Influence of Ligand Steric Bulk in the Synthesis of Transition-Metal Borylene Complexes

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The differing steric requirements of phenyl and mesityl substituents have been shown to influence reactivity in asymmetric transition-metal haloboryl complexes of the type $(\eta^5\text{-}C_5R_5)$-$Fe(CO)_2B(X)Ar$ (R = H, Me; X = Cl, Br; Ar = Ph, Mes). Hence substitution of *both* halides in $PhBCl_2$ can be achieved by reaction with an excess of the bulky organometallic nucleophile $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$, to generate $[(\eta^5\text{-}C_5Me_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}BPh)$ (**4c**), the first metal complex containing the phenylborylene ligand.

Introduction

A fuller understanding of the bonding between transition metals and low-coordinate ligands containing group 13 or 14 donor atoms continues to be the driving force for significant research effort.[1−10] In stark contrast to their group 14 counterparts, however, the bonding in terminally bound group 13 diyl systems (ER_n = BR, AlR, GaR, InR) remains a matter of some debate.[4−8] The description of superficially similar complexes as being bound via multiple bonds (e.g. $L_nM{=}ER$ or $L_nM{\equiv}ER$) or via donor/acceptor interactions ($L_nM{\leftarrow}ER$), for example, reflects not only the fundamental questions of structure and bonding posed by such complexes but also the scarcity of structural data available.[4,5,7]

Within this area compounds containing boranediyl (or borylene, BR) or allanediyl (AlR) ligands are a relatively recent addition, with the first structurally characterized examples having been reported as late as 1995.[4,5,11−13] Since then, the dozen or so compounds reported in the literature have generally conformed to one of two structural types, viz. (i) complexes containing terminally bound ligands having sterically bulky or π-electron-releasing R substituents (e.g. $(OC)_5Cr{=}BSi(SiMe_3)_3$ and $(OC)_4Fe{\leftarrow}Al(\eta^5\text{-}C_5Me_5))$[4−6] and (ii) complexes containing bridging RE ligands spanning two (or more) metal centers which are typically also linked by a metal−metal bond or a second bridging ligand (e.g. $[(\eta^5\text{-}C_5H_4R)Mn\text{-}(CO)_2]_2(\mu\text{-}BX)$ (X = NMe$_2$, R = H; X = OEt, R = Me; X = Cl, R = Me) and $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(\mu\text{-}AlEt)_2Ir\text{-}(PMe_3)(\eta^5\text{-}C_5Me_5))$.[11−13]

We have recently been interested in developing new routes to transition-metal complexes containing the borylene ligand in a variety of novel coordination modes

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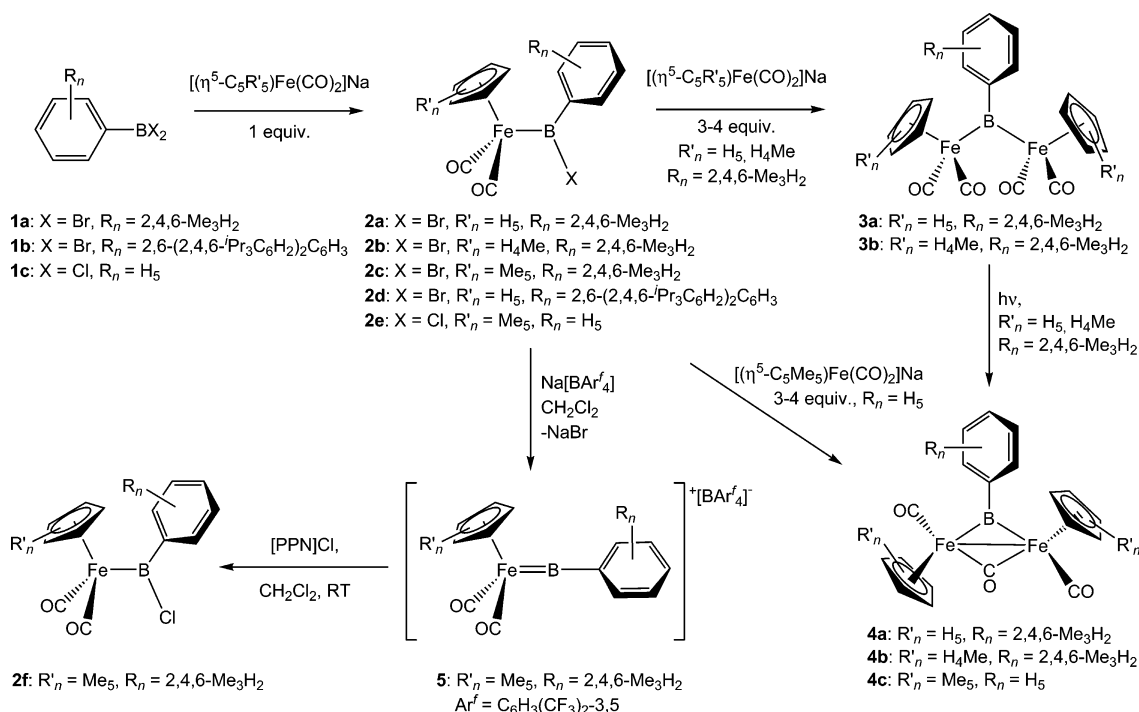
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Scheme 1. Halide Substitution and Abstraction Chemistry of Iron Haloboryl Complexes

