

The new international standards are expected to help genebanks worldwide to conserve crop diversity in a more efficient and cost-effective manner. They provide a basis for establishing the norms and standards essential for the smooth operation of a genebank. They can be used by genebank curators as a source of guidance for developing standard operating procedures. They would also be helpful for developing quality management systems in genebanks. A systematic application of these standards will, however, require strong national,

regional and global commitment and continuous financial support for capacity development and upgrading professional skills. After approval of the CGRFA, the *Genebank Standards for Plant Genetic Resources for Food and Agriculture* is expected to be published by the FAO and widely disseminated amongst decision-makers and relevant stakeholders. All genebanks are expected to adopt these standards, as far as possible, to ensure conservation of genetic resources under optimal conditions, for perpetuity. It is further expected that species-specific

standards be developed in future for further fine-tuning of this endeavour.

FAO/IPGRI, *Genebank Standards*, Food and Agriculture Organization of the United Nations, Rome, International Plant Genetic Resources Institute, Rome, 1994, p. 12.

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RESEARCH NEWS

The fascinating story of boron–boron triple bond

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Modern chemistry has enriched human lives in innumerable ways. From medicine to materials, chemistry plays a key role in determining and manipulating their properties at the molecular level. Though these achievements may reflect our success in utilizing chemistry, we are yet far from understanding numerous fundamental aspects of the subject. The quest of chemists to answer numerous fundamental, unanswered questions seems to be an endless voyage to search for and reach new destinations. Here, we focus on one of the simplest questions for which the answer could finally be provided only very recently: *with only three valence electrons, can boron form a true boron–boron triple bond?*

The stability of homoatomic triple bonds¹ is beyond any question for carbon and nitrogen. Triple bond-containing alkynes form a distinct class of numerous stable organic compounds and are regarded as an indispensable part of synthetic organic chemistry. The triple bond in dinitrogen is one of the strongest bonds in nature and as a result, dinitrogen is used to provide inert environment in laboratories. However, the stability of the triple bond does not apply in the case of other main group elements. Extreme steric protection is essential to stabilize homoatomic triple bonds in low-valent main group elements. Even if the synthetic difficulties can be overcome, they

are often severely trans-bent, reducing their triple bond character^{2,3}.

Boron, however, is unique in this regard (Figure 1)⁴. Having only three valence electrons, it lacks the ability to attain a closed-shell noble-gas electronic configuration in its trivalent state. Three coordinate organoboron compounds like boronic acids gain their stability from extensive B–O p_{π} – p_{π} overlap which diminishes the reactivity of the boron centre^{4e,4g}. Kinetic stability in triorganyl boranes can also be achieved using bulky aryl substitutions. The sterically protected empty p_{π} orbital greatly influences the optoelectronic properties of triarylboranes, which makes them potential candidates for electroluminescent materials and a receptor for smaller anions^{4b–f,4j}. Boron can also be stabilized in the organic backbone via chelation in borate form. The chelation process not only stabilizes the boron centre, it also assists to rigidify the organic moiety, forming highly emissive dyes. The BODIPY dyes must be mentioned in this context^{4c}, as they have been extensively studied in recent years and have already been commercialized in biomedical applications. In elemental form, boron forms icosahedral clusters^{4a,4i} (Figure 2) and this tendency is also manifested in carboranes which are promising candidates in medicinal chemistry as delivery agents in BNCT (boron–neutron capture therapy)^{4h}.

Boron forms a wide range of sigma bonds with other elements. Apart from conventional B–X sigma bonds, it also forms three-centre-two-electron B–H–B bonds in B₂H₆ which is an extreme example of the high electron deficiency of the element. Boron–boron σ -bonding in stable molecules is well known. Similar to boron-clusters and carboranes, B–B single-bonded compounds such as bis-(pinacolato)-diboron (Figure 2) or tetrachlorodiborane can be easily handled in general laboratory conditions. However, due to its highly electron-deficient nature, boron resists multiple bonding⁵ and rarely forms B–B π -bonds. Successful attempts to prepare stable homoatomic multiple-bonded group 13 element compounds have been based on populating the empty π -bonding orbital between the atoms. In 1992, Moezz *et al.*⁶ were able to form a B=B for the first time in anion-stabilized ‘diborenes’, which was described as a diborane dianion analogue of substituted ethylene (see below).

