

## Supporting Information

### The influence of S-to-S bridge in diiron dithiolate models on the oxidation reaction: A mimic of the H<sub>ox</sub><sup>air</sup> state of [FeFe]-hydrogenases

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## Experimental Section

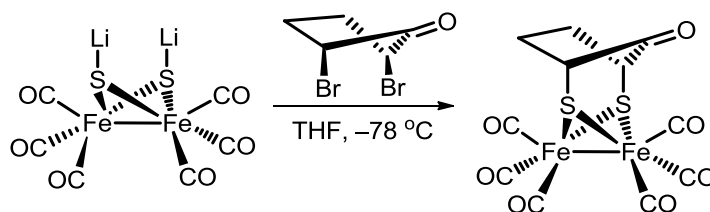
### Materials and instruments

**Materials.** Preparation of ( $\mu$ -cpdt)Fe<sub>2</sub>(CO)<sub>6</sub>, **1** and **2** was carried out under dry oxygen-free dinitrogen with standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. The reagents PMe<sub>3</sub> and Cp<sub>2</sub>Co were purchased from Aldrich and LiB(H)Et<sub>3</sub> from Acros. The other reagents such as cyclopentanone, Fe(CO)<sub>5</sub>, FcBF<sub>4</sub>, FcPF<sub>6</sub>, and Cp<sub>2</sub>Fe were purchased from local companies. All reagents were used as received. Compounds *cis*-2,5-dibromocyclopentanone,<sup>S1</sup> Fe<sub>2</sub>(SLi)<sub>2</sub>(CO)<sub>6</sub>,<sup>S2</sup> and FcBAr<sup>F</sup><sub>4</sub> were synthesized according to the literature procedures.<sup>S3,S4</sup>

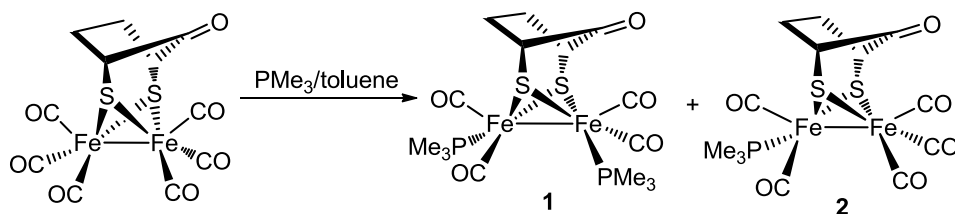
**Instruments.** Infrared spectra were recorded with a JASCO FT/IR 430 spectrophotometer. <sup>1</sup>H and <sup>31</sup>P NMR spectra were collected with a varian INOVA 400 NMR spectrometer. Mass spectra were recorded on a HP1100LC/MSD. Elemental analyses were performed with a Thermoquest-Flash EA 1112 elemental analyzer.

## Synthesis

**Synthesis of  $(\mu\text{-cpdt})\text{Fe}_2(\text{CO})_6$**  (cpdt = cyclopentanone-2,5-dithiolate). Compound *cis*-2,5-dibromocyclopentanone (0.72 g, 3.0 mmol) was added to a freshly prepared  $\text{Fe}_2(\text{SLi})_2(\text{CO})_6$  (~3 mmol) in THF (30 mL) at  $-78\text{ }^\circ\text{C}$  with stirring under the protection of nitrogen. The color of the solution immediately turned from dark green to red. The mixture was stirred for 1 h and then the bottle was removed from the cooling bath. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using hexane/ $\text{CH}_2\text{Cl}_2$  (1:1, V/V) as eluent. Yield of  $(\mu\text{-cpdt})\text{Fe}_2(\text{CO})_6$ : 35% (0.45 g). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2076 (m), 2036 (s), 1997 (m), 1731 (w)  $\text{cm}^{-1}$ . MS (API-ESI in  $\text{CHCl}_3$ ):  $m/z$  426.3  $[\text{M}+\text{H}]^+$  (calcd. for  $\text{C}_{11}\text{H}_6\text{Fe}_2\text{O}_7\text{S}_2$ :  $m/z$  425.8).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.18 (s br, 2H),  $\delta$  2.06 (d br, 2H),  $\delta$  1.50 (d br, 2H).



