Supplementary Information for: Isolation and electronic structures of derivatized manganocene, ferrocene and cobaltocene anions

Conrad A. P. Goodwin,1,2 Marcus J. Giansiracusa,1 Samuel M. Greer,2,3,4 Hannah M. Nicholas,1 Peter Evans,1 Michele Vonci,1 Stephen Hill,3,5 Nicholas F. Chilton,1,* David P. Mills1,*

Affiliations:

1Department of Chemistry, School of Natural Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK.

2Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

3National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA.

4Department of Chemistry & Biochemistry, Florida State University, Tallahassee, FL 32306, USA.

5Department of Physics, Florida State University, Tallahassee, FL 32306, USA.

*Correspondence to: nicholas.chilton@manchester.ac.uk; david.mills@manchester.ac.uk.
## Contents

1. Synthesis .................................................. 3
2. Crystallography ........................................... 9
3. Molecular structures of 1-7, and [K(2,2,2-crypt)][Cp⁷⁺] (8) .... 13
4. NMR spectra of 3-6 ........................................ 18
5. Decomposition of 2 studied by \(^1\)H NMR spectroscopy at room temperature ..... 25
6. UV-Vis-nIR spectra of 1-6 ................................. 27
7. ATR-IR spectra of 3-6 ...................................... 31
8. Raman spectra of 4-6 ....................................... 34
9. Cyclic voltammetry measurements .......................... 37
   9.1 Full scans of 1-3 ....................................... 40
   9.2 Investigations of [(Cp*)₂Fe], FeH, and 8 ............... 43
   9.3 Peak-isolation, and scan-rate dependent measurements of 1-3, and FeH⁺⁸⁺ calibrations .............................................. 49
10. Electronic Structure ......................................... 64
11. \(^{57}\)Fe Mössbauer spectroscopy of 2 and 5 ............... 86
12. EPR spectroscopy .......................................... 89
13. References ................................................. 98
1. Synthesis

**General.**

All syntheses and manipulations were conducted under argon with rigorous exclusion of oxygen and water using Schlenk line and glove box techniques. THF and hexane were purged with Nitrogen (BOC), passed through columns containing activated alumina and molecular sieves, stored over K mirrors (hexane) or 4 Å molecular sieves (THF) and degassed before use. DME was dried by refluxing over potassium and was stored over 4 Å molecular sieves and degassed before use. C₆D₆ and C₄D₈O for NMR spectroscopy were dried by refluxing over K, and both were vacuum transferred then degassed by three freeze-pump-thaw cycles before use. 2.2.2-cryptand was dried under vacuum for 4 hours, and stored in a glovebox before use. Anhydrous MCl₂ (M = Mn, Fe or Co) were purchased from Alfa Aesar and were used as received. KCp₃ and KC₆ were prepared according to literature methods.¹ ¹H (400 or 500 MHz) and ¹³C{¹H} (100 MHz and 125 MHz) NMR spectra were obtained on an Avance III 400 MHz or 500 MHz spectrometer at 298 K with 5 mm BBO Prodigy probes. These were referenced to the solvent used, or to external TMS (¹H, ¹³C), UV-Vis-NIR spectroscopy was performed on samples in Youngs tap-appended 10 mm pathlength quartz cuvettes on an Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer from 175 – 3300 nm. ATR-Fourier Transform Infra-Red (ATR-FTIR) spectra were recorded as microcrystalline powders using a Bruker Tensor 27 spectrometer. Raman spectra were recorded on crystalline samples pressed between two quartz slides sealed with vacuum grease using a XploRA+ PLUS Horiba Scientific spectrometer. Cyclic voltammetry was performed using a Metrohm µAUTOLABIII. Elemental analyses were performed by Mrs Anne Davies and Mr Martin Jennings at The University of Manchester, UK.

**Synthesis of 1-8**

[(Cp₃)₂Mn] (1): In a modification of published procedures,⁴ THF (20 mL) was added to a pre-cooled (-78 °C) mixture of MnCl₂ (0.378 g, 3.0 mmol) and KCp₃ (1.635 g, 6.0 mmol) in a grease-free Teflon stoppered vessel (Rotaflo), then allowed to warm slowly to room temperature. As the mixture warmed the solution slowly turned bright yellow. The mixture was heated at 80 °C for 16 hrs, which produced
a bright yellow solution with a pale precipitate. The mixture was cooled, and the volatiles were removed in vacuo to afford a flowing yellow powder. Hexane (30 mL) was added to the powder and heated at 80 °C for 3 hrs, cooled to room temperature, and filtered away from pale solids. The solution was concentrated to ~1.5 mL and stored at 5 °C for 16 hrs, giving 1 as large yellow plates (1.020 g, 65%). Analytical data was in agreement with those previously reported.

\[ [(\text{Cp}^\text{m})_2\text{Fe}] \ (2): \text{In a modification of published procedures}\,^5, \text{THF (20 mL) was added to a pre-cooled (-78 °C) mixture of FeCl}_2 (0.317 g, 2.5 mmol) and KCp^\text{m} (1.363 g, 5.0 mmol) in a grease-free Teflon stoppered vessel (Rotaflo), then allowed to warm slowly to room temperature. As the mixture warmed the solution slowly turned ruby red. The mixture was heated at 80 °C for 16 hrs, which produced an intense red solution with a pale precipitate. The mixture was cooled, and the volatiles were removed in vacuo to afford a flowing red powder. Hexane (30 mL) was added to the powder and heated at 80 °C for 3 hrs, cooled to room temperature, and filtered away from pale solids. The solution was concentrated to ~1 mL and stored at 5 °C for 16 hrs, giving 2 as large red cubes (0.888 g, 68%). Analytical data was in agreement with those previously reported.\]

\[ [(\text{Cp}^\text{m})_2\text{Co}\cdot\text{C}_6\text{H}_{14}) \ (3\cdot\text{C}_6\text{H}_{14}): \text{THF (20 mL) was added to a pre-cooled (-78 °C) mixture of CoCl}_2 (0.390 g, 3.0 mmol) and KCp^\text{m} (1.635 g, 6.0 mmol) in a grease-free Teflon stoppered vessel (Rotaflo), then allowed to warm slowly to room temperature. As the mixture warmed the solution slowly turned dark brown. The mixture was heated at 80 °C for 16 hrs, which produced dark brown solution with a pale precipitate. The mixture was cooled, and the volatiles were removed in vacuo to afford a brown solid. Hexane (30 mL) was added, and the mixture heated at 80 °C for 3 hrs, cooled to room temperature, and filtered away from pale solids. The solution was concentrated to ~1.5 mL and stored at 5 °C for 16 hrs, giving 3·(C\_6H\_14) as large brown plates (1.076 g, 59%). Anal. Calcd (%) for C\_34H\_58Co·C\_6H\_14: C, 78.51; H, 11.86. Found: C, 79.36; H, 11.82. \]^1H NMR (C\_6D\_6, 400 or 500 MHz, 298 K): δ = 3.50 (br. s), 3.67 (br. s). \]^13C\{\^1H\} NMR (C\_6D\_6, 125 MHz) No peaks were observed. FTIR (ATR, microcrystalline): \^v = 402 (w), 424 (w), 436 (w), 453 (w), 477 (w), 494 (w), 504 (w), 524 (m), 538 (w), 549 (w), 565 (w), 598 (m), 612 (w), 620 (w), 632 (w), 640 (w), 659 (w), 675 (w), 693 (w), 702 (w), 708 (w), 718 (w), 724
H NMR spectroscopy was in agreement with earlier reports.6,7 [K(2.2.2-crypt)]2[(Cp^nn)2Mn][Cp^nn] (4): THF (2 mL) was added to a mixture of 1 (0.365 g, 0.7 mmol), and 2.2.2-cryptand (0.264 g, 0.7 mmol) to give a bright yellow solution. This solution was added rapidly to a pre-cooled (-78 °C) Schlenk vessel containing KC8 (0.095 g, 0.7 mmol) and a Teflon-coated stirrer bar. The slurry was stirred rapidly and allowed to warm to -40 °C over the course of 10 minutes, during which time the colour changed from bright yellow to dark orange. The mixture was stirred at -40 °C for 10 minutes, and then allowed to settle for a further 5 minutes. The orange solution was filtered cold to a pre-cooled (-40 °C) vessel, and concentrated at this temperature to ca. 1 mL. Hexane (4 mL) was carefully layered on top, which caused some crystals to immediately form. The vessel and cold bath were transferred to a freezer (-25 °C), to warm slowly to -25 °C overnight. Orange plates of 4 were isolated by cold filtration (0.189 g, 16%). Anal. Calcd (%) for C87H159O12N4K2Mn·C4H8O: C, 65.90; H, 10.15; N, 3.38. Found: C, 65.99; H, 10.59; N, 3.27. 1H NMR (C4D8O, 400 MHz, 298 K): δ = 0.91, 1.00, 1.12, 2.29, 2.48, 7.13, 7.29. 13C{1H} NMR (C4D8O, 125 MHz) 28.35, 30.52, 57.44, 70.51, 71.87, 129.13, 129.93. FTIR (ATR, microcrystalline): ν̃ = 418 (w), 434 (w), 447 (w), 453 (w), 467 (w), 481 (w), 489 (w), 508 (w), 524 (m), 545 (w), 565 (w), 598 (w), 608 (w), 620 (w), 630 (w), 649 (w), 665 (w), 689 (w), 702 (w), 714 (w), 722 (w), 753 (w), 777 (w), 793 (w), 802 (w), 830 (w), 850 (w), 863 (w), 873 (w), 932 (m), 950 (s), 983 (w), 995 (w), 1026 (w), 1077 (s), 1103 (vs), 1132 (m), 1177 (w), 1195 (w), 1201 (w), 1234 (m), 1260 (m), 1297 (m), 1315 (w), 1328 (w), 1354 (s), 1385 (w), 1409 (w), 1446 (m), 1458 (w), 1477 (m), 1509 (w), 1540 (w), 1577 (w), 1589 (w), 1632 (vw), 1674 (vw), 1697 (w), 1730 (vw), 1752 (vw), 1781 (vw), 1819 (w), 1846 (w), 1858 (w), 1872 (w), 1893 (w), 1909 (w), 1931 (w), 1940 (w), 1960 (w), 1976 (m), 2009 (w), 2035 (w), 2048 (w), 2068 (w), 2729 (vw), 2743
(vw), 2759 (w), 2815 (w), 2882 (m), 2947 (w), 3016 (w), 3039 (vw), 3049 (vw), 3057 (w), 3067 (w), 3076 (w), 3096 (vw), 3104 (vw), 3114 (vw), 3123 (vw). On one occasion a few crystals of 8 were identified in a second crop of crystalline 4.

