

## Boron Cations

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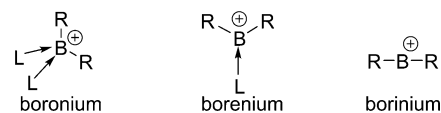
## Using Ylide Functionalization to Stabilize Boron Cations

Thorsten Scherpf, Kai-Stephan Feichtner, and Viktoria H. Gessner\*

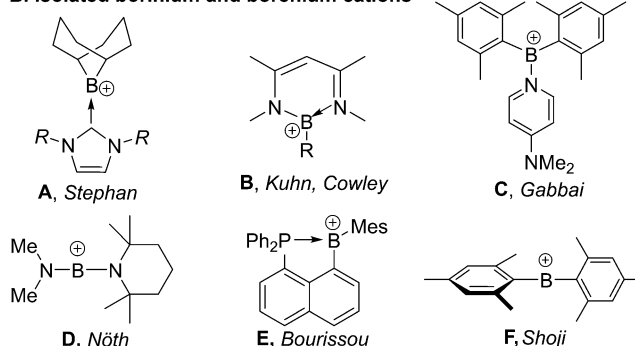
**Abstract:** The metalated ylide  $YNa$  [ $Y = (Ph_3PCSO_2Tol)^-$ ] was employed as  $X,L$ -donor ligand for the preparation of a series of boron cations. Treatment of the bis-ylide functionalized borane  $Y_2BH$  with different trityl salts or  $B(C_6F_5)_3$  for hydride abstraction readily results in the formation of the bis-ylide functionalized boron cation  $[Y-B-Y]^+$  (**2**). The high donor capacity of the ylide ligands allowed the isolation of the cationic species and its characterization in solution as well as in solid state. DFT calculations demonstrate that the cation is efficiently stabilized through electrostatic effects as well as  $\pi$ -donation from the ylide ligands, which results in its high stability. Despite the high stability of **2**  $[Y-B-Y]^+$  serves as viable source for the preparation of further borenium cations of type  $Y_2B^+ \leftarrow LB$  by addition of Lewis bases such as amines and amides. Primary and secondary amines react to tris-(amino)boranes via  $N-H$  activation across the  $B-C$  bond.

The chemistry of boron compounds is strongly connected with their exceptional Lewis acidity. Hence, their general properties, bonding modes and reactivities are dictated by their tendency to overcome their intrinsic electron deficiency, such as by adduct formation or oligomerization. Cationic boron species are naturally even more reactive due to their higher electron deficiency.<sup>[1]</sup> Depending on the coordination number, boron cations are classified into three classes.<sup>[2]</sup> While borinium species are highly reactive, two-coordinate compounds, boronium and borenium cations are four- and three-coordinate species, that are additionally stabilized by coordination of neutral donor ligands (L, Figure 1 A). Particularly borenium cations have fostered intense research interest over the past five years<sup>[3]</sup> due to the discovery of a series of applications in stoichiometric as well as catalytic transformations.<sup>[4]</sup> For example, the research groups of Curran, Vedejs, and Ingleson reported on borenium-catalyzed hydroboration<sup>[5]</sup> and haloboration<sup>[6]</sup> reactions, while the research groups of Stephan and Crudden established hydro-

## A. Classes of boron cations



## B. Isolated borenium and borinium cations



**Figure 1.** A) Classes of boron cations and B) isolated borenium and borinium cations.

genation reactions proceeding through FLP-type mechanisms (FLP = frustrated Lewis pair<sup>[7]</sup>).<sup>[8]</sup>

