EDGE ARTICLE

Dimeric boroles: effective sources of monomeric boroles for heterocycle synthesis†

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Monomeric boroles have been gaining attention as reagents for the synthesis of heterocycles due to their ability to insert atoms into the BC_4 ring in a single step. Although unique boron frameworks can be accessed *via* this methodology, the products feature aryl substitution on the carbon centers as steric bulk is required to preclude borole dimerization. This work demonstrates that insertion chemistry is possible with Diels–Alder dimeric boroles and that such reactivity is not exclusive to monomeric boroles with bulky groups. With 1-phenyl-2,3,4,5-tetramethylborole dimer, the formal 1,1-insertion of a nitrene and sulfur generate the six-membered aromatic 1,2-azaborine and 1,2-thiaborine, respectively. The isolation of the 1,2-thiaborine enabled the synthesis of an η^6-chromium complex. Benzophenone and diphenylketene readily insert a CO unit to generate BOC_5 seven-membered rings confirming dimeric boroles can serve as monomeric synthons in 1,2-insertion reactions. An epoxide did not furnish the anticipated eight-membered BOC_6 ring, instead provided a bicyclic system with a BOC_3 ring. The insertion chemistry was demonstrated with two other borole dimers featuring different substitution with diphenylketene as a substrate. This work elevates borole insertion chemistry to a new level to access products that do not require bulky substitution.

Boroles are reactive BC_4 heterocycles that feature a three-coordinate boron center linking a 1,3-butadiene backbone first disclosed by Eisch in his seminal report in 1969.[1] The four π-electron ring results in an anti-aromatic species high in thermodynamic energy making boroles attractive reagents for more stable species. Within the central ring, the boron center is highly Lewis acidic, the BC_4 ring can be reduced, and the diene engages in Diels–Alder reactions.[2–4] It has been demonstrated that Lewis acid–base adducts can rearrange if a reactive functionality is pendent on the Lewis base (*e.g.* imine, nitrile) to access ring expanded products.[2c] This is particularly significant as boron heterocycles are in small molecule drugs[5] and are being investigated in electronic materials.[6] Despite this interest, accessing heterocycles containing tricoordinate boron centers is challenging due to the propensity of boron reagents to react with nucleophiles to form four-coordinate species.

Boroles can be accessed through three general routes, one being the direct salt metathesis with a substituted 1,4-dilithio-1,3-butadiene and dihaloborane or organotrifluoroborate.[2d,7] Borolide dianions can undergo a two electron oxidation to the neutral boroles and the third method is transmetallation from tin or zirconium precursors.[3,8] The transmetallation route is the

most popular method due to the ease in manipulating the precursors including compatibility with non-coordinating solvents that enable the isolation of tricoordinate species.[8b]

Although boroles have been effective reagents for the preparation of ring systems of six to eight atoms,[2c,9] a major limitation has been the bulk on the boroles required to kinetically preclude dimerization (*e.g.* **A**, Fig. 1).[1,10] Boroles bearing a halide on boron (*e.g.* **B**) undergo complex decomposition at low temperatures[11] while those with organic groups dimerize *via* [4 + 2] cycloaddition with one equivalent acting as the diene and the other as the dienophile (*e.g.* $\mathbf{C_2}$).[3,12] The latter process is dictated by bulk on the carbon centers and is reminiscent of the dimerization of cyclopentadiene. In contrast to cyclopentadiene, the monomers are not isolable, however, reactivity studies suggest that the retro Diels–Alder process can be thermally induced.[3,13] Despite these dimers being known since 1985, the only studies have been heating the dimers in the presence of metal precursors to access η^5-metal complexes[14] or examining their Diels–Alder reactivity.[3,13] If dimeric boroles could be utilized as reagents for ring expansion reactions, it would circumvent the requirement of bulky substituted monomeric boroles enabling access to a diverse library of products. We herein investigate the ability of Diels–Alder dimeric boroles to serve as sources of monomers in ring expansion reactions.

