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Non-planar Boron Lewis Acids Taking the Next Step: Development of Tunable Lewis Acids, Lewis Superacids and Bifunctional Catalysts

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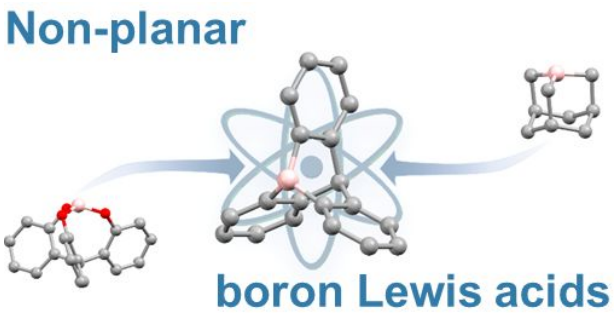
This paper is dedicated to Prof. Paul Knochel with respect and admiration



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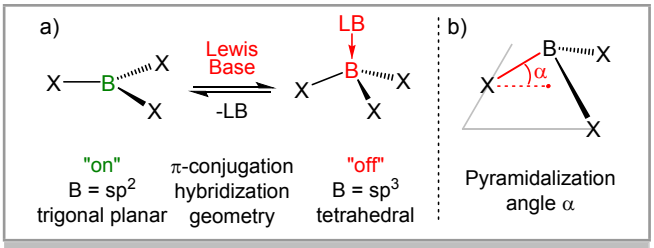
Abstract Though boron **Lewis acids are commonly adopting a trigonal planar geometry, a number of compounds were the trivalent boron atom is located in a pyramidal environment have been described. This review will highlight the recent developments of the chemistry and applications of non-planar boron Lewis acids, including a series of non-planar triarylboranes derived from the triptycene core. A thorough analysis of the properties and of the influence of the pyramidalization of boron Lewis acids on their stereoelectronic properties and reactivities are discussed on the basis of recent theoretical and experimental studies.**

Key words Boron Lewis acids, structural constraint, Lewis superacids, triarylboranes, boratriptycenes

Due to their unique chemical reactivities and physical properties, organoboron compounds are playing an important role in organic chemistry and materials sciences.[1] Trivalent boron compounds are among the most ubiquitous main-group Lewis acids and are widely used as catalysts and chemosensors for coordinating and detecting a large variety of anions, Lewis bases and chemical functionalities.[2]

Coordination of a Lewis base with a trigonal planar boron Lewis acid produces a tetrahedral Lewis adduct, or ate-complex if the Lewis base is anionic, in which the tetravalent boron atom is in a tetrahedral environment. During the Lewis acid-base association event, a large structural reorganization of both constituents occurs and the overlap of the vacant $2p_z$ boron orbital with the orbitals of the adjacent π-system (aryl, vinyl) or atom lone pair (nitrogen, oxygen, halogens) is disrupted because of the formation of a tetrahedral saturated boron atom in the Lewis adduct (Scheme 1).



Scheme 1. a) Association of a Lewis base LB with boron Lewis acid; b) Definition of the pyramidalization angle α.

On one hand, constraining boron Lewis acids into a fully planar geometry by linking the three boron substituents, or embedding the boron atom in flat polyaromatic structures,[3] are recent strategies to design new π-conjugated materials with high chemical stability and low Lewis acidity, featuring unprecedent chemical and photophysical properties.[4] Although the boron atom is readily accessible in such planarized systems, its coordination with Lewis bases is enthalpically disfavoured,

because very large molecular deformations and distortions of the highly planarized edifices would be required for forming a tetrahedral boron atom.[5]

On the other hand, constraining a tricoordinate boron atom in a cage-shaped or pyramidal scaffold for obtaining boron Lewis acids with enhanced Lewis acidity and pyramidal geometry (Scheme 1b) is an underexplored strategy for the design of new Lewis acids and boron materials.

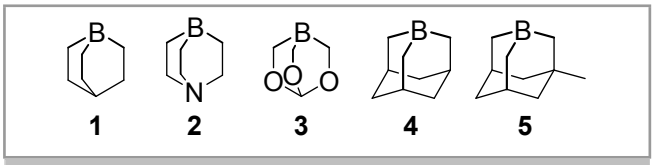
The scope of this article is to review the developments of the chemistry and applications of non-planar boron Lewis acids and highlight the latest developments of non-planar triarylboranes by our research group.

1. Non-planar trialkylboranes

Ring or cage-strained trialkylboranes with a pyramidal trivalent boron atom such as the borabicyclo[2.2.2]octanes **1**-**3** and the 1-boraadamantane **4-5** (Scheme 2) were the focus of several quantum chemical calculations. Paddon-Row, Radom and Gregory were the first to study a cage-shaped boron compound in the form of aza-borabicyclo-[2.2.2]octane **2**.[6] The goal of their investigation was to study bond-stretch isomerism in propellane derivatives based on the assumption that such compound would be less prone to decomposition than **1**.[7]

Schulman and Disch later investigated the structures of a series of bora-azapropellanes for understanding the nature of the B-N bonding with inverted tetrahedral configurations. More recently, trioxa-borabicyclo octane **3** and other tricylic boranes with a pre-pyramidalization of the boron center were computed to be ideal Lewis acids for the formation of unsupported donor–acceptor complexes with Lewis basic metal fragments such as [Pt(NHC)$_2$] (see section 4).[8]

Both 1-borabicyclo[2.2.2]octane (**1**) and 1-boraadamantane (**4**) are almost equally pyramidal (pyramidalization angles ~10°)[9] and have free energies of complexation with pyridine $\Delta G°_{py}$ of ≈ -12 kcal mol^{-1}, illustrating that they are stronger Lewis acids than their planar analogue BEt_3 ($\Delta G°_{py}$ = -5 kcal mol^{-1}).[9e]



Scheme 2 Cage-shaped trialkylboranes **1-5** with trivalent pre-pyramidalized boron centers.