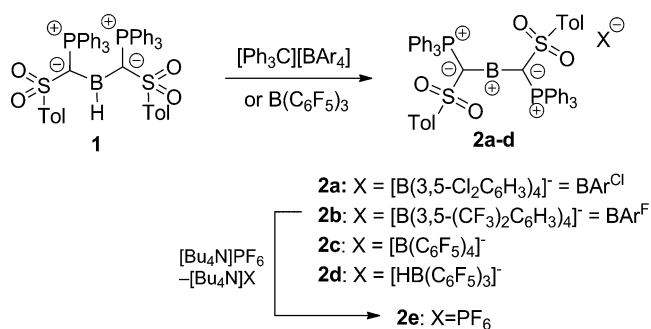
Despite these advances in the application of boron cations, these species—particularly the two- and three-coordinate systems—are still relatively underexplored with only a limited number being isolated.<sup>[9]</sup> Their chemistry has particularly benefited from the development of sterically demanding substituents and new ligand systems, such as strong (and often bulky or multidentate) N-donor ligands,<sup>[10]</sup> N-heterocyclic carbenes (NHC)<sup>[11]</sup> or carbodiphosphoranes (e.g. **A–F**, Figure 1 B).<sup>[12]</sup> These ligands facilitated their stabilization and thus their isolation.<sup>[13,14]</sup> Nevertheless, almost all isolated boron cations rely on the use of amido or aryl groups as anionic substituents at boron. They are capable to efficiently stabilize the cation by minimizing the electron deficiency at boron through additional  $\pi$ -donation. Our group has become interested in the coordination chemistry of ylidic donor ligands. Particularly, metalated ylides with two lone pairs of electrons at the central carbon atom seemed to be ideal ligands for the stabilization of electron-deficient species due to their potential ability to function as carbon-centered  $\sigma$ - and  $\pi$ -donor ligands.<sup>[15]</sup> Herein, we challenged this donor capacity of metalated ylides and their applicability as a novel class of  $X,L$ -type ligands for the stabilization of cationic boron species.

For the preparation of an ylide-stabilized boron cation we chose a synthetic strategy via hydride abstraction from the bis(ylide)-functionalized borane **1** (Scheme 1). **1** is conveniently accessible from the metalated ylide  $YNa$  [ $Y = (Ph_3PCSO_2Tol)^-$ ] and  $BH_3 \cdot THF$ .<sup>[15]</sup> To access the correspond-

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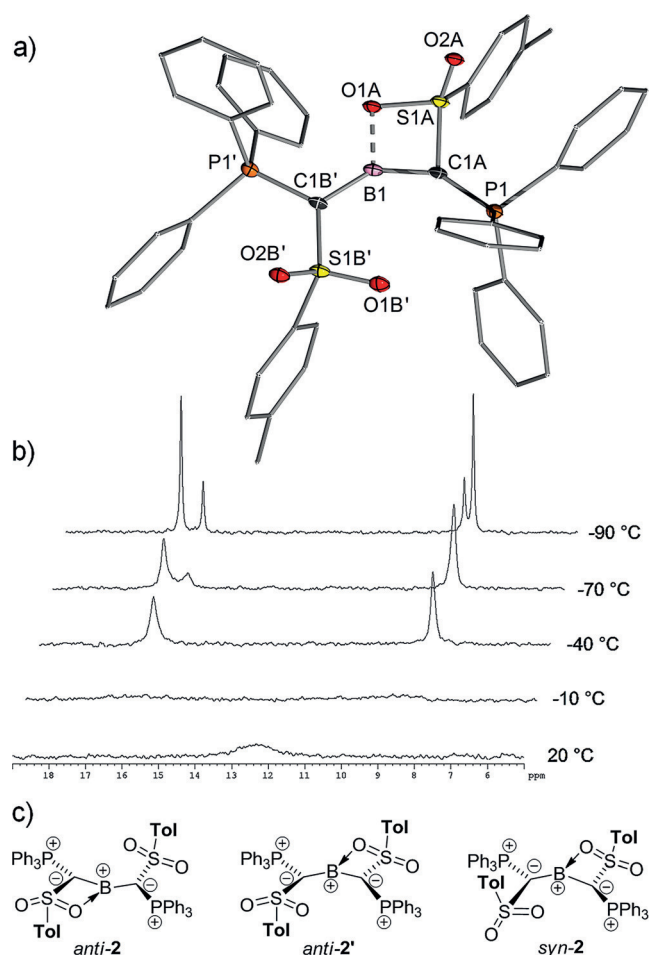
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**Scheme 1.** Preparation of boron cation **2** with different counterions.

