Synthesis of Ferrocenyl Boranes and their Application as Lewis Acids in Epoxide Rearrangements

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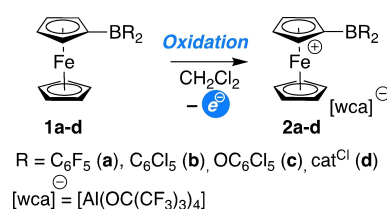*Dedicated to Joachim Podlech on the occasion of his 60th birthday.*

A series of substituted ferrocenyl boron derivatives was synthesized. The oxidation of the ferrocenyl unit resulted in a significant increase of the boron-centered Lewis acidity. The neutral and cationic Lewis acids were characterized by NMR spectroscopy, crystal structure analysis and by computational methods. The new Lewis acids were then applied in the Meinwald rearrangement of epoxides, predominantly furnishing aldehydes as the kinetic products.

Introduction

The ferrocene/ferrocenium couple (Fc/Fc$^+$) has gained widespread recognition as a stimuli-responsive, redox-switchable system.[1] Its remarkable stability and reversible redox properties make it an appealing candidate for incorporation into catalysts with variable reactivity, contingent upon the oxidation state.[2] Recent findings have demonstrated the conversion of relatively weak boron-centered Lewis acids, derived from ferrocenyl boron compounds,[3] into potent Lewis superacids through oxidation to their corresponding ferrocenium derivatives, as illustrated in Scheme 1.[4]

This substantial enhancement of Lewis acidity has facilitated the activation of challenging bonds, such as C—F or S—F bonds. Notably, the versatility of the ferrocene unit extends to the utilization of its cyclopentadienyl rings (Cp) to finely tune electronic properties, thus enabling precise adjustments to molecular characteristics and catalytic performance.[2c] Remarkably, the incorporation of such modifications into the Fc-borane system has yet to be reported, leaving a promising avenue for further refinement of Lewis acid catalysts tailored to specific applications. With this objective in view, we selected the pentamethyl cyclopentadienyl (Cp*) and the *t*Bu-substituted Cp

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Scheme 1. Boron-centered Lewis superacids featuring a redox-active ferrocene unit.

derivatives for the direct comparison with the parent derivatives **1a** and **1d** (Figure 1).

Results and Discussion

Synthesis and Characterization

The ferrocene derivatives **1e**–**g** were synthesized according to methods reported earlier.[3c,9,4] The two boranes **1e** and **1f** were obtained by reaction of the substituted ferrocene derivatives **3a** and **3b** with Piers' borane (HB(C$_6$F$_5$)$_2$, **4**)[5] in 89% and 39% yield as blue and red solids, respectively (Scheme 2a).

The boronic acid ester derivative **1g** was accessed in 79% yield following literature precedence[4] as yellow solid by the reaction of the *in situ* generated dilithio tetrachlorocatecholate (**5**) with the ferrocenyl dibromoborane **3c**. All three ferrocene derivatives were susceptible to oxidation by Ag[Al(OC$_4$F$_9$)$_4$] (**6**) and gave clean conversion into the corresponding ferrocenium derivatives (Scheme 3).
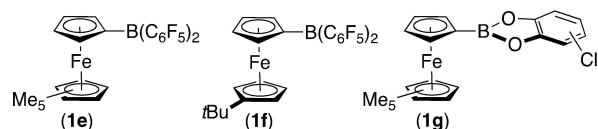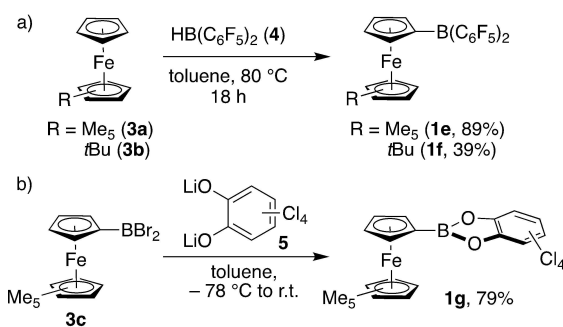

Figure 1. Substituted ferrocenyl boron derivatives.

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Scheme 2. Synthesis of the substituted a) ferrocenyl boranes **1e–f** and b) of the boronic acid ester **1g**.
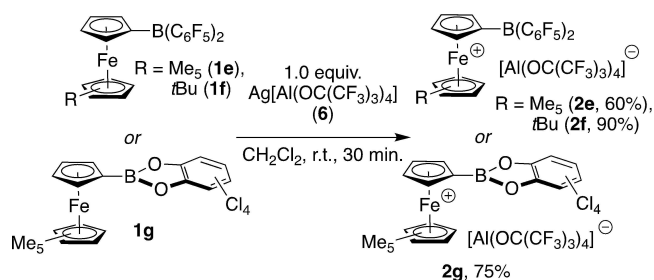
Scheme 3. Synthesis of the ferrocenium derivatives **2e–g**.

The ferrocenium derivatives **2e–g** were obtained in 60–90% yields as dark brown (**2e**), dark grey (**2f**) or dark green (**2g**) solids after layering the reaction mixture with n-hexane and storage at −20 °C.

Cyclovoltammetric investigations revealed fully reversible redox processes for all three investigated ferrocenyl boranes. As expected, the additional aliphatic substituents on the cyclopentadienyl (Cp) moiety significantly influence the observed Fc-based redox chemistry, counterpoising the influence of the electron-withdrawing halogenated boron scaffolds (Table 1). While for **1a** a quasi-reversible redox potential of $E^0_{1/2} = +450$ mV (in trifluorotoluene vs. Fc/Fc$^+$) was reported,[3g] the substitution of one Cp moiety by the permethylated Cp* lead to a cathodically shifted potential of $E^0_{1/2} = +137$ mV (in CH$_2$Cl$_2$ vs. Fc/Fc$^+$) for **1e**. The influence of the tert-butyl substituent in **1f** is even more pronounced ($E^0_{1/2} = +26$ mV). Compared to **1d**

($E^0_{1/2} = +270$ mV),[4] **1g** possesses a half-wave potential of $E^0_{1/2} = +97$ mV. We note in passing that **1e** shows a second, fully reversible redox process centered at $E^0_{1/2} = -269$ mV, which is attributed to pentamethyl ferrocene[6] as decomposition product formed by minor traces of humidity during the CV measurements. This exposes the much more pronounced sensitivity of **1e** compared to the other derivatives.

