Lewis Acids

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Pushing the Lewis Acidity Boundaries of Boron Compounds With Non-Planar Triarylboranes Derived from Triptycenes

*Ali Ben Saida[+], Aurélien Chardon[+], Arnaud Osi, Nikolay Tumanov, Johan Wouters, Abel I. Adjieufack, Benoît Champagne, and Guillaume Berionni**

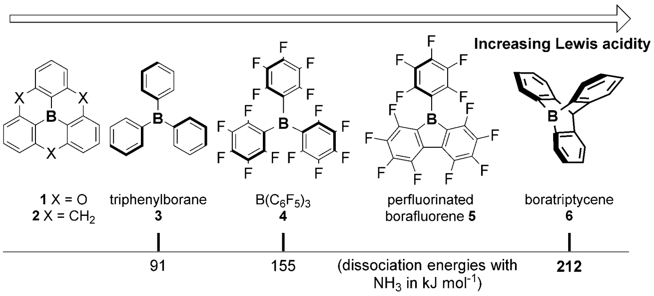
Dedicated to Professor Alain Krief on the occasion of his 77th birthday

Abstract: *Bending the planar trigonal boron center of triphenylborane by connecting its aryl rings with carbon or phosphorus linkers gave access to a series of 9-boratriptycene derivatives with unprecedented structures and reactivities. NMR spectroscopy and X-ray diffraction of the Lewis adducts of these non-planar boron Lewis acids with weak Lewis base revealed particularly strong covalent bond formation. The first Lewis adduct of a trivalent boron compounds with the Tf_2N^- anion illustrates the unrivaled Lewis acidity of these species. Increasing the pyramidalization of the boron center and using a cationic phosphonium linker resulted in an exceptional enhancement of Lewis acidity. Introduction of a phosphorus and a boron atom at each edge of a triptycene framework, allowed access to new bifunctional Lewis acid-base 9-phospha-10-boratriptycenes featuring promising reactivity for the activation of carbon-halogen bonds.*

Trivalent organoboron compounds are readily available Lewis acids of importance in academia and industry.[1] In contrast to triphenylborane (**3**), which has a propeller-like structure,[2] enforced planarization of the aryl rings with three linkers results in air and water stable planar boranes **1**–**2**, which are unreactive towards most Lewis bases (Scheme 1).[3]

Perfluorinated aryl rings considerably increase the boron Lewis acidity, as in tris(pentafluorophenyl)borane **4**, and connecting two aryl rings as in borafluorene **5** further increases the Lewis acidity (Scheme 1).[4] More remarkably, a CH linker connecting all three phenyl rings of triphenylborane **3** would provide the 9-boratriptycene **6** featuring a pyramidal coordination environment around the trivalent boron atom (Scheme 1).[5]

Quantum-chemical calculations revealed that **6** may have a huge potential in catalysis as a constituent of either cryptands or frustrated Lewis pairs with potential applications for the activation of H_2[6] and N_2O,[7] as well as in materials sciences for the design of new classes of donor-acceptor complexes of noble gases.[8] Owing to its strongly pyramidalized boron center integrated at the bridgehead position of a triptycene scaffold, the NH_3 affinity of **6** was computationally predicted to surpass by far that of $B(C_6F_5)_3$ **4** (Scheme 1).[5]

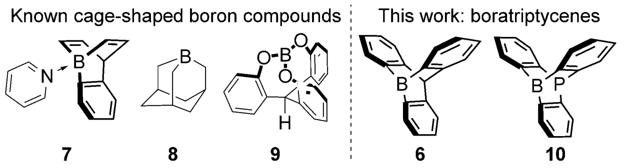


Scheme 1. Representative triarylboranes and computed NH_3 affinities.[5b]

