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Diiron Complexes Bearing Bridging Hydrocarbyl Ligands as Electrocatalysts for Proton Reduction

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Diiron Complexes Bearing Bridging Hydrocarbyl Ligands as Electrocatalysts for Proton Reduction

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Abstract: diiron complexes with bridging hydrocarbyl ligands and containing CO and Cp ligands (Cp = C₅H₅) have been investigated as possible electrocatalyst for H₂ production. In particular, studies included the vinyliminium complexes [Fe₂{μ-η¹:η³-C(R')=CRC=NMe₂}(μ-CO)(CO)(Cp)₂][SO₃CF₃] (R' = Tol, R = H, **1a**, Tol = 4-MeC₆H₄; R' = CH₂OH, R = H, **1b**; R' = CH₂OH, R = SPh, **1c**), the vinylalkylidene [Fe₂{μ-η¹:η³-C(Tol)CH=CHNMe₂}(μ-CO)(CO)(Cp)₂] (**2**), the aminoalkylidene [Fe₂{μ-CN(Me)(R)}(μ-CO)(CO)(L)(Cp)₂][SO₃CF₃] (R = Me, L = CO, **3a**; R = Me, L = NCMe, **3b**; R = Xyl, L = CO, **3c**, Xyl = 2,6-Me₂C₆H₃), [Fe₂{μ-CN(Me)₂}(μ-L')(CO)(L)(Cp)₂] (L' = CO, L = CN, **4**; L' = H, L = CO, **5**), the thiocarbyne complexes [Fe₂(μ-CSEt)(μ-CO)(CO)₂(Cp)₂][BF₄], (**6**) and [Fe₂(μ-CSMe)(μ-CO)(CO)(CN)(Cp)₂] (**7**), and the alkylidene complexes [Fe₂{μ-C(CN)(SMe)}(μ-CO)(CO)₂(Cp)₂][SO₃CF₃] (**8**) and [Fe₂{μ-C(SMe)(PMe)}(μ-CO)(CO)₂(Cp)₂][SO₃CF₃] (**9**). Cyclic voltammograms (CV) of the above complexes in CH₃CN have been recorded in the presence of increasing amounts of acetic acid to evidence electrocatalytic proton reduction. In spite of the fact that the above diiron complexes do not resemble the typical diiron dithiolate model system the aminocarbyne **4** and the thiocarbyne complex **7** exhibit significant properties as electrocatalyst for proton reduction (e.g., for **4**, the turnover number (TON) is 15.5).

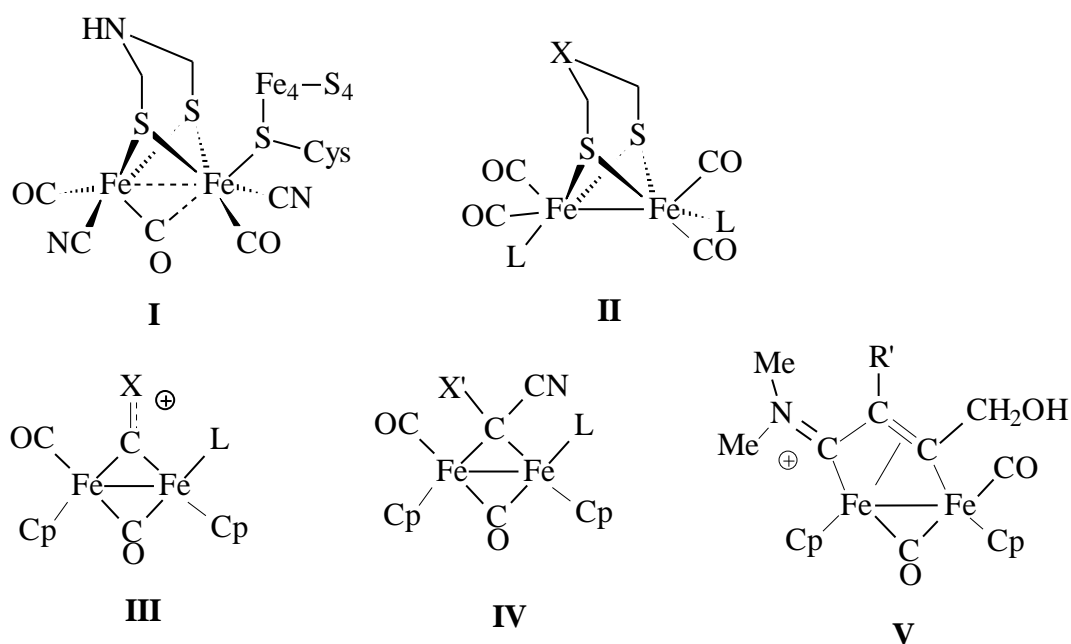
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Introduction

Large-scale use of hydrogen as an alternative clean energy vector is an attractive but challenging issue in many aspects (e.g., production from renewable sources and storage).¹ One major issue for the development of both H₂ generation from water splitting and fuel cells is the replacement of platinum (and other noble metals) with catalysts based on abundant and sustainable metals.² Natural hydrogenases, which are recognized as the most efficient catalysts for the conversion of protons and electrons into hydrogen, and the reverse reaction³ have inspired a multitude of works aimed at the design and synthesis of structural and functional models.⁴ In particular, since the first X-ray crystallographic structures for the [FeFe]-hydrogenase active site were reported,⁵ diiron dithiolate model systems have been very actively investigated.⁶ The cores of these diiron units, although rarely matching that of the enzyme subsite (Scheme 1), are usually designed to mimic the natural systems, in that they contain dithiolate ligands, carbon monoxide, and cyanide. The number of dithiolate model systems has grown exponentially, based on either modification of the bridgehead group or substitution of carbonyls and cyanides with other ligands such as phosphines, isocyanides, and N-heterocyclic carbenes (NHCs).^{6,7} Studies have produced a considerable amount of structural and mechanistic information concerning important aspects of the [FeFe]-H₂ases, but progress in the development of efficient electrocatalysts for H₂ production has been less effective. Although it is reasonable that diiron complexes which closely resemble the active site of natural [FeFe]-H₂ases might act as electrocatalysts for H₂ production, this should not be assumed as a “paradigm”. In other words, it cannot be excluded that other diiron complexes, which do not resemble, or resemble only in part, the natural enzymes should exhibit even remarkable electrocatalytic properties. If this possibility is realistic, the research field for efficient electrocatalysts for H₂ production based on diiron complexes would considerably expand. For example, there are a large number of diiron complexes that exhibit classic organometallic ligands such as cyclopentadienyls (η^5 -C₅H₅, Cp), bridging and/or terminal CO, and bridging hydrocarbyl ligands (e.g., alkyl, alkynyl, alkenyl, allyl, allenyl, etc.) which might be considered as potential electrocatalysts for H₂ production.⁸ In comparison to typical hydrogenase models, the presence of Cp ligands should produce effects not so dissimilar, at least in terms of electron donor ability, to those evidenced by CO replacement with phosphines or isocyanides. The most striking change, in comparison to the classic model system, is replacement of dithiolate ligands with bridging hydrocarbyls, which might be crucial in consideration of the major role of dithiolate ligands in model systems. Thiolates have been replaced by diphosphide,⁹ diselenide,¹⁰ and diamide ligands,¹¹ but the effects of bridging hydrocarbyl ligands in place of dithiolates can be hardly

