# Synthetic and reaction chemistry of heteroatom stabilized boryl and cationic borylene complexes<sup>†</sup>

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The synthesis, spectroscopic and structural characterization of the aryloxy and amino functionalized chloroboryl complexes ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>B(OMes)Cl (R = H, 2a; R = Me, 3a) and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(N<sup>7</sup>Pr<sub>2</sub>)Cl (7a) are reported. Compound 2a is shown to be a versatile substrate for further boron-centred *substitution* chemistry leading to the asymmetric boryl complexes ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(OMes)ER<sub>n</sub> [ER<sub>n</sub> = OC<sub>6</sub>H<sub>4</sub>'Bu-4, 2c; ER<sub>n</sub> = SPh, 2d] with retention of the metal–boron bond. The reactivities of 2a, 3a and 7a towards the halide *abstraction* agent Na[BAr<sup>f</sup><sub>4</sub>] have also been examined, in order to investigate the potential for the generation of cationic heteroatom-stabilized terminal borylene complexes. The application of this methodology to the mesityloxy derivatives 2a and 3a gives rise to B–F containing products, presumably *via* fluoride abstraction from the [BAr<sup>f</sup><sub>4</sub>]<sup>-</sup> counter-ion. By contrast, amino-functionalized complex 7a is more amenable to this approach, and the thermally robust terminal aminoborylene complex [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(N<sup>7</sup>Pr<sub>2</sub>)][BAr<sup>f</sup><sub>4</sub>] (9) can be isolated in *ca*. 50% yield. The reactivity of 9 towards a range of nucleophilic and/or unsaturated reagents has been examined, with examples of addition, protonolysis and metathesis chemistries having been established.

#### 1 Introduction

There has been much recent interest in the chemistry of transition metal boryl complexes (L<sub>n</sub>M-BX<sub>2</sub>),<sup>1</sup> in part due to their implication in the hydroboration and diboration of carbon-carbon multiple bonds,<sup>2,3</sup> and also in the highly selective stoichiometric and catalytic functionalization of hydrocarbons.<sup>4</sup> As a result of the remarkable activity exhibited by such species, the reactivity of boryl compounds towards a variety of substrates has therefore been investigated in some depth.1 Notwithstanding this, fundamental reactions that proceed with retention of the metal-boron linkage are still relatively rare.1 Generally, to exhibit such reactivity, the boryl ligand must feature weakly  $\pi$  donor groups such as chloride or bromide which are labile under conditions which leave the M-B bond intact. Asymmetric haloboryl species  $[L_n M - B(R)X]$  (X = Cl, Br), although relatively rare, are therefore potential precursors to a range of boron-containing complexes through substitution and abstraction chemistries.

In particular, given the elegant chemistry reported by Tilley and co-workers in the synthesis of a range of base-free silylene complexes,<sup>5</sup> we have been seeking to exploit the abstraction methodology outlined in Scheme 1 towards the synthesis of cationic unsaturated group 13 ligand systems.<sup>6-10</sup> Such an approach has previously been shown to be effective for cationic aryl- and metalla-diyl complexes of boron, gallium and indium, and herein we report on attempts to extend this chemistry to heteroatom (O, N) stabilized boranediyl complexes,<sup>10</sup> with a view to probing the role of the heteroatom in their structural and reaction chemistry. Thus, synthetic routes to precursor complexes of the type ( $\eta^{s}$ -C<sub>5</sub>R'<sub>5</sub>)Fe(CO)<sub>2</sub>B(ER<sub>n</sub>)X (ER<sub>n</sub> = OR, NR<sub>2</sub>) have been developed and their reactivities with respect to halide substitution and abstraction have been probed.

#### 2 Experimental

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry-box techniques. Solvents were pre-dried over sodium wire (hexanes, toluene) or molecular sieves (dichloromethane) and purged with nitrogen prior to distillation from the appropriate drying agent (hexanes: potassium, toluene: sodium, dichloromethane: CaH<sub>2</sub>). Benzene-d<sub>6</sub> and dichloromethane- $d_2$  (both Goss) were degassed and dried over potassium (benzene- $d_6$ ) or molecular sieves (dichloromethane- $d_2$ ) prior to use. Mesitol (MesOH, 2,4,6-trimethylphenol) (Aldrich) was sublimed under high vacuum (ca. 100 °C at 10<sup>-4</sup> Torr) prior to use; <sup>*n*</sup>BuLi (1.6 M solution in hexanes), BCl<sub>3</sub> (1.0 M in heptane) and BBr<sub>3</sub> (Aldrich) were used as received. TIF, Na[BPh<sub>4</sub>] and [PPN]Cl ([PPN]<sup>+</sup> = bis(triphenylphosphoranylidene)ammonium, [Ph<sub>3</sub>PNPPh<sub>3</sub>]<sup>+</sup>) (all Aldrich) were dried under high vacuum for 12 h prior to use. Na[ $(\eta^5-C_5H_5)Fe(CO)_2$ ], Na[ $(\eta^5-C_5Me_5)Fe(CO)_2$ ],  ${}^{i}Pr_{2}NBCl_{2}$ , tmpBBr<sub>2</sub> (tmp = 2,2,6,6-tetramethylpiperidyl) and Na[BAr<sup>f</sup><sub>4</sub>] were prepared according to literature methods.<sup>11-14</sup>

NMR spectra were measured on a Bruker AM-400 or JEOL 300 Eclipse Plus FT-NMR spectrometer. Residual signals of solvent were used as reference for <sup>1</sup>H and <sup>13</sup>C NMR, while a sealed tube containing a solution of  $["Bu_4N][B_3H_8]$  in CDCl<sub>3</sub> was used

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Scheme 1 Contrasting reactivity of haloboryl complexes towards nucleophilic and weakly coordinating anion substitution and abstraction chemistries.

as an external reference for <sup>11</sup>B NMR; <sup>19</sup>F NMR spectra were referenced to external CFCl<sub>3</sub>. Infrared spectra were measured for each compound pressed into a disk with an excess of dried KBr or as a solution in an appropriate solvent on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. Perfluorotributylamine was used as a standard for high-resolution EI mass spectra. Despite repeated attempts, satisfactory elementary microanalysis for new boryl and borylene complexes was frustrated by their extreme air, moisture and (in some cases) thermal instability. With the exception of oils 2e and 4, characterization of the new compounds is therefore based upon multinuclear NMR, IR and mass spectrometry data (including accurate mass measurement of molecular ions), supplemented by single-crystal X-ray diffraction studies in the cases of 2a, 2d, 3, 7a, 10 and 13. In all cases the purity of the bulk material was established by multinuclear NMR to be >95%. Abbreviations: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, pcq =partially collapsed quartet, quin = quintet, m = multiplet, fwhm = frequency width at half maximum.

#### Synthesis of MesOBX<sub>2</sub> (1a: X = Cl; 1b: X = Br)

The two compounds were prepared in a similar fashion, exemplified for 1a. To a solution of mesitol (1.01 g, 7.3 mmol) in hexanes (40 cm<sup>3</sup>) at -78 °C was added dropwise a solution of "BuLi in hexanes (5.5 cm<sup>3</sup> of a 1.6 M solution, 8.8 mmol); the resulting mixture was warmed slowly to 20 °C and stirred for 16 h. The supernatant was filtered from the solid product, which was then washed with hexanes  $(2 \times 20 \text{ cm}^3)$  and dried *in vacuo*. To a suspension of this lithium salt in toluene (40 cm<sup>3</sup>) was added BCl<sub>3</sub> in heptane (7.3 cm<sup>3</sup> of a 1.0 M solution, 7.3 mmol) and the mixture stirred at 20 °C for a further 16 h. Filtration of the supernatant provided a stock solution of 1a in toluene which could be used for further reactions. Due to redistribution of the OMes groups in the product under continuous pumping, the pure compound could not be isolated. <sup>11</sup>B NMR (96 MHz, toluene)  $\delta$  31.1. Stock solutions of 1b in toluene were prepared in a similar manner, with analogous redistribution of the OMes groups occurring under continuous pumping. <sup>11</sup>B NMR (96 MHz, toluene)  $\delta$  26.7.

### Syntheses of $(\eta^5-C_5R_5)Fe(CO)_2B(OMes)Cl (R = H, 2a; R = Me, 3a)$ and $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)Br, 2b$

The three compounds were prepared in a similar fashion, exemplified for **2a**. Typically, to a suspension of Na[ $(\eta^5-C_5H_5)Fe(CO)_2$ ] (1.035 g, 5.18 mmol) in toluene (15 cm<sup>3</sup>) was added a solution of **1a** in toluene (43 cm<sup>3</sup> of a 0.12 M solution, 5.18 mmol) and the resulting mixture stirred at 20 °C for 16 h. Filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (*ca.* 20 cm<sup>3</sup>) at -30 °C yielded **2a** and **3a** as pale yellow crystals suitable for X-ray diffraction, and **2b** as a pale yellow microcrystalline solid.

Yields were typically in the order of 40-50% (e.g. 0.879 g, 47%) for 2a). Data for 2a: <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ )  $\delta$  2.12 (s, 3H, para-CH<sub>3</sub>), 2.28 (s, 6H, ortho-CH<sub>3</sub>), 4.24 (s, 5H, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 6.75 (s, 2H, aromatic CH). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>) δ 17.0 (ortho-CH<sub>3</sub>), 20.5 (para-CH<sub>3</sub>), 84.7 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 129.2 (aromatic CH), 127.6, 132.7 (aromatic quaternary), 152.3 (ipso-aromatic quaternary), 214.1 (CO). <sup>11</sup>B NMR (96 MHz,  $C_6D_6$ )  $\delta$  61.5. IR (KBr disk, cm<sup>-1</sup>) v(CO) 2002, 1940. Mass spec. (EI) M<sup>+</sup> = 358 (weak), isotope pattern corresponding to 1 Fe, 1 B and 1 Cl atom. Exact mass: calc. for M<sup>+</sup> 358.0225, measd 358.0236. Data for **3a**: <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 1.91 (s, 15H, η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>), 2.13 (s, 3H, para- $CH_3$ ), 2.23 (s, 6H, ortho- $CH_3$ ), 6.83 (s, 2H, aromatic CH). <sup>13</sup>C NMR (76 MHz,  $CD_2Cl_2$ )  $\delta$  9.9 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 17.0 (*ortho*-CH<sub>3</sub>), 20.4 (para-CH<sub>3</sub>), 96.5 (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>), 128.8 (aromatic CH), 127.7, 129.9 (aromatic quaternary), 132.6 (ipso-aromatic quaternary), 217.8 (CO). <sup>11</sup>B NMR (96 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  63.7. IR (KBr disk, cm<sup>-1</sup>) v(CO) 1971, 1925. Mass spec. (EI) M<sup>+</sup> = 428 (weak), isotope pattern corresponding to 1 Fe, 1 B and 1 Cl atom, fragment ion peaks at m/z 400 [(M – CO)<sup>+</sup>, 55%] and 372 [(M – 2CO)<sup>+</sup>, 100%]. Exact mass: calc. for M<sup>+</sup> 428.1007, measd 428.1017. Data for **2b**: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.11 (s, 3H, para-CH<sub>3</sub>), 2.27 (s, 6H, ortho-CH<sub>3</sub>), 4.25 (s, 5H,  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 6.75 (s, 2H, aromatic CH). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>) δ 17.1 (para-CH<sub>3</sub>), 20.5 (ortho-CH<sub>3</sub>), 85.2 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 129.3 (aromatic CH), 127.7, 132.9 (aromatic quaternary), 153.2 (ipso-aromatic quaternary), 213.8 (CO). <sup>11</sup>B NMR (96 MHz, C<sub>6</sub>D<sub>6</sub>) δ 59.3. IR (KBr disk, cm<sup>-1</sup>) ν(CO) 2015, 1961. Mass spec. (EI) M<sup>+</sup> not observed, fragment ion peaks at m/z $374 [(M - CO)^+, 30\%], 346 [(M - 2CO)^+, 30\%], isotope patterns$ corresponding to 1 Fe, 1 B and 1 Br atom. Exact mass: calc. for  $(M - CO)^+$  373.9771, measd 373.9781.

