Electronic Supporting Information

A structural and functional mimic of the active site of NiFe hydrogenases†

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Experimental Section

Materials. All reactions were routinely performed under an inert atmosphere of argon using standard Schlenk techniques. Solvents were degassed and distilled under argon. Diethyl ether was distilled by refluxing over Na/benzophenone and dry dichloromethane and pentane were obtained by distillation on CaH_2. NMR solvents (Eurisotop) were deoxygenated by three freeze-pump-thaw cycles and stored over molecular sieves. Commercial dimethylformamide (DMF) for electrochemistry was degassed by bubbling nitrogen through it. [Ni(xbsms)][1] and $[CpFe(CO)_2(thf)](BF_4)$[2] were prepared according to previously reported procedures. Trifluoroacetic acid (TFA, Aldrich) was used as received. The supporting electrolyte $(n\text{-}Bu_4N)BF_4$ was prepared from $(n\text{-}Bu_4N)HSO_4$ (Aldrich) and $NaBF_4$ (Aldrich) and dried overnight at 80 °C under vacuum.

Methods and Instrumentation: NMR spectra were recorded at room temperature in 5 mm tubes on a Bruker AC 300 spectrometer equipped with a QNP probehead, operating at 300.13 MHz for ^1H and 75.5 MHz for ^{13}C. Solvent peaks are used as internal references relative to Me_4Si for ^1H and ^{13}C chemical shifts (listed in ppm). ESI mass spectra were recorded with a Finnigan LCQ thermoquest ion-trap. Elemental analyses were performed by the “Service Central d’Analyse du CNRS” (Vernaison, France). All electrochemical measurements were carried out under nitrogen at room temperature. A standard three-electrode configuration was used consisting of a glassy carbon (3 mm in diameter) or platinum (2 mm in diameter) disk as the working electrode, an auxiliary platinum wire and an Ag/AgCl/aqueous $AgCl_{sat}$ + KCl 3M (denoted as Ag/AgCl throughout this text) reference electrode closed by a Vycor frit and dipped directly into the solution.The internal reference system Fc^+/Fc was found at 0.53 V vs. Ag/AgCl in DMF. Cyclic voltammograms were recorded with a EG&G PAR 273A instrument. Solution concentrations were approximately 1 $mmol.L^{-1}$ for the catalyst and 0.1 $mol.L^{-1}$ for the supporting electrolyte $(n\text{-}Bu_4N)BF_4$. Electrodes were polished with an MD-Nap polishing pad with 1-µm monocrystalline diamond DP suspension and DP lubricant blue (Struers). Additions of TFA (50 mM solution in DMF) were made by syringe. Cyclic voltammograms of the supporting electrolyte and CF_3COOH in DMF are given in Figures S5 and S6. Bulk electrolysis experiments and coulometry were carried out on an EG&G PAR 273A instrument in DMF, using a mercury pool cathode. The platinum-grid counter electrode was placed in a separate compartment connected by a glass-frit and filled with a 0.1 $mol.L^{-1}$ solution of $(nBu_4N)BF_4$ in degassed DMF. A made-to-measure electrolysis cell with a cylindrical reservoir was used. The mercury pool surface was therefore identical from one experiment to another. The mercury surface was measured as 1.23 cm^2 and the electrolysis cell constant was determined to be 2.34×10^{-4} s^{-1} by performing bulk electrolysis of methylviologen hexafluorophosphate.[3] The following procedure was followed: a degassed DMF solution (7 mL) containing $(nBu_4N)BF_4$ ($_($0.1 mol.L^{-1}) and TFA (0,1 mol.L^{-1}) was first electrolyzed at the desired potential until the current reached 1% of its initial value. The catalyst (1 mmol.L^{-1}) was then added and electrolysis was performed at the same potential with coulometric monitoring. In parallel, the volume of H_2 evolved was measured at atmospheric pressure. Hydrogen was tested for purity using a Delsi Nermag DN200 GC chromatograph equipped with a 3 m Porapack column and a thermal conductivity detector (TCD). Nitrogen under 1 bar was used as the carrier gas. The whole apparatus was thermostated at 45°C. Under these conditions, pure hydrogen has an elution time of 77 s.

