

# Fe=B Double Bonds: Synthetic, Structural, and Reaction Chemistry of Cationic Terminal Borylene Complexes

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Application of halide abstraction chemistry to asymmetric haloboryl complexes ( $\eta^5\text{-C}_5\text{-Me}_5\text{Fe}(\text{CO})_2\text{B}(\text{ER}_n)\text{X}$ ) leads to the first synthetic route to cationic multiply bonded group 13 diyl species,  $[(\eta^5\text{-C}_5\text{Me}_5\text{Fe}(\text{CO})_2\text{B}(\text{ER}_n))]^+$ . The roles of steric bulk and  $\pi$  electron release within the  $\text{ER}_n$  substituent in generating tractable borylene complexes have been probed, as has the nature of the counterion. A combination of spectroscopic, structural, and computational techniques leads to the conclusion that the bonding in complexes such as  $[(\eta^5\text{-C}_5\text{Me}_5\text{Fe}(\text{CO})_2\text{B}(\text{Mes}))]^+$  is best described as an Fe=B double bond composed of B $\rightarrow$ Fe  $\sigma$  donor and Fe $\rightarrow$ B  $\pi$  back-bonding components. An extended study of the fundamental reactivity of cationic borylene systems reveals that this is dominated not only by nucleophilic addition at boron but also by iron-centered substitution chemistry leading to overall displacement of the borylene ligand.

## Introduction

The quest for transition metal complexes incorporating multiply bonded main group ligands has excited much recent interest, not only due to the fundamental questions of structure and bonding posed by such systems but also due to their implication as reagents or potential catalytic intermediates in important synthetic processes.<sup>1–6</sup> Although the chemistries of carbon-based ligand systems [e.g., alkylidenes or Fischer carbenes ( $\text{R}_2\text{C}$ )<sup>1</sup>] and more recently their heavier con-

geners [e.g., silylenes ( $\text{R}_2\text{Si}$ )<sup>2</sup>] dominate this area, recent studies have sought to develop the related chemistry of group 13 diyl ligands ( $\text{RE}$ ).<sup>3–10</sup> Numerous complexes

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have been reported featuring diyl ligands adopting bridging modes of coordination [e.g.,  $(L_nM)_2(\mu-ER)$ ],<sup>7–10</sup> but the synthetic, structural, and reaction chemistry of analogous compounds containing terminally bound ligands is less thoroughly understood.<sup>3–6</sup> Within this field, terminal borylene systems ( $L_nMBR$ ) represent a very recent and numerically small addition,<sup>3,4</sup> with the highly Lewis acidic boron center typically being stabilized by sterically bulky or  $\pi$  donor R groups or by coordination of a tethered base. Systematic studies of the metal–boron bond in two-coordinate borylene complexes such as these have been severely hampered by the paucity of synthetic routes available and by the narrow range of compatible metal fragments (predominantly metal carbonyls). The lack of *suitable* borane precursors of the type  $(RE)_n$  rules out one of the principal synthetic approaches available to the heavier group 13 elements,<sup>6,10</sup> and the scope of the salt elimination methodology used to give access to complexes such as  $(\eta^5-C_5Me_5)BFe(CO)_4$ <sup>3a</sup> or  $(OC)_5WBN(SiMe_3)_2$ <sup>3b</sup> has been shown to be limited to a very narrow range of boron dihalide and metal dianion precursors. Although photolytic borylene transfer has recently been shown to offer a potentially versatile new synthetic route [e.g., to previously inaccessible species such as  $(\eta^5-C_5H_5)V(CO)_3BN(SiMe_3)_2$ <sup>3c</sup>], structurally characterized terminal borylene complexes still number no more than a handful.

In recent work we have demonstrated that asymmetric haloboryl complexes  $L_nMB(R)X$  not only are readily accessible but also prove to be versatile substrates for boron-centered *substitution* chemistry,<sup>8,11</sup> leading to a range of novel bridging borylene and asymmetric boryl complexes. Given that halide (or pseudo-halide) *abstraction* from coordinated ligand fragments has previously been used to great effect in the synthesis of low-coordinate or unsaturated group 14 systems,<sup>2</sup> we speculated that a similar methodology applied to haloboryl complexes might offer a versatile new route to terminally bound group 13 diyl complexes. Such an approach proves to be viable, leading to the development of a new route to terminal borylene complexes and to the first examples of cationic group 13 diyls  $[L_nMER]^+ \cdot [(\eta^5-C_5Me_5)Fe(CO)_2(BMes)]^+ [BAR^f]^-$  [ $Mes = 2,4,6-Me_3C_6H_2$ ,  $Ar^f = C_6H_3(CF_3)_2-3,5$ ], for example, contains the shortest M–B distance yet reported (a feature that is indicative of a novel Fe=B double bond) and is the first borylene complex containing a  $\sigma$ -bound hydrocarbyl substituent.<sup>4a</sup> Herein we report an extended investigation of this synthetic approach to both aryl- and heteroatom-stabilized borylenes, together with an in-depth study aimed at elucidating fundamental patterns of reactivity. Although isolated reports of substitution chemistry for base-stabilized borylenes and of elegant metal-to-metal borylene transfer chemistry have appeared in the recent literature,<sup>3</sup> the fundamental reactivity of group 13 diyl complexes remains a largely uncharted area. Given the superficial similari-

ties between cationic borylene complexes  $[L_nMBR]^+$  and electrophilic carbenes and silylenes  $[L_nMER_2]^+$ , and their more strictly isolobal relationship with carbonyl complexes,  $[L_nMCO]^+$ , we have sought to determine patterns of reactivity toward both nucleophilic and multiply bonded reagents.

## Experimental Section

**(i) General Considerations.** All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or drybox techniques. Solvents were predried 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:  $CaH_2$ ). 3,3-Dimethyl-1-butene was dried over a potassium mirror and  $Me_2S_2$  over molecular sieves prior to use. Benzene- $d_6$  and dichloromethane- $d_2$  (both Goss) were degassed and dried over potassium (benzene- $d_6$ ) or molecular sieves (dichloromethane- $d_2$ ) prior to use. Benzophenone, [PPN]Cl ([PPN]<sup>+</sup> = bis(triphenylphosphoranylidene)ammonium,  $[Ph_3PNPPPh_3]^+$ ),  $[Ph_4P]Br$ ,  $[nBu_4N]I$ ,  $Na[BPh_4]$ ,  $[nBu_4N]BF_4$ , and  $Ag[BF_4]$  (all Aldrich) were dried under high vacuum (ca.  $10^{-4}$  Torr) for 12 h prior to use; CO (BOC) was used without further purification.  $Na[BAR^f_4]$ , [PPN][BPh<sub>4</sub>],  $(\eta^5-C_5H_5)Fe(CO)_2B(Mes)Br$  (**1**),  $(\eta^5-C_5Me_5)Fe(CO)_2B(Mes)Br$  (**2**),  $(\eta^5-C_5H_5)Fe(CO)_2B(C_6H_3Trp_2-2,6)Br$  (**3**) (Trp = 2,4,6-*Pr*<sub>3</sub>C<sub>6</sub>H<sub>2</sub>),  $(\eta^5-C_5Me_5)Fe(CO)_2B(Ph)Cl$  (**4**), and  $(\eta^5-C_5Me_5)Fe(CO)_2B(NMe_2)Br$  (**7**) were prepared by literature methods.<sup>8,11–14</sup>

NMR spectra were measured on a JEOL 300 Eclipse Plus FT-NMR spectrometer. Residual protons of solvent were used for reference for <sup>1</sup>H and <sup>13</sup>C NMR, while a sealed tube containing a solution of  $[nBu_4N][B_3H_8]$  in  $CDCl_3$  was used as an external reference for <sup>11</sup>B NMR. <sup>19</sup>F and <sup>31</sup>P NMR spectra were referenced to external  $CFCl_3$  and  $H_3PO_4$ , respectively. 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, polyethylenimine, and sodium trifluoroacetate were used as the standards for high-resolution EI, ES+, and ES– mass spectra, respectively. Despite repeated attempts, satisfactory elemental microanalysis for new boryl and borylene complexes was frustrated by their extreme air, moisture, and (in some cases) thermal instability. 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 **5**, **10**, **12**, **14**, **15**, and **16**. In all cases the purity of the bulk material was established by multinuclear NMR to be >95%. Abbreviations: st = strong, md = medium, b = broad, s = singlet, d = doublet, q = quartet, pcq = partially collapsed quartet, m = multiplet, fwhm = frequency width at half-maximum.

**(ii) Syntheses. Synthesis of  $[(\eta^5-C_5Me_5)Fe(CO)_2(BMes)]^+ [BAR^f]^-$  (**5**).** A solution of  $(\eta^5-C_5Me_5)Fe(CO)_2B(Mes)Br$  (**2**) (0.046 g, 0.1 mmol) in  $CH_2Cl_2$  (10 cm<sup>3</sup>) was added slowly to a suspension of  $Na[BAR^f_4]$  (0.089 g, 0.1 mmol) in  $CH_2Cl_2$  (10 cm<sup>3</sup>) at  $-78$  °C, and the resulting mixture warmed slowly to room temperature and stirred for 1 h. After this time the reaction was judged to be complete by <sup>11</sup>B NMR spectroscopy, and the reaction mixture was filtered, layered with hexanes, and cooled

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to  $-50\text{ }^{\circ}\text{C}$  for 1 week to yield **5** as colorless crystals suitable for X-ray diffraction (0.070 g, 56%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.01 (s, 15H,  $\eta^5\text{-C}_5\text{Me}_5$ ), 2.34 (s, 3H, para- $\text{CH}_3$ ), 2.63 (s, 6H, ortho- $\text{CH}_3$ ), 6.92 (s, 2H, aromatic CH), 7.54 (s, 4H, para-H of  $\text{BAr}_4^-$ ), 7.70 (s, 8 H, ortho-H of  $\text{BAr}_4^-$ ).  $^{13}\text{C}$  NMR (76 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.7 ( $\eta^5\text{-C}_5\text{Me}_5$ ), 20.8 (ortho- $\text{CH}_3$ ), 21.4 (para- $\text{CH}_3$ ), 97.1 ( $\eta^5\text{-C}_5\text{Me}_5$  quaternary), 116.7 (para-CH of  $\text{BAr}_4^-$ ), 123.8 (q,  $^1J_{\text{CF}} = 271\text{ Hz}$ ,  $\text{CF}_3$  of  $\text{BAr}_4^-$ ), 125.1 (meta-CH of mesityl), 128.6 (q,  $^2J_{\text{CF}} = 31\text{ Hz}$ , meta-C of  $\text{BAr}_4^-$ ), 134.0 (ortho-CH of  $\text{BAr}_4^-$ ), 147.9, 150.1 (quaternary C's of mesityl), 160.9 (q,  $^1J_{\text{CB}} = 49\text{ Hz}$ , ipso-C of  $\text{BAr}_4^-$ ), 211.4 (CO) (ipso-C of mesityl ligand not observed).  $^{19}\text{F}$  NMR (283 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$   $-62.8$  ( $\text{CF}_3$ ).  $^{11}\text{B}$  NMR (96 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$   $-7.6$  ( $\text{BAr}_4^-$ ), 145.0 (b, fwhm ca. 750 Hz,  $\text{BMe}_2$ ). IR ( $\text{CH}_2\text{Cl}_2$  solution,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2055 st, 2013 st. MS (EI): 349 [(M - CO) $^+$ , 15%], 321 [(M - 2CO) $^+$ , 5%], correct isotope distribution for 1 Fe, 1 B atoms. MS (ES neg): 863 [ $\text{BAr}_4^-$ , 100%].

**Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})\text{Br}$  (**2**) with Na[BPh $_4$ ].** A solution of **2** (0.030 g, 0.07 mmol) in  $\text{CH}_2\text{Cl}_2$  (4  $\text{cm}^3$ ) was added slowly to a suspension of Na[BPh $_4$ ] (0.022 g, 0.07 mmol) in  $\text{CH}_2\text{Cl}_2$  (2  $\text{cm}^3$ ) at  $-78\text{ }^{\circ}\text{C}$ , and the resulting mixture was warmed slowly to room temperature and stirred for 16 h. After this time, the reaction was judged to be complete by the disappearance of the resonance due to **2** and the appearance of a single peak at  $\delta_{\text{B}}$  66.0. The compound giving rise to this resonance was subsequently shown to be BPh $_3$  by comparison of spectroscopic data with those reported previously.<sup>15</sup> Volatiles were removed in vacuo, and the remaining solid was extracted with hexanes (5  $\text{cm}^3$ ). Cooling this solution to  $-50\text{ }^{\circ}\text{C}$  yielded orange crystals of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Ph}$ , the identity of which was confirmed by comparison of spectroscopic data with those reported previously.<sup>16</sup>

**Attempted Borylene Syntheses Using Other Aryl(halo)boryl Precursors and Halide Abstraction Reagents.** The reactions of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})\text{Br}$  (**1**),  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{B}(\text{C}_6\text{H}_3\text{Trp}_2, 2, 6)\text{Br}$  (**3**), and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Ph})\text{Cl}$  (**4**) with Na[BAr $_4^-$ ] and of **2** with Ag[BF $_4$ ] were carried out using a common method. Thus for example, a solution of **3** (0.048 g, 0.06 mmol) in  $\text{CH}_2\text{Cl}_2$  (5  $\text{cm}^3$ ) was added slowly to a suspension of Na[BAr $_4^-$ ] (0.056 g, 0.06 mmol) in  $\text{CH}_2\text{Cl}_2$  (5  $\text{cm}^3$ ) at  $-78\text{ }^{\circ}\text{C}$ . The resulting mixture was warmed slowly to room temperature and stirred for 1 h. After this time the  $^{11}\text{B}$  NMR resonance due to **3** ( $\delta_{\text{B}}$  114.9) had disappeared, but no new resonances attributable to borylene or boryl products were observed. In situ monitoring of the halide abstraction process by multinuclear NMR revealed that complete consumption of the boryl starting material is typically achieved very rapidly even at  $-70\text{ }^{\circ}\text{C}$ ; even at such temperatures it proved impossible to detect any products containing Fe=B bonds.

**Reaction of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{NMe}_2)\text{Br}$  (**7**) with Na[BAr $_4^-$ ].** A solution of **7** (0.054 g, 0.14 mmol) in  $\text{CH}_2\text{Cl}_2$  (4  $\text{cm}^3$ ) was added slowly to a suspension of Na[BAr $_4^-$ ] (0.123 g, 0.14 mmol) in  $\text{CH}_2\text{Cl}_2$  (2  $\text{cm}^3$ ) at  $-78\text{ }^{\circ}\text{C}$ . The resulting mixture was warmed slowly to room temperature and stirred for 1 h. After this time the  $^{11}\text{B}$  NMR resonance corresponding to **7** ( $\delta_{\text{B}} = 56.0$ ) had disappeared and had been replaced by a single broad peak at  $\delta_{\text{B}}$  88.0 (fwhm ca. 620 Hz). Monitoring of the progress of the reaction by infrared spectroscopy revealed the accompanying growth of two new carbonyl bands at 2050 (st) and 2006 (st)  $\text{cm}^{-1}$ . The reaction mixture was filtered, layered with hexanes, and cooled to  $-50\text{ }^{\circ}\text{C}$ , but the compounds isolated from repeated crystallizations were shown by  $^{11}\text{B}$  NMR to be hydrolysis products.

