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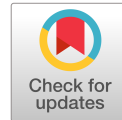
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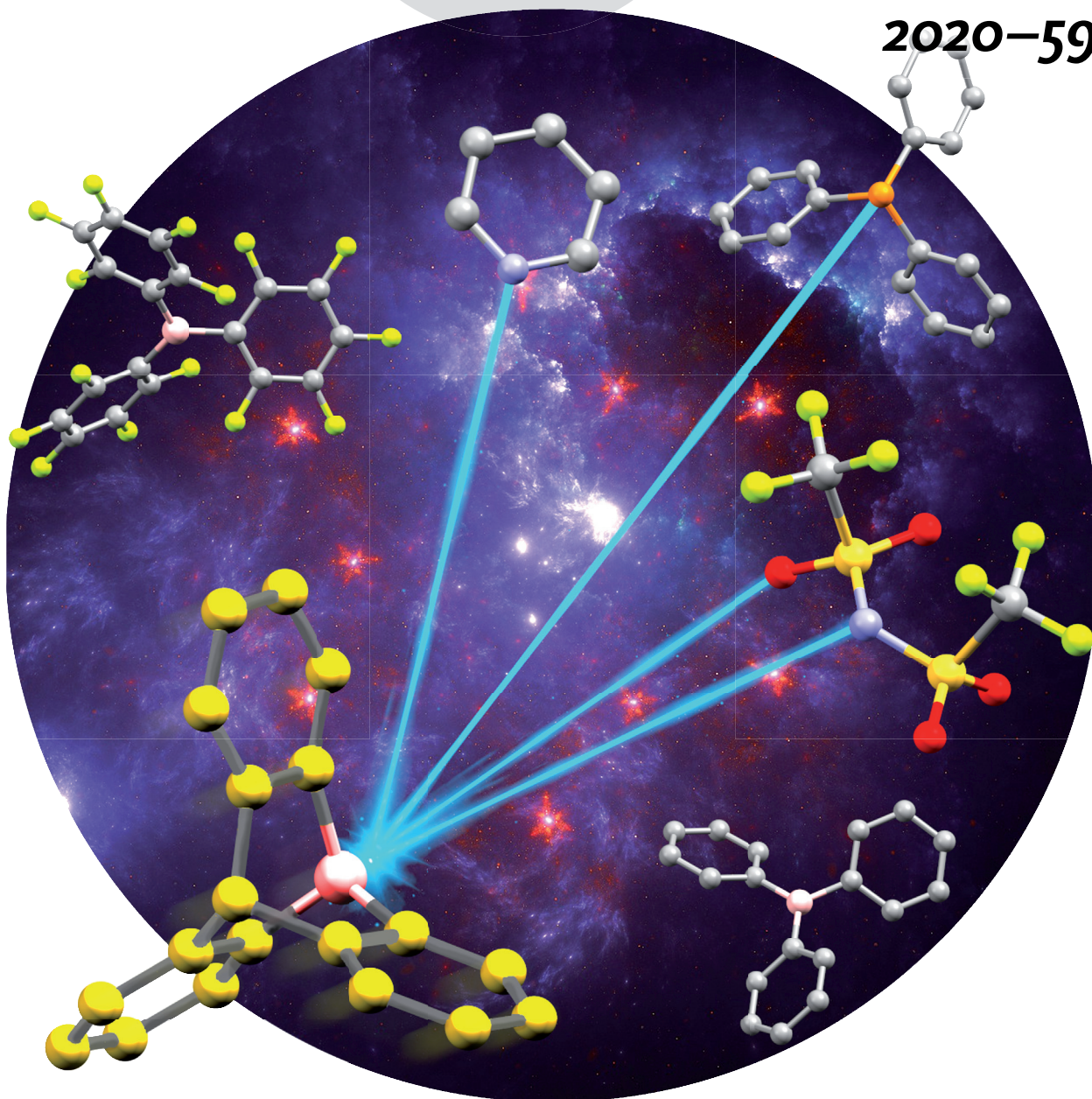
Escaping from the planar geometry ...