1a: X = Br, R_n = 2,4,6-Me$_3$H$_2$
1b: X = Br, R_n = 2,6-(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$
1c: X = Cl, R_n = H$_5$

2a: X = Br, R'$_n$ = H$_5$, R_n = 2,4,6-Me$_3$H$_2$
2b: X = Br, R'$_n$ = H$_4$Me, R_n = 2,4,6-Me$_3$H$_2$
2c: X = Br, R'$_n$ = Me$_5$, R_n = 2,4,6-Me$_3$H$_2$
2d: X = Br, R'$_n$ = H$_5$, R_n = 2,6-(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$
2e: X = Cl, R'$_n$ = Me$_5$, R_n = H$_5$

3a: R'$_n$ = H$_5$, R_n = 2,4,6-Me$_3$H$_2$
3b: R'$_n$ = H$_4$Me, R_n = 2,4,6-Me$_3$H$_2$

2f: R'$_n$ = Me$_5$, R_n = 2,4,6-Me$_3$H$_2$

5: R'$_n$ = Me$_5$, R_n = 2,4,6-Me$_3$H$_2$
Ar^f = C$_6$H$_3$(CF$_3$)$_2$-3,5

4a: R'$_n$ = H$_5$, R_n = 2,4,6-Me$_3$H$_2$
4b: R'$_n$ = H$_4$Me, R_n = 2,4,6-Me$_3$H$_2$
4c: R'$_n$ = Me$_5$, R_n = H$_5$

(Scheme 1).[14,15] To this end asymmetric haloboryl complexes (**2**) have proved to be valuable synthetic intermediates, available in high yield from the corresponding arylboron dihalide and displaying a range of useful further reactivity.[14−16] Thus, halide *abstraction* from the sterically hindered derivative **2c**, containing both η^5-C$_5$Me$_5$ (Cp*) and mesityl (2,4,6-Me$_3$C$_6$H$_2$, Mes) fragments, gives access to the cationic Fe=B double-bonded Fischer carbene analogue **5**.[17] Furthermore, in the case of the less congested η^5-C$_5$H$_5$ (Cp) and η^5-C$_5$H$_4$-Me (Cp′) derivatives **2a** and **2b**, halide *substitution* is possible, leading first to the novel unsupported bridged borylene systems **3a** and **3b** and then (under photolytic conditions) to the Fe−Fe-bonded species **4a** and **4b**.[14,15]

Very hindered systems such as Cp*Fe(CO)$_2$B(Br)Mes (**2c**) and CpFe(CO)$_2$B(Br)(2,6-Ar$_2$C$_6$H$_3$) (**2d**, Ar = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) have been shown to be inert toward boron-centered substitution chemistry.[15,16] Therefore, to further investigate patterns of structural and reaction chemistry in borylene systems, we have focused on less sterically demanding RB ligands. Phenyl- and methyl-borylene systems have previously been the subject of extensive computational study,[5e−g] and herein we present the first experimental realization of the PhB ligand.

