

# Migratory insertion of $[B(C_6F_5)_2]$ into C–H bonds: CO promoted transfer of the boryl fragment†

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The reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{B}(\text{C}_6\text{F}_5)_2$  with CO has been shown to proceed *via* ligand substitution at the metal with accompanying transfer of the boryl fragment (*via* C–H insertion) to the Cp ring, thereby generating the zwitterion  $[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2\text{H}]\text{Fe}(\text{CO})_3$  in quantitative yield.

Reactions of transition metal boryl complexes with C–H bonds and the exploitation of such reactivity in hydrocarbon functionalization represent exciting recent steps towards the realization of one of the ‘Holy Grails’ of organometallic chemistry.<sup>1–3</sup> Initial reports of stoichiometric alkane and arene functionalization by group 6–8 metal boryl complexes<sup>1</sup> have been followed by the development of catalytic systems typically employing Rh or Ir metal centres and either photolytic or thermal activation.<sup>2,3</sup> Mechanistically, such reactivity has been shown to occur *via* processes involving oxidative addition of B–X (X = H or B) and C–H bonds, followed by facile reductive elimination of the B–C bonded product.<sup>4</sup>

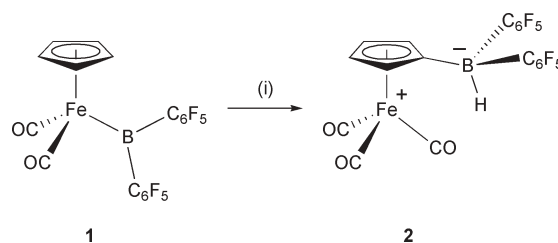
The fundamental reaction steps which lead to attack by transition metal boryl systems at C–H bonds have therefore been investigated in some depth. By contrast, reactions which result in the synthetic equivalent of boryl anion transfer are extremely rare.<sup>5</sup> Unlike the corresponding gallium ligand systems for example, reagents constituting the ‘free’  $[\text{BR}_2]^-$  anion are at best poorly defined.<sup>6</sup> In this paper we present preliminary results of the reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{B}(\text{C}_6\text{F}_5)_2$  with CO, which imply a new mechanism for attack at C–H bonds by a transition metal boryl complex. Migratory insertion of the  $[\text{B}(\text{C}_6\text{F}_5)_2]$  fragment into a C–H bond of the ancillary Cp ligand is driven by coordination of CO at the metal centre.

In the course of examining the photo-initiated reactivity of the perfluoroaryl boryl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{B}(\text{C}_6\text{F}_5)_2$ , **1**,<sup>7</sup> towards arenes we have observed the formation of small, but reproducible quantities of two boron-containing products. NMR data ( $\delta_{\text{B}} -24.8$ ,  $^1J_{\text{BH}} = 90$  Hz for the former,  $\delta_{\text{B}} -2.2$ ,

$^1J_{\text{BF}} = 66$  Hz,  $\delta_{\text{F}} -188.7$  for the latter) are consistent with species of the type  $[\text{Ar}_3\text{BX}]^-$  (X = H or F),<sup>8b,c</sup> additionally, monitoring of photolytic or thermal reactions over a prolonged timeframe (*ca.* 36 h) implies that the initially formed BH-containing product is converted into the latter BF species. Postulating that these two compounds might result from the reaction of **1** with small quantities of photolytically generated CO, we examined the behaviour of the parent boryl complex to exposure to carbon monoxide. Previous studies of the related complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{B}(\text{C}_6\text{H}_5)_2$  have been characterized by ‘immediate’ reaction with CO, although the iron and boron-containing products in this case were not identified.<sup>9</sup>

In the event, the reaction of **1** with CO at 1 atm pressure at room temperature leads to quantitative conversion (by  $^1\text{H}$  and  $^{11}\text{B}$  NMR) to a single compound having the same spectroscopic signals as the BH-containing species formed under photolytic conditions. A combination of multinuclear ( $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ) NMR, IR, mass spectrometry (including exact mass determination) and X-ray crystallography has been used to confirm that this compound is the zwitterionic complex  $[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2\text{H}]\text{Fe}(\text{CO})_3$  (**2**) featuring a hydroborate functionalized Cp ligand (Scheme 1).§

