Hydrogenase biomimetics: \( \text{Fe}_2(\text{CO})_4(\mu-\text{dppf})(\mu-\text{pdt}) \) (dppf = 1,1′-bis(diphenylphosphino)ferrocene) both a proton-reduction and hydrogen oxidation catalyst†

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\( \text{Fe}_2(\text{CO})_4(\mu-\text{dppf})(\mu-\text{pdt}) \) catalyses the conversion of protons and electrons into hydrogen and also the reverse reaction thus mimicking both types of binuclear hydrogenase enzymes.

Hydrogenases are enzymes capable of reversibly converting protons and electrons into hydrogen\(^2\) and over the past two decades their active sites have been discerned primarily from crystallographic studies,\(^2–4\) with three phylogenetically different enzyme types being identified. The two most widely studied of these are the so-called [FeFe]H\(_2\)ase and [NiFe]H\(_2\)ase enzymes (Chart 1) the active sites of which contain two transition metal atoms. Both enzyme types are able to catalyse both the reduction of protons and oxidation of hydrogen, [FeFe]H\(_2\)ase enzymes are more efficient with respect to the former, while [NiFe]H\(_2\)ase enzymes are favoured for the oxidation of hydrogen.\(^5\)

Over the past 15 years, a range of structural and functional biomimetics of the active sites of these enzymes have studied\(^5,6\) with key insights into the likely mechanism(s) being determined\(^7\) and recently some impressive turnovers for the electrocatalytic reduction of protons being reported.\(^8\) However, as far as we are aware, no biomimetic has yet been shown to both be catalytic for the reduction of protons and electrons to hydrogen and also the oxidation of hydrogen to protons and electrons.\(^9\) We herein describe Fe\(_2\)(CO)\(_4\)(\mu-\text{dppf})(\mu-\text{pdt})\) (dppf = 1,1′-bis(diphenylphosphino)ferrocene) which we have shown is a catalyst for both of these transformations.

Heating a toluene solution of equimolar amounts of Fe\(_2\)(CO)\(_4\)(\mu-\text{pdt})\) with dppf initially leads to formation of the linked tetranuclear complex \{Fe\(_2\)(CO)\(_4\)(\mu-\text{pdt})\}(\mu,\kappa^1,\kappa^1-\text{dppf})\) and unreacted dppf, which slowly rearranges to afford Fe\(_2\)(CO)\(_4\)(\mu-\text{dppf})(\mu-\text{pdt})\) in moderate yields\(^†\) as an air-stable orange solid (Scheme 1) being characterised by analytical and spectroscopic data together with a single-crystal X-ray diffraction study, the results of which are summarised in Fig. 1. The molecule is as expected and bond lengths and angles are generally within the ranges of those seen in related complexes.\(^10,11\) The iron–iron bond length of 2.6133(6) Å is, however, some 0.1 Å longer than is generally the case\(^10–12\) suggesting that the flexible nature of the dppf ligand allows this bond to relax. The non-bonding iron–iron interactions of 4.581 and 4.613 Å suggest that there is no direct contact between the two redox centres in the molecule.

Cyclic voltammograms (CVs) of 2 were recorded in acetonitrile at various scan rates as shown in Fig. 2. The complex undergoes an electrochemically reversible oxidation at \(E_{1/2} = 0.05\) V (\(\Delta E = 60\) mV) and a further reversible oxidation at \(E_{1/2} = 0.685\) V (\(\Delta E = 70\) mV). The former is associated with oxidation of the diiron centre and the latter most likely with the ferrocene moiety (see later). The reversibility of both oxidative processes is maintained at all scan rates. The complex also shows two overlapping irreversible reduction peaks at \(E_R = −2.10\) V and \(E_R = −2.19\) V which become separated at higher scan rates (≥0.25 V s\(^−1\)) (Fig. 2). Two small oxidation peaks are also

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**Scheme 1** Preparation of Fe\(_2\)(CO)\(_4\)(\mu-\text{dppf})(\mu-\text{pdt})\) (dppf = 1,1′-bis(diphenylphosphino)ferrocene).
observed at $E_p = -1.80$ V and $E_p = -1.53$ V on the return scan being due to the product formed in the reductive processes, whilst the small reduction peak appeared at $E_p = -0.35$ V on the return scan is associated with the first oxidation product.

