Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2020, **11**, 1542

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 3rd August 2019
Accepted 17th December 2019

DOI: 10.1039/c9sc03870a

rsc.li/chemical-science

Borane-induced ring closure reaction of oligomethylene-linked bis-allenes†

Xin Tao, Karel Škoch, Constantin G. Daniliuc, Gerald Kehr and Gerhard Erker *

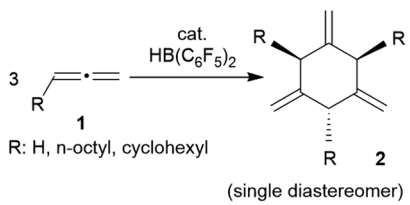
The trimethylene-linked bis-allene **3a** reacts with Piers' borane [$HB(C_6F_5)_2$] by a hydroboration/allylboration sequence to generate the cyclization product **5a**. Its pyridine adduct was isolated and characterized by X-ray diffraction. Compound **5a** undergoes a typical frustrated Lewis pair 1,2-P/B alkene addition reaction with PPh_3 to give the heterobicyclic bridged olefinic zwitterionic product **9a**. The tetramethylene-linked bis-allene **3b** and its phenylene annulated analogue **3c** react with $HB(C_6F_5)_2$ 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_3. Compound **12a** is oxidatively converted to the boron-free alcohol.

Introduction

Allenes are important building blocks in organic synthesis.[1] They show interesting and useful stereochemical properties.[2] We had recently shown that the borane $[HB(C_6F_5)_2]$[3] 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).[1,4,5]

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_2 or O) were reported to rearrange to **II** thermally induced.[6a] They added R_3Si-$SnBu_3$/or -GeR_3 reagents Pd(0) catalysed or radical induced to give the products **III**.[6b,c] With H_2NR nucleophiles cyclization to medium-sized rings (*e.g.* **IV**) was reported.[6d] The products **V** and **VI** of internal [2 + 2] cycloaddition were formed under the influence of Au(I)[6e] or Pd(0)[6a] catalysis, respectively. In some cases coupling between two bis-allenes occurred to give hetero-steroidal frameworks.[6f,g] It should be noted that the vast majority of these reaction is metal catalysed.

This posed the question what the favoured reaction pathway would be if we treated *e.g.* oligomethylene-linked bis-allenes with $HB(C_6F_5)_2$,[7] *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.



Scheme 1 $HB(C_6F_5)_2$-catalyzed cyclotrimerization of alkyl-substituted allenes.

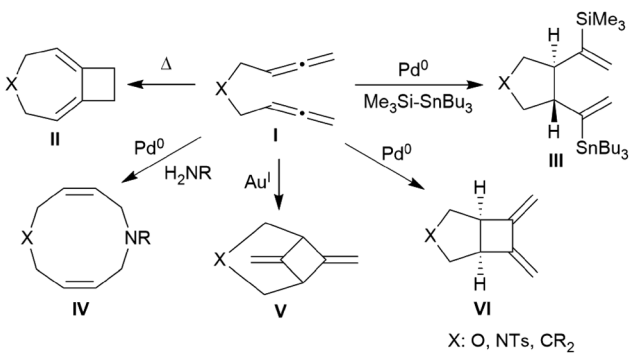


Chart 1 Examples of cyclization reactions of bis-allenes.

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany. E-mail: erker@uni-muenster.de

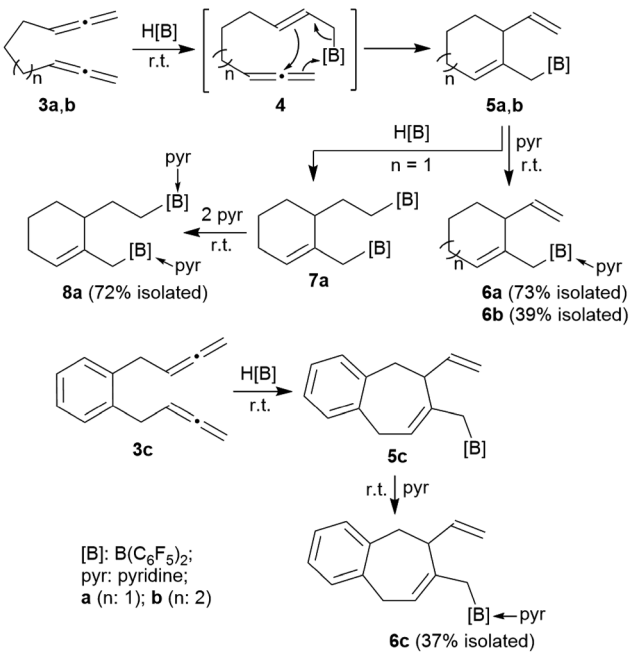
† Electronic supplementary information (ESI) available: Additional experimental details, further spectral and crystallographic data. CCDC deposition numbers are 1922906–1922913 and 1957134. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc03870a

