

## Lewis Acids

# Boron-Centered Lewis Superacid through Redox-Active Ligands: Application in C–F and S–F Bond Activation

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Dedicated to Herbert C. Brown on the occasion of his 111th birthday.

**Abstract:** A series of redox-responsive ferrocenyl-substituted boranes and boronic esters were synthesized. Oxidation of the ferrocenyl ligand to the ferrocenium resulted in a drastic increase in the Lewis acidity beyond the strength of SbF<sub>5</sub>, which was investigated experimentally and computationally. The resulting highly Lewis acidic boron compounds were used for catalytic C–F and S–F bond activation.

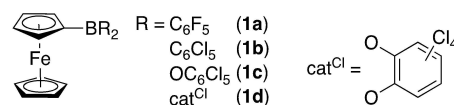
The ability of main group element compounds to activate molecular dihydrogen has sparked new interest in Lewis acid/Lewis base (LA/LB) catalysis.<sup>[1]</sup> Stephan demonstrated the heterolytic splitting of H<sub>2</sub> by these so-called frustrated Lewis pairs (FLP) and their first applications in hydrogenation.<sup>[2]</sup> Although B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>[3]</sup> is the most often applied Lewis acid,<sup>[1,4]</sup> it may not always be the optimal, since the reactivity of an FLP is strongly dependent on the Lewis acidity and Lewis basicity of its individual components.<sup>[2b,5,6]</sup> Whereas boron-derived LAs weaker than B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> allow for hydrogenations of functionalized molecules,<sup>[5,7]</sup> stronger LAs, mainly phosphorus-based, have enabled e.g. highly challenging bond activations.<sup>[8]</sup> And although cationic phosphonium or borenium ions often exceed the Lewis acidity of SbF<sub>5</sub> and are thus Lewis superacids (LSA), there are very few borane examples.<sup>[9]</sup> The reason has been the inherent high reactivity of boranes, which makes their synthesis and purification challenging.<sup>[9b,i]</sup> In this light, the generation of LSA by an electrochemical

process is the most practical way to circumvent this challenge. Redox-active groups can be useful in altering chemical entities.<sup>[10]</sup> Also boranes carrying peripheral cationic groups<sup>[11]</sup> or cationic boranes<sup>[12]</sup> show significantly increased Lewis acidity. It was envisaged that the synthesis and handling of potential LSAs might be tremendously simplified by applying redox processes at a late stage or e.g. just prior to catalytic application.<sup>[13]</sup> The ferrocenyl group (Fc)<sup>[14]</sup> is a widely recognized reversible redox-active group and had the potential to build the Lewis acid we sought. Several ferrocenyl boranes<sup>[15]</sup> have already been synthesized, among them Fc–B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**1a**)<sup>[16]</sup> and Fc–B(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub> (**1b**).<sup>[17]</sup> Although the (quasi) reversible redox behavior of **1a** has been reported,<sup>[16]</sup> studies regarding the level of Lewis acidity or potential catalytic applications have not yet been reported. However, Jäkle has reported Lewis acidity enhancement of organoboranes via oxidation of appended ferrocene moieties.<sup>[18]</sup> We here disclose the Lewis superacidity of ferrocenyl/ferrocenium boranes and boronic esters as well as their application in catalyzing challenging C–F and S–F bond activations for novel C–C and S–C bond formation reactions.

We started our investigation with synthesis of the four boron derivatives **1a–d** (Figure 1).

Cyclic voltammetry revealed quasi-reversible redox behavior for all compounds under study, with half-wave potentials of  $E_{1/2}^0 = +450$  mV (**1a**),<sup>[16,17]</sup>  $+550$  mV (**1b**),<sup>[17]</sup>  $+250$  mV (**1c**) and  $+270$  mV (**1d**) vs. the Fc/Fc<sup>+</sup> couple. Thus the C<sub>6</sub>Cl<sub>5</sub> group shows the strongest electron-withdrawing effect, which is in line with previous observations.<sup>[19]</sup> The corresponding Fc<sup>+</sup>-based cationic species **2a–d** were obtained by oxidation of **1a–d** with silver salts of weakly coordinating anions (wca), e.g. Ag[Al(OC<sub>4</sub>F<sub>9</sub>)<sub>4</sub>] or Ag[SbF<sub>6</sub>] (Scheme 1).