Overall, the influence of a specific additional substituent on the absolute redox potential does not only depend on its electronic nature, but also on the nature of the boron scaffold as the Cp by Cp* substitution causes a shift of $\Delta E = 313$ mV for **1d** to **1e** and only $\Delta E = 173$ mV for **1d** to **1g**. These findings clearly witness the potential fine-tuning of the redox chemistry in stimuli-responsive boranes, which was expected to influence the subsequent Lewis-acid chemistry. Besides electronic effects also sterics have to be taken into account as relevant characteristics of the introduced substituents as the Fe···B distance may be affected, which was already reported to be accompanied by an altered Lewis acidity on the boron atom.[7]

When the molecular structures[8] of the parent neutral Fc–B(C$_6$F$_5$)$_2$ (**1a**) and the Cp* derivative **1e** are compared (Table 2 and Figure 2), it can be observed that the tilt angle is significantly decreased by 9° (compare Table 2, **1a** and **1e**), which may be predominantly ascribed to the steric interactions of the bulky Cp* substituent with the diaryl boron unit. Although the magnitude of the tilt angle cannot be exclusively attributed to the Fe···B interactions, it has a substantial impact on the Fe–B distance (compare Table 2, **1a**, **1e** and **2a**). The reduced Fe···B interaction in **1e** results consequently in a significant increase in Lewis acidity as supported by the Gutmann-Beckett studies (vide infra) and possesses a comparable Lewis acidity to the archetypal boron-centered Lewis acid B(C$_6$F$_5$)$_3$. Indeed, the reaction of **1e** with 1.0 equiv. O=PEt$_3$ provided the Lewis adduct **1e·O=PEt$_3$** and clearly shows that the boron atom is still accessible for donors, offering potential catalytic activity (Figure 2). Suitable crystals of the corresponding ferrocenium ion **2e** could only be obtained as THF adduct (**2e·THF**). The Fe···B distance is by 18 pm larger in comparison to **1e·OPEt$_3$**.

Table 1. Half-wave potentials and peak potential differences and corresponding i_{pa}/i_{pc} values of **1e–g** in CH$_2$Cl$_2$ compared to reported values for **1a** and **1d**. Potentials given in mV vs. the Fc/Fc$^+$ redox couple (internal standard Fc*/Fc*$^+$ or Fc/Fc$^+$, Fc*=decamethyl ferrocene; conditions: Pt/[NBu$_4$][Al(OC$_4$F$_9$)$_4$]/Ag, $v = 100$ mV/s).

	$E^0_{1/2}$ [mV]	ΔE_p [mV]	i_{pa}/i_{pc}
1a[a][7g]	+450	–	~1
1d[8]	+270	200	~1
1e	+137	120	~0.8
1f	+26	52	~1
1g	+97	195	~0.9

[a] solvent trifluorotoluene.

Table 2. Summarized crystallographic data.

	d(Fe···B) [pm]	d(B–Cp) [pm]	α^{*}[a] [°]
1a[3g]	292.4	150.1(4)	16
1d[4]	304.8	149.6(7)	8
1e	312.4	151.0(14)	7
1g	308.1	151.3(6)	7
2a[3g]	315.8	154.7[b]	6
2d[4]	322.4	154.0(58)	0
2f	322.2	153.5(3)	−3.1
2g	318.2	154.0(7)	2

