



Fluorinated models of the iron-only hydrogenase: An electrochemical study of the influence of an electron-withdrawing bridge on the proton reduction overpotential and catalyst stability [☆]



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ABSTRACT

Here we report the synthesis, electrochemistry and electrocatalytic activity of $\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_6\text{F}_5)_2$ (**1**) where the highly fluorinated bridge is electron-withdrawing, resulting in decreased electron-density at the iron–iron bond. Additionally we discuss the related substituted complexes $\text{Fe}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-SC}_6\text{F}_5)_2$ (**2**) and $\text{Fe}_2(\text{CO})_4(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\mu\text{-SC}_6\text{F}_5)_2$ (**3**). As none of the complexes could be protonated in their neutral form it was found that proton reduction catalysis in the presence of strong acid (HBF_4) took place at the potential of the first reduction of complex **1** and **3**, following an EC mechanism. Complex **2** was unstable in the presence of strong acid. For **1** the potential at which proton reduction took place represented a relatively mild reduction potential (-1.15 V vs. Fc/Fc^+ in acetonitrile) that was comparable to examples of similar complexes in the literature. Complex **1** generated a small concentration of a highly catalytic species after electrochemical reduction, which we attribute to cleavage of the Fe–Fe bond and formation of a mono-nuclear iron species or to Fe–S bond breakage generating a vacant coordination site. The contributions to the catalytic currents were simulated using DigiSim, where it was found that the rate limiting step for **3** was the elimination of H_2 . It was also found that the highly catalytic species generated after reduction of **1** was more basic than $\mathbf{1}^-$ and also that protonation of this species was faster.

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1. Introduction

[Fe–Fe] hydrogenase enzymes rapidly and reversibly reduce protons to form hydrogen with negligible overpotential in neutral pH solution conditions [1]. With hydrogen increasingly cited as a clean and renewable energy source, low energy routes to its generation attract considerable interest. Understanding how hydrogenase enzymes are able to generate hydrogen with such remarkable efficiency is an ongoing research effort, particularly using protein film voltammetry techniques [2]. An alternate approach is to study the electrocatalytic activity of model compounds mimicking the enzyme active site [3]. First efforts were concentrated on producing faithful structural models of the active site known as the ‘H cluster’, which is a dithiolate bridged diiron cluster, ligated with biologically unusual CO and CN^- (Chart 1a) [4]. Although chemists have risen to the synthetic challenge of producing almost exact structural models of the H-cluster [5] so far the

performance of the mimic compounds, when studied as homogeneous proton reduction catalysts in non-aqueous solvents, has generally been disappointing. However very recently Dey and co-workers have achieved proton reduction catalysis in aqueous solution using an electrode-immobilised azadithiolate-bridged model with an onset potential of -0.36 V vs. NHE and with impressive Faradaic efficiency and turnover frequency [6].

Catalysis can take place either *via* initial reduction followed by protonation (an EC mechanism) or, if the complex has sufficient basicity, by protonation followed by electrochemical reduction (a CE mechanism). Hexacarbonyl complexes such as $\text{Fe}_2(\text{CO})_6(\mu\text{-pdt})$ (Chart 1b) are not usually basic enough to be protonated except by acids derived from strong Lewis acids [7]. Therefore, for catalysis to take place the complex must first be reduced, resulting in increased electron-density at the iron–iron bond and subsequent protonation [8]. Catalysis therefore takes place at the potential of the first reduction of the complex, which usually represents a considerable overpotential from the ideal thermodynamic potential of proton reduction. The basicity of the complex can be increased by substitution with electron-donating ligands, such as cyanide [4] and phosphines [9], resulting in protonation across the iron–iron bond without prior reduction. Protonation of these basic complexes can be quite rapid, but in some cases is still rate-limiting

