Selective synthesis of 1-stanna-2-boraferrocenes: novel bidentate Lewis acids *via* an unexpected rearrangement reaction

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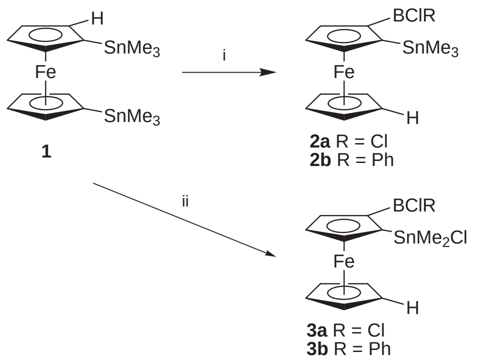
Ferrocene based bidentate Lewis acids of the general formula 1,2-fc(BR_2)(SnR_3) are obtained in one step from 1,1′-distannaferrocenes and chloroboranes *via* an unexpected rearrangement reaction.

Bidentate Lewis acids have attracted increasing attention owing to their potential in selective anion recognition,[1] self-assembly with Lewis bases,[2] as catalysts in acid catalyzed organic transformations[3] and as cocatalysts in Ziegler–Natta olefin polymerization.[4] Systems with two different acidic centers are still very rare although they might give rise to very specific binding properties.[5–7] In particular, the combination of Lewis acidic tin(IV) and boron centers permits fine-tuning of the Lewis acidity by well known selective substituent exchange reactions at either of the metal centers. As part of our general interest in the area of tin- and boron-substituted ferrocene derivatives, here, we report on a selective, one step synthesis of ferrocene based bidentate Lewis acids from readily available 1,1′-disubstituted stannaferrocenes.[8,9]

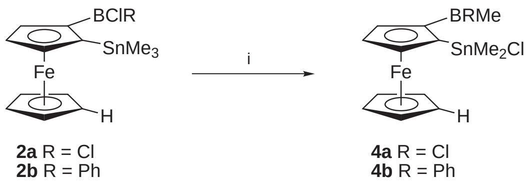
When 1,1′-bis[trimethylstannyl]ferrocene **1**[10] was treated with 1 equiv. of BCl_3 or $PhBCl_2$ in hexanes at −78 °C and the reaction mixture was allowed to slowly warm to 0 °C, the 1-stanna-2-boraferrocenes **2a** and **2b** were obtained as red oils after removal of all volatile material in high vacuum (Scheme 1). During the course of this reaction, one of the stannyl groups is replaced by a boryl substituent, which is accompanied by an unexpected rearrangement reaction. The boryl group in **2a** and **2b** is found exclusively *ortho* to the remaining stannyl substituent whereas the proton has transferred to the other Cp ring leaving an unsubstituted Cp ligand in **2a** and **2b**.† The reactions were conveniently followed by ^1H, ^{11}B and ^{119}Sn NMR spectroscopy.‡ The ^{11}B NMR spectra of **2a** and **2b** display a broad signal (**2a**: δ 51.1, **2b**: δ 57.2) in the expected range for aryldichloroboranes and diarylchloroboranes, respectively. In the ^{119}Sn NMR spectra of **2a** and **2b** a singlet (**2a**: δ −5.1, **2b** δ −9.9) is found at a similar chemical shift as observed for the starting material **1** (δ −6.3) indicating that a trimethylstannyl moiety is still attached to the ferrocene core. The most striking feature in the ^1H NMR spectra is a singlet with the intensity of five protons in the region typical of unsubstituted ferrocene Cp rings (**2a**: δ 3.92, **2b**: δ 3.93). The NMR signals for the methyl protons are particularly useful to monitor the substitution pattern on tin and boron, because of coupling between the ^{117}Sn and ^{119}Sn nuclei and adjacent methyl groups. For **2a** and **2b** one singlet with tin satellites is found [**2a**: δ 0.28, (9H), **2b**: δ 0.18, (9H)].



Scheme 1 *Reagents and conditions*: i, $RBCl_2$, hexanes, −78 °C to room temp.; ii, 2 $RBCl_2$, hexanes, −78 °C to room temp.

In order to investigate whether a second tin-boron exchange can take place, **1** was reacted with 2 equiv. of the haloboranes. If a similar reaction path as described for the formation of **2** is followed, either the formation of a 1,2-diboraferrocene or a rearranged 1,1′-diboraferrocene would be expected (Scheme 1). However, a ligand exchange on the remaining tin center to form **3a** and **3b** (73 and 53% isolated yield after recrystallization from hexanes at −55 °C, respectively) took place and no spectroscopic evidence for the formation of bisborylated ferrocenes was found.‡§ The ^{11}B NMR spectra of **3a** and **3b** show broad singlets (**3a**: δ 49.8, **3b**: δ 56.6) in the same range as observed for **2a** and **2b**. However, the exchange of a methyl for a chloro substituent on tin is evidenced by a pronounced high field shift in the ^{119}Sn NMR spectra (**3a**: δ 102.1, **3b**: δ 85.9). The planar chirality of **3a** and **3b** leads to two different signals in the ^1H NMR spectra for the methyl groups on tin [**3a**: δ 0.69, (3H), δ 0.52, (3H), **3b**: δ 0.82, (3H), δ 0.66 (3H)]. It is significant to note that **3b** was also detected as a byproduct in the 1 : 1 reaction between **1** and $PhBCl_2$ accompanied by a small amount of unreacted **1** accounting for a relatively low yield of **2b** in comparsion to **2a** (estimated yields based on ^1H NMR spectroscopy for **2a**: 95%, **2b**: 50%). By contrast, **3a** is only formed if **1** is reacted with an excess of BCl_3.

