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Bridgehead isomer effects in bis(phosphido)-bridged diiron hexacarbonyl proton reduction electrocatalysts

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Electronic Supporting Information (ESI)

Additional ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra and simulations

Experimental. Spectra were simulated using the NUMMRIT module[1] in the SpinWorks (v4.2) program.[2] Note: swapping the shifts of the two P atoms and the sign of the JHH at the same time gives the same results.

1. J. S. Martin and A. R. Quirt*, J. Magn. Reson.* 1971, **5**, 318.

2. *SpinWorks 4.2.0*, Copyright © 2015, Kirk Marat, University of Manitoba

***a,e*-$[Fe_2(CO)_6\{(\mu_2\text{-}P(PhH\}_2]$, 1a(Ph).**

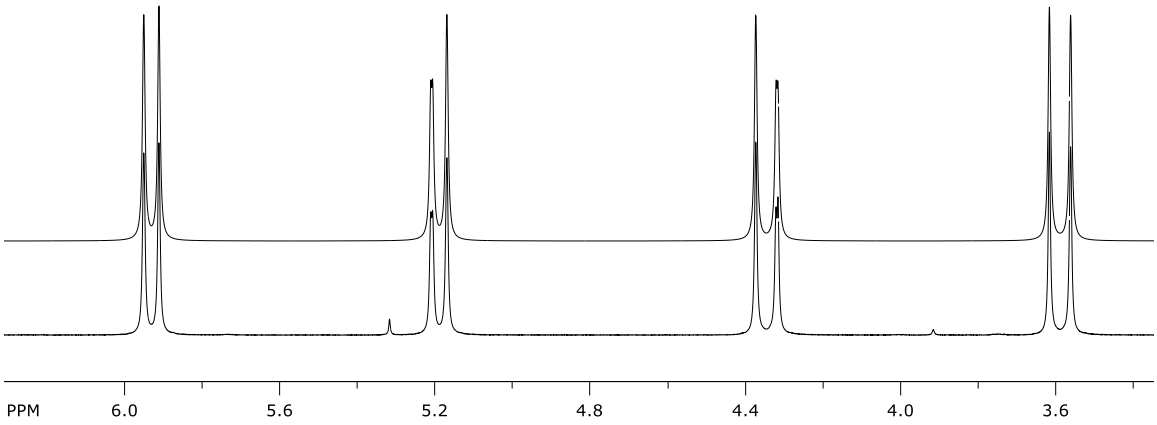

Figure 1S. Experimental (bottom trace) and simulated (top trace) for the P–H region of the 500 MHz ^{1} H NMR spectrum.

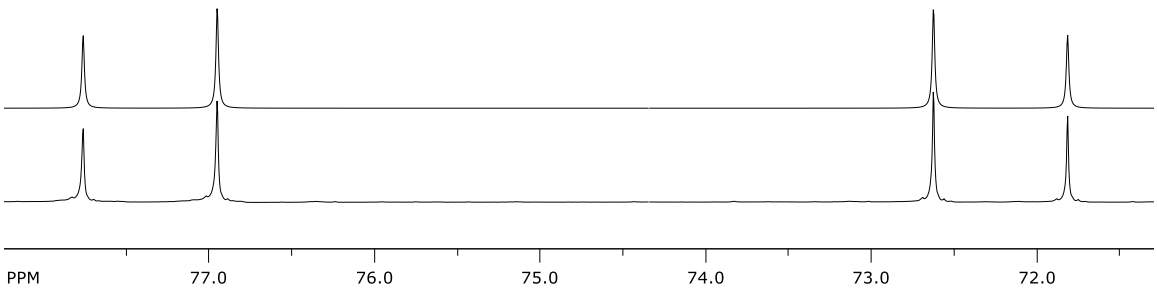

Figure 2S. Experimental $^{31}P\{^{1}H\}$ spectrum (bottom trace) and its simulation (top trace).

Simulation data.

Groups and chemical shifts:

#	name	shift (Hz)	spins	species	spin	sym	shift (ppm)
1	Ha	2778.620	1	1	1	1	4.560
2	Hb	1982.512	1	1	1	1	3.967
3	Pa	14616.615	1	2	1	1	72.244
4	Pb	15643.431	1	2	1	1	77.319

Scalar coupling constants: (round up to 1 dec pl)

j[1, 2] =	j[Ha,Hb] =	-1.000000
j[1, 3] =	j[Ha,Pa] =	373.487870
j[1, 4] =	j[Ha,Pb] =	17.018000
j[2, 3] =	j[Hb,Pa] =	24.834120
j[2, 4] =	j[Hb,Pb] =	380.817250
j[3, 4] =	j[Pa,Pb] =	-163.963000

Linewidth: 3.5 Hz

***a,e*-[$Fe_2(CO)_6\{\mu_2$-PH(*R*-2´-methoxy-1,1´-binaphthyl)$\}_2$], 1a(bn´).**

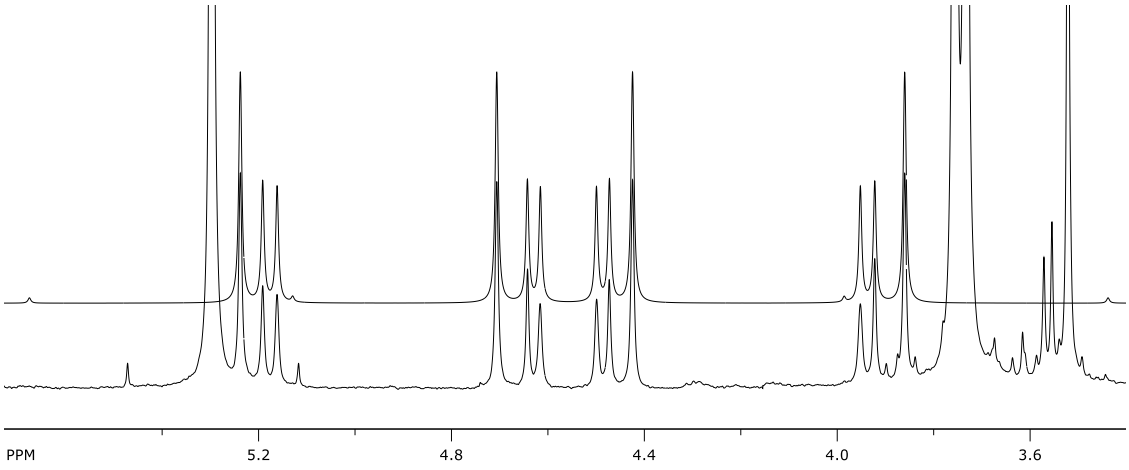

Figure 3S. Experimental (bottom trace) and simulated (top trace) for the P–H region of the 500 MHz ^{1}H NMR spectrum.