\[ \text{[K(2.2.2-crypt)][(Cp^w)_2Fe]} \] (5): THF (2 mL) was added to a mixture of 2 (0.366 g, 0.7 mmol), and 2.2.2-cryptand (0.264 g, 0.7 mmol) to give a bright ruby-red solution. This solution was added rapidly to a pre-cooled (-78 °C) Schlenk vessel containing KC₈ (0.095 g, 0.7 mmol) and a Teflon-coated stirrer bar. The slurry was stirred rapidly and allowed to warm to -40 °C over the course of 10 minutes, during which time the colour changed from ruby-red to dark brown. The mixture was stirred at -40 °C for 10 minutes, and then allowed to settle for a further 5 minutes. The brown solution was filtered cold to a pre-cooled (-40 °C) vessel, and concentrated at this temperature to ca. 1 mL. Hexane (4 mL) was carefully layered on top, which caused some crystals to immediately form. The vessel and cold bath were transferred to a freezer (-25 °C), to warm slowly to -25 °C overnight. Brown blocks of 5 were isolated by cold filtration (0.140 g, 21%). Anal. Calcd (%) for C₉₂H₉₄O₆N₂KFe: C, 66.57; H, 10.10; N, 2.99. Found: C, 66.60; H, 10.47; N, 3.03. ¹H NMR (CD₃O, 400 MHz, 298 K): \( \delta = -8.12 \) (s, 18H, FWHM = 186 Hz, C₅H₂(CMe₃)), -2.70 (s, 36H, FWHM = 423 Hz, (C₅H₂(CMe₃)₂), 2.28 - 2.78 (36H, 2.2.2-cryptand), Cp^w.CH not observed. ¹³C{¹H} NMR (CD₃O, 125 MHz) 35.76, 55.45, 57.43, 69.59, 70.51, 71.85, 72.96, 126.19, 127.00. FTIR (ATR, microcrystalline): \( \tilde{\nu} \) = 406 (m), 414 (w), 428 (m), 447 (w), 459 (w), 467 (w), 483 (w), 524 (m), 563 (m), 591 (w), 661 (w), 667 (w), 753 (m), 777 (m), 791 (m), 832 (m), 850 (w), 930 (m), 950 (s), 983 (m), 995 (m), 1026 (m), 1077 (s), 1085 (s), 1103 (vs), 1132 (s), 1195 (w), 1234 (m), 1260 (m), 1275 (w), 1295 (m), 1328 (w), 1352 (m), 1385 (m), 1446 (m), 1458 (m), 1477 (m), 1509 (w), 1542 (w), 1575 (w), 1591 (w), 1630 (w), 1644 (w), 1674 (w), 1699 (w), 1719 (w), 1734 (w), 1754 (w), 1781 (w), 1791 (w), 1821 (w), 1836 (w), 1852 (w), 1878 (w), 1895 (w), 1905 (w), 1915 (w), 1938 (w), 1962 (w), 1978 (w), 2009 (w), 2035 (w), 2046 (w), 2068 (w), 2164 (w), 2168 (w), 2239 (w), 2280 (w), 2317 (m), 2341 (w), 2372 (w), 2815 (m), 2882 (m), 2949 (m), 3018 (w), 3049 (w), 3059 (w), 3067 (w), 3076 (w), 3086 (w), 3096 (w), 3104 (w), 3114 (w), 3123 (w).
[K(2.2.2-crypt)][(Cp")₄]Co (6): THF (2 mL) was added to a mixture of \(\text{3·}(\text{C}_6\text{H}_{14})\) (0.428 g, 0.7 mmol), and 2.2.2-cryptand (0.264 g, 0.7 mmol) to give a brown solution. This solution was added rapidly to a pre-cooled (-78 °C) Schlenk vessel containing KC₈ (0.095 g, 0.7 mmol) and a Teflon-coated stirrer bar. The slurry was stirred rapidly and allowed to warm to -40 °C over the course of 10 minutes, during which time the brown colour developed a red hue. The mixture was stirred at -40 °C for 10 minutes, and then allowed to settle for a further 5 minutes. The brown solution was filtered cold to a pre-cooled (-40 °C) vessel, and concentrated at this temperature to ca. 1 mL. Hexane (4 mL) was carefully layered on top, which caused some crystals to immediately form. The vessel and cold bath were transferred to a freezer (-25 °C), to warm slowly to -25 °C overnight. Brown blocks of 6 were isolated by cold filtration (0.456 g, 66%). Anal. Calcd (%) for \(\text{C}_{52}\text{H}_{94}\text{O}_{6}\text{N}_{2}\text{KCo·(C}_6\text{H}_{14})_{0.5}\): C, 67.10; H, 10.34; N, 2.85. Found: C, 66.71; H, 10.51; N, 3.03. \(^1\)H NMR (\(\text{C}_4\text{D}_8\text{O}\), 400 MHz, 298 K): \(\delta = 2.35\) (s), 3.46 (s), 10.18 (br. s, FWHM = 367 Hz), 19.50 (br. s, FWHM = 185 Hz), 24.09 (br. s, FWHM = 159 Hz). \(^{13}\)C\(^{\{1\}H}\) NMR (\(\text{C}_4\text{D}_8\text{O}\), 125 MHz) 33.71, 33.96, 35.54, 53.46, 56.37, 69.43, 70.19, 70.76, 125.23, 128.10, 128.82. FTIR (ATR, microcrystalline): \(\tilde{\nu} = 408\) (m), 430 (m), 436 (m), 445 (w), 453 (w), 473 (w), 483 (w), 512 (w), 524 (m), 540 (w), 549 (w), 561 (w), 571 (w), 594 (w), 616 (w), 630 (w), 644 (w), 661 (w), 673 (w), 689 (w), 702 (w), 710 (w), 724 (w), 753 (m), 777 (m), 791 (m), 820 (w), 830 (w), 850 (w), 873 (w), 881 (w), 930 (m), 950 (s), 995 (m), 1026 (w), 1077 (s), 1085 (s), 1101 (vs), 1130 (m), 1152 (w), 1169 (w), 1195 (w), 1201 (w), 1232 (s), 1260 (s), 1275 (w), 1295 (m), 1328 (w), 1352 (s), 1385 (m), 1411 (w), 1444 (m), 1458 (m), 1477 (m), 1509 (w), 1540 (w), 1575 (w), 1589 (w), 1636 (w), 1646 (w), 1672 (w), 1683 (w), 1697 (w), 1730 (w), 1781 (w), 1791 (w), 1819 (w), 1854 (w), 1872 (w), 1885 (w), 1903 (w), 1915 (w), 1929 (w), 1940 (w), 1962 (w), 1976 (m), 2009 (m), 2023 (w), 2033 (m), 2046 (w), 2072 (w), 2095 (vw), 2101 (vw), 2123 (w), 2137 (w), 2148 (w), 2154 (w), 2174 (vw), 2182 (vw), 2211 (vw), 2223 (vw), 2233 (vw), 2241 (vw), 2252 (vw), 2266 (vw), 2276 (vw), 2290 (vw), 2303 (vw), 2680 (vw), 2694 (w), 2715 (w), 2749 (w), 2764 (w), 2815 (w), 2880 (m), 2925 (m), 2947 (m), 2976 (w), 3016 (m), 3047 (w), 3057 (w), 3067 (w), 3076 (w), 3086 (w), 3094 (w), 3104 (w), 3112 (w), 3123 (w), 3131 (w). On one occasion several crystals of [K(2.2.2-crypt)\(_2\)][(Cp")₄]Co][Cp"] (7) co-crystallized with 6.
[K(2.2.2-crypt)][Cp^m] (8): KCp^m (0.273 g, 1 mmol) was slurried in THF (4 mL) in a 10 mL glass vial, and solid 2.2.2-cryptand (0.376 g, 1 mmol) was added portion wise with manual agitation of the solution. The solution gradually turned clear from the initial colourless suspension, and a very pale peach/yellow colour could be seen. The solution was filtered through a glass pipette loaded with a small piece of filter paper into another 10 mL scintillation vial, and stored at -35 °C overnight, which afforded several colourless crystals of 8. Due to the low yield, only the identity of 8 was confirmed via single crystal X-ray diffraction. As we only sought to establish that the [Cp^m] anion could be outer-sphere for electrochemical experiments (vide infra), no attempt was made to optimize the yield or determine purity.
2. Crystallography

The crystal data for complexes 1-8 are compiled in Supplementary Tables 1-3. Datasets for 1-3 have been reported previously.\textsuperscript{4,5,7} Crystals of 1-4 and 6-8 were examined with a Rigaku XtalLAB AFC11 diffractometer, equipped with CCD detector and mirror-monochromated Cu Kα radiation ($\lambda = 1.54178$ Å) or mirror-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystals of 5 were examined using an Oxford Diffraction Supernova diffractometer, equipped with CCD area detector and a mirror-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Intensities were integrated from data recorded on 0.5° (1, 2, 6, 7), 0.7° (5), 0.8° (3, 4) or 1° (8) frames by $\omega$ rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. An analytical (1) or Gaussian grid face-indexed (2-8) absorption correction with a beam profile was applied through CrysAlisPro\textsuperscript{8}. The structures were solved using SHELXT\textsuperscript{9,10}; the datasets were refined by full-matrix least-squares on all unique $F^2$ values, with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; $U_{	ext{iso}}$(H) was set at 1.2 (1.5 for methyl groups) times $U_{	ext{eq}}$ of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. CrysAlisPro\textsuperscript{8} was used for control and integration, and SHELX\textsuperscript{9,10} was employed through OLEX2\textsuperscript{11} for structure solution and refinement, and also for molecular graphics. Crystallographic data for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 1951767 (1), 1951768 (2), 1951769 (3), 1951770 (4), 1951771 (5), 1951772 (6), 1951773 (7) and 1951774 (8). Copies of the data can be obtained free of charge from the CCDC via [www.ccdc.cam.ac.uk/getstructures](http://www.ccdc.cam.ac.uk/getstructures).
|             | 1          | 2          | 3          |
|-------------|------------|------------|------------|
| CCDC number | 1951767    | 1951768    | 1951769    |
| Formula     | C₃₄H₆₈Mn   | C₃₄H₆₈Fe  | C₃₄H₆₈Co(C₆H₁₄)₀.₅ |
| Fw          | 521.74     | 522.65     | 568.82     |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | P2₁/c      | P2₁/c      | P2₁/c      |
| a, Å        | 20.2442(4) | 16.4890(6) | 15.0105(4) |
| b, Å        | 17.5974(2) | 11.2307(3) | 14.1693(3) |
| c, Å        | 19.2721(3) | 17.7236(5) | 18.7143(6) |
| α, °        |            |            |            |
| β, °        | 112.443(2) | 107.283(4) | 107.100(3) |
| γ, °        |            |            |            |
| V, Å³       | 6345.6(2)  | 3133.92(18)| 3804.36(19)|
| Z           | 8          | 4          | 4          |
| ρ(calcd), g cm⁻³ | 1.092     | 1.108      | 0.993      |
| μ, mm⁻¹     | 0.435      | 3.969      | 0.471      |
| F(000)      | 2296       | 1152       | 1256       |
| Cryst size, mm | 0.38 x 0.48 x 0.58 | 0.05 x 0.18 x 0.28 | 0.11 x 0.18 x 0.42 |
| no. reflections (unique) | 36685 (11355) | 22424 (5733) | 17917, 6904 |
| R(int)      | 0.025      | 0.047      | 0.016      |
| R₁(F² > 2σ(F²)) | 0.0345 (0.0960) | 0.0612 (0.1724) | 0.0395 (0.1241) |
| S            | 1.07       | 1.06       | 1.07       |
| min./max. diff map, Å⁻³ | -0.32, 0.35 | -0.41, 1.03 | -0.43, 0.86 |

*R = \sum|Fo| - |Fc|/\sum|Fo|; \text{R}_{\text{w}} = \left[\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2\right]^{1/2}; S = \left[\sum w(Fo^2 - Fc^2)^2/(\text{no. data} - \text{no. params})\right]^{1/2} for all data.
Table 2. Crystallographic data for 4-6.

|       | 4               | 5               | 6               |
|-------|-----------------|-----------------|-----------------|
| CCDC number | 1951770         | 1951771         | 1951772         |
| Formula   | C₉₁H₁₆₇N₄O₁₃K₂Mn | C₅₂H₆₈N₄O₆KFe  | C₅₂H₆₈N₂O₆KCo  |
| Fw        | 1658.42         | 938.24          | 941.32          |
| Crystal system | Monoclinic      | Monoclinic      | Monoclinic      |
| Space group | P2₁/n           | P2₁/c           | P2₁/c           |
| a, Å      | 13.7471(3)      | 16.4355(13)     | 16.4529(6)      |
| b, Å      | 32.6921(7)      | 16.4631(19)     | 16.3213(7)      |
| c, Å      | 22.0618(4)      | 20.0365(16)     | 20.0312(7)      |
| α, °      | 105.279(2)      | 92.528(7)       | 92.950(4)       |
| β, °      | 92.28(7)        |                 |                 |
| γ, °      | 87.10(7)        |                 |                 |
| V, Å³     | 9564.6(4)       | 5416.2(9)       | 5371.9(4)       |
| Z         | 4               | 4               | 4               |
| ρcalc, g cm⁻³ | 1.152            | 1.151            | 1.164            |
| μ, mm⁻¹   | 2.356           | 0.401           | 0.443           |
| F(000)    | 3632            | 2052            | 2056            |
| Cryst size, mm | 0.07 × 0.10 × 0.14 | 0.08 × 0.10 × 0.19 | 0.05 × 0.09 × 0.13 |
| no. reflections (unique) | 39114 (17126) | 30231 (9914) | 27171 (9827) |
| Rint      | 0.077           | 0.180           | 0.119           |
| R₁(F² > 2σ(F²)) | 0.0917 (0.2586) | 0.0801 (0.1868) | 0.0546 (0.1274) |
| S         | 0.97            | 0.96            | 0.94            |
| min./max. diff map, Å⁻³ | -1.22, 0.45      | -0.60, 0.40     | -0.44, 0.43     |

\[^a\text{R} = \sum|F_o| - |F_c|/\sum|F_o|; \text{R}_W = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}; S = [\sum w(F_o^2 - F_c^2)^2/(\text{no. data} - \text{no. params})]^{0.5} \text{ for all data.}\]
Table 3. Crystallographic data for 7-8.

