Selective Ring-Opening Reactions of [1]Ferrocenophanes with Boron Halides: A Novel Route to Functionalized Ferrocenylboranes and Boron-Containing Oligo- and Poly(ferrocene)s

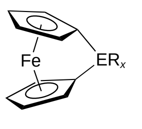
Frieder Jäkle, Andrea Berenbaum, Alan J. Lough, and Ian Manners*[a]

Abstract: The reactivity of strained [1]ferrocenophanes, $[Fe(\eta\text{-}C_5H_4)_2ER_x]$ ($ER_x = SiMe_2$, **1a**; SiMePh, **1b**; SnR_2, **1c**), towards boron halides has been investigated and has been shown to provide a facile pathway to ferrocene derivatives functionalized with Lewis acidic boron centers. The boron halides RBX_2 (R = Cl, Ph, fc; X = Cl, Br) (fc = $Fe(\eta\text{-}C_5H_4)_2$) lead to selective cleavage of the Si–Cp bonds in **1a** and **1b** to give, depending on the reaction stoichiometry, functionalized mono- or diferrocenylboranes $R_nB[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4SiMe_2Cl)]_{3-n}$ (**2a**: R = Cl, $n = 2$; **2b**: R = Cl, $n = 1$; **2c**: R = Ph, $n = 1$) and $R_nB[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4SiMePhCl)]_{3-n}$ (**2d**: R = Cl, $n = 2$) in high yields. Compounds **2a**–**d** were characterized by multinuclear NMR spectroscopy, mass spectrometry, and by single-crystal X-ray diffraction (for **2b**). Most likely due to steric constraints, a triferrocenylborane was not obtained even from the reaction of BCl_3 with an excess of **1a**, whereas facile formation of the diferrocenylphenylborane **2c** from $PhBCl_2$ and two equivalents of **1a** was observed. Selective hydrolysis of the B–Cl bonds of chlorodiferrocenylborane **2b** in the presence of trace amounts of water led to the silylated tetranuclear ferrocene complex $[(ClMe_2Sifc)_2B\text{-}O\text{-}B(fcSiMe_2Cl)_2]$ (**3**) without cleavage of the Si–Cl bonds. The structure of **3** was confirmed by an X-ray diffraction study. Studies of the reactivity of the higher Group 14 homologue of **1a** and **1b**, the tin-bridged [1]ferrocenophane **1c**, revealed that facile addition of B–Cl bonds occurs across the Sn–Cp bonds to yield the 1-stannyl-1′-borylferrocenes $[(ClMes_2Sn)fc(BClR)]$ (**4a**: R = Cl; **4b**: R = Ph; Mes = 2, 4, 6-$Me_3C_6H_2$). The new synthetic methodology can be extended to bifunctional Lewis acids such as the bis(boryl)ferrocene 1,1′-$fc(BBr_2)_2$, which affords the linear boron-bridged ferrocene trimer 1,1′-$[fc\{B(Br)fcSiMe_2Br\}_2]$ **5** in 54% isolated yield. In order to incorporate the functionalized ferrocenylboranes into polymer structures, compound **2c** was reduced with $Li[BEt_3H]$ to give the silicon-hydride functionalized species $[PhB\{(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_4SiMe_2H)\}_2]$ (**6**), which was then used as a capping reagent in the transition metal catalyzed polymerization of **1a**. This process leads to the incorporation of the ferrocenylborane unit into the main chain of a poly(ferrocenylsilane) to afford $[PhB\{(fcSiMe_2)_{n-1}fcSiMe_2H\}_2]$ (**7**).

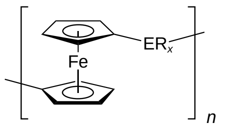
Keywords: boron · [1]ferrocenophanes · Lewis acids · ring-opening addition · tin

Introduction

[1]Ferrocenophanes **A** are interesting, strained organometallic molecules, in which the presence of a single bridging atom connecting the two Cp (Cp = cyclopentadienyl) rings leads to a tilted structure. Since the first example **A** ($ER_x = SiPh_2$) was synthesized in 1975,[1] the range of [1]ferrocenophanes has been expanded to species bridged with heavier main group elements of the second period and below from Group 14 (Ge, Sn),[2–6] Group 15 (P, As),[2, 3, 7, 8] and Group 16 (S, Se)[9, 10] as well as with Group 4 elements (Ti, Zr, Hf).[11, 12] Recently, the first-row-element boron has also been introduced as a bridging element.[13, 14] Whereas strained organic molecules are generally well-studied,[15] much less is known about the chemistry of corresponding organometallic species, particularly those that contain transition elements. The accessibility of a variety of [1]ferrocenophanes therefore provides a valuable opportunity to gain insight in this unexplored area.



A



B

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[a] Prof. I. Manners, Dr. F. Jäkle, A. Berenbaum, Dr. A. J. Lough
Department of Chemistry, University of Toronto
80 St. George Street, Toronto, ON, M5S 3H6 (Canada)
Fax: (+1)416 978-6157
E-mail: imanners@alchemy.chem.utoronto.ca

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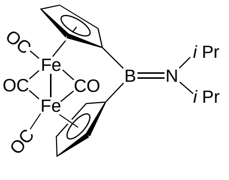

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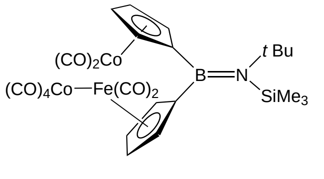

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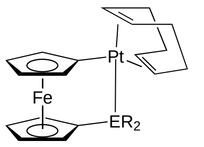

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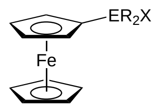


F

To date, studies of [1]ferrocenophanes have revealed a range of interesting reactivity. For example, thermal, anionic, and transition metal catalyzed ring-opening polymerization (ROP) of these species has been shown to result in stable, high-molecular-weight poly(ferrocene)s **B**.[16, 17]

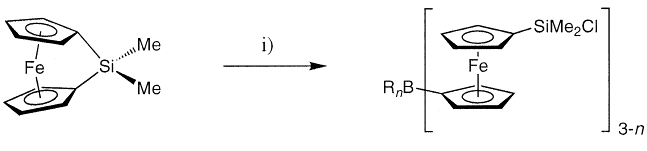
Insertion reactions can be observed at two different positions of the metallacycles, either at the Cp–E or the Fe–Cp bonds. The actual site of attack strongly depends on the nature of the bridging element. For instance, highly strained, boron-bridged ferrocenophanes (tilt angles between the Cp rings: α ca. 32°; for sila[1]ferrocenophanes: α ca. 20°) undergo facile insertion reactions into the Fe–Cp bond with transition metal carbonyl fragments (**C** from $Fe_2(CO)_9$ and **D** from $[Co_2(CO)_8]$).[18] However, insertion reactions into the B–Cp bonds have not yet been observed. On the other hand, with electron-rich Pt^0 species such as $Pt(cod)_2$ (cod = 1,5-cyclooctadiene) insertion of the metal center occurs into a Si–Cp bond of **A** ($ER_2 = SiMe_2$) or a Sn–Cp bond of **A** ($ER_2 = Sn\textit{t}Bu_2$) resulting in a platinasila[2]ferrocenophane **E** ($ER_2 = SiMe_2$)[19] or platinastanna[2]ferrocenophane **E** ($ER_2 = Sn\textit{t}Bu_2$)[4b], respectively. Ring-opening addition reactions with silicon- and tin-bridged [1]ferrocenophanes also occur with water, methanol, or silanol groups at the Cp–E bond to generate monosubstituted ferrocenylsilane species **F** containing E–O bonds.[20, 21] This synthetic strategy has, for example, been exploited to generate ferrocenyl-substituted mesoporous silica and has been utilized in the fabrication of novel composites and magnetic nanostructures.[21, 22] Similarly, chlorosilyl- and chlorogermyl-substituted ferrocenes **F** (E = Si or Ge) have recently been prepared in unusually high yield from silicon- and germanium-bridged [1]ferrocenophanes through a ring-opening addition reaction with HCl.[23] These monosubstituted ferrocene derivatives, which have been applied in the synthesis of ferrocenylsilane oligomers and for silica and electrode derivatization are very difficult to prepare by other, less selective synthetic routes.[24]

However, apart from reactions with protic species, the reactivity of [1]ferrocenophanes towards electrophiles is virtually unexplored. With other electrophiles, novel mixed-metal 1,1′-disubstituted ferrocenes may be accessible.[25] These species are of interest as bidentate Lewis acids in the selective recognition of anions and Lewis bases, and as catalysts in organic transformations.[26–28] Herein we describe the first studies on the reactivity of [1]ferrocenophanes towards boron halides and report on the synthesis, structures, and properties of the resulting functionalized ferrocenylboranes. We also report on our initial attempts to generate boron-bridged multinuclear ferrocene complexes and to incorporate Lewis acidic boron centers into poly(ferrocenylsilane) polymer backbones.