predicted. Indeed, among cyclopentadienyl diiron complexes, only the compound $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2(\text{Cp})_2]$ has been investigated and found to be a precatalyst for electrocatalytic hydrogen evolution. However, in this case, the real active catalytic species are mononuclear intermediates generated upon reduction of the diiron precursor.¹² Conversely, diiron complexes with bridging hydrocarbyl ligands (such as complexes III–V in Scheme 1) are expected to be more stable toward fragmentation and thus are better candidates to undergo redox transformation maintaining the Fe centers in close proximity.



Scheme 1

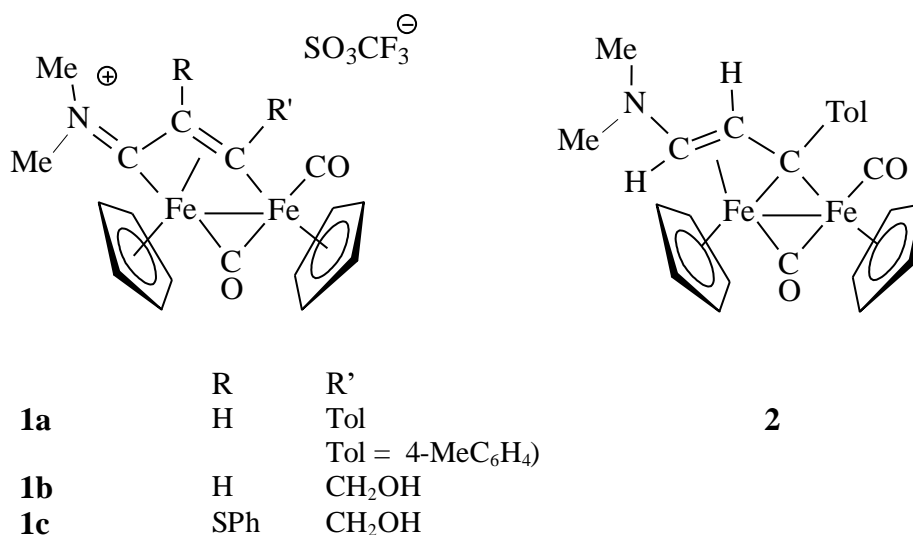
Moreover, diiron complexes with bridging hydrocarbyl ligands can be easily obtained by well-known synthetic protocols;¹³ the bridging frame can be of different sizes and lengths (C_1 , C_2 , and C_3 bridging chains) and can include extended π -delocalized systems. Bridging hydrocarbyls can be decorated by heteroatoms, functional groups, and positive or negative charges, providing plenty of possibilities to properly design and fine tune the properties of the ligand, in order to obtain the desired catalytic activity.¹⁴ Having these considerations in mind, we decided to investigate the electrochemical behavior of a few diiron complexes (III–V in Scheme 1) in order to establish if any of them exhibit activity as electrocatalysts for H_2 evolution. The results are reported herein.

Results and discussion

Diiron complexes of the type III–V with hydrocarbonyl ligands have been investigated by cyclic voltammetry, which is the usual way to demonstrate electrocatalytic ability for hydrogen evolution.¹⁵ Cyclic voltammograms (CVs) of the studied complexes in CH₃CN have been recorded in the presence of increasing amounts of acetic acid (HOAc). Catalytic activity in hydrogen evolution is normally evidenced by the appearance of an irreversible wave that grows with increasing acid concentrations, whereas the position of the peak can be used to evaluate the overpotential.

Cyclic Voltammograms of Vinyliminium and Vinylalkylidene Complexes.

Complexes containing bridging C₃ ligands (vinyliminium **1a–c** and vinylalkylidene **2**) investigated by cyclic voltammetry are reported in Scheme 2. Complexes **1a**,¹⁶ **1b**,¹⁷ **1c**,¹⁸ and **2**¹⁹ have been obtained according to reported procedures. The crystal structures of **1c** and **2** have been also reported previously.¹⁸ The presence of a bridging conjugated iminium ligand, with a positive charge, is expected to cause a decrease in the cathodic potential. Moreover, the bridging ligands in complexes **1b,c** contain heteroatoms and functions (S, OH) which, in theory, might facilitate proton capture and favor the catalytic conversion.



Scheme 2

The CV (Figure 1A) of complex **1a** displays two reversible redox processes with formal potentials of -1.30 and $+0.57$ V.

The redox waves observed at about -0.2 V are generated by degradation products that are produced by the oxidized/reduced states of complex **1a**. Indeed, they were not observed when CV was carried out between -1 and $+0.2$ V: i.e., in a potential range where no redox processes occur. The process on the cathodic side ($E = -1.30$ V) represents the reduction of the starting complex and involves one electron, as suggested by a ΔE_p value of 59 mV. Similarly, the process on the anodic side ($E = +0.57$ V) corresponds to an oxidation again involving one electron. The compounds **1b,c** and **2** display comparable behavior, and the formal potentials of the relevant redox couples are reported in Table 1; CVs are reported in the Supporting Information.