A particularly appealing class of molecules are hybrid inorganic/organic analogues of benzene in which a C=C unit is replaced by boron and lone pair bearing heteroatom.[15] Pentaarylboroles have been effective in their preparation by 1,1-insertion

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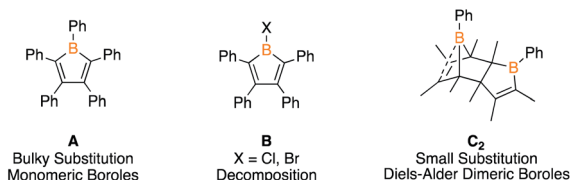
Fig. 1 Examples of boroles and a summary of their stability.

Fig. 2 Solid-state structures of **1** (left) and **2·Cr(CO)₃** (right). Hydrogen atoms are omitted for clarity and ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å) for **1**: B(1)–N(1) 1.443(4), N(1)–C(1) 1.399(4), C(1)–C(2) 1.370(4), C(2)–C(3) 1.442(5), C(3)–C(4) 1.377(5), C(4)–B(1) 1.513(4); for **2·Cr(CO)₃**: B(1)–S(1) 1.828(2), S(1)–C(1) 1.757(3), C(1)–C(2) 1.397(3), C(2)–C(3) 1.441(3), C(3)–C(4) 1.416(4), B(1)–C(4) 1.515(3), B(1)–Cr 2.388(3), S(1)–Cr 2.4367(6), C(1)–Cr 2.175(2), C(2)–Cr 2.223(3), C(3)–Cr 2.251(3), C(4)–Cr 2.273(2).
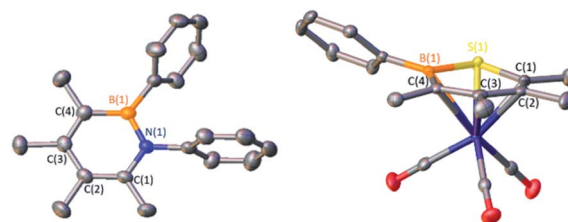
reactions but result in products with five bulky groups.[16] We envisioned that a dimeric borole, 1-phenyl-2,3,4,5-tetramethylborole dimer **C₂**, may also be an effective synthon of its monomer **C** to generate six-membered heteroaromatic targets. To target 1,2-azaborines, a 2 : 1 stoichiometric mixture of phenyl azide with dimer **C₂** in toluene was heated to 100 °C and monitored by *in situ* ¹¹B NMR spectroscopy (Scheme 1). The consumption of **C₂** was observed after 12 h by the disappearance of the peaks at −6.3 and 69.8 ppm coupled with the emergence of a new peak at 35.5 ppm, representative of 1,2-azaborine species.[16d–g] The identity of the insertion product was confirmed by a single crystal X-ray diffraction study (Fig. 2) and upon workup, the product was isolated as a yellow powder in 70% yield. ¹H NMR spectroscopy of the solid redissolved in CDCl₃ indicated a simplified methyl region with four signals integrating in equivalent ratios in contrast to eight signals for dimer **C₂**. 1,2-Azaborines are gaining attention for utility in materials and medicinal chemistry and this reaction demonstrates an efficient manner to access these heterocycles in a single step.

To determine if **C₂** is capable of acting as a source of **C** in other 1,1-insertion reactions it was reacted with excess elemental sulfur in toluene.[17] Monitoring the reaction by *in situ* ¹¹B NMR spectroscopy indicated that upon heating to 100 °C for 24 h a major peak at 49.8 ppm emerged, which lies in the range of reported 1,2-thiaborines (35.8–51.1 ppm).[15f,16c,18] Upon work-up, a yellow oil was isolated in 49% yield. The liquid state at room temperature prevented obtaining a solid state structure. Since 1,2-thiaborines are a six-π-electron aromatic system, we postulated that the π-system could coordinate to a transition metal. A suite of 1,2-azaborine metal complexes have been prepared,[19] but there is not an example of a 1,2-thiaborine complex in the literature, or any chalcogenaborine metal complexes.[15e,15f,20] Our attempts to prepare a 1,2-thiaborine chromium complex from Cr(CO)₃(CH₃CN)₃ and pentaaryl 1,2-thiaborines derived from monomeric pentaarylboroles were

