

# Linking of metal centres through boryl ligands: synthesis, spectroscopic and structural characterisation of a symmetrically bridged boryl complex $\text{CpFe}(\text{CO})_2\text{BO}_2\text{C}_6\text{H}_2\text{O}_2\text{BFe}(\text{CO})_2\text{Cp}$

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The synthesis, spectroscopic and structural characterisation of the symmetrically bridged boryl complex  $\text{CpFe}(\text{CO})_2\text{BO}_2\text{C}_6\text{H}_2\text{O}_2\text{BFe}(\text{CO})_2\text{Cp}$  are reported, together with analysis of the bonding by structural and DFT methods.

Transition metal boryl complexes ( $\text{L}_n\text{MBR}_2$ ) have been the subject of considerable recent research effort,<sup>1</sup> in part because of their involvement in versatile organic transformations such as the metal-catalysed hydroboration and diboration of multiple bonds.<sup>1,2</sup> Furthermore, derivatives of the type  $(\text{C}_5\text{R}_5)\text{M}(\text{CO})_n\text{BO}_2\text{C}_6\text{H}_2\text{Me}_2$  ( $\text{M} = \text{Fe}, \text{Ru}, n = 2$ ;  $\text{M} = \text{W}, n = 3$ ) have been shown to functionalise alkanes under photolytic conditions, with the unusual activity and regiochemistry of the reaction being tentatively ascribed to the presence of a ligand with Lewis acidic properties.<sup>3,4</sup> Recent studies have sought to probe the nature of the metal–boron interaction in metal boryl complexes by spectroscopic and crystallographic methods.<sup>1</sup> Almost exclusively,<sup>5</sup> such studies have focussed on monodentate boryl ligands adopting a terminal mode of coordination with respect to the metal centre.<sup>1</sup> Here, we describe a novel synthetic route to metal complexes featuring bidentate boryl ligands together with the structural and spectroscopic characterisation of the symmetrically bridged ( $\mu_2, \eta^1, \eta^1$ ) boryl system  $\text{CpFe}(\text{CO})_2\text{BO}_2\text{C}_6\text{H}_2\text{O}_2\text{BFe}(\text{CO})_2\text{Cp}$  **4**. Comparison of the mode of coordination of the bridging boryl ligand with that found for terminally bound analogues allows significant insight into the nature of the metal–boron interaction.

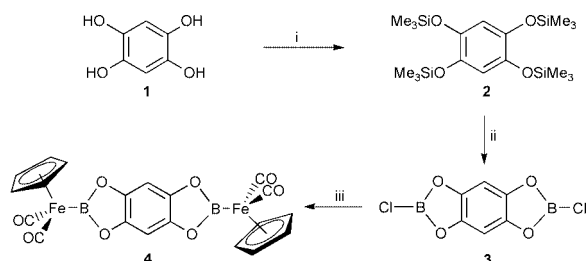
In our recent work we have been seeking to develop synthetic approaches to multifunctional boranes and boron halides based on polyhydroxybenzene frameworks (e.g. **3**) as potential precursors to multinuclear metal boryl complexes.<sup>6</sup> The synthetic route to compound **4** is outlined in Scheme 1; fuller details of the preparation of the trimethylsilyl and chloroborane precursors have been reported recently.<sup>6</sup> Addition of a toluene solution of **3** to 2 equivalents of  $\text{CpFe}(\text{CO})_2\text{Na}$  suspended in toluene at  $-30^\circ\text{C}$ , followed by warming to room temperature and stirring for 1 week led to the formation of an orange–red solution and a beige precipitate. Removal of the supernatant by filtration, extraction of the beige precipitate with  $\text{CH}_2\text{Cl}_2$  and

subsequent crystallisation by layering with 40/60 petroleum led to the formation of **4** in 45% yield. This compound is air sensitive, although thermally robust enough to survive unchanged at room temperature for several weeks under an argon atmosphere. It is sparingly soluble in non-polar organic media and decomposes rapidly in donor solvents such as thf or diethyl ether. Compound **4** has been characterised† by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{11}\text{B}$  NMR, IR spectroscopy, high-resolution mass spectrometry, elemental analysis and single crystal X-ray diffraction.

