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Perfluoroaryl boryl complexes: synthesis, spectroscopic and structural characterisation of a complex containing the bis(pentafluorophenyl)boryl ligand†

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The synthesis, spectroscopic and structural characterisation of the bis(pentafluorophenyl)boryl derivative CpFe$(CO)_2B(C_6F_5)_2$ are reported.

Transition metal boryl complexes ($L_nM–BX_2$) have been the centre of intense recent research activity,[1] partly because of their involvement in the hydro- and diboration of carbon–carbon multiple bonds,[2] but also because of their implication in highly selective stoichiometric and catalytic functionalization of alkanes under either photolytic or thermal conditions.[3–5] Such studies of reactivity have been complimented by numerous structural investigations in which the nature of the metal–boron bond has been probed by crystallographic, spectroscopic and computational methods.[1,6] One of the significant questions investigated by such studies is the potential for the extremely strongly σ-donor boryl ligand also to act as a π acid by utilizing the vacant boron-based orbital of π-symmetry. For complexes bearing π donor boryl substituents (*e.g.* X_2 = cat, *ortho*-$O_2C_6H_4$) research to date implies a relatively minor role for π back bonding;[1] to what extent the nature of the M–B bond can be altered by variation in the electronic properties of X is the subject of this and other studies.[7] Ultimately a better understanding of the nature of the M–B bond may help to rationalize the unusual reactivity of such complexes.

Pentafluorophenyl substituted boranes have received much recent attention due to the robustness of the B–C bond, the exploitation of their high Lewis acidity in a variety of catalytic applications and reports that $(\eta^5\text{-}C_5Me_5)$Ir derivatives mediate the activation of alkanes and arenes by $[HB(C_6F_5)_2]_2$.[4] Given that $B(C_6F_5)_3$ is reported to have a Lewis acidity intermediate between that of BCl_3 and BF_3,[8] and that complexes containing the BF_2 ligand have only recently been reported,[9] we have sought to develop synthetic routes to metal complexes containing the $B(C_6F_5)_2$ ligand. Such complexes would be expected to contain a highly Lewis acidic boron centre and might therefore act as useful probes of the potential for boryl ligands to act as π acids.

The reaction between CpFe$(CO)_2$Na and Cl$B(C_6F_5)_2$[10] **1** in toluene at 20 °C over a period of 3 h was monitored by ^{11}B NMR spectroscopy; the resonance due to the chloroborane precursor **1** was replaced by a low-field signal at δ_B 121.5, in the region characteristic of alkyl and aryl substituted transition metal boryl complexes. After work up CpFe$(CO)_2B(C_6F_5)_2$ **2** was obtained as air-, moisture- and photolytically-sensitive golden yellow crystals in yields of up to 42%.‡ **2** has been characterised§ by ^1H, ^{13}C, ^{11}B and ^{19}F NMR, IR, mass spectrometry, elemental analysis and single crystal X-ray diffraction.¶

The formula of **2** was evident from multinuclear NMR data and the structure was confirmed by the results of a single crystal X-ray diffraction study. The asymmetric unit consists of two very similar but independent molecules, each of which adopts the expected half sandwich geometry at the iron centre with the coordination sphere being completed by two carbonyls and one bis(pentafluorophenyl)boryl ligand (one of the two molecules is shown in Fig. 1). The geometry of the $B(C_6F_5)_2$ ligand is such that the planes of the C_6F_5 and BC_2 units are inclined at an average angle of 67.1(3)° to one another. This compares to an average value of 34.3° for Cl$B(C_6F_5)_2$,[10] and almost certainly reflects the greater steric demands of CpFe$(CO)_2$ compared to Cl. **2** represents, to our knowledge, the first example of a crystallographically characterized transition metal complex containing the $B(C_6F_5)_2$ ligand. Fe–B distances for the two independent molecules are 1.965(5) and 1.964(4) Å, values which are comparable to the distances found in CpFe$(CO)_2$B(cat) **3** [1.959(6) Å],[5] Cp*Fe$(CO)_2$B(cat) [1.980(2) Å],[5] and CpFe$(CO)_2BO_2C_6H_2O_2BFe(CO)_2$Cp [1.971(2) Å].[11] This compares to an average value of 2.015(6) Å found for related boryl complexes,‖ and the significantly longer bond found in the analogous diphenylboryl complex, CpFe$(CO)_2BPh_2$ **4** [2.034(3) Å].[5] The carbonyl stretching frequencies for **2** (2014 and 1968 cm^{-1}) are also comparable to those for **3** and **4** (2024, 1971 and 2021, 1951 cm^{-1}),[5] and somewhat higher than the average values for CpFe$(CO)_2$ boryl complexes (2007 and 1949 cm^{-1}).‖