unsuccessful, presumably due to the bulky substituents which has also been reported in attempts to coordinate metals to the central ring of hexaphenylbenzene.[21] To determine if the smaller 1,2-thiaborine could act as a ligand, the reaction of excess Cr(CO)₃(CH₃CN)₃ with 1,2-thiaborine (**2**) was conducted in THF at 23 °C and *in situ* monitoring by ¹¹B NMR spectroscopy revealed an upfield shift from free **2** at 49.8 ppm to 29.1 ppm with the reaction complete after 24 h (Scheme 2). The resonance is consistent with η⁶-bound 1,2-azaborine metal complexes.[19] A single ¹³C{¹H} NMR shift at 229.83 ppm was detected for the three carbonyl groups indicating chemical equivalency on the NMR timescale, attributed to rapid rotation about the BSC₄ ring. Upon work up a red solid was isolated in 76% yield and an X-ray diffraction study gratifyingly confirmed the product as the half-sandwich tricarbonylchromium complex **2·Cr(CO)₃** (Fig. 2).

The solid state structure of **2·Cr(CO)₃** confirms η⁶-coordination to chromium with a planar ring (max. deviation from planarity = 0.04 Å), although the chromium bonds to boron [Cr–B = 2.388(3) Å] and sulfur [Cr–S = 2.4367(6) Å] are longer than those to the four carbon atoms [B–C range 2.175(2)-2.273(2) Å]. The bond lengths within the 1,2-thiaborine ring of **2·Cr(CO)₃** are marginally longer in comparison to the only non-disordered uncomplexed 1,2-thiaborine, which is expected upon coordination.[16c] The carbonyl stretching frequencies are a gauge of the donor properties of aromatic ligands.[22] FT-IR spectroscopy revealed C–O stretching frequencies of 1964, 1908 and 1873 cm⁻¹ for **2·Cr(CO)₃** which are lower than those of the chromium complex with 1,2-dihydro-1-methyl-2-phenyl-1,2-azaborine (1979, 1916, 1900 cm⁻¹).[19a] This indicates that 1,2-thiaborine **2** induces more π-backbonding to the CO ligands by enriching the electron density at chromium more than the 1,2-azaborine.

Scheme 1 Reactions of borole dimer **C₂** with phenyl azide and elemental sulfur.
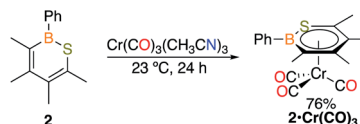
Scheme 2 Reaction of 1,2-thiaborine **2** with Cr(CH₃CN)₃(CO)₃.
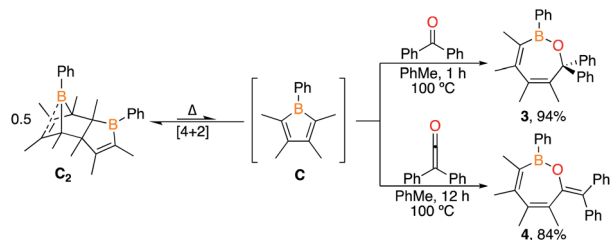
Scheme 3 Reaction of dimer C_2 with benzophenone and diphenylketene.

The resiliency of the π-coordination of the 1,2-thiaborine to chromium was investigated. No decomposition or migration to the B-phenyl group was observed at room temperature. Heating a THF-d_8 solution of $2 \cdot Cr(CO)_3$ resulted in free **2** by ^{1}H NMR spectroscopy and an insoluble grey precipitate, indicating slow decomposition of $2 \cdot Cr(CO)_3$ with no evidence of migration of the chromium center. Adding excess benzene as an extraneous π-donor into a solution of $2 \cdot Cr(CO)_3$ in THF-d_8 did not result in any reaction at room temperature. During the course of heating, *in situ* ^{1}H NMR spectroscopy revealed that $2 \cdot Cr(CO)_3$ decomposed by generating (benzene)chromium tricarbonyl, free **2**, and a similar grey precipitate. Attempts to access η^1-coordination chemistry *via* the sulfur atom in **2** were unsuccessful due to the relatively weak sulfur donor (see ESI†).

