King's Research Portal

DOI:

[10.1016/j.ica.2018.11.002](https://doi.org/10.1016/j.ica.2018.11.002)

Document Version

Peer reviewed version

[Link to publication record in King's Research Portal](#)

Citation for published version (APA):

Ghosh, S., Rana, S., Kabir, S. E., Richmond, M. G., & Hogarth, G. (2019). Highly efficient electrocatalytic proton-reduction by coordinatively and electronically unsaturated Fe(CO)(2-dppn)(2-tdt). *INORGANICA CHIMICA ACTA*, 486, 435-440. <https://doi.org/10.1016/j.ica.2018.11.002>

Citing this paper

Please note that where the full-text provided on King's Research Portal is the Author Accepted Manuscript or Post-Print version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version for pagination, volume/issue, and date of publication details. And where the final published version is provided on the Research Portal, if citing you are again advised to check the publisher's website for any subsequent corrections.

General rights

Copyright and moral rights for the publications made accessible in the Research Portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognize and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the Research Portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the Research Portal

Take down policy

If you believe that this document breaches copyright please contact librarypure@kcl.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Accepted Manuscript

Research paper

Highly efficient electrocatalytic proton-reduction by coordinatively and electronically unsaturated $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$

Shishir Ghosh, Shahed Rana, Shariff E. Kabir, Michael G. Richmond, Graeme Hogarth

PII: S0020-1693(18)31358-6
DOI: <https://doi.org/10.1016/j.ica.2018.11.002>
Reference: ICA 18617

To appear in: *Inorganica Chimica Acta*

Received Date: 30 August 2018
Revised Date: 2 November 2018
Accepted Date: 4 November 2018

Please cite this article as: S. Ghosh, S. Rana, S.E. Kabir, M.G. Richmond, G. Hogarth, Highly efficient electrocatalytic proton-reduction by coordinatively and electronically unsaturated $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$, *Inorganica Chimica Acta* (2018), doi: <https://doi.org/10.1016/j.ica.2018.11.002>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Highly efficient electrocatalytic proton-reduction by coordinatively and electronically unsaturated $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$

Shishir Ghosh^{a,b,c,*}, Shahed Rana^b, Shariff E. Kabir^b, Michael G. Richmond^d, Graeme Hogarth^{a*}

^a Department of Chemistry, King's College London, Britannia House, 7 Trinity Street, London SE1 1DB, UK

^b Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh

^c Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

^d Department of Chemistry, University of North Texas, 1155 Union Circle, Box 305070, Denton, TX 76203, USA

E-mail: sghosh_006@yahoo.com, graeme.hogarth@kcl.ac.uk

Abstract

Coordinatively and electronically unsaturated square-pyramidal $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$ (**2**) is shown to be amongst the most efficient proton-reduction catalysts reported to date. It is formed from the reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-tdt})$ ($\text{tdt} = 3,4\text{-toluenedithiolate}$) with 1,8-bis(diphenylphosphino)naphthalene (dppn) in presence of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ affording $\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppn})(\mu\text{-tdt})$ (**1**) as the major product, together with smaller but reproducible amounts of **2**. Both have been characterized by single crystal X-ray diffraction. The electrochemistry of **2** is solvent dependent but in both CH_2Cl_2 and in a 1:1 mixture of $\text{CH}_2\text{Cl}_2/\text{MeCN}$ it shows a reversible reduction at $E_{1/2} = -1.54$ V and $E_{1/2} = -1.68$ V respectively. While **2** degrades in the presence of the strong acid $\text{HBF}_4\cdot 2\text{H}_2\text{O}$ it is catalytically active for proton-reduction using $\text{CF}_3\text{CO}_2\text{H}$. Catalysis occurs at the first reduction potential and it displays an impressive $i_{\text{cat}}/i_{\text{p}}$ ratio of 33 after addition of 20 equivalents $\text{CF}_3\text{CO}_2\text{H}$. It is amongst the most efficient molecular proton-reduction catalysts reported to date.

Keywords: Square-pyramidal; proton reduction; diphosphine; redox-active ligand; DFT

1. Introduction

The development of mononuclear iron complexes as electrocatalysts for proton-reduction is spurred on by the findings that mononuclear cobalt and nickel complexes can act as efficient catalysts for this transformation as can dithiolate-bridged diiron biomimetics of the [FeFe]-hydrogenases [1-10]. While formally electronically saturated diiron biomimics can bind a proton across the iron-iron bond, coordinatively saturated mononuclear species don't contain a free coordination site and hence a typical feature of such catalysts is reduction-induced ligand loss. Thus coordinatively unsaturated mononuclear complexes are particularly attractive targets and recently square-pyramidal iron complexes have been shown to be catalytically active by both Ott [6,7] and Jones [8] (Chart). Such systems are attractive as they operate at relatively mild reduction potentials, appear to be more robust than related diiron complexes with respect to degradation during catalysis, and hydrogen formation can be achieved using a wide range of acids.

