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Aromatic 1,2-Azaborinin-1-yls as Electron-Withdrawing Anionic Nitrogen Ligands for Main Group Elements

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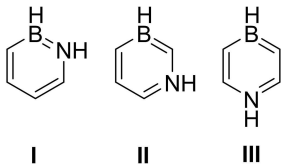
Abstract: The 2-aryl-3,4,5,6-tetraphenyl-1,2-azaborinines **1-EMe$_3$** and **2-EMe$_3$** (E = Si, Sn; aryl = Ph (**1**), Mes (= 2,4,6-trimethylphenyl, **2**)) were synthesized by ring-expansion of borole precursors with N_3EMe_3-derived nitrenes. Desilylative hydrolysis of **1-** and **2-SiMe$_3$** yielded the corresponding N-protonated azaborinines, which were deprotonated with *n*BuLi or $MN(SiMe_3)_2$ (M = Na, K) to the corresponding group 1 salts, **1-M** and **2-M**. While the lithium salts crystallized as monomeric Lewis base adducts, the potassium salts formed coordination polymers or oligomers via intramolecular K···aryl π interactions. The reaction of **1-M** or **2-M** with CO_2 yielded N-carboxylate salts, which were derivatized by salt metathesis to methyl and silyl esters. Salt metathesis of **1-M** or **2-M** with methyl triflate, [Cp*BeCl] (Cp* = C_5Me_5), BBr_2Ar (Ar = Ph, Mes, 2-thienyl), ECl_3 (E = B, Al, Ga) and PX_3 (X = Cl, Br) afforded the respective group 2, 13 and 15 1,2-azaborinin-2-yl complexes. Salt metathesis of **1-K** with BBr_3 resulted not only in N-borylation but also Ph-Br exchange between the endocyclic and exocyclic boron atoms. Solution ^{11}B NMR data suggest that the 1,2-azaborinin-2-yl ligand is similarly electron-withdrawing to a bromide. In the solid state the endocyclic bond length alternation and the twisting of the C_4BN ring increase with the sterics of the substituents at the boron and nitrogen atoms, respectively. Regression analyses revealed that the downfield shift of the endocyclic ^{11}B NMR resonances is linearly correlated to both the degree of twisting of the C_4BN ring and the tilt angle of the N-substituent. Calculations indicate that the 1,2-azaborinin-1-yl ligand has no sizeable π-donor ability and that the aromaticity of the ring can be subtly tuned by the electronics of the N-substituent.

Introduction

Since the first report of the inorganic benzene analogue borazine by Stock,[1] in which all CC units have been replaced by isosteric BN units, this relationship has been exploited to synthesize a vast library of BN-doped aromatic compounds and materials.[2] While the replacement of one or more endocyclic CC units by BN units reduces the aromaticity of the system,[3] the intrinsic polarization of the B–N bond and electron-deficiency of boron also endow aromatic CBN heterocycles with novel properties, which have found applications in optoelectronics[4] and increasingly in bioactive molecules.[5]

Among the azaborinine derivatives, i.e., C_4BN analogues of benzene,[6] the 1,2 isomers **I** (Figure 1) are the most stable and easiest to synthesize due to the direct electronic stabilization of the electron-deficient boron atom by the neighboring π-donating nitrogen atom.[3d] In contrast, the synthesis and



I II III

Figure 1. Isomeric forms of the parent azaborinine.

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chemistry of the less stable monocyclic 1,3- (**II**) and 1,4-azaborinines (**III**) is much less developed.[7,8] After Dewar's successful synthesis of a benzo-fused 1,2-azaborinine derivative in 1959,[5] the first monocyclic analogues were obtained in 1962 by Dewar via desulfurization of a thiophene-fused azaborinine,[10] and 1963 by White via the dehydrogenation of a 1,2-azaboracyclohexane obtained by dehydrocoupling/hydroboration of 3-butenylamine with phenylborane (Scheme 1a).[11] It wasn't until the advent of ring-closing metathesis that an efficient synthetic route to 1,2-azaborinines from 1,2-diallylaminoboranes was reported by Ashe and Fang in 2000[12] and later derivatized by the group of Liu (Scheme 1b).[13] Another route via the ring-expansion of 1,2-azaborolates has been reported by Ashe.[14] More recently our group has reported the rhodium-catalyzed or -mediated synthesis of 1,2-azaborinines from the [2+2+2] cycloaddition of a bulky iminoborane with two alkynes (Scheme 1c),[15] while both we and Martin have synthesized 1,2-azaborinines via the insertion of organoazides or diazoalkanes into the endocyclic B–C bond of boroles (Scheme 1d).[16,17]

In recent years the chemistry of 1,2-azaborinines has thus seen great advances,[18] including the isolation of the parent 1,2-azaborinine, C_4BNH_6,[19] and the first report of biologically active 1,2-azaborinines.[20] The groups of Liu and Ashe, in particular, have worked on the late-stage derivatization of 1,2-azaborinines, whereby most of the focus has been on the functionalization of the endocyclic boron atom or electrophilic aromatic substitution at the endocyclic C_4 moiety.[21] Thus far, the substitution pattern at the endocyclic nitrogen atom has been mainly limited to H, alkyl, aryl and silyl groups,[21a] with only a few more exotic derivatives, including azo,[16a,d] imino[17] and boryl groups.[16b]

In this work we present several methodologies for the late-stage derivatization of 1,2-azaborinines at the endocyclic nitrogen atom, including hydrolysis, tin-boron exchange, deprotonation followed by salt metathesis and spontaneous 1,2-addition, enabling the isolation of N-derivatives of groups 1–2 and 13–15. NMR-spectroscopic analyses and DFT calculations reveal that, unlike conventional anionic N-ligands the 1,2-azaborinin-1-yl ligand is highly electron-withdrawing and displays negligible π-donor ability. Furthermore, while the planarity of the azaborinine ring is highly dependent on the combined sterics of the adjacent substituents at the boron and nitrogen atoms, the degree of π conjugation and the aromaticity of the ring are mainly influenced by the electronics of the N-substituent.

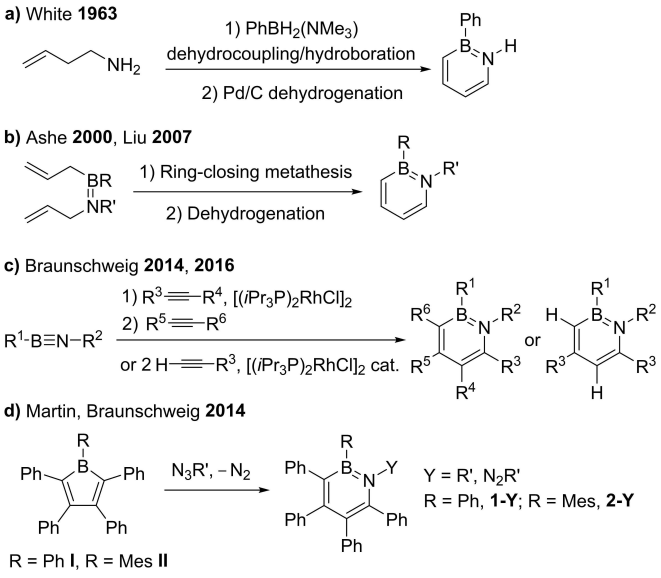
Results and Discussion

Synthesis and NMR-spectroscopic analyses

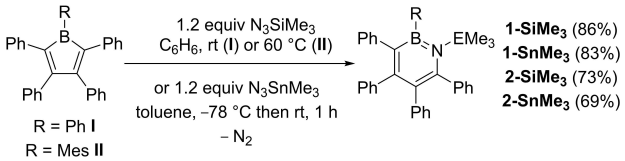
The trimethyltin derivatives **1-SnMe$_3$** and **2-SnMe$_3$** were synthesized using a procedure adapted from the literature synthesis of the lighter trimethylsilyl derivatives **1-SiMe$_3$** and **2-SiMe$_3$**[16e] by the insertion of the corresponding azide-derived trimethyltin nitrene into the endocyclic B–C bond of the borole precursors **I** and **II**,[22] respectively (Scheme 2). Because of the higher reactivity of N_3SnMe_3 compared to N_3SiMe_3, the reactions had to be carried out at −78 °C. **1-SnMe$_3$** and **2-SnMe$_3$** were isolated in good yields as colorless crystalline solids with ^{11}B NMR shifts of 38.8 and 40.7 ppm, respectively, in the same range as the analogous trimethylsilyl derivatives (δ_{11B} = 39.8 and 41.4 ppm, respectively).[16e]

