

Access to B=S and B=Se Double Bonds via Sulfur and Selenium Insertion into a B–H Bond and Hydrogen Migration

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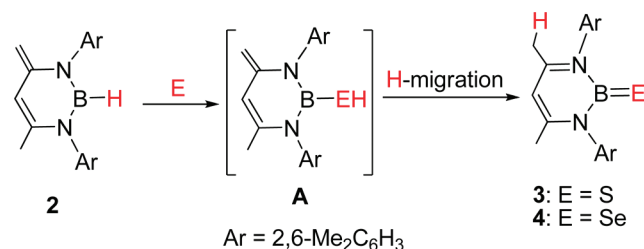
Abstract: Stable compounds with a boron–chalcogen (S or Se) valence double bond have been prepared via sequences involving insertion of the chalcogen into a B–H bond and subsequent hydrogen migration. X-ray diffraction studies and density functional theory calculations on the resulting compounds provide convincing evidence for the boron–chalcogen multiple bonding.

The synthesis and isolation of main-group compounds containing multiple bonding to group 16 elements have attracted much attention.¹ Monomeric oxoboranes and their heavy analogues RBE (E = S, Se, Te) have long been known to be extremely reactive and unstable under normal conditions. Recent isolation and structural characterization of the oxoboryl complex *trans*-[(Cy₃P)₂BrPt(BO)] (Cy = cyclohexyl) and the AlCl₃-stabilized oxoborane [HC(CMe)₂(NC₆F₅)₂]BO→AlCl₃ represent breakthroughs in oxoborane chemistry.^{2,3} However, even though reports on boron–chalcogen double-bond species RBE as reactive intermediates⁴ and high-temperature gas-phase species⁵ have appeared, such room-temperature-stable compounds are still elusive, probably because of their intrinsic high reactivity and the lack of suitable synthetic approaches. Herein we report on the synthesis and isolation of the first isolable monomeric thioxo- and selenoxoboranes featuring well-defined B=E (E = S, Se) double bonds from an N-heterocyclic borane via sequences involving sulfur and selenium insertion into the B–H bond and subsequent hydrogen migration, as shown in Scheme 1.

Bulky β -diketiminato ligands have proved to be effective for the stabilization of heavy group 13 element carbene analogues,⁶ but the analogous boron compounds have not been obtained to date. Theoretical calculations indicate that such boron analogues should have a very small singlet–triplet energy gap and be extremely reactive, unlike their heavy analogues.⁷ In the course of our studies on the boron analogues, we attempted to generate the species by dehydrohalogenation of the β -diketiminato chloroborane LBHCl (**1**, L = [HC(CMe)₂(NAr)₂][–], Ar = 2,6-Me₂C₆H₃) with N-heterocyclic silylenes following the protocol for the synthesis of N-heterocyclic silylenes developed by us.⁸ Thus, the desired chloroborane **1** was synthesized by the reaction of LLi⁹ with Me₂S·BHCl₂ in diethyl ether. Treatment of **1** with 1 equiv of 1,4-di(*tert*-butyl)imidazol-2-ylidene¹⁰ in THF indeed yielded a dehydrohalogenated product, as indicated by the formation of the insoluble imidazolium salt. Analysis of the resulting soluble product by multinuclear NMR spectroscopy, however, indicated the formation of borane **2** (Scheme 1) rather than the expected boron carbene analogue LB. Apparently, one of the β -methyl groups on the β -diketiminato ligand backbone is deprotonated during the reaction. The similar dehydrohalogenation of β -diketiminato silicon and germanium halides has been reported to yield novel N-heterocyclic silylene and germylene species, respectively.^{11a,b} **2** can be considered as the intramolecular C–H activation product of the isomeric monovalent species LB. We reasoned