Chart Square-pyramidal iron complexes previously used as electrocatalysts for proton-reduction [6-8].

The diphosphine, 1,8-bis(diphenylphosphino)naphthalene (dppn), has attracted considerable interest as a chelating ligand due to its rigid naphthalene backbone [14-26]. During our investigations on dithiolate-bridged diiron chelate complexes, we found from the reaction of

$\text{Fe}_2(\text{CO})_6(\mu\text{-tdt})$ and dppn, in addition to the expected diiron product $\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppn})(\mu\text{-tdt})$ (**1**), small amounts of $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$ (**2**) were also formed. The highly delocalized nature of bonding in this complex, involving both chelating ligands, makes it significantly different from those studied previously [6-8] prompting us to investigate its electrocatalytic properties, the results of which are detailed herein.

2. Results and discussion

2.1. Synthesis and structure

The $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ initiated reaction between $\text{Fe}_2(\text{CO})_6(\mu\text{-tdt})$ [27] and dppn in boiling MeCN afforded binuclear $\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppn})(\mu\text{-tdt})$ (**1**) (35%) together with smaller amounts of 16-electron mononuclear $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$ (**2**) (12%) (Scheme 1). Characterisation of both was made primarily on the basis of their crystal structure as shown in Figs. 1 and 2. Complex **1** contains a diiron framework linked by a tdt-bridge. The diphosphine chelates one iron centre, Fe(1), occupying apical-basal coordination sites with a bite angle of $87.41(3)^\circ$ [Fe(1)–P(1) 2.1913(8) and Fe(1)–P(2) 2.1948(8) Å]. The Fe–Fe vector [2.5282(5) Å] is slightly elongated as compared to that in $\text{Fe}_2(\text{CO})_6(\mu\text{-tdt})$ [2.4754(14) Å] [27] and consequently Fe–S bond distances [av. 2.278(8) Å] are also slightly longer than those in $\text{Fe}_2(\text{CO})_6(\mu\text{-tdt})$ [av. 2.267(2) Å] [27]. The IR spectrum of **1** shows absorption bands at 2021s, 1950m and 1907w cm^{-1} , characteristic of $\text{Fe}_2(\text{CO})_4(\kappa^2\text{-diphosphine})(\mu\text{-dithiolate})$ complexes, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at δ 69.5 due to rapid apical-basal site interconversion at room temperature.

Scheme 1 Synthesis of $\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppn})(\mu\text{-tdt})$ (**1**) and $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$ (**2**).

Complex **2** co-crystallises with a molecule of chloroform and there are two short interactions between the hydrogen of this and a sulfur (2.669 Å) and carbon (2.857 Å) of the dithiolate

ligand. Complex **2** favours square-pyramidal geometry over trigonal-bipyramidal arrangement in the solid-state with the carbonyl ligand in apical position. The diphosphine and dithiolate ligands constitute the base of the pyramid and lie mutually *trans*. Metric parameters are very similar to those of related square-pyramidal complexes reported by Ott [6,7] and Jones [8].

Fig. 1. ORTEP diagram of **1** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°): Fe(1)–Fe(2) 2.5282(5), Fe(1)–P(1) 2.1913(8), Fe(1)–P(2) 2.1948(8), Fe(1)–S(1) 2.2891(7), Fe(1)–S(2) 2.2680(7), Fe(2)–S(1) 2.2704(8), Fe(2)–S(2) 2.2825(8), P(1)–Fe(1)–P(2) 87.41(3), P(1)–Fe(1)–Fe(2) 154.88(3), P(2)–Fe(1)–Fe(2) 112.55(2), P(1)–Fe(1)–C(1) 94.25(9), P(2)–Fe(1)–C(1) 89.14(9), P(1)–Fe(1)–S(1) 107.64(3), P(1)–Fe(1)–S(2) 104.82(3), S(1)–Fe(1)–S(2) 79.94(3), S(1)–Fe(2)–S(2) 80.04(3), S(1)–Fe(1)–Fe(2) 55.97(2), S(1)–Fe(2)–Fe(1) 56.68(2).

