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Binding Cooperativity of Two Different Lewis Acid Groups at the Edge of Ferrocene

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Abstract: The binding properties of heteronuclear bidentate Lewis acids, in which an organoboron and an organotin moiety are attached adjacent to each other at one of the Cp rings of ferrocene, have been studied. Treatment of [1,2-fc($SnMe_2Cl$)(BClMe)] (**1-Cl**) (fc = ferrocenediyl) with one equivalent of pyridine or 4-dimethylaminopyridine (DMAP) resulted in diastereoselective complexation of boron. Adducts **2** and **3** have been studied by multinuclear NMR, and the stereoselectivity of complexation was further confirmed by single crystal X-ray diffraction of **2**. The importance of cooperative effects that involve an intramolecular B-Cl···Sn interaction on the diastereoselectivity is evident from comparison with binding studies on the phenyl-substituted analogue [1,2-fc($SnMe_2Cl$)(BPhMe)] (**1-Ph**). Complexation of **1-Ph** led to diastereomeric mixtures of adducts **4** and **5**, respectively, which were identified by multinuclear NMR including NOESY experiments. The solid-state structure of one of the diastereomers of **5** was confirmed by X-ray crystallography. Facile isomerization was found in solution and the barrier of activation was determined by VT NMR studies (**4**: $\Delta G^{\neq}_{298} = 54.9 \pm 0.4\ kJ\,mol^{-1}$; **5**: $\Delta G^{\neq}_{298} = 70.3 \pm 0.1\ kJ\,mol^{-1}$). Competitive binding of pyridine to **1-Cl** and [FcB(Cl)Me] (Fc = ferrocenyl) showed that cooperative effects between tin and boron lead to significant Lewis acidity enhancement. Binding of a second nucleophile in the presence of excess of base occurred also at boron. The novel zwitterionic complexes [1,2-fc($BMe(py)_2$)($SnMe_2Cl_2$)] (**6**) and [1,2-fc($BMe(dmap)_2$)-($SnMe_2Cl_2$)] (**7**) formed, which consist of boronium cation and stannate anion moieties. The structure of **7** in the solid-state was confirmed by X-ray crystallography. Multinuclear NMR data and competition experiments indicate weak binding of chloride to tin in **7** and partial dissociation in solution.

Keywords: boranes · chirality · cooperative phenomena · ferrocenes · Lewis acids

Introduction

Multifunctional Lewis acids are promising candidates for chemo- and stereoselective Lewis acid catalysis and have proven useful as activators in olefin polymerization, and as substrates for selective anion recognition.[1–3] Among the emerging class of bidentate Lewis acids, those with a metallocene backbone are particularly intriguing owing to the unique geometric features and the opportunity to influence the binding process through the oxidation state of the central metal atom. The latter has, for example, been exploited for the development of electrochemical fluoride and saccharide sensors.[4] In general, two possibilities exist for the design of a ferrocene-based bidentate Lewis acid. The Lewis acidic groups may either be attached in the 1,1′-positions with one Lewis acid group at each Cp ring (**A**), or, alternatively, they may be placed at the 1,2-positions of the same Cp ring (**B**). The ferrocene-based bifunctional Lewis acids studied to date almost exclusively possess identical Lewis

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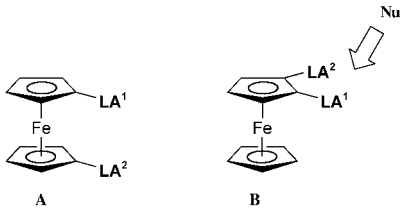
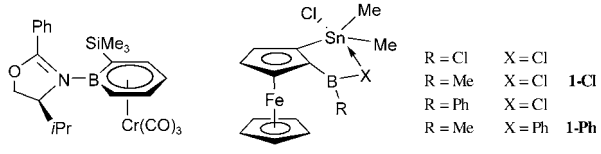
acidic groups that are attached in the 1,1′-positions of the metallocene.[5] The scarcity of studies on the respective 1,2-disubstituted ferrocenes of type **B** is primarily due to a lack of convenient synthetic routes.[6]



A B

A particularly intriguing aspect of bidentate Lewis acids **B** is the planar chirality,[7] which arises if two different Lewis acid groups LA^1 and LA^2 are attached at the edge of the ferrocene molecule. Since nucleophiles (Nu) are expected to predominantly attack from the sterically more accessible *exo*-side of ferrocene, unusual stereospecific binding phenomena may be observed. Indeed, a lot of attention has recently been devoted to the study of planar and central chiral ferrocene ligands, in which two different donor groups D are attached to the same Cp ring. These chiral ferrocene ligands play a major role in various catalysis applications.[8] However, the Lewis acid analogues **B** are underdeveloped and only few examples of planar chiral Lewis acids are known. The latter are typically monofunctional Lewis acids such as the (borabenzene)chromiumtricarbonyl species **C** reported by Fu and co-workers.[9,10]

We have shown that heteronuclear bidentate Lewis acids **D**, which are comprised of both Lewis acidic boron and tin groups,[11] can readily be obtained with good selectivity through a rearrangement reaction from 1,1′-bis(trimethylstannyl)ferrocene and boron halides.[12–14] We also demonstrated that the Lewis acidic organoboron moiety in species **D** is stabilized by an interaction with the electron-rich ferrocene fragment leading to a significant bending of the boryl group toward iron[15] and a strong red-shift and enhanced intensity of the visible absorption bands relative to those of ferrocene.[13] Moreover, we deduced from X-ray crystallography and multinuclear NMR studies that the adjacent organotin moiety adopts a pseudotrigonal bipyramidal structure both in the solid state and in solution as a result of a weak intramolecular interaction with the boron-bound substituent X (X = Cl, Ph).[13,16] In this paper, we describe our results on the competition of external nucleophiles with the intramolecular interactions in **D** and the observation of unusual cooperative and stereoselective binding processes.

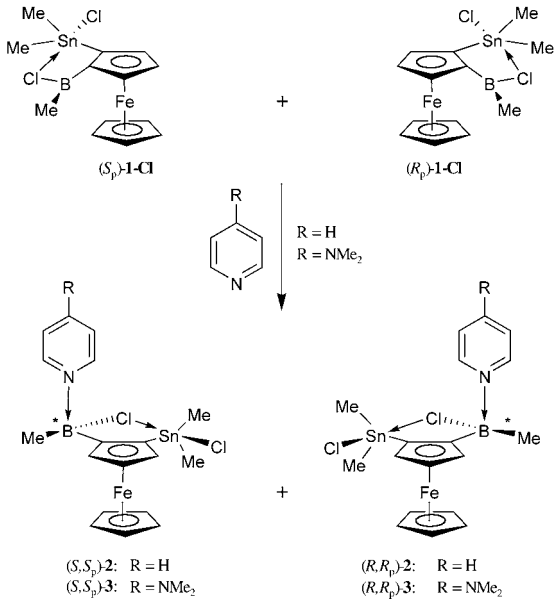


C D

R = Cl X = Cl
R = Me X = Cl **1-Cl**
R = Ph X = Cl
R = Me X = Ph **1-Ph**

Results and Discussion

Regio- and diastereoselective complexation of the heteronuclear bidentate Lewis acid 1-Cl with pyridine: The bidentate Lewis acid **1-Cl** readily reacts with equimolar amounts of pyridine and 4-dimethylaminopyridine (DMAP), respectively, to form the 1:1 complexes **2** and **3** (Scheme 1). The binding process can be monitored visually as the solution changes from red to a less intense orange color. The red color of ferrocenylboranes is generally associated with the attachment of the electron withdrawing group.[13,17] The observed color change is indicative of coordination of the nucleophile to boron, which turns the boryl group into an electron-donating substituent.[18] The coordination of pyridine to **1-Cl** is further confirmed by a strong upfield shift of the ^{11}B NMR signal from δ 61.5 in **1-Cl** to δ 9.5 in **2** and δ 8.4 in **3**, respectively, which is indicative of tetracoordination of boron (Table 1).[19] At the same time the ^{119}Sn NMR signal is shifted upfield from δ 95.0 for **1-Cl** to δ 68.8 in **2** and δ 57.2 in **3**, respectively, which suggests enhanced hypercoordination of tin (cf. [$FcSnMe_2Cl$] δ 130).[20] A strengthening of the chloride bridge in **2** and **3** is further indicated by an increase of the ^{119}Sn–^{13}C coupling constant for one of the two diastereotopic methyl groups on tin from 473 Hz for **1-Cl** to 502 Hz in **2** and 506 Hz in **3**. The second methyl group shows nearly identical coupling constants in **1-Cl** (429 Hz), **2** (425 Hz), and **3** (431 Hz), which are similar to that for [$FcSnMe_2Cl$] (415 Hz).[13]



Scheme 1. Formation of B-chiral complexes **2** and **3**.

The observation of only one set of signals in the ^1H, ^{13}C, and ^{119}Sn NMR spectra of **2** and **3** is intriguing since diastereomers are expected to form upon binding of a nucleophile to the organoboron moieties of the racemic mixture of

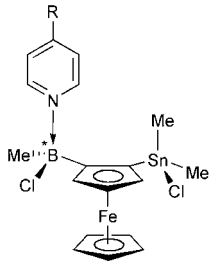
Table 1. ^{1}H, ^{119}Sn, and ^{11}B NMR data of complexes **2**–**8** in comparison to the free acids **1** and model compounds.[a]

		$\delta(^{1}H)$					$\delta(^{119}Sn)$[b]	$\delta(^{11}B)$
	C_5H_5	H3	H4	H5	Sn-Me			
1-Cl	3.83	4.67	5.03	5.23	0.76	0.97	95.0	61.5
		(11.0)	(7.0)	(15.0)	(60/63)	(63/66)		
1-Ph	4.20	4.94	5.06	5.04	0.68	−0.07	102.3	67.5
		(11.0)	(nr)	(15.0)	(57/60)	(61/64)		
2	4.27	4.37	4.55	4.78	0.06	1.02	68.8	9.5
		(14.0)	(8.8)	(12.8)	(59/62)	(65/68)		
3	4.25	4.26	4.49	4.72	0.23	1.01	57.2	8.4
		(14.0)	(9.0)	(13.0)	(61)	(68)		
4 (+55 °C)	4.10	4.19	4.58	4.68	0.47	0.47	121.4	6.6
		(br)	(br)	(br)	(59)	(59)		
4a (−50 °C)	4.19	4.25	4.54	4.71	0.40	0.02	119.3	1.0
		(nr)	(nr)	(nr)	(57)	(63)		
4b (−50 °C)	4.00	3.91	4.44	4.50	0.90	0.44	135.9	1.0
		(nr)	(nr)	(nr)	(58)	(58)		
5a	4.17	4.12	4.46	4.67	0.25	0.42	121.0	−1.6
		(nr)	(nr)	(nr)	(56)	(62)		
5b	4.01	3.87	4.39	4.51	0.89	0.30	131.0	−1.6
		(nr)	(nr)	(nr)	(56)	(58)		
6 (+30 °C)[c]	4.53	3.44	4.55	5.15	1.36		61.6	3.9
		(nr)	(nr)	(nr)	(73/76)			
7	4.08	3.58	4.47	4.51	0.70		100.9	3.3
		(12.0)	(7.2)	(14.0)	(59/61)			
8	4.07	3.62	4.52	4.50	0.70/1.29		128.8/	3.3
		(12.5)	(8.0)	(14.0)	(55/58)/(86/89)		−106.8	