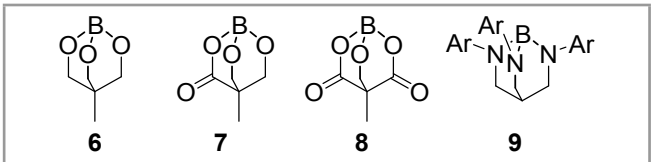
Only a few non-planar trialkylboranes derived from 1-bora-adamantane **4** have been isolated and investigated experimentally,[9] and the derivative **5** is the only structurally characterized Lewis base free boraadamantane derivative.[9f] Gas-phase electron diffraction structural determination showed that the B-C bonds in compound **5** are shorter than those in trimethylborane and triallylborane and are close to those in trivinylborane due to σ(C-C)→p(B) hyperconjugation.[9f]

On the basis of DFT calculations and NMR spectroscopy, Wrackmeyer and Tok found further evidences that the boron atom of trialkylboranes is involved in hyperconjugation with the vicinal C-C sigma bonds and that hyperconjugation was the strongest in the case of **4**.[10] For applications of bora-adamantane derivatives, see *section 4*.

2. Non-planar trialkyl and triaryl boronates

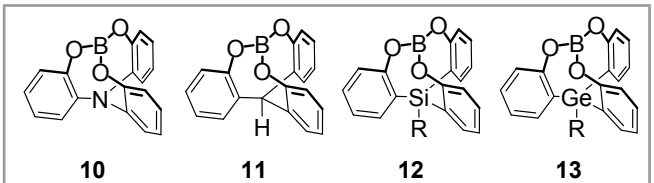
Cage-shaped triol and carboxylic ester boronates **6-9** were recently employed as boron Lewis acids with strong affinity for binding small anions such as F$^-$ (Scheme 3).[11] This binding was exploited for developing anion carriers for batteries in non-aqueous solvents (typically aprotic solvents) that have little ability to solvate such anions. In this context, boranes R_3B and Ar_3B have limited application due to their instability in strongly reducing conditions. Compounds **6-9** are easily accessible and their Lewis acidity is modulated by the substitution of the triol precursors. The association of **7** (^{11}B NMR = 21.6 ppm) with various F$^-$ sources lead to the formation of fluoroborate complexes with ^{11}B chemical shifts at ≈ −50 ppm.[11]

The group of Chen developed analogous tripodal amido-boron complexes **9** based on Gade's tripodal triamido ligands.[12] They successfully obtained the trivalent boron compound **9** which exhibited Lewis acidic properties and was characterized by X-ray diffraction analysis.



Scheme 3 Cage-shaped triol, carboxylic ester and amino boronates **6-9.**

Triarylboronate derivatives with a tethered central carbon atom were studied theoretically and experimentally. The cage-shaped aryl boronates **10-13** of Burgi[13] and Yasuda[14] are exhibiting a high Lewis acidity due to their geometry which prevent the overlap and the donation of the oxygen atoms lone pairs in to the boron 2p$_z$ vacant orbital as in classical arylboronates $(ArO)_3B$ (Scheme 4). For example, the complexation of pyridine with the cyclic arylboronate **11** (R = H) is much stronger (ΔE = −19 kcal mol^{-1}) than for the open-shaped $B(OPh)_3$ (ΔE = −5 kcal mol^{-1}).



Scheme 4 Cage-shaped triaryl boronates **10-13**.

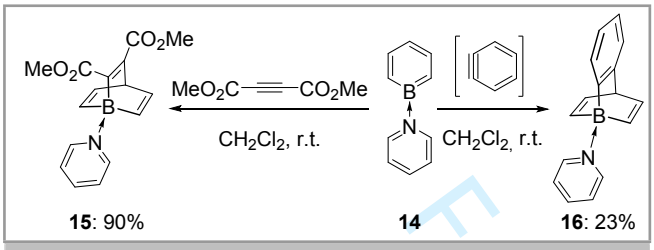
The group of Yasuda performed a series of structural modifications aiming at increasing the Lewis acidity of the boron center of the cage-shaped borate esters **11-13**.[14] They found that a) a weakened π-conjugation between the vacant *p* orbital of the boron and the lone pairs of the neighboring oxygens and b) a transannular p$_\pi$-σ* interaction with a tethered heteroatom (Si, Ge) allowed to further increase and fine-tune the reactivity of the boron center.[14]

The cage-shaped boronates **10**-**13** were efficient catalysts for the Diels-Alder reaction and showed significantly improved catalytic activities in comparison with common triarylboronates such as $B(OPh)_3$.[14b-c]

3. Non-planar alkenyl and aryl-boranes

3.1 Previous investigations on bora barrelenes and triptycenes

In the past two decades, several computational investigations of the stereoelectronic properties and reactivities of iptycenes-embedded boranes highlighted their unprecedent stereoelectronic properties and Lewis acidities. In 2006, Piers reported a synthetic protocol in order to access 1-borabarrelene **15** and 1-borabenzobarrelene **16** *via* a Diels-Alder reaction between Lewis bases stabilized borabenzene **14** and benzyne or electron deficient alkynes respectively (Scheme 5).[15]



Scheme 5 Piers synthesis of pyridine-1-borabarrelene Lewis adduct **15** and pyr-1-borabenzobarrelene **16**.