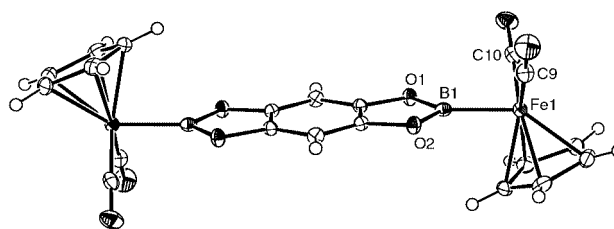
The single  $^{11}\text{B}$  NMR shift at  $\delta_{\text{B}}$  48 is entirely consistent with the formation of a symmetrically bridged molecule in which both of the B–Cl linkages in **3** have been replaced by Fe–B bonds, being very similar to those reported by Hartwig *et al.* for the terminally coordinated Bcat (cat = *ortho*- $\text{O}_2\text{C}_6\text{H}_4$ ) complexes  $(\text{C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{Bcat}$  [ $\delta_{\text{B}}$  51.8 ( $\text{R} = \text{H}$ )<sup>4</sup> and 54.3 ( $\text{R} = \text{Me}$ )<sup>4</sup> respectively]. Similar chemical shifts have also been reported by Braunschweig *et al.* for other terminal boryl ligands bound to iron.<sup>7,8</sup>

A single crystal X-ray diffraction study was undertaken on **4**,‡ the results of which confirm the formulation predicted on the basis of spectroscopic data and are illustrated in Fig. 1. The molecular structure consists of two piano-stool  $\text{CpFe}(\text{CO})_2\text{X}$  fragments linked in  $\mu_2, \eta^1, \eta^1$  fashion by the  $\text{BO}_2\text{C}_6\text{H}_2\text{O}_2\text{B}$  ligand.

The synthesis and structural characterisation of **4** allows, for the first time, the opportunity to compare the coordination behaviour of a bridging boryl ligand ( $\text{BO}_2\text{C}_6\text{H}_2\text{O}_2\text{B}$ ) with that of the analogous terminally bound ligand (Bcat). The complex  $\text{CpFe}(\text{CO})_2\text{Bcat}$  features near co-planarity of O–B–O and B–Fe–Cp centroid moieties consistent with the existence of a Fe–B  $\pi$  interaction involving the  $\text{CpFe}(\text{CO})_2$  HOMO and the ligand-based LUMO.<sup>4</sup> In the case of **4**, however, the crystal structure reveals a near orthogonal relationship [ $82.2(1)^\circ$ ] between the corresponding planes and implies no  $\pi$  interaction between ligand LUMO and Cp HOMO. This observation is consistent with the fact that the  $\nu(\text{CO})$  stretching frequencies for **4** are somewhat lower than those observed for  $\text{CpFe}(\text{CO})_2\text{Bcat}$  (2006 and  $1954\text{ cm}^{-1}$  vs. 2024 and  $1971\text{ cm}^{-1}$ ).<sup>4</sup> Given that the steric



**Scheme 1** Synthesis of the bridged boryl complex **4**. Reagents and conditions: i,  $\text{Me}_3\text{SiCl}$  (10 equiv.),  $\text{Et}_3\text{N}$ , toluene, 12 h at room temp., 78%; ii,  $\text{BCl}_3$  (2 equiv.), 40/60 petroleum, 3 h at  $50^\circ\text{C}$ , 89%; iii,  $\text{CpFe}(\text{CO})_2\text{Na}$  (2 equiv.), toluene, 1 week at room temp., 45%.



