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A free boratriptycene-type Lewis superacid

By exploiting the facile self-assembly of the pyrazabole scaffold, authors have devised a straightforward route to boratriptycene-type precursors that have two pyrazole bridges and one 1,1'-ferrocenylene linker between two bridgehead BH moieties. Single hydride abstraction generates ferrocene-stabilized borenium cations with an unprecedentedly large dip angle and exceptional Lewis acidity that can nevertheless be isolated in free form. Exceptional acidity of the prepared borenium salts stems from the structural strain imparted by the bridging rigid pyrazabole moieties, while weak Fe(3d)→B(2p) bonding prevents the planar borenium center from interaction with weakly-coordinated counterions.

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A free boratriptycene-type Lewis superacid†

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Bicyclic pyrazabole-bridged ferrocenes with BH groups at their bridgehead positions were prepared from [Li(thf)]₂[1,1'-fc(BH₃)₂] and pyrazole or 3,5-dimethylpyrazole in the presence of Me₃SiCl (**1** or **1Me**, respectively; 1,1'-fc = 1,1'-ferrocenylene); Me₃SiH and H₂ are released as byproducts. Treatment of **1** or **1Me** with 1 eq. of the hydride scavenger [Ph₃C][B(C₆F₅)₄] afforded the borenium salts [**2**][B(C₆F₅)₄] (72%) and [**2Me**][B(C₆F₅)₄] (77%). According to X-ray crystallography, [**2Me**]⁺ contains one trigonal-planar borenium cation, the cyclopentadienyl (Cp) rings of the 1,1'-fc fragment remain parallel to each other, but the Cp–B bond vector is bent out of the Cp plane by an unprecedentedly large dip angle α* of 40.6°. The Fe...B(sp²) distance is very short (2.365(4) Å) and the ¹¹B NMR signal of the cationic B(sp²) center is remarkably upfield shifted (23.4 ppm), suggesting a direct Fe(3d) → B(2p) donor–acceptor interaction. Although this interpretation is confirmed by quantum-chemical calculations, the coupling between the associated orbitals corresponds to an energy of only 12 kJ mol^{−1}. Accordingly, both the experimental (e.g., Gutmann–Beckett acceptor number AN = 111) and theoretical assessment (e.g., Et₃PO and F[−]-ion affinities) of the Lewis acidity proves that [**2**]⁺ is among the strongest boron-based Lewis acids available to date.

Introduction

The rise to prominence of boron-based Lewis acids began when their application potential as activators for metal-catalyzed homogeneous olefin polymerization was recognized.¹ The advent of the 'Frustrated Lewis Pairs' led to a further surge of interest, which has remained at a high level ever since.^{1,2} Among all the remarkable developments in the field, we focus here particularly on Lewis acidic organoboranes ('Lewis superacids').³

One way to increase the affinity of a triorganylborane (BR₃) for even weak Lewis bases is to introduce electronegative halogen substituents at the periphery.⁴ Classic examples include the compounds B(C₆F₅)₃ of Massey and Park⁵ or B(C₆Cl₅)₃ of Ashley and O'Hare.⁶ As an alternative, mesomerically electron-withdrawing substituents have also been employed.⁷ The affinity of a boron center (in particular) for anionic ligands can

also be increased by the Coulomb attraction of an adjacent positively charged group.⁸ Gabbai *et al.* took advantage of this effect when they used the phosphonium borane ([A]⁺; Fig. 1) to bind F[−] ions in water despite their high hydration enthalpy.^{9,10} Our group combined a high fluorine load with the positive charge of a phosphonium center to create a Lewis acid [B]⁺, stronger than B(C₆F₅)₃ and suitable as a catalyst for Diels–Alder

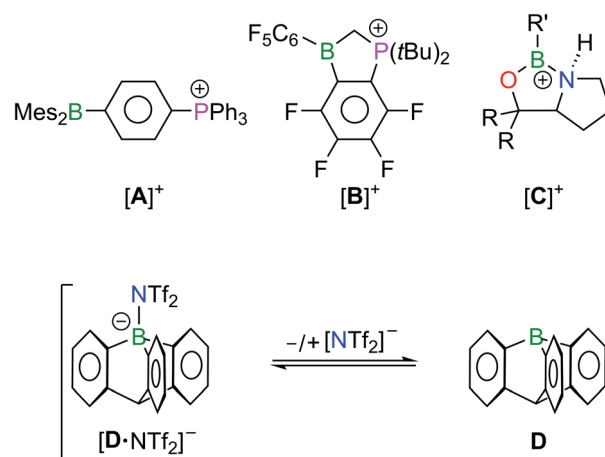


Fig. 1 Organoboranes of particularly high Lewis acidity due to introduced positive charges and fluorine substituents ([A]⁺, [B]⁺, [C]⁺) or structurally enforced pyramidalization (D). Mes = 2,4,6-Me₃C₆H₂, Tf = O₂SCF₃.