|                | 7                  | 8                  |
|----------------|--------------------|--------------------|
| CCDC number    | 1951773            | 1951774            |
| Formula        | C$_{91}$H$_{167}$N$_{13}$O$_{13}$K$_{2}$Mn | C$_{39}$H$_{72}$N$_{6}$O$_{3}$K |
| Fw             | 1662.41            | 721.09             |
| Crystal system | Monoclinic         | Triclinic          |
| Space group    | $P2_1/n$           | $P\bar{1}$         |
| $a$, Å         | 13.7140(3)         | 15.5407(17)        |
| $b$, Å         | 32.7193(6)         | 17.6505(16)        |
| $c$, Å         | 22.1005(5)         | 18.624(2)          |
| $\alpha$, °    | 63.484(10)         |                    |
| $\beta$, °     | 105.463(2)         | 72.496(10)         |
| $\gamma$, °    |                    | 76.511(9)          |
| V, Å$^3$       | 9557.8(4)          | 4330.1(9)          |
| Z              | 4                  | 4                  |
| $\rho_{\text{calc}}$, g cm$^{-3}$ | 1.155             | 1.106             |
| $\mu$, mm$^{-1}$ | 0.325             | 1.425             |
| $F(000)$       | 3640               | 1584               |
| Cryst size, mm | 0.10 x 0.12 x 0.21 | 0.07 x 0.11 x 0.23 |
| no. reflections (unique) | 61610 (17510) | 43539 (15269) |
| $R_{\text{int}}$ | 0.035             | 0.135              |
| $R_1$(wR$_2$) ($F^2 > 2\sigma(F^2)$) | 0.0369 (0.0915) | 0.0798 (0.2460) |
| $S$            | 1.02               | 0.96               |
| min./max. diff map, Å$^3$ | -0.34, 0.63       | -0.61, 0.63       |

$^a$ $R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|; \; R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}; \; S = [\Sigma w(F_o^2 - F_c^2)^2/(\text{no. data} - \text{no. params})]^{0.5}$ for all data.
3. Molecular structures of 1-7, and [K(2.2.2-crypt)][Cp^m] (8)

**Fig. 1.** Molecular structure of 1 (CCDC number 1951767 and also refcode BUBGUB) with selective atom labelling (C = grey, Mn = purple). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Mn(1)···Cp^m_centroid(1) = 2.111(2) Å, Mn(1)···Cp^m_centroid(2) = 2.100(2) Å, Cp^m_centroid(1)···Mn(1)···Cp^m_centroid(2) = 169.63(3)°.

**Fig. 2.** Molecular structure of 2 (CCDC number 1951768 and also refcode UZONUT) with selective atom labelling (C = grey, Fe = orange). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Fe(1)···Cp^m_centroid(1) = 1.716(2) Å, Fe(1)···Cp^m_centroid(2) = 1.715(2) Å, Cp^m_centroid(1)···Fe(1)···Cp^m_centroid(2) = 174.91(8)°.
Fig. 3. Molecular structure of 3 (CCDC number 1951769 and also refcode VOTZOW)\textsuperscript{7} with selective atom labelling (C = grey, Co = dark blue). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Co(1)···Cp\textsuperscript{iii} centroid(1) = 1.801(2) Å, Co(1)···Cp\textsuperscript{iii} centroid(2) = 1.802(2) Å, Cp\textsuperscript{iii} centroid(1)···Co(1)···Cp\textsuperscript{iii} centroid(2) = 174.77(4)°.

Fig. 4. Molecular structure of 4 (CCDC number 1951770) with selective atom labelling (C = grey, K = violet, Mn = purple, N = blue, O = red). Displacement ellipsoids set at 30 % probability level and hydrogen atoms, second [K(2.2.2-crypt)]\textsuperscript{+} cation, THF molecule, and a [Cp\textsuperscript{iii}]\textsuperscript{−} anion removed for clarity (see Supplementary Fig. 5 below). Mn(1)···Cp\textsuperscript{iii} centroid(1) = 1.749(2) Å, Mn(1)···Cp\textsuperscript{iii} centroid(2) = 1.750(2) Å, Cp\textsuperscript{iii} centroid(1)···Mn(1)···Cp\textsuperscript{iii} centroid(2) = 174.68(9)°.
Fig. 5. Molecular structure of 4 (CCDC number 1951770) with selective atom labelling (C = grey, K = violet, Mn = purple, N = blue, O = red). Displacement ellipsoids set at 30 % probability level. Hydrogen atoms, and a THF molecule are omitted for clarity.

Fig. 6. Molecular structure of 5 (CCDC number 1951771) with selective atom labelling (C = grey, K = violet, Fe = orange, N = blue, O = red). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Fe(1)···Cp^m_centroid(1) = 2.065(3) Å, Fe(1)···Cp^m_centroid(2) = 2.062(3) Å, Cp^m_centroid(1)···Fe(1)···Cp^m_centroid(2) = 169.38(11).
**Fig. 7.** Molecular structure of 6 (CCDC number 1951772) with selective atom labelling (C = grey, K = violet, Co = dark blue, N = blue, O = red). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity. Co(1)···Cp^{centroid}(1) = 1.933(2) Å, Co(1)···Cp^{centroid}(2) = 1.983(2), C^{centroid}(1)···Co(1)···C^{centroid}(2) = 176.04(4).

**Fig. 8.** Molecular structure of 7 (CCDC number 1951773) with selective atom labelling (C = grey, K = violet, Co = dark blue, N = blue, O = red). Displacement ellipsoids set at 30 % probability level. Hydrogen atoms, and a THF molecule are omitted for clarity.
**Fig. 9.** Molecular structure of 8 (CCDC number 1951774) with selective atom labelling (C = grey, K = violet, N = blue, O = red). Displacement ellipsoids set at 30 % probability level and hydrogen atoms are omitted for clarity.
4. NMR spectra of 3-6

The \(^1\)H and \(^{13}\)C\(^{\text{\footnotesize{1\text{H}}}}\) NMR spectra of 3 in C\(_6\)D\(_6\) could not be fully assigned due to paramagnetic broadening. Although the \(^1\)H NMR spectrum of 4 at 240 K in C\(_4\)D\(_8\)O contains signals in the diamagnetic region that are consistent with a low spin 18e\(^-\) system, its rapid decomposition to 1 and other paramagnetic products at 298 K thwarted confident assignment. The \(^1\)H and \(^{13}\)C\(^{\text{\footnotesize{1\text{H}}}}\) NMR spectra of 5 and 6 at 240 K in C\(_4\)D\(_8\)O could not be interpreted due to significant paramagnetic broadening; these samples were rapidly raised in temperature to 298 K and \(^1\)H NMR spectra were collected that could be tentatively assigned, but thermal decomposition precluded the collection of \(^{13}\)C\(^{\text{\footnotesize{1\text{H}}}}\) NMR spectra at this temperature.

Fig. 10. \(^1\)H NMR spectrum of complex 3 in C\(_6\)D\(_6\), zoomed in the region -29 to 20 ppm. Solvent residual denoted.
Fig. 11. \(^1\)H NMR spectrum of complex 3 in C\(_6\)D\(_6\) centred at +150 ppm. Solvent residual denoted.

Fig. 12. \(^1\)H NMR spectrum of complex 3 in C\(_6\)D\(_6\) centred at -150 ppm. Solvent residual denoted.
**Fig. 13.** $^{13}$C-$^1$H NMR spectrum of complex 3 in C$_6$D$_6$. Solvent residual denoted.

**Fig. 14.** Left: $^1$H NMR spectrum of complex 4 in C$_4$D$_8$O, zoomed in the region -2 to 9 ppm. Regardless of containment method, the sample began to rapidly evolve gas, decolorize from dark red to pale yellow, and precipitate pale insoluble material once it was warmed from 0°C to room temperature; Right: A side-by-side comparison of a fresh solution of 4 in C$_4$D$_8$O at 0°C, and an aged sample after 20 minutes at room temperature.
Fig. 15. $^1$H NMR spectrum of complex 5 in C$_4$D$_8$O, zoomed in the region -8.5 to 5 ppm. Solvent residual denoted. * denotes residual 2 impurity. Collected at 400 MHz, unlike other $^1$H spectra for 5.

Fig. 16. $^1$H NMR spectrum of complex 5 in C$_4$D$_8$O centred at +150 ppm. Solvent residual denoted.
Fig. 17. $^1$H NMR spectrum of complex 5 in C$_4$D$_8$O centred at -150 ppm. Solvent residual denoted.

Fig. 18. $^{13}$C($^1$H) NMR spectrum of complex 5 in C$_4$D$_8$O. Solvent residual denoted.
**Fig. 19.** $^1$H NMR spectrum of complex 6 in C$_4$D$_8$O, zoomed in the region -10 to 8 ppm. Solvent residual denoted. * denotes residual 2.2.2-cryptand impurity.

**Fig. 20.** $^1$H NMR spectrum of complex 6 in C$_4$D$_8$O centred at +150 ppm. Solvent residual denoted.
Fig. 21. $^1$H NMR spectrum of complex 6 in C$_4$D$_8$O centred at -150 ppm. Solvent residual denoted.

Fig. 22. $^{13}$C($^1$H) NMR spectrum of complex 6 in C$_4$D$_8$O. Solvent residual denoted.
5. Decomposition of 2 studied by $^1$H NMR spectroscopy at room temperature

![NMR spectrum comparison and image of NMR sample](image)

**Fig. 23.** Left: A comparison of the $^1$H NMR spectrum of 5 at $T = 0$, and $T = 110$ minutes at room temperature in C$_4$D$_8$O collected at 400 MHz for both spectra. The arrow denotes the region associated with 2, and shows that there is a modest ingrowth as 5 converts to 2 over time at room temperature. The significant broadening of most of the peaks is due to the deposition of insoluble dark material; Right: A photograph of the NMR sample at the conclusion of the experiment.
Fig. 24. $^1$H NMR spectrum of 5 after 7 days at room temperature in C$_4$D$_8$O. Peaks corresponding to 5 are completely absent, and significant ingrowth of 2 is apparent along with new paramagnetic species that we have not been able to crystallize or identify. Exposure to air appears to decompose the new paramagnetic species and allows the recrystallization of 2 (confirmed by unit cell determination) from the mixture by slow evaporation of the solvent.
6. UV-Vis-nIR spectra of 1-6

![UV-Vis-nIR spectra of 1-6](image)

**Fig. 25.** UV-vis spectra of 1-3 between 13,000 – 47,400 cm⁻¹ (770 – 211 nm) recorded as a 0.19 mM solution in THF for all complexes. An empirical correction has been applied to the baseline.

![UV-Vis-nIR spectra of complexes 4-6](image)

**Fig. 26.** UV-vis spectra of complexes 4-6 between 13,000 – 44,000 cm⁻¹ (770 – 227 nm) recorded as a 0.20 mM solution in THF for 4 and 6; and 0.21 mM for 5. An empirical correction has been applied to the baseline.
**Fig. 27.** UV-vis spectrum of complex 1 between 13,000 – 42,000 cm\(^{-1}\) (770 – 238 nm) recorded as a 0.19 mM solution in THF. An empirical correction has been applied to the baseline.

**Fig. 28.** UV-vis spectrum of complex 2 between 13,000 – 42,000 cm\(^{-1}\) (770 – 238 nm) recorded as a 0.19 mM solution in THF. An empirical correction has been applied to the baseline.
Fig. 29. UV-vis spectrum of complex 3 between 13,000 – 47,400 cm\(^{-1}\) (770 – 211 nm) recorded as a 0.19 mM solution in THF. An empirical correction has been applied to the baseline.

Fig. 30. UV-vis spectrum of complex 4 between 13,000 – 42,000 cm\(^{-1}\) (770 – 238 nm) recorded as a 0.20 mM solution in THF. An empirical correction has been applied to the baseline.
**Fig. 31.** UV-vis spectrum of complex 5 between 13,000 – 42,000 cm$^{-1}$ (770 – 238 nm) recorded as a 0.21 mM solution in THF. An empirical correction has been applied to the baseline.