Results and Discussion

Electrophilic substitution of aromatic systems with boron trihalides in most cases can only be achieved under drastic conditions even in the presence of a catalyst.[29] Reaction of BI_3 and BBr_3 with ferrocene has been shown to proceed under reflux conditions in solvents such as CS_2, hexanes, and CH_2Cl_2.[30] Borylation of ferrocene with BCl_3 does not proceed as readily as with the preceeding halides, however, it has been shown to be accelerated in the presence of $AlCl_3$/Al as a catalyst.[31] We anticipated that reaction of boron halides with strained [1]ferrocenophanes might permit ambient temperature access to ferrocenylboranes.

Ring-opening addition reactions of silicon-bridged [1]ferrocenophanes 1a and 1b with boron halides: Initially, we investigated the reactivity of the dimethylsilyl-bridged [1]ferrocenophane **1a** towards BCl_3 and $PhBCl_2$. Depending on the stoichiometry of the reactants, ring-opening addition occurred with $RBCl_2$ (R = Cl, Ph) giving mono- or diferrocenylboranes **2** (Scheme 1). Low-temperature reaction of **1a** with a large excess (5 equiv) of BCl_3 led to selective formation of $Cl_2BfcSiMe_2Cl$ (**2a**) which was isolated as a deep red oil. Lower ratios of BCl_3 to ferrocenophane **1a** led to increasing amounts of the red, crystalline diferrocenyl species $ClB(fcSiMe_2Cl)_2$ (**2b**), which can be selectively obtained from reaction of BCl_3 with two equivalents of **1a**. Similarly, addition of $PhBCl_2$ to two equivalents of **1a** resulted in the formation of the analogous diferrocenylphenylborane $PhB(fcSiMe_2Cl)_2$ (**2c**). However, attempts to form a triferrocenylborane from **1a** were unsuccessful, even when an excess of **1a** was used (4 equiv). Considering that triferrocenylborane[32] and even the tetracoordinate ferricenyl(III)tris(ferrocenyl(II))borate[33] are known in the literature, we assume that the formation of a triferrocenylborane by the ring-opening addition reaction is kinetically unfavorable due to steric constraints in the reaction transition state and possibly, in addition, the lower



1a

2a: $n = 2$; R = Cl
2b: $n = 1$; R = Cl
2c: $n = 1$; R = Ph

Scheme 1. Reaction of $RBCl_2$ (R = Cl, Ph) with **1a**. i) **2a**: excess BCl_3, 0 °C to 25 °C, hexanes; **2b**: 0.5 equiv BCl_3, −30 °C to 25 °C, hexanes; **2c**: 0.5 equiv $PhBCl_2$, 20 °C, hexanes.

reactivity of the B−Cl bond in the presence of electron-releasing ferrocenyl substituents at the boron center.

Borylsilylferrocenes **2a–c** were characterized by ^{1}H, ^{13}C, ^{11}B, and ^{29}Si NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction. The ^{1}H NMR spectra are consistent with the proposed structures of ring-opened ferrocenophanes with different substituents on the Cp rings. For instance, the monoaddition product **2a** shows four pseudotriplets ($\delta = 4.39, 4.37, 4.11, 3.93$) of equal intensity in the Cp region of the ^{1}H NMR spectrum. Similarly, the ^{1}H NMR spectrum of diferrocenylborane **2b** consists of four pseudotriplets of equal intensity at slightly lower field ($\delta = 4.68, 4.47, 4.22, 4.03$). The ^{29}Si NMR spectra exhibit signals of almost identical chemical shift (**2a**: $\delta = 22.6$; **2b**: $\delta = 22.8$; **2c**: $\delta = 22.3$) as the previously described $FcSiMe_2Cl$ ($\delta = 22.3$)[23] (Fc = (η-C_5H_4)Fe(η-C_5H_5)). The ^{11}B NMR signal for compound **2b** ($\delta = 56.5$) is shifted significantly downfield in comparison to that of **2a** ($\delta = 51.7$), which shows a similar chemical shift to that of $Fe(C_5H_4BCl_2)_2$ ($\delta = 50.1$).[30a] The ^{11}B NMR signal of the triarylborane **2c**, is the most downfield-shifted ($\delta = 60.5$) of the three. In order to further confirm the structure of compounds **2** a single-crystal X-ray diffraction study was undertaken on **2b**. The molecular structure of this species is shown in Figure 1.

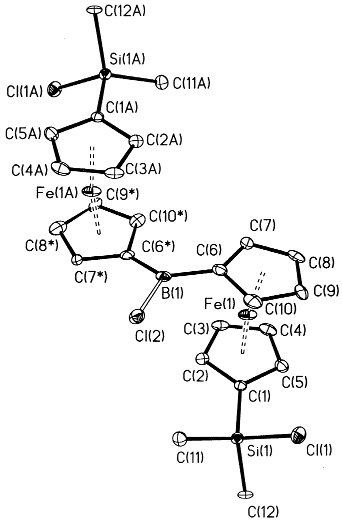


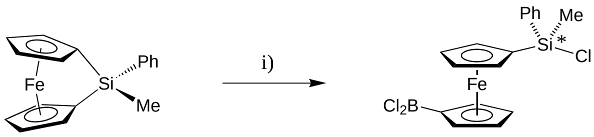
Figure 1. Molecular structure of **2b** with thermal ellipsoids at the 30% probability level.

The crystal structure of **2b** confirms the ring-opening reaction of [1]ferrocenophane **1a** with BCl_3 under attachment of two ferrocenyl groups to the boron center and transfer of chloro substituents to silicon. In contrast to the parent triferrocenylborane[32c], the ferrocene substituents are found in a *trans* position with regard to the trigonal planar boron center. This effect and the large angle between the ferrocenyl substituents and the central boron atom (C(6)-B(1)-C(6*): 128.4(6)°) may be attributed to the bulk of the ferrocene moieties. This may well explain the lack of a further reaction between **2b** and **1a**. Interestingly, the dimethylsilyl groups are not found in a *trans* orientation to the B−Cp bonds but make angles of about 90° with the latter (C(6)−B(1)//C(1)−Si(1) 84.0(5)° and C(6*)−B(1)//C(1A)−Si(1A) 101.0(5)°). The boron atom is bent out of the attached Cp plane by an angle α^* of 11.9(6)° ($\alpha^* = 180° -$ centroid(C(6) – C(10))-C(6)-B(1)), whereas the dimethylchlorosilyl substituents are essentially in the same plane ($\alpha^* = 180° -$ centroid(C(1) – C(5))-C(1)-Si(1) 1.3(3)). This effect was previously observed for borylated ferrocenes and attributed to some degree of iron – boron interaction.[34] The bending of the boryl group is smaller than for the monosubstituted ferrocenylborane $FcBBr_2$ ($\alpha^* = 17.7$, 18.9°)[34a], but is in a similar range as for the analogous stannylated derivatives (see below and reference [27d]). In agreement with a smaller degree of interaction than in $FcBBr_2$, the boron−carbon distances of 1.554(10), 1.564(10) Å, and the iron−boron distance of 2.857(8) Å are slightly longer than in $FcBBr_2$ (average d(B−C) 1.478 Å; average d(Fe−B) 2.840 Å). The Cp rings in **2b** are slightly tilted with respect to each other with interplanar angles of 4.1(7)° (C(1)−C(5)//C(6)−C(10)) and 6.7(8)° (C(1A)−C(5A)// C(6*)−C(10*)) and, accordingly, the angles between the Cp centroids and the central iron atom are only 168.9(2)° and 162.6(2)°, respectively (Table 1).

Table 1. Selected bond lengths, interatomic distances [Å], and angles [°] for **2b**.

Si(1)−Cl(1) 2.080(1)	B(1)−C(6)* 1.564(10)	C(1)-Si(1)-Cl(1) 107.6(1)
Si(1)−C(1) 1.852(3)	Fe(1) ··· Si(1) 3.517(1)	C(11)-Si(1)-Cl(1) 107.4(1)
Si(1)−C(11) 1.859(4)	Fe(1) ··· B(1) 2.857(8)	C(12)-Si(1)-Cl(1) 105.8(1)
Si(1)−C(12) 1.886(3)	C(1)-Si(1)-C(11) 112.2(2)	C(6)-B(1)-Cl(2) 115.8(6)
B(1)−Cl(2) 1.798(8)	C(1)-Si(1)-C(12) 110.6(1)	C(6)*-B(1)-Cl(2) 115.7(6)
B(1)−C(6) 1.554(10)	C(11)-Si(1)-C(12) 112.8(2)	C(6)-B(1)-C(6)* 128.4(6)

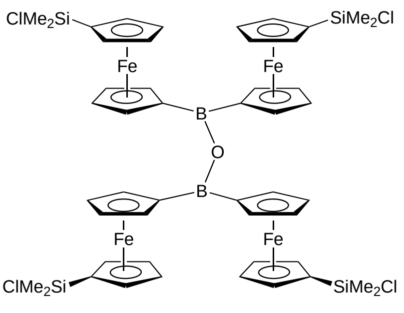
Ring-opening addition reactions of the unsymmetrically substituted silicon-bridged [1]ferrocenophane 1b with BCl_3: Interestingly, if an unsymmetrically substituted [1]ferrocenophane such as **1b** (R = Me, R′ = Ph) is used in the ring-opening addition reaction, the formation of a product containing a chiral silicon center can be expected. We found that the addition of a large excess of BCl_3 to the sila[1]ferrocenophane **1b** resulted in the formation of the ring-opened species **2d** (Scheme 2). This compound, which was isolated as a dark red oil, exists as a pair of enantiomers resulting from the chiral nature of the silicon center. This effect is reflected particularly in the ^{13}C NMR spectrum, as 10 separate, closely spaced signals are observed in the Cp region.