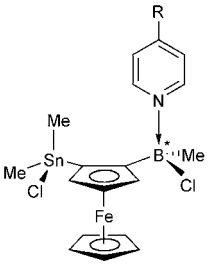
	C_5H_5	H2,5	H3,4	Sn-Me	$\delta(^{119}Sn)$	$\delta(^{11}B)$
[FcB(Cl)Me][d]	3.86	4.48	4.74			61.7
[FcB(Cl)Me]·Py	4.19	4.3–4.2	4.3–4.2			7.8
[FcB(Cl)Me]·DMAP	4.16	4.3–4.1	4.3–4.1			6.4
[FcB(Ph)Me]	4.08	4.48	4.73			63.0
[FcB(Ph)Me]·Py	3.94	4.02	4.27			2.9
[FcB(Ph)Me]·DMAP	3.92	3.94/3.86	4.16/4.15			−3.8
$[FcBMe(dmap)_2]Cl$	3.91	3.82	4.27			3.5
$[FcSnMe_2Cl]$	4.19	4.21 (11)	4.48 (8)	0.84 (58/61)	130.0	
$[FcSnMe_2Cl]/[PPh_4]Cl$	4.19	4.54 (12)	4.28 (9)	0.89 (68/71)	3.1	

[a] In $CDCl_3$ at 25 °C unless noted otherwise; coupling constants $J(^{117/119}Sn,H)$ are given in brackets. [b] Concentrations for the ^{119}Sn NMR spectra were about 0.02 M. [c] In $[D_5]$pyridine. [d] See ref. [33].

planar chiral **1-Cl** (see Scheme 1). While, for example, a B-Cl···Sn bridge in the enantiomers (S,S_p)-**2** and (R,R_p)-**2** should lead to the experimentally observed upfield-shift of the ^{119}Sn NMR resonance, a hyper-coordination effect is not expected if the boron-bound chlorine substituent pointed away from the tin atom, which would be the case in the other possible isomers (R,S_p)-**2** and (S,R_p)-**2** (see below). The absence of a second ^{119}Sn NMR signal in the spectra of **2** and **3** thus clearly indicates that only one enantiomer pair is formed, the (S,S_p)-**2**/(S,S_p)-**3** and (R,R_p)-**2**/(R,R_p)-**3** isomers. This conclusion is further supported by the fact that only one set of Cp signals is observed in the ^{1}H and ^{13}C NMR spectra of **2** and **3**.[21]



(R,S_p)-**2**: R = H
(R,S_p)-**3**: R = NMe_2



(S,R_p)-**2**: R = H
(S,R_p)-**3**: R = NMe_2

The X-ray crystal structure of **2** (Figure 1, Table 2) shows that pyridine indeed is coordinated to the boron atom from the sterically more accessible *exo*-side of the ferrocene. The stereochemistry of the chiral tetracoordinate organoboron moiety[22] thus generated is determined by both the steric requirements of the ferrocene unit and an interaction between the boron-bound chlorine and the electron-deficient organotin moiety with a distance of Cl(2)···Sn(1) 3.144(1) Å, which is comparable to that in **1-Cl** with Cl···Sn 3.138(1) Å. This interaction in turn results in a pyramidalization of tin as evident from the sum of the equatorial angles of 353.1° (78 % TBP_e[23]), which is close to that of **1-Cl** (350.6°; 71 % TBP_e).[24,25] The Sn–Cl(1) bond length of 2.417(1) Å for the tin-bound chlorine in *trans*-position and the intramolecular Sn···Cl(2) distance of 3.144(1) Å are also similar to those found for **1-Cl** (2.403(1) Å and 3.138(1) Å). The most strik-

ing difference between the structure of **2** and that of the free acid **1-Cl** is the bending of the boron atom away from the iron atom by $\beta = 180° - \text{angle}(\text{cent}_{Cp}\text{-C2-B1}) = 4.0(2)°$ (cent = center of gravity) in **2**, which stands in sharp contrast to the strong tilting of $\beta = 13.8(2)°$ toward the iron atom in **1-Cl**.[13] This effect is a result of the electronic saturation of boron in **2**, which is further reflected in significantly longer B–C(2) and B–Cl(2) distances of 1.580(4) Å (**1-Cl**: 1.523(7) Å) and 1.923(3) Å (**1-Cl**: 1.808(5) Å), respectively.

Role of the chloride bridge in diastereoselective binding: The X-ray crystallographic and solution NMR results suggested that the stannyl group plays an important role in the binding of nucleophiles to **1-Cl** as a result of formation of a halide bridge from boron to tin. In this context it is of interest to note that low temperature NMR studies on the bidentate Lewis acid **1-Cl** itself neither led to signal doubling of the Cp resonances nor to a change in the ^{119}Sn NMR shift. By contrast, for the monofunctional ferrocenylborane [FcB(Cl)Me] hindered rotation about the B–Cp bond gives rise to signal splitting of the Cp-H2,5 and Cp-H3,4 resonances in the low temperature ^{1}H NMR spectra ($T_c = -54$ and $T_c = -69\,°C$) and an activation barrier of $\Delta G^{\neq}_{298} = 46.6 \pm 0.3\ \text{kJ mol}^{-1}$ was determined.[26] This indicates that the rotamer of **1-Cl** with the chlorine substituent pointing toward the tin atom is strongly favored over that with the boron-bound methyl group adjacent to tin. The preference for this rotamer would then in turn be responsible for the observed diastereoselective binding of nucleophiles.

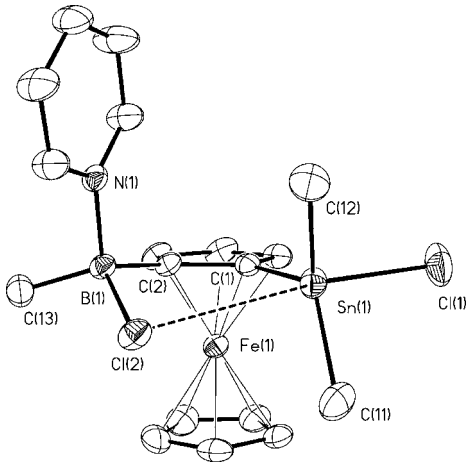


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

In order to unequivocally confirm the importance of the chloride bridge on the stereochemical outcome of the bind-

Table 2. Selected bond lengths [Å], interatomic distances [Å] and angles [°] of **2**, **5b**, and **7**.

2		**5b**		**7**	
Sn(1)–Cl(1)	2.4170(9)	Sn(1)–Cl(l)	2.3841(7)	Sn(1)–Cl(1)	2.5546(13)
Sn(1)–C(1)	2.097(3)	Sn(1)–C(1)	2.108(3)	Sn(1)–C(1)	2.129(5)
Sn(1)–C(11)	2.121(3)	Sn(1)–C(11)	2.128(3)	Sn(1)–C(11)	2.116(5)
Sn(1)-C(12)	2.122(3)	Sn(1)–C(12)	2.138(3)	Sn(1)–C(12)	2.119(5)
Sn(1)···Cl(2)	3.144(1)			Sn(1)–Cl(2)	2.783(1)
B(1)–C(2)	1.580(4)	B(1)–C(2)	1.626(4)	B(1)–C(2)	1.604(7)
B(1)–C(13)	1.594(4)	B(1)–C(13)	1.628(4)	B(1)–C(13)	1.614(7)
B(1)–N(1)	1.635(3)	B(1)–N(1)	1.644(3)	B(1)–N(1)	1.591(6)
B(1)–Cl(2)	1.923(3)	B(1)–C(14)	1.627(4)	B(1)–N(3)	1.618(6)
C(1)-Sn(1)-C(11)	123.91(12)	C(1)-Sn(1)-C(11)	119.94(12)	C(1)-Sn(1)-C(11)	113.9(2)
C(11)-Sn(1)-C(12)	114.83(15)	C(11)-Sn(1)-C(12)	112.54(15)	C(11)-Sn(1)-C(12)	120.4(2)
C(1)-Sn(1)-C(12)	114.22(12)	C(1)-Sn(1)-C(12)	115.09(12)	C(1)-Sn(1)-C(12)	123.93(19)
C(1)-Sn(1)-Cl(1)	97.98(7)	C(1)-Sn(1)-Cl(1)	101.47(7)	C(1)-Sn(1)-Cl(1)	102.77(12)
C(11)-Sn(1)-Cl(1)	96.94(11)	C(11)-Sn(1)-Cl(1)	101.40(11)	C(11)-Sn(1)-Cl(1)	90.22(15)
C(12)-Sn(1)-Cl(1)	101.98(11)	C(12)-Sn(1)-Cl(1)	102.88(10)	C(12)-Sn(1)-Cl(1)	90.51(15)
C(12)-Sn(1)···Cl(2)	90.1			C(12)-Sn(1)-Cl(2)	87.80(15)
C(11)-Sn(1)···Cl(2)	79.9			C(11)-Sn(1)-Cl(2)	86.06(15)
C(1)-Sn(1)···Cl(2)	74.5			C(1)-Sn(1)-Cl(2)	82.55(12)
Cl(1)-Sn(1)···Cl(2)	167.7			Cl(1)-Sn(1)-Cl(2)	174.42(4)
C(2)-B(1)-Cl(2)	109.03(18)	C(2)-B(1)-C(14)	111.2(2)	C(2)-B(1)-N(3)	110.4(4)
C(2)-B(1)-C(13)	117.6(2)	C(2)-B(1)-C(13)	114.9(2)	C(2)-B(1)-C(13)	115.3(4)
C(2)-B(1)-N(1)	108.52(18)	C(2)-B(1)-N(1)	103.7(2)	C(2)-B(1)-N(1)	108.04(4)
C(13)-B(1)-N(1)	107.8(2)	C(13)-B(1)-N(1)	108.1(2)	C(13)-B(1)-N(1)	111.9(4)
C(13)-B(1)-Cl(2)	110.22(17)	C(13)-B(1)-C(14)	111.3(2)	C(13)-B(1)-N(3)	106.5(4)
N(1)-B(1)-Cl(2)	102.71(16)	N(1)-B(1)-C(14)	107.0(2)	N(1)-B(1)-N(3)	104.2(3)
C(1)-C(2)-B(1)	127.6(2)	C(1)-C(2)-B(1)	127.1(2)	C(1)-C(2)-B(1)	129.3(4)
C(2)-C(1)-Sn(1)	126.77(12)	C(2)-C(1)-Sn(1)	126.8(2)	C(2)-C(1)-Sn(1)	134.5(3)
Cp staggering angle	31.4	Cp staggering angle	17.2	Cp staggering angle	33.5
Cent-C(2)-B(1)[a]	176.0[b]	Cent-C(2)-B(1)	169.5[b]	Cent-C(2)-B(1)[a]	177.0[b]
Cent-C(1)-Sn(1)[a]	177.1	Cent-C(1)-Sn(1)	177.7	Cent-C(1)-Sn(1)[a]	168.3[b]
(Cl(1)Sn(1)Cl(2))//(C1-C5)	48.2	(Cl(1)Sn(1)C(13))//(C1-C5)	31.0	(Cl(1)Sn(1)Cl(2))//(C1-C5)	64.5
(C(1)Sn(1)C(11)C(12))//(C1-C5)	82.7	(C(1)Sn(1)C(11)C(12))//(C1-C5)	85.6	(C(1)Sn(1)C(11)C(12))//(C1-C5)	24.2
(C(2)B(1)N(1))//(C1-C5)	78.6	(C(2)B(1)N(1))//(C1-C5)	71.1	(C(2)B(1)N(3))//(C1-C5)	74.5

[a] Cent = centroid of substituted Cp ring. [b] The substituent is pointing away from the iron atom.

ing of nucleophiles to boron, we decided to study the binding properties of the related heteronuclear bidentate Lewis acid **1-Ph**, in which the chloride substituent on boron is replaced with a phenyl group.[27] Treatment of **1-Ph** with pyridine and DMAP, respectively, led to the expected diastereomeric adducts **4** and **5** (see below; the S_p enantiomer of the racemic mixture of **1-Ph** forms the respective complexes (S,S_p)-**4a**, (R,S_p)-**4b**, (S,S_p)-**5a**, and (R,S_p)-**5b**). The ^{11}B NMR spectra showed signals characteristic of tetracoordinate boron (**4**: δ 6.6; **5**: δ −1.6; cf. **1-Ph**: δ 67.5) thus confirming the binding of the pyridine ligand to boron.[19] However, the ^{119}Sn NMR spectra of both **4** and **5** revealed two signals with slightly different chemical shifts and intensities at ambient temperature (**4**: δ 117.9, 128.8; **5**: δ 121.0, 131.0; cf. **1-Ph**: δ 102.3), which is indicative of the formation of diastereomers with different tin environments. Two sets of signals with different intensities were also found in the ^{1}H and ^{13}C NMR spectra of **5**, whereas broad signals were obtained in the case of the pyridine complex **4** at ambient temperature. At −50 °C two distinct sets of signals were observed for both complexes.