Theoretical studies [7] show that simple monodentate phosphines favour hexa-coordinate complexes in reaction with dithiolate-bridged diiron complexes as the loss of CO from these octahedral complexes is energetically unfavourable, whereas the use of strongly chelating diphosphines leads to selective formation of penta-coordinate square-pyramidal complexes. Spectroscopic data for **2** are in accord with the solid-state structure. The IR spectrum shows single carbonyl absorption at 1918 cm⁻¹, being similar to those observed for related complexes [6-8]. On the basis of the solid-state structure, the two phosphorus atoms of the dppn ligand would be expected to be inequivalent, but the ³¹P{¹H} NMR spectrum shows only a singlet at 67.9 ppm (at room temperature). This suggests that **2** is fluxional in solution

interchanging between square-pyramidal (2_{sp}) and trigonal-bipyramidal (2_{tbp}) geometries *via* a Berry pseudo-rotation. In support of this, Jones found that while $\text{Fe}(\text{CO})\{\kappa^2\text{-(Ph}_2\text{PCH}_2)_2\text{NCH}_2\text{C}_2\text{Me}\}(\kappa^2\text{-bdt)}$ (Chart) was square-planar in the solid state, the bis(diphenylphosphino)ferrocene (dppf) derivative (not shown) adopts a trigonal-bipyramidal geometry, with DFT studies revealing a small (*ca.* 6.6 kcalmol⁻¹) energy difference between conformers [7].

Fig. 2. ORTEP diagram of **2** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°): Fe(1)–P(1) 2.2049(7), Fe(1)–P(2) 2.1939(8), Fe(1)–S(1) 2.1889(8), Fe(1)–S(2) 2.2029(7), Fe(1)–C(1) 1.722(3), P(1)–Fe(1)–P(2) 87.97(3), S(1)–Fe(1)–S(2) 88.98(3), P(1)–Fe(1)–S(1) 88.10(3), P(2)–Fe(1)–S(2) 88.62(3), P(1)–Fe(1)–S(2) 166.59(3), P(2)–Fe(1)–S(1) 152.59(3), C(1)–Fe(1)–P(1) 90.51(9), C(1)–Fe(1)–P(2) 93.58(10), C(1)–Fe(1)–S(1) 113.57(10), C(1)–Fe(1)–S(2) 102.64(9).

2.2. Electrochemistry and DFT calculations

The redox chemistry of **2** was studied by cyclic voltammetry in both CH_2Cl_2 and a 1:1 mixture of $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (the complex is sparingly soluble in MeCN). The CV of **2** in CH_2Cl_2 at 0.1 V/s shows a reversible reduction at $E_{1/2} = -1.54$ V ($i_{\text{an}}/i_{\text{ca}} \sim 1$) and an irreversible oxidation at $E_p = 0.57$ V (Fig. 3) and a reductive feature was observed at $E_p = -0.23$ V on the return scan associated with the irreversible oxidation process (Fig. S1).

Fig. 3. CV of **2** in CH_2Cl_2 (1 mM solution, supporting electrolyte $[\text{NBu}_4][\text{PF}_6]$, scan rate 0.1 V s^{-1} , glassy carbon electrode, potential vs Fc^+/Fc).

The oxidative wave shows some reversibility at higher scan rates ($\geq 0.5 \text{ V/s}$), linear i_p vs $\sqrt{v}$ plots indicating that both the reductive and oxidative processes are diffusion controlled (Figs. S2 and S3). The current function ($i_p/\sqrt{v}$) associated with reduction deviates from linearity at slow scan rates ($< 0.05 \text{ V/s}$), indicating that more than one electron may be involved in reduction at longer time scales (Fig. S4); otherwise reduction is a one-electron electrode process (in CH_2Cl_2). In a 1:1 mixture of $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (Fig. 4) some further redox features are observed, the first reversible reduction now appearing at $E_{1/2} = -1.68 \text{ V}$ ($i_{\text{an}}/i_{\text{ca}} \sim 0.7$). A second irreversible reduction wave was also now observed at $E_p = -2.21 \text{ V}$ together with two oxidative waves, a reversible oxidation at $E_{1/2} = 0.22 \text{ V}$ ($i_{\text{ca}}/i_{\text{an}} \sim 0.8$) followed by an irreversible wave at $E_p = 0.52 \text{ V}$. A small reductive feature on the return scan at $E_p = -0.47 \text{ V}$ being associated with the second (irreversible) oxidative wave (Fig. S5). The enhanced reversibility of the oxidation in MeCN is probably due to metal coordination generating $[\text{Fe}(\text{CO})(\text{NCMe})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})]^+$, which may be sufficiently basic to stabilise against CO loss; the second irreversible oxidation wave resulting from oxidation of this solvated species. No additional features were observed when the scan rate was varied between 0.025 to 0.5 V/s (Fig. S6) and the peak current of the reversible processes exhibit a linear relationship with the square root of scan rate suggesting that both processes are diffusion controlled (Fig. S7). The current function ($i_p/\sqrt{v}$) associated with the first reductive process shows only slight deviation from linearity at very slow scan rates ($< 0.05 \text{ V/s}$), indicating that the first reduction in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ is a one-electron electrode process (Fig. S4).