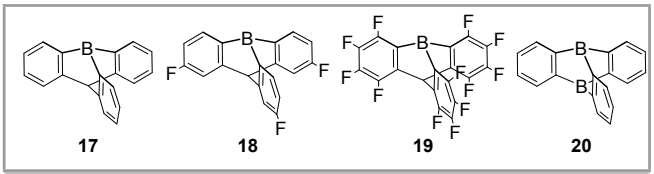
Though the trivalent bora-barrelenes Lewis acids could not be obtained, numerous experimental evidences highlighted their exceptionally high affinity for Lewis bases. First, DSC/TGA analysis shows that the dissociation of pyridine in **16** started at a very high temperature (222 °C), where **15** started melting at 216 °C with a mass loss of 11.3 % which corresponds to a retro Diels-Alder process with loss of acetylene. Furthermore, metrical data derived from X-ray structure determination revealed that the B-N distance in **15** was the shortest observed for a neutral boron Lewis acid.[15]

Boron Lewis acids possessing a partially pyramidal boron atom are expected to exhibit high Lewis acidity, because of lowering of the structural reorganization energy involved during the association with a Lewis base. If the Lewis acid is already pyramidal it has less structural reorganizations to reach a tetrahedral geometry with a sp^3 boron hybridization.

Such effects were already conjectured in a seminal review by Massey in 1989, who described 9,10-bis-boratriptycene **20** (Scheme 6) as an intriguing boron Lewis acid with untypical pyramidal structure and potentially interesting reactivity.

Theoretical calculations by Timoshkin *et al.* in 2012 indeed showed that 9-boratriptycene **17** is a stronger Lewis acid than BPh_3, and even than $B(C_6F_5)_3$, though not having electron-withdrawing substituent on its aryl rings (See Table 1).[16] The boron atom of **17** is at the bridgehead position of a triptycene scaffold, which constrained the trivalent boron atom to adopt a strongly pyramidal geometry, with a pyramidalization angle α of 16° (pyramidalization angle = 0° for BPh_3 and $B(C_6F_5)_3$). The boron atom pyramidalization is defined as the angle formed between the C–B bonds and the plane spanned by the *ipso*-carbon atoms of the three triptycene benzene rings (illustrated in Scheme 1b).

Timoshkin *et al.* took advantage of the pre-pyramidalization (*i.e.* the non-planarity) of the boron Lewis acids to propose a strategy for increasing the Lewis acidity of main group Lewis acids and to design *in-silico* new boron Lewis acids and superacids.[17] Using dissociation energies of the Lewis adduct with NH_3 as a criterion of Lewis acidity strength, they observed that the Lewis acidity of the reference compound BPh_3 was dramatically enhanced (>150 kJ mol^{-1}) when increasing the pyramidalization of the boron atom as in 9-boratriptycene **17**. This structural effect was combined with the substituents effect to design the perfluoro-9-boratriptycene **19** as a new Lewis superacid with higher Lewis acidity than SbF_5 in the gas-phase (Scheme 6).[16]



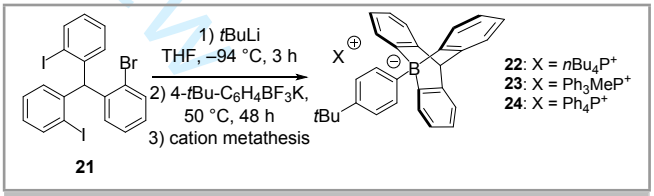
Scheme 6 Cage-shaped boron compounds derived from triptycene with trivalent pre-pyramidalized boron atoms.

The reorganization energy of the acceptor molecule, defined by Timoshkin as "the energy required to transform the geometry of the free Lewis acid into the geometry of the Lewis acid in the donor acceptor complex" is deeply reduced if the Lewis acid is already partially or strongly pyramidal in the initial ground state geometry.[18] Reorganization energies are generally larger for boron-based Lewis acids than for aluminium- and gallium-based Lewis acids due to the smaller size and C-B bond lenghts.

Thus, the gain in reorganization energy when using non-planar boron Lewis acids explains in part the large increase in their Lewis acidity.

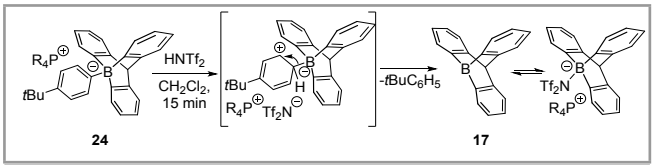
3.2 Recent work on boratriptycenes from our research group.

For synthesizing 9-boratriptycene derivatives and study their properties,[19] we started from a tris-*ortho*-halogenated triphenylmethane precursor **21** and developed a one-pot halogen/lithium exchange reaction followed by a quenching with an electrophilic boron source to obtain a series of 9-boratriptycene ate-complexes **22**-**24** (Scheme 7).