**Fig. 32.** UV-vis spectrum of complex 6 between 13,000 – 44,000 cm$^{-1}$ (770 – 227 nm) recorded as a 0.20 mM solution in THF. An empirical correction has been applied to the baseline.
7. ATR-IR spectra for 3-6

Fig. 33. ATR-IR spectra of complexes 4-6, with insert (1,600 – 400 cm\(^{-1}\)) highlighting the superimposable fingerprint regions. Recorded as microcrystalline powders.

Fig. 34. ATR-IR spectrum of complex 3, recorded as a microcrystalline powder.
Fig. 35. ATR-IR spectrum of complex 4, recorded as a microcrystalline powder.

Fig. 36. ATR-IR spectrum of complex 5, recorded as a microcrystalline powder.
Fig. 37. ATR-IR spectrum of complex 6, recorded as a microcrystalline powder.
8. Raman spectra for 4-6

Fig. 38. Raman spectrum of 4 (solid sample, quartz slide). The spectrum was acquired using a 638 nm red diode laser, 1200 g/mm grating, 10 s exposure and 10 accumulations.

Fig. 39. Raman spectrum of 5 (solid sample, quartz slide). The spectrum was acquired using a 638 nm red diode laser, 1200 g/mm grating, 5 s exposure and 2 accumulations.
Fig. 40. Raman spectrum of 6 (solid sample, quartz slide). The spectrum was acquired using a 638 nm red diode laser, 1200 g/mm grating, 5 s exposure and 2 accumulations.

Fig. 41. Raman spectrum of \([\text{Cp}_2\text{Co}][\text{PF}_6]\) (solid sample, quartz slide). The spectrum was acquired using a 638 nm red diode laser, 1200 g/mm grating, 10 s exposure and 10 accumulations.
Fig. 42. Raman spectrum of a blank quartz slide. The spectrum was acquired using a 638 nm red diode laser, 1200 g/mm grating, 10 s exposure and 10 accumulations.
9. Cyclic voltammetry measurements

All electrochemical measurements are quoted vs. the FcH+/FcH (henceforth FcH+/0 for brevity) couple for consistency with convention in the literature, however we note that the [Cp*₂Fe]⁺/0 couple would be preferable for future studies of such systems, as the redox peak positions are essentially invariant to the solvent used, and also to temperature (see Supplementary Fig. 47). Furthermore, convention dictates that processes are described in terms of reduction events, e.g. FcH+/0.

Before deciding to use DME as our solvent for cyclic voltammetry experiments, we first tried THF as the solvent. Preliminary scans with 2 showed larger than expected baseline current density, as well as irreproducible and poorly resolved peaks (Supplementary Fig. S43). This was despite repeated purification (boiling over K metal followed by vacuum distillation) of the solvent, while the electrolyte was the same as used for all experiments including the later measurements in DME. We also settled upon a routine measurement temperature of -50 °C, which was manually controlled and checked. Measurements at room temperature never showed resolved reduction peaks in either THF or DME, thus lower temperatures were needed to obviate decomposition pathways that could occur on the electrochemical time scale. A search of the literature showed that -50 °C was a sensible starting point. Furthermore, colder temperatures lead to rapid precipitation of the electrolyte out of the DME solvent.
Fig. 43. Cyclic voltammogram of 2 in THF (1 mM) with ["Bu₄N][BF₄] (0.5 M) electrolyte. The collection temperature and scan rate are denoted for each scan. Arrows indicate scan direction. Regardless of temperature or scan rate, we could not observe the [(Cp₃ttt)₂Fe]⁰⁻ couple, and the baseline current is less uniform than in following measurements conducted in DME. Additionally, the window is limited to smaller anodic potentials than DME, so the [(Cp₃ttt)₂Fe]²⁺⁻ couple was also not be observed.

Fig. 44. Calibration cyclic voltammogram of 2 in THF (1 mM), with ["Bu₄N][BF₄] (0.5 M) electrolyte and a crystal of FeH, at -50 °C. Collected at 200 mV/s.
We initially assessed the batch of electrolyte and solvent (DME henceforth) we used for all experiments; scans to the limits of the solvent window induced minor decomposition, evidenced on the second scan by spurious peaks at -1.62 and 0.38 V (vs FcH\(^{+0}\), Supplementary Fig. S45), thus only the first scan was used in all instances.

![Cyclic voltammogram of \([n^\text{Bu}_4\text{N}][\text{BF}_4]\) (0.5 M) in DME (1 mM), at -50 °C. Collected at 200 mV/s. Peaks indicated (p1 and p2) appear on second scan only.](image)

**Fig. S45.** Cyclic voltammogram of \([n^\text{Bu}_4\text{N}][\text{BF}_4]\) (0.5 M) in DME (1 mM), at -50 °C. Collected at 200 mV/s. Peaks indicated (p1 and p2) appear on second scan only.
9.1 Full scans of 1-3

A well-defined reversible oxidation process was seen at cathodic potentials vs FeH^+/0 for 2 (at -0.25 V, Supplementary Fig. 47) that compares well with the literature value reported for the [(Cp^III)Fe]/[(Cp^II)2Fe] couple (-0.38 V vs FeH^+/0) in DCM, 0.1 M [N^Bu4][PF6] \textsuperscript{17,18}. As expected, the six inductively donating 'Bu groups in 2 shift redox events to negative potentials vs FeH^+/0 (0.00 V by definition). Intrigued by the electrochemical stability of the Cp^III complexes 1-3 (Fig. 1 in main text, and Supplementary Fig. 46-48, 55-67), and the reported instability of [Cp^*2Fe]^2+ in organic solvents\textsuperscript{19}, we assessed whether 1-3 could also be doubly-oxidized. Complexes 1 and 2 exhibited additional quasi-reversible oxidation events at potentials more anodic (E_\text{1}\textsubscript{1/2} = 0.71 V, 1; 1.34, 2 vs FeH^+/0) than those for the established [(Cp^III)2M]/[(Cp^II)2M] couples, whilst 3 showed only a small irreversible oxidation wave (E_p1 = 0.54 V vs FeH^+/0) that we attributed to decomposition. We assign these redox couples in 1 and 2 to the reversible formation of [(Cp^III)2M]^2+: we have not attempted to synthesise these doubly cationic metallocenium di-cations.

![Cyclic voltammogram of 1 in DME (1 mM) with [N^Bu4][BF4] (0.5 M) electrolyte at -50 °C. Collected at 200 mV/s. Arrows indicate scan direction, black dot denotes suspected oxidation of [Cp^III], the * denotes the reduction peak from a second scan.](image-url)
The peaks $E_{p1}$ (-3.26 V) and $E_{p2}$ (-2.50 V) are labelled at the point of peak current density for these processes. Due to the significant separation ($\Delta E_{\text{ox/red}} = 760$ mV) it is unlikely that they represent a simple, outer sphere electron transfer as is the hallmark of metallocene chemistry. We think that given the persistent presence of additional [K(2.2.2-crypt)][Cp]$^\text{III}$ in samples of 4, that the separation between these peaks is due to a reorganization process involving one or both of the Cp$^\text{III}$ rings. Due to experimental limitations we have not been able to study the mechanistic aspects of this (i.e. temperature dependence of peak separation), however given that 4 is the most thermally sensitive of these metallocenates, such a future study could lead to evidence for the decomposition mechanism.

![Cyclic voltammogram](image)

**Fig. 47.** Cyclic voltammogram of 2 in DME (1 mM) with [$^\text{o}$Bu$_4$N][BF$_4$] (0.5 M) electrolyte, at -50 °C. Collected at 100 mV/s. Arrows indicate scan direction.
Fig. 48. Cyclic voltammogram of 3 in DME (1 mM) with [nBu₄N][BF₄] (0.5 M) electrolyte, at -50 °C. Collected at 200 mV/s. Arrows indicate scan direction. The couple at -1.34 V vs FcH⁺/₀ is in good agreement with a previous report (-1.25 V) for this complex (1 mM) in DCM with [nBu₄N][PF₆] (0.2 M) at room temperature. 

9.2 Investigations of [Cp*$_2$Fe], FcH, and [K(2.2.2-crypt)][Cp$^{	ext{III}}$]

[Cp*$_2$Fe] was prepared from commercial FeCl$_2$ (Alfa Aesar) and two equivalents of KCp* in THF. The product was crystallized from hexane as bright yellow plates, sublimed twice, and stored under Ar. [K(2.2.2-crypt)][Cp$^{	ext{III}}$] for cyclic voltammetry measurements was prepared *in-situ* from one equivalent of 2.2.2-cryptand and KCp$^{	ext{III}}$ in THF at room temperature.

During the course of our cyclic voltammetry experiments with 1-3, we decided to investigate whether the same apparent [(Cp$^R$)$_2$M]$^{2+/0}$ couples were available for both FcH and [Cp*$_2$Fe] as indeed [Cp*$_2$Fe]$^{2+}$ had been shown to be chemically accessible, but without electrochemical data due to the instability of the product in organic solvents. Additionally as the reversibility of the [Cp*$_2$Fe]$^{+0}$ couple is well-established$^{12,18}$, it provided a suitable case-study into the effects of electron and analyte transport at the reduced temperatures used in our electrochemical studies.

We additionally sought to check whether our putative [(Cp$^M$)$_2$M]$^{2+/+}$ (M = Mn or Fe) couple was in fact due to outer-sphere [Cp$^{	ext{III}}$] oxidation, as this anion is present in the structure of 1. Thus we performed CV experiments on solutions of [K(2.2.2-crypt)][Cp$^{	ext{III}}$] and found that small peaks in the scans of 1 and 3 could potentially be assigned as the [Cp$^{	ext{III}}$] oxidation by comparison however these experiments were complicated by suspected ligand scrambling between [K(2.2.2-crypt)][Cp$^{	ext{III}}$] and FcH, so no firm conclusions could be drawn.

Initial assessment of the [Cp*$_2$Fe] system under our conditions showed the [Cp*$_2$Fe]$^{+0}$ redox couple to be unaffected by solvent, electrolyte and temperature as expected (Supplementary Fig. S49)$^{12}$, with the exception of the magnitude of current transfer. The peak currents in both directions, at two different scan rates, are consistent.
Fig. 49. Cyclic voltammogram of \([\text{Cp}^*\text{Fe}]\) in DME (1 mM) with \([\text{NBu}_4\text{N}]\text{[BF}_4\text{]}\) (0.5 M) electrolyte, at -50 °C. Collected at the indicated scan rates. Arrows indicate scan direction.

Attempts to observe the \([\text{Cp}^*\text{Fe}]^{0/-}\) couple were unsuccessful even at -50 °C in both THF and DME solvents. The reduction potential clearly lies beyond our solvent window (Supplementary Fig. 50). Attempted chemical reduction with \(\text{KCe}_8\) in the presence of 2.2.2-cryptand in THF lead to no observable reaction. The bright yellow colour changed to green (yellow from the \([\text{Cp}^*\text{Fe}]\) and blue from the presence of solvated electrons), from which \([\text{Cp}^*\text{Fe}]\) could be recovered in good yield. This is in contrast to all other species investigated herein.
Given that [Cp\(^{+}\)\(_{2}\)Fe] can be doubly oxidized chemically\(^{19}\), though apparently not reduced either chemically or electrochemically, we attempted to see whether we could observe the double electrochemical oxidation of this complex at -50 °C in DME solvent. We were able to observe a second, irreversible, oxidation wave for [Cp\(^{+}\)\(_{2}\)Fe] at 1.06 V which we attribute to [Cp\(^{+}\)\(_{2}\)Fe\(^{2+}\)] formation, and found that on scans where this potential was exceeded, the [Cp\(^{+}\)\(_{2}\)Fe\(^{+}\)]/[Cp\(^{+}\)\(_{2}\)Fe] reduction wave was severely diminished (Supplementary Fig. 51, E\(_{p2}\)). We hypothesize that this is due to the chemical instability of [Cp\(^{+}\)\(_{2}\)Fe\(^{IV}\)]\(^{2+}\), in line with previous reports\(^{19}\).
**Fig. 51.** Cyclic voltammogram of \([\text{Cp}^*\text{Fe}^2]\) in DME (1 mM) with \([\text{nBu}_4\text{N}][\text{BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at 200 mV/s. Arrows indicate scan direction.