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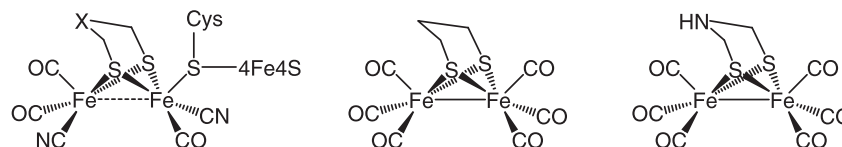


Chart 1. Left: Structure of H cluster (X now widely accepted as NH); Centre: structure of pdt hexacarbonyl; Right: structure of adt hexacarbonyl.

due to slow isomerisation processes [10]. The removal of electron-density from the bond by the proton allows reduction of the protonated complex to take place at 0.5–1 V more positive potential than the reduction of the non-protonated species. This CE mechanism could potentially result in lower overpotentials for catalysis, but unfortunately the increased electron-density provided by the ligands pushes the reduction potential of the complex more negative [11], so there is very little energetic gain from using this approach.

Researchers have addressed this issue by designing complexes with electron-withdrawing groups in the bridge. This results in less electron-density at the iron–iron bond, hence a less negative reduction potential [12–22]. Although the neutral complexes do not protonate at the iron centres and catalysis must take place by an EC mechanism, the potential at which this occurs is not prohibitively negative and represents an improved overpotential for proton reduction. One approach has been to introduce a basic N-containing moiety to the bridge that withdraws electron-density from the metal centres when it is protonated [12]. This approach may be considered biomimetic, as a similar mechanism may operate in the enzyme, where the dithiolate bridge is believed to be azadithiolate (adt) rather than propanedithiolate (pdt) (Chart 1c).

Other researchers have introduced more exotic bridges in an attempt to produce complexes with less negative reduction potentials [13–22]. From the perspective of reduction potential the most successful in literature to date is the *o*-carborane (1,2-*closo*- $C_2B_{10}H_{12}$) cluster bridged complex synthesised by Ott et al. [13], which undergoes reduction at $E_{1/2}^{\text{red}} = -0.88$ V vs. Fc/Fc^+ in MeCN and protonation and further reduction at the same potential in the presence of a strong acid. Other electron-withdrawing moieties have been introduced at the bridge, including benzenedithiolate (bdt) [14–16] and related chlorine-substituted arenedithiolates [17,18] and naphthalene [18]. Biphenyl, open-bridge complexes have also been reported including biphenyl-2,2-dithiolate [19], tetrachlorobiphenyl-dithiolate [20], $(\mu\text{-}S\text{-}2\text{-}R\text{CONHC}_6\text{H}_5)_2$ where $R = \text{CH}_3$, C_6H_5 and 4- FC_6H_4 [21] and others [22]. Wu has reported the synthesis and electrocatalysis of complexes of the form $\text{Fe}_2(\text{CO})_6(\mu\text{-SCH}_2\text{N}(\text{R})\text{CH}_2\text{S})$ with $R = \text{C}_6\text{F}_4\text{CF}_3\text{-}p$ or $\text{C}_6\text{H}_4\text{CF}_3\text{-}p$ where both electron-withdrawing moieties and a N site for protonation are incorporated into the bridge to achieve a mild reduction

potential [23]. Table 1 lists those complexes with the least negative reduction potentials reported to date and which have been tested for catalytic activity using HBF_4 or a similarly strong acid. Chart 2 shows the structures of those compounds included in Table 1.

Here we report the synthesis, electrochemistry and electrocatalytic activity of $\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_6\text{F}_5)_2$ (**1**) [24–26] where the highly fluorinated bridge is electron-withdrawing, resulting in decreased electron-density at the iron–iron bond. Additionally we discuss the related substituted complexes $\text{Fe}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-SC}_6\text{F}_5)_2$ (**2**) and $\text{Fe}_2(\text{CO})_4(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\mu\text{-SC}_6\text{F}_5)_2$ (**3**). The structures of these complexes are shown in Section 2.1 below. We address the following points in this paper: (a) whether the electron-withdrawing (SC_6F_5) bridge can lower the overpotential to proton reduction comparable to previously reported complexes; (b) if substitution with phosphine ligands can induce sufficient basicity for protonation across the iron–iron bond; (c) the relative stability of complexes **1**, **2** and **3** to electrochemical reduction and the generation of reduction products that show a high catalytic activity.

