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Ferrocene-Based Heteronuclear Bidentate Lewis Acids via Highly Selective *ortho*-Borylation of 1,1′-Bis(trimethylstannyl)ferrocene

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A new type of ferrocene-based heteronuclear bidentate Lewis acid with both Lewis acidic centers attached to the same cyclopentadienyl (Cp) ring is reported. Borylation of 1,1′-bis(trimethylstannyl)ferrocene (**1**) with BCl_3 in hexanes at −78 °C occurs with high selectivity at the α-position to give 1-(Me_3Sn)-2-(Cl_2B)fc (**2a-Cl**; fc = ferrocenediyl) as the major product in ca. 87% spectroscopic yield. Only minor amounts of the two other isomers, the 1-stannyl-3-boryl- (**2b-Cl**) and the 1-stannyl-1′-borylferrocene (**2c-Cl**), are observed. The reaction rate and selectivity strongly depend on the steric and electronic properties of the electrophile. With the bulkier electrophile $C_6F_5BCl_2$ larger amounts of the 1,3-product, 1-(Me_3Sn)-3-(C_6F_5-ClB)fc (**2b-Pf**; ca. 40%), form in addition to the 1,2-isomer 1-(Me_3Sn)-2-(C_6F_5ClB)fc (**2a-Pf**; ca. 60%). Use of the weaker electrophile $PhBCl_2$ results in a significantly lower reaction rate. Treatment of **1** with excess borane in hexanes yields 1-($ClMe_2Sn$)-2-(Cl_2B)fc (**3a-Cl**) and 1-($ClMe_2Sn$)-2-(ClPhB)fc (**3a-Ph**) as a result of preferred cleavage of an Sn−Me over the Sn−Cp bond in **2a-Cl** and **2a-Ph**. Facile Sn−Me bond cleavage also occurs during thermal treatment of **2a-Cl** (50 °C) and **2a-Ph** (80 °C), resulting in the rearranged species 1-($ClMe_2$-Sn)-2-(ClMeB)fc (**4a-Cl**) and 1-($ClMe_2Sn$)-2-(PhMeB)fc (**4a-Ph**). The heteronuclear bidentate Lewis acids **3a-Cl**, **3a-Ph**, **4a-Cl**, and **4a-Ph** were fully characterized by ^{1}H, ^{13}C, ^{11}B, and ^{119}Sn NMR spectroscopy, mass spectrometry, and elemental analysis. Single-crystal X-ray diffraction analyses of **4a-Cl** and **4a-Ph** reveal a dip angle between the Cp plane and the Cp−B vector of 13.8(2)° and 12.2(3)°, respectively, indicating a significant iron−boron interaction. The tin centers display a distorted trigonal bipyramidal arrangement as a result of short contacts to the boron-bound chloride (**4a-Cl**) and phenyl (**4a-Ph**) substituent, respectively. The ^{119}Sn NMR signals are upfield-shifted by 19−35 ppm relative to $FcSnMe_2$-Cl, suggesting a similar interaction to be present in solution. The presence of two Lewis acidic substituents on ferrocene is further reflected in a bathochromic shift and increase in the intensity of the visible absorption bands relative to ferrocene.

Introduction

Lewis acids play a vital role in many aspects of modern organic synthesis including polymerization reactions.[1] They are well-established and highly useful reagents in organic transformations involving carbonyl compounds such as Diels−Alder reactions, aldol condensations, or Michael additions and serve as cocatalysts in Ziegler−Natta polymerization. However, the use of bi- and multifunctional Lewis acids has been studied only recently.[2] This is surprising considering that their counterparts, the bi- and multidentate Lewis bases, play a major role as ligands in various transition metal catalyzed processes.

First investigations of bidentate Lewis acids were directed at the complexation of anions and neutral Lewis bases through chelating difunctional Lewis acids. Katz and co-workers showed in 1985 that 1,8-bis(dimethylboryl)naphthalene ("hydride sponge") binds hydride ions in a chelating fashion.[3] At the same time, Wuest and co-workers found that chloride ions could bridge two mercury centers in a complex with 1,2-bis(chloromercury)benzene.[4] The first structural evidence for chelating complexation between a bifunctional Lewis acid and a carbonyl functionality was presented in 1992 by Wuest and co-workers.[5] In this case, an interaction

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(2) For recent reviews see: (a) Kuivila, H. G. *In Heteroat. Chem.* [Int. Conf.] **1990**, 245. (b) Katz, H. E. *Inclusion Compd*. **1991**, *4*, 391. (c) Kaufmann, D. E.; Otten, A. *Angew. Chem*. **1994**, *106*, 1917. (d) Vaugeois, J.; Simard, M.; Wuest, J. D. *Coord. Chem. Rev.* **1995**, *145*, 55. (e) Schmidtchen, F. P.; Berger, M. *Chem. Rev*. **1997**, *97*, 1609. (f) Beer, P. D.; Smith, D. K. Prog. *Inorg. Chem*. **1997**, *46*, 11. (g) Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun*. **1998**, 443. (h) Wuest, J. D. *Acc. Chem. Res*. **1999**, *32*, 81. (i) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed*. **2001**, *40*, 486. For reviews on the use of bifunctional Lewis acids in Ziegler−Natta polymerization see: (j) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev*. **2000**, *100*, 1391. (k) Piers, W. E.; Irvine, G. J.; Williams, V. C. *Eur. J. Inorg. Chem*. **2000**, *10*, 2131.

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10.1021/om0204890 CCC: $22.00
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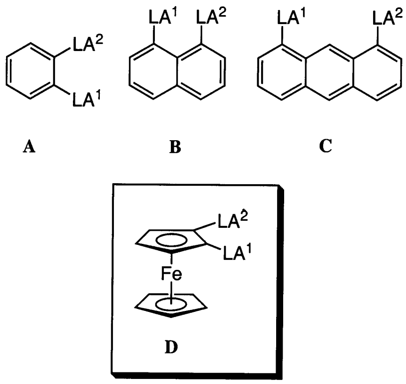
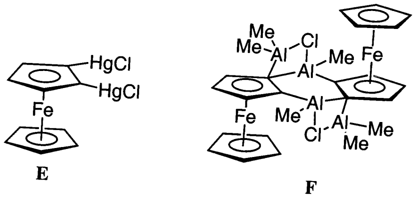
Chart 1



A **B** **C**

D

Chart 2



E **F**

between two aluminum centers and a carbonyl group is promoted by intramolecular chelation. This discovery led to a series of studies on the reactivity of bifunctional Lewis acids in organic transformations. Indeed, improved activation and increased stereoselectivity with bifunctional Lewis acids relative to their monofunctional counterparts have been reported.[6−8] Until now the variety of backbones for bidentate Lewis acids has been limited almost exclusively to Wuest's 1,2-phenylenediyl (**A**),[4,6] Katz's 1,8-naphthalenediyl (**B**),[3,8−10] and anthracenediyl (**C**)[11] bridges and closely related entities. These compounds have in common a very rigid two-dimensional backbone, in which the Lewis acidic centers are in well-defined positions within the plane of the molecule. We were intrigued by the fact that the Lewis acidic centers in 1,2-dimetalated ferrocenes (**D**) would *not* be part of a mirror plane, but rather at the "edge" of a cylindrical molecule, providing a unique geometric environment for the Lewis acidic centers.[12] The redox chemistry of the central iron atom in ferrocenes is an additional attractive feature, as it may provide an opportunity to fine-tune the Lewis acidity of these complexes.

Directed electrophilic aromatic substitution may be envisioned as a possible route to bidentate Lewis acids **D**.[13] Indeed, the directed synthesis of 1,2-disubstituted ferrocenes via lithiation of dimethylaminomethylferrocenes and related species has proven highly useful in the design and synthesis of planar chiral bifunctional amines and phosphines.[14] The dimethylaminomethyl group acts as an anchoring group directing the lithiation to the *ortho*-position. However, in the absence of this type of interaction, the *ortho*-selectivity in electrophilic aromatic substitutions is typically rather low.[15] The situation is even more complex when ferrocene is used as the substrate. The presence of the first electron-withdrawing group (LA^1) in **D** is expected to direct attack of the second electrophile to the other (more electron-rich) Cp ring. It is therefore not surprising that only a few reports on 1,2-dimetalated ferrocenes have appeared in the literature. The 1,2-bis(chloromercury)ferrocene **E** was first discovered as a byproduct in the mercuration of ferrocene with mercuric acetate by Rausch and co-workers in 1974.[16] However, the low yield of only ca. 2% limits the utility of this intriguing species. Another report on a 1,2-dimetalated ferrocene compound, the dialuminated species **F**, appeared in the literature shortly thereafter. Compound **F** was observed as one of the products in the reaction of 1,1′-bis(chloromercury)ferrocene with Me_2AlCl, and the structure was determined by X-ray crystallography.[17] However, **F** was not further characterized, nor were the properties of this unusual dimer studied. Cunningham and co-workers have recently reported that Friedel−Crafts acetylation of 1,1′-bis(trimethylsilyl)- and 1,1′-bis(tributylstannyl)ferrocene using acetyl chloride in the presence of $AlCl_3$ at −70 °C results in mixtures of three regioisomers, the 1,1′-, 1,2-, and 1,3-silylacetylferrocenes (31.0%, 15.5%, 53.0%) and the 1,1′-, 1,2-, and 1,3-stannylacetylferrocenes (28.5%, 13.0%, 44.0%), respectively.[18] This unusual observation encouraged us to investigate the reactivity of 1,1′-bis(trimethylstannyl)ferrocene (**1**) toward inorganic electrophiles, anticipating that reaction of **1** with a *stoichiometric* amount of group 13 halides might lead to similar products including the desired 1,2-dielement substituted ferrocenes.[19]

Results and Discussion

Selective *ortho*-Borylation of 1,1′-Bis(trimethylstannyl)ferrocene (1). 1,1′-Bis(trimethylstannyl)fer-

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(13) For an alternative approach via 1,2-dibromoferrocene see: Butler, I. R.; Drew, M. G. B. *Inorg. Chem. Commun.* **1999**, *2*, 234.

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(15) Notable exceptions include reactions involving the replacement of a sterically demanding group by a proton (release of steric strain leads to steric acceleration) and the formation of an intermediate complex between the solvent and the substituent, thereby leading to a strong +I effect of this group. The latter effect is for example believed to be responsible for the observed *ortho*-selectivity in the nitration of phenylboronic acid. See: Taylor, R. *Electrophilic Aromatic Substitution*; John Wiley & Sons: Chichester, 1990. For recent studies of regioselective electrophilic aromatic substitution reactions, see for example: (a) Yonehara, F.; Kido, Y.; Yamaguchi, M. *Chem. Commun.* **2000**, 1189. (b) Herrlich, M.; Mayr, H.; Faust, R. *Org. Lett.* **2001**, *3*, 1633. (c) Herrlich, M.; Hampel, N.; Mayr, H. *Org. Lett.* **2001**, *3*, 1629.

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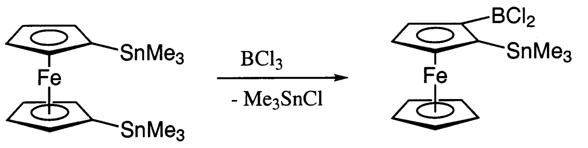
Scheme 1. Reaction of 1 with Boron Trichloride



1 **2a-Cl**

rocene (**1**)[20,21] was reacted with 1 equiv of BCl_3 in hexanes at −78 °C (Scheme 1). When the mixture was stirred at −78 °C for 1 h, the color of the solution gradually turned from light orange to red. The reaction mixture was allowed to slowly warm to 0 °C, and all volatile material was removed under reduced pressure (10^{-3} Torr). When the crude product was analyzed by ^{1}H NMR spectroscopy, we found to our surprise that the 1,2-isomer, **2a-Cl**,[22] was formed as the major product in an unusually high spectroscopic yield of ca. 87% (Scheme 1).

