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Synthetic, redox and coordination chemistry of bis(pentachlorophenyl)boryl ferrocene, FcB(C₆Cl₅)₂



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ABSTRACT

Two synthetic approaches to bis(pentachlorophenyl)boryl ferrocene have been explored. One mirrors that used in a novel approach to FcB(C₆F₅)₂ from FcBBr₂, but is less selective than its perfluorinated counterpart on account of the greater steric bulk of LiC₆Cl₅ over LiC₆F₅. This approach does, however, provide a viable route to unsymmetrical mono(pentachlorophenyl) derivatives of the type FcB(C₆Cl₅)_Ar through the intermediacy of the mono-substituted species FcB(C₆Cl₅)Br. FcB(C₆Cl₅)₂ itself is best synthesized from ferrocenyllithum and ClB(C₆Cl₅)₂ and is a violet—blue species featuring an extremely electron deficient Fe(II) centre ($E_{1/2} = +550$ mV with respect to ferrocene/ferrocenium). A combination of structural, spectroscopic and reactivity studies of these and related ferrocenylboranes allow some general comments to be made concerning the relative steric and electronic properties of the C₆Cl₅ group. Thus, in terms of their relative capabilities as electron-withdrawing groups the substituents examined can be ranked C₆Cl₅ > C₆F₅. Mes, while steric properties are ordered Mes > C₆Cl₅ > C₆F₅.

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Introduction

Functionalized ferrocenes play diverse roles in modern chemistry, with systems featuring pendant Lewis basic groups acting as donor ligands in various complexes exploited in homogenous catalysis, and those bearing Lewis acidic groups finding applications, for example, in polymer synthesis and in detection/sensing [1–4]. The latter field exploits cathodic shifts in the redox potential of the Fe(II) centre which can be induced, for example, on coordination of a Lewis base to a pendant boryl (-BX₂) unit [5,6]. The conversion of a mesomerically electron-withdrawing three-coordinate boryl function to an inductively donating four coordinate borate has been exploited in the design of systems used in the detection of anions such as fluoride and cyanide. More recently, bis(pentafluorophenyl)boryl ferrocene, FcB(C₆F₅)₂, originally synthesized by Piers and co-workers [7], has been exploited as one component of a 'frustrated Lewis pair' (FLP) capable of detecting nitrous oxide [8,9]. The formation of the ambiphilic N₂O adduct ${}^{t}Bu_{3}P \cdot NNO \cdot BFc(C_{6}F_{5})_{2}$ in the presence of ${}^{t}Bu_{3}P/FcB(C_{6}F_{5})_{2}$ brings about a selective colorimetric and electrochemical response [9].

The activation/trapping of small molecules using an FLP approach is known to be highly dependent on the cumulative acid/

base strength of the two components employed [8]. With this in mind, and given the recent syntheses of systems of the type $B(C_6F_5)_n(C_6Cl_5)_{3-n}$ [10], we sought to expand the current (very limited) pool of ferrocenylboranes possessing potent enough Lewis acidity for FLP chemistry. Thus in the current study we targeted bis(penta*chloro*phenyl)boryl ferrocene, FcB(C₆Cl₅)₂, and related systems [11].

Experimental

General procedures

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen, respectively. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS. Fluorobenzene was dried by refluxing over calcium hydride, distilled, sparged and stored over activated molecular sieves. NMR spectra were recorded in chloroform-*d*, benzene-*d*₆ or THF-*d*₈, which were dried over molecular sieves, potassium or calcium hydride respectively, and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H and ¹³C NMR spectra were recorded on Varian Mercury-VX-300 or Bruker AVII-500 spectrometers and referenced internally to residual protio-solvent (¹H) or solvent (¹³C)