ing boron cation a solution of **1** in  $\text{CHCl}_3$  was treated with one equiv. of a trityl salt with a weakly coordinating anion,  $[\text{Ph}_3\text{C}][\text{BAR}_4]$  ( $\text{Ar} = 3,5\text{-Cl}_2\text{C}_6\text{H}_3$ ,  $3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$  or  $\text{C}_6\text{F}_5$ ; see the Supporting Information for experimental details).<sup>[16]</sup> Reaction monitoring showed the consumption of the starting material and formation of one major new product exhibiting a broad signal at  $\delta_{\text{p}} = 12.5$  ppm in the  $^{31}\text{P}$  NMR spectrum (**1**:  $\delta_{\text{p}} = 23.8$  ppm) and a broad signal at  $\delta_{\text{b}} = 40.3$  ppm in the  $^{11}\text{B}$  NMR spectrum.  $^1\text{H}$  NMR spectroscopy clearly confirmed the formation of  $\text{Ph}_3\text{CH}$ , thus indicating successful formation of boron cation **2**. After 16 h reaction time at  $50^\circ\text{C}$  the conversion to **2** was found to be greater than 80%. Most remarkably, **2** could also be obtained from **1** with the strong Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>[17]</sup> This suggests that the formed boron cation **2d** is—owing to the donor capacity of the ylide ligands—less electron-deficient than  $\text{B}(\text{C}_6\text{F}_5)_3$  itself.

Despite the high-yielding formation of **2** its isolation revealed to be complicated due to the highly viscous nature of the obtained salts. To obtain **2** as solid material smaller counter-anions were tested to facilitate crystallization. Ion exchange by addition of  $[\text{Bu}_4\text{N}]\text{PF}_6$  to the crude reaction mixture led to **2e** as colorless solid and thus allowed its isolation in an overall yield of 61%. **2** exhibits a high thermal stability (also in refluxing toluene) and can be stored for months under inert conditions at room temperature without showing any decomposition reactions. A thermogravimetric analysis of **2e** showed no decomposition up to  $200^\circ\text{C}$  (see the Supporting Information). In the molecular structure, the asymmetric unit contains half a molecule which is assembled to **2e** through  $\text{C}_2$ -symmetry.<sup>[18]</sup> Thereby, the molecule features a disorder of the  $\text{B}-\text{C}-\text{SO}_2$  moiety, which however could be de-convoluted and the structure was refined satisfactorily. No interaction between the  $\text{PF}_6^-$  anion and the boron center is observed in the crystal structure (Figure 2 and the Supporting Information). However, **2e** features no two-coordinate boron atom. Instead, the sulfonyl groups of the ylide ligands coordinate to boron, thus leading to a slightly bent  $\text{C}-\text{B}-\text{C}$  moiety with a large angle of  $144.0(4)^\circ$ . Due to the disorder and the  $\text{C}_2$  symmetry in the molecular structure the sulfonyl moiety of both ylide ligands coordinate to the boron center, resulting in an all-planar  $\text{L}-\text{B}-\text{L}$  fragment ( $\text{L} = \text{PCS}$ ). Figure 2a shows only one possible arrangement. The two  $\text{C}-\text{B}1$  distances of 1.481(7) and 1.510(9) Å are both shorter than typical single bonds,<sup>[19]</sup> thus suggesting a considerable degree of  $\pi$ -donation from the ylide ligands to the boron center.



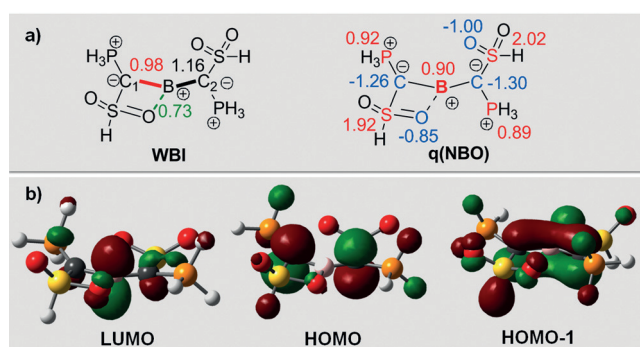
**Figure 2.** a) Molecular structure of **2-PF<sub>6</sub>** (disorder of the  $\text{CSO}_2$  moiety not depicted). Hydrogen atoms and the  $\text{PF}_6^-$  anion are omitted for clarity; 50% displacement parameters. Selected bond lengths [Å] and angles [°]:  $\text{C1B}-\text{B}'$  1.481(7),  $\text{C1A}-\text{B}$  1.510(9),  $\text{P}-\text{C1A}$  1.676(8),  $\text{P}-\text{C1B}$  1.781(8),  $\text{C1A}-\text{S1A}$  1.669(6),  $\text{C1B}-\text{S1B}$  1.701(6),  $\text{S1A}-\text{O2A}$  1.423(4),  $\text{S1A}-\text{O1A}$  1.592(5),  $\text{S1B}-\text{O1B}$  1.428(5),  $\text{S1B}-\text{O2B}$  1.444(4),  $\text{O1A}-\text{B}$  1.493(6),  $\text{S1A}-\text{C1A}-\text{P}$  124.3(4),  $\text{S1B}-\text{C1B}-\text{P}$  119.4(3);  $\text{C1A}-\text{B1}-\text{C1B}'$  144.0(4),  $\text{O1A}-\text{B}-\text{C1A}$  96.5(4). b)  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **2** at different temperatures. c) Different isomers of **2** in solution.

