Discovery of a two-coordinate borinium cation: a new frontier in boron chemistry

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In recent years there have been many exciting developments in the chemistry of boron[1–10]. We have previously discussed how the recent discovery of boron–boron triple bond by Braunschweig and coworkers has stimulated chemists to revisit the nature of chemical bonding[1]. Apart from this breakthrough, observation of B–C–B three-centre two-electron bonding interactions and evidence of bond-strengthening metal-to-ligand ($\pi_M \rightarrow \pi_B^*$) interactions, evolution of the chemistry of antiaromatic boroles, and metal–boron-bonded compounds have enriched our chemical perspective in innumerable ways[1]. These recent findings have been made possible owing to the unique and intriguing electronic nature of boron.

The intriguing structures of elemental boron and their compounds have excited experimental as well as theoretical studies for decades[1–3]. Boron, with only three valance electrons, is unable to attain an octet set or the noble gas (Ne) configuration in its tricoordinate state and retains a vacant p-orbital. Thus, tricoordinated boron compounds are inherently Lewis acidic in nature, a property that has been long exploited in catalysis, anion recognition and optoelectronic applications. The Lewis acidity of boron results in the formation of dimeric B_2H_6 from BH_3, boron clusters and borate anions in the presence of nucleophiles. Tricoordinate boron compounds can only be stabilized where there are extensive n–π/π–π^* interactions, e.g. boronic acids and kinetically inert compounds with bulky substituents, e.g. triarylboranes. Tricoordinate neutral boron resembles carbocation (carbenium ion, R_3C^+) in its electronic configuration; hence cationic two-coordinate boron species would resemble the linear dicationic carbon species R_2C^{2+} with strong Lewis acidic features. Would it be interesting to explore possibilities of two-coordinate boron cations or borinium cations? This question has motivated synthetic inorganic chemists for a long time[1,2].

Boron cations can be structurally classified into three types: two-coordinated borinium cations, tri-coordinated borenium cations and tetra-coordinated boronium cations (Figure 1). Among these classes, borenium and boronium cations are relatively easier to be generated owing to the partial neutralization of the Lewis acidity of the boron atom by coordination to solvent or ligand molecules[9,10]. However, generating borinium species is an extremely challenging task owing to their susceptibility towards nucleophiles. Low-coordinate boron compounds are generally accessible in the presence of strongly δ-basic ligands like NHCs (N-heterocyclic carbene), sterically encumbered amines, or in the presence of metal–boron bond due to the strong electron back-donation from metal centres. In the last few years, these strategies have been used for the synthesis of unusual boron–boron double (**1**) and triple-bonded (**2**) compounds[4]. Compound **2** is stabilized by the strong δ-donating NHC ligands and sterically protected by the bulky substituents, and is an example of neutral two-coordinate boron-containing compound. To obtain cationic two-coordinate borinium species, stabilization of the vacant p-orbitals on boron atom is an essential requirement. Recently, Braunschweig *et al.*[4] demonstrated (Figure 1) that careful design can also allow incorporation of boron in a cumulene-like structure (**3**).

Previously, two-coordinate boron atoms have been reported in strongly π-stabilized systems where the N–B–N or Fe–B–C units are stabilized by the strong electron donation of the neighbouring units (Figure 2)[1,3]. However, such thermodynamic stabilization of the boron centres diminishes their Lewis acidity. Recently, Shoji and co-workers demonstrated the synthesis, and structural characterization of a highly Lewis acidic borinium cation with C–B–C bonding motif[5]. The unusual Lewis acidity of the cationic boron enables direct activation of small molecules like carbon dioxide[5]. Although the finding is new, the journey towards this success began quite some time ago.

