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Metal-free Acetylene Coupling by Means of the $(C_6F_5)_2B$-X 1,2-Halogenoboration Reaction

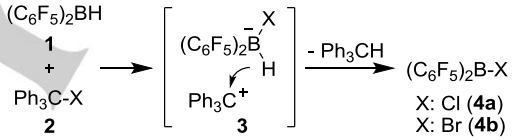
Atsushi Ueno, Jun Li, Constantin G. Daniliuc, Gerald Kehr, and Gerhard Erker*

Dedicated to the memory of Professor Takao Ikariya, Tokyo Institute of Technology, deceased April 21, 2017.

Abstract: $(C_6F_5)_2B$-halides were conveniently prepared by treatment of $(C_6F_5)_2BH$ with tritylchloride or -bromide, respectively. With cyclopropylacetylene $(C_6F_5)_2BBr$ underwent sequential *cis*-1,2-halogenoboration followed by 1,2-carboboration to give the 4-bromo-2,4-dicyclopropylbutadienyl-$B(C_6F_5)_2$ product. It reacted further with additional cyclopropylacetylene to give the linear triene and tetraene products in a metal free alkyne oligomerization reaction. The pyridine adduct of the initial diene product was characterized by X-ray diffraction. $(C_6F_5)_2BCl$ reacted analogously. Similar $(C_6F_5)_2BX$ induced oligomerization reactions were carried out with two conjugated enynes.

Boranes undergo two major types of reactions with acetylenes, both giving rise to the formation of alkenylborane derivatives. There are the variants of the 1,1-carboboration reaction.[1,2] These are characterized by attachment of a substituent from the borane and the remaining boryl group at the same acetylene carbon atom. Consequently, an acetylene substituent will undergo a 1,2-migration along the alkyne framework. More often encountered are the genuine 1,2-additions, most commonly the hydroboration reaction.[3] This is usually a *cis*-1,2-H[B] addition, but there are *trans*-1,2-H/BR_2 addition variants, as well.[4] 1,2-Diboration[5], 1,2-halogeno-[6,7] and 1,2-cyanoboration[8] reactions of alkynes are becoming increasingly important. These usually involve only XBR_2 addition reactions to acetylenes in a 1:1 stoichiometry. We have now found a novel very simple way of preparing the $(C_6F_5)_2BX$ reagents (X = Cl, Br)[9c,d,g] and found that they undergo *cis*-1,2-halogenoboration reactions that do not stop after the reaction with one alkyne equivalent but continue and add additional alkyne equivalents to give the respective linear oligomers. First examples of such sequences of halogenoboration reactions combined with subsequent alkyne/alkyne coupling will be presented in this account.

Chloro-bis(pentafluorophenyl)borane [$(C_6F_5)_2BCl$, **4a**] is a useful boron reagent. It had been synthesized in rather cumbersome ways using problematic organotin or organomercury reagents.[9] We have now developed a more convenient synthesis of **4a** and the related $(C_6F_5)_2BBr$ reagent **4b** by reacting Piers' borane [$(C_6F_5)_2BH$][9e] with trityl chloride or trityl bromide, respectively. This gave the $(C_6F_5)_2BX$ products, which we isolated in 79% (X: Cl) and 77% (X: Br) yield, respectively. Typically, one molar equivalent of triphenylmethyl bromide was added to a suspension of $(C_6F_5)_2BH$ in toluene. The mixture was stirred for 18 hours at r.t. Workup including vacuum distillation at 100 °C gave compound **4b** as a pale orange solid (1.9 g prepared in a typical procedure). We assume that the reaction is initiated by halide addition to the boron Lewis acid from the dissociative trityl halide equilibration, followed by hydride abstraction by the remaining trityl cation to give the respective $(C_6F_5)_2BX$ products and Ph_3CH (see Scheme 1), although this mechanistic description is not strictly proven. The $(C_6F_5)_2BH$ starting material for this synthesis was conveniently prepared by treatment of commercially available $(C_6F_5)_3B$ with triethylsilane by means of a variant of the procedure published by Piers et al. [9e]



Scheme 1. Synthesis of the bis(pentafluorophenyl)boron halides **4**.