**Fig. 1** Molecular structure of  $\text{CpFe}(\text{CO})_2\text{BO}_2\text{C}_6\text{H}_2\text{O}_2\text{BFe}(\text{CO})_2\text{Cp}$ , **4**. Relevant bond lengths (Å) and angles ( $^\circ$ ): Fe(1)–B(1) 1.971(2), Fe(1)–C(10) 1.751(2), Fe(1)–C(9) 1.758(2), Fe–Cp(centroid) 1.721(2), B(1)–O(1) 1.406(2), B(1)–O(2) 1.406(2); C(9)–Fe–C(10) 93.97(8), B(1)–Fe–C(9) 88.32(8), B(1)–Fe–C(10) 87.35(8), O(1)–B(1)–O(2) 109.15(14), O(1)–B(1)–Fe(1) 121.94(12), O(2)–B(1)–Fe(1) 125.79(13), O(1)–B(1)–Fe(1)–Cp(centroid) 82.2(1).

requirements at the iron centre of the terminal Bcat and bridging  $\text{BO}_2\text{C}_6\text{H}_2\text{O}_2\text{B}$  ligands are likely to be very similar it seems evident that the difference in ligand coordination is due to electronic factors. The presence of two extra oxygen-based substituents on the central benzene ring in **4** might be expected to render the ring more electron rich, thereby increasing the degree of O–B  $\pi$  interaction and reducing the  $\pi$  acidity of the boron centre with respect to the iron.

Interestingly, although these structural and spectroscopic observations imply a weaker Fe–B interaction, the Fe–B bond length is lengthened only marginally in **4** compared to the terminally bound  $\text{CpFe}(\text{CO})_2\text{Bcat}$  system [1.971(2) vs. 1.959(6) Å].<sup>4</sup> Conceivably this may reflect the fact that the bond length in such systems is relatively insensitive to the  $\pi$  contribution to bonding. However, the Fe–B distance in **4** is also significantly shorter than that found in any other terminally bound iron boryl complex for which the B–Fe–Cp centroid and  $\text{BR}_2$  planes are close to orthogonal [average 2.048(5) Å]. Such a shortening of the Fe–B bond might also be consistent with a weak  $\pi$  interaction between the boryl LUMO and the Fp HOMO – 2 (a  $1a'$   $\pi$  type MO which is perpendicular to the HOMO<sup>9</sup>). Such an interaction has been suggested for the complex  $\text{CpFe}(\text{CO})_2\text{BPh}_2$  [which, at 2.034(3) Å,<sup>4</sup> has a markedly longer Fe–B bond than **4**] and has been discussed by Hoffmann and coworkers in their analysis of ligand orientation in Fp–carbene complexes.<sup>9</sup>

Comparison of the bonding in **4** and  $\text{CpFe}(\text{CO})_2\text{Bcat}$  was further aided by DFT calculations<sup>10</sup> carried out for the model compound  $\text{CpFe}(\text{CO})_2\text{BO}_2\text{C}_2\text{H}_2$ , **5**, the preliminary results of which are reported here.¶ Total energies were calculated for various rotamers of the molecule **5** in which the angle between the B–Fe–Cp centroid and O–B–O planes was varied by rotation about the Fe–B bond in  $10^\circ$  intervals between 0 and  $90^\circ$ . Energy minima are found for  $\theta = ca. 10$  and  $80^\circ$ . These observations are indeed consistent with the presence of weak  $\pi$  type interactions between the Fp HOMO and boryl-based LUMO for the near parallel orientation of the B–Fe–Cp centroid and O–B–O planes and between the Fp HOMO – 2 and boryl LUMO for the perpendicular orientation. The calculated energy difference between these two minima is very small (0.1 kJ mol<sup>-1</sup> at the gradient corrected DFT level of theory), such that the adoption of one particular orientation in the solid state may well be influenced by crystal packing forces.

The structure of **4** illustrates the coordination behaviour of a symmetrical  $\mu_2, \eta^1, \eta^1$  boryl ligand and demonstrates significant differences in metal–boron interaction compared to terminal  $\eta^1$  analogues. The synthetic methodology outlined in Scheme 1, together with the recent synthesis of the *bis*(borane)  $\text{HBO}_2\text{C}_6\text{H}_2\text{O}_2\text{BH}$ ,<sup>6</sup> open up routes to a wide range of bridging boryl complexes *via* metathetical or oxidative addition pathways.