1b **2d**

Scheme 2. Reaction of BCl_3 with **1b**. i) excess BCl_3, −30 °C to 25 °C, hexanes.

Dimerization of chlorodiferrocenylborane 2b by controlled hydrolysis: At low temperature, the boron−chlorine bond of diferrocenylborane **2b** was selectively hydrolyzed with trace amounts of water to form the B-O-B-bridged tetraferrocene **3**.



3

The ^{11}B NMR spectrum of **3** shows a single signal at $\delta = 45.3$, which is significantly upfield-shifted with respect to the starting material (cf. **2b**; $\delta = 56.5$). This is in accordance with the formation of the boron–oxygen bonds.[35] A single signal is observed in the ^{29}Si NMR spectrum at $\delta = 22.8$ (cf. **2b**; $\delta = 22.8$) indicating the retention of the silicon–chlorine bonds. In order to confirm the assigned structure of **3**, a single-crystal X-ray diffraction study was performed on the orange crystals obtained from a solution in toluene at −55 °C. The molecular structure of compound **3** is shown in Figure 2.

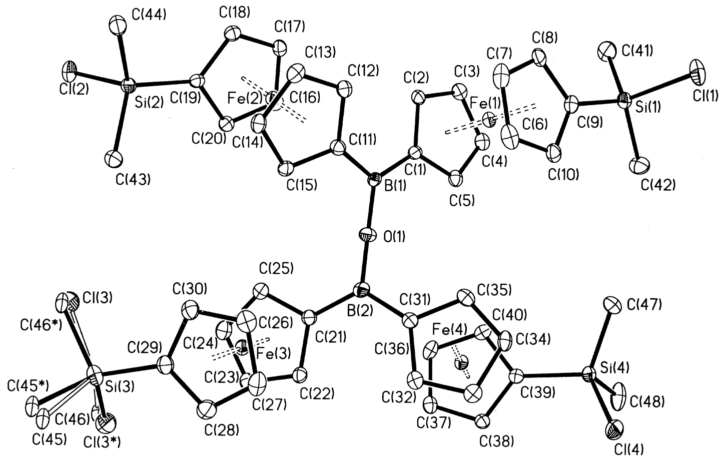


Figure 2. Molecular structure of **3** with thermal ellipsoids at the 30% probability level.

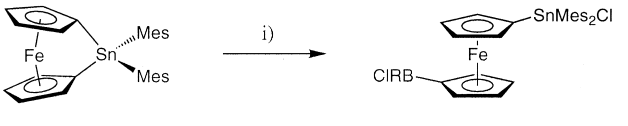
The crystal structure of **3** confirms the selective hydrolysis of **2b** to give a B-O-B bridged tetraferrocene derivative without hydrolysis of the Si–Cl bonds. Similar to the case of **2b**, the ferrocene substituents on each boron atom are found in a *trans* position with regard to the trigonal-planar boron center. In agreement with a diminished Lewis acidity of the boron centers in comparison to that in **2b**, the boryl groups are only slightly bent out of the Cp planes (average: 4.5°) and the Cp rings of the ferrocene moieties are only slightly tilted with respect to one another (average: 1.1°). Furthermore, the iron–boron distances are significantly longer in **3** (average d(Fe–B): 3.172 Å) than in **2b**, whereas the B–C distances are essentially unchanged (average d(B–C) 1.552 Å). The large B-O-B angle (161.0(5)°) and C-B-C angles (125.0(4), 125.5(5)°) reflect the steric bulk of the ferrocenyl substituents (Table 2).

Table 2. Selected bond lengths, interatomic distances [Å], and angles [°] for **3**.[a]

Si(1)–Cl(1) 2.080(2)	B(2)–C(31) 1.541(8)	C(43)-Si(2)-C(44) 115.1(3)
Si(1)–C(9) 1.838(5)	Fe(1)···Si(1) 3.508(2)	C(43)-Si(2)-Cl(2) 104.8(2)
Si(1)–C(41) 1.851(6)	Fe(2)···Si(2) 3.439(2)	C(44)-Si(2)-Cl(2) 106.2(2)
Si(1)–C(42) 1.856(5)	Fe(3)···Si(3) 3.503(2)	C(39)-Si(4)-Cl(4) 106.8(2)
Si(2)–Cl(2) 2.090 (2)	Fe(4)···Si(4) 3.478(2)	C(39)-Si(4)-C(47) 110.6(3)
Si(2)–C(19) 1.832(5)	Fe(1)···B(1) 3.222(6)	C(39)-Si(4)-C(48) 112.2(3)
Si(2)–C(43) 1.846(5)	Fe(2)···B(1) 3.171(6)	C(47)-Si(4)-C(48) 111.8(3)
Si(2)–C(44) 1.849(5)	Fe(3)···B(2) 3.218(6)	C(47)-Si(4)-Cl(4) 108.2(2)
Si(3)–C(29) 1.838(6)	Fe(4)···B(2) 3.077(6)	C(48)-Si(4)-Cl(4) 106.9(2)
Si(4)–Cl(4) 2.077(2)	C(9)-Si(1)-Cl(1) 104.7(2)	B(1)-O(1)-B(2) 161.0(5)
Si(4)–C(39) 1.835(5)	C(9)-Si(1)-C(41) 111.5(3)	O(1)-B(1)-C(1) 117.2(5)
Si(4)–C(47) 1.864(6)	C(9)-Si(1)-C(42) 113.1(3)	O(1)-B(1)-C(11) 117.8(5)
Si(4)–C(48) 1.852(6)	C(41)-Si(1)-C(42) 112.3(3)	O(1)-B(2)-C(21) 117.0(5)
B(1)–O(1) 1.367(6)	C(41)-Si(1)-Cl(1) 108.1(2)	O(1)-B(2)-C(31) 117.5(5)
B(2)–O(1) 1.367(7)	C(42)-Si(1)-Cl(1) 106.6(2)	C(1)-B(1)-C(11) 125.0(4)
B(1)–C(1) 1.563(7)	C(19)-Si(2)-Cl(2) 107.9(2)	C(21)-B(2)-C(31) 125.5(5)
B(1)–C(11) 1.555(7)	C(19)-Si(2)-C(43) 112.1(2)	
B(2)–C(21) 1.549(8)	C(19)-Si(2)-C(44) 110.2(2)	

[a] The geometric parameters of the disordered group are not included as restraints were used to partially model this group in the structure refinement.

Ring-opening addition reactions of tin-bridged [1]ferrocenophanes with boron halides: In order to explore the generality of the described ring-opening addition with Lewis acids, we investigated the reaction with tin-bridged [1]ferrocenophanes.[36] Indeed, reaction of tin-bridged [1]ferrocenophane **1c** with BCl_3 and $PhBCl_2$ gave the 1-stannyl-1′-borylferrocenes **4a** and **4b**, respectively (Scheme 3). The monoferrocenylborane **4a** was formed from the low-temperature reaction of **1c** with *one* equivalent of BCl_3. This stands in sharp contrast to the reaction of sila[1]ferrocenophane **1a**, for which a large excess (5 equivalents) of borane was necessary to selectively form the monoferrocenyl compound **2a**. The difference in reactivity may be attributed to the increased bulk of the bridging unit in **1c**, although the change of the bridging element may also play a significant role.



1c

4a: R = Cl
4b: R = Ph

Scheme 3. Synthesis of 1-stannyl-1′-borylferrocenes. i) $RBCl_2$, 0 °C to 25 °C, hexanes/toluene.

The Cp region of the ^{1}H NMR spectrum of **4a** and **4b** shows four pseudotriplets of equal intensity (**4a**: $\delta = 4.66, 4.45, 4.32, 4.25$; **4b**: $\delta = 4.78, 4.67, 4.30, 4.26$), which are slightly downfield-shifted from those of the analogous silicon species **2a** ($\delta = 4.39, 4.37, 4.11, 3.93$). A single signal was observed in the ^{119}Sn NMR spectra of **4a** and **4b** at $\delta = -34.1$ and at $\delta = -32.7$, respectively. The ^{11}B NMR signals are in the expected range for mono- and diarylchloroboranes (**4a**: $\delta = 51.9$; **4b**: $\delta = 58.7$).[35] To further confirm the assigned structure of **4a**, an X-ray diffraction study was undertaken on dark red single crystals obtained from a mixture of toluene and hexanes (40:60) at −30 °C. The molecular structure of compound **4a** is shown in Figure 3.

