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A cross-metathesis approach for polymetallic [FeFe]-hydrogenase mimics†

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A method has been developed for synthesizing [FeFe]-H2ase mimics with diverse structures and properties, employing cross-metathesis of olefins. Vinylmetallocenes (5 and 6) and vinyl half-sandwich complexes (10 and 11) have been used as cross-metathesis partners with [FeFe]-H2ase mimics (4, 8, and 9) bearing a double bond in the moiety attached to the ADT-bridge nitrogen. Electrochemical studies of these complexes, encompassing metallocene-type (7a-b, 12a-b, and 13a-b) as well as half-sandwich derivatives (12c and 13c-d), have demonstrated that the introduction of a redox unit has a marginal impact on the reduction potential of these [FeFe]-H2ase mimics. The application of this cross-metathesis approach has allowed the synthesis of [FeFe]-H2ase mimics featuring an Ir(III) electrochemical antenna (16-18) as well as systems having an electron-donor-photosensitizer structure (ED-PS) (23). The electrocatalytic properties of these complexes have been elucidated through electrochemical studies.

Introduction

Hydrogenases are a class of metalloenzymes capable of catalyzing one of the simplest reactions in chemistry, namely the conversion of protons to molecular hydrogen.¹ These enzymes play a fundamental role in the energy metabolism of several microorganisms, as well as in the modulation of the redox potential of the microorganism cell.² Depending on the metabolic and energetic requisites of the cell, hydrogenase metalloenzymes can promote the evolution or the decomposition of molecular hydrogen. Additionally, these enzymes play a key role in the modulation of transmembrane proton gradients.³ Reversible oxidation of molecular hydrogen occurs in the enzyme active metal-center.4

Depending on the nature of the metals present in this active centre, hydrogenases are classified into three different classes: [NiFe]- (A), [FeFe]- (B) and [Fe]-hydrogenases (C) (Fig. 1). The activity in the hydrogen evolution reaction (HER) depends on the enzyme type.2 Thus, [FeFe]-hydrogenases ([FeFe]-H2ases) are highly active in hydrogen production (up to

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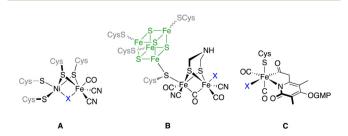


Fig. 1 The metal cores present in the three classes of hydrogenases. For [FeFe]-H₂ases, the Fe₄S₄ moiety has been drawn for clarity.

⁸⁰⁰⁰ μ mol H₂ min⁻¹ mg⁻¹),⁵ while [NiFe]-hydrogenases efficiently catalyse the oxidation of hydrogen.⁶ [Fe]-hydrogenases are present in some species of methanogenic archaea, catalysing the reduction of CO₂ to CH₄.⁷ In this regard, the similarity of [(μ-S)₂Fe₂(CO)₆] and the active centre of [FeFe]-H₂ases opened the possibility of using simplified models (mimics) of these enzymes to effect the HER. The use of these [FeFe]-H₂ase mimics has serious drawbacks with respect to the natural enzymes in the HER. Thus, different from the enzymes that can work at neutral pH, their mimics require lower pH values.8 The electrocatalytic reduction of protons by [FeFe]-H₂ase mimics occurs at more negative potentials than that in natural enzymes with the subsequent overpotential cost.9 Finally, the systems for H⁺ and e⁻ transfer that are present in the enzymes are absent in the [FeFe]-H2ase mimics. To solve these problems (knowing that the mimics present a higher tolerance to oxygen than the natural enzymes, which is one of

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the main shortcomings of these bio-catalysts) hundreds of [FeFe]-H₂ases have so far been designed and synthesised. ¹⁰

The general approaches for the preparation of [FeFe]- H_2 ases are limited to the direct reaction of Fe(CO)₅ or Fe₃(CO)₁₂ with sulphides and disulphides¹¹ to yield complexes **1** and to reactions of highly reduced species $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]^{2^-}$ with formal-dehyde imines (either as isolated species or as isolable trimers) or dichlorodimethyl amines, to form compounds **2**. The [2 + 2]-cycloaddition of $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]$ to alkenes and alkynes affords complexes **3**. This approach is less efficient but it tolerates a large array of functional groups (Scheme 1). The post-functionalization of simple [FeFe]- H_2 ase mimics has been restricted to ligand interchange in the inner coordination sphere of the $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]$ derivative, or in other condensation reactions to attach these complexes to more complex molecular scaffolds.

