Supporting Information

Dithiolato- and halogenido-bridged nickel-iron complexes related to the active site of [NiFe]-H$_2$ases: preparation, structures, and electrocatalytic H$_2$ production

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1. IR and $^1$H (31P) NMR spectra of 3a

**Fig. S1** IR spectrum of 3a.

**Fig. S2** $^1$H NMR spectrum of 3a.
Fig. S3 $^{31}$P NMR spectrum of 3a.
2. IR and $^1$H ($^{31}$P) NMR spectra of 4b

**Fig. S4** IR spectrum of 4b.

**Fig. S5** $^1$H NMR spectrum of 4b.
Fig. S6 $^{31}$P NMR spectrum of 4b.
3. Molecular structure of 3b and 4b.

**Fig. S7** Molecular structure of 3b. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ni1–P1 2.1257 (8), Ni1–Br1 2.3393(5), P1–N1 1.698(2), P1–Ni1–P1A 73.75(4), P1–Ni1–Br1 93.23(2), Br1–Ni1–Br1A 99.80(3), P1–N1–P1A 97.36(17).

**Fig. S8** Molecular structure of 4b. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Ni1–P1 2.1366(8), Ni1–P2 2.1285(8), Ni1–I1 2.5150(5), Ni1–I2 2.5094(5), P1–N1 1.699(2), P2–N1 1.699(2), P1–Ni1–P2 74.00(3), P1–Ni1–I1 92.66(3), I1–Ni1–I2 100.178(18), P1–N1–P2 98.12(10).
4. IR and $^1$H ($^{31}$P, $^{11}$B, $^{19}$F) NMR spectra of 5b.

Fig. S9 IR spectrum of 5b

Fig. S10 $^1$H NMR spectrum of 5b.
Fig. S11 $^{31}$P NMR spectrum of 5b.

Fig. S12 $^{11}$B NMR spectrum of 5b.
Fig. S13 $^{19}$F NMR spectrum of 5b.
5. IR and $^1$H ($^{31}$P, $^{11}$B, $^{19}$F) NMR spectra of 6a

Fig. S14 IR spectrum of 6a.

Fig. S15 $^1$H NMR spectrum of 6a.
**Fig. S16** $^{31}$P NMR spectrum of 6a.

**Fig. S17** $^{11}$B NMR spectrum of 6a.
Fig. S18 $^{19}$F NMR spectrum of 6a.
6. IR and $^1$H ($^{31}$P, $^{11}$B, $^{19}$F) NMR spectra of 7a

Fig. S19 IR spectrum of 7a.

Fig. S20 $^1$H NMR spectrum of 7a.
Fig. S21 $^{31}$P NMR spectrum of 7a.

Fig. S22 $^{11}$B NMR spectrum of 7a.
Fig. S23 $^{19}$F NMR spectrum of 7a.
7. Bulk electrolysis for the two-electron reduction of \([\text{CpFe(CO)}_2]_2\) and the one-electron reductions of 5a–7a.

The reduction events for 5a–7a is a one-electron process since their final Q values determined by bulk electrolysis are close to half that of the known two-electron reduction process of dimer \([\text{CpFe(CO)}_2]_2\).\textsuperscript{1,2}

![Graph showing bulk electrolysis for the two-electron reduction of \([\text{CpFe(CO)}_2]_2\) and the one-electron reductions of 5a–7a.]

**Fig. S24** Bulk electrolysis for the two-electron reduction of \([\text{CpFe(CO)}_2]_2\) and the one-electron reductions of 5a–7a.
8. Bulk electrolysis for the two-electron reduction of $[\text{CpFe(CO)}_2]_2$ and the one-electron oxidations of 5a–7a.

The oxidation events for 5a–7a are also a one-electron process since the final Q values determined by bulk electrolysis are close to half that of the known two-electron reduction of dimer $[\text{CpFe(CO)}_2]_2$.$^{1,2}$

![Graph showing Q/C vs Time/s for different compounds](image)

**Fig. S25** Bulk electrolysis for the two-electron reduction of $[\text{CpFe(CO)}_2]_2$ and the one-electron oxidations of 5a–7a.
9. Plots of $i_p$ versus $v^{1/2}$ for the reduction peaks of 5a–7a.