Complete assignment of the two sets of signals to the isomers **5a** (56 % by ^{1}H NMR integration at 25 °C) and **5b** (44 %) was possible through a combination of low temperature 2D NMR correlation techniques (DQF-COSY, HMQC, NOESY). Most notably, the NOESY spectrum shows a strong cross-peak for the major isomer (**5a**) between the boron-bound methyl group and the Cp-proton adjacent to boron (Cp-H3), whereas a similar peak is not observed for the minor isomer (**5b**) (Figure 2). Weak cross-peaks between the boron-bound methyl groups and the unsubstituted Cp ring confirm the positions of the methyl groups pointing toward the iron atom in both isomers. Similarly, the *ortho*-protons of the phenyl group of the major isomer show cross-peaks with one of the methyl groups on tin and with the protons on the unsubstituted Cp ring. Importantly, all observed NOESY cross-peaks are consistent with the assignment of the major isomer as **5a** and of the minor isomer as **5b**. The two sets of signals for the pyridine complex **4** at −50 °C are readily assigned to the respective isomers **4a** and **4b** by comparison with the data for **5a** and **5b** (Table 1).

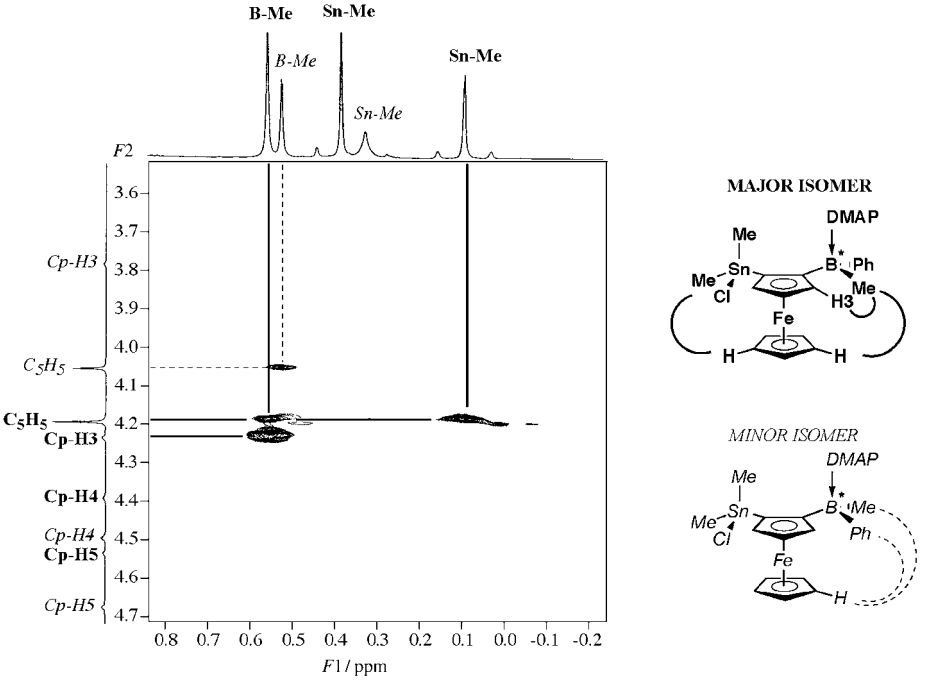
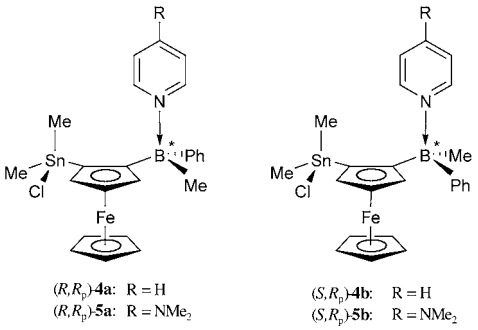


Figure 2. Methyl/Cp-region of the NOESY spectrum of **5** ($CDCl_3$; −50 °C); signals for the major isomer **5a** are indicated in bold font, those for the minor isomer **5b** are in italics.



Crystallization of **5** by slow solvent evaporation from a CH_2Cl_2/pentanes mixture gave yellow single crystals in nearly quantitative yield. Surprisingly, the X-ray structure analysis showed that the minor isomer **5b** had formed (Figure 3, Table 2). Packing effects are likely responsible for the preferred crystallization of the minor isomer. Indeed, when crystals of **5b** are redissolved in $CDCl_3$, immediate isomerization occurs yielding a 56:44 mixture of **5a**:**5b**.

The observation of signal broadening in the room temperature spectra of **4** and the apparent formation of a mixture of **5a** and **5b** from isolated crystals of **5b** indicated facile isomerization in solution.[28] To probe the mechanism of this process we performed variable temperature ^{1}H NMR studies on **4** and **5** (Figure 4).

As shown in Figure 4, two sets of sharp signals corresponding to the two isomers **4a** and **4b** are observed at low temperature. All resonances gradually undergo coalescence within the temperature range from −10 to +35 °C. The

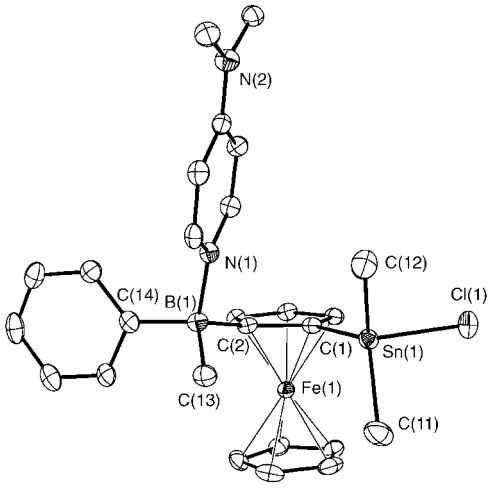


Figure 3. Molecular structure of the minor isomer **5b** with thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity.

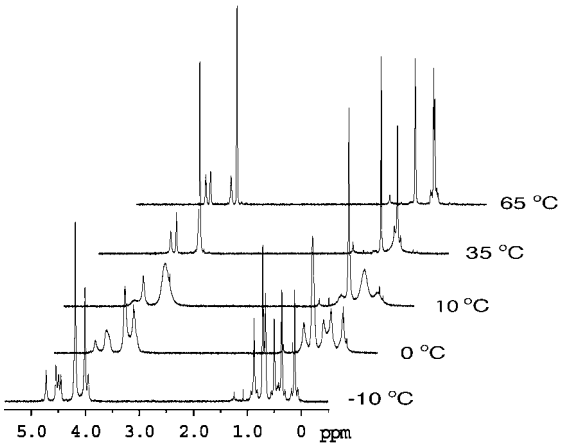


Figure 4. Variable temperature ^{1}H NMR spectra for **4** (methyl and Cp region).

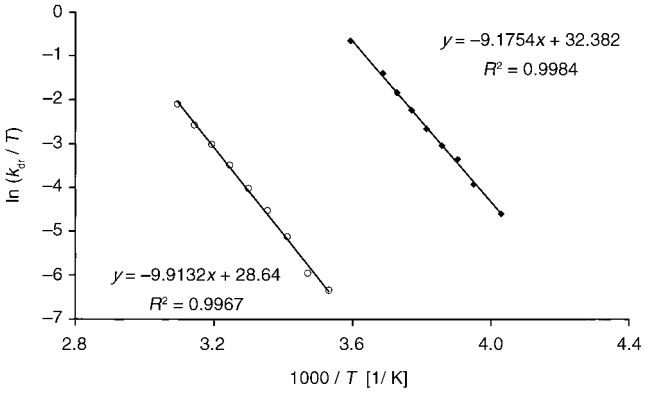


Figure 5. Eyring plots for the isomerization kinetics of **4** (◆) and **5** (○) in $CDCl_3$; the Cp (**4**) and NMe protons (**5**) were used as the probe and data were averaged for the two isomers.

spectrum at 65 °C represents the fast exchange limit as only one set of sharp signals is observed. By contrast, two sets of sharp signals are observed for the DMAP complex **5** at room temperature and only some of the signals undergo coalescence within the temperature range accessible in $CDCl_3$ solution. Isomerization of the DMAP complex **5** thus occurs much more slowly than in the case of the pyridine complex **4**. Thermodynamic data for the isomerization processes of **4** and **5** were determined by using standard line shape analysis techniques (see Supporting Information).[29] A significantly lower average energy barrier for the two isomers of **4** of $\Delta G^{\ddagger}_{298} = 54.9 \pm 0.4$ kJ mol^{-1} relative to those of **5** with $\Delta G^{\ddagger}_{298} = 70.3 \pm 0.1$ kJ mol^{-1} was deduced from the corresponding Eyring plots (Figure 5, Table 3).[30,31] These results are consistent with the seminal work by Brown and co-workers, who showed that the binding strength of organoborane adducts with substituted pyridine derivatives strongly depends on both electronic and steric factors.[32] A comparison with thermodynamic data for the monofunctional ferrocenylborane [FcB(Ph)Me] and the respective complexes [FcB(Ph)Me]·Py and [FcB(Ph)Me]·DMAP is instructive: The barrier of rotation about the Cp–B bond for [FcB(Ph)Me] was found to be comparatively low ($\Delta G^{\ddagger}_{rot}$ was estimated to be <40 kJ mol^{-1}; cf. for FcB(Cl)Me $\Delta G^{\ddagger}_{rot(298)} = 46.6 \pm 0.3$ kJ mol^{-1}).[26] The activation energies for isomerization of the complexes [FcB(Ph)Me]·Py ($\Delta G^{\ddagger}_{298} = 51.4 \pm 0.8$ kJ mol^{-1}) and [FcB(Ph)Me]·DMAP ($\Delta G^{\ddagger}_{303} = 65.3 \pm 1.5$ kJ mol^{-1}) on the other hand are higher than the rotational barrier for [FcB(Ph)Me] and similar to the barriers determined for our bifunctional Lewis acid complexes **4** and **5** (Table 3). They also follow the same trend with a significantly larger barrier for [FcB(Ph)Me]·DMAP than [FcB(Ph)Me]·Py, which is consistent with bond dissociation as the rate-limiting step.

Table 3. Thermodynamic parameters of the isomerization of **4** and **5** in comparison with data of monofunctional ferrocenylboranes.

	$\Delta G^{\ddagger}_{298}$ [kJ mol^{-1}][a]	$\Delta H^{\ddagger}$ [kJ mol^{-1}][a]	$\Delta S^{\ddagger}$ [J mol^{-1} K^{-1}][a]
4	54.9 ± 0.4	76.3 ± 2.7	72 ± 10
5	70.3 ± 0.1	82.4 ± 2.4	41 ± 8
[FcB(Ph)Me]·Py	51.4 ± 0.8	64.5 ± 4.9	44 ± 19
[FcB(Ph)Me]·DMAP	65.3 ± 1.5[b]		
[FcB(Ph)Me][c]	≦40[b]		
[FcB(Cl)Me][c]	46.6 ± 0.3	37.3 ± 0.8	−31 ± 4

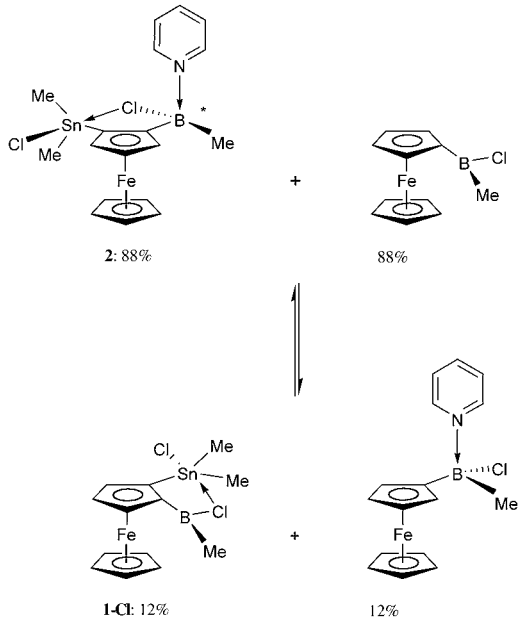
[a] Data were obtained in $CDCl_3$ (**4**, **5**, and FcB(Ph)Me·DMAP) or CD_2Cl_2 (FcB(Ph)Me·Py, FcB(Ph)Me, FcB(Cl)Me) through full VT NMR line shape analysis unless noted otherwise; data for **4** and **5** are averaged for the two isomers. [b] Estimated based on the coalescence temperature method.[36] [c] Data correspond to rotation about the B–C(Cp) bond.