Since the synthesis of $B(C_6F_5)_3$ **4** by Massey et al. in 1963,[9] the main approaches for increasing the acidity strength of boron Lewis acids essentially remained to use electron-withdrawing groups (p-$C_6F_4CF_3$, $OC(CF_3)$),[2–10a] cationic substituents (NR_3^+, PR_3^+, SMe_2^+, BR_2^+),[3a,10b,11] or anti-aromatic borole rings.[4]

The large number of electron-withdrawing groups however increases the molecular weight of these triarylboranes, and perfluorinated scaffolds are often problematic in terms of synthetic approaches, side-products formation by rearrangements, or fluorine substitutions by strong Lewis bases or nucleophiles.[12]

Knowing that several free or coordinated non-planar boron Lewis acids are known, such as borabenzobarrelene **7** (Scheme 2),[13] 1-bora adamantane **8**,[14] and **9**,[15a,b] we have been stimulated to generate the boratriptycene Lewis acid **6** and to design Lewis acid/base bifunctional molecules such as



Scheme 2. Cage-shaped boron compounds **6**–**10**.

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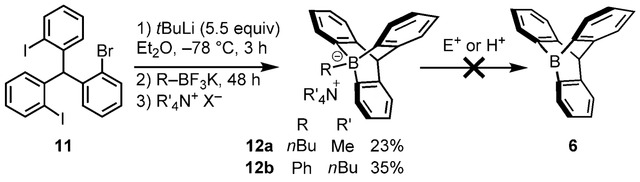
[*] A. Ben Saida,[+] Dr. A. Chardon,[+] A. Osi, Dr. N. Tumanov,
Prof. J. Wouters, A. I. Adjieufack, Prof. B. Champagne,
Prof. G. Berionni
Department of Chemistry, Namur Institute of Structured Matter
University of Namur
5000 Namur (Belgium)
E-mail: guillaume.berionni@unamur.be

[+] These authors contributed equally to this work.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201910908.

10 with a B atom and a P atom at each edge of the triptycene framework (Scheme 2).

The tris(*ortho*-halogeno)trityl derivative **11**[16] was subjected to a triple halogen/lithium exchange with *t*BuLi and was treated with potassium organotrifluoroborates to provide the 9-boratriptycene ate-complexes **12a–b** after cation metathesis and recrystallization (Scheme 3) which have been unambiguously characterized by X-ray diffraction analysis (see the Supporting Information and Figure 1). We next attempted to remove the *n*Bu and Ph groups on the tetravalent boron atom of **12a–b** by using various deborylation strategies.

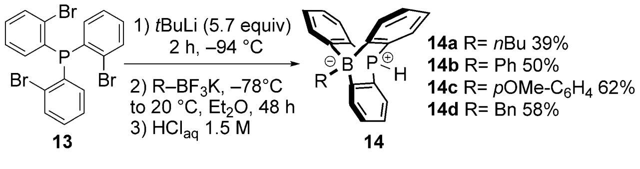


Scheme 3. Synthesis of 9-boratriptycene ate-complexes **12a,b** and attempted synthesis of 9-boratriptycene **6** via deprotection of **12a** or **12b**. $\mathrm{E^+ = Ph_3C^+BF_4^-}$, $\mathrm{Me_3O^+BF_4^-}$, Barluenga's reagent, $\mathrm{I_2}$; $\mathrm{H^+ = HBF_4}$, $\mathrm{HNTf_2}$, HCl. For the synthesis of **11** via a modification from a literature procedure,[16] see the SI.

Though the *n*Bu chain in triphenylboron ate-complexes $\mathrm{[Ph_3(\mathit{n}Bu)B^-X^+]}$ are readily cleaved via α or β-hydride abstraction and elimination by carbenium and oxonium ions,[17] this route proved to be unrewarding for the deborylation of **12a** (Scheme 3). Submitting **12b** to strong Brønsted acids or electrophiles only provided complex mixtures resulting from unselective deborylations (see the Supporting Information for full details).

