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Synthetic, structural and reaction chemistry of transition metal complexes containing the mesitylborylene ligand†

Deborah L. Coombs, Simon Aldridge* and Cameron Jones

Department of Chemistry, Cardiff University, PO Box 912, Park Place, Cardiff, UK CF10 3TB

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The synthesis, spectroscopic and structural characterization of the bromo-boryl complexes (η^5-C_5R_4R')Fe(CO)$_2$-B(2,4,6-$Me_3C_6H_2$)Br (R = R′ = H, **2**; R = H, R′ = Me, **3**; R = R′ = Me, **4**) are reported. These are shown to be versatile substrates for the synthesis of both asymmetric boryl complexes [*e.g.* (η^5-C_5H_5)Fe(CO)$_2$B(2,4,6-$Me_3C_6H_2$)OC_6H_4^{t}Bu-4, **6**], and bridging borylene complexes {*e.g.* [(η^5-C_5H_4R)Fe(CO)$_2$]$_2$B(2,4,6-$Me_3C_6H_2$), R = H, **7**; R = Me, **8**} *via* substitution chemistry with retention of the metal–boron bond. Complexes **7** and **8** are the first reported examples of structurally characterized bridging borylene complexes without a supporting M–M bond. Photolytically induced CO loss from [(η^5-C_5H_5)Fe(CO)$_2$]$_2$B(2,4,6-$Me_3C_6H_2$) yields the complex [(η^5-C_5H_5)Fe(CO)]$_2$(μ_2-CO)[μ_2-B(2,4,6-$Me_3C_6H_2$)] (**11**), which features a supported bridging borylene ligand.

1 Introduction

Investigation of the bonding between transition metals and low coordinate ligands of groups 13 and 14 continues to be the driving force for considerable research effort.[1–8] Whereas multiple bonding ($L_nM{=}ER_n$) involving alkylidene (ER_n = CR_2)[1] and more recently silylene ligands (ER_n = SiR_2)[2] is now well understood, 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 *via* donor/acceptor interactions ($L_nM{\leftarrow}ER$) 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] In some respects the arguments are reminiscent of those related to Fischer and Schrock carbenes.[1b]

Transition metal complexes containing diyls of the heavier group 13 elements (particularly gallium and indium) are relatively numerous with examples of both terminal and bridging modes of coordination having been demonstrated crystallographically.[7–10] Analogous compounds containing boranediyl (or borylene, BR) or alanediyl (AlR) ligands are much less common, 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) terminally bound BR (or AlR) ligands containing sterically bulky or π electron releasing R substituents [*e.g.* $(OC)_5Cr{=}BSi(SiMe_3)_3$ or $(OC)_4Fe{\leftarrow}Al(\eta^5\text{-}C_5Me_5)$];[4,6] and (ii) RE ligands adopting a bridging mode of coordination between two (or more) metal centres which are typically also linked by a metal–metal bond or a second bridging ligand {*e.g.* [(η^5-C_5H_4R)Mn(CO)$_2$]$_2$(μ_2-BX) (X = NMe_2, R = H; X = OEt, R = Me; X = Cl, R = Me) or (η^5-C_5Me_5)Ir(PMe_3)(μ-AlEt)$_2$Ir(PMe_3)(η^5-C_5Me_5)}.[11–13]

We have recently been interested in the coordination chemistry of ligands containing trigonal boron centres and in particular the influence of substituents X on the structural and reaction chemistry of boryl ligands BX_2.[14] Asymmetric boryl complexes [L_nM–B(R)X, X = halide], although rare, are potential precursors to a range of borylene complexes of the type L_nM–B(R)–$M'L'_n$ *via* boron-centred substitution chemistry. Choice of appropriately bulky aryl substituents (R) and labile halide (*e.g.* X = Br) has allowed us to isolate a range of asymmetric boryl complexes which prove to be versatile substrates in the synthesis of hitherto unreported unsupported bridging borylene complexes.[15]

2 Experimental

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry box techniques. Solvents were pre-dried over sodium wire and purged with nitrogen prior to distillation. Hexanes were distilled from potassium, and toluene was distilled from sodium prior to use. C_6D_6 (Goss) was degassed and dried over potassium prior to use. 2,4,6-$Me_3C_6H_2BBr_2$ ($MesBBr_2$, **1**), 2,4,6-^{t}$Bu_3C_6H_2BBr_2$, $NaOC_6H_4$^{t}Bu-4, Na[(η^5-C_5R_4R')Fe(CO)$_2$] (R = R′ = H; R = H, R′ = Me; R = R′ = Me) and Na[Mn(CO)$_5$] were prepared by minor modification of literature methods.[16–18]

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_4N)(B_3H_8)] in $CDCl_3$ was used as an external reference for ^{11}B NMR measurements. 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 and by the departmental service. 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 new compounds is based upon multinuclear NMR, IR and mass spectrometry data, supplemented by single crystal X-ray diffraction studies for compounds **2**, **3**, **4**, **6**, **7**, **8** and **11**. In all cases the purity of the bulk material was established by multinuclear NMR to be >95%.

Abbreviations: st = strong, md = medium, w = weak, sh = shoulder, s = singlet, d = doublet, m = multiplet.

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† Dedicated to Professor Tom Fehlner on the occasion of his 65th birthday.

Electronic supplementary information (ESI) available: logarithmic plot for the photolytic conversion of **7** to **11**. See http://www.rsc.org/suppdata/dt/b2/b206348b/

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Synthesis of $(\eta^5\text{-}C_5R_4R')Fe(CO)_2B(2,4,6\text{-}Me_3C_6H_2)Br$ ($R = R' = H$, 2; $R = H$, $R' = Me$, 3; $R = R' = Me$, 4)

