Fluoride-Promoted Aryl and Allyl Migration from Boron to Tin in 1-Stannyl-2-borylferrocenes

Ramez Boshra, Ami Doshi, and Frieder Jäkle*

Department of Chemistry, Rutgers University-Newark, 73 Warren Street, Newark, New Jersey 07102

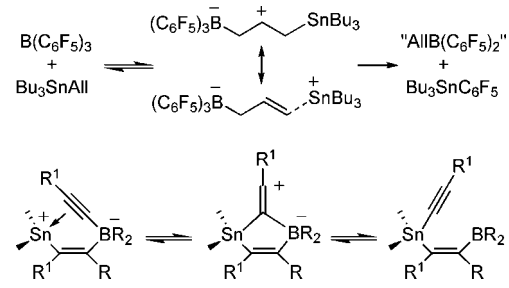
Received September 28, 2007

Transmetalation reactions where organotin reagents are used for the transfer of organic groups to boron halides are among the most selective and hence synthetically useful methods for the preparation of organoboranes. We describe here a rare example of the reverse reaction, where migration of the organic group from boron to tin is promoted by addition of fluoride. The bidentate Lewis acids Fc(BMeR)($SnMe_2Cl$) (Fc = 1,2-ferrocenediyl; R = phenyl (Ph), thienyl (Th), allyl (All)) react with KF at 45 °C to give the rearranged fluoroboranes Fc(BMeF)($SnMe_2R$) as oily liquids. With an excess of KF, the fluoroborate complexes K[Fc($BMeF_2$)($SnMe_2R$)] are obtained, which are readily isolated as light yellow solids in good to high yields. For the phenyl derivative it was demonstrated that the borate salt can be converted back to the fluoroborane by treatment with Me_3SiOTf or addition of pyridine, which gives the adduct Fc(BMeF)($SnMe_2Ph$)·Py as a crystalline solid. The fluoride and pyridine complexes have been characterized by multinuclear NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction (for R = Ph). Preliminary mechanistic studies suggest an intramolecular process and indicate that Lewis acid induced Sn−F bond activation may play an important role.

Introduction

Transfer of organic groups from tin to boron is one of the most useful tools for the preparation of organoboron compounds, including that of polymeric materials, with the main benefits being the mild reaction conditions and high selectivity commonly achieved.[1] In contrast, the reverse reaction, the transfer of organic groups from boron to tin, is only rarely encountered.[2] An interesting example is the reaction of $B(C_6F_5)_3$ with $AllSnBu_3$ studied by Piers, which leads to formation of $C_6F_5SnBu_3$ along with $AllB(C_6F_5)_2$, which in turn reacts further to a mixture of unidentified organoboron products (Chart 1).[3,4] Wrackmeyer demonstrated that intramolecular transfer of an alkynyl group from boron to a tin cation occurs readily in 1-stannyl-2-borylalkene derivatives.[5] In fact, these compounds establish an equilibrium between the neutral form and a zwitterionic species, in which a formally cationic tin moiety is stabilized by side-on coordination of the boron-bound alkynyl group (Chart 1). Intriguingly, the equilibrium can be shifted

Chart 1



with complete transfer of the alkynyl group to tin by addition of pyridine, which coordinates to boron. Migration of phenyl groups from boron to carbon has been observed, for example, in reactions of organoboranes with chiral sulfonium ylides and in the base-promoted bromide replacement of α-bromo alkylborates.[6] Related to these migration reactions are also 1,3-isomerization reactions of allylic stannanes[7] and ligand redistribution reactions between organotin species and organotin halides.[8] The latter are especially facile with allyltin reagents.[9]

We are interested in ferrocene-based bidentate Lewis acids, in which two Lewis acid sites are attached adjacent to one another at one of the Cp rings.[10,11] During the course of our studies we found that the heteronuclear bidentate Lewis acids Fc(BMeR)($SnMe_2Cl$) (R = Cl, **1-Cl**; R = Ph, **1-Ph**), which contain neighboring stannyl and boryl groups attached to

* To whom correspondence should be addressed. E-mail: fjaekle@rutgers.edu.

(1) (a) Köster, R. *Methods of Organic Chemistry (Houben-Weyl)*; G. Thieme Verlag: Stuttgart, New York, 1982; Vol. 13/3a. (b) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988. (c) Matteson, D. S. *Stereodirected Synthesis with Organoboranes*; Springer: Berlin, Heidelberg, New York, 1995. (d) Kaufmann, D. E., Matteson, D. S., Eds. *Organometallics: Boron Compounds*; G. Thieme Verlag: Stuttgart, New York, 2004; Science of Synthesis Vol. 6. (e) Jäkle, F. Boron: Organoboranes In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed.; Wiley: Chichester, U.K., 2005; pp 560–598. (f) Jäkle, F. *Coord. Chem. Rev.* **2006**, *250*, 1107–1121.

(2) The use of $Na[BEt_4]$ for the qualitative and quantitative determination of organotin species in aqueous medium through conversion to the ethylated tetraorganotin derivatives has been described; see: Carlier-Pinasseau, C.; Lespes, G.; Astruc, M. *Appl. Organomet. Chem.* **1996**, *10*, 505–512.

(3) Blackwell, J. M.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 1295–1306.

(4) Morrison, D. J.; Blackwell, J. M.; Piers, W. E. *Pure Appl. Chem.* **2004**, *76*, 615–623.

(5) Wrackmeyer, B.; Kehr, G.; Willbold, S. *J. Organomet. Chem.* **1999**, *590*, 93–103.

(6) (a) Aggarwal, V. K.; Fang, G. Y.; Schmidt, A. T. *J. Am. Chem. Soc.* **2005**, *127*, 1642–1643. (b) Robiette, R.; Fang, G. Y.; Harvey, J. N.; Aggarwal, V. K. *Chem. Commun.* **2006**, 741–743. (c) Matteson, D. S.; Mah, R. W. *J. Am. Chem. Soc.* **1963**, *85*, 2599–2603.

(7) Marshall, J. A.; Gill, K. *J. Organomet. Chem.* **2001**, *624*, 294–299.

(8) Davies, A. G. *Organotin Chemistry*; 2nd ed.; Wiley-VCH: Weinheim, Germany, 2004.

(9) (a) Gambaro, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1981**, *210*, 57–62. (b) Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *Tetrahedron* **1989**, *45*, 1067–1078.

10.1021/om700967a CCC: $40.75
Publication on Web 03/04/2008

ferrocene, are readily obtained through regioselective borylation of 1,1′-bis(trimethylstannyl)ferrocene in α-position with BCl_3 and $PhBCl_2$, respectively.[12,13] The initial electrophilic attack of the boron halide is followed by a proton migration and elimination of Me_3SnCl, leading to the 1,2-disubstituted species $Fc(BCl_2)(SnMe_3)$ and $Fc(BPhCl)(SnMe_3)$. Subsequent moderate heating of the reaction mixture results in migration of one of the methyl groups from tin to boron.[14] This process follows the typical reactivity pattern of tin/boron exchange reactions and is believed to proceed through intramolecular activation of one of the Sn−Me groups in the "trans" position to a bridging boron-bound chlorine atom leading to intermolecular transfer of the methyl group and intramolecular migration of the chlorine atom to tin.

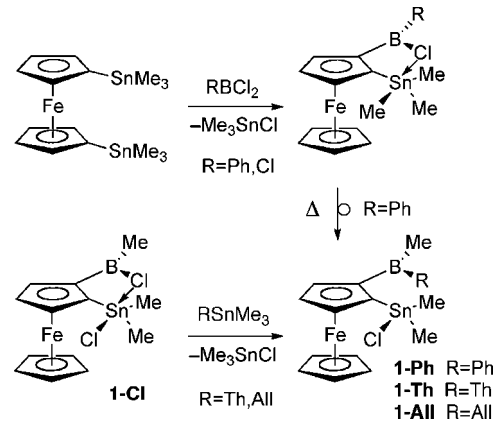
Currently we are investigating the binding properties of the resulting heteronuclear bidentate Lewis acids **1** and studying their use in asymmetric synthesis.[15–17] When they are reacted with KF in the presence of 18-crown-6, **1-Cl** and **1-Ph** form stable fluoride complexes in which the fluoride anion assumes a bridging position between boron and tin.[16,18] Here we demonstrate that, surprisingly, in the absence of 18-crown-6 a very different reactivity path is observed in that compounds $Fc(BMeR)(SnMe_2Cl)$ (R = Ph, Th, All) undergo an unusual and highly selective fluoride-promoted rearrangement reaction that involves facile transfer of the R group from boron to tin.