Careful analysis of the NMR data of the crude reaction mixture revealed formation of small amounts of the two other regioisomers, the stannylborylferrocenes **2b-Cl** and **2c-Cl** (Table 1). The 1,3-disubstituted isomer (**2b-Cl**) was formed in ca. 10% spectroscopic yield, whereas only trace amounts of the 1-stannyl-1′-borylferrocene (**2c-Cl**) were observed. The oily nature of the product and the inherent sensitivity toward air and moisture prevented separation of the isomers by crystallization or column chromatography. However, using 2D NMR spectroscopic techniques (dqfCOSY, HMQC, NOESY), we were able to conclusively assign the observed NMR signals to the three different isomers and to fully characterize each isomer by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy.

Three sets of signals were observed in the ^{1}H NMR spectrum of the isomer mixture **2-Cl** (Figure 1). The most striking feature is a large singlet with the intensity of five protons in the region typical of unsubstituted ferrocene Cp rings ($\delta = 3.93$). This signal can be attributed to the major isomer **2a-Cl** and corresponds to a set of three Cp resonances ($\delta = 4.46$, 4.53, 4.71) in the expected range for downfield-shifted protons attached to a boron-substituted Cp ring.[23] Particularly insightful is the coupling pattern consisting of double doublets for the resonances at $\delta = 4.46$ and 4.71 ($J =$ 1.2/2.4 Hz) and a pseudotriplet for the resonance at $\delta = 4.53$ ($J = 2.4$ Hz). The observed coupling constant of 2.4 Hz for the pseudotriplet is consistent with a ^{3}J(H, H) coupling in ferrocene species[16] and clearly indicates the formation of a 1,2-disubstituted species. A detailed analysis of the three Cp signals reveals satellites due to coupling to a tin center. The coupling constant of $J(^{117/119}\mathrm{Sn}, \mathrm{H}) = 13$ Hz for the resonance at $\delta = 4.46$ is considerably larger than the coupling constants for the other two signals ($J = 5$ and $J = 6$ Hz). Consequently, the double doublet at $\delta = 4.46$ may be attributed to the Cp proton adjacent to a trimethylstannyl group.[21,24] A similar set of signals of much lower intensity (ca. 10%) consisting of a singlet (5 H), two double doublets, and a pseudotriplet is detected in the same spectral region. However, the smaller coupling constant of the pseudotriplet at $\delta = 4.47$ (1.2 Hz) is indicative of a ^{4}J(H, H) coupling in a 1,3-disubstituted isomer. A third set of signals of very low intensity (ca. 3%) consists of four pseudotriplets at $\delta = 3.88$, 4.18, 4.36, and 4.44 ($^{3/4}J =$ 1.8 Hz) and can be attributed to the 1,1′-disubstituted isomer. The three isomers give rise to three singlets in the methyl region of the spectrum (**2a-Cl**, $\delta = 0.28$; **2b-Cl**, $\delta = 0.12$; **2c-Cl**, $\delta = 0.14$) with intensities that correlate well with those of the Cp resonances. Tin satellites flank these signals with ^{2}J(Sn, H) coupling constants identical to the one reported for starting material **1** (55−56 Hz).[21] Accordingly, a single ^{119}Sn NMR resonance is found for each isomer at a chemical shift similar to that for **1** (**2a-Cl**, $\delta = -5.1$; **2b-Cl**, $\delta = -10.1$; **2c-Cl**, $\delta = -7.2$; **1**, $\delta = -6.0$[21]), providing further evidence for the presence of unreacted trimethylstannyl groups in the products. In the ^{11}B NMR spectrum a broad resonance is observed at $\delta = 51$. Signals for the individual isomers could not be resolved as may be expected considering the broad nature of the resonance ($h_{1/2}$ ca. 320 Hz).

The facile and highly selective *ortho*-borylation of **1** is very unusual considering that Ar−Sn bonds are typically much more reactive toward boron halides than Ar−H bonds.[26] The 1-stannyl-1′-borylferrocene **2c-Cl** would therefore be expected as the major product. Moreover, the *ortho*-attack of the electrophile is remarkable considering the steric bulk and electronic properties of a trimethylstannyl group. A similar directing effect into the *ortho*-position of stannylated arenes has to our knowledge not been previously reported. In comparison, borylation of the less hindered 1,1′-dibromoferrocene and of alkylated ferrocenes exclusively takes place in the 3,4-positions, yielding 1,1′-dibromo-3,3′-diborylferrocene and 1-alkyl-3,1′,3′-triborylferrocenes, respectively.[27] Similarly, diborylation of ferrocene with boron tribromide leads to the 1,1′-diborylferrocene and small amounts of the 1,3-diborylated isomer, whereas a larger excess of boron tribromide results in the formation of 1,3,1′-triborylated and 1,3,1′,3′-tetraborylated ferrocenes.[28] The trimethylstannyl group is characterized by a weak −I and +M effect with a Hammett parameter of $\sigma_o^{+} = -0.12$ that does not account for the observed high reactivity of the α-positions.[29] Indeed, the α:β ratio for the acetylation of **1** is relatively low (1:4.3) and compa-

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(22) The 1-stannyl-2-borylferrocenes and 1-stannyl-3-borylferrocenes form as racemic mixtures as a result of their planar chirality. Only one of the two enantiomers will be shown in the schemes and figures.

(23) See, for example: (a) Ruf, W.; Renk, T.; Siebert, W. *Z. Naturforsch.* **1976**, *31b*, 1028. (b) Wrackmeyer, B.; Dörfler, U.; Herberhold, M. *Z. Naturforsch.* **1993**, *48b*, 121. (c) Appel, A.; Nöth, H.; Schmidt, M. *Chem. Ber.* **1995**, *128*, 621.

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(25) The pseudotriplet at $\delta = 4.46$ ($J = 1.2$ Hz) for isomer **2b-Cl** is overlapping with the double doublet at $\delta = 4.46$ for isomer **2a-Cl**. The signal is clearly visible in enriched samples of **2b-Cl**, and the assignment has been further confirmed by 2D NMR spectroscopy (dqfCOSY). The CpSn−H2,5 protons for **2c-Cl** resonate outside the spectral range shown in Figure 1 at $\delta = 3.88$.

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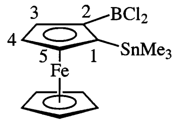
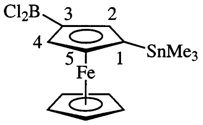
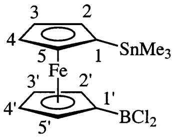
Table 1. ^{1}H NMR Data and Spectroscopic Yields for the Regioisomers 2a-Cl, 2b-Cl, and 2c-Cl

		
2a-Cl	**2b-Cl**	**2c-Cl**
87%	10%	3%
0.28 (Me)	0.12 (Me)	0.14 (Me)
3.93 (CpH)	3.93 (CpH)	
		3.88 (H2,5, ps.t, 1.8 Hz)
4.46 (H5, dd, 1.2/2.4 Hz)	4.36 (H5, dd, 1.2/2.4 Hz)	4.18 (H3,4, ps.t, 1.8 Hz)
4.53 (H4, ps.t, **2.4 Hz**)	4.47 (H2, ps.t, **1.2 Hz**)	4.36 (H3',4', ps.t, 1.8 Hz)
4.71 (H3, dd, 1.2/2.4 Hz)	4.60 (H4, dd, 1.2/2.4 Hz)	4.44 (H2',5', ps.t, 1.8 Hz)

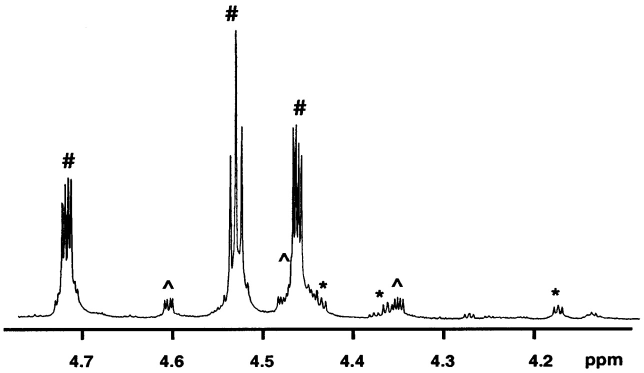


Figure 1. Region of substituted Cp rings in the ^{1}H NMR spectrum of crude **2-Cl**; **2a-Cl** (#); **2b-Cl** (∧); **2c-Cl** (*).[25]

rable to the reactivity ratio of 1:4.5 for isopropylferrocene and of 1:12.7 for *tert*-butylferrocene.[18] We reasoned that an evaluation of the influence of steric and electronic factors on the selectivity of the borylation of **1** might allow us to gain further insight into the characteristics of this unusual reaction.[30] We therefore extended our studies to the investigation of organoboron halides.

Dependence of Selectivity on Steric and Electronic Factors. $C_6F_5BCl_2$ represents an organoboron halide of Lewis acidity comparable to that of BCl_3, yet it is a considerably more sterically demanding Lewis acid. Upon addition of $C_6F_5BCl_2$ to a solution of **1** in hexanes at −78 °C, the reaction mixture immediately turned dark orange-red and a deep red color gradually developed upon warming to room temperature. The ^{1}H NMR spectrum of the crude product showed in addition to the expected 1,2-isomer **2a-Pf** a large amount of the 1,3-isomer, **2b-Pf**, whereas the 1,1′-isomer was not detected. The ratio of **2a-Pf** to **2b-Pf** was estimated to be ca. 55:45. The two isomers can readily be distinguished through analysis of the coupling patterns in the ^{1}H NMR spectrum as described above for the isomers **2a-Cl** and **2b-Cl**. Interestingly, the Cp signals adjacent to the boryl substituent are broadened at ambient temperature. This effect can be attributed to the presence of the bulky pentafluorophenyl group on boron, leading to a high rotational barrier around the Cp−B bond and the B−C_6F_5 bond. A similar line broadening, though at far lower temperature, has been reported for ferrocenylboranes with two different substituents on boron.[31] For instance, the coalescence temperature for rotation around the Cp−B bond in FcB(I)Ph was determined to be $T_c = -42$ °C ($\Delta G^\ddagger = 12.2$ kcal mol^{-1}).[31] The rotational hindrance of the pentafluorophenyl group in **2b-Pf** is also reflected in the ^{19}F NMR spectrum, which shows a broadened resonance for the fluorine atoms in *ortho*-position.

We then turned our attention to an evaluation of electronic factors and their effect on the selectivity of the borylation and the product distribution. We chose $PhBCl_2$, which is a much weaker electrophile in comparison to BCl_3 and $C_6F_5BCl_2$. Upon treatment of **1** with $PhBCl_2$ in hexanes at −78 °C, we did not observe any detectable conversion of the starting material. Only when the mixture was allowed to warm to ambient temperature, the reaction slowly proceeded as indicated by a gradual color change of the solution to dark red. However, complete conversion of $PhBCl_2$ was confirmed by ^{1}H NMR spectroscopy only after extended reaction time (ca. 5 days) at room temperature. A slightly faster reaction was observed in toluene leading to full conversion within ca. 2 days. Interestingly, in either toluene or hexanes, the product distribution for the reaction with $PhBCl_2$ was more complex than in the case of the above-described reactions with boron trichloride and $C_6F_5BCl_2$. ^{1}H NMR spectroscopy revealed that ca. 33% of 1,3-product **2b-Ph** and trace amounts of the 1,1′-isomer **2c-Ph** were formed in addition to **2a-Ph**. Furthermore, we detected a large amount of unreacted starting material **1** (ca. 20%) and formation of a new 1,2-disubstituted species (ca. 30%) containing a chloride substituent on tin, as confirmed by a downfield-shifted ^{119}Sn NMR signal at $\delta = 85.9$ (for details on the synthesis and isolation of this species with excess borane see vide infra). The amount of byproduct could be minimized by use of only 0.5 equiv of $PhBCl_2$. With this procedure, the two isomers **2a-Ph** and **2b-Ph** were formed almost exclusively. Our observations indicate that the steric bulk of the phenyl or the pentafluorophe-

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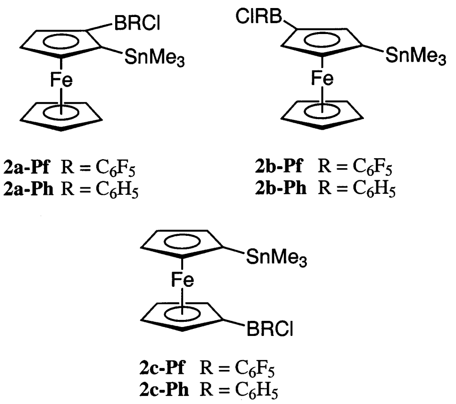
(30) More detailed mechanistic studies are currently under way and will be reported in a future contribution.