**Fig. 52.** Calibration cyclic voltammogram of \([\text{Cp}^*\text{Fe}]\), with a crystal of FeH, in DME (1 mM) with \([\text{nBu}_4\text{N}][\text{BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at 200 mV/s.
We were able to observe a well-reversible putative FcH\textsuperscript{IV/0} couple at -3.48 V vs FcH\textsuperscript{+0} (Supplementary Fig. 53) which is in good agreement with other measurements performed in this solvent\textsuperscript{13}, however attempts to access this species chemically under the same conditions used for [K(2.2.2-crypt)][(Cp\textsuperscript{iii})\textsubscript{2}Fe] (treatment with KC\textsubscript{8} in the presence of stoichiometric 2.2.2-cryptand) lead to the formation initially of dark purple solutions. Layering this solution with hexane and storage at -25°C lead to the deposition of black microcrystalline material that appeared to produce X-ray fluorescence when irradiated with Cu K\textalpha~ radiation (\(\lambda = 1.54178 \text{ Å}\)), as well as poorly resolved powder rings which suggests at least, the presence of metallic iron and amorphous/powdery material. We were unable to unambiguously identify this material.

![Cyclic voltammogram of FcH in DME (1 mM) with [\textsuperscript{6}BuN]\[BF\textsubscript{4}\] (0.5 M) electrolyte, at -50 °C. Collected at 200 mV/s. Arrows indicate scan direction.](image_url)

Fig. 53. Cyclic voltammogram of FcH in DME (1 mM) with [\textsuperscript{6}BuN]\[BF\textsubscript{4}\] (0.5 M) electrolyte, at -50 °C. Collected at 200 mV/s. Arrows indicate scan direction.
Fig. 54. Isolated scans in the cyclic voltammogram of FcH in DME (1 mM) with [$^{n}$Bu$_4$N][BF$_4$] (0.5 M) electrolyte, at -50 °C. Collected at indicated scan rates.

Isolation of the putative FcH$^{0/-}$ redox couple indicates only a modest scan-rate dependence, which suggests the reduced species remains intact on the experimental time scale. We suggest that given appropriate experimental conditions this species could be isolated chemically; however, we were not successful in our attempts.
9.3 Peak-isolation, and scan-rate dependent measurements of 1-3, and FcH⁺/0 calibrations

![Graph](image_url)

**Fig. 55.** Isolated scans in the cyclic voltammogram of 1 in DME (1 mM) with \([\text{nBu}_4\text{N}]\text{[BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at indicated scan rates. Showing the [(\(\text{Cp}^{\text{m}}\))\(_2\text{Mn}\)]\(^{0/0}\) redox couple.

![Graph](image_url)

**Fig. 56.** Isolated scans in the cyclic voltammogram of 1 in DME (1 mM) with \([\text{nBu}_4\text{N}]\text{[BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at indicated scan rates. Showing the [(\(\text{Cp}^{\text{m}}\))\(_2\text{Mn}\)]\(^{1+/0}\) redox couple.
**Fig. 57.** Isolated scans in the cyclic voltammogram of 1 in DME (1 mM) with \[^{n}Bu_4N\][BF_4] (0.5 M) electrolyte, at -50 °C. Collected at indicated scan rates. Showing the [(Cp^III)_2Mn]^+/0 redox couple. Circles indicate oxidation of the outer-sphere [Cp^III^-] anion.

**Fig. 58.** Cyclic voltammogram of 1 in DME (1 mM) with \[^{n}Bu_4N\][BF_4] (0.5 M) electrolyte, at -50 °C. Collected at 500 mV/s. Showing the [(Cp^III)_2Mn]^{+0} and [(Cp^III)_2Mn]^{2+/3} redox couples.
Fig. 59. Calibration cyclic voltammogram of 1, with a crystal of FcH, in DME (1 mM) with \([\text{Bu}_4\text{N}][\text{BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at 200 mV/s.

Fig. 60. Isolated scans in the cyclic voltammogram of 2 in DME (1 mM) with \([\text{Bu}_4\text{N}][\text{BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at indicated scan rates. Showing the \([(\text{Cp}^{\text{II}})_2\text{Fe}]^{\text{IV}}\) redox couple.
Fig. 61. Isolated scans in the cyclic voltammogram of 2 in DME (1 mM) with \([^n\text{Bu}_4\text{N}][\text{BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at indicated scan rates. Showing the \([(\text{Cp}^{\text{iii}})_2\text{Fe}]^{+0}\) redox couple.

Fig. 62. Isolated scans in the cyclic voltammogram of 2 in DME (1 mM) with \([^n\text{Bu}_4\text{N}][\text{BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at indicated scan rates. Showing the \([(\text{Cp}^{\text{iii}})_2\text{Fe}]^{2+/+}\) redox couple.
Fig. 63. Cyclic voltammogram of 2 in DME (1 mM) with \([\text{nBu}_4\text{N}][\text{BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at 500 mV/s. Showing the \([(\text{Cp}^{\text{m}})_2\text{Fe}]^{1+}/0\) and \([(\text{Cp}^{\text{m}})_2\text{Fe}]^{2+/+}\) redox couples.

Fig. 64. Calibration cyclic voltammogram of 2, with a crystal of FcH, in DME (1 mM) with \([\text{nBu}_4\text{N}][\text{BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at 100 mV/s.
Fig. 65. Isolated scans in the cyclic voltammogram of 3 in DME (1 mM) with $[^n$Bu$_4$N][BF$_4$] (0.5 M) electrolyte, at -50 °C. Collected at indicated scan rates. Showing the [(Cp$^{iii}$)$_2$Co]$^{0/+}$ redox couple. Peak drift is attributed to loss of [Cp$^{iii}$]$^-$ and poor thermal control/diffusion of ions during collection. Repeated runs showed the same behaviour.

Fig. 66. Isolated scans in the cyclic voltammogram of 3 in DME (1 mM) with $[^n$Bu$_4$N][BF$_4$] (0.5 M) electrolyte, at -50 °C. Collected at indicated scan rates. Showing the [(Cp$^{iii}$)$_2$Co]$^{-0/+}$ redox couple.
Fig. 67. Calibration cyclic voltammogram of 3, with a crystal of FcH, in DME (1 mM) with \([\text{Bu}_4\text{N}]\text{[BF}_4]\) (0.5 M) electrolyte, at -50 °C. Collected at 100 mV/s. The significant drift of the FcH\(^{\pm}\) couple when compared to previous samples (reproducibly) is evidence of significant sample degradation during the scans. This is not seen when more typical scan windows are used, only when strongly negative potentials were reached.
10. Electronic Structure

Methodology

For 1, there are two unique molecules in the asymmetric unit (using CCDC700167), so calculations were performed on both. SA-CASSCF calculations were performed for an active space of 9 electrons in 12 orbitals for one sextet, 17 quartets and 13 doublets. These calculations showed one low-lying sextet, two low-lying quartets and two low-lying doublets, so the SA-CASSCF calculations were performed averaging only these states. We found that the 3d$_{xz}$ and 3d$_{yz}$ (π, e$_{1g}$) orbitals and the excited 4d orbitals rotated out of the active space for fully-occupied 3p orbitals and unoccupied 4f orbitals, respectively, so the SA-CASSCF calculations were finally refined for one sextet, two quartets and two doublets using a 5 in 5 active space (3d$_{z^2}$ (σ, a$_{1g}$), 3d$_{xy}$ and 3d$_{c2-y^2}$ (δ, e$_{2g}$), and 3d$_{xz}$ and 3d$_{yz}$ (π*, e$_{1g}$), Tables S5 and S6). A CI expansion in this active space showed 20 quartets and 10 doublets were below 30,000 cm$^{-1}$ (relative to the lowest root of each multiplicity, for both unique Mn ions, Supplementary Table 4), and so these states were mixed with the sextet under SOC.

For 2, there are also two unique molecules in the asymmetric unit (using CCDC824919), so calculations were performed on both. SA-CASSCF calculations were performed for an active space of 10 electrons in 12 orbitals for 5 quintets, 35 triplets and 28 singlets. These calculations showed two low-lying quintets, four low-lying triplets and only one low-lying singlet, so the SA-CASSCF calculations were performed averaging only these states. This showed that an active space of 3d$_{xz}$ and 3d$_{yz}$ (π, e$_{1g}$), 3d$_{c2}$ (σ, a$_{1g}$), 3d$_{xy}$ and 3d$_{c2-y^2}$ (δ, e$_{2g}$), and 3d$_{xz}$ and 3d$_{yz}$ (π*, e$_{1g}$) and five ligand-hybridised 4d/5d orbitals was indeed most appropriate for these lowest states (Supplementary Table 8 and 9). Note that for the singlet state the two least-occupied active orbitals had 0.00 occupancy and in-fact are dominated by 5d functions (cf. these orbitals for the triplets and quintets which are dominated by 4d functions with occupancy ca. 0.01, similar to all other complexes). A CI expansion in this active space showed 5 quintets, 17 triplets and one singlet were below 30,000 cm$^{-1}$ (relative to the lowest root of each multiplicity, Supplementary Table 7), and so these states were mixed with SOC.

For 3, SA-CASSCF calculations were performed for an active space of 11 electrons in 12 orbitals for the lowest 10 quartets and 40 doublets. These calculations showed two low-lying quartets
and two low-lying doublets, so SA-CASSCF calculations were repeated for these states. This showed
that an active space of 3d_{xz} and 3d_{yz} (\pi, e_{1g}), 3d_{d_{2}} (\sigma, a_{1g}), 3d_{xy} and 3d_{x^{2}-y^{2}} (\delta, e_{2g}), and 3d_{xz} and 3d_{yz} (\pi^{*}, e_{1g}) and five ligand-hybridised 4d orbitals was indeed the most appropriate for these lowest states (Supplementary Table 11). A CI expansion in this active space showed seven quartets and 11 doublets were below 30,000 cm^{-1} (relative to the lowest root of each multiplicity, Supplementary Table 10), and so these states were mixed with SOC.

For 4, SA-CASSCF calculations were performed for an active space of 10 electrons in 12 orbitals for the lowest 5 quintets, 35 triplets and 28 singlets. SA-CASSCF calculations showed two low-lying quintets, two low-lying triplets and one low-lying singlet, so the SA-CASSCF calculations were repeated for these states. This showed that an active space of 3d_{xz} and 3d_{yz} (\pi, e_{1g}), 3d_{d_{2}} (\sigma, a_{1g}), 3d_{xy} and 3d_{x^{2}-y^{2}} (\delta, e_{2g}), and 3d_{xz} and 3d_{yz} (\pi^{*}, e_{1g}) and five ligand-hybridised 4d orbitals was indeed the most appropriate for these lowest states (Supplementary Table 13). A CI expansion in this active space showed three quintets, 19 triplets and 3 singlets were below 30,000 cm^{-1} (relative to the lowest root of each multiplicity, Supplementary Table 12), and so these states were mixed with SOC.

For 5, SA-CASSCF calculations were performed for an active space of 11 electrons in 12 orbitals for the lowest 10 quartets and 40 doublets. These calculations showed two low-lying quartets and two low-lying doublets, so SA-CASSCF calculations were repeated for these states. This showed that an active space of 3d_{xz} and 3d_{yz} (\pi, e_{1g}), 3d_{d_{2}} (\sigma, a_{1g}), 3d_{xy} and 3d_{x^{2}-y^{2}} (\delta, e_{2g}), and 3d_{xz} and 3d_{yz} (\pi^{*}, e_{1g}) and five ligand-hybridised 4d orbitals was indeed the most appropriate for these lowest states (Supplementary Table 15). A CI expansion in this active space showed nine quartets and 26 doublets were below 30,000 cm^{-1} (relative to the lowest root of each multiplicity, Supplementary Table 14), and so these states were mixed with SOC.

For 6 and 7, SA-CASSCF calculations were performed for an active space of 12 electrons in 12 orbitals for the lowest 10 triplets and 25 singlets. These calculations showed one low-lying triplet and two low-lying singlets, so SA-CASSCF calculations were repeated for these states. This showed that an active space of 3d_{xz} and 3d_{yz} (\pi, e_{1g}), 3d_{d_{2}} (\sigma, a_{1g}), 3d_{xy} and 3d_{x^{2}-y^{2}} (\delta, e_{2g}), and 3d_{xz} and 3d_{yz} (\pi^{*}, e_{1g}) and five ligand-hybridised 4d orbitals was indeed the most appropriate for these lowest states (Supplementary Tables 17 and 18). A CI expansion in this active space showed nine triplets and 14
singlets were below 30,000 cm$^{-1}$ (relative to the lowest root of each multiplicity, for both 6 and 7; note that for 7 two of the highest singlets are just over 30,000 cm$^{-1}$ and are included for consistency with 6, Supplementary Table 16), and these states were mixed with SOC.