As with all phenyl and mesityl analogues **1-Y** and **2-Y** presented herein, the ^{11}B NMR resonance of the latter is downfield-shifted by ca. 2.5 ppm compared to that of the former. This is due to the steric strain imposed by the mesityl substituent, which leads to an elongation of the endocyclic B–C bond and higher deviation from planarity in the C_4BN ring of **2-Y** (see **X-ray crystallographic analyses**). The ^{119}Sn NMR spectra show singlets at 74.0 and 65.8 ppm, respectively, with ^{13}C satellites ($^1J_{C-119Sn}$ = 389.1 and 383.5 Hz, respectively). **1-SnMe$_3$** and **2-SnMe$_3$** are the first examples of 1,2-azaborinin-1-yl tin complexes.

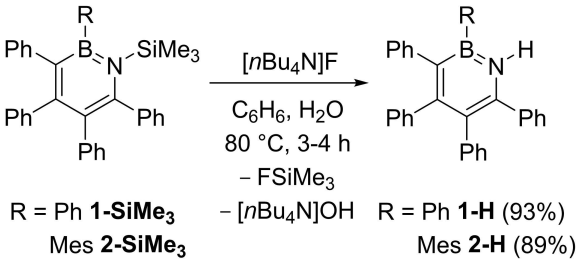
Protonation of the endocyclic nitrogen atom was achieved by refluxing **1-SiMe$_3$** and **2-SiMe$_3$** with tetra(*n*-butyl)ammonium fluoride in a 1:2 benzene/water mixture for 3–4 h (Scheme 3).[19a] Aqueous workup provided the protonated azaborinines **1-H** and **2-H**, in excellent yields (89%–93%). The ^{11}B NMR resonances are downfield-shifted to 34.6 and 37.0 ppm, respectively, compared to those of the trimethylsilyl precursors or the parent 1,2-azaborinine (δ_{11B} = 31.0 ppm).[19a] **2-H** had previously been obtained from the decomposition of **2-**



Scheme 1. Synthetic routes to 1,2-azaborinines. Mes = 2,4,6-trimethylphenyl.



Scheme 2. Synthesis of heavier tetrel-substituted 1,2-azaborinines.



Scheme 3. Synthesis of N-protonated azaborinines.

N_2Mes into **2-H** and 5,7-dimethyl-1H-indazole, the latter resulting from a Jacobsen-like indazole formation.[16d] The ^{1}H NMR spectra of **1-H** and **2-H** show characteristic deshielded N*H* singlets at 8.15 and 7.89 ppm, respectively, in line with the aromatic nature of the 1,2-azaborinine rings, and slightly upfield from that of the parent 1,2-azaborinine (δ_{1H} = 8.44 ppm).[19a] While **2-H** crystallized with a terminal N–H bond, **1-H** crystallized as the diethyl ether adduct, which presents N1–H1···O1 hydrogen bonding (N1···O1 ca. 2.97 Å, Figure 2).

Deprotonation of **1-H** and **2-H** with methyl lithium and *n*-butyl lithium, respectively, in THF yielded the corresponding lithium salts **1-Li(thf)$_2$** and **2-Li(thf)$_2$** (Scheme 4a).[23] Their sensitivity towards hydrolysis prompted us to also synthesize the TMEDA (N,N,N′,N′-tetramethylethylenediamine)-stabilized derivative **1-Li(tmeda)**. While deprotonation of **1-H** with NaHMDS (sodium bis(trimethylsilyl)amide) at 0 °C yielded the sodium salt **1-Na** in good yield, the analogous reaction with **2-H** only afforded small amounts of **2-Na** (Scheme 4b). Whereas **1-H** could also be deprotonated with KHMDS to yield **1-K** (Scheme 4c), no deprotonation was observed in the analogous reaction with **2-H**. The lower reactivity of **2-H** towards NaHMDS and KHMDS may be due to a combination of the lower acidity of its N*H* proton, as evidenced by its lower ^{1}H NMR N*H* chemical shift, and the steric repulsion of the mesityl and HMDS ligands. Instead, **2-K** was obtained in excellent yield by transmetallation of **2-Li(thf)$_2$** with potassium *tert*-butoxide (Scheme 4d). The

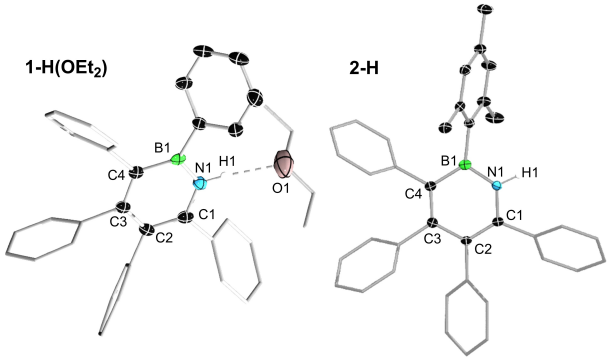
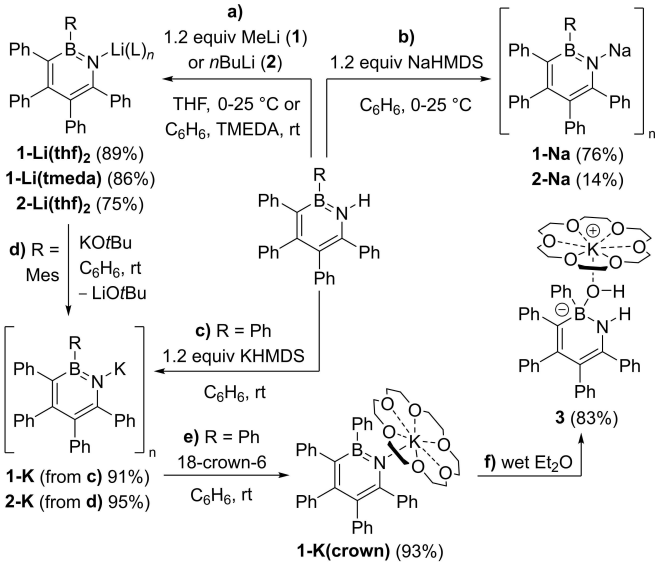


Figure 2. Crystallographically-determined solid-state structures of the diethyl ether adduct of **1-H** and **2-H**. Thermal displacement ellipsoids represented at 50% probability. Ellipsoids of peripheral phenyl and ethyl groups and hydrogen atoms omitted for clarity, except for the N1-bound proton H1.



Scheme 4. Deprotonation of **1-H** and **2-H** with group 1 bases. TMEDA = N,N,N′,N′-tetramethylethylenediamine; HMDS = hexamethyldisilazide.

sodium and potassium salts **1-M** and **2-M** (M = Na, K) are insoluble in hydrocarbon solvents. The solid-sate structures of the linear coordination polymer **[1-K]$_n$** and hexameric **[2-K]$_6$**, in which the monomers are joined by K···aryl π interactions (Figure 3), suggest that the sodium derivatives are also likely to be coordination polymers or oligomers in the solid state. In THF, they are soluble and most likely broken down into THF-solvated monomers. The addition of 18-crown-6 to the coordination polymer **1-K** led to the formation of the monomeric benzene-soluble potassium salt **1-K(crown)** (Scheme 4e). The ^{11}B NMR shifts of the alkali metal salts presented in Scheme 3 range from 33.7 to 37.2 ppm and decrease down group 1, as the N–metal interaction weakens and less electron density is removed from the azaborinine ring.