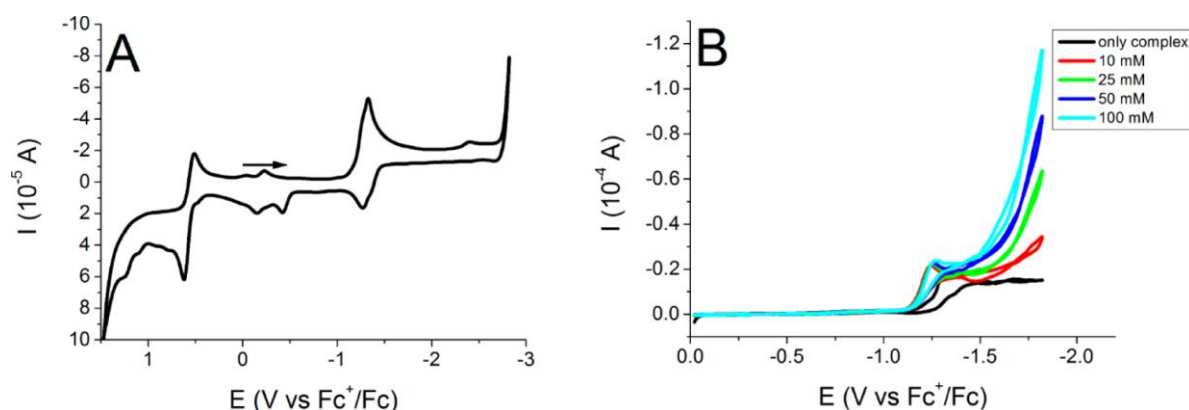


Figure. 1. CVs recorded in a 2 mM solution (in CH_3CN) of complex **1a** in the absence (A) and in the presence (B) of acetic acid at different concentrations. The arrow shows the direction of the first scan.

The one-electron nature of the first cathodic system was confirmed by performing controlled-potential electrolysis of a **1b** solution (2 mM) in CH_3CN at -1.50 V, as described in the Experimental Section. Electrocatalytic properties were studied recording CVs in the presence of increasing amounts of acetic acid (HOAc) (Figure 1B) in the cathodic region of the potential. No catalytic effect is observed at the peak current, and hydrogen evolution occurs at the same potentials recorded for the blank signal.

The absence of catalytic activity for H_2 evolution, in spite of the reversible electron reduction at a relatively accessible potential, is probably a consequence of the fact that reduction and protonation events take place at the bridging frame rather than at the iron atoms. Therefore, active metal-hydride species, which are necessary for hydrogen formation and evolution, are not formed. For this reason we turned our attention to diiron complexes with simpler bridging ligands, still

containing heteroatoms but with less extended π -bound systems, in order to address the electrochemical events at the Fe–Fe core.

Cyclic Voltammograms of μ -Alkylidyne Complexes.

Bridging aminoalkylidyne diiron complexes are generally robust, in that they do not undergo fragmentation of the Fe–Fe bond upon either reduction or nucleophilic addition.²⁰ Aminoalkylidyne ligands steadily occupy the bridging coordination position and exhibit a remarkable electrophilic character, which might contribute to lowering the reduction potential.

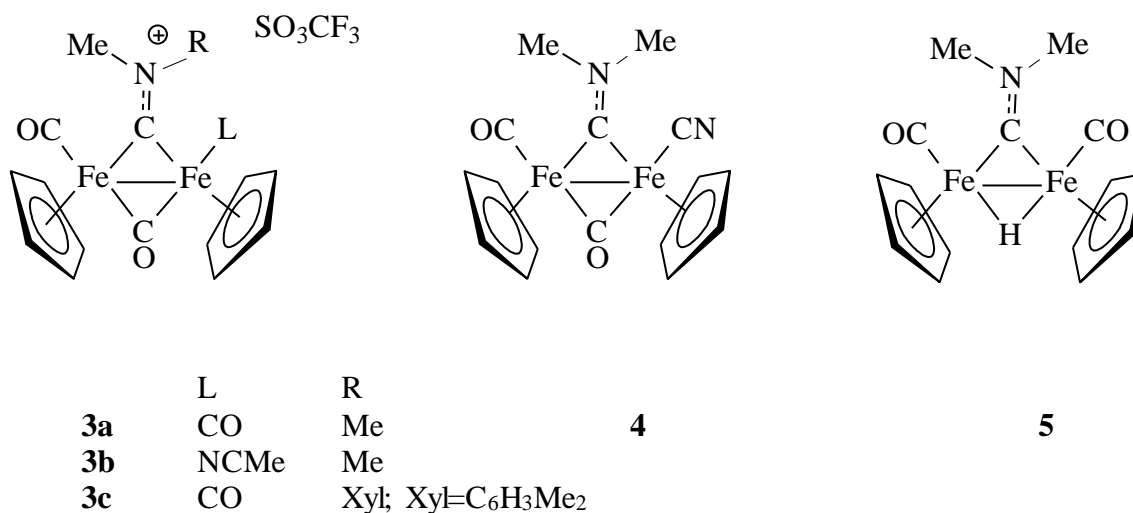
The aminoalkylidyne complexes selected for this work (Scheme 3) contain different ligands and substituents, which are expected to influence the redox and catalytic behavior of the diiron complexes. The complexes **3a**,²¹ **3b**,²² **3c**,²¹ **4**,²² and **5**²² have been obtained according to procedures previously reported.

Table 1. Formal potentials of electrochemical processes involving the complexes **1a-c** and **2**.

	E_{red}° (V vs Fc ⁺ /Fc)	E_{ox}° (V vs Fc ⁺ /Fc)
1a	-1.30	+0.57
1b	-1.35	+0.60*/+0.99**
1c	-1.28*	+0.70*
2	-2.10*	+1.35*

E_{ox}° refers to the anodic process, while E_{red}° refers to the cathodic one.* The process is irreversible (the peak potential is given). ** This potential corresponds to the peak of the second wave.

The structure of **4** has also been reported in the literature.²² The presence of anionic ligands, such as cyanide and hydride, in place of CO (complexes **4** and **5** in Scheme 3) produces neutral complexes. These ligands have been selected in that they are relevant in natural [FeFe]-H₂ase and might provide a most suitable environment for the Fe–Fe core. Other modifications that we have considered in the design of possible catalytically active species are the presence of N substituents with different electron-withdrawing character (Me or Xyl) and replacement of CO with a more labile ligand (NCMe in complex **3b**).