Recently, we approached the synthesis of some complex [FeFe]-H₂ase mimics by preparing the versatile reagent $[(\mu-ADT)^RFe_2(CO)_6]$ ($R=p\text{-}N_3C_6H_4$), and using this azide to introduce the [FeFe]-moiety into several substrates through a Cu-catalysed azide–alkyne cycloaddition.¹⁶ In parallel, the use of easily available phosphites having three [FeFe]-moieties allowed the coordination of these polymetallic ligands to different square-planar and piano-stool complexes.¹⁷ Moreover, the synthesis of heterometallic [FeFe]-mimics was carried out using tetranuclear complexes, in which the two [FeFe]-moieties were tethered by a bipyridine moiety suitable to complex different metals.¹⁸ The electronic and electrocatalytic properties of these compounds were highly influenced by the presence of additional transition metal complexes either enhancing the electronic communication between the [FeFe] centers or inhibiting it, depending on the metal.

Pursuing the idea of developing new methodologies to access heterometallic [FeFe]-H₂ase mimics in an easy way and within the concept of precision chemistry, herein we report the preparation of several heteropolymetallic [FeFe]-H₂-ase mimics through a simple and efficient cross-metathesis (CM) reaction,

 $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]$ $\begin{array}{c} \text{RSH} \\ \text{OC} \\ \text{2. TFA} \\ \text{OC} \\ \text{CO} \\ \text{C$

Scheme 1 The three main approaches for preparing [FeFe]- H_2 as m_1 mimics.

also including a new triad having an [ED-PS-F₂S₂] structure with electron donor (ED) and photosensitizer (PS) moieties, as well as their electrochemical and electrocatalytic properties.

Results and discussion

The initial study was aimed to assess the viability (and optimization of the reaction conditions) of a cross-metathesis reaction (CM) between a vinylmetallocene and an [FeFe]-H2ase mimic having a double bond attached to the nitrogen moiety of the adt-bridge. The reaction was studied using complex 4 19 and vinylferrocene 5.20 The Grubbs GBI catalyst led to low yields of the desired product 7a, requiring extended reaction times. The Hoveyda-Grubbs catalyst was more efficient but the main reaction products were homocoupling derivatives that were of little interest to fulfil our objectives. Finally, the use of the GBII catalyst led to the desired cross-metathesis product 7a in an acceptable yield (52%, isolated), minimizing the formation of homocoupling reaction products. The optimum solvent for the cross-metathesis process using the GBII catalyst was dichloromethane. These reaction conditions were subsequently applied to the reaction of complex 4 with vinyl ruthenocene 6, forming the cross-metathesis product 7b in 42% yield (Scheme 2).

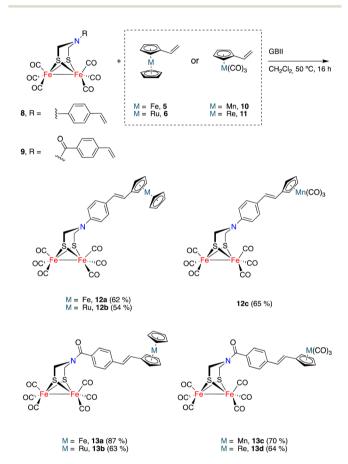
Complexes 7a and 7b are air-stable and were characterized by spectroscopic and spectrometric techniques. It is remarkable that both [FeFe]-H₂ase mimics were formed exclusively as their *E*-isomers. The signals of the olefinic protons for 7a are clearly identified at 6.19 and 5.57 ppm (J = 15.6 Hz), while those for complex 7b are observed at 6.07 and 5.57 ppm (J = 15.6 Hz). The structure of complex 7a was unambiguously determined by X-ray diffraction (Fig. 2).