While **1-K(crown)** was successfully recrystallized from benzene, a recrystallization attempt from diethyl ether led to the isolation of the 2-hydroxy-2-phenyl-1,2-azaborinin-2-ate salt **3**, which is formed by hydrolysis of **1-K(crown)** with trace water from the recrystallization solvent into **1-H** and KOH(18-crown-6) and subsequent nucleophilic attack of the KOH hydroxyl group at the boron center of **1-H** (Scheme 3f). The sharp ^{11}B NMR singlet of **3** at −0.3 ppm confirms the quaternization of the boron atom. Its ^{1}H NMR N*H* proton is upfield-shifted by ca. 3.3 ppm compared to **1-H**, reflecting the loss of π conjugation in the C_4BN ring. Finally, the strongly shielded ^{1}H NMR BO*H* singlet at 0.91 ppm and ^{13}C NMR resonance of one BPh *ipso*-carbon at 108 ppm are indicative of OH···K and *ipso*-C_{Ph}···K bonding, respectively, which is confirmed by the solid-state structure (Figure 3).

As previously shown by Liu and Ashe, N-lithiated 1,2-azaborinines are versatile precursors for nucleophilic aromatic substitution reactions at the endocyclic nitrogen atom.[23] Similarly, the potassium salt **1-K** underwent facile salt metathesis with methyl triflate (MeOTf) to yield the corresponding N-

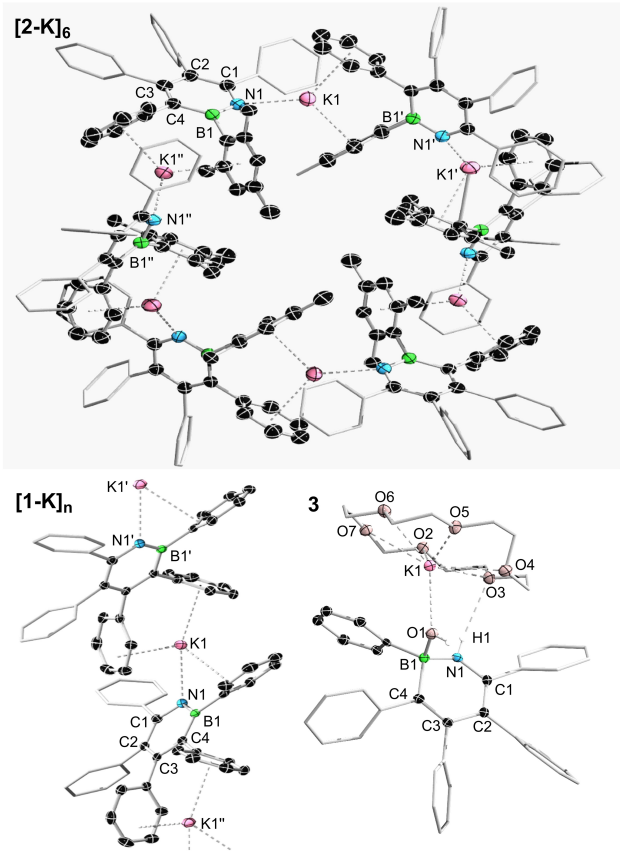
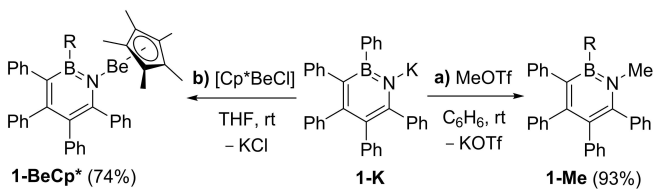


Figure 3. Crystallographically-determined solid-state structures of the **[2-K]$_6$** hexamer, the coordination polymer **1-K** and monomeric crown ether complex **3**. Thermal displacement ellipsoids represented at 50% probability for **[1-K]$_n$** and **3**, 30% for **[2-K]$_6$** (data quality insufficient for discussion of structural parameters). Ellipsoids of peripheral phenyl and ethyl groups and hydrogen atoms omitted for clarity, except for the N1-bound proton H1, π interactions between aryl groups and potassium represented as dotted lines.

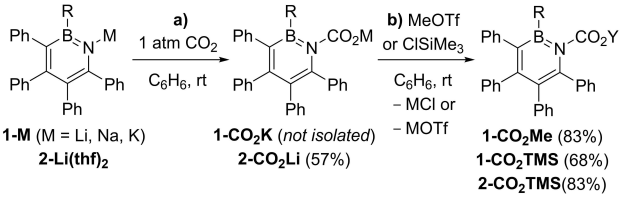
methylated **1-Me** (Scheme 5a). The ^{11}B NMR shift of **1-Me** at 35.5 ppm is slightly downfield-shifted from **1-H** (δ_{11B} = 34.6 ppm) and the N-methylation was confirmed by the C*H*$_3$ singlet at 3.21 ppm in the ^{1}H NMR spectrum. Liu et al. obtained their N-methylated 2-*n*-butyl-1-methyl-1,2-azaborinine by successive nucleophilic aromatic substitution with *n*BuLi and salt metathesis of the parent 1,2-azaborinine with methyl iodide.[23b] Similarly, salt metathesis of **1-K** with (pentamethylcyclopentadienyl)beryllium chloride, [Cp*BeCl], yielded the beryllium half-sandwich complex **1-BeCp*** (Scheme 5b). The ^{11}B NMR shift of **1-BeCp*** at 39.1 ppm is considerably deshielded compared to the alkali-metal complexes shown in Scheme 3. This is due to the strong polarization of the N–Be bond by the very electropositive and small beryllium dication, which draws electron density out of the C$_4$BN ring. The broad ^{9}Be NMR resonance at −14.9 ppm (fwmh ≈160 Hz) is slightly downfield-shifted from the half-sandwich beryllium halide complexes [Cp*BeX] (X = Cl, Br, I, δ_{9Be} = −15.1 to −15.9 ppm)[24] or the methyl complex [Cp*BeMe] (δ_{9Be} = −16.7 ppm),[25] indicating a lower electron density at beryllium and a strong electron-withdrawing ability of the 1,2-azaborinin-1-yl ligand. Complex **1-BeCp*** is also the first example of a beryllium half-sandwich complex with a nitrogen ligand.

Beyond salt metathesis, the N-metallated 1,2-azaborinines **1-M** (M = Li, Na, K) and **2-Li(thf)$_2$** also underwent insertion of CO$_2$ into the N–M bond, yielding the carboxylate salts **1-CO$_2$K** and **2-CO$_2$Li**, respectively (Scheme 6a). **2-CO$_2$Li** was isolated as a colorless solid with an ^{11}B NMR shift of 37.2 ppm, ca. 2 ppm downfield of that of **1-Me**, as expected with the electron-withdrawing carboxylate group. The ^{13}C NMR carboxylate resonance was observed at 160.5 ppm. **1-CO$_2$K** was not isolated but reacted in situ with methyl triflate and trimethylchlorosilane to generate the corresponding methyl and silyl esters **1-CO$_2$Me** and **1-CO$_2$TMS**, respectively (Scheme 6b). Similarly, salt metathesis between **2-CO$_2$Li** and ClSiMe$_3$ yielded **2-CO$_2$TMS**. The ^{11}B NMR shifts of these ester-substituted azaborinines appear at 35–37 ppm and the ^{13}C NMR resonances of their carboxylate carbon nuclei at 155–157 ppm. Furthermore, their IR spectra each show a strong C=O stretching band in the 1740–1760 cm^{-1} region, in the range typical for aliphatic esters. For comparison, Liu and co-workers have reported the synthesis of the related 1-*tert*-butylester-2-methyl-1,2-azaborinine from the salt metathesis of the N-potassiated azaborinine precursor with di-*tert*-butyldicarbonate, with an ^{11}B NMR shift of 41 ppm and an IR C=O stretching frequency of 1741 cm^{-1}.[26]