Experimental Section

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$_2$). d_6-Benzene and d_8-toluene (both Goss) were degassed and dried over potassium prior to use. PhBCl$_2$ and bis-(triphenylphosphoranyl)ammonium chloride, [PPN]Cl (both Aldrich) were used without further purification; [(η^5-C$_5$-Me$_5$)Fe(CO)$_2$BMes]$^+$[BAr$^f_4$]$^-$ and Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] were prepared by literature methods.[17,18] NMR spectra were measured on a JEOL 300 Eclipse Plus FT-NMR spectrometer. Residual protons of solvent were used for reference for ^{1}H and ^{13}C NMR, while a sealed tube containing a solution of [(^{n}Bu$_4$N)-(B$_3$H$_8$)] in CDCl$_3$ was used as an external reference for ^{11}B NMR. Infrared spectra were measured for each compound pressed into a disk with an excess of dried KBr on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, U.K. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. 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 **2e**, **2f**, and **4c** is therefore based upon multinuclear NMR, IR, and mass spectrometry data (including accurate mass measurement), supplemented by single-crystal X-ray diffraction studies in the case of **2e** and **4c**. In all cases the purity of the bulk material was established by multinuclear NMR to be >95%.

Abbreviations: vs = very strong, st = strong, m = medium, b = broad, s = singlet, d = doublet, t = triplet.

Synthesis of (η^5-C$_5$Me$_5$)Fe(CO)$_2$B(Cl)Ph (2e). To a suspension of Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] (185 mg, 0.69 mmol) in toluene (15 cm^3) at room temperature was added by syringe PhBCl$_2$ (105 mg, 0.66 mmol), and the reaction mixture was stirred for 4 h. Filtration, removal of volatiles in vacuo, and recrystallization from hexanes (ca. 20 cm^3) at −30 °C yielded **2e** as yellow crystals suitable for X-ray diffraction. Isolated yields were typically on the order of 95 mg (39%). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.46 (s, 15H, C$_5$*Me$_5$*), 7.22 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, aromatic *p*-CH), 7.31 (virtual t, $^3J_{H-H}$ = 7.5 Hz, 2H, aromatic *m*-CH), 8.17 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, aromatic *o*-CH). ^{13}C NMR (76 MHz, C$_6$D$_6$): δ 9.4 (η^5-C$_5$*Me$_5$*), 95.7 (η^5-*C$_5$*Me$_5$

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quaternary), 127.7, 131.0, 134.1 (aromatic CH), 216.3 (CO). ^{11}B NMR (96 MHz, C_6D_6): δ 111 (b, fwhm = 400 Hz). IR (KBr disk, cm^{-1}): ν(CO) 1995 st, 1929 st. MS (EI): 342 [(M − CO)$^+$, 30%], isotope pattern corresponding to 1 Fe, 1 B, 1 Cl atoms.