that **2**, by insertion of an electronegative fragment into the B–H bond, may be synthetically useful as an LB equivalent since the resulting acidic hydrogen atom may migrate to the exocyclic methylene group. To prove the hypothesis, the reactions of **2** with sulfur and selenium were investigated, as sulfur and selenium are known to undergo insertion reactions with a B–H bond. Reaction of **2** with 1 equiv of elemental sulfur in *n*-hexane at room temperature proceeded slowly to give an orange-yellow solution after stirring at room temperature overnight, from which yellow crystals of **3** were obtained after workup. The reaction with selenium was carried out at 70 °C in toluene, and the selenoxoborane **4** was obtained as orange crystals after crystallization from THF. Compounds **3** and **4** are extremely air- and moisture-sensitive. They were fully characterized by ¹H, ¹³C, and ¹¹B NMR spectroscopies, elemental analysis, and single-crystal X-ray analysis.

Scheme 1



The ¹H and ¹³C NMR spectra of **3** and **4** showed the characteristic patterns for the β -diketiminato ligand L, indicating that the exocyclic C=CH₂ group in **2** had been hydrogenated. The ¹¹B NMR spectra of **3** and **4** exhibited broad resonances at 36.79 and 40.88 ppm, respectively, which are downfield-shifted relative to the value of 29.3 ppm found in hydroborane **2** but fall in the range for three-coordinate diamino-substituted boron species.¹² The B=S and B=Se stretching vibration modes of **3** and **4** (1161 and 1136 cm^{–1})

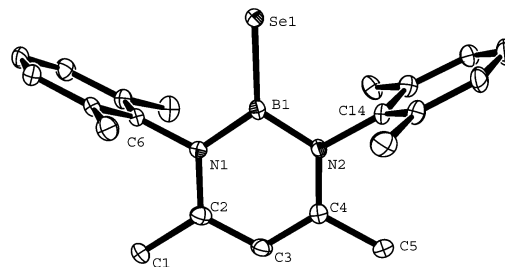


Figure 1. ORTEP drawing of **4** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **3**: B1–S1, 1.741(2); B1–N1, 1.483(3); B1–N2, 1.484(3); N1–B1–S1, 124.35(18); N2–B1–S1, 124.13(18); N1–B1–N2, 111.52(18). For **4**: B1–Se1, 1.896(4); B1–N1, 1.489(6); B1–N2, 1.476(6); N1–C2, 1.358(5); C2–C3, 1.406(7); C3–C4, 1.365(7); N2–C4, 1.343(5); N1–B1–Se1, 123.8(4); N2–B1–Se1, 123.6(4); N1–B1–N2, 112.6(3).

observed in their IR spectra are well-correlated with the theoretical predictions (see Figures S3 and S4 in the Supporting Information). These spectroscopic data are consistent with the structures of **3** and **4**. The molecular structures of **3** and **4** were unambiguously verified by single-crystal X-ray analysis.

Crystals of **3** and **4** suitable for X-ray diffraction studies were obtained from THF at $-40\text{ }^{\circ}\text{C}$. Compounds **3** and **4** are isomorphous and have similar molecular geometries. The structure of **4** is representatively shown Figure 1, where selected bond parameters for **3** and **4** are given. Both **3** and **4** are monomeric, with terminal S and Se atoms, respectively. The B–S bond length of $1.741(2)\text{ }\text{\AA}$ is significantly shorter than the sum of the covalent radii of boron and sulfur ($\sim 1.87\text{ }\text{\AA}$) and shorter than those in the three-coordinate boron compounds containing a B–SR bond ($1.77\text{--}1.805\text{ }\text{\AA}$),¹³ in which lone-pair donation from the sulfur atom to the boron atom may exist. The B1–Se1 bond length [$1.896(4)\text{ }\text{\AA}$] in **4** is shorter than the B–Se bond lengths ($1.960\text{--}2.13\text{ }\text{\AA}$) found in a small number of structurally characterized organic compounds containing a B–Se bond.^{4c–e,14} The geometry around the boron atom in both **3** and **4** was found to be approximately trigonal-planar [the sum of the angles = $360.00(18)^{\circ}$ for **3** and $360.0(4)^{\circ}$ for **4**]. These structural features are consistent with the multiply bonded character of the B–S(Se) bond.