**Synthesis of **1** and **2**.** The solution of  $\text{PMe}_3$  (3.0 M, 1.3 mL, 4.0 mmol) in hexane was added to a toluene solution (20 mL) of  $(\mu\text{-cpdt})\text{Fe}_2(\text{CO})_6$  (0.43 g, 1.0 mmol) at room temperature. The mixture was refluxed for 8 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/ $\text{CH}_2\text{Cl}_2$  (2:3, V/V) as eluent. Pure complexes **1** and **2** were obtained as red needle crystals by recrystallization of crude products in hexane/ $\text{CH}_2\text{Cl}_2$  (3:2, V/V), respectively.



Yield of **1**: 37% (0.19 g). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{CO})$  1986 (m), 1958 (s), 1913 (m), 1718 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.00 (s br, 2H), 1.90 (d br, 2H),  $\delta$  1.50–1.56 (m, 20H). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  24.20, 27.78. Anal. calcd. for C<sub>15</sub>H<sub>24</sub>Fe<sub>2</sub>O<sub>5</sub>S<sub>2</sub>P<sub>2</sub>: C, 35.51%; H, 4.63%; Found: C, 35.40%; H, 4.59%.

Yield of **2**: 52% (0.25 g). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{CO})$  2043 (m), 1986 (s), 1967 (m), 1715 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.11 (s br, 2H), 1.96 (d br, 2H),  $\delta$  1.50–1.55 (m, 11H). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  25.17. Anal. calcd. for C<sub>13</sub>H<sub>15</sub>Fe<sub>2</sub>O<sub>6</sub>S<sub>2</sub>P: C, 32.94%; H, 3.19%; Found: C, 33.11%; H, 3.14%.

**Synthesis of [1(OH)]BAR<sup>F</sup><sub>4</sub>.** Ferricinium salt [Cp<sub>2</sub>Fe](BAR<sup>F</sup><sub>4</sub>) (Ar<sup>F</sup> = 3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>) (420 mg, 0.4 mmol) and H<sub>2</sub>O (10  $\mu$ L) were added to the solution of **1** (100 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) under nitrogen. The solution changed immediately from red to dark green. After the mixture was stirred for 15 min, 90 mL of hexane was added. The suspension was stirred for 5 min and the green precipitate was filtered. The solid was washed with hexane (2  $\times$  10 mL) and dried under vacuum. Yield of [1(OH)]BAR<sup>F</sup><sub>4</sub>: 88% (0.25 g). The single crystal was obtained from a saturated solution of [1(OH)]BAR<sup>F</sup><sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>14</sub> (1/4, V/V) at room temperature. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{CO})$  2053 (m), 2014 (s), 1959 (m) cm<sup>-1</sup>. <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  31.07, 11.54. API-ESI-MS (in CH<sub>2</sub>Cl<sub>2</sub>):  $m/z$  538.9282 [M–BAR<sup>F</sup><sub>4</sub>]<sup>+</sup> (calcd. for C<sub>15</sub>H<sub>25</sub>Fe<sub>2</sub>O<sub>6</sub>P<sub>2</sub>S<sub>2</sub>:  $m/z$  538.9267). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.75 (s, 1H), 3.32 (s, 1H), 2.95 (s, 1H), 2.32 (s, 2H), 2.01 (s, 1H),  $\delta$  1.64–1.73 (2s, 18H).

### X-Ray structure determination of **1**, **2** and [1(OH)]BAR<sup>F</sup><sub>4</sub>

The single crystal X-ray diffraction data were collected with an Bruker Smart Apex II

CCD diffractometer with a graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.071073 \text{ \AA}$ ) at 298 K using the  $\omega$ - $2\theta$  scan mode. Data processing was accomplished with the SAINT processing program.<sup>S5</sup> Intensity data were corrected for absorption by the SADABS program.<sup>S6</sup> All structures were solved by direct methods and refined on  $F^2$  against full-matrix least-squares methods by using the SHELXTL 97 program package.<sup>S7</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by geometrical calculation. Details of crystal data, data collections and structure refinements are summarized in Tables S1 and S2. CCDC-798238 (**1**), 798239 (**2**) and -926091 ( $[\mathbf{1}(\text{OH})]\text{BAr}_4^{\text{F}}$ ) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1** Crystallographic data processing parameters for **1**, **2**, and **[1(OH)]BAr<sup>F</sup><sub>4</sub>**