The NMR data for **2** are consistent with a Cp-pendant  $[\text{B}(\text{C}_6\text{F}_5)_2\text{H}]^-$  function {e.g.  $\delta_{\text{B}} -24.8$ ,  $^1J_{\text{BH}} 90$  Hz, cf.  $\delta_{\text{B}} -23.4$ ,  $^1J_{\text{BH}} 86$  Hz for  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2\text{H}]\text{WH}_3\}$ <sup>10c</sup> and the IR stretching frequencies are also consistent with  $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_3]^+$  and  $[\text{ArB}(\text{C}_6\text{F}_5)_2\text{H}]^-$  fragments  $\{\nu(\text{CO}) 2114, 2064, 2053\text{ cm}^{-1}$ , cf.  $2120, 2068\text{ cm}^{-1}$  for  $[\text{CpFe}(\text{CO})_3]^+[\text{PF}_6]^-$ ;  $\nu(\text{BH}) 2374\text{ cm}^{-1}$  cf.  $2365\text{ cm}^{-1}$  for  $[(\text{C}_6\text{F}_5)_3\text{BH}]^-$ .<sup>8a,b</sup> In addition, EI mass spectra display the expected isotopic profiles for each of the series of ions  $[\text{M} - \text{H}]^+$  and  $[\text{M} - n\text{CO}]^+$  ( $n = 1\text{--}3$ ). The solid state structure of **2** (Fig. 1) reveals the expected piano-stool geometry at iron and pendant four-coordinate hydroborate fragment. There is no evidence for any intramolecular interaction of the boron-bound



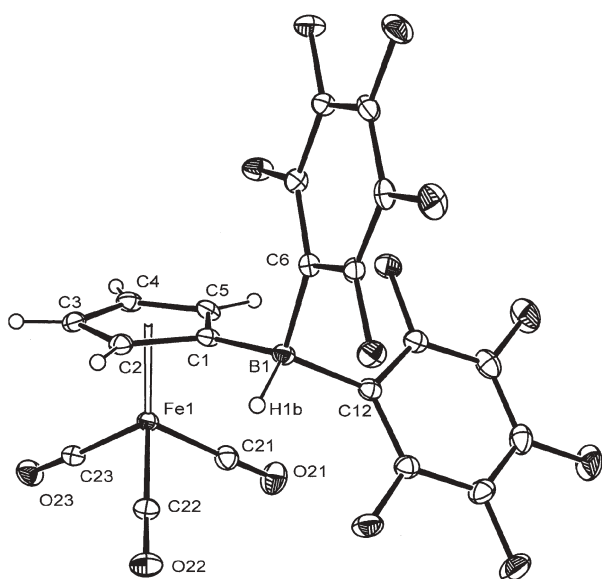
**Scheme 1** Synthesis of  $[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2\text{H}]\text{Fe}(\text{CO})_3$  (**2**) from **1** *via* CO-promoted boryl migration. Reaction conditions: (i) CO (1 atm),  $\text{C}_6\text{D}_6$ , 20 °C, quantitative by NMR ( $^1\text{H}$ ,  $^{11}\text{B}$ ), 74% isolated yield.

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**Fig. 1** Structure of  $[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2\text{H}]\text{Fe}(\text{CO})_3$  (**2**) with ORTEP ellipsoids set at the 50% probability level. Relevant bond lengths (Å) and angles (°) Fe–C(21) 1.799(2), Fe–centroid 1.721(2), B(1)–C(1) 1.615(3), B(1)–C(6) 1.646(3), B(1)–H(1b) 1.16(2), C(21)–Fe(1)–C(22) 97.4(1).

