

Boron-Boron Double and Triple Bonds

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Literature Seminar

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Main group elements like carbon, nitrogen, and oxygen are able to form a large number of different homo- and heteronuclear multiple bonds making up some of the most prominent functional groups in chemistry.¹ None of these is more ubiquitous than the carbon-carbon double and triple bonds which undergo a wide variety of reactions including various additions, cycloadditions, cross-couplings, and metatheses. However its group 13 neighbor, boron, had little evidence of neutral, homonuclear multiple bonding until recently despite its predicted stability. While the mono- and dianions of a small set of boron-boron double bonded compounds was reported two decades ago², and computational studies supported the evidence of neutral boron-boron double bonds³, it wasn't until 2007 that the Robinson group realized the experimental synthesis and characterization of a diborene molecule, Figure 1.⁴

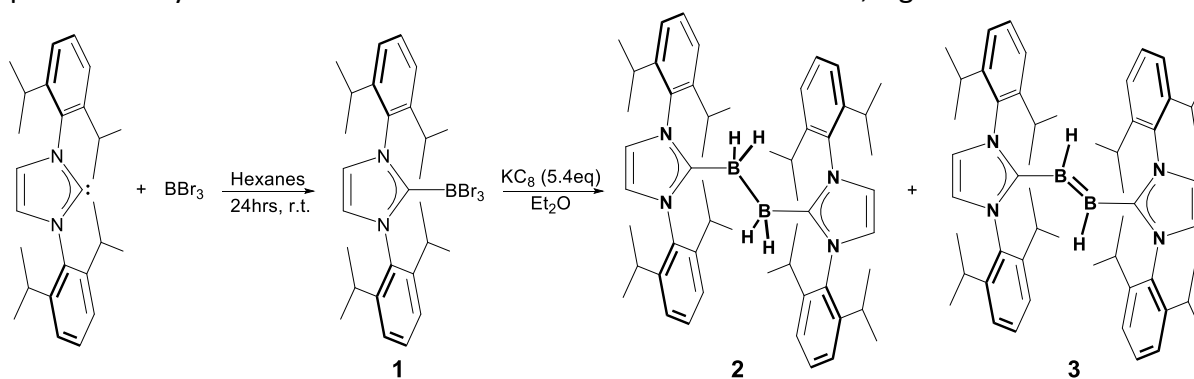


Figure 1. Synthesis of an NHC stabilized diborene.

This compound represents the first example of a stable, neutral diborene molecule. It is stabilized by two *N*-heterocyclic carbenes (NHCs) with additional bulk provided by the diisopropylphenyl flanking moieties. These ligands act as Lewis bases to help stabilize the boron-boron double bond and provides a compound that, while air sensitive, is quite stable. This complex was characterized by ¹H, ¹¹B, and ¹³C nuclear magnetic resonance (NMR) spectroscopy, X-ray crystallography, and DFT studies to probe the molecular orbital bonding. Evidence in support of the B=B double bond was the NMR shift in the ¹¹B NMR and bond distances determined by crystallography.

A similarity can be drawn when comparing the differences between single, double, and triple bonded boron-boron bond lengths in reference to carbon-carbon bonding. The difference between the single and doubly bonded boron molecule is approximately 0.27 Å and the double to triple is 0.11 Å. Looking at the carbon-carbon analogs the difference from single to double and double to triple (computationally) are 0.2 Å and 0.1 Å, respectively. This draws an

interesting comparison between these two close main group neighbors that is currently being explored.