[a] $\alpha^* = 180° - \alpha$, with α = angle between the centroid of the Cp ring, ipso C atom and B atom; [b] standard deviation not reported in reference.
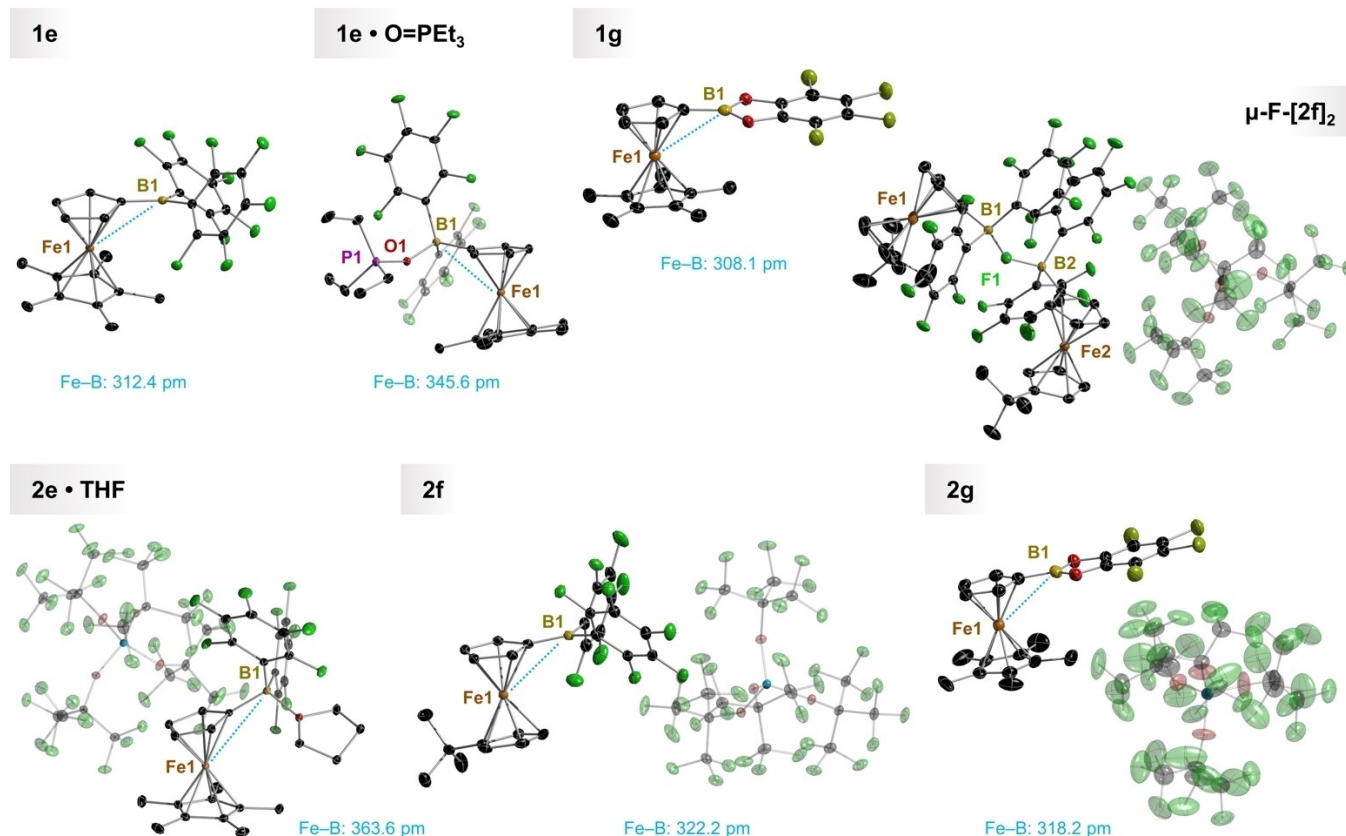
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Figure 2. Molecular structures in the solid state of **1e**, **1e·O=PEt₃**, **1g**, **2f**, **2g**, and μ-F-[**2f**]₂ determined by SC-XRD. Thermal ellipsoids are given at the 30% probability level. Hydrogen atoms and non-coordinated solvent molecules are omitted for clarity. The anion [Al(OC₄F₉)₄]⁻ is depicted with 70% transparency for clarity. The Fe···B distances are displayed in bright blue. For detailed information about bond lengths and angles, see Table 2 or the Supporting Information.[8]

However, the molecular structure of the uncoordinated *t*Bu derivative **2f** could be determined (Figure 2). The Fe···B distance in **2f** is by 6.4 pm longer than in the unsubstituted cation **2a**. Together with the distortion of the Fc unit from parallel arrangement and the out-of-plain bend by 3° of the Cp–B(C₆F₅)₂ angle, this hints towards strong steric interactions of the *t*Bu–Cp and the Cp–B(C₆F₅)₂ units. Upon prolonged storage of **2f** in solution, one of the anions is decomposed by fluoride abstraction yielding the fluoride-bridged, cationic dinuclear complex μ-F-[**2f**]₂. The molecular structure clearly shows that despite the high steric loading Lewis bases can still be accommodated at the boron center.

The Lewis acidity of the neutral as well as of the cationic ferrocene-derived boranes was investigated by the Gutmann-Beckett method[9] (see SI) and by computations. The results are summarized in Table 3.

Most unexpectedly, the neutral B(C₅F₅)₂-substituted boranes **1e** and **1f** exhibit comparable Lewis acidity compared to B(C₆F₅)₃ according to the Gutmann-Beckett method with similar acceptor numbers (AN) of 80 and 75, indicating comparable Lewis acidity to B(C₆F₅)₃ (see Supporting Information). These values are significantly higher compared to the parent Fc-derived system **1a** with an AN of 74,[3e] despite the fact that our cyclic voltammetry investigations clearly depicted **1e** as more electron-rich compound than **1a**. This may arise from the steric

Table 3. Computed hydride (HIA) and fluoride ion affinities (FIA)[10] using the TMS-F system as anchor point (TPSSh/def2-QZVPP/D3BJ).

Compound	HIA [kJ/mol]	HIA$_{solv}$[a] [kJ/mol]	FIA [kJ/mol]	FIA$_{solv}$[a] [kJ/mol]	NH₃ affinity [kJ/mol]	AN[b]
SbF₅	–	–	492	315	–	–
B(C₆F₅)₃	507	297	444	216	113	80
1a[4]	446	245	394	172	89	68[3b]
1d[4]	368	181	372	164	32	–
1e	435	230	378	151	69	80
1f	448	245	398	173	90	75
1g	360	170	364	153	27	32
2a[8]	786	331	732	255	121	82
2d[8]	703	236	691	226	49	–
2e	759	313	693	227	98	92
2f	775	329	721	251	41	86
2g	663	234	662	216	120	86

[a] Solvation enthalpies were calculated for CH₂Cl₂ using the conductor-like polarizable continuum model (CPCM) in combination with the SMD solvation method as implemented in the ORCA 5.0.3 package.[11] [b] Calculation of acceptor number (AN): AN = 2.21 (δ (³¹P NMR) − 41).

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interactions of the Cp* substituent with the $B(C_6F_5)_2$ group in **1e**, resulting in the reduced through-space interaction of a metal-centered filled d-orbital with the empty boron-centered p-orbital. The same rational was reasoned for the explanation of the comparably high Lewis acidity of **1f**, in which the rotation of the *t*Bu–Cp substituent results in repulsion of the $B(C_6F_5)_2$ fragment. The weakest Lewis acid in the series according to the Gutmann-Beckett method is the boronic acid derivative **1d** (AN = 32). However, the computed fluoride ion affinity (FIA)[10] does not provide such a clear-cut picture. The FIA_{solv} is by ca. 40–60 kJ mol^{-1} lower for the neutral Fc-boranes **1a**–**g** when compared to $B(C_6F_5)_3$ as expected for an electron-rich Fc-substituent attached to the boron center. The FIA_{solv} of the substituted Cp-derivatives **1e**–**g** is lower than for the parent derivatives **1a** and **1d**, accounting for the electron-donating nature of the substituted Cp-ligands. This trend is also found for the cationic Lewis acids **2a**–**g**. The Gutmann-Beckett analysis needs to be considered with care because of the paramagnetic nature of the ferrocenium-derivatives, affecting NMR resonances considerably (see SI). Again, the computed FIA_{solv} of **2e**–**g** are lower than for the Cp-derivative **2a** and **2d**. Surprisingly, in this series the *t*Bu-derivative **2f** exhibits the highest Lewis acidity according to our computations.

