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journal homepage: www.elsevier.com/locate/apcatb[Fe(C₅Ar₅)(CO)₂Br] complexes as hydrogenase mimics for the catalytic hydrogen evolution reactionE.B. Hemming^a, B. Chan^b, P. Turner^c, L. Corcilius^a, J.R. Price^c, M.G. Gardiner^d,
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ABSTRACT

A new iron-based hydrogenase mimic, [Fe(C₅(*p*-C₆H₄Br)₅)(CO)₂Br], was synthesised and characterised using X-ray crystallography. Two analogous catalytic precursors, [Fe(C₅Ar₅)(CO)₂Br] (Ar = C₆H₅; *p*-C₆H₄Br), were also analysed electrochemically in order to investigate how bulkier and more electron withdrawing C₅Ar₅ ligands affect the catalytic generation of hydrogen from trichloroacetic acid. Compared to previously reported iron-based cyclopentadienyl analogues, these complexes were found to have smaller overpotentials and larger turnover numbers. The [Fe(C₅(*p*-C₆H₄Br)₅)(CO)₂Br] complex was found to be the most efficient of the two catalytic precursors with a turnover number of 25, an overpotential of around 310 mV and a faster rate of reaction compared to [Fe(C₅Ph₅)(CO)₂Br].

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1. Introduction

Modern society is heavily reliant on a steady supply of energy in all aspects of daily life. Currently 82% of energy consumed globally is supplied by the combustion of fossil fuels [1]. However, with increasing energy demands, a finite supply of fossil fuels and growing concern about global warming, there is much interest in long-term, sustainable, and cost-effective alternative energy sources and carriers.

An alternative energy carrier which shows great potential is hydrogen. The benefits of using hydrogen over more conventional fuels include its elemental abundance, high energy content and potential for zero greenhouse gas emissions, with water the only by-product from direct combustion [2,3]. While hydrogen can be produced from a range of sources, including fossil fuels and biomass, one of the simpler methods of production involves the splitting of water [4]. By utilising this process, hydrogen could potentially provide a method for the storage and transport of energy from intermittent sources, such as wind or solar energy, a strategy which would provide flexibility in the utilisation of these renewable energy sources [5]. During the electrolysis of water,

hydrogen is produced by the hydrogen evolution reaction (HER, Eq. (1)):



Currently the preferred catalysts for the HER are platinum-based catalysts, which are capable of catalysing the HER at overpotentials close to zero [4,5]. However, the scarcity and high material cost of platinum makes it unfeasible for widespread industrial application, as there are insufficient platinum reserves to sustain a substantial large-scale hydrogen producing industry [4]. Over the last few decades, much research has focused on the development and improvement of HER catalysts based around cheaper and more abundant metals, such as the first row transition metals.

However, several efficient HER catalyst already exist in nature. These are members of a class of metalloenzymes called hydrogenases [6]. These enzymes are found in a range of microorganisms, including bacteria and archaea, and are capable of reversibly catalysing the HER at overpotentials that rival those of the platinum-based catalysts [6–8]. There are three types of hydrogenases, which are classed, based on the structure of their active sites, the [NiFe]-, [FeFe]- and [Fe]-hydrogenases, with active sites illustrated in Fig. 1 [8,9]. These three classes have been shown to be evolutionarily unrelated, though they possess some analogous features within their respective active sites [10,11]. The three forms of hydrogenase contain either a mononuclear or a dinuclear

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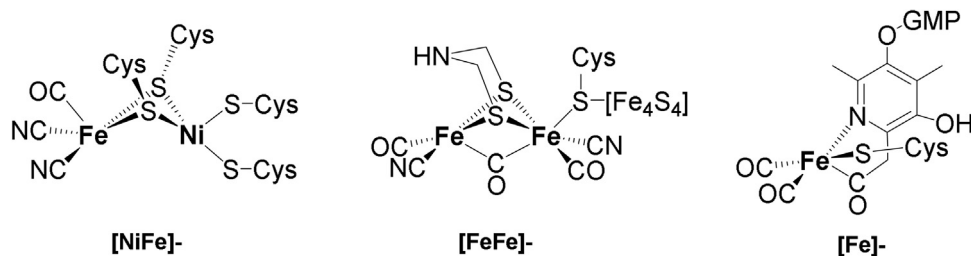