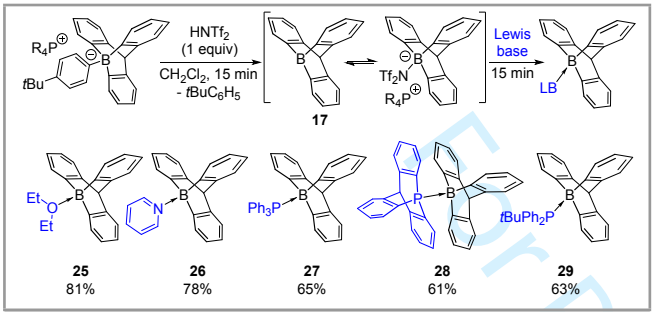
Scheme 7 Synthesis of phosphoniums-9-boratriptycene-ate-complexes **22**-**24**.

When performing the protodeboronation of the exocyclic C–B bond of the *para*-tertbutyl benzene ring of **22**-**23** by the strong bis(trifluoromethane)sulfonimide Brønsted acid ($HNTf_2$) in CD_2Cl_2 or benzene-d_6 the 9-boratriptycene **17** was observed in solution (Scheme 8). Variable temperature NMR spectroscopy measurements combined with quantum chemical calculations highlighted that 9-boratriptycene **17** exists in solution under its free form in equilibrium with its Lewis adduct with the triflimidate counter anion (Scheme 8).[19]



Scheme 8 Generation of 9-boratriptycene as a triflimidate-complexe *via* the selective protodeboronation of **22-24**.

Various 9-boratriptycene Lewis adducts **25-29** were obtained by adding selected Lewis bases to the above reaction mixture, showing that the association of **17** with Tf_2N^- is fast and highly reversible (Scheme 9).



Scheme 9 Formation and isolation of the Lewis adducts **25-29**.

The X-ray diffraction analysis showed that the pyridine Lewis adduct **26** had a B–N distance of 1.594(2) Å, slightly shorter than in the pyridine-$B(C_6F_5)_3$ Lewis adduct (1.614(2) Å) and similar to that in the pyridine Lewis adduct **15** (1.584(2) Å),[15] one of the shortest B-N bond lengths reported with a neutral boron Lewis acid (Figure 1). 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 **26** (23.8°) is higher than in the pyridine Lewis adduct of $B(C_6F_5)_3$ (22.2°) and comparable with the borabarrelene Lewis adduct **15** (24.5°).[15]

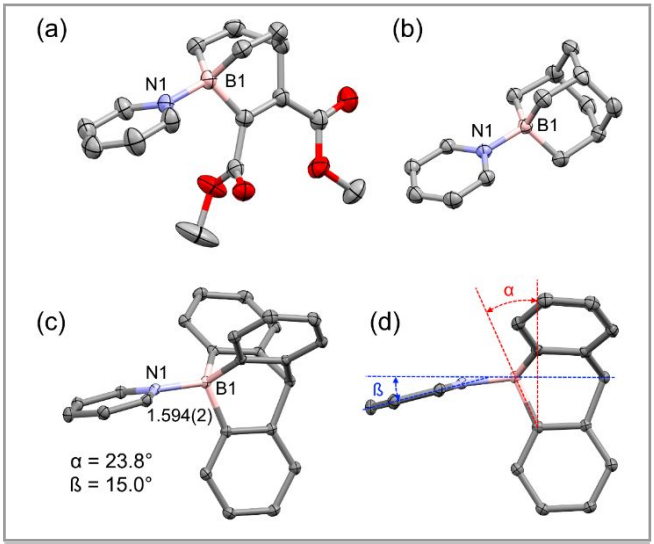
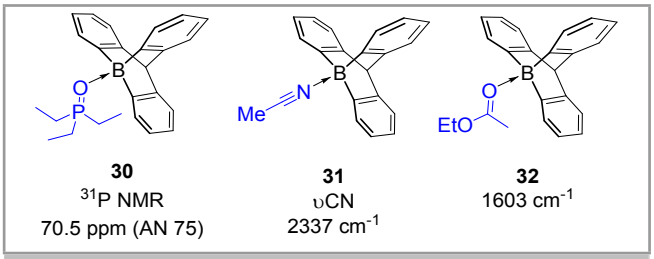


Figure 1 Molecular structures of the Lewis adducts of pyridine : a) with 1-borabarrelene-diester (**15**);[15] b) with 1-boraadamantane Lewis adduct;[9] c) with 9-boratriptycene with pyridine (**26**);[19] d) side view of **26** showing the out of plane twisting of pyridine (tilt angle β) and the pyramidalisation of the boron atom (defined as pyramidalisation angle α). Structures are shown in thermal ellipsoids representation with 50% probability level. H-atoms and solvate molecules are omitted for clarity, bond lengths in Å.

Beside their unique metrical properties derived from X-ray diffraction analysis and the very high dissociation energies of the Lewis bases in the case of **25** and **26**, further experimental evidences of the high Lewis acidity of 9-boratriptycene were derived from the spectroscopic analysis of its Lewis adducts **30-32** (Scheme 10).