Scheme 3

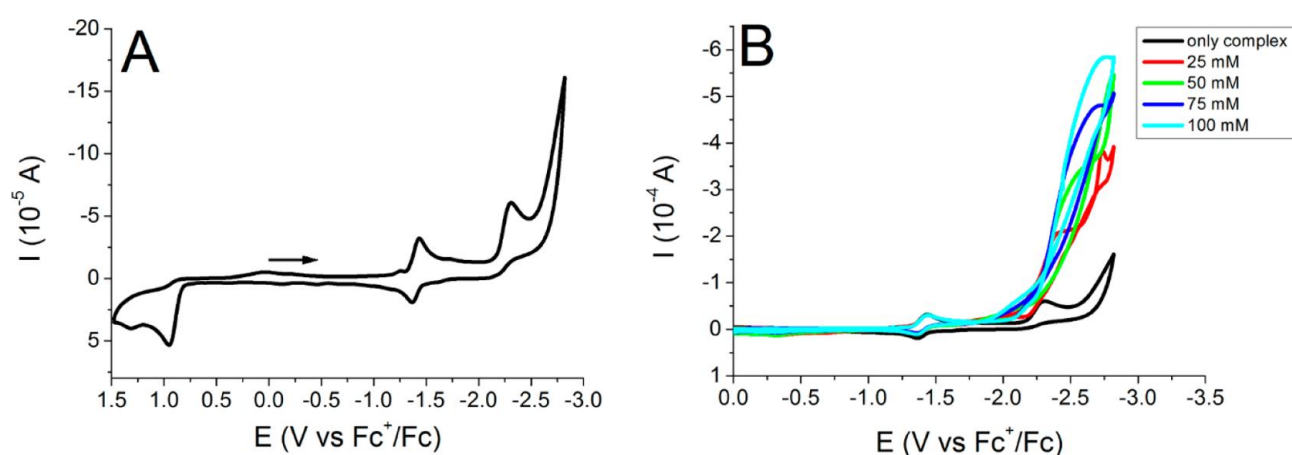


Figure 2. CVs recorded in a 2 mM solution (in CH₃CN) of complex 3a in the absence (A) and in the presence (B) of acetic acid at different concentrations. The arrow shows the direction of the first scan.

Table 2. Formal potentials of electrochemical processes involving the complexes **3a-c**.

	E_{red1}° (V)	E_{red2}° (V)	E_{ox1}° (V)	E_{ox2}° (V)	C.E.
3a	-1.40	-1.84*	+1.43*	+1.79*	0
3b	-1.67	-2.07	+0.32	+1.13*	0.11
3c	-1.40	-2.28*	+0.864*	+1.23*	0

E_{ox1}° and E_{ox2}° refer to the first and second anodic processes, respectively, while E_{red1}° and E_{red2}° refer to the first and second reduction waves, respectively. C.E. column reports the catalytic efficiency calculated in agreement with the method proposed by Felton et al.¹⁴ The process is irreversible and the peak potential is reported.

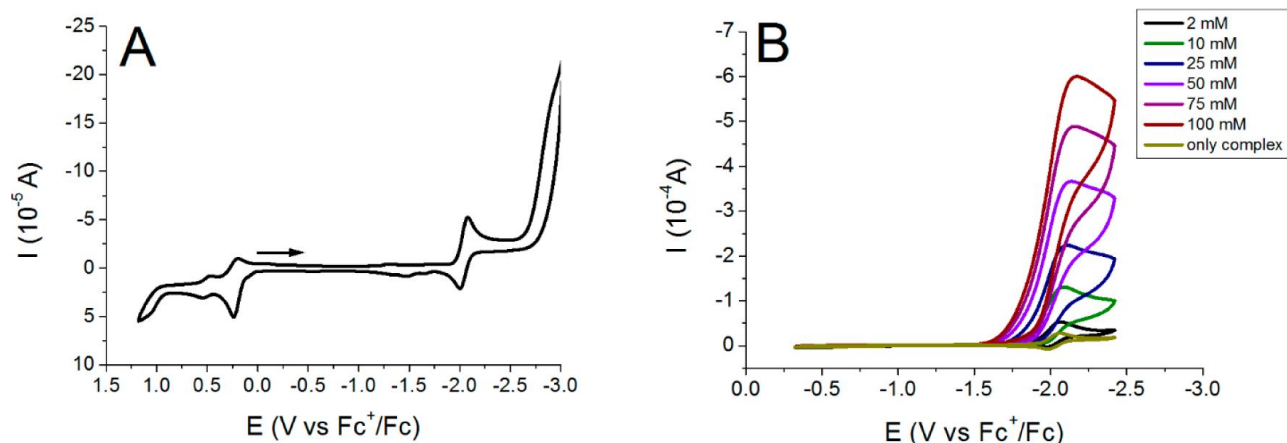


Figure 3. CVs recorded in a 2 mM solution of complex **4** (in CH₃CN) in the absence (A) and in the presence (B) of acetic acid at different concentrations. The arrow shows the direction of the first scan.

In spite of the modifications on the ancillary ligands, the electrochemical properties of complexes **3a–c** are quite similar (see Table 2 and the Supporting Information) and are well exemplified by the behavior of **3a**, shown in Figure 2. The CV (Figure 2A) shows two waves on the cathodic side and two waves on the anodic side. The first process in the anodic region is irreversible, occurs at a peak potential of +0.96 V, and involves two electrons, whereas the second process exhibits a peak potential equal to +1.31 V.

On the cathodic side complex **3a** shows a reversible process ($E^{\circ'} = -1.40$ V) which involves one electron and a second apparently irreversible process ($E_p = -2.07$ V) which involves two electrons, suggesting a complex kinetics (ECE; electrochemical–chemical–electrochemical). Since the latter occurs at a potential higher than the value of spontaneous hydrogen evolution on glassy carbon (GC), only the first redox couple might be of interest for the electrocatalysis occurrence. Indeed, no catalytic effect was observed for **3a** when the CV was recorded in the presence of acetic acid. Likewise, complex **3c** did not display electrocatalytic activity. On the other hand, compound **3b** displays a low activity for H₂ evolution, and the saturation of the catalyst was observed at low acetic acid concentrations (>25 mM). In the case of **3b**, the observed activity, although very limited, might be associated with the presence of the more labile ligand CH₃CN (in place of CO).

This might provide a coordination site which is not accessible in the analogous complexes **3a,c**.