The novel compounds **1c**, **1d** and **2a–d** were characterized by X-ray diffraction (Figure 2 and Supporting Information, see selected results in Table 1).



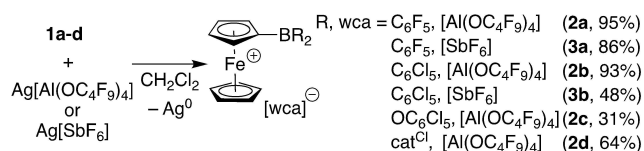
**Figure 1.** Boron-centered Lewis acids with a redox-active ferrocenyl moiety. For synthetic details see Supporting Information.

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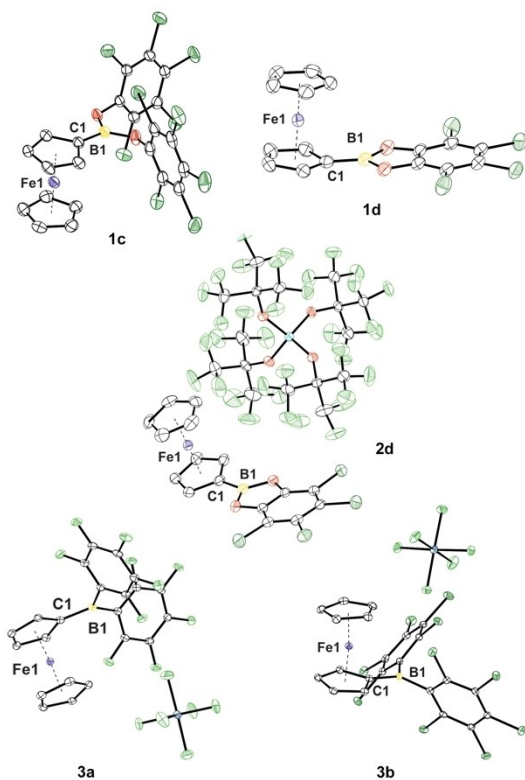
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**Scheme 1.** Synthesis of ferrocenium-derived boron-centered Lewis acids.



**Figure 2.** Molecular structures of the neutral (**1c** and **1d**) and cationic (**2a**, **3a** and **3b**) complexes. Thermal ellipsoids are given at the 30% probability level. Hydrogen atoms omitted for clarity.

**Table 1:** Selected distances, bond lengths and angles of **1a-d**, **2a-d** and **3a,b**.

	$d(\text{Fe}\cdots\text{B})$ [pm]	$d(\text{B}-\text{Cp})$ [pm]	$\alpha^*$ [°] <sup>[a]</sup>	$d(\text{Fe}-\text{Cp})$ [pm]	$d(\text{Fe}-\text{CpB})$ [pm]
<b>1a</b> <sup>[16]</sup>	292.4	150.1(4)	16	n.a.	n.a.
<b>2a</b> <sup>[b]</sup>	315.8	154.7	6.2	171.2	171.5
<b>3a</b>	317.6	1.538(3)	3.4	170.9	171.5
<b>1b</b> <sup>[17]</sup>	3.185(3)	1.514(4)	2.6	165.4	164.7
<b>2b</b> <sup>[b]</sup>	333.9	155.2	6.2	171.5	171.8
<b>3b</b>	329.7	1.545(3)	3.8	170.7	171.3
<b>1c</b>	316.69(62)	152.22(67)	3.1	165.2	165.5
<b>2c</b>	325.48(73)	154.17(1)	3.5	171.1	170.8
<b>1d</b>	304.82(42)	149.58(7)	7.9	164.2	163.5
<b>2d</b>	322.44(4)	154.02(58)	0.3	170.7	170.9

[a]  $\alpha^* = 180^\circ - \alpha$ , with  $\alpha$  = angle between the centroid of the Cp ring, ipso C atom and B atom. [b] Average of the structural parameters of several molecules in the asymmetric unit.

