
Breaking Rules – Making Bonds

A G Samuelson

Boron-containing molecules discovered recently have new types of dative bonds between carbenes and borylenes. At the same time, they show that traditional thumb rules regarding acids and bases are no longer valid.

In an interview, a teacher asked a student if an amine would behave as an acid or a base. The student confidently said, “An amine would behave as an acid”. The puzzled teacher, hoping to help the student arrive at the right answer, asked about the nature of trialkyl boron. Pat came the reply: “Boranes? Boranes are basic. A for acid and B for base”.

The student’s answer did not go down well with the teacher as the generally observed phenomenon is that boranes are Lewis acids and amines are Lewis bases. However, stereotyping molecules as acids and bases has to be done with care! Several recent discoveries have helped us improve our understanding of molecules containing main group elements as simple acids or bases. Guy Bertrand and Gernot Frenking describe one such discovery in the journal *Science* [1]. It explains how a tricoordinate boron compound could very well be a base!

Let us briefly look at what is understood by referring to a molecule as an acid or a base. There are different ways to ‘qualify and quantify’ the acidity or basicity of a molecule. The simplest and the first definition of acids and bases a chemistry student learns is based on the Brønsted theory which refers to proton-donors as acids and proton-acceptors as bases. The second and more general definition of an acid comes from the concepts developed by Lewis. A Lewis base donates a pair of electrons and a Lewis acid accepts a pair of electrons. Now, this is not always a pair of electrons. According to the Usanovitch definition, we can even include molecules that donate a single electron as a base. For a full discussion of acids and bases, one should refer an



A G Samuelson is a faculty member in the department of Inorganic and Physical Chemistry at the Indian Institute of Science, Bengaluru.

Keywords

Lewis acids and bases, boron, N-heterocyclic carbene, chemical bonding.

The student should have asked, “Are you referring to amines in the gas phase or dissolved in a solvent? And if dissolved, which solvent should I consider?”

elementary chemistry textbook [2].

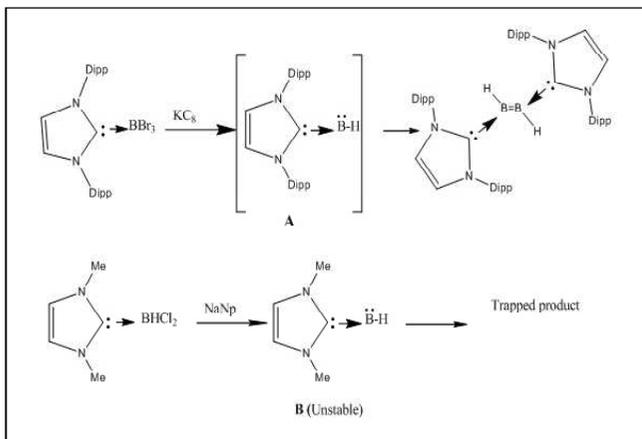
As a result of the many definitions that are accepted, the environment of the molecule in question can affect its acidity or basicity and hence the answer to the question on boranes and amines. The question posed to the student (mentioned above) was, strictly speaking, incomplete. The student should have asked, “Are you referring to amines in the gas phase or dissolved in a solvent? And if dissolved, which solvent should I consider?”

Acidity and basicity are relative to other molecules in the environment. However, especially in the gas phase, electron counting can give us a quick answer. A molecule with a non-bonded pair of electrons might be considered a base (e.g., ammonia) and a molecule with an incomplete octet (e.g., BR_3) might be considered an acid in the Lewis sense. The molecule that we are going to discuss here is a tricoordinate boron compound, but it is unusual because it has a pair of non-bonding electrons. So we would classify it as a base in the general sense! But Bertrand and Frenking have not indulged in just electron counting or semantics, they have shown that the reactivity of the tricoordinate boron fully fits the description of a base even when it is dissolved in solvents! Let us see how this comes about.