Scheme 10 NMR and infrared spectroscopy measurements of Lewis adducts **30-32.**

According to the Guttmann-Becket method the 9-boratriptycene **17** has an acceptor number of 75, and is less Lewis acidic than $B(C_6F_5)_3$ (acceptor number = 80).[2a,21] Infrared spectroscopy measurements of Lewis adducts **31** and **32** show however that the Lewis acidity of 9-boratriptycene is significantly higher than $B(C_6F_5)_3$ when considering MeCN and EtOAc as reference Lewis bases.[21]

Quantum chemical calculations allowed a better understanding of the origins of the high Lewis acidity of 9-boratriptycene (Table 1).[19] Reorganization energy of 9-boratriptcene **17** was significantly lower than that of triphenylborane **34** and tris(pentafluorophenyl)borane **35** for all Lewis bases considered (Table 1). The 9-boratriptycene exhibited a higher affinity for NH_3, fluoride, PPh_3 and pyridine than the propeller shaped triarylborane $B(C_6F_5)_3$ **35**. Interestingly, the 1-borabarrelene **33** has a similar boron pyramidalization than 9-boratriptycene **17** but is a weaker Lewis acid.

Table 1 Pyramidalization of the boron atom α. Gas phase reorganisation energy (RE) upon complexation with Lewis bases of selected boron

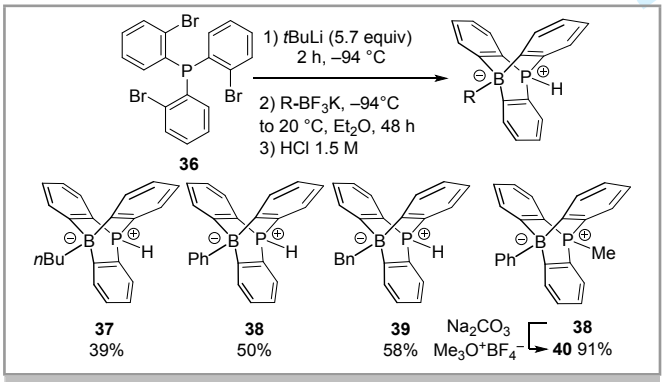
Boron Lewis acids		REs with Lewis bases (kJ mol⁻¹)					Lewis bases affinities (kJ mol⁻¹) and global and local electrophilicities (eV)						
	α[a]	H⁻	F⁻	NH_3	PPh_3	C_5H_5N	HIA[b]	FIA[b]	NH_3	PPh_3	C_5H_5N	GEI	ω_B
triethylborane (BEt_3)	0.90	125	118	72	81	86	292	285	92	38	86	0.97	-0.67
1-boraadamantane **4**	11.0	101	91	48	54	59	326	282	74	85	116	0.88	-0.57
1-borabarrelene **33**	15.4	95	87	45	50	52	412	395	172	164	176	1.02	-1.23
9-boratriptycene **17**	15.5	92	87	45	55	58	496	476	206	194	200	1.20	-1.50
BPh_3 **34**	0	130	174	74	69	113	352	333	88	72	79	1.53	-0.65
$B(C_6F_5)_3$ **35**	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.

Lewis acids and hydride, fluorine, ammonia, pyridine and PPh_3 affinities ΔH^0 (kJ mol^{-1}), global (GEI) and local electrophilicity index ω_B of the boron atom (eV).[19]

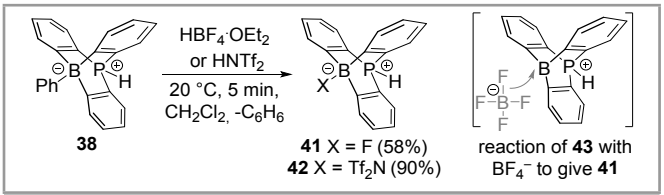
The global electrophilicity index (GEI)[22] showed that the 9-boratriptycene (GEI = 1.20 eV) is more electrophilic than 1-borabarrelene (GEI = 1.02 eV) and 1-boraadamantane **4** (GEI = 0.88 eV). This striking difference may overcompensate the small lack of pyramidalization in **33** thus conferring to **17** a higher Lewis acidity with the respect to 1-borabarrelene **33**.

Aiming that the boron pyramidalization was a key parameter, conferring to 9-boratriptycene a very high Lewis acidity, we then reasoned that switching the atom at the second bridged position of the triptycene should have a significant impact on the boron atom ground state properties and thus deeply affect its Lewis acidic properties.[23] Accordingly, a series of 9-phosphonium-10-boratriptycene-ate-complexes was prepared following the seminal method of Sawamura (Scheme 11).[24]



Scheme 11 Synthesis of 9-phosphonium-10-boratriptycene-ate-complexes **37**-**40**.

The protodeborylation of the exocyclic aryl ring of **38** proceeded very cleanly with HBF_4 leading to the fluoro-borate complexe **41**, therefore unambiguously supporting a mechanistic scenario involving a C-B bond cleavage via an electrophilic *ipso*-protonation and subsequent abstraction of a fluoride from the BF_4^- counteranion. Surprisingly, treatment with the super Brønsted acid $HNTf_2$ led to the formation of the unique triflimidate ate complex **42** (Scheme 12).



Scheme 12 Protodeboronation of **38** by using HBF_4 and $HNTf_2$

Whereas the binding of 9-boratriptycene **17** with the weakly basic NTf_2^- counteranion is highly reversible, the complex **42** shows high stability indicating a very high Lewis acidity of **43**. The Lewis adduct **42** is the first example of a triarylborane binded to NTf_2^-, demonstrating further the exceptional Lewis acidity of the intermediate 9-phosphonium-10-boratriptycene Lewis acid **43**.