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.*[8] Copper(I) induced treatment of 1,6-heptadiyne with *para*-formaldehyde as C_1-building block and dicyclohexylamine gave the trimethylene-linked bis-allene **3a**[6h] (40% isolated). The analogous reaction starting from 1,7-octadiyne gave the tetramethylene-linked bis-allene **3b**[6i] (63% isolated, see the ESI† for details). The phenylene containing bis-allene **3c** was synthesised analogously.

We reacted compound **3a** with one molar equivalent of Piers' borane [$HB(C_6F_5)_2$]. The rapid reaction (r.t., minutes, in CD_2Cl_2) gave the cyclized product **5a**. It was not isolated but characterized by spectroscopy [^{1}H NMR: δ 5.55 (olefinic =CH–) (C6–H, see Fig. 1 for the unsystematic atom numbering scheme), δ 5.52, 5.03, (–CH=CH_2 substituent); ^{11}B NMR: δ 69.3; $\Delta\delta^{19}F_{m,p} = 13.1$ 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 –$CH_2B(C_6F_5)_2$(pyridine) substituent adjacent to it at the olefinic ring carbon atom C4 (Fig. 1). In solution (CD_2Cl_2) we monitored the typical ^{1}H/^{13}C NMR features of the vinyl group at carbon atom C3 and the central doubly substituted cyclohexene core. The ^{1}H NMR features of the coordinated pyridine moiety show up at δ 8.67, 8.11 and 7.65 (^{11}B: δ −0.6). Due to the chiral centre (ring carbon C3) the C_6F_5 groups at boron are diastereotopic and give rise to a 1 : 1 set of the respective *o*,*p*,*m*-C_6F_5 ^{19}F NMR signals.



Scheme 2 $HB(C_6F_5)_2$-induced ring closure of the bis-allenes **3**.

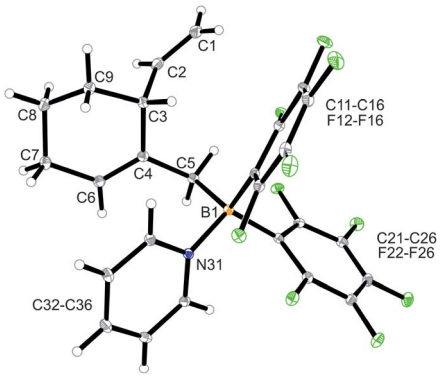


Fig. 1 A view of the molecular structure of the borane pyridine adduct **6a**. Selected bond lengths (Å) and angles (°): B1–N31 1.613(3), B1–C5 1.651(3), C1–C2 1.322(4), C4–C6 1.337(3), B1–C5–C4 117.7(2).

We assume that the reaction started with hydroboration of the terminal $=CH_2$ unit of one allenyl group by the $HB(C_6F_5)_2$ 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 allylboration 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 $B(C_6F_5)_2$ group gave **6a** (Scheme 2).

We reacted the tetramethylene-linked bis-allene **3b** with $HB(C_6F_5)_2$ 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 (Fig. 2). It shows the newly formed seven-membered ring in a typical cycloheptene boat-like conformation.[9] The –$CH_2B(C_6F_5)_2$ moiety is attached at the sp^2-carbon atom C4 (the boron atom bears a pair of C_6F_5 groups and the coordinated

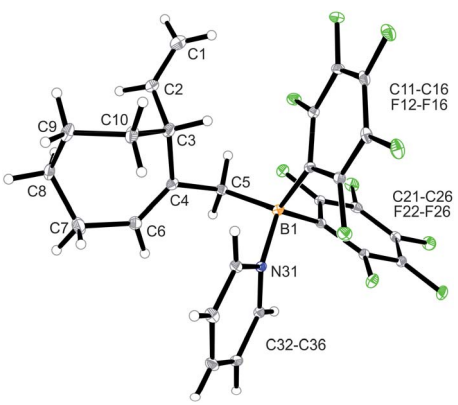


Fig. 2 Molecular structure of compound **6b**. Selected bond lengths (Å) and angles (°): B1–N31 1.627(5), B1–C5 1.645(6), C1–C2 1.285(8), C4–C6 1.340(6), B1–C5–C4 119.9(3).

pyridine ligand in a pseudo-tetrahedral geometry). The vinyl substituent is bonded to carbon atom C3.