Synthesis of [(η^5-C$_5$Me$_5$)Fe(CO)]$_2$(μ-CO)(μ-BPh) (4c). To a suspension of Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] (297 mg, 1.1 mmol) in toluene (15 cm^3) at room temperature was added by syringe PhBCl$_2$ (60 mg, 0.4 mmol) in toluene (3 cm^3), and the reaction mixture was stirred for 72 h. Filtration, removal of volatiles in vacuo, and recrystallization from hexanes (ca. 20 cm^3) at −50 °C yielded **4c** as red crystals suitable for X-ray diffraction. Isolated yields were typically on the order of 145 mg (65%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.53 (s, 30H, C$_5$Me$_5$), 7.23 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, aromatic *p*-CH), 7.37 (virtual t, $^3J_{H-H}$ = 7.4 Hz, 2H, aromatic *m*-CH), 7.76 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, aromatic *o*-CH). ^{13}C NMR (76 MHz, C_6D_6): δ 8.9 (η^5-C$_5$Me$_5$), 96.8 (η^5-C$_5$Me$_5$ quaternary), 127.4, 128.0, 129.1 (aromatic CH), 215.2 (terminal CO), 280.9 (bridging CO). ^{11}B NMR (96 MHz, C_6D_6): δ 159 (b, fwhm = 840 Hz). IR (KBr disk, cm^{-1}): ν(CO) 1917 vs, 1889 m, 1754 vs. MS (EI): M$^+$ = 554 (40%), isotope pattern corresponding to 2 Fe, 1 B atoms, fragment ion peaks at *m/z* 526 [(M − CO)$^+$, 12%], 498 [(M − 2CO)$^+$, 15%], 470 [(M − 3CO)$^+$, 30%]. Exact mass: calculated 554.1373, measured 554.1370.

Synthesis of (η^5-C$_5$Me$_5$)Fe(CO)$_2$B(Cl)Mes (2f). To a solution of [PPN]Cl (74 mg, 0.13 mmol) in dichloromethane (2 cm^3) was added a solution of [(η^5-C$_5$Me$_5$)Fe(CO)$_2$BMes]$^+$[BAr$^f_4$]$^-$ (160 mg, 0.13 mmol) in dichloromethane (8 cm^3) at room temperature, and the reaction mixture was stirred for 1.5 h. Filtration, removal of volatiles in vacuo, and recrystallization from hexanes (ca. 10 cm^3) at −50 °C yielded **2f** as a pale yellow microcrystalline material. Isolated yields were typically on the order of 45 mg (85%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.35 (s, 15H, C$_5$Me$_5$), 2.20 (s, 3H, *p*-CH$_3$), 2.28 (s, 6H, *o*-CH$_3$), 6.74 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 9.0 (η^5-C$_5$Me$_5$), 21.0 (*p*-CH$_3$), 21.6 (*o*-CH$_3$), 97.1 (η^5-C$_5$Me$_5$), 127.7 (aromatic CH), 133.2, 136.2 (aromatic quaternary), 216.2 (CO). ^{11}B NMR (96 MHz, C_6D_6): δ 112 (b, fwhm = 580 Hz). IR (KBr disk, cm^{-1}): ν(CO) 1996 m, 1936 m. MS (EI): 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: calculated 412.1058, measured 412.1055.

Reaction of (η^5-C$_5$Me$_5$)Fe(CO)$_2$B(Cl)Mes (2f) with Excess Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$]. To a suspension of Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] (70 mg, 0.3 mmol) in a Young NMR tube was added a solution of **2f** (15 mg, 0.04 mmol) in d_8-toluene (ca. 0.8 cm^3). The reaction mixture was monitored by ^{11}B NMR after 2.5 h at room temperature and then periodically over 1 week at 40 °C. At room temperature only the resonance due to **2f** was observed (δ_B 112); on heating no conversion to any other Fe−B-containing species was observed. Ultimately, after prolonged heating a reduction in intensity of the resonance due to **2f** was observed, although no corresponding new features grew in.

General Crystallographic Method. Data for compounds **2e** and **4c** were collected on an Enraf-Nonius Kappa CCD diffractometer; data collection and cell refinement were carried out using DENZO and COLLECT[19,20] and structure solution and refinement using SHELXS-97 and SHELXL-97, respectively.[21] 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, and complete details of each structure have been deposited with the CCDC (Nos. 211359 (**2e**) and 209269 (**4c**)).