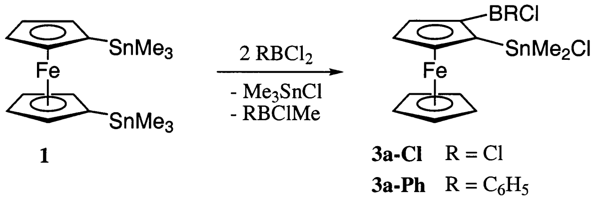
(31) Renk, T.; Ruf, W.; Siebert, W. *J. Organomet. Chem.* **1976**, *120*, 1.

Chart 3



2a-Pf R = C_6F_5
2a-Ph R = C_6H_5
2b-Pf R = C_6F_5
2b-Ph R = C_6H_5
2c-Pf R = C_6F_5
2c-Ph R = C_6H_5

Scheme 2. Reaction of 1 with 2 Equiv of $RBCl_2$ (R = Cl, Ph)



1

3a-Cl R = Cl
3a-Ph R = C_6H_5

nyl group directs the attack of the electrophile to some degree to the more accessible 3,4-positions in **1**. The presence of a relatively electron-rich phenyl group on boron considerably attenuates the borylation of **1**. We can conclude that steric factors to some extent determine the position, in which the electrophile attacks, whereas electronic effects play a major role in determining the overall reaction rate and the product distribution. In a continuation of this trend $MesBCl_2$ (Mes = 2,4,6-Me_3Ph) entirely fails to react with **1** at room temperature even after extended reaction time (5 days).

Formation of Ferrocene-Based Heteronuclear Bifunctional Lewis Acids. Compounds **2a** do not meet the requirements of a ferrocene-based bidentate Lewis acid of type **D** (Chart 1) since the trimethylstannyl group in these species is relatively electron rich. To develop methods for the functionalization of the remaining trimethylstannyl group and ultimately to increase the Lewis acidity of the tin center, we decided to further investigate the reactivity of species **2a**.

(i) Reaction of 1 with Excess Borane. The formation of a byproduct containing an Sn−Cl bond in the reaction of **1** with $PhBCl_2$ suggested that one of the Sn−Me bonds of the remaining trimethylstannyl substituent in **2a** can be cleaved with boron halides. Alternatively, cleavage of the remaining Sn−Cp bond with excess borane may lead to diborylated compounds. This reaction path was described by Deck and co-workers for the reaction of 1,1′-bis(trimethylsilyl)ferrocene with excess BCl_3 in dichloromethane, yielding mixtures of 1,1′- and 1,3-diborylated ferrocenes.[32] We reacted **1** with 2 equiv of BCl_3 in hexanes at −78 °C (Scheme 2). Interestingly, not the second Cp−Sn bond but one of the Sn−Me bonds was cleaved, and the novel heteronuclear bidentate Lewis acid **3a-Cl** was formed as the major product. A reaction at the second Sn−Cp bond did not take place under these conditions even when a larger excess of BCl_3 was applied.[33] Dark red crystals of the analytically pure isomer **3a-Cl** were isolated after repeated recrystallization from hexanes at −78 °C, and the structure of **3a-Cl** was confirmed by multinuclear and two-dimensional NMR spectroscopy, mass spectrometry, and elemental analysis. The ^1H NMR spectrum of **3a-Cl** shows a similar pattern in the Cp region as observed for the 1,2-disubstituted ferrocene **2a-Cl**. However, the signal for the Cp proton adjacent to the tin center is downfield-shifted in comparison to that for **2a-Cl** (**3a-Cl**, $\delta = 5.24$; **2a-Cl**, $\delta = 4.46$). The two methyl groups on tin are diastereotopic and show two distinct NMR signals at $\delta = 0.52$ ($J = 62$ Hz) and $\delta = 0.69$ ($J = 64$ Hz) as a result of the planar chirality of **3a-Cl**. A strongly downfield-shifted resonance in the ^{119}Sn NMR spectrum further confirms the presence of an electron-withdrawing substituent on tin and indicates an increased Lewis acidity of the stannyl group (**3a-Cl**, $\delta = 102.1$; **2a-Cl**, $\delta = -5.1$).

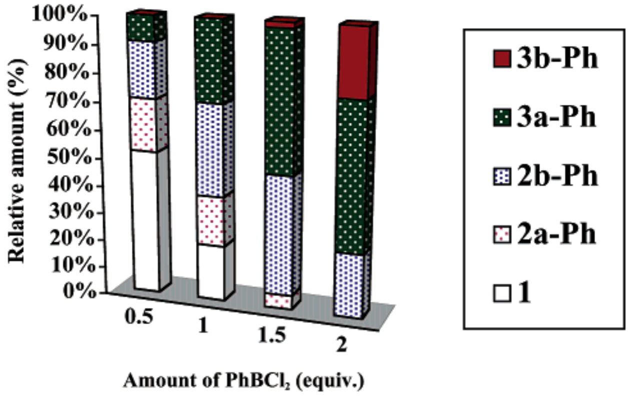
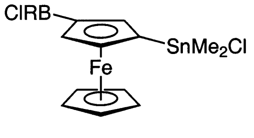


Figure 2. Product distribution for the reaction of **1** with varying amounts of $PhBCl_2$ in toluene at 25 °C.

Chart 4



3b-Ph R = C_6H_5

The formation of almost equal amounts of the 1,2- and 1,3-isomer in the reaction of **1** with $PhBCl_2$ provided us with an opportunity to directly compare the reactivity of a trimethylstannyl group in α-position with that in β-position to the boron substituent. Hence, we decided to study the product distribution for the reaction of **1** with $PhBCl_2$ as a function of stoichiometry (Figure 2). The two isomers **2a-Ph** and **2b-Ph** were formed almost exclusively with 0.5 equiv of $PhBCl_2$ in toluene. As the amount of $PhBCl_2$ was increased, **2a-Ph** reacted further under cleavage of an Sn−Me bond to give **3a-Ph** (Scheme 2). However, the 1,3-isomer **3b-Ph** (Chart 4) was formed only after extended reaction time when a 2-fold excess of $PhBCl_2$ was applied. The analytically pure isomer **3a-Ph** was isolated by repeated recrystallization from hexanes at −37 °C and fully characterized

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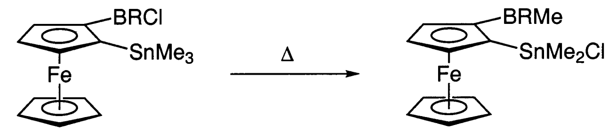
(32) Deck, P. A.; Fisher, T. S.; Downey, J. S. *Organometallics* **1997**, *16*, 1193.

(33) For related heteronuclear bifunctional Lewis acids with an organic backbone, see for example ref 10 and the following: (a) Katz, H. E. *J. Am. Chem. Soc.* **1986**, *108*, 7640. (b) Wrackmeyer, B.; Maisel, H.; Milius, W.; Badshah, A.; Molla, E.; Mottalib, A. *J. Organomet. Chem.* **2000**, *602*, 45.

Scheme 3. Thermal Rearrangement of 1-Stannyl-2-borylferrocenes



2a-Cl R = Cl
2a-Ph R = Ph

4a-Cl R = Cl
4a-Ph R = Ph

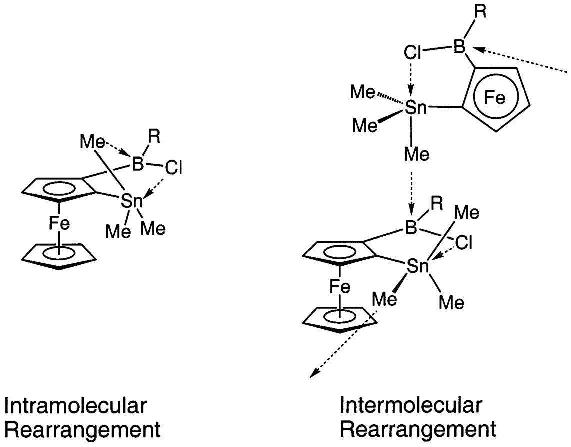
by multinuclear NMR spectroscopy, mass spectrometry, and elemental analysis.

(ii) Thermal Rearrangement of Stannylborylferrocenes 2a-Cl and 2a-Ph. Initially we kept the crude products **2** for 3 h at ca. 50 °C under high vacuum in order to remove any traces of Me_3SnCl or Me_2SnCl_2. Surprisingly, this procedure led to another rearrangement reaction to give **4a-Cl** and **4a-Ph** (Scheme 3), providing a simple alternate route for the introduction of electron-withdrawing substituents on tin. The rearrangement of **2a-Cl** to form **4a-Cl** slowly proceeded even below room temperature, whereas **2a-Ph** was stable at room temperature and required prolonged heating to ca. 80 °C for complete conversion to **4a-Ph**. In both cases, only the 1,2-isomers were isolated after repeated recrystallization from hexanes, indicating that this rearrangement reaction may have occurred specifically for the 1,2-isomers. Indeed, ^1H NMR spectroscopic analysis of the filtrate after crystallization of **4a-Ph** confirmed the presence of unchanged 1,3-isomer **2b-Ph**.

An increased Lewis acidity of the stannyl groups in the rearranged species **4a-Cl** and **4a-Ph** is reflected in a downfield shift of the ^{119}Sn NMR signal in comparison to **2a-Cl** and **2a-Ph** (**2a-Cl**, $\delta = -5.1$; **4a-Cl**, $\delta = 89.8$; **2a-Ph**, $\delta = -8.5$; **4a-Ph**, $\delta = 94.1$). Similarly, introduction of a methyl group on boron leads to the expected downfield shift[34] in the boron NMR spectra (**2a-Cl**, $\delta = 51.1$; **4a-Cl**, $\delta = 61.5$; **2a-Ph**, $\delta = 57.2$; **4a-Ph**, $\delta = 67.5$). The diastereotopic methyl groups on tin give rise to two signals with tin satellites in the ^1H NMR spectra of both **4a-Cl** and **4a-Ph**. An additional methyl resonance without tin satellites can be assigned to the methyl group that was transferred from tin to boron (**4a-Cl**, $\delta = 0.86$; **4a-Ph**, $\delta = 1.07$).

Cleavage of Sn−C(sp^3) versus Sn−C(sp^2) Bonds in 1-Stannyl-2-borylferrocenes. Preferred cleavage of an Sn−C(sp^3) bond over an Sn−C(sp^2) bond as observed in the formation of species **3a-Cl** and **3a-Ph** is rare.[35] An Sn−C(sp^2) bond is generally believed to be significantly more reactive toward electrophiles.[36] Attack of an electrophile at the Sn−Cp bond and subsequent formation of a cationic Wheland-type intermediate should be disfavored in the presence of a strongly electron-withdrawing boryl group at the same Cp ring. On the other hand, the apparent lower reactivity of the Sn−Me bonds in the 1,3-isomer, **2b-Ph**, in comparison to **2a-Ph** provides evidence for an activation that is unique to the Sn−Me bonds in 1-trimethylstannyl-2-borylferrocenes. The unusually low reactivity of the Sn−Cp bonds in **2a-Cl** and **2a-Ph** in comparison to the Sn−Me bonds suggests a combination of two effects: an intramolecular activation of the Sn−Me bonds and a deactivation of the Sn−Cp bond adjacent to an electron-withdrawing boryl substituent.