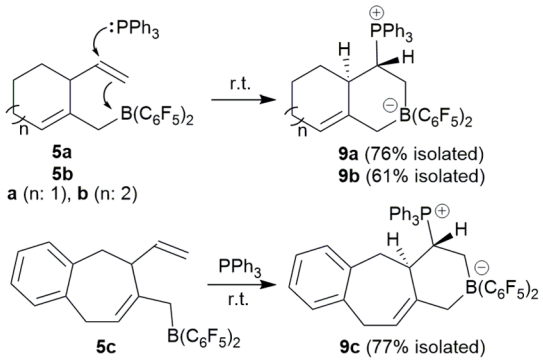
The reaction of the bis-allene **3a** responded to the stoichiometry of the $HB(C_6F_5)_2$ reagent since the primary ring-closure product **5a** contained a reactive pendant vinyl group. Therefore, the reaction of **3a** with two molar equivalents of Piers' borane gave the bis-borane product **7a**. Its ^{11}B NMR spectrum showed two signals (δ 73.3 and δ 69.4) that are attributed to the pair of Lewis acidic planar-tricoordinate boron centres. Consequently, we observed two sets of ^{19}F NMR resonances of the pairs of the C_6F_5 substituents at the two $B(C_6F_5)_2$ 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 C_6F_5 groups at each $B(C_6F_5)_2$(-pyridine) moiety are diastereotopic and, consequently, we observed four sets of *o*,*m*,*p*-C_6F_5 ^{19}F NMR signals of compound **8a**. We observed two sets of pyridine $^{1}H/^{13}C$ NMR resonances and located the single olefinic ^{1}H NMR signal (C6–H) at δ 4.35 (t, $J_{HH} = 3.3$ Hz, 1H).

We performed the reaction of the phenylene bridged bis-allene system **3c** in a similar way. The reaction of **3c** with one molar equiv. of $HB(C_6F_5)_2$ was carried out in CD_2Cl_2 at r.t. and the almost instantaneously *in situ* generated product was characterized by NMR spectroscopy [^{1}H: δ 5.48/5.13/5.08 (vinyl substituent), 5.72 (ring-CH=), ^{11}B: δ 71.9, ^{19}F: $\Delta\delta^{19}F_{m,p} = 13.2$]. 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}B NMR resonance in the typical range of tetracoordinate boron (δ −0.5) and the C_6F_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[10] reaction, namely a 1,2-borane/phosphane addition to the C=C double bond.[11]

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 $-B(C_6F_5)_2$ Lewis acid had been added to the $=CH_2$ terminus of the alkene and the external PPh_3 nucleophile to the –CH= carbon atom. The resulting zwitterionic heterobicyclo[4.4.0]decene type system features



Scheme 3 FLP reaction of the boranes **5** with PPh_3.

a bridgehead C=C double bond (C4–C6). There is a borate system inside the heterocyclic six-membered ring that was formed in the FLP addition reaction. Consequently, the $-PPh_3^+$ 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 (Fig. 3). In solution compound **9a** shows the NMR heteronuclear resonances at δ −12.3 (^{11}B) and δ 27.9 (^{31}P). A diastereotopic pair of C_6F_5 substituents is bonded at boron, giving rise to two separate sets of ^{19}F NMR resonances. The ^{1}H NMR [P]–CH– signal is found at δ 3.64 and the single olefinic =CH– signal at δ 5.17.