DFT calculations were performed with the Jaguar quantum chemistry program (version 5.2) using the crystallographic structure of [Ni(xbsms)FeCp(CO)](BF_4).[4] Calculations were carried out with two different functionals, B3LYP and BP86, and the LACV3P**++ basis set, which is of triple-zeta quality and has polarization and diffuse functions. For each modelled species in the catalytic cycle, geometry optimizations were carried out first in the gas-phase followed by optimization with an implicit solvent model (Poisson-Boltzmann solver) corresponding to DMF.

Comparison of [(CO)(dppe)Fe(pdt)(μ-H)Ni(dppe)]$^{+}$[5] with 2^+ in terms of overpotential for hydrogen evolution: Because the standard potential of the TFA/H_2 couple in CH_2Cl_2 (the solvent used for studying the catalytic activity of [(CO)(dppe)Fe(pdt)(μ-H)Ni(dppe)]$^+$) is not determined, we first used a platinum electrode to catalyze H_2 evolution from TFA in both DMF and CH_2Cl_2. Rotating disk electrode measurements showed that hydrogen evolves in CH_2Cl_2 at potentials 500 mV more positive than in DMF. We know that $E^0(TFA/H_2) = -1.01$ V vs Fc$^{+/0}$ in DMF[6] so that $E^0(TFA/H_2)$ can be estimated to –0.5 V vs Fc$^{+/0}$ in CH_2Cl_2. The reported potential for hydrogen evolution catalyzed by [(CO)(dppe)Fe(pdt)(μ-H)Ni(dppe)]$^+$ ($E_{pc}\sim-1.5$ V vs Fc$^{+/0}$ in the presence of 3 mmol^{-1} TFA) then corresponds to an overpotential of ~1V.

Syntheses

[Ni(xbsms)FeCp(CO)$_2$](BF_4) **1**(BF_4)

A solution of [(Cp)Fe(CO)$_2$(thf)](BF_4) (51,8 mg, 0,154 mmol) and [Ni(xbsms)] (61,4 mg, 0,152 mmol) in dichloromethane (10 mL) was stirred for 15 minutes at room temperature and then filtered through canula. The product was then precipitated with pentane, isolated by filtration, washed with pentane and dried in vacuum to afford a red powder (87 mg, 85%).

NMR ^{1}H (300 MHz, $CDCl_3$, 24°C): δ 7.35 (s, 4H, Ar), 5.33 (s, 5H, Cp), 4.11 (broad s, 2H, $ArCH_2S$), 3.93 (broad s, 2H, $ArCH_2S$), 2.43 (s, 2H, $(CH_3)_2CC\underline{H_2}$), 2.30 (s, 2H, $(CH_3)_2CC\underline{H_2}$), 1.77 (s, 6H, -$CH_3$), 1.74 (s, 6H, -$CH_3$). IR ($CH_2Cl_2$): ν_{CO} = 2054 (F), 2008 (F) cm^{-1}; IR (KBr): ν_{CO} = 2044 (F), 1996 (F) cm^{-1}. ESI-MS : m/z (%) 579 (70) [M]$^+$, 551 (8) {[M]–CO}$^+$, 523 (100) . Elemental analysis: calculated for **1**·0,5CH_2Cl_2·H_2O : $C_{23,5}H_{32}BClF_4FeNiO_3S_4$ (727.56) : C 38.79; H 4.43; B 1.49; F 10.44; Fe 7.68; Ni 8.07; S 19.23. Experimental: C 39.11; H 4.38; B 1.64; F 9.52; Fe 8.02; Ni 7.25; S 18.50.

[Ni(xbsms)FeCp(CO)](BF_4) **2**(BF_4)

Crystals of **2**(BF_4)·CH_2Cl_2 were obtained from a dichloromethane solution of complex **1**(BF_4) exposed to daylight, through slow diffusion of vapour of diethylether.