Based on the above considerations we propose the isomerization mechanism shown in Scheme 2. Dissociation of the pyridine ligand from boron is the rate limiting step as in-

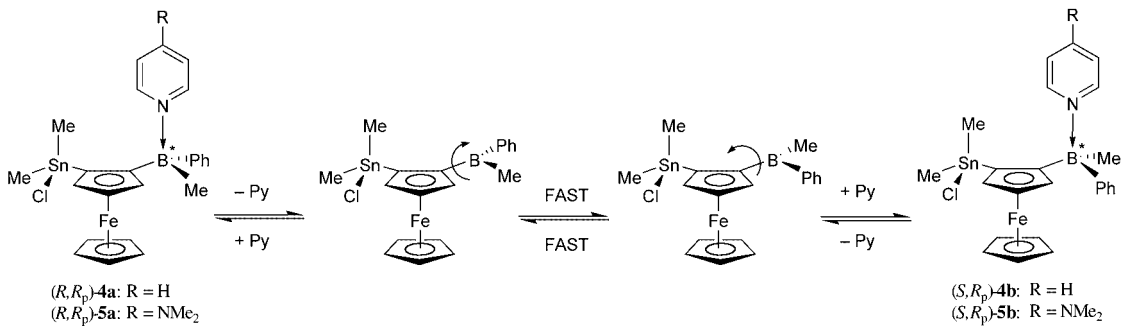
dicated by the significant difference in the measured activation energies ΔG^{+} for the DMAP and the pyridine complex, respectively, and further supported by the increase in entropy ΔS^{+}. Dissociation is followed by rotation about the B–C(Cp) bond, which despite the partial double-bond character[33,34] in the free acid **1-Ph** is fast in comparison to the dissociation step. The pyridine molecule then reattaches to boron from the *exo*-side of the ferrocene.[35] The slightly larger relative amount of isomers **4a** and **5a** is likely due to more favorable steric interactions of the phenyl group with the organotin moiety in comparison to the methyl group.

Lewis acidity enhancement of the heteronuclear bidentate Lewis acid 1-Cl: In order to probe the Lewis acidity enhancement[37] of the organoboron moiety in the bidentate Lewis acid **1-Cl** we compared the binding propensity with that of the monofunctional Lewis acid [FcB(Cl)Me],[33] which does not feature an adjacent Lewis acidic organotin group. In a competition experiment we treated a 1:1 mixture of **1-Cl** and [FcB(Cl)Me] with one equivalent of pyridine in $CDCl_3$ and allowed the mixture to equilibrate over a period of 24 h. The ^{119}Sn and ^{1}H NMR spectra confirm that the adduct **2** and the free acid [FcB(Cl)Me] are the predominant species (ca. 88%), whereas only small amounts (ca. 12%) of **1-Cl** and the adduct [FcB(Cl)Me]·Py are present (Scheme 3).[38] Coordination of pyridine to the bidentate Lewis acid **1-Cl** is thus slightly more favorable than complexation of the monodentate Lewis acid [FcB(Cl)Me]. When a similar competition experiment was performed with **1-Ph** and [FcB(Ph)Me], almost equal amounts of the mono- and bidentate Lewis acids were complexed with pyridine (ratio of [FcB(Ph)Me]·Py:**4** 60:40). These results are consistent with the observation discussed above that the activation energies ΔG^{+} for isomerization of **4** and **5** are quite similar to those for [FcB(Ph)Me]·Py and [FcB(Ph)Me]·DMAP, respectively. We conclude that Lewis acidity enhancement in **1-Cl** is unique and to a large extent due to the intramolecular chloride bridge in **1-Cl**.

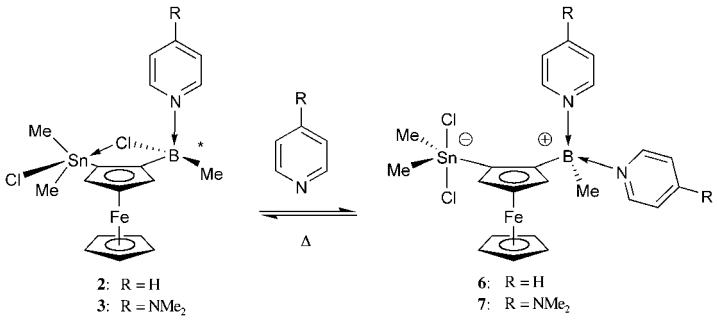
Thermoreversible binding of a second pyridine donor to 1-Cl: One of the key questions with regard to the binding of nucleophiles to a heteronuclear bidentate Lewis acid is whether both Lewis acidic groups are indeed readily accessible. In order to address this issue we decided to study the reaction of **1-Cl** with two equivalents of the pyridine donors. The second pyridine molecule may either coordinate to the Lewis acidic tin group or to boron thus replacing chloride under formation of a boronium cation. Coordination of pyridine to tin has, for example, been recently reported by Gabbaï and co-workers for a heteronuclear bifunctional Lewis acid featuring tin and gallium atoms adjacent to each other.[39] Formation of boronium cations from organoboron halides on the other hand is a common process,[40] and we indeed found that the monofunctional Lewis acid [FcB(Cl)Me] readily forms a boronium cation with two equivalents of pyridine (see vide infra). Surprisingly, coordination of a second pyridine molecule to **2** under formation of a boronium cation **6** was not detected in $CDCl_3$. Treatment of **1-Cl** with an excess of the more electron-rich base DMAP on the other hand led to formation of a new species **7** as evident from a shift of the ^{11}B NMR signal relative to that of the 1:1 DMAP adduct **3** from δ 8.4 to 3.3 and of the ^{119}Sn NMR signal from δ 57.2 to 100.9 (Scheme 4). Two sets



Scheme 3. Competitive binding of pyridine to **1-Cl** and [FcB(Cl)Me].



Scheme 2. Proposed isomerization pathway for **4** and **5**.



Scheme 4. Reversible binding of a second pyridine donor.

of DMAP signals are observed in the ^{1}H NMR spectrum of **7**, because the two DMAP ligands at the tetrahedral boronium moiety are diastereotopic. Integration of the DMAP signals relative to those of the ferrocene moiety further confirms that two molecules of DMAP are coordinated to **1-Cl**. Moreover, a characteristic shielding of the proton adjacent to the boronium cation (Cp-H3, δ 3.58) may be attributed to the anisotropy effect of the DMAP ligands. The methyl groups on tin, which are diastereotopic in **1-Cl** and also in the complexes **2** and **3**, give rise to only one signal in the pentacoordinate tin environment in **7**.

To gain further insight into the structural features of species **7** we performed an X-ray analysis on single crystals obtained by recrystallization from hot chloroform. The X-ray structure of **7** (Figure 6, Table 2) confirmed that not a bis-adduct, but a novel zwitterionic species had formed. Coordination of both DMAP molecules to boron yielded a cationic boronium moiety[41] and transfer of the chloride substituent to tin led to formation of a pentacoordinate stannate anion[42,43] (Scheme 4). While the chlorine atoms in species **1-Cl** and **2** show only a weak interaction with the tin atom, attack of a second molecule of DMAP apparently triggers the transfer of the chloride substituent to tin.[44] Steric congestion around tin results in rotation of the stannyl moiety thereby providing maximum space for the two axial chloride ligands. However, significant steric strain in the zwitterion **7** is still encountered as reflected in a strong upward tilt of the stannyl group of 11.7° relative to the Cp plane as well as strong distortions of the angles C(2)-C(1)-Sn(1) of 134.5(3)° and C(5)-C(1)-Sn(1) of 117.0(3)° between tin and the Cp ring (undistorted angle: 126°).[45] The Sn–Cl(2) distance of 2.7827(12) Å is significantly longer than that observed for Sn–Cl(1) of 2.5549(13) Å. Both bonds are elongated in comparison to the ones for **1-Cl** and **2** (ca. 2.4 Å), but much shorter than the intramolecular distances between the boron-bound chlorine and the tin atom in **1-Cl** and **2** (ca. 3.1 Å). The preference of chloride substituents for the axial positions is well-documented in the literature and dissimilar Sn–Cl distances have been reported for several other organostannate anions of type $[R_3SnCl_2]^-$, although this feature is not observed in all cases.[46] A closely related system is that of $[tmpH_2]^+[Me_3SnCl_2]^-$ with Sn–Cl distances of 2.454(2) and 3.043(3) Å reported by Johnson and Nöth.[47] The authors concluded that hydrogen-bonding interactions between one of the axial chlorine substituents and the $[tmpH_2]^+$ counterion are likely responsible for the elongation of the Sn–Cl bond. Inspection of the extended solid state structure of **7** indeed showed a short distance between the chlorine atom Sn–Cl(2) and the deuterium atom of a $CDCl_3$ solvent molecule. The Cl···D distance of 2.420 Å is well below the sum of the van der Waals radii (3.0 Å).

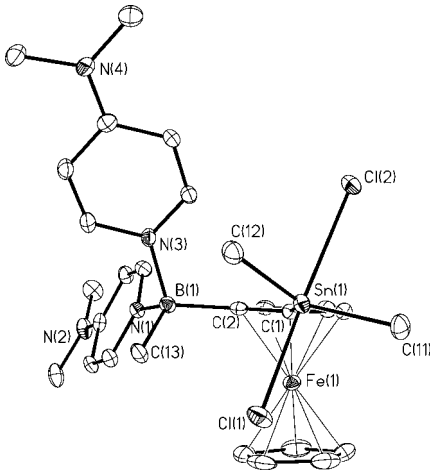


Figure 6. Molecular structure of **7** with thermal ellipsoids at the 30% probability level. Cocrystallized solvent molecules ($CDCl_3$) and hydrogen atoms are omitted for clarity.