The story starts with the recent study of borylenes ($:\text{BR}$) by Robinson who isolated a dimer stabilized by a carbene [4] and Braunschweig who trapped an intermediate borylene with boron in the +1 oxidation state [5] (*Scheme 1*). The species ($:\text{BR}$) is analogous to a carbene ($:\text{CR}_2$). Carbenes have been shown to be a stable species especially if they are sterically protected and have π donors in the adjacent position [6].

Guy Bertrand reasoned that the species **B** was unstable due to the presence of a vacant orbital, which could be stabilized with another donor. To make life simple, they decided to use one more carbene than what was used by Braunschweig as a donor. They also made it more bulky to afford steric protection. So instead of the simple carbene used by Braunschweig and coworkers





Scheme 1. Studies on borylenes by Robinson (**top**) and Braunschweig (**bottom**).

(Figure 1a), Bertrand used a very bulky carbene called cyclic (alkyl) (amino) carbene (CAAC) shown in Figure 1b. Bertrand's choice was also based on his earlier work that these molecules can donate the pair of electrons on carbon (nucleophilic) very easily. At the same time, they can accept a pair of electrons through the vacant orbital on carbon.

The result of their experiments is outlined in Scheme 2. Counterintuitively, they obtained the proposed product **3** when they reduced the adduct **2** with potassium (added as KC₈, which is potassium metal intercalated in graphite) without adding the extra ligand in 33% yield. When they carried out the reaction by adding some extra ligand **1** (CAAC), the yield of the expected product reduced! One would have expected better yields of the product with the extra ligand!

Since single crystals suitable for a crystallographic study were available, they quickly obtained the three dimensional structure

The species (:BR) is analogous to a carbene (:CR₂).

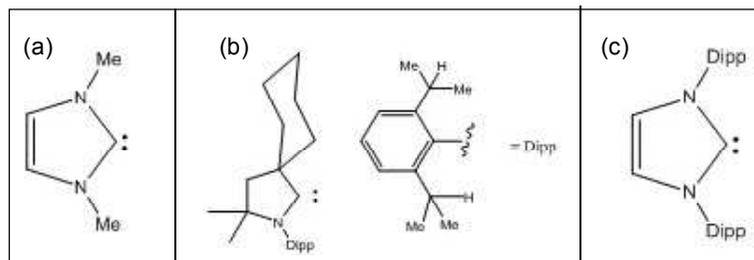
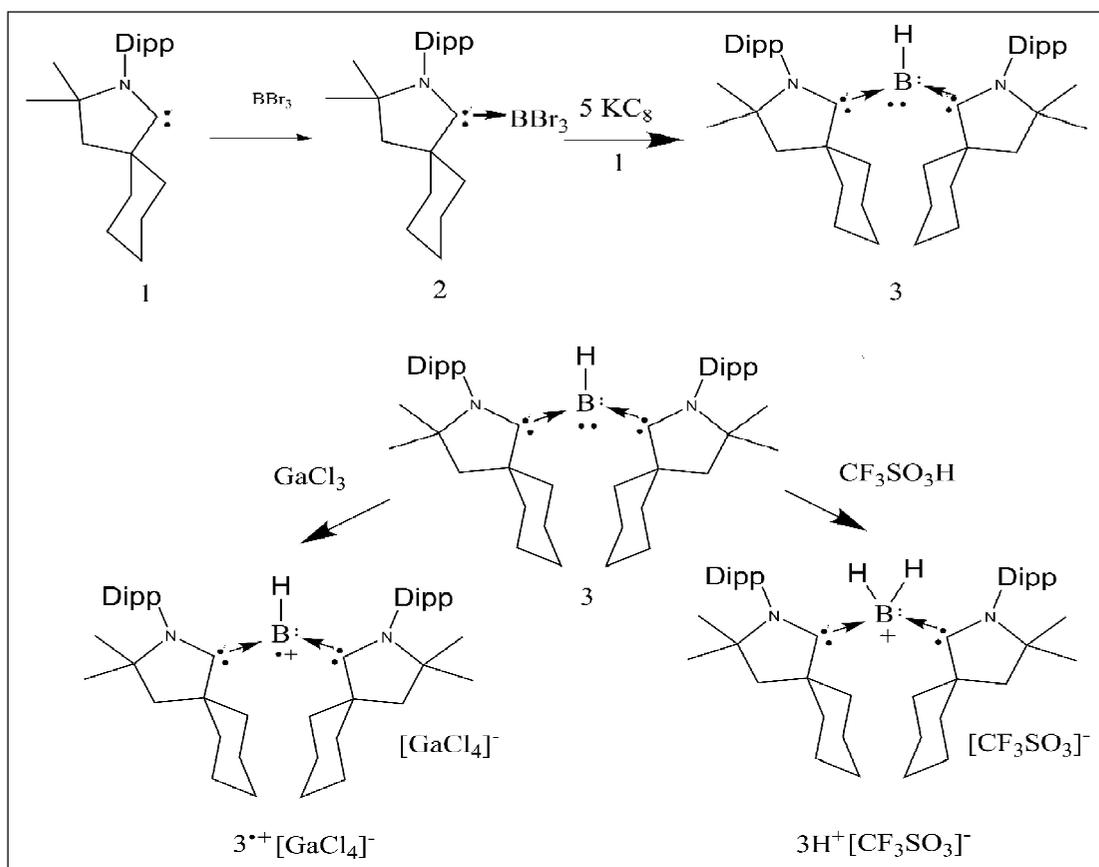


