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Proton reduction catalysis by manganese vinylidene and allenylidene complexes

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Abstract

The present paper reports the unprecedented observation of a catalytic electrochemical proton reduction based on metallocumulene complexes. Manganese phenylvinylidene $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Mn{=}C{=}C(H)Ph$ (**1**) and diphenylallenylidene $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C{=}C{=}CPh_2$ (**3**) are shown to catalyze the reduction of protons from HBF_4 into dihydrogen in CH_2Cl_2 or CH_3CN media at -1.60 and -0.84 V (in CH_3CN) vs. Fc, respectively. The working potential for **3** (-0.84 V vs. Fc in CH_3CN) is the lowest reported to date for protonic acids reduction in non-aqueous media. The similar catalytic cycles disclosed here include the protonation of **1**, **3** into the carbyne cations $[(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Mn{\equiv}C{-}CH_2Ph]BF_4$ ($[\mathbf{2}]BF_4$), $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{\equiv}C{-}CH{=}CPh_2]BF_4$ ($[\mathbf{4}]BF_4$) followed by their reduction to the corresponding 19-electron radicals $\mathbf{2}^{\cdot}$, $\mathbf{4}^{\cdot}$, respectively. Both carbyne radicals undergo a rapid homolytic cleavage of the C_β–H bond generating an H-radical producing molecular hydrogen with concomitant recovery of the neutral metallocumulenes thereby completing a catalytic cycle.
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1. Introduction

Hydrogen production by water electrolysis is an important challenge of both fundamental and economical significance in the quest for alternative energy sources. Though Pt-based catalysts are known to achieve such a reaction, their replacement by cheaper homogeneous transition metal catalysts is becoming highly desirable [1]. To date, only hydrogenases effectively catalyze this process with TOF up to 10^3–10^4 molecules H_2 s^{-1} per site [2]. However, the known biomimetic models for the active site of [Fe]-only hydrogenases based on iron dithiolate clusters $(\mu\text{-}SCH_2XCH_2S\text{-}\mu)Fe_2(CO)_6$ (X = CH_2 [3], O [4], NR [5]) are much less active than the native enzymes and are char-

acterized by an excessive overvoltage for hydrogen production.

To date, all proposed catalytic cycles for electrochemical proton reduction involve the formation of transition metal hydrido intermediates and their subsequent transformation resulting in dihydrogen elimination (Scheme 1). Depending on the catalyst structure such processes can proceed via various catalytic pathways differing in the sequences of the electrochemical and chemical elemental steps.

For complexes containing polydentate nitrogen ligands [6] and [Fe]-only hydrogenase model compounds $(\mu\text{-}SCH_2XCH_2S\text{-}\mu)Fe_2(CO)_6$ (X = CH_2, O) [3b,3c,3d,4] of low basicity the reduction step (c) producing anionic complexes precedes the protonation step (d) that affords terminal hydride species [M]H. The reverse order – protonation (a) preceding reduction (b) – was encountered for [1.1]ferrocenophane [7] and the anionic iron complex $[Fe(CO)_2(PMe_3)(\mu\text{-}S(CH_2)_3S\text{-}\mu)Fe(CO)_2CN]^-$ [3a]. In the latter case
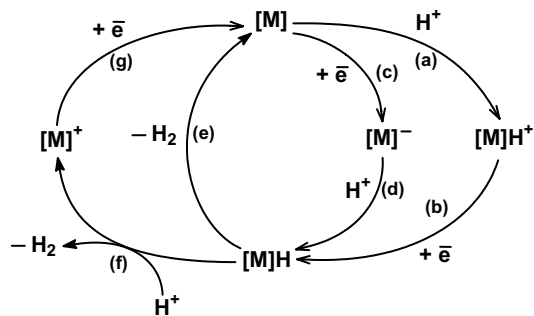
Scheme 1.