Results and Discussion

Compounds **1-Cl** and **1-Ph** were prepared as previously reported.[12,13] Transmetalation of **1-Cl** with $ThSnMe_3$ (Th = 2-thienyl) afforded $Fc(BMeTh)(SnMe_2Cl)$ (**1-Th**) as a red crystalline solid in 65% yield (Scheme 1). Using a similar procedure, the allyl derivative $Fc(BMeAll)(SnMe_2Cl)$ (**1-All**) was obtained from **1-Cl** and $AllSnMe_3$ as an orange-red oil in ca. 95% spectroscopic yield. The latter was used directly in subsequent reactions without further purification.

Each of the bidentate Lewis acids **1-R** (R = Ph, Th, All) was treated with 1 equiv of KF in THF at 45 °C for 3 h in an attempt at preparing the fluorostannane derivatives through replacement of the tin-bound chlorine for a fluorine substituent.[19] After filtration from insoluble salts, removal of the solvents, and extraction into hexanes the products were obtained as orange oils. Surprisingly, multinuclear NMR spectroscopy revealed the formation of the fluoroboranes **2-R** due to concomitant migration of the aryl/allyl group from boron to tin (Scheme 2, Table 1).[20]

Scheme 1



Scheme 2

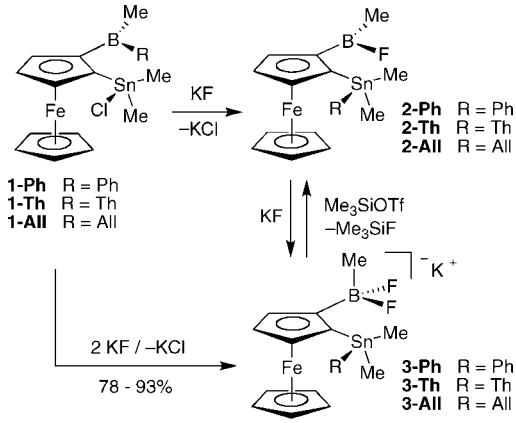


Table 1. Comparison of NMR Data for Compounds 1-R, 2-R, and 3-R

	$\delta(^{11}B)$ ($w_{1/2}$)	$\delta(^{19}F)$	$\delta(^{119}Sn)$
1-Ph[a]	68 (500)		102.3
1-Th[a]	62 (430)		95.4
1-All[a]	70 (600)		130.8
2-Ph[a]	53 (500)	−55.8	−32.1
2-Th[a]	53 (490)	−55.8	−33.5
2-All[a]	53 (530)	−55.8	−9.9
3-Ph[b]	9.2 (230)	−137.5/−142.6	−39.0
3-Th[b]	13.5 (210)	−130.9/−135.6	−46.5
3-All[b]	9.0 (160)	−132.0/−137.0	−12.5

[a] Data acquired in $CDCl_3$ at 25 °C. [b] Data acquired in CD_3CN at 25 °C.

Attachment of fluorine to boron in **2-R** is evident from a ^{19}F NMR signal at –55.8 ppm that is in a region typical of organofluoroboranes[21] and is further supported by a considerable upfield shift of the ^{11}B NMR resonances from a range of 62 to

(10) (a) Venkatasubbaiah, K.; Bats, J. W.; Rheingold, A. L.; Jäkle, F. *Organometallics* **2005**, *24*, 6043–6050. (b) Venkatasubbaiah, K.; Zakharov, L. N.; Kassel, W. S.; Rheingold, A. L.; Jäkle, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5428–5433. (c) Venkatasubbaiah, K.; DiPasquale, A. G.; Bolte, M.; Rheingold, A. L.; Jäkle, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 6838–6841. (d) Venkatasubbaiah, K.; Nowik, I.; Herber, R. H.; Jäkle, F. *Chem. Commun.* **2007**, 2154–2156.

(11) Heteronuclear bidentate Lewis acids with stannyl and boryl groups attached to vinylene, phenylene, and naphthalene scaffolds have been reported. See ref 14 and: (a) Köster, R.; Seidel, G.; Boese, R.; Wrackmeyer, B. *Chem. Ber.* **1988**, *121*, 597–615. (b) Wrackmeyer, B.; Kerschl, S.; Maisel, H. E.; Milius, W. *J. Organomet. Chem.* **1995**, *490*, 197–202. (c) Schulte, M.; Gabbaï, F. P. *Can. J. Chem.* **2002**, *80*, 1308–1312.

(12) Jäkle, F.; Lough, A. J.; Manners, I. *Chem. Commun.* **1999**, 453–454.

(13) Gamboa, J. A.; Sundararaman, A.; Kakalis, L.; Lough, A. J.; Jäkle, F. *Organometallics* **2002**, *21*, 4169–4181.

(14) For related studies with 1-stannyl-2-borylbenzene derivatives, see: Eisch, J. J.; Kotowicz, B. W. *Eur. J. Inorg. Chem.* **1998**, 761–769.

(15) Boshra, R.; Sundararaman, A.; Zakharov, L. N.; Incarvito, C. D.; Rheingold, A. L.; Jäkle, F. *Chem. Eur. J.* **2005**, *11*, 2810–2824.

(16) Boshra, R.; Venkatasubbaiah, K.; Doshi, A.; Lalancette, R. A.; Kakalis, L.; Jäkle, F. *Inorg. Chem.* **2007**, *46*, 10174–10186.

(17) Boshra, R.; Doshi, A.; Jäkle, F. *Angew. Chem., Int. Ed.* **2008**, *17*, 1134–1137.

(18) For related work with Hg/B heteronuclear bidentate Lewis acids see: (a) Solé, S.; Gabbaï, F. P. *Chem. Commun.* **2004**, 1284–1285. (b) Melaïmi, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2005**, *127*, 9680–9681.

(19) For examples of Sn−Cl for Sn−F exchange, see: (a) Krause, E. *Ber. Dtsch. Chem. Ges.* **1918**, *51*, 1447–1456. (b) Altmann, R.; Gausset, O.; Horn, D.; Jurkschat, K.; Schurmann, M.; Fontani, M.; Zanello, P. *Organometallics* **2000**, *19*, 430–443. (c) Beckmann, J.; Horn, D.; Jurkschat, K.; Rosche, F.; Schürmann, M.; Zachwieja, U.; Dakernieks, D.; Duthie, A.; Lim, A. E. K. *Eur. J. Inorg. Chem.* **2003**, 164–174. (d) Chaniotakis, N.; Jurkschat, K.; Müller, D.; Perdikaki, K.; Reeske, G. *Eur. J. Inorg. Chem.* **2004**, 2283–2288.

(20) Treatment of **1-Cl** with KF under similar conditions resulted in full recovery of the starting material, indicating that transfer of alkyl groups does not occur under these conditions.

(21) Bardin, V. V.; Frohn, H.-J. *Main Group Met. Chem.* **2002**, *25*, 589–613.

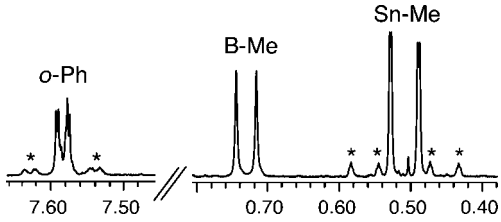


Figure 1. Ortho phenyl resonance (left) and methyl region (right) of the ^{1}H NMR spectrum of **2-Ph**. The $^{117/119}$Sn satellites are marked with asterisks.

70 ppm to ca. 53 ppm, which is attributed to enhanced π-overlap of boron and fluorine. Migration of the aryl group from boron to tin, on the other hand, results in a strong upfield shift of the ^{119}Sn NMR signals to ca. –10 to –34 ppm (**1-R** from 95 to 131 ppm). These data are consistent with formation of diarylstannanes, and for example, the value of –32.1 ppm for **2-Ph** compares favorably to that of −34.6 ppm for the nonborylated analogue $Fc(SnMe_2Ph)$. Aryl group transfer to tin is also evident from the ^{1}H NMR spectra, which display tin satellites for the ortho phenyl and thiophene protons in **2-Ph** ($J(^{117/119}Sn, H)$ = 46 Hz; Figure 1) and **2-Th** ($J(^{117/119}Sn, H)$ = 25 Hz), respectively, that are absent in the starting materials. Tin satellites are also found for the α-protons of the allyl group in **2-All** but are not well resolved. As a result of fluorine attachment to boron a doublet with a coupling constant of $^{3}J(^{19}F, H)$ of ca. 14 Hz is observed for the B−Me groups in compounds **2-R** (Figure 1).