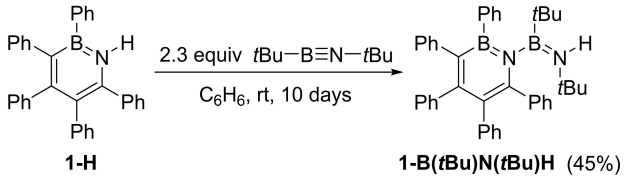
The polar B≡N triple bond of iminoboranes is known to undergo spontaneous 1,2-addition of protic N–H bonds.[27] The reaction of **1-H** with an excess of 1,2-di-*tert*-butyliminoborane in benzene at room temperature proceeded very slowly to the desired N-borylated 1,2-azaborinine **1-B(*t*Bu)N(*t*Bu)H** by addition of the N–H bond across the iminoborane B≡N triple bond (Scheme 7). The ^{11}B NMR spectrum of **1-B(*t*Bu)N(*t*Bu)H** shows two broad resonances at 40.8 and 36.7 ppm, the former being attributed to the exocyclic and the latter to the endocyclic boron atoms. The N*H* functionality appears as a singlet at 3.46 ppm in the ^{1}H NMR spectrum. The only other N-borylated



Scheme 5. Nucleophilic aromatic substitution reactions with [Cp*BeCl] (Cp* = C$_5$Me$_5$) and MeOTf (OTf = triflate) at the nitrogen atom of **1-K**.



Scheme 6. Insertion of CO$_2$ into N-metallated 1,2-azaborinines and subsequent carboxylate functionalization.

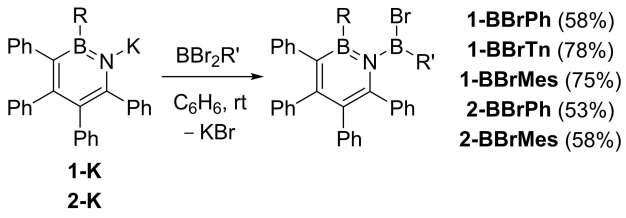


Scheme 7. N-Borylation of the 1,2-azaborinine ring by N–H bond addition across an iminoborane.

1,2-azaborinine, **1-B(NMesCH)$_2$**, was synthesized by reaction of **I** with the azidoborane $N_3B(NMesCH)_2$ and shows an ^{11}B NMR shift of 40.3 ppm for the endocyclic boron atom,[16b] significantly downfield from that of **1-B(*t*Bu)N(*t*Bu)H**. Since the 1,3-diazaborolide substituent $B(NMesCH)_2$ is less electron-withdrawing than the B(*t*Bu)N(*t*Bu)H substituent, this downfield-shift of **1-B(NMesCH)$_2$** is likely owed to steric influences disrupting the planarity of the C_4BN ring (see **X-ray crystallographic analyses**).

Compounds **1-K** and **2-K** also proved useful precursors for the N-borylation of the 1,2-azaborinine ring by salt metathesis with aryl(dibromo)boranes (Scheme 8). The resulting 1-boryl-1,2-azaborinines **1-BBrAr** (Ar = Ph, Mes, Tn; Tn = 2-thienyl) and **2-BBrAr** (Ph, Mes) were isolated as colorless solids in moderate to good yields. Their ^{11}B NMR spectra show two broad resonances at 36–38 ppm for the endocyclic and 53–56 ppm for the exocyclic boron nuclei. Since the exocyclic boron ^{11}B NMR resonances of **1-BBrPh** and **2-BBrPh** at 55.0 and 56.4 ppm, respectively, are similar to that of BBr_2Ph (δ_{11B} = 56.2 ppm),[28] the electronic effect on the boron atom of the 1,2-azaborinin-1-yl ligands may be deemed comparable to that of an electron-withdrawing bromide ligand. A notable exception is **2-BBrMes**, for which the endocyclic boron resonance is significantly downfield-shifted to 44 ppm. An X-ray crystallographic analysis reveals that this is due to the distortion of the C_4BN ring caused by the steric repulsion of the two mesityl substituents (see **X-ray crystallographic analyses**). The salt metathesis of **1-K** with the heteroaryl derivative dibromo(2-thienyl)borane (BBr_2Tn) yielded the corresponding borylated **1-BBrTn**, which shows a similar ^{11}B NMR shift to **1-BBrAr** for the endocyclic boron nucleus at 36.4 ppm and a more upfield-shifted resonance for the thienylboryl moiety at 49.3 ppm.

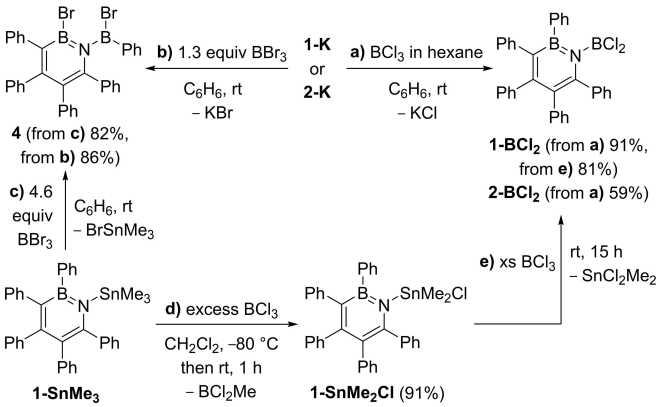
Salt metathesis of **1-K** and **2-K** with a hexane solution of BCl_3 also afforded the expected 1-dichloroboryl-1,2-azaborinines **1-BCl$_2$** and **2-BCl$_2$**, respectively, with ^{11}B NMR resonances around 46–47 and 36–38 ppm for the exocyclic and endocyclic boron



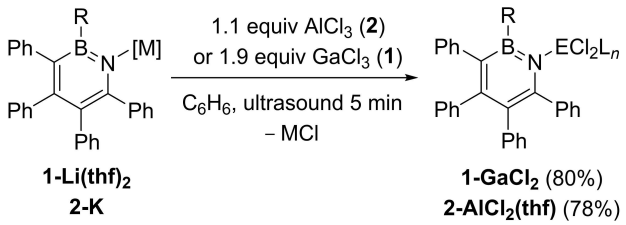
Scheme 8. N-Borylation of the 1,2-azaborinine ring by salt metathesis. Tn = 2-thienyl.

nuclei, respectively (Scheme 9a). The ^{11}B NMR shift of the exocyclic boron atom is slightly downfield from that of BCl_2Br (δ_{11B} = 44.7 ppm),[29] confirming once again that the 1,2-azaborinin-1-yl ligand is as, if not more, electron-withdrawing than a bromide when bound to boron. In contrast, the analogous reaction with BBr_3 did not yield **1-BBr$_2$** but led to the rearrangement product **4**, in which the phenyl substituent at the endocyclic boron atom and one bromide at the exocyclic boron atoms have been exchanged (Scheme 9b). As a result, the ^{11}B NMR resonance of the endocyclic boron nucleus is upfield-shifted to 30.4 ppm, which is in the range observed for related 3,4-benzo-fused 2-bromo-1,2-azaborinines (30–37 ppm),[30] while the resonance of the exocyclic boryl moiety appears at 55.7 ppm, similar to those of **1-** and **2-BBrAr**. Furthermore, the latter is also comparable to that of BBr_2Ph (δ_{11B} = 56.2 ppm),[28] once more highlighting the similar electronic effect on the boron atom of the 1,2-azaborinin-1-yl and bromide ligands. In another attempt to obtain **1-BBr$_2$** the 2-stannyl-1,2-azaborinine precursor **1-SnMe$_3$** was combined with BBr_3 in benzene. While the tin-boron exchange was successful, the only product obtained was again the 2-bromo-1,2-azaborinine **4** (Scheme 9c). The analogous reaction with BCl_3 at −80 °C, however, did not lead to the formation of **1-BCl$_2$**. Instead, a Me-Cl ligand exchange between the $SnMe_3$ moiety and BCl_3 was observed, leading to the formation of **1-SnMe$_2$Cl** (δ_{11B} = 38.8 ppm, δ_{119Sn} = 50.5 ppm) and BCl_2Me (δ_{11B} = 62.0 ppm, Scheme 9d).[31] Further addition of BCl_3 at room temperature then resulted in tin-boron exchange and the formation of **1-BCl$_2$** and the byproduct $SnMe_2Cl_2$ (Scheme 9e). The Me–Cl ligand exchange between a methylstannane and a chloroborane has been observed previously in the reaction of aryl(dichloro)boranes with $SnMe_4$.[32]

