	OX $E_{1/2}$ / V[a]	ΔFc[b]	$-I_p^c/I_p^a$ [c]	I_p vs. (scan rate)$^{1/2}$ (R^2)[d]	Square wave / V	OX' (E_p^a) / V	RED (E_p^c) / V	OX'' (E_p^a) / V
1Cl	-0.42 (0.09)	(0.10)	1.03	1.000, 0.998	-0.42	+1.08	-2.50	-1.20
1Br	-0.38 (0.10)	(0.10)	1.05	1.000, 0.997	-0.38	+1.12	-2.49	-1.20
1I	-0.34 (0.09)	(0.10)	1.04	0.999, 0.997	-0.34	+1.09[g]	-2.32(sh), -2.48	-1.21
1H	-0.50 (0.09)	(0.09)	1.03	1.000, 0.994	-0.51	+0.73	-	-
1SIP[f]	+0.26 (0.09)	(0.07)			+0.27	-0.01	-2.10	-
2Cl	-0.59 (0.10)	(0.10)	0.99	0.999, 0.999	-0.59	+0.87[h]	-2.64	-1.29
2Br	-0.55 (0.09)	(0.09)	0.96	0.999, 0.999	-0.55	+0.95[g]	-2.55	-1.30
2I	-0.51 (0.09)	(0.10)	1.02	0.998, 0.998	-0.51	+0.81[i]	-2.42(sh), -2.57	-1.29
2H	-0.71 (0.09)	(0.10)	1.05	0.999, 0.991	-0.71	+0.57	-	-
2SIP[f]	+0.06 (0.09)	(0.07)			+0.06	-	-2.20	-
3Cl	-0.45 (0.09)	(0.10)	1.01	1.000, 0.997	-0.45	+0.51[p]	-2.49	-1.10
3Br	-0.41 (0.09)	(0.10)	1.04	0.999, 0.996	-0.41	+1.06	-2.49	-1.10
3I	-0.37 (0.09)	(0.09)	1.00	0.998, 0.998	-0.37	+0.99[j]	-2.51	-1.07
3H	-0.50 (0.09)	(0.09)	0.84	0.994, 0.985	-0.50	+0.56[g]	-	-
3SIP[f]	+0.25 (0.1)	(0.07			+0.25	+0.01	-2.05	-1.33
4Cl	-0.44 (0.09)	(0.10)	0.96	0.996, 0.998	-0.44	+0.51[k]	-2.47	-1.01
4Br	-0.40 (0.09)	(0.10)	0.91	0.996, 0.999	-0.39	-	-2.50[l]	-1.01
4I	-0.36 (0.10)	(0.10)	1.06	0.996, 0.999	-0.35	+0.38	-2.26, -2.47[m]	-1.03
4H	-0.53 (0.15)[e]	(0.16)	-	0.955, -	-0.50	-	-	-
4SIP[f]	+0.26 (0.08)	(0.07			+0.27	0.00	-1.93	-1.27
5Cl	-0.54 (0.08)	(0.09)	0.77	0.992, 0.974	-0.54	-0.10[p]	-[n]	-1.07[p]
5Br	-0.50 (0.09)	(0.09)	0.76	0.998, 0.983	-0.51	+0.54	-1.85[p]	-1.10[p]
5I	-0.46 (0.09)	(0.09)	0.89	0.999, 0.996	-0.46	-	-[o]	-
5H	-0.62 (0.09)	(0.09)	1.05	0.998, 0.999	-0.62	+0.77	-	-
5SIP[f]	+0.20 (0.08)[q]	(0.07			+0.20	+0.06	-2.05	-1.31

