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Reductive Insertion of Elemental Chalcogens into Boron–Boron Multiple Bonds**

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Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: *The syntheses of sulfur- and selenium-bridged cyclic compounds containing boron stabilized by N-heterocyclic carbenes (NHCs) have been achieved by the reductive insertion of elemental chalcogens into boron–boron multiple bonds. The three pairs of bonding electrons between the boron atoms in the triply bonded diboryne enabled six-electron reduction reactions, resulting in the formation of [2.2.1]-bicyclic systems wherein bridgehead boron atoms are spanned by three chalcogen bridges. A similar reaction using a diborene (boron–boron double bond) resulted in the reductive transfer of both pairs of bonding electrons to three sulfur atoms, yielding a NHC-stabilized trisulfidodiborolane. The demonstration of these six- and four-electron reductions lends support to the presence of three and two pairs of bonding electrons between the boron atoms of the diboryne and diborene, respectively, a fact that may be useful in future discussions on bond order.*

The most oft-used textbook definition of bond order is given as half the difference in the number of electrons occupying the bonding orbitals of a particular bond and the electrons occupying antibonding orbitals for the same bond.[1] However, the basis for bond order, the concept of multiple bonding, was initially developed by Lewis[2] and Langmuir[3] in the early part of the 20th century as a way to reconcile known chemical formulae with the octet rule, which Lewis credits to Abegg.[4] The importance of these ideas is demonstrated by the fact that Lewis structures drawn with discrete multiple bonds remain pedagogical building blocks in the early stages of chemical education nearly one-hundred years since their initial conception. In the 1930s, Pauling,[5] Coulson,[6] Hückel,[7] and Penney[8] re-worked the idea of valence within a quantum mechanical framework to describe compounds for which a single proper Lewis structure was inadequate. It is in this work that the concept of bond order as a non-integer quantity was introduced as a way to quantify the partial multiple bonds observed in molecules (predominantly organic molecules) with multiple energetically relevant resonance structures.

The distinction between verbal descriptors (single, double, and triple bonds) and a numeric non-integer quantity defined as bond order became increasingly important as inorganic and organometallic chemists demonstrated multiple bonding in both metallic[9] and main-group systems.[10] In the main-group systems, differences in the spatial extents of the s and p orbitals in the elements below the second row of the Periodic Table played a central role, as they led to poor π-bonding and *trans*-bent equilibrium geometries for structures consisting of heavier elements.[11] This divergence from the idealized picture of planar double bonds composed of one σ and one π bond, and linear triple bonds consisting of one σ bond and two orthogonal π bonds, immediately raised eyebrows regarding the bond order in these compounds, as did their often weak bond strengths.

In 1997, Robinson's publication of a molecule he proposed to contain the first triple bond between two gallium atoms[12] kicked off a small flurry of debate over the accuracy of this label.[13,14] Distinct ideas emerged regarding the definition of bond order as either a mechanical property (the length and strength of the bond) or as an electronic property (the number of electrons that can be said to hold the atoms together). Even within these communities there was a lack of agreement, as different electronic models and computational techniques led to different assignments of bond order.[13,14a] This debate again flared after Sekiguchi's claim of the first structurally characterized disilyne,[15] which was *trans*-bent, but noticeably less so than alkyne analogues composed of Ge, Sn, and Pb.[16]

In 2012, a report from our group detailed the synthesis and characterization of the first stable diboryne (**1**, B_2IDip_2, IDip = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[17] a molecule containing a triple bond between two boron atoms, which computational study had previously predicted to be stable.[18] The compound displayed a very short B≡B bond, was linear across its central C-B-B-C core, and orbital analysis indicated an alkyne-like assembly of one σ and two π bonds. The linear geometry in **1** circumvented arguments over the effects of *trans*-bending on bond order, and fell in line with the idea that the co-residence of boron and carbon in the second row of the periodic table would result in a similar

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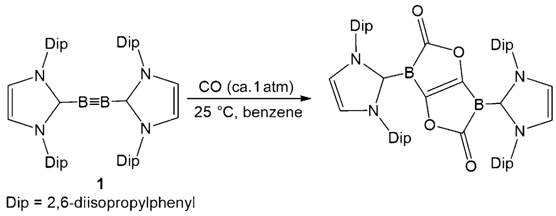
capacity for strong π bonding.[11] If the π bonds in an alkyne give it a bond order of three, the same should be true for **1**. A very recent NMR spectroscopy study of the scalar ^{11}B–^{11}B coupling between the boron atoms in **1** closely links the electronic structure of the B≡B bond to the C≡C bonds of alkynes.[19]