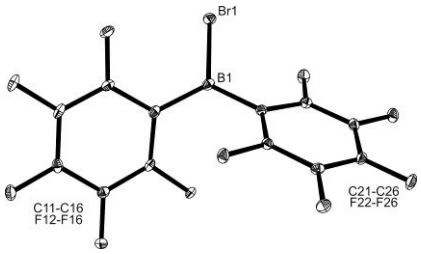


Figure 1. A view of the molecular structure of $(C_6F_5)_2BBr$ (**4b**) (thermal ellipsoids are shown at the 30% probability level).

In CD_2Cl_2 solution, compound **4b** shows a ^{11}B NMR signal at δ 60.5 (cf. **4a**: δ 58.1) and a set of three ^{19}F NMR resonances with a $\Delta\delta\ ^{19}F_{m,p}$ = 16.3 ppm chemical shift difference. Both these NMR features are typical for a strongly Lewis acidic planar-tricoordinate boron compound. Single crystals suited for the characterization of $(C_6F_5)_2BBr$ (**4b**) by X-ray diffraction were obtained from slow diffusion of pentane into a saturated CH_2Cl_2 solution of **4b**. The X-ray crystal structure analysis shows the presence of a planar-tricoordinate geometry around boron (see Figure 1). The structure is close to C_2-symmetric (but not crystallographically exact). The B1–Br1 bond length amounts to 1.908(2) Å. The pair of B1–C11/C21 bonds to the C_6F_5 rings are equal in length (both 1.566(3) Å). The sum of bond angles at the boron atom B1 is

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Supporting information for this article is given via a link at the end of the document. CCDC 1821915 (**8a**), 1821916 (**4b**), 1821917 (**8b**), 1834994 (**8f**),1834995 (**8c**), and 1834996 (**8e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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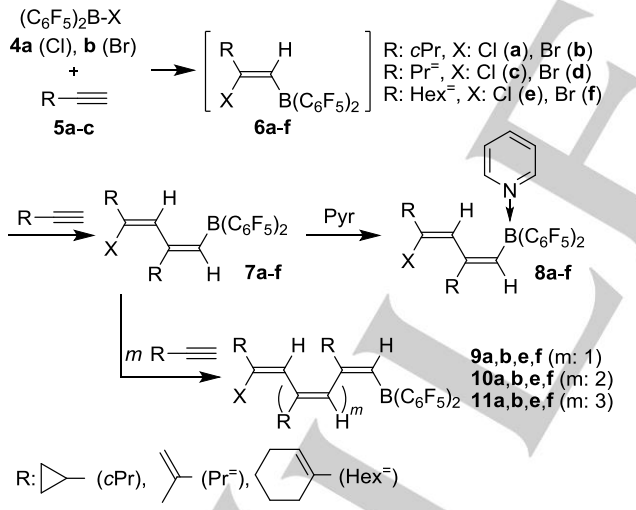
360.0° with the individual bond angles found within a small range [C11-B1-Br1: 119.0(2)°, C21-B1-Br1: 118.7(2)°, C11-B1-C21: 122.3(2)°]. The angle between the two C_6F_5 planes amounts to 60.3° in compound **4b**.

We chose cyclopropylacetylene (**5a**) to investigate the halogenoboration reactions of the strongly electrophilic halogenoboranes **4a** and **4b**. It turned out that in both cases the reaction took an uncommon course. We first treated the $(C_6F_5)_2BBr$ borane **4b** with one molar equiv. of cyclopropyl-acetylene (**5a**, d_6-benzene, r.t., 1h) and observed the clean formation of the *cis*-1,2-bromoboration product **6b**, which was characterized by NMR spectroscopy [^{1}H: δ 6.85 (s, =CH), δ 1.46, 0.80, 0.44 (cyclopropyl-H); ^{13}C: δ 163.5 (=CBr), δ 130.6 (=CH), ^{11}B: δ 57.4]. The reaction of compound **4b** with two molar equiv. of **5a** (or alternatively the addition of one equiv. of **5a** to the *in situ* formed halogenoboration product **6b**) under analogous conditions resulted in "alkyne-insertion" into the C(sp^2)–B bond of **6b** to give the carbon-carbon coupling product **7b**. The reaction was first carried out in C_6D_6 and the outcome investigated directly by NMR spectroscopy without workup. The 2:1 mixture of **5a** and **4b** in C_6D_6 was stirred for 2 h at room temperature. The NMR spectra showed that two acetylene equivalents had become coupled to give the 2,4-bis-cyclopropyl substituted butadiene, bearing a bromide and a -B$(C_6F_5)_2$ functional group at its ends. Compound **7b** apparently features an extended conformation that prohibits internal -Br/-B$(C_6F_5)_2$ interaction. The NMR features of the -B$(C_6F_5)_2$ group in **7b** point to a Lewis acidic planar-tricoordinate geometry at boron (see Table 1).