The oily nature of species **2-R** prevented further characterization by elemental analysis or X-ray crystallography. Hence, we converted the products to the respective fluoroborate complexes **3-R** by reaction with another 1 equiv of KF in THF. Alternatively, the bidentate Lewis acids **1-R** may be directly treated with 2 equiv of KF in THF for 6 h at 45 °C (Scheme 2). The rearranged fluoride complexes **3-Ph**, **3-Th**, and **3-All** were obtained as light yellow microcrystalline solids in 78%, 89%, and 94% isolated yields, respectively, and fully characterized by multinuclear NMR, elemental analysis, and X-ray crystallography (for **3-Ph**).

The NMR data of compounds **3-R** are given in Table 1. An upfield shift of the ^{11}B NMR signals (9.0 to 13.5 ppm) in comparison to the signals for compounds **1-R** and **2-R** is consistent with tetracoordination at boron.[22] As expected for the formation of difluoroborate complexes, the ^{19}F NMR spectra reveal two distinct broad signals for the diastereotopic fluorine atoms. The ^{1}H NMR spectra display pseudotriplets for the boron methyl group as a result of coupling to the diastereotopic fluorines and, as in the case of compounds **2-R**, tin satellites are observed for the ortho protons of the organic group that is transferred to tin. Attachment of the aryl substituents to tin is also evident from the NOESY spectra for compounds **3-Ph** and **3-Th**, which display strong cross peaks between the ortho phenyl and thiophene protons, respectively, and the Cp proton adjacent to tin.

Various attempts at obtaining single crystals of compounds **3-R** resulted in light orange, microcrystalline precipitates that were not suitable for X-ray analysis. Suitable crystals were, however, readily obtained for the crown ether complex $[K(18\text{-crown-}6)]^{+}[Fc(BMeF_2)(SnMe_2Ph)]^{-}$ (**3-Ph′**) by addition of 1 equiv of 18-crown-6 to **3-Ph** and slow diffusion of hexanes into a toluene solution of the product.[23] The molecular structure of **3-Ph′** confirms the phenyl group migration from boron to tin (Figure 2). This migration results in a change from the distorted-trigonal-bipyramidal tin environment observed for **1-Ph** to an almost perfect tetrahedral structure in **3-Ph′**. The latter is, for example, evident from a sharp decrease in the degree of pentacoordination ($\%TBP_{eq} = [(120° - Avg_{eq})/(120° - 109.5°)] \times 100\%$, where Avg_{eq} is the average of the equatorial-to-equatorial angles)[24] from 74.3% for **1-Ph** to 34.2% for **3-Ph′**. The geometry change is further reflected in a significant increase of the tin atom displacement[25] from the plane defined by C(1), C(12), and C(13) from 0.352 Å for **1-Ph** to 0.571 Å for **3-Ph′**.

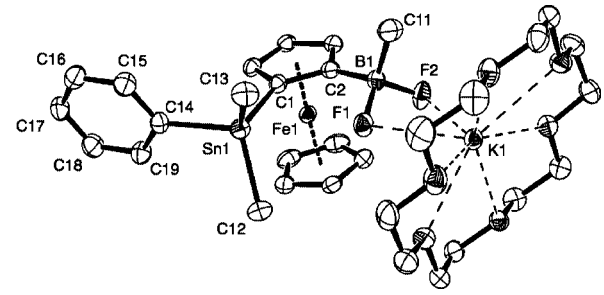


Figure 2. Molecular structure of **3-Ph′** (ORTEP, 30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−C(1) = 2.122(2), Sn(1)−C(12) = 2.140(3), Sn(1)−C(13) = 2.142(2), Sn(1)−C(14) = 2.157(3), B(1)−C(2) = 1.603(3), B(1)−C(11) = 1.605(4), B(1)−F(1) = 1.448(3), B(1)−F(2) = 1.450(3), Sn(1)···F(1) = 3.142(2), K(1)···F(1) = 2.8116(15), K(1)···F(2) = 2.6295(15); C(1)−Sn(1)−C(12) = 117.50(10), C(1)−Sn(1)−C(13) = 112.67(10), C(12)−Sn(1)−C(13) = 109.13(10), C(13)−Sn(1)−C(14) = 106.99(11), C(1)−Sn(1)−C(14) = 101.79(9), C(12)−Sn(1)−C(14) = 107.93(10), C(2)−B(1)−C(11) = 113.7(2), C(2)−B(1)−F(1) = 109.7(2), C(11)−B(1)−F(1) = 108.3(2), C(2)−B(1)−F(2) = 110.4(2), C(11)−B(1)−F(2) = 109.1(2), F(1)−B(1)−F(2) = 105.2(2), F(1)···Sn(1)−C(14) = 168.01(7).

The complex **3-Ph′** displays a coordination mode where electrostatic interactions lead to simultaneous interaction of both boron-bound fluorine atoms to the potassium ion and no additional donor ligands are found in the trans position. This arrangement results in unusually short K···F distances of 2.8116(15) and 2.6295(15) Å for K(1)···F(1) and K(1)···F(2), respectively.[26] Furthermore, the K ion is displaced by 0.629 Å from the plane defined by O(1)−O(6) toward the fluoride substituents. An even larger K displacement (0.8296 Å) has been previously observed for the fluoride complex $[K(18\text{-crown-}6)]^{+}[Fc(BMeF_2)]^{-}$.[16] The decrease in the K atom displacement in **3-Ph′** as compared to the monodentate $[K(18\text{-crown-}6)]^{+}[Fc(BMeF_2)]^{-}$ may be a consequence of a weak intermolecular interaction between the phenyl group and the neighboring K atom through C(17) and C(18) with intermolecular distances measuring 3.565 and 3.875 Å, respectively. For $[K(18\text{-crown-}6)]^{+}[Fc(BMePhF)]^{-}$ similar intermolecular phenyl/K contacts have been observed, which give rise to a polymeric structure in the solid state.[16]

(22) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372–11375.

(23) The ^{1}H NMR of $[K(18\text{-crown-}6)]^{+}[Fc(BMeF_2)(SnMe_2Ph)]^{-}$ (**3-Ph′**) displays chemical shifts that are very similar to those of $K^{+}[Fc(BMeF_2)(SnMe_2Ph)]^{-}$ (**3-Ph**).

(24) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *Organometallics* **1992**, *11*, 2099–2114.

(25) Altmann, R.; Jurkschat, K.; Schürmann, M.; Dakternieks, D.; Duhtie, A. *Organometallics* **1998**, *17*, 5858–5866.

(26) Related literature complexes: (a) Groux, L. F.; Weiss, T.; Reddy, D. N.; Chase, P. A.; Piers, W. E.; Ziegler, T.; Parvez, M.; Benet-Buchholz, J *J. Am. Chem. Soc.* **2005**, *127*, 1854–1869. (b) Fei, Z.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *Eur. J. Inorg. Chem.* **2005**, 860–865.

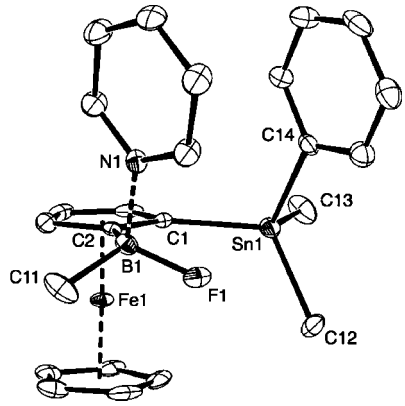


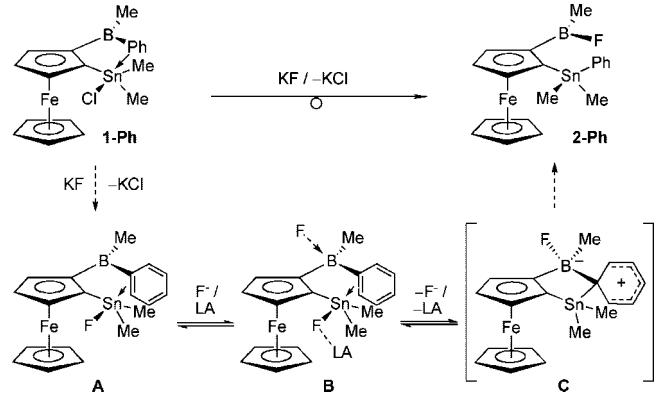
Figure 3. Molecular structure of **2-Ph·Py** (ORTEP, 30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−C(1) = 2.113(5), Sn(1)−C(13) = 2.152(6), Sn(1)−C(12) = 2.148(6), Sn(1)−C(14) = 2.158(5), B(1)−C(2) = 1.600(7), B(1)−C(11) = 1.598(8), B(1)−F(1) = 1.417(7), B(1)−N(1) = 1.665(6), Sn(1)···F(1) = 3.059(3), C(1)−Sn(1)−C(12) = 117.0(2); C(1)−Sn(1)−C(13) = 105.5(2), C(12)−Sn(1)−C(13) = 107.4(3), C(1)−Sn(1)−C(14) = 107.81(17), C(12)−Sn(1)−C(14) = 109.9(2), C(13)−Sn(1)−C(14) = 108.9(2), F(1)−B(1)−C(11) = 112.3(5), F(1)−B(1)−C(2) = 110.5(4), C(11)−B(1)−C(2) = 116.9(4).