## Substitution chemistry of 2a: syntheses of $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)OC_6H_4'Bu-4$ , 2c and $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)SPh 2d$

To a suspension of NaOC<sub>6</sub>H<sub>4</sub><sup>t</sup>Bu-4 (0.068 g, 0.40 mmol) in toluene  $(10 \text{ cm}^3)$  was added a solution of **2a** (0.142 g, 0.40 mmol) in toluene (10 cm<sup>3</sup>) and the resulting mixture was stirred for 72 h. Filtration, removal of volatiles in vacuo and recrystallization from hexanes (ca. 20 cm<sup>3</sup>) at -50 °C gave rise to 2c as a colourless microcrystalline solid (0.147 g, 79%). 2d was prepared in an analogous fashion from NaSPh (0.041 g, 0.31 mmol) and 2a (0.112 g, 0.31 mmol) and isolated as colourless crystals suitable for X-ray diffraction (0.117 g, 83%). Data for 2c: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.17 (s, 9H, 'Bu), 2.16 (s, 3H, para-CH<sub>3</sub>), 2.41 (s, 6H, ortho-CH<sub>3</sub>), 4.19 (s, 5H, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 6.79 (s, 2H, mesityl CH), 6.86 (d, J = 8.5 Hz, OC<sub>6</sub>H<sub>4</sub> 2H, meta-CH), 7.10 (d, J = 8.5 Hz, 2H, OC<sub>6</sub>H<sub>4</sub> ortho-CH). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>) δ 15.4 (ortho-CH<sub>3</sub>), 18.6 (para-CH<sub>3</sub>), 29.4 (CH<sub>3</sub> of 'Bu), 32.0 (quaternary of <sup>t</sup>Bu), 80.9 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 121.0, 126.0 (OC<sub>6</sub>H<sub>4</sub> aromatic CH), 128.5, 131.5 (mesityl aromatic quaternary), 129.1 (mesityl aromatic CH), 145.4, 153.2 ( $OC_6H_4$  aromatic quaternary), 153.2 (mesityl aromatic quaternary), 213.3 (CO). <sup>11</sup>B NMR (96 MHz,  $C_6D_6$ )  $\delta$ 47.4. IR (KBr disk, cm<sup>-1</sup>) v(CO) 2006, 1944. Mass spec. (EI): M<sup>+</sup> not observed, fragment ion peaks at m/z 444 [(M - CO)<sup>+</sup>, weak], isotope pattern corresponding to 1 Fe and 1 B atom. Data for 2d. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.08 (s, 3H, para-CH<sub>3</sub>), 2.24 (s, 6H, ortho-CH<sub>3</sub>), 4.20 (s, 5H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 6.63 (s, 2H, mesityl aromatic CH), 6.93 (m, 3H, SPh *meta-* and *para-*CH), 7.46 (d, J = 7.3 Hz, 2H, SPh ortho-CH). <sup>13</sup>C NMR (76 MHz,  $C_6D_6$ )  $\delta$  17.0 (ortho-CH<sub>3</sub>), 20.5 (para-CH<sub>3</sub>), 83.7 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 126.7, 129.2, 134.4 (SPh aromatic CH), 127.6 (mesityl aromatic CH), 128.4, 132.4, 152.8 (mesityl aromatic quaternary), 134.8 (SPh aromatic quaternary), 214.6 (CO). <sup>11</sup>B NMR (96 MHz,  $C_6D_6$ )  $\delta$  69.1. IR (KBr disk, cm<sup>-1</sup>) v(CO) 1996, 1930. Mass spec (EI): M<sup>+</sup> not observed, fragment ion peaks at m/z 404 [(M - CO)<sup>+</sup>, 100%], 376 [(M - 2CO)<sup>+</sup>, 20%]. Exact mass: calc. for  $(M - CO)^+$  404.0699, measd 404.0700.

#### Reaction of $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)Cl(2a)$ with Na[BAr<sup>4</sup><sub>4</sub>]

A mixture of Na[BAr<sup>f</sup><sub>4</sub>] (0.070 g, 0.08 mmol), 2a (0.028 g, 0.08 mmol) and dichloromethane- $d_2$  (1.5 cm<sup>3</sup>) in a J. Young's NMR tube was sonicated at 20 °C for 16 h. After this time, the reaction was found to be complete by the conversion of the NMR signal at  $\delta_{\rm B}$  61.5 (2a) to a broad doublet at  $\delta_{\rm B}$  45.7, and by the appearance of a partially collapsed quartet at  $\delta_{\rm F}$  –9.1. The reaction was repeated on a preparative scale (0.350 g, 0.39 mmol of Na[BAr<sup>f</sup><sub>4</sub>]), whereupon filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (ca. 20 cm<sup>3</sup>) at -50 °C yielded a red oil (yield: 0.064 g, 47%), characterized by multinuclear NMR and IR spectroscopies as  $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)F$ , 2e. <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ )  $\delta$  2.17 (s, 3H, para-CH<sub>3</sub>), 2.29 (s, 6H, ortho-CH<sub>3</sub>), 4.23 (s, 5H,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 6.74 (s, 2H, aromatic CH). <sup>13</sup>C NMR (76 MHz,  $C_6D_6$ )  $\delta$  17.0 (para-CH<sub>3</sub>), 20.4 (ortho-CH<sub>3</sub>), 83.4 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 129.3 (aromatic CH), 132.2, 134.7 (aromatic quaternary), 216.7 (CO), ipso-C of mesityl ring not observed. 11B NMR (96 MHz,  $C_6 D_6$ )  $\delta$  45.7 (d, J = 181 Hz). <sup>19</sup>F NMR (283 MHz,  $C_6D_6$ )  $\delta -9.1$  (pcq, J = 181 Hz). IR ( $C_6D_6$  soln, cm<sup>-1</sup>) 2013, 1954.

### Reaction of $(\eta^5-C_5Me_5)Fe(CO)_2B(OMes)Cl$ (3a) with Na[BAr<sup>f</sup><sub>4</sub>]; identification of $(\eta^5-C_5Me_5)Fe(CO)_2BF_2$

A mixture of Na[BAr<sup>f</sup><sub>4</sub>] (0.042 g, 0.05 mmol), 3a (0.020 g, 0.05 mmol) and dichloromethane- $d_2$  (1.5 cm<sup>3</sup>) in a J. Young's NMR tube was sonicated at 20 °C for 30 min. Multinuclear NMR monitoring of the reaction mixture at this point revealed, in addition to unreacted **3a** ( $\delta_{\rm B}$  63.7), the appearance of a broad doublet at  $\delta_{\rm B}$  50.3 and a quartet at  $\delta_{\rm F}$  -5.8 (J = 160 Hz). Further sonication was necessary to bring about consumption of the remaining 3a, with the additional consequence that a mixture of boron and fluorine-containing products was formed. In addition to the species responsible for the resonances at  $\delta_{\rm B}$  50.3/ $\delta_{\rm F}$  –5.8, a second significant component was observed giving rise to a well-defined triplet at  $\delta_{\rm B}$  47.8 and a quartet at  $\delta_{\rm F}$  –3.4 (J  $\approx$  200 Hz). The latter resonances were observed to increase in intensity at the expense of the former on prolonged sonication, although complete conversion to a single iron/boron containing product could not be achieved. By comparison of data with the product obtained from the independent reaction

of Na[ $(\eta^5-C_5Me_5)Fe(CO)_2$ ] with BF<sub>3</sub>·OEt<sub>2</sub> these latter resonances are attributed to  $(\eta^5-C_5Me_5)Fe(CO)_2BF_2$ , **4**.<sup>15</sup>