the protonation was found to occur at the Fe–Fe bond to form a bridging μ_2-H framework. Some remarkable biomimetic catalysts with azadithiolate bridge $(\mu\text{-SCH}_2\text{N(R)}\text{-}$ $\text{CH}_2\text{S-}\mu)\text{Fe}_2(\text{CO})_6$ (R = para-$\text{CH}_2\text{C}_6\text{H}_4\text{Br}$, 2-furyl, $\text{CH}_2\text{-}$ CH_2OCH_3, t-Bu, etc.) [5] undergo protonation at the basic nitrogen atom first, facilitating the subsequent reduction step. Further protonation at the Fe–Fe bond and transfer of the second electron causes dihydrogen elimination. The involvement of cationic intermediates decreases the working potential for the catalytic hydrogen production exhibiting the lowest overvoltage values reported so far [5]. The crucial H_2 production step can proceed via the formation of the dihydrogen ligand and its further substitution (heterolytic way (f), possible for both mono- and binuclear catalysts [3–6]) or via binuclear reductive elimination (homolytic way (e), restricted to binuclear models like [1.1]ferrocenophane [7]). Most of catalytic systems considered above function only in non-aqueous media with high working potential for hydrogen production and includes the intermediate formation of oxygen-sensitive carbonyl-metallate-anions and metal hydrides, thus remaining far from the practical applicability.

We are now proposing a new catalytic system for electrochemical proton reduction based on metallocumulene complexes involving the formation and subsequent activation of a C–H bond rather than an M–H bond. This new approach is illustrated for the manganese phenylvinylidene $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Mn}=\text{C}=\text{C(H)Ph}$ (1) and diphenylallenylidene $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}=\text{C}=\text{C}=\text{CPh}_2$ (3) complexes.

2. Results and discussion

We have reported earlier [8] that the reduction of the cationic manganese carbyne complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{-}$ $(\text{PPh}_3)\text{Mn}\equiv\text{C–CH}_2\text{Ph}]\text{BF}_4$ (2^+) leads quantitatively to the neutral vinylidene complex $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{-}$ $\text{Mn}=\text{C}=\text{C(H)Ph}$ (1) with concomitant evolution of dihydrogen. The reaction can be understood in terms of a homolytic cleavage of the C_β–H bond in 19-electron (19-e) carbyne complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{Mn}\equiv\text{C–CH}_2\text{Ph}]$ (2) generating an H-radical, which undergoes rapid dimerization into H_2. Few examples of related C–H bond activation processes in 19-e Mn [8a] and Re [9] radicals yielding hydrogen have been previously reported. Related homo-

lytic reactions for 19-e vinylidenes affording 18-e σ-alkynyl products are also known for Co, Rh, and Ru complexes [10]. As a rule such homolytic C_β–H bond cleavage processes are fast on the CV time scale and are supposed to be favored by the instability of the reactive 19-e metal moiety.

Considering that complex 2^+ can be restored from 1 upon simple protonation we reasoned that the stepwise transformation $1 \rightarrow 2^+ \rightarrow 2^\cdot \rightarrow 1$ (Scheme 2) might emerge as a viable catalytic cycle for hydrogen production via electrochemical proton reduction.

This prompted us to investigate the electrochemical behavior of complex 2^+ in dichloromethane and acetonitrile solutions in the presence of acid HBF_4. In CH_2Cl_2 the CV of 2^+ shows the irreversible one-electron reduction peak **B** at −1.78 V vs. Fc/Fc^+ (Fig. 1b) and the oxidation peak **A** of the vinylidene complex 1 at −0.06 V vs. Fc/Fc^+ is observed on the reverse scanning of potential thus indicating a fast rate for the C_β–H bond homolysis. In acetonitrile the reduction of 2^+ proceeds in the same manner at −1.60 V vs. Fc/Fc^+ but the reduction peak of the acid proton is observed at −2.13 V vs. Fc/Fc^+ probably due to partial deprotonation of 2^+ with this more basic solvent.

Upon addition of acid ($HBF_4 \cdot Et_2O$), the catalytic current in the reduction peak **B** of 2^+ appeared both in CH_2Cl_2 and CH_3CN media together with the increasing intensity of the proton reduction peak **C** (Fig. 2 for CH_3CN). The oxidation peak of 1 disappears in acidic solution due to the fast protonation of 1 into 2^+. The increase of acidity induces a cathodic shift of reduction potentials for 2^+ and proton (for 5 equivalents of HBF_4 in CH_3CN for −0.07 and 0.15 V, respectively). Such observations provide reliable evidence for proton reduction catalysis [3–6]. We can thus conclude that the catalytic process follows the CEC (chemical–electrochemical–chemical) pathway (Scheme 2).