The generality of the process exemplified in Scheme 2 was proven by affecting the CM reactions of [FeFe]-hydrogenase mimics 8 and 9 with vinylmetallocenes 5 and 6 and half-sand-wich complexes 10 and 11 (Scheme 3). Metallocene derivatives containing the [FeFe]-H₂ase mimic moiety 12a-b and 13a-b were obtained in good yields and, consistently, exclu-

Scheme 2 Synthesis of [FeFe]-hydrogenase mimics 7a and 7b.

C3 C5 C5 Fe3 C1 Fe3 Fe2 Fe2

Fig. 2 The X-ray structure of polynuclear complex 7a (30% displacement ellipsoids). Selected bond distances (Å): Fe1–Fe2 2.515(1), Fe1–S1 2.250(2), Fe1–S2 2.256(2), Fe2–S1 2.260(2), Fe2–S2 2.248(2), C1–N1 1.44 (1), C1–S1 1.829(8), C2–N1 1.433(9), C2–S2 1.845(7), C3–N1 1.485(9), C3–C4 1.492(10), C4–C5 1.32(1).



Scheme 3 Syntheses of [FeFe]-H₂ases bearing sandwich and half-sandwich moieties.

sively as their *E*-isomers. The analogous complexes 12c and 13c-d, having a half-sandwich moiety tethered to the [FeFe]-H₂ase mimic, were also obtained in good yields and again as their *E*-isomers. Yields for heterometallic mimics 13a (87%) and 13b (63%), derived from amides 9, were higher than those of their amine analogues 12a (62%) and 12b (54%).

Complexes **12c** and **13c–d** show two signals in the M-CO region of their $^{13}C\{^1H\}$ NMR spectra. One, at around 207.0 ppm, is attributable to the six equivalent CO ligands of the [FeFe] moiety and the other is attributable to the M(CO)₃

moiety (224.1 ppm for Mn derivatives **12c** and **13c**, 193.9 ppm for the Re derivative **13d**). The X-ray structure of half-sandwich **12c** and metallocene **13b** confirm the proposed molecular structures and the geometry of the double bond (Fig. 3).

The possibility of applying the CM approach for the synthesis of [FeFe]- H_2 ase mimics having octahedral Ir(III) moieties was next tested. [FeFe]- H_2 ase mimics combining an octahedral photoactive moiety tethered to a [(μ -ADT)Fe₂(CO)₆] fragment have been previously reported, ²³ since the idea of the octahedral moiety acting as a photocatalyst to induce the electron transfer processes to the [FeFe] moiety is very attractive. Unfortunately, to date, efficient catalytic systems in the HER have not yet been achieved using this approach. ^{24,25}

Ir(III) complex **15** acting as a partner in the CM approach was prepared from [Ir(μ-Cl)(C^N)₂]₂ **14** and 2-(4-vinylphenyl) pyridine²⁶ in the presence of Ag(CF₃SO₃) in boiling 2-ethoxyethanol. Complex **15** was obtained in 83% yield as an orange solid and as a single isomer, and is a thermodynamically favored²⁵ *fac* complex. Reactions of complex **15** with [FeFe]-mimics **4**, **8** and **9**, under the conditions reported above, gave heterotrimetallic complexes **16–18** in good yields (Scheme 4). Complexes **16–18** were air-stable and were characterized using spectroscopic techniques. Again, these complexes were obtained as *E*-isomers (1 H NMR $_{CH=CH}$ = 15.8 Hz), showing the characteristic 13 C{ 1 H} NMR CO signals for the [(μ-ADT) Fe₂(CO)₆] moiety in the 207–208 ppm range. These spectroscopic data together with the HRMS data support the heterotrimetallic structure proposed for complexes.

Finally, the CM approach for preparing [FeFe]- H_2 ase mimics was also used to prepare the [ED-PS-Fe₂S₂] system **23** (Scheme 5), where ED is an electron donor moiety (ferrocene) and PS is a photoactive moiety (Ir(III) complex). The synthesis began with the preparation of dimeric Ir(III) complex **19** (having formyl groups) by the reaction of 2-(4-formylphenyl)