hydride (H1b) with the metal centre or with any of the co-ligands, as has previously been observed for unsaturated group 4 systems bearing pendant hydroborate functions.<sup>11</sup> The closest *intermolecular* contact involving H1b (2.32 Å to the hydrogen attached to Cp carbon C4) is within the sum of the conventional van der Waals radii (2.4 Å) but is longer than distances typically associated with unconventional hydrogen bonds (>2.2 Å).<sup>12</sup> A number of borate-functionalized cyclopentadienyl metal systems have been reported previously from attack by a strongly Lewis acidic hydrido- or halo-borane at an existing Cp ligand.<sup>10</sup> In addition, transfer of a metal-bound boron-containing fragment to a Cp spectator ligand has been postulated to account for the observed products in a number of systems. Thus, for example, the much lower activity of  $\text{CpFe}(\text{CO})_2\text{Bcat}'$  compared to  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{Bcat}'$  ( $\text{cat}' = 3,5\text{-}^i\text{Bu}_2\text{C}_6\text{H}_2\text{O}_2\text{-}1,2$ ) in stoichiometric alkane borylation chemistry has been ascribed to ready functionalization of Cp C–H bonds, and the formation of  $[\text{CpFe}(\text{CO})(\mu\text{-CO})_2\text{Fe}(\text{CO})(\eta^5\text{-C}_5\text{H}_4\text{BPh}_3)]^-$  from  $[\text{CpFe}(\text{CO})_2]^-$  and  $\text{BPh}_3$  is thought to occur *via* the initially formed adduct  $[\text{CpFe}(\text{CO})_2(\text{BPh}_3)]^-$ .<sup>1d,13</sup>

To our knowledge the conversion of **1** to **2** represents the first structurally authenticated example of migratory insertion into a C–H bond for an isolated transition metal boryl complex. Preliminary data for the reaction of **1** with the isonitrile (2,6- $\text{Me}_2\text{C}_6\text{H}_3$ )NC are also consistent with an analogous migratory insertion reaction. In both reactions, evidence that the boron-bound hydrogen atom in **2** is initially derived from the Cp ligand (rather than from the benzene solvent) is obtained from the formation of the same  $^1\text{H}$  isotopomer in benzene- $\text{d}_6$ . Reactivity towards CO or (2,6- $\text{Me}_2\text{C}_6\text{H}_3$ )NC which occurs *via* boryl ligand displacement has been observed previously, albeit with the boron containing product being formed *via* B–B reductive elimination rather than insertion chemistry.<sup>14</sup> For the chemistry presented herein, the net chemical transformation of **1** into **2** involves a very rare example of overall transfer of the boryl anion,  $[\text{BR}_2]^-$

(although the precise mechanism for transfer of the boryl fragment awaits more detailed kinetic and computational study).<sup>5</sup> Precedent for this type of migratory insertion chemistry can, however, be found for the isoelectronic carbene fragment,  $[\text{CR}_2]$ . Addition of  $\text{PF}_3$  to the rhodium carbene complex  $\text{CpRh}(\text{P}^i\text{Pr}_3)\text{CPh}_2$  leads to the formation of  $[\eta^5\text{-C}_5\text{H}_4(\text{CPh}_2\text{H})\text{Rh}(\text{P}^i\text{Pr}_3)(\text{PF}_3)]$  *via* insertion of  $[\text{CPh}_2]$  into one of the C–H bonds of the ancillary Cp ligand.<sup>15c</sup> An intramolecular process involving  $\text{PF}_3$  coordination and carbene ligand migration to the Cp ligand is proposed to operate in this system and an analogous concerted intramolecular process represents a plausible mechanism for the formation of **2**.

Finally, in order to determine the identity of the second formed (BF-containing) product in the initial photochemical experiments, isolated samples of **1** were subjected to photolysis in benzene. From these studies the identity of this second species was confirmed crystallographically as  $[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2\text{F}]\text{Fe}(\text{CO})_3$  (**3**, see electronic supplementary information, ESI),<sup>†</sup> which presumably originates from B–H/C–F exchange chemistry.

In conclusion, we have elucidated a new mode of reactivity for transition metal boryl compounds, one which is more characteristic of group 14 ligands,<sup>15</sup> and which demonstrates an alternative mechanism for attack on arene C–H bonds by metal boryl systems. Further studies designed to probe the scope and mechanism of this reactivity will be reported in a full account.