**Generation of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{NMe}_2)[\text{BAr}_4^-]$  (**8**) and Trapping with [PPN]Cl.** A solution of **7** (0.020 g, 0.05 mmol) in  $\text{CD}_2\text{Cl}_2$  (2  $\text{cm}^3$ ) was added slowly to a suspension of Na[BAr $_4^-$ ] (0.046 g, 0.05 mmol) in  $\text{CD}_2\text{Cl}_2$  (0.5  $\text{cm}^3$ ) in a Young's

NMR tube at  $-78\text{ }^{\circ}\text{C}$ . The reaction mixture was warmed to  $-40\text{ }^{\circ}\text{C}$ , at which point monitoring by  $^{11}\text{B}$  NMR revealed partial conversion of **7** ( $\delta_{\text{B}}$  56.0) to **8** ( $\delta_{\text{B}}$  88.0); further warming to  $-20\text{ }^{\circ}\text{C}$  and a 30 min period at this temperature led to quantitative conversion of **7** to **8**, as judged by  $^{11}\text{B}$  and  $^1\text{H}$  NMR. Complete NMR characterization of **8** was achieved at this temperature.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.93 (s, 15H,  $\eta^5\text{-C}_5\text{Me}_5$ ), 2.83 (s, 6H,  $\text{NMe}_2$ ), 7.55 (s, 4H, para-H of  $\text{BAr}_4^-$ ), 7.70 (s, 8 H, ortho-H of  $\text{BAr}_4^-$ ).  $^{13}\text{C}$  NMR (76 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  10.3 ( $\eta^5\text{-C}_5\text{Me}_5$ ), 33.3 ( $\text{NMe}_2$ ), 101.8 ( $\eta^5\text{-C}_5\text{Me}_5$  quaternary), 117.6 (para-CH of  $\text{BAr}_4^-$ ), 124.6 (q,  $^1J_{\text{CF}} = 273\text{ Hz}$ ,  $\text{CF}_3$  of  $\text{BAr}_4^-$ ), 128.8 (q,  $^2J_{\text{CF}} = 30\text{ Hz}$ , meta-C of  $\text{BAr}_4^-$ ), 134.8 (ortho-CH of  $\text{BAr}_4^-$ ), 161.8 (q,  $^1J_{\text{CB}} = 50\text{ Hz}$ , ipso-C of  $\text{BAr}_4^-$ ), 207.6 (CO).  $^{19}\text{F}$  NMR (283 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$   $-62.6$  ( $\text{CF}_3$ ).  $^{11}\text{B}$  NMR (96 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$   $-7.7$  ( $\text{BAr}_4^-$ ), 88.0 (b, fwhm ca. 620 Hz,  $\text{BNMe}_2$ ). Cooling the solution to  $-80\text{ }^{\circ}\text{C}$  at this point resulted in no observable splitting of the  $^1\text{H}$  or  $^{13}\text{C}$  resonances attributable to the  $\text{NMe}_2$  group (singlets at  $\delta_{\text{H}}$  2.74 and  $\delta_{\text{C}}$  32.5, respectively). The reaction mixture was then warmed back to  $-20\text{ }^{\circ}\text{C}$  and filtered while cold into a solution of [PPN]Cl (0.150 g, 0.25 mmol) in  $\text{CD}_2\text{Cl}_2$  (1  $\text{cm}^3$ ). After warming to room temperature and stirring for 5 min the reaction mixture was analyzed spectroscopically, revealing clean and complete conversion of **8** to  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{NMe}_2)\text{Cl}$  (**9**). **9** was identified by comparison of spectroscopic data with those reported previously by Braunschweig:<sup>7d</sup>  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.73 (s, 15H,  $\eta^5\text{-C}_5\text{Me}_5$ ), 2.92 (s, 3H,  $\text{NMe}_2$ ), 3.03 (s, 3H,  $\text{NMe}_2$ ).  $^{13}\text{C}$  NMR (76 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.7 ( $\eta^5\text{-C}_5\text{Me}_5$ ), 41.2 ( $\text{NMe}_2$ ), 43.8 ( $\text{NMe}_2$ ), 95.5 ( $\eta^5\text{-C}_5\text{Me}_5$  quaternary), 217.5 (CO).  $^{11}\text{B}$  NMR (96 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  58.6. IR ( $\text{CD}_2\text{Cl}_2$  solution,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1983 st, 1923 st.

**Synthesis of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})\text{Cl}$  (**10**) from **5** and [PPN]Cl.** Details of the synthesis of **10** from **5** and [PPN]Cl have previously been reported by us.<sup>8c</sup> Data are reproduced here solely for comparative purposes. In addition, after our earlier report we have managed to obtain X-ray quality crystals of **10** by repeated recrystallization from hexanes at  $-30\text{ }^{\circ}\text{C}$ . Details of this structure are therefore reported here for the first time. Characterizing data for **10**:  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.35 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 2.20 (s, 3H, para- $\text{CH}_3$ ), 2.28 (s, 6H, ortho- $\text{CH}_3$ ), 6.74 (s, 2H, aromatic CH).  $^{13}\text{C}$  NMR (76 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  9.0 ( $\eta^5\text{-C}_5\text{Me}_5$ ), 21.0 (para- $\text{CH}_3$ ), 21.6 (ortho- $\text{CH}_3$ ), 97.1 ( $\eta^5\text{-C}_5\text{Me}_5$  quaternary), 127.7 (aromatic CH), 133.2, 136.2 (aromatic quaternary), 216.2 (CO).  $^{11}\text{B}$  NMR (96 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  112.1 (b, fwhm ca. 580 Hz). IR (KBr disk,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1996 md, 1936 md. MS (EI):  $\text{M}^+ = 412$  (5%), isotopic pattern corresponding to 1 Fe, 1 B, 1 Cl atoms, strong fragment ion peaks at  $m/z$  384 [(M - CO) $^+$ , 60%] and 356 [(M - 2CO) $^+$ , 100%]. Exact mass: calcd 412.1058, measd 412.1055. In addition, spectroscopic data for the hexane-insoluble product of this reaction are consistent with those reported previously for [PPN][BAr $_4^-$ ].<sup>17</sup>

**Synthesis of **2** from **5** and [Ph $_4\text{P}$ ]Br.** To a solution of [Ph $_4\text{P}$ ]Br (0.045 g, 0.1 mmol) in  $\text{CD}_2\text{Cl}_2$  (2  $\text{cm}^3$ ) was added a solution of **5** (0.040 g, 0.03 mmol) in  $\text{CD}_2\text{Cl}_2$  (2  $\text{cm}^3$ ). The resulting mixture was stirred at room temperature for 2 h, after which the  $^{11}\text{B}$  resonance due to **5** ( $\delta_{\text{B}}$  145.0) was found to be completely converted into a single signal at  $\delta_{\text{B}}$  113.0 characteristic of **2**. Further comparison of multinuclear NMR and IR data (for the isolated compound) with those obtained for an authentic sample of **2** in  $\text{CD}_2\text{Cl}_2$  confirmed the identity of **2** as the sole boron-containing product.<sup>8b</sup>

**Reaction of **5** with [ $^n\text{Bu}_4\text{N}$ ]I.** To a solution of [ $^n\text{Bu}_4\text{N}$ ]I (0.049 g, 0.13 mmol) in  $\text{CH}_2\text{Cl}_2$  (3  $\text{cm}^3$ ) was added a solution of **5** (0.161 g, 0.13 mmol) in  $\text{CH}_2\text{Cl}_2$  (6  $\text{cm}^3$ ). The reaction mixture was stirred for 2 h, at which point  $^{11}\text{B}$  NMR monitoring revealed complete conversion of **5** ( $\delta_{\text{B}}$  145.0) to a single boron-containing species at  $\delta_{\text{B}}$  110.7. Filtration, removal of

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volatiles in vacuo, and recrystallization from hexanes (ca. 10 cm<sup>3</sup>) at -30 °C initially yielded a small quantity (<<0.010 g) of a dark red crystalline solid subsequently identified crystallographically as ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>I (**13**) (full crystallographic details are included in the Supporting Information).<sup>18</sup> Subsequent cooling of the supernatant solution to -50 °C then yielded pale yellow crystals of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(Mes)I (**11**) (0.038 g, 56%). Characterizing data for **11**: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.26 (s, 15H,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 2.22 (s, 6H, ortho-CH<sub>3</sub>), 2.24 (s, 3H, para-CH<sub>3</sub>), 6.70 (s, 2H, aromatic CH). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.9 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 20.9 (para-CH<sub>3</sub>), 21.1 (ortho-CH<sub>3</sub>), 95.5 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> quaternary), 130.6 (aromatic CH), 129.0, 136.4 (aromatic quaternary), 216.3 (CO). <sup>11</sup>B NMR (96 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  110.7. IR (KBr disk, cm<sup>-1</sup>):  $\nu$ (CO) 2005 st, 1955 st. MS (EI): fragment ion peaks at *m/z* 476 [(M - CO)<sup>+</sup>, 25%], 448 [(M - 2CO)<sup>+</sup>, 5%]. Periodic sampling of the reaction mixture by infrared spectroscopy revealed, in addition to bands attributable to **11** [ $\nu$ (CO) 2005 and 1955 cm<sup>-1</sup>], weaker shoulders at 2017 and 1969 cm<sup>-1</sup>, which were present even at short reaction times (ca. 30 min) and whose relative intensities (with respect to the bands at 2005 and 1955 cm<sup>-1</sup>) appeared to vary little. For comparative purposes ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>I (**13**) in CH<sub>2</sub>Cl<sub>2</sub> has been reported to give rise to bands at 2019 and 1971 cm<sup>-1</sup>,<sup>18</sup> in addition those measured for a sample of **13** prepared independently from [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>]Na and **I**<sub>2</sub> are at 2017 and 1971 cm<sup>-1</sup>.

**Synthesis of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(Mes)F (**12**) from **5** and [<sup>7</sup>Bu<sub>4</sub>N]BF<sub>4</sub>.** To a solution of [<sup>7</sup>Bu<sub>4</sub>N]BF<sub>4</sub> (0.056 g, 0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) was added slowly a solution of **5** (0.212 g, 0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 cm<sup>3</sup>). The reaction mixture was stirred for 2 h, at which point <sup>11</sup>B NMR monitoring revealed complete conversion of **5** to a single boron-containing species at  $\delta_B$  90.4. Filtration, removal of volatiles in vacuo, and recrystallization from hexanes (ca. 10 cm<sup>3</sup>) at -50 °C yielded yellow crystals of **12** suitable for X-ray diffraction (0.043 g, 63%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.49 (s, 15H,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 2.16 (s, 3H, para-CH<sub>3</sub>), 2.43 (s, 6H, ortho-CH<sub>3</sub>), 6.73 (s, 2H, aromatic CH). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.4 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 21.0 (para-CH<sub>3</sub>), 21.6 (ortho-CH<sub>3</sub>), 96.3 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> quaternary), 128.8 (aromatic CH), 135.9 (d, <sup>3</sup>J<sub>CF</sub> = 3.5 Hz), 136.9 (aromatic quaternary), 216.7 (CO). <sup>19</sup>F NMR (283 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  56.2 (pcq). <sup>11</sup>B NMR (96 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  90.4 (b, d, <sup>1</sup>J<sub>BF</sub> = 180 Hz). The resonance observed in the <sup>11</sup>B{<sup>1</sup>H} spectrum of **12** in C<sub>6</sub>D<sub>6</sub> room temperature was broad, with coupling to the <sup>19</sup>F nucleus not completely resolved. Warming to 60 °C however allows the two components of the doublet to be resolved and the coupling constant to be determined (<sup>11</sup>B{<sup>1</sup>H} spectra at 20, 40, and 60 °C are included in the Supporting Information). IR (KBr disk, cm<sup>-1</sup>):  $\nu$ (CO) 1989 st, 1931 st. MS (EI): M<sup>+</sup> = 396 (5%), isotopic pattern corresponding to 1 Fe, 1 B atoms, fragment ion peaks at *m/z* 368 [(M - CO)<sup>+</sup>, 15%], 340 [(M - 2CO)<sup>+</sup>, 100%], and 325 [(M - 2CO - Me)<sup>+</sup>, 30%]. Exact mass: calcd 396.1354, measd 396.1356.

**Reaction of **5** with [PPN][BPh<sub>4</sub>].** To a solution of [PPN][BPh<sub>4</sub>] (0.150 g, 0.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 cm<sup>3</sup>) was added slowly a solution of **5** (0.217 g, 0.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) at -78 °C and the resulting mixture warmed slowly to room temperature and stirred for 1 h. After this time, the reaction was judged to be complete by the disappearance of the resonance due to **5** and the appearance of a single peak at  $\delta_B$  66.0. The compound giving rise to this resonance was subsequently shown to be BPh<sub>3</sub> by comparison of spectroscopic data with those reported previously.<sup>15</sup> Volatiles were removed in vacuo, and the remaining solid was extracted with hexanes (5 cm<sup>3</sup>). Cooling this solution to -50 °C yielded orange crystals of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>Ph, the identity of which was confirmed by comparison of spectroscopic data with those reported previously.<sup>16</sup>

**Reaction of **5** with CO.** A solution of **5** (0.217 g, 0.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was stirred for 6 h under a continuous flow of CO, after which the reaction was judged to be complete by <sup>11</sup>B NMR (by the complete replacement of the peak due to the starting material with a single peak at  $\delta_B$  17). Volatiles were removed in vacuo and the remaining solid washed successively with hexanes, toluene, and dichloromethane (ca. 10 cm<sup>3</sup> of each). No boron-containing products could be detected in any of the washings by <sup>11</sup>B NMR, thus implying significant volatility for the species giving rise to the resonance at  $\delta_B$  17 in the original reaction mixture. The red dichloromethane-soluble fraction was filtered, layered with hexanes, and cooled to -30 °C, whereupon red crystals of [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>3</sub>][BAR<sub>4</sub><sup>-</sup>] (**14**) suitable for X-ray diffraction were isolated (0.053 g, 75%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.00 (s, 15H,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 7.56 (s, 4H, para-H of BAR<sub>4</sub><sup>-</sup>), 7.71 (s, 8H, ortho-H of BAR<sub>4</sub><sup>-</sup>). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.8 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 104.5 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> quaternary), 117.5 (para-CH of BAR<sub>4</sub><sup>-</sup>), 124.6 (q, <sup>1</sup>J<sub>CF</sub> = 273 Hz, CF<sub>3</sub> of BAR<sub>4</sub><sup>-</sup>), 128.9 (q, <sup>2</sup>J<sub>CF</sub> = 31 Hz, meta-C of BAR<sub>4</sub><sup>-</sup>), 134.8 (ortho-CH of BAR<sub>4</sub><sup>-</sup>), 161.8 (q, <sup>1</sup>J<sub>CB</sub> = 53 Hz, ipso-C of BAR<sub>4</sub><sup>-</sup>), 204.0 (CO). <sup>19</sup>F NMR (283 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -62.7 (CF<sub>3</sub>). <sup>11</sup>B NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -7.6 (BAR<sub>4</sub><sup>-</sup>). IR (CH<sub>2</sub>Cl<sub>2</sub> solution, cm<sup>-1</sup>):  $\nu$ (CO) 2105 st, 2046 st. MS (ES pos): M<sup>+</sup> = 275 (100%), isotopic pattern corresponding to 1 Fe atom. MS (ES neg): 863 [BAR<sub>4</sub><sup>-</sup>, 100%]. Exact mass (cation): calcd 275.0365, measd 275.0365.

