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## ARTICLE

## Borane-induced Ring Closure Reaction of Oligomethylene-linked Bis-allenes

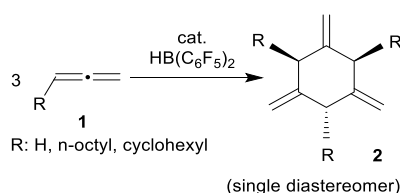
Xin Tao,<sup>a</sup> Karel Škoch,<sup>a</sup> Constantin G. Daniliuc,<sup>a</sup> Gerald Kehr,<sup>a</sup> Gerhard Erker<sup>\*a</sup>Received 00th January 20xx,  
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The trimethylene-linked bis-allene **3a** reacts with Piers' borane [HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] by a hydroboration/allylboration sequence to generate the cyclization product **5a**. Its pyridine adduct was isolated and characterized by X-ray diffraction. Compound **5a** undergoes a typical frustrated Lewis pair 1,2-P/B alkene addition reaction with PPh<sub>3</sub> to give the heterobicyclic bridged olefinic zwitterionic product **9a**. The tetramethylene-linked bis-allene **3b** and its phenylene annulated analogue **3c** react with HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> to give the analogous seven-membered ring products **5b,c** under mild conditions. The cyclization product **5a** undergoes a series of sequential allylboration reactions with two equivalents of allene followed by ring-closure to give the four-component coupling product **12a**. It undergoes FLP addition to an exo-methylene group upon treatment with PPh<sub>3</sub>. Compound **12a** is oxidatively converted to the boron-free alcohol.

## Introduction

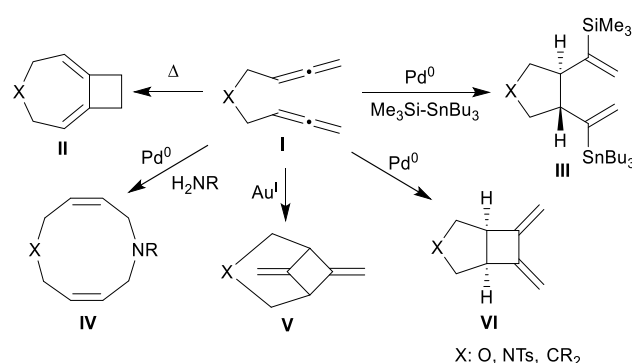
Allenes are important building blocks in organic synthesis.<sup>1</sup> They show interesting and useful stereochemical properties.<sup>2</sup> We had recently shown that the borane [HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>3</sup> catalyses the cyclotrimerization of allene as well as a small series of mono-alkyl-substituted allenes **1** to selectively give the respective 1,3,5-trimethylene cyclohexanes **2** as single isomers under metal-free conditions (Scheme 1).<sup>1,4,5</sup>



**Scheme 1.** HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-catalyzed cyclotrimerization of alkyl-substituted allenes.

There is a rich cyclization chemistry of bis-allenes reported in the literature (see Chart 1). Systems **I** (mostly with X = NTs, less frequently CR<sub>2</sub> or O) were reported to rearrange to **II** thermally induced.<sup>6a</sup> They added R<sub>3</sub>Si-SnBu<sub>3</sub>/ or -GeR<sub>3</sub> reagents Pd(0) catalysed or radical induced to give the products **III**.<sup>6b,c</sup> With H<sub>2</sub>NR nucleophiles cyclization to medium-sized rings (e.g. **IV**) was reported.<sup>6d</sup> The products **V** and **VI** of internal [2+2] cycloaddition were formed under the influence of Au(I)<sup>6e</sup> or Pd(0)<sup>6a</sup> catalysis, respectively. In some cases coupling between two bis-allenes occurred to give hetero-steroidal

frameworks.<sup>6f,g</sup> It should be noted that the vast majority of these reaction is metal catalysed.



**Chart 1.** Examples of cyclization reactions of bis-allenes.

This posed the question what the favoured reaction pathway would be if we treated e.g. oligomethylene-linked bis-allenes with HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>,<sup>7</sup> i.e. under metal-free conditions. We have now performed these reactions starting from two examples of that bis-allene family. It turned out that a different cyclization type prevailed under these conditions. The outcome of these reactions will be presented and discussed below.

