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Substitution chemistry of sterically demanding boryl ligands†

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The synthetic and reaction chemistry of the asymmetric aryl(bromo)boryl complexes (η^5-C_5H_5)Fe(CO)$_2$B(Ar)Br [Ar = 2,4,6-$Me_3C_6H_2$, Mes (3); 2,6-(2,4,6-$^iPr_3C_6H_2$)C_6H_3, 2,6-Trip$_2C_6H_3$ (4)] are reported. In particular, the scope for substitution at boron by main-group nucleophiles is probed. The synthesis and characterization of (η^5-C_5H_5)Fe(CO)$_2$B(Mes)ER$_n$ [ER$_n$ = O^{t}Bu, (5); ER$_n$ = SPh (6)] confirm that substitution at boron can be accomplished with retention of the Fe–B bond. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: boryl; boron; iron; cyclopentadienyl; substitution

INTRODUCTION

Transition metal boryl complexes (L_nM–BX_2) have been the subject of intense research effort[1–5] due to their implication in the hydroboration and diboration of carbon–carbon multiple bonds,[1–10] and also in the highly selective stoichiometric and catalytic functionalization of hydrocarbons.[11–19] The reactivity of boryl complexes towards a variety of substrates has, therefore, been investigated in some depth,[2,5] although the intrinsic reactivity of this bond is such that substitution reactions at the boron centre that occur with *retention* of the M–B linkage are still relatively rare.[2,4,5,20–23] Generally, to exhibit such reactivity, the boryl ligand has to contain labile, weakly π donor groups such as chloride or bromide. Haloboryl species [L_nM–BX_2 and L_nM–B(R)X (X = halide)], although rare, are therefore potential precursors to a range of boryl complexes through boron-centred substitution chemistry. With this in mind, we have developed the asymmetric (bromo)boryl complexes (η^5-C_5H_5)Fe(CO)$_2$B(Ar)Br [Ar = Mes (**3**); 2,6-Trip$_2C_6H_3$ (**4**)] and probed their reactivity with a range of nucleophiles.

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. Potassium *tert*-butoxide (Lancaster), NaH, $Me_2Si(H)Cl$ and Et_3SiH (Aldrich) were used as received without further purification. MesBBr$_2$ (**1**), 2,6-Trip$_2C_6H_3BBr_2$ (**2**), Na[(η^5-C_5H_5)Fe(CO)$_2$], NaSPh and lithium diisopropylamide were prepared by minor modification of literature methods.[24–29] (η^5-C_5H_5)Fe(CO)$_2$B(Mes)Br (**3**) was prepared as described previously.[30,31]

NMR spectra were measured on a Jeol 300 Eclipse Plus FT-NMR spectrometer. Residual protons of solvent were used for reference for ^1H and ^{13}C NMR, and a sealed tube containing a solution of [($^nBu_4N$)(B_3H_8)] in $CDCl_3$ was used as an external reference for ^{11}B NMR. IR 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. Despite repeated attempts, satisfactory elemental microanalysis for new boryl complexes was frustrated by their extreme instability with regard to air, moisture and (in some cases) heat. Characterization of new compounds is based upon multinuclear magnetic resonance, IR and mass spectrometry data, supplemented by single crystal X-ray diffraction studies for compound **5**. In all cases the purity of the bulk material was established by multinuclear NMR to be >95%.

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Abbreviations: st = strong; s = singlet; d = doublet; t = triplet; m = multiplet; sept = septet.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{B(2,6-Trip}_2\text{C}_6\text{H}_3)\text{Br}$ (4)