Despite the larger steric demands of the $B(C_6F_5)_2$ ligand compared to $B(C_6H_5)_2$, the shorter Fe–B distance in **2**

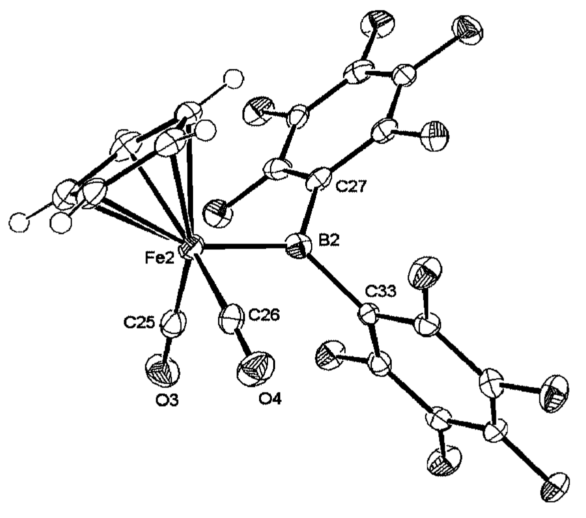

Fig. 1 Molecular structure of one of the two independent molecules of **2**. Relevant bond lengths (Å) and angles (°): Fe(2)–B(2) 1.965(5), Fe(2)–centroid 1.739(4), Fe(2)–C(25) 1.760(4), Fe(2)–C(26) 1.751(4), B(2)–C(27) 1.595(5), B(2)–C(33) 1.598(5); C(25)–Fe(2)–C(26) 95.0(2), Fe(2)–B(2)–C(27) 122.7(3), Fe(2)–B(2)–C(33) 125.8(2), C(27)–B(3)–C(33) 111.4(3), centroid–Fe(2)–B(2)–C(27) 28.4(3).

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† Electronic supplementary information (ESI) available: computational methodology, bond order calculations, calculated and crystallographically determined structural parameters and experimentally determined CO stretching frequencies for iron–boryl complexes. See http://www.rsc.org/suppdata/cc/b1/b106881b/

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Table 1 Calculated bonding parameters for complexes **2**–**4**

Compound	BDE (D_0)[a]/ kJ mol^{-1}	Mayer bond order	Breakdown of covalent contribution to bond[b] (%)		Electrostatic contribution to BDE[c]/kJ mol^{-1}
			σ	π	
2	224.2	0.999	81.9	18.0	66.7
3	274.6	0.957	89.2	10.7	12.0
4	231.2	0.888	90.4	9.5	40.4

[a] Bond dissociation energy (D_0) associated with homolytic cleavage of the Fe–B bond. [b] Decomposition of bonding density according to σ and π symmetry calculated using the method described in ref. 7 and also in the ESI.† [c] Electrostatic contribution to BDE calculated on an atom pair interaction basis, taking atomic charges from the Mulliken analysis.

(compared to **4**) testifies to the greater Lewis acidity of the boron centre. In addition, the torsion angle (θ) between the Cp centroid–Fe–B and BC_2 planes is significantly smaller in **2** [average value of 28.2(3)° for **2** *vs.* 75° for **4**]. Hoffmann and coworkers have concluded that a value of $\theta = 0°$ provides for best overlap between metal and ligand π orbitals in the pseudo-isoelectronic $CpFe(CO)_2CH_2^+$ system.[12] The smaller angle measured for **2** may therefore also be indicative of a stronger π interaction than in **4**, although almost certainly the high steric demands of the $B(C_6F_5)_2$ ligand prevent the attainment of a virtually coplanar arrangement such as that found in **3** (7.9°).

Further investigation of the bonding in $CpFe(CO)_2B(C_6F_5)_2$ and comparison with the related species **3** and **4** was carried out by the use of density functional theory,** the preliminary results of which are reported here. Calculated structural parameters for **2**–**4** are in good agreement with those measured crystallographically and are included in the ESI.† The bonding interaction between the Fe and B atom was calculated using an approach based on Mulliken analysis but with an additional subdivision of the bonding density into σ and π contributions. This was achieved by aligning the Fe–B bond with the *z*-axis and then calculating the bonding density for atomic orbital pairs of σ and π symmetry separately. The results of analysis of the calculated density are reproduced in Table 1. In comparison with **3** and **4**, the Fe–B bond in **2** shows significantly increased contributions not only from π symmetry covalent interactions but also from electrostatic attraction between the organometallic and boryl fragments. On the other hand it is worth mentioning that even in this system the barrier to rotation about the Fe–B bond is such that there is no sign of restricted rotation from VT-NMR experiments even at −110 °C.