2. Results

2.1. Synthesis and characterisation

The hexacarbonyl complex $\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_6\text{F}_5)_2$ (**1**) is easily prepared as an air-stable bright red solid in good yields upon heating $\text{Fe}_3(\text{CO})_{12}$ and pentafluorothiophenol in toluene [24]. The IR spectrum of **1** in dichloromethane shows absorption bands at 2089, 2059, 2022 and 2012 cm^{-1} , representing the stretching modes of the carbonyl ligands. The analogous pdt-bridged complex $\text{Fe}_2(\text{CO})_6(\mu\text{-pdt})$ displays absorptions at 2074, 2036 and 1995 cm^{-1} [4a] indicating that the force constant for the CO bonds is increased by substitution of the pdt bridge for the electron-withdrawing SC_6F_5 groups. For such thiolate-bridged complexes *anti* and *syn* isomers are present in solution in equilibrium (Chart 3) as confirmed by the ^{19}F NMR spectrum [27].

A common strategy in the development of hydrogenase biomimics is to sequentially replace one or more carbonyls for the more electron-donating phosphine ligands [9] in order to increase the basicity of the diiron centre and make proton binding more favourable. Heating **1** and a slight excess of PPh_3 in toluene at 80 °C resulted in the slow formation of $\text{Fe}_2(\text{CO})_5(\text{PPh}_3)(\mu\text{-SC}_6\text{F}_5)_2$ (**2**) as a red solid in 26% yield. Complex **2** shows IR absorption bands at lower wavenumbers than **1**: 2058, 2008, 1996, 1981 and 1944 cm^{-1} , carbonyl substitution for PPh_3 as expected increasing the electron-density on diiron centre. In the ^{31}P NMR spectrum two singlets were observed at 29.2 and 65.8 ppm in an approximate 19:1 ratio which we associate with *anti* and *syn* isomers of **2** respectively.

Heating **1** and a slight excess of dppm in toluene for 2 h lead to the formation of an intense red solution from which $\text{Fe}_2(\text{CO})_4(\mu\text{-SC}_6\text{F}_5)_2(\mu\text{-dppm})$ (**3**) was isolated as a brick red solid in 43% yield. Crystals suitable for X-ray diffraction were grown upon slow diffusion of methanol into saturated dichloromethane solutions and the results of the crystallographic study are summarised in Fig. 1 and its caption (see Supplementary materials for more details). The

Table 1

Table showing the reduction potentials and potential of proton reduction for selected diiron hexacarbonyl complexes. All potentials vs. Fc/Fc^+ .

Reference	Bridge	Solvent	$E_{1/2}^{\text{red}}$	Acid	E_{cat}
[13]	<i>o</i> -Carborane	MeCN	−0.88 V	–	–
[20]	Tetrachlorobiphenyl $S_2C_2(CO_2Me)_2$	DCM	−1.05 V	HBF_4	−1.3 V
[15]	3,6-Dichlorobiphenyl	MeCN	−1.20 V	HOTS	−1.20 V
[14]	bdt	MeCN	−1.27 V ^b	HBF_4	−1.27 V
[23]	$(\mu\text{-SCH}_2)_2\text{N}(\text{C}_6\text{F}_4\text{CF}_3\text{-}p)$	MeCN	−1.54 V	HBF_4	−1.29 V ^c
This work	$(\text{SC}_6\text{F}_5)_2$	MeCN	−1.10 V	HBF_4	−1.10 V
		DCM	−1.31 V	HBF_4	−1.31 V

^a Acid-dependent peak at −1.1 V is not catalytic (ECE).

^b Ref. [16] reports $E_{1/2}^{\text{red}}$ as −1.32 V for this complex.

^c Protonates at the N, best compared to adt bridged complexes [11].

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