Fig. 4. CV of **2** in a 1:1 mixture of $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (1 mM solution, supporting electrolyte $[\text{NBu}_4][\text{PF}_6]$, scan rate 0.1 Vs^{-1} , glassy carbon electrode, potential vs Fc^+/Fc).

To gain insight into the redox processes we have calculated the ground state electronic structure of **2** and also the radical anion $\mathbf{2}^-$ using DFT calculations. The HOMO of **2** is delocalized over iron, one sulfur and the tolyl ring, whereas the LUMO is primarily localized on the naphthalene backbone of dppn with only a small contribution from iron (Fig. 5). Reduction of **2** results in structural modification from favoured square-pyramidal structure to a trigonal bipyramidal conformation in $\mathbf{2}^-$. The HOMO of $\mathbf{2}^-$ is similar to that in **2**, whereas the SOMO is again primarily localized on the naphthalene backbone of dppn ligand (Fig. 5). The HOMO-LUMO gap in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (1.90 V) is *ca.* 0.2 V smaller than in CH_2Cl_2 (2.11 V), which is expected due to the coordinating nature of MeCN, which also stabilizes ionic species.

Fig. 5. HOMO (left) and LUMO (right) of **2** (top) and HOMO (left) and SOMO (right) **2^{•-}** (bottom) (orbitals are printed with an isovalue of 0.55).

2.3. Proton-reduction catalysis

Mononuclear **2** is not protonated by a range of acids and the DFT calculations suggest that reduction is primarily ligand based, and hence it might not be expected to be an efficient proton reduction catalyst. Nevertheless, the proton reduction by **2** was tested in a 1:1 mixture of CH₂Cl₂/MeCN using CF₃CO₂H and somewhat surprisingly was found to be an efficient catalyst at around the first reduction potential (Figs. 6 and S8). Upon addition of CF₃CO₂H, two new reduction peaks were observed at $E_p = -1.60$ and -1.70 V (Fig. 6a) the first of which we assume corresponds to the reduction of **2** to **2^{•-}** (as the reduction potential often displays a slight positive shift in presence of acid). At lower acid concentrations, the peak height of the first reduction was smaller than that of the second, but the peak height of the former increases as the concentration of acid is increased and surpasses the later with 10 equivalents of CF₃CO₂H, both peaks merging at higher acid concentrations (Fig. 6b). Similar behaviour was noted by Jones for related Fe(CO)(κ^2 -diphosphine)(κ^2 -bdt) complexes at low *p*-TsOH concentrations [7]. Since **2** does not protonate by CF₃CO₂H, then an EC mechanism is expected; reduction at $E_p = -1.60$ V generating **2^{•-}** being likely followed by rapid protonation to give HFe(CO)(κ^2 -dppn)(κ^2 -tdt) (**2H**). Thus, although DFT calculations suggest that the reduction of **2** is dppn-centred, the HOMO of the radical anion is partially based on iron which is necessary for metal protonation. An explanation for the two closely space catalytic events could be that different isomers of **2H** are accessible resulting from proton trapping of the anion before and after Berry pseudo-rotation. Processes occurring after the initial

protonation are not accessible to us and in the absence of detailed DFT calculations we prefer not to speculate on later parts of the catalytic cycle.

Fig. 6. CVs of **2** – (a) in the absence acid and in the presence of 1-7 equivalents of $\text{CF}_3\text{CO}_2\text{H}$, (b) in the absence acid and in the presence of 1-7, 9, 10, 12, 16 and 20 equivalents of $\text{CF}_3\text{CO}_2\text{H}$ (in 1:1 $\text{CH}_2\text{Cl}_2/\text{MeCN}$, 1 mM solution, supporting electrolyte $[\text{NBu}_4][\text{PF}_6]$, scan rate 0.1 V s^{-1} , glassy carbon electrode, potential vs Fc^+/Fc). Response of 20 equivalents $\text{CF}_3\text{CO}_2\text{H}$ alone is shown with the red dashed line.