… of trivalent boron Lewis acids is enabled by incorporating a boron atom at the edge of the triptycene scaffold. In their Communication on page 12402, G. Berionni and co-workers describe the preparation of the elusive 9-boratriptycene, a triarylborane with unprecedented structure and high Lewis acidity, due to the very low reorganization energy of the triptycene core and the absence of conjugation of its B atom orbitals with the orthogonally oriented aryl rings.

Controlled Generation of 9-Boratriptycene by Lewis Adduct Dissociation: Accessing a Non-Planar Triarylborane

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In memory of Professor Rolf Huisgen

Abstract: *A highly bent triarylborane, 9-boratriptycene, was generated in solution by selective protodeboronation of the corresponding tetra-aryl boron ate complex with the strong Brønsted acid HNTf$_2$. The iptycene core confers enhanced Lewis acidity to 9-boratriptycene, making it unique in terms of structure and reactivity. We studied the stereoelectronic properties of 9-boratriptycene by quantifying its association with small N- and O-centered Lewis bases, as well as with sterically hindered phosphines. The resultant Lewis adducts exhibited unique structural, spectroscopic, and photophysical properties. Beyond the high pyramidalization of the 9-boratriptycene scaffold and its low reorganization energy upon Lewis base coordination, quantum chemical calculations revealed that the absence of π donation from the triptycene aryl rings to the boron vacant p$_z$ orbital is one of the main reasons for its high Lewis acidity.*

Boron Lewis acids are archetypal trigonal planar Lewis acids with numerous applications in materials sciences and catalysis.[1] Numerous stereoelectronic factors affect the boron atom Lewis acidity, such as lone pair donation to the boron vacant orbital in boronates[2] and haloboranes,[3] the steric shielding of the substituents, the extent of conjugation with contiguous aromatic π-systems,[4] and the reorganization energy (RE) upon coordination with a Lewis base.[5]

Preventing structural reorganization by coercing boron Lewis acids into a rigid and fully planar geometry with linkers and tethers between the boron substituents was recently shown to be a powerful strategy to design new π-conjugated materials with high robustness and stability.[4] In contrast, embedding a tricoordinate boron atom in cage-shaped or pyramidal scaffolds, thus forcing the boron environment to adopt an unconventional pyramidal geometry, enhance Lewis acidity strikingly, as in 1-boraadamantane **1** (Scheme 1).[5,6]
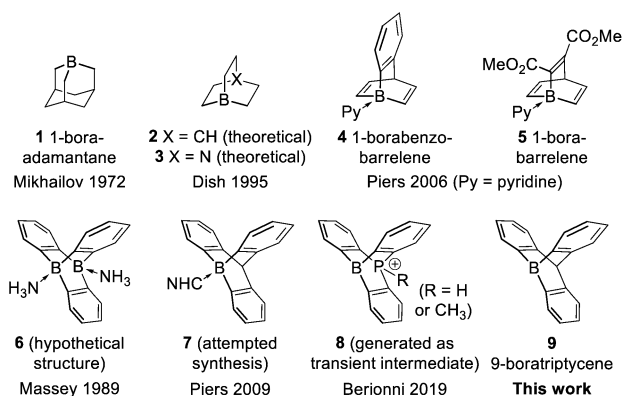
Scheme 1. Known and theoretical pyramidal boron Lewis acids **1**–**9**.

The out-of-plane distortion of the boron atom is smaller in **1** and in the borabicyclo[2.2.2]octane derivatives **2**–**3**[7] than in the Lewis base free borabarrelene derivatives **4**–**5** (Scheme 1). However, the Lewis-base-free borabarrelene and benzoborabarrelene Lewis acids have not been obtained experimentally in their trivalent form because of the high dissociation energies of the attached pyridine (or phosphine) Lewis bases.[8]

Non-planar triarylboranes belonging to the triptycene family, such as the 9,10-bis-boratriptycene **6** first mentioned by Massey in 1989,[9] and the *N*-heterocyclic carbene (NHC)-protected 9-boratriptycene **7** nearly reached by Piers in 2009,[10] are not experimentally known. The synthesis of the parent 9-boratriptycene **9** has remained an open challenge for the past three decades (Scheme 1).