We found that the zwitterion formation upon coordination of a second molecule of DMAP to **3** is a reversible process in $CDCl_3$ solution, which is strongly temperature and concentration dependent. Thermodynamic parameters for the coordination of DMAP to **3** were obtained through variable temperature ^{1}H NMR spectroscopy. The results from the van't Hoff plot shown in Figure 7 confirm that the

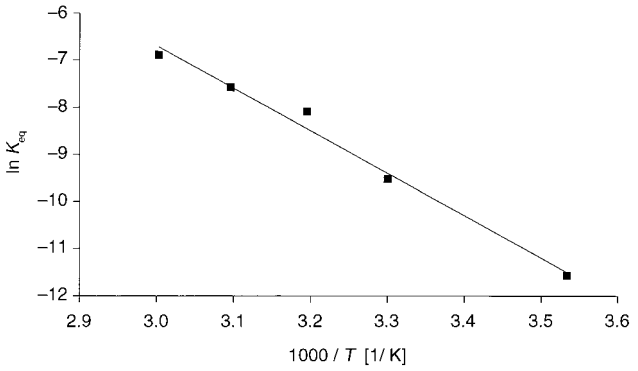
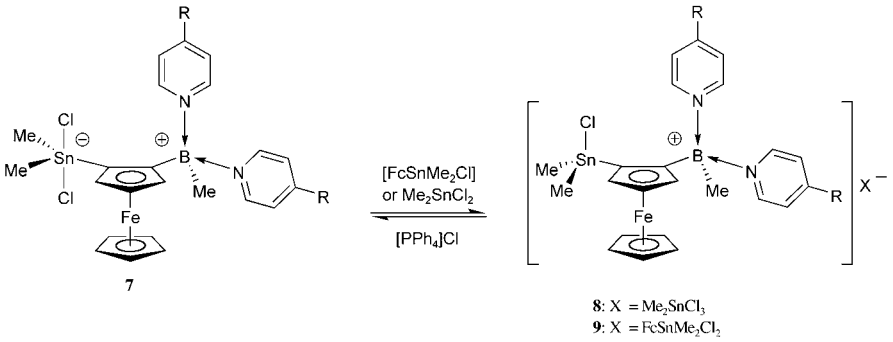


Figure 7. van't Hoff plot for the equilibrium between **3** and **7**.

binding of the second DMAP molecule is an exothermic process with $\Delta H_{as} = -75 \pm 15\ kJ\,mol^{-1}$, while the negative value of $\Delta S_{as} = -170 \pm 50\ J\,mol^{-1}\,K^{-1}$ is consistent with the associative nature of the binding of a DMAP molecule to boron (see Scheme 4).[48] Formation of a zwitterionic pyri-

dine complex **6** analogous to **7** is unfavorable in $CDCl_3$ as pointed out above, but could be observed in neat [D_5]pyridine. The binding constant $K_{298}=(1.7\pm0.4)\times10^{-1}\,\text{M}^{-1}$ for formation of **6** is several magnitudes smaller than that for **7** ($K_{298}=(2.0\pm0.5)\times10^{4}\,\text{M}^{-1}$), and even in neat pyridine complex **6** dissociates into **2** and pyridine at RT (**6**:**2** 62:38).[49]

Competition of external Lewis acids for the chloride ion in 7: The comparatively long Sn–Cl distances in the crystal structure of **7** in combination with the surprisingly large ^{119}Sn NMR shift of δ 100.9 in solution suggested that the chloride ion is relatively weakly bound to the organotin moiety.[50] Indeed, the ^{119}Sn NMR signal is only shifted slightly upfield relative to the monofunctional species [$FcSnMe_2Cl$] (δ 130), which does not display any Sn···Cl interactions. Treatment of **7** with an equimolar amount of the stronger Lewis acid Me_2SnCl_2 in $CDCl_3$ resulted in chloride abstraction under formation of the salt [1,2-fc(BMe(dmap)$_2$)-($SnMe_2Cl$)]$^+$[Me_2SnCl_3]$^-$ (**8**) (Scheme 5). Formation of the stannate anion [Me_2SnCl_3]$^-$ was evident from a signal at -106.8 ppm in the ^{119}Sn NMR spectrum, which is in a similar region as reported previously in the literature for the salt [Ph_4P]$^+$[Me_2SnCl_3]$^-$.[51] A second resonance at a chemical shift of $\delta(^{119}\text{Sn})=128.8$ is assigned to the "decomplexed" boronium cation [1,2-fc(BMe(dmap)$_2$)($SnMe_2Cl$)]$^+$. The coupling constant for the Sn-Me group $J(^{119}\text{Sn,H})=58$ Hz is slightly lower than that found for **7** ($J(^{119}\text{Sn,H})=61$ Hz), which is consistent with decomplexation of the tin atom.



Scheme 5. Chloride abstraction from **7** with Me_2SnCl_2 and [$FcSnMe_2Cl$].

The relative Lewis acidity of the tin atom in the boronium cation [1,2-fc(BMe(dmap)$_2$)($SnMe_2Cl$)]$^+$ can be assessed through a competition experiment with the related monofunctional Lewis acid [$FcSnMe_2Cl$] (Scheme 5). An equimolar amount of [$FcSnMe_2Cl$] was added to a solution of **7**, and the resulting mixture was studied by multinuclear NMR spectroscopy. As in the case of Me_2SnCl_2 addition, two different signals are observed in the ^{119}Sn NMR spectrum, one at $\delta(^{119}\text{Sn})=27$ (broad) and another at $\delta(^{119}\text{Sn})=120$ (sharp). However, none of the signals correlates with the ^{119}Sn NMR shifts for either **7** ($\delta(^{119}\text{Sn})=100.9$), **8** ($\delta(^{119}\text{Sn})=128.8$), or $FcSnMe_2Cl$ ($\delta(^{119}\text{Sn})=130$). This indicates that the external Lewis acid $FcSnMe_2Cl$ does compete with **7** for the chloride ion, though less effectively than Me_2SnCl_2. The fast dynamics of complexation apparently results in an averaged chemical shift of $\delta(^{119}\text{Sn})=27$, which is between the limits of $\delta(^{119}\text{Sn})=130$ for free $FcSnMe_2Cl$ and of about $\delta(^{119}\text{Sn})=-73$ for the fully complexed stannate [$FcSnMe_2Cl_2$]$^-$. The latter was determined by extrapolation from a titration study with [Ph_4P]Cl (Figure 8). Correlation of the chemical

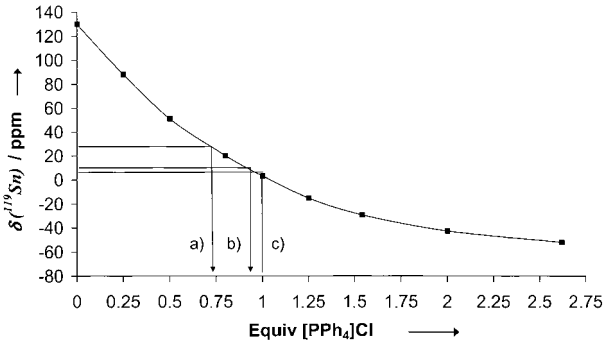
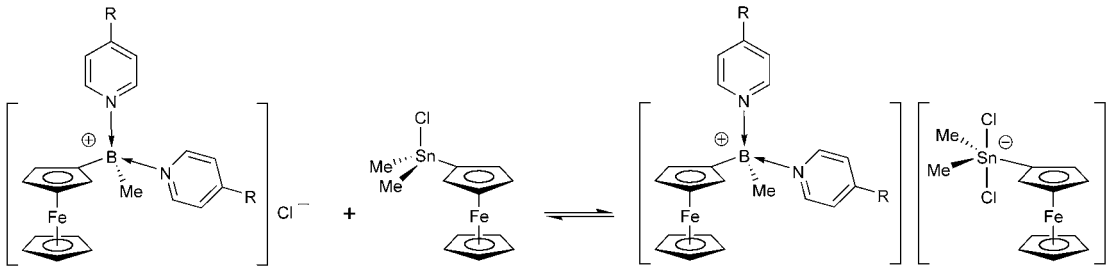


Figure 8. Titration of [$FcSnMe_2Cl$] with [PPh_4]Cl in $CDCl_3$ at ca. 0.02 M concentration. a) [$FcSnMe_2Cl$]+**7**, b) [$FcSnMe_2Cl$]+[FcBMe(dmap)$_2$]Cl, c) [$FcSnMe_2Cl$]+[PPh_4]Cl.

shift with the amount of chloride available, using the binding curve in Figure 8, indicates that about 0.7 equivalents of chloride from **7** are available for coordination to [$FcSnMe_2Cl$]. The second signal in the ^{119}Sn spectrum at $\delta(^{119}\text{Sn})=120$ may be interpreted as an averaged signal for the zwitterion **7** ($\delta(^{119}\text{Sn})=100.9$ with 1 equiv chloride) and the decomplexed species [1,2-fc(BMe(dmap)$_2$)($SnMe_2Cl$)]$^+$ ($\delta(^{119}\text{Sn})=128.8$). Thus only a small fraction of the chloride produced through boronium cation formation still contributes to the binding in **7**. These results clearly show that [$FcSnMe_2Cl$] is indeed a stronger Lewis acid toward chloride than the organotin moiety in the boronium cation [1,2-fc(BMe(dmap)$_2$)($SnMe_2Cl$)]$^+$.

Comparison with monofunctional Lewis acids: To directly assess the consequences of the arrangement with a tin and a boron atom adjacent to each other in **1-Cl** on the ability to form boronium stannate complexes, we also compared our results with the binding of DMAP to the respective monofunctional Lewis acids [$FcSnMe_2Cl$] and [FcB(Cl)Me] (Scheme 6). Mixing of a solution of [FcB(Cl)Me] with two equivalents of DMAP resulted in facile formation of [FcBMe(dmap)$_2$]Cl. The boronium cation was confirmed by the observed upfield shift in the ^{11}B NMR spectrum to δ 3.3,



Scheme 6. Formation of an intermolecular boronium–stannate complex (R = H, NMe_2).

which correlates well with that for **7** (δ 3.3). Moreover, a characteristic shielding of the protons in 2,5-position of the substituted Cp ring (δ 3.82) results from the presence of two DMAP ligands attached to boron, an effect that was also observed for **7**. However, in contrast to the dynamic equilibrium between **3** and **7** described above, full complexation under formation of [FcBMe(dmap)$_2$]Cl was observed in $CDCl_3$ without any evidence of dissociation into free DMAP and the mono-adduct [FcB(Cl)Me]·DMAP even at elevated temperature.

To the resulting solution was added one equivalent of the "external" Lewis acid $FcSnMe_2Cl$, and the mixture was studied by multinuclear NMR spectroscopy. Most notably, a strong upfield shift was observed in the ^{119}Sn NMR spectrum ($\delta(^{119}Sn) = 8.6$) relative to the free Lewis acid $FcSnMe_2Cl$ ($\delta(^{119}Sn) = 130$). Again, the fast dynamics of complexation result in an averaged chemical shift between the limits of ($\delta(^{119}Sn) = 130$ for free $FcSnMe_2Cl$ and of ca. ($\delta(^{119}Sn)$ −73 for the fully complexed species $[FcSnMe_2Cl_2]^-$. A high degree of chloride complexation to $FcSnMe_2Cl$ is evident from the large upfield shift ($\Delta\delta(^{119}Sn) = 121$ ppm) of the ^{119}Sn NMR signal relative to the free acid $FcSnMe_2Cl$.

Correlation of the ^{119}Sn NMR shift with the degree of chloride binding using the titration curve in Figure 8 confirms that chloride binding in the intermolecular complex $[FcBMe(dmap)_2]^+[FcSnMe_2Cl_2]^-$ is of the same magnitude as found for the phosphonium chloride complex $[PPh_4]^+[FcSnMe_2Cl_2]^-$. This stands in sharp contrast to the strongly diminished affinity of **7** for chloride ion binding. The latter is most likely due to severe steric strain as apparent from the crystal structure of **7**.

Summary and Conclusions

We have shown that intermolecular coordination of neutral monodentate donors such as pyridine to the bidentate Lewis acid **1-Cl** occurs regio- and stereoselectively at boron thereby compensating for the Fe–B interaction observed in the free acid **1-Cl**. The stannyl group not only enhances the Lewis acidity of **1-Cl** through a chloride bridge to boron, but also is responsible for the diastereoselectivity of the binding process. In the absence of such an intramolecular chloride interaction, two diastereomers are formed as shown for the complexation of **1-Ph** with pyridine and DMAP, respectively.

Binding of a second pyridine donor also occurs at boron rather than tin. This thermally reversible process involves the transfer of the chlorine substituent from boron to tin with generation of an unusual zwitterionic boronium–stannate complex. Zwitterion formation is favorable in the case of the strong base DMAP, but dissolution of **1-Cl** in neat pyridine is required in order to form a significant amount of a boronium species. While the presence of the organotin moiety enhances the Lewis acidity of boron in **1-Cl** towards binding of pyridine, severe steric crowding leads to diminished Lewis acidity of the tin atom itself, which only weakly coordinates chloride ions. Thus chloride binding in the intermolecular boronium-stannate complex $[Fc(BMe(dmap)_2)]^+[FcSnMe_2Cl_2]^-$ is stronger than in the boronium-stannate zwitterion **7**.