Chart 5. Possible Transition States for an Intra- versus Intermolecular Thermal Rearrangement Reaction



The thermal rearrangement of species **2a-Cl** and **2a-Ph** represents a similar process, except that Sn−Me bond cleavage is brought about by the chloroborane functionality in the molecule itself. A mechanism involving a transition state with four-coordinate boron and five-coordinate tin centers (see “intramolecular rearrangement” in Chart 5) has been postulated for the rearrangement of the analogous 1-stannyl-2-borylbenzene derivatives.[36] Indeed, the formation of stable pentacoordinate tetraorganostannanes through intramolecular coordination has been reported previously.[37] However, we believe that the proposed intramolecular transition state is less likely considering that the coordination of nucleophiles is known to lead to elongated tin−carbon bonds *trans* to the incoming nucleophile, which consequently display enhanced reactivity.[38] We thus favor a mechanism involving (i) intramolecular transfer of a chloride substituent from boron to tin and (ii) intermolecular transfer of the activated methyl group in *trans*-position to the boryl group of another molecule (Chart 5). This mechanism is further supported by a study on the concentration dependence of the rate of rearrangement of **2a-Cl**. Neat **2a-Cl** is fully converted to **4a-Cl** within 3 h at 60 °C. In contrast, a 0.2 M solution in deuterated benzene shows 70% conversion within 12 h and a 0.02 M solution gives only 25% conversion over the same period at 60 °C. These results clearly support an intermolecular mechanism for

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[34] Nöth, H., Wrackmeyer, B., Eds. *NMR, Basic Principles and Progress*; Springer-Verlag: Berlin, 1978; Vol. 14.

[35] A similar phenomenon has been observed for the reaction of stannylated zirconocenes with boron halides and for the borylation of 1,2-bis(trimethylstannyl)benzene: (a) Cheng, X.; Slebodnick, C.; Deck, P. A.; Billodeaux, D. R.; Fronczek, F. R. *Inorg. Chem.* **2000**, *39*, 4921. (b) Eisch, J. J.; Kotowicz, B. W. *Eur. J. Inorg. Chem.* **1998**, 761.

[36] See ref 35b.

[37] See, for example: (a) Tzschach, A.; Jurkschat, K. *Pure Appl. Chem.* **1986**, *58*, 639. (b) Jurkschat, K.; Tzschach, A.; Meunier-Piret, J. *J. Organomet. Chem.* **1986**, *315*, 45. (c) Kumar-Das, V. G.; Mun, L. K.; Wei, C.; Blunden, S. J.; Mak, T. C. W. *J. Organomet. Chem.* **1987**, *322*, 163. (d) Kumar-Das, V. G.; Mun, L. K.; Wei, C.; Mak, T. C. W. *Organometallics* **1987**, *6*, 10.

[38] See, for example: (a) Jastrzebski, J. T. B. H.; van Koten, G. *Adv. Organomet. Chem.* **1993**, *35*, 241. (b) Podesta, J. C.; Chopa, A. B.; Koll, L. C. *J. Chem. Res. (S)* **1986**, 308. (c) Jastrzebski, J. T. B. H.; Boersma, J.; Esch, P. M.; van Koten, G. *Organometallics* **1991**, *10*, 930. (d) Steenwinkel, P.; Jastrzebski, J. T. B. H.; Deelman, B.-J.; Grove, D. M.; Kooijman, H.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 5486. (e) Yoshida, J.; Izawa, M. *J. Am. Chem. Soc.* **1997**, *119*, 9361.

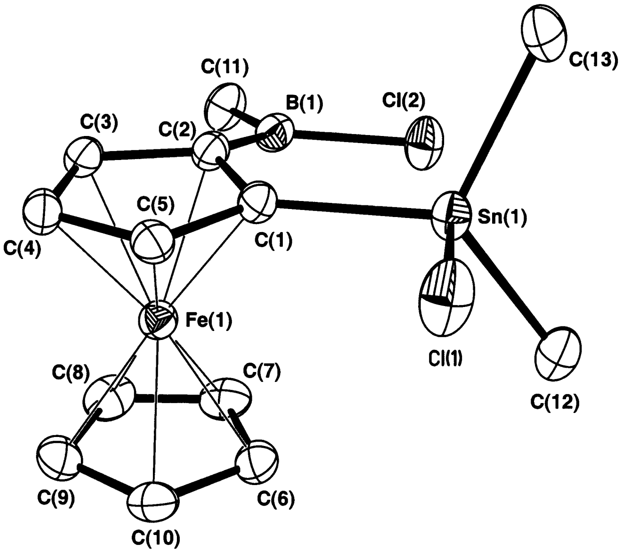

Figure 3. Molecular structure (ORTEP drawing) of **4a-Cl**.

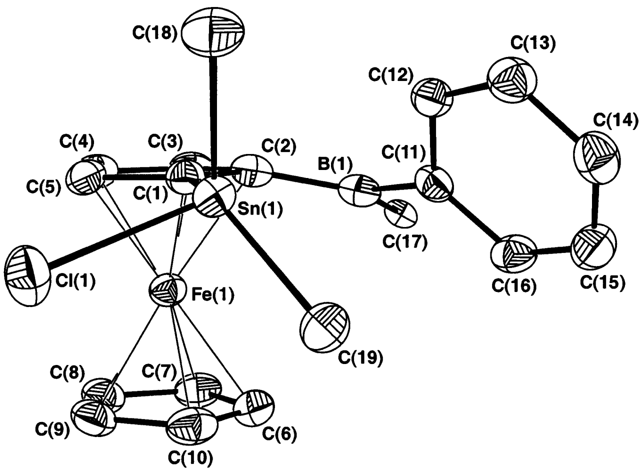

Figure 4. Molecular structure (ORTEP drawing) of **4a-Ph**.

the rearrangement of species **2a**. The lower reactivity of **2a-Ph** in comparison to **2a-Cl** may be traced back to the increased steric bulk and decreased Lewis acidity of the boryl group, which should disfavor the transfer of a methyl group to the boron center.

Properties of Ferrocene-Based Heteronuclear Bifunctional Lewis Acids. (i) Solid State Structure of 1-Stannyl-2-borylferrocenes. Single-crystal structure determinations were performed on dark red crystals of **4a-Cl** and **4a-Ph** obtained from hexanes at −37 °C. The structures in Figure 3 and Figure 4 unambiguously show that the proposed rearrangement reactions had taken place leading to an unsubstituted Cp ring and a 1-stannyl-2-borylcyclopentadienyl ligand on iron. A methyl group is attached to the boryl groups in **4a-Cl** and **4a-Ph** as a result of the substituent rearrangement reaction between the stannyl and the boryl group outlined in Scheme 3. Accordingly, a chloride substituent is found next to two methyl groups on the tin center. We anticipated that the solid state structure of the rearranged stannylborylferrocenes, **4a-Cl** and **4a-Ph**, may show an interaction between the Lewis acidic boron center and the chloride substituent on tin, thereby allowing us to gain insight into the nature of the transition state involved in their formation. An interaction between the tin-bound chlorine atom and the Lewis acidic boron center is not observed. In both structures, the chloride substituent on tin points away from the boron center. However, the boron-bound chloride substituent in **4a-Cl** points toward the Lewis acidic tin center (Cl(2)···Sn(1) = 3.1380(12) Å), leading to a pyramidalization on tin as reflected in the large equatorial angles C(1)−Sn(1)−C(12) of 121.7(2)°, C(1)−Sn(1)−C(13) of 113.1(2)°, and C(12)−Sn(1)−C(13) of 115.8(2)° (sum of equatorial angles: 350.6°). A similar effect is observed for the phenyl group in **4a-Ph**, which exhibits two relatively short contacts with the tin center (Sn(1)···C(11) = 3.516(4) Å; Sn(1)···C(12) = 3.216(4) Å).[39] The resultant pyramidalization of the tin center in **4a-Ph** is reflected in a sum of equatorial angles of 351.9°. In both structures the chloride substituent on tin is placed in the axial position *trans* to the chloro and phenyl group on boron, respectively. The angles Cl(1)−Sn(1)···Cl(2) of 172.54(4)° in **4a-Cl** and Cl(1)−Sn(1)···C(12) of 175.26(7)° in **4a-Ph** are close to the expected angle of 180° in an ideal trigonal bipyramidal arrangement. Accordingly, the Sn(1)−Cl(1) bonds in **4a-Cl** (2.4026(12) Å) and **4a-Ph** (2.4036(12) Å) are slightly elongated in comparison to a typical Sn−Cl bond in a tetrahedral environment (Me_3SnCl monomer: 2.351 Å[40]). It is worth noting that our structural results correlate nicely with the data reported for the structure of Me_3SnCl, which forms polymer chains in the solid state as a result of Sn···Cl bridges (Sn−Cl 2.430(2); 3.269 Å; Cl−Sn···Cl 176.85(6)°).[40]

Interestingly, in both structures the boron atom is bent out of the Cp plane toward the iron atom in a fashion similar to that observed in the crystal structures of dibromoborylferrocene[41] and bis(pentafluorophenyl)borylferrocene[42] (**4a-Cl**, $\alpha^* = 13.8(2)°$; **4a-Ph**, $\alpha^* = 12.2(3)°$; $FcBBr_2$, $\alpha^* = 17.7°$ and 18.9°; $FcB(C_6F_5)_2$, 16°; $\alpha^* = 180° -$ centroid(C1−C5)−C(2)−B angle), suggesting the presence of a weak, but significant iron−boron interaction.[41,43] A slightly lower degree of iron−boron interaction in **4a-Cl** and **4a-Ph** in comparison to $FcBBr_2$ and $FcB(C_6F_5)_2$ is reflected in a larger Fe−B distance (**4a-Cl**, 2.952(5) Å; **4a-Ph**, 3.087(5) Å; $FcBBr_2$, 2.840 Å; $FcB(C_6F_5)_2$, 2.924 Å). Similarly, the B−C(Cp) bonds (**4a-Cl**, 1.523(7) Å; **4a-Ph**, 1.536(6) Å) are slightly longer than in $FcBBr_2$ (1.474 and 1.482 Å) and $FcB(C_6F_5)_2$ (1.501(4) Å). The presence of both a ferrocenyl and a phenyl group in **4a-Ph** allows for a direct comparison of the B−Cp bond with the B−Ph bond. The B−Cp bond (1.536(6) Å) is qualitatively shorter than the B−Ph bond (1.571(5) Å), indicating a larger degree of π-interaction with the ferrocenyl group. This effect may be attributed to the contribution of a boratafulvene-like resonance structure (**I**, Chart 6), as further supported by the

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[39] For examples of intramolecular π-coordination of an alkynyl group to an organotin cation see: (a) Wrackmeyer, B.; Kundler, S.; Milius, W.; Boese, R. *Chem. Ber.* **1994**, *127*, 333. (b) Wrackmeyer, B.; Kundler, S.; Boese, R. *Chem. Ber.* **1993**, *126*, 1361. (c) Wrackmeyer, B.; Kehr, G.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1370.

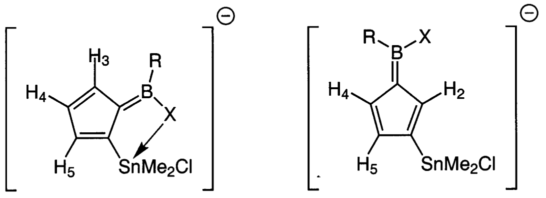
[40] Lefferts, J. L.; Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J. *J. Organomet. Chem.* **1982**, *240*, 349.

[41] Appel, A.; Jäkle, F.; Priermeier, T.; Schmid, R.; Wagner, M. *Organometallics* **1996**, *15*, 1188.

[42] Carpenter, B. E.; Piers, W. E.; Parvez, M.; Yap, G. P. A.; Rettig, S. J. *Can. J. Chem.* **2001**, *79*, 857.

[43] Silver, J.; Davies, D. A.; Roberts, R. M. G.; Herberhold, M.; Dörfler, U.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *590*, 71.