The complexes **3-R** can be readily converted back to the free bidentate Lewis acids as illustrated for **3-Ph**. The compound Fc(BMeF)($SnMe_2$Ph) (**2-Ph**) was obtained by treatment of the fluoride complex **3-Ph** with 1 equiv of Me_3SiOTf in toluene in 94% yield.[27] Alternatively, a strong Lewis base may be applied to replace the fluoride. Treatment of **3-Ph** with excess pyridine in toluene resulted in elimination of KF and the formation of the pyridine adduct [Fc(BMeF)($SnMe_2$Ph)]·Py (**2-Ph·Py**) in 52% isolated yield. The latter was identified by multinuclear NMR and further characterized by X-ray diffraction analysis of orange single crystals obtained from toluene/hexanes at –35 °C. The most striking feature of the structure of **2-Ph·Py** is the apparent π-stacking of the phenyl and pyridine rings, which adopt an almost coplanar conformation at an interplanar angle of 7.26° (Figure 3). A slight slippage is observed, and the shortest C−C distances are in the range of 3.6− 3.7 Å. The B−N bond distance of 1.665(6) Å is relatively long, suggesting only weak binding of pyridine to boron.[28]

Mechanistic Aspects. We have carried out a series of experiments in an attempt to probe the unusual aryl/allyl migration from boron to tin and to answer the following questions. (1) What is the significance of the fluoride anion and does solvent polarity play a role? (2) Does the reaction proceed inter- or intramolecularly and what effect does the 1,2-substitution pattern have on the course of the reaction? (3) What are the likely intermediates of this process?

Fluoride shows a unique ability to promote the observed rearrangement, as other salts such as KH, KCl, and KBr do not give any reaction with **1-Ph** under similar conditions. Solvent polarity was found to be also of great importance. Reactions of **1-Ph** in acetonitrile proceeded more quickly, whereas those in toluene resulted in full recovery of the starting material even after prolonged treatment at higher temperatures. This may be related to the poor solubility of KF in nonpolar solvents. The need for polar solvents might also suggest the involvement of charged intermediate(s) that require solvent stabilization.

Scheme 3. Proposed Mechanism for the Fluoride-Induced Rearrangement of 1-Ph[a]



[a] LA = BR_3 from another ferrocenylborane molecule.

To assess whether the reaction proceeds through an intra- or intermolecular process, we conducted parallel experiments with varying amounts of THF as the solvent. At higher dilution the rearrangement of **1-Ph** proceeded considerably more slowly, consistent with an intermolecular component to the migration process. Next we reacted the monofunctional Lewis acid Fc(BMePh) with Fc($SnMe_2$Cl) and KF under similar conditions. Almost no conversion was found after 3 h at 45 °C, and the ^{1}H NMR spectrum taken after 2 days revealed a mixture of the following major components: Fc($SnMe_2$Cl) (∼20%), Fc(BMePh) (∼40%), Fc($SnMe_2$F) (∼25%), and Fc($SnMe_2$Ph) (∼15%). This suggests that there is also an intramolecular component to the migration process and that cooperativity of the neighboring Lewis acid groups facilitates the rearrangement reaction.

On the basis of the unique ability of fluoride to promote the rearrangement, we propose that the initial step involves replacement of the Sn-bound chlorine for fluorine (Scheme 3). Exchange reactions of Sn−Cl for Sn−F are well-known and occur readily with aqueous KF.[19] Moreover, fluoride-promoted phenyl group migrations from silicon to carbon are commonly observed and known to proceed through either nucleophilic or electrophilic activation.[29] These reactions are commonly referred to as Meerwein−Wagner type rearrangements and in some cases have been dubbed as "relay substitution" reactions. To further probe this step, we reacted the preformed fluoride complex $[K(18\text{-crown-6})]^+[Fc(BMePh)(SnMe_2F)F]^-$[16] with organoborane Lewis acids: e.g., $FcB(C_6F_5)_2$[30] and $B(C_6F_5)_3$. These Lewis acids should be able to effectively compete for the complexed fluoride

(27) Defluoridation of potassium fluoroborates can be accomplished by treatment with fluoride anion acceptors. (a) With BF_3: Frohn, H.-J.; Bailly, F.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2002**, *628*, 723–724. (b) With AsF_5: Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2001**, *627*, 15–16. (c) With Me_3SiCl: Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020–3027. (d) With Me_3SiOTf: Burgos, C. H.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044–8049.

(28) Höpfl, H. *J. Organomet. Chem.* **1999**, *581*, 129–149.

(29) See, for example: (a) Corey, J. Y.; Corey, E. R.; Chang, V. H. T.; Hauser, M. A.; Leiber, M. A.; Reinsel, T. E.; Riva, M. E. *Organometallics* **1984**, *3*, 1051–1060. (b) Eisch, J. J.; Chingchen, S. C. *Heteroat. Chem.* **1994**, *5*, 265–274. (c) Damrauer, R.; Yost, V. E.; Danahey, S. E.; O'Connell, B. K. *Organometallics* **1985**, *4*, 1779–1784. (d) Märkl, G.; Horn, M.; Schlosser, W. *Tetrahedron Lett.* **1986**, *27*, 4019–4022. (e) Hudrlik, P. F.; Abdallah, Y. M.; Kulkarni, A. K.; Hudrlik, A. M. *J. Org. Chem.* **1992**, *57*, 6552–6556. (f) Morihata, K.; Horiuchi, Y.; Taniguchi, M.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1995**, *36*, 5555–5558. (g) Aronica, L. A.; Morini, F.; Caporusso, A. M.; Salvadori, P. *Tetrahedron Lett.* **2002**, *43*, 5813–5815. (h) Aronica, L. A.; Raffa, P.; Caporusso, A. M.; Salvadori, P. *J. Org. Chem.* **2003**, *68*, 9292–9298.

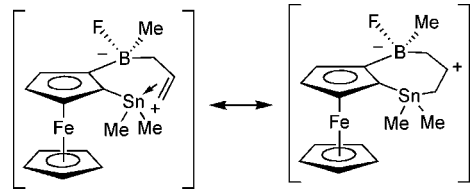
(30) Carpenter, B. E.; Piers, W. E.; Parvez, M.; Yap, G. A.; Rettig, S. J. *Can. J. Chem.* **2001**, *79*, 857–867.

and hence lead to (partial) liberation of the neutral fluorostannane [Fc(BMePh)($SnMe_2F$)] (**A**). However, the reaction resulted in formation of the rearranged product **2-Ph**, which suggests the presence of **A** as an intermediate in the observed rearrangement. It is important to point out that similar treatment of the chloro derivative $[K(18\text{-crown-6})]^+[Fc(BMePh)(SnMe_2Cl)F]^-$ with $FcB(C_6F_5)_2$ or Me_2SnCl_2 did not result in phenyl migration but rather in quantitative decomplexation of fluoride with formation of the unrearranged species **1-Ph**.

Partial tetracoordination of the boryl groups by fluoride is likely to be important to activate the aryl/allyl group in the actual rearrangement step. Precedents of Wagner−Meerwein type rearrangements of organoborates can be found in the literature (see ref 6). The observation that $Na[BPh_4]$ reacts slowly with R_3SnCl (R = Me, Bu) in THF at elevated temperature (85 °C) over a period of 2 days to give Ph_3B and $PhSnR_3$ is also in agreement with the proposed involvement of a borate intermediate.[31] Given the demonstrated ability of tetraorganoborates to transfer an aryl group from boron to tin, attack of a catalytic amount of F^- (or of a Sn−F moiety of another molecule) in **B** is likely to promote aryl (allyl) migration to the electron-deficient organotin moiety through a Wheland-type intermediate[32] (**C**; Scheme 3).