**Reaction of **5** with 3,3-Dimethyl-1-butene.** To a solution of 3,3-dimethyl-1-butene (0.015 g, 0.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) was added slowly a solution of **5** (0.223 g, 0.18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 cm<sup>3</sup>). The reaction mixture was stirred for 16 h, at which point complete consumption of the starting material **5** was confirmed by <sup>11</sup>B NMR. Volatiles were removed in vacuo, and the remaining solid was washed successively with hexanes, toluene, and dichloromethane (ca. 10 cm<sup>3</sup> of each). No boron-containing products could be detected in any of the washings by <sup>11</sup>B NMR. The orange dichloromethane-soluble fraction was filtered, layered with hexanes, and cooled to -30 °C, whereupon deep yellow crystals of [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>C=CH-Bu)][BAR<sub>4</sub><sup>-</sup>] (**15**) suitable for X-ray diffraction were isolated (0.125 g, 63%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.06 (s, 9H, <sup>t</sup>Bu), 1.82 (s, 15H,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 2.68 (d, <sup>3</sup>J<sub>HH</sub> = 8.3 Hz (cis), 1H, <sup>t</sup>BuHC=CH<sub>2</sub>), 3.11 (d, <sup>3</sup>J<sub>HH</sub> = 15.1 Hz (trans), 1H, <sup>t</sup>BuHC=CH<sub>2</sub>), 3.99 (dd, <sup>3</sup>J<sub>HH</sub> = 8.3 (cis), 15.1 Hz (trans), 1H, <sup>t</sup>BuHC=CH<sub>2</sub>), 7.55 (s, 4H, para-H of BAR<sub>4</sub><sup>-</sup>), 7.71 (s, 8H, ortho-H of BAR<sub>4</sub><sup>-</sup>). <sup>13</sup>C NMR (76 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.8 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 30.2 (quaternary C of <sup>t</sup>Bu), 35.6 (CH<sub>3</sub> of <sup>t</sup>Bu), 98.7 ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> quaternary), 102.5 (CH<sub>2</sub> of alkene), 117.5 (para-CH of BAR<sub>4</sub><sup>-</sup>), 124.6 (q, <sup>1</sup>J<sub>CF</sub> = 272 Hz, CF<sub>3</sub> of BAR<sub>4</sub><sup>-</sup>), 128.9 (q, <sup>2</sup>J<sub>CF</sub> = 32 Hz, meta-C of BAR<sub>4</sub><sup>-</sup>), 134.7 (CH of alkene), 134.9 (ortho-CH of BAR<sub>4</sub><sup>-</sup>), 161.7 (q, <sup>1</sup>J<sub>CB</sub> = 50 Hz, ipso-C of BAR<sub>4</sub><sup>-</sup>), 213.1 (CO). <sup>19</sup>F NMR (283 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -62.7 (CF<sub>3</sub>). <sup>11</sup>B NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -7.6 (BAR<sub>4</sub><sup>-</sup>). IR (CH<sub>2</sub>Cl<sub>2</sub> solution, cm<sup>-1</sup>):  $\nu$ (CO) 2033 md, 1997 md. MS (ES pos): M<sup>+</sup> = 331 (50%), isotopic pattern corresponding to 1 Fe atom, fragment ion peaks at *m/z* 275 [(M - 2CO)<sup>+</sup>, 100%], 247 [(M - alkene)<sup>+</sup>, 40%]. MS (ES neg): 863 [BAR<sub>4</sub><sup>-</sup>, 100%]. Exact mass (cation): calcd 331.1355, measd 331.1352.

**Reaction of **5** with Benzophenone.** To a solution of benzophenone (0.028 g, 0.15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) was added slowly a solution of **5** (0.191 g, 0.15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 cm<sup>3</sup>). The reaction mixture was stirred for 3 h, after which the reaction was judged to be complete by <sup>11</sup>B NMR (by the replacement of the peak due to the starting material with a single peak at  $\delta_B$  17). Volatiles were removed in vacuo, and the remaining solid was washed successively with hexanes, toluene, and dichloromethane (ca. 10 cm<sup>3</sup> of each). No boron-containing products could be detected in any of the washings by <sup>11</sup>B NMR. The red dichloromethane-soluble fraction was filtered, layered with hexanes, and cooled to -30 °C, whereupon red crystals of [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>( $\eta^1$ -O=CPh<sub>2</sub>)] [BAR<sub>4</sub><sup>-</sup>] (**16**) suitable for X-ray diffraction were isolated (0.109 g, 56%).

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$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.75 (s, 15H,  $\eta^5\text{-C}_5\text{Me}_5$ ), 7.39 (m, 2H, para-H of benzophenone), 7.56 (m, 8H, overlap of meta-H of benzophenone and para-H of  $\text{BAr}_4^-$ ), 7.73 (m, 12H, overlap of ortho-H of benzophenone and ortho-H of  $\text{BAr}_4^-$ ).  $^{13}\text{C}$  NMR (76 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  9.3 ( $\eta^5\text{-C}_5\text{Me}_5$ ), 98.0 ( $\eta^5\text{-C}_5\text{Me}_5$  quaternary), 117.5 (para-CH of  $\text{BAr}_4^-$ ), 124.6 (q,  $^1J_{\text{CF}} = 272$  Hz,  $\text{CF}_3$  of  $\text{BAr}_4^-$ ), 128.3 (para-C of benzophenone), 128.7 (q,  $^2J_{\text{CF}} = 27$  Hz, meta-C of  $\text{BAr}_4^-$ ), 129.1 (meta-C of benzophenone), 129.4 (ortho-C of benzophenone), 134.0 (ortho-CH of  $\text{BAr}_4^-$ ), 136.4 (ipso-C of benzophenone), 161.8 (q,  $^1J_{\text{CB}} = 50$  Hz, ipso-C of  $\text{BAr}_4^-$ ), 210.1 (CO of benzophenone), 215.1 (metal bound CO).  $^{19}\text{F}$  NMR (283 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -62.7 ( $\text{CF}_3$ ).  $^{11}\text{B}$  NMR (96 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -7.6 ( $\text{BAr}_4^-$ ). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2050 md, 2004 md, 1612 md (benzophenone). MS (ES pos):  $\text{M}^+ = 429$  (75%), isotopic pattern corresponding to 1 Fe atom, fragment ion peaks at  $m/z$  401 [ $(\text{M} - \text{CO})^+$ , 20%], 373 [ $(\text{M} - 2\text{CO})^+$ , 30%]. MS (ES neg): 863 [ $\text{BAr}_4^-$ , 100%]. Exact mass (cation): calcd 429.1153, measd 429.1149.

**Thermolysis of 5 in Dichloromethane Solution.** A solution containing **5** (0.152 g, 0.12 mmol) in  $\text{CD}_2\text{Cl}_2$  (1  $\text{cm}^3$ ) was transferred to a flame-dried Young's NMR tube.  $^{11}\text{B}\{^1\text{H}\}$  and  $^1\text{H}$  spectra were measured at room temperature and then periodically over a period of ca. 24 h at 40 °C. The relative concentration of **5** in solution was assessed by integration of the signal at  $\delta_{\text{H}}$  2.63 due to the six ortho methyl protons of the mesityl substituent. The procedure was repeated in  $\text{CH}_2\text{Cl}_2$ , using a sealed internal deuterium lock. First-order rate constants were then obtained from the (linear) plots of  $\ln([\mathbf{5}]/[\mathbf{5}]_0)$  versus time.

**Chemical Trapping of the Mesitylborylene Fragment: Reaction of 5 with  $\text{Me}_2\text{S}_2$ .** To a solid sample of **5** (0.206 g, 0.17 mmol) was added a solution of  $\text{Me}_2\text{S}_2$  (0.262 g, 0.28 mmol) in hexanes and the reaction mixture stirred at room temperature for 2 h. At this point the  $^{11}\text{B}$  NMR spectrum of the hexane-soluble fraction showed a single strong resonance at  $\delta_{\text{B}}$  66.0, characteristic of  $\text{MesB}(\text{SMe})_2$  (**17**).<sup>19</sup> Filtration and removal of volatiles in vacuo led to the isolation of a colorless oil, which was confirmed to be  $\text{MesB}(\text{SMe})_2$  by further comparison of spectroscopic data with those reported previously.<sup>19</sup>

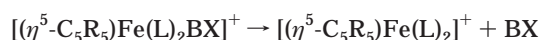
**(iii) General Crystallographic Method.** Data for compounds **5**, **10**, **12**, **13**, **14**, **15**, and **16** were collected on an Enraf Nonius Kappa CCD diffractometer; data collection and cell refinement were carried out using DENZO and COLLECT,<sup>20,21</sup> and structure solution and refinement using SHELXS-97 and SHELXL-97, respectively.<sup>22</sup> With the exception of ( $\eta^5\text{-C}_5\text{Me}_5$ )- $\text{Fe}(\text{CO})_2\text{I}$  (**13**) details of each data collection, structure solution, and refinement can be found in Table 1. Relevant bond lengths and angles are included in the figure captions (figures for compounds **14** and **15** are included in the Supporting Information), and complete details of each structure have been deposited with the CCDC (numbers as listed in Table 1). In addition complete details for each structure (including CIF files) have been included in the Supporting Information. The structure of compound **13** has previously been reported,<sup>18</sup> and the crystallographic study undertaken here merely served to unambiguously confirm the identity of a minor (yet chemically significant) side product isolated in low yield. Details of this structure are included in the Supporting Information.

The crystal structure of compound **5** was solved and refined in the monoclinic space group  $C2/c$ . Two crystallographically independent cations and anions, in addition to one molecule

of dichloromethane, were located and refined in the asymmetric unit. There were no significant geometric differences found between the two independent cations or the two independent anions. The relatively high *R*-factor for the crystal structure arises from the fact that the crystal chosen for the experiment was found to diffract weakly at high angle. This is despite the crystal being relatively large ( $0.35 \times 0.35 \times 0.15$  mm) and of relatively good quality. Prior to the collection of data on this crystal, data collections on a number of other samples of the compound were attempted, but all samples showed similar problems. Despite the poor quality of the data all indicators point toward a well-behaved structure and the molecular connectivity is unambiguous. A number of the fluorine atoms within the  $\text{CF}_3$  groups on both anions showed high anisotropic temperature factors, suggesting disorder within these groups. Attempts were made to model this disorder in all such  $\text{CF}_3$  groups with limited success. The disorder in three of the  $\text{CF}_3$  groups was successfully modeled, but in all others it was not possible to do so, presumably due to dynamic disorder within these groups. The fluorine atoms on these groups were, however, refined anisotropically.

**(iv) Computational Methodology.** The computational approach utilized for geometry optimization and bond dissociation energy (BDE) calculations on **5**, **8** and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PMe}_3)_2(\text{BMes})]^+$  was identical to that reported previously for similar studies on metal complexes containing boron-based ligand systems.<sup>4b,23</sup> The ADF2002.03 code was employed, together with BLYP exchange–correlation functionals,<sup>24,25</sup> a basis set derived from Slater-type orbitals with a triple- $\zeta$  valence shell and two polarization functions per atom was used in all cases, except for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PMe}_3)_2(\text{BMes})]^+$ , where, due to the larger number of atoms, a smaller basis set was chosen for the peripheral hydrogen and carbon atoms of the  $\text{PMe}_3$  ligands (double- $\zeta$  valence shell with one polarization function per atom). The frozen core approximation was employed for atoms other than hydrogen. For the atoms of the second period (B, C, N, O) the core orbitals were defined as 1s, while for phosphorus and iron orbitals up to the 2p and 3p, respectively, were included in the core. All structures were fully optimized based on unrestricted electronic structure calculations with complexes in the singlet ground state.

The bond dissociation energy for given MB bonds was calculated by estimating the energy change associated with the bond cleavage reaction:



The structures of the products from this reaction were independently optimized to allow for the inclusion of any molecular relaxation.<sup>23</sup> The  $\sigma$  and  $\pi$  contributions to the bonding energies were determined in the same way as reported previously for transition metal boryl complexes.<sup>23</sup> In each case a single-point calculation was carried out with the optimized structure aligned so that the  $\text{M}=\text{B}$  bond was along the *z*-axis. A specially developed analysis program was then used to carry out an adapted Mulliken analysis, which separates the bonding density into contributions from atomic orbitals of  $\sigma$  and  $\pi$

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**Table 1. Crystallographic Data for Compounds 5, 10, 12, 14, 15, and 16**