Further evidence for the activity of 1 in catalytic hydrogen production was obtained by preparative electrolysis of CH_2Cl_2 solutions of 1 (2 mM) and HBF_4 (10 equiv, 20 mM) at −1.75 V vs. Fc/Fc^+ on Hg-electrode. The initial rate of the electrolysis of $[2]BF_4$ becomes ~6 times higher
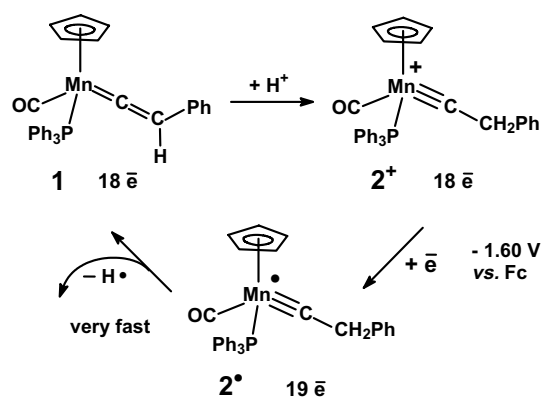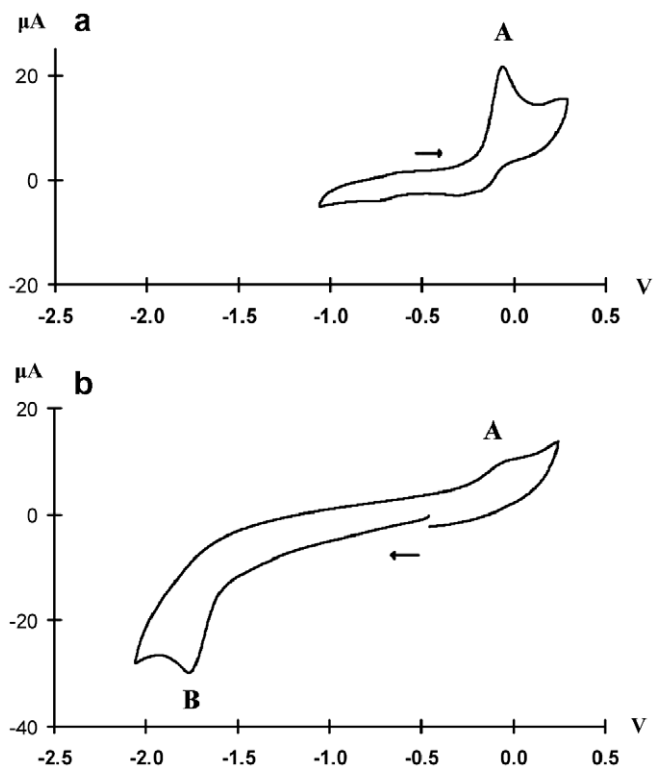

Scheme 2.

Fig. 1. Cyclic voltammograms of complexes **1** (a) and **2$^+$** (b). (GC-electrode, CH$_2$Cl$_2$, 0.1 M Bu$_4$NPF$_6$, 1×10^{-3} M, 0.2 V s^{-1}, potentials vs. Fc/Fc$^+$.)
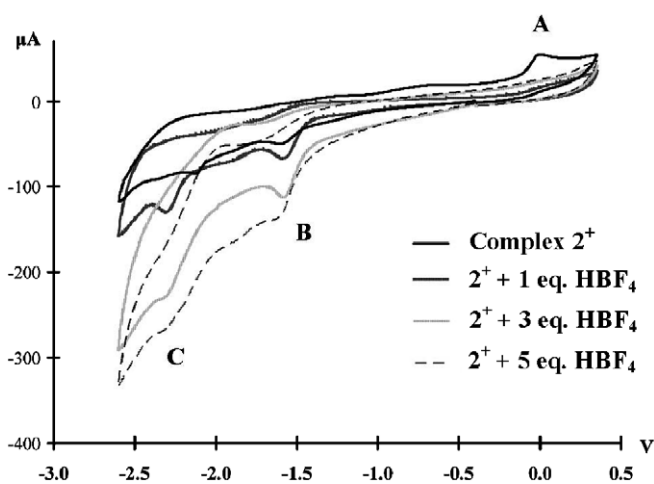
Fig. 2. Cyclic voltammogram of complex **2$^+$** in the presence of HBF$_4$. (GC-electrode, CH$_3$CN, 0.1 M Bu$_4$NPF$_6$, 2×10^{-3} M, 0.2 V s^{-1}, potentials vs. Fc/Fc$^+$.)

after addition of HBF$_4$ and gradually slows down as the acid concentration decreases. In such bulk experiments hydrogen bubbles can be clearly seen. During 1 h of electrolysis about 5 F per mol of **1** were passed through the solution, corresponding to ∼5 turnovers. The presence of [**2**]BF$_4$ in the concentrated solution after the electrolysis was detected by IR-spectroscopy. The working potential for catalytic proton reduction with **1** (−1.60 V vs. Fc/Fc$^+$

in CH$_3$CN) is within the range of those found for most [Fe]-only biomimetic models (−1.4 to −1.7 V vs. Fc/Fc$^+$) [3–5].