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reactions.¹¹ By shifting the positive charge even closer to the boron center, Corey *et al.* obtained chiral oxazaborolidinium cations $[C]^+$ that serve as broadly applicable catalysts in (enantioselective) $[4 + 2]$ - and $[3 + 2]$ -cycloaddition reactions.¹² Most trivalent compounds BR_3 with an empty boron 2p orbital adopt trigonal planar configurations. Only after coordination of a Lewis basic donor (Do) is the BC_3 moiety pyramidalized to allow for a (distorted) tetrahedral geometry of the $BR_3 \cdot Do$ adduct. However, when a rigid organic framework is designed to impose a structural constraint on the B atom that forces the BC_3 core out of planarity, the free Lewis acid becomes destabilized but also better preorganized for ligand coordination. As a consequence, the organoborane becomes a better electron-pair acceptor. Mikhailov realized such a structural motif by the synthesis of

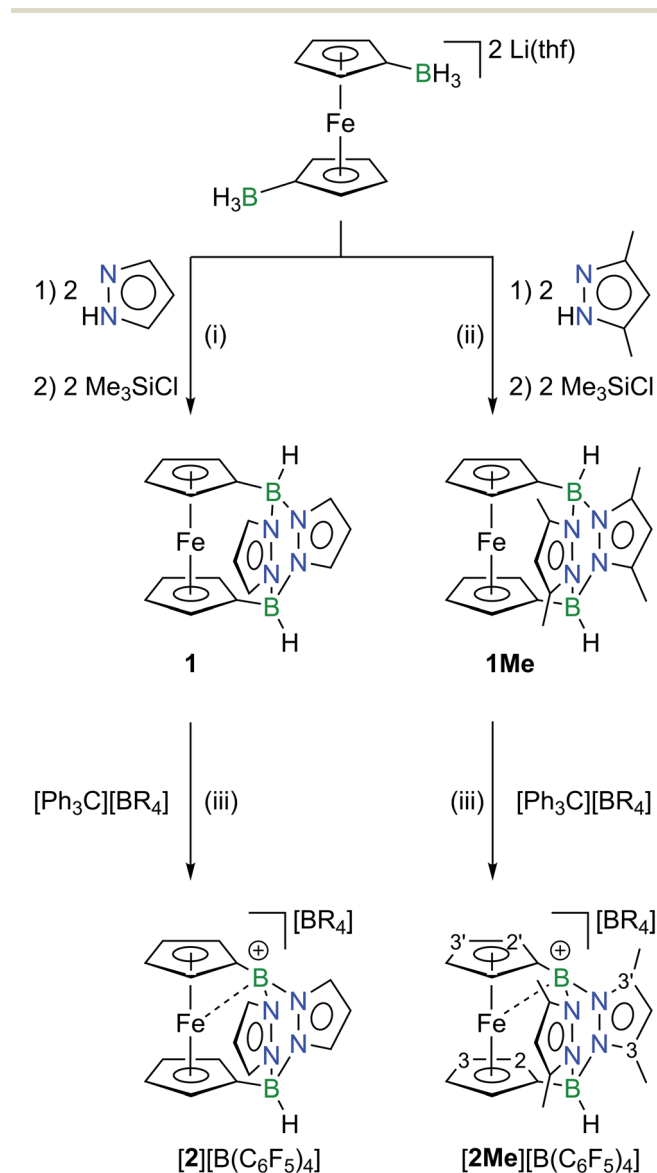
1-boraadamantane,^{14,15} while Berionni *et al.* released a non-planar 9-boratriptycene (**D**) by *in situ* protonolysis of corresponding borate-complexes $[R_4P][tBuC_6H_4-D]$ with $HNTf_2$ in CH_2Cl_2 ($Tf = O_2SCF_3$).¹⁶ In the resulting mixture, **D** is in an association–dissociation equilibrium with the weakly coordinating $[NTf_2]^-$ ion and was isolated in the form of its trapping products with various N-, P-, or O-centered Lewis bases.¹⁷ Structural data from X-ray crystallography are not available for either free 1-boraadamantane or **D**. Gas-phase electron diffraction on 3-methyl-1-boraadamantane at 100 °C revealed that the B atom in the equilibrium structure has a (slightly) pyramidal configuration with $\sum(C-B-C) = 349.4(4)^\circ$ and av. $d(B-C) = 1.556(5)$ Å.¹⁸ The experimentally determined structural parameters were confirmed by quantum-chemical calculations, which further indicate significant hyperconjugation between the vacant boron 2p orbital and its adjacent C–C σ bonds (average stabilization energy: 64.4 kJ mol^{−1}; electron occupancy $q(B(2p))$: 0.17 e[−]).^{18,19} Compared to 1-boraadamantane, the computed molecular structure of **D** shows a more pyramidalized BC_3 core ($\sum(C-B-C) = 339.3^\circ$) while $q(B(2p))$ is lower (0.08 e[−]).¹⁶