Recent quantum chemical investigations indicated that, owing to its unique tricyclic polyaromatic iptycene core, 9-boratriptycene **9** may potentially be applied to the development of new cryptands,[11] frustrated Lewis pairs[12] and donor–acceptor complexes of noble gases;[13] hence, **9** could be a key boron Lewis acid for unlocking many applications in catalysis and materials chemistry.

In an effort to access 9-boratriptycene derivatives, we recently developed a method to generate the strongly pyramidalized 9-bora-10-phosphatriptycene **8** as a transient Lewis acid with exceptionally high Lewis acidity (Scheme 2a).[14] Though the protodeboronation of **10** proceeded selectively at the exocyclic C–B bond (Scheme 2a), disappointingly, protodeboronation of the 9-phenyl-boratriptycene

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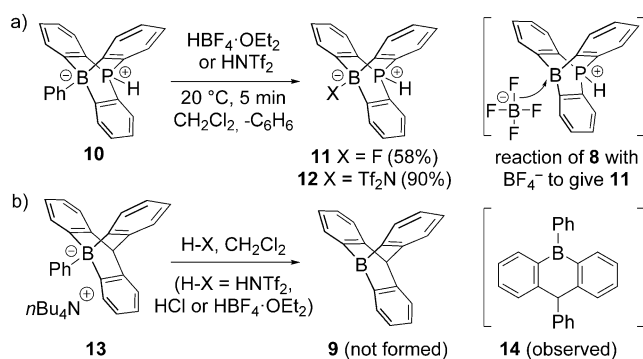
Scheme 2. a) Generation of 10-phosphonium-9-boratriptycene **8**.
b) Unsuccessful attempts to generate 9-boratriptycene **9** and formation of **14**.[14]

ate complex **13** lacking a phosphonium bridge occurred at an intracyclic C−B bond, thus preventing the formation of 9-boratriptycene **9** (Scheme 2 b).[14]

We designed a synthetic route for production of **9** in solution and trapped it with a series of O-, N-, and P-centered Lewis bases. Characterization of these Lewis adducts by X-ray diffraction, nuclear magnetic resonance (NMR), infrared (IR), and UV/Vis spectroscopies revealed that **9** exhibits a higher Lewis acidity than all non-planar boranes known to date. Quantum chemical calculations revealed that the absence of π donation from the triptycene aryl rings to the orthogonal p_z B vacant orbital is a key factor, in addition to the strain that avoids the planar geometry, conferring very high Lewis acidity to **9**.

To produce 9-boratriptycene **9**, we reasoned that replacing the phenyl ring in **13** with a more electron-rich[15] -C_6H_4tBu ring, as in the boron ate complexes **15a–c**,[16] should favor a selective exocyclic C−B bond protodeboronation (Scheme 3) and avoid a competing protodeborylation leading to the cleavage of the C−B bond part of the triptycene skeleton. When treating **15a** with one equivalent of $HNTf_2$ in CD_2Cl_2, the colorless solution became deep yellow in color and ^1H NMR spectroscopy indicated spontaneous consumption of **15a** and formation of tBuC$_6$H$_5$.