NMR ^1H (300 MHz, CD_2Cl_2, −35°C): δ 7.34 (m, 4H, Ar), 4.74 (s, 5H, Cp_1), 4.64 (s, 5H, Cp_2), 4.73 (d, 2H, $ArC(H_2)_2S$), 4.19 (d, 2H, $ArC(H_1)_2S$), 3.79 (d, 2H, $ArC(H_2)_2S$), 3.63 (d, 2H, $ArC(H_1)_2S$), 2.41 (d, 2H, $(CH_3)_2CC(\underline{H_2})_2$), 2.13 (d, 2H, $(CH_3)_2CC(\underline{H_2})_2$), 2.09 (d, 2H, $(CH_3)_2CC(\underline{H_1})_2$), 1.83 (d, 2H, $(CH_3)_2CC(\underline{H_1})_2$), 1.75 (s, 6H, $-CH_3$), 1.46 (s, 6H, $-CH_3$). IR (CH_2Cl_2): ν_{CO} = 1939 (F); IR (KBr): 1934 cm^{-1} (F). ESI-MS : m/z (%) 551 (100) $[M]^+$, 523 (2) $\{[M]–CO\}^+$.

Crystal Structure Analysis: Crystallographic data are summarized in Table S1. Data collection was performed at 298 K with a Bruker SMART diffractometer with a CCD area detector and with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Empirical absorption correction (Sadabs[7]) was performed. Molecular structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with the SHELXTL package,[8, 9] with anisotropic thermal parameters. Hydrogen atoms were generally found and refined isotropically. The hydrogen atoms of the methyl groups of the xbsms^{2-} ligand and the solvent molecules were placed in ideal positions and refined as riding atoms. The asymmetric unit of $\mathbf{2}(BF_4)\cdot CH_2Cl_2$ contains a $\mathbf{2}^+$ cation, one BF_4^- anion disordered over two positions around the boron atom with relative occupancies 0.917/0.083, and one CH_2Cl_2 molecule.

Selected bond lengths (Å) and angles (°): Ni-S(1) 2.1670(9), Ni-S(4) 2.1717(8), Ni-S(3) 2.1803(8), Ni-S(2) 2.1807(8), Fe-C(26) 1.764(3), Fe-C(Cp) 2.073(3)-2.102(3), Fe-S(4) 2.2862(9), Fe-S(1) 2.3017(9), O(1)-C(26) 1.143(4), S(1)-Ni-S(4) 80.92(3), S(4)-Ni-S(3) 91.38(3), S(1)-Ni-S(2) 91.02(3), S(3)-Ni-S(2) 95.52(3), Ni-S(1)-Fe 82.94(3), Ni-S(4)-Fe 83.21(3), C(26)-Fe-S(4) 96.58(10), C(26)-Fe-S(1) 100.31(10), S(4)-Fe-S(1) 75.71(3)

Table S1. Crystal data and structural refinement details for complex $\mathbf{2}(BF_4)\cdot CH_2Cl_2$

Compound	$\mathbf{2}(BF_4)\cdot CH_2Cl_2$
Formula	$C_{23}H_{31}BCl_2F_4FeNiOS_4$
Molecular mass	723.99
Color	dark brown
Crystal size (mm)	0.40 x 0.35 x 0.10
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	10.161 (2)
b [Å]	22.746 (5)
c [Å]	13.340 (3)
α [°]	90
β [°]	105.252 (4)
γ [°]	90
V [Å]^3	2974.5 (12)
Z	4
ρ_{calcd} [g.cm^{-3}]	1.617
μ [cm^{-1}]	16.24
Reflections collected	18506
Unique reflections (R_{int})	7024 (0.0274)
Observed reflections [I>2σ(I)]	5640
Refined parameters	475

R indices (all data)	R1 =0.0544, wR2 =0.0901
Final R indices (observed reflections)	R1 =0.0406, wR2 =0.0860
Goodness of fit S	1.104
$\Delta\rho$ (max/min) [e Å^{-3}]	0.532 and –0.593

$R1 = \Sigma \mid \mid F_0 \mid - \mid F_c \mid \mid / \Sigma \mid F_0 \mid$

$wR2 = \{\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2]\}^{1/2}$.

$w = 1 / [\sigma^2(F_0^2) + (aP)^2 + bP]$ où $P = [2F_c^2 + \mathrm{Max}(F_0^2, 0)] / 3$ (See CIF for a and b values)

Figure S1. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2, −35°C) of **2**(BF_4) with two sets of signals (aliphatic H and aromatic Cp) for isomers 1 and 2.