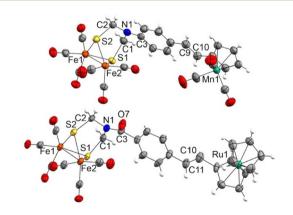


Fig. 3 X-ray structures of heterometallic complexes 12c (top) and 13b (bottom) (30% displacement ellipsoids). Selected bond distances (Å): 12c: Fe1-Fe2 2.5070(8), Fe1-S1 2.2620(11), Fe1-S2 2.2580(11), Fe2-S1 2.2723(10), Fe2-S2 2.2533(11), C1-N1 1.428(6), C1-S1 1.870(4), C2-N1 1.420(6), C2-S2 1.871(5), C3-N1 1.397(6), C9-C10 1.311(8). 13b: Fe1-Fe2 2.4944(18), Fe1-S1 2.249(2), Fe1-S2 2.257(3), Fe2-S1 2.271(2), Fe2-S2 2.268(2), C1-N1 1.427(12), C1-S1 1.850(10), C2-N1 1.452(10), C2-S2 1.846(9), C3-N1 1.352(12), C3-O7 1.240(12), C10-C11 1.249(19).

17 (48%)

18 (69%)

 $\begin{tabular}{ll} \textbf{Scheme 4} & \textbf{The synthesis of heterometallic [FeFe]-H}_2$ as e mimics. \\ \end{tabular}$

16 (46%)

Scheme 5 The synthesis of the $[ED-PS-Fe_2S_2]$ system 23.

pyridine²⁷ with IrCl₃.nH₂O in boiling 2-ethoxyethanol. This complex was obtained in 36% yield as a red solid. The dimeric structure of 19 was established using spectroscopic techniques. Its ¹H and ¹³C{¹H} NMR spectra show a single set of signals, which pointed to the coexistence of a diastereomeric mixture of compounds in solution. The reaction of dimeric complex 19 with 2-(4-vinylphenyl)pyridine in boiling 2-ethoxvethanol in the presence of silver triflate formed complex 20. The obtained solid was washed with EtOH and purified by silica gel chromatography (using DCM as the eluent) to obtain pure 20 as a red solid (47% yield). The structure of complex 20 was spectroscopically determined. The ¹H NMR spectrum shows the characteristic vinyl protons at 5.54 (dd, J_1 = 17.6, J_2 = 1,3 Hz) and 5.01 (dd, I = 10.8, $I_2 = 1.3$ Hz) ppm. The ${}^{13}C\{{}^{1}H\}$ NMR spectrum contains two signals, at 194.3 and 194.2 ppm, attributable to inequivalent aldehyde groups. This is consistent with a fac-disposition (thermodynamically favoured isomer).

Complex **20** was then reacted with alkene **9** under the CM conditions developed in this work. The CM product, namely complex **21**, was obtained in 62% yield. The HRMS and spectroscopic data were consistent with the proposed structure. Thus, a signal corresponding to the six CO groups of the [FeFe]-moiety appeared at 207.0 ppm in the 13 C{ 1 H} NMR spectrum, while the two signals appearing at 194.5 and 194.3 ppm correspond to the inequivalent formyl groups. Finally, the signal for the amide-CO group appeared at 162.9 ppm. The *E*-geometry was derived from the coupling of the protons attached to the double bond (I = 15.8 Hz).

To achieve the synthesis of the [ED-PS-Fe₂S₂] system 23, complex 21 was condensed with p-aminophenyl ferrocene 19 28 (2 equiv.) in a boiling solution of 3:1 EtOH/Cl₂CH₂. The desired complex was isolated as a red solid in 82% yield. Its structure was established using spectroscopic and HRMS techniques. Again, significant signals were observed for the two inequivalent imine protons at 8.29 and 8.23 ppm in the 1 H NMR spectrum and a sharp signal at 207.0 ppm was observed in the 13 C{ 1 H} NMR spectrum, supporting the integrity of the [(μ -ADT)Fe₂(CO)₆] moiety in the imine formation reaction.