The boryl substituent in Fc boranes tends to be bent out of the cyclopentadienyl (Cp) ring plane towards the iron center.<sup>[20]</sup> However, a clear trend for the dip angle  $\alpha^*$  was not found, as the bending depends on not merely the Fe...B interaction but a number of factors such as through-space interactions with the second Cp ring. The only trend that holds for all the investigated boranes is an increase of the bond length of 2.1 pm to 4.6 pm between the B atom and the Cp moiety upon oxidation (Table 1). This can be attributed to a weakened  $\pi$  interaction, as the oxidized Fe<sup>III</sup> atom draws more electron density from the Cp ring.<sup>[20]</sup> By comparing the oxidized boranes of different counterions [SbF<sub>6</sub>]<sup>-</sup> and [Al{OC(CF<sub>3</sub>)<sub>3</sub>]<sub>4</sub>]<sup>-</sup>, it could be seen that crystal packing has a clear impact on  $\alpha^*$ , e.g. **2a** and **3a**. In order to gauge the Lewis acidities of the title compounds,<sup>[21]</sup> we calculated the fluoride ion affinities (FIA and FIA<sub>solv</sub>), hydride ion affinities (HIA and HIA<sub>solv</sub>) and binding energy to the neutral Lewis base NH<sub>3</sub> of the title compounds and compared them against benchmark systems such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and SbF<sub>5</sub> (Table 2).

Antimony pentafluoride has been established as the threshold LSA, with a calculated FIA of 492 kJ mol<sup>-1</sup> (493 kJ mol<sup>-1</sup> at the BP86/SVP level using Krossing's method).<sup>[23]</sup> The Lewis acidities of the neutral Fc boranes **1a-d** are lower than that of SbF<sub>5</sub> and of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (444 kJ mol<sup>-1</sup>), most likely due to the electron-rich Fc moiety.<sup>[20]</sup> This is consistent with the calculated HIAs in the gas phase. However, upon oxidation, the calculated Lewis acidities of **2a** and **2b** largely exceed that of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> by a factor of 1.7 to 1.6. The estimated FIA for **2a** and **2b** is by 240 kJ mol<sup>-1</sup> and 209 kJ mol<sup>-1</sup> higher than that of SbF<sub>5</sub>, respectively. Therefore, these boranes can be classified as LSAs. The calculated Lewis acidities in solution (HIA<sub>solv</sub> and FIA<sub>solv</sub>) differ significantly from the gas phase calculations due to stronger stabilization of ionic species by the solvent model.<sup>[9]</sup> Nonetheless, the oxidized Fc<sup>+</sup> derivatives **2a**, **2b** and **2d** are stronger LAs than B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, based on the

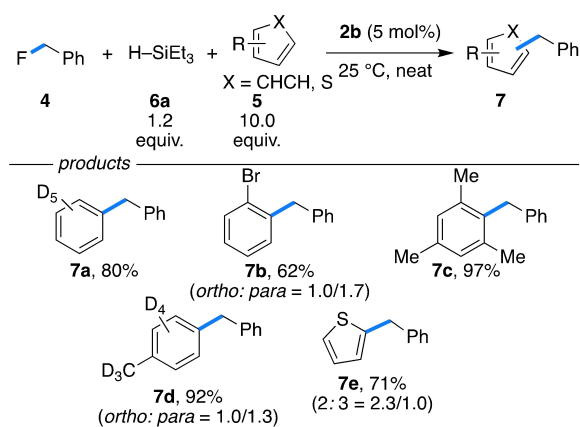
**Table 2:** Determination of Lewis acidity (TPSSH/def2-QZVPP/D3BJ).<sup>[a,b]</sup>

Compound	HIA [kJ mol <sup>-1</sup> ]	HIA <sub>solv</sub> <sup>[c]</sup> [kJ mol <sup>-1</sup> ]	FIA [kJ mol <sup>-1</sup> ]	FIA <sub>solv</sub> <sup>[c]</sup> [kJ mol <sup>-1</sup> ]	NH <sub>3</sub> affinity <sup>[d]</sup> [kJ mol <sup>-1</sup> ]
SbF <sub>5</sub>	–	–	492	315	–
B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	507	297	444	216	113
<b>1a</b> <sup>[16]</sup>	446	245	394	172	89
<b>1b</b> <sup>[17]</sup>	444	240	382	157	71
<b>1c</b>	376	169	370	144	44
<b>1d</b>	368	181	372	164	32
<b>2a</b>	786	331	732	255	121
<b>2b</b>	767	326	701	238	109
<b>2c</b>	680	237	674	208	65
<b>2d</b>	703	236 <sup>[c,d]</sup>	691	226	49