Taking into account the above developments over the last two decades, we have now designed a novel ferrocenylborane-based^{10h,20,21} Lewis superacid $[2]^+$ guided by the following criteria (Scheme 1): (i) facile synthesis inspired by the self-assembly of pyrazaboles or scorpionate ligands;²² (ii) a positively charged B center with electronegative N(sp²) atoms in its first coordination sphere, which cannot donate π -electron density to the vacant p orbital on the B atom due to the orthogonal positions of the filled p orbitals on the N atoms;^{23–25} (iii) a strained scaffold analogous to boratriptycene. The 1,1'-ferrocenylene bridge in $[2]^+$ has two functions to prevent the molecule from exceeding its stability limits: (i) a weak and easily displaced $Fe \rightarrow B^+$ through-space interaction should help to buffer the electron deficiency of the free borenium cation in its resting state.^{10h,20} (ii) Because of the facile distortion of the normally parallel cyclopentadienyl rings toward a tilted orientation, the 1,1'-ferrocenylene unit can act as a hinge that mitigates an overly strained pyramidal configuration of the B atom. The synthesis and key properties of $[2]^+$ -type compounds will be described herein.

Results and discussion

Synthesis of $[2][B(C_6F_5)_4]$ and $[2Me][B(C_6F_5)_4]$

Treatment of the readily available hydridoborate salt $[Li(thf)]_2[1,1'-fc(BH_3)_2]$ ²⁶ with pyrazole or 3,5-dimethylpyrazole and Me_3SiCl afforded the pyrazabole-bridged *ansa*-ferrocenes **1** and **1Me** in yields of 39% and 55%, respectively (Scheme 1; 1,1'-fc = 1,1'-ferrocenylene); Me_3SiH and H_2 are formed as the byproducts. Clean and quantitative hydride abstraction was achieved through the reaction of **1** or **1Me** with the hydride scavenger $[Ph_3C][B(C_6F_5)_4]$ in CH_2Cl_2 . After precipitation with *n*-pentane, $[2][B(C_6F_5)_4]$ (72%) and $[2Me][B(C_6F_5)_4]$ (77%) were isolated in good yields. Crystals of the borenium salts suitable for X-ray analysis were grown by layering their concentrated solutions in CH_2Cl_2 with *n*-hexane.²⁷

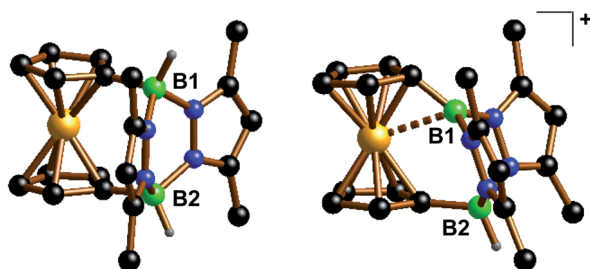


Scheme 1 Synthesis of pyrazabole-bridged *ansa*-ferrocenes **1** and **1Me**; hydride abstraction to afford the borenium-ion salts $[2][B(C_6F_5)_4]$ and $[2Me][B(C_6F_5)_4]$. Reagents and conditions: (i) THF, $-78^\circ C$ (30 min) to $70^\circ C$ (6 h). (ii) THF, room temperature (overnight) to $70^\circ C$ (3 h). (iii) CH_2Cl_2 , room temperature, 1 min. R = C_6F_5 .

The 1,1'-ferrocenylene moieties in **1Me**/**[2Me]**⁺ adopt almost perfectly staggered conformations with torsion angles $C_i - \text{COG} - \text{COG}' - C'_i$ close to zero (C_i = B-bonded C atom; COG = cyclopentadienyl-ring centroid). No significant differences are also observed between the B–C (av. 1.596 Å) or B–N (av. 1.567 Å) bond lengths in **1Me** and the B(2)–C (1.613(6) Å) or B(2)–N (av. 1.568 Å) bond lengths in **[2Me]**⁺. The configuration of the second B atom, however, changes fundamentally from tetrahedral to trigonal-planar upon going from **1Me** to **[2Me]**⁺ (sum of angles around B(1) = 359.7°). Accordingly, the B(1)–C (1.497(6) Å) and B(1)–N (av. 1.506 Å) bonds of **[2Me]**⁺ are contracted relative to the corresponding bonds at B(2). This contraction is about twice as pronounced for B(1)–C (Δ = 0.116 Å) as for B(1)–N (Δ = 0.062 Å). The B(1)–C bond of **[2Me]**⁺ is also considerably shorter than the exocyclic B–C bond between the orthogonally positioned planes in 9-Mes-9-borafluorene (1.562 Å), which we take as an archetypal B(sp²)–C(sp²) single bond.²⁸ The B(1)–N bonds of **[2Me]**⁺ are still longer than the average B–N bond in propeller-shaped B(pyrMe₂)₃ (1.443 Å; pyrMe₂ = 2,5-dimethylpyrrolyl), for which B=N π bonding is negligible.²⁹ The most important structural features of **[2Me]**⁺ are the pronounced dip angle $\alpha^* = 40.6^\circ$ and the short