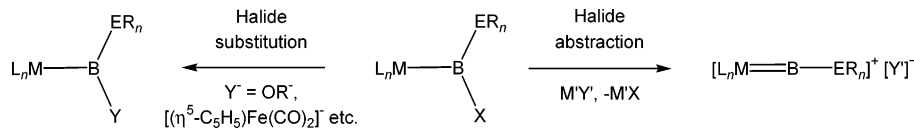
	5·1/2CH <sub>2</sub> Cl <sub>2</sub>	10	12
empirical formula	C <sub>53.5</sub> H <sub>39</sub> B <sub>2</sub> ClF <sub>24</sub> FeO <sub>2</sub>	C <sub>21</sub> H <sub>26</sub> BClFeO <sub>2</sub>	C <sub>21</sub> H <sub>26</sub> BFFeO <sub>2</sub>
CCDC deposit number	213762	210381	229790
fw	1282.77	412.53	396.08
temperature (K)	150(2)	120(2)	150(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic
space group	<i>C2/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P1</i>
unit cell dimens: <i>a</i> (Å)	36.301(7)	9.5840(2)	8.0000(16)
<i>b</i> (Å)	25.675(5)	17.3711(3)	8.6770(17)
<i>c</i> (Å)	23.956(5)	12.9997(2)	14.650(3)
$\alpha$ (deg)	90	90	92.67(3)
$\beta$ (deg)	93.81(3)	111.249(1)	101.17(3)
$\gamma$ (deg)	90	90	97.57(3)
volume (Å <sup>3</sup> )	22278(8)	2017.11(6)	986.3(3)
<i>Z</i>	16	4	2
density(calc) (Mg/m <sup>3</sup> )	1.530	1.358	1.334
abs coeff (mm <sup>-1</sup> )	0.440	0.892	0.785
<i>F</i> (000)	10320	864	416
cryst color, habit	colorless plate	yellow plate	yellow plate
cryst size (mm <sup>3</sup> )	0.35 × 0.35 × 0.15	0.40 × 0.20 × 0.08	0.20 × 0.15 × 0.10
$\theta$ range for data colln (deg)	2.91 to 25.02	3.27 to 27.48	3.43 to 26.34
index ranges ( <i>h</i> , <i>k</i> , <i>l</i> )	-43 to 43, -30 to 27, -28 to 28	-12 to 12, -22 to 22, -16 to 16	-9 to 9, -10 to 10, -18 to 18
no. of reflns collected	34 393	35 998	12 594
no. of indep reflns/ <i>R</i> <sub>int</sub>	19 345 (0.0553)	4627 (0.0516)	3933 (0.0907)
completeness to $\theta_{\max}$ (%)	98.3	99.8	98.1
absorp corr	Sortav	semiempirical from equivalents	Sortav
max. and min. transmn	0.9370, 0.8613	0.8321, 0.7168	0.9856 to 0.4788
refinement method	full matrix least squares on <i>F</i> <sup>2</sup>	full matrix least squares on <i>F</i> <sup>2</sup>	full matrix least squares on <i>F</i> <sup>2</sup>
no. of data/restraints/params	19 345/111/1560	4627/0/244	3933/0/244
goodness-of-fit on <i>F</i> <sup>2</sup>	1.030	1.030	1.041
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0888, w <i>R</i> 2 = 0.1974	<i>R</i> 1 = 0.0286, w <i>R</i> 2 = 0.0713	<i>R</i> 1 = 0.0446, w <i>R</i> 2 = 0.1059
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1679, w <i>R</i> 2 = 0.2356	<i>R</i> 1 = 0.0353, w <i>R</i> 2 = 0.0754	<i>R</i> 1 = 0.0544, w <i>R</i> 2 = 0.1111
largest diff peak and hole (e Å <sup>-3</sup> )	0.756 and -0.561	0.319 and -0.313	0.811 and -0.567
	<b>14</b>	<b>15</b>	<b>16·1/4C<sub>6</sub>H<sub>14</sub></b>
empirical formula	C <sub>45</sub> H <sub>27</sub> BF <sub>24</sub> FeO <sub>3</sub>	C <sub>50</sub> H <sub>39</sub> BF <sub>24</sub> FeO <sub>2</sub>	C <sub>58.5</sub> H <sub>40.5</sub> BF <sub>24</sub> FeO <sub>3</sub>
CCDC deposit number	229791	229792	229793
fw	1138.33	1194.47	1314.07
temperature (K)	150(2)	150(2)	150(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	monoclinic
space group	<i>P2<sub>1</sub>/c</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/n</i>
unit cell dimens: <i>a</i> (Å)	12.286(3)	17.935(4)	21.5502(3)
<i>b</i> (Å)	19.347(4)	19.412(4)	12.5448(2)
<i>c</i> (Å)	20.360(4)	29.048(6)	22.8344(5)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	104.19(3)	90	106.4300(10)
$\gamma$ (deg)	90	90	90
volume (Å <sup>3</sup> )	4691.9(16)	10 113(4)	5921.04(18)
<i>Z</i>	4	8	4
density(calc) (Mg/m <sup>3</sup> )	1.612	1.569	1.474
absorp coeff (mm <sup>-1</sup> )	0.457	0.427	0.373
<i>F</i> (000)	2272	4816	2650
cryst color, habit	yellow plate	yellow cube	red cube
cryst size (mm <sup>3</sup> )	0.20 × 0.20 × 0.10	0.35 × 0.30 × 0.25	0.25 × 0.20 × 0.18
$\theta$ range for data colln (deg)	2.95 to 25.35	2.97 to 25.34	3.07 to 26.04
index ranges ( <i>h</i> , <i>k</i> , <i>l</i> )	-14 to 14; -23 to 23; -24 to 24	-21 to 21, -23 to 23, -34 to 34	-26 to 26; -15 to 15; -28 to 28
no. of reflns collected	31 959	50 616	47 003
no. of indep reflns/ <i>R</i> <sub>int</sub>	8579 (0.0413)	9212 (0.0866)	11 596 (0.0682)
completeness to $\theta_{\max}$ (%)	99.7	99.6	99.1
absorp corr	Sortav	Sortav	Sortav
max. and min. transmn	0.9557, 0.9141	0.933, 0.692	0.953 and 0.876
refinement method	full matrix least squares on <i>F</i> <sup>2</sup>	full matrix least squares on <i>F</i> <sup>2</sup>	full matrix least squares on <i>F</i> <sup>2</sup>
no. of data/restraints/params	8579/36/712	9212/624/712	11 596/168/974
goodness-of-fit on <i>F</i> <sup>2</sup>	1.025	1.035	1.039
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0814, w <i>R</i> 2 = 0.2196	<i>R</i> 1 = 0.0744, w <i>R</i> 2 = 0.1938	<i>R</i> 1 = 0.0547, w <i>R</i> 2 = 0.1392
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1007, w <i>R</i> 2 = 0.2358	<i>R</i> 1 = 0.1151, w <i>R</i> 2 = 0.2180	<i>R</i> 1 = 0.0867, w <i>R</i> 2 = 0.1520
largest diff peak and hole (e Å <sup>-3</sup> )	0.931 and -0.606	1.326 and -0.495	0.492 and -0.316

symmetry.<sup>23,26</sup> In addition total Mulliken charges for all atoms and Mayer bond orders were obtained for comparison with the ADF output to ensure the accuracy of the analysis program.

## Results and Discussion

**(i) Synthetic Chemistry.** Asymmetric haloboryl complexes **1–4** have proved to be versatile substrates for boron-centered *substitution* chemistry, leading to a

(26) Dickinson, A. A. Ph.D. Thesis, Cardiff University, 2003.

Scheme 1. Substitution and Abstraction Chemistry of Asymmetric Haloboryl Complexes,  $L_nM-B(ER_n)X$ Scheme 2. Syntheses of Asymmetric Aryl(halo)boryl Complexes **1–4**<sup>a</sup>

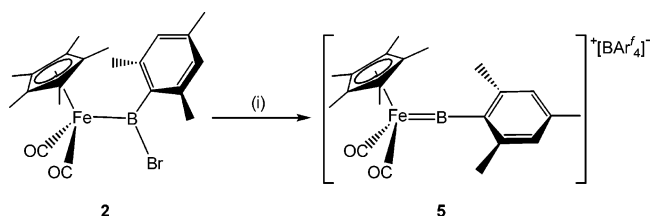
- 1 X = Br,  $R_n = H_5$ ,  $R' = R'' = Me$
- 2 X = Br,  $R_n = Me_5$ ,  $R' = R'' = Me$
- 3 X = Br,  $R_n = H_5$ ,  $R' = 2,4,6\text{-}iPr_3C_6H_2$ ,  $R'' = H$
- 4 X = Cl,  $R_n = Me_5$ ,  $R' = R'' = H$

<sup>a</sup> Reaction conditions: (i)  $Na[(\eta^5-C_5R_5)Fe(CO)_2]$  1 equiv, toluene, 18 °C, 4–96 h.

range of novel bridging borylene and asymmetric boryl complexes.<sup>8,11</sup> Given that *abstraction* of anionic fragments from coordinated ligands has previously been used to great effect in the synthesis of low-coordinate or unsaturated systems (e.g., silylenes and germylenes<sup>2</sup>), we speculated that a similar methodology applied to haloboryl complexes might offer a versatile new route to terminally bound group 13 diyl complexes (Scheme 1). Although relatively electron-rich phosphine-containing metal fragments have typically been employed, for example in the synthesis of terminal silylenes {e.g.,  $[(\eta^5-C_5Me_5)Ru(PMe_3)_2(=SiMe_2)]^+ 2b$ }, our initial attempts to produce analogous cationic terminal borylene complexes have utilized the more readily accessible  $[(\eta^5-C_5R_5)Fe(CO)_2]^+$  moiety ( $R = H, Me$ ).

Asymmetric haloboryl complexes incorporating aryl functions of varying steric bulk (e.g., **1–4**) have been shown in previous work to be readily and cleanly accessible by simple substitution chemistry (Scheme 2).<sup>8,11</sup> Thus, such species appeared to represent suitable precursors for the halide abstraction chemistry outlined in Scheme 1. In practice, both the steric properties of the putative borylene substituent (and of the metal fragment) and the inherent coordinating properties/reactivity of the counterion employed appear to play key roles in the isolation (or otherwise) of stable, tractable cationic borylene complexes. Thus, attempted halide abstraction from complexes **1**, **3**, and **4**, which contain steric shielding at *either* the boron or the iron center (but not both), leads to the generation of no observable borylene products even at  $-78$  °C. In the case of boryl precursor **2**, however, which contains sterically bulky substituents at both metal and boron centers [i.e., both mesityl and  $(\eta^5-C_5Me_5)$  groups], reaction with  $Na[BAR^t_4]$ , filtration, layering with hexanes, and cooling to  $-50$  °C for one week led to the isolation of **5** as colorless crystals in yields of ca. 55% (100 mg scale) (Scheme 3).<sup>4a</sup>

IR-measured carbonyl stretching frequencies for **5** (2055 and 2013  $cm^{-1}$ ) are shifted to significantly higher wavenumber compared to the starting boryl complex **2** (2006 and 1961  $cm^{-1}$ )<sup>8b</sup> and are consistent with the presence of a cationic complex containing the  $(\eta^5-C_5-$

Scheme 3. Synthesis of Cationic Mesitylborylene Complex  $[(\eta^5-C_5Me_5)Fe(CO)_2(BMes)][BAR^t_4]$  (**5**) by Bromide Abstraction<sup>a</sup>

<sup>a</sup> Reaction conditions: (i)  $Na[BAR^t_4]$  1 equiv, dichloromethane,  $-78$  to 18 °C, 1 h.

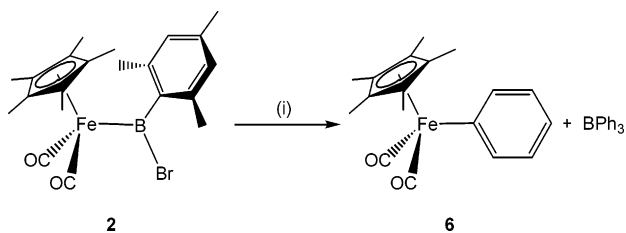
$Me_5)Fe(CO)_2$  unit.<sup>27</sup>  $^1H$  and  $^{13}C$  NMR data for **5** confirm the presence of mesityl,  $(\eta^5-C_5Me_5)$ , and CO fragments, and mass spectra display peaks consistent with  $[M - CO]^+$  and  $[M - 2CO]^+$  (EI) and  $[BAR^t_4]^-$  ions (ES<sup>-</sup>). Additionally, the strongly downfield  $^{11}B$  NMR shift ( $\delta_B$  145.0) is similar to that observed previously for iron complexes containing mesitylborylene ligands, albeit adopting a  $\mu_2$  bridging mode of coordination {cf.  $\delta_B$  158.0 and 161.9 for  $[(\eta^5-C_5H_5)Fe(CO)_2]_2(\mu-BMes)$  and *trans*- $[(\eta^5-C_5H_5)Fe(CO)]_2(\mu-BMes)(\mu-CO)$ , respectively}.<sup>8b</sup>  $^{11}B$  shifts in the range  $\delta_B$  87–204 have previously been reported by Braunschweig for terminal borylene complexes containing metals from groups 5, 6, and 8;<sup>3b–f</sup> lower field values have typically been obtained for borylene ligands containing weakly  $\pi$  donor substituents. The measured  $^{11}B$  shift for **5** is therefore consistent with a terminally bound BMes ligand, a structural inference that has subsequently been confirmed by X-ray crystallography (vide infra).

Attempts to generate similar cationic complexes using the commercially available halide abstraction reagents  $Na[BPh_4]$  and  $Ag[BF_4]$  proceed with rapid and complete consumption of the starting material **2**, but lead to the isolation of no tractable borylene products. In the case of  $Ag[BF_4]$  spectroscopic data are inconsistent with the presence of either boryl or borylene species in solution. Additionally, subsequent studies have revealed that the highly Lewis acidic boron center in  $[(\eta^5-C_5Me_5)Fe(CO)_2(BMes)]^+$  is incompatible with the tetrafluoroborate counterion; reaction of **5** with  $[^nBu_4N][BF_4]$  generates the neutral fluoroboryl complex  $(\eta^5-C_5Me_5)Fe(CO)_2B(Mes)F$  in high yield by fluoride exchange (vide infra). By contrast, the reaction of **2** with a suspension of  $Na[BPh_4]$  in dichloromethane leads to the generation of  $BPh_3$  and  $(\eta^5-C_5Me_5)Fe(CO)_2Ph$  (**6**) (Scheme 4).

A possible pathway for the formation of these products involves initial removal of bromide from boryl precursor **2**, yielding the cationic borylene as the tetraphenylborate salt, i.e.,  $[(\eta^5-C_5Me_5)Fe(CO)_2(BMes)][BPh_4]$ ; abstraction of phenyl anion from tetraphenylborate and displacement of the mesitylborylene ligand would then yield the observed products. Displacement of the mesitylborylene fragment from the coordination sphere of the  $[(\eta^5-C_5Me_5)Fe(CO)_2]^+$  unit by nucleophiles is found to be one of its principal modes of reactivity (vide infra),



**Scheme 4. Reaction of Bromoboryl Complex 2 with Na[BPh<sub>4</sub>]<sup>a</sup>**

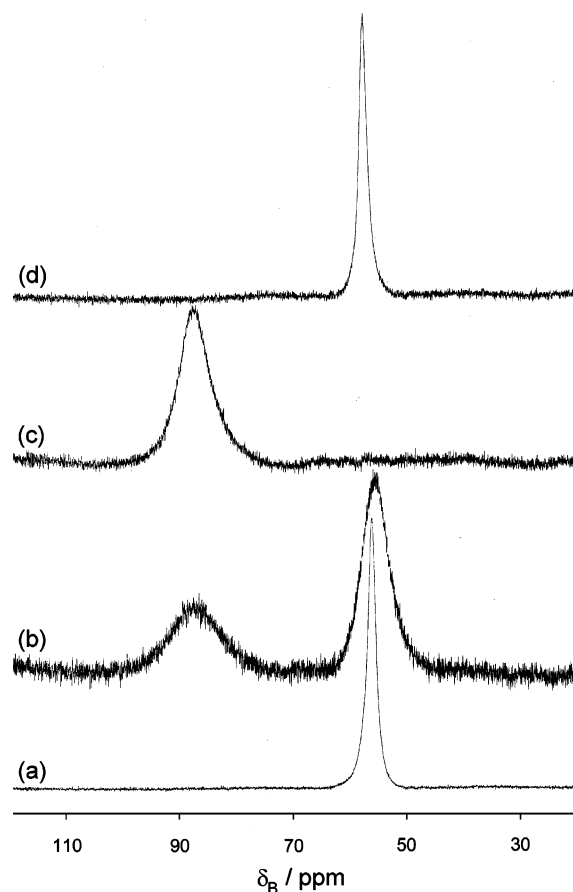


<sup>a</sup> Reaction conditions: (i) Na[BPh<sub>4</sub>] 1 equiv, dichloromethane, -78 to 18 °C, 30 min.

and consistent with the proposed mechanism, independent reaction of the [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup> salt of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>(BMes)]<sup>+</sup> (**5**) with [PPN][BPh<sub>4</sub>] (a dichloromethane-soluble [BPh<sub>4</sub>]<sup>-</sup> source) leads to very rapid generation of BPh<sub>3</sub> and (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>Ph. Further details of this and other reactions of complex **5** are outlined below.