However, the interplay between electronic effects and steric repulsion in **1e** seems to provide a species with much more pronounced sensitivity towards ambient conditions compared to the other members of the ferrocenyl borane family (vide supra). Additionally, to its surprisingly high Lewis acidity, it seems to show a narrow HOMO/LUMO gap (highest occupied molecular orbital/lowest unoccupied molecular orbital), which

results in an absorption at $\lambda_{max} = 580$ nm (Figure 3a) giving the compound an intense royal blue color.

TD-DFT computations revealed that this absorption arises from a HOMO/LUMO transition from a metal-centered orbital into the low-energy mostly B-centered LUMO (Figure 3b, left), as also indicated by the difference density plot (Figure 3b, right).

Application in Catalysis

Finally, we investigated the application of the Lewis acids in catalytic reactions. Epoxides are versatile intermediates and can be readily transformed in other functional groups.[12] A plethora of metal-catalyzed and organocatalytic transformations has been elaborated, providing access to versatile synthetic building blocks.[13] An elegant approach is the rearrangement of epoxides into carbonyl compounds since it offers the access to aldehydes or ketones dependent on the conditions and catalyst. This so-called Meinwald rearrangement can be catalyzed by various Brønsted acids[14] or Lewis acids, such as $BF_3 \cdot Et_2O$,[15] $ZnBr_2$,[16] $MgBr_2$,[17] $InCl_3$,[18] iridium,[19] chromium[20] or nickel complexes.[21] Notably, also $B(C_6F_5)_3$ was applied in the Meinwald rearrangement of stilbene oxide and alkyl epoxides.[22]

In our hands, the $B(C_6F_5)_3$-catalyzed rearrangement of styrene oxide (**7a**) provided the aldehyde **8a** in 45% yield in 15 min. (Table 4, entry 1).

In comparison to the literature precedence ($> 99\%$, 60 °C, 2 h in THF) this yield is significantly lower, but it should be noted that the reaction was run in dichloromethane at r.t. for 15 min. The neutral Fc-boranes **1a**–**g** provided the products in only 10% yield, but the catalyst's performance was improved when the cationic species **2a** were employed (compare entries 2–5 and 6–9). Consequently, we carried on with the cationic ferrocenium compounds **2e**–**g**. The catechol derivative **2g** showed the best reactivity and the product was obtained in 70% yield. The cationic catechol derivative **2g** also proved as most active for the conversion of *trans*-stilbene oxide (**7b**) to the aldehyde **8b** (entry 12). In addition, the styrene oxide derivatives **7c** and **7d** were converted into the aldehydes **8c** and **8d** in 90% yields (entries 15 and 18). However, for the two epoxides **7e** and **7f**, the cationic Cp* derivative **2e** was most active and yielded the rearrangements products **8e** and **8f** in 80 and 65% yield respectively, but prolonged reaction times of ca. 20 h were required (entries 21 and 24). The rearrangement of **7e** provided product mixtures of 1.7:1.0 of aldehyde and ketone. In comparison to the commercially available $BF_3 \cdot Et_2O$, which is usually applied in 1.0 or 0.5 equivalents,[15] the presented boron centered ferrocenium Lewis acids resemble an efficient alternative.

Conclusions

In conclusion, we have shown that also substituted Fc-borane derivatives display an increase of Lewis-acidity upon oxidation to the ferrocenium species. Interestingly, the *t*Bu-substituted Fc-
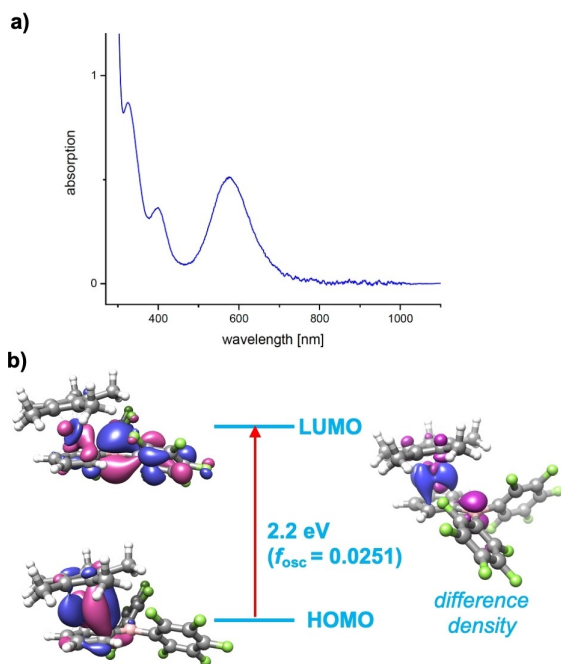

Figure 3. a) UV/vis spectrum of **1e** ($\sim10^{-3}$ M in CH_2Cl_2); b) results of the TD-DFT calculation (PBE0-D4/def2-TZVP): Kohn-Sham orbitals of the HOMO and LUMO; energy of the HOMO/LUMO excitation and difference density plot.