We reasoned that replacing the CH bridgehead position in **12** by a $\mathrm{P^+R}$ phosphonium linker should decrease the electron density of the triptycene aromatics and favor the selective exocyclic phenyl C–B bond protodeboronation. A series of 9-phosphonium-10-boratriptycene aryl and alkyl ate-complexes **14a–d** were thus prepared following the method of Sawamura (Scheme 4).[18]

The boron atom pyramidalization, defined as the distance between B and the plane spanned by the *ipso*-carbon atoms of the three triptycene benzene rings (gray plane in Figure 1), normalized by average B–C bond length is greater in boratriptycenes **12a,b** [0.445(3)] than in the phosphorus analogues **14a,b** [0.407(3)]. The higher boron pyramidalization in **12a** is due to the shorter triptycene back-side C–C bonds (1.524(5) Å) compared to longer C–P bonds (1.781(2) Å) in **14a** (Figure 1).



Scheme 4. Synthesis of 9-phosphonium-10-boratriptycene ate-complexes **14**.

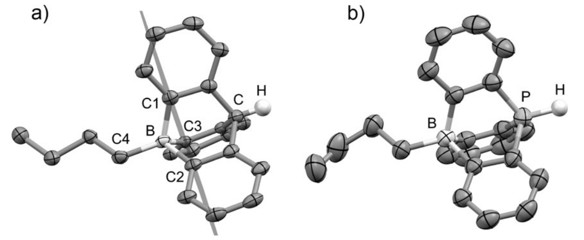
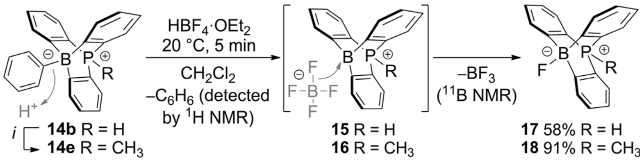


Figure 1. a) Molecular structure of the 10-*n*-butyl-boratriptycene **12a**; plane spanned by the *ipso*-carbon atoms of the three triptycene benzene rings shown as a gray plane. b) Molecular structure of the 9-phosphonium analogue **14a**. Here and further structures are shown with thermal ellipsoids set at the 50% probability level. See the Supporting Information for further details and CCDC numbers. The cation in **12a**, aromatic and alkyl chain H-atoms omitted for clarity. Selected bond lengths [Å] in **12a**: B–C1 1.652(5), B–C2 1.641(5), B–C3 1.650(5), B–C4 1.612(5), and in **14a** (atom numbering as for **12a**): B–C1 1.655(2), B–C2 1.661(2), B–C3 1.652(2), B–C4 1.624(2).

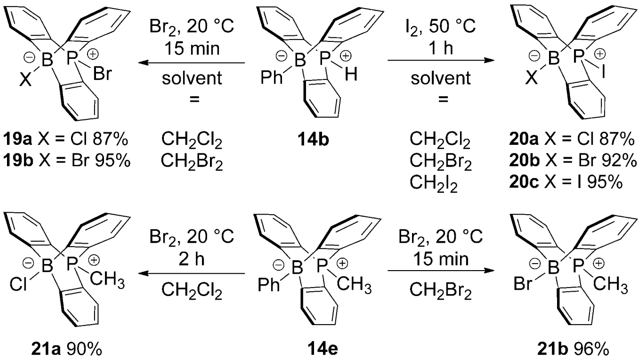
The phosphonium-borate **14b** (and analogue **14e**, Scheme 5) smoothly underwent selective phenyl protodeboronation with $\mathrm{HBF_4}$ to yield the fluoroborates **17–18** (Scheme 5). Their ^{19}F NMR spectrum showed a resonance at –235 ppm consistent with a $\mathrm{F–BAr_3^-}$ bond but low shifted by 45 ppm from the F–B resonance in $\mathrm{F–B(C_6F_5)_3^-}$.[19] Their formation supported a mechanistic scenario involving the transient formation of the highly Lewis acidic cationic boratriptycenes **15–16** which abstracted a fluoride from $\mathrm{BF_4^-}$.