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## Notes and references

§ Synthesis of  $[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2\text{H}]\text{Fe}(\text{CO})_3$  (**2**): Room temperature reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{B}(\text{C}_6\text{F}_5)_2$  (**1**, 100 mg, 0.19 mmol) with CO (1 atm) in benzene or benzene- $\text{d}_6$  in the absence of light for 12 h leads to quantitative conversion (by  $^1\text{H}$  and  $^{11}\text{B}$  NMR) to **2**. Layering of the reaction mixture with hexanes and cooling to  $-30^\circ\text{C}$  leads to the isolation of **2** as pale yellow plates suitable for X-ray crystallography (isolated yield 78 mg, 74%). Spectroscopic data for **2**:  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  3.30 [b, 1H, BH], 3.71, 4.58 [m, both 2H,  $\text{C}_5\text{H}_4$ ].  $^{13}\text{C}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  83.5 [quaternary of  $\text{C}_5\text{H}_4$ ], 85.0, 94.8 [CH of  $\text{C}_5\text{H}_4$ ], 121.7 [*ipso*-C of  $\text{C}_6\text{F}_5$ ], 136.1, 138.0, 147.0 [CF of  $\text{C}_6\text{F}_5$ ], 202.3 (CO).  $^{11}\text{B}$  (160 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -24.8 [d,  $^1J_{\text{BH}} = 90$  Hz].  $^{19}\text{F}$  NMR (283 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -130.8 [d,  $^3J_{\text{FF}} = 20.8$  Hz, *ortho*-CF], -160.3 [t,  $^3J_{\text{FF}} = 20.8$  Hz, *para*-CF], -164.5 [m, *meta*-CF]. IR (KBr,  $\text{cm}^{-1}$ )  $\nu(\text{BH})$  2374 w,  $\nu(\text{CO})$  2114 st, 2064 m sh, 2053 vs. EIMS  $m/z$  548.9 [(M – H)<sup>+</sup>, 3%], correct isotope distribution for 1Fe and 1B atoms, significant fragment ions at  $m/z$  521.9 [(M – CO)<sup>+</sup>, 25%], 493.9 [(M – 2CO)<sup>+</sup>, 85%] and 465.9 [(M – 3CO)<sup>+</sup>, 100%]. Exact mass [(M – H)<sup>+</sup>; calc. 548.9438, meas. 548.9444]. Crystallographic data for **2**:  $\text{C}_{20}\text{H}_5\text{BF}_{10}\text{FeO}_3$ , triclinic,  $P\bar{1}$ ,  $a = 7.4491(3)$ ,  $b = 8.4985(4)$ ,  $c = 15.6646(5)$  Å,  $\alpha = 103.233(2)$ ,  $\beta = 90.730(2)$ ,  $\gamma = 92.815(2)^\circ$ ,  $U = 963.88(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_c = 1.895$  Mg m<sup>-3</sup>,  $M_r = 549.90$ ,  $T = 120(2)$  K. 19657 reflections collected, 4417 independent [ $R(\text{int}) = 0.0369$ ] which were used in all calculations.  $R_1 = 0.0319$ ,  $wR_2 = 0.0726$  for observed unique reflections [ $F^2 > 2\sigma(F^2)$ ];  $R_1 = 0.0393$ ,  $wR_2 = 0.0761$  for all unique reflections. Max. and min. residual electron densities: 0.29 and -0.46 e Å<sup>-3</sup>. Crystallographic data for **3**:  $\text{C}_{20}\text{H}_4\text{BF}_{11}\text{FeO}_3$ , triclinic,  $P\bar{1}$ ,  $a = 7.5733(4)$ ,  $b = 8.4751(4)$ ,  $c = 15.5751(7)$  Å,  $\alpha = 103.050(2)$ ,  $\beta = 90.431(2)$ ,  $\gamma = 92.131(2)^\circ$ ,  $U = 937.06(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_c = 1.938$  g cm<sup>-3</sup>,  $M_r = 567.9$ ,  $T = 120$  K,  $\lambda = 0.6751$  Å. 10183 reflections collected, 5501 independent [ $R_{\text{int}} = 0.0198$ ] which were used in all calculations.  $R = 0.0358$ ,  $R_w = 0.0992$  for observed unique reflections [ $F^2 > 2\sigma(F^2)$ ];  $R = 0.0378$ ,  $R_w = 0.1011$  for all unique reflections. Max. and min. residual electron density: 0.37 and -0.45 e Å<sup>-3</sup>. CCDC 602510 and 602511. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604141h

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