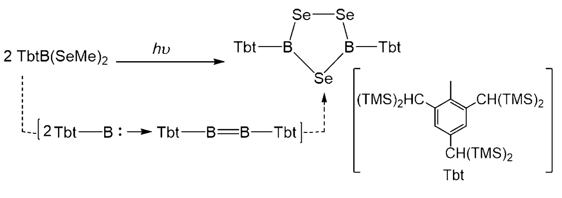
Recently, a report has surfaced in which the assignment of a triple bond in **1** is questioned through thermodynamic comparison with a stabilized two-atom segment of α-boron, and through the use of calculated vibrational data.[20] This work concluded that the bond order between the boron atoms in **1** was approximately 1.5; however, the methods in that report have not been universally accepted,[21] and a separate study of the mechanical strength of the bond, based on recorded Raman spectra, indicated no reason to doubt the triple bond assignment as the derived force constant of the B≡B bond falls in line with the trend established by the triple bonds in alkynes and dinitrogen.[22,23]

Clearly, there is no single functioning definition of bond order, but as covalent bonds consist of shared electrons, one way to probe the number of covalent bonds present between two atoms is to demonstrate the localization of multiple electron-pairs through reactivity studies.[24] In fact, this has already been achieved in the case of **1**, as its reaction with excess CO resulted in a six-electron redox reaction between the boron atoms, reductively linking four CO molecules in the formation of a bisboralactone [Eq. (1)].[25,26] With the capacity of **1** to perform multi-electron reduction reactions thus demonstrated, we sought to expand this chemistry both in the hope of synthesizing interesting and potentially useful molecules, and in providing further evidence for the residence of three bonding electron pairs between the boron atoms of **1**.



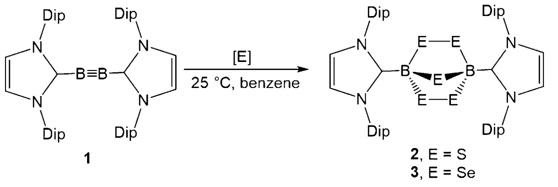
(1)

Elemental chalcogens, particularly O$_2$, S$_8$, and Se^0, are oxidants and their reductive insertion into redox active covalent bonds has been demonstrated for metal–metal single and multiple bonds,[27] metal–element multiple bonds,[28] and main-group homo- and heteroatomic bonds.[29] The ozonolysis of alkenes and alkynes demonstrates that this concept extends to familiar unsaturated organic systems.[30] A triselenodiborolane was synthesized by the UV-irradiation of a bulky di(methylseleno)arylborane [Eq. (2)] as part of a study into the utilization of the photolability of the B−Se bond to generate free borylene (R−B:) and, through coupling two such units, a diborene (R−B=B−R) sterically shielded by bulky R substituents.[31] It was postulated that the formation of the triselenodiborolane resulted from the insertion of elemental selenium, produced during the course of the irradiation, into the B=B bonds of diborenes formed in situ. Identical irradiation in the presence of a sulfur source (Me$_2$S$_2$) yielded the trisulfidodiborolane.



(2)

The inferred reductive activity of the unstable B=B double bond suggested a much more controlled addition of chalcogens to the comparatively stable, yet highly reductive, B≡B bond in **1**. The reaction of **1** with excess elemental sulfur (S$_8$) at room temperature [Eq. (3)] resulted in a rapid color change from green to yellow and a shift in the ^{11}B NMR resonance signal of the mixture from the broad peak at $\delta = 39$ ppm representative of **1** to a sharp signal at $\delta = 3$ ppm. Upon completion, the mixture was filtered to remove the residual sulfur, the solvent was removed in vacuo, and the residual oil was extracted with hexane. Pure **2** was recrystallized from a concentrated hexane solution. Single-crystal X-ray analysis of **2** (Figure 1) showed the insertion of five sulfur atoms between the two boron atoms, yielding a bicyclo[2.2.1] system with base-stabilized boron in the bridgehead positions.



