Pentacoordinate Iron Complexes as Functional Models of the Distal Iron in [FeFe] Hydrogenases

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Supporting information

1. Experimental

General Methods. Solvents and chemicals were of best commercially available grade and used without further purification (unless mentioned). Thin layer chromatography was carried out using pre-coated polymeric sheets of silica gel (Macheray-Nagel, POLYGRAM, SIL G/UV$_{254}$). Preparative column chromatography was carried out using silica gel (Merck Kieselgel, silica gel 60, 0.063-0.200 mm).

Nuclear Magnetic Resonance (NMR) spectra for ^{1}H were acquired on JEOL Eclipse β 400 MHz spectrometer. The spectra were referenced to residual proton-solvent references (^{1}H: CD_2Cl_2: 5.32 ppm, $CDCl_3$: 7.26 ppm, CD_3CN: 1.94 ppm). In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, q: quadruplet, m: multiplet), the number of protons implied, the value of the coupling constants in Hertz if applicable, and finally the assignment. ^{31}P NMR data were also measured on a JEOL Eclipse β 400 MHz instrument at 161.8 MHz, with chemical shifts referenced to 85% H_3PO_4 as an external standard.

IR absorption spectra were recorded between 850 and 4500 cm^{-1} on a Perkin Elmer Spectrum one spectrometer (IFS 66 v/S) with the sample as solution in a liquid-sample-cell between CaF_2 windows and a path length of 0.5 mm.

All electrochemical measurements were conducted in acetonitrile (Sigma-Aldrich, spectroscopic grade, dried over 3 Å molecular sieves). Cyclic voltammetry and controlled potential coulometry were carried out using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). The working electrode was a glassy carbon disc (diameter 3 mm, freshly polished) for voltammetry. For electrolysis experiments a carbon rod was used. A glassy carbon rod in a compartment separated from the bulk solution by a fritted disk was used as counter electrode. The reference electrode was a non-aqueous Ag^+/Ag electrode (CH Instruments, 0.01 M in $AgNO_3$ in acetonitrile) with a potential of -0.08 V vs. the ferrocenium/ferrocene (Fc^+/Fc) couple in acetonitrile as an external standard. All solutions were prepared from dry acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) as supporting electrolyte that was oven dried at 383 K.

Crystallographic data set was collected from a single crystal sample mounted on a loop fiber and coated with N-paratone oil (Hampton Research). Collection was performed using a Bruker SMART APEX diffractometer equiped with an APEXII CCD detector, a graphite monochromator and a 3-circles goniometer. The crystal-to-detector distance was 5.0 cm, and the data collection was carried out in 512 x 512 pixel mode. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0 degrees scan in 33 frames over three different parts of the reciprocal space (99 frames total). Cell refinement and data reduction were performed with SAINT V7.68A (Bruker AXS). Absorption correction was done by multi-scan methods using SADABS96 (Sheldrick). The structure was solved by direct methods and refined using SHELXL97 (Sheldrick). All non-H atoms were refined by full-matrix least-squares with anisotropic displacement parameters while hydrogen atoms were placed in idealized positions. Refinement of F^2 was performed against all reflections. The weighted R-factor *w*R and goodness of fit S are based on F^2. Crystal structures data were deposited at the Cambridge Crystallographic Data Centre, and allocated the deposition number CCDC 811891.

2. Synthesis and characterization

Compound 2. A solution of $FeCl_2$ (64 mg, 0.5 mmol) and bis-phosphane (206 mg, 0.5 mmol) in 10 mL of methanol under CO was treated with a methanolic solution of 3,6-dichloro-1,2-benzenedithiol (Cl_2bdt) (106 mg, 0.5 mmol) and Et_3N (0.14 mL, 1 mmol). The reaction turned to violet then to black. After one hour stirring at room temperature, the solvent was removed and the residue was purified by column chromatography on silica column with CH_2Cl_2/hexane (8:2) as eluent. A dark green powder was obtained after removal of solvent with 41 % yield (150 mg).