At this point the following question arises: why are stable fluoride complexes formed in the presence of 18-crown-6 and rearrangement only occurs when an organoborane is added as an external Lewis acid? We propose that in the presence of 18-crown-6 a stable and soluble fluoroborate complex is formed,[16] while in the absence of 18-crown-6 only a fraction of the organoborane is converted to the borate at any given time.[33] Given the pronounced ability of organoboranes to form complexes with fluoride,[34] the remaining uncomplexed borane (or the added external Lewis acid in the experiment with $[K(18\text{-crown-6})]^+[Fc(BMePh)(SnMe_2F)F]^-$) may then be able to activate the organotin moiety.

Chart 2. Possible Intermediate for the Fluoride-Induced Rearrangement of 1-All



Partial abstraction of the tin-bound fluorine by another ferrocenylborane molecule (**B**, LA = [Fc(BMePh)($SnMe_2F$)] in Scheme 3) should result in an activated organotin moiety that is stabilized by π-complexation with the adjacent aryl/allyl substituent on boron. Complexes of triorganotin cations with aromatic species are well-known and typically form upon generation of the highly reactive cations in aromatic solvents, unless prevented by extremely bulky substituents on tin.[35] In this context we should also reemphasize that alkynyl groups have been shown to coordinate to adjacent cationic Sn atoms in the zwitterionic alkynylborates reported by Wrackmeyer and bridging of allyl groups between $B(C_6F_5)_3$ and $-SnBu_3$ moieties has been demonstrated by Piers, as outlined in Chart 1.[3,4] π-Complexation of tin is further supported by the X-ray structure of the precursor **1-Ph**,[12,13] which already shows relatively short contacts between the meta and para carbon atoms of the boron-bound phenyl group and tin ($C_{meta}\cdots Sn$ = 3.516(4) Å and $C_{para}\cdots Sn$ = 3.216(4) Å). ^{119}Sn NMR measurements for **1-Ph**[13] also suggest the presence of such interactions in solution, as evidenced by an upfield shift to 102 ppm as compared to 130 ppm for the monodentate $Fc(SnMe_2Cl)$.[36]

The Wheland-type intermediate **C** allows for transfer of the aryl/allyl group and is itself likely stabilized by additional coordination of solvent (THF). Bridging aryl groups of this type are believed to be key intermediates in electrophilic substitution of arylstannanes with boron halides (the reverse aryl transfer reaction)[8] and commonly observed in organoaluminum chemistry: for example, in the dimeric structure of Ph_3Al, bis(μ-phenyl)bis(diphenylaluminum).[37] The ability of allyl groups to assume a bridging position as outlined in Chart 2 has been demonstrated by Piers[3] for the adduct of $B(C_6F_5)_3$ with $AllSnBu_3$ shown in Chart 1.

Conclusions

We have discovered a facile migration of aryl and allyl groups from boron to tin in 1,2-disubstituted ferrocenes. This process is promoted by addition of KF to the triorganoborane and leads to selective formation of fluoroboranes in high yields. The reaction resembles the so-called Meerwein−Wagner rearrangements that are commonly observed in organosilicon chemistry and also referred to as "relay substitutions".[29] Migration is believed to proceed through an intramolecular reaction pathway that likely involves Lewis acid activation of a fluorostannane intermediate with formation of a transient triorganotin cation

(31) Not surprisingly, these intermolecular reactions proceed considerably more slowly at the temperature of 45 °C used for the synthesis of compounds **2-R**.

(32) Rathore, R.; Hecht, J.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 13278–13279.

(33) Indeed, the mixture with KF in the absence of 18-crown-6 remains turbid throughout the reaction, indicating the presence of insoluble potassium salts.

(34) For recent examples of anion binding to organoboranes see: (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372–11375. (b) Suri, J. T.; Cordes, D. B.; Cappuccio, F. E.; Wessling, R. A.; Singaram, B. *Angew. Chem., Int. Ed.* **2003**, *42*, 5857–5859. (c) Kubo, Y.; Yamamoto, M.; Ikeda, M.; Takeuchi, M.; Shinkai, S.; Yamaguchi, S.; Tamao, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2036–2040. (d) Herberich, G. E.; Englert, U.; Fischer, A.; Wiebelhaus, D. *Eur. J. Inorg. Chem.* **2004**, 4011–4020. (e) Zhu, L.; Zhong, Z.; Anslyn, E. V. *J. Am. Chem. Soc.* **2005**, *127*, 4260–4269. (f) Koskela, S. J. M.; Fyles, T. M.; James, T. D. *Chem. Commun.* **2005**, 945–947. (g) Kubo, Y.; Ishida, T.; Kobayashi, A.; James, T. D. *J. Mater. Chem.* **2005**, *15*, 2889–2895. (h) Liu, Z.-Q.; Shi, M.; Li, F.-Y.; Fang, Q.; Chen, Z. H.; Yi, T.; Huang, C. H. *Org. Lett.* **2005**, *7*, 5481–5484. (i) Melaïmi, M.; Gabbaï, F. P. *Adv. Organomet. Chem.* **2005**, *53*, 61–99. (j) Bresner, C.; Aldridge, S.; Fallis, I. A.; Jones, C.; Ooi, L.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 3606–3609. (k) Bresner, C.; Day, J. K.; Coombs, N. D.; Fallis, I. A.; Aldridge, S.; Coles, S. J.; Hursthouse, M. B. *Dalton Trans.* **2006**, 3660–3667. (l) Neumann, T.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006**, *8*, 495–497. (m) Sakuda, E.; Funahashi, A.; Kitamura, N. *Inorg. Chem.* **2006**, *45*, 10670–10677. (n) Liu, X. Y.; Bai, D. R.; Wang, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 5475–5478. (o) Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 12879–12885. (p) Chiu, C.-W.; Gabbaï, F. P *J. Am. Chem. Soc.* **2006**, *128*, 14248–14249. (q) Agou, T.; Kobayashi, J.; Kawashima, T. *Inorg. Chem.* **2006**, *45*, 9137–9144. (r) Lee, M. H.; Agou, T.; Kobayashi, J.; Kawashima, T.; Gabbaï, F. P. *Chem. Commun.* **2007**, 1133–1135. (s) Sun, Y.; Ross, N.; Zhao, S.-B.; Huszarik, K.; Jia, W.-L.; Wang, R.-Y.; Macartney, D.; Wang, S. *J. Am. Chem. Soc.* **2007**, *129*, 7510–7511.

(35) (a) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001–5008. (b) Lambert, J. B.; Lin, L.; Keinan, S.; Müller, T. *J. Am. Chem. Soc.* **2003**, *125*, 6022–6023. (c) Henderson, L. D.; Piers, W. E.; Irvine, G. J.; McDonald, R. *Organometallics* **2002**, *21*, 340–345. (d) Müller, T. *Adv. Organomet. Chem.* **2005**, *53*, 155–215.

(36) A similar interaction was observed in the case of **1-Th** but not for **1-All**, as evidenced by ^{119}Sn NMR chemical shifts of 95.4 ppm for the former and 130.8 ppm for the latter.

(37) Malone, J. F.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2646–2648.

Table 2. Crystal Data and Structure Refinement Details of 3-Ph′ and 2-Ph·Py

compd	**3-Ph′**	**2-Ph·Py**
empirical formula	$C_{31}H_{46}BF_2FeKO_6Sn$	$C_{24}H_{27}BFFeNSn$
M_r	777.13	533.82
T, K	100(2)	100(2)
wavelength, Å	1.54178	1.54178
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$Pbca$
a, Å	10.6477(3)	12.0378(3)
b, Å	13.3122(3)	15.8820(3)
c, Å	24.4814(6)	23.9342(5)
α, deg	90	90
β, deg	93.1760(10)	90
γ, deg	90	90
V, Å^3	3464.77(15)	4575.84(17)
Z	4	8
ρ_{calcd}, g cm^{-3}	1.490	1.550
μ(Cu Kα), mm^{-1}	10.584	13.897
F(000)	1592	2144
cryst size, mm	0.18 × 0.33 × 0.12	0.29 × 0.13 × 0.06
limiting indices	$-12 \le h \le 12$	$-14 \le h \le 11$
	$-15 \le k \le 15$	$-18 \le k \le 16$
	$-29 \le l \le 29$	$-27 \le l \le 28$
θ range, deg	4.44−68.22	3.69−67.72
no. of rflns collected	23 820	19 748
no. of indep rflns	6268 (R(int) = 0.0545)	3962 (R(int) = 0.0445)
abs cor	numerical	numerical
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	6268/0/391	3962/0/265
goodness of fit on F^2	1.027	1.091
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0305, wR2 = 0.0737	R1 = 0.0435, wR2 = 0.1076
R indices (all data)[a]	R1 = 0.0344, wR2 = 0.0761	R1 = 0.0506, wR2 = 0.1117
peak/hole (e Å^{-3})	0.956/−0.483	1.795/−0.975

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

species that is partially stabilized by π-interaction with the aryl/allyl group. The respective rearranged fluoroborate complexes are accessible in the presence of excess of KF. These complexes are readily purified and can be converted back to the fluoroboranes via treatment with Me_3SiOTf or an excess of pyridine. Future work will focus on expanding the applications of this synthetic strategy to other group 13 and 14 elements.