Scheme 5. Protodeborylation of **14b** and **14e** by $\mathrm{HBF_4{\cdot}OEt_2}$ and formation of the zwitterionic fluoroborates **17** and **18**. Conditions: i): $\mathrm{Na_2CO_3}$, $\mathrm{Me_3O^+BF_4^-}$ (see the Supporting Information for full details).

Treatment of **14b** with $\mathrm{Br_2}$ or $\mathrm{I_2}$ resulted in the in situ formation of HBr or HI, respectively, due to the strong Brønsted acidity of the phosphonium moiety, with release of the phosphine which trapped the electrophilic halenium ions $\mathrm{X^+}$. Simultaneous protodeborylation of the phenyl C–B bond by the in situ formed HBr or HI gave **19–20** in high yields (Scheme 6) and the formation of benzene was detected by ^{1}H NMR spectroscopy (see the Supporting Information and Figure 2 for the solid-state structures). Translation of those conditions to the methylated analog **14e** furnished the halogeno-borates **21a–b** via halogeno-dephenylation reaction (Scheme 6), showing that selective deboronation by direct halogenation with $\mathrm{Br_2}$ is also successful.

Remarkably, the halide attached to the boron atom was not originating from the $\mathrm{Br_2}$ or $\mathrm{I_2}$ reagents, but from the reaction solvent $\mathrm{CH_2X_2}$. The transient boratriptycene Lewis acid thus abstracted a halide from the halogenated solvents



Scheme 6. a) Proto-dephenylation of **14b** by in situ formed HX; b) Halogeno-dephenylation of **14e** by Br_2 (solid-state structure of **21b** in Supporting Information).

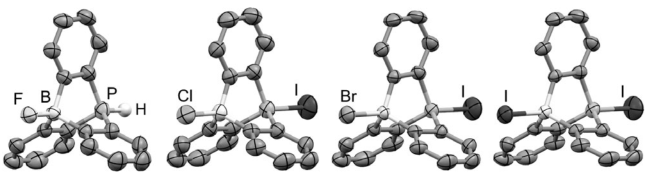


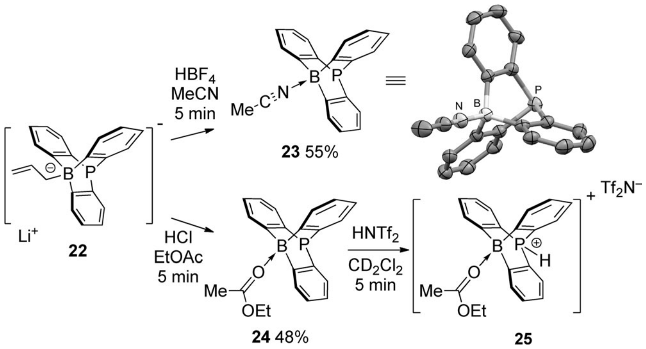
Figure 2. Left to right: Molecular structures of **17** and **20a–c**. Aromatic H-atoms are omitted for clarity. Selected bond lengths [Å]: P–H 1.330(3), B–F 1.403(3) in **17**; P–I 2.364(12), B–Cl 1.928(5) in **20a**; P–I 2.366(11), B–Br 2.065(4) in **20b**; P–I 2.362(13), B–I 2.260(5) in **20c**.

assisted by S_N2 substitution of the Br^- or I^- anions from HBr or HI.[20]

The 9-phosphonium-10-borates **19–21** were characterized by single-crystal X-ray diffraction, providing the B–X bond lengths for the complete halogen series of boron ate-complexes F^-, Cl^-, Br^- and I^-. The B–F (1.403(3) Å) and B–Cl (1.928(5) Å) distances in **17** and **20a** were shorter or comparable than in the $F\text{–}B(C_6F_5)_3^-$ (1.418(5) Å) and $Cl\text{–}B(C_6F_5)_3^-$ (1.919(18) Å) anions, respectively.[21]

Systematic X-ray diffraction, NMR and IR spectroscopy investigations of the 9-phospha-10-boratriptycene Lewis adducts with a series of Lewis bases were performed to gather quantitative information on the stereoelectronic properties of their boron atom.