Results

For 1 there are two unique molecules in the asymmetric unit (using CCDC700167), so calculations were performed on both; the first values are for Mn1 and those in braces are for Mn2. Using CAS(5,5)+SOC (Supplementary Tables 5 and 6), the ground state was found to be high-spin $S = 5/2$ (6A), and is well-separated from the first excited $S = 3/2$ state lying at ca. 23,200 cm$^{-1}$ \{23,200 cm$^{-1}$\}. The zero-field splitting for the ground $S = 5/2$ state is parameterised by $D = -0.19$ cm$^{-1}$ and $|E| < 0.01$ cm$^{-1}$ \{$D = -0.18$ cm$^{-1}$ and $|E| = 0.01$ cm$^{-1}$\}, where the magnetic z-axis is practically parallel to the centroid-Mn-centroid vectors. The $g$-value for the $S = 5/2$ state is predicted to be isotropic with $g = 2.00$ \{$g = 2.00$\}.

For 2 there are also two unique molecules in the asymmetric unit (using CCDC824919), so calculations were performed on both. Using CAS(10,12)+SO (Tables S8 and S9) the ground state was found to be low-spin $S = 0$ (1A), with a first excited $S = 1$ state lying at ca. 14,000 cm$^{-1}$ \{14,000 cm$^{-1}$\}. Thus, the electronic structure of 2 is low-spin diamagnetic in common with all other ferrocene derivatives\(^4\).\(^5\)

For 3, CAS(11,12)+SO (Table S11) calculations show the ground state is low-spin $S = 1/2$ (2E), but due to the low-symmetry of the molecule the orbital degeneracy of 3d$_{xz}$ and 3d$_{yz}$ pair is partly lifted, thus the second $S = 1/2$ state lies at ca. 1,800 cm$^{-1}$ which strongly mixes with two $S = 3/2$ states that lie between 1,900 – 3,000 cm$^{-1}$, while subsequent states lie above ca. 12,000 cm$^{-1}$. The $g$-value for the ground $S = 1/2$ state is anisotropic with $g_x \approx g_y = 2.1(1)$, $g_z = 1.61$, where the magnetic z-axis is practically parallel to the Cp$^{iii}_{\text{centroid}}$–Co–Cp$^{iii}_{\text{centroid}}$ vectors.
Table 4. Relative root energies (excluding sextet), calculated from a CI expansion in the refined active space for 1. All energies in cm\(^{-1}\). Active orbitals were optimised for each multiplicity by SA-CASSCF using the roots shown in grey.

| Mn1 | Mn2 |
|-----|-----|
|     |     |
| Quartet | Doublet | Quartet | Doublet |
| 0   | 0   | 0       | 0       |
| 155 | 117 | 305     | 118     |
| 3474 | 9551 | 3504 | 9464 |
| 3480 | 9551 | 3510 | 9464 |
| 7345 | 13673 | 7310 | 13571 |
| 7673 | 13705 | 7626 | 13636 |
| 7707 | 13945 | 7660 | 13858 |
| 8826 | 13951 | 8791 | 13864 |
| 8828 | 19932 | 8793 | 19812 |
| 9818 | 19973 | 9836 | 19878 |
| 9922 | 9989 |
| 13259 | 13186 |
| 13553 | 13504 |
| 13579 | 13577 |
| 16931 | 16888 |
| 20396 | 20171 |
| 20567 | 20470 |
| 28122 | 28070 |
| 28295 | 28275 |
| 28341 | 28320 |
Table 5. SA-CASSCF active space for the $S = 5/2$ ground state of 1 (Mn1).

| Orbital | Rendering | Occupation |
|---------|-----------|------------|
| 142     | ![Image](image1.png) | 1.00       |
| 143     | ![Image](image2.png) | 1.00       |
| 144     | ![Image](image3.png) | 1.00       |
| 145     | ![Image](image4.png) | 1.00       |
| 146     | ![Image](image5.png) | 1.00       |
Table 6. SA-CASSCF active space for the \( S = 5/2 \) ground state of \( 1 \) (Mn2).

| Orbital | Rendering | Occupation |
|---------|-----------|------------|
| 142     | ![Orbital 142 Rendering](image1) | 1.00       |
| 143     | ![Orbital 143 Rendering](image2) | 1.00       |
| 144     | ![Orbital 144 Rendering](image3) | 1.00       |
| 145     | ![Orbital 145 Rendering](image4) | 1.00       |
| 146     | ![Orbital 146 Rendering](image5) | 1.00       |
Table 7. Relative root energies for 2 (excluding singlet), calculated from a CI expansion in the refined active space. All energies in cm$^{-1}$. Active orbitals were optimised for each multiplicity by SA-CASSCF using the roots shown in grey.

|       | Fe1 | Fe2       |       |       |
|-------|-----|----------|-------|-------|
|       | Quintets | Triplets | Quintets | Triplets |
| 0     | 0    | 0        | 0     | 0     |
| 168   | 314  | 216      | 175   |       |
| 6221  | 912  | 6216     | 843   |       |
| 25224 | 966  | 24990    | 922   |       |
| 25541 | 7997 | 25524    | 7847  |       |
|       | 8361 | 21797    | 8470  |       |
|       | 22279 | 22089   |       |       |
|       | 22297 | 22113   |       |       |
|       | 23131 | 22923   |       |       |
|       | 23280 | 23116   |       |       |
|       | 24458 | 24178   |       |       |
|       | 24555 | 24374   |       |       |
|       | 25478 | 25348   |       |       |
|       | 26277 | 26085   |       |       |
|       | 29099 | 28893   |       |       |
|       | 29106 | 28906   |       |       |
Table 8. CASSCF active space for the ground $S = 0$ state of 2 (Fe1).

| Orbital | Rendering | Occupation |
|---------|-----------|------------|
| 140     | ![Orbital 140](image1.png) | 1.94       |
| 141     | ![Orbital 141](image2.png) | 1.93       |
| 142     | ![Orbital 142](image3.png) | 1.92       |
| 143     | ![Orbital 143](image4.png) | 0.08       |
| 144     | ![Orbital 144](image5.png) | 1.97       |
| 145 | ![Image](145.png) | 0.08 |
|-----|------------------|------|
| 146 | ![Image](146.png) | 1.92 |
| 147 | ![Image](147.png) | 0.03 |
| 148 | ![Image](148.png) | 0.06 |
| 149 | ![Image](149.png) | 0.06 |
| 150 | ![Image](150.png) | 0.00 |
Table 9. CASSCF active space for the ground $S = 0$ state of 2 (Fe2).

| Orbital | Rendering | Occupation |
|---------|-----------|------------|
| 140     | ![Image](image1.png) | 1.94       |
| 141     | ![Image](image2.png) | 1.94       |
| 142     | ![Image](image3.png) | 0.08       |
| 143     | ![Image](image4.png) | 1.97       |
| 144     | ![Image](image5.png) | 1.92       |
| 145 | ![Image](image1.png) | 0.08 |
|-----|----------------------|------|
| 146 | ![Image](image2.png) | 1.92 |
| 147 | ![Image](image3.png) | 0.03 |
| 148 | ![Image](image4.png) | 0.06 |
| 149 | ![Image](image5.png) | 0.06 |
| 150 | ![Image](image6.png) | 0.00 |
Table 10. Relative root energies for 3, calculated from a CI expansion in the refined active space. All energies in cm\(^{-1}\). Active orbitals were optimised for each multiplicity by SA-CASSCF using the roots shown in grey.

| Quartets | Doublets |
|----------|----------|
| 0        | 0        |
| 423      | 1857     |
| 9389     | 15009    |
| 17736    | 16562    |
| 17925    | 16802    |
| 18618    | 17885    |
| 19182    | 18818    |
|          | 19322    |
|          | 19716    |
|          | 19975    |
|          | 25339    |
Table 11. SA-CASSCF active space for two $S = 1/2$ states of 3.

| Orbital | Rendering | Occupation |
|---------|-----------|------------|
| 140     | ![Image](140.png) | 1.94       |
| 141     | ![Image](141.png) | 1.93       |
| 142     | ![Image](142.png) | 1.95       |
| 143     | ![Image](143.png) | 1.95       |
| 144     | ![Image](144.png) | 0.58       |
|    |     |     |
|----|-----|-----|
| 145|     | 1.97|
| 146|     | 0.58|
| 147|     | 0.02|
| 148|     | 0.03|
| 149|     | 0.03|
| 150|     | 0.01|
Table 12. Relative root energies for 4, calculated from a CI expansion in the refined active space. All energies in cm$^{-1}$. Active orbitals were optimised for each multiplicity by SA-CASSCF using the roots shown in grey.

| Quintets | Triplets | Singlets |
|----------|----------|----------|
| 0        | 0        | 0        |
| 484      | 1324     | 29030    |
| 10543    | 3422     | 29632    |
|          | 3634     |          |
|          | 5736     |          |
|          | 6788     |          |
|          | 21290    |          |
|          | 21981    |          |
|          | 22389    |          |
|          | 23475    |          |
|          | 23492    |          |
|          | 24858    |          |
|          | 25007    |          |
|          | 25236    |          |
|          | 26540    |          |
|          | 28049    |          |
|          | 28051    |          |
|          | 29749    |          |
|          | 29798    |          |
Table 13. SA-CASSCF active space for three $S = 0$ states of 4.

| Orbital | Rendering | Occupation |
|---------|-----------|------------|
| 140     | ![Orbital 140](image1) | 1.94       |
| 141     | ![Orbital 141](image2) | 1.95       |
| 142     | ![Orbital 142](image3) | 1.91       |
| 143     | ![Orbital 143](image4) | 1.90       |
| 144     | ![Orbital 144](image5) | 1.95       |
Table 14. Relative root energies for 5, calculated from a CI expansion in the refined active space. All energies in cm\(^{-1}\). Active orbitals were optimised for each multiplicity by SA-CASSCF using the roots shown in grey.

| Quartets | Doublets |
|----------|----------|
| 0        | 0        |
| 996      | 569      |
| 10155    | 7431     |
| 12970    | 8005     |
| 13215    | 8147     |
| 14348    | 8435     |
| 14473    | 8539     |
| 24432    | 9642     |
| 25239    | 10981    |
|          | 11369    |
|          | 14884    |
|          | 17958    |
|          | 18066    |
|          | 18698    |
|          | 18786    |
|          | 20569    |
|          | 20981    |
|          | 22038    |
|          | 22096    |
|          | 22272    |
|          | 22286    |
|          | 23157    |
|          | 23435    |
|          | 24753    |
|          | 25034    |
|          | 26457    |
Table 15. SA-CASSCF active space for two $S = 3/2$ states of 5.

| Orbital | Rendering | Occupation |
|---------|-----------|------------|
| 140     | ![Image](image1.png) | 2.00       |
| 141     | ![Image](image2.png) | 2.00       |
| 142     | ![Image](image3.png) | 1.00       |
| 143     | ![Image](image4.png) | 1.48       |
| 144     | ![Image](image5.png) | 1.96       |
|    | Image | Value |
|----|-------|-------|
| 145| ![Image](145.png) | 1.00  |
| 146| ![Image](146.png) | 1.48  |
| 147| ![Image](147.png) | 0.04  |
| 148| ![Image](148.png) | 0.02  |
| 149| ![Image](149.png) | 0.02  |
| 150| ![Image](150.png) | 0.01  |
Table 16. Relative root energies for 6 and 7, calculated from a CI expansion in the refined active spaces.

