

Supporting information

***rac*-1,2-*fc*(BMe₂)Br (**2**):** To a solution of 1,1'-dibromoferrocene (1.09 g, 3.16 mmol) in thf (18 mL) at -78°C was added *n*BuLi (1.98 mL of a 1.6M solution in hexanes, 3.16 mmol). After 30 min. tetramethylpiperidine (0.533 mL, 3.16 mmol) was added and the resulting mixture allowed to warm to -40°C. The temperature of the reaction was then *carefully* maintained between -40 and -30°C for 2 h. After this time, the reaction was again cooled to -78°C and FBMe₂ (1.13 g, 4.21 mmol, 90% purity as received from Sigma Aldrich) added as a solution in tetrahydrofuran (10 mL); the reaction mixture was allowed slowly to warm to 20°C and stirred for a further 15 h. The resulting red solution was diluted with ether (100 mL) and washed with water (50 mL) and brine (50 mL), before being dried *in vacuo* yielding the crude product as a dark red solid. Purification using column chromatography (hexane to 10% ethyl acetate/hexane) yielded **2** as a dark red amorphous solid. Yield: (1.225 g, 76%. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution in diethyl ether. Spectroscopic data for **2**: ¹H NMR (300 MHz, [D]chloroform, 20°C) δ_H 6.75 (s, 4H, aromatic CH of Mes), 4.98 (m, 1H, C₅H₃), 4.51 (virtual t, *J* = 2.5 Hz, 1H, C₅H₃), 4.38 (m, 1H, C₅H₃), 4.25 (s, 5H, Cp), 2.30 (s, 12H, ortho-CH₃ of Mes) and 2.26 (s, 6H, para-CH₃ of Mes). ¹³C NMR (75 MHz, [D]chloroform, 20°C) δ_C 139.5 (ortho-quaternary of Mes), 137.4 (para-quaternary of Mes), 127.9 (aromatic CH of Mes), 78.7, 77.0 (C₅H₃), 71.9 (Cp), 70.5 (C₅H₃), 24.3 (ortho-CH₃ of Mes), 21.1 (para-CH₃ of Mes), boron-bound quaternary carbons not observed. ¹¹B (96 MHz, [D]chloroform, 20°C): δ 78. UV-vis (dichloromethane): λ_{max} = 502 nm, ε = 1028 mol⁻¹ cm⁻¹ dm³. MS (EI⁺) 512 (100 %) M⁺; exact mass (calc. for M⁺, ¹¹B isotopomer) 512.0973, (meas.) 512.0981; Elemental microanalysis: (calc. for C₂₈H₃₀BBrFe C 65.54, H 5.89; (meas.) C 65.50, H 5.92. Crystallographic data for **2**: C₂₈H₃₀BBrFe, triclinic, P-1, *a* = 11.6882(2), *b* = 13.3858(2), *c* = 17.8620(3) Å, α 70.2595(7), β 75.9181(7), γ 67.4647(8)°, *V* = 2408.61(7) Å³, *Z* = 4, *D_x* = 1.415 Mg m⁻³, *M_r* = 513.11, *T* = 150(2) K. 19594 reflections collected, 10994 independent [R(int) = 0.066], 9258 observed [*I* > 2σ(*I*)]. *R*₁ = 0.1175, *wR*₂ = 0.2498 for observed unique reflections [*I* > 2σ(*I*)]; *R*₁ = 0.1285, *wR*₂ = 0.2555 for all unique reflections. Goodness of fit = 1.502. Max. and min. residual electron densities: 5.39 and -1.80 e Å⁻³. CCDC 742657. The ten largest q peaks are scattered across the asymmetric unit, with the largest peak being located ca. 1.14 Å from H173. The largest trough is located approximately in the centre of the phenyl group defined by C48, C49, C51, C52, C54 and C55. The residual peaks and troughs are probably due to poor data quality resulting e.g. from a damaged crystal, unresolved twinning etc. (i.e. from the poor quality of the crystal) Attempts to model these peaks were made, but without success. Despite the issues outlined above it seems unlikely that the overall connectivity of **2** is incorrect (especially given the reliability of the spectroscopic data), and no attempt is made to discuss the metrics obtained from the structure.

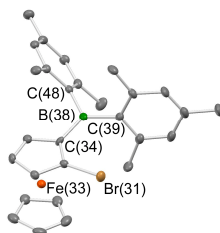


Fig. S1 Crystallographically determined molecular structure of **2**; hydrogen atoms omitted for clarity and thermal ellipsoids at the 30% probability level.

Crystallographic data for **4**: C₄₀H₄₀BF₂FeP, triclinic, P-1, *a* = 10.8437(3), *b* = 11.0155(3), *c* = 13.9298(4) Å, α 103.677(1), β 98.476(1), γ 95.908(1)°, *V* = 1582.54(8) Å³, *Z* = 2, *D_x* = 1.298 Mg m⁻³, *M_r* = 618.39, *T* = 150(2) K. 24749 reflections collected, 7156 independent [R(int) = 0.089], 4419 observed [*I* > 2σ(*I*)]. *R*₁ = 0.0495, *wR*₂ = 0.0880 for observed unique reflections [*I* > 2σ(*I*)]; *R*₁ = 0.1073, *wR*₂ = 0.1057 for all unique reflections. Goodness of fit = 0.956. Max. and min. residual electron densities: 1.19 and -1.03 e Å⁻³. CCDC 742658.

Crystallographic data for **5**: C₃₅H₃₇BF₂FeOS, orthorhombic, P 2₁2₁2₁, *a* = 9.3714(2), *b* = 11.8431(2), *c* = 25.5848(5) Å, *V* = 2839.57(10) Å³, *Z* = 4, *D_x* = 1.339 Mg m⁻³, *M_r* = 572.40, *T* = 150(2) K. 20354 reflections collected, 6016 independent [R(int) = 0.064], 4476 observed [*I* > 2σ(*I*)]. *R*₁ = 0.0441, *wR*₂ = 0.0990 for observed unique reflections [*I* > 2σ(*I*)]; *R*₁ = 0.0536, *wR*₂ = 0.1055 for all unique reflections. Goodness of fit = 0.980. Max. and min. residual electron densities: 1.64 and -0.87 e Å⁻³. Flack parameter = 0.022(19). CCDC 742659.