## Results and discussion

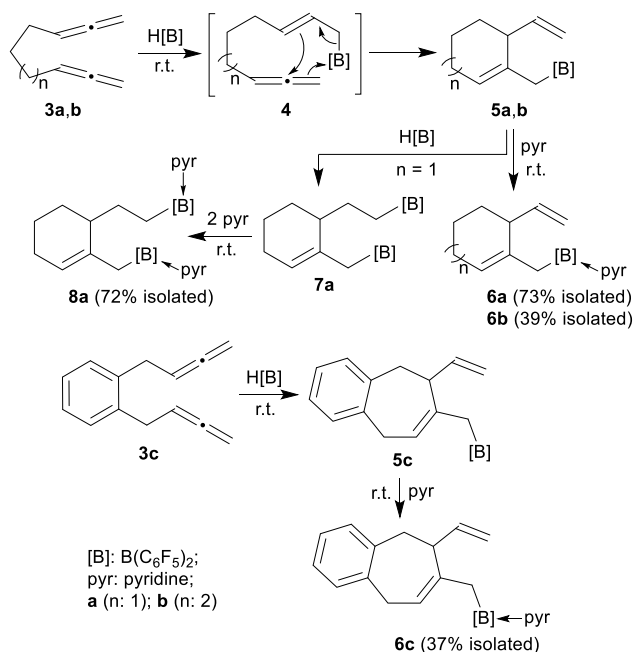
## Borane-induced ring-closure reaction of the bis-allenes

The allenes **3a** and **3b** (Scheme 2) were prepared by a variant of the Crabbé reaction as described by Ma et al.<sup>8</sup> Copper (I) induced treatment of 1,6-heptadiyne with para-formaldehyde as C<sub>1</sub>-building block and dicyclohexylamine gave the trimethylene-linked bis-allene **3a**<sup>6h</sup> (40% isolated). The analogous reaction starting from 1,7-octadiyne gave the

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tetramethylene-linked bis-allene **3b**<sup>6i</sup> (63% isolated, see the ESI for details). The phenylene containing bis-allene **3c** was synthesised analogously.

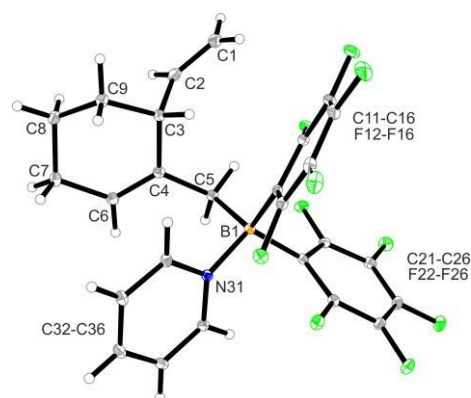


**Scheme 2.**  $\text{HB}(\text{C}_6\text{F}_5)_2$ -induced ring closure of the bis-allenes **3**.

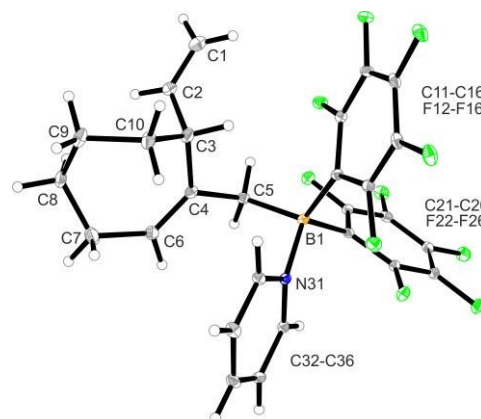
We reacted compound **3a** with one molar equivalent of Piers' borane  $[\text{HB}(\text{C}_6\text{F}_5)_2]$ . The rapid reaction (r.t., minutes, in  $\text{CD}_2\text{Cl}_2$ ) gave the cyclized product **5a**. It was not isolated but characterized by spectroscopy [ $^1\text{H}$  NMR:  $\delta$  5.55 (olefinic  $=\text{CH}-$ ) ( $\text{C}_6\text{-H}$ , see Figure 1 for the unsystematic atom numbering scheme),  $\delta$  5.52, 5.03,  $-\text{CH}=\text{CH}_2$  substituent);  $^{11}\text{B}$  NMR:  $\delta$  69.3;  $\Delta\delta^{19}\text{F}_{\text{m,p}} = 13.1$  ppm]. Compound **5a** was then generated *in situ* on a preparative scale and trapped by subsequent addition of pyridine. We isolated the pyridine adduct **6a** as a white crystalline solid in 73% yield. The X-ray crystal structure analysis of compound **6a** showed the newly formed cyclohexene core that has a vinyl group attached in the allylic position and it bears the  $-\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2(\text{pyridine})$  substituent adjacent to it at the olefinic ring carbon atom  $\text{C}_4$  (Figure 1). In solution ( $\text{CD}_2\text{Cl}_2$ ) we monitored the typical  $^1\text{H}/^{13}\text{C}$  NMR features of the vinyl group at carbon atom  $\text{C}_3$  and the central doubly substituted cyclohexene core. The  $^1\text{H}$  NMR features of the coordinated pyridine moiety show up at  $\delta$  8.67, 8.11 and 7.65 ( $^{11}\text{B}$ :  $\delta$   $-0.6$ ). Due to the chiral centre (ring carbon  $\text{C}_3$ ) the  $\text{C}_6\text{F}_5$  groups at boron are diastereotopic and give rise to a 1:1 set of the respective o,p,m- $\text{C}_6\text{F}_5$   $^{19}\text{F}$  NMR signals.