^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ 7.09-7.80 (m, 20 H, Ph), 7.16 (s, 2 H, Cl_2bdt), 2.96 (m, 2 H, Ph_2P-$(CH_2)_3$-PPh_2), 2.60 (m, 2 H, Ph_2P-$(CH_2)_3$-PPh_2), 2.30 (m, 1 H, Ph_2P-$(CH_2)_3$-PPh_2), 2.00 (m, 1 H, Ph_2P-$(CH_2)_3$-PPh_2).

^{31}P {^{1}H} NMR (CD_2Cl_2, 400 MHz, 298 K): δ 50.9 (s)

Anal. Calcd for $C_{34}H_{28}OCl_2FeP_2S_2$ C 57.89 H 4.00 %. Found C 58.29 H 5.74 %.

Compound 3.

Method 1 (Scheme 1a): The CO-removing agent $Me_3NO.2H_2O$ (61.0 mg, 0.55 mmol) was added to a solution of $Fe_2(CO)_6(Cl_2bdt)$ (244.5 mg, 0.50 mmol) in 15 mL of acetonitrile. The resulting dark red solution was stirred for 15 minutes before adding the bis-phosphane (235.0 mg, 0.55 mmol). The solution turned slowly from red to green. After one hour stirring at room temperature, the solvent was removed. The residue was purified by column chromatography on silica eluted with CH_2Cl_2/hexane (8:2). A dark green powder was obtained after removal of solvent. Yield: 135.0 mg (36 %)

Method 2 (Scheme 1b): The complex was synthesized following the same procedure as that used for the preparation of compound **2**. Complex **3** was obtained in 63 % yield (232 mg).

^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ 6.95-7.3 (m, 20 H, Ph), 7.22 (s, 2 H, Cl_2bdt), 3.96 (m, 2 H, ^{2}J = 14.6 Hz, PCH_2N), 3.20 (d, 2 H, ^{2}J = 14.6 Hz, PCH_2N), 2.20 (s, 3 H, NCH_3).

^{31}P {^{1}H} NMR (CD_2Cl_2, 400 MHz, 298 K): δ 50.40 (s)

Anal. Calcd for $C_{34}H_{29}NOCl_2FeP_2S_2$ C 56.68 H 4.06 N 1.94 %. Found C 56.38 H 4.20 N 1.87 %.

Compound 4. The complex was synthesized following the same procedure as for compound **4** except that the residue was purified with a mixture CH_2Cl_2/hexane (7:3) as eluent. A dark green powder was isolated with 50 % yield (232 mg).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 6.95-7.65 (m, 20 H, Ph), 7.16 (s, 2 H, Cl_2bdt), 4.14 (quintet, 2 H, J_{H-F} = 6.6 Hz, CH_2CF_3), 3.70 (m, 2 H, ^2J= 7.0 Hz, PCH_2N), 3.30 (q, 2 H, ^2J= 7.0 Hz, PCH_2N).

^{31}P {^{1}H} NMR ($CDCl_3$, 400 MHz, 298 K): δ 51.00 (s)

Anal. Calcd for $C_{35}H_{28}NOF_3Cl_2FeP_2S_2$ C 53.32 H 3.58 N 1.78 %. Found C 53.65 H 3.98 N 1.59 %.

Compound 5. The complex was synthesized following the same procedure as compound **2** from benzene-1,2-dithiol (bdt) instead of Cl_2bdt. The residue was purified with a mixture CH_2Cl_2/hexane (7:3) as eluent. A dark green powder **5** was isolated with 58 % yield (219 mg).

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.06 (m, 2 H, bdt), 7.67 (m, 4 H, Ph), 7.48 (m, 6 H, bdt + Ph), 6.90-7.20 (m, 12 H, Ph), 4.70 (t, 1 H, ^3J = 4.7 Hz, $CH0_2$), 4.10 (m, 2 H, CH_2CH_3), 3.63 (m, 2 H, ^2J= 7.2 Hz, PCH_2N), 3.48 (m, 2 H, ^2J= 7.2 Hz, PCH_2N), 3.42 (m, 2 H, CH_2CH_3), 2.88 (d, 2 H, ^3J = 3.1 Hz, NCH_2), 1.12 (t, 6 H, ^3J = 1.2 Hz, CH_3).