The three complexes were synthesized in a similar manner. Typically, to a suspension of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (0.32 g, 1.6 mmol) in toluene (20 cm^3) was added a solution of $2,4,6\text{-}Me_3C_6H_2BBr_2$ (0.46 g, 1.6 mmol) in toluene (10 cm^3) and the reaction mixture was stirred at room temperature for 12 h. Filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (*ca.* 20 cm^3) at −30 °C yielded **2**, **3** and **4** as pale yellow crystals suitable for X-ray diffraction. Yields of **2**–**4** were typically in the order of 50–60%. **2**: ^1H NMR (300 MHz, C_6D_6): δ 2.17 (s, 6H, *ortho*-CH_3), 2.20 (s, 3H, *para*-CH_3), 4.00 (s, 5H, $\eta^5\text{-}C_5H_5$), 6.69 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 20.9 (*para*-CH_3), 21.2 (*ortho*-CH_3), 86.8 ($\eta^5\text{-}C_5H_5$), 128.0 (aromatic CH), 131.1, 136.6 (aromatic quaternary), 213.8 (CO). ^{11}B NMR (96 MHz, C_6D_6) δ 111.4. IR (KBr disk, cm^{-1}) ν(CO) 2016 st, 1962 st. EI-MS: $M^+ = 386$ (weak), isotopic pattern corresponding to 1 Fe, 1 B, 1 Br atoms, strong fragment ion peaks at *m*/*z* 358 [$(M - CO)^+$, 25%] and 330 [$(M - 2CO)^+$, 100%]. **3**: ^1H NMR (300 MHz, C_6D_6): δ 1.32 (s, 3H, $\eta^5\text{-}C_5H_4\text{-}C\mathit{H}_3$), 2.20 (s, 9H, overlap of *ortho*- and *para*-CH_3), 3.97 (s, 4H, overlap of both sets of CH protons $\eta^5\text{-}C_5\mathit{H}_4CH_3$), 6.70 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 12.4 ($\eta^5\text{-}C_5H_4\mathit{C}H_3$), 20.9 (*para*-$CH_3$), 21.2 (*ortho*-$CH_3$), 86.7, 86.9 (CH of $\eta^5\text{-}C_5H_4CH_3$), 104.2 ($\eta^5\text{-}C_5H_4CH_3$ quaternary), 131.2 (aromatic CH), 129.9, 136.5 (aromatic quaternary), 214.3 (CO). ^{11}B NMR (96 MHz, C_6D_6) δ 111.3. IR (KBr disk, cm^{-1}) ν(CO) 2009 st, 1961 st. EI-MS: $M^+ = 400$ (weak), isotopic pattern corresponding to 1 Fe, 1 B, 1 Br atoms, fragment ion peaks at *m*/*z* 372 [$(M - CO)^+$, 30%] and 344 [$(M - 2CO)^+$, 70%]. **4**: ^1H NMR (300 MHz, C_6D_6): δ 1.31 (s, 15H, $\eta^5\text{-}C_5Me_5$), 2.21 (s, 3H, *para*-CH_3), 2.26 (s, 6H, *ortho*-CH_3), 6.73 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 9.0 ($\eta^5\text{-}C_5\mathit{Me}_5$), 20.9 (*para*-$CH_3$), 21.5 (*ortho*-$CH_3$), 97.4 ($\eta^5\text{-}\mathit{C}_5Me_5$ quaternary), 127.6 (aromatic CH), 132.3, 136.3 (aromatic quaternary), 216.0 (CO). ^{11}B NMR (96 MHz, C_6D_6) δ 113.2. IR (KBr disk, cm^{-1}) ν(CO) 2006 st, 1961 st. EI-MS: $M^+ = 456$ (weak), isotopic pattern corresponding to 1 Fe, 1 B, 1 Br atoms, fragment ion peaks at *m*/*z* 428 [$(M - CO)^+$, 100%] and 400 [$(M - 2CO)^+$, 50%].

Synthesis of $(OC)_5MnB(2,4,6\text{-}Me_3C_6H_2)Br$ 5

A solution of $2,4,6\text{-}Me_3C_6H_2BBr_2$ (0.14 g, 0.5 mmol) in toluene (5 cm^3) was added to a suspension of $Na[Mn(CO)_5]$ (0.11 g, 0.5 mmol) in toluene (20 cm^3) and stirred at room temperature for 12 h. Filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (*ca.* 10 cm^3) at −30 °C yielded yellow crystals of **5** (0.06 g, 29%). ^1H NMR (300 MHz, C_6D_6): δ 2.11 (s, 6H, *ortho*-CH_3), 2.49 (s, 3H, *para*-CH_3), 6.64 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 20.7 (*para*-CH_3), 21.4 (*ortho*-CH_3), 128.4 (aromatic CH), 130.6, 137.7 (aromatic quaternary), 210.5 (CO). ^{11}B NMR (96 MHz, C_6D_6) δ 119.4. IR (KBr disk, cm^{-1}) ν(CO) 2101 w, 2046 m, 2015 s, 1981 m sh, 1952 w.

Synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2B(2,4,6\text{-}Me_3C_6H_2)OC_6H_4{}^tBu\text{-}4$ 6

A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2B(2,4,6\text{-}Me_3C_6H_2)Br$, **2**, (0.14 g, 0.4 mmol) in toluene (10 cm^3) was added to a suspension of $NaOC_6H_4{}^tBu\text{-}4$ (0.07 g, 0.4 mmol) in toluene (2 cm^3) at room temperature. The resulting mixture was stirred at 65 °C for 21 d, at which point the reaction was judged to be complete by ^{11}B NMR. Filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (*ca.* 10 cm^3) at −30 °C yielded **6** as pale yellow crystals suitable for X-ray diffraction (0.11 g, 60%). ^1H NMR (300 MHz, C_6D_6): δ 1.01 (s, 9H, ^tBu), 2.02 (s, 3H, *para*-CH_3), 2.31 (s, 6H, *ortho*-CH_3), 4.11 (s, 5H, $\eta^5\text{-}C_5H_5$), 6.55 (s, 2H, mesityl CH), 6.98 (s, 4H, overlap of both sets of aromatic protons $OC_6\mathit{H}_4$). ^{13}C NMR (76 MHz, C_6D_6): δ 20.9 (*para*-CH_3), 21.9 (*ortho*-CH_3), 31.1 ($C\mathit{C}H_3$), 33.8 ($\mathit{C}CH_3$), 85.6 ($\eta^5\text{-}C_5H_5$), 119.0, 126.1 (OC_6H_4 aromatic CH), 127.7 (mesityl aromatic CH), 133.7, 136.3 (mesityl aromatic quaternary), 145.5, 155.1 (OC_6H_4 aromatic quaternary), 215.9 (CO). ^{11}B NMR (96 MHz, C_6D_6) δ 80.3. IR (KBr disk, cm^{-1}) ν(CO) 1997 st, 1933 st. EI-MS: $M^+ = 456$ (weak), isotopic pattern corresponding to 1 Fe, 1 B atoms, fragment ion peaks at *m*/*z* 428 [$(M - CO)^+$, 25%] and 400 [$(M - 2CO)^+$, 85%].

Synthesis of $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2B(2,4,6\text{-}Me_3C_6H_2)$ ($R = H$, 7; $R = Me$, 8)

Both complexes were synthesized in a similar manner. Typically, a solution of $2,4,6\text{-}Me_3C_6H_2BBr_2$ (0.29 g, 1.0 mmol) in toluene (5 cm^3) was added slowly to a suspension of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (1.00 g, 5.0 mmol) in toluene (20 cm^3) and the reaction mixture was heated to 40 °C for 4 d. Filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (*ca.* 20 cm^3) at −30 °C gave **7** and **8** as pale yellow crystals suitable for X-ray diffraction in yields of up to 35%. **7**: ^1H NMR (300 MHz, C_6D_6): δ 2.08 (s, 6H, *ortho*-CH_3), 2.27 (s, 3H, *para*-CH_3), 4.03 (s, 10H, $\eta^5\text{-}C_5H_5$), 6.74 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 20.8 (*para*-CH_3), 23.0 (*ortho*-CH_3), 86.6 ($\eta^5\text{-}C_5H_5$), 128.1 (aromatic CH), 126.0, 128.5, 134.0 (aromatic quaternary), 217.3 (CO). ^{11}B NMR (96 MHz, C_6D_6) δ 158.0. IR (KBr disk, cm^{-1}) ν(CO) 2010 st, 1997 md sh, 1949 st, 1931 w sh. EI-MS: $M^+ = 484$ (weak), isotope pattern corresponding to 2Fe, 1B atom, fragment ion peaks at *m*/*z* 456 [$(M - CO)^+$, 20%], 428 [$(M - 2CO)^+$, weak], 400 [$(M - 3CO)^+$, 30%], 378 [$(M - 4CO)^+$, 35%]. **8**: ^1H NMR (300 MHz, C_6D_6): δ 1.49 (s, 6H, $\eta^5\text{-}C_5H_4C\mathit{H}_3$), 2.12 (s, 6H, *ortho*-$CH_3$), 2.28 (s, 3H, *para*-$CH_3$), 3.94 (s, 2H, 2H of $\eta^5\text{-}C_5\mathit{H}_4CH_3$), 3.99 (d, 2H, 2H of $\eta^5\text{-}C_5\mathit{H}_4CH_3$), 5.96 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 12.6 ($\eta^5\text{-}C_5H_4\mathit{C}H_3$), 20.8 (*para*-$CH_3$), 23.0 (*ortho*-$CH_3$), 86.5, 87.8 (CH of $\eta^5\text{-}C_5H_4CH_3$), 102.2 (quaternary in $\eta^5\text{-}C_5H_4\text{-}CH_3$), 126.1 (aromatic CH), 128.5, 128.9, 133.8 (aromatic quaternary), 217.9 (CO). ^{11}B NMR (96 MHz, C_6D_6) δ 157.9. IR (KBr disk, cm^{-1}) ν(CO) 1999 st, 1967 st, 1942 st, 1923 st. EI-MS: $M^+ = 512$ (weak), isotope pattern corresponding to 2Fe, 1B atoms, fragment ion peaks at *m*/*z* 484 [$(M - CO)^+$, 10%], 456 [$(M - 2CO)^+$, 10%], 428 [$(M - 3CO)^+$, 5%], 400 [$(M - 4CO)^+$, weak].