We assume that the reaction started with hydroboration of the terminal  $=\text{CH}_2$  unit of one allenyl group by the  $\text{HB}(\text{C}_6\text{F}_5)_2$  reagent. This resulted in the formation of the functionalized borane **4** which contained a reactive allylborane unit opposite to a reactive allene unit. This situation was set up for an internal allylboronation reaction of the allene, which directly opened a pathway to the observed cyclization product **5a**. Addition of the pyridine Lewis base to the strongly Lewis acidic  $\text{B}(\text{C}_6\text{F}_5)_2$  group gave **6a** (Scheme 2).

We reacted the tetramethylene-linked bis-allene **4b** with  $\text{HB}(\text{C}_6\text{F}_5)_2$  and found that the seven-membered cyclization product **5b** was formed analogously. Treatment of the *in situ* generated borane **5b** with pyridine gave the respective pyridine adduct **6b**, which we isolated crystalline in 39% yield. Compounds **5b** and **6b** were characterized by spectroscopy (see the ESI for details); product **6b** was characterized by C,H,N elemental analysis and by an X-ray crystal structure analysis (Figure 2). It shows the newly formed seven-membered ring in a typical cycloheptene boat-like conformation.<sup>9</sup> The  $-\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$  moiety is attached at the  $\text{sp}^2$ -carbon atom  $\text{C}_4$  (the boron atom bears a pair of  $\text{C}_6\text{F}_5$  groups and the coordinated pyridine ligand in a pseudo-tetrahedral geometry). The vinyl substituent bonded to carbon atom  $\text{C}_3$ .



**Figure 1.** A view of the molecular structure of the borane pyridine adduct **6a**. Selected bond lengths (Å) and angles (°): B1-N31 1.613(3), B1-C5 1.651(3), C1-C2 1.322(4), C4-C6 1.337(3), B1-C5-C4 117.7(2).



**Figure 2.** Molecular structure of compound **6b**. Selected bond lengths (Å) and angles (°): B1-N31 1.627(5), B1-C5 1.645(6), C1-C2 1.285(8), C4-C6 1.340(6), B1-C5-C4 119.9(3).

The reaction of the bis-allene **3a** responded to the stoichiometry of the  $\text{HB}(\text{C}_6\text{F}_5)_2$  reagent since the primary ring-closure product **5a** contained a reactive pendant vinyl group. Therefore, the reaction of **3a** with two molar equivalents of Piers' borane gave the bis-borane product **7a**. Its  $^{11}\text{B}$  NMR spectrum showed two signals ( $\delta$  73.3 and  $\delta$  69.4) that are attributed to the pair of Lewis acidic planar-tricoordinate boron centres. Consequently, we observed two sets of  $^{19}\text{F}$  NMR resonances of the pairs of the  $\text{C}_6\text{F}_5$  substituents at the two  $\text{B}(\text{C}_6\text{F}_5)_2$  groups. The *in situ* generated bis-borane **7a** was then treated with two molar equivalents of pyridine to give the



respective double pyridine adduct **8a** (isolated as a white solid in 72% yield). It was characterized by C, H, N elemental analysis, by X-ray diffraction (the structure is shown in the ESI) and by spectroscopy. Due to the chiral centre (C3) the pair of  $\text{C}_6\text{F}_5$  groups at each  $\text{B}(\text{C}_6\text{F}_5)_2$ (pyridine) moiety are diastereotopic and, consequently, we observed four sets of *o,m,p*- $\text{C}_6\text{F}_5$   $^{19}\text{F}$  NMR signals of compound **8a**. We observed two sets of pyridine  $^1\text{H}/^{13}\text{C}$  NMR resonances and located the single olefinic  $^1\text{H}$  NMR signal (C6-H) at  $\delta$  4.35 (t,  $J_{\text{HH}} = 3.3$  Hz, 1H).