The dichloroaluminyl and -gallyl derivatives **2-AlCl$_2$(thf)** and **1-GaCl$_2$** were synthesized in a similar manner to **1-BCl$_2$** by salt metathesis of **2-K** and **1-Li(thf)$_2$**, respectively, with the corresponding group 13 trihalides under sonication in benzene (Scheme 10). While the ^{11}B NMR resonance of **2-AlCl$_2$(thf)** at 42.1 ppm is significantly downfield-shifted from that of **2-BCl$_2$** (δ_{11B} = 37.6 ppm), that of **1-GaCl$_2$** at 35.7 ppm is similar to that of **1-BCl$_2$** (δ_{11B} = 36.2 ppm). The upfield-shift of the endocyclic



Scheme 9. N-Borylation of **1-K** with trihaloboranes.

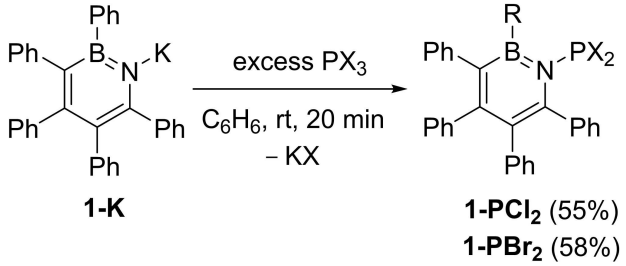


Scheme 10. Salt metathesis of **1-Li(thf)$_2$** or **2-K** with heavier group 13 trihalides.

boron atom in **2-AlCl$_2$(thf)** reflects a lower degree of π delocalization onto the boron atom, presumably due to the strong steric repulsion between the quaternary aluminyl moiety and the mesityl substituent, which causes an elongation of the B–N bond (see **X-ray crystallographic analyses**). The ^{27}Al NMR shift of **2-AlCl$_2$(thf)** at 85.5 ppm is downfield-shifted compared to AlCl$_3$(thf) (δ_{27Al} = 74.2 ppm),[33] reflecting once again the strongly electron-withdrawing nature of the 1,2-azaborinin-1-yl ligand.

Finally, the N-dihalophosphino derivatives **1-PCl$_2$** and **1-PBr$_2$** were synthesized by salt metathesis from **1-K** with PX$_3$ (X = Cl, Br, Scheme 11). **1-PCl$_2$** and **1-PBr$_2$** both show a broad ^{11}B NMR resonance around 41 ppm and a ^{31}P NMR singlet at 163.0 and 166.8 ppm, respectively. The latter are slightly upfield-shifted compared to the ^{31}P NMR shifts of PCl$_2$(NMe$_2$) and PBr$_2$(NMe$_2$) at 165 and 174 ppm, respectively.[34]

Examination of the **1-Y** and **2-Y** series presented herein as well as in the literature[16] shows that the ^{11}B NMR shift of the azaborinine boron nucleus varies in a relatively narrow range



Scheme 11. Salt metathesis of **1-K** with trihalophosphines.

between 33.8 and 44.2 ppm (Figure 4). For compounds with identical Y substituents, the ^{11}B NMR resonance of **2-Y** is on average downfield-shifted by 2.0 ppm compared to the **1-Y** derivative. Since the methyl substituents on the mesityl group are actually electron-donating, this downfield-shift must be due to sterics rather than electronics, as steric repulsion between the mesityl and N-substituent causes a slight distortion of the azaborinine ring, thus somewhat disrupting π overlap between the endocyclic nitrogen and boron atoms (see **X-ray crystallographic analyses**). The lowest shifts are observed for the group 1 series (Y = H, Li, Na, K) and, in the case of **2-Y**, compound **2-N$_2$Mes** (δ_{11B} = 35.1 ppm), which bears a strongly electron-donating azo substituent at nitrogen. The highest shift is observed for the most sterically crowded congener, **2-BBrMes** (δ_{11B} = 44.2 ppm). Overall, steric effects seem to have a stronger influence on the shielding of the endocyclic boron atom than electronic ones, as seen in the unexpected downfield shift of **2-AlCl$_2$(thf)** (δ_{11B} = 42.1 ppm) compared to the less sterically crowded but much more electron-withdrawing **2-BCl$_2$** (δ_{11B} = 37.6 ppm) or that of the strongly electron-donating **1-SiMe$_3$** (δ_{11B} = 39.8 ppm) compared to the much smaller yet less electron-donating **1-Me** (δ_{11B} = 35.6 ppm). Electronic effects are, however, visible when comparing compounds with similar steric crowding at nitrogen and boron but with peripheral electron-donating and -withdrawing substituents, such as **2-(4-*i*PrC$_6$H$_4$)** (δ_{11B} = 37.2 ppm) and the much more electron-withdrawing and deshielded **2-(4-FC$_6$H$_4$)** (δ_{11B} = 39.4 ppm).[16b,e]

X-ray crystallographic analyses

The solid-state structures of **1-Y** (Y = SnMe$_3$, H, Li(thf)$_2$, Li(tmeda), K, BeCp*, Me, CO$_2$Me, BCl$_2$, BBrAr (Ar = Ph, Tn, Mes), GaCl$_2$), **2-Y** (Y = SnMe$_3$, H, Li(thf)$_2$, BCl$_2$, BBrMes, AlCl$_2$(thf)) and **3** were determined by single-crystal X-ray crystallographic analyses (Figures 2, 3 and 5 and Figures S210–S231 in the Supporting Information). The solid-state structures of several **1-Y** analogues (**1-Li(thf)$_2$**, **1-Li(tmeda)** and **1-B(*t*Bu)N(*t*Bu)H**) present a flip disorder in the B1-N1-C1 moiety of the azaborinine ring as the C1-Ph and B1-Ph moieties have interchangeable steric profiles, thus preventing the discussion of bonding parameters within this fragment. Furthermore, the structures of **1-BCl$_2$** and **1-AlCl$_2$(thf)** both present whole-molecule disorder precluding all