The formation of hydrogen atoms followed by their recombination into dihydrogen constitutes a rather uncommon sequence for hydrogen production. Though the elimination of H might be regarded as thermodynamically unfavorable process we tentatively propose that reformation of the stable 18-e metal atom configuration constitutes the driving force of the C–H homolysis and provides the appropriate energy balance. The concerted pathway of dihydrogen formation directly from transition state consisting of two molecules of **2** should also be considered. The nature of "real" intermediate hydrogen species remains unclear and further detailed studies are to be done to gain mechanistic insight into the factors governing these specific radical processes.

In order to expand the scope of such catalysts, we investigated in parallel a closely related cycle based on the manganese diphenylallenylidene complex **3** for which a more positive reduction potential of the diphenylvinylcarbyne **4$^+$** could be expected (Scheme 3) [12].

CV of the diphenylallenylidene complex **3** in CH$_2$Cl$_2$ solution shows two one-electron oxidation steps: the first one, reversible at +0.35 V vs. Fc/Fc$^+$ (Fig. 3a, peak **D$_1$**) and the second one, irreversible at +1.19 V (not shown). The same pattern is observed for its reduction occurring at −1.55 V (Fig. 3a, peaks **D$_2$**, reversible) and at −2.20 V (irreversible, not shown). The vinylcarbyne cation **4$^+$** undergoes the irreversible one-electron reduction (Fig. 3b, peak **E**) at −0.84 V vs. Fc/Fc$^+$ (CH$_3$CN) and −0.93 V (CH$_2$Cl$_2$), and all representative peaks of neutral allenylidene **3** are observed thus the C$_\beta$–H bond activation process in **4** (Scheme 3) is also fast on the CV time scale.

CVs in acetonitrile in the presence of acid also reveal characteristic catalytic currents in the reduction peak of vinylcarbyne **4$^+$** (Fig. 4, peak **E**, −0.84 V vs. Fc/Fc$^+$) indicative of the catalytic proton reduction process, as for **1**.

The working potential for catalytic proton reduction for **3** is ∼0.7 V more positive than for **1** but catalytic currents in the case of **3** are generally by 30–50% lower thus reveal-
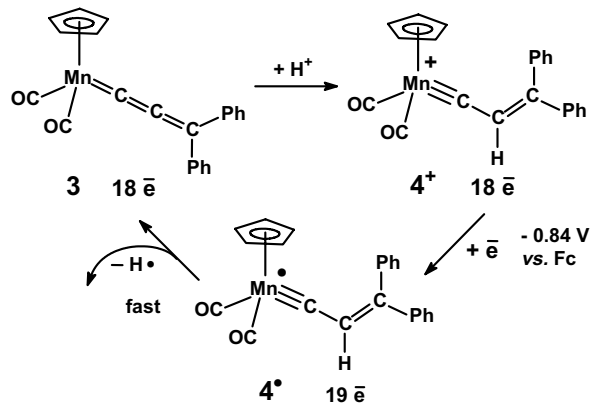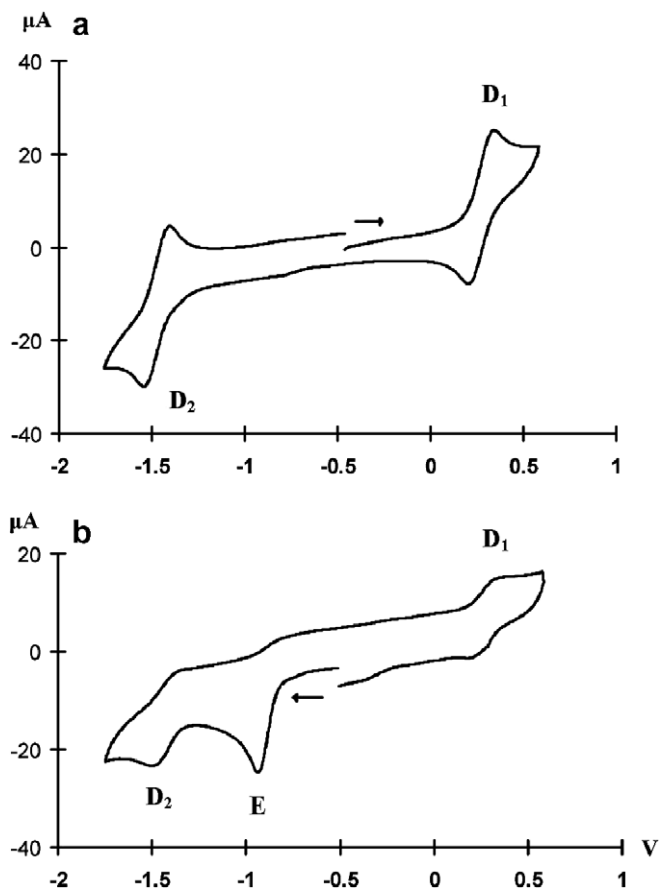