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Table 1. Crystallographic Data for 2e and 4c

	2e	**4c**
empirical formula	$C_{18}H_{20}BClFeO_2$	$C_{29}H_{35}BFe_2O_3$
fw	370.45	554.08
temp (K)	120(2)	120(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2_1$	$P\bar{1}$
unit cell dimens		
a (Å)	7.6864(4)	9.2733(4)
b (Å)	16.4353(8)	9.2964(5)
c (Å)	3.9744(6)	17.1859(9)
α (deg)	90	104.092(2)
β (deg)	102.373(3)	92.461(3)
γ (deg)	90	114.425(3)
V (Å^3)	1724.36(13)	1290.96(11)
Z	4	2
density (calcd) (Mg/m^3)	1.427	1.425
abs coeff (mm^{-1})	1.034	1.153
F(000)	768	580
cryst color, habit	pale yellow plate	red plate
cryst size (mm^3)	0.16 × 0.16 × 0.04	0.20 × 0.14 × 0.02
θ range for data colln (deg)	1.94−24.12	2.92−27.47
index ranges (*h, k, l*)	−8 to +8, −17 to +18, −16 to +16	−11 to +12; −12 to +11; −22 to +22
no. of rflns collected	16 024	21 173
no. of indep rflns/R_{int}	5177 (0.0928)	5789 (0.0592)
completeness to θ_{max} (%)	99.8	98.3
abs cor	semiempirical from equivalents	Sortav
max and min transmissn	0.9598, 0.8520	0.9773, 0.8022
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	5177/13/426	5789/0/327
goodness of fit on F^2	1.088	0.984
final *R* indices (*I* > 2σ(*I*))	R1 = 0.0786, wR2 = 0.1895	R1 = 0.0675, wR2 = 0.1638
R indices (all data)	R1 = 0.0962, wR2 = 0.1989	R1 = 0.0840, wR2 = 0.1719
largest diff peak and hole (e Å^{-3})	2.052 and −0.504	1.466 and −0.540

Results and Discussion

Reaction of PhBCl$_2$ with 1 equiv of Na[(η^5-C$_5$Me$_5$)Fe(CO)$_2$] in toluene at room temperature leads to the formation of a single boron-containing species (by ^{11}B NMR) with the observed chemical shift (δ_B 111) being consistent with the selective replacement of one halide by an (η^5-C$_5$Me$_5$)Fe(CO)$_2$ fragment (cf. δ_B 61.6, 56.0, and 113.2 for **1a**, **1c**, and **2c**, respectively[15]). ^{1}H and ^{13}C NMR, IR, and mass spectral data are also consistent with a formulation as the asymmetric phenyl(chloro)-boryl complex (η^5-C$_5$Me$_5$)Fe(CO)$_2$B(Cl)Ph (**2e**), and these inferences were confirmed by the results of a single-crystal X-ray diffraction study (see Figure 1 and Table 1).

The crystal structure of **2e** features two (essentially identical) molecules within the asymmetric unit with the half-sandwich coordination geometry at iron being completed by two carbonyls and a novel phenylchloroboryl ligand. **2e** therefore represents a rare example of a chloroboryl complex and is the first to contain the −B(Cl)Ph unit. Interestingly, the orientation of this ligand differs considerably from that of the mesitylbromoboryl ligand found in complexes **2a**−**c**. Whereas the −B(Br)Mes ligand is essentially coplanar with that defined by the Cp centroid−Fe−B unit in all cases ($\angle$centroid−Fe−B−C$_{ipso}$ = 10.2(2), 3.8(2), and 2.3(2)° for
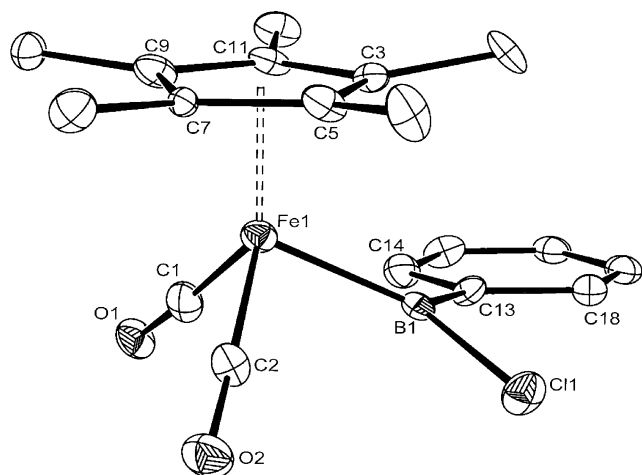
Figure 1. Structure of one of the two independent molecules in the asymmetric unit of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2B\text{-}(Cl)Ph$ (**2e**). Relevant bond lengths (Å), bond angles (deg), and torsion angles (deg): Fe(1)−B(1) = 2.006(10), B(1)−Cl(1) = 1.812(12), B(1)−C(13) = 1.561(15), Fe(1)−$(\eta^5\text{-}C_5\text{-}Me_5)$ centroid = 1.716(8); C(13)−B(1)−Fe(1)−$(\eta^5\text{-}C_5Me_5)$ centroid = 78.6(7), C(14)−C(13)−B(1)−Fe(1) = 31.3(9). Hydrogen atoms are omitted for clarity.