The ^{11}B NMR spectra showed a broad signal at 60 ppm consistent with a three-coordinated boron atom[17] but downshifted from the predicted value of 92 ppm (GIAO-DFT at

the B3LYP/6–311 + G(2d,p)//M06-2X/6–311G(d) level of theory), suggesting a reversible coordination of **9** with Tf_2N^- (Scheme 3; Supporting Information).
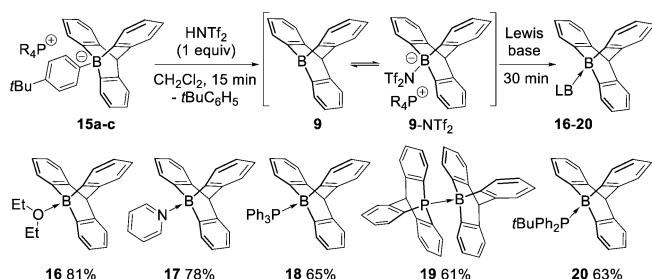
Subsequently, we performed the addition of selected Lewis bases to **9** and observed the rapid disappearance of the ^{11}B NMR signal at 60 ppm and the formation of the Lewis adducts **16–20**, which have been isolated in good yields after flash chromatography (Scheme 3).

The molecular structures of **16–19** in the solid state were determined by single-crystal X-ray diffraction (Figures 1 and 2). The B−N distance in **17** (1.594(2) Å) is shorter than in the pyridine−B(C$_6$F$_5$)$_3$ Lewis adduct (1.614(2) Å)[18] and similar to that in the pyridine Lewis adduct **4** (1.584(2) Å),[8] which is one of the shortest B−N bond lengths reported with a neutral boron Lewis acid.

Steric repulsions between the boratriptycene peri-hydrogen atoms and the pyridine moiety caused its deviation by a tilt angle β of 15° from the triptycene central B···C axis (Figures 1 c,d). The pyramidalization angle α in **17** (23.8°) is higher than in the Lewis adducts of pyridine with B(C$_6$F$_5$)$_3$ (17.6°)[18] or 1-boraadamantane (20.0°)[19] and comparable to that in the borabarrelene adduct **5** (24.5°).[8]

The 9-boratriptycene−PPh$_3$ Lewis adduct **18** featured one of the shortest B−P bonds (1.976(4) Å) reported to date for Ar$_3$B−PAr$_3$ Lewis adducts (Figure 2). For minimizing steric repulsions, the 9-boratriptycenyl aryl rings and the phosphine phenyl groups adopted a staggered conformation with CPBC torsion angles of 44° in the solid state.

The Lewis adduct **19** of 9-phosphatriptycene[20] with 9-boratriptycene is a unique P/B isostructural analogue of the highly congested 9,9′-bistriptycene[21] where the rotation around the Csp^3−Csp^3 bond (1.558(3) Å) connecting the two triptycenes is locked (rotation barrier > 225 kJ mol^{-1}). In the case of **20**, the tBu substituent precluded rotation around the
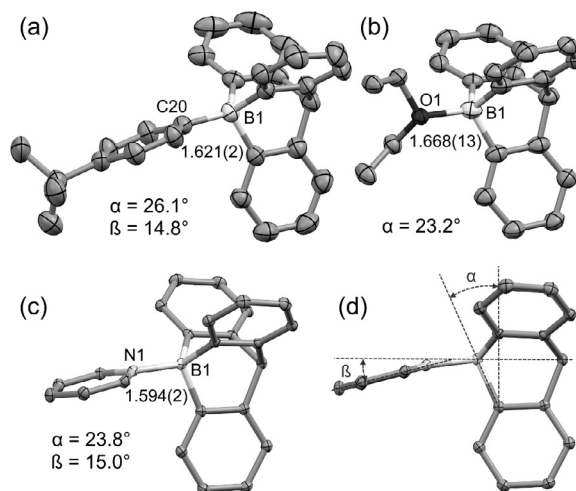

