Synthesis of unsymmetrical $B_2E_2$ and $B_2E_3$ heterocycles by borylene insertion into boradichalcogeniranes†

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We report the selective insertion of a range of borylene fragments into the E–E bonds ($E = S, Se, Te$) of cyclic boron dichalcogenides. This method provides facile synthetic access to a variety of symmetrical and unsymmetrical four- and five-membered rings.

Introduction

1,3-Dithietanes — four-membered [C$_2$S$_2$] cyclic molecules — comprise a scarce class of compounds. This, however, is at odds with the fact that the cyclic 1,3-dithiotetral moieties is found in bioactive compounds such as antibacterial and hepatoprotective agents and pesticides. Even more rare are the heavier analogues of 1,3-dithietanes, 1,3-diselenetane and 1,3-ditelluretane, which typically arise from the dimerization of a handful of selenones and tellurones. In the main group, Group 13 analogues of these heterocycles are known but remain limited in scope due to a dearth of options for their selective synthesis.

Molecular compounds of aluminium and gallium that feature a central planar M$_2$E$_2$ ring surrounded by organic substituents may be accessed by reaction of dihydride or dimethyl precursors with elemental chalcogens. Substituents may be accessed by reaction of dihydride or dimethyl precursors with elemental chalcogens. Substituents may be accessed by reaction of dihydride or dimethyl precursors with elemental chalcogens.

We have recently reported the reactivity of the N-heterocyclic-carbene-stabilized manganese borylene complex [Cp(OC)$_2$Mn=BrBu(IMe)]$^{10}$ with chalcogens (S, Se, Te), selectively affording a range of unusual boron chalcogenides, including a family of novel free and metal-bound boradichalcogenanes ([Cp(OC)$_2$]Mn[k$_1$-cyclo-TeTeB(Bu)(IMe)] (1) and [cyclo-EEBBrBu(IMe)] (E = S (2a), S (2b))]. We now report that these complexes selectively react with a number of different transition metal borylene complexes to afford a range of unsymmetrically substituted B$_2$E$_2$ four-membered rings under mild conditions (Fig. 1).

Results and discussion

Borylene complexes of the group VI metals figure among the most studied metal-stabilized sources of borylene fragments.
In recent years, borylene complexes of chromium, molybdenum and tungsten have been shown to engage in metal-to-metal, metal-to-carbon and metal-to-nitrogen borylene transfer, in C–H activation and in [2 + 1] addition reactions. Towards our study of the reactivity of boryl complexes with low-valent boron fragments, the sterically protected borylene complex \([\text{OC}]_2\text{Cr}–\text{BTp}\) (3) (Tp = 2,6-bis(2,4,6-trimethylphenyl)phenyl) was deemed a good starting point. Treatment of boraditellurirane complex 1 with one equivalent of 3 in toluene allowed us to isolate cyclo-[(\text{Bu})(\text{IMe})\text{B–Te–B(Tp)–Te}] (4) after recrystallization from a toluene/pentane mixture (yield: 24%).

High-resolution mass spectrometry (HRMS) and single-crystal X-ray diffraction analysis allowed us to identify 4 as an NHC-stabilized 1,3-ditellurabenzene arising from the insertion of a [BTp] fragment into the Te–Te bond of 1. To the best of our knowledge, 4 represents the first example of such a four-membered \(\text{B}_2\text{Te}_2\) ring (Fig. 2).

This new species features two resonances in its \(^{11}\text{B}\) NMR spectrum (δ = −33.0 and 61.1) which differ considerably from those of both starting materials (δ = −2.0 (1) and 147 (3)), as expected for its unsymmetrical substitution pattern. The new signal at −33.0 ppm is attributable to the sp\(^3\)-hybridized tetrahedral boron atom that is coordinated by an IMe ligand (B2), while the peak at 61.1 ppm can be assigned to the BTp moiety. In the solid state, 4 features a near-planar four-membered cycle which is close to perpendicular with the CBC plane of the (Bu)B2(IMe) group. The Tp substituent is rotated approximately 15° from perpendicularity with the B2E2 cycle. Interestingly, the B–Te distances are different for both boron centers. Indeed, the TpB1–Te bonds are significantly shorter (2.153(2) and 2.139(2) Å) than the corresponding (Bu)(IMe)B2–Te distances (2.358(2) and 2.331(2) Å), likely owing to Te-to-B π-donation, which is not present in the case of the sp\(^3\)-hybridized B2.