Fig. 7 shows a plot of catalytic current/noncatalytic current ratio ($i_{\text{cat}}/i_{\text{p}}$) vs acid concentration for the first catalytic wave. The $i_{\text{cat}}/i_{\text{p}}$ value (used to measure the efficiency of a catalyst) increases to 33 after addition of 20 equivalents $\text{CF}_3\text{CO}_2\text{H}$, being similar to the most efficient cobalt and nickel mononuclear catalysts such as $(\text{dmgBF}_2)_2\text{Co}(\text{NCMe})_2$ (dmgBF_2 = difluoroboryl-dimethylglyoxime) ($i_{\text{cat}}/i_{\text{p}} \sim 30$) [28], $[(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}})_2\text{Co}(\text{MeCN})_3]^{2+}$ ($\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}$ = 1,3,6-triphenyl-1-aza-3,6-diphosphacycloheptane) ($i_{\text{cat}}/i_{\text{p}} \sim 30$) [29] and $[(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}})\text{Ni}]^{2+}$ ($i_{\text{cat}}/i_{\text{p}}$ 38) [30].

Fig. 7. Dependence of i_{cat}/i_p on CF_3CO_2H concentration for **2** at potentials of the first catalytic wave (in 1:1 $CH_2Cl_2/MeCN$, 1 mM solution, 1-20 equivalents $HBF_4 \cdot Et_2O$, supporting electrolyte $[NBu_4][PF_6]$, scan rate 0.1 Vs^{-1} , glassy carbon electrode).

3. Conclusions

In summary, coordinatively and electronically unsaturated square-pyramidal $Fe(CO)(\kappa^2\text{-dppn})(\kappa^2\text{-tbt})$ (**2**) has been synthesised and structurally characterised. It adopts a square-pyramidal geometry in the solid-state but is fluxional in solution being proposed to interconvert with a trigonal bipyramidal isomer. Cyclic voltammetry shows that it undergoes a reversible one-electron reduction, with DFT calculations showing that this is primarily ligand-based, the added electron being delocalised over the naphthalene backbone of the dppn ligand. This marks **2** out as being significantly different to related $Fe(CO)(\kappa^2\text{-diphosphine})(\kappa^2\text{-dithiolate})$ complexes studied as proton-reduction catalysts, where the LUMO is primarily metal-centred and hence reduction affords an $Fe(I)$ radical anion [6-8]. Nevertheless, **2** is found to be a highly efficient proton-reduction catalyst generating hydrogen from CF_3CO_2H at relatively mild potentials. Work is continuing to address the mechanism of proton-reduction, especially regarding the role of the redox-active dppn ligand [31], and hence to further develop this class of coordinatively and electronically unsaturated complexes as proton-reduction catalysts.

4. Experimental

4.1. General

Unless otherwise stated, all manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Reagent-grade solvents were dried using appropriate drying agents and distilled prior to use by standard methods. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Bruker DPX 400 instrument. Elemental analysis was performed by Microanalytical Laboratories, University College London. $\text{Fe}_2(\text{CO})_6(\mu\text{-tdt})$ was prepared according to a published procedure [32].

4.2. Reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-tdt})$ with dppn

An acetonitrile solution (15 mL) of $\text{Fe}_2(\text{CO})_6(\mu\text{-tdt})$ (100 mg, 0.23 mmol), $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (18 mg, 0.23 mmol) and dppn (114 mg, 0.23 mmol) was heated to reflux for 1 h. The reaction mixture was then allowed to cool at room temperature. The solvent was removed by rotary evaporation under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (4:1, v/v) developed two bands. The red band gave $\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppn})(\mu\text{-tdt})$ (**1**) (70 mg, 35 %) as deep red crystals, while the green band gave $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$ (**2**) (20 mg, 12%) as dark green crystals after recrystallization from hexane/ CH_2Cl_2 at 4 °C. Data for **1**: Anal. calc. for $\text{C}_{45}\text{H}_{32}\text{Fe}_2\text{O}_4\text{P}_2\text{S}_2$ (found): C 61.80 (62.39), H 3.69 (3.76). IR (νCO)(CH_2Cl_2): 2021s, 1950m, 1907w cm^{-1} . ^1H NMR (CDCl_3): δ 8.12 (d, J 8.0, 2H), 7.92 (d, J 8.0, 1H), 7.88 (s, 1H), 7.48 (m, 13H), 6.89 (m, 3H), 6.66 (m, 9H), 2.34 (3H, s). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 69.5 (s). Data for **2**: Anal. calc. for $\text{C}_{42}\text{H}_{32}\text{FeOP}_2\text{S}_2\cdot\text{CHCl}_3$ (found): C 60.48 (60.93), H 3.89 (3.97). IR (νCO)(CH_2Cl_2): 1918s cm^{-1} . ^1H NMR (CDCl_3): δ 8.16 (d, J 7.04 Hz, 2H), 7.96 (d, J 8.08 Hz, 2H), 7.91 (s, 1H), 7.58-7.51 (m, 14H), 6.95 (m, 3H), 6.69 (m, 7H), 2.37 (s, 3H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 67.9 (s).