Electrochemistry

Complexes **7a-b**, **12a-c** and **13a-d** show a quasireversible reduction wave in the range of -1.70~V to -1.60~V ($\nu s.~Fc^{+/0}$). This wave is attributable to the [Fe^IFe^I] to [Fe^IFe⁰] reduction (Fig. S-1† and Table 1). ²⁹ Complexes **4**, **8** and **9** have been included for comparison. The small displacement in the reduction wave of complex **13a** with respect to **7a** agrees with the reported scarce influence of the substituent R attached to the nitrogen of the ADT-bridge of [(μ -ADT)N^RFe₂(CO)₆] complexes in their reduction potential. ³⁰

All complexes show a second irreversible reduction wave at $-2.10~V~(\nu s.~Fc^{+/0})$, attributable to the reduction of $[Fe^0Fe^I]$ to $[Fe^0Fe^0]$, and a quasireversible oxidation wave at around 0.50 V, attributable to the $[Fe^IFe^I]$ to $[Fe^IFe^I]$ oxidation. ²⁹ Additionally, complexes **4a**, **12a** and **13a** show the oxidation waves characteristic of the ferrocene moiety at 0.0 V ($\nu s.~Fc^{+/0}$), while rutheno-

Table 1 Electrochemical data (first reduction). Potentials in V vs. Fc^{+/0}

Complex	$E_{ m pc1}$	$E_{ m pa1}$	$E_{(1)}$
4	-1.76	-1.65 (0.11)	-1.70
7a	-1.74	-1.64(0.10)	-1.70
7 b	-1.74	-1.64(0.10)	-1.69
8	-1.70	-1.62(0.08)	-1.66
12a	-1.69	-1.62(0.07)	-1.65
12b	-1.69	-1.62(0.07)	-1.66
12c	-1.69	-1.62(0.07)	-1.65
9	-1.64	-1.57(0.07)	-1.61
13a	-1.64	-1.55 (0.09)	-1.60
13b	-1.64	-1.59(0.05)	-1.62
13c	-1.64	-1.58(0.06)	-1.61
13d	-1.64	-1.58(0.06)	-1.61

cene derivatives **4b**, **12b** and **13b** show the quasireversible oxidation wave at around 0.20 V (νs . Fc^{+/0}), corresponding to the Ru(II) to Ru(III) oxidation.

The electrocatalytic behavior of complexes 7, 12 and 13 in the presence of mild (AcOH, $pK_a^{MeCN} = 22.3^{31}$) and strong (CF₃COOH, $pK_a^{MeCN} = 12.6^{32}$) acids was next studied. Fig. 4 compiles the results of both experiments. The electrochemistry in the presence of AcOH was the standard for related [(μ -ADT) N^R Fe₂(CO)₆] complexes.³³ The current intensity for the first wave is independent of the amount of AcOH, while a strong increase in the current intensity was observed in the second wave (above 2.0 V). This behaviour is compatible with two successive reduction processes resulting in the HER.

Complexes 7, 12 and 13 behave differently in the presence of TFA. Now the first reduction wave in the range of -1.60 to -1.70 V (vs. Fc^{+/0}) experiences a strong electrocatalytic response (Fig. S-3†). Moreover, this wave splits into two waves upon increasing the concentration of the acid, which is consistent with the reduction of the protonated species.

The different electrocatalytic responses were evaluated through the increase of the current intensity with the acid concentration of the first reduction process (i_{cat}) with respect to the basal current intensity of the same process in the absence the acid (i_{p}) (Fig. 4). Similarly, plotting of i_{cat}/i_{p} vs. [H⁺] allowed

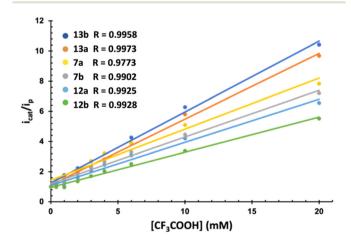


Fig. 4 Representation of i_{cat}/i_p for complexes 7, 12 and 13 vs. TFA

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the calculation of the TOF for the reduction of H⁺ (Table 2).³⁴ In all cases, the response increases linearly (Fig. 4), showing different sensibilities to the increase of [H⁺]. Amide derivatives 13b and 13a showed a stronger electrocatalytic response.