To a suspension of $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]$ (0.038 g, 0.2 mmol) in toluene (15 cm^3) was added a solution of **2** (0.122 g, 0.2 mmol) in toluene (10 cm^3) and the reaction mixture was stirred at room temperature for 4 days. Filtration, removal of volatiles *in vacuo* and recrystallization from hexanes (*ca* 10 cm^3) at −50 °C yielded pale yellow crystals of **4** (0.06 g, 45%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.08 (d, 6H, CHCH_3), 1.18 (d, 6H, CHCH_3), 1.22 (d, 12H, CHCH_3), 1.48 (d, 6H, CHCH_3), 1.54 (d, 6H, CHCH_3), 2.81 (sept, 2H, *para*-CHCH$_3$), 3.28 (sept, 2H, *ortho*-CHCH$_3$), 3.38 (sept, 2H, *ortho*-CHCH$_3$), 3.96 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 7.18 (s, 4H, *meta*-H, Trip), 7.21 (t, 1H, *para*-H, Ph), 7.33 (d, 2H, *meta*-H, Ph). ^{13}C NMR (76 MHz, C_6D_6): δ 22.2, 23.0, 23.9, 24.2, 26.5, 27.8 (CHCH_3), 30.6, 31.3, 34.6 (CHCH_3), 86.8 ($\eta^5\text{-C}_5\text{H}_5$), 120.4, 120.5 (*meta*-C, Trip), 125.5 (*para*-C, Ph), 130.7 (*meta*-C, Ph), 137.4 (*ortho*-C, Ph), 137.5 (*ipso*-C, Trip), 146.9 (*para*-C, Trip), 148.6 (*ortho*-C, Trip), 213.9 (CO). ^{11}B NMR (96 MHz, C_6D_6): δ 114.9. IR (KBr disk, cm^{-1}): ν(CO) 2013 st, 1951 st. EI-MS: m/z 693 [$(\text{M} - 2\text{CO})^+$, 5%].

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{B(Mes)O}^t\text{Bu}$ (5)

A solution of **3** (0.09 g, 0.2 mmol) in toluene (10 cm^3) was added to a suspension of KO^tBu (0.02 g, 0.2 mmol) in toluene (5 cm^3) at room temperature. The resulting mixture was stirred at 60 °C for 12 h, 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) yielded **5** as pale yellow crystals suitable for X-ray diffraction (0.05 g, 59%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.21 (s, 9H, ^{t}Bu), 2.17 (s, 3H, *para*-CH$_3$), 2.29 (s, 6H, *ortho*-CH$_3$), 4.04 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 6.68 (s, 2H, aromatic CH). ^{13}C NMR (76 MHz, C_6D_6): δ 20.9 (*para*-CH$_3$), 22.3 (*ortho*-CH$_3$), 30.3 (CCH_3), 79.8 (CCH_3), 85.3 ($\eta^5\text{-C}_5\text{H}_5$), 128.8 (aromatic CH), 133.2, 135.8 (aromatic quaternary), 216.8 (CO). ^{11}B NMR (96 MHz, C_6D_6): δ 72.9. IR (KBr disk, cm^{-1}): ν(CO) 1987 st, 1918 st. EI-MS: m/z 365 [$(\text{M} - \text{CH}_3)^+$, 45%], 335 [$(\text{M} - 3\text{CH}_3)^+$, 40%] and 307 [$(\text{M} - \text{O}^t\text{Bu})^+$, 100%].

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{B(Mes)SPh}$ (6)

A solution of **3** (0.09 g, 0.2 mmol) in toluene (10 cm^3) was added to a suspension of NaSPh (0.03 g, 0.2 mmol) in toluene (5 cm^3) at room temperature. The resulting mixture was heated to 50 °C for 7 days, 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) yielded **6** as pale yellow crystals (0.04 g, 44%). ^{1}H NMR (300 MHz, C_6D_6): δ 2.05 (s, 3H, *para*-CH$_3$), 2.15 (s, 6H, *ortho*-CH$_3$), 4.16 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 6.59 (s, 2H, aromatic CH), 6.73–6.81 (m, 5H, SC$_6H_5$). ^{13}C NMR (76 MHz, C_6D_6): δ 20.9 (*para*-CH$_3$), 22.2 (*ortho*-CH$_3$), 85.7 ($\eta^5\text{-C}_5\text{H}_5$), 127.7 (mesityl aromatic CH), 131.5, 132.6 (mesityl aromatic quaternary), 126.8, 135.9, 137.8 (SPh aromatic CH), 215.5 (CO). ^{11}B NMR (96 MHz, C_6D_6): δ 103.5. IR (KBr disk, cm^{-1}): ν(CO) 2000 st, 1935 st. EI-MS: m/z 416 [$(\text{M})^+$, 30%].