The four B–N bond lengths [$1.483(3)$ and $1.484(3)\text{ }\text{\AA}$ in **3**; $1.489(6)$ and $1.476(6)\text{ }\text{\AA}$ in **4**] are almost equal to each other, and the C–C and C–N bonds in the planar B–N–C–C–C–N ring tend to equalize in each of the two molecules; this indicates the electron delocalization in the N–C–C–C–N backbone. The B–N bond lengths in **3** and **4** are within the reported range for β -diketiminato boron compounds.^{3,15}

Although π bonding between boron and sulfur has been proposed in the three-coordinate boron compounds having the formula R_2BSR (R = alkyl, aryl),^{1a} compounds **3** and **4** represent the first well-defined stable compounds containing a valence double bond between boron and heavy chalcogens. Because of the electron delocalization in the central six-membered heterocycle, there is no structural distinction between the dative and covalent B–N bonds that can be observed. Nevertheless, **3** and **4** can be formally described as having an intramolecular donor-stabilized boron–chalcogen double bond. The syntheses of several N-heterocyclic carbene-stabilized silanechalcogenones supported by a closely related N-heterocyclic ligand via chalcogenation of the corresponding silylenes have recently been reported.¹⁶

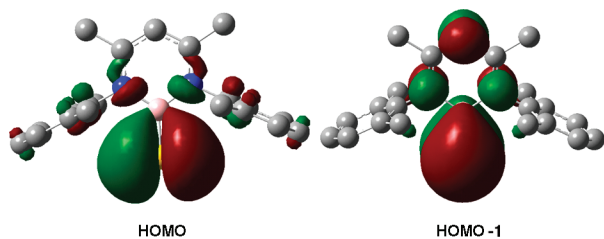


Figure 2. Representations of the frontier orbitals of **3** obtained from DFT calculations.

To analyze the bonding situation, theoretical calculations were performed for compound **3** using density functional theory (DFT) at the B3LYP/6-31++G (d,p) level.¹⁷ The optimized geometry for **3** is in good agreement with the X-ray results for **3** (see Figure S1 in the Supporting Information). The computed N–B–N (110.79°) and N–B–S (124.60°) angles are in line with those determined by X-ray diffraction analysis. The calculated B–S bond length ($1.72680\text{ }\text{\AA}$) is only slightly shorter and the B–N bond length ($1.51291\text{ }\text{\AA}$) slightly longer than the corresponding lengths found by the X-ray analysis. Natural bond order (NBO) analysis of **3** indicates highly filled σ ($1.98e$)

and π orbitals ($1.97e$) for the B–S double bond, with the π orbital being strongly polarized toward the sulfur atom (77.31%). The two B–N σ bonds are formed by the high-p-character hybrid orbitals ($sp^{2.52}$) of the boron atom with the $sp^{1.61}$ hybrid orbitals of the nitrogen atoms. Inspection of the frontier Kohn–Sham orbitals (Figure 2) shows that the HOMO corresponds mainly to the sulfur lone pair and the HOMO-1 to the B–S π bond with the ligand π^* components. The calculated ^{11}B and ^{77}Se NMR chemical shifts are in good agreement with the experimental values (see Table S2 in the Supporting Information).

In summary, the first stable molecular compounds with a boron–chalcogen valence double bond have been prepared via insertion of chalcogen into a B–H bond followed by hydrogen migration through the use of a bulky β -diketiminato ligand. **3** and **4** feature short B–E distances and a trigonal-planar geometry around the boron atom, thereby providing convincing evidence for the boron–chalcogen multiple bonding. Reactivity studies of these compounds and extension of the synthetic route to other systems are currently in progress.

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Supporting Information Available: Experimental details for the synthesis and characterization of the compounds in this paper, CIFs for **3** and **4**, and calculation details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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