Scheme 3.

Fig. 3. Cyclic voltammograms of complexes **3** (a) and **4**$^+$ (b). (GC-electrode, CH$_2$Cl$_2$, 0.1 M Bu$_4$NPF$_6$, 1×10^{-3} M, 0.2 V s^{-1}, potentials vs. Fc/Fc$^+$.)

ing a reduced activity of this catalyst. However, the complex **3** represents the lowest working potential (-0.84 V vs. Fc/Fc$^+$ in CH$_3$CN) for reduction of protonic acids in non-aqueous media catalyzed by homogeneous transition metal complexes (the best example reported so far was -1.13 V vs. Fc/Fc$^+$ for [(μ-SCH$_2$)$_2$N(2-C$_4$H$_3$O)]Fe$_2$(CO)$_6$ in CH$_3$CN [5c]).
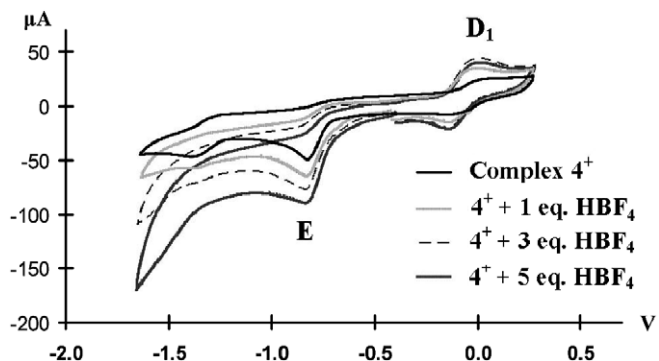
Fig. 4. Cyclic voltammogram of complex **4**$^+$ in the presence of HBF$_4$. (GC-electrode, CH$_3$CN, 0.1 Bu$_4$NPF$_6$, 2×10^{-3} M, 0.2 V s^{-1}, potentials vs. Fc/Fc$^+$.)
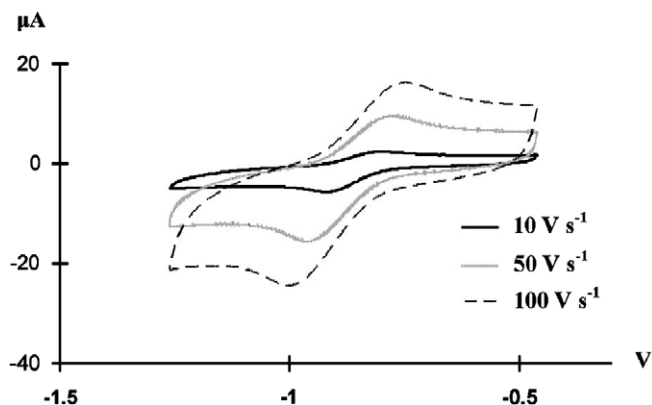
Fig. 5. Cyclic voltammogram of complex **4**$^+$ at high scan rates. (Pt-electrode, CH$_2$Cl$_2$, 0.1 M Bu$_4$NPF$_6$, 1×10^{-3} M, potentials vs. Fc/Fc$^+$.)

The reduction of the carbyne cations **2**$^+$ and **4**$^+$ under CV conditions at higher scan rates revealed some differences in the rate of homolytic C$_\beta$–H bond cleavage in 19-e radicals. The reduction peak for **2**$^+$ is completely irreversible even at 100 V s^{-1} so, the life-time of **2**$^{\cdot}$ is very short and the C$_\beta$–H cleavage proceeds at high rate. At the same time the I_a/I_c ratio for the reduction peak of **4**$^+$ becomes ca. 50% at 10 V s^{-1} and 100% at 100 V s^{-1} (Fig. 5) illustrating the greater life-time of **4**$^{\cdot}$ compared to **2**$^{\cdot}$.