Complex	<b>[1]</b> <sub>2</sub>	<b>2</b>	<b>[1(OH)]BAr<sup>F</sup><sub>4</sub> CH<sub>2</sub>Cl<sub>2</sub></b>
Formula	C <sub>30</sub> H <sub>48</sub> Fe <sub>4</sub> O <sub>10</sub> P <sub>4</sub> S <sub>4</sub>	C <sub>13</sub> H <sub>15</sub> Fe <sub>2</sub> O <sub>6</sub> PS <sub>2</sub>	C <sub>48</sub> H <sub>39</sub> BCl <sub>2</sub> F <sub>24</sub> Fe <sub>2</sub> O <sub>6</sub> P <sub>2</sub> S <sub>2</sub>
<i>F</i> <sub>w</sub>	1044.20	474.04	1487.26
Crystal system	triclinic	triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/c
<i>a</i> (Å)	10.158(4)	8.9553(15)	12.6932(8)
<i>b</i> (Å)	12.393(5)	10.2137(16)	18.5417(14)
<i>c</i> (Å)	17.576(6)	11.056(3)	25.8275(18)
<i>α</i> (deg)	92.450(6)	105.403(3)	90.00
<i>β</i> (deg)	92.727(6)	93.507(3)	91.440(4)
<i>γ</i> (deg)	95.945(6)	112.215(2)	90.00
<i>V</i> (Å <sup>3</sup> )	2195.7(14)	887.6(3)	6076.7(7)
<i>Z</i>	2	4	4
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.579	1.774	1.626
Crystal size (mm)	0.3/ 0.3 / 0.2	0.32/ 0.29 / 0.2	0.25/ 0.18 / 0.12
<i>μ</i> (mm <sup>-1</sup> )	1.697	1.985	0.805
<i>θ</i> Range (deg)	2.02 / 24.69	1.94 / 25.0	2.08 / 25.0
Reflns collected	10766	3080	23223
Independent reflns	7730	3028	10260
Parameters refined	469	217	788
<i>F</i> (000)	1072	480	2976
GOF on <i>F</i> <sup>2</sup>	0.96	1.011	1.087
<i>R</i> <sub>int</sub>	0.049	0.0250	0.0677
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0686	0.0390	0.0935
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	0.1733	0.1078	0.2370
Residual electron density (e Å <sup>-3</sup> )	0.899 / 0.459	1.125 / 0.629	0.918 / 0.737

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c||$ . <sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$ .

**Table S2** Selected bond lengths (Å) and angles (°) for **1**, **2**, and **[1(OH)]BAr<sup>F</sup><sub>4</sub>**

Complex	<b>1</b>	<b>2</b>	<b>[1(OH)]BAr<sup>F</sup><sub>4</sub></b>
Bond lengths			
Fe1–Fe2	2.5748(18)	2.5369(7)	2.6202(18)
Fe1–S1	2.252 (3)	2.2438(11)	2.216(2)
Fe1–S2	2.251 (3)	2.2552(10)	2.194(2)
Fe2–S1	2.260 (3)	2.2688(10)	2.292(2)
Fe2–S2	2.264 (3)	2.2678(9)	2.333(2)
Fe1–P1	2.237 (3)	2.2300(10)	2.272(3)
Fe2–P2	2.225 (3)	–	2.264(2)
Fe1–C6	1.784 (10)	1.770(4)	1.760(12)
Fe1–C7	1.759 (10)	1.770(4)	1.804(11)
Fe1–C9	–	–	2.609
Fe2–C8	1.755(10)	1.189(4)	1.828(10)
Fe2–C9	1.734(10)	1.797(4)	1.769(10)
Fe2–O1	3.717	3.715	1.928(5)
S...S	3.019	3.3035	3.114
O1...O8	3.023	3.027	3.530
Bond angles			
S1–Fe1–S2	84.02(9)	84.85(3)	89.83(9)
Fe1–S1–Fe2	69.60(8)	68.41(3)	71.05(7)
S1–Fe2–O1	–	–	85.31(18)
S2–Fe2–O1	–	–	84.39(16)
Fe1–C9–Fe2	–	–	70.6
S1–Fe2–C8	104.4(3)	–	171.0(2)
S2–Fe2–C8	108.2(3)	–	87.1(2)
S1–Fe2–C9	90.3(3)	–	95.7(3)
Torsional angle			
C6–Fe1–Fe2–C8	34.1	28.3	0
S1–Fe1–Fe2–S2	108.4	107.5	115.7