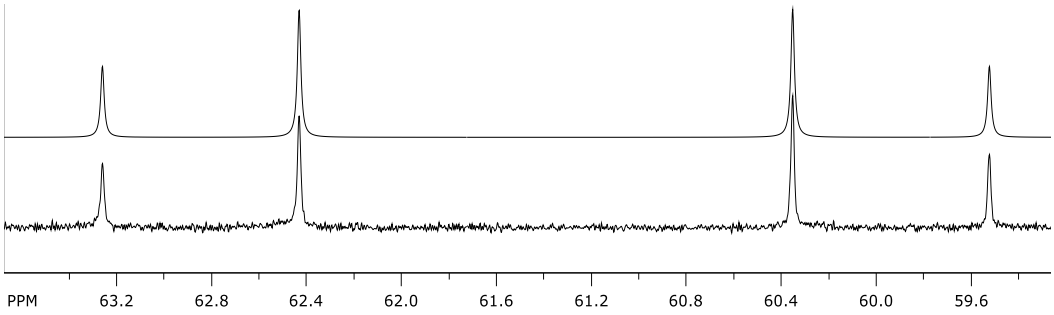

Figure 4S. Experimental $^{31}P\{^{1}H\}$ spectrum (bottom trace) and its simulation (top trace).

Simulation data.

Groups and chemical shifts:

#	name	shift (Hz)	spins	species	spin	sym	shift (ppm)
1	Ha	2414.676	1	1	1	1	4.832
2	Hb	2140.390	1	1	1	1	4.283
3	Pa	12702.067	1	2	1	1	62.781
4	Pb	12137.683	1	2	1	1	59.992

Scalar coupling constants: (round up to 1 dec pl)

j[1, 2] =	j[Ha,Hb] =	-0.750000
j[1, 3] =	j[Ha,Pa] =	388.164760
j[1, 4] =	j[Ha,Pb] =	18.885710
j[2, 3] =	j[Hb,Pa] =	26.704100
j[2, 4] =	j[Hb,Pb] =	396.675760
j[3, 4] =	j[Pa,Pb] =	-167.793220

Linewidth: 3.5 Hz

***e,e*-[$Fe_2(CO)_6(\mu_2\text{-}PHPh)_2$], 1b(Ph).**

The ^1H NMR spectrum was modelled as a AA'XX' system for the two P-H groups with coupling to *ortho* protons of the phenyl substituent; *i.e*., overall as a AA'(MM')2XX' spin system. There will be some extra small couplings to the *meta* and *para* protons that may broaden the multiplets, but will not change the larger evaluated couplings. The $^{31}P\{1H\}$ spectrum shows a singlet at 86.4 ppm.

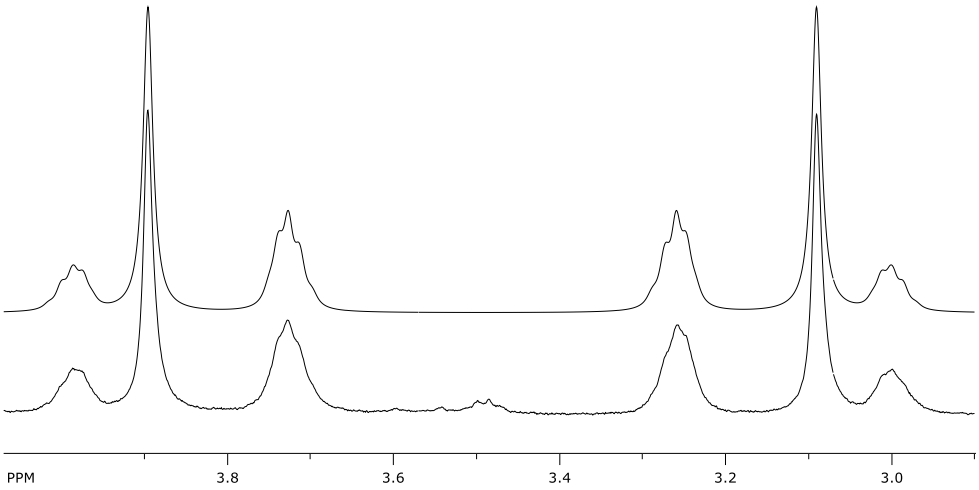

Figure 5S. Experimental (bottom trace) and simulated (top trace) for the P–H region of the 500 MHz ^1H spectrum.