In conclusion, our results clearly show that adjacent Lewis acid groups may act in a cooperative fashion even in the binding of monofunctional nucleophiles. The mutual interactions between Lewis acid groups attached to the same Cp ring in ferrocenes in particular are intriguing due to the possibility for stereoselective binding processes. Both bridging interactions and steric effects have to be taken into consideration when assessing the affinity of the individual Lewis acid groups for binding of nucleophiles.

Experimental Section

Materials and general methods: BCl_3 (1 M in hexanes), pyridine (anhydrous grade), 4-dimethylaminopyridine (DMAP), and $[PPh_4]Cl$ were purchased from Acros; $PhBCl_2$ and [D_5]pyridine were obtained from Aldrich; Me_3SnCl from Strem Chemicals; and $CDCl_3$ (>99.7%) from Cambridge Isotope Laboratories (CIL). The deuterated solvents were degassed via several freeze-pump-thaw cycles and stored over 3 Å molecular sieves. $PhBCl_2$ was distilled under vacuum prior to use, $[PPh_4]Cl$ was carefully dried under high vacuum at 150 °C, and all other chemicals were used as received. The compounds 1,2-fc($SnMe_2Cl$)(BClMe),[13] 1,2-fc($SnMe_2Cl$)(BMePh),[13] FcB(Cl)Me,[33] FcB(Cl)Ph,[33] and $FcSnMe_2Cl$[52] were prepared according to literature procedures. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen by using either Schlenk techniques or an inert-atmosphere glove box (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified by 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.

All 499.9 MHz ^{1}H NMR, 125.7 MHz ^{13}C 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 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). The 400 MHz ^{1}H NMR spectra and 100.5 MHz ^{13}C NMR spectra were recorded on a Varian VXR-S spectrometer. Two-dimensional NMR spectra were acquired on the Varian INOVA NMR spectrometer. All solution ^{1}H 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 $BF_3{\cdot}Et_2O$ ($\delta = 0$) in C_6D_6, respectively.

2D Proton correlation spectroscopy, COSY,[53] proton NOE spectroscopy, NOESY,[54] and one bond proton–carbon correlation spectroscopy, HMQC,[55] measurements were recorded in the absolute value mode (COSY) or the phase sensitive mode (NOESY, HMQC) by employing the TPPI improvement[56] of the States-Haberkorn-Ruben hypercomplex method.[57] Selection of desirable coherences and artifact suppression were accomplished by *z* gradients (COSY, echo N-type coherence selection[58]), or phase cycles of 32 (NOESY) or 16 (HMQC) steps. The NOESY data set was acquired by using a 500 ms mixing time. The HMQC pulse sequence included the BIRD filter to suppress signals from C12-attached protons[59] and C13-decoupling during proton acquisition, using a 3.6 kHz field strength and the GARP decoupling scheme.[60] Typically, 256 *t*1 increments of 2 K complex data points over 5.5 kHz (proton) and 22.5 kHz (carbon) spectral widths were collected with 1 (COSY), 32 (NOESY) or 16 (HMQC) scans per *t*1 increment, preceded by 16 or 32 dummy scans, and a relaxation delay of 2 s. Baseline distortion was addressed by properly adjusting the sampling delay and the signal phase.[61] Data sets were processed on a Sun Blade 100 workstation (Sun Microsystems Inc., Palo Alto, CA) by using the VNMR software package (Varian Inc., Palo Alto, CA). In order to decrease *t*1 ridges arising from incorrect treatment of the first data point in the discrete Fourier transform (FT) algorithm, the spectrum corresponding to the first *t*1 value was divided by 2 prior to FT along *t*1.[62] Shifted (COSY) or unshifted (NOESY, HMQC) Gaussian window functions were used in both dimensions. Data sets were zero-filled in the *t*1 dimension yielding 1 K × 1 K final matrices that have not been symmetrized. NMR signals; pst: pseudo-triplet, dpst: doublet of pseudo-triplet, nr: not resolved.

UV/Vis 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 glove box. Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

Treatment of 1-Cl with 1 equiv of pyridine—Synthesis of 2: Neat pyridine (60 mg, 0.76 mmol) was added dropwise to solution of **1-Cl** (300 mg, 0.70 mmol) in chloroform (2 mL). Pentanes (6 mL) were added and the reaction mixture was kept at −37 °C overnight. The yellow crystals formed overnight were washed successively with a mixture of pentanes and chloroform (2:1) and dried under high vacuum overnight to yield adduct **2** (180 mg, 51 %). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 8.65$ (d, $J = 6.8$ Hz, 2H, Py-H_o), 8.00 (t, $J = 7.8$ Hz, 1H, Py-H_p), 7.57 (pst, $J = 7.2$ Hz, 2H, Py-H_m), 4.78 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, $J(^{117/119}Sn,H) = 12.8$ Hz, 1H, Cp-H5), 4.55 (pst/dpst, $J = 2.4$ Hz, $J(^{117/119}Sn,H) = 8.8$ Hz, 1H, Cp-H4), 4.37 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, $J(^{117/119}Sn,H) = 14.0$ Hz, 1H, Cp-H3), 4.27 (s, 5H, Cp), 1.02 (s/d, $J(^{117/119}Sn,H) = 65/68$ Hz, 3H, Sn-Me), 0.70 (s, 3H, B-Me), 0.06 (s/d, $J(^{117/119}Sn,H) = 59/62$ Hz, 3H, Sn-Me); ^{13}C NMR (100.5 MHz, $CDCl_3$, 20 °C): $\delta = 145.3$ (Py-C_o), 141.4 (Py-C_p), 125.3 (Py-C_m), 90.0 (br, *ipso*-CpB), 77.1 (s/d, $J(^{117/119}Sn, C) = 704/736$ Hz, *ipso*-CpSn), 77.0 (overlapping, Cp-C5), 76.2 (s/d, $J(^{117/119}Sn, C) = 65$ Hz, Cp-C4), 73.1 (s/d, $J(^{117/119}Sn, C) = 57$ Hz, Cp-C3), 69.2 (Cp), 12.1 (br, B-Me), 4.5 (s/d, $J(^{117/119}Sn, C) = 476/502$ Hz, Sn-Me), 2.5 (s/d, $J(^{117/119}Sn, C) = 405/425$ Hz, Sn-Me); ^{11}B NMR (128.3 MHz, $CDCl_3$, 20 °C): $\delta = 9.5$ ($w_{1/2} = 400$ Hz); ^{119}Sn NMR (149.1 MHz, $CDCl_3$, 20 °C): $\delta = 68.8$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 442 (190), 312 nm (sh, 310); elemental analysis calcd (%) for: C 42.42, H 4.55, N 2.75; found C 42.44, H 4.27, N 2.60.

Treatment of 1-Cl with 1 equiv of DMAP—Synthesis of 3: Neat 4-dimethylaminopyridine (DMAP) (14.2 mg, 0.116 mmol) was added to a solution of **1-Cl** (50 mg, 0.116 mmol) in chloroform (3 mL). The reaction mixture was layered with pentanes (3 mL) and left to stand overnight at room temperature. The yellow crystals formed overnight were washed successively with a mixture of pentanes and chloroform (2:1) and dried under high vacuum overnight to yield adduct **3** (30 mg, 47 %). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 7.97$ (d, $J = 7.6$ Hz, 2H, DMAP-H_o), 6.46 (d, $J = 7.6$ Hz, 2H, DMAP-H_m), 4.72 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, $J(^{117/119}Sn,H) = 13$ Hz, 1H, Cp-H5), 4.49 (pst/dpst, $J = 2.4$ Hz, $J(^{117/119}Sn,H) = 9$ Hz, 1H, Cp-H4), 4.26 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, $J(^{117/119}Sn,H) = 14$ Hz, 1H, Cp-H3), 4.25 (s, 5H, Cp), 3.11 (s, 6H, NMe_2), 1.01 (s/d, $J(^{117/119}Sn,H) = 68$ Hz, 3H, Sn-Me), 0.63 (s, 3H, B-Me), 0.23 (s/d, $J(^{117/119}Sn,H) = 61$ Hz, 3H, Sn-Me); ^{13}C NMR (125.7 MHz, $CDCl_3$, 20 °C): $\delta = 155.3$ (DMAP-C_o), 143.9 (DMAP-C_p), 105.8 (DMAP-C_m), 91.0 (br, *ipso*-CpB), 77.3 (s/d, $J(^{117/119}Sn, C) = 690/722$ Hz, *ipso*-CpSn), 76.2 (s/d, $J(^{117/119}Sn, C) = 72$ Hz, Cp-C5), 72.5 (s/d, $J(^{117/119}Sn, C) = 59$ Hz, Cp-C3), 75.5 (s/d, $J(^{117/119}Sn, C) = 67$ Hz, Cp-C4), 68.8 (Cp), 39.5 (N-Me), 11.1 (br, B-Me), 4.6 (s/d, $J(^{117/119}Sn, C) = 483/506$ Hz, Sn-Me), 3.0 (s/d, $J(^{117/119}Sn, C) = 413/431$ Hz, Sn-Me); ^{11}B NMR (128.3 MHz, $CDCl_3$, 20 °C): $\delta = 8.4$ ($w_{1/2} = 400$ Hz); ^{119}Sn NMR (149.1 MHz, $CDCl_3$, 20 °C): $\delta = 57.2$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 448 (290), 339 nm (sh, 550 L mol^{-1} cm^{-1}); elemental analysis calcd (%) for: C 43.54, H 4.93, N 5.08; found C 43.34, H 4.79, N 4.88.

Treatment of 1-Ph with 1 equiv of pyridine—Synthesis of 4: Neat pyridine (16.7 mg, 0.212 mmol) was added to a solution of **1-Ph** (100 mg, 0.212 mmol) in CH_2Cl_2 (2 mL) via syringe. Pentanes (1 mL) were added and the reaction mixture was kept at −36 °C for 2 d. Light yellow crystals (102 mg, 87 %) of the desired complex were obtained and dried under vacuum for several hours. For **4a** (major isomer, ca. 60 % at −50 °C): ^{1}H NMR (500 MHz, $CDCl_3$, −50 °C): $\delta = 8.30$–8.29 (overlapping, 2H, Py-H_o), 8.01–7.96 (overlapping, 1H, Py-H_p), 7.52 (pst, $J = 7$ Hz, 2H, Py-H_m), 7.19–7.29 (m, 3H, Ph-H_p, Ph-H_m), 7.04 (d, 2H, $J = 7.0$ Hz, Ph-H_o), 4.71 (nr, 1H, Cp-H5), 4.54 (nr, 1H, Cp-H4), 4.25 (nr, 1H, Cp-H3), 4.19 (s, 5H, Cp), 0.68 (s, 3H, B-Me), 0.40 (s/d, $J(^{117/119}Sn,H) = 57$ Hz, 3H, Sn-Me), 0.02 (s/d, $J(^{117/119}Sn,H) = 63$ Hz, 3H, Sn-Me); ^{119}Sn NMR (186.4 MHz, $CDCl_3$, −50 °C): δ = 119.3; for **4b** (minor isomer, ca. 40 %): ^{1}H NMR (500 MHz, $CDCl_3$, −50 °C): $\delta = 8.30$–8.29 (nr, 2H, Py-H_o), 8.01–7.96 (nr, 1H, Py-H_p), 7.50 (pst, $J = 7$ Hz, 2H, Py-H_m), 7.29–7.19 (m, 3H, Ph-H_p, Ph-H_m), 7.16 (d, 2H, $J = 7.0$ Hz, Ph-H_o), 4.50 (nr, 1H, Cp-H5), 4.44 (nr, 1H, Cp-H4), 4.00 (s, 5H, Cp), 3.91 (nr, 1H, Cp-H3), 0.90 (s/d, $J(^{117/119}Sn,H) = 58$ Hz, 3H, Sn-Me), 0.63 (s, 3H, B-Me), 0.44 (s/d, $J(^{117/119}Sn,H) = 58$ Hz, 3H, Sn-Me); ^{119}Sn NMR (186.4 MHz, $CDCl_3$, −50 °C): δ = 135.9.