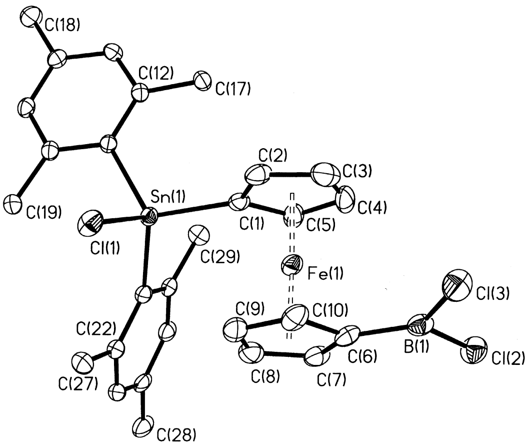


Figure 3. Molecular structure of **4a** with thermal ellipsoids at the 30% probability level.

The crystal structure of **4a** confirms the addition of BCl_3 across the Sn–C bond in **1c**. The bulky stannyl group adopts a *trans* position with respect to the boryl substituent (Sn(1)–C(1)// B(1)–C(6) 173.4(5)°), which is different from the structure of **2b** discussed above. As in **2b** and the 1,2-substituted analogue 1-($ClMe_2Sn$)-2-(MePhB)fc,[27d] the boryl group but not the stannyl substituent is bent towards the iron atom ($\alpha^* = 180° -$ centroid(C(6) – C(10))-C(6)-B(1) = 6.2(4)°; $\alpha^* = 180° -$ centroid(C(1) – C(5))-C(1)-Sn(1) = 1.9(1)°). The iron–boron distance of 3.087(5) Å is similar to that in the above-mentioned 1-stannyl-2-borylferrocene, but is slightly longer than in **2b** (2.857(8) Å) (Table 3).

Table 3. Selected bond lengths, interatomic distances [Å], and angles [°] for **4a**.

Sn(1)–Cl(1) 2.377(1)	B(1)–C(6) 1.505(6)	C(11)-Sn(1)-C(21) 110.4(1)
Sn(1)–C(1) 2.121(4)	Fe(1) ··· Sn(1) 3.6967(6)	C(11)-Sn(1)-Cl(1) 103.09(9)
Sn(1)–C(11) 2.150(3)	Fe(1) ··· B(1) 3.087(5)	C(21)-Sn(1)-Cl(1) 113.9(1)
Sn(1)–C(21) 2.164(4)	C(1)-Sn(1)-C(11) 116.8(1)	C(6)-B(1)-Cl(2) 121.5(3)
B(1)–Cl(2) 1.753(5)	C(1)-Sn(1)-C(21) 112.0(1)	C(6)-B(1)-Cl(3) 122.4(4)
B(1)–Cl(3) 1.752(5)	C(1)-Sn(1)-Cl(1) 100.2(1)	Cl(2)-B(1)-Cl(3) 116.1(3)

Reactivity of silicon-bridged [1]ferrocenophanes towards bifunctional boron halides: We were interested to explore whether strained [1]ferrocenophanes would also undergo selective ring-opening with bifunctional Lewis acids allowing the direct generation of multinuclear complexes. Indeed, reaction of 1,1′-bis(bromoboryl)ferrocene with two equivalents of the sila[1]ferrocenophane **1a** resulted in the ring-opening addition of one silaferrocene functionality to each boron atom to form the linear tri(ferrocene) **5** (Scheme 4).

As expected from the symmetry of the molecule, the ^1H NMR spectrum shows six Cp resonances of equal intensity ($\delta = 4.68$, 4.60, 4.53, 4.45, 4.18, 3.98) corresponding to six different types of protons. Two-dimensional NMR techniques (COSY, HSQC, HMBC, NOESY) allowed the assignment of three sets of signals to the three different pairs of Cp rings (see Scheme 4: $\delta(^1H/^{13}C)$: A 4.68/78.4, 4.53/77.6, 73.5; B 4.60/77.5 4.45/76.5, 72.5; C 4.18/74.7, 3.98/74.3, 70.7). Importantly, the connectivity between the ferrocene units was confirmed by an NOE peak ($\delta = 4.68/4.60$) between the *ortho* protons of the two pairs of Cp rings attached to the boron center (Cp-rings A, B in Scheme 4; see Figure 4). The ^{29}Si NMR spectrum shows a single signal at $\delta = 18.5$ which is upfield-shifted from those of the chorosilyl-substituted compounds **2a – c** and **3** ($\delta =$ ca. 22) correlating to the decreased electronegativity of the bromine atom. A single signal in the ^{11}B NMR was observed at $\delta = 56.5$, which is at the same chemical shift as that observed for chlorodiferrocenylborane **2b** ($\delta = 56.5$). Further evidence for the formation of the trinuclear complex **5** stems from the mass spectrometric

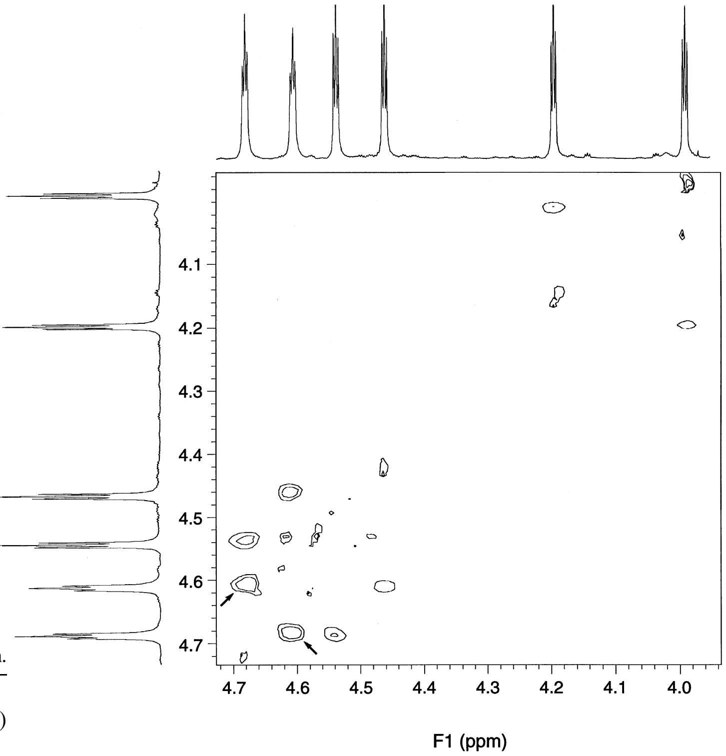
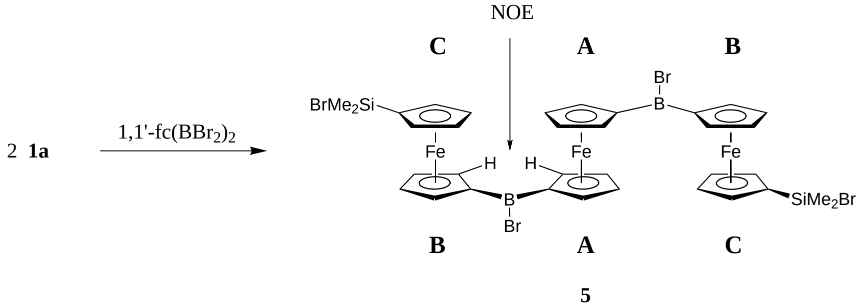


Figure 4. Ferrocene region of the NOESY NMR spectrum of **5** in C_6D_6. Arrows indicate the discussed NOE peaks.



Scheme 4. Reaction of 1,1′-fc(BBr_2)$_2$ with two equivalents of **1a**.

(EI-MS) analysis which showed the molecular ion at *m/z* 1010 as the most intense peak.

The attempted formation of a linear trimer analogous to **5** with dimethylamino or mesityl substituents on boron in place of bromine was not successful. NMR spectra of the reaction mixtures of 1,1′-fc$(BBrNMe_2)_2$ and 1,1′-fc$(BBrMes)_2$ with **1a** showed even after extended reaction time and elevated temperature (toluene, 100 °C) only signals for the starting material. As discussed above for the reaction of silicon-bridged [1]ferrocenophanes with varying amounts of BCl_3, sterically very demanding substituents on boron appear to prevent this reaction. The diminished Lewis acidity, present in 1,1′-fc$(BBrNMe_2)_2$, apparently has a similar effect as even at elevated temperature no reaction was detected with **1a**.

Incorporation of functionalized ferrocenylboranes into organometallic polymer structures; synthesis of boron-containing poly(ferrocene)s: Previously, in collaboration with Braunschweig and co-workers we have shown that the thermal ROP of boron-bridged [1]ferrocenophanes **A** ($ER_x = BN(SiMe_3)_2$) results in cyclic oligomers and insoluble polymeric material.[13, 18] A possible method for incorporation of boron centers into ferrocene polymers without decrease of solubility was envisaged to be the formation of a poly(ferrocenylsilane)-ferrocenylborane hybrid material.[37] We have previously shown that the addition of hydride-functionalized silanes provides a facile route for molecular weight control in transition metal catalyzed ring-opening polymerizations of sila[1]ferrocenophanes.[38] Accordingly, transition metal catalyzed polymerization of [1]ferrocenophane **1a** in the presence of a hydrosilyl-functionalized diferrocenylborane was expected to result in a boron-containing poly(ferrocenylsilane).

