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

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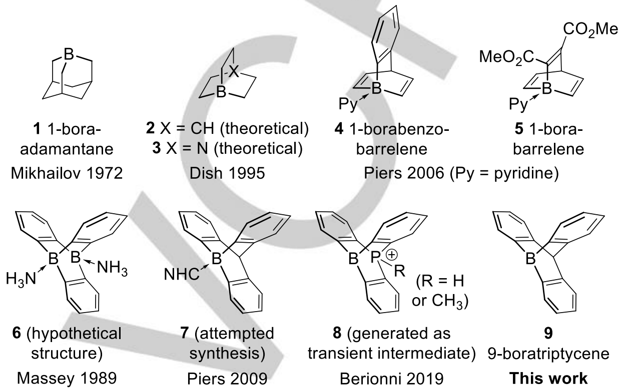
Dedicated to the memory of Professor Rolf Huisgen

Abstract: A highly bent neutral triarylborane, 9-boratriptycene, has been 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-centred 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 Lewis acidity such as the 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 upon coordination with a Lewis base.[5]

Preventing structural reorganization by coercing boron Lewis acids in 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, strikingly enhance its Lewis acidity as in 1-boraadamantane **1** (Scheme 1).[5,6]

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 bora-barrelene derivatives **4**-**5** (Scheme 1). However, the Lewis base free borabarrelene and benzo-borabarrelene Lewis acids have not been obtained experimentally under their trivalent form because of the high dissociation energies of the attached pyridine (or phosphine) Lewis bases.[8]

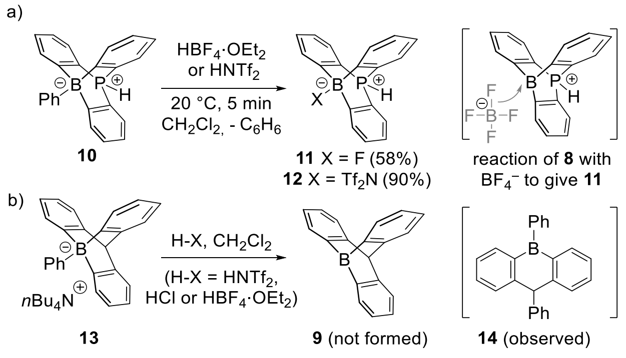


Scheme 1. Known and theoretical pyramidal boron Lewis acids **1**-**9**.

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 NHC-protected 9-boratriptycene **7** nearly reached by Piers in 2009[10] are not experimentally known, and the synthesis of the parent 9-boratriptycene **9** remained an open challenge in the past three decades (Scheme 1).

Recent quantum chemical investigations showed that owing to its unique tricyclic polyaromatic iptycene core, 9-boratriptycene **9** may potentially be applied for developing new cryptands,[12] frustrated Lewis pairs[13] and donor-acceptor complexes of noble gases[14], hence being 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).[11] Though the protodeboronation of **10** proceeded selectively at the exocyclic C-B bond (Scheme 2a), disappointingly, the proto-deboronation of the 9-phenyl-boratriptycene ate-complex **13** lacking the phosphonium bridge occurred at an intracyclic C-B bond, thus preventing the formation of 9-boratriptycene **9** (Scheme 2b).[11]



Scheme 2. a) Generation of 10-phosphonium-9-boratriptycene **8**; b) Unsuccessful attempts to generate 9-boratriptycene **9** and formation of **14**.[11]

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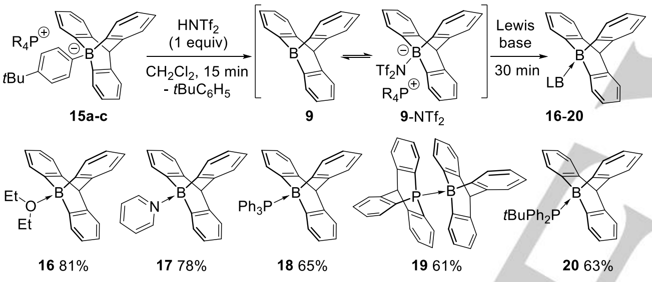
We now designed a synthetic route for producing **9** in solution and trapped it with a series of O-, N- and P-centred Lewis bases. Characterization of these Lewis adducts by X-ray diffraction, NMR, IR and UV-Vis spectroscopy revealed that **9** exhibits a higher Lewis acidity than all non-planar boranes known so far. Quantum chemical calculations showed 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 to **9** its very high Lewis acidity.

For producing 9-boratriptycene **9**, we reasoned that replacing the phenyl ring in **13** by a more electron-rich[15] -C_6H_4*t*Bu ring as in the boron ate-complexes **15a**-**c**[16] should favour a selective exocyclic C-B bond proto-deboronation (Scheme 3) and avoid a competing protodeborylation leading to the cleavage of a C-B bond part of the triptycene skeleton. When treating **15a** with one equivalent of $HNTf_2$ in CD_2Cl_2, the colourless solution turned to deep yellow and ^1H NMR spectroscopy indicated the spontaneous consumption of **15a** and the formation of *t*BuC_6H_5.