Scheme 2. $(C_6F_5)_2B$–halide induced linear oligomerization reaction of terminal acetylenes **5a-c**.

Treatment of **7b** with pyridine resulted in the formation of the pyridine adduct **8b**. This was synthesized on a preparative scale and isolated as a white solid in 82%. The X-ray crystal structure analysis showed the core structure that was formed by head to tail coupling of two cyclopropylacetylene units. Carbon atoms C2 and C4 have the pair of cyclopropyl substituents attached. Noteworthy is that the individual olefinic π-systems C1=C2 and C3=C4 are markedly rotated from conjugation (see Table 2).[10] The cyclopropyl group at C4 is found in a bisected orientation to allow π-conjugation of the cyclopropyl Walsh orbitals with the adjacent olefinic π-bond. The other cyclopropyl group was found disordered. The boron atom attached at carbon atom C1 is tetracoordinated. The stereochemistry at the olefinic double bonds indicates a pathway of formation of compound **7b** that involves an initial *cis*-1,2-bromoboration to give the intermediate **6b**, followed by a rare example of a *cis*-1,2-carboboration reaction[11] to give the observed product **7b** (see Scheme 2 and Figure 2).

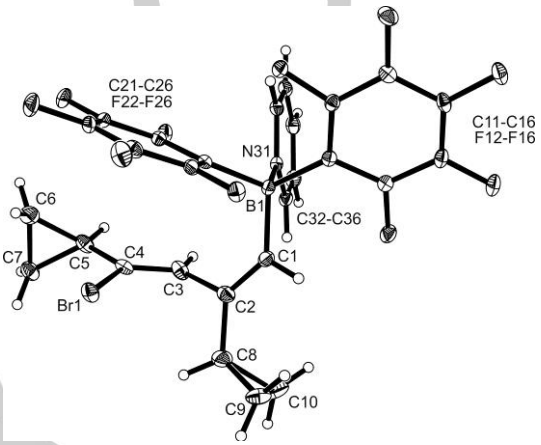


Figure 2. A view of the molecular structure of compound **8b** (thermal ellipsoids are shown at the 30% probability level).

Table 1. Selected NMR data[a] of the acetylene coupling products **7a**,**b** and their pyridine adducts **8a**,**b**

	7a (X: Cl)[b]	**8a** (Pyr)[c]	**7b** (X: Br)[b]	**8b** (Pyr)[c]
^{11}B	56.3	-3.2	55.3	-3.4
1-H	6.58	6.09	6.57	6.08
3-H	5.53	5.56	5.73	5.84
^{13}C1	130.6	132.3	130.7	131.8
^{13}C2	175.3	146.9	176.8	147.6
^{13}C3	121.2	124.3	124.3	127.6
^{13}C4	141.3	136.5	135.8	130.9
$\Delta\delta^{19}F_{m,p}$[d]	11.9	5.5	12.0	5.5

[a] ^{1}H/^{13}C NMR chemical shifts rel. TMS, δ-scale, ^{11}B rel. $BF_3{\cdot}Et_2O$; [b] in C_6D_6 (299 K); [c] in CD_2Cl_2 (299 K); [d] in ppm.

In solution the pyridine adduct **8b** shows the typical ^{1}H NMR signals of a pair of inequivalent cyclopropyl substituents. They show ^{13}C NMR resonances at δ 20.7/6.8 and δ 19.2/7.3, respectively. The ^{11}B NMR resonance is in the typical range of a tetracoordinate boron center. We note that pyridine coordination to boron has resulted in a marked shift of the β-^{13}C NMR feature of the directly attached alkenyl moiety to smaller δ-values relative to its active alkenylborane Lewis acid precursor **7b** [Δδ(C2) = 29.2 ppm, see Table 1].

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The cyclopropylacetylene coupling product **7b** reacted further with additional monomer **5a**. When one more equiv. of the alkyne was added to a solution of **7b** (r.t., 1h) we observed the formation of a mixture of the respective linear threefold (**9b**) and tetrafold acetylene coupling products (**10b**) in addition to some remaining **7b**. During this process the color of the reaction mixture changed from yellow to orange and then to dark red; addition of more acetylene equivalents gave a dark red-brown solution. The generated polyene products were characterized from the mixture by NMR spectroscopy (see the Supporting Information for details).