Attempted reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{B(Mes)Br}$ (3) with LiN^iPr_2

A solution of **3** (0.13 g, 0.3 mmol) in toluene (10 cm^3) was added to a solution of LiN^iPr_2 (0.03 g, 0.3 mmol) in toluene (10 cm^3) at room temperature and the reaction mixture was heated to 50 °C for 7 days. Measurement of the ^{11}B NMR spectrum at this point revealed a single resonance at δ_B 111.4 due to the starting material **3**. Extensive variation of reaction conditions (temperature, time, ratio of reagents) did not lead to any noticeable conversion of **3** to substitution products.

Attempted reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{B(Mes)Br}$ (3) with hydride sources

The three reactions with hydride sources [NaH, $\text{Me}_2\text{Si(H)Cl}$ and Et_3SiH] were carried out in a similar manner. In a typical reaction, a solution of **3** (0.15 g, 0.4 mmol) in toluene (10 cm^3) was added to a suspension of NaH (0.10 g, 4.0 mmol) in toluene (5 cm^3) and the resulting reaction mixture was heated to 65 °C for 7 days. At this point, only a single resonance at δ_B 111.4 due to the starting material **3** was observed. For all three hydride sources used, extensive variation of reaction conditions (temperature, time, ratio of reagents) did not lead to the formation of any hydrido-boryl products.

General crystallographic method

Data for compound **5** were collected on an Enraf Nonius Kappa CCD diffractometer; data collection and cell refinement were carried out using DENZO and COLLECT,[32] and structure solution and refinement using SHELXS-97 and SHELXL-97 respectively.[33] Fuller details of the data collection, structure solution and refinement can be found in Table 1, relevant bond lengths and angles are included in figure captions and complete details have been deposited with the CCDC (reference number 199224).

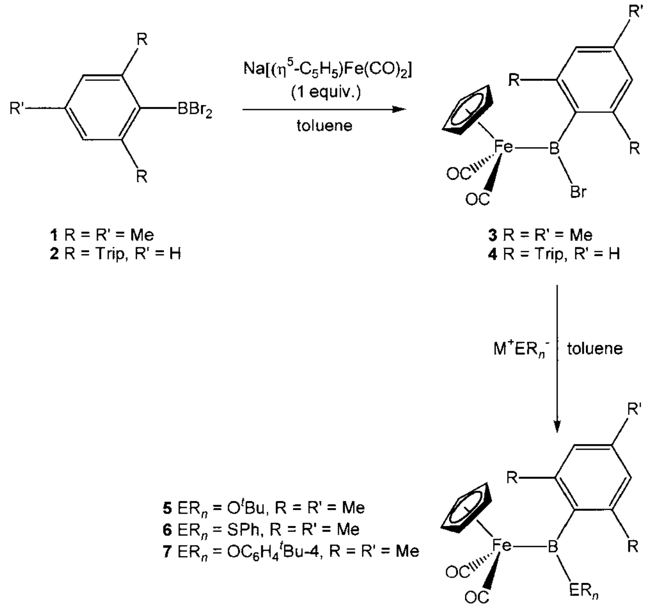
RESULTS AND DISCUSSION

As has previously been reported, selective substitution of a single halide in boranes of the type ArBBr_2 can be accomplished by the use of one equivalent of an organometallic nucleophile.[30,31] Thus, asymmetric (bromo)boryl complexes of the type $(\eta^5\text{-C}_5\text{R}_4\text{R}')\text{Fe(CO)}_2\text{B(Mes)Br}$ (R = R′ = H; R = R′ = Me; R = H, R′ = Me) are readily accessible from MesBBr_2. This chemistry can be extended to more bulky aryl groups; the asymmetric (bromo)boryl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{B(2,6-Trip}_2\text{C}_6\text{H}_3)\text{Br}$ (**4**) can be synthesized in moderate yields (*ca* 45%) by the reaction of $(2,6\text{-Trip}_2\text{C}_6\text{H}_3)\text{BBr}_2$ (**2**) with one equivalent of $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]$ in toluene over a period of 4 days at room temperature (see Scheme 1). The longer reaction time required

