Supplementary information for:

“The unusual redox properties of fluoroferrocenes revealed through a comprehensive study of the haloferrocenes”

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ELECTROCHEMISTRY

Figure S1. Overlaid cyclic voltammograms for mixed FcX and ferrocene solutions (V vs. $\text{FcH}/[\text{FcH}]^+$; conditions – 0.1 M TBAPF_6 in CH_3CN , WE: glassy carbon, RE and CE: Pt; potentials corrected for R_u ; current scaled for clarity as noted).

Figure S2. Overlaid cyclic voltammogram (blue solid line) and differential pulse voltammogram (black dotted line) for a mixture of ferrocene and fluoroferrocene (V vs. $\text{FcH}/[\text{FcH}]^+$; conditions – 0.1 M TBAPF_6 in CH_3CN , WE: glassy carbon, RE and CE: Pt; potentials corrected for R_u).

NMR SPECTRA

Figure S3. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) for **FeCl**.

Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3 , 298 K) for **FeCl**.

Figure S5. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) for **FcF**.

Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3 , 298 K) for **FcF**.

Figure S7. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (377 MHz, CDCl_3 , 298 K) for **FcF**.

Figure S8. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) for **fcCl₂**.

Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3 , 298 K) for fcCl_2 .

Figure S10. ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) for fcF_2 .

Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3 , 298 K) for fcF_2 .

Figure S12. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (377 MHz, CDCl_3 , 298 K) for fcF_2 .

UV-VIS SPECTROSCOPY

Figure S13. UV-vis spectra (MeCN, rt) of FcX (X = H, F, Cl, Br, I), at (a) ~1-2 mM and (b) ~0.1-0.2 mM (inset in (a), spectra normalized for clarity).

Figure S14. UV-vis spectra (MeCN, rt) of fcX₂ (X = H, F, Cl, Br, I), at (a) ~1-2 mM and (b) ~0.1-0.2 mM (inset in (a), spectra normalized for clarity).

IR SPECTROSCOPY

Figure S15. IR spectra (ATR) for parent, non-halogenated materials.

Figure S16. IR spectra (ATR) for haloferrocenes (FcX).

Figure S17. IR spectra (ATR) for halobenzenes.

Figure S18. IR spectra (ATR) for 1,1'-dihaloferrocenes (fcX₂).

Table S1. Selected IR (ATR) absorptions and their assignments.^a

compound	C-H stretch	C-C stretch ^b	ring deformation	C-H deformation ^b	C-H out-of-plane bend	C-X stretch
FcH	3096	1408	1105	999	813	-
FcF	3103	1409 1370 1241	1105	1019 1000 928	804	1468
FcCl	3094	1410 1383 1358 1346	1166 (CpCl) 1105 (CpH)	1019 1000	812	880 ^c
FcBr	3104	1406 1378 1354 1340	1150 (CpBr) 1105 (CpH)	1052 1019 1000	841 829 812	870 ^c
FcI	3093	1403 1378 1356 1339	1138 (CpI) 1105 (CpH)	1046 1020 999	816	863 ^c 852 ^c
fcF ₂	3110	1415 1381 1364 1210	1243 ^d 1210 ^d	1022 932	835 806	1465
fcCl ₂	3103	1416 1387 1367 1351	1168	1024	846 805	891 ^c 874 ^c
fcBr ₂	3086	1406 1380 1357 1340	1149	1023 1005	841 816 802	877 ^c 865 ^c
fcI ₂	3098	1403 1379 1345	1143	1020	822	864 ^c

^a Assignments aided using calculated IR spectra. ^b C–C stretch/C–H deformations in substituted ferrocenes often encompass partial C–X bond stretching. ^c C–X stretch combined with C–H out-of-plane bending. ^d Combined partial ring deformation/C–F stretch.

X-RAY CRYSTALLOGRAPHY

The structure of **FcF** was found to be completely disordered across a centre of symmetry, and additionally the fluorine atom was discovered to be located at multiple sites around the C₅H₄ ring (though only two sites were modelled). The structure was modelled using a single 50% occupancy orientation for the iron centre and two Cp rings that was allowed to be displaced from the centre of symmetry, along with two partial occupancy positions (of *ca.* 38 and 12% occupancy) for the fluorine atom (the occupancies of the adjacent Cp hydrogen atoms were adjusted accordingly). The geometries of the Cp rings were idealised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the non-hydrogen atoms, with the exception of the 12% occupancy fluorine atom, were refined anisotropically (the remainder were refined isotropically). As a result of this extensive disorder, none of the geometric data for this structure is reliable. In an effort to improve the structure, new crystals were grown and new data sets collected; in total three data sets were obtained from crystals from three different samples. All three data sets gave the same unit cell, and unfortunately, all of them showed exactly the same problems.