Table 2 compiles the overpotentials (η) and the TOFs for the corresponding processes of all complexes. Amide derivatives 13d and 13b show higher TOFs. These values are 200% higher than that of 12a, which clearly demonstrates the strong influence that the substituent in the ADT-bridge of [(μ-ADT) $N^{R}Fe_{2}(CO)_{6}$] exerts on the kinetics (TOF) of these processes. These results may be explained by the fact that protonating the amide nitrogen of 13d and 13b is more difficult than protonating the amine moiety of complexes 7a-b and 12a-c. This difficulty may direct the protonation directly to the Fe nucleus or may trigger the proton transfer from the more acidic protonated amide to the Fe-nucleus.

The electrochemistry of [FeFe]-H2ase mimics having octahedral Ir(III) moieties was next studied. Firstly, we registered the electrochemistry of complex 15. Fig. 5 shows a reversible oxidation wave at 0.33 V (IrIII to IrIV) (vs. Fc+/0) and two reduction waves at -2.69 and -2.92 V (vs. Fc^{+/0}), attributable to both types of ppy ligands (ppy = 2-phenylpyridine).

Complexes 16-18 show a quasireversible reduction wave between -1.48 and -1.57 V (vs. Fc^{+/0}) (Fig. 6 and Table 3) that are attributable to the [Fe^IFe^I] to [Fe^IFe⁰] reduction. Comparing with the reference voltammogram shown in Fig. 5, the additional reduction processes at around -1.98 and -2.09 V (vs. Fc^{+/0}) are attributable to the [Fe^IFe^I] to [Fe⁰Fe⁰] reduction. Reduction of the Ir(III) moiety was not seen in the window used. The oxidation waves of these compounds appeared in the range expected for the oxidation of Ir(III) to Ir(IV) moieties (0.33 V vs. Fc^{0/+}).³⁵ The main difference between complexes 15 and 16-18 in their oxidation waves is the irreversibility of the Ir(III) to Ir(IV) process observed for complex 16, while complex 18 maintains the reversibility of the oxidation wave. Obviously, this behaviour should be related to the linker that connects the Ir and the FeFe centers, which is efficient in the case of the amide linker (probably due to its iminol tautomer), but it fails in the case of the enamine linker.

Table 2 Electrochemical data for complexes 7, 12 and 13. Potentials in V vs. Fc^{+/0}

			_	
Complex	$E_{\text{Catalytic}}^{a}(V)$	$\eta^{b}(V)$	$TOF^{c}(s^{-1})$	
7a	-1.74	0.85	12.1	
7 b	-1.67	0.78	10.2	
12a	-1.65	0.76	6.0	
12b	-1.64	0.75	9.9	
12c	-1.69	0.80	8.9	
13a	-1.64	0.75	18.2	
13b	-1.65	0.76	21.4	
13c	-1.66	0.77	16.6	
13 d	-1.64	0.75	20.8	

^a Data obtained from Fig. S-3.† ^b Overpotential (η) calculated using $E_{\rm HA}^{\circ} = -0.89 \, \text{V.}^{10} \, ^{c} \, \text{TOF calculated with 20 mM TFA}.$

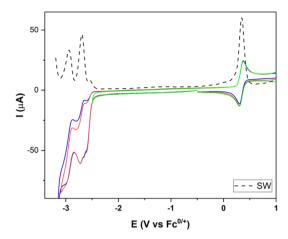


Fig. 5 CVs and SW of complex 15 in 10^{-3} M MeCN solutions containing $[^{n}Bu_{4}N]PF_{6}$ 10⁻¹ M as the supporting electrolyte (25 °C), Pt as the counter electrode, vitreum carbon as the working electrode; potentials in V vs. Fc⁺/Fc; scan rate: 100 mV s⁻¹.

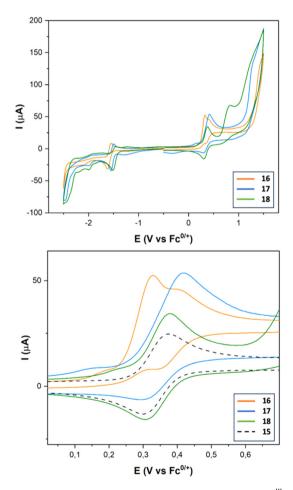


Fig. 6 CVs of complexes 16-18 (top) and expansion of the Ir^{III} to Ir^{IV} oxidation wave for 16-18 vs. 15 (bottom), obtained from 10-3 M solutions in MeCN containing $[^{n}Bu_{4}N]PF_{6}$ 10^{-1} M as the supporting electrolyte, recorded at 25 °C. Counter-electrode: Pt; working electrode: vitreous carbon; potentials given in V vs. Fc^+/Fc ; scan rate: 100 mV s⁻¹.