Simulation data

Groups and chemical shifts:

#	name	shift (Hz)	spins	species	spin	sym	Shift (ppm)
1	Ha	1738.943	1	1	1	2	3.480 (P-H)
2	Ho1	3817.990	1	1	1	2	ortho protons
3	Ho2	3817.990	1	1	1	2	ortho protons
4	Pb	15643.431	1	2	1	2	86.4 (31P)

Scalar coupling constants:

j[1, 1] =	j[Ha,Ha] =	1.500000 (approx.; < 2Hz)
j[1, 2] =	j[Ha,Ho1] =	0.000000 (4 bonds) not fitted
j[1, 3] =	j[Ha,Ho2] =	0.000000
j[1, 4] =	j[Ha,Pb] =	371.050000
j[2, 1] =	j[Ho1,Ha] =	0.000000
j[2, 2] =	j[Ho1,Ho1] =	-1.500000 (4 bonds, not fitted, and makes no difference)
j[2, 3] =	j[Ho1,Ho2] =	0.000000
j[2, 4] =	j[Ho1,Pb] =	0.000000
j[3, 1] =	j[Ho2,Ha] =	0.000000
j[3, 2] =	j[Ho2,Ho1] =	0.000000
j[3, 3] =	j[Ho2,Ho2] =	-1.500000
j[3, 4] =	j[Ho2,Pb] =	14.000000

j[4, 1] =	j[Pb,Ha] =	31.580000
j[4, 2] =	j[Pb,Ho1] =	14.000000
j[4, 3] =	j[Pb,Ho2] =	0.000000
j[4, 4] =	j[Pb,Pb] =	-129.750000

<u>*e,e*-[$Fe_2(CO)_6\{\mu_2$-PH(*R*-2´-methoxy-1,1´-binaphthyl)$\}_2$]</u>, 1b(bn´).

The methoxybinapthyl group was modelled as a substituted phenyl group with one *ortho* proton (Ho, 7.83ppm) and one *meta* proton (Hm, 7.94 ppm)

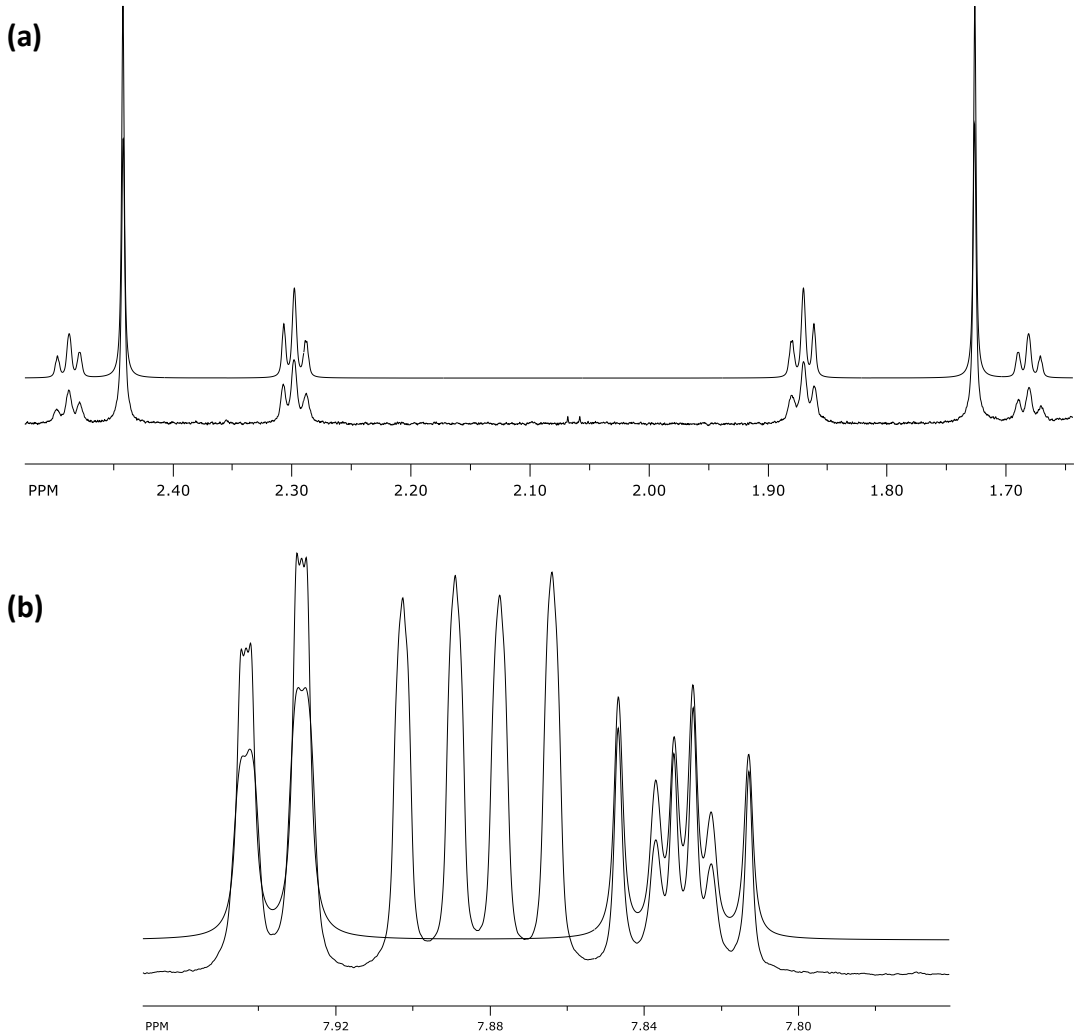

Figure 6S. Experimental (bottom trace) and simulated (top trace) of the 500 MHz ^{1}H spectrum of *e,e*-[$Fe_2(CO)_6(\mu_2$-PHPh$)_2$], **1b(bn'):** (a) the P–H region, (b) part of aryl region (the peak at 7.88 ppm was not required for the simulation in the P–H region).