The seven-membered ring compounds **5b** and **5c** react analogously with 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

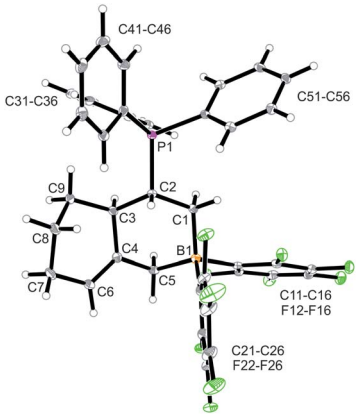


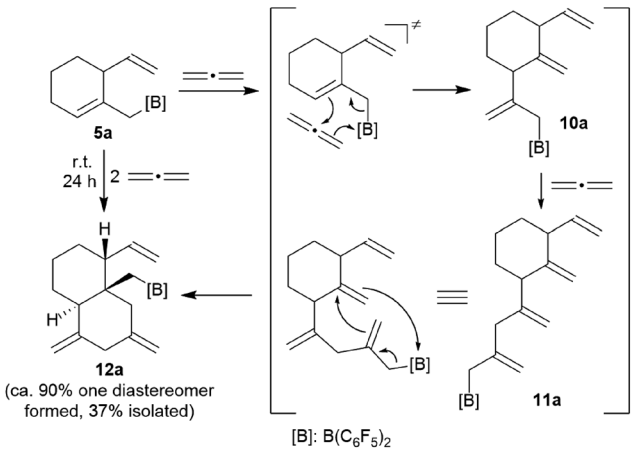
Fig. 3 Molecular structure of the P/B FLP addition product **9a**. Selected bond lengths (Å) and angles (°): B1–C1 1.647(2), B1–C5 1.640(2), P1–C2 1.856(2), C1–C2 1.549(2), C4–C6 1.333(2), C1–B1–C5 105.7(1), B1–C1–C2 114.6(1), C1–C2–C3 112.4(1), C2–C3–C4 109.2(1), C3–C4–C5 114.9(1), C4–C5–B1 108.9(1),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

δ −13.3 (^{11}B) and δ 30.5 (^{31}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[12] 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 allylborane 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 $H_2C{=}C{=}CH_2$. 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 °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 (Fig. 4) that the endocyclic allylborane moiety of the starting material **5a** had reacted with two molar equivalents of $H_2C{=}C{=}CH_2$ 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[4] to directly give the observed product **12a** (Scheme 4).

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 $-CH_2B(C_6F_5)_2$ group is attached at the bridgehead carbon (C4 in Fig. 4).



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

In solution (CD_2Cl_2) compound **12a** shows the typical NMR features of the vinyl substituent. The pair of $=CH_2$ exo-methylene groups shows a total of four ^{1}H NMR resonances (δ 4.85/4.61 and δ 4.68/4.42). The $-CH_2$[B] substituent shows the ^{1}H NMR signals of a pair of diastereotopic hydrogen atoms (AB system at δ 2.30/2.15; ^{13}C: δ 36.7). The corresponding ^{11}B NMR feature is at δ 76.4, *i.e.* in a typical range of a strongly Lewis acidic tri-coordinated boron atom in this substituent situation.[13] Consequently, we observed three ^{19}F NMR signals of the pair of the C_6F_5 substituents at boron with a large $\Delta\delta^{19}F_{m,p}$ = 11.5 ppm chemical shift separation.

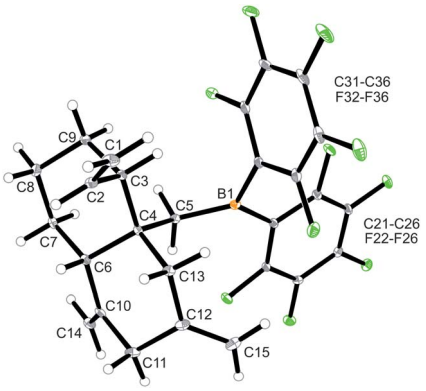
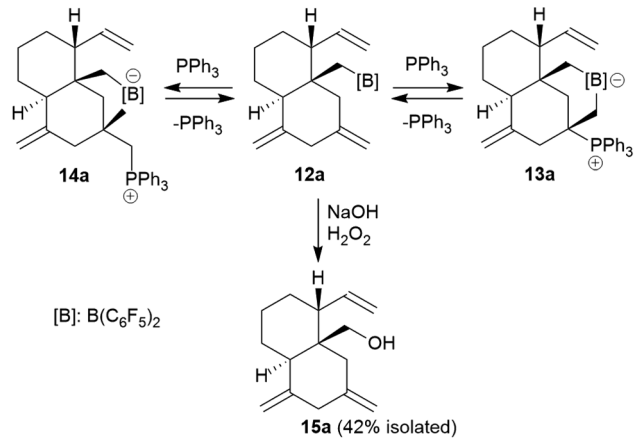


Fig. 4 Molecular structure of compound **12a**. Selected bond lengths (Å) and angles (°): B1–C5 1.554(3), C1–C2 1.313(3), C4–C5 1.557(3), C4–C6 1.566(3), C10–C14 1.324(3), C12–C15 1.324(3), B1–C5–C4 123.2(2), C5–C4–C6 109.0(2).