$\text{Fe}\cdots\text{B}(\text{sp}^2)$ contact of 2.365(4) Å ($\alpha^* = 180^\circ - \alpha$; $\alpha = \text{COG-C}_f\text{-B}(1)$). Corresponding distortions have already been observed for other ferrocenylboranes, but the dip angles are much smaller even in the most extreme cases, *i.e.*, FcBBr_2 : $\alpha^* = 18.9^\circ$,^{20a} 9-Fc-9-borafluorene: $\alpha^* = 25.5^\circ$,^{20d} FcBC_4Ph_4 : $\alpha^* = 29.4^\circ$ (Fc = ferrocenyl).^{20f} The planarization of one bridgehead B atom does not result in a substantial tilting of the ferrocenylene unit: **1Me**/[**2Me**]⁺ show largely coplanar cyclopentadienyl rings with Cp//Cp' angles of 5.2(2)/5.4(2)°. The 'hinge-effect' of the 1,1'-fc bridge, which was assumed in the design of the molecular framework, obviously does not play a major role. Considerable differences are observed for the pyrazabole moieties of **1Me** vs. [**2Me**]⁺: the gap between the two pyrazol-1-yl (pz) rings is significantly wider in **1Me** than in [**2Me**]⁺ (pz//pz' = 146.8(1)° vs. 118.7(2)°) and the dihedral angle between the best plane through the four N atoms and the B(2)-bonded Cp ring amounts to a value of 88.3° in **1Me**, but only to 71.6° in [**2Me**]⁺.

H⁻ ion abstraction leads to a symmetry breaking that renders the two Cp rings of [2Me]⁺ chemically inequivalent. The assignment of resonances to Cp⁻B⁺ or Cp-B(H) was achieved by means of a NOESY spectrum (*cf.* Scheme 1 for the atom labeling): an intense cross peak was observed between a pzCH₃ signal at δ(¹H) = 2.56 and a CpH resonance at δ(¹H) = 4.11 ppm; a second, significantly weaker, cross peak was detected between the second pzCH₃ signal (2.48 ppm) and a CpH resonance at 3.31 ppm (pz = pyrazol-1-yl). Through-space interactions of two nuclear spins that are in closer proximity to each other tend to result in a more pronounced NOE. Since we know from the solid-state structure of [2Me][B(C₆F₅)₄] that the average distance between CpH-2' and pzCH₃-3' is 2.94 Å and thus approximately 30% shorter than the distance between CpH-2 and pzCH₃-3 (4.19 Å), we assign the proton signals at 4.11/3.31 ppm to



parameter	1Me	[2Me][B(C₆F₅)₄]
B(1)–C [Å]	1.593(3)	1.497(6)
B(2)–C [Å]	1.598(3)	1.613(6)
B(1)–N [Å]	1.565(2)	1.505(5)
	1.568(2)	1.506(5)
B(2)–N [Å]	1.562(2)	1.566(6)
	1.570(2)	1.569(6)
Fe⋯B(1) [Å]	3.241(2)	2.365(4)
α^* [°]	1.6	40.6

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Chem. Sci., 2022, 13, 1608–1617 | 1611

with the vacant B(2p) orbital. The 3c2e bond thus can be viewed as a donor-acceptor interaction (see Fig. 3b for the composition of corresponding NLMO orbitals). In contrast, the corresponding 3c2e bond in structurally related $[\text{Fc-SiR}_2]^+$ ions is formed with the C_i atom of the other Cp ring. This difference might be attributed to the larger covalent/ionic radii of tricoordinated Si^+ compared to tricoordinated B^+ ions.

The metal \rightarrow B interaction found for $[2]^+$ is computed to become significantly stronger when the Fe(II) center in the metallocene scaffold is replaced by heavier Ru(II) or Os(II) ions with more diffuse 4d or 5d valence orbitals, respectively. This is concluded mainly from the shorter $\text{M}\cdots\text{B}^+$ contacts ($\text{M} = \text{Ru}, \text{Os}$) despite the larger ionic radii of these M(II) centers, and also from the larger $\text{M}\cdots\text{B}^+$ covalency revealed by the larger QTAIM delocalization indices and Mayer bond orders (Table S4†).