Simulation data

Groups and chemical shifts:

#	name	shift (Hz)	spins	species	spin	sym	atom type, shift
1	Ha	1250.756	1	1	1	2	P-Ha, 2.0841 ppm
2	Ho	4699.200	1	1	1	2	ortho protons, 7.8303 ppm
3	Hm	4762.418	1	1	1	2	meta protons, 7.9356 ppm
4	P	46510.331	1	2	1	2	^{31}P, 77.5 ppm

Scalar coupling constants (Hz):

j[1, 1] =	j[Ha,Ha] =	0.500000	(approx. Say < 2Hz)
j[1, 2] =	j[Ha,Ho] =	0.500000	(approx. Say < 2Hz)
j[1, 3] =	j[Ha,Hm] =	0.000000	
j[1, 4] =	j[Ha,P] =	391.280000	1J P-Ha
j[2, 1] =	j[Ho,Ha] =	0.000000	
j[2, 2] =	j[Ho,Ho] =	0.000000	
j[2, 3] =	j[Ho,Hm] =	8.680000	(3J Ho-Hm))
j[2, 4] =	j[Ho,P] =	11.820000	3J P-Ho
j[3, 1] =	j[Hm,Ha] =	0.000000	
j[3, 2] =	j[Hm,Ho] =	0.000000	
j[3, 3] =	j[Hm,Hm] =	0.000000	
j[3, 4] =	j[Hm,P] =	1.700000	4J P-Hm
j[4, 1] =	j[P,Ha] =	38.600000	2J P-Ha
j[4, 2] =	j[P,Ho] =	0.000000	
j[4, 3] =	j[P,Hm] =	0.000000	
j[4, 4] =	j[P,P] =	-113.650000	2J P-P

additional Figures From Electrochemical Studies

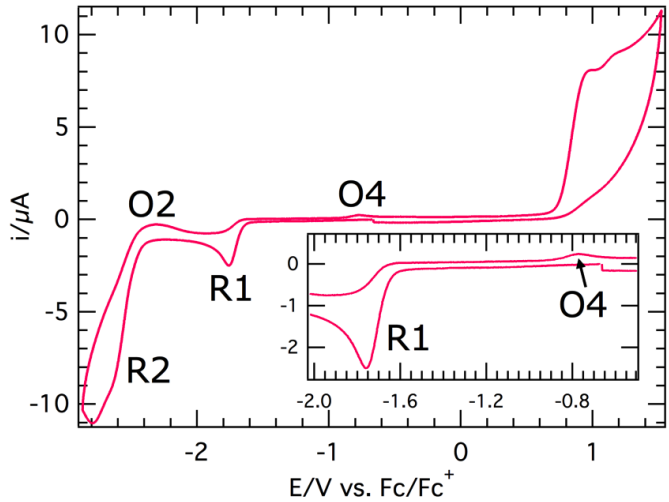

Figure 7S. CV of dimer *a,e*–$[Fe_2(CO)_6(\mu_2\text{-}PHPh)_2]$, **1a(Ph)**, with extended potential range recorded at v = 100 mV s^{-1}. All other conditions are identical to those listed in the caption to Figure 7 in the paper.

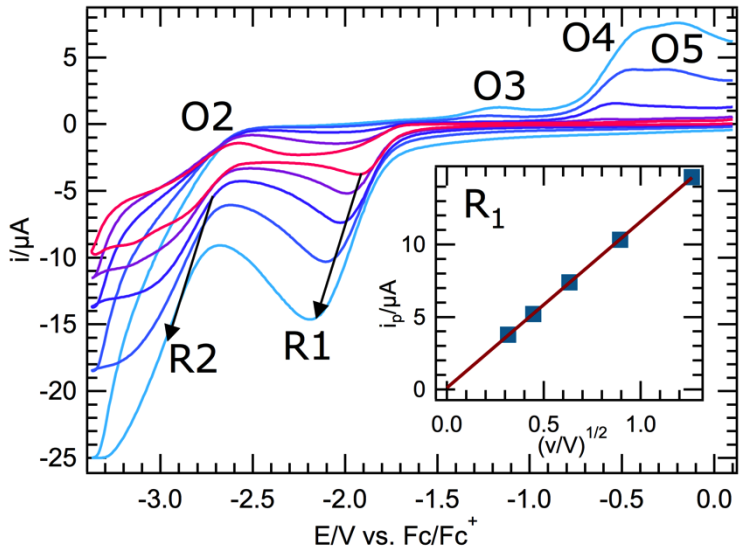

Figure 8S. CVs of *e,e*-[$Fe_2(CO)_6(\mu_2$-PHPh)$_2$], **1b(Ph)**, at different scan rates: v = 100, 200, 400, 800, 1600 mVs^{-1} with other conditions as in Figure 7 in paper. The inset shows a plot of i_p versus $v^{1/2}$ for peak R1.

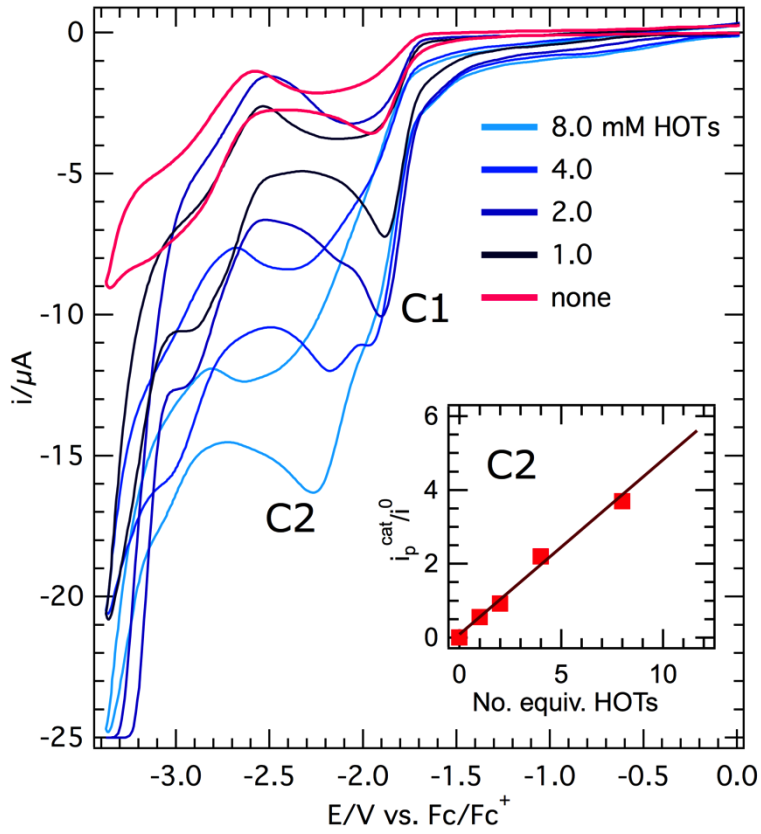

Figure 9S. Electrocatalysis of proton reduction: CVs of *e,e*-[$Fe_2(CO)_6(\mu_2$-PHPh)$_2$], **1b(Ph)**, (1.0 mM) and added TsOH. Inset: Current data for the catalytic wave *C2* versus equiv. of acid.

