Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Support Information

Three diiron complexes bearing an aromatic ring as the mimics of the diiron subunit of [FeFe]-hydrogenase: synthesis, electron transfer and coupled chemical reactions

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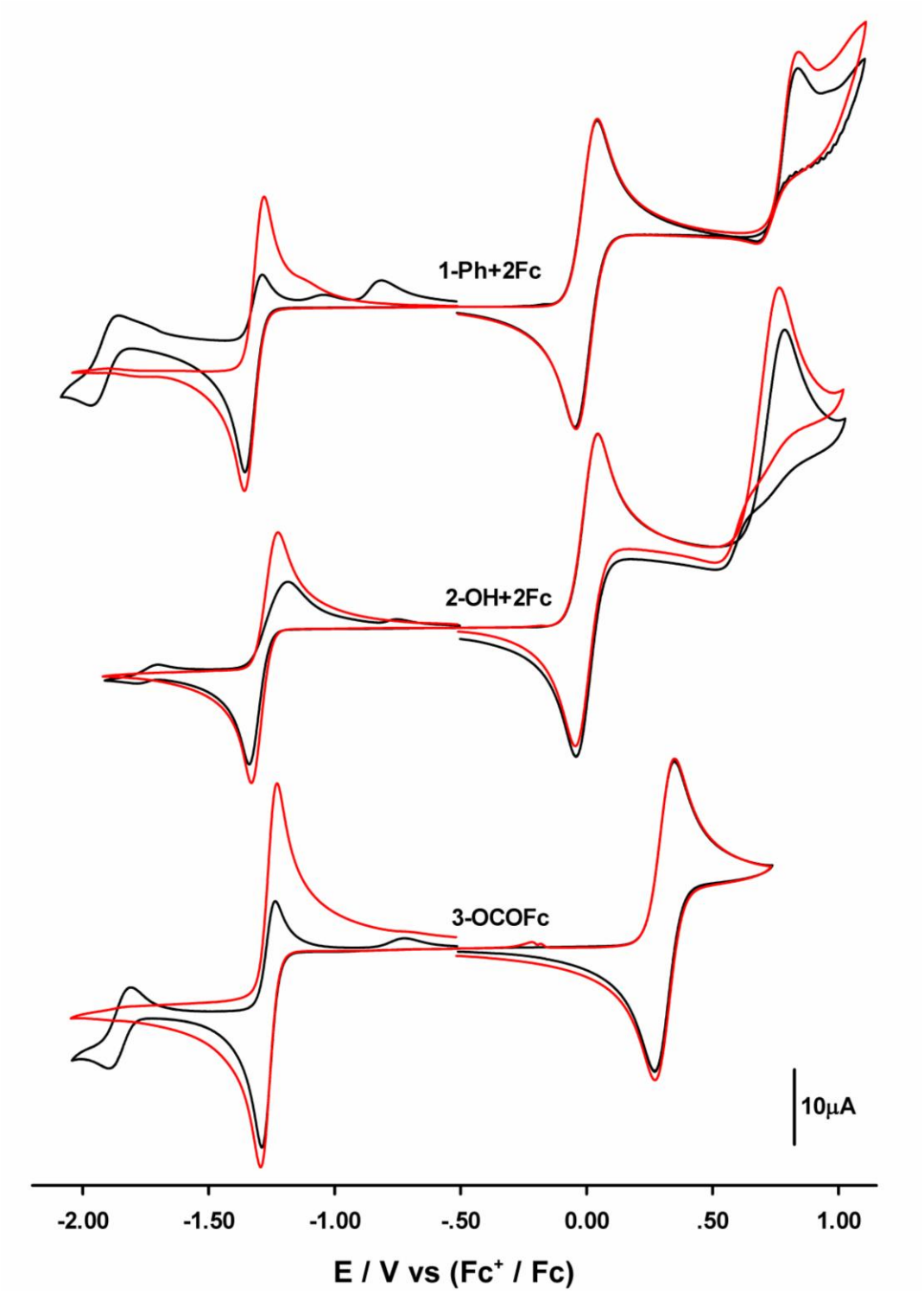

Fig. S1 Cyclic voltammograms of complexes **1-Ph+2Fc**, **2-OH+2Fc**, and **3-OCOFc** (3 mmol L^{-1}) in 0.1 mol L^{-1} $[NBut_4]BF_4$ / MeCN under Ar atmosphere (red line) and CO atmosphere (black line) at various ranges of scanning potentials (scanning rate = 0.1 Vs^{-1}, 298 K).