Despite the existing $\text{Fe}(3d) \rightarrow \text{B}(2p)$ interaction and a hence conceivable charge transfer leading to the generation of $\text{Fe}(\text{III})/\text{B}^+$ radical pairs, the electronic ground states of $[2]^+$ and $[2\text{Me}]^+$ remain diamagnetic with Fe(II) and B^+ centers, which is confirmed by computed and experimental NMR shifts as well as ^{57}Fe Mössbauer spectral parameters (Fig. S51, S52 and Tables S1, S6†). The electron-spin density in the lowest-lying triplet state of $[2]^+$ (147 kJ mol^{-1} above the singlet ground state) resides almost exclusively on the Fe(II) center, with just small positive/negative fractions at the C atoms of both Cp rings (Fig. S65†). The same holds for higher-lying triplet excited states and thus,

even upon singlet-triplet excitation, the $\text{Fe}(3d) \rightarrow \text{B}(2p)$ interaction would not be expected to promote the formation of an $\text{Fe}(\text{III})/\text{B}^+$ radical pair. A qualitatively similar picture, but with notably larger energy gap between singlet and triplet states, is obtained for the ruthenocene analogue of $[2]^+$ ($\Delta E = 280 \text{ kJ mol}^{-1}$). In striking contrast, the osmocene congener (which is also predicted to feature a singlet ground state with Os(II) and B^+ centers) is computed to display a distinct Os(III)/ B^+ character in its relaxed triplet excited state ($\Delta E = 238 \text{ kJ mol}^{-1}$).

Finally, we propose that the $\text{Fe}(3d) \rightarrow \text{B}(2p)$ interaction in $[2]^+/[2\text{Me}]^+$, while not significantly reducing the Lewis acidity of the ferrocenyl borenium ions (see below), may nevertheless provide the very extra stability needed to isolate the free Lewis acids (compare the case of the $[\text{D-NTf}_2]^- \leftrightarrow \text{D} + [\text{NTf}_2]^-$ equilibrium shown in Fig. 1).

Assessment of the Lewis acidity of the borenium cation $[2]^+$ by the Gutmann-Beckett NMR method, competition experiments with $\text{B}(\text{C}_6\text{F}_5)_3$ and computational studies

The sterically less encumbered borenium-ion derivative $[2]^+$ was selected for a comparative assessment of Lewis acidities. We first determined the acceptor number (AN) of $[2]^+$ on the scale developed by Gutmann and Beckett.³⁵ To this end, mixtures of $[2][\text{B}(\text{C}_6\text{F}_5)_4]$ and Et_3PO were prepared in CD_2Cl_2 and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded (see the ESI† for full details). We consistently observed a resonance at $\delta(^{31}\text{P}) = 91.0 \text{ ppm}$ for the adduct $[2\cdot\text{OPEt}_3][\text{B}(\text{C}_6\text{F}_5)_4]$. The signal is shifted to lower field by 40.7 ppm and 50.0 ppm, compared to the resonance of pure Et_3PO in CD_2Cl_2 (50.3 ppm) or *n*-hexane (41.0 ppm), respectively. From these data, an acceptor number $\text{AN}([2]^+) = 111$ was calculated, which is significantly higher than the acceptor number of $\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{AN} = 77\text{--}82$; CD_2Cl_2), higher than the acceptor numbers of so far reported Fc-borenium ions (cf. Table S7 in ESI†), and close to that of neat BBr_3 ($\text{AN} = 109$) or BI_3 ($\text{AN} = 115$).³⁶

The pyridine adduct $[2\cdot\text{py}][\text{B}(\text{C}_6\text{F}_5)_4]$ was synthesized on a preparative scale and characterized by NMR-spectroscopy and X-ray crystallography (Scheme 2). Five ^1H and five ^{13}C resonances are observed for the pyridine ligand in the corresponding room-temperature NMR spectra, demonstrating a sterically restricted rotation about the B-N(py) bond on the NMR time scale (CD_2Cl_2). The *p*-CH group of the coordinated pyridine molecule should be least affected by magnetic anisotropy effects originating from the surrounding π -electron clouds. Its continuous deshielding upon going from free pyridine ($\delta(^1\text{H})/\delta(^{13}\text{C}) = 7.67/136.1 \text{ ppm}$)^{11b} to $\text{B}(\text{C}_6\text{F}_5)_3\cdot\text{py}$ (8.21/143.2 ppm)^{11b} and $[2\cdot\text{py}][\text{B}(\text{C}_6\text{F}_5)_4]$ (8.56/147.8 ppm) therefore indicates increasing charge polarization induced by increasingly strong N-B donor-acceptor binding (cf. $[\text{Hpy}]\text{Cl}$: 8.51/146.1 ppm (ref. 11b)). Consistent with this, the N(py)-B bond in $[2\cdot\text{py}][\text{B}(\text{C}_6\text{F}_5)_4]$ (1.603(3) Å) is shorter than that in $\text{B}(\text{C}_6\text{F}_5)_3\cdot\text{py}$ (1.614(2) Å,³⁷ 1.628(2) Å (ref. 38)), but identical to the N-B bond in the adducts $[\text{B}\cdot\text{py}][\text{O}_3\text{SCF}_3]$ (1.599(4) Å (ref. 11b)) and $\text{B}(\text{C}_6\text{F}_5)_3\cdot\text{DMAP}$, which contains the stronger donor *p*-dimethylaminopyridine (1.602(6) Å (ref. 39)).