Synthesis of Si–H functionalized diferrocenylborane 6: The chlorosilyl-substituted diferrocenylborane **2c** was reduced by treatment with two equivalents of Li[BEt_3H]. Compound **6** was obtained as an orange powder in 61 % yield. Selective reduction of the Si–Cl functionality was confirmed by an upfield shift of the ^{29}Si NMR signal in comparison to **2c** (**6**: δ = -18.7; **2c**: $\delta = 22.3$), as well as the presence of an upfield-shifted signal for the methyl group protons, which is split into a doublet by coupling to the Si-H proton (**6**: $\delta = 0.13$, $J_{H,H} = 4$ Hz; **2c**: $\delta = 0.34$). The ^{11}B NMR signal at $\delta = 59.5$ was found to be only slightly shifted in comparison to that of **2c** ($\delta = 60.5$) which indicated that the boryl group was unaffected under the reaction conditions.

Transition metal catalyzed ROP of dimethylsila[1]ferrocenophane 1a in the presence of 6: Transition metal catalyzed ring-opening polymerization (ROP) of sila[1]ferrocenophane **1a** (15 equiv) in the presence of **6** was performed in toluene using $PtCl_2$ as a catalyst (Scheme 5). After overnight reaction, the poly(ferrocene) **7** was isolated as a light orange powder after precipitation into hexanes in a yield of about 50 %. The structure of **7** was clearly confirmed by multinuclear NMR spectroscopy. The ^1H NMR spectrum of **7** (Figure 5) shows four signals in the methyl region, three of which are of equal and much lower intensity than the main peak assigned to interior main chain silicon centers (**b**, see Figure 5 for labeling) ($\delta = 0.55$; cf. **B** $ER_x = SiMe_2$: $\delta = 0.53$).[39] The terminal $SiMe_2H$ groups (**d**) give rise to a doublet at $\delta = 0.30$ and the remaining two signals at $\delta = 0.29$ and 0.41 may be attributed to the dimethylsilyl groups next to the borane (**a**), and the silane termini (**c**), respectively. The Cp region of the ^1H NMR spectrum shows two large singlets ($\delta = 4.27$, 4.10) corresponding to the Cp protons of the poly(ferrocenylsilane) chain (ferrocenes **II**) (cf. **B** $ER_x = SiMe_2$: $\delta = 4.25$, 4.10).[39] Signals of lower intensity are detected at $\delta = 4.58$, and $\delta = 4.55$ which can be assigned to the Cp rings nearest to the boron atom (**I**) (cf. **6**: $\delta = 4.57$, 4.51). Shoulders on the Cp resonances assigned to ferrocenes **II** were attributed to further switching groups (**III**, **IV**). Importantly, the resonance for the Si–H (**d**) proton was observed at $\delta = 4.69$, which is significantly downfield-shifted from that of the starting material ($\delta = 4.50$). The ^{29}Si NMR spectrum shows a dominant signal at $\delta = -6.7$ which was assigned to the $SiMe_2$ groups of the poly(ferroce-

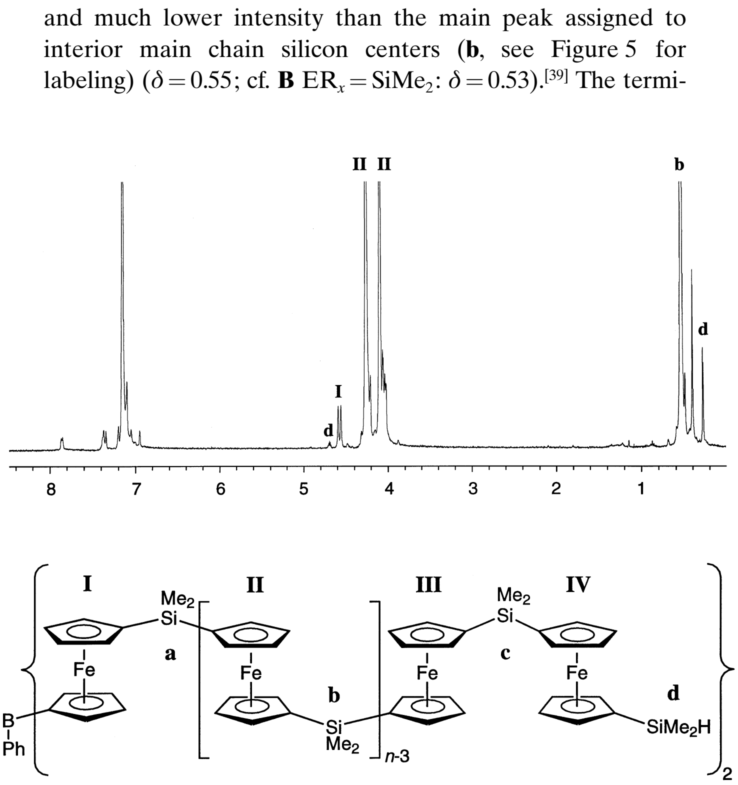
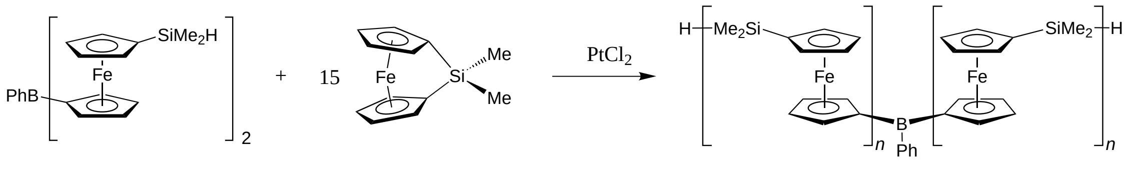


Figure 5. ^1H NMR spectrum of polymer **7** in C_6D_6 (n = ca. 17); resonances for environments II and b are only partially displayed.



6 **1a** **7**

Scheme 5. Synthesis of **7**.

nylsilane) main chain (**b**) (cf. **B** $ER_x = SiMe_2$: $\delta = -6.4$).[39] A signal of much lower intensity at $\delta = -6.8$ was attributed to a switching group. The signal due to the $SiMe_2H$ groups (**d**) was observed at $\delta = -18.7$ which is comparable to that found in other Si–H terminated poly(ferrocenyldimethylsilane)s.[38] No signal was observed in the ^{11}B NMR spectrum, which is most likely due to the extreme broadening that would be expected for a boron atom in this environment. The peak width at half height for **6** is 1000 Hz, and with incorporation of this moiety into a polymer chain, one would expect a shorter relaxation (T_1) time, and thus, an even broader signal. Importantly, the phenyl substituent on boron was clearly observed in both, ^1H and ^{13}C NMR spectra, supporting that the boryl group was indeed incorporated into the polymer structure **7**. ^1H NMR integration of the Me group resonances (**b** vs. **d**) showed that this material consists of a central boron atom with two chains of approximately 17 repeat units radiating from each side. This would indicate an absolute molecular weight (M_n) of approximately 8300 gmol^{-1}. GPC analysis of **7** indicated values of $M_n = 3500$, and $M_w = 6000$, with a PDI (PDI = polydispersity index M_w/M_n) of 1.72 which are significantly lower values. This is consistent with the results we obtain for other poly(ferocenylsilane) systems as the calibrations against polystyrene standards underestimate the molecular weight of ring-opened poly(ferrocene)s.[17a]

Conclusion

The reactions of silicon- and tin-bridged [1]ferrocenophanes with boron halides has led to the development of a new, mild synthetic route to functionalized monomeric and oligomeric ferrocenylboranes. Depending on the reaction stoichiometry and the bulk of the substituents on boron and the bridging element of the ferrocenophane, one or two, but not three ferrocene groups could be selectively attached to boron. The importance of subtle differences in steric bulk was indicated by the facile formation of a diferrocenylphenylborane (**2c**) from phenyldichloroborane, which can be ascribed to the lower steric bulk of a phenyl group in comparison to a ferrocenyl substituent. Essential for this reaction to occur is also the presence of a strongly Lewis acidic boron center as dimethylamino-substituted boranes did not undergo ring-opening reactions with the [1]ferrocenophanes. Interestingly, extension of the chemistry to bifunctional Lewis acids such as diborylferrocenes allowed for the selective introduction of multiple ferrocene groups to a Lewis acid functionalized molecular building block in a single step. Reduction of a chlorosilyl-substituted ferrocenylborane to give the silicon hydride end-functionalized species **6** allowed the facile incorporation of boron centers into the main chain of poly(ferrocenylsilane)s to generate novel hybrid materials **7**.

The new chemistry reported may be useful for the synthesis of ferrocene derivatives with Lewis acidic substituents for applications in molecular recognition and catalysis.[26–28] Current work in our laboratory involves the exploration of analogous ring-opening addition reactions of Lewis acids based on other main group and transition metals. Detailed studies on the properties of boron-bridged oligomers and polymers such as **7** and related materials are also underway.