Fig. 1. Active sites of the [NiFe]-, [FeFe]- and [Fe]-hydrogenases [8,9].

redox-active metal centre, as well as cyanide and/or carbonyl ligands bound to the metal centre [12]. These ligands are thought to be important in tuning the reactivity of the metal centres, with the arrangement around the metal centre allowing for good overlap between the π^* -orbitals of the ligands and the filled metal d -orbitals stabilising the metal centre, so enabling hydrogen activation [12–14]. The primary interest in these hydrogenases is the inclusion in the active site of iron and nickel, which are relatively abundant and inexpensive first row transition metals.

Much research has focussed on mimicking the active site of the hydrogenase enzymes in the effort to design an efficient and stable catalyst from the abundant first row transition metals [6,15]. One hydrogenase mimic that is capable of catalysing the HER is the $[\text{CpFe}(\text{CO})_2(\text{THF})](\text{BF}_4)$ (Cp = cyclopentadienyl anion) complex and its analogues [16]. However, one of the major drawbacks of this catalyst is its rapid deactivation, through the dimerisation of the catalytically active species, which results in a low turnover number (TON) of 2 [16]. In addition, the reduction of this complex to the active catalytic species, $[\text{CpFe}(\text{CO})_2]^-$, has been reported to occur at -0.80 V vs Ag/AgCl in DMF, which corresponds to a relatively large overpotential and, hence, low catalytic efficiency [16].

Different approaches by which the catalytic efficiency of these hydrogenase mimics could be improved include the use of bulky ligands to hinder dimerisation, the addition of more electron withdrawing groups to reduce the overpotential, and the addition of functional groups to link the complex to a solid support to inhibit dimerisation. This paper will focus on exploring the first two approaches and the identification of a possible route to the third. One way to increase the steric bulk around the metal centre could be through the use of a pentaphenylcyclopentadienyl (Cp^{**}) ligand. These ligands have previously been reported to improve the kinetic stability of organometallic complexes through their additional steric bulk when compared to the Cp ligand [17]. Furthermore, the Cp^{**} ligand is known to be more electron withdrawing than the Cp ligand, a difference which has been shown to result in a positive shift in the reduction potentials of Cp^{**} palladium complexes [17]. For the catalytic generation of hydrogen this would correspond to a decrease in the overpotential and an increase in catalytic efficiency. The presence of the phenyl groups on the Cp^{**} ligand allows for additional tuning of the catalytic properties by further substitution of these phenyl rings. This paper presents the synthesis and electrochemical study of two related HER catalyst precursors; $[\text{Cp}^{**}\text{Fe}(\text{CO})_2\text{Br}]$ and $[\text{Fe}(\text{C}_5(p\text{-C}_6\text{H}_4\text{Br})_5)(\text{CO})_2\text{Br}]$.

2. Experimental

2.1. Materials

Unless stated otherwise all chemicals were used as received. Tetrahydrofuran (THF) and toluene were dried by passage through a column of activated alumina under 10 bar of nitrogen pressure; in addition the THF was distilled under nitrogen before use. The supporting electrolyte, tetrabutylammonium hexafluorophos-

phate (TBAPF_6 , 98%) (Fluka), was recrystallised from ethanol and water before drying under vacuum at 80°C for a minimum of 12 h. Trichloroacetic acid (Merck) was recrystallised from chloroform and dried over diphosphorus pentoxide (Merck) under vacuum at room temperature.