We performed the reaction of phenylene bridged bis-allene system **3c** in a similar way. The reaction of **3c** with one molar equiv. of  $\text{HB}(\text{C}_6\text{F}_5)_2$  was carried out in  $\text{CD}_2\text{Cl}_2$  at r.t. and the almost instantaneously *in situ* generated product was characterized by NMR spectroscopy [ $^1\text{H}$ :  $\delta$  5.48/5.13/5.08 (vinyl substituent), 5.72 (ring-CH=),  $^{11}\text{B}$ :  $\delta$  71.7,  $^{19}\text{F}$ :  $\Delta\delta^{19}\text{F}_{\text{m,p}} = 13.2$ ]. The latter heteroatom NMR signals are typical for the presence of strongly Lewis acidic tricoordinate boron with this substituent pattern. Compound **5c** was treated with pyridine and the respective pyridine/borane Lewis adduct **6c** was isolated in 37% yield after workup involving pentane extraction. The NMR spectra now show a  $^{11}\text{B}$  NMR resonance in the typical range of tetracoordinate boron ( $\delta$  -0.5) and the  $\text{C}_6\text{F}_5$  substituents at boron are diastereotopic (see the ESI for further details).

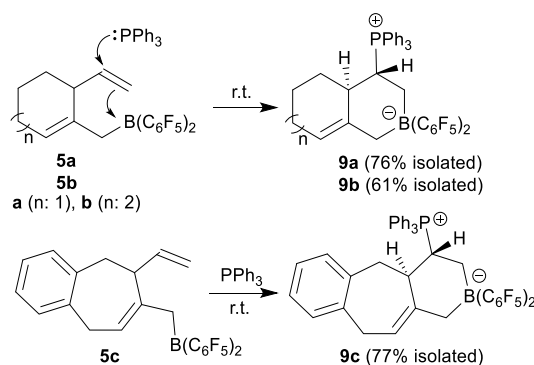
### Subsequent FLP ring-closure reactions

The compounds **5** each contain a sterically encumbered, strongly Lewis acidic borane functionality and in its vicinity an accessible reactive vinyl group. We used this for carrying out a typical frustrated Lewis pair<sup>10</sup> reaction, namely a 1,2-borane/phosphane addition to the  $\text{C}=\text{C}$  double bond.<sup>11</sup>

We reacted the *in situ* generated cyclization product **5a** with triphenylphosphane at room temperature. The reaction was practically instantaneous under these typical conditions and we isolated the P/B addition product **9a** to the internal vinyl group as a white powder in 76% yield (Scheme 3). Single crystals of compound **9a** that were suited for the X-ray crystal structure analysis were obtained at room temperature from a solution in dichloromethane that was layered with pentane. It showed that 1,2-phosphane/borane addition to the vinyl substituent had occurred. The internal  $-\text{B}(\text{C}_6\text{F}_5)_2$  Lewis acid had been added to the  $=\text{CH}_2$  terminus of the alkene and the external  $\text{PPh}_3$  nucleophile to the  $-\text{CH}=\text{C}$  carbon atom. The resulting zwitterionic heterobicyclo[4,4,0]decene type system features a bridgehead  $\text{C}=\text{C}$  double bond (C4–C6) and a borate system inside the heterocyclic six-membered ring that was formed in the FLP addition reaction. Consequently, the  $-\text{PPh}_3^+$  -phosphonium substituent is found attached at the same ring at carbon atom C2. We have isolated a single diastereoisomer of **9a** from this reaction; it features the hydrogen atoms at carbon atoms C2 and C3 oriented *trans* to each other at the heterobicyclic framework (Figure 3). In solution compound **9a** shows the NMR heteronuclear resonances at  $\delta$  -12.3 ( $^{11}\text{B}$ ) and  $\delta$  27.9 ( $^{31}\text{P}$ ). A diastereotopic pair of  $\text{C}_6\text{F}_5$  substituents is bonded at boron, giving rise to two separate sets of  $^{19}\text{F}$  NMR resonances. The  $^1\text{H}$

NMR [P]–CH– signal is found at  $\delta$  3.64 and the single olefinic  $=\text{CH}$ – signal at  $\delta$  5.17.

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Scheme 3. FLP reaction of the boranes **5** with  $\text{PPh}_3$ .

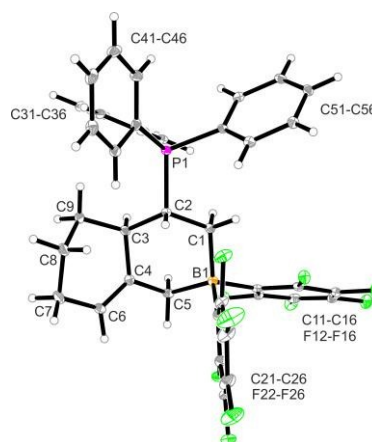


Figure 3. Molecular structure of the P/B FLP addition product **9a**. Selected bond lengths (Å) and angles (°): B1–C1 1.647(2), B1–C5 1.640(2), P1–C2 1.856(2), C1–C2 1.549(2), C4–C6 1.333(2), C1–B1–C5 105.7(1), B1–C1–C2 114.6(1), C1–C2–C3 112.4(1), C2–C3–C4 109.2(1), C3–C4–C5 114.9(1), C4–C5–B1 108.9(1), P1–C2–C1 109.3(1), P1–C2–C3 111.9(1), P1–C2–C3–C4 174.9(1), P1–C2–C1–B1 175.9(1).