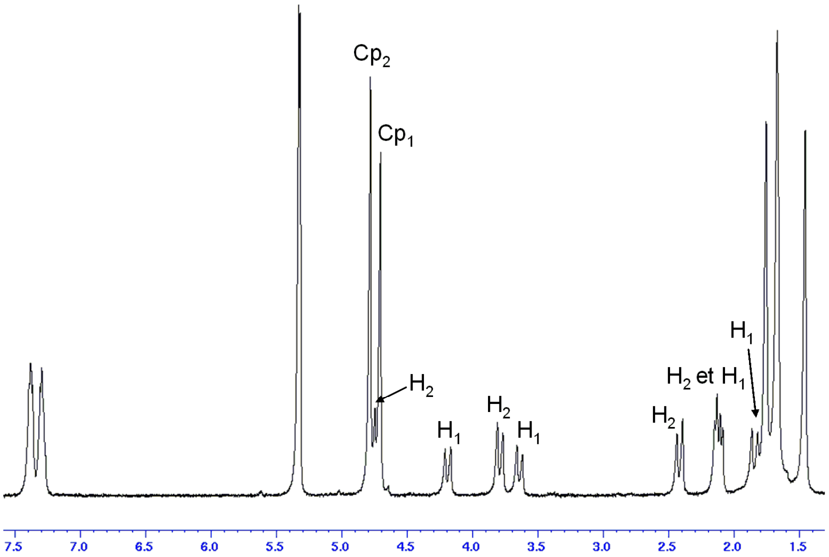


Figure S2. Evolution of the first reductive process of **2**(BF_4) (1.0 mmol.L^{-1}) in the presence of various amounts of CF_3COOH recorded in a DMF solution of n-Bu_4NBF_4 (0.1 mol.L^{-1}) on a glassy carbon electrode at 100 mV.s^{-1} : a) without acid; b) 1.5 equiv.; c) 5 equiv.

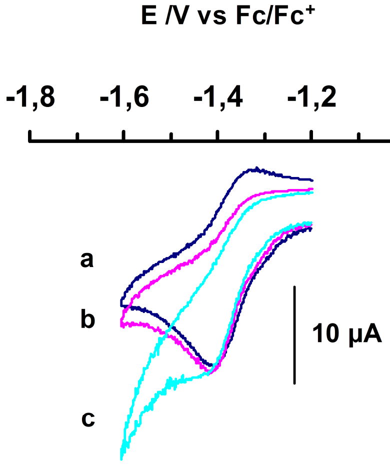
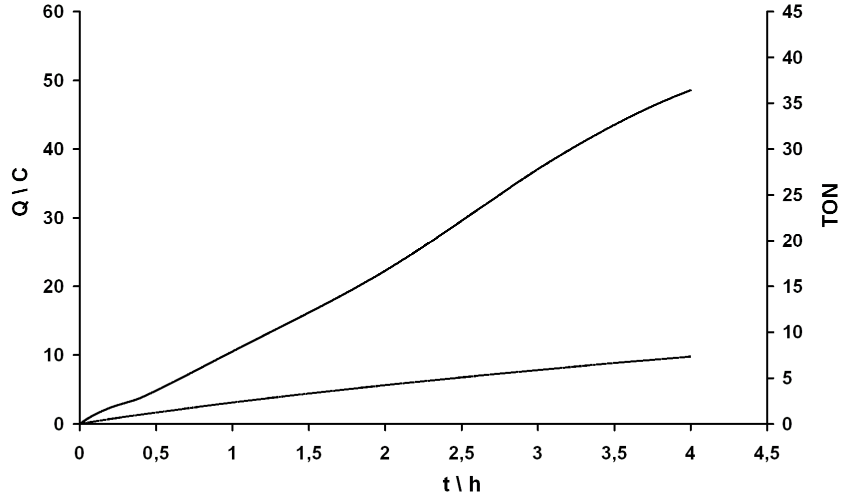


Figure S3. A.Coulometry for bulk electrolysis at –1.83 V vs Fc$^{+/0}$ of a DMF solution (7 mL) of CF_3COOH (0.7 mmol) and n-Bu_4NBF_4 (0.1 mol.L^{-1}) on a mercury pool electrode (~1.23 cm^2) in the absence and in the presence of **2**(BF_4) (1 mmol.L^{-1}). 1 turnover corresponds to 1.35 C. B. Volume of the evolved hydrogen as a function of the charge passed through the cell.