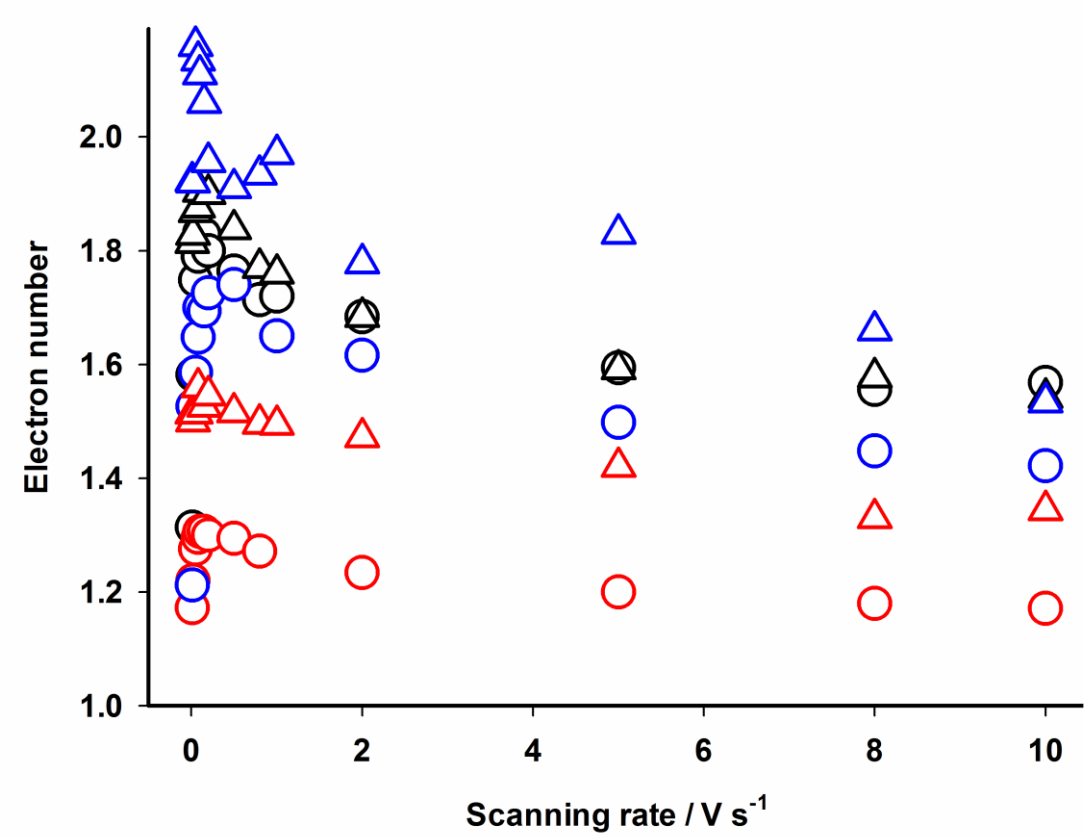

Fig. S2 Variation of electron numbers with scanning rate for the first reduction of complexes, **1-Ph** (black, 3 mmol L^{-1}), **2-OH** (red, 3 mmol L^{-1}), and **3-OCOFc** (blue, 1.64 mmol L^{-1}), under Ar (triangle) or CO (circle) atmosphere (298 K) in 0.1 mol L^{-1}-MeCN. Please note that for complexes **1-Ph** and **2-OH**, the calibrated electron numbers are only for reference since the diffusion coefficients may be significantly different between the complexes and externally added ferrocene.