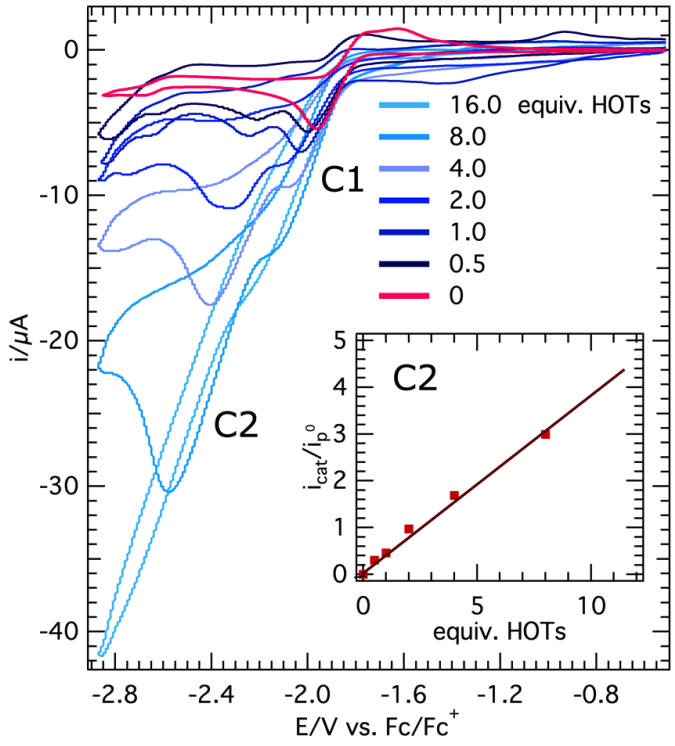

Figure 10S. Electrocatalysis of proton reduction: CVs of *a,ei*-[$Fe_2(CO)_6\{\mu_2$-P(bn')H$\}_2$] **1a(bn')** (1.0 mM) and added TsOH. Inset: Catalytic current ratio data for the catalytic wave *C2* versus equiv. of added acid.

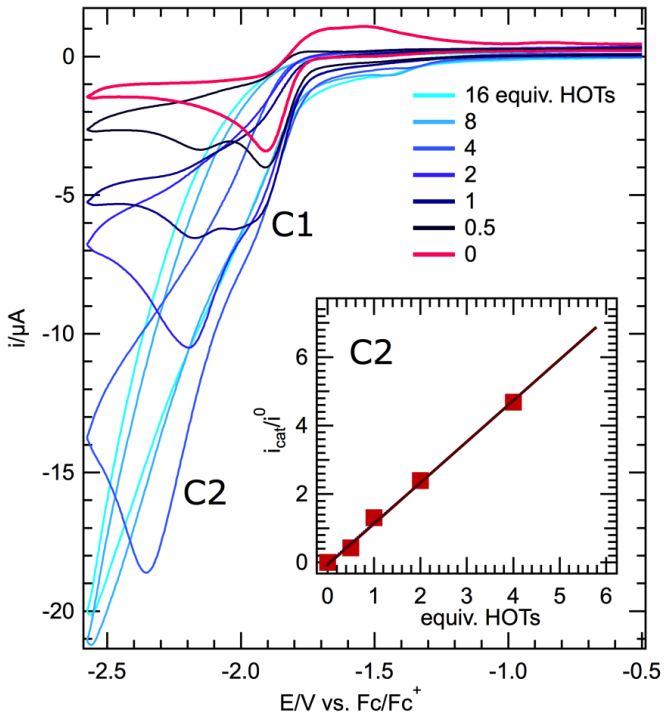

Figure 11S. Electrocatalysis of proton reduction: CVs of *e,e*-[$Fe_2(CO)_6\{\mu_2$-P(bn')H$\}_2$], **1b(bn´)**, (1.0 mM) and added TsOH. Inset: Catalytic current ratio data for the catalytic wave *C2* versus equiv. of added acid

Further spectra from studies of [$Fe_2(CO)_6\{\mu_2$-1,2-$(FcCH_2PCH_2)_2C_6H_4\}$] (4)

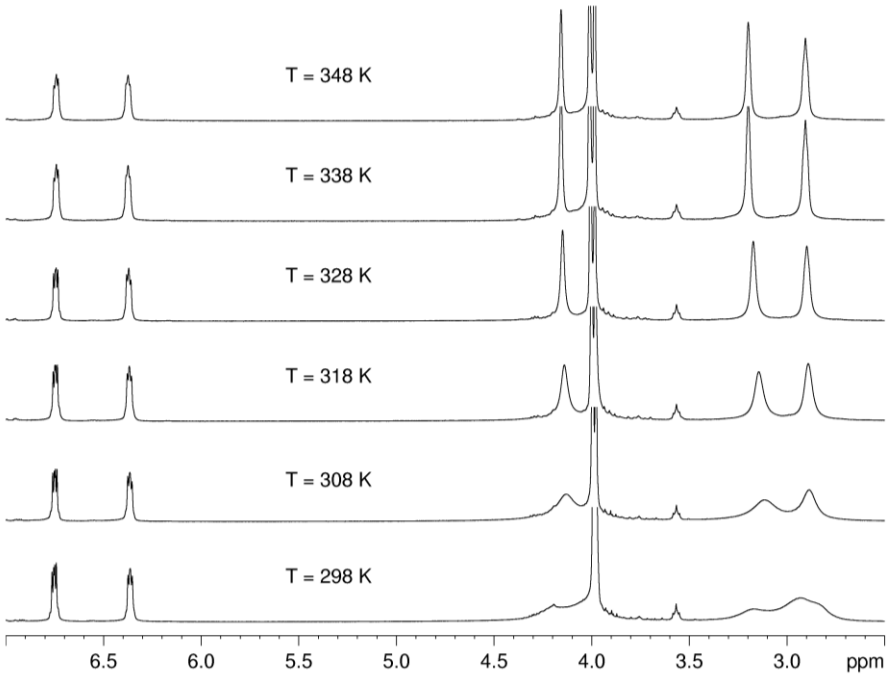

Figure 12S. Spectra from a variable temperature 400 MHz ^{1}H NMR study of **4** in benzene-d_6.