The ^{11}B NMR spectra showed a broad signal at 60 ppm, consistent with a three coordinated boron[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^- (See Scheme 3 and SI).

We next performed the addition of selected Lewis bases to **9**, and observed the fast vanishing 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).



Scheme 3. Generation of 9-boratriptycene **9** in equilibrium with Tf_2N^- in solution and formation of its Lewis adducts **16**-**20**.[16] R_4P^+ = $MePh_3P^+$, *n*Bu_4P^+ or Ph_4P^+, respectively in **15a**-**c**.

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-$B(C_6F_5)_3$ Lewis adduct (1.614(2) Å)[18] and similar to that in the pyridine Lewis adduct **4** (1.584(2) Å),[8] 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 (Figure 1c-d). The pyramidalisation angle α in **17** (23.8°) is higher than in the pyridine Lewis adduct of $B(C_6F_5)_3$ (22.2°)[19] and comparable to that in the borabarrelene **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 so far for Ar_3B-PAr_3 Lewis adducts. 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 (Figure 2).

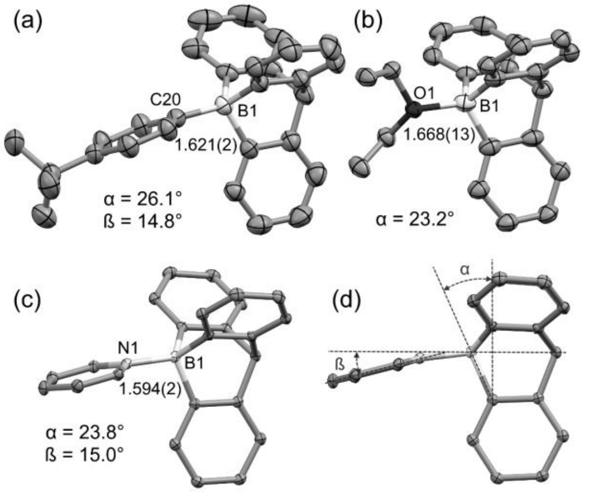


Figure 1. Molecular structures: a) of **15a** with the Ph_4P^+ counter ion omitted; b) of the Lewis adduct of 9-boratriptycene with Et_2O (**16**); c) of 9-boratriptycene with pyridine (**17**); d) side view of **17** showing the out of plane twisting of pyridine (tilt angle β) and the pyramidalisation of the boron atom (defined as pyramidalisation angle α). Here and further structures in Figure 2 are shown in thermal ellipsoids representation with 50% probability level. H-atoms and solvate molecules are omitted for clarity, bond lengths in Å.

The Lewis adduct **19** of 9-phosphatriptycene[20] with 9-bora-triptycene 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 *t*Bu substituent precluded rotation around the P-B bond on the NMR time scale, as evidenced by ^1H, NOESY, TOCSY and VT-NMR spectroscopy measurements up to 75 °C (see the SI).

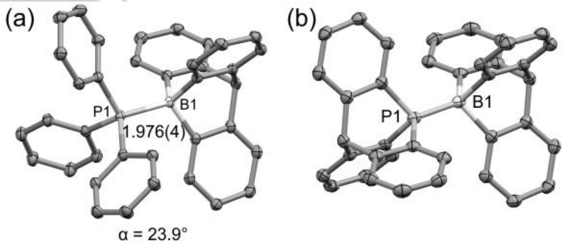
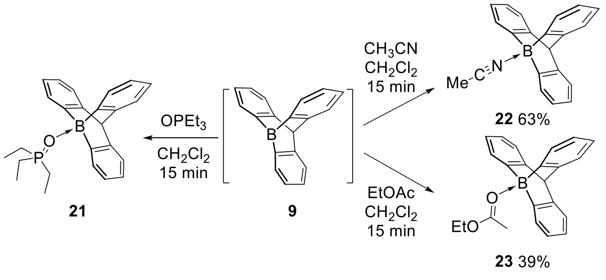


Figure 2. Molecular structure of the Lewis adducts a) **18** and; b) **19**. H-atoms and solvate molecules are omitted for clarity, bond lengths in Å.

TGA analysis 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 $OP(Et)_3$, CH_3CN and EtOAc (Scheme 4 and Figure 3).



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

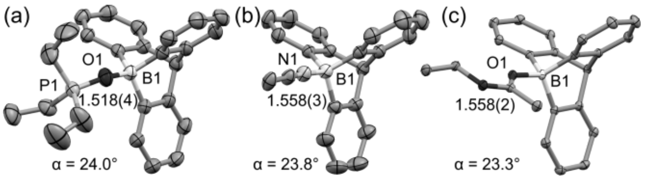


Figure 3. Molecular structures of the Lewis adducts **21**-**23**. Structures are shown in thermal ellipsoids representation with 30% probability level.