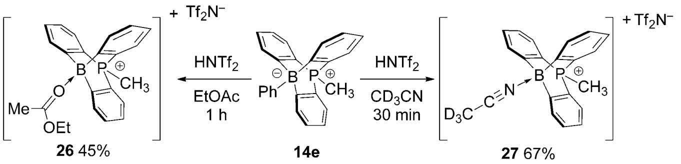
Inspired by the techniques of silylium cations generation via the allyl leaving group strategy,[22] the MeCN and EtOAc Lewis adducts **23–24** were synthesized by treating the allylborate **22** with HCl or HBF_4 in the desired solvents (Scheme 7). Both B–N and B–O bonds in **23** and **24** were much shorter than in the corresponding $B(C_6F_5)_3$ adduct[23] with the B–N bond length in **23** (1.569(9) Å) being one of the shortest reported in the Cambridge structural database, even shorter than in the Lewis adduct of CH_3CN with perfluoroborafluorene **5** (Scheme 1, 1.581(5) Å)[4] and in the Lewis adduct **7** (cf. Scheme 2, 1.589(2)).[4b]



Scheme 7. Formation of Lewis adducts **23–24** via deallylation of **22**. Selected bond lengths in [Å]: B–N 1.569(9) in **23**, B–O 1.565(18) in **24**, 1.548(3) in **25**.

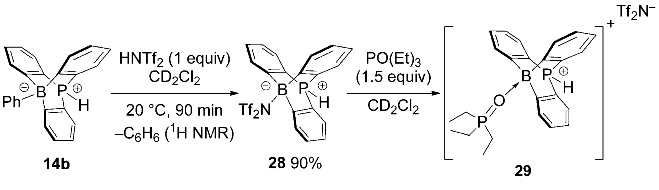
Though the phosphorus protonation had no effect on the boron atom pyramidalization according to the CBC angles (ca. 108.0° in **24** and **25**, see solid-state structures in Supporting Information), the boron Lewis acidity dramatically increased as indicated by the large shift of the $\nu_{C=O}$ stretching frequency of the coordinated EtOAc from 1607 cm^{-1} in **24** to 1581 cm^{-1} in **25**.[24] The $\nu_{C=O}$ stretching frequency in **25** is even lower than in $AlCl_3{\cdot}EtOAc$ (1624 cm^{-1}).[24] This strong Lewis acidity enhancement is the result of the electron-withdrawing effect of the phosphonium linker and to a transannular overlap[1c,15a] between the vacant p-orbital of boron and σ* orbital of the phosphonium in the triptycene scaffold.

As both $\nu_{C=O}$ stretching frequencies (ca. 1580 cm^{-1}) and both C=O ^{13}C chemical shifts (ca. 187 ppm) of the coordinated ethyl acetate in **25** and **26** were nearly identical, we concluded that the phosphorus atom quaternarization by H^+ or CH_3^+ had a comparable effect on the boron atom Lewis acidity (Scheme 8).



Scheme 8. Formation of Lewis adducts **26–27** via protodeboronation of **14e**. B–O length in **26** 1.548 Å (solid-state structure of **26** in the Supporting Information). IR spectroscopy, $\nu_{CN} = 2379\ cm^{-1}$ for **27**.