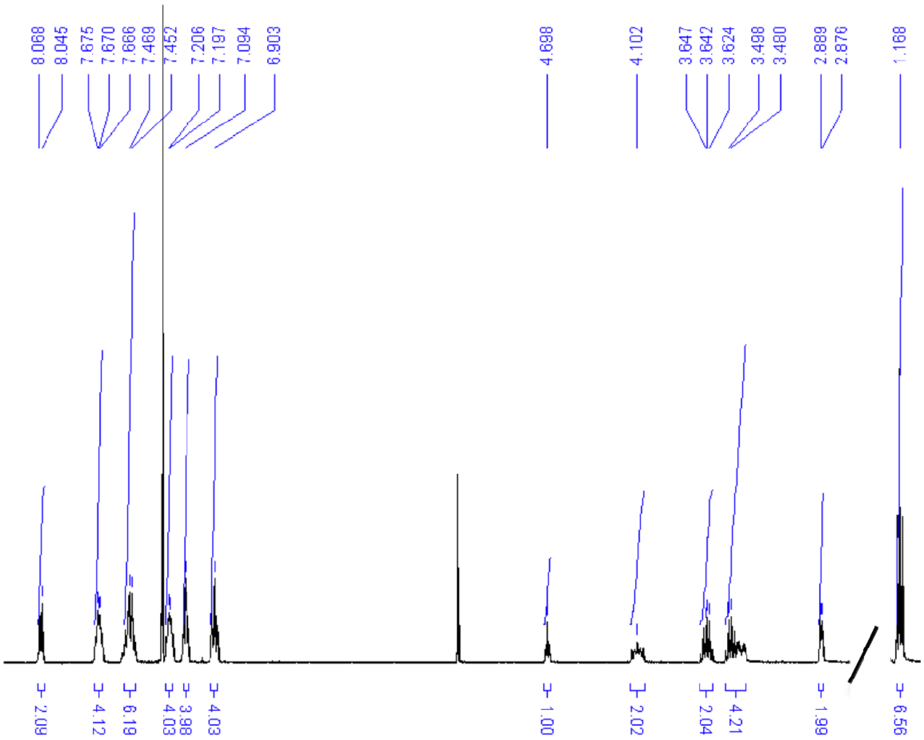


Figure S1. ^{1}H NMR spectra of the **5** (400 MHz, CDCl3, 298 K).

^{31}P {^{1}H} NMR ($CDCl_3$, 400 MHz, 298 K): δ 51.32 (s)

Anal. Calcd for $C_{39}H_{41}NO_3FeP_2S_2$ + 1/6 CH_2Cl_2 C 61.27 H 5.43 N 1.82 %. Found C 61.35 H 5.49 N 1.81 %.

3. IR-spectra of complexes 2-5 in the CO region

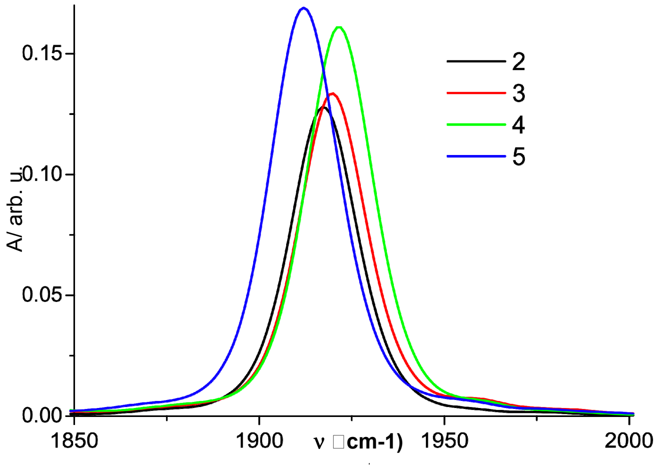


Figure S2. IR spectra of the CO region for solutions (2 mM) of **2-5** in CH_2Cl_2.