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## Notes and references

† Spectroscopic data for **4**: MS(EI):  $M^+ = 514$ , isotopic pattern corresponding to 2 B, 2 Fe atoms, fragment ion peaks at  $m/z$  486, 458, 430, 402 corresponding to sequential loss of four CO molecules, exact mass (calculated)  $m/z$  513.9417, (observed) 513.9424. <sup>1</sup>H NMR (<sup>2</sup>H<sub>6</sub>]benzene, 21 °C),  $\delta$  4.95 (s, 10H, Cp), 6.99 [s, 2H,  $\text{CpFe}(\text{CO})_2\text{BO}_2\text{C}_6\text{H}_2\text{O}_2\text{BFe}$

$(\text{CO})_2\text{Cp}$ ]. <sup>13</sup>C NMR (<sup>2</sup>H<sub>6</sub>]benzene, 21 °C),  $\delta$  82.85 (Cp), 94.68 (aromatic CH), 143.83 (aromatic quaternary), 212.54 (CO). <sup>11</sup>B NMR (toluene, 21 °C),  $\delta$  48 (br). IR(KBr disk, cm<sup>-1</sup>)  $\nu(\text{CO})$  2006s, 1954s. Elemental analysis: calc. for  $\text{C}_{20}\text{H}_{12}\text{B}_2\text{Fe}_2\text{O}_8$ , C, 46.74, H, 2.35. Found: C, 46.22, H 2.14%.

‡ Crystallographic data for **4**:  $\text{C}_{20}\text{H}_{12}\text{B}_2\text{Fe}_2\text{O}_8$ , monoclinic, space group  $P2_1/n$ ,  $a = 6.4542(3)$ ,  $b = 12.2543(4)$ ,  $c = 12.4180(6)$  Å,  $\beta = 93.604(3)^\circ$ ,  $U = 980.22(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.740$  Mg m<sup>-3</sup>,  $M = 513.94$ ,  $T = 100$  K. 6704 reflections collected, 2243 independent ( $R_{\text{int}} = 0.0340$ ) which were used in all calculations.  $R_1 = 0.0257$ ,  $wR_2 = 0.0582$  for observed unique reflections [ $I > 2\sigma(I)$ ] and  $R_1 = 0.0315$ ,  $wR_2 = 0.0605$  for all 2243 unique reflections. The max. and min. residual electron densities on the final difference Fourier map were 0.331 and  $-0.255$  e Å<sup>-3</sup>, respectively.

CCDC 182/1684. See <http://www.rsc.org/suppdata/cc/b0/b003901m/> for crystallographic data in .cif format.

§ Reported Fe–B distances (Å) for iron boryl complexes in which B–Fe–Cp centroid and  $\text{BR}_2$  planes are close to orthogonal [torsion angle ( $^\circ$ ) in square brackets]:  $\text{CpFe}(\text{CO})_2\text{BPh}_2$  2.034(3) [75],<sup>4</sup>  $\text{CpFe}(\text{CO})_2\text{B}(\text{NMe}_2)\text{B}(\text{NMe}_2)\text{Cl}$  2.090(3) [92.4],<sup>7</sup>  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{B}(\text{NMe}_2)\text{Cl}$  2.027(5) [87.4],<sup>8</sup>  $[\text{CpFe}(\text{CO})_2]_2\text{B}_3\text{N}_3\text{H}_3\text{Cl}$  2.041(1) [90.6 and 94.5].<sup>5</sup> The complex  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{BH}_2\text{PMe}_3$ , containing four-coordinate boron<sup>11</sup> was not included in this analysis.

¶ Details of DFT calculations: The ADF 1999.02<sup>12,13</sup> suite of programs was used for DFT calculations, employing Becke's gradient-corrected exchange functional<sup>14</sup> and Lee–Yang–Parr's correlation functional (BLYP).<sup>15</sup> Triple-zeta Slater type orbitals were used as basis functions with a polarisation function added for H through Ar and Ga through Kr. The level of frozen core approximation for C and O was the 1s orbital and for Fe orbitals up to 2p were fixed. The geometry of each molecule was optimised at the BLYP level of theory with no symmetry restrictions.

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