To remove any traces of Me_3SnCl or Me_2SnCl_2 from crude **2a** and **2b**, both compounds were kept at 50 °C for 3 h in high vacuum. Surprisingly, this led to another very selective rearrangement reaction giving almost exclusively **4a** and **4b**, which are obtained in good isolated yields by recrystallization from hexanes (Scheme 2). In both compounds a chloro substituent on boron has exchanged with a methyl group on the tin center.



Scheme 2 *Conditions*: i, 50 °C in high vacuum, 3 h.

The ^{11}B NMR spectra of **4a** and **4b** display a broad singlet (**4a**: δ 61.5, **4b** δ 67.5) which is shifted by about 10 ppm to lower field in comparison to **2a**,**b** and **3a**,**b**. On the other hand, the ^{119}Sn NMR spectrum of **4a** and **4b** (**4a** δ 89.8, **4b** δ 95.3) shows a singlet at a similar chemical shift as for **3a** and **3b**. Three singlets are observed for the methyl groups in the ^1H NMR spectra of **4a** and **4b**, but only two of them display tin satellites.§ The NMR spectroscopic data therefore clearly confirm a rearranged structure in comparison to **1** and the proposed substituent exchange reactions between **2**, **3** and **4**.

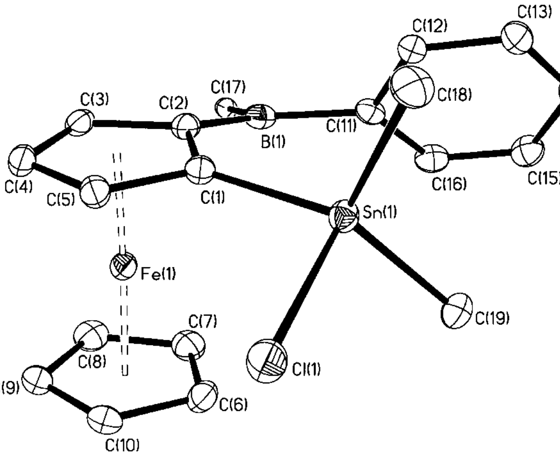


Fig. 1 Molecular structure (ORTEP drawing) of **4b**. Selected bond lengths (Å): Sn(1)–C(1) 2.121(4), Sn(1)–C(18) 2.130(4), Sn(1)–C(19) 2.121(4), Sn(1)–Cl(1) 2.404(1), B(1)–C(2) 1.536(6), B(1)–C(11) 1.571(5), B(1)–C(17) 1.623(5).

In order to further confirm the assigned rearranged structures and to distinguish unambiguously between a 1,2-substituted and a 1,3-substituted ferrocene moiety, a single crystal X-ray diffraction study of compound **4b** was undertaken.¶ Dark red crystals of **4b** were obtained from hexanes at −30 °C. A racemic mixture of both of the two possible enantiomers due to the planar chirality in **4b** is found in the single crystal used for X-ray crystallography. The structure (Fig. 1) confirmed that the proposed rearrangement reactions (see Schemes 1 and 2) had taken place. No interaction between the tin bound chlorine atom and the Lewis acidic boron center is evident. However, the boron atom is bent towards the iron atom as observed previously in the crystal structure of dibromoborylferrocene [**4b**: α^* = 12.2(3)°, $FcBBr_2$: α^* = 17.7, 18.9°; α^* = 180° − centroid (C1–C5)–C(2)–B angle] suggesting some iron–boron interaction.[11] A smaller degree of iron–boron interaction in **4b** in comparison to $FcBBr_2$ is reflected in a significantly longer B–C(Cp) bond length [**4b**: 1.536(6) Å, $FcBBr_2$: 1.474(9), 1.482(8) Å] and a longer Fe–B distance [**4b**: 3.087(5) Å, $FcBBr_2$: 2.840 Å]. The tin atom is only slightly bent away from the Cp plane [**4b**: α^* = 2.7(2)°, α^* = 180° − centroid(C1–C5)–C(1)–Sn angle].

In summary, reaction of **1** with haloboranes provides a mild, simple one step synthesis of novel bidentate ferrocene based Lewis acids. In contrast, the direct borylation of ferrocene with BCl_3 requires extended reaction times at elevated temperature.[12] The reaction sequence involves an interesting substituent rearrangement from one Cp ring to the other. Currently, we are investigating mechanistic details of the observed rearrangement reactions, the use of 1-stanna-2-boraferrocenes as bidentate Lewis acids in selective anion recognition including the effect of their planar chirality[13] and their potential as precursors for other 1,2-substituted ferrocenes.