Figure 1. Carbenes used to study borylenes.



Scheme 2. Synthesis of (top) the parent borylene-bis (CAAC) adduct **3**, and (bottom left) its conversion to the radical cation $3^+ [\text{GaCl}_4]^-$, and (bottom right) boronium $3\text{H}^+ [\text{CF}_3\text{SO}_3]^-$.

of **3**. The molecular structure is dominated by the steric requirement of the two CAAC groups around boron. Several unusual features of **3** need to be pointed out. The structure reveals a tricoordinate boron with three ligands in a plane around the boron. The angle between the CAAC ligands is 140° , whereas the angle between the CAAC ligands and hydrogen is 110° . Some key parameters are given in *Table 1*.

The structural parameters suggest that the lone pair of electrons on B is present in a pure $2p$ orbital. Based on the bonding picture

Molecule	$[3]^+ \cdot [\text{GaCl}_4]^-$	3	$[3\text{H}]^+ \cdot [\text{CF}_3\text{SO}_3]^-$
B-C: (Å)	1.58, 1.58	1.52, 1.52	1.61, 1.61
:C-N (Å)	1.36, 1.35	1.38, 1.39	1.31, 1.31
C:-B:-C ($^\circ$)	137.8	138.8	133.7

Table 1. Molecular parameters for the three borylenes stabilized by NHC ligands.

you would expect the boron to be electron rich with a formal oxidation state of only 1! Surprisingly, the computational study estimates a partial charge of +0.05 on the BH moiety. But the computational study also provides some insight into this unusual situation. As there is an empty orbital on each one of the CAAC ligands, the boron is able to donate electrons to the empty orbitals on the carbene. (You might recall that in BX_3 , where X is a halogen, there is donation of electrons from X to the empty orbital on B making BX_3 stable.) In this case, the reverse situation is true. The boron is donating electrons to the carbene!