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2][(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]B\text{-}(2,4,6\text{-}Me_3C_6H_2)$ 9

A solution of $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2B(2,4,6\text{-}Me_3C_6H_2)Br$ (0.21g, 0.5 mmol) in toluene (20 cm^3) was added slowly to a suspension of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (0.41 g, 2.1 mmol) in toluene (10 cm^3). The mixture was heated to 40 °C, for 6 d, at which point the reaction was judged to be complete by ^{11}B NMR. Filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (*ca.* 20 cm^3) at −30 °C yielded **9** as yellow crystals (0.19 g, 76%). ^1H NMR (300 MHz, C_6D_6): δ 1.47 (s, 3H, $\eta^5\text{-}C_5H_4C\mathit{H}_3$), 2.11 (s, 6H, *ortho*-$CH_3$), 2.28 (s, 3H, *para*-$CH_3$), 3.93 (m, 2H, 2H of $\eta^5\text{-}C_5\mathit{H}_4CH_3$), 3.98 (m, 2H, 2H of $\eta^5\text{-}C_5\mathit{H}_4CH_3$), 4.04 (s, 5H, $\eta^5\text{-}C_5H_5$), 6.75 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 12.6 ($\eta^5\text{-}C_5H_4\mathit{C}H_3$), 20.8 (*para*-$CH_3$), 23.0 (*ortho*-$CH_3$), 86.6 (CH of $\eta^5\text{-}C_5\mathit{H}_4CH_3$), 86.8 ($\eta^5\text{-}C_5H_5$), 87.7 (CH of $\eta^5\text{-}C_5\mathit{H}_4CH_3$), 102.3 (quaternary in $\eta^5\text{-}C_5H_4CH_3$), 126.0, 133.9 (aromatic CH), 128.5 (aromatic quaternary), 217.4, 217.8 (CO). ^{11}B NMR (96 MHz, C_6D_6) δ 157.6. IR (KBr disk, cm^{-1}) ν(CO) 2003 st, 1968 md, 1944 md, 1927 md. EI-MS: $M^+ = 498$ (weak), isotope pattern corresponding to 2 Fe, 1 B atoms, fragment ion peaks at *m*/*z* 470 [$(M - CO)^+$, weak], 442 [$(M - 2CO)^+$, weak], 414 [$(M - 3CO)^+$, 5%], 386 [$(M - 4CO)^+$, weak].

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu_2\text{-}CO)[\mu_2\text{-}B(2,4,6\text{-}Me_3\text{-}C_6H_2)]$ 11

A solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2B(2,4,6\text{-}Me_3C_6H_2)$, **7**, (0.04 g, 0.1 mmol) in C_6D_6 (2 cm^3) was photolysed for 5 d using a standard 100 W light source, at which point the reaction was judged to be complete by ^{1}H NMR. Removal of volatiles *in vacuo* and recrystallization from hexanes (*ca.* 10 cm^3) at −30 °C yielded **11** as single red crystals suitable for X-ray diffraction. The yield of **11** was typically in the order of 90%, based on the amount of **7** used. ^{1}H NMR (300 MHz, C_6D_6): δ 2.22 (s, 3H, *para*-CH_3), 2.52 (s, 6H, *ortho*-CH_3), 4.31 (s, 10H, η^5-C_5H_5), 6.86 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 21.0 (*para*-CH_3), 24.4 (*ortho*-CH_3), 86.9 (η^5-C_5H_5), 129.0 (aromatic CH), 136.6, 138.7 (aromatic quaternary), 214.7 (terminal CO), 272.7 (bridging CO). ^{11}B NMR (96 MHz, C_6D_6) δ 161.9. IR (KBr disk, cm^{-1}) ν(CO) 1947 md, 1924 st, 1780 md sh, 1773 st. EI-MS: $M^+ = 455$ (5%), isotope pattern corresponding to 2 Fe, 1 B atoms, fragment ion peaks at *m*/*z* 427 [$(M - CO)^+$, weak], 399 [$(M - 2CO)^+$, 10%], 371 [$(M - 3CO)^+$, 15%]. Kinetic data for the conversion of **7** to **11** were obtained by periodic measurement of the ^{1}H NMR spectrum of the reaction mixture and integration of the resonances due to the *ortho* methyl groups of the mesityl substituents of each compound.

Reaction of $(OC)_5MnB(2,4,6\text{-}Me_3C_6H_2)Br$, 5, with $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$

A solution of $(OC)_5MnB(2,4,6\text{-}Me_3C_6H_2)Br$, **5**, (0.186 g, 0.46 mmol) in toluene (15 cm^3) was added to a suspension of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (0.380 g, 1.90 mmol) in toluene (10 cm^3). The mixture was heated to 40 °C for 6 d, at which point the ^{11}B NMR spectrum of the reaction mixture showed complete conversion of the signal due to **5** (δ_B 119.4) to a single downfield resonance at δ_B 158.0. Filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (20 cm^3) at −30 °C yielded $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2B(2,4,6\text{-}Me_3C_6H_2)$, **7**, as the sole boron-containing product. The identity of **7** was confirmed by comparison of multinuclear NMR, IR and crystallographic cell parameters with those of an authentic sample prepared from $2,4,6\text{-}Me_3C_6H_2BBr_2$, **1**, and excess $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$.

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2B(2,4,6\text{-}Me_3C_6H_2)Br$, 2 with $Na[Mn(CO)_5]$

A solution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2B(2,4,6\text{-}Me_3C_6H_2)Br$, **2**, (0.125 g, 0.325 mmol) in toluene (10 cm^3) was added to a suspension of $Na[Mn(CO)_5]$ (0.272 g, 1.24 mmol) in toluene (5 cm^3). The mixture was heated to 40 °C for 3 d, at which point the ^{11}B NMR spectrum of the reaction mixture showed complete conversion of the signal due to **2** (δ_B 111.4) to a single downfield resonance at δ_B 160.7. Filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (10 cm^3) at −30 °C yielded a pale yellow powder in *ca.* 20% yield. Despite repeated attempts it proved impossible to isolate the product of this reaction as a crystalline material, or to obtain complete characterization data due to its extreme thermal and moisture sensitivity and its tendency to decompose with generation of $Mn_2(CO)_{10}$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ even at −30 °C. The downfield shift of *ca.* 50 ppm in the ^{11}B NMR spectrum does suggest the formation of a second metal–boron bond, although definitive evidence for the formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2][(OC)_5Mn]B(2,4,6\text{-}Me_3C_6H_2)$ (**10**) is clearly lacking.