To examine the ability of borole synthon C_2 to undergo 1,2-insertions to access seven-membered rings, the 1 : 2 stoichiometric reactions of C_2 with benzophenone and diphenylketene in toluene-d_8 at room temperature were investigated. No reaction occurred at room temperature but upon heating the solutions to 100 °C (1 h for benzophenone and 12 h for diphenylketene), ^{1}H NMR spectroscopy revealed consumption of dimer C_2, corroborated by ^{11}B NMR spectroscopy with new resonances at 43.6 ppm for benzophenone and 43.2 ppm for diphenylketene (Scheme 3). Both are consistent with a three-coordinate boron bound to an oxygen.[9e,16b] Single crystals grown for X-ray diffraction studies identified the products as the seven-membered BOC_5 rings **3** and **4** in which the 1,2-dipolar CO unit is inserted into the endocyclic B–C bond of the monomeric borole (Fig. 3). Both species adopt boat-like conformations.
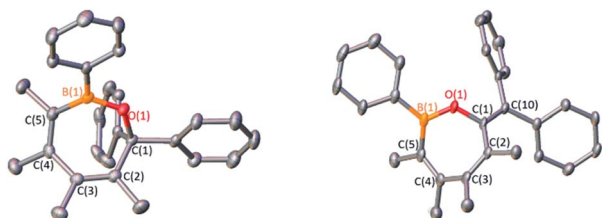

Fig. 3 (a) Solid-state structure of **3** (left) and **4** (right) hydrogen atoms are omitted for clarity and ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å) for **3**: B(1)–O(1) 1.366(5), O(1)–C(1) 1.452(5), C(1)–C(2) 1.542(5), C(2)–C(3) 1.348(5), C(3)–C(4) 1.486(5), C(4)–C(5) 1.347(5), C(5)–B(1) 1.563(5); for **4**: B(1)–O(1) 1.368(2), O(1)–C(1) 1.392(3), C(1)–C(2) 1.484(2), C(2)–C(3) 1.346(2), C(3)–C(4) 1.489(2), C(4)–C(5) 1.353(3), C(5)–B(1) 1.558(3), C(1)–C(10) 1.345(3).

1,1-Diphenylethylene oxide reacts with pentaphenylborole to generate a rare eight-membered boron heterocycle from the insertion of the C_2O unit.[9a] In the reaction of two equivalents of 1,1-diphenylethylene oxide with C_2 at 100 °C in toluene, *in situ* ^{11}B NMR spectroscopy revealed the complete consumption of C_2 after 14 h and a new signal at 59.4 ppm, differing from the eight-membered boracycle in the corresponding reaction with pentaphenylborole (46.3 ppm).[9a] Single crystal X-ray diffraction identified the product as a bicyclic compound composed of fused BC_4 and BOC_3 rings (**5**, Fig. 4) with a boron and carbon atom at the ring junctions. The boron center is essentially trigonal planar with the sum of angles about boron being 358.0(6)°. The presence of the phenyl group on the carbon adjacent to boron, C(6), suggests a rearrangement occurred. The B(1)–O(1) bond [1.353(3) Å] is consistent with a B–O single bond.[9a,23] The carbon–carbon bond lengths in the BC_4 ring derived from the borole alternate [C(3)–C(4) = 1.530(3), C(4)–C(5) = 1.342(4), C(5)–C(6) = 1.546(3) Å] which is consistent with 1-bora-cyclopent-3-ene ring systems.[9d,24] BOC_3 rings with a fused ring have been gaining attention with the effective drugs Kerydin® (onychomycosis) and Eucrisa® (eczema) containing such bicyclic systems.[5d,5e]

A proposed mechanism can be drawn that proceeds through an initial Lewis acid–base adduct **Int1** (Scheme 4). The epoxide ring opens *via* the oxygen–carbon bond of the diphenyl carbon to furnish the resonance stabilized carbocation **Int2**. The diene attacks the carbocation to forge the bicyclic framework and the
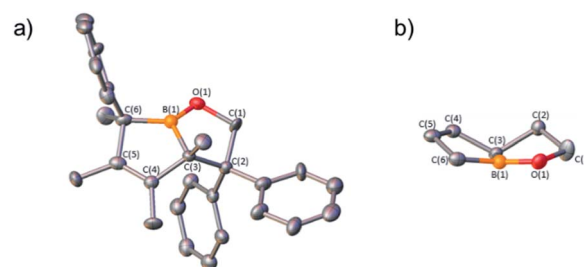