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Table 4. Catalytic Meinwald rearrangement.

entry	cat.	substrate	product	Time [h]	Yield [%]
1	B(C$_6$F$_5$)$_3$	Ph—(epoxide) **7a**	Ph—CH$_2$CHO **8a**	0.25	45[a]
2	**1a**	"	"	"	10[a]
3	**1e**	"	"	"	10[a]
4	**1f**	"	"	"	10[a]
5	**1g**	"	"	"	0[a]
6	**2a**	"	"	"	35[a]
7	**2e**	"	"	"	60[a]
8	**2f**	"	"	"	60[a]
9	**2g**	"	"	"	70[a]
10	**2e**	Ph—(epoxide)—Ph **7b**	Ph—CH(Ph)CHO **8b**	20	60[a]
11	**2f**	"	"	2	80[a]
12	**2g**	"	"	0.25	90[a], 86
13	**2e**	Ph/Me—(epoxide) **7c**	Ph—CH(Me)CHO **8c**	0.25	75[a]
14	**2f**	"	"	2	50[a]
15	**2g**	"	"	0.25	90[a], 45
16	**2e**	Ph/iPr—(epoxide) **7d**	Ph—CH(iPr)CHO **8d**	0.25	75[a]
17	**2f**	"	"	20	75[a]
18	**2g**	"	"	0.25	90[a], 74
19	**2e**	Ph—(epoxide)—Me **7e**	**8ea** / **8eb**	22	80 (1.7:1)[a]
20	**2f**	"	"	22	55 (1.8:1)[a]
21	**2g**	"	"	19	0
22	**2e**	(bicyclic epoxide) **7f**	**8f**	20	65[a]
23	**2f**	"	"	20	60
24	**2g**	"	"	19	75 (1.2:1)[a]

[a] determined by NMR spectroscopy using hexamethyl benzene as internal standard.

borane exhibits comparable Lewis acidity to the native Fc-borane in the neutral as well as in the cationic form. Even more surprising is the finding that the Lewis acidity increases for the boronic acid derivative when one cyclopentadienyl ring is exchanged by a pentamethylcyclopentadienyl group. The Lewis acids were utilized in the Meinwald rearrangement of epoxides and provided the aldehydes as kinetic products in 45–86% yield.

Experimental Section

General information: All preparations containing moisture or air sensitive compounds were carried out in oven dried glassware under an atmosphere of inert gas (Argon 5.0, AIR LIQUIDE) employing SCHLENK line techniques. Catalytic reactions were prepared in a GLOVEBOX SYSTEMS inert atmosphere glovebox. For NMR scale experiments Teflon cap sealed J. YOUNG NMR tubes were used. Flash chromatography was performed under excess pressure of 0.8 bar with silica gel or using an automated chromatography system by BCHI (Pure C-810 Flash). All commercially available reagents were purchased from SIGMA ALDRICH, ABCR, ALFA AESAR, BLDPHARM or TCI CHEMICALS and were used as received without further purification unless stated otherwise.

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B(C$_6$F$_5$)$_3$ was purchased from Boulder Scientific Company and used as received. NMR spectra were recorded on a Bruker AV 300 (300 MHz), a Bruker AV 500 (500 MHz) or a Bruker Ascend 700 (700 MHz) spectrometer as solutions in spinning mode (standard tubes) or non-spinning mode (J. Young NMR tubes). IR-spectra were measured using the ATR technique (attenuated total reflection) on a Bruker Vertex 70 spectrometer in the range from 4000 cm^{-1} to 400 cm^{-1}. Cyclic voltammetry measurements were performed with an Autolab potentiostat by Metrohm (AUT40259) and an electrochemical cell within a glovebox. UV/VIS spectra were recorded using a Mettler-Toledo spectrophotometer UV7 within quartz cuvettes (d = 1 cm) in solution. Diffraction data for **1 g** and **2 g** were measured using a STOE IPDS II diffractometer and graphite-monochromated MoK$_\alpha$ (0.71073 Å) radiation. Intensity data of **1 e**, **1 e**·O=PEt$_3$, 1e·THF, **2 e**·THF, **2 f** and μ-F-[**2 f**]$_2$ were collected on a Bruker Venture D8 three-cycle diffractometer equipped with a Mo K$_\alpha$ μ-source (0.71073 Å), an Incoatec multilayer monochromator and a Photon III detector. More detailed information about the structures is given in the Supporting Information. Due to the high fluorine content of many samples, no satisfactory elemental analysis could be obtained.

Computational Details

All calculations have been performed with the ORCA 5.0.3 program.[23] Geometry optimizations were performed with the functional TPSS[24] and the basis set def2-TZVP[25] including D3BJ dispersion correction.[26] All calculated geometries have been proven as minimum on the potential surface by numerical calculation of harmonic frequencies at the TPSS/TZVP-Level. The FIAs, HIAs and NH$_3$ affinities were calculated on TPSSh[24,27]/QZVPP[26]/D3BJ (with def2/J auxiliary basis set)[28] level of theory. The FIAs (HIAs) where calculated towards the isodesmic reaction with the Me$_3$Si$^+$/Me$_3$SiF (Me$_3$SiH) (FIA of Me$_3$Si$^+$ 958 kJ/mol; HIA of Me$_3$Si$^+$ 959 kJ/mol) system.[10] For solvent corrected (CH$_2$Cl$_2$) FIAs (FIA$_{solv}$) and HIAs (HIA$_{solv}$) the CPCM-SMD[29] method as implemented in ORCA where used on the TPSSh/QZVPP-level.

Synthesis of the Ferrocenyl Boranes

Ag[Al(OC(CF$_3$)$_3$)$_4$],[30] Cp*FeCp,[31] HB(C$_6$F$_5$)$_2$[32] and Cp*Fe(C$_5$H$_4$BBr$_2$)[33] were prepared according to previously described procedures and the obtained NMR data were in agreement with the literature.