Figure 1. Molecular structures of a) **15a** with the Ph$_4$P$^+$ counter ion omitted, b) the Lewis adduct of 9-boratriptycene with Et$_2$O (**16**), and c) 9-boratriptycene with pyridine (**17**). d) A side view of **17** showing the out-of-plane twisting of pyridine (tilt angle β) and the pyramidalization of the boron atom (defined as pyramidalization angle α). H-atoms and solvate molecules are omitted for clarity; thermal ellipsoids are represented with a 50% probability level; bond lengths [Å].
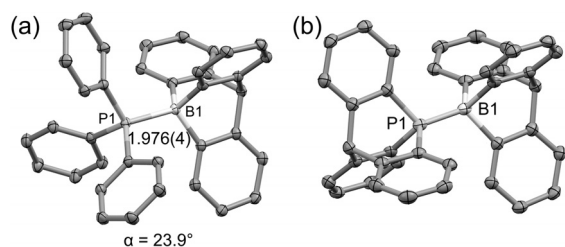

Scheme 3. Generation of 9-boratriptycene **9** in equilibrium with Tf$_2$N$^-$ in solution and formation of its Lewis adducts **16–20**.[16] In **15a–c** R$_4$P$^+$ = MePh$_3$P$^+$, nBu$_4$P$^+$, or Ph$_4$P$^+$, respectively.

Figure 2. Molecular structures of the Lewis adducts a) **18** and b) **19**. H-atoms and solvate molecules are omitted for clarity; thermal ellipsoids are represented with a 50% probability level; bond lengths [Å].

P–B bond on the NMR timescale, as evidenced by ^{1}H, nuclear Overhauser effect spectroscopy (NOESY), total correlation spectroscopy (TOCSY), and variable-temperature NMR (VT-NMR) spectroscopy measurements up to 75°C (Supporting Information).

Thermogravimetric analysis (TGA) showed that the Lewis adduct **16** undergoes a mass loss beginning at 175°C with a 20.6% weight loss consistent with the Et_2O dissociation (calc. 22.0%), while for **17** a single-stage decomposition process is observed (180–250°C). The Lewis acidity of **9** was quantified by IR and NMR spectroscopy investigations of its Lewis adducts with $OPEt_3$, CH_3CN, and EtOAc (Scheme 4, Figure 3).

According to the Gutmann–Becket scale,[22] the δ^{31}P chemical shift of 75 ppm in **21** indicated that 9-boratriptycene **9** has a smaller acceptor number (AN = 76) and is apparently a weaker Lewis acid than $B(C_6F_5)_3$ (AN = 80)[2a] for the $OPEt_3$ Lewis base.

In contrast, IR spectroscopy showed that the CN stretching vibration (2337 cm^{-1}) of **22** is similar to Greb's bis(perchlorocatecholato)silane (2335 cm^{-1}),[23] and blue shifted by
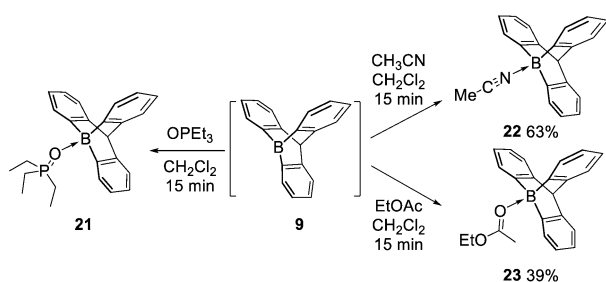
88 cm^{-1} with respect to free CH_3CN.[24] The $\nu_{C=O}$ stretching vibration of EtOAc in **23** (1603 cm^{-1})[25] and in $B(C_6F_5)_3$ (1648 cm^{-1})[14] also indicated that **9** is a stronger Lewis acid than $B(C_6F_5)_3$.

Quantum chemical calculations were thus undertaken to evaluate the RE of **9** and of other boron Lewis acids upon complexation with H$^-$, F$^-$, NH_3, PPh_3, and pyridine (Table 1). With NH_3, a RE of 45 kJ mol^{-1} is calculated for **9**, which is nearly identical to that of 1-boraadamantane **1** and 1-borabarrelene **24** (Table 1) and consistent with the data of Timoshkin.[5a] The RE of **9** increases up to 55 and 58 kJ mol^{-1} upon coordination with PPh_3 and pyridine, respectively, again similar to that of **1** and **24**. The REs of **9** are 14 to 87 kJ mol^{-1} lower than those of BPh_3 **25**, showing that structural REs account for up to 50% of their Lewis acidity difference in terms of Lewis bases affinities (Table 1).