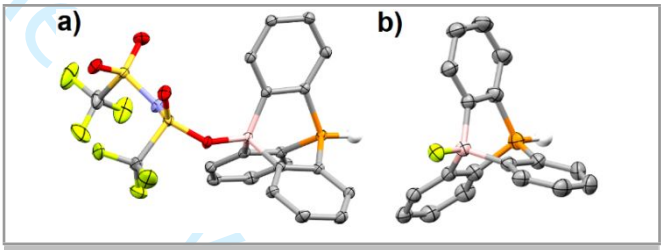
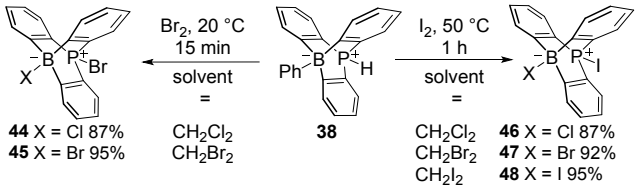


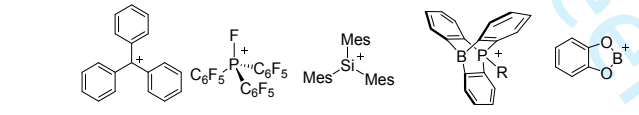
Figure 2 Molecular structure of a) the 9-phosphonium-10-boratriptycene Tf_2N^- Lewis adduct **42** as a toluene solvate (average values for CPC angles = 103.6°, CBC angles = 107.7°); b) F^- Lewis adduct complex **41** (average values for CPC angles = 103.2°, CBC angles = 106.6°). H-atoms (except P-H groups) and toluene solvate molecule are omitted for clarity, bond lengths in Å.

The treatment of **38** by Br_2 or I_2 resulted in the *in-situ* formation of HBr or HI which subsequently induced the dephenylation by protodeboronation of the exocyclic C–B bond to provide **44**-**48** in high yields (Scheme 13). Remarkably, the halide anion attached to the boron atom in **44**-**48** was originating from the reaction solvent, indicating that the intermediately generated phosphonium boratriptycenes **43** abstracted a halide ion from the reaction solvent CH_2X_2.[23]



Scheme 13 Synthesis of halogenoboranes **44**-**48** by dephenylation of **38**.

The Lewis acidity of **43** was quantified accurately by computing its fluoride and hydride ion affinities and comparing them with those of other cationic Lewis acids (Scheme 14).[25] The fluoride ion affinity (FIA) of the catechol borenium ion **53**[26] substantially surpassed that of **43** and **52** showing that the highly pyramidalized boron atom in addition to the cationic phosphonium linker backside could not compensate a cationic charge on the boron atom as in **53**. However, the FIA values of 845 and 830 kJ mol^{-1} for **43** and **52** show that the 9-phosphonium-10-boratriptycenes reach the Lewis acidities of unsolvated electrophilic phosphonium and silylium cations.[21] The computed hydride affinity of 903 and 888 kJ mol^{-1} for **43** and **52** are also higher than the triphenylcarbenium carbocation **49**, a key hydride and methyl anion abstracting reagent.[27]



ΔH_0 / kJ mol^{-1}	**49**	**50**	**51**	**43**: R = H **52**: R = Me	**53**
H^-	(846)[27]	-	577[26]	903[23]	888[23]	1011[26]
F^-	608[21]	779[21]	800[21]	845[23]	830[23]	997[26]

Scheme 14 Isodesmic (COF_2, $HSiEt_3$, $FSiEt_3$ or BEt_3 as anchor points) computed gas phase fluorine and hydride affinity of 9-phosphonium-10-boratriptycenes and reference cationic Lewis acids using. In parenthesis: non-isodesmic hydride affinity of carbenium **49**.

In essence, bending the archetypal planar trigonal boron atom environment results in a strong enhancement of the Lewis acidity without requiring perfluorinated scaffolds or electron-withdrawing groups as in 9-boratriptycene **17**. When in the case of 9-phosphonium-10-boratriptycenes **43** and **52**, the proximity of a cationic charge on the phosphonium bridge and a transannular overlap between the empty *p* orbital of boron and σ* orbital of the phosphonium back-side atom bond are also implemented, it results for **43** and **52** in the strongest ever known Lewis acidic properties for trivalent boron centers.

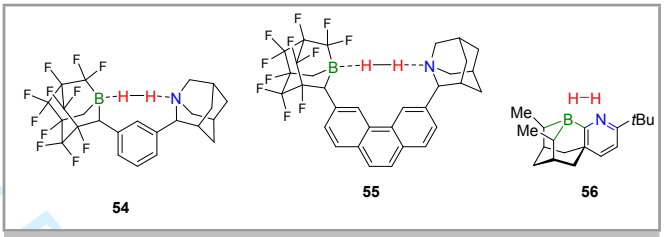
4. Applications of non-planar boranes

4.1 Applications of non-planar alkyl boranes and boronates

Bubnov improved the synthesis of the 1-boraadamantane **4** and performed extensive studies about this cage-shaped Lewis acid.[9] The Lewis adducts of 1-boraadamantane with 1-aminoadamantane or amino acids, exhibited interesting biological activity.[28] Another application, developed by Shea, is the homologation of 1-boraadamantane in order to synthesize oligomeric and polymeric boracyclanes and carbocycles.[29]