The structure of **fcCl₂** was found to have crystallography *C*₂ symmetry about an axis that passes through the iron centre and bisects the Cl1...Cl1A vector.

The crystal of **FcSO₂Ph** that was studied was found to be a two component twin in a *ca.* 67:33 ratio, with the two lattices related by the twin law [1 0 0 0 -1 0 0 0 -1]. The structure of was found to contain two crystallographically independent complexes, **FcSO₂Ph-A** and **FcSO₂Ph-B**, both shown in Fig. S4.

Crystal data for FcF: C₁₀H₉FFe, *M* = 204.02, monoclinic, *P*2₁/*n* (no. 14), *a* = 6.0054(4), *b* = 7.5812(5), *c* = 9.0629(6) Å, β = 96.034(6)°, *V* = 410.33(5) Å³, *Z* = 2 [*C*_i symmetry], *D*_c = 1.651 g cm⁻³, μ(Mo-Kα) = 1.785 mm⁻¹, *T* = 173 K, orange blocks, Agilent Xcalibur 3E diffractometer; 821 independent measured reflections (*R*_{int} = 0.0153), *F*² refinement,¹ *R*₁(obs) = 0.0383, *wR*₂(all) = 0.1024, 655 independent observed absorption-corrected reflections [|*F*_o| > 4σ(|*F*_o|)], 2θ_{max} = 56°, 97 parameters. CCDC 1419413.

Crystal data for fcF₂: C₁₀H₈F₂Fe, *M* = 222.01, monoclinic, *P*2₁/*n* (no. 14), *a* = 6.8600(4), *b* = 10.6829(5), *c* = 11.3933(6) Å, β = 106.195(5)°, *V* = 801.82(7) Å³, *Z* = 4, *D*_c = 1.839 g cm⁻³, μ(Mo-Kα) = 1.852 mm⁻¹, *T* = 173 K, orange blocks, Agilent Xcalibur 3E diffractometer; 1612

independent measured reflections ($R_{\text{int}} = 0.0228$), F^2 refinement,¹ $R_1(\text{obs}) = 0.0296$, $wR_2(\text{all}) = 0.0754$, 1359 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{\text{max}} = 56^\circ$], 119 parameters. CCDC 1419414.

*Crystal data for **fcCl₂***: $\text{C}_{10}\text{H}_8\text{Cl}_2\text{Fe}$, $M = 254.91$, monoclinic, $C2/c$ (no. 15), $a = 13.5151(9)$, $b = 7.3764(4)$, $c = 9.7375(7)$ Å, $\beta = 110.152(8)^\circ$, $V = 911.33(11)$ Å³, $Z = 4$ [C_2 symmetry], $D_c = 1.858$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 2.180$ mm⁻¹, $T = 173$ K, orange blocks, Agilent Xcalibur 3E diffractometer; 958 independent measured reflections ($R_{\text{int}} = 0.0146$), F^2 refinement,¹ $R_1(\text{obs}) = 0.0200$, $wR_2(\text{all}) = 0.0511$, 921 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{\text{max}} = 56^\circ$], 61 parameters. CCDC 1419415.

*Crystal data for **FcSO₂Ph***: $\text{C}_{16}\text{H}_{14}\text{FeO}_2\text{S}$, $M = 326.18$, monoclinic, $P2_1/c$ (no. 14), $a = 12.7625(2)$, $b = 10.8996(2)$, $c = 19.5864(6)$ Å, $\beta = 90.0276(19)^\circ$, $V = 2724.60(10)$ Å³, $Z = 8$ [two independent complexes], $D_c = 1.590$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.257$ mm⁻¹, $T = 173$ K, orange blocks, Agilent Xcalibur 3E diffractometer; 5712 independent measured reflections ($R_{\text{int}} = 0.0230$), F^2 refinement,¹ $R_1(\text{obs}) = 0.0289$, $wR_2(\text{all}) = 0.0614$, 5275 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{\text{max}} = 56^\circ$], 362 parameters. CCDC 1419416.

Figure S19. The crystal structure of **FcF** (50% probability ellipsoids).

Figure S20. The crystal structure of **fcF₂** (50% probability ellipsoids).

Figure S21. The crystal structure of the C_2 -symmetric complex **FeCl₂** (50% probability ellipsoids). The C_2 axis passes through the iron centre and bisects the Cl1...Cl1A vector.

Figure S22. The crystal structure of **FcSO₂Ph** showing the two independent complexes **FcSO₂Ph-A** and **FcSO₂Ph-B** (50% probability ellipsoids).

REFERENCES

1. (a) *SHELXTL*, Bruker AXS, Madison, WI; (b) *SHELX-2013*, <http://shelx.uni-ac.gwdg.de/SHELX/index.php>.