A



B

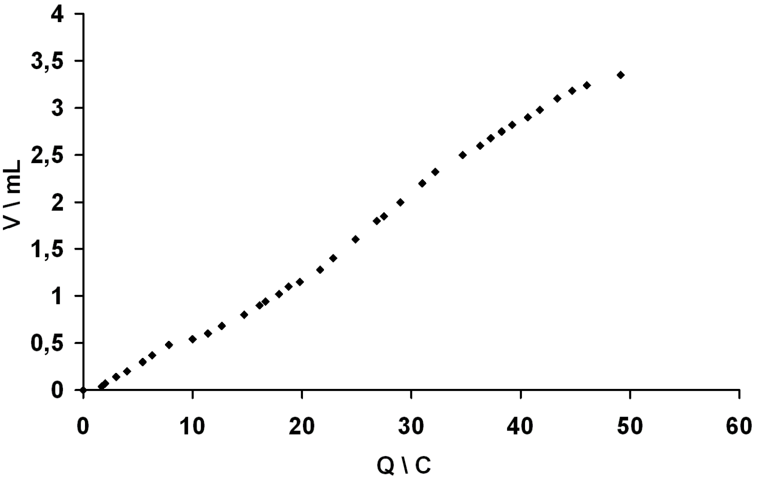


Figure S4. Evolution of the ratio i_c/i_p between the catalytic peak current i_c and the current of a monoelectronic wave i_p as a function of the number of equivalents of CF_3COOH added for **2**(BF_4), **3**(PF_6), [Ni(xbsms)] and [(CO)(dppe)Fe(pdt)(μ-H)Ni(dppe)](BF_4) (pdt = propanedithiolato dianion, dppe = diphenylphosphinoethane)

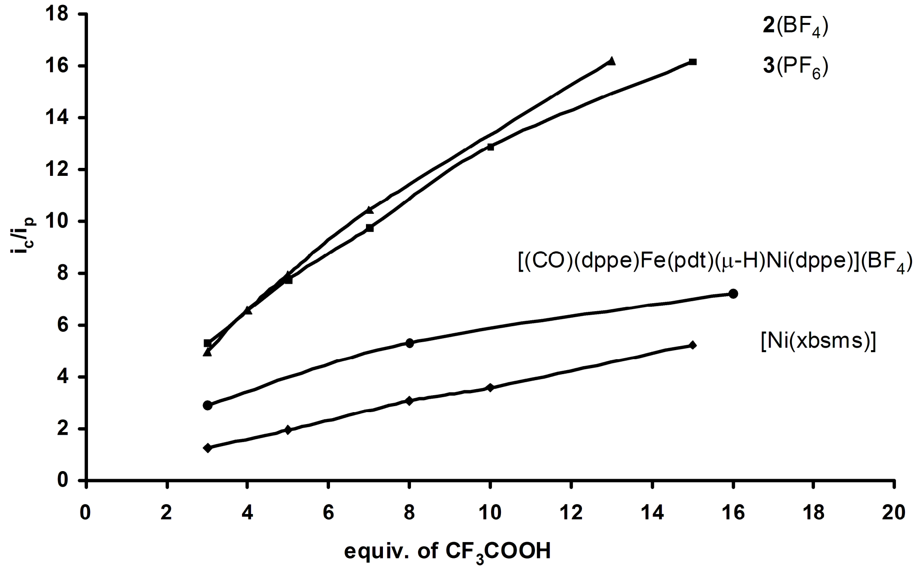


Figure S5. Cyclic voltammograms of CF_3COOH (a) 0 mM; b) 1.5 mM ; c) 3 mM; d) 5 mM ; e) 7 mM ; f) 10 mM) recorded in a DMF solution of n-Bu_4NBF_4 (0.1 mol.L^{-1}) on a glassy carbon electrode at 100 mV.s^{-1}.