## Electrochemistry studies of **1** and [1(OH)]BAr<sup>F</sup><sub>4</sub>

Cyclic voltammograms were carried out in a three-electrode cell under Ar using CHI 630D electrochemical work station. The working electrode was a glassy carbon disc (diameter 3 mm) polished with 3 and 1  $\mu\text{m}$  diamond pastes and sonicated in ion-free water for 15 min prior to use. The reference electrode was a non-aqueous  $\text{Ag}^+/\text{Ag}$  (0.01 M  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$ ) electrode and the counter electrode was platinum wire. A solution of 0.1 M  $n\text{Bu}_4\text{NPF}_6$  (Fluka, electrochemical grade) in  $\text{CH}_2\text{Cl}_2$  was used as supporting electrolyte, which was degassed by bubbling with dry argon for 10 min before measurement. The ferricinium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) couple was used as an internal reference and all potentials given in this work are referred to the  $\text{Fc}^{+/0}$  potential.

## Chemical reduction of [1(OH)]BAr<sup>F</sup><sub>4</sub>

The process of chemical reduction of [1(OH)]BAr<sup>F</sup><sub>4</sub> was monitored by in situ IR spectroscopy using a Mettler-Toledo ReactIR<sup>TM</sup> 15 System equipped with an MCT detector and a DsubAgXSiComp<sup>TM</sup> in situ probe. Two equiv. of  $\text{Cp}_2\text{Co}$  was added to the solution of [1(OH)]BAr<sup>F</sup><sub>4</sub> (14 mg, 0.01 mmol), which was in situ generated in  $\text{CH}_2\text{Cl}_2$  (2 mL). All typical  $\nu(\text{CO})$  absorptions of [1(OH)]BAr<sup>F</sup><sub>4</sub> disappeared within 15 min and in the meantime, the  $\nu(\text{CO})$  bands of **1** almost completely recovered in the IR spectra (Fig. S4<sup>†</sup>).