Experimental Section

Materials and General Methods. 18-crown-6 and KF were purchased from Sigma Aldrich and dried under high vacuum for 24 h. Trimethylsilyl triflate (Me_3SiOTf) was purchased from Acros and used without further purification. CD_3CN and $CDCl_3$ (>99.7%) were obtained from Cambridge Isotope Laboratories (CIL). The deuterated solvents were degassed via several freeze–pump–thaw cycles and stored over 3 Å molecular sieves. The compounds 1,2-Fc($SnMe_2Cl$)(BClMe),[12,13] 1,2-Fc($SnMe_2Cl$)(BMePh),[12,13] Fc(BMePh),[15] Fc($SnMe_2Cl$),[38] [K(18-crown-6)]$^+$[Fc(BMePh)($SnMe_2F$)F]$^-$,[16] and [K(18-crown-6)]$^+$[Fc(BMePh)($SnMe_2Cl$)F]$^-$ [16] were prepared 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 glovebox (MBraun). Ether solvents were distilled from Na prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns for hydrocarbon solvents), and the chlorinated solvents were subsequently degassed via several freeze–pump–thaw cycles.

The 499.9 MHz ^{1}H NMR, 470.36 MHz ^{19}F NMR, 186.4 MHz ^{119}Sn NMR, and 160.3 ^{11}B NMR spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution ^{1}H spectra were referenced internally to the solvent signals, and ^{19}F, ^{119}Sn, and ^{11}B NMR spectra were referenced externally to α,α′,α″-trifluorotoluene (0.05% in C_6D_6; δ −63.73), $SnMe_4$ (δ 0), and $BF_3 \cdot Et_2O$ (δ 0) in C_6D_6, respectively. Splittings of NMR signals are abbreviated as pst (pseudotriplet), dpst (doublet of pseudotriplets), nr (not resolved). Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

Crystal Structure Determinations. X-ray data were collected on a Bruker SMART APEX CCD diffractometer using Cu Kα (1.541 78 Å) radiation. Crystallographic data for **3-Ph′** and **2-Ph·Py** and details of X-ray diffraction experiments and crystal structure refinements are given in Table 2. Numerical absorption correction was applied in both cases. Structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. All software and source scattering factors are contained in the SHELXTL program package.[39] Crystallographic data for the structures of **2-Ph·Py** and **3-Ph′** have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-669585 and CCDC-669586, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Synthesis of 2-Ph. A solution of **1-Ph** (21 mg, 0.044 mmol) in 1 mL of THF was mixed with KF (2.8 mg, 0.048 mmol, 1.1 equiv) in 1 mL of THF. The reaction mixture was stirred at 45 °C for 3 h, followed by removal of insoluble salts by filtration. The product was obtained as an orange oil. Yield: 18 mg (90%), purity 95% by ^{1}H NMR. ^{1}H NMR (500 MHz,

(38) Kabouche, Z.; Dinh, N. H. *J. Organomet. Chem.* **1989**, *375*, 191–195.

(39) Sheldrick, G. M. SHELXTL, Version 6.14; Bruker AXS, Inc., Madison, WI, 2004.

$CDCl_3$, 25 °C): δ 7.58 (dd, J = 1.5 Hz, 7.5 Hz, $J(^{117/119}Sn,H)$ = 46 Hz, 2 H, Ph H_o), 7.36 (overlapped, 3 H, Ph $H_{m,p}$), 4.74 (m, 1 H, Cp H), 4.60 (m, 1 H, Cp H), 4.46 (dd, J = 1.5, 2.5 Hz, $J(^{117/119}Sn,H)$ = 12.5 Hz, 1 H, Cp H), 4.11 (s, 5 H, Cp), 0.73 (d, $^3J(^{19}F,H)$ = 14.0 Hz, 3 H, B−Me), 0.53 (d, $J(^{19}F,H)$ = 1.0 Hz, $J(^{117/119}Sn,H)$ = 55 Hz, 3 H, Sn−Me), 0.49 (d, $J(^{19}F,H)$ = 1.5 Hz, $J(^{117/119}Sn,H)$ = 56 Hz, 3 H, Sn−Me). ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ −32.1. $^{19}F\{^1H\}$ NMR (470.36 MHz, $CDCl_3$, 25 °C): δ −55.8. ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ 53 ($w_{1/2}$ = 500 Hz).

Synthesis of 3-Ph. A solution of **1-Ph** (100 mg, 0.212 mmol) in 1 mL of THF was mixed with KF (27 mg, 0.47 mmol, 2.2 equiv) in 1 mL of THF. The reaction mixture was stirred at 45 °C for 6 h, followed by removal of insoluble salts by filtration. The solvents were removed under high vacuum, and the remaining yellow microcrystalline solid was washed with hexanes (3 × 2 mL). Yield: 102 mg (0.198 mmol; 94%). ^1H NMR (500 MHz, CD_3CN, 25 °C): δ 7.67 (dd, J = 1.5, 8.0 Hz, $J(^{117/119}Sn,H)$ = 41 Hz, 2 H, Ph H_o), 7.30 (overlapped, 3 H, Ph $H_{m,p}$), 4.10 (nr, 2 H, Cp H), 3.97 (s, 5 H, Cp), 3.78 (m, $J(^{117/119}Sn,H)$ = 13 Hz, 1 H, Cp H), 0.42 (s/nr, $J(^{117/119}Sn,H)$ = 55 Hz, 3 H, Sn−Me), 0.38 (s/nr $J(^{117/119}Sn,H)$ = 56 Hz, 3 H, Sn−Me), −0.25 (pst, $^3J(^{19}F,H)$ = 12 Hz, 3 H, B−Me). ^{119}Sn NMR (186.4 MHz, CD_3CN, 25 °C): δ −39.0. $^{19}F\{^1H\}$ NMR (470.36 MHz, CD_3CN, 25 °C): δ −137.6, −142.7. ^{11}B NMR (160.3 MHz, CD_3CN, 25 °C): δ 9.2 ($w_{1/2}$ = 230 Hz). Anal. Calcd for $C_{19}H_{22}BF_2FeKSn$ (512.84): C, 44.50; H, 4.32. Found: C, 44.18; H, 4.14.

Synthesis of 1-Th. A solution of 2-(trimethylstannyl)thiophene (115 mg, 0.465 mmol) in 2 mL of acetonitrile was added dropwise to a solution of **1-Cl** (200 mg, 0.465 mmol) in 2 mL of acetonitrile. The reaction mixture was stirred for 48 h at room temperature, followed by removal of all volatile components under high vacuum. Dark red crystals were obtained from a 1:3 mixture of CH_2Cl_2/hexanes at −35 °C. Yield: 144 mg (0.301 mmol; 65%). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.81 (dd, J = 1.0, 4.5 Hz, 1 H, γ-Th), 7.52 (dd, J = 1.0, 3.5 Hz, 1 H, α-Th), 7.28 (dd, J = 3.5, 4.5 Hz, 1 H, β-Th), 5.03 (pst, J = 2.5 Hz, $J(^{117/119}Sn,H)$ = 7.0 Hz, 1 H, Cp H), 4.98 (dd, J = 1.0, 2.5 Hz, $J(^{117/119}Sn,H)$ = 12 Hz, 1 H, Cp H), 4.97 (dd, J = 1.0, 2.5 Hz, $J(^{117/119}Sn,H)$ = 14 Hz, 1 H, Cp H), 4.22 (s, 5 H, Cp), 1.22 (s, 3 H, B−Me), 0.73 (s/d, $J(^{117/119}Sn,H)$ = 58/61 Hz, 3 H, Sn−Me), 0.26 (s/d, $J(^{117/119}Sn,H)$ = 60/63 Hz, 3 H, Sn−Me). ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ 95.4. ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ 62 ($w_{1/2}$ = 430 Hz). Anal. Calcd for $C_{17}H_{20}BClFeSSn$ (477.23): C, 42.79; H, 4.22. Found: C, 42.76; H, 4.34.