Attempted reaction of $2,4,6\text{-}{}^t Bu_3C_6H_2BBr_2$ with $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$

To a suspension of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ (0.110 g, 0.55 mmol) in toluene (10 cm^3) was added a solution of $2,4,6\text{-}{}^t Bu_3C_6H_2BBr_2$ (0.226 g, 0.54 mmol) in toluene (5 cm^3) and the reaction mixture was stirred at room temperature for 12 h. Measurement of the ^{11}B NMR spectrum of the reaction mixture at this point revealed a single resonance at δ_B 59.7 due to the starting material ${}^t Bu_3C_6H_2BBr_2$. Extensive variation in reaction conditions (temperature, time, ratio of reagents) did not lead to the formation of any products containing an Fe–B bond (as judged by ^{11}B NMR).

General crystallographic method

Data for all compounds were collected on an Enraf Nonius Kappa CCD diffractometer; data collection and cell refinement were carried out using DENZO and COLLECT,[19] and structure solution and refinement using SHELXS-97 and SHELXL-97, respectively.[20] Details of each data collection, structure solution and refinement can be found in Table 1, relevant bond lengths and angles are included in figure captions. The poor quality of the data for compound **7** is due to the fact that the crystal was found to be a multiple. It was not possible to deconvolute the diffraction patterns of each component. This problem was found to be inherent in several crystals selected. The asymmetric unit contains two crystallographically independent molecules. All attempts to refine the structure in higher symmetry space groups failed. Despite the poor quality of the data the gross molecular framework of the molecule is unambiguous and fully supported by the spectroscopic data.

CCDC reference numbers 179292, 179293 and 187963–187967.

See http://www.rsc.org/suppdata/dt/b2/b206348b/ for crystallographic data in CIF or other electronic format.

3 Results and discussion

(i) Synthesis and reactivity

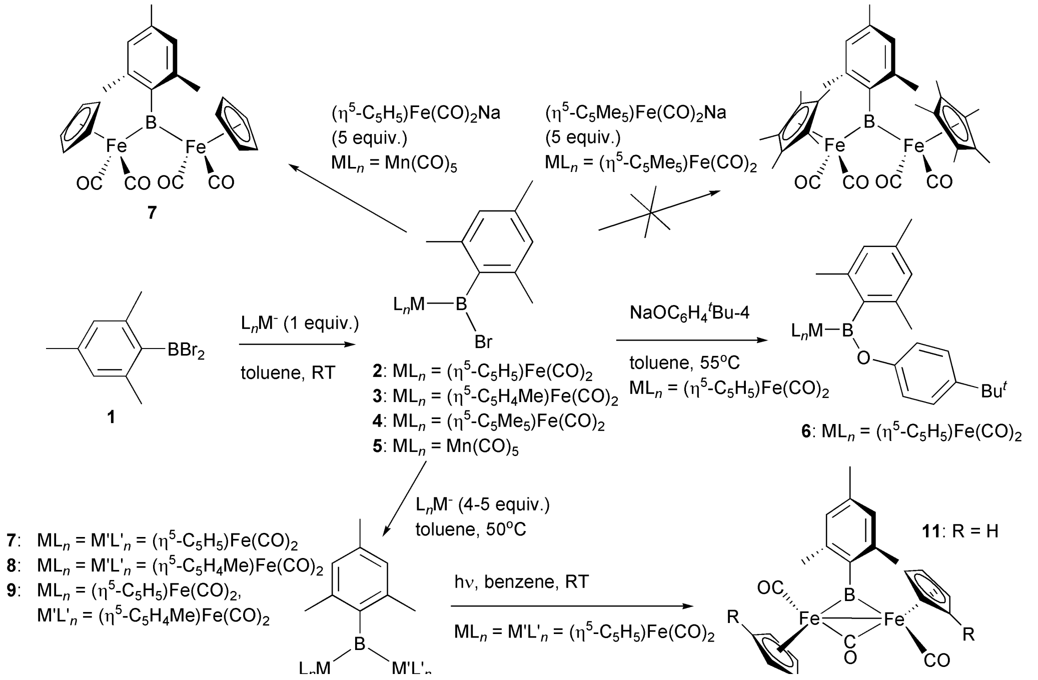
The asymmetric mesityl(bromo)boryl complexes **2**–**5** can be synthesised in moderate to good yields (29–60%) by the reaction of mesitylboron dibromide ($2,4,6\text{-}Me_3C_6H_2BBr_2$, $MesBBr_2$, **1**) with one equivalent of the appropriate organometallic anion in toluene at room temperature (see Scheme 1). Under these conditions substitution is selective for a single bromide, with negligible quantities of the disubstituted species **7** and **8** being formed (as determined by ^{11}B NMR spectroscopy). Interestingly the analogous reaction with super-mesityl boron dibromide ($2,4,6\text{-}{}^t Bu_3C_6H_2BBr_2$) fails to bring about substitution of either bromide under these or more forcing conditions.

Complexes **2**–**5**, bearing a single remaining bromide at boron, prove to be versatile substrates for further substitution chemistry. Reaction with main group nucleophiles, such as the phenoxide anion $4\text{-}{}^t BuC_6H_4O^-$, results in high yielding synthesis of further asymmetric mesitylboryl complexes. Formation of the mesityl(aryloxo)boryl complex **6**, for example, proceeds cleanly, although the high steric demands of the reagents ensure that reaction is slow (*ca.* 21 days for completion). Not surprisingly, the corresponding reaction with 4-*tert*-butyl phenol, $4\text{-}{}^t BuC_6H_4OH$, yields no products containing an Fe–B bond. Presumably the presence of reagents containing a relatively acidic hydrogen brings about Fe–B bond cleavage. Such reactivity would parallel that observed previously for Fe–B-containing systems.[3,21a]

Reaction with *organometallic* nucleophiles proceeds in most cases *via* displacement of bromide, resulting in the synthesis of complexes **7**–**9** containing bridging borylene ligands. Yields are of the order of 35% (overall from $MesBBr_2$) and this methodology gives access not only to symmetrically substituted derivatives, but also to asymmetric borylene complexes such as **9**. Two notable exceptions to this are (i) the inability to effect substitution of the second bromide with $(\eta^5\text{-}C_5Me_5)Fe(CO)_2^-$ as the nucleophile, presumably on steric grounds; and (ii) the reaction of the manganese boryl complex $(OC)_5MnBMes(Br)$, **5**, with an excess of $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ which gives rise to the symmetrical diiron complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2BMes$ rather than to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2][(OC)_5Mn]BMes$, **10**. Presumably displacement of the manganese carbonyl fragment reflects the superior nucleophilicity of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ anion and