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.[11] We, consequently, reacted the *in situ* generated borane **12a** with triphenylphosphane in dichloromethane. The reaction with 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 (Fig. 5). It showed that a P/B FLP addition had taken place at the proximal $C{=}CH_2$ moiety (C12=C15 in compound **12a**, see Fig. 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 $C{=}CH_2$ terminus and, consequently, phosphane addition to the 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 PPh_3^+ moiety is found attached at the new bridgehead atom C12 (Fig. 5).



Scheme 5 Reaction of compound **12a** with PPh_3 and oxidative replacement of the boryl group.

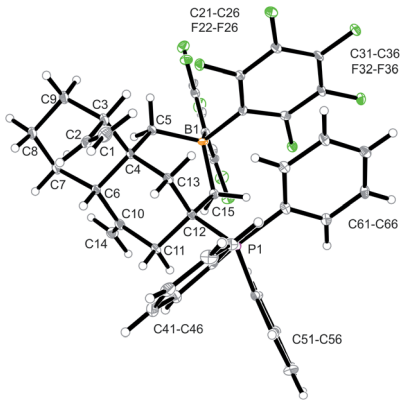


Fig. 5 A view of the P/B FLP alkene addition product **13a**. Selected bond lengths (Å) and angles (°): B1–C5 1.640(6), B1–C15 1.667(6), P1–C12 1.858(4), C1–C2 1.302(6), C4–C6 1.565(5), C10–C14 1.328(6), C12–C15 1.555(5), C5–B1–C15 110.3(3), C12–C15–B1 114.3(3), P1–C12–C15–B1 −129.8(3).

Compound **13a** shows a typical borate ^{11}B NMR resonance at δ −15.1 in solution (CD_2Cl_2, 273 K) and a phosphonium ^{31}P NMR signal at δ 31.1. It shows the ^{19}F NMR features of a pair of diastereotopic C_6F_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 has been formed under kinetic control. When we stored the CD_2Cl_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 PPh_3, *ca.* 8 mol%) and the new compound **14a** (*ca.* 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., CH_2Cl_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.

The X-ray crystal structure analysis of **14a** shows the presence of a 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 C12=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 PPh_3 addition had taken place at the $=CH_2$ terminus of the exo-methylene group concurrent with borane addition to its adjacent doubly substituted sp^2-carbon atom. The structure of the resulting P/B zwitterion **14a** is depicted in Fig. 6.

The ^1H NMR spectrum of compound **14a** (in CD_2Cl_2, at 299 K) shows the P-coupled system of the exocyclic $-CH_2-[P]$ moiety at δ 4.18/2.70 and the resonances of the endocyclic $-CH_2-[B]$ group at δ 1.32/0.35. The heteroatom NMR signals occur at δ −6.8 (^{11}B) and 19.9 (^{31}P), respectively and we observed two sets of ^{19}F NMR signals of the pair of diastereotopic C_6F_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.[14] This was carried out in the usual way of oxidative deborylation as it is done in conventional hydroboration chemistry.[15] Treatment of the strongly electrophilic $-B(C_6F_5)_2$ borane **12a** with $NaOH/H_2O_2$ 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**[6c,h,j] with $HB(C_6F_5)_2$. The reaction was carried out in CD_2Cl_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 $HB(C_6F_5)$ 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 $(C_6F_5)_2B-O-CH_2-CH=C=CH_2$ cleavage product **17** (see Scheme 6) and butadiene (**18**) as primary products. The latter was then subsequently converted by added $HB(C_6F_5)_2$ 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 $HB(C_6F_5)_2$ (see the ESI† for details). We also investigated briefly the reaction of the