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Table 3 Electrochemical data for 16–18. Potentials in V vs. Fc^{+/0}

	$E_{(1)}$	E_{cat}	η^a	TOF _(10 equiv.)	TOF _(20 equiv.)
16	-1.57	-1.60	-0.71	2.5	2.5
17	-1.52	-1.61	-0.72	11.5	11.5
18	-1.48	-1.63	-0.74	17.4	53.3

Data obtained from Fig. S-4.† a Overpotential (η) calculated using $E_{\rm HA}^{\circ}=-0.89\,{\rm V.}^{10}$

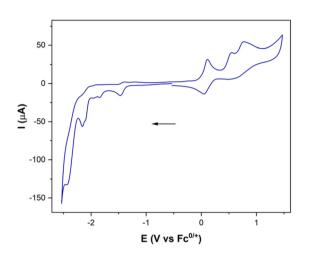


Fig. 7 CV of complex 23, obtained from 10^{-3} M solutions in MeCN containing ["Bu₄N]PF₆ 10^{-1} M as the supporting electrolyte, recorded at 25 °C. Counter-electrode: Pt; working electrode: vitreous carbon; potentials given in V vs. Fc⁺/Fc; scan rate: 100 mV s⁻¹.

To assess the electrocatalytic properties, an electrochemical study was conducted in the presence of a strong acid (CF₃COOH, $pK_a^{MeCN} = 12.6^{32}$). Complexes **16–18** exhibit a strong electrocatalytic response (see Fig. S-4†). TOF values were calculated using the same H⁺ source. Complex **18** shows the highest value (200-fold with respect to that of **16**), like the series of complexes **7**, **12** and **13**. Evidently, the nature of the linker between the new metal and the FeFe centres determine the electrocatalytic activity of these complexes.

To complete the study, the electrochemical response of the [ED-PS-Fe₂S₂] system **23** was measured. The [Fe^IFe^I] to [Fe^IFe⁰] reduction appears at -1.43 V (νs . Fc^{+/0}) and the [Fe^IFe⁰] to [Fe⁰Fe⁰] reduction process appears at -1.95 V (νs . Fc^{+/0}). The successive oxidation processes at 0.08 V (reversible) and 0.53 V (νs . Fc^{+/0}) correspond to the ferrocene and iridium moieties (Fig. 7).

Conclusions

The cross-metathesis coupling of [FeFe]-H₂ase mimics having double bond-containing moieties attached to the nitrogen of the adt bridge with vinyl metallocenes and half-sandwich and octahedral Ir(III) complexes having a vinyl functionality enables the syntheses of diverse heteropolymetallic [FeFe]-H₂ase

mimics in an easy and efficient way. The new complexes have an *E*-stereochemistry across the formed double bond.

Electrochemical studies on both metallocenes (7a-b, 12a-b, and 13a-b) and half-sandwich derivatives (12c and 13c-d) have revealed that the placement of a redox unit has only a minimum impact on the reduction potentials of these [FeFe]- H_2 ase mimics.

The application of this cross-metathesis approach also allowed the synthesis of complexes having an electron-donor-photosensitizer structure (ED-PS) (23) bonded to the nitrogen of the adt-bridge. The electrocatalytic properties of these complexes have been elucidated. We observed a clear increase in the electrocatalytic response (a 200-fold increase in the TOF values for the HER) upon replacing an amine group with an amide group. This significant enhancement is attributed to the potential of the iminol tautomer to act as an efficient proton transfer group. In summary, an easy, efficient and versatile synthetic approach for [FeFe]- H_2 ase mimics has been developed.

Author contributions

M. A. S. and L. C. designed and supervised the experimental work. S. A. performed the synthetic and characterisation experiments. J. A. C. and P. G.-A. determined the X-ray structures. All authors contributed to writing the manuscript.

Conflicts of interest

There are no conflicts to declare.

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