Fig. S26 Plots of $i_p$ versus $v^{1/2}$ for the reduction peaks of 5a ( ), 6a ( ) and 7a ( ▲ ).
10. Cyclic voltammograms and overpotential determinations of 6a,b and 7a,b with Cl$_2$CHCO$_2$H in MeCN.

Since the pK$_a$ and the standard redox potential of Cl$_2$CHCO$_2$H in MeCN (pK$_{a,MeCN}^\text{H} = 13.2$, $E^{0\text{H}_2^+/\text{H}_2} = -0.14$ V)$^3$ are known, the equilibrium potential ($E^{0\text{HA}}_\text{cat} = -0.92$ V vs Fc/Fc$^+$) can be calculated according to eq.S1 using Evans’ relationship.$^3$

The overpotentials of the electrocatalytic proton reductions catalyzed by 6a,b and 7a,b were measured using eq.S2 from the potential at 0.5 ($i_{pc}$), where $i_{pc}$ is the cathodic peak current in the cyclic voltammogram recorded after addition of 40 mM or 68 mM of Cl$_2$CHCO$_2$H.

$$E^{0\text{HA}}_\text{cat} = E^{0\text{H}_2^+/\text{H}_2} - (2.303RT/F)pK_{a,HA}$$  \hspace{1cm} \text{eq.S1}

$$\text{overpotential} = |E^{0\text{HA}}_\text{cat} - E_{\text{cat/2}}|$$  \hspace{1cm} \text{eq.S2}

![Cyclic voltammograms of 6a,b and 7a,b](image)

**Fig. S27** Cyclic voltammograms of 6a,b and 7a,b (1.0 mM) with varying amount of Cl$_2$CHCO$_2$H (denoted on right) in 0.1 M n-Bu$_4$NPF$_6$/MeCN at a scan rate of 0.1 V s$^{-1}$. 

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11. TOF calculations

The turnover frequency (TOF) was calculated using a ratio of $i_{\text{cat}}/i_p$ (eqs. S3 and S4), where $i_{\text{cat}}$ is the peak current of the reduction wave in the presence of acid and $i_p$ is the peak current in the absence of acid. The value of $i_{\text{cat}}/i_p$ is in the regime where the catalytic rate is independent of $[\text{H}^+]$.

$$\frac{i_{\text{cat}}}{i_p} = (n/0.446)(RTk/Fv)^{1/2}$$  \hspace{1cm} \text{eq. S3}

$$\text{TOF} = 1.94v\left(\frac{i_{\text{cat}}}{i_p}\right)^2$$  \hspace{1cm} \text{eq. S4}

$n =$ number of electrons transferred  \hspace{1cm} $R =$ ideal gas constant in $\text{K}^{-1}\text{mol}^{-1}$

$T =$ temperature in $\text{K}$  \hspace{1cm} $k =$ rate constant

$v =$ scan rate in $\text{V/s}$

$\text{TOF}_{5a} = 1.94v\left(\frac{i_{\text{cat}}}{i_p}\right)^2 = 1.94 \left(V^{-1}\right) \times 0.1 \left(Vs^{-1}\right) \times (7.0)^2 = 9.5$

$\text{TOF}_{5b} = 1.94v\left(\frac{i_{\text{cat}}}{i_p}\right)^2 = 1.94 \left(V^{-1}\right) \times 0.1 \left(Vs^{-1}\right) \times (9.3)^2 = 16.8$

$\text{TOF}_{6a} = 1.94v\left(\frac{i_{\text{cat}}}{i_p}\right)^2 = 1.94 \left(V^{-1}\right) \times 0.1 \left(Vs^{-1}\right) \times (6.0)^2 = 7.0$

$\text{TOF}_{6b} = 1.94v\left(\frac{i_{\text{cat}}}{i_p}\right)^2 = 1.94 \left(V^{-1}\right) \times 0.1 \left(Vs^{-1}\right) \times (8.1)^2 = 12.7$

$\text{TOF}_{7a} = 1.94v\left(\frac{i_{\text{cat}}}{i_p}\right)^2 = 1.94 \left(V^{-1}\right) \times 0.1 \left(Vs^{-1}\right) \times (5.4)^2 = 5.7$

$\text{TOF}_{7b} = 1.94v\left(\frac{i_{\text{cat}}}{i_p}\right)^2 = 1.94 \left(V^{-1}\right) \times 0.1 \left(Vs^{-1}\right) \times (7.9)^2 = 12.1$

12. References