Thereby, the shorter  $\text{C}-\text{B}$  distance corresponds to the *exo*-cyclic boron carbon bond ( $\text{B1}-\text{C1B}'$ ). The  $\text{P1}-\text{C1}$  and  $\text{S1}-\text{C1}$  bond lengths in the ligand backbone are in average longer (e.g.  $\text{S1}-\text{C1}$  (average): 1.685(6) Å) than in the metalated ylide  $[\text{Ph}_3\text{PCSO}_2\text{Ph}]\text{Na}$  (e.g.  $\text{S}-\text{C1}$ : 1.626(2) Å). This is consistent with a reduced negative charge at  $\text{C1}$  and reduced electrostatic interactions within the  $\text{P}-\text{C}-\text{S}$  backbone, which is conform with the  $\pi$ -interaction between the ylide ligand and the boron center.<sup>[15]</sup>

NMR spectroscopic studies of **2** revealed that the structure observed in solid-state is also preserved in solution. As such, dichloromethane (DCM) solutions of **2** showed—independent of the counter-anion—only a single broadened peak in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at  $\delta_{\text{p}} = 12.5$  ppm as well as broadened signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra at room temperature. This is consistent with a dynamic behavior and the alternating coordination of one of the two sulfonyl moieties to boron. This fluxional behavior can be followed by

VT NMR studies. Already at  $-30^{\circ}\text{C}$  the broad  $^{31}\text{P}$  NMR signal splits into two signals ( $\delta_{\text{P}} = 8.40$  and  $16.0$  ppm) due to the now prevented oscillation of the boron atom between the two sulfonyl moieties (*anti-2* and *anti-2'* in Figure 2). Further cooling to  $-90^{\circ}\text{C}$  results in a further splitting of the two signals in an approximate 7:3 ratio. This presumably corresponds to the now hindered rotation about the C–S bond and the formation of two isomers with both tolyl groups of the sulfonyl moiety either being located on the same (*syn-2*) or opposite side (*anti-2/2'*) of the YBY plane. In the crystal structure only the *syn*-isomer is found due to the interactions of the aryl groups with the  $\text{PF}_6$  anion.

DFT calculations were performed to get insights into the structure and bonding situation in the borenium cation (see the Supporting Information). The calculated geometrical parameters of  $2^{\text{Ph}}$  (Ph instead of the tolyl groups at sulfur) match the experimental values very well. The isomer *syn-2<sup>Ph</sup>* observed in the crystal structure is clearly energetically favored over a borinium system with a linear C–B–C moiety and no sulfonyl coordination ( $\Delta G = 49$  kJ mol $^{-1}$ ), but equal in energy with the *anti*-isomer *anti-2<sup>Ph</sup>* ( $\Delta G = -2.7$  kJ mol $^{-1}$ ).<sup>[20]</sup> The oscillation of the C–B–C unit between the two sulfonyl groups showed an activation barrier of only  $\Delta G^{\ddagger} = 97$  kJ mol $^{-1}$ , thus being well in line with the NMR studies. The calculated charges derived from the natural bond orbital (NBO) analysis of a hydrogen substituted model system  $2^{\text{H}}$  indicate that electrostatic effects play an important role in the stabilization of the C–B–C linkage (Figure 3). As