The seven-membered ring compounds **5b** and **5c** react analogously with  $\text{PPh}_3$ . Compound **5b** was *in situ* generated and triphenylphosphane was added. We isolated the product **9b** in 61% yield by crystallization. It was characterized by C, H, elemental analysis, by spectroscopy and by X-ray diffraction. The molecular structure is similar to that of **9a**. It also contains a *trans*-relationship of the C3-H and C2-H hydrogen atoms of the heterobicyclic ring system. The hetero-NMR signals occur at  $\delta$  -13.3 ( $^{11}\text{B}$ ) and  $\delta$  30.5 ( $^{31}\text{P}$ ). Compound **9c** was prepared analogously from **5c** (see Scheme 3). It was isolated as a white solid in 77% yield after workup and characterized by NMR spectroscopy and by an X-ray crystal structure analysis. For further details of the characterization of the compounds **9b** and **9c** including their depicted molecular structures see the ESI.

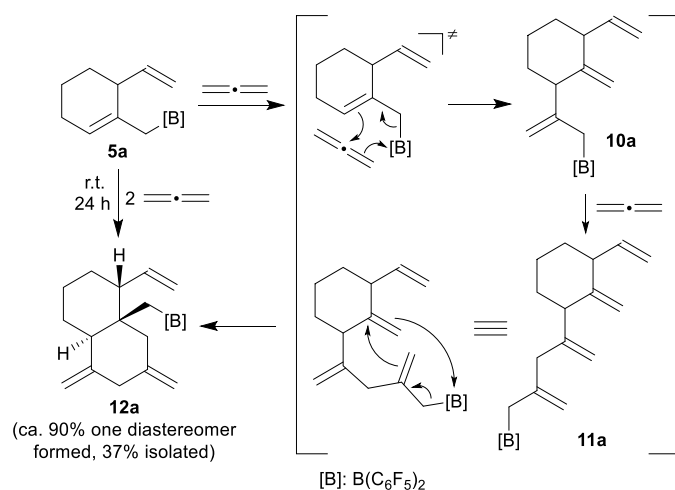
### Subsequent cyclooligomerization reaction with allene

Internal allene allylboration<sup>12</sup> represents the important step of the ring-closure reaction sequence starting from **3** to form the products **5**. The compounds **5** themselves each contain an allylboration functionality which might show the respective reactivity towards added allene reagents. Therefore, we exposed the cyclization product **5a** to an excess of the parent

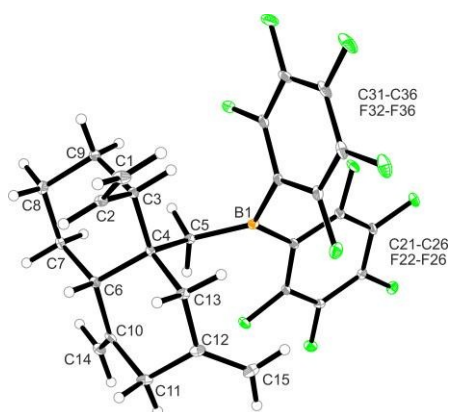




allene  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ . An NMR experiment revealed a close to complete conversion to the new product **12a** within 24 h at room temperature. We carried out this reaction on a preparative scale under analogous conditions. Workup involving crystallization from pentane at  $-35^\circ\text{C}$  (3 d) gave the crystalline product **12a**, which we isolated in 37% yield. Compound **12a** was characterized by C, H elemental analysis, by spectroscopy and by an X-ray crystal structure analysis. This showed (Figure 4) that the endocyclic allylborane moiety of the starting material **5a** had reacted with two molar equivalents of  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$  to give the functionalized decalin derivative **12a**. Apparently, compound **5a** had undergone an allylboration reaction with allene to generate the intermediate **10a**. This itself represents an "elongated" allylborane system, that subsequently took up another allene equivalent to give **11a**. The intermediate **11a** could in principle have reacted with further allene, but instead its allylborane "found" the remaining exo-methylene group at the six-membered core with which it underwent a favoured intramolecular allylboration reaction<sup>4</sup> to directly give the observed product **12a** (Scheme 4).