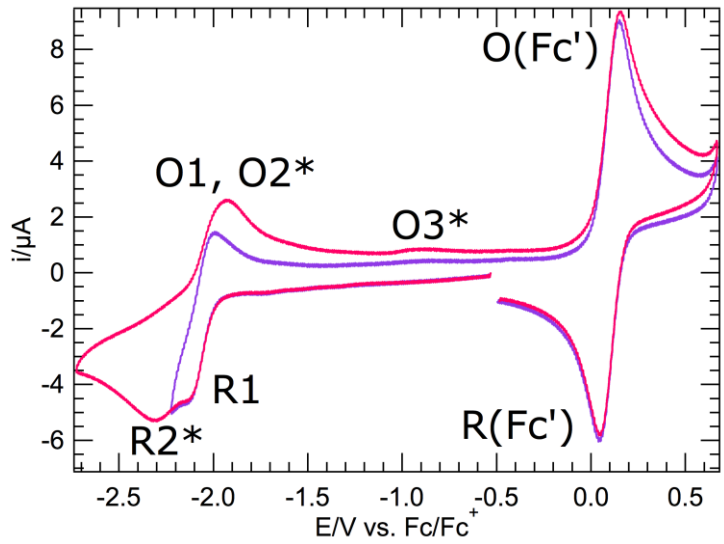

Figure13S. CVs of **4** (1.3 mM) in THF–[(n-Bu)$_4$N][PF_6] (0.4 M) showing the effect of switching before the second reduction process (*R2**); all other conditions as for Fig 7 in the paper.

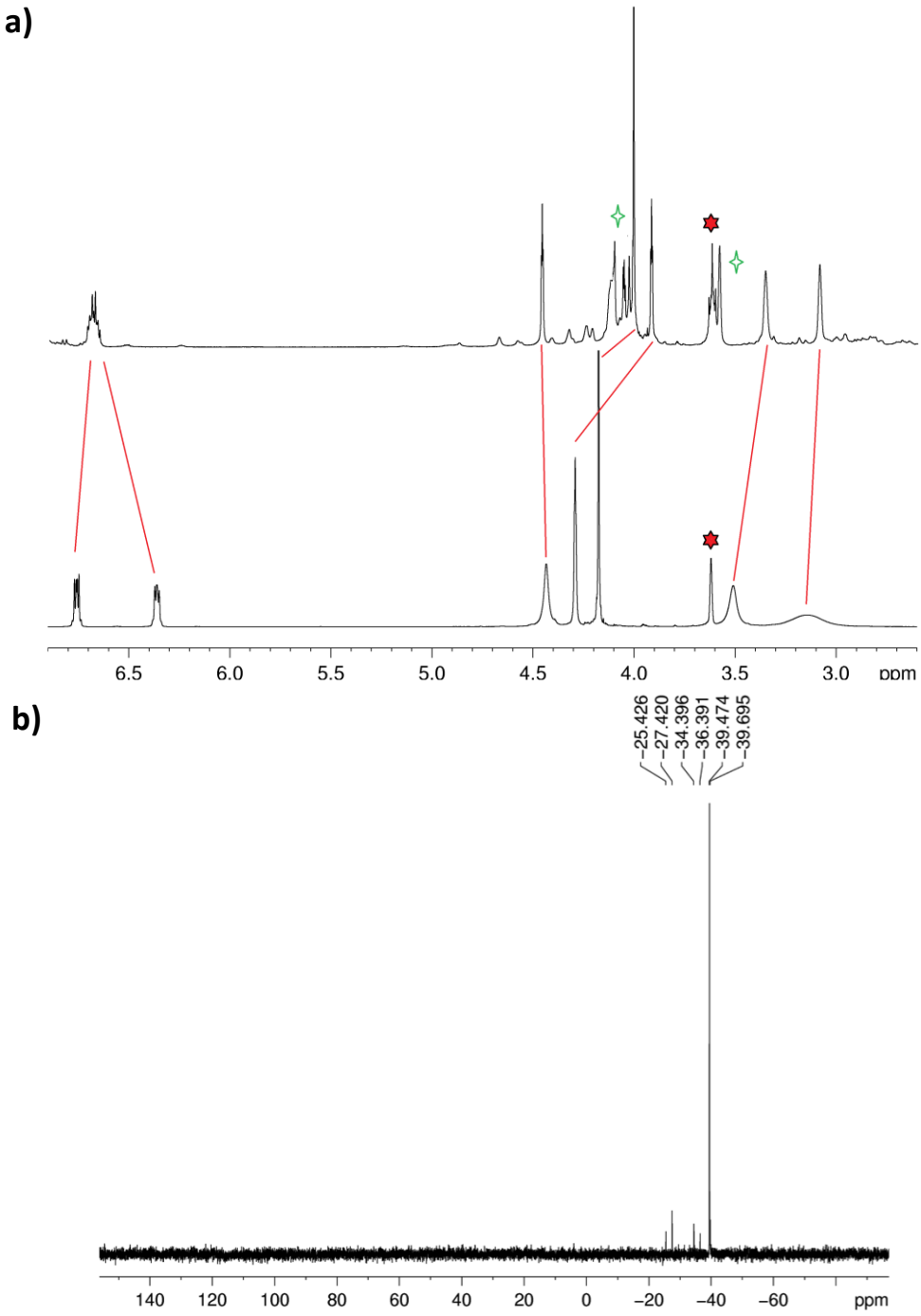

Figure 14S. a) ^{1}H NMR spectrum of **4** (bottom trace) and product(s) generated upon reduction of **4** with a Na mirror (top trace) in THF-*d8* (400 MHz, 298 K); **b)** $^{31}P\{^{1}H\}$ NMR spectrum of products generated after reduction of **4** with a Na mirror in THF-*d8* (161.9 MHz, 298 K).