Borylene complex 3 was also reacted with the Se and S compounds 2a and 2b under the same conditions as for 1.

Interestingly, in these cases the Se and S analogs of the four-membered \(\text{B}_2\text{Te}_2\) compound 4 were only observed as minor products, which we were unable to isolate, however we were able to obtain a few crystals of the selenium-containing analog of 4, which allowed us to determine a solid-state structure and...
confirm its connectivity (see ESIf). In these reactions, after crystallization from a THF/pentane mixture, the five-membered rings cyclo-[(tBu)(IMe)E–E–B(Tp)–E] (E = Se (5a) and S (5b)) were obtained (yield 22% in both cases). In the 1,2,4-triselena-3,5-diborolane 5a, the $^{11}$B NMR signals for the two boron atoms were found at 6.2 and 72.1 ppm. Similarly, in 5b, they are found at 7.7 and 66.2 ppm. The five-membered rings 5a and 5b are likely to arise from the initial formation of Se and S analogues of 4, which then undergo ring expansion using the starting materials or reaction intermediates as sacrificial chalcogen sources. While $^{11}$B NMR monitoring of the reaction showed the formation of other boron chalcogenide species – as is predicted from the stoichiometry of the reaction – these byproducts could not be identified. 5a and 5b can however be reliably crystallized from the reaction mixture and isolated.

In the solid state, 5a is structurally comparable to the three previously reported examples of crystallographically characterized 8Se8Se8Se non-cluster five-membered rings. Interestingly, it represents, to our knowledge, the first example of such a cycle with an unsymmetrical substitution pattern. The planar sp$^2$-hybridized TpB site features B–Se distances (1.919(5) and 1.921(4) Å) that are close to those reported by Tokioka and coworkers in a symmetrical five-membered ring of selenium and sp$^2$ boron. In contrast, on the tBu(IMe)B side of 5a, the B–Se distances (2.115(4) and 2.106(4) Å) are analogous to those found in triselena-1,3-diborolanes with sp$^3$ boron atoms. Unfortunately, while we were able to grow crystals of 5b, their poor quality, combined with the absence of heavy elements, did not yield crystallographic data of a precision that would allow us to discuss structural parameters. Instead, the single-crystal X-ray diffraction analysis only allows us to confirm the connectivity and the substitution pattern in the molecule.

Since the insertion of TpB fragments into 2a and 2b did not allow us to selectively synthesize unsymmetrical B–Se dichalcogenadiboretane rings, we elected to react these precursors with other borylene sources. Thus, the Group 6 aminoborylene complexes 11,12-{

![Image](https://example.com/image.png)

**Fig. 3** Reactions of boradichalcogeniranines 2a and 2b with borylene complexes 6 and 8 (top). Pov-Ray depictions of the crystallographically determined structures of compounds 7a (bottom left) and 7b (bottom right). Atomic displacement ellipsoids depicted at 50% probability level. Hydrogen atoms and ellipsoids of peripheral groups omitted for clarity. Selected bond distances (Å) and angles (°): 7a: B1–CtBu 1.628(6), B1–CtMe 1.631(6), B1–Se1 2.116(5), B1–Se2 2.112(5), B2–N 1.442(7), B2–Se1 1.957(5), B2–Se2 1.958(5), B1–Se1–B2 81.7(2), B2–Se2–B1 81.8(2), B2–Se1–B1 92.8(2); 7b: B1–CtBu 1.632(5), B1–CtMe 1.633(5), B1–S1 1.998(4), B1–S2 1.990(3), B2–N 1.440(5), B2–S1 1.855(3), B2–S2 1.844(4), B1–S1–B2 80.8(2), S1–B2–S2 104.0(2), B2–S2–B1 81.2(2), S2–B1–S1 94.0(2).

other side of the molecule, the (tBu)(IMe)B–Se distances (2.115(2) and 2.116(5) Å) are considerably longer, consistent with the presence of an sp$^3$ boron center. In the case of 7b, $^{11}$B NMR signals were found at −6.1 and 49.8 ppm. The solid-state structure of 7b is comparable to that of 7a, with (Me$_3$Si)$_2$NB–S bond distances of 1.844(4) and 1.855(3) Å, tBu(IMe)B–S distances of 1.990(3) and 1.998(4) Å and a B–N bond measuring 1.440(5) Å (Fig. 3).