4. X-ray data of compound 5

Crystal structures data for **5** has been deposited at the Cambridge CrystallographicData Centre, and allocated the deposition number CCDC 811891.

Formula	$C_{39}H_{41}FeNO_3P_2S_2$
M_w (g/mol); F(000)	753.64; 3152
T (K); wavelength (Å)	100; 0.71073
Crystal System	Monoclinic
Space Group	$P2_1/c$
Unit Cell: a (Å)	16.8541(8)
b (Å)	21.4065(10)
c (Å)	20.3977(10)
β (°)	95.7610(10)
V (Å^3); Z, Z'; $d_{\mathrm{calcd.}}$ (g/cm^3)	7322.1(6); 8; 1.367
θ range (°); completeness	1.21 to 31.16; 0.949
collected reflections; R_s	139249; 0.1406
unique reflections; R_{int}	22443; 0.102
m (mm^{-1}); Abs. Corr.	0.652; Semi-empirical from equivalents
$R_1(F)$; w$R(F^2)$ [$I > 2\sigma(I)$]	0.0384; 0.1040
$R_1(F)$; w$R(F^2)$ (all data)	0.0579; 0.0704
GoF(F^2)	0.796
Residual electron density (e$^-$/Å^3)	0.358; -0.425

Table S1. Crystallographic data for compound **5.**

Fe(1)-S(1)	2.1868(6)
Fe(1)-S(2)	2.1874(6)
Fe(1)-P(1)	2.2078(6)
Fe(1)-P(2)	2.2123(6)
Fe(1)-C(1)	1.713(2)
C(1)-O(1)	1.170(2)
S(1)-Fe(1)-S(2)	89.32(2)
S(1)-Fe(1)-P(1)	87.79(2)
S(2)-Fe(1)-P(2)	87.01(2)
P(1)-Fe(1)-P(2)	89.59(2)

S(1)-Fe(1)-C(1)	108.47(7)
P(1)-Fe(1)-C(1)	92.62(7)

Table S2. Selected bond lengths (Å) and bond angles (˚) for **5**.

5. p*Ka* determination of 5

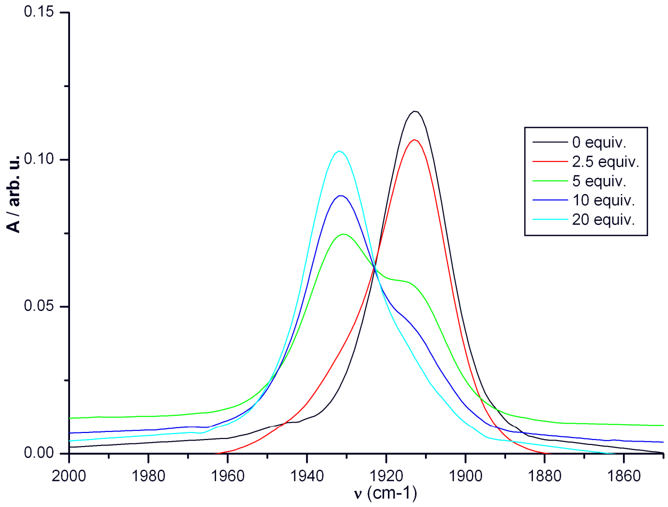


Figure S3. IR spectra of complex **5** (2 mM) with *p*-toluenesulfonic acid (0-20 eq.) in CH_3CN.

6. Electrochemistry

6.1 Overpotentials

The half-wave potentials $E_{1/2}$ of the catalytic waves were compared to (i) the corresponding $E^{Pt}_{1/2}$ obtained on a freshly polished Pt electrode under the same conditions and to (ii) theoretical half-wave potentials computed from the acid's pK_a and its homoconjugation constant K_c. The computed potentials refer to a reversible electrode process and provide reference potentials for evaluating the overpotential of the catalytic reaction.

