Abstract: The reactions of a diborene with elemental selenium or tellurium are shown to afford a diborasantirane or diboratellurirane, respectively. These reactions are reminiscent of the sequestration of sub-valent oxygen and nitrogen in the formation of oxiranes and aziridines; however, such reactivity is not known between alkenes and the heavy chalcogens. While carbon is too electronegative to affect the reduction of elements of lower relative electronegativity, the highly reducing nature of the B-B double bond enables reactions with Se and Te. The capacity of multiple bonds between boron to donate electron density is highlighted in reactions where diborynes behave as nucleophiles, attacking one of the two Te atoms of diarytellurides, forming salts consisting of diboratellurirane cations and aryttellurane anions.

The energy stored in small, highly strained cyclic molecules has made them an integral part of modern synthetic chemistry. Since this “strain energy” increases with decreasing ring size, it is greatest for three-membered rings, and when these rings are heterocyclic the charge-asymmetry induced in the molecule provides sites ready for reaction. Accordingly, an enormous amount of research has gone into both the synthetic methods to, and reactions of, members of this class of compounds, most prominently oxiranes (C=O rings) and aziridines (C=NR rings). The most common route to these materials is the oxidation of olefins using, in the case of oxirane formation, subvalent oxygen species such as O₃ peroxides, peroxyacids, and ozone, or with reagents that impart a degree of electron deficiency to an oxygen atom, such as chlorite or iodosylbenzene. Aziridination of olefins is most frequently accomplished through the in situ generation of nitrenes from azides or other electron deficient nitrogen sources such as iodinanes, hydroxylamines, and hydrazines. These alkene-oxidations are made possible by the relatively high electronegativity of oxygen and nitrogen, (\(X_{\text{Pauling}}\) = 3.44 and 3.04, respectively), relative to carbon (\(X_{\text{Pauling}}\) = 2.55).

Thiranes (C=S rings) are comparatively less common, and though examples of the direct addition of elemental sulfur to alkanyl double bonds are not unknown, their syntheses are more likely than their first row neighbors to involve non-redox routes. The similar electronegativities of carbon and sulfur (\(X_{\text{Pauling}}\) = 2.58) decreases the thermodynamic driving force for alkene oxidation, further exemplified by the noted willingness of thiranes to thermally extrude atomic sulfur and by their utility as sulfur atom transfer reagents. Three-membered heterocycles featuring heavier chalcogens (Se and Te) are even less prevalent. Though seleniranes have been proposed as reactive intermediates in a handful of transformations, the isolated examples of these compounds are few and none have been crystallographically verified. To date, there are no known examples of telluriranes. The heavy chalcogens have roughly equal (\(X_{\text{Se}} = 2.55\)) or smaller (\(X_{\text{Te}} = 2.10\)) electronegativities than carbon. As such, there is little or no driving force for the transfer of electron density from the alkene to form C=Se or C=Te rings, and hypothetical seleniranes or telluriranes would logically be thermodynamically unstable toward the alkene reclaiming its electrons by expelling the electropositive chalcogen.

For some time our group has been interested in the syntheses and utilities of diborones. In comparison to alkenes, the B-B bonds of diborones have been found to be exceptionally reducing, which is not surprising when considering both the formal +1 charge on boron and the lower electronegativity of boron (\(X_{\text{Pauling}}\) = 2.04) than carbon. Indeed, while direct oxidation of alkenes to thiranes with elemental sulfur is rare, the reaction of diborones with S₈ results in the transfer of all four reducing equivalents of the double bond to three sulfur atoms in the formation of a five-membered trithiaborolane. Might these highly reductive double bonds be capable of reaction with elemental Se and Te to form stable diborasantiranes and diboratelluriranes?

When a thienyl-substituted, N-heterocyclic carbene (NHC) stabilized diborone (1, IMes=5-(Me₂Si)C₆H₄SiMe₂) was reacted with excess elemental selenium in benzene, a color change from the deep purple of 1 to yellow was observed, along with the emergence of a new signal at ~14 ppm in its \(^{11}B\) NMR spectrum. An equivalent reaction with elemental tellurium evidenced a similar change, with the emergence of a signal at ~13 ppm in the \(^{11}B\) NMR spectrum concomitant with the change of color from purple to yellow. After filtration to remove the excess chalcogen, recrystallization from acetonitrile yielded pure 2 and 3, the desired diborasantirane and diboratellurirane, respectively. Both were structurally characterized by single-crystal X-ray crystallography (Figure 1). Though neither \(^{77}Se\) nor \(^{125}Te\) nuclei could be detected by NMR spectroscopy with 2 and 3, likely a result of extensive quadrupolar broadening induced by proximity to multiple boron nuclei, the \(^1H\) NMR spectra of the...
The B–B bonds in 2 (1.707(3) Å) and 3 (1.713(5) Å) are elongated with respect to the normal range of B–B lengths in diborene compounds (~1.58 – 1.61 Å), just slightly short of the normal range for B–B single bonds in base-stabilized neutral diboranes (1.72 – 1.84 Å). This mirrors the geometries of oxiranes, which tend to have C–C bond distances (1.438(4) Å, ethylene oxide) between those of alkanes (1.532 Å, ethane) and alkenes (1.3142(3) Å, ethylene). The typical C–C bonds in aziridines (~1.48 Å) and thiirane (~1.49 Å) are similarly situated between ethane and ethylene.