## References

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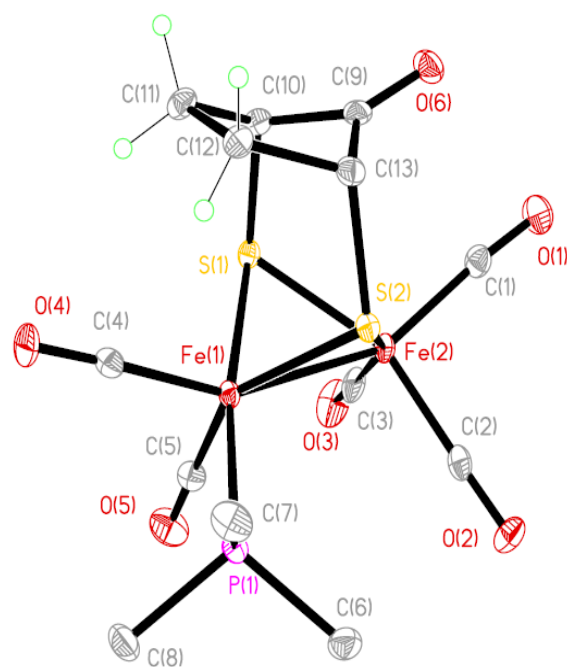
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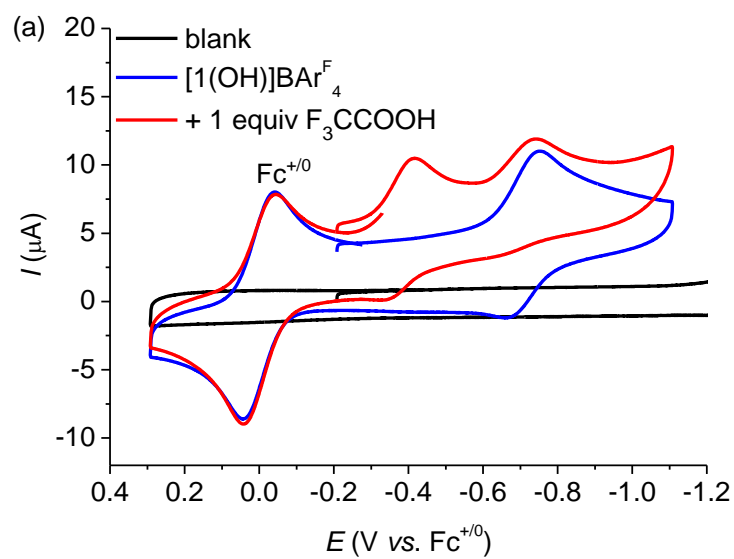
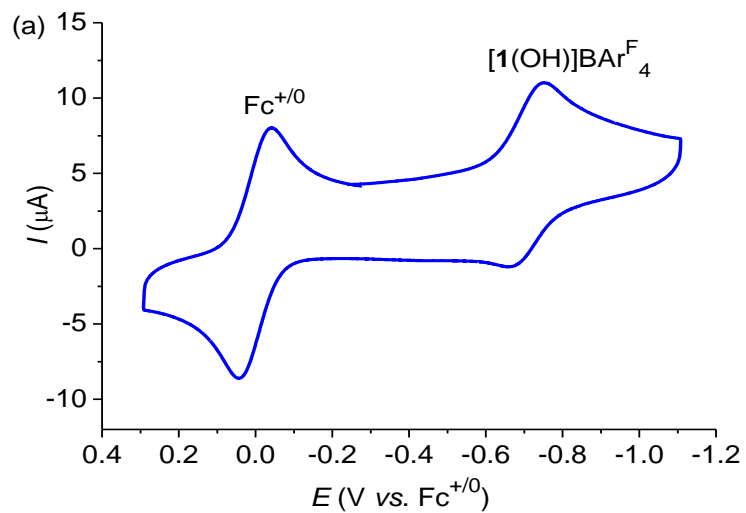
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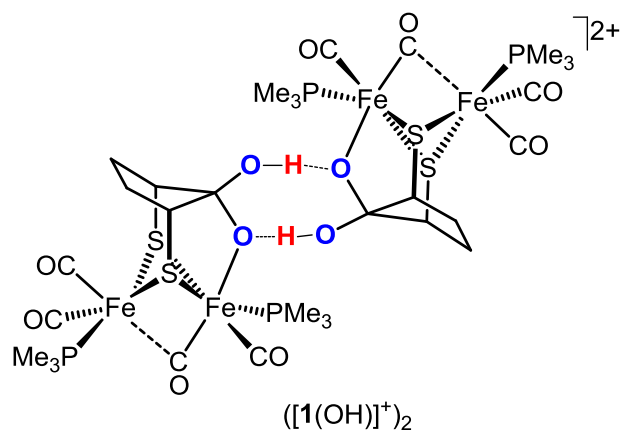
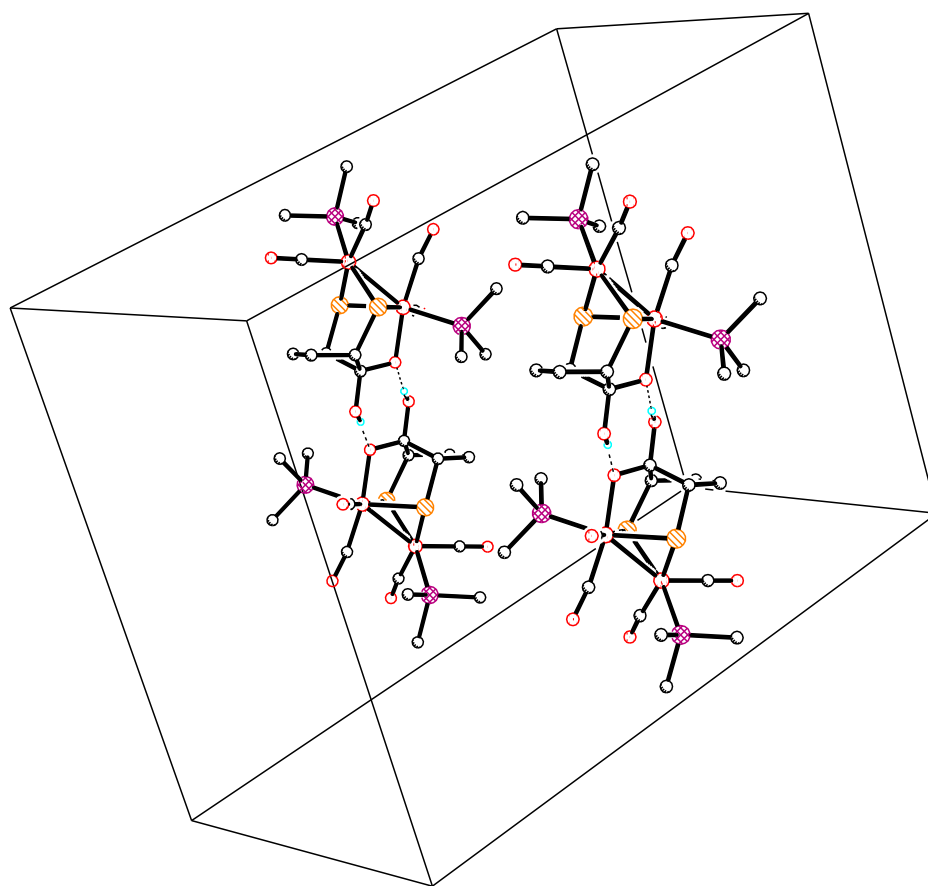