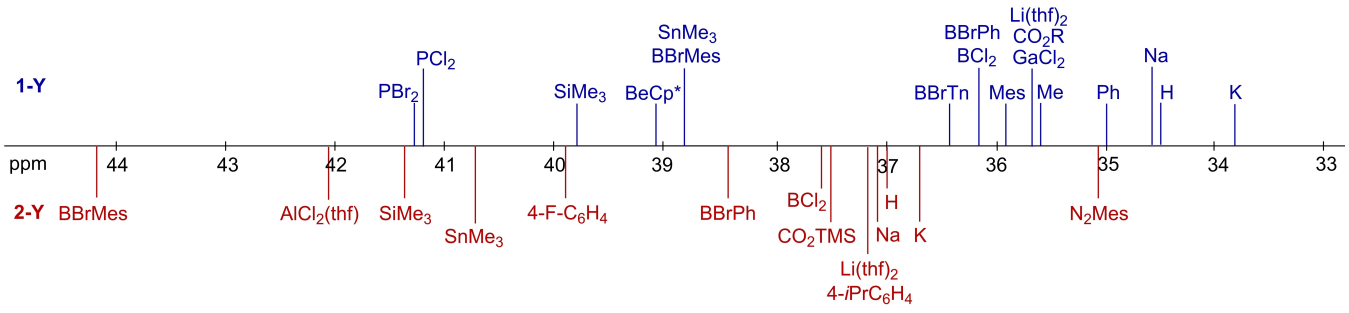


Figure 4. Distribution of ^{11}B NMR shifts of **1-Y** (top, Y in dark blue) and **2-Y** (bottom, Y in dark red) from this work and the literature: **1-Ph**,[16e] **1-Mes**, **1-SiMe$_3$**,[16e,f] **2-N$_2$Mes**,[16d] **2-(4-*i*PrC$_6$H$_4$)**,[16e] **2-(4-FC$_6$H$_4$)**,[16b] **2-SiMe$_3$**.[16e]

Table 1. ^{11}B NMR shifts (ppm) of the azaborinine boron nucleus, as well as selected bond lengths (Å), bond angles (°) and torsion angles (°) of the crystallographically-characterized compounds presented herein. Structures presenting a B1-N1-C1 flip disorder in the azaborinine ring (**1-Li(thf)$_2$**, **1-Li(tmeda)**, **1-BNH(tBu)$_2$**) or whole-molecule disorders (**1-BCl$_2$**, **2-AlCl$_2$(thf)**) are excluded.

	δ_{11B}	N1–E	B1–N1	N1–C1	C1–C2	C2–C3	C3–C4	C4–B1	Σ(∠B1)	Σ(∠N1)	C4–B1–N1–C1	C2–C1–N1–E	C3–C4–B1–C_R
1-SnMe$_3$[a]	38.8	2.141(3)	1.431(4)	1.397(4)	1.411(5)	1.419(5)	1.398(5)	1.486(5)	359.8(3)	358.2(3)	−9.3(5)	−158.1(2)	−169.7(3)
2-SnMe$_3$[a]	40.7	2.141(7)	1.434(12)	1.393(12)	1.353(14)	1.446(11)	1.371(12)	1.528(12)	359.9(8)	359.2(8)	7.9(1)	162.4(7)	174.1(7)
1-H[b]	34.6	[c]	1.414(5)	1.382(4)	1.399(5)	1.411(5)	1.396(5)	1.505(5)	360.0(3)	[c]	1.2(4)	[c]	175.5(3)
2-H[b]	37.0	0.910(16)	1.4240(19)	1.3764(17)	1.3807(18)	1.4486(18)	1.3843(19)	1.519(2)	360.0(1)	360.0(3)	3.1(2)	178(1)	178.9(1)
2-Li(thf)$_2$[e]	37.2	1.941(4)	1.424(3)	1.349(3)	1.400(3)	1.431(3)	1.386(3)	1.526(3)	360.0(2)	360.0(2)	1.9(3)	178.1(2)	173.7(2)
1-K[f]	33.8	2.7205(15)	1.404(2)	1.359(2)	1.434(3)	1.420(2)	1.404(2)	1.493(3)	360.0(2)	345.0(2)	−0.4(3)	−133.6(2)	−176.9(2)
1-BeCp*[h]	39.1	1.632(5)	1.420(4)	1.388(4)	1.446(4)	1.430(4)	1.392(4)	1.459(5)	359.5(3)	357.0(3)	10.5(4)	151.2(3)	168.6(3)
1-Me[i,j]	35.6	1.482(4)	1.407(3)	1.414(3)	1.447(4)	1.411(3)	1.410(3)	1.434(4)	[d]	360.0(2)	−4.3(4)	−177.9(3)	[d]
		1.482(3)	1.413(4)	1.408(3)	1.451(4)	1.410(4)	1.416(4)	1.447(4)	[d]	360.0(2)	5.5(4)	−179.9(3)	[d]
1-CO$_2$Me[l]	35.7	1.441(6)	1.423(7)	1.406(6)	1.414(6)	1.435(6)	1.406(6)	1.468(7)	360.0(4)	360.0(4)	−1.4(7)	−173.1(4)	179.5(5)
1-BBrPh[k]	36.2	[d]	1.421(5)	1.422(5)	1.428(7)	1.416(5)	1.415(5)	1.436(6)	359.9(4)	[d]	−3.3(6)	[d]	−174.2(4)
1-BBrTn[k]	36.4	1.489(6)	1.432(5)	1.415(6)	1.443(7)	1.415(6)	1.414(6)	1.444(6)	359.9(4)	359.9(4)	3.5(7)	176.8(5)	174.1(5)
1-BBrMes[k]	38.8	1.476(3)	1.450(3)	1.411(3)	1.377(3)	1.439(3)	1.379(3)	1.525(3)	359.9(2)	357.2(2)	−9.7(3)	−152.1(2)	179.9(2)
2-BBrMes[k,j]	44.2	1.465(7)	1.462(8)	1.414(7)	1.369(8)	1.453(8)	1.367(8)	1.536(8)	360.0(5)	358.1(5)	11.3(8)	151.9(5)	175.7(5)
		1.469(8)	1.453(8)	1.420(7)	1.376(8)	1.435(8)	1.384(8)	1.536(8)	359.9(5)	357.0(5)	−14.4(8)	−145.7(5)	−172.6(5)
2-BCl$_2$[k]	37.6	1.472(8)	1.451(8)	1.396(8)	1.379(8)	1.455(8)	1.365(8)	1.535(9)	359.9(5)	359.5(5)	−6.3(9)	172.5(6)	167.3(6)
1-GaCl$_2$[l]	35.7	1.876(3)	1.405(5)	1.380(4)	1.428(5)	1.427(5)	1.411(5)	1.469(5)	360.0(3)	359.6(3)	−1.4(5)	−173.4(2)	−178.9(3)

[a] E = Sn; [b] E = H; [c] N-bound hydrogen modelled with HFIX in idealized position; [d] bonding parameters cannot be discussed due to structural disorder; [e] E = Li; [f] E = K; [g] tetrahedral boron atom; [h] E = Be; [i] E = C; [j] two molecules present in the asymmetric unit; [k] E = B; [l] E = Ga.

discussion of their bonding parameters. Relevant bond lengths, bond angles and torsion angles of the compounds without any disorder within the azaborinine ring are listed in Table 1. The C_4BN ring atoms in all compounds are numbered as in Figures 2 and 3.

The C_4BN rings of **1-H** and **2-H** (Figure 2) are quasi-planar, with small endocyclic torsion angles, $<2.7°$ and $<4.8°$, respectively. The steric influence of the larger mesityl substituent at boron is mostly reflected in the significant increase in C–C bond length alternation within the C_4BN rings of **2-H** (C1–C2 1.3807(18), C2–C3 1.4486(18), C3–C4 1.3843(19) Å) compared to that of **1-H** (C1–C2 1.399(5), C2–C3 1.411(5), C3–C4 1.396(5) Å). This is also in line with the downfield shift of its ^{11}B NMR resonance (δ_{11B} = 37.0 (**2-H**), 34.6 (**1-H**) ppm) as less π electron density is delocalized from N1 onto B1. The same trend is observed for all the compounds **2-Y**, which show significantly more pronounced endocyclic C–C bond length alternation (avg. C1–C2 1.38, C2–C3 1.44, C3–C4 1.38 Å) than **1-H** (avg. C1–C2 1.42, C2–C3 1.42, C3–C4 1.40 Å). The highest degree of bond length alternation in each of the **1-Y** and **2-Y** series is observed for the compounds with the most sterically demanding substituent Y, **1-BBrMes** (C1–C2 1.377(3), C2–C3 1.439(3), C3–C4 1.379(3) Å) and **2-BBrMes** (avg. C1–C2 1.373(8), C2–C3 1.444(8), C3–C4 1.375(8) Å).