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Notes and references

† The similarity of the Cp proton NMR resonances of **2a**,**b**, **3a**,**b** and **4a**,**b** suggests a 1,2-substitution pattern analogous to that found by X-ray diffraction for **4b**.

‡ *Selected spectroscopic data*: For **2a**: ^1H NMR (400 MHz, C_6D_6, 20 °C): δ 4.71 [dd, J (HH) = 1.2, 2.4 Hz, 1H, Cp-H3], 4.53 [ps.t, J (HH) 2.4 Hz, 1 H, Cp-H4), 4.46 [dd, J (HH) 1.2, 2.4 Hz, 1 H, Cp-H5], 3.92 (s, 5H, Cp), 0.28 [s/d, J (^{117}SnH) 52, J (^{119}SnH) 55 Hz, 9 H, SnMe]; ^{13}C NMR (100.5 MHz, C_6D_6, 20 °C): δ 85.2 (Cp-C3), 80.8, 79.4 (Cp-C4,5), 70.7 (Cp), −1.7 (SnMe), not observed (*ipso*-Cp); ^{11}B NMR (160.4 MHz, C_6D_6, 20 °C): δ 51.1 ($h_{1/2}$ 320 Hz); ^{119}Sn NMR (111.8 MHz, C_6D_6, 20 °C): δ −5.1. **3a**: ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 5.24 [dd, J (HH) 1.2, 2.4 Hz, 1 H, Cp-H3], 4.51–4.55 (m, 2H, Cp-H4,5), 3.87 (s, 5 H, Cp), 0.69 [s/d, J (^{117}SnH) 61, J (^{119}SnH) 64 Hz, 3H, SnMe), 0.52 [s/d, J (^{117}SnH) 60, J (^{119}SnH) 62 Hz, 3H, SnMe]; ^{13}C NMR (75.5 MHz, C_6D_6, 20 °C): δ 86.2 (Cp-C3), 81.1, 80.7 (Cp-C4,5), 71.7 (Cp), 2.5, 1.1 (SnMe), not observed (*ipso*-Cp); ^{11}B NMR (160.4 MHz, C_6D_6, 20 °C): δ 49.8 ($h_{1/2}$ 350 Hz); ^{119}Sn NMR (111.8 MHz, C_6D_6, 20 °C): δ 102.1; MS (70 eV, EI): *m/z* (%): 450 (100) [M^+], 435 (28) [$M^+ - CH_3$], 420 (73) [$M^+ - 2\ CH_3$]. **4a**: ^1H NMR (400 MHz, C_6D_6, 20 °C): δ 5.33 [dd, J (HH) 1.2, 2.4 Hz, 1 H, Cp-H3], 4.54 [ps.t, J (HH) 2.4 Hz, 1H, Cp-H4,] 4.22 [dd, J (HH) 1.2, 2.4 Hz, 1H, Cp-H5], 3.85 (s, 5H, Cp), 0.86 (s, 3H, BMe), 0.82 [s/d, J (^{117}Sn, H) 63, J (^{119}SnH) 65 Hz, 3H, SnMe], 0.65 [s/d, J (^{117}SnH) 60, J (^{119}SnH) 62 Hz, 3H, SnMe]; ^{13}C NMR (75.5 MHz, C_6D_6, 20 °C): δ 84.8 (Cp-C3), 80.0 (Cp-C4,5), 70.3 (Cp), 2.7, 1.3 (SnMe), not observed (*ipso*-Cp, BMe); ^{11}B NMR (160.4 MHz, C_6D_6, 20 °C): δ 61.5 ($h_{1/2}$ 400 Hz); ^{119}Sn NMR (111.8 MHz, C_6D_6, 20 °C): δ 89.8; MS (70 eV, EI): *m/z* (%): 430 (100) [M^+], 415 (27) [$M^+ - CH_3$], 400 (78) [$M^+ - 2\ CH_3$].

§ Satisfactory elemental analyses for compounds **3a**,**b** and **4a**,**b** have been obtained.

¶ *Crystallographic data*: $C_{19}H_{22}BClFeSn$, M = 471.2, monoclinic, space group $P2_1/n$, a = 11.051(1), b = 14.166(1), c = 11.791(1) Å, β = 95.83(1)°, U = 1836.3(6) Å^3, Z = 4, D_c = 1.704 g cm^{-3}, μ = 2.291 mm^{-1}, 3145 observed reflections [$I > 2\sigma(I)$], R = 0.0307; R_w = 0.0786, GOF = 1.068. Data were collected on a Nonius Kappa CCD diffractometer at 150.0(1) K. The structure was solved by direct methods (SHELXS97) and refined by full-matrix least squares (SHELXL97) based on F^2 with all reflections. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions. CCDC 182/1154. See http://www.rsc.org/suppdata/cc/1999/453/ for crystallographic files in .cif format.

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