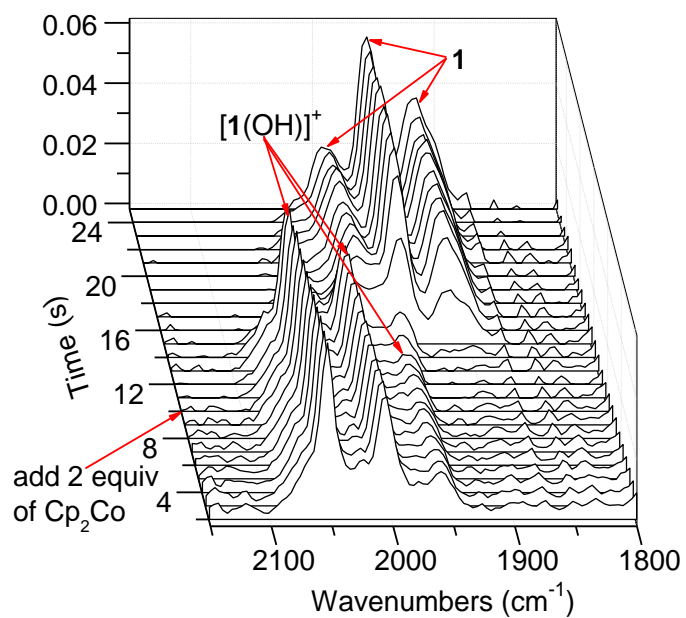
**Fig. S1** ORTEP drawing of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity except the hydrogen atoms at the C(11) and C(12).



**Fig. S2** Cyclic voltammograms of (a)  $[1(\text{OH})]\text{BARF}_4$  (1.0 mM) in  $\text{CH}_2\text{Cl}_2$  and (b)  $[1(\text{OH})]\text{BARF}_4$  + 1 equiv. of  $\text{CF}_3\text{COOH}$  in the presence of ferrocene as an internal standard, with 0.1 M  $n\text{Bu}_4\text{NPF}_6$  as electrolyte, scan rate  $100 \text{ mV s}^{-1}$ .



**Fig. S3** A view of the O–H  $\cdots$  O bonds between two molecules of  $[1(\text{OH})]^+$ . The structure is represented as standard ball and stick mode (O, red, small ball; H, sky-blue; C, grey; P, purple; S, yellow; Fe, red). Hydrogen atoms not involving in H-bond are omitted for clarity.



**Fig. S4** Sample-stacked IR spectra for the reduction of the in situ generated  $[1(\text{OH})]\text{BAR}_4^{\text{F}}$  (5 mM in  $\text{CH}_2\text{Cl}_2$ ) by 2 equiv. of  $\text{Cp}_2\text{Co}$ .