Table 1 Crystallographic data for **2**–**4**, **6**–**8** and **11**

	2	**3**	**4**	**6**	**7**	**8**	**11**
Empirical formula	$C_{16}H_{16}BBrFeO_2$	$C_{17}H_{18}BBrFeO_2$	$C_{21}H_{26}BBrFeO_2$	$C_{26}H_{29}BFeO_3$	$C_{23}H_{21}BFe_2O_4$	$C_{25}H_{25}BFe_2O_4$	$C_{22}H_{21}BFe_2O_3$
Formula weight	386.86	400.88	456.99	456.15	483.91	511.96	455.90
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	293(2)	120(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$Pbca$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	11.628(3)	8.315(2)	9.664(2)	17.798(4)	11.938(2)	9.372(2)	8.099(2)
b/Å	15.439(3)	15.283(3)	17.437(4)	10.551(2)	12.404(3)	21.143(4)	10.959(2)
c/Å	17.803(4)	14.113(3)	13.127(3)	12.427(3)	15.431(3)	11.672(2)	11.035(2)
α/°	90	90	90	90	111.56(3)	90	80.39(3)
β/°	90	104.89(3)	110.41(3)	91.57(3)	97.15(3)	90.39(3)	84.48(3)
γ/°	90	90	90	90	90.83(3)	90	84.96(3)
Volume/Å^3	3196.1(11)	1733.2(6)	2073.2(7)	2332.7(8)	2104.1(7)	2312.8(8)	958.6(3)
Z	8	4	4	4	4	4	2
D_c/Mg m^{-3}	1.608	1.536	1.464	1.299	1.528	1.470	1.579
Absorption coefficient/mm^{-1}	3.443	3.177	2.666	0.671	1.406	1.283	1.534
F(000)	1552	808	936	960	992	1056	468
Crystal size/mm	0.15 × 0.10 × 0.04	0.25 × 0.20 × 0.20	0.30 × 0.30 × 0.20	0.20 × 0.20 × 0.10	0.20 × 0.10 × 0.10	0.20 × 0.15 × 0.10	0.15 × 0.15 × 0.05
Theta range for data colln./°	3.17 to 27.46	3.39 to 27.49	3.24 to 27.46	3.00 to 25.35	3.13 to 25.00	2.94 to 25.23	3.03 to 27.05
Index ranges	$-15 \leqslant h \leqslant 13$ $-16 \leqslant k \leqslant 20$ $-23 \leqslant l \leqslant 22$	$-10 \leqslant h \leqslant 10$ $-19 \leqslant k \leqslant 19$ $-18 \leqslant l \leqslant 18$	$-12 \leqslant h \leqslant 12$ $-22 \leqslant k \leqslant 22$ $-17 \leqslant l \leqslant 17$	$-21 \leqslant h \leqslant 21$ $-12 \leqslant k \leqslant 12$ $-14 \leqslant l \leqslant 14$	$-14 \leqslant h \leqslant 14$ $-14 \leqslant k \leqslant 14$ $-17 \leqslant l \leqslant 18$	$-10 \leqslant h \leqslant 11$ $-23 \leqslant k \leqslant 25$ $-12 \leqslant l \leqslant 13$	$-10 \leqslant h \leqslant 10$ $-14 \leqslant k \leqslant 14$ $-14 \leqslant l \leqslant 13$
Reflections collected	21 250	31 913	34 838	42 154	29 366	10 628	10 805
Independent reflections	3641	3963	4735	4273	7309	2079	4221
R_{int}	0.1467	0.0588	0.0516	0.0980	0.0953	0.0466	0.0640
Completeness to theta max. (%)	99.7	99.4	99.7	99.8	98.7	99.5	95.6
Absorption correction	Sortav	Sortav	Sortav	Sortav	Sortav	Sortav	Sortav
Max. and min. transmission	1.36, 0.83	0.54, 0.39	0.59, 0.50	0.94, 0.72	0.94, 0.82	0.93, 0.87	0.88, 0.73
Refinement method	Full matrix least squares on F^2	Full matrix least squares on F^2	Full matrix least squares on F^2	Full matrix least squares on F^2	Full matrix least squares on F^2	Full matrix least squares on F^2	Full matrix least squares on F^2
Data/restraints/parameters	3641/0/193	3963/0/203	4735/0/243	4273/0/286	7309/0/548	2079/0/150	4221/18/256
Goodness-of-fit on F^2	0.969	1.030	1.069	1.042	1.187	1.062	1.025
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0481$ $wR2 = 0.0925$	$R1 = 0.0448$ $wR2 = 0.0923$	$R1 = 0.0316$ $wR2 = 0.0674$	$R1 = 0.0366$ $wR2 = 0.0879$	$R1 = 0.0932$ $wR2 = 0.2638$	$R1 = 0.0320$ $wR2 = 0.0697$	$R1 = 0.0617$ $wR2 = 0.1593$
R indices (all data)	$R1 = 0.1012$ $wR2 = 0.1080$	$R1 = 0.0555$ $wR2 = 0.0974$	$R1 = 0.0401$ $wR2 = 0.0704$	$R1 = 0.0482$ $wR2 = 0.0941$	$R1 = 0.1110$ $wR2 = 0.2712$	$R1 = 0.0419$ $wR2 = 0.0750$	$R1 = 0.0859$ $wR2 = 0.1744$
Largest diff. peak and hole/e Å^{-3}	0.770 and −0.752	1.941 (near Br1) and −1.813	0.480 and −0.773	0.263 and −0.338	2.578 (near Fe3) and −0.997	0.256 and −0.387	2.549, −0.680



Scheme 1 Outline of the boron-centred substitution chemistry used to synthesize mesitylboryl and mesitylborylene complexes **2**–**11**.

the better leaving group properties of $Mn(CO)_5^-$. ^{11}B NMR data suggest the asymmetric complex **10** as a possible candidate for the sole boron-containing product obtained from the alternative reaction of excess $NaMn(CO)_5$ with the iron mesityl(bromo)boryl derivative **2**. However, the extreme thermal- and air-sensitivity of this compound prevented its complete characterization. In general, complexes containing the $Mn(CO)_5$ fragment were found to be significantly more susceptible to decomposition than their $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ analogues; all attempts, for example, to isolate the dimanganese complex $[(OC)_5Mn]_2BMes$ were unsuccessful.

The substitution chemistry at boron implicit in the synthesis of complexes **6**–**10** generally proceeds in reasonable yield without scission of the existing metal–boryl linkage. Such substitution chemistry is relatively rare for transition metal boryl complexes, with these and most other reported examples occurring for complexes containing B–Cl or B–Br bonds.[4c,11f,14d] Presumably the relative lability of the B–halogen linkage and the high leaving group ability of Cl^- or Br^- facilitates halide substitution under conditions which allow the existing M–B bond to remain intact.