Me$_5$FcB(C$_6$F$_5$)$_2$ (1 e): In a glovebox, a Schlenk bomb with Teflon tap was charged with Cp*FeCp (512 mg, 2.00 mmol, 1.00 equiv.), HB-(C$_6$F$_5$)$_2$ (692 mg, 2.00 mmol, 1.00 equiv.) and toluene (12 mL, 0.17 M). The reaction mixture was heated to 80 °C for 19 h. The solvent was removed under vacuum and the dark violet residue was extracted with hexane. The solution was reduced in volume and stored overnight at −20 °C. The supernatant was removed, and the dark blue crystals were dried under vacuum. Yield: 89 % (1.07 g, 1.78 mmol). Crystals suitable for X-ray diffraction were obtained by self-crystallization in hexane at −20 °C. ^{1}H NMR (700 MHz, 298 K, CDCl$_3$) δ = 4.56 (br, 2H, C$_5$H$_4$B), 4.23 (br, 2H, C$_5$H$_4$B), 1.78 (s, 15H, CH$_3$); ^{11}B NMR (160 MHz, 303 K, CDCl$_3$) δ = 59.0 (s); ^{13}C NMR (176 MHz, 298 K, CDCl$_3$) δ = 145.4 (d, $^1J_{CF}$ = 243.9 Hz, Cq, CF), 141.5 (d, $^1J_{CF}$ = 254.0 Hz, Cq, CF), 137.6 (d, $^1J_{CF}$ = 252.4 Hz, Cq, CF), 116.2 (Cq, ipso-C$_6$F$_5$), 83.7 (Cq, Cp*), 83.7 (CH), 80.3 (CH), 11.4 (CH$_3$); No signal was observed for the boron bound carbon of C$_5$H$_4$B; ^{19}F NMR (659 MHz, 298 K, CDCl$_3$) δ = −128.13−−128.18 (m), −152.30−−152.36 (m), −161.81−−161.89 (m).

tBuFcB(C$_6$F$_5$)$_2$ (1 f): In a glovebox, a Schlenk bomb with Teflon tap was charged with (tBuC$_5$H$_4$)FeCp (484.3 mg, 2.00 mmol, 1.00 equiv.), HB(C$_6$F$_5$)$_2$ (692 mg, 2.00 mmol, 1.00 equiv.) and toluene (12 mL,

0.17 M). The reaction mixture was heated to 80 °C for 19 h. The solvent was removed under vacuum and the residue was extracted with hexane. The solution was reduced in volume and stored overnight at −20 °C. The supernatant was removed, and the red crystals were dried under vacuum. Further purification was achieved by recrystallization from pentane. Yield: 39 % (455 mg, 0.78 mmol). ^{1}H NMR (700 MHz, 298 K, CDCl$_3$) δ = 5.10 (t, $^3J_{HH}$ = 1.9 Hz, 2H, C$_5$H$_4$B), 4.46 (t, $^3J_{HH}$ = 1.9 Hz, 2H, C$_5$H$_4$tBu), 4.27 (t, $^3J_{HH}$ = 1.9 Hz, 2H, C$_5$H$_4$B), 4.24 (t, $^3J_{HH}$ = 1.9 Hz, 2H, C$_5$H$_4$tBu), 1.06 (s, 9H, C(CH$_3$)$_3$); ^{11}B NMR (160 MHz, 303 K, CDCl$_3$) δ = 55.2 (s); ^{13}C NMR (176 MHz, 298 K, CDCl$_3$) δ = 145.6 (d, $^1J_{CF}$ = 243.2 Hz, Cq, CF), 141.6 (d, $^1J_{CF}$ = 254.4 Hz, Cq, CF), 137.5 (d, $^1J_{CF}$ = 251.8 Hz, Cq, CF), 115.0 (Cq, ipso-C$_6$F$_5$), 105.6 (Cq, C$_5$H$_4$tBu), 79.9 (CH, C$_5$H$_4$B), 77.4 (CH, C$_5$H$_4$B), 68.7 (CH, C$_5$H$_4$tBu), 67.2 (CH, C$_5$H$_4$tBu), 31.0 (CH$_3$), 30.5 (Cq, C(CH$_3$)$_3$); No signal was observed for the boron bound carbon of C$_5$H$_4$B; ^{19}F NMR (659 MHz, 298 K, CDCl$_3$) δ = −128.95−−128.99 (m), −152.68−−152.74 (m), −161.66−−161.72 (m).

Me$_5$FcB(O$_2$C$_6$Cl$_4$) (1 g): C$_6$Cl$_4$(OH)$_2$ (236 mg, 0.95 mmol, 1.00 equiv.) was dissolved in toluene (20 mL, 0.05 M) and cooled to −78 °C. A solution of nBuLi (2.5 M in hexane, 0.76 mL, 1.90 mmol, 2.00 equiv.) was added and the mixture warmed to ambient temperature. After 30 minutes of stirring, the reaction mixture was cooled again to −78 °C and added to a solution of Cp*Fe(C$_5$H$_4$BBr$_2$) (405 mg, 0.95 mmol, 1.00 equiv.) in toluene (20 mL) at −78 °C. The mixture was warmed to ambient temperature, stirred for one hour and filtered. The solvent was removed under reduced pressure and the residue was washed with small amounts of hexane. After drying, the product was obtained as a yellow solid. Yield: 79 % (385 mg, 0.75 mmol). ^{1}H NMR (700 MHz, 298 K, CDCl$_3$) δ = 4.24 (t, $^3J_{HH}$ = 1.8 Hz, 2H, C$_5$H$_4$B), 4.16 (t, $^3J_{HH}$ = 1.7 Hz, 2H, C$_5$H$_4$B), 1.77 (s, 15H, CH$_3$); ^{11}B NMR (160 MHz, 303 K, CDCl$_3$) δ = 35.4 (s); ^{13}C NMR (176 MHz, 298 K, CDCl$_3$) δ = 145.3 (Cq, CO), 126.6 (Cq, CCl), 116.2 (Cq, CCl), 81.5 (Cq, Cp*), 77.9 (CH), 76.6 (CH), 11.0 (CH$_3$); No signal was observed for the boron bound carbon of C$_5$H$_4$B. FT-IR (cm^{-1}) $\tilde{v}$ = 2245 (vw), 2197 (vw), 2177 (vw), 2122 (vw), 2036 (vw), 1991 (vw), 1959 (vw), 1507 (w), 1487 (m), 1425 (s), 1378 (s), 1318 (m), 1134 (vw), 1107 (s), 1019 (w), 990 (m), 890 (m), 849 (vw), 818 (w), 793 (m), 695 (vw), 670 (vs), 601 (vw), 586 (vw), 552 (vw), 508 (m), 487 (vs), 457 (m), 437 (m), 419 (w), 406 (w). Elemental analysis (C$_{21}$H$_{19}$BCl$_4$FeO$_2$) calculated (found): 49.28 (49.83), 3.74 (3.57).