In line with the calculated NH_3, PPh_3, HIA, and FIA affinities, the global electrophilicity index (GEI) predicts that **9** (1.20) is more electrophilic than **1** (0.88) and **24** (1.02). However, as GEIs are global quantities based on the ground-state properties of Lewis acids (highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital energy levels) in their initial geometries, reorganization energies are not considered, and GEI values erroneously indicated that BPh_3 **25** and $B(C_6F_5)_3$ **26** are stronger Lewis acids than **9** (Table 1), contradictory to experimental spectroscopic data and calculated Lewis bases affinities. In contrast, the local electrophilicity index ω_B of the B atom reflected the Lewis acidity trends for all boranes correctly.

Competition experiments showed that **9** is a weaker Lewis acid than $B(C_6F_5)_3$ **26** for the small and anionic Lewis bases H$^-$ and F$^-$, but it is stronger than **26** for neutral Lewis bases from NH_3 to PPh_3, which agrees with the computed values (Supporting Information).

As a consequence of the strained nature of **9**, the p_π orbitals of the triptycene aryl rings and the formally vacant $2p_z$ orbital of the boron atom are nearly orthogonal to each other, precluding any stabilizing overlap or π-electron delocalization. This is clearly visualized when comparing the HOMO-5 and LUMO orbitals of BPh_3 **25** and 9-boratriptycene **9** (Figure 4). In **9**, the LUMO is principally located on the $2p_z$ boron orbital (Figures 4 a,b), whereas it is distributed over the whole p_π carbon orbital of its phenyl substituents in BPh_3 **25** (Figure 4 c), indicating a high contribution of the p_π orbitals to the LUMO. The HOMO-5 of **25** shows an entire distribution and an overall orbital overlap over the B atom and aromatic π-system (Figure 4 d), which is not the case in **9**.

Calculations of natural bond orbital (NBO)[28] and of natural charges on the boron atom confirmed the low contribution of the p_π to the formally empty orbital of the boron in **9** (Scheme 5).

Indeed, the electron occupancy of the $2p_z$ boron orbital of triphenyl boranes increases linearly from 0.22 to 0.26 e$^-$ when adding up to three electron-donating -NMe$_2$ groups at the *para* positions. In contrast, the electron occupancy of the $2p_z$ boron orbital of boratriptycenes is very low (0.08 e$^-$) and independent on the number of -NMe$_2$ substituents (Scheme 5, right). The natural charge of the substituted boratriptycenes B atom is equal to +1 and is strictly independent of their NMe$_2$

Scheme 4. Synthesis of the $OPEt_3$, CH_3CN, and EtOAc Lewis adducts of **9**.
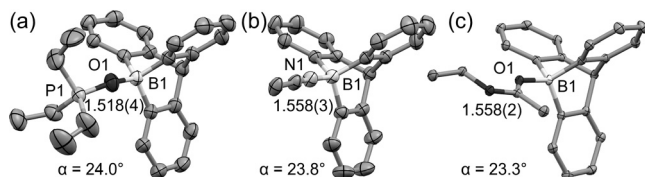

Figure 3. Molecular structures of the Lewis adducts **21**–**23**. Structures are represented as thermal ellipsoids with a 30% probability level; bond lengths [Å].