#### Synthesis of (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(N<sup>i</sup>Pr<sub>2</sub>)Cl, 7a

Reaction of  ${}^{i}Pr_{2}NBCl_{2}$  (1.199 g, 6.6 mmol) with Na[( $\eta^{5}$ - $C_5H_5$ )Fe(CO)<sub>2</sub>] (1.318 g, 6.6 mmol) in toluene (40 cm<sup>3</sup>) at 20 °C for 20 h, followed by filtration, removal of volatiles in vacuo and extraction with hexanes (ca. 40 cm<sup>3</sup>) yielded crude 7a as an oily brown solid. Yellow crystals suitable for X-ray diffraction were obtained by sublimation under high vacuum (40  $^{\circ}$ C at 10<sup>-4</sup> Torr). Yield (of sublimed material): 0.259 g, 12%. <sup>1</sup>H NMR (400 MHz,  $C_6 D_6 \delta 1.11$  (d, J = 6.7 Hz, 6H, CH<sub>3</sub> of <sup>*i*</sup>Pr), 1.39 (d, J = 6.7 Hz, 6H, CH<sub>3</sub> of 'Pr), 3.40 (sept, J = 6.7 Hz, 1H, CH of 'Pr), 4.44 (sept, J = 6.7 Hz, 1H, CH of <sup>*i*</sup>Pr), 4.69 (s, 5H,  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>) δ 21.2 (CH<sub>3</sub> of <sup>i</sup>Pr), 23.9 (CH<sub>3</sub> of <sup>i</sup>Pr), 47.8 (CH of <sup>*i*</sup>Pr), 55.2 (CH of <sup>*i*</sup>Pr), 88.2 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 215.6 (CO). <sup>11</sup>B NMR (96 MHz,  $C_6D_6$ )  $\delta$  55.4. IR ( $C_6D_6$  soln, cm<sup>-1</sup>) v(CO) 2001, 1941. Mass spec. (EI): M<sup>+</sup> not observed, fragment ion peaks at m/z 295  $[(M - CO)^+, 65\%], 288 [(M - Cl)^+, weak], 267 [(M - 2CO)^+, weak]]$ 10%], 223 [ $(M - N^{i}Pr_{2})^{+}$ , 100%]. Exact mass: calc. for  $(M - CO)^{+}$ 295.0592, measd 295.0595; calc. for  $(M - Cl)^+$  288.0853, measd 288.0856. The corresponding ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me) compound (7b) can be prepared in an analogous manner: <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$ 1.07 (d, J = 6.7 Hz, 6H, CH<sub>3</sub> of 'Pr), 1.66 (d, J = 6.9 Hz, 6H, CH<sub>3</sub> of <sup>*i*</sup>Pr), 1.72 (s, 3H, CH<sub>3</sub> of  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 3.34 (sept, J =6.7 Hz, 1H, CH of 'Pr), 4.17 (m, 2H, CH of n<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 4.30 (m, 2H, CH of  $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 4.60 (sept, J = 6.7 Hz, 1H, CH of <sup>*i*</sup>Pr). <sup>13</sup>C NMR (76 MHz,  $C_6D_6$ )  $\delta$  12.8 (CH<sub>3</sub> of  $\eta^5$ - $C_5H_4CH_3$ ), 21.3 (CH<sub>3</sub> of <sup>i</sup>Pr), 23.9 (CH<sub>3</sub> of <sup>i</sup>Pr), 47.8 (CH of <sup>i</sup>Pr), 55.1 (CH of <sup>*i*</sup>Pr), 82.4 (CH of  $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 84.6 (CH of  $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 100.9 (quaternary C of  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>), 216.1 (CO). <sup>11</sup>B NMR (96 MHz,  $C_6D_6$ )  $\delta$  55.0. IR ( $C_6D_6$  soln, cm<sup>-1</sup>) v(CO) 1998, 1938. Mass spec. (EI): M<sup>+</sup> 377 (weak), isotopic pattern corresponding to 1 Fe, 1 Cl and 1 B atom, strong fragment ion peaks at m/z 309 [(M - CO)<sup>+</sup>, 65%], 281 [(M - 2CO)<sup>+</sup>, weak], 237 [(M - N<sup>*i*</sup>Pr<sub>2</sub>)<sup>+</sup>, 100%]. Exact mass: calc. for  $(M - CO)^+$  309.0749, measd 309.0747.

#### Synthesis of [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)]<sub>2</sub>(μ-CO)(μ-Btmp), 8

To a suspension of  $Na[(\eta^5-C_5H_5)Fe(CO)_2]$  (0.300 g, 1.5 mmol) in toluene (20 cm<sup>3</sup>) was added a solution of tmpBBr<sub>2</sub> (0.47 g, 1.5 mmol) in toluene (5 cm<sup>3</sup>) and the resulting mixture was stirred at 45 °C for 192 h. Filtration, removal of volatiles in vacuo and recrystallization from hexanes (ca. 20 cm<sup>3</sup>) at -30 °C gave rise to 8 as dark red crystals (0.059 g, 8%). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  0.96 (quin, J = 6 Hz, 2H, CH<sub>2</sub>), 1.54 (t, J = 6 Hz, 4H, CH<sub>2</sub>), 1.58 (s, 12H, CH<sub>3</sub> of tmp), 4.58 (s, 10H, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C NMR (76 MHz,  $C_6D_6$ )  $\delta$  16.0 (para-CH<sub>2</sub>), 33.4 (CH<sub>3</sub> of tmp), 37.6 (*meta*-CH<sub>2</sub>), 55.3 (quaternary of tmp), 88.3 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 217.6 (terminal CO), 274.7 (bridging CO). <sup>11</sup>B NMR (96 MHz,  $C_6D_6$ )  $\delta$  115.3. IR (KBr disk, cm<sup>-1</sup>)  $\nu$ (CO) 1911, 1762. Mass spec (EI): M<sup>+</sup> 477 (15%), isotopic pattern corresponding to 2 Fe and 1 B atom, strong fragment ion peaks at m/z 449 [(M - CO)<sup>+</sup>, 20%], 421 [(M - 2CO)<sup>+</sup>, 15%], 393 [(M - 3CO)<sup>+</sup>, 5%], 328 [(M - $(\eta^{5}-C_{5}H_{5})FeCO)^{+}$ , 10%], 300 [(M -  $(\eta^{5}-C_{5}H_{5})Fe(CO)_{2})^{+}$ , 5%], 272 [(M - ( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>3</sub>)<sup>+</sup>, 25%]. Exact mass: calc. for M<sup>+</sup> 477.0856, measd 477.0864.

#### Synthesis of $[(\eta^5-C_5H_5)Fe(CO)_2B(N^iPr_2)]^+[BAr_4]^-$ , 9

Reaction of 7a (0.259 g, 0.80 mmol) and Na[BAr<sup>f</sup><sub>4</sub>] (0.710 g, 0.80 mmol) in dichloromethane (15 cm<sup>3</sup>) from -78 to 20 °C over a period of 30 min leads to quantitative conversion (by <sup>11</sup>B NMR) of 7a ( $\delta_B$  55.4) to 9 ( $\delta_B$  93.5). Filtration, and recrystallization from dichloromethane-hexanes (or fluorobenzene-hexanes) at -30 °C leads to the isolation of 9 as a spectroscopically pure colourless oil. Isolated yield: 0.465 g, 50%. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$ 1.39 (d, J = 6.6 Hz, 12H, CH<sub>3</sub> of 'Pr), 3.32 (sept, J = 6.6 Hz, 2H, CH of <sup>*i*</sup>Pr), 5.33 (s, 5H,  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 7.55 (s, 4H, para-CH of BAr<sup>*f*</sup><sub>4</sub><sup>-</sup>), 7.70 (s, 8H, ortho-CH of BAr<sup>f</sup><sub>4</sub><sup>-</sup>). <sup>13</sup>C NMR (76 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ 24.4 (CH<sub>3</sub> of <sup>i</sup>Pr), 51.0 (CH of <sup>i</sup>Pr), 87.1 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 117.6 (para-CH of BAr<sup>f<sub>4</sub>-</sup>), 124.6 (q, J = 272 Hz, CF<sub>3</sub> of BAr<sup>f<sub>4</sub>-</sup>), 128.8 (q, J =34 Hz, meta-C of BAr<sup> $f_{4}$ -), 134.8 (ortho-CH of BAr<sup> $f_{4}$ -), 161.8 (q,</sup></sup> J = 49 Hz, *ipso*-C of BAr<sup>f</sup><sub>4</sub><sup>-</sup>), 205.6 (CO). <sup>11</sup>B NMR (96 MHz,  $CD_2Cl_2$ )  $\delta -7.7$  (BAr<sup>f</sup><sub>4</sub><sup>-</sup>), 93.5 (b, fwhm *ca*. 615 Hz, BN<sup>*i*</sup>Pr<sub>2</sub>). <sup>19</sup>F NMR (283 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -62.6 (CF<sub>3</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub> soln, cm<sup>-1</sup>) v(CO) 2070, 2028. Mass spec. (ES): M<sup>+</sup> 288.1 (10%).

### Reaction of $[(\eta^5-C_5H_5)Fe(CO)_2B(N^iPr_2)]^+[BAr_4^f]^-$ , 9, with [PPN]Cl

To a solution of [PPN]Cl (0.010 g, 1.67 equiv.) in dichloromethaned<sub>2</sub> in a J. Young's NMR tube was added a solution of **9** (0.012 g) in dichloromethane-d<sub>2</sub> at 20 °C. Monitoring of the reaction by <sup>11</sup>B NMR spectroscopy revealed that after 10 min the resonance characteristic of **9** ( $\delta_B$  93.5) had been quantitatively replaced by a signal at  $\delta_B$  55.4. Further examination of the reaction mixture by <sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C NMR and by IR revealed spectroscopic features characteristic of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(N'Pr<sub>2</sub>)Cl(**7a**), which were indistinguishable from samples synthesized from Na[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>] and 'Pr<sub>2</sub>NBCl<sub>2</sub> (*vide supra*).

#### Reaction of $[(\eta^5-C_5H_5)Fe(CO)_2B(N^iPr_2)]^+[BArf_4]^-$ , 9, with H<sub>2</sub>O

To a solution of 9 (0.012 g, 0.01 mmol) in dichloromethane- $d_2$  $(2 \text{ cm}^3)$  in a J. Young's NMR tube was added H<sub>2</sub>O (0.01 cm<sup>3</sup>), 0.01 g, 0.5 mmol) and the resulting mixture was sonicated at 20 °C for 2 h. At this point <sup>1</sup>H and <sup>11</sup>B monitoring of the reaction revealed complete consumption of 9; filtration, layering of the of the resulting solution with hexanes and storage at -30 °C led to the formation of  $[H_2N^iPr_2]^+[BAr^f_4]^-$ , 10, as colourless crystals suitable for X-ray diffraction (see ESI<sup>†</sup>) Isolated yield: 0.007 g, 72%. Identification of the boron- and iron-containing products as  $B(OH)_3$  and  $[(\eta^5-C_5H_5)Fe(CO)_2]_2$  was confirmed by comparison of IR and multinuclear NMR data with reported values.<sup>16</sup> Data for 10: <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.25 (d, J = 6.5 Hz, 12H, CH<sub>3</sub> of 'Pr), 3.37 (sept, J = 6.5 Hz, 2H, CH of 'Pr), 4.99 (t, J = 52.9 Hz, 2H, NH<sub>2</sub>), 7.44 (s, 4H, para-CH of BAr<sup>f</sup><sub>4</sub><sup>-</sup>), 7.63 (s, 8H, ortho-CH of BAr<sup>f</sup><sub>4</sub><sup>-</sup>). <sup>13</sup>C NMR (76 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 20.0 (CH<sub>3</sub> of <sup>*i*</sup>Pr), 51.9 (CH of 'Pr), 117.6 (para-CH of BAr<sup>f</sup><sub>4</sub><sup>-</sup>), 124.6 (q, J = 272 Hz,  $CF_3$  of  $BAr_{4}^{r}$ ), 128.9 (q, J = 32 Hz, meta-C of  $BAr_{4}^{r}$ ), 134.9 (ortho-CH of BAr<sup>f</sup><sub>4</sub><sup>-</sup>), ipso-C of BAr<sup>f</sup><sub>4</sub><sup>-</sup> not observed. <sup>11</sup>B NMR  $(96 \text{ MHz}, \text{CD}_2\text{Cl}_2)\delta - 7.6 (\text{BAr}_4^{\text{f}})$ . <sup>19</sup>F NMR (283 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -62.6 (CF<sub>3</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub> soln, cm<sup>-1</sup>) v(NH) 3340, 3123. Mass spec. (ES+):  $[H_2N^iPr_2]^+$  102 (100%); (ES-):  $[BAr_4^f]^-$  863 (100%). Exact mass: calc. for  $[H_2N^iPr_2]^+$  102.1277, measd 102.1277; calc. for [BAr<sup>f</sup><sub>4</sub>]<sup>-</sup> 863.0654, measd 863.0642.