Table 2. Selected structural parameters[a] of the pyridine adducts **8a**,**b**,**c**,**f** of the acetylene coupling products **7a**,**b**,**c**,**f**.

	8a (X: Cl)[b]	**8b** (X: Br)[b]	**8c** (X: Cl)	**8f** (X: Br)
B1–N31	1.637(3)	1.638(2)	1.626(2)[c]	1.641(5)[c]
B1–C1	1.607(4)	1.615(3)	1.618(3)	1.612(5)
C1–C2	1.338(3)	1.345(3)	1.347(3)	1.351(5)
C2–C3	1.498(4)	1.491(3)	1.512(3)	1.496(5)
C3–C4	1.320(4)	1.325(3)	1.313(4)	1.331(5)
C4–X1	1.752(2)	1.905(2)	1.740(3)	1.921(3)
B1-C1-C2-	6.5(4)	6.0(3)	11.5(3)	4.9(5)
C2-C3-C4-	2.8(4)	2.7(3)	-3.1(4)	-1.7(5)
C1-C2-C3-	-108.1(3)	-109.2(2)	-97.5(3)	-107.2(4)

[a] bond length in Å, angles in deg, [b] values of molecule A. [c] B1-N1

The chloroborane **4a** reacted in a similar way with cyclopropylacetylene (**5a**). When we reacted $(C_6F_5)_2BCl$ (**4a**) with **5a** in a 1:1 molar ratio in deuterated benzene at r.t. we monitored the formation of a ca. 1:1 mixture of the conventional *cis*-1,2-chloroboration product **6a** with the extended product **7a** (see Scheme 2 and Figure 3). The ^{19}F NMR spectra indicated the presence of some residual chloroborane **4a** in this experiment.

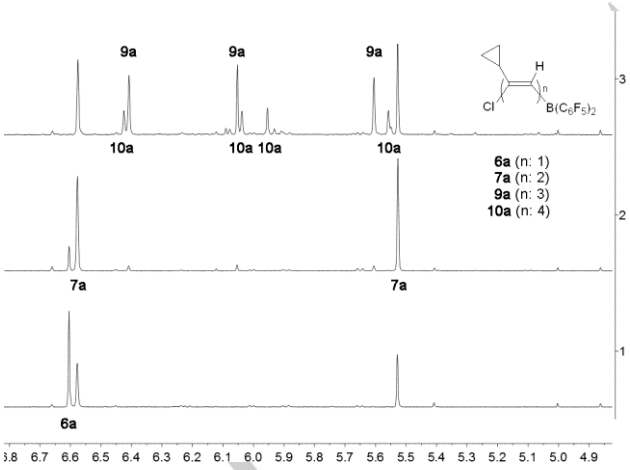
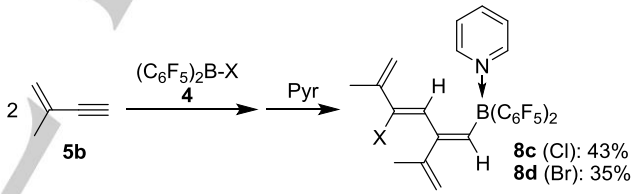


Figure 3. Olefinic section of the ^1H NMR (600 MHz, d_6-benzene, 299 K) spectra of the reaction of $ClB(C_6F_5)_2$ (**4a**) with (1) 1 equiv. cyclopropylacetylene (**5a**), (2) a second equiv. **5a**, and (3) a third equiv. **5a** (for details see the text and the Supporting Information).

The reaction of $(C_6F_5)_2BCl$ (**4a**) with cyclopropylacetylene in a 1:2 ratio gave the diene **7a**, which was apparently formed by sequential *cis*-1,2-chloroboration followed by *cis*-1,2-carboboration. We characterized the *cis*-1,2-chloroboration/ alkyne coupling product **7a** spectroscopically from an *in situ* experiment (see Table 1) and isolated the corresponding pyridine adduct **8a** in 81% yield from an experiment on a preparative scale. Compound **8a** was characterized by X-ray diffraction (see Table 2). The structure is depicted in the Supporting Information. Addition of one molar equiv. of cyclopropylacetylene to a solution of **7a** in d_6-benzene (r.t., 1h) resulted in building up the linear alkyne oligomer chain by further 1,2-carboboration. Under our typical reaction conditions, we observed the formation of the substituted linear triene **9a** as the major product admixed with the tetraene **10a** and some residual diene **7a**. The characteristic olefinic section of the ^1H NMR spectra of the oligomers is depicted in Figure 3.