**Scheme 4.** Formation of compound **12a** and allene by sequential allylboration reactions.



**Figure 4.** Molecular structure of compound **12a**. Selected bond lengths (Å) and angles (°): B1-C5 1.554(3), C1-C2 1.313(3), C4-C5 1.557(3), C4-C6 1.566(3), C10-C14 1.324(3), C12-C15 1.324(3), B1-C5-C4 123.2(2), C5-C4-C6 109.0(2).

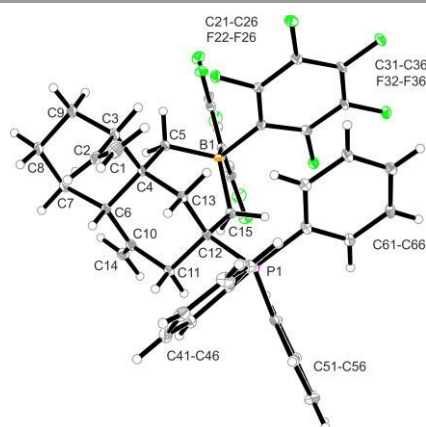
The X-ray crystal structure analysis of compound **12a** shows the newly formed *trans*-decalin framework that was formed by the

consecutive C-C coupling between **5a** and two molar equivalents of allene. The ring carbon atom C3 bears the remaining vinyl substituent; carbon atoms C10 and C12 are both part of the pair of exo-methylene groups 1,3-positioned in the second ring. The  $-\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$  group is attached at the bridgehead carbon (C4 in Figure 4).

In solution ( $\text{CD}_2\text{Cl}_2$ ) compound **12a** shows the typical NMR features of the vinyl substituent. The pair of  $=\text{CH}_2$  exo-methylene groups shows a total of four  $^1\text{H}$  NMR resonances ( $\delta$  4.85/4.61 and  $\delta$  4.68/4.42). The  $-\text{CH}_2[\text{B}]$  substituent shows the  $^1\text{H}$  NMR signals of a pair of diastereotopic hydrogen atoms (AB system at  $\delta$  2.30/2.15;  $^{13}\text{C}$ :  $\delta$  36.7). The corresponding  $^{11}\text{B}$  NMR feature is at  $\delta$  76.4, i.e. in a typical range of a strongly Lewis acidic tri-coordinated boron atom in this substituent situation.<sup>13</sup> Consequently, we observed three  $^{19}\text{F}$  NMR signals of the pair of the  $\text{C}_6\text{F}_5$  substituents at boron with a large  $\Delta\delta^{19}\text{F}_{\text{m,p}} = 11.5$  ppm chemical shift separation.

#### Some typical reactions of the borane **12a**

Compound **12a** is a reactive borane and it contains C=C double bond functionalities. Therefore, it should be suitable to undergo typical FLP addition to one of the olefinic units in the presence of an external phosphane nucleophile.<sup>11</sup> We, consequently, reacted the *in situ* generated borane **12a** with triphenylphosphane in dichloromethane. The reaction with  $\text{PPh}_3$  was instantaneous. The volatiles were removed and the residue was washed with pentane to give the P/B addition product **13a**, which we isolated as a white solid in 56% yield (see Scheme 5). Compound **13a** was characterized by C, H-elemental analysis, by spectroscopy and by X-ray diffraction (Figure 5). It showed that a P/B FLP addition had taken place at the proximal  $\text{C}=\text{CH}_2$  moiety (C12=C15 in compound **12a**, see Figure 4) by using the adjacent pendent internal borane and the external phosphane. Compound **13a** is the isomer that was formed by borane addition to the  $\text{C}=\text{CH}_2$  terminus and, consequently, phosphane addition to the  $\text{sp}^2$ -ring carbon atom. This resulted in the formation of a heterocyclic six-membered ring-system that had become 1,3-attached at the "lower" six-membered decalin ring of compound **12a**. The phosphonium  $\text{PPh}_3^+$  moiety is found attached at the new bridgehead atom C12 (Figure 5).

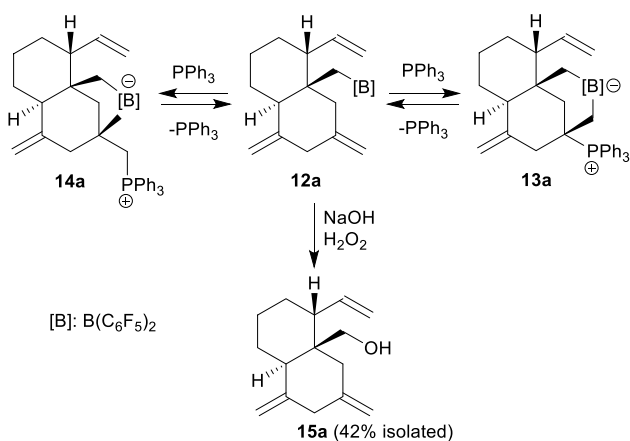


**Figure 5.** A view of the P/B FLP alkene addition product **13a**. Selected bond lengths (Å) and angles (°): B1-C5 1.640(6), B1-C15 1.667(6), P1-C12 1.858(4), C1-C2 1.302(6), C4-C6 1.565(5), C10-C14 1.328(6), C12-C15 1.555(5), C5-B1-C15 110.3(3), C12-C15-B1 114.3(3), P1-C12-C15-B1 -129.8(3).