Experimental Section

Materials and methods: The compounds TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine), $PhBCl_2$, and BCl_3 (1M in hexanes) were purchased from Aldrich and $PtCl_2$ from Strem and used without further purification. Dilithioferrocene · *n*TMEDA,[40] $fcSiMe_2$,[20] fcSiMePh,[41] $fcSnMes_2$,[4b] 1,1′-fc$(BBr_2)_2$,[30] 1,1′-fc$(B(NMe_2)Br)_2$,[14e] and 1,1′-fc$(BBrMes)_2$[42] were synthesized according to literature procedures. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box. Solvents were dried by standard methods and were distilled and stored over molecular sieves prior to use. The 300 and 400 MHz ^1H NMR spectra were recorded on either a Varian Gemini 300 or a Varian Unity 400 spectrometer. ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer (75.5 MHz) or a Varian Unity 400 spectrometer (100.4 MHz), ^{119}Sn NMR spectra (111.8 MHz) were recorded on a Varian Gemini 300 spectrometer, ^{11}B NMR spectra (160.4 MHz) were recorded on a Varian Unity 500 spectrometer, and ^{29}Si NMR spectra (79.3 MHz) on a Varian Unity 400 spectrometer. Two-dimensional NMR experiments were carried out on a Varian Unity 500 spectrometer. All solution ^1H and ^{13}C NMR spectra were referenced internally to protonated solvent shifts. ^{11}B NMR spectra were referenced externally to $BF_3 \cdot OEt_2$, ^{29}Si NMR spectra to $SiMe_4$ and ^{119}Sn NMR spectra to $SnMe_4$. Mass spectra were obtained with the use of a VG 70–250S mass spectrometer operating in an Electron Impact (EI) mode. The molecular weight of the polymer was estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6 K injector, ultrastyragel columns with a pore size between 10^3–10^5 Å, and a Waters 410 differential refractometer. A flow rate of 1.0 mL min^{-1} was used and the sample was dissolved in THF. Polystyrene standards were used for calibration purposes.

Reaction of five equivalents of BCl_3 with 1a: synthesis of 2a: A solution of **1a** (1.0 g, 4.1 mmol) in hexanes (50 mL) was added dropwise to a solution of BCl_3 (1.0M, 20 mL, 20 mmol) in hexanes (100 mL) at 0 °C. The reaction mixture was allowed to slowly warm up to room temperature and stirred for an additional hour. All volatile material was removed under vacuum leaving behind a dark red oil. Crystallization from hexanes at −55 °C, decanting of the solution and warming up to ambient temperature afforded **2a** (0.56 g; 40 %) as a dark red oil (95 % pure by NMR analysis). Attempts to further purify **2a** by distillation or crystallization were not successful and prevented accurate elemental analysis. For **2a**: ^1H NMR (400 MHz, C_6D_6, 20 °C): $\delta = 4.39, 4.37, 4.11, 3.93$ (ps. t, 4 × 2H; Cp), 0.36 (s, 6H; Me); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C): $\delta = 77.9, 76.6, 75.2, 74.7$ (Cp), 71.8 (*ipso*-Si-Cp), 2.7 (Me), not observed (*ipso*-B-Cp); $^{11}B\{^1H\}$ NMR (160.4 MHz, C_6D_6, 20 °C): $\delta = 51.7$ ($h_{1/2} = 300$ Hz); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C): $\delta = 22.6$; MS (70 eV, EI): *m/z* (%): 358 (100) [M^+].

Reaction of BCl_3 with two equivalents of 1a: synthesis of 2b: A solution of **1a** (2.50 g, 10.3 mmol) in hexanes (50 mL) was added dropwise to a solution of BCl_3 in hexanes (1.0M, 5.2 mL, 5.2 mmol) at −30 °C. The reaction mixture was allowed to slowly warm up to room temperature, stirred for 1 h, and filtered through a fritted glass disk. Dark red crystals of **2b** (2.35 g, 76 %) were obtained from the filtrate at −30 °C. For **2b**: ^1H NMR (400 MHz, C_6D_6, 20 °C): $\delta = 4.68, 4.47$ (ps. t, J(H,H) = 1.2 Hz, 2 × 4H; Cp), 4.22, 4.03 (ps. t, J(H,H) = 1.2 Hz, 2 × 4H; Cp), 0.42 (s, 12H; Me); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C): $\delta = 76.5, 75.9, 74.6, 73.9$ (Cp), 70.7 (*ipso*-Si-Cp), 2.9 (Me), not observed (*ipso*-B-Cp); $^{11}B\{^1H\}$ NMR (160.4 MHz, C_6D_6, 20 °C): $\delta = 56.5$ ($h_{1/2} = 1000$ Hz); ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C): $\delta = 22.8$; MS (70 eV, EI): *m/z* (%): 600 (100) [M^+], 585 (6) [$M^+ - CH_3$], 565 (3) [$M^+ - Cl$]; elemental analysis (%) for $C_{24}H_{28}BCl_3Fe_2Si_2$ (601.5): calcd: C 47.92, H 4.69; found: C 48.41, H 4.72.

Reaction of $PhBCl_2$ with two equivalents of 1a: synthesis of 2c: A solution of phenyldichloroborane (1.64 g, 10.3 mmol) in hexanes (25 mL) was added dropwise to a solution of **1a** (5.00 g, 20.6 mmol) in hexanes (100 mL) at room temperature. The reaction mixture was allowed to stir for a further 30 min, filtered through a fritted glass disk, and washed twice with hexanes. The residue was dried under vacuum to give **2c** (4.8 g; 72 %) as an orange microcrystalline solid. For **2c**: ^1H NMR (300 MHz, C_6D_6, 20 °C): $\delta = 7.71$ (m, 2H; *ortho*-Ph), 7.29 (m, 3H; *meta*-Ph, *para*-Ph), 4.53 (br., 8H; Cp), 4.16 (ps. t, J(H,H) = 1.2 Hz, 4H; Cp), 3.98 (ps. t, J(H,H) = 1.2 Hz, 4H; Cp), 0.34 (s, 12H; Me); $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 20 °C): $\delta = 133.2, 128.9,$

127.4 (Ph), 78.2, 75.6, 73.9, 73.3 (Cp), 69.9 (*ipso*-Si-Cp), 2.7 (Me), not observed (*ipso*-Ph), (*ipso*-B-Cp); ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6, 20°C): $\delta = 60.5$ ($h_{1/2} = 1000$ Hz); ^{29}Si NMR (79.3 MHz, C_6D_6, 20°C): $\delta = 22.3$; MS (70 eV, EI): *m/z* (%): 642 (100) [M^+]; elemental analysis (%) for $C_{30}H_{33}BCl_2Fe_2Si_2$ (643.2): calcd C 56.02, H 5.17; found C 56.19, H 5.08.

Reaction of five equivalents of BCl_3 with 1b: synthesis of 2d: A solution of **1b** (0.25 g, 0.82 mmol) in hexanes (25 mL) was added dropwise to a solution of BCl_3 (1.0 M, 4.2 mL, 4.2 mmol) in hexanes (25 mL) at −30°C. The reaction mixture was allowed to slowly warm up to room temperature and stirred for an additional hour. All volatile material was removed under vacuum leaving behind a red oil. Crystallization from hexanes at −55°C, decanting of the solution and warming up to ambient temperature afforded **2d** (0.12 g; 35%) as a dark red oil (95% pure by NMR analysis). Attempts to further purify **2d** by distillation were unsuccessful and prevented accurate elemental analysis. For **2d**: ^{1}H NMR (400 MHz, C_6D_6, 20°C): $\delta =$ 7.53, 7.13 (m, 5H; Ph), 4.44 (m, 2H; Cp), 4.37 (m, 2H; Cp), 4.15 (m, 2H; Cp), 4.07, 3.98 (s, 2 × 1H; Cp), 0.64 (s, 3H; Me); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 20°C): $\delta = 135.4$ (*ipso*-Ph), 133.7, 130.7, 128.3 (Ph), 78.3, 78.2, 76.8, 76.8, 75.8, 75.7 (Cp), 75.1 (*ipso*-B-Cp), 74.9, 74.9 (Cp), 70.7, (*ipso*-Si-Cp), 1.3 (Me); ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6, 20°C): $\delta = 51.6$ ($h_{1/2} = 500$ Hz); ^{29}Si NMR (79.3 MHz, C_6D_6, 20°C): $\delta = 12.8$; MS (70 eV, EI): *m/z* (%): 420 (100) [M^+].

Reaction of BCl_3 with four equivalents of 1a: A solution of BCl_3 in hexanes (2.6 mL, 1.0 M, 2.6 mmol) was added dropwise to a solution of **1a** (2.5 g, 10.3 mmol) in toluene (200 mL) at room temperature. The reaction mixture was kept under reflux for 72 h. Analysis by multinuclear NMR spectroscopy showed the formation of a complex mixture of products including the chlorodiferrocenylborane **2b**.