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resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ¹¹B, ¹⁹F and ³¹P NMR spectra were referenced with respect to Et₂O·BF₃, CFCl₃ and 85% aqueous H₃PO₄, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. UV-vis spectra were collected on a Scintio UV S-2100 UV/Vis spectrometer. Elemental analyses were carried out at London Metropolitan University. 1-bromo-2.3.4.5.6-pentafluorobenzene and ferrocene were sourced commercially and used without further purification. FcBBr₂ [12], ClB(C₆Cl₅)₂ [10], FcBMes₂[6d] and MesLi [13] were prepared by literature routes $[Fc = ferrocenyl = (\eta^5 - C_5H_5)Fe(\eta^5 - C_5H_4); Mes = mesityl = 2,4,6-$ Me₃C₆H₂]. Ferrocenyllithium, FcLi, was prepared by a modified literature route [14]: ^tBuLi (45 mL of a 1.6 M solution in hexanes, 72 mmol) was added over 15 min to a suspension of ferrocene (16.0 g, 86 mmol) in THF (80 mL) at 0 °C. Immediately after the addition of *t*-BuLi, hexane (150 mL) was added and the suspension cooled to -78 °C. The resulting pyrophoric orange precipitate was separated by filtration at -78 °C, washed with pre-cooled hexane $(4 \times 50 \text{ mL})$ at $-78 \text{ }^\circ\text{C}$ and volatiles removed *in vacuo* to afford an orange powder (approximately 15 g). This powder was continuously extracted with hexane (200 mL) using a Soxhlet apparatus over a period of 12 h, until the extracts were colourless. The remaining solid was dried in vacuo to afford the target material as a highly pyrophoric orange powder. Yield 8.17 g, 59%.

Novel syntheses

Novel route to $FcB(C_6F_5)_2$ (**1**) from $FcBBr_2$

^{*n*}BuLi (1.6 M, 17.5 mL in hexanes, 28 mmol) was added dropwise to a solution of 1-bromo-2,3,4,5,6-pentafluorobenzene (3.47 mL, 28 mmol) in hexane (30 mL) at -78 °C. The resulting mixture was stirred at -78 °C for 45 min; a solution of FcBBr₂ (5.00 g, 14 mmol) in hexane (150 mL) was then added dropwise at -78 °C. The resulting mixture was allowed to warm to room temperature over a period of 12 h. Volatiles were removed *in vacuo* and the residue was extracted with hexane (3 × 50 mL). The combined organic extracts were concentrated *in vacuo* and the residue cooled to -20 °C to produce maroon crystals, which were separated by filtration at -20 °C and dried *in vacuo*. Yield: 4.80 g, 65%. ¹H, ¹¹B and ¹⁹F NMR data were in agreement with the literature values [7].

$FcB(C_6Cl_5)_2$ (2)

