Fe₂(CO)₄(μ-dppf)(μ-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 and over the past two decades their active sites have been discerned primarily from crystallographic studies, with three phylogenetically different enzyme types being identified. The two most widely studied of these are the so-called [FeFe]-H₂ase and [NiFe]-H₂ase enzymes (Chart 1) the active sites of which contain two transition metal atoms. While both enzyme types are able to catalyse both the reduction of protons and oxidation of hydrogen, [FeFe]-H₂ase enzymes are more efficient with respect to the former, while [NiFe]-H₂ase enzymes are favoured for the oxidation of hydrogen.

Over the past 15 years, a range of structural and functional biomimetics of the active sites of these enzymes have studied with key insights into the likely mechanism(s) being determined and recently some impressive turnovers for the electrocatalytic reduction of protons being reported. 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. We herein describe Fe₂(CO)₄(μ-dppf)(μ-pdt) (1) with dppf initially leads to formation of the linked tetranuclear complex Fe₂(CO)₄(μ-pdt)(μ,μ,μ,μ-dppf) and unreacted dppf, which slowly rearranges to afford Fe₂(CO)₄(μ-dppf)(μ-pdt) (2) 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. The iron–iron bond length of 2.6133(6) Å is, however, some 0.1 Å longer than is generally the case suggesting that the flexible nature of the dppf ligand allows this bond to relax. The non-bonding iron–iron distances 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 E₁/₂ = 0.05 V (ΔE = 60 mV) and a further reversible oxidation at E₁/₂ = 0.685 V (ΔE = 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 E₁/₂ = −2.10 V and E₁/₂ = −2.19 V which become separated at higher scan rates (≥0.25 V s⁻¹) (Fig. 2). Two small oxidation peaks are also present (0.05 V and 0.31 V) which become larger at higher scan rates (≥0.25 V s⁻¹) (Fig. 2).

As well as the redox processes, a single-wavelength electrochemical reaction was monitored at 110 °C and 5 d to investigate the catalytic nature of the complex. It was found that it reduces protons to produce molecular hydrogen. It is proposed that this process occurs at the Fe₄(pdt) site (Scheme 1) and that it is not due to the Fe₄(dppf) site.

Scheme 1 Preparation of Fe₂(CO)₄(μ-dppf)(μ-pdt).
Complex 2 was first tested as a proton reduction catalyst in the presence of HBF4Et2O 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 (≥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 HBF4Et2O 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 H2 activation can be favoured by the presence of a mild and chemically inert oxidant in the diiron models. The concept was recently experimentally implemented by Camara and Rauchfuss16 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 $\text{Fe}^{IIII}$ couple ($E_{1/2} = -0.59$ V) of which lies closer to the $\text{H}_{2}/\text{H}^+$ couple vs. the Fc'/Fc couple.18 They showed that the dication of $\text{Fe}_{2}(\text{CO})_{4}[\mu^{2-}\text{Ph}_{3}\text{PCH} = \text{CHPPPh}_{2})[\mu^{3-}\text{FeP}]^{+}[\mu-\text{SCH}_{2}\text{N(Bz)CH}_{2}\text{S}]^{-}$ (A) cleaves $\text{H}_{2}$, being facilitated by an intramolecular electron-transfer in its doubly oxidised state, the electron transferring from the diiron unit to the pendent Fc* ligand i.e. switching from Fe(n)Fe(n)Fe(i) to Fe(n)Fe(n)Fe(n).18 In contrast, an analogue of A in which Fe* is replaced by PMe3 is catalytically inactive towards $\text{H}_{2}$ oxidation. 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 $\text{H}_{2}$ in presence of a base (pyridine) in its $2^{2+}$ state (Fig. 4). Thus, addition of equimolar amount of pyridine to an acetonitrile solution of 2

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**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) 2.2679(6), P(1)‚Fe(1)‚S(1) 174.34(2), P(2)‚Fe(2)‚S(1) 167.79(2).

**Fig. 2** CVs of 2 in MeCN (1 mM solution, supporting electrolyte [NBu4][PF6]), glassy carbon electrode, potential vs. Fe+/Fc” at various scan rates.

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 FePF6 to a CH2Cl2 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 CO band to higher energy is indicative of oxidation of the diiron centre allowing assignment of the couple at 0.05 V vs. Fc”/Fc to this process. The second oxidation we believe is associated with the dpff ligand. Uncoordinated dpff undergoes an irreversible oxidation at 0.20 V which becomes reversible and shifts to more positive potentials upon coordination to a metal centre.13 The relative position of the second oxidative process vs. Fc”/Fc and its chemical reversibility is consistent with the Fe$^{IIII}$ couple of the ferrocene moiety.

We next assessed the ability of 2 to bind a proton. Addition of one molar equivalent of HBF4Et2O to a CH2Cl2 solution of 2 (or two to an MeCN solution) resulted in the rapid and clean formation of the cationic-hydride $\text{[Fe}_{2}(\text{CO})_{4}[\mu-H][\mu-dppf][\mu-pdt]]^{+}[\text{BF}_{4}]_{2}$ (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 $\text{Fe}_{2}(\text{CO})_{4}[\mu-\text{Cy}_{2}\text{PCH}_{2}\text{PCy}_{2}]$[µ-pdt] and $\text{Fe}_{2}(\text{CO})_{4}[\mu-\text{Ph}_{2}\text{P(CH}_{2})_{2}\text{PPPh}_{2}]$[µ-pdt] containing basic and flexible diphosphines respectively.11 Thus, the greater flexibility of dpff in 2 appears to be the reason for its ability to bind a proton.

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**Fig. 3** CVs of 2 in the absence and presence of 1–10 molar equivalents of HBF4Et2O (1 mM solution in MeCN, supporting electrolyte [NBu4][PF6]), scan rate 0.1 V s$^{-1}$, glassy carbon electrode, potential vs. Fe+/Fc”.

Complex 2 was first tested as a proton reduction catalyst in the presence of HBF4Et2O 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 (≥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 HBF4Et2O by the glassy carbon electrode as this electrode becomes catalytically active beyond ~2.00 V in presence of strong acids. 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.

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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, ESI†) or H₂ (Fig. S6, ESI†). Similarly Fe₂(μ-H₃PCH₂P̊P̊H₃)₂[μ-pd]²⁺ 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 dihydride.

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 bio-mimetics containing different secondary 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 dpdf (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 product, which reaches 22

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