2a, **2b**, and **2c**, respectively), the −B(Cl)Ph unit in **2e** adopts a near-perpendicular orientation (∠centroid−Fe−B−C_{ipso} = 77.6(7)° (mean)). Furthermore, there is a marginal (at the 3σ level) lengthening of the Fe−B bond on going from mesityl(bromo)boryl complex **2c** (1.972(2) Å) to the phenyl(chloro)boryl species **2e** (2.005-(10) Å (mean)), consistent with the boryl ligand becoming a slightly poorer σ-donor and/or π-acceptor. Additionally, it is worth noting that the near-perpendicular orientation of aryl and boryl planes enforced in mesityl complexes **2a**−**c** (presumably on steric grounds) is not in evidence for the smaller phenyl substituent (∠Fe−B−C_{ipso}−C_{ortho} = 29.5(9)° (mean) for **2e**, cf. 89.5(2)° for **2c**).

A comparison of the steric and electronic properties expected for the −B(Cl)Ph ligand with those of related species might have been expected to result in an Fe−B distance for **2e** shorter than those found in $(\eta^5\text{-}C_5H_5)Fe(CO)_2BPh_2$ (2.034(3) Å) and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2B\text{-}(Cl)NMe_2$ (2.027(5) Å).[11d,22] Although the relatively poorly determined Fe−B distance for **2e** means that any differences are not statistically significant, a comparison of carbonyl stretching frequencies with those for $(\eta^5\text{-}C_5\text{-}Me_5)Fe(CO)_2B(Cl)NMe_2$ (1988, 1928 cm^{-1} vs 1995, 1929 cm^{-1} for **2e**) is consistent with −B(Cl)Ph being a slightly better π-acceptor ligand than −B(Cl)NMe$_2$.[11d]

Selective replacement of a single chloride in the phenyldichloroborane precursor **1c** with 1 equiv of Na-$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ therefore mirrors the reactivity observed for aryldibromoboranes **1a** and **1b**.[14−16] The reaction of PhBCl$_2$ with 5 equiv of Na$[(\eta^5\text{-}C_5Me_5)Fe\text{-}(CO)_2]$ in toluene over a period of 12 h at room temperature also results in the formation of a single boron-containing species. In this case, the observed chemical shift (δ_B 159) is consistent with replacement of both B−Cl bonds by B−Fe linkages.[15] ^{13}C NMR and IR data are consistent with a compound containing both bridging and terminal carbonyls, and mass spectroscopic data