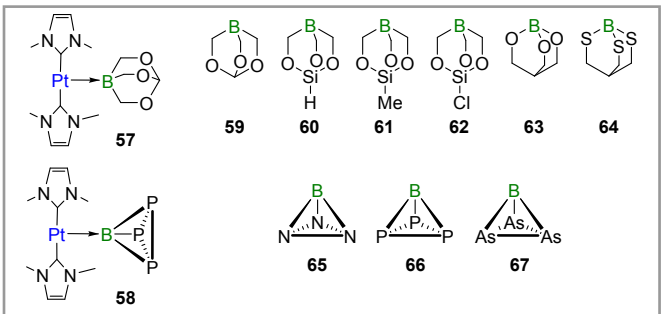
Cryptands based on boraadamantanes and aza-adamantanes were computationally studied for their abilities to activate and heterolytically split dihydrogen (Scheme 15).[30] The combination of non-fluorinated 1-ala- and 1-boraadamantane with 1-azaadamantane spaced by a linker being a benzene, anthracene or phenanthrene moiety were highlighted to allow the hydrogen heterolytic splitting via an endergonic process.

Investigations of the same process with fluorinated 1-ala- and 1-boraadmantane showed a drastic lowering of the reaction free energy, becoming a strongly exergonic process. The major lowering of the reaction free energy was observed with perfluorinated 1-boraadamantane and 1-azaadamantane spaced by benzene **54** and phenanthrene **55** moiety with a ΔG^0 of −172 kJ mol^{-1} and −174 kJ mol^{-1}, respectively. In 2016, Timoskin studied the heterolytic molecular hydrogen splitting by several 1-ala- and 1-boraadamantane derivatives Lewis acids and nitrogen based Lewis bases (Scheme 15).[31] They showed that the best candidates were perfluorinated 1-boraadamantane and 1-azaadmantane as Lewis acid and base respectively, leading to an endothermic splitting of H_2 by only 18 kJ mol^{-1}.



Scheme 15 Applications of cage-shaped 1-bora-adamantane for dihydrogen activation.

The group of Phukan recently studied the application of boron compounds as acceptor molecules in unsupported transition metal-boron complexes (Scheme 16).[8] If transition metals (TM) are well known as Lewis acidic sites in coordination chemistry able to coordinate with electron-donating ligands, they can also act as Lewis bases and thus participate in so-called "metal-to-ligand" dative bonding. The concept of unsupported bonding means that no secondary interactions are involved in the bonding between the metal and the ligand, only a single donor-acceptor bond.



Scheme 16 Non-planar compounds as acceptor molecules in unsupported Pt→B complexes and representative examples of two such complexes.

One hypothesis for the unstability of such complexes is the large "preparation energy" (*i.e.* reorganization energy) of planar boranes to get to the four-coordinated pyramidal geometry.[8] Phukan *et al.* proposed to use pre-pyramidalized boron compounds in order to favour the formation of unsupported Pt–boron donor–acceptor complexes. Their formation was evaluated in part by B–Pt bond dissociation energies (BDE). Non-planar compounds **59-64** gave higher BDEs than planar BCl_3, indicating more stable complexes. Eventually, a good correlation was observed between reorganization energy and BDE.

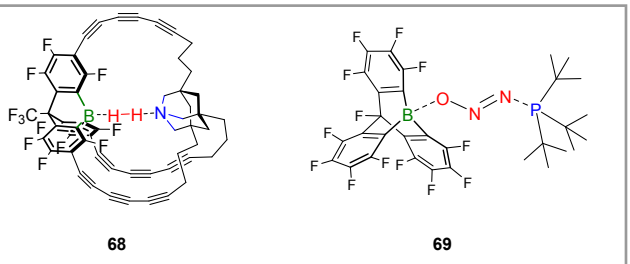
Building on this work, the group of Guha published in 2020 three new structures of non-planar boron supported by cyclic N_3, P_3 and As_3 (Scheme 16, **65-67**) that were predicted to form stable unsupported Pt–B donor–acceptor complexes.[32]

4.2 Applications of non-planar triarylboranes (boratriptycenes)

In 2012, Timoshkin started to study *in-silico* the dihydrogen heterolytic splitting reaction using combinations of group 13 Lewis acids (including fluorinated 9-boratriptycene derivatives) and group 15 Lewis bases.[33] Their first computational study aimed at evaluating the best Lewis acid/base pairs for H_2 splitting.

Pyramidalized Lewis acids, such as 9-boratriptycenes, compared to planar triaryl derivatives, lead to a decrease of the Gibbs free energies and free energies of activation for molecular hydrogen splitting, regardless of the Lewis base used. They next investigated the ideal distance between the Lewis acids and bases for H_2 splitting and designed numerous bifunctional molecules and disclosed that cryptands such as **68** are ideal systems for trapping and activating H_2 (Scheme 17).