4.3. Crystal structure determinations

Single crystals of **1** and **2** suitable for diffraction analysis were grown by slow diffusion of hexane into a dichloromethane solution at 4 °C. All geometric and crystallographic data for **1** were collected at 150 K on a Bruker SMART APEX CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$). Data collection, indexing and initial cell refinements were all done using SMART [33] software. Data reduction were carried out with SAINT PLUS [34] and absorption corrections applied using the programme SADABS [35]. Structures were solved

by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package [36]. A suitable single crystal of **2** was mounted on an Agilent Super Nova dual diffractometer (Agilent Technologies Inc., Santa Clara, CA) using a Nylon Loop and the diffraction data were collected at 134(1) K using Cu-K α radiation ($\lambda = 1.54184$). Unit cell determination, data reduction, and absorption corrections were carried out using CrysAlisPro [37]. The structures were solved with the ShelXS [36] structure solution program by direct methods and refined with the XL [36] refinement package using Least Squares minimisation within the OLEX2 [38] graphical user interface. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included using a riding model. The details of the data collection and structure refinement are given in Table 1.

4.4. Density functional theory (DFT) calculations

All calculations were performed with the hybrid DFT functional B3LYP, as implemented by the Gaussian 09 program package [39]. This functional utilizes the Becke three-parameter exchange functional (B3) [40], combined with the correlation functional of Lee, Yang and Parr (LYP) [41]. The iron atom was described by Stuttgart–Dresden effective core potential (ecp) and SDD basis set, while the 6-31+G(d') basis set was employed for the remaining atoms. All computed species were established as intermediates or minima based on zero imaginary frequencies (positive eigenvalues). The computed frequencies were used to make zero-point and thermal corrections to the electronic energies; the reported energies are quoted in kJ mol⁻¹ relative to the specified standard. The natural charges and Wiberg bond indices reported here were computed using Weinhold's natural bond orbital (NBO) program [42,43]. The geometry-optimized structures have been drawn with the JIMP2 molecular visualization and manipulation program [44,45].

4.5. Electrochemical Studies

Electrochemistry was carried out either in deoxygenated CH₂Cl₂ or a 1:1 mixture of CH₂Cl₂/MeCN with 0.1 M TBAPF₆ as the supporting electrolyte. The working electrode was a 3 mm diameter glassy carbon electrode that was polished with 0.3 μ m alumina slurry prior to each scan. The counter electrode was a Pt wire and the quasi-reference electrode was a

silver wire. All CVs were referenced to the Fc^+/Fc redox couple. An Autolab potentiostat (EcoChemie, Netherlands) was used for all electrochemical measurements. Catalysis studies were carried out by adding equivalents of $\text{CF}_3\text{CO}_2\text{H}$ (Sigma-Aldrich).

Acknowledgements

We thank the Commonwealth Scholarship Commission for the award of a Commonwealth Scholarship to SG. MGR acknowledges financial support from the Robert A. Welch Foundation (Grant B-1093) and the NSF (CHE-0741936). Prof. Michael B. Hall (TAMU) is thanked for providing us a copy of his JIMP2 program, which was used to prepare the geometry optimized structures reported here. GH thanks King's College London for Funding.

Appendix A. Supplementary material

CCDC 1825298 (for **1**) and CCDC 1825299 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystallographic data for **1** and **2**