In an attempt to extend the halide abstraction methodology to the synthesis of further cationic borylene complexes, we have examined the reactivity of amino(bromo)boryl complex (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(NMe<sub>2</sub>)Br (**7**) with Na[BAR<sup>f</sup><sub>4</sub>]. **7** is readily synthesized from Me<sub>2</sub>NBBR<sub>2</sub> according to literature procedures<sup>14</sup> and reacts readily with Na[BAR<sup>f</sup><sub>4</sub>] in dichloromethane at -20 °C. The complex so generated is characterized by two <sup>11</sup>B NMR resonances, a sharp signal at δ<sub>B</sub> -7.7 characteristic of the [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup> anion and a broad signal at δ<sub>B</sub> 88.0. The position of the latter resonance is very similar to those reported previously for charge neutral terminal aminoborylene complexes [e.g., δ<sub>B</sub> 98.3, 92.3, 86.6, and 88.2 for L<sub>n</sub>M(BN(SiMe<sub>3</sub>)<sub>2</sub>), L<sub>n</sub>M = (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>3</sub>, (OC)<sub>5</sub>Cr, (OC)<sub>5</sub>W, and (OC)<sub>4</sub>Fe, respectively<sup>3b,c,e,f</sup>]. Additionally IR-measured carbonyl stretching frequencies for the new species (2050 and 2006 cm<sup>-1</sup>) are similar to those reported for **5**, being similarly indicative of a cationic [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>]<sup>+</sup> fragment.<sup>27</sup>

In our hands, attempts to isolate this complex as a pure solid material have met with no success, due to its extreme moisture and air sensitivity. NMR monitoring of the reaction of **7** with Na[BAR<sup>f</sup><sub>4</sub>] in CD<sub>2</sub>Cl<sub>2</sub> over the temperature range -70 to -20 °C, however, allows the new complex (**8**) to be synthesized in solution in very high purity; complete conversion of **7** to **8** is achieved by warming the reaction mixture to -20 °C (see Figure 1), and full multinuclear NMR data for **8** can thus be obtained. These data are consistent with the presence of the [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup> counterion, with (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) and CO ligands at the metal center, and with *equivalent* nitrogen-bound methyl substituents. In addition, further characterization of the new complex was attempted by examining the products of its reaction with [PPN]Cl in CD<sub>2</sub>Cl<sub>2</sub>. The reaction of cationic mesitylborylene complex **5** with the same reagent has been shown to generate (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(Mes)Cl by chloride addition to the boron center (vide infra). Hence the formation of the known compound (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(NMe<sub>2</sub>)Cl (**9**)<sup>7d</sup> would provide further evidence that the new species (**8**) is the [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup> salt of the cationic aminoborylene [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>(BNMe<sub>2</sub>)]<sup>+</sup> (Scheme 5). In practice this reaction proceeds very cleanly as expected



**Figure 1.** <sup>11</sup>B{<sup>1</sup>H} NMR monitoring of the conversion of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(NMe<sub>2</sub>)Br (**7**) to [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>(BNMe<sub>2</sub>)] [BAR<sup>f</sup><sub>4</sub>]<sup>-</sup> (**8**) and ultimately (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(NMe<sub>2</sub>)Cl (**9**) in CD<sub>2</sub>Cl<sub>2</sub>. The spectra reproduced are (a) **7** at 18 °C prior to mixing with Na[BAR<sup>f</sup><sub>4</sub>]; (b) a mixture of **7** and **8** at -40 °C, 30 min after mixing of **7** with Na[BAR<sup>f</sup><sub>4</sub>]; (c) **8**, after a further 30 min reaction time at -20 °C; and (d) **9**, after subsequent addition of [PPN]Cl to the reaction mixture and warming to room temperature.

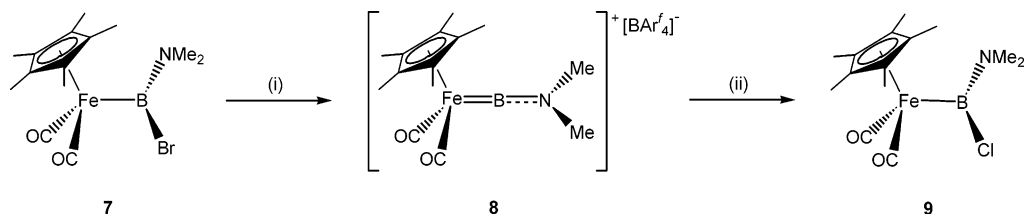
(see Figure 1), with complete conversion of **7** to **8** being achieved by reaction with 1 equiv of Na[BAR<sup>f</sup><sub>4</sub>] at -20 °C and chloroboryl complex **9** subsequently being formed quantitatively on addition of [PPN]Cl and warming to room temperature. Identification of final product **9** was made by comparison of its spectroscopic data with those reported previously by Braunschweig.<sup>7d</sup>

The observation of equivalent methyl groups within the amino substituent of **8** even at -80 °C (sharp singlets at δ<sub>H</sub> 2.74 and δ<sub>C</sub> 32.5 at -80 °C) contrasts with the situation found in boryl complexes **7** and **9**,<sup>7d,14</sup> but is consistent with that found for the analogous SiMe<sub>3</sub> groups in (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>3</sub>BN(SiMe<sub>3</sub>)<sub>2</sub>.<sup>3e</sup> As such, these data are consistent either with a static structure in which the methyl groups are related by a plane of symmetry encompassing the (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) centroid, Fe, B, and N atoms, or with a freely rotating NMe<sub>2</sub> unit and a low barrier to rotation about the Fe-B bond. The feasibility of both of these possibilities has been demonstrated by DFT calculations. A very low barrier to rotation (ca. 2.2 kcal mol<sup>-1</sup>) has been predicted around the V-B bond in the model vanadium aminoborylene complex (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>3</sub>BNH<sub>2</sub>.<sup>3e</sup> Additionally the minimum energy conformation of the cation [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>(BNMe<sub>2</sub>)]<sup>+</sup> has been calculated to feature a (η<sup>5</sup>-

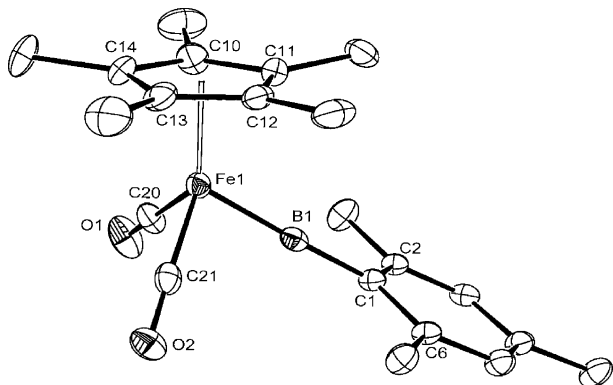
(27) See, for example: Nlate, S.; Guerschais, V.; Lapinte, C. *J. Organomet. Chem.* **1992**, 434, 89. (b) McArdle, P.; MacHale, D.; Cunningham, D.; Manning, A. R. *J. Organomet. Chem.* **1991**, 419, C18.



**Scheme 5. Generation and Trapping of Cationic Aminoborylene Complex**  
 $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BNMe}_2)][\text{BAR}^f_4]$  (**8**)<sup>a</sup>



<sup>a</sup> Reaction conditions: (i) Na[BAR<sup>f</sup><sub>4</sub>] 1 equiv, *d*<sub>2</sub>-dichloromethane, -20 °C, 30 min; (ii) [PPN]<sup>+</sup>Cl<sup>-</sup> ca. 5 equiv, *d*<sub>2</sub>-dichloromethane, -20 to 18 °C, 30 min.



**Figure 2.** Structure of one of the two crystallographically independent cations in the asymmetric unit of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BMes})][\text{BAR}^f_4]$ , **5**. Relevant bond lengths (Å), angles (deg), and torsion angles (deg): Fe(1)–B(1) 1.792(8), Fe(1)–C(20) 1.768(7), Fe(1)–( $\eta^5\text{-C}_5\text{Me}_5$ ) centroid 1.733(7), B(1)–C(1) 1.491(10), Fe(1)–B(1)–C(1) 178.3(6), ( $\eta^5\text{-C}_5\text{Me}_5$ ) centroid–Fe(1)–C(1)–C(2) 91.3(6). Hydrogen atoms are omitted for clarity.

$\text{C}_5\text{Me}_5$ ) centroid–Fe–N–C torsion angle of ca. 90° (84.6°) (see Supporting Information).<sup>4b</sup>

**(ii) Bonding Description.** The solid state structure of **5** (see Figure 2 and Table 1) is based around an asymmetric unit containing two (essentially identical)  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BMes})]^+$  cations, two  $[\text{BAR}^f_4]^-$  anions, and a molecule of  $\text{CH}_2\text{Cl}_2$  solvent. There are no short cation–anion or cation–solvent contacts. Of particular interest is the near linear Fe–B–C unit [ $\angle\text{Fe}(1)\text{–B}(1)\text{–C}(1) = 178.3(6)^\circ$ ] and the Fe–B distance [1.792(8) Å], which is significantly shorter than any transition metal to boron linkage previously reported. It is also 11% shorter than that found in  $(\eta^5\text{-C}_5\text{Me}_5)\text{BFe}(\text{CO})_4$  [2.010(3) Å] (a compound that contains a B→Fe donor/acceptor linkage), 18% shorter than the  $\sigma$ -only single bond found in the four-coordinate boryl complex  $(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Fe}(\text{CO})_2\text{BH}_2\cdot\text{PMe}_3$  [2.195(14) Å], and 8.5% shorter than the shortest Fe–B distance found for any three-coordinate boryl complex [1.959(6) Å for  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Bcat}$ ].<sup>3a,5d,28,29</sup> By means of comparison, the Fe–C distance in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(=\text{CCl}_2)]^+$  [1.808(12) Å] is ca. 12% shorter than found in typical  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$  alkyl complexes,<sup>30,31</sup> and the Ru–Si distance in  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2(=\text{SiMe}_2)]^+$  [2.238(2) Å] is 6% shorter than that found in  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2(\text{SiMe}_2\text{CH}_2\text{-$

$\text{PPh}_3)]^+$  [2.381(2) Å].<sup>2b,e</sup> The shortening of the Fe–B distance in **5** compared to Fe–B  $\sigma$ -type bonds is therefore as expected for a ligand containing a first-row element and is consistent with the presence of an Fe=B double bond.

Tilley has proposed that the Ru=Si double bond in the cationic silylene complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2(=\text{SiMe}_2)]^+$  is composed of a Si→Ru donor/acceptor  $\sigma$  component supplemented by Ru→Si  $\pi$  back-bonding into the vacant Si-based p orbital.<sup>2b</sup> A similar bonding arrangement for **5** would imply a significantly greater Fe→B back-bonding component than is found in  $(\eta^5\text{-C}_5\text{Me}_5)\text{BFe}(\text{CO})_4$ .<sup>3a,5d</sup> Such an arrangement is conceivable given the highly electrophilic nature of the boron center in **5** and the significantly higher DFT-predicted  $\pi$  bonding capability of the BPh ligand compared to B( $\eta^5\text{-C}_5\text{H}_5$ ).<sup>5i</sup> The presence of an appreciable Fe→B back-bonding component for **5** is implied by carbonyl stretching frequencies (2055, 2013  $\text{cm}^{-1}$ ) in excess of those of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(=\text{CMe}(\text{OMe}))]^+$  (2045, 1999  $\text{cm}^{-1}$ ).<sup>27a</sup> That these values are still short of those reported for  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_3]^+$  (2105, 2045  $\text{cm}^{-1}$ ), however, almost certainly reflects the stronger  $\sigma$  donor nature of BR over CO.<sup>27b</sup> Stronger  $\sigma$  donor properties than CO have been predicted by Hoffmann and Baerends for the borylene ligands BX (X = F, NH<sub>2</sub>, NMe<sub>2</sub>) on the basis of DFT calculations. Such properties are thought to reflect the higher HOMO energy for the boron-based ligands.<sup>5a–c</sup>

The orientation of the mesityl fragment in **5** [torsion,  $\angle(\eta^5\text{-C}_5\text{Me}_5)$  centroid–Fe(1)–C(1)–C(2) = 91.3(6)°] is such that an Fe→B  $\pi$  interaction involving the HOMO of the  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]^+$  fragment<sup>32</sup> could populate one of the two perpendicular vacant p orbitals at boron, with the other being stabilized by  $\pi$  interaction with the mesityl ring. Consistent with this, the distance B(1)–C(1) [1.491(10) Å] is significantly shorter than that found in **2** [1.569(3) Å].<sup>8b</sup> To explore more rigorously the bonding situation in **5**, DFT calculations were carried out for the cation  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BMes})]^+$  at the BLYP/TZP level of theory using methods previously described. The agreement between (fully optimized) calculated [Fe(1)–B(1) 1.843 Å, B(1)–C(1) 1.495 Å,  $\angle\text{Fe}(1)\text{–B}(1)\text{–C}(1) = 177.8^\circ$ , torsion = 81.6°] and measured geometric parameters is generally very good, with a 2–3% overestimate in the Fe–B bond length mirroring previous studies.<sup>23,33</sup> On the basis of a population analysis of the molecular orbitals at the DFT relaxed

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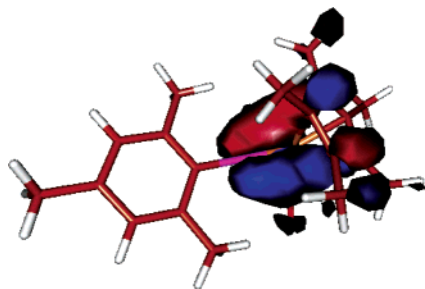
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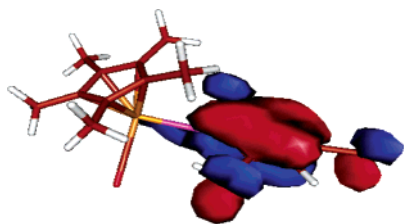
(31) For example, an Fe–C bond length of 2.069(10) Å has been reported for the complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(n\text{-C}_5\text{H}_{11})$ : Hill, R. O.; Marais, C. F.; Moss, J. R.; Naidoo, K. J. *J. Organomet. Chem.* **1999**, 587, 28.

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**Figure 3.** DFT (BLYP/TZP) calculated HOMO-3 for the cation  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BMes})]^+$  showing Fe–B  $\pi$  bonding character.



**Figure 4.** DFT (BLYP/TZP) calculated HOMO-9 for the cation  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BMes})]^+$  showing C–B  $\pi$  bonding character.

geometry, the Fe–B bond has a 62:38  $\sigma$ : $\pi$  breakdown of the covalent contribution to bonding {cf. 64:36 for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(=\text{CH}_2)]^+$ }. For the lowest energy conformation of the complex **5**, examination of the relevant molecular orbitals (Figures 3 and 4) reveals that the Fe–B bond is characterized by (i) a deep lying orbital (HOMO-7,  $-10.56$  eV) with considerable Fe–B  $\sigma$  bonding character (21.4% Fe  $3d_z^2$ , 12.8% B  $2p_z$ ) and (ii) a  $\pi$  type interaction predominantly featuring the Fe  $3d_{xz}$  and B  $2p_x$  orbitals. Both the HOMO-3 ( $-9.21$  eV) and the HOMO-6 ( $-9.85$  eV) feature significant in-phase contributions from these atomic orbitals (HOMO-3: 17.6% Fe  $3d_{xz}$ , 4.9% B  $2p_x$ ; HOMO-6: 18.1% Fe  $3d_{xz}$ , 3.1% B  $2p_x$ ). The LUMO+3 is the corresponding orbital of predominantly  $\pi^*$  character (10.4% Fe  $3d_{xz}$ , 35.4% B  $2p_x$ ). In addition it is possible to identify molecular orbitals [chiefly the HOMO-9 ( $-10.98$  eV) and HOMO-2 ( $-8.91$  eV)] that possess C–B  $\pi$  bonding character characterized by in-phase contributions from the  $2p_y$  atomic orbitals of the boron and ipso carbon atoms which lie perpendicular to the Fe–B  $\pi$  bond. These calculations therefore support a bonding model in which boron engages in  $\pi$  bonding to both  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]^+$  and Mes moieties.