Fig. 4 (a) Solid-state structure of **5**. Hydrogen atoms are omitted for clarity and ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å): B(1)–O(1) 1.353(3), O(1)–C(1) 1.460(3), C(1)–C(2) 1.567(3), C(2)–C(3) 1.609(3), C(3)–C(4) 1.530(3), C(4)–C(5) 1.342(4), C(5)–C(6) 1.546(3), C(6)–B(1) 1.582(4), B(1)–C(3) 1.565(4); (b) View of the fused bicyclic core along the boron plane.
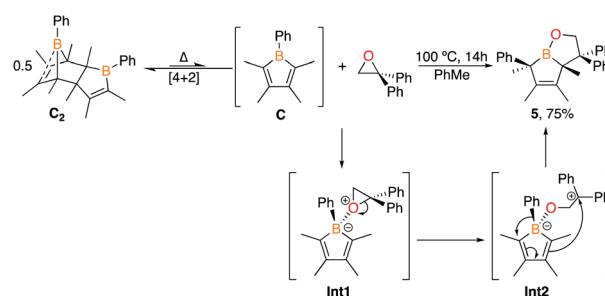
Scheme 4 Reaction of 1,1-diphenylethylene oxide with C_2 and proposed mechanism.

Scheme 5 Synthesis of borole dimers D_2 and E_2.

Fig. 6 (a) Solid–state structure of **6** (left) and **7** (right) hydrogen atoms are omitted for clarity and ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å) for **6**: B(1)−O(1) 1.368(2), O(1)−C(1) 1.398(2), C(1)−C(2) 1.489(2), C(2)−C(3) 1.351(2), C(3)−C(4) 1.500(2), C(4)−C(5) 1.351(2), C(5)−B(1) 1.561(1), C(1)−C(10) 1.345(2); for **7**: B(1)−O(1) 1.372(2), O(1)−C(1) 1.398(2), C(1)−C(2) 1.483(2), C(2)−C(3) 1.341(2), C(3)−C(4) 1.482(2), C(4)−C(5) 1.355(2), C(5)−B(1) 1.563(2), C(1)−C(10) 1.340(2).

phenyl group migrates to the adjacent carbon to give **5**. The migration occurs on the same face rationalizing the anti-stereochemistry of the methyl groups observed in the solid state structure. The centrosymmetric $P2_1/n$ space group indicates that both enantiomers are generated. This differs from the pentaphenylborole product in which the endocyclic B−C bond of the borole attacks the carbocation in **Int2** to generate an eight-membered ring.[9a,25] Although this bicyclic framework has not been observed previously in a product from a borole reaction, it has been proposed as an intermediate in insertion reactions and may provide insight into other reaction mechanisms.[16e,26]

To determine if other Diels–Alder dimeric boroles are capable of generating insertion products, two other Diels–Alder borole dimers, 1-phenyl-2,3,4,5-tetraethylborole dimer (**D_2**) and 1-biphenyl-2,3,4,5-tetramethylborole dimer (**E_2**), were prepared *via* transmetallation of zirconium precursors (Scheme 5). The identity of the tetraethyl dimer **D_2** was established by obtaining

an X-ray diffraction structure that is similar to **C_2** with the notable feature of a C=C bond coordinating to the bridgehead boron (Fig. 5). A ^{13}C DEPT experiment showed eight distinct resonances for both methylene and methyl groups indicating the presence of eight chemically inequivalent ethyl groups, consistent with the structure. The identity of 1-biphenyl dimer **E_2** was confirmed by multinuclear NMR spectroscopy and elemental analysis. The anticipated eight methyl signals were observed for **E_2** by ^1H NMR and ^{13}C NMR spectroscopy. Obtaining ^{11}B NMR spectra for **D_2** and **E_2** revealed two resonances, one for the tricoordinate boron center and another for the pseudo-five coordinate bridgehead boron akin to **C_2** (**D_2** = 68.5, −2.7 ppm; **E_2** = 70.4–5.8 ppm; *cf*. **C_2** = 69.8, −6.3 ppm).