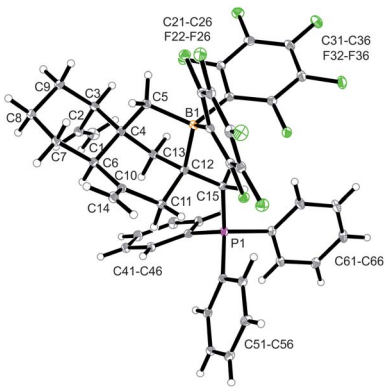
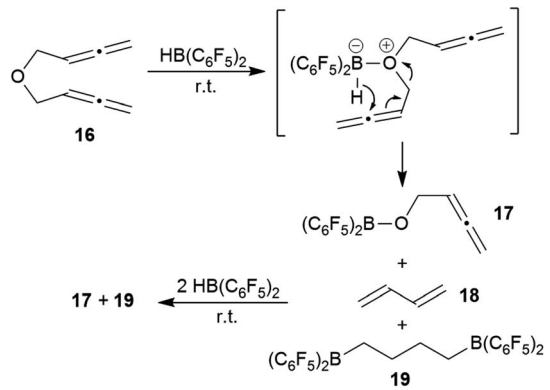


Fig. 6 A projection of the molecular structure of compound **14a**. Selected bond lengths (Å) and angles (°): B1–C5 1.657(4), B1–C12 1.695(3), P1–C15 1.823(2), C1–C2 1.301(13), C4–C6 1.556(3), C10–C14 1.325(4), C12–C15 1.540(3), C5–B1–C12 99.9(2), C12–C15–B1 112.1(2), B1–C12–C15–P1 179.1(2).



Scheme 6 Reaction of the bis-allenic ether **16** with $HB(C_6F_5)_2$.

respective bis-allenic *N*-tosyl amine with $HB(C_6F_5)_2$, but that gave a complicated mixture of as yet unidentified products.

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[16] to a terminal allene $=CH_2$ group by the strongly electrophilic $HB(C_6F_5)_2$ 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 $H_2C{=}C{=}CH_2$. 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.

Notes and references

1 (*a*) A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, 2000, **39**, 3590; (*b*) *Modern Allene Chemistry*, ed. N. Krause, and A. S. K. Hashmi, Wiley-VCH, Weinheim, Germany, 2004; (*c*) S. Ma, *Chem. Rev.*, 2005, **105**, 2829; (*d*) N. Krause and C. Winter, *Chem. Rev.*, 2011, **111**, 1994; (*e*) S. Yu and S. Ma, *Angew. Chem., Int. Ed.*, 2012, **51**, 3074; (*f*) W. Yang and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2014, **43**, 2941.

2 C. Gropp, N. Trapp and F. Diederich, *Angew. Chem., Int. Ed.*, 2016, **55**, 14444.

3 (*a*) D. J. Parks, R. E. H. Spence and W. E. Piers, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 809; (*b*) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492; (*c*) M. Hoshi, K. Shirakawa and M. Okimoto, *Tetrahedron Lett.*, 2007, **48**, 8475; (*d*) A. Schnurr, K. Samigullin, J. M. Breunig, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2011, **30**, 2838; (*e*) J. Zhang, S. Park and S. Chang, *Angew. Chem., Int. Ed.*, 2017, **56**, 13757.

4 (*a*) X. Tao, G. Kehr, C. G. Daniliuc and G. Erker, *Angew. Chem., Int. Ed.*, 2017, **56**, 1376; (*b*) See also: X. Tao, C. Wölke, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Sci.*, 2019, **10**, 2478.

5 Arylallenes react differently, see: X. Tao, C. G. Daniliuc, D. Dittrich, G. Kehr and G. Erker, *Angew. Chem., Int. Ed.*, 2018, **57**, 13922.

6 (*a*) X. Jiang, X. Cheng and S. Ma, *Angew. Chem., Int. Ed.*, 2006, **45**, 8009; (*b*) S.-K. Kang, T.-G. Baik, A. N. Kulak, Y.-H. Ha, Y. Lim and J. Park, *J. Am. Chem. Soc.*, 2000, **122**, 11529; (*c*) Y.-T. Hong, S.-K. Yoon, S.-K. Kang and C.-M. Yu, *Eur. J. Org. Chem.*, 2004, 4628; (*d*) J. Cheng, X. Jiang and S. Ma, *Org. Lett.*, 2011, **13**, 5200; (*e*) S. M. Kim, J. H. Park, Y. K. Kang and Y. K. Chung, *Angew. Chem., Int. Ed.*, 2009, **48**, 4532; (*f*) S. Ma, P. Lu, L. Lu, H. Hou, J. Wei, Q. He, Z. Gu, X. Jiang and X. Jin, *Angew. Chem., Int. Ed.*, 2005, **44**, 5275; (*g*) S. Ma and L. Lu, *Chem.–Asian J.*, 2007, **2**, 199; (*h*) X. Lian and S. Ma, *Chem.–Eur. J.*, 2010, **16**, 7960; (*i*) V. A. D'yakonov, G. N. Kadikova, L. M. Khalilov and U. M. Dzhemilev, *Russ. J. Org. Chem.*, 2013, **49**, 1139; (*j*) S.-K. Kang, Y.-H. Ha, D.-H. Kim, Y. Lim and J. Jung, *Chem. Commun.*, 2001, 1306.