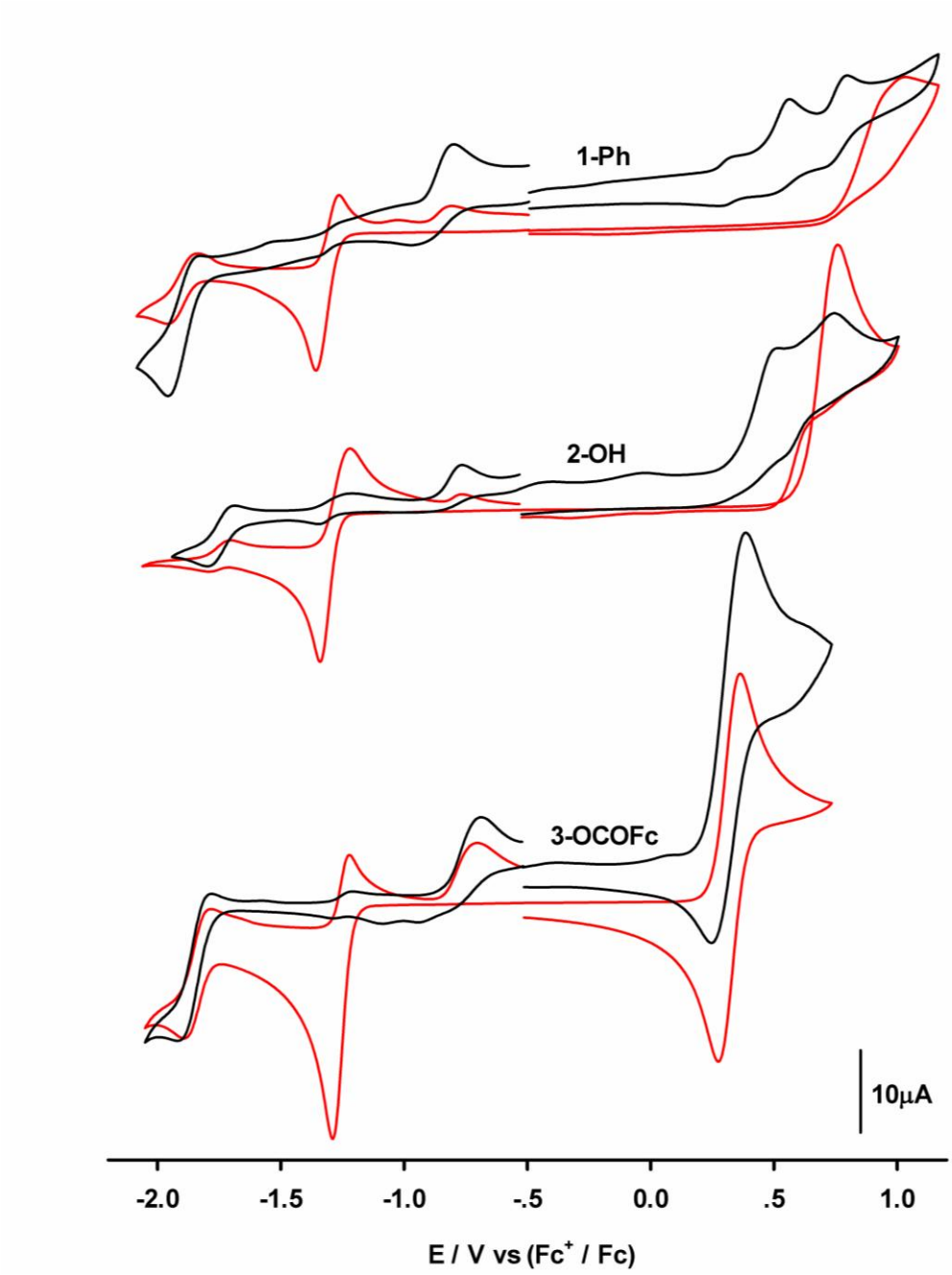

Fig. S3 Cyclic voltammograms of compounds **1-Ph**, **2-OH**, **3-OCOFc** (red line) and their electrolysis product at –1.5 V (black line) (3 mmol L^{-1}) in 0.1 mol L^{-1} $[NBut_4]BF_4$–CH_3CN under CO atmosphere (scanning rate = 0.1 Vs^{-1} 298 K).