We propose that the greater stability of **4**$^{\cdot}$ is caused by the lower electron density on the metal atom and the delocalization of the unpaired electron at the C$_\gamma$ atom and phenyl substituents of the ligand. This is probably the main reason for the lower activity of **3** in proton reduction catalysis.

3. Concluding remarks

In summary, we have shown for the first time that proton reduction catalysis can be achieved with metallocumulene complexes. The catalytic cycle includes the protonation of manganese complexes **1**, **3** into cationic carbynes **2**$^+$, **4**$^+$ and their further reduction to the corresponding 19-e radicals **2**$^{\cdot}$, **4**$^{\cdot}$, respectively. Hydrogen elimination leads to regeneration of the stable neutral 18-e complexes **1** and **3** which can be easily protonated again. The tendency of the metal to achieve an 18-e configuration appears as the main driving force in such homolytic processes and is typical for odd-electron σ,π- and π-complexes [8a,11]. The presence of PPh$_3$ ligand in **1** increases the stability of the active species but shifts negatively the working potential.

The advantages of the catalytic systems presented in Schemes 2 and 3 are the cationic nature of the key intermediates **2**$^+$ and **4**$^+$ facilitating the reduction without formation of unstable carbonylmetallate or metal hydride species. It is noteworthy that all factors influencing proton reduction catalysis – basicity and stability of the catalytic center, the reduction potential of cationic intermediate – can be tuned by varying the ligand set giving a good opportunity for the design of new effective and economically viable catalysts.

4. Experimental

All manipulations were carried out under purified Ar atmosphere using standard Schlenk techniques. Solvents grade CH_2Cl_2 and CH_3CN were distilled over CaH_2 prior to use. Bu_4NPF_6 and $HBF_4 \times Et_2O$ was purchased from Aldrich Chemical Co. Vinylidene $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)$-Mn=C=C(H)Ph and allenylidene $(\eta^5\text{-}C_5H_5)(CO)_2Mn=$C=C=CPh_2$ compounds and their protonated carbyne derivatives were prepared by published methods [8b,12].

Cyclic voltammetry measurements were carried out using a Autolab PGSTAT100 instrument controlled by GPES 4.09 software. Experiments were performed under Ar atmosphere in CH_2Cl_2 or CH_3CN solutions using three-electrode cell consisted of a glassy carbon working electrode ($d = 3$ mm), a platinum wire ($S = 1$ cm^2) as counter electrode, and a SCE electrode as a reference. For high scan rate experiments a platinum ($d \approx 0.5$ mm) working electrode was used. 0.1 M solution of Bu_4NPF_6 was used as the supporting electrolyte. The sample concentrations used were 1×10^{-3} M (CH_2Cl_2) and 2×10^{-3} M (CH_3CN). All peak potentials are given relative to the ferrocene/ferrocenium couple ($E = +0.46$ V (CH_2Cl_2) or $E = +0.40$ V (CH_3CN) vs. SCE). The number of electrons consumed was estimated by comparison of the currents of the peaks observed with those of the one-electron Fc/Fc^+ or $(\eta^5\text{-}C_5Me_5)_2Fe/(\eta^5\text{-}C_5Me_5)_2Fe^+$ couples at the same concentrations. Before each measurement the working electrode was polished with a polishing machine (Presi P230). For the proton reduction experiments the diluted solution of $HBF_4 \times Et_2O$ was prepared (70 µL of $HBF_4 \times Et_2O$ in 1 mL of the appropriate solvent) and added via syringe directly to the electrochemical cell. The values of the catalytic current in the proton reduction experiments were strongly dependent on the electrode surface quality (the values of the catalytic current obtained on the freshly polished electrode are 2–3 times greater than those for the next repetitive scan) thus all cyclic voltammograms were reproduced several times affording the same results.

Controlled potential electrolysis was carried out in 20 mL cell in CH_2Cl_2-Bu_4NPF_6 solution using unstirred Hg pool electrode (the surface area ca. 10 cm^2) at -1.3 V vs. SCE (-1.75 V vs. Fc). The typical concentration of catalyst and acid were 2 mM and 20 mM, respectively.

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