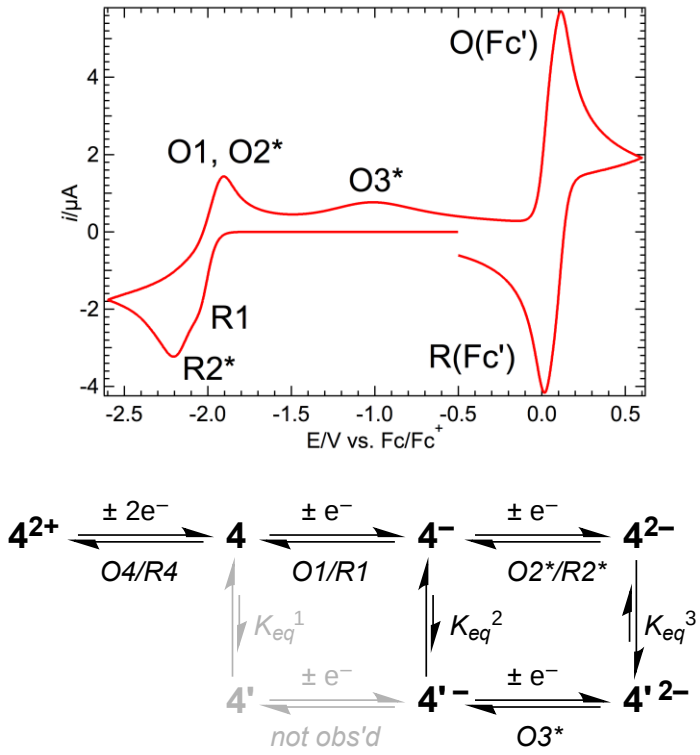

Figure 15S. a) Simulated CV of **4** using *DigiElch 6.F* software and the following input parameters: [**4**] = 2.6 mM, D = 10^{-5} cm^2 s^{-1}; 100 mV s^{-1}; A(electrode planar) = 0.0078 cm^2; E (**4**/**4**$^-$) = –2.00 V, α = 0.45, k_s = 3.5x10^{-4} cm s^{-1}; K_{eq}^1 = 5 x 10^4 and k_f = 1; E ([**4**$^{\bullet-}$]'/**4'**$^{2-}$) = –1.52 V, α = 0.86, k_s = 4x10^{-5} cm s^{-1}; K_{eq}^2 = 2.59 x 10^3 and k_f = 10^3; E (**4**$^{2+}$/**4**) = 0.03 V, α = 0.5, k_s = 10^{-1} cm s^{-1}; **b)** Mechanism used in simulation of the electrochemistry of **4.**