2.2. Synthesis

Tetraphenylcyclopentadienone was synthesised following a procedure by Johnson and Grummit [18]. 1,2,3,4,5-Pentaphenylcyclopentadien-1-ol was synthesised using a method adapted from Field et al. [19] The diethyl ether solvent was substituted with THF and the formation of the Grignard was initiated using a heat gun at 100°C before further heating the solution for 30 min at 70°C . 1-Bromo-1,2,3,4,5-pentaphenylcyclopentadiene was synthesised following a method derived from Field et al. [19] 1-Bromo-1,2,3,4,5-penta(*p*-bromophenyl)cyclopentadiene was synthesised following a procedure adapted from Carella et al. [20]

The two iron complexes $[\text{Cp}^{**}\text{Fe}(\text{CO})_2\text{Br}]$ and $[\text{Fe}(\text{C}_5(p\text{-C}_6\text{H}_4\text{Br})_5)(\text{CO})_2\text{Br}]$ were synthesised from their respective ligand precursors using a method adapted from McVey and Pauson, with benzene replaced by toluene as the solvent [21]. $[\text{Cp}^{**}\text{Fe}(\text{CO})_2\text{Br}]$ was recrystallised from dichloromethane and hexane rapidly using a rotary evaporator, while $[\text{Fe}(\text{C}_5(p\text{-C}_6\text{H}_4\text{Br})_5)(\text{CO})_2\text{Br}]$ was recrystallised from dichloromethane and hexane at -20°C .

$[\text{Fe}(\text{C}_5(p\text{-C}_6\text{H}_4\text{Br})_5)(\text{CO})_2\text{Br}]$ data: dark red crystals, decomposed without melting. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 6.9 (10H, d, $^3J_{\text{HH}} = 8.4\text{ Hz}$, ArH), 7.3 (10H, d, $^3J_{\text{HH}} = 8.1\text{ Hz}$, ArH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 99.9, 123.6, 128.0, 131.6, 133.5 ppm. **Selected APCI-MS data m/z (%):** 841 (29), 762 (13), 705 (21), 689 (100). **Selected IR data (neat):** 3043 (νCH ; w, b), 2034 (νCO ; s), 1994 (νCO ; s), 1655 (m), 1587 (w), 1493 (m), 1431 (w), 1385 (m), 1264 (w), 1182 (w), 1070 (s), 1009 (s), 825 (s), 770 (s), 751 (m) cm^{-1} . **Anal. Calc. for $\text{C}_{37}\text{H}_{20}\text{Br}_6\text{FeO}_2$:** C, 43.07; H, 1.95. **Found:** C, 42.53; H, 2.17.

2.3. Characterisation

A single crystal X-ray diffraction structural analysis for $[\text{Fe}(\text{C}_5(p\text{-C}_6\text{H}_4\text{Br})_5)(\text{CO})_2\text{Br}]$ was performed by using an Agilent SuperNova Dual diffractometer equipped with an Atlas detector and employing mirror monochromated Cu ($K\alpha$) radiation from a micro-source. Cell constants were obtained from least squares refinement against 47017 reflections located between 6 and $152^\circ 2\theta$. Data were collected at 150(1) Kelvin with ω scans to $152^\circ 2\theta$. The data processing was undertaken with CrysAlis Pro[22] and subsequent computations were carried out using the WinGX[23] and ShelXle interfaces [24]. A multi-scan absorption correction was applied to the data [22]. The structure was solved by direct methods with SHELXT[25] and extended and refined with SHELXL-2014/7 [26]. An ORTEP depiction with 50% displacement ellipsoids is provided in Fig. 2 [27,28]. Details for the structural characterisation for both $[\text{Cp}^{**}\text{Fe}(\text{CO})_2(\text{FBF}_3)]$ and $[\text{Cp}^{**}\text{Fe}(\text{CO})_2(\text{OH}_2)](\text{BF}_4)$ can be found in the ESI. The data for the three complexes have been deposited with

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