A substantial bond dissociation energy (BDE,  $D_0$ ) of  $147.5$  kcal mol $^{-1}$  has been calculated for the removal of the mesitylborylene ligand from **5**. This figure is elevated slightly on replacement of the ancillary carbonyl ligands by trimethylphosphines {e.g.,  $153.0$  kcal mol $^{-1}$  for model compound  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PMe}_3)_2(\text{BMes})]^+$ } but is significantly smaller for the removal of  $\text{BNMe}_2$  from  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BNMe}_2)]^+$  (**8**) ( $125.9$  kcal mol $^{-1}$ ). These changes are primarily due to differences in the orbital (covalent) contribution to the Fe–B bond; these in turn reflect the expected trends in the  $\sigma$  and  $\pi$  properties of the BX ligand and the electronic properties of the metal center.<sup>4b</sup> Consistent with this, the calculated Fe–B distances for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PMe}_3)_2(\text{BMes})]^+$  and **8** are, respectively, 2.4% shorter and 1.4% longer than in **5**, and the B–C<sub>ipso</sub> distance in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$

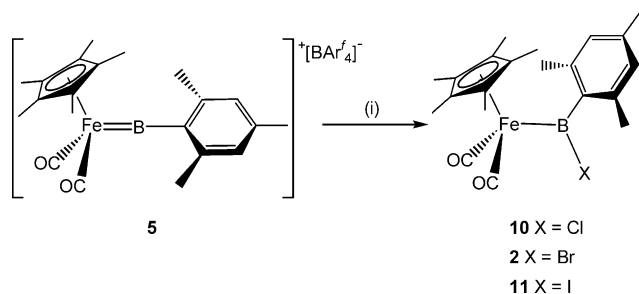
$(\text{PMe}_3)_2(\text{BMes})]^+$  shows a complementary lengthening by 2.3%. Additionally, the BDE predicted for **5** is significantly greater than that calculated for removal of the very similar BPh ligand from the most stable (axial) isomer of the charge neutral complex  $(\text{OC})_4\text{FeBPh}$  ( $110.3$  kcal mol $^{-1}$ ).<sup>51</sup> Energy decomposition analyses indicate that this is almost entirely accounted for by a reduction in the repulsive Pauli term. This in turn is associated with the more contracted nature of the frontier orbitals of the metal and borylene fragments in the cationic complex.<sup>4b</sup> Finally, comparison of iso-electronic Fe=B and Fe=C containing systems {e.g., **8** and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{CCMe}_2)]^+$ } reveals a ca.  $10$  kcal mol $^{-1}$  higher BDE for the boron-based ligand.<sup>4b</sup> This finding is entirely consistent with the stronger  $\sigma$  donor properties and comparable  $\pi$  acceptor role predicted for the  $\text{BNR}_2$  ligand by previous studies.<sup>5a</sup>

Previous computational studies have predicted significant boron-centered reactivity toward nucleophiles for terminal borylene complexes due to the high positive charge and LUMO amplitude at boron.<sup>5b</sup> On the other hand, the current study shows that in the presence of suitable steric shielding, even complexes bearing a net positive charge can be isolated. Indeed, it seems likely that the combination of charge and steric shielding in **5** retards the dimerization process observed for the putative iso-electronic manganese system  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{-Mn}(\text{CO})_2(\text{BCl})]$ .<sup>34</sup> The calculated partial charge at boron ( $+0.356$ , Mulliken method) in **5** is certainly consistent with a highly electrophilic boron center, although the composition of the LUMO (29.3% Fe  $3d_{x^2-y^2}$ , 4.6% Fe  $3d_{xz}$ , 4.4% Fe  $3d_{yz}$ , 4.2% B  $2p_x$ ) suggests that attack by nucleophiles at the iron center may also be feasible.

**(iii) Reactivity.** The reactivity of cationic borylene complex **5** toward a number of different types of reagent has been investigated, with the aim of elucidating fundamental patterns of reactivity for this class of compound. Although some reports of substitution chemistry for base-stabilized borylenes<sup>3g,h</sup> and of elegant metal-to-metal borylene transfer chemistry have appeared in the recent literature,<sup>3c,e,f</sup> the *fundamental* reactivity of group 13 diyl complexes remains a largely uncharted area. A number of extensive theoretical studies have predicted thermodynamically strong M–E bonds for diyl complexes,<sup>5</sup> but point to probable kinetic lability stemming from the buildup of positive charge at the group 13 element on coordination.<sup>5b</sup> With this in mind we have examined the reactivity of **5** toward a range of anionic and neutral nucleophiles, with the aim of exploiting the electrophilicity of the boron center toward the controlled synthesis of complexes containing new B–X bonds. In addition, given the similarities between cationic borylene complexes such as **5** and silylene and Fischer carbene complexes of the type  $[\text{L}_n\text{M}=\text{EX}_2]^+$  (E = Si, C) we were interested in examining the reactivity of **5** toward unsaturated substrates. Of particular interest, given the known highly indiscriminate reactivity of the “free” borylene fragment, is the development of controlled metal-mediated reactivity toward organic or organometallic substrates.

**(a) Reactivity toward Nucleophiles.** The likelihood of nucleophilic attack at the boron center in **5**,

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**Scheme 6. Reactivity of Cationic Borylene 5 toward Halide Anions<sup>a</sup>**


<sup>a</sup> Reaction conditions: (i) halide source ([PPN]Cl, [Ph<sub>4</sub>P]Br, or [t<sup>n</sup>Bu<sub>4</sub>N]I) 1 equiv, dichloromethane, 18 °C, 1.5–2 h.

widely predicted for analogous charge neutral systems, would appear to be increased by the net positive charge and a calculated Mulliken charge at boron of +0.356. We therefore set out, in the first instance, to examine its reactivity toward a range of anionic nucleophiles. The reaction of **5** with convenient soluble sources of halide anions in dichloromethane leads, as expected, to nucleophilic addition at the boron center (Scheme 6). The chloro-, bromo-, and iodoboryl complexes are formed very rapidly (as judged by the <sup>11</sup>B NMR spectrum of the reaction mixture) and can be isolated in reasonable yields (60–80%). In the case of the reaction with [Ph<sub>4</sub>P]Br, the known (structurally characterized) precursor bromoboryl complex **2** is formed;<sup>8b</sup> reaction with [PPN]Cl or [t<sup>n</sup>Bu<sub>4</sub>N]I leads to the isolation of the new boryl complexes **10** and **11**, together with the appropriate [BAR<sub>f</sub>]<sup>−</sup> salt (e.g., [PPN][BAR<sub>f</sub>]<sup>−</sup> in the case of **10**). Furthermore, a similar type of halide transfer reactivity is observed with [t<sup>n</sup>Bu<sub>4</sub>N][BF<sub>4</sub>]. Abstraction of fluoride from the tetrafluoroborate anion leads to the formation of fluoroboryl complex **12** in good yield (Scheme 7).

Thus the chemistry outlined in Schemes 6 and 7 represents a new synthetic route to asymmetric boryl complexes, and one which gives access to the complete range of halide-substituted complexes (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(Mes)X (X = F, Cl, Br, I). Spectroscopic data for the new compounds **10–12** are in agreement with the proposed formulations, and in the cases of **10** and **12**, these inferences have been confirmed by the results of a single-crystal X-ray diffraction study (see Figures 5 and 6 and Table 1).

The molecular structure of chloroboryl complex (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(Mes)Cl (**10**) has much in common with that reported previously for bromoboryl analogue **2** and for most other complexes of the type (η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>)Fe(CO)<sub>2</sub>B(Mes)X (X = halide, alkoxide, aryloxy, etc.).<sup>8b,11</sup> As such, the plane defined by the boryl ligand [i.e., by atoms B(1), C(1), and Cl(1)] is essentially coplanar with that defined by the cyclopentadienyl centroid, Fe(1) and B(1) [∠centroid–Fe(1)–B(1)–C(1) = 179.5(2)°] and nearly perpendicular to that defined by the mesityl fragment [∠Cl(1)–B(1)–C(1)–C(8) = 89.5(2)°]. This ligand orientation seems to be influenced to a large degree by minimizing steric interactions between the bulky mesityl and pentamethylcyclopentadienyl substituents. The molecular structure of fluoroboryl complex **12**, however, offers an instructive contrast with those of related compounds. A significantly longer Fe–B distance [2.017(3) vs 1.985(2) Å for **10**] and a markedly different orientation of the boryl ligand [∠centroid–

Fe(1)–B(1)–F(1) = 37.6(2)°] allow for the presence of an intramolecular C–H⋯F hydrogen bond incorporating the fluorine substituent and one of the methyl groups of the (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) ligand (Figure 6). The H⋯F and C⋯F distances [2.44 and 3.054(4) Å] and the C–H⋯F angle (120.4°) fall within the ranges expected for such an interaction.<sup>35</sup> The ability of a relatively weak C–H⋯X hydrogen bond to influence conformational geometry in organometallic boryl systems finds precedent in the solid state structure of tetrachlorocatecholboryl complex (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)Fe(CO)<sub>2</sub>BO<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub> and provides further experimental evidence for the relatively low barrier to rotation about the Fe–B bond that has been predicted by DFT.<sup>23,36</sup> It should be noted that there is no evidence on the basis of spectroscopic data for the existence of an intramolecular hydrogen bond in solution. The packing of **12** in the solid state is also influenced by π stacking, this interaction being characterized by interplanar distances (ca. 3.5 Å) that are similar to those reported for analogous systems.<sup>37</sup>

The synthesis and characterization of the complete series of haloboryl complexes (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>B(Mes)X [X = F (**12**), Cl (**10**), Br (**2**), I (**11**)] offers a unique opportunity to investigate the electronic influence of the boron-bound substituents in organometallic boryl complexes. Relevant spectroscopic and structural data for the four complexes are included in Table 2.

The most obvious structural trend is the sequential increase in the Fe–B distance on going from bromoboryl complex **2** to its chloro- and fluoro-substituted analogues **10** and **12**. Such a trend can be rationalized in terms of the expected reduction of both σ donor and π acceptor properties along the series of ligands –B(Mes)Br, –B(Mes)Cl, and –B(Mes)F. Hence complex **12** features easily the longest Fe–B bond (with presumably the smallest absolute π back-bonding component), a factor that allows for greater rotational freedom by reducing steric interactions between the bulky metal- and boryl-bound substituents. This then helps explain the markedly different conformation adopted by the fluoroboryl complex and the presence of an intramolecular C–H⋯F hydrogen bond in the solid state.

Carbonyl stretching frequencies for these complexes decrease from values for iodoboryl **11** (2005 and 1955 cm<sup>−1</sup>), which are similar to those of corresponding alkyl compounds,<sup>38</sup> to values that are somewhat lower (e.g., 1989 and 1931 cm<sup>−1</sup> for fluoroboryl **9**). Such a trend mirrors the expected decrease in the π acceptor properties of the boryl ligand on going from –B(Mes)I to –B(Mes)F, this in turn being determined by competing X→B π donation from the halide. <sup>11</sup>B NMR shifts are also known to be strongly influenced by the π donor

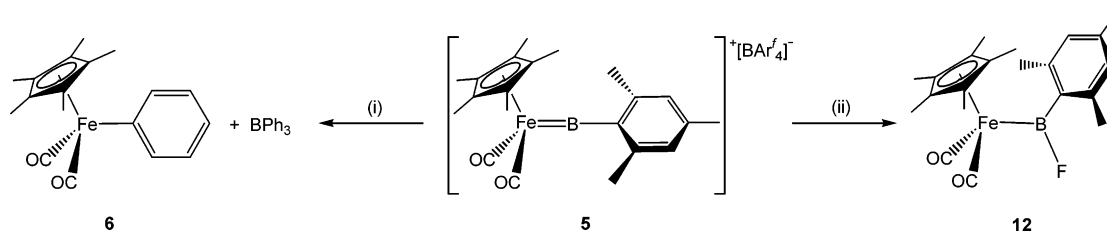
(35) See, for example: (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290. (b) Jeffrey, G. A. *J. Mol. Struct.* **1999**, *485–486*, 293. (c) Vargas, R.; Garza, J.; Dixon, D. A.; Hay, B. P. *J. Am. Chem. Soc.* **2000**, *122*, 4750.

(36) Aldridge, S.; Calder, R. J.; Baghurst, R. E.; Light, M. E.; Hursthouse, M. B. *J. Organomet. Chem.* **2002**, *694*, 9.

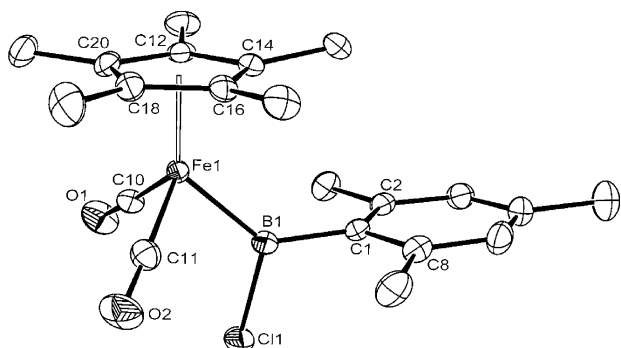
(37) See, for example: Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

(38) Carbonyl stretching frequencies for alkyl compounds of the type (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Fe(CO)<sub>2</sub>R typically fall in the ranges 2005–1999 and 1944–1938 cm<sup>−1</sup>; DeLuca, N.; Wojcicki, A. *J. Organomet. Chem.* **1980**, *193*, 359.

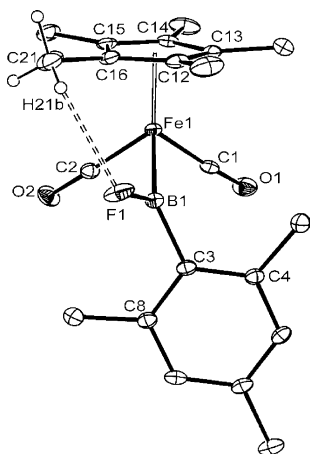


Scheme 7. Contrasting Reactivity of Cationic Borylene **5** toward the Borate Anions  $[\text{BPh}_4]^-$  and  $[\text{BF}_4]^-$ <sup>a</sup>

<sup>a</sup> Reaction conditions: (i)  $[\text{PPN}][\text{BPh}_4]$  1 equiv, dichloromethane, 18 °C, 1 h; (ii)  $[\text{nBu}_4\text{N}][\text{BF}_4]$  1 equiv, dichloromethane, 18 °C, 2 h.



**Figure 5.** Molecular structure of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})\text{Cl}$ , **10**. Relevant bond lengths (Å), angles (deg), and torsion angles (deg): Fe(1)–B(1) 1.985(2), B(1)–Cl(1) 1.834(2), B(1)–C(1) 1.569(2), Fe(1)– $(\eta^5\text{-C}_5\text{Me}_5)$  centroid 1.748(2),  $(\eta^5\text{-C}_5\text{Me}_5)$  centroid–Fe(1)–B(1)–Cl(1) 179.5(2), Cl(1)–B(1)–C(1)–C(8) 89.5(2). Hydrogen atoms are omitted for clarity.



**Figure 6.** Molecular structure of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})\text{F}$ , **12**, showing intramolecular C–H $\cdots$ F hydrogen bonding. Relevant bond lengths (Å), angles (deg), and torsion angles (deg): Fe(1)–B(1) 2.017(3), B(1)–F(1) 1.350(3), B(1)–C(3) 1.581(4), Fe(1)– $(\eta^5\text{-C}_5\text{Me}_5)$  centroid 1.736(3), H(21b)–F(1) 2.44, C(21) $\cdots$ F(1) 3.054(4), C(21)–H(21b)–F(1) 120.4,  $(\eta^5\text{-C}_5\text{Me}_5)$  centroid–Fe(1)–B(1)–F(1) 37.6(2), F(1)–B(1)–C(3)–C(8) 70.7(2). Hydrogen atoms except those attached to C(21) are omitted for clarity.

properties of boron-bound substituents;<sup>39</sup> the strongly upfield resonance measured for fluoroboryl complex **12** compared to **2**, **10**, and **11** therefore reflects the known

(39) For a discussion of the influence of  $\pi$  donor substituents on  $^{11}\text{B}$  chemical shifts in boryl systems see, for example: Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685. In the case of boron-bound iodine substituents, relativistic effects can also be important: Kaupp, M.; Malkina, O. L.; Malkin, V. G. *Chem. Phys. Lett.* **1997**, *265*, 55.