***Table S1**: [a] In THF containing $[NBu^n_4][BF_4]$ (0.5 M) as supporting electrolyte. At ambient temperature. Potentials quoted against $E_{1/2}$ Fc^+/Fc at 0.10 Vs^{-1} used as the internal standard unless stated otherwise. Values in brackets are ΔE (= $E_p^a - E_p^c$); $E_{1/2} = (E_p^a + E_p^c)/2$; E_p^a = peak anodic (oxidation) potential; E_p^c = peak cathodic (reduction) potential. [b] $\Delta Fc = E_p^a - E_p^c$ for the Fc^+/Fc couple at 0.10 Vs^{-1}. [c] at 0.1 Vs^{-1}. [d] from data recorded at 0.1, 0.2, 0.3, 0.05 and 0.02 Vs^{-1}, R^2 values for I_p^a and I_p^c, respectively. [e] at 1.00 Vs^{-1} and $[CoCp_2][PF_6]$ used as the internal standard to avoid overlap of couples. Potential quoted against the Fc^+/Fc couple using an independent calibration where $E_{1/2}$ $[CoCp_2]^+/[CoCp_2]$ = -1.359 V vs. Fc^+/Fc under identical conditions. [f] In MeCN containing $[NBu^n_4][BF_4]$ (0.1 M) as supporting electrolyte and $[Fe(\eta^5$-*

$C_5Me_5)_2$] used as the internal standard to avoid overlap of couples. Potentials quoted against the Fc^+/Fc couple using an independent calibration where $E_{1/2}$ [Fe(η^5-$C_5Me_5)_2$]$^+$/ [Fe(η^5-$C_5Me_5)_2$] = -0.505 V vs. Fc^+/Fc under identical conditions. Current analysis not performed due to the presence of overlapping iodide electrochemistry. [g] increase in current but not resolved as a well-defined peak. [h] return wave noted for this oxidation process in reduction half-cycle: $E_{1/2}$ +0.81 V (0.13) (ΔFc 0.12) at 0.3 Vs^{-1}. [i] return wave noted for this oxidation process in reduction half-cycle: $E_{1/2}$ +0.76 V (0.13) (ΔFc 0.13) at 0.3 Vs^{-1}. [j] return wave noted for this oxidation process in reduction half-cycle: $E_{1/2}$ +0.94 V (0.11) at 0.1 Vs^{-1} ($E_{1/2}$ +0.94 V (0.12) (ΔFc 0.12) at 0.3 Vs^{-1}). [k] small couple noted at $E_{1/2}$ +0.09 V (0.08). [l] a small return wave was associated with this reduction at E_p^a -2.37 V. [m] return wave noted for this reduction process in oxidation half-cycle: $E_{1/2}$ +2.42 V (0.10) at 0.1 Vs^{-1}. [n] no defined peak but small current noted at potentials more cathodic than ca. -1.15 V. [o] asymmetric couple noted E_p^c -1.22 V (broad) E_p^a -1.11 V (sharp) at 0.1 Vs^{-1}. [p] small feature. [q] overlaps with an additional feature at E_p^a +0.36 V.

DFT Experimental and Supplementary Information

Compound	Fe1-Ct	Fe1-Cl1	Fe1-P1	Fe1-P2	Ct-Fe1-Cl1	Cl1-Fe1-P1	Cl1-Fe1-P2
1Cl	1.699(3) 1.711	2.3317(9) 2.343	2.1963(10) 2.191	2.1846(10) 2.181	123.9(9) 121.64	87.90(3) 88.73	89.11(3) 89.26
2Cl	1.732 1.744	2.346(1) 2.358	2.197(1) 2.202	2.210(1) 2.216	119.06 118.6	87.23(5) 87.47	86.03(4) 85.83
3Cl	1.716(5) 1.72	2.3298(16) 2.343	2.198(16) 2.202	2.1881(15) 2.186	123.8(19) 123.19	90.18(6) 88.96	86.15(6) 86.08
4Cl	1.704(7) 1.742	2.294(2) 2.348	2.184(2) 2.201	2.194(2) 2.213	121.24(2) 120.47	89.09(9) 89.57	87.64(8) 87.62
5Cl	1.739(4) 1.759	2.3423(10) 2.351	2.2358(10) 2.235	2.2107(11) 2.221	122.8(11) 121.48	89.18(4) 89.94	84.18(4) 85.08

***Table S2**: Representative comparison of experimental and theoretical bond lengths (Å) and angles (°) of **1Cl-5Cl** where Ct = centroid.*