Chart 6



I

II

Table 2. Selected Bond Lengths (Å), Interatomic Distances (Å), and Angles (deg) for 4a-Cl and 4a-Ph[a]

4a-Cl		4a-Ph	
Sn(1)−Cl(1)	2.4026(12)	Sn(1)−Cl(1)	2.4036(12)
Sn(1)−C(1)	2.130(4)	Sn(1)−C(1)	2.121(4)
Sn(1)−C(12)	2.123(5)	Sn(1)−C(18)	2.130(4)
Sn(1)−C(13)	2.139(5)	Sn(1)−C(19)	2.121(4)
B(1)−Cl(2)	1.808(5)	B(1)−C(17)	1.623(5)
B(1)−C(2)	1.523(7)	B(1)−C(2)	1.536(6)
B(1)−C(11)	1.562(7)	B(1)−C(11)	1.571(5)
C(1)−Sn(1)−C(12)	121.71(19)	C(1)−Sn(1)−C(19)	122.7(2)
C(1)−Sn(1)−C(13)	113.10(18)	C(1)−Sn(1)−C(18)	113.1(2)
C(12)−Sn(1)−C(13)	115.8(2)	C(18)−Sn(1)−C(19)	116.1(2)
C(12)−Sn(1)−Cl(1)	100.37(15)	C(18)−Sn(1)−Cl(1)	100.65(13)
C(1)−Sn(1)−Cl(1)	99.17(12)	C(1)−Sn(1)−Cl(1)	98.52(10)
C(13)−Sn(1)−Cl(1)	101.41(15)	C(19)−Sn(1)−Cl(1)	99.54(12)
C(2)−B(1)−Cl(2)	117.1(4)	C(2)−B(1)−C(17)	121.2(3)
C(2)−B(1)−C(11)	127.4(4)	C(2)−B(1)−C(11)	120.4(3)
C(11)−B(1)−Cl(2)	115.5(4)	C(11)−B(1)−C(17)	118.3(3)
(C1−C5) // (C6−C10)	1.1(2)	(C1−C5)//(C6−C10)	2.5(2)
Cent−C(2)−B(2)	166.2(2)	Cent−C(2)−B(1)	167.8(3)
Cent−C(1)−Sn(1)	182.2(4)	Cent−C(1)−Sn(1)	182.7(2)
Cp-staggering angle	5.9(5)	Cp-staggering angle	0.7(5)
Fe(1)···B(1)	2.952(5)	Fe(1)···B(1)	3.087(5)
Sn(1)···Cl(2)	3.1380(12)	Sn(1)···C(11)	3.516(4)
		Sn(1)···C(12)	3.216(4)

[a] Cent = centroid(C1−C5)

Table 3. ^{1}H, ^{119}Sn, and ^{11}B NMR Data of Compounds 3a and 4a[a]

	δ^{1}H							
	CpH	H3	H4	H5	Sn−Me		δ^{119}Sn	δ^{11}B
3a-Cl	3.87	4.55 (10)	4.53 (7)	5.24 (15)	0.52 (62)	0.69 (64)	102.1	49.8
3a-Ph	3.86	4.57 (11)	4.63 (8)	5.46 (15)	0.66 (63)	0.82 (66)	85.9	56.4
4a-Cl	3.83	4.22 (11)	4.54 (7)	5.33 (15)	0.65 (63)	0.82 (66)	89.8	61.5
4a-Ph	4.02	4.70 (13)	4.72 (6)	5.20 (14)	−0.16 (64)	0.54 (60)	94.1	67.5

	CpH	H2,5	H3,4	Sn−Me	δ^{119}Sn	δ^{11}B
FcSnMe$_2$Cl	3.94	4.00 (11)	4.17 (8)	0.48 (60)	121.1	
FcBCl$_2$[31]	3.86	4.38	4.28			49.8
FcBClPh[31]	3.86	4.62	4.41			55.9

[a] In C_6D_6 at 20 °C, coupling constants $J(^{119}Sn, ^{1}H)$ are given in parentheses.

Table 4. ^{13}C NMR Data of Compounds 3a and 4a[a]

	CpH	C1	C3	C4	C5	Sn-Me		B-Me
3a-Cl	71.7	82.1	80.7 (43)	81.1 (49)	86.2 (48)	1.1 (420)	2.5 (462)	
3a-Ph	70.3	83.8	80.9 (47)	80.6 (52)	85.4 (53)	1.4 (430)	2.6 (473)	
4a-Cl	70.3	81.8	80.0 (nr)	80.0 (nr)	84.8 (52)	1.3 (427)	2.7 (473)	9.3
4a-Ph	69.9	77.9	83.0 (57)	79.1 (54)	83.6 (58)	−0.6 (454)	2.4 (411)	10.7

	CpH	C1	C2,5	C3,4	Sn-Me
FcSnMe$_2$Cl	68.6	69.0	74.0 (69)	71.9 (52)	−1.7 (415)
FcBCl$_2$[31]	71.0		76.2	77.3	
FcBClPh[31]	70.4		76.8	77.4	

[a] In C_6D_6 at 20 °C, coupling constants $J(^{119}Sn, ^{13}C)$ are given in parentheses; nr = not resolved.

observation of a bond length alternation within the substituted Cp rings of both **4a-Cl** and **4a-Ph**. The tin atom does not show an interaction with the iron atom in **4a-Cl** or **4a-Ph**, but is slightly bent away from the iron center (**4a-Cl**, $\beta^* = -2.2(4)°$; **4a-Ph**, $\beta^* = -2.7(2)°$; $\beta^* = 180° -$ centroid(C1−C5)−C(1)−Sn angle).

(ii) NMR Spectroscopic Studies of 1-Stannyl-2-borylferrocenes. A comparison between the NMR spectroscopic properties of the bifunctional Lewis acids **3a** and **4a** and their monofunctional counterparts FcBCl$_2$, FcBClPh, and FcSnMe$_2$Cl was expected to give us some insight as to whether the two Lewis acidic centers influence each other in solution (Table 3 and Table 4). The ^{11}B NMR resonances of **3a-Cl** ($\delta = 49.8$) and **3a-Ph** ($\delta = 56.4$) are very similar to those observed for FcBCl$_2$ ($\delta = 49.8$) and FcBClPh ($\delta = 55.9$), respectively, and therefore do not seem to be very sensitive to the substitution pattern of the ferrocene moiety. In contrast, the ^{119}Sn NMR signals vary from 85.9 to 102.1 ppm for species **3a** and **4a** and are strongly upfield-shifted in comparison to FcSnMe$_2$Cl ($\delta = 121.1$). Interestingly, this effect seems to be unique for the 1,2-isomers, as the chemical shift of $\delta = 118.9$ for the 1,3-isomer **3b-Ph** is very close to that of FcSnMe$_2$Cl. An influence of the boryl on the stannyl group is also evident in the proton NMR spectra of **3a** and **4a**, all of which show two distinct signals for the methyl groups on tin. With the exception of those for **4a-Ph**, the methyl groups are downfield-shifted (δ ranges from 0.52 to 0.82) relative to those in FcSnMe$_2$Cl ($\delta = 0.48$) and the coupling constants of 60−66 Hz are slightly larger than in FcSnMe$_2$Cl ($^{2}J(^{119}Sn, H) = 60$ Hz), indicating an increased s-character of the Sn−C bonds.[21,24] A similar yet more pronounced effect is observed in the ^{13}C NMR spectra. Two methyl resonances with tin satellites are observed for each compound. The coupling constant for one of these signals ranges from 411 to 430 Hz, which is very close to the one for FcSnMe$_2$Cl ($J(^{119}Sn, C) = 415$ Hz). The second methyl resonance exhibits an unusually large coupling of 454−473 Hz to tin.

The strong dependence of the ^{119}Sn NMR shift on the substitution pattern on boron in combination with a significant upfield shift indicates that an interaction between the boron substituents and the Lewis acidic tin center as discussed above for the solid state structures of **4a-Cl** and **4a-Ph** also plays a role in solution. This conclusion is further supported by the observed strong coupling of the tin center to the methyl groups in the 1-stannyl-2-borylferrocenes, which is typical of equatorial ligands in pentacoordinate tin compounds.[38]

The Cp-H5 proton adjacent to the stannyl group is strongly downfield-shifted (δ ranges from 5.20 to 5.46) relative to the chemical shift of $\delta = 4.00$ observed for FcSnMe$_2$Cl.[44] Furthermore, an unusually strong coupling of the CpH3 and CpH5 protons to the tin center is observed (^{3}J(Sn, H5) ranges from 14 to 15 Hz; ^{4}J(Sn, H3) ranges from 10 to 13 Hz; for FcSnMe$_2$Cl, $^{3}J = 11$ Hz, $^{4}J = 8$ Hz). This suggests that the boratafulvene-

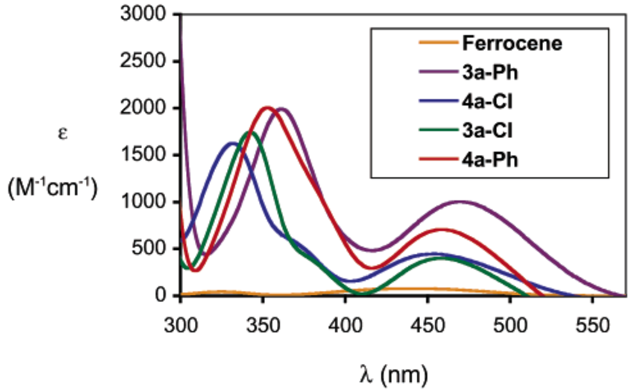


Figure 5. Absorption spectra of 1-stannyl-2-borylferrocenes (region from 300 to 570 nm shown).

like resonance structure (**I**, Chart 6) significantly contributes not only in the solid state but also to the structure in solution. An enhanced Sn−H coupling is not observed for the 1,3-isomer **3b-Ph** (δ (Cp-H5) = 4.51; ^3J(Sn, H) = 11 Hz). A possible explanation is that coupling between tin and the Cp protons is not promoted by extended delocalization in the boratafulvene-like resonance structure of the 1,3-disubstituted species (**II**, Chart 6).

(iii) UV−Visible Absorption Characteristics of 1-Stannyl-2-borylferrocenes. The 1-stannyl-2-borylferrocenes **3a-Cl**, **3a-Ph**, **4a-Cl**, and **4a-Ph** are dark orange-red in the solid state as well as in solutions of noncoordinating solvents. Hence, their visible absorption spectrum is markedly different from that of ferrocene, which gives a light yellow solution as a result of two weak absorption bands at λ_{max} = 441 (ϵ = 49) and λ_{max} = 325 (ϵ = 91).[45] In contrast, for the 1-stannyl-2-borylferrocenes strong absorption bands are observed in the range 454−471 nm (ϵ = 400−1000) and 332−361 (ϵ = 1600−2000) (Figure 5; see also Supporting Information). For the parent molecule, ferrocene, these bands have been assigned to symmetry-forbidden d−d transitions.[45] When substituents are introduced at the Cp rings, the transitions become formally allowed and the intensity consequently increases. For instance, the bands observed for phenylferrocene at 446 nm (310) and 339 nm (850) are significantly more intense than those for ferrocene.[45] It has also been noted that introduction of electron-withdrawing groups on ferrocene leads to a bathochromic shift of the visible absorption maxima.[46] This effect is pronounced for the stannylborylferrocenes, which show a red-shift of 13 to 30 nm relative to ferrocene for the band at 454−471 nm. The extent of the bathochromic shift depends on the substituents on boron and increases in the order Me < Cl < Ph, with **3a-Ph** displaying the strongest and lowest energy band (Figure 5). Interestingly, the bathochromic shift not only is due to the presence of a boryl group but can in part be traced back to the presence of the Lewis acidic stannyl group. The maxima for **3a-Cl** at λ_{max} = 458 nm and **3a-Ph** at λ_{max} = 471 nm are slightly red-shifted relative to those for $FcBCl_2$ (λ_{max} = 454 nm) and FcBClPh (λ_{max} = 464 nm), respectively. A similar effect is also observed for the lowest energy absorption in the UV region of the spectrum, which for the stannylborylferrocenes ranges from 332 to 361 nm with shoulders reaching into the visible region. Again, the extent of the bathochromic shift of this band increases in the order Me < Cl < Ph and is more pronounced than in the parent ferrocenylboranes (**3a-Cl**, λ_{max} = 342 nm; $FcBCl_2$, λ_{max} = 331 nm; **3a-Ph**, λ_{max} = 361 nm; FcBClPh, λ_{max} = 353 nm). The strong dependence of λ_{max} on the substitution pattern on boron indicates a significant charge-transfer contribution to these d−d transitions. Three strong absorption bands between 200 and 267 nm for **3a-Cl** and **4a-Cl** can be assigned to charge-transfer bands. The UV region of the spectra for **3a-Ph** and **4a-Ph** are further complicated by absorption bands due to the phenyl group.