**Table 2. Comparison of Structural and Spectroscopic Data for Haloboryl Complexes of the Type  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})\text{X}$**

	<b>11</b>	<b>2</b>	<b>10</b>	<b>12</b>
X in –B(Mes)X	I	Br	Cl	F
$\nu(\text{CO})/\text{cm}^{-1}$	2005, 1955	1999, 1942	1996, 1937	1989, 1931
$d(\text{Fe}–\text{B})/\text{Å}$	–	1.972(2)	1.985(2)	2.017(3)
$\delta_{\text{B}}/\text{ppm}$	110.7	113.0	112.1	90.4

$\pi$  donor properties of fluoride. Very similar trends have been observed previously, for example in the reported resonances of the phenylboron dihalides  $\text{PhBX}_2$  [ $\delta_{\text{B}}$  23.8–24.5, 54.1–55.9, 56.1–60.6, and 44.6–48.2 for X = F, Cl, Br, and I, respectively<sup>40</sup>].

In the case of the reaction of **5** with  $[\text{nBu}_4\text{N}]\text{I}$ , periodic monitoring of reaction mixture by IR spectroscopy reveals that a second, minor product is also formed (albeit in low yield). This product is present even at short reaction times (ca. 30 min), and its relative concentration (with respect to that of the major product, iodoboryl **11**) does not appear to vary significantly with time. This second compound gives rise to two carbonyl stretching bands (2017 and 1969  $\text{cm}^{-1}$ ) which are in agreement both with the values reported previously by Akita, Morooka, and co-workers for  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{I}$  in  $\text{CH}_2\text{Cl}_2$  (2019 and 1971  $\text{cm}^{-1}$ )<sup>18</sup> and with those measured for a sample of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{I}$  prepared independently from  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]\text{Na}$  and  $\text{I}_2$  (2017 and 1971  $\text{cm}^{-1}$ ). Additional confirmation of the identity of this compound was obtained crystallographically; the less soluble  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{I}$  can be separated from **11** by fractional crystallization from a hexane solution. Although there are minor differences from the literature data, the crystal structure obtained (and which is reproduced in the Supporting Information) unambiguously identifies the minor product as  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{I}$  (**13**).<sup>18</sup> Given the patterns of reactivity that emerge for **5** toward *neutral* two-electron-donor ligands (vide infra), together with the seemingly invariant relative concentrations of **11** and **13** in the reaction mixture, it seems likely that **13** is formed by competing attack of iodide at the iron center of **5**, rather than by decomposition of boryl complex **11**. Although nucleophilic attack at iron formally involves reaction at an 18-electron metal center, an interchange type mechanism involving concerted loss (and scavenging) of the  $\text{BMe}_3$  ligand is implied by kinetic data for other reactions of this type (vide infra).

The notion of the iron center as a competing site of electrophilicity is given further impetus by examination

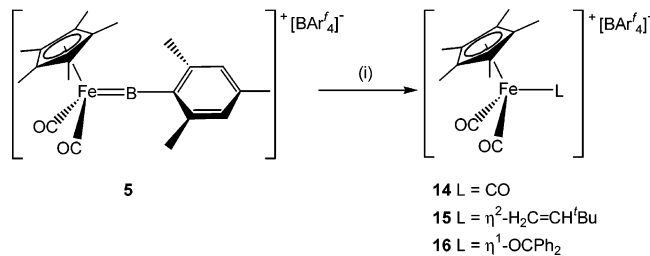
(40) Nöth, H.; Wrackmeyer, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978; Vol. 14.

of the reaction of **5** with  $[\text{BPh}_4]^-$  (Scheme 7). Thus the reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BMes})][\text{BAR}'_4]$  with a single equivalent of the soluble  $[\text{PPN}]^+$  salt of  $[\text{BPh}_4]^-$  in dichloromethane proceeds very rapidly (as judged by  $^{11}\text{B}$  NMR) to the formation of  $\text{BPh}_3$  and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Ph}$  (**6**). Reaction of the tetraphenylborate counterion with an electrophilic metal center to generate  $\text{BPh}_3$  finds precedent, for example, in the chemistry of cationic vanadocene complexes.<sup>41</sup> In monitoring the reaction of **5** with  $[\text{BPh}_4]^-$  by  $^{11}\text{B}$  NMR spectroscopy, no evidence was obtained for any competing reaction involving nucleophilic transfer of the  $\text{Ph}^-$  moiety to the boron center. It might reasonably be expected that the product of such a reaction,  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})\text{Ph}$ , might give rise to a  $^{11}\text{B}$  resonance similar to that reported previously by Hartwig for the diphenylboryl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{BPh}_2$  ( $\delta_{\text{B}}$  121).<sup>29</sup> In the event no signals in this region of the spectrum were observed at any time. Although it is not possible to rule out conclusively a mechanism involving *initial* transfer of  $\text{Ph}^-$  to the boron center followed by rapid decomposition of the boryl complex,  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})\text{Ph}$ , so formed, such a pathway would appear unlikely because (i) thermolysis of the related compound  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{BPh}_2$  proceeds rapidly only at elevated temperatures (75–95 °C)<sup>29,42</sup> and (ii) decomposition of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{BPh}_2$  under either thermal or photochemical conditions has been reported to generate (in addition to  $\text{BPh}_3$ ) the dimer  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  rather than  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Ph}$ .<sup>29</sup>

The experimental observation of alternative sites of reactivity toward nucleophiles finds ample precedent, for example in the chemistry of closely related carbonyl complexes. Thus displacement of CO from the metal center in  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})(\text{L})_2]^+$  by an incoming two-electron donor is a textbook reaction, with alternative carbon-centered reactivity being observed, for example, in the reaction with hydroxide to generate metalcarboxylates such as  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{CO}_2)]^-$ .<sup>43</sup> What is particularly intriguing in the case of **5** is that reactivity toward the borate anions  $[\text{BPh}_4]^-$  and  $[\text{BF}_4]^-$  should apparently lead to highly selective, but opposing sites of attack. Given the calculated partial charges at boron and iron (+0.356 and -0.338, respectively) and the composition of the LUMO (38.3% total from Fe  $3d_{x^2-y^2}$ ,  $3d_{xz}$ , and  $3d_{yz}$ ; 4.2% from B  $2p_x$ ), an attractive (if simplistic) interpretation is that attack by the harder nucleophile  $[\text{BF}_4]^-$  is charge driven (toward boron), while that by the softer nucleophile  $[\text{BPh}_4]^-$  is influenced by the predominant localization of the LUMO at iron.

The reactivity of **5** toward archetypal *neutral* two-electron ligands such as phosphines and CO has also been examined. In the case of tertiary phosphines (exemplified by  $\text{PPh}_3$ ) an oily mixture of products was obtained on addition of 1 equiv of the ligand to a solution of **5** in dichloromethane. The analogous reaction of **5** with CO over a period of 6 h also proceeds with complete consumption of the starting material (as judged by  $^{11}\text{B}$

### Scheme 8. Displacement of the Mesitylborylene Ligand from **5** by Neutral Two-Electron-Donor Ligands<sup>a</sup>



<sup>a</sup> Reaction conditions: (i) excess ligand (CO,  $\text{H}_2\text{C}=\text{CH}'\text{Bu}$ , or  $\text{O}=\text{CPh}_2$ ), dichloromethane, 18 °C, 2–16 h.

NMR), but in this case results in the formation of a single metal-containing species. Filtration of the reaction mixture, removal of volatile components in vacuo, and recrystallization from a dichloromethane/hexane mixture at -30 °C leads to the isolation of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_3][\text{BAR}'_4]$  (**14**) as a red crystalline material in ca. 75% yield. **14** has been characterized by IR and multinuclear NMR spectroscopies and by mass spectrometry, with unambiguous confirmation being obtained by single-crystal X-ray diffraction (see Table 1 and Supporting Information). Structural and spectroscopic data for the  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_3]^+$  cation in **14** are very similar to those reported previously by McArdle for the corresponding  $[\text{BF}_4]^-$  salt.<sup>27b</sup>

The isolation of **14** as the metal-containing product from the reaction of **5** with CO implies that displacement of the BMes ligand from the coordination sphere of iron is not limited to its reactions with anionic nucleophiles such as  $[\text{BPh}_4]^-$  or  $\text{I}^-$  (see Scheme 8). Similar reactivity has been reported by Tilley for cationic ruthenium silylene complexes toward ligands containing nitrogen or phosphorus donor atoms. Thus reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2(\text{SiMe}_2)]^+$  with  $\text{PMe}_3$  or  $\text{PPh}_3$  ultimately leads to  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2(\text{PR}_3)]^+$  (R = Me, Ph) through decomposition of the initially formed Si-ligated complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2(\text{SiMe}_2\text{-PR}_3)]^+$ .<sup>2e</sup> Although no analogous intermediate species could be definitively identified in the reaction of **5** with either  $\text{PPh}_3$  or CO, it is not possible to rule out an overall substitution pathway involving initial formation of a labile B-ligated complex.

**(b) Reactivity toward Unsaturated Substrates.** The versatile and widely exploited reactivity toward unsaturated substrates of organometallic complexes containing  $\text{M}=\text{C}$  double bonds,<sup>1</sup> together with the obvious similarities between electrophilic Fischer carbene and borylene complexes, prompted us to examine the reactivity of **5** toward simple unsaturated species containing  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ , or  $\text{C}=\text{O}$  bonds. However these studies reveal that the predominant mode of reactivity of **5** toward compounds of this type does not involve the cyclopropanation or metathesis chemistry typical of  $\text{M}=\text{C}$  bonds,<sup>1,44</sup> but rather involves borylene ligand displacement, even by substrates that are typically thought of as forming weak metal–ligand bonds.

Reaction of **5** with 3,3-dimethyl-1-butene over a period of 16 h leads to complete consumption of the starting

(41) Choukroun, R.; Douziech, B.; Pan, C.; Dahan, F.; Cassoux, P. *Organometallics* **1995**, *14*, 4471.

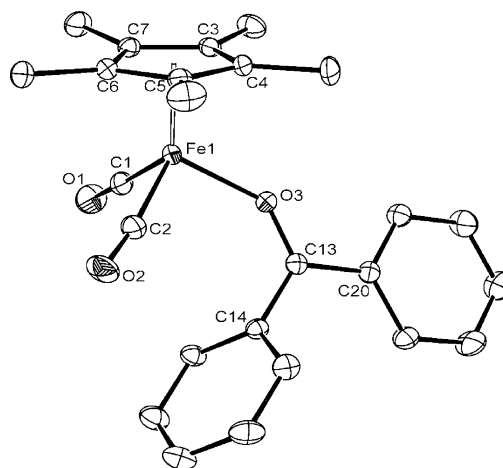
(42) Additionally, in our experience boryl complexes of the type  $(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Ar})\text{X}$  tend if anything to be thermally more stable for R = Me than R = H (see ref 8b).

(43) See, for example: Gibson, D. H.; Ong, T.-S.; Ye, M. *Organometallics* **1991**, *10*, 1811.

(44) See, for example: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 1987.

material, as judged by  $^{11}\text{B}$  NMR. The metal-containing product isolated from dichloromethane solution displays  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR resonances indicative of the  $[\text{BAR}^f_4]^-$  anion, and the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are consistent with the presence of  $(\eta^5\text{-C}_5\text{Me}_5)$ , CO, and coordinated alkene moieties. In particular, the  $^1\text{H}$  resonances for the three alkene protons of the  $^t\text{Bu}(\text{H})\text{C}=\text{CH}_2$  unit are shifted significantly upfield ( $\delta_{\text{H}}$  2.68, 3.11, 3.99) compared to the free alkene ( $\delta_{\text{H}}$  4.82, 4.92, 5.85), as expected for coordination to the iron center. Similar upfield shifts are observed for the alkene moiety on coordination to the  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]^+$  fragment for ethylene and styrene (e.g.,  $\delta_{\text{H}}$  5.24, 5.75, 6.72 to 3.03, 3.97, 4.89 for styrene).<sup>45</sup> In addition the ES+ mass spectrum displays prominent features corresponding to the molecular ion  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{H}_2\text{C}=\text{CH}^t\text{Bu})]^+$  ( $\text{M}^+$ ,  $m/z$  331, 50%) and to fragment ions formed by loss of either alkene or carbonyl ligands ( $[\text{M} - \text{alkene}]^+$ ,  $m/z$  247, 40%;  $[\text{M} - 2\text{CO}]^+$ ,  $m/z$  275, 100%). Carbonyl stretching frequencies of 2033 and 1997  $\text{cm}^{-1}$  are slightly lower than those reported for  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{H}_2\text{C}=\text{CHR})][\text{PF}_6]$  ( $\text{R} = \text{H}$ , 2050, 2020  $\text{cm}^{-1}$ ;  $\text{R} = \text{Ph}$ , 2060, 2020  $\text{cm}^{-1}$ )<sup>45</sup>, for which an  $\eta^2$  mode of alkene coordination might be expected by comparison with the structurally authenticated ruthenium styrene complex,<sup>45</sup> but are similar to those reported for the crystallographically characterized complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-bicyclo[3.2.2]non-1-ene})][\text{CF}_3\text{SO}_3]$  (2030, 2010  $\text{cm}^{-1}$ ).<sup>46</sup> Thus the available spectroscopic data point to a cationic complex featuring an  $\eta^2$ -coordinated alkene fragment, i.e.,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^2\text{-H}_2\text{C}=\text{CH}^t\text{Bu})][\text{BAR}^f_4]$  (**15**), an inference that was subsequently confirmed crystallographically. The structure of **15** (see Table 1 and Supporting Information) features a C–Fe–C angle [ $37.4(2)^\circ$ ] and Fe–C [2.096(6) and 2.233(7) Å] and C–C distances [1.393(9) Å] for the coordinated alkene ligand that are consistent with previous examples of  $\eta^2$  coordination to a  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2]^+$  fragment.<sup>46–48</sup> Additionally the angles subtended at the iron center by the carbonyl ligands and by the alkene C=C centroid [ $92.6(3)$ – $96.8(3)^\circ$ ] are consistent with a three-legged piano stool geometry at the metal.

The reactivity of **5** toward more polar multiple bonds was also examined, with a similar outcome being observed. Thus, reaction with benzophenone in dichloromethane over a 3 h period leads to complete consumption of the starting material; recrystallization from dichloromethane/hexane generates the dark red benzophenone complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-O}=\text{CPh}_2)][\text{BAR}^f_4]$  (**16**) as the metal-containing product in 55–60% yield. The identity of **16** was established by multinuclear NMR, IR, and mass spectrometry and confirmed crystallographically. In particular the stretching frequencies for the CO ligands (2050, 2004  $\text{cm}^{-1}$ ) show the expected shift to lower wavenumber in comparison with those reported for the analogous  $(\eta^5\text{-C}_5\text{H}_5)$  complex (2078,



**Figure 7.** Molecular structure of the cationic component of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-OCPh}_2)][\text{BAR}^f_4]$ , **16**. Relevant bond lengths (Å), angles (deg), and torsion angles (deg): Fe(1)–C(1) 1.801(5), Fe(1)–C(2) 1.793(5), Fe(1)–O(3) 1.982(3), Fe(1)– $(\eta^5\text{-C}_5\text{Me}_5)$  centroid 1.723(4), O(3)–C(13) 1.256(5), Fe(1)–O(3)–C(13)  $136.6(3)^\circ$ ,  $(\eta^5\text{-C}_5\text{Me}_5)$  centroid–Fe(1)–O(3)–C(13)  $141.3(4)^\circ$ . Hydrogen atoms are omitted for clarity.