FcLi (0.33 g, 1.7 mmol) prepared as described above was added slowly at 6 °C to a suspension of ClB(C₆Cl₅)₂ (0.95 g, 1.7 mmol) in benzene (100 mL). The resulting purple suspension was allowed to warm to room temperature over 15 min, and then stirred for 15 h. The precipitate was separated by filtration and then extracted with benzene (2 \times 50 mL). The filtrate and extracts were combined and dried in vacuo to afford a purple solid (0.49 g), which was analysed by ¹H NMR and found to consist of a mixture ferrocene and the target material. The ferrocene impurity was removed by sublimation (at 70 °C and 10^{-2} mbar) to afford FcB(C₆Cl₅)₂ (**2**) as a violet solid. Yield: 0.33 g, 27%. Crystals of 2 · C₆D₆ suitable for X-ray diffraction were obtained by cooling a saturated solution in benzene. ¹H NMR (300 MHz, chloroform-*d*, 20 °C): $\delta_{\rm H}$ 5.00 (t, 2H, ${}^{3}J_{H-H} = 1.8$ Hz, C₅H₄B), 4.71 (t, 2H, ${}^{3}J_{H-H} = 1.8$ Hz, C₅H₄B), 4.32 (s, 5H, C₅H₅). ¹H NMR (300 MHz, benzene- d_6 , 20 °C): δ_H 4.52 (t, 2H, ${}^{3}J_{H-H} = 1.8$ Hz, C₅H₄B), 4.49 (t, 2H, ${}^{3}J_{H-H} = 1.8$ Hz, C₅H₄B), 3.95 (s, 5H, C₅H₅). ¹¹B{¹H} NMR (96 MHz, chloroform-*d*, 20 °C): δ_B 62. ¹³C {¹H} NMR (75 MHz, THF- d_8 , 20 °C): δ_C 139.9 (C₆Cl₅), 132.4 (C₆Cl₅), 129.6 (C₆Cl₅), 124.2 (C₆Cl₅), 77.9 (C₅H₄B), 74.2 (C₅H₄B), 67.8 (C₅H₅). No signal was observed for the boron bound carbon of C₅H₄B. MS (CI negative), m/z (%): 249.8 (43) $[C_6Cl_5]^-$, 537.7 (39) [C₅H₄B(C₆Cl₅)(C₆Cl₄)]⁻, 628.6 (100) [Fe(C₅H₄B(C₆Cl₅)₂)]⁻, 693.6 (16) $[FcB(C_6Cl_5)_2]^-$; accurate mass: calc. (for M⁺, ¹⁰B, ³⁵Cl, ⁵⁶Fe, isotopomer) 688.7081; meas. 688.7066. Elemental microanalysis: calc. for C₂₂H₉BCl₁₀Fe, C 38.05%, H 1.31%; meas. C 37.85, 37.92%, H 1.20, 1.21%. UV–vis (fluorobenzene) λ_{max} , nm (ε): 546 (358 L mol⁻¹ cm⁻¹). $E_{1/2}$ (0.05 M [^{*n*}Bu₄N][B(C₆F₅)₄] electrolyte in α, α, α -trifluorotoluene) = +550 mV, relative to FcH/FcH⁺. Crystallographic data for **2**·C₆D₆: C₂₈H₉BCl₁₀D₆Fe, M_r = 778.65, monoclinic, *P* 2₁/c, *a* = 9.2004(1), *b* = 22.2839(2), *c* = 14.7467(1) Å, β = 101.7501(4)°, *V* = 2960.03(5) Å³, *Z* = 4, ρ_c = 1.747 Mg m⁻³, *T* = 150 K, λ = 0.71073 Å. 12,403 reflections collected, 6721 independent [R(int) = 0.000] which were used in all calculations. R_1 = 0.0381, wR₂ = 0.0987 for observed unique reflections [*I* > 2 σ (I)] and R_1 = 0.0506, wR₂ = 0.1067 for all unique reflections. Max. and min. residual electron densities 0.52 and -0.56 e Å³. CSD reference: 1001876.