Gilbert independently investigated the enthalpies of association of fluorinated 9-boratriptycenes and other triarylboranes with sterically hindered Lewis base, in particular with P*t*Bu$_3$. The Gibbs free energies of nitrous oxide N_2O complexation by these Lewis acid/base systems was screened.[34] The perfluorinated 9-boratriptycene/N_2O/P*t*Bu$_3$ **69** complex is more stable by 12 kJ mol^{-1} and 168 kJ mol^{-1}, respectively, than the complexes with $B(CF_3)_3$ and $B(C_6F_5)_3$, highlighting the potential of this type of non-planar Lewis acids for the activation of small molecules.



Scheme 17 Applications of cage-shaped boron compounds with trivalent pre-pyramidalized B centers for hydrogen activation and N_2O trapping.

5. Other non-planar group 13 Lewis acids

Although not a boron compound, the group of Frenking designed a very interesting cryptand scaffold based on a pyramidalized aluminium center predicted to be capable of chelating noble gases.[17] Donor-acceptor complexes of noble gases of the form A←Ng←D (where A, Ng and D stand respectively for acceptor, noble gas and donor) have already been isolated experimentally but are generally unstable. Explanations of these observations include a significant reorganization energy of the acceptor molecule and repulsive Ng←D interactions that ultimately lead to an exothermic evolution of free Ng. To prevent this and any direct A←D bonding, they proposed a new push-pull cryptand featuring both a pyramidal acceptor part, in the form of a perfluoro-9-alatriptycene moiety, linked to a donor part in the form of an 1-azaadamantane. This remarkable structure is predicted to form thermodynamically stable Ar and Kr complexes. (Figure 1) The bonding situation is described as a 3-center 4-electrons bond.

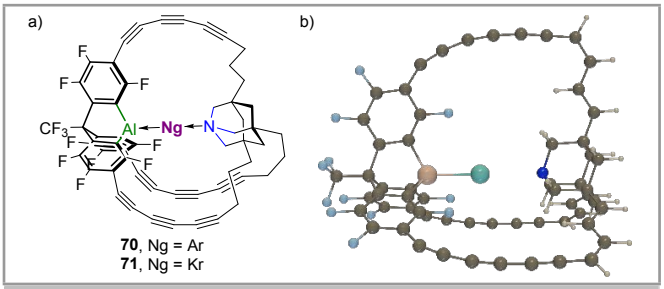


Figure 1 a) Pyramidalized Al-N cryptand in complex with Ar **70** and Kr **71** in the form of a 3-center 4-electrons interaction b) Visual representation (using the program Drawmol) of complex **71** in its optimized geometry as reported by Frenking.[17]

6 Further work and perspectives

Main group Lewis acids and superacids, such as carbenium, silylium and borenium ions and electrophilic phosphoniums cations recently enabled numerous catalytic applications. The 9-boratriptycene and its cationic derivatives, which are covering a wide range of Lewis acidity from that of $B(C_6F_5)_3$ to that of the tris(mesityl)silylium ion are foreseen to become competent catalysts for several processes such as catalytic C-F bond activation, arylation of hydrocarbons, activation of small molecules, hydrosilylations, Diels-Alder and Nazarov reactions.[35]

Owing to the very low energies of reorganization of cage-shaped Lewis acids upon association/dissociation with Lewis bases, all intrinsic reactions barriers are decreased and lower than conventional planar triarylboranes and may favour the kinetics and thermodynamics of the catalytic transformations cited above.

As discussed in the previous sections, quantum chemical computation showed that non-planar boranes are potentially interesting new constituents of bifunctional catalysts and of FLPs for the activation of H_2 and N_2O. In contrast to most of the highly Lewis acidic triarylboranes which are partially fluorinated or perfluorinated, no fluorine atoms are required for enhancing the Lewis acidity of non-planar boranes. Thus, the Lewis acid decomposition and the formation of side-products by substitutions of fluorine atoms by strong Lewis bases or nucleophiles could be avoided.[36]

The development of thermally robust and sterically hindered boratriptycene and of FLPs derived from it might become thus feasible. For example, the catalytic dehydrogenation of amine-boranes and the production,[37] storage and transfer of H_2 for hydrogenation reactions can also benefit from bifunctional

Lewis acid/base catalyst requiring very low reorganization energies during the dehydrogenation/hydrogenation processes.

In conclusion, non-planar triarylboranes may open novel directions in main-group chemistry, and enable the design of new modulable Lewis acids and superacids by taking advantage of transannular interactions in cage-shaped compounds and by controlling the bending of the boron atom environment.

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Biosketches

Paste photo in this space	Prof. Guillaume Berionni received his PhD in 2010 from the University of Versailles, France. He then moved to the Ludwig Maximilian University of Munich as a Humboldt postdoctoral fellow and became independent PI under the guidance of Prof. H. Mayr and Prof. P. Knochel. Since 2018, he is Professor of chemistry at the University of Namur, Belgium. His research interests are organoboron chemistry, main-group compounds, and organometallic reactivity. He is actively involved in teaching, especially at the master's level. Dr. Aurélien Chardon received his PhD from the University of Caen Normandie, France. He made a postdoctoral research project under the supervision of Prof. G. Berionni in UNamur focusing on the synthesis of 9-boratriptycenes derivatives. Damien Mahaut started his PhD in 2019 and is working on the development of new frustrated Lewis pairs base on the triptycene scaffold. Arnaud Osi started his PhD in 2019 on the development of non-planar boron Lewis acids for activating C-F bonds. Ali Ben Saida started his PhD in 2018 and his research project focuses on the development of bifunctional Lewis acid-base triptycene derivatives.

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