### Reaction of $[(\eta^5-C_5H_5)Fe(CO)_2B(N^iPr_2)]^+[BAr_4^f]^-$ , 9, with Ph\_3P=S and Ph\_3As=O

In a typical reaction **9** (0.068 g, 0.06 mmol) and Ph<sub>3</sub>P=S (1.0 equiv.) were stirred together in dichloromethane for 30 min at 20 °C, after which time the reaction was judged to be complete by <sup>11</sup>B and <sup>31</sup>P NMR (conversion of signals at  $\delta_{\rm B}$  93.5 and  $\delta_{\rm P}$  43.7 to  $\delta_{\rm B}$  35.6 and  $\delta_{\rm P}$  60.8). Removal of volatiles *in vacuo* and extraction into hexanes gives <sup>i</sup>Pr<sub>2</sub>NB( $\mu$ -S)<sub>2</sub>BN<sup>i</sup>Pr<sub>2</sub> (**12a**) which was identified by comparison of <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B NMR and mass spectrometry data with those reported previously.<sup>171</sup>H, <sup>13</sup>C, <sup>11</sup>B, <sup>19</sup>F and <sup>31</sup>P NMR and IR of the hexane-insoluble product confirmed it to be [( $\eta^{5}-C_{5}H_{5}$ )Fe(CO)<sub>2</sub>(PPh<sub>3</sub>)]<sup>+</sup>[BAr<sup>f</sup><sub>4</sub>]<sup>-</sup> (**11a**).<sup>18</sup> Our data for the known compounds **11a** and **12a** are included in the ESI.† A similar procedure was adopted for the reaction of **9** with Ph<sub>3</sub>As=O and details of the characterizing data for **11b** and **12b** are also included in the ESI.†<sup>17,18</sup>

### Reaction of $[(\eta^5-C_5H_5)Fe(CO)_2B(N^iPr_2)]^+[BAr_4^{f_4}]^-$ , 9, with Ph<sub>3</sub>P=O

The reaction of 9 with Ph<sub>3</sub>PO proceeds along similar lines to those reported above for Ph<sub>3</sub>PS and Ph<sub>3</sub>AsO, with the caveat that the increased temperature (480 h at 35 °C) required to drive the reaction to completion (i) allows for the isolation of the intermediate species  $[(\eta^5-C_5H_5)Fe(CO)_2\{B(N^iPr_2)(OPPh_3)\}]^+[BAr_4^f]^-$ , 13; and (ii) results in appreciable conversion of the ironcontaining product  $[(\eta^5-C_5H_5)Fe(CO)_2(PPh_3)]^+$  into dinuclear  $(\eta^5-C_5H_5)Fe(CO)_2(PPh_3)]^+$  $C_5H_5)_2Fe_2(CO)_3(PPh_3)$ .<sup>19</sup> Data for 13: Reaction of 9 (0.199 g, 0.17 mmol) and Ph<sub>3</sub>PO (0.048 g, 0.17 mmol) in dichloromethane (5 cm<sup>3</sup>) at 20 °C over a period of 30 min, followed by filtration and recrystallization from dichloromethane-hexanes at -30 °C leads to the isolation of 13 as pale yellow crystals. Isolated yield: 0.105 g, 43%. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$  1.06 (d, J = 6 Hz, 6H,  $CH_3$ of <sup>*i*</sup>Pr), 1.20 (d, J = 6 Hz, 6H, CH<sub>3</sub> of <sup>*i*</sup>Pr), 3.25 (sept, J = 6 Hz, 1H, CH of <sup>*i*</sup>Pr), 4.10 (sept, J = 6 Hz, 1H, CH of <sup>*i*</sup>Pr), 4.50 (s, 5H,  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 7.38–7.48 (m, 9H, ortho and para-CHs of Ph<sub>3</sub>PO), 7.55 (s, 4H, para-CH of BAr<sup>f</sup><sub>4</sub><sup>-</sup>), 7.60–7.78 (m, 6H, meta-CH of Ph<sub>3</sub>PO), 7.73 (s, 8H, ortho-CH of BAr<sup>f</sup><sub>4</sub><sup>-</sup>). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>)δ 22.4, 23.9 (CH<sub>3</sub> of <sup>*i*</sup>Pr), 47.2 (CH of <sup>*i*</sup>Pr), 84.4 (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 117.5 (para-CH of BAr<sup> $f_4^-$ </sup>), 122.6 (*ipso*-C of Ph<sub>3</sub>PO), 124.6 (q, J = 272 Hz, CF<sub>3</sub> of  $BAr_{4}^{f_{-}}$ ), 128.9 (q, J = 34 Hz, meta-C of  $BAr_{4}^{f_{-}}$ ), 130.1 (meta-CH of Ph<sub>3</sub>PO), 133.5 (*ortho*-C of Ph<sub>3</sub>PO), 134.9 (*ortho*-CH of BAr<sup>f</sup><sub>4</sub><sup>-</sup>), 135.9 (*para*-C of Ph<sub>3</sub>PO), 161.8 (q, J = 49 Hz, *ipso*-C of BAr<sup>f</sup><sub>4</sub><sup>-</sup>), 214.7 (CO). <sup>11</sup>B NMR (96 MHz,  $CD_2Cl_2$ )  $\delta$  -7.7 (BAr<sup>f</sup><sub>4</sub>), 48.9 (b, fwhm ca. 480 Hz, B(OPPh<sub>3</sub>)N<sup>i</sup>Pr<sub>2</sub>). <sup>19</sup>F NMR (283 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -62.7 (CF<sub>3</sub>). IR (CD<sub>2</sub>Cl<sub>2</sub> soln, cm<sup>-1</sup>) v(CO) 2004, 1949. Mass spec. (ES): M<sup>+</sup> 566.1 (5%).

#### 3 Results and discussion

#### (i) Synthesis and substitution chemistry of boryl complexes

The boranes MesOBX<sub>2</sub> (X = Cl **1a**, X = Br **1b**) can readily be synthesized by the reaction of MesOLi with BX<sub>3</sub> in toluene. However, isolation of either **1a** or **1b** as a pure compound proves impossible as exposure to continuous vacuum facilitates substituent redistribution, presumably driven by the loss of volatile BX<sub>3</sub>. Thus, for example, in the case of **1a** attempted removal of solvent yields an oily mixture containing **1a** ( $\delta_B$  31.1) and a



Scheme 2 Synthesis and reactivity of mesityloxy(halo)boryl complexes. *Reagents and conditions*: (i) BX<sub>3</sub> (1 equiv.), toluene, 20 °C, 16 h; (ii) Na[( $\eta^{5}$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>] (1 equiv.), toluene, 20 °C, 16 h, 40–50%; (iii) **2a**, [R<sub>n</sub>E]<sup>-</sup> (NaOC<sub>6</sub>H<sub>4</sub>'Bu-4 or NaSPh) (1 equiv.), toluene, 20 °C, 48–72 h, 79–83%; (iv) **2a**, Na[BAr<sup>4</sup><sub>4</sub>] (1 equiv.), dichloromethane, 20 °C, 16 h, 47%; (v) **3a**, Na[BAr<sup>4</sup><sub>4</sub>] (1 equiv.), dichloromethane, 20 °C, 16 h, 47%; (v) **3a**, Na[BAr<sup>4</sup><sub>4</sub>] (1 equiv.), dichloromethane, 20 °C, 16 h, (vi) **2a**, Na[BPh<sub>4</sub>] (1 equiv.), dichloromethane, 20 °C 168 h; (vii) **2a** or **2b**, excess Na[( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>], toluene, 50 °C, >72 h.

species giving rise to a second resonance at  $\delta_B$  22.3, which on the basis of the known rearrangement chemistry of boranes of the type (RO)BX<sub>2</sub>,<sup>20</sup> and the reported shift for (PhO)<sub>2</sub>BCl ( $\delta_B$ 22.0),<sup>20</sup> is tentatively identified as (MesO)<sub>2</sub>BCl. Further support for this assignment comes from the fact that the reactions can be driven in the reverse direction by the addition of excess BCl<sub>3</sub> (in heptane) with subsequent stirring for 12 h. The rate of substituent redistribution under vacuum is significantly lower for **1b** compared to **1a**, presumably due to the less volatile nature of BBr<sub>3</sub> (*cf*. BCl<sub>3</sub>).

Despite this redistribution chemistry, both **1a** and **1b** can conveniently be obtained as stock solutions in toluene by filtration of the BX<sub>3</sub>–MesOLi reaction mixture, and used for further reaction chemistry (Scheme 2). Accordingly, the asymmetric haloboryl complexes ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>B(OMes)X (**2a**: R = H, X = Cl; **2b**: R = H, X = Br; **3a**: R = Me, X = Cl) can be synthesized in moderate yields (39–50%) by the reaction of a toluene solution of **1a** or **1b** with one equivalent of the appropriate organometallic anion (Scheme 2). Under these conditions, substitution is selective for a single halide, with negligible quantities of the disubstituted species [( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub>B(OMes) being formed (as determined by the <sup>11</sup>B NMR spectrum of the reaction mixture). **2a**, **2b** and **3a** have been characterized by multinuclear NMR, IR and mass spectrometry (including exact mass determination) and in the cases of **2a** and **3a** by single-crystal X-ray diffraction.

As has been found for the analogous mesityl(bromo)boryl complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(Mes)Br, ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(OMes)Cl (**2a**) is a versatile substrate for further substitution chemistry with anionic main group nucleophiles.<sup>21</sup> Thus, reaction with one equivalent of NaOC<sub>6</sub>H<sub>4</sub>'Bu-4 or NaSPh in toluene at 20 °C leads to the asymmetric boryl complexes ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(OMes)ER<sub>n</sub> (ER<sub>n</sub> = OC<sub>6</sub>H<sub>4</sub>'Bu = **2c**; ER<sub>n</sub> = SPh = **2d**) in good yield.