$FcB(C_6Cl_5)Br(3)$

ⁿBuLi (88 mL of a 1.6 M solution in hexanes, 14 mmol) was added dropwise to a suspension of hexacahlorobenzene (4.01 g, 14 mmol) in a 1:1 hexane/diethyl ether mixture (100 mL of each) at -78 °C. The resulting suspension was allowed to warm to approximately -40 °C, until the white insoluble material was consumed, yielding a yellow solution, which was quickly transferred to a suspension of FcBBr₂ (5.01 g, 14 mmol) in hexane (100 mL) at -78 °C. The resulting red suspension was allowed to warm to room temperature over 2 h, darkening noticeably around -30 °C, and was then stirred at room temperature for a further 12 h. Volatiles were removed in vacuo to afford a dark maroon tar. Condensing argon onto the tar (ca. 20 mL), subsequent mechanical manipulation of the solid to give a fine suspension in argon and then evacuation for a period of 1 h gave rise to a maroon powder. Yield 6.92 g, 93%. ¹H NMR (300 MHz, chloroform-*d*, 20 °C): $\delta_{\rm H}$ 4.87 (t, 2H, ${}^{3}J_{\rm H-H}$ = 1.8 Hz, C₅H₄B), 4.47 (t, 2H, ${}^{3}J_{\rm H-H}$ = 1.8 Hz, C₅H₄B), 4.32 (s, 5H, C₅H₅). ¹¹B{¹H} NMR (96 MHz, chloroform-*d*, 20 °C): δ_B 61. ¹³C{¹H} NMR (75 MHz, THF-*d*₈, 20 °C): δ_C 139.8 (C₆Cl₅), 134.1 (C₆Cl₅), 132.0 (C₆Cl₅), 76.6 (C₅H₄B), 76.4 (C₅H₄B), 73.0 (C₅H₄B), 70.8 (C₅H₅). MS (ESI positive) *m*/*z* (%): 185.9 (100) [FcH]⁺, 249.8 (34) [C₆Cl₅H]⁺, 461.8 (59) [FcB(C₆Cl₅)(OH)]⁺, 523.8 (16) [FcB(C₆Cl₅)Br]⁺; accurate mass: calc. (for M⁺, ¹⁰B, ³⁵Cl, ⁵⁴Fe, ⁷⁹Br isotopomer) 518.7850; meas. 518.8750. Elemental microanalysis: calc. (for C₁₆H₉BBrCl₅Fe) C 36.60%, H 1.73%; meas. C 36.13, 36.21%, H 1.32, 1.37%. *E*_{1/2} (0.05 M [^{*n*}Bu₄N][B(C₆F₅)₄] electrolyte in α,α,α. trifluorotoluene) = +382 mV, relative to FcH/FcH⁺.

$FcB(C_6Cl_5)(Mes)$ (4)

A suspension of FcB(C₆Cl₅)Br (0.858 g, 1.6 mmol) and MesLi (0.205 g, 1.6 mmol) in benzene (50 mL) was heated under reflux for 2 h. The reaction mixture was cooled to room temperature, volatiles removed in vacuo and the residue transferred as a suspension in a minimal amount of hexane onto a silica/hexane column. Elution with hexane gave rise to three bands which were isolated, the volatiles removed in vacuo from each and their composition analysed by ¹H NMR spectroscopy. The first, yellow band (0.03 g) was found to be ferrocene, the second, maroon band (0.39 g, 42%) was found to be the target material and the last, red band (0.08 g) was found to be unreacted starting material. 4 was isolated as a maroon solid in >95% purity (by multinuclear NMR) after removal of the hexane solvent. ¹H NMR (500 MHz, benzene d_{6} , 20 °C): δ_{H} 6.79 (s, 2H, CH of Mes), 4.49 (t, 2H, ${}^{3}J_{H-H} = 2.0$ Hz, C_5H_4B), 4.42 (t, 2H, ${}^3J_{H-H} = 2.0$ Hz, C_5H_4B), 3.95 (s, 5H, C_5H_5), 2.52 (s, 6H, ortho-CH₃ of Mes), 2.15 (s, 3H, para-CH₃ of Mes). ¹¹B{¹H} NMR (96 MHz, benzene- d_6 , 20 °C): δ_B 72 (br s). ¹³C{¹H} NMR (125 MHz, benzene-d₆, 20 °C): δ_C 140.4 (para-C of Mes), 139.5 (Ar-C), 138.2 (ortho-C of Mes), 133.6 (Ar-C), 133.4 (Ar-C), 132.2 (Ar-C), 129.6 (Ar-C), 129.1 (meta-C of Mes), 80.2 (C₅H₄B), 75.1



Scheme 1. A novel synthetic route to FcB(C₆F₅)₂ (1) and attempted route to FcB(C₆Cl₅)₂ (2).

(C₅H₄B), 70.3 (C₅H₅), 25.3 (*ortho*-CH₃ of Mes), 21.1 (*para*-CH₃ of Mes). The boron bound carbon of C₅H₄B was not observed. MS (ESI positive) m/z (%): 185.9 (31) [FcH]⁺, 249.8 (16) [C₆Cl₅H]⁺, 563.9 (100) [FcB(C₆Cl₅)Mes]⁺; accurate mass: calc. (for M⁺, ¹⁰B, ³⁵Cl, ⁵⁴Fe, ⁷⁹Br isotopomer) 558.9529; meas. 558.9525. UV–vis (fluorobenzene) λ_{max} , nm (ε): 529 (364 L mol⁻¹ cm⁻¹).