A direct iron−boron interaction in the stannylborylferrocenes **4a-Cl** and **4a-Ph** has been deduced from strong bending of the boryl substituent out of the Cp plane toward the iron atom. Furthermore, charge transfer from iron to boron has been substantiated by theoretical calculations on the parent molecule, $FcBH_2$ (Fc = ferrocenyl), which indicate orbital overlap between the $d_{x^2-y^2}$ (HOMO-1) and d_{z^2} (HOMO-2) orbitals on iron and the empty p-orbital on boron.[41] This interaction may in part be responsible for the unusual absorption characteristics of the described stannylborylferrocenes, including the strong absorptions in the visible part of the electronic spectra and their dependence on the substitution pattern on boron.

Conclusions

We have investigated the borylation of 1,1′-bis(trimethylstannyl)ferrocene (**1**) as a potential route to 1,2-disubstituted ferrocenes. Borylation of **1** does not involve direct tin−boron exchange, as is typically observed with arylstannanes, but occurs with unprecedented selectivity at the α-position. Steric and electronic factors determine the selectivity and overall rate of the reaction. With more sterically demanding substituents on boron, increased amounts of the 1,3-product are formed. A decrease in Lewis acidity of the electrophile on the other hand leads to a considerably lower reaction rate and, in the case of $PhBCl_2$, results in side-reactions involving the Sn−Me bonds. A further increase of steric bulk and decrease of Lewis acidity as in the case of $MesBCl_2$ prevent the reaction entirely.

Whereas compounds **2a** are examples for 1,2-dielement-substituted ferrocenes, only the boryl group is truly Lewis acidic. To increase the Lewis acidity of the tin center, functionalization of the remaining trimethylstannyl group was necessary. We found that the presence of a boryl group adjacent to a trimethylstannyl group in **2a** decreases the ability of an electrophile to attack at the Sn−Cp bond. However, selective cleavage of an Sn−Me bond can be brought about either with excess borane or via an unusual thermal rearrangement, in which a methyl group is transferred from tin to boron and a chloride substituent from boron to tin. The resulting heteronuclear bidentate Lewis acids **3a** and **4a** consist of two Lewis acidic groups, a dimethylchlorostannyl and a boryl group, both of which are attached to the same Cp ring of ferrocene.

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[44] The assignments of the Cp protons have been further confirmed through the presence of a cross-peak between the Cp-H2 protons and the *ortho*-protons on the phenyl group in the NOESY spectrum of **3a-Ph**.

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The presence of two Lewis acidic centers is reflected in the solution and solid state characteristics of these novel bifunctional Lewis acids. Structural studies of the rearranged species **4a-Cl** and **4a-Ph** reveal a significant iron−boron interaction, as deduced from the dip angles of 13.8° and 12.2° between the Cp plane and the Cp−boron vector. An interaction between the tin-bound chloride and the Lewis acidic boron center could not be deduced from the solid state structure of the stannylborylferrocenes **4a-Cl** and **4a-Ph**. Our findings suggest that the iron−boron interaction is energetically more favorable than a boron−chlorine interaction in the ferrocene-based systems **4a-Cl** and **4a-Ph**. However, in the case of the higher homologues the situation may well be different. Indeed, Gabbaï and co-workers[10] have recently reported a related “iron-free” stannagallacycle that readily forms a chloride bridge from tin to gallium, which consequently displays a tetrahedral geometry. We are currently developing synthetic routes to the analogous aluminum- and gallium-functionalized ferrocenes.

Whereas the boron centers in **4a-Cl** and **4a-Ph** can draw electron density from the electron-rich iron atom, a similar interaction is not observed for tin. However, short contacts between the boron-bound chloride and the tin center in **4a-Cl** as well as the phenyl group and the tin center in **4a-Ph** result in a distorted trigonal bipyramidal geometry around tin in the solid state. A similar interaction between the boron substituents and the tin center in solution can be deduced from a comparison of the NMR data of compounds **3a** and **4a** with the “boron-free” compound $FcSnMe_2Cl$. Particularly revealing is the observed strong upfield-shift of 19−35 ppm for the ^{119}Sn NMR signals relative to $FcSnMe_2Cl$. Interestingly, this hypercoordination of tin may be responsible for the observed high reactivity of the Sn−Me bonds in **2a**, leading to facile formation of species **3a** with excess borane and of **4a** via thermal rearrangement.

The presence of two strongly electron-withdrawing substituents in compounds **3a** and **4a** is reflected in the UV−visible spectra of the 1-stannyl-2-borylferrocenes. Intense absorptions are observed in the range 453−470 and 333−362 nm. Absorption bands in this range have been assigned to weak, symmetry-forbidden d−d transition in the parent ferrocene molecule. These bands are red-shifted for the stannylborylferrocenes relative to ferrocene, and their position strongly depends on the substitution pattern on boron, indicating a significant charge-transfer contribution. A comparison with the absorption spectra of the related ferrocenylboranes suggests that both the boryl and the stannyl group contribute to the observed bathochromic shift.

A particularly appealing feature of compounds **3a** and **4a** is that the chloride substituents on tin and boron lend themselves to fine-tuning of the Lewis acidity via substituent exchange reactions. In addition, the redox chemistry of the ferrocene backbone may prove valuable for further manipulation of the Lewis acidic centers. However, probably the most intriguing aspect of the described stannylborylferrocenes is their planar chirality.[47] Racemic mixtures are obtained for all compounds **2a**, **3a**, and **4a**. A critical step will be to develop methods for the isolation of enantiomerically pure species. One route that we are currently exploring is the separation of the enantiomers via formation of complexes with chiral amines or phosphines.

Experimental Section

Materials and General Methods. The compounds $PhBCl_2$, BCl_3 (1 M in hexanes), and Me_3SnCl were purchased from Acros and BBr_3 and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were purchased from Aldrich. $PhBCl_2$ and BBr_3 were distilled under vacuum prior to use. The compounds $MesBCl_2$,[48] $FcBCl_2$,[49] $C_6F_5BCl_2$,[50] and $FcSnMe_2Cl$[51] were prepared according to literature procedures. 1,1′-Bis(trimethylstannyl)ferrocene was obtained from dilithioferrocene·*n*TMEDA[52] and 2 equiv of Me_3SnCl in Et_2O according to a literature procedure[20] (purity >97%). All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies). TMEDA and all ether solvents were distilled from Na prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies), and the chlorinated solvents were subsequently degassed via several freeze−pump−thaw cycles. All 400 or 500 MHz ^1H NMR spectra and 100.5 or 125.7 MHz ^{13}C NMR spectra were recorded on a Unity 400 and a Unity 500 spectrometer, respectively. Two-dimensional NMR data were acquired on a Unity 500 spectrometer. The 149.1 MHz ^{119}Sn NMR, 376.2 MHz ^{19}F NMR, and 128.3 MHz ^{11}B NMR spectra were recorded on a Unity 400 spectrometer. All solution ^1H and ^{13}C NMR spectra were referenced internally to the solvent signals. ^{119}Sn and ^{11}B NMR spectra were referenced externally to $SnMe_4$ ($\delta = 0$) and $BF_3 \cdot Et_2O$ ($\delta = 0$), respectively, and the ^{19}F NMR spectra were referenced to α,α',α''-trifluorotoluene (0.05% in C_6D_6; $\delta = -67.73$). UV−visible absorption data were acquired on a Varian Cary 500 UV−vis/NIR spectrophotometer. Solutions (10^{-3} and 10^{-4} M) were prepared using a microbalance (±0.1 mg) and volumetric glassware and then charged into quartz cuvettes with sealing screw caps (Starna) inside the glovebox. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in an electron impact (EI) mode. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

Reaction of 1 with BCl_3. Synthesis of 1-Stannyl-2-borylferrocenes 2a-Cl, 2b-Cl, and 2c-Cl. A solution of BCl_3 (1.0 mL, 1.0 M in hexanes) was added dropwise to a solution of 1,1′-fc$(SnMe_3)_2$ (0.51 g, 1.00 mmol) in hexanes (10 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and then allowed to slowly warm to 0 °C. All volatile material was removed under reduced pressure (10^{-3} Torr), and the product was subsequently kept under dynamic vacuum at ambient temperature over a period of 1 h. The crude product was obtained as a dark red oil and characterized by NMR spectroscopy without further purification. The isomer ratios for compounds **2a-Cl** (87%), **2b-Cl** (10%), and **2c-Cl** (3%) were estimated via integration of the $SnMe_3$ proton NMR signal. For **2a-Cl**: ^1H NMR (400 MHz, C_6D_6, 20 °C): δ 4.71 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, $J(^{117/119}Sn, H) = 6$ Hz, 1 H, Cp-H3), 4.53 (pst/dpst, $J = 2.4$ Hz, $J(^{117/119}Sn, H) = 5$ Hz, 1 H, Cp-H4), 4.46 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, $J(^{117/119}Sn, H) = 13$ Hz, 1 H, Cp-

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H5), 3.93 (s, 5 H, Cp), 0.28 (s/d, J($^{117/119}$Sn, H) = 52/55 Hz, 9 H, Sn-Me). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 85.2 (s/d, J($^{117/119}$Sn, C) = 45 Hz, Cp-C5), 80.8 (s/d, J($^{117/119}$Sn, C) = 31 Hz, Cp-C3), 80.3 (*ipso*-CpSn), 79.4 (s/d, J($^{117/119}$Sn, C) = 41 Hz, Cp-C4), 70.7 (Cp), −6.8 (s/d, J($^{117/119}$Sn, C) = 349/366 Hz, Sn-Me), not observed (*ipso*-CpB). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ −5.1. For **2b-Cl**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 4.60 (dd, J = 1.2 Hz, 2.4 Hz, 1 H, Cp-H4), 4.47 (pst, J = 1.2 Hz, 1 H, Cp-H2), 4.36 (dd, J = 1.2 Hz, 2.4 Hz, 1 H, Cp-H5), 3.93 (s, 5 H, Cp), 0.12 (s/d, J($^{117/119}$Sn, H) = 53/56 Hz, 9 H, Sn-Me). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 83.4 (s/d, J($^{117/119}$Sn, C) = 47 Hz, Cp-C5), 82.7 (s/d, J($^{117/119}$Sn, C) = 46 Hz, Cp-C2), 78.7 (s/d, J($^{117/119}$Sn, C) = 35 Hz, Cp-C4), 76.9 (*ipso*-Cp), 70.9 (Cp), −9.0 (s/d, J($^{117/119}$Sn, C) = 346/361 Hz, Sn-Me). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ −10.1. For **2c-Cl**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 4.44 (pst, J = 1.8 Hz, 2 H, CpB-H3,4), 4.36 (pst, J = 1.8 Hz, 2 H, CpB-H2,5), 4.18 (pst, J = 1.8 Hz, 2 H, CpSn-H3,4), 3.88 (pst, J = 1.8 Hz, 2 H, CpSn-H2,5), 0.14 (s/d, J($^{117/119}$Sn, H) = 53/56 Hz, 9 H, Sn-Me). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ −7.2. Reliable ^{13}C NMR data for **2c-Cl** could not be obtained, as the amount of the 1,1′-disubstituted isomer in the reaction mixture is very small. The ^{11}B NMR signals for the individual isomers could not be resolved. The following assignment is made for the isomer mixture: ^{11}B NMR (128.3 MHz, C$_6$D$_6$, 20 °C): 51 ($h_{1/2}$ = 320 Hz).