We also performed competition experiments using the combinations $[2\cdot\text{Do}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{B}(\text{C}_6\text{F}_5)_3$ and $[2][\text{B}(\text{C}_6\text{F}_5)_4]/\text{B}(\text{C}_6\text{F}_5)_3\cdot\text{Do}$

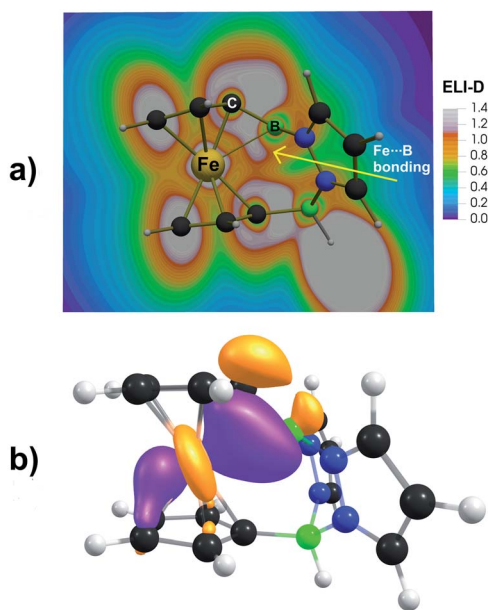


Fig. 3 (a) Electron localizability indicator (ELI-D) analysis of bonding in $[2]^+$. The selected plane includes the Fe and two B atoms. The gray-white regions represent ELF maxima (bonding attractors), showing a donor-acceptor $\text{Fe}\cdots\text{B}$ interaction. (b) Natural localized molecular orbital (NLMO) corresponding to a 3c2e bond between Fe(II), B(sp^2), and the adjacent C_i atom in $[2]^+$ (isosurface plot: $\pm 0.05 \text{ au}$). NLMO composition is as follows: 51% Fe (99% d), 15% B (10% s, 90% p), 26% C (99% p). A similar NLMO picture was obtained for $[2\text{Me}]^+$ with the following composition: 50% Fe (99% d), 14% B (10% s, 90% p), 28% C (99% p).



Scheme 2 Synthesis and solid-state structure of the pyridine adduct [2·py][B(C₆F₅)₄]; C-bonded H atoms and the [B(C₆F₅)₄][−] anion are omitted for clarity. Reagents and conditions: (i) CHCl₃, room temperature. R = C₆F₅.

in CD₂Cl₂ (Do = Et₃PO or pyridine). Irrespective of the ligand employed, we found that the transfer of Do from B(C₆F₅)₃ to [2]⁺ was faster and occurred to a much higher extent than *vice versa*, which clearly points to a higher Lewis acidity of [2]⁺ compared to B(C₆F₅)₃ (see the ESI[†] for plots of corresponding NMR spectra). A quantitative determination of exchange-equilibrium constants was not possible, because [2][B(C₆F₅)₄] is not stable over the long term toward B(C₆F₅)₃. An observed slow increase in the amount of B(C₆F₅)₃·Do over the course of several days may therefore well be preceded by a slow B(C₆F₅)₃-induced degradation of [2]⁺/[2·Do]⁺ and subsequent trapping of the released ligand by B(C₆F₅)₃.

To confirm the exceptionally strong Lewis acidity of [2]⁺ indicated by the above experiments, we compared the Et₃PO affinities and Gutmann–Beckett acceptor numbers for [2]⁺/[2Me]⁺, the Ru/Os congeners of [2]⁺, a series of structurally related neutral/ionic Fe–B Lewis acids, and variously substituted boranes also on the basis of quantum-chemical calculations (Table S7 and Fig. S67, S68[†]). When taking into account the solvation and counterion effects (where appropriate), we observe a very good correlation between experimental and computed ³¹P NMR shifts for a range of 28 Lewis acid adducts with Et₃PO (Table S7 and Fig. S67[†]); the linear regression is improved almost to perfection (*R*² = 0.991) when the data points for the boron trihalides BX₃ are omitted (X = F, Cl, Br, I). In accordance with the experimental NMR studies, the DFT calculations indicate that [2]⁺ is one of the strongest Lewis acids among hitherto reported boron-containing species.