In the last few decades, there have been many attempts to synthesize stable (structurally characterized) low-valent cationic main-group compounds. The interest in these species stems from their fundamental and unique chemical features as well as potential applications. The stepwise breakthroughs in the fields of one element (e.g. silicon) have

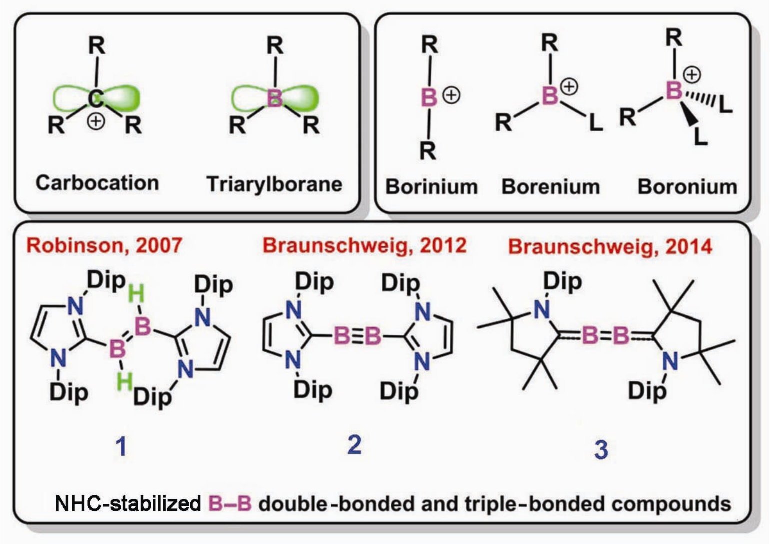

Figure 1. (Top left) Isoelectronic tri-coordinate boron and carbenium ions. (Top right) Schematic representation of borinium, borenium and boronium species (L represents ligand/solvent coordination). (Bottom) B–B double- and triple-bonded compounds **1**, **2** and **3** (Dip = 2,6-diisopropyl phenyl group).

subsequently enriched the chemistry of other elements (e.g. boron). There is a gradual variation in the properties of elements belonging to the same group. For instance, almost all halogens (e.g. fluorine, chlorine, bromine and iodine) are readily available in their anionic halide forms. However, this analogy does not hold for all main-group elements. For example, carbon readily forms cationic carbonium species which can be easily generated, detected and even isolated in innumerable ways. However, the analogous cationic silylium species has long eluded structural characterization. Although silylium cations were postulated and even detected in mass spectrometric analyses, the debate on the existence of silylium species has lasted for a long time. Only in 2002, Lambert and coworkers first reported the isolation and structural characterization of a free silylium species[6]. The goal was achieved using sterically bulky substituents around the silicon core (i.e. mesityl groups) along with a large and chemically inert anionic counterpart (e.g. $[HCB_{11}Me_5Br_6]$, where Me represents methyl)[7]. Although it appears seemingly unrelated to the chemistry of borinium ions, this discovery has served the chemistry of borinium cations in two crucial ways. First, the introduction of inert anions such as carboranes has become an important part for stabilizing cationic species without any undesirable cation–anion coordination. Secondly, the known fluoride affinity of silicon has been directly used in the synthesis of borinium cations.

Fluoride compounds such as TBAF (tetrabutylammonium fluoride) are often used for the deprotection of O–Si bonds in organic synthesis. Similarly, silicon compounds are also often used for fluoride anion capture from solution media. The chemistry of boron compounds is also inseparably related to fluorine. Tetra-coordinate boron compounds such as borondipyrromethene (BODIPYs) contains N_2BF_2 motif. Further, dimesitylfluoroborane (Mes_2BF) is a commercially available and stable synthetic precursor for the synthesis of triarylboranes with terminal boron atoms. Thus, the reaction of Mes_2BF with defluorinating agents like silylium compounds can be expected to be a smooth synthetic route for preparation of the two-coordinate Mes_2B^+ cation. However, the choice of anionic counterpart and solvent is crucial in obtaining such high Lewis acidic cationic species. Commonly used anionic species like triflate anions can show unwanted coordination towards cationic species as well as nucleophilic reactivity in several cases. In 1985, Noth and Narula showed that triflate can bind to borinium cations resulting in a tri-coordinate boron atom[8]. However, the triflate can be replaced with pyridines to obtain $R_2B\text{-}Py^+$-type borenium cations (Py – pyridine compounds). In 2008, Gabbai and Chiu utilized the reaction of Mes_2BF with Me_3SiOTf (trimethylsilyltriflate) in the presence of DMAP (*p*-dimethylaminopyridine) in order to obtain $Mes_2B\text{-}DMAP^+$ complex, a borenium cation[9]. Later, in 2009, they showed that similar strategy of using Me_3SiOTf can be followed in order to obtain NHC (N-heterocyclic carbene)-stabilized borenium cation (**4**, Figure 2)[10]. However, the isolation of a two-coordinate borinium cation was achieved only recently by Shoji and co-workers in 2014.