(3)

An equivalent reaction with elemental selenium required ultrasonic agitation, but resulted in a color change from green to deep red and an upfield shift of the ^{11}B NMR resonance signal to $\delta = -9$ ppm. Filtration of the reaction mixture, followed by concentration in vacuo and recrystallization at −30 °C from a mixture of toluene and hexane furnished **3**, the structure of which was verified by single-crystal X-ray analysis

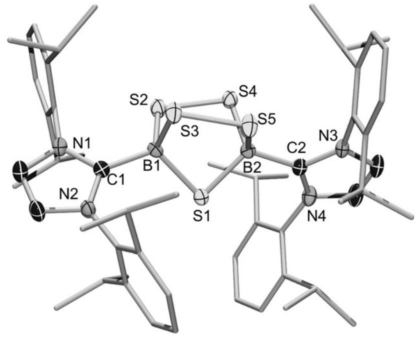


Figure 1. Crystallographically determined structure of **2**, H atoms and some thermal ellipsoids are omitted for clarity, thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: B1–C1 1.614(4), B2–C2 1.618(4), B1–S2 1.923(3), B1–S3 1.875(3), S2–S4 2.080(1); S3-S5 2.092(1), C1-B1-S1 115.1(2), C1-B1-S2 111.4(2), C1-B1-S3 106.1(2), B1-B1-B2 87.9(1), B1-S2-S4-B2 13.4(2), B1-S3-S5-B2 13.9(1).

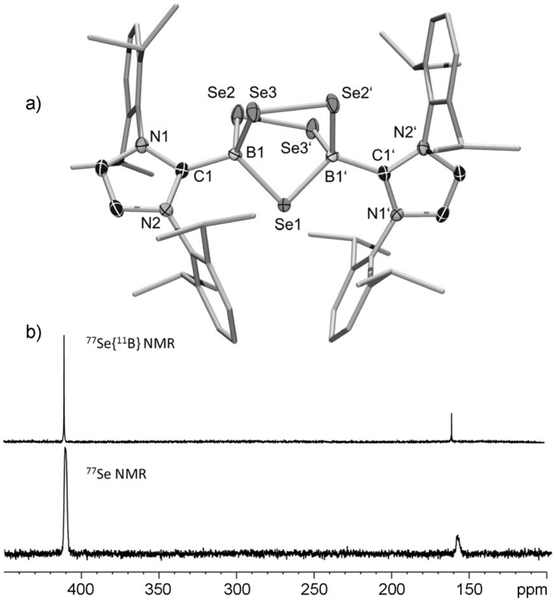


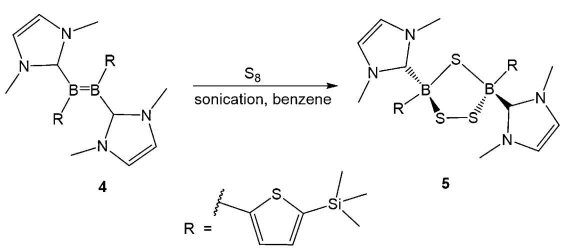
Figure 2. a) Crystallographically determined structure of **3**, All H atoms and some thermal ellipsoids are omitted for clarity, thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: B1–C1 1.603(4), B1–Se1 2.031(3), B1–Se2 2.072(3), B1–Se3 2.097(3); C1-B1-Se1 116.8(2), C1-B1-Se2 110.5(2), C1-B1-Se3 103.7(2), Se1-B1-Se2 109.2(1), Se1-B1-Se3 106.4(1), Se2-B1-Se3 110.1(1); b) Top: ^{11}B-decoupled and bottom: ^{11}B-coupled ^{77}Se NMR spectra of **3**.

(Figure 2a). The cyclic voltammograms of **2** and **3** were very complicated, showing a number of irreversible peaks in both the oxidative and reductive directions.[32]

The ^{77}Se NMR spectrum of **3** showed two signals in a 4:1 ratio at $\delta = 411$ and $\delta = 161$ ppm, which narrowed upon ^{11}B decoupling (Figure 2b). The large downfield resonance corresponding to the two symmetrical diselenide bridges is shifted upfield with respect to the Se atoms of the diselenide bridge in the monocyclic 3,5-diethyl-1,2,4-triselena-3,5-diborolane, which resonate at $\delta = 555$ ppm. The Se^{2-} bridge in **3** is significantly upfield-shifted in comparison to the single-selenide bridge in the triselenadiborolane ($\delta = 417$ ppm).[33] The signal observed at $\delta = 161$ ppm is comparable with other compounds in which one Se^{2-} is bound to two boron atoms in non-cyclic systems, for example, the signal at $\delta = 181$ ppm measured for bis(9-borabicyclo[3.3.1]nonanyl)selenium ((9-BBN)$_2$Se), but the similarities do not extend to the diselenide group in the related (9-BBN)$_2$Se$_2$, which resonates at $\delta =$ 260 ppm.[34] The differences are perhaps a consequence of the coordination between two tetrahedral boron atoms in **3**, though quarternization of the boron atoms of a triselenadiborolane with pyridine gave a compound showing only one ^{77}Se NMR resonance at $\delta = 211$ ppm.[33]