Synthesis of 2-Th. A solution of **1-Th** (19 mg, 0.039 mmol) in 1 mL of THF was mixed with KF (2.5 mg, 0.043 mmol, 1.1 equiv) in 1 mL of THF. Using a procedure similar to that for the preparation of **2-Ph**, the product was obtained as an orange oily material. Yield: 18 mg (98%), purity 90% by ^1H NMR. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.70 (d, J = 4.0 Hz, $J(^{117/119}Sn,H)$ = 13 Hz, 1 H, γ-Th), 7.33 (d, J = 3.0 Hz, $J(^{117/119}Sn,H)$ = 25 Hz, 1 H, α-Th), 7.29 (pst, J = 4.0 Hz, 1 H, β-Th), 4.75 (m, 1 H, Cp H), 4.62 (m, 1 H, Cp H), 4.50 (dd, J = 1.0, 2.5 Hz, $J(^{117/119}Sn,H)$ = 13 Hz, 1 H, Cp H), 4.14 (s, 5 H, Cp), 0.76 (d, $^3J(^{19}F,H)$ = 14.5 Hz, 3 H, B-Me), 0.62 (d, $^3J(^{19}F,H)$ = 1.5 Hz, $J(^{117/119}Sn,H)$ = 58 Hz, 3 H, Sn-Me), 0.53 (nr, $J(^{117/119}Sn,H)$ = 58 Hz, 3 H, Sn−Me). ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ −33.5. $^{19}F\{^1H\}$ NMR (470.36 MHz, $CDCl_3$, 25 °C): δ −55.8. ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ 53 ($w_{1/2}$ = 490 Hz).

Synthesis of 3-Th. A solution of **1-Th** (25 mg, 0.052 mmol) in 1 mL of THF was mixed with KF (7.6 mg, 0.13 mmol, 2.5 equiv) in 1 mL of THF. Using a procedure similar to that for the preparation of **3-Ph**, the product was obtained as a yellow microcrystalline solid. Yield: 24 mg (0.046 mmol; 89%). ^1H NMR (500 MHz, CD_3CN, 25 °C): δ 7.67 (d, J = 5.0 Hz, 1 H, γ-Th), 7.34 (d, J = 3.5 Hz, $J(^{117/119}Sn,H)$ = 22 Hz, 1 H, α-Th), 7.25 (dd, J = 3.5, 4.5 Hz, 1 H, β-Th), 4.09 (br, 2 H, Cp H), 4.00 (s, 5 H, Cp), 3.82 (br, 1 H, Cp H), 0.55 (s/d, $J(^{117/119}Sn,H)$ = 61 Hz, 3 H, Sn−Me), 0.38 (s/d, $J(^{117/119}Sn,H)$ = 60 Hz, 3 H, Sn−Me), −0.25 (pst, $^3J(^{19}F,H)$ = 12 Hz, 3 H, B-Me). ^{119}Sn NMR (186.4 MHz, CD_3CN, 25 °C): δ −46.6. $^{19}F\{^1H\}$ NMR (470.36 MHz, CD_3CN, 25 °C): δ −130.9, −135.6. ^{11}B NMR (160.3 MHz, CD_3CN, 25 °C): δ 13.6 ($w_{1/2}$ = 210 Hz). Elemental analysis was performed on crystals grown from a solution of THF/ether in the presence of 1.0 equiv of 18-crown-6 at −38 °C. Anal. Calcd for $C_{29}H_{44}BF_2FeKO_6SSn$ (783.18): C, 44.47; H, 5.66. Found: C, 44.61; H, 5.75.

Synthesis of 1-All. A solution of $AllSnMe_3$ (58 mg, 0.28 mmol) in 2 mL of dichloromethane was added dropwise to a solution of **1-Cl** (119 mg, 0.28 mmol) in 2 mL of dichloromethane. The reaction mixture was stirred for 24 h at room temperature followed by removal of all volatile components under high vacuum. An orange oily material was obtained after solvent removal. Yield: 114 mg (95%), purity 95% by ^1H NMR. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 6.09 (m, 1 H, allyl-β), 4.99 (m, 2 H, allyl-γ), 4.93 (overlapping, 2 H, Cp H), 4.77 (dd, J = 1.5, 2.5 Hz, $J(^{117/119}Sn,H)$ = 14 Hz, 1 H, Cp H), 4.19 (s, 5 H, Cp), 2.29 (d, J = 8.0 Hz, 2 H, allyl-α), 0.91 (s/d, $J(^{117/119}Sn,H)$ = 58/60 Hz, 3 H, Sn-Me), 0.88 (s, 3 H, B−Me), 0.78 (s/d, $J(^{117/119}Sn,H)$ = 56/58 Hz, 3 H, Sn−Me). ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ 130.8. ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ 70 ($w_{1/2}$ = 600 Hz).

Synthesis of 2-All. A solution of **1-All** (21 mg, 0.048 mmol) in 1 mL of THF was mixed with KF (3.1 mg, 0.053 mmol, 1.1 equiv) in 1 mL of THF. Using a procedure similar to that for the preparation of **2-Ph**, the product was obtained as an orange oily material. Yield: 19 mg (94%), purity 90% by ^1H NMR. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 5.98 (m, 1 H, allyl-β), 4.85 (m, 1 H, allyl-γ), 4.77 (m, 1 H, Cp H), 4.73 (m, 1 H, allyl-γ), 4.60 (br, 1 H, Cp H), 4.52 (dd, J = 1.0 Hz, 2.5 Hz, $J(^{117/119}Sn,H)$ = 12 Hz, 1 H, Cp H), 4.18 (s, 5 H, Cp), 1.96 (m, 2 H, allyl-α), 0.72 (d, $^3J(^{19}F,H)$ = 13.5 Hz, 3 H, B−Me), 0.29 (nr, 6 H, Sn−Me). ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ −9.9. $^{19}F\{^1H\}$ NMR (470.36 MHz, $CDCl_3$, 25 °C): δ −55.8. ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ 53 ($w_{1/2}$ = 530 Hz).

Synthesis of 3-All. A solution of **1-All** (68 mg, 0.16 mmol) in 1 mL of THF was mixed with KF (23 mg, 0.40 mmol. 2.5 equiv) in 1 mL of THF. Using a procedure similar to that for the preparation of **3-Ph**, the product was obtained as a yellow microcrystalline solid. Yield: 58 mg (78%), purity 90% by ^1H NMR. ^1H NMR (500 MHz, CD_3CN, 25 °C): δ 6.05 (m, 1 H, allyl-β), 4.76 (m, 1 H, allyl-γ), 4.59 (m, 1 H, allyl-γ), 4.10 (br, 1 H, Cp H), 4.07 (dd, J = 1.0, 2.5 Hz, $J(^{117/119}Sn,H)$ = 9 Hz, 1 H, Cp H), 3.98 (s, 5 H, Cp), 3.89 (dd, J = 1.0, 2.5 Hz, $J(^{117/119}Sn,H)$ = 12 Hz, 1 H, Cp H), 1.90 (m, 2 H, allyl-α), 0.18 (s/d, $J(^{117/119}Sn,H)$ = 54 Hz, 3 H, Sn−Me), 0.16 (s/d, $J(^{117/119}Sn,H)$ = 55 Hz, 3 H, Sn−Me), −0.27 (pst, $^3J(^{19}F,H)$ = 11 Hz, 3 H, B−Me). ^{119}Sn NMR (186.4 MHz, CD_3CN, 25 °C): δ −12.5. $^{19}F\{^1H\}$ NMR (470.36 MHz, CD_3CN, 25 °C): δ −132.0, −137.0. ^{11}B NMR (160.3 MHz, CD_3CN, 25 °C): δ 9.0 (pst, $J(^{11}B,^{19}F)$ = 72 Hz, $w_{1/2}$ = 160 Hz). Elemental analysis was performed on crystals grown from a solution of toluene in the presence of 1.0 equiv of 18-crown-6 at −38 °C. Anal. Calcd

for $C_{28}H_{46}BF_2FeKO_6Sn$ (741.12): C, 45.38; H, 6.26. Found: C, 45.04; H, 6.21.