Experimental values of $E_{1/2}$ were determined from the inflection point (minimum of the derivative di/dE) of the voltammograms' forward scan by subtracting 0.015V for peak shaped CVs.[1] For catalytic CVs closer to the S-shape characteristic of kinetic control without substrate limitations the inflection point was directly taken as $E_{1/2}$.

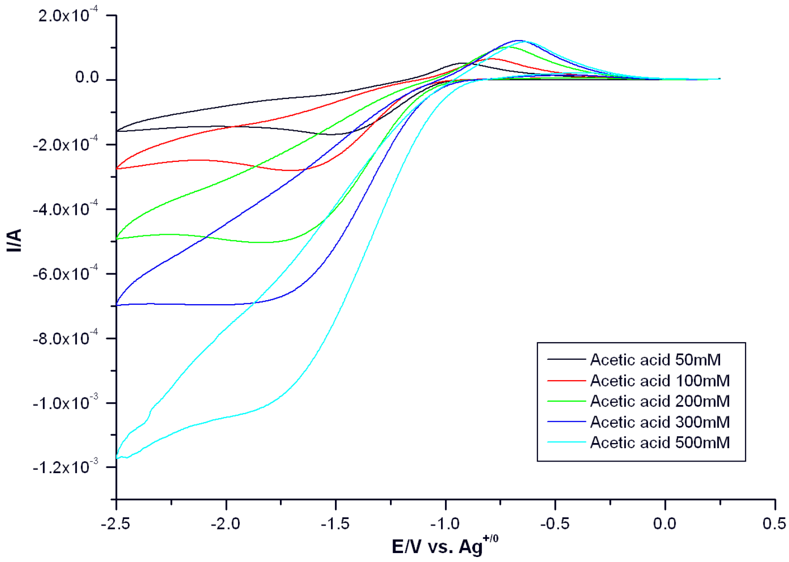


Figure S4. Cyclic voltammograms (0.1 V.s^{-1}) of acetic acid (50-500 mM) on Pt electrode (3 mm diameter) in CH_3CN with $[N(n\text{-}C_4H_9)_4][PF_6]$ (0.1 M) as supporting electrolyte.

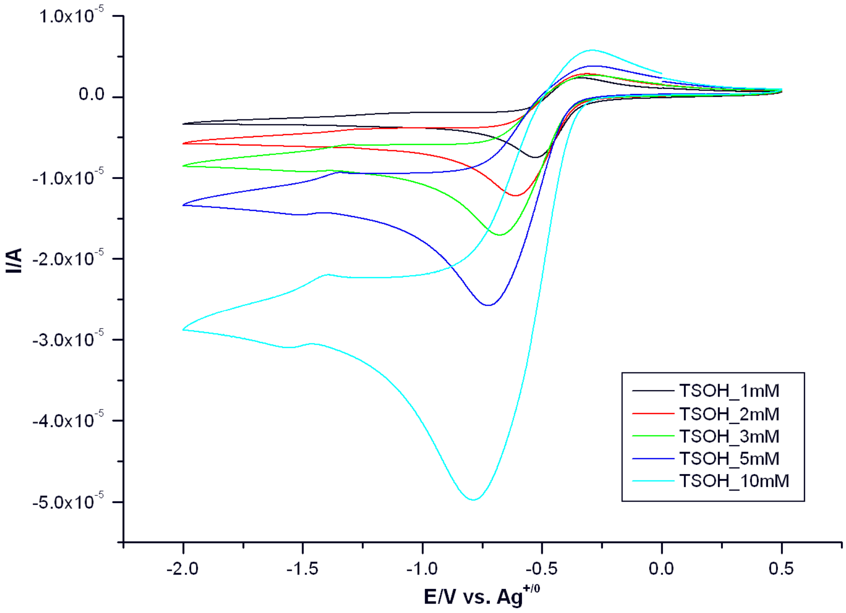


Figure S5. Cyclic voltammograms (0.1 V.s^{-1}) of *p*-toluenesulfonic acid (1-10 mM) on Pt electrode (3 mm diameter) in CH_3CN with $[N(n\text{-}C_4H_9)_4][PF_6]$ (0.1 M) as supporting electrolyte.