7 For examples of thermally induced reactions of bis-allenes, see: (*a*) L. Skattebol and S. Solomon, *J. Am. Chem. Soc.*, 1965, **87**, 4506; (*b*) W. R. Roth, M. Heiber and G. Erker, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 504; (*c*) S. Sakai, *J. Phys. Chem. A*, 2006, **110**, 9443.

8 (*a*) J. Kuang and S. Ma, *J. Org. Chem.*, 2009, **74**, 1763; for the original Crabbé reaction see *e.g.*; (*b*) P. Crabbé, H. Fillion, D. André and J.-L. Luche, *J. Chem. Soc., Chem. Commun.*, 1979, 859; see also; (*c*) S. Kitagaki, M. Komitzu and C. Mukai, *Synlett*, 2011, 1129.

9 *Basic Organic Stereochemistry*, ed. E. L. Eliel, S. H. Wilen and M. P. Doyle , John Wiley & Sons, Inc., New York, 2001.

10 (*a*) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46; (*b*) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400.

11 (*a*) J. S. J. McCahill, G. C. Welch and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 4968; (*b*) J. B. Sortais, T. Voss, G. Kehr, R. Fröhlich and G. Erker, *Chem. Commun.*, 2009, 7417; (*c*) T. Voss, J.-B. Sortais, R. Fröhlich, G. Kehr and G. Erker, *Organometallics*, 2011, **30**, 584; (*d*) X. X. Zhao and D. W. Stephan, *J. Am. Chem. Soc.*, 2011, **133**, 12448; (*e*)

G. Ménard, L. Tran, J. S. J. McCahill, A. J. Lough and D. W. Stephan, *Organometallics*, 2013, **32**, 6759.

12 (*a*) B. M. Mikhailov and Y. N. Bubnov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, **13**, 1874; (*b*) *Organoboron Compounds in Organic Synthesis*, ed. B. M. Mikhailov and Y. N. Bubnov, Harvood, Chur, 1984; (*c*) Y. N. Bubnov, *Pure Appl. Chem.*, 1987, **59**, 895; (*d*) R. W. Hoffmann, *Pure Appl. Chem.*, 1988, **60**, 123; (*e*) Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207; (*f*) S. Y. Erdyakov, M. E. Gurskii, A. V. Ignatenko and Y. N. Bubnov, *Mendeleev Commun.*, 2004, **14**, 242; (*g*) M. E. Gurskii, S. Y. Erdyakov, T. V. Potapova and Y. N. Bubnov, *Russ. Chem. Bull.*, 2008, **57**, 802.

13 For a comparison, the ^{11}B NMR signal of $B(C_6F_5)_3$ is δ 59.5. (*a*) G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245; (*b*) A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1966, **5**, 218.

14 We had previously shown that alkenyl-$B(C_6F_5)_2$ derivatives undergo typical borane reactions, *e.g.* Pd-catalyzed cross-coupling with iodobenzene: (*a*) C. Chen, G. Kehr, R. Fröhlich and G. Erker, *J. Am. Chem. Soc.*, 2010, **132**, 13594; (*b*) C. Chen, T. Voss, R. Fröhlich, G. Kehr and G. Erker, *Org. Lett.*, 2011, **13**, 62.

15 (*a*) H. C. Brown and B. C. Rao, *J. Am. Chem. Soc.*, 1956, **78**, 5694; (*b*) H. C. Brown and B. C. Rao, *J. Org. Chem.*, 1957, **22**, 1136; (*c*) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 1959, **81**, 247.

16 For an example of a rare alternative 1,1-hydroboration reaction, see: A. Ueno, J. Yu, X. Tao, C. G. Daniliuc, G. Kehr and G. Erker, *Organometallics*, 2018, **37**, 2665.