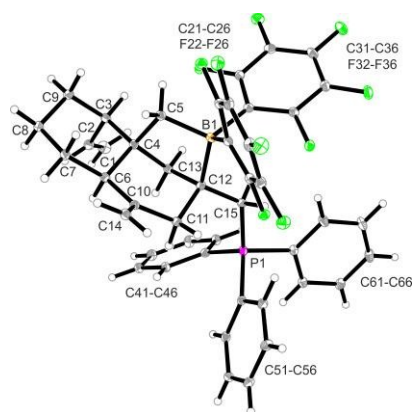


Compound **13a** shows a typical borate  $^{11}\text{B}$  NMR resonance at  $\delta -15.1$  in solution ( $\text{CD}_2\text{Cl}_2$ , 273 K) and a phosphonium  $^{31}\text{P}$  NMR signal at  $\delta 31.1$ . It shows the  $^{19}\text{F}$  NMR features of a pair of diastereotopic  $\text{C}_6\text{F}_5$  groups at the boron atom (for further details of the NMR characterization of compound **13a** see the ESI).

Compound **13a** is the P/B FLP addition product that is formed under kinetic control. When we stored the  $\text{CD}_2\text{Cl}_2$  solution of compound **13a** for 7 days at room temperature the resulting NMR spectra showed the formation of an equilibrium mixture of **13a** (ca. 20 mol%), the starting material **12a** (plus  $\text{PPh}_3$ , ca. 8 mol%) and the new compound **14a** (65 mol%) (plus some minor contaminants). The major product **14a**, apparently formed under thermodynamic control, was prepared similarly on a preparative scale (24 h, r.t.,  $\text{CH}_2\text{Cl}_2$  layered with pentane) and crystallized from the mixture. Crystalline compound **14a** was isolated in 60% yield and the product was characterized by C, H-elemental analysis, by spectroscopy and by X-ray diffraction.



**Scheme 5.** Reaction of compound **12a** with  $\text{PPh}_3$  and oxidative replacement of the boryl group.



**Figure 6.** A projection of the molecular structure of compound **14a**. Selected bond lengths (Å) and angles (°): B1–C5 1.657(4), B1–C12 1.695(3), P1–C15 1.823(2), C1–C2 1.301(13), C4–C6 1.556(3), C10–C14 1.325(4), C12–C15 1.540(3), C5–B1–C12 99.9(2), C12–C15–B1 112.1(2), B1–C12–C15–P1 179.1(2).

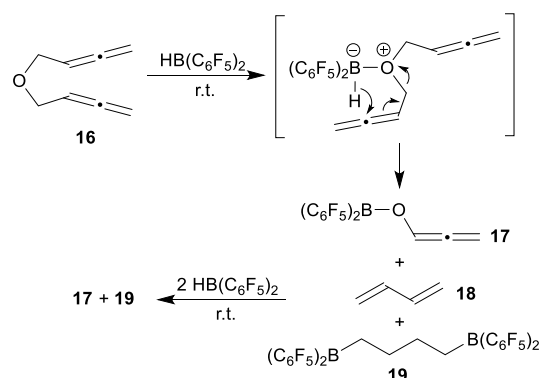
The X-ray crystal structure analysis of **14a** shows the presence of five-membered boratacycle that is 1,3-annulated to the “lower” six-membered ring of the *trans*-decalin framework. It was apparently formed by a 1,2-P/B FLP addition to the  $\text{C12}=\text{C15}$  carbon-carbon double bond of the starting material

**12a**, similar as we had seen it in the formation of its isomer **13a**, only that in this case  $\text{PPh}_3$  addition had taken place at the  $-\text{CH}_2$  terminus of the exo-methylene group concurrent with borane addition to its adjacent doubly substituted  $\text{sp}^2$ -carbon atom. The structure of the resulting P/B zwitterion **14a** is depicted in Figure 6.