The 1,2-insertion reactions of borole dimers **D_2** and **E_2** with two equivalents of diphenylketene were investigated (Scheme 6). Upon heating the toluene-d_8 solutions to 100 °C (1 h for **D_2** and 8 h for **E_2**), ^1H and ^{11}B NMR spectroscopy revealed the consumption of the borole dimers. The ^{11}B signals at 43.7 and 44.9 ppm for the reactions with **D_2** and **E_2**, respectively, are reminiscent of **4** (43.2 ppm). The reactions were scaled up and X-ray diffraction studies confirmed the products from **D_2** and **E_2** as the seven-membered BOC_5 rings **6** and **7**, respectively (Fig. 6). The experiments confirm that insertion reactions are effective with other dimeric boroles although the reaction times differ. The reactions with the dimers featuring methyl groups on carbon were completed in 12 h (**C_2**) and 8 h (**E_2**) while the reaction with the dimer bearing ethyl groups on the carbon centers (**D_2**) was complete within an hour.[17]
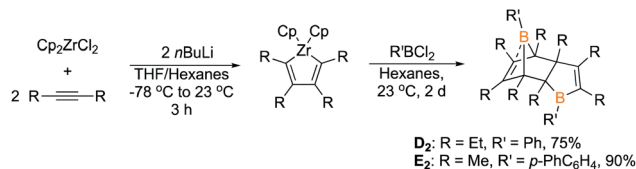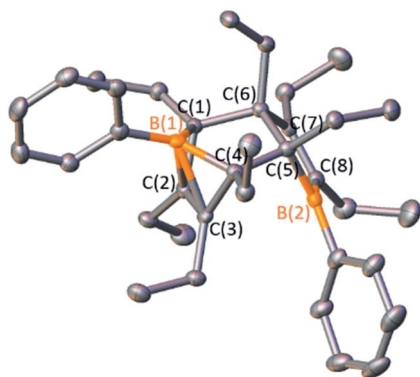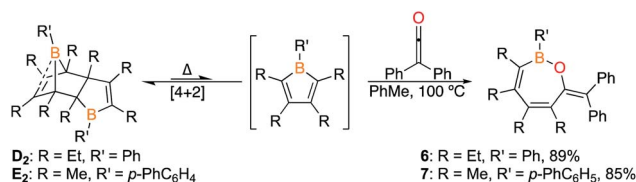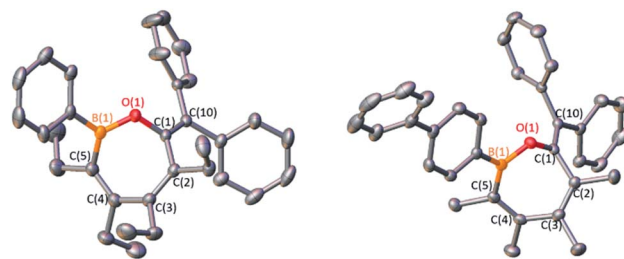

Fig. 5 Solid-state structure of D_2. Hydrogen atoms are omitted for clarity and ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å) for D_2: B(1)−C(1) 1.619(4), B(1)−C(4) 1.611(4), C(1)−C(2) 1.514(4), C(2)−C(3) 1.380(4), C(3)−C(4) 1.524(4), C(4)−C(5) 1.585(3), C(5)−C(6) 1.573(4), C(6)−C(7) 1.527(4), C(7)−C(8) 1.357(4), B(2)−C(5) 1.599(5), B(2)−C(8) 1.540(4).

Conclusions

In conclusion, we report the first examples of ring expansion reactions with borole dimers as precursors, specifically the 1,1-insertion with elemental sulfur and an azide as well as the 1,2-insertion with benzophenone and diphenylketene to access six- and seven-membered boracycles, respectively. The sulfur insertion product, a 1,2-thiaborine, could be coordinated to chromium in an η^6 fashion. It is notable that this complex could not be accessed from the peraryl-substituted monomeric

Scheme 6 Reaction of diphenylketene with D_2 and E_2. Reaction times: 1 h for **6** and 8 h for **7**.

borole products. An attempt to access an eight-membered ring was unsuccessful with 1,1-diphenylethylene oxide, instead forging a new BOC_3 ring that is a component in effective pharmacophores. The reactions all required heat to crack the dimer but were all complete within 24 h at 100 °C. Dimers with different substitution on boron and carbon are also capable of insertion reactions, exemplified in the reactions with diphenylketene. These studies solidify that bottleable monomeric boroles are not essential for insertion chemistry and that dimers have great potential to act as borole synthons to furnish a wealth of heterocycles with less restrictions on the substitution.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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