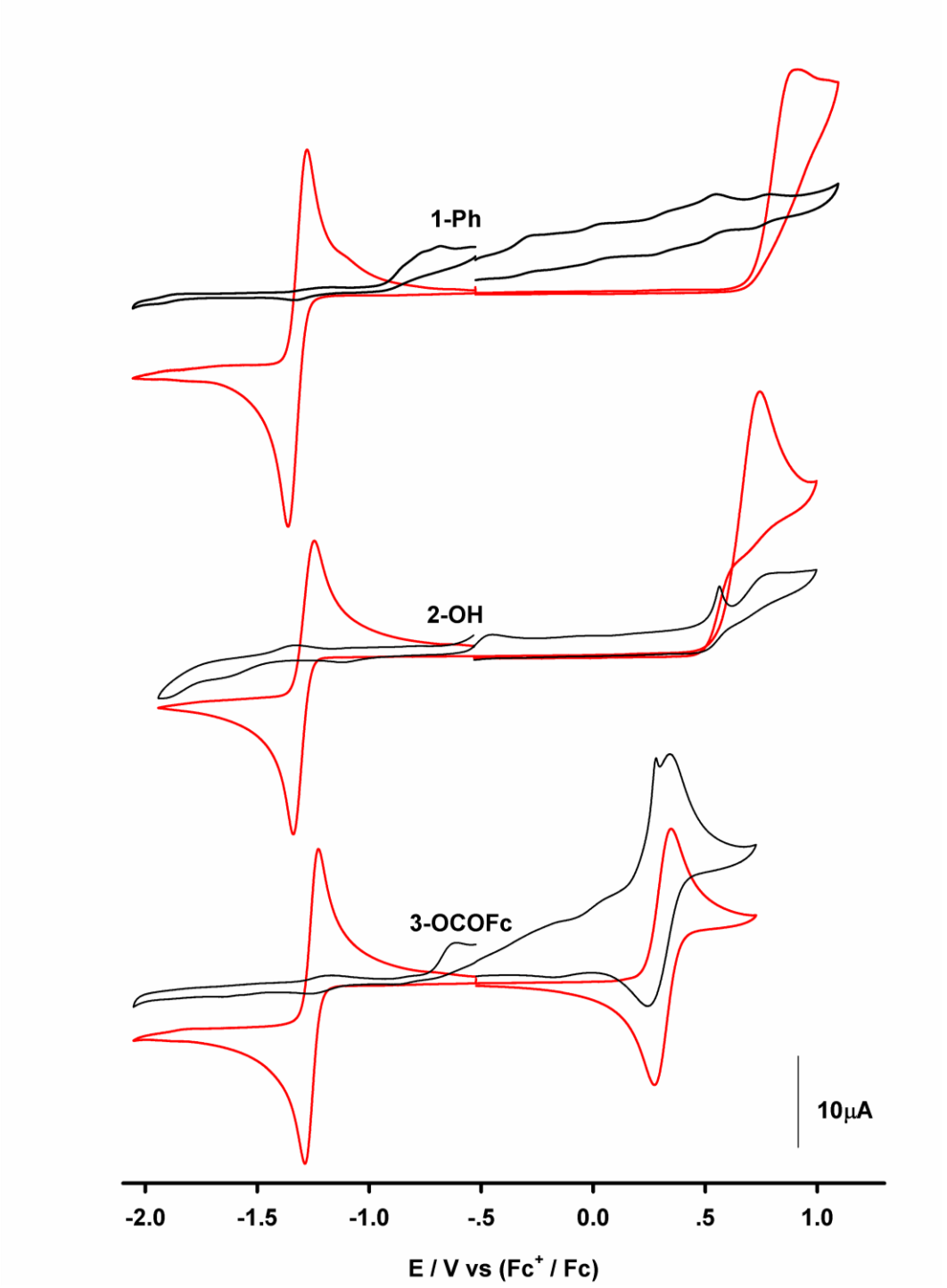

Fig. S4 Cyclic voltammograms of compounds **1-Ph**, **2-OH**, **3-OCOFc** (red line) and their electrolysis product at −1.5 V (black line) (3 mmol L^{-1}) in 0.1 mol L^{-1} $[NBut_4]BF_4$–CH_3CN under Ar atmosphere (scanning rate = 0.1 Vs^{-1} 298 K).