Oxidation of Ferrocenyl Boranes

In a glovebox, the ferrocenyl borane (200 μmol, 1.00 equiv.) and Ag[Al(OC(CF$_3$)$_3$)$_4$] (200 μmol, 1.00 equiv.) were dissolved in CH$_2$Cl$_2$ (2 mL, 0.1 M). After stirring at room temperature for 30 minutes, the reaction mixture was filtered. The resulting solution was layered with hexane and stored overnight at −20 °C. The supernatant was removed, the crystalline solid was washed with hexane and dried under reduced pressure.

[Me$_5$FcB(C$_6$F$_5$)$_2$][Al(OC(CF$_3$)$_3$)$_4$] (2 e): Yield: 60 % (189 mg, 120 μmol). ^{1}H NMR (500 MHz, 303 K, CD$_2$Cl$_2$) δ = 22.30 (br, 2H, C$_5$H$_4$B), 15.17 (br, 2H, C$_5$H$_4$B), −42.65 (br, 15H, CH$_3$); ^{11}B NMR (160 MHz, 303 K, CD$_2$Cl$_2$) δ = 47.8 (s); ^{13}C NMR (176 MHz, 298 K, CD$_2$Cl$_2$) δ = 387.8 (CH, C$_5$H$_4$B), 315.1 (CH, C$_5$H$_4$B), 246.6 (Cq, C$_5$H$_4$B), 209.5 (Cq, Cp*), 142.5 (Cq, ipso-C$_6$F$_5$), 137.9 (d, $^1J_{CF}$ = 261.6 Hz, Cq, C$_6$F$_5$), 136.4 (d, $^1J_{CF}$ = 262.9 Hz, Cq, C$_6$F$_5$), 129.4 (d, $^1J_{CF}$ = 247.0 Hz, Cq, C$_6$F$_5$), 121.9 (q, $^1J_{CF}$ = 294.7 Hz, Cq, CF$_3$), 79.4 (Cq, C(CF$_3$)$_3$), 24.7 (CH$_3$); ^{19}F NMR (282 MHz, 298 K, CD$_2$Cl$_2$) δ = −75.80 (s), −123.95 (br), −150.43−−150.57 (m), −162.10 (br); ^{27}Al NMR (182 MHz, 298 K, CD$_2$Cl$_2$) δ = 34.8 (s).

[tBuFcB(C$_6$F$_5$)$_2$][Al(OC(CF$_3$)$_3$)$_4$] (2 f): Yield: 90 % (279 mg, 180 μmol). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated solution of the borane in DCM. ^{1}H NMR (500 MHz, 303 K, CD$_2$Cl$_2$) δ = 44.34 (br, 2H, C$_5$H$_4$B),

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37.22 (br, 2H, C_5H_4B), 30.06 (br, 2H, C_5H_4tBu), 28.11 (br, 2H, C_5H_4tBu), −11.54 (br, 9H, $C(CH_3)_3$); ^{11}B NMR (160 MHz, 303 K, CD_2Cl_2) δ=45.0 (s); ^{13}C NMR (176 MHz, 298 K, CD_2Cl_2) δ=406.7 (Cq, C_5H_4tBu), 349.9 (CH, C_5H_4B), 298.4 (CH, C_5H_4B), 232.3 (Cq, C_5H_4B), 215.1 (CH, C_5H_4tBu), 206.8 (CH, C_5H_4tBu), 136.1 (d, $^1J_{CF}$=252.1 Hz, Cq, C_6F_5), 135.72 (d, $^1J_{CF}$=257.9 Hz, Cq, C_6F_5), 135.66 (Cq, ipso-C_6F_5), 125.3 (d, $^1J_{CF}$=249.4 Hz, Cq, C_6F_5), 121.7 (q, $^1J_{CF}$=294.8 Hz, Cq, CF_3), 79.3 (Cq, $C(CF_3)_3$), 29.8 (Cq, $C(CH_3)_3$), −12.8 (CH_3); ^{19}F NMR (282 MHz, 298 K, CD_2Cl_2) δ=−76.09 (s), −125.49 (br), −150.26−−150.40 (m), −162.21 (br); ^{27}Al NMR (182 MHz, 298 K, CD_2Cl_2) δ=34.5 (s).