A B–B triple bond in compounds like LBBL (L = substituent) seems to be rather far-fetched as boron has only three valence electrons (Figure 3) available for bonding. In 2002, the B₂ entity could be isolated in an argon matrix at 8 K by stabilization with Lewis base CO in the form of OCBBCO⁷ (Figure 3). It was found to be a neutral molecule with some boron–boron triple bond character. In

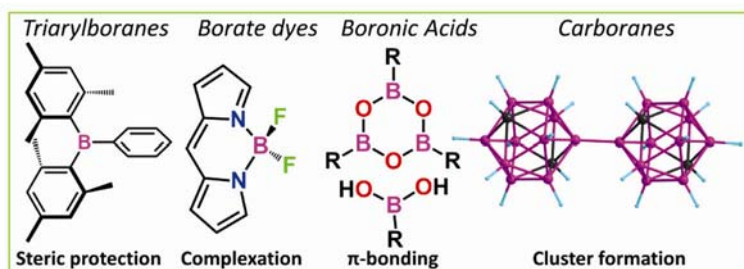


Figure 1. General classification of stable boron containing molecules (colour code for carborane: C, Black, B, Magenta and H, Cyan).

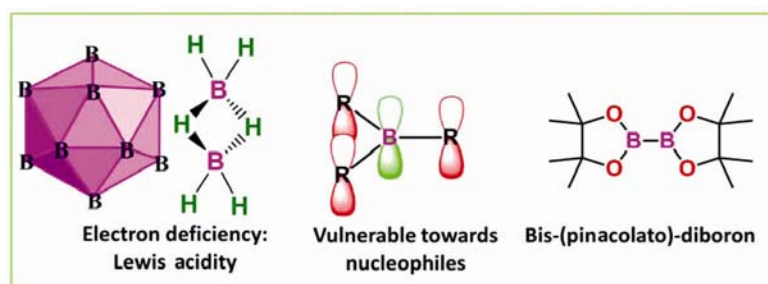


Figure 2. (From left to right) Electron deficiency of boron-containing systems, resulting in the icosahedral structure of elemental boron and dimerization of BH_3 . Empty p_x orbital in BR_3 compounds. Bis-(pinacolato)-diboron, a commonly used reagent having B–B single bond.

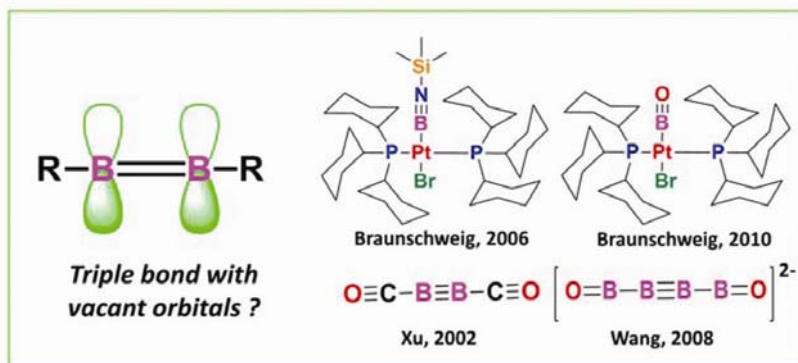


Figure 3. The logical problem of formation of a boron–boron triple bond and some of the boron-containing molecules that are believed to show considerable triple-bond character in B–B or B–X bonds.

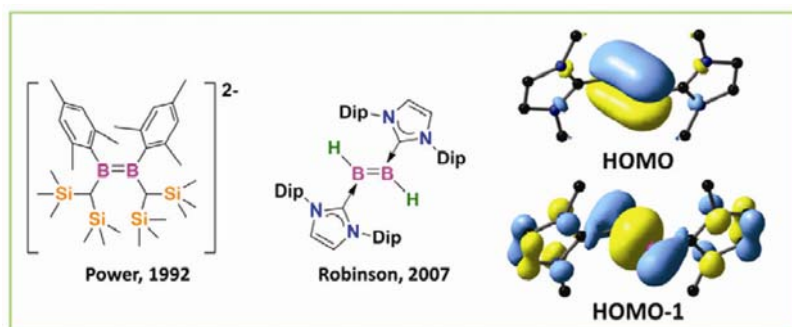


Figure 4. An anionic 'diborene' (left) and sterically demanding *N*-heterocyclic carbene stabilized 'diborene' (right) and selected MOs of the same (hydrogens omitted for clarity; dip fragments replaced by methyl groups for simplicity).

2008, similar structural features were also observed in a dianionic species $\text{OBBBBO}^{2,7b}$. The reported molecules containing the so-called $\text{B}\equiv\text{B}$ were only characterized in extremely controlled conditions and could not be isolated for detailed studies. However, the findings prompted a number of theoretical studies, considering $\text{L} \rightarrow \text{B}\equiv\text{B} \leftarrow \text{L}$ systems in which the donors L were diatomic molecules (CO , CS , BO^-), phosphines (PCl_3 , PMe_3), *N*-heterocyclic carbenes (NHCs), etc.⁷. The NHC-stabilized $\text{L} \rightarrow \text{B}\equiv\text{B} \leftarrow \text{L}$ compounds were predicted to have linear and very short B–B bond distance, in particular, true boron–boron triple bond. Later on, successful syntheses of compounds containing $\text{B}\equiv\text{N}$ (2006) and $\text{B}\equiv\text{O}$ (2010) entities were achieved by Braunschweig *et al.*⁸ in the coordination sphere of Pt and their structural characterizations revealed the true potential of the electron-rich boron centres for forming genuine triple bonds (Figure 3).