The CV of **4** (Figure 3A) displays a reversible redox process on the cathodic side with a formal potential of -2.04 V, whereas two almost reversible processes are observed on the anodic side with formal potentials of +0.21 and +0.51 V, respectively. When the CVs (Figure 3B) were recorded in the presence of increasing amounts of acetic acid, a meaningful electrocatalytic behavior was

observed for the redox couple with a formal potential of -2.04 V. The forward peak (negative I values) increases, indicating that the neutral form of the complex is regenerated by the catalytic reaction pathway. At the same time, the backward peak decreases because the reduced form of the complex is consumed by H_2 evolution. The ratio between the currents in the presence and in the absence of acetic acid (100 mM), at a potential corresponding to the complex peak, was equal to 20. This value is so high as to rule out the possibility that the current is ascribable only to other possible reactions involving **4**. The recorded current is directly proportional to the acetic acid concentration up to 100 mM, and the catalytic efficiency was estimated to be equal to 0.34.¹⁵ The overpotential with respect to the thermodynamic value of acetic acid (-1.46 V vs Fc^+/Fc) was determined in agreement with the method reported in the literature¹⁵ and gave a value of -0.58 V. The CV of complex **5** (Figure 4) displays three redox processes on the anodic side and only one on the cathodic side.

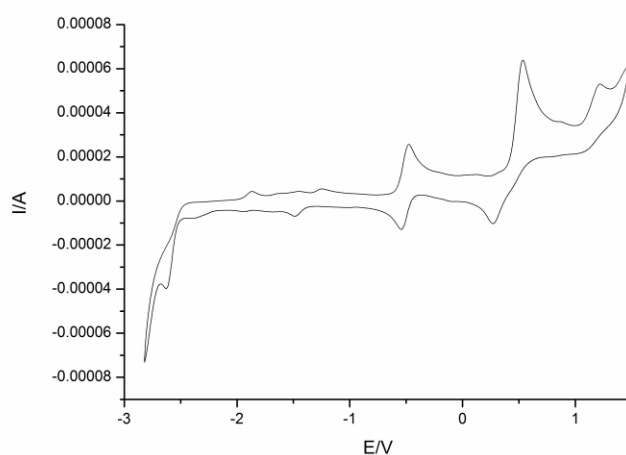


Figure 4. CV recorded in 2 mM solution (in CH_3CN) of complex **5**.

In the anodic region the first process is practically reversible and occurs at a formal potential of -0.50 V and the second process is partially irreversible ($E_p = +0.53$ V), whereas the third process is irreversible ($E_p = +1.23$ V). The only cathodic process is irreversible and displays a peak potential at -2.63 V.

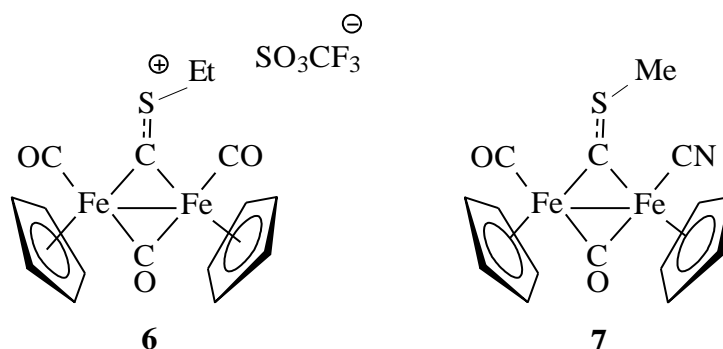
This potential value is more cathodic than that for the spontaneous H_2 evolution on glassy carbon, indicating that complex **5** cannot be exploited for electrocatalytic H_2 production. The absence of catalytic activity for complex **5**, in spite of the fact that hydride intermediates are expected to play a key role in electrocatalytic H_2 production, might be associated with bridging hydride coordination. Indeed, the reactivity and stability of terminal vs bridging iron hydrides in dithiolate model systems

are a matter of discussion, and evidence suggests that terminal hydride is more electron rich than the μ -hydrido ligand and, consequently, more catalytically active.^{6c,23} In addition to considerations of the hydride coordination mode, it has to be outlined that **5** exhibits a remarkable stability and inertness toward ligand replacement. Thus, it is perhaps not too surprising that **5** does not act as a catalyst, since strong Fe–H bonds and stable hydride complexes would be an obstacle to fast catalysis.

There are two major observations concerning the electrochemical behavior of the bridging aminoalkylidene diiron complexes described above. The first is that cationic complexes (**3a–c**) can be easily reduced in a reversible one-electron process but do not display electrocatalytic properties, except for **3b**, containing a more labile acetonitrile ligand in place of CO.

A rather obvious conclusion is that the absence of a vacant coordination site can be a major obstacle to the development of complex shows an appreciable catalytic activity. Cyanide in place of CO makes the diiron complexes less easily reducible but increases electron density at the Fe–Fe core, thus favoring protonation, which is the subsequent required step for H₂ evolution. Interestingly, although aminocarbene diiron complexes are quite dissimilar to natural [Fe–Fe]-H₂ase, also in this case cyanide ligand provides the most suitable environment to observe H₂ catalytic production.

Encouraged by the results described above, we extended investigations to the thio-alkylidene complexes **6** and **7** (Scheme 4), which allowed us to observe the influence of S in place of N in the bridging ligand. Cationic thiocarbene complexes [Fe₂(μ -CSR)(μ -CO)(CO)₂(Cp)₂]⁺ have been described in the literature,²⁴ and the structure of [Fe₂(μ -CSEt)(μ -CO)(CO)₂(Cp)₂][BF₄], which differs from **6** only in the counteranion, has been reported.^{24a}



Scheme 4

Cationic diiron thiocarbene complexes display a remarkable electrophilic character and undergo both nucleophilic addition²⁵ and olefin incorporation.²⁶ Moreover, it has been shown that thiocarbene diiron complexes can undergo one-electron reduction to form relatively stable radical

species, such as $[\text{Fe}_2(\mu\text{-CSMe})\text{-}(\text{CO})_3(\text{Cp})_2]^\bullet$,²⁷ which has been exploited to promote substitution of terminally coordinated CO with other ligands.

Details on the synthesis of **7**, which has been not reported in the literature, together with its spectroscopic data, are given in the Experimental Section.

On the cathodic side the CV (Figure 5A) of **6** displays two redox processes; the first is reversible with a formal potential of -1.20 V, and the second is irreversible ($E_p = -1.99$ V). Two irreversible processes are observed on the anodic side with peak potentials of $+0.96$ and $+1.30$ V, respectively.