The selected solid-state structures viewed along the C_4 plane of the azaborinine ring in Figure 5 exemplify the increasing twisting of the azaborinine ring and increasing tilt angle of the N-substituent with increasing sterics. While the endocyclic boron atom B1 remains perfectly planar in all the azaborinine derivatives, the nitrogen atom N1 deviates slightly from planarity for the more sterically demanding substituents Y, namely BeCp* and BBrMes (Σ(∠N1) 357.0(3)–357.5(5)°). Within the **1-Y** series the absolute value of the C4–B1–N1–C1 torsion angle, which is indicative of the degree of planarity of that

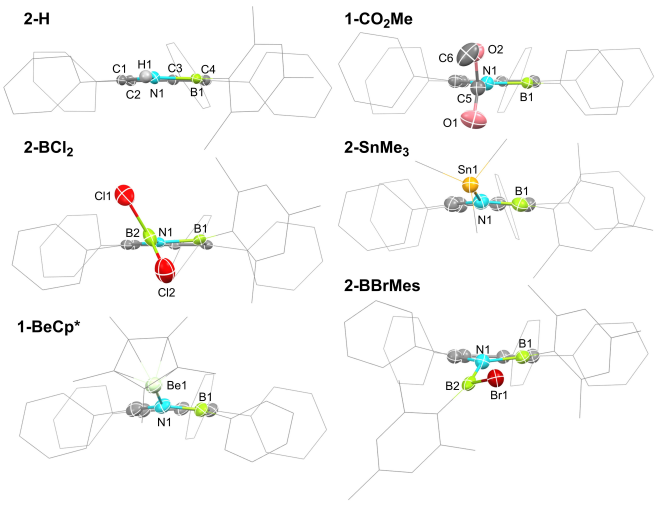


Figure 5. Crystallographically determined solid-state structures of **2-H**, **1-CO$_2$Me**, **2-BCl$_2$**, **2-SnMe$_3$**, **1-BeCp***, and **2-BBrMes**, viewed along the azaborinine C_4 plane. Thermal displacement ellipsoids represented at 50% probability. Peripheral groups shown in wireframe representation and hydrogen atoms omitted for clarity.

portion of the C_4BN ring, and thereby of the π overlap between the lone pair of the endocyclic nitrogen and the empty p-orbital at boron, increases with the increasing steric demand of Y in the order of $Y = H \approx K < Li(thf)_2 \approx CO_2Me < BBrPh \approx BBrTn < SnMe_3 \approx BeCp^* < BBrMes$ (**1-Me** is an outlier due to a disorder in the boron-bound phenyl group).

Furthermore, for compounds with the same Y substituent, the absolute value of the C4–B1–N1–C1 torsion angle is higher in the **2-Y** than in the **1-Y** series (e.g., **1-BBrMes** 9.7(3)° < **2-BBrMes** 12.9(8)°) as the sterics of the mesityl substituent collide with those of Y, increasing the distortion of the C_4BN ring. It is also noteworthy that the larger substituents Y are increasingly tilted out of the azaborinine plane, as quantified by a decrease in the absolute value of the torsion angle C2–C1–N1–E with increasing sterics of Y. Thus, while |C2–C1–N1–E| is close to 180° for the smaller substituents Y = H, $Li(thf)_2$ and Me in the **1-Y** series, it decreases to 158.1(2)° for **1-SnMe$_3$**, all the way down to 152.1(2) and 151.2(3)° for **1-BBrMes** and **1-BeCp***, respectively. The only outlier is the coordination polymer **[1-K]$_n$**, for which an additional π interaction with the boron-bound phenyl substituent leads very strong tilting out of the azaborinine plane (C2–C1–N1–K1 −133.6(2)°). The degree of tilting of the boron-bound phenyl or mesityl substituent out of the azaborinine plane, quantified by the absolute value of the torsion angle C3–C4–B1–C_R, does not seem to follow a clear steric or electronic trend for either R or Y.

Plotting the ^{11}B NMR shifts of **1-Y** and **2-Y** (new and literature-known compounds) against the torsion angles C2–C1–N1–E and C4–B1–N1–C1 showed an upfield shift with increasing C2–C1–N1–E, i.e., with decreasing tilting of E out the azaborinine plane, and a downfield shift with increasing C4–B1–N1–C1, i.e., with increasing distortion of the C_4BN ring. The trends could in each case be fitted linearly with good correlation (Figure 6). It may therefore be concluded that the degree of planarity of the azaborinine ring within itself and with the substituent at the nitrogen atom, which are mainly governed by the sterics of the exocyclic substituents at both the endocyclic boron and nitrogen atoms, are the major factors determining the ^{11}B NMR shift of 1,2-azaborinine derivatives:

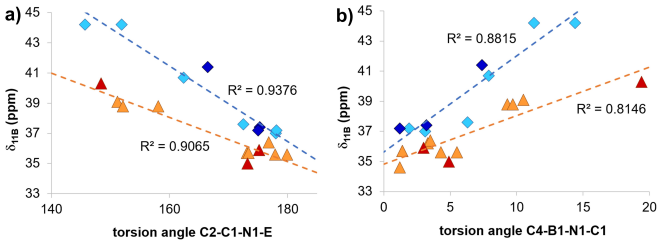


Figure 6. Plots of δ_{11B} (ppm) versus absolute values of torsion angles a) C2–C1–N1–E and b) C4–B1–N1–C1 (°) for crystallographically-characterized compounds of the series **1-Y** (compounds presented herein in orange, **1-K** excluded; literature-known **1-Y** in dark red, Y = Ph, Mes, $B(NMesCH)_2$) and **2-Y** (compounds presented herein in light blue; literature-known **2-Y** in dark red, Y = $SiMe_3$, 4-$OMeC_6H_4$, 4-$iPrC_6H_4$). The dotted lines represent the best fit of linear regression for each data set, R^2 is the square of the trendline correlation coefficient.

the closer to planarity the more upfield-shifted the ^{11}B NMR resonance, indicating a higher electron density at boron.

DFT calculations

As shown by the experimental results, the 1,2-azaborinin-1-yl ligand is rather unusual in that, unlike the vast majority of anionic N-ligands, which are 2π-electron donors through their available lone pair, it has electron-withdrawing ability similar to a bromide ligand. The lack of π donation was confirmed by DFT calculations on **1-ECl$_2$** (E = B, Al, Ga) optimized at the B3LYP-D3(BJ)-def2-SVP level of theory (see Supporting Information for details). The calculated Wiberg bond indices (WBIs) for the N–E bonds of these three complexes are 1.07, 0.78 and 0.78, respectively, indicating essentially single bonds, with at most a very small double bond character for the exocyclic N–B bond. The partial double bond character of the endocyclic N–B bonds, however, is confirmed by the calculated WBIs of 1.21, 1.25 and 1.26 for E = B, Al, Ga, respectively. Unlike the N–E bonds in **1-ECl$_2$**, those in ECl_2NMe_2 (E = B, Al, Ga) have WBIs of 1.42, 1.15 and 1.17, respectively, indicating strong double bond character for the N–B bond and lower but non-negligible double bond character for the N–Al and N–Ga bonds.

This is also borne out by the inspection of the frontier molecular orbitals (MOs) of **1-ECl$_2$** involved in the π delocalization over the C_4BN ring (HOMO, HOMO-1 and HOMO-11), which show no π-bonding contribution between the azaborinine nitrogen atom and the exocyclic boron atom (see Figure 7 for **1-BCl$_2$** and Figure S234 in the Supporting Information for **1-AlCl$_2$** and **1-GaCl$_2$**). The lack of π donation to the ECl_2 fragment is also reflected in the negligible energy differences ($\Delta E \leq \pm$ 0.07 eV) between the three compounds for these three MOs. In contrast, the HOMO of the amino-substituted group 13 dichlorides, ECl_2NMe_2, corresponds in all three cases to the N–E π bond. Furthermore, the HOMO of BCl_2NMe_2 is stabilized by 0.67 eV compared to that of $AlCl_2NMe_2$ due to the better p orbital overlap between N and B (see Figure S233 in the Supporting Information). Thus, unlike the vast majority of anionic nitrogen ligands the 1,2-azaborinin-1-yl ligand has no significant π-donor ability.