Crystallography

Data for $2 \cdot C_6 D_6$, $Fc(C_6 Cl_5)B(\mu_2-O)B(C_6 Cl_5)Fc \cdot \frac{1}{2}C_6 H_6$ and DMAP·B($C_6 F_5$)₂Fc were collected on a Nonius KappaCCD diffractometer at 150 K. Data collection and reduction were carried out using Collect and Denzo/Scalepack, respectively, structure solution using either Sir92 or Superflip, and refinement using CRYSTALS [15]. Complete details of all structures are contained within the respective CIFs which have been deposited with the CCDC (1001876–1001878).

Determination of Lewis acid acceptor number (AN)

A modified Gutmann method utilizing the ³¹P NMR signal of Et₃PO and a 1:3 ratio of Lewis base to Lewis acid was employed, following the protocol of Adamczyk-Woźniak et al. [16].

Electrochemistry

Electrochemical measurements were performed on a PAR AMETEK VersaSTAT 3 potentiostat under nitrogen within a Saffron Omega Scientific glove-box. The cyclic voltammetry measurements were carried out in a supporting electrolyte of 0.05 M [n Bu₄N] [B(C₆F₅)₄] in α , α , α -trifluorotoluene, using a silver quasi-reference electrode, a platinum working electrode and a platinum wire auxiliary electrode.

Results and discussion

Synthetic and structural studies

 $FcB(C_6F_5)_2$ (1) can be synthesised conveniently and in good yield (65%) by the treatment of FcBBr₂ with two equivalents LiC₆F₅, itself generated *in situ* from either C₆F₆ or C₆F₅Br and ⁿBuLi at -78 °C (Scheme 1). This synthetic route avoids the use of either ClB(C₆F₅)₂ or [HB(C₆F₅)_{2]n} (and associated tin-containing precursors) which are inherent in either of the published routes to 1 [7]. In addition, it points to a simple, versatile approach for variation in the boronbound aryl substituents starting from a common intermediate, i.e.

FcBBr₂. Thus, initial attempts to synthesize the novel borane FcB(C_6Cl_5)₂ (**2**) sought to exploit the analogous route from FcBBr₂ and two equivalents of LiC₆Cl₅. However, under all reaction conditions screened, mixtures of the target compound FcB(C_6Cl_5)₂ (**2**), unreacted FcBBr₂ and partially substituted FcB(C_6Cl_5)Br (**3**) were obtained. Attempts to separate **2** from **3** proved unsuccessful: attempts at fractional recrystallization resulted in co-precipitation, while column chromatography could not adequately separate the two compounds and led additionally to contamination with traces of Fc(C_6Cl_5)B(μ_2 -O)B(C_6Cl_5)Fc (see ESI).

That the reaction of FcBBr₂ with two equivalents of LiC_6F_5 proceeds without issue, while the analogous reaction with LiC₆Cl₅ does not, is thought to be a consequence of steric effects. Consistently, when only one equivalent of LiC₆Cl₅ is employed, the reaction with FcBBr₂ allows for the facile, controlled introduction of a single perchlorophenyl group. The compound so generated, FcB(C₆Cl₅)Br (3), is a maroon solid, available in good yield (90-95%) and has been characterized by ¹H, ¹¹B and ¹³C NMR spectroscopy, mass spectrometry and elemental microanalysis. Although the thermal frailty of LiC₆Cl₅ prevents the subsequent use of forcing conditions to substitute the remaining boron-bound bromide (to generate **2**) [17], the reaction of **3** with one equivalent of the more robust lithium arvl LiMes in refluxing benzene vields $FcB(C_6Cl_5)(Mes)$ (4: Scheme 2). After work-up, compound 4 was isolated in moderate vield (35-45%) as a maroon solid, and characterized by ¹H, ¹¹B and ¹³C NMR spectroscopy and mass spectrometry (including accurate mass determination). Thus, under more forcing conditions, a second aryl group can indeed be assimilated by the $[FcB(C_6Cl_5)]$ fragment.