When the CV (Figure 5B) was recorded in the presence of acetic acid, the backward peak decreased, suggesting the occurrence of a chemical process after the electron transfer that removes the reduced complexes. At the same time the forward peak increases, suggesting that more electrons are involved in the electrochemical process. Therefore, we can say that the process follows an ECE reaction pathway; i.e., an electrochemical process is followed by a chemical reaction which is in turn followed by an additional electron transfer. After that the hydrogen evolution could occur, but it is too slow to be evidenced using our experimental setup.

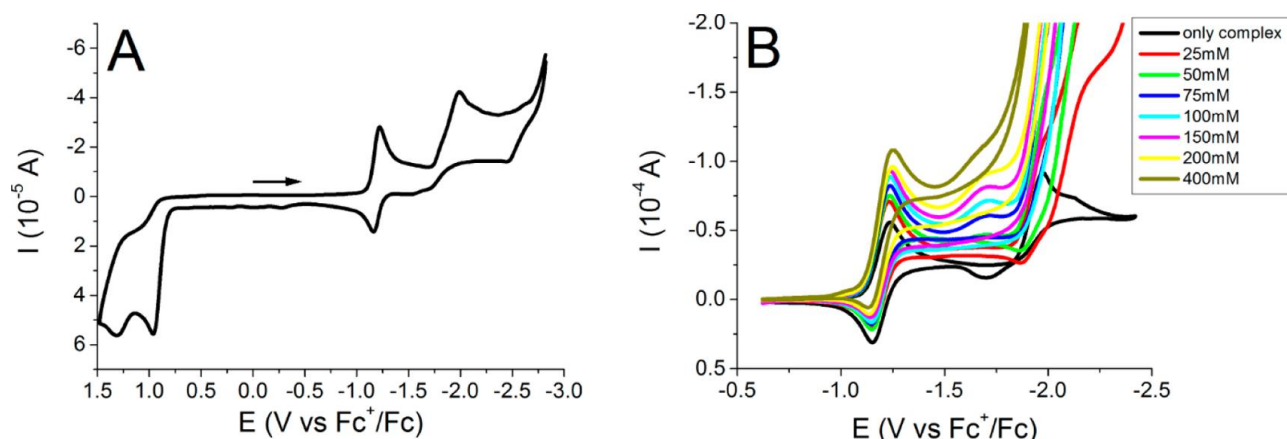


Figure 5. CVs recorded in a 2 mM solution (in CH_3CN) of complex **6** in the absence (A) and in the presence (B) of acetic acid at different concentrations. The arrow shows the direction of the first scan.

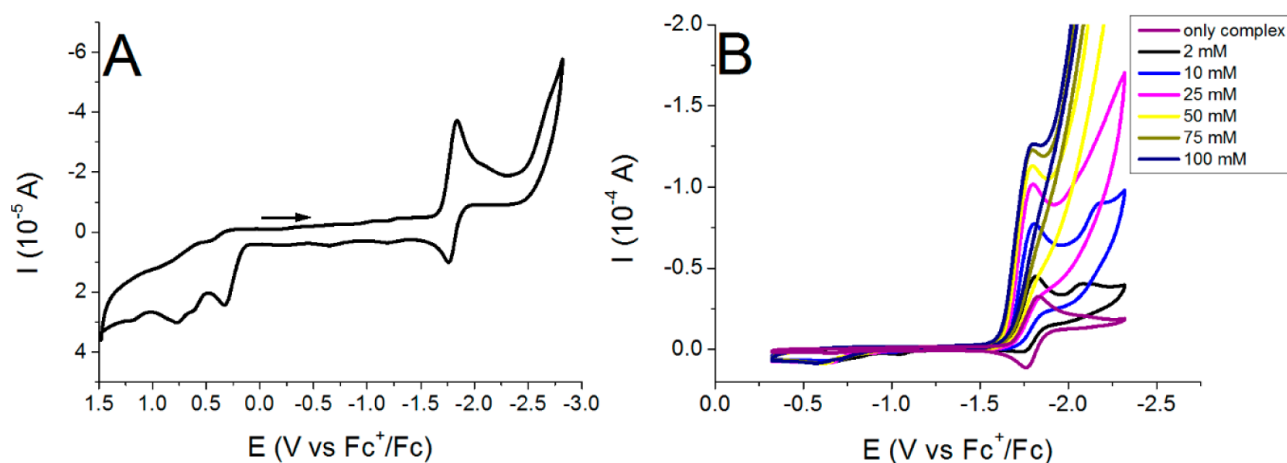


Figure 6. CVs recorded in a 2 mM solution (in CH₃CN) of complex **7** in the absence (A) and in the presence (B) of acetic acid at different concentrations. The arrow shows the direction of the first scan.

The CV of complex **7** (Figure 6A) displays two irreversible redox waves at least in the anodic region with peak potentials at +0.34 and +0.78 V. On the cathodic side complex **7** shows only a reversible process involving one electron, with a formal potential of -1.80 V. When the CVs (Figure 6B) were recorded in a solution of complex **7** wherein increasing amounts of HOAc were added, the redox couple exhibited electrocatalytic properties. The ratio between the currents in the presence and in the absence of acetic acid (100 mM) at a potential corresponding to the complex peak was greater than **4**. The value observed for **7** is not as high as the value for **4**, but no reaction, among the possible ones, would require such a high number of electrons. For example, hydrogenation of the bridging ligand requires only two electrons, as well as hydride formation at the diiron center. Moreover, the forward peak current depended linearly on acetic acid concentration up to 20mM, the catalytic efficiency was equal to 0.32, and the overpotential was particularly low (-0.34 V).

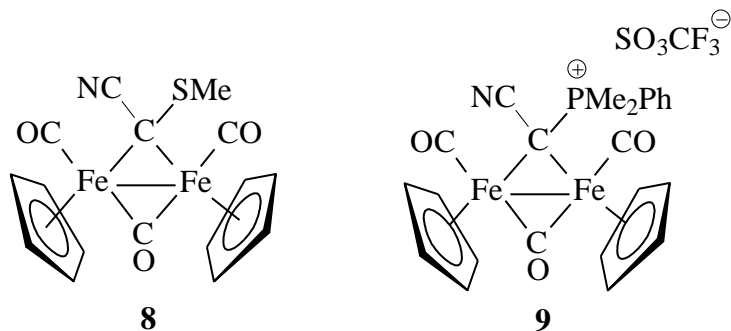
Therefore, complex **7** displays the most remarkable catalytic properties among the complexes we have examined. The overpotential is very close to the best values exhibited by dithiolate model complexes recently reviewed by Felton et al.,¹⁵ and the catalytic efficiency is similar to the average value reported in the same review.