Complexes **7**–**9** feature a novel unsupported bridging mode of coordination of the borylene ligand. Previously reported iron and manganese complexes containing a bridging BX moiety typically also feature a M–M bond.[11,12] Thus, for example, the complex $[(\eta^5\text{-}C_5H_4Me)Fe(CO)]_2(\mu_2\text{-}CO)[\mu_2\text{-}BN(SiMe_3)_2]$ features iron centres linked not only *via* a bridging $BN(SiMe_3)_2$ ligand, but also by an Fe–Fe bond and a μ_2 carbonyl ligand.[11d] The synthetic route to this compound is very similar to that reported here for complexes **7** and **8**, involving the reaction of two equivalents of $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2^-$ with $Cl_2BN(SiMe_3)_2$.[11d] In the case of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)]_2(\mu_2\text{-}CO)[\mu_2\text{-}BN(SiMe_3)_2]$, however, chloride displacement is also accompanied by loss of one CO ligand. Although spontaneous loss of CO is not observed during the formation of **7** (or **8**), photolysis in benzene at room temperature does lead to the evolution of one equivalent of CO. The exclusive organometallic product in the case of **7** is the *trans* isomer (*vide infra*) of the supported bridging borylene complex **11**. This result contrasts with that observed on photolysis of the analogous gallium-containing complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2GaMes$, which is reported to yield a mixture of *cis*- and *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu_2\text{-}CO)(\mu_2\text{-}GaMes)$.[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 [2.528(1) *vs.* 2.635(1) Å[9b]]. This in turn would bring about enhanced steric interactions between the cyclopentadienyl ligands and the mesityl 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 mesityl ligand such as to minimize unfavourable inter-ligand contacts (*vide infra*). Consistent with this observation, $[(\eta^5\text{-}C_5H_4Me)Fe(CO)]_2(\mu_2\text{-}CO)[\mu_2\text{-}BN(SiMe_3)_2]$ synthesized by Braunschweig *et al.* is also obtained exclusively as the *trans* isomer.[11d]

The course of the photolytic conversion of **7** to **11** can be followed by NMR spectroscopy; integration of the ^1H resonances due the *ortho* methyl protons of each compound allows the concentration/time dependence illustrated in Fig. 1 to be obtained. Complete conversion is obtained over a period of *ca.* 80 h and a logarithmic plot for [**7**] confirms the expected first order kinetics and yields a value of 1.8×10^{-5} s^{-1} for the corresponding rate constant (logarithmic plot included with ESI †).

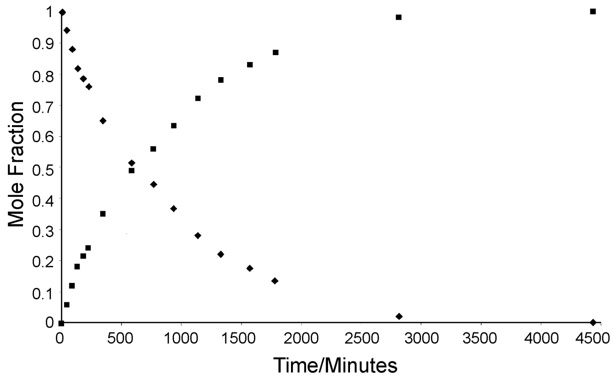


Fig. 1 Plot of mole fraction against time in minutes for the photolytic conversion of unsupported borylene **7** to Fe–Fe bonded species **11**, as determined by integration of the ^1H NMR signals of the *ortho* methyl groups of each compound (◆, compound **7**; ■, compound **11**).

(ii) Structural and spectroscopic studies

^{11}B NMR spectroscopy proves to be an informative probe of the substitution chemistry outlined in Scheme 1. Replacement of a single bromide by an organometallic fragment results in the 50–60 ppm downfield shift typically observed on formation of a M–B single bond. Further substitution chemistry results in an upfield shift on replacement of bromide by a better π donor aryloxo substituent (δ_B 111.4 for **2**, 80.3 for **6**) or in a further downfield shift of *ca.* 50 ppm on formation of a second M–B linkage. Interestingly, although the coordination environment at the boron centre is significantly altered on Fe–Fe bond formation (*e.g.* **11** from **7**) there is little change in the measured ^{11}B resonance (δ_B 162 and 158, respectively).

Single crystals of the precursor mesityl(bromo)boryl complexes **2**–**4**, the mesityl(aryloxo)boryl complex **6**, the unsupported bridging borylenes **7** and **8** and the photolytically generated Fe–Fe bonded borylene **11** proved to be accessible by controlled cooling of concentrated solutions in hexanes. Molecular structures are depicted in Figs. 2–8 and details of data collection, structure solution and refinement are included in Table 1. The structures of compounds **3** and **7** have previously been communicated.[15]

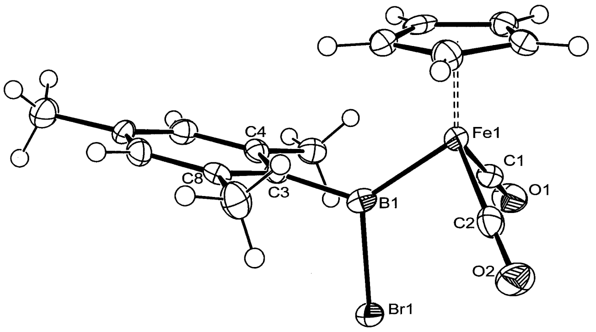


Fig. 2 Molecular structure of (η^5-C_5H_5)Fe(CO)$_2$BMes(Br), **2**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 1.964(5), B(1)–Br(1) 2.013(4), B(1)–C(3) 1.563(6), Fe(1)–(η^5-C_5H_5) centroid 1.729(4); C(3)–B(1)–Fe(1)–(η^5-C_5H_5) centroid 10.2(2), C(4)–C(3)–B(1)–Fe(1) 91.9(3).

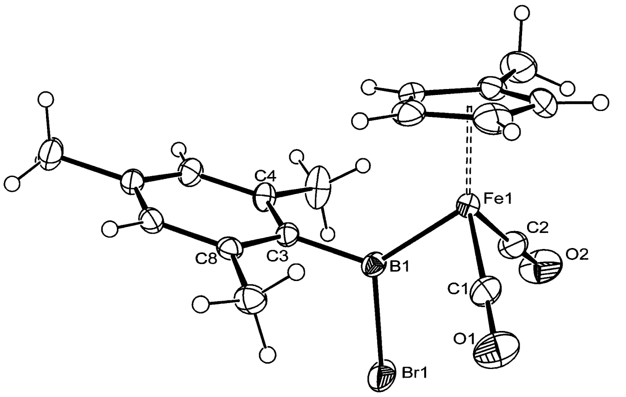


Fig. 3 Molecular structure of (η^5-C_5H_4Me)Fe(CO)$_2$BMes(Br), **3**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 1.962(4), B(1)–Br(1) 2.005(3), B(1)–C(3) 1.571(4), Fe(1)–(η^5-C_5H_4Me) centroid 1.735(4); C(3)–B(1)–Fe(1)–(η^5-C_5H_4Me) centroid 3.8(2), C(4)–C(3)–B(1)–Fe(1) 88.3(2).

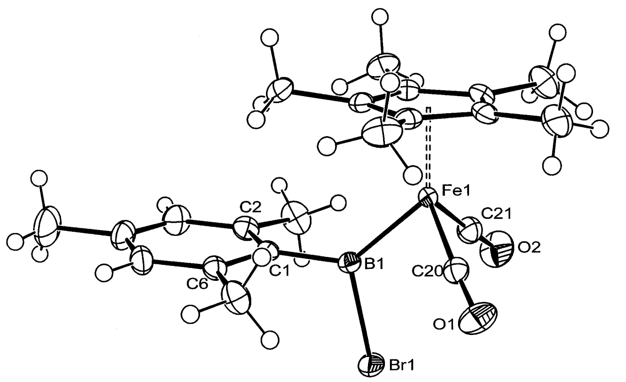


Fig. 4 Molecular structure of (η^5-C_5Me_5)Fe(CO)$_2$BMes(Br), **4**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 1.972(2), B(1)–Br(1) 2.018(2), B(1)–C(1) 1.569(3), Fe(1)–(η^5-C_5Me_5) centroid 1.746(2); C(1)–B(1)–Fe(1)–(η^5-C_5Me_5) centroid 2.3(2), C(2)–C(1)–B(1)–Fe(1) 89.5(2).