Both complexes have been spectroscopically characterized, and the structure of 2d confirmed by X-ray diffraction. Given the lower steric requirements of the mesityloxo substituent, it is somewhat surprising that unlike  $(\eta^5-C_5H_5)Fe(CO)_2B(Mes)Br$ , 2a and 2b do not undergo substitution with a second equivalent of an organometallic nucleophile to form the corresponding bridging borylene species {*i.e.*  $[(\eta^5-C_5H_5)Fe(CO)_2]_2B(OMes)$ }. Presumably, this reflects  $\pi$  electron release by the aryloxy substituent and hence the lower electrophilicity of the boron centre in the B(OMes)X ligand compared to B(Mes)Br. Given its relevance to halide abstraction chemistry (vide infra), attempts were made to synthesize the fluoroboryl complex  $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)F$ (2e) by the reaction of 2a with sources of fluoride (such as TlF), a transformation which has previously been reported by Braunschweig for  $(\eta^5-C_5H_5)Fe(CO)_2B(Cl)Si(SiMe_3)_3$ <sup>22</sup> In the case of 2a however this approach was unsuccessful, leading instead to the decomposition of all Fe-B bonded species.

#### (ii) Halide abstraction chemistry

Given the success of halide abstraction methodology in the synthesis of novel terminal borylene species,<sup>6,7</sup> the reactivity of the boryl complexes **2a** and **3a** towards Na[BPh<sub>4</sub>] and Na[BAr<sup>f</sup><sub>4</sub>] was also investigated (Scheme 3). No reaction of **2a** with Na[BPh<sub>4</sub>] in dichloromethane was observed under any conditions, presumably due to the low solubility of the tetraphenylborate reagent; **2a** does, however, react with Na[BAr<sup>f</sup><sub>4</sub>] in dichloromethane over a period of 16 h. This reaction does not lead to the isolation of the expected cationic terminal borylene species, however, yielding instead a red oil, the identity of which is suggested by spectroscopic data to be the asymmetric fluoroboryl complex ( $\eta^{5}-C_{5}H_{5}$ )Fe(CO)<sub>2</sub>B(OMes)F



Scheme 3 Synthesis and reactivity of amino(halo)boryl complexes. *Reagents and conditions*: (i)  $NR_2 = tmp$ ,  $Na[(\eta^5-C_5H_5)Fe(CO)_2]$  (1 equiv.), toluene, 45 °C, 192 h, 8%; (ii)  $NR_2 = N'Pr_2$ ,  $Na[(\eta^5-C_5H_5)Fe(CO)_2]$  (1 equiv.), toluene, 20 °C, 20 h, 12% (after sublimation); (iii)  $Na[BAr_4^r]$  (1 equiv.), dichloromethane- $d_2$ , -78 °C to 20 °C, 30 min, 50%.

(2e). The formation of 2e is assumed to occur by the abstraction of a fluoride anion from  $[BAr^{f}_{4}]^{-}$  by the highly reactive putative terminal borylene complex  $[(\eta^{5}-C_{3}H_{3})Fe(CO)_{2}B(OMes)]^{+}$ . Such reactivity towards the weakly coordinating  $[BAr^{f}_{4}]^{-}$  counterion has precedent in the literature for highly electrophilic species,<sup>23</sup> and cationic borylene complexes of the type  $[(\eta^{5}-C_{3}R_{3})Fe(CO)_{2}BX]^{+}$  have previously been shown to abstract both F<sup>-</sup> and Ph<sup>-</sup> from borate anions of the type  $[BX_{4}]^{-}$ .<sup>7</sup> No trace of any intermediate was observed by multinuclear NMR monitoring of the reaction, even at -80 °C.

Given the increased steric shielding and electron donation offered by the  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ligand, the corresponding halide abstraction reaction with the more sterically encumbered boryl complex 3a was also examined by multinuclear NMR spectroscopy. Slow warming of **3a** with Na[BAr<sup>f</sup><sub>4</sub>] in dichloromethane- $d_2$  from -78to 20 °C gives a mixture of two major boron-containing products. The first of these is characterized by a broad doublet at  $\delta_{\rm B}$  50.3 and a quartet at  $\delta_{\rm F}$  –5.8 (<sup>1</sup> $J_{\rm BF}$  = 160 Hz), which by comparison with the very similar data measured for  $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)F$ (2e,  $\delta_{\rm B}$  45.7,  $\delta_{\rm F}$  -9.1,  ${}^{1}J_{\rm BF}$  = 181 Hz) suggests an analogous formulation as  $(\eta^5 - C_5 Me_5)Fe(CO)_2B(OMes)F(3b)$ . As the reaction progresses, the resonances associated with 3b diminish, with signals at  $\delta_{\rm B}$  47.8 (triplet) and  $\delta_{\rm F}$  -3.4 (quartet,  ${}^{1}J_{\rm BF}$  = 201 Hz) being observed to grow in. Comparison of multinuclear NMR and IR data with those reported for  $(\eta^5-C_5Me_5)Fe(CO)_2BF_2$  (prepared from Na[ $(\eta^5-C_5Me_5)Fe(CO)_2$ ] and BF<sub>3</sub>·OEt<sub>2</sub>)<sup>15</sup> and for other – BF<sub>2</sub> complexes,<sup>24</sup> strongly suggests that this second species is the diffuoroboryl complex  $(\eta^5-C_5Me_5)Fe(CO)_2BF_2$ , 4. Although 4 is the major boron-containing component of the reaction mixture after 1 h, complete conversion to a single iron/boron product proved impossible.

The unusual reactivity displayed by boryl complexes **2a** and **3a** towards Na[BAr<sup>*t*</sup><sub>4</sub>] contrasts with that observed for the mesityl complex ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(Mes)Br, which cleanly generates [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>BMes]<sup>+</sup>[BAr<sup>*t*</sup><sub>4</sub>]<sup>-,6,7</sup> Presumably, given the differing steric and electronic properties of the Mes and OMes substituents, this behaviour is dominated by the smaller degree of steric shielding at the highly electrophilic boron centre afforded by the OMes group, leading to a more reactive putative borylene species in [( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>B(OMes)]<sup>+</sup>.

Given the lability demonstrated by the putative aryloxyborylene complexes  $[(\eta^5-C_5R_5)Fe(CO)_2B(OMes)]^+$ , we have sought to exploit the greater steric shielding afforded by amino substituents at the boron centre. We have previously shown that the aminoborylene complex  $[(\eta^5-C_5Me_5)Fe(CO)_2B(NMe_2)]^+$  is accessible by halide abstraction chemistry and stable enough below -30 °C to permit spectroscopic characterization and subsequent chemical trapping.<sup>7</sup> By increasing the steric bulk of the amino substituents we have therefore sought to exploit this methodology towards the synthesis of more robust cationic borylene species. In a similar fashion to its NMe<sub>2</sub> substituted counterpart,<sup>25a</sup> the asymmetric chloroboryl complex  $(\eta^5 - C_5 H_5)Fe(CO)_2B(N^iPr_2)Cl$ (7a) can be synthesized by the reaction of  ${}^{i}Pr_{2}NBCl_{2}$  with one equivalent of  $Na[(\eta^5-C_5H_5)Fe(CO)_2]$  in toluene (Scheme 3). As with anyloxyboryl complexes 2a, 2b and 3a, this reaction proceeds with the selective substitution of one chloride substituent, with negligible quantities of the disubstituted species  $[(\eta^5-C_5H_5)Fe(CO)_2]_2B(N^iPr_2)$  being formed (as determined by <sup>11</sup>B NMR). Indeed, all attempts to substitute the second chloride to form the bridging borylene complex, even by using very forcing conditions failed to produce  $[(\eta^5-C_5H_5)Fe(CO)_2]_2B(N^iPr_2)$ . Due to the high solubility of 7a in hexanes, clean samples could not easily be isolated by crystallization at low temperatures. However, sublimation of the crude product (10<sup>-4</sup> Torr, 45 °C) yielded crystalline samples of pure 7a, which have been characterized by multinuclear NMR, IR mass spectrometry (including exact mass determination) and single-crystal X-ray diffraction.

By contrast, the corresponding reaction of the more bulky aminoborane tmpBBr<sub>2</sub> with one equivalent of Na[( $\eta^5$ - $C_5H_5$ )Fe(CO)<sub>2</sub>] in toluene does not yield the analogous boryl complex  $(\eta^5-C_5H_5)Fe(CO)_2B(tmp)Br$ , but leads instead to the supported bridging borylene  $[(\eta^5-C_5H_5)Fe(CO)]_2(\mu-CO)(\mu-Btmp)$ 8 (Scheme 4). The structure of 8 in solution is derived from spectroscopic measurements, including mass spectrometry data and exact mass measurements. In addition to the presence of  $\eta^5$ - $C_5H_5$  and 2,2,6,6-tetramethylpiperidyl moieties in the <sup>1</sup>H and <sup>13</sup>C NMR spectra in the expected 2:1 ratio, the <sup>11</sup>B NMR spectrum of **8** shows a resonance at  $\delta_{\rm B}$  115.3, which is characteristically shifted downfield ca. 90 ppm from the starting material, indicating the replacement of both bromides by  $(\eta^5-C_5H_5)Fe(CO)_2$  fragments.<sup>21a,26</sup> This chemical shift value is very similar to that for other bridging aminoborylene complexes [e.g.,  $\delta_{\rm B}$  118.4, 119.1 and 105.9 for {( $\eta^{5}$ - $C_5R_5$ )Fe(CO) $_2(\mu$ -CO)( $\mu$ -BN $_3P_2$  ( $R_5 = H_5$  or  $H_4$ Me) and { $(\eta^5-C_5H_5)Ru(CO)$ }<sub>2</sub>( $\mu$ -CO)( $\mu$ -BN{SiMe<sub>3</sub>}<sub>2</sub>, respectively].<sup>25</sup> The <sup>13</sup>C NMR data for **8** shows both terminal and bridging carbonyl signals ( $\delta_{\rm C}$  217.6 and 274.7, respectively) and this together with the carbonyl stretches (1911 and 1762 cm<sup>-1</sup>) provides strong evidence for the proposed structure,  $[(\eta^5-C_5H_5)Fe(CO)]_2(\mu-CO)(\mu-Btmp)$ . The carbonyl stretching frequencies for 8 are very similar to those for the bridging aminoborylene complexes  $\{(\eta^5 - C_5 R_5)Fe(CO)\}_2(\mu - \theta)$ CO)( $\mu$ -BN{SiMe<sub>3</sub>}<sub>2</sub> (R<sub>5</sub> = H<sub>5</sub>, 1924 and 1770 cm<sup>-1</sup>; R<sub>5</sub> = H<sub>4</sub>Me, 1925 and 1770 cm<sup>-1</sup>), and in common with these species a *trans* arrangement of the terminal CO ligands in 8 would be expected on steric grounds.<sup>25</sup> Intriguingly, no evidence of the intermediate boryl complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(tmp)Br is seen in the <sup>11</sup>B NMR spectrum of the reaction mixture at any time, indicating that if