Hydrolysis of 2b: Orange crystals of compound **3** were obtained from a toluene solution of the chlorodiferrocenylborane **2b** with trace amounts of water at −55°C. Single crystals suitable for an X-ray diffraction study were grown from toluene at −30°C. For **3**: ^{1}H NMR (400 MHz, C_6D_6, 20°C): $\delta = 4.78$ (ps.t, J(H,H) = 1.2 Hz, 8H; B-Cp-H2,5), 4.47 (m, 16H; B-Cp-H3,4, Si-Cp-H2,5), 4.22 (ps.t, J(H,H) = 1.2 Hz, 8H; Si-Cp-H3,4), 0.50 (s, 24H; Me); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 20°C): $\delta = 75.4$, 73.9, 73.9, 73.1 (Cp), 70.7 (*ipso*-Si-Cp), 2.9 (Me), not observed (*ipso*-B-Cp); ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6, 20°C): $\delta = 45.3$ ($h_{1/2} = 1500$ Hz); ^{29}Si NMR (79.3 MHz, C_6D_6, 20°C): $\delta = 22.8$; MS (70 eV, EI): *m/z* (%): 1148 (100) [M^+]; elemental analysis (%) for $C_{48}H_{56}B_2Cl_4Fe_4OSi_4$ (1148.1): calcd C 50.21, H 4.92; found C 50.15, H 5.03.

Reaction of BCl_3 with 1c: synthesis of 4a: BCl_3 (0.50 mL, 1 M in hexanes, 0.50 mmol) was added quickly to a solution of **1c** (272 mg, 0.50 mmol) in toluene/hexanes (1 mL/4 mL) at 0°C. The reaction mixture was slowly warmed to ambient temperature, allowed to stir for 30 min, and a small amount of insoluble material was removed by filtration through glass wool. The resulting solution was kept at −30°C to give **4a** (0.19 g, 58%) as a red crystalline solid. For **4a**: ^{1}H NMR (300 MHz, C_6D_6, 20°C): $\delta = 6.65$ (s/d, J($^{117/119}$Sn, H) = 26 Hz, 4H; *meta*-Mes), 4.66, 4.45 (ps.t, J(H,H) = 1.2 Hz, 2 × 2H; B-Cp), 4.32, 4.25 (ps.t, J(H,H) = 1.2 Hz, 2 × 2H; Sn-Cp), 2.44 (s/d, J($^{117/119}$Sn, H) = 8 Hz, 12H; *ortho*-Me), 2.03 (br., 6H; *para*-Me); ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 20°C): $\delta = 143.8$ (s/d, J($^{117/119}$Sn,^{13}C) = 46 Hz; *ortho*-Mes), 140.0 (*para*-Mes), 139.2 (*ipso*-Mes), 129.4 (s/d, J($^{117/119}$Sn,^{13}C) = 59 Hz; *meta*-Mes), 80.2 (*ipso*-Sn-Cp), 78.5, 77.0 (B-Cp), 76.3 (s/d, J ($^{117/119}$Sn,^{13}C) = 68 Hz; Sn-Cp), 74.6 (s/d, J($^{117/119}$Sn,^{13}C) = 52 Hz; Sn-Cp), 25.1 (s/d, J($^{117/119}$Sn,^{13}C) = 41 Hz; *ortho*-Me), 21.0 (*para*-Me), not observed (*ipso*-B-Cp); ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6, 20°C): $\delta = 51.9$ ($h_{1/2} = 500$ Hz); ^{119}Sn NMR (111.8 MHz, C_6D_6, 20°C): $\delta = -34.1$; MS (70 eV, EI): *m/z* (%): 658 (100) [M^+], 576 (32) [$M^+ - HBCl_2$]; elemental analysis (%) for $C_{28}H_{30}BCl_3FeSn$ (658.3): calcd: C 51.09, H 4.59; found: C 49.40, H 4.70.

Reaction of $PhBCl_2$ with 1c: synthesis of 4b: Phenyldichloroborane (75 mg, 0.47 mmol) was added quickly to a solution of **1c** (255 mg, 0.47 mmol) in toluene (2 mL) at 0°C. The reaction mixture was slowly warmed to ambient temperature, allowed to stir for 30 min, and a small amount of insoluble material was removed by filtration through glass wool. All volatile material was removed under vacuum and the crude product was redissolved in hexanes (3 mL). The resulting solution was kept at −30°C to give **4b** (0.24 g, 73%) as a dark red crystalline solid. For **4b**: ^{1}H NMR (300 MHz, C_6D_6, 20°C): $\delta = 8.00$ (m, 2H; *ortho*-Ph), 7.28–7.14 (m, 3H; *meta*-Ph, *para*-Ph), 6.64 (s/d, J($^{117/119}$Sn,H) = 26 Hz, 4H; *meta*-Mes), 4.78, 4.67 (ps.t, J(H,H) = 1.2 Hz, 2 × 2H; B-Cp), 4.30, 4.26 (ps.t, J(H,H) = 1.2 Hz, 2 × 2H; Sn-Cp), 2.43 (s/d, J($^{117/119}$Sn,H) = 8 Hz, 12H; *ortho*-Me), 2.05 (br., 6H; *para*-Me); ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 20°C): $\delta = 143.8$ (s/d, J($^{117/119}$Sn,^{13}C) = 46 Hz; *ortho*-Mes), 139.8 (*para*-Mes), 139.4 (*ipso*-Mes), 135.1 (*ortho*-Ph), 131.9 (*para*-Ph), 129.3 (s/d, J($^{117/119}$Sn,^{13}C) = 58 Hz; *meta*-Mes), 128.1 (*meta*-Ph), 79.6 (*ipso*-Sn-Cp), 78.0, 77.9 (B-Cp), 75.8 (s/d, J($^{117/119}$Sn,^{13}C) = 70 Hz; Sn-Cp), 74.2 (s/d, J($^{117/119}$Sn,^{13}C) = 52 Hz; Sn-Cp), 25.1 (s/d, J($^{117/119}$Sn,^{13}C) = 41 Hz; *ortho*-Me), 21.0 (*para*-Me); not observed (*ipso*-B-Cp, *ipso*-B-Ph); ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6, 20°C): 58.7 ($h_{1/2} = 1000$ Hz); ^{119}Sn NMR (111.8 MHz, C_6D_6, 20°C): $\delta = -32.7$; MS (70 eV, EI): *m/z* (%): 700 (100) [M^+]; elemental analysis (%) for $C_{34}H_{35}BCl_2FeSn$ (699.9): calcd: C 58.35, H 5.04; found: C 58.39, H 5.36.

Reaction of 1,1′-fc(BBr_2)$_2$ with two equivalents of 1a: synthesis of 5: A solution of 1,1′-fc(BBr_2)$_2$ (1.05 g, 2.00 mmol) in toluene (20 mL) was added dropwise to a solution of **1a** (0.99 g, 4.11 mmol) in toluene (50 mL) at −20°C. The reaction mixture was allowed to slowly warm up to room temperature, stirred for 3 h and filtered through a fritted glass disk. Hexanes (35 mL) was added and the reaction mixture was kept at −55°C to give **5** (1.1 g, 54%) as a dark red microcrystalline solid. For **5**: ^{1}H NMR (400 MHz, C_6D_6, 20°C): $\delta = 4.68$ (ps.t, J(H,H) = 1.2 Hz, 4H; Cp^{A}), 4.60 (ps.t, J(H,H) = 2 Hz, 4H; Cp^{B}), 4.53 (ps.t, J(H,H) = 2 Hz, 4H; Cp^{A}), 4.45 (ps.t, J(H,H) = 2 Hz, 4H; Cp^{B}), 4.18 (ps.t, J(H,H) = 2 Hz, 4H; Cp^{C}), 3.98 (ps.t, J(H,H) = 2 Hz, 4H; Cp^{C}), 0.50 (s, 12H; Me); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 20°C): $\delta = 78.4$ (Cp^{A}), 77.6 (Cp^{A}), 77.5 (Cp^{B}), 76.5 (Cp^{B}), 74.7 (Cp^{C}), 74.3 (Cp^{C}), 70.7 (*ipso*-Cp^{C}), 3.7 (Me), not observed (*ipso*-B-Cp^{A,B}); the *ipso*-B-Cp signals were observed in the HMBC spectrum (499.8 MHz) in form of cross peaks with the proton resonances of the respective Cp rings: $\delta = 73.5$ (*ipso*-B-Cp^{A}), 72.5 (*ipso*-B-Cp^{B}); ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6, 20°C): $\delta = 56.5$ ($h_{1/2} = 1000$ Hz); ^{29}Si NMR (79.3 MHz, C_6D_6, 20°C): $\delta = 18.5$; MS (70 eV, EI): *m/z* (%): 1010 (100) [M^+], 686 (30) [$M^+ -$ HfcSiMe$_2$Br], 598 (85) [$MH^+ -$ BBr(fcSiMe$_2$Br)]; elemental analysis (%) for $C_{34}H_{36}B_2Br_4Fe_3Si_2$ (1009.6): calcd: C 40.45, H 3.59; found: C 39.48, H 4.51. The slightly inaccurate analysis for compound **5** may be attributed to the extreme moisture sensitivity of this compound; however, incomplete combustion and formation of boron-containing ceramics may also play a role.