In 2007, Wang *et al.*⁹ used the strategy of stabilizing the boron atoms using NHC donors. Isolation of the bis(carbene)-stabilized diborene (Figure 4) could be possible by the reduction of an NHC-BBr_3 adduct. The reduction process was expected to be via boron-based intermediate radical formation as abstraction of hydrogen, presumably from the reaction solvent, was observed. The MO analysis of the 'diborene' clearly demonstrates the B=B double bond formation. As evident from Figure 4, the HOMO-1 constitutes B–B σ -bond and the HOMO is actually a filled B–B π -orbital; this is similar to C=C double-bond formation in alkenes. Interestingly, a true 'diboryne' is yet to be found, which they might have if the proton abstraction during synthesis could be avoided. The choice of ligands was perfect, but proper choice of the synthetic route is yet to be achieved.

Recent studies^{10,11} have successfully avoided the hydrogen abstraction by starting with a molecule with a pre-formed B–B bond (Figure 5). Addition of two equivalents of NHC 1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene in B_2Br_4 furnished the bis(carbene)-stabilized diborene (1). The reduction of 1 with two or four equivalents of one electron-reducing agent $\text{Na}(\text{C}_{10}\text{H}_8)$ in THF gave bis(NHC)-stabilized dibromodiborene (2) and bis(NHC)-stabilized diboryne (3).

Unlike the previously known examples, compound **3** was found to be highly stable at ambient temperature (decomposes at 234°C) in the absence of air and water. The stability of **3** enabled^{10,11}, the authors to determine its actual molecular

structures by single crystal X-ray diffraction (Figure 6). Compound **3** shows an effective linear C → B≡B ← C core with only a slight BBC bending ($173.0^\circ \pm 0.2^\circ$ and $173.3^\circ \pm 0.2^\circ$), as predicted by theory. The B–B distance of $1.449 \pm 0.003 \text{ \AA}$ is

much shorter than that in **2** ($1.561 \pm 0.018 \text{ \AA}$) corresponding to a contraction of ~6%.

Apart from alkynes and dinitrogen, compound **3**, if it consists of a true B≡B, will be the most recent class of compounds having genuine homoatomic triple bond, which can also be modified experimentally by modifying the stabilizing ligand. Is it really a boron–boron triple bond? If we consider the MO picture of B₂ molecule (Figure 7), it can be easily realized that the bond order must be 1, rather than 3. However, in its third excited state, the $1\sigma_u^+$ orbital being vacant and the p_π bonding orbitals being completely occupied, it must have a bond order of 3. Is it possible that the NHC ligands force the B₂ unit to achieve its third excited state configuration?

A closer look at the MOs (Figure 7) of model NHC-stabilized diboryne (where the dip fragments are replaced by methyl groups for convenience) would reveal that the four highest occupied MOs are B–B bonding (HOMO, HOMO-1, HOMO-6 and HOMO-14), whereas HOMO-13 is B–B antibonding. Thus, the overall B–B bond order is 3 ($(8 - 2)/2 = 3$). It is also evident how NHC ligands donate electron density into the vacant $1\sigma_u^+$ (HOMO-13) and $2\sigma_g^+$ (HOMO-14) orbitals of the third excited state of B₂. The $2\sigma_g^+$ orbitals are stabilized compared to the π -bonding orbitals due to charge donation from the carbenes. Thus, the B₂(NHC)₂ molecule contains a genuine B≡B triple bond.

Is it actually an end to our journey? No, rather it might be a start; only a further step into the unrevealed world of main-group chemistry. The remarkable achievement of B–B multiple bonding introducing NHCs has already prompted scientists to revisit the foundations of chemical bonding and structural possibilities. Recent work by Tai and Nguyen¹² shows that B(NHC) unit can be utilized like a CH fragment if allowed by the synthetic boundaries. Similar to the known aromatic and antiaromatic C_nH_n molecules, B_n(NHC)_n compounds are feasible and electronically close in nature to their carbon analogues. Figure 8 shows the similarity in π -electron delocalization in benzene (C₆H₆) and isostructural B₆(NHC)₆. If experimental chemists are able to address the synthetic challenges of these hypothetical molecules in the near future, we may expect to witness a whole new era of main-group organometallic chemistry.