Nucleus-independent chemical shift (NICS)[35] calculations were performed on structures optimized at the B3LYP-D3(BJ)-def2-SVP level of theory to assess the aromaticity of the 1,2-

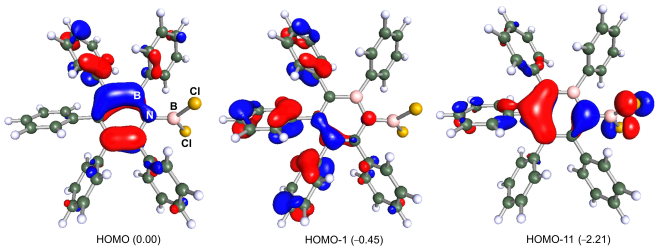


Figure 7. Plots of the frontier HOMOs of **1-BCl$_2$** involved in the π delocalization over the C_4BN ring, calculated at the B3LYP-D3(BJ)-def2-SVP level of theory. Relative energies in parentheses in eV. Isovalues at 0.04.

Table 2. Wiberg bond indices (WBIs) of the endocyclic B–N bond, NICS(−1)$_{zz}$, NICS(1)$_{zz}$ and NICS(±1)$_{zz}$ (= mean of NICS(−1)$_{zz}$ and NICS(1)$_{zz}$) values of benzene and selected 1,2-azaborinines calculated at the B3LYP-D3(BJ)-def2-SVP level of theory.

Compound	WBI(N1-B1)	NICS(-1)$_{zz}$	NICS(1)$_{zz}$	NICS(±1)$_{zz}$
benzene	–	−29.27	−29.27	−29.27
1,2-azaborinine	1.30	−20.45	−20.45	−20.45
1-H	1.31	−13.30	−13.54	−13.42
2-H	1.32	−14.04	−14.17	−14.11
1-BeCp*	1.29	−13.79	−15.68	−14.74
1-Me	1.27	−14.72	−14.32	−14.47
1-CO$_2$Me	1.19	−12.95	−12.95	−12.95
1-SnMe$_3$	1.25	−13.19	−14.97	−14.08
1-BCl$_2$	1.21	−12.91	−12.85	−12.88
2-BBrMes	1.16	−13.21	−12.17	−12.69
1-GaCl$_2$	1.26	−14.61	−14.00	−14.31
1-PCl$_2$	1.15	−11.46	−10.38	−10.92

azaborinine ring in several of the derivatives presented herein and compare it to that of benzene and the parent 1,2-azaborinine. The calculated NICS(-1)$_{zz}$, NICS(1)$_{zz}$ and NICS(±1)$_{zz}$ (= mean of NICS(−1)$_{zz}$ and NICS(1)$_{zz}$) values (ppm) are listed in Table 2 together with the calculated WBIs of the endocyclic B–N bond.

The NICS(±1)$_{zz}$ values confirm that the aromaticity of **1-Y** and **2-Y** ($-10.92 \leq$ NICS(±1)$_{zz} \leq -14.74$) is significantly lower than that of the parent 1,2-azaborinine (−20.45), itself significantly less aromatic than benzene (−29.27), as reported in the literature.[3d,36] The lower aromaticity of **1-Y** and **2-Y** compared to the parent compound is owed to the electron-withdrawing effect of their five aryl substituents. The least negative NICS(±1)$_{zz}$ values, indicative of the lowest degree of aromaticity, are observed for highly electron-withdrawing substituents with good orbital overlap with the endocyclic nitrogen atom (**1-CO$_2$Me** −12.95; **1-BCl$_2$** −12.88; **2-BBrMes** −12.69; **1-PCl$_2$** −10.92). The more negative NICS(±1)$_{zz}$ value of **1-GaCl$_2$** (-14.31) may result from the lack of orbital overlap between Ga and N, which leaves the π electron density of the ring essentially undisturbed.

Electron-donating or electronically saturated substituents seem to slightly increase the aromaticity of **1-Y**, as suggested by the more negative NICS(±1)$_{zz}$ values of **1-SnMe$_3$** (−14.08) and **1-Me** (−14.47) and **1-BeCp*** (−14.74) compared to **1-H** (−13.42). Examination of the WBIs of the endocyclic B–N bonds suggests a rough correlation (when excluding the extreme cases of **1-H**, **2-H** and **1-BBrMes**) between the degree of endocyclic B–N π bonding and the NICS(±1)$_{zz}$ values, the latter tending to become more negative as the former increases. It is noteworthy that the degree of distortion of the C_4BN ring or of tilting of the substituent Y out of the C_4BN plane seems to have little effect on the NICS(±1)$_{zz}$ values. Thus, the aromaticity of the 1,2-azaborinine ring can be up- or down-tuned with an appropriate choice of substituent at the nitrogen atom.

Conclusion

In this study we have shown that N-protonated 1,2-azaborinines provide a versatile platform for further functionalization at the endocyclic nitrogen atom with various main group elements (E). Deprotonation with group 1 bases affords the corresponding azaborinin-1-yl salts, which are oligo- or polymeric in the absence of stabilizing Lewis bases and monomeric in the presence of the latter. Insertion of CO_2 into the exocyclic N–M bond provides access to carboxylate-substituted azaborinine salts, which can be further derivatized into azaborinine-substituted alkyl or silyl esters. Salt metathesis of the group 1 azaborininyl salts with an organoberyllium halide, methyl triflate, aryl(dihalo)boranes, group 13 trichlorides and phosphorus trihalides yields the corresponding N-beryllated, N-methylated, N-borylated, N-aluminylated, N-gallylated and N-phosphanylated azaborinines. Alternatively, N-borylated azaborinines were obtained by tin-boron exchange between the N-trimethylstannyl derivative and the corresponding haloborane. The salt metathesis of the 2,3,4,5,6-pentaphenyl-1,2-azaborinin-1-yl potassium salt or its trimethylstannyl derivative with BBr_3 resulted in an additional Ph-Br exchange between the endocyclic and exocyclic boron atoms, yielding a 2-bromo-1,2-azaborinine. Structural analyses showed that the azaborinine C_4BN ring displays increasing bond length alternation with increasing sterics of the substituent at the endocyclic boron atom, as well as increasing distortion from planarity and out-of-plane tilt of the nitrogen substituent with increasing sterics of the latter. This is also reflected in an increasing downfield shift of the ^{11}B NMR resonance of the endocyclic boron atom as π donation from the lone pair at nitrogen to the empty p orbital at boron is increasingly disrupted, a trend which can be modelled by linear correlations between the endocyclic ^{11}B NMR shift and the C4–B–N–C1 and C2–C1–N1–E torsion angles, respectively. DFT calculations show that the 1,2-azaborinin-1-yl ligand is an unusually electron-withdrawing anionic nitrogen ligand lacking π-donor ability. NICS calculations indicate that the aromaticity of the C_4BN ring can be subtly decreased with electron-withdrawing substituents at the nitrogen atom and increased with electron-donating ones.

Experimental

All experimental details provided in the Supporting Information in a separate file (pdf): synthetic procedures, NMR, IR and X-ray crystallographic data, as well as details of the computations.

Deposition Number(s) 2213410-2213431 and 2213438 contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service. See Table S1 in the Supporting Information for the correspondence between CCDC and compound numbers

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: 1,2-azaborinine · aromaticity · crystallographic analyses · N-functionalization · salt metathesis

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