The synthesis of a stable diboryne molecule has only recently been reported by Braunschweig and co-workers using this same system but starting with the tetrabromodiborane molecule with sodium naphthalenide as the reducing agent in THF instead of KC_8 and diethylether as previously reported by Robinson and co-workers, Figure 2.^{4,5}

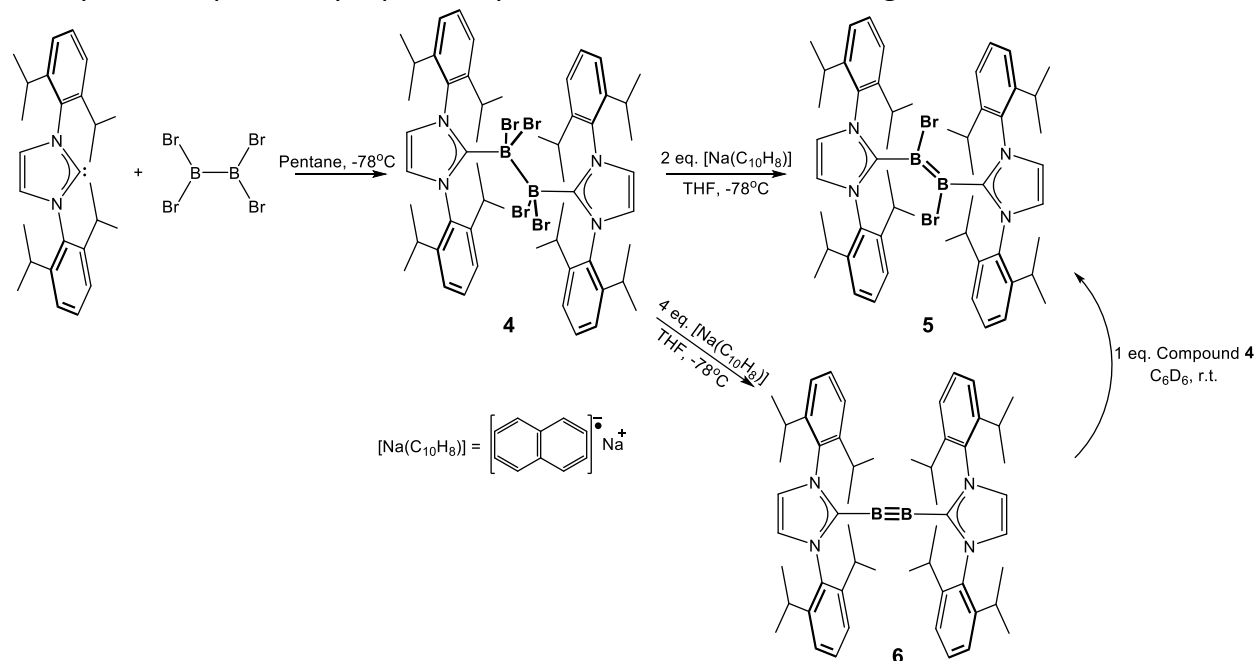


Figure 2. Synthesis of an NHC stabilized diborene and the first diboryne.

They hypothesize that Robinson and co-workers could well have achieved a triply bonded diboryne compound if not for the abstraction of hydrogen, likely from the etherate solvent, by their tribromoborane. They isolated both the diborene and diboryne using either two or four equivalents of their reducing agent and characterized both of these by ^1H , ^{11}B , and ^{13}C NMR spectroscopy, elemental analyses, X-ray crystallography, solid-state infrared spectroscopy (IR), UV-vis, and DFT calculations to support and explain the spectral data from obtained from UV-vis analysis. All of these results support formation of the desired triply bonded molecule.

Finally the most recent work by Braunschweig and co-workers looked into the reactivity of this diboryne with small molecules and found it had interesting reactivity with carbon monoxide.⁶ Simply treating the compound with 1 atm of CO at room temperature yielded a red-orange solid that contained four CO molecules in a bis(boralactone) core that were not just joined head-to-head but actually in a head-to-tail (C-O-C) fashion. Additionally an intermediate was also synthesized by adding 2 equivalents of CO at -78°C to yield a single bridging CO across the now double bond of the boron atoms, Figure 3. Both complexes were characterized by ^1H , ^{11}B , and ^{13}C NMR spectroscopy, elemental analyses, X-ray crystallography, solid-state infrared spectrum (IR), UV-vis, fluorescence, and DFT calculations.