The  $^1\text{H}$  NMR spectrum of compound **14a** (in  $\text{CD}_2\text{Cl}_2$ , at 299 K) shows the P-coupled system of the exocyclic  $-\text{CH}_2-[\text{P}]$  moiety at  $\delta 4.18/2.70$  and the resonances of the endocyclic  $-\text{CH}_2-[\text{B}]$  group at  $\delta 1.32/0.35$ . The heteroatom NMR signals occur at  $\delta -6.8$  ( $^{11}\text{B}$ ) and 19.9 ( $^{31}\text{P}$ ), respectively and we observed two sets of  $^{19}\text{F}$  NMR signals of the pair of diastereotopic  $\text{C}_6\text{F}_5$  groups at boron (for further details see the ESI).

We eventually converted the borane-induced multi-component cyclization product **12a** to a boron-free derivative.<sup>14</sup> This was carried out in the usual way of oxidative deborylation as it is done in the conventional hydroboration chemistry.<sup>15</sup> Treatment of the strongly electrophilic  $-\text{B}(\text{C}_6\text{F}_5)_2$  borane **12a** with  $\text{NaOH}/\text{H}_2\text{O}_2$  gave the alcohol **15a** that we isolated as a white solid in 42% yield after workup (see the ESI for its characterization by NMR spectroscopy).

We briefly investigated the reaction of the bis-allenic ether **16**<sup>c,h,j</sup> with  $\text{HB}(\text{C}_6\text{F}_5)_2$ . The reaction was carried out in  $\text{CD}_2\text{Cl}_2$  solution at r.t. The products of the reaction were not isolated but directly identified in situ generated from the solution. We subsequently added a total of three molar equivalents of  $\text{HB}(\text{C}_6\text{F}_5)_2$  to eventually achieve a complete conversion of compound **16** with a clean product formation. The NMR analysis (for details see the ESI) revealed that the by far predominant reaction was ether cleavage. This gave the  $(\text{C}_6\text{F}_5)_2\text{B}-\text{O}-\text{CH}_2-\text{CH}=\text{C}=\text{CH}_2$  cleavage product **17** (see Scheme 6) and butadiene (**18**) as primary products. The latter was then subsequently converted by added  $\text{HB}(\text{C}_6\text{F}_5)_2$  to the bis-hydroboration product **19**. The boryl ether **17** also was not stable under the reaction conditions, probably due to subsequent ether cleavage with additional  $\text{HB}(\text{C}_6\text{F}_5)_2$  (see the ESI for details). We also investigated briefly the reaction of the respective bis-allenic N-tosyl amine with  $\text{HB}(\text{C}_6\text{F}_5)_2$ , but that gave a complicated mixture of as yet unidentified products.



**Scheme 6.** Reaction of the bis-allenic ether **16** with  $\text{HB}(\text{C}_6\text{F}_5)_2$ .



## Conclusions

With this study we have found a new variant of our borane induced carbon-carbon coupling reactions between allene building blocks. In this case the reaction starts as it is commonly observed in our systems by 1,2-[B]-H addition<sup>16</sup> to a terminal allene =CH<sub>2</sub> group by the strongly electrophilic HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> hydroboration reagent to probably generate a reactive allylborane intermediate *in situ*, which is set for undergoing rapid intramolecular ring-closure with the pendant second allenyl moiety to generate the products **5a** to **5c**, respectively. These are then obviously protected by their special geometry from undergoing further intermolecular allylborane coupling under the applied reaction conditions, so that the reaction stopped at the functionalized six- or seven-membered ring products. The compounds **5** are, however, in principle still active allylboration reagents. This we could show by the rapid reaction of the example **5a** with the parent allene H<sub>2</sub>C=C=CH<sub>2</sub>. Two equivalents of allene were consumed in a sequence of consecutive intramolecular allylboration reactions, followed by a final intramolecular allylboration ring-closure reaction to give the four-component coupling product **12a**. This in turn was oxidatively converted to the boron-free product **15a**. These metal-free reactions are markedly different from the common metal catalysed bis-allenic cyclization reactions reported in the literature (see Chart 1 and the respective references). We will see how the products of our metal free cyclization reactions and their follow-up products (and related systems) might become easily available useful reagents for further external C-C coupling reactions using either of the newly generated functionalities.

## Conflicts of interest

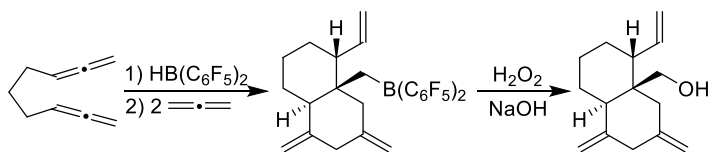
There are no conflicts to declare.

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## TOC



Text for TOC: The borane induced cyclization of the bis-allene followed by reaction with two molar equivalents of allene gives the functionalized decalin product.