An alternative, more selective, pathway to the target compound 2 was therefore investigated as shown in Scheme 3. This route utilizes the chloroborane, $ClB(C_6Cl_5)_2$, reported by Ashley et al. [10] and FcLi, itself synthesized by a modified procedure from that reported in the literature [14]. A complication arises from the reaction of lithioferrocene with a C-Cl rather than with the B-Cl bond. This unwanted side reaction was encountered when the two reagents were mixed as solutions at -78 °C and slowly warmed to room temperature; its extent could, however, be minimized by adding FcLi as a solid powder to a benzene solution of ClB(C6Cl5)2 at 6 °C. After work-up, 2 could be isolated as a purple solid, albeit in relatively low yield (25–30%). The measured ¹H and ¹³C NMR spectra are fully consistent with the proposed structure, with further confirmation of identity and purity coming from mass spectrometry and elemental analysis, respectively. The structure of 2 in the solid state was subsequently determined by X-ray crystallography (Scheme 3).



Scheme 2. Synthetic route to FcB(C₆Cl₅)Br (3) and FcB(C₆Cl₅)(Mes) (4).



Scheme 3. Synthesis of FcB(C₆Cl₅)₂ (2) from FcLi. Molecular structure of 2 · C₆D₆ as determined by X-ray crystallography. Hydrogen atoms and benzene-*d*₆ solvate molecule omitted for clarity and thermal ellipsoids drawn at the 50% probability level. Key geometric parameters are given in Table 1.

The ¹¹B NMR spectrum of **2** in benzene- d_6 features a broad peak at $\delta_B = 62$ ppm, i.e. somewhat downfield of that reported for FcB(C₆F₅)₂ (**1**; $\delta_B = 53$ ppm) [7]. In the case of **1**, the chemical shift is thought to reflect a degree of pyramidalization at boron caused by the presence in solution of a weak Fe \rightarrow B donor/acceptor interaction [7]. In the case of **2**, however, crystallographic evidence in the solid state argues against the presence of an analogous interaction (vide infra) and the ¹¹B shift in solution is more in line with those reported for unperturbed three-coordinate triarylboranes [7].

In certain aspects the molecular structure of **2** in the solid state is similar to that reported for its pentafluorophenyl counterpart, 1 (Table 1). Thus, for example, the B–C bond lengths involving both the ferrocenvl and arvl substituents are not significantly different for the two systems. The structure of 1, however exhibits a noticeable bending of the borane unit toward the iron centre, such that the Cp centroid– C_{ipso} –B angle deviates significantly from linearity (by ca. 16°). Piers and co-workers ascribe this effect to a degree of electron donation from iron-based orbitals to the highly electron deficient boron centre [7,18]. In the case of 2, however, the corresponding Cp centroid-Cipso-B angle is essentially linear (177.4°) and the Fe…B contact much longer [3.185(3) Å, cf. 2.924 Å for 1 [7]. Moreover, the sum of the C–B–C angles for $2(359.8^{\circ})$ is reflective of a strictly planar borane fragment. Thus, there is no evidence for an analogous $Fe \rightarrow B$ donor/acceptor formulation for 2. These differences we again ascribe primarily to steric factors, with the bulkier pentachlorophenyl substituents preventing any structurally significant interaction.

Probes of the relative electron deficiency and Lewis acidity of $FcB(C_6Cl_5)_2$

Comparisons with $FcB(C_6F_5)_2(1)$

The electrochemical properties of **1** and **2** have been compared as solutions in α , α , α -trifluorotoluene using a [${}^{n}Bu_{4}N$][B(C₆F₅)₄] electrolyte ([${}^{n}Bu_{4}N$][PF₆] has been shown previously to react with the cation formed by single electron oxidation of **1** leading to

Table 1

Comparison of key bond lengths (Å) and angles (°) of $FcB(C_6F_5)_2$ (1) [7] and $FcB(C_6Cl_5)_2$ (2).