Theoretical values $E^{t}_{1/2}$ can be approximated by the standard potential E° of the AH/H_2 couple that is given by eq. 1 where $E^{\circ}(H^+/H_2)$ is the standard potential for the reduction of protons.[2]

$$E^{o}_{(HA/H_2,A^-)} = E^{o}_{(H^+/H_2)} - 2.303\frac{RT}{F}\mathrm{p}K_{a(HA)} \qquad (1)$$

While Evans and co-workers have proposed a value of $E^{\circ}(H^+/H_2)$ = -0.14 V *vs.* $Fc^{+/0}$ in acetonitrile, recent work by Artero and co-workers[3] suggests corrections that results in $E^{\circ}(H^+/H_2)$ = 0.07 V *vs.* $Fc^{+/0}$.

The exact value of $E^{t}_{p/2}$ depends on the bulk concentration C_0 of the acid and the concentration C°_{H2} of dissolved H_2 (at $p(H_2)$ = 1 bar) and also on differences in diffusion coefficients of the involved species as pointed out by Artero and co-workers (eq. 2 and 3).

$$E^{\mathrm{t}}_{1/2\,(\mathrm{HA/H_2,A^-})} = E^{o}_{(\mathrm{H^+/H_2})} - 2.303\frac{RT}{F}\mathrm{p}K_{\mathrm{a(HA)}} + \varepsilon_{\mathrm{D}} - \frac{RT}{2F}\ln\frac{C_0}{C^{\mathrm{o}}_{\mathrm{H_2}}} \qquad (2)$$

$$\varepsilon_{\mathrm{D}} = \frac{RT}{3F}\ln\frac{8D^2_{\mathrm{A^-}}D_{\mathrm{H_2}}}{D^3_{\mathrm{HA}}} \approx 0.040\ \mathrm{V\ in\ CH_3CN} \qquad (3)$$

The same authors have also emphasized that in situations where the dissociation of HA is significantly affected by homoconjugation ($K_cC_0 > 1$), half-wave potentials will also depend on the homoconjugation constant K_c. Values of $E^{t,c}_{1/2}$ that include the effect of homoconjugation can be approximated by eq. 4 and 5 for the reduction of AH and its homoconjugate AHA^-, respectively.

$$E^{\mathrm{t},c}_{1/2\,(\mathrm{HA/H_2,AHA^-})} = E^{o}_{(\mathrm{H^+/H_2})} - 2.303\frac{RT}{F}\mathrm{p}K_{\mathrm{a(HA)}} + \varepsilon_{\mathrm{D}} + \frac{RT}{2F}\ln(2K^2_{\mathrm{C}}C_0C^{\mathrm{o}}_{\mathrm{H_2}}) \qquad (4)$$

$$E^{\mathrm{t},c}_{1/2\,(\mathrm{AHA^-/H_2,A^-})} = E^{o}_{(\mathrm{H^+/H_2})} - 2.303\frac{RT}{F}\mathrm{p}K_{\mathrm{a(HA)}} + \varepsilon_{\mathrm{D}} + \frac{RT}{2F}\ln\left(\frac{2C^{\mathrm{o}}_{\mathrm{H_2}}}{3K^2_{\mathrm{C}}C_0}\right) \qquad (5)$$

In Table S3 we have compiled experimental data for (i) the reduction of AcOH and TsOH catalyzed by complex **5**, (ii) reduction of these acids on a Pt electrode, and (iii) the theoretical reference potentials that can be used to infer the overpotential for the catalytic reduction. The calculated potentials are based on $E^{\circ}(H^+/H_2)$ = -0.07 V *vs.* $Fc^{+/0}$ and 0.07 V must be subtracted to compare these values to potentials calculated with the previously widely used standard potential $E^{\circ}(H^+/H_2)$ = -0.14 V *vs.* $Fc^{+/0}$.