2030  $\text{cm}^{-1}$ ).<sup>49</sup> Although no data were reported for the C=O stretch of the coordinated benzophenone ligand for this compound, the measured value for **16** (1612  $\text{cm}^{-1}$ ) is very similar to that reported for the structurally characterized yttrium complex  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Y}(\text{O}=\text{CPh}_2)\text{-Cl}$  (1614  $\text{cm}^{-1}$ ), which contains an O-bound  $\eta^1\text{-O}=\text{CPh}_2$  ligand.<sup>50</sup> The crystal structure of **16** (Figure 7 and Table 1) confirms this mode of attachment for the benzophenone ligand; the Fe–O distance and Fe–O–C angle [ $1.982(3)$  Å and  $136.6(3)^\circ$ ] are very similar to those reported previously for cationic  $\eta^1$ -ketone complexes {e.g.,  $1.983(5)^\circ$  and  $136.9(4)^\circ$ , respectively, for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{O}=\text{CC}_6\text{H}_6)][\text{BF}_4]$ }, and the lengthening of the benzophenone C=O bond [1.256(5) Å in **16**] compared to the free ligand (1.23 Å) mirrors that seen in  $\text{Tb}[\text{N}(\text{SiMe}_3)_2]_3(\eta^1\text{-O}=\text{CPh}_2)$  [1.264(14) Å].<sup>51,52</sup> Although a number of ketone and aldehyde complexes of iron have been reported, complex **16** represents the first structurally characterized iron-containing benzophenone complex.

Within the context of the current study the conversion of **5** to **16** in particular appears somewhat surprising, especially given that the charge neutral chromium aminoborylene complex  $(\text{OC})_5\text{CrBN}(\text{SiMe}_3)_2$  can be recovered unchanged from acetone solution.<sup>53</sup> Strong binding of group 13 diyl ligands to transition metal centers has been predicted by a number of recent computational studies,<sup>5</sup> and a bond dissociation energy of 147.5  $\text{kcal mol}^{-1}$  has been predicted for the mesitylborylene ligand in  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BMe}_3)]^+$ .<sup>4b</sup> That the reactivity of **5** toward a number of neutral two-electron-donor ligands (including relatively weak donors such as ketones) is undoubtedly characterized by sub-

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stitution of the mesitylborylene ligand would therefore appear to be thermodynamically counterintuitive. On the other hand, extrusion of the MesB fragment from the coordination sphere of a cationic group 8 metal center has some precedent in silylene chemistry, with  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2(\text{SiMe}_2)]^+$  ultimately undergoing substitution at ruthenium with tertiary phosphines.  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2(\text{PR}_3)]^+$  (R = Me or Ph) and oligomeric  $(\text{Me}_2\text{Si})_n$  are the final products identified in this case.<sup>2e</sup> A similar irreversible extrusion of the MesB fragment from **5** is conceivable, although given the observation of a common boron-containing product from all of the displacement reactions described above, together with the known (high) reactivity of “free” borylenes toward hydrocarbons, a more likely possibility is irreversible reaction of the BMes fragment with the common dichloromethane solvent. A number of experimental observations add weight to this hypothesis.

Although complete characterization of the common boron-containing product was prevented by its high volatility and extreme moisture sensitivity, its measured <sup>11</sup>B chemical shift ( $\delta_{\text{B}}$  17.0) is consistent with a species such as  $[\text{Mes}(\text{Cl}_2\text{CH})\text{B}(\mu\text{-H})_2]$  formed by dimerization of the initial product of BMes insertion into one of the C–H bonds of dichloromethane (cf. chemical shifts of  $\delta_{\text{B}}$  17.5 and 25.9 for  $\text{B}_2\text{H}_6$  and  $(\text{MesBH}_2)_2$ , respectively<sup>40,54</sup>).<sup>55</sup> Additionally, <sup>1</sup>H signals consistent with mesityl and BH protons show similar concentration/time profiles, and rapid insertion reactions of “free” borylenes into C–H and C–C bonds have previously been reported in a number of studies.<sup>56</sup> Of particular relevance is the intramolecular C–H insertion reaction undergone by the putative borylene  $(\text{Me}_3\text{Si})_3\text{CB}$  to generate the hydride-bridged dimer  $[(\text{Me}_3\text{Si})_2\text{C}(\text{Me}_2\text{Si})\text{CH}_2\text{B}(\mu\text{-H})_2]$ .<sup>57</sup> Although other insertion reactions of the MesB fragment (e.g., into the C–Cl bond of dichloromethane) can be envisaged, we believe that kinetic data in particular are most consistent with a C–H insertion process (vide infra).

The fact that the same boron-containing product is generated in each of the borylene displacement reactions (even with relatively poor donors such as benzophenone) prompted us to examine whether, under forcing conditions, a similar substitution of the borylene ligand might be brought about by the dichloromethane solvent alone.<sup>58</sup> At room temperature **5** is stable in dichloromethane solution over a period of several days. However at 40 °C, a solution of **5** in  $\text{CD}_2\text{Cl}_2$  decomposes over a period of ca. 24 h. This decomposition process, monitored by <sup>11</sup>B and <sup>1</sup>H NMR reveals not only that the same boron-containing product is formed as in other ligand displacement reactions but that the decomposition process is first order in **5** (Figure 8). This result renders

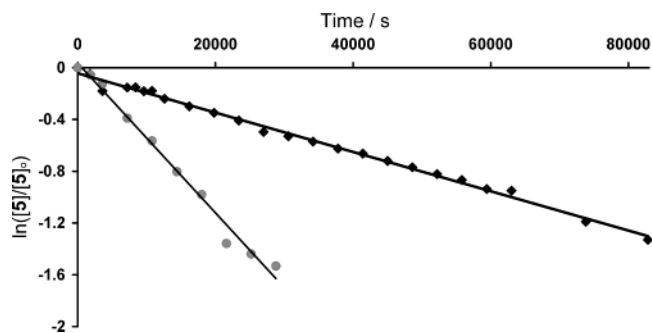
(54) Entwistle, C. D.; Marder, T. B.; Howard, J. A. K.; Fox, M. A.; Mason, S. A. *J. Organomet. Chem.* **2003**, *680*, 165.

(55) The species giving rise to the resonance at  $\delta_{\text{B}}$  17 does not appear to be the product of a hydrolysis reaction. Independent hydrolysis of **5** generates  $(\text{MesBO})_3$  and  $\text{MesB}(\text{OH})_2$ , which give rise to <sup>11</sup>B NMR resonances at ca. 30 ppm.

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(58) Dichloromethane complexes of the type  $[(\eta^5\text{-C}_5\text{R}_5)\text{Fe}(\text{CO})_2(\text{CH}_2\text{-Cl}_2)]^+$  have previously been reported: (a) Reger, D. L.; Coleman, C. J. *Organomet. Chem.* **1977**, *131*, 153. (b) Johnston, P. Hutchings, G. J.; Denner, L.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1987**, *6*, 1292.



**Figure 8.** Plots of  $\ln([5]/[5]_0)$  versus time (s) for the thermolysis of cationic borylene **5** in deuterio (◆) and normal dichloromethane (●). The linear plots ( $R^2 = 0.994$  and  $0.988$ , respectively) yield values of  $1.52 \times 10^{-5}$  and  $5.78 \times 10^{-5} \text{ s}^{-1}$  for the first-order rate constants  $k_{\text{D}}$  and  $k_{\text{H}}$ , respectively.

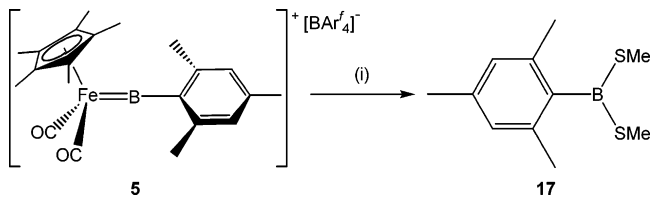
unlikely a bimolecular decomposition process involving interaction between two molecules of **5**. Furthermore, comparison of the kinetic data for the reactions in  $\text{CD}_2\text{Cl}_2$  and  $\text{CH}_2\text{Cl}_2$  reveals a primary kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}} = 3.8$ ), an observation consistent not only with involvement of the dichloromethane solvent in the rate-determining step of the borylene displacement reaction but also with a significant degree of C–H bond breakage in the transition state. It therefore seems probable that insertion of the BMes fragment into one of the C–H bonds of the  $\text{CH}_2\text{Cl}_2$  solvent is occurring during the ligand displacement process. Clearly, given the high BDE calculated for **5**, the observation of facile ligand displacement at 40 °C must imply significant involvement of the dichloromethane molecule during the displacement of the BMes fragment from the metal coordination sphere. The thermodynamics of the insertion process (i.e., the formation of B–H and B–C bonds) would then explain the displacement of the BMes ligand even by relatively poor donors.

An alternative approach to determining the fate of the boron-containing fragment in ligand displacement reactions of **5** is the use of trapping reagents which might be expected to give tractable and readily characterized products on reaction with any mesitylborylene generated. West has previously reported the trapping of “free” borylene by an internal alkyne to generate a stable boracyclopene, and we initially investigated the reaction of **5** with similar trapping agents.<sup>59</sup> However, the course of such reactions using either neat alkyne [e.g., bis(trimethylsilyl)acetylene] or a solution in dichloromethane did not appear to be straightforward, and no spectroscopic evidence was obtained at any point for the generation of a boracyclopene,  $\text{Mes-BC}_2\text{R}_2$ .<sup>59</sup> Tokitoh and co-workers, on the other hand, have reported the photolytic generation of sterically encumbered arylborylenes and their trapping with dialkyldichalcogenides (e.g.,  $\text{Me}_2\text{S}_2$ ) to generate species of the type  $\text{ArB}(\text{ER})_2$ .<sup>60</sup> Hence we investigated the use of such trapping agents in the chemistry of **5**. Accordingly, the reaction of **5** with  $\text{Me}_2\text{S}_2$  in hexane at room temperature leads to quantitative and very rapid (by

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**Scheme 9. Reactivity of **5** toward Dimethyl Disulfide: Chemical Trapping of the Borylene Fragment<sup>a</sup>**



<sup>a</sup> Reaction conditions: (i) Me<sub>2</sub>S<sub>2</sub> 1.5 equiv, hexane, 2 h.

<sup>11</sup>B NMR) conversion to a single boron-containing species, giving rise to a broad signal at  $\delta_B$  66.0. Isolation of the oily hexane-soluble product and comparison of spectroscopic data with those reported previously confirm that this product is the bis(methylthio)borane MesB(SMe)<sub>2</sub> (**17**) (Scheme 9).<sup>19</sup> A similar reaction with Me<sub>2</sub>Se<sub>2</sub> also generates a single boron-containing product, the <sup>11</sup>B NMR resonance of which ( $\delta_B$  75.4) is appropriate for a bis(methylseleno)aryl borane [e.g.,  $\delta_B$  76.6 and 70.3 for 2,4,6-(R<sub>2</sub>HC)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>B(SeMe)<sub>2</sub> (R = SiMe<sub>3</sub>) and PhB(SeMe)<sub>2</sub>, respectively].<sup>40,60</sup> Chemical trapping experiments therefore mirror the results of thermolysis studies in being consistent with rapid insertion of the ejected BMes ligand into reactive available linkages.

### Conclusions

Application of halide abstraction chemistry to asymmetric haloboryl complexes of the type  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{ER}_n)\text{X}$  leads to the development of the first synthetic route to *cationic* multiply bonded group 13 diyl complexes. Thus, abstraction of bromide from  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})\text{Br}$  (**2**) by Na[BAR<sup>f</sup><sub>4</sub>] leads to the isolation of colorless crystalline  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Mes})][\text{BAR}^f_4]$  (**5**) in 50–60% yield, while similar chemistry applied to  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{NMe}_2)\text{Br}$  (**7**) at –20 °C leads to the generation of the highly reactive aminoborylene  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BNMe}_2)][\text{BAR}^f_4]$  (**8**), which can be characterized in solution by multinuclear NMR and IR spectroscopies and chemically trapped by chloride to yield the known compound  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{NMe}_2)\text{Cl}$  (**9**). In the case of arylborylene complexes, both the steric properties of the putative borylene substituent (and of the metal fragment) and the inherent coordinating properties/reactivity of the counterion employed appear to play key roles in the isolation (or otherwise) of stable, tractable cationic borylene complexes. Thus the need for suitable steric shielding of *both* boron and metal centers is demonstrated by the reactions of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Ph})\text{Cl}$  (**4**) or  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Ar})\text{Br}$

(Ar = Mes or 2,6-Trp<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with Na[BAR<sup>f</sup><sub>4</sub>], which lead to the generation of no detectable borylene products. On the other hand, the use of alternative halide abstraction agents containing more reactive anions such as [BPh<sub>4</sub>]<sup>–</sup> or [BF<sub>4</sub>]<sup>–</sup> leads to the isolation of complexes derived from attack at either the boron or iron center.

Crystallographic, spectroscopic, and DFT studies of **5** are consistent with an Fe=B double bond comprising a B→Fe  $\sigma$  interaction, supplemented by Fe→B  $\pi$  back-bonding into one of the formally vacant p orbitals at boron. On the basis of a DFT population analysis the Fe–B bond has a 62:38  $\sigma$ : $\pi$  breakdown of the covalent contribution to bonding compared to a 64:36 breakdown for archetypal Fischer carbene  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(=\text{CH}_2)]^+$ .

DFT-based analyses of the charge distribution and LUMO composition for **5** indicate that both boron and iron centers may be likely centers for nucleophilic attack. Such predictions are borne out in practice by an investigation of the reactivity of **5** toward a number of different classes of reagent. Thus reactions proceeding to  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{B}(\text{Ar})\text{X}$  via nucleophilic addition at the boron center predominate for the halide ions Cl<sup>–</sup>, Br<sup>–</sup> and I<sup>–</sup> and for BF<sub>4</sub><sup>–</sup>, whereas substitution of the borylene ligand at the iron center is observed for BPh<sub>4</sub><sup>–</sup>, CO, H<sub>2</sub>C=C(H)Tbu, and Ph<sub>2</sub>C=O. Despite unfavorable ligand binding thermodynamics, the latter chemistry is thought to be driven by irreversible removal of the MesB ligand, which can be trapped, for example, by insertion into the S–S bond of Me<sub>2</sub>S<sub>2</sub> trapping agent.

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**Supporting Information Available:** Full details (including CIF files) of the crystallographic studies of compounds **5**, **10**, **12**, **14**, **15**, and **16**, together with those for **13** (not reported in main text); variable-temperature NMR spectra for fluoroboryl complex **12**; details of the DFT optimized structures for **5**, **8**, and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PMe}_3)_2(\text{BMes})]^+$ ; and a complete listing of the molecular orbital energies and compositions for **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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