Attempted reaction of 1,1′-fc(B(NMe$_2$)Br)$_2$ with two equivalents of 1a: A solution of 1,1′-fc(B(NMe$_2$)Br)$_2$ (0.94 g, 2.06 mmol) in toluene (1 mL) was added dropwise to a solution of **1a** (0.99 g, 4.11 mmol) in toluene (3 mL) at ambient temperature. ^{1}H NMR analysis (C_6D_6) after heating the solution to 100°C for 2 h showed only signals for the starting materials.

Attempted reaction of 1,1′-fc(BBrMes)$_2$ with two equivalents of 1a: A mixture of 1,1′-fc(BBrMes)$_2$ (60 mg, 100 μmol) and **1a** (48 mg, 200 μmol) was dissolved in toluene (0.6 mL) at ambient temperature. ^{1}H NMR analysis (C_6D_6) after heating the solution to 65°C for 2 h showed only signals for the starting materials.

Synthesis of 6: A solution of Li[BEt$_3$H] (3.5 mL, 3.5 mmol) was added dropwise to a stirred solution of **2b** (1.0 g, 1.7 mmol) in THF (250 mL) at −78°C. The reaction mixture was allowed to stir overnight at room temperature prior to removal of all volatile material under high vacuum. The residue was extracted with toluene, and the solvent was removed from the filtrate to give **6** as an orange solid (yield: 0.60 g; 61%; purity: 95%). For **6**: ^{1}H NMR (400 MHz, C_6D_6, 20°C): $\delta = 7.79$ (m, 2H; *ortho*-Ph), 7.32 (m, 3H; *meta*-Ph, *para*-Ph), 4.57 (ps.t, J(H,H) = 1.6 Hz, 4H; Cp), 4.52–4.49 (m, 6H; Si-H, Cp), 4.20 (ps.t, J(H,H) = 1.6 Hz, 4H; Cp), 3.98 (ps.t, J(H,H) = 1.6 Hz, 4H; Cp), 0.13 (d, J(H,H) = 4 Hz, 12H; Me); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 20°C): $\delta = 146.0$ (*ipso*-Ph), 133.3, 128.6, 127.3 (Ph), 78.1, 75.2, 74.4, 72.8 (Cp), 69.1 (*ipso*-Si-Cp), −3.2 (Me), not observed (*ipso*-B-Cp); ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6, 20°C): $\delta = 59.5$ ($h_{1/2} =$ 1000 Hz); ^{29}Si NMR (79.3 MHz, C_6D_6, 20°C): $\delta = -18.7$; MS (70 eV, EI): *m/z* (%): 574 (31) [M^+], 332 (38) [$M^+ -$ HMe$_2$SiFc], 242 (80) [fcSiMe$_2^+$].

Preparation of boron-containing poly(ferrocenylsilane) 7: A catalytic amount of PtCl$_2$ (ca. 0.1 wt.%) was added to a solution of **6** (50 mg, 87 μmol, 1 equiv) and **1a** (0.32 g, 1.3 mmol, 15 equiv) in toluene (20 mL) and stirred at room temperature. A color change from red to dark orange was noted after 0.5 h, and the reaction mixture was allowed to stir for a further 12 h in order to ensure complete reaction. The solution was reduced in volume, and the product precipitated twice into hexanes. The resulting light orange powder (**7**) was dried under vacuum (0.18 g; 49%). For **7**: ^{1}H NMR (400 MHz, C_6D_6, 20°C): $\delta = 7.84$ (m, 2H; *ortho*-Ph), 7.37 (m, 3H;

Table 4. Crystal data and structure refinement.

	2b ClB(fcSiMe$_2$Cl)$_2$	**3** [(fcSiMe$_2$Cl)$_2$B]$_2$O	**4a** Cl$_2$BfcSnMes$_2$Cl
formula	$C_{24}H_{28}BCl_3Fe_2Si_2$	$C_{48}H_{56}B_2Cl_4Fe_4OSi_4$	$C_{28}H_{30}BCl_3FeSn$
M_r	601.50	1148.11	658.22
T [K]	150.0(1)	150.0(1)	100.0(1)
crystal system	orthorhombic	triclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	*P*21/*c*
a [Å]	11.0823(2)	10.5444(2)	9.7660(4)
b [Å]	10.9321(3)	15.0013(5)	15.1067(8)
c [Å]	21.3922(5)	17.4139(6)	18.8598(7)
α [°]	90	112.678(1)	90
β [°]	90	96.852(2)	103.304(3)
γ [°]	90	91.890(2)	90
V [Å^3]	2591.73(10)	2514.0(1)	2707.8(2)
Z	4	2	4
ρ_{calcd} [g cm^{-1}]	1.542	1.517	1.615
$\mu(Mo_{K\alpha})$ [mm^{-1}]	1.533	1.475	1.770
$F(000)$	1232	1180	1320
crystal size [mm]	0.34 × 0.32 × 0.28	0.27 × 0.25 × 0.20	0.32 × 0.22 × 0.22
θ range [°]	4.12–26.36	4.10–26.37	4.20–25.02
limiting indices	$0 \leq h \leq 13, 0 \leq k \leq 13, -26 \leq l \leq 0$	$0 \leq h \leq 13, -18 \leq k \leq 18, -21 \leq l \leq 21$	$0 \leq h \leq 11, 0 \leq k \leq 17, -22 \leq l \leq 21$
reflns collected	16429	24233	11977
independent reflns	2637 ($R_{int} = 0.053$)	10151 ($R_{int} = 0.065$)	4735 ($R_{int} = 0.032$)
GoF on F^2	1.229	1.033	1.020
$R1$[a] [$I > 2\sigma(I)$]	0.0445	0.0544	0.0316
$wR2$[b] (all data)	0.1024	0.1472	0.0817
peak/hole [e Å^{-3}]	0.456/−0.662	0.988/−0.577	0.782/−0.486

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

meta-Ph, *para*-Ph), 4.69 (m, 2H; Si-H), 4.58, 4.55 (br.s, 2 × 4H; B-Cp^{I}), 4.27, 4.21, 4.10, 4.06 (m, $16(n-1)$H; Cp^{II,III,IV}), 0.55–0.40 (m, $12(n-1)$H; Me^{a,b,c}), 0.29 (d, J(H,H) = 4 Hz, 12H; Me^{d}); see Figure 5 for numbering (n = ca. 17); ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6, 20 °C): $\delta = 146.2$ (*ipso*-Ph), 133.4, 128.7, 127.4 (Ph), 78.0 (B-Cp), 75.3 (B-Cp), 74.2 (B-Cp), 73.6 (Si-Cp), 72.8 (B-Cp), 71.8 (Si-Cp), 68.6 (*ipso*-Si-Cp), −0.5 (SiMe$_2$), −2.8 (SiMe$_2$H), not observed (*ipso*-B-Cp); ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6, 20 °C): *no signal observed*; ^{29}Si NMR (79.3 MHz, C_6D_6, 20 °C): $\delta = -6.7$ (SiMe$_2$), −6.8 (SiMe$_2$), −18.7 (SiMe$_2$H); M_n = 8,300 (from ^{1}H NMR spectrum); M_n = 3500, M_w = 6000, PDI = 1.72 (from GPC).

X-ray structural characterization: A summary of selected crystallographic data is given in Table 4. Data were collected on a Nonius KappaCCD diffractometer using graphite monochromatic $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). A combination of 1° phi and omega (with kappa offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using Denzo-SMN package.[43] The structures were solved and refined using the SHELXTL\PC V5.1 package.[44] Refinement was done by full-matrix least-squares based on F^2 using all data (negative intensities included). Hydrogen atoms were included in calculated positions.For **2b**: In space group P*bca* with $Z = 4$ the molecules must lie across one of the types of inversion centers. Since the molecules do not possess crystallographic inversion symmetry they are disordered. The cyclopentadienyl rings (C(6) through C(10) and C(6*) through C(10*)) and the boron and chlorine atoms, by which they are bridged, are disordered about the inversion center with occupancies of 50:50 but all other atoms are ordered with occupancies of 1.0. For **3**: The chlorodimethylsilyl group is rotationally disordered by approximately 60° about the Si(3)−C(29) bond. The atoms C(45), C(46), and Cl(3) are disordered over two sites with occupancies of 0.5. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-140049, CCDC-140050, and CCDC-140051. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Acknowledgement

We thank the donors of the Petroleum Research Fund (PRF) administered by the American Chemical Society, for financial support of this work. We also wish to acknowledge a DFG postdoctoral fellowship for F.J., a University of Toronto Open Fellowship for A.B., and I. M. is grateful to NSERC for an E. W. R. Steacie Fellowship (1997–1999), the University of Toronto for a McLean Fellowship (1997–2003), and the Ontario Government for a PREA Award (1999–2003).

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Received: February 7, 2000 [F2283]