On the basis of the electrochemical data, a possible mechanism for the electrocatalytic process involving complex **7** can be proposed. The first reaction step is the monoelectronic reduction clearly evidenced in the CV recorded for the diiron complex alone (redox waves with $E^{\circ} = -1.80$ V). This process is followed by a reaction with the proton to form an adduct that can be easily reduced. Consequently, the catalyst undergoes a further reduction that involves the transfer of a second electron which is highlighted in the CVs of **7** recorded in the presence of HOAc. The redox waves observed in Figure 6B at about -0.6 V are ascribed to the reoxidation of this reduced adduct, and this kind of response is typical of an ECE process.²⁸ The final step of the reaction is the hydrogen evolution that leads also to the regeneration of the catalyst, thus making it again available to be reduced. The increase of the cathodic current in the presence of HOAc indicates the process occurrence. Therefore, we believe that the overall electrocatalytic process takes place through an ECECcat mechanism. It is worth noting that **4** and **7**, which can be considered the most active electrocatalysts for H₂ evolution among the complexes investigated herein, are characterized by a perfectly reversible active redox system. This property is fundamental to allow a catalytic process

with the best efficiency,²⁹ and it is not a common feature even in many complexes already described in the literature for hydrogen production.³⁰ Moreover, we estimated the turnover number (TON) for **4**, by a controlled-potential electrolysis of **4** (2 mM) in a CH₃CN solution at -2.10 V, as described in the Experimental Section. In particular, electrolysis in the presence of acetic acid (100 mM) consumed 31 electrons per molecule of catalyst (complex **4**) per hour, corresponding to 15.5 turnovers per hour, which is consistent with results obtained in analogous experiments on dithiolate model systems.³¹ The TON value was obtained from the linear region of the coulogram (see the Supporting Information, Figure S33) by subtraction of the Coulombs relevant to the experiment carried out at -2.1 V in 100 mM HOAc, in the absence of complex (control experiment), to those relevant to the experiment carried out in the presence of complex **4**. Furthermore, the experiment was repeated four times with the same catalyst, for a total of 130 min, with no significant loss of activity.

Cyclic Voltammograms of μ -Alkylidene Complexes.

Bridging alkylidene (carbene) ligands are usually less reactive in comparison to bridging alkylidynes, in that the bridging carbon can be viewed as a saturated sp³ carbon. Thus, diiron μ -alkylidenes generally do not display a noticeable electrophilic character and are rather stable complexes.^{13c} In particular, we investigated complexes **8** and **9** (Scheme 5), in that they display some special features which might be beneficial to catalysis.



Scheme 5

The bridging alkylidene **8**³² contains both CN and SMe substituents, which are expected to display some electronwithdrawing effects and favor the reduction process. On the other hand, the presence of S might also favor proton uptake.

In addition, the phosphonium-carbene complex $[\text{Fe}_2\{\mu\text{-C}(\text{CN})(\text{PMe}_2\text{Ph})\}\{\mu\text{-CO}\}(\text{CO})_2\text{Cp}_2][\text{SO}_3\text{CF}_3]$ (**9**)³³ is positively charged and PR₃ acts as a good leaving group, being

easily displaced by a variety of nucleophiles. Therefore, complex **9** should exhibit unique properties, between those of bridging carbynes and carbenes.

In spite of the above considerations, the electrochemical properties of complexes **8** and **9** were quite similar. Therefore, only the CV of complex **9** is reported as an example in Figure 7. There are two reversible waves in the cathodic region with formal potentials at -1.11 and -1.93 V. On the anodic side an irreversible redox process is observed with a peak potential at $+1.11$ V. Unfortunately, no catalytic effect by the first cathodic process was observed when acetic acid was added to the solution.

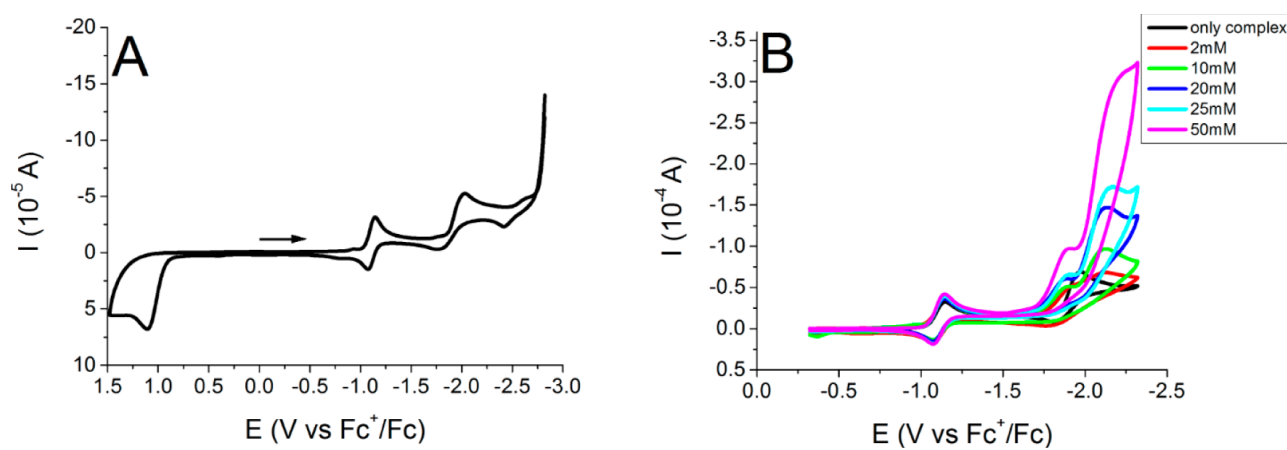


Figure 7. CVs recorded in a 2 mM solution (in CH₃CN) of complex **9** in the absence (A) and in the presence (B) of acetic acid at different concentrations. The arrow shows the direction of the first scan.

Conclusions

Diiron complexes containing bridging hydrocarbyl ligands (vinylalkylidenes, alkylidenes, aminoalkylidynes, and thioalkylidynes) and also Cp and CO ligands have been investigated as potential electrocatalysts for hydrogen production. The aim was to demonstrate that diiron complexes which do not closely resemble natural [Fe–Fe]-H₂ases might act as catalysts and that the search for efficient, iron based catalysts for H₂ production is not necessarily restricted to the realm of iron dithiolate model systems. Having examined a number of different complexes, we found that in a couple of cases (namely complexes **4** and **7**) the electrocatalytic properties are significant and comparable to those of many common dithiolate systems.