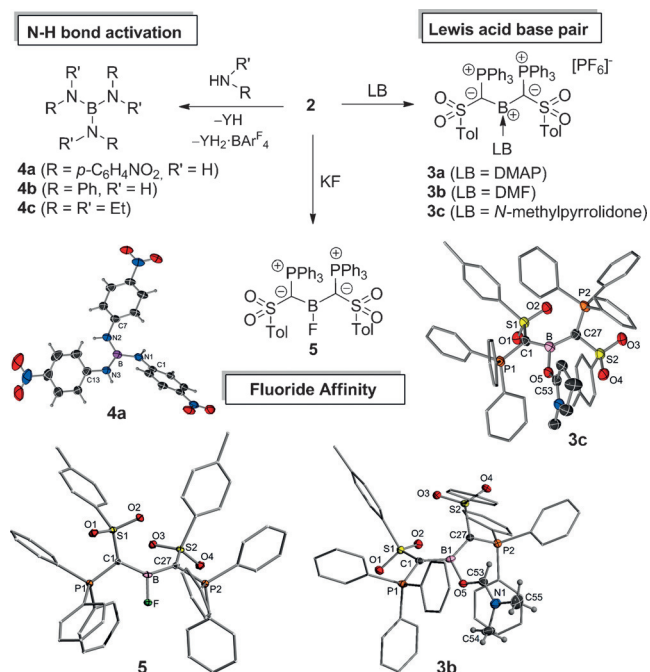
**Figure 3.** a) Calculated Wiberg bond indices (WBI) and NBO charges and b) frontier molecular orbitals of  $2^{\text{H}}$  (M062X/6-311 + G(d,p)).

such, high negative charges are observed at the carbon atoms ( $q_{\text{C}} = -1.26$  and  $-1.30$ ) and a positive charge of  $q_{\text{B}} = +0.90$  at boron. The calculated Wiberg bond indices (WBI) of the B–C bonds amount to 0.98 and 1.16, thus suggesting some double bond character within the C–B–C linkage. The WBI of the B–O interaction of 0.73 underlines its importance for the stabilization of the boron cation. The NBO analysis of  $2^{\text{H}}$  confirms the highly unsymmetrical bonding situation within the C–B–C linkage, showing a C–B single and a C=B double bond. However, both bonds [for example, the double bond by 69 ( $\sigma$ -bond) and 86% ( $\pi$ -bond)] are strongly polarized towards the carbon end, thus reflecting the high negative charges observed at the ylidic carbon atoms. The molecular

orbitals show that the lowest unoccupied orbital (LUMO) is predominantly localized at the boron center. Hence, the boron atom remains—independent of the degree of  $\pi$ -delocalization and coordination of the sulfonyl moiety—the most electrophilic center in the molecule (c.f.  $q_{\text{B}} = +0.90$ ). The two highest occupied molecular orbitals (HOMOs) illustrate the strongly polarized  $\pi$ -delocalization in the C–B–C moiety. The HOMO represents the two lone pairs at the carbon atoms, while the HOMO-1 is the bonding  $\pi$ -interaction over the whole C–B–C linkage. Hence, the calculations and experimental data argue for a C–B–C moiety with highly polarized C=B double bonds.

Next, we addressed the reactivity of the boron cation. At first, its Lewis acidity was probed by reaction with different Lewis bases. Dimethylaminopyridine (DMAP) quantitatively delivered the corresponding borenium ion **3a**, as evidenced by a shift in the  $^{31}\text{P}\{^1\text{H}\}$  (12.6 ppm for **2** and 21.0 ppm for **3a**) and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum (47.0 ppm for **3a**). Adduct formation was also observed with amides (DMF or *N*-methylpyrrolidone, NMP), while, no adduct formation was observed with ketones or phosphines ( $\text{PMe}_3$ ,  $\text{PPh}_3$ ). The coordination of NMP and DMF was found to be reversible. As such, evaporation of a DMF solution of **3c** at room temperature resulted in the re-formation of **2e** and the liberation of DMF. This is confirmed by DFT studies on the adduct formation with different Lewis bases, which yielded an exergonic process for amines, but a slightly endergonic reaction with amides (see the Supporting Information). The obtained borenium salts **3a–c** could be isolated by crystallization at low temperature and their composition was unambiguously confirmed by NMR spectroscopy as well as XRD analysis. In all cases, no double coordination of two molecules of the Lewis base to form a boronium ion was observed, even when using an excess of Lewis base.<sup>[21]</sup> The structures of **3b** and **3c** are given in Figure 4, **3a** in the Supporting Information. Upon coordination of the Lewis base the intramolecular sulfonyl coordination is broken to provide selective access to borenium ions with two equivalent ylide ligands. Thus and in contrast to **2e**, the B–C distances are almost equal and range between 1.51 and 1.54 Å. These bond lengths are slightly longer than the average bond length in **2e**, but still in between a typical B–C single and double bond,<sup>[19]</sup> thus indicating still present  $\pi$ -interaction between boron and the ylide ligands in **3**. Compared to **2e**, the C–B–C angles in **3a–c** are smaller and the ylide ligands are not coplanar, but slightly twisted arranged to each other. The C=O bonds in DMF and *N*-methylpyrrolidone experience a slight lengthening upon coordination to the boron center, thus indicating some degree of Lewis acid activation.