For **4a**/**4b** (fast exchange limit): ^{1}H NMR (500 MHz, $CDCl_3$, 55 °C): $\delta = 8.46$ (br, 2H, Py-H_o), 7.88 (t, $J = 7.0$ Hz, 1H, Py-H_p), 7.43 (br, 2H, Py-H_m), 7.69–7.22 (m, 5H, Ph-$H_{o,m,p}$), 4.67 (br, 1H, Cp-H5), 4.58 (br, 1H, Cp-H4), 4.19 (br, 1H, Cp-H3), 4.11 (s, 5H, Cp), 0.79 (s, 3H, B-Me), 0.47 (s/d, $J(^{117/119}Sn,H) = 59$ Hz, 6H, Sn-Me); ^{13}C NMR (125.7 MHz, $CDCl_3$, 60 °C): δ = 147.2 (Py-C_o), 139.5 (Py-C_p), 132.8 (Ph-C_o), 127.9 (Ph-C_m), 126.2 (Ph-C_p), 124.9 (Py-C_m), 78.3, 77.4 (Cp-C3,5), 74.8 (*ipso*-CpSn), 72.8 (Cp-C4), 68.8 (C_5H_5), 12.7 (br, B-Me), 2.7 (nr, Sn-Me), 1.01 (nr, Sn-Me), not observed *ipso*-CpB, *ipso*-PhB; ^{11}B NMR (160.3 MHz, $CDCl_3$, 55 °C): δ = 6.6 ($w_{1/2} = 450$ Hz); ^{11}B NMR (160.3 MHz, $CDCl_3$, −50 °C): $\delta = 1.0$ ($w_{1/2} = 830$ Hz); ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 55 °C): $\delta = 121.4$; elemental analysis calcd (%) for **4**: C 52.38, H 4.95, N 2.54; found C 51.40, H 4.57, N 2.40.

Treatment of 1-Ph with 1 equiv of DMAP—Synthesis of 5: DMAP (13.0 mg, 0.106 mmol) was added to (50 mg, 0.106 mmol) of **1-Ph** in CH_2Cl_2 (1 mL) and pentanes (1 mL). Yellow crystals (61 mg, 97 %) were obtained upon slow evaporation of the solvents and found by X-ray crystallography to correspond to the minor isomer **5b**; however, fast equilibration occurred in solution. For **5a** (major isomer ca. 56 % at +25 °C): ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.84$ (d, $J = 7$ Hz, 2H, DMAP-H_o), 7.25–7.17 (m, 3H, Ph-H_p, Ph-H_m), 7.10 (d, $J = 7.0$ Hz, 2H, Ph-H_o), 6.45 (d, 2H, $J = 7$ Hz, DMAP-H_m), 4.67 (nr, 1H, Cp-H5), 4.46 (nr, 1H, Cp-H4), 4.17 (s, 5H, Cp), 4.12 (nr, 1H, Cp-H3), 3.09 (s, 6H, NMe_2), 0.59 (s, 3H, B-Me), 0.42 (s/d, $J(^{117/119}Sn,H) = 62$ Hz, 3H, Sn-Me), 0.25 (s/d,

$J(^{117/119}Sn,H) = 56$ Hz, 3H, Sn-Me); ^{13}C NMR (125.7 MHz, $CDCl_3$, −50 °C): $\delta = 158.5$ (Ph-Ci), 154.7 (overlapping, DMAP-C_P), 145.3 (overlapping, DMAP-C_o), 132.9 (Ph-C_o), 128.6 (Ph-C_m), 126.3 (Ph-C_p), 106.2 (overlapping, DMAP-C_m), 98.5 (br, *ipso*-CpB), 76.7 (s/d, $J(^{117/119}Sn,C) = 73$ Hz, Cp-C5), 76.5 (s/d, $J(^{117/119}Sn, C) = 67$ Hz, Cp-C3), 75.4 (s/d, $J(^{117/119}Sn,C) = 615/641$ Hz, *ipso*-CpSn), 72.3 (s/d, $J(^{117/119}Sn,C) = 54$ Hz, Cp-C4), 68.8 (s, Cp), 40.2 (overlapping, N-Me), 11.8 (br, B-Me), 4.2 (nr, Sn-Me), 1.1 (s/d, $J(^{117/119}Sn,C) = 416/423$ Hz, Sn-Me); ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): $\delta = 121.0$; ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 60 °C): $\delta = 120.9$; ^{119}Sn NMR (186.4 MHz, $CDCl_3$, −50 °C): $\delta = 122.1$. For **5b** (minor isomer ca. 44 %): ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.78$ (d, $J = 7$ Hz, 2H, DMAP-H_o), 7.17–7.25 (m, 3H, Ph-H_p, Ph-H_m), 7.15 (d, $J = 7$ Hz, 2H, Ph-H_o), 6.41 (d, 2H, $J = 7$ Hz, DMAP-H_m), 4.51 (nr, 1H, Cp-H5), 4.39 (nr, 1H, Cp-H4), 4.01 (s, 5H, Cp), 3.87 (nr, 1H, Cp-H3), 3.06 (s, 6H, NMe_2), 0.89 (s/d, $J(^{117/119}Sn,H) = 56$ Hz, 3H, Sn-Me), 0.55 (s, 3H, B-Me), 0.30 (s/d, $J(^{117/119}Sn,H) = 58$ Hz, 3H, Sn-Me); ^{13}C NMR (125.7 MHz, $CDCl_3$, −50 °C): $\delta = 157.5$ (Ph-C_i), 154.7 (overlapping, DMAP-C_P), 145.3 (overlapping, DMAP-C_o), 132.5 (Ph-C_o), 127.0 (Ph-C_m), 124.8 (Ph-C_p), 106.2 (overlapping, DMAP-C_m), 96.9 (br, *ipso*-CpB), 78.9 (s/d, $J(^{117/119}Sn,C) = 75$ Hz, Cp-C5), 76.0 (s/d, $J(^{117/119}Sn,C) = 70$ Hz, Cp-C3), 74.0 (s/d, $J(^{117/119}Sn,C) =$ n.d., *ipso*-CpSn), 71.9 (s/d, $J(^{117/119}Sn,C) = 56$ Hz, C4), 68.7 (s, Cp), 40.2 (overlapping, N-Me), 12.7 (br, B-Me), 2.7 (nr, Sn-Me), 2.1 (nr, Sn-Me); ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 25 °C): $\delta = 131.0$; ^{119}Sn NMR (186.4 MHz, $CDCl_3$, 60 °C): $\delta = 128.5$; ^{119}Sn NMR (186.4 MHz, $CDCl_3$, −55 °C): $\delta = 137.9$.

For **5a/5b**: ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): $\delta = -1.6$ ($w_{1/2} = 1120$ Hz).

Treatment of 1-Cl with excess of pyridine—Synthesis of 6: Compound **1-Cl** (5.3 mg, 12 μmol) was dissolved in [D_5]pyridine (1.0 g) yielding an equilibrium mixture of species **6** and **2** (ca. 62:38 at 30 °C according to ^1H NMR spectroscopy). For **6**: ^1H NMR (400 MHz, [D_5]pyridine, 30 °C): $\delta = 5.15$ (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, Cp-H5), 4.55 (pst/dpst, $J = 2.4$ Hz, 1H, Cp-H4), 4.53 (s, 5H, Cp), 3.44 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, 1H, Cp-H3), 1.57 (s, 3H, B-Me), 1.36 (s/d, $J(^{117/119}Sn,H) = 73/76$ Hz, 6H, Sn-Me); ^{119}Sn NMR (149.1 MHz, [D_5]pyridine, 30 °C): $\delta = 61.6$ (12 mM); ^{11}B NMR (160.3 MHz, $CDCl_3$, 30 °C): $\delta = 3.9$ ($w_{1/2} = 720$ Hz); compare to **2** in [D_5]pyridine: ^1H NMR (400 MHz, [D_5]pyridine, 30 °C): $\delta = 5.10$ (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, 1H, Cp-H5), 4.64 (pst/dpst, $J = 2.4$ Hz, 1H, Cp-H4), 4.52 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, 1H, Cp-H3), 4.43 (s, 5H, Cp), 0.91 (s, 3H, B-Me), 0.8 (very broad, 6H, Sn-Me).

Orange crystals of species **6** were isolated from a hot solution of **1-Cl** (50 mg, 0.12 mmol) in pyridine (5 mL). The crystals of **6** thus obtained contain 2.5 molar equivalents of pyridine according to ^1H NMR spectroscopy (dissolution in $CDCl_3$ yielded one molar equivalent of **2** and 1.5 molar equivalents of free pyridine) and elemental analysis: calcd (%) for **6**·0.5 pyridine: C 48.82, H 4.74, N 5.58; found: C 48.97, H 4.64, N 6.08.

Treatment of 1-Cl with 2 equiv of DMAP—Synthesis of 7: Neat DMAP (85.3 mg, 0.698 mmol) was added to a solution of **1-Cl** (100 mg, 0.233 mmol) in chloroform (3 mL). The reaction mixture was layered with pentanes (3 mL) and left to stand overnight at room temperature. The yellow crystals formed were successively washed with a mixture of pentanes and chloroform (2:1) and dried under high vacuum overnight to yield yellow crystals of **7**·1.5 $CHCl_3$ (130 mg, 65 %). X-ray quality crystals were obtained by recrystallization from chloroform. ^1H NMR (500 MHz, $CDCl_3$, 30 °C): $\delta = 7.79$, 7.69 (2×d, 2×2H, $J = 7.5$ Hz, DMAP-H_o), 6.92, 6.69 (2×d, 2×2H, $J = 7.5$ Hz, DMAP-H_m), 4.51 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, $J(^{117/119}Sn,H) = 14$ Hz, 1H, Cp-H5), 4.47 (pst/dpst, $J = 2.4$ Hz, $J(^{117/119}Sn,H) = 7.2$ Hz, 1H, Cp-H4), 4.08 (s, 5H, Cp), 3.58 (dd/ddd, $J = 1.2$ Hz, 2.4 Hz, $J(^{117/119}Sn,H) = 12$ Hz, 1H, Cp-H3), 3.27, 3.17 (2×s, 2×6H, NMe_2), 0.79 (s, 3H, B-Me), 0.70 (s/d, $J(^{117/119}Sn,H) = 59/61$ Hz, 6H, Sn-Me); ^{13}C NMR (125.7 MHz, $CDCl_3$, 20 °C): $\delta = 155.7$, 155.6 (DMAP-C_o), 144.0, 142.9 (DMAP-C_p), 107.3, 107.0 (DMAP-C_m), 91.0 (br, *ipso*-CpB), 77.6 (s/d, $J(^{117/119}Sn,C) = 73.0$, Cp-C5), 76.9 (s/d, $J(^{117/119}Sn,C) =$ n.d., *ipso*-CpSn), 74.8 (s/d, $J(^{117/119}Sn,C) = 65.0$ Hz, Cp-C4), 71.8 (s/d, $J(^{117/119}Sn,C) = 56.0$ Hz, Cp-C3), 68.5 (Cp), 40.0 (NMe_2), 39.9 (NMe_2), 10.7 (br, B-Me), 2.9 (s/d, $J(^{117/119}Sn,C) = 428/447$ Hz, Sn-Me); ^{11}B NMR (128.3 MHz, $CDCl_3$, 20 °C): $\delta = 3.3$ ($w_{1/2} = 400$ Hz); ^{119}Sn NMR (149.1 MHz, $CDCl_3$, 20 °C): $\delta = 100.9$ (20 mM); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 448 (160), 333 nm (sh, 560 $L\,mol^{-1}\,cm^{-1}$); elemental analysis calcd (%) for **7**·1.5$CHCl_3$: C 40.13, H 4.55, N 6.57; found: C 40.13, H 4.38, N 6.45.

General procedure for NMR binding studies: Stock solutions of **1-Cl**, **1-Ph**, FcB(Cl)Me, FcB(Ph)Me, $FcSnMe_2Cl$, pyridine, and DMAP were prepared by dissolving substrates in a sufficient amount of $CDCl_3$. Exact quantities for each particular experiment are listed below.