Upon chemical oxidation, by addition of FePF$_6$ to a CH$_2$Cl$_2$ solution of 2, new IR absorption bands appear at 2044 and 2013 cm$^{-1}$ (Fig. S1, ESI†). The 60 cm$^{-1}$ shift of the first $\nu_{CO}$ band to higher energy is indicative of oxidation of the diiron centre allowing assignment of the FeII/III couple to 0.05 V.

The second oxidative reaction we believe is associated with the dppf ligand. Uncoordinated dppf undergoes an irreversible oxidation at 0.20 V which becomes reversible and shifts to more positive potentials upon coordination to a metal centre. The relative position of the second oxidative process vs. Fe$^2$/Fe and its chemical reversibility is consistent with the Fe$^{IV}$/III couple of the ferrocene moiety.

We next assessed the ability of 2 to bind a proton. Addition of one molar equivalent of HBF$_4$ Et$_2$O to a CH$_2$Cl$_2$ solution of 2 (or two to an MeCN solution) resulted in the rapid and clean formation of the cationic-hydride $\text{Fe}_2(\text{CO})_4(\mu-H)(\mu-\text{dppf})(\mu-\text{pdt})$ (BF$_4$)$_2$ (3). Further, and unlike most related cationic complexes, 11 addition of base leads to regeneration of the neutral complex. This suggests that while 2 is able to bind a proton, it is relatively weakly held. Related $\text{Fe}_2(\text{CO})_4(\mu-$diphosphine)(\mu-dithiolate) complexes do not generally form stable cationic hydrides, the exceptions being $\text{Fe}_2(\text{CO})_4(\mu-\text{C}_5\text{Me}_5\text{CH}_2\text{PEt}_2)$ (FcP*) as the intramolecular oxidant, the Fe$^{IV}$/III couple ($E_{1/2} = -0.59$ V) of which lies closer to the H$_2$/H$^+$ couple vs. the Fe$^{II}$/Fe couple. 18 They showed that the dication of $\text{Fe}_2(\text{CO})_4(\mu-$d-pdt)$\text{Fe}(\text{CO})_4(\mu-$d-pdt)$15 which either protonates or undergoes a further reduction before second protonation to liberate hydrogen. The peak heights of the oxidative processes do not change during the experiment showing the robustness of 2 under the operating conditions.

Complex 2 was first tested as a proton reduction catalyst in the presence of HBF$_4$ Et$_2$O in MeCN. Fig. 3 shows the CVs upon addition of between 1–10 equivalents of acid. A new reduction wave appears at $E_p = -1.70$ V upon addition of acid being associated with reduction of 3, its height growing with increasing amounts of acid, being characteristic of electrocatalytic proton reduction. At higher amounts of acid ($\geq 7$ molar equivalents) this wave splits into two distinct peaks possibly resulting from reduction of the putative cation $\text{HFe}_2(\text{CO})_4(\mu-H)(\mu-$dppf)(\mu-pdt)]$ (see below). Another catalytic wave is also observed at $E_p = -2.10$ V which competes with the direct reduction of HBF$_4$ Et$_2$O by the glassy carbon electrode as this electrode becomes catalytically active beyond ~2.00 V in presence of strong acids. 14 On the return scan a further catalytic wave is seen at $E_p = -1.55$ V implying that the species responsible for the first catalytic wave is regenerated. Thus it appears that 2 enters into the catalytic cycle via a CE mechanism to generate the neutral paramagnetic complex $\text{Fe}_2(\text{CO})_4(\mu-H)(\mu-$dppf)(\mu-pdt)]$ which either protonates or undergoes a further reduction before second protonation to liberate hydrogen. The peak heights of the oxidative processes do not change during the experiment showing the robustness of 2 under the operating conditions.

