauchfuss T B 2011 *Nat. Chem.* **4** 26
28. Capon J F, Gloaguen F, Schollhammer P and Talarmin J 2004 *J. Electroanal. Chem.* **566** 241
29. Capon J F, Gloaguen F, Schollhammer P and Talarmin J 2006 *J. Electroanal. Chem.* **595** 47
30. Gloaguen F, Morvan D, Capon J F, Schollhammer P and Talarmin J 2007 *J. Electroanal. Chem.* **603** 15
31. Charreteur K, Kdider M, Capon J F, Gloaguen F, Pétilion F Y, Schollhammer P and Talarmin J 2010 *Inorg. Chem.* **49** 2496
32. Orain P Y, Capon J F, Gloaguen F, Schollhammer P and Talarmin J 2010 *Int. J. Hydrogen Energy* **35** 10797
33. Chen L, Wang M, Gloaguen F, Zheng D, Zhang P and Sun L 2012 *Chem. Eur. J.* **18** 13968
34. Felton G A N, Vannucci A K, Chen J, Lockett L T, Okumura N, Petro B J, Zakai U I, Evans D H, Glass R S and Lichtenberger D L 2007 *J. Am. Chem. Soc.* **129** 12521
35. Streich D, Astuti Y, Orlandi M, Schwartz L, Lomoth R, Hammarström L and Ott S 2010 *Chem. Eur. J.* **16** 60
36. Vannucci A K, Wang S, Nichol G S, Lichtenberger D L, Evans D H and Glass R S 2010 *Dalton Trans.* **39** 3050
37. Kumar B, Beyler M, Kubiak C P and Ott S 2012 *Chem. Eur. J.* **18** 1295
38. Liu Y-C, Yen T-H, Tseng Y-J, Hu C-H, Lee G-H and Chiang M-H 2012 *Inorg. Chem.* **51** 5997
39. Adam F I, Hogarth G and Richards I 2007 *J. Organomet. Chem.* **692** 3957
40. Almazahreh L R, Apfel U-P, Imhof W, Rudolph M, Görls H, Talarmin J, Schollhammer P El-khateeb M and Weigand W 2013 *Organometallics* **32** 4523
41. King R B 1963 *J. Am. Chem. Soc.* **85** 1584
42. Hasan M M, M B Hursthouse, S E Kabir and K M A Malik 2001 *Polyhedron* **20** 97
43. Schwartz L, Singh P, Eriksson L, Lomoth R and Ott S 2008 *C. R. Chimie* **11** 875
44. Sheldrick G M, SHELX-97 1997 *A Program for Crystal Structure Solution and Refinement*; University of Göttingen, Germany
45. Frisch M J et al. Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2004. Gaussian 09, Revision A.02, Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, Li X, Hratchian H P, Izmaylov A F, Bloino J, Zheng G, Sonnenberg J L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery, Jr. J A, Peralta J E, Ogliaro F, Bearpark M, Heyd J J, Brothers E, Kudin K N, Staroverov V N, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J C, Iyengar S S, Tomasi J, Cossi M, Rega N, Millam N J, Klene M, Knox J E, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Martin R L, Morokuma K, Zakrzewski V G, Voth G A, Salvador P, Dannenberg J J, Dapprich S, Daniels A D, Farkas Ö, Foresman J B, Ortiz J V, Cioslowski J and Fox D J 2009 *Gaussian, Inc.* Wallingford CT
46. Becke A D 1988 *Phys. Rev. A* **38** 3098
47. Becke A D 1993 *J. Chem. Phys.* **98** 5648
48. Lee C, Yang W and Parr R G 1998 *Phys. Rev. A* **37** 785
49. Hay P J and Wadt W R 1985 *J. Chem. Phys.* **82** 270
50. Hay P J and Wadt W R 1985 *J. Chem. Phys.* **82** 299
51. Dunning Jr. T H and Hay P J 1977 In *Methods of Electronic Structure Theory* Vol. 3 H F Schaeffer (Ed.) (Plenum Press: New York)
52. Wolinski K, Hinton J F and Pulay P 1990 *J. Am. Chem. Soc.* **112** 8251
53. Cheeseman J R, Trucks G W, Keith T A and Frisch M J 1996 *J. Chem. Phys.* **104** 5497
54. Ezzaher S, Gogoll A, Bruhn C and Ott S 2010 *Chem. Commun.* **46** 5775
55. Ezzaher S, Capon J-F, Gloaguen F, Pétilion F Y, Schollhammer P, Talarmin J, Pichon R and Kervarec N 2007 *Inorg. Chem.* **46** 3426
56. Zhao Z, Wang M, Dong W, Li P, Yu Z and Sun L 2009 *J. Organomet. Chem.* **694** 2309
57. Adam F I, Hogarth G, Kabir S E and Richards I 2008 *C. R. Chim.* **11** 890
58. Song L C, Ge J H, Zhang X G, Liu Y and Hu Q M 2006 *Eur. J. Inorg. Chem.* 3204