Given that the assessment of Lewis acidity based on the Gutmann–Beckett method is sometimes under criticism, in particular when comparing the Lewis acidity of ionic and neutral borane species,⁴⁰ we also calculated the F[−]-ion affinities (FIAs) for the above series of Lewis acids (Table S9[†]). The calculations were performed along the lines of Christie's method using F₂CO as the standard, which avoids the theoretical treatment of free F[−] in the gas phase.^{41,42} Fig. S69 and S70[†] show that there is a reasonably good correlation between the computed FIAs and the ³¹P NMR shifts, acceptor numbers, and Et₃PO affinities for all compounds

studied. Thus, also according to the FIAs, [2]⁺ is one of the strongest Lewis acids among the boron-containing systems: Apart from Ingleson's transient [CatB][CbBr₆] (Cat = catecholato, [CbBr₆][−] = [*closo*-1-H-CB₁₁H₅Br₆][−]),⁴³ [2]⁺ outperforms all neutral and ionic Fe–B species as well as variously substituted boranes and borenium ions, including Corey's oxazaborolidinium cations [C]⁺,⁴² and Jäkle's borenium Lewis acids.⁴⁰ A borderline case is the hypothetical free 9-phosphonium-10-boratriptycene cation, which could not yet be isolated (*cf.* the structural motif of **D** featuring a [PH]⁺ rather than a CH group at the bridgehead position; Fig. 1):^{17a} while the computed Gutmann–Beckett acceptor number of [2]⁺ is higher than that of 9-phosphonium-10-boratriptycene (AN_{calcd} = 110 *vs.* 83; Table S7[†]), the FIA of [2]⁺ is lower (FIA = 396 *vs.* 474 kJ mol^{−1}; Table S9[†]).

We finally note that replacing the Fe(II) center in [2]⁺ with Ru(II) or Os(II) leads to more shielded ³¹P nuclei in corresponding Et₃PO adducts, which indicates a reduced Lewis acidity of the B⁺ centers, consistent with stronger M → B donation (see above).

Optoelectronic properties of 1/[2][B(C₆F₅)₄] and 1Me/[2Me][B(C₆F₅)₄]

Cyclic voltammograms and UV/vis spectra were recorded in CH₂Cl₂ at room temperature. The Fe(II)/Fe(III) transitions of **1** and **1Me** occur at half-wave potentials of *E*_{1/2} = −0.23 V and −0.32 V, respectively (*vs.* FcH/FcH⁺). Their 1,1'-fc moieties are therefore easier to oxidize than the reference compound ferrocene, indicating a net electron-donating effect of the two tetracoordinated B substituents. Jäkle *et al.* reported on a pronounced Lewis acidity enhancement of neutral dibora-diferrocenes upon oxidation of their 1,2-ferrocenylenes moieties.⁴⁴ In a similar vein, we have also attempted the Fe-centered oxidation of [2][B(C₆F₅)₄] and [2Me][B(C₆F₅)₄] with the goal of generating dicationic borenium ions, but have not been successful so far. The longest-wavelength absorptions of **1** and **1Me** in CH₂Cl₂ are broad and appear at λ_{max} = 451 nm, near the most bathochromic band in the UV-vis spectrum of parent ferrocene (441 nm).⁴⁵ The experimentally determined absorption maximum is well reproduced by TD-DFT calculations on **1**, which predict a transition at λ_{max}(calc) = 447 nm (*f*_{OSC} = 0.001), attributable to a charge transfer from the 1,1'-fc unit to the pyrazole rings (HOMO−1 → LUMO). [2][B(C₆F₅)₄] and [2Me][B(C₆F₅)₄] show their longest-wavelength absorptions at λ_{max} = 378 and 391 nm, respectively (CH₂Cl₂; Fig. 4). According to TD-DFT calculations, the first absorption peak of [2]⁺ at λ_{max} = 378 nm (λ_{max}(calc) = 383 nm; *f*_{OSC} = 0.004) is mainly associated with a charge transfer from Fe(II) d-orbitals (HOMO−2) to the Cp rings (LUMO+1). The second intense peak at 309 nm (λ_{max}(calc) = 317 nm; *f*_{OSC} = 0.082) can be attributed to an Fe(II) → B₂p_z (HOMO−2 → LUMO) transfer (Fig. 4). However, the transferred electron density accumulates predominantly at the p_z moieties, and the charge at the B⁺ center does not change much upon excitation (Table S12[†]) due to the delocalized nature of the corresponding MOs (ground-state [2]⁺: *q*(B(2p)) = 0.90 e[−], excited-state [2]⁺: *q*(B(2p)) = 0.91 e[−]).