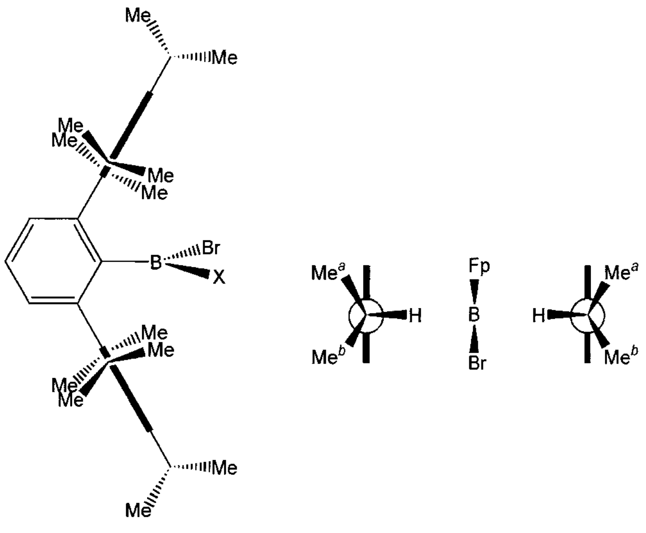
Table 1. Crystallographic data for **5**

Empirical formula	$C_{20}H_{25}BFeO_3$
Formula weight	380.06
Temperature (K)	150(2)
Wavelength (Å)	0.710 73
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.967(2)
b (Å)	8.191(2)
c (Å)	26.530(5)
β (°)	99.06(3)
Volume (Å^3)	1924.3(7)
Z	4
Density (calc.) (Mg m^{-3})	1.312
Absorption coefficient (mm^{-1})	0.798
F(000)	800
Crystal size (mm^3)	0.10 × 0.20 × 0.20
θ range for data collection (°)	2.9 to 27.4
Index ranges	
h	−11 to 11
k	−11 to 10
l	−33 to 34
Reflections collected	14 895
Independent reflections	4385
R_{int}	0.0620
Completeness to $\theta_{\max}$ (%)	99.5
Absorption correction	Sortav
Max. and min. transmission	0.92, 0.86
Refinement method	Full matrix least squares on F^2
Data/restraints/parameters	4385/0/232
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.042$, $wR_2 = 0.093$
R indices (all data)	$R_1 = 0.070$, $wR_2 = 0.103$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.36 and −0.35

for the synthesis of this complex (compared with the mesityl derivative **3** under analogous conditions) reflects the enhanced steric bulk around the boron centre. Spectroscopic data for **4** are entirely consistent with the proposed formulation (Fig. 1). In particular, multinuclear NMR data for **4** are highly indicative of selective replacement of a single bromide in **2** with an (η^5-C_5H_5)Fe(CO)$_2$ unit. The ^{11}B NMR shift for **4** (δ_B 114.9) is very similar to those observed for the analogous structurally characterized mesityl species (η^5-C_5R_4R')Fe(CO)$_2$B(Mes)Br [R = R′ = H (**3**) δ_B 111.4; R = R′ = Me δ_B 113.2; R = H, R′ = Me δ_B 111.3], showing the expected *ca* 50 ppm downfield shift on coordination to



Scheme 1. Outline of the boron-centred substitution chemistry used to synthesize complexes **3**–**7**.



2 X = Br
4 X = (η^5-C_5H_5)Fe(CO)$_2$, Fp

Figure 1. Extremely bulky terphenyl boranes. Structure of (η^5-C_5H_5)Fe(CO)$_2$B(2,6-Trip$_2$C$_6$H$_3$)Br (**4**) proposed on the basis of spectroscopic data and accounting for the inequivalence of methyl groups within each *para* ^{i}Pr unit.