Competitive binding of pyridine to 1-Cl and FcB(Cl)Me: A stock solution of pyridine (24 μmol) in $CDCl_3$ was slowly added to a mixture of FcB(Cl)Me (24 μmol) and **1-Cl** (24 μmol) in $CDCl_3$ (1.5 g). The mixture was allowed to equilibrate over a period of 24 h and subsequently studied by ^1H and ^{11}B NMR spectroscopy. Integration of the ^1H NMR signals revealed product ratios of **1-Cl** (12 %), **2** (88 %), FcB(Cl)Me (88 %), and FcB(Cl)Me·Py (12 %) for the resulting mixture. Note that since the mode of addition has some influence on the initially observed ratios, the system was equilibrated for an adequate period of time.

Competitive binding of pyridine to 1-Ph and FcB(Ph)Me: The pyridine complex FcB(Ph)Me·Py (4.2 mg, 11 μmol) and **1-Ph** (5.0 mg, 11 μmol) were dissolved in $CDCl_3$ (0.7 mL). The mixture was allowed to equilibrate over a period of 24 h and subsequently studied by low temperature ^1H NMR spectroscopy. Integration of the ^1H NMR signals at −50 °C revealed product ratios of **1-Ph** (40 %), **4** (60 %), FcB(Ph)Me (60 %), and FcB(Ph)Me·Py (40 %) for the resulting mixture.

Treatment of 7 with 1 equiv Me_2SnCl_2: Me_2SnCl_2 (5.1 mg, 23 μmol) was added to **7** (31 mg, 23 μmol) in $CDCl_3$ (1.57 g). The resulting mixture was studied by multinuclear NMR spectroscopy. For **8**: ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.80$, 7.63 (2×d, 2×2H, $J = 8.0$, 7.5 Hz, DMAP-H_o), 6.88, 6.64 (2×d, 2×2H, $J = 7.5$, 8.0 Hz, DMAP-H_m), 4.52 (pst/dpst, $J = 2.5$ Hz, $J(^{117/119}Sn,H) = 8.0$ Hz, 1H, Cp-H4), 4.50 (dd/ddd, $J = 1.0$ Hz, 2.2 Hz, $J(^{117/119}Sn,H) = 14.0$ Hz, 1H, Cp-H5), 4.07 (s, 5H, Cp), 3.62 (dd/ddd, $J = 1.0$ Hz, 2.0 Hz, $J(^{117/119}Sn,H) = 12.5$ Hz, 1H, Cp-H3), 3.25, 3.17 (2×s, 2×6H, NMe_2), 1.29 (s/d, $J(^{117/119}Sn,H) = 86/89$ Hz, 6H, Sn-Me), 0.78 (s, 3H, B-Me), 0.70 (s/d, $J(^{117/119}Sn,H) = 55/58$ Hz, 6H, FcSn-Me); ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): $\delta = 156.2$, 156.1 (DMAP-C_p), 144.1, 143.3 (DMAP-C_o), 107.7, 107.5 (DMAP-C_m), 91.6 (br, *ipso*-CpB), 77.8 (s/d, $J(^{117/119}Sn,C) = 79$ Hz, Cp-C5), 75.9 (s/d, $J(^{117/119}Sn,C) = 63$ Hz Cp-C3), 74.2 (nr, *ipso*-CpSn), 72.7 (s/d, $J(^{117/119}Sn$,Cp-C4) = 57 Hz, Cp-C4), 68.8 (Cp), 40.3, 40.2 (NMe_2), 18.4 (s/d, $J(^{117/119}Sn,C) = 686/719$ Hz, Sn-Me), 10.9 (br, B-Me), 1.2 (s/d, $J(^{117/119}Sn,C) = 388/405$ Hz, FcSn-Me); ^{11}B NMR (128.3 MHz, $CDCl_3$, 25 °C): $\delta = 3.3$ ($w_{1/2} = 640$ Hz); ^{119}Sn NMR (149.1 MHz, $CDCl_3$, 25 °C): $\delta = 128.8$, −106.8 (21 mM).

Treatment of 7 with 1 equiv $FcSnMe_2Cl$: A solution of DMAP (6.4 mg, 52 μmol) in $CDCl_3$ (0.65 g) was added to a well-stirred mixture of $FcSnMe_2Cl$ (9.7 mg, 26 μmol) in $CDCl_3$ (0.986 g) and **1-Cl** (11.5 mg, 0.026 mmol) in $CDCl_3$ (1.529 g). The resulting mixture was studied by multinuclear NMR spectroscopy. For **9**: ^1H NMR (500 MHz, $CDCl_3$, 30 °C): $\delta = 7.75$, 7.62 (2×d, 2×2H, $J = 7.3$ Hz, DMAP-H_o), 6.87, 6.63 (2×d, 2×2H, $J = 7.3$ Hz, DMAP-H_m), 4.51–4.52 (overlapping, 2H, CpBSn-H4,5), 4.44 (pst/dpst, $J = 1.5$ Hz, $J(^{117/119}Sn,H) = 12$ Hz, 2H, Cp-SnH3,4), 4.35 (pst/dpst, $J = 1.5$ Hz, $J(^{117/119}Sn,H) = 12$ Hz, 2H, CpSn-H2,5), 4.20 (s, 5H, Cp), 4.07 (s, 5H, Cp), 3.59 (dd/ddd, $J = 1.5$, 2.5 Hz, $J(^{117/119}Sn,H) = 12$ Hz, 1H, CpBSn-H3), 3.16, 3.03 (2×s, 2×6H, NMe_2), 0.85 (s/d, $J(^{117/119}Sn,H) = 65/69$ Hz, 6H, FcSn-Me), 0.77 (s, 3H, B-Me), 0.70 (s/d, $J(^{117/119}Sn,H) = 56/59$ Hz, 6H, FcBSn-Me); ^{11}B NMR (128.3 MHz, $CDCl_3$, 25 °C): $\delta = 3.3$ ($w_{1/2} = 670$ Hz); ^{119}Sn NMR (149.1 MHz, $CDCl_3$, 25 °C): $\delta = 120.4$, 27.3 (12 mM).

Treatment of [Fc(BMe(dmap)$_2$)]Cl with $FcSnMe_2Cl$: A solution of DMAP (13.2 mg, 108 μmol) in $CDCl_3$ (1.328 g) was added to FcB(Cl)Me (13.4 mg, 54 μmol) in $CDCl_3$ (1.00 g). Formation of the boronium cation was confirmed by ^1H and ^{11}B NMR spectroscopy (for [Fc(BMe(dmap)$_2$)]Cl: ^1H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 7.80$ (d, $J = 7.0$ Hz, 4H, DMAP-H_o), 6.79 (d, $J = 7.5$ Hz, 4H, DMAP-H_m), 4.27 (pst, $J = 2$ Hz, 2H, Cp-H3,4), 3.91 (s, 5H, Cp), 3.82 (pst, $J = 2$ Hz, 2H, Cp-H2,5), 3.21 (s, 6H, NMe_2), 0.63 (s, 3H, B-Me); ^{11}B NMR (160.3 MHz, $CDCl_3$, 25 °C): $\delta = 3.5$ ($w_{1/2} = 740$ Hz)); $FcSnMe_2Cl$ (20.1 mg, 54 μmol) in $CDCl_3$ (2.09 g) was added to the boronium cation [Fc(BMe(dmap)$_2$)]Cl thus generated. The resulting mixture was studied by multinuclear NMR spectroscopy. ^1H NMR (500 MHz, $CDCl_3$, 30 °C): $\delta = 7.76$ (d, 4H, $J = 7.3$ Hz, DMAP-H_o), 6.73 (d, 4H, $J = 7.3$ Hz, DMAP-H_m), 4.50 (pst/dpst,

2H, $J=1.7$ Hz, $J(^{117/119}Sn,H)=12$ Hz, CpSn-H2,5), 4.32 (pst/dpst, 2H, $J=1.7$ Hz, $J(^{117/119}Sn,H)=9$ Hz, CpSn-H3,4), 4.29 (pst, $J=1.7$ Hz, 2H, CpB-H3,4), 4.20 (s, 5H, Cp), 3.93 (s, 5H, Cp), 3.82 (pst, $J=1.7$ Hz, 2H, CpB-H2,5), 3.19 (s, 12H, NMe_2), 0.86 (s/d, $J(^{117/119}Sn,H)=66/69$ Hz, 6H, Sn-Me), 0.62 (s, 3H, B-Me); ^{11}B NMR (128.3 MHz, $CDCl_3$, 25 °C): $\delta=3.4$ ($w_{1/2}=690$ Hz); ^{119}Sn NMR (149.1 MHz, $CDCl_3$, 25 °C): $\delta=8.6$ (20 mM).

Crystal structure determinations: Data were collected on Bruker P4/CCD (**2**) and Smart Apex CCD (**5b**, **7**) diffractometers at 223 and 100 K, respectively. Crystallographic data and details of X-ray studies are given in Table 4. The structures were solved by direct methods and refined by full-matrix least squares based on F^2 with all reflections (SHELXTL V5.1; G. Sheldrick, Siemens XRD, Madison, WI). Except for a disordered $CDCl_3$ solvent molecule in **7**, non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contribution. SADABS (G. M. Sheldrick, SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption correction was done for all data ([$T_{min}/T_{max}=0.623/1.000$ (**2**), 0.787/1.000 (**5b**), and 0.7343/0.9222 (**7**)]. The main molecule of **7** co-crystallized with 1.5 $CDCl_3$ solvent molecules; one of them is disordered over two positions related by a two-fold axis.

CCDC-216761 (**2**), -250640 (**5b**), and -216760 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 4. Experimental data for the X-ray diffraction studies of **2**, **5b**, and **7**.

	2	**5b**	**7**
empirical formula	$C_{18}H_{22}BCl_2FeNSn$	$C_{26}H_{32}BClFeN_2Sn$	$C_{28.5}H_{39}BCl_{6.5}FeN_4Sn$
M_W	508.62	593.34	853.41
T [K]	223.0(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$
a [Å]	10.3464(7)	7.3178(4)	31.948(5)
b [Å]	13.9832(9)	22.8309(12	12.667(2)
c [Å]	13.9403(10)	15.0124(8)	17.763(3)
β [°]	95.0750(10)	92.4090(10)	102.366(3)
V [Å^3]	2008.9(2)	2505.9(2)	7021(2)
Z	4	4	8
ρ_{calcd} [g cm^{-3}]	1.682	1.573	1.615
$\mu(Mo_{K\alpha})$ [mm^{-1}]	2.231	1.699	1.646
$F(000)$	1008	1200	3436
crystal size [mm]	$0.30\times0.30\times0.10$	$0.20\times0.05\times0.05$	$0.20\times0.10\times0.05$
θ range [°]	2.07–28.35	1.62–27.52	1.31–27.53
limiting indices	$-13\le h\le 13$	$-8\le h\le 9$	$-26\le h\le 41$
	$-17\le k\le 18$	$-29\le k\le 19$	$-15\le k\le 16$
	$-18\le l\le 17$	$-18\le l\le 15$	$-8\le l\le 22$
reflns collected	14590	11114	13316
independent reflns	4868	5494	7436
R(int)	0.0308	0.0227	0.0416
absorption correction		SADABS	
refinement method		full-matrix least-squares on F^2	
data/restraints/parameters	4868/0/217	5494/0/417	7436/0/384
goodness-of-fit on F^2	1.106	1.044	1.037
final R indices [$I>2\sigma(I)$][a]			
$R1$	0.0362	0.0293	0.0552
$wR2$	0.0991	0.0660	0.1324
R indices (all data)[a]			
$R1$	0.0410	0.0347	0.0692
$wR2$	0.1028	0.0683	0.1408
peak$_{max}$/hole$_{min}$ [e Å^{-3}]	1.322 and −0.956	0.707 and −0.347	1.990 and −1.071

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

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