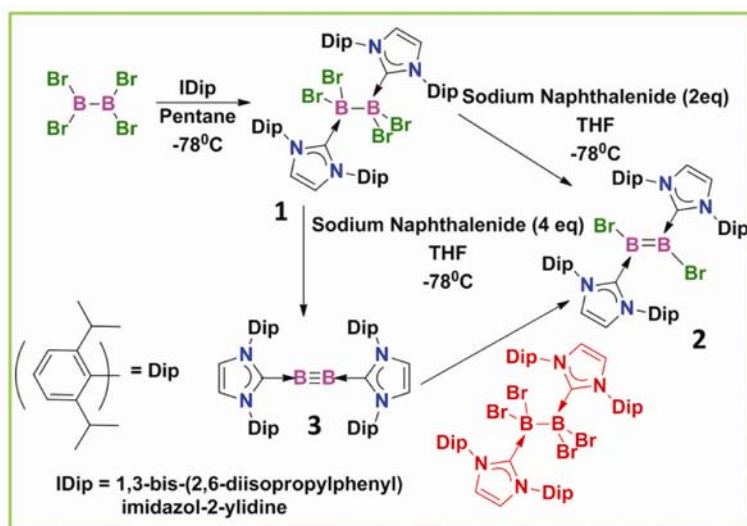


Figure 5. Synthetic scheme for NHC-stabilized 'diboryne'.

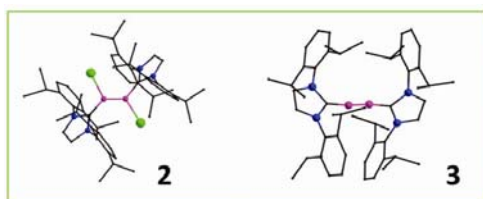


Figure 6. Solid-state structures (X-ray) of diborene **2** and diboryne **3** (colour code: C, Black, B, Magenta and N, Blue).

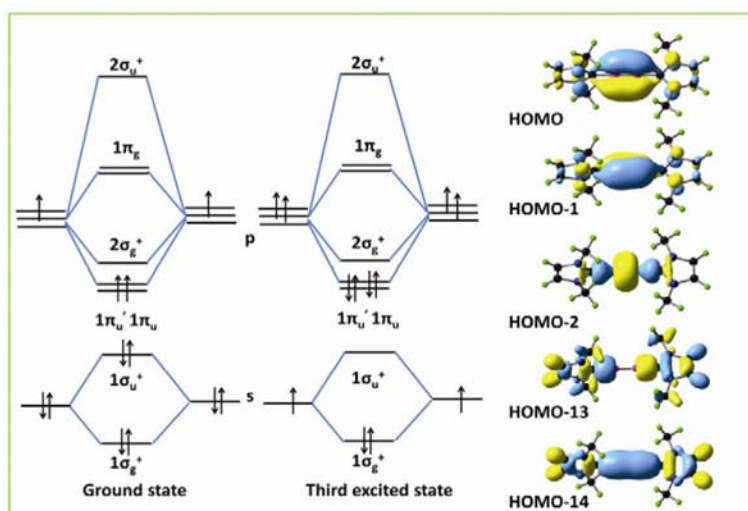


Figure 7. MO diagram for ground state and third excited state of B₂ (left) and selected MOs of model NHC-stabilized diboryne (dip fragments replaced by methyl groups for simplicity).

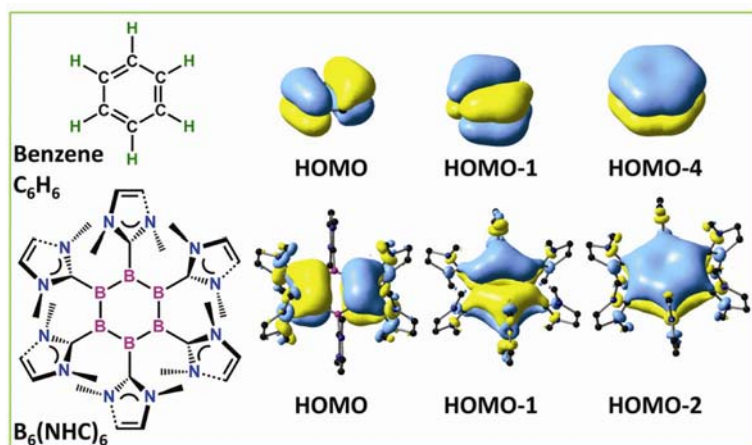


Figure 8. Comparison of selected filled π -MOs of benzene (C_6H_6) and hypothetical $B_6(NHC)_6$ (hydrogen atoms omitted for clarity).

The synthesis and structural characterization of **3** is a ground-breaking realization in respect of fundamental chemistry. It redefines our fundamental understanding of chemical bonding and will inspire further insights into the very basic concepts of chemistry. The NHC ligands have once again proved their versatility and significance in main-group and fundamental chemistry. We can look forward to further studies on the reactivity of $B=B$ triple bond in **3**, the newest member of the family of true homoatomic triple bonds.

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