They showed (Figure 3) that the reaction of Mes_2BF with 1 equiv. triethylsilylium carborane ($Et_3Si[HCB_{11}Cl_{11}]$) at 298 K in *o*-DCB (ortho-dichlorobenzene) for 5 min gave $Mes_2B^+[HCB_{11}Cl_{11}]$ (compound **5**). The air sensitive compound is stable up to 593 K under inert atmosphere. Under argon, compound **3** does not show any decomposition even after 1 year. The ^{11}B NMR signal of the Mes_2B^+ cation in *o*-DCB-*d*4 appears as a broad peak at $\delta = 93.3$ ppm, indicating strong electron deficiency of the boron centre and is significantly shifted to the downfield region with respect to previously reported two-coordinate boron compounds. A single-crystal X-ray diffraction study shows well-separated cationic and anionic parts (Figure 4). The shortest distance between the boron atom of Mes_2B^+ and a chlorine atom of the carborane anion (4.562(2) Å) is considerably longer than the sum of their van der Waals radii (3.67 Å). The expected sp hybridization of the boron atom results in a near-linear Cipso–B–Cipso geometry with an angle of 172.1(2)°. Like compound **3**, isolation of the Mes_2B^+ cation was also found to be feasible in the presence of another large inert anionic species, i.e. $[(C_6F_5)_4B]$ (compound **6**). However, in this case, the compound was less stable and found to decompose at ~465 K.

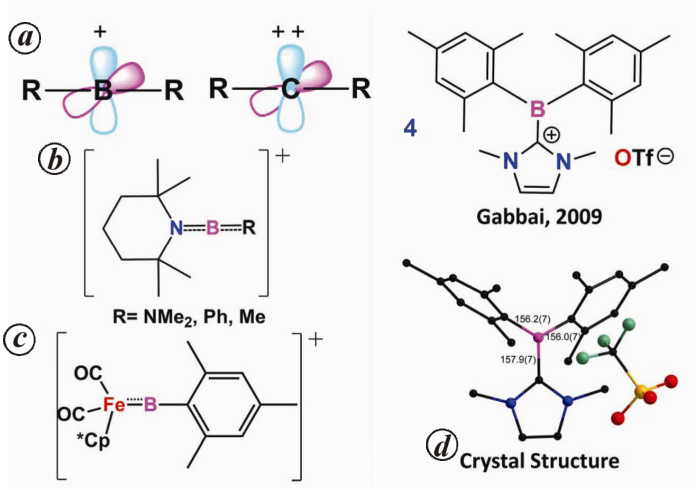

Figure 2. ***a***, Schematic representation of borinium cation R_2B^+ and isoelectronic R_2C^{++}. ***b***, ***c***, Previously reported examples of linear borinium cations. ***d***, Structural formula of compound **4** and its crystal structure (solvent molecules omitted for clarity).

Figure 3 shows the electronically important molecular orbitals (MOs) of the cationic Mes_2B^+ system (C_2 symmetry). The HOMO-2 and HOMO-3 orbitals of the system show π back-donation from the aromatic moieties to the boron centre, which can well explain the quinoidal geometry of the mesityl ring systems. As expected, the LUMO and LUMO+1 orbitals are localized on the boron centres and bear the signatures of vacant p_y and p_z orbitals. The gauge-independent atomic orbital calculation on the counterion-free model of Mes_2B^+ in vacuum (89.7 and 102.4 ppm at the B3LYP/6-311++G(3df,2pd) and M06-2X/6-311++G(3df,2pd) level of computation respectively) nearly reproduced the chemical shift of the boron centre of Mes_2B^+ observed in *o*-DCB-*d*4 ($\delta = 93.3$ ppm).