the metal centre. ^{1}H and ^{13}C NMR data are also consistent with a lowering of symmetry implicit in monosubstitution at boron. Hence, whereas the structurally characterized 2,6-Trip$_2$C$_6$H$_3$BBr$_2$ (**2**, Fig. 1) shows three methyl and three methine signals for the pendant ^{i}Pr groups in both ^{1}H and ^{13}C NMR spectra, the ^{13}C spectrum of **4** shows six methyl and three methine signals. This observation is consistent with both Trip (2,4,6-^{i}Pr$_3$C$_6$H$_2$) arms being equivalent. It is, however, consistent with inequivalence of the 'up' and 'down' *ortho* ^{i}Pr groups of each Trip moiety, as would be expected for replacement of a single bromide by (η^5-C$_5$H$_5$)Fe(CO)$_2$ (**4**, Fig. 1). Intriguingly, inequivalence of the two methyl groups within each *para* ^{i}Pr unit is also implied by these data. Such a phenomenon is not observed for 2,6-Trip$_2$C$_6$H$_3$BBr$_2$, and effectively reflects diastereotopic inequivalence of each methyl group within the *para* ^{i}Pr unit (*i.e.* Me^a and Me^b are inequivalent whatever the angle of rotation about the C–C bond, Fig. 1). Such inequivalence implies slow interconversion between the positions of Fp and Br groups at boron on the NMR time scale (*i.e.* slow rotation about the B–C bond). This is not unexpected given the steric bulk at boron and variable-temperature NMR measurements reveal no sign of coalescence in the ^{13}C NMR spectrum at temperatures up to 95 °C. IR data for **4** are similar to those for **3** [ν(CO) 2013, 1951 cm^{-1} for **4** versus 2016, 1962 cm^{-1} for **3**] and, therefore, are consistent with a similar weakly π acceptor –B(Ar)Br boryl ligand.

The asymmetric mesityl(bromo)boryl complex **3** is a versatile substrate for further substitution chemistry *via* metathetical reaction with main-group nucleophiles (Scheme 1). Complex **5** can be synthesized in good yield from the reaction of **3** with KO^{t}Bu in toluene at 50 °C. Judging by ^{11}B NMR, this reaction is complete in 12 h, whereas the corresponding reaction with NaOC$_6$H$_4$^{t}Bu-4 to form **7** takes 21 days.[30,31] Similarly, complex **6** is formed in moderate yield from the analogous reaction of **3** with NaSPh at 50 °C over a period of 7 days. Presumably, these differing rates reflect not only the classical influences of sterics and electronics on nucleophilicity, but also the relative solubilities of the reagents in non-polar solvents and/or the kinetics of reactivity at the solid–solution interface. Intriguingly, **3** shows no reactivity towards amido or hydridic reagents [exemplified by LiN^{i}Pr$_2$, NaH, Me$_2$Si(H)Cl and Et$_3$SiH]. Whereas the lack of reactivity towards LiN^{i}Pr$_2$ might be understood on steric grounds, the resistance of **3** to attack by hydride sources is more difficult to rationalize. Steric factors are also likely to be reflected in the lack of clean substitution chemistry observed for **4**. At room temperature, **4** is resistant to attack even by nucleophiles that react quickly with **3**; significant elevation of temperature merely results in the destruction of all Fe–B-bonded species.

Spectroscopic data for **5** and **6** are consistent with the proposed formulation and, in the case of **5**, single crystals suitable for X-ray diffraction were obtained by controlled cooling of a concentrated solution in hexanes. The molecular structure and relevant bond lengths and angles are given in Fig. 2.

The molecular structure of **5** reveals the expected half-sandwich geometry at iron, with the coordination sphere completed by two carbonyls and one mesityl(*tert*-butoxy)boryl ligand. In common with related structures,[30,31] the trigonal planar [$\sum$ (angles at boron) = 360.0(2)°] boryl moiety is essentially perpendicular to the plane of the mesityl group [$\angle$Fe(1)–B(1)–C(1)–C(6) = 84.6(2)°], presumably on steric grounds. Significant elongation of the Fe–B bond [2.056(2) Å] is observed with respect to that found in **3** [1.964(5) Å] and (η^5-C$_5$H$_5$)Fe(CO)$_2$B(Mes)(OC$_6$H$_4$^{t}Bu-4) (**7**) [2.040(2) Å].[30,31] Conceivably, this reflects not only changes in ligand bulk but also the differing π acceptor properties of the boryl ligand. Alkoxoboryl ligands have previously been shown to be significantly poorer π acceptors than their aryloxo counterparts, with concomitantly longer Fe–B bonds.[34]