(22) Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908.
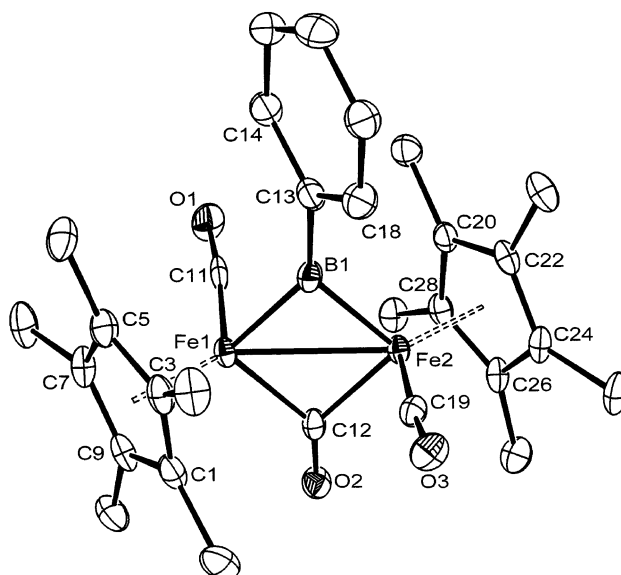
Figure 2. Structure of $[(\eta^5\text{-}C_5Me_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}BPh)$ (**4c**). Relevant bond lengths (Å), bond angles (deg), and torsion angles (deg): Fe(1)−B(1) = 1.934(6), Fe(2)−B(1) = 1.936(6), Fe(1)−C(12) = 1.924(5), Fe(2)−C(12) = 1.930(5), Fe(1)−$(\eta^5\text{-}C_5Me_5)$ centroid = 1.757(5), Fe−Fe = 2.573(3), B(1)−C(13) = 1.542(8); Fe(1)−B(1)−Fe(2) = 83.3(2), Fe(1)−B(1)−C(4)−C(5) = 59.4(3). Hydrogen atoms are omitted for clarity.

imply the structure **4c**, containing three CO ligands. These spectroscopic inferences were confirmed by the results of a single-crystal X-ray diffraction study (see Figure 2).

Spectroscopic data are consistent with the presence of a single isomer in solution, and the results of the diffraction study imply that this is the trans isomer. This result is in line with that found previously for the mesitylborylene species $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}BMes)$ (**4a**)[15] but contrasts with the gallium complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}GaMes)$, which is reported to be formed as a mixture of cis and trans isomers by the photolysis of $[(\eta^5\text{−}C_5H_5)Fe(CO)_2]_2GaMes$.[9b] Conceivably this difference reflects the differing geometric constraints imposed by bridging borylene and gallylene ligands. The shorter Fe−E bond lengths imposed for E = B lead to a significantly compressed Fe−Fe distance (2.573(3) (**4c**) and 2.528(1) Å (**4a**) vs 2.653(1) Å for *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}GaMes)$). This in turn brings about enhanced steric interactions between the cyclopentadienyl ligands and the aryl substituent of the bridging borylene ligand. This factor would be expected to be less important for the trans isomer, in which rotation about the B−C_{ipso} bond could place the plane of the aryl group parallel to those of the cyclopentadienyl ligands so as to minimize unfavorable interligand contacts (see Figure 2). Consistent with this, increasing the steric bulk of the cyclopentadienyl ligand in the gallium system has been reported to alter the product distribution; photolysis of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2GaMes$ yields exclusively *trans*-$[(\eta^5\text{-}C_5Me_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}GaMes)$.[9b]

The Fe−B distances for **4c** (1.936(6) and 1.934(6) Å) are, to our knowledge, the shortest reported for a bond between iron and any three-coordinate boron ligand system. Hence, for example, these distances are significantly shorter than those found in **4a** (1.956(5) and 1.966(5) Å[15]) or in $[(\eta^5\text{-}C_5H_4Me)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}BN\text{-}$

$(SiMe_3)_2]$ (2.007(3) and 2.002(3) Å[11d]), despite the increased bulk of the Cp* ligand at iron. Clearly, the smaller steric constraints of the BPh ligand allow for a noticeable contraction of the Fe_2B unit. The smaller steric bulk of the phenyl unit compared to mesityl would also appear to influence the course of the synthetic chemistry outlined in Scheme 1. Thus, mesityl compound **2c** has been found to be inert to further substitution chemistry with organometallic nucleophiles,[15] whereas replacement of both chloride groups with bulky organometallic fragments is possible for $PhBCl_2$. Conceivably this might also reflect the differing labilities of the B–Cl and B–Br bonds in $(\eta^5\text{-}C_5Me_5)Fe(CO)_2B$-(Cl)Ph (**2e**) and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2B(Br)Mes$ (**2c**), although B–Br bonds would, if anything, be expected to be more labile than analogous B–Cl linkages.[23] That these differences in reactivity *are* due to steric rather than electronic factors has been confirmed by independent synthesis of the complex $(\eta^5\text{-}C_5Me_5)Fe(CO)_2B(Cl)$-Mes (**2f**) and examination of its reactivity toward further B–Fe bond formation.