Scheme 4 Reactivity of terminal aminoborylene complex 9. *Reagents and conditions*: (i) [PPN]Cl (1.67 equiv.), dichloromethane- $d_2$ , 20 °C, 10 min, quantitative (by NMR); (ii) H<sub>2</sub>O (*ca.* 50 equiv.), dichloromethane- $d_2$ , 20 °C, 2 h, 72%; (iii) Ph<sub>3</sub>P=S or Ph<sub>3</sub>As=O (1 equiv.), dichloromethane, 20 °C, 30 min, quantitative by NMR; (iv) Ph<sub>3</sub>P=O (1 equiv.), dichloromethane, 20 °C, 30 min, 43%; (v) 35 °C, 480 h.

this species is an intermediate in the formation of **8**, it never achieves measurable concentration. The difference in reactivity between the two aminoboranes 'Pr<sub>2</sub>NBCl<sub>2</sub> and tmpBBr<sub>2</sub> towards Na[( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>] is difficult to rationalize in terms of the (similar) electronic properties of the two amino substituents, and the greater steric demands of tmp over N<sup>7</sup>Pr<sub>2</sub>, but presumably reflects the differences in reactivities of B–Cl and B–Br bonds. Moreover, the lability of the putative tmp(halo)boryl complex ( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(tmp)Br is somewhat surprising given the likely degree of steric shielding at the boron centre towards attack by a second equivalent of the organometallic nucleophile.<sup>27</sup>

The reactivities of amino(halo)boryl complexes 5a and 7a towards Na[BAr<sup>f</sup><sub>4</sub>] have also been investigated. Reaction of ( $\eta^5$ - $C_5Me_5$ )Fe(CO)<sub>2</sub>B(NMe<sub>2</sub>)Cl (5a) with Na[BAr<sup>4</sup><sub>4</sub>] in CD<sub>2</sub>Cl<sub>2</sub> at -20 °C yields the cationic terminal borylene complex [( $\eta^5$ - $C_5Me_5)Fe(CO)_2B(NMe_2)]^+[BAr_4]^-$  (6), the synthesis of which has previously been reported.<sup>7</sup> Due to the lack of steric shielding around the low-coordinate boron centre, 6 is thermally fragile, but has been characterized by multinuclear NMR and IR spectroscopy at -20 °C and by its reaction with [PPN]Cl in CD<sub>2</sub>Cl<sub>2</sub> to yield the known chloroboryl complex  $(\eta^5-C_5Me_5)Fe(CO)_2B(NMe_2)Cl$ (5b).7 Increased steric shielding was therefore thought to be paramount in the stabilization of the extremely electrophilic boron centre found in these cationic B/N vinylidene analogues. Reaction of 7a with Na[BAr<sup>f</sup><sub>4</sub>] in dichloromethane results in quantitative conversion (by <sup>1</sup>H and <sup>11</sup>B NMR) to  $[(\eta^5 C_5H_5$ )Fe(CO)<sub>2</sub>(BN<sup>i</sup>Pr<sub>2</sub>)]<sup>+</sup>[BAr<sup>f</sup><sub>4</sub>]<sup>-</sup> (9). 9 (along with its  $C_5H_4$ Me counterpart) is a colourless oil at (or close to) 20 °C, but its formulation can be definitively established from spectroscopic and reactivity data. Thus the <sup>11</sup>B chemical shift ( $\delta_B$  93.5) is very close to those reported by Braunschweig for neutral terminal aminoborylene systems of the type  $L_n M = BN(SiMe_3)_2 (\delta_B 86.6-98.3)^{28}$  and the downfield shift on chloride abstraction ( $\Delta \delta_{\rm B}$  38.1 between 7a

and 9) mirrors that found for  $(\eta^5-C_5Me_5)Fe(CO)_2B(Mes)Cl/[(\eta^5-C_5Me_5)Fe(CO)_2B(Mes)Fe(CO)_2B(Mes)Fe(CO)_2B(Mes)Fe(CO)_2B(Mes)Fe(CO)_2B(Mes)Fe(Mes)Fe(CO)_2B(Mes)Fe(CO)_2B(Mes)Fe(CO$  $C_5Me_5$  [Fe(CO)<sub>2</sub>(BMes)]<sup>+</sup> ( $\delta_B$  112.1 and 145.0) and for ( $\eta^5$ - $C_5Me_5)Fe(CO)_2B(NMe_2)Cl/[(\eta^5-C_5Me_5)Fe(CO)_2(BNMe_2)]^+$  ( $\delta_B$ 58.6 and 88.0).<sup>6,7</sup> <sup>1</sup>H and <sup>13</sup>C NMR data are consistent with the presence of  $(\eta^5 - C_5 H_5)$ , N<sup>*i*</sup>Pr<sub>2</sub> and  $[BAr_4^{f_4}]^-$  moieties in a 1 : 1 : 1 ratio, and the ES+ mass spectrum shows the presence of the  $[(\eta^5 C_5H_5$ )Fe(CO)<sub>2</sub>(BN<sup>i</sup>Pr<sub>2</sub>)]<sup>+</sup> cation. The observation of equivalent <sup>i</sup>Pr amino substituents is consistent with the structure of the related neutral system  $(\eta^5-C_5H_5)V(CO)_3=BN(SiMe_3)_2$ <sup>28c</sup> and agrees with the results of DFT calculations for the model compounds  $[(\eta^5 C_5R_5$ )Fe(CO)<sub>2</sub>(BNMe<sub>2</sub>)]<sup>+</sup> (R = H, Me) for which a minimum energy structure close to  $C_s$  symmetry [ $\angle$ centroid-Fe–N–C  $\approx$  $90^{\circ}$  (84.6° for R = Me)] and a low barrier to rotation about the Fe-B-N axis (ca. 2.2 kcal mol<sup>-1</sup>) have been calculated.<sup>29</sup> Additionally, the IR spectrum of 9 shows carbonyl stretching frequencies (2070, 2028 cm<sup>-1</sup>) which are significantly blue-shifted with respect to 7a (2001, 1941 cm<sup>-1</sup>) {*cf*.  $\Delta v \approx 50$  cm<sup>-1</sup> for  $(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}B(Mes)Cl/[(\eta^{5}-C_{5}Me_{5})Fe(CO)_{2}(BMes)]^{+}$  and which are very similar to those reported for archetypal Fischer carbene systems such as  $[(\eta^5-C_5H_5)Fe(CO)_2=CH(SPh)]^+[PF_6]^-$ (2073, 2034 cm<sup>-1</sup>).<sup>30</sup> Further evidence for the nature of 9 is obtained (i) from its reaction with [PPN]Cl which in common with the analogous reaction for structurally characterized cationic derivatives,<sup>6,7</sup> generates a haloboryl complex (in this case 7a) by halide addition at boron; and (ii) from its reaction with  $Ph_3P=O$ which proceeds via the structurally characterised adduct  $[(\eta^5 C_5H_5$ )Fe(CO)<sub>2</sub>{B(N<sup>*i*</sup>Pr<sub>2</sub>)(OPPh<sub>3</sub>)}]<sup>+</sup>[BAr<sup>f</sup><sub>4</sub>]<sup>-</sup> (vide infra).

#### (iii) Reactivity of terminal aminoborylene complex 9

Reports of the fundamental chemistry of M=B double bonds have been somewhat limited, predominantly to metal-metal transfer reactions and addition/substitution reactivity towards nucleophiles.<sup>7,28,31</sup> Thus, for example, the chemistry of  $[(\eta^5-C_5Me_5)Fe(CO)_2(BMes)]^+$  (Mes =  $C_6H_2Me_3$ -2,4,6) is dominated by electrophilic character at both Fe and B centres, while neutral aminoborylene complexes of the type (OC)<sub>5</sub>MBN(SiMe<sub>3</sub>)<sub>2</sub> (M = Cr or W) act as effective sources of the [BN(SiMe<sub>3</sub>)<sub>2</sub>] fragment towards metal complexes bearing labile ligands, and towards C=C triple bonds.<sup>7,28,32</sup> Hence it was with a view to further exploring the scope of reactivity of these highly unsaturated complexes, that we set about investigating the synthesis of cationic aminoborylene systems,  $[L_nM=BNR_2]^+$ . The reactivity of  $[(\eta^5-C_3H_3)Fe(CO)_2(BN^iPr_2)]^+$  [BAr<sup>4</sup><sub>4</sub>]<sup>-</sup>, 9, towards a range of nucleophilic and/or unsaturated reagents has been examined (see Scheme 4), with examples of addition, protonolysis and metathesis chemistries having been established.