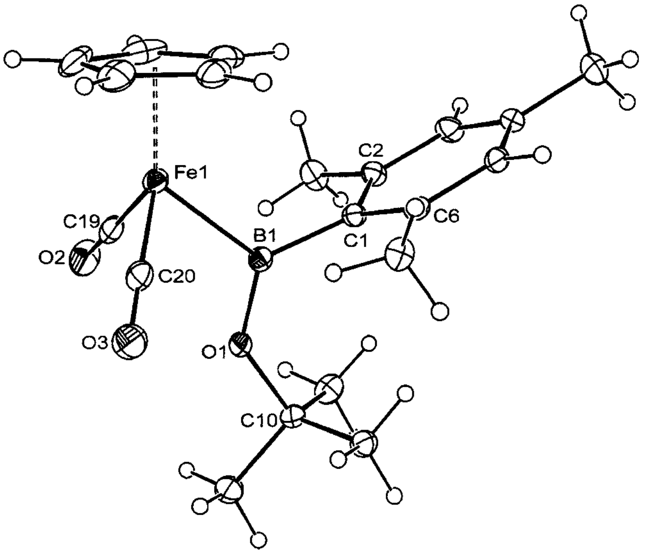


Figure 2. Molecular structure of (η^5-C$_5$H$_5$)Fe(CO)$_2$B(Mes)O^{t}Bu (**5**). Relevant bond lengths (Å) and angles (°): Fe(1)–B(1) 2.056(2), B(1)–O(1) 1.364(3), B(1)–C(1) 1.583(3), Fe(1)–(η^5-C$_5$H$_5$) centroid 1.735(3), (η^5-C$_5$H$_5$) centroid–Fe(1)–B(1)–C(1) 2.8(2), Fe(1)–B(1)–C(1)–C(6) 84.6(2).

Indeed, the influence of ligand π acceptor properties on the spectroscopic and structural properties of boryl complexes (η^5-C$_5$H$_5$)Fe(CO)$_2$B(Mes)ER$_n$ (ER$_n$ = O^{t}Bu, OC$_6$H$_4$^{t}Bu-4, SPh, Br) can be gauged by reference to Table 2. The decreasing π donor ability of the substituents ER$_n$ (O^{t}Bu > OC$_6$H$_4$^{t}Bu-4 > SPh > Br) is reflected in successive downfield shifts in the ^{11}B NMR resonances of these complexes. The Fe–B distances and carbonyl stretching frequencies of these complexes also reflect, at least in part, the π acceptor capability of the–B(Mes)ER$_n$ fragment. The highest carbonyl stretching frequencies and the shortest Fe–B bond length are found for **3** (ER$_n$ = Br), reflecting the weakly π donating ability of bromide leading to the highest π acceptor capability for this boryl ligand. Successively lower carbonyl stretching frequencies (and longer Fe–B bond lengths) for ER$_n$ = SPh, OC$_6$H$_4$^{t}Bu-4, O^{t}Bu reflect a reduction in Fe–B π back-bonding as a result of enhancement of the competing R$_n$E–B π interaction.

Table 2. Comparison of structural and spectroscopic data for complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2B(Mes)ER_n$

	3	**6**	**7**	**5**
ER_n in$-B(Mes)ER_n$	Br	SPh	$OC_6H_4{}^tBu\text{-}4$	O^tBu
$\nu(CO)/cm^{-1}$	2016, 1962	2000, 1935	1997, 1933	1987, 1918
$d(Fe-B)/Å$	1.964(5)	—	2.040(2)	2.056(2)
δ_B/ppm	111.4	103.5	80.3	72.9

CONCLUSIONS

This study reveals that bromo-substituted boryl complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2B(R)Br$ can be used to synthesize transition metal compounds containing novel boryl ligands *via* boron-centred substitution chemistry with retention of the M–B linkage. Reaction of **3** with appropriate main-group nucleophiles yields the asymmetric boryl complexes **5** and **6** in modest yields, thereby facilitating spectroscopic and structural probes of the variation in electronic properties possible for boryl ligands of the type $-B(Mes)ER_n$. The synthesis of the bulkier asymmetric (bromo)boryl complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2B(2,6\text{-}Trip_2C_6H_3)Br$ (**4**) has also been reported, although substitution chemistry is, in this case, curtailed by substituent bulk.