Reaction between the highly electrophilic terminal borylene complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2BMes]^+[BAr^f_4]^-$ (**5**) and 1 equiv of [PPN]Cl in dichloromethane at room temperature leads to the generation of $(\eta^5\text{-}C_5Me_5)Fe$-$(CO)_2B(Cl)Mes$ (**2f**) in good (85%) isolated yield. Boron-centered reactivity toward anionic nucleophiles for **5** is consistent with the predictions of several theoretical studies[5] and proves to be one of the dominant features of its chemistry.[24] Spectroscopic data for **2f** are entirely consistent with the proposed structure, and further support for this assignment comes from the observation of similar spectroscopic features for the analogous (structurally characterized) phenyl compound $(\eta^5\text{-}C_5$-$Me_5)Fe(CO)_2B(Cl)Ph$ (**2e**) (vide supra). In this respect, similarities in ^{11}B NMR (δ_B 111 and 112 for **2e** and **2f**, respectively) and IR data (1995, 1929 cm^{-1} and 1996, 1936 cm^{-1} for **2e** and **2f**, respectively) are particularly revealing.

In common with its bromo-substituted counterpart **2c**, **2f** does not undergo any further Fe–B bond formation on heating with excess $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ in toluene. It therefore seems likely that the contrasting reactivity of phenyl-substituted **2e** is steric in its origins. Finally, it is interesting to note that in our investigation of the $PhBCl_2/Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ system we were unable to identify any intermediate species analogous to the unsupported mesitylborylene complexes **3a** and **3b**.[14,15] A similar situation was reported by Braunschweig and co-workers, who isolated only $[(\eta^5\text{-}C_5H_4R)Fe$-$(CO)]_2(\mu\text{-}CO)[\mu\text{-}BN(SiMe_3)_2]$ from the reaction of $Na[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]$ (R = H, Me) with $Cl_2BN(SiMe_3)_2$ in benzene.[11d] In the case of the arylborylene ligands, it would appear that only by utilizing the less bulky Cp or Cp′ ligands at iron is it possible to isolate the unsupported bimetallic systems. Previous work has shown that the degree of steric crowding at boron is maximized in unsupported bridged systems such as **3a** and **3b**,[14,15] and it is therefore logical that this mode of coordination is only accessible in conjunction with the less sterically bulky iron fragments.

Conclusions

The differing steric requirements of phenyl and mesityl substituents have been shown to influence reactivity in asymmetric transition metal haloboryl complexes. Hence, substitution of *both* halides in $PhBCl_2$ can be achieved by reaction with an excess of the bulky organometallic nucleophile $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$, whereas the mesityl species $(\eta^5\text{-}C_5Me_5)Fe(CO)_2B(X)Mes$ (X = Cl, Br) are seemingly inert to further Fe–B bond formation. Use of phenyl-substituted precursors allows the synthesis of **4c**, the first metal complex containing a phenylborylene ligand—a model system which has previously been the subject of several computational studies.[5e–g] Fe–B distances in **4c** are the shortest yet reported for any three-coordinate boron ligand system containing iron and are significantly shorter than those found in the analogous mesityl complexes.

Supporting Information Available: Tables and structures giving crystallographic data for the structural analyses of compounds **2e** and **4c** and figures giving ^{1}H, ^{13}C and ^{11}B NMR spectra for compounds **2e**, **2f**, and **4c**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for **2e** and **4c** have also been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 211359 and 209269, respectively).

OM030489F

(23) See, for example: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1990.
(24) Aldridge, S.; Coombs, D. L. Unpublished results.