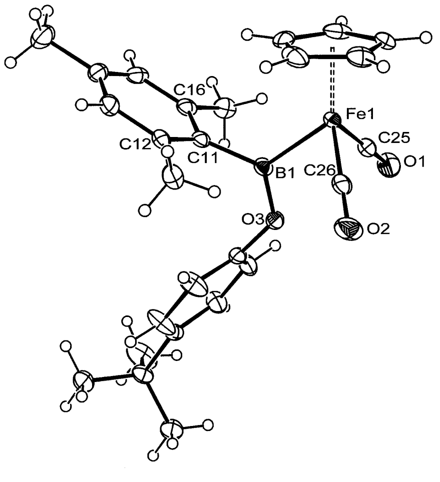


Fig. 5 Molecular structure of (η^5-C_5H_5)Fe(CO)$_2$BMes(OC$_6$H$_4$^{t}Bu-4), **6**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 2.040(2), B(1)–O(3) 1.377(3), B(1)–C(11) 1.577(3), Fe(1)–(η^5-C_5H_5) centroid 1.739(3); C(11)–B(1)–Fe(1)–(η^5-C_5H_5) centroid 4.8(2), C(16)–C(11)–B(1)–Fe(1) 89.1(2).

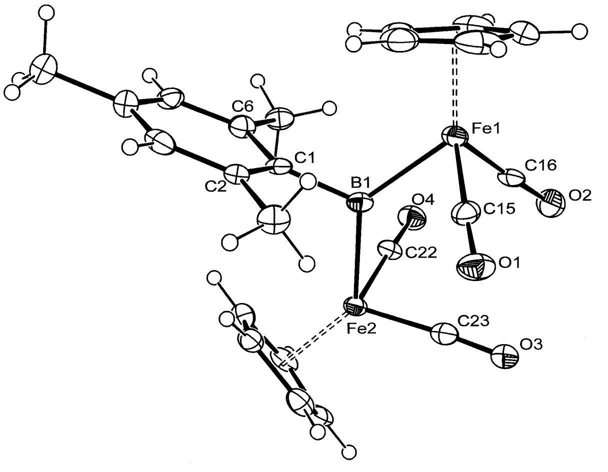


Fig. 6 Molecular structure of one of the two crystallographically independent molecules of [(η^5-C_5H_5)Fe(CO)$_2$]$_2$BMes, **7**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 2.090(10), Fe(2)–B(1) 2.091(10), Fe(1)–C(15) 1.730(10), Fe(1)–(η^5-C_5H_5) centroid 1.745(10), Fe(1) ··· Fe(2) 3.802(10), B(1)–C(1) 1.571(14); Fe(1)–B(1)–Fe(2) 130.8(5), C(1)–B(1)–Fe(1) 115.7(6), C(1)–B(1)–Fe(2) 113.5(6), C(1)–B(1)–Fe(1)–(η^5-C_5H_5) centroid 18.7(6), Fe(1)–B(1)–C(1)–C(2) 83.6(6).

The structures of boryl complexes **2**–**4** (Figs. 2–4) display the expected half sandwich geometry at the iron centre with the coordination sphere being completed by two carbonyls and one mesityl(bromo)boryl ligand. Iron–boron distances for the three compounds are short [1.964(5), 1.962(4) and 1.972(2) Å, respectively],[21] and this together with Cp centroid–Fe–B–C$_{ipso}$ angles close to 0° (10.2, 3.8 and 2.3°, respectively) and relatively high carbonyl stretching frequencies (2016, 1962; 2009, 1962; and 2006, 1961 cm^{-1}) indicates a modest Fe–B π back bonding interaction from the metal-based HOMO.[21a,22] In each case there is clearly little π interaction between the boron centre and the mesityl fragment, as manifested by Fe–B–C$_{ipso}$–C$_{ortho}$ angles of 91.9, 88.3 and 89.5°, respectively. This almost certainly

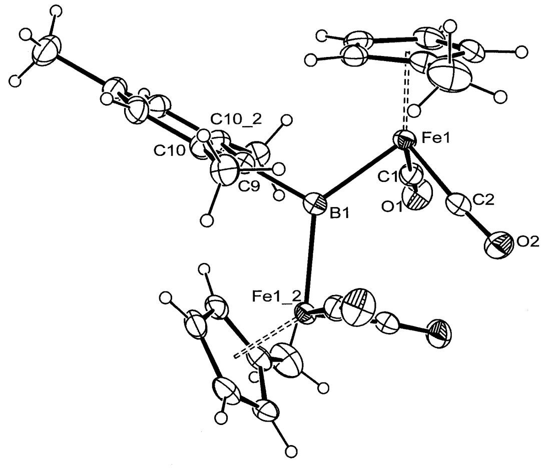


Fig. 7 Molecular structure of [(η^5-C_5H_4Me)Fe(CO)$_2$]$_2$BMes, **8**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 2.093(2), Fe(1_2)–B(1) 2.093(2), Fe(1)–C(1) 1.745(3), Fe(1)–(η^5-C_5H_5) centroid 1.749(3), Fe(1) ··· Fe(1_2) 3.800(2), B(1)–C(9) 1.580(5); Fe(1)–B(1)–Fe(1_2) 130.4(2), C(9)–B(1)–Fe(1)–(η^5-C_5H_5) centroid 21.3(3), Fe(1)–B(1)–C(9)–C(10) 83.8(2).

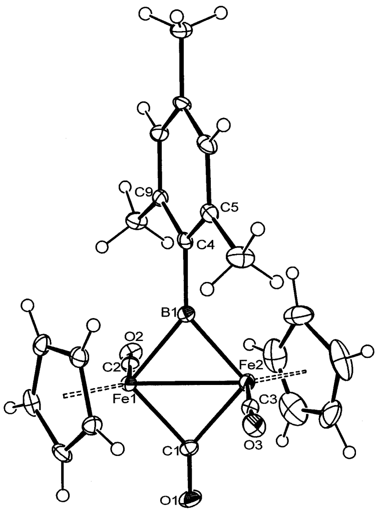


Fig. 8 Molecular structure of [(η^5-C_5H_5)Fe(CO)]$_2$(μ-CO)(μ-BMes), **11**. Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 1.956(5), Fe(2)–B(1) 1.966(5), Fe(1)–C(1) 1.919(5), Fe(2)–C(1) 1.920(5), Fe(1)–(η^5-C_5H_5) centroid 1.739(3), Fe(1) ··· Fe(2) 2.528(1), B(1)–C(4) 1.556(7); Fe(1)–B(1)–Fe(2) 80.3(2), Fe(1)–B(1)–C(4)–C(5) 60.4(2).

reflects the high steric requirements of the (η^5-C_5R_5)Fe(CO)$_2$ moiety, as the corresponding torsion angle in (MesBO)$_3$, for example, is 35.3°.[23] To our knowledge complexes **2**–**4** represent the first crystallographically characterized transition metal complexes containing a bromide-substituted boryl ligand – B(Br)X,[24] and feature B–Br distances [2.103(4), 2.005(3) and 2.018(2) Å, respectively] which are towards the longer end of those reported for trigonal boron.[25]

Replacement of the bromide substituent in **2** by a 4-*tert*-butyl phenoxide group (giving **6**; Fig. 5) leads to significant elongation of the Fe–B distance [from 1.964(5) to 2.040(2) Å], as expected for a boryl ligand which is both a poorer π acceptor and of greater steric bulk. The orientation of mesityl and (η^5-C_5H_5)-Fe(CO)$_2$ fragments with respect to the boryl ligand remain essentially unaltered.