All energies in cm⁻¹. Active orbitals were optimised for each multiplicity by SA-CASSCF using the roots shown in grey.

|       | 6       |       | 7       |       |
|-------|---------|-------|---------|-------|
|       | Triplets | Singlets | Triplets | Singlets |
| 0     | 0        | 0      | 0        | 0      |
| 11070 | 44       | 11897  | 20       |        |
| 11206 | 7192     | 12159  | 7254     |        |
| 11411 | 9707     | 12478  | 10654    |        |
| 11462 | 10320    | 12518  | 10982    |        |
| 23708 | 13903    | 24742  | 14741    |        |
| 23801 | 14734    | 25042  | 15305    |        |
| 25140 | 15732    | 26453  | 16597    |        |
| 25483 | 15803    | 26690  | 16625    |        |
|       | 22546    |        | 23822    |        |
|       | 23604    |        | 25401    |        |
|       | 23803    |        | 25550    |        |
|       | 28344    |        | 30263    |        |
|       | 28353    |        | 30267    |        |
Table 17. SA-CASSCF active space for the $S = 1$ ground state of 6.

| Orbital | Rendering | Occupation |
|---------|-----------|------------|
| 140     | ![Orbital 140](image1.png) | 2.00       |
| 141     | ![Orbital 141](image2.png) | 2.00       |
| 142     | ![Orbital 142](image3.png) | 1.95       |
| 143     | ![Orbital 143](image4.png) | 1.95       |
| 144     | ![Orbital 144](image5.png) | 1.97       |
|   |   |   |
|---|---|---|
| 145 | ![Diagram](image1) | 1.02 |
| 146 | ![Diagram](image2) | 1.02 |
| 147 | ![Diagram](image3) | 0.01 |
| 148 | ![Diagram](image4) | 0.03 |
| 149 | ![Diagram](image5) | 0.03 |
| 150 | ![Diagram](image6) | 0.03 |
Table 18. SA-CASSCF active space for the $S = 1$ ground state of 7.

| Orbital | Rendering | Occupation |
|---------|-----------|------------|
| 140     | ![Orbital 140](image1) | 2.00       |
| 141     | ![Orbital 141](image2) | 2.00       |
| 142     | ![Orbital 142](image3) | 1.95       |
| 143     | ![Orbital 143](image4) | 1.97       |
| 144     | ![Orbital 144](image5) | 1.02       |
S11. $^{57}$Fe Mössbauer spectroscopy of 2 and 5.

To corroborate the data, we repeated the measurement on a second sample of 5; whilst the relative amounts of the two signals differ between experiments, the best fit parameters are identical in both datasets (See Supplementary Table 19 and Supplementary Fig. 68). However, the unambiguous spectra allow us to show that there are no Fe-containing decomposition products for 5, other than 2.

**DFT Calculations of $^{57}$Fe Mössbauer Parameters**

Calculations for 2 and 5 were performed using the atomic coordinates determined by X-Ray crystallography (with hydrogen positions optimized). These calculations were performed using ORCA V4.1 with the B3LYP and BP86 functionals along with the def2-tzvp (Fe,C)/def2-svp (H) basis sets. The resolution of the identity approximation (RI for BP86 and RIJCOSX for B3LYP) was used along with auxiliary basis sets generated using the ‘autoaux’ command. The quadrupole splitting and isomer shifts were then calculated using the same basis sets described above but with CP(PPP) on Fe. A recent report has suggested that the RI approximation can cause changes in the calculated parameters, so, we have performed all calculations of the quadrupole splitting and isomer shifts with and without use of the RI approximation. The computed density at the Fe nucleus was converted to experimental values of the isomer shift using the calibration curve described by Römelt et al. A summary of these results is presented here (Supplementary Table 20). The results presented in the main text refer to those obtained using BP86 without the RI approximation.
Table 19. Experimentally determined $^{57}$Fe Mossbauer Parameters.*

| Sample  | Site° | δ (mm/s) | $\Delta E_Q$ (mm/s) | $\Gamma_L$ (mm/s) | $\Gamma_R$ (mm/s) | Weight (%) |
|---------|-------|----------|---------------------|------------------|------------------|------------|
| Fe(II)  | N     | 0.66(2)  | 2.60(2)             | 0.30             | 0.30             | 100        |
| Sample 1| A     | 1.25(2)  | 1.23(2)             | 0.60             | 0.38             | 59.3       |
|         | N     | 0.66(2)  | 2.60(2)             | 0.30             | 0.30             | 40.7       |
| Sample 2| A     | 1.25(2)  | 1.23(2)             | 0.60             | 0.38             | 74.8       |
|         | N     | 0.66(2)  | 2.60(2)             | 0.30             | 0.30             | 25.2       |

*Numbers in parentheses indicate the estimated uncertainty in the last digit.

°N refers to the parameters of the neutral molecule, 2 while A refers to the anionic molecule, 5.

Fig. 68. Experimental (black) and simulated (red) $^{57}$Fe Mössbauer spectra recorded under zero applied field and 80 K of: Top, pure complex 2. Middle and Bottom, Samples 1 and 2, complex 5 contaminated with complex 2 that forms by thermal decomposition. The blue traces correspond to the quadrupole doublet assigned to 5 (~75%) whilst the green traces originate from the decay product 2 (~25%). The red traces are the weighted sum of the two sub-spectra.
As described in the main text, the asymmetric quadrupole doublet observed for 5, is likely due to relaxation effects. Other alternative explanations could include sample texture or the Goldanskii-Karyagin effect\textsuperscript{30}. In our experimental results we observe that the low mm/sec peak is broadened; this is expected when the $\Delta E_Q$ value is negative. This observation is consistent with our DFT calculations that produce negative values of $\Delta E_Q$. Lowering the temperature to 4 K could confirm the presence of slow relaxation, but in order to fully interpret this splitting variable field measurements would need to be performed.

| S  | R.I.† | $\rho(0)$ (a.u.\textsuperscript{3}) | $\delta$ (mm/s) | $\Delta E_Q$ (mm/s) |
|----|-------|-----------------------------------|-----------------|-------------------|
| 2  | Experiment | 0.66(2) | 2.60(2) | |
|    | BP86 | 0 | yes | 11826.9945 | 0.69 | 2.51 |
|    |      |   | no | 11827.1100 | 0.64 | 2.52 |
|    | X-ray | B3LYP | 0 | yes | 11816.1254 | 0.61 | 3.37 |
|    |      |   | no | 11816.1256 | 0.61 | 3.37 |
| 5  | Experiment | 1.25(2) | 1.23(2) | |
|    | BP86 | $\frac{1}{2}$ | yes | 11825.5465 | 1.31 | 2.34 |
|    |      |   | no | 11825.9389 | 1.14 | 2.36 |
|    | B3LYP | $\frac{1}{2}$ | yes | 11814.4226 | 1.23 | 2.01 |
|    |      |   | no | 11814.4225 | 1.23 | 2.01 |
|    | X-ray | BP86 | $\frac{3}{2}$ | yes | 11825.6336 | 1.27 | 0.67 |
|    |      |   | no | 11826.0519 | 1.09 | 0.65 |
|    |      | B3LYP | $\frac{3}{2}$ | yes | 11814.4771 | 1.21 | 0.68 |
|    |      |   | no | 11814.4769 | 1.21 | 0.68 |

\textsuperscript{*}Fe (CP(PPP)) C (def2-tzvp) H (def2-svp) \textsuperscript{†}RIJCOSX (B3LYP) and ‘RI’ (BP86) in ORCA terminology.
12. EPR spectroscopy

A powder Q-band EPR spectrum for 1 is visible at room temperature, and shows a multitude of transitions across the entire field range (Supplementary Fig. 69); this unambiguously indicates a high-spin $S = 5/2$ ground state for Mn$^{2+}$ with significant zero-field splitting (ZFS) that can be parameterised with rhombic ZFS parameters $D = -0.435$ and $E = -1.5 \times 10^{-3} \text{ cm}^{-1}$ using the PHI code (Supplementary Fig. 69)$^{31}$. When cooled to 11 K, the spectrum is substantially changed from that at room temperature and gives $D = -0.547$ and $E = -7.8 \times 10^{-3} \text{ cm}^{-1}$ (Supplementary Fig. 69); there is a smooth change in the $D$ parameter as a function of temperature (Supplementary Fig. 70 and 71, Supplementary Table 21), suggesting that there is gradual structural variation with temperature. The experimental ZFS values, $D \sim -0.5 \text{ cm}^{-1}$ and negligible $E$, are in good agreement with those calculated by CASSCF as around $D = -0.2 \text{ cm}^{-1}$ with very small $|E| \leq 0.01 \text{ cm}^{-1}$. Our experiments are also in good agreement with literature studies of previous [[(Cp$^3$)$_2$Mn] variants, where both high and low temperature $D$ and $E$ parameters were determined (300 K: $D = -0.42(3)$ and $E = 0.014(4) \text{ cm}^{-1}$ and 4 K: $D = -0.65(1)$ and $E = 0.0083(7) \text{ cm}^{-1}$)$^{32}$.

![Fig. 69. Powder Q-band EPR spectra (black) of 1 at: a) 294 K (33.936855 GHz, red line is a simulation with $D = -0.435 \text{ cm}^{-1}$, $E = -1.5 \times 10^{-3} \text{ cm}^{-1}$, $D_{\text{strain}} = 5.14 \times 10^{-2}$, $I_{\text{iso}} = 2.5 \text{ GHz using PHI}$); and, b) at 11 K (33.932480 GHz, red line is a simulation with $D = -0.547 \text{ cm}^{-1}$, $E = -7.8 \times 10^{-3} \text{ cm}^{-1}$, $D_{\text{strain}} = 8.69 \times 10^{-3}$, $I_{\text{iso}} = 2.5 \text{ GHz using PHI}$).](image)
Fig. 70. Variable temperature continuous wave powder Q-band EPR spectra of 1 collected from 11 to 294 K. Refer to Table S20 below for frequencies and fitting parameters obtained using PHI ($g_{iso} = 2$ and $\hbar \nu_{iso} = 2.5$ GHz).

Fig. 71. Plots of the variation with temperature of the $D$ (left) and $E$ (right) fitting parameters of 1 obtained from Q-band data.
Table 21. Q-band fitting parameters for 1 obtained using PHI software ($g_{iso} = 2$ and $lw_{iso} = 2.5$ GHz).

| Temp (K) | D (cm$^{-1}$) | E (cm$^{-1}$) | $D$ strain | Frequency (GHz) |
|----------|---------------|---------------|------------|-----------------|
| 294      | -0.435        | -1.5x10$^{-3}$ | 5.14x10$^{-2}$ | 33.93686       |
| 250      | -0.437        | -1.5x10$^{-3}$ | 5.50x10$^{-2}$ | 33.94635       |
| 225      | -0.446        | -3.9x10$^{-3}$ | 4.43x10$^{-2}$ | 33.94721       |
| 200      | -0.455        | -3.6x10$^{-3}$ | 3.67x10$^{-2}$ | 33.94950       |
| 175      | -0.462        | -5.0x10$^{-3}$ | 1.20x10$^{-2}$ | 33.95284       |
| 150      | -0.480        | -5.6x10$^{-3}$ | 1.41x10$^{-2}$ | 33.93995       |
| 125      | -0.494        | -6.0x10$^{-3}$ | 7.54x10$^{-3}$ | 33.94195       |
| 100      | -0.510        | -5.8x10$^{-3}$ | 2.61x10$^{-9}$ | 33.93997       |
| 75       | -0.517        | -6.7x10$^{-3}$ | 6.18x10$^{-3}$ | 33.94118       |
| 50       | -0.531        | -7.9x10$^{-3}$ | 1.47x10$^{-2}$ | 33.94181       |
| 25       | -0.544        | -7.6x10$^{-3}$ | 4.96x10$^{-8}$ | 33.94048       |
| 15       | -0.546        | -8.0x10$^{-3}$ | 6.99x10$^{-3}$ | 33.93497       |
| 11       | -0.547        | -7.8x10$^{-3}$ | 8.69x10$^{-3}$ | 33.93248       |

Fig. 72. Continuous wave powder X-band (9.390418 GHz) EPR spectrum of 3 at 5 K. Note that a c.w. X-band EPR spectrum of 3 in frozen DCM solution at 100 K has previously been reported<sup>6</sup>. Fitted using Easyspin with $S = \frac{1}{2}$, $g_{iso} = 1.89$, $A_{iso} = 21$ MHz and $lw_{iso} = 31$ mT.
**Fig. S73.** Continuous wave Q-band (34.034311 GHz) EPR spectrum of 5 mM 3 frozen solution in Tol:Hex (9:1) collected at 20 K. Fitted using Easyspin with $S = 1/2$, $g_x = 2.029$, $g_y = 1.954$ and $g_z = 1.742$ with $A_x = 400$, $A_y = 0$ and $A_z = 240$ MHz and $h\nu_{iso} = 36$ mT.