$[Me_5FcB(O_2C_6Cl_4)][Al(OC(CF_3)_3)_4]$ (2 g): Yield: 75% (223 mg, 151 μmol). ^1H NMR (500 MHz, 303 K, CD_2Cl_2) δ=24.66 (br, 2H, C_5H_4B), 21.45 (br, 2H, C_5H_4B), −43.27 (br, 15H, CH_3); ^{11}B NMR (160 MHz, 303 K, CD_2Cl_2) δ=34.5 (s); ^{13}C NMR (176 MHz, 298 K, CD_2Cl_2) δ=375.5 (CH, C_5H_4B), 343.6 (CH, C_5H_4B), 298.5 (Cq, C_5H_4B), 233.4 (Cq, Cp*), 133.2 (Cq, CO), 123.6 (Cq, CCl), 121.7 (q, $^1J_{CF}$=292.7 Hz, Cq, CF_3), 108.8 (Cq, CCl), 79.4 (Cq, $C(CF_3)_3$), 15.5 (CH_3); ^{19}F NMR (282 MHz, 298 K, CD_2Cl_2) δ=−75.71 (s); ^{27}Al NMR (182 MHz, 298 K, CD_2Cl_2) δ=34.9 (s). FT-IR (cm^{-1}) $\tilde{v}$=2197 (vw), 1993 (vw), 1414 (vw), 1392 (vw), 1352 (vw), 1298 (w), 1274 (m), 1213 (vs), 1165 (w), 1123 (w), 1023 (vw), 971 (vs), 888 (vw), 833 (vw), 796 (vw), 755 (vw), 726 (vs), 692 (vw), 671 (vw), 560 (w), 536 (w), 439 (m), 400 (vw).

Isomerization of Epoxides

Epoxides **7 a**, **7 b** and **7 f** were commercially available and used without purification. Epoxides **7 c**,[34] **7 e**[34] and **7 d**[35] were synthesized according to literature procedures. The obtained NMR data were in agreement with the literature.

Catalyst screening and substrate scope: In a glovebox, the borane (5.0 μmol, 10 mol%) was dissolved in CD_2Cl_2 (0.2 mL) and transferred to a J. Young NMR tube. A solution of the epoxide (50 μmol, 1.0 equiv.) and HMB (1.6 mg, 10 μmol, 0.2 equiv.) in CD_2Cl_2 (0.3 mL) was added. After the given time at room temperature, the yield was determined by ^1H NMR spectroscopy using HMB as internal standard. The formation of aldehyde and, if applicable, the formation of ketone was further supported by GC-MS.

General procedure for isomerization of epoxides: In a glovebox, a crimp seal glass vial was charged with the ferrocenium borane **2 g** (22.2 mg, 15.0 μmol, 5.00 mol%) and CH_2Cl_2 (1 mL). A solution of the epoxide (300 μmol, 1.00 equiv.) in CH_2Cl_2 (2 mL) was added and the reaction mixture was stirred at room temperature for 15 minutes. The mixture was transferred to a round bottom flask, loaded with a small portion of silica and the solvent was removed under reduced pressure. After column chromatography (silica, mixtures of CH and EA), the aldehydes were obtained as colorless or slightly yellow oils.

2,2-diphenylacetaldehyde (8 b): Starting from trans-stilbene oxide (**7 b**), yield: 86% (50.4 mg, 257 μmol). ^1H NMR (700 MHz, 298 K, $CDCl_3$) δ=9.96 (d, $^3J_{HH}$=2.3 Hz, 1H, CHO), 7.40–7.37 (m, 4H, H_{Ar}), 7.33–7.31 (m, 2H, H_{Ar}), 7.24–7.23 (m, 4H, H_{Ar}), 4.90 (d, $^3J_{HH}$=2.3 Hz, 1H, PhCH); ^{13}C NMR (176 MHz, 298 K, $CDCl_3$) δ=198.7 (CH, CHO), 136.4 (Cq), 129.3 (CH), 129.1 (CH), 127.8 (CH), 64.3 (CH). The NMR data are in agreement with the literature.[34]

2-phenylpropanal (8 c): Starting from 2-methyl-2-phenyloxirane (**7 c**), yield: 45% (18.2 mg, 136 μmol). ^1H NMR (500 MHz, 303 K, $CDCl_3$) δ=9.70 (d, $^3J_{HH}$=1.3 Hz, 1H, CHO), 7.40–7.37 (m, 2H, H_{Ar}), 7.32–7.29 (m, 1H, H_{Ar}), 7.23–7.20 (m, 2H, H_{Ar}), 3.64 (qd, $^3J_{HH}$=7.1 Hz, $^3J_{HH}$=1.3 Hz, 1H, $CHCH_3$), 1.45 (d, $^3J_{HH}$=7.1 Hz, 3H, CH_3); ^{13}C NMR (176 MHz, 298 K, $CDCl_3$) δ=201.2 (CH, CHO), 137.9 (Cq), 129.2 (CH), 128.5 (CH), 127.7 (CH), 53.2 (CH), 14.8 (CH_3). The NMR data are in agreement with the literature.[34]

3-methyl-2-phenylbutanal (8 d): Starting from 2-isopropyl-2-phenyloxirane (**7 d**), yield: 74% (36.1 mg, 223 μmol). ^1H NMR (700 MHz, 298 K, $CDCl_3$) δ=9.71 (d, $^3J_{HH}$=3.3 Hz, 1H, CHO), 7.37–7.35 (m, 2H, H_{Ar}), 7.31–7.28 (m, 1H, H_{Ar}), 7.20–7.18 (m, 2H, H_{Ar}), 3.18 (dd, $^3J_{HH}$=9.5 Hz, $^3J_{HH}$=3.3 Hz, 1H, PhCH), 2.42 (dqq, $^3J_{HH}$=9.5 Hz, $^3J_{HH}$=6.6 Hz, $^3J_{HH}$=6.6 Hz, 1H, $CH(CH_3)_2$), 1.05 (d, $^3J_{HH}$=6.6 Hz, 3H, CH_3), 0.77 (d, $^3J_{HH}$=6.6 Hz, 3H, CH_3); ^{13}C NMR (176 MHz, 298 K, $CDCl_3$) δ=201.3 (CH, CHO), 135.6 (Cq), 129.5 (CH), 129.0 (CH), 127.6 (CH), 67.0 (CH), 28.9 (CH), 21.3 (CH_3), 20.2 (CH_3). The NMR data are in agreement with the literature.[34]

Supporting Information

Synthetic procedures and analytical data are available in the Supporting Information of this article. Additional references cited within the Supporting Information.[36–42]

Conflict of Interests

The authors declare no conflict of interests.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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