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Table 1: Pyramidalization of the boron atom α, reorganization energies (REs), and Lewis bases affinities ($-\Delta H^0$)[26] of selected boron Lewis acids with anionic and neutral Lewis bases, as well as the global (GEI) and local (ω_B) electrophilicity index of the B atom of the Lewis acids.[27]

Boron Lewis acids							Lewis bases affinities [kJ mol^{-1}]						
		REs with Lewis bases [kJ mol^{-1}]					Global and local electrophilicities [eV]						
	α[a]	H$^-$	F$^-$	NH$_3$	PPh$_3$	C$_5$H$_5$N	HIA[b]	FIA[b]	NH$_3$	PPh$_3$	C$_5$H$_5$N	GEI	ω_B
BEt$_3$	0.90	125	118	72	81	86	292	285	92	38	86	0.97	−0.67
1-Boraadamantane **1**	11.0	101	91	48	54	59	326	282	74	85	116	0.88	−0.57
1-Borabarrelene **24**	15.4	95	87	45	50	52	412	395	172	164	176	1.02	−1.23
9-Boratriptycene **9**	15.5	92	87	45	55	58	496	476	206	194	200	1.20	−1.50
BPh$_3$ **25**	0	130	174	74	69	113	352	333	88	72	79	1.53	−0.65
B(C$_6$F$_5$)$_3$ **26**	0	144	132	97	82	121	516	466	159	133	144	2.79	−1.23

[a] Pyramidalization angle in degrees (α), [b] hydride ion affinity (HIA), and fluorine anion affinity (FIA). Pseudo-isodesmic reactions have been used, with the HIA of SiMe$_3$H and the FIA of SiMe$_3$F as the anchor point evaluated at the reference G3 level.[2c, 26]
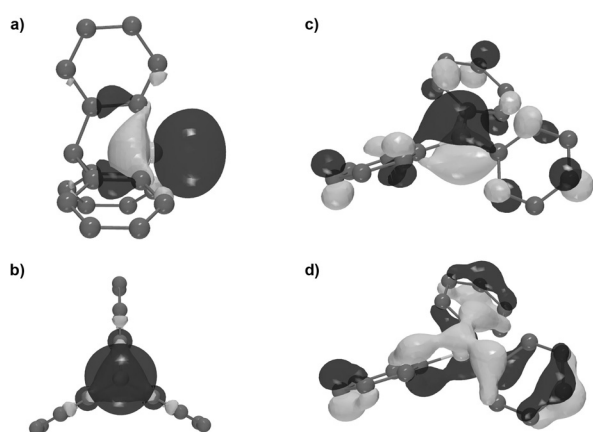
Figure 4. a) A plot of the LUMO (−0.64 eV) of 9-boratriptycene **9**. b) A side view of the LUMO of **9**. c) A plot of the LUMO (−1.12 eV) of triphenylborane **25**. d) A plot of the HOMO-5 (−8.71 eV) of **25**. All plots were derived after M06-2X/6–311G(d) geometry optimization (isosurface value of 0.045 a.u.).[26a]

Number of NMe$_2$ groups	0	1	2	3		0	1	2	3
Occupancy of B	0.22	0.24	0.25	0.26		0.08	0.08	0.08	0.08
B natural charge	0.92	0.89	0.88	0.86		1.00	1.00	1.00	1.00

Scheme 5. Electron occupancy at the formally vacant p empty orbital of the boron atom (in electrons) and natural charge of boron. Calculations at the M06-2X/6–311G(d) level of theory using the Gaussian NBO 3.1 program.[28]

substitution pattern, unambiguously demonstrating the absence of orbital overlap between the π-system and the boron atom because of the geometry (and symmetry) constraints of the triptycene core.

In summary, 9-boratriptycene is a non-conjugated tri-arylborane with no electron delocalization between its aryl rings and the boron 2p$_z$ orbital. In spite of the absence of fluorine substituents, 9-boratriptycene can exhibit a higher Lewis acidity than B(C$_6$F$_5$)$_3$ because of its pyramidal boron

atom, its strained triptycene scaffold with large spaces between the aryl rings, and its low energy of reorganization during coordination with a Lewis base (especially for neutral and large Lewis bases).

The unprecedented reactivity and stereoelectronic properties of boratriptycenes are particularly appealing for the conception of strongly acidic boron Lewis acids. Work is ongoing in our laboratories toward functionalization of the triptycene core with bulky substituents for the design of new sterically hindered and unsymmetrically substituted boron-chirogenic Lewis acids.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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