Parameter	FcB(C ₆ F ₅) ₂ (1) [7]	$FcB(C_6Cl_5)_2(2)$
d(B-Caryl)/Å	1.604(4), 1.584(4)	1.609(3), 1.617(3)
$d(B-C_{Fc})/Å$	1.501(4)	1.514(4)
$\angle (C_{aryl} - B - C_{aryl})/^{\circ}$	118.4(2)	118.4(2)
$\angle (C_{aryl} - B - C_{Fc})/^{\circ}$	118.0(2), 122.5(2)	120.3(2), 121.1(2)
$\Sigma{(C-B-C)}/{\circ}$	358.9	359.8
d(Fe…B)/Å	2.924	3.185(3)

irreversible electrochemical processes) [7]. In line with the findings reported for $B(C_6X_5)_3$ (X = F, Cl) [10], we find that the C_6Cl_5 substituent is more electron withdrawing than its perfluorophenyl analogue. Accordingly, the oxidation potential of the pendant ferrocenyl group in 2 is +550 mV (with respect to ferrocene/ferrocenium), while that 1 is +450 mV. Thus, 2 is shown to be intrinsically more electron deficient than 1. In addition, the Lewis acidities determined for 1 and 2 by the Gutmann-Beckett method using Et_3PO reveal that **2** is also the stronger Lewis acid [19]. Thus, the acceptor numbers determined for 1 and 2 using this approach are 71.9 and 81.0, respectively. The value determined for 1 can be put into context by that previously reported for $B(C_6F_5)_3$ (78.2) [16], and presumably reflects not only the more electron rich nature of the ferrocenyl group (compared to C_6F_5), but also the retention in solution of the Fe \rightarrow B interaction [7], which further biases binding thermodynamics against Et₃PO coordination. Consistently, Piers and co-workers report a Lewis acidity for 1 on the Childs scale of 0.37 [cf. 0.77 for B(C₆F₅)₃ and 1.00 for BBr₃] The greater steric demands of the C_6Cl_5 group (over C_6F_5) are presumably responsible for the lack of any significant Fe \rightarrow B interaction in **2**, which consequently renders it more Lewis acidic, provided the incoming Lewis base is not itself sterically impeded.

While studies of the reduction potentials of $B(C_6F_5)_3$ and $B(C_6Cl_5)_3$ are (in keeping with our CV studies of **1** and **2**) indicative of the greater electron-withdrawing capabilities of the C_6Cl_5 group, it is also known (i) that $B(C_6F_5)_3$, but not $B(C_6Cl_5)_3$, will bind Et_3PO in dichloromethane- d_2 solution [10]; and (ii) that $B(C_6F_5)_3$ has a greater fluoride ion affinity than $B(C_6Cl_5)_3$ [20]. Both of these observations are consistent with the dominance of steric (rather than electronic) factors in Lewis base coordination by *tris*(pentahalophenyl)boranes, in that the bulkier but more electron deficient system $B(C_6Cl_5)_3$ binds more weakly. That $FcB(C_6Cl_5)_2$ (**2**) not only binds Et_3PO [unlike $B(C_6Cl_5)_3$], but is determined to be a stronger Lewis acid than $FcB(C_6F_5)_2$ (**1**) – at least with this particular Lewis basic 'probe' – would imply that the incorporation of the ferrocenyl group markedly reduces the steric congestion at the boron centre compared to $B(C_6X_5)_3$ systems.

Comparisons within the series $FcB(C_6Cl_5)(Mes)_{2-x}$

While we have been unable to access the mixed Lewis acid $FcB(C_6F_5)(C_6Cl_5)$, due to the explosive [21] incompatibility of LiC_6F_5 with the forcing conditions required to substitute the remaining bromide in $FcB(C_6Cl_5)Br$ (3), the related series of boranes $FcB(C_6Cl_5)_2$ (2), $FcB(C_6Cl_5)(Mes)$ (4) and $FcBMes_2$ (5)[6d] has now been synthesized. We therefore sought to explore the trends in electron deficiency and Lewis acidity at boron as a function of the formal C_6Cl_5/Mes substitution process.