According to the Gutmann-Becket scale,[22] the $\delta^{31}P$ 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 than in Greb's bis(perchloro-catacholato)silane (2335 cm^{-1})[24] and blue shifted by 88 cm^{-1} with respect to free CH_3CN.[23] The $\nu_{C=O}$ stretching vibration of EtOAc in **23** (1603 cm^{-1})[25] and in $B(C_6F_5)_3$ (1648 cm^{-1})[11] also indicated that **9** is a stronger Lewis acid than $B(C_6F_5)_3$.

Quantum chemical calculations were thus undertaken to evaluate the reorganization energy (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**, nearly identical to that of **1** and **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 ground-state properties of Lewis acids (HOMO and LUMO 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), in contradiction with experimental spectroscopic data and calculated Lewis bases affinities. In contrast, the local electrophilicity index ω_B of the B atom reflected correctly the Lewis acidity trends for all boranes.

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 is stronger than **26** for neutral Lewis bases from NH_3 to PPh_3, in agreement with the computed values (see the SI).

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

Boron Lewis acids		REs with Lewis bases (kJ mol^{-1})					Lewis bases affinities (kJ mol^{-1}) and global and local electrophilicities (eV)						
	α^a	H^-	F^-	NH_3	PPh_3	C_6H_5N	HIA^b	FIA^b	NH_3	PPh_3	C_6H_5N	GEI	ω_B
triethylborane (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
$B(C_6F_5)_3$ **26**	0	144	132	97	82	121	516	466	159	133	144	2.79	-1.23

[a] α = pyramidalization angle in degrees, [b] HIA= hydride ion affinity, FIA = fluorine anion affinity. Pseudo-isodesmic reactions have been used, with the HIA of $SiMe_3H$ and the FIA of $SiMe_3F$ as the anchor point evaluated at the reference G3 level[2c,26]

Due 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 (Figure 4a-b) whereas it is distributed over the whole pπ carbon orbital of its phenyl substituents in BPh_3 **25** (Figure 4c), 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 4d), which is not the case in **9**.

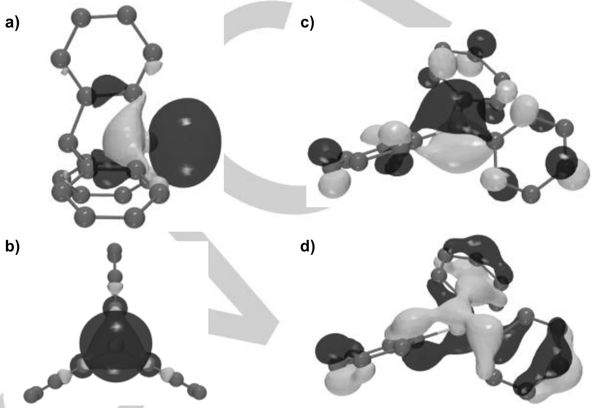
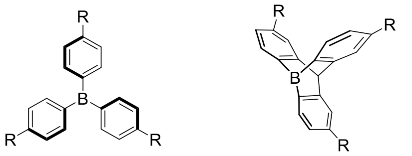


Figure 4. a) Plot of the LUMO (-0.64 eV) of 9-boratriptycene **9**; b) side view of the LUMO of **9**; c) plot of the LUMO (-1.12 eV) of triphenylborane **25**; d) plot of the HOMO-5 (-8.71 eV) of **25**. All were derived after M06-2X/6-311G(d) geometry optimization (isosurface value of 0.045 a.u).[26a]

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).



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]

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). Natural charge of the substituted boratriptycenes B atom is equal to +1 and is strictly independent of their NMe_2 substitution pattern, unambiguously demonstrating the absence of orbital overlap between the π-system and the boron atom due to the geometrical (and symmetry) constraints of the triptycene core.

In summary, 9-boratriptycene is a non-conjugated triarylborane, with no electron delocalization between its aryl rings and the boron $2p_z$ orbital. Due to its pyramidal boron atom, its strained triptycene scaffold with large spaces between the aryl rings, and its low energy of reorganisation during coordination with a Lewis base, 9-boratriptycene, though not having any fluorine substituents, can exhibit a higher Lewis acidity than $B(C_6F_5)_3$ especially for neutral and large Lewis bases.

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

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Keywords: Triarylborane • Non planar boron Lewis acids • Main group chemistry • Triptycene • Lewis adducts

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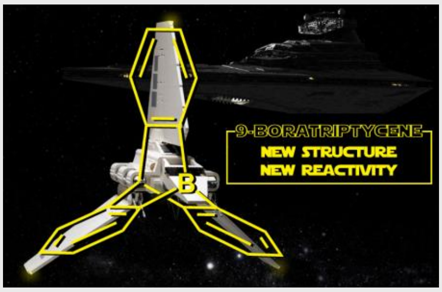

Breaking B-π conjugation: 9-boratriptycene is a uniquely bent and non-conjugated triarylborane with unprecedented geometrical shape, providing it a low reorganisation energy and high Lewis acidity power.

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