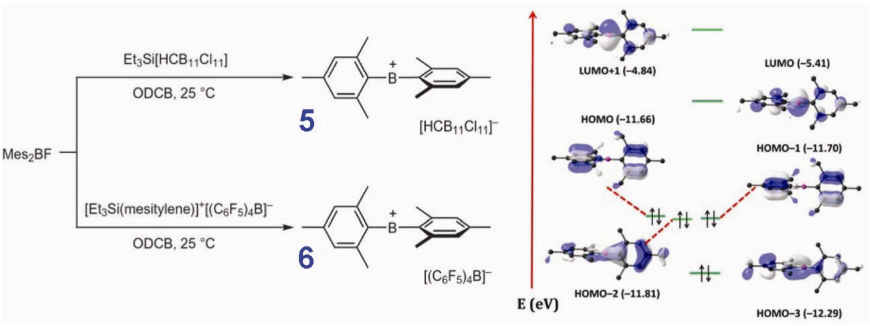

Figure 3. (Left) Synthesis of borinium compounds **5** and **6**. (Right) Selected important molecular orbitals of cationic Mes$_2$B$^+$.

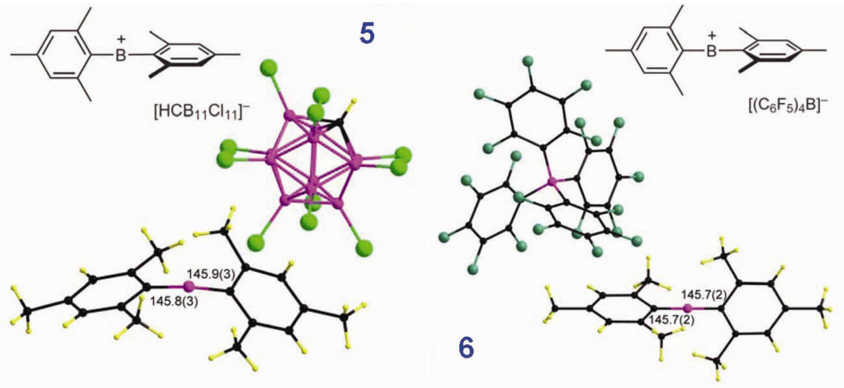

Figure 4. Structures of compound **5** and **6**.

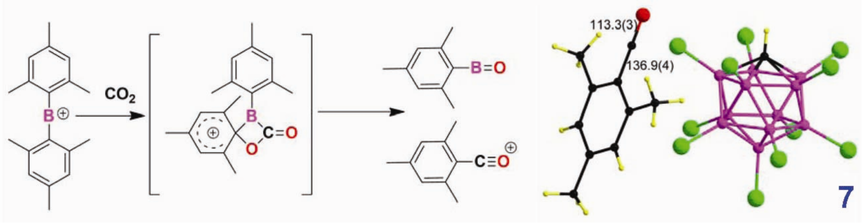

Figure 5. (Left) Proposed mechanism of CO$_2$ activation by Mes$_2$B$^+$. (Right) Single-crystal X-ray diffraction structure of compound **7**, i.e. [MesC≡O] + [HCB$_{11}$Cl$_{11}$].

Thus, it was concluded that even in the solution state, the boron atom does not experience any solvent coordination under experimental conditions. Although compounds **5** and **6** do not show any solvent or anion coordination under these controlled conditions, the Lewis acidic features of the Mes$_2$B$^+$ are well unveiled even in the presence of a passive reactant such as CO$_2$. When a solution of compound **5** in *o*-DCB at 298 K is exposed to CO$_2$ gas at 1 bar pressure, immediate formation of colourless crystals was observed. X-ray crystallography revealed that the resulting compound **7** is a salt of the MesC≡O$^+$ aroyl cation with [HCB$_{11}$Cl$_{11}$]$^-$ as a counterion (Figure 5). The reaction is expected to proceed through the coordination of an oxygen atom of CO$_2$ to the boron centre of Mes$_2$B$^+$, leading to polarization of CO$_2$.

In summary, in recent times, the fundamental chemistry of boron has progressed at a pace never seen before. Isolation and characterization of these borinium cations is only one example of countless hidden possibilities. Although we have started exploiting boron compounds decades ago in synthesis, catalysis and medicine, and recently in materials science, recent developments in the fundamental chemistry of boron opens up further opportunities for various applications.

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