The $(C_6F_5)_2B$–halide induced cyclopropylacetylene oligomerization reactions are not the only examples of this reaction type. We found a similar behaviour upon treatment of the compounds **4a** and **4b** with the conjugated enyne 2-methylbutenyne **5b**, as well. The reaction of **5b** with $(C_6F_5)_2BCl$ **4a** in a 2:1 molar ratio followed by addition of the pyridine trapping reagent (one molar equiv.) gave the acetylene coupling product **8c** (Scheme 3), which we isolated as a white solid in 43% yield. The ^1H NMR spectrum of compound **8c** shows a pair of methyl group singlets, four olefinic exo-methylene resonances and two singlets of the olefinic =CH- units within the main carbon chain.



Scheme 3. $(C_6F_5)_2B$-halide induced carbon-carbon coupling of two 2-methylbutenyne units.

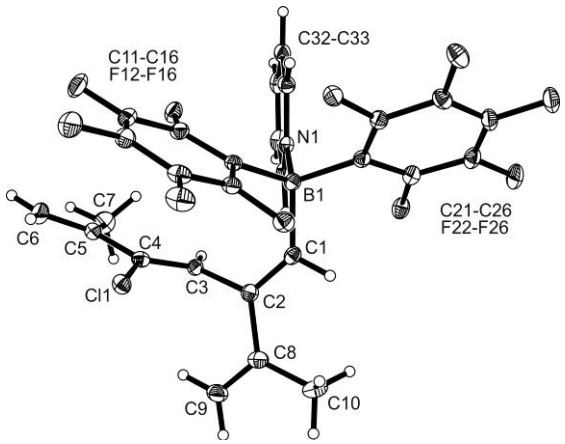


Figure 4. A view of the molecular structure of the acetylene coupling product **8c** (thermal ellipsoids are shown at the 30% probability level). Selected bond lengths (Å) and angles (°) are described in Table 2.

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Compound **8c** was characterized by X-ray diffraction (single crystals were obtained from pentane/dichloromethane by the diffusion method). The solid state structure (see Fig 4) shows the central C_4-π-system constructed by C-C coupling of the two substituted acetylene monomer units. We note that the two conjugated four-electron π-systems originating from the two enyne monomers are oriented close to orthogonal to each other θ C1-C2-C3-C4 = -97.5°). Carbon atom C1 bears the $–B(C_6F_5)_2$ group (with pyridine attached to the boron Lewis acid), and chloride originating from the **4a** reagent is found bonded to C4.

The reaction of compound **5b** with $(C_6F_5)_2BBr$ (**4b**) proceeded analogously and furnished the product **8d** (for details see the Supporting Information). We reacted the conjugated enyne ethynylcyclohexene (**5c**) with each of the $(C_6F_5)_2B$-halide reagents **4a**/**4b**. In reactions under direct NMR control using increasing enyne to halogenoborane ratios we could observe the initial 1,2-halogenoboration products **6e**,**f** admixed with the "dimers" **7e**,**f**, followed by the formation of a mixture of higher "oligomers" at higher **5c**/**4** ratios (for details including the depicted NMR spectra see the Supporting Information). On a preparative scale we synthesized the pyridine adducts of the "dimeric" products and isolated them as white solids in 75% (**8e**, X = Cl) and 92% (**8f**, X = Br) yield, respectively. Both the products **8e** and **8f** were characterized by X-ray crystal structure analyses. The structure of compound **8f** is shown in Figure 5; the structure of compound **8e** is depicted in the Supporting Information). Each of these compounds shows a set of four olefinic ^{1}H NMR signals in solution at 299 K (for further details see the Supporting Information).