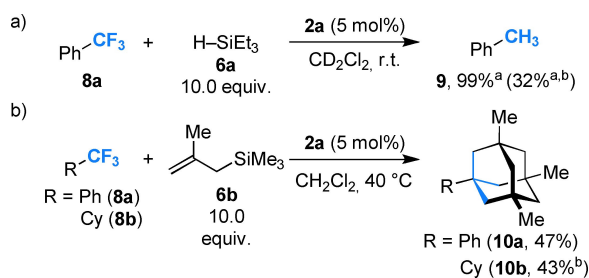
[a] The Global Electrophilicity Index (GEI) recently reported by Stephan and co-workers<sup>[22]</sup> turned out to be unreliable for the cationic open-shell title compounds (details in Supporting Information); [b] Only the cationic compounds of **2a-d** were calculated; [c] Solvation enthalpies were calculated for CH<sub>2</sub>Cl<sub>2</sub> using the conductor-like polarizable continuum model (CPCM) in combination with the solvent model based on density (SMD) method as implemented in the ORCA 4.2.1 package; [d] TPSS/TZVP/D3BJ.

$FIA_{solv}$ . Calculating affinities for a neutral Lewis base,<sup>[22]</sup> **2a** also has a larger affinity, with a  $\Delta G$  for the dissociation of  $NH_3$  of  $121 \text{ kJ mol}^{-1}$ , compared to  $113 \text{ kJ mol}^{-1}$  for  $B(C_6F_5)_3$  ( $109 \text{ kJ mol}^{-1}$  for **2b**). However, the  $FIA_{solv}$  for  $SbF_5$  was calculated to be  $60 \text{ kJ mol}^{-1}$  and  $77 \text{ kJ mol}^{-1}$  higher than for **2a** and **2b**, respectively. Taking the computational error in the comparison of neutral and positively charged entities into account, the Lewis acidities appear to be of the same magnitude. To demonstrate that **2a** and **2b** are stronger LAs than  $SbF_5$  in solution, we synthesized the corresponding  $[SbF_6]^-$  salts by reacting **1a** or **1b** with  $Ag[SbF_6]$  (Scheme 1). The corresponding  $[SbF_6]^-$  salts **3a** and **3b** proved to be unstable and decomposed under inert atmosphere at room temperature (r.t.), potentially as a result of the Lewis superacidity. As control experiment, **2a** or **2b** were reacted with 1.0 equiv  $[Ph_4P][SbF_6]$  in  $CD_2Cl_2$  at r.t.  $^{11}B$  NMR experiments revealed the formation of paramagnetic compounds featuring a tetragonal boron, as indicated by the peak at  $\delta = -11.0 \text{ ppm}$  (**3a**) or  $-9.6 \text{ ppm}$  (**3b**) attributed to a B–F resonance. This finding strongly supports the significantly higher Lewis acidity of the  $Fc^+$  boranes compared to  $SbF_5$  in solution. Finally, we evaluated the LSAs for C–F and S–F bond activation.<sup>[8]</sup> All neutral ferrocene-derived LAs were inactive when benzyl fluoride (**4**) was reacted with the aromatic compounds **5** (neat) at r.t. (Scheme 2).

However, reactivity was observed for all four  $Fc^+$  derivatives **2a–d**, but **2a** and **2b** performed slightly better (70% vs. 60% yield; see Supporting Information for de-