The reactivity of 9 towards anionic nucleophiles, exemplified by chloride, mirrors that observed for the arylborylene complex [ $(\eta^5$ - $C_5Me_5$ )Fe(CO)<sub>2</sub>(BMes)]<sup>+</sup>[BAr<sup>f</sup><sub>4</sub>]<sup>-</sup>, being characterized by addition at the boron centre. Thus, reaction of 9 with [PPN]Cl regenerates chloroboryl complex 7a, the identity of which was confirmed by spectroscopic data indistinguishable from authentic samples synthesized from Na[ $(\eta^5-C_5H_5)Fe(CO)_2$ ] and <sup>*i*</sup>Pr<sub>2</sub>NBCl<sub>2</sub>. The reactivity of 9 towards water also displays similarities to the chemistry observed for related M-B bonds towards protic reagents. Thus, the reaction proceeds via scission of the Fe-B linkage,17 although somewhat surprisingly this is also accompanied by breakage of the B-N bond. The nitrogen-containing product isolated from the reaction has been shown by spectroscopic and crystallographic studies (see ESI<sup>†</sup>) to be the diisopropylammonium salt  $[H_2N^iPr_2]^+[BAr_4]^-$  (10); the boron- and iron-containing products can be shown by comparison with previously reported data to be B(OH)<sub>3</sub> and [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub>, respectively.<sup>16</sup> B-N bond breakage under these mild conditions is somewhat unexpected; <sup>*i*</sup>Pr<sub>2</sub>NBCl<sub>2</sub> for example undergoes hydrolysis to yield a mixture of  $({}^{i}Pr_{2}NBO)_{3}$  and  $({}^{i}Pr_{2}NBCl)_{2}(\mu-O)$  under aqueous basic conditions after prolonged stirring at room temperature.17b

Although the reactivity of cationic aminoborylene complex **9** towards Cl<sup>-</sup> is indicative of the electrophilic character known to dominate the chemistry of  $[(\eta^5-C_5Me_5)Fe(CO)_2(BMes)]^+[BAr^f_4]^-$ , its reactivity towards unsaturated substrates suggests a broader scope for its chemistry. Thus, the reaction of **9** with Ph<sub>3</sub>P=S in dichloromethane at 20 °C leads to the formation of  $[(\eta^5-C_5H_5)Fe(CO)_2(PPh_3)]^+[BAr^f_4]^-$  (**11a**) and  ${}^{i}Pr_2NB(\mu-S)_2BN^iPr_2$  (**12a**) with >95% conversion (as determined by <sup>1</sup>H, <sup>11</sup>B and <sup>31</sup>P NMR spectroscopies). The identities of the isolated products **11a** and **12a** were confirmed by comparison of multinuclear NMR (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>19</sup>F and <sup>31</sup>P), IR and mass spectrometry data with those reported for authentic samples.<sup>17,18</sup> Similar reactivity towards Ph<sub>3</sub>As=O leads to the isolation of  $[(\eta^5-C_5H_5)Fe(CO)_2(AsPh_3)]^+[BAr^f_4]^-$  (**11b**) and (<sup>i</sup>Pr\_2NBO)\_3 (**12b**).<sup>17,18</sup>

The reactions of **9** with Ph<sub>3</sub>P=S and Ph<sub>3</sub>As=O represent, to our knowledge, the first examples of net metathesis chemistry for a terminal borylene complex.<sup>33</sup> Although metathesis chemistry has been reported for isoelectronic vinylidene systems ( $\eta^{5}$ -C<sub>3</sub>H<sub>3</sub>)M(CO)<sub>2</sub>=C=CH<sub>2</sub> (M = Mn, Re),<sup>34</sup> and for B=C double bonds,<sup>33</sup> no such chemistry has been reported for neutral aminoborylene complexes.<sup>28</sup> The origins of the differing reactivity of **9** and an idea of the likely mechanism can be gauged by examining the analogous reactivity towards Ph<sub>3</sub>P=O. This reaction proceeds at a significantly slower rate than those with Ph<sub>3</sub>P=S or Ph<sub>3</sub>As=O, presumably reflecting the greater strength of the P=O bond. In this case, however, it is possible to identify a reaction intermediate which is characterized by NMR signals at  $\delta_{\rm B}$  48.9 and  $\delta_{\rm P}$  48.3. The former resonance is consistent with values previously reported for base-stabilized terminal borylene complexes (e.g.  $\delta_{\rm B}$  51.7–53.2 for N-donor adducts of osmium aminoborylenes),<sup>31</sup> whereas the  $^{31}P$ chemical shift is as expected for donor/acceptor adducts of Ph<sub>3</sub>PO with boron-centred Lewis acids ( $\delta_P$  43.6–46.7).<sup>35</sup> In addition, the observations of inequivalent 'Pr groups by 'H and ''C NMR and of significantly lower carbonyl stretching frequencies (2004, 1949 cm<sup>-1</sup>) are both consistent with the formation of a trigonal planar boron centre by coordination of a Lewis base. Confirmation that the intermediate species is indeed the B-bound Ph<sub>3</sub>PO adduct  $[(\eta^5-C_5H_5)Fe(CO)_2\{B(N^iPr_2)(OPPh_3)\}]^+[BAr_4^f]^-(13)$  has been obtained crystallographically (vide infra). Given the isolation of 13, it is plausible that the first step in the reaction mechanism involves coordination of  $Ph_3E=X$  (E = P, As; X = O, S) at boron, and that the overall metathesis chemistry of 9 therefore occurs via a combined addition/substitution pathway (Scheme 5). Such a proposal contrasts with the concerted metallacyclobutane mechanism known to operate for M=C/C=C metathesis,<sup>36</sup> but is plausible given the polar nature of the M=B and E=X bonds involved, and the previously demonstrated propensity of cationic borylenes to undergo addition at boron and substitution at the metal centre.7



Scheme 5 Proposed addition/substitution pathway for metathesis reactions of  $[(\eta^5-C_5H_5)Fe(CO)_2B(N'Pr_2)]^+[BAr'_4]^-$ , 9 (exemplified by Ph<sub>3</sub>P=S).

#### (iv) Spectroscopic and structural studies

Single-crystal X-ray diffraction studies were undertaken on compounds 2a, 2d, 3a, 7a, 10 and 13; of these, the structure of  $[H_2N'Pr_2]^+[BAr'_4]^-$ , 10 was obtained predominantly for compound verification and shows geometric features very similar to related derivatives. Hence this structure together with that of 3a (which closely resembles that of 2a) have been included only in the ESI.† For the remaining compounds, details of data collection, structure solution and refinement parameters are given in Table 1; relevant bond lengths and angles are included in the figure captions. Complete details of *all* structures are given in the ESI‡ and have been deposited with the Cambridge Structural Database.

The structures of mesityloxy(chloro)boryl complexes **2a** and **3a** (see Fig. 1 and ESI†) display the expected half sandwich geometry at the iron centre with the coordination sphere being completed by two carbonyls and the B(OMes)Cl ligand. The ironboron distances for **2a** and **3a** are relatively short [1.977(4) Å for both compounds];<sup>1</sup> however in each case the orientation of the boryl plane (*i.e.* that defined by the B, O and Cl atoms) relative to that defined by the cyclopentadienyl centroid, Fe and B atoms [torsion angles are 67.1(2) and 87.6(2)° for **2a** and **3a**, respectively] and the relatively low carbonyl stretching frequencies (2002, 1940 and 1971, 1925 cm<sup>-1</sup>, respectively) indicate little or no Fe  $\rightarrow$  B  $\pi$ 

| Table 1         Crystallographic data | t for 2a, 2d, 7a | and <b>13</b>  |  |  |  |
|---------------------------------------|------------------|--|--|--|--|
|                                       |                  | 2a   | 2d   | 7a   | 13   |
| Empirical formula                     |                  | C <sub>16</sub> H <sub>16</sub> BCIFeO <sub>3</sub>    | $C_{22}H_{21}BFeO_3S$                                  | C <sub>13</sub> H <sub>19</sub> BCIFeNO <sub>2</sub>   | $\mathrm{C}_{63}\mathrm{H}_{46}\mathrm{B}_{2}\mathrm{F}_{24}\mathrm{FeNO}_{3}\mathrm{P}$ |
| CCDC deposit number                   | L                | 282086   | 282087   | 277456   | 277457   |
| $M_r$                                 |                  | 358.40   | 432.11   | 323.40   | 1429.45  |
| T/K                                   |                  | 180(2)   | 180(2)   | 150(2)   | 150(2)   |
| λ/Å                                   |                  | 0.71073  | 0.71073  | 0.71073  | 0.71073  |
| Crystal system                        |                  | Triclinic  | Monoclinic   | Orthorhombic   | Triclinic  |
| Space group                           |                  | $P\overline{1}$  | $P2_1/n$   | Pbca   | $P\overline{l}$  |
| a/Å                                   |                  | 7.8325(3)  | 14.4401(4)   | 11.7410(4)   | 13.0324(2)   |
| $b/ m \AA$                            |                  | 8.0671(3)  | 9.7496(3)  | 13.9170(4)   | 13.9949(2)   |
| $c/ m \AA$                            |                  | 13.6886(6)   | 14.5657(12)  | 19.0830(7)   | 19.1002(3)   |
| $a/^{\circ}$                          |                  | 81.631(2)  | 06   | 06   | 68.7080(10)  |
| $\beta /^{\circ}$                     |                  | 81.424(2)  | 91.901(1)  | 06   | 83.7430(10)  |
| y/°                                   |                  | 75.958(2)  | 90   | 90   | 87.4800(10)  |
| $V/Å^3$                               |                  | 824.29(6)  | 2049.51(12)  | 3118.15(18)  | 3226.47(8)   |
| Z                                     |                  | 2  | 4  | 8  | 2  |
| $D_{ m c}/{ m Mg}~{ m m}^{-3}$        |                  | 1.444  | 1.400  | 1.378  | 1.471  |
| $\mu/\mathrm{mm}^{-1}$                |                  | 1.084  | 0.857  | 1.134  | 0.373  |
| F(000)                                |                  | 368  | 896  | 1344   | 1444   |
| Crystal size/mm                       |                  | 0.23 	imes 0.23 	imes 0.05                             | 0.35 	imes 0.12 	imes 0.10                             | 0.25 	imes 0.10 	imes 0.10                             | $0.38 \times 0.25 \times 0.20$   |
| $\theta$ Range for data collec        | stion/°          | 2.93 - 27.49   | 3.49–27.43   | 3.57-26.37   | 2.81–27.54   |
| Index ranges (hkl)                    |                  | -9 to 10, -10 to 10, -16 to 17                         | -18 to 18, -9 to 12, -18 to 18                         | -14 to $14$ , $-17$ to $17$ , $-23$ to $23$            | -16 to 16, $-17$ to 18, $-24$ to 24  |
| No. reflections collecte              | p                | 13020  | 12489  | 22231  | 51247  |
| No. indep. reflns/ $R_{\rm int}$      |                  | 3685 (0.0678)  | 4272 (0.0699)  | 3175 (0.1524)  | 14704(0.1118)  |
| Completeness to $\theta_{\max}$ (     | (%)              | 97.4   | 99.5   | 99.8   | 99.0   |
| Max. and min. transm                  | ISSION           | 0.9478 and 0.7887                                      | 0.9192 and 0.7535                                      | 0.8950 and 0.7647                                      | 0.910 and 0.871  |
| No. of data/restraints,               | /params          | 3685/0/202   | 42/2/0/253   | 31/5/0/1/6   | 14/04/15//913  |
| Goodness-of-fit on $F^2$              |                  | 1.160<br>21  | 1.03/  | 1.038  |  |
| Final K indices $ I > 26$             | تر( <i>1</i> )]  | K1 = 0.0516, WR2 = 0.1113<br>D1 = 0.0013,, D2 = 0.1250 | RI = 0.0534, wR2 = 0.1088<br>BI = 0.1027, wB2 = 0.1085 | KI = 0.0572, WK2 = 0.1157<br>PI = 0.1048, WP2 = 0.1338 | R1 = 0.0718, WR2 = 0.1791<br>P1 = 0.1223, WR2 = 0.1701                                   |
| Largest diff. peak and                | hole∕e Å⁻³       | 0.518 and $-0.588$                                     | 0.398  and  -0.520                                     | 0.505  and  -0.537                                     | 1.086 and -0.608   |
|                                       |                  |  |  |  |  |
| Absorption correction: semi-en        | npirical from e  | equivalents; rennement method: full-r                  | matrix least squares $(F^{z})$ .                       |  |  |
|                                       |                  |  |  |  |  |