Compound	HOMO (eV)	Total Fe (%)	Fe s (%)	Fe p (%)	Fe d (%)	Total X (%)	X s (%)	X p (%)	X d (%)	Total Cp (%)	Cp s (%)	Cp p (%)	Cp d (%)	Total dppe (%)	dppe s (%)	dppe p (%)	dppe d (%)
1Cl	-3.73	70.23	0	0.95	69.28	14.35	0	13.95	0.40	9.38	0.04	8.93	0.41	6.04	1.05	3.96	1.02
2Cl	-3.53	72.68	0	0.80	71.88	11.11	0	10.70	0.41	10.13	1.60	7.98	0.53	6.09	0.82	4.18	1.09
3Cl	-3.69	70.06	0.04	0.84	69.18	13.22	0	12.82	0.41	10.45	0.19	9.64	0.62	6.27	0.92	4.34	1.01
4Cl	-3.74	69.14	0	0.73	68.41	12.02	0	11.63	0.39	12.42	0.41	11.18	0.83	6.44	0.88	4.51	1.04
5Cl	-3.54	73.07	0	0.83	72.24	12.29	0	11.88	0.41	9.15	0.42	8.30	0.43	5.48	0.74	3.79	0.95
1Br	-3.78	67.96	0	0.94	67.02	17.27	0	16.72	0.55	8.94	0.02	8.53	0.39	5.83	1.04	3.78	1.00
2Br	-3.56	72.00	0	0.83	71.19	13.44	0	12.88	0.57	9.46	1.43	7.53	0.50	5.10	0.69	3.42	1.00
3Br	-3.74	68.84	0.02	0.85	67.96	13.93	0	13.33	0.60	10.80	0.20	9.96	0.64	6.42	0.81	4.57	1.04
4Br	-3.78	67.29	0	0.75	66.55	13.69	0	13.13	0.56	12.58	0.46	11.29	0.84	6.43	0.82	4.58	1.04
5Br	-3.66	68.14	0	0.91	67.23	11.96	0	11.37	0.59	12.97	0.69	11.73	0.56	6.91	1.01	4.87	1.02
1I	-3.83	61.91	0	0.86	61.05	25.05	0	24.92	0.12	7.96	0.08	7.52	0.35	5.09	0.88	3.31	0.91
2I	-3.62	68.26	0	0.88	67.39	17.80	0	17.68	0.12	8.87	1.2	7.21	0.47	5.05	0.53	3.55	0.98
3I	-3.78	61.96	0.01	0.71	61.24	22.86	0	22.74	0.12	9.70	0.15	8.93	0.62	5.47	0.60	3.94	0.92
4I	-3.86	63.87	0.01	0.76	63.10	18.08	0	17.96	0.12	11.93	0.41	10.72	0.80	6.12	0.56	4.58	0.98
5I	-3.74	66.17	0	0.98	65.21	14.24	0	14.12	0.13	12.47	0.58	11.35	0.54	7.11	1.01	5.09	1.01
1H	-3.84	73.36	0.61	3.45	69.30	0.76	0.35	0.42	0	10.01	0.45	9.12	0.44	15.87	0.79	10.99	4.09
2H	-3.56	70.71	0.54	3.79	66.38	0.86	0.50	0.36	0	11.92	1.98	9.32	0.62	16.58	0.25	12.18	4.09
3H	-3.79	73.96	0.82	3.76	69.38	0.09	0.08	0.01	0	9.63	0.28	8.93	0.42	16.32	0.70	11.57	4.05
4H	-3.70	72.50	1.25	3.64	67.60	0.58	0.20	0.38	0	11.47	0.22	10.55	0.70	15.46	0.28	11.39	3.80
5H	-3.64	68.13	0.75	4.68	62.71	0.57	0.37	0.21	0	13.96	0.80	12.53	0.62	17.34	0.35	12.82	4.18

***Table S3**: Energies and compositions of the HOMO in **1Cl-5Cl**, **1Br-5Br**, **1I-5I** and **1H-5H**. Calculated using AOMix*