Acid (C_0/mM)	Potential[a] / V *vs.* $Fc^{+/0}$							
	exptl.[b]				calc.[c]			
	$E_{1/2}$ [5]/mM			$E^{Pt}_{1/2}$	E° (HA/ H_2, A^-)	$E^{t}_{1/2}$ (HA/ H_2, A^-)	$E^{t,c}_{1/2}$ (HA/ H_2, AHA^-)	$E^{t,c}_{1/2}$ (AHA^-/ H_2, A^-)
	0.25	0.5	1.0					
AcOH (50)	-1.65	-1.65	-1.63	-	-1.39	-1.38	-1.33	-1.53
AcOH (100)	-1.65	-1.65	-1.63	-1.48	-1.39	-1.39	-1.32	-1.55
AcOH (200)	-1.65	-1.65	-1.63	-1.48	-1.39	-1.40	-1.31	-1.58
AcOH (300)	-1.64	-1.64	-1.63	-1.47	-1.39	-1.40	-1.31	-1.60
AcOH (500)	-1.64	-1.64	-1.63	-1.40	-1.39	-1.41	-1.30	-1.62
TsOH (1)	-1.31 (-1.57)	-1.27 (-1.48)	-1.25 (-)	-0.52	-0.58	-0.53	-0.52	-0.53
TsOH (2)	-1.29 (-1.51)	-1.23 (-1.52)	-1.22 (-1.49)	-0.58	-0.58	-0.54	-0.51	-0.56
TsOH (3)	-1.29 (-1.53)	-1.23 (-1.53)	-1.21 (-1.52)	-0.62	-0.58	-0.54	-0.51	-0.57
TsOH (5)	-1.29 (-1.55)	-1.23 (-1.55)	-1.22 (-1.54)	-0.62	-0.58	-0.55	-0.50	-0.59
TsOH (10)	-1.28 (-1.57)	-1.25 (-1.57)	-1.23 (-1.57)	-0.63	-0.58	-0.56	-0.49	-0.62

[a] In CH_3CN solution with 0.1 M $TBAPF_6$ as supporting electrolyte

[b] All exptl. potentials corrected for IR drop.

[c] Calculated with $E^{\circ}(H^+/H_2)$ = -0.07 V.

Table S3. Experimental half-wave potentials for reduction of AcOH (pK_a = 22.3, $\log(K_c)$ = 3.7) and TsOH (pK_a = 8.3, $\log(K_c)$ = 2.95) on a glassy carbon electrode catalyzed with complex **5** ($E_{1/2}$) or on a Pt electrode ($E^{Pt}_{1/2}$), and theoretical potentials computed from the acids' pKa (E°, $E^{t}_{1/2}$) or its pK_a and its homoconjugation constant K_c ($E^{t,c}_{1/2}$), T = 298 K.

6.2 Catalytic rate constants

For the catalytic reduction of acetic acid a bimolecular rate constant was obtained with eq. 6 (D = 1×10^{-5} cm^2/s, A=0.071 cm^2) from the slopes of the plots in Figure S1b at the highest substrate concentrations ($C_S{}^0$). The bimolecular rate constant describes the reaction of **5**$^-$ with AcOH based on a two-step mechanism with the first homogeneous step being rate-limiting.[4]