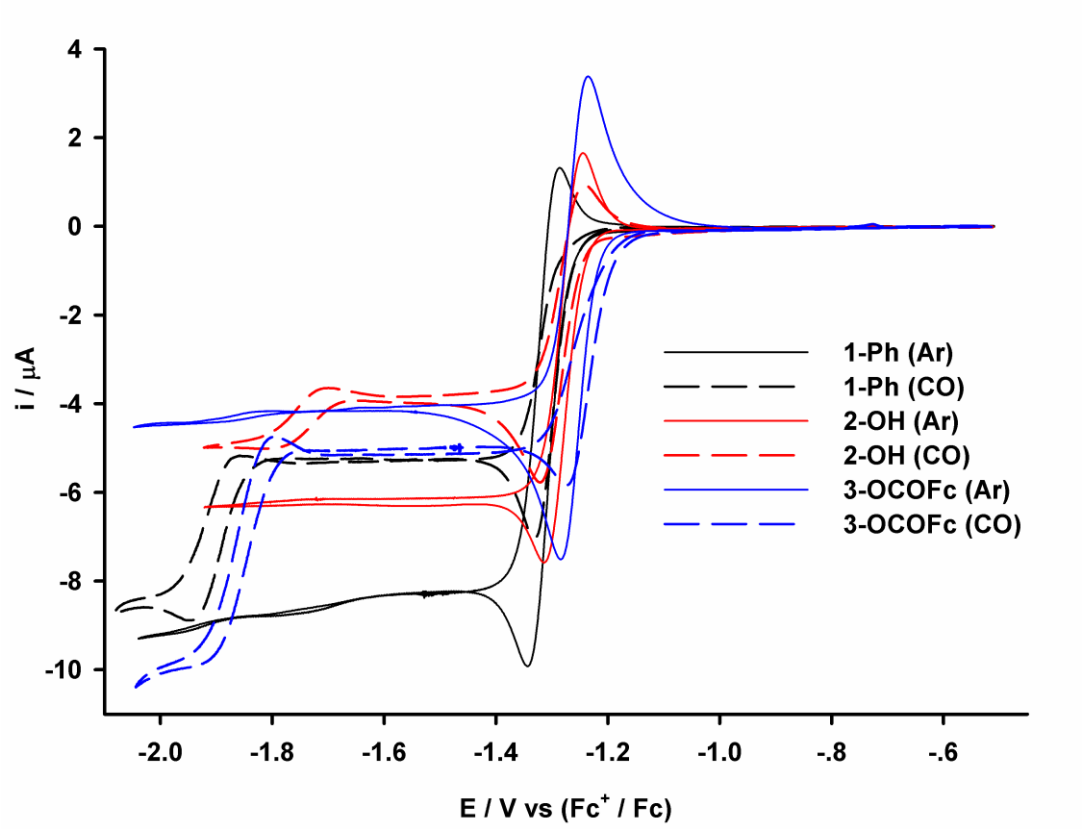

Fig. S5 Cyclic voltammograms of complexes **1-Ph**, **2-OH**, and **3-OCOFc** (3 mmol L^{-1}) in 0.1 mol L^{-1} $[NBut_4]BF_4$ / MeCN under Ar atmosphere (solid line) and CO atmosphere (dash line) (v = 0.01 Vs^{-1}), respectively.