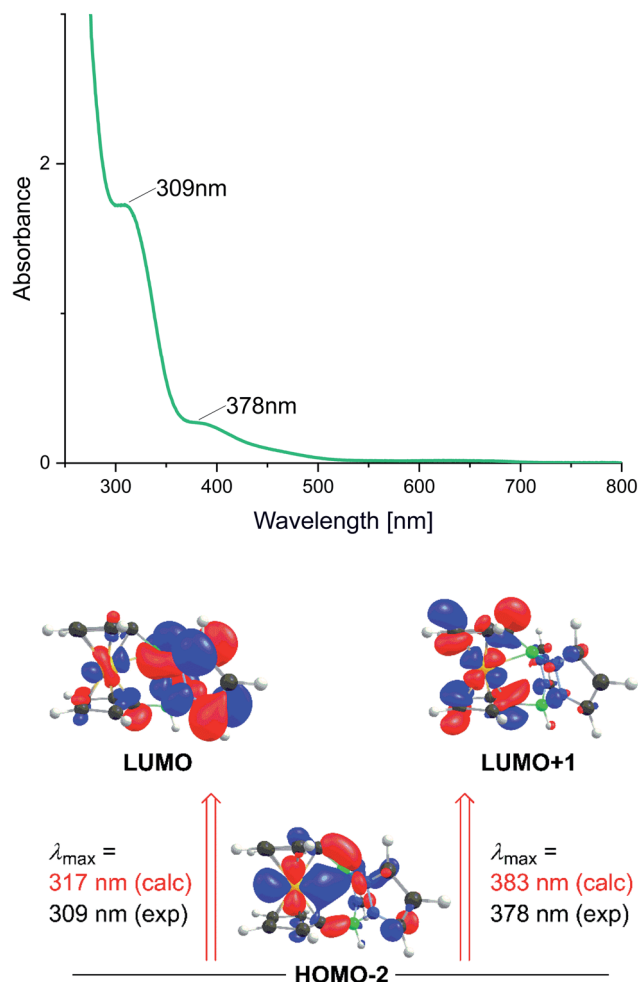


Fig. 4 Top: experimentally determined UV/vis absorption spectrum of $[2][B(C_6F_5)_4]$ in CH_2Cl_2 . Bottom: computed key molecular orbitals of $[2]^+$ and lowest energy electronic transitions (TD-DFT PBE0-10HF/def2-TZVP/ CH_2Cl_2).

Conclusions

By exploiting the facile self-assembly of the pyrazabole scaffold, we have devised a straightforward route to boratriptycene-type precursors that have two pyrazole bridges and one 1,1'-ferrocenylene linker between two bridgehead BH moieties (**1**, **1Me**). H^- abstraction with the $[Ph_3C]^+$ cation generates bridgehead borenium cations of exceptional Lewis acidity that can nevertheless be isolated in free form ($[2][B(C_6F_5)_4]$, $[2Me][B(C_6F_5)_4]$). A weak Fe–B(sp^2) through-space interaction likely assists in stabilizing the systems without appreciably diminishing their electron-pair affinities. Although the borenium centers of $[2]^+$ and $[2Me]^+$ adopt trigonal-planar configurations (X-ray crystallography, DFT calculations), huge dips of the B atoms with respect to their attached Cp rings indicate pretensioned 'entatic' states of the molecules,⁴⁶ which should significantly promote Lewis acid–base pairing. Since a plethora of pyrazole derivatives are available, the degree of steric protection of the electrophilic borenium center can be varied easily (*cf.* $[2]^+$ with pyrazole bridges *vs.* $[2Me]^+$ with bulky 3,5-dimethylpyrazole

bridges). By using chiral substituents in the 3,5-positions of the pyrazole rings, even chiral Lewis acids should be within reach. As an outlook, we note that an exchange of Fe for Os would lead to a related Lewis acid that is computed to exhibit a distinct $Os(III)/B^+$ character in its relaxed triplet excited state and thus could open new avenues for exploring the evolving chemistry of *in situ*-generated boron radicals.⁴⁷

Data availability

Experimental and computational data associated with this article have been provided in the ESI.[†]

Author contributions

M. H. synthesized and characterized all compounds. J. N. and P. H. performed all quantum-chemical calculations. A. O. and V. S. recorded and interpreted the Mössbauer spectra. M. B. performed the X-ray crystal structure analyses. H.-W. L. and M. W. supervised the project. The manuscript was written by M. W. and P. H. and edited by all the co-authors.

Conflicts of interest

There are no conflicts of interest to declare.

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