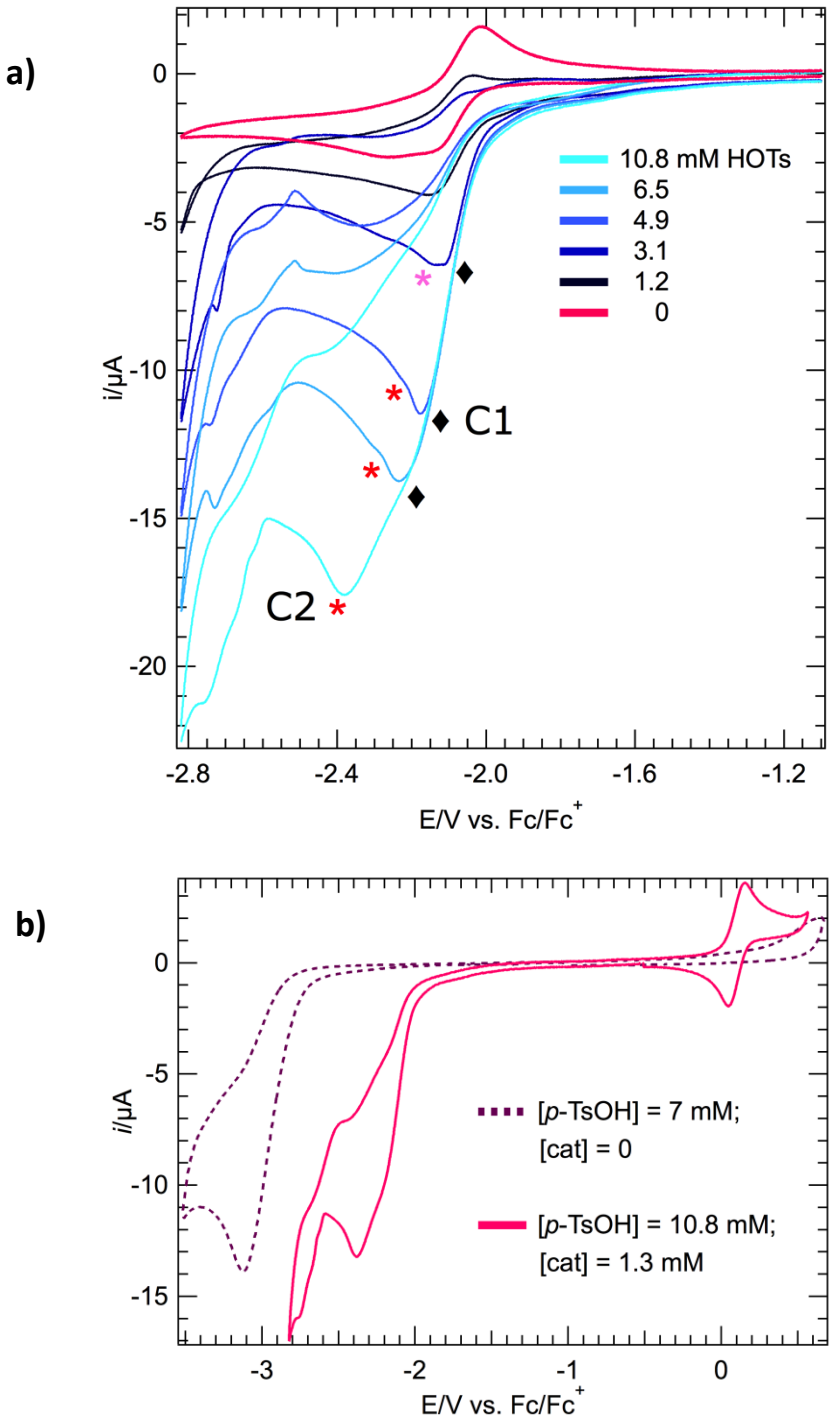

Figure 16S. (a) CVs of **4** (1.3 mM) with added TsOH in tetrahydrofuran–0.4 M $[Bu_4N][PF_6]$; *v* = 100 mV s^{-1}, other conditions as in Figure 7. The black diamonds indicate the peaks *C1* and the red asterisks indicate peaks *C2*. (b) CVs TsOH in tetrahydrofuran–0.4 M $[Bu_4N][PF_6]$ in the absence and presence of **4**.

Electrocatalysis using [Fe$_2$(CO)$_6${μ-P(CH$_2$Fc)H}$_2$] and [Fe$_2$(CO)$_6${μ-P(CH$_2$Fc)Me}$_2$]

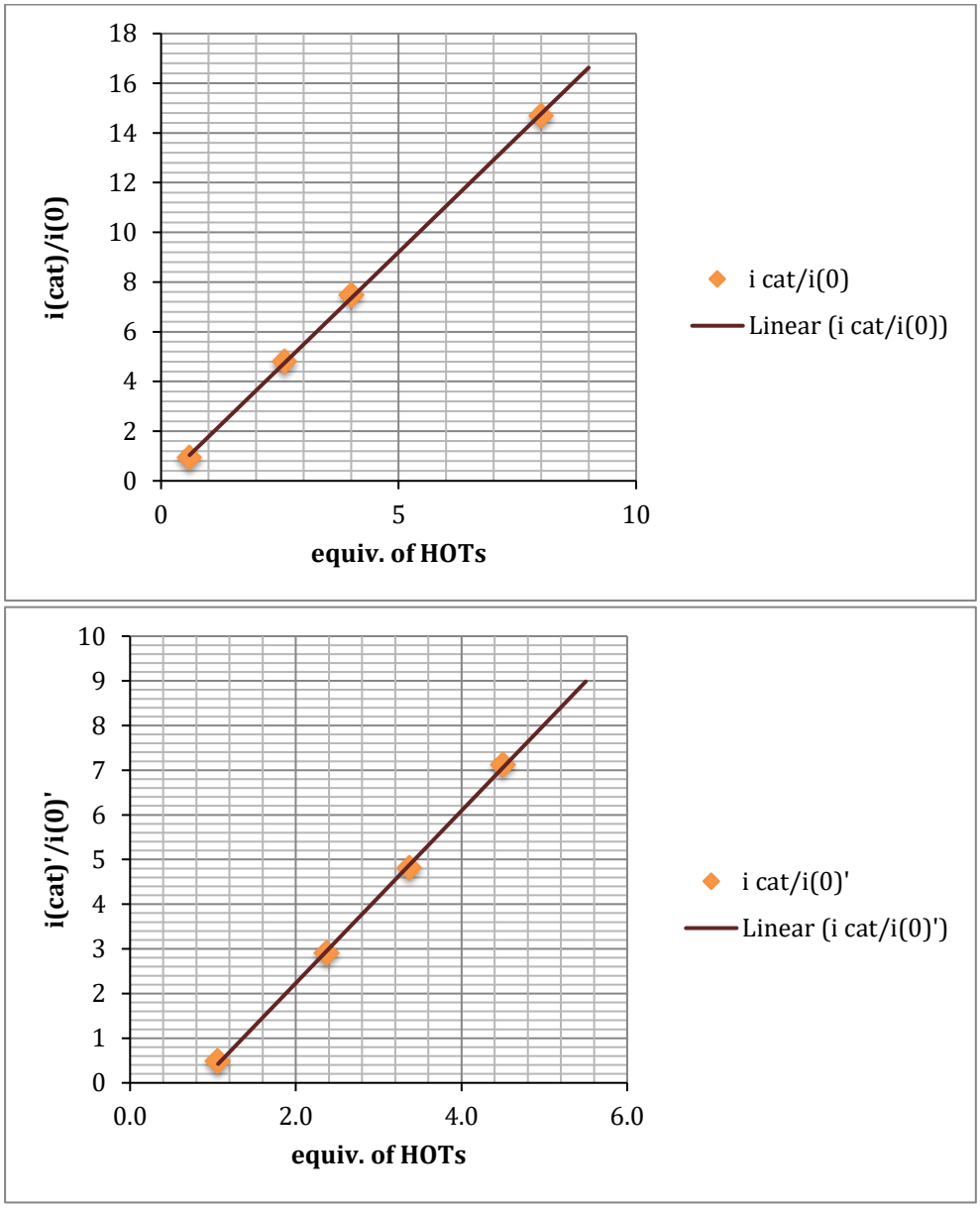

Figure 17S. Plots of catalytic current ratio against equiv. of added acid for [Fe$_2$(CO)$_6$(μ-P(CH$_2$Fc)H)$_2$] (top) and [Fe$_2$(CO)$_6$(μ-P(CH$_2$Fc)Me)$_2$)] (bottom) using data taken from Figure 7 in Gimbert-Suriñach *et al. Organometallics* 2012, **31**, 3480-3491.