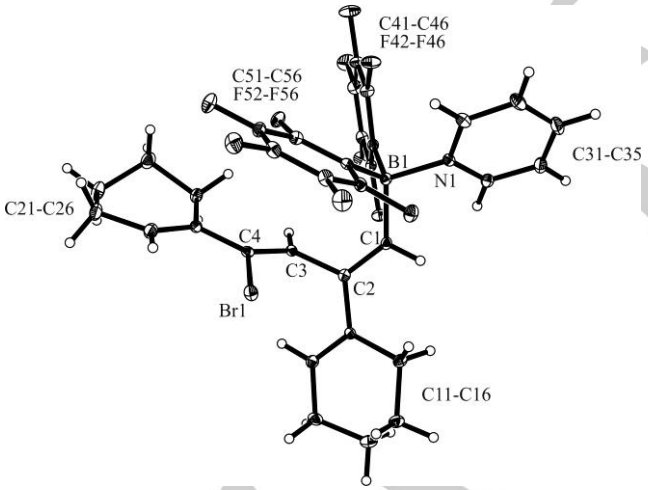

Figure 5. Molecular structure of compound **8f** (thermal ellipsoids are shown at the 15% probability level). Selected bond lengths (Å) and angles (°) are described in Table 2.

In this study we developed a convenient way of preparing the $(C_6F_5)_2B$–halide reagents **4a** and **4b** by treatment of Piers' borane $[(C_6F_5)_2BH]$ with trityl chloride or -bromide. We assume that the reaction proceeds by halide capture from the dissociative equilibrium between $Ph_3C–X$ with the trityl cation and halide anion by the $(C_6F_5)_2BH$ Lewis acid to generate $[(C_6F_5)_2B(H)X]^-$, although this has not yet been strictly proven. Hydride abstraction by the Ph_3C^+ cation would then directly lead to the $(C_6F_5)_2BCl$ or $(C_6F_5)_2BBr$ products with formation of the stoichiometric triphenylmethane co-product.

Our study shows that the $(C_6F_5)_2B$–halides may serve as useful reagents, which are now easily available by a reaction scheme that avoids the hazardous C_6F_5–Li reagent and potentially problematic organotin or organomercury reagents.[9] The $(C_6F_5)_2B$–halides **4a** and **4b** readily undergo the *cis*-1,2-halogenoboration reaction with cyclopropylacetylene to give the respective β-chloro- or bromoalkenylboranes **7a**,**b**. Their subsequent reactions with additional equivalents of the alkyne are unusual. They form series of linear alkyne oligomers that are apparently formed by successive 1,2-carboboration reactions with the added alkyne. Similar reaction sequences were observed with the conjugated enynes **5b** and **5c**. 1,2-Carboboration reactions in general are not too frequently observed; they seem to require rather electrophilic boranes in order to proceed with acceptable rates.[11] In addition there seems to be a steric component.

Alkyne oligomerization and polymerization is usually a domain of transition metal catalysis. Many transition metal systems have been shown to induce the thermodynamically favourable cyclotrimerization of alkynes to give benzene derivatives.[12] Acetylene polymerization and linear oligomerization of substituted alkynes is mostly carried out with specific Ziegler-Natta catalysts[13] or by metathesis reactions.[14] In our case this can be achieved in a stoichiometric way simply by the action of the $(C_6F_5)_2B$–halide reagents with the here chosen alkyne derivatives. The sequence of 1,2-halogenoboration combined with multiple 1,2-carboboration results in the formation of series of linear alkyne oligomers that feature pairs of halide and –boryl functional groups at the terminal carbon atoms of the oligo-ene π-systems. We will see if this new reaction scheme will lead to interesting applications of the resulting conjugated functionalized olefinic systems.

Acknowledgements

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Keywords: 1,2-halogenoboration • carboboration • metal-free oligomerization • oligo-acetylenes • boron halide synthesis

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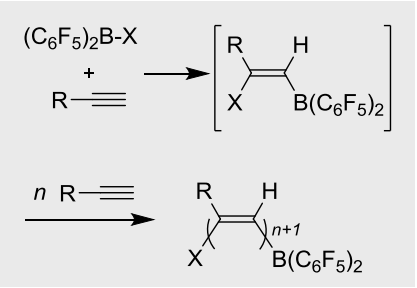
Treatment of Piers' borane [$HB(C_6F_5)_2$] with trityl halides gave the X-$B(C_6F_5)_2$ reagents (X: Cl or Br). They reacted with terminal acetylenes under mild conditions by sequential 1,2-halogenoboration followed by multiple alkyne addition to give series of the linear conjugated alkyne oligomers in a metal-free synthesis.



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Metal-free Acetylene Coupling by Means of the $(C_6F_5)_2B$-X 1,2-Halogenoboration Reaction

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