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Fig. 1 Structure of  $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)Cl$ , 2a. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (°) for 2a: Fe(1)-B(1) 1.977(4), B(1)-Cl(1) 1.816(4), B(1)-O(3) 1.350(4); B(1)-O(3)-C(8) 124.6(3), centroid-Fe(1)-B(1)-Cl(1) 67.1(2).

back bonding interaction from the metal–based HOMO.§ The Fe–B bond length for **2a** is similar to that measured for the catecholboryl complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Bcat [cat = O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-1,2; 1.959(6) Å] but the higher carbonyl stretching frequencies (2024 and 1971 cm<sup>-1</sup>) and the near zero torsion angle (7.9°) measured for the Bcat complex imply that, in contrast to **2a**, this species features a modest but significant HOMO-derived Fe $\rightarrow$ B  $\pi$  interaction.<sup>39</sup> The torsion angle measured for **2a** is similar to that found for the dichloroboryl complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>BCl<sub>2</sub> (77.7°),<sup>40</sup> implying possible  $\pi$  overlap with the HOMO–2 molecular orbital of the [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sup>+</sup> fragment.<sup>37</sup> However, the significantly shorter Fe–B length [1.942(3) Å] for this compound compared with **2a** is presumably due to the greater  $\pi$  acceptor capability of the –BCl<sub>2</sub> ligand compared to –B(OMes)Cl.<sup>40</sup>

Substitution of the chloride substituent in 2a with para *tert*-butyl phenoxide leads to the new boryl complex ( $\eta^5$ - $C_5H_5)Fe(CO)_2B(OMes)(OC_6H_4^{t}Bu-4)$ , 2c, characterized by an upfield shift in the 11B NMR to 47.4 ppm, indicative of replacement of the chloride with a more  $\pi$  electron releasing phenoxide group. In similar fashion, replacement of the chloride with a thiophenolate group yields 2d, characterized by an <sup>11</sup>B NMR chemical shift of 69.1 ppm. The marked downfield shift of the sulfur-substituted boryl complex 2d (compared to 2c) reflects the greater Lewis acidity of the -B(OMes)SPh ligand compared to  $-B(OMes)OC_6H_4^{T}Bu-4$  and is consistent with the <sup>11</sup>B NMR chemical shifts reported for the platinum(II) bis-boryl complexes  $(Ph_3P)_2Pt(Bcat)_2$  ( $\delta_B$  47.0) and  $(Ph_3P)_2Pt\{B(1,2-S_2C_6H_4)\}_2$  ( $\delta_B$ 72.0).<sup>41</sup> 2d is only the second crystallographically characterized example of a thio-substituted boryl complex,41b and is the first fully characterized boryl to contain mixed oxygen/sulfur substituents (Fig. 2). 2d has a significantly longer Fe-B bond distance than



Fig. 2 Structure of  $(\eta^5-C_5H_3)Fe(CO)_2B(OMes)SPh, 2d$ . Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (°): Fe(1)–B(1) 2.034(4), B(1)–S(1) 1.848(4), B(1)–O(3) 1.349(5); B(1)–O(3)–C(8) 128.4(3), B(1)–S(1)–C(17) 107.8(2), centroid-Fe(1)–B(1)–Cl(1) 57.0(3).

precursor 2a [2.034(4) and 1.977(4) Å, respectively], presumably reflecting, at least in part, the greater steric requirements of the SPh substituent.

Due to its very high solubility in hexanes, it was not possible to crystallize **7a** by cooling even of very concentrated solutions. It did prove possible, however, to obtain crystals of X-ray quality by sublimation of the crude mixture at 40 °C under high vacuum (10<sup>-4</sup> Torr). The molecular structure of **7a** (Fig. 3 and Table 1) reveals a relatively long iron-boron distance [2.054(4) Å] indicative of little Fe–B  $\pi$  interaction in the solid state; this is further evidenced by the near 90° torsion angle [∠centroid-Fe(1)–B(1)–N(1) = 72.5(5)°]. Indeed, similar values are reported by Braunschweig for ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(NMe<sub>2</sub>)Cl [Fe–B = 2.027(5) Å, interplanar



Fig. 3 Structure of  $(\eta^5-C_5H_5)Fe(CO)_2B(N'Pr_2)Cl$ , 7a. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (°): Fe(1)–B(1) 2.054(4), B(1)–Cl(1) 1.841(4), B(1)–N(1) 1.389(5), centroid-Fe(1)–B(1)–N(1) 83.7(4).

<sup>§</sup> The HOMO of the  $[(\eta^5-C_5H_3)Fe(CO)_2]^+$  fragment is an orbital of a" symmetry lying approximately co-planar with the cyclopentadienyl ring; the HOMO–2 is of a' symmetry and is perpendicular to the HOMO.<sup>37</sup> For a recent analysis of  $\pi$  back-bonding in half-sandwich boryl systems of the type  $(\eta^5-C_5H_3)Fe(CO)_2BX_2$  as a function of the centroid-Fe–B–X torsion angle, see ref. 38.

angle =  $87.4^{\circ}$ ] and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(NMe<sub>2</sub>)B(NMe<sub>2</sub>)Cl [Fe-B = 2.090(3) Å, interplanar angle = 92.4°] for which little or no Fe-B  $\pi$  back bonding is proposed.<sup>25,42</sup> The relatively low carbonyl stretching frequencies for **7a** (2001, 1941 cm<sup>-1</sup>), are similar to those for ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(E{SiMe<sub>3</sub>}<sub>3</sub>)Cl (2009, 1956 cm<sup>-1</sup> for both E = Si, Ge), and ( $\eta^5$ -C<sub>3</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>B(NMe<sub>2</sub>)Cl (2006, 1946 cm<sup>-1</sup>) and give further evidence that there is little Fe–B  $\pi$  back bonding.<sup>22,25</sup> As found for related derivatives,<sup>25,42</sup> the B– N bond distance for **7a** is relatively short [1.389(5) Å], revealing appreciable  $\pi$  bond character in the solid state; this increased B–N bond order is also apparent in solution—the <sup>1</sup>H and <sup>13</sup>C NMR spectra for **7a** show two sets of signals for the isopropyl CH and CH<sub>3</sub> groups, consistent with slow rotation about the B–N bond on the NMR timescale.

The structure of the Ph<sub>3</sub>PO adduct  $[(\eta^5-C_5H_5)Fe(CO)_2-{B(N^iPr_2)(OPPh_3)}]^+[BAr^f_4]^-(13)$  has also been determined (see Fig. 4 and Table 1). Consistent with related complexes,<sup>31,43</sup> the Fe–B bond length for 13 [2.057(4) Å] is more akin to that expected for a single bond than a double bond {*cf.* 2.054(4) and 1.792(8) Å for 7a and  $[(\eta^5-C_5Me_5)Fe(CO)_2(BMes)]^+$ , respectively}.<sup>6,7</sup> Such a phenomenon has previously been ascribed to significant contributions from resonance forms incorporating a formal M–B single bond (as in Scheme 5),<sup>31</sup> and a description of 13 as an amino(oxy)boryl species featuring a pendant cationic phosphorus centre is probably most apt. Consistent with this, the PO distance in 13 is significantly longer then that found in free Ph<sub>3</sub>PO [1.540(2) *vs.* 1.493 Å (mean)].<sup>44</sup>



Fig. 4 Structure of the cationic component of  $[(\eta^5-C_3H_3)Fe(CO)_2-\{B(N'Pr_2)(OPPh_3)\}]^*[BAr^f_4]^-$ , 13. Hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 50% probability level. Important bond lengths (Å) and angles (°): Fe(1)–B(1) 2.057(4), B(1)–O(3) 1.469(4), B(1)–N(1) 1.397(5), P(1)–O(3) 1.540(2); P(1)–O(1)–B(1) 148.0(2), centroid-Fe(1)–B(1)–N(1) 72.5(5).

#### 4 Conclusions

Heteroatom stabilized asymmetric haloboryl complexes of the types  $(\eta^5-C_5R_5)Fe(CO)_2B(OMes)X$  and  $(\eta^5-C_5H_5)Fe(CO)_2$ -

 $B(N^{i}Pr_{2})Cl$  can be formed via salt elimination reactions of the haloboranes MesOBX<sub>2</sub> or <sup>i</sup>Pr<sub>2</sub>NBCl<sub>2</sub> with the appropriate transition metal anion. Conversely, reaction of tmpBBr<sub>2</sub> with  $Na[(\eta^5-C_5H_5)Fe(CO)_2]$  yields only the bridging borylene species  $[(\eta^5-C_5H_5)Fe(CO)]_2(\mu-CO)(\mu-Btmp)$  seemingly independent of reaction conditions.  $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)Cl$  is found to be a versatile substrate for substitution chemistry with retention of the Fe-B bond, leading to the formation of new asymmetric boryl complexes  $(\eta^5-C_5H_5)Fe(CO)_2B(OMes)ER_n$  $(ER_n = OC_6H_4^{T}Bu-4 \text{ or SPh})$ , the latter complex being the first crystallographically characterized example of a boryl species containing mixed oxygen/sulfur substituents. The reaction of complexes  $(\eta^5 - C_5 R_5)Fe(CO)_2B(OMes)Cl$  (R = H or Me) with Na[BAr<sup>f</sup><sub>4</sub>] leads to the formation of fluoroboryl complexes ( $\eta^5$ - $C_5R_5$ )Fe(CO)<sub>2</sub>B(OMes)F and ( $\eta^5$ - $C_5Me_5$ )Fe(CO)<sub>2</sub>BF<sub>2</sub>, presumably due to halide abstraction from  $[BAr_4^f]^-$  by the putative cationic terminal borylene species  $[(\eta^5-C_5R_5)Fe(CO)_2BOMes]^+$ . Application of halide abstraction to  $(\eta^5 - C_5 H_5)Fe(CO)_2B(N^i Pr_2)Cl$ on the other hand yields the cationic terminal borylene complex  $[(\eta^5-C_5H_5)Fe(CO)_2BN^iPr_2]^+[BAr_4]^-$ , which displays a range of novel reaction chemistries including metathesis.

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