Recent developments in hydrogenase biomimics suggest that H$_2$ activation can be favoured by the presence of a mild and chemically inert oxidant in the diiron models. 16 The concept was recently experimentally implemented by Camara and Rauchfuss 17,18 who utilised ($\text{C}_5\text{Me}_5\text{Fe}(\text{C}_5\text{Me}_4\text{CH}_2\text{PEt}_2$ (FcP*)) as the intramolecular oxidant, the Fe$^{IV}$/III couple ($E_{1/2} = -0.59$ V) of which lies closer to the H$_2$/H$^+$ couple vs. the Fe$^{II}$/Fe couple. 18 They showed that the dication of $\text{Fe}_2(\text{CO})_4(\kappa^2-$Ph$_2$PCH$_2$CH$_2$) (A) cleaves H$_2$, being facilitated by an intramolecular electron-transfer in its doubly oxidised state, the electron transferring from the diiron unit to the pendant FcP* ligand i.e. switching from Fe(n)Fe(n)Fe(t) to Fe(n)Fe(t)Fe(n).18 In contrast, an analogue of A in which FeP* is replaced by PMe$_3$ is catalytically inactive towards H$_2$ oxidation.18 That there is electronic communication between the diiron core and the ferrocene in A despite the presence of a methylene linker unit prompted us to investigate the possibility of electronic communication between the two redox-active metal centres in 2. Indeed we found that 2 catalytically cleaves H$_2$ in presence of a base (pyridine) in its 2$^+$ state (Fig. 4). Thus, addition of equimolar amount of pyridine to an acetonitrile solution of 2

![Fig. 1 Molecular structure of 2. Selected bond lengths (Å) and bond angles (°): Fe(1)–Fe(2) 2.6133(6), Fe(1)–P(1) 2.2256(6), Fe(2)–P(2) 2.6797(6), P(1)–Fe(1)–S(1) 174.34(2), P(2)–Fe(2)–S(1) 167.79(2).](image1.png)

![Fig. 2 CVs of 2 in MeCN (1 mM solution, supporting electrolyte [NBu$_4$][PF$_6$]), glassy carbon electrode, potential vs. Fe$^2$/Fe at various scan rates.](image2.png)

![Fig. 3 CVs of 2 in the absence and presence of 1–10 molar equivalents of HBF$_4$ Et$_2$O (1 mM solution in MeCN, supporting electrolyte [NBu$_4$][PF$_6$]), scan rate 0.1 V s$^{-1}$, glassy carbon electrode, potential vs. Fe$^2$/Fe.](image3.png)
under H₂ results in an increase of the oxidative peak current of the second oxidation process of 2 by 10 μA, which reaches 22 μA upon addition of 10 equivalents of pyridine. No such catalytic wave was observed when the same experiment was carried out in absence of base (Fig. S5, ES†) or H₂ (Fig. S6, ES†). Similarly Fe₂(CO)₉[μ-P₃HCH₂P₃B]₂[μ-pdt]¹¹ does not show catalytic waves under the same conditions even when ferrocene is added. At this stage we do not have a clear view of the likely mechanism operating. It has been proposed¹⁸ and examined theoretically¹⁹ that A²⁺ heterolytically cleaves H₂ to afford a terminal hydride and nitrogen-bound proton. This clearly cannot occur in the case of 2 and thus we tentatively propose the intermediate formation of a cationic dilydride.

In summary we have shown that a biomimetic of the diiron hydrogenase can catalyse both the reduction of protons and H₂ oxidation. We are currently developing a range of related biomimetics containing different second redox-active centres²⁰ and using density functional theory calculations in order to more fully understand the electronic structure of 2²⁺ and the nature of the H₂ oxidation process.

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Notes and references

† Synthesis of 2. A mixture of 1 (0.10 g, 0.26 mmol) and dpff (0.14 g, 0.26 mmol) in toluene (100 ml) was heated at reflux for 5 d resulting in a colour change from orange to red-brown. After cooling to room temperature, volatiles were removed under reduced pressure to give a dark oily red solid (0.12 g, 52%).

‡ 1H NMR (CDCl₃) δ 8.01 (t, J = 8.2, 2H, Ph), 7.67–6.99 (m, 18H, Ph), 4.93 (brs, 2H, CH), 4.46 (s, 2H, CH), 4.44 (s, 2H, CH), 4.01 (s, 2H, CH), 2.60 (br, 2H, CH₂), 2.31 (m, 2H, CH₂), 2.13 (br, 2H, CH₂).

²³P{¹H}NMR (CDCl₃) 51.3 (s) ppm. Elemental analysis calc. for Fe₂(CO)₉[μ-P₃HCH₂P₃B] 2 = 0.091; found 0.092. 31P{¹H} NMR (CDCl₃) 44.8 (s) ppm.

Supplementary information is available at the ChemComm web site.