2a and 2b also react with [Cp(OC)$_2$Mn=]BtBu ([Cp = cyclopentadienyl] BtBu) to a manganese borylene complex that has a rich reactivity and that is a precursor of 1, 2a and 2b. While we were not able to obtain high-quality crystals from this reaction, HRMS of the isolated products revealed a formula consistent with cyclo-[(tBu)(IMe)E–E–B(tBu)–] (E = Se (9a) and S (9b)), arising once again from the transfer of a borylene fragment (tBuB) from 8 to 2a and 2b. The solution $^1$H and $^{13}$C NMR spectra of 9a and 9b are consistent with the formula assignment from HRMS, revealing a 1 : 1 : 1 ratio of IMe and two inequivalent tBu groups. The $^{11}$B NMR resonances of 9a (δ = −10.8 and 77.5) and 9b (δ = −3.6 and 72.9) reveal a similar environment for the sp$^3$ boron atom as that in the corresponding four-membered rings 7a and 7b, which leads us to...
postulate that products 9a and 9b are indeed the cyclic compounds \( \text{cyclo-}[\text{CAAC}][\text{BCN}][\text{E}][\text{E}][\text{E}][\text{E}] \).

Finally, 2a was also found to react with the macrocyclic complex \( \text{cyclo-}[\text{CAAC}][\text{BCN}][\text{E}][\text{E}][\text{E}][\text{E}] \). This metal-free tetrameric borylene was previously shown to be a useful source of the corresponding monomer \( \text{[CAAC][BCN]} \) in its reaction with Lewis bases and to generate of one of the few reported examples of \( \text{cyclo-}[\text{BSe}] \), complexes by reaction with elemental selenium. Thus, the reaction of 2 and 10 in toluene led to the isolation of the new, 1,3-diseleno-2,4-diborolane \( \text{cyclo-}[\text{CAAC}][\text{BSe}][\text{E}][\text{E}][\text{E}][\text{E}] \) in a 34% yield. While once again unsymmetrically substituted, this compound is the first of the series reported herein to feature two sp\(^3\)hybridized boron atoms. The \( ^{11}\text{B} \) NMR spectrum of 11 shows two signals at \(-9.5 \) and \(-32.8 \) ppm. While both signals lie within the typical range for sp\(^3\) boron atoms, we can assign the former to the \{\text{Bu}\}[\text{Me}][\text{B}] \) group by comparison to 7a and 9a, while the latter is similar to signals of both isomers of the previously reported \( \text{cyclo-}[\text{CAAC}][\text{CN}][\text{E}][\text{E}][\text{E}][\text{E}] \) (\( \delta = -31.8 \) and \(-33.5 \) ppm).

Rather surprisingly, and in contrast with other 1,3-diseleno-2,4-diborolanes,\(^{9,b,10} 11 \) adopts a clearly bent butterfly structure in the solid state. This situation is plausibly a consequence of the unsymmetrical substitution pattern, which gives rise to a large difference in steric bulk on both faces of the cycle. The B-Se distances are slightly shorter on the \{\text{CAAC}\}[\text{CN}][\text{B}] \) side (2.067(1) \( \AA \)) than around the \{\text{Bu}\}[\text{Me}][\text{B}] \) moiety (2.114(1) \( \AA \)) [Fig. 4].

Conclusions

In conclusion, we demonstrate that borylene fragments can be inserted into the E–E bonds (E = Te, Se and S) of boradichalcogeniranes. This reaction gives unprecedented synthetic access to unsymmetrically substituted 1,3-dichalcogena-2,4-diborolates and 1,2,4-dichalcogena-3,5-diborolanes. We have thus reported the synthesis of heterocycles featuring unsymmetrical boron centers in sp\(^3\)-sp\(^3\) and sp\(^3\)-sp\(^3\) hybridization combinations. Given the lack of methods for the synthesis of such unsymmetrical compounds, this approach will provide us with a useful platform to study the properties and applications of these unusual heterocycles.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