As a demonstration of the exceptional Lewis acidity of these 9-phosphonium-10-boratriptycenes, the protodeborylation of **14b** with $HNTf_2$ yielded a unique triflimidate Lewis adduct **28** (Scheme 9; Figure 3). This unprecedented Lewis adduct between a trivalent boron Lewis acid and an oxygen atom of the very non-nucleophilic Tf_2N^- anion[25] showcases the extreme Lewis acidity of the boron atom in 9-phosphonium-10-boratriptycenes.



Scheme 9. Generation of the triflimidate Lewis adduct **28** and subsequent Lewis base exchange with $PO(Et)_3$ to give **29** (solid-state structures in Figure 3).

Addition of $PO(Et)_3$ on **28** resulted in the displacement of the Tf_2N^- anion and produced the Lewis adduct **29** (Scheme 9; solid-state structures in Figure 3) which can be employed for probing by ^{31}P NMR spectroscopy the boron Lewis acidity according to the Gutmann-Becket method.[26]

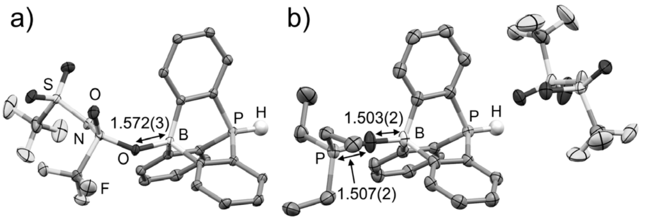
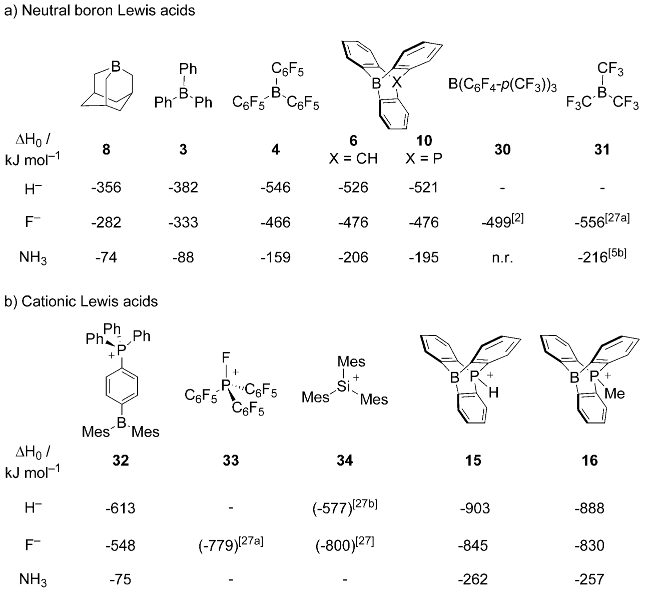


Figure 3. Molecular structure of a) the 9-phosphonium-10-boratriptycene Tf_2N^- Lewis adduct **28** as a toluene solvate (average values for C-P-C angles = 103.6°, C-B-C angles = 107.7°); b) of the $PO(Et)_3$ adduct **29** (average values for CPC angles = 103.2°, CBC angles = 106.6°). H-atoms (except P—H groups) and toluene solvate molecule are omitted for clarity, bond lengths in [Å].

The ^{31}P NMR chemical shift of 79.3 ppm for $PO(Et)_3$ in **29** corresponded to an Acceptor Number[26] of 84.7 showing that the Lewis acidity of tris(perfluorotolyl)borane **30** (AN = 85.0)[2] is reached when considering $PO(Et)_3$ as a reference Lewis base.