**Scheme 2.** Catalytic C–F bond arylation.



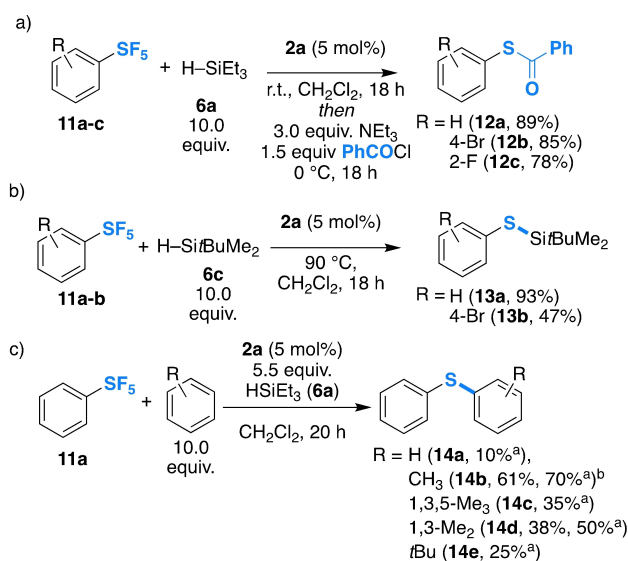
**Scheme 3.** C–F bond a) reduction and b) alkylation; <sup>a</sup> determined by  $^1H$  NMR with hexamethylbenzene as internal standard, <sup>b</sup> with 5 mol% **2b**.

tails). In the presence of 5 mol% **2b**, the aromatic compounds were converted into the benzylated products **7a–e** in 62–97% yield. Low regioselectivities were observed for the substituted benzo **7b** and thiophene **7e** derivative.

The  $CF_3$  group in **8a** became reactive in the presence of the more Lewis acidic borane **2a** and triethyl silane (**6a**). Toluene (**9**) was produced within less than 5 min. in quantitative yield at r.t. (Scheme 3a).

The chloro derivative **2b** was less efficient and reduced **8a** in 32% yield within 22 h. All three C–F bonds of **8a** were able to be exploited for C–C bond formation by reacting with allyl silane **6b** under catalytic conditions (Scheme 3b). Surprisingly, the tris allylated product was not produced but the corresponding adamantyl derivative **10a** was obtained in 47% yield. Similarly, trifluoromethyl cyclohexane (**9b**) was converted into **10b** in 43% yield. These products most likely arise from the triple allylation of the  $CF_3$  group and subsequent Lewis acid-catalyzed trimerization through carbocationic species.<sup>[24]</sup> We also challenged the activation of the exceptionally stable pentafluorosulfanyl group ( $SF_5$ ).<sup>[25]</sup> So far, only drastic reductive Birch conditions had enabled the conversion of an  $SF_5$  group to a thiol.<sup>[26]</sup> Again, among the tested LAs, the strongest proved to be most active. Under mild conditions with 5 mol% **2a**, the pentafluorosulfanyl benzene derivatives **11a–c** were converted into the thiols (Scheme 4a).

The products were isolated as the benzoyl-protected thiols **12a–c** in 78–89% yield. A control experiment using 5 mol% of the silylium salt  $[Et_3Si][B(C_6F_5)_4]$  displayed comparable performance in the conversion of **11a** to **12a** so that **2a** probably acts as initiator (see Supporting Information).<sup>[27]</sup> The silane-protected thiols **13a** and **13b** were directly accessible in 93% and 47% yield, respectively, using the more sterically hindered *tert*-butyldimethyl silane (TBDMS silane (**6c**, Scheme 4b). Furthermore, the corresponding diaryl thioethers **14a–e** were formed when the



**Scheme 4.** S–F bond functionalization; <sup>a</sup> determined by GC; <sup>b</sup> performed in toluene.

reaction was performed in the presence of the aromatic compound, 5.5 equiv triethyl silane and 5 mol % **2a** (Scheme 4c). Although yields were low to medium, these examples represent the first catalytic conversion of SF<sub>5</sub> groups into new C–S bonds. The mechanism of the SF<sub>5</sub> group activation has not yet been investigated, but the formation of these products suggests an in situ generation of cationic organosulfur species.

In summary, we have shown that Lewis superacids are readily available from redox-active ferrocenyl boranes. The Fc-based one-electron oxidation process increases the Lewis acidity by a factor of 1.4–1.5 (FIA<sub>solv</sub>) and results in a Lewis superacid. The diaryl ferrocenium boranes **2a–b** are active in C–F and S–F bond activations, offering a broad spectrum of transformations, from reductions to alkylations and arylations. For the first time, organo-SF<sub>5</sub> groups were catalytically converted into thiols and silyl and diaryl thioethers. The mechanism of the SF<sub>5</sub> group activation is currently under investigation.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

**Keywords:** C–F Bond Activation · Ferrocene · Fluorine · Lewis Superacids · S–F Bond Activation

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