Fig. 1. UV-Vis spectra (left to right) of FcBMes₂ (5), FcB(C₆Cl₅)(Mes) (4) and FcB(C₆Cl₅)₂ (2) in fluorobenzene solution (ca. 1.3 mM).

Cyclic voltammetry measurements readily testify to the expected increase in electron-withdrawing capabilities for the C₆Cl₅ group over mesityl (e.g. $E_{1/2}$ for $\mathbf{5} = +180$ mV with respect to ferrocene/ferrocenium, cf. +550 mV for 2),[6d] and such electronic factors are also shown to have pronounced spectroscopic consequences. Thus, on increasing the number of perchlorophenyl groups, the wavelength corresponding to maximum absorption intensity in the UV-vis spectrum (λ_{max}) undergoes successive red shifts, with maxima at 507 nm, 529 nm and 546 nm being measured for fluorobenzene solutions of 5, 4 and 2 respectively (Fig. 1). Accordingly, while such solutions of 5 are red and those of 4 maroon, those of 2 are unusual for a neutral ferrocene-derived species in being blue-violet in colour (SI). Typically the LUMO of a borane of this type is known to feature a large contribution from the formally vacant p orbital at boron [4]. Thus, successive replacement of mesityl substituents with more electronwithdrawing C₆Cl₅ groups lowers the LUMO energy and shifts the radiation absorbed to longer wavelength.

While the values of λ_{max} measured for **5**, **4** and **2** reflect a continuous progression in terms of electronic properties, the Gutmann-Beckett determined Lewis acidities reveal a much less smooth trend. Thus, the apparent acceptor numbers (ANs) determined for these three compounds are 11.5, 12.0 and 81.0, respectively. What is striking are the very low (and remarkably similar) Lewis acidities determined for the mesityl containing systems $FcBMes_2$ (5) and $FcB(C_6Cl_5)(Mes)$ (4). To put these numbers in perspective, the ANs determined even for relative weak boronate ester Lewis acids tend to be in the range 65–75 [16]. The data (for 4 and **5**) are consistent with the high steric demands of the mesityl substituent: we hypothesize that mesityl-containing Lewis acids of this type are too sterically demanding for facile adduct formation with the Et₃PO probe. A similar explanation can be offered, for example, for the markedly different acceptor numbers determined using the same method for the ortho-(14.0), meta-(69.6) and para-(69.0) isomers of the catecholate esters of fluorophenylboronic acid [16].

Conclusions

Two synthetic approaches to bis(pentachlorophenyl)boryl ferrocene have been explored: one mirroring that used in a novel approach to FcB(C₆F₅)₂ (**1**) from FcBBr₂, is less selective than its perfluorinated counterpart on account of the greater steric bulk of LiC₆Cl₅. This approach does however, provide a viable route to unsymmetrical mono(pentachlorophenyl) derivatives of the type FcB(C₆Cl₅)X (X = Br, Mes). FcB(C₆Cl₅)₂ (**2**) is best synthesized from ferrocenyllithum and ClB(C₆Cl₅)₂ and is a violet–blue species characterized by an extremely electron deficient Fe(II) centre ($E_{1/2} = +550$ mV with respect to ferrocene/ferrocenium). A combination of structural, spectroscopic and reactivity studies of these and related ferrocenylboranes allow some general comments to be made concerning the relative steric and electronic properties of the C₆Cl₅ group. Thus, it is apparent that in terms of their capabilities as electron-withdrawing groups the substituents examined can be

ranked $C_6Cl_5>C_6F_5>$ Mes, while steric properties are ordered Mes $>C_6Cl_5>C_6F_5.$

Appendix. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.07.003.

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