It is not surprising that only in a limited number of cases have we found a positive response. The catalytic H₂ production involves many steps and has so many structural, thermodynamic, and kinetic requirements that our rather naïve and tentative approach should have hardly produced much better results. Nevertheless, our findings indicate that a proper combination of bridging hydrocarbyl

ligands and cyclopentadienyls, together with CO and CN^- , can be used in place of dithiolates, providing a favorable electron density at the Fe–Fe core. Indeed, electron donor ligands shift the reduction potentials to more negative values, which is disadvantageous; on the other hand, they favor protonation at the metal, so that a most appropriate compromise has to be found. The mechanism of the reaction and structural changes involved have not been investigated, although all the complexes examined (except **5**) show a common structural motif, based on the $\text{cis-Fe}_2(\text{Cp})_2(\mu\text{-CO})(\text{CO})$ frame. In spite of these limits, a few clear indications have emerged from our work, and are outlined as follows.

(I) Bridging hydrocarbyl ligands are effective in preventing Fe–Fe fragmentation during electron and proton transfer (as suggested by the high reversibility of the redox system), so that possible advantages associated with metal–metal cooperative effects are maintained.

(II) Most structures of bridging ligands (e.g., vinylalkylidenes) containing π -extended systems and functional groups are not advantageous, in that reduction and protonation events occur at the ligand in place of the metal and, consequently, they do not result in H_2 production.

(III) Structural changes occurring at the $\text{Fe}_2(\text{Cp})_2(\text{CO})_2$ frame, along with reduction and protonation, are still not well understood; nevertheless, the lack of readily available coordinative sites in our diiron complexes clearly limits the catalytic activity.

(IV) Replacement of CO with cyanide substantially improves the catalytic activity, presumably for the same reason that makes the cyanide so effective in natural [FeFe]- H_2 ase. In other words, despite the fact that we deliberately looked for diiron species not resembling natural systems, it seems that some common features (e.g., CN^- and CO ligands) are beneficial.

Likewise, the presence of a S atom in the bridging ligand (e.g., in the μ -thioalkylidyne **7**) seems to favor the catalytic activity.

In conclusion, our findings indicate that organometallic diiron complexes with bridging hydrocarbyl ligands are of potential interest to expand the field of iron-based electrocatalysis for H_2 production.

Experimental Section

General Data. All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded on a PerkinElmer Spectrum 2000 FT-IR spectrophotometer, and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA instrument. NMR spectra were recorded on a Mercury Plus 400

instrument. Chemical shifts for ^1H and ^{13}C were referenced to internal TMS. All reagents were commercial products (Aldrich) of the highest purity available and were used as received.

Synthesis of $[\text{Fe}_2(\mu\text{-CSMe})(\mu\text{-CO})(\text{CO})(\text{CN})(\text{Cp})_2]$ (7**).** A solution of $[\text{Fe}_2(\mu\text{-CSMe})(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{CF}_3\text{SO}_3]$ (150 mg, 0.28 mmol), in THF (15 mL), was irradiated by a UV lamp for 2 h. Afterward, the mixture was treated with NBut4CN (84 mg, 0.33 mmol) and the mixture was stirred for 1 h. Solvent removal under reduced pressure gave a solid residue which was dissolved in CH_2Cl_2 and chromatographed on alumina. Elution with $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ (1/1 v/v) afforded a greenish brown band corresponding to **7** as a mixture of cis and trans isomers in almost equimolar amounts (cis and trans refer to the mutual Cp positions with respect to the Fe–Fe bond (yield 73 mg, 66%). Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{Fe}_2\text{NO}_2\text{S}$: C, 47.04; H, 3.42; N, 3.66. Found: C, 46.99; H, 3.43; N, 3.69. IR (CH_2Cl_2): $\nu(\text{CN})$ 2100 (vs); $\nu(\text{CO})$ 1999 (vs), 1981 (vs), 1819 (s) cm^{-1} . ^1H NMR (CDCl_3): δ 4.91, 4.96, 4.90, 4.86 (s, 10H, Cp); 3.49, 3.54 (s, 3H, SMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 408.3 ($\mu\text{-CSMe}$), 259.6 ($\mu\text{-CO}$); 210.1, 209.2 (CO); 136.2 (CN); 91.90, 89.88 (Cp); 34.2 (SMe).

Electrochemical Studies. Cyclic voltammograms were recorded at a scan rate of 0.05 V s^{-1} on a BAS-100A electrochemical analyzer using a three-electrode cell: a glassy-carbon disk (0.071 cm^2) as the working electrode, a Ag/AgNO₃ (0.1 M) reference electrode, and a platinum-wire counter electrode. All experiments were performed under a nitrogen atmosphere in CH_3CN containing 0.1 M nBu₄NPF₆ at room temperature. Ferrocene (Fc) was the internal reference, and all potentials have been quoted relative to the Fc/Fc⁺ couple set at 0.00 V. Glacial acetic acid was added in molar equivalent increments via microsyringe. Cyclic voltammograms of the complexes not shown in the main text are reported in the Supporting Information. All of the CVs have been recorded starting from the open circuit potential. Bulk electrolysis was carried at -1.50 V , in a three-electrode cell with stirring, to evaluate the number of electrons exchanged by complex **1b** (2 mM) during the first cathodic process using a rectangular GC electrode with a geometric area of 4.9 cm^2 and was stopped when the recorded current decreased to 5% of the initial value. Bulk electrolysis for the electrocatalytic reaction of hydrogen evolution in the presence of complex **4** was carried at -2.10 V , for 2000 s, under hydrodynamic conditions. The cell was the same and contained 20 mL of CH_3CN , which was 2.0 mM in complex **4**. Acetic acid was added until a concentration of 100 mM was obtained. After the first electrolysis the experiment was repeated three more times by adding acetic acid to the same solution in order to evaluate the stability of the catalyst.

Supporting Information

Figures giving cyclic voltammograms of all complexes (**1a–c**, **2**, **3a–c**, **4–9**) in the absence and in the presence of increasing amounts of acetic acid, bulk electrolysis of **1b** and **4**, and ^1H and ^{13}C

NMR spectra of complex **7**, not previously reported. The Supporting Information is available free of charge on the ACS Publications website ...

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