As the Fluoride (FIA) and Hydride Ion Affinity (HIA) constitute well-established Lewis acidity scales with a repertoire of hundreds of Lewis acids,[27a] we computed the F^- and H^- affinities of $B(C_6F_5)_3$, $B(CF_3)_3$, and of boratriptycenes in the gas phase. Their affinities (ΔH^0) toward ammonia were also evaluated (Scheme 10). In the case of fluoride, pseudo-isodesmic reactions have been used, with the FIA of $SiMe_3F$ as the anchor point evaluated at a reference G3 level.[27a]



a) Neutral boron Lewis acids

ΔH_0 / kJ mol^{-1}	**8**	**3**	**4**	**6** X = CH	**10** X = P	**30**	**31**
H^-	-356	-382	-546	-526	-521	-	-
F^-	-282	-333	-466	-476	-476	-499[2]	-556[27a]
NH_3	-74	-88	-159	-206	-195	n.r.	-216[5b]

b) Cationic Lewis acids

ΔH_0 / kJ mol^{-1}	**32**	**33**	**34**	**15**	**16**
H^-	-613	-	(-577)[27b]	-903	-888
F^-	-548	(-779)[27a]	(-800)[27]	-845	-830
NH_3	-75	-	-	-262	-257

Scheme 10. Gas phase hydride, fluoride, and ammonia affinities, of selected, a) neutral and, b) cationic Lewis acids (ΔH^0 in kJ mol^{-1}) evaluated using density functional theory with the M06-2X exchange-correlation functional[28a] and the 6-311G(d) atomic basis set. Values in parenthesis from the literature with pseudo-isodesmic reactions with COF_2 and BEt_3, respectively.[27] Non-isodesmic FIA in CH_2Cl_2 (IEFPCM solvation model) equal to 278 kJ mol^{-1} for **4**.

The considerably higher Lewis acidity of 9-boratriptycene **6** than of BPh_3 **3** and of boraadamantane **8** (CBC angles 116°) is linked with the stronger pyramidalization of its boron atom environment (CBC angles 113° in **6**). The neutral boratriptycenes **6** and **10** are even more Lewis acidic than $B(C_6F_5)_3$ when considering their FIAs and is approaching that of SbF_5 (536 kJ mol^{-1})[27a] and of the "super-$B(C_6F_5)_3$" **30** in the gas phase.[2]

The non-isodesmic FIA of **4**, **15** and **31** in CH_2Cl_2 (IEFPCM solvation model)[28b] have also been calculated since Coulombic attraction and charge effect contribution are reduced in condensed-phase, and the Lewis acidity of **15** (513 kJ mol^{-1}) was slightly lower than in $B(CF_3)_3$ **31** (529 kJ mol^{-1}). Gas-phase result FIAs clearly showed that 9-phosphonium-10-boratriptycenes **15** and **16** are stronger Lewis acids than some electrophilic phosphonium and silylium cations (Scheme 10b).[27]

In essence, bending the archetypal planar trigonal boron coordination environment results in exceptional Lewis acidity enhancements without requiring perfluorinated scaffolds or electron-withdrawing groups. Three factors are combined to reach one of the strongest trivalent boron Lewis acid (compound **15**), which is even able to bind very weakly nucleophilic anions, such as Tf_2N^-: i) pyramidalized boron coordination environment; ii) transannular overlap between the empty p orbitals of boron and the σ* orbital of the phosphonium back-side atom, and iii) cationic charge on the phosphonium bridge in close proximity to the B atom. The unprecedented reactivity of 9-phospha-10-boratriptycene may open innovative avenues in bifunctional Lewis and Brønsted acid/base catalysis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boron · Lewis acids · Lewis superacid · non-planar · triarylboranes

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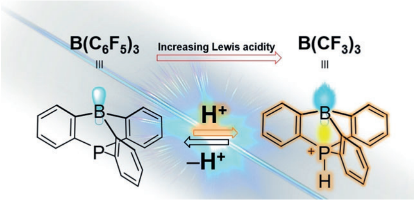
Communications

Lewis Acids



Pyramid power: Owing to the drastic pyramidalization around their trivalent boron atom and to the presence of a cationic phosphonium back-side bridge, the Lewis acidity of the cage-shaped 9-bora-10-phosphonium triptycenes surpasses that of all trivalent boron Lewis acids generated to date.