X- and Q-band powder EPR spectra for 4 show identical spectral features to 1 with the addition of some sharp signals at $g = 2$ (Supplementary Fig. 74, cf. Supplementary Fig. 71); thus, we suggest that the 18e$^{-}$ manganocenate anion (isoelectronic to ferrocene) is EPR silent and the spectral features owe to the Mn$^{2+}$ decomposition product 1 and some radical impurities, respectively. We note that this is consistent with the independent observation of Fe$^{2+}$ decomposition products in 5 from $^{57}$Fe Mössbauer spectroscopy. This agrees with the CASSCF results that find an $S = 0$ ground state for 4, and the previous reports of the analogous derivatised manganocene anion [Cp*$_2$Mn]$^{-}$ being diamagnetic$^{33,34,35}$. 
Fig. 74. Continuous wave powder Q-band (34.033169 GHz) EPR spectrum of 4 collected at 5 K with simulation parameters from 1 at 11 K. Sharp line at ca. 1.2 T is due to radical impurities.

Fig. 75. Variable temperature continuous wave powder X-band EPR spectrum of 5 collected at 5, 10 and 20 K using frequencies of 9.432402, 9.432511 and 9432537 GHz, respectively. Simulation fitted simultaneously with Q-band data using PHI with $S = 3/2$, $D = -4.42$ cm$^{-1}$ with $E = 0$ cm$^{-1}$ and $g_{x/y} = 2.06$ and $g_z = 2.37$ and $h\omega_{x/y} = 9.46(5)$ and $h\omega_z = 6.7(1)$ GHz. Sharp lines at ca. 0.3 T are due to radical impurities.
The Q-band EPR spectrum for 6 at 5 K (Supplementary Fig. 76) shows a sharp absorption-like feature at ca. 0.3 T ($g \sim 4$) and a broad derivative feature at ca. 1.2 T ($g \sim 2$). There are several smaller features between these two strong signals which are influenced by the orientation of the sample (indicating polycrystallinity of the sample, Supplementary Fig. 77), as well as showing signs of magnetic torque on multiple field scans (Supplementary Fig. 78). The broad feature at ca. 1.2 T is consistent with a broadened Q-band spectrum of 3 (Fig. 4a and Supplementary Fig. 76), thus we suspect that this signal is due to the presence of 3 as a decomposition product of 6 (as observed by EPR spectroscopy for 4 and by Mössbauer spectroscopy for 5). At X-band, a broad feature at ca. 0.34 T ($g \sim 2$) is visible (Supplementary Fig. 79), as well as a feature at 1.2 T; the former is consistent with the X-band spectrum of 3 (Supplementary Fig. 72), while the latter arises from condensation of paramagnetic O$_2$ in the sample tube holder (1.8 mm Q-band tube within a 4 mm X-band tube). No other features are observable at X-band which is curious given the ca. 0.3 T ($g \sim 8$) resonance observed at Q-band.

Starting from the CASSCF-predicted ground $S = 1$ state, simulations with $|D| = 1.4$ cm$^{-1}$ and $E = 0$ can reproduce the 0.3 T Q-band resonance for 6, however, this is accompanied by a strong feature at 0.75 T at X-band, which is clearly absent in the experimental data (Supplementary Fig. 80). However, if a rhombic ZFS of ca. $|E| > 0.15$ cm$^{-1}$ is present, then the $m_S = \pm 1$ states would be split in zero field by an amount larger than the X-band microwave energy, and a feature could be observable at Q-band (ca. 1.1 cm$^{-1}$) but not at X-band (ca. 0.3 cm$^{-1}$). Indeed, in this model (if $g = 2.0$ is fixed), then the position of the Q-band resonance measures $|E| = 0.51$ cm$^{-1}$, and any value of $|D| > 6$ cm$^{-1}$ is possible (N.B. as the sample must be rotated for each temperature change to negate alignment in the magnetic field, absolute intensities cannot be directly compared and we are thus unable to perform reliable variable temperature measurements to determine an approximate value for $D$ in this case). For $6 < |D| < 15$ cm$^{-1}$, features owing to transitions between $m_s = \pm 1$ states with a perpendicular magnetic field can be observed between 0.5 and 1 T, but due to the weak experimental intensity in this region we suspect that $|D| > 15$ cm$^{-1}$. These results are in reasonable agreement with the CASSCF-SO calculations which suggest that $D = 24 – 26$ cm$^{-1}$ and $|E| = 0.2 – 0.4$ cm$^{-1}$.
Fig. 76. Continuous wave powder Q-band (33.984321 GHz) EPR spectrum of 6 with simulation in PHI using $S = 1$, $|D| = 15$ cm$^{-1}$, $|E| = 0.51$ cm$^{-1}$ and $I_{iso} = 1.5$ GHz, accounting for the observed Q-band spectrum and giving no spectrum at X-band. Features at ca. 1.2 T correspond to decomposition to 3.

Fig. 77. Evidence of polycrystallinity for 6 at Q-band (34.122766 and 34.118435 GHz), showing changes in peak intensities in subsequent scans under identical scan conditions following rotation of the sample relative to the applied magnetic field.
**Fig. 78.** Evidence of magnetic torque for 6 at Q-band (34.122766 and 34.122239 GHz), showing changes in peak intensities in subsequent scans under identical scan conditions.

**Fig. 79.** Continuous wave powder X-band (9.441592 GHz) EPR spectrum of 6 collected at 5 K. Features at ca. 0.3 T and 1.2 T correspond to decomposition to 3 and oxygen, respectively.
Fig. 80. Simulation of 6 using PHI with \( S = 1, |D| = 1.4 \, \text{cm}^{-1}, |E| = 0 \, \text{cm}^{-1} \) and \( h\nu_{iso} = 1.5 \, \text{GHz} \) at (left) X- and (right) Q-band (9.441869 and 33.984321 GHz). This accounts for the strong feature observed at Q-band but is accompanied by a strong feature at 0.75 T at X-band, which is not observed experimentally. Features at ca. 0.3 T and 1.2 T in the X-band spectrum (left) correspond to decomposition to 3 and oxygen, respectively, while features at ca. 1.2 T in the Q-band spectrum (right) correspond to decomposition to 3.
13. References

1. Jaroschik, F., Nief, F., Le Goff, X.-F. & Ricard, L. Synthesis and Reactivity of Organometallic Complexes of Divalent Thulium with Cyclopentadienyl and Phospholyl Ligands. *Organometallics* **26**, 3552–3558 (2007).

2. Bergbreiter, D. E. & Killough, J. M. Reactions of potassium-graphite. *J. Am. Chem. Soc.* **100**, 2126–2134 (1978).

3. Sitzmann, H., Schar, M., Dormann, E. & Kelemen, M. High Spin-Manganocenes with Bulky, Alkylated Cyclopentadienyl Ligands. *Z. Anorg. Allg. Chem.* **623**, 1609–1613 (1997).

4. Walter, M. D., Sofield, C. D., Booth, C. H. & Andersen, R. A. Spin Equilibria in Monomeric Manganocenes: Solid-State Magnetic and EXAFS Studies. *Organometallics* **28**, 2005–2019 (2009).

5. Walter, M. D. & White, P. S. [Cp'FeI]₂ as convenient entry into iron-modified pincer complexes: bimetallic η⁶,κ¹-POCOP-pincer iron iridium compounds. *New J. Chem.* **35**, 1842–1854 (2011).

6. Schneider, J. J. et al. Synthesis, structure and spectroelectrochemistry of bis(η⁶-1,4-tri-tert-butyl-benzene)chromium(0) and bis(η⁵-1,2,4-tri-tert-butyl-cyclopentadienyl)cobalt(II). Dia- and paramagnetic sandwich complexes derived from sterically highly demanding π-ligands. *J. Organomet. Chem.* **590**, 7–14 (1999).

7. Peters, M. et al. Pogo-Stick Iron and Cobalt Complexes: Synthesis, Structures, and Magnetic Properties. *Inorg. Chem.* **58**, 16475–16486 (2019).

8. *CrysAlisPRO*, version 39.27b (Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, 2017).

9. Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr., Sect. A* **64**, 112–122 (2008).

10. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C* **71**, 3–8 (2015).

11. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42**, 339–341 (2009).

12. Aranzaes, J. R., Daniel, M. -C. & Astruc, D. Metallocenes as references for the determination of redox potentials by cyclic voltammetry – Permethylated iron and cobalt sandwich complexes, inhibition
by polyamine dendrimers, and the role of hydroxy-containing ferrocenes. Can. J. Chem. 84, 288–299 (2006).

13. Ito, N., Saji, T. & Aoyagui, S. Electrochemical formation of stable ferrocene anion and the formal rate constant of the ferrocene0/− electrode. J. Organomet. Chem. 247, 301–305 (1983).

14. Mugnier, Y., Moise, C., Tirouflet, J. & Laviron, E. Reduction electrochimique du ferrocene. J. Organomet. Chem. 186, C49 (1980).

15. Geiger Jr, W. E. Electrocatalysis of cobaltocene. Evidence for a metallocene anion. J. Am. Chem. Soc. 96, 2632–2634 (1974).

16. Bard, A. J., Garcia, E., Kukharenko, S. & Strelets, V. V. Electrochemistry of metallocenes at very negative and very positive potentials. Electrogeneration of 17-electron Cp2Co2+, 21-electron Cp2Co2−, and 22-electron Cp2Ni2− species. Inorg. Chem. 32, 3528–3531 (1993).

17. Kreye, M. et al. Synthesis and Reactivity of Sterically Encumbered Diazaferrrocenes. Organometallics 32, 5887–5898 (2013).

18. Connelly, N. G. & Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. Chem. Rev. 96, 877–910 (1996).

19. Malischewski, M., Adelhardt, M., Sutter, J., Meyer, K. & Seppelt, K. Isolation and structural and electronic characterization of salts of the decamethylferrocene dication. Science 353, 678–682 (2016).

20. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 98, 5648–5652 (1993).

21. Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B 37, 785–789 (1988).

22. Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. Phys. Rev. B 33, 8822–8824 (1986).

23. Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. J. Chem. Phys. 98, 1372–1377 (1993).

24. Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A 38, 3098–3100 (1988).
25. Weigend, F. & Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. Phys. Chem. Chem. Phys. 7, 3297–3305 (2005).

26. Neese, F. Software update: the ORCA program system, version 4.0. Wiley Interdiscip. Rev. Comput. Mol. Sci. 8, e1327 (2018).

27. Stoychev, G. L., Auer, A. A. & Neese, F. Automatic Generation of Auxiliary Basis Sets. J. Chem. Theory Comput. 13, 554–562 (2017).

28. McWilliams, S. F., Brennan-Wydra, E., Cory MacLeod, K. & Holland, P. L. Density Functional Calculations for Prediction of 57Fe Mössbauer Isomer Shifts and Quadrupole Splittings in β-Diketiminate Complexes. ACS Omega 2, 2594–2606 (2017).

29. Römelt, M., Ye, S. & Neese, F. Calibration of Modern Density Functional Theory Methods for the Prediction of 57Fe Mössbauer Isomer Shifts: Meta-GGA and Double-Hybrid Functionals. Inorg. Chem. 48, 784–785 (2009).

30. Gütlich, P., Bill, E. & Trautwein, A. Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Application. Springer, Berlin (2011).

31. Chilton, N. F., Anderson, R. P., Turner, L. D., Soncini, A. & Murray, K. S. J. Comput. Chem. 34, 1164–1175 (2013).

32. Ammeter. J. H, J. Magn. Res. 30, 299-325 (1978).

33. Smart, J. C. & Robbins, J. L. A low spin manganocene and its novel anionic derivative. Synthesis and characterization of decamethylmanganocene complexes. J. Am. Chem. Soc. 100, 3936–3937 (1978).

34. Robbins, J. L., Edelstein, N. M., Cooper, S. R. & Smart, J. C. Syntheses and electronic structures of decamethylmanganocenes. J. Am. Chem. Soc. 101, 3853–3857 (1979).

35. Malischewski, M. & Seppelt, K. Structural characterization of potassium salts of the decamethylmanganocene anion Cp*2Mn−. Dalton Trans. 48, 17078–17082 (2019).