In contrast to the coordination of tertiary amines, **2** shows a totally different behavior towards primary and secondary amines, which however reflects the high polarity of the C–B bond. Treatment of **2b**<sup>[22]</sup> with an excess of *p*-nitroaniline results in N–H activation across the B–C bond and cleavage of both ylide substituents from the boron center.<sup>[23]</sup> This leads to the formation of tris(amino)borane **4a** together with ylide YH and the corresponding phosphonium salt ( $[\text{YH}_2][\text{BAR}^{\text{F}}_4]$ ). **4a** is the only product formed in this reaction. Employing a 1:1 ratio of amine and **2b** delivered **4a** and unreacted



**Figure 4.** Reactivity of boron cation **2**. Molecular structures of **3b**, **3c**, **4a**, and **5**. H-atoms, PF<sub>6</sub><sup>-</sup>, and solvent molecules omitted for clarity. 50% displacement parameters. Selected bond lengths [Å] and angles for **3b**: S1-C1 1.720(2), P1-C1 1.750(2), C1-B 1.512(3), B-O5 1.478(3), O1-C27 1.522(3), S2-C27 1.714(2), P2-C27 1.735(2), N-C53 1.283(3), O5-C53 1.295(2), O5-B-C1 111.7(2), O5-B-C27 116.1(2), C1-B-C27 132.2(2), S1-C1-P1 114.4(1), S2-C27-P2 113.3(1). **5**: S1-C1 1.703(2), P1-C1 1.735(2), F-B 1.387(2), B-C27 1.527(3), B-C1 1.531(3), S2-C27 1.708(2), P2-C27 1.733(2), F-B-C27 112.2(2), F-B-C1 112.2(2), C27-B-C1 135.6(2), S1-C1-P1 115.1(1), S2-C27-P2 113.8(1).

borenium cation **2b**. The same reactivity of **2b** was also observed with aniline or the secondary amines, diethyl amine or pyrrole, while pyrrole directly leads to the formation of the corresponding borate [B(pyrrole)<sub>4</sub>]<sup>-</sup>. Thus, despite the high thermal stability of **2** it still functions as highly reactive boron cation. Besides the coordination of different Lewis bases and the N-H addition across the B-C bond, **2** also acts as fluoride acceptor. Reaction with KF selectively delivered fluoroborate **5**, while keeping the Y-B-Y moiety intact.

In conclusion, we have shown that metalated ylides can be employed as strong electron-donating X<sub>L</sub>-type ligands. Their donor capacity allowed the isolation of a boron cation of type Y-B<sup>+</sup>-Y with a remarkable thermal stability due to the efficient stabilization through the ylide substituents. DFT calculations indicate that electrostatic interactions as well as π-delocalization within the C-B-C linkage play the most important role for the stability of the cationic species. Despite this stability the boron cation remains its reactivity as cationic species. As such, it forms Lewis acid base adducts with amines and amides and reacts with primary and secondary amines by N-H addition across the B-C bond. Overall, the facile isolation of ylide-functionalized boron cations demonstrates the unique donor properties of metalated ylides, which should also be beneficial for the stabilization of further electron-deficient compounds.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** boron · boron cations · carbanions · Lewis acid base pairs · ylide ligands

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