$$I_\mathrm{p} = FAC^0_\mathrm{cat}\sqrt{D}\sqrt{2kC^0_\mathrm{S}} \qquad (6)$$

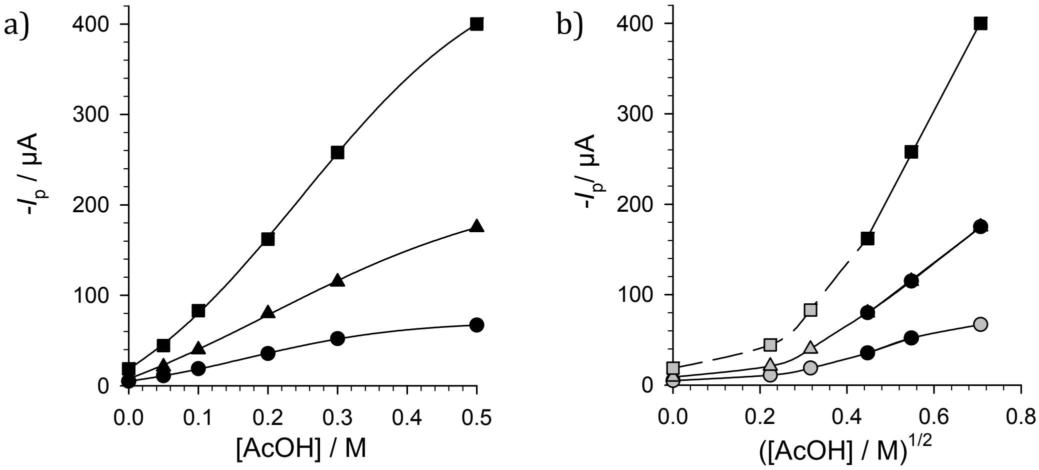
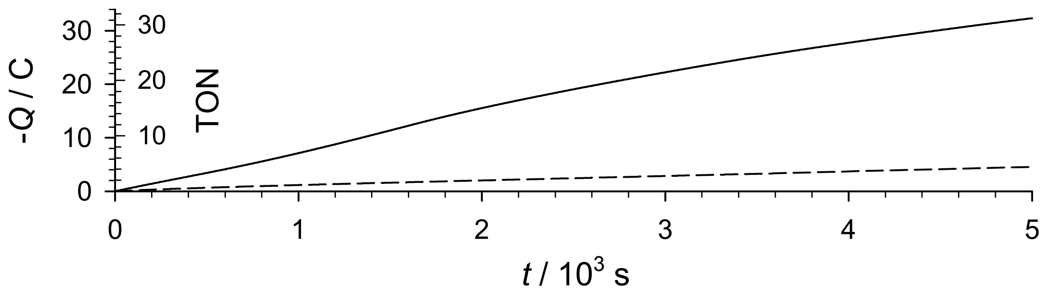


Figure S6. Peak/plateau current with 0.25 mM **5** (●), 0.50 mM **5** (▲), and 1.0 mM **5** (■) as function of [AcOH] (a) and ([AcOH])$^{1/2}$ (b).

For the total catalysis peaks with TsOH the catalytic rate constant was estimated with eq. 7 and E_p = -1.505, -1.563, -1.606 V ($C_S{}^0$ = 3, 5, 10 mM, $C_\mathrm{cat}{}^0$ = 1 mM, v = 0.100V/s).[4]

$$E_\mathrm{p} = E^0_{\mathrm{cat/cat}^-} - 0.409\frac{RT}{F} + \frac{RT}{F}\ln\left(\frac{RT}{F}\frac{k\,(C^0_\mathrm{cat})^2}{C^0_\mathrm{S}\,v}\right) \qquad (7)$$

7. **Controlled potential electrolysis coupled to gas chromatography.**



Charge and turnover number during controlled potential electrolysis (-1.70 V) of AcOH (0.50 M) with **5** (1.0 mM) and without catalyst (---).

8. References

1. S. E Treimer and D. H Evans, *J. Electroanal. Chem*., 1998, **449**, 39.
2. G. A. N. Felton, R. S. Glass, D. L. Lichtenberger and D. H. Evans, *Inorg. Chem.*, 2006, **45**, 9181.
3. V. Fourmond, P.-A. Jacques, M. Fontecave and V. Artero, *Inorg. Chem.*, 2010, **49**, 10338.
4. J.-M. Savéant, Elements of molecular and biomolecular electrochemistry: An electrochemical approach to electron transfer chemistry, John Wiley & Sons, Hoboken, N.J, 2006.