Diborynes, molecules containing a boron-boron triple bond, are likewise known to be highly reducing. In fact, the reaction of the bis-NHC-stabilized diborane BuIDip is a reaction pathway wherein the B=B bond acts as a nucleophile, attacking one of the tellurium atoms of the ditelluride, forcing out a [PhTe]+ leaving group. Such a process has been suggested as the pathway for the epoxidation of alkenes with peracids, though controversy surrounding this assertion still exists.

**Figure 1.** Synthesis and crystallographically determined structures of 2 and 3. The ellipsoids represent 50% probability, and have been omitted from the ligand periphery. For clarity, all hydrogen atoms are likewise omitted. Selected bond lengths (Å) and angles (°): (2) B1–B2 1.707(3), C2–B1 1.604(2), C1–B1 1.586(2), B1–Se1 2.115(2): (3) B1–B2 1.713(5), C1–B1 1.584(4), C2–B1 1.598(4), B1–Te1 2.360(3).

**Figure 2.** Crystallographically determined structures of [5]+ and [6]+ (aryltelluride anions, with anionic phenyltelluride. An equivalent reaction utilizing the more electron-poor di-[4-fluorophenyl]-ditellurium showed identical reactivity, allowing the isolation and characterization of 6.

The boron-boron bond lengths in 5 and 6 were found to be 1.490(6) Å and 1.494(10) Å, respectively. These are moderately longer than the B=B length in 1 (1.449(3) Å), yet substantially shorter than those typically found in diborenes (~1.58 – 1.61 Å). Similar structural features are found in the organic anion.
tellurium, which has a central C–C bond measuring 1.288(14) Å \cite{24} – longer than the central bond in di-tert-butyl acetylene (1.202(2) Å \cite{25}) but significantly shorter than the ~1.34 Å typical of the double bond in alkenes.\cite{25} The B–B–C angles in 5 and 6 (~163 – 165°) are only slightly bent from linearity, though it is possible that the steric bulk of the two IDip groups prevents more acute bending. These angles are slightly more linear than the C–C–C angles in I, which measure 1.555(10) and 1.576(9) Å \cite{24}. The Te atoms of 5 and 6 are highly pyramidalized, which is unsurprising since a planar tricoordinate Te atom would necessarily place two electrons into the τ-system between the boron atoms, resulting in an antiaromatic electron count of four.

The relatively slight deviation from linearity induced by the complexity of [PhTe]\textsuperscript{+} led us to seek additional information about the boron-boron bonds in 5 and 6. The Raman spectrum of 4, previously used to study the strength of the B≡B triple bond,\cite{26} shows identifiable peaks at 1628, 1657 and 1685 cm\textsuperscript{-1} corresponding to the symmetric stretch of the three possible isotopomeric combinations of \textsuperscript{11}B and \textsuperscript{10}B. The spectra recorded with 5 and 6 showed a similar diagnostic isotopic pattern, shifted to lower wavenumbers, as a result of bond lengthening and a decrease in bond order. The spectrum of 5, in combination with the predicted spectra of its isotopomers, is presented in Figure 3, showing B≡B frequencies of 1511, 1531 and 1555 (tentatively) cm\textsuperscript{-1} for the \textsuperscript{11}B/\textsuperscript{11}B, \textsuperscript{11}B/\textsuperscript{10}B, and \textsuperscript{10}B/\textsuperscript{10}B isotopomers, respectively. Compound 6 showed a very similar spectrum, which is provided in Figure S3. For comparison, the stretching frequencies attributed to the B≡B stretch in 4 are given in Figure 3 in green. Though direct comparison to organic tellurium species such as 7 was not possible, as these compounds lack Raman data, the redshifting of the B≡B stretch (Δν = ~120 cm\textsuperscript{-1}) upon going from 4 to 5 is significantly smaller than the redshift observed between C≡C triple bonds and the central C≡C stretch in similarly structured selenenium ions (Δν = ~380 cm\textsuperscript{-1}) \cite{24}.

In conclusion, the use of highly reducing boron-boron multiple bonds has enabled the formation of new, small heterocycles incorporating the heavy chalcogens, which are too electropositive to form similar compounds with carbon. The willingness of these τ-bonds between boron atoms to donate electrons was explicitly shown in their capacity to act as nucleophiles in conjunction with ditellurides in the formation of diborate tellurenum cats by anionic telluride anions. These reactions serve to highlight both the similarities and differences between boron-boron multiple bonds and their conventional unsaturated organic analogs. Both are capable of sequestering chalcogen atoms into three membered rings, but the specific chalcogens employed, and the mechanism of their insertion, depends on the relative electronegativities of the chalcogen in question and boron or carbon. With this lesson learned, we continue to seek out reactions which fail with electron poor alkenes, in hopes that increasing the reductive power of the double bond may enable the chemistry to flourish.

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Keywords: Boron • Multiple Bonds • Heterocycles • Selenium • Tellurium

\[\text{[Reference List]}\]

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[12] The calculated frontier molecular orbitals of compounds 2, 3, and 5 are given in Figures S1 and S2 of the Supplementary information


Heavy heterocycles: The reaction of diborenes with Se and Te resulted in the formation of diboraseleniranes and diboratelluriranes, while the reaction of diborynes with diarylditellurides yields diboratellurenium cations with arytelluride anions. Such reactions are unique to boron-boron multiple bonds due to their reducing nature and the relatively low electronegativity of boron.

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Highly Strained Heterocycles
Built from Boron-Boron
Multiple Bonds and Heavy
Chalcogens