In conclusion the synthesis, spectroscopic and structural characterization of the first transition metal complex containing the $B(C_6F_5)_2$ ligand are reported. As expected the electron withdrawing nature of the pentafluorophenyl substituents leads to an enhanced π interaction with the metal centre, although even here this still represents only a small contribution to the overall metal ligand bond. Further studies aimed at extending the known chemistry of this ligand are currently underway.

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Notes and references

‡ Dropwise addition of a solution of $ClB(C_6F_5)_2$[10] (0.4 g, 1.05 mmol) in 12 cm^3 toluene to 1 equivalent of $CpFe(CO)_2Na$ suspended in toluene at 20 °C led to the evolution of an orange–red solution and an off-white precipitate. Examination of the ^{11}B NMR spectrum of the solution after 3 h revealed that the signal at δ_B 59.1 characteristic of **1** had disappeared, the sole resonance observed being at δ_B 121.5. Filtration of the reaction mixture at this point, removal of volatiles *in vacuo* and recrystallization from hexanes at −30 °C afforded golden yellow crystals of **2** in yields of *ca.* 42%. Crystals suitable for X-ray crystallography could be grown by careful cooling of concentrated solutions in either toluene or hexanes.

§ *Spectroscopic data* for **2**: MS(EI): M$^+$ = 522 (weak), isotopic pattern corresponding to 1 B and 1 Fe atom, strong fragment ion peaks at *m*/*z* 494 [(M − CO)$^+$, 60%] and 466 [(M − 2CO)$^+$, 18%]. ^1H NMR ([$^2H_6$]benzene, 21 °C), δ 3.91 (s, C_5H_5). ^{13}C NMR ([$^2H_6$]benzene, 21 °C), δ 86.3 (C_5H_5), 137.3, 139.9, 140.7 (aromatic CF), 211.0 (CO). ^{11}B NMR (toluene, 21 °C), δ 121.5 (br). ^{19}F NMR (toluene, 21 °C), δ −132.9 (virtual dq, *ortho*-CF, *J* 21.2, 6.1 Hz), −153.7 (tt, *para*-CF, *J* 20.8, 6.1 Hz), −161.5 (m, *meta*-CF). IR (KBr disk, cm^{-1}) ν(CO) 2014s, 1968s. Elemental analysis: calc. for $C_{19}H_5BF_{10}FeO_2$, C, 43.72; H, 0.97%. Found: C, 43.55; H, 0.97%. No significant changes in the ^{19}F NMR spectrum were observed on cooling to −110 °C.

¶ *Crystallographic data* for $C_{19}H_5BF_{10}FeO_2$, **2**: triclinic, space group $P\bar{1}$, a = 10.6895(2), b = 13.4060(2), c = 13.6885(2) Å, α = 93.628(3), β = 93.588(3), γ = 113.060(3)°, U = 1793.08(5) Å^3, Z = 4, D_c = 1.933 Mg m^{-3}, M = 521.89, T = 120(2) K. 12458 reflections collected, 6094 independent (R_{int} = 0.0589) which were used in all calculations. R_1 = 0.0431, wR_2 = 0.0741 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0829, wR_2 = 0.0858 for all 6094 unique reflections. The max. and min. residual electron densities on the final difference Fourier map were 0.356 and −0.431 e Å^{-3}, respectively. Bond lengths (Å) and angles (°) not included in caption: Fe(1)–B(1) 1.964(4), Fe(1)–centroid 1.729(3), Fe(1)–C(6) 1.760(4), B(1)–C(8) 1.589(5); C(6)–Fe(1)–C(7) 93.98(17), centroid–Fe(1)–B(1)–C(14) 27.9(3). CCDC reference number 168238. See http://www.rsc.org/suppdata/cc/b1/b106881b/ for crystallographic data in CIF or other electronic format.

‖ Average Fe–B bond length measured for crystallographically characterized complexes of the type (η^5-C_5R_5)$Fe(CO)_2BX_2$; average symmetric and antisymmetric CO stretching frequencies measured for complexes of the type (η^5-C_5H_5)$Fe(CO)_2BX_2$.[5,11,13–15]

** *Details of DFT calculations*: gradient corrected DFT calculations were carried out using the ADF2000.01 code,[16] with functionals for exchange and correlation due to Becke[17] and Lee, Yang and Parr,[18] respectively. A basis set was constructed from Slater type orbitals with triple zeta valence shell and a single polarization function per atom (ADF IV). All structures were fully optimised at the BLYP level of theory with no symmetry restrictions. Convergence criteria: (i) energy change on next step $< 1 \times 10^{-3}$ E_h; (ii) gradient $< 1 \times 10^{-3}$ E_h Å^{-1}; and (iii) uncertainty in Cartesian coordinates $< 1 \times 10^{-2}$ Å.

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