Reaction of 1 with C$_6$F$_5$BCl$_2$. Neat C$_6$F$_5$BCl$_2$ (122 mg, 0.49 mmol) was added dropwise to a solution of 1,1′-fc(SnMe$_3$)$_2$ (250 mg, 0.50 mmol) in hexanes (10 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and then allowed to slowly warm to 0 °C. All volatile material was removed under reduced pressure (10^{-3} Torr), and the product was subsequently kept under dynamic vacuum at ambient temperature over a period of 1 h. The crude product was obtained as a dark red oil and characterized by NMR spectroscopy without further purification. The isomer ratios for compounds **2a-Pf** (55%) and **2b-Pf** (45%) were estimated via integration of the SnMe$_3$ proton NMR signal. The 1,1′-isomer **2c-Pf** was not observed. For **2a-Pf**: ^{1}H NMR (500 MHz, C$_6$D$_6$, 70 °C): δ 4.70 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 14 Hz, 1 H, Cp-H5), 4.61 (pst/dpst, J = 2.4 Hz, J($^{117/119}$Sn, H) = 5 Hz, 1 H, Cp-H4), 4.16 (br, 1 H, Cp-H3), 4.05 (s, 5 H, Cp), 0.29 (s/d, J($^{117/119}$Sn, H) = 53/56 Hz, 9 H, Sn-Me). ^{19}F NMR (376.2 MHz, C$_6$D$_6$, 20 °C): −130.3 (dd, J(F, F) = 26 Hz, J(F, F) = 8 Hz, 2 F, *ortho*-F), −152.5 (t, J(F, F) = 22 Hz, 1 F, *para*-F); −162.3 (m, 2 F, *meta*-F). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 146.9 (d, J(C, F) = 246 Hz, C$_6$F$_5$), 142.2 (d, J(C, F) = 255 Hz, C$_6$F$_5$), 137.6 (d, J(C, F) = 252 Hz, *para*-C$_6$F$_5$), 113.5 (br, *ipso*-C$_6$F$_5$), 86.5 (s/d, J($^{117/119}$Sn, ^{13}C) = 49 Hz, Cp-C5), 81.8 (*ipso*-CpSn), 81.0 (s/d, J($^{117/119}$Sn, ^{13}C) = 33 Hz, Cp-C3), 80.5 (s/d, J($^{117/119}$Sn, ^{13}C) = 40 Hz, Cp-C4), 77.5 (br, *ipso*-CpB), 70.5 (Cp), −6.8 (s/d, J($^{117/119}$Sn, ^{13}C) = 351/368 Hz, Sn-Me). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ −6.0. For **2b-Pf**: ^{1}H NMR (500 MHz, C$_6$D$_6$, 70 °C): δ 4.53 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 10 Hz, 1 H, Cp-H5), 4.46 (br, 1 H, Cp-H4), 4.42 (br, 1 H, Cp-H2), 4.08 (s, 5 H, Cp), 0.15 (s/d, J($^{117/119}$Sn, H) = 53/56 Hz, 9 H, Sn-Me). ^{19}F NMR (376.2 MHz, C$_6$D$_6$, 20 °C): δ −130.3 (br, 2 F, *ortho*-F), −151.9 (br, 1 F, *para*-F), −162.3 (m, 2 F, *meta*-F). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 146.7 (d, J(C, F) = 245 Hz, C$_6$F$_5$), 142.1 (d, J(C, F) = 255 Hz, *para*-C$_6$F$_5$), 137.6 (d, J(C, F) = 252 Hz, C$_6$F$_5$), 113.5 (br, *ipso*-C$_6$F$_5$), 84.4 (s/d, J($^{117/119}$Sn, ^{13}C) = 45 Hz, Cp-C2), 82.9 (s/d, J($^{117/119}$Sn, ^{13}C) = 46 Hz, Cp-C5), 81.2 (*ipso*-CpSn), 79.0 (s/d, J($^{117/119}$Sn, ^{13}C) = 35 Hz, Cp-C4), 75.2 (br, *ipso*-CpB), 70.5 (Cp), −9.1 (s/d, J($^{117/119}$Sn, ^{13}C) = 346/362 Hz, Sn-Me). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ −9.9. The ^{11}B NMR signals for the individual isomers could not be resolved. The following assignment is made for the isomer mixture: ^{11}B NMR (128.3 MHz, C$_6$D$_6$, 20 °C): 52.0 ($h_{1/2}$ = 500 Hz).

Reaction of 1 with 0.5 Equiv of PhBCl$_2$. Synthesis of 1-Stannyl-2-borylferrocenes 2a-Ph, 2b-Ph, and 2c-Ph. A solution of PhBCl$_2$ (0.17 g, 1.00 mmol) in toluene (5 mL) was added dropwise to a solution of 1,1′-fc(SnMe$_3$)$_2$ (1.02 g, 2.00 mmol) in toluene (20 mL) at ambient temperature. The reaction mixture was allowed to stir for 12 h, and subsequently all volatile material was removed under reduced pressure at ambient temperature. A dark red oil was obtained and characterized by NMR spectroscopy without further purification. The ratios for compounds **1** (52), **2a-Ph** (19), **2b-Ph** (20), and **2c-Ph** (9) were estimated via integration of the SnMe$_3$ proton NMR signal. For **2a-Ph**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 8.01 (d, J = 8.0 Hz, 2 H, *ortho*-Ph), 7.25−7.23 (m, 3 H, *para*-Ph, *meta*-Ph), 4.68 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 8 Hz, 1 H, Cp-H3), 4.61 (pst, J = 2.4 Hz, J($^{117/119}$Sn, H) = nr, 1 H, Cp-H4), 4.61 (dd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = nr, 1 H, Cp-H5), 3.93 (s, 5 H, Cp), 0.34 (s/d, J($^{117/119}$Sn, H) = 52/54 Hz, 9 H, Sn-Me). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 140.5 (br, *ipso*-Ph), 134.9 (*ortho*-Ph), 131.5 (*para*-Ph), 128.1 (*meta*-Ph), 84.5 (s/d, J($^{117/119}$Sn, ^{13}C) = 53 Hz, Cp-C5), 81.6 (s/d, J($^{117/119}$Sn, ^{13}C) = 36 Hz, Cp-C3), 81.1 (*ipso*-CpSn), 78.8 (s/d, J($^{117/119}$Sn, ^{13}C) = 42 Hz, Cp-C4), 70.3 (Cp), −6.4 (s/d, J($^{117/119}$Sn, ^{13}C) = 348/365 Hz, Sn-Me), not observed (*ipso*-CpB). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ −8.5. For **2b-Ph**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 8.14 (d, J = 8.0 Hz, 2 H, *ortho*-Ph), 7.25−7.23 (m, 3 H, *para*-Ph, *meta*-Ph), 4.85 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 8 Hz, 1 H, Cp-H4), 4.73 (pst/dpst, J = 1.2 Hz, J($^{117/119}$Sn, H) = 11 Hz, 1 H, Cp-H2), 4.49 (dd/ddd, J = 1.2/2.4 Hz, J($^{117/119}$Sn, H) = 10 Hz, 1 H, Cp-H5), 3.93 (s, 5 H, Cp), 0.18 (s/d, J($^{117/119}$Sn, H) = 54/56 Hz, 9 H, Sn-Me). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 139.8 (br, *ipso*-Ph), 135.0 (*ortho*-Ph), 131.8 (*para*-Ph), 128.3 (*meta*-Ph), 83.7 (s/d, J($^{117/119}$Sn, ^{13}C) = 46 Hz, Cp-C2), 82.9 (s/d, J($^{117/119}$Sn, ^{13}C) = 47 Hz, Cp-C5), 79.7 (s/d, J($^{117/119}$Sn, ^{13}C) = 37 Hz, Cp-C4), 79.2 (*ipso*-CpSn), 70.3 (Cp), −9.0 (s/d, J($^{117/119}$Sn, ^{13}C) = 345/360 Hz, Sn-Me), not observed (*ipso*-CpB). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ −10.6. For **2c-Ph**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 8.08 (d, J = 8.0 Hz, 2 H, *ortho*-Ph), 7.25−7.00 (m, 3 H, *para*-Ph, *meta*-Ph), 4.66 (pst, J = 1.8 Hz, 2 H, CpB-H3,4), 4.61 (pst, = 1.8 Hz, 2 H, CpB−H2,5), 4.18 (pst, J = 1.8 Hz, 2 H, CpSn-H3,4), 3.89 (pst, J = 1.8 Hz, 2 H, CpSn−H2,5), 0.21 (s/d, J($^{117/119}$Sn, H) = 55/58 Hz, 9 H, Sn-Me). Reliable ^{13}C and ^{119}Sn NMR data for **2c-Ph** could not be obtained since the relative ratio of the 1,1′-disubstituted isomer in the reaction mixture is very low. The ^{11}B NMR signals for the individual isomers could not be resolved. The following assignment is made for the isomer mixture: ^{11}B NMR (128.3 MHz, C$_6$D$_6$, 20 °C): 57.2 ($h_{1/2}$ = 500 Hz).

Reaction of 1 with 2 Equiv of BCl$_3$. Synthesis of 3a-Cl. A solution of BCl$_3$ (7.2 mL, 1.0 M in hexanes) was added dropwise to a solution of 1,1′-fc(SnMe$_3$)$_2$ (1.84 g, 3.60 mmol) in hexanes (20 mL) at −78 °C. The reaction mixture was allowed to slowly warm to ambient temperature and allowed to stir for 12 h. All volatile material was removed under reduced pressure (10^{-3} Torr), and the product was subsequently kept under dynamic vacuum at room temperature over a period of 12 h. The red oily product was redissolved in hexanes (20 mL) and filtered through a glass frit. After repeated recrystallization at −78 °C dark red crystals of 1-stannyl-2-borylferrocene **3a-Cl** (0.63 g, 35%) were isolated. For **3a-Cl**: ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ 5.24 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 14 Hz, 1 H, Cp-H5), 4.55 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 10 Hz, 1 H, Cp-H3), 4.53 (pst/dpst, J = 2.4 Hz, J($^{117/119}$Sn, H) = 7 Hz, 1 H, Cp-H4), 3.87 (s, 5 H, Cp), 0.69 (s/d, J($^{117/119}$Sn, H) = 61/64 Hz, 3 H, Sn-Me), 0.52 (s/d, J($^{117/119}$Sn, H) = 60/62 Hz, 3 H, Sn-Me). ^{13}C NMR (125.7 MHz, C$_6$D$_6$, 25 °C): δ 86.2 (s/d, J($^{117/119}$Sn, C) = 48 Hz, Cp-C5), 82.1 (*ipso*-CpSn), 81.1 (s/d, J($^{117/119}$Sn, C) = 49 Hz, Cp-C4), 80.7 (s/d, J($^{117/119}$Sn, C) = 43 Hz, Cp-C3), 77.6 (br, ipso-CpB), 71.7 (Cp), 2.5 (s/d, J($^{117/119}$Sn, C) = 441/462 Hz, Sn-Me), 1.1 (s/d, J($^{117/119}$Sn, C) = 402/420 Hz, Sn-Me). ^{11}B NMR (128.3 MHz, C$_6$D$_6$, 20 °C): δ 49.8 ($h_{1/2}$ = 350 Hz). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ 102.1. MS (70 eV, EI): *m/z* (%) 450 (100) [M$^+$] 435 (28) [M$^+$ − CH$_3$], 420 (73) [M$^+$ − 2 CH$_3$]; $C_{12}H_{14}BCl_3FeSn$ (450.0) calcd C 32.03, H 3.14; found C 32.40, H 3.33.