Having discussed the structure of this unusual compound, let us look into its chemistry. It is interesting that the lone pair leads to electrochemistry consistent with the availability of a non-bonded pair of electrons on boron. The compound is very easily oxidized to form the radical cation $[3]^{+\bullet}$ at the very low potential of -0.9 V w.r.t. a standard calomel electrode (SCE). For comparison, one can look at the oxidation potential of ferrocene that is oxidized at $+0.5$ V vs. SCE. Surprisingly, the complex **3** can be stabilized in this state by a suitable counter ion and so addition of $GaCl_3$ allowed them to isolate the radical cation $[3]^{+\bullet} \cdot [GaCl_4]^-$ and characterize the same by X-ray crystallography. Not surprisingly, some of the metrical details of structure $[3]^{+\bullet} \cdot [GaCl_4]^-$ remains almost the same as of **3**. Probably the most convincing evidence that compound **3** is a base comes from its reaction with a proton to form $[3H]^+ \cdot [CF_3SO_3]^-$. They have characterized the protonated species also by crystallography, which shows that the central boron is now a distorted tetrahedral species. It is distorted from an ideal tetrahedron (the structure adopted by the ammonium ion), because unlike $[NH_4]^+$, this molecule now has two very large CAAC groups and two sterically accommodating hydrogen atoms.

Before we finish this discussion, we should point out a very important difference between the boron chemistry discussed in textbooks till date, which relates to the chemistry of boron in its usual oxidation state, +3, and this unusual structure. Boron has

Boron has been stabilized in an oxidation state of +1. So the basic nature of boron is associated with the low oxidation state of the element.



been stabilized in an oxidation state of +1. So the basic nature of boron is associated with the low oxidation state of the element. So it should not surprise us that boron in the unusual oxidation state +1 is electron rich and so behaves as an electron donor and a base. Frenking and coworkers have asked themselves a hypothetical follow up question. Can other first row elements be stabilized with an extra pair of electrons to form stable molecules? In a computational study, they show that many are possible, and surprisingly, some of them are already known [5]! Consider, for example, the singly ionized nitrogen atom. It now has two pairs of electrons and it is positively charged. Can we stabilize this ion $[:N:]^+$? The answer is yes! They discuss several examples. One of them, the molecule $[N_5]^+$, is already familiar to the readers of *Resonance*. This molecule can be considered as a singly ionized nitrogen, $[:N:]^+$ stabilized by coordination of two electrons each from two dinitrogen molecules. This molecule was very explosive and so it was more than a handful! The resonance structures and some of its chemistry were discussed in this journal, a while ago [7].

Suggested Reading

- [1] R Kinjo, B Donnadieu, M A Celik, G Frenking, G Bertrand, Synthesis and characterization of a neutral tricoordinate organoboron isoelectronic with amines, *Science*, Vol.333, pp.610–613, 2011.
- [2] J E Huheey, R L Keiter, E A Keiter and O K Medhi, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th Edition, Pearson Education, 2008.
- [3] P Bissinger, H Braunschweig, K Kraft, T Kupfer, Trapping the elusive parent borylene, *Angew. Chem. Int. Ed.*, Vol.50, No.20, pp.4704–4707, 2011.
- [4] Y Wang, B Quillian, P Wei, Y Xie, C S Wannere, R B King, H F Schaefer III, P v R Schleyer, G H Robinson, Planar, twisted, and trans-bent: conformational flexibility of neutral diborenes, *J. Am. Chem. Soc.*, Vol.130, p.3298, 2008.
- [5] A J Elias, Molecule Matters - N-heterocyclic carbenes - the stable form of $R_2C:$, *Resonance*, Vol.13, No.5, pp.456–467, 2008.
- [6] M A Celik, R Sure, S Klein, R Kinjo, G Bertrand and G Frenking, Borylene complexes $(BH)L_2$ and nitrogen cation complexes $(N^+)L_2$: isoelectronic homologues of carbones CL_2 , *Chem. Eur. J.*, Vol.18, p.5676, 2012.
- [7] A G Samuelson and J Jabadurai, Molecule Matters - Dinitrogen, *Resonance*, Vol.12, No.3, pp.70–76, 2007.

Address for Correspondence
A G Samuelson
Department of Inorganic and
Physical Chemistry
Indian Institute of Science,
Bengaluru 560 012
Email:
ashoka.samuelson@
gmail.com