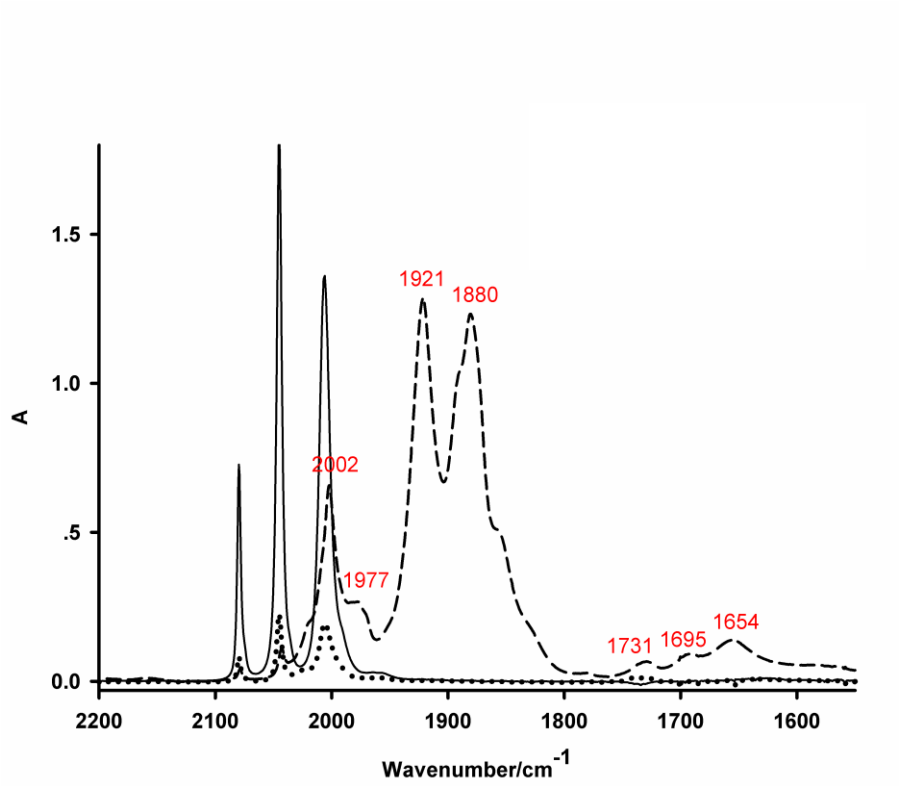

Fig. S6 Infrared spectra of complex **1-Ph** (black line), reduced product (THF, dash line), and unreacted precursor (Et_2O, dot line) under CO and with sodium as reducing agent.

Table S1 Electron numbers (n) per molecule derived from bulk electrolysis in 0.1 mol L^{-1} $[NBut_4]BF_4$ / MeCN at room temperature.

Complex	μmol	[a]Q_{cal}	[a]Q_{exp}	n	Average
Under CO					
1-Ph	23.82	4.60	2.18	0.95	0.99 ± 0.04
	35.73	6.90	3.34	0.97	
[b]**1-Ph**	12.62	2.44	1.29	1.05	
	11.91	2.30	1.15	1.00	
2-OH	10.40	2.01	0.96	0.96	1.05 ± 0.06
[b]**2-OH**	11.10	2.14	1.12	1.05	
	11.10	2.14	1.15	1.07	
3-OCOFc	11.42	2.21	1.03	0.93	0.98 ± 0.06
	5.71	1.10	0.56	1.02	
Under Ar					
1-Ph	11.9	2.30	1.98	1.72	1.8 ± 0.2
[b]**1-Ph**	7.86	1.52	1.52	2.00	
	10.48	2.02	1.73	1.71	
2-OH	7.53	1.45	1.11	1.53	1.48 ± 0.07
[b]**2-OH**	10.40	2.02	1.44	1.43	
3-OCOFc	5.71	1.10	0.87	1.58	1.57 ± 0.01
	5.71	1.10	0.86	1.56	

[a] Q_{cal} is the charge (C) calculated by assuming two electrons per molecule in the

reduction and Q_{exp} the charge (C) obtained from bulk electrolysis.

[b] 2 equivalents ferrocene added externally to calibrate the electron number.