Reaction of 1 with a Large Excess of BCl$_3$. A solution of **1** (1.02 g, 2.00 mmol) in hexanes (25 mL) was cooled to −78 °C, and BCl$_3$ (10.0 mL, 1.0 M in hexanes) was slowly added via syringe. The reaction mixture was allowed to slowly warm to ambient temperature and allowed to stir for 12 h. All volatile material was removed under reduced pressure (10^{-3} Torr), and the product was subsequently kept under dynamic vacuum at room temperature over a period of 12 h. The red oily product was redissolved in hexanes (20 mL) and filtered through a glass frit. An NMR spectroscopic investigation of the crude product revealed species **3a-Cl** as the major component.

Reaction of 1 with 2 Equiv of PhBCl$_2$. Synthesis of 3a-Ph. Neat PhBCl$_2$ (3.34 g, 21.0 mmol) was added dropwise to a solution of 1,1′-fc(SnMe$_3$)$_2$ (5.12 g, 10.0 mmol) in toluene (50 mL) at −78 °C. The reaction mixture was allowed to slowly warm to ambient temperature and stirred for 2 days. All volatile material was removed under high vacuum at ambient temperature over a period of 12 h. The red oily product was redissolved in hexanes (20 mL), a small amount of insoluble green material was removed via filtration through a glass frit, and the solvent was removed under high vacuum. A dark red oil was obtained and characterized by NMR spectroscopy. The isomer ratios were estimated via integration of the SnMe$_3$ proton NMR signal to ca. 60/40 for 1,2-isomers/1,3-isomers. Repeated recrystallization of the crude product from hexanes yielded dark red crystals (1.53 g, 31%) of the analytically pure isomer **3a-Ph**. For **3a-Ph**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 7.89 (d, J = 8.0 Hz, 2 H, *ortho*-Ph), 7.23 (t, J = 7.5 Hz, 1 H, *para*-Ph), 7.18 (pst, J = 7.8 Hz, 2 H, *meta*-Ph), 5.46 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 15 Hz, 1 H, Cp-H5), 4.63 (pst/dpst, J = 2.4 Hz, J($^{117/119}$Sn, H) = 8 Hz, 1 H, Cp-H4), 4.57 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 11 Hz, 1 H, Cp-H3), 3.86 (s, 5 H, Cp), 0.82 (s/d, J($^{117/119}$Sn, H) = 63/66 Hz, 3 H, Sn-Me), 0.66 (s/d, J($^{117/119}$Sn, H) = 60/63 Hz, 3 H, Sn-Me). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 138.7 (*ipso*-Ph), 134.7 (*ortho*-Ph), 132.0 (*para*-Ph), 128.3 (*meta*-Ph), 85.4 (s/d, J($^{117/119}$Sn, ^{13}C) = 53 Hz, Cp-C5), 83.8 (*ipso*-CpSn), 80.9 (s/d, J($^{117/119}$Sn, ^{13}C) = 47 Hz, Cp-C3), 80.6 (s/d, J($^{117/119}$Sn, ^{13}C) = 52 Hz, Cp-C4), 75.8 (br, *ipso*-CpB), 70.3 (Cp), 2.6 (s/d, J($^{117/119}$Sn, ^{13}C) = 453/473 Hz, Sn-Me), 1.4 (s/d, J($^{117/119}$Sn, ^{13}C) = 409/430 Hz, Sn-Me). ^{11}B NMR (128.3 MHz, C$_6$D$_6$, 20 °C): δ 56.4 ($h_{1/2}$ = 500 Hz). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ 85.9. MS (70 eV, EI): *m/z* (%) 492 (100) [M$^+$], 477 (15) [M$^+$ − CH$_3$], 462 (53) [M$^+$ − 2 CH$_3$]; $C_{18}H_{19}BCl_2FeSn$ (491.6) calcd C 43.98, H 3.90; found C 43.55, H 3.90. For **3b-Ph**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 8.08 (d, J = 8.0 Hz, 2 H, *ortho*-Ph), 7.3−7.1 (m, 3 H, *meta*-Ph, *para*-Ph), 4.83 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 7 Hz, 1 H, Cp-H4), 4.73 (pst/dpst, J = 1.2 Hz, J($^{117/119}$Sn, H) = 12 Hz, 1 H, Cp-H2), 4.51 (dd/ddd, J (H, H) = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 11 Hz, 1 H, Cp-H5), 3.94 (s, 5 H, Cp), 0.41 (s/d, J($^{117/119}$Sn, H) = 62 Hz, 3 H, Sn-Me), 0.40 (s/d, J($^{117/119}$Sn, H) = 62 Hz, 3 H, Sn-Me). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 139.3 (br, *ipso*-Ph), 135.1 (*ortho*-Ph), 132.2 (*para*-Ph), 128.2 (*meta*-Ph), 82.9 (s/d, J($^{117/119}$Sn, ^{13}C) = 66 Hz, Cp-C2), 81.8 (J($^{117/119}$Sn, ^{13}C) = 62 Hz, Cp-C5), 80.2 (J($^{117/119}$Sn, ^{13}C) = 49 Hz, Cp-C4), 78.7 (*ipso*-CpSn), 74.2 (br, *ipso*-CpB), 70.7 (Cp), −1.8 (s/d, J($^{117/119}$Sn, ^{13}C) = 398/417 Hz, Sn-Me), −1.6 (s/d, J($^{117/119}$Sn, ^{13}C) = 398/417 Hz, Sn-Me). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ 118.9.

Attempted Reaction of 1 with MesBCl$_2$. A solution of 1,1′-fc(SnMe$_3$)$_2$ (0.51 g, 1.00 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with neat MesBCl$_2$ (0.20 g, 1.00 mmol) at −78 °C. The reaction mixture was allowed to slowly warm to ambient temperature and stirred for 2 days. A proton NMR spectroscopic investigation of the reaction mixture revealed only signals for the two precursors.

Synthesis of 4a-Cl. A solution of BCl$_3$ (14.5 mL, 1.0 M in hexanes) was added dropwise to a solution of 1,1′-fc(SnMe$_3$)$_2$ (7.34 g, 14.5 mmol) in hexanes (20 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and then allowed to slowly warm to ambient temperature. All volatile material was removed under reduced pressure (10^{-3} Torr), and the product was subsequently kept under dynamic vacuum at 50 °C over a period of 3 h. The red oily product was redissolved in hexanes (20 mL) and filtered through a glass frit to remove a small amount of insoluble material. After repeated recrystallization at −37 °C dark red crystals of 1-stannyl-2-borylferrocene **4a-Cl** (2.43 g, 39%) were isolated. For **4a-Cl**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 5.33 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 15 Hz, 1 H, Cp-H5), 4.54 (pst/dpst, J = 2.4 Hz, J($^{117/119}$Sn, H) = 7 Hz, 1 H, Cp-H4), 4.22 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 11 Hz, 1 H, Cp-H3), 3.83 (s, 5 H, Cp), 0.86 (s, 3 H, B-Me), 0.82 (s/d, J($^{117/119}$Sn, H) = 63/66 Hz, 3 H, Sn-Me), 0.65 (s/d, J($^{117/119}$Sn, H) = 60/63 Hz, 3 H, Sn-Me). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 84.8 (s/d, J($^{117/119}$Sn, C) = 52 Hz, Cp-C5), 81.8 (*ipso*-CpSn), 80.3, 80.0 (Cp-C3,4), 70.3 (Cp), 9.3 (br, B-Me), 2.7 (s/d, J($^{117/119}$Sn, C) = 443/473 Hz, Sn-Me), 1.3 (s/d, J($^{117/119}$Sn, C) = 408/429 Hz, Sn-Me), not observed (*ipso*-CpB). ^{11}B NMR (128.3 MHz, C$_6$D$_6$, 20 °C): δ 61.5 ($h_{1/2}$ = 400 Hz). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ 89.8. MS (70 eV, EI): *m/z* (%) 430 (100) [M$^+$], 415 (27) [M$^+$ − CH$_3$], 400 (78) [M$^+$ − 2 CH$_3$], 246 (59) [MH$^+$ − SnMe$_2$Cl]; $C_{13}H_{17}BCl_2FeSn$ (429.6) calcd C 36.35, H 3.99; found C 36.35, H 4.10.

Synthesis of 4a-Ph. A solution of PhBCl$_2$ (1.58 g, 9.95 mmol) in hexanes (30 mL) was added dropwise to a solution of 1,1′-fc(SnMe$_3$)$_2$ (5.12 g, 10.0 mmol) in hexanes (80 mL) at −78 °C. The reaction mixture was allowed to slowly warm to ambient temperature and stirred for another 12 h. All volatile material was removed under reduced pressure (10^{-3} Torr), and the product was subsequently kept under dynamic vacuum at 80 °C over a period of 5 h. The red oily product was redissolved in hexanes (20 mL) and filtered through a glass frit. After repeated recrystallization at −37 °C dark red crystals of 1-stannyl-2-borylferrocene **4a-Ph** (1.09 g, 23%) were isolated. For **4a-Ph**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 7.38 (d, J = 7.6 Hz, 2 H, *ortho*-Ph), 7.08−7.04 (m, 3 H, *para*-Ph, *meta*-Ph), 5.20 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 14 Hz, 1 H, Cp-H5), 4.72 (pst/dpst, J = 2.4 Hz, J($^{117/119}$Sn, H) = 6 Hz, 1 H, Cp-H4), 4.70 (dd/ddd, J = 1.2 Hz, 2.4 Hz, J($^{117/119}$Sn, H) = 13 Hz, 1 H, Cp-H3), 4.02 (s, 5 H, Cp), 1.07 (s, 3 H, B-Me), 0.54 (s/d, J($^{117/19}$Sn, H) = 57/60 Hz, 3 H, Sn-Me), −0.16 (s/d, J($^{117/119}$Sn, H) = 62/64 Hz, 3 H, Sn-Me). ^{13}C NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 147.3 (*ipso*-Ph), 132.8 (*ortho*-Ph), 130.7 (*para*-Ph), 129.1 (*meta*-Ph), 83.6 (s/d, J($^{117/119}$Sn, ^{13}C) = 58 Hz, Cp-C5), 83.0 (s/d, J($^{117/119}$Sn, ^{13}C) = 57 Hz, Cp-C3), 80.9 (br, *ipso*-CpB), 79.1 (s/d, J($^{117/119}$Sn, ^{13}C) = 54 Hz, Cp-C4), 77.9 (*ipso*-CpSn), 69.9 (Cp), 10.7 (br, B-Re), 2.4 (s/d, J($^{117/119}$Sn, ^{13}C) = 396/411 Hz, Sn-Me), −0.6 (s/d, J($^{117/119}$Sn, ^{13}C) = 438/454 Hz, Sn-Me). ^{11}B NMR (128.3 MHz, C$_6$D$_6$, 20 °C): δ 67.5 ($h_{1/2}$ = 500 Hz). ^{119}Sn NMR (149.1 MHz, C$_6$D$_6$, 20 °C): δ 94.1. MS (70 eV, EI): *m/z* (%) 472 (100) [M$^+$], 457 (10) [M$^+$ − CH$_3$], 442 (50) [M$^+$ − 2 CH$_3$]; $C_{19}H_{22}BClFeSn$ (471.2) calcd C 48.43, H 4.71; found C 48.02, H 4.70.

Crystal Structure Determination for 4a-Cl and 4a-Ph. Data were collected on a Nonius Kappa-CCD diffractometer and were integrated and scaled using the Denzo-SMN package.[53] The structures were solved by direct methods (SHELXS97) and refined by full-matrix least squares (SHELXTL V5.1[54]) based on F^2 with all reflections. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publications nos. 188 727 (**4a-Cl**)

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(53) Otwinowski, Z.; Minor, W. *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A; Carter, C. W., Sweet, R. M., Eds.; Academic Press: London, 1997; pp 307−326.

(54) Sheldrick, G. M. *SHELXTL/PC*, Version 5.1, Windows NT Version; Bruker AXS Inc.: Madison, WI, 1999.

and 182/1154 (**4a-Ph**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data for compound **4a-Cl**, including tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. UV−visible data and selected 2D NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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