Compound	1	2
Empirical formula	C ₄₅ H ₃₂ Fe ₂ O ₄ P ₂ S ₂	C ₄₂ H ₃₂ FeOP ₂ S ₂ ·CHCl ₃
Formula weight	874.47	853.95
Temp (K)	150 (2)	134(1)
Wavelength (Å)	0.71073	1.54184
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ /c
<i>a</i> (Å)	10.6010(9)	15.78692(17)
<i>b</i> (Å)	13.1222(11)	13.69980(17)
<i>c</i> (Å)	15.4847(13)	18.0806(2)
α (°)	91.417(2)	90
β (°)	106.046(1)	102.5994(11)
γ (°)	108.993(1)	90
Volume (Å ³)	1941.8(3)	3816.27(8)
<i>Z</i>	2	4
Calculated density (gcm ⁻³)	1.496	1.486
Absorption coefficient (mm ⁻¹)	0.982	7.191
<i>F</i> (000)	896	1752
Crystal size (mm ³)	0.10 × 0.09 × 0.04	0.27 × 0.11 × 0.05
2 θ range for data collection (°)	5.52 to 56.52	8.17 to 134.984
Index ranges	-14 ≤ <i>h</i> ≤ 14 -17 ≤ <i>k</i> ≤ 17 -20 ≤ <i>l</i> ≤ 20	-18 ≤ <i>h</i> ≤ 18 -16 ≤ <i>k</i> ≤ 10 -19 ≤ <i>l</i> ≤ 21
Reflections collected	17013	12220
Independent reflections (<i>R</i> _{int})	8946 (<i>R</i> _{int} = 0.0303)	6718 (<i>R</i> _{int} = 0.0364)
Data/restraints/parameters	8946 / 0 / 496	6718 / 0 / 470
Goodness-of-fit on <i>F</i> ²	1.068	1.036
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0471, <i>wR</i> ₂ = 0.0988	<i>R</i> ₁ = 0.0426, <i>wR</i> ₂ = 0.1036
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.04603, <i>wR</i> ₂ = 0.1041	<i>R</i> ₁ = 0.0517, <i>wR</i> ₂ = 0.1116
Largest difference in peak and hole (e Å ⁻³)	0.548 and -0.361	0.70 and -0.53

References

- 1 I. Bhugun, D. Lexa and J.-M. Saveant, *J. Am. Chem. Soc.*, 1996, **118**, 3982-3983.
- 2 M.J. Rose, H.B. Gray and J.R. Winkler, *J. Am. Chem. Soc.*, 2012, **134**, 8310-8313.
- 3 V. Artero and M. Fontecave, *C. R. Chimie*, 2008, **11**, 926-931.
- 4 G.P. Connor, K.J. Mayer, C.S. Tribble and W.R. McNamara, *Inorg. Chem.*, 53 (2014) 5408-5410.
- 5 S. Kaur-Ghumaan, L. Schwartz, R. Lomoth, M. Stein and S. Ott, *Angew. Chem. Int. Ed.*, 2010, **49**, 8033-8036.
- 6 M. Beyler, S. Ezzaher, M. Karnahl, M.-P. Santoni, R. Lomoth and S. Ott, *Chem. Commun.*, 2011, **47**, 11662-11664.
- 7 A. Orthaber, M. Karnahl, S. Tschierlei, D. Streich, M. Stein and S. Ott, *Dalton Trans.*, 2014, **43**, 4537-4549.
- 8 S. Roy, S.K.S. Mazinani, T.L. Groy, L. Gan, P. Tarakeshwar, V. Mujica and A.K. Jones, *Inorg. Chem.*, 2014, **53**, 8919-8929.
- 9 L. Gan, T.L. Groy, P. Tarakeshwar, S.K.S. Mazinani, J. Shearer, V. Mujica and A.K. Jones, *J. Am. Chem. Soc.*, 2015, **137**, 1109-1115.
- 10 G.-G. Luo, Y.-H. Wang, J.-H. Wang, J.-H. Wu and R.-B. Wu, *Chem. Commun.*, 2017, **53**, 7007-7010.
- 11 S. Gao, J. Fan, S. Sun, F. Song, X. Peng, Q. Duan, D. Jiang and Q. Liang, *Dalton Trans.*, 2012, **41**, 12064-12074.
- 12 A. Rana, B. Mondal, P. Sen, S. Dey and A. Dey, *Inorg. Chem.*, 2017, **56**, 1783-1793.
- 13 S. Ghosh, N. Hollingsworth, M. Warren, K.B. Holt and G. Hogarth, *Polyhedron*, 2017, **137**, 140-146.
- 14 V.W.-W. Yam and S.W.-K. Choi, *J. Chem. Soc., Dalton Trans.*, 1996, 4227-4232.
- 15 S.L. James, A.G. Orpen and P.G. Pringle, *J. Organomet. Chem.*, 1996, **525**, 299-301.
- 16 V.W.-W. Yam, C.-L. Chan, S.W.-K. Choi, K.M.-C. Wong, E.C.-C. Cheng, S.-C. Yu, P.-K. Ng, W.-K. Chan and K.-K. Cheung, *Chem. Commun.*, 2000, **1**, 53-54.
- 17 V.W.-W. Yam, C.-K. Li, C.-L. Chan and K.-K. Cheung, *Inorg. Chem.*, 2001, **40**, 7054-7058.
- 18 M.I. Bruce, P.A. Humphrey, S. Okucu, R. Schmutzler, B.W. Skelton and A.H. White, *Inorg. Chim. Acta*, 2004, **357**, 1805-1812.