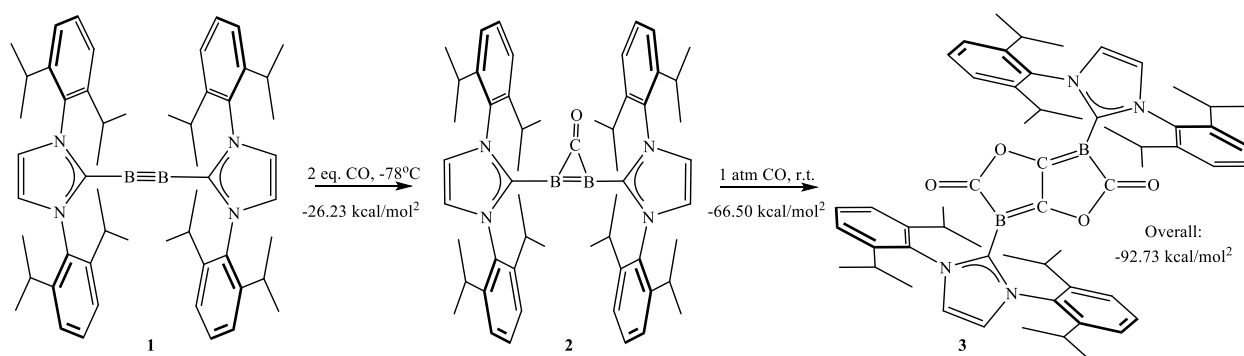


Figure 3. Reaction of diboryne stepwise with CO.

Overall these diborene and diboryne compounds were synthesized and characterized as highly stable compounds as predicted by early computational studies. Furthermore the diboryne has shown small molecule reactivity with carbon monoxide in a rare head-to-tail fashion to form the bis(boralactone) product. These systems, in addition to being interesting analogues to the well-studied carbon-carbon double and triple bonds, have provided relatively unique reactivity that may lead to new understanding of main group chemistry.

References:

1. Fischer, R. C.; Power, P. P. π -bonding and the Lone Pair Effect in Multiple Bonds Involving Heavier Main Group Elements: Developments in the New Millenium. *Chem. Rev.* **2010**, *110*, 3877-3923.
2. (a) Moezzi, A.; Olmstead, M. M.; Power, P. P. Boron-boron double bonding in the species $[B_2R_4]^{2-}$: synthesis and structure of $[(Et_2O)Li]_2\{Mes_2BB(Mes)Ph\}$, a diborane(4) dianion analog of a substituted ethylene. *J. Am. Chem. Soc.* **1992**, *114*, 2715-2717. (b) Moezzi, A.; Bartlett, R. A.; Power, P. P. Reduction of a Boron-Nitrogen 1,3-Butadiene Analogue: Evidence for a Strong B-B π -Bond. *Angew. Chem., Int. Ed.* **1992**, *31*, 1082-1083.
3. (a) Kaufmann, E.; Schleyer, P. v. R. Dilithioborane (6) ($Li_2B_2H_4$). An experimentally viable species with a B=B double bond. Planar no-bond-double-bond isomers with pentacoordinate boron? *Inorg. Chem.* **1998**, *27*, 3987-3992. (b) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, Y.; King, B. R. Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. Stable Neutral Diborene Containing a B=B Double Bond. *J. Am. Chem. Soc.* **2007**, *129*, 12412-12413.
4. Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, Y.; King, B. R. Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. Stable Neutral Diborene Containing a B=B Double Bond. *J. Am. Chem. Soc.* **2007**, *129*, 12412-12413.
5. Braunschweig, H.; Dewhurst, R. D.; Mies, J.; Radacki, K.; Vargas, A. Ambient-Temperature Isolation of a Compound with a Boron-Boron Triple Bond. *Science* **2012**, *336*, 1420-1422.
6. Braunschweig, H.; Dellermann, T.; Dewhurst, R. D.; Ewing, W. C.; Hammond, K.; Jimenez-Halla, J. O. C.; Kramer, T.; Kruppenacher, I.; Mies, J.; Phukan, A. K.; Vargas, A. Metal-free binding and coupling of carbon monoxide at a boron-boron triple bond. *Nat. Chem.* **2013**, *5*, 1025-1028.