The bicyclic structures of **2** and **3** are reminiscent of the common organic norbornane, with the exception that **2** and **3** are twisted away from the C_{2v} symmetry of norbornane into a less-symmetric C_2 conformation. While the two di-carbon bridges in norbornane are parallel to one another,[35] the S4-S3-S2-S5 dihedral angle in **2** is approximately 17°. The same twist is evident in **3**, with an approximately equal magnitude (ca. 16°). The C–B bonds in **2** and **3** (**2**, 1.618(3) Å; **3**, 1.603(4) Å) are elongated in comparison to the original boron–NHC bond in **1** (1.495(3) Å, 1.487(3) Å), moving into the normal range for IDip-stabilized tetrahedral boron (e.g., 1.585(4) Å, IDip-BH$_3$; 1.623(7) Å, IDip-BBr$_3$).[36] The disulfide bonds in **2** (2.092(1) Å, 2.080(1) Å) fit into the common range for organic S–S bonds[37] and are similar to the S–S bond in the monocyclic dimethyl-1,2,4-trithia-3,5-diborolane (2.076(3) Å).[38] The diselenide bond in **3** measures 2.3393(4) Å, well inside the normal range of organic diselenides.[39]

If the NHC-stabilized triple bond is capable of delivering six reducing equivalents, it stands to reason that an NHC-stabilized diborene (compound containing a B=B bond), should be capable carrying out four-electron reductions. To test this logic we treated a NHC-stabilized diborene with elemental sulfur. When a thienyl-substituted, IMe-stabilized diborene (**4**)[40] was treated with elemental sulfur by sonication, the clean formation of the IMe-stabilized 1,2,4-trithia-3,5-diborolane **5** (Figure 3) was observed, resulting from the reductive transfer of four equivalents of electrons to three sulfur atoms [Eq. (4)].



(4)

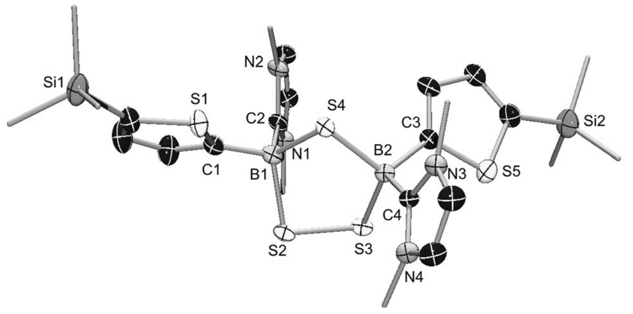


Figure 3. Crystallographically determined structure of one of the two independent molecules of **5**. H atoms are omitted for clarity and some thermal ellipsoids are omitted for clarity, thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: B1–C1 1.607(8), B1–C2 1.647(7), B1–S4 1.942(6), B1–S2 1.935(6), S2–S3 2.085(2); S4-B1-S2 104.6(3), B1-S4-B2 102.2(2).

The ^{11}B NMR shift of **5** ($\delta = -2$ ppm) is consistent with tetrahedral coordination at the boron atoms. Slow evaporation of a benzene solution resulted in the isolation of crystals of **5** suitable for single-crystal X-ray crystallography (Figure 3). Useful parallels may be drawn between **5** and the structure of the five-membered cyclic ozonide intermediate in the ozonolysis of alkenes,[30] as both result from reductive insertions of chalcogens into double bonds.

In summary, we report herein the syntheses of three new Group 13/16 cyclic systems produced by the reductive insertion of elemental chalcogens into redox-active bonds between boron atoms. The B≡B bond furnished six reducing equivalents; the B=B bond provided four. In our view, this reactivity is one more piece of evidence for the concept of traditional multiple bonding in boron, and particularly of the existence of a triple bond in **1**.

Keywords: bicyclic compounds · bond order · boron · multiple bonds · redox chemistry

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