Conversion of 3-Ph to 2-Ph. A solution of Me_3SiOTf (44 mg, 0.199 mmol) in 1 mL of toluene was added to **3-Ph** (102 mg, 0.199 mmol) in 1 mL of toluene with stirring. The reaction mixture was stirred at room temperature for 1 h, followed by removal of insoluble salts by filtration. Toluene was removed under high vacuum, and the remaining oily material was extracted with hexanes (1 mL). Yield: 85 mg (94%), purity 95% by ^{1}H NMR.

Synthesis of 2-Ph·Py. A solution of pyridine (16 mg, 0.202 mmol) in 1 mL of toluene was added to **3-Ph** (32 mg, 0.062 mmol) in 1 mL of toluene with stirring. The reaction mixture was stirred for 1 h at room temperature, followed by removal of insoluble salts by filtration. The reaction mixture was layered with 1 mL of hexanes and kept at −35 °C for several days. Light orange crystals were collected and dried under vacuo. Yield: 17 mg (0.032 mmol; 52%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.43 (d, J = 5.5 Hz, 2 H, Py H_o), 7.75 (t, J = 8.0 Hz, 1 H, Py H_p), 7.38 (d, J = 7.0 Hz, $J(^{117/119}Sn,H)$ = 43 Hz, 2 H, Ph H_o), 7.27 (overlapped, 1 H, Ph H_m), 7.20 (overlapped, 3 H, Py H_m, Ph H_p), 4.44 (br, 1 H, Cp H), 4.39 (br, 1 H, Cp H), 4.15 (overlapped, 6 H, Cp H), 0.41 (d, J = 2.0 Hz, $J(^{117/119}Sn,H)$ = 56 Hz, 3 H, Sn−Me), 0.40 (nr, $J(^{117/119}Sn,H)$ = 54 Hz, 3 H, Sn−Me), 0.32 (d, $^3J(^{19}F,H)$ = 14 Hz, 3 H, B−Me). ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ −33.6. $^{19}F\{^1H\}$ NMR (470.36 MHz, $CDCl_3$, 25 °C): no signal detected. ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): δ 14.7 ($w_{1/2}$ = 520 Hz). Anal. Calcd for $C_{24}H_{27}BFFeNSn$ (553.84): C, 54.00; H, 5.10; N, 2.62. Found: C, 53.90; H, 5.02; N, 2.57.

Synthesis of Fc(SnMe$_2$Ph). A solution of PhMgBr (57 μL, 1 M in THF, 0.057 mmol) was added via syringe to $Fc(SnMe_2Cl)$ (20 mg, 0.054 mmol) in 1 mL of THF. The reaction mixture was stirred at room temperature for 2 h, followed by removal of all volatile components. The product was extracted by adding 1 mL of hexanes, followed by removal of insoluble magnesium salts by filtration. An orange oil was obtained after evaporation of the solvents. Yield: 22 mg (99%), purity >95% by ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.58 (dd, J = 1.5 Hz, 7.0 Hz, $J(^{117/119}Sn,H)$ = 45 Hz, 2 H, Ph H_o), 7.36 (overlapped, 3 H, Ph $H_{m,p}$), 4.39 (pst, J = 1.5 Hz, 2 H, Cp H), 4.12 (pst, J = 1.5 Hz, 2 H, Cp H), 4.09 (s, 5 H, Cp), 0.51 (s/d, $J(^{117/119}Sn,H)$ = 54/56 Hz, 6 H, Sn−Me). ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 142.0 (*ipso*-Ph), 136.2 (s/d, $J(^{117/119}Sn,C)$ = 37 Hz, meta Ph), 128.7 (s/d, $J(^{117/119}Sn,C)$ = 9.5 Hz, para Ph), 128.4 (s/d, $J(^{117/119}Sn,C)$ = 48 Hz, ortho Ph), 74.4 (s/d, $J(^{117/119}Sn,C)$ = 51 Hz, Cp C2,5), 71.0 (s/d, $J(^{117/119}Sn,C)$ = 41 Hz, Cp C3,4), 68.3 (C_5H_5), 67.8 (Cp C2,5), −9.1 (s/d, $J(^{117/119}Sn,C)$ = 358/375 Hz, Sn−Me). ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): δ −34.6. GC-MS (70 eV, EI): *m*/*z* (%) 412 (86) [M^+], 397 (89) [$M^+ - CH_3$], 382 (14) [$M^+ - 2CH_3$], 305 (100) [$M^+ - 2CH_3 - Ph$].

Reaction of [K(18-crown-6)THF]$^+$[Fc(BMePh)(SnMe$_2$F)F]$^-$ with FcB(C$_6$F$_5$)$_2$. A solution of $[K(18\text{-crown-6})THF]^+[Fc(BMePh)(SnMe_2F)F]^-$ (16 mg, 0.019 mmol) in 1 mL of THF was added to $FcB(C_6F_5)_2$ (10 mg, 0.019 mmol) in 1 mL of THF with stirring. The reaction mixture was stirred at room temperature for 30 min, followed by removal of all volatile components under high vacuum. The residue was extracted three times with 3 mL of hexanes. The product obtained upon removal of solvent from the combined extracts was identified as **2-Ph** by ^{1}H NMR analysis. Similar results were obtained when the reaction was carried out in C_6D_6.

Reaction of [K(18-crown-6)THF]$^+$[Fc(BMePh)(SnMe$_2$Cl)F]$^-$ with FcB(C$_6$F$_5$)$_2$. A solution of $[K(18\text{-crown-6})THF]^+[Fc(BMePh)(SnMe_2Cl)F]^-$ (8.2 mg, 9.4 μmol) in 1 mL of THF was added to $FcB(C_6F_5)_2$ (5.0 mg, 9.4 μmol) in 1 mL of THF with stirring. Using a procedure analogous to that for the preparation of **2-Ph** from $[K(18\text{-crown-6})THF]^+[Fc(BMePh)(SnMe_2F)F]^-$, the product **1-Ph** was obtained as a red microcrystalline solid. Similar results were also obtained when the reaction was carried out with Me_2SnCl_2 as the Lewis acid.

Reaction of Fc(SnMe$_2$Cl) with Fc(BMePh) in the Presence of KF. A mixture of $Fc(SnMe_2Cl)$ (2.5 mg, 6.7 μmol, 3.4 mM), Fc(BMePh) (1.9 mg, 6.7 μmol), and KF (0.4 mg, 6.9 μmol) in 1 mL of THF was stirred at 45 °C for 3 h, followed by removal of insoluble salts by filtration. Only the starting materials were observed by ^{1}H NMR. The reaction was repeated with an excess of KF (1 mg, 17 μmol) and run for 2 days. The ^{1}H NMR spectrum now showed the presence of the following ferrocene-containing species: $Fc(SnMe_2Cl)$ (∼20%), Fc(BMePh) (∼40%), $Fc(SnMe_2F)$ (∼25%), and $Fc(SnMe_2Ph)$ (∼15%). In a similar experiment that was run for 3 days at 45 °C using 6.5 mg of $Fc(SnMe_2Cl)$, 5.1 mg of Fc(BMePh), and 2.3 mg of KF a larger amount of $Fc(SnMe_2Ph)$ (∼40%) was produced.

Concentration Dependence of the Rearrangement Reactions. Two samples, each of which contained the compound **1-Ph** (10 mg, 0.021 mmol, 21.2 mM) and KF (1.4 mg, 0.024 mmol, 1.1 equiv), were prepared and 1 and 4 mL of THF were added as the solvent, respectively. The mixtures were stirred at 45 °C for 1.5 h, followed by removal of insoluble salts by filtration. The conversion was estimated by ^{1}H NMR to be 95% for the sample prepared with 1 mL of THF and 70% for the sample with 4 mL of THF.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research. F.J. thanks the Alfred P. Sloan foundation for a research fellowship and the National Science Foundation for a CAREER award (Grant No. CHE-0346828). Funding of an X-ray diffractometer was possible through a grant from the National Science Foundation (Grant No. NSF CRIF-0443538). We are indebted to Prof. Lalancette for helpful discussions and Dr. Krishnan Venkatasubbaiah for acquisition of X-ray data for **2-Ph·Py**.

Supporting Information Available: Figures giving NMR spectra of the compounds **1-All**, **2-Ph**, **2-Th**, **2-All**, and $Fc(SnMe_2Ph)$ and CIF files and tables giving crystallographic data, including crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700967A