The crystal structures of the disubstituted species **7** (Fig. 6) and **8** (Fig. 7) each consists of two piano stool (η^5-C_5H_4R)-Fe(CO)$_2$ (R = H, Me) fragments linked in μ_2,η^1,η^1 fashion by a single bridging mesitylborylene ligand [(2,4,6-$Me_3C_6H_2$)B]. Metal–metal distances in both compounds [3.802(10) and 3.800(2) Å, respectively] are long enough to preclude any direct interaction between the metal centres. The corresponding distances for [(η^5-C_5H_4R)Mn(CO)$_2$]$_2$(μ_2-BX) (X = NMe$_2$, R = H; X = OEt, R = Me; X = Cl, R = Me) each of which contains a single Mn–Mn bond and in [(η^5-C_5H_4Me)Fe(CO)]$_2$(μ_2-CO)[μ_2-BN(SiMe$_3$)$_2$], which contains both an Fe–Fe linkage and a bridging carbonyl, are 2.790(2), 2.817(1), 2.824(2) and 2.548(1) Å, respectively.[11a–d,g] As such **7** and **8** represent to our knowledge the first reported structurally characterized transition metal complexes containing an unsupported bridging borylene ligand.[26] Indeed, this particular structural motif is extremely rare among dinuclear complexes of the group 8 metals containing bridging ligands of the lighter main group elements; the overwhelming majority of complexes containing bridging alkylidene (CR$_2$), silylene (SiR$_2$) or alanediyl (AlR) ligands also feature a metal–metal bond or additional bridging ligands.

Photolysis of **7** results in loss of CO and formation of compound **11** (Fig. 8). Crystallographic analysis of **11** confirms the more conventional bridging geometry implied by infrared spectroscopy, with an Fe–Fe distance of 2.528(1) Å being similar to that found in [(η^5-C_5H_4Me)Fe(CO)]$_2$(μ_2-CO)[μ_2-BN(SiMe$_3$)$_2$] [2.548(1) Å [11d]] and therefore entirely consistent with an Fe–Fe single bond. **11** is formed in solution exclusively as a single isomer (as shown by multinuclear NMR), with the results of the crystallographic study implying that this features a *trans* arrangement of cyclopentadienyl ligands. The underlying steric reasons for the formation of the *trans* isomer can be understood by reference to Fig. 9 which shows the view along the B–C_{ipso} axis. The sterically favourable coplanar orientation of cyclopentadienyl and mesityl groups would not be possible for the *cis* isomer.

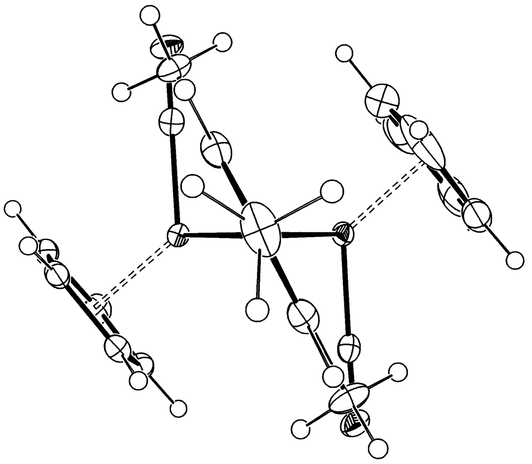


Fig. 9 Molecular structure of [(η^5-C_5H_5)Fe(CO)]$_2$(μ-CO)(μ-BMes), **11** viewed along the axis of the B(1)–C(4) bond.

There are two major differences between the different types of bridging mesitylborylene complex. Firstly the Fe–B–Fe angle is significantly wider in **7** or **8** [132.7(5) and 130.4(2)°, respectively] than is typically found in bridging borylenes which form part of a three-membered MBM metallacycle {*e.g.* 80.3(2) and 78.9(1)° for **11** and [(η^5-C_5H_4Me)Fe(CO)]$_2$(μ_2-CO)[μ_2-BN(SiMe$_3$)$_2$], respectively[11d]}. The opening out of the M–B–M angle in the absence of a constraining metal–metal bond mirrors the behaviour of analogous gallium and indium systems. The slightly wider angle found in **7** and **8** than in [(η^5-C_5R_5)Fe(CO)$_2$]$_2$GaX (X = Mes, R = Me, θ = 124.4°; X = ^{t}Bu, R = H, θ = 122.4°) or in [(OC)$_4$Co]$_2$In(2,4,6-^{t}Bu$_3C_6H_2$) (θ = 122.2°),[9,10] for example, almost certainly reflects the smaller covalent radius of boron. The shorter M–E distances found for E = B necessitate greater opening out of the M–E–M angle to minimize steric interaction between the bulky organometallic fragments.

Secondly, the Fe–B distances in the unsupported complexes **7** and **8** [2.089(9) and 2.093(2) Å] are significantly longer than those found in similar complexes containing a metal–metal bond {*cf.* mean values of 1.961(5) and 2.003(3)Å for **11** and [(η^5-

$C_5H_4Me)Fe(CO)]_2(\mu_2\text{-}CO)[\mu_2\text{-}BN(SiMe_3)_2]$, respectively[11d]}. That the Fe–B distances in **7** and **8** are also significantly greater than those found in the mesityl(bromo)boryl precursors **2** and **3** implies that steric repulsion between $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ fragments contributes to bond lengthening. π-Stabilisation of the boron centre in **7** and **8** is therefore clearly minimal, with Fe–B distances among the longest measured for trigonal boron,[21] and the orientation of the mesityl fragment reflecting little overlap with the aromatic π system [torsion angle, $Fe–B–C_{ipso}–C_{ortho}$ = 83.6(4)°]. Steric shielding would therefore appear to be a crucial factor in the isolation of complexes **7** and **8**. The use of sterically demanding substituents in the isolation of labile borylene complexes has previously been suggested in theoretical studies by Baerends and co-workers.[5a] From a synthetic viewpoint, however, choice of the appropriate level of steric shielding is clearly important. In our hands the complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2BX$ [X = Mes (**7**), Ph and Cl] are accessible *via* metathesis chemistry,[27] but the latter two compounds are significantly more sensitive to decomposition; on the other hand $(\eta^5\text{-}C_5H_5)Fe(CO)_2BR(Br)$ [R = $2,6\text{-}(2,4,6\text{-}{}^iPr_3C_6H_2)_2C_6H_3$] is inert to further substitution chemistry at boron,[28] and $2,4,6\text{-}{}^tBu_3C_6H_2BBr_2$ is unreactive towards substitution of either bromide by organometallic fragments.

4 Conclusions

The chemistry undertaken during this study reveals (i) that bromo-substituted boryl complexes prove to be versatile substrates for the synthesis of transition metal compounds containing novel boryl or borylene ligands; (ii) that boron-centred substitution chemistry in these boryl systems can generally be carried out with retention of the M–B linkage; (iii) that the steric properties of the mesityl substituent are ideal for the synthesis of novel unsupported bridged borylene systems; and (iv) that photolytic conversion to a more conventional bridging system can easily be accomplished. Attempts to further broaden the synthetic scope of mesityl(bromo)boryl complexes are ongoing and will be reported in due course.

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