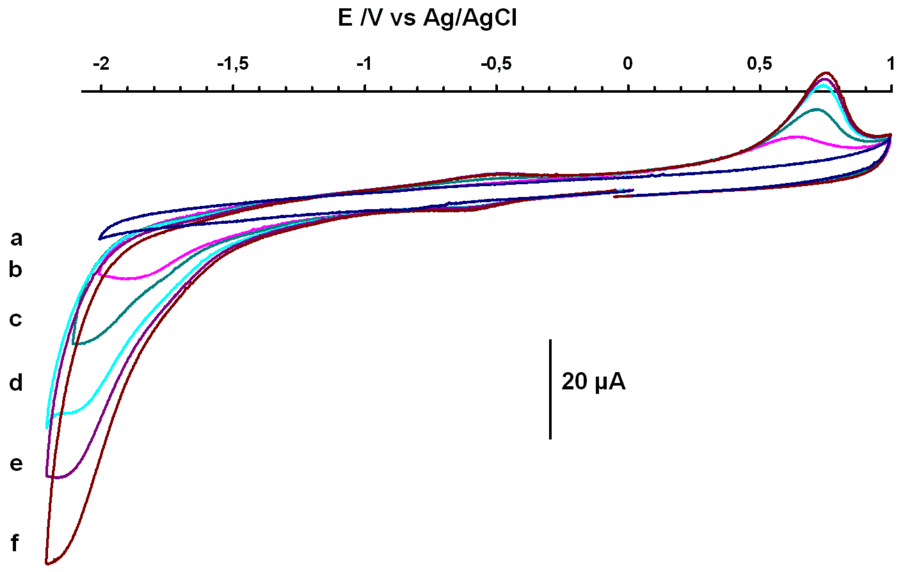
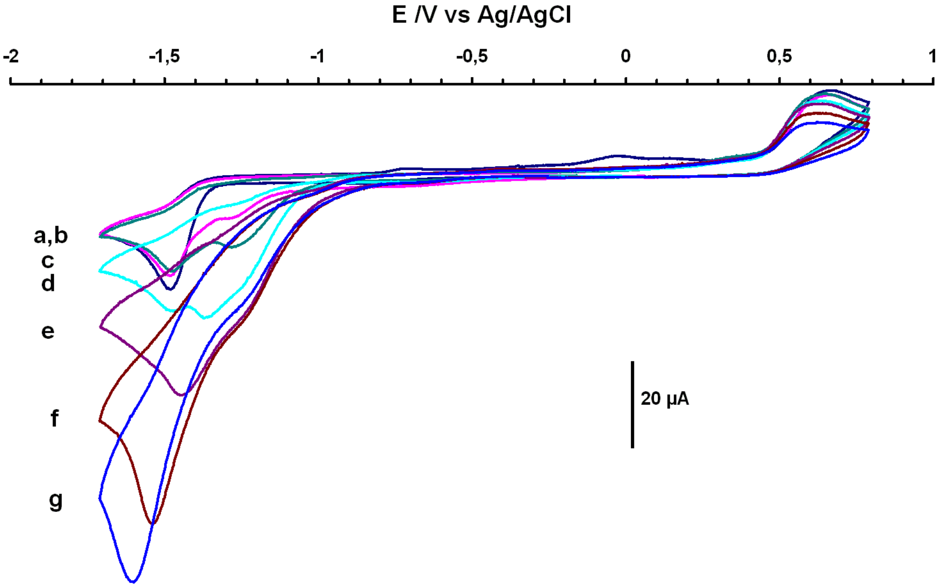


Figure S6. Cyclic voltammograms of [Ni(xbsms)] (1.0 mmol.L^{-1}) in the presence of various amounts of CF_3COOH recorded in a DMF solution of n-Bu_4NBF_4 (0.1 mol.L^{-1}) on a glassy carbon electrode at 100 mV.s^{-1} : a) 0 equiv.; b) 1.0 equiv.; c) 1.5 equiv.; d) 3.0 equiv.; e) 5 equiv. f) 8 equiv. g) 10 equiv.



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