- 19 M.I. Bruce, P.A. Humphrey, R. Schmutzler, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, 2004, **689**, 2415-2420.
- 20 W.H. Watson, S. Kandala and M.G. Richmond, *J. Organomet. Chem.*, 2007, **692**, 968-975.
- 21 V.N. Nesterov, W.H. Watson, S. Kandala and M.G. Richmond, *Polyhedron*, 2007, **26**, 3602-3608.
- 22 S.E. Kabir, F. Ahmed, S. Ghosh, M.R. Hassan, M.S. Islam, A. Sharmin, D.A. Tocher, D.T. Haworth, S.V. Lindeman and T.A. Siddiquee, *J. Organomet. Chem.*, 2008, **693**, 2657-2665.
- 23 S. Ghosh, G. Hogarth, S.E. Kabir, A.L. Miah, L. Salassa, S. Sharmin and C. Garino, *Organometallics*, 2009, **28**, 7047-7052.
- 24 A. Rahaman, F.R. Alam, S. Ghosh, D.A. Tocher, M. Haukka, S.E. Kabir, E. Nordlander and G. Hogarth, *J. Organomet. Chem.*, 2014, **751**, 326-335.
- 25 A. Rahaman, S. Ghosh, D.G. Unwin, S. Basak-Modi, K.B. Holt, S.E. Kabir, E. Nordlander, M.G. Richmond and G. Hogarth, *Organometallics*, 2014, **33**, 1356-1366.
- 26 J.M. Camara and T.B. Rauchfuss, *J. Am. Chem. Soc.*, 2011, **133**, 8098-8101.
- 27 M.M. Hassan, M.B. Hursthouse, S.E. Kabir and K.M.A. Malik, *Polyhedron*, 2001, **20**, 97-101.
- 28 X. Hu, B. S. Brunschwig and J. C. Peters, *J. Am. Chem. Soc.*, 2007, **129**, 8988-8998.
- 29 G.M. Jacobsen, J.Y. Yang, B. Twamley, A.D. Wilson, R.M. Bullock, M. Rakowski-DuBois and D.L. DuBois, *Energy Environ. Sci.*, 2008, **1**, 167-174.
- 30 M.L. Helm, M.P. Stewart, R.M. Bullock, M. Rakowski-DuBois and D.L. DuBois, *Science*, 2011, **333**, 863-866.
- 31 S. Ghosh, S. Rana, N. Hollingsworth, M.G. Richmond, S.E. Kabir and G. Hogarth, *Inorganics*, submitted.
- 32 R.B. King, *J. Am. Chem. Soc.*, 1963, **85**, 1584-1587.
- 33 SMART Version 5.628; Bruker AXS, Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373, 2003.
- 34 SAINT Version 6.36A; Bruker AXS, Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373, 2002.
- 35 G.M. Sheldrick, SADABS Version 2.10; University of Göttingen, Göttingen, Germany, 2003.
- 36 G.M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122.
- 37 CrysAlisPro; Oxford Diffraction: Yarnton, England, 2015.

- 38 O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
- 39 M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski and D.J. Fox, GAUSSIAN 09 (Revision A.02), Gaussian, Inc., Wallingford, CT, 2009.
- 40 A.D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
- 41 C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785-789.
- 42 A.E. Reed, L.A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899-926.
- 43 K.B. Wiberg, *Tetrahedron*, 1968, **24**, 1083-1096.
- 44 JIMP2, version 0.091, a free program for the visualization and manipulation of molecules: M.B. Hall and R.F. Fenske, *Inorg. Chem.*, 1972, **11**, 768-775.
- 45 J. Manson, C.E. Webster and M.B. Hall, Texas A&M University, College Station, TX, 2006, <http://www.chem.tamu.edu/jimp2/index.html>.

Graphic abstract

Coordinatively and electronically unsaturated square-pyramidal $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$ is shown to be amongst the most efficient proton-reduction catalysts reported to date. Catalysis occurs at the first reduction potential and it displays an impressive $i_{\text{cat}}/i_{\text{p}}$ ratio of 33 after addition of 20 equivalents $\text{CF}_3\text{CO}_2\text{H}$.

Graphic

Highlights

- Synthesis of coordinatively and electronically unsaturated $\text{Fe}(\text{CO})(\kappa^2\text{-dppn})(\kappa^2\text{-tdt})$
- CV and DFT studies reveal nature of mono-anion
- Efficient proton-reduction catalyst at first reduction potential

ACCEPTED MANUSCRIPT