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REFERENCES

1. Wadepohl H. *Angew. Chem. Int. Ed. Engl.* 1997; **36**: 2441.
2. Irvine GJ, Lesley MJG, Marder TB, Norman NC, Rice CR, Robins EG, Roper WR, Whittell G, Wright LJ. *Chem. Rev.* 1998; **98**: 2685.
3. Braunschweig H. *Angew. Chem. Int. Ed. Engl.* 1998; **37**: 1787.
4. Braunschweig H. *Coord. Chem. Rev.* 2001; **223**: 1.
5. Smith MR. *Prog. Inorg. Chem.* 1999; **48**: 505.
6. Brown HC, Singaram B. *Pure Appl. Chem.* 1987; **59**: 879.
7. Burgess K, Ohlmeyer MJ. *Chem. Rev.* 1991; **91**: 1179.
8. Beletskaya I, Pelter A. *Tetrahedron* 1997; **53**: 4957.
9. Marder TB, Norman NC. *Top. Catal.* 1998; **5**: 63.
10. Ishiyama T, Miyaura N. *J. Organometal. Chem.* 2000; **611**: 392.
11. Waltz KM, Hartwig JF. *Science* 1997; **277**: 211.
12. Chen H, Hartwig JF. *Angew. Chem. Int. Ed. Engl.* 1999; **38**: 3391.
13. Chen H, Schlecht S, Semple TC, Hartwig JF. *Science* 2000; **287**: 1995.
14. Waltz KM, Hartwig JF. *J. Am. Chem. Soc.* 2000; **122**: 11 358.
15. Kawamura K, Hartwig JF. *J. Am. Chem. Soc.* 2001; **123**: 8422.
16. Ishiyama T, Tagaki J, Ishida K, Miyaura N, Anastasi NR, Hartwig JF. *J. Am. Chem. Soc.* 2002; **124**: 390.
17. Iverson CN, Smith MR. *J. Am. Chem. Soc.* 1999; **121**: 7696.
18. Cho JY, Tse MK, Holmes D, Maleczka RE, Smith III MR. *Science* 2002; **295**: 305.
19. Shimada S, Batsanov AS, Howard JAK, Marder TB. *Angew. Chem. Int. Ed. Engl.* 2001; **40**: 2168.
20. Irvine GJ, Rickard CEF, Roper WR, Williamson A, Wright LJ. *Angew. Chem. Int. Ed. Engl.* 2000; **39**: 948.
21. Braunschweig H, Colling M, Kollann C, Englert U. *J. Chem. Soc., Dalton Trans.* 2002; **2289**.
22. Rickard CEF, Roper WR, Williamson A, Wright LJ. *Organometallics* 2002; **21**: 1714.
23. Aldridge S, Calder RJ, Baghurst RE, Light ME, Hursthouse MB. *J. Organometal. Chem.* 2002; **649**: 9.
24. Gerrard W, Howarth M, Mooney EF, Pratt DE. *J. Chem. Soc.* 1963; 1583.
25. Grigsby WJ, Power PP. *J. Am. Chem. Soc.* 1996; **118**: 7981.
26. King RB, Bisnette MB. *J. Organometal. Chem.* 1967; **8**: 287.
27. King RB. *Acc. Chem. Res.* 1970; **3**: 417.
28. Dean PAW, Vittal JJ, Payne NC. *Can. J. Chem.* 1985; **63**: 394.
29. Ojima I, Kwon HB. *J. Am. Chem. Soc.* 1988; **110**: 5617.
30. Aldridge S, Coombs DL, Jones C. *Chem. Commun.* 2002; 856.
31. Coombs DL, Aldridge S, Jones C. *Dalton Trans.* 2002; 3851.
32. Otwinowski Z, Minor W. *Methods in Enzymology* vol. 276, Carter CW, Sweet RM (eds). Academic Press: New York, 1996; 307.
33. Sheldrick GM. *Acta Crystallogr. Sect. A* 1990; **46**: 467.
34. Aldridge S, Calder RJ, Rossin A, Dickinson AA, Willock DJ, Jones C, Evans DJ, Steed JW, Light ME, Coles SJ, Hursthouse MB. *J. Chem. Soc., Dalton Trans.* 2002; 2020.